PHYSICAL PROPERTIES OF A ROCK SALT LATTICE MADE UP OF DEFORMABLE IONS

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The energy of interaction between neighbor ions has been determined in the approximation of strongly bound electrons, as a function of the ionic dipole moments and the ion-to-ion distance. The equations of lattice vibrations have been solved taking interaction retardation into account. In the long-wave case, the resulting spectrum of characteristic frequencies of the crystal lattice differs substantially from that obtained in the framework of the Born theory. The Born relationship between the dielectric constant and the limiting vibration frequency changes as well. The dispersion law and the moduli of elasticity for six alkali halide crystals have been determined. A comparison between the theory and the experiment has been made.

1. Introduction

Almost all the works dealing with crystal lattice dynamics proceed from the assumption that the potential energy of an ion pair $v = v(\mathbf{R}_1 - \mathbf{R}_2)$ depends only on the coordinates of ions' nuclei $\mathbf{R}_1$ and $\mathbf{R}_2$. However, this energy substantially depends on properties of the electron shells of ions as well. When the lattice vibrates, those shells become deformed, and the law of interaction between them changes. Since the shape of the electron shells in any ion pair is also governed by displacements of all its neighbors, it is incorrect, in principle, to write down the crystal energy as a sum of ion pair energies. The influence of ion deformation is not at all small. This becomes evident from the fact that the quantities n_0^2 and $\varepsilon - n_0^2$, where ε is the dielectric constant and n_0 the optical refractive index, are of the same order of magnitude. Hence, the same order of magnitude must be inherent to dipole forces originated from the polarization and the displacement of ions.

In the opinion of some authors [1–3], neglecting or taking this deformation, as well as the overlapping of neighbor electron shells, into account incorrectly while calculating the effective field acting on each ion brings

about the situation, where the Born relationship

$$\frac{\varepsilon - n_0^2}{(n_0^2 + 2)^2} m \omega_0^2 = \frac{4\pi e^2}{9\Delta} \tag{1}$$

is usually no more valid. Here, ω_0 is the limiting frequency of ion oscillations; $m = m_1 m_2 / (m_1 + m_2)$ is the reduced mass of an ion pair; Δ is the volume of a unit cell containing two ions with opposite charges (in the considered case, i.e. two face-centered lattices inserted into each other, this parameter is equal to $2a^3$); and a is half the lattice constant. These issues have been discussed in work by Skanavi [4] in detail. The cited authors [1–3] formally "removed" the discrepancies with experiment by modifying the effective Lorentz field $(4\pi/3)\mathcal{P}$ and introducing fitting parameters.

It seems expedient to assign, to every ion, the internal degrees of freedom, which describe its shape, and define the crystal energy as a function of nuclear coordinates and internal coordinates of all ions. In the first approximation, it suffices to take the components of dipole moments $\mathbf{P}_1$ and $\mathbf{P}_2$ of both ions for such internal coordinates. Really, when calculating the energy of an ion in an electric field and without knowing the distribution of the ionic charge density, we have to consider this field to be approximately uniform within the ion limits. In this case, higher multipole moments can be neglected as well, because their energy in a uniform field is equal to zero. The multipole interaction is substantial only between the nearest neighbors and will be taken into consideration approximately in this case.

Supposing the displacement $\mathbf{u}_k^l$ and the dipole moment $\mathbf{P}_l^k$ of every ion to be small (l is the number of a cell and $k = 1, 2$ is the number of an ion in the cell), we can confine the expression for the potential energy of the crystal U to quadratic terms with respect to $\mathbf{u}_k^l$ and $\mathbf{P}_l^k$. Then, every term of the U-expansion will include $\mathbf{u}_k^l$ and $\mathbf{P}_l^k$ associated with no more than two ions, so that U will become decomposed into a sum of

pair energies $v = v(\mathbf{R}_k^l, \mathbf{P}_k^l, \mathbf{R}_{k'}^{l'}, \mathbf{P}_{k'}^{l'})$, where $\mathbf{R}_k^l$ stands for the coordinates of the nucleus of the $\frac{l}{k}$-th ion.

The most natural way to define the function v consists in the consideration of two isolated ions. We will carry out the corresponding calculation in the framework of the model of strongly bound electrons.

2. Energy of an Ion Pair

Let $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_{N_1})$ and $\phi(\mathbf{r}_1', \mathbf{r}_2', \ldots, \mathbf{r}_{N_2}')$ be the wave functions of ions of the Na^+ and Cl^- types, which contain N_1 and N_2 electrons, respectively.

We take the antisymmetrized product of Ψ and ϕ as an approximate wave function Φ for a system of two closely located ions,

$$\Phi = \frac{1}{\sqrt{N}} \sum_\nu \sum_{\substack{\mu_i < \mu_\nu \\ \lambda_i < \lambda_\nu}} \Psi(\mathbf{r}_{\lambda_1}' \mathbf{r}_{\lambda_2}' \ldots \mathbf{r}_{\lambda_\nu}' \mathbf{r}_{t_1} \ldots \mathbf{r}_{t N_1 - \nu}) \times$$

$$\times \phi(\mathbf{r}_{\mu_1} \mathbf{r}_{\mu_2} \ldots \mathbf{r}_{\mu_\nu} \mathbf{r}_{S_1}' \ldots \mathbf{r}_{S N_2 - \nu}'). \tag{2}$$

The expressions for Ψ and ϕ as functions of the ion-to-ion distance $|\mathbf{R}_1 - \mathbf{R}_2|$ will be determined making use of the variational principle. In every term of formula (2), ν radius-vectors $\mathbf{r}_{\mu_1}, \ldots, \mathbf{r}_{\mu_\nu}$ of electrons belonging to the first ion are swapped with the same number of radius-vectors $\mathbf{r}_{\lambda_1}', \ldots, \mathbf{r}_{\lambda_\nu}'$ of electrons belonging to the second ion, and summation is carried out over all permutations. N is the total number of permutations. Since the dimensions of the region, where Ψ and ϕ are different from zero simultaneously, are relatively small, we can confine the consideration to the permutations with $\nu = 0$ and 1, while calculating any matrix elements.

Let $\mathbf{E}_{01}$ and $\mathbf{E}_{02}$ be the strengths of the external electric field at the center of the first and the second ion, respectively. The field is considered to be approximately uniform within the limits of each ion. Then, the average value of the system Hamiltonian is equal to

$$\bar{H} = \bar{H}_1 + \bar{H}_2 + \bar{W} - (\mathbf{E}_{01}, \mathbf{P}_1 + e\mathbf{R}_1) - (\mathbf{E}_{02}, \mathbf{P}_2 - e\mathbf{R}_2). \tag{3}$$

Here, H_1 and H_2 are the Hamiltonians of isolated ions,

$$W = \sum_{i,\kappa} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_\kappa'|} - \sum_\kappa \frac{e^2 Z_1}{|\mathbf{R}_1 - \mathbf{r}_\kappa'|} -$$

$$- \sum_i \frac{e^2 Z_2}{|\mathbf{r}_i - \mathbf{R}_2|} + \frac{Z_1 Z_2 e^2}{|\mathbf{R}_1 - \mathbf{R}_2|}$$

is the potential energy of interaction (in the case $\nu = 0$), and $Z_1 = N_1 + 1$ and $Z_2 = N_2 - 1$ are the charges of ion nuclei. In the approximation concerned, $\bar{W}$ is equal to the sum of Coulomb Q ($\nu = 0$) and exchange J ($\nu = l$) energies (the "correlation energy" is neglected).

Let the expansions of Ψ and ϕ into series of the characteristic functions of isolated ions look like

$$\Psi = c_0 \psi_0 + \sum_x \sum_{i=1}^\infty c_{xi} \psi_{xi} + \sum_k c_k \psi_k,$$

$$\phi = b_0 \varphi_0 + \sum_\xi \sum_{i=1}^\infty b_{\xi i} \varphi_{\xi i} + \sum_\kappa b_\kappa \varphi_\kappa. \tag{4}$$

Here, the functions ψ_{xi} and $\varphi_{\xi i}$ describe various "p-states" of the ions which are chosen in such a way that the matrix elements of coordinate x_i,

$$(0|x_1|xi) = \int \psi_0^* x_1 \psi_{xi} d\tau,$$

and ξ_1,

$$(0|\xi_1|\xi i) = \int \varphi_0^* \xi_1 \varphi_{\xi i} d\tau,$$

are different from zero (for instance, in the Fock approximation, the angular-dependent multipliers of these functions are $\sin\theta \cos\varphi$ rather than usual $\sin\theta\ e^{i\varphi}$). The subscripts x and ξ run through three values (x, y, z) and (ξ, η, ζ), respectively. The functions ψ_k and φ_κ describe other excited states.

Let $E_0, E_{xi}, E_k, \varepsilon_0, \varepsilon_{\xi i}$, and ε_κ denote the energy levels for those states: $H_1 \psi_0 = E_0 \psi_0, H_2 \varphi_{\xi i} = \varepsilon_{\xi i} \varphi_{\xi i}$, and so on. We suppose that the shape of ions does not differ much from the nonperturbed one (spherical): $(|c_{xi}|, |c_k|) \ll c_0 \approx 1$ and $(|b_{\xi i}|, |b_\kappa|) \ll b_0 \approx 1$. Now, we expand $\bar{H}_1$ and $\bar{H}_2$ in the power series in $c_{xi}, c_k, b_{\xi i}$, and b_κ up to the second and J up to the first order inclusive (the exchange integrals calculated making use of the functions $(\psi_0 \varphi_{\xi i})$, and so on are supposed small). It is the indicated coefficients that will play the role of approximation parameters in the functions Ψ and ϕ and will be determined from the variational conditions $\partial \bar{H} / \partial c_{xi} = 0$, and so on.

Certainly, this way does not enable one to obtain the exact wave function for the pair of ions, because the freedom in the choice of Φ has already been restricted by formula (2) and by the condition that $c_{xi}, c_k, \ldots$ are small. However, the accuracy of this method, at least for large distances $|\mathbf{R}_1 - \mathbf{R}_2|$, exceeds considerably that of

the Heitler–London method, where the approximation $(\Psi = \psi_0, \phi = \varphi_0)$ is adopted. The resulting $\bar{H}_{\min}$ is identified with the required $U(\mathbf{R}_1, \mathbf{P}_1, \mathbf{R}_2, \mathbf{P}_2)$. Since we are interested in the interaction energy at arbitrary $\mathbf{P}_1$ and $\mathbf{P}_2$, the extremum of $\bar{H}$ is to be searched, provided that six following conditions are fulfilled:

$$\mathbf{P}_{1x} = -eN_1 \sum_{i=1}^{\infty} 2\mathrm{Re}[(0|x_1|xi)] = \mathrm{const},$$

$$\mathbf{P}_{2\xi} = -eN_2 \sum_{i=1}^{\infty} 2\mathrm{Re}[(0|\xi_1|\xi i)] = \mathrm{const}. \tag{5}$$

Carrying out these calculations, which are not too difficult, separating the interaction between point charges and dipoles from the Coulomb energy Q, and combining all other terms in $\bar{H}_{\min}$, which depend on $\mathbf{R}_1$ and $\mathbf{R}_2$, but not on $\mathbf{P}_1$ and $\mathbf{P}_2$, into a function $u(|\mathbf{R}_1 - \mathbf{R}_2|)$, we obtain

$$\bar{H}_{\min} = \sum_x \frac{\mathbf{P}_{1x}^2}{2\alpha_x} + \sum_\xi \frac{\mathbf{P}_{2\xi}^2}{2\alpha_\xi} - \sum_x \mathbf{P}_{1x}\beta_x - \sum_\xi \mathbf{P}_{2\xi}\beta_\xi +$$

$$+u(|\mathbf{R}_1 - \mathbf{R}_2|) - \frac{e^2}{|\mathbf{R}_1 - \mathbf{R}_2|} + \frac{(\mathbf{P}_1, \mathbf{P}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|^3} -$$

$$-\frac{3e(\mathbf{P}_1, \mathbf{R}_1 - \mathbf{R}_2)(\mathbf{P}_2, \mathbf{R}_1 - \mathbf{R}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|^5} +$$

$$+\frac{e(\mathbf{R}_1 - \mathbf{R}_2, \mathbf{P}_1 + \mathbf{P}_2)}{|\mathbf{R}_1 - \mathbf{R}_2|^3} -$$

$$-(\mathbf{E}_{01}, \mathbf{P}_1 + e\mathbf{R}_1) - (\mathbf{E}_{02}, \mathbf{P}_2 - e\mathbf{R}_2), \tag{6}$$

where

$$\alpha_x = 2eN_1^2 \sum_{i=1}^{\infty} \frac{|(0|x_1|xi)|^2}{E_{xi} - E_0},$$

$$\beta_x = \frac{N_1^2 N_2 e^3}{2\alpha_x} \sum_{i=1}^{\infty} \frac{2\mathrm{Re}[\omega_{xi}^*(0|x_1|xi)]}{E_{xi} - E_0},$$

$$\omega_{xi} = \int \cdots \int \psi_0^*(\mathbf{r}\ldots)\varphi_0^*(\mathbf{r}'\ldots)\omega(\mathbf{rr}')\times$$

$$\times\psi_{xi}(\mathbf{r}'\ldots)\varphi_0(\mathbf{r}\ldots)d\tau,$$

$$\omega_{\xi i} = \int \cdots \int \psi_0^*(\mathbf{r}\ldots)\varphi_0^*(\mathbf{r}'\ldots)\omega(\mathbf{rr}')\times$$

$$\times\psi_0(\mathbf{r}'\ldots)\varphi_{\xi i}(\mathbf{r}\ldots)d\tau, \tag{7}$$

the quantities α_ξ and β_ξ can be obtained by substituting $(0|x_1|xi), \omega_{xi}, E_0$, and E_{xi} in these formulas by $(0|\xi_1|\xi i), \omega_{\xi i}, \varepsilon_0$, and $\varepsilon_{\xi i}$, respectively; and

$$\omega(\mathbf{rr}') = \frac{Z_1}{|\mathbf{R}_1 - \mathbf{r}'|} + \frac{Z_2}{|\mathbf{R}_2 - \mathbf{r}|} - \frac{1}{|\mathbf{r} - \mathbf{r}'|} - \ldots. \tag{8}$$

For the reasons of symmetry, we can put

$$\alpha_x = \alpha_y = \alpha_z = \alpha_1, \quad \alpha_\xi = \alpha_\eta = \alpha_\zeta = \alpha_2.$$

If the x- and ξ-axes coincide with each other and with the direction $\mathbf{R}_1 - \mathbf{R}_2$, then, owing to the suggestion made above that the functions $\psi_{yi}, \psi_{zi}, \varphi_{\eta i}$, and $\varphi_{\zeta i}$ are odd with respect to the relevant coordinates, the integrals $\omega_{yi}, \omega_{zi}, \omega_{\eta i}$, and $\omega_{\zeta i}$ vanish (consequently, so do the quantities $\beta_y, \beta_z, \beta_\eta$, and β_ζ), whereas the integrals ω_{xi} and $\omega_{\xi i}$, together with the quantities β_x and β_ξ, turn out to have different signs. The quantities β_x and β_ξ depend on the properties of and the distance between ions. Generally speaking, $|\beta_x|$ and $|\beta_\xi|$ grow with the increase of ionic dimensions and sharply decrease with increase in the distance $|\mathbf{R}_1 - \mathbf{R}_2|$. The quantities α_1 and α_2 are approximately proportional to the ionic volumes, and $\alpha_1 \leq \alpha_2$ for the majority of alkali halide crystals. Since ω_{xi} and $\omega_{\xi i}$, being exchange integrals, are much more sensitive to ionic dimensions than the matrix elements $(0|x_1|xi)$ and $(0|\xi_1|\xi i)$, and $\alpha_1\beta_x$ differs from α_1 in that $(0|x_1|xi)$ in every term of the sum over i is substituted by ω_{xi}, it is natural to expect that $0 < -\beta_x \leq \beta_\xi$ in the majority of cases. (The positive and negative ions under investigation have similar electron shells and approximately equal polarizabilities at identical dimensions.)

Consider both limiting cases:

$$\beta_x = -\beta_\xi \tag{9a}$$

and

$$\beta_x = 0. \tag{9b}$$

For ions close by dimensions, case (9a) is more preferable. However, if $\alpha_1 \ll \alpha_2$, case (9b) is more

adequate to reality; although, in such a case, due to the smallness of $\mathbf{P}_1$, the value of β_x is of no importance at all, and formulas (9a) and (9b) bring about almost the same results. Below, the calculations are carried on for case (9a).

We suggest that the aggregation of ions into a crystal can change only the values of the parameters $\alpha_1, \alpha_2, \beta_x, \beta_\xi$, and $u(|\mathbf{R}_1 - \mathbf{R}_2|)$, but not the kind of the dependence of $\bar{H}_{\min}$ on $\mathbf{P}_1$ and $\mathbf{P}_2$. Let us write down the potential energy of the crystal in the form

$$U = \sum \bar{H}_{\min} = \sum_l \left\{ \frac{\left(\mathbf{P}_1^l\right)^2}{2\alpha_1} + \frac{\left(\mathbf{P}_2^l\right)^2}{2\alpha_2} + \right.$$

$$+ \sum_{l'}^{(6)} \beta_\xi \left(\left|\mathbf{R}_1^l - \mathbf{R}_2^{l'}\right| \right) \frac{(\mathbf{P}_1^l - \mathbf{P}_2^{l'}, \mathbf{R}_1^l - \mathbf{R}_2^{l'})}{\left|\mathbf{R}_1^l - \mathbf{R}_2^{l'}\right|} -$$

$$- \left(\mathbf{E}_{01}^l + \frac{1}{2}\mathbf{E}_1^l, \mathbf{P}_1^l + e\mathbf{R}_1^l \right) - \left(\mathbf{E}_{02}^l + \frac{1}{2}\mathbf{E}_2^l, \mathbf{P}_2^l - e\mathbf{R}_2^l \right) +$$

$$+ \left. \sum_{l'}^{(6)} u \left(\left|\mathbf{R}_1^l - \mathbf{R}_1^{l'}\right| \right) \right\}. \tag{10}$$

Here, $\mathbf{E}_k^l$ $(k = 1, 2)$ is the strength of the electric field created at the center of the $_k^l$-th ion by other ions considered as point charges e_k and dipoles $\mathbf{P}_{k'}^{l'}$. In the sums over l', the exchange interaction and higher multipole ones with only six nearest neighbors are taken into account.

3. Equations for Lattice Vibrations

Let us put $\mathbf{R}_k^l = \mathbf{r}_k^l + \mathbf{u}_k^l$, where $\mathbf{r}_k^l$ is the radius-vector of the lattice site, expand U into a series up to terms of the order of $\left(\mathbf{u}_k^l\right)^2$, and write down the equations of vibrations:

$$m_k \ddot{\mathbf{u}}_k^l = -\frac{\partial U}{\partial \mathbf{u}_k^l}, \quad 0 = -\frac{\partial U}{\partial \mathbf{P}_k^l}. \tag{11}$$

Both mechanical and optical properties of crystals can be obtained by considering free lattice vibrations. However, the optical phenomena are closely related to the interaction retardation. It turns out that the latter can be taken into account, if one uses Eqs. (11), where U is described by formula (10), and the quantities $\mathbf{E}_1^l$ and

$\mathbf{E}_2^l$ in the latter are interpreted as exact strength values of the field radiated by all oscillating dipoles.

$$\Pi_k^l(\mathbf{r}, t) = \sum_{k'=1,2} \sum_{l'}' \frac{1}{|\mathbf{r} - \mathbf{r}_{k'}^{l'}|} \times$$

$$\times \left[e_{k'} \mathbf{u}_{k'}^{l'} \left(t - \left|\mathbf{r} - \mathbf{r}_{k'}^{l'}\right| / c \right) + \mathbf{P}_{k'}^{l'} \left(t - \left|\mathbf{r} - \mathbf{r}_{k'}^{l'}\right| / c \right) \right] \tag{12}$$

is the Hertz vector created by all ions, except for the $_k^l$-th one. Then,

$$\mathbf{E}_k^l = \left[\nabla \left(\nabla \Pi_k^l \right) - \frac{1}{c^2} \ddot{\Pi}_k^l \right]_{\mathbf{r}=\mathbf{r}_k^l}. \tag{13}$$

Provided that the external field is absent, Eqs. (11) have plane-wave solutions:

$$\mathbf{u}_k^l(t) = \mathbf{u}_k e^{-i\omega t + i(\mathbf{K}\mathbf{r}_k^l)}, \quad \mathbf{P}_k^l(t) = \mathbf{P}_k e^{-i\omega t + i(\mathbf{K}\mathbf{r}_k^l)}. \tag{14}$$

In this case, Π_k^l reads

$$\Pi_k^l(\mathbf{r}, t) = e^{-i\omega t + i(\mathbf{K}\mathbf{r})} \left[(\mathbf{p}_k + \mathbf{P}_k) S_1(\mathbf{r} - \mathbf{r}_k) + \mathbf{p}_{k'} + \right.$$

$$\left. + \mathbf{P}_{k'}) S_2(\mathbf{r} - \mathbf{r}_k) \right], \tag{15}$$

where $k' \neq k, \mathbf{p}_k = e_k \mathbf{u}_k$, and $\mathbf{r}_k = \mathbf{r}_k^l$ at $l = 0$.

S_1 and S_2 are slowly convergent series, the form of which can be easily obtained by substituting Eq. (14) into Eq. (12). Ewald [5] transformed them into rather quickly and uniformly convergent series. However, his result is too complicated. It is more convenient to expand Ewald's formulas (rewritten for a crystal of the definite type) in a power series in the dimensionless wave number $\mathbf{k} = a_2 \mathbf{K}$. The expansion terms of the order of $\mathbf{K}^2$ are sufficient for our purposes, and the quantity $k_0^2 = (a\omega/c)^2$ can be neglected in comparison with unity. For the given lattice of the NaCl type, after elementary but very long numerical calculations, we obtain (see details in work [6])

$$\mathbf{E}_k^l(t) = \frac{2}{\Delta} e^{-i\omega t + i(\mathbf{K}\mathbf{r}_k^l)} \mathbf{F}_k, \tag{16}$$

where

$$\mathbf{F}_k = \frac{2\pi}{3} \mathbf{P} - 2\pi \frac{(\mathbf{P}, \mathbf{k})\mathbf{k} - \mathbf{P}k_0^2}{k^2 - k_0^2} +$$

$+\mathbf{E}_1(\mathbf{k}; \mathbf{p}_k + \mathbf{P}_k) + \mathbf{E}_2(\mathbf{k}; \mathbf{p}_{k'} + \mathbf{P}_{k'}) + \ldots,$

$(k' \neq k)$. Here,

$$\mathbf{P} = \mathbf{p}_1 + \mathbf{p}_2 + \mathbf{P}_1 + \mathbf{P}_2, \qquad (17a)$$

$$\mathbf{E}_1(\mathbf{k}; \mathbf{p}) = -0.237\mathbf{p}k^2 + 0.290(\mathbf{p}\mathbf{k})\mathbf{k} + 0.421(\mathbf{p}; \mathbf{k}\mathbf{k}), \qquad (17b)$$

$$\mathbf{E}_2(\mathbf{k}; \mathbf{p}) = 0.402\mathbf{p}k^2 + 0.986(\mathbf{p}\mathbf{k})\mathbf{k} - 2.191(\mathbf{p}; \mathbf{k}\mathbf{k}), \qquad (17c)$$

the notation $(\mathbf{p}; \mathbf{k}\mathbf{k})$ stands for the vector $\mathbf{e}_x p_x \mathbf{k}_x^2 + \mathbf{e}_y p_y \mathbf{k}_y^2 + \mathbf{e}_z p_z \mathbf{k}_z^2$, and $\mathbf{e}_x, \mathbf{e}_y, \mathbf{e}_z$ are the axis unit vectors. The first term in Eq. (16) is the Lorentz field, the second one is the macroscopic strength of the field $\vec{\mathcal{E}}$. Unlike other terms, it cannot be expanded into a power series in $\mathbf{k}_x, \mathbf{k}_y$, and $\mathbf{k}_z$. This circumstance is related to the fact that Coulomb forces diminish slowly with increase in the distance. Therefore, the analysis of the equations of vibrations made by Born [7,8] on the basis of such an expansion is not applicable in this case. In particular, the conclusion that the given crystals have only one limiting frequency is wrong.

Taking Eqs. (10) and (16) into account, Eqs. (11) read

$$-M_k \mathbf{p}_k k_0^2 = \mathbf{F}_k - G\mathbf{p} + f(\mathbf{P}_2 - \mathbf{P}_1) +$$

$$+ \frac{1}{2}(G + 6H)(\mathbf{p}_{k'}; \mathbf{k}\mathbf{k}) - H\mathbf{p}_{k'}k^2 +$$

$$+ (-1)^k \left\{ \frac{1}{2}f(\mathbf{P}_{k'}; \mathbf{k}\mathbf{k}) - h[3(\mathbf{P}_{k'}; \mathbf{k}\mathbf{k}) - \mathbf{P}_{k'}k^2] \right\}, \quad (18a)$$

$$\mathbf{P}/A_k = \mathbf{F}_k + (-1)^k f\mathbf{p} - (-1)^k \left\{ \frac{1}{2}f(\mathbf{p}_{k'}; \mathbf{k}\mathbf{k}) - \right.$$

$$\left. - h[3(\mathbf{p}_{k'}; \mathbf{k}\mathbf{k}) - \mathbf{p}_{k'}k^2] \right\}, \qquad (18b)$$

where $k = 1, 2, \; k' \neq k$. Here,

$$M_k = m_k \frac{ac^2}{e^2}, \quad A_k = \frac{\alpha_k}{a^3}, \quad H = -\frac{c^2}{e^2}\left[\frac{du(r)}{dr}\right]_{r=a},$$

$$h = \frac{a^2}{e}\beta_\xi(a), \quad f = \frac{2a^3}{e}\left[\frac{d\beta_\xi(r)}{dr}\right]_{r=a} + 4h,$$

$$G = \frac{a^3}{e^2}\left[\frac{d^2u(r)}{dr^2}\right]_{|r|=a} - 4H, \quad \mathbf{p} = \mathbf{p}_1 + \mathbf{p}_2. \qquad (19)$$

The parameter H is determined from the condition that, if $\mathbf{P}_k^l = 0$, the positions of ions at lattice sites $\mathbf{r}_k^l$ correspond to the minimum of U. Considering the uniform expansion $a \to a + \delta$ ($|\delta| \ll a$), we obtain from the condition $(\partial U/\partial \delta)_{\delta=0} = 0$ that $H = \alpha^0/6 = 0.291$, where α^0 is the Madelung constant. For the compressibility of the crystal χ, we similarly obtain

$$\frac{1}{\chi} = \frac{a^2}{18}\left[\frac{\partial^2}{\partial\delta^2}\left(\frac{U}{V}\right)\right]_{\delta=0} =$$

$$= \frac{1}{36a}\left[-\frac{2e^2\alpha^0}{r^3} + 6\frac{d^2u(r)}{dr^2}\right]_{r=a} = \frac{e^2}{6a^4}G, \qquad (20)$$

where V is the crystal volume.

4. Optical Vibrations of the Lattice

Consider long waves. Neglecting the terms of the order of k^2 in Eqs. (18); expanding k_0^2 into the power series in k^2; expressing $\mathbf{p}_1, \mathbf{p}_2, \mathbf{P}_1$, and $\mathbf{P}_2$ in terms of $\mathbf{P}$; and taking Eq. (17a) into account, we obtain

$$k_0^2 = k_{00}^2 + k_{01}^2 + k_{02}^2 + \ldots,$$

$$\left[\left(1 - \frac{2\pi}{3}A\right)\left(G - Af^2 - Mk_{00}^2\right) - \frac{2\pi}{3}\beta^2\right]\mathbf{P} +$$

$$+ 2\pi\left[\beta^2 + A\left(G - Af^2 - Mk_{00}^2\right)\right]\frac{(\mathbf{P}, \mathbf{k})\mathbf{k} - \mathbf{P}k_{00}^2}{k^2 - k_{00}^2} = 0, \qquad (21)$$

where

$$M = M_1 M_2/(M_1 + M_2),$$

$$A = A_1 + A_2, \; \beta = 1 + f(A_2 - A_1).$$

Since, in this approximation, the right-hand side of Eq. (18a) does not depend on the k-value ($k = 1$ or 2), it follows that

$$k_{00}^2(M_1\mathbf{p}_1 - M_2\mathbf{p}_2) = 0. \qquad (22)$$

For optical vibrations, $k_{00} \neq 0$, so that $M_1\mathbf{p}_1 = M_2\mathbf{p}_2$. From Eq. (21), one can see that $\mathbf{P}$ is either
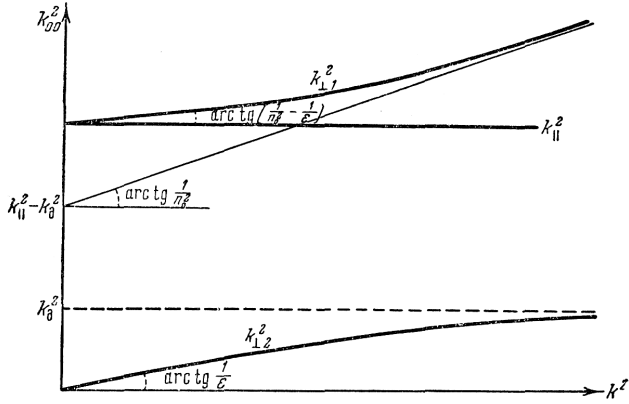
Fig. 1. Illustrative dependence of the frequency on the wave number for extremely long waves $k_{\perp 1}^2$ and $k_{\perp 2}^2$ calculated by formula (26). The dashed line corresponds to neglecting the retardation

parallel or perpendicular to $\mathbf{k}$. In the former case, by putting $k_{00} = k_\parallel$, we have

$$Mk_\parallel = G - Af^2 + \frac{(4\pi/3)\beta^2}{1 + (4\pi/3)A}. \tag{23}$$

On the other hand, in the case of transverse vibrations, we obtain a biquadratic equation for the dimensionless frequency $k_{00} = k_\perp$. In the limiting case $Mk_\perp \gg G$ (the visible and near infra-red ranges), it is reduced to the equation

$$\frac{k^2}{k_\perp^2} = n_\infty^2 = \frac{1 + (4\pi/3)A}{1 - (2\pi/3)A}. \tag{24}$$

If the wave vector $k_\perp$ approaches the dispersion frequency k_∂, we have $k^2/k_\perp^2 \to \infty$, and Eq. (21) brings about

$$Mk_\partial^2 = G - Af^2 - \frac{(2\pi/3)\beta^2}{1 - (2\pi/3)A}. \tag{25}$$

In terms of notations (23)–(25), the solution of the equation mentioned is

$$k_\perp^2 = \frac{1}{2}\left(k_\parallel^2 + \frac{k^2}{n_\infty^2}\right) \pm \sqrt{\frac{1}{4}\left(k_\parallel^2 + \frac{k^2}{n_\infty^2}\right) - \frac{k^2 k_\partial^2}{n_\infty^2}} \approx$$

$$\approx \begin{cases} k_\parallel^2 + \dfrac{k^2}{n_\infty^2} - \dfrac{k^2 k_\partial^2}{k_\parallel^3 n_\infty^2 + k^2} + \ldots \\ \dfrac{k^2 k_\partial^2}{k_\parallel^2 n_\infty^2 + k^2} + \ldots . \end{cases} \tag{26}$$

In Fig. 1, the dependence of k_{00}^2 on k^2 is depicted. The dashed line corresponds to neglecting the retardation, which is evidently eligible only if $k^2 \gg k_{00}^2$, i.e. when the wavelength is much shorter than the wavelength of light of the same frequency in vacuum. In this case, $\mathcal{E} = 0$, and the vibration is purely mechanical. Moving along the second branch towards large wavelengths, we progressively enter into the radiowave range: $k \to 0$ and $k_\perp^2/k^2 \to k_\partial^2/(n_\infty^2 k_\parallel^2) = 1/\varepsilon$. The first branch has no analog in the mechanical theory at all. Its asymptote corresponds to pure oscillations of light in an insulator: $k_\perp^2 = k_\parallel^2 - k_\partial^2 + k^2/n_\infty^2$. In this case, $\mathbf{p}_1 = \mathbf{p}_2 = 0$, so that only $\mathbf{P}_1$ and $\mathbf{P}_2$ oscillate. Each branch of the $k_\perp(\mathbf{k})$-dependence corresponds to two vibrations with different polarizations. Hence, the total number of optical vibrations equals five. This circumstance is associated with the fact that the equations of motion with retardation are not linear differential equations, and two degrees of freedom of radiation join, so to say, three mechanical degrees of freedom. The range $k_0 < k_\perp < k_\parallel$ is a "forbidden gap". For real-valued $k_\perp$, the quantity $\mathbf{k}$ will be imaginary, which means both a decrease of the vibration amplitude with increase in the distance and the absence of the energy transfer. As is known from experiment, crystals effectively reflect light in approximately this frequency range. However, the issues of the light transmission through a crystal with finite dimensions go beyond the scope of this consideration. In this range, the light absorption is substantial, so that an account of vibration anharmonicity is necessary to be made. One can only assert with confidence that the absorption is maximal at $k_\perp \approx k_0$, because a high refractive index $n = k/k_\perp$ corresponds to the large amplitudes of $\mathbf{p}_1$ and $\mathbf{p}_2$, when the anharmonicity-induced transmission of energy to other vibrations is extremely large.

5. Wave Dispersion. Determination of Theory Parameters

We substitute $k_\parallel^2$ by $(\varepsilon/n_\infty^2)k_0^2$ and solve Eq. (21) with $(\mathbf{Pk}) = 0$ to find $n^2 = k^2/k_{00}^2$. This gives us the dispersion law

$$n^2 = n_\infty^2 + \frac{(\varepsilon - n_\infty^2)k_\partial^2}{k_\partial^2 - k_1^2}. \tag{27'}$$

The derivation of the law given above is more rigorous than the conventional one, which is based on the consideration of forced oscillations. It is so, because the presented derivation contains neither an ineligible

identification of the external force acting upon an ion with the strength of the light wave field, nor a doubtful introduction of an "effective field", which would inevitably include some part of ionic interaction.

A comparison of formula (27′) with experiment is expedient to be carried out in the range $k_\perp^2 \gg k_0^2$. Here, the absorption is not high, and the experimental data are the most exact. However, n_∞ cannot be more considered as constant for visible light. Making allowance for the electron dispersion, n_∞^2 is expressed by a multiterm dispersion formula. At $\hbar\omega \ll (E_{xi} - E_0, \varepsilon_{\xi i} - \varepsilon_0)$, this formula can be reduced to a one-term one. Substituting n_∞ by n_0 in the second term of formula (27′)—here, n_0 corresponds to the previous, static definitions of α_1 and α_2; and such an operation is admissible, because this term is small at those frequencies, at which $n_\infty \neq n_0$—we finally obtain

$$n^2 = 1 + \frac{(n_0^2 - 1)\omega_\partial'^2}{\omega_\partial'^2 - \omega^2} + \frac{(\varepsilon - n_0^2)\omega_\partial^2}{\omega_\partial^2 - \omega^2}, \quad \omega_\partial = \frac{c}{a}k_\partial, \quad (27)$$

where ω_∂' is the effective frequency of electron dispersion.

In Fig. 2, the experimental $n(\omega)$-values for NaCl, KCl, KBe, and KJ taken from the Landolt–Börnstein Handbook and for LiF and NaF taken from works [9,10] are exhibited. The curves were drawn by formula (27), where the parameters $n_0, \omega_\partial', \omega_\partial,$ and ε acquire the values that give the best agreement with experiment in the middle section of the range $\omega_\partial \ll \omega \ll \omega_\partial'$. In so doing, the value of n_0^2 is determined with an accuracy of about 0.01%, those of $\omega_\partial'^2$ and $(\varepsilon - n_0^2)\omega_\partial^2$ with an accuracy of no more than 1%, while those of ε and ω_∂^2 separately with an accuracy of 5–7%, i.e. within the spread limits of experimental data obtained at the static determination of ε. From Eqs. (23) and (25), we have

$$G - Af^2 = Mk_\partial^2 \frac{\varepsilon + 2}{n_0^2 + 2}, \tag{28a}$$

$$\beta^2 = \frac{9}{2\pi} \frac{\varepsilon - n_0^2}{(n_0^2 + 2)^2} Mk_\partial^2. \tag{28b}$$

If we neglected the dependence of the exchange energy J on the dipole moments $\mathbf{P}_1$ and $\mathbf{P}_2$, we would obtain—in accordance with Eq. (19)—that $f = 0$ and, hence, $\beta = 1$; so that Eq. (28b) would reduce to Eq. (1). It is this neglect that is implicitly contained, in essence, in all works dealing with the theory of crystals; and just this neglect is responsible for the discrepancy between the Born relation (1) and the experimental data.
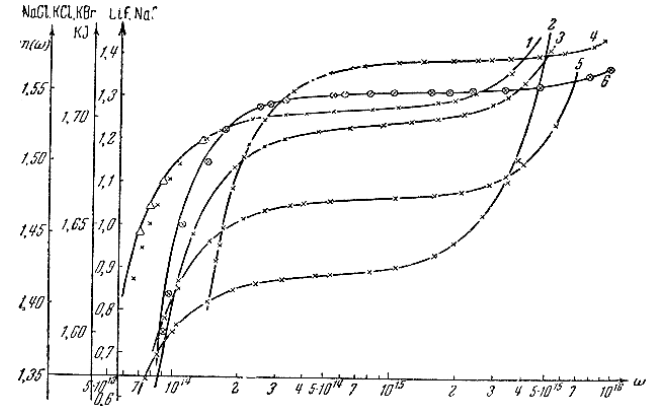

Fig. 2. Comparison of $n(\omega)$ experimental data with curves drawn by formula (27) for the parameters listed in Table 2: KBr (*1*), KJ (*2*), NaCl (*3*), LiF (*4*), KCl (*5*), and NaF (*6*). In the case of curve *1*, crosses correspond to data of work [11], and triangles to data of work [12]

The deviation sign can be easily predicted. Namely, since $\beta_\xi(\mathbf{r}) > 0$ and drastically decreases with the growth of $\mathbf{r}$, $f < 0$ according to Eq. (19), and, therefore, $\beta < 1$ (because $A_2 > A_1$).

To find f, one has to know both A_2 and A_1 separately. Various authors determined the α_1- and α_2-values following independent ways (see works [2, p. 14] and [8, p. 299]). Table 1 demonstrates that all the methods bring about almost identical values for α_1. Since $\alpha_1 \ll \alpha_2$, a small determination error for α_1 almost does not influence the determination accuracy for α_2 calculated by the formula $\alpha_2 = Aa^3 - \alpha_1$. A comparison of α_2 calculated in such a way (the value of A was determined by Eq. (24) assuming $n_\infty \to n_0$, and that of α_1 was taken from the work by J. Mayer and M. Göppert-Mayer) with α_2's obtained by other authors testifies to a sufficient accuracy of formula (16) for the actual field and for all six crystals.

Skanavi [4] drew a conclusion that the Lorentz formula is applicable only to crystals, where the ions are close by dimensions. However, he proceeded from the assumption that the polarizabilities are additive:

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4\pi}{3\Delta}(\alpha_1 + \alpha_2 + \alpha),$$

where α is the polarizability associated with displacements of ions. However, as is evident from more general formulas (18), there is no additivity: owing to the terms $f(\mathbf{P}_2 - \mathbf{P}_1)$ and $(-1)^k f\mathbf{p}$, the displacements of ions give rise to the emergence of a polarization, and vice versa.

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T a b l e 1. Ionic polarizabilities

Crystal	$\alpha_1 \times 10^{24}$ cm^3				$\alpha_2 \times 10^{24}$ cm^3		$A_1 = \alpha_1/a^3$	A by Eq. (24)	α_2 calc.
	Fajans and Joos	Pauling	Born, Heisenberg	Mayer	Fajans and Joos	Pauling			
LiF	0.08	0.029	0.075	0.025	0.98	1.04	0.0031	0.1126	0.89
NaF	0.196	0.179	0.21	0.17	0.98	1.04	0.0137	0.0948	1.01
NaCl	0.196	0.179	0.21	0.17	3.53	3.66	0.0076	1.1467	3.10
KCl	0.88	0.83	0.87	0.80	3.53	3.66	0.0260	0.1344	3.34
KBr	0.88	0.83	0.87	0.80	4.97	4.77	0.0225	0.1488	4.50
KJ	0.88	0.83	0.87	0.80	7.55	7.10	0.0183	0.1639	6.62

T a b l e 2. Most important crystal parameters

Crystal	$a \times 10^8$ cm	$M \times 10^9$	ε	n_0^2	$\omega_\partial \times 10^{-13}$	$\omega_\parallel \times 10^{-13}$	β	f	G	$\omega_d \times 10^{-13}$
LiF	2.01	0.665	8.14	1.9257	6.08	12.51	0.800	-1.875	3.26	5.78
NaF	2.315	1.562	5.26	1.7430	4.42	7.67	0.811	-2.810	4.29	4.64
NaCl	2.814	2.546	5.80	2.3302	3.09	4.88	0.753	-1.877	4.38	3.09
KCl	3.135	3.780	4.78	2.1748	2.68	3.98	0.797	-2.463	5.64	2.66
KBr	3.290	5.601	4.81	2.3585	2.14	3.06	0.756	-2.353	5.65	2.13
KJ	3.525	6.832	5.20	2.6481	1.83	2.56	0.730	-2.003	5.58	1.85

T a b l e 3. Elastic constants of the crystals[†]

Crystal	Calculated						Experimental					Source
	ε	$C_{12}=C_{44}$ (in 10^{11} CGS)	For Eq. (9a) $C_{11}\times10^{-11}$	$\chi\times10^{12}$	For Eq. (9b) $C_{11}\times10^{-11}$	$\chi\times10^{12}$	$C_{12}\times10^{-11}$	$C_{44}\times10^{-11}$	$C_{11}\times10^{-11}$	$\chi\times10^{12}$	T, K	
LiF	8.14	4.92	13.2	1.30	13.0	1.32	4.04	5.54	9.74		300	[13]
	8.73	4.92	12.7	1.37	12.4	1.35	4.33	6.28	11.77	1.467	300	[14]
										1.53	300	
										1.4	extrapol. to 0 K	
NaF	5.26	2.79	12.0	1.74	10.4	1.88				2.11 (powder)	300	
NaCl	5.80	1.28	5.50	3.72	5.35	3.79	1.306	1.281	4.97	4.14	300	[15]
								1.27		4.11	300	
							1.23	1.19	4.67		290	[14]
	6.00	1.28	5.29	3.82	5.15	3.89	1.23	1.265	4.85		300	[13]
							1.31	1.27	4.99		290	[16]
							1.30	1.278	5.06		270	[17]
							1.17	1.332	5.76		80	[17]
KCl	4.78	0.83	5.08	4.46	4.56	4.82	0.64	0.63	3.77		300	
								0.64	3.63		300	
							0.6	0.63	4.08		290	[17]
	4.94	0.83	4.86	4.60	4,34	5.00	0.6	0.66	4.81		80	[17]
										5.52	300	
										5.1		
								0.70	4.71	4.92	extrapol. to 0 K	
KBr	4.81	0.69	4.19	5.40	3.85	5.75	0.54	0.508	3.45		300	[18]
							0.58	0.621	3.33		300	
								0.523	4.175		extrapol. to 0 K	[18]
							0.57		3.46		300	
KJ	5.20	0.52	3.13	7.20	2.97	7.49		0.362	2.69		300	[13]
								0.421	2.67		300	

[†]Unreferenced data were taken from the Landolt–Börnstein Handbook

Different values calculated for the polarizability α_2 of the same anion in different compounds (see the last column in Table 1) are associated with the influence of the cation on the anion properties; the effect was left beyond consideration in Section 2 as an effect of the second order. This cation influence also results in that the value of α_2 for an ion in the crystal is less than that for an isolated one.

To summarize, in Table 2, we list the values of $\varepsilon, n_0^2, \omega_\partial$, and $\omega_\parallel = ck_\parallel/a$ which were obtained from a comparison of formula (27) with experimental results, as well as values for the parameters G, f, and β calculated by formulas (28). The last column contains the values for the frequencies of maximal absorption ω_d taken from work [8]. One can see that the agreement between the ω_d- and ω_∂-values is excellent.

6. Elastic Properties of Crystals

We can obtain an additional confirmation that the deduced law of interaction (6) is correct, by comparing the elastic constants of the crystals with experimental data. We can do it, because all parameters of the theory are already determined. For this purpose, let us consider acoustic vibrations which correspond to putting $k_{00} = 0$ in Eq. (22). Then, from Eq. (21), we obtain, in the zero-order approximation, that $\mathbf{P}^{(0)} = 0$, $\mathbf{P}_1^{(0)} = \mathbf{P}_2^{(0)} = 0$, and $\mathbf{p}_2^{(0)} = -\mathbf{p}_1^{(0)}$. Let $k_0^2 = k_{01}^2$, $\mathbf{p}_1 = \mathbf{p}_1^{(0)} + \mathbf{p}_1'$, $\mathbf{p}_2 = -\mathbf{p}_1^{(0)} + \mathbf{p}_2'$, $\mathbf{P}_1 = \mathbf{P}_1'$, $\mathbf{P}_2 = \mathbf{P}_2'$, and $\mathbf{P} = \mathbf{P}'$.

The first pair of Eqs. (18) looks like

$$\frac{2\pi}{3}\mathbf{P}' - 2\pi\frac{(\mathbf{P},\mathbf{k})\mathbf{k} - \mathbf{P}k_{01}^2}{k^2 - k_{01}^2} - G\mathbf{p}' + f(\mathbf{P}_2' - \mathbf{P}_1') =$$

$$= (-1)^k M_k k_{01}^2 \mathbf{p}_1^{(0)} +$$

$$+ (-1)^k \left\{ E_1(\mathbf{k}; \mathbf{p}_1^0) - E_2(\mathbf{k}; \mathbf{p}_1^0) + H\mathbf{p}_1^0 k^2 - \right.$$

$$\left. - \frac{1}{2}(G + 6H)(\mathbf{p}_1^{(0)}; \mathbf{k}\mathbf{k}) \right\}, \quad (k = 1, 2). \quad (29)$$

For this pair to be consistent, the relevant condition is

$$\frac{1}{2}(M_1 + M_2)k_{01}^2\mathbf{p}_1^{(0)} = 0.348\mathbf{p}_1^{(0)}k^2 + 0.696(\mathbf{p}_1^{(0)}\mathbf{k})\mathbf{k} +$$

$$+ \left(\frac{1}{2}G - 1.739\right)(\mathbf{p}_1^{(0)}, \mathbf{k}\mathbf{k}). \quad (30)$$

This relationship is equivalent to the equation of elastic wave propagation in a continuous anisotropic medium,

$$\rho\frac{\partial^2 \mathbf{q}}{\partial t^2} = C_{44}\Delta\mathbf{q} + (C_{12} + C_{44})\nabla(\nabla\mathbf{q}) +$$

$$+(C_{11} - C_{12} - 2C_{44})\left(\mathbf{e}_x\frac{\partial^2 \mathbf{q}_x}{\partial x^2} + \mathbf{e}_e\frac{\partial^2 \mathbf{q}_y}{\partial y^2} + \mathbf{e}_z\frac{\partial^2 \mathbf{q}_z}{\partial z^2}\right), \quad (31)$$

where ρ is the density, and C_{ik} are the moduli of elasticity. The former equation is reduced to the latter one by substituting $\mathbf{q} = \mathbf{p}_1^{(0)}e^{-i\omega t + i(\mathbf{Kr})}$.

By comparing Eqs. (30) and (31), and making allowance for the relationships between $(\mathbf{k}, M_k, k_{01})$ and $(\mathbf{K}, m_k, \omega)$ given in Section 3, we find that

$$C_{44} = 0.348\frac{e^2}{a^4} = C_{12}, \quad (32a)$$

$$C_{11} = \left(\frac{1}{2}G - 0.655\right)\frac{e^2}{a^4}, \quad (32b)$$

$$\frac{3}{\chi} = C_{11} + 2C_{12} = \frac{e^2}{2a^4}G, \quad (32c)$$

in accordance with Eq. (20).

In Table 3, we give the values for C_{11}, C_{44}, and χ calculated by those formulas both in case (9a), for which all the calculations were carried out, and in case (9b)[1]. Since $\alpha_1 \ll \alpha_2$ for all crystals, the second assumption is closer to the truth. It is also confirmed by the comparison with experiment. However, the discrepancy between those two cases is small. The influence of a probable error in the determination of ε is illustrated making use of LiF, NaCl, and KCl crystals as examples. In so doing, together with the corresponding values $\varepsilon = 8.14, 5.80$, and 4.78, which provide the best results for the dispersion, the values $\varepsilon = 8.73, 6.00$, and 4.94, which are also acceptable in formula (25) without producing a large error, were also used.

While comparing with experiment, one should bear in mind that the theory, in which the thermal motion and even zero oscillations are ignored, should give the best match with experiment at $T = 0$ K. There are no relevant experiments for $n(\omega)$. Meanwhile, the dependence of C_{11} and χ on T is stronger and that of C_{44} is weaker than the temperature dependences of optical constants. The systematic error also stems from neglecting the non-electrostatic interaction between ions located at distances $a\sqrt{2}$ and $a\sqrt{3}$ from one another. At last, the real crystals possess plenty of structural distortions, which are capable to affect $n(\omega)$ and C_{11}, C_{44}, χ differently. So, there are no reasons to exactly identify the values calculated for an ideal lattice with the macroscopical values measured

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[1] See work [6] for more details.

making use of real crystals. This circumstance manifests itself in rather a substantial spread of experimental data.

Having all those considerations in view, the agreement with experimental data should be adopted as good. Thus, the theory of a lattice composed of deformable ions, which operates with four parameters $(A_1, A_2, G,$ and $f)$, provides a good agreement with experiment for seven quantities: $\alpha_1, \alpha_2, \varepsilon, \omega_d, C_{11}, C_{12},$ and C_{44}, as well as for the dispersion curve.

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