══════ *Semiconductor physics* ══════

Model phonon spectra of Cu_7SiS_5I and Ag_7SiS_5I crystals

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Abstract. In the concept of superspatial symmetry the crystal structure of Cu_7SiS_5I and Ag_7SiS_5I superionic conductors has been analyzed. To calculate the phonon spectra, the model of FCC superlattice ($8a$, $8a$, 0; $8a$, 0, $8a$; 0, $8a$, $8a$) in the metric of protocrystal (a, a, 0; a, 0, a; 0, a, a) has been developed. For the developed model, the general (3+3)-dimensional basis, the array of modulation vectors and mass modulation functions have been presented. The model calculations of phonon spectra dispersion for Cu_7SiS_5I and Ag_7SiS_5I crystals in schemes with various partial occupation of crystallographic orbits by Cu(Ag) atoms have been performed. The dispersion dependences of phonon spectra for Cu_7SiS_5I and Ag_7SiS_5I crystals in the high-symmetric directions of Brillouin zone have been presented. The genesis of phonon branches of vibrational spectra has been analyzed.

Keywords: superionic conductor, phonon spectra, crystal structure, superlattice, protocrystal.

1. Introduction

Numerical modelling of vibrational spectra opens up prospects in terms of forecasting the physical properties of new materials, which is especially important for studying the lattice dynamics of disordered systems with the variations of both structure and chemical composition. Investigations of argyrodites, namely, Cu_7SiS_5I and Ag_7SiS_5I superionic crystals [1-3] that possess the high ionic conductivity, attract interest not only among the researches, but among the specialists in theoretical physics. The attention is caused by the ever-increasing possibilities of their practical application as the solid electrolytes in supercapacitors and accumulator batteries as well as in the fuel cell membranes. It should be noted that for these applications the main attention should be paid to preparation of argyrodites not only in crystalline forms, but in the forms of various types of composites, ceramics and thin films [4-7].

Besides, for the fundamental studies the specific attention is attracted by the crystalline superionic conductors, for which the presence of high-temperature phase with high ionic conductivity is typical. It should be noted that physical and chemical properties of crystalline Cu_7SiS_5I and Ag_7SiS_5I superionic conductors are defined by their crystal structure, the main characteristic of which is the partial occupation of position of the certain crystallographic orbits by atoms of one type [1].

The purpose of this work is to theoretically study lattice dynamics for Cu_7SiS_5I and Ag_7SiS_5I superionic conductors with taking into account the peculiarities of their crystal structure.

2. Material and methods

Sequential inclusion of additional "physical" parameters (colour, phase, charge sign, spin, *etc.*) in symmetry description led to creation of the theory of colour symmetry [8] and the concept of superspatial symmetry [9]. Among the varieties of generalized symmetry, the latter is convenient and obvious in the construction of (3+*d*)-dimensional models for describing complex crystalline formations united by a single metric and scale of the function of the protocrystal carrier [10]. Formation of the (3+*d*)-dimensional metric is based on its higher symmetry
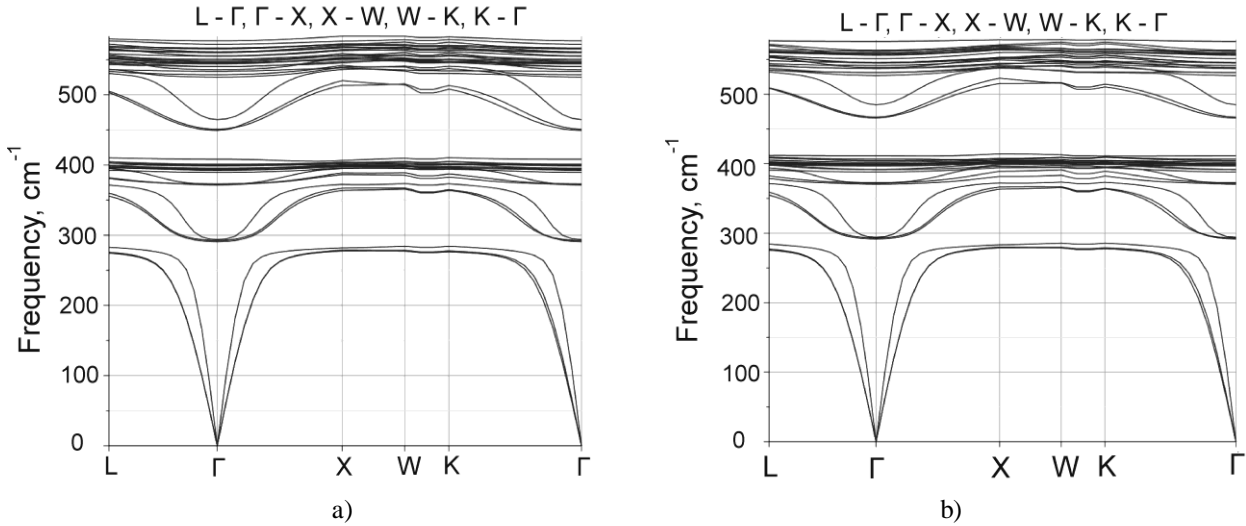
Fig. 1. Model phonon dispersion dependences for Cu$_7$SiS$_5$I crystal, calculated for the high-symmetric directions of the Brillouin zone in different schemes: (a) (5+2) scheme (5 Cu atoms localized in orbit 18 (4a, 4a, 0) and 2 Cu atoms in orbit 10 (3a, 3a, 0)); (b) (6+1) scheme (6 Cu atoms localized in orbit 18 (4a, 4a, 0) and 1 Cu atom in orbit 10 (3a, 3a, 0)) at the selection of equal values of power constants (power constants: = [82.1, 0, 0, 0, 0, 3.1, 2.2, 1.7, 1, 1, 0, 0, 0, 0, 0.7, 0, 1, 5, 0, 0, 0, 2, 0, 0, 10.0, 53, 0.6, 19]).

and is associated with an additional internal "phase" d-dimensional space, which enables to describe complex crystals and systems as natural ($sa \times sa \times sa$)-superlattices.

Compositional peculiarities of complex crystals and systems of solid solutions by the mechanism of filling with different sorts atoms and vacancies of translationally equivalent positions given by the basis of the protocrystal are covered by the concept of superspatial symmetry. Different combinations of protocrystal bases and real crystalline formation together with all possible variants of compositional filling of crystallographic positions can be taken into account. Using the complete set of modulation vectors allows to determine the amplitudes of mass modulation functions and on their basis to generate the generalized dynamic matrix of real physical object as well as mass pertur-bation matrix: the first one is given as a superposition of the dynamic matrix of the protocrystal, defined at different points of the Brillouin zone related by modulation vectors, while the second one is described by amplitudes of mass modulation functions [11, 12].

In the concept of superspatial symmetry, the dispersion curves of the phonon spectrum of crystalline formation are defined as solutions of the matrix equation under the condition of equality to zero of the determinants belonging to the following type:

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

where $D_{\alpha\beta}\left(k+q_i\right)$ are dynamic matrices of the monoatomic protocrystal determined at the points of ZB $(k+q_i)$, $\rho_{(i-j)} = \rho_i\left(q_i, \Delta^* b_{ij}^*\right)$ are the amplitudes of the

mass modulation function specified for the modulation vector $(q_i - q_j)$, k is the wave vector, q_j are the modulation vectors, α, β – coordinates x, y, z. The solution of the matrix equation relatively to $\omega^2(k)$ allows to determine the dispersion dependences of the phonon spectrum, and taking into account the various variants of compositional filling – to monitor their genesis [12].

Dynamic matrices of the protocrystal $D_{\alpha\beta}(k+q_i)$ are determined from the equation:

$$D_{\alpha\beta}\left(k+q_i\right) = \sum_{(n\neq0)} \alpha_n \frac{n_\alpha n_\beta}{n^2}\left(1 - e^{i(k+q_i)n}\right), \quad (2)$$

where α_n is the power constant of the atom interaction in 0 position and n – adjacent atom, n_α, n_β are the projections of the vector n on the axis α, β.

In equidistant approximation to the model, the power characteristic depends only on the distance between atoms, and then interaction of different sort atoms in equidistant positions is the same. This enables to form a dynamic matrix in a quasi-diagonal form. In a non-equidistant approximation, α_n is defined by both the distance between positions and the difference between the physical characteristics of the objects occupying them.

The values of amplitudes of mass characteristics $\rho(q_j)$ are obtained by solving the system of equations with respect to the amplitudes of mass modulation functions $\rho(q_j) = \rho_j$:

$$m\left(r_k\right) = \sum_{j=1}^{s^3} \rho(q)e^{iq_j r_k}, \quad (3)$$

where s is the number of possible positions of atoms in

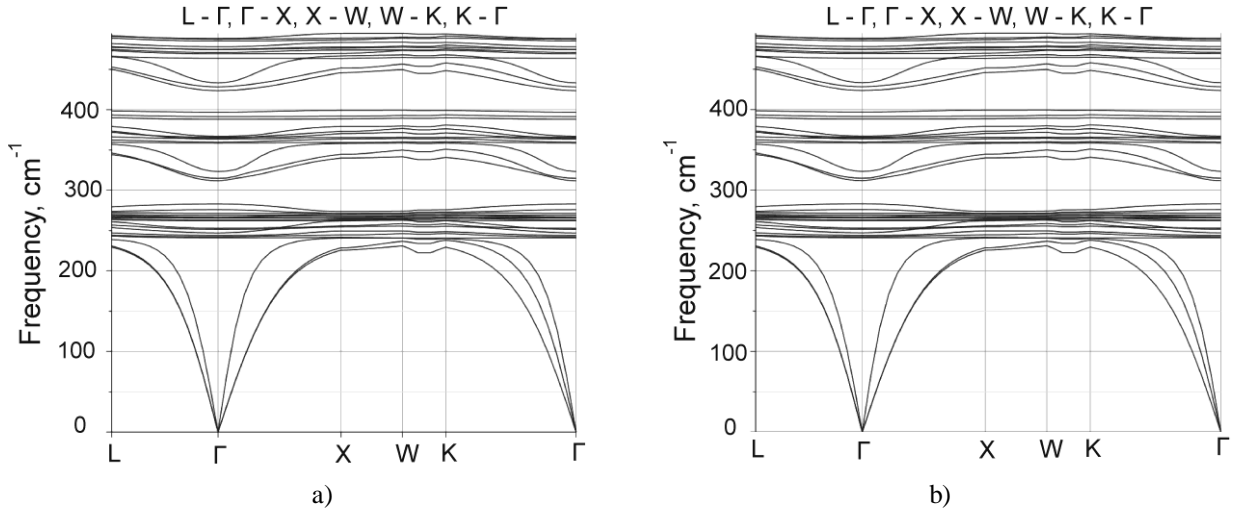*Nebola I.I., Katanytsia A.F., Shteyfan A.Ya. et al. Model phonon spectra of Cu$_7$SiS$_5$I and Ag$_7$SiS$_5$I crystals*

Fig. 2. Model phonon dispersion dependences for Ag_7SiS_5I crystal, calculated for the high-symmetric directions of the Brillouin zone in different schemes: (a) (5+2) scheme (5 Ag atoms localized in orbit 18 (4a, 4a, 0) and 2 Ag atoms in orbit 10 (3a, 3a, 0)); (b) (6+1) scheme (6 Ag atoms localized in orbit 18 (4a, 4a, 0) and 1 Ag atom in orbit 10 (3a, 3a, 0)) at the selection of equal values of power constants (power constants: = [52.1, 0, 0, 0, 0, 0.1e–1, 9, 0.1e–1, 9, 0.1e–1, 0, 0, 0, 0, 1, 0, 1, 5, 0, 0, 0, 2, 0, 0, 0.8e–1, 3, 1, 23.5]).

the superlattice, $m(r_k)$ are mass characteristics in these positions, q_j is an array of modulation vectors, the number of which coincides with the number of positions in the superlattice.

3. Results and discussion

Let us describe some representatives of the family of argyrodite in the concept of superspatial symmetry, based on the model of natural FCC (16a×16a×0)-superlattice, when considering the power field in an equidistant approximation.

Representatives of the argyrodite family belong to the crystalline structures characterized by the partial occupancy of a part of crystallographic orbits by atoms of one sort. The crystalline structure of the argyrodite type Cu_7SiS_5I and Ag_7SiS_5I superionic conductors [1] consists of an anionic frame and the cationic frame typical for crystals of the argyrodite family by filling atoms Cu(Ag) into their positions. In Paterson's images, the peaks specify the occupancy of the following sites: 24–x degenerated position (g), 48–x degenerated position (h), 16–x degenerated position (e) and two of the four 4–x degenerated positions (a), (b), (c) and (d). According to this, the following positions of atoms are chosen: Cu1 (Ag1) to 24 (g), Cu2 (Ag2) to 48 (h), 16 of 20 S to 16 (e) s x = 3/8, and 4 S to 4 (c), I to 4 (a), atoms Si in 4 (b) [12].

When calculating the phonon spectra of Cu_7SiS_5I and Ag_7SiS_5I crystals for the crystal structure description, the model of FCC superlattice (8a, 8a, 0; 8a, 0, 8a; 0, 8a, 8a) in the protocrystal metric (a, a, 0; a, 0, a; 0, a, a) with (3+3)-dimensional basis was chosen:

$$a_1 = \left(a, a, 0, \bar{b}/8, \bar{b}/8, 0\right); \quad a_1^* = \left(\bar{\pi}/a, \pi/a, \pi/a, 0, 0, 0\right);$$

$$a_2 = \left(a, 0, a, \bar{b}/8, \bar{b}/8\right); \quad a_2^* = \left(\pi/a, \bar{\pi}/a, \pi/a, 0, 0, 0\right);$$

$$a_3 = \left(0, a, a, 0, \bar{b}/8, \bar{b}/8\right); \quad a_3^* = \left(\pi/a, \pi/a, \bar{\pi}/a, 0, 0, 0\right);$$

$$a_4 = \left(0, 0, 0, b, b, 0\right); \quad a_4^* = \left(\bar{\pi}/8a, \pi/8a, \pi/8a, \bar{\pi}/b, \pi/b, \pi/b\right);$$

$$a_5 = \left(0, 0, 0, b, 0, b\right); \quad a_5^* = \left(\pi/8a, \bar{\pi}/8a, \pi/8a, \pi/b, \bar{\pi}/b, \pi/b\right);$$

$$a_6 = \left(0, 0, 0, 0, b, b\right); \quad a_1^* = \left(\pi/8a, \pi/8a, \bar{\pi}/8a, \pi/b, \pi/b, \bar{\pi}/b\right)$$

and with 512-fold multiplication.

The total of 512 possible positions of atoms covers 30 orbits, and the set of 512 modulation vectors is separated into 30 stars (Table 1). In Table 2, the atoms coordinates and occupancy of the orbit for Cu_7SiS_5I and Ag_7SiS_5I compounds in accordance with Ref. [1] and our paper are presented.

Consideration of the structure and calculations for the superspatial model were carried out by solving the secular Eq. (1) of the order 1536×1536 with the involvement of 512 potential positions, 14 of which are occupied by the atoms of structures Cu_7SiS_5I and Ag_7SiS_5I, namely: I [0, 0, 0], Cu2 (Ag2) (142) [3, 0], Cu2 (Ag2) (153) [0, –3], Cu1 (Ag1) (471) [1, –1, –6], Cu1 (Ag1) (472) [6, –1, –1], Cu1 (Ag1) (Ag1) (Ag1) (Ag1) 473) [–1, 6, –1], Cu1 (Ag1) (474) [–1, –1, 6], Cu1 (Ag1) (475) [–6, –1, –1], S2 (490) [6, 2, 2], S2 (491) [2, 6, 2], S2 (493) [–6, 2, 2], S1 (498) [4, 4], Si (512) [8, 0, 0]. Dynamic matrices of the protocrystal were calculated at 512 points of the Brillouin zone. By modifying the occupancy of crystallographic positions with atoms and correcting the values of power constants in the equidistant approximation, the phonon spectra for high-symmetric directions of the FCC lattice Brillouin zone were obtained (Fig.1 and Fig. 2).

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Table 1. The array of positions arranged into orbits and modulation vectors in the stars of Cu_7SiS_5I and Ag_7SiS_5I structure with $(8a \times 8a \times 0)$ superlattice of the argyrodite family to take into account the partial occupancy of Cu(Ag).

Atoms	Orbit (position) number	Positions of atoms arranged into orbits	Star number (dimension)	Modulation vectors arranged into stars
I	1(1)	$[0,0,0]$	1(1)	$[0,0,0]$
	2(2–13)	$[a,a,0]$	2(12)	$[\pi/8a, \pi/8a, 0]$
	3(14–19)	$[2a,0,0]$	3(6)	$[\pi/4a, 0, 0]$
	4(20–43)	$[2a,a,a]$	4(24)	$[\pi/4a, \pi/8a, \pi/8a]$
	5(44–55)	$[2a,2a,0]$	5(12)	$[\pi/4a, \pi/4a, 0]$
	6(56–79)	$[3a,a,0]$	6(24)	$[3\pi/8a, \pi/8a, 0]$
	7(80–87)	$[2a,2a,2a]$	7(8)	$[\pi/4a, \pi/4a, \pi/4a]$
	8(88–135)	$[3a,2a,a]$	8(48)	$[3\pi/8a, \pi/4a, \pi/8a]$
	9(136–141)	$[4a,0,0]$	9(6)	$[\pi/2a, 0, 0]$
Cu2(Ag2) $(2/12^*, 1/12^{**})$	10(142–153)	$[3a,3a,0]$	10(12)	$[3\pi/8a, 3\pi/8a, 0]$
	11(154–177)	$[4a,a,a]$	11(24)	$[\pi/2a, \pi/8a, \pi/8a]$
	12(178–201)	$[4a,2a,0]$	12(24)	$[\pi/2a, \pi/4a, 0]$
	13(202–225)	$[3a,3a,2a]$	13(24)	$[3\pi/8a, 3\pi/8a, \pi/4a]$
	14(226–249)	$[4a,2a,2a]$	14(24)	$[\pi/2a, \pi/4a, \pi/4a]$
	15(250–297)	$[4a,3a,a]$	15(48)	$[\pi/2a, 3\pi/8a, \pi/8a]$
	16(298–321)	$[5a,a,0]$	16(24)	$[5\pi/8a, \pi/8a, 0]$
	17(322–369)	$[5a,2a,a]$	17(48)	$[5\pi/8a, \pi/4a, \pi/8a]$
Cu1(Ag1) $(5/6^*, 1^{**})$	18(370–375)	$[4a,4a,0]$	18(6)	$[\pi/2a, \pi/2a, 0]$
	19(376–399)	$[4a,3a,3a]$	19(24)	$[\pi/2a, 3\pi/8a, 3\pi/8a]$
	20(400–411)	$[5a,3a,0]$	20(12)	$[\overline{3\pi/8a}, 3\pi/8a, 0]$
	21(412–423)	$[4a,4a,2a]$	21(12)	$[\pi/2a, \pi/2a, \pi/4a]$
	22(424–429)	$[6a,0,0]$	22(6)	$[3\pi/4a, 0, 0]$
	23(430–453)	$[5a,3a,2a]$	23(24)	$[\overline{3\pi/8a}, 3\pi/8a, \pi/4a]$
	24(454–477)	$[6a,a,a]$	24(24)	$[3\pi/4a, \pi/8a, \pi/8a]$
	25(478–489) +1	$[6a,2a,0]$	25(12)	$[3\pi/4a, \pi/4a, 0]$
S2	26(490–497)	$[6a,2a,2a]$	26(8)	$[3\pi/4a, \pi/4a, \pi/4a]$
S1	27(498)	$[4a,4a,4a]$	27(1)	$[\pi/2a, \pi/2a, \pi/2a]$
	28(499)	$[-4a,-4a,-4a]$	28(1)	$[\overline{\pi}/2a, \overline{\pi}/2a, \overline{\pi}/2a]$
	29(500–511)	$[7a,a,0]$	29(12)	$[\overline{\pi}/8a, \pi/8a, 0]$
Si	30(512)	$[8a,0,0]$	30(1)	$[\pi/a, 0, 0]$

*Occupancy of the orbit in (5+2) scheme; **occupancy of the orbit in (6+1) scheme

The values of power constants α_n are given in order of increasing the distances between the positions of orbits $1(0, 0, 0)$ and $n + 1$, taking into account all possible variants of distances between pairs of occupied atoms. Power constants were selected in equidistant approximation, the interaction was determined only by the distances and did not depend on the variety of interacting pairs of atoms. For example, for the Cu_7SiS_5I compound (α_{26n} – power constant describing the interaction at the distance $4a\sqrt{3}$ equal to 3.1 N/m, and others, respectively): (power constants: = [82.1, 0, 0, 0, 3.1, 2.2, 1.7, 0.6, 1, 0, 0, 0, 0, 0.7, 0, 1, 5, 0, 0, 0, 2, 0, 0, 0, 10.0, 53, 0.6, 19]). Similarly, for Ag_7SiS_5I compound: (power constants: = [52.1, 0, 0, 0, 0.01, 9, 0.01, 1, 1, 0, 0, 0, 0, 0.7, 0, 0, 7, 5, 0, 0, 0, 0, 0, 0.08, 3, 1, 23.5]).

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Table 2. The atoms coordinates and occupancy of the orbit for Cu_7SiS_5I and Ag_7SiS_5I compounds.

Atom	Coordinates [1]	Occupancy [1]	Coordinates [this paper]	Occupancy [this paper]
Cu1(Ag1)	(0.02362, 0.25, 0.25)	0.624	(0.0, ¼, ¼)	$5/6^*, 1^{**}$
Cu2(Ag2)	(0.01914, 0.30918, 0.30918)	0.376	(0, 5/16, 5/16)	$2/12^*, 1/12^{**}$
Cu3(Ag3)	(0.0116, 0.1917, 0.1917)	0.376		0.0
I	(0, 0, 0)	0.989	(0, 0, 0)	1.0
S1	(0.25, 0.25, 025)	0.989	(¼, ¼, ¼)	1.0
S2	(0.62183, 0.62183, 0.62183)	1.0	(5/8, 5/8, 5/8)	1.0
Si	(0.5, 0.5, 0.5)	1.0	(½, ½, ½)	1.0

As a result of the model analysis of Cu_7SiS_5I and Ag_7SiS_5I structures, taking into account the different occupancy schemes of the orbit of Cu(Ag) atoms in the metric of the FCC protocrystal with $(a, a, 0)$, $(a, 0, a)$, $(a, a, 0)$ and real structure in superlattice with FCC basis $((8a \times 8a \times 0), (8a \times 0 \times 8a), (0 \times 8a \times 8a))$, the transformation of the phonon spectra for Cu_7SiS_5I and Ag_7SiS_5I crystals was observed, caused by changes in the corresponding mass characteristics of Cu and Ag atoms in various positions and a certain correlation of power constants. All the calculations give a satisfactory match of the frequency range with the experimental frequency values at the point Γ (427 cm^{-1} (the most intense band), 306 cm^{-1}, 567 cm^{-1} for Cu_7SiS_5I crystal; 240 cm^{-1} (the most intense band), 470 cm^{-1} for Ag_7SiS_5I crystal).

4. Conclusions

The calculated dispersion curves have shown the similarity of results for both schemes in two cases of Cu_7SiS_5I and Ag_7SiS_5I crystals. It can reflect insignificant transformation when varying the occupation positions by Cu(Ag) atoms, accompanied with high ionic conductivity in the superionic phase of Cu_7SiS_5I and Ag_7SiS_5I crystals ("jumping" of atoms between orbits under consideration). The partial occupancy of the different orbits leads to lowering the symmetry, removal of degeneration and appearance of energy close to spectral branches, which can also stimulate the mobility of Cu(Ag) atoms.

Acknowledgements

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Модель фононного спектра кристалів Cu₇SiS₅I та Ag₇SiS₅I

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Анотація. У концепції надпросторової симетрії проаналізовано кристалічну структуру суперіонних провідників Cu₇SiS₅I та Ag₇SiS₅I. Для розрахунку фононних спектрів розроблено модель надгратки ГЦК ($8a$, $8a$, 0; $8a$, 0, $8a$; 0, $8a$, $8a$) у метриці протокристала (a, a, 0; a, 0, a; 0, a, a). Для розробленої моделі представлено загальний (3+3)-вимірний базис, масив векторів модуляції та функції модуляції маси. Проведено модельні розрахунки дисперсії фононних спектрів для кристалів Cu₇SiS₅I та Ag₇SiS₅I у схемах з різним частковим заповненням кристалографічних орбіт атомами Cu(Ag). Наведено дисперсійні залежності фононних спектрів для кристалів Cu₇SiS₅I та Ag₇SiS₅I у високосиметричних напрямках зони Бриллюена. Проаналізовано походження фононних гілок коливних спектрів.

Ключові слова: суперіонний провідник, фононні спектри, кристалічна структура, надгратка, протокристал.

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