Model phonon spectra and densities of states of Nb_3Sn and Nb_3Ge structures

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Abstract

The efficiency of combining the concept of superspatial symmetry and the ideas of the lattice model for the calculation of the model phonon spectra of complex crystalline formations is shown. $3+3$ - dimensional bases, sets of modulation vectors and $(4 \times 4a \times 4a)$ lattice model for the description of crystal structure are presented and calculations of model phonon spectra and state densities of Nb_3Sn and Nb_3Ge structures at different combinations of force constants are given. As a result of the analysis it is shown that at the choice of certain combinations of power constants, mainly α_4, α_5 and α_6, it is possible to obtain phonon spectra with optical frequencies in 150 - 240 cm^{-1} range, which correlates with the experimental data. However, the distribution of densities in the spectra of phonon states is significantly different, which may reflect the significant lability of the chemical bond in these compounds, despite the binary nature of their composition.

1 Introduction

Simplification of mathematical description, the ascertainment of certain rules of selection, reference points and exact relationships in physical theory, including the theory of condensed matter, are related with the theory of symmetry and its generalizations [1]. No less productive in recent years has been the idea of lattice models [2, 3] which also allows for a number of simplifications and exact solutions. Let us show the possibility of obtaining additional simplifications in the method of calculating the model phonon spectra of complex crystals, in the concept of superspatial symmetry [4]–[9] using the idea of lattice models [2, 3].

Crystallographic description of the complex crystals structure in a certain spatial group is associated with the choice of unit cell type and set of Weisskopf's positions, the latter determine the crystallographic orbits and thus the number of atoms in the unit cell and their coordinates [10]. The inclusion of Weisskopf's positions only with rational values allows us to form an elementary cell of a complex crystal in the form of a lattice model of a certain order. In complex crystals of cubic syngony, these models can be selected with sufficiently reasonable accuracy and with a not very large value of the lattice model order.

To describe the structure of the unit cell, we use a combination of the idea of superspatial symmetry and the lattice model. Let's define a lattice model with the minimum possible order n (for cubic syngony) in the metric of the convenient protocrystal, which will provide setting the positions of atoms at the selected accuracy. We will describe the minimum lattice model in the concept of superspatial symmetry [4]–[9].

2 Calculation method

Consideration of complex crystals of cubic syngony in the concept of superspatial symmetry makes it possible to combine them into families having one order of n of lattice model ($na \times na \times na$) and to describe their physical properties from a single point of view. The analysis showed that NaTl, BiF_3, CaF_2, ZnS, Ge, Cu_2O, Nb_3Sn (A-15) crystals and some others can be attributed to ($4a \times 4a \times 4a$)-family.

Let's illustrate the calculation method of the crystals model phonon spectra of this family on the structure A15 example [10]. Representatives of this family are interesting as the most high-temperature superconductors. The ancestor of this family is aluminum niobium Nb_3Al, a typical superconductor with A15 structure (cubic structure of β-W type with space group Pm3n № 200). A simple cubic unit cell (SC) contains 8 atoms in the Weisskopf positions (1 am$\bar{3}$. [0,0,0], 1, b m$\bar{3}$, [1/2, 1/2 ,1/2] 2 and 6 g mm2, [-x,1/2,0], [0,x,1/2], [0,-x,1/2], [1/2,0,x], [1/2, 0,-x]) where x=1/4. It is convenient to set all these positions in the lattice model of the order 64 ($4 \times 4a \times 4a$).

The use of lattice model allows us to use the interatomic interaction as the first approximation according to [11].

Compositional features of realization of complex crystals and systems of solid solutions according to the mechanism of filling the lattice model given by protocrystal basis with mixed atoms and vacancies of translationally equivalent positions are covered by the concept of superspatial symmetry [4]–[9]. Different combinations of protocrystal bases of the lattice model [2, 3] and real crystal formation together with all possible variants of compositional filling the crystallographic positions (lattice models) can be taken into account. Using the complete set of modulation vectors [4]–[9] allows determining the amplitudes of mass modulation functions and on their basis to generate a generalized dynamic matrix of a real physical object and a matrix of mass perturbation [6]–[9]. The first is given in the form of a superposition of dynamic protocrystalline matrices defined at different points in the Brillouin zone (BZ), connected by modulation vectors. The second is described by the amplitudes of mass modulation functions [5]–[9].

The solution of the matrix equation relatively $\omega^2(k)$ allows to determine the dispersion dependences of the phonon spectrum, and taking into account different variants of compositional filling and combinations of values of force constants tracking their genesis [5]–[9].

In the concept of superspatial symmetry, the dispersion curves of the phonon spectrum of crystal formation are defined as solutions of the matrix equation under the condition of zero equality of the determinant of the form [5, 7, 9]:

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

where $D_{\beta\gamma}(k+q_i)$ – dynamic matrices of a monoatomic protocrystal determined at points in the Brillouin zone (BZ), $(k+q_i)$, $\rho(q_i - q_j) = (q_s)$ - the amplitudes of the mass modulation function given for the modulation vector $(q_i - q_j)$, k – wave vector, q_i – modulation vectors β, γ – coordinates x, y, z.

Dynamic matrices of protocrystal $D_{\beta\gamma}(k+q_i)$ in the first approximation are determined by the equation:

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

where α_n is the force constant of the atom interacting in the 0-position and the l-th neighboring atom, l_β,l_γ – projections of the vector l on the axis β, γ.

In the equidistant approximation for the model, the force characteristic depends only on the distance between the atoms and, then, the interaction of different kinds of atoms that are in equidistant positions is the same. Note that this situation in this structure is realized only at a distance multiple $4a$ when there is an interaction of different single-type atoms (Nb - Nb and Sn - Sn). This allows us to form a dynamic matrix in quasi-diagonal form. In the non-equidistant approximation, α_l is determined by both the distance between the positions and the difference between the physical characteristics, the objects that occupy them (in this paper, this situation is not considered).

The values of the amplitudes of the mass characteristics $\rho(q_i)$ are obtained by solving the system of equations

$$m(r_j) = \sum_{i=1}^{n} \rho(q_i) e^{iq_i r_j} \tag{3}$$

relative to the amplitudes of mass modulation functions $\rho(q_i) = \rho_i$, n is the number of possible positions of atoms in the lattice model, where $m(r_j)$ are the mass characteristics at these positions, q_j – the array of modulation vectors, the number of which coincides with the number of positions in the lattice model.

Thus, the construction of generalized dynamic matrix of $(3n \times 3n)$ dimensionality is the basis for calculating the dynamics of the lattice, and its elements depend on the force constants α_l [3]–[5],[8].

Let's consider the most general case of crystals with the $(4a \times 4a \times 4a)$- superlattice (lattice model of the order 64), in which we will describe positions of atoms using the $(3+3)$-dimensional direct and inverse basis:

$$
\begin{aligned}
a_1 &= (a,0,0,-\frac{b}{4},0,0) \qquad & a_1^* &= (\frac{2\pi}{a},0,0,0,0,0)\\
a_2 &= (0,a,0,0,-\frac{b}{4},0) \qquad & a_2^* &= (0,\frac{2\pi}{a},0,0,0,0)\\
a_3 &= (0,0,a,0,0,-\frac{b}{4}) \qquad & a_3^* &= (0,0,\frac{2\pi}{a},0,0,0)\\
a_4 &= (0,0,0,b,0,0) \qquad & a_4^* &= (\frac{\pi}{2a},0,0,\frac{2\pi}{b},0,0)\\
a_5 &= (0,0,0,0,b,0) \qquad & a_5^* &= (0,\frac{\pi}{2a},0,0,\frac{2\pi}{b},0)\\
a_6 &= (0,0,0,0,0,b) \qquad & a_6^* &= (0,0\frac{\pi}{2a},0,0,\frac{2\pi}{b})
\end{aligned}
\tag{4}
$$

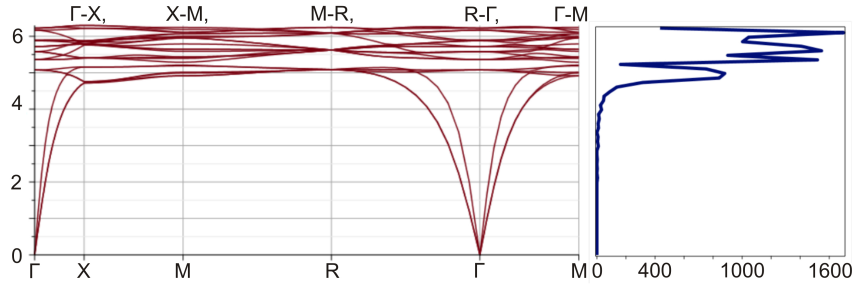
For V_E and V_d, the bases of simple cubic lattice (SCL), the first three-dimensional components a_1, a_2, a_3 and the last three components a_4, a_5, a_6, respectively, were chosen.

All 64 possible combinations of modulation vectors can be divided into 10 stars, namely: 2 single- rayed stars
$\{q_{000}\}(q_{000}=0,0,0)$, $\{q_{222}\}(q_{222}=\pi/a,\pi/a,\pi/a)$;
two three-rayed $\{q_{200}\}(q_{200}=\pi/a,0,0,q_{020}=0,\pi/a,0,q_{002}=0,0,\pi/a)$
and $\{q_{220}\}(q_{220}=\pi/a,\pi/a,0,q_{202}=\pi/a,0,\pi/a,q_{022}=0,\pi/a,\pi/a)$;
two six-rayed $\{q_{100}\}(q_{100}=\pi/2a,0,0,q_{010}=0,\pi/2a,0,etc.)$ and $\{q_{122}\}(q_{122}=\pi/2a,\pi/a,\pi/a,etc.)$;
one octave-rayed $\{q_{111}\}(q_{111}=\pi/2a,\pi/2a,\pi/2a,etc.)$
and three twelve-rayed $\{q_{110}\}(q_{110}=\pi/2a,\pi/2a,0,etc.)$,
$\{q_{112}\}(q_{112}=\pi/2a,\pi/2a,\pi/,etc.)$, $\{q_{120}\}(q_{120}=\pi/a,\pi/a,0,etc.)$.
Similarly, all 64 positions of the n lattice model can be plotted in orbits.

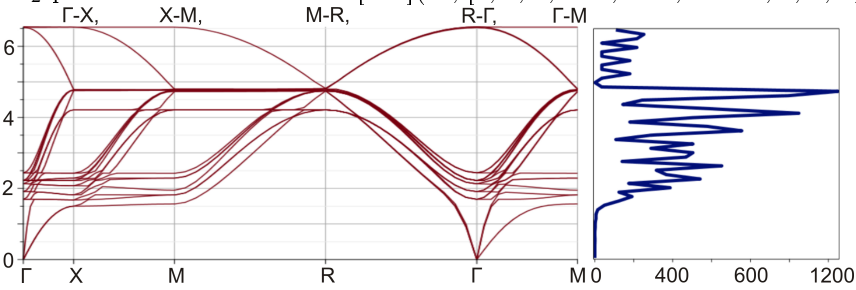
Consideration of the structure and calculations of dispersion dependences for the superspatial model were performed by solving a secular equation of type (1) similarly [12], of the order of 192×192, involving 64 possible positions, 8 of which are occupied by atoms of structures. Occupied Weisskopf's positions are marked with asterisks.

Dynamic matrices of protocrystal were calculated at 64 points in the Brillouin zone. By modifying the values of the force constants in the equidistant approximation, the phonon spectra were obtained for the highly symmetric directions of the Brillouin zone of a simple cubic lattice and the phonon states density.

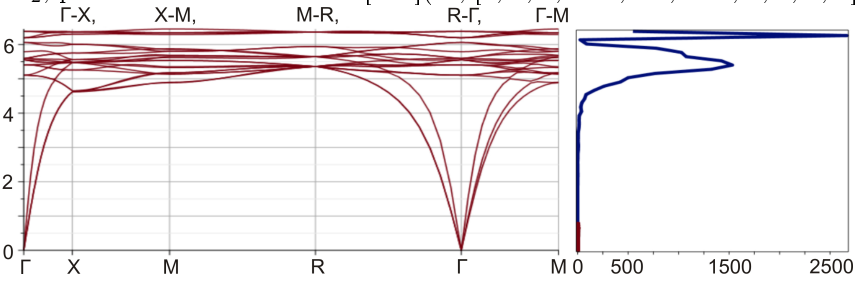
The values of the force constants α_l are given in order of increasing the distances between the orbit positions of $1(0,0,0)$ and $l+1$, taking into account all possible variants of the distances between pairs of positions occupied by atoms. The power constants were chosen in the equidistant approximation; the interaction was determined only by distance and did not depend on the type of interacting pairs of atoms. For example, for the Nb_3Sn structure, the power constant α_4 that describes the interaction at a distance of $4a$ (Nb – Nb) is equal to 10.9 n/m, and the others accordingly :(powerConstants := Vector[row](34, [0, 0, 0, 10.9, 10.1,



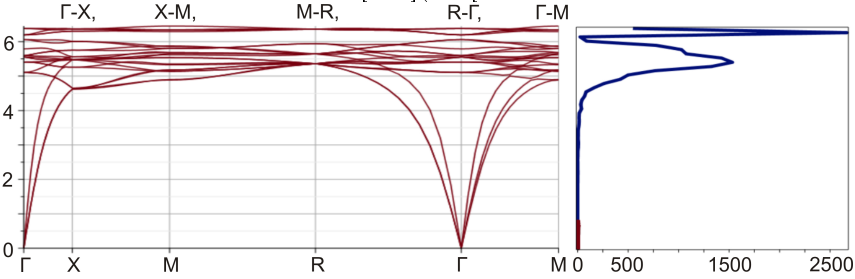
Nb_6Sn_2 powerConstants := Vector[row](34, [0, 0, 0, 10.9, 10.1, 10.955, 0, 0, 0, 0])



Nb_6Sn_2, powerConstants := Vector[row](34, [0, 0, 0, 60.9, 1.0, 1.05, 0, 0, 0, 0])



Nb_6Ge_2 powerConstants := Vector[row](34, [0, 0, 0, 15.9, 10.0, 10.05, 0, 0, 0, 0])



Nb_6Ge_2 powerConstants := Vector[row](34, [0, 0, 0, 63.0, 12.50, 5.5, 0, 0, 0, 0])

Figure 1: Model phonon dispersion dependences and phonon states densities of Nb_3Sn and Nb_3Ge crystals are calculated for highly symmetric directions of the Brillouin zone in schemes with different combinations of force constants values.

10.95, 0, 0, 0, 0] for Nb_3Sn)). For all other combinations of compounds Nb_3Sn and Nb_3Ge, the force constants are chosen similarly (Fig. 1).

Conclusions

The efficiency of combining the superspatial symmetry concept and the ideas of the lattice model for the calculation of model phonon spectra of complex crystalline formations is shown. As a result of the analysis of the calculated dispersion dependences of the phonon spectra and states densities of Nb_3Sn and Nb_3Ge structures at different combinations of force constants, it is shown that by choosing the certain combinations of force constants, mainly α_4, α_5 (Nb-Sn) and α_6 (Nb-Nb), it is possible to obtain the phonon spectra with the optical frequencies in 150 - 240 cm^{-1} range (4.5 – 7.2 THz), which coincides with the experimental data [10]. At the same time, the distribution of densities in the spectra of phonon states is significantly different, which may reflect the significant lability of the chemical bond in these compounds.

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