Short Notes

Light scattering in LiCoPO$_4$ single crystal: analysis of the vibrational spectrum

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In a single crystal of LiCoPO$_4$ Raman scattering has been studied in a wide temperature range. Thirty-two of the 36 Raman-active vibrational modes predicted by group-theory analysis were detected. The experimental lines are identified on the basis of their polarization rules, frequency position, and temperature behavior.

The recent interest in the family of lithium orthophosphates LiMePO$_4$ (Me = Fe, Mn, Co, Ni) stems from the fact that (i) they could have been good candidates for the observation of the so-called piezomagnetoelectric effect [1], and (ii) LiCoPO$_4$ crystals have rather high linear magnetoelectric coefficients [2], which were previously observed mainly in rare-earth compounds, e.g., TbPO$_4$ (Ref. 3). The high value of the magnetoelectric effect may be due to the particular arrangement of the energy levels of the magnetic ions in LiCoPO$_4$. That is why the study of the energy spectrum features of lithium orthophosphates is important.

In this paper we report the results of a Raman study of a LiCoPO$_4$ single crystal in a wide frequency and temperature ranges. As a result of the incomplete $3d^n$ shell of transition metal ions, the low-temperature Raman spectra may contain lines corresponding to electronic crystal field transitions. Because of the phase transition to the magnetically ordered state, the light scattering on spin waves, and on excitons was expected to be observed. On the one hand, there are reasons to believe that the high magnetoelectric coefficients of LiCoPO$_4$ are connected with the electronic energy level arrangement of the magnetic Co^{2+} ion. On the other hand, the above-mentioned frequency region of the electronic excitations overlaps with that of the vibrational spectra. This circumstance makes it necessary to study the phonon spectra in the paramagnetic and magnetically ordered states. Since the vibrational spectra of LiCoPO$_4$ have not yet been studied, our aim is to study the spectra in detail in order to detect the phonon modes predicted by group-theory analysis and to identify them.

Experimental procedure

The Raman spectra were measured on a single crystal of LiCoPO$_4$ of high optical quality. The sample was cut as a rectangular parallelepiped with edges parallel to the crystallographic axes of the orthorhombic cell a, b, c with 0.96, 1.22, and 1.76 mm length, respectively. The system of coordinates was chosen to be $X \parallel a$, $Y \parallel b$ and $Z \parallel c$. Since the absorption spectrum of this crystal has strong

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lines at 470–580 nm and weaker ones at 700–800 nm [2], the 632.8-nm line of the He-Ne (~ 30 mW) laser was used in the experiments to reduce the beam-induced heating of the sample and to enhance the scattered light intensity. The scattered light was analyzed with a double Jobin Yvon U1000 monochromator and detected with a cooled photomultiplier and a photon counting system. In order to avoid the polarizing effect of the spectrometer, a depolarization wedge was placed in front of the entrance slit. The temperature interval 4.2–300 K was ensured using a special optical cryostat with a wide-angle aperture micro-objective. The sample was kept in an exchange gas atmosphere.

Structural features of LiCoPO$_4$ and group-theory analysis of fundamental vibrations

The crystal LiCoPO$_4$ is isomorphic with other lithium orthophosphates LiMePO$_4$ (Ref. 4), which belong to the olivine structure type. At room temperature the orthorhombic unit cell contains four formula units and is described with space group *Pnma*. One of the structural features is a layer-like arrangement of oxygen atoms in the planes parallel to (001), the atom distribution is similar to the hexagonal close packing. Each phosphorus atom in the crystal is surrounded by four oxygen atoms, creating a distorted tetrahedral PO$_4^{3-}$ complex with $C_s(m \perp b)$ point symmetry. The Co and Li atoms are surrounded by six oxygen atoms which occupy the positions with site symmetry C_s and C_i, respectively. The antiferromagnetic ordering of the Co^{2+} spins [$T_N = 21.9$ K (Ref. 2); magnetic space group *Pnma'* (Ref. 5)] does not induce multiplication of the crystallographic primitive cell.

The group-theory analysis of the fundamental vibrations in the crystal LiCoPO$_4$ was performed in terms of external and internal vibrations of the ion complexes and single ions. Let us introduce the internal vibrations as vibrations which are caused by the motion of atoms which induces deformation or a change in the PO$_4^{3-}$ volume (the position of the mass center and the orientation of the inertia axes are assumed to be undisturbed). This is valid in the case where the internal and external vibration frequencies differ considerably. The so-called external vibrations describe the translational motion of the mass center of PO$_4^{3-}$, Li$^+$, and Co^{2+} ions and the hindered rotations (librations) of the PO$_4^{3-}$ ions. Such separation is rather arbitrary and may be used in the group-theory analysis for clarity only. In

fact, these vibrations are not completely independent. The group-theory results are given in Table 1 using the above-mentioned terms. As seen in Table 1, 36 optic modes with the symmetries A_g, B_{1g}, B_{2g} and B_{3g} are expected in the Raman spectra, which correspond to the polarization of the excited and scattered light in the chosen coordinate system as: $A_g - (XX), (YY), (ZZ), B_{1g} - (XY), (YX), B_{2g} - (XZ), (ZX),$ and $B_{3g} - (YZ), (ZY)$.

Table 1

The symmetry of fundamental vibrations of a LiCoPO$_4$ crystal

Type of vibrations	Symmetry of vibrations							
	A_g	B_{1g}	B_{2g}	B_{3g}	A_u	B_{1u}	B_{2u}	B_{3u}
Acoustic						1	1	1
Optic	11	7	11	7	10	13	9	13
Internal PO$_4$	6	3	6	3	3	6	3	6
External:								
Translational	4	2	4	2	5	6	4	6
Librational PO$_4$	1	2	1	2	2	1	2	1

Experimental results and discussion

The Raman spectra of the LiCoPO$_4$ crystal shows many well-polarized lines of different intensities (Fig. 1). It should be noted, however, that the strongest Raman lines can infiltrate into the spectra with other polarizations, which are forbidden for them by selection rules. This is mainly connected with the use of collecting wide-angle aperture optics required for the experiment under the conditions of strong excited and scattered light absorption by the crystal.

The intense lines which persist when the temperature rises from $T < T_N$ to room temperature are identified here as first-order vibrational excitations. Since the test crystal undergoes no structural phase transitions, the phonon lines show only a weak frequency shift and broadening with increasing temperature (Figs. 2 and 3).

Internal vibrations of the free tetrahedron PO$_4$ contain, according to Herzberg [6], the nondegenerate mode $A_1(\nu_1)$, double-degenerate mode $E(\nu_2)$, and two triple-degenerate modes F_2 (ν_3 and ν_4) in terms of irreducible representations of point group T_d of the tetrahedron. The fundamental mode frequencies ν_1, ν_2, ν_3, and ν_4 are 980, 365, 1082, 515 cm^{-1}, and 938, 420, 1017, 515 cm^{-1}, as obtained in Refs. 6 and 7, respectively. In the crystal these modes generate 18 Raman-active vibrational branches. On the basis of the frequencies estimated above and the comparison between the number of experimentally
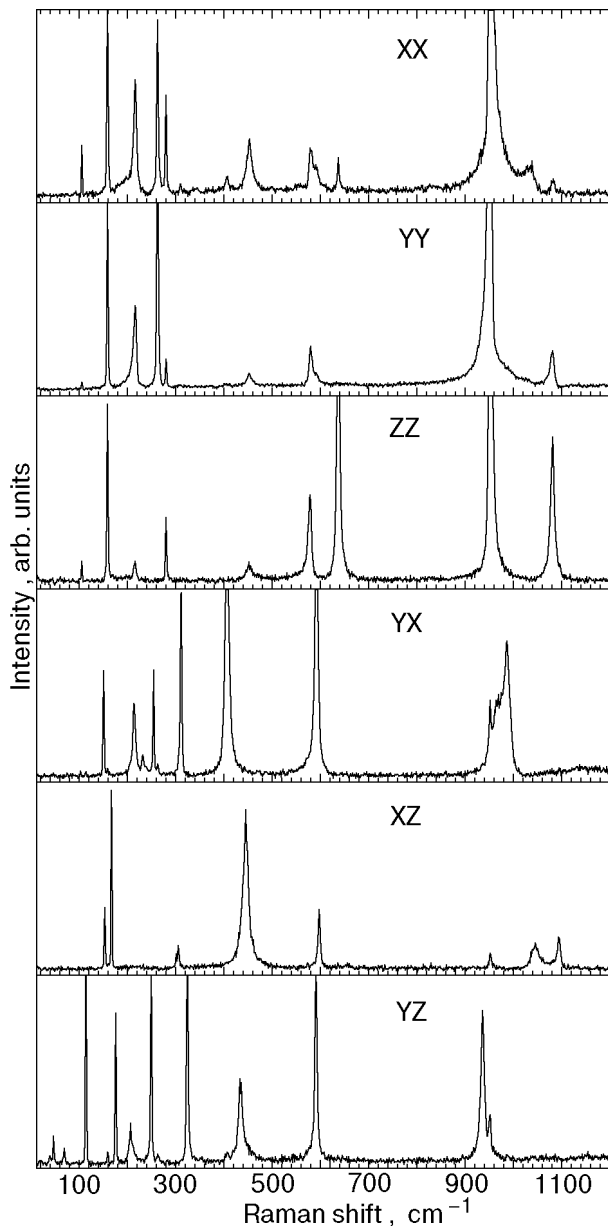
Fig. 1. Low temperature (10 K) polarized Raman spectra of the crystal $LiCoPO_4$. Spectral resolution is 2.0 cm^{-1}.

Fig. 2. Temperature behavior of the Raman spectrum of the crystal $LiCoPO_4$ with the component of the scattering tensor YZ (B_{3g} modes) in the region of external vibrations. The numbers indicate the spectra at temperatures, K: 300 (*1*); 250 (*2*); 200 (*3*); 150 (*4*); 82 (*5*); 40 (*6*); 10 (*7*).

observed and theoretically predicted modes, the frequency region of vibrational excitations in the crystal $LiCoPO_4$ is arbitrarily separated into two subregions, which correspond to the external (0–350 cm^{-1}) and the internal PO_4 complex vibrations (above 400 cm^{-1}).

Following the scheme given above, it is assumed that in the first subregion the Raman spectrum involves the translational modes of the Co^{2+} and PO_4^{3-} ions and the PO_4^{3-} complex librations. Since the Li^+ ions are embedded at the positions with a symmetry center, their vibrations are not active in the first-order Raman scattering. It is known [8] that the temperature dependence of the phonon line width may mainly be determined via two mecha-
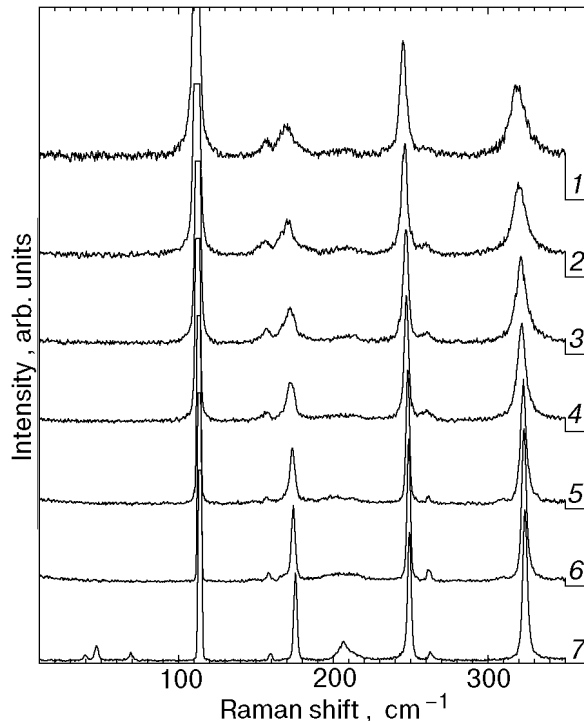
nisms: (i) anharmonicity of the corresponding vibrational mode and (ii) relaxation processes which may be related to many-particle decays of the oscillation or reorientation motions typical of atomic complexes. The first mechanism provides the linear part of the spectral line widening dependence of temperature, while the second one represents the Arrhenius-like part. Since the reorientation motions in the crystal are accomplished only by the PO_4 complexes during their hindered rotations, the 174.5 and 323 cm^{-1} lines (T = 10 K) in the low-frequency region of the B_{3g} spectrum were preferentially assigned to librations on the grounds that the temperature dependence of their width is described mainly by mechanism (ii) (Fig. 3). In the other polarizations the temperature behavior of the line widths cannot clearly be assigned to each mechanism. We should note that 214.5 cm^{-1} (A_g) and 310 cm^{-1} (B_{1g}) lines have large width (contrary to other lines in the low-frequency region) in the whole temperature range studied. We can therefore assume that they have librational character also.

In the high-frequency region of the phonon spectrum the observed lines were identified in accordance with their closeness to the fundamental oscillation frequencies of the free PO_4 complex (see

above) and with allowance for the polarization selection rules following from group-theory analysis.

The frequencies of all phonon lines detected in this experiment along with the symmetries and identification of the corresponding vibration modes are presented in Table 2. Of the 36 predicted modes ($11A_g$, $7B_{1g}$, $11B_{2g}$, $7B_{3g}$) 32 Raman-active phonon modes ($11A_g + 6B_{1g} + 8B_{2g} + 7B_{3g}$) were detected. The absence of some lines from the spectra may be attributed either to their extremely weak intensity or to the masking with the infiltrated strong lines that belong to another Raman polarization.

Table 2

Experimentally observed frequencies (cm^{-1}) of vibrational excitations of a LiCoPO$_4$ single crystal at 10 K (300 K) and their classification

Type of vibrations	Symmetry of vibrations			
	A_g	B_{1g}	B_{2g}	B_{3g}
External	104.5(102)			113(111)
		149.5(143)		
			151.5(151)	
	157.5(156)			
			166(164)	
				174.5(169)
	216(209)			248(244.5)
		253(250.5)		
	261(260)			
	279(272)			
			300(299)	
			304.5(299)	
		310(300.5)		
				323(318.5)
Internal PO$_4$ — $E(\nu_2)^*$		405(402)		433(432)
			444.5(446.5)	
	451.5(448)			
$F_2(\nu_4)^*$	577.5(577.5)			589.5(589)
		591(590)		
			596(596)	
	636(634.5)			
$A_1(\nu_1)^*$	951(950.5)			
$F_2(\nu_3)^*$				935(939)
		986(986.5)		
	~1030(~1009)			
			1044(1037)	
		1080(1075)		
			1093(1088)	

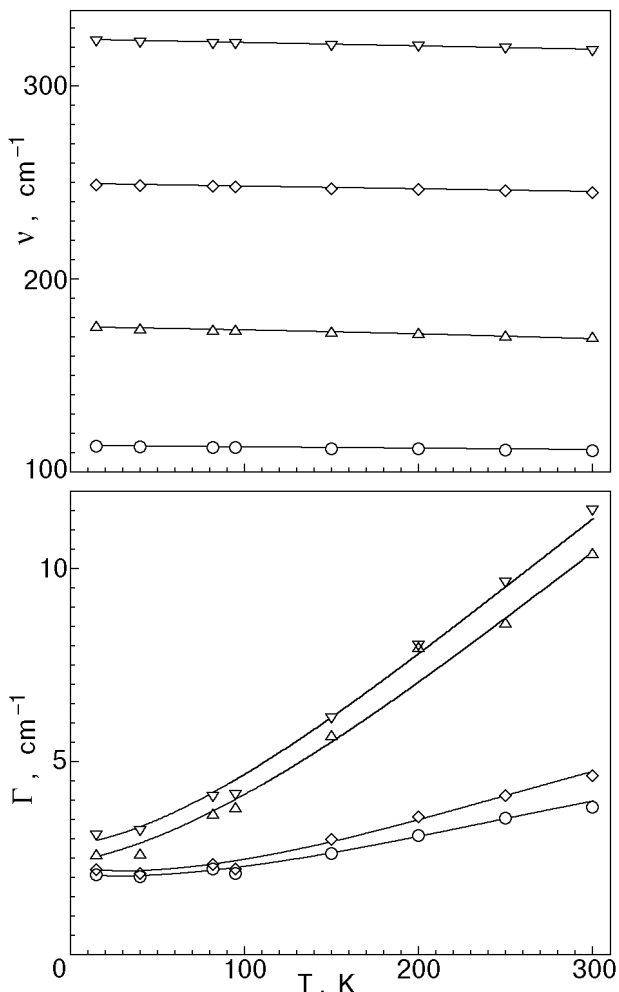* Irreducible representations and the internal mode indexes of a free PO$_4$ tetrahedron [6].

Fig. 3. Temperature dependence of the frequency ν and width at half maximum Γ of the phonon lines in the low-frequency B_{3g} spectrum (see Fig. 2).

It should be noted that the low-temperature spectra have features in their temperature behavior of the intensity that differ from that of phonons. We assign the lines appearing at $T < T_N$ in the spectral region below 100 cm^{-1} to the scattering by spin waves. Their temperature behavior and frequency position require further experimental and theoretical investigations. If all the three lines observed in the spectrum have single-particle nature, the description of the magnetic structure of LiCoPO$_4$ requires the consideration of more than two nonequivalent sublattices.

In the region above 100 cm^{-1} some lines may be assigned to scattering by electron (exciton at $T < T_N$) excitations. Their typical feature is the tendency to rapidly widen as the temperature rises above T_N.

An additional point to emphasize is that some phonon lines observed in the experiment exhibit an asymmetric shape. This may result from the crystal

lattice inharmonicity or from a strong hybridization of electronic and vibrational excitations in the $LiCoPO_4$ crystal. In order to separate the contributions of the above mechanisms, it is interesting to study vibrational spectra of other members of the lithium orthophosphate family in which paramagnetic ions of metals have no low-frequency electron excitations, which can overlap in energy with that of the phonons.

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