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Ab initio and Experimental Study of Vibrational Properties of In_2Se_3

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The results of investigation of the vibrational properties of the semiconductor compound In_2Se_3: by the density functional perturbation theory (DFPT) and experimentally using Raman spectroscopy are presented. Comparison of Raman scattering measurements and results of calculations of lattice dynamics allowed us to identify four Raman active modes found at 91.28, 104.5, 182.68 and 193.6 cm^{-1}. The phonon modes were identified by considering the point group symmetry. The results of identification of phonon modes confirmed the R3m-symmetry of the α-In_2Se_3 phase. A comparison is also made with the results of the experimental data available in the literature obtained by the method of Raman spectroscopy. The calculated frequencies and symmetries of the phonon modes at the center of the Brillouin zone are in good agreement with the experimental data.

Keywords: In_2Se_3, Raman scattering, IR- and Raman active modes, phonon dispersion, phonon density of states.

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1. Introduction

Semiconductor compound In_2Se_3 attracts attention as a material for photovoltaic solar cells [1], ion batteries [2], photodetectors [3,4], phase random access memories [5–7], thermoelectric materials [8,9].

In_2Se_3 bulk crystals are characterized by various modifications of the crystal structure, are not very uniform and do not have mirror cleavage surfaces. Due to technological difficulties in growing, these crystals are still little studied.

With the help of DFPT and Raman spectroscopy, in this article we study the lattice dynamics of the semiconductor compound α-In_2Se_3 with a rhombohedral structure.

The electronic, optical and dynamic properties of this compound are well studied experimentally, while theoretical studies of vibrational properties, which play an important role in the interpretation of Raman scattering (RS), infrared reflection (IR) spectra and in the refinement of crystal structures, are almost absent. The RS spectra of α-In_2Se_3 have been studied experimentally in articles [10–16], but there are no clear conclusions about the spatial symmetry of α-phases, since theoretical calculations for the interpretation of experimental data have not been carried out. Theoretically, the vibrational state was studied only in the article [17], but only for the center of the Brillouin zone (BZ). Therefore, theoretical studies of the dynamic properties of this compound are still relevant, which was the motivation for this article.

The purpose of this article is to study phonon spectra, determine the symmetry of phonon modes at the center of BZ, compare the results with experimental data obtained from the RS-spectrum, and, based on this, refine the crystal symmetry of this In_2Se_3 sample.

2. Crystal structure and calculation method

In_2Se_3 crystals have several modifications: α and β — rhombohedral, γ and δ — hexagonal [16,18–21]. Under normal conditions, α-In_2Se_3 is a stable phase. It is problematic to distinguish between the R3m- and R$\bar{3}$m-phases by X-ray diffraction analysis, since the positions of their diffraction maxima are almost the same. Therefore, the question of whether the rhombohedral phase α-In_2Se_3 has a center of symmetry with space group R$\bar{3}$m (No. 166) or belongs to the non-centrosymmetric rhombohedral space group R3m (No. 160), remains open. To clarify the crystal structure of the obtained sample, RS measurements and theoretical calculations of the phonon spectrum were carried out to interpret the experimental results.

For the synthesis, elements with the following purity were used: In-000, Se-XT 17-4. Synthesis of compound In_2Se_3 was carried out as follows. The ampoule of molten quartz was first washed with a mixture of HF + distilled water, dried for 24 hours in an oven at 1000°C and cooled. The cleaned ampoule was filled with elements according to the

Table 1. Optimized and experimental lattice parameters and z-coordinates of In_2Se_3 crystal atoms (in hexagonal coordinates)

Parameters	Experiment [18]	Theory
a, Å	4.05	3.9602
c, Å	28.77	28.4238
In1	0.242	0.251
In2	0.718	0.712
Se1	0.0	0.0
Se2	0.525	0.540
Se3	0.818	0.801

stoichiometric composition, pumped out to 0.0113 Pa and sealed. In order to reduce the risk of ampoule explosion, the mixture was heated in a crucible from 200 to 910°C at a rate of 0.5°C/min, kept at this temperature for 36 hours for ensuring homogenization. Then the crucible was cooled to room temperature by slowly moving from the warm zone to the cold one at a rate of 0.6 mm/hour. The microrelief of the surface of the obtained compound was studied by X-ray diffraction analysis. Analysis of the X-ray diffraction pattern of the sample under study showed that this compound crystallizes in the rhombohedral α-phase. Measurements of the Raman scattering spectra in α-In_2Se_3 were carried out on Nanofinder 30 confocal Raman microspectrometer (Tokyo Instr., Japan). The research was carried out in backscattering geometry. The excitation source was a YAG : Nd laser with a second-harmonic radiation wavelength of $\lambda = 532$ nm, a maximum power of 10 mW, and a beam diameter of $4\,\mu$m. The radiation receiver was a cooled (−70°C) CCD camera (charged-coupled device) operating in the photon counting mode. The exposure time was usually 1 min. The spectrometer used a diffraction grating 1800 lines/mm, the accuracy of determining the spectral position of the lines was 0.5 cm^{-1} or better.

The phonon spectra were calculated using the density functional perturbation theory (DFPT) [22–24] using the pseudopotential method based on plane waves implemented in the ABINIT code [25]. Norm-concerving Hartwigsen-Goedecker-Hutter [26] pseudopotentials were used as pseudopotentials. The exchange-correlation interaction was described in the generalized gradient approximation (GGA) according to the scheme [27]. In the expansion of the wave functions, plane waves with a maximum kinetic energy of up to 80 Ry were used, which ensure a satisfactory convergence of the total energy. Integration over BZ was replaced by summation using $4 \times 4 \times 4$ partitioning with a shift from the origin according to the Monkhorst-Pack scheme [28]. The equilibrium positions of atoms inside the lattice cell of the crystal and the lattice parameters were determined based on the condition of minimizing the Gellmann-Feynman forces acting on the atoms. The equilibrium positions of atoms were determined by the BFGS (Broyden–Fletcher–Goldfarb–Shanno) method using experimental data as initial values (Table 1) [18].

The minimization procedure has performed until the force moduli were below 10^{-8} Ry/Bohr. Calculations of the phonon states density were carried out on a grid of $40 \times 40 \times 40$ points in BZ. LO−TO splittings at the BZ center for polar modes are calculated taking into account the long-range Coulomb field and the non-analytical term added to the dynamic matrix, which depends on the effective Born charge and electron permittivity tensors. The dependence of the convergence of the total energy and Gellmann-Feynman forces on the Monkhorst-Pack grid and on the plane wave maximum energy, taking into account the optimal computer time consumed for calculations, showed that the grid of $4 \times 4 \times 4$ and the plane waves maximum energy of 80 Ry in the expansion of wave functions give results that are in good agreement with the experimental data on the dynamic properties of α-In_2Se_3.

3. Vibrational properties

The primitive cell of α-In_2Se_3 R3m-symmetry contains five atoms, and therefore the phonon spectrum has 15 normal phonon modes. Group-theoretic analysis leads to the following expansion of phonon modes: $\Gamma = 5A_1 + 5E$, acoustic modes $\Gamma_{\text{acoustic}} = A_1 + E$ and optical modes $\Gamma_{\text{optic}} = 4A_1 + 4E$. The phonon symmetry modes E are doubly degenerated. All optical modes are active in both infrared reflection and Raman scattering, are polar modes and, therefore, exhibit longitudinal-transverse optical splitting (LO−TO). An analysis of the atoms displacement vector shows that in fully symmetric A-modes the atom displacement occurs perpendicular to the layers along the crystallographic axis z, accompanied by changes in the lengths of valence bonds, while in E-modes atoms are displaced along the layers in the plane xy with bending of covalent bonds. Figure 1 shows the Raman scattering spectrum α-In_2Se_3. As can be seen in Fig. 1, the following frequencies of RS-active phonon modes are observed: 91.28, 104.5, 182.68 and 193.6 cm^{-1}. Four of the twelve Raman active modes have been detected and identified using the results of calculations of the phonon spectrum ab initio (Table 2).

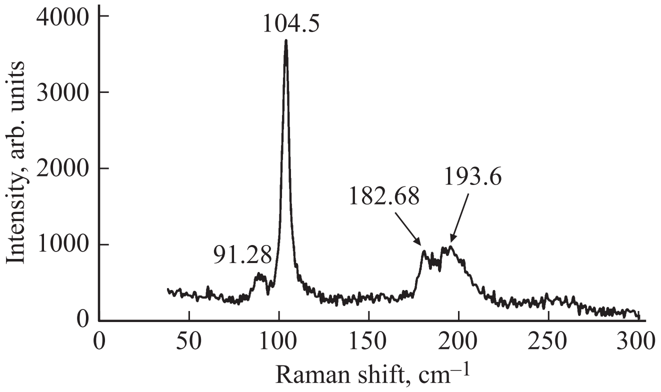

Figure 1. Raman light scattering spectrum α-In_2Se_3.

Table 2. Frequencies of optical phonons α-In_2Se_3 experimentally determined and calculated taking into account the macroscopic electric field in the directions of the wave vector [100] and [001] (in Cartesian coordinates). The slash indicates LO–TO splitting

Mode	ω_{theo}, cm^{-1}	ω_{exp}, cm^{-1}		
	This article	[12]	[14]	This article
A_1(R, IR)	104.75	104	104.2	104.5
	–	144	–	–
	178.74/180.1	180/182	–	–
	191.11/200.06	193/203	192.6	193.6
	240.38/253.47	237	–	–
E(R, IR)	30.38	27	–	–
	95.85/97.29	91	88.2	91.28
	151.49/172.51	–	–	–
	185.32/206.65	187	180.9	182.68

Phonon mode dispersion and phonon density of states (PDOS) α-In_2Se_3 are shown in Figs. 2 and 3, respectively. As can be seen in Fig. 2, the phonon spectrum can be divided into three groups separated by small energy gaps. In addition, the dispersion of phonons in all directions in BZ exhibits anisotropy due to the strong covalent bond between the In and Se atoms along the plane of the atomic layers. The maximum phonon frequency is $\sim 240\,\text{cm}^{-1}$. Analysis of eigenvectors and PDOS shows that acoustic and low-frequency optical branches with E-modes in the frequency range from 0 to $90\,\text{cm}^{-1}$ with maxima at 45, 70 and $85\,\text{cm}^{-1}$ are related to the vibration of the In atom, with a small contribution of Se. The average frequency interval from 90 to $150\,\text{cm}^{-1}$ with a maximum at $106\,\text{cm}^{-1}$ is mainly associated with vibration of the Se atom, with an insignificant contribution of the In atom. The high-frequency third region includes the movement of In and Se atoms. In this frequency interval, the contribution of the lighter Se atom is the main one. The most intense spectrum peak at $106\,\text{cm}^{-1}$ corresponds to the A-mode, to which vibrations of Se atoms make a more significant contribution. Table 2 shows the theoretically calculated phonon frequencies taking into account the macroscopic electric field (with the [100] and [001] directions in Cartesian coordinates) and the phonon frequencies from experimental studies of the Raman scattering spectra α-In_2Se_3. As can be seen in the table, the theoretically and experimentally determined frequencies are in satisfactory agreement.

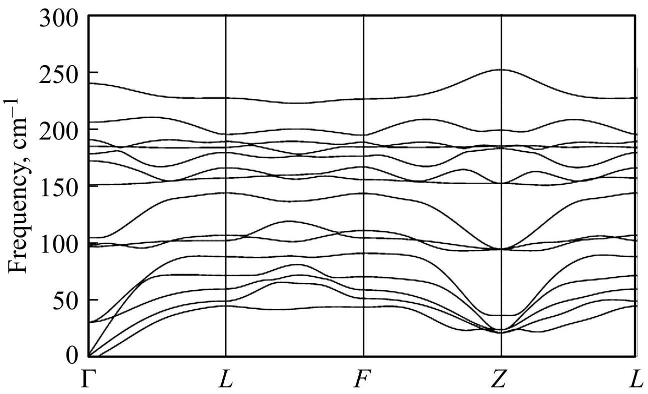

Figure 2. Phonon dispersion in α-In_2Se_3.

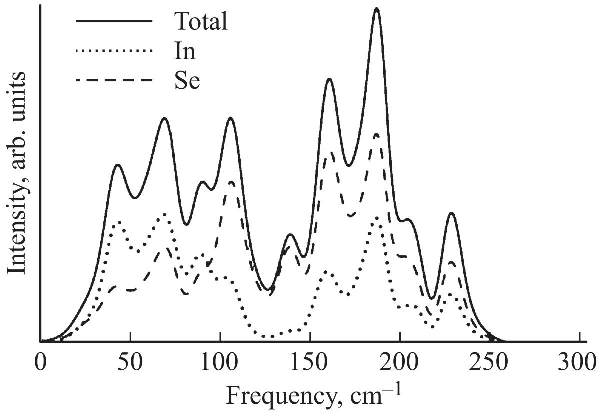

Figure 3. Total phonon states density and phonon states density projected onto atoms in α-In_2Se_3.

4. Conclusion

In this article, we carried out a joint experimental and theoretical study of the vibrational properties of α-In_2Se_3 using measurements of Raman scattering, as well as lattice dynamics calculations *ab initio*. Comparison of the results of Raman scattering with calculations ab initio, as well as group-theoretical analysis, allowed us to identify the phonon modes α-In_2Se_3. Our study confirmed the R3m-symmetry of the α-In_2Se_3 phase as a suitable space group.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] J. Herrero, J. Ortega. Sol. Energy Mater. **16**, *6*, 477 (1987).
[2] M.S. Whittingam. Prog. Solid State Chem. **12**, *1*, 41 (1978).
[3] Q.L. Li, Y. Li, J. Gao, S.D. Wang, X.H. Sun. Appl. Phys. Lett. **99**, *24*, 243105 (2011).

[4] T. Zhai, X. Fang, M. Liao, X. Xu, L. Li, B. Liu, Y. Koide, Y. Ma, J. Yao, Y. Bando, D. Golberg. ACS Nano **4**, *3*, 1596 (2010).

[5] H. Lee, D.H. Kang, L. Tran. Mater. Sci. Eng. B **119**, *2*, 196 (2005).

[6] B. Yu, S. Ju, X. Sun, G. Ng, T.D. Nguyen, M. Meyyappan, D.B. Janes. Appl. Phys. Lett. **91**, *13*, 133119 (2007).

[7] Y.T. Huang, C.W. Huang, J.Y. Chen, Y.H. Ting, K.-C. Lu, Y.L. Chueh, W.W. Wu. ACS Nano **8**, *9*, 9457 (2014).

[8] J. Cui, X. Liu, X. Zhang, Y. Li, Y. Deng. J. Appl. Phys. **110**, *2*, 023708 (2011).

[9] J. Cui, X. Zhang, Y. Deng, H. Fu, Y. Yan, Y. Gao, Y. Li. Scripta Mater. **64**, *6*, 510 (2011).

[10] Y. Zhou, D. Wu, Y. Zhu, Y. Cho, Q. He, X. Yang, K. Herrera, Z. Chu, Y. Han, M.C. Downer, H. Peng, K. Lai. Nano Lett. **17**, *9*, 5508 (2017).

[11] X. Tao, Y. Gu. Nano Lett. **13**, *8*, 3501 (2013).

[12] R. Lewandowska, R. Bacewicz, J. Filipowicz, W. Paszkowicz. Mater. Res. Bull. **36**, *15*, 2577 (2001).

[13] D. Wu, A.J. Pak, Y. Liu, Y. Zhou, X. Wu, Y. Zhu, M. Lin, Y. Han, Y. Ren, H. Peng. Nano Lett. **15**, *12*, 8136 (2015).

[14] S.V. Solanke, R. Soman, M. Rangarajan, S. Raghavan, D.N. Nath. Sensors Actuators A **317**, 112455 (2021).

[15] E. Mafi, A. Soudi, Y. Gu. J. Phys. Chem. C **116**, *42*, 22539 (2012).

[16] K. Kambas, C. Julien, M. Jouanne, A. Likforman, M. Guittard. Phys. Status Solidi B **124**, *2*, K105 (1984).

[17] R. Vilaplana, S. Gallego Parra, A. Jorge-Montero, P. Rodríguez-Hernández, A. Munoz, D. Errandonea, A. Segura, F.J. Manjón. Inorg. Chem. **57**, *14*, 8241 (2018).

[18] K. Osamura, Y. Murakami, Y. Tomie. J. Phys. Soc. Jpn **21**, *9*, 1848 (1966).

[19] S. Popovic, A. Tonejc, B. Grezeta-Plenkovic, B. Celustka, R. Trojko. J. Appl. Crystallogr. **12**, *4*, 416 (1979).

[20] C. Julien, M. Eddrief, M. Balkanski, A. Chevy. Phys. Rev. B **46**, *4*, 2435 (1992).

[21] S. Popovic, B. Celustka, D. Bidjin. Phys.Status Solidi **6**, *1*, 301 (1971).

[22] P. Gianozzi, S. de Gironcoli, P. Pavone, S. Baroni. Phys. Rev. B **43**, *9*, 7231 (1991).

[23] S. Baroni, S. de Gironcoli, A. Dal Corso, P. Gianozzi. Rev. Mod. Phys. **73**, *2*, 515 (2001).

[24] X. Gonze. Phys. Rev. B **55**, *16*, 10337 (1997).

[25] X. Gonze, J.M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jallet. Comput. Mater. Sci. **25**, *3*, 478 (2002).

[26] C. Hartwigsen, S. Goedecker, J. Hutter. Phys. Rev. B **58**, *7*, 3641 (1998).

[27] J.P. Perdew, A. Zunger. Phys. Rev. B **23**, *10*, 5048 (1981).

[28] H. Monkhorst, J. Pack. Phys. Rev. B **13**, *12*, 5188 (1976).

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