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CONSIDERATION OF THE VIBRATIONAL PROPERTIES OF GERMANIUM DICHALCOGENIDES ON BASE OF VIBRATIONAL PROPERTIES OF GeX_4 (X = S, Se) TETRAHEDRA

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Vibrational properties of the single crystals GeS_2 and $GeSe_2$ have been analysed on ground of their properties of the crystal structure (the basic building blocks in GeX_2 are GeX_4 tetrahedra, which are interconnected via common edge or a common corner). There have been analysed the Raman and infrared spectra of an isolated GeS_4 tetrahedra, of single crystals $SnGeS_3$ and $PbGeS_3$, (whose GeS_4 tetrahedra are connected via common corners), then the Raman spectra of a Ge_2S_6 molecule, (built of two GeS_4 tetrahedra connected via common edge) and the Raman and infrared spectra of *a* — of and *c* — GeX_2. It has been concluded that molecular vibrations of the variously connected GeX_4 tetrahedra are not only present in the single crystals GeS_2 and $GeSe_2$, too, but they also play a dominant role in vibrational properties of the germanium dichalcogenides.

1. *Introduction*

The germanium dichalcogenides (GeS_2, $GeSe_2$) are semiconducting, layered compounds, whose vibrational properties have been an object of increasing interest for the last few years. The interest for examination of the vibrational properties of these materials are related to specific properties of the crystal structure of these compounds.

GeS_2 and $GeSe_2$ crystallise in an monoclinic system with 16 molecules per unit cell, space group $P2_1/c$. In these compounds germanium atoms are surrounded by 4 chalcogen atoms, while the chalcogen atoms are surrounded by two germanium atoms. Thus the crystal structure of these compounds can be presented by GeX_4 tetrahedra, in the way it was schematically displayed in Fig. 1a.

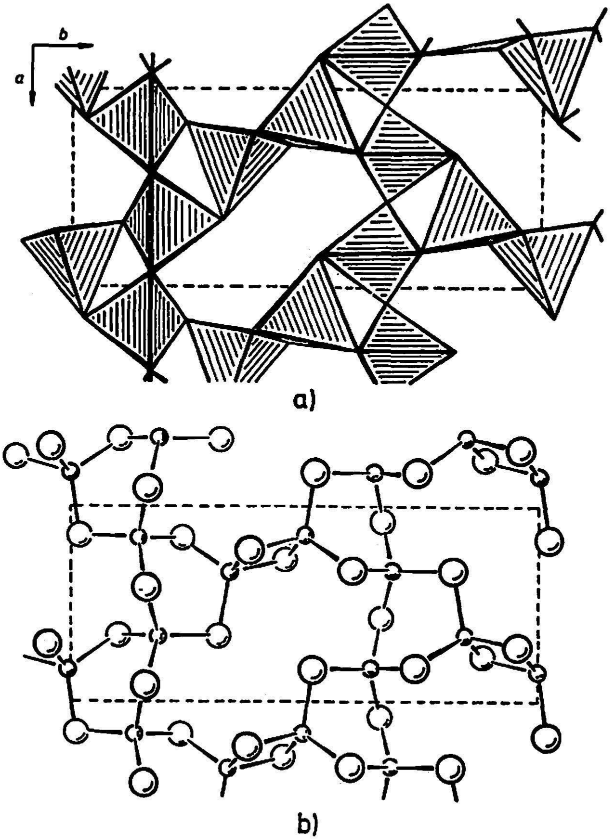

Fig. 1. Structure of single layer of Ge (S, Se)$_2$ shown with the coordination tetrahedra (*a*) and with atoms (*b*).

As Fig. 1a shows, one layer of germanium dichalogenide consists of GeX_4 tetrahedra, which are connected via corners along the *a*-axis of crystal and form continuous chains. These chains that are equivalent by the symmetry operation around the 2_1 axes are bridged via corners by edge-sharing tetrahedra. Thus a layer of GeX_2 is built of the GeX_4 tetrahedra, interconnected either via a common corner, or a common edge. The units cell of GeX_2 contains two such layers, within identity period along the *c*-axis.

In our previous paper[1], the Raman and infrared spectra of GeX_2 were given and the vibrational properties discussed in the aspect of their layer structure. In this work, the vibrational properties of GeX_2 are considered in the aspect of the existence of molecular effects, i. e. vibrations of the GeX_4 tetrahedra. In this respect besides the *R* and *IR* spectra of GeX_2, the Raman and infrared spectra of Sn (Pb) GeS_3 (in which the GeX_4 tetrahedra are connected via a common corner) were measured and analysed in this work. The vibrational properties of a GeS_4 isolated tetrahedron in solution $Na_4GeS_4 \cdot 14H_2O$[2], and in the crystals Ba_2GeS_4[3], Sr_2GeS_4[4] and Pb_2GeS_4[4], the vibrational properties of a Ge_2S_6 molecule in solution $Na_4Ge_2S_6 \cdot 14H_2O$[5], as well as the vibrational properties of amorphous GeS_2[6-9] then were also analysed.

In the case of $GeSe_2$, vibrational properties of only amorphous and single crystal $GeSe_2$ will be analysed only applying the analysis and conclusions derived for the case of the vibrational properties of GeS_2.

2. *Experimental details*

The obtaining of single crystals GeS_2, $GeSe_2$[1], as well as Sn (Pb) GeS_3[10], used in this work, was described earlier.

Raman spectra of GeS_2, $GeSe_2$ and Sn (Pb) GeS_3 at room and liquid helium temperature were taken in the back scattering geometry with a Spex model 1401 double monochromator employing holographic gratings, a cooled *RCA C31C34A02* photomultiplier and associated photon counting electronics. The 514.5 nm line of an argon ion laser was used as excitation source.

The room temperature infrared reflectivity spectra in the range between 100 and 500 cm^{-1} were taken on a Bruker model *ITS114* spectrometar with a resolution of 4 cm^{-1}.

3. *Results and discussion*

3.1. *Vibrational properties of GeS_2*

We shall first consider the vibrational properties of GeS_4 molecules. The XY_4 molecule has a T_d point symmetry, which for the distribution of normal modes gives

$$\Gamma_{T_d} = 1A_1 + 1E + 2F_2. \qquad (1)$$

$\nu_1 (A_1)$ is nondegenerate, $\nu_2 (E)$ is doubly degenerate, while $\nu_3 (F_2)$ and $\nu_4 (F_2)$ are triply degenerate modes. ν_1 and ν_2 modes are only Raman active, and ν_3 and ν_4 modes are active both in the Raman and infrared spectra. It is also known that ν_3 mode appears at the highest frequency, and that the other modes can be arranged, according to the frequency height at which they appear, as follows:

$$\nu_3 > \nu_1 > \nu_4 > \nu_2. \qquad (2)$$

The ν_3 and ν_1 modes are high-frequency modes and occur due to the bond stretching vibrations of atoms. The ν_2 and ν_4 modes are low-frequency modes and they occur due to the bond bending vibrations of atoms of the XY_4 tetrahedra.

These modes occur at lower frequencies due to the easier distortion of the valence angle than the elongation and shortening of the valence bonds between atoms in XY_4 tetrahedra. Possible vibrational modes of the XY_4 tetrahedra are shown in Fig. 2.

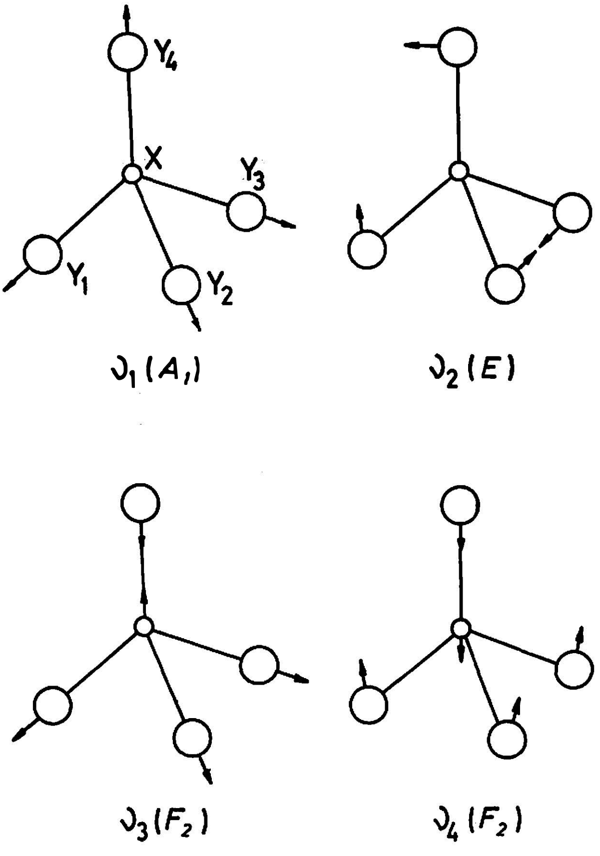

Fig. 2. Vibrational modes of XY_4 tetrahedral molecule; non-degenerate ν_1 (A_1) mode, doubly degenerate ν_2 (E) mode and triply degenerate ν_3(F_2) and ν_4 (F_2) modes.

The vibrational properties of the GeS_4 molecule have been poorly studied in the literature. As far as we know, only in Ref. 2 the vibrational properties of the GeS_4 tetrahedra, present as an isolated ion in the solution $Na_4GeS_4 \cdot 14H_2O$, were analysed. From Raman spectra$^{2)}$, it was found out that the ν_1 mode appears at 386 cm^{-1} and the ν_3 mode at 417 cm^{-1}. Position of low-frequency modes was not experimentally established due to a long tail of the scattered laser light. Frequencies of the bond bending modes ν_2 and ν_4 at 170 and at 205 cm^{-1}, respectively, were obtained by calculation on base of comparison to the Raman spectra of the AsS_4 molecule$^{2)}$.

In addition to the mentioned Raman spectra of a free GeS_4^- ion, Raman spectra of the GeS_4 molecule, present in the crystals $Ba_2GeS_4$$^{3,4)}$, $Sr_2GeS_4$$^{4)}$ and $Pb_2GeS_4$$^{4)}$, are known, too. In these crystals the GeS_4 tetrahedra are strongly distorted. Distances between the atoms Ge and S are in the range from 0.2197 to 0.2206 nm in SrGSe$_4$[11], from 0.125 to 0.237 nm in Ba$_2$GeS$_4$[11], and from 0.218 to 0.222 nm in Pb$_2$GeS$_4$[12].

An A_1 mode in Ba$_2$GeS$_4$ is observed at 393 cm^{-1}, in Sr$_2$GeS$_4$ at 382 cm^{-1}, and in Pb$_2$GeS$_4$ at 361 cm^{-1}. The A_1 mode frequency shifting of the GeS$_4$ molecule in these crystals probably comes, as a result of the influence of surrounding metal atoms. Since the distance between the atoms Pb and S is the shortest (0.287 nm) in comparison to Ba-S (0.327 nm) and Sr-S (0.306 nm), that means that the A_1 mode shifting in Pb$_2$GeS$_4$ is the greatest[1]. The values of angles and distances between atoms in the GeS$_4$ tetrahedra in these crystals are given at the bottom of Table 1. As it can be seen from Table 1, the GeS$_4$ tetrahedra in Sr$_2$GeS$_4$ and GeS$_4^{4-}$ free ions have very similar structural properties. Consequently, their vibrational modes are observed at almost the same frequencies. On base of the existing literature data, collected in Tab. 1, it can be accepted that the bond stretching modes of a GeS$_4$ tetrahedra are at 386 cm^{-1} and 417 cm^{-1}. The GeS$_4$ bond bending modes cannot be so clearly determined, since these modes in the GeS$_4^{4-}$ ion at 205 and 170 cm^{-1} were determined by calculation, while in Ba (Sr, Pb)$_2$GeS$_4$ a considerable number of modes exist that could be the ν_4 and ν_2 modes of the GeS$_4$ tetrahedra. Frequencies of these modes are also given in Table 1.

For analysis of the vibrational properties of GeS$_2$, besides the vibrational properties of GeS$_4$ tetrahedra, one must also know, the vibrational properties of the GeS$_4$ tetrahedra connected via corners and via common edges (Fig. 1).

For that reason we measured Raman and infrared spectra of SnGeS$_3$ and PbGeS$_3$. In these crystals, GeS$_4$ tetrahedra are linked together by sharing corners, thus forming (GeS$_2$S$_{2/2}^{2-}$) tetrahedral chains parallel to the crystallographic *c*-axis[13,14]. The unit cell of Sn(Pb)GeS$_3$ is monoclinic (space group P2$_1$/c, Z = 4) and contains two such chains with two tetrahedra each. The same building blocks of GeS$_4$ tetrahedra are present in GeS$_2$[15]. Nonpolarized Raman spectra of Sn(Pb)GeS$_3$ at liquid helium temperature and room temperature nonpolarized infrared spectra of Sn(Pb)GeS$_3$ are given in Figs. 3 and 4. The frequencies of the Raman and infrared modes of these crystals are given in Table 1.

The (GeS$_2$S$_{2/2}^{2-}$) chains in the crystal structure of GeS$_2$ are connected with two edge sharing tetrahedra. The edge-sharing tetrahedra form a Ge$_2$S$_6$ molecule. Raman spectra of the Ge$_2$S$_6$ molecule which has the same structural properties[16] as the edge-sharing GeS$_4$ tetrahedra in GeS$_2$, were published only in Ref. 5. The frequencies of the Raman modes of Ge$_2$S$_6$ molecule are also given in Table 1.

In consideration of influence of the molecular vibrations of GeS$_4$ tetrahedra on vibrational properties of GeS$_2$, the Raman spectra of an isolated GeS$_4^{4-}$ ion, SnGeS$_3$, Ge$_2$S$_6$ molecule and GeS$_2$, are shown, one under another, in Fig. 5.

As it can be seen in Fig. 5 there are two spectral regions due to the bond stretching vibrations (above 350 cm^{-1}) and bond bending vibrations (under 250 cm^{-1}) of the GeS$_4$ tetrahedra. We shall first consider the modes which originate from the bond stretching vibrations.

The ν_1 (A_1) and ν_3 (F_2) modes of an isolated GeS$_4^-$ ion appears at 386 cm^{-1} and 417 cm^{-1}, respectively[2]. Since the GeS$_4^{4-}$ ion is in solution, there is practically no influence of the surrounding medium on its vibrational properties. For Ba$_2$GeS$_4$ and Sr$_2$GeS$_4$, as the distances *M*-*S* are farther than 0.3 nm, it can also be stated that the surrounding medium is of no considerable influence on vibra-

TABLE 1.

Compounds	GeS_4	Ba_2GeS_4		Sr_2GeS_4		Pb_2GeS_4	$SnGeS_3$		$PbGeS_3$		Ge_2S_6	GeS_2		a-GeS_2					
Ref.	2	3,4		4		4	17		26		5	1		6		8		9	
Activity	*R*	*R*	*R*	*R*	*IR*	*R*	*R*	*IR*	*R*	*IR*	*R*	*R*	*IR*	*R*	*IR*	calc.	*R*	calc.	*R*
											457	455	450				440		
								440			452	442	440						
					428		432		428			434	430	432					
ν_3		422										421							
	417	413	415	415	416							414	414						
				402	400		406	408	403	404		410	410						
		383		398		385	397	387	399	396	402	405	406		405				408
	386	393	393	382	388							389	388			388			
											378	376	378	375			375		374
ν_1							370	374	370			369	372		367			367	
						361	364	363	355	360		355	364						
							352	350	345	341	350	352	352						
												348	338	342	328	342	345	342	345
			254	260	272		255	272				256							
				253	244	237	237	248	239			237							
		227							232			227	228						
ν_4 (*R*, *IR*)	(205)		202	210	216		223	222	224	214	221	223	212						
		198		198	196	199	193	195		196	191	194	191						
		183					182		181		180	183	182						
												174	174						

	(170)			163		162			163	164				
$\nu_2\,(R)$					156		156		154	156				
		152				146		147	150	150		149	147	
				142		141			143	140				
					134				134					
									125	124				
									122					
				118					120	117				
						113	112		114	114			114	
				107	110				104	106	105			
						103		101	100	103				
									97	98				
				89		86			90	92				
				82	84	78		81	77	77				
				71	76	70			68	67				
					62	63		58	56	58				
									53					
				48	46	49			49					
									44					
									39					
				32		32			32					
									28					
Ge-S distance (nm)	0.222	0.215—0.237	0.2197—0.2206	0.218—0.222			0.220—0.225			0.217—0.225			0.217—0.226	0.2218—0.2232
S-Ge-S angle (°)	109,47	93—126	109—116	102—117			102—119			101—118			94—117	97—116
Ge-S-Ge angle (°)							99			103			86	82—102
Ref..	2	3,4	11	12			18			14			16	15

Phonon frequencies (cm^{-1}) and some crystallographic data of compounds which consists GeS_4 tetrahedra.

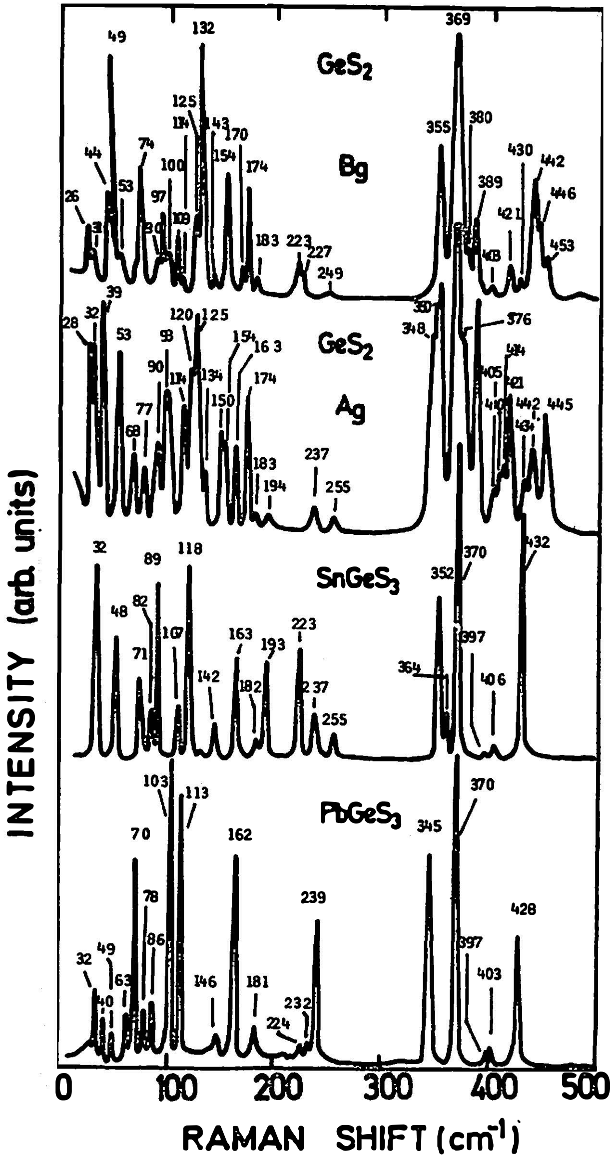

Fig. 3. Raman spectra of GeS_2 at 300 K (*a* and *b*) and non-polarized Raman spectra of Sn(Pb)GeS_3 at 4.2 K (*c* and *d*).

tional properties of the GeS_4 molecule, thus the bond stretching modes occurs practically at the same frequency as in GeS_4^{4-} ion. For that reason we can be sure that the ν_1 (A_1) and ν_3 (F_2) modes of GeS_4 tetrahedra are at 386 cm^{-1} and 417 cm^{-1}, respectively. These modes of an isolated GeS_4 tetrahedra at coupling of tetrahedra via common corner as in Sn (Pb) GeS_3, or common edge as in Ge_2S_6,

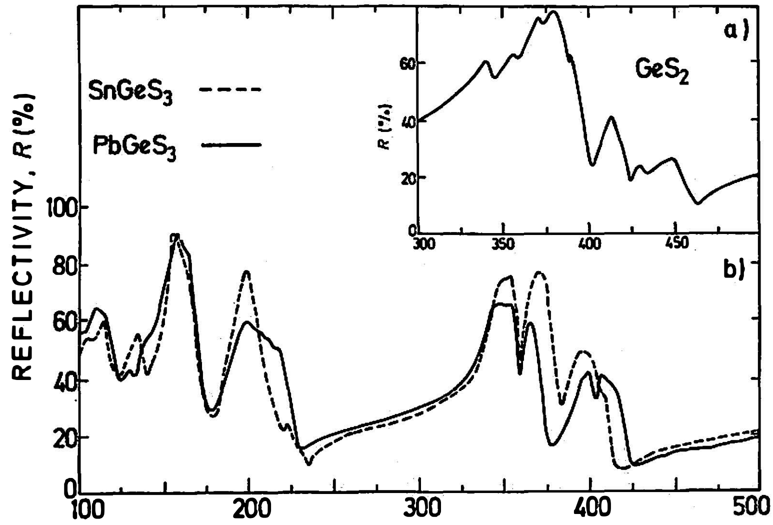

Fig. 4. Non-polarized far-infrared spectra of GeS_2 (*a*) and Sn (Pb) GeS_3 (*b*) at room-temperature.

shift toward shorter wave numbers and decompose into several surrounding modes (Fig. 5).

Two GeS_4 tetrahedra which are connected via common corner form Ge_2S_7 molecule with D_{3d} point symmetry. The distribution of the normal modes of Ge_2S_7 molecule with D_{3d} symmetry is:

$$\Gamma_{D_{3d}} = 3A_{1g} + 3E_g + 1A_{1u} + 3A_{2u} + 4E_u. \qquad (3)$$

$3A_{1g}$ and $3E_g$ are Raman active modes, $3A_{2u}$ and $4E_u$ are infrared active modes and $1A_{1u}$ is inactive mode. The correlation diagram between T_d and D_{3d} point groups is presented in Fig. 6a. According to this diagram A_1 mode of the isolated tetrahedra splits into A_{1g} (R) and A_{1u} (O), A_{2u} (IR) and E_u (IR) modes of Ge_2S_7 molecule. The highest intensity Raman modes of Sn(Pb)GeS_3 at 370 and 432 (428) cm^{-1} could be taken as A_{1g} modes of Ge_2S_7 molecule. As shown in Figs. 3 and 4 these modes are only Raman active.

The other Raman modes, in this spectral region at 352, 364, 397, 406 cm^{-1} in $SnGeS_3$, that is at 345, 355, 399 and 403 in $PbGeS_3$, have corresponding infrared pairs (Fig. 4) at 350, 363, 387, and 408 cm^{-1} ($SnGeS_3$) and 341, 360, 369 and 404 cm^{-1} ($PbGeS_3$). Because of that these modes are Raman and infrared active, they probably originate from ν_3 (F_2) mode of the GeS_4 tetrahedra. A more detailed analysis of vibrational properties of Sn(Pb)GeS_3 has been given in Ref. 17.

Two GeS_4 tetrahedra which are connected via common edge form Ge_2S_6 molecule with D_{2h} point symmetry[5]. The distribution of the normal modes of Ge_2S_6 molecule with D_{2h} symmetry is:

$$\Gamma_{D_{2h}} = 4A_g + 2B_{1g} + 1B_{2g} + 2B_{3g} + 1A_u + 2B_{1u} + 3B_{2u} + 3B_{3u}. \qquad (4)$$

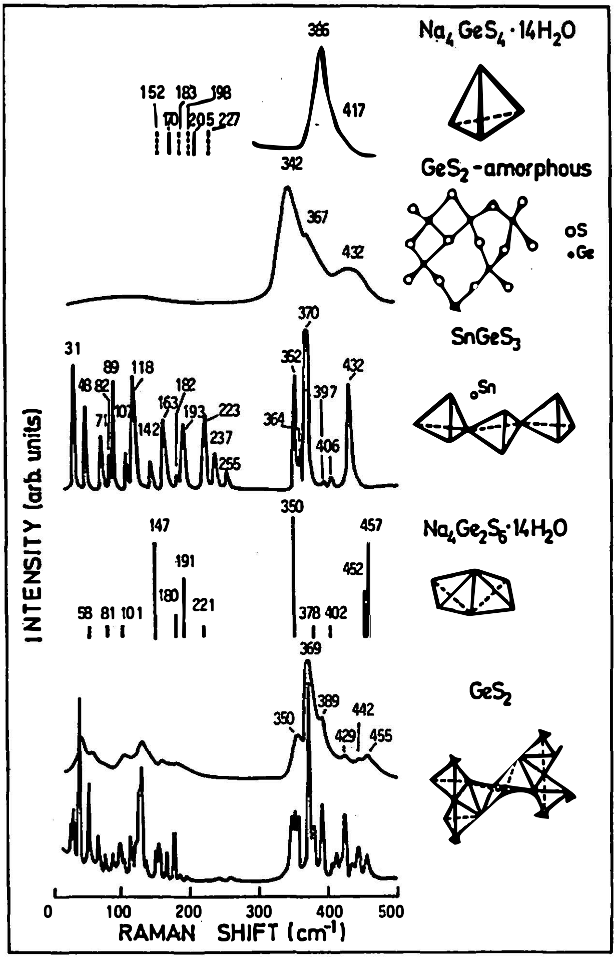

Fig. 5. Raman spectra of some compounds which consists GeS_4 tetrahedra.

$4A_g$, $2B_{1g}$, $1B_{2g}$ and $2B_{3g}$ are Raman active modes, $2B_{1u}$, $3B_{2u}$ and $3B_{3u}$ are infrared active modes and $1A_u$ is inactive mode. The correlation diagram between T_d and D_{2h} point groups is presented in Fig. 6b. According to this diagram A_1 mode of the isolated tetrahedra splits into $A_g\,(R)$ and $A_u(O)$ modes of Ge_2S_6 molecule. The strongest intensity Raman modes of Ge_2S_6 molecule in BS of spectral region at 350cm^{-1} and 457 cm^{-1} (Fig. 5) could be taken as A_g modes of Ge_2S_6 molecule. Since the infrared spectra of Ge_2S_6 molecule are unknown, it is difficult to distinguish from other Raman modes in the BS region those ones which originate from the ν_3 (F_2) mode (417 cm^{-1}) of an isolated GeS_4 molecule. For the same reason, a more complete analysis of vibrational properties of the Ge_2S_6 molecule is not possible.

Let us refer back to Fig. 5, where the Raman spectra of the Ge_2S_6 molecule where given$^{5)}$. A mode of the strongest intensity is at 350 cm^{-1}. That means that the ν_1 (A_1) mode of an isolated GeS_4 tetrahedra (386 cm^{-1}) shifts, at coupling of the tetrahedra via a common edge, in direction of shorter wave numbers for 36 cm^{-1}, which makes 20 cm^{-1} more than at coupling of the GeS_4 tetrahedra via a common corner (370 cm^{-1}).

Now we shall refer back to Figs. 3 and 5, where the Raman spectra of GeS_2 are shown. In the *BS* spectral region, the existence of fifteen various modes has been stated. Comparing the *BS* spectral range of GeS_2 with the same spectral range in Sn(Pb)GeS_3 and Ge_2S_6 it can be concluded that the Raman mode of GeS_2, of the strongest intensity at 369 cm^{-1} which is the mode of strongest intensity in Sn(Pb)GeS_3 too, represents the A_{1g} mode of the corner-connected GeS_4 tetrahedral chains. The modes of GeS_2 at 352, 355, 405 and 421 cm^{-1} also can be characterised as the modes of $(GeS_2S_{2/2}^{2-})$ tetrahedral chains. The Raman modes of GeS_2 at 350, 376, (380), 403, 442 and 455 cm^{-1} could be modes originating from vibrations of the edge-sharing GeS_4 tetrahedra (Ge_2S_6 molecule). In order to emphasize only the strongest intensity Raman modes in Fig. 5, a Raman spectra of GeS_2 with a very bad resolution is given. In this spectra clearly noticeable

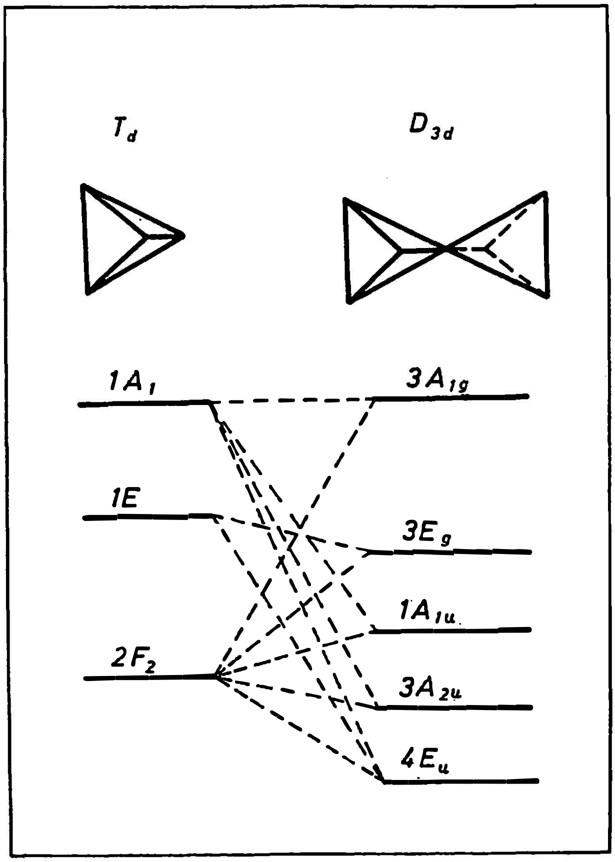

Fig. 6a. The correlation diagram between T_d and D_{3d} points groups.

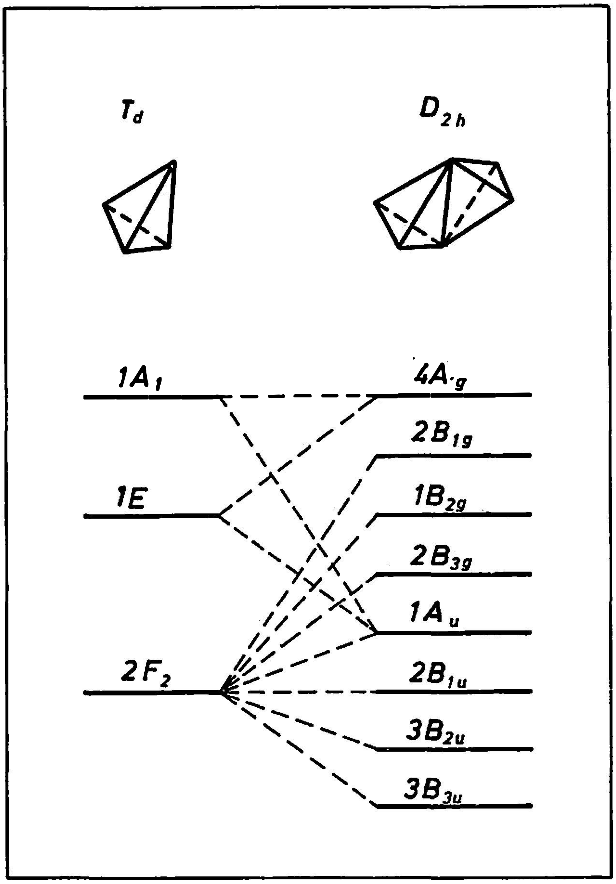

Fig. 6b. The correlation diagram between T_d aud D_{2h} points groups.

are only the modes at 350, 369, 389, 429, 442, and 445 cm^{-1}. The Raman mode of GeS_2 at 350 cm^{-1} is strongest mode of the Ge_2S_6 molecule, and it appears as an intensive mode in $Sn(Pb)GeS_3$, too. The existence of this mode originating probably from vibrations of structure which form by coupling of GeS_4 tetrahedra both via common corner and via common edge (f. e. S_{free}—Ge—S_{free} bridge). As we have already stated, the mode at 369 cm^{-1} originates from vibration of atoms of the corner-connected GeS_4 tetrahedra. Besides this mode, an A_g (B_g) mode of GeS_2 of considerably lower intensity was acertained at 376 (380) cm^{-1}. Since in the Ge_2S_6 molecule the existence of a mode at 378 cm^{-1} has also been determined, while it is not the case with $Sn(Pb)GeS_3$, this mode of GeS_2 can be ascribed to vibration of atoms of the edge-sharing GeS_4 tetrahedra. The mode at 429 cm^{-1} (it is in fact the mode of GeS_2 at 421 cm^{-1}, but shifts because of the bad resolution) appears in $Sn(Pb)GeS_3$ at 432 (428) cm^{-1} and it is also caused by vibration of atoms of ($GeS_2S^{2-}_{2/2}$) chains. The last two modes at 442 and 455 cm^{-1} could, as we have already stated, be ascribed to vibrations of the edge-sharing GeS_4

tetrahedra. It is interesting that the mode of GeS$_4$ at 389 cm^{-1} has a corresponding mode neither in Sn(Pb)GeS$_3$, nor in Ge$_2$S$_6$ molecules. Probably, this mode originates from a vibration of structure, composed of atoms of several different tetrahedra (16-membered rings, Fig. 1). Other modes in this spectral region are of very low intensity and occur, due to the complex coupling of GeS$_4$ tetrahedra in GeS$_2$, as companion modes of tetrahedral vibrations.

In Fig. 4a the nonpolarized reflectivity spectra of GeS$_2$ is shown[1,18]. All *IR* modes in Sn(Pb)GeS$_3$, noticed in Fig. 4b, are also present in GeS$_2$, (Fig. 4a). For other infrared-active modes in GeS$_2$ we cannot perform an analysis similar to that one for Raman modes because the infrared spectra of the Ge$_2$S$_6$ molecule are unknown. However, due to the particular symmetry of the crystal lattice of GeS$_2$, each of the Raman modes has a corresponding infrared pair[1], so everything that will be further said for Raman modes relates to infrared modes as well.

It is especially difficult to analyse a bond bending spectral region since the localisation of bound bending modes, due to disagreement in literature data, is not reliable. In a free GeS_4^- ion, it has been determined calculatively that bond bending modes are at 205 and 170 cm^{-1}, while in B$_2$GeS$_4$, Sr$_2$GeS$_4$ and Pb$_2$GeS$_4$ they are at 254 and 202, 258 and 206, and at 237 and 199, respectively. Referring back to the Raman and infrared spectra of Sn(Pb)GeS$_3$ (Fig. 3); Ge$_2$S$_6$ (Fig. 5) and of GeS$_2$[1], we can choose a big number of candidates for bond bending modes. In the Raman spectra of SnGeS$_3$, the modes at 163, 182, 193, 223, 237 and 255 cm^{-1} represent candidates for bond bending modes. In PbGeS$_3$ modes at 162 cm^{-1} and 239 cm^{-1} also can be clasified as bond bending modes because they greatly surpass the other modes in intensity. In Ge$_2$S$_6$ the modes of the strongest intensity in this region are at 147 and 191 cm^{-1}. In GeS$_2$, due to complexity of the crystal structure, the number of candidates for bond bending modes increases. As we could not determine with certainty the localization of the bond bending modes, only those regions in which these modes appeared were pointed out in Table 1.

The modes which appear under 150 cm^{-1} probably originate from the vibration of the structures composed of atoms of several corner-connected or edge-sharing tetrahedra. Besides these modes, interlayer modes (rigid-layer modes) were established at 28, 39 and 44 cm^{-1} [1].

The Raman and infrared spectra of amorphous GeS$_2$ (a-GeS$_2$) have been presented by a few authors[6–9]. In these papers the experimental spectra are in accordance (Tab. 1) but interpretations of the presented spectra differ. The Raman spectra of a-GeS$_2$[6] is also given in Fig. 5. Lucovsky et al.[6,7] describe modes at 342 cm^{-1} and 375 cm^{-1} as the A_1 and F_2 modes of the GeS$_4$ molecule. They assume that the mode at 432 cm^{-1} appears due to intermolecular coupling due to the three-dimensional nature of a-GeS$_2$. Arai et al.[8] are of the opinion that the observed modes in the Raman spectra of a-GeS$_2$ results from vibration of atoms of the GeS$_4$ tetrahedra, connected in the same way as in the crystalline GeS$_2$. Applying the already given analysis of vibrational properties of the cristalline GeS$_2$ on the vibrational properties of a-GeS$_2$, we can support the assertion given in Ref. *8*, claiming that a dominant role in the vibrational properties of a-GeS$_2$ have vibrations of edge sharing and corner-connected tetrahedra.

The Raman mode of the strongest intensity in a-GeS$_2$ is at 342 cm^{-1}. Since the shifting of the ν_1 (A_1) mode of the GeS$_4$ tetrahedra (386 cm^{-1}) towards shorter wave number is bigger at coupling of the GeS$_4$ tetrahedra via common edge (350 cm^{-1}) than via common corner (370 cm^{-1}), we may assume that the Raman mode of the strongest intensity in a-GeS$_2$ results from the vibrations of the structure built of atoms of the edge-sharing GeS$_4$ tetrahedra. The modes of a-GeS$_2$ at 367 and 432 cm^{-1} (strongly expressed in Sn(Pb)GeS$_3$, too), result from vibrations of the strucure built of atoms of the corner-connected GeS$_4$ tetrahedra.

According to that we come to a conclusion that in a-GeS$_2$ the atoms distribute in a way similar to that one in the single crystal GeS$_2$, i. e. in the GeS$_4$ tetrahedra, connected either via common edge, or common corner.

3.2. *Vibrational properties of GeSe$_2$*

We shall not be able to analyse the vibrational properties of GeSe$_2$ using the same procedure as with GeS$_2$, because vibrational properties of either isolated or in different ways coupled GeSe$_4$ tetrahedra are not known so far. So we shall perform our analysis of the vibrational properties of GeSe$_2$ on base of the conclusions derived for vibrational properties of the isostructural GeS$_2$. The Raman and infrared spectra of GeSe$_2$, as well as an appropriate analysis of vibrational properties of GeSe$_2$ on ground of its layer-structure, were given in our previous papers[1,19,20]. The (XY) component at 300 K, and (XX) component at 4.2 K of the Raman tensor of GeSe$_2$[1] are given in Fig. 7. As it can be seen in Fig. 7, the two spectral regions are distinctly noticable: the bond stretching between 190 and 330 cm^{-1} and bond bending under 150 cm^{-1}. We shall first consider the bond stretching region. A mode of the strongest intensity is at 212 cm^{-1}. Analogously to what has been stated for the strongest intensity mode in GeS$_2$, it can be assumed that the mode of GeSe$_2$ at 212 cm^{-1}, results from vibrations of the corner-connected GeSe$_4$ tetrahedra. Owing to its intensity, this mode masks

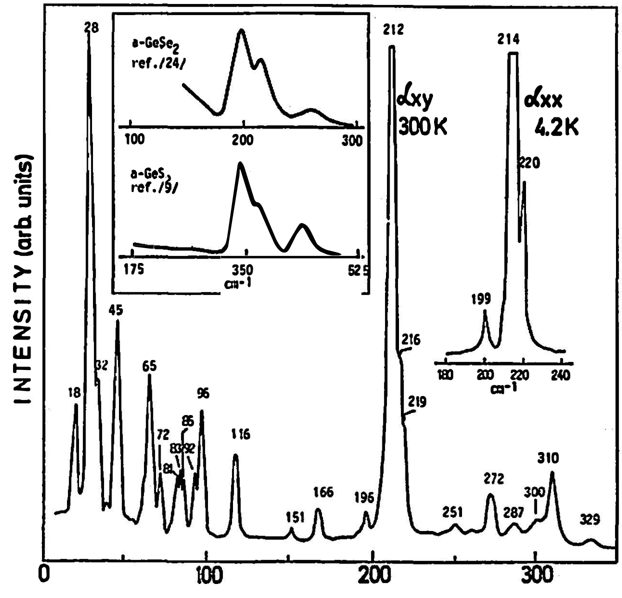

Fig. 7. Raman spectra of crystalline and amorphous GeSe$_2$.

the modes in its surroundings. For that reason it is very difficult to detect the modes at 216 and 219 cm^{-1}, as shown Fig. 7. Existence of a mode quite close to the mode at 212 cm^{-1} is even more noticeable from the (XX) component determined at 4.2 K, and it is also given in Fig. 7. Referring to what has been already said for GeS$_2$, a consequential statement relating the modes of GeSe$_2$ at 196, 212, 216 and 219 cm^{-1} could be given. The Raman mode of GeSe$_2$ at 196 cm^{-1} is analogical to the mode of GeS$_2$ at 250 cm^{-1} and can be said that this mode originates from vibration of structure which is built by coupling of GeSe$_4$ tetrahedra both via common corner and via common edge.

The mode of GeSe$_2$ at 219 cm^{-1} (220 cm^{-1} at 4.2 K) is analogical to the mode of GeS$_2$ at 389 cm^{-1}, and it results from vibration of the structure built of atoms of several tetrahedra (probably 16-membered rings). The modes of GeS$_2$ between 250 and 340 cm^{-1} probably result, like in GeS$_2$, from the ν_3 (F_2) mode of either corner-connected or edge-sharing GeSe$_4$ tetrahedra.

Analysis of the bond bending region of GeSe$_2$ is very complicated for the same reasons valid for GeS$_2$. Besides, no data concerning BB modes of GeSe$_4$, except for the case of a-GeSe$_2$[25], are available in the literature.

Vibrational properties of amorphous GeSe$_2$ have been studied by the authors[9,21–25]. The Raman spectra of amorphous GeS$_2$ and GeSe$_2$ are depicted in an insert of Fig. 7, and the frequencies of the Raman modes of amorphous and single crystal GeSe$_2$ are given in Tab. 2. Various models for explanation of

TABLE 2

	Amorphous — GeSe$_2$				Single crystal	
Ref.	9	24	25	23	Raman[1]	IR
ν_1 (R)					220	
					216	
	219	198	212	217	212	
	201		198	197	203	
					196	
ν_2 (R)					85	
					80	
	—	80	82	72	72	
		(IR)			61	
					55	
ν_3 (R, IR)					329	331
						320
					310	313
						304
	254	255	304	263	300	296
					288	282
					272	272
					261	260
					251	256
ν_4 (R, IR)					117	118
					103	104
	—	100		104	96	96
					92	

Phonon frequencies (cm^{-1}) of single crystal and amorphous GeSe$_2$.

vibrational properties of a-$GeSe_2$ have been suggested[9,21-25]. The most often opinion was that the observed modes of a-$GeSe_2$ originate from tetrahedral vibrations of free $GeSe_4$ molecule. The greatest difficulty arising in this matter was how to explain the existence of two modes at 198 and 213 cm^{-1} as the ν_1 modes of $GeSe_4$ tetrahedra. Quite recently[25], the modes at 198 and 212 cm^{-1} have been classified as modes resulting from vibrations of the corner-connected and edge-sharing $GeSe_4$ tetrahedra, respectively. Referring to what has been said for the vibrational properties of a-GeS_2 for the modes of a-$GeSe_2$ at 198, 212 and 255 cm^{-1}, the following applies: the mode at 198 cm^{-1} is analogical to the mode at 342 cm^{-1} of a-GeS_2 and it results from atom vibrations of the edge-sharing tetrahedra. The modes at 212 and 255 cm^{-1} result from vibrations of the corner-connected $GeSe_4$ tetrahedra.

It was determined in single crystal GeS_2 and $GeSe_2$ that the frequency ratio of the strongest intensity Raman modes (ν_1 modes) is: $\nu_1 (GeS_2)/\nu_1 (GeSe_2) = 1.75$[1]. The same ratio can also appear with the modes in a-$GeS_2(Se)_2$. Since this ratio has been determined for the A_1 modes, and as it applies the modes in a-$GeS_2(Se)_2$, it can be said that all modes in the BS region of Raman spectra of a-$GeS(Se)_2$ result from A_1 modes of the coupled $GeSe_4$ tetrahedra (either via a common edge or a common corner).

By analysis of vibrational properties of GeS_2 it was shown that the mode at 432 cm^{-1} is an A_1 mode of the corner-connected GeS_4 tetrahedra. In $GeSe_2$ too an analogical mode will be obtained if we divide 432 cm^{-1} by 1.75, thus getting the mode at 251 cm^{-1}. Raman spectra of a-GeS_2 and a-$GeSe_2$ are depicted in the insert of Fig. 7 one under another. On purpose to confirm the analogy between these spectra, the axis of wave numbers for the case of a-$GeSe_2$ was enlarged for the factor 1.75.

In the end we can emphasize that since the vibrational properties of a-$GeSe_2$ are similar to those of single crystal $GeSe_2$, that means that also the structure of a-$GeSe_2$ is similar to the structure of the single crystal $GeSe_2$.

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RAZMATRANJE VIBRACIONIH OSOBINA GERMANIJUM DIHALKOGENIDA NA BAZI VIBRACIONIH OSOBINA GeX_4 ($X = S, Se$) TETRAEDARA

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Vibracione osobine GeS_2 i $GeSe_2$ proučavane su na bazi osobina njihove kristalne strukture (izgrađivački elementi kod GeX_2 su GeX_4 tetrahedri koji se međusobno povezuju preko zajedničke ivice ili zajedničkog roglja). Analizirani su Raman i infracrveni spektri izolovanog GeS_4 tetraedra, monokristalnih jedinjenja $SnGeS_3$ i $PbGeS_3$ u kojima su GeS_4 tetraedri spojeni preko zajedničkog roglja, zatim Raman spektri Ge_2S_6 molekula koji je izgrađen iz dva GeS_4 tetraedra spojena preko zajedničke ivice i Raman i infracrveni spektri *a*- i *c*-$GeS(Se)_2$. Utvrđeno je da molekularne vibracije na različite načine spregnutih GeX_4 tetraedra ne samo što su prisutne i kod GeS_2 i $GeSe_2$, već u vibracionim osobinama germanijum dihalkogenida igraju dominantnu ulogu.