

Contribution to the Theory of the Dielectric Properties of the Alkali Halides

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(Received April 11, 1960)

In this paper some relations between dielectric properties of diagonal cubic ionic crystals are derived on the basis of the shell model for ions of Dick and Overhauser. The relations, which contain no model constants, are in a good agreement with experimental data. Also it is shown that Dick and Overhauser overestimated the number of electrons in the shells of the ions, which accounts for the failure of their quantitative treatment. In the appendix the paper of Hanlon and Lawson on the same subject is discussed.

a. INTRODUCTION

WITH the use of the simple classical ionic model it is possible to derive, for diagonal cubic crystals AB , the following relation (Szigeti¹):

$$\epsilon_0 - \epsilon_\infty = \left(\frac{\epsilon_\infty + 2}{3} \right)^2 \frac{4\pi N}{\mu\omega_i^2} Z^2 e^2 s^2. \quad (1)$$

Here N is the number of pairs of ions AB per unit volume with a reduced mass μ and charges $\pm Ze$, ϵ_0 is the dielectric constant at low and ϵ_∞ the extrapolated value of the dielectric constant at optical frequencies and $\omega_i/2\pi$ is the frequency of maximum light absorption in the infrared. The parameter s has been introduced because of the failure of the experimental data to satisfy the relation with $s=1$ (for the alkali halides the values of s are in the range $0.7 < s < 0.9$); formally it is an effective charge parameter, with no further relation to the model. This has recently prompted some authors to develop a somewhat more complicated model of the ions.

Dick and Overhauser² assumed that an ion consists of a spherical shell of n outermost electrons and a core consisting of the nucleus and tightly bound inner electrons. In an electric field the shell is supposed to retain its spherical shape, and to move bodily with respect to the core (see Fig. 1). The polarizability of the ion is made finite by a harmonic restoring force of spring constant k which acts between the core and the shell. In a crystal the repulsive forces between the ions are assumed to act between the shells, and not between the cores (or masses) as in the old model; therefore they modify the electronic polarization of the ions. This assumption is based on a quantum mechanical calculation on the origin of the repulsive forces between two helium atoms: the interaction between the exchange-charge and the nuclei appears to be the main component, and the exchange-charge clearly is a very sensitive function of the distance between the shells of the atoms.

As a further correction they included the "exchange-charge polarization": when repelling ions are moved with respect to one another there is a change in the

exchange-charge distribution, leading to a dipole moment. They calculated the influence of both effects on s and found that about half of the deviations of s from unity could be explained in this way, the influence of the "short range interaction polarization" being somewhat larger than that of the "exchange-charge polarization."

In this paper we will make use of the shell model of Dick and Overhauser to derive some new relations. These relations do not contain model constants and are in good agreement with experimental data. We have neglected "exchange-charge polarization" because so many arbitrary assumptions are needed to calculate this effect, that even its order of magnitude is uncertain. Moreover the success of our relations shows that the effect must be of minor importance or compensated by other unknown effects. Further we will show that the method used by Dick and Overhauser to estimate the number of electrons in the outer shells of the different ions leads to higher values than other more direct methods. The approximate values we found lead to an effect of repulsive forces on the value of s of the right magnitude. Also an interesting figure about the relative importance of the different polarization processes at low frequencies is obtained.

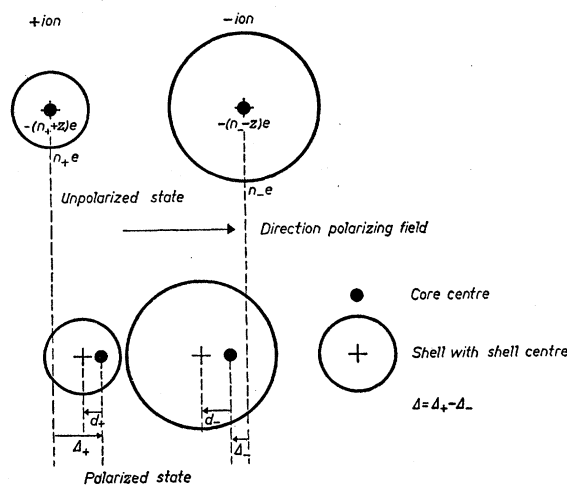


FIG. 1. Dick and Overhauser's shell model for ions. In the unpolarized state the centers of cores and shells coincide. In the polarized state they are separated by a distance d ; so the distance between the cores (the masses) has been diminished by an amount Δ , the distance between the shells by an amount $\Delta - d_- + d_+$.

¹ B. Szigeti, Trans. Faraday Soc. **45**, 155 (1949); Proc. Roy. Soc. (London) **A204**, 51 (1950).

² B. J. Dick, Jr., and A. W. Overhauser, Phys. Rev. **112**, 90 (1958).

Hanlon and Lawson³ have used a model only slightly different: they stated that because of the large curvature of the repulsive fields the influence of a repulsive force on the polarization of an ion will be larger—say f times—than that of an electric force of equal magnitude. They adjusted f for NaCl to make their formulas fit the value of s from relation (1), and with this value of f they got a good agreement for all other alkali halides. However, in the Appendix it is shown that this model leads to a formula that is different from the relation for s they derived, which makes the value of the agreement obtained questionable. Moreover our success with the model of Dick and Overhauser shows that this extra complication is not necessary to obtain agreement.

b. DERIVATION OF THE RELATIONS

b.1. Free Ion Polarizability

If an atom (ion) is in an electric field $E = E_0 e^{i\omega t}$ the equation of motion of its shell of n electrons relative to the core is:

$$neE - kd = -nm\omega^2 d, \quad (2)$$

where d is the distance between the centers of core and shell and m and e the electronic mass and charge, respectively. So we have a polarizability

$$\alpha_{\omega}^{\text{free}} = \frac{P}{E} = \frac{ned}{E} = \frac{(ne)^2}{k} \left(1 - \omega^2 \frac{mn}{k}\right)^{-1}. \quad (3)$$

At lower frequencies where $\omega^2(mn/k) \ll 1$ we obtain

$$\alpha^{\text{free}} = (ne)^2/k. \quad (4)$$

From Eq. (3) it is clear that n and k can be calculated if one knows the free ion polarizability and its dispersion;

$$\alpha = \frac{\frac{(n_+ + Z)^2}{k_+} + \frac{(n_- - Z)^2}{k_-} + \frac{Z^2}{A} - \mu\omega^2 \left(\frac{n_+^2}{Ak_+} + \frac{n_-^2}{Ak_-} + \frac{(n_+ + n_-)^2}{k_+ k_-} \right)}{1 - \mu\omega^2 \left(\frac{1}{A} + \frac{1}{k_+} + \frac{1}{k_-} \right)}. \quad (11)$$

In the limit $\omega = \infty$, Eq. (11) gives the value of the polarizability α_{∞} to be inserted in the Lorentz-Lorentz formula:

$$\frac{\epsilon_{\infty} - 1}{\epsilon_0 + 2} \frac{3}{4\pi N} = \alpha_{\infty} = \frac{(n_+ e)^2}{k_+} + \frac{(n_- e)^2}{k_-} - \frac{\left(\frac{n_+ e}{k_+} - \frac{n_- e}{k_-} \right)^2}{\frac{1}{A} + \frac{1}{k_+} + \frac{1}{k_-}}. \quad (12)$$

In the limit $\omega = 0$, the static polarizability α_0 of the Clausius-Mosotti relation is obtained:

$$\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \frac{3}{4\pi N} = \alpha_0 = \frac{(n_+ + Z)^2 e^2}{k_+} + \frac{(n_- - Z)^2 e^2}{k_-} + \frac{Z^2 e^2}{A}. \quad (13)$$

³ J. E. Hanlon and A. W. Lawson, Phys. Rev. **113**, 472 (1959).

this has been actually used by Dick and Overhauser for rare gas atoms.

b.2. Polarization in Crystals

We denote quantities referring to anions with a suffix $-$ and to cations with a suffix $+$; let further the spring constant of the repulsive force between the shells per ion pair be A and the local field be E_l . In the cases we consider we may approximate E_l by $E_l = E_0 + (4\pi/3)P$; where E_0 is the applied field and P the dipole moment per unit volume. Further $\Delta = \Delta_+ - \Delta_-$ is the relative displacement of the masses M_+ and M_- of the ions, or of the cores.

The equations of motion of the ion shells, if we neglect the inertia of electrons, are

$$n_- e E_l - k_- d_- + A(\Delta - d_- + d_+) = 0, \quad (5)$$

$$n_+ e E_l - k_+ d_+ - A(\Delta - d_- + d_+) = 0. \quad (6)$$

For the cores

$$-(n_- - Z)e E_l + k_- d_- = -M_- \omega^2 \Delta_-, \quad (7)$$

$$-(n_+ + Z)e E_l + k_+ d_+ = -M_+ \omega^2 \Delta_+. \quad (8)$$

As only the relative displacement Δ is relevant, we can eliminate Δ_+ and Δ_- ; with the use of Eqs. (5), (6), (7), and (8) we obtain

$$\mu\omega^2 \Delta = Ze E_l + A(\Delta - d_- + d_+). \quad (9)$$

The dipole moment per ion pair is

$$p = -Ze\Delta + n_- e d_- + n_+ e d_+. \quad (10)$$

For the polarizability per ion pair $\alpha = p/E_l$ we get from Eqs. (5), (6), (9), and (10)

The infrared absorption frequency ω_i occurs when there is a finite polarization without application of a field; for transverse waves there is no depolarizing field and so we have $E = (4\pi/3)P$ or $\alpha_i = 3/4\pi N$. Then Eq. (11) yields, with the use of Eqs. (12) and (13), the relation

$$\mu\omega_i^2 = \frac{\epsilon_{\infty} + 2}{\epsilon_0 + 2} \frac{1}{\frac{1}{A} + \frac{1}{k_+} + \frac{1}{k_-}}. \quad (14)$$

Simple algebraic manipulation of Eqs. (12), (13), and (14) leads to an equation of the form of the Szegedi relation (1), s is the following function of the model

parameters:

$$s-1 = \frac{\frac{n_+}{k_+} - \frac{n_-}{k_-}}{\frac{Z}{A} + \frac{Z}{k_+} + \frac{Z}{k_-}} = \frac{\frac{\alpha_+^{\text{free}}}{n_+} - \frac{\alpha_-^{\text{free}}}{n_-}}{Ze^2 \left(\frac{1}{A} + \frac{1}{k_+} + \frac{1}{k_-} \right)}. \quad (15)$$

Here it should be remarked that if in the formulas III-1, V-33, 32, 28, and 31 of Dick and Overhauser's paper we put the value of D equal to zero (thus neglecting the "exchange-charge polarization") we get our formulas (3), (12), (13), (14), and (15), respectively.

b.3. New Expressions for s

Making use of Eqs. (4), (12), and (14), Eq. (15) can be written as a function containing no model parameters:

$$(1-s)^2 = \frac{\epsilon_0 + 2}{\epsilon_\infty + 2} \frac{\mu\omega_i^2}{Z^2 e^2} (\alpha_+^{\text{free}} + \alpha_-^{\text{free}} - \alpha_\infty). \quad (16)$$

Now we may assume that, for all alkali halides of Table III,

$$\frac{\alpha_-^{\text{free}}}{n_-} > \frac{\alpha_+^{\text{free}}}{n_+} \quad \text{and therefore} \quad s < 1.$$

Then Eq. (16) can be used to calculate the values of s

TABLE I. Comparison of s values, calculated from Eqs. (1) and (16). The values of ϵ_∞ used are those of Tessman, Kahn, and Shockley,^a which differ somewhat from Szigeti's. (In the two first columns all other factors are equal, in the cases of LiF and RbI Szigeti probably has made a calculation error.) $\langle |\Delta| \rangle$ is the mean absolute deviation of s values from those of column 2.

Compound	s from Eq. (1)			s from Eq. (16)	
	Szigeti ^b	Roberts ^c	Haussühl ^d	α^{free} -data Fajans-Joos	α^{free} -data Pauling ^e
LiF	0.87	0.83	0.81	0.77	0.77
NaF	0.93	0.93	0.83	0.96	0.85
NaCl	0.74	0.73	0.76	0.74	0.68
NaBr	0.69	0.71	0.74	0.69	0.71
NaI	0.71	0.71	0.77	0.64	0.64
KCl	0.80	0.78	0.80	0.83	0.80
KBr	0.76	0.75	0.77	0.78	0.81
KI	0.69	0.70	0.72	0.72	0.74
RbCl	0.84	0.83	0.84	0.86	0.76
RbBr	0.82	0.81	0.79	0.80	0.80
RbI	0.89	0.79	0.81	0.75	0.76
CsCl	0.84	0.86		0.91	0.80
CsI	0.79	0.82		0.83	0.83
$\langle \Delta \rangle$			3.9%	4.2%	5.6%

^a See reference 8.

^b See reference 1.

^c See reference 6.

^d See reference 7.

^e See reference 4.

⁴ L. Pauling, Proc. Roy. Soc. (London) **A114**, 181 (1927).

⁵ K. Fajans and G. Joos, Z. Physik **23**, 1 (1924).

⁶ S. Roberts, Phys. Rev. **76**, 1215 (1949).

⁷ S. Haussühl, Z. Naturforsch. **A12**, 445 (1957).

⁸ J. R. Tessman, A. H. Kahn, and W. Shockley, Phys. Rev. **92**, 890 (1953).

TABLE II. Comparison of s values from Eq. (1) and Eq. (17). The data used are from Landolt-Börnstein.^a

Compound	Variable quantity	s [Eq. (17)]	s [Eq. (1)]
NaCl	Temperature	0.66	0.73
NaCl	Pressure	0.64	0.73
KCl	Temperature	0.74	0.78

^a See reference 9.

directly. The results, for two sets of polarizabilities of the free ions (those of Pauling⁴ and of Fajans and Joos⁵) are given in Table I.⁶⁻⁸ It is clear that the agreement between these values and those calculated from Eq. (1) is good; nearly as good as between s values from Eq. (1) calculated with two different sets of dielectric constants.

Formulas relating $(1-s)^2$ directly to experimentally measurable quantities are obtained in the following way: As n and k are specific properties of the ions, it is to be expected that their relative dependence on temperature and pressure will be small, and to a first approximation negligible in comparison with that of A , the interionic force constant. Differentiation of Eqs. (12) and (13) and combination with Eq. (15) then gives

$$(1-s)^2 = \frac{\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \gamma + \frac{3}{(\epsilon_\infty + 2)^2} \frac{\partial \epsilon_\infty}{\partial T}}{\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \gamma + \frac{3}{(\epsilon_0 + 2)^2} \frac{\partial \epsilon_0}{\partial T}} = \frac{\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \beta + \frac{3}{(\epsilon_\infty + 2)^2} \frac{\partial \epsilon_\infty}{\partial p}}{\frac{\epsilon_0 - 1}{\epsilon_0 + 2} \beta + \frac{3}{(\epsilon_0 + 2)^2} \frac{\partial \epsilon_0}{\partial p}}, \quad (17)$$

where $\gamma = (1/V)(\partial V/\partial T)$ and $\beta = (1/V)(\partial V/\partial p)$.

Unfortunately only few data are available; the results are given in Table II.⁹ Further and more accurate measurements are needed to reach a conclusion about the adequacy of the assumptions.

We can apply the same assumptions and differentiate Eq. (14); the results can be written as

$$\frac{\partial \ln \omega_i^2}{\partial T} = \frac{\partial \ln [(\epsilon_\infty + 2)/(\epsilon_0 + 2)]}{\partial T} - \frac{3V\mu\omega_i^2}{4\pi Z^2 e^2 (\epsilon_\infty + 2)} \times \left[(\epsilon_0 - 1)\gamma - 3 \frac{\partial \ln(\epsilon_0 + 2)}{\partial T} \right]. \quad (18)$$

However there is a complete lack of experimental data to test this equation.

⁹ H. H. Landolt and R. Börnstein, Physikalisch-Chemische Tabellen (Julius Springer, Berlin, 1923), 5th ed.

TABLE III. Approximate number of electrons (n_-) in the outer shells of halide ions, from uv dispersion data.

Ion	Corr. rare gas atom D.O. ^a	n_- Eq. (22)	Com- pound	uv abs. (Å) ^b	Data used		$A \times 10^4$ cgs ^a
					Vol. (Å) ^c	α_{free} (Å) ^d	
F ⁻	4.8	0.9	NaF	1170	24.65	1.04	6.34
Cl ⁻	8.7	4.3	LiCl	1430	33.75	3.66	4.35
Cl ⁻		2.8	NaCl	1580	44.61		3.80
Br ⁻	9.9	3.8	LiBr	1730	41.37	4.77	3.82
Br ⁻		2.6	NaBr	1880	52.93		3.43
I ⁻	11.3	4.0	LiI	2210	54.00	7.10	3.00
I ⁻		2.9	NaI	2280	67.40		2.66

^a See reference 2.^b See reference 10^c See reference 5.^d See reference 4.

c. COMPARISON WITH THE RESULT OF DICK AND OVERHAUSER

c.1. Introduction

The success of our relations (16) and (17) suggests, that the shell model offers a nearly quantitative explanation of the deviations of s from unity. On the other hand Dick and Overhauser² made an estimation of all constants in Eq. (15) and found that only a part of the deviations was explained. They proceeded in the following way. The values of n and k for the noble gas atoms can directly be calculated from the known dispersion of the dielectric constant and the atomic polarizabilities [Eq. (3)]. Now Dick and Overhauser assumed that the number of electrons in the shell of an ion is the same as that in the shell of the iso electronic noble gas atom, the difference in polarizability being due to a difference in the value of the spring constant k only. Then k values for the different ions were calculated, using the values of Pauling⁴ for the free ion polarizabilities. The values of A for the compounds were obtained from the parameters B and ρ in the Born-Mayer repulsive potentials between ions. In this way they arrived at values for all constants in Eq. (15). However, the calculated values of $(1-s)$ turned out to be only about 30% of those obtained from Eq. (1), and the inclusion of the effect of "exchange-charge polarization" raised this figure only to about 50%.

Therefore we have made some more direct estimations of the number of electrons in the shells of the ions, where we have avoided the arbitrary assumption of equal number for isoelectronic ions and atoms. This will be outlined in the following paragraphs.

c.2. Ultra-Violet Dispersion in Crystals

The ultraviolet dispersion in solid alkali halides is generally ascribed to the anions. The equation of motion of the anion shell with nuclei at rest, and without neglecting the inertia of electrons, is

$$n_-eE_+ - k_-d_- + A(d_+ - d_-) = -m\omega^2 n_-d_- \quad (19)$$

Now for the Li salts and perhaps also the Na salts we can safely assume that $|d_+| \ll |d_-|$ and so to a first approximation we may neglect Ad_+ . Then

$$\alpha_- = \frac{n_-ed_-}{E_+} = \frac{(n_-e)^2}{k_- + A - m\omega^2 n_-} \quad (20)$$

Here again we have maximum absorption if

$$3/4\pi N = \alpha_+ + \alpha_- \approx \alpha_-.$$

We obtain, with ω_0 denoting the first ultraviolet absorption peak,

$$K_- - (n_-e)^2(4\pi N/3) = -A + n_-m\omega_0^2. \quad (21)$$

Combination with Eq. (4) gives us a quadratic equation in n_- :

$$n_-^2 \left(\frac{e^2}{\alpha_{\text{free}}} - \frac{4\pi}{3} Ne^2 \right) - n_- \frac{4\pi^2 mc^2}{\lambda_0^2} + A = 0. \quad (22)$$

For the different Li and Na salts the higher values of the roots of this equation are given in Table III.¹⁰ The lower roots, in the range $0.3 < n_- < 0.5$, are unacceptable, as they result in values for k_- lower than A , which would mean that shell electrons move principally under influence of the repulsive force between the ions, which also would be the case for cations and therefore in contradiction with the assumptions underlying Eq. (22).

c.3. Static Polarizability

Another method of estimating the number of electrons in the shell of the halide ions makes use of Eq. (13). If we assume that, where for the Li salts $\alpha_{\text{Li}} \ll \alpha_{\text{halogen}}$ we have also $(n_+ + 1)^2/k_+ < (n_- - 1)^2/k_-$, and that A is given sufficiently accurately by the values obtained by Dick and Overhauser from the Born Mayer parameters B and ρ , we can calculate $(n_- - 1)^2e^2/k_-$. As on the other hand $n_-^2e^2/k_-$ is known (free ion polarizability) the value of n_- can be calculated. The results are given in Table IV, and it is seen that there is, in fact, rough agreement with the results of the preceding paragraph. The values obtained are rather low; if one thinks of a shell of 8 outer s and p electrons, then the values of Dick and Overhauser seem more reasonable. However, the model is a strongly idealized one, and therefore one cannot expect that all features will be physically significant. On the other hand values between 2 and 4 might be explained by the argument, that repulsive forces are due only to the electrons in the outer p orbital extended in

¹⁰ E. G. Schneider and H. M. O'Bryan, Phys. Rev. **51**, 293 (1937).

TABLE IV. Estimation of the number of electrons in outer shells of halide ions from the static polarizabilities.

Compound	Ion	ϵ_0^a	$\alpha_0 (\text{\AA}^3)$	$\frac{e^2}{A} (\text{\AA}^3)$	$\frac{(n_- - 1)^2}{k_-} e^2 (\text{\AA}^3)$	$\frac{n_-^2 - e^2}{k_-} (\text{\AA}^3)$	n_-	uv n_- Eq. (22)	Corr. rare gas atom D.O. ^b
LiF	F ⁻	8.9	2.810	2.355	0.455	1.04	3.0	0.9	4.8
LiCl	Cl ⁻	11.95	6.324	5.301	1.023	3.66	2.1	4.3	8.7
LiBr	Br ⁻	13.25	7.933	6.037	1.869	4.77	2.7	3.8	9.9
LiI	I ⁻	16.85	10.839	7.687	3.152	7.10	3.0	4.0	11.2

^a See reference 7.^b See reference 2.

the direction of the displacement, and, with a lower weight factor, to the electrons in the outer s orbitals.

It is interesting to note that the term $Z^2 e^2 / A$, which in the old theory allows for the "ionic" polarizability makes up about 80% of the total polarizability. This is also true for the other alkali halides. (NaF is an exception, here e^2 / A is a little larger than α_0 , which is impossible in the theory, but perhaps there are some errors in the experimental data.) If in the shell model the extra charge of an ion is located on its shell, then $Z^2 e^2 / A$ is the polarizability due to the motion of the shells towards each other, and the terms $(n_+ + Z)^2 e^2 / k_+$ and $(n_- - Z)^2 e^2 / k_-$ are the effective polarizabilities of the ions. Clearly the repulsive forces are very effective in suppressing the polarization of the negative ion.

c.4. Discussion

It is clear from Table IV that the approximate values we obtained for the numbers of electrons in the shell of the anions (n_-) are about 2 or 3 times smaller than those found by Dick and Overhauser. Now it is unlikely that the values for n_+ (the number of electrons in the shell of the cations) are much lower than our values of n_- , the latter being already very low. Therefore it is probable that the estimation of Dick and Overhauser of $|\alpha_+ / n_+ - \alpha_- / n_-|$ in Eq. (15) is about 2 or 3 times too small and, as always holds $1/A \gg 1/k_+ + 1/k_-$, the same applies for their values of $1 - s$. We may thus conclude that the shell model does indeed lead to effects on s of the right magnitude.

APPENDIX. THE HANLON-LAWSON MODEL

This model differs from the model of Dick and Overhauser in that the authors state that owing to the large curvature of the repulsion potential a repulsive force will have a larger polarizing power than an electric force of equal magnitude. So if the shell is connected with the core by a spring with constant k for electric forces, its constant will be $k/f < k$ for the repulsive forces.

In this case we get for the shell of the anion in a crystal the two equations

$$n_- e E_i - k(d_- - \delta_-) = 0, \quad (\text{A1})$$

$$A(\Delta - d_- + d_+) - (k/f)\delta_- = 0, \quad (\text{A2})$$

where δ_- is the part of the displacement of the shell due to the "mechanical" force. Multiplication of the latter formula with f and adding to the first one gives

$$n_- e E_i - k_- d_- + fA(\Delta - d_- + d_+) = 0, \quad (\text{A3})$$

which is the same as Eq. (5), if A in that equation is replaced by fA . For the shell of the cation the equation is obtained from Eq. (6) in an analogous manner. The cores obey the equations

$$-(n_- - Z)e E_i + k_-(d_- - \delta_-) + (k_-/f)\delta_- = -M_- \omega^2 \Delta_-, \quad (\text{A4})$$

$$-(n_+ + Z)e E_i + k_+(d_+ - \delta_+) + (k_+/f)\delta_+ = -M_+ \omega^2 \Delta_+. \quad (\text{A5})$$

We again eliminate Δ_+ and Δ_- and, with the use of Eqs. (A1) and (A2), we obtain

$$-\mu \omega^2 \Delta = -Ze E_i - A(\Delta - d_- + d_+), \quad (\text{A6})$$

which is the same as Eq. (9). Making the calculation in the same way as before we finally get

$$\alpha_0 = \frac{[n_+^2 + (1+f)Zn_+ + fZ^2]e^2}{k_+} + \frac{[n_-^2 - (1+f)Zn_- + fZ^2]e^2}{k_-} + \frac{Z^2 e^2}{A}, \quad (\text{A7})$$

$$\alpha_\infty = \frac{n_+^2 e^2}{k_+} + \frac{n_-^2 e^2}{k_-} - \frac{\left(\frac{n_+ e}{k_+} - \frac{n_- e}{k_-}\right)}{\frac{1}{fA} + \frac{1}{k_+} + \frac{1}{k_-}}, \quad (\text{A8})$$

$$\mu \omega_i^2 = \frac{\epsilon_\infty + 2}{\epsilon_0 + 2} \frac{1}{\frac{1}{A} + \frac{f}{k_+} + \frac{f}{k_-}}. \quad (\text{A9})$$

By simple algebra a relation of the form of Eq. (1), of

Szigeti, can be obtained; for s^2 we get

$$s^2 = 1 - (1+f)t + ft^2, \quad (\text{A10})$$

where

$$t = \frac{\frac{n_+}{k_+} - \frac{n_-}{k_-}}{\frac{Z}{A} + \frac{Zf}{k_+} + \frac{Zf}{k_-}}. \quad (\text{A11})$$

If we compare these results with those of Hanlon and Lawson, it turns out that Eqs. (A8) and (A9) are the same as Eqs. (21) and (29) in their paper. However, for s

they obtained [Eq. (25)], in our notation,

$$s^2 = 1 - 2ft + f^2t^2 = (1-ft)^2. \quad (\text{A12})$$

The reason for this difference is that they did not calculate the expression for the static polarizability, which is also altered by the change in the model.

That they obtained agreement between s values from Eq. (1) and those from Eq. (A12) is therefore no support for the model, but possibly also with Eq. (A10) a value of f can be selected that is in agreement with experimental data. However, as the more simple model of Dick and Overhauser already gives good results, we do not think it necessary to include this complication.

Vibrational Modes Near Impurities

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(Received March 25, 1960)

In many cases, the interaction between the electronic state of an impurity in a solid and the motion of the atoms in the lattice is controlled by the relative motion of the impurity with respect to its nearest neighbors. We therefore examine the nature of the vibrations of the lattice near an impurity. In particular, two problems are considered: First, the direct absorption of light by the "localized" mode introduced by the presence of the impurity, and the relation of its frequency to that of the "reststrahlen" absorption; second, the relative importance of the "localized" modes and of the "lattice" modes in producing the observed broadening of the spectra due to electronic transitions of the impurity center. It is found that the large number of lattice modes together produce a mean displacement of the same order of magnitude as do the very few local ones. The implications for the "configuration coordinate" model for phosphors are examined; both theory and experiment suggest that if only one mode, or group of modes, are effective in producing broadening, their frequency is substantially lower than that of the localized modes which are optically active.

I. INTRODUCTION

WE wish to discuss here the nature of the vibrations of a lattice near an impurity. Many of the properties of impurities in a lattice depend on interaction of the electronic state of the impurity with that of the lattice vibrations; the mechanism of this interaction has been discussed by many people.¹ Here we shall not concern ourselves with the detailed nature of these interactions; we shall merely note that this interaction, whatever it is, will be the result, in many cases, of the relative motion of the impurity atom with respect to its nearest neighbors, and ask what our knowledge of the lattice vibrations can tell us about this.

Two problems in particular are considered: First, the optical absorption by impurity centers is considered and the relation of the frequency of this absorption to the mass of the imperfection is computed. Second, an

attempt is made to assess the relative importance of local vibrational modes and of lattice modes in producing the observed broadening of optical spectra. This leads to an examination of the rationale for the "configuration coordinate" model for phosphors.

In most cases we shall have to work with rather simplified models, since more realistic ones are mathematically too complicated. However, many of our conclusions can be taken over qualitatively to more physical situations, as we shall point out as we go along. The results of this analysis will be compared with experimental data on the optical properties of KCl containing F centers, hydride ions, and thallium.

II. "BREATHING" MODES

One assumption we shall make throughout is that introduction of the impurity atom does not change the force constants in any way. This is strictly correct only for impurities which are isotopes of the regular constituents of the lattice, but may be approximately true also for impurities chemically similar to them.

We shall also confine ourselves to a cubic lattice and

¹ For a review, see M. Lax, in the *Proceedings of the Conference on Photoconductivity, Atlantic City, November 4-6, 1954*, edited by R. G. Breckenridge, B. R. Russell, and E. E. Hahn (John Wiley & Sons, New York, 1956), p. 111.