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Thermionic Constants of Semi-Conductors

In some recent papers[1], we have described a convenient method of determining the thermionic constants of metals. The method consists essentially in determining, at different known temperatures, the rate of effusion of electrons through a small hole in a thin wall of a chamber made of the metal, instead of determining the direct emission from the surface. The advantage of the effusion method over the emission method is this. The expression for emission involves the transmission coefficient of the surface for electrons having the requisite momentum to cross the surface. This coefficient is very sensitive to adsorption of gases at the surface, and may differ considerably from unity. This coefficient, however, is eliminated in the expression for effusion, in the same manner in which the emissivity of the surface for electromagnetic radiations is eliminated when we take the electromagnetic radiations from a cavity through a small hole, instead of directly from the radiating surface. When the transmission coefficient is eliminated, any observed deviation of the A-coefficient in Richardson's equation from its theoretical value may be attributed to a small linear variation of the work function with temperature. Thus one is enabled by this method to determine not only the work function correctly, but also its temperature coefficient.

The thermionic constants of several metals have been determined by this method, using for this purpose a graphite chamber the walls of which were coated completely with the metal under study, by thermal or electrolytic deposition.

The main purpose of this communication is to direct attention to a new application of this method, namely, for the determination of the thermionic constants of semi-conductors, and to report some preliminary results obtained with nickel ribbons coated with the triple carbonates of barium, strontium and calcium in the molar percentages 47·5, 46·0 and 6·5 respectively. The ribbons were kindly supplied by Dr. D. A. Wright, of the Research Laboratories of the General Electric Co., Ltd., at Wembley. The ribbons were cut into pieces about 2 cm. in length, and a sheaf of them, held together at one end by a platinum foil, was fixed to the back of the graphite chamber, so that the ribbons did not come directly in-

to contact with the graphite surface. The total surface area of these ribbons was more than twenty-five times the area of the effusion hole in our earlier measurements, and about fifty times in our later ones. The coated filaments were activated in the usual manner, and the effusion currents, corresponding to the saturation electronic vapour pressure of the oxide coat, in the temperature range 950°–1,160° K., were measured in the same manner as in our measurements on metals. (The electronic vapour pressure due to graphite, or platinum, is negligible at these temperatures.)

The currents corresponding to zero field were found to fit well with Richardson's equation, with $\varphi = 1{\cdot}55$ eV., and $A = 48$ amp. cm.$^{-2}$ deg.$^{-2}$. The latter value corresponds to a temperature coefficient of the work function $d\varphi/dT = 8 \times 10^{-5}$ eV. per deg., which is of the same order as in many metals. At 1,000° K. the current corresponding to effusion over the whole of the 2π-solid angle would be about 0·75 amp. per sq. cm. The corresponding current obtained by Elizabeth Grey[2] for maximum space-charge-limited pulsed emission directly from the surface of the oxide coat is 8 amp. per sq. cm., which is about eleven times as great. This ratio is of the order to be expected.

We thank Dr. Wright for supplying the coated ribbons, and for helpful discussions.

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Nov. 27.

[1] Jain, S. C., and Krishnan, Sir K. S., *Proc. Roy. Soc.*, A, **213**, 143, and **215**, 431 (1952).
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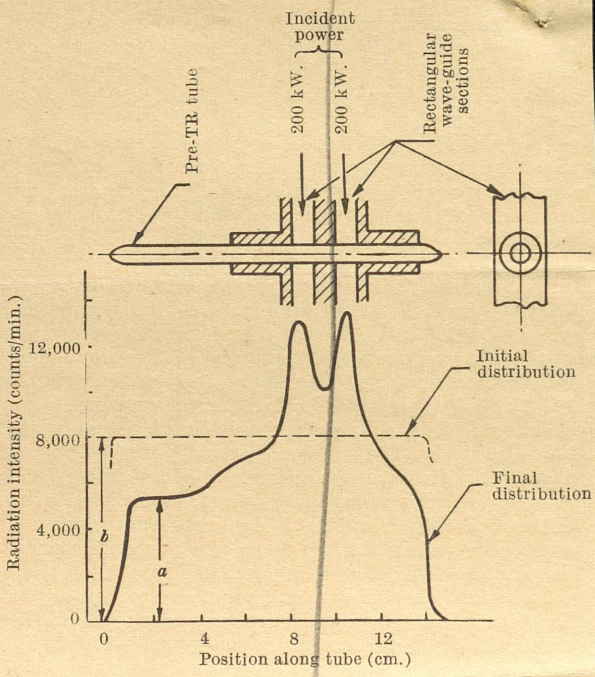

Fig. 1

Measurements using radioactive krypton can give information regarding the clean-up rate of this particular gas under certain conditions, and also enable a comparison to be made of the ability of different discharge conditions to clean-up rare gases.

Two techniques have been used to monitor the clean-up rate in pre-T.R. valves having walls of silica 0·020 in. thick: (*a*) The collimated beta radiation from a section of the valve remote from the discharge and gas clean-up region is monitored during the life of the valve, by Geiger counter. The activity then measured is due to free gas in the valve only, and hence the count-rate is proportional to the free gas density. (*b*) For low clean-up rates, a break-open test is most convenient. After a known period of life, the total activity of the valve is measured before and after breaking it open to the atmosphere. The residual activity of the valve after the free gas has escaped then corresponds to the quantity of gas cleaned-up into the walls of the valve.

A typical example of technique (*a*) is shown in Fig. 1. A silica tube pre-T.R. crosses two wave-guides, with 200 kW. of 3 cm. microwave power incident on each section of the tube. The tube contained 7 mm. mercury pressure of krypton. The lower diagram shows the distribution of the radiation emitted in a radial direction as a function of position

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decrease linearly within the experimental error.

New observations have been made at room temperature and at approximately 95° K. with a 'Norelco' high-angle goniometer diffractometer. In the front reflexion region, there is no ambiguity in indexing, and the changes in position of the 110 and

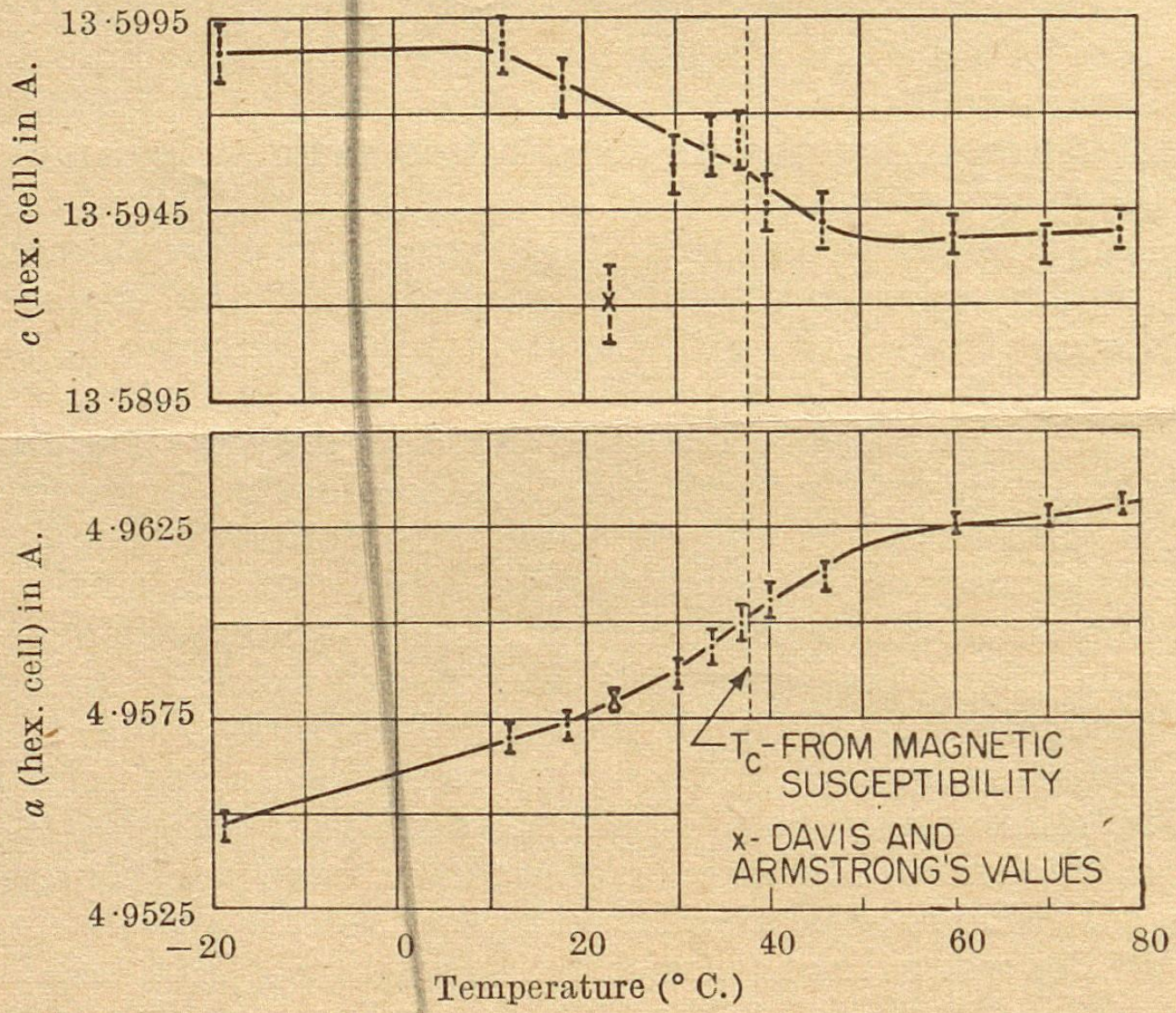

Fig. 1. Lattice parameters (hexagonal setting) of Cr_2O_3 as a function of temperature

NATURE

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The Drude Dispersion Formula shown to be Applicable to any Medium irrespective of the Polarization Field

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[Received April 10, 1956]

ABSTRACT

It is shown that the well known dispersion formula of Drude is applicable to a dense medium even when the polarization fields associated with the different types of oscillators may all be different. The parameters involved in the formula are naturally the frequencies and the oscillator strengths of the oscillators in the medium, both of them as influenced by the mutual interactions between the oscillators, i.e. as influenced by the polarization fields. The observed data on dispersion will enable us to determine these parameters. In the Lorentz type of dispersion formula, on the other hand, the frequencies and the oscillator strengths involved are those of the *isolated* oscillators, which naturally are independent of the polarization field, and hence the effect of the polarization field on dispersion has to be taken into account explicitly. Because of this, the Lorentz type of formula needs for its formulation explicit information regarding the polarization field, which cannot be supplied by the observed dispersion data alone. The reduction of the Drude formula to one of the Lorentz type, and the appropriate information regarding the polarization field that is needed for this purpose, are also discussed in the paper.

§ 1. THE DISPERSION FORMULAE OF DRUDE AND OF LORENTZ

THE well known dispersion formula of Lorentz for a dense medium is

$$\frac{K_\omega - 1}{K_\omega + 2} = \frac{4\pi}{3}\sum_{i=1}^{n}\frac{N_i F_i e_i^2}{\mu_i(\Omega_i^2 - \omega^2)} = \frac{4\pi}{3}\sum_{i=1}^{n}\frac{A_i}{(\Omega_i^2 - \omega^2)}, \text{ say} \quad . \quad . \quad (1)$$

where K_ω is the dielectric constant of the medium for frequency ω, N_i is the number per unit volume, F_i the oscillator strength, and μ_i the reduced mass, of oscillators of frequency Ω_i. This formula is derived on the basis that the actual field acting on an oscillator in the medium is not merely the field in the medium but includes in addition the polarization field, which is further taken to be $4\pi/3$ times the polarization per unit

† Communicated by the Authors.

volume. This introduces in the expression for $K_\omega - 1$ a multiplying factor $[1+(4\pi/3)\chi_\omega]=(K_\omega+2)/3$, where χ_ω is the polarization of the medium per unit volume per unit field in the medium.

On the other hand the Drude formula, namely

$$K_\omega - 1 = 4\pi \sum_{i=1}^{n} \frac{N_i f_i e_i^2}{\mu_i(\omega_i^2 - \omega^2)} = 4\pi \sum_{i=1}^{n} \frac{a_i}{\omega_i^2 - \omega^2}, \text{ say, } \ldots \quad (2)$$

which had been derived much earlier, did not naturally contemplate the presence of a polarization field. Hence the Drude formula is generally regarded as a special case of the Lorentz formula, applicable to media in which the polarization field is known to be zero.

For convenience in discussion we shall refer to the quantities A_i and a_i briefly as the oscillator strengths of the oscillators concerned in the two formulae, though actually they refer to N_i oscillators.

Many years ago Herzfeld and Wolf (1925) showed, however, that formula (1) *can always be reduced algebraically to* (2), the ω_i's and a_i's appearing in (2) being calculable functions of Ω_i's and A_i's. They derived (2) from (1) in the simple case when the number of frequencies involved in the formula is just two, but as they themselves pointed out, the reduction of (1) to (2) can be done also in the general case when the frequencies are more than two.

Further since the number of parameters involved in the two formulae is the same, it should be possible conversely to reduce (2) to (1), though the actual reduction, as we shall see later in the present paper, is not quite so simple as the reduction of (1) to (2).

From these considerations it follows that if the experimental data for the dispersion of any substance can be fitted with one of these formulae, they can be fitted equally well with the other formula too. The characteristic frequencies appearing in the two formulae will naturally be very different. From this circumstance it has been concluded by some of the later workers that by comparing the frequencies occurring in the two formulae with the observed frequencies of the medium it should be possible to decide between the two formulae : in other words to decide whether there is a polarization field of magnitude $4\pi/3$ times the polarization per unit volume, as contemplated in the derivation of the Lorentz formula, or it is zero as is taken to be implied by the Drude formula.

§ 2. The Dispersion Data can give no Information regarding the Polarization Field

In some earlier papers (Krishnan and Roy 1952, 1953) we have shown that such an appeal to observation, namely to find which set of frequencies deduced from the observed dispersion agrees with the observed resonance frequencies, whether it is the Ω_i's or the ω_i's, will not enable us to decide

on the existence or otherwise of a polarization field in the medium, and much less to determine its magnitude. Irrespective of whether a polarization field occurs or not, and irrespective of its magnitude when it occurs, the Drude formula (2) will always express correctly the observed dispersion, and the frequencies appearing in this formula will be the actual resonance frequencies of the medium. Since (2) can always be reduced algebraically to (1), again irrespective of the presence or not of an actual polarization field, the observed validity of (1) has by itself no physical significance, *unless the magnitude of the polarization field can be verified independently, or the frequencies Ω_i, whose significance will be stated presently, are known from other considerations.*

This arises from the following circumstance. The effect of the polarization field, whatever may be its magnitude, on the dielectric constant, can be taken into account in two alternative ways, which are mathematically equivalent, and which lead to the Lorentz and the Drude formulae respectively :

(1) The frequencies and the oscillator strengths may be taken to be those of the oscillators when isolated from one another, namely Ω_i and A_i respectively, and the effect of the polarization field on the dielectric constant is then taken into account explicitly.

(2) Alternatively, one may use the frequencies and the oscillator strengths, of the oscillators as influenced by the mutual interactions of the oscillators, i.e. as influenced by the polarization field, namely ω_i and a_i, in which case the whole effect of the polarization field on the dielectric constant is taken into account automatically.

The difference between the two approaches lies in this : whereas ω_i and a_i can be obtained directly from the dispersion data, Ω_i and A_i cannot be.

§ 3. Scope of the Present Paper

It was also emphasized in these papers that the polarization fields associated with the different types of oscillators present in the medium, as for example the electronic and the reststrahlen oscillators in the alkali halide crystals, may be widely different. It was further mentioned, without a statement of the proof, that the Drude formula (2) will hold even in the most general case when the polarization field acting on an oscillator of type i due to all the oscillators of type j in the medium is p_{ij} times χ_j, where χ_j is the contribution from oscillators of type j to the polarization per unit volume per unit field in the medium, and the p_{ij}'s *may all be different.* Since this result is of some importance, and the proof is not obvious, the proof is given in the present paper.

The conditions under which the Drude formula, which is generally applicable to any medium, can be reduced to one of the Lorentz type are also discussed in this paper.

§ 4. The Basic Expression for Refractivity and its Reduction to the Drude Formula

When the different p_{ij}'s, which we may refer to as the polarization field factors, may be different, the basic expression for the dielectric constant of the medium takes the form

$$K_\omega - 1 = 4\pi\chi = 4\pi \sum_{i=1}^{n} \chi_i, \qquad \ldots\ldots (3)$$

where

$$\chi_i = \frac{N_i F_i e_i^2}{\mu_i(\Omega_i^2 - \omega^2)}\left(1 + \sum_{j=1}^{n} p_{ij}\chi_j\right) \qquad \ldots\ldots (4)$$

Obviously the χ's, like K, would be functions of the incident frequency ω, but for convenience in writing, we have dropped the subscripts ω except in the case of K.

We now proceed to demonstrate that the basic eqns. (3) and (4) can be reduced to formula (2) of Drude.

Using the n equations similar to (4), and using also (3), one can eliminate all the χ_i's and obtain therefrom

$$\begin{vmatrix} -\chi & 1 & 1 & \ldots & \ldots & 1 \\ 1 & p_{11} - \frac{1}{b_1} & p_{12} & \ldots & \ldots & p_{1n} \\ 1 & p_{21} & p_{22} - \frac{1}{b_2} & \ldots & \ldots & p_{2n} \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots & \ldots \\ 1 & p_{n1} & p_{n2} & \ldots & \ldots & p_{nn} - \frac{1}{b_n} \end{vmatrix} = 0, \qquad \ldots (5)$$

where

$$b_i = \frac{N_i F_i e_i^2}{\mu_i(\Omega_i^2 - \omega^2)} = \frac{A_i}{\Omega_i^2 - \omega^2} \qquad \ldots\ldots (6)$$

Let

$$\Delta = \begin{vmatrix} p_{11} - \frac{1}{b_1} & p_{12} & \ldots & \ldots & p_{1n} \\ p_{21} & p_{22} - \frac{1}{b_2} & \ldots & \ldots & p_{2n} \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ p_{n1} & p_{n2} & \ldots & \ldots & p_{nn} - \frac{1}{b_n} \end{vmatrix} \qquad \ldots (7)$$

which is a polynomial of degree n in ω^2, which cannot be zero for all values of ω^2.

Now let P_{ij} be the co-factor of the $_{ij}$th element in the determinant Δ. One then obtains from (5)

$$\chi = -\sum_{i,j=1}^{n} P_{ij}/\Delta. \quad \ldots\ldots\ldots \quad (8)$$

In (8) the P_{ij}'s are polynomials of degree $n-1$ in ω^2, whereas Δ is of degree n in ω^2. Hence the right-hand side of (8) can be expanded into partial fractions, thus leading to the expression

$$K_\omega - 1 = 4\pi\chi = 4\pi \sum_{i=1}^{n} \frac{a_i}{{\omega_i}^2 - \omega^2}, \quad \ldots\ldots \quad (9)$$

where ${\omega_1}^2, {\omega_2}^2, \ldots {\omega_n}^2$ are the n roots of the equation $\Delta(\omega^2)=0$. ω_i and a_i will be functions of the Ω's, the A's and the p's, and will be independent of ω.

Equation (9) can be immediately recognized as the Drude formula.

§ 5. The Dispersion Data in Relation to the Polarization Field

This derivation emphasizes the basic nature of the Drude formula for dispersion. Far from being a special case of the Lorentz formula for zero polarization field, it is physically a more significant formula than Lorentz's, even when there is a polarization field, which may be large and complicated. Just as for the isolated oscilators, their optical behaviour is determined uniquely by their characteristic frequencies Ω_i and their oscillator strengths A_i, so also the optical behaviour of a dense assemblage of such oscillators is determined by the corresponding quantities ω_i and a_i characteristic of the medium. The parameters involving explicitly the polarization fields get eliminated.

For the same reason the dispersion data by themselves cannot give any information regarding the polarization field. If the medium has n characteristic frequencies, the observed dispersion data, which obviously should fit into (9), can supply $2n$ parameters, namely the ω_i's and the a_i's which would be just sufficient to determine the frequencies Ω_i and the oscillator strengths A_i of the n oscillators, *when all the p_{ij}'s are known.*

Now if the p_{ij}'s were all different their number would be n^2, in which case, the p's would be too numerous to be calculated from the $2n$ parameters available from the dispersion data, even if all the Ω_i's and the A_i's were known ; except in the trivial case when $n=1$. But actually the p_{ij}'s are not quite so many, since in general p_{ij} should be equal to p_{ji}, in which case the number of different p_{ij}'s reduces to $\frac{1}{2}n(n+1)$. If the Ω_i's and the A_i's are known, then all the p_{ij}'s should be determinable from the dispersion data when $n \leqslant 3$. With $n=3$ or even with $n=2$, it would be possible in practice to describe satisfactorily the dispersion over a fairly wide region of the spectrum.

The result obtained just now may be of even deeper practical interest. Till now we have been concerning ourselves with the dispersion formula alone, i.e. the expression for K as *a function of the frequency* ω, which

enables us directly to determine only the parameters ω_i and a_i, and in which the polarization fields do not appear explicitly. On the other hand the expression for K as *a function of the density of the medium* would involve the polarization field explicitly. In particular, for molecular substances like benzene, naphthalene and other organic compounds, in which the molecules retain their individuality in the condensed state, one can obtain the Ω_i's and the A_i's from the dispersion in the vapour state, in which the polarization fields are negligible, and the corresponding ω_i's and a_i's in the condensed phase from the dispersion data for this phase. A comparison of the two sets, referring respectively to the two phases, should enable us to determine all the p_{ij}'s, provided we choose a spectral region in which 3 frequencies would be adequate to represent correctly the dispersion data.

On the other hand the variation of dispersion with density, in the condensed phase, which may be secured by varying the temperature, would not be so helpful, since the p's also are functions of the density.

§ 6. Reduction of the Basic Formula to One of the Lorentz Type

Having shown that the basic formulae of dispersion, namely (3) and (4), do reduce to Drude's even when the p_{ij}'s are all different, we may proceed to enquire whether in this general case, (3) and (4) can also be reduced to one of the Lorentz type, by which we mean a formula of the type

$$\phi(K)=4\pi\sum_{i=1}^{n}\frac{A_i}{\Omega_i^2-\omega^2}; \qquad \ldots\ldots\ldots \quad (10)$$

in which the Ω_i's and the A_i's refer to the *isolated* oscillators, and have the same significance as in (1). The answer is that this can not be done in the general case when the p_{ij}'s are all different.

The problem is really one of finding an expression for K, i.e. for χ, which will not involve the component polarizabilities χ_i separately. One obvious method of doing this is to eliminate the χ_i's between (3) and (4), and this procedure, as we have seen, yields the Drude formula, which involves the characteristic frequencies ω_i of the medium, and not the frequencies Ω_i of the isolated oscillators, which we now wish to retain. On a closer examination of (4) and (3) one can see that the separate χ_i's can be eliminated, without at the same time eliminating the Ω_i's also, only when the p_{ij}'s have all the same value, say p.

When this is the case, the explicit expression for $\phi(K)$ appearing in (10) becomes

$$\frac{\chi}{1+p\chi}=\sum_{i=1}^{n}\frac{A_i}{\Omega_i^2-\omega^2} \qquad \ldots\ldots\ldots \quad (11)$$

or

$$\frac{K-1}{K+\alpha}=p\sum_{i=1}^{n}\frac{A_i}{\Omega_i^2-\omega^2} \qquad \ldots\ldots\ldots \quad (12)$$

where $\alpha=4\pi/p-1$.

§ 7. Reduction of the Drude Formula to one of the Lorentz Type

We have shown that the basic formulae of dispersion, namely (3) and (4), can be reduced to the Drude formula (9) even when the p_{ij}'s are all different, and that in the special case when they have all the same value p, (3) and (4) reduce to (12) also. Hence it follows when all the p_{ij}'s have the same value, it should be possible directly to reduce (9) to (12), i.e. to obtain the constants Ω_i and A_i in terms of ω_i and a_i when $\alpha=4\pi/p-1$ is known. The reduction is done in the following manner.

Starting with (10), and remembering that $\alpha=4\pi/p-1$, one obtains immediately

$$\frac{K-1}{K+\alpha}=\left(p\sum_{i=1}^{n}\frac{a_i}{\omega_i^2-\omega^2}\right)\Big/\left(1+p\sum_{i=1}^{n}\frac{a_i}{\omega_i^2-\omega^2}\right)$$

$$=\frac{p\sum_{i=1}^{n}a_i\prod_{\substack{j=1\\j\neq i}}^{n}(\omega_j^2-\omega^2)}{\prod_{i=1}^{n}(\omega_i^2-\omega^2)+p\sum_{i=1}^{n}a_i\prod_{\substack{j=1\\j\neq i}}^{n}(\omega_j^2-\omega^2)} \quad . \quad . \quad . \quad . \quad (13)$$

Now knowing ω_i and a_i and knowing further that every p_{ij} has the same value $p=4\pi/(\alpha+1)$, we may put the denominator on the right-hand side of (13)$=0$, and treating it as an equation in ω^2, obtain the n roots of the equation, namely M_1^2, M_2^2, . . . M_n^2, and thence obtain

$$\frac{K-1}{K+\alpha}=\frac{p\sum_{i=1}^{n}a_i\prod_{\substack{j=1\\j\neq i}}^{n}(\omega_j^2-\omega^2)}{\prod_{i=1}^{n}(M_i^2-\omega^2)} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Since the M_i's are now known, the numerator on the right hand side can be put equal to $p\sum_i C_i\prod_{\substack{j=i\\j\neq i}}^{n}(M_j^2-\omega^2)$ where the C_i's can be readily obtained. We thus obtain

$$\frac{K-1}{K+\alpha}=p\sum_{i=1}^{n}\frac{C_i}{M_i^2-\omega^2}, \quad . \quad . \quad . \quad . \quad (15)$$

in which the C_i's are obviously independent of ω.

Comparing (15) with (12) one can immediately see that if the basic assumption that every p_{ij} has the same value, namely p, is correct, then every M_i and C_i appearing in (15) should be identical with every Ω_i and A_i respectively.

But the important point to emphasize is that the values of M_i and C_i thus obtained will represent correctly the frequencies and the oscillator strengths of the isolated oscillators only to the extent to which our knowledge of the polarization field is dependable. Since the dispersion data themselves do not supply any information regarding the polarization

field, one may choose any arbitrary α, and find the corresponding M_i and C_i which will make (15) algebraically identical with (9). Since the Drude formula (9) represents correctly the observed dispersion, (15) too, with the appropriate choice of the M_i's and C_i's corresponding to our choice of α, will represent equally well the observed dispersion, and this will be so irrespective of the actual values of the different p_{ij}'s ; but then the M_i's and C_i's that appear in the formula will not be the actual Ω_i's and the A_i's of the isolated oscillators.

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THE POLARIZATION FIELD IN AN IONIC CRYSTAL AND ITS INFLUENCE ON THE RESTSTRAHLEN FREQUENCY

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ABSTRACT

By displacing the lattice of positive ions in an ionic crystal like the alkali halide with reference to the lattice of negative ions, one naturally produces a polarization in the medium. When the displacement is small the polarization may be regarded as due to point-dipoles located at the lattice points of the crystal. Associated with the polarization there will naturally be a polarization field acting on the ions tending to increase this displacement. Knowing the potential energy corresponding to a small displacement, one obviously obtains the reststrahlen frequency of the crystal. In calculating this potential energy, however, one has to include in addition to the work done against the forces due to the Coulomb and the repulsion interactions between the ions, also the work done by the polarization field in effecting this displacement. If the latter work were not included, the frequency that one would get would be that of the individual dipoles isolated from one another, whereas the reststrahlen frequency is that of the assemblage of such dipoles. Owing to their mutual interactions in the assemblage the latter frequency may be markedly different from that of the isolated dipoles. It is precisely these interactions that are taken into account when the effect of the polarization field is included in the calculation of the potential energy.

The characteristic frequencies that appear in the well-known Drude formula for dispersion are the resonance frequencies of the medium, in which the effect of the polarization field has been included automatically, and hence the formula will be of general validity irrespective of the magnitude of the polarization field acting on the oscillators. On the other hand in the Lorentz formula, in which the polarization field is taken into account explicity, the characteristic frequencies that occur are those which the oscillators constituting the medium would have if they had been isolated from one another, *i.e.*, if there had been no polarization field to influence them.

The paper includes also a discussion on the nature of the polarization field in ionic crystals.

1. INTRODUCTION

Some years ago we calculated the frequency and the anharmonicity of the polar oscillations of the alkali halide crystals (Krishnan and Roy 1950 ab, 1951) on the basis of the following simple model. The positive and the negative ions in the crystal lattice are regarded as held in their respective positions of equilibrium by the electrostatic and the repulsion interactions between the ions. Whereas the electrostatic interactions are long range ones, the repulsion interactions are practically confined to the adjacent ions only. Now displacing the lattice of positive ions in the crystal with respect to that of the negative ions by a small distance r, the potential energy due to such a relative displacement may be readily calculated on the basis of this model, and expressed as a power series in r, in which, owing to the centre of symmetry of the lattice points of the crystal, the terms involving the odd powers of r will be absent. The coefficient of the r^2 term in this expression will obviously determine the frequency, and that of the r^4 term the anharmonicity, of the polar oscillations of the crystal. For most of the alkali halides, the frequency thus obtained was found to agree closely with the known reststrahlen frequency of the crystal. It was further found that the sign and the magnitude of the anharmonicity calculated in this manner for KCl crystal fitted well with the known decrease of the specific heat

of the crystal at constant volume with increase of temperature at high temperatures. Among the alkali halides this happens to be the only crystal for which such specific heat data are available.

Now the relative displacement r of the positive and the negative lattices naturally leads to a homogeneous polarization of the crystal, and in calculating the r^2 term in the expression for the potential energy we had to take into account, in the paper referred to, besides the electrostatic and the repulsion interactions between the ions, separately the work done by the polarization field also in effecting this displacement.

A question has been raised in the course of some discussions on the subject whether in considering the electrostatic interactions with all the surrounding ions in the crystal, all of them occupying their respective displaced positions, the effect of the polarization field also has not been indirectly taken into account. The answer to this question is an unambiguous one, namely, that in calculating the reststrahlen frequency one should take into account explicitly the effect of the polarization field, in addition to taking into account the effect of the electrostatic and the repulsion interactions. Even so, the very posing of the question points to the need for a further elucidation of the issues involved. Such an elucidation incidentally helps also to clarify some of the basic concepts regarding the nature of the polarization field itself.

2. CALCULATION OF THE RESTSTRAHLEN FREQUENCY

Since our main purpose is the elucidation of the basic issues, and it can be done with any typical crystal, we shall confine attention for the present to a crystal of the NaCl type. Again, since we are concerned here with the calculation of the frequency only, and not its anharmonicity, we shall retain the r^2 term alone in the expression for the potential energy. Knowing the potential energy W per pair of ions, the frequency of the polar oscillations of the crystal may be readily obtained from the relation

$$W = \tfrac{1}{2}\mu\omega_0^2 r^2, \tag{1}$$

where ω_0 is 2π times the frequency, and μ is the reduced mass of the ion-pair.

Considering now the calculation of W, it is found that the contribution to W from the electrostatic interactions between the ions is nothing, owing to the centre of symmetry of the lattice points, and that from the repulsion interactions is given by $a_1 r^2$, where

$$a_1 = 3/(2\,N\,\beta\,d^2) = \alpha\,e^2\,(\delta-2)/(6d^3)\,; \tag{2}$$

d is the distance between the neighbouring ions, α is the Madelung constant, N is the number of ion-pairs per unit volume of the crystal, β is the compressibility, and δ is a number which defines the repulsion interaction between two adjacent ions as a function of the distance of separation R between them :

$$\phi = A \exp(-\delta R/d). \tag{3}$$

Now the relative displacement of the two lattices will produce a homogeneous polarization in the medium, both directly as a result of this separation, and indirectly by polarizing the ions themselves, *i.e.*, by displacing the electronic cloud in each ion relatively to its nucleus. As a result of this polarization there will be a polariz-

ation field acting on the ions, which will be in a direction that will help the further relative separation of the ions. Hence $a_1 r^2$ will be correspondingly too high an estimate of the potential energy W required for the calculation of the reststrahlen frequency ω_0 with the help of equation (1).

Let Br be the total polarization per unit volume. Then pBr will be the polarization field acting on an ion, where p is the polarization field factor. The corresponding contribution to the potential energy will then be

$$a_2 r^2 = -\tfrac{1}{2} e\, pB\, r^2, \tag{4}$$

where e is the magnitude of the electronic charge. Hence the net value of the potential energy per pair of ions, due to the relative displacement r of the two lattices, will be given by

$$W = (a_1 + a_2) r^2 = a r^2, \text{ say.} \tag{5}$$

We shall quote here some of the major results obtained in the papers referred to, relating to the quantities involved in (5) and relevent to our purpose.

1. Since the relative displacement r of the two lattices is small in comparison with the inter-ionic distance d, the detailed structure of the polarization due to this displacement corresponds to locating at each point of the lattice of positive ions a point-dipole, of moment er, with its direction along that or r.

2. The polarization field associated with the ionic displacements r was found to have just the Lorentz value, namely $4\pi/3$ times the polarization per unit volume, which is to be expected since the medium consists now of point-dipoles occupying the points of a simple cubic lattice, and Lorentz's original calculation which led to the factor $4\pi/3$ was concerned specifically with this case.

3. It was further found that the relative displacement of the two lattices does not induce any electronic polarization in the ions, and hence the total polarization per unit volume is just Ner.

The experimental evidence for this finding is this. The observed reststrahlen frequency is just what should be expected if the total polarization of the medium had been Ner per unit volume. Any appreciable electronic polarization induced by the ionic displacements r, would have lowered correspondingly the reststrahlen frequency below its observed value.

In other words the mutual interactions between the displacement dipoles $e\,r$ correspond to a polarization field factor $p=4\pi/3$, whereas the interactions between these dipoles and the electronic cloud of the ions correspond to $p\approx 0$. This is due to the following circumstance. The polarization due to the displacement of the electronic cloud with respect to its nucleus cannot be replaced by a point-dipole, except for its effect at large distances. The extent of overlap of the electronic clouds of neighbouring ions is obviously such as to make $p=0$ for interactions involving electronic polarizations.

In view of these findings, one obtains

$$a_2 r^2 = -\tfrac{2}{3}\pi N e^2 r^2 \tag{6}$$

The reststrahlen frequencies of all the alkali halide crystals were calculated in this manner using (1) and (5), and including in (5) explicitly the contribution $a_2 r^2$ from the polarization field to the potential energy. The calculated frequencies were found to agree well with the observed ones.

3. THE FREQUENCIES INVOLVED IN THE DISPERSION FORMULAE OF DRUDE AND LORENTZ

Just as one obtains from the potential energy $W=ar^2$ a certain frequency ω_0 which can be identified with the resonance frequency of the crystal, one can also calculate another characteristic frequency Ω_0 from the expression $W_1 = a_1 r^2$ using a relation analogous to (1). The difference between ω_0 and Ω_0 is that in calculating the former the contribution to the protential energy from the polarization field has been included, whereas in calculating Ω_0 this contribution has not been included. As was shown by us in some later papers (Krishnan and Roy 1952, 1953) Ω_0 also has a physical significance. It is the frequency which the individual dipoles located at the lattice points would have, had they been isolated from one another, as distinguished from the reststrahlen frequency ω_0 which is that of the assemblage of these oscillators. That the resonance frequency ω_0 of the assemblage is different from the frequency Ω_0 of the isolated dipoles is indeed to the expected, and is due to the mutual interactions of the dipoles in the assemblage. It was further shown in the papers referred to that the effect of their mutual interactions on their frequency is equivalent to the effect of the polarization field in the assemblage on the frequency.

This manner of distinguishing between ω_0 and Ω_0 throws new light on the well-known dispersion formulae of Drude and Lorentz. Again, since we are concerned here with illustrating the basic results, it will be convenient to take the simple case when the medium has just one frequency, namely, the reststrahlen frequency ω_0, the corresponding frequency of the isolated oscillators calculated from $W_1=a_1r^2$ being Ω_0. Now the dielectric constant of such a crystal for any applied frequency ω is given by the relation,

$$K_\omega = 1 + 4\pi x, \tag{7}$$

where x is the polarization that would be induced in unit volume, per unit field in the medium' as usually defined. If γ is the moment induced in an isolated oscillator per unit field incident on it, then obviously

$$\gamma = \frac{e^2}{\mu(\Omega_0^2-\omega^2)}. \tag{8}$$

There are N such oscillators in the medium but x will not be merely N times γ, but may differ from it considerably, owing to the mutual interactions of these oscillators.

The effect of these interactions on x, and hence also on $K\omega$, can be taken into account in two alternative, but equivalent, ways.

1. The actual field producing the polarization in each of the oscillators in the medium, still regarded as retaining its natural frequency Ω_0, is not the field in the medium, say E, but will be greater by $\frac{4}{3}\pi xE$, so that

$$x=N\gamma\ (1+\tfrac{4}{3}\pi x)=N\gamma\ (K_\omega + 2)/3. \tag{9}$$

The expression for K_ω then takes the well-known Lorentz form

$$\frac{K_\omega-1}{K_\omega+2} = \tfrac{4}{3}\pi N \frac{e^2}{\mu(\Omega_0^2-\omega^2)}.$$

2. The alternative way in which the mutual interactions between the dipoles can be regarded as influencing the dielectric constant, is through their effect on the frequency of the oscillators, their frequency ω_0 in the assemblage being different from that in the isolated state, namely Ω_0. The field that produces the polarization in the oscillator is now just the field in the medium E.

In this cae $$\varkappa = \frac{Ne^2}{\mu(\omega_0^2 - \omega^2)} \tag{11}$$

and hence $$K_\omega - 1 = 4\pi N \frac{e^2}{\mu(\omega_0^2 - \omega^2)}. \tag{12}$$

The two expressions (10) and (12) will become idential when

$$\Omega_0^2 - \omega^2 = \frac{K_\omega + 2}{3}(\omega_0^2 - \omega^2), \tag{13}$$

From (12) one can readily obtain

$$\frac{K_0 - 1}{K_\omega - 1} = \frac{\omega_0^2 - \omega^2}{\omega^2} \tag{14}$$

Eliminating ω between (13) and (14) one can see that the criterion for securing the identity of (10) and (12), namely (13), reduces to

$$\Omega_0^2 = \frac{K_0 + 2}{3}\omega_0^2. \tag{15}$$

It can be readily seen that the values of Ω_0^2 and ω_0^2 obtained from a_1 and a respectively would lead to precisely this relation, since

$$a_1 = \tfrac{1}{2}\mu\,\Omega_0^2 = a + \tfrac{2}{3}\pi N e^2 = \tfrac{1}{2}\mu\omega_0^2\,\left(1 + \frac{K_0 - 1}{3}\right). \tag{16}$$

Thus one can readily see that by including in the expression for the potential energy W the contribution from the polarization field, one obtains the reststrahlen frequency ω_0 of the medium, *i.e.* of the assemblage of oscillators, whereas without it one gets the frequency Ω_0 which the same oscillators would have, had they been isolated from one another.

4. THE NATURE OF THE POLARIZATION FIELD

We now return to the question posed in an earlier section. If the polarization of the medium arises from the relative separation of the lattices of positive and negative ions, and if in obtaining the potential energy from which the reststrahlen frequency is to be calculated the contribution to it from all the positive and the negative ions, in their displaced positions, has been taken into account, is not the effect of the polarization field also included in it automatically? The answer is supplied indirectly by the results obtained in the previous section, and it is quite definite, namely, that the polarization field has to be taken into account separately, since the frequency that we are trying to calculate is the resonance frequency ω_0 of the crystal, and not Ω_0 of the corresponding isolated oscillators.

One can also approach the question from certain direct considerations regarding the mechanism of the polarization field. Consider a medium of induced point-dipoles arranged in a simple cubic lattice. Consider one of these lattice points, say O. Now the field in the medium E as usually defined, is that at O when it is made the centre of a very thin long cylindrical cavity scooped out of the medium with its axis along the direction of the polarization. Hence E will consist of the applied field, if any, and the field due to the charges developed on the surface of the medium as a consequence of the polarization of the medium. The surface charges, and hence the field at O due to them, will obviously be determined by *all* the dipoles in the medium, *including that at O also.* On the other hand, the inner field E_i, again as usually defined, will be the field at O when the dipole at O is removed without disturbing the surrounding dipoles. Obviously the difference between E and E_i is this : whereas the former includes a certain averaged self-field at O due to the dipole at O, the latter does not include it. Since this self-field is negative, E will be smaller than E_i. The excess of E over E is by definition the polarization field. For a cubic distribution of point-dipoles, as Lorentz has shown,

$$E_i = E + \tfrac{4}{3}\pi \varkappa E, \tag{17}$$

where $\varkappa E$ is the total polarization per unit volume.

Now one can readily appreciate the equivalence of the two alternative ways described earlier in this paper, of taking into account the effect of the mutual interaction of the dipoles. Consider one of the dipoles say the one at O. It may be regarded as having the frequency Ω_0 and placed in the cavity, created by removing the dipole at O, and thus subject to a field E_i, or alternatively as being an intergral part of the medium with its frequency the same as that of the medium, namely ω_0, the field that determines its polarization being now the field in the medium E. The difference between E_i and E, as we have seen, is $\frac{4}{3}\pi$ times the polarization per unit volume, *i. e.* $\frac{4}{3}\pi \mathcal{N} e r$.

One thus obtains the relations

$$\left.\begin{aligned} 2a_1 r &= \mu \Omega_0^2 r = E_i e \\ 2ar &= \mu\omega_0^2 r = Ee \end{aligned}\right\} \tag{18}$$

from which one further obtains

$$a - a_1 = a_2 = \tfrac{1}{2}(E - E_i)\, e/r = -\tfrac{2}{3}\pi \mathcal{N} e^2, \tag{19}$$

which is just equation (6).

The relations will again be consistent with the expression for the potential energy per unit volume of the crystal due to the relative separation of the lattices of positive and negative ions, namely,

$$\mathcal{N}W = \mathcal{N}ar^2 = \tfrac{1}{2}\mathcal{N}\mu\omega_0^2 r^2 = (K_0 - 1) E^2/(8\pi), \tag{20}$$

from which one obtains

$$K_0 - 1 = \frac{4\pi \mathcal{N} e^2}{\mu\omega_0^2}, \tag{21}$$

which is just relation (12) in the relevant special case when $\omega = 0$.

5. SOME GENERAL CONSIDERATIONS

Returning to the calculation of the potential energy W, one may re-examine here the contributions from the electrostatic and the repulsion interactions. The repulsion interactions are confined practically to the nearest neighbours, and there is no ambiguity in culculating them. On the other hand, the electrostatic interactions are long-range ones, and in calculating for example the interactions between any two distant ions we have taken the force between them to be given by $\pm e^2/R^2$, as though they were *in vacuo*, and we have ignored the presence of the intervening ions. For very distant ions one may take the intervening medium as having the appropriate dielectric constant K so that the force between them is now $\pm e^2/(KR^2)$. But for the nearer ions the effective value of the dielectric constant to be used in this expression will be difficult to estimate. In any case the usual calculation of the interactions in which the presence of the intervening ions is ignored, which is equivalent to putting $K=1$, is obviously not justifiable. It may appear at first sight that by taking the influence of the intervening ions into account in calculating the electrostatic interactions it may not be necessary to take account explicitly the effect of the polarization field.

This conclusion also would not be justified. It is sufficient to mention in this connection that the actual contribution from the electrostatic interactions to the r^2 term in the expression for W is nothing, and even if the appropriate dielectric constants were to be taken into account in calculating the electrostatic forces their contribution to the r^2 term would still be zero because of the cubic symmetry of the lattice, though the contribution to the r^4 term will be affected.

Thus we are forced to the same conclusion as previously, namely, that in calculating the potential energy W, and thence the reststrahlen frequency ω_0, the contribution to W from the polarization field has to be explicitly taken into account. Otherwise the frequency that one obtains would be that of the isolated oscillators, namely Ω_0, whereas the reststrahlen frequency is the resonance frequency ω_0 of the assemblage of these oscillators, which owing to the mutual interaction of these oscillators, may be markedly different from the frequency Ω_0 of the isolated oscillators.

6. THE OVERLAP OF THE ELECTRONIC CLOUDS OF ADJACENT IONS

In the foregoing discussions we have taken the charges on the ions to be $\pm e$, where e is the electronic charge. This will be the case rigorously if the neighbouring ions did not influence each other, *i.e.*, if the electronic clouds of adjacent ions did not overlap appreciably. But actually the overlap will be considerable. The major effect of the overlap from the point of view adopted by us comes to this. As a result of the separation of the positive and the negative lattices there is polarization of the crystal. This polarization might induce the electronic polarization of the ions, *i.e.* produce a shift of the electronic cloud of an ion relatively to the nucleus of the ion. The effect of the overlap is to make the electronic polarization induced by the relative displacement of the two lattices negligible; while the charges on the ions retain the magnitude of the electronic charge. This method of taking the overlap into account is simple, and fits well, as we have seen, with observation.

On the other hand one may, alternatively, assume the polarization fields, associated not only with the ionic displacement, but also with the shift of the electrons with respect to their nuclei, to have the Lorentz value, and the effective

charges to be correspondingly smaller than $|e|$ in magnitude. There are some major difficulties in accepting this view. Apart from the difficulty of determining theoretically the magnitude of the overlap, and thence the effective charges on the ions, the polarization field associated with the electronic polarization is known from other phenomena to deviate considerably from the Lorentz field. For exmple, considering the temperature variation of refractivity, which is practically the variation due the change in density accompanying the change in temperature— it is found that the terms involving the electronic frequencies behave very differently from the term involving the reststrahlen frequency.

From a detailed analysis of the experimental data for the dispersion, and for its temperature variation, in the alkali halides, Ramachandran (1947) found that in the expression for $dK\omega/dt$ the term involving the reststrahlen frequency ω_0 is proportional to $1/(\omega_0^2-\omega^2)$, whereas the terms involving the ultraviolet frequencies ω_i are proportional to $1/(\omega_i^2-\omega^2)^2$, which points to a marked difference in the behaviour of the two sets of frequencies. The difference can be attributed to the reststrahlen oscillators being practically point-dipoles, whereas the electronic oscillators are not. The result will be that the polarization field corresponding to the mutual interactions of the reststrahlen oscillators will have just the Lorentz value, as we have seen, whereas the interactions between the reststrahlen oscillators and the electronic oscillators, or between the electronic oscillators themselve, would be much smaller. Actually the experimental finding quoted above, obtained from the temperature variation of the dispersion, points to the interactions involving the electronic oscillators being negligible. This was precisely also the conclusion to which we were led from the magnitude of the contribution to W from the polarization field, *i.e.*, the magnitude of a_1 required to explain the observed reststrahlen frequency.

Indeed all the observational data receive a natural and quantitative explanation on the basis of the approximation that the effective charges on the ions are just $\pm e$ and that the whole affect of the overlap of the electronic clouds of the neighbouring ions is to suppress completely the interactions between the reststrahlen oscillators and the electronic ones, and also those among the electronic oscillators themselves. On the other hand, the mutual interactions between the reststrahlen oscillators among themselves are considerable, and correspond to a polarization field having just the Lorentz value.

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