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Field-induced magnetic phases and electric polarization in LiNiPO$_4$

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Neutron diffraction is used to probe the ($H$, $T$) phase diagram of magnetoelectric (ME) LiNiPO$_4$ for magnetic fields along the $c$ axis. At zero field the Ni spins order in two antiferromagnetic phases. One has commensurate (C) structures and general ordering vectors $k_{C}=(0,0,0)$; the other one is incommensurate (IC) with $k_{IC}=(q,0,0)$. At low temperatures the C order collapses above $\mu_{0}H=12$ T and adopts an IC structure with modulation vector parallel to $k_{IC}$. We show that C order is required for the ME effect and establish how electric polarization results from a field-induced reduction in the total magnetoelastic energy.

Materials with both magnetic and electric orders as found in magnetoelectric (ME) multiferroics have received growing interest in recent years. It is expected that the coupling of magnetic and electric orders in multiferroics will be of technological use, but will also lead to rich physics with multiorder phase transitions and excitations such as electromagnons. Often ferroelectric and magnetic phases have very different ordering temperatures, suggesting that they are driven by different microscopic interactions, but for some they coincide and ferroelectricity is generated by magnetic long-range order.

In the lithium orthophosphates, LiMPO$_4$ ($M$=Mn,Fe,Co,Ni), a strong ME effect is observed in the antiferromagnetic phases. Mercier explained the temperature dependence of the ME coefficients for LiMnP$_4$ and LiCoP$_4$ and to lesser extent for LiFeP$_4$ with a microscopic model adapted from Cr$_2$O$_3$. However, the ME effect in LiNiP$_4$ differs from that in the other lithium phosphates and was not modeled as successfully. In Li$_{12}$, we use the detailed information of the magnetic structures and lead to staggered magnetic moments in applied magnetic fields. Then we establish that electric polarization is only allowed in the field-induced C structure, but not in the high-temperature IC and the zero-field C structures. Finally we show that the electric polarization is driven by the magnetic symmetry and propose a model that accounts for the temperature dependence of the ME constants.

Measurements were performed on a high-quality 0.4 g single crystal. Zero-field measurements were performed in a closed cycle cryostat on a four-circle goniometer at the TriCS single-crystal diffractometer, using neutron wavelength $\lambda=1.18$ Å for the C structure determination at $T=5$ K, and $\lambda=2.318$ Å for the IC structure at $T=21$ K. For diffraction measurements on the triple-axis spectrometer RITA-II, the sample was mounted in a 15 T magnet with the vertical field along the crystallographic $c$ axis. The ($H$, $T$) phase diagram was determined using neutrons with $\lambda=4.04$ Å. The high-field magnetic structure was studied with $\lambda=2.02$ Å neutrons.

To understand the ME effect in LiNiP$_4$, we have studied the ($H$, $T$) phase diagram and the magnetic structures for fields $H||c$ up to $\mu_{0}H=14.7$ T. We first present the ($H$, $T$) phase diagram and show that off-diagonal single-ion anisotropies and Dzyaloshinsky-Moriya (DM) interactions allowed by symmetry are consistent with the observed magnetic structures and lead to staggered magnetic moments in applied magnetic fields. Then we establish that electric polarization is only allowed in the field-induced C structure, but not in the high-temperature IC and the zero-field C structures.

Symmetry properties. LiNiP$_4$ crystallizes in the orthorhombic $Pnma$ (No. 62) crystal structure with lattice parameters $a=10.02$ Å, $b=5.83$ Å, and $c=4.66$ Å. The magnetic Ni$^{2+}$ ions with spin $S=1$ are situated on 4($c$) sites forming buckled planes perpendicular to the $a$ axis. The positions of the four Ni$^{2+}$ in each unit cell are $r_1=(0.275,0.25,0.98)$, $r_2=(0.725,0.75,0.02)$, and $r_3=(0.225,0.75,0.48)$, as shown in Fig. 1(a). The low crystal-field symmetry in LiNiP$_4$ leads to a magnetic-susceptibility tensor that contains staggered off-diagonal terms, $\chi_{ab}$ and $\chi_{ac}$. This allows for a single-ion anisotropy of the type...
magnetic moments are nearly parallel to the $c$ axis. However, the data do not exclude an elliptically polarized collinear spin-density wave belonging to a $D_{xz}$ symmetry.

**Field-induced staggered moments.** Magnetic fields along the $c$ axis induce an antiferromagnetic ($1,1,0$) peak that grows as $(\mu_B H)^2$ in the C phase [Fig. 3(e)]. High-energy (100 keV) x-ray diffraction at the BWS beam line at HASYLAB, DESY, detected no field-dependent signal at (1,1,0), showing that the neutron signal is of magnetic origin. Structural refinements reveal that the ($1,1,0$) peak reflects an additional staggered magnetic $a$ component, $m^a$, with $(+,+,+,−)$ symmetry, and an ordered moment increasing linearly with field to a value of $m^a = 0.17 \mu_B$ at 12 T. Assuming that, to first order, the field rotates the magnetic moments without changing their magnitude, the magnetic structure [Fig. 1(c)] has a total ferromagnetic moment of $\sim (0,0,0.6\mu_B)$ per unit cell and the magnetization is $M_c = (0,0,2.0)$ G at 12 T. This is consistent with bulk measurement, showing that the magnetization grows almost linearly with $\mathbf{H}$ and is $\sim 0.03$ G at 0.1 T. At 40 K, where the system is paramagnetic, there is still field-induced (1,1,0) intensity [Fig. 3(e)]. We interpret this as staggered magnetic fields at the Ni position due to off-diagonal elements of the local susceptibility tensor or the DM interactions, as previously observed in antiferromagnetic $S = \frac{1}{2}$ chains.

The IC magnetic order at zero field is a transversely polarized collinear spin-density wave belonging to a single representation of $k_c$, determined from 112 magnetic peaks at 5 K. The magnetic moments are nearly parallel to the $c$ axis with $m_c = (0.3(1),0.2(2)) \mu_B$. The $c$ component, $m^c$, has a $(+,+,+,−)$ order and the $a$ component, $m^a$, has a $(+,+,−,−)$ order on the sites $r_i$ with increasing $i = 1, \ldots, 4$ [Figs. 1(a) and 1(b)]. Earlier structural analysis using powder diffraction found $m^c$, but not the smaller $m^a$. The presence of $m^a$ may be explained by single-ion anisotropies and DM interactions. Inserting $m_c^a$ of $(+,+,−,−)$ symmetry into Eqs. (1) and (2), we find that $\mathcal{H}^{\text{DM}}_{12} = -D_{12}(S_i^a - S_j^a + S_k^a + S_l^a)$ and $\mathcal{H}^{\text{DM}}_{12} = -D_{12}(S_i^a - S_j^a - S_k^a + S_l^a)$, which both favor that $m^a$ is of $(+,+,−,−)$ symmetry.

**Phase diagram.** The $(H,T)$ phase diagram for fields $\mathbf{H}\parallel c$ including a C and an IC antiferromagnetic phase, and a paramagnetic (P) phase, which at zero field supports short-range fluctuations up to $T=40$ K (Ref. 13). [(b) and (c)] $T$ and $H$ dependences of the $(0,1,0)$ magnetic Bragg peak intensity at three temperatures and fields.

![Graphical representation](image-url)
supported by analysis of higher-order harmonics and indirectly by a mean-field calculation predicting a phase boundary between the EP IC structure and a high-temperature linearly polarized (LP) IC structure around 15 K at 14.7 T. Coexisting with the IC order is a field-induced, (1,1,0) intensity [Figs. 3(e) and 3(f)] signaling a (+,−,+−) C-type moment along the a axis of approximately 0.11\(\mu_B\).

Phenomenology. The zero-field C structure breaks inversion symmetry, but is invariant under \(2_p\) (180° screw axis along b), thus preventing electric polarization perpendicular to b. However, for \(H||c\) the invariance under \(2_p\) is broken and electric polarization is allowed. The LP IC structures leave at least one point of inversion invariant and do not allow for electric polarization—even in the presence of the C staggered moments. This is consistent with a more formal treatment developed by Harris. 8

Magnetoelectric effect. The main features of the ME effect in LiNiPO\(_4\) can be explained by connections between superexchange (SE), DM spin interactions, and elastic distortions. At zero field \(|S_1|=|S_2|=|S_3|=|S_4|=|S|\), the thermal mean value of the spin operator, and the angles between \(S_1\) and \(S_2\) and between \(S_1\) and \(S_4\) are identical, \(\theta_3=\theta_4=\theta\). In the C phase a magnetic field \(H||c\) rotates the spins as shown in Fig. 4(c). Here \(\theta_1=\theta+\Delta \theta\) and \(\theta_2=\theta-\Delta \theta\), and \(\Delta \theta\) is proportional to the magnetization \(\chi\) if we assume that

\[
[S_1]=|S_1|=|S_3|=|S_4| \quad \text{even at nonzero fields. The SE energy for } H_{12,34}^{SE}=J_{12}S_1S_2+J_{34}S_3S_4 \quad \text{in this spin configuration is}
\]

\[
E_{12,34}^{SE} = (J_{12}+J_{34})(S)^2\left(1 - \frac{1}{2}(\theta^2 + \Delta \theta^2)\right)
\]

\[-(J_{12}-J_{34})(S)^2\theta\Delta \theta. \quad (3)
\]

SE energy (3) can be lowered by a uniform displacement of exchange mediating ions such as the translation of all PO\(_4\) tetrahedra along a by a small distance x [Fig. 4(b)]. The symmetry of the Ni-O-P-O-Ni exchange paths implies that a uniform translation of the tetrahedra, leading to an electric polarization \(P_x\) along a simultaneously increases \(J_{12}\) and reduces \(J_{34}\), or vice versa. To first order \(J_{12}=J+\delta\) and \(J_{34}=J-\delta\), where \(\delta=\lambda x\) for small values of x. Introducing an elastic energy \(\epsilon_i x^2\) for the tetrahedra displacements gives a SE-elastic interaction energy \(-2\lambda x(S)^2\theta\Delta \theta + \epsilon_i x^2\), which is minimum for \(x=\lambda(S)^2\theta\Delta \theta\). Noting that \(P_x \propto x\) and \(\Delta \theta \propto \chi\), we obtain an electrical polarization \(P_x \propto \epsilon_i x(S)^2\chi\), and thereby a ME coefficient \(\alpha_{xz} \propto \epsilon_i(S)^2\chi\). An equivalent expression for \(\alpha_{xz}\) can also be obtained from the DM interaction term \(H_{12,34}^{DM}\). These ME coefficients are similar to the phenomenological expressions suggested by Rado,25 but are here established from a microscopic point of view related to Ref. 11. Figure 4(c) compares the temperature dependence of the measured ME coefficient \(\alpha_{xz}\) (Ref. 13) to \(\epsilon_i(S)^2\chi\)
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(dashed line), assuming a constant elastic coefficient \( \epsilon \), and using the magnetic order parameter \( S \) determined in Ref. 19 and the magnetic susceptibility \( \chi \) from Refs. 20 and 26. A more elaborate calculation of \( \alpha_\epsilon \), assuming the angle difference \( \Delta \theta \) fixed at the low-temperature value, while the spins have nonidentical lengths at finite temperatures, gives significantly better agreement with the experimental data [solid line in Fig. 4(c)]. Here the expressions for SE and DM are not equivalent and both terms are needed in the best fit to the data.

To explain the elastic distortions in the C phase for \( H \parallel a \) we first assume, as for \( H \parallel c \), that the magnetization of the sample results from a rotation of the magnetic moments. This way we obtain the C spin structure sketched in Fig. 4(d).

Similar arguments, now on the pairs \( (S_1, S_2) \) and \( (S_1, S_3) \), and \( (S_2, S_3) \), find for identical spin lengths a ME coefficient \( \alpha_{\epsilon_{\parallel}} \propto \epsilon \langle S \rangle^2 \chi_\epsilon \) (dashed line), which is compared to the measured ME coefficient \( \alpha_{\epsilon_{\parallel}} \) (Ref. 13) in Fig. 4(d). Once again the elaborate calculation (solid line) improves the agreement with the experimental data.

The proposed mechanism for ME distortions is not effective for \( H \parallel b \) in the C phase, nor for any field direction in the LP IC phase. In the former case, all spins will cant with the same amount in the field direction and have the same lengths, leading to no energy differences between any pairs of spins and no magnetostriction. In the LP IC case, the observed spin structures are superpositions of C and IC components, which are uncoupled in the energy terms because of translational symmetry. The symmetries of the C and the IC components considered separately do not produce the needed energy differences and ME distortions are therefore not induced.

Conclusions. The symmetries of the established magnetic structures do not support an electric polarization in the C and zero-field IC phases. Applying a magnetic field along \( c \) in the C phase creates a polar axis and allows for electric polarization. Symmetry analysis show that electric polarization is possible in the C phase structure, but not in the LP IC phase. A microscopic model explains the temperature dependence of the ME constants, providing evidence that the electric polarization in LiNiPO_4 results from field-induced changes in the magnetic structure.

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