Experimental Investigation of Vibrational Properties of In_2Se_3

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***Abstract*—The results of the study of vibrational properties of the semiconductor compound In_2Se_3 are presented: theoretically, by the density functional perturbation theory (DFPT) method, and experimentally, using Raman spectroscopy. Comparison of Raman scattering measurements and lattice dynamics calculations allowed us to identify four Raman-active modes detected at 91.28, 104.5, 182.68 and 193.6 cm^{-1}. Identification of phonon modes was carried out by considering the point symmetry group. The results of phonon mode identification confirmed the R3m symmetry of the α-In_2Se_3 phase. A comparison of the results with the experimental data available in the literature, obtained by the Raman spectroscopy method, is also performed. The calculated frequencies and symmetries of the phonon modes in 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.

I. INTRODUCTION

The semiconductor compound In_2Se_3 attracts attention as a material for photovoltaic solar cells, ion batteries, photodetectors [1,2], random access phase memories [3-5], and thermoelectric materials [6,7].

Bulk crystals of In_2Se_3 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, they have not been studied much so far.

Using DFPT and Raman spectroscopy, the lattice dynamics of the semiconductor compound α- In_2Se_3 with a rhombohedral structure is studied in this work.

The electronic, optical and dynamic properties of this compound have been well studied experimentally, while theoretical studies of the vibrational properties, which play an important role in the interpretation of Raman spectra, infrared reflection (IR) spectra and in refining the crystal structures, are almost absent. The Raman spectra of α- In_2Se_3 have been studied experimentally in [8-12], but there are no clear conclusions about the spatial symmetry of the α phase, since theoretical calculations have not been carried out to interpret the experimental data. The vibrational state was theoretically studied only in, but only for the center of the Brillouin zone (BZ). Therefore, theoretical studies of the dynamic properties of this compound still remain relevant, which served as the motivation for this work.

The aim of this work is to study the phonon spectra, determine the symmetry of the phonon modes in the center of the BZ, compare the results with experimental data obtained from the Raman spectrum, and, based on this, refine the crystal symmetry of this In_2Se_3 sample.

II. CRYSTAL STRUCTURE AND CALCULATION METHOD

In_2Se_3 crystals have several modifications: α and β are rhombohedral, γ and δ are hexagonal. 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 the diffraction maxima are almost identical. Therefore, the question of whether the rhombohedral phase of α- In_2Se_3 has a symmetry center with the 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, Raman measurements and theoretical calculations of the phonon spectrum were carried out to interpret the experimental results.

Elements of the following purity were used for the synthesis: In-000, Se-XT 17-4. The In_2Se_3 compound was synthesized as follows. An 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 purified ampoule was filled with elements according to the 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 and kept at this temperature for 36 hours to ensure 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 surface microrelief of the obtained compound was studied by X-ray phase analysis. Analysis of the X-ray diffraction pattern of the sample showed that this compound crystallizes in the rhombohedral α-phase. Raman spectra of α- In_2Se_3 were measured on a Nanofinder 30 confocal Raman microspectrometer (Tokyo Instr., Japan). The studies were carried out in backscattering geometry. A YAG:Nd laser with a second harmonic wavelength of λ = 532 nm, a maximum power of 10 mW, and a beam diameter of 4 μm was used as an excitation source. A cooled (−70◦C) charged-coupled device (CCD) camera operating in photon counting mode served as a radiation receiver. The exposure time was usually 1 min. The spectrometer used a diffraction grating of 1800 lines/mm, the accuracy of determining the spectral position of the lines was no worse than 0.5 cm−1.

The phonon spectra were calculated using the density functional perturbation theory (DFPT) [22–24] using the plane-wave pseudopotential method implemented in the ABINIT code. The norm-preserving Hartwigsen–

Goedecker–Hutter pseudopotentialswere used as pseudopotentials. The exchange-correlation interaction was described in the generalized gradient approximation (GGA) according to the scheme. In the expansion of the wave functions, plane waves with a maximum kinetic energy of up to 80 Ry were used, ensuring satisfactory convergence of the total energy. Integration over the ZB was replaced by summation using a 4 × 4 × 4 partition with a shift from the origin according to the Monkhorst–Pack scheme.

TABLE. OPTIMIZED AND EXPERIMENTAL LATTICE PARAMETERS AND Z-COORDINATES OF ATOMS OF THE In_2Se_3 CRYSTAL (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

The equilibrium positions of atoms within the unit cell of the crystal and the lattice parameters were determined from the condition of minimizing the Hellman–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).

The minimization procedure was carried out until the force moduli were less than 10^{-8} Ry/Bohr. The phonon density of states calculations were performed on a 40 × 40 × 40 grid in the BZ. The LO−TO splittings in the BZ center for polar modes were calculated taking into account the long-range Coulomb field and a non-analytical term added to the dynamic matrix, which depends on the Born effective charge tensors and the electron permittivity. The dependence of the convergence of the total energy and Hellman–Feynman forces on the Monkhorst–Pack grid and on the maximum plane wave energy taking into account the optimal consumed computer time for calculations showed that the 4 × 4 × 4 grid and the maximum plane wave 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.

III. Oscillatory properties

The phonon mode dispersion and phonon density of states (PDOS) of α-In_2Se_3 are shown in Fig. 2 and 3, respectively. As can be seen from Fig. 2, the phonon spectrum can be divided into three groups separated by small energy gaps. In addition, the phonon dispersion in all directions in the ZB exhibits anisotropy due to the strong covalent bonding between In and Se atoms along the plane of the atomic layers. The maximum phonon frequency is ~ 240 cm^{-1}. The eigenvector and PDOS analysis shows that the acoustic and low-frequency optical branches with E-modes in the frequency range from 0 to 90 cm^{-1} with maxima at 45, 70, and 85 cm^{-1} are related to the vibration of the In atom, with a small contribution from Se. The middle frequency range from 90 to 150 cm^{-1} with a maximum at 106 cm^{-1} is mainly due to the vibration of the Se atom, with an insignificant contribution from the In atom. The high-frequency third region includes the motion of the In and Se atoms. In this frequency range, the contribution of the lighter Se atom is the main one. The most intense peak of the spectrum at 106 cm^{-1} corresponds to the A-mode, to which a more significant contribution is made by the vibrations of the Se atoms.

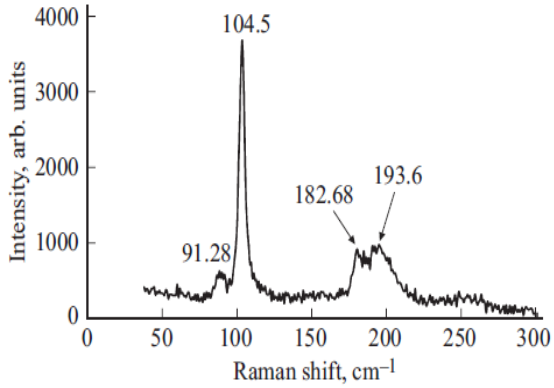

Fig. 1. Raman spectrum of α-In_2Se_3.

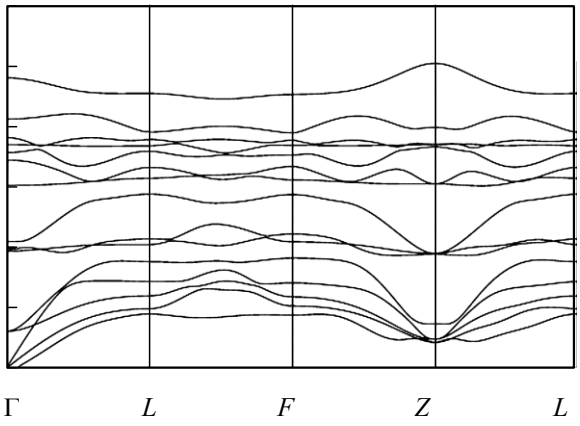

Fig. 2. Phonon dispersion in α- In_2Se_3.

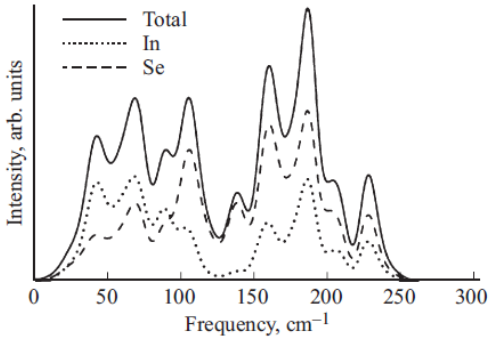

Fig. 3. Total and projected onto atoms densities of phonon states in α- In_2Se_3.

IV. Conclusion

In this work, a combined experimental and theoretical study of the vibrational properties of α- In_2Se_3 was performed using Raman measurements and ab initio calculations of the lattice dynamics. Comparison of the Raman results with first-principles calculations and group-theoretical analysis allowed us to identify the phonon modes of 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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