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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 $k_{IC} = (0,q,0)$. 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.

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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. However, the ME effect in LiNiPO$_4$ differs from that in the other lithium phosphates and was not modeled as successfully. In the present study we determine the field-induced magnetic structures in LiNiPO$_4$ for fields $\mathbf{H} \parallel \mathbf{c}$ 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. 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.

Symmetry properties. LiNiPO$_4$ 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 $r_1 = (0.275,0.25,0.98)$, $r_2 = (0.725,0.25,0.52)$, $r_3 = (0.725,0.75,0.02)$, and $r_4 = (0.225,0.75,0.48)$, as shown in Fig. 1(a). The low crystal-field symmetry in LiNiPO$_4$ leads to a magnetic-susceptibility tensor that contains staggered off-diagonal terms, $\chi_{ac}$ and $\chi_{ca}$. This allows for a single-ion anisotropy of the type...
resulting in a magnetization $\mathbf{M}$ of the crystal, as described in the text. (d) Linearly polarized (LP) IC magnetic structure at zero field seen along the $a$ axis.

\[
\mathcal{H}_{\text{ami}}^{\text{m}} = -D_{\text{z}}(S_1^a S_2^d - S_2^a S_1^d + S_3^a S_4^d - S_4^a S_3^d),
\]

and two DM interactions

\[
\begin{align*}
\mathcal{H}_1^{\text{DM}} &= D_1(S_1^a S_2^d - S_2^a S_1^d + S_3^a S_4^d - S_4^a S_3^d), \\
\mathcal{H}_2^{\text{DM}} &= -D_2(S_1^a S_3^d - S_2^a S_4^d - S_3^a S_1^d + S_4^a S_2^d).
\end{align*}
\]

\textit{Phase diagram.} The $(H, T)$ phase diagram for fields $\mathbf{H} \parallel \mathbf{c}$ up to $\mu_B H = 14.7$ T is shown in Fig. 2. The C phase is characterized by commensurate Bragg peaks associated with ordering vector $\mathbf{k}_C$, such as $(0,1,0)$ but shifted $(-0.25, -0.25, 0)$ compared to the values given in the text. [(b) and (c)] Projected C structure at zero and finite field $\mathbf{H} \parallel \mathbf{c}$ seen along the $b$ axis. Spin angles are exaggerated for clarity. The applied field causes the Ni$^{2+}$ moments to rotate, resulting in a magnetization $\mathbf{M}$ of the crystal, as described in the text. (d) Linearly polarized (LP) IC magnetic structure at zero field seen along the $a$ axis.

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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 mode along the a axis of approximately 0.11 μB.

Phenomenology. The zero-field C structure breaks inversion symmetry, but is invariant under 2p (180° screw axis along b), thus preventing electric polarization perpendicular to b. However, for H||c the invariance under 2p 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.24

Magnetoelastic effect. The main features of the ME effect in LiNiPO4 can be explained by connections between superexchange (SE), DM spin interactions, and elastic distortions. At zero field |S1|=|S2|=|S3|=|S4|=⟨S⟩, the thermal mean value of the spin operator, and the angles between S1 and S2 and between S1 and S4 are identical, θ12=θ34=θ. In the C phase a magnetic field H||c creates the spins as shown in Fig. 4(c). Here θ12=θ+Δθ and θ34=θ−Δθ, and Δθ is proportional to the magnetization χcH if we assume that

\[ |S_1|=|S_2|=|S_3|=|S_4|=|S| \]

even at nonzero fields. The SE energy for \( J_{12,34}=J_{12}S_1S_2+J_{34}S_3S_4 \) in this spin configuration is

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

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

SE energy (3) can be lowered by a uniform displacement of exchange mediating ions such as the translation of all PO4 tetrahedra along a by a small distance x. Introducing an elastic energy \( e_i x^2 \) for the tetrahedra displacements gives a SE-elastic interaction energy \(-2\lambda_iS^2\theta^2 + e_i x^2 \), which is minimum for \( x=\lambda_i/S^2 \theta^2 \lambda \). Noting that \( P_i \propto \chi \) and \( \Delta \theta \propto H_c \), we obtain an electrical polarization \( P_i \propto e_i S^2 \chi^2 \), and thereby a ME coefficient \( \alpha_{xz} \propto e_i (S^2 \chi^2 \). An equivalent expression for \( \alpha_{yx} \) can also be obtained from the DM interaction term H_{DM}^{0}. These ME coefficients are similar to the phenomenological expressions suggested by Rado 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 \( e_i (S^2 \chi^2 \).
(dashed line), assuming a constant elastic coefficient $\epsilon_c$ and using the magnetic order parameter ($S$) determined in Ref. 19 and the magnetic susceptibility $\chi_m$ from Refs. 20 and 26. A more elaborate calculation of $\alpha_{zz}$ 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 $\mathbf{H} \parallel \mathbf{a}$, we first assume, as for $\mathbf{H} \parallel \mathbf{c}$, that the magnetization of the sample results from a rotation of the magnetic moments. This way we obtain the spin structure sketched in Fig. 4(d). Using similar arguments, now on the pairs $(S_1, S_2)$ and $(S_2, S_3)$, we find for identical spin lengths a MO coefficient $\alpha_{zz} \propto \epsilon_c (S)^2 \chi_m$ (dashed line), which is compared to the measured MO coefficient $\alpha_{zz}$ (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 $\mathbf{H} \parallel \mathbf{b}$ 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 LP IC phase. In the latter case, all spins will cant with the same amount in the field direction and have the same LP IC phase. Similarly, in the C phase, the magnetic susceptibility

$$\chi_m$$

19 and the magnetic susceptibility

$$\chi_m$$

20 and 26. This Brief Report was authored, in whole or in part, under Contract No. DE-AC02-07CH11358 with the U.S. Department of Energy. This research project is based on experiments performed at the Swiss spallation neutron source SINQ, Paul Scherrer Institute, Villigen, Switzerland.

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