Raman Scattering in Layered CdInGaS$_4$

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Abstract

Raman scattering spectra of CdInGaS$_4$ crystals grown by the chemical transport method were measured at room and liquid-nitrogen temperatures. Band pairs at 29-38, 43-48 and 60-65 cm^{-1} are reported for the first time. The origin of these bands is attributed to the Davydov doublets, arising due to a small interlayer interaction. Seventeen bands observed in the Raman spectra are assigned to normal modes on the basis of the C$_{3v}^1$ space group. This modification contains two layers per unit cell and do not have inversion symmetry. It is shown that the crystals grown from the vapor phase and by the Bridgman method belong to different modifications.

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Key Words: Raman scattering, layered crystals, CdInGaS$_4$.

1. Introduction

CdInGaS$_4$ was first synthesized by Shand [1]. The interest to study this material originates from its unique physical properties which make it promising in optoelectronics. Among these are: high sensitivity in the UV and VIS range of spectra [2, 3]; intense red and blue photoluminescence at room and low-temperatures [1, 4]; stability in high temperature atmospheres and isotropic thermal expansion inspire evident layered structures [5, 6]; high birefringence in the visible and near IR range of spectra [7] and a laminated structure resulting in a possibility to grow and study different polytypes. The crystals grown by the vapor chemical transport reactions have C$_{3v}^5$ space group (SG), whereas melt-grown crystals may develop to C$_{3v}^1$ or D$_{3d}^1$[8].

The atomic arrangement in one pack is shown in Figure 1 [3]. Vibrational properties of CdInGaS$_4$ were published in a number of articles. Normal modes of vibrations observed in $E\perp c$ and $E||c$ geometry's (where E is the electric field vector of the incident electromagnetic wave, c is in the direction of the optical axis) by measuring the near-normal room-temperature reflectivity in the spectral range from 45 to 500 cm^{-1} were associated to the basis C$_{3v}^1$ SG [8]. Taking into consideration the results of [8] and the results of polarized Raman scattering measurements, the authors of [9] came to conclusion that the Bridgman grown crystals may have D$_{3d}^1$ SG. Raman scattering spectrum; and IR reflectivity (measured only for $E\perp c$ geometry) for CdInGaS$_4$ crystals grown by the chemical vapor transport reaction were reported in [10]. Observed phonon modes were compared with those for cubic CdIn$_2$S$_4$ and were associated to the spinel-type structure with the O$_h^7$ SG [10]. Of the results presented in [10], two points can be made: first, it is rightful to interpret the vibrational properties of layered crystals on the basis of the spinel structure; second, according to the irreducible representations of the O$_h$ point group, there are 5 Raman (A$_{1g}$, E$_g$ and 3F$_{2g}$ and 4F$_{1u}$ IR)

active modes. Nine Raman modes observed in [10] are in contradiction with the prediction of the theory of symmetry for the O_h point group.
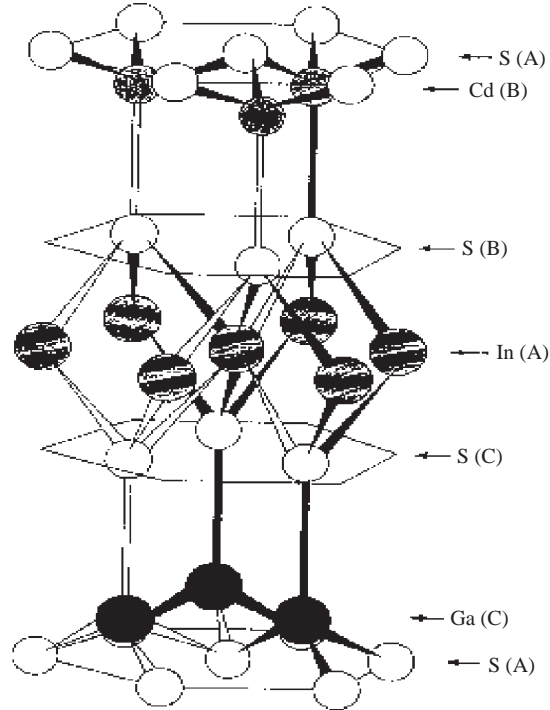

Figure 1. The unit cell of CdInGaS$_4$.

Table summarizes the vibrational frequencies of CdInGaS$_4$ crystal and their assignment given by different authors. Some controversy arises when comparing the results given in Table for the frequency positions, number of lines and their assignment. At this stage it would seem that a new, high resolution Raman investigation of CdInGaS$_4$ is needed, with the determination of the peak frequencies using the deconvolution method of the observed spectra.

In the present paper are presented the results of Raman scattering measurements of CdInGaS$_4$ crystals grown by the chemical transport reactions method at room temperature and 77 K. Far IR transmission spectra of thin plates were also measured at room temperature and 77 K. The symmetry of modes are assigned using the data existing in literature.

2. Experimental

Single crystals were grown by the chemical vapor method, using iodine as a transport element in an evacuated (10^{-5} Torr) quartz tubes. The color of crystals was transparent yellow. All obtained crystals were in the form of soft plane-parallel plates. The plates were easily cleaved into thin samples with mirror-like surfaces oriented right angle to the optical c-axis. Non-polarized Raman scattering spectra were excited with the 6471 Å line of a Kr$^+$ laser in order to see as many lines as possible. The optical set-up consisted of a SPEX 1401 double monochromator (1800 grooves/mm) equipped with a EDG 1433-c CCD cryogenic detector system. The spectra were recorded in back scattering geometry. The accuracy of measurements was ± 1 cm^{-1}. The wave number peak positions of the bands were determined by fitting Lorentzian lines shapes to the experimental data. Raman spectra were measured at room and liquid-nitrogen temperatures. Frequencies of the IR active modes were also determined by transmission measurements of thin cleaved (~ 50 μm) crystals in E$\perp c$ geometry. For this purposes the vacuum grating spectrometer FIS-3 was used in

the spectral range of 50–400 cm^{-1}. The resolution in the investigated range was not worse than 3 cm^{-1}. Low-temperature cryostat was used for transmission measurements.

Table. Raman and IR active optical phonon frequencies ω_0 (cm^{-1}) and their symmetries for CdInGaS$_4$ crystal at room temperature, according to different references. For each reference the space group (SG) is indicated in the respective column. The transverse (TO) and longitudinal (LO) mode assignments are indicated. The frequencies of the IR active phonons from the absorption measurements of thin plates are shown in brackets. m.a. denotes mode assignment. "sh", "w", "vw", "md", "st", "vst" and "sts" denote the intensity of lines: "shoulder", "weak", "very weak", "middle", "strong", "very strong" and "strongest," respectively.

Polarized IR reflection and absorption SG-C$^1_{3v}$ [8]		Polarized Raman scattering, SG-D$^1_{3d}$ [9]		IR reflection, E$\perp$c geometry SG-O^7_h [10]		Non-polarized Raman scattering SG-O^7_h [10]		Present work, non-polarized Raman scattering	
m.a.	ω_0	m.a.	ω_0	m.a.	ω_0	m.a.	ω_0	m.a.	ω_0
-	-	E^1_g	17	-	-	-	-	E^1	21 w
-	-	E^2_g	27	-	-	-	-	E^2	29 md
-	-	E^3_g	37	-	-	-	39	E^{2,1}	38 md
-	-	-	-	-	-	-	-	E^3	43 w
-	-	-	-	-	-	-	-	E^{3,1}	48 w
-	-	A$^1_{1g}$	62	-	-	-	-	A^1	60 w
-	-	-	-	-	-	-	-	A^{1,1}	65 w
-	-	-	-	F$^1_{1uTO}$	80	-		A^2	82 w
E^1	(100)	A$^2_{1g}$	104	F$^1_{1uLO}$	103	F$^3_{2g}$	104	E^4	102 sts (103)
E^2	(120)	-	-	-	-	-	-	E^5	120 sh (125)
-	-	A$^2_{1g}$	133	-	-	-	-	-	-
-	-	-	-	F$^2_{1uTO}$	167	-	-	-	
-	-	E^4_g	179	-	-	-	-	-	-
E$^3_{TO}$	202 (202)	-	-	-	-	-	-	-	-
A$^1_{TO}$	208	-	-	-	-	-	-	-	-
E$^3_{LO}$	217	-	-	-	-	-	-	-	-
-	-	E^5_g	221	-	-	-	-	-	-
E$^4_{TO}$	235 (230)	-	-	F$^2_{1uLO}$	238	F$^2_{2g}$	229	E^6	230 sh
E$^4_{LO}$	244	-	-	-	-	-	-	-	-
A$^1_{LO}$	252	A$^4_{1g}$	250	-	-	F$^2_{2g}$	249	A^3	250 vst
E$^5_{TO}$	300 (298)	A$^5_{1g}$	304	F$^3_{1uTO}$	292	F$^1_{2g}$	298	E^7	300 vst
A$^2_{TO}$	320	-	-	-	-	-	-	-	-
E$^5_{LO}$	328	A$^6_{1g}$	330	F$^3_{1uLO}$	325	-	330	E^8	329 vw
A$^2_{LO}$	334	-	-	F$^4_{1uTO}$	338	-	-	-	-
E$^6_{TO}$	348 (350)	A$^7_{1g}$	350	-	-	-	-	-	-
E$^6_{LO}$	366	-	-	F$^4_{1uLO}$	365	A$_{1g}$	369	E^9	360 w
A$^3_{LO}$	386	-	-	-	-	-		A^4	382 vw
E^6_g	401	-	-	-	-	A$_{1g}$	394	A^5	399 w

3. Results and Discussion

Figures 2, 3 and 4 show the room temperature Raman spectrum of CdInGaS$_4$ crystal taken in backscattering geometry. No noticeable changes were observed when the temperature of the crystal was cooled down

to 77 K. At this temperature, the lines became narrower and their frequency peak positions shifted slightly to higher frequencies (~ 1 to 1.5 cm^{-1}). No new bands were observed at low temperature.
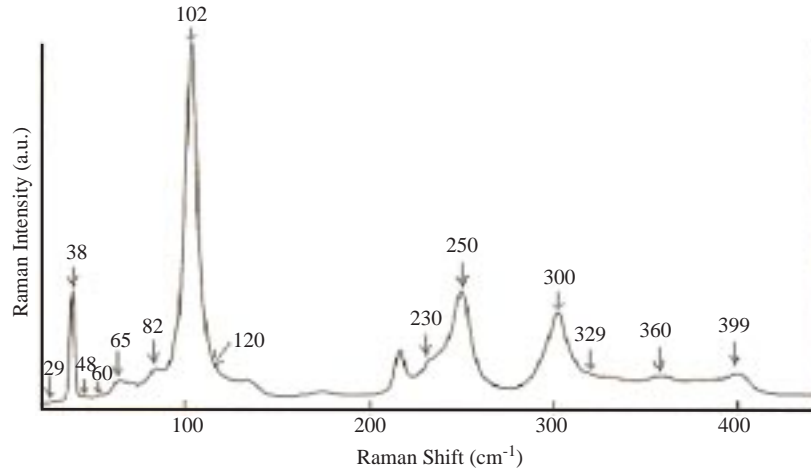

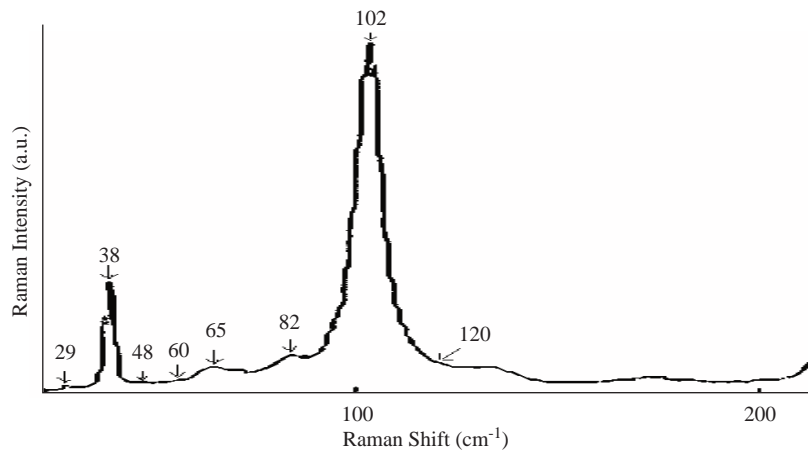**Figure 2.** Raman spectrum of CdInGaS$_4$.

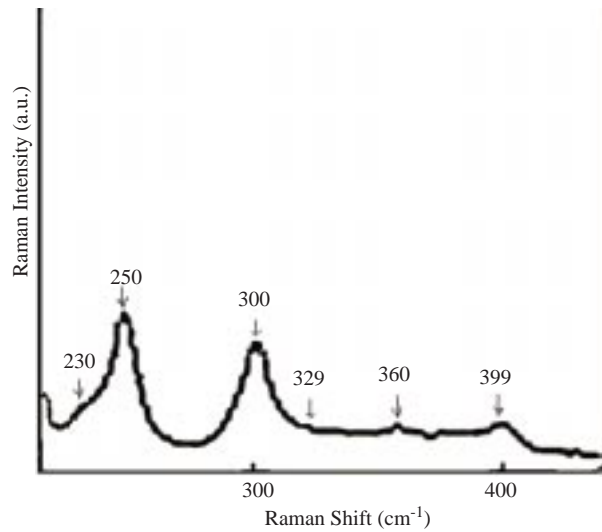
Figure 3. Raman spectrum of CdInGaS$_4$.

Figure 4. Raman spectrum of CdInGaS$_4$.

Such a behavior denotes that at least, in the temperature range 77–300 K, CdInGaS$_4$ crystal does not undergo the phase transition, as it was reported for ternary layered TlGaSe$_2$-type crystals in [11].

Absorption measurements at 300 and 77 K showed that the lines at 103 and 125 cm^{-1} do not exhibit strong temperature dependence. With decreasing the temperature the peak positions of the transmission spectra for both lines shifted to higher frequency ($\sim$ 1.5 cm^{-1}), the lines became narrower and the transmission decreased to about 3% of the room temperature values. That is why we attributed these lines as arising due to one phonon resonance.

Eight Raman bands were observed in the low-frequency range (less than 100 cm^{-1}). The lines at 17, 27, 37, 62 and 80 cm^{-1} were reported also in [9] and [10], respectively. A pair of lines at 29-38, 43-48 cm^{-1} and 60-65 cm^{-1} are reported for the first time.

Raman scattering in CdInGaS$_4$ under pressure showed that the lowest frequency mode at 17 cm^{-1} has a highest value of the frequency shift parameter γ_j with pressure [$\gamma_j = (1/\nu_j)(\mathrm{d}\nu_j/\mathrm{d}P)$, where ν_j is the frequency of jth phonon at ambient pressure, P is the pressure] and hence may be attributed to a rigid-layer (RL) mode [15]. Taking this result into consideration, we also attribute the lowest frequency phonon at 21 cm^{-1} (see Table) as a mode in which the entire layer vibrates rigidly out of phase with respect to its neighbor layer. The frequency of this mode gives information about the strength of the layer-layer interaction in CdInGaS$_4$. Occurrence of the low-frequency RL mode voices in favor of the fact that the unit cell of studied crystals consists of at least two layers. This fact excludes the one-layer modification reported in [12].

We may use the frequency of the lowest Raman mode at 21 cm^{-1} to estimate a frequency of splitting between a Davydov-pair in the similar way as it was done for GaSe [14]. According to [14], one can estimate the value $\delta\nu_j$ of splitting of the mode with frequency ν_j by means of the relation $\delta\nu_j = \nu_{RL}^2/2\nu_j$, where ν_{RL} is the frequency of the RL mode. Estimated values are: for the mode at 29 cm^{-1}, $\delta\nu = 7.6$ cm^{-1}; for 43 cm^{-1}, 5.1 cm^{-1}; for 60 cm^{-1}, 3.7 cm^{-1}, for 82 cm^{-1}, 2.7 cm^{-1}, for 102 cm^{-1}, 2.2 cm^{-1}. With increasing phonon frequency this difference decreases and equals 0.7 cm^{-1} for phonons at 300 cm^{-1}. From Table it is seen that the differences between the experimental values of observed pairs at 29-38 cm^{-1}, 43-48 cm^{-1}, 60-65 cm^{-1}, and calculated according to the above given formulae, are in reasonable agreement. For this reason we attribute the above mentioned pairs to a Davydov pairs, which take place in the vibrational spectra of layered (molecular, chain) crystals which contain at least two layers per unit cell. Due to low intensities of these lines at low temperature, it was rather uncertain to determine the experimental values of the splitting at 77 K. But the tendency was towards a negligible increase the splitting at 77 K. As it is seen from Table calculated frequency separation of the Davydov pairs for the phonons at 82, 102 and 120 cm^{-1} is higher than the limit of the spectral resolution we used (1 cm^{-1}). Despite this, we did not observe the pairs for these bands. It may be due to very low intensities of the other pair for these bands in the same way, as it was in case of GaSe [16]. Concerning the absence of the pair for modes at 230, 250, 300 cm^{-1} and higher frequencies, the calculations showed that the frequency separation of the Davydov pair for these phonons should be about 1 cm^{-1} (230 cm^{-1}) and less (for 300 cm^{-1} mode $\delta\nu_j = 0.7$ cm^{-1}). These values lie just within the limit of the spectral resolution we used.

Let us consider the symmetry assignment of the modes. First, we assume that the crystal has one of C_{3v}^1 or C_{3v}^5 SG, as suggested in [1] and [12], respectively. According to these articles, a unit cell of crystal contains one layer and the crystal structure does not posses inversion symmetry. If the crystal has one of the above-mentioned SG, then the phonon spectra should not reveal a RL mode. The assignment of lowest frequency mode at 21 cm^{-1} to a RL mode is in contradiction to one-layer modifications such as C_{3v}^1 and C_{3v}^5. D_{3d}^1 modification has a center of symmetry [9]. It is known, that in centrosymmetric crystals, due to the exclusion principle, the doublets resulting from a small interaction between the layers are such that only one component is Raman active. We believe that the observation of both components of the doublets in Raman spectra is due to a lack of inversion symmetry in the crystal. In favor of this is also the fact that we have observed a weak second harmonic signal generated in crystals excited with a pulsed YAG:Nd^{3+} laser

operated at 1.06 μm. According to [9], the presence of inversion symmetry in the crystals grown by the Bridgman method was supported by the absence of the second harmonic signal in the crystals excited by a 1.06 μm of a pulsed YAG:Nd^{3+} laser. It seems that the crystals grown by the Bridgman and chemical vapor methods belong to different modifications. The situation looks the same in the case of layered GaSe; vapor-grown crystals have R3m SG, whereas melt grown predominantly contains D$_{3h}^1$ (ε-type).

The symmetry assignment given below takes into account also the results of polarized IR reflection (transmission) and Raman scattering measurements given in [8] and in [6, 9], respectively. We assume that the layer unit cell contains one formula (7 atoms) and in the C$_{3v}$ symmetry of the individual layer the division of the 21 long-wavelength normal modes of vibrations is $\Gamma \equiv 7A_1+7E$. Excluding A_1+E acoustic vibrations, we have $6A_1+6E$ phonons, which are simultaneously active in IR and Raman spectra. Then we assume that symmetry of crystal is C$_{3v}^1$ (which contains two layers) and it is the same as the symmetry of the C$_{3v}$ layer. In this case the crystalline structure of the two layers may give rise to a small splitting of each intralayer frequency into two bands—similar to a case for ε-GaSe, where the symmetry of layer is D$_{3h}$ and the symmetry of the crystal is D$_{3h}^1$. For the two-layer modification the result is simply $\Gamma \equiv 14A_1+14E$. Excluding the acoustic vibrations, one has 13A$_1$ and 13 E-type simultaneously active IR and Raman active phonons. A list of all observed modes is given in Table. As the reader may see, we observed 17 Raman and 2 IR active phonons predicted by the theory of symmetry. The back scattering geometry from the cleaved plain, which we used in our experiments, exhibits greater preference for the detection of E-type phonons over A-type phonons. Hence our observation of more E-type vibrations than A-type vibrations.

4.   Conclusion

Seventeen bands observed in the Raman scattering spectra of vapor grown crystals were assigned to normal modes on the basis of the C$_{3v}^1$ space group. This modification of the CdInGaS$_4$ crystal does not contain inversion symmetry and contains two layers per elementary unit cell. CdInGaS$_4$ crystals grown from the vapor phase, and from the melt, belong to different crystallographic modifications. A pair of bands observed in the low-frequency range (below 100 cm^{-1}) of CdInGaS$_4$ are attributed to the Davydov doublets, arising due to a small interlayer interaction.

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