

1 / 1 AUG 1952

7th August, 1952.

Dear Krishnan,

I acknowledge receipt of the paper by Dr. Roy and yourself on "The Polarization Fields and the Resonance Frequencies of the Alkali Halide Crystals", submitted for publication in the Philosophical Magazine.

Yours sincerely,

*H. P. Mott*



1 AUG 1952

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AIR LETTER

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Professor Sir K.S. Krishnan, F.R.S.,

National Physical Laboratory  
of India,

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New Delhi 12,

INDIA.

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Sender's name and address:-

Professor N.F.Mott,

University of Bristol,

H.H.Wills Physical  
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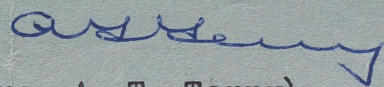
9th August, 1952

Sir K. S. Krishnan, F.R.S.  
National Physical Laboratory of India.  
NEW DELHI.

Dear Sir,

Professor Mott asks me to acknowledge  
the receipt of your paper with S.K. Roy "The Polarization  
Fields and the Resonance Frequencies of the Alkali Halide  
Crystals" which you have communicated to the Philosophical  
Magazine.

Yours faithfully,



(Mrs. A. T. Terry)  
Secretary

DELIVERED  
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WRITE TO THE  
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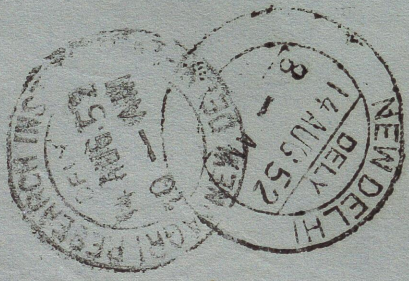
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Ref. No. P.M. 723

The Philosophical Magazine

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Sir K. S. Krishnan, F.R.S.,  
National Physical Laboratory of India,  
Hillside Road,  
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INDIA.

*usu.*  
22 SEP 1952

Dear Sir,

We beg to acknowledge the receipt the paper entitled "The Polarization Fields and the Resonance Frequencies of Alkali Halide Crystals" by Sir K. S. Krishnan, F.R.S. and S. K. Roy, which has been accepted for publication in the Philosophical Magazine.

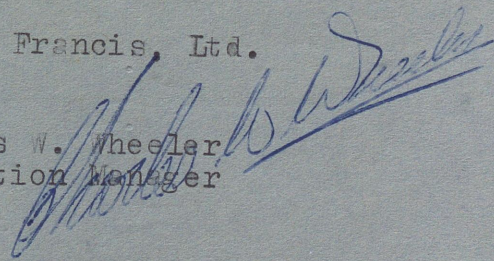
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Yours faithfully,

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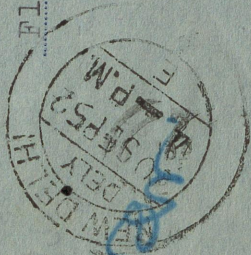
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Oct. 6, 1952

M/s Taylor & Francis, Ltd.,  
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Dear Sirs,

Herewith I am returning the corrected proof of the paper by me and Dr S.K.Roy, entitled "The Polarization Fields and the Resonance Frequencies of the Alkali Halide Crystals" (P.M.723). The major corrections to be made in the galley proof which are indicated in their proper places in the proof, are collected together here for convenience in checking the final proof of the paper.

1. The last part of eq.(2) should read

$$= a_1 \text{ say,} \quad \text{-----} \quad (2)$$

2. The eqns. appearing in § 4 should read

$$Na r^2 = \frac{1}{2} N \mu \omega_i^2 r^2 = \frac{1}{2} P E$$

3. The last two lines in § 4 should read

"polarization field, namely  $\mu P^2/2$  ( $= 2\pi P^2/3$  in the case of the alkali halides) before it can be equated to  $\frac{1}{2} N \mu \omega_i^2 r^2$ "

4. Eqn.(17) should read:

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

5. Eqn.(22) should read:

$$-\left(\frac{4\pi}{3} + f\right)P = -\mu P \quad \text{-----} \quad (22)$$

6. Eqn.(24) should read :

(24)

$$4\pi\chi_i = \frac{C_i}{\Omega_i^2 - \omega^2} \left(1 + \sum_j \rho_{ij}\chi_j\right) \quad (24)$$

7. Eqn.(25) should read:

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

8. Eqn.(27) should read:

$$B_i = \frac{\rho C_i}{4\pi}; \quad \alpha = \frac{4\pi}{\rho} - 1. \quad (27)$$

9. The second and third rows of Table I should read:

$C_i \times 10^{-26}$ from (11)	210	68	28	15	10
$C_i \times 10^{-26}$ from dispersion	230	74	33	18	11

10. Eqn.(37) should read

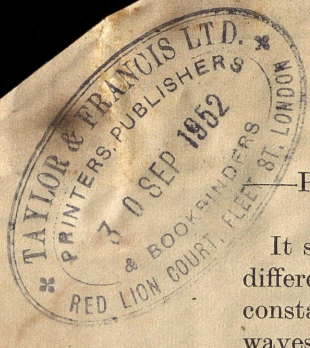
$$\psi_j = -\omega_j \frac{\partial \omega_j}{\partial t} \quad (37)$$

11. Under REFERENCES the first line should read:

Born, M. and Mayer, G.M. 1933 Handbuch der Physik, 24/2 623

Yours faithfully,

U8u



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  $\Omega_i$  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  $p_{ij}, p_{jk}, \dots$  will be much less than  $p_{ii}=4\pi/3$ , and the factors  $p_{jj}, p_{kk}, \dots$  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

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

where the electronic resonance frequencies  $\omega_j, \omega_k, \dots$  will be practically the same as for the individual (not isolated) atoms, namely,  $\Omega_j, \Omega_k, \dots$  respectively, whereas the lattice frequency  $\omega_i$  will naturally be very different from  $\Omega_i$ .

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

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

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

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

or alternatively,

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

the relation between  $\Omega_i$  and  $\omega_i$  being given as before (see (12) and (13)) by

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

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

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

§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.

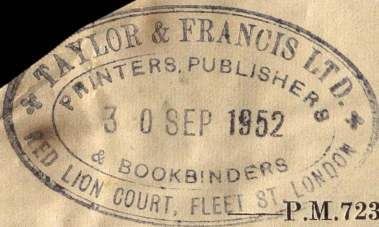
(1) When the data are fitted into a dispersion formula of the Drude type, the characteristic frequencies that appear in the formulae are found to agree well with the observed resonance frequencies. Since the fitting is done empirically, it will be more correct to say that the available experimental data 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 dispersion	230	68	28	15	10
$C_i \times 10^{-26}$ from (11)	230	75	33	18	11

(3) Now the measurements on dispersion usually extend at the infra-red end to about  $22 \mu$  for some of the crystals, and to about  $9 \mu$  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	2.4

§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  $\alpha$  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  $-\alpha e(\partial n/\partial\rho)$  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\*

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

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

where

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

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  $\rho$ , 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  $\omega_j$ '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 variation 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.

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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