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ABSTRACT
Below its Neél temperature, the frustrated magnet CdCr₂O₄ exhibits an antiferromagnetic spin-spiral ground state. Such states can give rise to a sizable magnetoelectric coupling. In this report, we measure the electric polarization induced in single-crystalline CdCr₂O₄ by large applied magnetic field. Because the detection of a macroscopic polarization is hindered by the structural domains in the tetragonal spin-spiral phase, we have pioneered an alternative method of measuring polarization induced by high magnetic fields, using electrostatic force microscopy. This method enables us to measure polarization from nanoscale areas of the sample surface, as well as imaging how charge inhomogeneities change with magnetic field.

Materials with strong magneto-electric coupling hold the promise of revolutionizing information storage through electric field control of magnetism. However, such coupling is often weak, since ferroelectricity and magnetism derive from breaking of different symmetries.1 Non-collinear magnetic ground states, such as spin-spirals, often found in frustrated magnets, can provide a route to strong magnetoelectric coupling.2,3

In chromium spinels Al₄X₄ (A = Zn, Cd, and Hg: X = O, S, and Se), the Cr-ions form a pyrochlore lattice of corner-sharing tetrahedra, leading to spin frustration in the antiferromagnetic members of the family. Many of these compounds present a spin-spiral ground state, including ZnCr₂Se₄.1 The oxide compounds also exhibit a half-magnetization “plateau” state under applied magnetic field.1,2,3 In the antiferromagnetic compound CdCr₂O₄, there is a transition to an incommensurate spin-spiral below the Neél temperature T_N of 7.8 K,6 at low temperature, the spin-spiral disappears at a magnetic field of 28 T, where the material enters the plateau state.6 The plateau state has a spin structure in which three of the spins in each tetrahedron point “up,” and one points “down.”6,7,10–12

In this paper, we present the generation of electric polarization by applied magnetic field in the spin-spiral ground state of the frustrated spinel CdCr₂O₄. We measure the field-induced electric polarization both via a standard polarization current (pyrocurrent) technique and by measuring the contact potential difference (CPD) between the sample surface and the tip of a scanning probe microscope (SPM), in a static magnetic field up to 30 T generated by a Bitter magnet. In order to perform these measurements, we employed a high-field scanning probe microscope (HF-SPM).13 The SPM technique has the advantage of being able to measure the surface polarization within an area smaller than the structural domains, circumventing the problems these domains present for traditional polarization measurements.

In an initial experiment, we measured polarization on a single-crystal sample of CdCr₂O₄ as a function of temperature and magnetic field. The magnetic field was applied parallel to the [111] direction via a superconducting magnet. On the [111] surfaces of the sample (A = 16 mm²), we applied silver paint electrodes and measured the pyrocurrent using an electrometer (Keithley 6517). The change of the
polarization is obtained by integrating the field or temperature dependent current normalized to the sample area $A$ via

$$\Delta P(T, H) = 1/A \int_{t_0}^{t} I(T(t), H(t))dt.$$  \hspace{1cm} (1)

In Figs. 1(a) and 1(b), the polarization current (pyrocurrent) and the resulting polarization are plotted, while warming the sample through the Neel temperature $T_N$, at 2 K/min, at zero magnetic field and at 10 T. No poling voltage was applied; the magnetic field was applied both during cooling and warming. Figure 1(b) shows that at zero magnetic field no polarization is present, but at 10 T, a small polarization of 0.12 $\mu$C/m$^2$ is observed below the Neel temperature. Measurements were attempted with a poling voltage applied while cooling down, but there was no indication of any switchable spontaneous polarization emerging below $T_N$ at zero magnetic field. The inset in Fig. 1(b) shows the dielectric constant, derived from the sample capacitance, measured by a capacitance bridge (Andeen-Hagerling AH2500A) at a fixed frequency of 1 kHz. A sharp decrease in the dielectric constant is seen while cooling down through $T_N$.

We also measured polarization in CdCr$_2$O$_4$ at high magnetic fields, using a pulsed magnet capable of reaching 56 T. We maintained the same experimental conditions presented above: the electrodes were applied on the (111) surfaces of the samples, and the magnetic field applied in the [111] direction. Measurements were made at 1.5 K: samples were cooled through the Neel temperature $T_N$, at 2 K/min, at zero magnetic field and at 10 T. No poling voltage was applied; the magnetic field was applied both during cooling and warming. Figure 1(b) shows that at zero magnetic field no polarization is present, but at 10 T, a small polarization of 0.12 $\mu$C/m$^2$ is observed below the Neel temperature. Measurements were attempted with a poling voltage applied while cooling down, but there was no indication of any switchable spontaneous polarization emerging below $T_N$ at zero magnetic field. The inset in Fig. 1(b) shows the dielectric constant, derived from the sample capacitance, measured by a capacitance bridge (Andeen-Hagerling AH2500A) at a fixed frequency of 1 kHz. A sharp decrease in the dielectric constant is seen while cooling down through $T_N$.

We can understand the generation of electric polarization with magnetic field in CdCr$_2$O$_4$ as being due to its spin-spiral ground state. Non-collinear spin states can produce an electric polarization either via the spin-current model or an inverse Dzyaloshinskii–Moriya-type interaction. In either case, the spin-induced polarization has the form

$$P = a \sum_{i,j} e_{ij} \times (S_i \times S_j),$$  \hspace{1cm} (2)

where $e_{ij}$ is the unit vector connecting the neighboring spins $S_i$ and $S_j$ and $a$ is a constant, which determines the coupling strength.

Below its Neel temperature, CdCr$_2$O$_4$ exhibits a spin-flop transition at around 5 T, for magnetic fields applied away from the [010] easy plane. This has been observed in magnetization and neutron diffraction data, by magnetostriction and by ESR and optical spectroscopy measurements. We observe an increase in polarization at the spin flop [Figs. 1(c) and 1(d)]. This indicates a transition to a tilted conical spin structure, where the spin rotation plane $S_i \times S_j$ is canting toward the field direction, increasing the angle to $e_{ij}$, and thus per Eq. (2), producing an increased polarization. Above the spin flop, only a gradual increase in polarization is seen with higher fields, indicating that the spin rotation plane is close to parallel to the [111] axis by 10 T and thus that the field-induced polarization is almost saturated. At 28 T, CdCr$_2$O$_4$ enters the plateau magnetic state, which is collinear and therefore generates no polarization.

Figure 2 shows the effect on the magnetic-field induced polarization of poling voltage and field orientation. It is possible to invert the sample polarization by applying an opposite poling voltage. By contrast, inverting the magnetic field orientation does not change the polarization direction. We observed that the response of the CdCr$_2$O$_4$ polarization to poling voltage produced results with a high degree of sample dependence. In some samples, for example, it was not possible to invert the polarization, but the polarization direction was apparently...
“pinned.” We observed also some history dependence, in terms of the magnitude of the polarization obtained. We attribute these effects to the presence of structural domains in the low-temperature tetragonal antiferromagnetic phase: such domains have been identified in neutron diffraction data. Different orientations of domains affect the total polarization, since the spin spiral vector is locked to the tetragonal lattice. Additionally, domain walls can act as charge trapping sites. Since domains are erased every time T increases above 8 K, there is a degree of stochasticity in the pattern of domains created each time. This may account for the difference between field-increasing and -decreasing plots seen in Fig. 1, since the domains are also erased on the field-induced transition. This sample- and history-dependence made more detailed studies of the total polarization difficult, for example, its field-orientation dependence.

A way to avoid the problems associated with domain structures is to perform local polarization measurements within an area much smaller than the size of the domain. To this end, we performed field dependent electrostatic force microscopy (EFM), on the as-grown (111) surface of CdCr₂O₄ single crystals in a range of static fields up to 28 T. We also recorded the contact potential difference (CPD) between the tip and the sample at each field. The CPD is the bias, applied to the sample, that is needed to nullify the electrostatic forces, measured as phase or frequency shift, between the tip and the sample. This technique is normally used to compensate for a work-function difference which is typically ~1 V, but in this experiment, we recorded the CPD voltage in order to measure a surface charge induced by bulk polarization. The CPD was measured at a single point in the scan area, before recording the image, and it was kept constant during the scan. For this purpose, an SPM able to work in a high magnetic field generated by a Bitter magnet was employed. We operated the HF-SPM at 4.4 K, in He-exchange gas at a pressure of around 10⁻² mbar. A Co-coated cantilever was used, with 300 kHz resonance frequency and a Q-factor of 3800 at zero field. The images were collected in amplitude modulation (AM)-AFM with tapping mode at a fixed frequency of 320 kHz. EFM images and CPD voltage were recorded in lift mode at 100 nm above the sample surface. The sample bias was applied to the sample via silver paste. The magnetic field was parallel to the CdCr₂O₄ (111) direction. The high field SPM has previously demonstrated a topographic resolution better than 20 nm at 30 T; the resolution of the EFM images will be similar to the lift height of 100 nm.

Figure 3(a) shows topographic and EFM images of CdCr₂O₄. The topographic images show some structures several tens of nm high, which are thought to be multiple unit cell-high “mesas.” Between the mesas, the terraces are flat to within the z resolution of 0.14 nm determined from contact-mode AFM measurements. In order to obtain the EFM images, we recorded the phase shift image at field increments between zero and 28 T. Since the Q-factor changed with field, we translated the phase measurements into frequency shift. We then extracted the frequency shift values calculating the RMS image contrast and plotted it as a function of field, see Fig. 3(b). No clear correlation is observed between the features seen in the EFM images and the topography, and no qualitative change in the EFM images is seen with field. However, the image contrast does change, being low at 28 T and zero field, and higher at intermediate fields. We see no indication of tetragonal domain walls in the images of Fig. 3(a), which in the observed [111] orientation would be expected to present linear features along 120° domain boundaries. Existing neutron diffraction data do not offer a measure of the size of the tetragonal domains, so we infer that the size of the domains is larger than the 4 μm scan area.

Figure 3(c) presents the CPD voltage as a function of field. Normally, we would not expect the CPD to vary with magnetic field B, but here we recorded a clear change in the CPD with B, which increases with field up to 26 T and then goes back to zero. The recorded CPD values are also strongly enhanced, reaching up to 30 V, compared to typical CPD values due to work-function differences of ~1 V. This curve can be compared to polarization data derived from pyrocurrent from a similar sample, in a pulsed field at 1.5 K, Fig. 3(d). Both datasets show a continuously increasing signal in polarization or bias up to the transition to the plateau phase. Once the plateau phase is reached, the polarization and bias both drop back to zero. The magnetostuctural transition occurs at different fields between Figs. 3(c) and 3(d) due to the temperature dependence of the transition. To identify precisely the magnetostuctural transition field in the SPM experiment, we used the HF-SPM as a dilatometer. From this comparison, we can conclude that CPD voltage measurements with SPM are qualitatively equivalent to polarization measurement of the bulk.

The measurement of CPD in Fig. 3(c) provides a single point measurement of the bulk polarization. We can also investigate the surface charge distribution via the EFM images in Fig. 3(a). The EFM images do not resemble the topography, but indicate an inhomogeneous distribution of surface charges, likely due to the presence of defects at or near the surface. The pattern of defects does not change with magnetic field, but as the polarization increases with field, the presence of defects leads to an increasing charge inhomogeneity and hence increased image contrast. The effect of the defects is apparently less pronounced at high fields, leading to a diminished EFM image contrast above 10 T [Fig. 3(b)], whereas the CPD and polarization peak just before the transition at 28 T. At the transition to the plateau state, both the CPD and image contrast revert to their values at zero magnetic field. In the present study, we do not attempt to determine the precise nature of these defects, but note that they are observed in all areas of the sample surface studied. Since the sample was studied “as grown” without surface processing, we infer that the defects are produced during growth. A future spectroscopic study, for example, electron energy loss spectroscopy, might be able to uncover the nature of the charge-trapping defects.

To conclude, we have observed electric polarization induced by magnetic field in the frustrated spinel CdCr₂O₄. Polarization arises due to the non-collinear spin spiral state. We see no evidence for spontaneous polarization at zero magnetic field. Also the sign of polarization does not change with magnetic field direction, but only with poling voltage sign. Thus in terms of the electric polarization generated via Eq. (2), the spin-spiral ground state of CdCr₂O₄ behaves like a simple proper screw, as per ZnCr₂Se₄ and not like a spin cycloid as in CoCr₂O₄. This is despite CdCr₂O₄ having in fact a somewhat more complex incommensurate spin spiral.

In polarization, we observe clearly the effect of the spin flop transition at ~5 T. Based on ESR and optical spectroscopy measurements, the spin-flop has been interpreted as a transition from a helical structure to a commensurate canted spin structure. This would imply the disappearance of polarization above 5 T, which is not observed in our polarization data. Therefore, we can conclude that a spin spiral state survives as a canted conical spiral up to the transition to the collinear half-magnetization plateau at 28 T. This conclusion is...
supported by neutron diffraction experiments. A schematic of the field evolution of the spin-spiral structure of a single spin sublattice in CdCr\textsubscript{2}O\textsubscript{4} is shown in Fig. 4. The role of tetragonal domains and domain walls in the magnetoelectric effect in CdCr\textsubscript{2}O\textsubscript{4} remains to be fully explored, since in the present experiment, the scan area is smaller than the domain size: larger-area SPM, optical or polarized x-ray imaging techniques could be employed.

We have demonstrated that high magnetic field electrostatic force microscopy provides a viable alternative way of measuring electric polarization. By enabling polarization measurements to be made on a length scale of less than 100 nm, it was possible in this study to measure polarization within domains. The technique could readily be improved by the addition of Kelvin probe feedback: this would allow to record CPD at each pixel while imaging, or to make continuous measurements of CPD while sweeping the field. This method for measuring polarization will be a valuable tool for studying multiferroic samples with nano- and meso-scale inhomogeneities such as multiferroic domain walls and engineered nanostructures.

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**DATA AVAILABILITY**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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