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Phonon spectra near metal-insulator phase transition in $Li_{1+x}Ti_{2-x}O_4$ system

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The phonons of two end members of $Li_{1+x}Ti_{2-x}O_4$ spinel system, i.e., the metallic $LiTi_2O_4$ and the insulating $Li[Li_{1/3}Ti_{5/3}]O_4$, are calculated in superspace symmetry approach using a short-range force constant model. The composition dependence of zone-centre optical phonons in $Li_{1+x}Ti_{2-x}O_4$ near phase transition and $Li_{1-x}Mg_xTi_2O_4$ has been investigated using different models of substitution. One- and two-mode behavior is therefore predicted for F_{1u} and F_{2u} modes in case of tetrahedral and octahedral substitution, respectively.

Key words: *superspace symmetry, phonon spectra, spinel, $Li_{1+x}Ti_{2-x}O_4$*

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1. Introduction

A large class of solid spinels XY_2O_4 are of technological and geological interest having widely variable occupations of two (tetrahedral A and octahedral B) sites by various cations (figure 1). Normally in most spinels there are occupations of the octahedral and tetrahedral sites preferred by different atoms.

Among a large number of spinel compounds only a few show metallic behavior and $Li_{1+x}Ti_{2-x}O_4$ system is the only one to be superconducting with a $T_C \approx 13$ °K. The replacement of Ti ions by additional Li ions carries the system through a metallic-insulator transition at $x \approx 0.1 - 0.15$ [1–3]. Although many experimental studies have been done in connection with the transition [1–4], the origin of the metal-insulator transition is still not fully understood. In order to study the mechanism of superconductivity and metal-insulator transition in $Li_{1+x}Ti_{2-x}O_4$ the investigations of its phonons are quite important. Therefore, the phonons of two end members of $Li_{1+x}Ti_{2-x}O_4$ spinel system, i.e., the metallic $LiTi_2O_4$ and the insulating $Li[Li_{1/3}Ti_{5/3}]O_4$, are calculated using a simple short-range force constant model.

The simple force constant models are widely used in studying the phonons in spinel type oxides, sulphides and selenides [5,6]. Lattice dynamic calculations of

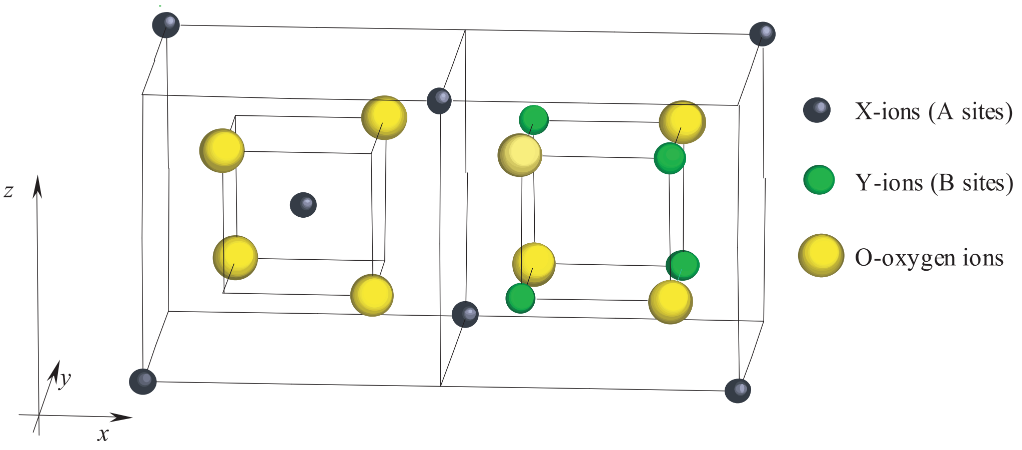


Figure 1. Primitive cell of XY_2O_4 spinel structure.

inverse spinels had been performed in [7]. The phonons in superconducting oxide spinel $LiTi_2O_4$ were also investigated using three short-range force constants α_1, α_2, α_3 by Gupta et al. [8]. The theoretical Raman frequencies and superconducting transition temperature T_C agree satisfactorily with the observed values in paper [8].

In accordance with the above, the simple model with three central force constants for interatomic interaction between the first, second and third nearest neighbors is used in the present work to investigate the phonons in $Li[Li_xTi_{2-x}]O_4$ and $Li_{1-x}Mg_x[Ti_2]O_4$ systems.

The analysis of the phonon spectra of the $Li_{1+x}Ti_{2-x}O_4$ spinel system, in particular, as well as of many other spinels, becomes complicated by disordering of the cations between A and B sites, which may depend upon the temperature, conditions of synthesis and chemical composition [9].

In this paper for the first time the Superspace Symmetry Approach (SSA) [10–12] has been used in constructing the simplified dynamic matrix of spinel structure. The dynamic matrix elements are calculated, using the experimental data of Raman spectra of $Li_{1+x}Ti_{2-x}O_4$ solids near metal-insulator phase transition.

The SSA approach takes into account the composition freedom of the sites occupied by different atoms. Thus, we have computed the compositional variations of zone-centre phonon frequencies with different kinds of substitutions in $Li[Li_xTi_{2-x}]O_4$ and $Li_{1-x}Mg_x[Ti_2]O_4$ lithium spinel systems.

2. Theory

XY_2O_4 type crystals have the cubic lattice (space group $Fd3m$ (O_h)) the primitive cell of which contains 14 atoms (figure 1).

One can consider a spinel structure as a suitable model object for the study of phonon spectra in SSA approach due to the presence of equidistant sites, occupied by various sorts of atoms and vacancies.

We can regard the real structure in terms of SSA as a compositional modulated one from the basic "simpler" structure with a smaller period of translations [13]. So, the complex crystal is the compositional natural superlattice in this approach.

Let us select a Volume-Centered Cubic (VCC) lattice as the basic structure. $(3+d)$-dimensional superspace description [10–13] of given crystals is realized, using the basis in the direct space:

$$\begin{bmatrix} \mathbf{a}_1 \\ \mathbf{a}_2 \\ \mathbf{a}_3 \\ \mathbf{a}_4 \\ \mathbf{a}_5 \\ \mathbf{a}_6 \end{bmatrix} = \begin{bmatrix} -a & a & a & b/4 & -b/4 & -b/4 \\ a & -a & a & -b/4 & b/4 & -b/4 \\ a & a & -a & -b/4 & -b/4 & b/4 \\ 0 & 0 & 0 & 0 & b & b \\ 0 & 0 & 0 & b & 0 & b \\ 0 & 0 & 0 & b & b & 0 \end{bmatrix}, \tag{1}$$

where a is a parameter of basic one atom lattice; $b/4$ is a lattice parameter in the additional 3-dimensional phase space.

3-dimensional components of the last three vectors in reciprocal basis define the elementary modulation vectors:

$$\mathbf{q}_1 = (-\frac{\pi}{4a}, \frac{\pi}{4a}, \frac{\pi}{4a}), \qquad \mathbf{q}_2 = (\frac{\pi}{4a}, -\frac{\pi}{4a}, \frac{\pi}{4a}), \qquad \mathbf{q}_3 = (\frac{\pi}{4a}, \frac{\pi}{4a}, -\frac{\pi}{4a}). \tag{2}$$

The linear combinations of these vectors in the limits of basic structure BZ will derivate the set of 32 modulation vectors.

The primitive spinel cell has 18 vacancies concerning a VCC lattice of the basic structure. Let us consider that the vacancy contains an atom with zero mass and is surrounded by a zero force field whether atoms are included in first, second or third coordination group or not. Such an atom does not carry changes into a dynamic matrix.

In terms of SSA approach a phonon spectrum of crystal lattice is defined by the solutions of the generalized eigenvalue problem [11]:

$$|D^{\mathrm{SSA}}(\mathbf{k}) - \omega^2(\mathbf{k})\mathrm{M}| = 0, \tag{3}$$

where M is a matrix of the mass defect operator [10–12], responsible for mass modulation of basic one-atom lattice. The structure of $D^{\mathrm{SSA}}(\mathbf{k})$ matrix is [12]:

$$D^{\mathrm{SSA}}(\mathbf{k}) = \begin{bmatrix} D_{q_1}(\mathbf{k}-\mathbf{q_1}) & D_{q_2}(\mathbf{k}-\mathbf{q_1}) & \cdots & D_{q_{32}}(\mathbf{k}-\mathbf{q_1}) \\ D_{q_i}(\mathbf{k}-\mathbf{q_2}) & D_{q_1}(\mathbf{k}-\mathbf{q_2}) & \cdots & D_{q_m}(\mathbf{k}-\mathbf{q_2}) \\ \vdots & \vdots & \ddots & \vdots \\ D_{q_j}(\mathbf{k}-\mathbf{q_{32}}) & D_{q_n}(\mathbf{k}-\mathbf{q_{32}}) & \ldots & D_{q_1}(\mathbf{k}-\mathbf{q_{32}}) \end{bmatrix}. \tag{4}$$

Here $D_{q_j}(\mathbf{k}-\mathbf{q}_i)$ – j-th fragment of a dynamic matrix of basic one-atom structure, averaged at mass and force field, defined in $\mathbf{k}-\mathbf{q}_i$ points of BZ $(i, j = 1, 2, \ldots, 32)$.

We can write the set of matrices $D_{q_j}(\mathbf{k}-\mathbf{q}_i)$, using simple short-range force constants model. Each force constant parameter describes the interaction in a corresponding coordination group. The mass modulation and modulation of force constants in the averaged basic structure leads to the correct parameters of the complex crystal.

Hereinafter we shall view the interaction in the limits of the first three coordination groups of a VCC basic lattice, that corresponds to interactions X–O, Y–O, and Y–Y (O–O).

Using the position and modulation vectors $\mathbf{r}_j$ and $\mathbf{q}_i$ we get the Fourier transformation F

$$F_{ij} = \frac{1}{\sqrt{32}} \exp(\mathrm{i}\mathbf{q}_i \mathbf{r}_j) \tag{5}$$

and apply in the equation (3). We obtain:

$$|F^{-1} D^{\mathrm{SSA}}(\mathbf{k}) F - \omega^2(\mathbf{k}) F^{-1} \mathrm{M} F| = |D^{\mathrm{cl}}(\mathbf{k}) - \omega^2(\mathbf{k}) M| = 0. \tag{6}$$

M is diagonal mass matrix. The structure for the force part of dynamic matrix D^{cl} is:

$$D^{\mathrm{cl}} = \left[\begin{array}{c|c|c|c c|c} D^{\mathrm{cl}}_{11} & 0 & D^{\mathrm{cl}}_{12} & 0 & \cdots & D^{\mathrm{cl}}_{1m} \\ \hline 0 & 0 & 0 & 0 & \cdots & 0 \\ \hline D^{\mathrm{cl}}_{21} & 0 & D^{\mathrm{cl}}_{22} & 0 & \cdots & D^{\mathrm{cl}}_{2m} \\ \hline 0 & 0 & 0 & 0 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \hline D^{\mathrm{cl}}_{n1} & 0 & D^{\mathrm{cl}}_{n2} & 0 & \cdots & D^{\mathrm{cl}}_{nm} \end{array}\right]. \tag{7}$$

The zero columns and strings correspond to the places, in which the vacancies are disposed, and coincide with zero diagonal elements of mass matrix M. Therefore, these columns and strings can be eliminated. Such a block matrix becomes equivalent to a classical dynamic matrix. Apparently, its order equals $3 \times (32 - 18) = 42$.

The group theoretical treatment of the optical zone-centre ($\mathbf{k}$=0) phonon modes for the spinel structure yields [14]

$$\Gamma(0) = \mathrm{A}_{1\mathrm{g}}(R) + \mathrm{E}_{\mathrm{g}}(R) + 3\mathrm{F}_{2\mathrm{g}}(R) + 4\mathrm{F}_{1\mathrm{u}}(IR) + \mathrm{F}_{1\mathrm{g}} + 2\mathrm{A}_{2\mathrm{u}} + 2\mathrm{E}_{\mathrm{u}} + 2\mathrm{F}_{2\mathrm{u}}. \tag{8}$$

Five modes $\mathrm{A}_{1\mathrm{g}}$, E_{g} and $3\mathrm{F}_{2\mathrm{g}}$ are Raman-active (marked as R) and four $4\mathrm{F}_{1\mathrm{u}}$ are infrared active (marked as IR).

As mentioned above, in the present investigation the dynamic matrix elements are calculated using a simple short-range force constant model. For this purpose we have obtained the evaluation of three parameters of interatomic interaction in the way pointed in [8], based on the experimental Raman data [2] by analytical expressions [6]:

$$\left\{ \begin{array}{lcl} m_{\mathrm{O}} \omega^2_{\mathrm{A}_{1\mathrm{g}}} & = & \alpha_1 + \alpha_2 + 8\alpha_3 \,, \\ m_{\mathrm{O}} \omega^2_{\mathrm{E}_{\mathrm{g}}} & = & \alpha_2 + 2\alpha_3 \,, \end{array} \right. \tag{9}$$

where $\omega_{\mathrm{A}_{1\mathrm{g}}}$ and $\omega_{\mathrm{E}_{\mathrm{g}}}$ are the observed Raman $\mathrm{A}_{1\mathrm{g}}$ and E_{g} modes; m_{O} is the mass of oxygen atom; α_1, α_2, α_3 represent the central force constants for interatomic interaction between the first, second and third nearest neighbors. We can take the values of the O–O and Ti–Ti force constants to be $\alpha_3 = 20.0$ N/m, based on earlier studies [8] of oxides spinel and the semi-empirical treatment by Oda et al. [15].

Table 1. Experimental phonon modes A_{1g}; E_g [2,8] and calculated short-range force constants α_1, α_2, α_3 for $LiTi_2O_4$ and $Li[Li_{1/3}Ti_{5/3}]O_4$ spinel systems.

Spinel system	A_{1g}, cm^{-1}	E_g, cm^{-1}	α_1, N/m	α_2, N/m	α_3, N/m
$LiTi_2O_4$ [8]	628	429	80.0	135.0	20.0
$Li[Li_{1/3}Ti_{5/3}]O_4$	675 [2]	427 [2]	139.5	133.1	20.0

The force constants for different spinel systems calculated by using the value $\alpha_3 = 20.0$ N/m and Raman data [2,8] are given in table 1.

As an example of using SSA approach, in a short-range force constant model we calculate the phonon frequencies in spinel systems in the following cases:

(i) The zone-centre phonon frequencies of lithium spinel $LiTi_2O_4$;

(ii) The dispersion curves of phonons for the end members of $Li_{1+x}Ti_{2-x}O_4$ spinel system above and below the point of metal-insulator phase transition;

(iii) The composition dependence of zone-centre phonons in $Li_{1+x}Ti_{2-x}O_4$ system ($0 \leqslant x \leqslant 1/2$) and $Li_{1-x}Mg_xTi_2O_4$ system ($0 \leqslant x \leqslant 1/2$) with a different type of substitutions.

3. Results and discussion

Using three force constants (see table 1), the phonon frequencies of $LiTi_2O_4$ at the zone centre are calculated in the framework of superspace symmetry and classified according to irreducible representations. These are given in table 2 along with the observed Raman measurements [2] and calculations of Gupta et al. [8] with the same parameters α_1, α_2, α_3.

A simple short-range force constant model, as was shown in papers [5–8], in spinel cases gives the similar frequencies for zone centre vibrations and Raman data. The consideration of a long-range Coulomb interatomic interaction may reduce the existing difference. One can see that the present results also practically coincide with calculations [8]. It testifies to the equivalence of dynamic matrices constructed in different approaches.

The phonon dispersion curves calculated for $LiTi_2O_4$ and $Li[Li_{1/3}Ti_{5/3}]O_4$ are shown in figure 2. The mass of the introduced Li ion in $Li[Li_{1/3}Ti_{5/3}]O_4$ system is averaged on all occupied octahedral sites. We have made our calculations of $LiTi_2O_4$ for comparison with the corresponding one, which used a short-range Buckingham potential and a long-range Coulomb interaction [4]. The given model enables us to observe the qualitative difference in the phonon spectrum of insulator $Li[Li_{1/3}Ti_{5/3}]O_4$ and metallic $LiTi_2O_4$ spinels.

The detailed analysis of our calculations shows (see figure 2) that the movement from Γ point in Γ–R direction is associated with the splitting of each of triple

Table 2. Observed [2] and calculated zone-centre frequencies of $LiTi_2O_4$ in cm^{-1}.

Species	Measurements [2]	Calculations [8]	Our calculations
A_{1g}	628	628.0	628.4
A_{2u}	—	664.6	664.5
	—	323.8	323.7
F_{1g}	—	429.0	429.3
F_{1u}	—	668.3	668.3
	—	508.6	508.5
	—	424.9	424.9
	—	210.3	210.2
F_{2g}	—	652.4	652.5
	494	542.4	542.3
	339	344.2	344.2
F_{2u}	—	542.5	542.4
	—	165.0	165.0
E_g	429	429.0	429.3
E_u	—	603.3	603.1
	—	236.8	236.7

generated modes $3F_{2g}$, $4F_{1u}$, F_{1g}, $2F_{2u}$ into doubly generated and single generated. It leads to 28 dispersion curves in the direction Γ–R (14 doubly generated and 14 single generated branches).

The movement from point Γ in Γ–X direction is associated with similar splitting of triple-generated modes and additional splitting of doubly generated modes $2E_u$. In the total we have 30 branches in Γ–X direction (12 doubly generated and 18 single generated).

In Γ–K direction one can observe 42 modes (all modes are single generated).

The $Li_{1+x}Ti_{2-x}O_4$, spinel system ($0 \leqslant x \leqslant 1/3$) undergoes a metal-insulator transition near $x \approx 0.15$. In $LiTi_2O_4$ Li and Ti ions occupy tetrahedral and octahedral sites, respectively. In $Li[Li_{1/3}Ti_{5/3}]O_4$ an additional substitution of Ti ions by Li leads to a loss of metallic properties [1–3].

In order to determine an effect of mass distribution in cationic sublattice on the phonons in superconducting lithium spinel $LiTi_2O_4$, we have carried out a series of model examinations of substitution in octahedral and tetrahedral sites (figure 3).

The masses of atoms in the sites of substitutions are calculated by assuming the linear variation from one atom mass to the other with composition x:

$$m^o(Li_{1+x}Ti_{2-x}O_4) = (1-x)m^o(LiTi_2O_4) + xm^o(Li[Li_{1/3}Ti_{5/3}]O_4), \quad (0 \leqslant x \leqslant 1/2),$$
$$m^t(Li_{1-x}Mg_xTi_2O_4) = (1-x)m^t(LiTi_2O_4) + xm^t(MgTi_2O_4), \quad (0 \leqslant x \leqslant 1/2),$$

where m^o and m^t are the masses of atoms of corresponding systems in octahedral

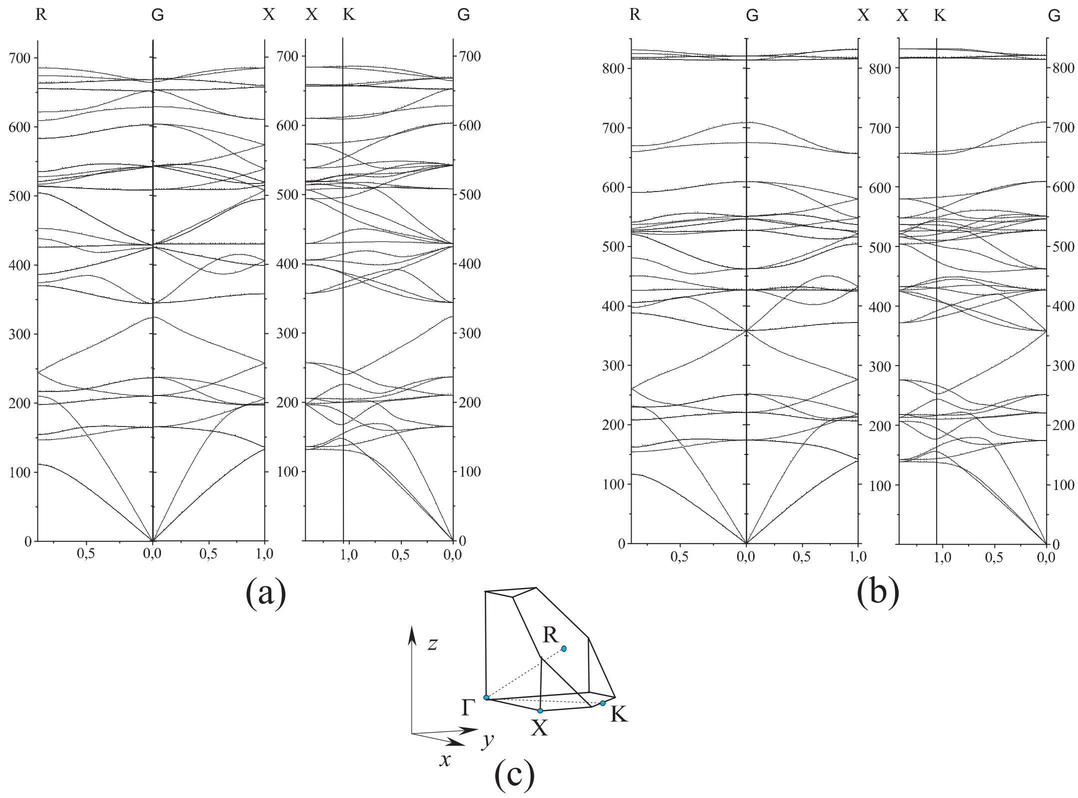


Figure 2. Phonon spectrum of crystals in symmetry directions, calculated using a short-range force constant model. Wave vector defined in terms of $\pi/4a$. a) $Li[Ti_2]O_4$, (α_1 = 80.0 N/m, α_2 = 135.0 N/m, α_3 = 20.0 N/m); b) $Li[Li_{1/3}Ti_{5/3}]O_4$, ($\alpha_1 = 139.5$ N/m, $\alpha_2 = 133.1$ N/m, $\alpha_3 = 20.0$ N/m); c) 1/8 of Brillouin zone for FCC spinel lattice with lattice parameter $4a$. The length of an edge of an octant along the x-axes is $\pi/4a$.

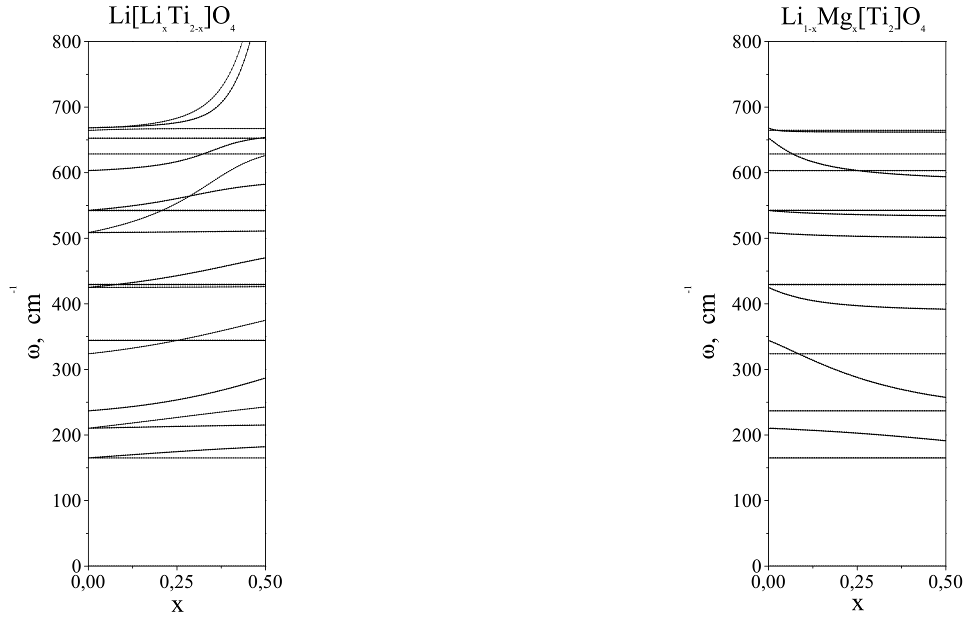
and tetrahedral sites, locally involved in the given substitutions.

The force constants are taken corresponding to the end members of spinel systems $Li[Li_xTi_{2-x}]O_4$ and $Li_{1+x}Mg_x[Ti_2]O_4$ with $x = 0$ (In both cases $LiTi_2O_4$ (see table 1)). We do not change them during the whole composition range.

By modeling different types of substitution we can find the anomaly of the phonon frequencies in the system $Li[Li_xTi_{2-x}]O_4$, which undergoes a metal-insulator transition contrary to $Li_{1-x}Mg_x[Ti_2]O_4$ with the saved metallic properties [2,4].

As we can see in figure 3a the energy of some modes (F_{1u}) sharply increases in the field of anomaly. It does not provide advantage to the system as a whole. The light atoms Li ($M_{Li} = 6.9$) are not inclined to occupy the octahedral sites relative to oxygen framework ($M_O = 16.0$) together with heavy atoms of Ti ($M_{Ti} = 47.9$). One can assume the F_{1u} modes will indicate the phase transition by taking into account the adequate model of interatomic interaction.

The calculations shown in figure 3a should not be viewed as the ones simulating the metal-insulator phase transition. The present model of lattice dynamics is very simple in predicting or simulating any phase transition. The anomaly just shows



(a) (b)

Figure 3. Compositional variation of zone-centre phonon frequencies in mixed systems: a) $Li[Li_xTi_{2-x}]O_4$; b) $Li_{1-x}Mg_x[Ti_2]O_4$.

the dynamical instability of spinel lattice with given parameters when octahedral substitutions occur by light atoms. It can be balanced by the renormalization of force constants that one can interpret as a phase transition.

In $Li_{1-x}Mg_x[Ti_2]O_4$ the substitution of cations occurs in tetrahedral sites. Figure 3*b* shows no anomaly of phonon branches. The given lattice model in this case does not guarantee any transition in a spinel system.

Finally, as we can see in figure 3*a* that some phonon branches (F_{1u} and F_{2u}) of the system $Li[Li_xTi_{2-x}]O_4$ exhibit two-mode behavior in which two sets of phonon frequencies are observed for the whole composition range. On the other hand, only one set of phonon frequencies varies with the concentration of the components in $Li_{1-x}Mg_x[Ti_2]O_4$ system (see figure 3*b*). Thus, our calculations in mixed spinel systems predict for F_{1u} and F_{2u} modes, one- and two-mode behaviors in case of tetrahedral and octahedral substitution, respectively. However, precise infrared and inelastic-neutron-scattering experiments are required to confirm the predicted behavior of phonons in $Li[Li_xTi_{2-x}]O_4$ and $Li_{1-x}Mg_x[Ti_2]O_4$ systems.

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Фононний спектр в околі фазового переходу метал-діелектрик системи $Li_{1+x}Ti_{2-x}O_4$

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У надпросторовому підході, використовуючи модель короткодіючих силових постійних, розраховані фонони двох крайніх членів шпінелевої системи $Li_{1+x}Ti_{2-x}O_4$: металічної $LiTi_2O_4$ та діелектричної $Li[Li_{1/3}Ti_{5/3}]O_4$. Застосовуючи різні моделі заміщення, досліджена композиційна залежність оптичних фононів в центрі зони Бриллюєна для $Li_{1+x}Ti_{2-x}O_4$ в околі фазового переходу та $Li_{1-x}Mg_xTi_2O_4$. Одно- та двомодову поведінку передбачено для F_{1u} та F_{2u} мод у випадку тетраедричного та октаедричного заміщення відповідно.

Ключові слова: *надпросторова симетрія, фононний спектр, шпінель, $Li_{1+x}Ti_{2-x}O_4$*

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