PHASE TRANSITION AND CORRELATION BETWEEN PHONON SPECTRA OF α-SnS AND β-SnS

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Analysis of the phase transition from α to β modification orthorhombic crystals SnS carry out. Correlation between normal modes of lattice vibrations both modification SnS and SnSe is given.

1. Introduction

It was shown by authors [1] at high temperature β modification of SnS and SnSe crystals has the symmetry $Cmcm(D_{2h}^{17})$. As distinct from low-temperature α modification, there is one layer in unit cell base-centered orthorhombic crystal lattice of β–SnS.

Phase transition is due to displacement of cation and anions from the equilibrium positions in the direction of crystallographic axis "a".

Although of different coordination number (nearest neighbors) of atoms in the structures α-SnS and β-SnS, the main interaction between neighbors atoms, denoted by letters A, B, C, D and E by authors [1], is preserved.

Phase transition from α- to β-modification is a second order, with negligible thermal effect near critical point. There is a very small change in unit cell dimension over a narrow range of temperature near critical point.

In the following paper [2] authors touched upon the problem of mechanism of $\alpha \rightarrow \beta$ phase transition. It was shown that the transition is responsibled by totally symmetric irreducible representation (irrep) of the group of the zone-boundary wave-vector $\vec{k}\left(\frac{2\pi}{a},0,0\right)$. The number of symmetry elements is reduced twice as a consequence of the change of the translational symmetry of lattice from base-centered to simple orthorhombic lattice.

In present work the phase transition $\beta \rightarrow \alpha$ for SnS is analysed in detail and correlation between normal modes of lattice vibration both modification is established.

2. The group-theoretical analysis of $\beta \rightarrow \alpha$ phase transition for SnS.

The factor-group of the crystal space group $Cmcm$ upon the translation group contained the following elements:

- $(E/0)$-identity, $(C_{2x}/0)$, (C_{2y}/τ), (C_{2z}/τ),-π rotation about "a", "b" and "c" axis, correspondingly,
- $(J/0)$-inversion, $(JC_{2x}/0)$, (JC_{2y}/τ), (JC_{2z}/τ)-mirror plane perpendicular to "a", "b" and "c" axis, correspondingly.

Here $\vec{k}(0, b/2, 0)$-nonprimitive translation. Primitive translation vectors are:

$$\vec{T}_1(a/2,0, c/2),\ \vec{T}_2(0, b,0),\ \vec{T}_3(-a/2,0, c/2)$$

It is convenient to carry out group-theoretical analysis of the second order phase transition upon the general scheme suggested by Ljubarskij [3].

For realize this it is necessary to have the tables of matrix of irrep of the group of the wave vectors of Brillouin zone of the high symmetrically phase.

In our case the problem is simplified because character table for the factor group of the point $X\left(\frac{2\pi}{a},0,0\right)$ has the same form as for point group D_{2h}. Yet it is important to remind that the character of translation T_1 or T_3 equal to 1.

According to [3] second order phase transition is possible if:

1) antisymmetrized quadratic power of the irrep do not contain the vector rep, and

2) symmetrized cubic power of the irrep do not contain the identity rep.

The first requirement is fulfilled for all one-dimensional reps of the group of wave vector X. Second requirement is fulfilled only for identity rep but we must take the element $C_{2x}C_{2z}$ and JC_{2x}, JC_{2z} accompanied together with primitive translation T_1 or T_3. As for as the character of this translation is negative, we have deal with c irrep B_{2g} , rather but not the identity irrep Ag of the point group D_{2h}.

In conclusion we obtain the set of elements that is characterized for the space group $Pnma$- D_{2h}^{16}:

$$(E/0),(C_{2x}/(a/2,0,c/2)),(C_{2y}/(0,b/2,0)),(C_{2z}/(a/2,b/2,c/2)),$$
$$(JC_{2x}/(a/2,0,c/2)),(JC_{2y}/(0,b/2,0)),(JC_{2z}/(a/2,b/2,c/2)),(J/0)$$

with primitive translations:

$$\vec{T}_1(a,0,0),\ \vec{T}_2(0, b,0),\ \vec{T}_3(0,0, c)$$

3. Symmetrized coordinates of lattice vibration and phase transition

Now we consider in what way the $\beta \rightarrow \alpha$ phase transition takes place. In β -modification of SnS cations and anions are in following positions:

$$1.(0,1/4,z), \quad 2.(0.-1/4,-z) \qquad (1)$$

in units of "a", "b" and "c", correspondingly.

Group theoretical analysis of the symmetry of normal modes bring to result that decomposition of vibrational rep in symmetrically points $\Gamma(0,0,0)$ and $X\left(\frac{2\pi}{a},0,0\right)$ (or equivalent point $Z\left(0,0,\frac{2\pi}{c}\right)$) has the form

$$\Gamma_{vibr} = 2\left(A_g + B_{1g}^{(yz)} + B_{2g}^{(xz)} + B_{1u}^{(x)} + B_{2u}^{(y)} + B_{3u}^{(z)}\right) \qquad (2)$$

Here we used common spectroscopic symbols for irreps (see, for example, [4]), in parenthesis it is shown that the transformation properties of bases functions of irreps.

By standard projection operator method we construct the bases of irreps through lattice displacements.

For cations and anions we have:

$$\begin{aligned} e_{A_g} &= \frac{1}{\sqrt{2}}(z_1 - z_2), \; e_{B_{3u}} = \frac{1}{\sqrt{2}}(z_1 + z_2) \\ e_{B_{1g}} &= \frac{1}{\sqrt{2}}(y_1 - y_2), \; e_{B_{2u}} = \frac{1}{\sqrt{2}}(y_1 + y_2) \\ e_{B_{2g}} &= \frac{1}{\sqrt{2}}(x_1 - x_2), \; e_{B_{1u}} = \frac{1}{\sqrt{2}}(x_1 + x_2) \end{aligned} \qquad (3)$$

where x, y, z-Cartesian coordinates.

Now we can see in what way the symmetry change occurs. Indeed, in vibration B_{2g} atoms number 1 and 2 moves in opposite directions along "a" axis. Atoms 1' and 2', which are translationally equivalent atoms from the neighbor unit cell (by T_1 or T_3) shifts in opposite direction from owns translationally equivalent atoms 1 and 2. So, from the structure:

$$\begin{aligned} &1.(0,1/4,z), \; 2.(0,-1/4,-z) \\ &1\;.(1/2,1/2,1/2+z), \; 2\;.(1/2,-1/4,1/2-z) \end{aligned} \qquad (4)$$

owing to displacements in B_{2g} mode we get:

$$\begin{aligned} &1.(x,1/4,z) \; 2.(-x,-1/4,-z) \\ &3.(1/2-x,1/4,1/4+z) \; 4.(1/2+x,-1/4,1/2-z) \end{aligned} \qquad (5)$$

that is the structure of α-modification of SnS.

Evidently both cations and anions shifts from equilibrium positions, but as stated in [1] that anions shift are negligible as compared with cations shift which is equal 0,12a.

4. The relations between normal modes of α- and β-SnS

After reducing the Brilloin zone of base-centered orthorhombic lattice of β-SnS, irreps of the symmetry point $X\left(\frac{2\pi}{a},0,0\right)$ turns out in centre of Brillouin zone simple orthorhombic lattice α-SnS. Taking into account that the part of symmetry elements are accompanied by translation T_1 and T_3 we obtain the following comparability relations for irreps α-SnS and β-SnS.

$$\begin{aligned} A_g^{\alpha}(\Gamma) &\rightarrow A_g^{\beta}(\Gamma) \text{ or } B_{2g}^{\beta}(X) \\ B_{1g}^{\alpha}(\Gamma) &\rightarrow B_{1g}^{\beta}(\Gamma) \text{ or } B_{3g}^{\beta}(X) \\ B_{1u}^{\alpha}(\Gamma) &\rightarrow B_{2u}^{\beta}(\Gamma) \text{ or } B_{2g}^{\beta}(X) \\ B_{2u}^{\alpha}(\Gamma) &\rightarrow B_{2u}^{\beta}(\Gamma) \text{ or } A_u^{\beta}(X) \end{aligned} \qquad (6)$$

As we know the decomposition of vibrational rep α-SnS in symmetry point $\Gamma(0,0,0)$ has a form:

$$\Gamma_{vib}^{\alpha} = 4A_g + 4B_{2g} + 2B_{1g} + 2B_{3g} + 2A_u + 4B_{1u} + 4B_{3u} + 2B_{2u} \qquad (7)$$

Using fig. (4) of the work [5] and the scheme of enlargement zone the phonon dispersion of hypothetical crystal β-GeS can be found as a first approximation (see fig.).

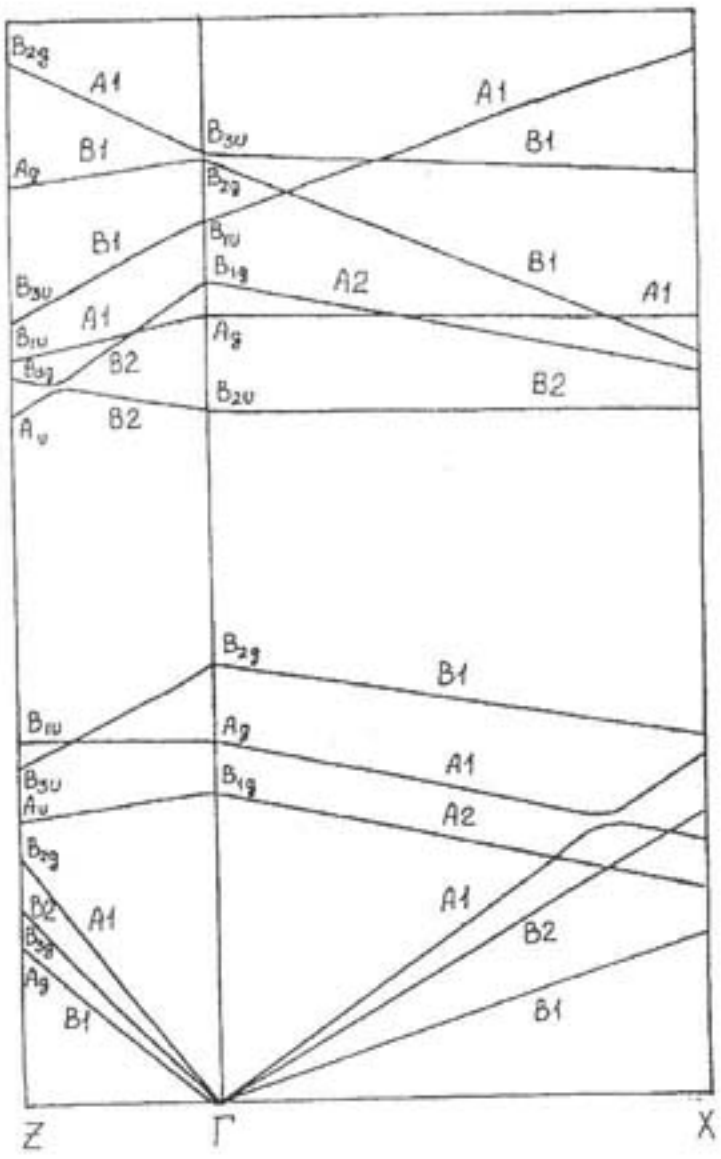

Fig. Phonon spectrum of α-GeS in enlargement Brilloin zone.

Hence, we see that all modes B_{3g}^{α}, small optical modes B_{1u}^{α}, B_{3u}^{α}, A_g^{α} and B_{2g}^{α} as well the largest mode A_g^{α} and B_{2g}^{α} occurs in point $X\left(\frac{2\pi}{a},0,0\right)$. Applying this rule for α-SnS and β-SnSe we find the phonon spectra of β-SnS and β-SnSe (table). The value of vibrational frequency for α-modification we get from [4].

Table 1

The frequency of vibrational modes of β-SnS and α-SnSe obtained by comparability relations from vibrational modes of α-modifications (in cm^{-1})*

Modes	Symmetry point	β-SnS	β-SnSe
A_g^1	Γ/X	192/290	130/-
A_g^2	Γ/X	95/70	71/-
B_{2g}^1	Γ/X	160/218	-/151
B_{2g}^2	Γ/X	85/40	-/33
B_{1g}^1	Γ/X	208/164	133/108
B_{1g}^2	Γ/X	70/49	57/37
B_{1u}^1	Γ/X	222/188	150/130
B_{1u}^2	Γ/X	0/68	0/56
B_{2u}^1	Γ/X	145/-	96/-
B_{2u}^2	Γ/X	0/-	0/-
B_{3u}^1	Γ/X	220/178	142/123
B_{3u}^2	Γ/X	0/99	0/80
B_{2g}^1			
B_{2g}^2			

*) The frequencies of Au modes for α-SnS and β-SnSe and B_{2g} modes for α-SnSe unknown

It stands to reason we suppose that the force constants for interatomic interactions singhtly changes as we goes from α-SnS to β-SnS.

For checking this we construct the model of lattice dynamic of β-SnS taking into account radial and transverse components of the force constants for all types A, B, C, D and E interactions. From this model the relations are followed

$$\begin{aligned} Tr\ B_{2g}(\Gamma)+Tr\ B_{1u}(\Gamma)&=Tr\ B_{2g}(X)+Tr\ B_{1u}(X)\\ Tr\ A_g(\Gamma)+Tr\ B_{3u}(\Gamma)&=Tr\ A_g(X)+Tr\ B_{3u}(X)\\ Tr\ B_{1g}(\Gamma)+Tr\ B_{2u}(\Gamma)&=Tr\ B_{1g}(X)+Tr\ B_{2u}(X) \end{aligned} \qquad (8)$$

where $Tr\ B_{2g}(\Gamma)$ is mean the trace of matrix for vibration mode B_{2g} in symmetry point Γ and so on. The relations (8) that are reminiscent of Brounts rule [6] are fulfilled with an accuracy 10 %.

5. Conclusion

The analysis of β-α phase transition for orthorhombic crystals SnS and SnSe carry out. Correlation between vibrational modes of both modification are obtained.

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FAZA KEÇİDLƏRİ VƏ α-SnS İLƏ β-SnS KRİSTALLARININ FONON SPEKTRLƏRİ ARASINDA ƏLAQƏ

SnS tipli ortorombik kristallarda $\beta \rightarrow \alpha$ faza keçidi təhlil edilmişdir. Hər iki fazanın fonon spektrləri arasında əlaqə tapılmışdır.

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ФАЗОВЫЕ ПЕРЕХОДЫ И КОРРЕЛЯЦИЯ МЕЖДУ ФОНОННЫМИ СПЕКТРАМИ α-SnS И β-SnS

Проведен анализ фазового перехода $\beta \rightarrow \alpha$ для орторомбических кристаллов типа SnS. Найдены корреляции между частотами решеточных колебаний обеих модификаций SnS и SnSe.

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