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Abstract. In this paper the Raman vibrational spectra for all actually realized geometries of $PbGa_2S_4$ and $MgGa_2S_4$ crystals at 77 K, and infrared reflectivity spectra for both $E \| c$ and $E \perp c$ polarizations in the range from 50 to 4000 cm^{-1} at 300 K have been investigated. The contours of the reflectivity spectra are calculated by means of the classical dispersion relations of the multi-oscillator model, and the fundamental phonon parameters and the static (ε_0) and high-frequency (ε_∞) dielectric constants are determined as well. Davydov multiplet vibrational modes have been revealed in both crystals.

1. Introduction

$PbGa_2S_4$, $CdGa_2S_4$ and $MgGa_2S_4$ are semiconductors with strong anisotropy in their properties, each containing three species of atom. These materials look promising as regards use in non-linear optical devices for doubling, summation and extraction of radiation frequencies, parametric generation, radiation selection of photodetectors for IR etc [1–5]. The $CdGa_2S_4$, $PbGa_2S_4$ and $MgGa_2S_4$ crystals are crystallized in lattices with S_4^2 [6], D_{2h}^{24} [6] and C_{2h}^6 [7] symmetry, respectively. All three are wide-band materials. The minima of the energy gaps of $CdGa_2S_4$ and $PbGa_2S_4$ crystals are formed by direct transitions [8–10]. Three exciton series were found in $PbGa_2S_4$ in the energy gap region [9]. At present, the $CdGa_2S_4$ crystal is the most investigated. Electron transitions in the region of fundamental absorption have been investigated in references [4, 5, 10–12]. The dynamics of the crystal lattice was studied in references [13–19]. Investigation of the dynamical properties of such crystal types is of interest for determination of the degree of ionicity of atoms and the anisotropy of chemical bonding in the crystal lattice, which determine the nature of the vibrational modes [20, 21]. Infrared- and Raman-active vibrational modes in $PbGa_2S_4$ have been reported in reference [22]. The vibrational properties of $MgGa_2S_4$ crystals have not been investigated up to now.

In this paper, the Raman vibrational spectra for all actually realized geometries of $PbGa_2S_4$ and $MgGa_2S_4$ crystals at 77 K, and infrared reflectivity spectra for both $E \| c$ and $E \perp c$ polarizations in the range from 50 to 4000 cm^{-1} at 300 K have been investigated. The contours of the reflectivity spectra are calculated by means of the classical dispersion relations of the multi-oscillator model, and the fundamental phonon parameters and the static (ε_0) and high-frequency (ε_∞) dielectric constants are determined as well. Davydov multiplet vibrational modes have been revealed in both crystals.

2. Experimental details

The $PbGa_2S_4$ crystals obtained by the vertically directed crystallization technique were easily cleaved in the (100) plane and prepared in the form of cubic ($2 \times 2 \times 4$ cm) samples. The crystal symmetry (D_{2h}^{24}) was verified by x-ray structure analysis and the lattice parameters ($a = 20.69$ Å, $b = 20.51$ Å, $c = 12.23$ Å) were determined. These parameters coincide with reference data [6]. Other crystal phases are not observed and are not known from the literature.

The $MgGa_2S_4$ crystals were needle shaped, with the C_{2h}^6 space group and lattice parameters that are the same as in reference [7]. Infrared reflectivity spectra were taken for mosaic surfaces made of 3–4 crystals. The surface was polished to a mirror finish. Then, the absolute values of the reflectivity coefficients for the LO and TO vibrational modes are both a few per cent ($\sim$5–7%) lower, while the change in the mode frequencies was negligible. Our estimation for $MgGa_2S_4$ crystals gave values less than ± 1 cm^{-1}. In the present paper, our preliminary data for $MgGa_2S_4$ are the first results on vibrational spectra of $MgGa_2S_4$ crystals.

The infrared reflectivity spectra were measured by a computer-controlled KSDI–82 vacuum spectrometer (250–50 cm^{-1}) and by a Specord-M80 spectrometer (4000–200 cm^{-1}). The spectra were discretely recorded, and at each wavelength mathematical processing of the signal was carried out. The Raman scattering spectra were measured by a DFS-32 spectrometer with two excitation sources: He–Ne and Ar$^+$ lasers with $\lambda = 6328$ Å and $\lambda = 5145$ Å, respectively.

3. Vibrational properties of $PbGa_2S_4$

$PbGa_2S_4$, as mentioned above, crystallizes in the orthorhombic structure: space group D_{2h}^{24} with lattice parameters $a = 20.706$ Å, $b = 20.380$ Å, $c = 12.156$ Å. The number of vibrational modes of each symmetry has not been evaluated theoretically because the coordinates of the Pb, Ga and S atoms in $PbGa_2S_4$ crystals are unknown. X-ray structure investigations are difficult because of the strong absorption by Pb atoms. Therefore, the number of vibrational modes of each symmetry is determined only approximately. From the observed total number of vibrational modes ($\sim$60) in infrared and Raman spectra, we assume that this number of modes is close to that of the full series of Γ vibrations. We can also assume that the primitive cell of $PbGa_2S_4$ contains three formula species. In this case the number of vibrational modes has to be 63 (60 optical and 3 acoustic) vibrations. Therefore, approximately nine vibrational modes should be expected in each symmetry. Exactly that number of modes have been observed in the experiment.

According to the selection rules, modes of A_g, B_{1g}, B_{2g} and B_{3g} symmetry are Raman active, and modes of B_{1u}, B_{2u} and B_{3u} symmetry are active in IR reflection and absorption. Phonons of A_u symmetry are forbidden in infrared, as well as in Raman scattering. Phonons of B_{1u} symmetry are active in $E\|c$ polarization. In $E\perp c$ polarization, phonons of $B_{2u}+B_{3u}$ symmetry are active, i.e. B_{2u} phonons are active for $E\|b$ polarization, and B_{3u} phonons are active for $E\|a$ polarization.

The Raman scattering tensors of the first order for crystals of D_{2h} symmetry are

$$\begin{vmatrix} a & 0 & 0 \\ 0 & b & 0 \\ 0 & 0 & c \end{vmatrix} \sim A_g \qquad \begin{vmatrix} 0 & d & 0 \\ d & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \sim B_{1g}$$
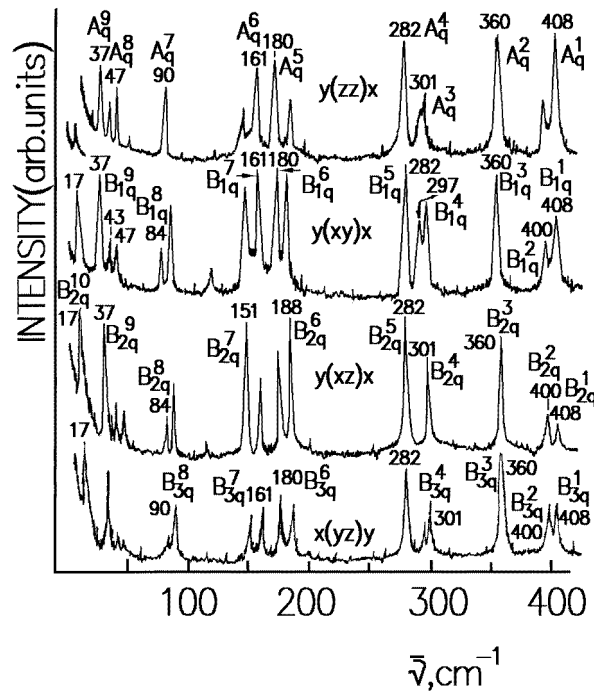
Figure 1. The Raman scattering spectra of PbGa$_2$S$_4$ crystals for actually realized geometries at 77 K.

$$\begin{vmatrix} 0 & 0 & e \\ 0 & 0 & 0 \\ e & 0 & 0 \end{vmatrix} \sim B_{2g} \qquad \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & f \\ 0 & f & 0 \end{vmatrix} \sim B_{3g}.$$

The Raman spectra of the PbGa$_2$S$_4$ crystals are presented in figure 1 for different geometries at 77 K. In $y(zz)x$ geometry the most intense modes are A_g^1–A_g^9. The high-frequency mode at 408 cm^{-1} is observed in all geometries, with lower intensity for $y(xz)x$ and $x(yz)y$ geometries. A band at 360 cm^{-1} with almost the same intensity is observed for all orientations. The vibrational mode at 400 cm^{-1} has higher intensity for three B$_{1g}$, B$_{2g}$ and B$_{3g}$ geometries. In all orientations the lines at 282 cm^{-1} and 301 cm^{-1} with A$_g$, B$_{1g}$, B$_{2g}$ and B$_{3g}$ symmetries are also observed. The B$_{1g}^4$ vibrational mode at 297 cm^{-1} is determined. In the range from 150 to 200 cm^{-1} four vibrational lines were distinguished, which appear as two pairs. At room temperature the polarization dependences of these lines are seen in the following manner: the lines at 151 cm^{-1} and 186 cm^{-1} [5] have the highest intensity for $y(xz)x$ geometry, while the lines at 161 and 180 cm^{-1} have high intensity in three other geometries. At the temperature 77 K (figure 1), all four lines for all orientations are resolved; however, they have different intensities. On the basis of these regularities we believe that the lines at 151 and 188 cm^{-1} have B$_{2g}$ symmetry, while the lines at 161 and 180 cm^{-1} are of A$_g$, B$_{2g}$ and B$_{3g}$ symmetry. The band at 90 cm^{-1} is due to A$_g^7$ and B$_{3g}^8$ modes, and the bands at 84 cm^{-1} have B$_{1g}$ and B$_{2g}$ symmetry. In the low-frequency region the lines at 17, 37, 43 and 47 cm^{-1} were observed; these also have different intensities for different orientations.

In the reflectivity spectra of the PbGa$_2$S$_4$ crystals in the range from 50 to 500 cm^{-1} for $\boldsymbol{E}\|\boldsymbol{c}$ and $\boldsymbol{E}\perp\boldsymbol{c}$ ($\boldsymbol{E}\|\boldsymbol{a}$) polarizations, there were observed nine and eight bands, respectively
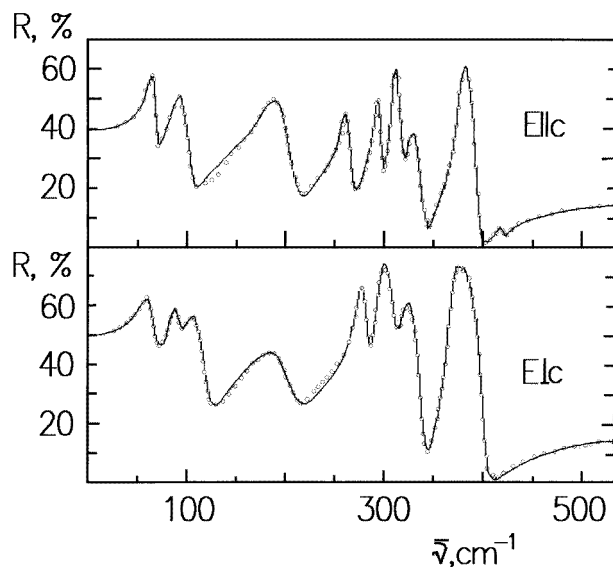
Figure 2. Reflectivity spectra of PbGa$_2$S$_4$ crystals for $E\|c$ and $E\perp c$ polarization. (Experimental values: open circles; theoretical calculation: solid line.)

(figure 2). Under the action of a macroscopic electric field due to optical vibrations, splitting of the vibrations of B$_{1u}$, B$_{2u}$ and B$_{3u}$ symmetry into longitudinal (LO) and transverse (TO) modes takes place.

To determine the phonon parameters (frequency, oscillator strength, damping and dielectric constants), the contours of the reflectivity spectra were calculated from the dispersion relationship:

$$\varepsilon(\omega) = \varepsilon_1 + i\varepsilon_2 = \varepsilon_\infty + \sum_{j=1}^{N} \frac{4\pi f_j \omega_{TOj}^2}{\omega_{TOj}^2 - \omega^2 - i\omega\gamma_j}.$$

Here ε_∞ is the high-frequency dielectric constant; ω_{TOj} is the transverse phonon frequency ($\omega = 2\pi\nu/c$); γ_j is the damping; j is the oscillator number; f_j is the oscillator strength; and ω_{LOj} is determined from the Im$(-\varepsilon(\omega)^{-1})$ condition. The dielectric constant ε_∞ in the high-frequency range is calculated from the relation

$$R(\omega) = \left| \frac{\sqrt{\varepsilon(\omega)} - 1}{\sqrt{\varepsilon(\omega)} + 1} \right|^2$$

where R is the reflectivity over the frequency range from 3000 to 4000 cm^{-1} for the corresponding light wave polarization.

The reflectivity spectra contours calculated from the dispersion relations are in good agreement with the experimental spectra. The values ω_{TOj}, f_j and γ_j were selected using a fitting procedure for measured contours and calculated ones. The low-frequency dielectric constant was calculated as the sum of the oscillator strengths, i.e. $\varepsilon_0 = \varepsilon_\infty + 4\pi f_j$.

From the spectra shown in figures 1 and 2 and from the data of table 1, we see that the 1, 2, 5–8 vibrational modes have the highest oscillator strength in $E\perp c$ ($E\|b$) polarization; that is, the magnitude of the static dielectric constant in this polarization is due to those modes. For $E\perp c$ polarization, the bands 2 and 7–9 have the highest oscillator strength, and

Table 1. The infrared parameters of active phonons in PbGa$_2$S$_4$ crystals.

Modes	ω_{TOj} (cm^{-1})	ω_{LOj} (cm^{-1})	γ_j (cm^{-1})	$4\pi f_j$	Parameters
B_{1u}^1	418	419	7	0.012	$R(4000\ \text{cm}^{-1}) = 0.19$
B_{1u}^2	375	395	8	0.369	$\varepsilon_\infty = 6.48$
B_{1u}^3	325	340	17	0.319	$\varepsilon_0 = 18.65$
B_{1u}^4	309	316	5	0.378	
B_{1u}^5	293	298	6	0.375	
B_{1u}^6	260	268	10	0.556	
B_{1u}^7	185	210	26	2.725	
B_{1u}^8	91	105	16	3.459	
B_{1u}^9	64	70	8	3.976	
B_{3u}^1	367	402	8	0.544	$R(4000\ \text{cm}^{-1}) = 0.22$
B_{3u}^2	318	340	15	0.349	$\varepsilon_\infty = 7.66$
B_{3u}^3	295	312	10	1.284	$\varepsilon_0 = 32.81$
B_{3u}^4	276	284	8	1.434	
B_{3u}^5	187	210	41	3.167	
B_{3u}^6	104	122	20	3.932	
B_{3u}^7	88	93	11	3.212	
B_{3u}^8	60	70	16	11.23	

Table 2. Atom coordinates in MgGa$_2$S$_4$ crystals.

Atom	x	y	z
S(1)	1/8	−1/8	0
S(2)	1/8	1/24	0
S(3)	1/8	5/24	0
S(4)	3/8	1/8	0
S(5)	3/8	−1/24	0
S(6)	3/8	−5/24	0
Ga(1)	0.31	−1/8	0.14
Ga(2)	0.31	1/24	0.14
Ga(3)	0.31	5/24	0.14
Mg(1)	0	−1/8	1/4
Mg(2)	0	1/24	1/4
Mg(3)	0	5/24	1/4

these provide the major contribution to the static dielectric constant ε_0. In the reflectivity spectra, the bands 5 and 7 and the bands 1 and 2 are at their most intense for $E \perp c$ and $E \| c$ polarizations, respectively. The bands 5 and 7 are located in the Raman scattering range from 151 to 188 cm^{-1}. In the range from 250 to 350 cm^{-1} in infrared reflectivity spectra, the 3–5 ($E \| c$) and 2–4 ($E \perp c$) group of vibrational modes have been observed, which have line shapes different from the traditional one. For the CdGa$_2$S$_4$ crystals, two bands, at 372, 323 cm^{-1} ($E \| c$) and at 362, 324 cm^{-1} ($E \perp c$), have been observed in approximately the same frequency region, and these have been ascribed to vibrational modes of B$_2$ and A symmetry of Ga–S molecules [4]. For CdGa$_2$S$_4$, the band at 324 (323) cm^{-1} is

approximately equal in intensity to the band at 372 (362) cm^{-1}. From comparing the shapes of the reflectivity spectra of $CdGa_2S_4$ and $PbGa_2S_4$, it is reasonable to assume that, for the latter crystal, Davydov multiplets of infrared-active modes are observed. The Davydov interaction leads to the splitting of infrared-active modes for several components—4 and 5 for $E\|c$ polarization and 3 and 4 for $E\perp c$ polarization. The weak bands at 322 cm^{-1} (band 2) and 328 cm^{-1} (band 3) are probably due to the existence of the vibrational B_{2u} modes measured in B_{3u} geometry or vice versa. Thus, we assume that the bands at 284–306 cm^{-1} for $E\perp c$ polarization and the bands at 298–314 cm^{-1} for $E\|c$ polarization are Davydov doublets, which are active in infrared spectra. In the latter case, the splitting of the infrared Davydov components is a little greater (22–16 cm^{-1}) than the splitting of the Raman components (4–10 cm^{-1}; see table 2).

4. Davydov multiplets of vibrational modes

Since the crystal structure of the complex $PbGa_2S_4$ crystal exhibits orthorhombic symmetry and its unit cell consists of four layers, between neighbouring layers there exist interlayer interactions. Here, strong modes, which determine the basic chain frequencies, appear in the form of Davydov multiplets. Coupling (strong interaction) of two layers leads to a series of two or four vibrational modes. Here Raman–Raman-, infrared–infrared- and Raman–infrared-active modes are possible and can manifest themselves. It is worth noting that all vibrational modes in the spectra under consideration are observed as allowed doublets in each geometry. The same situation is observed in molecular crystals and in crystals of In–S type [2]. In the $PbGa_2S_4$ crystals, D_{2h}^{24}-symmetric atom shifts are possible for all normal modes. For this symmetry group, pairs of modes, A_g and B_{1g}, B_{2g} and B_{3g}, B_{3u} and B_{2u}, involving conjugated symmetry elements and transferring non-equivalent translation packets from one to another, can form doublets analogous to Davydov doublets in molecular crystals. In $PbGa_2S_4$, due to symmetry rules, both polarized components of almost all of the Davydov doublets are active either in Raman or in infrared spectra. In the experimental spectra obtained, exactly the same tendency is observed. The bands at 400–408, 397–301, 180–188, 151–161 cm^{-1} are of the Raman–Raman kind. These modes are due to the vibration of both Ga–S and S–S molecules.

In the $PbGa_2S_4$ crystals with the space group D_{2h}^{24}, in which the positional atom symmetry is C_i, each allowed mode in an infrared spectrum band can have three Davydov components: B_{1u}, B_{2u}, B_{3u}. As the three transition moments are mutually perpendicular, when infrared irradiation falls on a single-crystalline plane only two Davydov components will be observed in the spectrum. The Davydov splitting magnitude is about 6–8% of the basic frequency magnitude. The vibrations of A_g, B_{1g}, B_{2g} and B_{3g} symmetry are Raman active. The vibrations of A_u symmetry are forbidden both in Raman and in infrared spectra.

The vibrational spectrum of the layered $PbGa_2S_4$ crystal is determined mainly by interlayer atom interaction. The intralayer interaction appears as a small perturbation, which leads to interlayer vibration splitting into Davydov doublets. The interlayer vibrational terms of A_1 symmetry are split into B_{3u}–A_g and B_{2u}–A_u pairs as a result of the lattice-field action. The A_u modes are forbidden, while B_{2u} modes should exist in infrared spectra for $E\|a$ polarization, which we did not take.

Intralayer vibrations of B_1 symmetry are split into B_{2g}–B_{1u} and B_{3g}–B_{1g} pairs by the D_{2h} crystal field. Comparing all observed Raman and infrared vibrational modes (figure 3), we see that they are divided into two groups. The first group is located in the regions from 280 to 420 cm^{-1} and we assign it to the internal vibrational modes (figure 3(a)) which are due to vibrations of S–S and Ga–S atoms; the second group in the range from 17 to
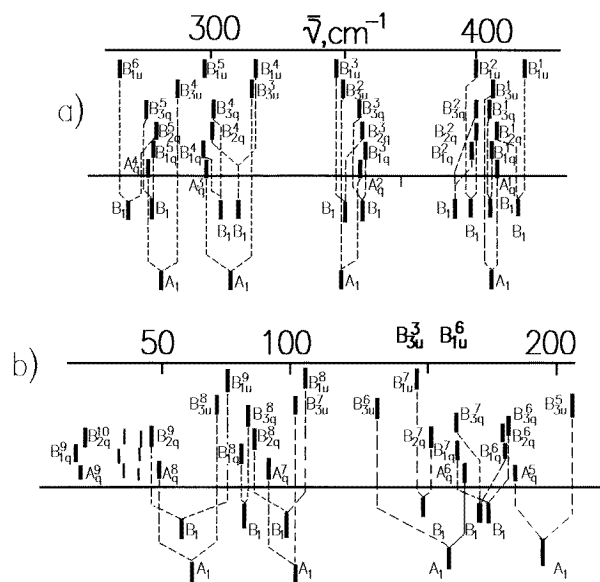
Figure 3. The splitting scheme of (a) internal and (b) external vibrational modes of PbGa$_2$S$_4$ crystals.

210 cm^{-1} we attribute to the external vibrational modes, which are formed by vibrations of Pb–Ga–S molecules (figure 3(b)). The internal vibrational modes of both TlGaS$_2$ and TlInS$_2$ crystals are observed in the frequency region from 300 to 250 cm^{-1} and from 200 to 150 cm^{-1}, and external vibrations are observed in the region from 50 to 130 cm^{-1} [23, 24]. The determination of internal vibrational modes is straightforward enough, because these have been attributed both to In$_4$S$_{10}$ and to Ga$_4$S$_{10}$ anion groups [25]. With account taken of possible combinations of the Davydov doublets, the observed modes are coupled in pairs. Four internal vibrational modes formed from the A$_1$ state (B$_{3u}$–A$_g$ pairs) have been observed, while B$_1$ terms form ten B$_{2g}$–B$_{1u}$ and B$_{3g}$–B$_{1g}$ pairs. We assume that six terms of A$_1$ type in the high-frequency region and two A$_1$ terms in the low-frequency region form eight pairs of B$_{2u}$–A$_u$ type. Therefore, in the infrared spectra for $E\|c$ polarization, eight vibrational modes of B$_{2u}$ symmetry should be observed. The internal vibrational modes are also revealed in the form of four groups of terms in the regions 270–290, 290–340, 340–370 and 390–420 cm^{-1}. In the low-frequency region, four mode pairs of B$_{3u}$–A$_g$ type and six mode pairs of B$_{2g}$–B$_{1u}$ and B$_{3u}$–A$_g$ type were observed and ascribed to the external vibrational modes (figures 3(a), 3(b)).

Table 3. Factor-group analysis for MgGa$_2$S$_4$ crystals.

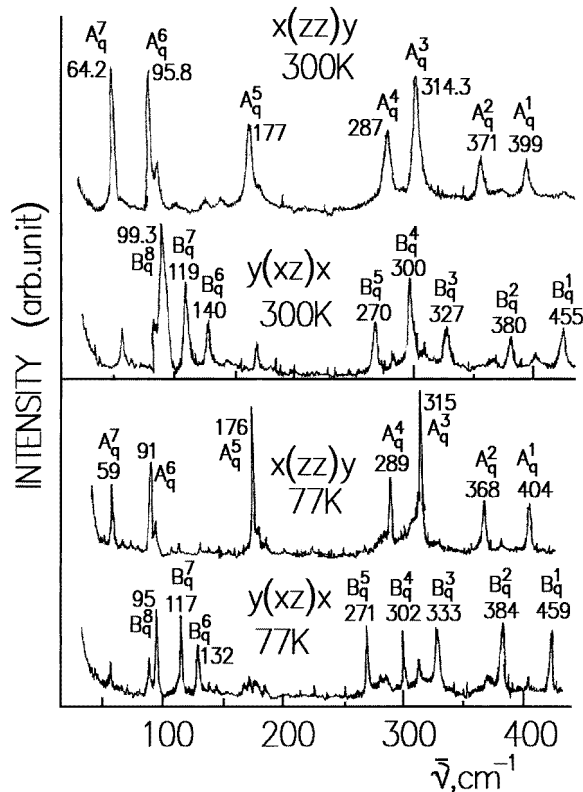| C$_{2h}$	Mg C$_2$	S C$_1$	Ga C$_1$	Mg	S	Ga	N	T	R
A$_g$	A	3A	3A	1	3	3	7		z
B$_g$	2B	3A	3A	2	3	3	8		x, y
A$_u$	A	3A	3A	1	3	3	7	z	
B$_u$	2B	3A	3A	2	3	3	8	x, y	

Figure 4. Raman scattering spectra of MgGa$_2$S$_4$ in two geometries at 77 and 300 K.

5. Vibrational properties of MgGa$_2$S$_4$

The MgGa$_2$S$_4$ compound crystallizes in a lattice with the space group $C_{2/c}$ (C_{2h}^6). The lattice parameters are $a = 12.74$ Å, $b = 22.54$ Å, $c = 6.43$ Å, $\beta = 108.8°$ [6]. The atom coordinates are listed in table 2. Mg atoms take the position 4e; Ga and S atoms take the common positions 8f. In this crystal with space group C_{2h}^6 the atoms can take positions from the set $4C_i(2)$, $C_2(2)$, $C_1(4)$. Therefore, S and Ga atoms have $C_1(4)$ positional symmetry, and Mg atoms have $C_2(2)$ symmetry. From correlation tables, A$_g$ and A$_u$ representations of the C$_{2h}$ symmetry group transform into A representations of the C$_2$ group, and both B$_g$ and B$_u$ representations transform into B representations. The irreducible B vector representations for C$_{2h}$ groups are twice degenerate for C$_2$ groups, and A states are degenerate (table 3). From correlation tables it is seen that all irreducible representations of C$_{2h}$ groups transform into A representations of C$_1$ groups. Simultaneously, it was discovered that the states of A representations are degenerate in the C$_1$ group (table 3). Therefore, on the basis of the factor-group analysis (table 3) for MgGa$_2$S$_4$ crystals, the vibrational modes of the symmetry

$$\Gamma = 7A_g + 8B_g + 7A_u + 8B_u$$

can be observed in the Brillouin zone centre. Thus, for MgGa$_2$S$_4$ one can expect to observe 30 phonons. In infrared spectra, seven phonons of A$_u$ symmetry for $\boldsymbol{E}\|\boldsymbol{c}$ polarization and eight phonons of B$_u$ symmetry for $\boldsymbol{E}\perp\boldsymbol{c}$ polarization could be observed. The phonons of A$_g$

and B$_g$ symmetry are Raman active. The tensors of Raman scattering for C$_{2h}$ symmetry are

$$A_g \sim \begin{vmatrix} a & d & 0 \\ d & b & 0 \\ 0 & 0 & c \end{vmatrix} \qquad B_g \sim \begin{vmatrix} 0 & 0 & e \\ 0 & 0 & f \\ e & f & 0 \end{vmatrix}.$$

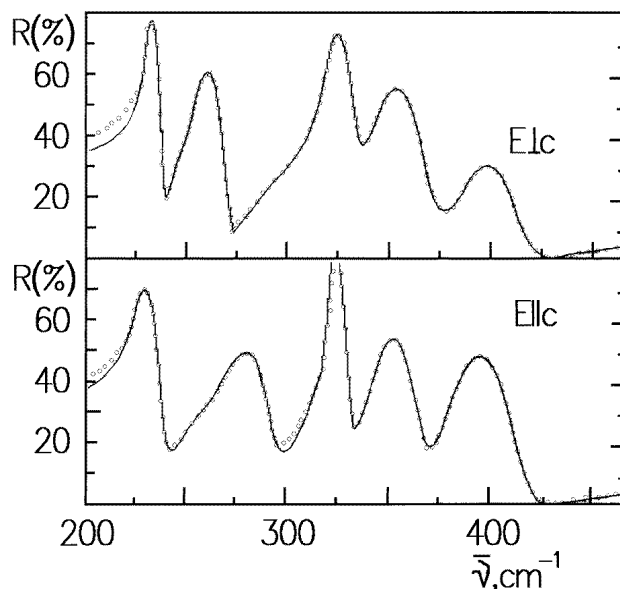The Raman scattering spectra in two geometries at 300 and 77 K are shown in figure 4.

Figure 5. Reflectivity spectra of MgGa$_2$S$_4$ crystals for $E\|c$ and $E\perp c$ polarization. (Experimental values: open circles; theoretical calculation: solid line.)

15 vibrational modes are observed at the temperatures 300 and 77 K, i.e. all of the expected vibrational modes were revealed. As is seen from the figures, the vibrational modes are divided in two groups, i.e. at 59–180 cm^{-1} and at 270–402 cm^{-1}. Comparing the Raman scattering spectra of MgGa$_2$S$_4$ with the vibrational modes of PbGa$_2$S$_4$, CdGa$_2$S$_4$ and CdAl$_2$S$_4$ crystals [4, 5, 7, 8], we can conclude that the high-frequency modes from 270 to 402 cm^{-1} are due to internal vibrational modes, and the low-frequency modes are due to external vibrational modes. The Ga ions are located along the line of tetrahedral slits. Their positions are more distorted than the Mg positions. The average Ga–S distance is equal to 2.28 Å [6] as in α-Ga$_2$S$_3$. Four anion types are varied within trigonal SGa$_3$ and SMgGa$_2$ configurations and irregular tetrahedral arrangements of both SMg$_2$Ga$_2$ and SMg$_3$Ga configurations. In MgGa$_2$S$_4$ crystal, the arrangement of S atoms is identical with their arrangement in α-Ga$_2$S$_3$. The Ga atoms are linked with S atoms (the distances between atoms are equal to 2.253, 2.318 and 2.310 Å). The similar positioning of Ga and S atoms generates a great number of internal vibrational modes. The Mg atoms are located in octahedra and the Mg–S distance is in the range from 2.52 to 2.71 Å, indicating that the octahedra are slightly distorted. The average value of the Mg–S separation is equal to 2.59 Å in good agreement with the value observed in the MgS structure of NaCl type (2.60 Å). Each Mg atom is octahedrally correlated with six S atoms in such a way that three edge parts of the octahedron are perpendicular to the (001) plane. There are three octahedron types with slightly different parameters. Octahedron planes in MgGa$_2$S$_4$ are arranged at

$x = 0$, $y = 0$ and at $x = 1/2$, $y = 1/2$ in accordance with centring of the (001) plane. This arrangement of the layers and the octahedra creates external vibrational modes in the range from 59 to 246 cm^{-1}. Infrared reflectivity spectra of the MgGa$_2$S$_4$ crystals are shown in figure 5 for both $\boldsymbol{E} \| \boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ polarizations in the range from 200 to 500 cm^{-1}.

Table 4. The infrared parameters of active phonons in MgGa$_2$S$_4$ crystals.

Modes	ω_{TOj} (cm^{-1})	ω_{LOj} (cm^{-1})	γ_j (cm^{-1})	$4\pi f_j$	Parameters
A_u^1	383	416	18	0.278	$R(4000\ \text{cm}^{-1}) = 0.145$
A_u^2	345	366	15	0.493	$\varepsilon_\infty = 4.97$
A_u^3	321	331	2	0.520	$\varepsilon_0 = 8.97$
A_u^4	277	295	18	1.157	
A_u^5	226	240	7	1.559	
B_u^1	390	416	25	0.231	$R(4000\ \text{cm}^{-1}) = 0.15$
B_u^2	344	370	18	0.488	$\varepsilon_\infty = 5.13$
B_u^3	320	333	6	0.950	$\varepsilon_0 = 8.77$
B_u^4	256	271	9	0.899	
B_u^5	230	238	3	1.074	

Five vibrational modes of A$_u$ symmetry for $\boldsymbol{E} \| \boldsymbol{c}$ polarization and five modes of B$_u$ symmetry for $\boldsymbol{E} \perp \boldsymbol{c}$ polarization have been observed in the range from 200 to 500 cm^{-1}. Two and three modes in the far-infrared region for $\boldsymbol{E} \| \boldsymbol{c}$ and $\boldsymbol{E} \perp \boldsymbol{c}$ polarization, respectively, were not revealed. From the observed modes, the modes A_u^4, A_u^5 and B_u^3, B_u^5 (figure 5, table 4) have the highest oscillator strength. The splitting between A_u^i and B_u^i modes is approximately the same as that between A_g^i and B_g^i modes. The values of ε_0 obtained in the two polarizations are slightly underestimated because not all of the modes were observed.

The unit cell of MgGa$_2$S$_4$ described by the factor group C_{2h}^6 contains four formula units. Each of the free vibrations of the Ga–S molecules is broken in the layer of C$_{2v}$ symmetry into both A$_1$ and A$_2$ vibrational terms, and in the MgGa$_2$S$_4$ crystal it is divided into four components (i.e. A$_g$, A$_u$, B$_g$ and B$_u$). The A$_1$ vibrational term of the C$_{2v}$ layer is split by the C$_{2h}$ crystal field into both A$_u$ and B$_g$ modes, and the A$_2$ vibrational term of the C$_{2v}$ layer is split into A$_g$ and B$_u$ modes.

Comparing the internal vibrational modes of MgGa$_2$S$_4$ and PbGa$_2$S$_4$ crystals, we conclude that the B_g^1 and A_u^1 modes are due to the A_1^1 state, and both the A_g^1 and B_u^1 modes are due to the A_2^1 term. Both the A_1^1 and the A_2^1 states are due to A^1 states in their turn. The B_g^2–A_u^2 and A_g^2–B_u^2 vibrational modes are also Davydov pairs, as are B_g^3–A_u^3 modes and A_g^3–B_u^3 modes, which appear as a result of the A^3-term splitting. B_g^4–A_u^4 and A_g^4–B_u^4 vibrations are Davydov multiplets of internal vibrations of Ga–S molecules in MgGa$_2$S$_4$ crystals as well.

Thus, PbGa$_2$S$_4$ is a strongly anisotropic layer crystal, whose unit cell contains four layers. Interlayer interaction takes place between the layers, leading to the appearance of Davydov multiplets in vibrational spectra. Taking into account that in PbGa$_2$S$_4$ crystals exciton series due to excitons of both large and small radius are observed, these crystals could be recommended as materials for use in the investigation of the effect of interlayer Davydov interaction on vibrational, electronic and electron–vibrational spectra.

References

[1] Levinze B F, Bethea C C and Kasper H M 1974 Nonlinear optical susceptibility of thiogalate-CdGa$_2$S$_4$ *IEEE J. Quantum Electron.* **10** 904

[2] Badikov V V, Matveev I N, Pschenichnikov S M, Suslikov L M, Kopinets I F and Slivka V Iu 1981 *Uzkopolosnyi Perestraivaemyi Opticheskii Filtr na Monokristale CdGa$_2$S$_4$* vol 8 (Moscow: Kvantovaia Elektronika) p 910

[3] Voroschilov Iu V and Slivka V Iu 1989 *Anoksidnye Materialy dlia Elektronnoi Tehniki* (Moscow: Livov University Press) p 123

[4] Georgobiane A N, Ozerov Iu V, Radautsan S I and Tigineanu I M 1981 *Fiz. Tverd. Tela* **23** 2094

[5] Georgobiane A N, Radautsan S I and Tigineanu I M 1985 *Sov. Phys.–Semicond.* **19** 191

[6] Peters T E and Baglio J A 1972 *J. Electrochem. Soc.* **119** 230

[7] Romers By C, Blaisse B A and Ijdo D J W 1967 *Acta Crystallogr.* **23** 634

[8] Karaman M I, Muschinskii V P and Golovei V M 1985 *Izv. Akad. Nauk SSSR Neorg. Mater.* **21** 1791

[9] Syrbu N N, Cebotari V Z and Bobrysheva A I 1998 unpublished

[10] Radautsan S I, Syrbu N N, Nebola I I, Tyrziu V G and Bercha D M 1977 *Sov. Phys.–Semicond.* **11** 69

[11] Gusenova D A, Kerimova T G and Nani R H 1977 *Sov. Phys.–Semicond.* **11** 1135

[12] Georgobiane A N and Tigineanu I M 1981 *Sb. Kratk. Soobshch. Fiz. Akad. Nauk SSSR, Fiz. Inst. P N Lebedeva* **2** 8

[13] Suslikov L M, Nebola I I, Peresch E Iu, Voroschilov Iu V, Bercha D M and Slivka V Iu 1978 *Fiz. Tverd. Tela* **20** 3186

[14] Nebola I I, Suslikov L M, Diordiai V S, Bysochanskii Iu A, Harhalis R R and Slivka V Iu 1982 *Fiz. Tverd. Tela* **24** 3631

[15] Lottici P P and Razzetti C 1983 *Solid State Commun.* **6** 681

[16] Suslikov L M, Gerasimenko V S and Slivka V Iu 1980 *Opt. Spectrosk.* **48** 789

[17] Haeuseler H, Waschenbach G and Lutz H D 1995 *Phys. Status Solidi* b **129** 549

[18] Neumann H, Sobotta H, Syrbu N N, Radautsan S I and Riede V 1984 *Cryst. Res. Technol.* **19** 709

[19] Syrbu N N, Tezlevan V E and Perchekli V I 1993 *Opt. Spectrosk.* **75** 355

[20] Jijin G N, Mavrin B N and Shabanov V F 1984 *Opticheskie Kolebatelinye Spektry Kristallov* (Moscow: Mir) p 232

[21] Levaniuk A P and Soblanin A A 1990 *Rasseianie Sveta Vblizi Tochek Fazovyh Perehodov* ed G Z Kaminz and A P Levaniuk (Moscow: Nauka) p 414

[22] Syrbu N N, Lvin V E, Zadnipru I B and Golovei V M 1991 *Sov. Phys.–Semicond.* **25** 1721

[23] Durnev Iu I, Kulibujiev B S, Torgaschev V I and Iudik Iu I 1989 *Izv. Akad. Nauk SSSR Ser. Fiz.* **33** 1300

[24] Syrbu N N, Neumann H, Sobotta N and Riede V 1993 *Sov. Phys.–Semicond.* **27** 41

[25] Krebs B, Hurter H M and Voelker D 1986 *Z. Kristallogr.* **154** 63