https://doi.org/10.15407/ujpe68.6.397

A.P. NAUMENKO, V.O. GUBANOV

Taras Shevchenko National University of Kyiv
(64/13, Volodymyrs'ka Str., Kyiv 01601, Ukraine; e-mail: a_naumenko@univ.kiev.ua)

SYMMETRY OF ENERGY STATES IN α-LiIO$_3$ CRYSTALS TAKING TIME-INVERSION INVARIANCE INTO ACCOUNT

Using the theory of the projective representations of groups, the non-degenerate representations of the wave vector groups at points Γ, Δ, and A of the Brillouin zone for the α-LiIO$_3$ crystal have been constructed, and their compatibility conditions have been found. The energy states of the α-LiIO$_3$ crystal at those points are classified taking the time-inversion invariance into account, and their corresponding classification in the large (Jones) zone is provided. Based on experimentally measured first-order Raman spectra, the dispersion curves of phonon branches in the $\Gamma - A$ direction are plotted. Contributions of overtones and components at points Γ and A to experimentally recorded second-order Raman spectrum have been discussed; their role in the second-order spectrum formation is associated with the considered features in the phonon state density at those points and the vibrational states of other critical points in the Brillouin zone. It has been concluded that the application of the quasi-molecular approximation is valid, when considering the lattice dynamics of α-LiIO$_3$ crystals.

Keywords: crystal lattice dynamics, Brillouin zone, Jones zone, Raman spectroscopy, lithium iodate.

1. Introduction

The energy spectra of vibrational states in gyrotropic hexagonal lithium iodate (α-LiIO$_3$) crystals have been thoroughly studied using the methods of infrared (IR) and Raman spectroscopies in a lot of works [1–4]. Extensive information has also been accumulated concerning the study of the energy spectra of polariton states in those crystals and their dispersion near the center of the Brillouin zone [5]. However, no theoretical calculations of the dispersion of elementary excitations over the Brillouin zone have been carried out for α-LiIO$_3$ crystals. The invariance of energy states with respect to the time inversion at points that are not located at the Brillouin zone center (point Γ) was also not taken into account.

In this work, to elucidate the indicated issues, the method of constructing irreducible projective representations of the wave vector groups has been applied for the first time to α-LiIO$_3$ crystals. This method makes it possible to consider the time-inversion invariance of energy states, introduce their classification in the large (Jones) zone, and draw conclusions at the qualitative level about the dispersion of phonon states; the latter can be studied experimentally via measuring the 2nd-order Raman spectra in those crystals. The approximate correlation method for estimating the form of phonon dispersion curves in the $\Gamma - A$ direction of the Brillouin zone in α-

Citation: Naumenko A.P., Gubanov V.O. Symmetry of energy states in α-LiIO$_3$ crystals taking time-inversion invariance into account. *Ukr. J. Phys.* **68**, No. 6, 397 (2023). https://doi.org/ 10.15407/ujpe68.6.397.

Цитування: Науменко А.П., Губанов В.О. Симетрія енергетичних станів з урахуванням інваріантності до інверсії часу та дисперсія фононних гілок у гіротропних кристалах α-LiIO$_3$. *Укр. фіз. журн.* **68**, №6, 398 (2023).

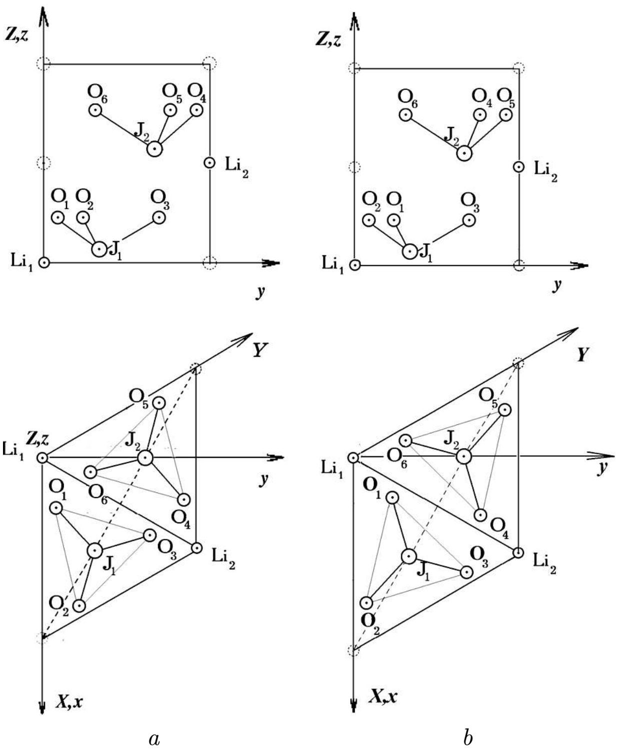


Fig. 1. Unit cells of α-LiIO$_3$ crystal: right- (a) and left-handed (b) enantiomorphic modifications

LiIO$_3$ crystals and the possibility of using the quasi-molecular approach to interpret the energy spectra of their elementary excitations are also discussed.

2. Symmetry and Crystalline Structure of α-LiIO$_3$ Crystals

The symmetry of both enantiomorphic structural modifications of hexagonal α-LiIO$_3$ crystals is described by the same space group $P6_3$ (C_6^6), and the crystal class to which they belong is presented by the point group $6C_6$. The optical activity of those crystals is associated with the chiral arrangement of $(IO_3)^-$ ions in their lattices. These ions form structural groups that are initially non-chiral and are not subjected to asymmetric deformations during the crystallization (i.e., they do not acquire a deformation-induced chirality). The $(IO_3)^-$ groups possess the $3m$ (C_{3v}) symmetry in the free state. Owing to the presence of reflection planes, those initially non-chiral groups, when being deformed at the crystallization in the α-LiIO$_3$ lattice, do not change their own symmetry. But they turn out somewhat rotated around the axes passing through them. As a result, they retain only the symmetry elements of the $3(C_3)$ group that are in common with the structure surrounding them and consisting of Li$^+$ ions. After the mutual loss of the rotation axes and reflection planes that do not coincide for both structures, the $(IO_3)^-$ groups become chirally arranged over the lattice.

The unit cells of both enantiomers of crystalline α-LiIO$_3$ contain 10 atoms each, which form two formula units. They differ from each other by the rotation of the $(IO_3)^-$ ions around the 3rd-order polar axes that pass through their centers and in parallel to the 6th-order axis. In particular, this orientation coincides spatially and by direction with the crystallographic axis OZ (we assume that the directions of the polar axes are determined, according to the sequence of the chemical symbol recording in the compound formula, by the direction from the atom I in the $(IO_3)^-$ groups to the center of the equilateral triangle formed by three oxygen atoms). The $(IO_3)^-$ ions are rotated by a small angle ϑ with respect to the orientation at which the Li, I, and O atoms would lie in the same planes that contain the c_6 axis. A counterclockwise rotation from the viewpoint of an observer looking against the polar axis direction corresponds to a positive angle value, whereas a clockwise rotation under the same observation conditions corresponds to a negative one. The former structural form will be called the right-handed enantiomorphic modification of α-LiIO$_3$, and the latter the left-handed one [1].

In Fig. 1, a, the unit cell (it coincides with the primitive one) of the α-LiIO$_3$ crystal in the right-handed enantiomorphic modification is shown in two projections. Its parameters are $a_1 = (5.170 \pm 0.002)$ Å, where $\mathbf{a}_1 \| OZ$, and $a_2 = (5.478 \pm 0.002)$ Å, where $\mathbf{a}_2 \| OX$ [6–9]. The atomic coordinates in the primitive cell in the crystallographic coordinate system are selected as follows: Li$_1$ at (X, Y, Z) (position a) and Li$_2$ at $(1-X, 1-Y, Z+1/2)$, where $X = 0$, $Y = 0$, and $Z = 0$, i.e., the origin of the crystallographic coordinate system coincides with the position of atom Li$_1$;

[1] The definition of the right- and left-handed enantiomorphic modifications of the crystalline structure is introduced here by postulating the polar axis direction and using only crystallographic data. Currently it is assumed that the right-handed enantiomorphic modification of α-LiIO$_3$ crystals, as well as many others among the corresponding gyrotropic classes, is always the modification with the positive piezoelectric coefficient $d_{33} > 0$.

Table 1. **Characters of irreducible representations of the point group 6**

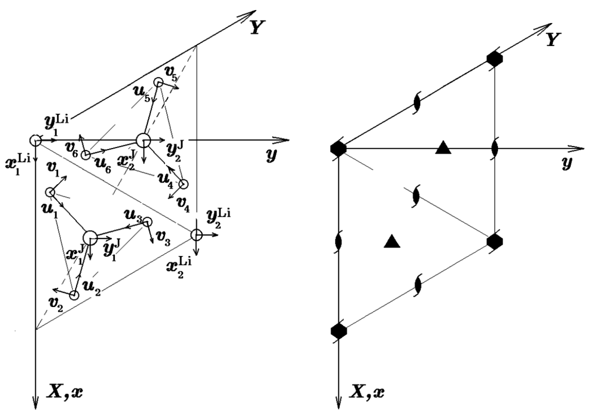
$6(C_6)$	e	c_3	c_3^2	c_2	c_6^5	c_6	$n_{\rm vib}$	$n_{\rm ac}$	$n_{\rm opt}$	Відбір
A_1	1	1	1	1	1	1	5	1	4	μ_z; α_{zz}, $\alpha_{xx}+\alpha_{yy}$
A_2	1	1	1	−1	−1	−1	5	0	5	v, ia
B_1	1	ε_3	ε_3^{-1}	1	ε_3	ε_3^{-1}	5	0	5	
E_1 B_2	1	ε_3	ε_3^{-1}	−1	$-\varepsilon_3$	$-\varepsilon_3^{-1}$	5	1	4	$\alpha_{xx}-\alpha_{yy}$, α_{xy}; ia
E_2 B_3	1	ε_3^{-1}	ε_3	1	ε_3^{-1}	ε_3	5	0	5	μ_x, μ_y; α_{zx}, α_{zy}
B_4	1	ε_3^{-1}	ε_3	−1	$-\varepsilon_3^{-1}$	$-\varepsilon_3$	5	1	4	
$\Gamma_{\rm vib}$	30	0	0	0	0	0				
$\Gamma_{\rm ac}$	3	0	0	−1	2	2				

I$_1$ at (X,Y,Z) and I$_2$ at $(1-X,1-Y,Z+1/2)$, where $X=2/3$, $Y=1/3$, and $Z=0.0727\pm0.0067$ (position b); O$_1$ at (X,Y,Z), O$_2$ at $(1-Y,\ X-Y,\ Z)$, O$_3$ at $(1-X+Y,1-X,\ Z)$, O$_4$ at $(X-Y,X,Z+1/2)$, O$_5$ at $(1-X,1-Y,Z+1/2)$, and O$_6$ $(Y,1-X+Y,Z+1/2)$, where $X=0.3437\pm0.0013$, $Y=0.0957\pm0.0013$, and $Z=0.2345\pm0.0023$ (position c). Figure 1,b illustrates the unit cell of the α-LiIO$_3$ crystal in the left enantiomorphic modification. Surely, its parameters do not differ from the above parameters for the unit cell of the α-LiIO$_3$ crystal in the right-handed modification.

In Fig. 2, a, the vectors of the generating basis are shown, which are used below to construct the forms of normal crystal-lattice vibrations. They are orthogonal vectors in the displacement space and transform into one another for various atoms of the same chemical nature at symmetry transformations [10].

Figure 2, b demonstrates a plot of the space symmetry group $P6_3$ [11]. It illustrates the positions of the symmetry elements in the primitive cell of the α-LiIO$_3$ crystal, which is determined by the choice of atomic coordinates used above. This plot characterizes the symmetry of the space group $P6_3$ and is identical for the right- and left-handed enantiomorphic structural forms of α-LiIO$_3$ provided a similar choice of atomic coordinates (with the coordinate swapping $X \rightleftarrows Y$, of course). In what follows, without loss of generality, we will analyze the dynamics of the crystal lattice of α-LiIO$_3$ crystals in the right-handed structural modification.

The characteristics of irreducible representations of the point group 6 are given in Table 1. This well-known table is exhibited in the form, where the irreducible representations are systematized accounting for the internal structure of the group 6, which is a direct product of the groups 3 and 2 ($6=3\times2$). The main axis in the group 6 is axis 3 (c_3), because it is the highest-order axis in the highest-order subgroup entering the direct product defining the group 6. Furthermore, the group 6 (C_6) is isomorphic to the group $\bar{3}$ (C_{3i}), which is a direct product of the groups 3 and $\bar{1}$ ($\bar{3}=3\times\bar{1}$). The isomorphic groups 6 and 3 must have the same table of characters of irreducible representations, and the method of its construction for the group $\bar{3}$ (the classification of representations into symmetric and antisymmetric ones with respect to inversion) is generally accepted. It is this systematics that is recommended for applications [12–15]. As one can see later, it is this systematics that is preferred, when constructing projective representations of point groups whose applications have become recently more and more widespread.



a *b*

Fig. 2. Generating basis (a) and graph of the space symmetry group for the right-handed enantiomorphic modification α-LiIO$_3$ crystal (b)

Unfortunately, the classification (several of its variants) that does not take the internal structure of group 6 into account remains widely applicable. In its framework, axis 6 (c_6) is considered to be the main axis in the cyclic Abelian group 6, and the number ordering of irreducible representations is carried out according to a formal attribute based on the order of counting the values of $\sqrt[6]{1}$ in the complex plane, which is ambiguous in principle [16,17]. Nevertheless, one of the variants of this classification was applied in work [1], where the experimental results obtained for phonon states in α-$LiIO_3$ crystals were presented and classified. The use of an unambiguous classification (we prefer this variant) results in that we consider the vibrational modes of symmetry E_2 from work [1] as vibrational modes of symmetry E_1 in the crystals of class 6 (C_6); and vice versa, we consider the vibrational modes of symmetry E_1 from work [1] as vibrational modes of symmetry E_2.

3. Correlation Analysis of the Phonon Spectrum of α-$LiIO_3$ Crystals. Symmetry Coordinates and Forms of Normal Vibrations

Let us first consider the commonly used approximate correlation method to analyze the phonon spectrum of α-$LiIO_3$ crystals. It is based on a quasi-molecular approach (hereafter, the structure of the right-handed enantiomorphic modification of the α-$LiIO_3$ crystal is used for calculations; for the left-handed enantiomorphic form, all calculations are identical). In this approach, two strongly coupled molecular structural formations are distinguished in the crystal unit cell: these are two ions $(IO_3)^-$ whose internal bonds are stronger than their external bonds with Li^+ ions and much stronger than the bonds between the quasi-molecular α-$LiIO_3$ formations. The classification of the bonds in the α-$LiIO_3$ lattice into strong and weak ones in the framework of this method makes it possible to find the approximate forms of normal vibrations used as a basis to interpret the phonon spectrum. In so doing, the fundamental normal vibrations of the crystal lattice are classified into "internal" and "external" with respect to the vibrations of their structural elements keeping their relative individuality. Internal vibrations are distinguished by their symmetry type, or, as is often the case, they can be classified into quasi-valent and quasi-deformational ones; external vibrations can be classified into translational and librational ones.

The phonon spectrum for α-$LiIO_3$ crystals in the selected direction in the **k**-space has 30 branches. At the point Γ, the fundamental vibrational modes described by the representation of the displacements of all atoms in the primitive cell are classified by the irreducible representations of group 6 as follows:
in general,

$$\Gamma_{\rm vib} = 5A_1 + 5A_2 + 5B_1 + 5B_2 + 5B_3 + 5B_4,$$

for acoustic vibrations,

$$\Gamma_{\rm ac} = A_1 + B_2 + B_4,$$

and for optical ones,

$$\Gamma_{\rm opt} = 4A_1 + 5A_2 + 5B_1 + 4B_2 + 5B_3 + 4B_4.$$

As a result of the time-inversion invariance of one-dimensional complex conjugate representations, by combining them into two-dimensional ones, we obtain

$$\begin{aligned}
&\Gamma_{\rm vib} = 5[A_1 + A_2 + (B_1 + B_3) + (B_2 + B_4)] = \\
&= 5A_1 + 5A_2 + 5E_1 + 5E_2, \\
&\Gamma_{\rm ac} = A_1 + (B_2 + B_4) = A_1 + E_2, \\
&\Gamma_{\rm opt} = 5[A_1 + 5A_2 + 5(B_1 + B_3) + 4(B_2 + B_4)] = \\
&= 4A_1 + 5A_2 + 5E_1 + 4E_2.
\end{aligned}$$

Among 27 fundamental optical vibrational modes, 12 modes are active in the IR absorption [modes $4A_1$ and $4E_2$ ($4B_2$ and $4B_4$)], 22 modes are Raman active [modes $4A_1$, $5E_1$ ($5B_1$ and $5B_3$), and $4E_2$ ($4B_2$ and $4B_4$)], and 5 modes are neither active in the IR absorption nor in Raman spectra (RS) (modes $5A_2$). Since modes A_1 and E_2 are simultaneously IR and Raman active, they can be additionally separated into $TO - LO$ pairs because of long-range Coulomb forces.

Let us construct the forms for the fundamental normal vibrations in the α-$LiIO_3$ crystal lattice. They are orthogonal vibrational functions that are linear combinations of symmetrized vibrational (dynamic) coordinates or symmetrized displacements [10, 16]. The latter, being classified by a symmetry type analogously to vibrational modes, look as follows:
for symmetry A_1,

$$s_1^{A_1} = \frac{1}{\sqrt{2}}(z_1^{\rm I} + z_2^{\rm I}),$$

$$s_2^{A_1} = \frac{1}{\sqrt{6}}(z_1^{\rm O} + z_2^{\rm O} + z_3^{\rm O} + z_4^{\rm O} + z_5^{\rm O} + z_6^{\rm O}),$$
$$s_3^{A_1} = \frac{1}{\sqrt{6}}(u_1^{\rm O} + u_2^{\rm O} + u_3^{\rm O} + u_4^{\rm O} + u_5^{\rm O} + u_6^{\rm O}),$$
$$s_4^{A_1} = \frac{1}{\sqrt{6}}(v_1^{\rm O} + v_2^{\rm O} + v_3^{\rm O} + v_4^{\rm O} + v_5^{\rm O} + v_6^{\rm O}),$$
$$s_5^{A_1} = \frac{1}{\sqrt{2}}(z_1^{\rm Li} + z_2^{\rm Li}),$$

for symmetry A_2,

$$s_1^{A_2} = \frac{1}{\sqrt{2}}(z_1^{\rm I} - z_2^{\rm I}),$$
$$s_2^{A_2} = \frac{1}{\sqrt{6}}(z_1^{\rm O} + z_2^{\rm O} + z_3^{\rm O} - z_4^{\rm O} - z_5^{\rm O} - z_6^{O}),$$
$$s_3^{A_2} = \frac{1}{\sqrt{6}}(u_1^{\rm O} + u_2^{\rm O} + u_3^{\rm O} - u_4^{\rm O} - u_5^{\rm O} - u_6^{\rm O}),$$
$$s_4^{A_2} = \frac{1}{\sqrt{6}}(v_1^{\rm O} + v_2^{\rm O} + v_3^{\rm O} - v_4^{\rm O} - v_5^{\rm O} - v_6^{\rm O}),$$
$$s_5^{A_2} = \frac{1}{\sqrt{2}}(z_1^{Li} - z_2^{\rm Li}),$$

for symmetry B_1,

$$s_1^{B_1} = (x_1^{\rm I} + iy_1^{\rm I}) - (x_2^{\rm I} + iy_2^{\rm I}),$$
$$s_2^{B_1} = \frac{1}{\sqrt{6}}(z_1^{\rm O} + \epsilon_3 z_2^{\rm O} + \epsilon_3^{-1} z_3^{\rm O} + z_4^{\rm O} + \epsilon_3 z_5^{\rm O} + \epsilon_3^{-1} z_6^{\rm O}),$$
$$s_3^{B_1} = (u_1^{\rm O} + \epsilon_3 u_2^{\rm O} + \epsilon_3^{-1} u_3^{\rm O} + u_4^{\rm O} + \epsilon_3 u_5^{\rm O} + \epsilon_3^{-1} u_6^{\rm O}),$$
$$s_4^{B_1} = (v_1^{\rm O} + \epsilon_3 v_2^{\rm O} + \epsilon_3^{-1} v_3^{\rm O} + v_4^{\rm O} + \epsilon_3 v_5^{\rm O} + \epsilon_3^{-1} v_6^{\rm O}),$$
$$s_5^{B_1} = (x_1^{\rm Li} + iy_1^{\rm Li}) - (x_2^{\rm Li} + iy_2^{\rm Li}),$$

for symmetry B_2,

$$s_1^{B_2} = (x_1^{\rm I} + iy_1^{\rm I}) + (x_2^{\rm I} + iy_2^{\rm I}),$$
$$s_2^{B_2} = (z_1^{\rm O} + \epsilon_3 z_2^{\rm O} + \epsilon_3^{-1} z_3^{\rm O} - z_4^{\rm O} - \epsilon_3 z_5^{\rm O} - \epsilon_3^{-1} z_6^{\rm O}),$$
$$s_3^{B_2} = (u_1^{\rm O} + \epsilon_3 u_2^{\rm O} + \epsilon_3^{-1} u_3^{\rm O} - u_4^{\rm O} + \epsilon_3 u_5^{\rm O} + \epsilon_3^{-1} u_6^{\rm O}),$$
$$s_4^{B_2} = (v_1^{\rm O} + \epsilon_3 v_2^{\rm O} + \epsilon_3^{-1} v_3^{\rm O} - v_4^{\rm O} - \epsilon_3 v_5^{\rm O} - \epsilon_3^{-1} v_6^{\rm O}),$$
$$s_5^{B_2} = (x_1^{\rm Li} + iy_1^{\rm Li}) + (x_2^{\rm Li} + iy_2^{\rm Li}),$$

for symmetry B_3,

$$s_1^{B_3} = (x_1^{\rm I} - iy_1^{\rm I}) - (x_2^{\rm I} - iy_2^{\rm I}),$$
$$s_2^{B_3} = (z_1^{\rm O} + \epsilon_3^{-1} z_2^{\rm O} + \epsilon_3 z_3^{\rm O} + z_4^{\rm O} + \epsilon_3^{-1} z_5^{\rm O} + \epsilon_3 z_6^{\rm O}),$$
$$s_3^{B_3} = (u_1^{\rm O} + \epsilon_3^{-1} u_2^{\rm O} + \epsilon_3 u_3^{\rm O} + u_4^{\rm O} + \epsilon_3^{-1} u_5^{\rm O} + \epsilon_3 u_6^{\rm O}),$$
$$s_4^{B_3} = (v_1^{\rm O} + \epsilon_3^{-1} v_2^{\rm O} + \epsilon_3 v_3^{\rm O} + v_4^{\rm O} + \epsilon_3^{-1} v_5^{\rm O} + \epsilon_3 v_6^{\rm O}),$$
$$s_5^{B_3} = (x_1^{\rm Li} - iy_1^{\rm Li}) - (x_2^{\rm Li} - iy_2^{\rm Li}),$$

and for symmetry B_4,

$$s_1^{B_4} = (x_1^{\rm I} - iy_1^{\rm I}) + (x_2^{\rm I} - iy_2^{\rm I}),$$
$$s_2^{B_4} = (z_1^{\rm O} + \epsilon_3^{-1} z_2^{\rm O} + \epsilon_3 z_3^{\rm O} - z_4^{\rm O} - \epsilon_3^{-1} z_5^{\rm O} - \epsilon_3 z_6^{\rm O}),$$
$$s_3^{B_4} = (u_1^{\rm O} + \epsilon_3^{-1} u_2^{\rm O} + \epsilon_3 u_3^{\rm O} - u_4^{\rm O} - \epsilon_3^{-1} u_5^{\rm O} - \epsilon_3 u_6^{\rm O}),$$
$$s_4^{B_4} = (v_1^{\rm O} + \epsilon_3^{-1} v_2^{\rm O} + \epsilon_3 v_3^{\rm O} - v_4^{\rm O} - \epsilon_3^{-1} v_5^{\rm O} - \epsilon_3 v_6^{\rm O}),$$
$$s_5^{B_4} = (x_1^{\rm Li} - iy_1^{\rm Li}) + (x_2^{\rm Li} - iy_2^{\rm Li}).$$

After combining the vibrational states and accounting for their time-inversion invariance ($B_1 + B_3 \Longrightarrow E_1$ and $B_2 + B_4 \Longrightarrow E_2$), the symmetrized displacements take the following forms:
for symmetry E_1,

$$s_{1\alpha}^{E_1} = \frac{1}{\sqrt{2}}\left(x_1^J - x_2^{\rm I}\right),$$
$$s_{2\alpha}^{E_1} = \frac{1}{\sqrt{12}}\left(2z_1^{\rm O} - z_2^{\rm O} - z_3^{\rm O} + 2z_4^{\rm O} - z_5^{\rm O} - z_6^{\rm O}\right),$$
$$s_{3\alpha}^{E_1} = \frac{1}{\sqrt{12}}\left(2u_1^{\rm O} - u_2^{\rm O} - u_3^{\rm O} + 2u_4^{\rm O} - u_5^{\rm O} - u_6^{\rm O}\right),$$
$$s_{4\alpha}^{E_1} = \frac{1}{\sqrt{12}}\left(2v_1^{\rm O} - v_2^{\rm O} - v_3^{\rm O} + 2v_4^{\rm O} - v_5^{\rm O} - v_6^{\rm O}\right),$$
$$s_{5\alpha}^{E_1} = \frac{1}{\sqrt{2}}\left(x_1^{\rm Li} - x_2^{\rm Li}\right),$$
$$s_{1\beta}^{E_1} = \frac{1}{\sqrt{2}}\left(y_1^J - y_2^J\right),$$
$$s_{2\beta}^{E_1} = \frac{1}{2}\left(z_2^{\rm O} - z_3^{\rm O} + z_5^{\rm O} - z_6^{\rm O}\right),$$
$$s_{3\beta}^{E_1} = \frac{1}{2}\left(u_2^{\rm O} - u_3^{\rm O} + u_5^{\rm O} - u_6^{\rm O}\right),$$
$$s_{4\beta}^{E_1} = \frac{1}{2}\left(\upsilon_2^{\rm O} - \upsilon_3^{\rm O} + \upsilon_5^{\rm O} - \upsilon_6^{\rm O}\right),$$
$$s_{5\beta}^{E_1} = \frac{1}{\sqrt{2}}\left(y_1^{\rm Li} - y_2^{\rm Li}\right).$$

and for symmetry E_2,

$$s_{1\alpha}^{E_2} = \frac{1}{\sqrt{2}}\left(x_1^{\rm I} + x_2^{\rm I}\right),$$
$$s_{2\alpha}^{E_2} = \frac{1}{\sqrt{12}}\left(2z_1^{\rm O} - z_2^{\rm O} - z_3^{\rm O} - 2z_4^{\rm O} + z_5^{\rm O} + z_6^{\rm O}\right),$$

$$s_{3\alpha}^{E_2} = \frac{1}{\sqrt{12}}\left(2u_1^{\mathrm{O}} - u_2^{\mathrm{O}} - u_3^{\mathrm{O}} - 2u_4^{\mathrm{O}} + u_5^{\mathrm{O}} + u_6^{\mathrm{O}}\right),$$
$$s_{4\alpha}^{E_2} = \frac{1}{\sqrt{12}}\left(2v_1^{\mathrm{O}} - v_2^{\mathrm{O}} - v_3^{\mathrm{O}} - 2v_4^{\mathrm{O}} + v_5^{\mathrm{O}} + v_6^{\mathrm{O}}\right),$$
$$s_{5\alpha}^{E_2} = \frac{1}{\sqrt{2}}\left(x_1^{\mathrm{Li}} + x_2^{\mathrm{Li}}\right),$$
$$s_{1\beta}^{E_2} = \frac{1}{\sqrt{2}}\left(y_1^{\mathrm{I}} + y_2^{\mathrm{I}}\right),$$
$$s_{2\beta}^{E_2} = \frac{1}{2}\left(z_2^{\mathrm{O}} - z_3^{\mathrm{O}} - z_5^{\mathrm{O}} + z_6^{\mathrm{O}}\right),$$
$$s_{3\beta}^{E_2} = \frac{1}{2}\left(u_2^{\mathrm{O}} - u_3^{\mathrm{O}} - u_5^{\mathrm{O}} + u_6^{\mathrm{O}}\right),$$
$$s_{4\beta}^{E_2} = \frac{1}{2}\left(v_2^{\mathrm{O}} - v_3^{\mathrm{O}} - v_5^{\mathrm{O}} + v_6^{\mathrm{O}}\right),$$
$$s_{5\beta}^{E_2} = \frac{1}{\sqrt{2}}\left(y_1^{\mathrm{Li}} + y_2^{\mathrm{Li}}\right).$$

The set of expressions for the linear combinations of symmetric displacements for all normal vibrations comprises a solution to the problem of finding the forms of normal vibrations.

It is convenient to begin the construction of expressions for normal vibrations $\varphi_{i\nu}^{\mu}$ – here, the indices μ, i, and ν denote, as it was for the symmetrized displacements, the representation type, the sequence number of the normal vibration, and the type of its partner functions, respectively – from the acoustic modes for which the linear combinations of symmetrized displacements are obvious. Then the approximate expressions for normal vibrations that are orthogonal to the previously found forms should be determined. They can be divided into quasi-valent and quasi-deformational ones. All forms for normal vibrations, both exact and approximate ones, expressed in terms of symmetrized displacements are given on the right-hand side of Table 2. The left-hand side of Table 2 contains a correlation diagram obtained by comparing the vibrational modes, which demonstrates the correspondence of the normal vibrations in the α-LiIO$_3$ crystal to the vibrations of an isolated XY_3 pyramid [10].

It is worth to note that, in the framework of this approach, we immediately obtain analytic expressions for the vibrations in the α-LiIO$_3$ crystal that form Davydov doublets, for example, $(A_1)_1 - (A_2)_1$, $(A_1)_2 - (A_2)_2$, and so on for pairs of vibrations. At the same time, for A-type oscillations, the second Davydov component is not observed in the spectra, because it is a "silent" mode.

Table 2. **Diagram of correspondence between normal vibrations in α-LiIO$_3$ crystal and vibrations of an isolated IO$_3$ ion**

$(\mathrm{IO}_3)^-$	$(\mathrm{IO}_3)^- + {}$ $+\mathrm{Li}^+$	α-LiIO$_3$ (crystal)
$(A_1)_1$	$(A)_1$	$(A_1)_1\ \varphi_1^{A_1} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_1} + s_2^{A_1}) + s_5^{A_1}\right]$
		$(A_2)_1\ \varphi_1^{A_2} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_2} + s_2^{A_2}) + s_5^{A_2}\right]$
	$(A)_2$	$(A_1)_2\ \varphi_2^{A_1} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_1} - s_2^{A_1}) + s_5^{A_1}\right]$
		$(A_2)_2\ \varphi_2^{A_2} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_2} - s_2^{A_2}) + s_5^{A_2}\right]$
$(A_1)_2$	$(A)_3$	$(A_1)_3\ \varphi_3^{A_1} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_1} - s_2^{A_1}) + s_3^{A_1}\right]$
		$(A_2)_3\ \varphi_3^{A_2} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_2} - s_2^{A_2}) + s_3^{A_2}\right]$
$(A_1)_3$	$(A)_4$	$(A_1)_4\ \varphi_4^{A_1} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_1} - s_2^{A_1}) - s_3^{A_1}\right]$
		$(A_2)_4\ \varphi_4^{A_2} = \frac{1}{\sqrt{2}}\left[\frac{1}{\sqrt{2}}(s_1^{A_2} - s_2^{A_2}) - s_3^{A_2}\right]$
A_2	$(A)_5$	$(A_1)_5\ \varphi_5^{A_1}(z - \mathrm{rot.}) = s_4^{A_1}$
		$(A_2)_5\ \varphi_5^{A_2}(\text{rigid pyram. rot.}) = s_4^{A_2}$
$(E)_1$	$(E)_1$	$(E_2)_1\ \varphi_{1\alpha}^{E_2} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_2} + \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_1} - s_{4\beta}^{E_1})\right] + s_{5\alpha}^{E_2}\right\}$
		$(E_1)_1\ \varphi_{1\alpha}^{E_1} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_1} + \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_2} - s_{4\beta}^{E_2})\right] + s_{5\alpha}^{E_1}\right\}$
	$(E)_5$	$(E_2)_5\ \varphi_{5\alpha}^{E_2} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_2} + \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_1} - s_{4\beta}^{E_1})\right] - s_{5\alpha}^{E_2}\right\}$
		$(E_1)_5\ \varphi_{5\alpha}^{E_1} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_1} + \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_2} - s_{4\beta}^{E_2})\right] - s_{5\alpha}^{E_1}\right\}$
$(E)_2$	$(E)_2$	$(E_2)_2\ \varphi_{2\alpha}^{E_2} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_2} - \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_2} - s_{4\beta}^{E_1})\right] - s_{2\alpha}^{E_1}\right\}$
		$(E_1)_2\ \varphi_{2\alpha}^{E_1} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_1} - \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_2} - s_{4\beta}^{E_2})\right] - s_{2\alpha}^{E_1}\right\}$
$(E)_3$	$(E)_3$	$(E_2)_3\ \varphi_{3\alpha}^{E_2} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_2} - \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_1} - s_{4\beta}^{E_1})\right] + s_{2\alpha}^{E_1}\right\}$
		$(E_1)_3\ \varphi_{3\alpha}^{E_1} = \frac{1}{\sqrt{2}}\left\{\frac{1}{\sqrt{2}}\left[s_{1\alpha}^{E_1} - \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_2} - s_{4\beta}^{E_2})\right] + s_{2\alpha}^{E_2}\right\}$
$(E)_4$	$(E)_4$	$(E_2)_4\ \varphi_{4\alpha}^{E_2} = \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_1} + s_{4\beta}^{E_1})$
		$(E_1)_4\ \varphi_{4\alpha}^{E_1} = \frac{1}{\sqrt{2}}(s_{3\alpha}^{E_2} + s_{4\beta}^{E_2})$

Graphic representations of the forms of normal vibrations in the lithium iodate crystal are shown in Figs. 3 (A-modes) and 4 ($E_{i\alpha}$-modes).

The Raman spectrum of the α-LiIO$_3$ crystal (Fig. 5) also demonstrates a good agreement with the use of the quasi-molecular approach for the interpretation of experimental results: the spectrum has three distinct regions in which the lines are grouped. The high-frequency region, which is separated from the others by an interval of about 300 cm^{-1}, is represented by bands arising due to quasi-valent vibrations of (IO$_3$)$^-$ groups. Quasi-deformation modes of groups (IO$_3$)$^-$ should be represented in the medium

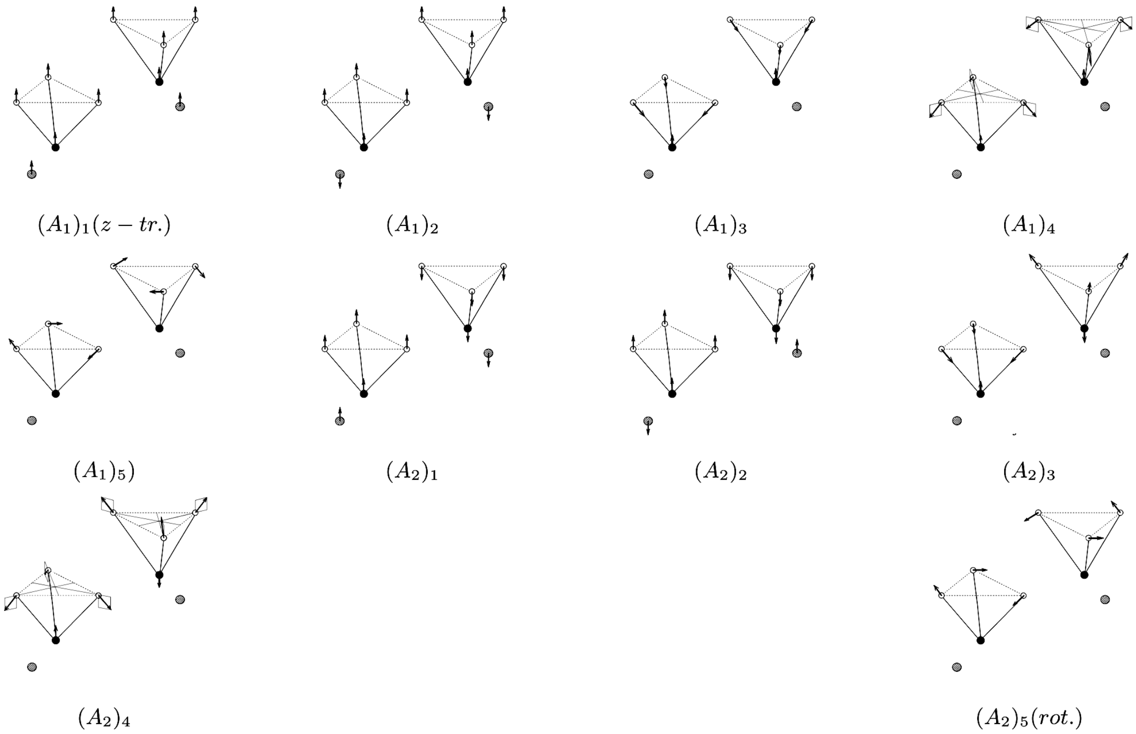


Fig. 3. Forms of non-degenerate vibrations in α-LiIO$_3$ crystal

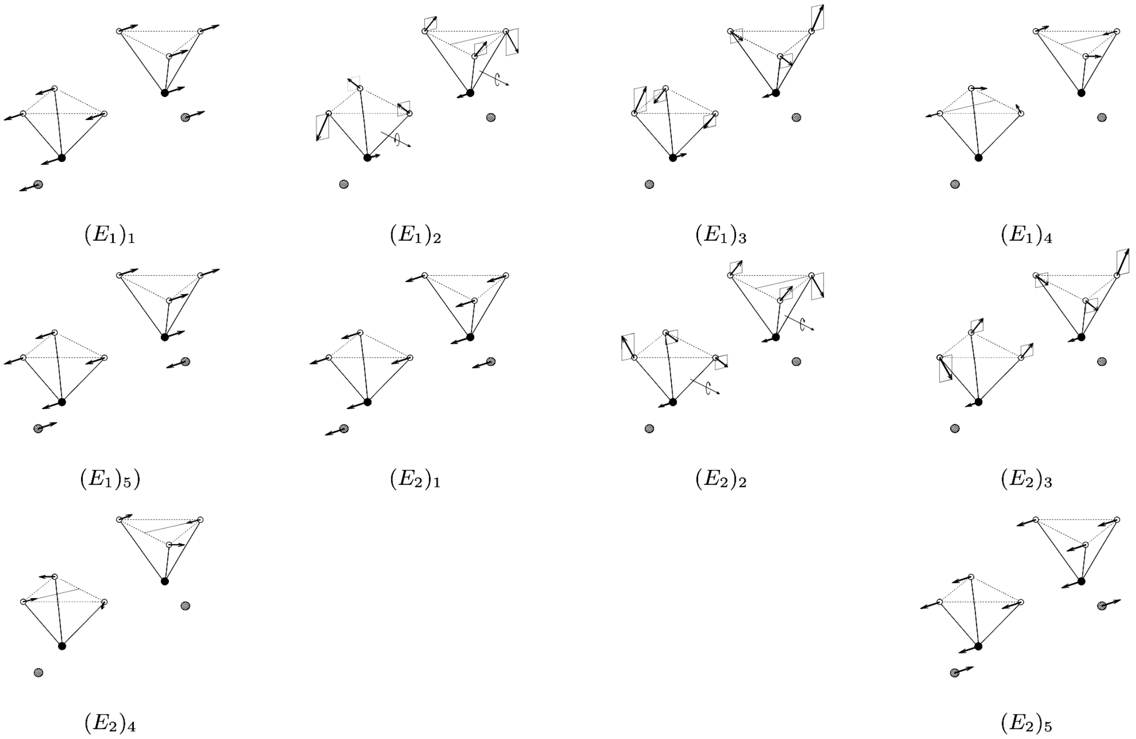


Fig. 4. Forms of normal vibrations in α-LiIO$_3$ crystal (degenerate modes)

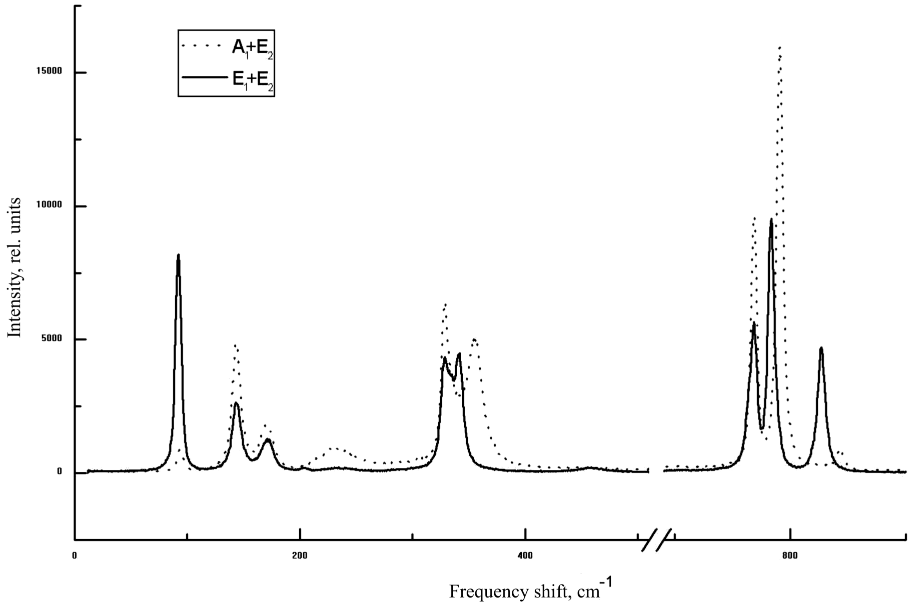


Fig. 5. 1st-order Raman spectrum of α-$LiIO_3$ crystal

wavelength range of the spectrum. The low-frequency spectrum belongs to external oscillations – translations and librations of $(IO_3)^-$ groups and Li^+ cations.

4. Classification of Energy States Along the Direction $\Gamma - A$ in the Brillouin Zone

Let us now turn from the approximate correlational consideration, where the quasi-molecular approach is applied, to a precise description. The latter is based on a more complete consideration of the symmetry properties of the crystalline space group and, in particular, a more complete consideration of the invariance of energy states with respect to time inversion (this result can be obtained by analyzing the properties of projective irreducible representations). In this case, the phonon states in the α-$LiIO_3$ crystal at the points of highest symmetry – first of all, these are points located on the $\Gamma - A$ line – due to their time-inversion invariance can be represented by dispersion curves in the zone of doubled length in the given direction, a large zone (the Jones zone), where the number of phonon branches is twice as small as in the ordinary Brillouin zone.

In order to get a more complete idea of the energy state classification in the large zone of α-$LiIO_3$ crystals, let us consider, in more details, the classification of those states along the direction $\Gamma - A$; namely, at points Γ, Δ, and A of the ordinary Brillouin zone.

4.1. Theory

Following the method described in work [12] and detailed in work [19] for the case of SiC crystals, let us construct the irreducible representations $D_{\mathbf{k}}$ of the groups of wave vectors $G_{\mathbf{k}}$ at points Γ, Δ, and A. These representations contain an infinite number of $D_{\mathbf{k}}(h)$ members for the elements $h \in G_k$. Any element h can be written in the form $h = (\boldsymbol{\alpha} + \mathbf{a} \mid r)$, where r is "a rotating element" (their set forms a point group $F_{\mathbf{k}}$, the isomorphic factor-group of the group $G_{\mathbf{k}}$ over the infinite invariant subgroup of translations), $\boldsymbol{\alpha}$ is a nontrivial translation vector corresponding to the rotating element r, and $\mathbf{a}$ is a trivial translation vector or a vector of the Bravais lattice. The values of matrices $D_{\mathbf{k}}(h)$ and their characters $\chi_{D_{\mathbf{k}}(h)}$ are

$$D_{\mathbf{k}}(h) = e^{-i\mathbf{k}(\boldsymbol{\alpha}+\mathbf{a})} w(r) D(r), \tag{1}$$

and

$$\chi_{D_{\mathbf{k}}(h)} = e^{-i\mathbf{k}(\boldsymbol{\alpha}+\mathbf{a})} w(r) \chi_{D(r)}. \tag{2}$$

The notations used here are as follows:

• for the representations describing the states without taking the spin into account (with an integer spin), $w(r) = u(r) \equiv u_1(r)$ is a function that reduces the factor-system $\omega(r_2, r_1) \equiv \omega_1(r_2, r_1)$ determined by the properties of the crystalline space group to the standard form $\omega'(r_2, r_1) \equiv \omega'_1(r_2, r_1)$;

• for the representations describing the states taking the spin into account (with a half-integer spin), $w(r) = u_s(r) = u_1(r)u_2(r)$ is a function that reduces the factor-system $\omega(r_2, r_1) = \omega_s(r_2, r_1) = \omega_1(r_2, r_1)\omega_2(r_2, r_1)$ determined by the transformations of spinors at the symmetry operations of directional groups of wave-vector groups $F_{\mathbf{k}}$ to the standard form $\omega'_2(r_2, r_1) = \omega'_s(r_2, r_1) = \omega'_1(r_2, r_1)\omega'_2(r_2, r_1)$;

• $u_2(r)$ is a function that reduces the factor-system $\omega_2(r_2, r_1)$ determined by the transformations of only the spin-dependent part of the wave function of spinors at the group $F_{\mathbf{k}}$ operations to the standard form $\omega'_2(r_2, r_1)$;

• are irreducible projective representations of the class to which the factor-system $\omega(r_2, r_1)$ belongs; they correspond to standard factor-systems;

• $\chi_{D(r)}$ are the characters of irreducible projective representations $D(r)$.

When finding the irreducible representations of the wave vector group at points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$, for the canonical values of the wave vectors, let us choose $\mathbf{k}_{\mathit{\Gamma}} = 0$, $\mathbf{k}_A = -\mathbf{b}_1/2$, and $\mathbf{k}_{\mathit{\Delta}}$, i.e., the first Brillouin zone – its center is at the point (0, 0, 0) – includes the points lying at its boundary and corresponding to negative **k**-values.

For points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$, the wave vector groups are identical and coincide with the complete space group G whose elements are usually denoted by the letter g. The basis elements $h_i = g_i$, which define those groups and can contain only trivial translations related to the selected non-trivial and trivial translations for the generating elements of directional groups of wave vector groups, are chosen in the form: $h_1 = (0 \mid e)$, $h_2 = (0 \mid c_3)$, $h_3 = (0 \mid c_3)$, $h_4 = (\mathbf{a}_1/2 \mid c_2)$, $h_5 = \left(\mathbf{a}_1/2 \mid c_6^5\right)$, and $h_6 = (\mathbf{a}_1/2 \mid c_6)$, where $\mathbf{a}_1$ is the primitive lattice vector directed along the Oz axis. Such a choice of generating basis elements h_i is associated with the standard selection of reference points in the crystal lattice, which are used to reckon the vectors of non-trivial and trivial translations. As standard reference points in the α-LiIO$_3$ lattice, let us choose the points lying on the highest-order axis (for the group $P6_3$, this is the axis of the 6th order) and in the Oxy plane. Let it be the point $(0, 0, 0)$.

For points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$, let us construct the factor-systems

$$\omega_1\left(r_2, r_1\right) = e^{i\left(\mathbf{k} - r_2^{-1}\mathbf{k}\right)\boldsymbol{\alpha}_1},$$

which are determined by the properties of the crystalline spatial group, and the factor-systems

$$\omega_2(r_2, r_1) = \begin{cases} 1 & \text{for} \quad 0 \le \vartheta < 2\pi, \\ -1 & \text{for} \quad 2\pi \le \vartheta < 4\pi, \end{cases}$$

which describe the transformations of spin variables at the symmetry operations of directional groups of wave-vector groups (ϑ is an angle of the rotation corresponding to the element product $r_2 r_1$).

Now, let us determine the functions $u_1(r)$ and $u_2(r)$ that reduce those factor-systems to the standard form. Since the group 6, which describes the directional symmetry of the wave vector groups coinciding for points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$, does not contain vector-changing elements, all elements of the factor-systems $\omega_1(r_2, r_1)$ for those points are equal to 1. This fact means that the factor-systems $\omega_1(r_2, r_1)$ for those points coincide with the standard factor-system $\omega'_{(0)}(r_2, r_1)$ of group 6 of class K_0, all of whose elements equal 1. Therefore, the functions $u_1(r)$ are also equal to 1 at points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$ for all elements of group 6.

The factor-systems $\omega_2(r_2, r_1)$, which are determined by the directional symmetry group of the wave-vector groups also coincide at points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$, being determined by the group 6 in each case. To obtain a factor-system $\omega_2(r_2, r_1)$ that would be common for points $\mathit{\Gamma}$, A, and $\mathit{\Delta}$, let the following elements be chosen as the generating elements of the group 6. Either these are two elements, $a = c_3$ and $b = c_2$ (choice 1, which accounts for the composition principle. According to it, group 6 can be represented as a direct product of groups 3 and 2, $6 = 3 \times 2$), or this is one element, $a = c_6$ (choice 2). Let us represent all symmetry elements of group 6 in the form $b^q a^p$, where $p = 0$, 1, 2 and $q = 0$, 1 (choice 1); or in the form a^p, where $p = 0$, 1, 2, 3, 4, 5 (choice 2). Making use of the definition relationships satisfied by the chosen generating elements, let us calculate all $\omega_2(r_2, r_1)$-values. It is important that, in this case, the relationships for the dual group 6 – either $a^6 = e$, $b^4 = e$, and $ab = ba$ (for choice 1) or $a^{12} = e$ (for choice 2) – should be taken as the definition ones.

Table 3. **Factor-system $\omega_2(r_2, r_1)$ for group 6**

$\omega_2(r_2,r_1)$ / r_2 \ r_1	e	c_3	c_3^2	c_2	c_6^5	c_6
e	1	1	1	1	1	1
c_3	1	1	−1	1	−1	1
c_3^2	1	−1	−1	−1	−1	1
c_2	1	1	−1	−1	−1	1
c_6^5	1	−1	−1	−1	−1	−1
c_6	1	1	1	1	−1	1

The factor-system $\omega_2(r_2, r_1)$ calculated for the group 6 is shown in Table 3. Since the group 6 is cyclic, all its projective representations, as well as the representations of any other cyclic group, are projectively equivalent (p-equivalent) to the ordinary (they are also called vector) ones and belong, as well as the vector representations, to the class K_0. This means that the factor-system $\omega_2(r_2, r_1)$ introduced for the group 6 in Table 3 also belongs to the class K_0. Indeed, for an arbitrary pair of commuting elements (in a cyclic group that is an Abelian one, any pair of elements commutes), all ratios $\omega_2(r_2, r_1)/\omega_2(r_1, r_2) = 1$ [i.e., the factor-system $\omega_2(r_2, r_1)$ is symmetric with respect to its diagonal determined by the elements $\omega_2(e, e)$ and $\omega_2(c_6, c_6)$], which features that the factor-system $\omega_2(r_2, r_1)$ belongs to the class K_0. Standard factor-systems of class K_0 in all groups are the systems all of which elements equal 1. It is easy to see that the factor system $\omega_2(r_2, r_1)$ of group 6 is reduced to a p-equivalent standard factor-systems $\omega'_2(r_2, r_1)$ [in this case, the latter coincides with the standard factor-system of class K_0 of group 6, i.e., the factor-system $\omega'_{(0)}(r_2, r_1)$ of group 6], via the transformation

$$\omega'_2(r_2, r_1) = \frac{\omega_2(r_2, r_1)u_2(r_2, r_1)}{u_2(r_1)u_2(r_2)},$$

where the function $u_2(r)$ equals 1, −1, 1, i, $-i$, and $-i$ for the elements e, c_3, c_3^2, c_2, c_6^5, and c_6, respectively [2]. Furthermore, the equality $\omega'_2(r_2, r_1) = \omega'_{(0)}(r_2, r_1)$, which holds in this case, is a criterion that the values of $u_2(r)$ determined above are correct.

[2] Since [12] $u_2(c_3^p) = e^{ip\pi}$ $(p = 0, 1, 2)$, $u_2(c_2^q) = \epsilon_4^q = (e^{i2\pi/4})^q = e^{iq\pi/2}$ $(q = 0, 1)$, $u_2(c_6^r) = [u_2(c_6)]^r$ ($r = 0$, 1, 2, 3 ,4, 5), and the equalities $u_2(c_3) = [u_2(c_6)]^2 = -1$ and $u_2(c_2) = [u_2(c_6)]]^3 = [u_2(c_6)]^2]\, u_2(c_6) = -u_2(c_6) = i$ must be obeyed, then $u_2(c_6) = -i$.

4.2. Point Γ

First, let us construct one- and two-valued irreducible projective representations of the wave vector group for α-LiIO$_3$ crystals at point Γ, where $\mathbf{k}_A = \mathbf{k}_\Gamma = 0$, so that the one-valued projective representations also coincide with ordinary vector representations, and two-valued projective representations coincide with spinor representations of the point group 6. Multiplying, in accordance with formulas (1) and (2), the characters of ordinary vector representations of group 6 (see Table 3; for the one-dimensional irreducible representations, those characters coincide, in this case, with their matrices) by the determined values of the function $u_2(r)$ (they are given in the upper part of Table 3), we can easily find the characters of the irreducible spinor representations of group 6 in terms of the characters of its projective representations (the primed quantities in Table 4).

For comparison, the characters of irreducible representations of the dual group 6′ are shown in Table 5. One can easily see that the characters of spinor representations that are given in Table 5 coincide with the calculated characters of two-valued projective representations of class K_0 of group 6 given in Table 4. It is important in this case that just the successive multiplication by the values of the function $u_2(r)$ determines the sequence numbers of the projective representations in Table 4, which are used to set the sequence numbers (or the sequence of recording) of spinor representations in the dual group 6′.

4.3. Points A and Δ

Finally, let us determine the characters of one- and two-valued irreducible representations of the wave vector groups for the α-LiIO$_3$ crystal at points A and Δ. The latter are characterized by the wave vectors $\mathbf{k}_A = -\mathbf{b}_1/2$ and $\mathbf{k}_\Delta$, respectively. These characters, which can be easily determined by calculating the values of the exponent $e^{i\mathbf{k}(\boldsymbol{\alpha}+\mathbf{a})}$ for the basis elements indicated above, are shown in Tables 6 (for point A) and 7 (for point Δ) [3].

[3] Note that Table 7 contains the general expressions for the characters of irreducible representations of wave vector groups for points in the direction $\Gamma-A$, whereas Tables 4 and 6 contain expressions for the limiting values of $\eta_k = e^{-ika_1/2}$ at points Γ and A.

Table 4. **Characters of irreducible projective representations of the wave vector group 6 (C_6) at point Γ**

$6(C_6)$				e	c_3	c_3^2	c_2	c_6^5	c_6
	Γ_1		A_1	1	1	1	1	1	1
	Γ_2		A_2	1	1	1	-1	-1	-1
	Γ_3		B_1	1	ε_3	ε_3^{-1}	1	ε_3	ε_3^{-1}
$\Gamma_3+\Gamma_5$	Γ_4	E_1	B_2	1	ε_3	ε_3^{-1}	-1	$-\varepsilon_3$	$-\varepsilon_3^{-1}$
$\Gamma_4+\Gamma_6$	Γ_5	E_2	B_3	1	ε_3^{-1}	ε_3	1	ε_3^{-1}	ε_3
	Γ_6		B_4	1	ε_3^{-1}	ε_3	-1	$-\varepsilon_3^{-1}$	$-\varepsilon_3$
$\Gamma_7+\Gamma_8$	Γ_7	$E_1'+E_2'$	E_1'	1	-1	1	i	$-i$	$-i$
	Γ_8		E_2'	1	-1	1	$-i$	i	i
	Γ_9		E_3'	1	$-\varepsilon_3$	ε_3^{-1}	i	ε_{12}	$-\varepsilon_{12}^{-1}$
$\Gamma_9+\Gamma_{12}$	Γ_{10}	$E_3'+E_6'$	E_4'	1	$-\varepsilon_3$	ε_3^{-1}	$-i$	$-\varepsilon_{12}$	ε_{12}^{-1}
$\Gamma_{10}+\Gamma_{11}$	Γ_{11}	$E_4'+E_5'$	E_5'	1	$-\varepsilon_3^{-1}$	ε_3	i	$-\varepsilon_{12}^{-1}$	ε_{12}
	Γ_{12}		E_6'	1	$-\varepsilon_3^{-1}$	ε_3	$-i$	ε_{12}^{-1}	$-\varepsilon_{12}$
	Γ_1		A_1	1	1	1	1	1	1
	Γ_2		A_2	1	1	1	-1	-1	-1
	$\Gamma_3+\Gamma_5$		E_1	2	-1	-1	2	-1	-1
	$\Gamma_4+\Gamma_6$		E_2	2	-1	-1	-2	1	1
	$\Gamma_7+\Gamma_8$		$E_1'+E_2'$	2	-2	-2	0	0	0
	$\Gamma_9+\Gamma_{12}$		$E_3'+E_6'$	2	1	-1	0	$\sqrt{3}$	$-\sqrt{3}$
	$\Gamma_{10}+\Gamma_{11}$		$E_4'+E_5'$	2	1	-1	0	$-\sqrt{3}$	$\sqrt{3}$
	$u_2(r)$			1	-1	1	i	$-i$	$-i$

Table 5. **Characters of irreducible representations of the dual group $6'(C_6')$**

$6'(C_6')$				e	q	c_3	qc_3	c_3^2	qc_3^2	c_2	qc_2	c_6^5	qc_6^5	qc_6	c_6
	Γ_1		A_1	1	1	1	1	1	1	1	1	1	1	1	1
	Γ_2		A_2	1	1	1	1	1	1	-1	-1	-1	-1	-1	-1
	Γ_3		B_1	1	1	ε_3	ε_3	ε_3^{-1}	ε_3^{-1}	1	1	ε_3	ε_3	ε_3^{-1}	ε_3^{-1}
$\Gamma_3+\Gamma_5$	Γ_4	E_1	B_2	1	1	ε_3	ε_3	ε_3^{-1}	ε_3^{-1}	-1	-1	$-\varepsilon_3$	$-\varepsilon_3$	$-\varepsilon_3^{-1}$	$-\varepsilon_3^{-1}$
$\Gamma_4+\Gamma_6$	Γ_5	E_2	B_3	1	1	ε_3^{-1}	ε_3^{-1}	ε_3	ε_3	1	1	ε_3^{-1}	ε_3^{-1}	ε_3	ε_3
	Γ_6		B_4	1	1	ε_3^{-1}	ε_3^{-1}	ε_3	ε_3	-1	-1	$-\varepsilon_3^{-1}$	$-\varepsilon_3^{-1}$	$-\varepsilon_3$	$-\varepsilon_3$
$\Gamma_7+\Gamma_8$	Γ_7	$E_1'+E_2'$	E_1'	1	-1	-1	1	1	-1	i	$-i$	$-i$	i	i	$-i$
	Γ_8		E_2'	1	-1	-1	1	1	-1	$-i$	i	i	$-i$	$-i$	i
	Γ_9		E_3'	1	-1	$-\varepsilon_3$	ε_3	ε_3^{-1}	$-\varepsilon_3^{-1}$	i	$-i$	ε_{12}	$-\varepsilon_{12}$	ε_{12}^{-1}	$-\varepsilon_{12}^{-1}$
$\Gamma_9+\Gamma_{12}$	Γ_{10}	$E_3'+E_6'$	E_4'	1	-1	$-\varepsilon_3$	ε_3	ε_3^{-1}	$-\varepsilon_3^{-1}$	$-i$	i	$-\varepsilon_{12}$	ε_{12}	$-\varepsilon_{12}^{-1}$	ε_{12}^{-1}
$\Gamma_{10}+\Gamma_{11}$	Γ_{11}	$E_4'+E_5'$	E_5'	1	-1	$-\varepsilon_3^{-1}$	ε_3^{-1}	ε_3	$-\varepsilon_3$	i	$-i$	$-\varepsilon_{12}^{-1}$	ε_{12}^{-1}	$-\varepsilon_{12}$	ε_{12}
	Γ_{12}		E_6'	1	-1	$-\varepsilon_3^{-1}$	ε_3^{-1}	ε_3	$-\varepsilon_3$	$-i$	i	ε_{12}^{-1}	$-\varepsilon_{12}^{-1}$	ε_{12}	$-\varepsilon_{12}$

4.4. Time-inversion invariance of energy states

In the absence of external magnetic fields, the additional conditions are imposed on the state wave functions and, accordingly, on the representations at points Γ, A, and Δ. These conditions emerge, if the invariance of energy states with respect to the time inversion is taken into account. As a result, there arises an additional degeneration of some states. Its appearance can be determined by means of the Herring criterion [12, 18]. The stages and results of calculations of the Herring criterion for the irreducible representations at points Γ and A are quoted in Table 8. At the point Δ, the combination of the representations of the complete space group does not give rise to the combination of the representations of the wave vector group, because there are no elements at this point that satisfy the relationship $g'\mathbf{k} = -\mathbf{k}$ [19].

The values of the Herring criterion quoted in Table 8 testify that the representations Γ_1 and Γ_2 are related to the case a_1; the representations Γ_3, Γ_4, ..., Γ_{12} and A_1, A_2, ..., A_6, A_9, ..., A_{12} to the case b_1, and the representations A_7 and A_8 to the case c_1. There is no additional degeneration of the states with the symmetries Γ_1 and Γ_2 at point Γ, if their time-inversion invariance is taken into account. States Γ_3 and Γ_5, Γ_4 and Γ_6, Γ_7 and Γ_8, Γ_9 and Γ_{12},

Table 6. **Characters of irreducible projective representations of the wave vector group at point *A***

$6\,(C_6)$		e	c_3	c_2^3	c_2	c_6^5	c_6
A_1+A_2	A_1	1	1	1	i	i	i
	A_2	1	1	1	$-i$	$-i$	$-i$
	A_3	1	ε_3	ε_3^{-1}	i	$-\varepsilon_{12}$	ε_{12}^{-1}
A_3+A_6	A_4	1	ε_3	ε_3^{-1}	$-i$	ε_{12}	$-\varepsilon_{12}^{-1}$
A_4+A_5	A_5	1	ε_3^{-1}	ε_3	i	ε_{12}^{-1}	$-\varepsilon_{12}$
	A_6	1	ε_3^{-1}	ε_3	$-i$	$-\varepsilon_{12}^{-1}$	ε_{12}
$((A_7))$	A_7	1	-1	1	-1	1	1
$((A_8))$	A_8	1	-1	1	1	-1	-1
	A_9	1	ε_3	ε_3^{-1}	-1	ε_3	ε_3^{-1}

Table 7. **Characters of irreducible projective representations of the wave vector group at point Δ**

Δ_n	e	c_3	c_3^2	c_2	c_6^5	c_6
Δ_1	1	1	1	$\eta_\mathbf{k}$	$\eta_\mathbf{k}$	$\eta_\mathbf{k}$
Δ_2	1	1	1	$-\eta_\mathbf{k}$	$-\eta_\mathbf{k}$	$-\eta_\mathbf{k}$
Δ_3	1	ε_3	ε_3^{-1}	$\eta_\mathbf{k}$	$\varepsilon_3\eta_\mathbf{k}$	$\varepsilon_3^{-1}\eta_\mathbf{k}$
Δ_4	1	ε_3	ε_3^{-1}	$\eta_\mathbf{k}$	$-\varepsilon_3\eta_\mathbf{k}$	$\eta_\mathbf{k}$
Δ_5	1	ε_3^{-1}	ε_3	$\eta_\mathbf{k}$	$\varepsilon_3^{-1}\eta_\mathbf{k}$	$\varepsilon_3\eta_\mathbf{k}$
Δ_6	1	ε_3^{-1}	ε_3	$\eta_\mathbf{k}$	$-\varepsilon_3^{-1}\eta_\mathbf{k}$	$-\varepsilon_3\eta_\mathbf{k}$
Δ_7	1	-1	1	$\eta_\mathbf{k}$	$\eta_\mathbf{k}$	$\eta_\mathbf{k}$
Δ_8	1	-1	1	$-i\eta_\mathbf{k}$	$i\eta_\mathbf{k}$	$i\eta_\mathbf{k}$
Δ_9	1	$-\varepsilon_3$	ε_3^{-1}	$i\eta_\mathbf{k}$	$\varepsilon_{12}\eta_\mathbf{k}$	$-\varepsilon_{12}\eta_\mathbf{k}$
Δ_{10}	1	$-\varepsilon_3$	ε_3^{-1}	$-i\eta_\mathbf{k}$	$-\varepsilon_{12}\eta_\mathbf{k}$	$\varepsilon_{12}^{-1}\eta_\mathbf{k}$
Δ_{11}	1	$-\varepsilon_3^{-1}$	ε_3	$i\eta_\mathbf{k}$	$-\varepsilon_{12}^{-1}\eta_\mathbf{k}$	$\varepsilon_{12}\eta_\mathbf{k}$
Δ_{12}	1	$-\varepsilon_3^{-1}$	ε_3	$-i\eta_\mathbf{k}$	$\varepsilon_{12}^{-1}\eta_\mathbf{k}$	$-\varepsilon_{12}\eta_\mathbf{k}$

Γ_{10} and Γ_{11}, and the states at point A for symmetries A_1 and A_2, A_3 and A_6, A_4 and A_5, A_9 and A_{11}, A_{10} and A_{12} become pairwise-combined, and states A_7 and A_8 become doubled (this doubling is marked by double parentheses). It is the indicated combinations and doublings of representations, which arise due to the account for the time-inversion invariance, that are marked in Tables 1, 4, and 6, whereas the characters of the combined and doubled representations are given in the bottom parts of Tables 4 and 6.

5. Classification of Energy States in the Large Zone

Let us turn from the classification of phonon and electronic states in the Brillouin zone of α-LiIO$_3$ crystals to their classification in the large (or Jones) zones [20]. The extension of the latter along the $\Gamma-\Delta$ direction in the wave vector space is twice as large as their extension in the ordinary zone. The main possibility of such a classification is provided by the pairwise merging of the dispersion branches of all energy states at point A owing to the time-inversion invariance for structures whose symmetry is described by the non-symmorphic space group $P6_3$. In the case of such a merging of energy zones, the dispersion branches originating from point Γ can be represented by dispersion branches reflected perpendicularly to the wave vector direction into the second Brillouin zone up to its boundary, point Γ' separated from point Γ by the wave vector $-\mathbf{b}_1$ ($\mathbf{k}_{\Gamma'} = -\mathbf{b}_1$, $\mathbf{k}_{\Gamma'} = 2\pi/\mathbf{a}_1$). It is essential that, for the large zone in the direction $\Gamma-A$, equivalent are those wave vectors that differ from each other by two rather than one vector of the reciprocal lattice. Naturally, the number of dispersion branches in the large zone is half as much as in the conventional Brillouin zone.

At the same time, when constructing the characters of irreducible representations at points Γ and Γ' with regard for the multiplier

$$\exp\left(i\mathbf{k}_{\Gamma'}\boldsymbol{\alpha}_r\right) = \begin{cases} 1 & \text{at} \quad \boldsymbol{\alpha}_r = 0, \\ -1 & \text{at} \quad \boldsymbol{\alpha}_r = \mathbf{a}_1/2, \end{cases}$$

then, at first glance, it seems that when changing from point Γ to point Γ' in the large zone, the following conditions of representation compatibility must be satisfied:

$$\Gamma_1 \longrightarrow \Delta_1 \longrightarrow A_1 + A_2 \longrightarrow \Delta_2 \longrightarrow \Gamma_2,$$

Table 8. **Stages and results of calculations of the characters $\chi_{\mathbf{k},D_\mu}[(g')^2]$ and $\chi_{\mathbf{k},D'_\mu}[(g')^2]$ and the corresponding Herring criterion values for irreducible representations at points Γ and A**

$(g')^2$	$e^{-i\mathbf{k}(\mathbf{ra}+\boldsymbol{\alpha})}$		$u(r^2) \equiv$ $\equiv u_1(r^2)$	$\chi_{D_\mu}(r^2) = \chi_{D'_\mu}(r^2)$			$\chi_{\mathbf{k},D_\mu}[(g')^2]$						$u_2(r^2)$	$v(r^2)$	$\chi_{\mathbf{k},D''_\mu}[(g')^2]$					
	Γ	A	Γ, A	$A_1^{(0)}$, $A_4^{(0)}$	$B_1^{(0)}(A_3^{(0)}$, $B_2^{(0)})(A_4^{(0)})$	$B_3^{(0)}(A_5^{(0)})$, $B_4^{(0)}(A_6^{(0)})$	Γ_1, Γ_2	Γ_3, Γ_4	Γ_5, Γ_6	A_1, A_2	A_3, A_4	A_5, A_6			Γ_7, Γ_8	Γ_9, Γ_{10}	Γ_{11}, Γ_{12}	A_7, A'_8	A_9, A_{10}	A_{11}, A_{12}
$(g'_1)^2$	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1
$(g'_2)^2$	1	1	1	1	ε_3^{-1}	ε_3	1	ε_3^{-1}	ε_3	1	ε_3^{-1}	ε_3	1	1	1	ε_3^{-1}	ε_3	1	ε_3^{-1}	ε_3
$(g'_3)^2$	1	1	1	1	ε_3	ε_3^{-1}	1	ε_3	ε_3^{-1}	1	ε_3	ε_3^{-1}	-1	-1	1	ε_3	ε_3^{-1}	1	ε_3	ε_3^{-1}
$(g'_4)^2$	1	-1	1	1	1	1	1	1	1	-1	-1	-1	1	-1	-1	-1	-1	1	1	1
$(g'_5)^2$	1	-1	1	1	ε_3^{-1}	ε_3	1	ε_3^{-1}	ε_3	-1	$-\varepsilon_3^{-1}$	$-\varepsilon_3$	1	-1	-1	$-\varepsilon_3^{-1}$	$-\varepsilon_3$	1	ε_3^{-1}	ε_3
$(g'_6)^2$	1	-1	1	1	ε_3	ε_3^{-1}	1	ε_3	ε_3^{-1}	-1	$-\varepsilon_3$	$-\varepsilon_3^{-1}$	-1	1	-1	$-\varepsilon_3$	$-\varepsilon_3^{-1}$	1	ε_3	ε_3^{-1}
							1	0	0	0	0	0			0	0	0	1	0	0
$\frac{1}{l}\sum_{(g')^2}\chi_{\mathbf{k}}\quad(g')^2\,\delta_{\mathbf{k},-g'\mathbf{k}}$							a_1	b_1	b_1	b_1	b_1	b_1			b_1	b_1	b_1	c_1	b_1	b_1

$\Gamma_2 \longrightarrow \Delta_2 \longrightarrow A_1 + A_2 \longrightarrow \Delta_1 \longrightarrow \Gamma_1$,

$\Gamma_3 \longrightarrow \Delta_3 \longrightarrow A_3 + A_6 \longrightarrow \Delta_6 \longrightarrow \Gamma_6$,

$\Gamma_4 \longrightarrow \Delta_4 \longrightarrow A_4 + A_5 \longrightarrow \Delta_5 \longrightarrow \Gamma_5$,

$\Gamma_5 \longrightarrow \Delta_5 \longrightarrow A_4 + A_5 \longrightarrow \Delta_4 \longrightarrow \Gamma_4$,

$\Gamma_6 \longrightarrow \Delta_6 \longrightarrow A_3 + A_6 \longrightarrow \Delta_3 \longrightarrow \Gamma_3$,

$\Gamma_7 \longrightarrow \Delta_7 \longrightarrow ((A_7)) \longrightarrow \Delta_7 \longrightarrow \Gamma_7$,

$\Gamma_8 \longrightarrow \Delta_8 \longrightarrow ((A_8)) \longrightarrow \Delta_8 \longrightarrow \Gamma_8$,

$\Gamma_9 \longrightarrow \Delta_9 \longrightarrow A_9 + A_{11} \longrightarrow \Delta_{11} \longrightarrow \Gamma_{11}$,

$\Gamma_{10} \longrightarrow \Delta_{10} \longrightarrow A_{10} + A_{12} \longrightarrow \Delta_{12} \longrightarrow \Gamma_{12}$,

$\Gamma_{11} \longrightarrow \Delta_{11} \longrightarrow A_9 + A_{11} \longrightarrow \Delta_9 \longrightarrow \Gamma_9$,

$\Gamma_{12} \longrightarrow \Delta_{12} \longrightarrow A_{10} + A_{12} \longrightarrow \Delta_{10} \longrightarrow \Gamma_{10}$.

However, as was already mentioned above, in contrast to Brillouin zones, the wave vectors at points Γ and Γ' in large zones are not equivalent: the wave vector at point Γ in the large zone corresponds to elementary excitations with the wavelength $\lambda_\Gamma = 2\pi/k_\Gamma = \infty$, whereas the wave vector at point Γ' corresponds to elementary excitations with the wavelength $\lambda_{\Gamma'} = 2\pi/k_{\Gamma'} = a_1$. This means that the phases of the wave functions at the points of the crystal lattice that are distant from each other by the distance $a_1/2$ (this is a conditional lattice constant for the classification of states in the large zone) along the $0Z$ direction can either coincide (at $\lambda = \infty$) or differ by π (at $\lambda = a_1$). These are the so-called "sum" and "difference" modes [21]; the former relate to point Γ, and the latter to point Γ'. Therefore, the modes of electronic states for each of the Γ_7 and Γ_8 symmetries can be divided into identical numbers of sum and difference modes, which, like the sum and difference partners, combine at point A into dual modes $((A_7))$ and $((A_8))$. Modes Γ_{10} and Γ_{11} belong to the sum ones, because $\Gamma_{10} + \Gamma_{11} = \Gamma_1 \times D_{1/2}$, and modes Γ_9 and Γ_{12} to the difference ones, because $\Gamma_9 + \Gamma_{12} = \Gamma_2 \times D_{1/2}$ (here Γ_1 is the sum mode, Γ_2 the difference mode, and $D_{1/2}$ the representation for the transformation of a completely symmetric spinor with $j = 1/2$). Modes Γ_1, Γ_4, Γ_6, Γ_7, Γ_8, Γ_{10}, and Γ_{11} belong to Γ, and modes Γ_2, Γ_3, Γ_5, Γ_7, Γ_8, Γ_9, and Γ_{12} to Γ'. Hence, if the center of the large zone is chosen at point Γ, the dispersion curves describing the transition from point Γ to point Γ' satisfy the following conditions:

$\Gamma_1 \longrightarrow \Delta_1 \longrightarrow A_1 + A_2 \longrightarrow \Delta_2 \longrightarrow \Gamma_2$,

$\Gamma_4 \longrightarrow \Delta_4 \longrightarrow A_4 + A_5 \longrightarrow \Delta_5 \longrightarrow \Gamma_5$,

$\Gamma_6 \longrightarrow \Delta_6 \longrightarrow A_3 + A_6 \longrightarrow \Delta_3 \longrightarrow \Gamma_3$,

$\Gamma_7 \longrightarrow \Delta_7 \longrightarrow ((A_7)) \longrightarrow \Delta_7 \longrightarrow \Gamma_7$,

$\Gamma_8 \longrightarrow \Delta_8 \longrightarrow ((A_8)) \longrightarrow \Delta_8 \longrightarrow \Gamma_8$,

$\Gamma_{10} \longrightarrow \Delta_{10} \longrightarrow A_{10} + A_{12} \longrightarrow \Delta_{12} \longrightarrow \Gamma_{12}$,

$\Gamma_{11} \longrightarrow \Delta_{11} \longrightarrow A_9 + A_{11} \longrightarrow \Delta_9 \longrightarrow \Gamma_9$.

On the other hand, if the center of the large zone is shifted to point Γ', the compatibility conditions for the transition from point Γ' to point Γ look like

$\Gamma_2 \longrightarrow \Delta_2 \longrightarrow A_1 + A_2 \longrightarrow \Delta_1 \longrightarrow \Gamma_1$,

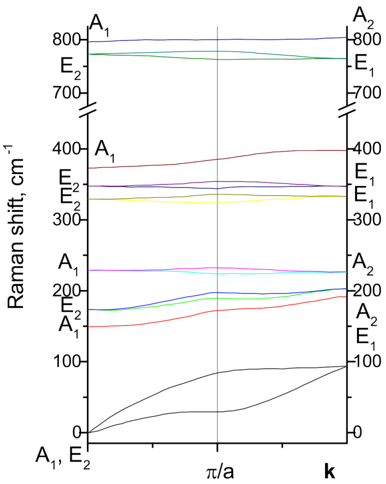


Fig. 6. Dispersion of phonon states in α-$LiIO_3$ crystal

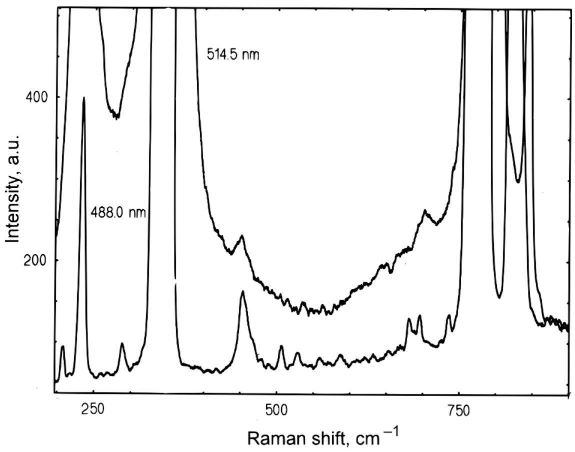


Fig. 7. Fragments of the spectra of α-$LiIO_3$ crystal at various excitation radiation wavelengths (indicated near the curves)

$$\varGamma_3 \longrightarrow \varDelta_3 \longrightarrow A_3 + A_6 \longrightarrow \varDelta_6 \longrightarrow \varGamma_6,$$

$$\varGamma_5 \longrightarrow \varDelta_5 \longrightarrow A_4 + A_5 \longrightarrow \varDelta_4 \longrightarrow \varGamma_4,$$

$$\varGamma_7 \longrightarrow \varDelta_7 \longrightarrow ((A_7)) \longrightarrow \varDelta_7 \longrightarrow \varGamma_7,$$

$$\varGamma_8 \longrightarrow \varDelta_8 \longrightarrow ((A_8)) \longrightarrow \varDelta_8 \longrightarrow \varGamma_8,$$

$$\varGamma_9 \longrightarrow \varDelta_9 \longrightarrow A_9 + A_{11} \longrightarrow \varDelta_{11} \longrightarrow \varGamma_{11},$$

$$\varGamma_{12} \longrightarrow \varDelta_{12} \longrightarrow A_{10} + A_{12} \longrightarrow \varDelta_{10} \longrightarrow \varGamma_{10}.$$

The process of constructing the dispersion curves for the phonon states in the large zone of α-$LiIO_3$ crystal is schematically illustrated in Fig. 6. Here, the frequencies of single-phonon spectra were taken from the 1st-order Raman spectra (Fig. 5), and the positions of the dispersion curves corresponding to point A from the 2nd-order Raman spectra (Fig. 7).

Thus, the dispersion of the energy states with various symmetries along the $\varGamma - A$ direction in the Jones zone of α-$LiIO_3$ crystals can be represented in the form of dispersion branches that merge in pairs at the points corresponding to the center and the boundary of the zone. In other words, the dispersion curves for this crystal form closed contours in the wave vector versus energy coordinates. As one can see from the construction procedure, enhanced values of the density of states on those dispersion curves correspond to points $\varGamma$ and A of the Brillouin zone.

6. Conclusions

The main results of this research are as follows.

In the framework of quasi-molecular approximation and making use of the group-theoretic method of projection operators, the analytic forms for normal vibrations in the α-$LiIO_3$ crystal lattice have been obtained. It is shown that the Raman spectra experimentally observed for those crystals can be completely interpreted on the basis of the calculated vibrational forms, and the spectra themselves undoubtedly testify to the validity of applying the quasi-molecular approximation when considering the lattice dynamics of this crystal.

Using the theory of projective representations of groups, the irreducible representations of wave vector groups are constructed at points $\varGamma$, $\varDelta$, and A of the Brillouin zone of the α-$LiIO_3$ crystal, and the conditions of their compatibility are found.

The energy states of α-$LiIO_3$ crystal in the large (Jones) zone are classified, which makes it possible to determine the dispersion of phonon states along the direction $\varGamma - A$ in the Brillouin zone.

On the basis of the experimentally measured 1st-order Raman spectra, the dispersion curves of phonon branches in the direction $\varGamma - A$ are plotted. Contributions of overtones and component tones at points $\varGamma$ and A to the experimentally recorded 2nd-order Raman spectrum are discussed. Their role in the formation of the 2nd-order spectrum is connected with the considered features in the density of phonon states at those points, as well as vibrational states at other critical points in the Brillouin zone.

1. W. Otaguro, E. Wiener-Avnear, C.A. Arguello, S.P.S. Porto. Phonons, polaritons, and oblique phonons in $LiIO_3$ by Raman scattering and infrared reflection. *Phys. Rev. B* **4**, 4542 (1971).
2. F.E.A. Melo, F. Cardeira, V. Lemos. Raman scattering from three phases in $LiIO_3$. *Solid State Commun.* **41**, 281 (1982).
3. D.F. Baisa, O.I. Barabash, V.P. Demyanenko, O.K. Zavadiyeva, G.O. Puchkovska, Yu.O. Frolkov, I.S. Rez. Study of spectral characteristics of hexagonal and tetragonal modifications of lithium iodide. *Ukr. Fiz. Zh.* **18**, 1610 (1973) (in Ukrainian).
4. K.E. Haller, E.M. Jarvekyulg, L.A. Rebane. Raman spectra and phase transitions in lithium iodate. *Fiz. Tverd. Tela* **18**, 1409 (1976) (in Russian).
5. Yu.N. Polivanov. Raman scattering of light by polaritons. *Usp. Fiz. Nauk* **126**, 185 (1978) (in Russian).
6. A. Rozenzweig, B. Morosin. A reinvestigation of the crystsl structure of $LiIO_3$. *Acta Crystallogr.* **20**, 758 (1966).
7. J.L. de Boer, F. van Bolhuis, R. Olthof-Hazkamp, A. Vos. A reinvestigation of the crystsl structure of lithium iodate. *Acta Crystallogr.* **21**, 841 (1966).
8. A. Emiraliev, A.G. Kocharov, I.I. Yamzin, V.A. Lyubimtsev. Neurodiffraction refinement of the α-$LiIO_3$ structure. *Krystallografiya* **18**, 1177 (1973) (in Russian).
9. A. Emiraliev, A.G. Kocharov, I.I. Yamzin, V.A. Lyubimtsev. Thermal parameters of atoms in α-$LiIO_3$. *Krystallografiya* **21**, 391 (1976) (in Russian).
10. T. Hahn. *International Tables for Crystallography. Vol. A. Space Group Symmetry* (Reidel, 1983).
11. V.O. Gubanov, A.P. Naumenko. Forms of normal vibrations of pyramidal molecules and XY_3 ions. *Visn. Kyiv. Univ. Ser. Fiz. Mat. Nauky* **4**, 342 (1997) (in Ukrainian).
12. G.L. Bir, G.E. Pikus. *Symmetry and Strain-Induced Effects in Semiconductors* (Wiley, 1974).
13. L.D. Landau, E.M. Lifshitz. *Quantum Mechanics. Non-Relativistic Theory* (Pergamon Press, 1981).
14. M. Hamermesh. *Group Theory and Its Application to Physical Problems* (Dover Publications, 1989).
15. G.F. Koster, J.O. Dimmock, R.C. Wheeler, H. Statz. *Properties of the Thirty-Two Point Groups* (MIT Press, 1966).
16. H. Poulet, J.P. Mathieu. *Vibration Spectra and Symmetry of Crystals* (Gordon and Breach, 1976).
17. S.L. Mayants. *Theory and Calculation of Molecular Vibrations* (Izd. Akad. Nauk SSSR, 1960) (in Russian).
18. C. Herring. Character tables for two space groups. *J. Franklin Inst.* **233**. 525 (1942).
19. D.S. Balchuk, M.M. Bilyi, V.P. Gryshchuk, V.O. Gubanov, V.K. Kononov. Symmetry of vibrational modes, time-inversion invariance of energy states, and Raman light scattering in 4h- and 6h-SiC crystals. 1. Classification of energy states in Brillouin zones. *Ukr. Fiz. Zh.* **41**, 146 (1996) (in Ukrainian).
20. H. Jones. *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing, 1960).
21. J.J. Sullivan. Lattice vibrations of wurtzite structure crystals. *J. Phys. Chem. Solids* **25**, 1039 (1964).

Received 25.05.23.
Translated from Ukrainian by O.I. Voitenko

А.П. Науменко, В.О. Губанов

СИМЕТРІЯ ЕНЕРГЕТИЧНИХ СТАНІВ З УРАХУВАННЯМ ІНВАРІАНТНОСТІ ДО ІНВЕРСІЇ ЧАСУ ТА ДИСПЕРСІЯ ФОНОННИХ ГІЛОК У ГІРОТРОПНИХ КРИСТАЛАХ α-LiIO$_3$

Із залученням теорії проективних представлень груп побудовано незвідні представлення груп хвильового вектора в точках Γ, Δ і A зони Бріллюена кристала α-$LiIO_3$ та знайдено умови їхньої сумісності. Із врахуванням інваріантності до інверсії часу проведено класифікацію енергетичних станів кристалів α-$LiIO_3$ в цих точках та надано відповідну їх класифікацію у великій зоні (зоні Джонса). На основі експериментально виміряних раманівських спектрів першого порядку побудовано криві дисперсії фононних гілок у напрямку Γ–A. Обговорюються внески в експериментально зареєстрований раманівський спектр другого порядку обертонів та складових тонів точок Γ і A, участь яких у формуванні спектра другого порядку зумовлена розглянутими особливостями розподілу густини фононних станів у цих точках, та коливальних станів інших критичних точок зони Бріллюена. Зроблено висновок про правомірність застосування квазимолекулярного наближення при розгляді динаміки ґратки кристалів α-$LiIO_3$.

Ключові слова: динаміка кристалічної ґратки, зона Бріллюена, зона Джонса, раманівська спектроскопія, йодат літію.