

A.A. STUPKA

Oles Honchar Dnipropetrovsk National University
(72, Gagarin Ave., Dnipropetrovsk 49050, Ukraine; e-mail: antonstupka@mail.ru)**FREQUENCIES OF LONG-WAVE
PHONON-POLARITONS AND OPTICAL PHONONS
IN DIATOMIC IONIC CRYSTALS**PACS 63.20. e; 71.36.+c;
72.30.+q

Long-wave phonon-polaritons and longitudinal optical phonons in ionic crystals with two atoms per unit cell have been considered. The model of the point charge and the self-consistent electromagnetic field in the dielectric medium is used. The standard dispersion laws for both branches of phonon-polaritons regarded as transversal waves are obtained. The frequency of longitudinal optical phonons is expressed in terms of the ion plasma frequency in an insulator multiplied by the factor $\sqrt{\varepsilon_0/(\varepsilon_0 - \varepsilon_\infty)}$, where ε_0 is the static dielectric constant, and ε_∞ is the high-frequency one. A good agreement between the found expression and tabulated data is found.

Keywords: ionic crystal, self-consistent electromagnetic field, long-wave vibrations, phonon-polaritons, longitudinal optical phonons, ion plasma frequency.

1. Introduction

In the framework of the general theory of phonons, we will calculate interatomic force constants in order to determine the force that acts on the atom after its small deviation from the equilibrium position [1, 2], which makes it possible to construct the dynamic matrix and obtain phonon frequencies as the roots of the secular determinant.

The importance to take the electromagnetic interaction into account, while considering long-wave, in comparison with the lattice constant, optical vibrations in solids was demonstrated in works [3, 4]. In the recent paper [5], high-frequency optical vibrations in ionic crystals with two atoms per elementary cell were proposed to be considered as plasma oscillations of point charges. The consideration given below aims at extending the results of work [5] to the low-frequency limit of phonon-polaritons and, in such a way, at obtaining the expression for the transverse phonon frequency in terms of the high-frequency and static dielectric constants from the standard relation for the static limit of the dielectric induction [4]. However, in contrast to the widely known model of rigid ions [6], no effective charges are introduced.

**2. System of Equations
for the Electromagnetic Field and Ions**

The fact that the elastic forces are proportional to the gradients of displacements is neglected in the long-wave approximation. The thermal motion of ions and the damping will also be neglected. Only small vibrations in non-magnetic media will be studied; therefore, the nonlinear magnetic part of the Lorentz force can be omitted at once. The short-range elastic forces are considered in the harmonic approximation. In the framework of the Born–Huang theory, the linearized equations of motion for ions look like

$$\partial \mathbf{v}_+ / \partial t = -(\omega_0^2 (\mathbf{u}_+ - \mathbf{u}_-) M - Ze\mathbf{E}) / M_+, \quad (1)$$

$$\partial \mathbf{v}_- / \partial t = -(\omega_0^2 (\mathbf{u}_- - \mathbf{u}_+) M + Ze\mathbf{E}) / M_-. \quad (2)$$

where the reduced mass of an elementary cell in the crystal, $M = \frac{M_+ M_-}{M_+ + M_-}$, was introduced, the subscript + or – corresponds to the ion charge sign, \mathbf{u}_\pm is the ion displacement from its equilibrium position, \mathbf{v}_\pm the ion velocity, M_\pm the ion mass, ω_0 the resonance frequency [7, (27.47)] (in such a macroscopic theory, this is an external parameter, as a rule), Z the difference between the proton and electron numbers in the ion, and e the elementary charge. The total time derivative coincides with the partial one after the linearization.

The self-consistent average electromagnetic field has to satisfy Maxwell's equations in the insulator,

$$\partial \mathbf{D}_\infty / \partial t = c \nabla \times \mathbf{B} - 4\pi \mathbf{j}, \quad (3)$$

$$\partial \mathbf{B} / \partial t = -c \nabla \times \mathbf{E}. \quad (4)$$

In our approach, the density of the current created by the ions with the definite charge sign is expressed in terms of the corresponding velocity as follows:

$$\mathbf{j}_\pm = \pm Z e n_0 \mathbf{v}_\pm, \quad (5)$$

where n_0 is the equilibrium density of ions with the given sign. In the isotropic case, Eq. (3) introduces the dielectric induction, which is linearly related to the electric field strength \mathbf{E} in the approximation of small vibrations [8, 9]. It is natural that the high-frequency dielectric permittivity ε_∞ describing the electron polarization of ions should be used in Eq. (3), because the motion of ions was taken into account through the electric current (5). In this case, the high-frequency dielectric induction equals $\mathbf{D}_\infty = \varepsilon_\infty \mathbf{E}$. However, we may introduce the ionic polarization density by rewriting the linearized current (5),

$$P_i = Z e n_0 \mathbf{u}, \quad (6)$$

where $\mathbf{u} = \mathbf{u}_+ - \mathbf{u}_-$ is the relative shift of sublattices. This circumstance allows us to determine the dielectric induction as follows:

$$\mathbf{D} = \varepsilon_\infty \mathbf{E} + 4\pi Z e n_0 \mathbf{u}. \quad (7)$$

One can easily see that Eqs. (1) and (2) give rise to

$$\partial^2 \mathbf{u} / \partial t^2 = -\omega_0^2 \mathbf{u} + Z e \mathbf{E} / M. \quad (8)$$

In order to find the resonance frequency, let us consider the static case where the time derivatives equal zero. In the electrostatic situation, we have the following expression for the dielectric induction (7) in terms of the dielectric constant:

$$\mathbf{D}_0 = \varepsilon_0 \mathbf{E} = \varepsilon_\infty \mathbf{E} + 4\pi Z e n_0 \mathbf{u}. \quad (9)$$

Neglecting the time derivative in Eq. (8), we obtain

$$0 = -\omega_0^2 \mathbf{u} + Z e \mathbf{E} / M. \quad (10)$$

By solving Eqs. (9) and (10) simultaneously, we arrive at the expression for the sought frequency,

$$\varepsilon_0 \mathbf{E} = \varepsilon_\infty \mathbf{E} + 4\pi Z e n_0 Z e \mathbf{E} / (M \omega_0^2); \quad (11)$$

whence

$$\omega_0 = \sqrt{\frac{4\pi Z^2 e^2 n_0}{M(\varepsilon_0 - \varepsilon_\infty)}}. \quad (12)$$

In the general case, Eq. (3) for an arbitrary frequency looks like

$$\partial \varepsilon_\infty \mathbf{E} / \partial t = c \nabla \times \mathbf{B} - 4\pi Z e n_0 (\mathbf{v}_+ - \mathbf{v}_-). \quad (13)$$

Hence, we have obtained a homogeneous system of time-dependent equations (8), (4), and (13) describing coupled vibrations of the ionic lattice and oscillations of the self-consistent electromagnetic field.

3. Optical Vibrations in the Ionic Crystal

Now, using the system of equations indicated above, we can derive an equation for the electric field waves. Differentiating Eq. (13) with respect to the time and substituting the derivative $\partial \mathbf{B} / \partial t$ from Eq. (4), we obtain

$$\partial^2 \varepsilon_\infty \mathbf{E} / \partial t^2 = -c^2 \nabla (\nabla \cdot \mathbf{E}) - 4\pi Z e n_0 \partial^2 \mathbf{u} / \partial t^2. \quad (14)$$

It is convenient to pass to the Fourier components in the obtained equations, by following the rule

$$\mathbf{E}(\mathbf{x}, t) = \int d^3 k d\omega \mathbf{E}(\mathbf{k}, \omega) e^{i\mathbf{k}\mathbf{x} - i\omega t} / (2\pi)^4. \quad (15)$$

Then, from Eq. (8), we obtain

$$\mathbf{u} = \frac{Z e}{(\omega_0^2 - \omega^2) M} \mathbf{E}. \quad (16)$$

Dividing the field into the potential and vortex parts, $\mathbf{E} = \mathbf{E}^\parallel + \mathbf{E}^\perp$, we obtain two linear homogeneous algebraic equations,

$$-\omega^2 \mathbf{E}^\perp = -\frac{c^2}{\varepsilon_\infty} k^2 \mathbf{E}^\perp - \frac{4\pi Z^2 e^2 n_0}{\varepsilon_\infty M} \mathbf{E}^\perp \frac{\omega^2}{\omega^2 - \omega_0^2}, \quad (17)$$

$$-\omega^2 \mathbf{E}^\parallel = -\frac{4\pi Z^2 e^2 n_0}{\varepsilon_\infty M} \mathbf{E}^\parallel \frac{\omega^2}{\omega^2 - \omega_0^2}. \quad (18)$$

Equation (17) gives us the dispersion law for phonon-polaritons in the high-frequency limit $\omega \gg \omega_0$,

$$\omega^2 = c^2 k^2 / \varepsilon_\infty + \Omega_i^2, \quad (19)$$

where the following notation was introduced for the ionic plasma frequency:

$$\Omega_i = \sqrt{4\pi Z^2 e^2 n_0 / (M \varepsilon_\infty)}. \quad (20)$$

This result coincides with that obtained in work [5, (13)].

Equation (17) gives the known dispersion law for transverse waves with an arbitrary frequency,

$$\omega^4 - \omega^2(\omega_0^2 + c^2 k^2 / \varepsilon_\infty + 4\pi Z^2 e^2 n_0 / (M \varepsilon_\infty)) + \omega_0^2 c^2 k^2 / \varepsilon_\infty = 0, \quad (21)$$

which coincides with Eq. (12.6) in work [2]. The bi-quadratic equation (21) has standard solutions for ω^2 [2, Eq. (12.7)],

$$\omega^2 = \frac{1}{2} \left(\omega_L^2 + \frac{c^2}{\varepsilon_\infty} k^2 \pm \sqrt{\left(\omega_L^2 + \frac{c^2}{\varepsilon_\infty} k^2 \right)^2 - 4\omega_0^2 \frac{c^2}{\varepsilon_\infty} k^2} \right), \quad (22)$$

where

$$\omega_L^2 = \omega_0^2 + \Omega_i^2. \quad (23)$$

The lower phonon-polariton branch has the frequency ω_0 in the short-wave limit, which corresponds to the frequency of transverse optical phonons.

Equation (18), besides the trivial root $\omega = 0$, gives the frequency of longitudinal vibrations,

$$\omega^2 = \omega_L^2, \quad (24)$$

which corresponds to longitudinal optical phonons. Using Eqs. (12) and (20), formula (23) can be rewritten in the form

$$\omega_L^2 = \frac{4\pi Z^2 e^2 n_0}{M} \frac{\varepsilon_0}{(\varepsilon_0 - \varepsilon_\infty)\varepsilon_\infty}, \quad (25)$$

in which one can easily recognize the known Lyddane–Sachs–Teller formula [10]

$$\omega_L^2 = \omega_0^2 \frac{\varepsilon_0}{\varepsilon_\infty}. \quad (26)$$

Formula (25) can be rewritten in the form

$$\omega_L^2 = \Omega_i^2 \frac{\varepsilon_0}{\varepsilon_0 - \varepsilon_\infty}. \quad (27)$$

Longitudinal optical frequencies for some ionic crystals

Crystal	ρ , g/cm ³	ε_0	ε_∞	ω_L^{tab} , THz	ω_L , THz	$\omega_L / \omega_L^{\text{tab}}$
LiH	0.78	12.9	3.6	210	213	1.02
LiF	2.64	8.9	1.9	120	119	0.99
LiCl	2.07	12.0	2.7	75	65.0	0.87
LiBr	3.46	13.2	3.2	61	52.0	0.85
NaF	2.79	5.1	1.7	78	76.9	0.99
NaCl	2.17	5.9	2.25	50	44.8	0.90
NaBr	3.21	6.4	2.6	39	34.5	0.88
KF	2.50	5.5	1.5	61	56.9	0.93
KCl	1.99	4.85	2.1	40	35.6	0.89
KI	3.12	5.1	2.7	26	22.8	0.88
RbI	3.55	5.5	2.6	19	15.8	0.83
MgO	3.58	9.8	2.95	14	13.7	0.98

Hence, the frequency of longitudinal phonons is always higher than the frequency of corresponding plasma oscillations, but tends to the latter under the condition $\varepsilon_0 \gg \varepsilon_\infty$.

In order to compare the obtained transverse phonon frequency with tabulated data on ω_L^{tab} , it is convenient to change from the density of ions with the same sign in expression (25) to the mass density of the crystal ρ using the formula $\frac{n_0}{M} = \frac{\rho}{M_+ M_-}$. Then, we may write

$$\omega_L = Z \sqrt{\frac{\rho \varepsilon_0}{M_+ M_- (\varepsilon_0 - \varepsilon_\infty) \varepsilon_\infty}} \times 1.70156 \times 10^{-9} \text{ s}^{-1}. \quad (28)$$

For the sake of comparison, we took the data on the frequency of longitudinal vibrations ω_L^{tab} from Table 5.1 in work [11] (see Table). The values for the ionic crystal density were taken from work [12].

4. Conclusions

Hence, the known dispersion laws for phonon-polaritons and longitudinal optical phonons can be obtained in the framework of the macroscopic model for ionic crystals without introducing the effective charge. The transverse frequency of optical phonons in a two-atom-per-cell ionic crystal is obtained from the electrostatic equilibrium condition. The table demonstrates a good agreement between the frequencies of longitudinal optical phonons calculated by formula (25) with the known data [11]. Certainly, the

macroscopic model of point charges gives better results for ions with smaller radii. The presented consideration is a generalization of work [5], in which ions were considered as free point charges.

1. Y. Wang, Sh. Shang, Z.-K. Liu, and L.-Q. Chen, *Phys. Rev. B* **85**, 224303 (2012).
2. A.S. Davydov, *Solid State Theory* (Academic Press, New York, 1980).
3. K. Huang, *Proc. Roy. Soc. A* **208**, 352 (1951).
4. M. Born and K. Huang, *Dynamical Theory of Crystal Lattices* (Clarendon Press, Oxford, 1954).
5. A.A. Stupka, *Ukr. Fiz. Zh.* **58**, 865 (2013).
6. K.V. Namjoshi, S.S. Mitra, and J.F. Vetelino, *Solid State Commun.* **9**, 185 (1971).
7. N.W. Ashcroft and N.D. Mermin, *Solid State Physics* (Saunders College Publ., Philadelphia, PA, 1976).
8. A.I. Akhiezer, I.A. Akhiezer, R.V. Polovin, A.G. Sitenko, and K.N. Stepanov, *Plasma Electrodynamics* (Pergamon Press, New York, 1975).
9. L.D. Landau and E.M. Lifshitz, *Electrodynamics of Continuous Media* (Pergamon Press, New York, 1984).
10. R.A. Lyddane, R.G. Sachs, and E. Teller, *Phys. Rev.* **59**, 673 (1941).
11. Ch. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1995).
12. V.A. Rabinovich and Z.Ya. Khavin, *Brief Chemical Handbook* (Khimiya, Leningrad, 1978), (in Russian).

Received 16.02.14.

Translated from Ukrainian by O.I. Voitenko

A.A. Ступка

ЧАСТОТИ ДОВГОХВИЛЬОВИХ
ФОНОН-ПОЛЯРИТОНІВ ТА ОПТИЧНИХ ФОНОНІВ
У ДВОАТОМНИХ ІОННИХ КРИСТАЛАХ

Резюме

Розглянуто довгохвильові фонон-поляритони і поздовжні оптичні фонони в іонних кристалах з двома атомами в елементарній комірниці. Використано модель точкових зарядів і самоузгодженого електромагнітного поля в діелектричному середовищі. Отримано стандартні закони дисперсії для обох гілок фонон-поляритонів як поперечних хвиль. Частоту поздовжніх оптичних фононів виражено через іонну плазмову частоту у діелектрику з множником $\sqrt{\varepsilon_0/(\varepsilon_0 - \varepsilon_\infty)}$ зі статичною ε_0 та високочастотною ε_∞ діелектричними сталими. Порівнянням з табличними даними показано добру точність зазначеного виразу.