Auxiliary boundary conditions for optical phonons in the theory of additional light waves

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The proposed derivation of the auxiliary boundary conditions is not based on the assumption that the interaction between cells of a crystal is weak, and therefore adds much to the earlier studies of the Frenkel exciton. Besides the crystal excitations (vibrations) that are at resonance with the light, nonresonant excitations that lead to numerous additional short low-amplitude light waves are considered for the first time ever. A method of excluding the short waves and of correspondingly decreasing the number of the auxiliary boundary conditions is proposed. The auxiliary boundary conditions are obtained without assuming predominance of the long-range or of the short-range interactions [S. I. Pekar, Crystal Optics and Additional Light Waves (in Russian), Kiev, Naukova Dumka, 1982], by taking into account an inhomogeneous solenoidal-field wave with $k^2 = 0$ [S. I. Pekar and V. I. Pipa, Sov. Phys. Solid State **25**, 206 (1983)].

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Pekar[1] has shown in 1957 that in the region of exciton absorption of light there exist, besides the two ordinary birefringence waves, supplementary solutions of Maxwell's equations, namely additional light waves (ALW). In Ref. 1 was introduced the concept of a generalized exciton—an elementary excitation of a dielectric, characterized by a single continuous quantum number, the quasimomentum **k**, while all the remaining quantum numbers are discrete. An optical phonon is a particular case of a generalized exciton, and all the general-theory results obtained for an infinite crystal can therefore be extended to include also this phonon. In particular, ALW appear in the vincinity of the frequency limit of the optical phonon (the IR band). In the problem of the passage and reflection of light at the vacuum-crystal interface the Maxwellian boundary conditions are insufficient for a unique determination of the amplitudes of the reflected and transmitted waves in terms of the amplitude of the incident wave. Auxiliary boundary conditions (ABC) are needed. It is known[1,2] that the latter depend on the particular model of the exciton. The ABC for a Frenkel exciton were obtained in Refs. 1–3. In the present paper we obtain ABC for another particular exciton case—the optical phonon. The phonons are obtained as a result of quantization of the harmonic crystal-lattice vibrations. This quantization, as is well known, can be effected also after first developing a classical theory of lattice vibrations. In a bounded crystal it is necessary to formulate and use the boundary conditions even in the classical treatment of normal lattice vibrations. The subsequent quantization does not change the boundary conditions. The classical theory of lattice vibrations is therefore sufficient for the formulation of the ABC.

Infrared optical-exciton waves in a crystal (polaritons) are described by the ion equations of motion

$$M_\mu \ddot{\mathbf{u}}_{\mathbf{m}\mu} = -\sum_{\mathbf{n},\nu=1}^{f} a_{\mathbf{m}\mu,\mathbf{n}\nu}\mathbf{u}_{\mathbf{n}\nu} + e_\mu \mathbf{E}_\perp(\mathbf{m}, t) \qquad (1)$$

and by Maxwell's equations

$$\mathbf{E}_\perp = -\frac{1}{c}\dot{\mathbf{A}}, \quad \Delta\mathbf{A} - \frac{1}{c^2}\ddot{\mathbf{A}} = -\frac{4\pi}{c}\dot{\mathbf{P}}_\perp, \quad \mathbf{E}_\parallel = -4\pi\mathbf{P}_\parallel, \quad (2)$$

$$\mathbf{P}(\mathbf{r}, t) = \frac{1}{v}\sum_{\nu=1}^{f} e_\nu(\mathbf{u}_{\mathbf{m}\nu})_{\mathbf{m}\to\mathbf{r}}. \qquad (3)$$

The integer lattice vectors **m** (or **n** number here the unit cells of the crystal, and the subscripts μ and ν number the ions within the cell boundaries. $\mathbf{u}_{\mathbf{m}\mu}$ is the vector of the displacement from the equilibrium position of the μ-th ion with mass M_μ and charge e_μ in the cell **m**; f is the number of ions in the cell; e is not necessarily a multiple of the unit charge;

$$a_{\mathbf{m}\mu,\mathbf{n}\nu} \equiv a_{\mu\nu,\mathbf{n}-\mathbf{m}}, \qquad (4)$$

$$\overset{xy}{a}_{\mathbf{m}\mu,\mathbf{n}\nu} = \overset{yx}{a}_{\mathbf{n}\nu,\mathbf{m}\mu}; \qquad (5)$$

$\mathbf{E}_\perp$ is the solenoidal part of the electric field; $\mathbf{P}(\mathbf{r},t)$ is the specific polarization of the crystal; v is the volume of the unit cell. The light waves are assumed to be long. We neglect the variation of $\mathbf{E}_\perp$ within the limits of the unit cell.

If the term $e_\mu \mathbf{E}_\perp$ in (1) is discarded, meaning that the retardation in the solenoidal part of the field is neglected, the system (1) describes not a light wave (an optical exciton), but an oscillating exciton. It can then be seen from (1) that the term $-a_{\mathbf{m}\mu,\mathbf{n}\nu}\mathbf{u}_{\mathbf{n}\nu}$ is a potential force acting on the ion **m** μ and caused by the displacement of the in **n**ν. If the distance $|\mathbf{n} - \mathbf{m}|$ is large, this force can be calculated as being the force acting on the charge e_μ in the electric field of the corresponding dipole produced in the cell **n** as a result of the displacement of the ion **n**ν. The value of $a_{\mathbf{m}\mu,\mathbf{n}\nu}$ so obtained will be designated by the symbol $\beta_{\mathbf{m}\mu,\mathbf{n}\nu}$. This value, however, calls for a correction that is larger the shorter the distance $|\mathbf{n} - \mathbf{m}|$. Using the symbol $\alpha_{\mathbf{m}\mu,\mathbf{n}\nu}$ for this correction we can write the exact equality

$$a_{\mathbf{m}\mu,\mathbf{n}\nu} = \beta_{\mathbf{m}\mu,\mathbf{n}\nu} + \alpha_{\mathbf{m}\mu,\mathbf{n}\nu}. \qquad (6)$$

Here $\alpha_{\mathbf{m}\mu,\mathbf{n}\nu}$ is large when $|\mathbf{n} - \mathbf{m}|$ is of the order of one or two lattice constants, and decreases rapidly with increasing $|\mathbf{n} - \mathbf{m}|$. We shall therefore call the terms β and α in the right-hand sides of (6) and (1) the contributions from the long-range and short-range interactions, respectively.

In an infinite crystal, the solution of (1) can be sought in the form

$$\mathbf{u}_{\mathbf{m}\mu} = \mathbf{u}_{0\mu} e^{i(\mathbf{k}\mathbf{m} - \omega t)}, \quad \mathbf{E}_{\perp} = \mathbf{E}_{\perp}{}^{0} e^{i(\mathbf{k}\mathbf{r} - \omega t)}. \tag{7}$$

Substitution of (7) in (1) yields the final system of equations for $\mathbf{u}_{0\mu}$

$$\omega^2 M_\mu \mathbf{u}_{0\mu} = \sum_{\nu=1}^{f} a_{\mu\nu}(\mathbf{k}) \mathbf{u}_{0\nu} - e_\mu \mathbf{E}_{\perp}{}^{0}, \tag{8}$$

where

$$a_{\mu\nu} \equiv \sum_{\mathbf{n}} a_{\mu\nu,\mathbf{n}} e^{i\mathbf{k}\mathbf{n}}, \quad a_{\mu\nu}^{xy} = a_{\nu\mu}^{yx*}. \tag{9}$$

In the right-hand side of (8) the contribution to the sum from the long-range interactions is equal to the product, with negative sign, of the charge e_μ by the electric field produced at the location of the ion 0_μ by an aggregate of electric dipoles with a dipole moment

$$\mathbf{p}_{\mathbf{n}\nu} = \mathbf{p}_{0\nu} e^{i\mathbf{k}\mathbf{n}}, \quad \mathbf{p}_{0\nu} = e_\nu \mathbf{u}_{0\nu} \tag{10}$$

and localized at all points $\mathbf{n}\nu$ except the point 0μ. This field can be calculated by Ewald's method and represented in the form

$$\mathbf{E}_{0\mu} = \mathbf{E}(0) + \sum_{\nu=1}^{f} e_\nu Q_{\mu\nu}(\mathbf{k}) \mathbf{u}_{0\nu}. \tag{11}$$

Here $\mathbf{E}(0)$ is the microscopic electric field in the zeroth cell. For long waves (i.e., small $|\mathbf{k}|$ compared with the reciprocal lattice constant), the only ones considered hereafter, this electric field can be calculated as continuous and is equal to[2]

$$\mathbf{E}(\mathbf{r}) = -\frac{4\pi}{v} \frac{\mathbf{k}(\mathbf{k}, \mathbf{p}_0)}{\mathbf{k}^2} e^{i\mathbf{k}\mathbf{r}}, \quad \mathbf{p}_0 = \sum_{\nu=1}^{f} e_\nu \mathbf{u}_{0\nu}. \tag{12}$$

The second term of (11) is an analytic function of $\mathbf{k}$ (Ref. 14) and its inclusion makes the macroscopic field exactly equal to the effective field. Without loss of generality, this term can be regarded as included in the term for the short-range interactions. The homogeneous system (8) can then be represented in the form

$$\omega^2 M_\mu \mathbf{u}_{0\mu} = \frac{4\pi e_\mu \mathbf{k}(\mathbf{k}, \mathbf{p}_0)}{v\mathbf{k}^2} + \sum_{\nu=1}^{f} \alpha_{\mu\nu}(\mathbf{k}) \mathbf{u}_{0\nu}, \tag{13}$$

$$\alpha_{\mu\nu}(\mathbf{k}) = \sum_{\mathbf{n}} \alpha_{\mu\nu,\mathbf{n}} e^{i\mathbf{k}\mathbf{n}} - e_\mu e_\nu Q_{\mu\nu}(\mathbf{k}). \tag{14}$$

At fixed $\mathbf{k}$, the system (13) determines $3f$ eigenfrequencies $\omega_l(\mathbf{k})$ and amplitudes $\mathbf{u}_{0\mu}^{(l)}$ ($l = 1,2,...,3f$). We orthonormalize the amplitudes as follows:

$$\sum_{\mu=1}^{f} M_\mu (\mathbf{u}_{0\mu}^{(l)*}, \mathbf{u}_{0\mu}^{(l')}) = \Omega \delta_{ll'}. \tag{15}$$

Three of the $3f$ amplitudes $\mathbf{u}_{0\mu}^{(l)}$ ($l = 1,2,...,3f$) pertain to acoustic vibrations for which the frequency and the dipole moment of the cell are equal to zero at $|\mathbf{k}| = 0$. They will be disregarded hereafter.

We seek the solution of three inhomogeneous system (8) in the form of an expansion in the complete system of vectors $\mathbf{u}_{0\mu}^{(l)}$ in $3f$-dimensional space. As a result we get

$$\mathbf{u}_{0\mu} = \frac{1}{\Omega} \sum_{l=1}^{3f} \frac{(\mathbf{p}_0^{(l)*}, \mathbf{E}_\perp{}^{0}) \mathbf{u}_{0\mu}^{(l)}}{\omega_l{}^2(\mathbf{k}) - \omega^2}, \tag{16}$$

where

$$\mathbf{p}_0^{(l)} = \sum_{\mu=1}^{f} e_\mu \mathbf{u}_{0\mu}^{(l)}.$$

The solution of the system (1)–(3) determines the dispersion law of all the light waves (vibrational optical excitons) in the crystal

$$\mathbf{k}_j = \mathbf{k}_j(\omega), \quad j = 1, 2, \ldots, N, \tag{17}$$

where j numbers the optical waves and N is their total number. The explicit form (17) of the solutions was obtained, subject to the generalized-exciton assumption, in Refs. 1 and 5–7.

We proceed now to consider light waves in a semi-infinite crystal located in the half-space $z > 0$. We seek the solution of the system (1)–(3) in this case in the form of a linear combination of the solutions for an infinite cyrstal. Inasmuch as translational symmetry in the xy plane is preserved in a semi-infinite crystal, we can seek the solution of these equations in the form

$$\mathbf{u}_{\mathbf{m}\mu} \infty e^{i(\mathbf{k}_\tau \mathbf{m} - \omega t)}, \quad \mathbf{E}_\perp \infty e^{i(\mathbf{k}_\tau \mathbf{r} - \omega t)}, \tag{18}$$

where $\mathbf{k}_\tau$ is an arbitrary vector in the xy plane. This means that the linear combination should include only the waves (7) and (17) with equal ω and with identical xy-plane projection $\mathbf{k}_j$ equal to $\mathbf{k}_\tau$ ($\mathbf{k}_j = \mathbf{k}_\tau + \mathbf{k}_{zj}$). To pick out the waves included in the linear combination it is therefore necessary to specify the values of ω and $\mathbf{k}_\tau$ in the dispersion law (17) and determine $\mathbf{k}_{zj}$ from the latter.

It is convenient to choose as the coefficients of the linear combination of the solutions the same light-field amplitudes $\mathbf{E}_\perp^0$ which are contained in (7) and in terms of which $\mathbf{u}_{\mathbf{m}\mu}$ are expressed in (7) and (16). As a result, the aforementioned linear combination of solutions should be of the form

$$\mathbf{u}_{\mathbf{n}\nu} = \sum_{j=1}^{N} \mathbf{u}_{\mathbf{n}\nu j} = \sum_{j=1}^{N} \mathbf{u}_{0\nu j} e^{i(\mathbf{k}_j \mathbf{n} - \omega t)}. \tag{19}$$

On going from an infinite crystal to a semi-infinite one no change occurs in Eqs. (2) and (3), while (1) becomes "truncated," i.e., the indices m_3 and n_3 in it take on only positive values: $m_3, n_3 = 1,2,3...$. In addition, in contrast to the Frenkel exciton, the interaction between the unit cells of the crystal is not assumed to be weak. Therefore an increase in the distance from the ions to the half-space $z < 0$ can substantially deform the near-surface cells of a semi-infinite crystal and alter the coupling coefficients $a_{\mathbf{m}\mu,\mathbf{n}\nu}$ for them. We designate these changes by $-\Delta a_{\mathbf{m}\mu,\mathbf{n}\nu}$. We stipulate that at positive m_3 the substitution $a_{\mathbf{m}\mu,\mathbf{n}\nu} \rightarrow a_{\mathbf{m}\mu,\mathbf{n}\nu} - \Delta a_{\mathbf{m}\mu,\mathbf{n}\nu}$ transform Eq. (1) into the equation for a semi-infinite crystal. To this end we must have $\Delta a_{\mathbf{m}\mu,\mathbf{n}\nu} = a_{\mathbf{m}\mu,\mathbf{n}\nu}$, at $m_3 > 0$ and $n_3 \leq 0$, while at $m_3 > 0$ and $n_3 > 0$ the quantity $-\Delta a_{\mathbf{m}\mu,\mathbf{n}\nu} = -\Delta \alpha_{\mathbf{m}\mu,\mathbf{n}\nu}$ is the aforementioned subsurface change of the coupling constant, a change included in this case in the short-range-interaction term.

The linear combination (19) certainly satisfies the equations for an infinite crystal. Therefore, if it is substituted in the corresponding truncated equations for the semi-infinite crystal, the latter will not be satisfied, and contain residual

terms

$$\mathbf{R_{m\mu}}'=\sum_{n\nu}\Delta a_{m\mu,n\nu}\mathbf{u}_{n\nu}, \qquad m_3=1,2,3,\ldots . \tag{20}$$

Substituting (19) in (20) and subdividing the coefficients $a_{m\mu,n\nu}$ in accord with (6) into long- and short-range interaction terms, we can represent the residue (20) in the form

$$\mathbf{R_{m\mu}}'=e^{-i\omega t}(\mathbf{R_{m\mu}}^{\beta}+\mathbf{R_{m\mu}}^{\alpha}), \quad \mathbf{R_{m\mu}}^{\beta}=\sum_{j=1}^{N}\mathbf{R}_{m\mu j}^{\beta}, \quad \mathbf{R_{m\mu}}^{\alpha}=\sum_{j=1}^{N}\mathbf{R}_{m\mu j}^{\alpha}, \tag{21}$$

where the contribution from the long-range interactions is

$$\mathbf{R}_{m\mu j}^{\beta}=\sum_{\substack{n\nu \\ n_3\leqslant 0}}\beta_{m\mu,\,n\nu}\mathbf{u}_{0\nu j}e^{i\mathbf{k}_j\mathbf{n}} \tag{22}$$

and that from the short-range interactions is

$$\mathbf{R}_{m\mu j}^{\alpha}=\sum_{n\nu}\Delta\alpha_{m\mu,n\nu}\mathbf{u}_{0\nu j}e^{i\mathbf{k}_j\mathbf{n}}. \tag{23}$$

The contribution (22), with the sign reversed, is equal to the force of the electric field acting on the ion $m\mu$ and produced by an aggregate of electric dipoles having dipole moments

$$\mathbf{p}_{n j}=\mathbf{p}_{0j}e^{i\mathbf{k}_j\mathbf{n}}, \qquad \mathbf{p}_{0j}=\sum_{\nu=1}^{f}e_{\nu}\mathbf{u}_{0\nu j}\equiv\nu\mathbf{P}_j \tag{24}$$

and localized in the half-space $n_3\leqslant 0$. Since $\mathbf{k}_j$ is small the aforementioned electric field can be calculated as continuous. The potential of this field is equal to[2]

$$\varphi_j(\mathbf{r})=-\frac{2\pi}{|\mathbf{k}_\tau|}\frac{L(\mathbf{P}_j)}{|\mathbf{k}_\tau|+ik_{zj}}e^{L(\mathbf{r})}, \tag{25}$$

$$L(\mathbf{r})=i(\mathbf{k}_\tau,\,\mathbf{r})-|\mathbf{k}_\tau|z. \tag{26}$$

Thus,

$$\mathbf{R}_{m\mu}^{\beta}=\sum_{j=1}^{N}e_{\mu}(\nabla\Delta_j)_{\mathbf{r}=\mathbf{m}}=\sum_{j=1}^{N}e_{\mu}\varphi_j(\mathbf{m})\,[\,\nabla L(\mathbf{r})\,]_{\mathbf{r}=\mathbf{m}}. \tag{27}$$

The residue $\mathbf{R}_{m\mu j}^{\beta}$ decreases with increasing $m_3>0$ as $\exp(-|\mathbf{k}_\tau|m_z)$. If the calculation of the potential φ were not restricted to the continuity approximation and were calculated by direct summation over $n_3\leqslant 0$, the residue (27), which decreases slowly with m_3, would acquire additional terms that decrease rapidly over one or two lattice constants. These terms can be included without loss of generality in the residue $\mathbf{R}_{m\mu}^{\alpha}$ that is due to the short-range interactions.

We consider now the contribution made to the residue by the short-range interactions. Since $\Delta\alpha_{m\mu,n\nu}$ decreases rapidly with increasing $|n_3-m_3|$, we can confine ourselves in the sum over n_3 in (23) to only a few terms with the smallest values of $|n_3|$. The exponential factor in (23) can then be replaced by $\exp(i\mathbf{k}_\tau\cdot\mathbf{n})$. Taking into account the translational symmetry of the semi-infinite crystal in the xy plane, we can represent (23) in the form

$$\mathbf{R}_{m\mu j}^{\alpha}=e^{i\mathbf{k}_\tau\mathbf{m}}\sum_{\nu=1}^{f}\Delta\alpha_{\mu\nu}(m_3)\mathbf{u}_{0\nu j}, \tag{28}$$

where

$$\Delta\alpha_{\mu\nu}(m_3)=\sum_{n}\Delta\alpha_{m\mu,n\nu}e^{i\mathbf{k}_\tau(\mathbf{n}-\mathbf{m})}. \tag{29}$$

On going from an infinite to a semi-infinite crystal, the changes in Eqs. (1) are not restricted to the fact that the sum over n in them becomes truncated, so that when (19) is substituted in the right-hand sides of Eqs. (1) the aforementioned residues $\mathbf{R}'_{m\mu}$ appear. As shown in Ref. 3, if some perturbation (light, ultrasound, or some other) produces in a semi-infinite crystal waves with specific polarization of the form

$$\mathbf{P}(\mathbf{r},t)=\sum_{j=1}^{N}\mathbf{P}_je^{i(\mathbf{k}_j\mathbf{r}-\omega t)}, \quad \mathbf{k}_j=\mathbf{k}_\tau+\mathbf{k}_{zj}, \tag{30}$$

there appears in the crystal an inhomogeneous perturbing-field wave

$$\mathbf{E}_{\perp}=\mathbf{k}_0Ce^{i(\mathbf{k}_0\mathbf{r}-\omega t)}, \qquad k_{0z}=i|\mathbf{k}_\tau|, \quad \mathbf{k}_0^2=0. \tag{31}$$

Here

$$C=-\frac{2\pi}{|\mathbf{k}_\tau|}\sum_{j=1}^{N}\frac{(\mathbf{k}_0,\mathbf{P}_j)}{|\mathbf{k}_\tau|+ik_{zj}}. \tag{32}$$

No such wave exists in an infinite crystal. Consequently, on going to a semi-infinite crystal there appears in the right-hand side of (1), besides the residue $\mathbf{R}'_{m\mu}$, an additional term $e_{\mu}\,\mathbf{k}_0C\exp\,[i(\mathbf{k}_0\cdot\mathbf{m}-\omega t)]$.

The peculiarity of the wave (31) is that its total electric field $\mathbf{E}$, the magnetic field $\mathbf{H}$, and the polarization $\mathbf{P}$ are equal to zero. Therefore if a wave equation is written for one of these quantities, say $\mathbf{E}$, the wave (31) will be included among the trivial (zero) solutions of the wave equation, and the dispersion equation will not have a corresponding root. The latter was the reason why this wave was unobserved for many years. The wave (31) was therefore called in Ref. 3 the "lost" wave. This wave is not connected with the spatial dispersion and with the spectral regions of the exciton resonances, and exists at all ω in the region where macro-electrodynamics is valid.

Since $\mathbf{k}_0^2=0$ at $\mathbf{k}=\mathbf{k}_0$, the denominator of the first term in the right-hand side of (13) is zero. Therefore $\mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_0)=0$, i.e., the wave (31), as can be seen from (16), does not cause ion displacement $\mathbf{u}_{0\mu}$ and makes no contribution whatever to the linear combination (19) and to the residue (20).

Writing (26) in the form $L(\mathbf{r})=i(\mathbf{k}_0,\mathbf{r})$ and using (21), (25), and (27) we easily rewrite the contribution made to $\mathbf{R}'_{m\mu}$ from the long-range interactions in the form

$$e^{-i\omega t}\mathbf{R}_{m\mu}^{\beta}=e_{\mu}\mathbf{k}_0e^{i(\mathbf{k}_0\mathbf{m}-\omega t)}\frac{2\pi}{|\mathbf{k}_\tau|}\sum_{j=1}^{N}\frac{(\mathbf{k}_0,\mathbf{P}_j)}{|\mathbf{k}_\tau|+ik_{zj}}. \tag{33}$$

This contribution is exactly cancelled out by the aforementioned additional term $e_{\mu}\,\mathbf{k}_0C\exp\,[i\mathbf{k}_0\mathbf{m}-\omega t)]$ that appears in (1) in the term with the perturbing field. The residue in (1) therefore will be only the contribution from the short-range interactions, given according to (21) and (23) by

$$e^{-i\omega t}\mathbf{R}_{m\mu}^{\alpha}=e^{i(\mathbf{k}_\tau\mathbf{m}-\omega t)}\sum_{\nu=1}^{f}\Delta\alpha_{\mu\nu}(m_3)\sum_{j=1}^{N}\mathbf{u}_{0\nu j}, \quad \begin{array}{l}\mu=1,2,\ldots,f \\ m_3=1,2,3,\ldots\end{array}. \tag{34}$$

In order that the linear combination (19) of the solution of Eqs. (1)–(3) for an infinite crystal be the solution of the problem for a semi-infinite crystal, the wave amplitudes

$|\mathbf{E}_{\perp j}{}^0|$ must be chosen such that the residues (34) vanish at all μ and at $m_3 > 0$. Equating these residues to zero at some value of m_3, we obtain a system of homogeneous equations relative to the quantities

$$\mathbf{u}_{0\nu} = \sum_{j=1}^{N} \mathbf{u}_{0\nu j}.$$

Since the determinant of the system differs from zero, we obtain the conditions $\mathbf{u}_{0\nu} = 0$. Using Eq. (16) for $\mathbf{u}_{0\nu j}$, we can express these conditions in the form

$$\mathbf{u}_{0\nu} = \sum_{j=1}^{N} \sum_{l=1}^{3f-3} \frac{(\mathbf{p}_{0j}^{(l)*}, \mathbf{E}_{\perp j}{}^0) \mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_j)}{\Omega[\omega_l{}^2(\mathbf{k}_j) - \omega^2]} = 0,$$

i.e., $\quad [\mathbf{u}_{m\nu}]_{m_3=0} = 0 \quad \nu = 1, 2, \ldots, f.$ \hfill (35)

In this case the residues (34) vanish also for the other values of m_3.

We substitute $\mathbf{p}_0^{(l)}(\mathbf{k}_j)$ and $\mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_j)$ in the numerators of the fractions of (35), assuming that $|\mathbf{k}_j| \to 0$; these vectors will depend only on the direction of $\mathbf{k}_j$. Then $\mathbf{p}_{0j} = 0$ for the three acoustic oscillation branches with numbers $l = 3f$, $3f - 1$ and $3f - 2$, i.e., the corresponding terms are absent from (35).

Equations (35) are in fact the sought auxiliary boundary conditions (ABC) that determine uniquely, in conjunction with the Maxwell boundary conditions, the amplitudes $|\mathbf{E}_{\perp j}{}^0|$ of all the wave that are produced in the crystals, as well as of the wave reflected into the vacuum, in terms of the amplitude of the wave incident from the vacuum on the crystal.

Using the second equation of (12) as well as Eqs. (7) and (16) for $\mathbf{u}_{0\nu j}$, we can obtain for the polarization-wave amplitudes the expression

$$\mathbf{P}_j = \beta(\omega, \mathbf{k}_j) \mathbf{E}_{\perp j}^0, \quad \beta(\omega, \mathbf{k}_j) = \sum_{l=1}^{3f-3} \frac{\overline{\mathbf{p}_{0j}^{(l)} \mathbf{p}_{0j}^{(l)*}}}{v\Omega[\omega_l{}^2(\mathbf{k}_j) - \omega^2]_1}. \quad (36)$$

The common bar over the two vectors denotes a tensor dyad. At such a value of β, if all the limiting natural frequencies $\omega_{ls} (\mathbf{s} = \mathbf{k}/|\mathbf{k}|)$ are close enough to one another and ω approaches all the ω_{ls} simultaneously, there exist in the crystal $3f - 3$ additional light waves (ALW).[7] It is therefore necessary that the ABC reduce just to $3f - 3$ scalar equations.

It seems at first glance that the ABC (35) constitute $3f$ scalar equations, and thus do not correspond to $3f - 3$ ALW. However, multiplying (35) by M_ν and summing over ν we obtain the known identity

$$\sum_{\nu=1}^{f} M_\nu \mathbf{u}_{0\nu} = 0$$

(at the limiting optical lattice vibration the mass center of the unit cell is at rest). It follows from this identity that three scalar equations in (35) are the consequence of the remaining ones. The number of independent equations obtained from the ABC (35) is $3f - 3$.

Multiplying Eqs. (35) by e_μ and summing over μ we can obtain from them the condition

$$[\mathbf{P}(\mathbf{r},t)]_{z=0} = 0, \quad \text{i.e.,} \quad \sum_{j=1}^{N} \sum_{l=1}^{3f-3} \frac{\mathbf{p}_{0j}^{(l)}(\mathbf{p}_{0j}^{(l)*}, \mathbf{E}_{\perp j}^0)}{v\Omega[\omega_l{}^2(\mathbf{k}_j) - \omega^2]} = 0. \quad (37)$$

If $f = 2$ we can obtain, conversely, (35) from (37). The conditions (35) and (37) are perfectly analogous to the corresponding ABC in the case of a Frenkel exciton.[1,2,3,7]

It can be shown that when the limiting frequency ω_{ls} of one of the excitons deviates from the remaining ones, as well as from ω, the refractive index n of one of the ALW becomes very large $(n \sim 10^2$ and larger). This light wave becomes excitonlike (see Ref. 7, § 17); it comes close to the normal vibration of the crystal lattice l, and in particular its dispersion law in the region of large $\mathbf{k}$ corresponding to large n tends to

$$\omega = \omega_l(\mathbf{k}). \quad (38)$$

We get thus a one-to-one correspondence between the vibrational exciton l, whose limiting frequency ω_{ls} moves away from ω, and one of the additional light waves, which coincides with this exciton in the limit as $n \to \infty$. We agree to assign to this ALW the same number as the exciton that moved off resonance, i.e., $j = l$. Equation (38) should then be written in the form $\omega = \omega_l(\mathbf{k}_l)$. The smallest (practically zero) denominator of all the fractions contained in (35) is then $\omega_l{}^2(\mathbf{k}_l) - \omega^2$, where l is the number of the aforementioned solitary *nonresonant* normal vibration, for which the difference $\omega_{ls}{}^2 - \omega^2$ is large. It can be shown that

$$\frac{\omega_l(\mathbf{k}_l) - \omega}{\omega} \sim \frac{\Delta_l}{2M_{ls}c^2} \frac{\omega}{\omega - \omega_{ls}} \sim 10^{-7} - 10^{-10},$$

where M_{ls} is the effective mass of the optical phonon and Δ_l is the longitudinal-transverse splitting of its energy (for details see Ref. 7, §§ 12 and 17).

Assume now that the limiting frequencies ω_{ls} with $l = 1, 2, \ldots, g \leqslant 3$ are degenerate and close to ω, while the remaining ω_{ls} with $l = g + 1, g + 2, \ldots, 3f - 3$ are far enough from ω (nonresonant). Each nonresonant normal vibration corresponds to an excitonlike ALW. The latter are numbered by the indices $j = g + 1, g + 2, \ldots, 3f - 3$. These waves have very large n and k, and will therefore be called short.[1] The other light waves will be called long. The sum over j in (35) can be broken up into a sum over long and a sum over short waves. In the latter it is possible to retain only the dominant terms $j = l$ whose denominators are almost zero. Next, since the short waves have very large n, all are directed normal to the crystal surface, i.e., their $\mathbf{k}_j$ have the same direction, and consequently $\mathbf{u}_{\mu\nu}^{(l)}(\mathbf{k}_j)$ is independent of j. We denote them by $\mathbf{u}_{\theta\nu}^{(l)}$. The ABC (35) can therefore be rewritten in the form

$$\sum_{\text{long}} \sum_{l=1}^{3f-3} \frac{(\mathbf{p}_{0j}^{(l)*}, \mathbf{E}_{\perp j}{}^0) \mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_j)}{\omega_l{}^2(\mathbf{k}_j) - \omega^2} + \sum_{l=g+1}^{3f-3} \frac{(\mathbf{p}_{0l}^{(l)*}, \mathbf{E}_{\perp j}{}^0) \mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_l)}{\omega_l{}^2(\mathbf{k}_l) - \omega^2} = 0;$$

$$\nu = 1, 2, \ldots, f. \quad (39)$$

Choosing as the basis the complete system of orthonormalized $3f$-dimensional vectors $\mathbf{u}_0^{(l)}(\ldots \mathbf{u}_{0\nu}^{(l)} \ldots)$, whose $\mathbf{k}$ is directed normal to the surface$(|\mathbf{k}| \to 0)$, we can expand in their terms any vector $\mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_j)$:

$$\mathbf{u}_{0\nu}^{(l)}(\mathbf{k}_j) = \sum_{l'=1}^{3f-3} A_j^{ll'} \mathbf{u}_{0\nu}^{(l')}. \quad (40)$$

Substituting (4) in (39) and equating to zero the coefficient of

each $u_{0\nu}^{(l)}$, we can rewrite (39) in the form

$$\sum_{\text{long}} \sum_{l=1}^{3f-3} \frac{(p_{0j}^{(l)*}, E_{\perp j}^{0}) A_j^{ll'}}{\omega_l^2(k_j) - \omega^2} = 0, \quad l'=1,2,\dots,g, \quad (41)$$

$$\sum_{\text{long}} \sum_{l=1}^{3f-3} \frac{(p_{0j}^{(l)*}, E_{\perp j}^{0}) A_j^{ll'}}{\omega_l^2(k_j) - \omega^2} + \frac{(p_{0l'}^{(l')*}, E_{\perp l'}^{0})}{\omega_{l'}^2(k_{l'}) - \omega^2} = 0,$$

$$l'=g+1, g+2, \dots, 3f-3. \quad (42)$$

Since the sum over j_{long} in (42) is finite and $\omega_{l'}^2(k_{l'}) - \omega^2 \approx 0$, their solutions are

$$E_{\perp l'}^{0} \approx 0, \quad l'=g+1, \ g+2, \dots, 3f-3. \quad (43)$$

The amplitudes of all the short ALW corresponding to non-resonant normal vibrations are thus equal to zero. Equations (41), on the other hand, are the sought ABC when not all the normal vibrations are at resonance with the light, but only g of them. In this case it is necessary in the second equation of (36) to replace that part of the sum

$$\overline{\sum_{l=g+1}^{3f-3} \frac{p_{0j}^{(l)} p_{0j}^{(l)*}}{v\Omega[\omega_l^2(k_j) - \omega^2]}},$$

which contains nonresonant denominators with small k_j by the "background"/polarizability $\beta_0(\omega, s_j)$. The ABC (41) contain amplitudes of only long light waves. The number of the equation is g, i.e., exactly the number of the ABC.

Equations (41) become simpler in the following three cases.

1. Normal incidence of the light, $u_{0\nu}^{(l)}(k_j) = u_{0\nu}^{(l)}$, i.e., $A_j^{ll'} = \delta_{ll'}$. and the $p_{0j}^{(l)}$ are independent of j. Equations (41) take the form

$$\sum_{\text{long}} \frac{(p_0^{(l)*}, E_{\perp j}^{0})}{\omega_l^2(k_j) - \omega^2} = 0, \quad l=1,2,\dots,g. \quad (44)$$

Multiplying these equations by $p_0^{(l)}$ and summing over l we obtain

$$[P_{ex}(r,t)]_{z=0} = 0, \quad \text{т. е.} \quad \sum_{\text{long}} [\beta(\omega, k_j) - \beta_0(\omega, s_j)] E_{\perp j}^{0} = 0, \quad (45)$$

where p_{ex} is the partial contribution of the resonant normal vibrations to the specific polarization.

When comparing the conditions (37) and (45) it must be emphasized that the total polarization (37) on the crystal surface is zero if account is taken of the contribution made to the polarization by all light waves, including the short ones. The exciton polarization (45), however, is equal to zero when account is taken of the contribution made to the polarization by only the long waves; the total long-wave polarization differs then from zero.

2. The light wave incident from vacuum and all the waves excited in the crystal are polarized perpendicular to the incidence plane (s-polarization). This is realized, e.g., when the incidence plane is a mirror symmetry plane of the crystal. The dipoles $p_0^{(l)}$ then either lie in the incidence plane and therefore do not interact with the light, or are perpendicular to the incidence plane. In the latter case the singular

term in (13) is zero, $\alpha_{\mu\nu}$ and ω_l do not depend on s in the limit as $|k| \to 0$, and $u_{0\nu}^{(l)}(k_j) = u_{0\nu}^{(l)}$, i.e., $A_j^{ll'} = \delta_{ll'}$. The $p_{0j}^{(l)}$ do not depend on j. Equations (41) take the form (44), (45).

3. Oblique incidence and arbitrary polarization of the light waves. Assume that the singular term in (13) is small compared with the sum and can be regarded as a small perturbation. Then, discarding this term in the zeroth approximation, $\alpha_{\mu\nu}$ and ω_l do not depend on s as $|k| \to 0$, therefore $u_{0\nu}^{(l)}(k_j)$ and $u_{0\nu}^{(l)}$ are solutions of one and the same system of linear equations. It is then possible to confine oneself in (4) at $1 \leqslant l \leqslant g$ to summation over only the degenerate solutions $u_{0\nu}^{(l)}$ with $1 \leqslant l' \leqslant g$. In other words,

$$A_j^{ll'} = 0 \quad \text{at} \quad l \leqslant g, \ l' > g \quad \text{and at} \quad l > g, \ l' \leqslant g. \quad (46)$$

Taking this formula into account, we easily obtain from (40)

$$p_{0j}^{(l)} = \sum_{l'=1}^{g} A_j^{ll'} p_0^{(l')}, \quad l=1,2,\dots,g, \quad (47)$$

and in (41) it is necessary to sum over l from 1 to g. Multiplying (41) from the right by $p_0^{(l')}$, summing over l', and using (47) we obtain

$$\sum_{\text{long}} \sum_{l=1}^{g} \frac{(p_{0j}^{(l)*}, E_{\perp j}^{0}) p_{0j}^{(l)}}{\omega_l^2(k_j) - \omega^2} = 0. \quad (48)$$

These ABC coincide with (45).

If we now introduce the singular term as a perturbation, the ABC are slightly modified: first, $u_{0\nu}^{(l)}(k_j)$, $A_j^{ll'}$ and $p_{0j}^{(l)}$ with $l, l' \leqslant g$ acquire corrections of first order of smallness. Second, small deviations from (46) appear, the values of $A_j^{ll'}$ with $l \leqslant g$, $l' > g$ will differ from zero but will be small. Therefore the ABC (41) will contain the part of the sum

$$\sum_{\text{long}} \sum_{l=g+1}^{3f-3} \frac{(p_{0j}^{(l)*}, E_{\perp j}^{0}) A_j^{ll'}}{\omega_l^2(k_j) - \omega^2}, \quad l'=1,2,\dots,g. \quad (49)$$

which was discarded in the zeroth approximation. This sum is of second order of smallness, since $A_j^{ll'}$ in it is of first order but the denominators of all fractions are nonresonant; in the case of long waves they are much larger than the resonant denominators contained in the remaining part of the sum (41). If we neglect the part (49) of (41) (retaining only terms of first order of smallness), the ABC (41) take the form

$$\sum_{\text{long}} \sum_{l=1}^{g} \frac{(p_{0j}^{(l)*}, E_{\perp j}^{0}) A_j^{ll'}}{\omega_l^2(k_j) - \omega^2} = 0, \quad l'=1,2,\dots,g. \quad (50)$$

These ABC reduce to (48), i.e., to (45).

Thus as a result of elimination of the short waves the initial ABC (35) were reduced with the aid of quite exact transformations to the conditions (41). The latter were reduced in cases 1 and 2 to the ABC (45), i.e., (48), without any approximations whatever. In case 3, however, substantial approximations had to be used to obtain the ABC (48) and (50).

There is another procedure of excluding the short waves and transforming the ABC. If account is taken of the third equation of (2), the first term of the right-hand side of (13) can be written in the form $-e_{\mu} E_{\parallel}^{0}$ and it yields, together

with the last term of (8), the force $-e_\mu \mathbf{E}^0$, where $\mathbf{E}^0$ is the amplitude of the total electric field. As a result, Eq. (8) takes the form

$$\omega^2 M_\mu \mathbf{u}_{0\mu} = \sum_{\nu=1}^f \alpha_{\mu\nu}(\mathbf{k}) \mathbf{u}_{0\nu} - e_\mu \mathbf{E}^0, \quad \mu = 1, 2, \ldots, f. \quad (51)$$

The force that causes the oscillations is here the total electric field of the light wave, and the matrix $\alpha_{\mu\nu}(\mathbf{k})$ takes into account only the interaction of the nearest cells of the crystal.[4] This matrix is not singular, i.e., as $|\mathbf{k}| \to 0$ this matrix itself, its eigenvectors $\tilde{\mathbf{u}}_{0\mu}^{(l)}(\mathbf{k})$, and the eigenfrequencies $\tilde{\omega}_l$ do not depend on s. Therefore in the formula analogous to (40), namely,

$$\tilde{\mathbf{u}}_{0\nu}^{(l)}(\mathbf{k}_j) = \sum_{l'} \tilde{A}_j^{ll'} \tilde{\mathbf{u}}_{0\nu}^{(l')}, \quad |\mathbf{k}_j| \to 0, \quad (52)$$

$\tilde{A}_j^{ll'} \neq 0$ only if the vibrations l and l' are of the same frequency (the sum has not more than three terms).

Since (51) and (8) are equivalent, their solutions $\mathbf{u}_{0\nu}$ and $\tilde{\mathbf{u}}_{0\nu}$ should coincide. Expressed in terms of $\mathbf{E}_j^0$, they are

$$\mathbf{u}_{0\nu} \equiv \tilde{\mathbf{u}}_{0\nu} = \sum_{j=1}^N \sum_{l=1}^{3f-3} \frac{(\tilde{\mathbf{p}}_{0j}^{(l)*}, \mathbf{E}_j^0) \tilde{\mathbf{u}}_{0\nu}^{(l)}(\mathbf{k}_j)}{\Omega[\tilde{\omega}_l^2(\mathbf{k}_j) - \omega^2]}, \quad \nu = 1, 2, \ldots, f, \quad (53)$$

where

$$\tilde{\mathbf{p}}_{0j}^{(l)} = \sum_{\nu=1}^f e_\nu \tilde{\mathbf{u}}_{0\nu}^{(l)}(\mathbf{k}_j). \quad (54)$$

In lieu of (36) we now obtain

$$\mathbf{P}_j = \varkappa(\omega, \mathbf{k}_j) \mathbf{E}_j^0, \quad \varkappa(\omega, \mathbf{k}_j) = \sum_{l=1}^{3f-3} \frac{\tilde{\mathbf{p}}_{0j}^{(l)} \tilde{\mathbf{p}}_{0j}^{(l)*}}{\nu\Omega[\tilde{\omega}_l^2(\mathbf{k}_j) - \omega^2]}, \quad (55)$$

and the ABC take as before the form $\mathbf{u}_{0\nu} = 0$. Transformations similar to those given in the first variant allow us to write the ABC, prior to exclusion of the short waves, in the form

$$\sum_{\text{long}} \sum_l \frac{(\tilde{\mathbf{p}}_{0j}^{(l)*}, \mathbf{E}_j^0) \tilde{A}_j^{ll'}}{\tilde{\omega}_l^2(\mathbf{k}_j) - \omega^2} + \sum_{\text{short}} \frac{(\tilde{\mathbf{p}}_{0j}^{(l')*}, \mathbf{E}_j^0)}{\tilde{\omega}_{l'}^2(\mathbf{k}_j) - \omega^2} = 0,$$

$$l' = 1, 2, \ldots, 3f-3. \quad (56)$$

Here l number the oscillations that are degenerate with l'. It is assumed that the limiting frequencies $\tilde{\omega}_l$ with $l = 1,2,\ldots,g$ are mutually degenerate and are close to ω, while $\tilde{\omega}_l$ with $l = g+1, g+2,\ldots,3f-3$ are far enough from ω.

Short waves are excitonlike, but in contrast to $\mathbf{E}_{1j}^0$ their $\mathbf{E}_j^0$ is not equal to zero. Therefore the short waves can be excluded from the ABC (56) only approximately, with much lower accuracy than in the first variant. Putting $\delta_{ls} \equiv \omega_{ls}^2 - \tilde{\omega}_l^2(0)$. we obtain for short waves $\tilde{\omega}_l^2(\mathbf{k}_l) - \omega^2 \approx -\delta_{ls}$. Assuming that at $g < l \leqslant 3f-3, j \neq l$ or $l \leqslant g, g < j \leqslant 3f-3$ we have

$$\left| \frac{\delta_{ls}}{\tilde{\omega}_l^2(\mathbf{k}_j) - \omega^2} \right| \ll 1. \quad (57)$$

We can approximately express from (56) with $l' > g$ the amplitudes $|\mathbf{E}_{j\,\text{short}}^0|$ in terms of $|\mathbf{E}_{j\,\text{long}}^0|$, and it turns out that $|\mathbf{E}_{j\,\text{short}}^0|/|\mathbf{E}_{j\,\text{long}}^0|$ is of the order of the ratio in the left-hand

side of (57). It can then be easily shown that in Eqs. (56) with $l' \leqslant g$ the sums over j_{short} are of second order of smallness compared with the sum over j_{long}. Discarding the sum over j_{short} we obtain ABC for only long waves:

$$\sum_{\text{long}} \sum_{l=1}^g \frac{(\tilde{\mathbf{p}}_{0j}^{(l)*}, \mathbf{E}_j^0) \tilde{A}_j^{ll'}}{\tilde{\omega}_l^2(\mathbf{k}_j) - \omega^2} = 0, \quad l' = 1, 2, \ldots, g. \quad (58)$$

They are similar and equivalent in accuracy to the ABC (50), but are more advantageous than (50) because by using (52) and (54) they can be rewritten in a more convenient form

$$[\tilde{\mathbf{P}}_{ex}]_{z=0} = 0, \quad \text{i.e.,} \quad \sum_{\text{long}} \sum_{l=1}^g \frac{\tilde{\mathbf{p}}_{0j}^{(l)}(\tilde{\mathbf{p}}_{0j}^{(l)*}, \mathbf{E}_j^0)}{\nu\Omega[\tilde{\omega}_l^2(\mathbf{k}_j) - \omega^2]}$$

$$= \sum_{\text{long}} [\varkappa(\omega, \mathbf{k}_j) - \varkappa_0] \mathbf{E}_j^0 = 0. \quad (59)$$

Here $\chi_0(\omega)$ is the "background" polarizability of the crystal.

Thus in case 1 considered above it is necessary to use the ABC (45) of the first variant, since they were obtained without the restrictions (57) and without the associated approximation. An exception is the case when the normal to the crystal surface coincides with the principal axis of the polarizability $\varkappa$. In this case, at normal incidence there exist in the crystals only transverse or only longitudinal long waves. For transverse waves $\mathbf{E}_j^0 = \mathbf{E}_{1j}^0$, $\delta_{ls} = 0$, i.e., the two variants coincide. In particular, the ABC (45) coincide with (59). The longitudinal waves have $\beta_{ss}(\omega, \mathbf{k}) = \infty$, so that it is more convenient to describe them by using the tensor $\varkappa_{ss} = -1/4\pi$ (see Ref. 7, § 11). They have $\mathbf{P}_{ex} = \mathbf{P}$. There can be no more than two longitudinal waves, and they differ in the sign of $\mathbf{k}: \mathbf{k}_2 = -\mathbf{k}_1$, with $\tilde{\omega}^2(\mathbf{k}_1) = \tilde{\omega}^2(\mathbf{k}_2)$. In this case both ABC $\mathbf{P}_{ex} = 0$ and the ABC $\tilde{\mathbf{P}}_{ex} = 0$ reduce to the condition

$$\sum_{j=1}^2 \mathbf{E}_j^0 = 0,$$

i.e., they are mutually equivalent.

In case 2 all the light waves excited in the crystal are also transverse, therefore the ABC (45) and (50) are equivalent.

In case 3 the ABC of the first variant (41) was obtained without the restrictions (57) and without the corresponding approximation, but these ABC are complicated. The result of their simplification, the ABC (50), were obtained subject to the restrictions (57) and are equivalent in accuracy to the ABC (59) of the second variant.

We note in conclusion that the vectors $\mathbf{P}_{0j}^{(l)}$ and their dependence on s_j can be determined by using § 17 of Ref. 7.

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[1] Nonetheless, $|\mathbf{k}|$ for them is small compared with the reciprocal of the lattice constant.

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