

THE PRESENT STATE OF THE THEORY OF POLARIZATION OF IDEAL IONIC AND VALENCE CRYSTALS

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Usp. Fiz. Nauk 74, 269-288 (June, 1961)

1. INTRODUCTION

ONE of the most important characteristics of non-conducting crystals is the dielectric constant  $\epsilon$ , defined as

$$\epsilon E = D = 1 + 4\pi P. \tag{1}$$

In varying fields  $\epsilon$  is a function of the frequency  $\omega$ , and is usually expressed in the form

$$\epsilon = \sum_i \frac{a_i}{\omega_i^2 - \omega^2},$$

or, when one includes absorption,

$$\epsilon = \sum_i \frac{a_i}{\omega_i^2 - \omega^2 + i\gamma\omega}.$$

A problem for theory is the determination of the polarization  $P$  of the crystal and the value of  $\epsilon$  as a function of the frequency of the variable field, and the establishment of the relation between the natural frequencies  $\omega_i$  and the coefficients  $a_i$  and various characteristics of the crystals.

In general, the field  $E$  varies not only with time, but also over space. For light waves or radio waves a significant variation of  $E$  occurs over a wave length  $\lambda$  which is many times greater than the lattice constant  $a$  of the crystal; we may therefore partially neglect the inhomogeneity of the field and the polarization. But if the field  $E$  is caused by some defects of the crystal structure (lattice vacancies, foreign ions with a different valence, or a moving charge), the field (and consequently also the polarization  $P$ ) is already inhomogeneous within a single elementary cell. This greatly complicates the theoretical computation of  $P$ . In any case, it is always of great practical convenience to expand the electric field in Fourier series and to find the polarization resulting from the individual components  $E_k \exp\{-i\omega t + iK \cdot r\}$ . For not too strong fields\* the polarization is equal to the sum of the corresponding components  $P_k \exp\{-i\omega t + iK \cdot r\}$ . In fields which are almost homogeneous, the ratio of the components  $P_k$  and  $E_k$  is conveniently written using a dielectric constant which is a function of frequency and wave length:

$$\epsilon(k, \omega) = 1 + 4\pi \frac{P_k}{E_k}. \tag{2}$$

\*In strong fields the additivity of the polarizations may no longer hold. Then  $\epsilon$ , defined by formula (1), will depend still on the magnitude of the field  $E$ .

The dependence of  $\epsilon(k, \omega)$  on  $k$ , which is called spatial dispersion, leads to various delicate effects in the optics of crystals in the neighborhood of the natural frequencies  $\omega_i$ . Thus already in 1878 Lorentz predicted theoretically the occurrence of double refraction of light in cubic crystals. For crystals without a center of inversion, the dependence of  $\epsilon(K)$  in the first approximation (linear in  $K$ ) leads to a rotation of the plane of polarization. A quantitative theory of this phenomenon was developed by Born for ionic crystals in the infrared region. Comparatively recently Pekar<sup>1</sup> considered the relation between  $P$  and  $E$  for frequencies near the exciton absorption line, and predicted the existence of several electromagnetic waves with different indices of refraction and a common frequency, the occurrence of longitudinal waves, and other effects.

For waves which are long compared to  $a$  ( $aK \ll 1$ ),  $\epsilon(K, \omega)$  can be written as an expansion in powers of the components  $k = aK$ . For example, for crystals of any crystal system,

$$\epsilon_{xy}(k, \omega) = \epsilon_{xy}(0, \omega) + \sum_z \epsilon_{xy,z}(\omega) k_z + \frac{1}{2} \sum_{\bar{x}, \bar{y}} \epsilon_{xy, \bar{x}\bar{y}} k_{\bar{x}} k_{\bar{y}} + \dots, \tag{3}$$

where the symbol  $\sum_z$  means that the symbol  $z$  shall run through all three values  $x, y, z$ . Using such an expansion, Ginzburg<sup>2</sup> treated theoretically the optical anisotropy of crystals in the neighborhood of the dispersion frequencies, considered the optical activity of crystals without a center of inversion, and the supplementary light waves.

In a phenomenological theory the quantities  $\epsilon_{xy}(0, \omega)$ ,  $\epsilon_{xy,z}(\omega)$  are parameters which can be determined from experiment.<sup>2</sup>

For fields which are essentially inhomogeneous, when  $Ka \sim 1$ , the dependence of  $P_k$  on  $E_k$  can no longer be found for the general case, and to find it is a separate theoretical problem for each crystal.

Most of the work on the theory of polarization of crystals has been devoted to finding the dependence  $\epsilon(\omega)$ , since the purpose was to apply it to the case of long electromagnetic waves. However, with the development of the theory of dielectrics, one has to deal more and more with the study of the behavior of various lattice defects. The calculation of the energy of formation of a defect (tearing out of an ion, etc.), the energy of ionization of an impurity atom, the determination of the mobility of current carriers in dielec-

trics (polarons) have inevitably included the computation of the polarization and the crystal polarization energy associated with such defects. Here one has to deal with the polarization in an essentially inhomogeneous field. However, the theory of this phenomenon is for the most part lacking at present. Nevertheless the treatment of polarization in inhomogeneous fields exhibits a whole variety of very interesting features. In the following we shall consider the theory of polarization for the general case of inhomogeneous fields, while we shall treat homogeneous fields by making the limiting transition  $K \rightarrow 0$ . In addition, we shall restrict our treatment to the simplest ionic and atomic crystals.

## 2. THE THEORY OF INERTIALESS POLARIZATION ON THE BASIS OF A MODEL OF A LATTICE OF POINT DIPOLES. THE DETERMINATION OF THE INTERNAL FIELD

The theory of polarization takes an especially simple form in the frequency range where  $\omega$  is small compared to the frequencies of electronic dispersion  $\omega_i$  (corresponding to the excitation of the valence electrons of the atoms) and large compared with the frequencies of oscillation of the nuclei. Then the induced dipole moments of the atoms follow the change of the field  $\mathbf{E}$  without any lag, while the nuclei remain fixed.

In ionic and molecular crystals, the constituent parts of which have saturated valence bonds and closed electron shells, we can introduce approximately the concept of the dipole moment of the electron shell of each lattice site:  $\mathcal{P}_s^l$  (the index  $l$  enumerates the lattice cell, while  $s$  denotes the various atoms within a single cell). Assuming that the electric field  $\mathbf{F}$  within each atom is approximately equal to its value at the nucleus  $q\mathbf{r}_s^l$ , we may write

$$\mathcal{P}_s^l = \alpha_s \mathbf{F}(\mathbf{r}_s^l). \quad (4)$$

The quantity  $\alpha_s$  is called the polarizability coefficient of the  $s$ -th atom. It can be calculated from the well-known formula if we know the ground state and some of the lowest-lying excited states of the atom. For an ionic crystal,  $\alpha_s$  is practically the same as for the isolated ions or for ions in solution.<sup>3</sup> The field  $\mathbf{F}$  at the lattice site  $\mathbf{r}_s^l$  is equal to the sum of the external field  $\mathbf{E}_0(\mathbf{r}_s^l)$  and the field  $\mathbf{E}_1$  produced by all the neighboring dipoles  $\mathcal{P}_{s'}^{l'}$ :

$$\mathbf{E}_1(\mathbf{r}_s^l) = \sum_{s'l'} \left\{ \frac{3(\mathcal{P}_{s'}^{l'} \cdot \mathbf{r}_{ss'}^{ll'})}{|\mathbf{r}_{ss'}^{ll'}|^5} \mathbf{r}_{ss'}^{ll'} - \frac{\mathcal{P}_{s'}^{l'}}{|\mathbf{r}_{ss'}^{ll'}|^3} \right\}. \quad (5)$$

The computation of the internal field  $\mathbf{E}_1$  in this approximation is a purely mathematical problem which for an ideal lattice of point ions is solved exactly in principle. The expression  $\mathbf{E}_1 = \mathbf{E} + (4\pi/3)\mathbf{P}$  is well known for cubic crystals and uniform polarization  $\mathbf{P}$  (Lorentz field). For inhomogeneous fields one knows the method

of Mott and Littleton<sup>4</sup> which reduces to a numerical summation of the fields (5) of the neighboring dipoles, for which one writes and solves exactly Eq. (4), while the field of more remote dipoles is expressed in terms of  $\mathbf{E}$  by the formulas of macroscopic electrostatics. A difficulty which appears here is the need to cross the boundary between macroscopic and microscopic treatments of polarization: as one includes more and more configuration spheres in the micro-calculation of the field and the polarization according to (4) and (5), the quantity of interest to us (for example, the polarization energy of the crystal) oscillates between rather wide limits. This results from the irregular oscillations of the numbers of atoms between successive configuration spheres. Rittner, Hunter, and duPré,<sup>5</sup> in calculating the polarization of a crystal by the field of a point charge, have used high-speed computers and gone out to the tenth configuration sphere. However, even then the fluctuations of the calculated quantities remain considerable.

We should remind the reader of the possibility of replacing the summation in (5) by an integration beginning from some radius  $R$ . Born proposed to eliminate the indeterminacy by choosing  $R$  so that the number of sites  $N$  inside the sphere of radius  $R$  was equal to  $(4\pi/3)(R_0^3/v_0)$ , where  $v_0$  is the average volume per atom.

Formula (5) should be applied with some care to the case of a homogeneous external field, since for  $\mathcal{P}_s^{l'}$ , independent of index  $l'$ , the summation over  $l'$  diverges. The reason for this is easy to understand if we consider a crystal of finite dimensions whose polarization is described by a plane wave with small  $\mathbf{k}$ :  $\mathbf{P}_\mathbf{k} e^{i\mathbf{k} \cdot \mathbf{r}}$ . For a longitudinal wave  $\mathbf{P}_\mathbf{k} \parallel \mathbf{k}$ , at the boundaries of the crystal perpendicular to  $\mathbf{P}_\mathbf{k}$  there appear surface charges which are the same over the whole surface. They produce a field which is equal to  $-4\pi\mathbf{P}_\mathbf{k}$  in the limit  $K \rightarrow 0$ . If, however,  $\mathbf{K} \perp \mathbf{P}_\mathbf{k}$ , then these surface charges will oscillate with a wave length  $2\pi/K$ , and their fields will on the average cancel one another in the crystal. Therefore if we set  $\mathbf{K} = 0$  to start with, the field is not unique. Considering the idealized case of an infinite crystal, we should set  $\mathbf{K}$  different from zero, and in going to the limit  $\mathbf{K} \rightarrow 0$  we should assume that the direction of  $\mathbf{K}$  is fixed. The difference between the internal fields for longitudinal and transverse polarizations is the reason for the difference in the limiting frequencies of the longitudinal and transverse vibrations of the crystal lattice, if the computation of the frequency is done without taking retardation into account.

The difficulty we have pointed out disappears if we go over from a static field to a field  $\mathbf{E}(\mathbf{r}, t)$  which varies in time. In this case, applying the Fourier expansion, we should assume that all of the dipoles  $\mathcal{P}_s^l$  are described by a sum of dipole waves

$$\mathcal{P}_s^l = \mathcal{P}_s^K e^{-i\omega t + i\mathbf{K} \cdot \mathbf{r}_s^l}. \quad (6)$$

Then in computing the internal field, we should take into account that the field of each dipole  $\mathcal{P}_{s'}^{l'}$  will arrive at the point  $\mathbf{r}_s^l$  at a different time  $(1/c)|\mathbf{r}_{ss'}^{l'l}|$ . The effect of retardation is unimportant so long as this time is much less than the period of oscillation of the field  $2\pi/\omega$ , but for  $\omega \neq 0$  the field from sufficiently remote dipoles (and this is the field which, as we have just seen, gives the finite contribution  $-4\pi\mathbf{P}$ ) will necessarily arrive with a large retardation. Therefore formula (5) cannot be used.

To compute the varying internal fields, the most practical method is that of Ewald,<sup>7</sup> proposed about thirty years ago. It consists in transforming the Hertz vector of the system of dipoles

$$\mathbf{\Pi}(\mathbf{r}, t) = \sum_{s'l'} \frac{\mathcal{P}_{s'}^{l'} \left( t - \frac{1}{c} |\mathbf{r} - \mathbf{r}_{s'}^{l'}| \right)}{|\mathbf{r} - \mathbf{r}_{s'}^{l'}|} \quad (7)$$

to two rapidly converging series: one series over the crystal and another over the reciprocal lattice of a crystal. Usually we are interested in the value of  $\mathbf{\Pi}_s^l$  at the point  $\mathbf{r}_s^l$ , produced by all the dipoles except for the  $l, s$ -th (the exciting field). To find  $\mathbf{\Pi}_s^l$  from (7) we should subtract the field of the dipole  $\mathcal{P}_s^l$  itself. For the dipole wave (6),

$$\mathbf{\Pi}_s^l(\mathbf{r}_s^l, t) = e^{-i\omega t + i\mathbf{K}\mathbf{r}_s^l} \left\{ \sum_{s' \neq s} \mathcal{P}_{s'}^{\mathbf{K}} S(\mathbf{r} - \mathbf{r}_{s'}) + \mathcal{P}_s^{\mathbf{K}} \bar{S}(\mathbf{r} - \mathbf{r}_s) \right\}_{\mathbf{r}=\mathbf{r}_s^l}. \quad (8)$$

Then

$$S(r) = \sum_{l'} e^{-i\mathbf{K}(\mathbf{r}-\mathbf{r}_{s'}^{l'})} \cdot \frac{2}{\sqrt{\pi}} \int_0^\infty e^{-|\mathbf{r}-\mathbf{r}_{s'}^{l'}|^2 x^2 + \frac{\omega^2}{4c^2 x^2}} dx + \frac{4\pi}{\Delta} \sum_m \frac{e^{i\mathbf{q}^m \mathbf{r} - \frac{1}{4\epsilon^2} [(q^m + \mathbf{K})^2 - \frac{\omega^2}{c^2}]} }{(q^m + \mathbf{K})^2 - \frac{\omega^2}{c^2}}, \quad (9)$$

$$\begin{aligned} \bar{S}(r) = & S(r) - \frac{2}{\sqrt{\pi}} e^{-i\mathbf{K}(\mathbf{r}-\mathbf{r}^l)} \int_0^\infty e^{-|\mathbf{r}-\mathbf{r}^l|^2 x^2 + \frac{\omega^2}{4c^2 x^2}} dx \\ & - e^{i\mathbf{K}(\mathbf{r}^l - \mathbf{r})} \left\{ i \frac{\sin \frac{\omega}{c} |\mathbf{r} - \mathbf{r}^l|}{|\mathbf{r} - \mathbf{r}^l|} \right. \\ & + \frac{1}{\sqrt{\pi}} \left[ e^{i \frac{\omega}{c} |\mathbf{r} - \mathbf{r}^l|} \int_0^{e + \frac{i\omega}{2\epsilon c}} e^{-|\mathbf{r}-\mathbf{r}^l|^2 x^2} dx \right. \\ & \left. \left. + e^{-i \frac{\omega}{c} |\mathbf{r} - \mathbf{r}^l|} \int_0^{e - \frac{i\omega}{2\epsilon c}} e^{-|\mathbf{r}-\mathbf{r}^l|^2 x^2} dx \right] \right\}, \quad (10) \end{aligned}$$

where  $\Delta$  is the volume of the unit cell,  $\mathbf{q}^m$  are the vectors of the reciprocal lattice. The quantity  $\bar{S}$  is finite for  $\mathbf{r} \rightarrow \mathbf{r}_s^l$ .

The sum over the lattice vectors  $\mathbf{r}^{l'}$  converges rapidly for large  $\epsilon$ , while the sum over the reciprocal lattice vectors converges for small  $\epsilon$ . For  $\epsilon \sim (1/a)\sqrt{\pi/2}$  both series converge quite rapidly. For approximate calculations it is sufficient to keep two configuration spheres in the space of  $\mathbf{r}^{l'}$  and  $\mathbf{q}^m$ . If one includes five spheres, then, as our calculations

for lattices of the NaCl type have shown, one obtains an accuracy to five places of decimals.<sup>8</sup>

Knowing the Hertz vector (8), one can easily calculate the electric field at any point of the lattice

$$\mathbf{E}_1(\mathbf{r}_s^l) = (\text{grad div } \mathbf{\Pi}_s^l(\mathbf{r}, t) - \frac{1}{c^2} \ddot{\mathbf{\Pi}}_s^l(\mathbf{r}, t))_{\mathbf{r}=\mathbf{r}_s^l}. \quad (11)$$

Performing the differentiation and making the limiting transition  $\mathbf{r} \rightarrow \mathbf{r}_s^l$ , we obtain

$$\mathbf{E}_1(\mathbf{r}_s^l) = \frac{2}{\Delta} e^{-i\omega t + i\mathbf{K}\mathbf{r}_s^l} \sum_{s'y} \varphi_{ss'xy}^{\mathbf{K}} \mathcal{P}_{s'y}^{\mathbf{K}}, \quad (12)$$

where the coefficients  $\varphi_{ss'xy}^{\mathbf{K}}$  form a tensor of second rank which depends only on the geometry of the lattice and on the wave vector  $\mathbf{K}$ . In our paper<sup>8</sup> it was computed for a lattice of the NaCl type through  $1/8$  of the length of the cell of the reciprocal lattice, neglecting retardation. An examination of formulas (9) and (11) shows that the quantity  $\omega^2/c^2$  is important only in the zeroth terms of the sum over  $\mathbf{q}^m$ :

$$\frac{4\pi}{\Delta} e^{-\frac{1}{4\epsilon^2} (K^2 - \omega^2/c^2)} \approx \frac{4\pi}{\Delta} \frac{1}{K^2 - \frac{\omega^2}{c^2}} - \frac{\pi}{\epsilon^2 \Delta}. \quad (13)$$

In formula (12) it gives a contribution to the internal field of

$$\mathbf{E}_{1,0} = -\frac{4\pi}{\Delta} \frac{(\mathcal{P}\mathbf{K})\mathbf{K} - \mathcal{P} \frac{\omega^2}{c^2}}{K^2 - \omega^2/c^2} + \dots, \quad (14)$$

where  $\mathcal{P} = \sum_s \mathcal{P}_s$  is the total amplitude of the dipole moment of the cell. When we neglect retardation,  $\mathbf{E}_{1,0}$  reduces to

$$-\frac{4\pi}{\Delta} \frac{(\mathcal{P}\mathbf{K})\mathbf{K}}{K^2} \quad (15)$$

and is undetermined at  $\mathbf{K} = 0$  within the limits  $\pm 4\pi\mathcal{P}/\Delta$ .

Thus the correction due to retardation results in the replacement of (15) by the exact expression (14). We see immediately that

$$\lim_{\mathbf{K} \rightarrow 0} \mathbf{E}_{1,0} = -\frac{4\pi}{\Delta} \mathcal{P} \quad (16)$$

independent of the directions of  $\mathcal{P}$  and  $\mathbf{K}$ . In the following we shall consider the effect of this point in the theory of lattice vibrations. But here we shall show that, by using (12), one can easily find the polarization of the crystal in any inhomogeneous field. For each Fourier component of field and polarization, formulas (4) and (12) give a system of simultaneous equations

$$\mathcal{P}_{sx}^{\mathbf{K}} = \alpha_s \left( E_{sx}^{\mathbf{K}} + \frac{2}{\Delta} \sum_{s'y} \varphi_{ss'xy}^{\mathbf{K}} \mathcal{P}_{s'y}^{\mathbf{K}} \right),$$

which can be written more briefly as follows:

$$\sum_{s'y} C_{ss'xy}^{\mathbf{K}} \mathcal{P}_{s'y}^{\mathbf{K}} = \frac{\Delta}{2} E_{sx}^{\mathbf{K}}. \quad (17)$$

Finding the matrix  $C^{-1}$ , which is reciprocal to  $C$ , we get

$$\mathcal{P}_{sx}^K = \frac{\Delta}{2} \sum_{s'y} C_{ss'xy}^{-1} E_{s'y}^K. \quad (18)$$

The polarization of each site  $l, s$  is obtained by summing the Fourier expansion

$$\mathcal{P}_{sx}^l = \sum_K \mathcal{P}_{sx}^K e^{i\mathbf{K}r_s^l - i\omega_K t} = \frac{2}{\Delta} \sum_K \sum_{s'y} C_{ss'xy}^{-1} E_{s'y}^K e^{i\mathbf{K}r_s^l - i\omega_K t}. \quad (19)$$

Usually it is not necessary to know all the quantities  $\mathcal{P}_{sx}^l$ , but only certain macroscopic quantities, for example, the polarization energy of the crystal. The energy of all the dipoles in the external field  $\mathbf{E}$  is obviously equal [using (12)] to

$$\begin{aligned} U^{(e)} &= - \sum_{slx} \mathcal{P}_{sx}^l E_x(r_s^l) = - \frac{\Delta}{2} \sum_{ss'xy} C_{ss'xy}^{-1} E_{s'y}^K e^{i\mathbf{K}r_s^l - i\omega_K t} E_x(r_s^l) \\ &= - \frac{\Delta}{2} N \sum_{ss'xyK} E_{sx}^{-K} C_{ss'xy}^{-1} E_{s'y}^K, \end{aligned} \quad (20)$$

where  $N$  is the number of cells in the crystal.

The internal energy of the crystal  $U^{(0)}$  is equal to half of this quantity with the opposite sign.

As an example, we give the values of the total energy  $U^{(e)} + U^{(0)}$  for a crystal of the NaCl type which is polarized without inertia by the field of a point charge  $e$  located at one of the sites. For this case, we calculated the values of the components  $\mathbf{E}_S^K$ . The value of the energy is given in Table I (in eV) for NaCl, KCl, and KBr. The index  $s_1 = 1$  means that the charge is located on the cation, while  $s = 2$  means that it is located on the anion. For comparison we give the values of Mott and Littleton and Ritter et al. These results differ only slightly from one another. The advantage of our method is that, after the complicated computation of  $C^{-1}$  and  $\mathbf{E}_S^K$ , one can easily solve miscellaneous problems.

As a second example, we consider the energy of interaction of two charges located at lattice sites. Here we must compute from formula (20) the energy of the crystal in the field of the two charges  $e_1$  and  $e_2$ . This energy splits into terms proportional to  $e_1^2$ ,  $e_2^2$ , and  $e_1 e_2$ . The first two terms give the energy of the crystal in the field of the point charges  $e_1$  and  $e_2$ , while the last term gives the correction via polarization to the energy of interaction of the charges. Adding the term  $e_1 e_2 / r$ , we obtain the total energy of interaction.

The first computations according to this method were done by Kucher<sup>18</sup> for KCl. The defect of his computation was the not entirely correct summation in the neighborhood of  $\mathbf{K} = 0$ .

In Table II we give both the results of Kucher and the more accurate ones obtained by V. N. Fedorchenko. For comparison we give the value of  $e^2/r$  (i.e., the energy in vacuum) and  $e^2/n^2 r$  (i.e., the energy computed using macroscopic electrostatics). In the last column we give the ratio (in %) of the microscopic and macroscopic computations. We see that, with increasing  $r$  from  $a$  to  $a\sqrt{3}$ , this difference decreases, but in all cases the microcalculation gives the larger value. This is related to the fact that the space between charges which are placed close to one another is not filled entirely with dielectric. It is interesting that the energy of interaction and the polarization energy of a crystal in the field of a charge depend on where the charges  $e_1$  and  $e_2$  are placed. This is related to the different polarizabilities of the immediate surroundings. The differences of the energies from the macroscopic expressions are significant for  $r = a$  and  $a\sqrt{2}$ , and must be taken into account in developing a theory of impurity centers.

### 3. THE THEORY OF INERTIAL POLARIZATION OF A CRYSTAL IN THE MODEL OF POINT IONS AND DIPOLES AND ITS DEFICIENCIES

In an electric field, static or variable, but with frequency small compared with the natural frequencies of the atoms, the polarization of a crystal has a component which is associated with the displacement of the nuclei. One can formally introduce a polarizability of the displacement of each ion  $\beta_S$  and by analogy with (4) write

$$\mathbf{p}_S^l = \beta_S \mathbf{F}(r_s^l). \quad (21)$$

Strictly speaking, however, the quantities  $\beta_S$  have no physical meaning, since the quasi-elastic force which brings the ion back to its equilibrium position depends not only on its displacement, but also on the displacements of all the surrounding ions. Therefore, to find the displacements of the nuclei  $\mathbf{u}_S^l$  and the corresponding dipole moments  $\mathbf{p}_S^l = e_S \mathbf{u}_S^l$  is a complicated static

Table I. Total energy of a crystal polarized by the field of a point charge located at one of the lattice sites

Location of charge	Crystal	Author and method of computation					Our method
		Macroscopic	Mott and Littleton	Rittner et al.			
				I approx.	II approx.	III approx.	
$s=1$	NaCl	-1.87	-2.02	-2.04	-2.02	-2.00	-2.444
	KCl						-1.954
	KBr						-2.018
$s=2$	NaCl		-1.44	-1.45			-1.487
	KCl						-1.385
	KBr						-1.432

**Table II.** Energy of interaction of two charges located at different sites of a crystal  $s_1^l$  and  $s_2^l$ , compared with the energy in vacuum and the energy calculated from Coulomb's law

Crystal	Distance	Location of charge	U according to Kucher	$e^2/r$	$\frac{e^2}{n^2 r}$	U	$U: \frac{e^2}{n^2 r}$ in %
NaCl	a	$s_1=1$	2.553	5.108	2.492	2.724	124.2
KCl		$s_2=2$		4.581	2.403	2.472	117.4
KBr				4.370	1.850	2.193	118.5
NaCl	$a\sqrt{2}$	$s_1=1$	1.665	3.612	1.550	1.671	107.8
KCl		$s_2=1$		3.239	1.489	1.612	108.2
KBr				3.090	1.308	1.435	109.7
NaCl	$a\sqrt{2}$	$s_1=2$	1.756	3.612	1.550	1.815	117.1
KCl		$s_2=2$		3.239	1.869	1.699	117.1
KBr				3.090	1.308	1.532	117.1
NaCl	$a\sqrt{3}$	$s_1=1$		2.949	1.266	1.312	103.7
KCl		$s_2=2$		2.645	1.216	1.244	102.4
KBr				2.523	1.068	1.108	103.7

(or dynamic in the case of variable fields) problem, which leads to a system of equations for all the displacements.

If we introduce a potential energy of the ions  $U^0$  as an expansion in powers of the displacements  $u_s^l$  up to terms of second order inclusive, we obtain a system of linear equations for determining the displacements  $u_s^l$ :

$$m_s \ddot{u}_{sx} = -\frac{\partial U^0}{\partial u_{sx}^l} + e_s E_x(r_s^l). \quad (22)$$

In order to avoid confusion, in both this and the preceding section, we have explicitly separated the following quantities: the external field  $E_0$ , the effective field  $E_1$ , and the macroscopic field intensity  $E_{\text{mac}}$ . For convenience in working with variable fields, it is useful to understand by  $U^0$  the potential energy of the ions excluding the Coulomb forces. Then by  $F$  in (22) we mean the total field intensity produced at the site  $r_s^l$  by both the external sources as well as the surrounding ions and dipoles. Denoting the field of all the ions and dipoles by  $E_1$ , we have

$$F = E_0(r_s^l) + E_1(r_s^l). \quad (23)$$

It is convenient to express the internal field  $E_1$  in terms of the Hertz vector

$$E_1 = \nabla \nabla \Pi_s^l - \frac{1}{c^2} \ddot{\Pi}_s^l, \quad (24)$$

where

$$\Pi_s^l(r, t) = \sum_{s'l'} \frac{p_{s'l'}^l \left( t - \frac{|r - r_{s'l'}^l|}{c} \right) + \mathcal{P}_{s'l'}^l \left( t - \frac{|r - r_{s'l'}^l|}{c} \right)}{|r - r_{s'l'}^l|}. \quad (25)$$

If we make a Fourier transformation of all the quantities  $p_{s'l'}^l$ ,  $\mathcal{P}_{s'l'}^l$ , and  $E_0$  and use Ewald's method, then the internal field will have, as before, a term dependent on the retardation of the interaction:

$$E_{1,0} = -\frac{4\pi}{\Delta} \frac{(\mathcal{P}K)K - \mathcal{P} \frac{\omega^2}{c^2}}{K^2 - \frac{\omega^2}{c^2}}, \quad \text{where } \mathcal{P} = \sum_s (p_s^K + \mathcal{P}_s^K). \quad (26)$$

It is easy to show that in dielectrics, in which there are no true charges, the quantity  $E_{1,0}$  is the macroscopic field intensity  $E_{\text{mac}}$ . In fact, combining Maxwell's equations in the absence of conduction currents,

$$\Delta E_{\text{mac}} - \frac{1}{c^2} \ddot{E}_{\text{mac}} = -4\pi \left( (\text{PK})K - \frac{1}{c^2} \ddot{\mathbf{P}} \right) + 4\pi \nabla \rho, \quad (27)$$

where  $\mathbf{P}$  is the dipole moment per unit volume. For  $\rho = 0$ , representing  $E_{\text{mac}}$  and  $\mathbf{P}$  as plane waves, we again obtain precisely formula (26). If we omit the case of external electromagnetic fields, then for  $\rho \neq 0$  the distribution of charges determines the so-called "external field" and, if  $E_0^K$  is its Fourier component, then from (27)

$$E_{\text{mac}} = -4\pi \frac{(\text{PK})K - \frac{\omega^2}{c^2} \mathbf{P}}{K^2 - \frac{\omega^2}{c^2}} + \frac{K(E_0^K)}{K^2}. \quad (28)$$

The last term is equal simply to  $E_0^K$ , since the field produced by the charge  $\rho$  is necessarily longitudinal.

Thus, the macroscopic field  $E_{\text{mac}}$  is equal to the sum of the external field and  $E_{1,0}$ , while the internal field  $E_1$  is the sum of  $E_{1,0}$  and a part which is regular in  $K$ . For cubic crystals for small  $K$  this part is equal to  $(4\pi/3)\mathbf{P}$ .

If the external field is an electromagnetic wave impinging on the crystal, then it appears at first glance that it is in general not possible to separate it, since the field comes from the vacuum with velocity  $c$ , while in the crystal there are only waves propagating with the velocity  $c/\sqrt{\epsilon}$ . There is a tendency among some authors to identify the external field with  $E_{\text{mac}}$ , which, as we have already seen, is completely unjustified. This problem was solved by Ewald on the basis of a treatment of a crystal of finite size. Ewald proved an extinction theorem according to which the field of a system of dipoles in a semi-infinite crystal is equal to the field of the system of dipoles in an infinite crystal  $E_1$  plus a field which is equal and opposite in sign

to the field of the incident wave. Thus, in a semi-infinite crystal, the incident waves are extinguished, while the sum of the external and internal fields is equal to the internal field for an infinite crystal and is given by formula (24). This theory thus enables us to treat the process of arrival of electromagnetic waves in a crystal as a problem of free oscillation of all the dipoles. The problem thus reduces to the system of equations

$$m_s \ddot{u}_{sx}^l = -\frac{\partial U^0}{\partial u_{sx}^l} + e_s E_{1x}^l(r_s^l), \quad \mathcal{P}_{sx}^l = \alpha_s E_{1x}^l(r_s^l), \quad (29)$$

to which we must still add Eqs. (24) and (25), which express the internal field  $\mathbf{E}_1$  in terms of the dipole moments due to displacements  $\mathbf{p}_s^l$  and electronic shells  $\mathcal{P}_s^l$ .

Thus the problem of determining the dielectric constant  $\epsilon$  as a function of  $\omega$  and  $\mathbf{K}$  reduces to equations for the propagation of electromagnetic waves together with equations for oscillation of the nuclei. To solve them we must know the potential energy of the non-electrostatic forces  $U^0$ . Thus the polarization properties of the crystal are closely related to the properties of the lattice and consequently to the whole variety of physical properties of the crystal. The non-electrostatic forces  $U^0$  can be subdivided into: 1) corrections to the law of interaction of point charges, because the ions have finite dimensions, 2) exchange forces of repulsion (these are also short range), and 3) Van der Waals forces having the dependence  $\sim 1/R^6$ . In practice all of these forces are different from zero only for nearest and next nearest neighbors. In the expansion of the potential energy in the displacements, for each pair of ions we obtain a function with three (and under the assumption of central forces — only two) parameters. Thus in the simplest case of binary cubic crystals, in the central force approximation when one takes into account the interaction of nearest neighbors, to know  $U^0$  we must assign two parameters, one of which can be eliminated by using the condition of equilibrium of the lattice in the absence of displacements. At the same time the number of experimental data is much greater: the elastic constants  $C_{ijk}$ , the dispersion frequency  $\omega_g$ , and the static dielectric constant  $\epsilon_0$ .

In 1949<sup>3</sup> we proposed a method for treating the physical properties of crystals by using the study of their long-wave acoustical and optical vibrations. At the All-Union Conference on the Physics of Dielectrics in Moscow (1958), we presented the results of a comparison of the theory with experiment for 25 ionic crystals. It appeared that the theory of a lattice of point ions does not enable one correctly to relate all the available experimental data. The situation is not essentially improved by introducing an effective fractional charge  $e^* \neq e$ . There is nothing surprising in this, since in actuality the electronic shells of the ions

overlap, and this overlapping is changed during the displacement and polarization of the ions. In the following section we shall treat various improvements of the theory which take these effects into account.

#### 4. METHODS FOR IMPROVING THE THEORY OF LATTICES, TAKING INTO ACCOUNT THE FINITE DIMENSIONS OF THE IONS

The majority of attempts to go beyond the limits of the theory of a point lattice are directed toward improving the formulas for the effective field. Heckmann<sup>9</sup> proposed to introduce a correction coefficient  $\beta$  into the Lorentz formula  $(4\pi/3)\mathbf{P}$ . Thus in our notation for long waves

$$\mathbf{F} = \mathbf{E}_{\text{mac}} + \frac{4\pi}{3} \beta \mathbf{P}. \quad (30)$$

A similar improvement was introduced by Højendahl.<sup>10</sup> The parameter  $\beta$  was determined from a comparison with experiment, and turned out to be very small. Mott and Gurney proposed to split the polarization  $\mathbf{P}$  into two parts:  $\mathbf{P}_1$  due to the displacements, and  $\mathbf{P}_2$  due to the deformation of the electron shells. Moreover, in calculating the effective field  $\mathbf{F}$ , acting on the ion coordinate, they set

$$\mathbf{F}_1 = \mathbf{E}_{\text{mac}} + \frac{4\pi}{3} (\mathbf{P}_1 + \gamma \mathbf{P}_2), \quad (31)$$

and in calculating the field producing the polarization of the ion —

$$\mathbf{F}_2 = \mathbf{E}_{\text{mac}} + \frac{4\pi}{3} (\mathbf{P}_2 + \gamma \mathbf{P}_1). \quad (32)$$

From a comparison with experiment it turns out that it is best to set  $\gamma = 0$ .

In the author's opinion, all of these operations are entirely too arbitrary. Moreover, the internal field  $4\pi\mathbf{P}/3$  is essentially due to the action of distant ions. (In the usual derivation of this formula, the atom is surrounded by a sphere, and one shows that the fields of all the dipoles inside this sphere cancel, while the field  $4\pi\mathbf{P}/3$  is caused by the surface charge on the sphere.) Therefore, the inclusion of the finite dimensions of the dipoles cannot change its value.

Szigeti,<sup>12,13</sup> on the other hand, proposed completely logically that the short-range forces can, just as well as the long-range forces, have a polarizing influence on the ions. For binary cubic crystals, he sets the dipole moment of a pair of ions resulting from the short-range forces proportional to their relative displacement. In our notation this part of the polarization  $\mathcal{P}_1 + \mathcal{P}_2$  is equal to:

$$\Delta (\mathcal{P}_1 + \mathcal{P}_2) = (s-1) ze (\mathbf{u}_1 - \mathbf{u}_2), \quad (33)$$

where  $z$  is the valence of the ion, and  $s$  is a parameter of the theory. From a comparison with experiment it turns out that  $s < 1$ , and thus, as the nuclei approach one another, their electron shells tend to

shift to opposite sides. Szigeti's theory gives better agreement with the observed values of the static ( $\epsilon_0$ ) and the high frequency ( $n^2$ ) dielectric constants, the dispersion frequency  $\omega_g$ , and the compressibility of crystals;  $s$  is determined from the relation

$$\frac{\epsilon_0 - n_0^2}{(n_0^2 + 2)^2} m\omega_g^2 = \frac{4\pi}{g} N |zse|^2. \quad (34)$$

The results of Szigeti's theory are sometimes interpreted in terms of an effective charge  $e^*$ . Thus, if we add the dipole moment resulting from the displacement to the quantity (33), we find

$$\mathcal{P} = sze(u_1 - u_2) = ze^*(u_1 - u_2), \quad (35)$$

where  $e^* = se$  plays the role of the charge of an ion in the theory of a point lattice. The value of  $s$  varies from 0.48 for ZnS to 1.10 for TlBr and for most alkali halide crystals lies in the range 0.7 - 0.8.

In our opinion, however, it is inconsistent to include the effect of displacements on polarization and not to include the reciprocal action of the polarization on the displacements. It is clear that by applying an electric field and causing the ions to polarize we, in agreement with (33), should obtain some force acting on the nucleus. However, Szigeti did not consider this effect.

The tendency to confuse two different concepts — the magnitude of the dipole moment divided by the relative displacement of the pair of ions  $\mathcal{P}/(u_1 - u_2)$  and the average charge of an ion — already appeared in the work of Eucken and Büchner<sup>14</sup> (1934) and Lundqvist.<sup>15</sup> Lundqvist using the Heitler-London method and the theory of rigid ions, treated the effect of overlapping of electron shells and came to the conclusion that it was necessary to assign fractional average charges to the ions. Phenomenologically, there is nothing to prevent one from introducing the concept of  $e^*$  according to formula (35). However, this quantity will have nothing in common with the true average charge of each ion. In addition, one cannot treat the dipole moments of the electron shells  $\mathcal{P}_1^l$  and  $\mathcal{P}_2^l$  as unique functions of the displacements of just these two ions. They may be changed, for example, by the external field which exists for undisplaced nuclei or as the result of the displacement of the surrounding nuclei. As we saw in Sec. 2, each  $\mathcal{P}_s^l$  is determined by the field produced by all the surrounding ions. This circumstance is masked to a certain extent in the case of homogeneous fields when all the displacements and dipole moments of the ions of the same type are identical, which permits us to apply formula (35), but shows itself completely in inhomogeneous fields. Therefore, to avoid misunderstandings one should strictly distinguish dipole moments produced by displacements of nuclei and those produced by polarization of the electron shells.

The relative independence of the quantities  $\mathcal{P}_s^l$  and  $u_s^l$  is shown very well from a consideration of the normal amplitudes of oscillation of the lattice. For dif-

ferent branches and different values of the wave vector  $\mathbf{K}$ , one obtains a whole variety of relations between the amplitudes  $\mathcal{P}_1$ ,  $\mathcal{P}_2$  and  $u_1$ ,  $u_2$ . For the longitudinal optical branch  $\mathcal{P}_2$  is of the order of  $p_2 = -eu_2$  and opposite in direction. For the transverse optical branches  $\mathcal{P}_1$ ,  $\mathcal{P}_2$  have the same direction as  $p_1$  and  $p_2$ , while their values are smaller. For the acoustical branches,  $\mathcal{P}_1/p_1$  and  $\mathcal{P}_2/p_2$  are much smaller than for the optical branches. It is clear that all this variety of relations cannot be described by means of a single parameter  $s - 1$ : one should assume an "effective charge" for each ion which is different for the different branches and the various values of the wave vector  $\mathbf{K}$ . A phenomenological description of the polarization of the unit cell by means of (35) is possible only in the limit of long waves.

We should also mention the work of Tenez<sup>16</sup> who considered the eigenfrequencies of oscillation of the KCl lattice and introduced the parameter  $e^*$  into the theory of a point lattice. This paper must be criticized for inconsistency for the same reasons.

## 5. THE QUANTUM-MECHANICAL BASIS OF THE DYNAMICS OF CRYSTAL LATTICES AND THE ADIABATIC APPROXIMATION

As we have seen in the preceding sections, the theory of the polarization of a crystal in an electric field through displacement of the nuclei is closely related to the dynamical properties of the crystal lattice, since for the determination of the displacements of the nuclei one must know the potential energy of the non-electrostatic forces  $U^0$ , and the assignment of  $U^0$  in a model with point ions turns out to be unsatisfactory.

Born and Huang<sup>6</sup> give a completely rigorous approach to the dynamics of crystal lattices based on quantum mechanics and the adiabatic approximation. It is assumed that it is possible to find the  $\Psi$  function and the energy  $U$  of a system of electrons in a crystal for arbitrary small deviations of the nuclei from their equilibrium positions. Because of the enormous difference in masses, when the nuclei move, the light electrons "adjust themselves" to each new position of the nuclei, and  $\Psi$  and  $U$  change adiabatically and without inertia as a result of the displacements of the nuclei. Obviously then the eigenvalue of the energy of the electrons  $U$  is a function of the displacements of the nuclei and will play the role of a potential energy when we treat their motion.

To realize this program in practice with complete precision is as yet impossible. Therefore at the present time the theory of Born and Huang unavoidably contains a very large number of unknown functions and parameters and requires simplification and specification for practical application.

Independently of these authors, in Kiev beginning in 1949 we developed the dynamics of a crystal lattice of special type by essentially equivalent methods.<sup>3,17-20</sup>

The wave function of the electrons in the crystal  $\Psi$  was constructed as an anti-symmetrized product of the  $\Psi$  functions of the individual ions, which differ slightly from the functions for isolated ions and can be subjected to small changes under the action of the external fields and the displacements of the nuclei. In this way one achieves an adiabatic approximation and takes account of the change in the  $\Psi$  function and the energy of the electrons as a result of nuclear displacements. The system of equations for the dynamics of a crystal has the form (29), (24), and (25). Here the non-electrostatic part of the potential energy  $U$  contains, in addition to the terms used earlier containing both  $\mathcal{P}_S^l$  and  $u_S^l$ , additional terms which were called exchange-dipole terms and represented the change in the exchange energy when the ions are polarized. The appearance of these terms led to a relation of the type of (33) in the limit of long waves. However, these terms could be used for any oscillations and took into account the reaction of the dipole moments on the displacements, which was omitted in the work of Szigeti. The results of a comparison of this theory with experiment for 25 crystals were presented at the Second All-Union Conference on the Physics of Dielectrics in Moscow (1958).<sup>21</sup> As one sees from these results, the concepts of a fractional charge of an ion  $e^*$  and of exchange-dipole forces in a phenomenological sense can, to a certain extent, replace one another. In particular, in our theory also one obtains a formula of the type of (34) for determining the parameter  $\beta$  of the exchange-dipole forces, which is approximately equal to Szigeti's parameter  $s$ , but the two hypotheses are not completely equivalent.

The picture of exchange-dipole forces, as we have seen,<sup>21</sup> leads to a somewhat better agreement with experiment for the elastic constants. Still, apparently, in all crystals one must take into account both these forces and some heteropolar binding and a difference of  $e^*$  from  $e$ .

A more detailed treatment of the coupling of the displacements of atoms with their polarization leads to entirely new effects in the theory of homopolar crystals. Together with V. S. Mashkevich<sup>22</sup> we have given an adiabatic treatment of homopolar crystals with lattice of the diamond type. From the point of view of the elementary theory of such a crystal which contains uncharged atoms, one should, for all frequencies, have only inertialess polarization described by the formulas and equations of Sec. 2. In actuality, although the electrostatic energy of such a crystal is described by a quadratic form in only the dipole moments of the electron shells  $\mathcal{P}_S^l$ , and does not contain the nuclear displacements, nevertheless the non-electrostatic part of the potential energy  $U$  contains exchange-dipole terms described by expressions which are bilinear in  $\mathcal{P}_S^l$  and  $u_S^l$ . The presence of such terms results in a coupling between the displacements and the polarizations of the atoms. During the displacements, dipole moments appear, and the polarization gives rise

to forces acting on the nuclei. Thus there appears an interaction of the nuclear displacements of a non-polar crystal with the electric field, and the complete difference between polar and non-polar crystals disappears.

For chemically homogeneous media (diamond, silicon, germanium) in the case of very long waves, the dipole moments of two atoms in the cell compensate one another completely for the optical vibrations of the lattice, and the interaction we have described disappears. However, with decreasing wave length, the dipole moment of the unit cell increases linearly with  $K$ , and for essentially inhomogeneous fields there is a sense to speaking of an inertial polarization of these crystals, just as in ionic dielectrics. In the case of electromagnetic waves with frequency close to the limiting frequency of the normal vibrations of the lattice, this interaction leads to peculiarities in the propagation of light (in the far infrared region): to dispersion, to a weak double refraction and absorption of light, to the appearance of marked anisotropy and dichroism.

Our papers in collaboration with Mashkevich<sup>22-24</sup> were criticized in a paper of M. Lax.<sup>25</sup> Lax correctly emphasized that in the limit of long waves ( $K = 0$ ) the dipole moment of optical vibrations in the linear approximation in the displacements should be absent in a lattice of the diamond type. (The crystal has a center of inversion which lies midway between the nearest neighbor atoms.) Therefore the energy of interaction of the light with the crystal  $\mathbf{E} \cdot \mathbf{P}$  should be of order  $aK$ , while the intensity of the one-phonon absorption is  $(aK)^2 \sim 10^{-8}$  of the intensity of absorption in ionic crystals. Therefore Lax insists that the principal infrared absorption in crystals of the diamond type is due to anharmonicity of the vibrations (two-phonon absorption), which is treated theoretically by him together with Burstein.<sup>26</sup>

Although we agree with this last conclusion, it should, however, be mentioned that one-phonon absorption due to the dipole moment  $\mathbf{P} \sim aK$  has a definite angular dependence and a clearly expressed dichroism which enables one to distinguish it experimentally. The corresponding band should be very narrow, and its integral intensity should be  $10^8$  times smaller than in ionic crystals (where this band is very broad), the absorption coefficient at the maximum is about  $1 \text{ cm}^{-1}$  which is entirely accessible to measurement. Thus, on the background of a broad weak band due to the anharmonicity, one should expect a narrow peak. Such a picture is actually observed in diamond, silicon, and germanium.<sup>26</sup> One might think that the peaks at  $1280 \text{ cm}^{-1}$ ,  $625 \text{ cm}^{-1}$ , and  $345 \text{ cm}^{-1}$  correspond to the one-phonon absorption predicted by theory.<sup>24</sup> To settle this question one must investigate experimentally the dependence of the absorption coefficient in the peak on the direction of propagation  $K$  and on the polarization of the light. Such an investigation would be of very great interest.



Even if the one-phonon absorption can be neglected in the infrared region, as Lax believes, this would not be an argument against the role of polarization effects and the coupling of displacements and polarization in non-polar crystals. These effects will be significant for short-wave oscillations: for example, in the problem of the dispersion of the natural frequencies and the temperature dependence of the specific heat or in the problem of the interaction of the displacements in a crystal with charged defects, and to ignore them is not possible. This is shown by a comparison with experiment of the theoretical dispersion law  $\omega(\mathbf{K})$  for germanium, of which we will speak further later on.

The picture is markedly changed if we go over to crystals of this same type, but with different atoms in the unit cell, for example SiC. Then as a result of the asymmetry of the exchange-dipole forces, the dipole moment of the unit cell is not cancelled even for the limiting long waves of the optical vibration branches. Therefore, such compounds should behave like polar compounds. The crystals should have different eigenfrequencies for the longitudinal and transverse oscillations and be characterized by different static and high-frequency dielectric constants  $\epsilon_0$  and  $n_0^2$ , and exhibit the usual dispersion in the infrared part of the spectrum  $\epsilon(\omega)$ , despite the fact that the atoms of the crystal are not charged! It is interesting that all these properties were actually observed in SiC by Spitzer, Kleinman, and Frosch.<sup>27</sup> These authors estimated the effective charge of each atom to be equal to 0.94e and concluded that they are dealing "definitely with an ionic crystal."

In Figs. 1 and 2 we show the initial part of the dispersion curves  $\omega(\mathbf{K})$  of the normal vibrations of ionic and non-polar crystals. The curves are obtained by solving the system (29), (24), and (25) by an expansion in powers of  $a\mathbf{K}$  with and without retardation (dashed curves). When the retardation is omitted, the optical frequencies of the ionic crystal are found to differ by a factor of  $\sqrt{\epsilon_0}/n_0$  for the longitudinal and transverse vibrations. When the retardation is included, the number of branches is increased by two, corresponding to the fact that the frequency  $\omega$  drops out in the denominator of the right side of (29)

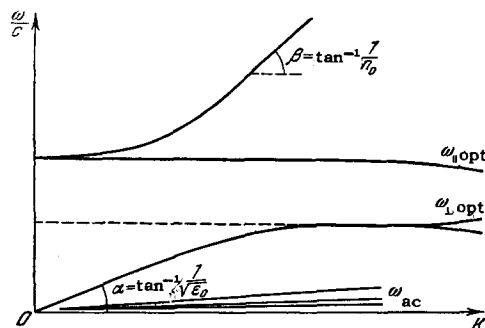


FIG. 1. Initial portion of the dispersion curves  $\omega(\mathbf{K})$  for ionic crystals. Dashed curve - neglecting retardation. Solid curves - including retardation.  $\omega_{ac}$  are the acoustic branches,  $\omega_{l,opt}$  and  $\omega_{t,opt}$  are the longitudinal and transverse optical branches.

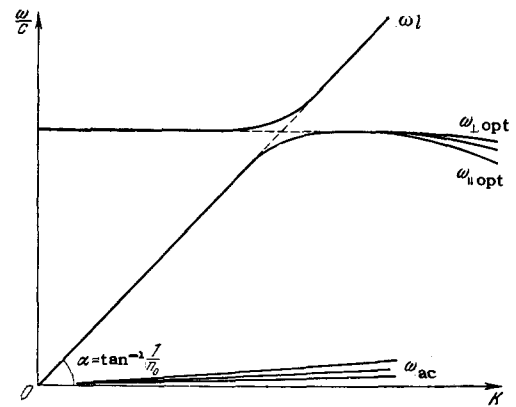


FIG. 2. Initial portion of the dispersion curves  $\omega(\mathbf{K})$  for non-polar crystals.  $\omega_l$  is the so-called "light branch." The other notations are the same as for Fig. 1.

and the order of the system is increased. The "superfluous" oscillations correspond to the two degrees of freedom of the electromagnetic field. We should remember here that over a broad region around  $\omega \sim \omega_g$  one cannot speak separately of electromagnetic vibrations and lattice vibrations. The process of propagation of the field and the oscillations of the nuclei are closely coupled with one another, since the oscillating ions produce a field and the field has an effect on the oscillations of the ions: we are dealing with a pair of tightly coupled systems whose individual motions can be detected only when we go far away from the given region of frequencies and wave lengths. This circumstance was pointed out by the author in his first paper.<sup>3</sup> In 1951 this result was stated again independently by Huang<sup>28</sup> on the basis of a macroscopic approach. As already stated, when one includes retardation the point  $\mathbf{K} = 0$  ceases to be singular, and the frequencies of longitudinal and transverse oscillations coincide there.

For homopolar crystals the effect of interaction of field and oscillations in the long-wave region are small, and analogous singularities in the behavior of the curves are observed only in the immediate neighborhood of the limiting frequency. There the oscillation takes on a mixed optical-mechanical character, there is a "mixing together" of light and optical oscillations, and one observes a small dispersion. The effect of double refraction is of order  $a\mathbf{K}$  and can be studied. (In crystals of the NaCl type, it is of order  $a^2\mathbf{K}^2$  and lies outside the limits of accuracy of measurement.) The double refraction is anisotropic in  $\mathbf{K}$  and vanishes in the [100] and [111] directions. For non-polar crystals with different atoms, the picture is intermediate between Figs. 1 and 2, but is closer to the case of ionic crystals.

## 6. POLARIZATION OF IONIC CUBIC CRYSTALS BY THE FIELD OF A CHARGE LOCATED AT A LATTICE SITE

For crystals in which the function  $U^0$  is known and the eigenfrequencies and amplitudes of oscillation

$\omega_{\alpha\mathbf{K}}$  and  $\mathbf{p}_{\mathbf{S}}^{\alpha\mathbf{K}}$ ,  $\mathcal{P}_{\mathbf{S}}^{\alpha\mathbf{K}}$  are calculated, one can easily find the deformation of the crystal by a field of arbitrary type. To do this, we introduce the normal coordinates  $q_{\alpha\mathbf{K}}$  ( $\alpha$  is the branch number and  $\mathbf{K}$  the wave vector), in terms of which the lattice energy is represented as a sum of squares, and the equations of oscillation under the action of an external electric field can be separated and take the form

$$q_{\alpha\mathbf{K}} + \omega_{\alpha\mathbf{K}}^2 q_{\alpha\mathbf{K}} = Q_{\alpha\mathbf{K}} = \sum_{\mathbf{s}} E_{\text{osx}} (P_{\text{sx}}^{\alpha\mathbf{K}} + \mathcal{P}_{\text{sx}}^{\alpha\mathbf{K}}). \quad (36)$$

In a static field

$$q_{\alpha\mathbf{K}} = \frac{Q_{\alpha\mathbf{K}}}{\omega_{\alpha\mathbf{K}}^2}. \quad (37)$$

The energy of all the dipoles in the external field is equal to twice the internal energy of the crystal with opposite sign, and leads to a sum of squares  $Q_{\alpha\mathbf{K}}^2 / \omega_{\alpha\mathbf{K}}^2$ . In Table III we give the results of a computation of the contribution of the inertial part of the polarization to the energy  $U_q$  of the crystal, and also the total energy of the crystal in the field of a point charge,

**Table III.** Contribution of the energy of displacements of the nuclei, and total energy of the crystals NaCl, KCl, and KBr, where there is a point charge at one of the lattice sites

Crystal	Excess charge on cation		Excess charge on anion	
	$U_q$ (in ev)	$U_{\text{tot}} = U_q + U$	$U_q$	$U_{\text{tot}} = U_q + U$
NaCl	-1.843	-4.287	-2.219	-3.706
KCl	-1.356	-3.310	-2.029	-3.414
KBr	-1.431	-3.449	-1.719	-3.251

computed in this fashion. This polarization energy, together with the Madelung energy, essentially determines the work required for removing an ion from the lattice. In completely analogous fashion, one can also compute the energy of interaction of two charges placed at lattice sites which are close to one another. To do

this one must, as in Sec. 2, find the energy of the crystal in the field  $E_0$  produced by the two charges  $e_1$  and  $e_2$ , and separate out the part which is proportional to the product  $e_1 e_2$ . The results of such a computation, also carried out by V. I. Fedorchenko, are given in Table IV. As one sees from the table, the energy of interaction for a minimal separation  $r = a$  is approximately 1.5 times greater than the energy computed using the Coulomb law. This difference decreases gradually as the distance  $r$  is increased. These results should be kept in mind in finding the binding energy of an electron to an impurity center which possesses a charge. In those cases where the radius of the electron state is comparable with the lattice constant, the potential energy differs essentially from the macroscopically computed value  $e^2/\epsilon r$ .

## 7. THE MOST PRESSING PROBLEMS OF THE THEORY OF POLARIZATION OF CRYSTALS

An analogous computation in other crystals is of interest, as well as a further study of the behavior of defects, including mobile defects, in more complicated systems and in particular in ceramic compounds, polymers, and dielectrics having large values of  $\epsilon$ . As we have seen, this is entirely possible in principle. It is necessary only to know the potential energy  $U$  of the non-electrostatic forces in the lattice. The advantage of binary cubic crystals is simply that for them  $U$  can be expressed by means of a small number of parameters. For their determination one can use the elastic constants of the lattice and the values of the dispersion frequencies. In more complicated systems (ternary, etc.) the number of parameters determining  $U$  increases markedly, and one begins to lack sufficient experimental data. Here the theorist is helped by the new, very effective method of neutron spectroscopy. By studying the scattering of slow neutrons (for  $T = 1 - 4^\circ\text{K}$ ) and measuring the energy loss as a function of scattering angle, one can simultaneously determine the change in energy and momentum of individual groups of neutrons. According to the conservation

**Table IV.** Energy of interaction of charges located at neighboring and next nearest sites of the lattice, including polarization and displacement of ions

Location of charges	Separation of charges	Crystal	Energy of interaction	Energy according to the Coulomb law	% of Coulomb energy
$s_1=1$	$r=a$	NaCl	1.377	0.873	157.8
KCl		1.448	0.941	154.0	
KBr		1.143	0.906	126.2	
$s_2=2$	$r=a\sqrt{2}$	NaCl	0.954	0.617	154.5
KCl		0.817	0.665	122.8	
KBr		0.909	0.640	141.9	
$s_1=1$	$r=a\sqrt{2}$	NaCl	1.006	0.617	162.9
KCl		0.633	0.665	95.2	
KBr		0.729	0.640	133.8	
$s_2=2$	$r=a\sqrt{3}$	NaCl	0.431	0.504	85.5
KCl		0.637	0.543	117.3	
KBr		0.532	0.532	101.8	

laws,  $\Delta\epsilon = -\hbar\omega_{\alpha\mathbf{K}}$  and  $\Delta\mathbf{P} = -\hbar\mathbf{K}$ , since the majority of scattering acts occur with the creation of a single phonon. Then one obtains the experimental dependence of  $\omega_{\alpha\mathbf{K}}$  on  $\mathbf{K}$ , i.e., the dispersion law for the normal oscillations of the crystal. One and certainly several such curves for various branches and directions of the wave vector (it is convenient to align  $\mathbf{K}$  with the [100], [110], and [111] directions) represent an invaluable addition for the theorist, since they make it possible to determine a large number of the parameters which appear in  $U$ , and thus to construct the dynamics of the lattice.

Quite recently there have appeared papers by Brockhouse and Iyengar<sup>29</sup> and Palevsky, Hughes, Kley, and Tunkelo,<sup>30</sup> in which they have investigated the dispersion of  $\omega(\mathbf{K})$  in the [100] and [111] directions for germanium and silicon. The nature of the curves of  $\omega(\mathbf{K})$ , and in particular the large difference between the frequencies of the short-wave oscillations of the transverse optical and acoustic branches are in contradiction with the theory which includes only the interaction of nearest neighbors. Although for non-polar crystals the assumption of short range forces is completely reasonable, the experimental curves of  $\omega(\mathbf{K})$ , as well as the temperature variation of the specific heat, differ significantly from the predictions of the theory of Hsieh,<sup>31</sup> which took account of the interactions only in the limit of the nearest and next nearest neighbors (first and second configuration spheres). To obtain good agreement with experiment it appears necessary to include interactions within the first six configuration spheres! The corresponding theory which contains 21 parameters was presented by Cole and Kineke<sup>32</sup> and by Herman.<sup>33</sup> These authors showed that to obtain good agreement with experiment it is not enough to include the interaction even within the first four spheres, but that it is important to include the contributions of the fifth and sixth spheres. However, a theory with such a large number of parameters to a very definite extent loses value and simply leads to a method for choosing an interpolation formula whose parameters may have no physical meaning. The only thing that remains unquestionable is the conclusion that the long range forces play an important role in this crystal.

From the point of view of our picture of the short-range valence binding it is quite impossible to understand why the interaction at such large distances is important. M. Lax<sup>34</sup> has proposed that these relatively long-range forces are due to quadrupolar polarization of atoms in the inhomogeneous field and the resulting quadrupole-quadrupole forces. So far, such forces have been taken into account only in the single paper of Herpin.<sup>35</sup> He treated quadrupolar polarization in crystals of the NaCl type and showed that it can explain the small deviation in these crystals from the Cauchy relation  $C_{12} = C_{44}$ .

We cannot completely agree with Lax's conclusion because with the relatively rapid fall-off of the quadrupole forces with distance, the main contribution to  $U$  must come from the interaction in the first four spheres. However, this interaction actually is taken into account in the theory<sup>32,33</sup> and nevertheless turns out to be insufficient. Obviously we are dealing here with a true long range interaction which may be simply a dipole-dipole interaction. This was convincingly shown by Cochran<sup>36</sup> on the example of germanium. Cochran started from a model proposed by Dick and Overhauser,<sup>37</sup> according to which a binary ionic cubic crystal can be characterized by a double set of coordinates: the coordinates of the framework (the nuclei) and the coordinates of the centers of the shells treated as spheres. All these coordinates are coupled by quasi-elastic forces, where the masses of the electron shells can be neglected in the equations of motion.

Carrying over this model to valence crystals, where the atomic shells are not closed, Cochran makes use of the results of Mashkevich and Tolpygo<sup>22</sup> where  $U$  is expressed as a quadratic function of the displacements and the dipole moments of all the atoms, and shows that the replacement of the variables of the "nuclear shell model"<sup>37</sup> reduces to the model of  $u_S^l \mathcal{P}_S^l$  in reference 22. However, the direct use of the results of reference 22 for germanium leads to incorrect results, to an infinite jump for  $\omega(\mathbf{K})$ . As was verified by T. I. Kucher, the matrix  $C_{SS}^{-1,xy}$ , by means of which one eliminates the dipole moments  $\mathcal{P}_S^l$  from the equations for the oscillations, is subjected to an infinite discontinuity on a certain surface  $F(k_x k_y k_z) = 0$  both in germanium and in silicon. Cochran treated a somewhat more general expression for  $U$ , which includes the non-electrostatic (exchange-dipole in our terminology) interaction of nearest dipoles  $\mathcal{P}_S^l$  (they were neglected in reference 22 for insufficient reason, as we see now). With a relatively small number of parameters, a portion of which are eliminated by means of the known values of the elastic moduli, Cochran obtained good agreement with experiment for the dispersion law.

Thus it appears sufficient to take account of the non-electrostatic interaction just for nearest neighbors and that the apparent "long range interaction in non-polar crystals" is caused by electrostatic forces between dipoles which arise as a result of displacements of the atoms.

Cochran's work clearly shows how important a role is played by exchange-dipole forces in atomic crystals. Because of the strong overlapping of electron shells of neighbors in the formation of valence bindings, there is a marked effect of mutually deforming forces of the atoms on one another. From this one may conclude that the polarization energy of these crystals in highly non-uniform fields will be large.

Thus we see that the main problems of the theory of polarization of crystals essentially reduce to the more general problem of constructing a lattice dynamics on the one hand, and to the study of the nature of defects which influence the polarization properties on the other hand. This latter problem has not been discussed by us here, but it is clear that the theory of defects is essentially contained in the problem of the dynamics of lattices. As for the problem of the internal field, in principle it is completely clear, and one needs only study methods for rapidly computing this field for different structures by using the already known formulas.

If these principal problems are solved, then one will also have solved the problem of the polarization of ideal crystals in an arbitrary fields, as well as obtained a basis for a correct study of the behavior of defects in a lattice.

On the other hand, we have seen that the problem of lattice dynamics becomes more and more complicated as the theory develops. We are already no longer satisfied with the theory of a point lattice or with the theory of point ions and dipoles. In certain cases one can take account of quadrupolar polarization and exchange-dipole forces. Finally, one should point out the most pressing problem, in our opinion, of constructing a dynamics of a crystal with an average charge which is equal to some fractional value. If the atomic crystals of diamond, graphite, Si, and Ge represent only an example of a crystal with uncharged atoms, then even in the "most heteropolar compounds," such as NaCl and other alkali-halide crystals, there is reason to assume that the charge on the ions is a fraction, equal to 0.9e.

A strictly heteropolar crystal is possibly an unobtainable limiting case, and most compounds, such as MgO, ZnS, InSb, and Cu<sub>2</sub>O, not to speak of more complicated compounds, such as BaTiO<sub>3</sub> etc., are only partially polar compounds. In addition to the work of Tenerz<sup>16</sup> and Lundqvist<sup>15</sup> which we have mentioned, the problem of incomplete heteropolarity has been treated by Löwdin<sup>38</sup> and also by Tomishima and Asano<sup>39</sup> for the ZnS crystal. In recent papers of Potter,<sup>40</sup> starting from an analysis of the experimental data on the dispersion of  $\epsilon$ ,  $n_0^2$  and elastic properties, there has been found the average charge in ZnS, InSb, and CaSb. Merten<sup>41</sup> made a calculation of the eigenfrequencies in ZnS in the approximation of an average ion charge.

In our opinion, all of the papers in this direction are distinguished by one main assumption: they are based on the use of a constant fractional charge. It is clear that if the joining of ions to form a crystal leads to a change in the charge, then every compression and expansion of the crystal and every deformation of more general type also should lead to a change in the value of the charge. Thus, during the lattice oscillations, in addition to the change in displacements

$u_s^l$  and dipole moments  $\mathcal{P}_s^l$  one should also consider change of the charges  $e_s^l$  and the forces resulting therefrom. In particular, the polarization of a crystal will partially be determined by the change in the charge of the ions. In reference 42 there is described an attempt made by the author to construct such a theory. Unfortunately, the mathematical difficulties in this case are very great, and the abundance of unknown parameters makes it difficult to obtain quantitative results.

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Translated by M. Hamermesh