

*The Polarization Fields and the Resonance Frequencies of the
Alkali Halide Crystals*

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[Received August 7, 1952]

ABSTRACT

The effect of the polarization field on the dielectric constant of a medium can be taken into account in two alternative ways, which are equivalent. It may be regarded as enhancing the actual field that produces the polarization, or as determining the resonance frequencies of the medium, which will be different from the frequencies of the individual oscillators that constitute the medium. The dispersions of the alkali halides are discussed from the latter point of view. Though the polarization factors defining the interactions between the infra-red oscillators have the Lorentz value $4\pi/3$, those defining the interactions of the *electronic* oscillators are found to be zero. The electronic overlap between the neighbouring ions in their equilibrium positions seems to be just the one that corresponds to negligible interactions between the electronic oscillators.

§1. INTRODUCTION

THE part played by the polarization field in dielectric phenomena has been discussed in detail by Lorentz (1908), and following him by several authors. (For a good account of the subject see Debye 1928, Fröhlich 1949, or Rosenfeld 1951.) An obvious method of considering the influence of the polarization field on the dielectric constant is to regard the effective field that produces the polarization as including the polarization field in addition to 'the field in the medium', to which the polarization field will naturally be proportional. The result will be an enhanced susceptibility and a correspondingly enhanced dielectric constant. This method of calculating the effect of the polarization field is the one usually adopted.

The polarization field is also known (Krishnan and Roy 1951) to play an important part in determining the observed resonance frequencies of the medium. Hence its effect on the dielectric constant may also be regarded as exercised indirectly through its influence on the resonance frequencies. The dispersion of the dielectric constant of the alkali halide crystals is discussed in the present paper from the latter point of view. The alkali halides are particularly suitable for this purpose.

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The point of view adopted here throws also some light on the relation between the different types of dispersion formulae, and in particular on the relation between the characteristic frequencies that appear in these formulae.

§ 2. THE EFFECT OF THE POLARIZATION FIELD ON THE PRINCIPAL LATTICE OSCILLATION OF AN ALKALI HALIDE CRYSTAL

In a recent paper (Krishnan and Roy 1951) the frequency of the principal mode of oscillation of an alkali halide crystal, in which the lattice of the alkali ions oscillates with respect to the lattice of the halide ions, was calculated on the basis of the simple Born model. It was found that the electric polarization of the crystal due to the separation of the charges accompanying the oscillation, plays an important part in determining the frequency. Separating the two lattices by a small distance r one can obviously express the potential energy of the crystal thus deformed as a power series in r , in which owing to the centre of symmetry of the lattice points of the undeformed crystal, terms involving odd powers of r will naturally be absent. We shall confine attention at present to the r^2 term, which is the first non-vanishing, and also the predominant, term involving r , and which determines the frequency. We shall denote this term in the potential energy per pair of ions by

$$W = ar^2 = \frac{1}{2}\mu\omega_i^2 r^2, \quad \dots \dots \dots (1)$$

where μ is the reduced mass of the pair given by $1/\mu = 1/m_1 + 1/m_2$ and m_1 and m_2 are the masses of the two ions, and ω_i is the angular frequency of the principal mode of oscillation.

The essential part of the problem is to evaluate the contributions to a from the different types of interactions. This has been done in the paper referred to, and we shall merely quote here the relevant results. It will be seen immediately, in view of the centre of symmetry of all the lattice points, that the electrostatic interactions contribute nothing to a . As regards the repulsion interactions, they may be taken to be of the form $Ae^{-R/\rho}$, where R is the distance between the interacting ions, and they are of short range, since ρ is found to be much shorter than the equilibrium distance d between the neighbouring ions. Hence these interactions may be regarded as confined to the immediate neighbours only. Their contribution to a is found to be equal to

$$\frac{3}{2N\beta d^2} = \frac{\alpha e^2(\delta - 2)}{6d^3} = a_1 \text{ say, } \dots \dots \dots (2)$$

where N is the number of ion-pairs per unit volume, β is the compressibility of the crystal, α is the Madelung constant, d is the equilibrium distance between neighbouring ions, $\delta = d/\rho$ and e is the electronic charge. The interactions of the van der Waals type involving the dipole moments induced in the ions contribute relatively little to a , and they are neglected throughout.

Had a_1 been the whole of the contribution to a , the frequency of the principal lattice oscillation of the crystal would be given by

$$a_1 = \frac{1}{2} \mu \Omega_i^2. \quad (3)$$

But actually the contribution to a from the polarization field is considerable. For a given relative displacement r between the two lattices the polarization per unit volume is given by

$$P = Ner. \quad (4)$$

In the paper referred to it was shown (1) that owing to the electronic overlap between the neighbouring ions, this polarization does not induce any *electronic* polarization in the ions, and (2) that the polarization field acting on an ion and tending to displace it as a whole, has just the Lorentz value, namely $(4\pi/3)P$, and hence (3) that the corresponding contribution to a is given by

$$a_2 = -\frac{2}{3} \pi Ne^2. \quad (5)$$

This term is negative since the polarization field is in a direction that tends to *increase* the relative displacement r between the two lattices.

In NaCl, for example, a_2 is found to be numerically nearly half of a_1 and since they are of opposite signs, a_2 is of almost the same magnitude as a , the net coefficient of the r^2 term, namely

$$a = a_1 + a_2. \quad (6)$$

For most of the alkali halide crystals the frequency ω_i calculated in this manner by taking the polarization field into account, agrees well with the observed reststrahlen frequency (Krishnan and Roy 1951).

§3. THE MAGNITUDE OF THE POLARIZATION FIELD

As is well known the internal field F in a dielectric may differ considerably from the field E in the medium, the difference between them being the polarization field

$$F = E + p\chi E, \quad (7)$$

in which χ is the susceptibility of the medium, i.e., the polarization per unit volume per unit field in the medium, and p is the polarization factor, which is rather difficult to evaluate except under certain simple conditions. When the elementary dipoles in the medium, which together make up the polarization of the medium, are *point*-dipoles, and when they are arranged in a cubic lattice, or are distributed at random, p , as Lorentz has shown, will be equal to $4\pi/3$ (see also Van Vleck 1937).

But actually, as was shown in the paper referred to, the dipoles concerned in refraction phenomena, for which Lorentz's theory was originally intended to apply, are by no means point-dipoles; they are due primarily to the displacement of the electrons in an atom with respect to its positively charged nucleus, and the separation of charges will be of atomic dimensions, and comparable with the distances between neighbouring dipoles. Thus the Lorentz polarization factor $p = 4\pi/3$ may fail

just where it was originally intended to apply, namely to electronic polarization as is involved in refraction phenomena in the visible and in the ultra-violet regions of the spectrum. But the polarization produced in ionic crystals like the alkali halides by a small relative displacement of the two lattices, with which we are concerned here, is in a different category altogether, since we can now regard the polarization as due to dipoles of small dimensions of the order of r located at the lattice points. This can be readily seen from the following considerations. Electrostatically the effect of deforming the original lattice, which we shall designate by A , into B will be equivalent to superposing on A the following two lattices: the lattice A' obtained from A by changing the signs of all the ions in it, and the lattice B . The superposition of A' and B will be equivalent to locating a small dipole of moment er at each of the positive, or each of the negative lattice points, which again will be equivalent to locating a dipole $er/2$ at every lattice point, whether positive or negative. Since r can be made as small as we desire, these dipoles will be practically point-dipoles, and the corresponding polarization factor p will therefore be expected to approximate closely to the Lorentz value $4\pi/3$, and this is just the value which we have used in the calculation of ω_i and which, as we mentioned, is confirmed experimentally.

§4. THE RESONANCE FREQUENCY OF AN ASSEMBLAGE OF HARMONIC OSCILLATORS

Coming back to the calculation of the energy ar^2 per pair of ions from which the resonance frequency ω_i of the crystal is evaluated using relation (1), it may appear at first sight that when the electrostatic interactions between all the ions of the positive and the negative lattices displaced relatively to each other by r are taken into account, the effect of the polarization field also, which is a direct result of this displacement, gets included in it automatically, and it should not therefore be necessary to invoke separately the effect of the polarization field. But actually the necessity arises from the following circumstance. It was shown just now that separating the two lattices by a small distance r is equivalent to developing small dipoles at the lattice points. The oscillating crystal will be equivalent to harmonic oscillators, all of the same moment, located one at each of the lattice points of the crystal. The frequency Ω_i which we would have obtained from a_1 with the help of relation (3), i.e. the frequency which we would have obtained by ignoring the polarization field, would be the frequency of these *individual* oscillators, whereas the frequency ω_i that we are trying to calculate is the resonance frequency of the assemblage of these oscillators, which will be different from Ω_i , and the difference is determined by the polarization field. (That Ω_i is itself dependent on the density of the medium does not affect the argument.)

Anticipating the results concerning the energies associated with the polarization of the medium to be given in § 6, we may mention immediately that

$$Nar^2 = \frac{1}{2}N\mu\omega_i^2r^2 = \frac{1}{2}PE,$$

where E is the field in the medium, whereas the energy that is obtained from the Coulomb and the repulsion interactions is equal to $PF/2$, where F is the internal field, which includes in addition to E the polarization field pP . Hence one has to subtract from Na_1r^2 the work done by the polarization field, namely $pP^2/2$ ($=2\pi P^2/3$ in the case of the alkali halides), before it can be equated to $\frac{1}{2}N\mu\omega_i^2r^2$.

§5. THE DIELECTRIC CONSTANT OF THE CRYSTAL AND THE DRUDE AND THE LORENTZ FORMULAE

Let us for the present ignore the electronic polarization, i.e. the polarization due to the displacements of the electrons in the ions with reference to their respective nuclei, and regard the medium as consisting of ions that can only be bodily displaced. For any given relative displacement r of the positive and the negative lattices the polarization per unit volume will be given by (4), namely $P=Ne r$. This polarization may also be regarded as produced by a field E in the medium, such that

$$Ee=2ar=\mu\omega_i^2r. \quad \dots \dots \dots (8)$$

The corresponding internal field F will be given by

$$Fe=Ee+\frac{4\pi}{3}Ne^2r=2a_1r=\mu\Omega_i^2r, \quad \dots \dots \dots (9)$$

where, as we have seen, Ω_i is the frequency which we would have obtained for the principal oscillation of the crystal if we had neglected the effect of the polarization field, as distinguished from the actual resonance frequency ω_i .

It will be seen from (8) that the susceptibility χ_0 of the medium for static electric fields will be given by

$$\epsilon_0-1=4\pi\chi_0=\frac{C_i}{\omega_i^2}, \quad \dots \dots \dots (10)$$

where

$$C_i=\frac{4\pi Ne^2}{\mu} \quad \dots \dots \dots (11)$$

and ϵ_0 is the corresponding dielectric constant. Equation (10) can be readily identified with the well-known expression of Born's (see *Handbuch der Physik*). The two frequencies Ω_i and ω_i are connected by the relation

$$\Omega_i^2=\omega_i^2+\frac{C_i}{3}, \quad \dots \dots \dots (12)$$

or

$$\Omega_i^2=\omega_i^2\frac{\epsilon_0+2}{3}. \quad \dots \dots \dots (13)$$

Similarly

$$\left. \begin{aligned} a_1 &= \bar{a} \frac{\epsilon_0+2}{3}, \\ a_2 &= -a \frac{\epsilon_0-1}{3}. \end{aligned} \right\} \dots \dots \dots (14)$$

Hence eqn. (10) can also be written in the form

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} = \frac{C_i/3}{\Omega_i^2} \dots \dots \dots (15)$$

Similarly the dielectric constant at any frequency ω can be expressed either in the form

$$\epsilon_\omega - 1 = \frac{C_i}{\omega_i^2 - \omega^2} \dots \dots \dots (16)$$

or, in view of (12), in the form

$$\frac{\epsilon_\omega - 1}{\epsilon_\omega + 2} = \frac{C_i/3}{\Omega_i^2 - \omega^2}, \dots \dots \dots (17)$$

which are indeed identical relations (Livens, 1912).

Just as the equivalence of (10) and (15) is based on relation (13), the equivalence of (16) and (17) corresponds to a relation which is analogous to (13), and which is a corollary to it, when we are concerned, as we are now, with only one frequency that influences the polarization, the relation being

$$\Omega_i^2 - \omega^2 = (\omega_i^2 - \omega^2) \frac{\epsilon_\omega + 2}{3} \dots \dots \dots (18)$$

It can be readily seen that (16) and (17) reduce to (10) and (15) respectively when $\omega \rightarrow 0$.

In (16) resonance occurs obviously when $\omega = \omega_i$ and in (17) when the right hand side tends to unity, i.e. when $\Omega_i^2 - \omega^2 = C_i/3$ which in view of (12) corresponds again to $\omega = \omega_i$ as it should.

One may thus take into account the effect of the polarization field on the dielectric constant explicitly by taking the field that is effective in producing the polarization as $(1 + 4\pi\chi_\omega/3)$ times E or $(\epsilon_\omega + 2)E/3$ where E is the field in the medium, in which case the formula obtained is of the Lorentz type, and the characteristic frequency appearing in the expression is the frequency Ω_i ; or *alternatively*, one may regard the effect of the polarization field as confined to changing Ω_i to the actual resonance frequency of the crystal ω_i such that the relation (18) is satisfied, in which case the formula is of the Drude type.

§6. THE ELECTRIC FIELDS ASSOCIATED WITH THE SEPARATION OF THE LATTICES

(Now the potential energy Nar^2 per unit volume, due to separating the two lattices by a small distance r can also be regarded as due to the incidence of a 'field E in the medium' such that eqn. (8) is satisfied, or such that

$$\begin{aligned} Nar^2 &= \frac{E^2}{8\pi} (\epsilon_0 - 1) \\ &= \frac{1}{2} EP. \dots \dots \dots (19) \end{aligned}$$

Similarly

$$Na_1 r^2 = \frac{1}{2} FP, \dots \dots \dots (20)$$

and the energy per unit volume associated with the occurrence of the polarization field will be given by

$$Na_2r^2 = -\frac{1}{2}pP^2, \dots \dots \dots (21)$$

where pP is the polarization field. In the alkali halides, as we have seen, $p=4\pi/3$.

As is well known, the field in the medium E at any given lattice point O includes not only the field due to all the surrounding dipoles, but also a certain averaged field at O due to the dipole at O also, i.e., the averaged self-field of the dipole at O also, whereas the inner field F does not include the latter (Fröhlich 1949). Though we refer to the latter field for convenience as the self-field, it depends very much on the polarization of the surroundings, which will be realized immediately when we remember that the self-field will be just compensated by the field that would obtain at the point O in the cavity produced by removing from the medium the doublet located at O .

Now the effect at O of all the dipoles including the one at O will be equivalent to the field at O due to the charges developed on the surface of the medium due to polarizing it. Hence the averaged self-field of the doublet at O will be just the difference between the field at O due to the charges developed on the surface of the medium as a result of polarizing it, and the field at the same point due to all the surrounding dipoles in the medium. Since the difference between F and E is the polarization field, the latter field can be regarded as equal to the averaged self-field, but of opposite sign to it.

Now the self-field of a dipole should depend only on the fine structure of the medium, and in particular should be independent of the external shape. One may, therefore, use any convenient shape like a sphere or an infinite parallel plate, and show that the self-field is equal to

$$-\left(\frac{4\pi}{3} + f\right)P = -pP, \dots \dots \dots (22)$$

where fP is the field at O due to all the surrounding doublets in an infinite medium. In the case of the alkali halides f will obviously be zero.

§7. THE DISPERSION FORMULAE FOR A DENSE MEDIUM

We have specifically discussed till now the case when the only frequency affecting the dielectric constant is that of the principal lattice oscillation of the crystal. One good reason for confining ourselves to this case is that the polarization factor involved here is very definite, and is known to be equal to $4\pi/3$. But the main results obtained are applicable equally well to the case when the medium has more than one resonance frequency, and when some or all of these are electronic frequencies, instead of lattice frequencies. Let us denote these frequencies and the physical constants associated with them by the subscripts $i, j, k, \dots n$. The polarization factor p_{ij} defining the polarization field acting on any oscillator i due

to the dipole moments of all the oscillators j in the medium will not in general be equal to $4\pi/3$ but will depend on both i and j . The dielectric constant of the medium will then be given by

$$\epsilon - 1 = 4\pi\chi = 4\pi \sum_i \chi_i, \dots \dots \dots (23)$$

where χ_i is the contribution to the susceptibility, i.e. to the polarization per unit volume per unit field in the medium, from the oscillators of type i .

$$4\pi\chi_i = \frac{C_i}{\Omega_i^2 - \omega^2} (1 + \sum_j p_{ij}\chi_{ij}), \dots \dots \dots (24)$$

in which the summation extends over all values of j namely $i, j, \dots n$.

$$C_i = \frac{4\pi n_i f_i e^2}{\mu_i}, \dots \dots \dots (25)$$

where n_i is the number of oscillators of type i present per unit volume of the medium, f_i is the oscillator strength, and μ_i is the effective mass of the oscillator. Ω_i is the frequency of the oscillator in the free state, to be more precise, the frequency which it will have if the influence of the interactions of the surrounding dipoles is eliminated.

In the special case when all the p_{ij} 's have the same value, say p , eqns. (23) and (24) reduce to

$$\frac{\epsilon - 1}{\epsilon + \alpha} = \sum_i \frac{B_i}{\Omega_i^2 - \omega^2}, \dots \dots \dots (26)$$

where

$$B_i = \frac{pC_i}{4\pi}; \alpha = \frac{4\pi}{p} - 1. \dots \dots \dots (27)$$

When further all the polarization factors have just the Lorentz value, namely $p = 4\pi/3$, it will be seen from (27) that α reduces to 2, and eqn. (26) to the well-known Lorentz formula.

Herzfeld and Wolf (1925) have shown that the simple Lorentz formula

$$\frac{\epsilon - 1}{\epsilon + 2} = \sum_i \frac{B_i}{\Omega_i^2 - \omega^2}, \dots \dots \dots (28)$$

is mathematically convertible into the Drude formula

$$\epsilon - 1 = \sum_i \frac{C_i}{\omega_i^2 - \omega^2} \dots \dots \dots (29)$$

and *vice versa*. Using the same method it can be readily shown that the more general formula corresponding to (23) and (24) in which the polarization factors p_{ij} may all be different, can also be reduced to the Drude formula (28) or to the simple Lorentz formula, and conversely the Drude or the simple Lorentz formula can also be transformed to a formula of the type (24), with any specified values of p_{ij} .

It will be seen immediately, whatever may be the actual polarization fields that may obtain in the medium, and even if there is no polarization field at all, that the dispersion data can be fitted, as may be desired, into

a Drude formula, or a simple Lorentz formula, or a generalized Lorentz formula of the type (23) and (24) with any postulated set of polarization factors p_{ij} . The characteristic frequencies that appear in these alternative formulae with which the same set of observational data can be fitted, will naturally be different; those that appear in the Drude formula will be the actual resonance frequencies ω_i of the medium, and in the other formulae the frequencies will differ from ω_i by amounts which are determined by the polarization fields postulated on which the formulae are based. Hence dispersion data by themselves can yield information regarding only the resonance frequencies of the medium and their oscillator strengths, and none at all regarding the polarization field.

It may not be out of place here to emphasise these results. Though the mathematical equivalence of the Drude and the simple Lorentz formulae, which was demonstrated long ago by Herzfeld and Wolf, is generally conceded, the agreement between the characteristic frequencies appearing in these formulae, and the observed absorption frequencies is sometimes invoked in order to decide between the alternative formulae as regards their experimental validity. On considerations of convenience, the Drude dispersion formula, in which the characteristic frequencies that appear are also the observed absorption frequencies, is naturally preferable to any alternative formulae, but the latter formulae too should be regarded as having the same experimental validity as Drude's.

It should be mentioned immediately that the equivalence between the different alternative formulae relates to the formulation of the dielectric constant as a function of the frequency of the incident electromagnetic waves, with which we are concerned here, and *does not extend to the expressions for the dielectric constant as a function of the density of the medium*. Since the polarization field will depend on the density the latter formula will be conditioned by the actual polarization field. Even here, the frequencies Ω_i of the individual oscillators, and the polarization field factors p_{ij} may also be dependent on the degree of close-packing. We shall postpone consideration of these aspects to a later section of the paper.

§8. THE CASE OF THE ALKALI HALIDES

The case of the alkali halides is exceptional, as we have mentioned already. The only infra-red resonance frequency that is involved in the dispersion formula is that of the principal lattice oscillation of the crystal. Making the subscript i refer to this frequency, p_{ii} as we have seen, has just the Lorentz value $4\pi/3$. The other frequencies, denoted by the subscripts j, k, \dots , will all be electronic and the separation of the charges in the corresponding dipoles will be comparable with the distance between the neighbouring ions. Hence the distribution of the field in the neighbourhood of any of the latter dipoles will differ considerably from that of a point-dipole. Indeed, even the order of magnitude of the field may become different when the approach to the dipole is close.

In other words, when there is considerable overlap of the electronic clouds of neighbouring ions, as is the case with the neighbouring ions in the alkali halide crystals, the polarization factors of the type p_{ij} , p_{ik} , . . . will be much less than $p_{ii}=4\pi/3$, and the factors p_{jj} , p_{kk} , . . . may be still smaller.

In the paper referred to, it was shown that in the alkali halides all the p 's except p_{ii} have practically zero values. This circumstance, namely, that only one of the p 's has a finite value, and the rest have zero value renders the case of the alkali halides exceptional.

The expression for the dielectric constant of these halides will, therefore, be of the form

$$\epsilon_\omega - 1 = \frac{C_i}{\omega_i^2 - \omega^2} + \sum_j \frac{C_j}{\omega_j^2 - \omega^2}, \quad \dots \dots \dots (30)$$

where the electronic resonance frequencies ω_j , ω_k , . . . will be practically the same as for the individual (not isolated) atoms, namely, Ω_j , Ω_k , . . . respectively, whereas the lattice frequency ω_i will naturally be very different from Ω_i .

In particular, in the region of very long wavelengths in which the contribution to the dispersion from the electronic frequencies, namely

$$n_\omega^2 - 1 = \sum_j \frac{C_j}{\omega_j^2 - \omega^2}, \quad \dots \dots \dots (31)$$

is practically independent of ω , and is nearly the same as for $\omega=0$, we obtain

$$\epsilon_\omega - n_0^2 = \frac{C_i}{\omega_i^2 - \omega^2}, \quad \dots \dots \dots (32)$$

or alternatively,

$$\frac{\epsilon_\omega - n_0^2}{\epsilon_\omega - n_0^2 + 3} = \frac{C_i/3}{\Omega_i^2 - \omega^2}, \quad \dots \dots \dots (33)$$

the relation between Ω_i and ω_i being given as before (see (12) and (13)) by

$$\Omega_i^2 = \omega_i^2 + \frac{C_i}{3} = \omega_i^2 \left(\frac{\epsilon_0 - n_0^2 + 3}{3} \right). \quad \dots \dots \dots (34)$$

In particular one obtains from (31) for the dielectric constant in a static field, the well-known expression of Born

$$\epsilon_0 = n_0^2 + \frac{C_i}{\omega_i^2}. \quad \dots \dots \dots (35)$$

§ 9. DISCUSSION OF THE AVAILABLE EXPERIMENTAL DATA

The available experimental data for the refractive indices of the alkali halides, which extend over a wide spectral range, have been discussed by Herzfeld and Wolf (1925), by Fuchs and Wolf (1928), and more recently by Ramachandran (1947) and by Radhakrishnan (1948). Attention may be drawn in particular to the following results.

(1) When the data are fitted into a dispersion formula of the Drude type, the characteristic frequencies that appear in the formulae are found to agree well with the observed resonance frequencies. Since the fitting is done empirically, it will be more correct to say that the available experimental data can be fitted satisfactorily into a Drude dispersion formula, using the *observed* resonance frequencies of the crystal as the characteristic ones that should appear in the formula. For details regarding the fitting with the experimental data reference may be made to the original papers. The formula in general, involves three frequencies in the far ultra-violet, and the principal lattice frequency in the infra-red.

(2) Since the only infra-red frequency involved in the formula is that of the principal lattice oscillation of the crystal the corresponding oscillator strength C_i will be that defined by (16), and given by (11). Hence it will be possible to compare the values of C_i calculated from (11) with the numerical values appearing in the empirical formulae given by Ramachandran and Radhakrishnan. They are collected together in table 1 which includes all the crystals for which experimental dispersion formulae are available.

Table 1

Crystal	LiF	NaF	NaCl	KCl	KBr
$C_i \times 10^{-26}$ from (11)	210	68	28	15	10
$C_i \times 10^{-26}$ from dispersion	230	74	33	18	11

(3) Now the measurements on dispersion usually extend at the infra-red end to about 22μ for some of the crystals, and to about 9μ only for most others. Since even at the former limit the contribution to $n^2 - 1$ from the infra-red term in the dispersion formula is very small, the experimental value of C_i appearing in the infra-red terms is slightly uncertain, except where the value of the dielectric constant for either steady fields or for the usual radio frequencies has also been utilized in determining the constants of the dispersion formula. Actually this has been done only for a few crystals, by Radhakrishnan. Hence it will be of interest to compare the calculated and observed values of $k_0 - n_0^2$ in which k_0 is the dielectric constant for static fields, and n_0^2 is the square of the refractive index extrapolated to $\omega \rightarrow 0$. The experimental value of n_0^2 is readily obtained from the dispersion formula by taking the contributions at $\omega = 0$ from all the terms except the infra-red one. The experimental values of $k_0 - n_0^2$ thus calculated are given in table 2 along with the values calculated from (34), in which we have used for the frequency of the principal lattice oscillation of the crystal the values calculated by us in an earlier paper, on the basis of Born's model, from

the known Coulomb and repulsion interactions between the ions (Krishnan and Roy 1951). The value as was shown in the paper agrees well with the observed reststrahlen frequency.

Table 2

Crystals	k_0	n_0^2	$k_0 - n_0^2 = Ne^2/\pi\mu\nu^2$	
			Observed	Calculated
LiF	9.3	1.9	7.4	7.6
NaF	6.0	1.7	4.3	4.5
NaCl	5.6	2.3	3.3	3.2
KCl	4.7	2.2	2.5	2.4
KBr	4.8	2.4	2.4	2.2

§10. DEPENDENCE ON DENSITY

Extensive data are also available for the temperature variation of the refractive index of the alkali halides, and for some of them for the variation of the refractive index with the density also. One may therefore compare the observed values of $(\partial n/\partial t)$ and $-\rho(\partial n/\partial \rho)\alpha$ where α is the coefficient of thermal expansion, in order to find whether the change of refractive index with temperature is due wholly to the change of density accompanying the temperature change, or whether there is in addition a pure temperature effect due to the thermal agitations of the ions. From the values of $\partial n/\partial t$ and of $-\alpha\rho(\partial n/\partial \rho)$ given in table 3 it will be seen that the pure temperature effect, if any, is practically negligible.

Table 3

Crystals	$10^5\alpha$	$\rho(\partial n/\partial \rho)$	$10^5(dn/dt)$	
			Observed	Calculated
NaCl	12.0	0.24	-3.8	-2.9
KCl	11.4	0.23	-3.6	-2.6
KBr	12.0	0.35	-3.6	-4.2
KI	13.5	0.43	-5.0	-5.8

Now the available data for the temperature variation of the refractive index which extend from the extreme quartz ultra-violet to the infra-red

in most crystals, have been analysed by Ramachandran and by Radhakrishnan. They find that the temperature variation can be expressed empirically in the form*

$$2n \frac{dn}{dt} = -\alpha(n^2 - 1) + \sum \frac{2C_j \psi_j}{(\omega_j^2 - \omega^2)^2} + \frac{2C_i \psi_i}{(\omega_i^2 - \omega^2)^2} + \frac{D}{\omega_i^2 - \omega^2}, \quad (36)$$

where

$$\psi_j = -\omega_j \frac{\partial \omega_j}{\partial t} \dots \dots \dots (37)$$

The first term on the right hand side of (36) is due directly to the change in density, since the expression for $n^2 - 1$ will contain a factor proportional to ρ , and this term accounts for the bulk of the temperature variation. Attention may be drawn here to the extra term involving the infra-red frequency and proportional to $1/(\omega_i^2 - \omega^2)$.

We have referred to the experimental finding that in the alkali halides all the polarization factors are zero except p_{ii} , which is equal to $4\pi/3$. Any change of density is not likely to affect p_{ii} . If the other factors also remain unchanged, i.e. continue to be zero, it will be difficult to explain either the change in the ω_j 's suggested by the analysis of the experimental data, or the extra infra-red term proportional to $1/(\omega_i^2 - \omega^2)$ which corresponds to a change of the oscillator strength with temperature. The obvious inference is that though all the p 's except p_{ii} are quite small, their variations with density, and therefore also with temperature, are considerable. Further the form of the empirical formula suggests that coefficients of the type $(\partial p_{jj}/\partial t)$, $(\partial p_{kk}/\partial t) \dots$ relating to the interactions of the electronic oscillators of the same frequency, and terms like $\partial p_{ij}/\partial t$ which define the interaction of the infra-red frequency with the other frequencies, are the predominant ones. These differential coefficients can be calculated from the experimental data. We shall merely mention that $\partial p/\partial t$ is of the order of 10^{-4} .

§11. FURTHER REMARKS ON THE ELECTRONIC OVERLAP OF THE NEIGHBOURING IONS

In the previous sections the effect of the electronic overlap between the neighbouring ions has been regarded as affecting the polarization field, and rendering it almost nothing when the ions are at their equilibrium positions. Alternatively, the effect of the overlap can also be regarded as reducing the effective charge on an ion from e to fe where f is a factor which is determined by the degree of overlap, and is less than unity, while the polarization field is allowed to have the Lorentz value (Fröhlich 1949). The former point of view, in which the overlap is regarded as reducing the polarization field to nothing, has certain advantages over the alternative point of view, and has therefore been adopted here.

* Actually these authors use wave-lengths instead of frequencies, but the latter are used here for convenience.

That in all the alkali halides the electronic polarization field is found to be practically zero when the ions are at their equilibrium positions may be theoretically significant. According to the simple Born model on which the foregoing discussions are based, the ions in the lattice are held in their equilibrium positions by the Coulomb electrostatic interactions between the charges carried by the ions, and the repulsion interactions between the neighbouring ions. When the ions have taken their equilibrium positions under the corresponding attractive and repulsive forces respectively, there will be a certain optimum overlap between the neighbouring ions, and this overlap is apparently also the one that corresponds to zero polarization field. This view receives strong support from the observation referred to in the previous section, namely this: though the polarization field is zero for the equilibrium positions of the ions, it varies rapidly about this value with change of density.

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Thermionic constants of metals and semiconductors III. Monovalent metals

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(Received 22 December 1952)

In this part are described measurements on the thermionic constants of the monovalent metals copper, silver and gold, made by the effusion method. Owing to the low melting-points of these metals, and the consequent low vapour pressure of the electron gas in thermal equilibrium with them, the effusion holes used had to be much larger than in the measurements with the other metals. The maximum size of the effusion hole that can be used with an electron gas chamber of given dimensions without disturbing appreciably the equilibrium condition in the chamber, and the effect of the large size of the effusion hole on the saturation current, are discussed in some detail.

For all the three metals, the A coefficient in Richardson's equation for thermionic emission is found to be only slightly short of the theoretical value of $120 \text{ amp cm}^{-2} \text{ deg}^{-2}$. This experimental finding is of significance, since the lowering of the thermodynamic potential of the degenerate electron assemblage in these metals, consequent on the thermal expansion of the metal, is considerable.

1. INTRODUCTION

In the earlier parts of this work (Jain & Krishnan 1952*a, b*) was described a new method for determining the thermionic constants of metals, which is based on measuring the rate of effusion of electrons through a small hole, from a chamber of electron gas in thermal equilibrium with the metal. The chamber is made from a thin-walled tube of graphite, and its inner walls (and the region adjoining the effusion hole) are coated completely with the metal to be studied. The chamber can be heated to any desired high temperature *in vacuo* by sending a suitable heavy electric current through the tube. In this part are described measurements on the monovalent metals copper, silver and gold, made by the same method. Since the conduction electrons in these metals are highly degenerate at all working temperatures, and they approximate closely to the model of a free-electron gas, the thermionic constants of these metals, and in particular the A coefficients in the Richardson equation for thermionic emission, are of special theoretical interest.

All the metals whose thermionic constants were determined earlier by this method were studied at high temperatures, up to about 1600°K , and this was possible because of their high melting-points. The metals studied in this part, however, have much lower melting-points, and since their thermionic constants are of the same order of magnitude as in the former metals, they have much lower electronic vapour pressures in the range of temperatures over which they can be studied. This necessitates certain modifications in the experimental technique, and these modifications raise questions regarding the maximum size of the effusion hole that can be used with a chamber of given dimensions without disturbing appreciably the equilibrium in the chamber, and also regarding the effect of a large effusion hole on

the magnitude of the saturation current. These questions also are discussed in this part.

It may be mentioned here that the usual diode method is particularly unsuitable for determining the thermionic constants of metals having low melting-points. Their surfaces have to be degassed by repeated heating before the thermionic emissions from them settle down to their proper values, and the heat treatment for degassing becomes efficient only at very high temperatures. On the other hand, the present method, as we have shown in parts I and II, is quite insensitive to surface adsorption.

It may be mentioned here that the actual vapour pressure of the electrons in the chamber is very small; and the effusion is into vacuum where the pressure of the residual gas also is very small. The mean free paths in both are much larger than the over-all dimensions of the apparatus. Hence the equilibrium in the electron gas chamber is maintained through collisions with the inner walls of the chamber, in much the same manner in which the density of electromagnetic radiations inside a hot chamber is maintained.

2. MODIFICATIONS REQUIRED IN THE EXPERIMENTAL TECHNIQUE

In the measurements reported in parts I and II, the chamber containing the electron gas was a cylinder of internal diameter 11.6 mm and of length about 30 mm. The effusion hole was circular and had a diameter of about 2.4 mm. A metal plate having a circular aperture of about 20 mm diameter, and placed at a distance of about 20 mm from the effusion hole, and coaxial with it, served to restrict the solid angle of effusion electrons reaching the Faraday cylinder to about $\frac{1}{2}\pi$ about the axis of the effusion hole. The metal plate bearing the diaphragm was kept in electrical contact with the graphite tube, so as to keep the region between the effusion hole and the metal diaphragm field-free. The dimensions given above varied slightly in the different measurements, but they serve to give an idea of the order of magnitude of these quantities in the previous experimental arrangement.

By applying a difference of potential between the Faraday cylinder and the diaphragm, the effusion electrons are collected in the cylinder. As was mentioned in part I, the current through the Faraday cylinder increases at first rapidly, and then slowly and linearly, with the increase of the applied voltage. It is therefore possible to extrapolate backwards from the linear portion, and obtain with accuracy the saturation current corresponding to effusion under zero applied potential.

For the monovalent metals studied here, whose work functions are in the range of 4.3 to 4.5 eV, and whose A coefficients have nearly the theoretical value of $120 \text{ amp cm}^{-2} \text{ deg}^{-2}$, the lowest temperature at which the saturation current corresponding to effusion can be measured with some precision with the dimensions given above for the effusion hole and for the solid angle of collection, is about 1350° K . Now, the melting-points of the monovalent metals studied in the present part are of this magnitude, and in order to be able to measure the saturation currents with accuracy it therefore becomes necessary to enlarge considerably either the solid angle of collection, or the size of the effusion hole. Enlarging the solid angle does not help much, but on the other hand introduces uncertainties regarding the

penetration of the applied field into the region behind the metal diaphragm, and consequently also uncertainties in the effective solid angle of effusion of the electrons collected by the Faraday cylinder. One has therefore to depend on enlarging the effusion hole, and this necessitates a corresponding enlargement of the size of the chamber containing the saturated electron gas from which effusion takes place.

We may mention immediately the dimensions of the apparatus finally adopted in the present measurements, with which the currents through the Faraday cylinder could be measured accurately in the range of temperatures studied. The cylindrical chamber had an internal diameter of 46 mm and a length of 100 mm, and the effusion hole was a circle of diameter 16 mm. These dimensions correspond to a total area W of the inner walls of the chamber about 87 times the area s of the effusion hole. Though the temperature range over which the present measurements extend is lower than in the measurements on the other metals, owing to the enlarged dimensions of the chamber, the electric current needed for heating was much heavier, namely 400 to 450 amp, as compared with about 250 amp in the previous measurements.

3. EFFECT OF THE LARGE SIZE OF THE EFFUSION HOLE ON THE SATURATION CURRENT

The use of a large effusion hole raises immediately two important points for consideration. First, how large can the effusion hole be in relation to the dimensions of the chamber without the saturation pressure of the electron gas in the chamber being disturbed by too rapid an effusion? This will be considered in detail in the next section. The other point is a geometrical one, and arises in the following manner. As we have seen, the effusion electrons collected by the chamber are restricted by an aperture of radius r_0 in a metal plate kept at a distance d from the plane of the effusion hole. As long as the effusion hole is small, the saturation current corresponding to the electrons passing through the restricting diaphragm and reaching the Faraday cylinder, will naturally be proportional to the area s of the effusion hole. This will not, however, be the case when this area is not small, as we shall see presently.

Now the rate of effusion of electrons from any given small element of area, per unit solid angle, at an angle θ to the normal to the plane of the effusion hole, is known to be proportional to $\cos \theta$. Let i be the saturation electric current corresponding to effusion per second, per unit area of the effusion hole, *over all directions*, i.e. over the whole of the 2π solid angle, corresponding to the range $\theta = 0$ to $\frac{1}{2}\pi$. This will be the current occurring in the Richardson equation

$$i = AT^2 e^{-\phi/kT}. \quad (1)$$

As a result of the cosine law, the corresponding value for effusion per unit area *per unit solid angle* along a direction θ will obviously be $(i/\pi) \cos \theta$.

Let I be the saturation current actually observed, which will correspond to effusion from the whole area of the effusion hole, the effusion being confined to directions restricted by the diaphragm used. *If the area s of the effusion hole is small and the hole is on the axis of the circular diaphragm, as was the case in the measure-*

ments described in parts I and II, one can immediately see (see equation (14) of part I) that

$$I = \frac{is}{\pi} \int \cos \theta d\omega = \frac{isr_0^2}{r_0^2 + d^2}. \quad (2)$$

In equation (2) $d\omega$ denotes the element of solid angle. Using this relation, i can be readily obtained from the observed value of I .

On the other hand, if s is not small, which is the case in the present measurements, it is easily shown that the relation between I and i is given by the more general expression

$$\begin{aligned} I &= \frac{i}{\pi} \iint \cos \theta ds d\omega \\ &= \frac{i}{\pi d^2} \iint \cos^4 \theta ds dS, \end{aligned} \quad (3)$$

where ds and dS are elements of area in the effusion hole and in the limiting aperture respectively, and θ is the angle which the line joining the two surface elements makes with the normal to the two planes.

Equation (3) may, for convenience in practical application, be expressed in the form

$$I = is \frac{r_0^2}{r_0^2 + d^2} f, \quad (4)$$

where f may be regarded as a correction factor which is determined by the dimensions of the effusion hole, and of the diaphragm, and their separation. We now proceed to evaluate the integral appearing in (3), and thence the correction factor f .

4. EVALUATION OF THE INTEGRAL

The integral may be evaluated in the following manner. Let the elements of area be defined by $ds = \rho d\rho d\alpha$ and $dS = r dr d\beta$ respectively. Then the integral may be expressed in the form

$$X = \iint \cos^4 \theta ds dS = d^4 \int_{\rho=0}^{\rho_0} \int_{r=0}^{r_0} \int_{\alpha=0}^{2\pi} \int_{\beta=0}^{2\pi} \frac{\rho r d\rho dr d\alpha d\beta}{(B - C \cos \gamma)^2}, \quad (5)$$

where

$$\left. \begin{aligned} B &= \rho^2 + r^2 + d^2, \\ C &= 2\rho r, \\ \gamma &= \beta - \alpha. \end{aligned} \right\} \quad (6)$$

One can immediately see that when ρ is small, X becomes proportional to the area $s = \pi\rho_0^2$ of the effusion hole.

Taking up first the integration over β , this may be replaced where ρ , r and α are kept constant, by integration over γ between the limits 0 and 2π . Substituting

$$\tan \frac{\gamma}{2} = t, \quad (7)$$

and remembering that the integration between the limits 0 and π gives the same value as integration between π and 2π , one obtains

$$\begin{aligned}
 Y &= \int_0^{2\pi} \frac{d\gamma}{(B - C \cos \gamma)^2} \\
 &= 2 \int_0^\infty \frac{2(1+t^2) dt}{[B(1+t^2) - C(1-t^2)]^2} \\
 &= \frac{4}{(B+C)^2} \int_0^\infty \frac{dt}{t^2 + \frac{B-C}{B+C}} + \frac{8C}{(B+C)^3} \int_0^\infty \frac{dt}{\left(t^2 + \frac{B-C}{B+C}\right)^2}. \tag{8}
 \end{aligned}$$

The first integral in (8) is directly evaluated, and the second by applying the reduction formula

$$2k(n-1) \int \frac{dx}{(x^2+k)^n} = \frac{x}{(x^2+k)^{n-1}} + (2n-3) \int \frac{dx}{(x^2+k)^{n-1}}. \tag{9}$$

One thus obtains
$$Y = \frac{2\pi B}{(B^2 - C^2)^{\frac{3}{2}}}. \tag{10}$$

Coming back to (5), the next step after integrating over β will be to integrate over α , which now is just equivalent to multiplying by 2π . Hence

$$X = 4\pi^2 d^4 \int_0^{\rho_0} Z \rho d\rho, \tag{11}$$

where

$$Z = \int_{r=0}^{r_0} \frac{B r dr}{(B^2 - C^2)^{\frac{3}{2}}}. \tag{12}$$

Now $B^2 - C^2$, which for convenience may be denoted by Q , may be written in the form

$$Q = B^2 - C^2 = r^4 + 2r^2(d^2 - \rho^2) + (d^2 + \rho^2)^2, \tag{13}$$

and B in the form

$$B = (r^2 + d^2 - \rho^2) + 2\rho^2. \tag{14}$$

Doing so, one obtains

$$Z = \int_{r=0}^{r_0} \frac{dQ}{4Q^{\frac{3}{2}}} + \int_{r=0}^{r_0} \frac{2\rho^2 r dr}{Q^{\frac{3}{2}}}. \tag{15}$$

By substituting

$$r^2 + d^2 - \rho^2 = 2\rho d \tan \delta, \tag{16}$$

and remembering that

$$(r^2 + d^2 - \rho^2)^2 + (2\rho d)^2 = Q,$$

the second integral in (15) also can be seen to reduce to a simple form, namely, to

$$\frac{1}{4d^2} \int_{r=0}^{r_0} \cos \delta d\delta.$$

The expression (11) for X thus reduces to

$$X = \pi^2 d^2 \int_0^{\rho_0} \rho d\rho - \pi^2 d^2 \int_0^{\rho_0} \frac{\rho^3 + \rho(d^2 - r^2)}{Q_0^{\frac{1}{2}}} d\rho, \tag{17}$$

where Q_0 is the value of Q for $r = r_0$, and as a function of ρ can be written in the convenient form

$$Q_0 = \rho^4 + 2\rho^2(d^2 - r_0^2) + (d^2 + r_0^2)^2, \tag{18}$$

from which it will be seen that the second term in (17) reduces to the simple form

$$-\frac{\pi^2 d^2}{4} \int_{\rho=0}^{\rho_0} \frac{dQ_0}{Q_0^{\frac{1}{2}}}.$$

One thus obtains finally

$$X = \frac{1}{2} \pi^2 d^2 (\rho_0^2 + r_0^2 + d^2 - \sqrt{(\rho_0^2 + r_0^2 + d^2)^2 - 4\rho_0^2 r_0^2}). \quad (19)$$

It is significant that ρ_0 and r_0 in the expression for X may be interchanged, which shows that the effusion hole and the collecting aperture may be interchanged without affecting the saturation current.

For any given values of ρ_0 , r_0 and d , X is readily evaluated from (19), and hence the correction factor f also, which as defined by equations (3) and (4) has the value

$$f = \frac{r_0^2 + d^2}{sSd^2} X, \quad (20)$$

where $s = \pi\rho_0^2$ and $S = \pi r_0^2$ are the areas of the effusion hole and the aperture respectively.

Again it will be seen from (19) that when ρ_0 is small in comparison with either r_0 or d , X reduces to $sSd^2/(r_0^2 + d^2)$, and hence f reduces to unity, as should be expected.

5. THE MAXIMUM SIZE OF THE EFFUSION HOLE THAT CAN BE USED WITH A CHAMBER OF GIVEN DIMENSIONS

As was pointed out in part I the relation between the effusion of electrons from a chamber of the saturated electron gas, through a small hole, and emission directly from an equal area of the surface of the metal, bears a close analogy to the relation between the black body radiation from a cavity through an aperture, and the direct radiation from the heated surface. Corresponding to the emissivity of the surface ϵ in the radiation problem, ϵ' may be taken to represent in the electronic case the ratio of direct emission from the surface to effusion from the chamber of saturated vapour through an equal area of the effusion hole. When the surface is an ideal one, i.e. when it has been completely degassed, ϵ' will obviously be equal to $1 - r$, where r is the reflexion coefficient of the surface of the metal for electrons incident on it, and $1 - r$ is its transmission coefficient. But for any normal surface, i.e. a surface which has not been specially treated for degassing, which is the case in our present measurements, ϵ' may be considerably smaller. We have made some quantitative measurements with a normal surface of nickel, and ϵ' is found to be about $1/5$, and it may be presumed that for the other metals also it will be of this order of magnitude. Graphite, however, is an extreme case, in which the emission coefficient ϵ' for the untreated surface is much smaller, about $1/15$ at 1300°K , about $1/70$ at 1600°K , and still smaller at higher temperatures.

The main purpose of invoking here the analogy of the relation between the electromagnetic radiation from the surface and from the cavity, with the corresponding relation between electronic emission from the surface and effusion from the chamber, is this. It is possible to utilize some of the results already available for the case of radiation from a cavity to our present problem, namely to determine the

maximum size of the effusion hole that can be used with a chamber of given dimensions without disturbing appreciably the equilibrium pressure of the electron gas in the chamber.

The type of source that has been studied in detail in the radiation problem is a cylindrical furnace closed at one end and open at the other. We should refer here in particular to the investigations of Buckley (1927, 1928*a, b*, 1934) and Yamauti (1933). Obviously the greater the ratio of the length l of the cylinder to its radius R , and the higher the emissivity of surface, the closer will be the approximation of the radiation from the cavity to that of an ideal black body. For example, for a permitted defect of 1% of the actual cavity radiation from that of a black body, the values of the ratio l/R corresponding to different values of ϵ , as obtained by Buckley, are given in table 1. The significance of the entries in the bottom row of the table will be made clear presently.

TABLE 1

ϵ	0.75	0.5	0.3	0.25
l/R	3.8	5.8	8.0	9.0
$W\epsilon/s$	6	6	5	5

One can also deduce from certain general considerations a rough criterion that the radiation from such a cylinder may approximate to that of a black body. The criterion is that the total radiation from the walls of the chamber, namely $W\epsilon$, where W is the area of the walls of the chamber, should be much larger than the emission from the aperture, which will be practically s . In other words $W\epsilon/s = p$ say, should be much larger than unity.

One has now to estimate for a given value of ϵ how large p should be in order that the radiation may approach that of a black body to any desired degree of approximation. As was mentioned above, the larger will p have to be the closer the approximation required. One can also see in a general way that p should depend on ϵ , which becomes obvious when one remembers that for an ideally black surface p can be as small as unity.

In the last row of the table are entered the values of $W\epsilon/s$, calculated from Buckley's data for an accuracy of 1%. In view of what was stated just now regarding the dependence of p on ϵ , the apparent constancy of the values of $W\epsilon/s$ entered in the last row of the table shows first that the variation of $W\epsilon/s$ with ϵ is small in the range considered, and that if ϵ is not much smaller than 0.25, a value of p of the order of 5 is ample to make the approximation to the black body as close as 1%.

It may not be permissible to extrapolate from these data to the case when the open end of the cylinder is restricted to a small aperture in the centre, or when ϵ' is small. But since one is concerned here with orders of magnitude only, $W\epsilon'/s > 5$ may safely be taken as a good enough general criterion for the electronic case also. Adopting this criterion, one can readily see that with the dimensions of the chamber and of the effusion hole used in the present measurements, i.e. with $W/s = 87$, the value of ϵ' can be as low as 1/17, and this requirement is clearly satisfied not only for the metals at all working temperatures, but also for the exceptional case of graphite up to about 1300° K. For graphite at higher temperatures the deviation from the ideal value may exceed 1%.

6. EXPERIMENTAL VERIFICATION OF THE EFFECT OF A WIDE EFFUSION HOLE

In the last section it was found that even in the extreme case of graphite, except probably at very high temperatures, the large size of the effusion hole that is used in the present measurements is small enough not to disturb the equilibrium in the chamber. In order to check this result experimentally, and incidentally also to check the geometrical correction factor calculated in an earlier section, we have made some systematic measurements on the saturation current for graphite, which as we have seen is an extreme case, using effusion holes varying in area from 4.5 to 314 mm², and at different temperatures. The effusion holes were circular holes punched in sheets of mica, and backed by a bigger hole in the end wall of the graphite chamber, as in the measurements made in part I. Three different sets of measurements were made, in which the size of the effusion hole was varied over the range given just now; the values of r_0 and d in the three sets were (22, 18), (16, 20) and (10, 18) respectively, in mm.

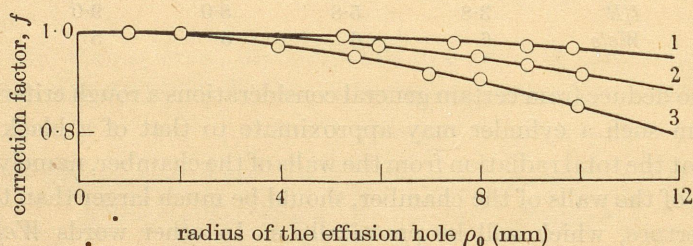


FIGURE 1

The full curves 1, 2 and 3 in figure 1 give the values of f corresponding to these three cases, calculated on the basis of equations (20) and (19). The circles in the figure denote the experimental values of f . Each such circle, corresponding to one of the sizes used for the effusion hole, represents the results obtained at different temperatures, and since they agree closely no attempt is made to indicate them separately in the figure. It will be seen that the experimental points lie practically on the theoretical curves, even for the largest value of the aperture used. This finding, besides verifying the relations (20) and (19) for the evaluation of f from the dimensions of the apparatus, also shows that even the largest effusion hole used is too small to disturb appreciably the equilibrium in the chamber.

Incidentally it is also found that for the small effusion holes used in the measurements described in parts I and II, the correction factor f differs negligibly from unity.

These measurements also throw light on an important point that arises in connexion with the use of effusion holes made in a mica sheet. The main purpose of using the mica sheet is to shield the Faraday cylinder from the electrons that would be emitted by the front surface of graphite if the effective effusion hole had been a hole in the graphite wall itself, since the wall also is at the same temperature as the chamber. The point that naturally arises in this connexion is the possibility of an accumulation of charge on the mica sheet, and the effect of this charge on the effusion of electrons. If the surface charge has any effect it will evidently be most pronounced with narrow effusion holes, and will be practically nothing with large

holes. The agreement of the experimental values plotted in figure 1 with the values calculated from the dimensions, suggests that the effect if any, of the surface charge on effusion even through holes of about 4.5 mm^2 area, which was the smallest hole used in any of our measurements, is negligible.

7. MEASUREMENTS WITH COPPER, SILVER AND GOLD

The thermionic constants of these metals were determined in the same manner as those of the transition metals in part II. The inner walls of the graphite chamber, and the regions adjoining the effusion hole, were coated with the metal to be studied, by thermal deposition, and in the case of copper and silver electrolytically also. The specimen of silver used was of spectroscopic purity and was supplied by Johnson, Matthey and Co. The specimen of gold used was of 99.99 % purity and was kindly

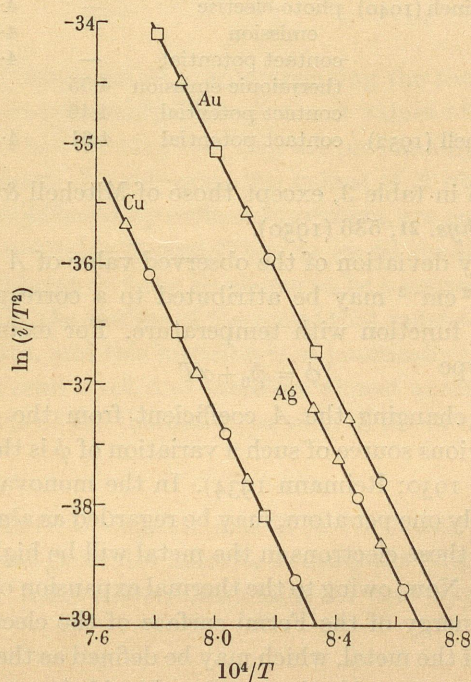


FIGURE 2

supplied by The Chief Assayer of the India Government Mint. The specimen of copper also was of high purity and was further purified by electrolysis. The Richardson plots of $\ln(i/T^2)$ against $1/T$ for the three metals are given in figure 2, in which the values of i used in the plotting have been corrected for the large size of the effusion holes used. The values of the thermionic constants of these metals deduced from these plots are entered in Table 2.

In table 3 are collected together the results obtained by other workers; those obtained earlier than 1938 are not included in this list. The available data for the A coefficients are very meagre, and they vary widely. They are all very low, the values reported earlier being 65 for copper (Goetz 1927), 0.76 for silver (Ameiser 1931) and 40 for gold (Goetz 1927), in the usual unit $\text{amp cm}^{-2} \text{ deg}^{-2}$. These low

values, as mentioned in the Introduction, may be due to the difficulty of effectively degassing the surfaces at temperatures below their melting-points, as these temperatures are not high enough for this purpose.

TABLE 2

metal	ϕ (eV)	A (amp cm ⁻² deg ⁻²)
copper	4.50 ± 0.02	110 ± 5
silver	4.31 ± 0.03	107 ± 6
gold	4.25 ± 0.02	100 ± 4

TABLE 3. EARLIER VALUES FOR THE WORK FUNCTIONS IN eV

author	method	copper	silver	gold
Klein & Lange (1938)	contact potential	4.46	4.44	4.46
Farnsworth & Winch (1940)	photo-electric	—	4.75 (111)	—
	emission	—	4.81 (100)	—
Anderson (1941)	contact potential	—	4.79 (100)	—
Dyke (1946)	thermionic emission	4.55	—	—
Anderson (1949)	contact potential	4.46	—	—
Mitchell & Mitchell (1952)	contact potential	4.61	4.35	—

All the data entered in table 3, except those of Mitchell & Mitchell (1952), are taken from *J. Appl. Phys.* 21, 536 (1950).

As is well known any deviation of the observed value of A from the theoretical value of 120 amp deg⁻² cm⁻² may be attributed to a corresponding small linear variation of the work function with temperature. For example, a temperature variation of ϕ of the type

$$\phi = \phi_0 + \alpha T \quad (21)$$

will be equivalent to changing the A coefficient from the theoretical value of A_0 to $A_0 e^{-\alpha/k}$. One obvious source of such a variation of ϕ is the thermal expansion of the metal (Herzfeld 1930; Reimann 1934). In the monovalent metals the conduction electrons, nearly one per atom, may be regarded as almost completely free, and the assemblage of these electrons in the metal will be highly degenerate at all working temperatures. Now, owing to the thermal expansion of the metal there will be a lowering of the energy of the Fermi surface of the electrons. If the energy barrier at the surface of the metal, which may be defined as the difference in energy between an electron at rest outside the metal and inside it, remains independent of the change of temperature, the lowering of the Fermi surface will lead to an equal increase in ϕ .

Now the energy ζ of the Fermi surface, measured from the bottom of the electronic energy band, will be proportional to $n^{2/3}$, where n is the number of electrons per unit volume, and therefore also practically the number of atoms per unit volume. Hence

$$\frac{1}{\zeta} \frac{d\zeta}{dT} = -\frac{2}{3} \Delta, \quad (22)$$

where $\Delta = -\frac{1}{n} \frac{dn}{dT}$ is the coefficient of thermal expansion of the metal. The corresponding thermal coefficient of ϕ will then be given by

$$\alpha = \frac{d\phi}{dT} = -\frac{d\zeta}{dT} = \frac{2}{3} \zeta \Delta, \quad (23)$$

where the Fermi energy ζ is given by the well-known expression

$$\zeta = \frac{\hbar^2}{2m} \left(\frac{3n}{8\pi} \right)^{\frac{2}{3}}. \quad (24)$$

The values of Δ , and of ζ and α calculated from (24) and (23) respectively, are given in table 3. On this basis the A coefficients should be a fraction $e^{-\alpha/k}$ of A_0 , and the values of this fraction are entered in the last column of the table.

TABLE 4

metal	$10^5 \Delta(\text{deg}^{-1})$	ζ (eV)	$10^4 \alpha(\text{eV deg}^{-1})$	$e^{-\alpha/k}$
copper	5.01	7.0	2.3	0.07
silver	5.76	5.5	2.1	0.09
gold	4.17	5.5	1.5	0.18

Such a lowering in the value of A accompanying the thermal expansion of the metal *is not verified experimentally*. Though the A values of these metals obtained by the usual diode method are very low, they are presumably due to the insufficient degassing of the surfaces. In any case, the values of A obtained by the present method, which are not affected by surface adsorption, are only slightly short of the theoretical value A_0 (see table 2), and this is so for all the three metals.

This finding is significant and can be shown to be a consequence of the lowering of the energy barrier at the surface of the metal that must accompany the thermal expansion of the lattice, and this lowering is of practically the same magnitude as the lowering of the Fermi level, and therefore almost exactly compensates for it. These and other effects of the thermal expansion of the lattice will be discussed in part IV.

We wish to thank Mr G. D. Joglekar and Dr K. N. Mathur for help in the installation of the high current generator used for heating the graphite chamber, and the Chief Assayer of the India Government Mint for the supply of gold of 99.99 % purity.

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Polarization Field in Ionic Crystals

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Reprinted from the

Proceedings of the International Conference of Theoretical Physics

Kyoto and Tokyo, September 1953

Held under the auspices of the I. U. P. A. P.

with a subvention from U. N. E. S. C. O.

Polarization Field in Ionic Crystals

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About two or three years ago, we published a series of papers^{1) 2) 3)} on the frequencies and the anharmonicities of the normal modes of oscillation of the alkali halide crystals, taking a simple model, which is justifiable in the case of most of the alkali halides, and in particular in the case of the halides where the two ions are situated on either side of a rare gas between them. We take the Coulomb interaction between the electrostatic subjects and the repulsive interaction, which can be taken to have an usual exponential form or any other convenient form, (it doesn't actually make much difference with function). The fall of the repulsive forces with increase of distance is so rapid that all repulsion interaction except between the nearest neighbours may be neglected. Further, in view of the spherical sym-

metry of the ions, we may regard both the electrostatic and the repulsive interactions to be central. These assumptions, which are good approximations, render the model simple.

We tried to calculate the frequencies and the anharmonicities and we got the interesting result that the frequencies calculated in that manner from the repulsive and the attractive forces were much larger than the observed *Reststrahlen* frequencies. Then we found that actually the polarization field, which is produced by the displacement of the ions, plays an important part in determining the force of restitution. When once you separate the two lattices, the polarization field increases in the direction to increase the separation, and therefore the calculated frequencies will be much too high because we haven't taken into account the effect of the polarization field. It is very gratifying that many of the results, which we deduced from a critical discussion of the observational data, are confirmed by the detailed calculations of Prof. Yamashita, who spoke just before me.

For example, we found, from the known frequency and the calculation of the frequency for these, that the polarization of the medium is due wholly to the displacements of the ions, and that these displacement do not induce any polarization in the ions and that the effective polarization field acting on an ion and tending to displace it has just the Lorentz value, namely $4\pi/3$ times the polarization per unit volume of the crystal.

It is understandable because, as far as I can see, when you displace the positive and the negative lattices relatively to each other, you can regard the effect of it as due to location of point dipoles equal to half er (r is the relative displacement) at each one of the lattice points. If that is so, this is the one case where the conditions postulated originally by Lorentz in deriving the Lorentz formula, namely that the dipoles should be point dipoles and should be arranged at the corners of the cubic lattice, are precisely satisfied. There is no similar case in other solids that I know of, because most of the polarizations, (even the cases which Lorentz himself had in view,) namely the displacement of the electrons with reference to the nuclei covers such a large distance, and it is not negligible in comparison with interatomic distance in the solids. On the other hand in the case of gases, they will satisfy the condition, but it ceases to be interesting, because the total polarization field becomes so small that one might actually neglect it and it makes no reference to the discussion. And so, we came to the conclusion that the polarization field is due only to the displacements of the positive and negative ions as a whole, as distinguished from the polarization due to the displacement of the electrons with respect to the nuclei, and the latter was found to be nothing.

And one gets a feeling, when we have taken the electrostatic interactions between the various ions, whether we have not already taken into account the effect of the dipole moment. It is not so, because the frequencies, which we calculate neglecting the polarization field, are the frequencies of the individual isolated doublets. Whereas, what we aim at is the calculation of the frequency of the assemblage of these oscillators, and the natural frequency of the assemblage as a

whole is very different from the frequency of the individual dipole oscillators which constitute the assembly.

Separating the two lattices by a small distance r one can obviously express the potential energy of the crystal thus deformed as

$$W = ar^2 = \frac{1}{2} \mu \omega_i^2 r^2$$

where μ is the reduced mass of the pair and ω_i is the angular frequency of the principal mode of oscillation.

The essential part of the problem is to evaluate the contributions to a from the different types of interactions. It will be seen immediately, in view of the centre of symmetry of all the lattice points, that the electrostatic interactions contribute nothing to a . As regards the repulsion interactions, they may be taken to be of the form $A \exp(-R/\rho)$, where R is the distance between the interacting ions. Their contribution to a is found to be equal to, say,

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

where N is the number of ion-pairs per unit volume, β is the compressibility of the crystal, α is the Madelung constant, d is the equilibrium distance between neighbouring ions, $\delta = d/\rho$ and e is the electronic charge. Had a_1 been the whole of the contribution to a , the frequency of the principal lattice oscillation of the crystal would be given by

$$a_1 = \frac{1}{2} \mu \Omega_i^2.$$

But actually the contribution to a from the polarization field is considerable. For a given relative displacement r between the two lattices the polarization per unit volume is given by $P = Ner$, and then the corresponding contribution to a is given by

$$a_2 = -\frac{2}{3} \pi Ne^2.$$

This polarization may also be regarded as produced by a field E in the medium, such that

$$Ee = 2ar = \mu \omega_i^2 r.$$

The corresponding internal field will be given by

$$Fe = Ee + \frac{4\pi}{3} Ne^2 r = 2a_1 r = \mu \Omega_i^2 r,$$

where Ω_i is the frequency which we would have obtained for the principal oscillation of the crystal if we had neglected the effect of the polarization field, as distinguished from the actual resonance frequency ω_i .

The two frequencies Ω_i and ω_i are connected by the relation

$$\Omega_i^2 = \omega_i^2 \frac{\epsilon_0 + 2}{3}.$$

Then the dielectric constant at any frequency ω can be expressed either in the form

$$\epsilon_\omega - 1 = \frac{C_i}{\omega_i^2 - \omega^2}$$

or in the form

$$\frac{\epsilon_\omega - 1}{\epsilon_\omega + 2} = \frac{C_i/3}{\Omega_i^2 - \omega^2}.$$

Thus we get a very satisfactory explanation of the old controversy as to the relative merits of the Drude and the other types of formulae. In the derivation of the Drude formula, we do not invoke the presence of the polarization field, and the other types of formulae are reduced to Drude formula in the special case when the polarization fields are neglected. We immediately drew the conclusion that the Drude formula implicitly takes the polarization field to be nothing. But actually the polarization field can be taken into account in two alternative but mathematically equivalent ways. Either we can make the polarization field adapt to the field in the medium, so that the effective field F that produces the polarization of the medium is much larger than the field E in the medium, or we can take the natural frequency of the individual oscillators to be affected by the presence of the polarization field, so that frequency of the medium as a whole ω_i is very different from the frequency of the individual oscillators Ω_i . And, when also we chose the frequency which is the frequency of the medium, we have already and completely taken into account the effect of the polarization field, and so, in the Drude formula. And indeed the validity of that formula is independent of whether there is a polarization field or not.

In addition we have calculated the frequencies for all the alkali halides even where the compressibility data are not available. The constants needed in the calculation of the frequencies are obviously d , δ and μ . For all the alkali halides the values of δ have already been calculated from certain general considerations by Pauling. So we can use Pauling's values of δ even in the case of crystals for which data are not available for the compressibility. We find it consistent and very convenient to use this value of δ consistently throughout for all the ionic crystals, and for the value of the *Reststrahlen* frequency, taking only the displacement polarization to be effective and having the Lorentz value and the other polarization nothing, we get a very good agreement between experimental data except for one of the fluorides and one of the iodides.

Moreover, the fact that γ is zero (γ is defined according to Prof. Mott as $F = E + (4\pi/3)Ner + \gamma P_e$, where P_e is the polarization due to the displacement of the electrons with respect to the nuclei) seems to be a criterion for equilibrium in the case of the monovalent ionic crystals, that is, under equilibrium conditions γ always is zero. When you change the density of the crystal by either compressing it or chang-

ing the temperature, the value of γ varies, though γ is near about zero and under the equilibrium distance γ is zero, — that is to say, the polarization field is zero under equilibrium conditions at very low temperature, but when once you have thermal agitation, the variation of γ with density, therefore also with temperature, is a finite quantity. That contributes largely to the variation of the dielectric constant with temperature.

One can calculate the precise variation of the dielectric constant with temperature and compare it with the experimental data. I thought that I might just give within the limited time some of the major results regarding the frequencies. Incidentally I may mention the effect of the anharmonicity. The contribution to the potential energy from the polarization of the medium is confined to the r^2 term, but both the repulsion and the Coulomb interaction will contribute to the r^4 term. It will be easily seen that this term is of the form

$$fr^4 = br^4 + cr^2(l^4 + m^4 + n^4),$$

and is thus a function of the direction of the relative displacement r of the two lattices.

As a result of calculation we have found that the effect of the anharmonicity also comes of the right sign and the right magnitude required to explain the observed fall in the specific heat at constant volume, at high temperatures of potassium chloride — that is the only case for which data seem to be available for finding the variation of specific heat at constant volume at high temperatures, and that is reported in most of the standard books, for example Prof. Seitz's book. It was conjectured by Prof. Born that the fall can be explained as due to an anharmonicity if the anharmonicity can be chosen appropriately in magnitude and in sign, but actually we find the anharmonicity has the correct sign and has the correct order of magnitude to explain the temperature fall.

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DISCUSSION

J. Yamashita: Professor Krishnan has talked about the temperature effect of the dielectric constant of ionic crystals. We have also computed the temperature coefficient of the dielectric constant of LiF. In this case we must determine the wave functions so as to minimize the change of the total free energy. The coefficients of our formula A , B and C depend upon temperature through the change

of inter-ionic distance by thermal expansion. When inter-ionic distance increases, the values of the constants become smaller (the repulsive force becomes smaller). By this reason the dielectric constant increases. Of course the density of the dipoles, which is proportional to $\frac{1}{2}a^3$, decreases by thermal expansion, but the former effects are larger than the latter. Thus the dielectric constant of the ionic crystals increases when the temperature increases. After some computations the temperature change of the dielectric constant of LiF becomes $1/\kappa \cdot d\kappa/dT = 3.2 \times 10^{-4}$, while the observed value is 3.75×10^{-4} .

Krishnan: It is very gratifying that many of the results deduced by us from certain simple considerations are now confirmed by the detailed quantum mechanical calculations made by Prof. Yamashita.

H. Fröhlich: I take it that the frequencies derived here refer to very long waves. In many problems concerning scattering of electrons we require the frequency of short waves. I wonder whether any calculations have been made in this connection.

Krishnan: In reply to Prof. Fröhlich I may mention that our programme is to determine the frequencies and the anharmonicities of all the normal modes of oscillation of ionic crystals; of the alkali halides in the first instance. Naturally we started with the homogeneous polar oscillations (i.e. the *Reststrahlen* oscillations) at one end, and the low frequency acoustic modes of oscillation at the other end, both of which correspond to wavelengths large in comparison with the interatomic distance. Since the polarization is now nearly homogeneous over distances large in comparison with the interatomic distance, its effect is easy to calculate. We have recently worked out the case of shorter wavelengths, particularly in the region of k -space close to the region of total reflection of the elastic waves: i.e. close to the boundaries of the Brillouin zone.

We are now trying to extend the calculation to the intermediate modes also, particularly with the view of demonstrating that in the optical branch, the frequency is practically independent of the wave-number k , not only close to the region of total reflection where the group velocity of the waves is known to be zero, but over much wider regions.

Yamashita: In general the computation of the frequency of short waves is very difficult. However, for some definite values of the wave vector, it is possible. Really Lyddane-Hertzfeld have computed the frequency for

$$(1) \quad \vec{s} = (\pi/2a, \pi/2a, \pi/2a)$$

$$(2) \quad \vec{s} = (\pi/a, 0, 0)$$

$$(3) \quad \vec{s} = (\pi/a, \pi/2a, 0)$$

under the assumption of rigid spheres of ions. We have performed a recalculation on taking account of the polarization and charge-overlap effect. The results are:

	Case 1.	Case 2.	Case 3.
(+)	4.59 (s) 2.56 (d)	3.51 (s) 2.72 (s)	2.38 (s) 3.05 (s)
(-)	2.97 (s) 2.06 (d)	3.24 (d) 1.62 (d)	3.37 (d) 2.33 (d)
(+)	4.59 2.56	4.26 3.21	2.46 3.05
(-)	3.71 2.06	3.27 1.83	3.55 2.82

s: single mode, *d*: double modes, unit: 10^{13} sec⁻¹. The upper half is the results of ours, the lower is those of L.—H.

The frequencies for many of modes are nearly the same, but for some modes two results are different. Then we may say that the assumption of rigid sphere model is good for short waves, though not very good.