KRISHNAN MEMORIAL LECTURES

NATIONAL PHYSICAL LABORATORY
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Lecture

by

K. R. RAMANATHAN

Thanks to Dr Joglekar and his colleagues for organising these Open Day Celebrations and for their kind invitation to me to deliver the First Krishnan Memorial Lecture on the completion of 15 years of work of the NPL in this famous campus. It is a proud privilege which I value greatly because of my long and intimate association with Dr Krishnan and of my many contacts with the NPL and the CSIR.

I am glad to see with us here today Dr K. N. Mathur who was associated with Dr K. S. Krishnan from the very early days of the NPL.

The Foundation Stone of NPL was laid by Panditji on 4 January 1947 and the formal opening of the building was made by Sardar Patel on 21 January 1950.

Dr K. S. Krishnan's association with Dr S. S. Bhatnagar goes back to 1940—in the early years of World War II when the Government of India had realised the importance of associating Indians in a responsible way with the development of Science, Technology and Industry in the country.

The Board of Scientific and Industrial Research was set up in 1940 and CSIR in 1942. Prof. A.V. Hill's visit to India took place in 1943-44. Fuel, Glass, Physics, Chemistry and Metallurgy were the first subjects to receive attention.

Dr K.S. Krishnan had joined the Allahabad University as Professor of Physics in 1942. His response to Dr S.S. Bhatnagar's request to join him in the work of the CSIR (1942) was sympathetic, but cautious.

"The scientific objectives were unexceptionable and I had myself frequently expressed in my discussions with him the need for organising various laboratories, and in particular a Bureau of Standards for India. When the latter was decided upon and a planning committee was appointed I did accept its membership. Following the British example, the proposed Bureau of Standards was to be designated as the NPL, though I would have preferred the former. I also accepted the membership of the BSIR. But the immediate background which prompted the organisation of the CSIR did not enthuse me. Moreover with my pronounced academic lean-

ings, there was a strong resistance in me on academic grounds, for putting the cart before the horse.

I felt the development of the Universities should have the higher priority. Otherwise we would eat out of the seed crop."

Although Dr Krishnan understood and appreciated Dr Bhatnagar's practical sense and keenness for urgent action, he desisted from joining him in the early forties. In 1945-46, Dr Krishnan was a Member of a Scientific Mission to UK and USA. He spent some time in the NPL, UK and in the Bureau of Standards, Washington.

After his return, he wrote in his Diary :

"In 1947, I seemed to relax, and in the flush of newly found independence, every problem seemed to recede to the background in the intense faith that in an independent India, every problem would get solved and every defect get rectified.

I was aware that the maintenance of the various physical standards, which involves considerable amount of constructive work—is not as exciting, or as attractive, as creative work. But in the growing industrial economy of the country, the organisation of the Bureau of Standards was one of national importance and I had no doubts in my own mind about it."

You all are aware how Dr Krishnan, after he took up the Directorship of the NPL, threw himself heart and soul to building up the NPL, from the days when he used to go by bus and foot to his couple of rooms in the Delhi University to the day of his death on 13 June 1961.

The organisation grew to large dimensions during his stewardship. Dr Krishnan's relationship to his colleagues and staff remained that of colleague to colleague or of teacher to student. His administration was by example rather than by office orders.

Dr Krishnan was well aware that Science and Technology are mutually dependent, and act and react on each other. From his own experience as a Scientist, he knew that 'knowing' and 'doing' should go together.

In a reminiscent mood, writing early in 1928, Dr Krishnan says "for a long time past, I have not done any experimental work; in fact, the last experiment I did was the one on the magnetic double refraction of nitric oxide, in the summer of 1926. Since then, I have been exclusively confined to my desk excepting for a short interval of about a week. Though the period has been

extremely fruitful regarding my scientific output, still, one must agree with Professor (Raman) that it is not quite healthy for a scientific man to be out of touch with actual experimenting of any length of time. It was mainly with a view to start immediately some experimental work that I took up at the suggestion of Professor (Raman) the general problem of the fluorescence of organic vapours..."

This attitude of mind remained with him throughout his life (of linking his thinking with doing and of his doing with thinking).

To appreciate Dr Krishnan's attitude to Science and Industry and to his work in the NPL, one has to understand that he was an integrated personality with well defined mental and spiritual outlook. He had grown up in an atmosphere of plain living and high thinking. His ideal of life was that of a scholar and a teacher, in continuous quest for deeper understanding of the phenomenal world and the problems of life. He believed that 'Swadhyaya' and 'Pravachana'—learning by research and expounding through lectures were the chosen way of life for him.

Dr K. S. Krishnan's Work in the NPL

Although our NPL was modelled on the NPL of the United Kingdom. Dr K. S. Krishnan had always in his mind the functions of the National Bureau of Standards (NBS) in USA. The US Act of Congress of 3 March 1901, amended in Public Law 619, 1950, state the objectives of NBS as follows :

(i) Development and maintenance of the international standards of measurement and the provisions of the means and methods of making measurements consistent with these standards.

(ii) The determination of Physical constants and properties of materials.

(iii) The development of methods and instruments of testing materials, devices, and structures.

(iv) Advisory services to Government agencies on scientific and technical problems.

(v) Invention and development of devices to serve special needs of the Government, and

(vi) The development of standard practices, codes, and specifications.

The work involves basic and applied research, development, engineering, instrumentation, testing, evaluation and calibration services and various consultation and information services.

Research projects are also undertaken for the Government agencies. When new subjects grow, means and methods of measurements and setting up of standards have to grow.

Except in the field of indigenous manufacturing of radio components and materials studies, I doubt Dr Krishnan envisaged the development and Industry as a function of the NPL. Helping an industry is one thing and founding an industry is something different.

NPL's Activities

There has already been so much said about the activities of the CSIR and National Laboratories that it would be presumptuous and even confusing to say anything more.

But as a colleague to colleagues, I often feel that it would be good if different, related divisions of a laboratory of a laboratory could work together on specific projects—the solution of many definite problems often requires the coordinated action of more than one discipline.

Here in NPL, we have a collection of personnel and facilities such as do not exist in many universities, so that more combined action should be possible.

One such area, in which concerted action is possible, is looming large in the near future; namely the growth of an Electronics Industry in India. Materials—Techniques and Instrumentation, Standardised equipment for quantitative measurement in various frequencies from audio to GHz ranges. For helping this development, help would be needed from Solid State Physics, Electronics, Electrical and Mechanical Engineering, Radio, Cryogenics, etc. Also cooperation between NPL and other laboratories such as the Pilani and CSIO, Chandigarh — communication and broadcasting services and competent radio and electronics industries.

I feel that the authorities of the NPL have a big programme ahead for helping developments in this field.

I, however, realise that a laboratory can help an established industry or point the way to new industries but cannot actually establish a new industry.

Friends, you have great task ahead. In solving them, I wish and pray that the understanding, conciliatory, ardent, and human spirit of Dr Krishnan be a source of inspiration to you.

As our late Prime Minister Pandit Jawaharlalji said of Dr Krishnan, "He was a dear friend and colleague, a great scientist and scholar, who had not lost that gentleness and humour which are the true marks of greatness."

Evolution of the Government-Science Relationship in the United States

by

PROF. FREDRICK SEITZ

Professor, University of Illinois
President, National Academy of Sciences, USA

I consider it a very great honour to give the Krishnan Memorial Lecture. I first met Dr Krishnan just after the War, and then again at a meeting in Tokyo in 1953, the very famous theoretical conference which was held there; in which for the first time since the War scientists from all over the world visited Japan. I had looked forward to seeing him here during my visit three years ago, but he passed away just before that visit.

Originally, I had intended to speak on Solid State Physics. I found, however, on arriving at Bombay and even more so in Delhi, a broad interest in India these days in the relationship between science and Government; and much of your science is government supported. Many individuals were asking me for some of the facts about the evolution of Government-Science Relationship in the United States.

Early Academies

Although the first settlers in North American region were from Western Europe—they did not bring with them the full appreciation of the methods of science. A century and a half after the first settlers, say by 1750, there were in the United States a few individuals who had a deep interest in science, but there were no full time professional scientists. The most remarkable man of that time was Benjamin Franklin. Benjamin Franklin was elected to the Royal Society of London. He decided, United States should have an academy; and founded the American Philosophical Society in Philadelphia. Another academy was formed in New England after the Revolution. The United States gained its independence in about 1784; the so-called American Academy of Arts and Sciences was founded in Boston in North Illinois, but it also was devoted to applied sciences. So, by 1800 it was quite clear that United States was the nation in which technology was important but there was no evidence whatever that it would take creative science seriously. There was, in fact, a vast gulf between United States and Western Europe which at that time had many great scientists.

In short, Western Europe was scientifically mature, United States was scientifically primitive. Even now it has an interest in technology. A number of individuals about that time proposed to our national government that it should create some kind of an institution devoted to science. It was all rejected by the Congress, our Parliament. It preferred to borrow basic science from Europe and devote efforts to the use of science.

Smithsonian Institute

Then a rather remarkable thing happened, quite an accident, which gave a cornerstone to our national structure in the inter-relation between science and the government. There was in England a chemist, who was a contemporary of Dalton by the name of Smithson. He was a good chemist, a member of the Royal Society of London. His mother was a wealthy woman, his father a nobleman. His house was in Northumberland, but his family—his father's family—never gave him recognition. He never married. As he approached the end of his life, he decided to do something with the wealth he inherited from his mother, a sum of half a million dollars that he wanted to devote to science. Although he never had been to USA, he apparently was inspired by this struggling classless society and he decided in 1827 to leave his fortunes to the Government of the United States to create an institution devoted to science and he said, "He hoped it would make the name of Smithson live for ever." By 1846, the Congress decided to create what is now called the Smithsonian Institution. They decided to choose the best scientist in United States to head it. The man, in fact, who was about the age of 50, was Joseph Henry. They asked him if he would serve as Head of the now national institute—The Smithsonian Institution. Seeing a new opportunity, he accepted the appointment even though he disliked leaving academic life and he became active in Washington. Eventually he became a close friend of President Lincoln during Civil War and helped the Federal Government in certain experiments concerned with signalling in light during the Civil War which broke out in 1861.

National Academy of Sciences

The struggle between the North and the South was over many issues. In this pressure of war the Northern Government decided to pay much more attention to science and technology. It passed, what is called, the Land Grant Act so that each State was given land to set up an institution of higher learning. The second step it took was to create the National Academy of Sciences of which I am the President now with a Federal Charter with the understanding that the members of the Academy will make themselves available without fee, without compensation to advise the Government on request. The Academy was created in 1863 right in the middle of Civil War. The Charter was signed by Abraham Lincoln.

The Academy, as I said, which was formed in 1863, had initially 14 members, expanded rapidly to 100 and each man worked with the various branches of Federal Government. When Joseph Henry was made President, not the whole time President,

he retained his position in Smithsonian Institution. He took the Academy in hand and decided that if he was to be the Principal Adviser to the Government, it would be absolutely necessary that men in it should be men of high integrity, who would not use the opportunity for their own ends but would think unselfishly of the Government. He was President for 10 years and during the course of those 10 years lasting to 1878, he established the principle that the first and foremost principles governing elections to the academy would be experience and confidence in research, pure and applied.

Between the time of Joseph Henry and World War I, the members of the Academy held their meetings in Smithsonian Institution and served the Federal Government in a number of ways.

Effect of Civil War

But in the main, the advances recorded before World War I were in the observational sciences—astronomy—the natural subject and then in chemistry. Let me also stress that in this period and partly as a result of the stimulus of the Civil Wars, industrial technology, independent of science was increasing very rapidly. To give you a picture of the scale of acceleration, when the Civil War broke out in 1861, both the North and the South purchased in the first year of the War all of their military supplies from Europe. The South never left this stage. It did not have its own industry. It had an economy based on slavery and around agriculture production of cotton. They had never developed the scientific technology. The North in the second year of the War produced half of its ordnances. In the third, it produced all and by the fourth year onwards it had military equipment of Northern manufacture in super abundance. All through the periods of World War I and II all the industrial economy, so to speak, was expanding rapidly, but without the same kind of scientific base that one found in Europe.

Emphasis on Science

One of the developments I should mention now, occurred in the year 1890. The University of Chicago was formed and a decision was made that it would put its emphasis on science. Now it was the new universities that hired all the good scientists on whom it could lay its hands on and pay them, by those days, very remarkable salaries. The standards set up in the university of Chicago was so significant that within 30 years it had given opportunity to three great physicists to win Nobel Prizes, namely : Michelson, Millikan and Compton. This created a great revolution in the academic scene because the competition it started made it necessary for the other universities to begin competing by the same standard.

Another transformation occurred about this time in 1890's. Some of the industrial companies which had depended primarily on borrowed knowledge from Europe and on indigenous engineering, decided that they ought to have a little more science and set up research laboratories. Particularly about 1900, the General

Electric Company, the Bell Telephone's and the Du-Pout's founded the research laboratories. In many respects they were better than some of the best universities; as you know, Langmuir, Davidson and others—great physicists and chemists—all did their key work in industrial laboratories of which any university would be proud.

Bureau of Standards and National Research Council

Parallel to this there was some activity within the Federal Government, and in 1892, on the advice of the Academy, the Federal Government created the Bureau of Standards and began to do research of significant kind within the Government. World War I, like the Civil War, created a revolution in relationship between the science and Government. Suddenly, in spite of its own developments, the United States found itself cut-off abruptly from Western Europe. It could no longer buy more sophisticated manufactured products like dyes, it could no longer send its young people abroad for study or its technically competent people to get technical information. Moreover, the Government feared that the United States would be involved in World War I. With these difficulties hanging over its head, President Wilson turned to the Academy and asked whether it could advise him to help accelerate what was obviously needed for revolution within the country—a complex revolution in the basis of its technology and industry. The leaders of the Academy decided that the Academy should recognise itself to advise the Government. The Academy members were men from academic institutions. They decided that the Academy should create within itself a new body, National Research Council which would call upon individuals, whether or not they were members of the Academy, to form advisory teams. This structure was the principal guiding structure in World War I. In 1918, President Wilson felt that the National Research Council has been the sole factory in aiding war effort and that it should be made a permanent part of the Academy and it was retained.

Following the Civil War, the Academy noted that it would create a revolution in transportation, provided the highway system could be developed and it created a Highway Research Board to advise the Federal Government on highway planning. That Board has been active since 1918 and is responsible for most of planning of the highways which exist in the United States.

Post Graduate Fellowships

In the 1920's, the Academy decided that it was wrong to stop serious interest in research as soon as a student completed his graduate training or his Ph. D. training and that there should be fellowships so that some of the very best research students could have one or two additional years beyond the doctorate, studying either in Europe or elsewhere in the United States. It created what is called the National Research Council Post-doctorate Fellowships.

National Institute of Cacner

When a depression occurred in 1928, President Roosevelt found himself in difficulty and he again turned to the National Academy for help. The Academy

recommended that the Government set up a series of agencies that would give money to private industries and to the universities to accelerate pure and applied science—science of industrial interest and interest in the public health. The National Institute of Cancer was formed and that Institute eventually became the National Institute of Health.

National Science Foundation

When World War II occurred, President Roosevelt called on exactly the same men to help him through. Those men, Compton and Vanaver Bush and James Conant, were the leaders in the Government-Science relationship during World War II. They created the National Defence Research Committee in 1940 and then had the Government create the office of the Scientific Research and Development to spend money to support research throughout the country in connection with military efforts, with the understanding that the office will disappear at the end of the War. The office of Scientific Research and Development was a body which essentially directed war research efforts. President Roosevelt asked Bush to head a Committee to decide what should happen in post-war period. The result of that study, presently available in the form of a book, drew a blue-print for the post-war period. It urged all Federal agencies to give contracts and approve programmes for the support of research in private industry and in the unversities as well as within the Government. It advised on the expansion in Federal laboratories and advised the creation of the new agency which would support pure science, that agency which eventually came into being in 1950 is the National Science Foundation.

Between 1945 and 1962 the Federal expenditures for research expanded over ten times, I should say, for research and development until it reached the level of about 3 per cent of the gross national product, about 10% of that going into the basic, pure and applied work.

Scientific Advisers

President Trueman established the post of Scientific Adviser in the Whitehouse to help him coordinate the science programmes through the various executive agencies. This was broadened and there had been four scientific advisers with Advisory Committees to report directly to the President. Two years ago, Congress established an Advisory Group within the Congress itself which is attached to the Library of Congress. In addition, two years ago, Congress entered into a contract with the Academy so that each year we advise various committees of Congress on request of areas of interest to them.

Present Problems

With this expansion that has occurred since the War, it has also created a number of great problems. As science and the expenditure on science has grown, the interest of Congress in those expenditures has also grown. In fact, each year

now we note a much more strenuous debate over the expenditure on science which indicates that there would be levelling off in certain areas.

There is also another great problem associated with the growth of what is called big science. As you know, there are certain kinds of research, space research, research with reactors, research with accelerators, oceanographic research, research involving large clinics, animal clinics and clinics with human subjects in which the annual costs are astronomical. There is a certain tendency to give preference to these big projects over the small scale research in which still lies the cornerstone of science. They tend to be favoured because they make a big impression at the political level. If the Congressman can get a large programme started in his district, it is easier to advertise.

There is a danger that the national programme would become unbalanced in that the independent scientists engaged in small research in fields, for example like chemistry, will be neglected. The Academy is very conscious of this danger and, in fact, this year in December, just a month ago, we issued report on chemistry which we hope will refocus the attention of Congress on the independent investigator and the chemist is perhaps the first and foremost of independent small investigators. I should say, on a sense of loyalty, that Solid State Physicist also is.

Thank you all.

Magnetic Effects in Crystals

by
DR S. BHAGAVANTAM
Scientific Adviser to the Minister of Defence

My association with the late Dr K. S. Krishnan goes back to nearly 40 years. It brings to my memory the days when scientific research in India, in all its aspects such as its tempo, its objectives, the resources behind it by way of men and money, was very different from what it is today. The occasion of the Krishnan Memorial Lecture brings to my mind the fact that Krishnan was a pioneer from those days of complete self reliance and I would like to pay my tribute to the memory of this great man. When I first came in contact with him, he was already in the forefront of Indian Science and used to express himself with great clarity. At that time, he was working in branches of crystal physics which were close to magnetism. After graduation, I myself started work on the magnetic properties of naphthalene crystals. Thus, my early work having been on magnetic properties of crystals and the fact that Krishnan's early interests were also in magnetocrystalline action may be considered as providing some justification for my choosing "Magnetic Effects in Crystals" as the title of this lecture. We shall mainly concern ourselves with what are called the thermo-galvano-magnetic effects.

Hall Effect

I would first like to deal with the Hall Effect which was discovered in 1879 by Hall. If we subject a crystal also to a magnetic field and pass an electric current in a direction perpendicular to the magnetic field, a potential difference is exhibited across the slab in the third direction at right angles to the above two. This potential difference is called the Hall voltage and constitutes a magnetic effect known for many years. Because the effect, that is the potential difference, arises as a result of an electric current and a magnetic field, it is described as a galvano-magnetic effect. One can measure this effect only with some effort, because if you took about 100th of an inch thick copper strip and send an electric current of one ampere through it and place the copper strip in a magnetic field of 12000 gauss, then the potential difference at the ends of the copper strip will be about a quarter of a microvolt.

Ettingshausen Effect

I will now pass on from the Hall effect to a slightly different effect called the Ettingshausen effect discovered in 1887. This effect manifests itself as a difference

in temperature between the two sides of the strip instead of a potential difference as in the previous case. If we take a copper strip, again a 100th of an inch thick and send a current of one ampere, using magnetic fields of the order of a few thousand gauss, a temperature difference of about 0.000075 degrees between the two ends can be expected. This effect is also quite difficult to measure. I want to emphasize that while these effects are difficult to observe and measure, they were being taught and learnt. One can see that potentially, this effect is capable of being used for purposes of cooling. If, however, I had said this some years ago, no one would have believed it because, one does not work in the field of practical refrigeration with temperature differences of the order of 0.000075 degrees.

Nernst Effect

There are two more effects which I would like to mention as part of this sequence. The first is called the Nernst effect. The situation here is slightly different, in as much as a magnetic field is still there but there is no electric current. Instead, we have a thermal current generated by establishing a thermal gradient. A potential difference then appears in the material. There are three vector quantities here as before, mutually perpendicular to each other, but this effect is called a thermo-magnetic effect for the simple reason that the agencies that cause the potential difference to occur are a thermal gradient and a magnetic field. This is different from the two galvano-magnetic effects, namely, the Hall and Ettingshausen effects, mentioned a little earlier. This was discovered by Nernst and the potential difference produced is called the Nernst voltage.

Righi-Leduc Effect

The last in the series is called the Righi-Leduc effect. This too is a thermo-magnetic effect. There is a thermal current and a magnetic field, both perpendicular to each other and we find that there is a temperature difference set up in a third direction perpendicular to both these.

Thus, these four principal magnetic effects are obtained simply by combining in two perpendicular directions a thermal current with a magnetic field, or an electric current with a magnetic field, and looking in the third direction for a difference either in temperature or in electric potential.

New Materials

These four effects have been known for about a hundred years. However, it is only in recent years that they have assumed great importance from a technical point of view. Unlike copper and other simple elemental substances which were known and studied during the past 100 years, we have today substances which are alloys or compounds of certain chosen materials, a good example being Indium Antimonide, wherein these effects are manifested with magnitudes which are millions of times large than what we were hitherto used to. To understand these

effects in such a way as to be able to exploit them, we should proceed in a logical manner. Then alone will one succeed in the search for new materials which may exhibit these effects in larger and larger measures.

Vector Quantities

In order to go about our experiments systematically, we should study the origin of these magnetic effects and the relationships, if any, that exist amongst themselves. We should be able to explain why certain crystals show these effects better than others. In this context, I wish to draw your attention to the simple Ohm's Law, relating current and potential through electrical resistance. Current and potential are vector quantities and hence each one of them must be expressed in ordinary space in terms of three components. This would mean that the resistance of a conductor is not a simple number. When we are dealing with directions in space, we will have in general to give its magnitude in terms of nine quantities.

If you heat a conductor, its resistance changes, and a coefficient giving the rate of change of resistance with respect to temperature can be determined, and you all know that this property is used for constructing resistance thermometers. As the resistance is not a simple number, one linear equation and a single coefficient with respect to temperature no longer suffice to describe the variation. In fact, experiments show that if we raise the temperature high enough, the variation of resistance ceases to be linear. Moreover, if we are dealing with a single crystal, this variation may be different for the different components of resistance connecting the current and potential difference vectors.

All the four quantities, namely, the electrical potential and the electric current, the thermal gradient and the thermal flow can be related to each other by suitable expressions as in (1). The dependence of all the coefficients on the magnetic field H is not to first power only but extends to higher powers, the four important relations being shown in (2).

$$E_i = \rho_{ik}(H)\, j_k + \alpha_{ik}(H)\, G_k$$
$$q_i = -\beta_{ik}(H)\, j_k + K_{ik}(H)\, G_k \qquad \ldots (1)$$

G_k in (1) stands for the negative temperature gradient $-\partial T/\partial x_k$.

$$\rho_{ik}(H) = \rho^0_{ik} + \beta_{ikl} H_l + \rho_{iklm} H_l H_m + \rho_{iklmn} H_l H_m H_n + \rho_{iklmnp} H_l H_m H_n H_p + \ldots$$

$$K_{ik}(H) = K^0_{ik} + K_{ikl} H_l + K_{iklm} H_l H_m + K_{iklmn} H_l H_m H_n + K_{iklmnp} H_l H_m H_n H_p + \ldots$$

$$\alpha_{ik}(H) = \alpha^0_{ik} + \alpha_{ikl} H_l + \alpha_{iklm} H_l H_m + \alpha_{iklmn} H_l H_m H_n + \alpha_{iklmn_p} H_l H_m H_n H_p + \ldots$$

$$\beta_{ik}(H) = \beta^{0}_{ik} + \beta_{ikl} H_l + \beta_{iklm} H_l H_m + \beta_{iklmn} H_l H_m H_n + \beta_{iklmnp} H_l H_m H_n H_p + \ldots \quad \ldots(2)$$

The quantities ρ^{0}_{ik}, ρ_{ikl}, ρ_{iklm}, ... and β^{0}_{ik}, β_{ikl}, β_{iklm}, ... are called the galvano-magnetic coefficients. The quantities K°_{ik}, K_{ikl}, K_{iklm}, ... and α°_{ik}, α_{ikl}, α_{iklm} ... are called the thermo-magnetic coefficients. In particular, ρ°_{ik} represents the electrical resistivity in the absence of a magnetic field and ρ_{ikl} gives the first order effect of a magnetic field on the electrical resistivity and is no other than the Hall effect. In Table 1 are given all the galvano-magnetic and thermo-magnetic coefficients, conveniently tabulated under columns and giving properties of increasing order effects in H, the magnetic field. All the four effects mentioned above, namely Hall, Ettingshausen, Nernst and Righi-Leduc effects as well as their higher orders are contained therein.

TABLE 1

	Composite tensor	Zero order component	First order component	Second order component	Third order component	Fourth order component
	$\rho_{ik}(H)$	Electrical resistivity	Hall effect	Magneto-resistance	Second order Hall effect	Second order Magneto-resistance
		ρ_{ik}°	ρ_{ikl}	ρ_{iklm}	ρ_{iklmn}	ρ_{iklmnp}
Galvanomagnetic effects	$\beta_{ik}(H)$	No name	Ettingshausen effect	No name	Second order Ettingshausen effect	No name
		β_{ik}°	β_{ikl}	β_{iklm}	β_{iklmn}	β_{iklmnp}
	$K_{ik}(H)$	Thermal Conductivity	Leduc-Righi effect	Magneto-thermal conductivity	Second order Leduc-Righi effect	Second order Magneto-thermal conductivity
		K_{ik}°	K_{ikl}	K_{iklm}	K_{iklmn}	K_{iklmnp}
Thermomagnetic effect	$\alpha_{ik}(H)$	Thermo-electric power	Nernst effect	Magneto-thermo-electric power	Second order Nernst effect	Second order Magneto-thermo-electric power
		α_{ik}°	α_{ikl}	α_{iklm}	α_{iklmn}	α_{iklmnp}

Applications

I wish to draw your attention to the fact that these magnetic effects have recently become technologically very important. I will illustrate this by one or two examples.

The Hall effect can be used to convert a direct current into an alternating current. We take a slice of a crystal of one of the substances which exhibit the

Hall effect prominently, send a direct current along its length and put it in the field of an electromagnet, excited by an alternating current. The magnetic field which is perpendicular to the crystal slice alternates upwards and downwards as frequently as the current alternates in the energising coils of the electromagnet. Therefore, the potential across the breadth of the Hall crystal also alternates, and thus an alternating voltage is produced while we send only a direct current through the crystal. The frequency of alternation will be the same as the frequency at which we energise the electromagnet and this device gives us a converter; not only a converter but an amplifier converter. There is no moving part here, and we can get amplification as well as a conversion of a direct current into an alternating current.

When we want to measure a current, the normal thing is to put in ammeter in that circuit. However, we can also use the Hall crystal for this purpose because, an electric current flowing will mean a magnetic field surrounding the conductor. The magnetic field thus generated can be made to cut the Hall crystal. And if in the Hall crystal, we maintain a steady electric current in a direction normal to the magnetic field, a Hall potential will be produced and it can be measured. This will be in direct proportion to the magnetic field which in turn will depend upon the electric current. Thus, a simple Hall crystal through which a steady electric current is flowing can be used as an ammeter.

The Ettingshausen effect consists in producing a temperature difference although in the case of copper, the effect is negligibly small. Today we have substances which show large temperature differences as a result of applying a magnetic field and passing an electric current in appropriate directions. In this, we find the potentiality of an application for refrigeration. In fact, technologists have succeeded in making compounds and alloys which give considerable differences in temperature when an electric current and a magnetic field are applied suitably and such alloys are being exploited for making specific cooling devices.

The present quest is to fully understand the nature of these magnetic effects. To look for and make new materials which exhibit these phenomena in a large measure and to apply such results to various practical needs are tasks engaging the attention of many people all over the world and in several laboratories. Some of the problems which are arising in connection with space technology are such that we do want very light elements and devices which can produce the required effects. The moral of this is that, although when Hall effect and Ettingshausen effect were discovered, they were obscure magnetic effects which interested only the theoretician, today, after a hundred years, with the persistent efforts to find out suitable materials exhibiting these effects in a large measure, we have entered fields where physicists are deeply interested in applying these principles for practical purposes.

Magnetic Symmetry

I have to introduce a post-script here. A brief mention is necessary of certain new concepts which have come up during the past few years. In my opinion, these will have an important influence on the understanding of physical properties of crystals with magnetic structure and in particular the magnetic effects we are considering.

A study of the magnetic state in crystals has revealed that the conventional notions of crystals symmetry are inadequate. We take a few examples to illustrate this. Caesium, iron and chromium have a body centred cubic structure, but caesium is diamagnetic, iron is ferromagnetic and chromium is antiferromagnetic. The differences arise due to the different orientations of the atomic magnetic moments in the latter two cases and complete absence of magnetic ions in the former case.

To take another example, the fluorides of manganese and nickel crystallize in the rutile structure and they are antiferromagnetic. We know that the magnetic moments of the atoms in manganese fluoride are in opposite directions to each other along the four-fold axis of symmetry and cancel each other. In nickel fluoride the atomic magnetic moments also cancel out but lie in a plane perpendicular to the symmetry axis. This takes a very important difference in as much as the former is always antiferromagnetic whereas the latter is capable of exhibiting weak ferromagnetism above a transition point.

The above two examples indicate that the conventional symmetry classification fails to take account of the differences in magnetic structure and cannot explain their very different behaviour.

During the last decade or so the Russian school of physicists (Landau, Lifshitz, Shubnikov, Belov, Dzialoshinskii) have realized the need for generalization of the concepts of symmetry of crystals taking their magnetic structure into account. It is realized that in addition to the symmetry of spatial disposition of atoms in a crystal, the symmetry of spatial orientation of the atomic magnetic moments is relevant. This necessitated introduction of new symmetry operations. The reversal of atomic magnetic moments is taken as a possible symmetry operation and is denoted by $\bar{1}$. The combination of $\bar{1}$ with conventional operations which may be denoted R, S, T, U, ... are called antisymmetry operations and are denoted by $\underline{R}$, $\underline{S}$, $\underline{T}$, $\underline{U}$ respectively. $\underline{1}$ is the anti operation corresponding to the identity 1.

Groups of all possible conventional operations and anti-operations are constructed. There are in all 122 generalized groups called Shubnikov point groups. Thirty two of them contain $\bar{1}$ explicitly. They are called double colour groups and since magnetic moment reversal is included as a symmetry operation, the para- and diamagnetic crystals are classified under them. Thirty two more of them, known as single colour

groups, consist of conventional operations only, i.e. they are like the classical groups. Each of the remaining 58 groups contains at least one anti-operation but not the anti-identity $\bar{1}$ itself. They are called double colour groups. The ferro-, ferri and antiferromagnetic crystals are classified under the 90 single colour and double colour groups.

The introduction of magnetic symmetry satisfactorily explains the structural differences and differences in behaviour pointed out in our examples. In our first example, caesium and iron in fact fall into different magnetic groups. Similarly in the second example, it can be shown that the magnetic point group of nickel fluoride admits the existence of a macroscopic resultant magnetic moment while that of manganese fluoride does not.

There is yet another example which in my opinion strongly supports the introduction of the concepts of magnetic symmetry. It is the case of piezomagnetism, which was pronounced to be impossible due to symmetry considerations. Landau and Lifshitz and Dzialoshinskii have shown that it was an erroneous conclusion resulting from the mistaken assumption that all crystals have a time symmetric structure. Magnetic moment reversal is equivalent to time reversal and ferro- and antiferromagnetic crystals which contain fixedly oriented atomic magnets are not time-symmetric. Taking the appropriate magnetic symmetry of such crystals, it can be shown that piezomagnetism is not forbidden in certain antiferromagnetic classes. In fact it was shown that it was possible in Cr_2O_3 crystals. This conjecture has been experimentally verified recently.

Magnetic Symmetry and Transport Properties

The recognition of magnetic symmetry of crystals gives rise to an anomaly in the understanding of the transport properties with which we have been mainly concerning ourselves in this lecture. We noted that the para- and diamagnetic crystals are time-symmetric. A common transport property like the electrical resistance ρ_{ik} which relates the time symmetric vector electric field E_i with the time-symmetric vector electric current J_i has to be a time-asymmetric tensor and therefore forbidden in these crystals.

To avoid this anomaly, Birss (1963) suggested that in the case of transport properties we should apply Neumann's principle with the restriction that only the conventional (ordinary) symmetry operations of the crystal should be taken into consideration while obtaining the symmetry restrictions on transport properties. I feel that the anomaly is only apparent. In the steady state of a constant current, the crystal is not in thermodynamic equilibrium and entropy is generated at a constant rate. The symmetry of the system in the steady state is the common symmetry of the crystal in its equilibrium state (given by its grey point group) and the symmetry of the time irreversible scalar, namely the constant rate of entropy production. The

common symmetry thus consists of the ordinary symmetry operations in the symmetry group of the crystal. The result is same as that suggested by Birss, but this approach is self-consistent.

Recently, Kleiner (1966) has brought out a deeper aspect of the situation. He suggested that the Onsagar relations which govern the intrinsic symmetry with respect to the first two indices of the transport property tensors, being consequences of the principle of microscopic reversibility of particle velocities, need appropriate modifications for magnetic crystals. He gave the generalized Onsager relations which are valid in the presence or in the absence of an external magnetic field for magnetic as well as non-magnetic crystals which incorporate the usual Onsager with the generalized Onsager relations, a new aspect of the transport property tensors subject to the double colour symmetry groups emerges. The clear distinction between the intrinsic and macroscopic symmetry of the tensor no longer exists. The symmetry restrictions on the property tensors due to Onsager relations include the restrictions due to the conventional symmetry operations of the crystal.

The existence of extraordinary Hall effect in certain ferromagnetic crystals, as pointed out by Kleiner, lends support to this generalization.

I may take this opportunity to point out a few interesting consequences of the generalized Onsager relations. We note that in para- and diamagnetic crystals, the symmetric and antisymmetric parts of the galvano-magnetic tensor $\rho_{ij}(H)$, are also respectively the even and odd parts of the function. Let us consider as an example the ρ_{ijk} tensor which describes the Hall effect and which is in the odd part of the function. In non-magnetic crystals, it does not give rise to Joule heat because it is also in the antisymmetric part of the tensor $\rho_{ij}(H)$. In magnetic crystals however, this is no longer so. We, therefore split the ρ_{ijk} into symmetric and antisymmetric parts. The symmetric part which may be observed in magnetic crystals is a kind of magnetoresistance which depends on the direction of the external magnetic field. Similarly there will be an antisymmetric part generated in the even part of the function which is a different kind of Hall effect that is unaffected by the direction of the magnetic field.

Several interesting possibilities are inherent in the generalized Onsager relations. A detailed experimental investigation of the thermo-galvano-magnetic effects of the antiferromagnetic single crystals should yield important results.

Nuclear Explosions

by

PROF. D. S. KOTHARI

It is more than an honour to be asked to give the Krishnan Memorial Lecture. Recalling how-so briefly the great work and example of Dr Krishnan is to uplift ourselves and strengthen our commitment to science, education and research. Dr Krishnan was a towering physicist, but his interests were not confined to physics alone. His idea of a 'complete physicist' was in tune with that of a complete man — an integration of scientific and humanistic cultures. In no small measure he personified this in himself.

I propose to speak about some aspects of nuclear weapons and the unprecedented danger to which human civilization is exposed because of their continued existence. We would only delude ourselves and imperil the whole future of mankind if we were to believe that because we have lived with A- and H-bombs for two decades, we could do so indefinitely or even for some decades more. It would be wholly irrational to ignore the possibility of some unpredictable or accidental happenings, some 'fluctuation' or aberration in the world political scene, unleashing a nuclear war. We may also recall that according to the work of L.F. Richardson [*Statistics of Deadly Quarrels* (1960)] the distribution of wars throughout history appears to be ruled by chance rather than fore-thought or planning. The frequency of wars conforms to a Poisson distribution.

It is well known that H-bomb laden planes are in the air as part of routine exercises. There have been a few accidental crashes but fortunately no explosion. The *New York Times* (April 3, 1962) reported that at the height of the Berlin crisis in 1961 nuclear-armed planes at US Strategic Air Command bases all over the world were alerted to take off in response to a radar alarm signal which, fortunately, within a few seconds, was discovered to be erroneous, caused by an electronic malfunctioning. False signals on early warning radar screens can arise from flock of birds, abnormal meteorological conditions, and unforeseen technical failures of electronic systems.

The current discussions of the problems of nuclear non-proliferation, and the draft treaty (prepared by the 18-Nation Disarmament Committee) before the UN, have lent additional interest and importance to the subject. The nuclear war

science and of power achieve a measure of real understanding, it is almost inevitable that major issues are often decided on superficial, and partisan, even irrational, considerations.

* * *

The progress of civilization has depended largely upon man's ability to harness energy to meet his diverse needs. The three kinds of energy processes known are gravitational energy, chemical energy which is essentially electrical in origin, and nuclear energy. The nuclear process is some million times more powerful than any chemical reaction. It may be observed that unlike gravitational and chemical energy, harnessing of nuclear energy is not possible without deep insight and considerable progress in fundamental science as distinct from empirical arts and crafts. Gravitational energy was adequate to meet the demands of tribal life. Chemical energy (burning of coal) led to the development of nation-states. It seems that nuclear energy will lead inevitably to one world or none at all.

Rutherford, in his Nobel Prize address in 1925, stated that nuclear transformations were of extraordinary scientific interest, but he could not envisage any possibility of their being ever harnessed commercially for production of energy. In September 1933, in his address to the British Association, he reiterated that anyone who looks upon nuclear transformations as a source of power is talking moonshine. Yet by the end of 1942 the atomic nucleus had become a source of energy in Fermi's historic uranium-graphite pile at Chicago. Since then progress in developing atomic energy has been truly phenomenal. The International Atomic Energy Agency (IAEA) lists 80 power reactors in operation today (USA has 18) of which the most powerful is of 475 MWe in Canada. (MWe = Megawatt, electric power output). The number under construction, according to IAEA, is 57, of which the most powerful single unit is of 1065 MWe in USA—this list also includes the three Indian reactors, at Tarapur (2 × 190 MWe) and Rana Pratap Sagar (200 MWe). The total power of the reactors in operation is 11,000 MWe and under construction 24,000 MWe. It is estimated that the world nuclear electrical-power by 1980 is likely to exceed 300,000 MWe (about a quarter of the *total* electrical power). This would mean fission of a few hundred tons of uranium a year, producing a comparable amount of plutonium every year. The present total electric power generation capacity in the world (thermal, hydro and nuclear) is around 650,000 MW.

At this point let me say a word about the discovery of uranium fission. The epochal idea of fission came to Otto Frisch in December 1938 in discussion with Lise Meitner who collaborated with Otto Hahn on chemical investigations on new elements produced on bombardment of uranium by neutrons. Frisch on his return after spending Christmas with Lise Meitner spoke about the new idea to Neils Bohr who was just leaving Copenhagen for the USA. Bohr's spontaneous comment was "Oh, what fools we have been! We ought to have seen that (fission) before." On January 26, 1938, at a theoretical physics conference in Washington, Bohr referred to

the discovery of Frisch-Meitner, and immediately everybody in the States who could do fission experiments started exploring vigorously the new field. Bohr soon recognised that it was the isotope U 235 which suffered fission on exposure of natural uranium to slow neutrons. Within a few months of the discovery, he in common with several other physicists foresaw the possibility of a chain process leading to a nuclear explosion. (The use of the word 'fission' by Frisch was based on the analogy of division of a biological cell.)

Fermi in Chicago achieved the first fission-chain reaction on December 2, 1942. This and the subsequent work leading to the atomic bomb test in July 1945 were carried out in utmost secrecy.

The first Soviet atomic pile went critical on December 24, 1946 under the leadership of Igor Kurchatov (1903-1960). He also played a leading role in the development of the A- and H-bombs and has been called the father of the Soviet nuclear weapons. The transuranic element of atomic number 104 which has been recently synthesised at Dubna (USSR) has been named Kurchatovium by the Soviet discoverers.

An interesting account of the history of the German effort to make an atomic bomb has appeared recently [David Irving, *The German Atomic Bomb* (1968)]. The Germans had an early lead in relevant basic knowledge, but curiously enough when it came to producing fissile material in quantity they rejected both the gaseous diffusion process and the graphite pile. These were the two processes which formed the basis of the American nuclear programme. The diffussion process probably did not receive serious attention because its discoverer, the physicist Gustav Hertz was a German Jew. The concept of the graphite-moderated pile was not pursued as Bothe, one of the leading German physicists of the time, had concluded on the basis of some wrong measurements by him on neutron cross-sections that scuh a pile could operate only with enriched uranium and not natural uranium. Almost the entire German effort was devoted to building heavy water reactor, but the project did not go far because of various difficulties including inadequate supply of heavy water.

Harry Truman, who was President of the USA at the time of the A-bombing of Japan wrote in his Memoirs in 1956 : "One event occurred in 1945 of such magnitude that it was to revolutionize our relations with the world and usher in a new era for humanity, the fruits and goals and problems of which we cannot even now grasp. It was the atomic bomb."

The Soviet Union successfully conducted its A-bomb test in *August 1949*, much earlier than many had thought possible. In his book *Nuclear Weapons and Foreign Policy* (1957), Henry Kissinger observed : "No conceivable acquisition of territory—not even the occupation of Western Europe—could have affected the strategic

balance as profoundly as did the Soviet success in ending our (USA) atomic monopoly."

The major events in the development of nuclear weapons are summarised in the following table :

Year	USA	USSR	UK	France	China
Aug. 1945	A [U, Pu; 20 KT]				
Apr. 1948	A [100 KT]				
Aug. 1949		A			
Oct. 1952			A [Pu]		
Nov. 1952	H [5MT]				
Aug. 1953		H [1 MT]			
Mar. 1954	H [15 MT]				
Nov. 1955		H [10 MT] air burst			
Nov. 1956	H [15 MT] air burst				
May 1957			H [5 MT] air burst		
Dec. 1960				A [Pu]	
Oct. 1964					
June 1967					A [U] H air burst [?]

A=Atomic bomb; H=Thermonuclear bomb;
Within brackets, U stands for Uranium 235, and Pu for Plutonium 239.
KT=Thousand tons of TNT equivalent.
MT=Million tons of TNT equivalent.

On October 16, 1964, the People's Republic of China detonated its first A-bomb at Lop Nor in the desert of western Sinkiang—it was the first Asian country to do so. The fissile material used was U 235. The Chinese thermonuclear explosion was achieved in June 1967. This was only two and a half years after the first fission explosion, whereas the corresponding period was 7 years for the USA and 4 for the USSR. The separation of uranium isotopes for making nuclear weapons is an extremely complex, a formidable, technical undertaking. It needs very highly developed metallurgical and engineering industries to produce special alloys, compressors, porous cells and so on, required for uranium hexafluoride gaseous diffusion plant. The possibility cannot be eliminated that the Chinese employed the

relatively simpler gas centrifuge process. Also sophisticated electronic computers are necessary to deal with calculations concerning thermonuclear devices and their testing. The Chinese emergence as a potentially major nuclear power (eventually in the category of USA and USSR) has added a new dimension to the complex problems and dangers facing a nuclear-armed world.

A limited test ban treaty, "Treaty banning nuclear weapon tests in the atmosphere, in outer space and under water", was signed in 1963 in Moscow by the USSR, USA and UK. The aim of the treaty is to renounce tests which result in fallout hazards. By the end of 1966, 116 countries of which 109 are members of the UN joined the treaty, but France and China are not parties to it. The treaty would have been hardly possible but for the initiative and effort of the scientific community generally. It may be mentioned that since signing the treaty, underground explosions even of megaton yields have been conducted by the superpowers to improve the efficiency of their weapons*.

An UN treaty to ban nuclear weapons from outer space was signed by USA, USSR and UK in January 1967.

* * *

A 20 kiloton atomic bomb liberates energy equal to that released in an explosion of 20,000 tons of chemical explosive (e.g. TNT). In an A-bomb this energy comes from the fission of one kilogram of fissile material. Of course, the actual amount of fissile material in a bomb is much more as it is only a relatively small fraction of the total which undergoes fission. The fission process can continue only so long as the fissile-mass configuration exceeds the "critical size". The more sophisticated a bomb-design, greater is the proportion of the fissile material utilized in fission. (Factors which increase the efficiency are improved geometry of the reacting mass, using a casing material which reflects neutrons and strengthening of the bomb envelope so that the moment of burst is not too early in relation to the build-up of the chain reaction.) It is believed that for a "crude" 20 kiloton bomb about 20 kilograms of uranium 235 are needed. If the bomb is of plutonium, the amount is somewhat less than 10 kilograms. Weapon-grade uranium is highly enriched, containing more than 90 per cent of uranium 235. Weapon-grade plutonium has to be relatively free from plutonium 240, which is non-fissile. Plutonium 240 has a half-life of $1{\cdot}2 \times 10^{11}$ years for spontaneous fission, whereas the value for plutonium 239 is $5{\cdot}5 \times 10^{15}$ years (35 spontaneous fissions per gram of plutonium 239 per hour). To produce weapon-grade plutonium, the burning time of uranium in a reactor has to be kept down resulting in a low efficiency of fuel utilisation. To give

*As an example of the military importance of tests we may recall US Defence Secretary McNamara's observations (*Time*, Aug. 23, 1963) that whereas the US could develop without further tests a 50 to 60 MT warhead for delivery by a B-52 bomber, it would need testing which could be underground to develop a 35 MT warhead for ICBM Titan II.

an example : the relative abundance of plutonium 240 in plutonium produced from irradiation of natural uranium in a thermal reactor (neutron flux $\sim 10^{13}/cm^2$-sec) for a burn-up time of 3000 Mwd/ton is about 20 per cent, whereas it is less than 10 per cent for a burn-up time of 1000 Mwd/ton. [Mwd = Megawatt days].

In an atomic bomb the process of energy liberation is a fission chain reaction which builds up exponentially, extremely fast, in a few micro-seconds, once the fissile mass exceeds its critical size. In a thermonuclear bomb, on the other hand, except for its triggering mechanism which is a fission chain explosion—an A-bomb as it were—the source of its tremendous energy is (i) fusion reaction and (ii) fission reaction in natural uranium (uranium 238). In uranium 238 there is no build-up of a chain process—it is not a fissile material like U 235. To produce fission in U 238 a supply of energetic neutrons is necessary and in a thermonuclear bomb these are provided by a fusion reaction. The main ingredients of the fusion process are heavy hydrogen and lithium 6. The intense heat of the triggering device initiates a thermonuclear reaction in heavy hydrogen (and tritium which comes from lithium 6 on its interaction with neutrons). A thermonuclear bomb is often called an H-bomb. The crucial idea which made the H-bomb project technically feasible was given by Edward Teller in 1951. It still remains highly classified. There is a possibility that the triggering of a thermonuclear bomb can be done with "shaped-charges" employing chemical explosives, but here is no clear evidence on this point. If the bulk of the energy comes from the fission of uranium 238, the bomb is called fission bomb or a "dirty" bomb. It is also referred to as a triple-F bomb (Fission-$\frac{U\ 235}{U\ 238}$ Fusion-Fission). If the bomb design is such that the bulk of its energy is derived from a fusion reaction, the quantity of radioactive fission products released from the explosion would be much less than in the case of a fission bomb. It appears that for triggering an H-bomb, U 235 is perhaps more suitable than plutonium. Pu 239 has a much stronger *alpha* activity than U 235; and as alpha particles on interaction with light impurity elements in the fissile material produce neutrons, a much stronger implosion may be possible with U than with Pu. For a massive nuclear programme of A- and H-bombs, it may be more economical to base it on U 235 than on plutonium. This presumably is the reason why the Chinese nuclear programme has been based on U 235.

The 'progress' in nuclear weapons technology from early 1940s to early 1950s may be summed up as : *From uranium 235 to uranium 238.* This made nuclear explosion energy a thousand times cheaper.

The spectrum of A-bombs extends from probably half a KT to a few hundred KT; and of H-bombs from a fraction of a MT to a hundred MT. A "standard" A-bomb is usually assumed to be 20 KT and a "standard" H-bomb of 20 MT.

The radius of destruction of an atomic bomb is of the order of a few miles and the destruction is almost entirely caused by blast and heat. In the case of a thermonuclear bomb, the destruction due to blast and heat alone covers a few hundred square miles, comparable in size to the largest of metropolitan cities. This is not all. The highly radioactive fall-out (specially from a "dirty" bomb) will cause fatalities over an area of several thousand square miles and significant damage over hundreds of thousands of square miles. A thermonuclear bomb detonated close to the ground sucks millions of tons of debris into the fire ball. For a ground burst the bulk of the fission products comes down as 'local fall-out', extending over a period of hours to days. But a small part is projected high into the atmosphere, gets widely scattered and gradually, over a year or so, settles down almost over the entire surface of the earth. This is called 'global fall-out'. For an air burst, the fire ball consists only of a few tons of bomb material, and the fall-out is largely global. An atomic bomb dropped over a city will kill around ten to hundred thousand people and a hydrogen bomb dropped over a metropolis will kill around a million people (omitting fatalities caused by local fall-out over a much larger area). Megaton bombs and megadeaths go together. To appreciate the order of magnitude of the radiological hazards from a nuclear explosion, a 20 MT bomb liberating its explosion energy from fission of 1000 kilograms of uranium produces an equal amount of fission products (and 10 kg of neutrons) at the time of detonation. The radioactivity of the fission products decays according to the $1/t^{1\cdot2}$ law. At eight hours after detonation the activity will be equivalent to about 80 million roentgen square miles. This means that if the explosion products were uniformly spread over an area of 100,000 square miles, any individual in that area, in the open, will receive a total radiation dose (gamma rays) of 800r. The lethal dose for a man is of the order of 600r. Further, one ton of fission products contains 13·5 kilograms of strontium 90 with an activity of 2 million curies. Strontium 90 constitutes a serious danger to men through contamination of vegetation, food and water. The maximum permissible body burden of strontium 90 is two microcuries.

The total explosion energy released in all wars including the two world wars is of the order of a few megatons. The three figures serve to illustrate the order of

5—500—50,000 MT

magnitude of three important aspects of nuclear explosions. 5 MT may be taken to be the total energy released in all wars, whereas 500 MT is nearly the total energy of nuclear test explosions so far conducted; and 50,000 MT gives the order of magnitude of the energy which may be unleashed if a full-scale nuclear war broke out. 50,000 MT is the symbol of the precarious 'balance of terror' between the super-powers.

An important concept is that of *assured destruction capability*, a term made familiar by Mr McNamara, the US Defence Secretary till recently. Assured destruction capability of a country A in relation to country B represents the level of

damage that the country A can certainly inflict on country B on the assumption that it was B which *first* attacked A with as much force as it could conceivably deploy. If the *assured destruction capability* of A *exceeds* what B believes to be the maximum damage that it could accept without collapsing completely, then B would be deterred from mounting a first attack on A. If the assured destruction capability of each of the two countries (as assessed by the other) exceeds unambiguously what the other *firmly* believes to be its maximum limit of acceptable damage, they would be mutually deterred from attacking one another. There will be between them a balance of terror. So long as decisions are taken rationally, they would not attack each other. To do so would be totally suicidal for both of them. But to suppose that decisions of the kind we are contemplating will be always taken rationally, is to make too big an assumption. And it would be folly to stake the whole future of mankind on such an assumption. Also, it ignores the crucial point that there is yet no rational theory of what constitutes a maximum acceptable damage; and, whatever the estimate based on cold calculations, whether it will not melt away in the emotional heat and stress of an unpredictable crisis. Further, whatever the danger, it is likely to be far more when instead of two there would be within a few decades, as is bound to happen on present trends, three super-powers in a triangle of terror balance.

The following table reproduced from McNamara's evidence before the US Senate Committee in January 1967 (see *Survival*, April 1967) provides a grim illustration of the US-SU terror balance. It shows that in a nuclear war between the super-powers the fatalities on either side would be of the order of tens to hundreds of millions.

Number of fatalities in an all-out strategic exchange
(in millions)†
(Assumes no Soviet reaction to US ABM deployment)

US programmes	Soviets strike first, US retaliates		US strikes first, Soviets retaliate*	
	US fat.	Sov. fat.	US fat.	Sov. fat.
Approved	120	120	100	70
Posture A	40	120	30	70
Posture B	30	120	20	70

†The fatality figures represent deaths from blast and fall-out; they do not include deaths resulting from fire-storms, disease, and general disruption of everyday life. The data in the table are highly sensitive to small changes in the pattern of attack and small changes in force levels.

*Assumes US minimizes US fatalities by maximizing effectiveness of strike on Soviet offensive systems.

The first line in the table assumes no anti-ballistic missile defence, whereas Posture A envisages a light and Posture B a more sophisticated ABM defence. The cost for Posture A has been estimated to be at least $ 12 billion, and for Posture B $22 billion.

According to McNamara, significant Chinese nuclear threat to the continental USA will not develop before the mid-1970's. It is unlikely that before that the Chinese could deploy operational ICBMs in significant numbers, though it may have within two or three years a couple of submarines with nuclear missiles of rather short range. The USA is planning to provide a somewhat elementary type of ABM defence consisting of about 10 missile batteries with radar installations costing about $4 billion, with the ostensible aim of neutralizing any possible Chinese threat in the coming decade. The effectiveness of this austere ABM defence in reducing US fatalities from a Red Chinese attack in the 1970's is shown below (according to McNamara) :

US fatalities—in millions	Chinese strike first (operational inventory)	
	X missiles	3X missiles
Without ABM	5	10
With ABM	0+	1

By 1980's China's nuclear capability, of which submarine launched missile is likely to be an important component, is expected to reach a level when it could cause 'unacceptable destruction' to the super-powers.

It is important to recognise a special characteristic of the nuclear arms race. The increasing sophistication and amplification of nucler weapons and the scaling up of defence preparedness and costs since Hiroshima have steadily *diminished*, and not improved, the security for the super-powers. What does this mean ? A nuclear attack and the inescapable counter-attack in the early 1950's could have inflicted casualties numbering a few millions on the two sides; in the late 1950's the numbers could have been in tens of millions, whereas today the casualties could be of the order of *hundreds* of millions. As J. B. Wiesner and H. York state (*Scientific American*, October 1964) : "*It is our considered professional judgement that this dilemma (increasing military power and decreasing national security) has no technical solutions.*" Wiesner has been Chairman of the U.S. President's Advisory Committee and Special Science Assistant to the late President Keneddy; York has been Chief Scientist of the Advanced Research Project Agency of the U.S. Department of Defence. Again, McNamara in his statement to the Senate Committee in January 1967 observed that any defensive measures, such as deployment of ABM, by the one super-power to reduce the assured destruction capability of the other super-power could be offset always by the opposing side improving its offensive

capability—increasing the number of weapons or size of war-heads or better penetration aids to defeat enemy defences; or any appropriate combination of these. And what is significant is that the cost of improved defence to reduce damage would be far more than the cost of offensive measures required to neutralize it. Referring to the question of US deployment of ABM system he said : "*In all probability, all we would accomplish would be to increase greatly both their defence expenditures and ours without any gain in real security to either side.*"

The present level of nuclear armouries of USA and USSR, as commonly depicted in current literature, is given in the following table :

Nuclear Armoury, USA and USSR in 1967

(Based on *US News & World Report*, July 24, 1967)

Category of Nuclear Warhead		USA		USSR	
		No. of Warheads	Total yield (in Mega-tons)	No. of Warheads	Total yield (in Mega-tons)
Inter-continental Ballistic Missiles	ICBM	1054	1650	300 to 500	4000
Intermediate Range Ballistic Missiles	IRBM	None	None	750	750
Submarine-Launched Ballistic Missiles	SLBM	656	460	247	196
Anti-Ballistic Missiles	ABM	None	None	Tallinin system (Galosh & Griffin missiles)	n. a.
Strategic Bombers		680	27,200	110	24,400
Space Weapons		None	None	SCRAG Orbital Weapon	30 (each)
Total		2390	29,310	2607	29,346

Despite the clear futility of the arms race there is no noticeable slowing down in the effort of the super-powers to improve and multiply their nuclear arsenals. The USA is developing a new generation of ICBMs. Multiple Independent Re-entry Vehicles (MIRV) are to replace within a few years existing ICBM war-heads.

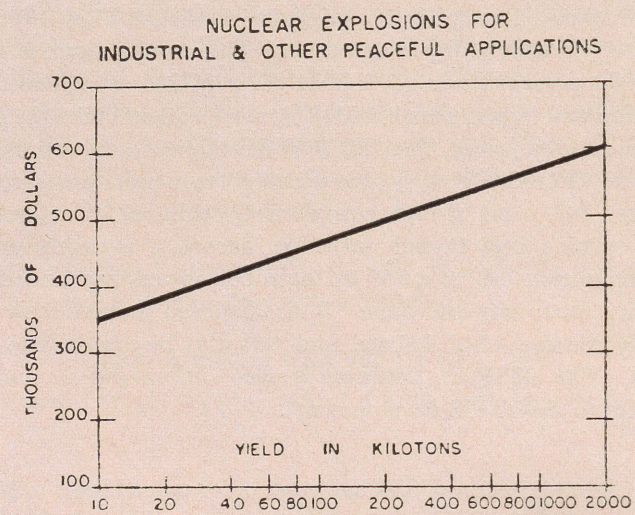
An MIRV will carry a number of megaton war-heads (5 to 10) which could be directed separately to widely dispersed targets. This would increase several-fold the effectiveness of the present stock of ICBMs. The ICBM *Poseidon* with increased targeting precision and larger, possibly MIRV, war-head will take the place of *Polaris* in nuclear-powered submarines. The USSR is developing a "fractional orbital bombardment system" (FOBS). The system which corresponds to a satellite trajectory just short of one full orbit would considerably enhance the element of surprise and cut down warning time, though targeting accuracy is likely to be poor. As noted earlier deployment of the ABM by the super-powers has added a new dimension to the arms race between them. It is believed that Moscow and Leningrad have a relatively massive ABM defence, and this may be extended to cover most of Western Russia. The USSR, it appears, is also improving its nuclear-submarine launched missiles to match US developments.

It will be observed that the USSR has gone in for much bigger megaton warheads, presumably to match the very hard emplacement of the US underground ICBMs. It seems that the strength of the nuclear arsenals of the two super-powers has increased more than four-fold since 1960. McNamara recently stated that USSR has now 720 ICBMs in operation, twice the number a year ago at the beginning of 1967. It had 30 long range nuclear submarines and 155 intercontinental bombers. By mid-1969 the USSR is likely to equal the USA in the number of land-based ICBMs, but the deployment of multiple warheads by the USA will give it a lead in striking power. There is no evidence of any scaling down of the arms race. [Professor Linus Pauling's estimate of the world's total nuclear stock is 500,000 MT (USA-320,000; USSR-120,000).

* * *

A word may be added about the cost and cost effectiveness of nuclear weapons. A basic quantity is the cost of weapon-grade fissile material. Its cost may be assumed as of the order of $10,000 per kilogram for a country such as the USA with large production of weapon-grade fissile material, tens to hundreds of tons a year. [By mid-1963 the total stock of US fissile material was about 600 tons of which 400 tons was for warheads (25,000 'tactical' and 700 'strategic' warheads.)] For a country with a small production programme, say a few A-bombs a year, the cost would be orders of magnitude higher, because of the huge cost of R & D and production installations. For a super-power an A-bomb would cost a few hundred thousand dollars, and a high-yield H-bomb about a million dollars. Fig. 1 gives the price of nuclear explosives for commercial applications, as indicated by the USAEC at the Third Plowshare Symposium, 1964*. For an H-bomb a major element of cost is that of its fission triggering device. It is apparent that nuclear explosives (whether used in war, or peace?) are hundreds of times cheaper than chemical explosives for the same amount of explosion energy; and the costs are likely to be much lower

*The AEC price of $350,000 for 10 KT explosion and $600,000 for 2 MT refer ' to a time when nuclear explosives will be purchased in quantity for routine commercial applications." [Dr Bhabha's figures (*Statesman*, Oct. 25, 1964) were Rupee-equivalents of these dollar prices].



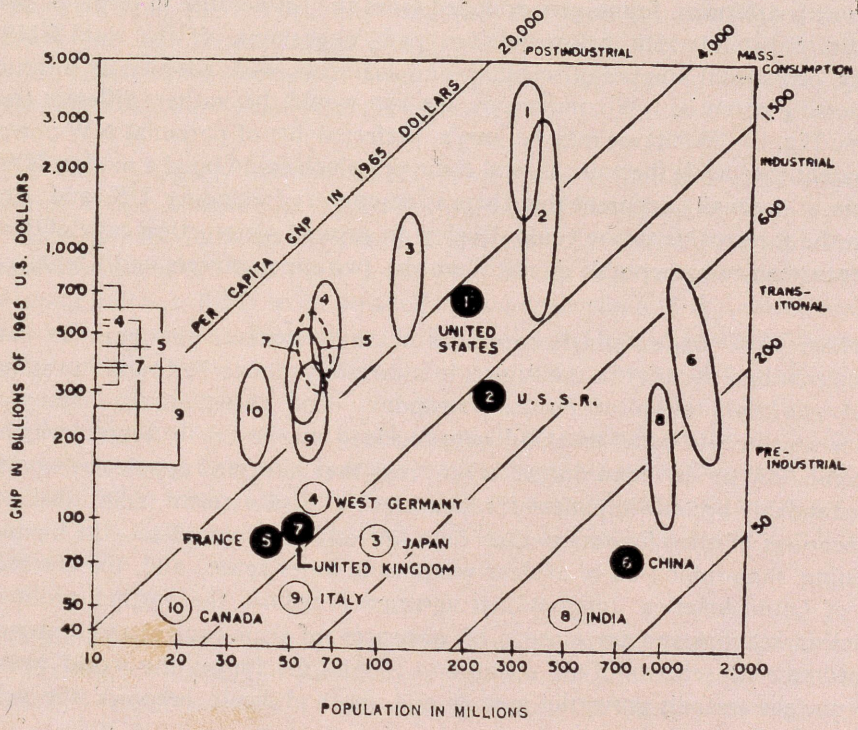
Source :—Proceedings of the "Third Plowshare Symposium Division of Tech. Information," USAEC, 1964, Page 9

Fig. 1

still because of continuing R & D effort. If we include the cost of delivery systems, *nuclear weapons are thousands of times cheaper than conventional weapons to produce the same effect.*

The USA, it may be noted, has been for over two decades spending on nuclear weapons and delivery systems from 25 per cent to now about 12 per cent of its annual military budget. This represents 2·4 to 1·2 per cent of its GNP. The corresponding UK figure is 0·7 per cent of GNP for 1963 and 0·3 per cent for 1967. A recent report (October 1967) prepared by a UN Panel of Experts (which included Dr V. A. Sarabhai, Chairman of the AEC) has discussed what it would cost a country with a relatively developed scientific and industrial base to go in for a modest nuclear weapons programme. The report gives two illustrative examples. The cost estimate for warheads and delivery system for what is called a *modest nuclear capacity*, consisting of 30 to 50 jet bombers, 50 medium range missiles of 3,000 km range in soft emplacements, and 100 plutonium warheads, is estimated at $1700 million (that is, about $2 billion) spread over a period of 10 years. The second example deals with a *small but high quality nuclear force* which would include 20 to 30 thermonuclear weapons, 100 intermediate range missiles and also 2 missile launching nuclear submarines. The cost is estimated at $5,600 million (that is, about $6 billion) over 10 years. The important point made in the report is that the time needed to develop even a modest nuclear capacity would be at least 10 years for "reasonably industrialized nations." A crucial element is of course the availability of competent scientists and engineers in relatively large numbers required for

PROJECTIONS FOR THE TEN MAJOR COUNTRIES



Circles refer to 1965 and ellipses represent estimate range for 2000 A.D.
Black circles represent nuclear powers.
Inclined (45 degree) lines denote (for 1965) per capita GNP in 1965 U.S. dollars.
[The vertical brackets on GNP axis are aid to projections of some of the ellipses].

[From *Daedalus*, Summer 1967]

Fig. 2

R & D work and production. The report, on the basis of a comparison of the national defence expenditures of different countries, concludes that at present 'there are only about six countries in the world', other than the five nuclear weapons powers, that could expect to develop even a modest nuclear capacity without jeopardising their national economies. The table at the end reproduced from the report gives defence, education, and health expenditures of different countries, expressed in equivalent dollars. For a small high quality nuclear capability referred to above, only six countries (besides the five nuclear powers) appear capable of finding the necessary resources in men and material. These six, according to the report, are India, Canada, Italy, Poland, Sweden and the Netherlands. (If we take the Rupee-Dollar exchange rate after devaluation in 1966, India would rank below Italy in the above list). In identifying countries which could develop

a nuclear weapons capability in the next decade or so, the criterion adopted in the report is arbitrary. Japan gets excluded from the list because in terms of defence expenditure it stands 15th, below Belgium and Yugoslavia. If the total GNP of a country, or its total number of scientists and engineers, were adopted as a criterion for assessing potential NW competency, the list would be rather different (*see* for example Fig. 2). Whatever may be one's preferred list of potential NW powers, it is apparent that while there are several countries which could build a modest NW programme, it is equally apparent that there is no country (including UK and France) that in the foreseeable future could develop an assured destruction capability which could cause an "unacceptable damage" on the two super-powers and China.

The report "unhesitatingly concludes .....that whatever the path to national and international security in the future, it is certainly not to be found in the further spread and elaboration of nuclear weapons. The threat of the immeasurable disaster which could befall mankind were nuclear war ever to erupt, whether by miscalculation or by mad intent is so real that informed people the world over understandably become impatient for measures of disarmament additional to the few measures of arms limitation that have already been agreed to—the limited ban on testing, the prohibition of nuclear weapons in outer space, and the nuclear-free zone of Latin America. International agreemeat against the further proliferation of nuclear weapons and agreements of measures of arms control and disarmament will promote the security of all countries..... And the longer the world waits, the more nuclear arsenals grow, the greater and more difficult becomes the eventual task."

* * *

The Non-Proliferation Treaty jointly drafted by the USA and the USSR, and under current discussion, has as its main aim the prevention of nuclear-weapon states from passing nuclear weapons or relevant technical knowledge to non-nuclear-weapon nations; and it commits the latter from accepting, or taking steps to produce, nuclear explosives. The treaty provides for inspection by the International Atomic Energy Agency (IAEA) of activities of non-nuclear-weapon nations to ensure fulfilment of the obligations under the treaty. The treaty recognises the right of all nations to engage in research and development on the peaceful uses of nuclear energy, and for that purpose to exchange to the fullest possible extent scientific and technological information. It contains an article to ensure that potential benefits from any peaceful applications of nuclear explosive will be available (at as low a cost as possible) bilaterally or through an appropriate international body to non-nuclear-weapon states parties to the treaty, on the basis of agreed international procedures. The treaty requires that after 5 years of its commencement a conference shall be held to review the operation of the treaty. After 25 years a conference shall be convened to decide whether the treaty shall be extended for a limited period or continue indefinitely. The decision shall be taken by the majority of the parties to the treaty.

A striking thing about the NPT is the strong support it has received from both the USA and the USSR. That for the first time the two super-powers are manifestly and with determination pursuing a common though admittedly a limited aim is something whose immediate and long-term importance, political, military and psychological, should not be under-estimated.

The NPT is clearly asymmetric between nuclear-weapon and non-nuclear-weapon states. It can, however, be argued that in the contemporary situation a measure of asymmetry is inevitable in any practical step towards lessening tension. Perhaps, the weakest element of the draft treaty lies in an inherent difficulty of sharply demarcating between R&D work directed towards peaceful and that which may lead to military applications. Weapon-grade fissile material would be needed for advanced type reactors. What about research and development, as also stock of fissile material, needed by industry in a non-nuclear weapon state to build fast reactors? How is one to label a stock of fissile material as peaceful or not so ? Recently the IAEA has agreed to supply enriched nuclear fuel to some countries. For instance, Spain is to receive 25 kilograms of uranium enriched to 93·5 per cent, and Pakistan 4·5 kilograms of 90 per cent enriched uranium for the research reactor at Islamabad.

Science cannot be divided into peaceful, not-so-peaceful, and hideous science. Even Ramanujan's formula of partitions found its application in understanding the properties of nuclei relevant to the realisation of the chain reaction. It is not science which is dangerous, but it is the misuse of science which is so. The Non-Proliferation Treaty attempts to draw an artificial distinction between peaceful and non-peaceful application. We must remember that science is universal and international. Scientific discoveries by non-nuclear nations and peaceful application of science can be put by nuclear powers to military use. The Non-Proliferation Treaty would imply that whereas non-nuclear powers would be denied the development of their own techniques of peaceful use of nuclear explosions, the nuclear powers would be free to put to military use the scientific discoveries made by non-nuclear nations.

What about chemical and biological weapons ? Recently serious concern was expressed by many US scientists including such internationally well-known names as John Edsall, Bentley Glass, Felix Bloch and E. L. Tatum who urged President Johnson to stop the employment of "anti-personnel and anti-crop chemical weapons in Vietnam." [see, *Science*, January 13 and 20, 1967; also Brig. Gen. J. H. Rothschild, USA (Retd), *Tomorrow's Weapons* (1964).] In the case of biological weapons a non-proliferation treaty would hardly make any sense as in the field of biology it is almost impossible to draw a line between peaceful work and its military applications.

The NPT may, some fear, divert and distract attention from the main goal which is to achieve, by gradual stages, complete and comprehensive disarmament.

In this direction there is no visible progress. At the same time it must be recognized that there is a strong contrary view that progress towards comprehensive disarmament has been thwarted because most of the effort so far has been towards proposing a step which must link demonstrably with other succeeding steps. On the other hand some progress might have been possible if each step was examined by itself rather than made a link in a chain which inevitably would be vague and raise hypothetical issues.

Nuclear-weapons and NPT alternatives

	To sign NPT	Not to sign NPT
To make nuclear weapons	USA, USSR, UK	China, France
Not to make nuclear weapons	Canada, Sweden, Japan	India (?)

* * *

The real danger which confronts the world today is the danger of 'poverty'. Some appear to think that whereas they could trust nuclear weapons in the hands of superpowers, they are not prepared to place the same trust when it comes to their being in the hands of less affluent or developing nations. Even assuming that this is a valid-assessment, what it truly implies is that the real danger is poverty. What is urgently necessary is that serious effort is devoted to seeing how advanced countries could help the economic developmet of the newly developing countries. Like the non-proliferation issue the problem is not technical, but largely political.

The solution to the great nuclear challenge of our times can be found only on the basis of hope and faith, trust and confidence, courage and wisdom. The only possible goal—to be attained by stages—can and ought to be comprehensive and complete disarmament. The world has to learn a new, and in the present nuclear context, the great lesson that Ashoka, one of the greatest emperors in world history, learned in Kalinga.

Ashoka (273 B.C.-232 B.C.) proclaimed in one of his famous Rock Edicts: "The country of the Kalinga was conquered by King Priyadarsi beloved of the Gods, eight years after his coronation. In this war in Kalinga men and animals numbering one hundred and fifty thousand were carried away captive from that country, as many as one hundred thousand were killed there in action, and many times that number perished. ...(But) Now the beloved of the Gods thinks that .. what is conquest through Dharma is now considered to be the best conquest... So, whatever conquest is achieved in this way, verily that conquest creates an atmosphere of satisfaction everywhere both among the victors and the vanquished. In the conquest through Dharma, satisfaction is derived by both parties."

As Bohr emphasised in his 1950 letter to the UN Secretary General, the terrifying prospect of nuclear competition between nations can only be avoided through a universal agreement in true confidence. In the present age of science and technology the fate of all nations is inseparably bound together. To think otherwise is only to delude ourselves. As Bohr observed: "... An open world where each nation can assert itself solely by the extent to which it can contribute to the common culture and is able to help others with experience and resources must be the goal to be put above everything else... .. The very fact that knowledge is in itself the basis for civilization points directly to openness as the way to overcome the present crisis. Whatever judicial and administrative international authorities may eventually have to be created in order to stabilize world affairs, it must be realized that full mutual openness, only, can effectively promote confidence and guarantee common security.....

"The efforts of all supporters of international co-operation, individuals as well as nations, will be needed to create in all countries an opinion to voice, with ever increasing clarity and strength, the demand for an open world."

The appendix gives some informatson about radiation units, radioactivity of fission products, damage effects, of high-yield fission explosions and other relevant and data summarised from *Nuclear Explosions and Their Effects*, Second Edition (1958).

I am grateful to Shri A. Nagaratnam for his assistance in preparation of this lecture.

NATIONAL EXPENDITURES IN EQUIVALENT UNITED STATES DOLLARS

(Reference—United Nations *Statistical Yearbook* : *1965*, Tables 192 and 185)

	Defence		Serial No.	Education		Health	
Year	$ millions	Country		$ millions	Country	$ millions	Country
1964	54,514	USA	1	35,528	USA	40,836	USA
,,	14,765	USSR	2	16,106	USSR	20,339	USSR
,,	5,615	UK	3	4,346	UK	3,231	Germany, F.R.
,,	4,016	Germany, F. R.	4	2,250	Germany, F. R.	3,138	UK
,,	3,891	France	5	2,003	Italy	1,207	Australia
,,	1,702	India	6	1,820	Canada	838	Poland
,,	1,568	Canada	7	1,033	Japan	415	Canada
,,	1,467	Italy	8	1,008	Netherlands	245	India
,,	924	Poland	9	1,002	Poland	183	Denmark
,,	774	Sweden	10	736	Belgium	173	Sweden
,,	734	Netherlands	11	582	India	172	Venezuela
,,	539	Australia	12	572	Sweden (1963)	165	Brazil
,,	496	Belgium	13	468	Australia	163	New Zealand
,,	443	Yugoslavia	14 (1963)	373	Brazil	136	Argentina
,,	427	Japan	15	301.5	Mexico (1963)	128	Bulgaria
(1963)	369	Spain	16	273	Finland	107	Finland
1964	340	Switzerland	17	262	Argentina	73	Yugoslavia
,,	320	Turkey	18	243	Denmark	64	Mexico
(1963)	314	Brazil	19 (1963)	221	Bulgaria	60.6	Turkey
1964	302	Argentina	20	219	Turkey	53.8	Peru
,,	267	UAR	21	217	Austria	50.8	UAR
,,	250.5	Israel	22 (1963)	205	Spain	47.5	S. Africa
,,	241	Pakistan	23	174	Venezuela	42	Belgium
,,	235	Denmark	24	164	Norway	38.6	Israel
(1962)	220	Bulgaria	25	149	Philippines	37.9	Norway
1964	208	Norway	26	140	UAR	36	Netherlands

(*Contd. on page* 39)

Defence			Serial No.	Education		Health	
Year	$ millions	Country		$ millions	Country	$ millions	Country
1964	193	Iran	27	115	New Zealand (1963)	35.7	Nigeria
,,	188	Greece	28	115	Peru	26	Pakistan
,,	176.3	Portugal	29	110	Chile	21.2	Thailand
,,	165	Indonesia	30	107	Yugoslavia	14.1	Portugal
,,	160	South Africa	31	105	Thailand	11.1	Austria
,,	144	Venezuela	32	94.6	Israel	6.0	Indonesia
,,	132	Austria	33 (1963)	89	Nigeria	3.7	Switzerland
,,	130	Mexico	34	75.1	South Africa		
,,	130	Finland	35	70	Pakistan		
,,	94.1	Thailand	36	42.3	Portugal		
,,	78.5	Chile	37	41.1	Switzerland		
,,	78.2	Peru	38	14	Indonesia		
,,	77	New Zealand	39				
,,	76	Philippines	40				
(1963)	53.3	Nigeria	41				

The Table is reproduced from "Report of the Secretary-General on the effects of the possible use of nuclear weapons and on the security and economic implications for States of the acquisition and further development of these weapons" (October, 1967).

APPENDIX

PHYSICS AND NUCLEAR WEAPONS—SOME BASIC INFORMATION

Units and Constants

Roentgen or *r*—Unit of dose of X-rays and gamma rays, employed in dealing with biological effects/damage. [It is the quantity of X- or gamma-radiation such that the associated corpuscular emission produces, per 0.001293 gram of air (1 cc of air at NTP) ions—in air—carrying one electrostatic unit of electricity of either sign]. A dose of about 400 *r* is lethal in 50 per cent of cases. Every person receives from the 'natural background radiation' a dose of about 0.1 *r* per year.

Milliroentgen or *mr*—One-thousandth of 1 *roentgen.*

Rad—Unit of dose of any ionizing radiation corresponding to an energy absorption of 100 ergs per gram of tissue or any other material. For X- and gamma rays 1 *r* is very nearly equal to 1 *rad.*

Rem (Roentgen-equivalent-man)—Unit of dose of any ionizing radiation which has the same biological effects as 1 *rad* of X-rays. [Dose in *rem* = (Modifying factor) × (Dose in *rad*). The modifying factor depends upon the Relative Biological Effectiveness of the radiation in question. It is practically unity for gamma and beta rays, 10 for fast neutrons, protons and alpha particles, and 20 for atomic nuclei. For X-rays it is unity by definition].

Curie or *Ci*—Unit of activity (radioactivity)--It is equal to that quantity of radioactive element or mixture of elements in which the number of disintegrations per second is 3.7×10^{10}. (1 gram of radium has an activity of 1 *curie.*)

Millicurie or *mCi*—One-thousandth of 1 *curie.*

Microcurie or μ*Ci*—One-millionth of 1 *curie.*

Micro-microcurie or $\mu\mu$Ci or pCi—One-millionth of 1 *microcurie* (1 pCi = 2.22 disintegrations per minute).

Strontium Unit or *S. U.*—Unit of *strontium* 90 *activity* equal to 1 pCi of strontium 90 per gram of calcium.

Megaton-Fission—One megaton-fission is equivalent in explosion energy to 1 million tons of chemical explosive (TNT)

$= 1.0 \times 10^{15}$ gram-calorie
$= 1.2 \times 10^{9}$ kilowatt-hour

Fission Products—Gamma activity at time *t* from detonation, of fission products liberated in 1 megaton-fission is $\frac{3.4 \times 10^{11}}{t^{1.2}}$ *curie* (*t* is in hours).

Dose (Gamma) from Fission Products—10,000 curies per square mile give gamma *dose rate* of about 1 *r* per day.

Strontium 90—One megaton-fission liberates 0.1 million curies of strontium 90

= 0.5 *mCi* per square mile (if uniformly distributed over earth's surface)

= 1 *strontium unit* (for 'average soil' containing 20 grams of calcium per square foot in top 2.5 inches).

mev (million-electron-volt)—Unit of energy useful in dealing with atomic phenomena : Equal to the energy of an electron falling through 1 million-volt $= 1.60 \times 10^{-6}$ erg.

NOMINAL HIGH-YIELD FISSION EXPLOSION (20 M. T.)

(Fission of 1,000 kg : Number of nuclei undergoing fission $= 2.6 \times 10^{27}$)

Total explosion energy	= 20 million ton of TNT
	$= 8.4 \times 10^{22}$ erg
Released in explosion :	
(i) Fission products	= 1,000 kilogram (2,200 lb)
(ii) Neutrons	= 10 kilogram (22 lb)

Gamma activity of fission products

Time from detonation	Rate of emission of gamma ray energy (mev per sec)	Gamma activity (curie)
1 minute	2.1×10^{25}	8.1×10^{14}
1 hour	1.5×10^{23}	6.0×10^{12}
1 day	3.4×10^{21}	1.3×10^{11}
1 week	3.3×10^{20}	1.3×10^{10}
1 month	5.8×10^{19}	2.2×10^{9}
1 year	2.9×10^{18}	1.1×10^{8}

The rate of emission of beta energy is about the same as of gamma energy, though the number of beta particles is about twice the number of gamma ray photons.

Beta activity of strontium 90 contained in fission products : 1.9×10^{5} curie (= 10 millicurie per square mile, if deposited uniformly over the earth's surface).

Gamma dose rate from active deposit on plane surface :

One roentgen per day corresponds to gamma ray energy of 10,000 mev per square centimeter per second ($= 2.6 \times 10^{14}$ mev per square mile per second). *Hence for fission products, 1 roentgen per day corresponds to gamma activity of* 10,000 *curie per square mile* (= 1 *millicurie per square meter*).

Beta dose : For a lightly clothed man the dose from beta rays emitted by fission products – unlike the gamma dose the beta dose is confined only to the body tissues within a centimeter or so from the skin — can be very roughly taken to be 10 times the gamma dose.

[From *Nuclear Explosions and Their Effects*, published by the Publications Division, Government of India (1958), p. 100].

EFFECTS (EXCEPT FALLOUT) OF 20 M.T. HIGH-YIELD EXPLOSION

(Air burst at a height of about 1½ miles)

Blast (Duration of positive phase of blast pressure : about 10 seconds)		Heat flash (Duration : about 20 seconds)	Initial nuclear radiation (Duration : about one minute)
Category of damage	Radius of damage (miles)	On a clear day fires and skin burns (on exposed skin) may extend up to a radius of 20 miles, that is, beyond the zone of heavy blast damage. On a hazy or cloudy day the effect would be substantially reduced.	The gamma rays will give a dose of about 400 r up to radius of 2 miles and no significant hazard beyond four miles. The radius of hazard due to neutrons would be such less (and as such their effect can be ignored).
(A) Total destruction of houses	5		
(B) Irreparable damage to houses	8		
(C) Houses not reparable in short-term (must be vacated for repairs)	13		
(D) Houses reparable in short-term (need not be vacated for repairs)	20		
(E) Light damage such as broken windows	80		

In the first minute of detonation, the fireball containing most of the fission products would travel upwards a distance of a few miles (say, 5 miles).

[From *Nuclear Explosions and Their Effects*, published by the Publications Division, Government of India (1958), p. 64]

GAMMA DOSE FROM LOCAL FALLOUT : 20 MT EXPLOSION

(ground burst, assuming one-fourth of fission products goes into local fallout)

Duration of exposure : 8 hours from detonation to (8+T) hours

Fallout is assumed to be uniformly distributed over A sq. miles

T	12 hr	48 hr	1 week	1 month	1 year
RA (roentgen—square miles, in millions)	3·5	6·6	9·5	12·3	15·5

[From *Nuclear Explosions and Their Effects* published by the Publications Division, Government of India (1958), p. 117]

ESTIMATED DETECTION RANGES FOR 1-MEGATON DETONATIONS IN SPACE*

Ground-Based Techniques

Method	Range in Miles	
	Unshielded	Shielded**
Direct visible light (daytime)	200,000 a	>200,000 a
Direct visible light (nighttime)	>2,000,000 a	>2,000,000 a
Fluorescence	6,000,000 b	60,000-600,000 b
Backscatter Radar	~10,000	~1,000
Cosmic Noise Absorption	~10,000	~1,000
Ionosonde Method	~10,000	~1,000
Electromagnetic Pulse	>1,000	>1,000
VLF Phase Anomaly	6,000,000	60,000-600,000
Electric and Magnetic Fields	~10,000	~10,000

Satellite-Based Techniques

Method	Ranges in Miles	
	Unshielded	Shielded**
Thermal X-rays	1,000,000,000	4,000,000
Prompt gamma rays	2,000,000	2,000,000
Delayed gamma rays	2,000,000	2,000,000
Prompt neutrons	1,000,000	1,000,000
Delayed neutrons	100,000	100,000
Trapped electrons	30,000	30,000

a) These estimates apply only if the line of sight is not obscured by cloud cover.
b) Fluorescence is less affected by cloud cover than is visible light.

*Except for the trapped-electron method, the estimated ranges for 1 to 10-kiloton detonations are roughly one-hundredth to one-tenth those for 1 megaton.

**A shielded explosion is one in which the nuclear device is surrounded by a thin sheet of lead or other material to reduce the amount of radiation emitted. Such a shield would be particularly effective for thermal X-rays.

[From *The Effect of Nuclear Weapons*
S. Glasstone, US-ABC (1962), p. 698]

COMPARATIVE RISKS FROM MAIN SOURCES OF IRRADIATION

(Relative to those from Natural Radiation, taken as 1)

Source	Hereditary[a] effects	Somatic effects[a]	
		Leukaemia	Bone tumour
Natural sources	1.00	1.00	1.00
Medical irradiation[b]	0.30	0.4-0.8	?
Fallout from tests up to December 1961	0.11	0.15	0.23
Fallout from continued testing	0·23	0.28	0.43

a) No comparison can be made between hereditary and somatic effects.

b) Calculated on the basis of all information received, largely from countries with advanced medical facilities.

[From *Report of the UN Scientific Committee on the Effects of Atomic Radiation* (1962), p. 30]

ESTIMATED DAMAGE TO WORLD POPULATION (2.5×10^9) FROM GLOBAL FALLOUT

(Assumed average strontium 90 level in man = 10 *strontium units*)

(i) Leukaemia	150,000	additional deaths over a period of 30 years
(ii) Bone-tumours	50,000	additional deaths over a period of 30 years
(iii) Life-shortening	2 weeks	per person : 100 million man-years for the world population
(iv) Genetic effect*	400,000	'genetic deaths', the number in the first generation being 10 per cent of the above figure

*Due to external exposure to fallout gamma radiation. (The strontium 90 contribution to genetic effect is negligible.)

NOTE—The numbers in the table—and these are indicative of the likely orders of magnitude—give the damage over a period of 30 years. It is readily seen, as the half-life of strontium 90 is about 30 years, that the total damage spread over a century or so (resulting from an initial stratospheric load of strontium 90 of the order of 100 megatons of fission energy) would be about twice that given in the table.

[From *Nuclear Explosions and Their Effects* published by the Publications Division, Government of India (1958), p. 204]

Lecture

by

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I was deeply moved and highly honoured to receive Dr Verma's invitation to give the K. S. Krishnan Memorial Lecture on this special occasion, to commemorate what would have been his 70th birthday. Dr Krishnan was a brilliant scientist, a friend of Mr Nehru, who made him a National Professor. He was greatly respected not only in his own country but all over the world. Yet he made no difference between the high and the low and was equally happy and friendly with all. He came to stay in our home in March, 1937 and my family loved him. He was so full of fun. I well remember his first coming into our house; my 2-year-old son took one look at him and then ran and flung his arms around Dr Krishnan's knees. My son is now 34 years of age, a medical man with a big country practice. I asked him whether he rememberd anything of Dr Krishnan's early visits. "Oh yes", he said, "he took salt with his grapefruit". Well, I don't think, he always took salt with his grapefruit, but perhaps he did once, because he liked to experiment. That year there was a late fall of snow, unusual in March; and he was delighted because he had never seen snow before except on distant mountain-tops. He went out into the garden and played with it like a child. My daughters also remember how, on a later occasion, he came with us by pleasure boat along with River Thames to see Windsor Castle. We all enjoyed that quiet journey on the water in the sunshine.

He was very much concerned about international affairs and was a widely-read and deeply-religious man. He had many conversations with my husband and myself on these subjects. But he could be absent-minded. My husband's most amusing memory is finding Dr Krishnan knocking on his own bedroom door and waiting for himself to tell him to come in.

I had first consulted him when I became interested in the magnetic anisotropy of crystals, a subject on which he was an authority. And I acted as his lecture assistant when he gave a course of lectures at the Royal Institution, London, on this subject. He was a clear lecturer and a fine teacher. But above all he was a great scholar, and I have therefore chosen as the subject of this Memorial Lecture a

scholarly subject in which I am sure that he would have been interested, because one of his main interests was the nature of the solid state.

I shall discuss the geometrical changes that occur in the structures of single crystals during phase transitions, the formation of mixed crystals, and various kinds of chemical reactions, such as isomerization, dimerization and decomposition, whether spontaneous or brought about by irradiation, by heat or by pressure.

First of all I should explain that a soild may be crystalline or amorphous. In both states the atoms or molecules will be approximately the same average distance apart. In both they will be individually vibrating about their average positions with frequencies and amplitudes which are dependent on temperature and pressure. A crystalline soild has a regular, symmetrical, periodic pattern of atoms, ions, molecules or groups of molecules in 3 dimensions. (Paracrystalline solids may be regular in only 1 or 2 dimensions.) It has a definite melting-point. An amorphous soild has no regular, periodic internal pattern, and no definite melting-point. As the temperature is raised it softens and becomes less viscous, becoming a liquid gradually. In a liquid there is the same lack of arrangement as in an amorphous soild; but in the latter the thermal vibrations are about fixed (though irregular) positions, whereas in a liquid the atoms or molecules can roll over one another and change places. Ideally, the pattern in a crystalline solid is perfectly regular. In reality it is nothing of the kind even apart from the disorder involved in thermal vibration. There will be regions of relative perfection, sometimes quite large; but there are also dislocations, vacant sites, impurities, changes of orientation and grain boundaries. These are of great importance in connection with many of the physical properties of real solids. They are also of importance in chemical reactions, which observation has shown to be initiated at these imperfections. As the temperature is raised the disorder involved in these imperfections increases and melting occurs when both disorder and thermal vibration amplitudes are sufficient to break down the interatomic or intermolecular forces that maintain the orientational order of the crystal. The dependence of chemical reactions in the solid state upon temperature may be as much the result of increased static disorder as of the increased dynamic vibrations.

I shall concentrate mainly on chemical reactions in single crystals.

Substitution

One of the simplest types of such chemical change is the substitution of one kind of atom, ion or group by another. As an example one may consider hydroxy-apatite, the crystalline component of bone material. In this structure the hydroxyl groups occur within hexagonal channels; and they may be replaced by flourine to form fluorapatite or by carbonate groups to form carbonate apatite in which some of the carbonates may also replace phosphate groups. The famous 'Piltdown

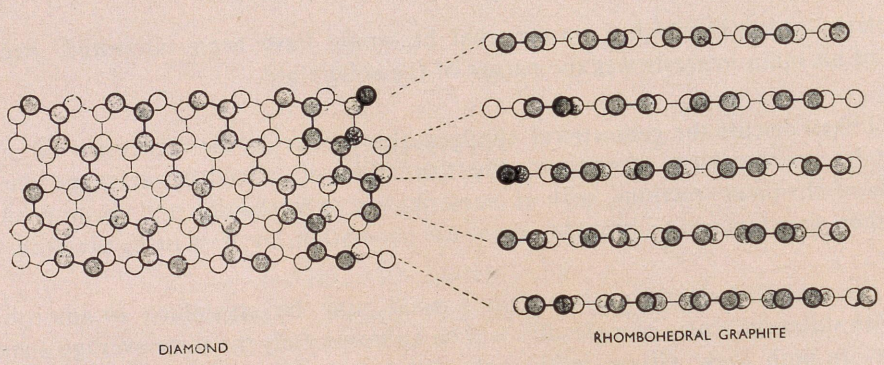


Fig. 1—The diamond-to-graphite transformation

Man' forgery was detected in part because the bones were found to contain insufficient fluorine for their alleged age.

Phase Transitions of First and Second Order

Diamond was one of the first substances the crystal structure of which was fully and correctly determined. Each carbon atom is surrounded tetrahedrally by four others. If heated to about 1500°C in vacuo it changes into graphite, in which the carbon atoms are arranged in plane hexagonal networks, separated by the van der Waals distance of 3.4 Å (the Å unit is 10^{-10}m). This first-order phase transition is chemically drastic and involves a large density change, but is geometrically simple (Fig. 1). In diamond there are puckered hexagons of carbon atoms in the {111} planes, which are parallel to the eight octahedral faces of the natural diamond habit. Diamond is the prototype of all the aliphatic carbon compounds. Its thermal vibration amplitudes are normally very small indeed and it is a very perfect, very hard substance. But when heated to 1500° (in vacuo so that it does not combine with the oxygen of the air) the thermal vibrations are large enough to allow the conversion to what is essentially the more stable low-pressure form, graphite, the prototype of the atomic compounds. The {111} puckered hexagons of the diamond become the (0001) plane hexagons of the graphite (Fig. 1), the transformation being one in which there is a considerable amount of preferred orientation in the final product.

The transformation of graphitic carbon to diamond, which is the basis of the synthetic diamond industry, is much more difficult. It does not occur by simple pressure except at very high pressures (shock-loading) or at very high temperatures, of the order of 5000°C. But it can be made to occur at much lower pressures and temperatures (of the order of 50 kilobars and 1500°C) if the carbon is first dissolved in a metal such as nickel which is able to act as a kind of catalyst because the network of the {111} octahedral planes of nickel fits very well both the (C001) hexagonal network of graphite and the {111} octahedral network of diamond, thus encouraging an epitaxial transition.

Epitaxy (Royer, 1928) comes into many chemical reactions very directly. It is the tendency of one crystalline substance to grow in an oriented way on another as a substrate because there is a simple geometrical relationship between the networks which are in contact. These will be naturally occuring faces for each substance, and $na \times mb$ for one substance should match $n'a' \times m'b'$ for the other, where a, b, a′, b′ are small crystal translations and n, m, n', m', are small integers. The match need not be exact; in certain circumstances over 10 per cent misfit can be tolerated (Newkirk and Turnbull, 1955) but usually the match is within 2 or 3 per cent. Chemical similarity between the two substances is not necessary, but it assists epitaxy if it exists (Kleber *et al.*, 1963). A well-known example of epitaxy is the growth of ice on silver iodide which is one basis of rain-making from supercooled clouds. Camphor can grow on quartz, anthraquinone on sodium chloride, urea on ammonium chloride, and so on, always in denite orientations.

Sometimes a phase transition involves only a minor geometrical adjustment, with no abrupt change of properties such as density or specific heat (although there may be a specific heat anomaly at the transition point). A typical example is the change from rhombohedral to hexagonal graphite, which can be brought about mechanically, since the only difference in structure is in the stacking of the hexagonal sheets of carbon atoms.

Diamond is cubic in structure. A very rare hexagonal arrangement of tetrahedral carbon atoms (which bears the same relationship to diamond as wurtzite does to zinc blende, both being crystalline ZnS) has recently been found and has been named *lonsdaleite* by the American scientists concerned in its discovery. It was first identified by Dupont scientists as a minor component, with diamond, of the conversion of well-oriented graphite by shock-loading at extremely high pressures. It was subsequently found, again in very small quantities, in meteoritic diamond. But it occurs almost free from diamond when a *single crystal* of graphite is subjected to relatively high pressures (Fig. 2) even at comparatively low temperatures. Here, however, the corresponding faces are not, as might have been supposed, the basal plane of graphite matching the basal plane of lonsdaleite. It is found that on release of compression the *basal* plane of graphite becomes the *prism* face of lonsdaleite, the reason being that the epitaxial fit in this direction is a very good one.

Most of the research work currently in progress in the Department of Crystallography at University College, London, is concerned with relatively simple organic compounds and with the geometrical changes that occur in single crystals of these when they are subjected to the various kinds of chemical change that I mentioned previously. I shall now discuss some examples of the different types of reaction studied.

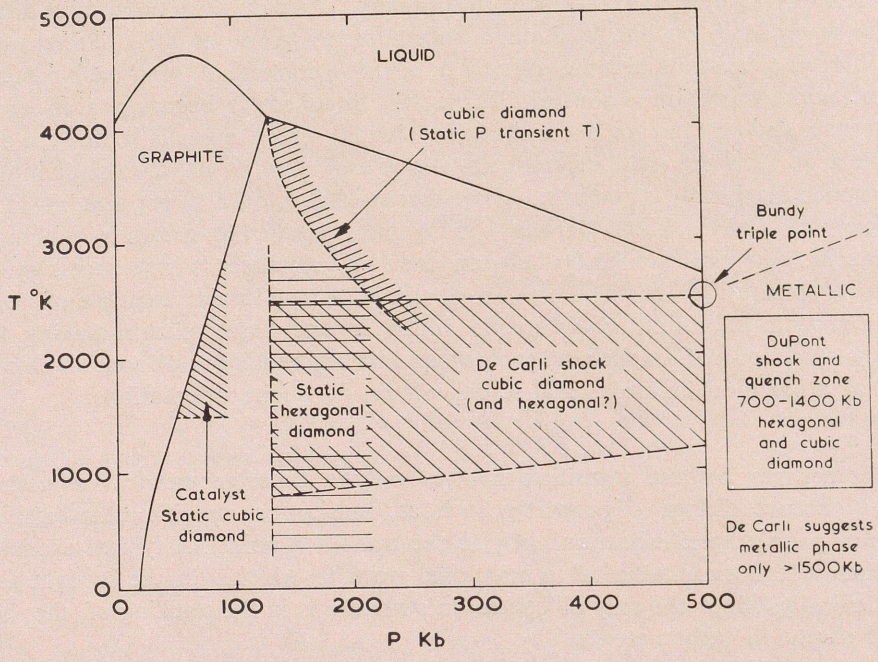


Fig. 2—Phase diagram for different forms of carbon

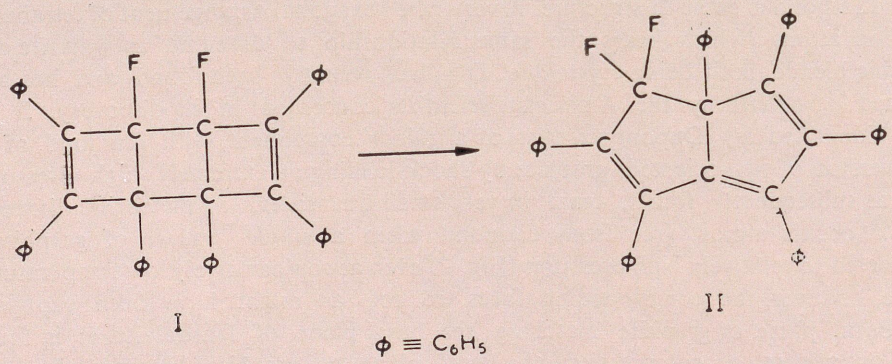


Fig. 3—Isomerisation which occurs rapidly on melting I, or slowly in single crystals of I below the M. P.

Isomerisation (Rummery, 1968)

One of the most curious changes is that shown in Fig. 3. Substance I is colourless, and melts at about 182°C. The melt, which is of a deep red colour, recrystallises within about 70 seconds giving yellow dichroic crystals of II, having a melting point about 220°C. Both substances are triclinic and their crystal structures have been determined by Dr E. W. Hughes and his colleagues (*see* Rummery, 1968 for references).

Dr Hughes noticed, however, that crystals of I began to turn yellow even before they melted and he suggested to me that some molecules in the single crystal I might be turning into molecules of II by spontaneous isomerisation. The question to be considered whether, if this occurred, the change took place in isolated molecules, or in little groups to form 3-dimensional inclusions, or in chains or planes to form some 'mesomeric' intermediate structure.

X-ray diffraction studies combined with observation of dichorism which develops in crystals of I as the temperature is raised show that molecules of II do form in crystals of I and that these isomeric molecules are parallel but isolated. It is a striking commentry on the imperfections that exist in real crystals that such a drastic change of shape of the molecule can occur without the breaking up of the crystal as a whole.

Dimerisation

Many of our studies have been of the dimerisation, in the solid state, of anthracene derivatives. One of the most interesting of these studies is the formation of dianthracene from anthracene (O'Donnell, 1968) when crystals are exposed to UV irradiation. This has been both affirmed and denied. We have found that it requires filtered UV radiation from which wavelengths greater than 3000 Å have been removed, in order to bring about the reaction. If the whole spectrum is used the reverse reaction take splace simultaneously with the dimerisation and the result is 'no change'. The dianthracene molecules are not isolated, but they form only moderately well-orientated inclusions within the initial single crystal of anthracene. There are two or three possible relative orientations, each having a different epitaxial fit on to the anthracene matrix. One of these gives much better orientated inclusions than the other two, and hence sharper diffraction spots.

Mixed-crystal formation and pseudo-symmetric short-range order

It is obvious that alloys and intermetallic compounds are different chemical substances from the pure metals of which they are formed. So also are mixed crystals (solid solutions) of different organic compounds. It is not always easy to form such mixed crystals in any desired proportions. One cannot do it simply by crystallizing from a melt of known composition, nor from a solution of the end compounds in known proportions (Glazer, 1968). The actual composition of the crystals formed can, however, be determined from their infra-red spectra. We have found, in two instances, that a miscibility gap exists in the mixed-crystal series even when the end compounds are isomorphous, if one of them has pseudo-symmetry and is therefore partly disordered. This occurs in the cases of anthrone, $C_{14}H_{10}O$ (Flack, 1968), which forms mixed crystals with anthraquinone, $C_{14}H_8O_2$; and of N-oxyphenazine $C_{12}H_8N_2O_2$ (Glazer, 1968) which forms mixed crystals with phenaxine, $C_{12}H_8N_2$. Anthrone and N-oxyphenazine both have pseudo-symmetric crystal structures. It is impossible for these molecules to be centro-symmetrical but they behave as if they

were. This must mean that they are disordered in such a way that equal numbers of asymmetric molecules are pointing in inverse directions. If we call a molecule pointing one way A, and its inverse molecule B then there are three possibilities. The first is a completely ordered arrangement:

A B A B A B A B etc. or A A B B A A B B etc.

The second is a completely random arrangement:

A A B A B B A B A A A B A B B B B A A B A B etc.

The third is an arrangement having regions of short-range order which are, however, only of an approximately uniform size and which are separated by random regions:

A B A B A B A B B A B A B A A B A B A B A A B B B A B A B etc.

The first would have a 'superlattice'. The second would have a definite pseudo-symmetrical structure, unit being (A+B)/2. Each of these would give a diffraction pattern consisting of sharp reflexions, although in the second case there would also be heavy diffuse background scattering. The third arrangement would be distinguished by some kind of *patterned* diffuse scattering. The question is whether this kind of short-range-order pattern could be distinguished from the diffuse thermal-vibration pattern, which is also, of course, due to another kind of short-range-order. The studies made by Flack and Glazer show that the *static* effect of the short-range order gives a diffuse pattern, which is readily distinguished, in general, from the *dynamic* effect due to thermal vibration (Fig. 4). Both effects are best observed on X-ray diffraction photographs of stationary single crystals taken with characteristic CuK radiation plus the continuous (white) spectrum. The sharp spots on Fig. 4 are Laue spots; the short diffuse streaks along horizontal 'layer-lines' are due to the short-range order; the remaining diffuse spots and patches are due to thermal vibration. From the shapes of the short-range-order streaks it is possible to calculate the approximate size of the regions concerned. In the case of anthrone it is found that the short-range order extends for about 36Å in the *b*-axis direction, and for about 25Å along the *c*-axis direction, whereas along *a* there is a complete disorder.

The question then arises : when anthraquinone is dissolved in anthrone (or phenazine in N-oxyphenazine) to form a solid solution, are these rods or sheets of short-range order broken up at once or do the solute atoms go first between them ? X-ray diffraction studies of the whole range of mixed crystals show that the short-range order persists, certainly to about a 60 : 40 mixture. When, however, anthrone is dissolved in anthraquinone no observable short-range order occurs : the solute molecules are probably randomly placed. Between these two extremes there is a region of immiscibility which seems to begin as soon as the proportion of anthraquinone is so high that the short-range order would have to break down. The sequence in the phenazine—N-oxyphenazine series is



Fig. 4—X-ray photograph of a stationary anthrone crystal (Flack, 1968)

0 to 10 per cent N-oxyphenazine : randam substitution

10 to 52 per cent N-oxyphenazine : miscibility gap

52 to 100 per cent N-oxyphenazine : sheets or rods of short-range order between which the phenazine molecules go.

Decomposition, Slowly or Explosively

The example of decomposition most completely studied by X-ray techniques is that of anthracene peroxide, $C_{14}H_{10}O_2$, (a photo-oxide) which when irradiated by X-rays, or heated, decomposes to a mixed crystal of anthraquinone and anthrone. This reaction was found accidentally. One of my research students, Mr J. Stephens, was studying the structure of anthracene peroxide, the molecule of which is bent, with a bridge of two oxygen atoms between the central, aliphatic carbon atoms. Initially, the crystals gave quite normal X-ray diffraction patterns, but after a few hours' X-irradiation at room temperature new spots appeared on the photographs (Fig. 5). Eventually the original X-ray pattern had disappeared almost completely and had been replaced by the new pattern, which appeared to be that of anthraquinone, $C_{14}H_8O_2$. The crystal itself had not changed its external appearance at all, although it had gone black. The final product was, therefore, completely pseudomorphic on the original.

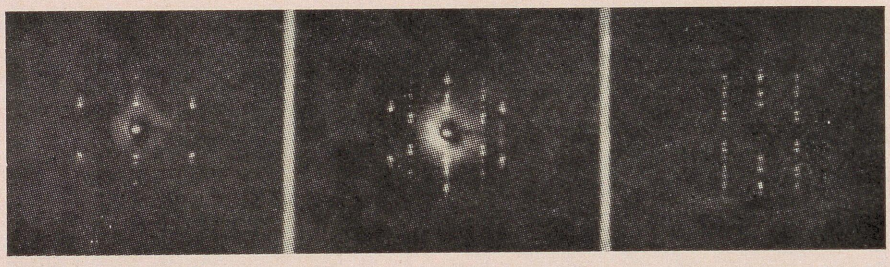


Fig. 5—X-ray photographs of the decomposition of anthracene peroxide

Shortly after this we saw, from a paper by Dr S. N. Srivastava (1964) that anthrone is isomorphous with anthraquinone and we found by experiment (Harris, 1965) that the two form mixed crystals. The product of the chemical decomposition of a single crystal of anthracene peroxide is a somewhat fibrous crystal and it would not be possible to distinguish by X-ray diffraction whether it is anthrone, anthraquinone or a mixed crystal or a mixture of the two. Moreover, since the crystal shape is unchanged, a density measurement would reveal nothing. However, a clear answer was obtained by mass spectrometry (Lonsdale, Nave and Stephens, 1966). The decomposition is ideally

$$2C_{14}H_{10}O_2 \rightarrow [C_{14}H_8O_2 + C_{14}H_{10}O] + H_2O$$

but in fact it is not so simple as this. The mixed crystal composition varies according to the history of the crystal and there are other, non-crystallised, products of decomposition, including some gaseous ones. The molecular volumes of the anthrone and anthraquinone are less than those of the peroxide. Since, however, the crystal shape does not change, there must be cracks and cavities, which develop in the structure. These would provide ample space to accommodate the water molecules and other gaseous products of the decomposition, provided that the reaction occurs slowly. At room temperatures, with intermittent X-irradiation, the reaction takes 300 hours or more to complete. As the temperature is raised, it goes more quickly, even without X-irradiation, but the course of the reaction and the products are similar. At about 800°C, for example, the reaction is effectively complete in about 7 hours. If the original crystal is heated fairly quickly to, say 110°C it falls to a powder; and if it is dropped on to a melting-point bar at about 163°C it melts and/or explodes almost simultaneously. Thus by examining the geometrical course of the reaction at room temperature one is able to see, in slow motion as it were, what occurs in the same reaction that leads to an explosion.

Details of the geometrical procedure can be obtained from Weissenberg and other types of X-ray diffraction pattern taken at intervals. The earliest stage of the reaction is one that produces fine continuous lines along k-constant festoons on Weissenberg photographs or continuous layer-lines on "stationary-crystal" patterns

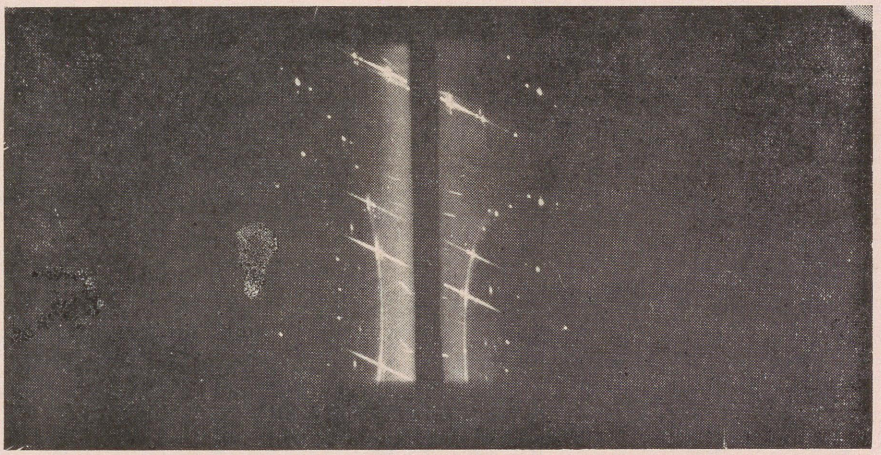


Fig. 6—Continuous lines on X-ray photograph of anthracene peroxide

(Fig. 6). The interpretation of these is that in the original anthracene peroxide matrix some *b*-axis strings of molecules have become disconnected with their neighbours — just an isolated string here and there. The intermolecular distance along the string does not change at this stage; the sharpness of the lines shows that the molecules are still peroxide molecules at the original distance apart. Fig. 7 shows why such a break-down of the structure might occur. Normal to the *b*-axis the oxygen bridges of neighbouring strings of molecules face one another at rather close quarters. Irradiation could partially ionise these atoms; increased thermal vibration will increase the change of their coming too close together and thus repelling one another, so that the crystalline attractions are overcome and the phase relationship breaks down locally.

As time goes on new continuous X-ray diffraction festoons appear which are characteristic of the final product. This means that some chains of photo-oxide molecules have been entirely converted into chains of anthraquinone, or anthrone or both. This is a genuine chain reaction. If the oxygen bridge of one molecule breaks, then the same break-down is triggered off all along the chain, probably because this means that along the chain hydrogen atoms are changing molecules or are being ejected. There is no intermediate stage observable between the long chain of photo-oxide molecules and the short chain of anthraquinone (or anthrone) molecules into which it is converted (Fig. 8). When there are enough chains of the end products formed, they 'crystallise', still within the anthracene peroxide matrix, into very small mixed crystals or perhaps into a mixture of crystals of anthraquinone and anthrone, in twinned orientations which are epitaxially related to the crystal of origin. Finally the change-over becomes complete except, presumably, for the original crystal surface layer which retains its exact shape. The molecular volume of an anthraquinone or anthrone molecule is 242Å^3. That of the original anthracene

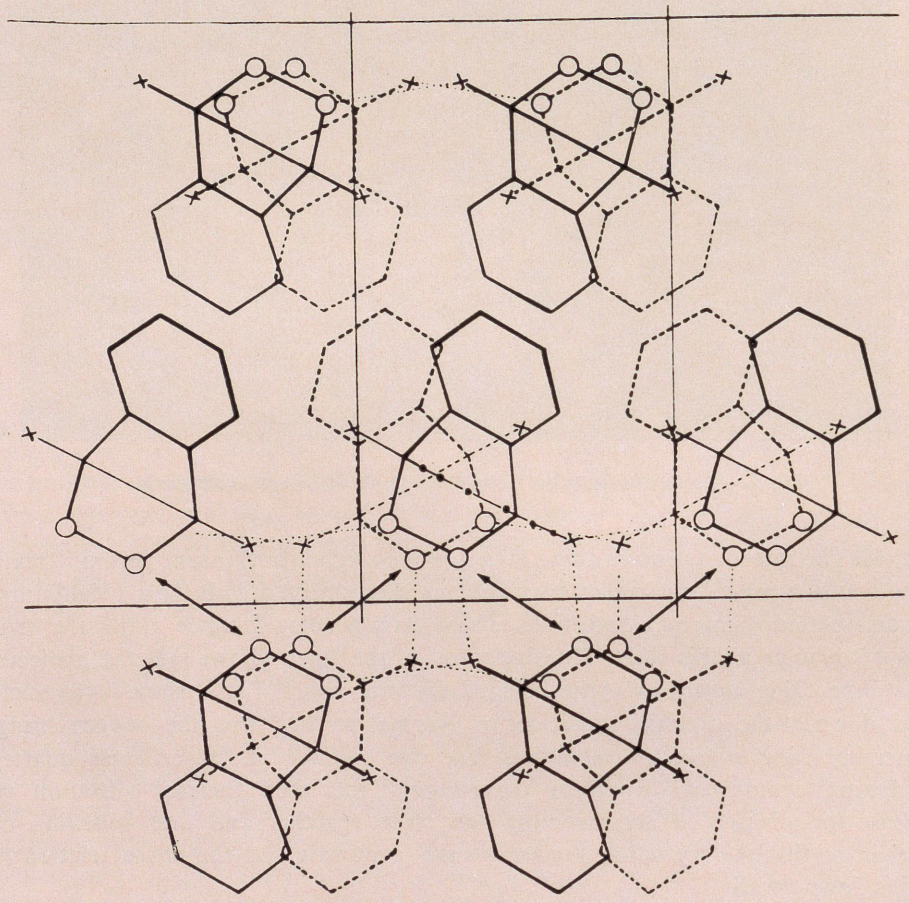


Fig. 7—Projection of the structure of anthracene peroxide normal to the *a* axis

peroxide molecule was 253Å^3. It follows that in recrystallising within the same single crystal 'skin' the final crystalline product takes up some five per cent less space than the original, so that there must be cracks or vacant sites; and these, given time for diffusion, would readily accommodate the 'gaseous' or amorphous part of the decomposition product, in particular, molecules of H_2O. If the temperature is raised so that the necessary time for diffusion to take place is not available, then the crystal falls to a powder or even explodes.

The variation of speed of decomposition with temperature is a property that it would be interesting to measure. So an attempt was made to find some X-ray diffraction pattern which was particularly sensitive to rate of change. Such a pattern is illustrated in Fig. 9. It shows the $k=0$ circle near to the primary beam trace, when the X-rays are nearly along the *b* axis, the crystal being stationary. The

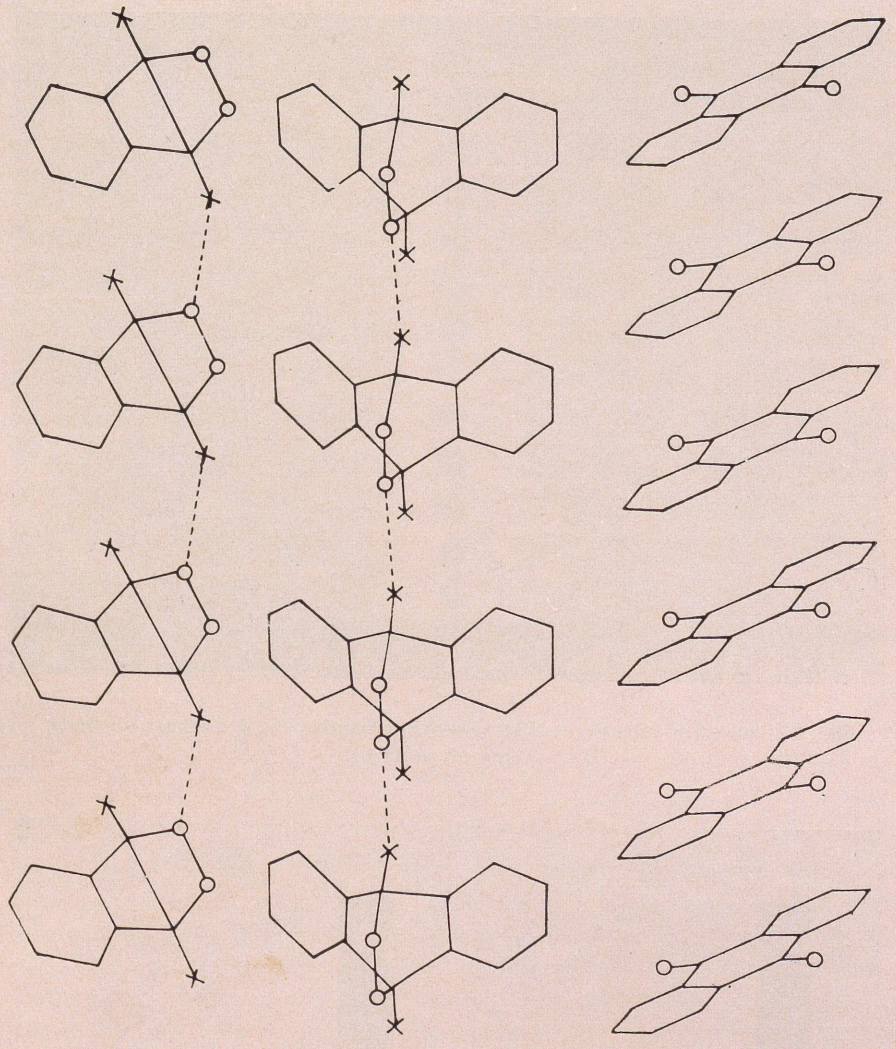


Fig. 8—Diagram showing two chains of anthracene peroxide molecules (unrelated by phase) and a chain of anthraquinone molecules

recording of intensity over a curved line or an extended area required a very specialized piece of equipment and it was found that the isodensitracer used by astronomers was very suitable for the purpose (Fig. 10). At present only tentative results are available, but it does seem that the 'stationary-crystal' method, using an X-ray beam which consists of a continuous spectrum with a very strong characteristic component, provides a powerful method of studying the types of disorder that occur in single crystals either resulting in pseudosymmetry or as the result of phase transitions or chemical reactions.

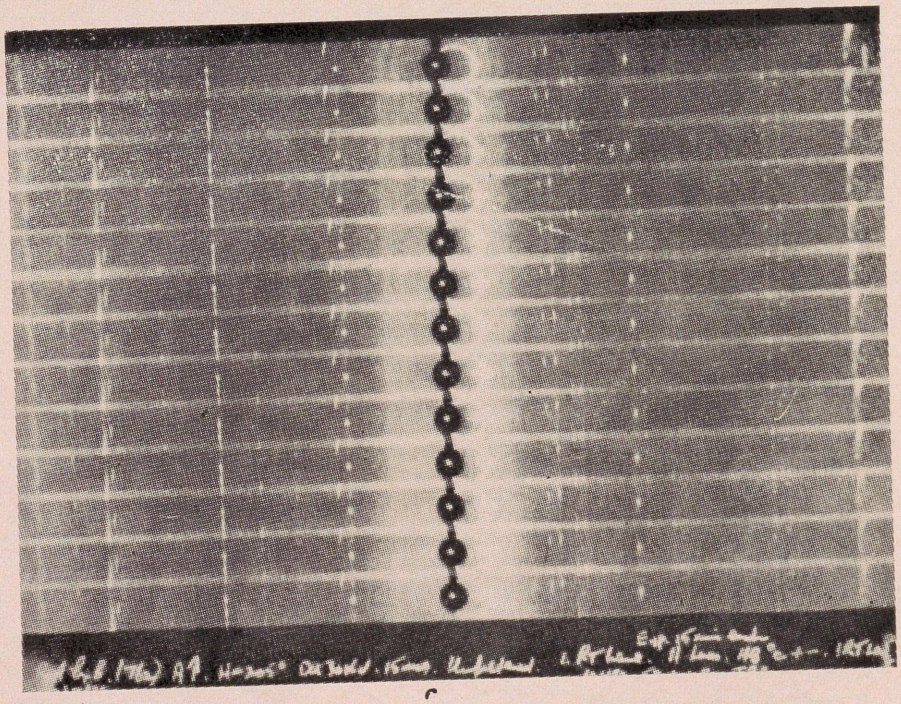


Fig. 9—Changes of intensity seen on sensitive diffraction circle as time progresses (Temp. about 80°C)

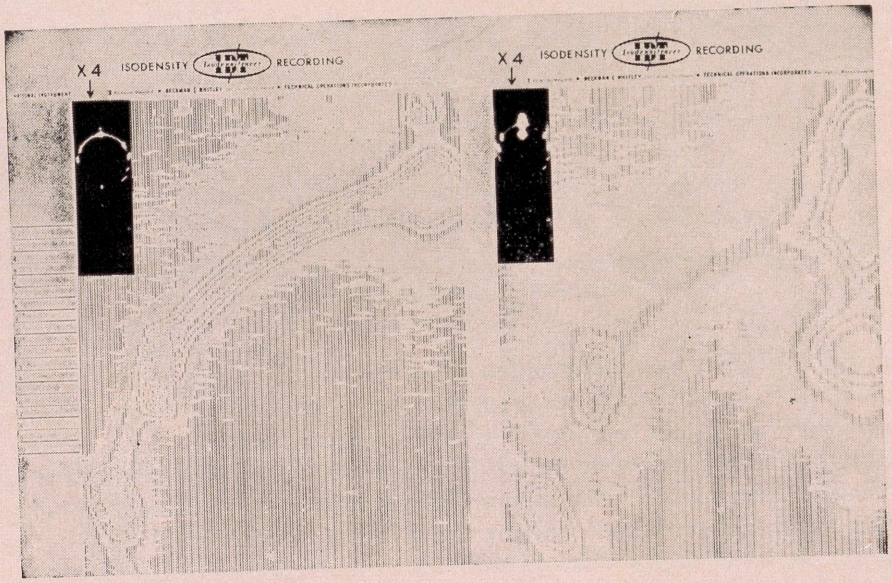


Fig 10—Isodensitracer intensity records of two half-circles

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Molecular Biophysics and Crystallography*

by

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Introduction

I will like to thank the National Physical Laboratory and in particular its Director, Dr A. R. Verma, for the honour they have done me in inviting me to deliver the Krishnan Memorial Lecture this year. Dr K. S. Krishnan was one of the foremost among the physicists of our country and a large number of workers in India in the field of Solid State Physics have been his students. Although I did not work with Professor Krishnan, I had the honour of having him as the member of the Selection Committee which made me Professor and Head of the Department of Physics in the University of Madras some 17 years ago. I porpose to tell you briefly today about some of the achievements of this laboratory, which started its work in the field of crystal physics, and which has now grown into a Centre of Advanced Study in Biophysics and Crystallography.

I have chosen the title of my talk as Molecular Biophysics and Crystallography. Molecular Biophysics is a field of comparatively recent origin. Several problems involving the physics of molecules, which are applicable to biological media, have been taken up for study, mainly by X-ray crystallographers, during the last thirty years. However, an understanding of the molecular structures occurring in biological materials and of the theory underlying the formation of such structures has emerged only during the last ten years. It is rather interesting that the development of this field of *bio*molecular structure has been the starting point of several innovations even in the study and solution of crystal structures itself. In fact, the methods of approach adopted by molecular biophysicists have turned out to be immensely fruitful in the evolution of new methods in crystallography—not only in the solution of crystal structures, but also in understanding the stability of periodic structures in crystals, and even the very process of crystallisation. It is my aim in this lecture to deal with some of the basic ideas in the field of molecular biophysics which are

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of particular applicability not only in biology, but also in physics and crystallography.

Biopolymer Helices

Although the study of crystal structures of inorganic and organic compounds progressed fairly rapidly, particularly during the 1930's and 40's, the developments in the study of biopolymer structures was not equally fast. Mainly because of the fact that the latter molecules were much larger than the molecules of the usual chemical compounds commonly met with, progress could be made only in those cases in which the molecular chain exhibited some simple symmetry properties. The best examples are those of cellulose, for which a preliminary structure was given by Meyer & Mark[1] in the 1920's and silk, for which the structure was given by Brill[2] and Meyer and Mark[3], also in the 1920's. In both these cases, the polymer chain had the symmetry of a twofold screw axis. Another example for which a structure with a twofold screw symmetry could be deduced was stretched hair (the so-called beta-keratin), proposed by Astbury and Woods.[4] Although the X-ray patterns of some other proteins like those in natural hair, muscle and tendon showed fairly clear diffraction patterns characteristic of a rotation photograph (fibre patterns, as they are called), their interpretation was not uniquely possible. Several attempts were made in the early days by well-known workers in this field, but all these suffered from the fact that some basic ideas required for their elucidation were lacking at that time. In fact, one of the central dogmas in crystallography, namely that a molecular structure in the solid state can have only screw axes of order 2, 3, 4, and 6 had to be completely revised. It is true that, if there is a 3-dimensionally periodic structure, then the above result is perfectly valid. On the other hand, it turns out that many of the biological fibres possess only structures having, what might be called, one-dimensional periodicity. These structures however coil up in the form of helices. The helices are packed side by side, but this packing often does not follow an exact lattice symmetry. When this happens, it can be shown that it is not necessary for the helix to have only 2, 3, 4 or 6 units per turn, but that it may have any number of units per turn—in fact the number of units per turn, n, may even be non-integral (say 10/3 or 18/5) and it may even be non-rational (e.g. a value such as 3.28...). This change in attitude did not take place all of a sudden, but it came as a result of a very slow evolution spread out over nearly a decade. In 1950, Bragg, Kendrew and Perutz[5] made an extensive study of the possible symmetries that may exist for helical chains of polypeptides (which are the synthetic analogous of natural proteins), but they considered only integral helices of the type acceptable to classical crystallographers. Within a year after that, the first revolution took place in this field, which was inaugurated by Pauling and Corey[6], who consider helices stabilised by conditions demanded by stereochemistry, rather than by crystallography. Putting in the condition that the helices must be stabilised by strong secondary valence bonds—in this case NH...O hydrogen bonds—they showed that a very stable type of folding of the chains is possible having about 3.6 to 3.7

residues per turn. This arrangement, the so-called alpha helix, is a very important secondary structure formed in almost every protein and is exhibited by a vast majority of synthetic polypeptides, which are analogous to the natural proteins. Pauling's idea of non-integral helices was almost immediately accepted, and, in fact, a general theory of the X-ray pattern to be expected from such helices was given by Cochran, Crick and Vand[7] in 1952. This theory was based on the idea that the number of residues per turn was some rational number and that the helices had some repeat distance (c) along the axis of the helix. Although the above authors indicated that this idea of rationality was not essential for the theory, it has been the custom of most of the workers in the field to take the number n to be rational and express it in the ratio of two integers. In a paper published in 1960, I put forward the idea[8] that there is no need at all for the number of residues to be rational and that its magnitude is determined only by stereo-chemical considerations, which may lead to any value, rational or irrational, for n. It was also shown in this paper that the description of the X-ray pattern can be given in a very simple manner by means of two parameters of the helix, namely the unit height (h) and the unit twist ($t=1/n$), as shown in Fig. 1, without any reference to a possible repeat spacing (c), as mentioned above. These two quantities h and n are directly related to measurable layer-

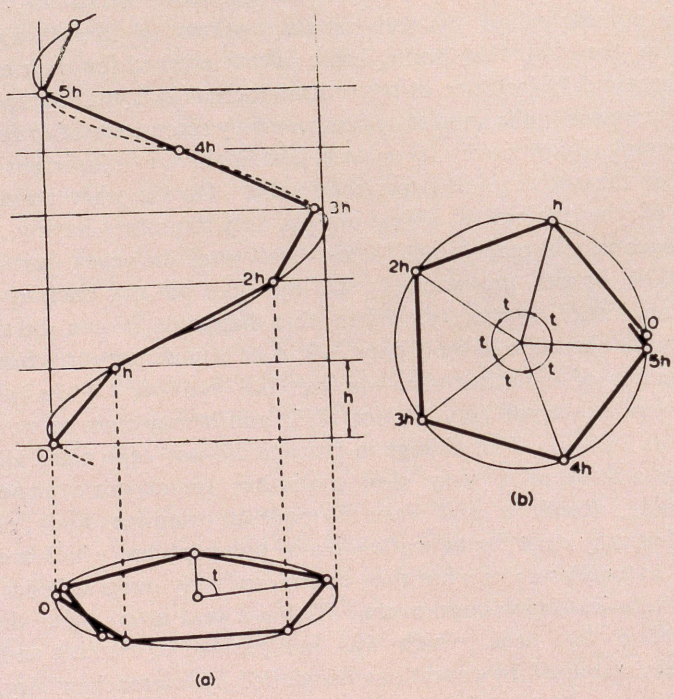


Fig. 1—Diagram showing the projections (a) parallel, and (b) perpendicular, to the helical axis, of a helix made up of straight links joined together. The joints, are marked by circles

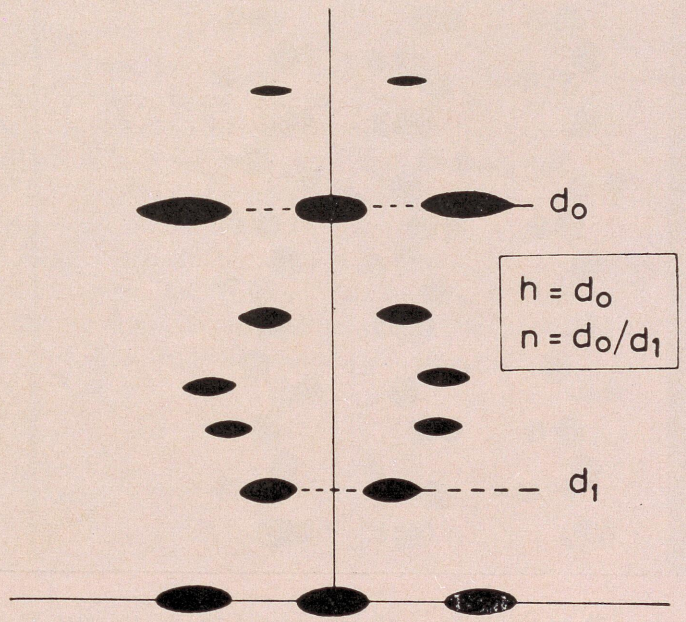


Fig. 2 – Idealized X-ray diffraction pattern of a simple-helical structure showing the layer lines of spacing d_0 and d_1

line spacing in the X-ray diffraction patterns by simple formulae. The spacing (d_0) of the prominent meridional reflection gives straightaway the quantity h. Similarly, the ratio of the spacing of the first layer-line (d_1) to the spacing (d_0) of the meridional reflection gives the number n ($=d_1/d_0$) (see Fig. 2).

This method of interpreting the X-ray pattern was adopted in our laboratory for determining the parameters of the helix which occurs in the protein collagen. In this case, d_1 is approximately 9·5 Å and d_0 is approximately 2·9 Å, so that we have $h=2{\cdot}9$ Å and $n=9{\cdot}3/2{\cdot}9$, approximately 3·3. These data formed the basis of the development of the triple-helical structure of collagen, which was proposed from our laboratory[9]. This structure has gone through several refinements[10] and is now accepted to be basically correct. [11a,b] Fig. 3 contains a picture of this structure, along with the other two standard types of structures found in fibrous proteins. Just as in the case of the alpha helix of Pauling, which is stabilised by hydrogen bonds, this structure is also rendered stable by the presence of hydrogen bonds which join each of the chains in the triple helix with the other two. I shall not go into more detail about the collagen structure except to point out that the knowledge of its triple-helical nature and the exact way in which the chain is twisted, which were deduced essentially from X-ray diffraction, have turned out to be of great importance in understanding the biochemistry and biology of this protein.

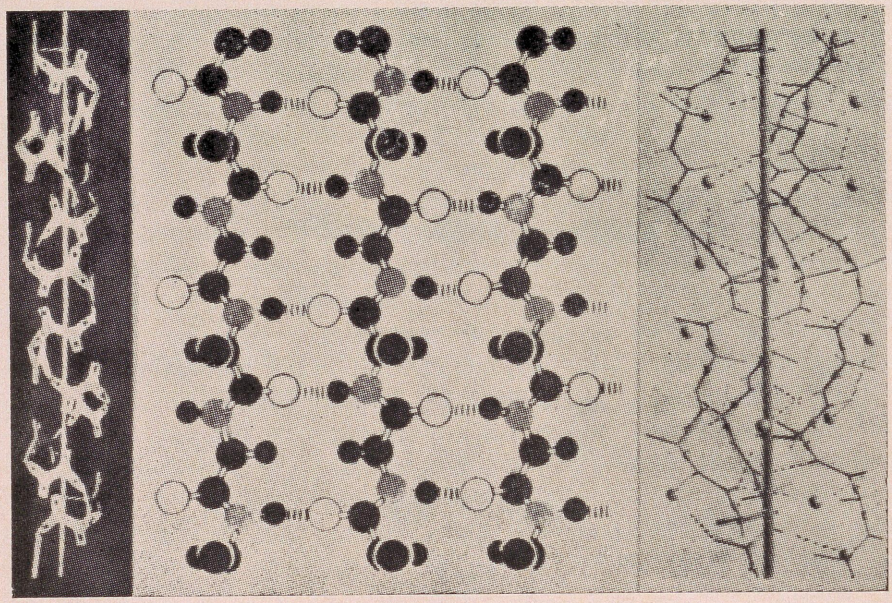


Fig. 3 – Diagrams illustrating the three standard types of protein structures. Three types of illustrations are shown : (a) Alpha helix, as in natural hair, (b) Beta structure, as in silk, (c) Triple-helical structure, as in collagen

In fact, a three-volume treatise on Collagen [12,13] has been published recently under my General Editorship.

Principles of Biopolymer Folding

We shall now consider more generally the ways in which biopolymers fold and aggregate and shall discuss both the description of the different types of folds that are observed, as well as the basic physical theory underlying the formation of the different conformations. As we have seen above, a helix is a commonly occurring form of folding of a polymer chain. It would be interesting to examine why the helix is so common and whether any other similar regular type of structure would be expected for a polymer chain, in general. The answer to this depends on a general mathematical problem, namely what would be the symmetry of a set of identical units which are spatially arranged in such a way that the relative orientation of any pair of them is exactly the same. It is easy to see that the condition stated above is satisfied by a helical arrangement. Considering, for instance, Fig. 1, it will be seen that a rotation by an angle $2\pi/n$ and a translation upwards by a distance h results in one unit being brought into superposition with the next unit. Consequently, a pair of units, which may be denoted by the indices $(j, j+1)$, are brought into superposition with a pair of units $(j+1, j+2)$ by this symmetry operation. Since j may be any number, it follows from this that every pair of units are spatially related with respect to each other in exactly the same way.

It would therefore be worthwhile to enquire if this is true more generally—namely that, if the condition of identical relative disposition of every pair of successive units in a chain is postulated, then the resulting structure would necessarily be a helix, or whether it might have some general class of symmetry. It can in fact be shown that the resulting structure would always have the symmetry of a simple helix[14], as depicted in Fig. 1. This follows from a theorem regarding the most general type of motion that a rigid body can have when it is brought from one place to another with a different orientation. Such a motion, which is designated in mathematics as an affine transformation, can be shown to be equivalent to a screw motion in three dimensions, i.e. rotation about an axis, followed by translation parallel to the axis. It would be realised that this screw motion is the elemenl of symmetry in a helix, and its successive applications would result in a helical symmetry for the structure.

General Geometrical Association of two Identical Bodies

(a) *Polypeptide chain*

This brings us to the question of how two identical bodies can be related by a symmetrical of screw motion, and a way of obtaining this, making use of the stereochemistry of its chemical structure. This is best illustrated by the case of a polypeptide chain, for which this relationship was first discussed in particular detail[15], in a study made in our laboratory. We may therefore consider two linked peptide units, which are the constituent units in the polypeptide chains, as shown in Fig. 4. The units themselves are planar, and rigid, although they contain the set of atoms C^{α}—CO—NH—C^{α}, and the only variable parameters which introduce changes in the configurational relation between the two are the pair of dihedral angles of rotation, ϕ and ψ, about the bonds meeting at the C^{α} atoms, as marked in Fig. 4. The two units are in fact joined at the common alpha carbon atom C^{α}. If the dihedral angles ϕ and ψ are defined with respect to a standard orientation, then the relative configuration of the pair of peptide units is uniquely specified. If now the pair of angles (ϕ, ψ) is the same at every alpha carbon atom, then clearly we have the conditions stated earlier for the formation of a helical structure. The resulting helical structure may therefore be represented by the values of the two parameters ϕ and ψ. It is quite easy to work out the relationship between the set (ϕ, ψ) and the elements of the helix (n, h)[16]. The result is shown in Fig. 5, in which lines of constant n and constant h are drawn. Incidentally, this figure also contains curves marking the boundaries of the allowed and disallowed regions in the (ϕ, ψ) plane which are decided by the so-called "contact criteria" conditions—namely that the atoms in the two neighbouring peptide units must be at distances larger than specified minimum values for each pair of atoms for a conformation (ϕ, ψ) to be allowed. A list for such limiting values are given in Table 1. This (ϕ, ψ) map is also called the "conformational map".

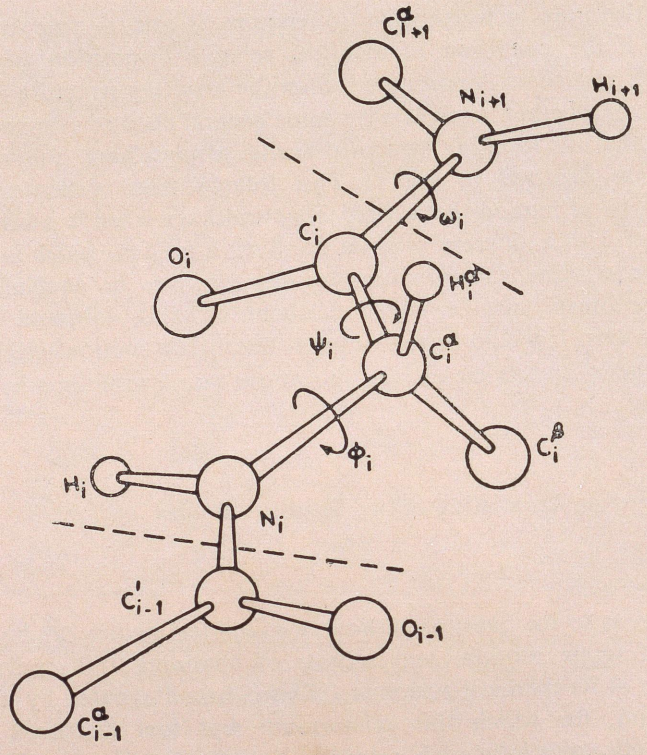


Fig. 4—Two linked peptide units, showing the dihedral angles of rotation ϕ and ψ

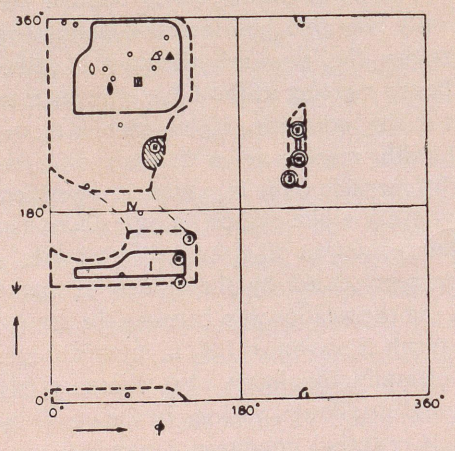


Fig. 5—(a) The conformational map in the (ϕ, ψ) plane. The thick continuous lines enclose the regions allowed by normal limits and the broken lines enclose those allowed by extreme limits

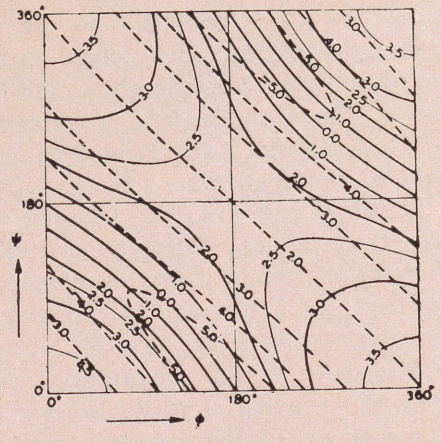


Fig. 5—(b) Contours of constant n and h, The continuous lines are for n, and the broken lines are for h, marked in Å

Table 1—List of limiting contact distances between different types of atoms*

Nature of contact	Limiting distance (Å)		Nature of contact	Limiting distance (Å)	
	Normal limit	Extreme limit		Normal limit	Extreme limit
H...H	2·00	1·90	C...S	3·30	3·10
H...C	2·40	2·20	N...N	2·70	2·60
H...N	2·40	2·20	N...O	2·70	2·60
H...O	2·40	2·20	N...P	3·20	3·10
H...P	2·65	2·50	N...S	3·10	3.00
H...S	2·65	2·50	O...O	2·70	2·60
C...C	3·00	2·90	O...P	3·20	3·10
C...N	2·90	2·80	O...S	3·10	2·90
C...O	2·80	2·70	P...P	3·50	3·30
C...P	3·40	3·20			

*Two types of contact distances, normal limits and extreme limits are given. The names are self-explanatory.

Table 2—Helical parameters of regular protein and polypeptide structures

Conformation		Helical Parameters		Example	
ϕ	ψ	n	h	Protein	Polypeptides
125°	130°	3·6	1·5Å	Keratin myosin	poly-L-alanine poly-L-glutamic acid
40°	320°	2·0	3·5Å	silk	poly-L-alanine poly-L-serine poly-L-lysine
120°	310°	—3·3	2·9Å	collagen	polyglycine poly (Gly-L-Pro-L-Pro) poly (Gly-L-Ala-L-Hyp)

From this map, it is readily seen that we can straightaway pick out what will be the types of helices that are possible for a polypeptide chain. These will correspond to values of the helical parameters (n, h) which occur inside the allowed regions in the map. Typical of such stable helices are the standard right-handed alpha helix, the collagen helix, silk helix, and the left-handed alpha helix, which are all marked in Fig. 5. Table 2 gives a list of the helical parameters of the regular

structures observed and some of the examples of materials which exhibit them. It is interesting that there are only three different types of regular structures observed in fibrous proteins. Fig. 3 (a), (b), (c) are diagrams illustrating these. Although a vast number of other types of helical structures are permitted by the contact criteria, they are not particularly stabilised by hydrogen bonds. Because of this reason, none of them occur in an extended region of the chain, although specific conformations (ϕ, ψ) corresponding to points occurring all over the allowed regions in the conformational map (Fig. 5) are found to occur in structures of globular proteins, which have irregularly folded chain structures.

Structure of Biopolymers other than Proteins

(a) *Polysaccharides*

The above ideas are readily extended to other biopolymers such as polysaccharides.[17,18] In this case, the repeating unit is not so simple as a peptide unit, but is much larger, namely the six-membered ring of a glucose sugar residue. Two types of such sugar residues are possible, namely those arising from α- and β-glucose, which are shown in Fig. 6. The possible rotations about the two bonds at the so-

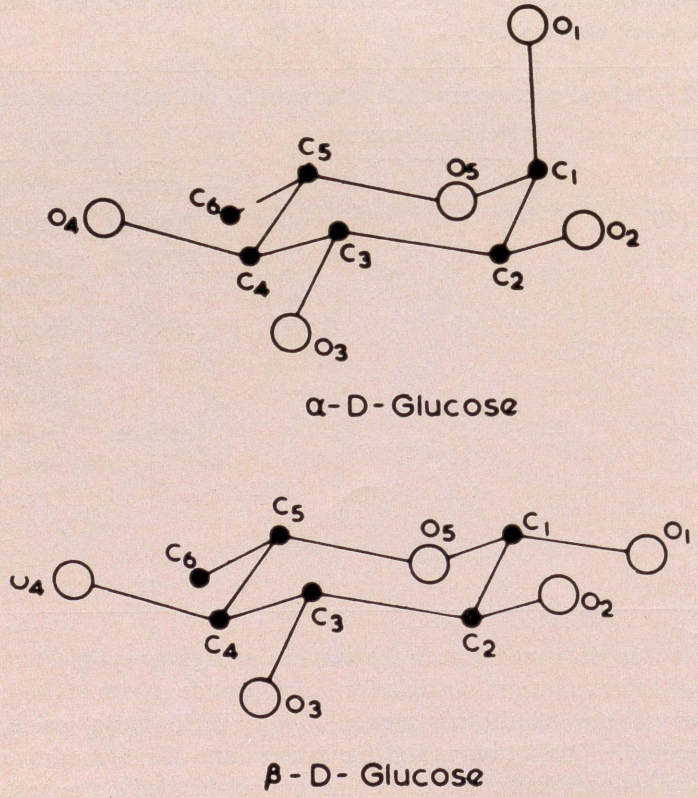


Fig. 6—Molecular structures of α-glucose and β-glucose

called glycosidic linkage at the oxygen atoms are similar to the two torsional rotations considered above for the peptide units, and may therefore be denoted by the same symbols (ϕ, ψ). The (ϕ, ψ)-maps for polysaccharide chains, both of the α- and β-types, have been calculated in our laboratory (not shown here, see Ref.19). It is found that the possible helices for the two types of linkages obtained with α- and β-glucose, respectively, are vastly different. This is because the angle between the bonds at either end of the residue leading to the bridge oxygen atoms is quite different in the two types of glucose residues—the two are nearly at right angles in α-, and nearly parallel in β-glucose. Therefore, if the β-linkage is taken, we get helical chains similar to those occurring in cellulose. These helices can have a value for the number of residues per turn, n, only between 2 and 3. They are therefore straight, and they form extended structures. Cellulose (a polymer of β-glucose) in fact has $n=2$. A related polysaccharide called xylan, a polymer of β-xylose, has $n=3$ (Ref. 20) On the other hand, if the α-linkage is taken, we observe an opposite effect, namely that the helices are highly coiled and are very flat and n can have values only from 4 to 6 or 7. A typical example of this form of polysaccharide is amylose, which occurs in starch. Two forms are known, one (V-amylose) with $n=6$,[21] and another (B-amylose complex) with $n=4$. The structure of all these have been worked out in our laboratory using the ideas of the dihedral angle rotations, ϕ and ψ, and employing methods similar to those developed for proteins.[22]

An interesting aspect of polysaccharide chemistry is that the β-polysaccharides, such as cellulose, are highly insoluble in water and are not digestible by human beings, while the α-polysaccharides (e.g. starch) form the essential food material for men. There is thus a complete difference in the biochemistry of the two types of molecular chains. It may be mentioned that, at the suggestion of our Centre, a study has been initiated to work out methods whereby the farm waste materials, which are essentially in the form of cellulose, may be broken down into sugars and then converted into protein food. If this succeeds, then practically the whole of the plant kingdom, including wood, stalk and leaves of the plants, can be converted into food suitable for human beings. We have made a feasibility survey and it is likely that the work may be taken up as a broad interdisciplinary project by a number of laboratories in our country, including three CSIR National Laboratories, the IARI, and two Centres of Advanced Study in Botany and Biophysics.

(b) *Nucleic Acid*

The other well-known biopolymer is nucleic acid, whose repeating unit is shown in Fig. 7. This unit, however, is not rigid and it is possible to have rotations ($\theta 1$, $\theta 2$ & $\theta 3$) inside the unit itself, apart from the standard dihedral angles (ϕ, ψ). We shall not discuss this subject more in detail, although the basic ideas of carrying out all these rotations have been developed in our laboratory.[23,24,19] These have served to explain the occurrence of various types of helices in nucleic acids and polynucleotides, whose existence has been extensively studied by workers in other laboratories.

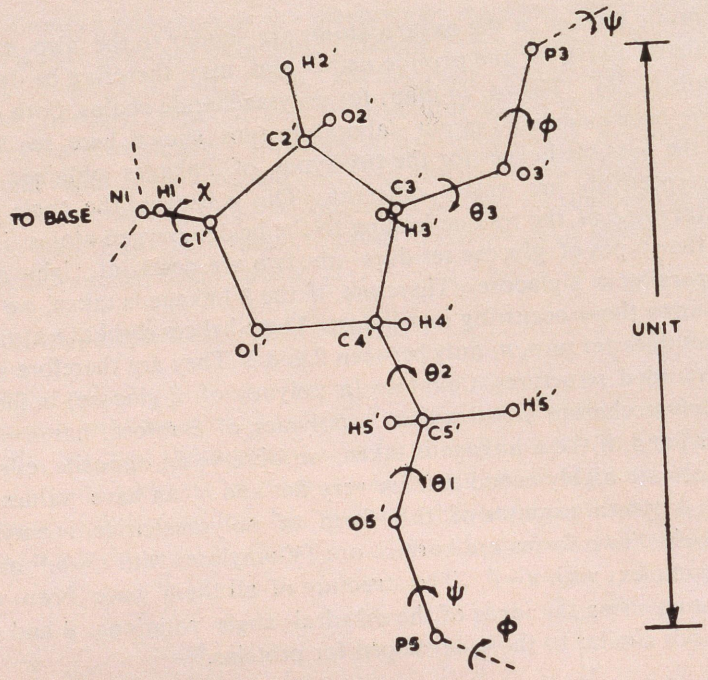


Fig. 7—The backbone of the repeating nucleotide unit in a nucleic acid chain, showing the various dihedral angles

Incidentally, these nucleic acid helices are also essentially stabilised by hydrogen bond formation—for instance, the occurrence of hydrogen bonds between base-pairs in the DNA double helix is too well-known to be discussed here.

Non-Helical Association in Biopolymers—Intermolecular Forces

As mentioned earlier, regular and periodic arrangements of the units often occur in biopolymer chains. However, there are a large number of examples, such as the metabolically active proteins, which do not have a regular arrangement of units throughout their structure. The chains in these materials are not very long, say as in collagen, which may have a thousand units, or as in nucleic acids, which may sometimes have a million units. The biologically active protein chains have between 50 and 300 units and should be considered to be finite molecules rather than as macromolecules. These protein chains exhibit a variety of conformations, containing sometimes portions of α-helices and sometimes portions of the β-structure. All these are folded together in a complicated manner leading to a compact globular structure for the molecule as a whole (Fig. 8). The theory of the formation of such globular structures is much more complicated than that of simple helices, and I shall not try to give it here in detail, except for the fundamental physical ideas that are involved in it. It is based on the calculation of the energy

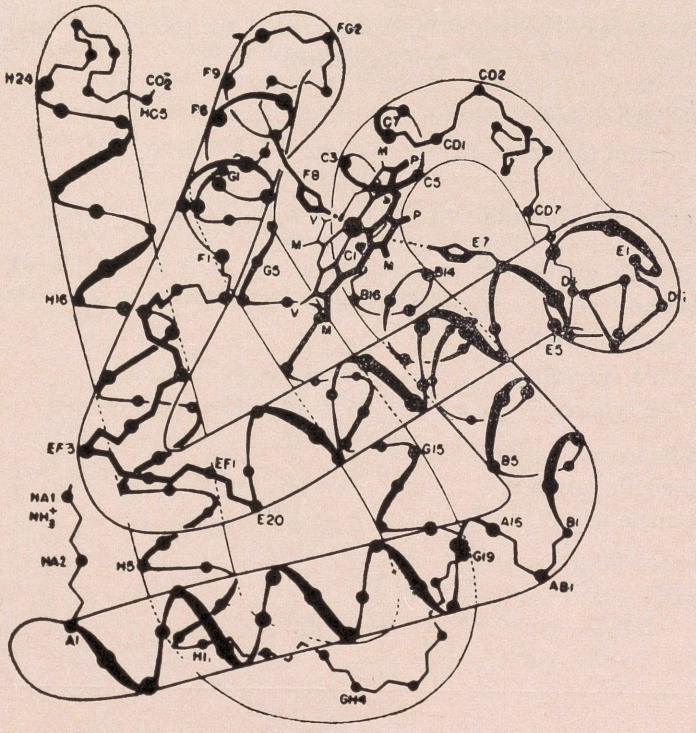


Fig. 8—The chain structure in a typical globular protein molecule (myoglobin)

of interatomic interactions between the various atoms and groups in such a structure and the determination of the particular conformation which leads to a minimum value for this energy. In fact, such ideas of energy minimisation are also required for an understanding of the relative stabilities of the different helical conformations. A vast amount of research has gone into the understanding of these interatomic and intermolecular interactions and the development of suitable formulae for their representation. Reference may be made to two recent reviews[25,26] from our laboratory, regarding the application of these ideas to proteins and polypeptides.

Table 3 gives a summary of the theoretical formulae for some of the types of the potential functions commonly used in such theories. The types of interactions between bonded atoms which are relevant in these studies may be classified as follows :

(i) *Non-bonded Interaction* : The principal component of this is the van der Waals attraction given by the inverse sixth power law. At short distances, there is a repulsion, which may be expressed either by an exponential, or an inverse twelfth power formula, as shown in Table 3. When both effects are combined, the energy is minimum at some finite distance, which is usually defined as the sum of the van der Waals radii of the two atoms concerned.

Table 3—Types of potential functions used in the theory of biopolymer conformations

(i) *Non-bonded interaction*

Buckingham formula $V_{nb} = -\frac{a}{r^6} + be^{-cr}$

Lennard-Jones formula $V_{nb} = -\frac{a}{r^6} + \frac{b}{r^{12}}$

(ii) *Electrostatic interaction*

$V_{es} = e_1 e_2 / \epsilon' r_{12}$, ϵ' = effective dielectric constant

(iii) *Torsional potentials*

Three-fold symmetry, e.g. $V\phi = \frac{1}{2} V\phi_1 \ (1 - \cos 3\phi)$

Two-fold symmetry, e.g. $V = \frac{1}{2} V\omega_1 \ (1 - \cos 2\omega)$

(iv) *Bond-distorsion energy*

Bond-length variation $V_l = \frac{1}{2} K_1 \ (\triangle l)^2$

Bond-angle variation $V = \frac{1}{2} K\tau \ (\triangle \tau)^2$

(v) *Hydrogen bond energy*

$V_{hb} = D\{1 - \exp[-n\,(r - r_o)^2/2r]\}$
$- D^* \{1 - \exp[-n^*\,(d - r - r_o^*)^2/2\,(d - r)]\}$
$+ Be^{-\mu d} - A/d^m$

(ii) *Electrostatic Interaction* : This type of interaction arises from the partial charges held by the various atoms in the structure, whose magnitudes are known either from dipole moment data of related molecules, or from quantum chemical calculations of such molecules or groups. It is also necessary to introduce an effective dielectric constant (ϵ') whose value is usually taken to be 4-5 for water solutions.

(iii) *Torsional Potentials* : It is not correct to say that the rotation about a single bond (e.g. N—C^α) is completely free. It has a variation with angle which may have a three-fold symmetry (as for the rotation about the C—C bond or ϕ- or ψ-rotations), or a two-fold symmetry (as for the rotation about the C—N partial double bond). The values of the constants for the corresponding expressions in Table 3 are not very accurately known, but are deduced from various available data on related compounds having these bonds.

(iv) *Bond Distortion Energy* : Both distortion of bond lengths and bond angles lead to increase in potential energy. The effective constants involved in the expressions associated with these energies are best obtained from data on infrared and Raman frequencies. In general, these energies are much larger than those involved in the categories (i), (ii) and (iii), and therefore this type of distortion is only used in refined calculations.

(v) *Hydrogen Bond Energy* : The theory of hydrogen bonds has only been worked out in outline and it has to be considerably refined (see next para). Therefore, only one form of the formulae, due to Lippincott and Schroeder, is given in Table 3. At present studies are under way in our laboratory for obtaining the most satisfactory hydrogen bond potential functions.

The need to obtain precise theories of biopolymer conformations, has, in fact, led to a survey of the available knowledge regarding intermolecular forces by various workers. It is found that there is a comparative lack of precise physical data to support the theories that are available. As a consequence, a large amount of work

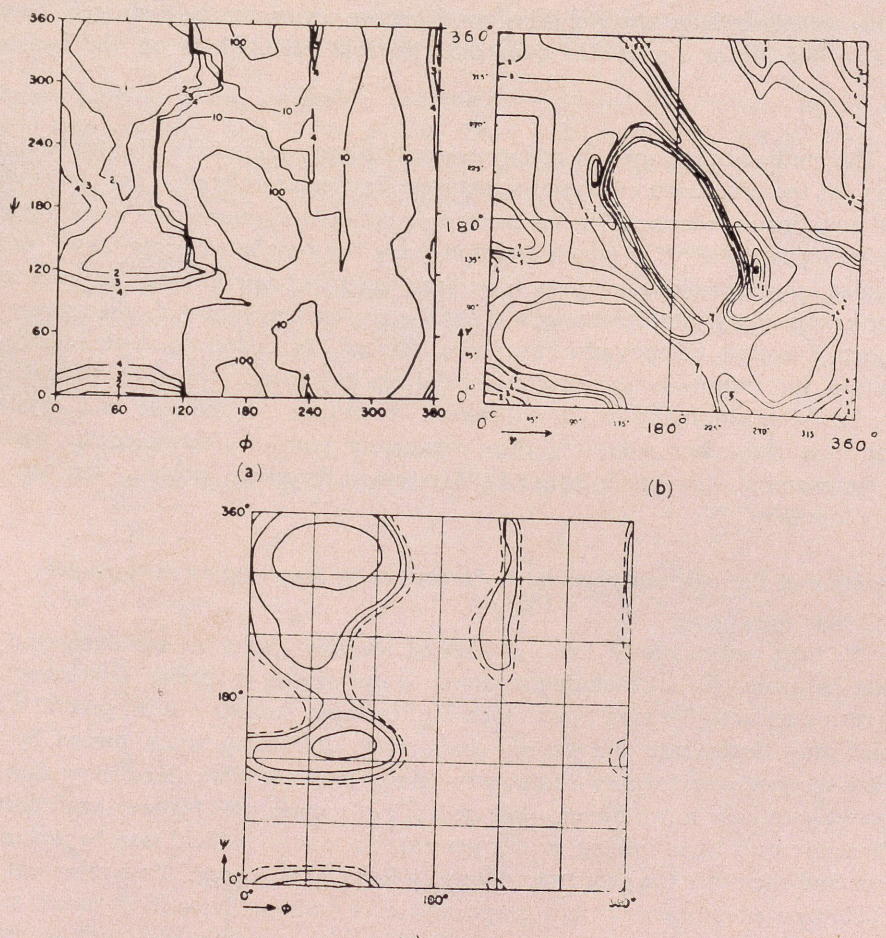


Fig. 9—Potential energy distribution in the (ϕ,ψ)—plane. (a) and (b) Calculated by quantum-chemical method by Hoffman[27] and Pullman[28] respectively, (c) Calculated using empirical potential functions of the type listed in Table 2

has been initiated both in theoretical studies (e.g. in the field of quantum chemistry) and in experimental studies dealing with molecular interactions, for example by the method of molecular beam scattering. I may mention, in particular, the results of two such theoretical studies. Fig. 9 (a,b) show the results of two calculations[27,28] of a quantum chemical nature (made using standard methods, in conjunction with the Schrödinger equation) in the shape of (ϕ, ψ) maps. It will be seen how closely the results of these studies concur with the empirical potential map (Fig. 9 c), and even the simple contact map of Fig. 5 (a). Similarly, at our suggestion, calculations have been made, using quantum chemical methods, of energies of hydrogen bonds and of their variation with the distance between the atoms and the angles that are involved in such a bond.[29] The authors of these studies, namely Dr C. N. R. Rao of Kanpur and his colleague, have also published an extensive review on the hydrogen bond.[31] (see also Ref. 30 for a review of quantum chemical calculations on the hydrogen bond.)

The methods developed in connection with biopolymers have also found application for the prediction of crystal structures. Particular reference may be made to some investigations reported at the latest International Congress of Crystallography held in August 1969[32,33] in which attempts have been made to apply these : (a) the formulae for intermolecular forces have been used for determining the orientation of molecules in a crystal structure; and (b) the crystal structure data themselves of a number of related compounds have been utilized for deducing more exactly the formulae for intermolecular interactions. I am mentioning these to indicate how there has been action and reaction between biophysics on one side and crystallography on the other side, *via* the connecting link of intermolecular forces—see, for example, the paper entitled "Molecular forces in protein structure and crystallography".[26]

Formation of Periodic and Symmetric Structures by Aggregation of Particles

(a) *Linear aggregates*

We have seen already how, if a set of identical particles are connected in a linear fashion such that each one is joined to the next in a specific relative orientation at a particular linking point, then the resulting structure is in general a helix (which may degenerate to a straight chain with alternating units turned by 180°, having the symmetry of a two-fold screw axis). It is not difficult to show that it is impossible to have a two-dimensional network of connections between such particles if there are only two linking points per particle, one of which may be called the donor and the other the acceptor. Applying ideas of topology, if we represent each particle by a point (vertex) in a graph and each linkage between a donor and an acceptor, which connects one particle with the next, by a line (edge) connecting the two vertices, then the resulting graph for the above arrangement will be, what is called, a linear graph, or a graph of degree 2. Every vertex will have only two edges meeting at it and therefore we can only have two possibilities : (a) the graph will be

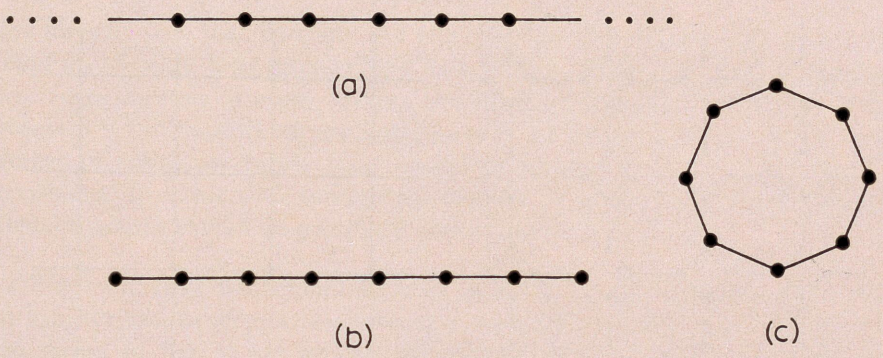


Fig. 10—Linear graphs of degree 2 (a) Infinite, (b) Finitely terminated with the bounding vertices of degree 1, (c) Cyclic

infinitely long, or it may be finitely terminated, with the two vertices at the either end of degree 1 (Fig. 10 a, b); or (b) the graph may be cyclic, with all vertices of degree 2 (Fig. 10 c). Since there are no more connections possible from each vertex, it is not possible to have a two-dimensional network.

(b) *Two-dimensional aggregation*

Similarly, from intuitive considerations it may be readily shown that an infinite two-dimensional network can be constructed if every vertex has three edges meeting at it (Fig. 11 a). A simple example of inter-connections of finite particles having this property is also shown in Fig. 11 (b).

More complicated regular networks having vertices, all of degree 3, are possible, e.g. as shown in Fig. 11 (c). [It is of course possible to have two-dimensional

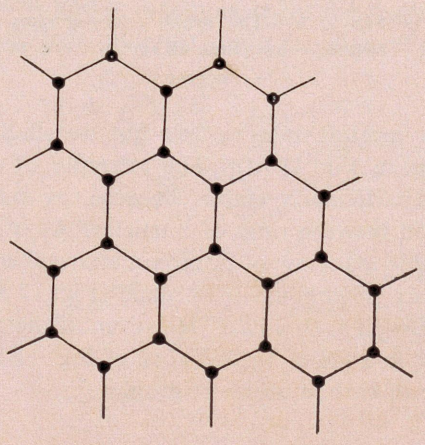


Fig. 11 (a)—A simple two-dimensional graph of degree 3

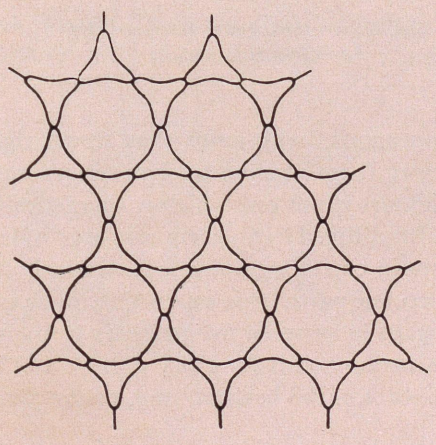


Fig. 11 (b)—A structure composed of particles, which can be represented by this graph

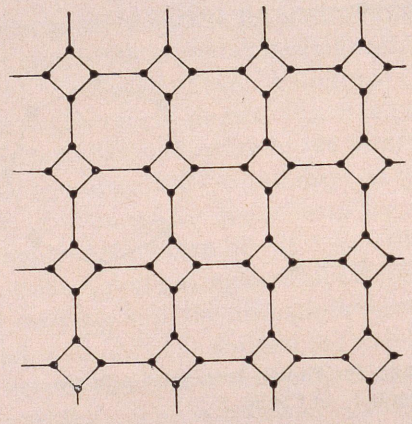


Fig. 11 (c) – A more eomplicated example of an infinite two-dimensional graph of degree 3

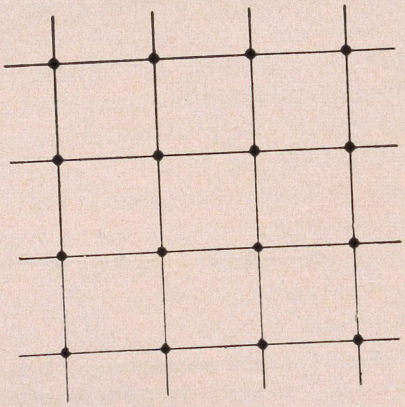


Fig. 11 (d) – Two-dimensional graph with vertices of degree > 3

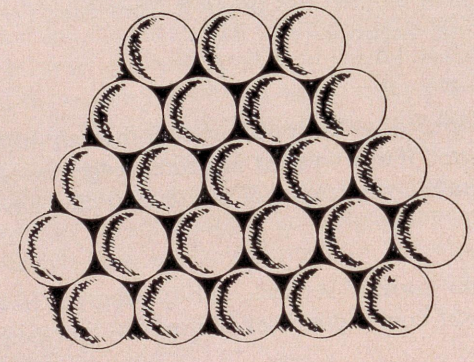


Fig. 12(a) – Hexagonal close-packing of balls in a sheet

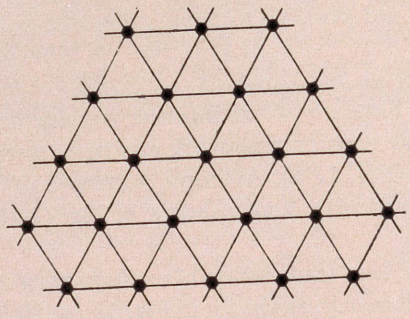


Fig. 12 (b)—The graph corresponding to this — note that all vertiecs are of degree 6

arrangements, with more than three edges meeting at a vertex, but we shall not consider these, except to show an example in Fig. 11 (d)]. The example of three neighbours is not one which is energetically particularly stable, because, as may be seen from Fig. 11 (b), there are large holes in between rings of particles. As is well-known in crystallography, a particularly stable packing of approximately spherical, or circular, particles is one which involves six neighbours in a plane (Fig. 12 a, b). The gaps in between the particles is minimum in such a case. However, if there are three strong bonds for every particle at 120° in a plane, the network of Fig. 11 (a) is possible (e.g. the benzene ring, or the plane of carbon atoms in graphite).

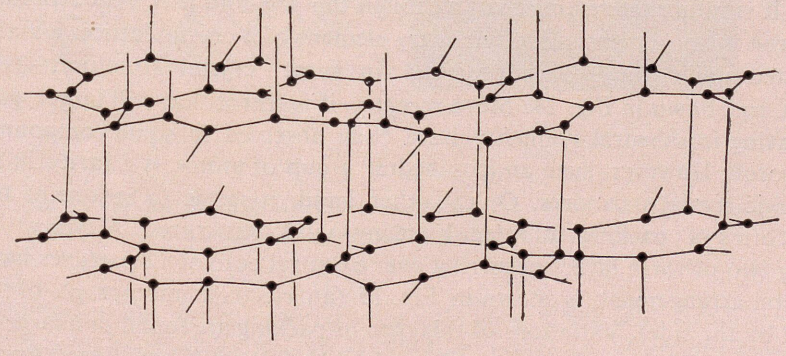
(c) *Three-dimensional structures*

We might ask ourselves the question; what is the minimum number of linkages per particle that is needed to build an extended three-dimensional structure? We

have already seen that two are not enough. On the other hand, as will be seen from Fig. 13 (a), it is possible to have such a three-dimensional network having only three edges meeting at every vertex. This again may not be a stable type of linkage, because it is too "open" but the question here is essentially one about the minimum number of edges per vertex that is needed. Since it is possible to have a three-dimensional structure with three edges meeting at every vertex, three-dimensionally extended graphs should be possible if their degree is greater than 3.

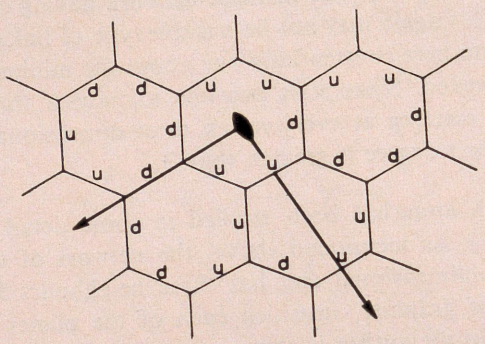
The number of neighbours for each atom has been studied in some detail in inorganic crystal structures. For example, as mentioned above, the network of the type shown in Fig. 11 (a), which is two-dimensional and has three neighbours for each atom, is observed in the structure of graphite, in which each of the planes of carbon atoms has this structure. As far as the author is aware, the type of structure shown in Fig. 13 (a) has not been noticed in crystallography. But the structures with the smallest number of neighbours that are known have four edges meeting at a vertex, e.g. the diamond structure (Fig. 13 b) This structure is also known to be highly open with vacant interstices, which is stabilised only because of the covalent tetrahedral character of the bonds. In most-close-packed structures in three dimensions, the number of neighbours is large, namely 8 to 12 or more.

Thus we see that there is a competition between the requirements of close packing and the number of definitely associating linkages. If there are no directed or specific associations, and only close packing predominates, then we would expect structures with a larger number of neighbours. On the other hand, if there are directed valence bonds, or there are linkages with restricted rotation, then the number of neighbours would be smaller and could be as small as 4, or even 3. It would be interesting to analyse the various standard structures of crystals from this point of view and to examine their topology in relation to graph theory. Perhaps one would find, purely from a topological point of view, that the observed structures



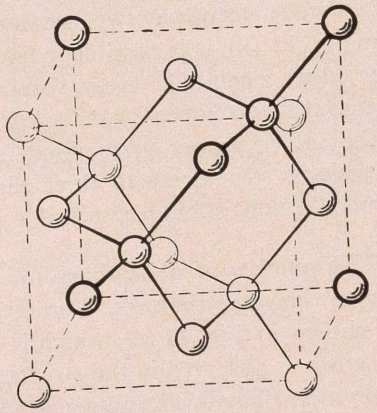
(a)

Fig. 13 (a)—A possible three-dimensional (periodic) network, having all vertices of degree 3



(b)

Fig. 13 (b)—The normal view of one of the layers (*u* and *d* represent bonds going up and down from the layer). The arrows indicate the unit cell translations



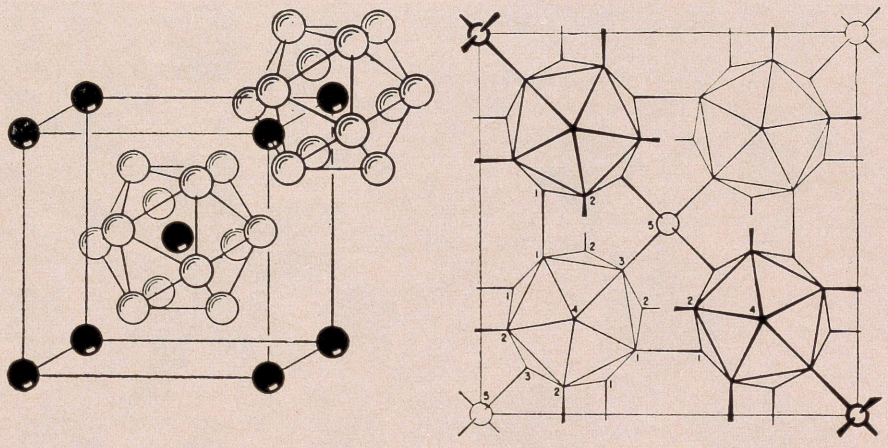
(c)

Fig. 13 (c)—The diamond structure network, which has all vertices of degree 4

may be classified into a small number of types, although some of them belonging to the same topological type may have different geometrical symmetries.

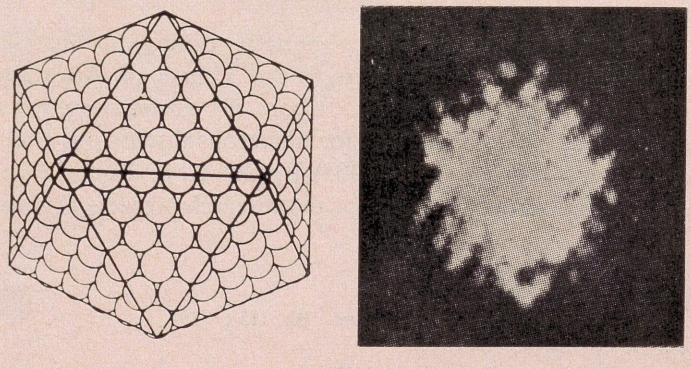
(d) *Packing in biological structures*

It is well-known from crystal structure studies that the close-packing that is possible for a periodic structure involves a coordination number of 12 which exists, for instance, in the face-centred cubic and the hexagonal close-packed structures. However, if the packing of just 12 neighbours around a central sphere is considered, there appears to be a slight superiority in the icosahedral packing than in the f.c.c. packing. It is rather interesting that, although the five-fold axis which occurs in an icosahedron is not a permissible symmetry element of a crystal lattice, icosahedrally coordinated units have been observed in some crystal structures—two such examples are shown in Fig. 14. More recently, it is learnt that still larger groups of atoms having icosahedral symmetry have been observed in some compounds containing boron. However, such an icosahedral group of atoms is a rarity in the field of inorganic crystal structures. On the other hand, it seems to be one of the commonest forms of packing adopted by many virus structures. A typical packing involving two or three layers occurring over a central core of 12 particles having the icosahedral arrangement, is shown in Fig. 15 (an electron micrograph of the virus is shown by the side). Variations of this type of packing are found in a large number of viruses, which have been extensively studied by Klug in Cambridge. Apparently, this packing arises not by any specific types of linkages between neighbouring particles, but rather by their packing together in the closest possible manner at the stage of the nucleus formation. It is rather interesting that several biological species



(a) (b)

Fig. 14—Crystal structures having an icosahedral arrangement of atoms, Structures of (a) $MoAl_{12}$ and (b) Tetragonal boron



(a) (b)

Fig. 15—(a) An icosahedral arrangement of spheres, (b) Electron micrograph of a virus, which has this type of packing of the particles

have structure at the microscopic level which have a five-fold symmetry, e.g. the five petals of a flower (see Fig. 16 a). In fact, books on symmetry (e.g. Ref. 34) often give photographs of sea animals which even exhibit icosahedral symmetry (Fig. 16 b). The origin of such symmetries in biological systems is certainly a very interesting and fruitful field for study.

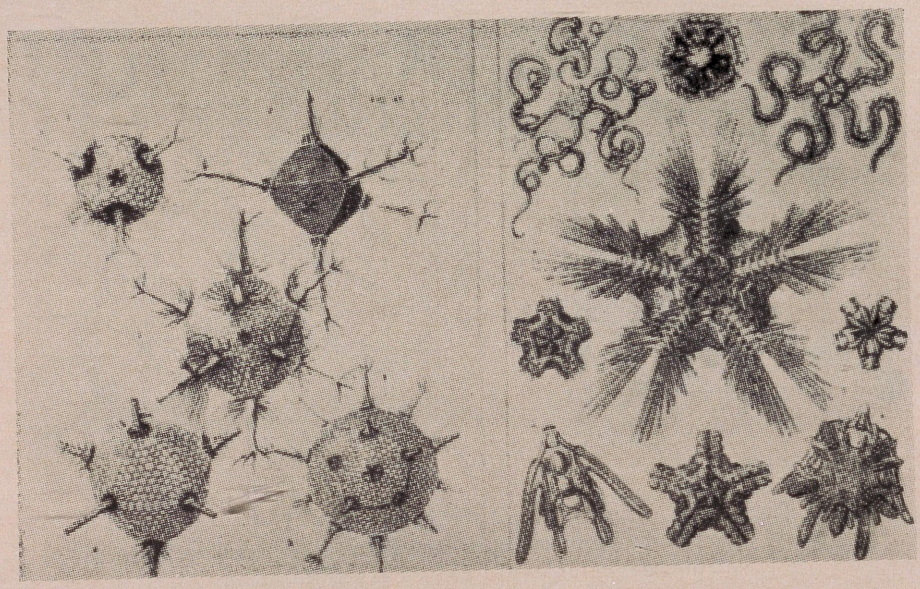


Fig. 16 (a) and (b) – Drawings of biological specimens, many of which exhibit icosahedral symmetry, or have a five-fold axis of symmetry (From Ref. 34)

Acknowledgements

The work reported in this lecture has been done during the last several years in collaboration with a number of workers in the Centre of Advanced Study in Biophysics, University of Madras. I wish to record my grateful appreciation of all the help and assistance given by them and for numerous discussions that I have had with them. The award of a grant (AM-10905) by the U. S. Public Health Service materially assisted in the conduct of some of the research projects reported here.

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Lecture

by

PROF. S. N. BOSE

Dear Director Verma and I see many familiar faces before me. I won't name them separately but to all of my friends, I say, I feel highly honoured for being asked to come among you and to say something on this very memorable day. I had a great sensation of pride being associated with the National Physical Laboratory where as Dr Verma has said by dint of merit and hard work, bands of young people are grouped together with the main purpose of solving many problems, either manufacture of highly sophisticated instruments which may ultimately be utilized for purposes of research or by finding out all about certain commercial processes to enable the manufacturers of our country to produce and thus to help our industry. our people, and incidentally help our countrymen also by saving a lot of foreign exchange. We had been discussing these problems together and I remember, years ago, when we began our life as students of science that there were no such facilities offered to the young and meritorious aspirants in those days. There had remained, besides the Government colleges, where alone to some extent facilities were provided for. But there had remained this solitary Indian Association founded by a doctor, a patriotic doctor, who had thought of the future of the country, of the possibilities that are provided by native talent and who had collected money and founded the Indian Association where people could be told news about the recent developments of science and where people may be given facilities for work. Then there was no question of utilizing the resources of the laboratory for research purposes for solving problems which defied the industrialists. It was more or less about a century ago that people were then thinking how to make our countrymen modern in the sense that they will be able to look at science with eyes not made to see, not half as troubled with superstitions they will be able to look at major and natural phenomena and reason as to how things are brought about, how things develop, how things are made and so on.

Dr Sircar had himself a history. He had begun as a doctor trained in western alopathic methods but very soon he convinced himself that it is possible to effect well cures by homeopathic methods and he was brave enough to adopt this method after he had carefully gone about and tested for himself the efficacies of these drugs. As a result he ran the risk of being thrown out of the cadre of the physicians who were (because he was a graduate himself of the medical science of Calcutta Univer-

sity) and the doctors were all up against him for having gone in favour of a method which they didn't vouch safe any reasonable efficacy. However he continued. He was a Dean of Faculty of the Medicine. He continued to be in that list and he valiantly collected private subscriptions and erected a modest building and laboratory. In this laboratory originally there were many short course lectures.

Sir Ashutosh himself (when he was a young man just out of the university), he delivered the course of lectures in mathematics on his research work. When we were students we found his name in the textbook as a person who has given a very ingenious and brilliant explanation of the equation of mass. He had ambitions. He wanted to do research work but then ultimately, then our country didn't offer any facilities, no avenue of progress nor of advancement being offered to any scientist. So he turned to law. Legal profession was then highly honoured and some how or other science had got curiously evaded to law in our country in the sense that not only Sir Ashutosh, a great lawyer as well as a great mathematician, he had brought about the revolution in the teaching of modern science but also there were too great lawyers whose statues are in the foreground of the College of Science who by their magnificent donations have made science possible in those days. Formerly before our days our students had mostly to rely on government facilities being offered and with the solitary exception of two great names gone down the history of science in our country—Sir Jagdish Chandra Bose and Prafulla Chandra Roy—who had continued to work, who had gone abroad, studied science elsewhere and then returned to our country but with the native equipment sharpened by western teaching, had continued to find new directions in their work and in their jurisdiction.

Sir Jagdish's name had remained connected with the application of science for unravelling of the mysteries of plant life. Sir P. C. Roy's name had remained associated with the first efforts of Indians to manufacture in our country drugs and the first ingredients which go towards basic industry, manufacture of sulphuric acid, etc. But the scientists usually then who had their training most of them had finished the training and gone to law. However, there was a great change in the history of our country; there came the partition and the Swadeshi Movement and then people at once thought how futile it was to go about learning things and at the same time remain thoroughly dependent upon others even for our own immediate necessities. There was a movement which wanted people to become completely independent so far as the daily necessities were concerned. There were students who had gone abroad to learn the technique of modern industry, to study how things are spun, how mills are erected, how chemical industries are developed, etc. etc. There were also others who had gone abroad to study sciences. They had hopes and ambitions that they would return and set up for themselves some industry. However, there was also, well, it did not find favour with the then rulers of the country and there were repressions, persecutions, and revolt. There was the university started at Jadavpur where people wanted to give complete education in mother tongue. Where people came, where people endowed their withals for the furtherance of education in

our country. Well there was suddenly at the same time a sort of revision of the curricula of the Calcutta University and the training of science was given a more modern look. Students had to work in the laboratories to justify the award of their degrees. Even for the first degree in science you have to do two years practical work. At that time the Indian Association laboratories had offered facilities for students who were anxious to learn science but could not find enough facilities in the modest colleges that were then existing in Calcutta. And Indian Association had offered facilities for working practical courses of the Intermediate subjects of Physics, Chemistry and Botany and students in large numbers had belonged to the Indian Association to do work. Well, I tell you all this simply as a sort of introduction to tell you to remind you that the facilities of the Indian Association were very modest indeed. And we had simply thought of it as a place where beginnings had been made but could not be very much improved because of the failing resources.

Mohinder Sircar had died and the laboratories were still having very modest resources. When we were students for master's degree in Calcutta about 1913 etc., then there were new things; there were new endowments and there were new persons, eminent scientists who had been invited to go down to Calcutta. Dr Ganesh Prasad had been appointed Rashbehari Ghosh professor. There were endowments given by the two eminent laywers and Sir Tarak Nath Palit—the names of Sir Tarak Nath Palit and Sir Rashbehari Ghosh will remain written in letters of gold in our history and there were the first selections made of the professors. Of course curiously enough when the appointments with the endowment were made and money had been given for the establishment of these professorship there was a clause which produced a great ire among our rulers because one of the clauses was that the person who would be appointed should be Indian. According to laws as Indians were defined, it was just barring for ever appointments of anybody other than Indians to these posts. Actually then most of our scientists—most of our science posts had gone to Europeans with the solitary exception of the two illustrious names which I just mentioned—Sir Jagdish Bose and Sir Prafulla Chandra Roy—all the other professors were mostly Europeans, and Scotch men, who had not very brilliant academic career but it was considered sufficient to be educated to teach the Indians in smattering of science. However, some money had already been spent for the teaching of science and when we were students we used to look through the almirahs in which were packed things at which we wondered, for example Echelon Grating or some other things which occasionally reverently they will be put on the lecture table and will be again put back inside the show case. The professors thought that if it would be touched by people there, it would be spoiled for ever and so much money wasted. Now that was science.

Well you have to respect and have reverent superstition and look at these things at the same time remember that these problems and these apparatus were manufactured not in India but elsewhere to be shown for our edification to be treasured and

to be always subjects of perpetual adulation. At that time about 1913 when we were students and of course Sir P. C. Roy was doing some research on the amine nitrides and Sir J. C. Bose was doing his magnetic crystallograph and then this endowment had come and Sir Ashutosh had to seek out certain probable recipients of these chairs— of these endowments.

And he had noted a brilliant young man who had come down to Calcutta not as a scientist but as an officer of the finance department but who had chosen to pass all his time that he could spare from his official work in the laboratory. I am mentioning Sir C. V. Raman's early debut in the scientific world as a person, as a volunteer who came in the science association. Who had the facility to be utilising all the facilities which Indian Association had offered. He had chosen to choose his dwelling house very near so that he could come and enter the association by the back door and continue his work in the long hours after sun set so that he could work there.

Sir Ashutosh had observed because, he was the then President of the Indian Association, and when his name was comparatively unknown among the professors of the various colleges he had predicted that this young man will go very far. I remember I had heard on a particular day when I had gone to see Sir Ashutosh and we were wondered about the new appointments he said "I know that he will go very far."

So we were all wondering. We were occasionally going to the Indian Association and already he was a name among the aspirants who wanted to do work. He was working like any other student of science, mornings and evenings, he was making his observations he was studying his what you call the asymmetric diffraction and publishing his papers in the Philosophical Magazine. And then to the young aspirants who had just passed out of the Calcutta University he had given problems to solve. He was a very keen observer, Sir C. V. Raman—for example, I remeber there was a very old apparatus in the Indian Association which was set up to show the effects of elasticity. There were two balls which were pulled apart and then allowed to come down and to have a collision and then rebound and jump upto certain distance depending upon how far it could retrace its position. Well you see that this is more elastic than the others. That was a very old apparatus.

Sir C. V. Raman had taken two of these elastic balls together, had locked one against the other and curiously enough had observed that it sounded very different if you hear it on the end rather than broad side position. It went very far on one side and sounded more metallic than the others and he was curious. Well things all set and knocked about in that apparatus, nobody had ever thought that there was this assymetry in the production and propagation of sound when two

balls collided. But he was curious. He had observed this thing. And he of course was not a master mathematician like Ganesh Prasad so he asked Ganesh Prasad. They were friends then. Usually people before they become great, they remain friendly, it was only afterwards that they quarrell. So Sir C. V. Raman was still friendly to Ganesh Prasad. So Dr Ganesh Prasad was consulted. He shook his head very wisely and then gave it as a problem to one of the young people. Result : Sudanshu Bannerjee got his doctorate.

Well he solved the problem. He explained how it has to be explained by regarding these balls as sources of short waves and he analysed the short waves being reflected one from the other and then by curious combination they got together, you see, and produce the sort of a double source and just as a magnet you had these magnetic lines proceeding more rapidly having greater force in one direction than on the other. He had deduced by means of analysis the cause as to why these short waves were very much stronger in one direction than the other. I just tell you this to illustrate the keen observation power of Sir C. V. Raman. How out of very modest things he could find certain things which needed explanation and how he could lead on to very abstruse calculations and thus furnish a sort of enduring results for science. There are such things which I remember, as for example, the Wolf Knot he used to show from the violin; how the maintenance of vibration should be very difficult when certain critical vibrations occur and so on. Then about the colour of the thin films etc. And for every such little things which one could observe he found something out of the argument and gave them as problems to be solved to young men and they were very glad; they were grateful because at least something were given for them to wet their own innate intelligence and to apply the newly acquired scientific methods which they learnt at the feet of their teachers. But the teachers had not been able to offer them any problems and problems were found for them and that was how names which we had admired in our young days, names like Sushil Mitra or Phani Ghosh. These people were given problems and they began their life as investigators and they got their inspiration from Sir C. V. Raman. They didn't remain tagged on to him but they developed these their own capacity for work and they developed and Sushil Mitra became one of the pioneers of the study of ionosphere and there are many students who will remember his name with respect who had their first lessons in wireless. In microwaves were given prizes in the National Physical Laboratory. He had begun the studies of these waves and then he finally passed out as a Fellow. Before he passed out he was a fellow of the Royal Society. Phani Ghosh had developed his powers of organization; he had started the department of Applied Physics which has grown to be of respectable dimensions now. Every year they are passing out students who are absorbed by the industries, by governmental departments, etc. However, Sir C. V. Raman had continued and had observed certain things about which he speaks himself—about the colour of seas, the blue colour of the seas which he thought was not the reflection of blue of the heavens and he went on, ultimately discovered the Raman Effect. And

in this discovery was associated a young man, comparatively young men, who was a very quiet sort of person, when we have found he was very much younger than us and found well ardent student when Professor Sommerfield had come and had lectured on the new developments of physics. He had taken down notes which the professor found suitable and valuable for the publication of a brochure combining these lectures, etc. He had continued his work in that modest Indian Association and Sir C. V. Raman had continued on the problems on the mysterious colour and he had guessed that there was not only a scattering of light, there was also a change of waves.

He had put various people on that problem; for example I suppose there are many illustrious people who had done that but the problem could not be solved. Ultimately he had found that there was actually a change of wave length. But some how or other he was not clear as to what was happening. The first paper which he published had talked vaguely about the change and something like the Compton effect—the Compton effect had recently been discovered and had reported about the change of wave length of X-rays. It was only by dint of very careful work at the Indian Association with very modest apparatus and with ordinary spectrograph in which exposures went over a 100 hours; that the actual discovery about the Raman Effect could be clinched to a successful issue and Krishnan had worked assiduously and without sparing himself and as a result he had almost blinded himself by this continuous work and the exposure to the ultra violet rays. However, that brought fame to India. Raman Effect was there and they were so energetic and organizationally so able was Sir C. V. Raman that as soon as he recognised that there was something very new he put into the problem various, all the resources that could be possibly utilized in putting, pressed into service and had the problem searched out. And Krishnan had remained associated with him with this work.

Of course some people had thought that it should be called Raman-Krishnan Effect. But Raman himself would have been very angry if anybody had said it is Raman-Krishnan Effect. Though there were the foreigners who wanted to say that was Raman-Smekal Effect. The German's had thought that Smekal had already thought of the possibility of a similar phenomena and had talked about it though of course he had done no experiments himself and the first work of Raman was not with atoms but with molecules and, however, the Germans continued to talk about it as Raman-Smekal effect making Sir C. V. Raman very angry. So nobody could talk about it other than Raman Effect. Though there were the Russians who talked about Landsberg and Mandelstam as the first to notice this effect—they put forward I suppose some sort of a claim that it was observed in the solids etc. But, however, so energetic were Raman and his pupils that they convinced the world that here was a new novel effect—effect which neither Stokes or Rayleigh had thought of and there were proof positive and there were hundreds of experiments done all with very modest apparatus at the Indian Association. Either with the old superanuated

apparatus which were treasured there or with some of the new apparatus which were bought for postgraduate work at the College of Science and then Sir C. V. Raman had proved completely that two things—that it is possible by modest means if only one really had a dissent of the new and the mysterious and were not daunted and went on solving problems he will be able to solve them and with even ordinary efforts. One need not wait for all the apparatus to come from abroad to have them for their research work purposes but if you are anxious you could do it. So Raman and Krishnan worked together and then after sometime when there was necessity at the newly instituted university at Dacca to make appointments for a reader of physics—Krishnan was taken in and Raman came and recommended Krishnan as one of the brainiest of his pupils.

Krishnan came, he thought for a few months about continuing the Raman Effect experiments there but then gave up. And then he took to a new problem and where he has made his name, where his pupils have developed methods, this method of making magnetic assymetric magnetic measurements and crystals. Now one of these pupils had talked about it yesterday and you should remember though they had now developed and got new things indented liquifiers etc. from abroad in which they intend to go down to the temperature of helium. The first measurements were made with apparatus with the coarse fibre which were drawn at the laboratory with the measurements done with ordinary instruments and so on. That demonstrated once more that if you have problems and if you really want them to solve, there will be methods by means of which you could really make a sort of brilliant beginnings. I don't mean to say, I don't want to discourage the government from giving grants to the science, saying, that it is not necessary. But what I mean to say that before such grants are given ample facilities exist in our country to prove the capacity of the various people and the immediate necessity of getting new things indented from abroad. Now a days the question of getting apparatus from abroad has become rather of second grade importance because of the development of our industries; because of a large number of trained technicians which are now available in our country. We remember when we were students then the professors used to hold on to his mechanic you see that, as something of his most precious possessions. For example, there was a mechanic of Sir J. C. Bose and he did very fine work indeed to the sort of amazement and because Sir C. V. Raman had cast his jealous eyes on this particular one mechanic or the other, he grew furious, he was very angry and Sir C. V. Raman had contented himself with getting a sort of somebody who had voluntarily given up the service because of higher emoluments at the Indian Association which he had procured for him. But this Sir J. C. Bose wouldn't forget and wouldn't forgive.

Now I tell you these simple, these curious little stories and anecdotes to remind you that about 70-80 years ago there was a paucity of even technicians in our country and we used to quarrel about the possession of a particularly gifted person or the other to be kept inside the laboratory rather than be given away to a com-

petitive person. Now there are a lot of technicians in our market and we are now finding it difficult how to suitably give employments to these technicians. And, if therefore, there were persons in our country who had problems which he wishes to solve which will require facilities and well, gifts of peculiar nature of ability, well, I think our among the many thousands or many hundreds of thousands of people who have now been trained during all these years there would not be any dearth of people who if suitably used, organized and put to work will produce, will solve problems which the country had to face.

Now I am telling you simply because reviewing the early history of the introduction of science in our country I remember among these great names then begun life very humbly who had very humble resources at their disposal but who had imagination, who had layers of genious, who had indomitable patience, who could solve problems for themselves, who would enthuse young men by their example and thereby place a goal among others before our young men and place India as you say in the map of science. Well gentlemen I have talked a great deal; talked only to remind you of the (since I have talked about Krishnan Memorial Lecture) the picture of K. S. Krishnan as he was then a modest investigator in the laboratory of Dacca, who loved his pupils, who lived like an Indian Guru surrounded by his students and thereby produced enthusiasm.

Thereby not only Krishnan had progressed, had solved problems, had created fresh problems, had been one of the founders of this National Physical Laboratory where we all have assembled but throughout the country there are students, his own pupils, who had worked, who had found work, found problems, who had been at it, who had more or less been inspired by his example and thereby had produced for India a rich resource with men and money. Men in the sense that there along with these people laboratories have sprung up all over the country where young men are trained and given suitable opportunities they will be able to solve problems. Only one thing somehow or other in our country, there is something, I suppose it is a sort of evil star in our country in which though we make very good beginnings somehow or other we finish rather a sort of a very third or something.

Though we had produced these brilliant young men but at the same time we have not been able to produce or to make as much progress as we could really hope, ultimately in the field of research and industries. As to why? However, if we only remember that when we were young, people used to point out, point a finger at Japan and we had a song that though these half savages they can boast of independence, we had no independence and so on. There was that celebrated song about Hemchandra. And, however, they had thought of western methods and resolutely by means of the few very far seeing statesmen who had chosen upon themselves the task of getting scientific knowledge from abroad. Result : within hundred years or so Japan had become a name to be respected in the history of science and even now though Japan had been humbled by the last war and had

been devastated, had been under the heels of the aggressor, but Japan had been able to maintain their supremacy and their place in the first ranks of the scientists by means of their own efforts. Well, I sometimes think why is it that India who had more or less, very often been able to see very much farther than the others who had seen the sun rise very much earlier than any other people; why India and the Indians had not been able to take advantage of the early seers and have not been able to continue this advantage and to maintain their pre-eminent position in our country.

Well, I leave these questions to the history and to the new generation of the young people who some how or other feel that they have got nothing in common with the old fogies. Now especially in Bengal they talk about the generation gap. The gap is there. One can not gain say it, and it is a challenge. It is a perpetual challenge to the Indian genious as to how even though the country is endowed with such natural resources, even a country which had such brilliant history why it continues to remain third rate inspite of so much and so many resources and so much of man power. Well, gentlemen I stop here with these questions asked to our young men.

Virtual Interactions Between Atoms and Electromagnetic Fields

by

PROF. A. KASTLER

We know that atoms can interact strongly with electromagnetic fields if the frequency of the oscillating field ν_0 is "on resonance" with the atoms, if it satisfies Bohr's condition $h\nu_0 = E_2 - E_1$, where $E_2 - E_1$ is an interval between two discrete energy states E_2 and E_1 of the atom.

In this case we observe "real processes" or "transitions". If the atom is in the lower state it can absorb radiation of frequency ν_0 and it is lifted to the upper state. If the atoms is in the upper state it can emit radiation of frequency ν_0 either spontaneously and this gives to the upper state a limited lifetime τ — or it can emit this radiation by stimulated emission. In all these real processes energy, momentum and angular momentum are conserved, the number of photons in the radiation field changes, and the populations of atoms N_1 and N_2 in the states E_1 and E_2 undergo changes. The Bohr-equation expresses conservation of energy.

Now let us look on a different case, where the atom is in presence of a radiation field of frequency ν, and where the Bohr condition is not fulfilled:

$$h\nu \neq E_2 - E_1$$

$$h\nu = E_2 - E_1 + \delta E$$

There is an energy discrepancy δE.

We know that in this case real transitions of absorption or emission cannot take place. They would violate the conservation of energy. We know that nevertheless there is some interaction. We know for example that in a transparent medium—a piece of glass—the velocity of light is not the same as in vacuum. The medium does not absorb photons, but it changes their properties, their speed.

The question arises:

What is in this interaction the action of the photons on the medium, on the molecules and the atoms of the medium?

This problem has been investigated theoretically and experimentally by Claude Cohen-Tannoudji and his coworkers, and I want to show you some experimental results obtained.

Virtual Processes

Interactions of photons which are "off resonance" with atoms violate the conservation of energy. But we know that if we look on an energy state of an atom during a very short time δt, this state gets a "fluffyness" δE according to Heisenberg's uncertainty relation

$$\delta E \times \delta t \simeq \hbar$$

Owing to this relation an interaction becomes possible, in spite of the energy discrepancy δE provided the time of interaction satisfies the condition.

$$\delta t \leqslant \frac{\hbar}{\delta E}$$

An atom is able to absorb for a short time a non-resonant photon provided it remits it again before time δt is over.

An atomic system in vacuum can emit photons of any frequency ν provided it reabsorbs them again in the time limit imposed by the uncertainty relation.

Such ultrashort process of interaction with non-resonant photons are called "virtual processes".

Virtual processes have real results:

In vacuum an atomic system is continually emitting and reabsorbing "virtual photons" of any frequency. We can look on the atom or on the electron as being surrounded by its "virtual photon cloud."

As a result of these virtual processes the magnetic moment of the electron, associated to its spin, remains not exactly one Bohr-magneton μ_B but becomes

$$\mu_S = \mu_B (1 + \epsilon)$$

Theory predicts that

$$\epsilon = \frac{\alpha}{2\pi} - 0{\cdot}3285 \frac{\alpha^2}{\pi^2} + 0{\cdot}19 \frac{\alpha^3}{\pi^3} + \ldots$$

where α is the fine-structure constant.

This "anomaly" of the magnetic moment of the electron was experimentally established by Kusch and his collaborators. ϵ was accurately measured by Crane who found:

$$\epsilon = 1{\cdot}1596 \times 10^{-3}$$

A consequence of this is that the Zeeman-splitting between the substate $m_S = +\frac{1}{2}$ and $m_S = -\frac{1}{2}$ in a magnetic field corresponds to a Lande-factor different from 2.

$$g_S = 2(1 + \epsilon)$$

Another result due to these virtual processes in vacuum is a shift produced on the energy levels of atoms $\tilde{E}_1 = E_1 + \delta E_1$.

We do not know E_1, we can only measure the position of the shifted level $\tilde{E}_1$. But there is the happy case of levels which according to Dirac's quantum mechanical theory should be coincident, and which, through the virtual processes, are submitted to different shifts. This is the case for the two levels $2\,^2S_{1/2}$ and $2\,^2P_{1/2}$ of the hydrogen atom. The difference of the two shifts appears in the "Lamb-shift" measured in the experiment of Lamb and Rutherford:

$$\tilde{E}_S - \tilde{E}_P = h\nu, \text{ where } \nu = 1057{\cdot}8 \text{ MHz.}$$

If the atom is in a radiation field, induced virtual processes of absorption and re-emission of photons will take place and produce analogous effects—changes of magnetic moments and displacements of energy levels. The magnitude of these effects will depend on the intensity of the radiation field surrounding the atoms.

Following Cohen-Tannoudji we call atoms surrounded by a non-resonant radiation field "dressed atoms".

As we will see the properties of "dressed atoms" may be very different from those of "bare atoms".

Atoms dressed by a non-resonant radiofrequency field

We are able to produce progressive or standing monochromatic electromagnetic waves in the radiofrequency range, and to produce such waves having a high intensity. If we put atoms in such an oscillating RF field, its magnetic moment is substantially changed. Let us take the case of a standing RF magnetic field

$$H_1 \cos \omega t$$

produced in a RF coil. Let us define $\omega_1 = \gamma H_1$ where γ is the gyromagnetic ratio of the atom.

Theory shows that the g-factor of the atom dressed by the RF field is given by:

$$g = g_0 J_0 \left(\frac{\omega_1}{\omega}\right) = g_0 J_0 \left(\frac{\gamma H_1}{\omega}\right)$$

where g_0 is the normal g-factor of the bare atom and where J_0 is the zero-order Bessel-function of the dimensionless variable ω_1/ω with the zero values 2.40—5.52 —8.65 etc.

If the amplitude of the RF field corresponds to one of these values, the g-factor of the atom is reduced to zero, the magnetic moment of the atom is made equal to zero.

The measurement of the g-factor can be done in different ways:

(a) by measuring the width of the Hanle-curve

(b) by measuring the Larmer frequency of a free precession in the magnetic field

(c) by measuring the frequency of a radiofrequency resonance.

An experiment is made in the following way:

In a collection of atoms (Hg-vapour containing the isotope ^{199}Hg) a magnetic moment M_0 is produced in the X-direction by optical pumping and a small magnetic field H_0 is applied in the Z-direction which produces the Larmor-precession of the moment M in the XY plane. This precessing moment decays with a decay-constant τ identical to the relaxation time. The moment in the X-direction is given by

$$M_X = \frac{M_0}{1 + (\omega_0 \tau)^2}$$

where $\omega_0 = \gamma H_0$ is the Larmor-precession frequency. γ is related to the g-factor by $\gamma = g\,(e/2m_0)$. The half-value width of the Hanle curve corresponds to $\omega_0 \tau = 1$ or $\gamma H_0 \tau = 1$. The corresponding field value is $H_0 = \gamma^{-1}\tau^{-1}$. τ being constant, this width varies proportionally to g^{-1}. The slide 4 shows Hanle-curves for ^{199}Hg corresponding to the nuclear paramagnetism in the ground state.

A different method has been used in the case of the ground state of an alkali-atom : ^{87}Rb, where the paramagnetism is due to the valence-electron and corresponds to 1 Bohr-magneton.

After a bulk magnetic moment is produced in the magnetic-field direction by optical pumping, a 90° pulse is applied, and the free precession signal is observed on a circularly polarized light beam in a transverse direction. By this technique one observes directly the change of the precession frequency (the modulation frequency) produced by the change of the H_1-amplitude.

In the case of alkali-atoms or of the hydrogen-atom still a third method can be used: the measure of the hyperfine-resonances between the two hyperfine levels of the ground state. A change of the Zeeman-intervals produced by dressing the

atoms, is reflected in the change of the HF resonances as is shown in slide 7. Slide 9 shows an application of this technique. In the ground state $^2S_{1/2}$ of an alkali-atom of nuclear spin i, the g-factor is given by

$$g_F = \frac{g_J}{2i+1} + \frac{2}{2i+1}$$

for ^{87}Rb, $i = \frac{3}{2}$ we have $g_F = \frac{1}{2}$

For ^{133}Cs, $i = \frac{7}{2}$ we have $g_F = \frac{1}{4}$

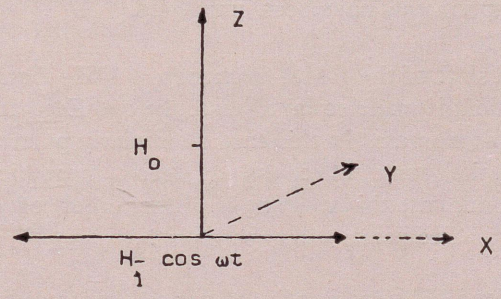
The two g-factors are different. The slide shows the Bessel-functions for both atoms. At a crossing point A the two g-factors have been equalized and the two atoms have the same Larmor-precession frequency. This can be checked in the following way:

Slide 10 : A mixture of Cs and Rb vapours is used. By optical pumping a longitudinal moment parallel to the steady field H_0 is induced in Cesium. By a 90° pulse it is transformed into a transversal precessing moment. Then the dressing field is applied equalizing the Larmor-speeds of both atoms. By exchange collisions the precessing moment of Cs is transferred coherently to the Rb-atoms. This precessing Rb-moment is monitored by an Rb-light beam whose intensity modulation is observed.

Slide 11 shows the experimental result.

Anisotropy of the Larmor-precession of a Dressed Atom

We have seen that by dressing the atom with a RF field we reduce the speed of the Larmor-precession.



The Larmor-precession takes place in the equatorial plane XY perpendicular to the steady H_0 field which is in the Z-direction. The dressing field is an oscillatory field in the X-direction of the equatorial plane. It changes the symmetry conditions for the atom. We have no more revolution symmetry around H_0. If we observe the components M_X and M_Y of the precessing transverse moment, we find that they are unequal. The magnetic-moment vector of the atom is precessing on an ellipse.

Atoms Dressed by Electromagnetic Fields of Optical Frequency

In the foregoing slides we have shown the effects on atoms of non resonant electromagnetic fields in the radiofrequency range. Analogous effects can be obtained by radiation fields of optical frequencies.

The frequency of the light beam inducing virtual processes must be "off resonance", but strong effects are obtained if the frequency k is near the frequency k_0 of optical resonance.

Let us take the example of the isotope ^{199}Hg of mercury whose ground state $6\,^1S_0$ shows only nuclear paramagnetism associated to the nuclear spin $i = 1/2$ and whose excited state $6\,^3P_1$ is split into two hyperfine levels $F = 1/2$ and $F = 3/2$. The two hyperfine components of the resonance line 2.537 Å : A ($i=1/2 \rightarrow F=1/2$) and B ($i=1/2 \rightarrow F=3/2$) are well separated, and one of the lines of the isotope ^{201}Hg is near component A of ^{199}Hg, the distance between the two lines being of the order of a Doppler width (1000 MHz). Irradiation with light of a ^{201}Hg light source produces a shift of the Zeeman sublevels of the ground state of ^{199}Hg. Which level is shifted? This depends on the polarization of the shifting light. σ^+ polarized light shifts the upper level $m_1=1/2$ upwards. σ^- polarized light shifts the lower level upwards. These shifts are detected by the change of the NMR frequency.

Slide 14 shows the experimental arrangement and slide 15 shows the shifting effects. The shift is proportional to the light intensity.

Slide 16 shows how the shift depends on k-k_0. The connection of this effect with anomalous dispersion is obvious. Here we observe the effect of the interaction on the atoms. If we measure the refraction index we are interested in the effect of the interaction on the light.

These shifting experiments have been improved.

Slide 17 shows a shift of the NMR frequency of ^{199}Hg from 33 Hz to 39 Hz.

If the magnetic field is made equal to zero, the two Zeeman levels $m_1 = -1/2$ and $m_1 = +1/2$ are degenerate. In this case a circularly polarized light beam "off resonance" produce the same effect as a steady magnetic field. It produces a Zeeman splitting. In our case this splitting is of the order of 6 Hertz. This effect has been observed by a free precession experiment.

A linearly polarized light beam, off resonance, can produce effects similar to those of a steady electric field. Such an effect has been observed on the ground state of ^{201}Hg of nuclear spin 3/2, where a magnetic field, produces a splitting into four equidistant Zeeman levels. A linearly polarized light beam of a ^{202}Hg-source produces shifts analogous to Stark shifts. Such a shift has been experimentally observed on the nuclear magnetic resonance line (by Cagnac, 1968) and on the level -crossing signals (by Cohen-Tannoudji, 1968).

In conclusion we can say that by dressing atoms with strong electromagnetic fields we can change their properties. We can either suppress the Zeeman splitting in spite of the presence of a steady magnetic field, or we can produce Zeeman splittings or Stark splittings in absence of any steady electric or magnetic field.

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ILLUSTRATIONS

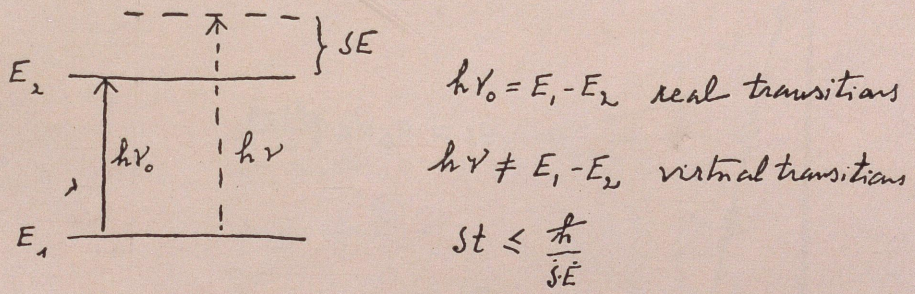


Fig. 1

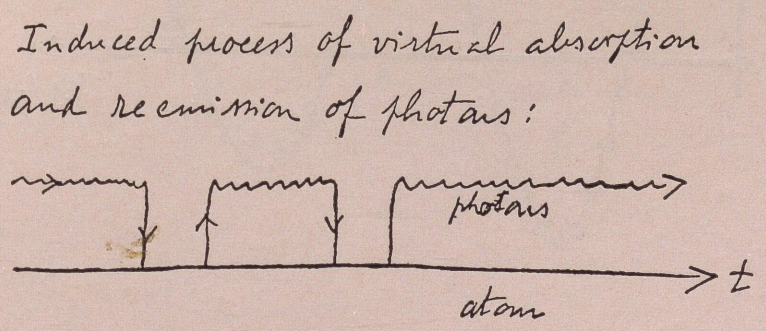


Fig. 2(a)

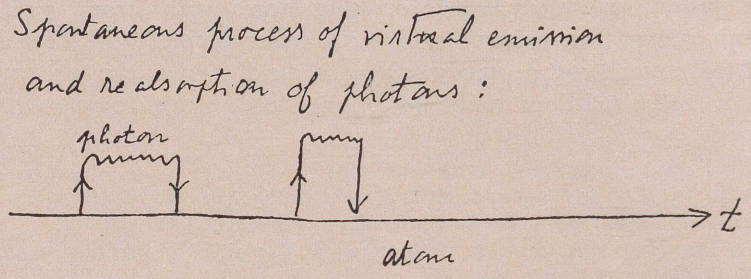

Spontaneous process of virtual emission
and reabsorption of photons :
photon
t
atom

Fig. 2(b)

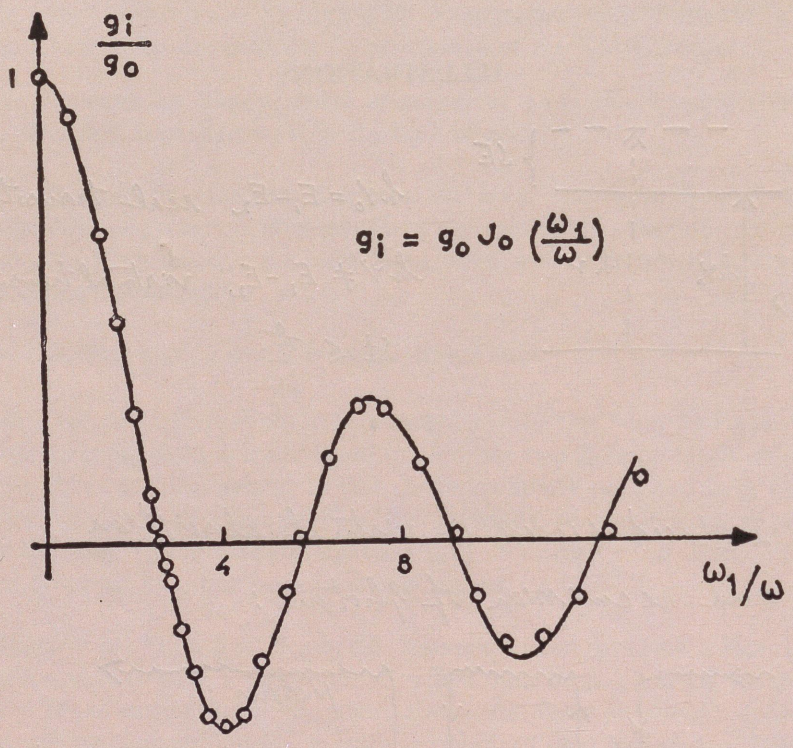

gi/g0
1
gi = g0 J0 (ω1/ω)
4
8
ω1/ω

Fig. 3

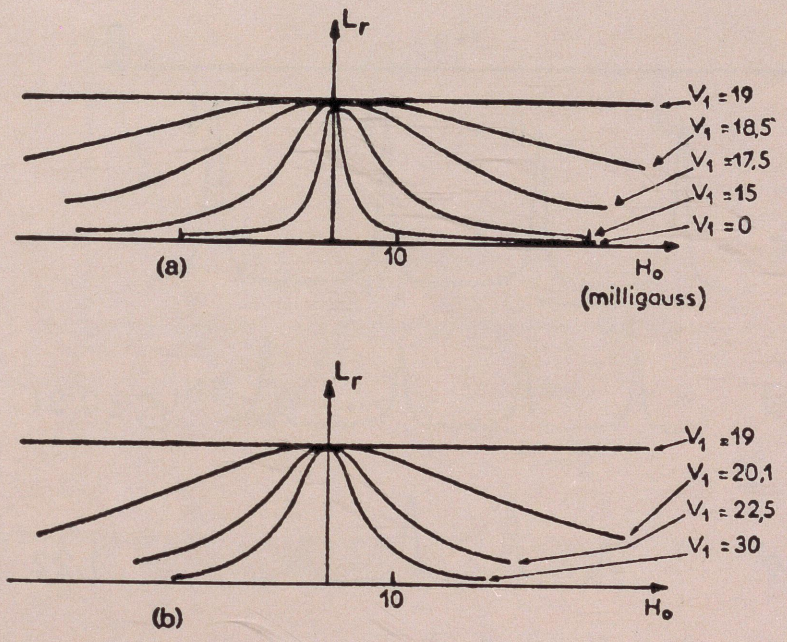

L_r
$V_1 = 19$
$V_1 = 18,5$
$V_1 = 17,5$
$V_1 = 15$
$V_1 = 0$
(a)
10
H_o
(milligauss)
L_r
$V_1 = 19$
$V_1 = 20,1$
$V_1 = 22,5$
$V_1 = 30$
(b)
10
H_o

Fig. 4

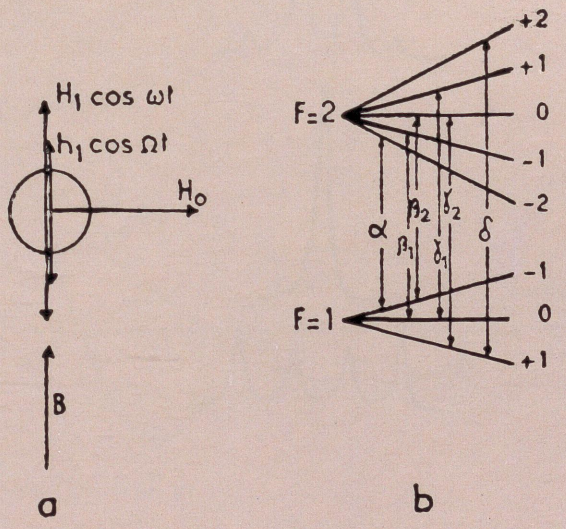

$H_1 \cos \omega t$
$h_1 \cos \Omega t$
H_o
B
a
+2
+1
0
-1
-2
F=2
-1
0
+1
F=1
α
β_2
β_1
γ_2
γ_1
δ
b

Fig. 6

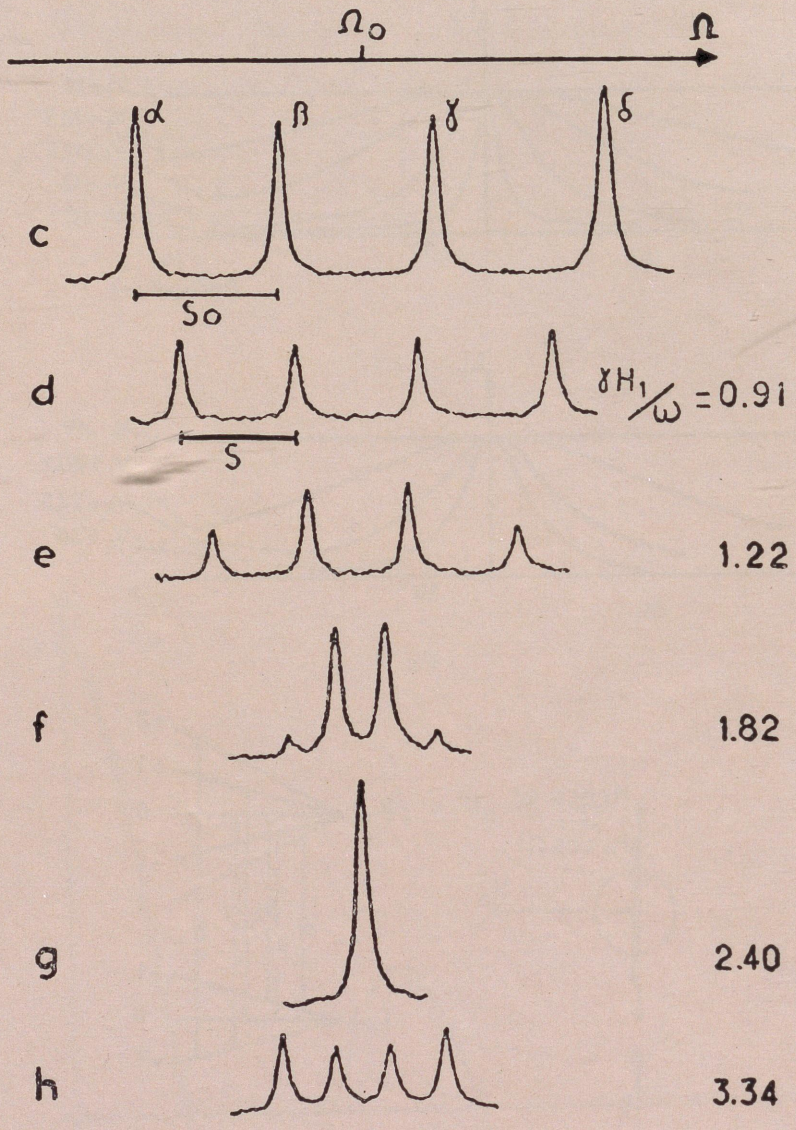


Fig. 7

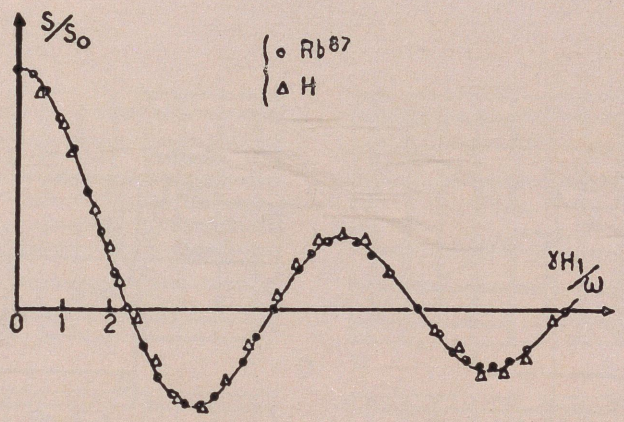


Fig. 8—Plot of the ratio s/s_0 as a function of $\gamma H_1/\omega$. The experimental points for Rb^{87} and H fit into the same theoretical curve

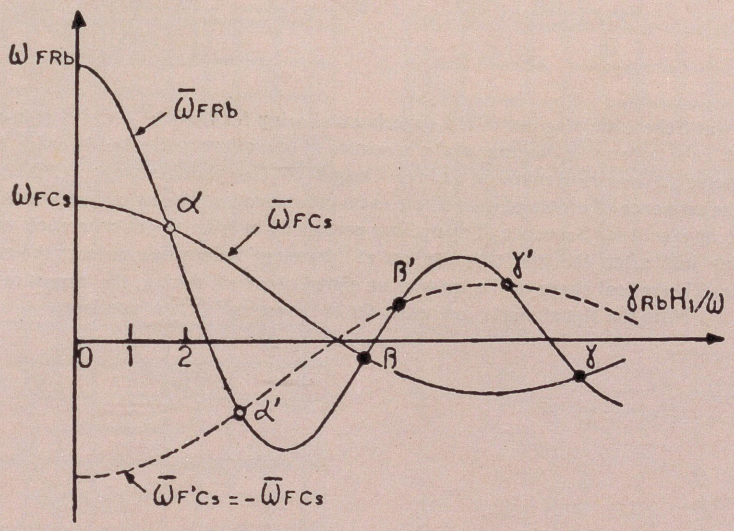


Fig. 9—Plot of Rb^{87} and Cs^{133} Larmor frequencies in a given static field H_0 as a function of the rf field amplitude measured by the dimensionless quantity $\gamma Rb H_1/\omega$ (γRb is the Rb gyromagnetic ratio). The Solidline curves gives the frequencies $\bar{\omega}_{FRb}$ aed $\bar{\omega}_{FCs}$ of upper hyperfine levels in both alkalis. The dashed-line curve represents the frequency $\bar{\omega}_{F'Cs} = -\bar{\omega}_{FCs}$ of the lower F' level of Cs

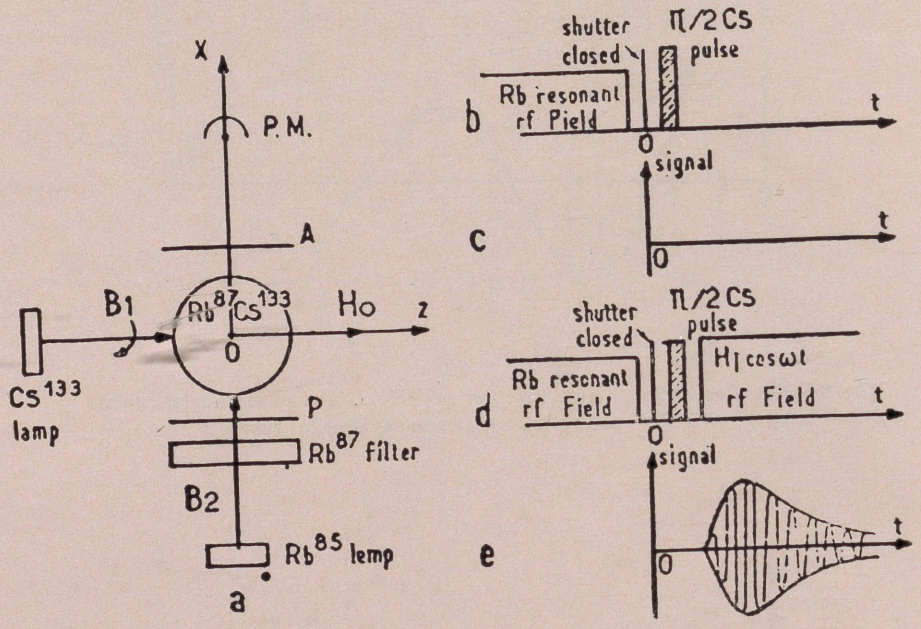


Figure 10—(a) Schematic diagram of the experimental setup for the Rb^{87}—Cs^{133} spin-exchange experiment. (b) Schematic diagram of the sequence of operations performed in order to introduce transverse angular momentum in Cs. (c) Output of the photomultiplier (P.M.) during and after the sequence of events of (b) : There is no coherence transfer at all and no signal is expected to appear. (d) Sequence of operations performed in order to get coherence transfer : One applies just after the $\pi/2$ cs pulse an rf "dressing" field which matches the atomic g factors. (e) Theoretical shape of the transfer ac signal obtained during the sequence of (d). Note the signal starts just when the rf "dressing" field is applied.

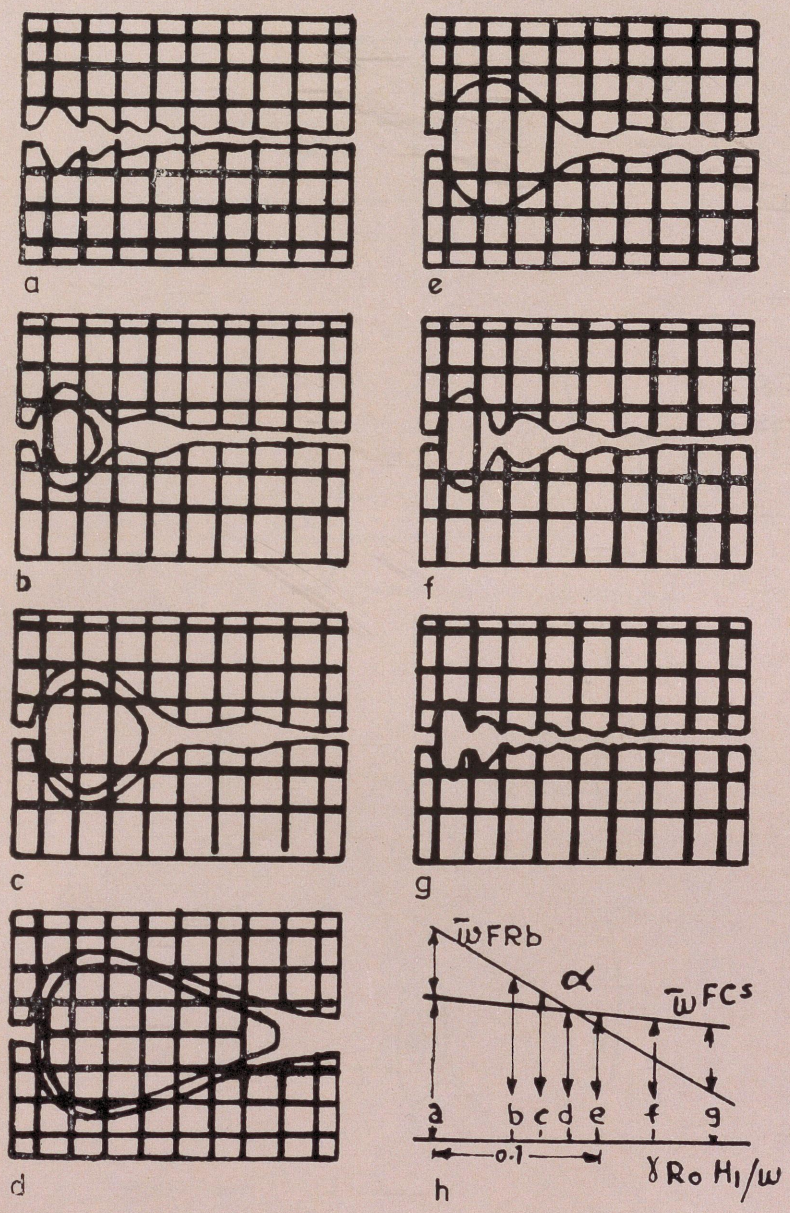

a
e
b
f
c
g
d
$\bar{\omega}_{FRb}$
α
$\bar{\omega}_{FCs}$
a
b
c
d
e
f
g
0.1
$\gamma_{Ro}\, H_1/\omega$
h

Fig. 11

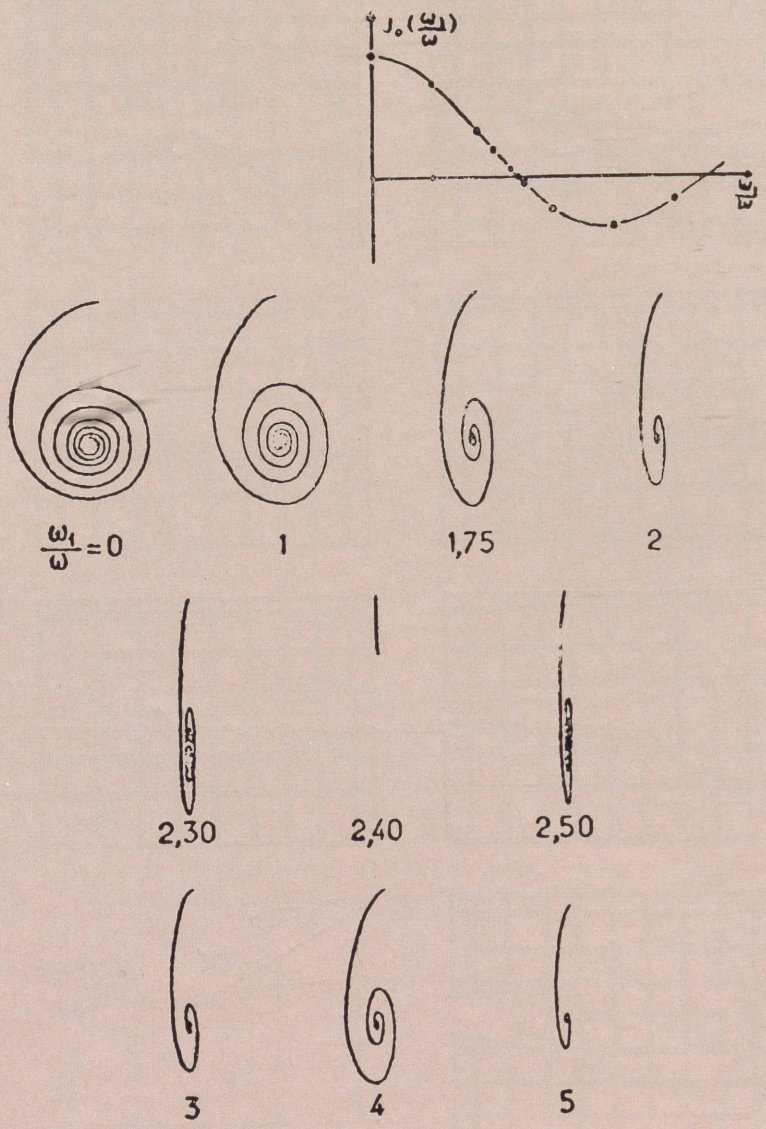

$J_0(\frac{\omega_1}{\omega})$
$\frac{\omega_1}{\omega}$
$\frac{\omega_1}{\omega}=0$
1
1,75
2
2,30
2,40
2,50
3
4
5

Fig. 12

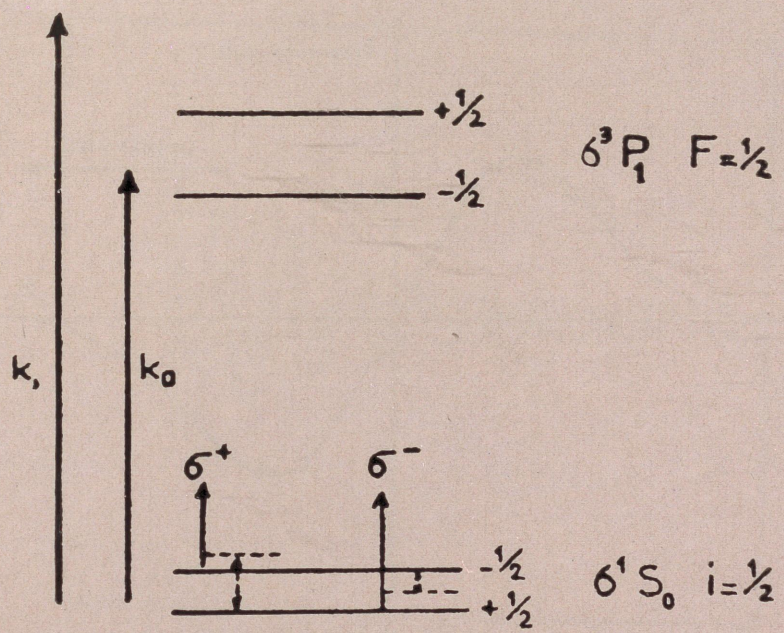


Fig. 14—Level shift produced by virtual transitions

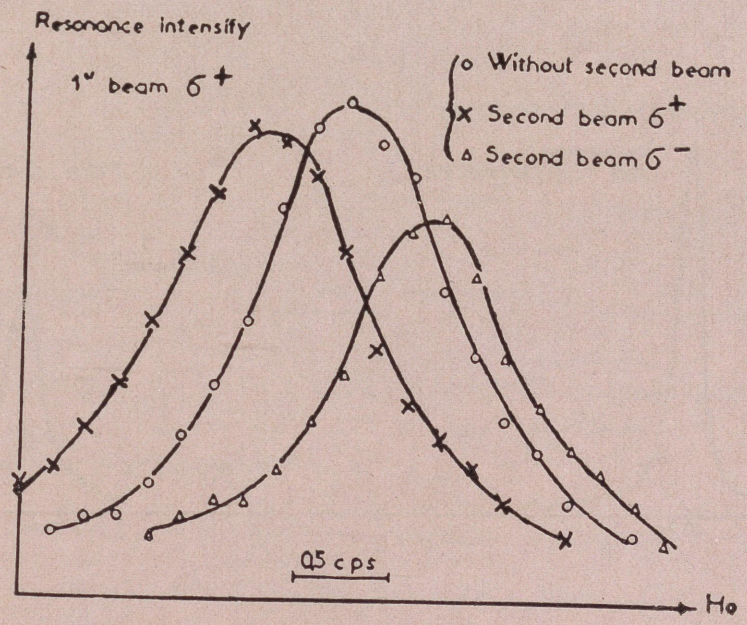


Fig. 15 – Shifts produced by σ^+ and by σ^- light

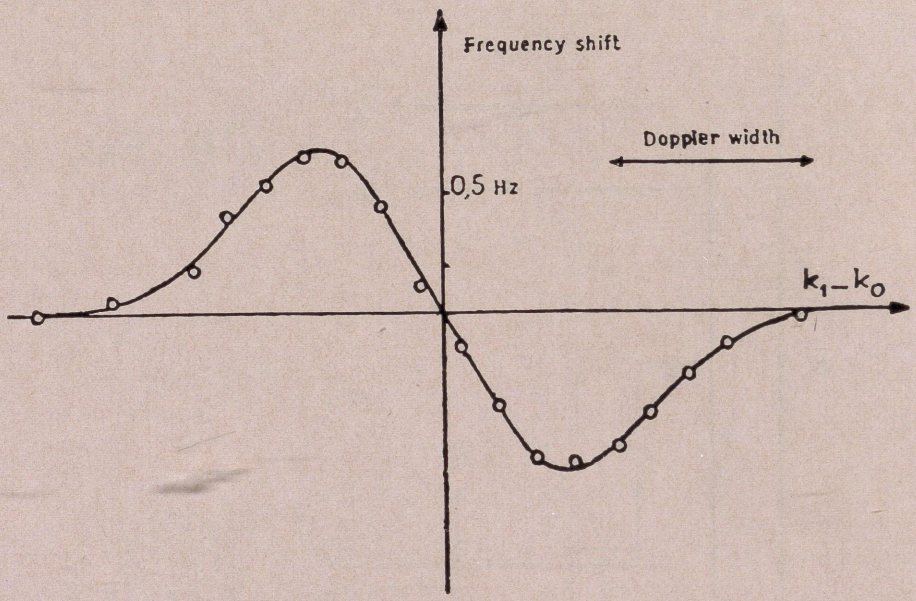

Frequency shift
Doppler width
0,5 Hz
$k_1 - k_0$

Fig. 16

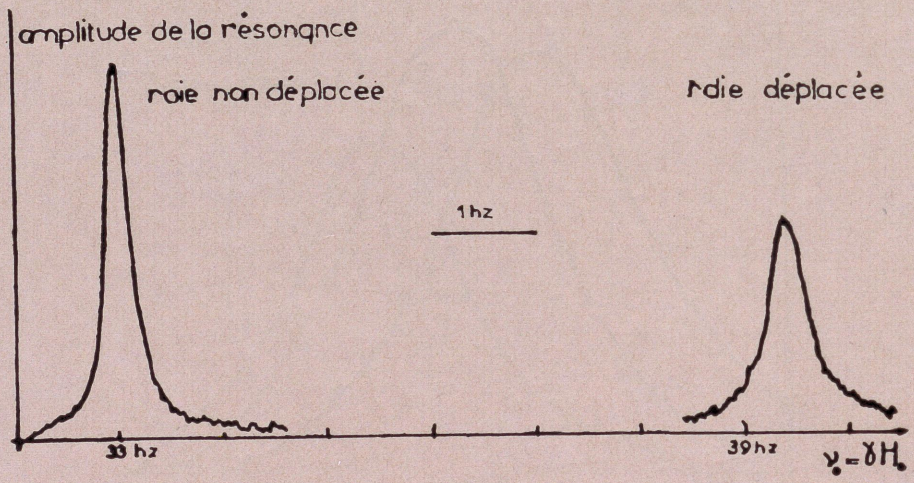

amplitude de la résonance
raie non déplacée
raie déplacée
1hz
38 hz
39hz
$\nu_0 = \gamma H_0$

Fig. 17

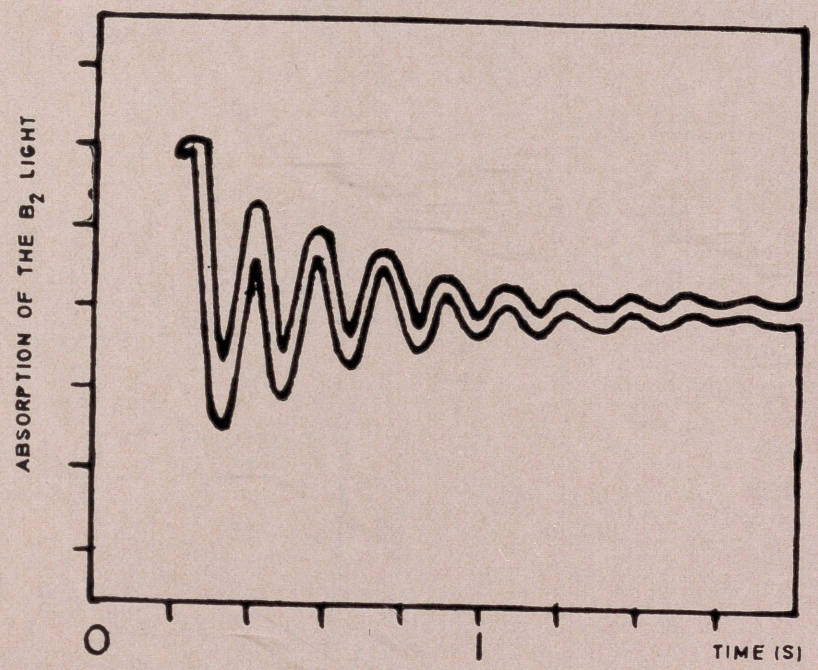

ABSORPTION OF THE B_2 LIGHT
0
1
TIME (S)

Fig. 18

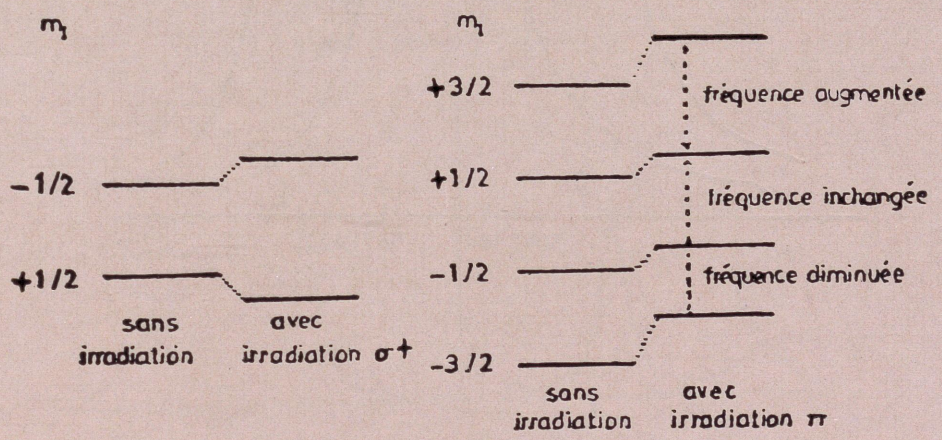

m_1
-1/2
+1/2
sans irradiation
avec irradiation σ+
m_1
+3/2
+1/2
-1/2
-3/2
fréquence augmentée
fréquence inchangée
fréquence diminuée
sans irradiation
avec irradiation π

Fig. 19

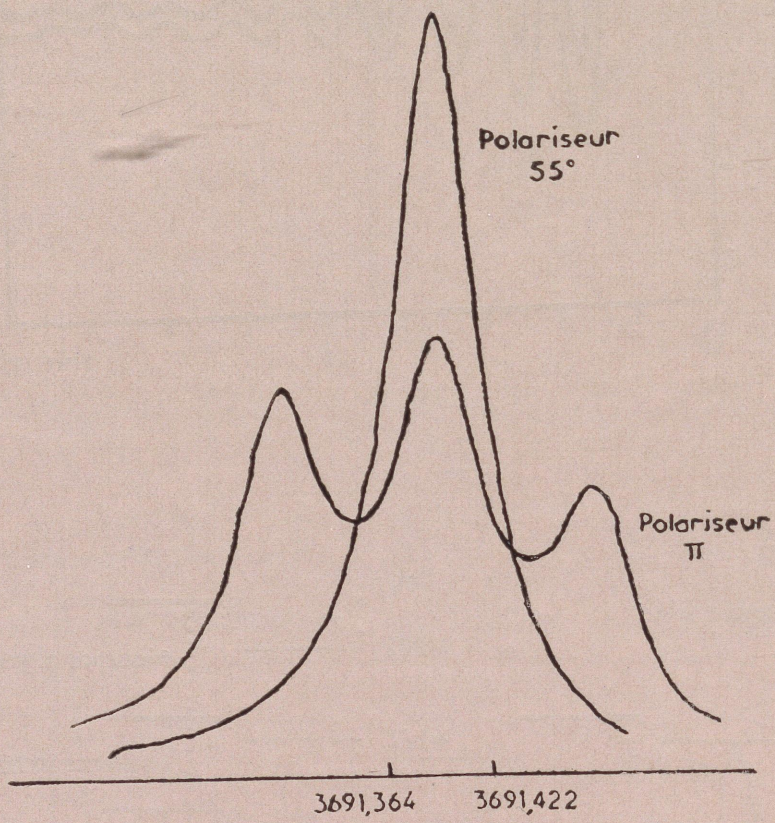


Fig. 20

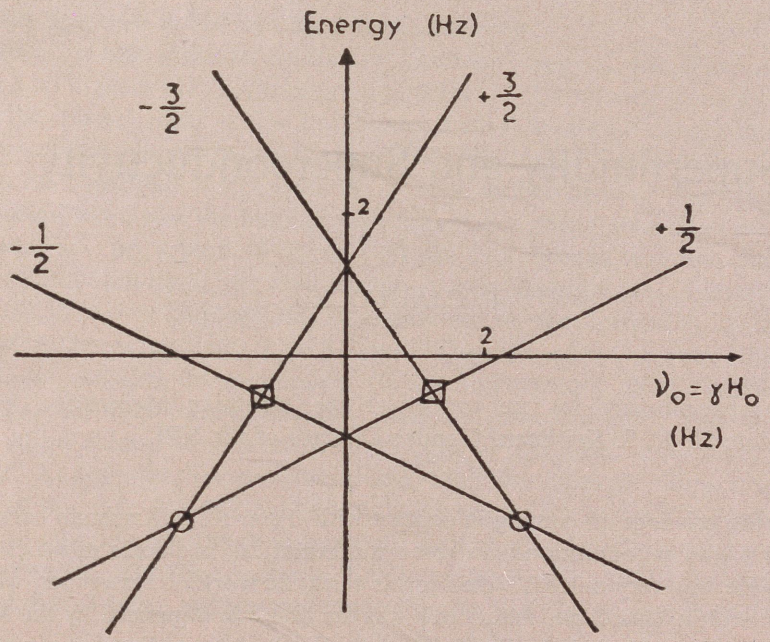


Fig. 21(a)

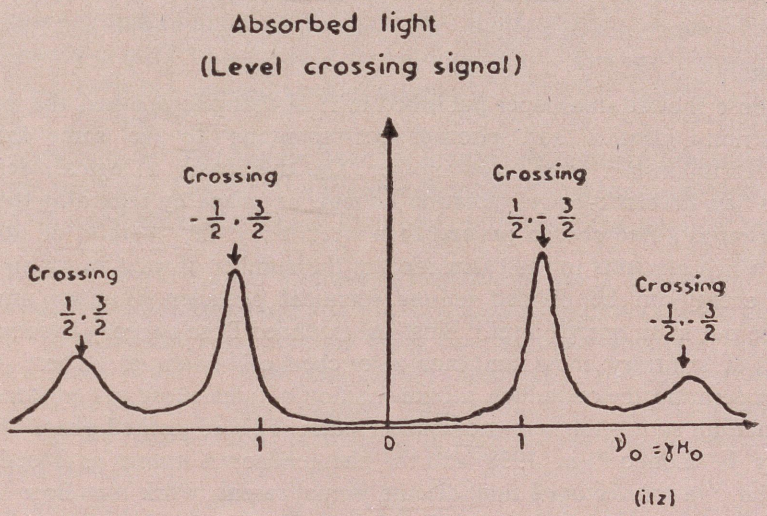


Fig. 21(b)

Superfluidity and Superconductivity

by

F. C. AULUCK

It is a great pleasure for me to deliver the Krishnan Memorial Lecture in honour of late Sir K. S. Krishnan, founder Director of the NPL.

I had the privilege of coming in contact with Prof. K. S. Krishnan early in my career. This was in connection with some mathematical problems in which he was interested. He was very much devoted to his scientific work. I remember we had a Summer School in Mussoorie, in fact this was the first one organised by the Ministry of Education, where Prof. S. N. Bose presided. We had long discussion among all the participants and Prof. Krishnan stayed throughout the duration of the Summer School. The last summer school on Theoretical Physics which Prof. K. S. Krishnan attended was held in Dalhousie in 1961. He was not well but even then he spoke for one hour. He returned to Delhi the next day. Probably he could not bear the strain of the journey and died the next day. I pay my homage in the memory of the noble scientist of international fame.

Introduction

S. N. Bose showed in a paper published in 1924 that photons had the property of being strictly identical and photons corresponding to the same frequency cannot be distinguished from one another. On this basis a logical derivation of Planck's 'law of black-body radiation' could be made by regarding the black-body radiation as a free photon gas and then treat it by the method of statistical mechanics which amounts to the calculation of the number of ways in which a given amount of energy can be divided among identical particles when any number of them can be put in an energy level. Einstein[2] extended Bose's theory to ideal gases of particles of arbitrary mass and non-zero chemical potential. There exists a critical temperature below which a finite fraction of ideal Bose gas condenses into a single quantum state—the zero-momentum state. This condensed phase was discovered by F. London[3] in 1938 and the phenomenon is known as Bose-Einstein condensation. In this lecture I shall discuss some recent work on Bose systems which undergo such change of phase like liquid He^4, liquid He^3, superconductors, excitons and one-dimensional systems.

Excitation Spectrum in He^4 and the Bose Condensate

I shall first talk about liquid Helium, London[3] applied the ideas of Bose-condensation to explain the properties of liquid He II. As is well known liquid He I goes to the phase He II at $T=2{\cdot}17$ K and there is an abrupt change in all properties. The condensate, consisting of the particles in the zero-momentum state, corresponds to the superfluid component. It is now well-recognised that Bose Einstein condensation represents the basis of the superfluid phenomena. However, an ideal gas would not be superfluid (that is, it can flow through very fine channels with apparently no viscosity at all) even though it may undergo Bose-Einstein condensation. As shown by Landau[4], this is no account of the instability in the flow due to the formation of elementary excitations. The interaction between the particles of Bose gas stabilize the condensate. In London's theory all the atoms go to the ground denotes state (zero-momentum state) at absolute zero, that is, if N_0 the number of particles with zero momentum and N the total number of particles, $N = N_0$. At any other temperature T less than the critical temperature T_c, the number of atoms in the condensate is finite and tends to zero as T tends to T_c. The theoretical estimates for the condensate N_0/N differ considerably varying from $0{\cdot}08$ as given by Penrose and Onsagar[5] to 0.71 as given by Byckling[6]. The theoretical calculations of Ker, Pathak and Singwi[7], and Girardea and Yoon[8] give the value 0.06.

The recent experiments of R.A. Cowley and A.D.B. Woods[9] have thrown a new light on the problem of Bose Condensate and excitation spectrum. By means of neutron scattering they have measured the momentum distribution of He^4 atoms and thereby the occupancy of the zero-momentum state. They have also found a new branch of a higher excitation spectrum together with the well-known lower phonon-spectrum. The new branch of the excitation spectrum is almost flat with an energy equal to about 20 K upto the wave number around 2.3 Å^{-1} and beyond it more or less equal to the free atom energy. The excitation spectrum in liquid helium, thus, has a two-branch structure.

The possibility of detecting the thermal excitations in liquid helium II was first pointed by Cohen and Feynman[10]. When a beam of monochromatic slow neutrons is incident on a sample of the liquid, each neutron is scattered creating an elementary excitation of momentum $\bar{h}\,\vec{k}$ and energy $\epsilon(k)$. By using the laws of conservation of momentum and energy one can obtain a dispersion curve for the excitations. The Fig. 1 gives the curve as deduced from the neutrons scattering experiments of Henshaw and Woods[11]. For small wave numbers k, the curve is linear. The curve does not end at the wave number 2.8Å^{-1}. The Fig. 2 gives the experimental results of the one-phonon excitations at 1.1 K and Fig. 3 also show the multiphonon peak.[9]

Neutrons act as microscopic probes whose resolution has a characteristic length $\lambda_{res} \sim 1/k$. This length may be compared with the interparticle distance in liquid

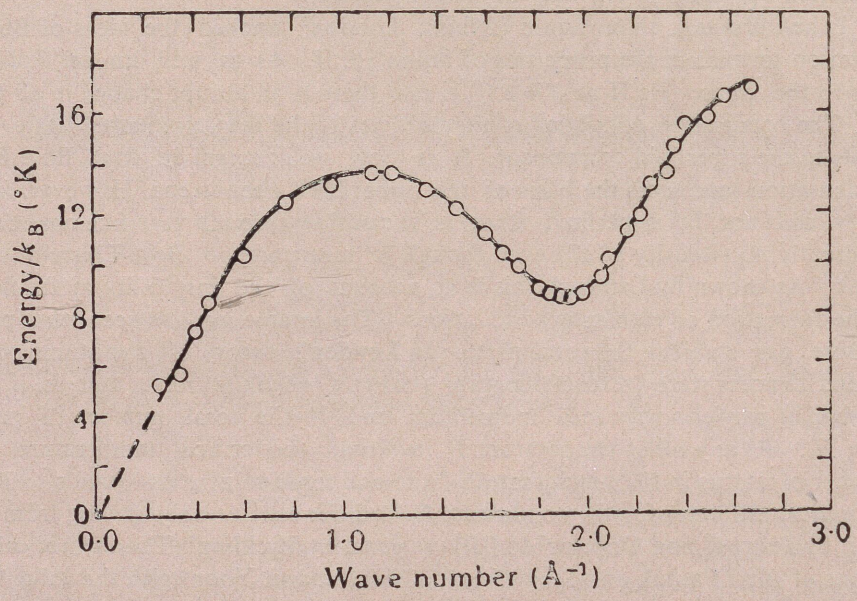


Fig. 1 – The dispersion curve for Thermal excitations in liquid Hell at 1.12 K, as deduced from the neutron scattering experiments (Reference 11)

helium. In the long wave length limit λ_{res} is greater than the interparticle distance λ_{int} and therefore the scattering takes place from a large number of atoms. The differential cross-section for scattering with momentum transfer $\bar{h}\vec{Q}$ and energy transfer $\bar{h}\omega$ is proportional to the structure factors $\vec{S}(Q, w)$ which gives information about the collective excitations in the liquid. However, in the short wave length limit ($\lambda_{res} << \lambda_{int}$) the scattering takes place from individual atoms and $\vec{S}(Q, w)$ gives information about the momentum distribution of the helium atoms. Thus when a high-energy neutrons (with energy 1 eV or more) scatters from an individual helium atom and is scattered when between collision, it experiences a Doppler shift due to the initial motion of the atom. If at $T=0$, all the atoms are in the ground state the differential cross-section reduces to a delta-function. Hohenberg and Platzman[12] have given an analysis of the conditions under which one can deduce the value of N_0, from such observations. The peak on the top of a broad back ground indicates the presence of a condensate. By using this data and the sum rules, they show that $N_0/N=0.062$ at $T=1.27$.

The problem of condensate is not even now fully understood inspite of a number of attempts. A complete understanding of the two (or possibly more) branches requires more work.

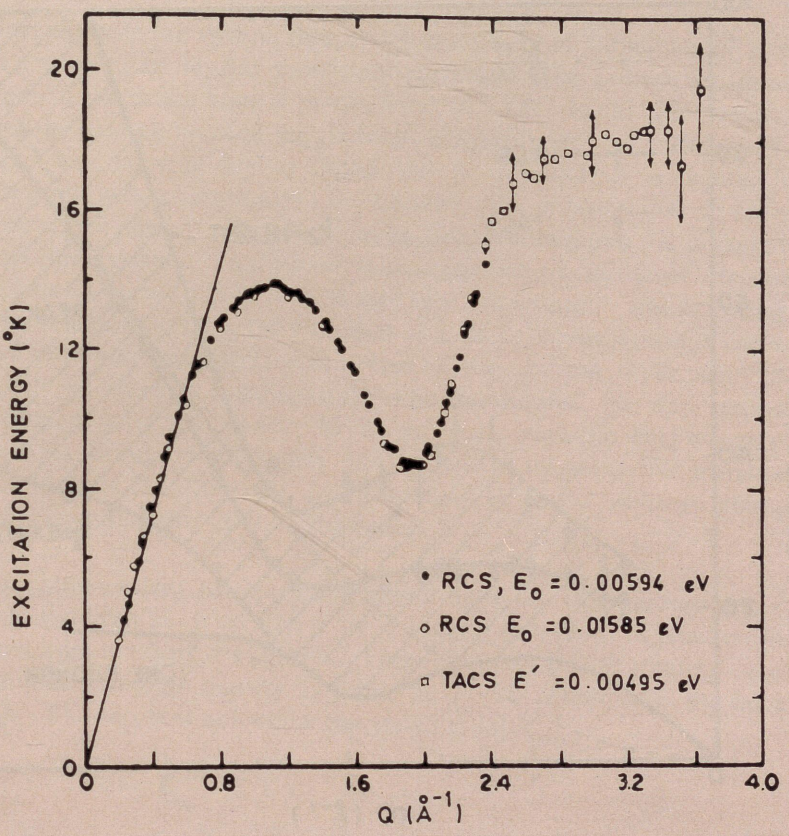


Fig. 2—The dispersion curve or the one-phonon excitations in superfluid helium at 1.1 K. $\hbar\vec{\phi}$ is momentum transfer (Reference 9); RCS—Rotating Crystal Spectrometer; TACS—Triple-axis Crystal Spectrometer; E_0 and E' are the energies of the incident and scattered neutrons

Superconductivity

It is now well recognised that Bose-Einstein condensation represents the basis of the superfluid and superconducting phenomenon. Superconductivity is a more general phenomenon. There are superconducting elements, solid solutions and intermetallic compounds. The transition temperatures vary from 0.0002 K to 23.2 K. In principle the transition temperature could be higher. Superfluids and superconductors possess many similar properties. The microscopic theory of Bardeen, Cooper and Schrieffer[13] has given an understanding of many diverse properties of superconductors. A superconductor can be made normal by the application of a magnetic field which at absolute zero is of the order of a few hundred gauss. The energy difference between the superconducting and the normal phase at absolute zero is of the order of 10^{-8} eV per atom. This may be compared with the Fermi energy of the conducting electrons in a normal metal which is of the order of

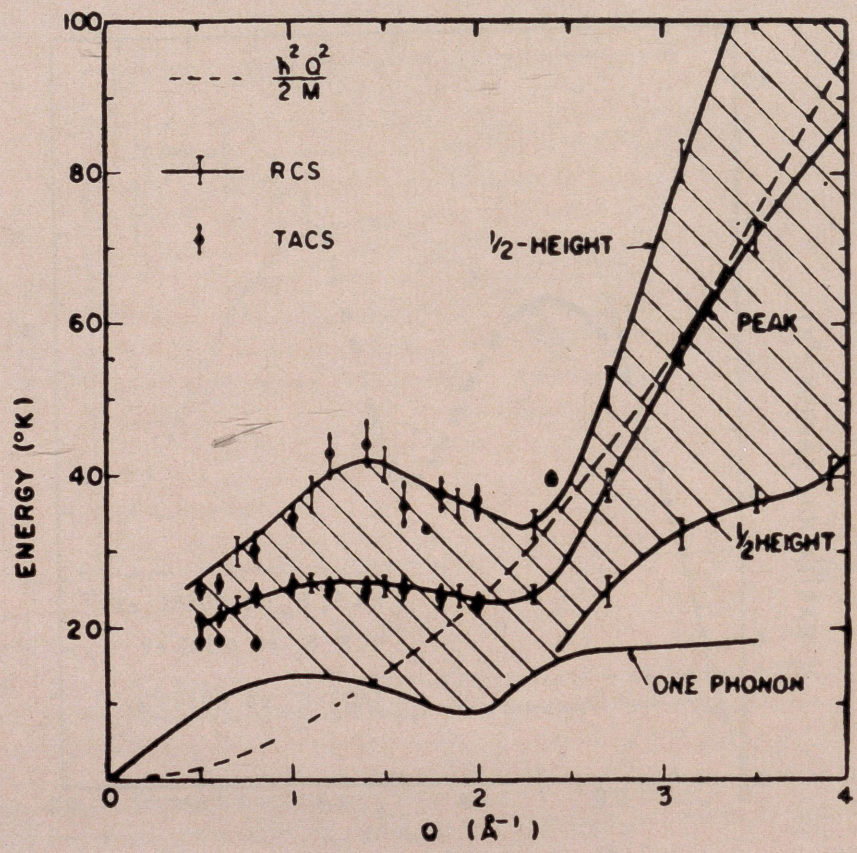


Fig. 3—The energy/wave vector dependence of the scattering at 1.1 K, energy of peak and of the high and low energy half-maxima of the multiphonon scattering

1—10 eV. Thus the energy involved is extremely small. The discovery of the isotope effect, that is the critical temperature T_c varies as $M^{-1/2}$ where M is the isotopic mass, showed that superconductivity is very largely due to an interaction between the electrons and the lattice. This is because the mean frequency is also proportional to $M^{-1/2}$. When an electron moves through the lattice it distorts the lattice and the lattice in turn acts on the electron by virtue of the electrostatic forces between them. This distortion of the lattice by an electron acts on the electron. The oscillations of the lattice can be quantized in terms of phonons; so in a lattice the interaction between two electrons can be visualised as due to exchange of phonons. According to the BCS theory the electrons in a superconductor, near the Fermi surface, experience an attractive interaction which dominates the screened repulsive Coulomb interaction and leads to the formation of Cooper pairs—electron pairs with equal and opposite momentum and with opposite spins. If the temperature is low enough, the pairing is energetically favourable. The energy

required to excite the system, then equals the energy of formation of a bound pair which acts as a gap in the excitation spectrum. The average separation between electrons in the bound state is of the order 10^{-4} cm. In the superconducting state the average spacing between the electrons is roughly 10^{-6} cm. The pairs therefore, overlap. The superfluidity of liquid He^4 is qualitatively accounted for by Bose condensation and, as emphasized by London, the condensation is an ordering in the momentum space and not a space-like condensation of clusters which then undergo condensation. In the case of superconductors, the inner structure of the pairs plays an essential role because electrons are fermions which distinguishes the pairing condensation from the spectrum of a Bose condensation. The existence of Cooper pairs was demonstrated in a striking way by the experiments of Doll and Nabauer[14], and Deaver and Fairbank[15] who showed that the flux trapped inside a hollow superconducting cylinder in an external magnetic field was quantized, the flux quanta being of magnitude $hc/2e$. As the magnetic field increased, the flux changed in units of $hc/2e$. The quantisation of flux also leads to the stability of persistent supercurrents in hollow cylinders.

Supraconductivity is a quantum phenomenon on the microscopic scale. The quantum state can be represented by assigning a single wave function $\psi=\psi\, e_i\, \phi$ to a macroscopic number of electrons. These electrons (Cooper pairs) condense into a single state and their density is given by $\rho=\psi^2$. They have the same quantum phase ϕ. The supercurrent which this state carries is

$$\vec{J} = \frac{e\,\bar{h}}{m}\,\psi^2\,\Delta\,\phi$$

This implies a direct connection between the quantum mechanical phase ϕ and experimentally observable parameters such as the supercurrent. In 1962 Josephson[16] predicted that the supercurrent tunnels between two superconductors separated by a thin insulating barrier. This current oscillates at a frequency ω which depends on the voltage V maintained across the barrier and the phase of oscillation would be determined by the magnetic field within the barrier. The Josephson frequency relation is $\omega = 2eV/\bar{h}$

The Josephson current relation is $j = j_0 \sin(\phi_1 - \phi_2)$

where ϕ_1 and ϕ_2 are the phases in the superconductors across the barrier and

$$\delta/\delta t\,(\phi_1-\phi_2) = 2eV/\bar{h}$$

δ_0 is the maximum zero-voltage current that can be passed by the junction, known as Josephson junction. When there is no applied field, a dc current will flow across the junction. However, when there is an applied field, the current would be

$$j = j_0 \sin\left(2e/\bar{h} \int_0^+ V(t)dt + \alpha\right)$$

where α is the phase difference at $t=0$. For a dc voltage V_0, the current oscillates rather rapidly and the near current is zero. However, when one applies a voltage at a very high frequency in addition to a dc voltage, the current-voltage characteristics show steps of constant current at voltages given precisely by the josephson's frequency relation $n\bar{h}\omega=2eV$. These steps were first observed by Sidney Shapiro[17]. By measuring the voltage at which the steps occur for a known frequency a precise measurement of e/h has been made correct to 1 in 10^9. This has been used for determining the values of the fundamental constants, which has resulted in the resolution of several discrepancies between theory and experiment in quantum electrodynamics and in the development of an 'atomic' voltage standard. There are a large number of applications of Josephson junctions in computer technology, microcircuit technology and fundamental investigations of superconductivity.

Attempts are being made to fabricate alloys with as high a critical temperature as possible. The critical temperatures now reported are higher than the boiling point of hydrogen which is very significant because the superconductivity applications can now be based on liquid hydrogen. John Gavaler[18] has obtained an alloy which has a critical temperature 22.3 K, and Wernick and W. Royer have raised it to 23.2 K.

However, these samples were produced by the sputtering process, which usually is not adaptable to fabricating large amounts of material in the thicknesses needed for devices that carry high electrical currents. L.R. Newkerk and F.A. Valencia[19] at Los Alamos have made superconductors in the form of a deposit of 25 to 30 micrometers in thickness in a copper tube 38 centimeters long by the chemical vapour deposition process. It is considered that this process lends itself to fabricate superconductors in commercial quantities for such as superconducting power transmission or high field superconducting magnets.

Attempts have also been made to prove the existence of superconductivity at very high pressures[20]. Kothari[21] in 1937 predicted that hydrogen in Jupiter may be in metallic state. The pressures in the interior of Jupiter are thought to reach 100 Mbar, and a number of scientists think that much of the planet is metallic hydrogen. The data sent by Pioneer 10 recently support known theories. The planet is mostly a Cauldron of liquid hydrogen except perhaps a small rocky iron bearing core. A number of experimenters in USA and the Soviet Union are trying to produce metallic hydrogen in the laboratory. The Russian experiments report to have produced metallic hydrogen at a pressure of 2.8 megabars. At the transition point the density changes from 1.08 to 1.3 g/cm^3. In USA metallic hydrogen has been produced at a pressure of 2 megabars at the density 1 g/cm^3. Two methods have been used for this purpose. In one method they use two concentric conducting cylinders that surround a cylinder of liquid hydrogen. The outer cylinder is driven inwards with high explosives shortly after a 60 kG magnetic field is applied between the cylinders. The magnetic field intensity increases to 10 MG in about 10 micro-

seconds. The field squeezes on the smaller cylinder, generating a pressure on the hydrogen sample. The pressure goes as high as 3.5 megabars and then relaxes in about 0.5 microsecond to 1.5 megabar. In the other method static pressures are used to obtain a pressure of 2.5 megabars. If metallic hydrogen turns out to be metastable, it will be extremely dangerous, because the stored energy may be 30 to 40 times greater than that of TNT. Some theorists[22] think that metallic hydrogen could be a room-temperature superconductor and may open entirely new vistas in technology.

One-Dimensional Superconductor

Considerable theoretical and experimental work has recently[23] been done on organic solids based on tetracyanoquinodimethane (TCNQ). The temperature dependence of their conductivity in metal-like above a critical temperature T_c and insulator like below this temperature; T_c is about 60K. A possible explanation of the phenomenon is the onset of Peierlsin stability, that is the system approaches T_c and is about to go semi-conducting it undergoes a doubling of the unit cell in which the molecules pairwise distort. The high conductivity which may be greater than 10^6/ohm cm observed just about T_c is attributed to fluctuating superconductivity arising from BCS-type pairing of the electrons associated with Peierls instability[24]. The metal-insulator transition temperature increases with pressure at the rate 1 K/kbar for the salt TTF (tetrathiofulvalinium)-TCNQ. The conductivity for this organic salt at 273 K increases by a factor at 20 kbar, while the peak conductivity near the metal-insulator transition remains independent of pressure. Theoretically, these properties can be explained as arising from an one-dimensional metallic model. But according to Matthias all the (TCNQ) compounds are ferroelectrics. The dielectric constants of these compounds vary between 350 and 800, a fantastically large value. There is at present no theory which explains the properties of these organic compounds.

Electron-hole Droplets in Germanium and Silicon

The condensation of excitons in germanium and silicon at low temperatures has been the subject of much interest recently. Since the first suggestion by L. V. Keldysh[25] ample experimental evidence has accumulated to show that electrons and holes in Ge and Si undergo a gas-liquid type transition. Both theorists[26] and experimenters have apparently confirmed the formation of conducting electron-hole droplets which are about 1 micron in size at temperatures of a few degrees Kelvin and the discovery of a condensed metallic phase in Ge and Si. Experiments have concentrated on proving the existence of the droplet phase and on measuring the condensation energy and the liquid-phase density. High electron-hole concentrations in germanium can be created by laser or electron beam excitation and study the luminescence lines as a function of increasing temperature. V. Marrello *et al.*[27] have demonstrated that the condensed phase of electrons and holes in germanium can be produced by electrical injection of holes and electrons from p- and n-doped contacts,

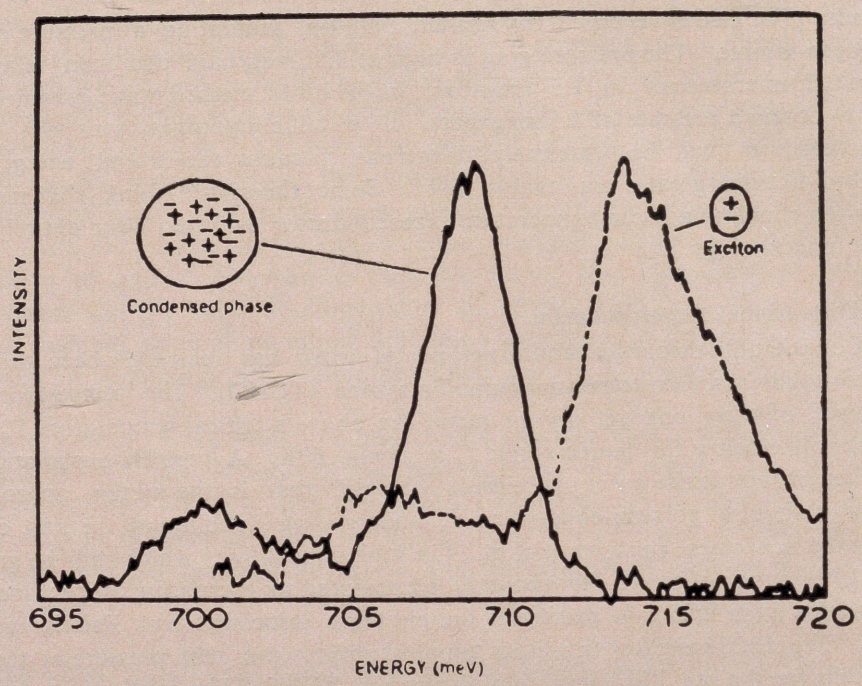


Fig. 4 —Electron-hole droplets. The dashed curve gives the intensity of exciton radiation corresponding to low electron-hole concentrations. The undashed curve gives the intensity characteristic of the condensed hole-electron phase at high concentrations and temperatures. The shift in energy is associated with the formulation of the condensed phase

current pulses that lasted ten millisec were used and radiation characteristic of the condensed phase was observed. This radiation came uniformly from the region between the contacts showing thereby that the condensed phase is present throughout the germanium sample. It is thought that eventually the droplet phenomenon may be of technological importance : whether exchange of virtual excitons or electron-hole pairs can lead to an effective attractive potential between electrons is still an open question.

On the Superfluidity of Liquid Helium^3

As is well known He^3 and He^4 remain liquid down to the lowest temperatures attained. Whereas the specific heat of liquid He^4 shows a lambda transition at 2.17 K, the specific heat of liquid He^3 does not exhibit any such behaviour about 1 K. It was thought that this difference is because of the fact that liquid He^3 is governed by Fermi statistics and liquid He^4 by Bose statistics. In 1972 Osheroff, Richardson and Lee[28] discovered two transitions below 3 milli degrees Kelvin. Measurements of the melting pressure of a sample of He^3, self-cooled to below 2 mK in a Pomeranchuk compression cell were taken. The Fig. 5 gives the time evolution and

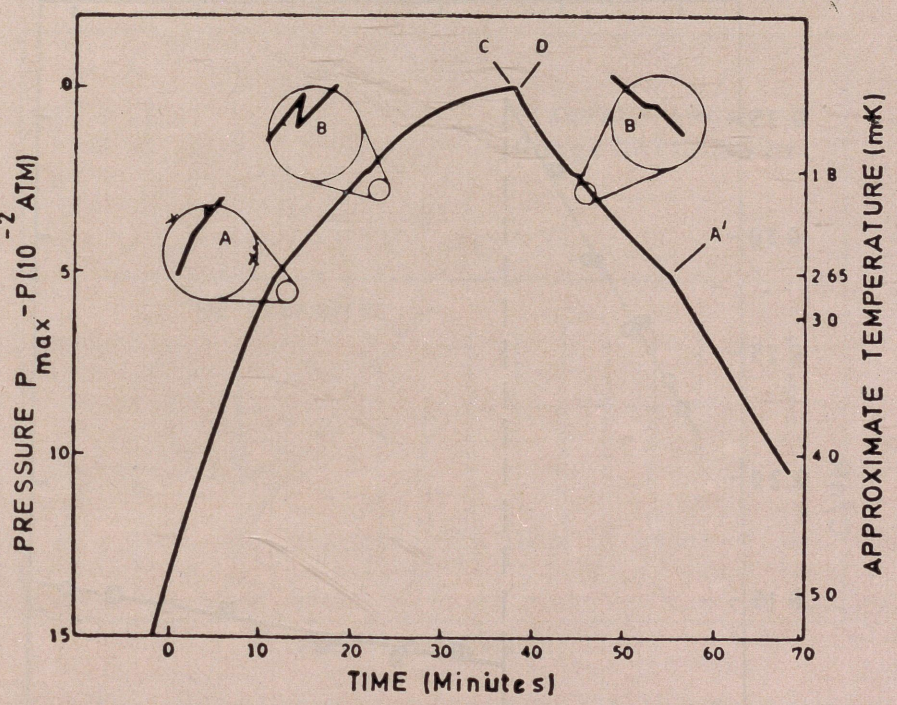


Fig. 5—The curve shows pressurization curve for He^3 on cooling and warming. At A and A′ there is a change of slope dp/dt. At B and B′ there is also a change of slope with a hysteresis in the compressive part

subsequent decompression. The rate dp/dt is constant initially. At the point A corresponding to pressure 33·9053 atmospheres there is a change in the slope dp/dt and this occurs at the temperature of 2·65 K. The change in slope, by roughly a factor of 1.8, occurs within a pressure interval of less then 3×10^{-4} atm. This indicates that there is a new phase below this temperature. Again at the point corresponding to the pressure 33.9279 atm and temperature below 2 mK there is a sudden drop in pressure of about 31×10^{-4} atmospheres on cooling. At C, 33.9575 atm, maximum pressure in the He^3 melting curve is observed. On warming through decompression no hysteresis is observed at B′ as is observed at B. All these features are reproducible and are independent of the rate of compression. Osheroff *et al.*[29], have made nuclear-magnetic resonance studies which show that both transitions A and B are related to the liquid He^3 and are not correct with the properties of solid Helium[3]. Webb *et al.*[31] have measured liquid He^3 specific heat and have observed a finite discontinuity in specific heat from 241 lb/in² to the melting pressure in the temperature range 2-3 mK. The ratio of the total He^3 specific heat just below to just above the critical temperature is about 2·9 at a pressure of 484·5 lb/in² (Fig. 6). From this result it follows that the A transition is a second order phase transition. The B transition is a first order transition phase.

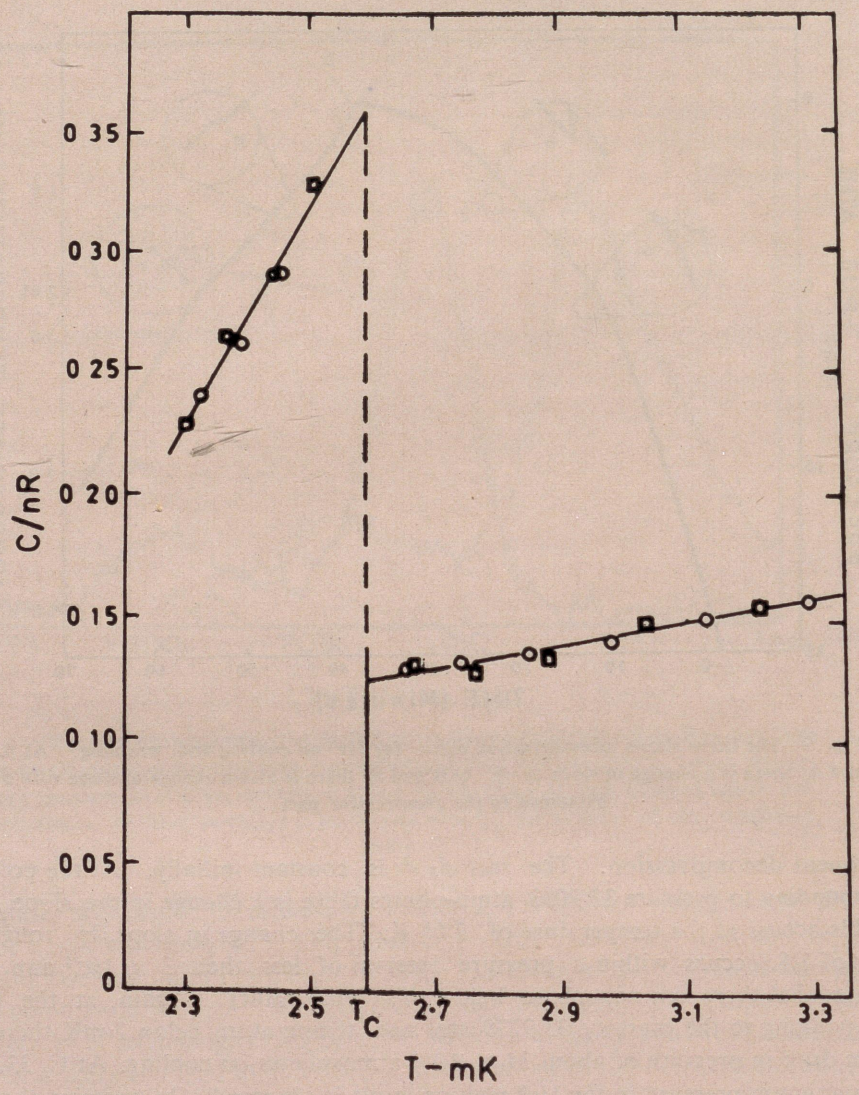


Fig. 6—Total molar heat capacity as a function of temperature of liquid He^3 show a discontinuity at the transition temperature A

The experiment done by Alvesala *et al.*[32] provide strong evidence that two superfluid transitions occur in liquid He^3 below 3 mK. These experimenters have measured the relative viscosity η of liquid He^3 along the melting curve from 10 mK to about 1 mK with a vibrating-string viscometer. The He^3 specimen was refrigerated inside a Pomeranchuk cell which had been precooled to 15 mK by means of a dilution refrigerator. In the He^3 chamber was a capacitative pressure gauge and a vibration-string viscometer made of niobium-titanium wire that was stretched so that it had a

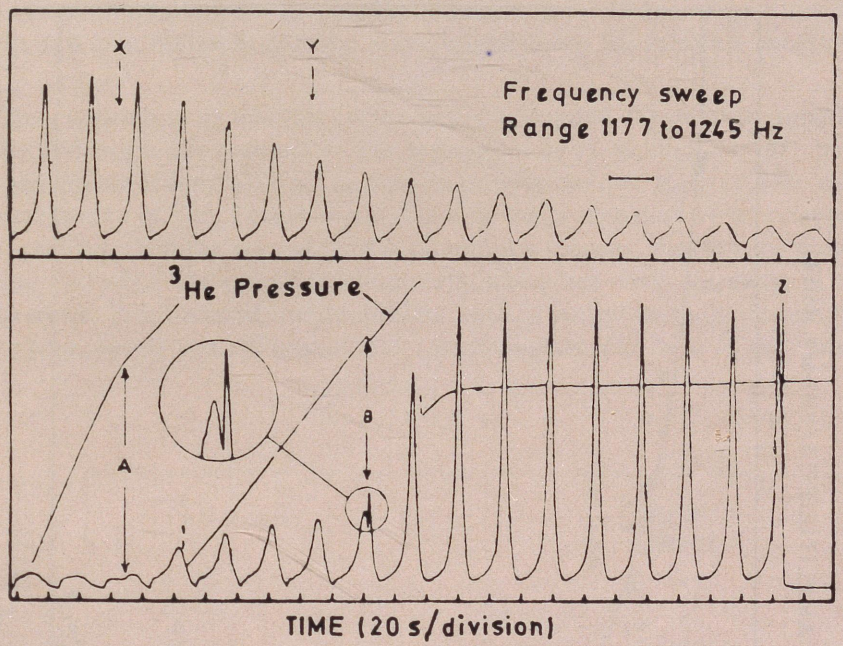


Fig. 7—Viscometer signal record as a function of time. The lower figure indicates pressure in He^3 cel. The melting curve is reached at X, and at Y the compression speed is changed. The transitions A and B are shown showing a discontinuous increase of the viscometer signal at B. At Z the vibrating string sticks

natural resonant frequency of 1245 Hz. Fig. 7 shows the actual chart recorder tracing of the viscometer signals as a function of time. The lower part of the figure gives the output from the capacitance bridge measuring the pressure in He^3 cell. The Pomeranchuk cooling starts cooling at X. At Y the compression speed is changed. The A and B transitions, and the point Z, where the signal stops on account of formation of solid He^3 are shown. When the He^3 was cooled the amplitude of the oscillations at resonance decreased (Fig. 7). At the temperature 2.6 mK the amplitude started to increase again which indicated the change of phase A. On further cooling the amplitude increased. At the point B there was a sudden jump in the signal amplitude and after that the amplitude increased rapidly. At 1 mK the amplitude was four times the amplitude at 10 mK. The normalised viscometer signal amplitudes against melting pressure are given in Fig. 8.

To a reasonable approximation the signal amplitude varies inversely as the square root of viscosity. According to the theory of Fermi liquid the viscosity varies as $1/T^2$. It follows that the expected value of the viscosity at 1 mK is about 1000 times smaller than the viscosity at the point A. This may be considered as a strong evidence for superfluidity. The double hysteresis loop corresponding to

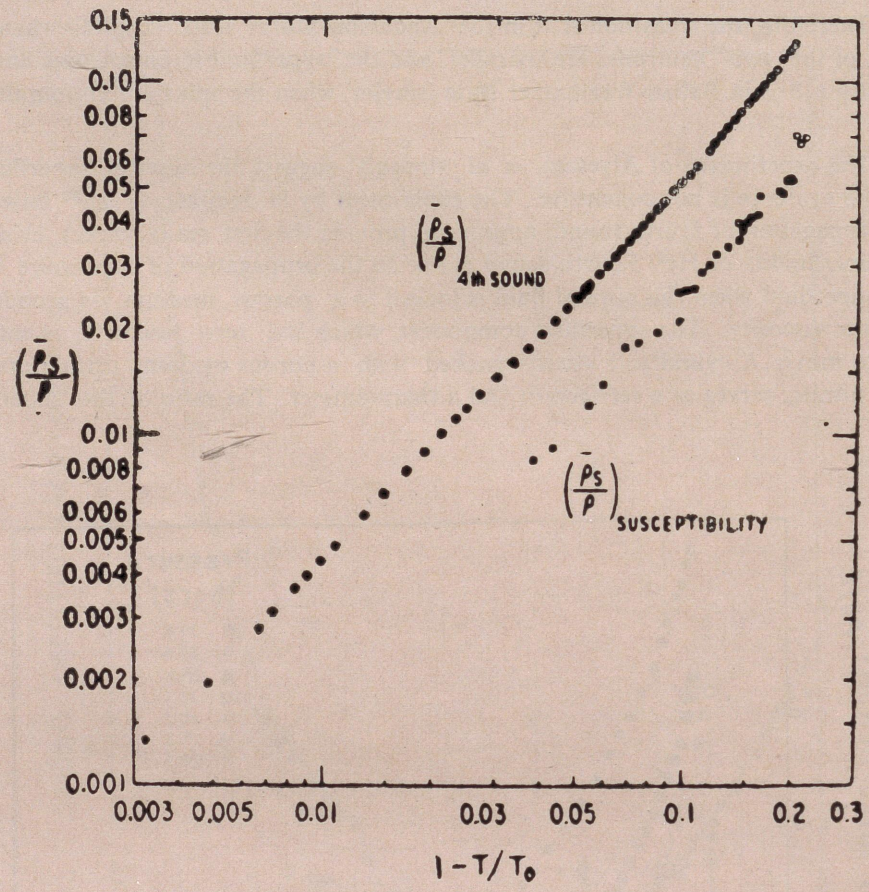


Fig. 10—ln $\bar{\rho}_s/\rho$ shown against ln (1-T/TC) for a pressure of 33.59 bar. The lower curve gives values of e_s/ρ deduced from susceptibility measurements for pressure of 23.8 bar (filled squares) and 29.9 bar (open squares)

density to the total density ρ_s/ρ can be calculated from a relationship based on the two-fluid model

$$\rho_s/\rho = C_4^2/C_1^2$$

where C_1 is the velocity of first sound and C_4 the velocity of fourth sound. The ratio ρ_s/ρ was measured along lines of constant pressure with the temperature decreasing down to as low as 0.8 times the critical temperature T_c. The transition A is near 2.6 mK and B near 2.0 mK (at a melting pressure near 34.4 bar). Fig. 9 gives ρ_s/ρ as function of the magnetic temperature in millikelvins. The arrows marked BA for pressure of 27.56, 25.50 and 23.09 bar are the expected positions of the B-A

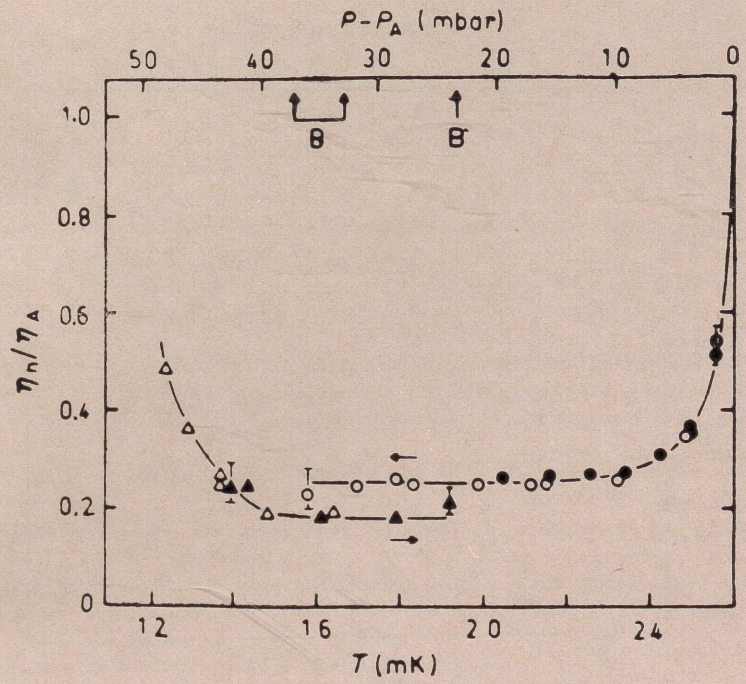


Fig. 11—The ratio $\bar{\eta}_n/\eta_A$ of the average viscosity of normal He^3 at the A point as a function of temperature. The pressure difference relative to the A transition is also indicated. Open symbols represent points taken upon cooling and filled ones during warming. Circles are for the A phase and triangles for the B phase

transitions. Fig. 10 gives the variation of log ρ_s/ρ versus log $(1 - T/T_c)$. It is seen that for all pressures $\rho_s/\rho \sim (1 - T/T_c)^{\alpha}$ when α is in the range 1.1—1.3. The values of ρ_s turn out to be small, since this also happens in fourth sound measure in He^4.

The viscosity and the density of the normal component of liquid He^3 in the A and B phases have also been determined at the melting curve with a vibrating-wire viscometer. The Fig. 11 shows the average viscosity $\bar{\eta}_n/\eta A$ of the normal component as a function of the temperature. $\bar{\eta}A$ is the viscosity of normal He^3 at the A point (open symbols represent point taken upon cooling and filled ones during warming). The circles are for in the A phase and triangles for in the B phase Fig. 12 gives the reduced average density $\bar{\rho}_n/\rho A$ of the normal component of superfluid He^3 at the melting curve as a function of temperature; ρA is the total density of He^3 at the A point. The results show that resistive flow of the liquid is accompanied by a flow of zero viscosity. The data prove superfluidity both in the A and in the B phase. With this discovery of the new phases of He^3, the number of known superfluids in nature has been doubled.

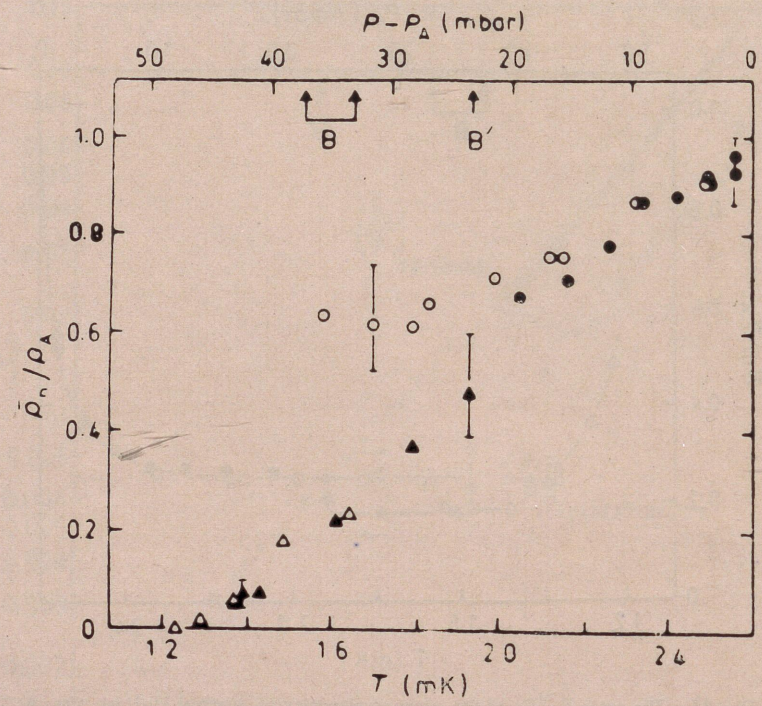


Fig. 12—The $\bar{\rho}_n/\rho_A$ of the average density of the normal component of superfluid He^3 at the melting curve as a function of temperature, ρ_A is the total density of He^3 at the A point. The symbols are the same as in Fig. 11

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The Metallic Phase of Planets and Meteorites

by

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Iron is widely disseminated throughout the Solar system and it takes 3rd place in it after silicon and magnesium, excluding gases. Iron can be found in metallic alloys with Ni and other elements in all meteorites—both iron and stone ones. The nuclei of the planets of the Earth group are made up of iron alloy. This fact has been acknowledged by the majority of scientists, and I have already had a chance to speak about it (4, 5, 6, 8, 11).

At the outset let us look into the specific properties of the metallic iron of meteorites, then let us go over to the origins of iron in the metallic nuclei of our planets, and finally, let us consider experimental foundations of the possible ways of formation of the iron metallic phase of planets and meteorites during the process of accretion of matter in the protoplanetic cloud.

Metallic alloy FeNi can be found in all iron, stone and stone-and-iron meteorites. Iron in those meteorites is found in two polymorphous varieties of hexahedrite (low temperature phase with a scant content of Ni $\sim$ 6%, the so-called a-Fe), and of kamacite and octahedrite, which emerge in the conditions of high temperature in the two-phase region of the diagram of condition FeNi — alloy rich in Ni ($\sim$30-50%) — the so-called taenite. Their mixture is known as plessite.

When the meteoric iron is etched by acids the so-called Widmanstätten figures (Figs 1, 2) emerge. In precisely the same way the metallic phase of stone meteorites (containing on the average iron metallic phase $\sim$ 10%) show the same picture—iron polymorphism — kamacite and taenite phase (Fig. 3).

It is a well-known fact, that up to 70 chemical elements can make alloys with iron. At the same time the analysis of iron-bearing alloys from various types of meteorites show that only up to 15-20 chemical elements, notably typical siderophiles (Ni, Co, Au, platinoids Sn, Sb, As, Ge, Ga, Mo, P) are regularly concentrated in metallic iron. At the same time some elements, much more widely spread in the protoplanetic cloud and also crystallized in the regular cubic system—Mn, Ti,



Fig. 1—Iron meteroite octahedrite Chebankal. Polished surface. Structure can be seen

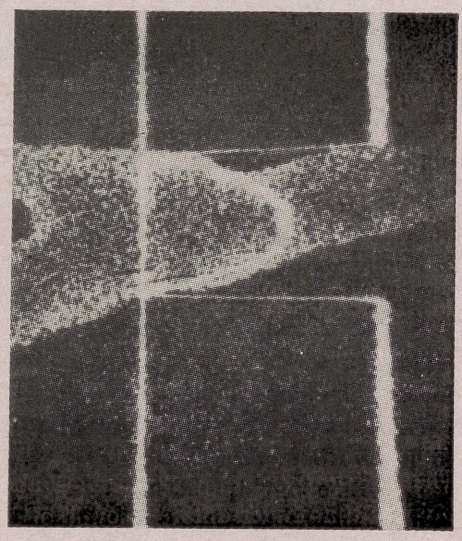


Fig. 2—Bar of taenite in kamacite FeNi in Sikhote–Alin meteorite. Grey streak of taenite. Concentration curve of Ni distribution can be seen

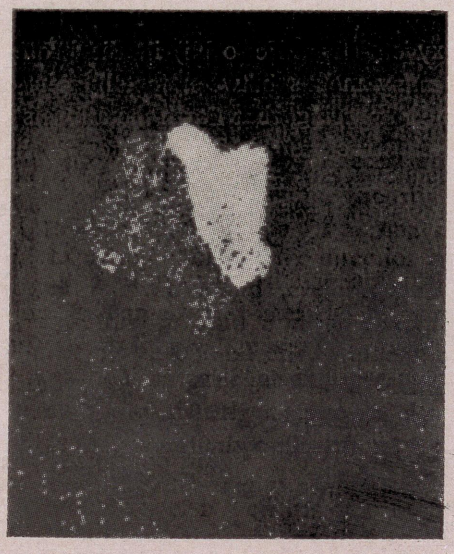


Fig. 3— Metallic phase of stone meteorite (chondrite) Gigailovka. Kamacite and taenite (light field)

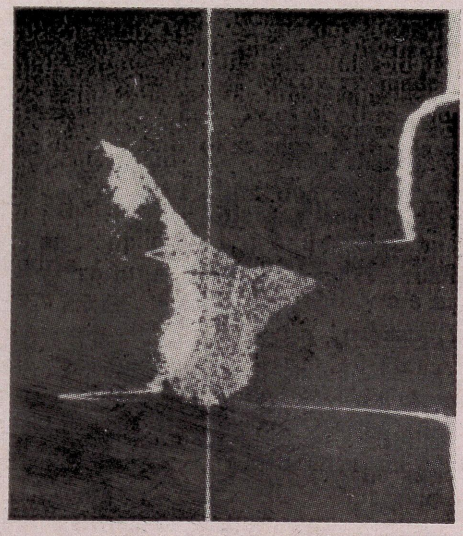


Fig. 4—Metallic phase of Gigailovks chondrite. Light taenite on the kamacite background. Concentration curve of Ni distribution

Cr, V, like many others entering into continuous solid solutions with Fe, are not found as components in meteoric iron. Experience as well as calculations show that chemical elements with partial pressure PO_2 in the reversible equilibrium of metal with oxide under the given temperature lower than for the system Fe-FeO produce oxides, namely TiO_2, CrO_3, V_2O_3, etc., therefore they do not further dissolve in FeNi alloys. At the same time the elements requiring for oxidation a higher PO_2 remain metals and dissolve in FeNi alloy (Table 1). In this way we explain the composition of meteoric iron.

At the same time both phases of kamacite and taenite (Fig. 4), frequently separate and with the same admixtures of chemical elements can be encountered in stone meteorites in primary FeNi alloy from the protoplanetic cloud. Exactly the same differences can be found in the meteoric matter of the Moon. The appearence of taenite is always connected with an increase of Ni over 8% in the alloy. The extent of the spread of Ni is about 6% of Fe in our Solar system. It is our opinion that under different levels of PO_2, that is, the depth of oxidation of ions of metals, there takes place a burning-out of a part of Fe in FeO in FeNi alloy with the result that the remaining alloy is enriched primarily with Ni. Parallel with this the content of some elements is increased in the alloy depending on the place in PO_2 row (Table 1), while other elements are converted into oxides and disappear from the alloy. It can be seen, for example, that platina and platinoids are accumulated (7), while Ga, Ge-decrease, etc.

Thus the range of partial pressure of oxygen (from Fe to Ni) in the protoplanetic cloud determines the distribution of many metals between metallic phase and silicates, and other compounds. Let me note in passing, that Earth metallurgists failed to produce Fe alloys with Widmanstätten structure (2). There emerged the so-called diffusion theory (3) of the formation of kamacite and taenite. In the iron nuclei of cosmic bodies of lunar size under the conditions of cooling with the rate of 0.2—2.0°C in 100 million years (with intial temperature $\sim$ 800-900°C) there takes place the diffusion of Ni in one direction while Fe diffuses in the other direction, which resulted in the formation of kamacite and taenite. Then these lunar bodies have been broken up by large cosmic bodies, which resulted in the formation of meteoric iron with kamacite and taenite, thus passing through the planetary stage.

At the same time a lower density of meteoric alloy FeNi as compared to Earth alloy, the presence in iron meteorites of, for example, tridymite and other minerals, capable of standing pressures of only 3 kilobars, and certain other data were at variance with the diffusion hypothesis. On the other hand, it is evident, that FeNi alloy in stone meteorites had not undergone such a process, as stone meteorites had not been subjected to high pressures and temperatures, but contain, as we have seen, kamacite and taenite. In FeNi alloy of chondrites or in FeNi alloy of iron

Table 1—Partial pressure of oxygen (PO_2) in reversible equilibrium of metals with their oxide (at a temp. of melting of 1803 K)

Elements	PO_2 (atmospheres)	Elements	PO_2 (atmospheres)
$La\text{-}La_2O_3$	$3{,}2.10^{60}$	$Mn\text{-}MnO$	4.10^{-15}
$Ta\text{-}Ta_2O_5$	2.10^{-41}	$Y\text{-}Y_2O_3$	4.10^{-14}
$Nb\text{-}NbO_2$	$6{,}3.10^{-34}$	$Cr\text{-}Cr_2O_3$	1.10^{-13}
$Th\text{-}ThO_2$	2.10^{-26}	$Zn\text{-}ZnO$	$3,\ 2.10^{-12}$
$Be\text{-}BeO$	1.10^{-25}	$W\text{-}WO_2$	1.10^{-11}
$Sc\text{-}Sc_2O_3$	5.10^{-23}	$Ga\text{-}Ga_3O_3$	1.10^{-10}
$U\text{-}UO_2$	$1{,}2.10^{-24}$	$Mo\text{-}MoO_2$	$7{,}4.10^{-9}$
$Ba\text{-}BaO$	2.10^{-23}	$Fe\text{-}FeO$	4.10^{-9}
$Al\text{-}Al_2O_3$	5.10^{-22}	$As\text{-}As_2O_3$	$3{,}2.10^{-8}$ (542°K)
$Zr\text{-}ZrO_2$	1.10^{-22}	$In\text{-}In_2O_3$	$3{,}2.10^{-8}$
$Ti\text{-}TiO_2$	$7{,}9.10^{-19}$	$Sn\text{-}SnO_2$	7.10^{-7}
$Si\text{-}SiO_2$	$6{,}3.10^{-17}$	$Gl\text{-}GlO_2$	2.10^{-7}
		$Ni\text{-}NiO$	2.10^{-5}
		$Sb\text{-}Sb_2O_3$	$1{,}3.10^{-5}$
		$Co\text{-}CoO$	$6{,}3.10^{-4}$
		$Cu\text{-}Cu_2O$	2.10^{-4}
		(Pt, Pd, Ir, Os, Ru, Rh, Au)	

Table 2—Satellites of planets and asteroids

	Mass	R	Density gr/cm
Moon	1,00	1,00	3,34
Io	0,985	1,0	3,22
Europa	0,641	0,85	3,02
Ganymede	2,112	1,6	1,73
Callisto	1,316	1,44	1,48
Titan	1,87	1,40	2,31

meteorites there are always present certain definite similar admixtures of elements with a distinctive distribution of them throughout the alloy phases.

When a theory required the destruction of one body, it could have been endured, but when it has become clear that it cannot be done with the destruction of only one body because of differences in metallic phases of Fe (in meteorites) of

other admixtures of elements through a considerable range of concentration — the doubts have become even more evident.

We should have expected, that cosmic bodies of lunar size with nuclei of FeNi alloy had, in accordance with this theory, strictly definite limits as far as their size, composition thermal balance and life span were concerned. At the same time the absolute age of stone meteorites, iron meteorites, the Moon and the Earth is close, if not identical, to $4{\cdot}5 \times 10^9$ years. And if even the Moon with its density of 3.34, i.e. lower than the density of stone meteorites (also taking into account the fact that about 10% of its density had been acquired due to compression) with the loss by the Moon, as we have shown (9), of a considerable amount of siderophile elements, the Moon, around which the solar plasma smoothly flows without any perturbation, lacks a metallic nucleus, than it is quite probable that lunar bodies of smaller size could have no metallic nuclei (Table 2).

Let us turn back to experimental possibilities of obtaining kamacite-taeinte structure on films FeNi system in a limited period of time. Here I give mainly those results that are interesting from the point of view of the way of formation of metallic phases in meteorites and planets. The technique of the experiment is explained in detail in (10). The films have been obtained by spraying a composite plate of Fe and Ni. The spraying regime—electric tension of 1500 volts on the

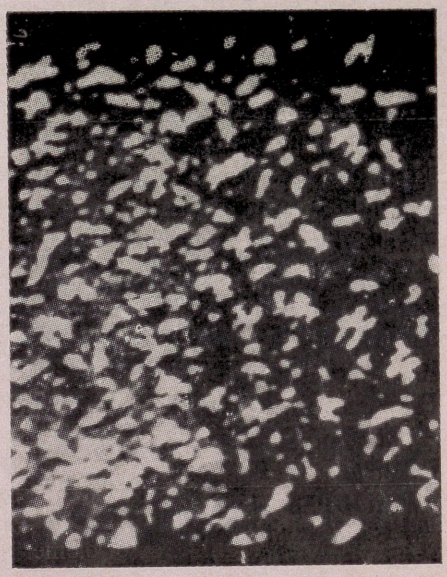


Fig. 5—Electronic view of the surface of the film, showing the differentitation of matter into two phases. Light-taenite, dark-kamacite. (Phase size up to 10-20 microns)

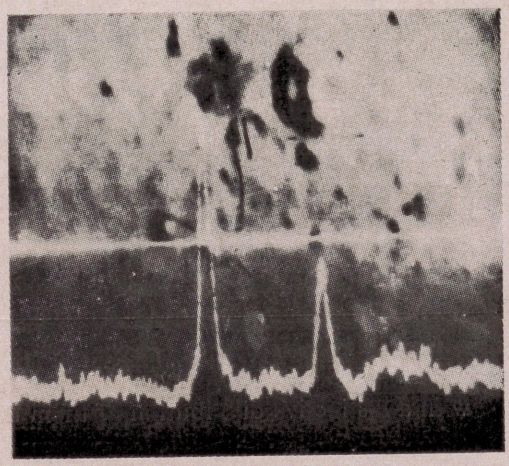


Fig. 6—Electronic view and concentration curve of Ni distribution along the A—B line

target. The pressure of argon — 4.10^{-4} torr. Distance target-layer equals about 6-7 centimeters. Spraying rate for films — 1-2 micron/hour. As a layer we used a glass plate from which a film with thickness of 5 microns could easily be separated for a further study. The temperature of the layer could be raised to 550°C. The X-ray analysis of the alloy demonstrated the structure of volume-concentrated cube with a low content of Ni in Fe, and the structure of facet-centred cube with a high content of Ni. When heating the layer up to 300°C there emerged areas of joint coexistence of α and γ phases (concentration of Ni 10-25%). Chemical analysis of the films has been done with micro-analysers (electronic probe). A series of experiments has been conducted. As an example you can see the picture of the local micro-analysis (Fig. 5) of the sprayed sample of FeNi (with 7% of Ni), where kamacite and taenite can be clearly differentiated (Fig. 6). Concentration curve obtained on the same sample are shown in Fig. 7. There was up to 15% of Ni in taenite about 5% of Ni in kamacite. Thus it can be asserted on the basis of all the data that FeNi alloy of stone and iron meteorites and planetary nuclei has been forming through accretion process from the protoplanetic cloud by a non-difussion way, independently and directly from the steam phase. It is being condensed at $\sim$ 1500°C crystallized in two modifications depending on PO_2 and it does not go through a planetary stage.

Let us come back to the method of formation of planetary nuclei. As we have already seen metallic (heavy) FeNi nuclei can be assumed for cosmic bodies, planets

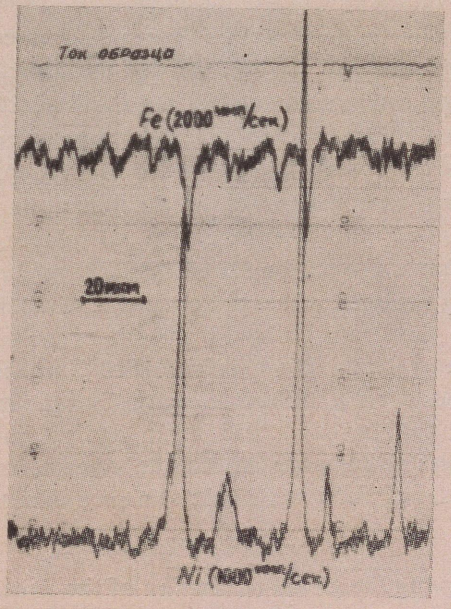


Fig. 7—Concentration curves of Ni distribution (lower curve) and of Fe distribution (middle curve) in the film (scale 20 micron in millimeter)

with a high density level. Again as we have already seen the moons and asteroids do not have sufficiently high density (Table 2).

Let me remind you, by the way, that it looks like that at present some very popular recently hypotheses the authors of which tried to substitute compressed H_2 or hydrides Si for metallic FeNi planetary nuclei seem to have disappeared. Experiments with the pressure of silicates $P \sim 10^6$ atmospheric did not result in the discovery of a sudden leap in the density of silicates. Evidently planets' nuclei cannot be provided only through the matter of stone meteorites, chondrites, which have on the average only 10% of metallic phase. Thus, for example according to calculations the Earths' nucleus contains 32% of the total mass (with Fe content in the Earth about 41%). In other words the Earths' nucleus could have been formed only on the basis of iron meteorites or similar material. It is a well-known fact that the mass of iron meteorites falling on the Earth is much greater than the mass of stone meteorites. More than that, iron meteorites falling on the surface of the Earth, often have masses in excess of hundreds of tons, while stone meteorites with the mass exceeding hundreds of kilograms is a rare occasion. Traditionally, evidently, think, that FeNi phase of an initially homogenous planet like Earth for example undergoes differentiation into layers under the influence of the heat of radio-active elements (secondary heating of matter) with the creation of a nucleus.

But the calculations for the heat required for such a process, i.e. lifting silicate matter from the Earths' centre to the periphery of the planet with a simultaneous sinking of metallic alloy down to the centre of the Earth enabling the metallic alloy to take the place of the silicate — show that the temperature of the Earth should reach up to 3000°C, and there is no known way to drain it. At the same time such temperatures haven't been observed during the differentiation of the Earths' matter in the silicate layer (mantle), otherwise the Earths' all volatile compounds like CO_2, H_2O etc. would have flown away a long time ago. Therefore, it should be agreed that metallic alloy FeNi emerges in the protoplanetic cloud independently (selectively) and directly from the steam phase Fe and Ni of the protoplanetic cloud. It has been condensed under temperature below 1500°C in the gas-and-dust cloud, where there grew a considerable difference in the temperature of solid particles (lower temperature) on the one hand, and steam and gas (higher temperature) on the other hand (1). Phases of kamacite and taenite emerged instantly. The distribution of elements in phases of FeNi and silicates in accordance with PO_2.

In all likelihood during the global separation of the matter in the protoplanetic cloud the magnetic field played its role in separating ferromagnetic particles from dielectrics. Later the iron particles easily stuck together and fused thanks to their heat conductivity.

All this makes us to look for a way of formation of metallic planetary nuclei in the formation of considerable masses of iron pieces in the protoplanetic cloud, their hitting each other and subsequent growth through accretion of the future planets nucleus. The ways to the solution of this problem have just been outlined.

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The Role of Crystallography in Solid State Physics

by

A. GUINIER

After the long period where crystals have been classified and studied only from their macroscopic properties (and especially the external forms of isolated specimens), the discovery of M. Von Laue opened the era of the determination of crystalline structures at an atomic scale. X-Ray Crystallography began in England around W.H. and W.L. Bragg and rapidly flourished in many countries, the initial impulse being often given by former students or collaborators of the Bragg's.

Structures more and more complex have been solved : NaCl in 1912, silicates in the twenties, organic crystals in the thirties, and finally in the last twenty years the enormous protein molecules containing thousands of atoms. These remarkable progresses are due to the continuous improvements of the methods. In fifty years, we have witnessed the passage from the Bragg spectrometer and its ionization chamber to the fully automatic 4-circles diffractometer; the theory progressed from the trial and errors techniques to the so called direct methods and the main change was brought by the appearance of the modern computers.

As a result of all these factors, it is hardly exaggerated to say that the problem of the determination of a crystal structure is now solved : in the majority of cases, it is a matter of routine rather than of research. So X-ray crystallography is now a technique at the disposal of the chemist who may find the structure of the molecule he is interested in, or more generally the nature of the atomic bonds. For the chemist, it is, of course a very valuable tool, the success of which is well known and it is certain that this part of crystallography, which we may call "crystal-chemistry" will continue to be more and more used in the future.

But this is only a partial description of crystallography, because there is another branch where the crystallographer works in collaboration with a Solid State Physicist instead a chemist. The nature of the problems, the techniques and the theories, are quite distinct from those of the classical crystallography. What I would like to do in this lecture, is to show to the physicist what are now the potentialities of the crystallography in his problems, being given the recent progresses

of the techniques. I do not intend to describe the methods or the theories involved but only to give an idea to the non-specialist in crystallography of what is now feasible.

It is trivial to say that the study of any physical properties of a crystal makes use of the knowledge of its crystalline structure. But it is well known that it is very far from being sufficient. The metallurgist must know that Aluminium has a face-centred cubic cell with a parameter of 4.04Å; however, that is of no help to understand the mechanical properties of Aluminium metal. The reason is that many physical properties depend primarily on the imperfections of the crystal, for instance, vacancies, dislocations, etc... and although these imperfections affect a very small proportion of atoms or are of very small amplitude, nevertheless, they may have a first order importance. Thus the Solid State Physicist is most eager to get any direct information about the *real* structure of the crystal and some X-ray crystallographic methods are able to answer to these questions. The atomic defects modify—in general—very slightly the diffraction figures of a perfect ideal crystal. Thus the X-ray crystallographer working for the physicist must focus his attention not on the main features of the diffraction pattern which could bring only informations trivial for him, but on small details, because it is from these data he will be able to detect the interesting defects of the crystal. This is the main object of the "Crystallography for the Physicist", which differs from the "Crystallography for the Chemist" by its methods as well as its aims. Generally, the modifications of the diffraction figure are relatively weak; the experiments are thus difficult. On the other hand it is well known that one cannot obtain a direct image of the defect and the search for a suitable atomic model is never simple. The result is that this branch of crystallography is in a much less advanced state than the classical one. However, in the previous recent years considerable progresses have been realized on the experimental side, mainly due to the appearance of new powerful sources of X-rays and of more efficient detectors.

On the other hand, neutron scattering made possible by the High Flux Reactors has been used in addition to X-ray scattering and is now a valuable complement of the X-ray investigations.

In the strictly limited frame-work of one lecture, it is of course impossible to give an exhaustive review of all the aspects of what we have called the crystallography for the physicist. Therefore, we have only picked up a small number of examples which are especially characteristics of the kind of interaction between Solid State Physics and the new possibilities of X-ray diffraction; Preference has been given to the domains which are likely to have an important development in the coming years.

Detection of localized defects (dislocations, stacking faults)

As a first example, we shall consider the case of localized defects : the atoms involved are in a very small proportion but undergo considerable displacements, of the order of the atomic diameter, as it occurs in the immediate vicinity of a dislocation line, whereas there are a few thousands of atoms between two neighbouring dislocations. It is well known that dislocations—or also stacking faults—are detectable by X-rays and electrons. Although we are not going to enter into the theory of the phenomenon, it is interesting to understand qualitatively the principle of the method. When a crystal is perfect, the diffraction obeys the "dynamical" theory : it predicts the same geometry for the diffracted beams but a much lower intensity. The atomic disorder along the dislocation line decreases very rapidly with the distance but it remains very slight deviations (10^{-4} or 10^{-5}) from the perfect lattice up to a distance of the order of the micron. Inside this cylinder, the diffracted intensity on any reflecting plane is considerably increased because of the imperfection of the crystal. Thus when a beam traverses the crystal, it suffers an apparent absorption along the dislocation line. Therefore, that line appears with a contrast sufficient to be easily seen on an image of the crystal. For electrons, this image is obtained in the electron microscope with a high magnification. For X-rays, the Lang method gives an image or rather a shadow, in natural size. So this special technique allows to reach experimentally the dislocation which is essential to account for the plastic properties of a crystal. In fact, the dislocation line is detected, localized, but the details of the nature of the atomic displacements in the core of the defective line are unknown. However, a very subtle analysis leads to models of structures' at atomic scale, that is much below the resolving power of the experiment.

It is interesting to note that these methods, so useful for the physicist, are based on the influence of the imperfection on the intensity of diffraction. But the same phenomenon gives much trouble to the crystallochemist because it introduces very important, and very difficult to correct, errors in the data necessary for the structure determination.

These experiments, initiated some 20 years ago by Hirsch and Whelan for the electron microscope and by Lang for X-rays, have given an experimental support to the concept at first only theoretical of dislocation. They constituted a turning point of the theory of metals, the origin of the development of what is called now microplasticity, the study of mechanical properties of materials from their real atomic structure.

Not ony these methods will continue to be in use as a fundamental tool for the Solid State Physicist, but their expansion will be more rapid because of technological progresses, namely the availability of more powerful X-ray sources : the rotating anode tubes, to-day commercially available are ten times more intense than the conventional tubes, and what is much more important, there will be soon in

operation, in a few places across the world, synchrotron radiation sources with an intensity factor of 1.000. One can reasonably hope now that many applications which are impeded by the prohibitively long term of the experiments will thus become feasible.

Metallic Solid Solutions

When a single-phased binary alloy A B is in the disordered state, one concludes from the conventional crystallographic methods that its structure is that of a regular crystal with one single fictitious atom, which is the average of A and B with the respective concentrations of the two species. Nevertheless that result cannot satisfy the metal physicist since he knows that, for a given lattice and a given composition, and the same diffraction pattern the solid solution may have very different physical properties depending on the heat-treatment. That shows that a more elaborate description of the structure is needed : one has to know the repartition of the two kinds of atoms A and B at the homologous nodes of the lattice because one must admit that it is not random and it varies with the state of the metal.

Experimentally the lack of periodicity due to the replacement of an A atom by a B atom at homologous sites in the crystal produces a diffuse scattering in between the Bragg diffraction spots corresponding to the average regular lattice. The variation of this scattered intensity with the diffraction angle is a function of the degree and nature of order between the A and B atoms. Moreover this scattering is generally very weak and is completely negligible in Debye-Scherrer or rotating crystal cameras. Special precautions and well adapted devices are indispensable and, measously, high intensity sources or sensitive detectors are of great help. From the measurement of the diffuse scattering it is sometimes possible to deduce directly the kind of partial ordering of the atoms. More generally, especially when this ordering is correlated with local distortions of the lattice, models of possible structure are tested and one selects the one which is compatible with the observed scattering, and with all the other available informations. The "diffuse scattering" method has been called sometimes "Monochromatic Laue Method" because one registers on a film all the rays emerging from a single crystal in a fixed position, as in a Laue camera, but, the incident beam is monochromatic instead of being polychromatic : it is a typical example of a special technique used only by the physicist.

The magnetic properties of a Fe-Ni alloy depend on the ordering of Fe and Ni, the mechanical properties of Al-Cu alloy (duralumin type) depend on the extent and nature of the segregation of the Cu atoms inside the solid solution crystal. The extreme possibilities of the method have been demonstrated in the case of pure copper containing a proportion of 10^{-4} vacancies distributed at random : the nature of the distortions of the lattice around the vacancies has been identified by their diffuse scattering (the "interstitialcy" configuration has been found the only one compatible experiment).

Mechanism of Phase Transition

We consider now a pure substance which undergoes a phase transition at a temperature Tc, the crystal structure changing at that temperature from one form ϕ_1 to another one ϕ_2. In many cases, the change is really discontinuous : one single ϕ_1 crystal transforms into several ϕ_2 crystals and the reverse transformation changes the ϕ_2 crystals into new ϕ_1 without any relation with the primitive ϕ_1 crystal, which has been broken into separate pieces. What is more interesting is the case where the transition is smoother : the crystal ϕ_1 is transformed into one or several ϕ_2 crystals remaining coherent and one finds back the primitive ϕ_1 crystal by the reverse operation.

That is the case, for example, of perovskite $Ba\,TiO_3$ for the para-ferroelectric transition at 120°C. A peculiar diffuse scattering is observed on the diffraction patterns of the $BaTiO_3$ crystal around the transition temperature. As the substance is pure and, the content of every cell is identical, the disorder responsible of the diffuse scattering must be due to displacements of homologous atoms, variable from one to another cell : effectively a model may be built which explains the observed scattering.

But one knows that the atoms, as in any crystal, are vibrating around their average positions, which are situated at the nodes of a regular lattice. It is possible to assume that the atomic displacements revealed by the diffuse scattering are due to these atomic vibrations because : at any time, the atoms are effectively out of their equilibrium positions, but these displacements are no more static but they vary with time. X-ray scattering is not capable to distinguish between these two models Fortunately neutron scattering does, because the atomic movements change the energy of the scattered neutron (inelastic neutron scattering) : the atomic vibrations may be analysed into *phonons* travelling through the crystal and one shows that the frequency of the phonons may be measured by the difference in energy between the scattered and the incident neutron.

The combination of neutron and X-ray scattering experiments has proved definitely that the disorder in the perovskites was dynamic. The phonons are very anisotropic : there exists certain modes—the soft modes—the frequency of which pecreases when the transition temperature is approached, and the amplitudes of which consequently increase (1) : that is the consequence of the softening of some atomic bonds which become so weak that a change of structure is possible.

This example shows that X-ray coupled with neutron diffraction experiments constitute an experimental tool for studying the dynamics of the crystals which is one of the clues of the understanding of the crystalline structure, and of their

(1) The equipartition of energy between phonons requires that the product of amplitude by frequency is a constant.

transformation. It shows again how special methods of X-ray crystallography become now an important auxiliary of Solid State Physics.

Intermediate states between crystalline and amorphous states

It is known that some structures cannot be considered neither as a crystal nor as a typical amorphous body, and it happens that some of these intermediate structures have very interesting applications, therefore, are now very actively studied and, in that field also, non-conventional X-ray methods play an important role. Let us give only few examples. Much attention has been given since a few years to non-metallic substances exhibiting a high conductivity. In an "ionic superconductors", like β-Alumina for instance, (β Al_2O_3, Na_2O) the charge carriers are the Na^+ ions which are extremely mobile at high temperature (> 300°C). The crystals are made by a stacking of layers of Al_2O_3 having well defined crystalline structures; the Na^+ ions are situated on planes between the Al_2O_3 layers, and in these planes their positions are not precisely determined, as if they formed a "two-dimensional" liquid : this freedom of movements for the Na^+ ions explains why they can move when an electric field is applied. Furthermore, the ionic conductivity is high only in directions parallel to the Al_2O_3 layers and not in the normal direction.

The crystal called K C P [$K_2Pt(CN)_4 Br_{0.3}$, 2.3 H_2O] is a good electrical conductor but only in the direction of the axis along which there are files of Pt atoms separated by a distance very near the atomic diameter of Pt in the pure metal. But these chains are separated by a much greater interval : Thus K C P may be considered as a one-dimensional conductor formed by the metallic Pt chains. Because there is no mobile ions, the charge carriers must be electrons. The "one-dimensional metal" has been thoroughly studied by theoreticists : there are electronic states characterized by their wave vector, parallel to the chain axis. They form a band limited by a Fermi level with momentum K_F. On the other hand, Pt atoms are vibrating and phonons propagate along the chain. Kohn had predicted that there is a coupling between electrons and phonons, which is responsible of an anomaly; the frequency of the phonon of wavelength 2 K_F is decreased (its amplitude being increased). The existence of these particular phonons is detectable by X-ray scattering because of their amplitude larger than the amplitude of phonons of other wavelength. It is also detectable by inelastic neutron scattering through their anomalously low frequency. Thus the phenomenon of the conductibility of this special compound, which has been recently discovered, is greatly enlightened by the combination of X-ray and neutron scattering.

Another example of a one dimensional conductor is the famous organic compound TTF-TCNQ which is so good a conductor at 50°K, that it had been considered some years ago as a supurconductor. In that case also, X-ray and neutron scattering brings important informations on a very complex phenomenon, not yet completely understood.

Up to now we have given examples of crystals having some defects of order. On the other side, there are amorphous substances in which some order exists. In the first case, the scattering due to the disorder is relatively easy to detect because the perfect crystal does not produce any scattering out of the regular Bragg diffraction. In the other case, the situation is less favourable because any amorphous body gives a continuous diffraction pattern and the modification of the state of order produces only variations which may be weak in relative value; it is more difficult to isolate the effect of a partial order. Nevertheless, some interesting results have been obtained with the various phases of "liquid crystals". In the nematic phase, molecules which have an elongated shape are all aligned but there is only a liquid like order between the molecules centres. In certain nematic liquids such as B.E.A., this positional disorder is not complete. It appears on the diffraction pattern diffuse streaks which are characteristic of ordered chains parallel to the molecule length. That shows that there is a tendency for the molecules to form strings of a few molecules attached to each other. The disorder of random close packed spheres, which is the model commonly used to describe liquids and amorphous bodies is certainly altered when the molecules are large, have anisotropic shapes (discs - or needle - like) and interact through directed bonds : it is, in fact, the situation of the majority of macromolecules and especially those of biological interest. It is obvious that the properties of these substances depend on the state of local order : hence, the interest of the development of these structural studies in spite of their difficulties.

The Crystallographers have now solved the problem of perfect crystals. The consequences of their work have been immense, mainly in chemistry, biochemistry, etc... But it is a fact the matter in our world is, in a very large proportion, neither completely ordered, nor completely disordered. To understand its physical properties, one must know not only an ideal simplified structure but the real one. The progresses of crystallography allow us to begin to characterize a state of partial order. Our knowledge is still at the present time limited, first because of the uncertainties of interpretation of experimental data, but also because the number of samples which have been studied is still low. There is still an immense field of research which is now open to a new, extended crystallography and it is certain that any advance in this domain will be very fruitful.

Raman Effect : Discovery and After

by

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At the outset I wish to express my sincere gratitude to Dr Ajit Ram Verma, Director of the National Physical Laboratory for having invited me to deliver the "Krishnan Memorial Lecture" this year which coincides with the 80th birth anniversary of the late Sir K. S. Krishnan, FRS. I have chosen "Raman Effect : Discovery and After" as the subject of my lecture today. The selection of the topic has a special significance since Prof. Krishnan was closely associated with the experiments carried out under Prof. Raman's guidence which finally led to the discovery of the Raman Effect. Besides, this year has a special significance for Raman Effect as it is Golden Jubilee year of the discovery.

In this lecture, I propose to describe briefly the history of the discovery and review the progress made during the last fifty years.

History of the Discovery

The starting point in the history of the discovery of the effect was Prof. Raman's voyage to Europe in the summer of 1921, when he was attracted by the blue opalescence of the Mediterranean Sea, which he later explained as due to the scattering of light by water molecules in the backward direction just as the blue colour of the sky on a clear day was attributed by the Lord Rayleigh to the scattering by air molecules. Immediately after his return, Prof. Raman started a series of systematic investigations on the scattering of light by samples of clear water in the Indian Association for the Cultivation of Science at 210, Bow Bazaar Street, Calcutta, where he was the Honorary Director and Professor. During the next six years Prof. Raman along with his brilliant students like Ramanathan, Krishnan, Ramdas, Venkateswaran, Kameswara Rao, Ramakrishna Rao, Ramachandra Rao, etc. established the various laws of molecular scattering in diverse media with particular reference to (a) structure of molecules, (b) state of matter, (c) pressure and temperature, and (d) phase transition at the critical temperature.

As early as in 1923, K. R. Ramanathan showed that when violet rays passed through carefully purified water or alcohols, there was an appreciable quantity of radiation in the green region of the scattered light which he termed as "weak fluore-

scence" and which was found to be a characteristic property of the subsatnce studied and not due to any fluorescent impurity. Two years later, K. S. Krishnan observed the same phenomenon while studying the scattering of light in a large number of carefully purified liquids. He also made another important observation that the new radiation was partially polarised unlike ordinary fluorescence. The technique used for observing the new phenomenon consisted of a beam of sunlight, a condensing lens of large aperture, a flask containing the liquid and a set of complementary filters, i.e. a violet blue filter in the path of the incident beam and a greenish yellow filter in the path of the transversely scattered light. Raman himself observed the phenomenon later in optical glasses and in a crystal of ice. In January 1928, S. Venkateswaran made a very remarkable observation that the colour of sunlight scattered in a highly purified sample of glycerine was a brilliant green which was strongly polarised. Raman and Krishnan detected the new radiation in a number of organic vapours and also in the gases CO_2 and N_2O under pressure in order to have sufficient density of scattering particles. They soon realised that they were dealing with a new phenomenon of a fundamental character and communicated their conclusions to "*Nature*", London on 16th February 1928 in a letter entitled "A new type of secondary radiation", which was published on 31 March 1928. (Copy reproduced in Appendix II).

On the 28th of February while continuing further studies on the subject, Prof. Raman and Krishnan used a direct vision spectroscope for examining the scattered track to find out the influence of the wavelength of the incident light on the phenomenon. Using a narrow range of wavelength in the violet blue region for excitation which was obtained by passing sunlight through a combination of filters, and viewing the transversely scattered light through a direct vision spectroscope, they were surprised to find that the modified scattering appearing in the blue green region was separated by a dark interval from the indigo violet region transmitted by the incident filter combination. This encouraged them to use monochromatic radiations from a quartz mercury arc for excitation. Using this source, they got a number of sharp lines in the scattered light from benzene and toluene which were not present in the spectrum of the incident mercury arc light, but manufactured by the molecules of the liquid. The scattered spectra from many liquids were photographed with the aid of a small Hilger spectrograph and measured. New lines were observed on either side of the exciting line. He immediately announced the results of the discovery to the press the next day. The above results were published by Prof. Raman in a letter to "*Nature*" sent on 8 March 1928, under the title "Change of wavelength in scattering", in which he had referred to the strong polarization of modified lines. The note was published on 21 April 1928.

The intense excitement and tireless energy with which the researches were pursued to the successful conclusion by Prof. Raman and his group during the month of February 1928 will be evident from a perusal of the diary maintained by

Prof. Krishnan at the time, from which extracts are reproduced in the Appendix I at the end of this paper. It also shows that Dr K. S. Krishnan was closely associated with Prof. Raman in the discovery of the new effect.

The Nature and Significance of the Effect

The first detailed announcement of discovery before a scientific audience with a description of the principal features of the new effect was made by Raman under the title "A New Radiation" on 16 March 1928, while inaugurating the South Indian Science Association at Bangalore. The full text of the lecture was subsequently communicated and published in the Indian Journal of Physics on 31 March 1928 along with photographs of the scattered spectrum of benzene. These spectra are reproduced as Figs. 1 to 4 here.

In this historic paper the following aspects of the new effect were clearly brought out. (i) The universality of the phenomenon, i.e. it is observed in all transparent substances irrespective of the state of aggregation of the molecules whether it be a gas, liquid, crystal or amorphous substance and also in largest possible varieties of chemical compounds. (ii) The modified radiation is of the same order of intensity as the unmodified Rayleigh scattering and it is strongly polarized. It should therefore be a scattering effect. (iii) Each incident radiation produces a different set of modified scattered radiations. (iv) The scattered radiations consist in many cases of fairly sharp lines in displaced positions. (v) The frequency differences between the incident and scattered radiations represent the absorption frequencies of the medium which normally lie in the infra-red. Part of the incident energy is absorbed by the molecule for raising it to an excited state and the balance is scattered. A possible relationship of the new phenomenon to Kramers and Heisenberg's quantum theory of dispersion was also indicated. (vi) A continuous wing is found accompanying the unmodified Rayleigh line, the intensity and width of which are found to depend on the anisotropy of the molecules involved. These observations of Raman established and emphasised the fundamental character of the new effect.

Prof. Raman concluded this epoch making paper in the following words: "We are only on the fringe of a fascinating new region of experimental research which promises to throw light on diverse problems relating to radiation and wave-theory, X-ray optics, atomic and molecular spectra, fluorescence and scattering, thermodynamics and chemistry. It all remains to be worked out.

I have to add in conclusion that I owe much to the valuable co-operation in this research of Mr K. S. Krishnan and the assistance of Mr Venkateswaran and other workers in the laboratory".

Reprints of the paper in the Indian Journal of Physics were posted to all important physicists and scientific institutions all over the world, thus ensuring Prof. Raman's priority of the discovery, for once announced many other scientists began

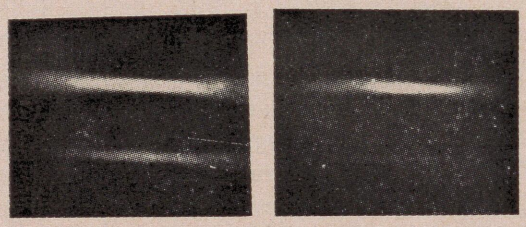


Fig. 1 Fig. 2

Polarisation
of
Scattering
Fig. 1 Unmodified
Fig. 2 Modified

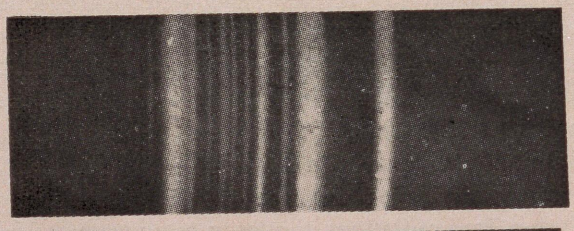


Fig. 3 (1)
Incident Spectrum

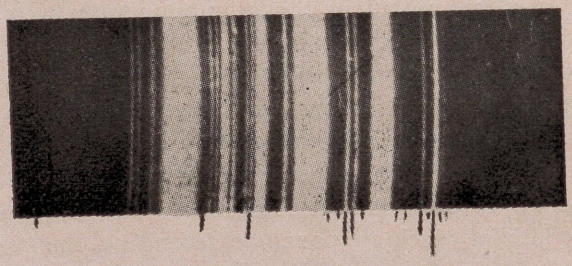


Fig. 3 (2)
Scattered Spectrum

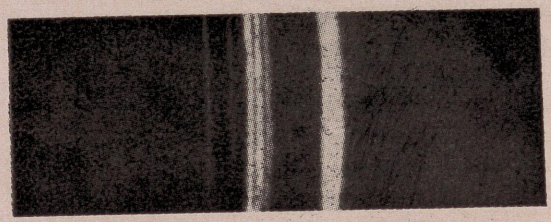


Fig. 4 (1)
Incident Spectrum

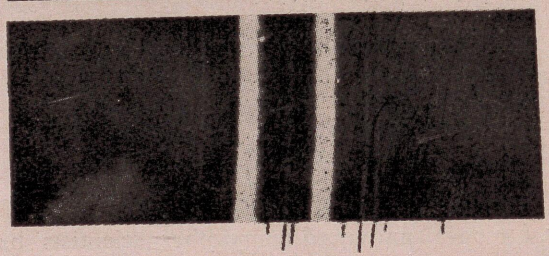


Fig. 4 (2)
Scattered Spectrum

to work on it. If this full paper had been sent abroad, it would have taken at least four months for the paper to appear in print. Prof. Raman and Krishnan indicated in a subsequent communication to "*Nature*" that the effect was somewhat analogous to Compton Effect. It was Prof. Rocard of Paris who attempted to give a theoretical explanation to Raman's observations and also indicated that new lines should appear on either side of the exciting line (April 1928). It was L. A. Ramdas (June 1928), who was the first to call the effect as "Raman Effect" while reporting the results obtained with ether vapours.

Explanation of Figures 1 to 4

These figures have been reproduced from the paper entitled "A New Radiation" by C. V. Raman which appeared in the Indian Journal of Physics, Vol. II, p. 387, 1928.

Fig. 1—A photograph of the scattering by toluene of sunlight filtered through a blue-violet glass. It was taken through a double image prism of calcite.

Fig. 2—The same as above with an additional complementary filter of green glass interposed in front of the camera lens. The polarisation of the scattered track is prominent in the two figures as seen by the striking difference in intensities of the two polarised tracks.

Fig. 3—(1) The spectrum of the direct mercury arc filtered through blue-violet glass and taken through small Hilger quartz spectrograph. (2) The spectrum of the mercury arc light scattered by benzene taken with the same instrument. The region transmitted by the blue-violet filter in the incident path covers the range from 3500 to 4400 A.U. The scattered benzene spectrum shows a number of sharp lines not present in Fig. 3 (1).

Fig. 4—(1) The spectrum of the mercury arc filtered through potassium permanganate solution. (2) The spectrum of light scattered by benzene under conditions specified in 4(1) above. The new lines which are not present in Fig. 4(1) are seen in this figure.

Immediately following the announcement, Raman and Krishnan carried out further experiments and established the following additional facts :

1. Each substance displayed a characteristic scattered spectrum which could serve to identify it unambiguously.

2. For a given substance the difference in frequency between any modified line and the exciting line was constant and independent of the frequency of the incident light. It is in this crucial respect that the new effect is distinguished from fluorescence for which the frequency and not the frequency shift is independent of the frequency of the exciting line.

3. The new lines are sharp and often occurred in pairs uniformly separated in frequency units from the exciting line. Those appearing on the lower frequency or higher wavelength side are called "Stokes Lines" and are generally more intense than their counterparts on the higher frequency side called "Anti-Stokes Lines".

4. The observed range of frequency shifts in any scattered spectrum extends from a few to about 3700 wavenumbers expressed in cm^{-1} corresponding to a maximum frequency of 1.11×10^{13} Hz or to a minimum wavelength of 2.7 μ.

5. The frequency shifts observed in the new effect are the frequencies of oscillation of the chemically bonded atoms of the molecule, which in turn depend on the geometry of the molecule and the forces binding the atoms together. They correspond to the frequencies of absorption of the molecule in the infra-red region of the spectrum.

6. The intensity and the depolarisation ratio are different for different lines.

7. According to the quantum theory of radiation, exchange of energy can take place between the molecule and the incident light quantum as follows :

Molecule + $h\nu_1 \rightleftharpoons$ Molecule* + $h\nu_2$. The exchange can take place in either direction. From left to right the molecule is receiving energy and goes over to the excited state indicated by the star and ν_2 the frequency of the modified line is less than the frequency ν_1 of the incident radiation. From right to left the molecule already in an excited state is giving up energy and ν_1 the frequency of the modified line will be more than ν_2 the frequency of the incident light. In the former case one observes Stokes lines, while in the latter case one observes anti-Stokes lines. Thus, Raman was the first to demonstrate that the energy of a photon can undergo partial transformation within matter. The ratio of the intensities of the corresponding Stokes and anti-Stokes Raman lines is proportional to the ratio of the population of states in terms of the Boltzmann distribution. Thus the processes giving rise to Raman effect have brought about a new and striking demonstration of the corpuscular aspect of radiations.

8. Raman scattering is in general feebler than Rayleigh scattering. The intensity of Raman scattering like Rayleigh scattering increases as the fourth power of the incident frequency except in the neighbourhood of the absorption band.

It became clear that the fundamental and most important aspect of Raman scattering is that it provided a tool for mapping the vibrational and rotational energy levels of chemical compounds which normally appear in the infra-red region of the spectrum and were not easily accessible at that time, and thus Raman effect opened up a wholly new field of study of molecular structure.

The importance of the discovery was immediately recognized by the authorities in optics and scattering, namely P. Pringsheim of Germany, Y. Rocard and J. Cabannes of France, J. C. McLennan of Canada and R. W. Wood of U.S.A. They confirmed Raman's findings. Pringsheim (August 1928), who compared Raman scattering with Tyndall effect, fluorescence and Compton effect, concluded that Raman scattering was an entirely new phenomenon which enabled one to record the characteristic molecular frequencies more conveniently in the visible region. He christened the same as Raman effect, the new lines as Raman lines and the spectrum of new lines as Raman spectrum. He concluded the classic paper in Naturwissenschaften with the following words :

"With the increasing number of new researchers coming into this field, new problems will show up in increasing proportions. One can state without doubt that through his discovery Raman has opened up a big and completely new field of spectroscopy."

R. W. Wood sent a cable to '*Nature*', the first and last sentences from which are quoted below : "Professor Raman's brilliant and surprising discovery that transparent substances illuminated by very intense monochromatic light scatter radiations of modified wavelength and that frequency difference between the emitted radiation and one exciting the medium is identical with frequency of the infra-red absorption bands, opens up wholly new field of study of molecular structure. I have verified his discovery in every particular... It appears to me that this very beautiful discovery which resulted from Raman's long and patient study of phenomena of light scattering is one of the most convincing proofs of quantum theory of light which we have at present time."

The apparatus used by Raman for the discovery consisted of a mirror for deflecting sunlight, a condensing lens, a pair of complementary glass filters, a flask containing benzene and a pocket spectroscope, the total cost not exceeding Rs 200. It would also be inferred from the above account that the discovery was not the result of an accident, but was the culmination of seven years of systematic and sustained work carried out by Raman and his band of students with devotion. The achievement is all the more creditable when one considers the fact that scientific research was not liberally supported by Government of that day as it is today.

The history of the discovery of Raman effect teaches us many lessons. Firstly, it teaches us humility. Secondly, hardly any discovery appears immediately in its clear and final form. The truth is approached step by step. Thirdly, it is the calibre of the scientist that matters for scientific progress and not the provision of very costly equipment. Fourthly, sustained effort in a single field only will ultimately lead to success and fame. Fifthly, great discoveries always appear incredibly simple, but only after some devoted person has made the discovery.

Prof. Raman was awarded the Hughes Medal of the Royal Society of England in 1930 and the Nobel Prize for Physics in the same year for his discovery. While presenting the Hughes Medal, Lord Rutherford of Nelson, President of the Royal Society made the following observation:

"Raman effect must rank among the best three or four discoveries in experimental physics of the last decade. It has proved and will prove an instrument of great power in the study of the theory of solids." This prophesy has been fully vindicated by the recent progress in Raman spectroscopy.

While delivering the Nobel Lecture, on 11th December, 1930 at Stockholm, Raman drew special attention to the universality of the phenomenon, the convenience of the experimental technique and the simplicity of the spectra obtained which enabled the effect to be used as an experimental aid to the solution of a wide range of problems in physics and chemistry. It is the simplicity of Raman spectra that gives to the study of Raman effect its special significance and value.

Nearly two months after the discovery, two Russian Physicists — G. Landsberg and L. Mandelstam, who were working on molecular scattering of light in crystals reported that they had independently observed modified lines in the spectrum of quartz when irradiated by light from a quartz mercury arc. They sent a note to Naturwissenschaften on 5 May 1928, which was published on 13 July 1928. In this note they had referred to Raman's two communications on the new radiation published in '*Nature*' of 31 March 1928 and 21 April 1928 and confessed that they were unable to appreciate any connection between their observation and that of Raman. They should have also received the reprint of the paper which appeared in the Indian Journal of Physics. It was obvious that they did not understand its significance either. Their full paper containing observations with quartz and calcite was sent on 12 July 1928 and was published in Zeitschrift fur Physik on 19 September 1928. Even in this they had not given due recognition to Raman's discovery. It is necessary to recall that the Russian physicists made their first communication on the subject after the publication of the notes in '*Nature*' of March 31st and April 21st and the full paper in the Indian Journal of Physics of March 31st. Their paper appeared in print after sixteen other papers on the subject had appeared in print in recognized scientific journals. The various observations of Raman and Krishnan listed in the paper under reference clearly demonstrated the fundamental character

and the significance of the phenomenon in a manner which any isolated observation with one or two substances like the one reported by Landsberg and Mandelstam would have quite failed to achieve. In spite of this fact, the Russians refused to accept the naming of the discovery as Raman effect for a quite long time. All the papers on the subject published from Russia till a few years ago were entitled 'Combination Scattering'.

Although the possibility of the occurrence of a process similar to Raman effect was envisaged by Smekal in 1923 while discussing the interaction of radiation with matter and later by Kramers and Heisenberg in the quantum theory of dispersion and also by Dirac in his radiation theory, its significance was not understood until the phenomenon was discovered quite independently by Raman in 1928. It was only after Raman's discovery that the full implications of the dispersion theory came to be recognized. A certain amount of prejudice did exist among some German Scientists towards Indian work and achievement. In spite of the fact that the entire scientific community was unanimous in calling the discovery of the new radiation just "Raman Effect", Julius Springer of Berlin published a book by K. W. F. Kohlraush entitled "Der Smekal-Raman Effekt", in 1931. A supplementary volume by the same author was also published by Julius Springer in 1939 again under the same title. It is gratifying to note that there is no controversy now.

Immediately following the discovery, Raman effect began to be used by physicists and chemists alike for solving a wide range of problems and many important contributions to our knowledge in physics and chemistry were reported in a short span of five years. This upsurge can be attributed to the fact that the data obtained from Raman effect depend essentially on the structure of the molecules of the scattering substance. It is thus possible to obtain information of great value to the physicists and more so to the chemists by a single observation of the Raman spectrum instead of a whole series of difficult experiments in infra-red. More than 2,500 chemical compounds were studied by Raman effect during the first decade.

It is not possible to enumerate all the important and fundamental contributions from Raman effect studies. A few striking ones made in the first two years are referred to here. One is the contribution to the development of nuclear physics. It was the rotational Raman spectrum of nitrogen recorded by Rasetti which gave definite proof that the nitrogen nuclei follow Bose-Einstein statistics. This in turn led to the conclusion for the first time unambiguously that electrons could not be present in the nuclei. This is the conclusive piece of evidence which led to the idea that atomic nucleus consists of protons and neutrons and not of protons and electrons. Another important contribution resulted from the work of McLennan and McLeod on the Raman effect in liquid hydrogen. This gave direct experimental proof for the existence of two forms of hydrogen, the ortho and para in which the nuclear spins of the two hydrogen nuclei in the molecule are parallel and anti-

parallel respectively. In many cases Raman spectrum gives an answer when infra-red and visible spectra fail. A typical example is the fluorine molecule which defied all attempts to determine its intermolecular distance and vibrational frequency until the Raman spectrum of the gas was obtained.

I shall now give a brief review of the techniques used in Raman spectroscopy and the important results obtained from Raman Effect studies during the past fifty years.

Techniques of Raman Spectroscopy

In any study on the Raman spectrum of a substance the important parameters to be measured for each Raman line are the following :

(1) Frequency shift from the exciting line expressed in wave numbers, i.e. cm^{-1}, (2) Degree of depolarisation, (3) Absolute intensity, and (4) Linewidth. These together with a knowledge of its appearance or otherwise in infra-red absorption are the five factors necessary for the identification and classification of the mode of vibration of the molecule giving rise to the particular Raman line.

Although the techniques used for measuring Raman spectra data have undergone many changes, the principal components for recording the spectra have remained the same during the last fifty years. They are : (1) A source of monochromatic radiation, (2) A container for the sample if it is a gas or a liquid, (3) A dispersing instrument, and (4) A detecting system. During the first thirtyfive years after the discovery almost all the studies were limited to vibrational and rotational spectra of molecules in liquid and gaseous phases and in solids. Such spectra were easily excited by the 253.7, 404.6 and 435.8 nm radiations of a mercury arc and were recorded photographically with the aid of high dispersion large aperture prism spectrographs. This simple technique is characterised by low signal to noise ratio and hence it is time consuming. In spite of the laborious and exotic nature of the experimental techniques used for recording the Raman spectra before 1963, Raman effect did find considerable applications for solving many physicochemical problems and for acquiring information concerning the properties of molecules and the dynamics of crystal lattices. But much weaker scattering phenomena associated with electronic energy levels, quasiparticles and other quantised systems, while expected theoretically could not be observed experimentally. Many coloured substances could not be studied at all because of the limitations of the experimental technique. Thus in the earlier days, Raman scattering was important more for the quantum mechanical and other fundamental principles it illustrated than for its practical applications.

The development and use of laser radiation as exciter for Raman effect studies for the first time by Porto and Wood in 1962 marked a new era or a revolution in light scattering research. The laser radiation is characterised by exceptionally

high specific intensity, negligible divergence, high monochromaticity, complete polarisation and nearly perfect coherence and hence forms an ideal source for studies on Raman effect. The most commonly used lasers for Raman excitation are the continuously operating He-Ne (632.8 nm), Ar^+ ion (488, 514.5 and 476.5 nm), and He-Cd (441.5 and 325 nm) gas lasers and the pulsed and continuously operating forms of the ruby (694.8 nm) and Nd-YAG or Nd glass (1060 nm) solid state lasers. The very recent development of tunable dye lasers the wavelength of whose output radiation is capable of being varied at will over the entire visible and ultraviolet regions of the spectrum has given a new dimension to the studies on Raman effect. Since an almost coherent laser beam can be focussed on to a region whose dimension could be of the order of a few wavelengths, the sample size can be smaller than a millionth part of a gram which could be easily maintained at any desired temperature and state. A new vista of micro Raman spectroscopic analysis has already begun enabling one to extend such studies to biological and biomedical samples available only in very small quantities or concentrations either by themselves or in solution. With the availability of laser radiations of any wavelength from the ultraviolet region to the near infra-red region of the spectrum, studies on Raman effect are now made with coloured and even opaque substances.

A major technical advance has been made in the sample handling techniques in recent years. With the use of an intense exciting source the main limitation in getting satisfactory Raman spectra of opaque, coloured or absorbing materials is the localised overheating and consequent decomposition of the sample. These difficulties are overcome by the introduction of devices which permit relative motion between the sample and the focussed laser beam. Techniques involving rotation of the sample if it is a solid and flow of the sample if it is a liquid are adopted. In some cases the focussed laser beam is scanned rapidly over the surface of the sample in either a linear or circular way.

Spectrographs have been replaced by holographic grating double and triple monochromators with efficient stray light elimination and the use of high speed and reproducible scanning mechanisms. There is a parallel development of sophisticated photon counting system consisting of a photomultiplier, associated electronic equipment, counter, recorder and a computer. Several types of computer interfaces have been developed. The computer interface should have the capacity for digitising at least two channels of analogue information, namely frequency shift and intensity. With the advent of the digital storage of spectra it is easy to redisplay the spectrum under high dispersion to see the separation of closely spaced lines. Redisplay on the same screen of the spectra taken with different concentrations or at different temperatures can also be done with the aid of the computer. With the modern laser Raman spectrometers, the spectrum of any substance can be recorded in a few minutes, whereas the time taken was a few hours or even days before the laser era.

Other improvements in the detection system enable one to obtain directly a difference Raman spectra as in a double beam infra-red spectrometer, addition Raman spectra, the depolarisation ratio versus frequency shift curve, derivative Raman spectra, etc.

Multichemical Raman spectroscopy has also been developed which has high sensitivity, no reciprocity effect and short response time of a few pico seconds and high storage capacity. Space resolution enables one to conduct Raman microscopic examination of heterogeneous samples.

Compared to the very simple equipment used by Prof. Raman for discovering the effect, the modern laser Raman spectrometer is more sophisticated and hence very costly.

Recent Developments

Using laser excitations Raman spectra of many substances have been reinvestigated and spectra of many more new substances including those which are coloured or opaque, polymers, nucleic acids, proteins, enzymes and other biological molecules have been studied for the first time and considerable information has been accumulated about their structure. New types of excitations such as electronic Raman effect, Resonance Raman effect, inverse Raman effect, etc. have been reported.

In normal Raman effect the vibrational and rotational energy levels of the system take part. With the aid of appropriate laser excitation, transitions in low lying electronic levels especially in rare earth salts can be induced by Raman effect. The electronic Raman spectra of many substances including semimetals and semiconductors have been recorded for getting information about their electronic levels.

Even in the pre-laser days, it was reported that the intensity of Raman lines did not always follow the λ^{-4} law. With the availability of powerful lasers which now provide a large number of different excitation frequencies, it is found that there is a progressive increase in intensity of the Raman lines as the exciting frequency approaches that of an electronic absorption band of the scattering system. When the exciting frequency coincides with the allowed broad electronic absorption band of the molecule, it leads to a rigorous resonance Raman scattering (RRS), which is characterised by an enormous increase in the intensity of the Raman line. RRS is accompanied by intense fluorescence also. Fluorescence has been eliminated in many cases by the use of picosecond gating of Raman scattering initiated by a mode locked pulsed laser, the pulse duration being of the order of nanoseconds or picoseconds. The life time for emission of Raman effect is very short compared to that of fluorescence. Although the phenomenon of the RRS was predicted by Placzek's theory of Raman scattering in 1934 and experimentally

observed as early as 1958, it is only with the availability of powerful tunable lasers the usefulness of RRS for structural studies has been fully exploited. A phenomenon called inverse Raman effect has also been reported. In this process Raman scattering appears as absorption lines in a continuum on the anti-Stokes side instead of the normal emission lines.

Raman Scattering Other Than By Phonons

In polar crystals electromagnetic waves and optical phonons interact strongly when their energies and wave vectors are nearly equal. This interaction removes the intersection of the uncoupled dispersion curves and results in an upper and lower branches which have mixed electromagnetic and mechanical nature. The crystal excitations in this mixed region have been called polaritons which give rise to Raman scattering when excited. The frequency of the polariton appearing as Raman shift varies with angle of scattering. Polariton Raman scattering enables us to understand the nature of the electric field inside the crystal and their interaction with lattice vibrations. Stimulated Raman scattering of polaritons would provide an intense coherent and variable source of infra-red and visible radiation. The existence of spin orbit interaction in magnetic crystal leads to a mechanism of Raman scattering from spin waves. Such magnon or collective excitations have been observed both in the first and second order Raman spectra of the transition metal fluorides below the Neel temperature using laser excitation.

Spin flip Raman scattering has been observed from magnetically split ground states of donors and acceptors, i.e. Raman scattering from plasma, i.e. from single particle electron and hole excitations in semiconductors such as GaAs and GaP have also been recorded. Some exciting new applications of Raman effect in the area of electronic processes in semiconductors namely p-type cubic crystals are in the offing.

Non Linear Effects

When giant pulses of short duration and high peak power from a ruby or Nd-YAG laser are used for excitation, various non-linear optical phenomena are observed. Of the many non-linear effects, the important ones as regards Raman scattering is concerned are the Stimulated Raman Effect (SRE), the Hyper Raman Effect (HRE) and Coherent Anti-Stokes Raman Scattering (CARS) of which the last one holds greater promise for future development and applications.

In stimulated Raman scattering if the incident intensity is above a threshold value a good fraction of the incident light is thrown as coherent stimulated Raman scattering close to the forward direction. Only a couple of Raman modes are excited in this process. This effect has been studied in many liquids and some solids. In hyper Raman effect, Raman lines appear on either side of the octave of the laser excitation frequency. It is a very feeble phenomenon and hence difficult to

record. All the vibrational modes of a system will be active in HRE unlike in ordinary Raman effect and infra-red absorption.

Coherent Anti-Stokes Raman spectroscopy (CARS) is a relatively new kind of Raman spectroscopy which is based on nonlinear conversion of two laser beams into a coherent, laser like Raman beam of high intensity in the anti-Stokes region. The technique consists in mixing two collinear laser beams of frequencies in a medium such that the difference in the laser frequencies is nearly equal to the frequency of a mode of vibration of the molecule active in Raman effect. New waves are generated in the forward direction at a frequency which corresponds to the anti-Stokes Raman line of the particular mode. The emission is often many orders of magnitude greater than normal scattering and because of the coherent and anti-Stokes character of the radiation, the CARS is potentially a powerful technique for obtaining analytical and spectroscopic information pertaining to Raman active resonance in gases, liquids and solids even if they are fluorescent. It is widely used to take Raman spectra of gases in discharges, plasmas, combustion and atmospheric chemistry. CARS techniques may be expected to be useful for studying fluctuations phenomena, reaction dynamics, photochemistry, kinetics, relaxation and energy transfer.

Applications

(a) *Physics of the Solid State*

Raman spectra of crystalline substances reflect not only the structure of the molecular species present but also the nature of the crystalline forces as well as the structure and symmetry of the crystal itself. The crystal spectrum consists of three groups of frequency : (1) the external or lattice frequencies normally (below 250 cm^{-1}), (2) internal frequencies of the complex ions or (molecules 250-3300 cm^{-1}), and (3) water bands (3300-3700 cm^{-1}). The Raman lines arising from individual molecules or ions coming under the second category will essentially be the same as those of the corresponding liquid.

In the earlier days, a number of Indian and French workers invesitgated the changes in the intensities of Raman lines arising from changing orientations of the crystal axes with reference to the direction of polarisation of incident electric vector. From group theoretical analysis they had worked out the Raman active vibrational symmetries and Raman tensors for the 32 crystal symmetry classes. Only after the advent of laser Raman spectroscopy precision measurements of polarisation characteristics and orientation effects could be carried in a variety of crystals and all the theoretical predictions including splitting of Raman modes in the crystalline field predicted by group theory could be satisfactorily verified.

Although with the use of mercury resonance radiation as excitor it was possible to record the first and second order Raman spectra of simple crystals, like

diomond, alkali halides, etc. by the author and his associates which led to the progressive development of the theory of the dynamics of the crystal lattices, very little work could be done on temperature dependence of Raman frequencies in crystals and on the other types of excitations in crystals. With the advent of laser Raman Spectroscopy, great insight has been obtained regarding the mechanisms responsible for Raman scattering in the solid state. Much activity has been directed towards the study of phase transitions and polaritons. It is well known that many structural phase transitions in the solids are accompanied by a so called soft mode. As the transition temperature is approached the frequency of this mode decreases. It is found that in many cases the soft mode tends to a hard core frequency at the phase transition. As this soft mode is a normal mode of lattice vibration, the dynamic and static properties can be investigated by measuring soft mode response using Raman technique. The two important categories of soft mode transitions that are being extensively studied are in ferroelectric and ferro-elastic crystals, the order parameter in the former being spontaneous plarization and that in the latter being spontaneous strain. By monitoring the intensity of Raman active phonon through transitions as a function of temperature and pressure, one could be able to say whether the transition is of first or second order. Thus one gets greater insight into the mechanism of phase transitions.

(b) *Chemical Applications*

One of the very first applications of Raman spectroscopy was for the solution of understanding of many physcochemical problems. Raman effect served as an aid for the analysis of unknown stiructures of molecules and also for the identification and estimation of the quantity of any substance present in any stationary state or during any transient process. Raman data of various molecules and ions have led to vibrational assignments and evaluation of their force constants and other thermodynamical properties. Chemical problems such as molecular interactions, nature of the chemical bond, constitution, tautomerism, isomerism, molecular rotations, hindered rotation, electrolytic dissociation, association, polymerisation, solvent effect, exchange interactions, hydrogen bonding, spectra structure correlation, kinetics of fast reactions, catalysis, absorption, phase transitions, etc. have been successfully solved. Recently, Raman spectroscopy has been applied for the determination of potential functions governing puckering and internal torsional modes and for getting information on intramolecular forces.

Extensive investigations carried out on the Raman spectra of a series of related organic compounds of similar structure and containing some types of bonds such as C—C, C=O, C=C, C—H, O—H, C≡C, CHO, COOH, etc. have shown that each bond can be identified by a characteristic frequency which is only little affected by the other part of the molecule. This requenchy will remain approximately constant throughout a series of molecules containing that group in common. The various group frequencies have been catalogued. The presence of or absence of a particular group frequency in Raman effect has been made use of for solving unknown struc-

tures, for identification, analysis and estimation in chemical industry and oil technology.

In the past, Raman spectroscopy of gases, was limited to the study of molecular structures only. The availability of powerful lasers, scanning spectrometers, and view techniques has greatly enlarged the scope of Raman spectroscopy of gases in recent years. More than 61 different molecules in the gaseous state have been examined for high resolution Raman spectroscopy and their molecular constants have been determined very accurately. Laser Raman spectroscopy of gases is now being applied to a variety of scientific and technological problems including the detection of molecular hydrogen in planetary atmospheres and interstellar space, determination of temperatures, particle densities, reaction kinetics and air pollution studies.

(c) *Biochemical, Biological and Polymer Sciences*

Recent developments in techniques of Raman spectroscopy have established that it is an invaluable tool for gaining information concerning molecular conformation of intermolecular interactions in nucleic acids and proteins, as well as in corresponding homopolymers, polynucleotides and polypeptides. In the 300-1700 cm^{-1} spectral region pure nucleic acid or protein gives about 30 to 40 Raman lines, some of which are strong and some weak. They are mostly identified even in a Raman spectrum of a complex system containing more than one kind of molecule. Some of the lines are useful for conformation and/or interaction studies.

The Raman lines characteristic of α-helix, β-form and random coil or non-helical portion have been catalogued in the literature. Comparing the observed Raman spectrum of any protein with the above catalogue, one can estimate the extent of each portion and thereby make a conformational analysis of the protein under study. Such an analysis is extremely useful for interpreting any change in the structure of the proteins brought about by a certain physical or chemical reaction.

Some typical problems for which Raman spectroscopy is capable of giving solutions are concerned with the conformation of RNA or DNA in the native virion, types of interactions between the nucleotides, dynamics of the conformation due to the viral infection and a host of such related ones. Greater speed, simplicity and versatility, ease with which spectra can be obtained equally well with amorphous solids, aqueous suspensions or solutions and the fact that the Raman spectrum of a virus contains resolvable features due to different molecular sub groups of both nucleic acid and protein components render the technique of Raman spectroscopy superior to and more useful than all other physicochemical methods of investigation.

Observation of the changes in the various Raman lines as the conformation of a biological macromolecule is changed from the order to disordered form by raising the temperature has been termed Raman-T jump experiment. It can be used

for determining the kinetics of order-disorder transition as a function of time in the nucleic acids and proteins. Biological importance of such studies is very well known.

Another interesting area of application is in polymer characterisation. Elucidation of chemical structure and compositions, study of stereoregularity of monosubstituted vinyl polymers $(CH_2—CHX)_n$, geometrical isomerism of repeat units, chain conformation in solid state, melt and in aqueous and other solutions and packing of polymer chains in a crystal are the major areas in polymer chemistry where Raman spectroscopy offers considerable scope. Underlying all these applications is the identification of certain intense scattering by nearly homo nuclear single and multiple bonds of carbon-carbon, sulphur-sulphur and nitrogen-nitrogen.

Concluding Remarks

Before it completed its Golden Jubilee, Raman effect had the unique privilege of having a renaissance nearly fifteen years ago as a consequence of the development of lasers and their use for exciting Raman spectra and another one after 1970 with the development of tunable lasers. Since 1928 upto the present day more than 20,000 original scientific papers have been published on various aspects of Raman effect and its application to different branches of science, of which two thirds have appeared after 1963. There are nearly 500 scientists working in the field now and about 1,600 papers are published every year. Although the early interest was exhibited by physicists, its gradual passage into the hands of chemists became quickly evident. The advent of the laser in 1963 completely revolutionised the practice of Raman spectroscopy and the interest began to spread to other fields. Biology, biochemistry, polymer science and medical science are some of the sciences to benefit from this renaissance. Even in sophisticated technology Raman effect is finding increasing applications. Raman effect is a typical example of a discovery made in one field of knowledge had repercussions very rapidly in a whole series of other fields. This proves the intimate solidarity which unites all branches of science.

After the completion of 50 years, one finds that the activities on Raman effect are expanding both in the direction of theory and applications. Continued technological innovation and development of more powerful tunable lasers may eventually lead another revolution in the history of Raman effect.

I wish to conclude this lecture by paying homage to the late Prof. C. V. Raman, FRS, Nobel Laureate and also to his brilliant student, the late Prof. K. S Krishnan, FRS, the two illustrious scientists of India.

APPENDIX I

EXTRACTS FROM PROF. K. S. KRISHNAN'S DIARY

5th February, 1928

For the last 3 or 4 days, I have been devoting all my time to fluorescence. The subject promises to open out a wide field for research, since at present, there is no theory of fluorescence which could explain even the outstanding facts.

Studied anthracens vapour. It exhibits strong fluorescence which does not show any polarisation, when viewed through a double image prism. Professor has been working with me all the time.

Recently, Professor has also been working Mr Venkateswaran on the fluorescence exhibited by many aromatic liquids in the near ultra-violet region present in sunlight and the fluorescence of some of the liquids are found to be strongly polarised. However, in view of the fact that the fluorescence of anthracens vapours does not show any polarisation, Professor has asked me to verify again his observations on the polarisation of liquids.

7th February, Tuesday

Tried to verify the polarisation of the fluorescence exhibited by some of the aromatic liquids in the near ultraviolet region. Incidentally, discovered that all pure liquids show a fairly intense fluorescence also in the visible region, and what is much more interesting, all of them are strongly polarised : the aromatics. In fact, the polarisation being the greater for the aliphatics than for the aromatics. In fact, the polarisation of the fluorescent light seems in general to run parallel with the polarisation of the scattered light, i.e. the polarisation of the fluorescent light is greater the smaller the optical anisotropy of the molecule.

When I told Professor about the results, he would not believe that all liquids can show polarised fluorescence and that in the visible region. When he came in up to the room, I had a bulb of pentane in the tank, a blue-violet filter in the path of incident light, and when he observed the track with a combination of green and yellow filters, he remarked "you do not mean to suggest, Krishnan, that all that is fluorescence". However, when he transferred the green yellow combination also to the path of the incident light, he could not detect a trace of the track. He was very much excited and repeated several times that it was an amazing result. One after another, the whole series of liquids were examined and every one of them showed the phenomenon without exception. He wondered how we missed discovering all that five years ago.

In the afternoon, took some measurements on the polarisation of fluorescence.

After meals at night, Venkateswaran and myself were chatting together in our room when Professor suddenly came to the house (at about 9.00 P.M.) and

called for me. When we went down, we found he was much excited and has come to tell me that what we had observed that morning must be the Kramers-Heisenberg Effect we had been looking for all these days. We, therefore, agreed to call the effect "modified scattering." We were talking in front of our house for more than a quarter of an hour when he repeatedly emphasised the exciting nature of the discovery.

8th February, Wednesday

Took some preliminary measurements of the polarisation of the modified cattering by some typical liquids.

9th February, Thursday

Set up this morning the long telescope and made preliminary arrangements for observing the effect with vapours. Before the arrangements were completed, Professor left for the College for his lecture.

In the afternoon, tried ether vapour and it was surprising that the modified radiation was very conspicuous. Tried a number of others in quick succession without however the same success.

When Professor came from the College at about three, I announced to him the result, and there was still enough sunlight all the time, that it was a first rate discovery, that he was feeling miserable during the lecture because he had to leave the experiment, and that however he was fully confident that I would not let the grass grow under my feet till I discovered the phenomenon in gases. He asked me to "call in every body in the place to see the Effect" and immediately arranged in a most dramatic manner, with the mechanics to make arrangements for examining the vapours at high temperatures.

Evening was busy and when Professor returned after his walk he told me that I ought tackle big problems like that and asked me to take up the problem of the experimental evidence for the spinding electron after this work over.

10th February to 15th February

Studied a number of vapours. though a number of them showed the effect, nothing definite could be said regarding the polarisation of the modified scattering.

16th February, Thursday

Studied today pentane vapour at high temperature and it showed a conspicuous polarisation in the modified scattering. We sent a note today to *Nature* on the subject under the title "A New Type of Secondary Radiation".

17th February, Friday

Professor confirmed the polarisation of fluorescence in pentane vapour. I am having some trouble with my left eye. Professor has promised to make all observa tions himself for sometime to come.

19th February to 26th February

Studied a number of other vapours.

27th February, Monday

Religious ceremony in the house. Did not go to the Association.

28th February, Tuesday

Went to the Association only in the afternoon. Professor was there and we proceeded to examine the influence of the wavelength of the incident light on the phenomenon. Used the usual blue violet filter couple with a uranium glass, the range of wavelengths transmitted by the combination being much narrower than that transmitted by the blue violet filter alone. On examining the track with a direct vision spectroscope we found to our great surprise the modified scattering was separated from the scattering corresponding to the incident light by a dark region.

EXTRACTS FROM PROF. RAMAN'S ADDRESS TO THE SOUTH INDIAN ASSOCIATION IN BANGALORE ON 16TH MARCH 1928

"This encouraged us to use monochromatic incident light. Using the mercury arc as source we get a number of sharp lines in the scattered light which were not present in the spectrum of the incident light. A quartz mercury lamp with a filter which completely cuts out all the visible lines of longer wavelengths the indigo line 4358 A.U. was found to be very effective. When the light from such a lamp was passed through the bulb containing a dust-free liquid and the spectrum of the scattered light was observed through a direct vision spectroscope, it was found to exhibit two or more sharp bright lines in the blue and green regions of the spectrum. These lines are not present in the spectrum of the incident light or in the unfiltered light of the mercury arc, and are manufactured by the molecules of the liquid

"There has, as yet, not been sufficient time for photographing the spectra from a large number of liquids, or even for measuring the photographs already obtained. Visual observations have however been made with a large number of liquids. There is an astonishing similarity between the spectra obtained with different liquids. When only the 4358 line was used, most liquids showed in the spectrum of the scattered light, a bright line in the blue-green region of the spectrum (about 5000 A.U.) whose position was practically the same for chemically similar liquids such as pentane, hexane and octane for instance. There was however recognizable difference in the position of the modified line when other liquids such as benzene or water were used. When the 4047 line of the mercury arc was set in by removing the quinine sulphate solution, a second modified line in the blue region of the spectrum was seen with most liquids...".

(Reproduced from the publication "*Science Week*" of the Andhra Pradesh Academy of Sciences, 1978).

APPENDIX II

A NEW TYPE OF SECONDARY RADIATION

If we assume that the X-ray scattering of the 'unmodified type observed by Prof. Compton corresponds to the normal or average state of the atoms and molecules, while the modified scattering of altered wavelength corresponds to their fluctuations from that state, it would follow that we should expect also in the case of ordinary light two types of scattering, one determined by the normal optical properties of the atoms or molecules, and another representing the effect of their fluctuations from their normal state. It accordingly becomes necessary to test whether this is actually the case. The experiments we have made have confirmed this anticipation, and shown that in every case in which the light is scattered by the molecules in dust free liquids or gases, the diffuse radiation of the ordinary kind, having the same wavelength as the incident beam, is accompanied by a modified scattered radiation of degraded frequency.

The new type of light scattering discovered by us naturally requires very powerful illumination for its observation. In our experiments a beam of sunlight was converged successively by a telescope objective of 18 cm aperture and 230 cm focal length and by a second lens of 5 cm focal length. At the focus of the second lens was placed the scattering material, which is either a liquid (carefully purified by repeated distillation in vacuo) or its dust free vapour. To detect the presence of a modified scattered radiation, the method of complementary light-filters was used. A blue-violet filter, when coupled with a yellow green filter and placed in the incident light, completely extinguished the track of the light through the liquid or vapour. The reappearance of the track when the yellow filter is transferred to a place in between it and the observer's eye is proof of the existence of a modified scattered radiation. Spectroscopic confirmation is also available.

Some sixty different common liquids have been examined in this way, and every one of them showed the effect in greater or less degree. That the effect is a true scattering and not a fluorescence is indicated in the first place by its feebleness in comparison with ordinary scattering and secondly by its polarisation, which is in many cases quite strong and comparable with the polarisation of the ordinary scattering. The investigation is naturally much more difficult in the case of gases and vapours, owing to the excessive feebleness of the effect. Nevertheless, when the vapour is of sufficient density, for example with ether or amylene, the modified scattering is readily demonstrable.

210, Bow Bazaar Street
Calcutta, India
February 16, 1928

C. V. RAMAN
K. S. KRISHNAN

(The first communication on Raman Effect reproduced from *Nature*, *London*, 31st March 1928, Vol. 121, p. 501-02).

Interaction between Scientific Disciplines : Can Study of Liquid Crystals Teach anything of Importance for Geophysics ?

by

F. C. FRANK

I am highly honoured in being invited to give the K. S. Krishnan Memorial Lecture. Krishnan himself I barely knew, though for his work his name was one I learnt to respect many years ago. I think that Neville Mott and I drank tea with him in Delhi Airport 26 years ago, and this was the only time we ever met. I have refreshed my memory of his fields of activity by reading that Biographical Memoir of him which was compiled for the Royal Society by Homi Bhabha, and completed after his death by Kathleen Lonsdale, both of them people whom I both knew and respected. Reading that account, I had a moment of doubt, whether I had done well in choosing Interaction of Disciplines for the theme of this lecture, because Krishnan was so completely and thoroughly a physicist: but for someone scholarly enough, more scholarly than I, there is indeed a lecture theme there, directly relevant to Krishnan. His disciplines were Physics, Mathematics and Literature, especially literature with a philosophic bent. The interactions of physics and mathematics are close and familiar, and it might be hard to say anything really new about them: but I would be fascinated to hear an analysis of the relationship between Krishnan's physics and his literary learning, though I suspect that only Krishnan himself might have been capable of making that analysis properly. His wide reading was in Tamil, Sanskrit and English, and for the latter I cull a list of authors from the Biographical Memoir: Scott, Dickens, Thackeray, Stevenson, Cervantes, Victor Hugo, Conan Doyle, Plato and Aristotle in translations, Shakespeare, Milton, Shelley, Swift, Addison, Boswell, Newman, Matthew Arnold, Walter Pater, Charles Lamb, Tolstoy, Ibsen, Bernard Shaw, John Stuart Mill, Whitehead, Lewis Carroll—I omit the more scientific writers.

It is a pet hypothesis of mine, though again one which requires more scholarship than I possess to investigate its validity, that different languages, especially those with significant structural difference, promote different ways of thought, so that science gains more benefits from its international pursuit than simple numerical multiplication. Even highly successful approaches to scientific problems

sooner or later come up against problems intractable to that approach, which may yet yield to another, perhaps more easily found from another cultural background.

Myself, I do not think I can take that theme further in its full width, and will confine myself to considering the interactions between one scientific discipline and another, which have come my way in my own far less disciplined approach to the disciplines than was Krishnan's.

Let me address myself immediately to my rhetorical question: 'Can study of liquid crystals teach us anything about the interior of the Earth?' : and answer it in the affirmative. In saying yes to the question, I am far from suggesting that any part of the Earth's interior is a liquid crystal (though there is enough still to be learnt about the properties of silicate melts that I ought not to say that is impossible). What I do want to say is that study of liquid crystals has revealed previously unsuspected facts about the dramatic consequences of a mild degree of anisotropy for the behaviour of thermally driven convection: and since thermo-convection is of unquestionable importance for the behaviour of the inner Earth, a substantial reconsideration of its principles is called for as a result of experiments in what might seem a totally unrelated field.

I have said that thermo-convection is of unquestionable importance in the Earth, and must defend that statement, since almost everything that can be said about the Earth's interior will, rightly, be questioned. Some have said that it is difficult to say whether convection will occur in the solid mantle of the Earth, because the creep-rate of rock under a given stress is a steeply exponential function of temperature, and we have no exact knowledge of temperature in the Earth. David Tozer inverts the argument. The Earth contains heat sources, the radioactive elements Uranium, Thorium and Potassium, and without convection that heat cannot escape, so that the temperature rises until convection *does* occur: and the sensitivity of creep-rate to temperature merely has the consequence of narrowing the uncertainty about what that temperatue is.

One may raise a doubt that perhaps the radioactive elements are only negligibly present in the lower Mantle: for it is known that they are very strongly concentrated into the surface. If the radioactivity of the average surface rocks were maintained to a depth of only 20 km. or so, it would suffice to generate the whole of the 50 mW per square metre of vertical heat flow observed in bore-holes everywhere over the Earth. We must consider, however, how that surface enrichment in radioactive elements has come about. It can only have happened, I think, in the Earth itself, and in the primitive Earth, four and a half thousand million years ago the elements were surely much more thoroughly mixed. I accept the scenario most generally accepted today, which I first learnt from von Weizsacker,

that the Earth and the other planets first formed by cool coagulation of dust from a spinning disc of gas around the sun, and that this body then gradually heated itself to melt its various constituents in turn, the lighter fluids rising towards the surface, to cool and freeze once more, the heavier fluids, particularly molten iron, sinking towards the centre.

It would not change the present-day picture much if I were to accept the alternative model still taught by some, that the initial Earth was fully molten, for it would soon cool and largely solidify: and a single stage of crystallization could not suffice to purify the interior from its radio-active impurities as fully as the evidence indicates. I am right to call them impurities, since they are minority elements in the total composition, and they will preferentially enter the liquid phase whenever partial melting occurs. I know of no other process which can have separated the elements to the degree which is indicated than *repeated* fractional crystallization: which must have operated on the whole of that shell of solid rock down to a depth of 2989 km, 85% of the volume of the Earth, which we call the mantle, to bring about its separation into a lower mantle, which may be chemically and mineralogically homogeneous, and an upper mantle, the uppermost 700 km, 35% of the mantle volume, which is not. Radioactive heat generation in the lifetime of the Earth, together with gravitational energy release from the descent of the heavier elements, have provided enough heat to melt the whole mantle some 10 or 20 times. I suppose that all of it has been repeatedly melted, but at no one time has more than a very small fraction of it been molten.

In the light of this scenario, in which partial melting plays an essential role, it is necessary to recognize two very distinct modes of convection. One is total convection, which overturns the whole material: the other is percolative convection, in which fluid moves through relatively motionless solid, as in the thermosyphoning of water through porous ground at hot springs: or, in the deeper Earth, the percolation of molten rock: provided, of course, that it can percolate.

Whether a small quantity of melt can percolate in a solid is a subtle question of capillarity, first analysed in a metallurgical context by C. S. Smith, who was considering two phase alloys at a temperature above the melting point of one of them. If the dihedral angle enclosing liquid where it meets two solid grains exceeds 60° then surface energy is minimized when it resides in discrete curved face tetrahedra between four solid grains at a time: but if that angle is 60° or less, then it forms an infinitely connected system of channels along the three grain junctions. In the latter case, which is the more usual when liquid and solid are chemically similar, an arbitrarily small fluid fraction can undergo percolation. When the fluid is the melt formed from the solid matrix, the percolation of even a very small fraction of fluid can provide the overwhelmingly predominant mechanism of heat transport, through the matrix melting wherever heat is

supplied, percolation of fluid transporting the latent heat of melting, and depositing it by freezing again where heat is extracted. The resulting heat transport is predominantly vertical, downwards if the fluid is heavier than the matrix (as is the case for melt-water in a glacier), upwards in the more usual case that the fluid is lighter than the solid from which it forms. We may presume that this is the general case for the mantle-rocks, and it corresponds with the upward direction of geothermal heat-flow. Now, as the flow proceeds, gravitational energy is dissipated by viscosity, causing local melting. The channels in which the flow principally occurs, which are predominantly the vertical ones, are thus enlarged. The drainage system which thus establishes itself will thus be a tributary system, a three-dimensional analogue of a river system on the surface of the Earth. Here also the principal channels, in the principal drainage direction, erode deeper, and collect tributary flow from channels in less favoured directions. Thus this predominant heat transport mechanism acquires anisotropy, favouring vertical flow.

Recent work on liquid crystals has shown that anisotropy in heat-transport properties has dramatic and unexpected consequences affecting the conditions for total convection.

In ordinary circumstances, when an isotropic heat conduction equation applies, the conditions for the occurrence of convection in a layer heated from below (if the material has a positive coefficient of thermal expansion) have been well-known since the problem was analysed by Lord Rayleigh at the beginning of this century. In a layer of thickness d, convection will occur if a certain dimensionless combination, known as the Rayleigh number, exceeds critical value which is about 1000. That is :

$$\mathrm{Ra} = \frac{g \alpha \Delta T^* d^3}{\nu K} > \mathrm{Ra}_c \sim 10^3$$

where g is the gravitational acceleration, α the coefficient of expansion, d the layer thickness, ν the kinematic viscosity which is viscosity divided by density, K the thermal diffusivity, which is thermal conductivity divided by density and specific heat, and

$$\Delta T^* = \Delta T - (\Delta T)_s$$

is the difference in effective temperature between bottom and top, that is the actual temperature difference less the temperature drop caused by adiabatic expansion in rising through the thickness d. The numerator in the Rayleigh number measures the driving force for convection and the denominator the two dissipative factors tending to bring it to a halt: viscous drag for one, and for the other heat conduction which conveys heat horizontally from the hot rising currents to the cool falling currents, thus reducing the convective drive.

In applying this formula to the interior of the Earth, geophysicists are of course conscious the rock is not a Newtonian fluid: but one substitutes for viscosity

the ratio of shear stress to creep rate, which may indeed be nearly proportional for slow creep in a hot rock. Then that simple argument due to Tozer says that since a body the size of the Earth cannot get rid of its heat except by convection, so long as any energy sources remain within it the temperature must rise until the effective viscosity, which is an exponentially decreasing function of temperature, becomes low enough for the Rayleigh number to reach its critical magnitude, causing convection to set in. And since convection brings the temperature gradient down towards its adiabatic value, the temperature distribution remains closely the same, with approximately the adiabatic gradient, thereafter.

Another rather firm geophysical conclusion has been that since the melting point gradient is in all probability an order of magnitude greater than the adiabatic gradient, and the effective viscosity of rocks at their melting point cannot be very high, a zone of partial melting must be limited in thickness to at most a very few tens of kilometres. It is usual to identify this limited zone of partial melting with the so-called Low Velocity Zone, a level in the Earth at a depth somewhere between 100 and 200 km where the seismic wave-velocity, which generally increases with depth, shows a minimum.

In reaching these conclusions, the possibility that anisotropy could dramatically modify the conditions for thermo-convection had not been contemplated. The experiments and theoretical analyses on liquid crystals which have brought this to light are those of Dubois-Violette and others, from 1973 onwards. MBBA is a nematic, that is to say a uniaxial liquid, with a preferential orientation of its molecules along one direction. Its thermal conductivity in this direction is 1.7 times what it is in the transverse directions. In a specimen with the unique axis horizontal the critical Rayleigh number is found to be about 1. That is to say, to set it into convection requires a temperature excess at the bottom surface about 1000 times smaller than would be needed for an isotropic oil of similar coefficient of expansion and mean viscosity and thermal conductivity. More remarkable still, in a specimen with *vertical* unique axis, there is no convection at the critical Rayleigh number for an isotropic fluid, but convection is induced with a very small *downward* heat current, when the specimen is heated from above, in spite of the fact that this makes the upper layers lighter than the lower : the critical Rayleigh number is about -1.

How is one to understand that ? This is not the kind of lecture in which I should attempt to present the mathematical analysis of the problem, which is not mine anyway. Let me indicate the qualitative physics involved :

In the isotropic case one of the factors inhibiting convection below the critical Rayleigh number is the horizontal heat conduction current, away from a hot rising current into a cool falling current.

The bodies of fluid to right and left of a rising current rotate to right and left respectively. When the fluid is anisotropic, the easy axes of heat conduction are correspondingly deflected to right and left from their initial orientations. There is then a new contribution to horizontal heat flow arising from the anisotropy : the tilted easy axes cause a deflection of the vertical heat conduction current, which is now no longer antiparallel to temperature gradient. With a horizontal initial orientation this effect focusses the upward heat conduction current into the rising convective current, enhancing its buoyancy : with a vertical initial orientation the upward heat conduction current is deflected away from rising fluid, and focussed into regions of falling fluid, so quenching their motion. These horizontal heat conduction currents are much stronger than those present in the isotropic case, even for the modest anisotropy of MBBA: so much so that a downward heat flow being focussed into rising fluid currents is able to support convection in spite of stable density stratification.

One conclusion I wanted to draw from this is that percolative convection will act to suppress total convection. If upward melt-drainge is occurring in a mass of partially molten rock, establishing preferentially vertical drainage-channels, then if some column begins to rise as a whole the drainage-channels at its periphery are deflected outwards, so as to drain the light fluid out of it, and destroy its buoyancy. That suggests that percolative convection inhibits total convection, and the usual Rayleigh criterion is no longer a good test for whether total convection will occur. This raises the possibility that partial melting, and the melting point gradient rather than the smaller adiabatic temperature gradient, may extend through a greater range of depths in the Earth than has been thought possible. Other explanations can be found for the limited extent of the Low Velocity Zone.

In its negative sense, destroying the validity of the ordinary Rayleigh criterion, I am sure that is right. Thermal conductivity ceases to be the right parameter to put into the criterion when another and more powerful heat transfer mechanism, percolation, obeying different equations, is present. In its more positive sense the argument may we wrong. Further theoretical and experimental work by Lekkerkerker and by Guyon *et al* on the case of the liquid crystal with vertical axis heated from below, published in the last year or so, has shown that at a critical Rayleigh number not very much larger that than for the isotropic case, the phenomenon called 'overstability' by convection theorists intervenes. This is what control egineers call 'hunting'. Because of time lags between cause and effect, the same couplings which prevent the establishment of steady-state convection, cells can promote an oscillatory convection, and this can become strong enough to overwhelm the primary alignment of anisotropy responsible for stability. This has been shown to happen in MBBA.

The system with percolative convection present is not governed by the same equations. I do not know whether it will 'hunt' or not. I will only draw the limited

conclusion that study of liquid crystals has sufficed to show geophysicists that some of their basic beliefs regarding convection are in need of deeper examination.

I have chosen Geophysics and Liquid Crystals studies as examples of branches of science which at first consideration one could have supposed to have no possible connection. As another example, at the present time physicists concerned with liquid crystals, with liquid helium-3, with phase-change theory, with the theory of fundamental particles, and with the mechanics of manybody systems are all busy learning algebraic topology, finding most unexpected meeting points there. I believe it to be a general principle that there is no telling in advance which branch of science will make a breakthrough of great importance for another. And it therefore behoves all scientists to endeavour to maintain communication between all branches of sciences.

This requires vigilance and positive effort. Without it, sciences tend to fragment. The subjects dynamic diffraction of X-rays and electron theory of metals had their origins together in the 1920s. Papers by Ewald, von Laue and Bethe in that period discussed both cases together. Then in the 1930s they separated. The detaild consideration of electrons diffracting in a crystal in the electron-microscope, which makes the bridge between them, did not come for another two decades. In the meantime, a tiny difference in convention broke the communication. Those doing electron-theory of metals drew the wave-vectors from the origin to an outer point in reciprocal space, those doing dynamic diffraction of X-rays drew the wave-vectors from the outer points in to the origin. The consequence was that though they were doing the same basic theory and drawing the same diagrams they did not know it and could not help each other.

That example tells me that physicists can be just as great sinners as everyone else in letting the lines of communication becomc attenuated : but they should conscientiously work against it, and they are in principle better placed than most for keeping communications open. In physics and mathematics most of the sciences meet sooner or later : and physics has the advantage that there are astonishingly few branches of mathematics which do not ultimately find physical application, and in those applications they become visualizable and so communicable to a larger number. I urge it as a duty upon all physists to express themselves in ways which will keep them in communication with as many of their scientific colleagues as possible.

There are those who argue that since all sciences are interrelated, all scientists should take degrees in General Science. I think not, myself. I fear that a man who studies mathematics, physics, chemistry and biology for three or four years will not have reached sufficient depth to enter a professional conversation in any of them, and he will make better contact with the practitioners of any if he can speak with some authority in one.

It is possible for the job to provide the unifying principle. I remember Stephen Bragg saying, when he was Research Director for Rolls-Royce, (and whatever else was wrong with Rolls-Royce, there was nothing wrong with its R and D), that if he put a mathematician, a physicist, a chemist and a metallurgist together as a team to solve some aero-engines problem, within three months he could not tell, from the ideas they were producing, which had come from which background.

There is a lot to be said for learning different subjects in sequence, if there is time enough. I always encourage a man who proposes to change subjects for a higher degree. I am very happy, myself, that I followed a first degree in chemistry with a D. Phil. taken in the Engineering Science Laboratory at Oxford : and it was my D. Phil. supervisor, E. B. Moullin, Reader in Electrical Engineering, who directed my attention to the importance of Crystal Defects, which became one of my principal concerns in Physics.

Conversely, there is no need to make an explicit change. The science itself, if it is one of the modern active sciences, changes enough in the course of a lifetime to give a man a widely varied career. I remember that I used to point out, in the days when Bristol had three Professors of Physics, whose first degrees were respectively in Mathematics (that was Maurice Pryce), Physics and Chemistry (myself), that it was the one who had been continuously a Physicist, Cecil Powell, who had earned a Nobel Prize : showing that there is advantage in a cobbler sticking to his last.

So my advice is : study one subject thoroughly, and others as they become necessary to you, and then talk to your colleagues about eveything under the Sun. And try to write your papers in such language that they are comprehensible to as wide a range of other scientists as possible.