Lattice stability and features of the dispersion of the phonon spectrum in different approximations of the force interaction

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Abstract

The consistent inclusion of additional physical parameters (color, phase, sign of charge, spin, etc.) into the symmetrical description has resulted to the creation of the theory of color symmetry [1] and the concept of superspace symmetry [2]. Among the types of generalized symmetry, the concept of superspace symmetry is quite convenient and visual when building $(3+d)$-dimensional models describing the structure of complex crystals and systems united by a single metric and the scale of the function of the protocrystal carrier [3]. Formation of the $(3+d)$-dimensional metric of a protocrystal is based on its higher symmetry and is associated with an additional d-dimensional space, which allows the description of real objects (crystals and systems) as natural (sa×sa×sa) superlattices.

1 Calculation method

The compositional features of the implementation of complex crystals and systems based on the mechanism of filling with atoms of various types and vacancies, translationally equivalent positions, given by the basis of the protocrystal, are covered by the concept of superspace symmetry. At the same time, various combinations of the bases of the protocrystal and the real physical object along with all possible variants of the compositional filling of the positions can be taken into account. The use of a complete set of modulation vectors makes it possible to determine the amplitudes of the mass modulation functions and, based on them, to generate a generalized dynamic matrix (GDM) of a family of complex crystals in the form of a superposition of the protocrystal dynamic matrices determined at various points of the Brillouin zone (ZB), related by the modulation vectors, and the mass perturbation matrix described by amplitudes of mass modulation functions.

A number of families of crystal structures are characterized by a combination of several crystallographic orbits with their partial filling with atoms of the same

type. As an example, the argyrodite family [4]. Let's consider the indicated situation based on a simpler model. Let's choose for analysis a model of crystal structures of the perovskite family (Fig. 1), which is characterized by an equidistant arrangement of atoms of various types. In the concept of superspace symmetry, the perovskite class can be considered as a natural (2a×2a×2a) superlattice [5].

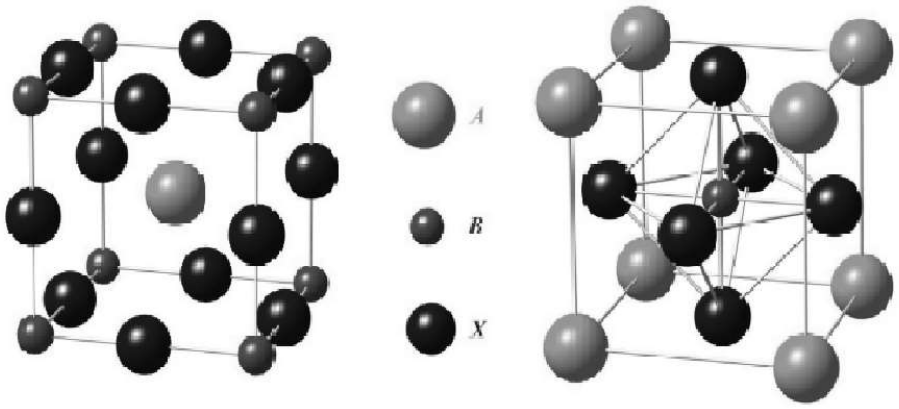

Figure 1: Crystal structure of type ABX_3 of an ideal cubic perovskite.

Since we are interested in the analysis of the situation with partial filling of different crystallographic orbits with atoms of the same type, we will describe the structure of perovskite in the basis of the (4a×4a×4a)-superlattice, introducing a number of additional crystallographic orbits into consideration. Thus, in addition to the composite superlattice obtained by modulating a monatomic PCG with the help of 8 modulation vectors [5] for the (2a×2a×2a)-superlattice, let's consider the modulated monatomic PCG with the help of 64 modulation vectors in the basis of the (4a×4a×4a)-superlattice.

Solving the matrix equation with respect to $\omega^2(k)$ allows us to define the dispersion dependences of the phonon spectrum, and taking into account different options for compositional filling allows us to trace their genesis [6].

Dispersion curves of the phonon spectrum of complex crystals of the perovskite structural type in the concept of superspace symmetry are defined as solutions of the matrix equation under the condition that the determinant is equal to zero, which has the form:

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

where $D_{\alpha\beta}(k+q_i)$ are the dynamic matrices of the monoatomic protocrystal (PCL), defined at $(k+q_i)$ points of ZB for the $BaTiO_3$ crystal: $(i = 1, \ldots, 8)$ – in the (2a×2a×2a) basis, $(i = 1, \ldots, 64)$ – in the basis of the (4a×4a×4a)-superlattice, respectively, $\rho_{(i-j)} = \rho_i(q_i, \Delta^* b^*_{ij})$ are the amplitudes of the mass modulation function given for modulation vectors $(q_i - q_j)$, $\alpha, \beta - x, y, z$, k – wave vector, q_i – modulation vectors [7].

The dynamic matrices of the protocrystal $D_{\alpha\beta}(k+q_i)$ are defined from the relation

$$D_{\alpha\beta}(k+q_i) = \sum_{(n\neq 0)} \alpha_n \frac{n_\alpha n_\beta}{n^2}(1 - e^{i(k+q_i)n}), \tag{2}$$

where α_n is the force constant between the atom at the position $(0,0,0)$ and its n neighbor, n_α, n_β are the projections of the vector $\vec{n}$ on the α, β axis.

The calculation of phonon mode frequencies can be obtained by equating to zero the determinant written in a slightly different form [7]:

$$|\rho_i^{(D)}(k-q_i, \Delta^* b_{ij}^*) - \omega^2 \delta_{\alpha\beta}\delta_{ij} - \omega^2 \rho_{(i-j)}\delta_{\alpha\beta}| = 0, \tag{3}$$

where $\rho_j^{(D)}(k-q_i, \Delta^* b_{ij}^*) = \rho_j^{(D)}$ are the amplitudes of the modulation functions of UDM of a complex crystal.

$$D_{\alpha\beta}^{r_k}(k+q_i) = \sum_{j=1}^{n} \rho_j^{(D)}(k-q_i, \Delta^* b_{ij}^*) e^{iq_j r_k}, \tag{4}$$

with respect to the amplitudes of the modulation functions $\rho_j^{(D)}$ of the dynamic matrix, we obtain solutions in the form of a superposition of the dynamic matrices defined for each of the n positions: for (2a×2a×2a)-superstructures $n = 8$; for (4a×4a×4a)-superstructures $n = 64$.

The implementation of a step-by-step complication of the description of real crystal structures by choosing the most obvious $(3+d)$-dimensional bases allows us to introduce a $(3+d)$-dimensional superspace, which covers the possibility of filling of all positions of the PCL structures with (sa×sa×sa)-superlattices.

The description of crystal formations of cubic syngonia with (sa×sa×sa)-superlattices is contained in $(3+d)$-dimensional bases [5]:

direct:

$$\begin{aligned} a_1 &= (a, 0, 0, -b/s, 0, 0);\\ a_2 &= (0, a, 0, 0, -b/s, 0);\\ a_3 &= (0, 0, a, 0, 0, -b/s);\\ a_4 &= (0, 0, 0, b, 0, 0);\\ a_5 &= (0, 0, 0, 0, b, 0);\\ a_6 &= (0, 0, 0, 0, 0, b), \end{aligned} \tag{5}$$

and reciprocal:

$$\begin{aligned} a_1^* &= (2\pi/a, 0, 0, 0, 0, 0);\\ a_2^* &= (0, 2\pi/a, 0, 0, 0, 0);\\ a_3^* &= (0, 0, 2\pi/a, 0, 0, 0);\\ a_4^* &= (2\pi/sa, 0, 0, 2\pi/b, 0, 0);\\ a_5^* &= (0, 2\pi/sa, 0, 0, 2\pi/b, 0);\\ a_6^* &= (0, 0, 2\pi/sa, 0, 0, 2\pi/b). \end{aligned} \tag{6}$$

The $(3+d)$-dimensional description of $BaTiO_3$ crystals with a (2a×2a×2a)-super/-lattice covers a set of eight modulation vectors, which can be divided into 4 stars:

1. $(0,0,0)$ – dimensionality one;
2. $(\pi/a, \pi/a, 0)$ – dimensionality three;

3. $(\pi/a, \pi/a, \pi/a)$ – dimensionality one;
4. $(\pi/a, 0, 0)$ – dimensionality three.

They correspond to four orbits defined by radius vectors: $r_{Ti} = (0,0,0)$, $r_O = 2a(1/2,0,0)$, $r_{Ba} = 2a(1/2,1/2,1/2)$, $r_{Vac} = 2a(1/2,1/2,0)$.

The Fig. 1 shows two equivalent setups for describing the structure of the $BaTiO_3$ crystal, which demonstrate the equivalence of the orbits $r_O = 2a(1/2,0,0)$ and $r_{Vac} = 2a(1/2,1/2,0)$. Obviously, the multiplication period of the composite superlattice is equal to 2.

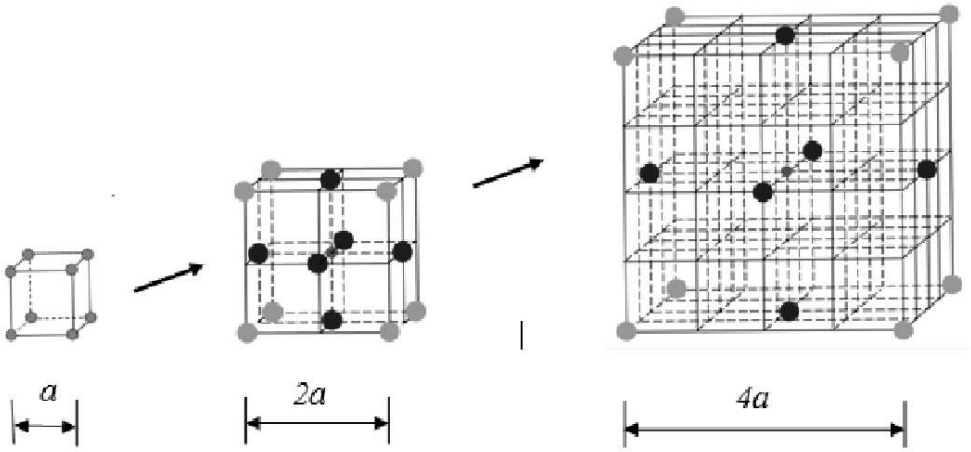

Figure 2: Structure of $BaTiO_3$ crystal: a) with (2a×2a×2a)-superlattice; b) with (4a×4a×4a)-superlattice.

When transitioning from the $BaTiO_3$ crystal structure with (2a×2a×2a)-superlattice to that with the (4a×4a×4a)-superlattice (Fig. 2), the volume of the direct lattice increases by 8 times, and the volume of the Brillouin zone decreases by 8 times, accordingly (Fig. 3).

Based on the PCL base, the full set of 64 combinations of modulation vectors can be divided into 10 stars [7]:

1. $(0,0,0)$ – dimensionality one;
2. $(\pi/2a, 0, 0)$ – dimensionality six;
3. $(\pi/a, 0, 0)$ – dimensionality three;
4. $(\pi/a, \pi/a, \pi/a)$ – dimensionality one;
5. $(\pi/a, \pi/a, 0)$ – dimensionality three;
6. $(\pi/2a, \pi/2a, \pi/2a)$ – dimensionality eight;
7. $(\pi/2a, \pi/a, \pi/a)$ – dimensionality six;
8. $(\pi/2a, \pi/2a, 0)$ – dimensionality twelve;
9. $(\pi/2a, \pi/2a, \pi/a)$ – dimensionality twelve;
10. $(\pi/2a, \pi/a, 0)$ – dimensionality twelve.

The phonon spectra were calculated in the Maple software environment. Fig. 4 shows the calculated model phonon spectrum of $BaTiO_3$ crystal with a (2a×2a×2a)-superlattice in the approximation of an equidistant force field along the $X - \Gamma - M - R - \Gamma$ lines with taking into account the interaction within the six first coordination groups for an ideal structure.

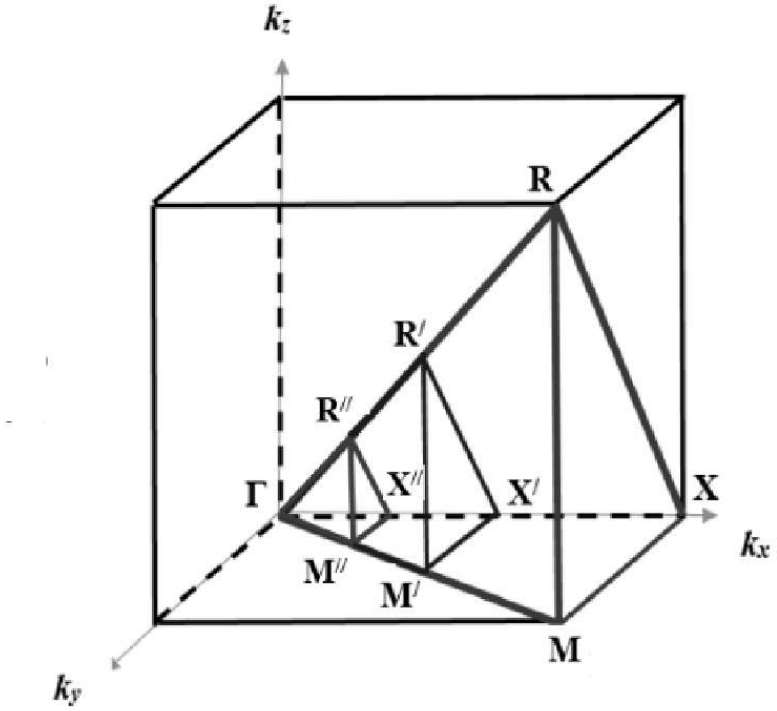

Figure 3: Transformation of the ZB PCL with a period a (red lines) when transitioning to (2a×2a×2a)-superlattice (blue lines), to (4a×4a×4a)-superlattice (green lines) 2.

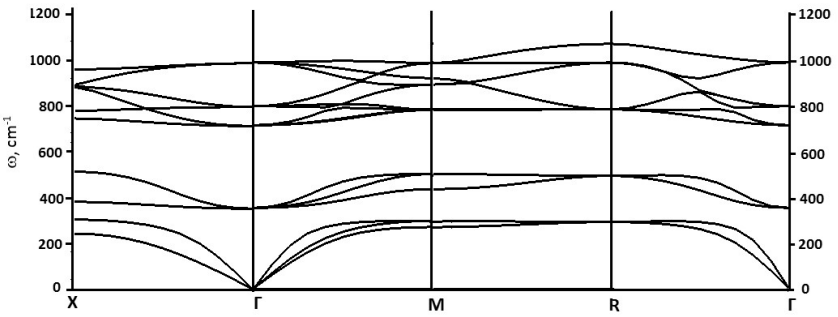

Figure 4: Phonon spectrum of $BaTiO_3$ crystal with (2a×2a×2a)-superlattice (ideal structure) ($\alpha_1 = 220$ (N/m), $\alpha_2 = 110.5$ (N/m), $\alpha_3 = 10$ (N/m), $\alpha_4 = 5$ (N/m), $\alpha_5 = 3.5$ (N/m), $\alpha_6 = 2$ N/m)).

The Fig. 5 shows the model phonon spectrum of $BaTiO_3$ crystal with a (2a×2a×2a)-superlattice for the case of a structure with two partially filled equivalent orbits $(0, a, 0)$ and $(a, 0, a)$ with oxygen atoms.

The Fig. 6 shows the change in the dispersion dependences in the direction of $\Gamma - R$ of ZB in the (4a×4a×4a)-metric when the orbit $(2a, 2a, 0)$ is populated with oxygen atoms (ideal structure) (a), the orbits are partially populated (two atoms are localized in a three-fold orbit $(2a, 2a, 0)$, and one – in a six-fold orbit $(2a, 2a, a)$ (b), and two atoms are localized in a three-fold orbit $(2a, 2a, 0)$, and one – in a twelve-fold orbit $(2a, a, 0)$ (c)).

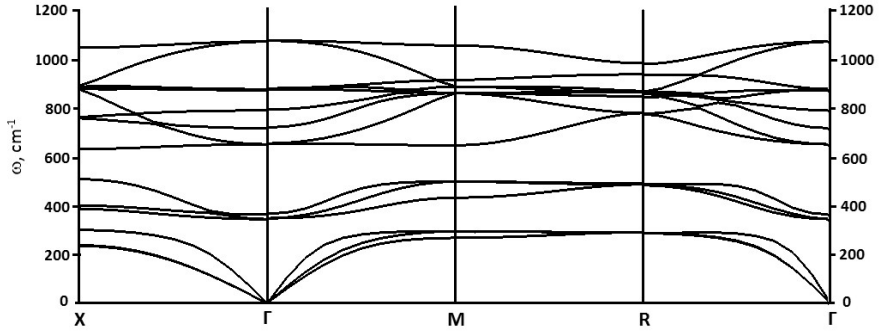

Figure 5: Model phonon spectrum of $BaTiO_3$crystal with (2a×2a×2a)-superlattice (case of structure with two partially filled orbits with oxygen atoms).

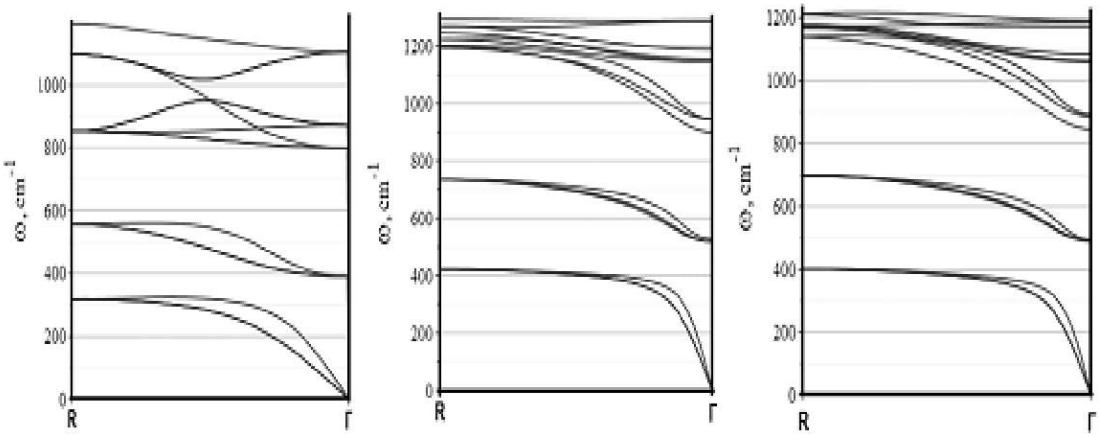

Figure 6: Dispersion dependences of the phonon spectrum of the $BaTiO_3$ crystal in the metric (4a×4a×4a). left) ideal structure, middle) localization of one oxygen atom in the $(2a, 2a, a)$ orbit, right) localization of one oxygen atom in the $(2a, a, 0)$ orbit.

Table 1: Coordinates of occupied positions in the (4a×4a×4a) superlattice and values of model force constants at the distances for the ideal structure of $BaTiO_3$ crystal.

Ideal structure	Relation (position 1)–(position 2)	Value of model force constant α_i(N/m)
Ba(0,0,0)	(0,0,0) - (2a,0,0)	$\alpha_4 = 220$(N/m)
O(2a,0,0)	(0,0,0) - (2a,2a,0)	$\alpha_8 = 110$(N/m)
O(0,2a,0)	(0,0,0) - (2a,2a,2a)	$\alpha_{12} = 10$(N/m)
O(0,0,2a)		
Ti(2a,2a,2a)		

Tables 1, 2, 3 show the coordinates of the occupied positions in the (4a×4a×4a)-superlattice and the values of the model force constants at the distances for various constructions of the $BaTiO_3$ crystal structure.

Table 2: Coordinates of occupied positions in the (4a×4a×4a) superlattice and values of model force constants at the distances for the structure of $BaTiO_3$ crystal (construction 1).

Construction 1	Relation (position 1)–(position 2)	Value of model force constant α_i(N/m)
Ba(0,0,0)	(0,0,0) - (a,0,0)	$\alpha_1 = 70$(N/m)
O(2a,0,2a)	(0,0,0) - (2a,0,0)	$\alpha_4 = 220$(N/m)
O(0,2a,2a)	(0,0,0) - (2a,a,0)	$\alpha_5 = 100$(N/m)
O(2a,2a,a)	(0,0,0) - (2a,2a,0)	$\alpha_8 = 10$(N/m)
Ti(2a,2a,2a)	(0,0,0) - (2a,2a,a)	$\alpha_9 = 4$(N/m)
	(0,0,0) - (2a,2a,2a)	$\alpha_{12} = 10$(N/m)

Table 3: Coordinates of occupied positions in the (4a×4a×4a)-superlattice and values of model force constants at the distances for the structure of $BaTiO_3$ crystal (construction 2).

Construction 2	Relation (position 1)–(position 2)	Value of model force constant α_i(N/m)
Ba(0,0,0)	(0,0,0) - (2a,0,0)	$\alpha_4 = 220$(N/m)
O(2a,a,0)	(0,0,0) - (2a,a,0)	$\alpha_5 = 100$(N/m)
O(2a,0,2a)	(0,0,0) - (2a,2a,0)	$\alpha_8 = 10$(N/m)
O(0,2a,2a)	(0,0,0) - (2a,2a,a)	$\alpha_9 = 4$(N/m)
Ti(2a,2a,2a)		

2 Conclusions

The performed studies demonstrated a slight rearrangement of the phonon spectrum of the $BaTiO_3$ crystal when the population changes between equivalent orbits in the (2a×2a×2a)-metric and a rather significant rearrangement when the population changes between orbits of different multiplicity in the (4a×4a×4a)-metric. Note that the model calculations in the (4a×4a×4a)-metric are related with the introducing into consideration the additional model force constants that specify the force interaction at additional distances. In the case of the (2a×2a×2a)-metric, additional force constants do not arise, since they are all included into the consideration of the ideal structure. What is interesting, at the same time, is the almost absent effect on the realization of the low-frequency part of the spectrum in the (4a×4a×4a)-metric and the significant restructuring of the high-frequency branches of the phonon spectrum. Along with this, modeling in the (4a×4a×4a)-metric is related with a significantly smaller value of the "jump" distance of oxygen atoms between the considered orbits.

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