Semiconductor Physics, Quantum Electronics & Optoelectronics, 2018. V. 21, N 2. P. 134-138.

Semiconductor physics

Model research of phonon spectra of argyrodites family

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Abstract. Cu_6PS_5Br compound belongs to the large family of complex chalcohalides crystallizing in the argyrodite structures. The main peculiarity of the copper-containing argyrodites is high ionic conductivity of Cu^+ ions, which makes it possible to use as the functional electronic materials. In the present study, the crystal structure of Cu_6PS_5Br argyrodite have been analyzed and described using the superspace symmetry concept. The program operating under the Maple environment and suitable for theoretically calculating the phonon spectra of the Cu_6PS_5Br argyrodite crystal has been developed. Zone structures have been calculated and presented for a series of model Cu_6PS_5Br phases. The eigenvalues of the generalized dynamic matrix have been found as well as the dispersion dependences have been built for the directions Γ–X–M–R–Γ–M of the Brillouin zone.

Keywords: argyrodites, crystal structure, protocrystal, phonon spectrum, Maple environment.

doi: https://doi.org/10.15407/spqeo21.02.134
PACS 61.66.Fn

Manuscript received 12.04.18; revised version received 05.05.18; accepted for publication 27.06.18; published online 03.07.18.

1. Introduction

In the recent years, investigations of superionic conductivity in solids have evolved into a broad interdisciplinary branch of science that encompasses physics, chemistry, materials science and instrumentation. Today, superionic conductors (SICs) are widely used in manufacturing rechargeable batteries, fuel cells, gas sensors, ion-selective electrodes, high-temperature heating elements, integrators and other devices [1-4]. One of the most prominent representatives of SICs is crystalline Cu_6PS_5Br compound that belongs to the structural family of argyrodites; and the main goal of this work was to investigate and model the phonon spectra inherent to the above mentioned compound.

2. Material and methods

The crystal structure of the high-temperature Cu_6PS_5Br phase was first reported in the papers [5 - 7], in which the lattice parameters, atomic coordinates, atomic displacement parameters (temperature factors) and site occupancy factors were given along with the interatomic distances and bond angles.

Analysis of the crystal structures typical for the argyrodite family has revealed high variability in the number of crystallographic positions and in the occupancy factors [8]. In our previous paper [9], for *ab initio* calculations of the phonon frequencies in the Γ point of the Brillouin zone of the Cu_6PS_5Br crystal, we have chosen the crystal structure model with the coordinates and occupancies presented in Table 1. In this paper, the same model was used for calculations of the dispersion dependences of the phonon spectrum in the Brillouin zone [8].

Such a crystal structure, according to [10], can be described as an occupancy-modulated face-centered cubic (FCC) superlattice with the base vectors (4*a*, 4*a*, 0), (4*a*, 0, 4*a*), and (0, 4*a*, 4*a*). In order to implement the above description, we have used the (3+3)-dimensional space with the bases of the direct and reciprocal space in the metrics of the body-centered cubic (BCC) lattice with the base vectors ((–*a*, *a*, *a*), (*a*, –*a*, *a*), (*a*, *a*, –*a*)) [11]:

Table 1. Atomic positions and occupancies of the model Cu_6PS_5Br crystal structure.

Atom	Coordinates [7]	Occupancies [7]	Coordinates [9]	Occupancies [9]	Coordinates [this paper]	Occupancies [this paper]
Cu(1)	(0.02362, 0.25, 0.25)	0.624	(0.01747, 0.25, 0.25)	1.0	(0.0, 1/4, 1/4)	1.0
Cu(2)	(0.01914, 0.30918, 0.30918)	0.376		0.0		0.0
Br	(0, 0, 0)	0.989	(0, 0, 0)	1.0	(0, 0, 0)	1.0
S(1)	(0.25, 0.25, 0.25)	0.989	(0.25, 0.25, 0.25)	1.0	(1/4, 1/4, 1/4)	1.0
S(2)	(0.62183, 0.62183, 0.62183)	1.0	(0.62183, 0.62183, 0.62183)	1.0	(5/8, 5/8, 5/8)	1.0
P	(0.5, 0.5, 0.5)	1.0	(0.5, 0.5, 0.5)	1.0	(1/2, 1/2, 1/2)	1.0

$$
\begin{aligned}
&a_1 = (-a, a, a, b/4, -b/4, -b/4);\\
&a_2 = (a, -a, a, -b/4, b/4, -b/4);\\
&a_3 = (a, a, -a, -b/4, -b/4, b/4);\\
&a_4 = (0, 0, 0, 0, b, b);\\
&a_5 = (0, 0, 0, b, 0, b);\\
&a_6 = (0, 0, 0, b, b, 0);\\
&a_1^* = (0, \pi/a, \pi/a, 0, 0, 0);\\
&a_2^* = (\pi/a, 0, \pi/a, 0, 0, 0);\\
&a_3^* = (\pi/a, \pi/a, 0, 0, 0, 0);\\
&a_4^* = (-\pi/4a, \pi/4a, \pi/4a, -\pi/b, \pi/b, \pi/b);\\
&a_5^* = (\pi/4a, -\pi/4a, \pi/4a, \pi/b, -\pi/b, \pi/b);\\
&a_6^* = (\pi/4a, \pi/4a, -\pi/4a, \pi/b, \pi/b, -\pi/b).
\end{aligned}
\qquad (1)
$$

3. Results and discussion

Using the bases (1), the relevant sets of (i) the superlattice positions and (ii) the modulation vectors $\mathbf{q}_i$ were generated (Table 2). A complete set of 32 possible positions of atoms covers 10 orbits, while the set of 32 modulation vectors is separated into 10 stars. It allows to write a system of equations for determining the amplitudes of the mass modulation function $\rho_i(\mathbf{q}_i, \mathbf{b}^*)$. For the three-dimensional projection of the structure:

$$M(n,0) = \sum_{l=1}^{10} \rho_l(\mathbf{q}_l, 0) \sum_{m=1}^{\text{by star}} e^{i(\mathbf{q}_{l_m} n)}, \qquad (2)$$

Table 2. Arrays of positions gathered in orbits and of modulation vectors gathered in stars.

Atom	No. of orbit (position)	Atomic positions gathered in orbits	No. of star (modul. vector)	Modulation vectors gathered in stars
Br	1 (1)	[0, 0, 0]	1 (1)	[0, 0, 0]
P	2 (2)	[4*a*, 0, 0]	2 (2)	[π/*a*, 0, 0]
S(1)	3 (3)	[2*a*, 2*a*, 2*a*]	3 (3)	[π/2*a*, π/2*a*, π/2*a*]
	4 (4)	[–2*a*, –2*a*, –2*a*]	4 (4)	[–π/2*a*, –π/2*a*, –π/2*a*]
	5 (5–10)	[2*a*, 0, 0]; [0, 2*a*, 0]; [0, 0, 2*a*]; [–2*a*, 0, 0]; [0, –2*a*, 0]; [0, 0, –2*a*];	5 (5–10)	[π/2*a*, 0, 0]; [0, π/2*a*, 0]; [0, 0, π/2*a*]; [–π/2*a*, 0, 0]; [0, –π/2*a*, 0]; [0, 0, –π/2*a*]
Cu(1)	6 (11–16)	[2*a*, 2*a*, 0]; [0, 2*a*, 2*a*]; [2*a*, 0, 2*a*]; [–2*a*, 2*a*, 0]; [0, 2*a*, –2*a*]; [–2*a*, 0, 2*a*]	6 (11–16)	[π/2*a*, π/2*a*, 0]; [0, π/2*a*, π/2*a*]; [π/2*a*, 0, π/2*a*]; [–π/2*a*, π/2*a*, 0]; [0, π/2*a*, –π/2*a*]; [–π/2*a*, 0, π/2*a*]
	7 (17–20)	[*a*, *a*, *a*]; [–*a*, –*a*, *a*]; [–*a*, *a*, –*a*]; [*a*, –*a*, –*a*]	7 (17–20)	[π/4*a*, π/4*a*, π/4*a*]; [–π/4*a*, –π/4*a*, π/4*a*]; [–π/4*a*, π/4*a*, –π/4*a*]; [π/4*a*, –π/4*a*, –π/4*a*]
	8 (21–24)	[–*a*, –*a*, –*a*]; [–*a*, *a*, *a*]; [*a*, *a*, –*a*]; [*a*, –*a*, *a*]	8 (21–24)	[–π/4*a*, –π/4*a*, –π/4*a*]; [–π/4*a*, π/4*a*, π/4*a*]; [π/4*a*, π/4*a*, –π/4*a*]; [π/4*a*, –π/4*a*, π/4*a*]
	9 (25–28)	[3*a*, 3*a*, 3*a*]; [–3*a*, –3*a*, 3*a*]; [–3*a*, 3*a*, –3*a*]; [3*a*, –3*a*, –3*a*]	9 (25–28)	[3π/4*a*, 3π/4*a*, 3π/4*a*]; [–3π/4*a*, –3π/4*a*, 3π/4*a*]; [–3π/4*a*, 3π/4*a*, –3π/4*a*]; [3π/4*a*, –3π/4*a*, –3π/4*a*]
S(2)	10(29–32)	[–3*a*, –3*a*, –3*a*]; [–3*a*, 3*a*, 3*a*]; [3*a*, 3*a*, –3*a*]; [3*a*, –3*a*, 3*a*]	10(29–32)	[–3π/4*a*, –3π/4*a*, –3π/4*a*]; [–3π/4*a*, 3π/4*a*, 3π/4*a*]; [3π/4*a*, 3π/4*a*, –3π/4*a*]; [3π/4*a*, –3π/4*a*, 3π/4*a*]

where $M(n, 0)$ is the mass of atom in the n position ($\Delta n = 0$), l defines the number of the star, and m is the number of the vector of the star.

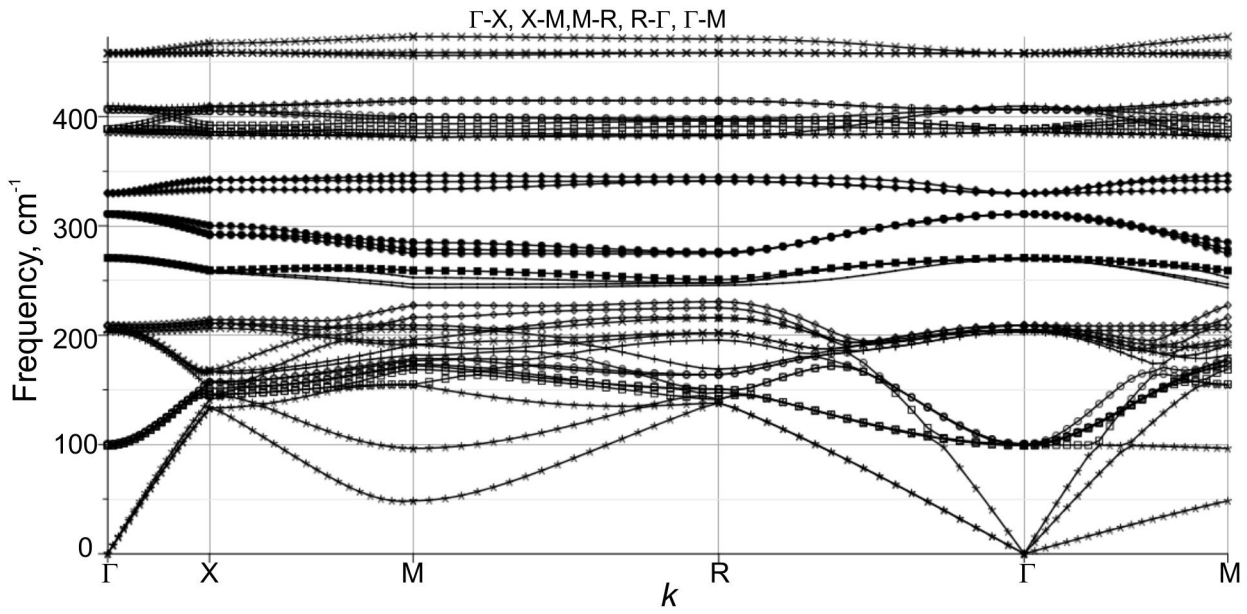

Fig. 1. Phonon spectra of the Cu_6PS_5Br crystal calculated for the selected power constants $\alpha_1 = 114$ N/m, $\alpha_2 = 2.4$ N/m, $\alpha_3 = 0.8$ N/m, $\alpha_4 = 0.6$ N/m, $\alpha_5 = 0.5$ N/m, $\alpha_6 = 0.6$ N/m in Eq. (6).

By solving the above system of equations, one can obtains ρ_i ($\mathbf{q}_i$, $\mathbf{b}^*$):

$$
\begin{aligned}
32\rho_1 &= M_1 + M_2 + M_3 + M_4 + 6M_5 + 6M_6 + \\
&\quad + 4M_7 + 4M_8 + 4M_9 + 4M_{10}\,, \\
32\rho_2 &= M_1 + M_2 + M_3 + M_4 + 6M_5 + 6M_6 - \\
&\quad - 4M_7 - 4M_8 - 4M_9 - 4M_{10}\,, \\
32\rho_3 &= M_1 + M_2 - M_3 - M_4 - 6M_5 + 6M_6 + \\
&\quad + 4iM_7 - 4iM_8 - 4iM_9 + 4iM_{10}\,, \\
32\rho_4 &= M_1 + M_2 - M_3 - M_4 - 6M_5 + 6M_6 - \\
&\quad - 4iM_7 + 4iM_8 + 4iM_9 - 4iM_{10}\,, \\
32\rho_5 &= M_1 + M_2 - M_3 - M_4 + 2M_5 - 2M_6\,, \\
32\rho_6 &= M_1 + M_2 + M_3 + M_4 - 2M_5 - 2M_6\,, \\
32\rho_7 &= M_1 - M_2 - M_3 + iM_4 + \sqrt{2}(1+i)M_7 + \\
&\quad + \sqrt{2}(1-i)M_8 - \sqrt{2}(1-i)M_9 - \sqrt{2}(1+i)M_{10}\,, \\
32\rho_8 &= M_1 - M_2 + M_3 - iM_4 + \sqrt{2}(1-i)M_7 + \\
&\quad + \sqrt{2}(1+i)M_8 - \sqrt{2}(1+i)M_9 - \sqrt{2}(1-i)M_{10}\,, \\
32\rho_9 &= M_1 - M_2 - M_3 + iM_4 - \sqrt{2}(1-i)M_7 - \\
&\quad - \sqrt{2}(1+i)M_8 + \sqrt{2}(1+i)M_9 + \sqrt{2}(1-i)M_{10}\,, \\
32\rho_{10} &= M_1 - M_2 + M_3 - iM_4 - \sqrt{2}(1+i)M_7 - \\
&\quad - \sqrt{2}(1-i)M_8 + \sqrt{2}(1-i)M_9 + \sqrt{2}(1+i)M_{10}\,.
\end{aligned}
\tag{3}
$$

The above-given solution defines a defect-free generalized structure with the chemical formula $VHEFC_6D_6A_4B_4K_4M_4$. In order to obtain the amplitudes of modulation functions for the superionic Cu_6PS_5Br structure, one has to make the following substitutions: $M_1 = M_{Br}$, $M_3 = M_P$, $M_4 = M_{S(1)}$, $M_6 = M_{Cu}$, $M_{10} = M_{S(2)}$, $M_2 = M_5 = M_7 = M_8 = M_9 = 0$. Then, one can obtain:

$$
\begin{aligned}
\rho_1 &= \tfrac{1}{32}\left(M_{Br} + M_P + M_{S(1)} + 6M_{Cu} + 4M_{S(2)}\right), \\
\rho_2 &= \tfrac{1}{32}\left(M_{Br} + M_P + M_{S(1)} + 6M_{Cu} - 4M_{S(2)}\right), \\
\rho_3 &= \tfrac{1}{32}\left(M_{Br} - M_P - M_{S(1)} + 6M_{Cu} + 4iM_{S(2)}\right), \\
\rho_4 &= \tfrac{1}{32}\left(M_{Br} - M_P - M_{S(1)} + 6M_{Cu} - 4iM_{S(2)}\right), \\
\rho_5 &= \tfrac{1}{32}\left(M_{Br} - M_P - M_{S(1)} - 2M_{Cu}\right), \\
\rho_6 &= \tfrac{1}{32}\left(M_{Br} + M_P + M_{S(1)} - 2M_{Cu}\right), \\
\rho_7 &= \tfrac{1}{32}\left(M_{Br} - iM_P + iM_{S(1)} - \sqrt{2}(1+i)M_{S(2)}\right), \\
\rho_8 &= \tfrac{1}{32}\left(M_{Br} + iM_P - iM_{S(1)} - \sqrt{2}(1-i)M_{S(2)}\right), \\
\rho_9 &= \tfrac{1}{32}\left(M_{Br} - iM_P + iM_{S(1)} + \sqrt{2}(1-i)M_{S(2)}\right), \\
\rho_{10} &= \tfrac{1}{32}\left(M_{Br} + iM_P - iM_{S(1)} + \sqrt{2}(1+i)M_{S(2)}\right).
\end{aligned}
\tag{4}
$$

Within the framework of the superspace symmetry concept, the dispersion curves of the phonon spectra of complex crystals are defined as the solutions of the matrix equation under the condition that the determinant is equal to zero [12]:

$$
\left| D_{\alpha\beta}(\mathbf{k} + \mathbf{q}_i) - \omega^2 \delta_{\alpha\beta}\delta_{ij} - \omega^2 \rho_{(i-j)}\delta_{\alpha\beta} \right| = 0\,, \tag{5}
$$

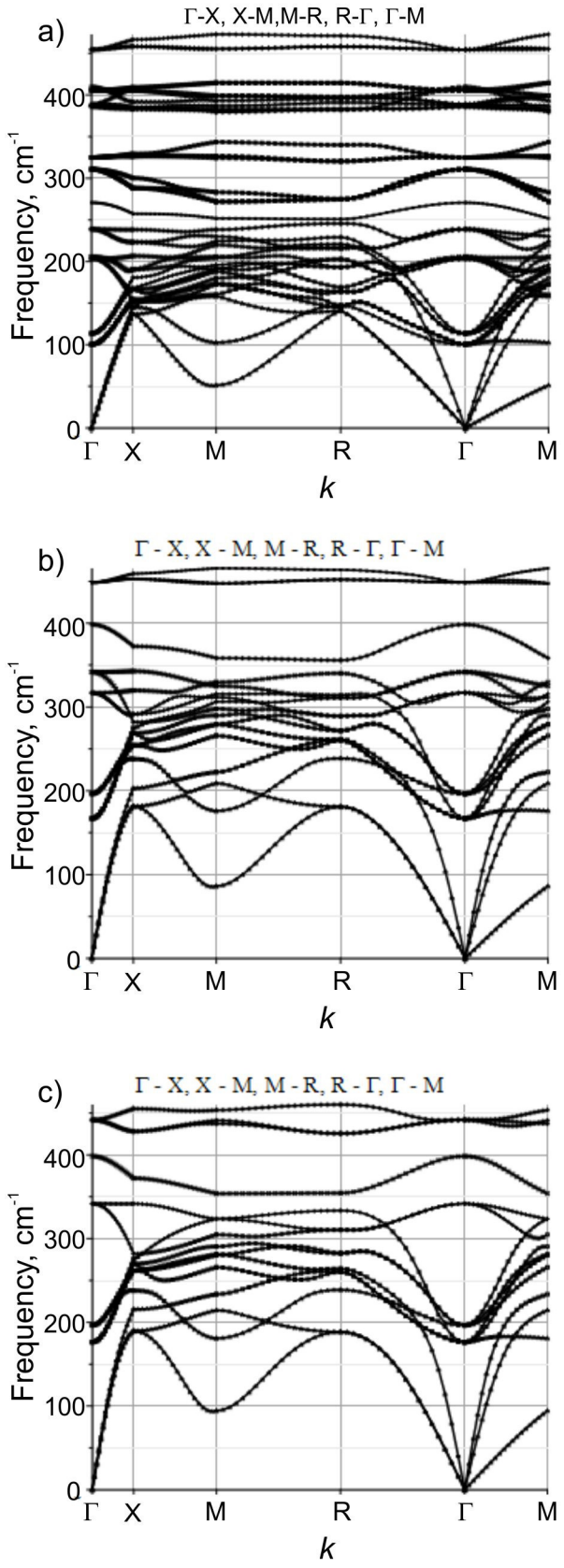

Fig. 2. Dispersion dependences for the crystal systems with the eliminated certain mass characteristics of subsystems and with the selected values of power constants for the Cu_6PS_5Br crystal: (a) $M_{Br} = 0$; (b) $M_{Br} = 0$, $M_{Cu} = 0$; (c) $M_{Br} = 0$, $M_{Cu} = 0$, $M_{S(1)} = 0$.

Table 3. Long-wave frequencies (cm^{-1}) in the cubic Cu_6PS_5Br crystal phase.

Symmetry	Theory [9]	Experiment [9]	Our data
F_2	72.3i (TO); 59i (LO)		99.0
F_1	51.7i (TO); 20i (LO)		100.4
F_2	74.2	74	205.1
F_1	80.8	78	209.1
F_2	109.2		269.7
E	147.6	156	203.2
A	206.0	234	270.7
F_2	211.0	245	310.8
F_1	317.5		329.8
F_2	320.0	316	388.6
E	347.0		386.0
F_2	348.9		406.5
A	415.4	427	409.6
F_2	511.3i (TO); 521i (LO)	547 (TO); 558 (LO)	458.0

where α, β are *x*, *y*, *z*; **k** is the wave vector; $\mathbf{q}_i$ are the modulation vectors; ρ_i ($\mathbf{q}_i$, $\mathbf{b}^*$) – amplitudes of the mass modulation function, which are defined for the modulation vectors $\mathbf{q}_i$, $-\mathbf{q}_i$; $D_{\alpha\beta}(\mathbf{k}+\mathbf{q}_i)$ – the dynamic matrixes of the monatomic BCC crystal, which are defined in the $\mathbf{k}+\mathbf{q}_i$ point of the Brillouin zone (i = 1, 2, ..., 32) as:

$$D_{\alpha\beta}(\mathbf{k}+\mathbf{q}_i) = \sum_{(n\neq 0)} a_n \frac{n_\alpha n_\beta}{n^2}\left(1 - e^{i(\mathbf{k}+\mathbf{q}_i)\mathbf{n}}\right), \qquad (6)$$

where α_n is the power constant between 0 and the n-th neighbor, n_α, n_β are the projections of the vector **n** on the α, β axes.

Calculations of the phonon spectra for the Cu_6PS_5Br crystal have been carried out in the Maple software environment. The calculated dispersion dependences of the phonon branches for the Cu_6PS_5Br crystal (along the lines Γ–X–M–R–Γ–M) are given in Fig. 1. The employed software allows one to distinguish phonon dependences associated with certain compositional-structural moieties (Fig. 2) by eliminating their mass characteristics. The results obtained for the Γ point and their comparison with the literature data are presented in Table 3.

4. 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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