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Field-induced reentrant magnetoelectric phase in LiNiPO₄

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Using pulsed magnetic fields up to 30 T we have measured the bulk magnetization and electrical polarization of LiNiPO₄ and have studied its magnetic structure by time-of-flight neutron Laue diffraction. Our data establish the existence of a reentrant magnetoelectric phase between 19 T and 21 T. We show that a magnetized version of the zero field commensurate structure explains the magnetoelectric response quantitatively. The stability of this structure suggests a field-dependent spin anisotropy. Above 21 T, a magnetoelectrically inactive, short-wavelength incommensurate structure is identified. Our results demonstrate the combination of pulsed fields with epitheal neutron Laue diffraction as a powerful method to probe even complex phase diagrams in strong magnetic fields.

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I. INTRODUCTION

The coupling between magnetization and ferroelectricity in magnetoelectric (ME) materials [1–3] suggests a wide range of prospects for applications [4]. Low-power ME memory devices are currently being realized [5–9] and electrically manipulating spin waves to process information has far-reaching perspectives [10–12]. These low-symmetry materials offer a menagerie of possible microscopic origins for the ME coupling, including incommensurate (IC) magnetic structures in frustrated magnets [13] and transition metal orbital magnetism [14]. For instance, TbMnO₃ has a complex magnetic phase diagram with two distinct multiferroic phases [15,16], where a cycloidal IC structure produces ferroelectric polarization [17]. Another example is MnWO₄, where electric polarization is generated by an elliptical spiral [18], the chirality of which can be controlled by an electric field [19]. In Cr₂O₃, multiple coexisting mechanisms may even be possible [20,21].

The S = 1 Ni²⁺ ions in orthorhombic LiNiPO₄ (space group Pnma with lattice parameters a = 10.02 Å, b = 5.83 Å, and c = 4.66 Å) [22–25] form a frustrated 3D antiferromagnetic network. Its spin dynamics is dominated by the competition between nearest (J₁) and next-nearest (J₂) neighbor interactions in the bc plane [26,27]. The c axis is the easy axis, but the anisotropy within the ac plane is weak. The combination of spin anisotropy and a prominent Dzyaloshinskii-Moriya (DM) interaction results in commensurate magnetic order below TN = 20.7 K and—for magnetic fields along the easy c-axis—in a ME response PC caused by field-induced canting of the spins [28]. The ratio of J₁ to J₂ leaves LiNiPO₄ near an instability to IC magnetic order. Indeed, the low-temperature commensurate phase is bordered by IC phases (with collinear and spiral spin structures, respectively) above TNC in zero field [29] and above 12 T parallel to c at 1.5 K [28,30]. Both of these phases are magnetoelectrically inactive. At 16 T the IC modulation of the spiral locks into a quintupling of the crystallographic unit cell along b. Pulsed field magnetization measurements at 4.2 K indicate the existence of additional magnetic phase transitions for fields in the range 14–22 T [31]. The ME properties and magnetic structures of the higher-field phases are unknown, but recent advances in pulsed-field diffraction [32–35] imply that the latter can now be investigated using neutron scattering.

We used pulsed magnetic fields to study the magnetization, electrical polarization, and magnetic structures of LiNiPO₄ up to 30 T along the c axis. Our results demonstrate how epitheal neutron Laue diffraction in pulsed fields allows an efficient and exhaustive identification of propagation vectors characterizing a complex sequence of magnetic phases. We show that magnetoelectricity reemerges in the field range 19–21 T and is accompanied by commensurate antiferromagnetic order with spins polarized along the applied field axis. This phase is supplanted by a magnetoelectrically inactive, short-wavelength IC structure above 21 T. Combining the bulk and neutron diffraction data, a quantitative model connecting the magnetic structures, magnetization process, and magnetoelectric response of LiNiPO₄ is developed. Finally, we discuss whether a drastic field dependence of the spin-anisotropy can explain the observed magnetic structure. Our results establish LiNiPO₄ as a model system with a complex phase diagram that is directly impacted by the spin-lattice coupling.

II. EXPERIMENTAL DETAILS

The neutron diffraction experiment was performed on the SEQUOIA direct time-of-flight spectrometer [36] at the Spallation Neutron Source, Oak Ridge National Laboratory. The instrument was operated in Laue mode with an epitheral neutron wavelength band λ = 0.1–0.8 Å. The pulsed magnetic field was generated by a solenoid coil, mounted in an insert for a standard ⁴He-flow cryostat, and connected to a capacitor.
bank delivering 4–5 ms pulses and a maximum field of 30 T. 
This setup \cite{32,33} allows the sample temperature to be 
controlled by the cryostat, while the solenoid is immersed in liquid 
nitrogen. A high-quality single crystal (\(m \approx 400 \text{ mg} \)) was 
mounted inside the 12 mm magnet bore with its crystallo-
graphic \(a\) axis vertical and the \(c\) axis at an angle \(\theta = 2.8^\circ\) away 
from the field axis, which in turn was parallel to the incident 
beam. With this crystal orientation, momentum transfers par-
allel to \((0,1,0)\) are probed at a horizontal scattering angle \(2\theta\).

The existence of specific Bragg peaks \(Q = (0, K, 0)\) can 
now be investigated by adjusting the maximum field \(\mu_0 H_{\text{max}}\) 
and the time delay \(\Delta t\) between the magnet pulse and the 
neutron pulse emanating from the spallation target (see 
Appendix A and Fig. 4). Neutrons fulfilling the condition \(Q = 
(2\pi/b)K = (4\pi/\lambda)\sin(\theta)\) then arrive at the sample position 
while the field takes on a value in the range of interest. 
Employing the time-of-flight method, the neutron wavelength 
\(\lambda\), and therefore \(K\), depends on time. With each setting, Bragg 
peaks are probed along a curve in a \(\mu_0 H_x\) versus \(K\) plane [see 
Fig. 2(a)].

The advantage of using epithermal neutrons is that the 
momentum range probed near the field maximum is 
comparable to typical Brillouin zone dimensions. Further, the 
decrease in Bragg peak reflectivity associated with the use 
of short-wavelength neutrons is partially compensated by a 
reduction in absorption and extinction losses \cite{37}. The cooling 
requirements of the coil limit the number of pulses to 6–10 per 
hour, leaving only the strongest Bragg peaks observable.

In addition to the diffraction experiment, the magnetization 
and electrical polarization were measured in pulsed fields up 
to 30 T applied along the \(c\) axis. The pulse durations (FWHM) 
were 5 ms and 2 ms, respectively. The absolute value of the 
magnetization \(m\) was scaled to previous results obtained with 
static fields \cite{30}. The electrical polarization was measured 
using a procedure similar to that described in Refs. \cite{38,39}. 
All measurements presented in this paper were obtained at 
\(T = 4.2\ \text{K}\).

III. RESULTS

The bulk magnetization shown in Fig. 1(a) indicates the 
existence of five phases at 4.2 K (enumerated I–V with 
increasing field) up to 30 T where the magnetization approaches 
\((1/3)m_s\), with the expected saturation magnetization per ion 
given by \(m_s \approx 2.2\mu_B\). The associated critical fields are in 
rough agreement with those reported in Ref. \cite{31}. The two 
lowest transition fields at 12 and 16 T are in agreement with 
our previous studies \cite{28,30}. The ME response \(P_x = \alpha_x H_x\) 
of the five phases is shown in Fig. 1(b). At low fields in 
phase I, the known linear ME effect of LiNiPO\(_4\) \cite{22,28}, is 
observed. At fields larger than \(\sim 6.5\ \text{T}\), a quadratic component 
develops before the polarization drops to zero at the transition 
from the commensurate phase I to the IC screw spiral phase 
II. \(P_x\) remains zero as the spiral structure reestablishes 
commensuration with the lattice \cite{30} in phase III. In phase 
IV a dramatic reentrance of ME effect is observed, with 
\(P_x\) increasing linearly with field before disappearing at the 
transition to phase V.

We note that there are slight variations between the transi-
tion fields seen in the magnetization and polarization measure-
ments. These are likely due to the differences in pulse duration 
and shape. Furthermore, phase coexistence and demagnetiza-
tion effects are expected to be more pronounced for pulsed 
fields as compared to static fields. Additionally, both data sets 
display hysteresis as is typical for first-order transitions.

Next, we describe the pulsed field neutron diffraction 
results. Figure 2(a) shows all data obtained for \(\mu_0 H_z > 10\ \text{T}\). 
Each circle represents a single neutron recorded by a small 
number of detector pixels near the horizontal scattering angle 
\(2\theta\) (see Appendix A for details). The curved, solid lines 
represent corresponding values of \((0, K, 0)\) and \(\mu_0 H_z\) for each 
field pulse setting. A clustering of neutrons near specific values 
of \(K\) is evident in each of the magnetic phases. Note in 
particular that the nuclear \((0,0,0)\) reflection is observed for 
all magnet pulses, in the field interval 0–21 T, demonstrating 
that the sample maintains its orientation throughout the 
experiment. In Figs. 2(b)–2(d) we integrate the detected 
neutron counts over the field ranges of phases III, IV, and V. The 
peak positions are then extracted by fitting the resulting curves 
to Gaussian line shapes. The peak widths were fixed to values 
observed by extrapolation from high-statistics measurements 
of the \((0,1,0)\) and \((0,2,0)\) Bragg peaks performed in zero field 
(see Appendix A).

From the data in Fig. 2(b), we verify the known propagation 
vector \((0,0,8,0)\) of phase III. Figure 2(c) shows a main result of 
our work: the novel magnetoelectric phase IV is characterized 
by a single propagation vector \((0,0,99(1),0)\) which is equal to 
\((0,1,0)\) within error. Therefore, the two magnetoelectric phases 
I and IV of LiNiPO\(_4\) are characterized by identical propagation 
vecors. Finally, Fig. 2(d) indicates the presence of two Bragg 
reflections, \((0,0,99(1),0)\) and \((0,1,33(1),0)\), in phase V. Due 
to the possibility of phase coexistence near phase boundaries, 
the existence of the former peak should be treated with caution 
and is subject to further investigation.

FIG. 1. Magnetization \(m\) (a) and electrical polarization \(P_x\) (b) at 
4.2 K versus \(\mu_0 H_z\). The solid vertical lines at \(\mu_0 H_z \approx 12\ T, 16\ T, 
19\ T,\) and \(21\ T\) are approximate transition fields deduced from the 
magnetization and its derivative. The polarization data indicate a finite 
ME response in phases I (\(\mu_0 H_z < 12\ T\)) and IV (\(19\ T < \mu_0 H_z < 
21\ T\)). The dashed line corresponds to the model calculation described 
in the text.
The measured magnetization and propagation vector allow us to establish a quantitative model for the electric polarization in phase IV. In this section we show how the most probable magnetic structure consistent with the measured magnetization and electric polarization in Fig. 1 can be identified.

We start by providing an argument showing that the propagation vector in phase IV is commensurate and not incommensurate. The hard axis in LiNiPO₄ is along \( b \) due to a single-ion anisotropy energy \( D_xS_x^2 \) with a large \( D_x = 1.423 \text{ meV} \) (see Ref. [30] and Appendix C). This serves to confine the magnetic moments to the \( ac \) plane. Hence, any magnetic structure characterized by \((0, K, 0) = (0, 1 \pm k, 0)\) has ordered moments perpendicular to the propagation vector. This is the case for the screw spiral structures observed in phases II and III, as well as the sinusoidally modulated structure observed in zero field just above \( T_N \) [29,30]. Neither of these structures support the linear ME effect [40]. On the other hand, the commensurate structure in phase I does support the ME effect. This suggests that because a finite electrical polarization is observed in phase IV, its propagation vector is truly commensurate and equal to \((0, 1, 0)\). The neutron diffraction data give rise to the same conclusion.

We proceed to determine the most probable structure by help of symmetry analysis [28,30]. The four \( \text{Ni}^{2+} \) ions reside in a nearly face-centered orthorhombic arrangement at \( r_1 = (0.275, 0.25, 0.98), r_2 = (0.775, 0.25, 0.52), r_3 = (0.725, 0.75, 0.02), \) and \( r_4 = (0.225, 0.75, 0.48) \). The magnetic reflections \((0, 1 \pm k, 0)\) exclusively reflect magnetic ordering of the four ions according to the pattern \( C_j = (+, +, - \beta, - \beta) \), where \( j \) denotes the moment direction and \( \beta = e^{i\pi k} \) is a phase factor. Here \( k \) can be a rational number, corresponding to commensurate propagation vectors, or an irrational number corresponding to an IC propagation vector. In the case of phase IV we have \( k = 0 \). Other possible symmetry components are \( G_j = (+, - , + \beta, - \beta), A_j = (+, - , - \beta, + \beta) \), and \( F_j = (+, +, + \beta, + \beta) \). For the momenta \((0, 1 \pm k, 0)\) probed in our experiment (see Fig. 2), the neutron scattering selection rules imply vanishing intensity contributions from any spin component parallel to \( b \). Thus, \((0, 1 \pm k, 0)\) peaks reflect only \( C_x \) and \( C_z \) components of the magnetic structure. As shown in Appendix A, the full \( Q \) range probed in the neutron scattering experiment included \((1, 1, 0)\) and \((1, 2, 0)\) reflecting \( G \) and \( A \) symmetry components, respectively. No intensity was observed at these positions and hence we can exclude any major components of these types. Based on the data shown in Figs. 2(b)–2(d) it is estimated that Bragg peaks of \( \sim 10 \) times less intensity than the \((0, 1, 0)\) peak would be impossible to observe in the pulsed-field experiment. On the other hand, the finite magnetization [see Fig. 1(a)] is represented by an \( F_z \) component, coexisting with the \( C_x \) or \( C_z \) component.

We can now exploit the symmetry constraints on the ME effect to choose between these two possibilities, \( C_x \) and \( C_z \), for the main magnetic structure components. These constitute two distinct magnetic point groups with two different magnetoelectric tensor components. Thus, a \( C_x \) component would lead to the absence of an \( \alpha_{1z} \) ME tensor component [22,41], in contrast to the observations. On the other hand, a \( C_z \) component allows a nonzero \( \alpha_{1z} \) element as indeed observed in phase IV. Therefore, we conclude that the main magnetic structure component in phase IV is \( C_z \), just as is the case for the zero-field structure. In zero field, an additional symmetry component, \( A_x \), was observed, resulting in a canting of spin pairs \((1, 2)\) and \((3, 4)\); see Fig. 3(a). In Ref. [28], a small applied field was shown to introduce an asymmetry in this canting angle—represented by a \( G_z \) component—in addition to a component \( F_z \) reflecting the field-induced magnetization. For phase IV, we propose the version of this structure shown in Fig. 3(b). Here, the spins on sites 1 and 2 are nearly parallel to the applied magnetic field, while those on sites 3 and 4 are rotated away from the \( c \) axis. This corresponds to the presence of two additional antiferromagnetic symmetry components of similar magnitude, \( A_x \sim G_x \), in addition to the \( C_z \) and \( F_z \) components deduced from the neutron diffraction and magnetization data, respectively. The squared structure factors for the Bragg peaks
reflecting the $A_x$ and $G_x$ symmetry components correspond to peak intensities about an order of magnitude smaller than the intensity of the observed (0,1,0) peak, and are thus too weak to be observed directly in pulsed fields. However, the existence of these symmetry components is made plausible by the quantitative model for the ME response in both phases I and IV as described in the next section.

Generally, in simple Heisenberg antiferromagnets a spin-flop transition is expected for magnetic fields applied along the easy axis [42,43]. The magnitude of the easy-axis anisotropy is therefore favorable in terms of the balance between Zeeman and exchange energy. In addition, the $C_x$ component is exper-

FIG. 3. (a) The magnetic structure in small applied fields in phase I, the difference in spin canting between spin pairs (1, 2) and (3, 4) produces the ME effect [28]. (b) The proposed magnetic structure in phase IV producing the reentrant polarization. The open arrows in (a) and (b) are translated copies of the moments on sublattices 1 and 3, illustrating the relative angles $\phi_1$, $\phi_0$, and $\Delta \phi(H)$ described in the text. (c) The calculated $c$ components of the IC structure in phase V with $k = 1/3$.

B. Magnetoelectric effect in phase IV

Our starting point for modeling the magnetoelectric effect in phase IV is inspired by the model previously developed for phase I in Ref. [28] and the similarities between the magnetic structures in phases I and IV. The magnetic structure in phase I, see Fig. 3(a), is predominantly described by $C_z$ with an additional minor symmetry component $A_x$ causing a small canting angle $\phi_c = 15.5^\circ = 0.27$ rad in zero magnetic field. The magnetic structure in phase IV is similar but with a much more pronounced canting angle; see Fig. 3(b). This canting of predominantly the spins on sites 3 and 4 is described by two distinct and similar antiferromagnetic components $A_x \sim G_x \sim 4C_z$. While these components are too small to be observable in the neutron data directly, their existence can be deduced from the following model encompassing the ME response in both phases I and IV. At the onset field $H_{c1} \approx 19$ T the magnetization in phase IV is $m = 0.45 \mu_B \approx (1/5)m_S$ corresponding to an angle between spins 3 and 4 of $\phi_c \approx 105^\circ$. In both phases the applied field along $c$ changes the canting angles by $\Delta \phi$, creating an asymmetry in the superexchange (SE) energy of the two spin pairs (1, 2) and (3, 4). As a result, the SE energy can be lowered by translating the exchange-mediated PO4 tetrahedra by a distance $x$ along the $c$ axis, leading to an increase (reduction) of the $J_{14}(J_{12})$ exchange couplings [28]. The corresponding SE energy of the two spin pairs in phase IV is $\Delta E_{SE} = J_{14}(S)^2 \cos(\phi_0 + \Delta \phi(H)) + J_{12}(S)^2 \approx J_{14}(S)^2[-0.26 - 0.97 \Delta \phi(H)] + J_{12}(S)^2$, where the last part is obtained by a Taylor expansion around $\phi_0$. $\Delta \phi(H)$ is the field-induced rotation of the moments on sites 3 and 4 in the $ac$ plane. The PO4 tetrahedra displacement $x$ introduces an asymmetry in the exchange paths increasing $J_{34} \rightarrow J + \lambda x$ and decreasing $J_{12} \rightarrow J - \lambda x$ ($\lambda$ is a proportionality constant). This leads to a reduction of the SE energy $\Delta E =$
The displacement of the PO$_4$ tetrahedra in the lattice is associated with an elastic energy $\epsilon_s x^2$. Minimizing the sum of the SE and elastic energy yields the equilibrium tetrahedral displacement $x$, proportional to the bulk polarization via $P_x = \frac{\kappa x}{\epsilon_s}$:

$$P_x = \frac{3K(S)^2}{\epsilon_s}[0.63 + 0.48\Delta\phi(H)],$$

where $\kappa$ connects the microscopic charge displacement of the PO$_4$ tetrahedra to bulk electric polarization. Since this model applies for both phases I and IV, we proceed to use the measured ME response in phase I to estimate the ratio $\frac{K}{\epsilon_s}$, enabling us to predict the ME response in phase IV. In phase I, the polarization is described by $P_x = \frac{K x}{\epsilon_s} = \frac{3K(S)^2}{\epsilon_s} \Delta\phi$. A quadratic onset of $P_x(H_z)$ is evident in Fig. 1. This is due to a constant angle between moments on sites 1 and 2 when $\Delta\phi \rightarrow 0$, where the low-angle quadratic terms of an expansion of the SE energy for the two ion pairs (3,4) and (1,2) no longer cancel out (see Appendix B). The quadratic response was fitted to set in at 6.5 T with increasing field, where the measured polarization is $P_x = \frac{3K x}{\epsilon_s} = 4.6 \times 10^{-7} \mu_C$. At $\Delta\phi = \phi_z = 0.27$ rad [28], we estimate $\frac{K x}{\epsilon_s} \approx 6.2 \times 10^{-6} \mu_C$. In phase IV, the magnetization increases from 0.45$\mu_B$ to 0.5$\mu_B$ representing a change in canting angle of $\Delta\phi = 0.13$ rad for ions 3 and 4. Using the estimate for $\frac{K x}{\epsilon_s}$, a linear change in the polarization in the interval $P_x = 3.9 - 4.3 \times 10^{-6} \mu_C$ going through phase IV is predicted. This corresponds well with the observed polarization in phase IV as evident in Fig. 1, strongly supporting the establishment of a longitudinal $C_z$ structure in phase IV.

C. Magnetic structure in phase V

The data shown in Fig. 1(a) indicate that the magnetization is $m \approx (1/3)m_C$ and slowly varying with field. The neutron diffraction data in Fig. 2(d) display two Bragg peaks at (0,1,0) and (0,4/3,0). As shown in Appendix A, no additional peaks were observed. It is therefore likely that the structure is a longitudinal spin-flip type structure, mainly composed of $k = 0$ ferromagnetic $F_z$ component (the magnetization) and a $C_z$ component with a commensurate ordering wave vector $k = 1/3$. Note that a $C_z$ component $(+, +, -\beta, -\beta)$ with $k = 1/3$ is equivalent to an $F_z$ component $(+, +, +, \beta, +, \beta)$ with $k = 2/3$, both being fully compensated AFM structures. The DM interaction is expected to produce weak components transverse to the $c$ axis, but the resulting low-intensity Bragg peaks reflecting these minor components are not observable. When using the weak $D_1 = 0.413$ meV anisotropy in a mean-field calculation similar to that presented in Ref. [30], a $k = 1/3 C_z$ magnetic structure with spins almost entirely aligned along the $c$ axis is stabilized. The spin components in the $bc$ plane are shown in Fig. 3(c) (see also Appendix C). Phase V does not display the ME effect and the calculated structure obeys this constraint. However it does not produce the observed (0,1,0) reflection. As mentioned earlier, this peak is probed only near the phase boundary between phases IV and V and could have its origin in phase coexistence. The existence of a (0,1,0) Bragg peak in phase V is therefore subject to further investigation. We emphasize that the zero-field Hamiltonian is unable to predict the magnetic structure in phase IV, and therefore the mean-field predictions for phase V should be treated with caution. Clarifying the magnetic structure in phase V requires additional neutron scattering studies.

V. CONCLUSION

To conclude, we have discovered the reentrance of a magnetoelectric response between 19 T and 21 T in LiNiPO$_4$ for fields applied along the $c$ axis. Pulsed-field neutron Laue diffraction reveals a commensurate magnetic structure in this phase, characterized by the propagation vector $(0,1,0)$. We have shown that a magnetized version of the zero-field structure is consistent with all data. This is confirmed by a quantitative model for $P_x(H_z)$ which is in excellent agreement with the data. For fields in the range between 21 T and 30 T we propose a spin-flip type structure with ordering vector $(0,1/3,0)$ and spins nearly parallel to the $c$ axis. In this phase the magnetoelectric effect is absent. A mean-field model employing the zero-field exchange couplings and single-ion anisotropies fails to predict the magnetic structure in the high-field magnetoelectric phase. This indicates that the couplings between magnetic and structural degrees of freedom have a strong influence on the physical properties of LiNiPO$_4$.

Note Added. A very recent paper [45] reports an experimental study of the magnetoelectric effect in LiNiPO$_4$ in pulsed fields. The paper confirms the existence of a magnetoelectric phase near 20 T as well as a nonlinear contribution to the magnetoelectric effect in phase I.

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R.T.-P. and E.F. contributed equally to this work.

FIG. 4. Experimental setup. (a) Scattering geometry with the magnetic field direction and crystallographic directions indicated. The red (blue) arrows represent the shortest (longest) accessible wavelengths. (b) Neutron travel distance and magnetic field strength as a function of time. The overlap of the neutron pulse (gray area) and magnet pulse (black curve) is determined by the maximum field strength, $\mu_H H_{\text{max}}$, and the time delay, $\Delta t$. The red (blue) dashed line corresponds to TOF of the shortest (longest) accessible wavelength.

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TABLE I. Magnet settings used in the neutron experiment. The field was generated by a 5.6 mF capacitor bank with a maximum charging level of 1.5 kV corresponding to $\mu_0 H_{\text{max}} = 30$ T.

<table>
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<tr>
<th>$\mu_0 H_{\text{max}}$ (T)</th>
<th>19.2</th>
<th>19.2</th>
<th>19.2</th>
<th>20.7</th>
<th>22.0</th>
<th>22.7</th>
<th>25.2</th>
<th>28.2</th>
</tr>
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<tbody>
<tr>
<td>$\Delta t$ ($\mu$s)</td>
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<td>600</td>
<td>750</td>
<td>1200</td>
<td>300</td>
<td>0</td>
<td>700</td>
<td>700</td>
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<tr>
<td>No. of pulses</td>
<td>193</td>
<td>73</td>
<td>117</td>
<td>151</td>
<td>119</td>
<td>127</td>
<td>163</td>
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APPENDIX A: FURTHER EXPERIMENTAL DETAILS

The scattering geometry in the pulsed-field experiment and the principle of controlling the overlap between the magnet and neutron pulses are illustrated in Fig. 4. Table I lists the magnet settings employed as well as the number of magnet pulses discharged for each setting.

In Fig. 5 we show a SEQUOIA detector image in which we have integrated over all field pulses. Only a small detector area around the forward-scattering direction is accessible. This is due to neutron-absorbing boron shielding around the magnet and the sample space. Within the illuminated portion of the detector we only observe Bragg peaks around the expected ($0,K,0$) position. A careful search for peaks of other forms, e.g., ($1,1,0$), ($1,1,33,0$), and ($1,2,0$), was conducted. No such peaks could be observed in this experiment.

In the interval between the field pulses, the instrument collected zero-field data. Due to the long waiting times, the statistical quality of these data, shown in Fig. 6, is very good.

As expected, we observe two Bragg peaks in phase I: a nuclear ($0,2,0$) peak and a magnetic ($0,1,0$) peak.

The limited statistics of having only counted 1274 neutrons for finite fields exclusively allows for the determination of the Bragg peak positions and not for any quantitative analysis of the intensities. The peak centers are determined by fitting Gaussian line shapes to the data. The peak widths were fixed to values obtained by a linear extrapolation based on the zero-field data shown in Fig. 6.

For each magnet setting, a curve in ($\mu_0 H,K$) space is probed. The scattered neutrons were recorded in event mode allowing us to assign a corresponding field value (at the sample position) for each individual detected neutron. In Fig. 2 it is evident that some neutron counts occur away from the solid lines representing the corresponding values of $Q = (0,K,0)$ and magnetic field, $\mu_0 H$. The reason is that the scattered neutrons are spread over two vertical detector tubes, each with signal in 10 pixels. The resulting variation in scattering angle gives rise to a slight difference in flight path. This, in turn, implies that for a given setting of the maximum field strength and dwell time, any given value of $Q = (0,K,0)$ is probed over a small distribution of fields. This is shown in Fig. 7 for the particular case of the data set obtained with $\mu_0 H_{\text{max}} = 28.2$ T and $\Delta t = 700 \mu$s.

FIG. 5. SEQUOIA detector image integrated over all magnetic field pulses. In the part of the detector not affected by the shielding around the magnet insert, only peaks of the type ($0,K,0$) were identified.

FIG. 6. All neutron counts obtained in zero field as a function of scattering vector $Q = (0,K,0)$.

FIG. 7. The effect of having the ($0,K,0$) Bragg peak signals distributed over multiple pixels in two adjacent detector tubes. The probed curve in ($\mu_0 H,K$) space is split into two curves which are broadened due to the spread in pixels, as indicated by the curve widths.
TABLE II. The exchange parameters (in units of meV) used in the mean-field model, including the number of neighbors \((Z)\) using the same notation as in Ref. [30].

<table>
<thead>
<tr>
<th>(J_{0n}^{\alpha} )</th>
<th>( J_{\delta} )</th>
<th>( J_{\gamma} )</th>
<th>( J_{\delta} )</th>
<th>( J_{\delta} )</th>
<th>( J_{\delta} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Z = 4 ) 2 2 2 2 2 2 4 4 4</td>
<td>( J(i,j) ) 1.002 1.13</td>
<td>0.40 0.321</td>
<td>-0.112</td>
<td>-0.23</td>
<td>-0.08</td>
</tr>
</tbody>
</table>

APPENDIX B: ONSET OF QUADRATIC POLARIZATION IN PHASE I

In phase I, the energy \( \mathcal{E}_{12,34}^{\text{SE}} \) of the Hamiltonian \( \mathcal{H}_{12,34}^{\text{SE}} = J_{12} S_{1} \cdot S_{2} + J_{34} S_{3} \cdot S_{4} \) can be Taylor expanded

\[
\mathcal{E}_{\text{SE}} = (J_{12} + J_{34})(S_{i})^{2} \left[ 1 - \frac{1}{2}(\phi_{c}^{2} + \Delta \phi^{2}) \right] - (J_{34} - J_{12})(S_{i})^{2} \phi_{c} \Delta \phi,
\]

where \( \Delta \phi \) is the field- induced change in canting angle. Assuming that the resulting asymmetry in canting angles changes \( J_{12} = J_{34} \) to produce \( J_{12} = J - \delta J_{34} = J + \delta J \), only the last term contributes to the resulting change in superexchange energy \( \Delta \mathcal{E}_{\text{SE}} = -\Delta(S_{i})^{2} \phi_{c} \Delta \phi. \) This linear dependence on \( \Delta \phi \) is shown in Ref. [28] to produce a linear ME response at low fields. However, if the field is strong enough, \( \Delta \phi \rightarrow \phi_{c} \), resulting in constant alignment of spins 1 and 2. This activates the first term in the Taylor expansion as a source of ME response. Using the same procedure as in the main text, a Taylor expansion of the superexchange energy around \( \phi_{c} \) now yields

\[
\mathcal{E}_{\text{SE}} = J_{12}(S_{i})^{2} \left[ \cos(2\phi_{c}) - 2\phi_{c} \Delta \phi - \frac{\cos(2\phi_{c})}{2} \Delta \phi^{2} \right] + J_{34}(S_{i})^{2}
\]

using the small-angle approximation for \( \sin(2\phi_{c}) \). Assuming the linear change in exchange constants the energy difference now becomes

\[
\Delta \mathcal{E}_{\text{SE}} = \langle S_{i} \rangle^{2} \left[ -0.15 - 2\phi_{c} \Delta \phi - \frac{\cos(2\phi_{c})}{2} \Delta \phi^{2} \right].
\]

Using the same assumptions as in the main text, this gives rise to a continuation of the lower-field ME response through the linear term, with an additional quadratic component as \( \Delta \phi \rightarrow \phi_{c} \), with tetrahedra displacement given by \( x = \frac{\sqrt{3}}{2} \times 0.15 + \phi_{c} \Delta \phi + \frac{\cos(2\phi_{c})}{2} \Delta \phi^{2} \). Assuming \( \Delta \phi \propto M = \chi_{c} H_{c} \), we can fit \( P_{x} \) vs \( H_{c} \) in phase I to the function \( P_{x} = c_{1} H_{c}^{\alpha} + c_{2} S_{y}(H_{c})^{2} - c_{3} \), where the \( c_{i} \) are variables and \( S_{y}(H_{c}) \) is a Heaviside step function centered at \( H_{c} = \phi_{c} \). The step function roughly represents the crossover regime between the two cases described. The quadratic onset thus has a clear justification using the employed model, and can be said to arise from \( \Delta \phi \rightarrow \phi_{c} \).

APPENDIX C: ELABORATION ON THE MEAN-FIELD MODEL

The mean-field model employed in this work was originally introduced in Ref. [30]. The Hamiltonian is assumed to be

\[
\mathcal{H} = \frac{1}{2} \sum_{i,j} J_{ij} S_{i} \cdot S_{j} + \mathcal{H}_{\text{DM}} + \sum_{a,i} D_{a} S_{a,i} - g \mu_{B} \sum_{i} \mathbf{H} \cdot S_{i}
\]

with \( g = 2.2. \) Assuming only nearest neighbors to contribute, the DM interaction allowed by symmetry is [28]

\[
\mathcal{H}_{\text{DM}} = D_{14} \sum_{ij \in \text{n.n.}} \left[ S_{i}(1i) S_{j}(4j) - S_{i}(1i) S_{j}(4j) \right] + S_{i}(3i) S_{j}(2j) - S_{i}(3i) S_{j}(2j),
\]

where, e.g., \( S_{i}(1i) \) only contributes to the sum if the \( i \)th site belongs to sublattice 1 consisting of ions on position \( \mathbf{r}_{1} \). The exchange constants used in the Hamiltonian are given in Table II. In order to stabilize structures with short modulation wavelengths, a weak next-nearest neighbor interaction along the \( b \) axis between sublattices 1 and 4 in the \( bc \) plane, \( J_{bc}^{\text{nnn}} \), is introduced. For calculating the structure in phase \( \mathcal{V} \), the modulation period along the \( b \) axis was fixed to 3 unit cells (\( K = 1/3 \)), which was also found to be the most stable modulation above approximately 23 T in the model with \( J_{bc}^{\text{nnn}} = -0.08 \text{ meV} \). The resulting components (thermal mean values) of \( S_{y} \) and \( S_{z} \) on each of the 12 sites are given in Table III. The \( S_{y} \) components of the spins have been omitted as they are all zero, due to the strong \( D_{y} \) term.


