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Neutron diffraction with static and pulsed magnetic fields is used to directly probe the magnetic structures in LiNiPO₄ up to 25 T and 42 T, respectively. By combining these results with magnetometry and electric polarization measurements under pulsed fields, the magnetic and magnetoelectric phases are investigated up to 56 T applied along the easy c axis. In addition to the already known transitions at lower fields, three new ones are reported at 37.6, 39.4, and 54 T. Ordering vectors are identified with magnetization measurements under pulsed fields, the magnetic and magnetoelectric phases are investigated up to 56 T applied along the easy c axis. In addition to the already known transitions at lower fields, three new ones are reported at 37.6, 39.4, and 54 T. Ordering vectors are identified with 

\[ M_{ij} = M_0 + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_i H_k + \ldots, \]

where \( i, j, k \in \{a, b, c\} \) and \( P_0 \) is a spontaneous polarization. In a similar way, the induced magnetization, \( M_i \), may be expressed as follows:

\[ M_i = M_0 + \alpha_{ij} E_j + \frac{1}{2} \gamma_{ijk} E_j E_k + \ldots, \]

where \( E_j \) is now the applied electric field and \( M_0 \) is a spontaneous magnetization. The linear ME coupling is described by \( \alpha_{ij} \) and the coefficients, \( \beta_{ijk} \) and \( \gamma_{ijk} \), account for the quadratic ME effect. Higher order terms may also occur. The allowed ME tensor forms are governed by the magnetic symmetry of the system and \( \beta_{ijk} \) has the same symmetry as the pyroelectric tensor.

In multiferroics with a strong coupling between magnetic and electric order, the mechanism is often explained by spin currents [5], the inverse Dzyaloshinskii-Moriya interaction [6], or \( p-d \) hybridization [7]—the former two are rooted in noncollinear magnetic order breaking spacial inversion symmetry [8,9]. Examples are incommensurate spiral magnets such as the rare-earth manganites \( R \)MnO₃ (\( R = \text{Gd, Tb, Dy} \)) [10–12] and \( R \)Mn₂O₅ (\( R = \text{Tb, Ho, Dy} \)) [13,14] or copper-based compounds such as \( \text{LiCu}_2\text{O}_2 \) [15] or \( \text{LiCuVO}_4 \) [16]. However less common, some ME materials have magnetic order where the magnetic unit cell coincides with the crystallographic unit cell. Among these are, e.g., tetragonal \( \text{Ba}_2\text{CoGe}_2\text{O}_7 \) [7] and \( \text{Cr}_2\text{O}_5 \) [17,18]. Another example is the lithium orthophosphates, \( \text{LiMPO}_4 \) with \( M = \text{Ni, Co, Mn, Fe} \). These orthorhombic compounds (space group \( \text{Pnma} \)) all have commensurate antiferromagnetic ground states below their respective ordering temperatures [19–21]. Although the magnetic orders have similar symmetry, the spin orientation differs, depending on the magnetic ion in question due to the single-ion anisotropy. For instance, in \( \text{LiNiPO}_4 \), the spins are along \( c \) and in \( \text{LiFePO}_4 \) they are along \( b \). The variations in spin orientation result in different ME tensor forms. For \( \text{LiNiPO}_4 \) the elements \( \alpha_{ab}, \alpha_{cb} \neq 0 \) are finite whereas for \( \text{LiFePO}_4 \) the elements \( \alpha_{ab}, \alpha_{bc} \neq 0 \) are finite [22]. The ME effect in the lithium orthophosphates has been studied using various methods such as electric polarization measurements [22], optical absorption spectroscopy [23,24], and density-functional theory [25,26]. The relative strength of the effect in these materials is linked to the spin-orbit interaction.

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I. INTRODUCTION

The fields of study centered on multiferroics and magnetoelectrics span both fundamental physics and applications with their potential for low-energy dissipative data storage and other multifunctional devices [1–4]. In materials displaying a magnetoelectric (ME) effect, an external magnetic or electric field can induce a finite magnetization or electric polarization, respectively. The effect is usually described using Landau theory where the magnetic polarization, \( P_i \), induced by an applied magnetic field, \( H_j \), is written as [1]

\[ P_i = P_0 + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_i H_k + \ldots, \]

where \( i, j, k \in \{a, b, c\} \) and \( P_0 \) is a spontaneous polarization. In a similar way, the induced magnetization, \( M_i \), may be expressed as follows:

\[ M_i = M_0 + \alpha_{ij} E_j + \frac{1}{2} \gamma_{ijk} E_j E_k + \ldots, \]

where \( E_j \) is now the applied electric field and \( M_0 \) is a spontaneous magnetization. The linear ME coupling is described by \( \alpha_{ij} \) and the coefficients, \( \beta_{ijk} \) and \( \gamma_{ijk} \), account for the quadratic ME effect. Higher order terms may also occur. The allowed ME tensor forms are governed by the magnetic symmetry of the system and \( \beta_{ijk} \) has the same symmetry as the pyroelectric tensor.

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with $\Delta g/g = 0, 0.1, 0.3$ and 0.1 for LiMnPO$_4$, LiFePO$_4$, LiCoPO$_4$, and LiNiPO$_4$ with maximum ME coefficients $|\alpha_{\text{max}}| = 0.8, 4.2, 30$ and 1.7 ps/m, respectively (see Fig. 1 in Ref. [27]). Following the discussion in Refs. [26,27], for magnetic fields perpendicular to the spin direction, the temperature dependence of the ME tensor element, $\alpha$, follows that of the antiferromagnetic order parameter. For magnetic fields parallel to the spin direction, the ME tensor element, $\alpha_\parallel \to 0$ for $T \to 0$. This is exactly what is observed for LiMnPO$_4$. However, it is not the case for the other compounds in the lithium orthophosphate family and the temperature dependencies of their respective ME tensor elements do not follow the behavior described above. Especially, $\alpha_\parallel$ is finite for $T \to 0$ for LiFePO$_4$, LiCoPO$_4$, and LiNiPO$_4$. We note that LiMnPO$_4$ has a quenched orbital moment whereas the other compounds have a sizable orbital moment. Previously, the field and temperature dependencies of the field-induced electric polarization in LiNiPO$_4$ [28,29] and LiFePO$_4$ [30] have been successfully described based on related models.

In this paper, we focus on LiNiPO$_4$, which displays a cornucopia of magnetic phases. The crystallographic unit cell contains four magnetic Ni$^{2+}$ ions ($S = 1$) placed in a nearly face-centered arrangement (see Fig. 1 with positions [31] given in the figure caption). Below $T_N = 20.8$ K, the spins order in an antiferromagnetic commensurate structure with propagation vector $Q = (0, 0, 0)$. The major spin component is along $c$ and with symmetry ($\uparrow\uparrow\downarrow\downarrow$) [20]. Here $\uparrow\downarrow$ denotes spin up/down for ions on sites 1–4 following the enumeration of Ref. [28]. A smaller spin-canting component along $a$ with symmetry ($\uparrow\downarrow\uparrow\downarrow$) was also reported [28]. Just above $T_N$, an incommensurate, linearly modulated phase exists in the narrow temperature interval up to 21.7 K [28,32,33].

Upon applying a magnetic field along the easy $c$ axis, the material goes through a series of magnetic phase transitions: At 12 T, it enters an incommensurate spiral phase with spins in the ($a, c$) plane and propagating along $b$ [28]. At 16 T, the spiral locks in to a period of five crystallographic unit cells. Upon further increasing the field, at 19.1 T the spiral gives way to another $Q_{IV} = (0, 0, 0)$ structure which, yet again, at 20.9 T, yields to a longer-period structure with a modulation of three unit cells along $b$ [29]. The magnetization in this phase is $\sim 1/4$ of the saturated value. THz absorption spectra recorded up to 33 T along $c$ show changes in the magnon absorption that coincide with the magnetic phase boundaries [34]. Phases I and IV (field intervals 0–12 T and 19.1–20.9 T) both support the ME effect which has previously been characterized and successfully modeled [22,28,29,35].

The magnetic dispersion of LiNiPO$_4$ in phases I and II is well described by the following Hamiltonian [33,36]:

$$\hat{H} = \sum_{\langle i,j \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{i,n} D_i^\nu (S_i^\nu)^2 + \sum_{\langle i,j \rangle} D_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) + g \mu_B \mathbf{H} \cdot \sum_i \mathbf{S}_i,$$

where $J_{ij}$ are the exchange interaction constants, $D_{ij}$ the Dzyaloshinskii-Moriya interaction vectors, and $\mathbf{H}$ the applied magnetic field. All parameters are given in Table I. The energy is dominated by $J_{xx}$ and $D_x$, but the Zeeman energy gets comparable in size already around 12 T where the first phase transition occurs. With yet higher fields, it is to be expected that the magnetic ground state is perturbed and the relative energy scales of the interactions may change. In fact, it was necessary to include an additional next-nearest-neighbor exchange interaction in a mean-field model describing phase V [29]. The single-ion anisotropy in LiNiPO$_4$ was studied from first principles [25] and the overall

![FIG. 1. Crystal structure of LiNiPO$_4$. The magnetic Ni$^{2+}$ ions are surrounded by oxygen ions in an octahedral environment. The unit cell contains four magnetic ions which form buckled sheets in the ($b, c$) plane. The ion positions are $r_1 = (1/4 + \epsilon, 1/4, 1/2 - \delta)$, $r_2 = (3/4 + \epsilon, 1/4, 1/2 + \delta)$, $r_3 = (3/4 - \epsilon, 3/4, \delta)$, and $r_4 = (1/4 - \epsilon, 3/4, 1/2 - \delta)$, where $\epsilon = 0.0256$ and $\delta = 0.0175$ [31]. The exchange interactions are mediated via couplings such as Ni-O-Ni (blue path) and Ni-O-P-O-Ni (red path).](image-url)

**TABLE I.** Single-ion anisotropy constants, Dzyaloshinskii-Moriya interaction and exchange parameters given in meV as derived from the measured dispersion relations in Ref. [33].

<table>
<thead>
<tr>
<th>$D_x$</th>
<th>$D_y$</th>
<th>$D_xD_y$</th>
<th>$J_{xx}$</th>
<th>$J_y$</th>
<th>$J_x$</th>
<th>$J_{xx}$</th>
<th>$J_{yy}$</th>
<th>$J_{xy}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.413</td>
<td>1.423</td>
<td>0.0320</td>
<td>1.002</td>
<td>0.67</td>
<td>−0.06</td>
<td>0.321</td>
<td>−0.112</td>
<td></td>
</tr>
</tbody>
</table>
The magnet coil was made from a copper-silver alloy. A duration and a peak field of 56 T were applied along the horizontal scattering plane. Magnetic field pulses of 40 ms limits the maximum field to 26 T [42–45]. In comparison, hybrid magnet technology combining supercon-ducting and resistive coils permits continuous operation, but reaches at the price of a very low duty cycle [40,41]. In hybrid solenoid magnet allowed for probing all magnetic phases up to 25.1 T DC field. The magnet has a 30° conical opening, which combined with magnet rotation with respect to the incident neutron beam gives access to a substantial region of reciprocal space. The sample was a high-quality 330 mg single crystal oriented with (0,1,0) and (0,0,1) in the horizontal scanning plane. Magnetic fields were applied along the c axis with temperatures in the interval 1.3 − 30 K. The magnet was rotated −6° with respect to the incoming beam with wavelength band 0.7 − 6.9 Å. A number of Bragg peaks were observed on the forward and backscattering area detectors: (±1, K, 0), (−2, −2, 0), (0, K, 0), (2, −1.33, 0), (1, −0.67, 0), (−2, −0.33, 0), (0, 0, 4), and (0, 0, 2) with K ∈ [−2, 0].

A second TOF neutron diffraction experiment was performed on the Neutron Beamline for Observation & Research Use (NOBORU) at the Japan Proton Accelerator Research Complex. The instrument was operated in Laue mode with wavelengths λ < 10.5 Å and an area detector (with 16 vertical PSDs of 128 pixels with 10 μs time bins) was placed in a forward scattering position. The pulsed magnetic field was generated by a copper coil mounted on an insert for a standard ³He cryostat controlling the sample temperature. The coil itself was immersed in liquid nitrogen and connected to a capacitor bank delivering 10 ms pulses and thereby generating fields up to 42 T. The sample was the same 330 mg single crystal also used in the HFM/EXED experiment. It was oriented with the a axis vertical and the c axis in the scattering plane rotated 6° away from the field direction to reach momentum transfers along (0, K, 0). This particular direction in reciprocal space was chosen since magnetic structures in the lithium orthophosphates have so far without exception been found to propagate along b [28,29,50]. The time delay, Δt, between neutron pulse and magnet pulse as well as the maximum field, μ₀Hmax, were adjusted such that the neutron TOF-dependent intensity collected in a small region on the area detector may be converted to intensity versus (0, K, 0). The relation between TOF and K goes as K = 2aLsinθ/TOF with a = 252.7 μs/m/Å. Data was collected using 14 different settings of μ₀Hmax and Δt and with 50−120 magnet pulses per setting. The experimental technique is also described in Refs. [29,40]. The setup is illustrated in Fig. 2.

III. RESULTS AND DISCUSSION

A. Magnetometry and electric polarization

Magnetic phase transitions are observed in the magnetization at 12.0, 16.0, 19.1, 20.9, 37.6, 39.4, and 54 T as shown in Fig. 3. Phases are enumerated using Roman numerals I–VIII.
FIG. 2. TOF Laue neutron diffraction under pulsed magnetic fields at NOBORU. Scattered neutrons are recorded using an area detector consisting of 16 tubes with 128 pixels each. The detector image shows accumulated data for 99 magnet pulses. Integrating neutron counts in the box yields data as shown in the histogram and with the red curve being the magnetic field pulse. At 40 T, there is a signal around 5 ms which corresponds to the (0,1,0) Bragg peak. The shown data is collected with the settings $\mu_0 H_{\text{max}} = 40.5$ T and $\Delta t = 1000 \mu$s.

Following the notation of Ref. [29]. Note that the material is magnetized by $\sim \frac{3}{4}$ of the saturation magnetization ($M_S = 2.2 \mu_B/$ion [28]) at the highest probed field strength. To our best knowledge, the transitions at 37.6, 39.4, and 54 T have not been reported earlier and phases VI, VII, and VIII are unknown. Pronounced hysteresis of about 1 T is observed in the magnetization at the 54 T transition but not at 37.6 and 39.4 T.

Figure 3 also shows the electric polarization along $a$ as a function of magnetic field applied along $c$. Phases I, IV, and VII display a ME effect with finite tensor elements, $\alpha_{ac}$ and/or $\beta_{acc}$. Hysteresis in the polarization is observed at 12.0, 19.1 and 39.4 T but not at 20.9 T. The bumps observed in the polarization around $\sim 23$, $\sim 33$ and $\sim 44$ T for decreasing fields are attributed to mechanical oscillations of the sample and probe in the experimental setup. Because of the delayed response, these disturbances often appear only for decreasing field as seen here.

Previously, the ME effects in phases I and IV have been studied in Refs. [22,29,35]. A model for the temperature dependence of $P_a$ in phase I was put forth in Ref. [28]. Expanding on this theoretical framework, a similar model for the field dependence of $P_a$ in phase IV was developed in Ref. [29]. In Sec. III D, we will explore if this model can explain the field dependence of $P_a$ in phase VII as well, despite the pronounced differences in characteristics that can be summarized as follows: In phase I, $P_a$ is approximately linear with field until around 6.5 T where a quadratic onset is evident [29] (we note that Ref. [35] reported the upturn to be cubic in field and not quadratic). In phase IV, $P_a$ is linear for the entire field interval. In both phases I and IV, $\frac{dP_a}{dH} > 0$, i.e., $\alpha_{ac}$ is positive and the quadratic tensor element, $\beta_{acc} > 0$, is also positive above 6.5 T in phase I. In phase VII, however, $P_a$ appears purely quadratic and $\frac{dP_a}{dH} < 0$, i.e., $\alpha_{ac} \approx 0$ and $\beta_{acc} < 0$.

FIG. 3. Magnetization (grey curve) and electric polarization data (red and blue curves). Magnetization (right axis) and electric polarization (left axis) along $a$ measured at 4.2 K as a function of magnetic field applied along $c$. Phase transitions as observed in the magnetization are indicated with vertical dashed lines and the ramp direction is shown with open arrows. Phase numbers are listed on top of the plot.
Before further discussing the ME effect in phase VII, we first present the results of our neutron-diffraction experiments in Secs. III B and III C.

B. Neutron diffraction

A pulsed-field neutron diffraction experiment was performed at NOBORU as described in Sec. II and an example of the raw data is shown in Fig. 4(a). Four distinct peaks are observed at 2.5, 3.7, 5.0, and 7.5 ms, corresponding to momentum transfers (0,2,0), (0, $\frac{4}{3}$, 0), (0,1,0), and (0, $\frac{2}{3}$, 0), respectively. The nuclear peak, (0,2,0), is present at all fields whereas the remaining peaks are magnetic and only appear in specific field intervals. The Bragg peak (0,1,0) is observed in phase VII whereas (0, $\frac{4}{3}$, 0) and (0, $\frac{2}{3}$, 0) are present in phases V and VI. Below 2 ms (not shown), the spectrum is dominated by background counts originating from high-energy particles, but at higher TOFs the background is extremely low: 0–1 counts per 100 pulses.

Figures 4(b)–4(d) show the integrated intensities for the field intervals 21 – 37 T (phase V), 38 – 39 T (phase VI) and > 40 T (phase VII), respectively. The intervals are chosen with approximately ±0.5 T distance to the phase boundaries obtained from the magnetization measurements. Due to the rapidly varying field, this was done as a precaution to exclusively sum up neutrons scattered while the field was well away from the phase boundaries. In phase V, a strong peak is observed at (0, $\frac{4}{3}$, 0) as well as weaker ones at (0,1,0), (0, $\frac{2}{3}$, 0), and (0,2,0). The situation is similar in phase VI with a strong peak at (0, $\frac{4}{3}$, 0) and weaker ones at (0,1,0) and (0, $\frac{2}{3}$, 0). Finally, in phase VII, the peaks at (0, $\frac{4}{3}$, 0) and (0, $\frac{2}{3}$, 0) give way to a sole peak at (0,1,0). Note that (0,2,0) was not probed in phases VI and VII.

Peak positions were obtained from fits to Gaussian profiles. The peak widths were fixed based on analysis of zero-field data which displayed nuclear peaks (0, K, 0) with K = 2, 4, 6, 8, 10 and magnetic peaks with K = 1, 3. These data (not shown) are of much higher statistical quality than the pulsed field data, and allow us to reduce the number of fitting parameters and thereby obtain stable fits. For K < 6, the peak widths approximately follow a linear trend: $\sigma(K) = \alpha K + \beta$, where $\alpha = 0.0143(1)$ and $\beta = 0.0023(7)$ r.l.u. were fitted. This relation is used for fixing the peak widths in the field-on data. The fitted peak positions in phase V are (0,0.6593(6),0), (0,0.987(4),0), (0,1.326(5),0), and (0,1.979(3),0). In phase VI, they are similarly (0,0.660(1),0), (0,1.00(1),0), and (0,1.300(8),0). In phase VII, a single peak is observed at (0,0.993(2),0). Note that the propagation vectors are assumed field independent for each individual phase. While this is experimentally verified up to 23 T for phase V [see color plot in Fig. 5(b)], it is an assumption at all higher fields.

The pulsed-field technique is limited by counting statistics since the setup has a 10 – 30 min cool-down period after each magnet pulse in which no data is collected. It is therefore impractical for detailed studies of phase boundaries. The HFM/EXED facility, on the other hand, is excellent for parametric studies and allowed for tracking magnetic phase boundaries in LiNiP$_2$O$_6$ up to 25.1 T. Examples of collected data are shown in Fig. 5. Moreover, the superior counting statistics at EXED enabled improved peak

![Figure 4](image-url)
FIG. 5. Temperature and field dependencies of the $(0, K, 0)$ Bragg peak. Top left-hand panels, (a) and (c), show neutron intensity profiles as a function of $(0, K, 0)$ at selected field values at 1.3 K and at selected temperatures at 19.7 T, respectively. Data sets are offset on the vertical axis for clarity. Gaussian profiles were fitted to the line shapes (solid lines) and the integrated intensity calculated. Panels (b) and (d) show the neutron intensities in a color plot with scattering vector position, $(0, K, 0)$, and field or temperature on the axes. Fitted positions are marked with black dots. Horizontal dashed lines indicate phase transitions. Righthand panels, (e) and (f), show integrated intensities for the identified scattering vectors: $(0, -1, 0)$, $(0, -1 \pm k, 0)$, and $(0, -2k, 0)$ for $k \approx 0.2$ and $(0, -1 \pm k, 0)$ for $k = 0.33$. Different phases are indicated with colored regions corresponding to the phase diagram in Fig. 6.
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FIG. 6. Magnetic phase diagram of LiNiPO₄ based on neutron diffraction, magnetization measurements in pulsed and static fields, as well as pulsed field electric polarization measurements. In all cases, the field was along the crystallographic c axis. The error bars of the vibrating sample magnetometry (VSM) data are comparable to the symbol size. The three phases with propagation vector (0,0,0) support the ME effect (grey regions) whereas all phases with larger periods do not (colored regions). The field-induced phases are enumerated I–VIII for increasing field. Note that the phase boundaries for temperatures \( T > 4.2 \) K and fields \( \mu_0H > 25.1 \) T have not been probed and the boundaries indicated here are merely a conjecture.

symmetry, respectively, both with spins polarized along a. The structure is illustrated in Fig. 7.

Apart from parametric studies of the \((0, K, 0)\) magnetic Bragg peak, the HFM/EXED experiment also allowed for the observation of additional magnetic Bragg peaks in phase IV. In addition to the \((0,1,0)\) peak already observed in our previous pulsed field experiment, magnetic intensity was thus observed at \((±1,−2,0)\) and \((±1,−1,0)\) in phase IV at HFM/EXED. Those peaks represent structure components \((↑↓↓↑)\) and \((↑↑↓↑)\), respectively, and with spin mostly oriented along a. Hence, the additional magnetic peaks are consistent with the structure proposed in Ref. [29].

Neutron diffraction, magnetization data, and mean-field theory presented in Ref. [29] lead to a proposal for the structure in phase V where the propagation vector is \((0, 1/3, 0)\), i.e., a period of three crystallographic unit cells along b. This spin structure consists of a ferromagnetic component along c and an antiferromagnetic symmetry component \((+−−)\) describing the modulated part of the structure. Here the notation is slightly altered like in Ref. [28] such that \(+\) (−) denotes spin \(↑\) \((↓)\) and \(β = e^{-iφ/3}\) is a phase factor.

The structure proposed in Ref. [29] was based on the observation of the \((0, 1/3, 0)\) magnetic Bragg peak and a magnetization which exhibits a near-plateau at \(1/3\) saturation magnetization. A number of additional magnetic Bragg peaks were observed at the HFM/EXED experiment and a somewhat sounder structure determination is in principle possible. Intensities are obtained using the MANTID software package [52] as follows: (1) rectangular masks are created for each individual peak, (2) a second-order polynomial is fitted to empirically describe the background of the TOF spectrum. Next, (3), the background is subtracted and, finally, (4) vanadium and Lorentz corrections are applied. Due to technical issues, not all the intensities could be reliably determined, e.g., the equivalent peaks \((±1,−1/3,0)\) differ by a factor of \(1.5\) and \((−2,−1/3,0)\) is placed near the edge of the detector. Still, the presence or absence of these additional peaks may in the least be used in the analysis. In an attempt to determine the magnetic structure in phase V, intensities for a number of model structures were refined using FULLPROF [53] and compared with the observed intensities (see Table II). The models count a spin-density wave with spins along \(c\) as well as circular and elliptical spiral structures with spins in the \((a, c)\) plane. The elliptical spiral has major axis along c. The propagation vector is \((0, 1/3, 0)\) in all cases. The spin-density
wave forbids neutron intensity for \((1, -\frac{3}{4}, 0)\) and \((\pm 1, -\frac{4}{3}, 0)\). Since these peaks are present, this model can readily be discarded. The circular and elliptical spiral structures both allow all observed Bragg peaks. Although the data quality does not allow for a conclusive distinction between the two, the circular spiral yields a better refinement.

Phase VI looks very similar to phase V [compare Figs. 4(b) and 4(c)]. Yet, the magnetic susceptibility, \(\frac{\Delta H}{\Delta T}\), is a factor \(\sim 10\) larger in phase VI compared to phase V (revisit the magnetization curve in Fig. 3). Furthermore, the period of the structure is possibly longer with a peak observed at \((0, 1.300(8), 0)\) in phase VI as compared to \((0, 1.326(5), 0)\) in phase V. When determining the peak position it was assumed field independent but as also previously pointed out, this might not be the case. If, e.g., \(K\) decreases with field from \(K = 1.33\) to \(K = 1.27\) within the field interval, the fitted position—given that the neutron intensity stays constant—would indeed be \(K = 1.30\). In such a case, the period of the magnetic structure would no longer be locked in with the crystal structure. However, if the peak is actually moving with field, a peak broadening is expected when integrating over the entire field interval. This does not appear to be the case when inspecting Fig. 4(c).

Having thus described phases IV, V, and VI, we now turn to phase VII. In many ways, this phase looks similar to phase IV: the magnetization is linear as a function of applied field (see Fig. 3) and a single magnetic Bragg peak—\((0, 1, 0)\)—was observed in the pulsed-field Laue neutron diffraction experiment. The magnetization is \(\sim 1.1\ \mu_B = \frac{1}{4} M_s\) \((M_s = 2.2\ \mu_B\ \text{for LiNiPO}_4 [28])\) at the phase transition at \(H_c = 39.4\ \text{T}\). This may be obtained by a further magnetized version of the structure in phase IV. In the proposed structure, spins 1 and 2 are aligned with the applied magnetic field and spins 3 and 4 are almost antiparallel to each other as well as perpendicular to the field (see Fig. 7). The angle between spins 3 and 4 is \(\phi_0 \approx \pi\) upon entering phase VII and increases, \(\phi_0 + \Delta \phi > \pi\), as the field is increased.

Finally, the presented data is insufficient to comment on the likely magnetic structure in phase VIII (\(>54\ \text{T}\)). Further work along this direction will have to await further developments in pulsed-field technology for neutron diffraction.

To summarize this section on magnetic structures, the magnetic phase diagram of LiNiPO4 is presented in Fig. 6. It consists of a series of alternating commensurate and incommensurate phases. Strikingly, all the observed \(Q = (0, 0, 0)\) phases display the ME effect and all phases with larger periods do not. In the next section, we will have a closer look at the quadratic ME effect discovered in phase VII.

D. Quadratic magnetoelectric effect

As already mentioned, a magnetic-field-induced electric polarization is observed in phases I, IV, and VII [revisit Fig. 3], precisely those phases with propagation vector \((0, 0, 0)\) and where the magnetic unit cell is identical to the crystallographic one. In all three cases, the measured polarization, \(P_{\text{ac}}\), is triggered by a magnetic field applied along \(c\). Thus, the nonzero ME tensor elements are \(\alpha_{ac}\) and/or \(\beta_{acc}\). However, as also pointed out in Sec. III A, the field dependencies of these tensor elements are different in phase VII as compared to phases I and IV. In phase I, the linear ME tensor element is \(\alpha_{ac} > 0\) and there is an onset of a second-order effect around \(6.5\ \text{T}\) with \(\beta_{acc} > 0\). In phase IV, \(\alpha_{ac} > 0\) and \(\beta_{acc} \approx 0\). In phase VII, however, the linear effect is entirely replaced by the quadratic effect and \(\alpha_{ac} \approx 0\), \(\beta_{acc} < 0\). This is demonstrated in the inset in Fig. 8 where the electric polarization is plotted as a function of the reduced field, \(h = \mu_0 (H - H_c)\), squared. It is also noteworthy that the quadratic ME tensor element has opposite sign in phase VII as compared to phase I. Since \(\beta_{acc} < 0, \alpha_{ac} \approx 0\) but \(P_{\text{ac}} > 0\) in phase VII, a constant term, \(B_0\), must exist. This means that phase VII is not only ME but in some sense also pyroelectric.

The appearance of both the linear and second-order ME effect is governed by the magnetic symmetry of the crystal. The magnetic point group of LiNiPO4 in phase I is \(m m m\), which allows linear ME coefficients \(\alpha_{ac}, \alpha_{ca} \neq 0\) but the quadratic effect is prohibited [54]. The proposed magnetic structures in phases IV and VII lead to the magnetic point group \(2' m m'\) and now both linear and quadratic ME effects are allowed with tensor elements \(\alpha_{ac}, \alpha_{ca} \neq 0\) and \(\beta_{aba}, \beta_{abb}, \beta_{acc}, \beta_{baa} = \ldots\)

\[P_{\text{ac}} \propto 1 - \frac{1}{2} \Delta S = 0\]

\[\phi_0 = \pi, \Delta S = 0\]

\[P_{\text{ac}} = AH^2 + C\]

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\[\phi_0 = \pi, \Delta S = 0\]
\( \beta_{\text{bab}}, \beta_{\text{cca}} = \beta_{\text{cc}} \neq 0 \) [55]. Thus, the observed nonzero elements \( \alpha_{\text{ac}} \) in phase IV and \( \beta_{\text{ace}} \) in phase VII are consistent with the magnetic point group of the proposed spin structures. Moreover, the magnetic point group in phase I also becomes \( 2/m \) upon applying a magnetic field as an asymmetry in the canting angles is introduced, i.e., in Fig. 7 spins 1 and 2 experience a decrease in canting angle whereas spins 3 and 4 obtain a larger canting angle. At low fields, the deviation from \( mm \) is negligible but starting at \( \sim 6.5 \text{T} \) a nonlinear response in the electric polarization is clearly seen. It should be mentioned that the branching away from the linear behavior in phase I was already reported in Ref. [35]. There, it was assumed that the point group remains \( mm \) and hence the quadratic term is prohibited. Instead, a cubic term is possible which was then used to describe the data in Ref. [35]. It is difficult to unambiguously determine whether the curve follows a quadratic or cubic behavior as a function of applied magnetic field. However, the magnetic point group symmetry in phases IV and VII does change and, as argued above, this change may take place already in phase I. In the following analysis, we carry on assuming that \( \beta_{\text{ace}} \neq 0 \) and disregard any possible cubic contributions to the ME response.

The change of sign in \( \beta_{\text{ace}} \) may be understood by considering a variation of the model that has previously been successful in describing the field dependence of the induced electric polarization in both phases I [28] and IV [29]. The exchange energy for spin pairs (1,2) and (3,4) is simply \( E_0 = J_{12}S_1^z S_2^z + J_{34} S_3^z S_4^z \cos (\varphi_0 + \Delta \varphi) \). This is upon entering phase VII where \( \varphi_0 \approx \pi, \Delta \varphi = 0 \) and \( J_{12} = J_{34} = J \) is assumed. When increasing the field, spins 3 and 4 rotate further and now \( \Delta \varphi > 0 \). This is assumed to introduce an asymmetry in the exchange interactions such that \( J_{12} \to J - \lambda \chi S \) and \( J_{34} \to J + \lambda \chi S \), where \( \lambda \) is a proportionality constant and \( \chi = \lambda x \) is the displacement of the PO4 tetrahedra. Since the spin pairs (1,2) and (3,4) are no longer equivalent, we also introduce the possibility for different thermal averages of the moment, \( S_{12} \to S \) and \( S_{34} \to S - \Delta S \). Now the exchange energy reads \( E_1 = (J - \lambda \chi S)^2 + (J + \lambda \chi S)(S - \Delta S)^2 \cos (\varphi_0 + \Delta \varphi) \). Ignoring higher order terms in \( \Delta S \), the change in exchange energy is then \( \Delta E = \lambda \chi [(-1 + (1 - 2 \Delta S/S)^2 \lambda \chi S) \cos (\varphi_0 + \Delta \varphi)] \). Moving the PO4 tetrahedra, which in our model is responsible for the occurrence of finite polarization, also introduces an elastic energy, \( \epsilon \chi^2 \). The equilibrium displacement is found by minimizing the overall change in exchange and elastic energies. Expanding the cosine, \( \cos (\varphi_0 + \Delta \varphi) \approx \cos \varphi_0 - \Delta \varphi \sin \varphi_0 - (\Delta \varphi)^2/2 \cos \varphi_0 \), then yields an expression for the electric polarization, \( P_a = \lambda \chi S \), as follows:

\[
P_a = \frac{K}{2 \epsilon \chi} \left( 1 - \frac{2 \Delta S}{S} \right) \left[ \cos \varphi_0 - \Delta \varphi \sin \varphi_0 - \frac{(\Delta \varphi)^2}{2} \cos \varphi_0 \right],
\]

where \( K \) is a proportionality constant. This simplifies to \( P_a = \frac{K}{2 \epsilon \chi} \left( 2 - \frac{2}{2} (\Delta \varphi)^2 \right) \) for \( \Delta S = 0 \) and \( \varphi_0 = \pi \) which is close to the value \( \varphi_0 = 165^\circ \) as deduced from the measured magnetization. Hence, the polarization decreases with \( (\Delta \varphi)^2 \). It is expected that the change in angle is proportional to the reduced field, i.e., \( \Delta \varphi \propto h \), such that the electric polarization decreases quadratically with the reduced field. The quadratic ME coefficient may then be identified as \( \beta_{\text{acc}} \propto \frac{\lambda \chi^2}{\epsilon \chi} \) and \( P_0 = \frac{\lambda \chi}{\epsilon \chi} \). Thus, the observed quantities \( \beta_{\text{ace}} < 0 \), \( P_0 > 0 \) as well as \( \alpha_{\text{ab}} = 0 \) in phase VII appear naturally as a result of Taylor expanding the cosine function around \( \varphi_0 = \pi \).

The above expression captures the qualitative behavior of \( P_a(h) \) but the model curve (blue line in Fig. 8) does not describe the measured curve well when going to higher magnetic fields and away from the phase transition. Various other attempts to fit the full expression for the electric polarization yields either bad fits, unphysical parameters, or results in disagreement with the measured magnetization. Instead, a general phenomenological function, \( P_a = A h^p + C \), with constant parameters \( A \) and \( C \), yields a fitted exponent \( p = 2.01 \), i.e., very close to the quadratic behavior obtained by the model. This function describes the data well (red line in Fig. 8).

In summary, although our model captures the qualitative behavior of the observed electric polarization, it lacks some elements to give a quantitatively accurate description. Nevertheless, it is remarkable that a model rooted in the same general assumptions can embrace the field dependencies of the induced electric polarization in all three observed ME phases in LiNiPO4. It shows that the ME effect in this compound is governed by a single mechanism which prevails at very high magnetic fields. The simple model is based on varying exchange couplings in certain ways and is as such an empirical description offering little in-depth understanding of the physical phenomenon at work. However, the model does describe our observations well and it is especially encouraging that models emanating from the same base point are able to describe several different ME phases. Therefore, we now speculate on plausible underlying microscopic mechanisms responsible for the ME effect in LiNiPO4.

The magnetic ions are located in a distorted octahedral environment (see Fig. 1). The superexchange bonds involved in the model calculation, \( J_{12} \) and \( J_{34} \), follow the path Ni-O-P-O-Ni. Two ways of altering the exchange path readily spring to mind: (i) displacing the PO4 tetrahedra along \( a \) as also suggested in Ref. [28] or (ii) rotating the NiO6 octahedra around the \( b \) axis. Rotations around other axes may also be possible but are not considered here. The effect on the \( J_{12} \) and \( J_{34} \) exchange paths of the above two mechanisms separately and combined are illustrated in Fig. 9. Displacing the PO4 tetrahedra changes the bond angles, which in turn changes the exchange integrals according to the Anderson-Goodenough-Kanamori rules [56] such that \( J_{12} \neq J_{34} \). Furthermore, there is an overall displacement of charge inside the unit cell. This way, the exchange integrals and charge displacement are directly coupled and a ME link is created. From the measured electric polarization in phase VII, we expect a displacement of the tetrahedra in the fm range. Similarly, tilting the NiO6 octahedra results in changes in the bond angles and again \( J_{12} \neq J_{34} \). However, the oxygen ions are displaced symmetrically such that there is zero net charge displacement and therefore no ME effect. The two mechanisms combined—PO4 displacement and NiO6 tilting—yields asymmetric exchange paths as well as asymmetric charge displacements. This enables asymmetric changes in the exchange interactions and in the ordered moment, as proposed in our model.
On a final note, we return to the consequences of the change of magnetic point group symmetry upon applying a magnetic field. In phase I, above 6.5 T and in phases IV and VII, the four Ni sites 1–4 are no longer equivalent but split up in two different sites with spins 1 and 2 on one site and spins 3 and 4 on the other. This means that the crystallographic symmetry is also reduced from \( Pnma \) (space group 62) to \( P2_1ma \) (space group 26). Although the system remains orthorhombic, such change in crystal symmetry would be associated with a change in the diffraction pattern and should therefore be identifiable, e.g., in an x-ray Laue diffraction experiment. Furthermore, tracking the change of symmetry as a function of field would allow us to study whether the system stays in the lower symmetry phase as soon as it is entered or whether it alternates with field, e.g., with \( Pnma \) in non-ME phases (II, III, V, VI) and \( P2_1ma \) in ME phases (I, IV, VII). However, performing such an experiment at elevated fields is yet to be carried out and poses a future challenge. To investigate the possibility for changes in the crystal symmetry as a function of applied field, it would also be interesting to measure other components in the ME tensor such as, e.g., \( P_c \) for \( H \parallel c \). Previous \textit{ab initio} calculations show that the local single-ion anisotropy may be responsible for the canted magnetic structure that in turn establishes the ME effect in LiNiPO\(_4\) at low fields applied along \( a \) [25]. It would be interesting to perform such theoretical study for high magnetic fields along \( c \) to understand the ME effect in phases IV and VII. Here one would also have to take into account the potential change in crystal symmetry.

**IV. CONCLUSIONS**

The magnetic phase diagram of LiNiPO\(_4\) was characterized by magnetization and electric polarization measurements up to 56 T as well as neutron diffraction up to 42 T applied along the easy axis \( c \). In addition to already established transitions, we discover phase transitions at 37.6, 39.4, and 54 T. Furthermore, magnetic structure refinements using integrated neutron intensities of Bragg peaks observed in phase V (20.9 – 37.6 T) indicate a circular spiral structure with spins in the \((a, c)\) plane. The spiral is propagating along \( b \) and has a period of three nuclear unit cells. Phase VI (37.6 – 39.4 T) is very similar to phase V but for an increased magnetic susceptibility and possibly a slightly longer period of the magnetic structure. In phase VII (39.4 – 54 T), yet another commensurate magnetic structure is established. This phase displays a quadratic ME effect and the proposed spin structure is similar to those found in the other ME phases I and IV.

A generalized version of the model describing the field-induced electric polarization in phases I and IV is developed. The ME effect in LiNiPO\(_4\) is clearly connected to phases where the magnetic unit cell is identical to the crystallographic unit cell and we speculate on the underlying physical mechanisms.

Further experimental work is required to investigate the magnetic structure in phase VIII (>54 T) as well as to search for evidence for field-dependent structural distortions.

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