LATTICE DYNAMICS OF THE TERNARY-LAYERED $TlGaSe_2$ COMPOUND

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Abstract

We present first-principles calculation of lattice dynamics of the $TlGaSe_2$ ternary semiconductor compounds. Calculations have been performed using open-source code ABINIT on the basis of the density functional perturbation theory within the plane-wave pseudopotential approach. Results on the frequencies of phonon modes in the center of the Brillouin zone and the dispersion of transverse shear acoustic branch of the phonon spectra agree well with experimental data on Raman scattering, infrared reflectivity, and ultrasound wave propagation in $TlGaSe_2$. The calculated and experimental temperature dependences of heat capacity are in a good agreement up to the room temperature. Along the layer, the low-frequency acoustic branch displays the bending wave behavior which is characteristic of the layer crystal structures. We have calculated elastic and compliances tensor, the directional Grüneisen functions, and the coefficients of the linear thermal expansion $TlGaSe_2$.

We obtained that both principal coefficients of linear thermal expansion are positive in the range of temperature above 5 K.

1. Introduction

In recent years, the semiconductor compound $TlGaSe_2$, as well as its structural analogue $TlInS_2$, is studied rather intensively. They attract interest because of structural phase transitions found in these crystals. The existence of structural phase transition in this compound, apparently, was first observed in [1] where temperature dependence of the Raman spectra and lattice absorption was studies. In [2], it was suggested that this is possibly a ferroelectric phase. To substantiate this assumption, the authors referred to the hypothesis by Orgel [3] who predicted the possibility of ferroelectric properties of the crystals containing univalent Tl ions with stereochemically active lone electron pair. Later, independently, a similar assumption was made in [4]. In [5], the displacement of atoms from their positions in the direction of crystallographic *a*-axis was drawn to explain the nature of the ferroelectric phase transition. The first proof of the ferroelectric phase transition in TlGaSe2 was obtained by the method of submillimeter dielectric spectroscopy in [6]. In addition to this work, it was argued that the observed behavior of dielectric dispersion in the temperature range of 120-107 K is typical for ferroelectrics with incommensurate phase. Final confirmation of these views was obtained in the X-ray diffraction studies [7]. As far as we know, despite the great diversity of experimental data on IR and Raman spectra, calorimetric measurements and thermal expansion for the compound $TlGaSe_2$, theoretical calculations of lattice dynamics, which would have helped to shed light on the nature

of phase transitions and negative thermal expansion at low temperatures [8], have not been reported in the literature. In this work, we perform these calculations from first principles in the framework of the density functional perturbation theory. We use the norm preserving pseudopotentials and local density approximation taking into account the exchange-correlation corrections. It is known that first-principles calculations of lattice dynamics based on the density functional perturbation theory are sufficiently accurate, and employing this method, the phonon dispersions for many crystals are reproduced quite well. In particular, this method was successfully applied to the calculation of lattice dynamics of layered crystal of graphite, which is characterized by weak van der Waals chemical binding between the layers [9].

2. Structural data and group-theoretical analysis of phonon spectrum of $TlGaSe_2$

Ternary $TlGaSe_2$ compound crystallizes in a monoclinic system with base-centered lattice and space group symmetry C_{2h}^6 at room temperature [10]. The primitive cell contains 8 formula units. The crystal structure consists of layers composed of tetrahedral complexes Ga_4Se_{10} linked together by the common atoms of selenium. Univalent thallium ions are in trigonal-prismatic voids between these complexes. Two layers within the unit cell are rotated relative to each other at 90° [10].

Each layer consists of two atoms of Tl1, Tl2, Ga1, Ga2, Se3, Se4, and Se5 and one atom of Se1 and Se2. A rotation about the second-fold axis accompanied by a shift along *c*-direction transforms each layer into itself. Unit cell parameters and reduced coordinates of atoms inside the unit cell (in units of the corresponding parameters of monoclinic unit cell) taken from [9], and our optimized data are given in Tables 1 and 2.

Table 1. Experimental and optimized unit cell parameters of $TlGaSe_2$.

a^{exp}(Å)	b^{exp} (Å)	c^{exp} (Å)	β^{exp}	a^{opt} (Å)	b^{opt} (Å)	c^{opt} (Å)	β^{opt}
10.772	10.771	15.636	100.06°	10.446	10.446	16.760	99.09°

Table 2. Experimental and optimized atomic coordinates of $TlGaSe_2$.

Atom	x^{exp}	y^{exp}	z^{exp}	x^{opt}	y^{opt}	z^{opt}
Tl1	0.4632	0.1885	0.1078	0.4605	0.1878	0.0949
Tl2	0.2163	0.0613	0.6158	0.2134	0.0617	0.6047
Ga1	0.3981	0.1880	0.8378	0.3953	0.1879	0.8260
Ga2	0.1461	0.0639	0.3391	0.1430	0.0644	0.3263
Se1	0	0.9295	0.2500	0	0.9270	0.2500
Se2	0	0.4468	0.2500	0	0.4496	0.2500
Se3	0.2047	0.4370	0.0695	0.2092	0.4380	0.0888
Se4	0.2588	0.1882	0.2508	0.2614	0.1884	0.2504
Se5	0.4541	0.3124	0.5732	0.4588	0.3118	0.5864

Pay attention to the extreme closeness of the cell parameters in the layer plane, which, together with a unique value of the monoclinic angle, allows a high-accuracy transformation of a base-centered monoclinic cell into a body-centered tetragonal one, as it is noted in [4]. As one can see from Table 2, the optimized parameters *a* and *b* are somewhat reduced, while the value of *c* significantly increased after optimization, with unit-cell volume increased by 1% approximately. Estimates show that the layer thickness and the unit cell size in the direction parallel to the layers decrease, as a result of optimization, approximately in equal measure, i.e. the layer shrinks as a whole but the distance between layers increases dramatically.

The Brillouin zone for base-centered monoclinic lattice [11] constructed on the reciprocal lattice vectors $\mathbf{g}_1 = 2\pi\ (a^{-1}, b^{-1}, a^{-1} \tan(\beta-\pi/2))$, $\mathbf{g}_2 = 2\pi\ (-a^{-1}, b^{-1}, -a^{-1} \tan(\beta-\pi/2))$ and $\mathbf{g}_3 = 2\pi\ (0, 0, c^{-1} \sec(\beta-\pi/2))$ is bounded by planes: $\pm 1/2\ \mathbf{g}_3$; $\pm 1/2\ \mathbf{g}_1$; $\pm 1/2\ \mathbf{g}_2$; $\pm 1/2\ (\mathbf{g}_1 - \mathbf{g}_3)$; $\pm 1/2\ (\mathbf{g}_2 + \mathbf{g}_3)$; $\pm 1/2\ (\mathbf{g}_1 - \mathbf{g}_2 - \mathbf{g}_3)$.

The coordinates of symmetric points and the matrix of irreducible representations are given in [12]. According to [12], the degeneracy of phonon branches occurs along line V at the boundary of the Brillouin zone (due to the symmetry with respect to time reversal the representations of V1 and V2 are degenerate).

3. Method of calculation

Calculation of the phonon spectrum of $TlGaSe_2$ was performed in the framework of the density perturbation functional theory [13] using the local-density approximation. We used the software package ABINIT [14] and the norm preserving pseudopotentials [15]. The basis of plane waves was truncated at electron kinetic energy of 40 Hartrees. Integration over the Brillouin zone was carried out using a 2×2×2 grid according to the scheme proposed by Monkhorst and Pack [16]. The equilibrium structure was determined by minimizing the total energy with respect to the lattice constants and the internal structural parameters. Dynamic matrix describing the phonon spectrum throughout the Brillouin zone was obtained by Fourier interpolation using the ANADDB program of the ABINIT software package. The calculated phonon spectrum is shown in Fig. 1.

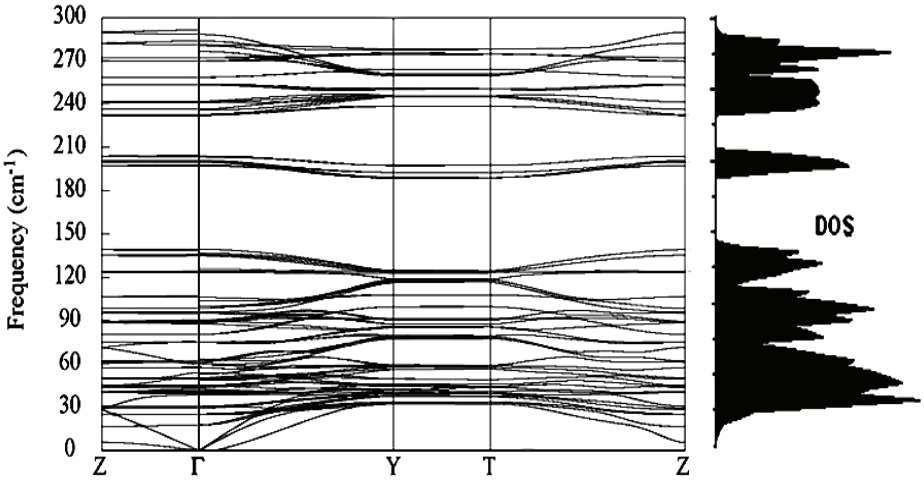

Fig. 1. Calculated phonon spectra and phonon density of states (inset to the right side) of $TlGaSe_2$.

4. Results and discussion

As one can see from Fig. 3, the dispersion of optical phonon branches along Λ line perpendicular to the layers is weak. In the direction parallel to the layers, all optical modes are split into pairs with nearly identical dispersion, which is, naturally, a consequence of stratification of the crystal structure and of the fact that the crystal unit cell contains two layers. In the direction of V, on the border of the Brillouin zone, these pairs are degenerate due to the symmetry with respect to time reversal. One of the transverse branches behaves as bending mode.

Figure 1 shows also the calculated phonon density of states. It consists of three separate bands. A remarkable feature is the presence of a very narrow band of frequences near 200 cm^{-1}, which we attribute to the vibrations of gallium atoms within selenium tetrahedrons.

Figure 2 shows the calculated (isochoric) and the experimental (isobaric) [17] temperature dependences of heat capacity. The inset shows the temperature dependence of heat capacity on the log scale, where the deviation from the cubic dependence (straight line) are clearly visible even at very low temperatures, which is characteristic of layered crystals and indicates the presence of bending vibrations in the phonon spectrum. In [18], it is stated that below 10 K the cubic law is observed, but it is possible that this is a pseudo-cubic law having no connection with the Debye law in general.

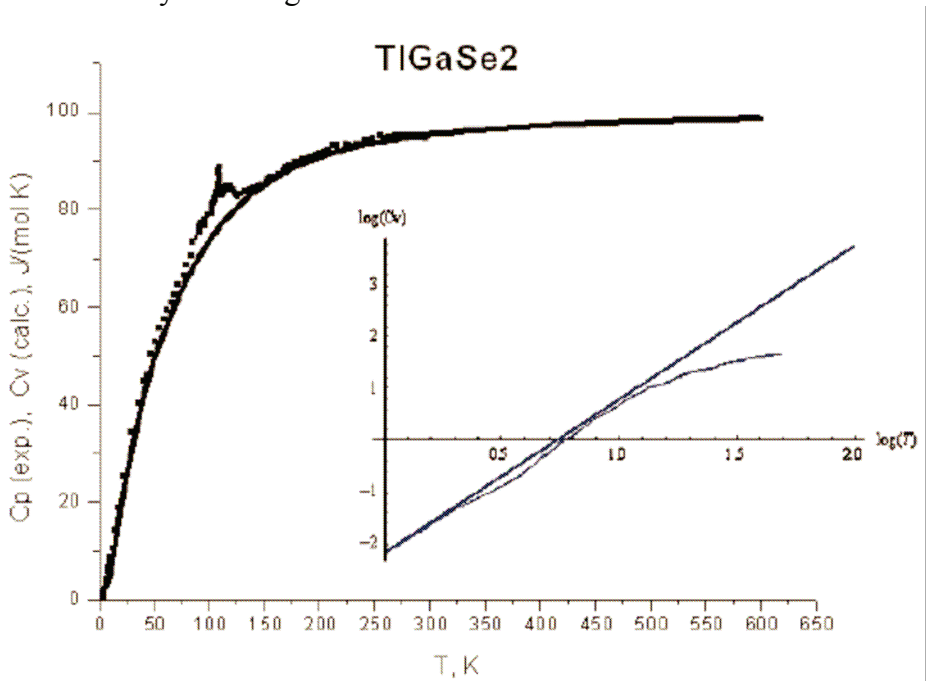

Fig. 2. Temperature dependence of heat capacity: the points correspond to experimental data, and the solid curve represents the results of calculation. Inset: the temperature dependence of heat capacity on the log scale; the straight line represents the Debye law.

Calculated elastic tensor components are given in Table 3 together with values from ultrasonic experiments [19, 20]

Table 3. Elastic tensor components (GPa) $TlGaSe_2$.

	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
clamped ion	62.9	45.3	40	81.6	40.3	45.0
relaxed ion	45.0	31.5	24.1	56.1	4.3	29.4
[19]	67.9	-	-	45.8	3.78	7.08
[20]	64.2	-	-	43.7	5.0	12.7

We have calculated the directional Grüneisen functions, which are strain derivatives of the entropy. In the calculations, we used the fact that $TlGaSe_2$ behaves as a quasi-tetragonal crystal, and, therefore [21]:

$$\gamma_{\perp} = \frac{1}{2C_i}\left(\frac{\partial S}{\partial \ln a}\right)_{c,T}; \quad \gamma_{\parallel} = \frac{1}{C_i}\left(\frac{\partial S}{\partial \ln c}\right)_{a,T},$$

where C_I is the heat capacity under constant stress.

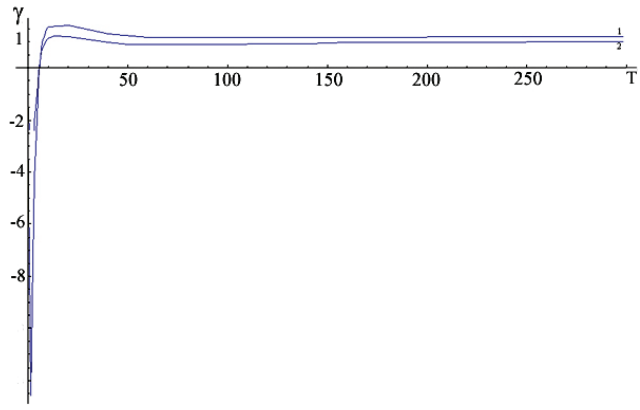

Fig. 3. Temperature dependence of directional Grüneisen functions. Upper curve 1 for $\gamma_{\parallel}$ and the lower one 2 for $\gamma_{\perp}$.

The coefficients of the linear thermal expansion can be expressed in terms of the linear compressibility and the coefficients of elastic compliance in the following way:

$$\alpha_{\perp} = \frac{C_i}{V}\{\chi_{\perp}\gamma_{\perp} + s_{13}(\gamma_{\parallel} - \gamma_{\perp})\}, \quad \alpha_{\parallel} = \frac{C_i}{V}\{\chi_{\parallel}\gamma_{\parallel} - 2s_{13}(\gamma_{\parallel} - \gamma_{\perp})\}.$$

Here $\chi_{\perp} = s_{11} + s_{12} + s_{13}$, $\chi_{\parallel} = 2s_{13} + s_{33}$ are the linear compressibility and s_{ij} are the components of the tensor of elastic compliance.

Figure 3 illustrates our calculations of the temperature dependence of Grüneisen constants. As one can see from the Fig. 3, in the range of temperature above 5 K, the difference between directional Grüneisen functions is small (<0.2γ) and, so far as $|s_{13}| < s_{11} + s_{12}$, cross-linking term is small as compared with first term in the expression for coefficients of thermal expansion, this implies that both principal coefficients of linear thermal expansion are positive at these temperatures.

The linear compressibility $\chi_{\perp}$ could be responsible for the negative thermal expansion (NTE) if inequality $c_{13} > c_{33}$ is fulfilled, because linear compressibility $\chi_{\perp}$ is proportional to the difference (c_{33}-c_{13}). The values of the elastic constants calculated theoretically satisfy an opposite inequality, which, incidentally, also follows from the empirical results by [22-24]. One is left to propose that in the range of temperatures (50-150 K) considered by the authors of [24], a strong anharmonism takes place, which leads to a sharp increase in the elastic constant c_{13}, compared to c_{33}. According to [24], this increase, indeed, takes place, however, the difference between the elastic constants c_{13} and c_{33} remains so that c_{13} is below c_{33}. This circumstance suggests that, perhaps, it is necessary to measure the linear thermal expansion in $TlGaSe_2$ more carefully. It is interesting to note that the X-ray data by [4] do not show any evidence of NTE in the entire range of temperature from 12.2 to 300 K, except for a jump of the lattice constants at the point of a phase transition. It is possible that precisely this jump could have led the authors of [8] to a false conclusion about the presence of NTE in $TlGaSe_2$ crystal.

5. Conclusions

We have calculated the phonon spectrum of ternary $TlGaSe_2$ compound in the framework of the density functional perturbation theory using ABINIT code. The lattice dynamic of monoclinic $TlGaSe_2$ shows many interesting features which are related to the layer crystal structure, for example, the occurrence of a bending mode in phonon spectra along the layer plane, a weak dispersion of optical phonon branches in the direction perpendicular to the lay-

ers, and splitting of all optical modes into pairs with nearly identical dispersion in the direction parallel to the layers, which is a natural consequence of stratification of the crystal structure and of the fact that the crystal unit cell contains two layers. The calculated and experimental temperature dependences of heat capacity are in a good agreement up to the room temperature (except the structure which appears in the experimental curve owing to a phase transition near T = 107 K). We calculated the directional Grüneisen functions and the coefficients of the linear thermal expansion $TlGaSe_2$.

We obtained that both principal coefficients of linear thermal expansion are positive in the range of temperature above 5 K.

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