Model Calculations of the Phonon Dispersion Curves for Cu_6AsS_5I Superionic Crystal

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Abstract—**The crystal structure of Cu_6AsS_5I crystal have been analyzed and described by using the superspace symmetry concept. The program operating under the Maple environment and suitable for theoretically calculating the phonon spectra of Cu_6AsS_5I crystal has been developed. The eigenvalues of the generalized dynamic matrix have been found as well as the dispersion dependencies have been built for the directions Γ – X – M – R – Γ – M of the Brillouin zone.**

Index Terms—**argyrodites, crystal structure, protocrystal, phonon spectrum, Maple environment.**

I. Introduction

It is convenient to describe and study complex crystal structures of a cubic crystal system within the model of natural superlattices. The structure of the relevant in recent years compounds with superionic conductivity is investigated and their phonon spectra are calculated. The class of such compounds includes crystals of the argyrodite family. The crystal of Cu_6AsS_5I compound is a bright representative of this family [1]. It is well-known that argyrodite crystals characterize by high ionic conductivity which determined the possibilities of their application in new devices for solid state ionics [2]. Due to the optical studies two low-temperature phase transitions (PTs) in Cu_6AsS_5I crystal were observed: a first-order PT at T_I=(153±1) K and a second-order PT at T_{II}=260–280 K [3]. The spectrometric investigation shown that an excitonic absorption band at low temperatures and high absorption levels is revealed and is fully smeared out at the first-order PT temperature. At $T>T_I$ the excitonic band is fully smeared out, absorption edge has an exponential shape and a characteristic Urbach bundle is observed. The complex impedance, complex electrical conductivity and complex dielectric permittivity of Cu6AsS5I crystal was studied in the temperature interval 291–400 K and frequency range 1 Hz – 3 GHz [4].

The main goal of the present work was to carry out the theoretical calculation of the phonon spectra for Cu_6AsS_5I within the superspace symmetry concept.

II. Material And Methods

The superlattice idea presupposes a composition (combination) of different types of Bravais lattices for describing the different kind atom orbits in complex crystals [5]. The use of the "sublattice" term in the supra-symmetry concept involves the use of the modulation vectors and functions [5, 6].

The study of the crystal structure of high temperature phase Cu_6AsS_5I compound is systematized in the paper [1], in which the lattice parameters, atomic coordinates, etc are provided.

Atom	Population	Position (in calc.)	x (in calc.)	y (in calc.)	z (in calc.)
Cu(1)	24g	0.658 (1)	0.0242 (0)	0.25 (1/4)	0.25 (1/4)
Cu(2)	48h	0.184 (0)	0.0192 (0)	0.200 (3/16)	0.200 (3/16)
S(1)	16e	1 (1)	0.373 (3/8)	0.373 (3/8)	0.373 (3/8)
S(2)	4d	1 (1)	0.75 (3/4)	0.75 (3/4)	0.75 (3/4)
I	4a	1 (1)	0 (0)	0 (o)	0 (0)
As	4b	1 (1)	0 (0)	0.5 (1/2)	0 (0)

The performed analysis of the Cu_6AsS_5I crystal structure indicates a significant change in population densities of several crystallographic positions, therefore, model studies can use the framework for Cu_6PS_5Br isostructural crystal that was proposed in previous Refs. [7, 8]. Such a crystal structure, according to the Ref. [6], can be described as occupation-modulated face-centered cubic (FCC) superlattice with underlying vectors: (4a,4a,0), (4a,0,4a), (0,4a,4a). For this

purpose the (3+3)-dimensional space with bases of direct and reciprocal space in the metric of body-centered lattice (BCC) ((-a,a,a), (a,-a,a), (a,a,-a)) will be used.

III. Results and discussion

Full set of 32 possible atom positions covers 10 orbits, and the plurality of 32 modulation vectors is divided into 10 stars. This allows to write the system of equations to determine the mass modulation function amplitudes $\boldsymbol{\rho}_i(\boldsymbol{q}_i, \boldsymbol{b}^*)$.

In this case, within the supra-symmetry concept, the dispersion curves of the phonon spectra are defined as solutions of matrix equations provided that the determinant is equal to zero [6]:

$$\left| D_{\alpha\beta}(\mathbf{k}+\mathbf{q}_i) - \omega^2 \delta_{\alpha\beta}\delta_{ij} - \omega^2 \rho_{(i-j)}\delta_{\alpha\beta} \right| = 0 \quad (1)$$

where α, β – x, y, z, $\boldsymbol{k}$ – the wave vector, $\boldsymbol{q}_i$ – modulation vectors, $\boldsymbol{\rho}_i(\boldsymbol{q}_i, \boldsymbol{b}^*)$ - the mass modulation function amplitudes specified for the modulation vectors $\boldsymbol{q}_i - \boldsymbol{q}_j$, and $D_{\alpha\beta}(\boldsymbol{k}+\boldsymbol{q}_i)$ - the dynamic matrixes of monatomic BCC crystal, defined in $\boldsymbol{k}+\boldsymbol{q}_i$ point of Brillouin zone (i = 1, 2, ..., 32) according to [9]:

$$D_{\alpha\beta}(\mathbf{k}+\mathbf{q}_i) = \sum_{(n\neq 0)} \alpha_n \frac{n_\alpha n_\beta}{n^2}(1 - e^{i(\mathbf{k}+\mathbf{q}_i)\mathbf{n}}) \quad (2)$$

where α_n - force constant between 0i n neighbor , n_α, n_β – projections of vector $\boldsymbol{n}$ on the axis α, β.

Calculation of phonon spectra was performed in the "Maple" software environment . The calculated energy dependences of the phonon dispersion branches of the Cu_6AsS_5I crystal along the Γ – X – M – R – Γ – M lines are shown in (Fig.1.). The software allows selecting phonon dependencies that are connected with particular composite structural formations (Fig.2.), by means of vanishing some mass characteristics.

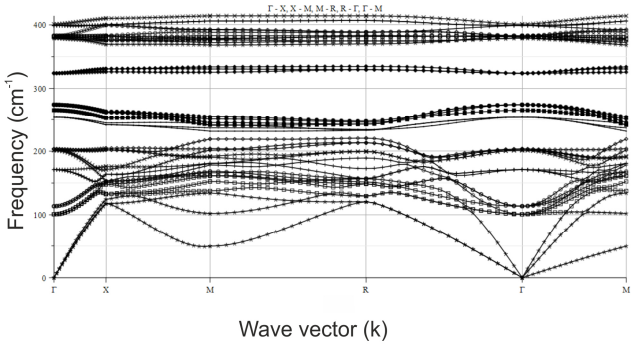

Fig.1. Phonon spectra of the crystal are calculated at choosing the force constants being equal to: α_1=108 N/m, α_2=3.4 N/m, α_3=0.8 N/m, α_4=0.6 N/m, α_5=0.5 N/m, α_6=0.6 N/m.

From the analysis of the results quite a satisfactory agreement of the calculated values and experimental data for the G-spot (A mode type (389 cm-1 experiment, 401 cm-1 calculation), three times degenerated F type (274 cm-1 experiment and 274см-1 and 254 cm-1 calculation) is seen. It is clearly seen that the fluctuations band that is connected with the Cu atoms is realized in wide energy band 400 – 400 cm-1 and is characterized by a complex behavior of mutually intersecting dispersion branches that may facilitate the activity of Cu atoms in superionic conductivity.

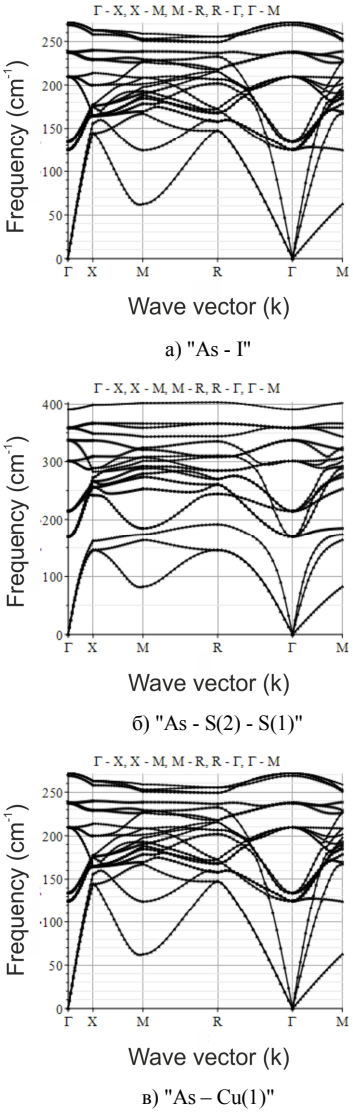

Fig.2. The dispersion dependence for crystal subsystems with the corresponding vanished mass characteristics and fixed for the Cu_6AsS_5I crystal values of the force constants (α_1=108 N/m, α_2=3.4 N/m, α_3=0.8 N/m, α_4=0.6 N/m, α_5=0.5 N/m, α_6=0.6 N/m)
(а) – $M_{S(1)}$=0, $M_{S(2)}$=0, M_{Cu}=0, б) – M_{Cu}=0, в) - $M_{S(1)}$=0, $M_{S(2)}$=0)

Taking into account the Cu(2) atoms population in 48h (0.184) position requires significant increasing the number of sets of positions and modulation vectors, since it is necessary to consider the the sublattice multiplication equal to 512, which corresponds to the transition from the FCC basic structure ((a,a,0), (a,0,a), (0,a,a)) to FCC superlattice real structure with basis ((8a,8a.0), (8a,0,8a), (0,8a,8a)).

IV. CONCLUSIONS

Comparison of the dispersion curves calculated here for the Cu_6PS_5Br crystal with the earlier data of the Raman scattering and the first-principle calculations shows that the results are in good agreement with each other. Additionally, the correlations of the values of the low-frequency optical branches F_2, F_1 with the values α_2=2.4 N/m for the system "P – S(2)" can be clearly observed.

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