the present theory. His formula agreed with experiment for values of e above 0.5. The present theory agrees with experiment over the entire investigated range. The present theory shows that e approaches zero only asymptotically as λ increases. The several cases of zero e recorded by Raman must be attributed to experimental difficulties in measuring small rebound velocities.

In our notation, Raman's formula is

$$e = (1 - 0.88\lambda)/(1 + 0.88\lambda).$$

In view of the success of this formula for small values of λ, it is of interest to see the relation between this formula and the present theory. This relation is given below.

According to the definition of e, the change in velocity of the sphere during impact is $(1+e)v_0$. It is also equal to $\int m^{-1}F dt$. Hence

$$(1+e)v_0 = \int m^{-1}F dt. \qquad (18)$$

Likewise, according to the definition of e, the energy lost by the sphere during impact is $(1-e^2)mv_0^2/2$. But this is equal to the energy absorbed by the plate, namely, $\int F(dU/dt)dt$, or by Eq. (1), $\alpha \int F^2 dt$. Hence

$$(1-e^2)mv_0^2/2 = \alpha \int F^2 dt. \qquad (19)$$

Upon dividing Eq. (19) by the square of Eq. (18), we obtain

$$(1-e)/(1+e) = R,$$

and hence

$$e = (1-R)/(1+R)$$

where

$$R = 2m\alpha \int F^2 dt / (\int F dt)^2,$$

or, by Eq. (17),

$$R = 2\lambda \{ \int \sigma^3 d\tau / (\int \sigma^{\frac{3}{2}} d\tau)^2 \}.$$

When the inelasticity parameter λ is small, the bracketed ratio will be only slightly different from its value for $\lambda = 0$. The value of this ratio has been calculated numerically for the case $\lambda = 0$, and found to be 0.42. Hence in the limit of small λ,

$$R = 0.84\lambda,$$

which is nearly the value used by Raman.

On the Polar Vibrations of Alkali Halides

R. H. LYDDANE, *University of North Carolina, Chapel Hill, North Carolina*

AND

R. G. SACHS* AND E. TELLER, *George Washington University, Washington, D. C.*

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The long wave-length, polar lattice vibrations of alkali halide crystals are discussed without making any specific assumptions about the detailed interactions between the ions. This is made possible by the introduction of the effective charge, e^*, of an ion defined as follows: All of the positive ions in a crystal slab are displaced by an equal amount in a direction perpendicular to the faces of the slab and all of the negative ions in the opposite direction. Then e^* is the ratio of the dipole moment per ion pair induced in the slab by this displacement to the relative displacement of the positive and the negative ions. Expressions are obtained for the frequency, ω_l, of the longitudinal vibration and the frequency, ω_t, of the transverse vibration in terms of the dielectric constant, k, of the crystal, the dielectric constant, k_0, obtained by extrapolating the square of the index of refraction of the crystal from high frequencies to zero frequency, and e^*. The ratio of the two frequencies is found to be independent of e^* and given by $\omega_l/\omega_t = (k/k_0)^{\frac{1}{2}}$.

THE calculation of a property of an ionic crystal which involves the lattice vibrations usually requires that detailed assumptions be made about the microscopic behavior of the crystal. However, statements that are independent of such a full knowledge can be made when the vibrations in question are of wave-length long compared to the lattice distance but short compared to the size of the crystal. Under

* Now at Purdue University, Lafayette Indiana.

these conditions there exist two sharply defined types of vibration, the longitudinal and the transverse. It has already been demonstrated by Lyddane and Herzfeld[1] and by Fröhlich and Mott[2] that in the case of the vibrations for which oppositely charged ions move in opposite directions (polar vibrations) the frequency of the longitudinal vibration is higher than that of the transverse because of the accumulation of charge near the nodes for the former. However, in these calculations, the polarizability of the ions has been neglected entirely or considered only in part.

The purpose of the present paper is to find the ratio of the frequencies of the longitudinal and transverse polar vibrations. It will be shown that this ratio can be derived without making any specific hypothesis about the detailed structure of the crystal.

I

First we consider the force on an ion when a crystal slab is placed in a uniform external field E_0 perpendicular to the faces of the slab. This force is defined as follows: If, in the presence of the field E_0, all the positive ions are displaced in one direction and all the negative ions in the opposite direction so that their relative displacement is the infinitesimal quantity dx, then the force on an ion is the total change in energy per ion pair caused by this displacement divided by the relative displacement dx.

When the ions are displaced as described above, there is a dipole field at great distances from the crystal corresponding to a dipole moment p of the crystal. The interaction energy of the polarized crystal with the field E_0 is the same as the interaction energy of the charges giving rise to E_0 with the field of the crystal. Assuming, then, that these charges are at a great distance from the crystal, the interaction energy is pE_0. This result is independent of the position of the charges giving rise to E_0 since it must be the same for any uniform field of magnitude E_0.

Since all displacements x which are to be considered are small, the dipole moment may be

[1] R. H. Lyddane and K. F. Herzfeld, Phys. Rev. 54, 846 (1938).
[2] H. Fröhlich and N. F. Mott, Proc. Roy. Soc. A171, 496 (1939).

expanded in powers of x and only the first term need be retained. Therefore the dipole moment per ion pair, that is, p divided by the number of ion pairs in the slab, is also proportional to x and may be written e^*x. The constant of proportionality, e^*, will be called the "effective charge" of an ion since for a crystal made up of nonpolarizable, infinitely small ions, e^* is just equal to the charge on an ion. The energy per ion pair is pE_0 divided by the number of ion pairs; thus it is equal to e^*xE_0 and the change in energy per ion pair due to the displacement dx is e^*dxE_0. Dividing by dx, we find that the force on an ion due to the external field is e^*E_0.

In addition to this force caused by the external field, there is a restoring force acting on the ions due to the presence of the other ions in the slab. If the latter force is assumed to be harmonic with force constant q, its contribution to the total force is $-qx$. When the slab is allowed to come to equilibrium in the presence of the field E_0, the total force on an ion vanishes, or

$$e^*E_0 = qx. \qquad (1)$$

The field E_0 may be expressed in terms of the density of polarization, P, in the slab and the dielectric constant, k, of the crystal. For the electric displacement in the slab is numerically equal to E_0 so that E_0 satisfies the relation

$$4\pi P = (1 - 1/k)E_0. \qquad (2)$$

The polarization P is the sum of two terms. The first is the contribution of the dipole moments e^*x and is equal to $e^*x/2a^3$ where a is the lattice distance and $2a^3$ is the volume per ion pair. The other is the contribution of the polarization induced on the ions by the external field. This may be measured in terms of the dielectric constant k_0 obtained by extrapolating the square of the index of refraction from high (visible) frequencies to zero frequency. k_0 is the dielectric constant that the crystal would have if the atomic nuclei were held fixed in the positions they had before the field was turned on. The density of polarization under this condition is equal to $P - e^*x/2a^3$ and this polarization satisfies the equation

$$4\pi(P - e^*x/2a^3) = (1 - 1/k_0)E_0. \qquad (2')$$

Subtracting Eq. (2') from Eq. (2), we obtain

$$(1/k_0 - 1/k)E_0 = 4\pi e^* x/2a^3,$$

and substituting for E_0, Eq. (1) becomes

$$q = \beta k k_0/(k - k_0), \qquad (3)$$

if $\beta = 2\pi e^{*2}/a^3$.

II

We now consider a large crystal slab[3] and assume that there is no external field present. The ions are displaced perpendicularly to the faces of the crystal into positions corresponding to the amplitudes in a longitudinal vibration with nodal planes parallel to these faces. Then there is a restoring force on each ion of magnitude $-\mu\omega_l^2 x$ where x is the relative displacement of the positive and the negative ions, μ the reduced mass of an ion pair, and ω_l the frequency of the longitudinal vibration. We wish to show that the force constant q defined above is just equal to $\mu\omega_l^2$ if the wave-length of the vibration is long compared to the lattice distance.

Consider the crystal to be divided into slabs parallel to the nodal planes and of thickness small compared to the wave-length of the vibration under consideration but large compared to the lattice distance. Then if the ions of the crystal are displaced as described above, each one of the slabs will be uniformly polarized. Such a uniformly polarized slab is equivalent to a parallel plate condenser so, disregarding end effects,[4] it gives rise to no external field. Thus the force on an ion pair in one slab is due only to the displaced ions in that slab. Therefore this force will be the same as that found in Section I for a uniformly polarized slab, that is, $-qx$. From this it follows that $q = \mu\omega_l^2$, and Eq. (3) becomes

$$\mu\omega_l^2 = \beta k k_0/(k - k_0). \qquad (3')$$

III

Those transverse modes of vibration of the large crystal slab that have their nodal planes parallel to the surface of the crystal will now be considered. In this case, the displacements of the ions are parallel to the crystal faces. It is assumed that the crystal wave-length is long compared to the lattice distance, but short compared to the thickness of the crystal.

A small slab with its faces perpendicular to the planes bounding the crystal is cut from within the crystal when its ions are in their equilibrium positions. All dimensions of the slab are chosen to be small compared to the wave-length of the vibration under consideration but large compared to the lattice distance. The ions in the crystal are now displaced according to the amplitudes in the transverse vibration and the displacements are chosen to be perpendicular to the face of the cavity. Then there will be a field in the cavity.

We now put the small slab back into the cavity and displace its ions in such a way as to complete the transverse displacement of the crystal. The force on an ion is then the sum of two forces, the first of which is the force due to the other ions within the slab. Since the ions in the slab are uniformly displaced, this force is the same as that discussed in the previous section, which is $-\mu\omega_l^2 x$. The second force is caused by the field that was present in the cavity so the difference between the longitudinal and the transverse frequencies is due to this field.

To calculate the field in the cavity, we observe that charges appear on the edges of the large crystal slab and the faces of the cavity. Since the former charges are alternatingly positive and negative, their field does not extend deeply into the crystal and their contribution to the field in the cavity may be neglected. The charge distribution on the face of the cavity is practically uniform, since the dimensions of the cavity are small compared to the wave-length. The corresponding charge density, σ, produces a field $4\pi\sigma$ in the cavity. Since σ is numerically equal to the density of polarization, P, in the neighborhood of the cavity, the field in the cavity is $4\pi P$.[5] The value of P is not affected by the removal or the replacement of the small slab because this slab acts like a condenser and produces no external fields.

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[3] It can be shown that the results to be obtained are independent of the shape of the crystal as long as the crystal is large compared to the wave-length of the vibration. The crystal slab will be considered throughout since the treatment in this case is particularly simple.

[4] At great distances from the slab the end effects become important and give rise to the dipole field discussed in Section I.

[5] Cf. R. H. Lyddane, K. F. Herzfeld and R. G. Sachs, Phys. Rev. **58**, 1008 (1940).

All of the considerations of Section I may be applied to the uniform field $4\pi P$, so, if the slab is replaced in this field, the force on an ion in the slab due to the field is $4\pi e^* P$. Therefore, when the ions have a relative displacement x, the difference in force for the longitudinal and the transverse displacements is

$$\mu(\omega_l^2 - \omega_t^2)x = 4\pi e^* P. \tag{4}$$

The density of polarization of the crystal around the cavity is the same as that of the slab. This polarization is made up of two parts. The first is that which would be obtained if the ions in the slab were held fixed. Its magnitude is $(1-1/k_0)/4\pi$ times the external field. The second part is due to the displacement of the ions, and its magnitude is $e^* x/2a^3$. Since in the present case the external field acting on the replaced slab is $4\pi P$ we obtain the equation

$$P = (1-1/k_0)P + e^* x/2a^3,$$

so that

$$4\pi e^* P = \beta k_0 x.$$

Thus Eq. (4) yields

$$\mu(\omega_l^2 - \omega_t^2) = \beta k_0. \tag{4'}$$

A relation that corresponds to the well-known Born[6] formula may be obtained by subtracting Eq. (4) from Eq. (3'). The result is

$$\mu\omega_t^2 = \beta k_0^2/(k-k_0), \tag{5}$$

which differs from the usual formula by the factor $e^{*2}k_0^2/e^2$ where e is the electronic charge.

Dividing Eq. (3') by Eq. (5) the quantity β and with it the unknown charge e^* drops out and we get for the relation between ω_l and ω_t

$$\omega_l^2/\omega_t^2 = k/k_0. \tag{6}$$

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[6] M. Born, Preuss. Akad. Wiss. (Berlin) 29, 604 (1918); Physik. Zeits. 19, 539 (1918). M. Born and M. Goeppert-Mayer, *Handbuch der Physik* 24/2, p. 646.

IV

In the previous considerations, it has been found convenient to define the effective charge, e^*, of an ion in terms of a polarized slab. It is apparent that an effective charge can be defined in the same way for a crystal of any other geometrical shape. In general, the effective charge will depend on the shape of the crystal considered. There are two configurations other than the slab that are of particular interest in any discussion of the dielectric behavior of a solid, the needle and the sphere. If we define the effective charges of the needle and the sphere to be e_n and e_s, respectively, and β_n, β_s to be $2\pi e_n^2/a^3$ and $2\pi e_s^2/a^3$, respectively, then all of the calculations can be carried out in a manner similar to the foregoing. The results of these calculations are the following: Eq. (5) is replaced by

$$\mu\omega_t^2 = \beta_n/(k-k_0) \tag{5'}$$

in the case of the needle and by

$$\mu\omega_t^2 = \beta_s(k_0+2)^2/9(k-k_0) \tag{5''}$$

in the case of the sphere. In all cases Eq. (6) remains, of course, the same.

It is of interest to note that Eq. (5') is of the same form as the Born formula and Eq. (5'') is the same as the corresponding equation given by Wolf and Herzfeld[7] if the quantity that they call p_4 is set equal to e_s^2/e^2. In order that Eqs. (5), (5') and (5'') be consistent, it is necessary that the effective charges satisfy

$$e_n = k_0 e^* = e_s(k_0+2)/3.$$

There is, of course, no generally valid reason why e^*, e_n, or e_s should be equal to the elementary charge.

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[7] K. L. Wolf and K. F. Herzfeld, *Handbuch der Physik* Vol. 20, p. 517.