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# Characteristics of Raman spectra of $2H$-$\alpha$-$In_2Se_3$ layered crystals of different thicknesses

© I.A. Eliseyev, G.V. Osochenko, A.N. Smirnov, V.Yu. Davydov, M.V. Rakhlin, L.V. Kotova,
K.A. Gasnikova, P.A. Alekseev, Yu.E. Kitaev

Ioffe Institute,
St. Petersburg, Russia
E-mail: ilya.eliseyev@mail.ioffe.ru

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The results of studies of the vibrational properties of layered $\alpha$-$In_2Se_3$ crystals when the number of constituent layers is varied are presented. The joint analysis of Raman spectroscopy and atomic force microscopy data, followed by theoretical group analysis of vibrational modes, has allowed us to establish the patterns of changes in the parameters of spectral lines in the range of high and ultra-low ($\omega < 50\,\mathrm{cm}^{-1}$) frequencies. It is shown for the first time that the position of the high-frequency line $A_1(3)$ ($\omega \sim 200\,\mathrm{cm}^{-1}$) can be used to estimate the thickness of $\alpha$-$In_2Se_3$ in the range of seven to several tens of layers.

**Keywords:** 2D materials, indium selenide, Raman spectoscopy, vibrational properties.

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## 1. Introduction

The popularity of the family of layered materials representing structures with covalent intralayer and van der Waals interlayer bond, is due to the widest range of existing and promising areas of their use. These materials and heterostructures on their base are used in leading areas, such as non-linear optics and optoelectronics [1], quantum computations [2] etc. Due to its ferroelectric and piezoelectric properties, $In_2Se_3$ is currently one of the most actively studied materials in this family. However, despite multiple scope of publications dedicated to the research of its electric, structural and mechanical properties (see reviews [3–8] and references therein), the area of its optical and vibrational properties, in our opinion, remains understudied.

The feature of the Raman spectra of most 2D layered materials, such as graphene, mono- and dichalcogenides of transition metal, hexagonal boron nitride etc., is the presence of the lines corresponding to the vibrations of the layers relative to each other. These lines usually manifest themselves in the region of ultralow ($< 50\,\mathrm{cm}^{-1}$) frequencies, which leads to certain difficulties in their observation. Nevertheless, using the example of the materials listed above, it was shown that the analysis of this area in the Raman spectrum is highly informative to detect the number of the layers [9]. Moreover, using the example of $MoS_2$ it was demonstrated that frequencies of the lines corresponding to the vibrations of the layers relative to each other are much less sensitive to the deformation of the crystalline lattice compared to the high-sensitive lines of intralayer vibrations [10]. Therefore, the position of low-frequency lines of intralayer vibrations in the Raman spectrum provides potentially more valid information about the quantity of monolayers.

The objective of this paper is the development of the method of optical non-destructive assessment of $In_2Se_3$ thickness using Raman spectroscopy. Flakes of $In_2Se_3$ were studied, which were made by the method of micromechanical cleavage from the bulk crystal ($\alpha$-$In_2Se_3$ made by HQ Graphene) and placed on the silicon substrates coated with 50-nm gold layer. Raman spectra were measured at room temperature in the backscattering geometry with Horiba LabRAM HREvo UV-VIS-NIR-Open spectrometer equipped with a confocal microscope with an Olympus MPLN100× lens (NA = 0.9). Use of a 2400 grooves/mm diffraction grating made it possible to acheive spectral resolution of $0.4\,\mathrm{cm}^{-1}$. The power of the exciting light of YAG:Nd laser with wavelength of 532 nm was less than 100 mW in a spot with a diameter of $1\,\mu$m. To cut off the component of Rayleigh scattering of exciting light and to register the spectra in the region of ultralow frequencies, a kit of BragGrate ultranarrow filters was used. For calibration, estimates of $In_2Se_3$ thickness were used, which were obtained from the data of atomic-force microscopy (AFM). AFM study was carried out on Ntegra AURA setup using HA_NC cantilever with curvature radius of less than 10 nm [11].

For the symmetry analysis of the phonon spectra of $In_2Se_3$, the original procedure was used, which was previously applied for GaSe [12]. Group-theoretical analysis was performed sequentially for the isolated layer, then for the bulk crystal, and finally the symmetrical compliance was established between the layer and crystalline modes. This makes it possible to identify the genesis of intralayer and low-frequency interlayer vibrations. It is important to note that the term layer in relation to $In_2Se_3$ in this paper refers to biperiodic (quasi-two-dimensional) crystal made of five successively arranged planes of Se-In-Se-In-Se atoms with covalent bonds between atoms.

Symmetry of the bulk $In_2Se_3$ crystal $In_2Se_3$ is described by space group $P6_3mc$ (SG 186). The unit cell of the crystal includes two formula units (10 atoms) and two layers, the symmetry of each being described by the layer symmetry group $p3m1$ (DG 69). Note that the layer group $p3m1$ (DG 69) is a subgroup of the space group $P3m1$ (SG 156).

This paper considers thin flakes with thickness of $N$ layers. Symmetry of both layers included in the unit cell of the bulk crystal is described by the same layer group. At the same time two layers included into the unit cell of the bulk crystal differ by placement of atoms in positions of symmetry (Wyckoff positions), and their coordinates are related to each other by a rotation by 60° and shift.

The structure made of $N$ layers may be presented as unit cell of virtual volume crystal with the space group $P3m1$ (SG 156).

Vibrational representation of the isolated layer is described by expressions

$$\Gamma^{\mathrm{L}} = 5A_1 + 5E;$$

for acoustic vibrations $\Gamma^{\mathrm{L}}_{\mathrm{ac}} = A_1 + E$, for optical $\Gamma^{\mathrm{L}}_{\mathrm{opt}} = 4A_1 + 4E$ ones.

Representation for the structure from $N$ layers looks as follows:

$$\Gamma^{\mathrm{NL}} = N(5A_1 + 5E);$$

for acoustic vibrations $\Gamma^{\mathrm{NL}}_{\mathrm{ac}} = A_1 + E$, for optical $\Gamma^{\mathrm{NL}}_{\mathrm{opt}} = (5N_{\mathrm{L}} - 1)(A_1 + E)$ ones.

Optical vibrations of symmetry $A_1$ are Raman-active in geometries of parallel polarization $(xx, yy, zz)$, and vibrations of $E$ symmetry — both in geometries of crossed — $xz, yz, xy$ and parallel — $xx, yy$ — polarizations.

Based on the above vibrational representations, we can obtain the expressions for the number of vibrational modes of the structure made of $N$ layers:

$$N_{\mathrm{LF}} = 4N(A_1 + E) \qquad (1)$$

for interlayer (low-frequency) vibrations and

$$N_{\mathrm{HF}} = (N - 1)(A_1 + E) \qquad (2)$$

for intralayer (high-frequency) vibrations.

Figure 1 presents experimentally measured Raman spectra of 20-layer $In_2Se_3$, crystal obtained in geometries of crossed and parallel polarization. Hereinafter geometry of polarization is given in Porto's notation, where $x$ and $y$ axes are mutually perpendicular and oriented randomly in the plane of the layer, and $z$ axis is perpendicular to the plane of the layer.

As one can see, in the low-frequency part of the spectra (Figure 1, $a$) the set of lines observed in parallel and crossed polarizations, matches fully. This enables us to assign the lines observed in spectra to shear interlayer vibrations of symmetry $E$ in the layer plane based on the above selection rules. Besides, the spectra show not more than four lines, while the expression (1) we obtained predicts the presence of 20 vibrational modes of $E$ symmetry in the 20-layer crystal of $In_2Se_3$. This contradiction may be explained by the effect of the limited spectral resolution of the instrument and related inability to register the lines located closely to each other. Absence of the substantial contribution of modes of $A_1$ symmetry in the spectra that correspond to the breathing vibrations of the layers in direction along the $z$ axis, may indicate a weak influence of such vibrations on changes in the polarizability tensor.

Figure 1, $b$ presents spectra measured in the region of high frequencies. Presence of a clearly marked line with frequency of $88\,\mathrm{cm}^{-1}$ indicates that the studied sample is $\alpha$-$In_2Se_3$ of polytype $2H$ [4]. One can see well that most observed lines are absent in the crossed geometry which makes it possible, according to the selection rules specified above, to relate them to the vibrations of the $A_1$ symmetry. Note that according to the classification existing in most papers [13,14] the lines with frequencies 180–182 and $186-187\,\mathrm{cm}^{-1}$ are related to vibrations of symmetry $E$ and $A_1$ respectively, while the data we obtained indicate the association of the line with frequency $180-182\,\mathrm{cm}^{-1}$ to vibrations of symmetry $A_1$, and line with frequency $186-187\,\mathrm{cm}^{-1}$ — vibrations of symmetry $E$.

In the region of high frequencies (Figure, $d, e$) the lines $A_1(3)$ ($\sim 195\,\mathrm{cm}^{-1}$), whose frequency in transition from 7-layer to 75-layer crystal decreases by more than $9\,\mathrm{cm}^{-1}$, and weak line $A_1(4)$, frequency of which in the spectrum of 7-layer crystal is $11\,\mathrm{cm}^{-1}$ higher than in the spectrum of the 75-layer one, are the most sensitive to changes in the number of layers. Frequency of line $A_1(2)$ with number of layers increasing from 7 to 75 decreases by $1.2\,\mathrm{cm}^{-1}$. At the same time frequencies of lines $E(1)$ and $E(2)$, and also $A_1(1)$ in the same range of the layer quantity change by no more than $0.5\,\mathrm{cm}^{-1}$ (Figure, $d$). It is known that the influence of the layer environment on vibrations with displacements of atoms in the layer plane is significantly smaller than on vibrations with displacements of atoms perpendicular to it. Based on the above, we may assume that modes $A_1(1)$, $A_1(3)$ and $A_1(4)$ correspond to vibrations with substantial contribution of atom displacements perpendicularly to the layer plane. In turn, the vibrational modes of $E$ symmetry and the mode $A_1(1)$ represent displacements of atoms predominantly in the layer plane, therefore their frequencies are practically independent on the number of layers.

Let us summarize the above. Within the framework of this paper, a systematic study of the Raman spectra of $2H$-$\alpha$-$In_2Se_3$ with different number of layers was carried out. The nature of dependences of the frequencies of spectral lines observed in the region of low ($10-50\,\mathrm{cm}^{-1}$) and high ($50-300\,\mathrm{cm}^{-1}$) frequencies on the number of $In_2Se_3$ layers was established. It was demonstrated that the modes corresponding to the vibrations of the $A_1$ symmetry are the most sensitive to the number of layers. It should be noted

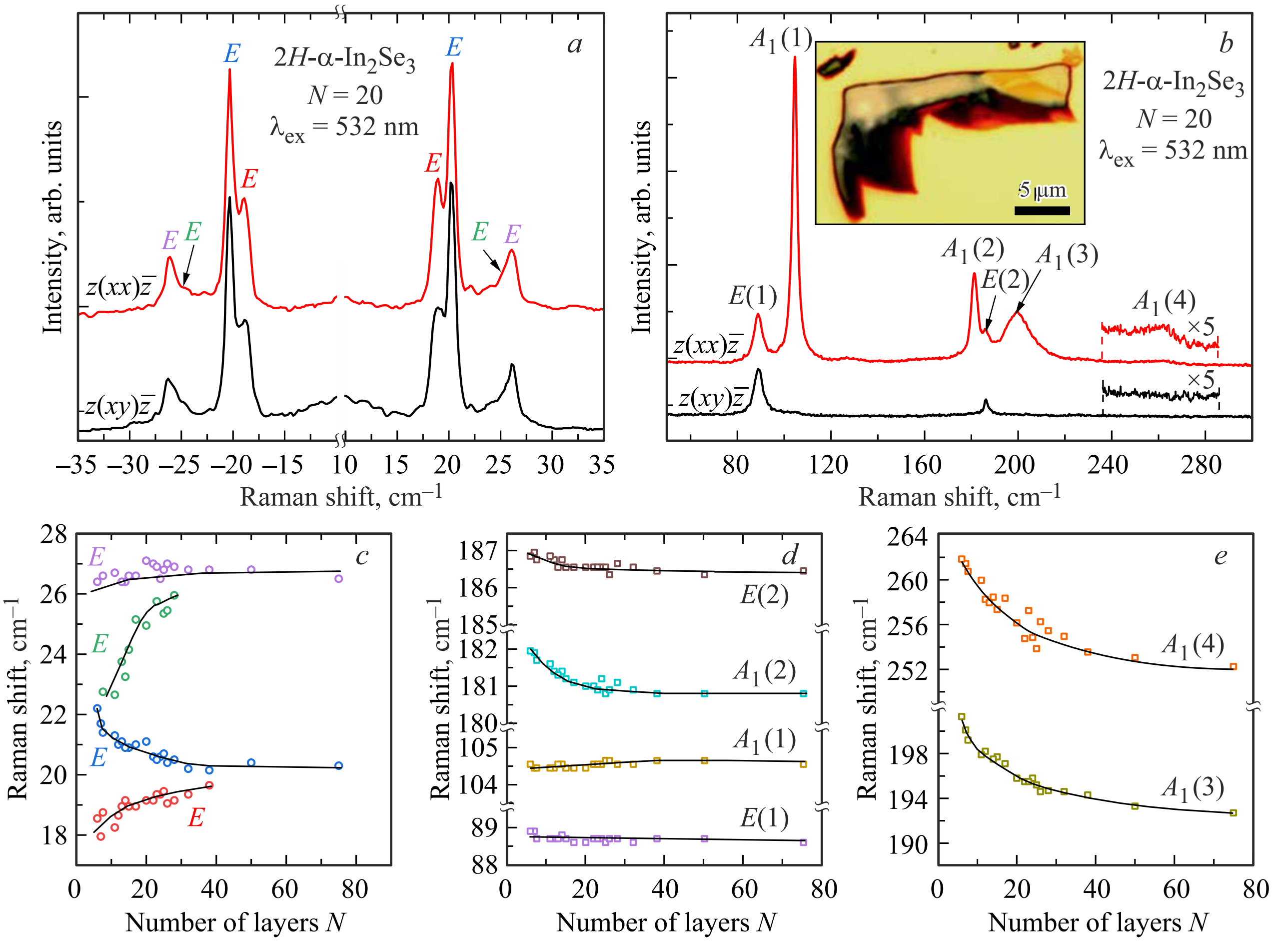

**Figure 1.** Raman spectra of 20-layer $In_2Se_3$ in the area of ultralow (*a*) and high (*b*) frequencies measured in parallel (red spectrum) and crossed (black spectrum) polarizations. The insert of panel (*b*) shows a photograph of one of the studied flakes. Dependences of the position of low-frequency (*c*) and high-frequency (*d, e*) lines on thickness of $In_2Se_3$, measured with AFM.

specifically that analysis of the mode $A_1(3)$, experiencing the strongest shift with the change of the number of layers makes it possible to assess thickness of $In_2Se_3$ without a triple monochromator or Bragg filters necessary to analyze the Raman spectrum in the region of ultralow ($< 50\,\mathrm{cm}^{-1}$) frequencies. Based on the data of group-theoretical analysis, expressions were obtained for the quantity of interlayer and intralayer vibrational branches depending on the number of layers, their symmetry was established, as well as the selection rules in the Raman spectra.

## Conflict of interest

The authors declare that they have no conflict of interest.

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