

SOME REGULARITIES OF RAMAN ACTIVE MODES
IN $A^{II}B_2^{III}C_4^{VI}$ COMPOUNDS

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On the bases of experimental and theoretical results of the study of the lattice dynamics, and also data from literature, regularities in the dependences of optical phonons frequencies on the masses of atoms in the $A^{II}B_2^{III}C_4^{VI}$ compounds are established.

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1. INTRODUCTION

Semiconducting compounds of the group $A^{II}B_2^{III}C_4^{VI}$ (A-Zn, Cd; B-Ga; C-S, Se), are thiogalates and crystallize into a tetragonal structure with a space group S_4^2 ($I\bar{4}$) [1]. This group of thiogalates is characterized by the presence of an ordered cation vacancy, which distinguishes them from crystal chemical and isoelectronic analogs with the structure of chalcopyrite and sphalerite, as a result of which the compounds of this group are also called defective chalcopyrite (DC). Compounds $A^{II}B_2^{III}C_4^{VI}$ (A-Zn, Cd; B-In, Ga; C-S, Se, Te) are promising in connection with the possibility of their use in semiconductor instrumentation [2].

2. RESULTS AND DISCUSSION

As it is known, there are 7 atoms in the unit cell of defective chalcopyrites of the $A^{II}B_2^{III}C_4^{VI}$ group. Therefore, the vibrational spectrum consists of 21 modes and is described at the center of the Brillouin zone (at $q=0$) by the following irreducible representations [3]:

$$\Gamma = 3A + 6B + 6E \tag{1}$$

All E symmetry modes are doubly degenerated, one B mode and one E mode are acoustic. All optical

modes (3A, 5B and 5E) are active in Raman spectra (RS). In the infrared absorption (IR) spectra, 5B symmetry modes are active, allowed in polarization parallel to the tetragonal C axis, and 5 doubly degenerated E symmetry modes. B and E modes are polar, while A modes are non-polar. Type A fully symmetrical vibrations are associated with displacements of the anionic sublattice atoms along the x, y, and z crystallographic axes, while the cationic sublattice atoms do not participate in vibrations. B type vibrations are associated with displacements of atoms in the cationic sublattice relative to the anionic sublattice along the tetragonal c axis (along the z axis). The doubly degenerated E_x and E_y modes are associated with the displacements of the atoms of the cationic sublattice along the x and y crystallographic axes, respectively [4].

Since the vibrations of the three A (1) symmetry modes are associated only with the displacements of the anionic atoms S, Se, and Te, it should be expected that in compounds of defective chalcopyrites of the $A^{II}B_2^{III}C_4^{VI}$ group containing the same anion atoms (for example, CdGa₂S₄, ZnGa₂S₄, HgGa₂S₄ or CdGa₂Se₄, ZnGa₂Se₄, HgGa₂Se₄), the corresponding frequencies of the A_1 , A_2 , and A_3 modes are differ little. Indeed, as can be seen from Table 1, the frequencies of the A_1 , A_2 , and A_3 modes in CdGa₂S₄, ZnGa₂S₄, HgGa₂S₄ compounds and in CdGa₂Se₄, ZnGa₂Se₄, and HgGa₂Se₄ compounds are very close in magnitude.

Table 1.

Frequencies of the A_1 , A_2 and A_3 modes in the $A^{II}B_2^{III}C_4^{VI}$ group compounds

Modes	CdGa ₂ S ₄ ref.[5]	ZnGa ₂ S ₄ ref.[3]	HgGa ₂ S ₄ ref.[6]	CdGa ₂ Se ₄ ref.[7]	ZnGa ₂ Se ₄ ref.[7]	HgGa ₂ Se ₄ ref.[8]
A_1	219	230	220	140	143	139
A_2	310	320	300	185	180	183
A_3	359	367	358	207	209	206

Already in early studies on the frequencies of Raman active modes in defective chalcopyrites [3, 9], it was noted that the frequencies of polar (E, B) and nonpolar (A) modes can be approximated by the following simple relationship:

$$\omega^2 = \frac{f}{M} \tag{2}$$

here f - force constants of interatomic interaction, M - masses of atoms. This relation has a greatly simplified form, but correctly reflects the characteristic

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regularities of frequencies for isostructural crystals, for example, compounds of the $A_2^{VI}B_3^{VI}$ group [10]. If we assume that the lowest-frequency mode A_1 in defective chalcopyrites is due to in-phase displacements of anion atoms, then in relation (2) we can take the mass $M=4m$, where m is the mass of the anion. Figure 1 shows the dependence of the experimentally determined frequencies of the A_1 mode of the $A^{II}B_2^{III}C_4^{VI}$ compounds on the value of $(4m)^{-1/2}$. As it can be seen from the fig.1, a satisfactory linear dependence (2) of the frequencies of the A_1 mode on the values of $(M)^{-1/2}$ is observed.

Similar conclusions can be drawn for the polar E and B modes. In the $A^{II}B_2^{III}C_4^{VI}$ compounds, the lowest

frequency E modes are most likely due to in-phase displacements of atoms of A cations (Zn, Cd, Hg) and C anions (S, Se, Te). In this case, in (2) in the approximation of a linear chain, we can assume $M=m_A+m_C$, where m_A is the mass of the cation, m_C is the mass of the anion, as was done in [9].

Table 2 and figure 2 show the dependence of the experimentally determined frequencies of the lowest frequency transverse E_{TO} modes of the $A^{II}B_2^{III}C_4^{VI}$ compounds on the value of $(m_A+m_C)^{-1/2}$. As it can be seen from the figure, in this case, the linear dependence (2) of the frequencies ν of the lowest frequency transverse E_{TO} modes on the values of $(M)^{-1/2}$ is also well observed.

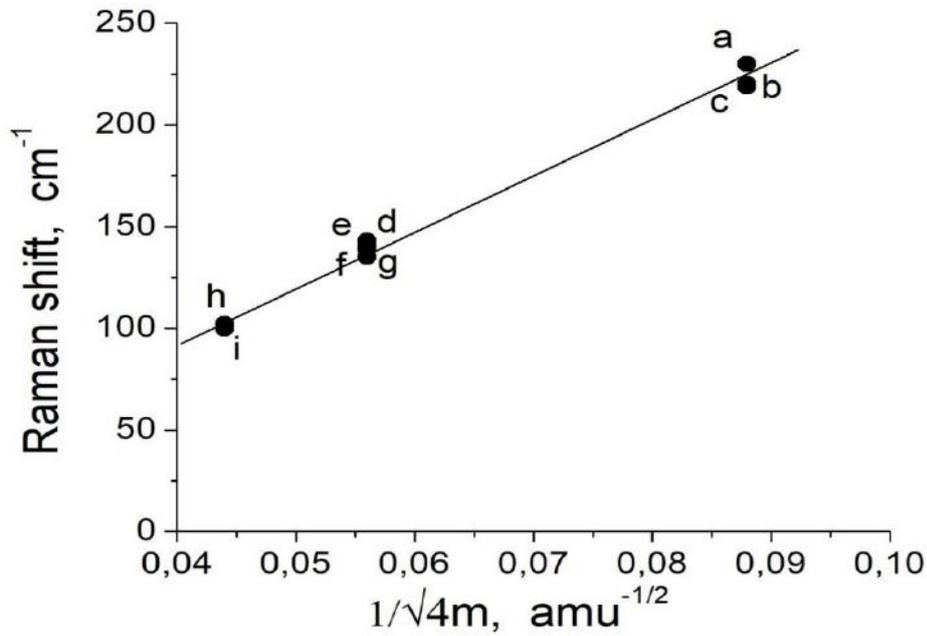


Fig. 1. Dependence of the experimentally determined frequencies of the A_1 mode of crystals $ZnGa_2S_4$ (a), $HgGa_2S_4$ (b), $CdGa_2S_4$ (c), $ZnGa_2Se_4$ (d), $CdGa_2Se_4$ (e), $HgGa_2Se_4$ (f), $ZnIn_2Se_4$ (g), $CdGa_2Te_4$ (h), $CdIn_2Te_4$ (i) on the value $(4m)^{-1/2}$.

Table 2.
Frequencies (cm^{-1}) of the lowest-frequency transverse E_{TO} modes and $(m_A+m_C)^{-1/2}$ (in $amu^{-1/2}$) values of the $A^{II}B_2^{III}C_4^{VI}$ group compounds.

	HgGa ₂ Se ₄ ref.[8]	HgGa ₂ S ₄ ref.[6]	CdGa ₂ Se ₄ ref.[3]	ZnGa ₂ Se ₄ ref.[9]	CdGa ₂ S ₄ ref.[3]	ZnGa ₂ S ₄ ref.[3]
Frequencies	51	61	68	84	86	108
$(m_A+m_C)^{-1/2}$	0.060	0.066	0.072	0.085	0.083	0.104

Table 3.
Frequencies (cm^{-1}) of highest-frequency longitudinal B_{LO} modes and $\mu^{-1/2}$ (in $amu^{-1/2}$) values of the $A^{II}B_2^{III}C_4^{VI}$ compounds

	CdGa ₂ Te ₄ ref.[5]	CdGa ₂ Se ₄ ref.[5]	ZnGa ₂ Se ₄ ref.[7]	CdGa ₂ S ₄ ref.[5]	ZnGa ₂ S ₄ ref.[7]
Freq.	234	275	285	389	396
$\mu^{-1/2}$	0.126	0.144	0.157	0.198	0.207

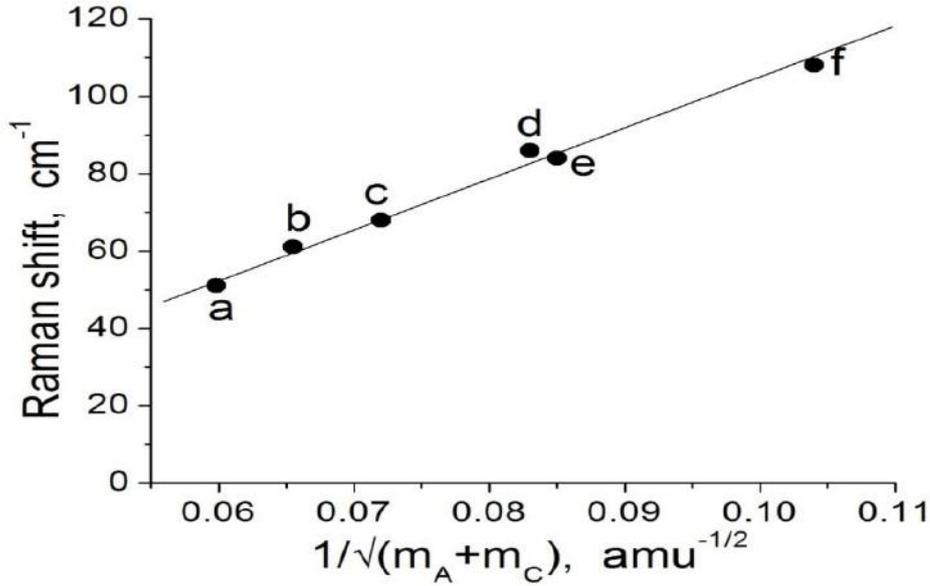


Fig. 2. Dependence of experimentally determined frequencies of the lowest frequency transverse E_{TO} modes of HgGa₂Se₄ (a), HgGa₂S₄ (b), CdGa₂Se₄ (c), ZnGa₂Se₄ (d), CdGa₂S₄ (e), ZnGa₂S₄ (f) crystals on the value $(m_A + m_C)^{-1/2}$.

In the $A^{II}B_2^{III}C_4^{VI}$ compounds, the highest-frequency longitudinal B_{LO} modes are probably due to antiphase displacements of A cation atoms (Zn, Cd, Hg) and C anions (S, Se, Te). In this case, the reduced mass μ is used. In [3], for calculating the reduced mass μ of high-frequency E and B symmetry modes of defective chalcopyrites $A^{II}B_2^{III}C_4^{VI}$, it is proposed to use the relation:

$$\frac{4}{\mu} = \frac{2}{m_A} + \frac{1}{m_B} + \frac{4}{m_C} \quad (3)$$

Table 3 and figure 3 show the dependence of the experimentally determined frequencies of the highest-frequency longitudinal B_{LO} modes of the $A^{II}B_2^{III}C_4^{VI}$

compounds on the value of the reduced mass μ calculated according to (3).

CONCLUSION

On the basis of our own data and data from the literature on the frequencies of optical phonons, linear dependences of the frequencies of Raman-active phonons on the masses of atoms of the $A^{II}B_2^{III}C_4^{VI}$ group compounds were established.

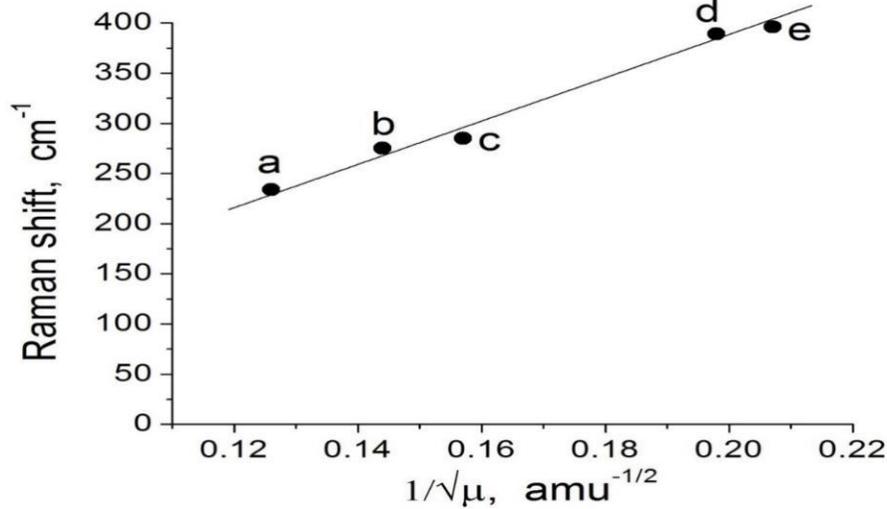


Fig. 3. Dependence of the experimentally determined frequencies of the highest-frequency longitudinal B_{LO} modes of CdGa₂Te₄ (a), CdGa₂Se₄ (b), ZnGa₂Se₄ (c), CdGa₂S₄ (d), ZnGa₂S₄ (e) crystals on the value of $\mu^{-1/2}$.

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