Raman study of magnetoelectric $LiCoPO_4$

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The olivine-type lithium orthophosphates Li*M*PO4 (*M*=Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}) family have intriguing magnetoelectric properties and the entangled spin excitations. It demonstrates a tight coupling of the phonon, electron and magnetic subsystems. The present work is dedicated to the Raman studies of the $LiCoPO_4$ single crystal possessing the highest magnetoelectric coefficient among the above-mentioned crystals of the Li*M*PO_4 family. Raman spectroscopy is the non-destructive highly informative method that can simultaneously probe the phonon, electron and magnetic excitations. In the present work, we discuss the magnetic scattering spectrum, electronic excitations of the Co^{2+} ion and additional phonon lines arising below T_N = 21.9 K.

Raman spectrum of the $LiCoPO_4$ single crystal was investigated in the frequency region of 3–1200 cm^{-1} in the temperature range between 5 and 300 K. A_g, B_{1g}, B_{2g} and B_{3g} modes are active in Raman tensor components: A_g –*XX*, *YY*, *ZZ*, B_{1g} –*XY*, *YX*, B_{2g} – *Z*, *ZX* and B_{3g} – *YZ*, *ZY*.

X ∥ a, Y ∥ b, Z ∥ c.

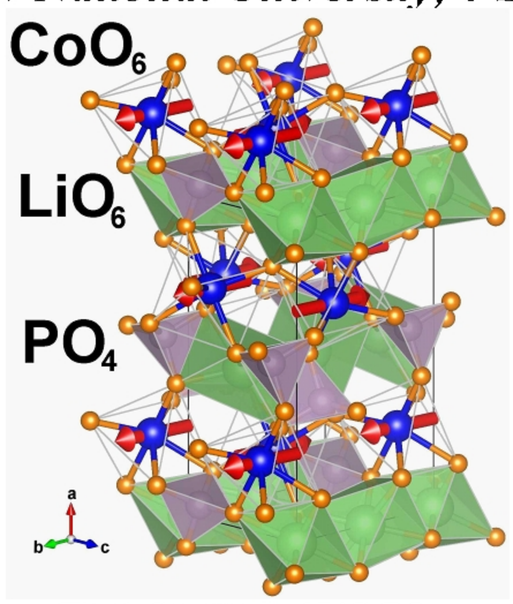


Fig. 1. Structure of $LiCoPO_4$.

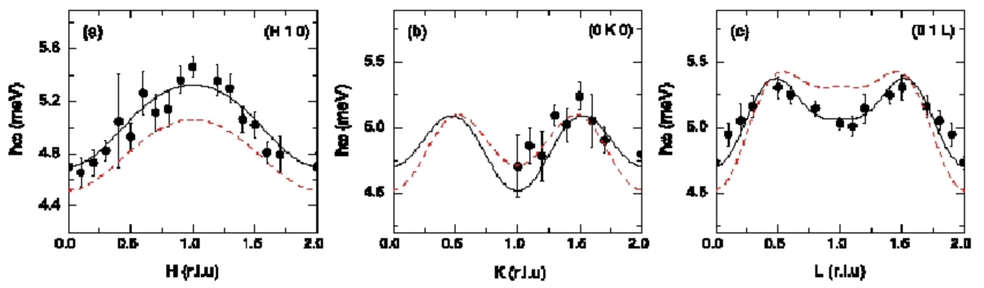


Fig. 2. Magnons dispersion curves in crystal $LiCoPO_4$ [1].

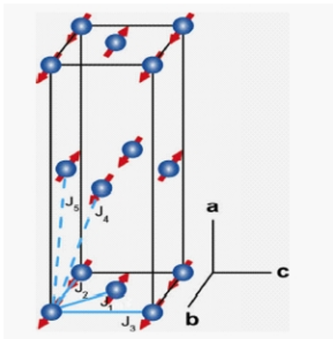
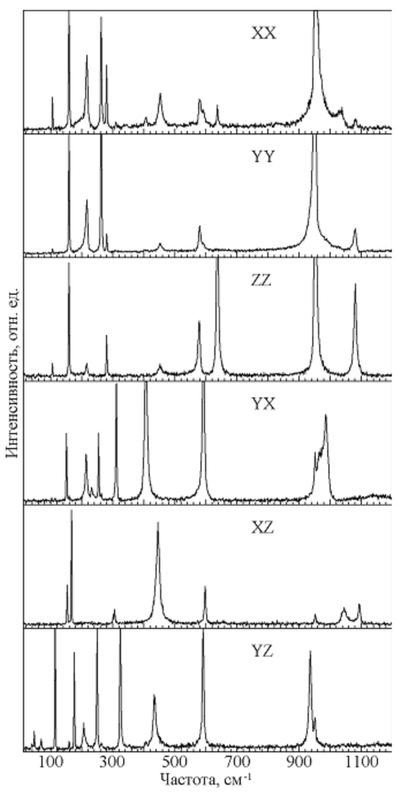
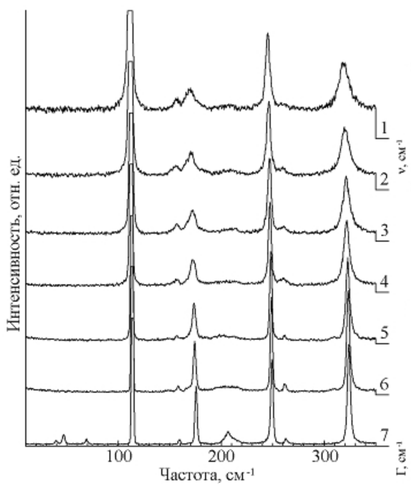
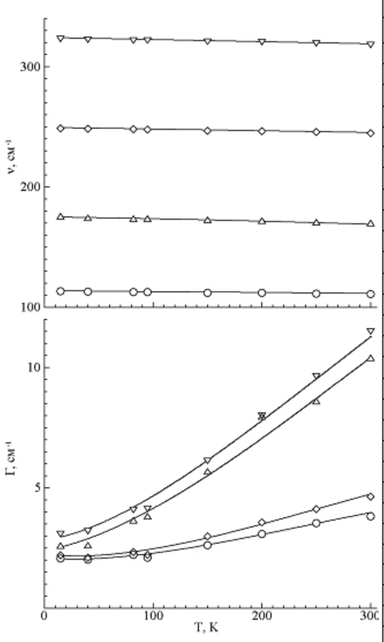


Fig. 3. Magnetic cell of $LiCoPO_4$ and scheme of exchange interactions. Co^{2+} ions are showed [1].
Parameters of model (in meV) [1]:
J_1 = 0.743 ± 0.187 , J_2 = 0.105 ± 0.159,
J_3 = 0.194 ± 0.131 , J_4 = -0.108 ± 0.08 ,
J_5 = -0.181 ± 0.105 ,
D_x = 0.718 ± 0.192 , D_y = 0.802 ± 0.208.

Previous Raman work [2, 3]







Frequency (in cm^{-1}) Compound			Factor-group symmetry	Site symmetry	Free PO_4 unit
$LiCoPO_4$ [2]	$LiNiPO_4$ [3]	ωNi / ωCo	D_{2h}*	C_s	T_d
1093 (1087)	1090 (1088)	1.0009	B_{2g}	A'	
1080 (1077)	1074.5 (1072)	0.9954	A_g	(1080)	
1044 (1028)	1023 (1022.5)	0.9946	B_{2g}	A'	F_2 (ν_3)
1030 (1009)	1011.5 (1010.5)	1.0015	A_g	(1016)	1082 cm^{-1}
986 (986.5)	986 (987.5)	1.0010	B_{1g}	A''	
935 (943)	953 (952)	1.0095	B_{3g}	(970)	
—	—		B_{2g}	A'	A_1 (ν_1)
951 (951)	948.5 (948.5)	0.9974	A_g		980 cm^{-1}
636 (634)	642 (640)	1.0095	A_g	A'	
596 (596)	603 (601)	1.0015	B_{2g}	(621)	
591 (590)	592.5 (591.5)	1.0025	B_{1g}	A''	F_2 (ν_4)
589.5 (589)	592 (591)	1.0034	B_{3g}	(591)	515 cm^{-1}
577.5 (577)	581.5 (580)	1.0052	A_g	A'	
—	—		B_{2g}		
451 (449)	462.5 (459)	1.0223	A_g	A'	
444.5 (448)	470.5 (467.5)	1.0435	B_{2g}	(455)	E (ν_2)
433 (432)	442.5 (437)	1.0116	B_{3g}	A''	363 cm^{-1}
405 (401)	422.5 (417.5)	1.0411	B_{1g}	(427)	
279 (272)	308 (303.5)	1.1158			
261 (260)	287.5 (282.5)	1.0865	A_g		
216 (209)	242.5 (238)	1.1388			
157.5 (156)	175.5 (175)	1.1218			
104.5 (102)	114 (111.5)	1.0931			
310 (300.5)	325 (320.5)	1.0666			
253 (250.5)	258 (256)	1.0220	B_{1g}		
181.5 (180)	199 (195)	1.0541			
149.5 (143)	—				
304.5 (299)	329.5 (325.5)	1.0886			
300 (299)	313 (310)	1.0368	B_{2g}		
—	255.5 (252)				
166 (164)	182 (181.5)	1.1067			
151.5 (151)	172 (170)	1.1258			
323 (318.5)	329 (324.5)	1.0188			
248 (244.5)	262 (258.5)	1.0573	B_{3g}		
174.5 (169)	193.5 (189)	1.1183			
113 (111)	122 (119.5)	1.0766			

External mode

Structure of $LiCoPO_4$: *Pnma* (D_{2h}^{16}), Z=4,
***a*=10.092 A, *b*=5.89 A, *c*=4.705 A at T=300 K.**
***a*=10.159 A, *b*=5.9 A, *c*=4.70 A at T=8 K.**

T_N = 21.9 K , magnetic group *Pnma'* (Z=4).
Linear magnetoelectric (ME) – $P_i = \alpha_{ij} H_j$
ME coefficients:
$|\alpha_{yx}|$ (4.2 K) =30.6 ps/m and $|\alpha_{xy}|$ (4.2 K) =18.4 ps/m.

Γ_{vib}=11A_g+7B_{1g}+11B_{2g}+7B_{3g}+10A_u+14B_{1u}+10B_{2u}+14B_{3u}
Γ_{int}= 6A_g + 3B_{1g} + 6B_{2g} +3B_{3g} + 3A_u +6B_{1u} +3B_{2u} +6B_{3u},
Γ_{tr} = 4A_g + 2B_{1g} + 4B_{2g} + 2B_{3g} + 5A_u + 6B_{1u} + 4B_{2u} +6B_{3u},
Γ_{lib}= A_g+2B_{1g}+B_{2g}+2B_{3g}+2A_u+B_{1u}+2B_{2u}+B_{3u}.

11A_g+7B_{1g}+11B_{2g}+7B_{3g} modes are active in Raman spectra.

Table 1. Symmetry and frequencies of the phonon modes in $LiCoPO_4$ [2] and $LiNiPO_4$ [3] crystals at T = 10 K (300 K).

New Raman data

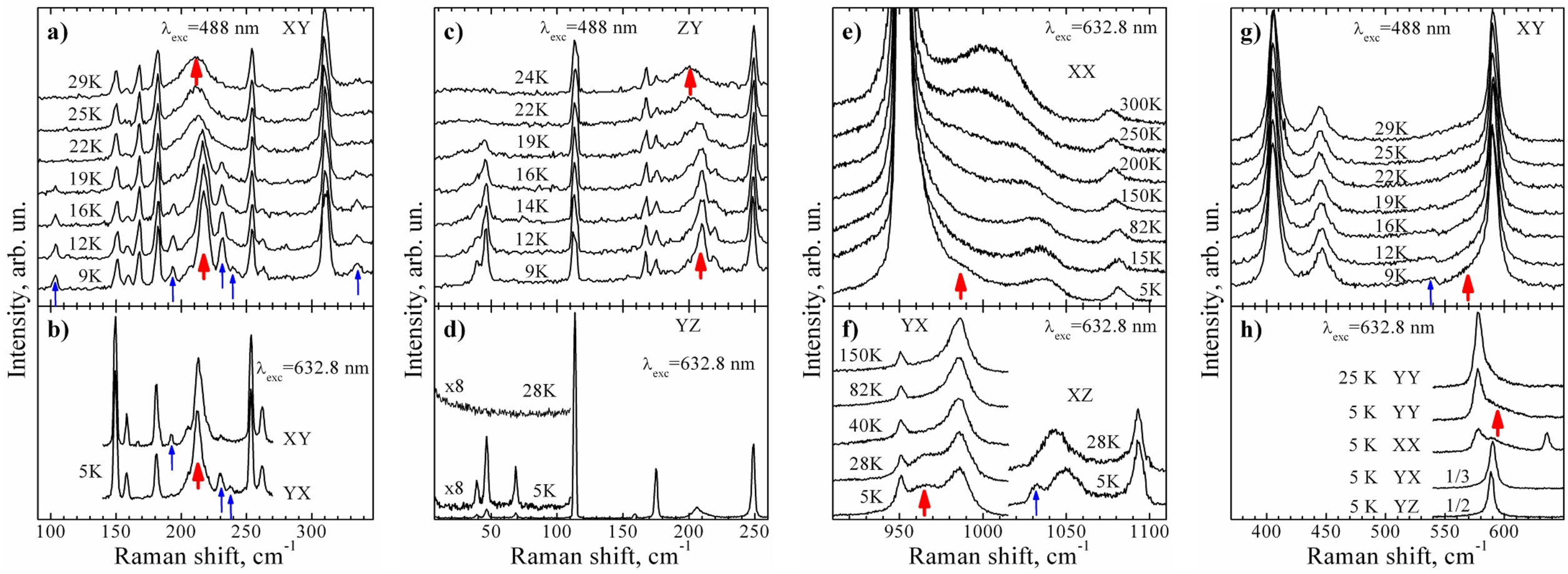


Fig. 4. Temperature dependence of polarized Raman spectra for: a), b) – B_{1g}; c), d) – B_{3g}; e) – A_g, f) – B_{1g} (*YX*) and B_{2g} (*XZ*), g) – B_{1g}; h) – A_g, (*YY*, *XX*), B_{1g} (*YX*), B_{3g} (*YZ*) modes. Spectral resolution: a), c), g) – 3.0 cm^{-1}; b), d), e), f), h) – 1.8 cm^{-1}. Blue thin arrows are related to the additional phonon lines. Red thick arrows are electronic excitations.

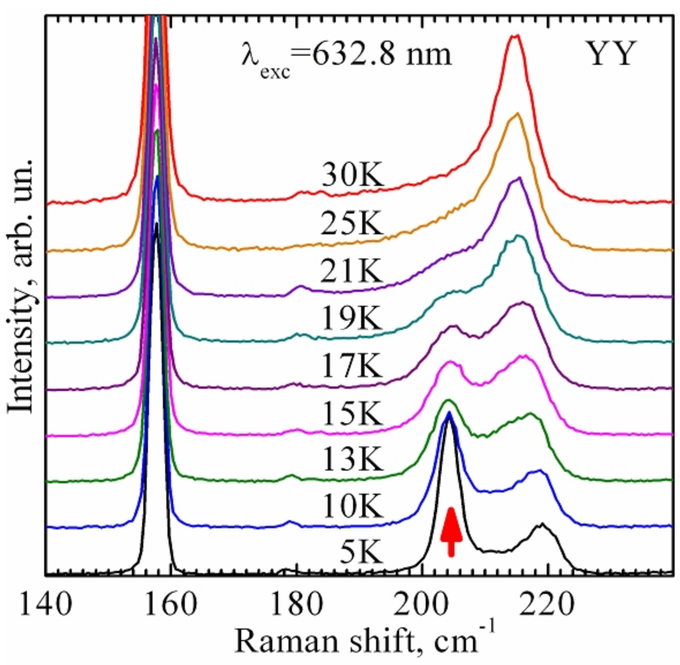


Fig. 5. Temperature dependence of A_g (*YY*) Raman spectra. Spectral resolution: 1.8 cm^{-1}. λ_{exc} = 632.8 nm.

Conclusions

The performed analysis of the taken Raman spectra in the different polarization configurations has revealed a number of additional phonon lines upon transition to a magnetically ordered state: 102.0, 192.2, 230.0, 237.5 and 333.5 cm^{-1} (Figs. 4a, 4b); 1031.5 cm^{-1} (Fig. 4f). It could be explained by the unit-cell multiplication below T_N=21.9 K as well as IR phonon leakage due to the magneto-electric effect.

These are observed three additional low-frequency lines 39.0, 46.0, 68.2 cm^{-1} disappearing above T_N (Figs. 4c, 4d). We suppose these lines could be assigned with magnetic excitations that is in good accordance with previous THz absorbance spectroscopy studies [4].

The linewidths of the 205.0 and 212.2 cm^{-1} (Figs. 4a-d); ~ 570 and 590.0 cm^{-1}; 965.0 and 987.0 cm^{-1} bands (Figs. 4e, 1f) are more than 5 times that the linewidths of the phonon lines. We believe, that they can be assigned with the electronic transitions between the crystal field split levels of the ground $^4T_1$ (^4F) state of Co^{2+} ion. Strong coupling between these electronic and phonon excitations have been revealed (Figs. 4e, 4g, Fig. 5).

Referenses:

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