High magnetic field evolution of ferroelectricity in CuCrO_2

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CuCrO_2 offers insights into the different types of spiral magnetic orderings that can form spontaneously due to frustration in triangular-lattice antiferromagnets. We explore the magnetic phase diagram up to 65 T along all the principal axes, and also use electric polarization to probe changes in the spiral order at high magnetic fields. It is known that at zero magnetic field a proper-screw spiral of the Cr $\mathbf{S} = \frac{3}{2}$ spins forms that in turn induces electric polarization with six possible orientations in the $\mathbf{ab}$ plane. Applied magnetic fields in the (hard) $\mathbf{ab}$ plane have been shown to induce a transition to cycloidal-spiral magnetic order above 5.3 T in those domains that have spins perpendicular to the applied magnetic field. We show that the cycloidal order remains unchanged all the way up to 65 T, which is one quarter of the extrapolated saturation magnetization. On the other hand, for magnetic fields along the (easy) $\mathbf{c}$ axis, we observe a transition in the electric polarization near 45 T, and it is followed by a series of steps and/or oscillations in the electric polarization. The data are consistent with a proper-screw-to-cycloidal transition that is pushed from 5.3 to 45 T by easy-axis anisotropy, and is in turn followed by stretching of the magnetic spiral through commensurate and incommensurate wave vectors. This work also highlights the ability of the magnetically induced electric polarization to probe complex magnetic orders in regimes of phase space that are difficult to reach with neutron diffraction.

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I. INTRODUCTION

Ferroelectricity can be induced by magnetic ordering that breaks spatial-inversion symmetry (SIS). These magnetic structures are often complex and result from geometrical magnetic frustration [1,2]. A well-studied SIS-breaking magnetic structure is the cycloidal-magnetic-spiral state that has been studied in TbMnO_3 [3] among others [4–14]. The microscopic mechanism in these compounds is thought to be an inverse Dzyaloshinskii-Moriya (DM) [15], also described as a spin-current model [16]. In these cycloidal spirals, the electric polarization $\mathbf{P}$ is perpendicular to the spiral propagation vector $\mathbf{q}$ and parallel to the spiral plane: $\mathbf{P} \perp \mathbf{q}$. However, recently it has been shown that aside from cycloidal spirals, proper screw-type spirals (PSS) can also create magnetic field induced ferroelectricity in crystals with certain symmetry [17–19], including the triangular-lattice antiferromagnets (TLAs) CuFeO_2 with Al and Ga doping and CuCrO_2 . A microscopic theory has been proposed for ferroelectricity induced by a magnetic PSS [20] where the metal-ligand $d-p$ hybridization is influenced by spin-orbit coupling. In this mechanism, $\mathbf{P}$ is parallel to the screw axis $\mathbf{q}$ and perpendicular to the spiral plane: $\mathbf{P} \parallel \mathbf{q}$.

The multiferroic CuCrO_2 compound exhibits both PSS order at zero field and cycloidal spiral order in applied magnetic fields. It is also an example of a system whose magnetoelectric properties are tunable by both an electric and magnetic field [21,22]. This material crystallizes in the rhombohedral $R\bar{3}m$ structure, forming a triangular lattice of Heisenberg Cr^{3+} ($3d^3$ $\mathbf{S} = \frac{3}{2}$) spins [23–25]. Along the $\mathbf{c}$ axis, each triangular plane is rotated from its neighbors by 30° and displaced such that the atoms of one layer reside in the center of the triangle of the neighboring layers. The structure of the Cr atoms is shown in Fig. 1(a).

Thermodynamic investigations for single-crystal samples of CuCrO_2 reveal that two successive magnetic transitions occur at $T_N = 24.2$ K and $T_{MF} = 23.6$ K, and nonzero $\mathbf{P}$ appears below T_{MF} [19,26,27]. The magnetic structure of CuCrO_2 at zero magnetic field has been identified by neutron diffraction studies as an incommensurate PSS spin order of the Cr $\mathbf{S} = \frac{3}{2}$ moments with a propagation vector $\mathbf{q} = (0.329, 0.329, 0)$ [21,28–31]. Within the spiral, the ordered moment reaches maximum values of $2.2 \mu_B$ along [1-10] and $2.8 \mu_B$ along [001] [32,33]. Single-crystal neutron diffraction measurements reveal that the spin structure between T_N and T_{MF} (where there is no ferroelectric order) is two dimensional (2D) with short-range magnetic correlations along the $\mathbf{c}$ axis [33]. However, in the multiferroic state below T_{MF} , the magnetic structure becomes three dimensional (3D) with long-range correlations along the $\mathbf{c}$ axis [33]. Analysis of the magnetic excitation spectrum revealed antiferromagnetic (AFM) nearest- and next-nearest-neighbor exchange coupling within the plane and further showed that AFM next-next-nearest-neighbor exchange couplings J_3 in the plane also have to be considered [32]. Additionally, it was shown that a small ferromagnetic (FM) interplane coupling ($J_z \ll J_1$) exists. The interplane interaction mediates the 3D order in the multiferroic state and is responsible for the incommensurate $\mathbf{q}$, deviating from the out-of-plane 120° spin structure ($\mathbf{q} = 4/3\pi\mathbf{x}$) following the analysis of Ref. [34]. The relevant exchange interaction paths are shown as a schematic cartoon in Fig. 1(b). Finally, there is an easy-axis anisotropy D_z along the $\mathbf{c}$ axis.

There is a threefold rotation symmetry with respect to the hexagonal $\mathbf{c}$ axis, and thus there are six equivalent magnetic spiral domains since the spiral propagation vector can point forward or backward along any of the three principal axes [33]. Since the electric polarization points along the spiral

FIG. 1. (Color online) (a) Simplified crystal structure of CuCrO_2 showing the $\mathbf{S} = \frac{3}{2}$ Cr spins. The interplane magnetic exchange interaction J_z is indicated. (b) The (001) projection of the Cr triangular-lattice plane, where dashed and solid lines represent the hexagonal lattice above and below the magnetic ordering temperature [35]. The parameters J_1 , J_2 , and J_3 indicate nearest-, next-nearest-, and next-next-nearest magnetic exchange interactions within the $\mathbf{ab}$ plane. (c) Schematic representation of ferroelectric domain configuration in zero electric $\mathbf{E}$ and magnetic $\mathbf{H}$ field. The propagation vectors of $(\mathbf{q}, \mathbf{q}, 0)$, $(\mathbf{q}, -2\mathbf{q}, 0)$, and $(2\mathbf{q}, -\mathbf{q}, 0)$, which are crystallographically equivalent to each other, are indicated by the different colored arrows.

propagation vector, there are also six electric domains as shown in Fig. 1(c). These domains can be selected by applied electric and/or magnetic fields, and the application of both an electric and a magnetic field parallel to each other in the $\mathbf{ab}$ plane is proposed to select a single domain [22]. A small lattice distortion was observed in the magnetically ordered phase by x-ray diffraction and magnetostriction measurements [35]. This distortion changes the equilateral triangles in the $\mathbf{ab}$ plane into isosceles triangles [Fig. 1(b)], thus impressing the lowered symmetry of the magnetic order of a given domain onto the lattice [35]. This distortion also induces an anisotropy D_x in the $\mathbf{ab}$ plane that is selected by the spiral propagation vector [32].

By applying magnetic fields $\mathbf{H} \parallel [1-10]$, the direction of $\mathbf{P}$ is changed from $[110]$ to $[1-10]$ at $H_f \sim 5.3$ T [19,21,22,36]. Neutron diffraction measurements find that this change in the direction of $\mathbf{P}$ is accompanied by a spin flop in the magnetic domain whose spins originally lay perpendicular to the applied magnetic field. This spin flop corresponds to a transition from a proper screw spiral with (110) spiral plane to a cycloidal-spiral spin structure with (1-10) spiral plane, keeping the propagation vector along the $[110]$ direction [31]. According to the inverse DM model, the cycloidal spiral could produce a $\mathbf{P}$ along $[001]$, however, in fact $\mathbf{P}$ in the cycloidal-spiral state points along the propagation vector $[1-10]$. Furthermore, no feature in the magnetostriction is observed at this spin-flop transition. Thus, no inverse DM interaction can be observed in this compound [35] and the multiferroic behavior appears to be dominated by the Arima mechanism [20].

In this study, we extend the phase diagram of CuCrO_2 to 65 T for all principal directions of $\mathbf{H}$ and $\mathbf{P}$ via measurements of magnetization and electric polarization in pulsed magnetic fields. We uncover additional magnetic and ferroelectric phase transitions.

II. EXPERIMENT

Single crystals of CuCrO_2 were grown by a flux method as described previously [33]. The temperature and magnetic field dependence of the magnetization $M(T, H)$ were measured in

a commercial SQUID (superconducting quantum interference device) magnetometer in a Quantum Design (QD) Magnetic Property Measurement System (MPMS) up to $\mu_0 H = 7$ T and down to $T = 2$ K. The magnetization data taken in the superconducting magnet are consistent with earlier reports [19,22], where two magnetic transitions are detected in dM/dT at $T_N = 24.2$ K and $T_{MF} = 23.6$ K and an anomaly is revealed in dM/dH curves around 5.3 T along $\mathbf{H} \parallel [1-10]$. In addition, $M(H)$ measurements were extended up to $\mu_0 H = 60$ T and down to $T = 0.6$ K in short-pulsed magnets with an extraction magnetometer [37] at the National High Magnetic Field Laboratory (NHMFL) at Los Alamos National Laboratory. The magnetization curves taken in pulsed magnetic field are calibrated by the SQUID data.

For the measurements of electric polarization and capacitance, samples were cut into thin plates with dimensions of $0.55 \times 1.17 \times 0.15$ mm³ for $\mathbf{P} \parallel [110]$, $0.58 \times 0.97 \times 0.31$ mm³ for $\mathbf{P} \parallel [1-10]$, and $0.89 \times 1.12 \times 0.38$ mm³ for $\mathbf{P} \parallel [001]$. The measurements for $\mathbf{P}$ in the $\mathbf{ab}$ plane were consistent across three different samples. Platinum electrodes were sputtered onto the samples and then the platinum wires were attached onto the opposite faces of the thin plate (see the inset of Fig. 2). The samples were characterized by temperature-dependent capacitance measurements with an AH 2500 Capacitance Bridge at 1 kHz. In zero magnetic field, the phase transitions are seen in capacitance measurement as shown in Fig. 2, where a distinct peak structure is observed at $T_{MF} = 23.6$ K. The magnetic susceptibility measurements show two transitions T_N and T_{MF} , whereas capacitance measurements only show the T_{MF} phase transition.

The electric polarization in pulsed magnetic fields up to 65 T was measured by integrating the magnetoelectric current induced by changing magnetic fields, recorded using a Stanford Research 570 current to voltage converter [38,39]. The magnetoelectric current is the magnetic field induced analog of the pyroelectric current, and it increases linearly with magnetic field sweep rate such that the signal to noise of the

FIG. 2. (Color online) Capacitance measurements in zero magnetic field for single crystals of CuCrO_2 . Platinum (Pt) electrodes were sputtered onto the opposite sides of the samples (see inset). Silver paint was used to make the electrical contact between sputtered Pt electrode and Pt wire. The sample was poled by applying external voltage V_p across the contacts.

FIG. 3. (Color online) (a) Magnetization vs magnetic field curves $M(H)$ taken in the up sweep of pulsed magnetic field for $\mathbf{H} \parallel [110]$, $[1-10]$, and $[001]$ at $T = 1.6$ K. The dashed line is a linear guide to the eye. Left upper inset shows dM/dH for $\mathbf{H} \parallel [110]$ and $[1-10]$, where symbols and lines are based on data taken in superconducting and pulsed field magnets, respectively, at $T = 2$ K. Right lower inset presents the $M(H)$ data for both the up sweep (symbol) and down sweep (line) of pulsed magnetic fields up to 60 T along $\mathbf{H} \parallel [110]$ at $T = 0.6$ K. (b), (c) $M(H)$ curves for $\mathbf{H} \parallel [001]$ and $\mathbf{H} \parallel [110]$ at selected temperatures. For clarity, the curves are shifted from each other by $0.1 \mu_B/\text{Cr}$.

electric polarization measurements is improved in our pulsed magnets compared to our dc magnets. Electric polarization was measured after first poling the sample by applying a constant external 200 V across the capacitor plates as the sample is cooled from 30 K to the measurement temperature. This corresponds to a poling electric field of $E_p \sim 1.3$ MV/m for $\mathbf{P} \parallel [110]$ and ~ 0.6 MV/m for $\mathbf{P} \parallel [1-10]$ and $[001]$.

III. RESULTS

A. Magnetization

Magnetization of CuCrO_2 in dc and pulsed fields are shown in Fig. 3. In Fig. 3(a), $M(H)$ to 60 T is plotted at 1.6 K, and is roughly linear to 60 T with no significant magnetic anisotropy between the three orientations of the magnetic field. No hysteresis is seen either, as shown in the right lower inset where $M(H)$ for up and down sweeps of $\mathbf{H} \parallel [110]$ is plotted for $T = 0.6$ K. M reaches $\sim 0.7 \mu_B/\text{Cr}$ at 60 T and the expected saturation magnetization of $\sim 3 \mu_B/\text{Cr}$ linearly extrapolates to $H = 270$ T. A slight deviation from a linear dependence of $M(H)$ is observed for $\mu_0 H > \sim 48$ T along $\mathbf{H} \parallel [001]$. Note that, for $\mathbf{H} \parallel [110]$, the observed magnetization curve is consistent with an earlier measurement at 1.6 K up to 50 T in pulsed magnetic field [36].

In the upper inset of Fig. 3(a), we show a feature in dM/dH at 5.3 T and 2 K for $\mathbf{H} \parallel [1-10]$, corresponding to the spin flop at H_f from a PSS to a cycloidal spiral structure, consistent with earlier results [22]. The temperature evolution of the $M(H)$ curves for $\mathbf{H} \parallel [001]$ and $[110]$ are plotted in Figs. 3(b) and 3(c) at selected temperatures. The general behavior of the $M(H)$ curves remains the same for different temperatures, although $M(H)$ curves show an increase in the slope with increasing temperature as the influence of the antiferromagnetic exchange interaction weakens.

B. Electric polarization at 4 K

In Figs. 4 and 5, we show the measured magnetoelectric current $d(\Delta P)/dt$ and its integral, the magnetic field

induced change in electric polarization $\Delta P(H)$ of CuCrO_2 at $T = 4$ K. The temperature evolution of $\Delta P(H)$ is shown in Figs. 6, 7, and 8.

When $\mathbf{H}$ is applied in the **ab** plane in Fig. 4 ($\mathbf{H} \parallel [1-10]$ and $\mathbf{H} \parallel [110]$), we observe transitions in $P(H)$ near ~ 5.3 T that are consistent with earlier results, and have been attributed to a spin flop of one magnetic domain from PSS to cycloidal order [22]. This transition occurs both for $\mathbf{P} \parallel$ and $\perp$ to $\mathbf{H}$. In these transitions, the electric polarization always becomes larger along the direction of the applied H , and smaller perpendicular to H . For magnetic fields above this transition, we find that $\mathbf{P}$ remains constant, but nonzero, up to 65 T.

When $\mathbf{H}$ is applied along $[001]$ (Fig. 4), we observe a previously unreported anomaly in $\Delta P(H)$ for $\mathbf{P} \parallel [110]$ and $[1-10]$. The electric polarization is extraordinarily hysteretic; it is suppressed at 45 T on the up sweep, and then regains most of its original value in a step near 3 T on the down sweep. Similar behavior was observed in three different samples.

For $\mathbf{P} \parallel [001]$, $\Delta P(H)$ for both $\mathbf{P} \parallel \mathbf{H}$ and $\mathbf{P} \perp \mathbf{H}$ is insensitive to the entire magnetic field range measured as shown in Fig. 5. This observation is consistent with earlier reports [19,22] that in zero magnetic field the electric polarization is absent $\mathbf{P} \parallel [001]$. We observed a very small change of $\Delta P(H)$ for $\mathbf{H} \parallel [001]$ near ~ 1.5 and ~ 40 T, as shown in the inset of Fig. 5. However, the variation is an order of magnitude smaller than that for other orientations of $\mathbf{P}$. We are assuming that the $\mathbf{P} \parallel [110]$ and $\mathbf{P} \parallel [1-10]$ components are intrinsic whereas the small $\mathbf{P} \parallel [001]$ component is due to a slight misalignment of the electrode. Therefore, the electric polarization vectors in CuCrO_2 are lying within the **ab** plane in applied magnetic field at least up to 65 T. Details about the variation of $\Delta P(H)$ as a function of temperature for $\mathbf{P} \parallel [110]$ and $\mathbf{P} \parallel [1-10]$ are described next.

1. Temperature dependence of $P(H)$ for $\mathbf{H} \parallel [110]$ and $[1-10]$

Previous works have discussed the electric polarization flop from $\mathbf{P} \parallel [110]$ to $\mathbf{P} \parallel [1-10]$ by application of magnetic field $H_f = 5.3$ T along $\mathbf{H} \parallel [1-10]$. However, details about the

FIG. 4. (Color online) Magnetic field variation of the electric polarization $\mathbf{P}$ of CuCrO_2 at $T = 4$ K for three different orientations of applied magnetic field $\mu_0 H$. Electric polarization change with time dP/dt for (a) $\mathbf{P} \parallel [110]$ and (b) $\mathbf{P} \parallel [1-10]$, plotted as a function of $\mu_0 H$. Solid and dotted lines represent up and down sweeps of magnetic field, respectively. The curves are shifted vertically for clarity. Note that the up sweep of the pulsed magnets is much faster than the down sweep, resulting in larger signatures in $d\Delta P/dt$ for the up sweep than the down sweep for the same ΔP . Electric polarization change $\Delta P(H)$ determined by integrating $d\Delta P/dt$ with respect to time for (c) $\mathbf{P} \parallel [110]$ and (d) $\mathbf{P} \parallel [1-10]$. The poling electric field E_p was ~ 1.3 MV/m for $\mathbf{P} \parallel [110]$ and ~ 0.6 MV/m for $\mathbf{P} \parallel [1-10]$. Open symbols and solid lines indicate up and down sweeps of magnetic field, respectively. Schematic experimental configurations, applied electric and magnetic field directions, on the (001) projection of the Cr triangular-lattice plane are shown in insets of (a) and (b).

temperature variation have not been reported. We find that H_f is insensitive to temperature from 1.6 K all the way to $T_{\text{MF}} = 23.6$ K, and in our pulsed field measurements H_f is also insensitive to the direction of magnetic field in the $\mathbf{ab}$ plane. Figures 6(a)–6(d) and 6(e)–6(h) show the $\Delta P(H)$ curves for

$\mathbf{P} \parallel [110]$ and $\mathbf{P} \parallel [1-10]$, respectively, at selected temperatures. Although the absolute value of the $\Delta P(H)$ is suppressed with increasing temperature, the peak position in $d\Delta P/dt$ remains the same for all measured temperatures.

The observed $\Delta P(H)$ curves show a large hysteresis, which is enhanced as the temperature is lowered, and has been attributed to the first-order nature of the phase transition [22]. Interestingly, for the down sweep of magnetic field, the $\Delta P(H)$ curves come back to zero for $\mathbf{P} \parallel \mathbf{H}$, whereas the $\Delta P(H)$ curves do not come back to zero for $\mathbf{P} \perp \mathbf{H}$. Note that this behavior with a large hysteresis loop is absent for the electric polarization measurements in superconducting magnets [22], where the $\Delta P(H)$ curves are back to zero with narrow region of hysteresis for both configurations of magnetic field. In addition, the electric polarization curve in Ref. [22] for $\mathbf{P} \parallel [110]$ and $\mathbf{H} \parallel [1-10]$ shows a clear anomaly at H_f , whereas the $\Delta P(H)$ curve in pulsed field measurements indicates a broad transition. The observed behavior in pulsed magnetic field might be related to the domain dynamics that can be affected by magnetic field-sweep rate.

2. Temperature dependence of $P(H)$ for $\mathbf{H} \parallel [001]$

FIG. 5. (Color online) Electric polarization change with time $d\Delta P/dt$ for $\mathbf{P} \parallel [001]$, plotted as a function of $\mu_0 H$. The curves are shifted vertically for clarity. Inset: $\Delta P(H)$ for $\mathbf{H} \parallel [001]$.

FIG. 5. (Color online) Electric polarization change with time $d\Delta P/dt$ for $\mathbf{P} \parallel [001]$, plotted as a function of $\mu_0 H$. The curves are shifted vertically for clarity. Inset: $\Delta P(H)$ for $\mathbf{H} \parallel [001]$.

Figures 7 and 8 show the temperature evolution of $\mathbf{P} \parallel [110]$ and $\mathbf{P} \parallel [1-10]$ along $\mathbf{H} \parallel [001]$ at selected temperatures. For

FIG. 6. (Color online) Electric polarization change for $\mathbf{P} \parallel [110]$ (a)–(d) and $\mathbf{P} \parallel [1-10]$ (e)–(h) with time $d\Delta P/dt$ plotted as a function of $\mu_0 H$ at selected temperatures. (a), (e) $\mathbf{P} \parallel \mathbf{H}$ and (c), (g) $\mathbf{P} \perp \mathbf{H}$. The vertical line is guided to the eye, indicating a transition $H_f \sim 5.3$ T for the up sweep of the magnetic field. (b), (d), (f), (h) $\Delta P(H)$ determined by integrating $d\Delta P/dt$ with respect to time. Open symbols and solid lines indicate up and down sweeps of the magnetic field, respectively.

FIG. 7. (Color online) (a) 3D plot of $d\Delta P/dt$ for $\mathbf{P} \parallel [110]$ along $\mathbf{H} \parallel [001]$, plotted as a function of $\mu_0 H$ and T . For clarity, only curves for up sweep of magnetic fields are plotted. Inset shows the $dP(H)/dt$ at $T = 23, 22, 14, 10$, and 4 K for both up (thick lines) and down sweep (thin lines) of magnetic field. (b), (c) $\Delta P(H)$ curves for up sweep of magnetic field at selected temperatures. For comparison, $\Delta P(H)$ at $T = 12$ K is plotted in both figures. Inset (b) shows the expanded plot for the dashed-square region ($T = 16, 14$, and 12 K).

FIG. 8. (Color online) (a) 3D plot of dP/dt for $\mathbf{P} \parallel [1-10]$ along $\mathbf{H} \parallel [001]$, plotted as a function of $\mu_0 H$ and T . For clarity, only curves for up sweep of the magnetic field are plotted. Inset shows $dP(H)/dt$ at $T = 23, 22, 14, 10$, and 4 K for both up (thick lines) and down sweep (thin lines) of magnetic field. (b), (c) $\Delta P(H)$ curves for up sweep of magnetic field at selected temperatures. For comparison, $\Delta P(H)$ at $T = 12$ K is plotted in both figures. Inset (b) shows the expanded plot for the dashed-square region ($T = 16, 14$, and 12 K).

$\mathbf{P} \parallel [110]$, a 3D plot of $d\Delta P/dt$ as a function of $\mu_0 H$ and T is shown in Fig. 7(a), and the integrated ΔP is shown in Figs. 7(b) and 7(c).

At the base temperature, there is one transition in the electric polarization on the up sweep at $H_{2,\text{up}} = 45$ T, and a transition of almost equal size at $H_{2,\text{down}} = 3$ T on the down sweep. Note that in the raw $d\Delta P(H)/dt$ data, these features appear to have different sizes due to the different magnetic field-sweep rates on the up and down sweeps. As the temperature is increased, H_2 shifts to lower magnetic fields, and then additional features at higher fields appear on the up sweep, marked H_1 , H_3 , and H_4 . Presumably, H_3 and H_4 occur above 65 T at base temperature, and then shift down to $H < 65$ T as the temperature is increased. As the temperature is raised towards T_{MF} , the hysteresis between $H_{2,\text{up}} = 45$ T and $H_{2,\text{down}} = 3$ T narrows until both become 18 T just below T_{MF} . The integrated electric polarization $\Delta P(H)$ in Figs. 7(b) and 7(c) shows steplike features corresponding to the peaks in $d\Delta P/dt$, and $\Delta P(H)$ actually becomes nonmonotonic in H for $T = 4, 6$, and 8 K.

For $\mathbf{P} \parallel [1-10]$, $d\Delta P/dt$ and $\Delta P(H)$ are very similar to the previously discussed case for $\mathbf{P} \parallel [110]$, also showing these additional anomalies at high temperatures (see Fig. 8). One difference is that the H_3 peak is negative for $\mathbf{P} \parallel [1-10]$, whereas it is positive for $\mathbf{P} \parallel [110]$. The resultant $\Delta P(H)$ is extremely nonmonotonic between 4 and 20 K.

IV. PHASE DIAGRAMS AND DISCUSSION

Our $H - T$ phase diagram of CuCrO_2 for $\mathbf{H}$ in the $\mathbf{ab}$ plane is shown in Fig. 9. The phase boundary was determined from the peaks in $dP(H)/dH$. For $H = 0$, the system becomes a correlated paramagnet below $T_N = 24.2$ K, and forms a 3D magnetic spiral structure with ferroelectricity below $T_{\text{MF}} = 23.6$ K [33]. There is no $\mathbf{P}$ along the $\mathbf{c}$ axis. For both directions of $\mathbf{P}$ in the $\mathbf{ab}$ plane, $\mathbf{P}$ is enhanced when $\mathbf{P} \parallel \mathbf{H}$ and suppressed when $\mathbf{P} \perp \mathbf{H}$. The previously reported PSS to cycloidal-spiral phase transition H_f observed in dc measurements near

FIG. 9. (Color online) Magnetic field temperature $H - T$ phase diagram of CuCrO_2 for $\mathbf{H} \perp [001]$. Open and closed symbols represent transitions observed in down and up sweeps of magnetic field, respectively. The gray area is a guide to the eyes. Star symbol indicates previously reported transition in dc fields. The horizontal dotted and dashed lines indicate the magnetic transition temperatures T_N and T_{MF} at zero magnetic field, respectively.

$\mathbf{H} = 5.3$ T when $\mathbf{H} \perp \mathbf{P}$ in the $\mathbf{ab}$ plane [35] is shown as a star in Fig. 9. Our pulsed-field data also show features at H_f and we find that H_f is independent of temperature up to T_{MF} . Although the location of the H_f phase transition is consistent between pulsed and dc magnetic field experiments, the shape of $P(H)$ at the H_f phase transition differs. For dc magnetic field measurements, a very sharp first-order transition at H_f is observed in $P(H)$ and dielectric constant $\epsilon(H)$, along $\mathbf{H} \parallel [1-10]$, whereas gradual transitions in $P(H)$ and $\epsilon(H)$ are observed for $\mathbf{H} \parallel [110]$. This behavior was explained by gradual domain rearrangement [22]. In pulsed magnetic field measurements, $P(H)$ varies more gradually up to ~ 10 T for all configurations we measured. In addition, $\Delta P(H)$ exhibits a very large hysteresis loop compared to dc magnetic field measurements, and does not return to its zero-field value for $\mathbf{P} \perp \mathbf{H}$. This discrepancy is probably due to the dynamics of the domain structure in CuCrO_2 . However, this effect does not change our main results. Since H_f agrees between dc and pulsed magnetic fields, the essentials of the different ferroelectric phases remain the same. The magnetization in pulsed magnetic fields is similar to the dc magnetic field measurements as shown in the inset of Fig. 3(a), where the peak height and width in dM/dH are similar between two different measurements. This is likely because the longitudinal magnetization results from spin canting within all of the domains, and thus is less sensitive to the domain dynamics.

Previous studies of CuCrO_2 suggest [19,31] that the polarization flop at H_f in CuCrO_2 can be interpreted as the rearrangement of multiferroic domains. The present observations can be explained by the same approach. In zero applied electric field, there are six possible ferroelectric domains as shown in Fig. 1(c). If the poling electric field $\mathbf{E}$ is applied along $[110]$, the three ferroelectric domains closest to $[110]$ are selected. By applying sufficiently high magnetic field $\mu_0 H > H_f$, all three domains will transform into the one domain parallel to $\mathbf{q}$ for $\mathbf{H} \parallel [110]$ and into the one domain perpendicular to $\mathbf{q}$ for $\mathbf{H} \parallel [1-10]$. When the poling electric field $\mathbf{E}$ is applied along $[1-10]$, two ferroelectric domains are selected. For $\mu_0 H > H_f$, these two domains will collapse into the single domain parallel to $\mathbf{q}$ for $\mathbf{H} \parallel [110]$ and into the single domain perpendicular to $\mathbf{q}$ for $\mathbf{H} \parallel [1-10]$, respectively. Thus, $\mathbf{P}$ increases for $\mathbf{H} \parallel \mathbf{P}$ and decreases for $\mathbf{H} \perp \mathbf{P}$. In Ref. [31], the neutron scattering experiments have shown that the domain undergoes spin flop for $\mathbf{H} \perp \mathbf{P}$, when $\mathbf{P} \parallel [110]$ and $\mathbf{H} \parallel [1-10]$.

Within the cycloidal phase above H_f , $\mathbf{P}$ is remarkably insensitive to H , despite the linearly increasing magnetization between 10 and 65 T. However, it is not so remarkable when we consider that 65 T corresponds to only about a quarter of the saturation magnetization, and also that in most magnetoelectric materials, especially those with magnetostrictive coupling mechanisms, the leading term in the expansion of $P(M)$ is $P \sim M^2$. Since M changes by only $\sim 1/6$ of its value between 10 and 65 T, P should only change by $\frac{1}{36}$ of its value. Given that the electric polarization is induced by SIS-breaking magnetic order, we expect that the electric polarization can be suppressed some time before reaching the full saturation magnetization in a ~ 270 -T applied magnetic field.

In Fig. 10, the $H - T$ phase diagram is shown for H along the $\mathbf{c}$ axis obtained from $P(H)$ for $\mathbf{P} \parallel [110]$ and $\mathbf{P} \parallel [1-10]$.

FIG. 10. (Color online) Magnetic field temperature $H - T$ phase diagram of CuCrO_2 for $\mathbf{H} \parallel [001]$. Solid circles and squares are based on the measurements for $\mathbf{P} \parallel [110]$ and $\mathbf{P} \parallel [1-10]$, respectively. Open and closed symbols represent transitions observed in up and down sweeps of magnetic field, respectively. Labels H_1 , H_2 , H_3 , and H_4 correspond to the anomalies observed in $dP(H)/dT$ (see Figs. 7 and 8). Thick lines and shaded areas are guides to the eyes.

The lines are defined by the peak positions in $dP(H)/dH$, and different transitions for up and down sweeps are shown.

The spin-flop transition observed for $\mathbf{H}$ in the $\mathbf{ab}$ plane of 5.3 T would also be expected to occur for $\mathbf{H}$ along the $\mathbf{c}$ axis, although at a different magnetic field due to magnetic anisotropy. Thus, we can speculate that the 45-T transition (H_2) observed for $\mathbf{H}$ along the $\mathbf{c}$ axis is the same PSS to cycloidal-spiral transition that occurred at 5.3 T for $\mathbf{H}$ in the $\mathbf{ab}$ plane. This speculation is also in agreement with the observed hysteresis. For the down sweep of magnetic field, an increase of the polarization is observed around 5 T, but initial polarization is not recovered. This can be understood that the polarized initial state was mainly one domain which is going through the PSS to cycloid transition for the up sweep of magnetic field. For the down sweep of magnetic field, the cycloid phase decays into a three-domain PSS state. Since the polarization of only one domain is measured, it would explain the observed reduction of P . Furthermore, the steps or oscillations in P above this transition are reminiscent of the anisotropic next-nearest-neighbor Ising model (ANNNI)-like behavior of incommensurate wave vectors due to frustration [40,41].

The assorted transitions observed in $\Delta P(H)$ for different directions of $\mathbf{P}$ and $\mathbf{H}$ are only weakly observable in the mostly linear $M(H)$ curves up to 65 T. In light of previous neutron diffraction measurements, we conclude that the difference between the $M(H)$ and $P(H)$ curves can be related to the fact that $P(H, E)$ results largely from domain physics of domains that have little net magnetization [21,31], whereas the measured longitudinal M is likely the result of spin canting that occurs in all domains.

Finally, we compare CuFeO_2 and CuCrO_2 , both of which have multiferroic properties that have been explained by the mechanism proposed by Arima [20]. They have the same crystal structure, where the magnetic Fe and Cr ions are located on triangular-lattice planes stacked along the $\mathbf{c}$ axis. The MF phase in CuFeO_2 is observed in an applied magnetic field between critical fields (7 and 13.5 T) or

through doping. By contrast, the CuCrO_2 is multiferroic at zero magnetic field. In addition, we observed in this study that the multiferroic phase in CuCrO_2 can be suppressed by applied magnetic fields $\mathbf{H} \parallel [001]$. Whereas the interplane coupling in CuCrO_2 is ferromagnetic, the interplane coupling in CuFeO_2 is antiferromagnetic, and nonfrustrated. The nearest-neighbor intralayer exchange interaction J_1 is one order of magnitude stronger in CuCrO_2 than CuFeO_2 [32]. Therefore, the critical field for the suppression of the multiferroic phase in CuCrO_2 is much larger than the critical fields in CuFeO_2 .

A theoretical work [42] has examined CuCrO_2 using a simplified two-dimensional triangular-lattice AFM considering intralayer exchange parameters up to third neighbor, but setting interlayer interactions to zero. This model qualitatively reproduces our phase diagrams, but does not predict the details we observe for $\mathbf{H} \parallel [001]$ (Fig. 10). In this model, the next stable magnetic state in applied magnetic fields is a three-sublattice phase with $M = \frac{1}{3} M_s$. At this phase transition, there is predicted to be a magnetization plateau, and the complete suppression of the electric polarization. If the prediction of this collinear three-sublattice phase is correct, then we can extrapolate from our magnetization data that the transition should occur at ~ 90 T. Based on the model, the magnetic structure is always in a three-sublattice spiral state in the whole field range of the phase diagram. When we interpret the transitions as the spin flop to the cycloidal state, then the emerging phase between H_2 and H_3 is especially interesting. Here, the magnetic structure is still a PSS, but with a strong reduced polarization. The applied magnetic field couples in the $\mathbf{c}$ direction to the ferromagnetic interlayer exchange interaction. The stronger interlayer exchange might lead to new stacking sequence with a $\mathbf{c}$ component of $\frac{1}{2}$ in the propagation vectors. According to Ref. [34], this would subsequently change the propagation vector from $(\frac{1}{3} - \epsilon, \frac{1}{3} - \epsilon, 0)$ to $(\frac{1}{3} - \epsilon, \frac{1}{3}, \frac{1}{2})$.

V. SUMMARY

The $H - T$ phase diagram of single-crystalline CuCrO_2 is explored up to 60 T in magnetization and 65 T in electric polarization for all the principal directions of $\mathbf{P}$ and $\mathbf{H}$. At low temperatures, ferroelectricity persists beyond 65 T for all directions of $\mathbf{P}$ and $\mathbf{H}$ (except for $\mathbf{P} \parallel [001]$, that shows no ferroelectricity for all $\mathbf{H}$). We find that the $P(H)$ curves for $\mathbf{H} \parallel [001]$ reveal a complex new phase diagram with features on the up sweep of the magnetic field. We speculate that magnetic fields along the $\mathbf{c}$ axis induce a PSS to cycloidal transition. At lower temperatures, the magnetic structure likely undergoes a stretching through incommensurate and commensurate wave vector. On the other hand, for $\mathbf{H}$ in the $\mathbf{ab}$ plane, we observe the previously reported spin-flop transition to a cycloidal-spiral magnetic phase near 5.3 T, and find that it is not sensitive to temperatures between 1.6 K and the ordering temperature at $T_{\text{MF}} = 23.6$ K. The electric polarization remains essentially constant between H_f and the maximum magnetic field of 65 T.

The $M(H)$ curves reveal a quasilinear isotropic magnetic field dependence up to 60 T, with very weak signature of the spin-flop transition for $\mathbf{H}$ along $[1 -1 0]$ at 5.3 T, and possibly a faint upward deviation from linear behavior at the 45-T transition for $\mathbf{H}$ along $[001]$. The magnetization

value at 60 T reaches $\sim 0.7 \mu_B/\text{Cr}$, which is far below the saturation value. By a simple linear extrapolation, any $\frac{1}{3} M_s$ plateaus should occur near ~ 90 T, and complete saturation by 270 T.

Our phase diagrams are in rough agreement with a recent two-dimensional model for CuCrO_2 that predicts a three-sublattice state at $\frac{1}{3} M_s$, and if this occurs, it would be at ~ 90 T. However, our phase diagram for $\mathbf{H} \parallel [001]$ shows that the multiferroic properties are much more complex than the predictions of just the magnetic properties, likely due to the interlayer exchange interactions.

CuCrO_2 shows strong magnetic frustration due to its triangular spin configuration in the **ab** plane, and evidenced by the discrepancy between the ~ 24 K 2D ordering temperature and the ~ 270 T saturation magnetization and ~ 200 K Curie-Weiss temperature. Thus, as expected we observe multiple magnetic and ferroelectric phases accessibly by relatively small magnetic fields relative to the saturation magnetic field. However, within most of the phases there is almost no observable variation of the electric polarization with magnetic field. This may be due to the fact that in most cases of magnetically induced electric polarization, the leading behavior of P is M^2 , and so P will show most of its magnetic

field dependence at higher magnetic fields that we have applied.

In conclusion, CuCrO_2 is a frustrated magnet with a rich variety of magnetic and ferroelectric phases that couple to each other and extend beyond 65 T.

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