The nature of the phonon dispersion relation anomalies of IV–VI compounds

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Abstract.   The nature of phonon dispersion relation anomalies of the IV–VI compounds in the high-symmetry phase is analysed in the framework of the vibronic theory of ferroelectricity. It is shown that the source of the phonon dispersion curve anomalies is the strong electron–phonon interaction of pseudo-Jahn–Teller type. The phonon spectra of the high-symmetry phase of PbTe are calculated for different temperatures. The calculated spectra are in agreement with experimental data. It is shown that the significant temperature dependence of the soft mode in IV–VI semiconductors is caused by the closeness of the lattice to structural instability.

1. Introduction

Notwithstanding noticeable advances in explaining the structural properties of binary IV–VI compounds (MeCh, where Me = Ge, Sn, Pb and Ch = chalcogenes S, Se, Te), the theory of the lattice dynamics of such substances is far from complete. These systems belong to the ferroelectric materials which undergo transitions to the lower-symmetry phase with lowering temperature [1]. The reason for the transition is the softening with lowering temperature of the frequency of a 'soft mode' which becomes zero at the transition point and causes a structural distortion. Most of the existing models [2, 3, 4] used for calculations of the phonon spectra are of purely phenomenological character, leaving intact the closeness of the compounds under consideration to the structural phase transitions. The model suggested in [5] takes into account in a phenomenological way the closeness to the structural phase transition but cannot explain neither the temperature dependence nor the microscopic origin of the structural changes. Since the contribution of the interactions which lead to the phase transition is connected with the symmetry of the structural instability [5] and the strength of this contribution depends on the closeness to the transition temperature, the phonon spectra of these compounds have to demonstrate the universal properties of the phonon anomalies. Therefore the model for the lattice dynamics has to be constructed on the basis of a microscopic theory which is valid for the description of the structural changes.

The common feature of the models which explain the structural properties of ferroelectrics is the assumption that the phase with the higher symmetry is unstable at zero temperature. The difference between these models is in the offered stabilization mechanism which switches on with increasing temperature and stabilizes the lattice against low-symmetry distortion. The first approach (see e.g. [6]) ascribes the stabilization factor to the lattice anharmonicity. This approach successfully explains the temperature dependence of the soft mode but cannot relate the changes of the vibrational spectrum to the symmetry of the structural distortion. Another approach is the 'polarization model' (see e.g. [7])

which explains the temperature dependence of the soft mode based on the assumption of the anharmonic electronic polarizability. The main drawback of both models is their purely phenomenological character which does not take into account the relation of the electronic structure of the ferroelectric compounds to the structural instability. Therefore, fine effects, connected e.g. with the influence of magnetic field on the transition temperature (see [8, 9]), cannot be explained within the framework of these theories. Besides, it is difficult to explain why the soft mode corresponds to long-wave vibrations in IV–VI compounds [10] but to phonons with finite wave vector in other substances (e.g. K_2SeO_4 [11, 12]).

One of the most successful models put forward for the description of structural instabilities of ferroelectric materials which is free from the aforementioned drawbacks is the vibronic theory [13, 14, 15]. According to this theory the structural transition is caused by the strong electron–vibrational pseudo-Jahn–Teller (PJT) interaction [16] in a case when the electronic configuration contains almost degenerate electronic states. This approach is justified both on the basis of microscopic models [17, 18] and on the results of the first-principles total-energy calculations [19]. The symmetry of the phase transition is defined within the framework of vibronic theory by the symmetry of the strongest mode in the electron–lattice interaction. This interaction leads to the phonon softening and the instability occurs when the frequency of the phonon mode reaches a zero value. This approach appears to be successful also in the explanation of the properties of the mixed-valence materials [20, 21], which also contain almost degenerate electronic configuration. In spite of the quantitative explanation of the properties of the soft mode the vibronic model has not been applied to the calculation of the influence of electron–vibrational interaction on a phonon with a general wave vector. Therefore to calculate the whole phonon spectra this theory has to be generalized to the case of an arbitrary phonon. Besides, it is still a matter of discussion whether the explanation of the soft-mode temperature dependence offered by vibronic theory [13, 14] is valid for IV–VI compounds [22], where the values of semiconducting gaps exceed significantly the thermal energy kT_R corresponding to room temperature T_R. Therefore, to prove the relevance of vibronic theory for 'wide gap' IV–VI ferroelectrics, one has to find a mechanism explaining the strong temperature dependence of the phonon spectra near the structural instability.

It has already been shown in [23] that the phonon spectra of the typical IV–VI compounds PbTe and PbS at room temperature can be successfully fitted within the framework of the model which puts into correspondence the phenomenological constants of the lattice dynamics model and the microscopic parameters of the vibronic approach. However, this model is inappropriate for the analysis of the temperature dependence of the phonon dispersion anomalies. Besides, since the model [23] is developed for zero temperature, the effective phenomenological constants, used for the fit of the room-temperature data, cannot be expressed in terms of the microscopic parameters of the vibronic Hamiltonian. Therefore, the method used in [23] can be considered as a semiphenomenological approach and the microscopic parameters obtained in [23] can be treated as the effective ones.

In this paper we apply the vibronic theory of ferroelectrics to obtain the microscopic description of the phonon anomalies of IV–VI compounds phonon spectra and analyse their temperature dependence in the high-symmetry phase. As an example the vibrational spectrum of PbTe, which is a typical representative of IV–VI compounds, is analysed. Although the following calculations are adapted to the specific case of IV–VI compounds, some peculiarities of the proposed model might be also valid for other segnetoelectrics (e.g. K_2SeO_4, $KTaO_3$ [11, 12, 24]). In the second section we calculate the electron–ion free energy of a cluster of a IV–VI compound which then is applied to the calculation of the

influence of the electronic system on the phonon frequencies in section 3. The complete model used for calculation of the phonon spectrum is specified in section 4. The results of calculation of the room-temperature phonon spectra of the typical IV–VI compound PbTe are presented in section 5. The temperature dependence of the phonon anomalies is analysed and discussed in sections 6 and 7. Some conclusions are presented in section 8.

2. Free energy of the cluster

Using the standard approach [14] let us consider the cluster ChMe$_6$ which in accordance with the band structure of the IV–VI compounds, contains six electrons distributed among p-orbitals of chalcogene $\{p_{0,x}^{Ch}, p_{0,y}^{Ch}, p_{0,z}^{Ch}\}$ and metal $\{p_{\varrho_i,x}^{Me}, p_{\varrho_i,y}^{Me} p_{\varrho_i,z}^{Me}\}$ ions. Here ϱ_i denote positions of Me ions in the cluster

$$\varrho_{\pm x} = [\pm 1, 0, 0] \qquad \varrho_{\pm y} = [0, \pm 1, 0] \qquad \varrho_{\pm z} = [0, 0, \pm 1].$$

To simulate the electronic structure of narrow-band IV–VI semiconductors we assume that the energies of chalcogene and metal orbitals are

$$E_{Ch} = -\Delta/2 \qquad E_{Me} = \Delta/2$$

respectively, where Δ is the parameter describing the effective width of the gap in the electronic spectrum.

To calculate the potential energy, we expand the electron–ion $V(r, Q)$ potential in distortions $\{Q_{\Gamma,\gamma}\}$ of the cluster high-symmetry ($Q = 0$) configuration up to the third power. Distortion Q_γ^Γ transforms according to the row γ of the Γ irreducible representation of the point group of the crystal. The potential energy of the cluster is the sum of the conventional ion–ion term:

$$U(Q) = \sum_\Gamma \mathcal{F}_\Gamma^{(0)} \sum_\gamma Q_{\Gamma,\gamma}^2$$

(with bare force constants $\mathcal{F}_\Gamma^{(0)}$) and a contribution from the Q-dependent energy of the electronic subsystem:

$$\Delta V(r, Q) = \sum_{\Gamma\gamma} V_{\Gamma,\gamma}(r) Q_{\Gamma,\gamma} + \sum_{\Gamma\gamma} \sum_{\Gamma'\gamma'} W_{\Gamma,\gamma;\Gamma',\gamma'}(r) Q_{\Gamma,\gamma} Q_{\Gamma',\gamma'}$$
$$+ \sum_{\Gamma\gamma} \sum_{\Gamma'\gamma'} \sum_{\Gamma''\gamma''} \xi_{\Gamma,\gamma;\Gamma',\gamma';\Gamma'',\gamma''}(r) Q_{\Gamma,\gamma} Q_{\Gamma',\gamma'} Q_{\Gamma'',\gamma''}. \qquad (1)$$

This term is represented in IV–VI compounds mainly by dipolar and shear symmetry [5].

For the dipolar contribution ($Q_{D,\gamma}$, $D = \Gamma_{15}^-$, $\gamma = x, y, z$) the expansion of $V(r, Q)$ can be reduced to the form

$$\Delta V(r, Q) = \sum_\gamma V(r) Q_{D,\gamma} + \sum_\gamma W(r) Q_{D,\gamma}^2 + \sum_\gamma \xi(r) Q_{D,\gamma}^3. \qquad (2)$$

We take into account only the strongest contributions to the electron–lattice interaction, which are due to distortion of the σ_γ-coupling caused by the displacement $Q_{D,\gamma}$ along the axis with the same index γ. This displacement mixes three p_γ orbitals, of which one, ψ_γ^{Ch}, belongs to the chalcogene and the other two, $\psi_{\rho=\pm\gamma}^{Me}$, are placed on two metal ions, which are situated along the direction with the same index γ ($\rho = \pm\gamma$). Since displacements do not mix the orbitals with different indexes γ, the eigenvalue problem can be factorized into three independent equations, each having the form

$$\begin{vmatrix} U(Q) + \Delta/2 - \varepsilon & \mathcal{T}_+ & 0 \\ \mathcal{T}_+ & U(Q) - \Delta/2 - \varepsilon & \mathcal{T}_- \\ 0 & \mathcal{T}_- & U(Q) + \Delta/2 - \varepsilon \end{vmatrix} = 0 \qquad (3)$$

$$\mathcal{T}_\pm = \pm V Q_{D,\gamma} + W Q_{D,\gamma}^2 \pm \xi Q_{D,\gamma}^3. \tag{4}$$

Here V, W and ξ are the matrix elements of potentials $V(r)$, $W(r)$ and $\xi(r)$ respectively between the chalcogene and metal wave functions connected by σ-coupling. The eigenvalues of (3) are

$$\varepsilon_{1,2} = U(Q) \pm \tfrac{1}{2} \left[\Delta^2 + 8 Q_{D,\gamma}^2 (V^2 + \widetilde{W}^2 Q_{,D\gamma}^2) \right]^{1/2}$$
$$\varepsilon_3 = U(Q) + \Delta/2$$

where

$$\widetilde{W} = \sqrt{2V\xi + W^2}. \tag{5}$$

It is seen that expansion of the dipolar electron–lattice potential up to the third order (2) leads to the renormalization (5) of the coupling constant W due to a contribution proportional to $V\xi$ which is connected with the joint action of linear and cubic terms of expansion (2). This contribution was neglected in the semiphenomenological approach [23] but has to be accounted for in the microscopic treatment.

It was shown in [23] that for large enough vibronic interaction the high-symmetry configuration can be unstable at zero temperature and the minimum of the electron–lattice system energy corresponds to the distorted cluster with equal values of $\left| Q_{D,\gamma} \right|$

$$\left| Q_{D,\gamma} \right| \equiv Q \qquad (\gamma = x, y, z). \tag{6}$$

These configurations are equivalent to displacement of two fcc sublattices relative to each other along e.g. the $\tau = [111]$ direction and, therefore, describe the dipolar distortion (see e.g. [19]).

The frozen-in dipolar shift induces the rhombohedral (R) or orthorhombic (O) unit cell distortion [17]. Both R- and O-distortions can be described as the joint action of the three shear modes $Q_{S,\beta}$ ($S = \Gamma_{25}^+$; $\beta = xy, xz, yz$) [5]. Since the shear distortions appear only in response to the dipolar shift τ [17, 5], it is natural to interpret the Γ_{25}^+ mode contribution as the second-order shear-dipolar (SD) terms of expansion (1). If we take into account that the energy relaxation in response to the dipolar shift along e.g. the x-direction appears only due to the xy- and xz-shear distortions, we arrive at the following expression for the SD contribution:

$$\Delta V_{SD}(r, Q) = \Omega(r) \left[Q_{D,x} \left(Q_{S,xy} + Q_{S,xz} \right) \right.$$
$$\left. + Q_{D,y} \left(Q_{S,yx} + Q_{S,yz} \right) + Q_{D,z} \left(Q_{S,zy} + Q_{S,zx} \right) \right] \tag{7}$$

where the SD coupling parameter

$$\Omega(r) = \Omega_{\Gamma_{15}^-,\gamma; \Gamma_{25}^+,\beta}(r) \equiv \partial^2 V(r, Q)/\partial Q_{D,\gamma} \partial Q_{S,\beta} \qquad \gamma = x, y, z. \tag{8}$$

Here $\beta = \gamma\gamma'$; $\gamma' \neq \gamma$.

In order to investigate the instability against the shear mode with a bare frequency ω_S, we consider the frozen-in dipolar $Q_{\tau=[111]}$ displacement and take into account only the the influence of distortions on σ-coupling between the chalcogene and metal ions. The Me ions tend to relax the distortions of σ-coupling bonds. Taking into account that in the case of e.g. $Q_{\tau=[111]}$ dipolar displacement three Me ions ($\rho = x, y, z$) are near neighbours and three others ($\rho = -x, -y, -z$) are the next-nearest neighbours one can factorize the eigenvalue problem into three independent equations. For example, for $\gamma = x$

$$\begin{vmatrix} U(Q) + A - \varepsilon & 2\Omega Q_{D,x} \left(Q_{S,xy} + Q_{S,xz} \right) & 0 \\ 2\Omega Q_{D,x} \left(Q_{S,xy} + Q_{S,xz} \right) & U(Q) - A - \varepsilon & 0 \\ 0 & 0 & U(Q) + \Delta/2 - \varepsilon \end{vmatrix} = 0 \tag{9}$$

$$A = \tfrac{1}{2}\left[\Delta^2 + 8Q_{D,x}^2(V^2 + \widetilde{W}^2 Q_{D,x}^2)\right]^{1/2}$$

where Ω is equal to half of the matrix element of SD coupling potential $\Omega(r)$ between the chalcogene and three near-neighbour metal wave functions. The eigenvalues of three determinants (9) for $\gamma = x, y, z$ are

$$\varepsilon_{1,2}^\gamma = U(Q) \pm \tfrac{1}{2}\left\{\Delta^2 + 8Q_{D,\gamma}^2(V^2 + \widetilde{W}^2 Q_{D,\gamma}^2) + 4\Omega^2\left[Q_{D,\gamma}(Q_{S,\beta_\gamma} + Q_{S,\beta_\gamma'})\right]^2\right\}^{1/2} \quad (10)$$

$$\varepsilon_3^\gamma = U(Q) + \Delta/2.$$

Here $\gamma = x, y, z$, $\beta_x = xy, \beta_x' = xz$; $\beta_y = yx, \beta_y' = yz$; $\beta_z = zy, \beta_z' = zx$.

It was shown in [23] that for large enough PJT parameters the cluster at zero temperature can be unstable against the shear modes and the symmetry of distortions corresponds to the R- and O-transformations [5]:

$$|Q_{S,xy}| = |Q_{S,xz}| = |Q_{S,yz}|. \quad (11)$$

Therefore the offered scheme of the electron–ion interaction gives a correct description of the symmetry of the structural instability.

Neglecting the terms which are independent of the distortions Q one obtains the following expression for the free energy of the cluster:

$$F(Q) = U(Q) + 2\sum_\gamma F_\gamma(Q)$$

$$F_\gamma(Q) = -kT\sum_{n=1}^{3}\ln\left(1 + \exp\left(-\frac{\varepsilon_n^\gamma}{kT}\right)\right). \quad (12)$$

Here k is the Boltzmann constant, T is the temperature and ε_n^γ are the eigenvalues (10). The factor of 2 in (12) is due to spin summation. The expression for $F_\gamma(Q)$ takes the form

$$F_\gamma(Q) = -kT\left[\ln 2\left(1 + \cosh\right.\right.$$

$$\left.\left.\times\frac{\left\{\Delta^2 + 8(V^2 + \widetilde{W}^2 Q_{D,\gamma}^2)Q_{D,\gamma}^2 + 4\Omega^2\left[Q_{D,\gamma}(Q_{S,\beta_\gamma} + Q_{S,\beta_\gamma'})\right]^2\right\}^{1/2}}{2kT}\right)\right].$$

Since we restrict ourselves to the description of the lattice dynamics in the high-symmetry phase where the minimum energy of the system corresponds to zero displacements $\{Q_{\Gamma,\gamma}\}$, one can expand the free energy in small distortions provided this approximation does not change the symmetry properties of the structural instability (6, 11). It was shown [23] that the approximate potential obtained by expansion in small distortions results in the same structural transition (6, 11) and, therefore, retains the symmetry properties of the exact one.

The expansion of the free energy up to the fourth order gives

$$F_\gamma \approx U(Q) - \mathcal{K}_{har}(T)Q_{D,\gamma}^2 - \mathcal{K}_{anhar}^D(T)Q_{D,\gamma}^4 - \mathcal{K}_{anhar}^{SD}(T)Q_{D,\gamma}^2\left(Q_{S,\beta_\gamma} + Q_{S,\beta_\gamma'}\right)^2 \quad (13)$$

where the electronic contribution to the lattice energy can be represented as the sum of harmonic and anharmonic terms with the temperature dependent coefficients

$$\mathcal{K}_{har}(T) = (2V^2/\Delta)\tanh(\alpha/2) \quad (14)$$

$$\mathcal{K}_{anhar}^D(T) = (2/\Delta)\tanh(\alpha/2)\left[\widetilde{W}^2 - (2V^4\Delta)\left(1 - \frac{\alpha}{\sinh\alpha}\right)\right] \quad (15)$$

$$\mathcal{K}_{anhar}^{SD}(T) = (\Omega^2/\Delta)\tanh(\alpha/2) \quad (16)$$

$$\alpha = \Delta/2kT.$$

The expressions (13)–(16) for the expansion of the free energy coincide for $T = 0$ with equations (3)–(5) of [23] if one substitutes the matrix element W for the effective one $\widetilde{W}$ (5).

3. Vibronic contribution to the interionic potential and lattice dynamics

To calculate the lattice dynamics in the cubic phase, it is sufficient to consider the case of the stable high-symmetry configuration ($Q = 0$). Therefore we expand the cluster energy in the small distortions Q of the equilibrium state up to the fourth order. Then the potential energy of the cluster is given by the sum of the harmonic terms

$$U^c(Q) = \left(\omega_0^2/2 - \mathcal{K}_{har}(T)\right) \sum_{\gamma} Q_{D,\gamma}^2 \tag{17}$$

where the PJT interaction results in softening of the phonon frequencies ω_0, and anharmonic contributions

$$\mathcal{U}_D^{app}(Q_D) = -\mathcal{K}_{anhar}^D(T) \sum_{\gamma} Q_{D,\gamma}^4 \tag{18}$$

$$\mathcal{U}_{SD}^{app}(Q_S) = -\mathcal{K}_{anhar}^{SD}(T) \Big[Q_{D,x}^2 \left(Q_{S,xy} + Q_{S,xz}\right)^2$$
$$+ Q_{D,y}^2 \left(Q_{S,yx} + Q_{S,yz}\right)^2 + Q_{D,z}^2 \left(Q_{S,zy} + Q_{S,zx}\right)^2 \Big]. \tag{19}$$

To consider the lattice dynamics one should generalize the cluster approach to the case of longitudinal and transverse phonon modes with an arbitrary wave vector q. Finite wave vector can be taken into account by the substitution of the distortions Q for the projection operators $\widetilde{Q}$ which correspond to the projection of the phonon modes on the cluster distortions with the definite point symmetries (see e.g. [25]). According to [25] one has to introduce different interaction constants λ_{long} and λ_{tr} for distortions which are connected with the the ionic displacement parallel and perpendicular to the wave vector q respectively. It was shown in [23] that in this case the dipolar distortion can be effectively decoupled into longitudinal $\widetilde{Q}_{D,\gamma}^{long}$ and transversal $\widetilde{Q}_{D,\gamma}^{tr}$ projection operators

$$\widetilde{Q}_{D,\gamma} = \widetilde{Q}_{D,\gamma}^{long} + \theta \widetilde{Q}_{D,\gamma}^{tr}$$

where

$$\theta = \lambda_{tr}/\lambda_{long}.$$

The projections of the phonon modes on the dipolar (e.g. for $\gamma = x$)

$$\widetilde{Q}_{D,x}^{long} = u_{0x}^{Ch} - \tfrac{1}{2} \left(u_{\varrho_1 \mathbf{x}}^{Me} + u_{\varrho_{-1} \mathbf{x}}^{Me}\right)$$

$$\widetilde{Q}_{D,x}^{tr} = u_{0x}^{Ch} - \tfrac{1}{4} \left(u_{\varrho_2 \mathbf{x}}^{Me} + u_{\varrho_{-2} \mathbf{x}}^{Me} + u_{\varrho_3 \mathbf{x}}^{Me} + u_{\varrho_{-3} \mathbf{x}}^{Me}\right)$$

and shear (e.g. for $\beta = xy$)

$$\widetilde{Q}_{S,xy} = \tfrac{1}{2} \left(u_{\varrho_1 \mathbf{y}}^{Me} - u_{\varrho_{-1} \mathbf{y}}^{Me} + u_{\varrho_2 \mathbf{x}}^{Me} - u_{\varrho_{-2} \mathbf{x}}^{Me}\right)$$

irreducible representations of the point group can be expressed in terms of the ionic displacements u. Here $u_{\varrho_{\pm j}\gamma}^{Me}$ is the displacement of ion Me_j along the γ direction ($j = \pm 1, \pm 2, \pm 3$ denote the Me ions in $[\pm 1, 0, 0]$, $[0, \pm 1, 0]$, $[0, 0, \pm 1]$ positions).

It is clear that the quadratic contributions (17) to the potential energy can be taken into account in terms of the temperature dependent renormalization of the phenomenological

parameters of the standard models. The anharmonic contribution (m is the unit cell index) is the sum of dipolar and shear-dipolar terms

$$\varepsilon_{PJT}(Q) = -\mathcal{K}^D_{anhar}(T) \sum_{\mathbf{m}\gamma} \widetilde{Q}^4_{D,\gamma}(m) - \mathcal{K}^{SD}_{anhar}(T)$$

$$\times \sum_{\mathbf{m}} \left\{ \widetilde{Q}^2_{D,x}(m)\left[\widetilde{Q}_{S,xy}(m) + \widetilde{Q}_{S,xz}(m)\right]^2 + \widetilde{Q}^2_{D,y}(m)\left[\widetilde{Q}_{S,yx}(m)\right. \right.$$

$$\left. + \widetilde{Q}_{S,yz}(m)\right]^2 + \widetilde{Q}^2_{D,z}(m)\left[\widetilde{Q}_{S,zy}(m) + \widetilde{Q}_{S,zx}(m)\right]^2 \Big\}. \tag{20}$$

Expression (20) is equivalent to (6) of [23] for $T = 0$ in temperature-dependent coefficients $\mathcal{K}^{D,SD}_{anhar}(T)$.

4. Model

To consider the lattice dynamics, we use the conventional shell model [2, 3]

$$\hat{\mathbf{M}}\omega^2\hat{\mathbf{U}} = (\hat{\mathcal{R}} + \hat{\mathbf{Z}}\hat{\mathcal{C}}\hat{\mathbf{Z}})\hat{\mathbf{U}} + (\hat{\mathcal{T}} + \hat{\mathbf{Z}}\hat{\mathcal{C}}\hat{\mathbf{Y}})\hat{\mathbf{W}}$$

$$\hat{\mathbf{m}}\omega^2\hat{\mathbf{W}} = (\hat{\mathcal{T}}^* + \hat{\mathbf{Y}}\hat{\mathcal{C}}\hat{\mathbf{Z}})\hat{\mathbf{U}} + (\hat{\mathcal{L}} + \hat{\mathbf{Y}}\hat{\mathcal{C}}\hat{\mathbf{Y}})\hat{\mathbf{W}} \tag{21}$$

$$\hat{\mathcal{L}}_{\alpha\beta}(tt') = \hat{\mathcal{S}}_{\alpha\beta} + \delta_{\alpha\beta}\delta_{tt'}\left[k_t + \left(\hat{\mathcal{T}}_{\alpha\alpha}(tt)\right) - \left(\hat{\mathcal{S}}_{\alpha\alpha}(tt)\right)\right]. \tag{22}$$

Here $\hat{\mathbf{U}}$ is the matrix of the displacements of the cores with masses and charges defined by matrices $\hat{\mathbf{M}}$ and $\hat{\mathbf{Z}}$, respectively. $\hat{\mathbf{W}}$ is the matrix of the shell displacements with respect to the atomic core. The matrices $\hat{\mathbf{m}}$ and $\hat{\mathbf{Y}}$ define the shell masses and charges respectively. $\hat{\mathcal{R}}$, $\hat{\mathcal{T}}$, $\hat{\mathcal{S}}$ are the matrices of short-range interaction: core–core, core–shell and shell–shell respectively; $\hat{\mathcal{C}}$ is the Coulomb matrix; k is the elastic constant of the interionic core-shell interaction; t is the sublattice index.

To treat the harmonic part of the potential energy, we use the model proposed in [5]. This model takes into account the interactions specific for the segnetoelectric compounds (i.e. the long-range non-coulombic interaction and stabilization of the lattice against the shear distortions by the next-nearest neighbour coupling).

In conventional treatment the PJT effect is characterized by the interaction of the electronic subsystem with displacements of the cores. However, it is known that the main contribution to the polarizability of IV–VI compounds is provided by the dipole moments of the electronic shells [5]. Thus, it is natural to use the model of the unconventional Jahn–Teller (UJT) effect [26] where the shell deformations adopt the role which in conventional Jahn–Teller systems is played by nuclear displacements. In order to treat the lattice dynamics in the framework of the UJT model, we include the anharmonic interactions (20) in the $\hat{\mathbf{S}}$–$\hat{\mathbf{S}}$ coupling matrix $\hat{\mathcal{S}}$ and, therefore, in the $\hat{\mathbf{W}}$–$\hat{\mathbf{W}}$ coupling matrix $\hat{\mathcal{L}}$ (see (22)).

For the sake of simplicity we treat the anharmonic contributions in the spirit of effective mean field decoupling [23]. The idea of this approximation is to represent the fourth-order term in distortions by the product of two quadratic multipliers and replace the ionic displacements with the partial ones in the first factor. The partial displacements of an ion belonging to the sublattice t of the unit cell m due to the phonon mode (q, ν) can be expressed in terms of the polarization vectors $e^t_{q,\nu}$:

$$u^{q,\nu}_{m,t} = \exp\left(iq \cdot R_m\right) e^t_{q,\nu}/\sqrt{M_t} \tag{23}$$

where M_t is the dimensionless ionic mass. The polarization vectors, in turn, can be obtained as the solutions of equations (21) and (22) where the anharmonic contributions are neglected.

The procedure of decoupling is equivalent at fixed temperature T_0 to that outlined in [23], although in the formalism suggested here the decoupling coefficients are temperature dependent due to temperature dependence of the anharmonic contribution (20).

This procedure gives the following expressions for dipolar

$$\mathcal{K}^D_{anhar}(T_0)\widetilde{Q}^4_{D,\gamma}\left(\{u_{m,t}\}\right)\Big|_{q,\nu} \approx \Lambda_D(T_0)\widetilde{Q}^2_{D,\gamma}\left(\{u_{m,t}\}\right)\left|\widetilde{Q}_{D,\gamma}\left(\{u^{q,\nu}_{m,t}\}\right)\right|^2 \tag{24}$$

and shear-dipolar

$$\mathcal{K}^{SD}_{anhar}(T_0)\widetilde{Q}^2_{D,\gamma}\left(\{u_{m,t}\}\right)\widetilde{Q}_{S,\beta}\left(\{u_{m,t}\}\right)\widetilde{Q}_{S,\beta'}\left(\{u_{m,t}\}\right)\Big|_{q,\nu}$$

$$\approx \Lambda_{SD}(T_0)\left|\widetilde{Q}_{D,\gamma}\left(\{u^{q,\nu}_{m,t}\}\right)\right|^2\widetilde{Q}_{S,\beta}\left(\{u_{m,t}\}\right)\widetilde{Q}_{S,\beta'}\left(\{u_{m,t}\}\right) \tag{25}$$

anharmonic contributions. Here $\Lambda_D(T_0)$ and $\Lambda_{SD}(T_0)$ are the phenomenological parameters for fixed temperature T_0. Thus, the suggested approximation leads to effective coupling constants

$$\widetilde{\Lambda}^{q,\nu}_{D,SD}(T) = \Lambda_{D,SD}(T)\left|\widetilde{Q}_{D,\gamma}\left(\{u^{q,\nu}_{m,t}\}\right)\right|^2 \tag{26}$$

which depend on the phonon wave vector q, branch index ν and temperature.

Since the UJT anharmonic contributions are treated as a part of $\hat{\mathbf{S}}$–$\hat{\mathbf{S}}$ or $\hat{\mathbf{W}}$–$\hat{\mathbf{W}}$ interactions, one has to use the partial displacement vectors of the shells for the evaluation of effective parameters (26). Therefore we use the shell displacement vectors $\hat{\mathbf{S}}$ for evaluation of the short-range shear-dipolar interaction. Since the shell polarizability is dominant in the dipolar response of ferroelectrics [5], one can use the relative displacement vectors of a shell with respect to the atomic core $\hat{\mathbf{W}}$.

The model suggested accounts for specific features of the lattice dynamics of the ferroelectric compounds which are connected with the closeness to the structural instability and has significant advantages in the treatment of the IV–VI compound phonon spectra in comparison with the purely phenomenological Cochran model [2, 3, 4]. In spite of more than 15 phenomenological parameters which were involved in the fit procedure within the standard Cochran model [2, 3], this model is unable to describe all types of anomaly observed in phonon dispersion curves. Besides, the parameters obtained as the result of the fit procedure, are incompatible with the related compounds PbTe and PbS.

On the other hand, within our approach the standard parameters of the conventional shell model are almost equal for these two compounds (see [5]), and the only parameters which significantly changed for different compounds are the constants which are connected with structural instability [23]. There are parameters which can be defined from the fit to the room-temperature T_R data: (i) dipolar ($\Lambda_D(T_R)$) constant; (ii) shear-dipolar ($\Lambda_{SD}(T_R)$) constant; (iii) ratio $\theta = \lambda_{tr}/\lambda_{long}$ (we use the same value of θ for dipolar and shear-dipolar anharmonic terms).

5. Room-temperature spectrum

Since the experimental data on the phonon spectra of PbTe [2] for all branches along the symmetry directions are available only for ambient temperature one should fit the model parameters to the dispersion curves at this temperature. We used for the description of the room-temperature phonon spectrum the constants which were obtained in [23].

To analyse the temperature dependence of the phonon spectrum of PbTe we reproduce in figure 1 the results of theoretical fitting (full line) together with the experimental data for room temperature T_R [23]. To compare the results of our approach with that of the standard
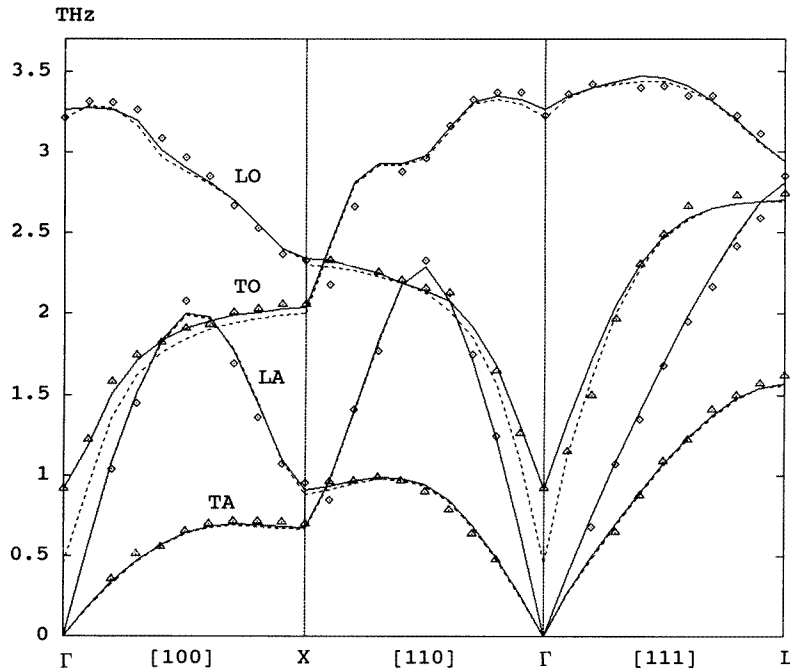
Figure 1. Calculated PbTe phonon spectrum for room temperature (solid lines) and 4 K (dashed lines) with the experimental data for room temperature.

ones one can note that the description of TO($q \sim 0$) anomalies is much better than the results of the models applied in [2, 3]. The phenomenological parameters of conventional shell model are close to those obtained in [5]. The values of the specific for PJT coupling parameters are $\Lambda_D(T_R) = 2.87 \left(e^2/2\mathcal{V}\right)$, $\Lambda_{SD}(T_R) = 11.3 \left(e^2/2\mathcal{V}\right)$, $\theta = 1.43$ ($\mathcal{V}$ is the volume of the elementary cell and e is the charge of the electron). The room-temperature phonon spectrum of another IV–VI compound PbS can also be reproduced theoretically with values of the phenomenological constants which are close to those of PbS [23].

One of the most interesting features of the suggested approach is that the LO($q \sim 0$) anomalies are also reproduced. These anomalies were explained previously in [2] by the interaction of the optic mode with the free carriers induced by imperfections. This explanation seems rather doubtful due to the absence of similar anomalies in other classes of compounds with imperfect lattices. In our approach both LO($q \sim 0$) and TO($q \sim 0$) anomalies can be ascribed to the dipolar PJT interaction specific for IV–VI compounds. These anomalies disappear for a zero value of parameter Λ_D.

The shear-dipolar coupling leads to the anomalies of TO[100] and TO[110] branches (see [23]). These anomalies cannot be reproduced without inclusion of the shear-dipolar coupling specific for the rhombohedral and orthorhombic distortions in the models (see e.g. results of [2, 3]).

6. Model for temperature dependence

To consider the temperature dependence of lattice dynamics one has to consider the temperature dependence of harmonic (14) and anharmonic (15) contributions to the shell–

shell interaction.

To reduce the number of model phenomenological parameters we assume that the relative changes of all shell–shell force constants with temperature can be described by the same universal function $\mathcal{K}_{har}(T)$ (see (14)) which depends only on the statistical distribution of electrons on the energy levels involved in the PJT interaction (14). Introducing the parameter (see e.g. (14))

$$\kappa = 2V^2/\Delta \tag{27}$$

describing the strength of the renormalization of the bare shell–shell force constants $\mathcal{F}_{SS}^{(0)}$, one can determine the temperature dependence of the force constants $\mathcal{F}_{SS}(T)$ by the relation

$$\left(\mathcal{F}_{SS}(T) - \mathcal{F}_{SS}^{(0)}\right)\big/\mathcal{F}_{SS}^{(0)} = -\kappa\,\tanh(\Delta/4kT).$$

The bare value of the force constant $\mathcal{F}_{SS}^{(0)}$ is not known but can be easily derived from the values of the parameters $\mathcal{F}_{SS}(T_R)$. These parameters were determined by the fit of the solutions of the shell model equations (21) and (22), including the additional contribution (17)–(19), to the room-temperature T_R data in [23]. Under the condition $(\mathcal{F}_{SS}(T) - \mathcal{F}_{SS}(T_R))/\mathcal{F}_{SS}(T_R) \ll 1$, which is valid for the specified set of parameters (see below), force constants can be expressed in terms of constants $\mathcal{F}_{SS}(T_R)$ and parameter κ found in the fit to the room-temperature experimental data:

$$\mathcal{F}_{SS}(T) = \mathcal{F}_{SS}(T_R)\left\{1 + \kappa\left[\tanh(\Delta/4kT_R) - \tanh(\Delta/4kT)\right]\right\}. \tag{28}$$

Since we neglect all anharmonic contributions except those which arise due to PJT interaction the temperature dependence of the anharmonic force constant $\Lambda_{D,SD}(T)$ can be expressed by

$$\Lambda_{D,SD}(T) = \Lambda_{D,SD}(T_R)\left[\mathcal{K}(T)/\mathcal{K}(T_R)\right] \tag{29}$$

(here the constants $\Lambda_{D,SD}(T_R)$ have been obtained by the fit to the room-temperature data of the model (17–19, 21, 22)) where, e.g., for dipolar mode

$$\mathcal{K}(T) = \tanh(\alpha/2)\left[\beta + (\alpha - \sinh\alpha)/\sinh\alpha\right]. \tag{30}$$

Here we have introduced the parameter

$$\beta = \widetilde{W}^2\Delta/2V^4 \tag{31}$$

describing the strength of the anharmonic PJT interaction.

The procedure of evaluation of the quantities κ and β, which define the temperature dependence and are expressed (27, 31, 5) in terms of the parameters of the microscopic Hamiltonian (1), is rather straightforward provided the room-temperature constants $\mathcal{F}_{SS}(T_R)$ and $\Lambda_{D,SD}(T_R)$ are determined and the value of the gap in the electronic spectrum Δ is known. The values of parameters of the microscopic Hamiltonian (1) are not known within the framework of our treatment. Nevertheless, one can unambiguously determine the constants κ and β provided the frequencies of the TO[$q = 0$] mode are known at least for two temperatures $T_{1,2} \neq T_R$. Then, the relevance of the model can be checked by comparison of the phonon spectra for all values of wave vectors in the high symmetry direction with experimental data in wide temperature range.

7. Discussion of the temperature dependence of the phonon spectrum

The models which postulate that stabilization of the high-symmetry phase occurs due to anharmonic contribution to the phonon frequencies $\hbar\omega_{ph}$ (see e.g. [27]) successfully explain the temperature dependence of the soft mode because the characteristic temperatures
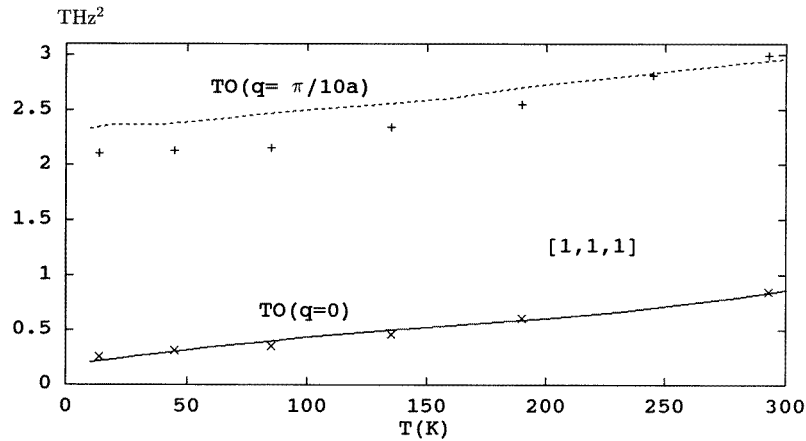
Figure 2. The calculated squares of TO[$q = 0$] (full line) and TO[$q = 2\pi/a(0.1, 0.1, 0.1)$] (dashed line) frequencies in comparison with experimental data [28] ($\times$ and $+$ respectively).

$T_{ph} \sim \hbar\omega_{ph}/k$ are comparable to the room temperature T_R. The function $\tanh\left(\hbar\omega_{ph}/2kT\right)$ entering the equations of the anharmonic models is sensitive to the temperature variations in the range 0 K $< T < 300$ K since $2kT_R \approx \hbar\omega_{ph} \approx 100$ K–300 K. The drawback of these models is that the simple explanation of the soft-mode temperature dependence cannot be connected either to the electronic or to the structural properties of the system.

On the other hand the models which are based on the vibronic interaction contain the ratio of the temperature and the electronic gap Δ. Therefore, in the case of IV–VI compounds, one has to explain how the sharp temperature (0 K $< T < 300$ K) dependence of the soft-mode frequency can be consistent with rather 'wide' ($\Delta \approx 1000$–3000 K) gaps in the electronic spectrum. It is clear that, unlike the case of models which involve the lattice anharmonicity as a source of structural instability and where the changes of characteristic temperature dependent factors is noticeable, the variations of the functions (28) and (29) does not exceed a few per cent.

To avoid this difficulty one can suggest that there is an ionic polarizability that is temperature dependent instead of ion–ion interaction constants [7]. In some sense the approach offered here is similar to the method of [7] since in our model the temperature dependent interaction is included in the shell–shell dynamical matrix. Therefore, the treatment offered here leads to the *temperature dependent polarizability*. It is clear that small variations with temperature of ion–ion force constants cannot produce significant changes of phonon frequencies. But even small changes of the shell–shell interactions can produce significant phonon renormalization provided the electronic polarizability, as in the case of IV–VI compounds, is high [5]. Moreover, inclusion of temperature dependent factors in the shell–shell dynamic matrix can give a natural explanation of the experimentally observed [28] sharp temperature dependence of transverse optic (TO) phonons which coexists with the weak temperature dependence of longitudinal optic (LO) branches. In compounds with large LO[$q = 0$]–TO[$q = 0$] splitting, which is equivalent to the high electronic polarizability, the LO mode is stabilized by long-range Coulomb forces whereas the TO mode is extremely sensitive to even small variations of shell–shell force constants.

To compare the calculations with experimental data we used the model parameters which were obtained from the fit [23] to the room-temperature experimental data and calculated
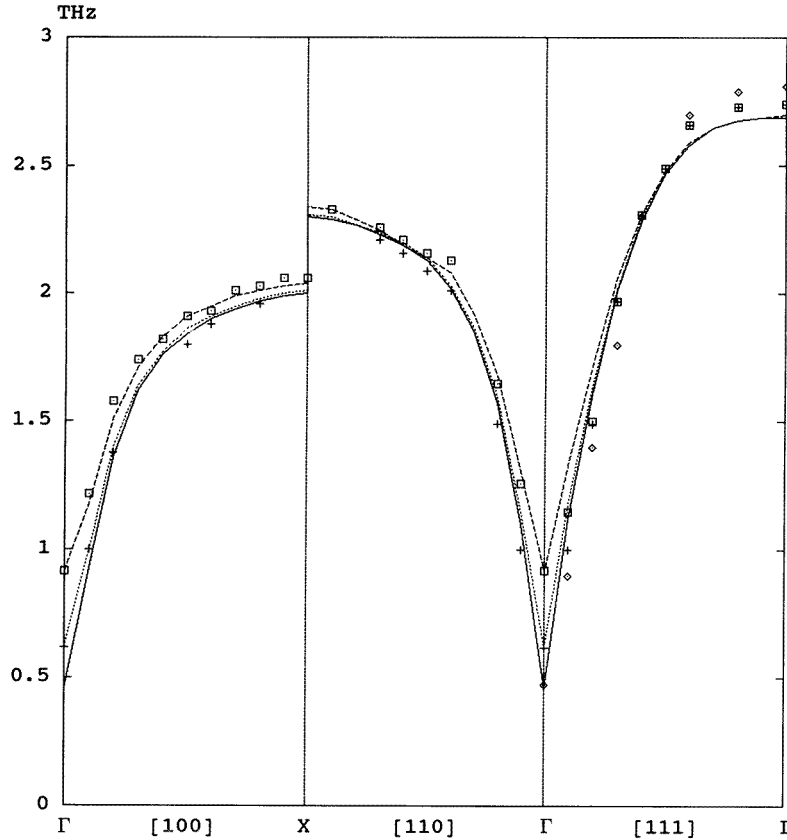
Figure 3. Theoretical and experimental frequencies of TO branches of PbTe for room temperature (dashed line and squares); 80 K (dotted and crosses) and 4 K (full line and diamonds). Experimental points for 293 K and 4 K were taken from [2] and [31] respectively. Experimental data for 80 K were obtained as the result of the procedure based on the re-scaling of the measurements of temperature dependence of $Pb_{0.82}Sn_{0.18}Te$ phonon branches to the PbTe lattice [32].

their temperature dependence according to relations (28)–(30). The value of the electronic gap $\Delta = 0.25$ eV was taken from [29]. The values of the parameters $\kappa = 0.2$ and $\beta = 0.08$ were obtained from the fit to the frequencies of the TO$[q = 0]$ mode at $T_R = 300$ K, $T_1 = 80$ K and $T_2 = 4$ K.

To check up whether our model is able to reproduce the temperature dependence of the soft mode we have calculated and compared with the experimental data [28] the temperature dependence of TO$[q = 0]$ and TO$[q = 2\pi/a(0.1, 0.1, 0.1)]$ phonon frequencies (see figure 2). Rather good agreement confirms that the chosen values of κ and β reproduces the temperature dependence of the soft mode in the whole temperature range. Model calculations also reproduce experimentally observed independence of temperature of LO branches

$$\left| \omega^2_{LO[q=0]}(4 \text{ K}) - \omega^2_{LO[q=0]}(300 \text{ K}) \right| / \omega^2_{LO[q=0]}(4 \text{ K}) \approx 0.03$$

in the temperature range where renormalization of TO phonons is significant

$$\left| \omega^2_{TO[q=0]}(4 \text{ K}) - \omega^2_{TO[q=0]}(300 \text{ K}) \right| / \omega^2_{TO[q=0]}(4 \text{ K}) \approx 2.78.$$

Moreover, TO[$q \approx 0$] phonons are the only part of the phonon spectra which, in accordance with the experiment, renormalizes significantly as the temperature decreases (see the dashed line in figure 1). The calculated temperature dependence of TO phonon branches in comparison with experimental data is presented in figure 3.

One of the most crucial differences between the 'lattice anharmonicity' and PJT models is the scale of the force constant renormalization which is necessary to drive a system into a structural instability. The deviation of the force constant from its room-temperature value is of the order of the bare constant in the former approach whereas it does not exceed a few per cent in the latter one. Therefore, the PJT model implies that even at room temperature the lattice is barely stable. Indeed the experimental data and theoretical considerations are in favour of this assumption. The experimental evidence of the closeness to the instability [30] is e.g. extremely high sensitivity of $Pb_{1-x}Sn_x Te$ properties with respect to the composition and pressure. Theoretical considerations (e.g. model treatment [5, 17, 18] and the *ab initio* [19] approach) also support the conclusion that IV–VI compounds are close to the structural instability even at ambient temperature.

8. Conclusions

In conclusion, it was shown that the phonon spectrum of the IV–VI compounds and its temperature dependence can be explained within the framework of the pseudo-Jahn–Teller model in spite of the comparably wide gap in the electronic spectrum. Although the electronic gap, which is fairly wide in comparison with room temperature, leads to a small renormalization of the force constants, the unconventional nature of the pseudo-Jahn–Teller effect, when the interaction is connected rather with the polarization of electronic shells than with the nuclei displacements, results in significant soft-mode temperature dependence. The model presented is able to describe the temperature dependence of the whole phonon spectrum. The quantitative agreement with experiment indicates that IV–VI compounds are close to structural instability even at room temperature.

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