INVESTIGATION OF ANHARMONICITY OF NORMAL VIBRATIONAL MODES IN [Sb$_2$S$_3$]$_2$ CLUSTER

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Theoretical investigation of the vibrational spectrum based on a chain model of the cluster with two Sb$_2$S$_3$ molecules in a cell is presented. For this purpose, symmetric and normal coordinates along the z (**c**) axis have been formed. The dependence of total energy $E(\Delta z)$ upon normal coordinates has been defined for four infrared and five Raman modes. The anharmonicity of these modes has been evaluated by calculating a ratio of quasi-harmonic $\widetilde{\omega}$ and harmonic frequencies ω_0.

1. Introduction

Infrared (IR) vibrational spectrum of Sb$_2$S$_3$ type crystals has been investigated experimentally using the Fourier spectrometer in [1, 2]. It was found that the reflectivity spectrum for polarization parallel to z (**c**) axis (**E**$\|$**c**) has four large intense and five small peaks. To explain the nature of these peaks, symmetrical coordinates of normal vibrational modes, four IR of A_u and five Raman of B_g symmetry, are defined.

2. Crystallochemical structure of Sb$_2$S$_3$ crystals

Antimony trisulphide Sb$_2$S$_3$ (stibnite), as a representative of the sulphides of low symmetry, is thought to be a semiconductor with strong chemical bonds. The crystal is formed from the infinite chains [Sb$_2$S$_3$]$_\infty$ along the z (**c**) axis, with shorter Sb–S and longer Sb–S covalent bonds.

A pair of single chains is coupled by longer bonds in a ribbon [(Sb$_2$S$_3$)$_\infty$]$_2$. The ribbons are weakly bound by longer Sb–S bonds, that constitute layers perpendicular to ac-plane. The unique property of this crystal is that atoms of the weakly bound chains are in nonequivalent positions. Therefore, Sb$_2$S$_3$ has a crystal lattice with complicated chemical binding.

3. Symmetrical coordinates of the molecule cluster [Sb$_2$S$_3$]$_2$ in a unit cell

A double chain is a certain cluster model formed of two molecules [Sb$_2$S$_3$]$_2$ in the unit cell. It contains ten atoms: Sb1, Sb2, Sb1A, Sb2A, S1, S2, S3, S1A, S2 A, S3A (Fig. 1). The space group of this chain is C_{2h}^2 with symmetry types A_g, B_g, A_u, B_u [5]. The total energy of the normal vibrational modes can be calculated using the cluster model. For this purpose we obtain symmetry coordinates of the molecular cluster [Sb$_2$S$_3$]$_2$ for all nine normal vibrational modes as shown in Table 1.

As mentioned above, the Sb$_2$S$_3$ crystal is composed of chains intercoupled by weak interaction. A single chain is formed of many simplified unit cells. One of such cells contains ten atoms. Symmetry operations of this unit cell belong to the space group C_{2h}^2 for the paraelectric phase of the crystal. They are $S_1 = E/(0, 0, 0)$, $S_2 = C_2(z)/(0, 0, 1/2)$, $S_3 = I/(0, 0, 0)$, $S_4 = \sigma z/(0, 0, 1/2)$. Operations S_1 and S_2 belong to the space group C_2^2 for the ferroelectric phase of the crystal.

Symmetry coordinates, associated with space groups C_{2h}^2 and C_2^2, are

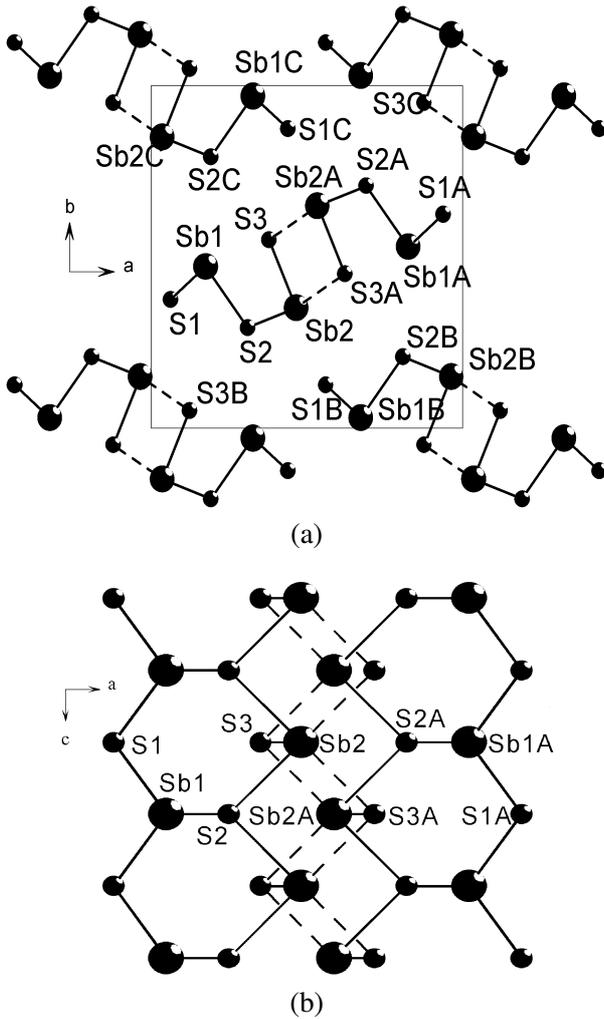$$\chi_j = N_j \sum_i c_{ji}^{\alpha} q_i. \qquad (1)$$

(a)

(b)

Fig. 1. Projection of the Sb_2S_3 crystal structure on (a) ab-plane and (b) ac-plane. The letters A, B, C show Sb and S atoms which are in the equivalent positions similarly as atoms having the same numbers: Sb1, Sb1A, Sb1B, Sb1C, Sb2, Sb2A, Sb2B, Sb2C, S1, S1A, S1B, S1C, S2, S2A, S2B, S2C, S3, S3A, S3B, S3C.

They are derived from the properties of irreducible representations $\Gamma_\alpha = A_u, A_g, B_u, B_g$ of group C_{2h}^2 and $\Gamma_\alpha = A, B$ of group C_2^2. Combinations of atomic displacements $q_i = z_i$ typically possess symmetry A_u and B_g, and the combinations of $q_i = x_i, y_i$ have symmetry A_g and B_u for C_{2h}^2. The coefficients are $c_{ji}^\alpha = 0, \pm 1/2, \pm 1$ (see Table 1).

Hence, the normal vibrations in the Sb_2S_3 chain of the paraelectric phase along the z (**c**) axis can be described by A_u and B_g symmetry coordinates, whereas the vibrations in the direction of x and y axes are associated with A_g and B_u symmetry coordinates. The modes $\chi_7(B_u)$ and $\chi_{13}(B_u)$ correspond to acoustic vibrations, while the remaining ones to the optical vibrations of the Sb_2S_3 chain.
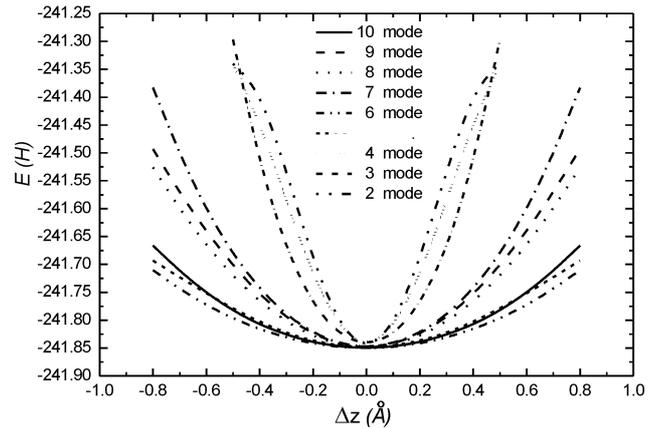

Fig. 2. The dependence of the total energy E of normal coordinates Δz along the z (**c**) axis. 1 H (Hartree) = 27.21 eV.

4. Investigation of normal modes in the vibrational spectrum of Sb_2S_3

The total energy of a crystal is the sum of kinetic and potential energy:

$$E = E_K + E_{ee} + E_{ne} + E_{nn}. \tag{2}$$

Here E_K is the kinetic energy of electrons, E_{ee} is the interelectron interaction energy, E_{ne} is the electron–nuclear interaction energy, and E_{nn} is the internuclear interaction energy.

They were evaluated for each position of nuclei using the unrestricted Hartree–Fock method (UHF) employing the computer program GAMESS described in [2].

The displacement Δz of atoms from their equilibrium position z_0 is

$$\Delta z = z - z_0. \tag{3}$$

The energy E of the $[Sb_2S_3]_2$ cluster was approximated by the fourth-degree polynomial

$$E = E_0 + b(\Delta z)^2 + c(\Delta z)^4. \tag{4}$$

Therefore, E is a function of normal coordinates (Fig. 2). The ratio of coefficients c/b given in Table 2 is the anharmonicity characteristic.

5. Evaluation of quasi-harmonic frequency of normal vibrational modes

The ratio of frequencies $\widetilde{\omega}/\omega_0$, like c/b, is an anharmonicity characteristic of normal modes.

The harmonic part of Eq. (4) determines the frequency of normal modes: $\omega_0^2 = b/M_r$, where M_r is the reduced mass of a mode. The anharmonic part of

Table 1. Symmetry coordinates of the $[Sb_2S_3]_2$ cluster.

Γ_α	F_S	N	Sb1	Sb2	Sb1A	Sb2A	S1	S2	S3	S1A	S2A	S3A	Mode
A_u	χ_1	$\frac{1}{\sqrt{10}}$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	$+1$	1
(C_{2h}^2)	χ_2	$\frac{1}{\sqrt{8}}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	-1	$+1$	-1	-1	$+1$	2
	χ_3	$\frac{1}{\sqrt{8}}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+1$	-1	-1	$+1$	-1	-1	3
	χ_4	$\frac{1}{\sqrt{8}}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$+\frac{1}{2}$	-1	$+1$	-1	-1	$+1$	-1	4
	χ_5	$\frac{1}{2}$	$+1$	-1	$+1$	-1	0	0	0	0	0	0	5
B_g	χ_6	$\frac{1}{\sqrt{10}}$	$+1$	$+1$	-1	-1	$+1$	$+1$	$+1$	-1	-1	-1	6
(C_{2h}^2)	χ_7	$\frac{1}{\sqrt{8}}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	-1	$+1$	$+1$	$+1$	-1	7
	χ_8	$\frac{1}{\sqrt{8}}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	$+1$	-1	-1	-1	$+1$	$+1$	8
	χ_9	$\frac{1}{\sqrt{8}}$	$+\frac{1}{2}$	$+\frac{1}{2}$	$-\frac{1}{2}$	$-\frac{1}{2}$	-1	$+1$	-1	$+1$	-1	$+1$	9
	χ_{10}	$\frac{1}{2}$	$+1$	-1	-1	$+1$	0	0	0	0	0	0	10

Table 2. Coefficients b, c and the ratios c/b and $\widetilde{\omega}/\omega_0$.

Mode	Activity	b (H/Å^2)	c (H/Å^4)	c/b (Å^{-2})	$\widetilde{\omega}/\omega_0$
10	R	0.25662	0.04909	0.19129	0.847973
9	R	0.60694	-0.08003	-0.13186	0.691603
8	R	0.51889	-0.02126	-0.04097	0.682178
7	R	0.63004	0.15303	0.24289	0.922911
6	R	0.20776	0.01767	0.08505	0.701430
5	IR	0.30488	-0.09445	-0.30979	0.952573
4	IR	3.43235	-5.58637	-1.62756	0.945749
3	IR	1.73525	-1.83695	-1.05861	0.992792
2	IR	4.46771	-9.61104	-2.15122	0.880855

Eq. (4) changes this frequency. The quasi-harmonic frequency can be evaluated by the following transformation [4]:

$$E = \left(b + c\langle(\Delta z)^2\rangle\right)(\Delta z)^2$$

$$= M_r(\Delta z)^2. \qquad (5)$$

The average $\langle(\Delta z)^2\rangle$ may by calculated by using the formula [4]

$$\langle(\Delta z)^2\rangle = \frac{\hbar}{2\omega_0}\cot\left[\frac{1}{2}\frac{\hbar\omega_0}{k_B T}\right], \qquad (6)$$

where T is temperature and k_B is the Boltzmann constant. So one obtains the transformed frequencies using the expression

$$\widetilde{\omega}^2 = \omega_0^2 + \frac{c}{\omega_0 M_r}\cot\left[\frac{1}{2}\frac{\hbar\omega_0}{k_B T}\right]. \qquad (7)$$

It is seen from Table 2, where values of $\widetilde{\omega}/\omega_0$ are given, that a considerable change in the frequency owing to the mode anharmonicity takes place.

6. Conclusion

Theoretical investigation using harmonical approach of the vibrational spectrum of the $[Sb_2S_3]_2$ cluster along the z (**c**) axis shows only four A_u modes active in IR. However, while investigating the experimental spectrum of reflectivity, we have observed nine peaks, wich may be caused by nine active vibrational IR modes. In this paper we demonstrate that all nine normal modes along the z (**c**) axis are anharmonic, and the ratio of frequencies $\widetilde{\omega}/\omega_0$ is found to be within the range from 0.682 to 0.993 for separate modes.

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[Sb$_2$S$_3$]$_2$ KLASTERIO VIBRACINIŲ NORMALIŲJŲ MODŲ TYRIMAS

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Santrauka

Teoriniam Sb$_2$S$_3$ kristalo vibracinio spektro tyrimui panaudotas vienos grandinėlės, sudarytos iš atomų [Sb1, Sb2, S1, S2, S3]$_2$ klasterio, modelis. Ištirtos tokio klasterio ortonormalinės simetrinės ir normalinės koordinatės z (**c**) ašies kryptimi. Apskaičiuotos keturių IR ir penkių Ramano modų energijos E verčių priklausomybės nuo normalinių koordinačių z (**c**) ašies kryptimi. Įvertintas šių modų anharmoniškumas, apskaičiuojant kvaziharmoninio $\widetilde{\omega}$ ir harmoninio ω_0 dažnių santykį.