Modern Views on the Structure of Metals*

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There are several striking properties that distinguish a metal from a non-metal. A metal is a good conductor of both heat and electricity; indeed in popular descriptions of electrical phenomena the term metal is used almost as a synonym for a good conductor. We speak of metallic reflection or metallic lustre, and also of a metallic sound or the ring of a metal and figuratively of a metallic voice. We speak also of the malleability of a metal. What is it that endows metals with these characteristic properties ? The first step towards an answer to this question was the recognition, made about the end of the last century, that these various properties characteristic of a metal are intimately connected with one another, and further that they can all be traced ultimately to the presence in the metal, of a large number of free electrons, i.e. electrons that can migrate freely over the whole body of the metal.

The mobility of these electrons accounts directly for the observed electrical conductivity of the metal, and also for its thermal conductivity. The optical behaviour of such a medium containing free electrons will be similar to the behaviour of the ionosphere with regard to wireless waves. As we know, the ionosphere, contain-

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* Some parts of this paper are based on a speech broadcast from the All India Radio Station, Dacca.

ing a fair number of charged particles, almost totally reflects all wireless waves whose wave-lengths are greater than a certain critical value. The facility with which wireless waves are propagated over the earth — indeed several times round it under favourable conditions — is due to the reflecting properties of the ionosphere. In the same manner a metal, with its large density of free electrons, has its critical wave-length in the ultra-violet region of the spectrum, and electromagnetic waves of longer wave-lengths, as for example light-waves, will therefore be totally reflected from the polished surface of the metal. This accounts for the peculiar sheen or lustre that is associated with a metal. The solid metal, which is crystalline, may be regarded as an assemblage of positive ions arranged in a regular manner, and embedded in a matrix of negatively charged free electrons, and this structure will account for the malleability of the metal, and also for its peculiar elastic properties.

The number of such free electrons is easily estimated, at least in some of the simple metals like the alkali metals. Thin films of these metals have been found to become transparent, as should be expected, beyond a certain critical wave-length in the ultra-violet, which is different for the different alkali metals. From these wave-lengths one can calculate the number of free electrons in these metals, in the same manner in which one can claculate, from the critical wave-length of penetration of wireless waves into the ionosphere, the density of charged particles in it. The number of free electrons in the alkali metals, thus estimated, comes out to be nearly one per atom, which, in view of the monovalency of these atoms, seems to be very reasonable.

With this estimate of the number of free electrons, one would naturally like to go further, and deduce quantitatively from a few simple postulates regarding the movements of these electrons, the various metallic properties. An obvious, and particularly simple, set of postulates would be to suppose that these electrons are moving about in a random, disorderly manner, much like the molecules in any ordinary gas. Then, the larger the temperature the greater will be the velocities and therefore the kinetic energies of these electrons. This picture, however, presents some fundamental difficulties. In the first place, measurements on the heat capacities of metals show that even with a large increase in temperature there is hardly any change in the kinetic energies associated with the electrons — a result which flatly contradicts the theoretical prediction.

Secondly, each of these electrons, by virtue of its spin, should behave like a small magnet, of a definite known strength. When a piece of any metal, like copper or silver —— I shall exclude for the present the ferrous metals, which have a complicated magnetic behaviour —— is placed between the poles of a magnet, the elementary electronic magnets in the metal will naturally tend to aline themselves along the direction of the magnetic field. This tendency to regular alinement will, however, be much hampered by the disorderly thermal movements of these magnets. When equilibrium is established, there will be, statistically, a preponderance of orientations along the field, as compared with orientations in other directions; with the result that the piece of metal will behave like an induced magnet. Now the lower the temperature, the less violent

will be the thermal movements, and consequently the feebler the disturbances to the regular alinement of the elementary magnets, and therefore the greater the magnetization of the piece of metal.

But actually the magnetization produced at all ordinary temperatures is found to be only one hundredth of the expected value, and further even this feeble magnetization, instead of being stronger at lower temperatures, remains practically independent of temperature.

From the low values for the specific heat and the magnetization of the free electrons in the metal, one may be tempted to infer that the number of these free electrons may not be really so large as that deduced from the optical data, but may be much smaller, only a hundredth of it. This alternative also presents a serious difficulty. The observed conduction properties of the metal will then require that the free electron must be capable of travelling enormous distances in the metal without suffering any collision —— distances about a hundred times the distance between neighbouring atoms in the metal. How an electron can travel in a straight line such large distances, and still dodge all the intervening atoms, which are fairly closely packed, and avoid colliding with them, is on this view incomprehensible.

The above considerations relating to the specific heat, magnetization, and distances of travel of the electrons in a metal will illustrate the kinds of difficulties that one meets with in trying to develop a simple kinetic theory.

On a closer examination of the problem, however, the failure of the simple theory is not surprising. With the large concentration of free electrons that ordinarily obtains in a metal — nearly

as large as the concentration of the atoms — and their low mass, the wave-aspect of the electrons will become very conspicuous, and we have to replace the ordinary kinetic postulates appropriate to an aggregate of particles, by suitable postulates that will take into account the wave-nature of these electrons.

The fundamental law governing wave-motions in an enclosure is very simple. Let me illustrate by some examples. It is well-known that if a stretched string is allowed to vibrate, those vibrations only will be maintained whose half-wave-lengths are equal to the length of the string, or half, or a third, or a fourth, etc., of the length. In other words, only those vibrations that form nodes at the two fixed ends of the string, will be maintained.

In the same manner, if we consider the vibrations of the air in a closed room, there are certain discrete notes which only can be maintained in the enclosure, as any one who sings in a small room will realize. By sounding various notes it is easy to locate some of these natural frequencies of vibration of the air in the room. According to Lord Rayleigh it is somewhat in this manner that blind people are able to guess about the sizes of rooms*.

Now the result that in any given enclosure certain discrete wave-lengths only can be maintained, is very general, and applicable

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* He quotes a remarkable instance recorded by Darwin. 'The late blind Justice ~~Mr~~ Fielding' writes Darwin 'walked for the first time into my room, when he once visited me, and after speaking a few words said, "This room is about 22 feet long, 18 wide, and 12 high"; all ~~of~~ which he guessed by the ear with great accuracy'.

not only to the sound-waves maintained in the air inside a closed chamber, but also to light-waves, or electron-waves, maintained in suitable enclosures.

An obvious question suggests itself at this stage. We found just now that only waves of certain discrete wave-lengths, depending on the size of the enclosure, can be maintained in it. Will all these waves be maintained in equal intensity, or will some of the waves be more intense than others ? In other words, how is the energy distributed among the different permitted vibrations ?

In the example of the sound-waves in an enclosure the answer is simple; the gravest notes will be the predominant notes. The corresponding problem in the case of light-waves is rather complicated and has indeed proved to be a major problem in physics. With electron-waves the problem becomes again simple. Each of the permitted wave-lengths for the electron-waves in the medium, as for other waves, will correspond to a definite kinetic energy, so that the law regarding the maintenance of waves of definite wave-lengths, will mean that the kinetic energies of the electrons in the metal can have certain discrete values only. There is a subtle principle of exclusion* governing these electrons according to which, in the whole assemblage, containing billions of billions of electrons, just two electrons, and no others, can have any particular permitted kinetic energy. These two may be regarded as a pair moving along opposite directions with the same kinetic energy, and with their spins opposed to each other.

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* The above statement of the Principle of Exclusion may be shown to be ultimately equivalent to the statement that no two electrons in the metal, having their spins parallel, can occupy the same position at the same time.

Now assigning one such pair of electrons to the gragest mode of vibration, i.e. to the lowest permitted level of kinetic energy, another pair to the next higher permitted energy level, and so on, one finds that the last pair of electrons in the metal has to be assigned on this scheme to an energy level that is enormously high. To give an idea of the magnitude of the highest energy possessed by the electrons, I may mention that in a metal like silver, the energy will be the same as the average energy of the molecule in any ordinary gas kept at a temperature of about 40,000° C. The corresponding velocity of the electron will be nearly 1/250 of the velocity of light, i.e. nearly 750 miles per second, which is a very high velocity indeed.

Thus all the permitted energy levels up to a certain large value will be occupied by electrons in pairs. A few stray electrons may occupy some of the immediately higher energy levels, and singly; their number being the smaller the lower the temperature. At room temperature their number will be about one per cent.

The enormous energies possessed by the free electrons in the metal will therefore persist practically unimpaired right down to the lowest temperatures.

The above model of the electronic structure obtaining in metals offers a satisfactory solution of the difficulties encountered before. In the first place, since the average kinetic energy already possessed by the electrons is at least a hundred times greater than the thermal energies possessed by molecules at ordinary temperatures, naturally until we reach temperatures of the order of a few thousand degrees, we can not appreciably add to their energy content.

Secondly, the majority of the electrons are paired in such a way that the spin magnetic moments of the components of a pair oppose each other. In the presence of a magnetic field it is only the few stray electrons (about one per cent at room temperature) that are unpaired, that can turn round in the magnetic field and contribute to the magnetization. It is therefore not surprising that the observed magnetization is so feeble.

Now the number of such single or celibate electrons will be the smaller the lower the temperature. On the other hand, the lower the temperature the less the disturbance from thermal agitations to the regular alinement of these magnets and hence the greater the magnetization. As a result of these two opposing factors, the first tending to decrease the number of effective magnets at low temperatures, and the second tending to improve their alinement at low temperatures, the observed feeble magnetization will be practically independent of temperature.

On this view, the number of free electrons that can take part in electrical conduction will in effect be small. We then have to meet the third difficulty that I mentioned, namely that observational data require that the electron should be capable of travelling large distances, without colliding with any of the numerous atoms in its path. The difficulty resolves itself in view of the wave nature of the electron which predominates under the conditions of close packing in the metal. When the wave-length is large in comparison with the inter-atomic distance, electron-waves, just like light-waves, will suffer very little loss of energy by passage through a homogeneous ~~medi~~ medium in which the constituent atoms, which will tend to scatter the waves, are regularly spaced as in the crystalline metal. If the

atoms are perfectly regularly arranged, the scattering of the electron-waves by them will be so small that the metal will have hardly any electrical resistance. Thus on this view the difficulty is not so much to explain how the electrons travel large distances in the medium, but to explain why they stop at all, i.e. why the metal has any electrical resistance at all . To explain this we have to invoke the deviations from the regular arrangement of the atoms, brought about by their thermal agitations; the higher the temperature, the larger will be the deviations, and hence the greater the scattering, and therefore the greater the electrical resistance of the medium. This is one of the characteristics of pure metals. The presence of any impurity, will naturally disturb the homogeneity of the scattering medium, and will thus tend to increase its resistance. This result also is experimentally verified.

Thus all the three difficulties mentioned in an earlier part of this paper as typical of those that one encounters in the classical electron theory of metals, vanish when the wave nature of the mobile electrons is taken tnto account. If further one can, on this basis, explain what can not be explained on the classical theory, namely why certain elements only are metallic and not the others, the new theory may be regarded as quite satisfactory.

The question raised above may be restated in the following form: why is the free electron density so large in certain elements and not in others ? If we might generalize from the results obtained for the alkali metals, we should expect the number of free electrons to be the same as the number of valency electrons. Why then are not all the elements metallic ?

We have already seen that electron-waves with certain definite wave-lengths only can be maintained in a given enclosure and that among these permitted wave-lengths, all those that range from the longest to a certain minimum, which is determined by the density of free electrons in the enclosure, will be represented in the motions of these electrons at ordinary temperatures. Assuming that all the valency electrons in a crystal are free, let us calculate this minimum wave-length. If this wave-length — to be more precise, half of it — comes out to be much greater than the distance between neighbouring atoms in the crystal, then evidently the influence of the crystal lattice on the electronic motions will be small, and the electronic behaviour will conform to that of an electron gas. The substance will then exhibit pronounced metallic properties. This is the case with the alkali metals, and the noble metals.

If, on the other hand, the minimum wave-length calculated from the electron density is not so large, the possibility of regular reflections from the crystal planes, of some of the short waves, has to be considered; in other words, the influence of the lattice becomes prominent. In the neighbourhood of those wave-lengths that can be reflected strongly, are set upt barriers that require much energy to cross over from the long wave-length side.

If, as frequently happens, the permitted wave-lengths on the long wave-length side of the barriers are <u>just</u> sufficient in number to be assigned one to each pair of electrons in the substance, then these electrons are as good as bound. They can not change their wave-lengths, or their momenta, except by crossing the barriers, i.e. except when supplied with the requisite large energy from outside.

Such substances will not conduct electricity, except in very high electric fields. In other words, they will behave as insulators. Diamond is a typical example of such a substance. The number of electrons to which can be assigned proper wave-lengths, without crossing the barriers, comes out in this crystal to be just four per carbon atom, i.e. just all the valency electrons; and the barriers are sufficiently high to prevent a normal crossing over of the electrons.

Thus the new theory provides us further with a criterion by which to decide whether the valency electrons in a given substance can be regarded as free, or as effectively bound, i.e. whether the substance will behave as a metal or as an insulator.