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Magnetoelectric properties of LiCoPO$_4$ and LiNiPO$_4$

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In strong magnetic fields up to 20 T quasistatic measurements of the magnetic-field-induced electric polarization have been performed in LiNiPO$_4$ single crystals between 4.2 and $\sim$25 K. The magnetoelectric (ME) effect has been studied in detail near the Néel temperature. The temperature hysteresis of the polarization induced by a magnetic field was found. An anomalous temperature dependence of the magnetoelectric susceptibility during the phase transition and the ME ''butterfly loop'' were observed. The phenomenological theory of the magnetoelectric effect in LiCoPO$_4$ and LiNiPO$_4$ has been developed. A tentative explanation of the existence of the magnetoelectric ''butterfly loop'' is given. It is shown that there is a non-Lifshitz invariant in the free energy expansion which is linear in the spatial derivatives. Hence the phase transition to a space-modulated spin structure is possible. The influence of such a structure on the linear magnetoelectric effect is examined.

I. INTRODUCTION

The magnetoelectric (ME) effect is characterized either by the linear change of the electric polarization resulting from the application of a magnetic field or by the linear change of a magnetic moment resulting from the application of an electric field and is basically one of the consequences of time invariance violating in materials.[1] An explicit prediction of the magnetoelectric effect for Cr$_2$O$_3$ was made by Dzyaloshinskii in 1959. The lithium orthophosphates occupy a unique place in the large family of magnetoelectrics because of their exceptionally large ME coefficients. At the moment there are only speculations whether this is related to the special character of the olivine crystal structure or to the particular arrangement of the energy levels of the magnetic ions.

The lithium orthophosphates of divalent cobalt and nickel belong to the olivine family of orthorhombic antiferromagnetics (AFM) with the general formula LiMPO$_4$ (where M = Fe^{++}, Mn^{++}, Co^{++}, Ni^{++}), which are known to be magnetoelectrics.[2] There are four formula units per unit cell and for LiCoPO$_4$ and LiNiPO$_4$ the lattice parameters are a = 10.20 Å, b = 5.92 Å, and c = 4.69 Å and a = 10.03 Å, b = 5.85 Å, and c = 4.68 Å, respectively. The standard space group is orthorhombic $Pnma$ ($\equiv D_{16}^{2h}$). The magnetic ions are crystallographically equivalent and occupy the 4(c) position:

$$1(x,1/4,z), 2(-x,3/4,-z), 3(x+1/2,1/4,-z+1/2), 4(-x+1/2,3/4,z+1/2), \quad (1)$$

where $x \approx 0.28$ and $z \approx 0.98$. The projection of the unit cell onto the XY plane is shown in Fig. 1. LiCoPO$_4$ and LiNiPO$_4$ were investigated extensively in the past.[2–4] At low temperature antiferromagnetic ordering takes place with preservation of the unit cell. Thus, the antiferromagnetic structure can be described in terms of four magnetic sublattices. Earlier papers on LiCoPO$_4$ have indicated that this crystal exhibits a simple two-sublattice antiferromagnetism with spins aligned along the b axis.[3,4] The magnetic Co-O-Co superexchange interactions couple the spins between planes parallel to (100). Only long-range interactions such as the Co-O-P-O-Co operate between these planes. The LiNiPO$_4$ magnetic structure differs only in spin direction (c axis) from that of LiCoPO$_4$. One of the interests in LiCoPO$_4$ came from the
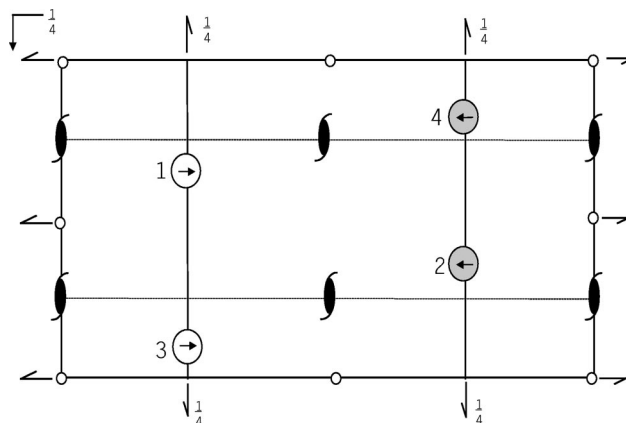

FIG. 1. Unit cell and spin configuration of LiCoPO$_4$ projected onto the XY plane. Only the positions of Co^{++} ions and symmetry elements are shown.

fact that it was considered as a likely candidate for measuring the so far not yet demonstrated piezomagnetoelectric effect,[5] which was not observed experimentally. However, a number of puzzles and unexplained anomalies in this compound have been observed.[6,7]

The paper is organized as follows:

In Sec. II, we briefly discuss the existing experimental data on a LiCoPO$_4$.

In Sec. III, the results of the investigations of the ME properties of a LiNiPO$_4$ single crystal are reported.

In Sec. IV, we present a phenomenological theory of the magnetoelectric effect. Though the most typical properties can be explained in the framework of the proposed approach for the description of the ME effect in Li phosphates, some experimental results cannot be deduced from the simplest model. Several of them could nevertheless be explained by use of the original approach provided we assume the transition parameter to be spatially inhomogeneous. We then go on to consider a model which assumes that the free energy expansion contains Lifshitz-like invariants.

In Sec. V, we summarize the conclusions obtained from the present investigation.

II. DISCUSSION OF FORMER, PUBLISHED DATA OF LiCoPO$_4$

Recently the magnetization of a LiCoPO$_4$ single crystal has been studied in magnetic fields up to 20 T and down to liquid helium temperatures.[7] The characteristic feature of those dependences is a magnetic-field-induced phase transition at about 12 T, followed by a second induced one at about 19 T at 6.5 K, for fields applied along the antiferromagnetic axis. It was suggested that two metamagnetic transitions occur, an antiferromagnetic to ferrimagnetic phase transition followed by a transition to the paramagnetic phase. It is clear that the magnetic behavior of LiCoPO$_4$ in high magnetic fields cannot be understood in the framework of just a two-sublattice model. It should be emphasized that in an external magnetic field the magnetic moment of Co^{++} ions does not reach the saturation value even for 20 T. Since the exchange field is so strong, it seems reasonable to suppose that the metamagnetic behavior could be due to special features of the exchange interaction, and that the biquadratic exchange plays an important role in the magnetic ordering of LiCoPO$_4$.[8] On the other hand, the theory we developed elsewhere[9] predicts a large anisotropy in the magnetic susceptibility, which is observed experimentally.[10] The great value of a zero-field splitting has allowed us to calculate a magnetoelectric effect in LiCoPO$_4$ using the one-ion approximation,[11] so the magnetocrystalline anisotropy also plays an important role in LiCoPO$_4$. It is well known that if the anisotropy energy is larger (or comparable) than the exchange energy, a metamagnetic transition takes place instead of a spin-flop transition. All these results suggest that magnetic and magnetoelectric properties of LiCoPO$_4$ are much affected by the crystal field and the exchange interaction of the same order of magnitude. The nature of the above transitions is still a subject for investigations.

Accurate ME measurements with a maximum field of 10 kOe show[6] that the coefficient $\alpha_{xy}(T)$ of LiCoPO$_4$ follows a power law from about $T_1 = 14$ K to $T_N = 21.9$ K with a criti-

cal exponent $\beta = 0.338$. It is remarkable that the nonclassical region extends here over more than 7 K so that $(T_N - T_1)/T_N = 0.36$. The ME susceptibility in crystals with olivine structure would be expected to be proportional to the sublattice magnetization rather than to the spin-spin correlation function. Thus we expect that the same critical exponent describes the critical behavior of the sublattice magnetization in LiCoPO$_4$.

Another unsolved problem is the specific behavior of the linear ME effect in LiCoPO$_4$. In recent studies an unexpected ME ''butterfly loop'' was observed between T_N and $T_N - 1$ K with a maximum magnetic field of 10 kOe (Ref. 6) and down to 4 K with higher fields.[7] Such a loop is usually the signature of the presence of a spontaneous magnetic moment, but for structures with magnetic symmetry mmm' weak ferromagnetism should not exist. In order to measure the magnetoelectric effect it is usually necessary to cool a sample through the Néel temperature with the simultaneous application of both an electric and a magnetic field. It is an important point that it was not necessary to perform a ME annealing procedure for LiCoPO$_4$. A sufficient condition for observing the ME effect and obtaining a single AFM domain state was the annealing with a magnetic field alone. Hence the material behaves like a weak ferromagnet, but neither a spontaneous magnetization nor a spontaneous polarization has so far been observed by direct measurements.[6]

To throw light on the nature of the above peculiarities and to understand whether these are related to the special character of the olivine crystal structure or essentially due to the presence of the $3d$ transition-metal ions ME measurements on isomorphic material LiNiPO$_4$ have been performed (see the next section).

III. HIGH MAGNETIC-FIELD-INDUCED PHASE TRANSITION, MONITORED BY THE LINEAR MAGNETOELECTRIC EFFECT IN THE ANTIFERROMAGNET LiNiPO$_4$

Magnetoelectric measurements have been performed in the temperature range of 4.2 K up to 25 K and up to an applied magnetic field of 20 T. The polarization induced by the magnetic field has been detected by a quasistatic technique.[12] The induced electric charge was recorded with an electrometer Keithley 642 operated in charge mode. The magnetic field was swept at a constant rate of about 15 kOe/min. The sample temperature was measured using a calibrated carbon-glass resistor. As was mentioned above, below T_N the magnetic symmetry of this compound allows a linear ME effect. The ME tensor has two nonzero components α_{xz} and α_{zx}, where x, y, and z are taken along the unit cell axes a, b, and c, respectively. The AFM single crystal LiNiPO$_4$ has been investigated on a (001)-cut single crystal plate. It is interesting to note that in this case it was not necessary to perform a ME annealing procedure with a view to ''poling'' the AFM domains, i.e., by applying simultaneous electric and magnetic fields. This method was first demonstrated on AFM Cr$_2$O$_3$.[13] For LiNiPO$_4$ a sufficient condition for observing the ME effect was an annealing with a magnetic field alone in order to obtain an AFM single-domain state. It is just the same situation as in LiCoPO$_4$ (Refs. 6 and 7) for observing the ME effect (α_{xy}).
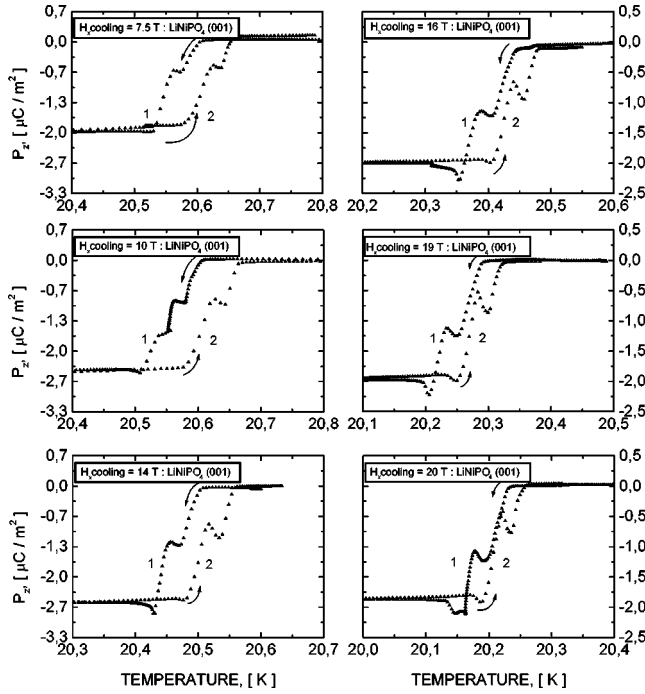
FIG. 2. Temperature dependence of the magnetoelectric polarization of LiNiPO$_4$ measured when cooling (curve 1) and heating (curve 2) in the magnetic field applied along the x-direction.

FIG. 3. Variation of the electric polarization P_z during the AFM phase transition induced by the magnetic field.

Figure 2 shows the temperature dependence of the induced electric polarization P_z on cooling (curve 1) and on heating (curve 2). The characteristic features of these dependences are the presence of the hysteresis loop of the induced electric polarization when cooling and heating through the antiferromagnetic phase transition point T_N and a peak in the temperature dependence of the polarization near the transition at $T=T_N$. It is easy to see from the figure that the magnetic field affects the phase transition temperature. In order to study this aspect the measurements of the induced polarization have been performed in the vicinity of the phase transition and a typical dependence is shown in Fig. 3. The magnetic fields was swept at a rate of about 20 kOe/min. The discrepancy of the induced polarization for forward and reverse magnetic fields is due to the nonstability of the temperature during the measurements. We believe that the small intermediate peaks on the hysteresis loop are due to pinning of the phase boundary and/or of domains. Another strong point is the existence of the ME ''butterfly loop.'' Such a loop is usually the signature of the presence of a spontaneous magnetic moment, but for the structure with $mm'm$ symmetry weak ferromagnetism should not exist. Figure 4 shows the dependence of the induced electric polarization P_z as a function of the magnetic field for $\mathbf{H}\|\mathbf{x}$ at various temperatures. From the figure one can see that the ME ''butterfly loop'' completely vanishes when the temperature approaches about 8 K. This may testify to a new phase transition in LiNiPO$_4$ at low temperature. To our mind there are at least two possible mechanisms which can be responsible for such a behavior of the ME susceptibility. One of them is the presence of the toroidal ordering. A peak just below the transition temperature in LiNiPO$_4$ has some similarity to the kind of behavior in boracites, e.g., Co-Cl boracite and Co-Br boracite.[14,15] Such a behavior has been explained by assum-
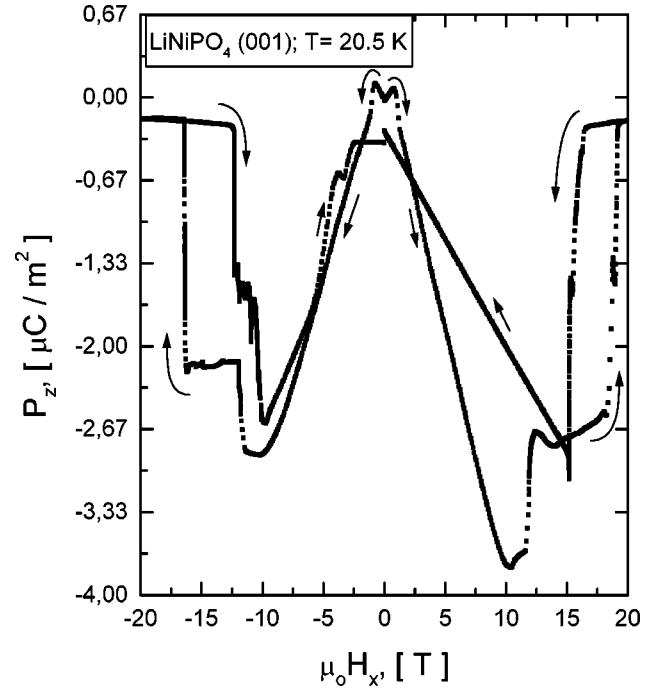
ing that an order parameter transforms as a toroidal moment.[16] The magnetic symmetry of the Li phosphates allows a spontaneous toroidal moment, and the above peculiarity, which was observed for the first time in those compounds, can be the sign of toroidal ordering. The other one is a space-modulated spin structure. The reason for such a structure is the presence of a non-Lifshitz invariant in the free energy expansion which is linear in the spatial derivatives. A more detailed analysis will be given in the next
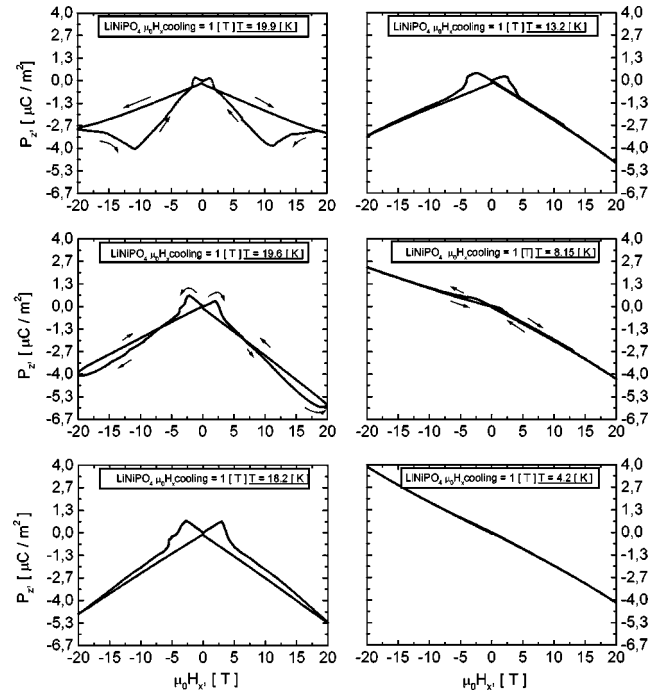

FIG. 4. The electric polarization P_z vs magnetic field $\mathbf{H}_x$ at various temperatures.

TABLE I. Magnetic symmetries associated with the irreducible corepresentations of the paramagnetic group $Pnma1'$ at $k=0$.

IC's	Magnetic groups Induced by IC's	Magnetic point groups induced by IC's	Basis of the IC's	Basis of the IR's [a] associated with IC's	Nonzero α_{ij}
τ_1^-	$Pnma/D_{2h}^{16}$	mmm/D_{2h}	L_{1Y}		
τ_2^-	$Pn'm'a'$ $D_{2h}^{16}/(D_2^4)$	$m'm'm'/$ $D_{2h}(D_2)$	L_{2X},L_{3Z}	xyz	α_{XX},α_{YY} α_{ZZ}
τ_3^-	$Pnm'a'$ $D_{2h}^{16}/(1C_{2h}^2)$	$mm'm'/$ $D_{2h}(1C_{2h})$	m_X,L_{1Z}	yz	
τ_4^-	$Pn'ma$ $D_{2h}^{16}/(1C_{2v}^9)$	$m'mm/$ $D_{2h}(1C_{2v})$	L_{3Y},T_x	x	α_{YZ},α_{ZY}
τ_5^-	$Pn'ma'$ $D_{2h}^{16}/(2C_{2h}^5)$	$m'mm'/$ $D_{2h}(2C_{2h})$	m_Y	xz	
τ_6^-	$Pnm'a$ $D_{2h}^{16}/(2C_{2v}^2)$	$mm'm/$ $D_{2h}(2C_{2v})$	L_{2Z},L_{3X},T_y	y	α_{XZ},α_{ZX}
τ_7^-	$Pn'm'a$ $D_{2h}^{16}/(3C_{2h}^5)$	$m'm'm/$ $D_{2h}(3C_{2h})$	m_Z,L_{1X}	xy	
τ_8^-	$Pnma'$ $D_{2h}^{16}/(3C_{2v}^7)$	$mmm'/$ $D_{2h}(3c_{2v})$	L_{2Y},T_z	z	α_{XY},α_{YX}

[a]Irreducible representations.

section. It is necessary to note that at low temperatures no phase transition was observed in strong magnetic fields when applied perpendicularly to the spin direction. Hence, it would be interesting to measure another component of the ME tensor, i.e., when the field is applied along the spin direction.

IV. PHENOMENOLOGICAL THEORY

Further we shall consider LiCoPO$_4$. All consideration is valid to equal degree for LiNiPO$_4$ as well as LiCoPO$_4$ if we make the substitutions $L_{2y}\to L_{2z}$, $m_y\to m_z$ and $p_y\to p_z$. The antiferromagnetic structure of LiCoPO$_4$ is shown in Fig. 1. The spins denoted by 1, 2, 3, and 4 differ only in sign, and their sum over the unit cell is equal to zero: $\mathbf{S}_1=-\mathbf{S}_2=\mathbf{S}_3=-\mathbf{S}_4$. The direction of the spins is along [010]. Consistent with experimental data,[3,4] we assume that the translational symmetry of the crystal does not change during the phase transition. This means that the order parameter transforms according to one of the irreducible corepresentations (IC's) of the point group of the crystal. Table I summarizes the magnetic symmetries associated with the IC's of the paramagnetic group $Pnma1'$ (No. 62) at $k=0$, where $\mathbf{m}=\mathbf{S}_1+\mathbf{S}_2+\mathbf{S}_3+\mathbf{S}_4$, $\mathbf{L}_1=\mathbf{S}_1+\mathbf{S}_2-\mathbf{S}_3-\mathbf{S}_4$, $\mathbf{L}_2=\mathbf{S}_1-\mathbf{S}_2+\mathbf{S}_3-\mathbf{S}_4$, and $\mathbf{L}_3=\mathbf{S}_1-\mathbf{S}_2-\mathbf{S}_3+\mathbf{S}_4$. Here $\mathbf{m}$ is the mean magnetic moment of the unit cell and $\mathbf{L}_1$, $\mathbf{L}_2$, and $\mathbf{L}_3$ are antiferromagnetic vectors associated with a two-sublattice distribution of spins. One can see from Table I that it is the component L_{2y} which coincides with the antiferromagnetic order in LiCoPO$_4$, i.e., the order parameter associated with the antiferromagnetic transition $Pnma1'\to Pnma'$, is associated with the vector $\mathbf{L}_2$. It is interesting to note that for that phase a toroidal momentum T_z is nonzero, i.e., has a spontaneous value. The invariant which is responsible for the spontaneous T_z in that phase has the form $L_{2y}T_z$. We shall not consider further this invariant. Now we can write the thermodynamic potential

$$\Phi_{EX}=\frac{1}{2}\Lambda\mathbf{L}_2^2+\frac{1}{4}B\mathbf{L}_2^4,$$

$$\Phi_{ex}^*=\frac{1}{2}D_1(\mathbf{L}_2\cdot\mathbf{m})^2+\frac{1}{2}D_2\mathbf{L}_2^2\mathbf{m}^2,$$

$$\Phi_{AN}=\frac{1}{2}\beta_1 L_{2y}^2+\frac{1}{4}\beta_2 L_{2y}^4+\gamma_1 L_{2x}L_{3z}+\gamma_2 L_{2z}L_{3x}. \quad (2)$$

We assume that only one coefficient Λ depends linearly on the temperature: $\Lambda=\Lambda_0(T-T_N)$. The remaining coefficients are assumed constant and equal to their values at the transition point. The relativistic γ_i terms show that two other canted AFM structures may arise in LiCoPO$_4$. These states result from a weak coupling of relativistic origin. For instance, for the magnetic structure with nonzero component L_{2z} according to Table I the components α_{xz} and α_{zx} of the magnetoelectric susceptibility tensor should be nonzero (further we shall put $\gamma_i=0$). However, for the magnetic group mmm' according to Table I, invariant components of the vector $\mathbf{m}$ are absent, which indicates a lack of weak ferromagnetism. Referring to Ref. 8 for details, we would like only to note that Eq. (2) gives an entirely correct qualitative description of the metamagnetic behavior of exchange origin if it is assumed that $D_1<0$, i.e., allows for the biquadratic exchange.

The ME effect in LiCoPO$_4$ requires the introduction of two additional contributions in the thermodynamic potential:

$$\Phi_{ME}=\lambda_1 L_{2y}m_y p_x+\lambda_2 L_{2y}m_x p_y+\frac{\mathbf{m}^2}{2\chi}+\frac{\mathbf{p}^2}{2K},$$

$$\Phi_{EH}=-\mathbf{E}\mathbf{P}-\mathbf{m}\mathbf{H}. \quad (3)$$

Minimization of $\Phi_{ME}+\Phi_{EH}$ with respect to the P_i and $m_i|_{H=0}$ yields

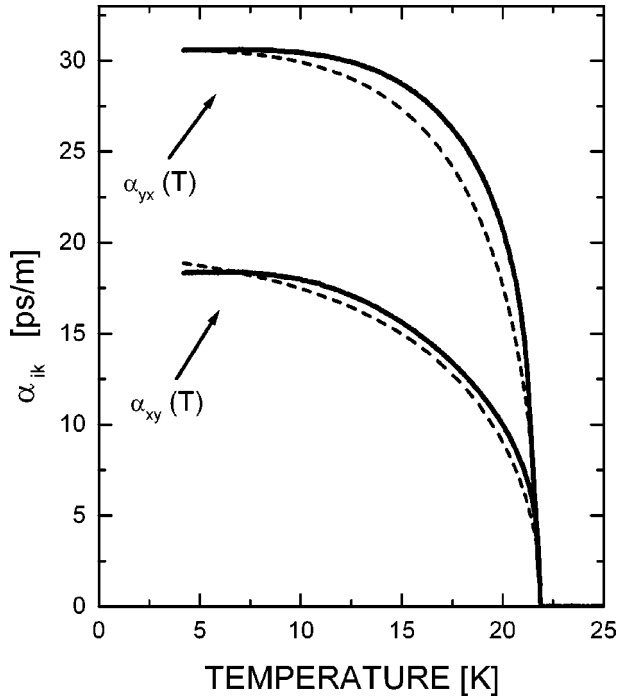FIG. 5. The best fit to the temperature dependence of the ME coefficients α_{xy} and α_{yx} measured by Rivera (Ref. 6). The solid lines represent the experimental data and the dashed lines represent the best fit according to Eq. (6).

$$p_y = -\lambda_2 K L_{2y} m_x, \quad p_x = -\lambda_1 K L_{2y} m_y,$$

$$m_y = -\lambda_1 \chi L_{2y} p_x, \quad m_x = -\lambda_2 \chi L_{2y} p_y. \quad (4)$$

From Eq. (4) we see that there is no difference in behavior between the spontaneous ME effect along x and y since both along x and y the symmetry breaking relativistic component L_{2y} relates $P_{y(x)}$ and $m_{x(y)}$. Let us stress that the linear relationship between P_i and m_i occurs via coefficients which vary as $(T_N - T)^{1/2}$.

Including the field contributions Φ_{EH} and Φ_{ex}^* we obtain

$$\alpha_{xy} = -\frac{K\chi\lambda_1 L_{2y}}{1 + (D^* - \lambda_1^2 K)\chi L_{2y}^2},$$

$$\alpha_{yx} = -\frac{K\chi\lambda_2 L_{2y}}{1 + (D_2 - \lambda_2^2 K)\chi L_{2y}^2}, \quad (5)$$

where $D^* = (D_1 + D_2) > 0$, $P_x = \alpha_{xy} H_y$, $P_y = \alpha_{yx} H_x$:

$$\alpha = -\frac{a(T_N - T)^{1/2}}{1 - b(T_N - T)}. \quad (6)$$

Equation (6) gives the temperature dependence of α (see Fig. 5) and the best fitting for α_{xy} (α_{yx}) (Ref. 6) is obtained with $a \approx -6.881$ (-14.72) and $b \approx -0.03$ (-0.561).

The theoretical analysis carried out cannot explain the existence of the ME ''butterfly loop'' in LiCoPO$_4$ and LiNiPO$_4$. In the following we provide an explanation of the above anomaly, taking into consideration a Lifshitz-like invariant in the free energy expansion. It means that we shall discuss a model in which the instability of the paramagnetic

phase occurs for a given wave number $\mathbf{k}_0$ quite close to the Γ point ($\mathbf{k}=0$). The symmetry analysis shows that the mechanism under study can be related to the presence of Lifshitz-like invariants which are linear in the spatial derivatives:

$$\sigma\left(\mathbf{L}_1 \cdot \frac{\partial \mathbf{L}_2}{\partial z} - \mathbf{L}_2 \cdot \frac{\partial \mathbf{L}_1}{\partial z}\right) + \varsigma\left(\mathbf{m} \cdot \frac{\partial \mathbf{L}_2}{\partial x} - \mathbf{L}_2 \cdot \frac{\partial \mathbf{m}}{\partial x}\right). \quad (7)$$

Invariants like these were introduced first in Ref. 17. We restrict the discussion here to the first term in Eq. (7), which means to the case of a one-dimensionally modulated incommensurate system. Adding that invariant to the usual thermodynamic potential we have

$$\Phi = \int f \, dz,$$

$$f = \frac{1}{2}\Lambda\mathbf{L}_2^2 + \frac{1}{4}B\mathbf{L}_2^4 + \frac{1}{2}\Lambda_1\mathbf{L}_1^2 + \frac{\alpha_1}{2}\left(\frac{d\mathbf{L}_2}{dx}\right)^2 + \frac{\alpha_2}{2}\left(\frac{d^2\mathbf{L}_2}{dx^2}\right)^2$$

$$- \sigma\left(\mathbf{L}_2 \cdot \frac{d\mathbf{L}_1}{dz} - \mathbf{L}_1 \cdot \frac{d\mathbf{L}_2}{dz}\right), \quad (8)$$

where α_1, α_2 and are the constants of the inhomogeneous exchange. Eliminating $\mathbf{L}_1$ we obtain

$$\mathbf{L}_1 = -2\sigma\Lambda_1^{-1}\frac{d\mathbf{L}_2}{dz},$$

$$f = \frac{1}{2}\Lambda\mathbf{L}_2^2 + \frac{1}{4}B\mathbf{L}_2^4 + \frac{1}{2}(\alpha_1 - 4\sigma^2\Lambda_1^{-1})\left(\frac{d\mathbf{L}_2}{dz}\right)^2$$

$$+ \frac{\alpha_2}{2}\left(\frac{d^2\mathbf{L}_2}{dz^2}\right)^2. \quad (9)$$

If in Eq. (9) $(\alpha_1 - 4\sigma^2/\Lambda_1) < 0$, then the transition to the incommensurate phase takes place. This is precisely the equation investigated earlier in Ref. 18 but the difference is that in Eq. (9) instead of a one-dimensional order parameter we have a three-dimensional one. In what follows we represent the AFM vector by the polar and azimuthal angles and the b axis coincides with the polar axis, $\mathbf{L}(\mathbf{r}) = (\sin\theta\sin\phi, \cos\theta, \sin\theta\cos\phi)$ and setting $\mathbf{L}_2 = \text{const}$.

Further we consider the case $\theta = \text{const}$ and $\phi = \phi(z)$. Taking into consideration the crystallographic anisotropy we get

$$f = K_2\sin^2\theta + K_4\sin^4\theta + \left(\frac{1}{2}(\alpha_1 - 4\sigma^2\Lambda_1^{-1})(\phi')^2\right.$$

$$\left. + \frac{1}{2}\alpha_2\{(\phi'')^2 + (\phi')^4\}\right)\sin^2\theta. \quad (10)$$

In Eq. (10) we do not take into account the external magnetic field. It means we do not consider phase transitions induced by the magnetic field.

The Euler-Lagrange equation for the free energy can now be written as

$$\alpha_2\phi^{IV} - \{(\alpha_1 - 4\sigma^2\Lambda_1^{-1})\phi'' + 6\phi''(\phi')^2\} = 0. \quad (11)$$

It is important for us that under certain correlations between the phenomenological constants in Eq. (10) the phase

transition to the conical helix phase take place, that is, θ = const $(0 < \theta < \pi)$ and $\phi = \phi(z)$,[19] and we have the solution

$$\phi(z) = qz, \quad q^2 = -(\alpha_1 - 4\sigma^2/\Lambda_1)/2\alpha_2,$$

$$(\alpha_1 - 4\sigma^2/\Lambda_1) < 0, \quad \alpha_2 > 0,$$

$$\sin^2\theta = \frac{\left(K_1 - \dfrac{\alpha_1 - 4\sigma^2\Lambda_1^{-1}}{4\alpha_2}\right)}{2K_2}. \quad (12)$$

The mixed invariant of exchange-relativistic origin which is responsible for the spontaneous P_{x0} in this phase has the form

$$\delta P_x(L_{1z}L_{2x} - L_{1x}L_{2x}). \quad (13)$$

Now we can determine the spontaneous polarization of the system:

$$P_{x0} = qK\delta(2\sigma\Lambda_1^{-1})\sin^2\theta \approx qK\delta(2\sigma\Lambda_1^{-1})\theta^2. \quad (14)$$

The spontaneous magnetization m_{y0} appears due to the ME interaction [see Eq. (4)] which is very small as well and it reduces to zero below the "lock-in" transition.

The existence of the nonzero spatial average electric polarization and magnetization can explain the above anomaly of the polarization induced by the magnetic field. To summarize, we get the following: (1) The space-modulated spin structure along the z axis is possible. (2) In this case the AFM vector $\mathbf{L}_2$ can be very close to the b axis in accordance to the neutron scattering data. (3) There is another antiferromagnetic structure with $\mathbf{L}_1 \neq 0$. But this vector is very small. (4) The ME susceptibility has approximately the same mathematical form in the case of the space-modulated spin structure as well as in the case of the uniform antiferromagnetic state. (5) There is nonzero spontaneous polarization (and spontaneous magnetization). (6) It is easy to show that for LiCoPO$_4$ we have $m_{y0} \neq 0$, $p_{x0} \neq 0$, while for LiNiPO$_4$ we have $m_{z0} \neq 0$, $p_{x0} \neq 0$. (7) The microscopic mechanism of the nonuniform exchange is the competition of the interactions generating the exchange structures $\mathbf{L}_2$ and $\mathbf{L}_1$.

V. CONCLUDING REMARKS

We have detected new features in the field and temperature dependences of the magnetoelectric effect in LiNiPO$_4$ and interpreted them in terms of a thermodynamic approach. Although difficulties and unsolved problems remain, we have found that there is no particular mystery about the coexistence of weak ferromagnetism and magnetoelectricity in Li phosphates. We showed that the observation of the magnetoelectric "butterfly loop" could be explained by inclusion of an incommensurate magnetic modulation. A general theoretical treatment of the problem of the symmetry of incommensurate phases and the possible full or partial canceling of the linear ME effect are not yet at hand and more theoretical work is needed, particularly for understanding the detailed form of the ME anomalies. Some experiments would allow further developments of the theory.

The following is of particular interest.

The angular and magnetic field dependences of the AFMR spectrum permit us to establish the magnetic ground state of compounds. The magnetic resonance can probably help us determine the local spin correlations and check the existence of the incommensurate phase because incommensurate modulation destroys the translational symmetry and the lineshape of the magnetic resonance signal will have a specific signature.[20] The phenomenological theory of the resonance ME effect in para-, antiferro-, and ferrimagnetic crystals and in crystals which allow the existence of a weak ferromagnetic moment was presented in Refs. 21 and 22. Of course, direct neutron scattering can solve this problem, too. Studying the ME effect in other compounds of the family will yield further valuable information to understand the special role played by the olivine crystal structure of these compounds and by the particular arrangement of the energy levels of the magnetic ions.

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