Multiferroicity and magnetoelectric coupling in α-$CaCr_2O_4$

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Ferroelectricity in the incommensurate helical magnetic phase (below T_N, 43 K) of alpha (α) $CaCr_2O_4$ has been confirmed by pyroelectric measurements. Magnetoelectric and magnetodielectric coupling exist below T_N and are proportional to the square of magnetic field. From symmetry analysis we suggest that the presence of an external electric field destabilizes the symmetrical $2221'$ phase and stabilizes $21'$ symmetry. This provides a unique system in which polarization varies as the *fourth-degree* of the order-parameter amplitude and exhibits a vanishingly small value below the first-order transition at T_N, as observed experimentally.

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I. INTRODUCTION

Today the fascinating interplay between ferroelectric and magnetic order-parameter makes multiferroic materials as one of the interesting topics of condensed matter physics. These materials have attracted immense attention due to strong magnetoelectric coupling and several potential technological applications.[1] The search of such materials has been initiated after the discovery of magnetoelectric coupling in $TbMnO_3$.[1] Such materials are very rare,[2] and on the basis of their microscopic origin these materials are classified into several groups.[3] Recently, different "*frustrated magnets*" exhibit magnetoelectric coupling: e.g., RMn_2O_5,[4] $Ni_3V_2O_8$,[5] $MnWO_4$,[6] $Ba_{0.5}Sr_{1.5}Zn_2F_{12}O_{22}$,[7] $CoCr_2O_4$,[8] ABX_2 (A = Cu, Ag; B = Fe, Cr; and X = O and S).[9–13] In all these systems the ferroelectricity has been observed in the incommensurate magnetic phase.

Among frustrated magnets, the triangular antiferromagnetic lattice has been studied extensively, especially delafossites. The crystal structure of α-$CaCr_2O_4$ has been reported long ago by Pausch *et al.*[14] It crystallizes in an orthorhombic-layered structure with triangular sheets of CrO_2 separated by Ca^{+2} and mostly resembles delafossites with a small distortion. Recently, the magnetic properties of α-$CaCr_2O_4$ have been investigated in detail by Chapon *et al.*[15] They exhibit a long-range antiferromagnetic-incommensurate helical magnetic phase below $T_N = 43$ K having magnetic propagation wave vector $q = (0,0.3317(2),0)$. Neutron diffraction data shows that the plane of rotation of spins is perpendicular to the wave vector. In some materials polarization exists in the incommensurate phases (e.g., Rb_2ZnCl_4, $(NH_4)_2BeF_4$, and K_2SeO_4).[16] These materials exhibit a first-order phase transition to a ferroelectric phase at low temperature. Similarly, ferroelectricity has been reported in $TbMnO_3$,[1] $YBaCuFeO_5$,[17] and $CuFeO_2$[9] in the incommensurate magnetic phase. Considering these observations, we could expect magnetic field-induced ferroelectricity in α-$CaCr_2O_4$ in the incommensurate phase below T_N, although the magnetic point group $2221'$ does not allow ferroelectricity. Until now, there is no report on the dielectric and ferroelectric studies of this system. In this context it is worth investigating dielectric and magnetoelectric properties of this system in detail. In this paper we report, for the first time, the temperature- and magnetic field-dependent dielectric and ferroelectric properties of α-$CaCr_2O_4$. A clear dielectric peak was observed at T_N in association with incommensurate magnetic phase. Our pyroelectric results confirm that this ferroelectric (incommensurate magnetic phase) to paraelectric (paramagnetic phase) transition is of first order.

II. EXPERIMENTAL

Polycrystalline α-$CaCr_2O_4$ were prepared by spark plasma-sintering method. The phase purity of the sample was studied by room temperature x-ray diffraction. DC magnetization measurement was performed in zero field cooling and field cooling mode at 0.3 T magnetic field by using Quantum Design superconducting quantum interference device. Clear antiferromagnetic transition was observed at 43 K (not shown here). Dielectric measurement was performed on a thin parallel plate capacitor. Silver paste was used to make electrodes. The dielectric and magnetodielectric studies were made by using Agilent 4284A LCR meter at four different frequencies (5 kHz–100 kHz) and different magnetic fields (0, 0.5, and 10 T) during heating and cooling (1 K/min). Isothermal magnetodielectric was performed at different temperatures between ±14 T with a sweep rate of 100 Oe/sec at 100 kHz. Ferroelectricity was confirmed from pyroelectric measurements using a Keithley 6517A electrometer. The sample was cooled from room temperature to 55 K without any electric field. A poling electric field of ±630 kV/m was applied at 55 K during cooling to align the electric dipoles and was removed at 8 K. Polarization vs time was recorded for 5000 sec to remove the stray charge (if any) before measuring the pyroelectric current. Magnetoelectric coupling was observed by measuring the polarization vs magnetic field at 42 K. The sample was cooled with same electric field up to 42 K in a similar way as mentioned for polarization vs temperature. Magnetic field was ramped between ±14 T (100 Oe/sec) many times to ensure the reproducibility of the data. In each case magnetic field was applied perpendicular to the direction of electric field.

III. RESULTS

We have observed a lamda (λ)-like peak in dielectric permittivity at T_N [Fig. 1(a)]. This peak is frequency independent (not shown here). A small hysteresis is observed during cooling and warming measurements (not shown here), indicating the signature of first-order transition. The losses are

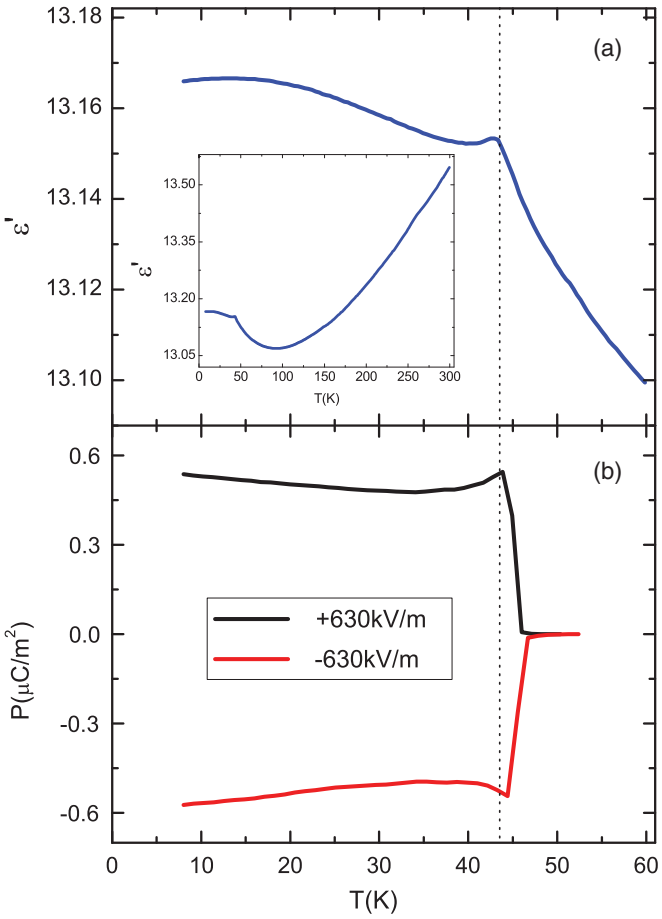

FIG. 1. (Color online) Temperature profiles of (a) dielectric permittivity measured at 100 kHz during warming (1 K/min); inset shows the overall temperature behavior (8 K to 300 K), and (b) remnant polarization (P) after poling with positive (black line) and negative electric field (red line) of α-$CaCr_2O_4$.

very small ($<10^{-4}$ below 250 K). This anomaly is consistent with the anomaly observed in magnetization and heat capacity measurements,[15] which indicates the coupling between charge and spin orders. The dielectric value decreases almost linearly from room temperature to 200 K and then decreases slowly up to 90 K. Below 90 K, dielectric permittivity again increases with decreasing temperature [inset of Fig. 1(a)]. The similar dielectric anomaly is also expected for related materials of this family, e.g., α-$SrCr_2O_4$, which has similar magnetic structure.[18]

The existence of ferroelectricity in the incommensurate helical magnetic phase is proved by pyroelectric measurements [Fig. 1(b)]. Although the remnant polarization value is very small, these results are highly reproducible and repeated many times. The direction of polarization flips by reversing the sign of poling electric field. The polarization decreases discontinuously at T_N, which is associated to the order of phase transition. For ferroelectric materials the order of transition can also be confirmed by pyroelectric measurement. In first-order transition, remnant polarization decreases discontinuously, while in second-order transition it decreases continuously from ferroelectric to paraelectric phase.[19] In this case polarization drops discontinuously to

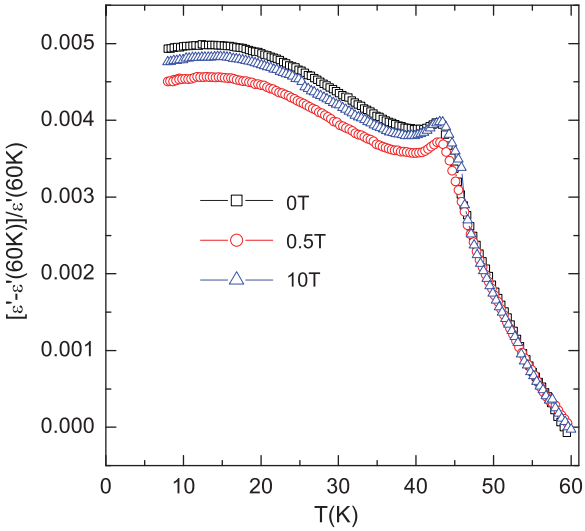

FIG. 2. (Color online) Relative dielectric permittivity vs temperature under different magnetic fields (0, 0.5, and 10T) at 100 kHz.

zero at T_N, such behavior has been observed at first-order ferroelectric to paraelectric-phase transition.[20] The first-order nature of this transition is confirmed from our pyroelectric measurements and also mentioned by Chapon *et al.*[15] The type of phase transition is different from delafossites, and the saturated polarization is also small as compared to delafossites. This difference could be related to a different magnetic-point group. The remnant polarization is comparable with spinel $CoCr_2O_4$.[8]

Recently, Dutton *et al.*[18] investigated magnetic and structural properties of α-$SrCr_2O_4$, which is analogous to α-$CaCr_2O_4$. They have studied the variation of lattice parameters with temperature and observed an inflection point at T_N in all lattice parameters without any change in symmetry and proposed spin-driven structural distortion. They also proposed the possibility of small domains with monoclinic or triclinic symmetry. However, there is no report on temperature-dependent lattice parameters of α-$CaCr_2O_4$. High resolution-diffraction measurement could be useful to state the lowering of the symmetry to monoclinic or triclinic symmetry, which could be favorable for ferroelectricity.

Dielectric permittivity was also measured under different magnetic fields to see whether or not T_N varies under magnetic field. Figure 2 represents the normalized dielectric permittivity $[(\varepsilon'-\varepsilon'_{60\,K})/\varepsilon'_{60\,K}]$ under a different magnetic field at 100 kHz. There is no shift in dielectric anomaly temperature when measured under high magnetic fields (up to 10 T). This illustrates the robust nature of antiferromagnetic interactions in this sample. To confirm the magnetoelectric coupling, we have measured isothermal polarization vs time by ramping magnetic field up to ± 14 T (100 Oe/sec) at 42 K (Fig. 3). In this figure we have presented the observed polarization, average remnant polarization (P_{avg}), and background signal. The upper panel of Fig. 3 shows observed polarization (raw data) for time and magnetic field dependence. To avoid the contribution of noise, we have averaged the observed polarization for all cycles by assuming symmetric behavior during increasing and decreasing magnetic field. The middle panel presents

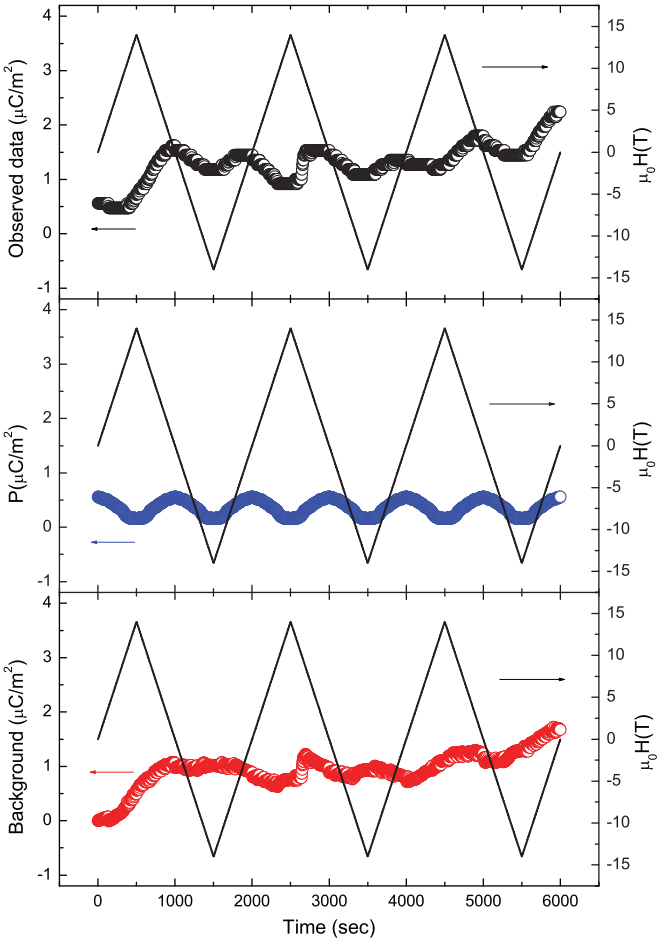

FIG. 3. (Color online) Time and magnetic field-dependence polarization of α-$CaCr_2O_4$ at 42 K ($\pm$14 T; 100 Oe/sec); arrows indicate the respective y-axis. Upper panel shows the as-observed polarization, middle panel shows average-remnant polarization (P_{avg}), and lower panel represents the background signal (see text for detail).

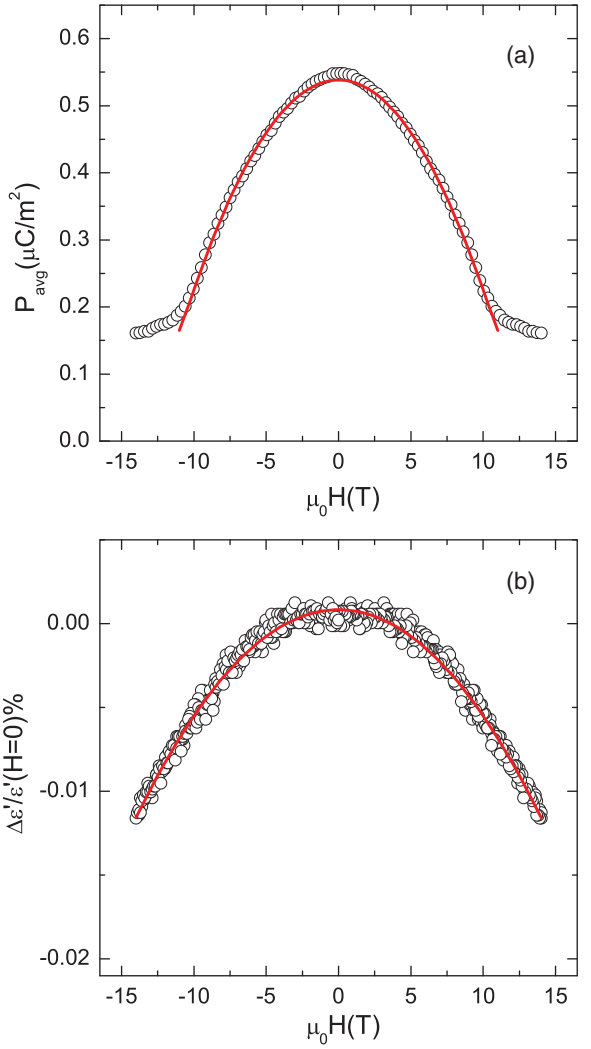

FIG. 4. (Color online) (a) Magnetic field-dependent P_{avg} at 42 K and (b) dielectric permittivity at 10 K with increasing and decreasing magnetic field (100 Oe/sec). Open circles represent experimental points and red line indicates the H^2 fitting. Here $\Delta\varepsilon' = \varepsilon'(H) - \varepsilon'(H=0)$.

P_{avg} as a function of time and magnetic field. Background is the difference between observed polarization and P_{avg} and is presented in the lower panel of Fig. 3. Such analysis is useful to see the clear effect of the magnetic field even for very small variations of polarization and also reported for delafossites $ACrO_2$ (A = Cu and Ag).[21] Figure 3 indicates the presence of magnetoelectric coupling. The magnetic field dependence P_{avg} at 42 K (extracted from Fig. 3, middle panel) and dielectric permittivity at 10 K is shown in Fig. 4(a) and 4(b), respectively. Figure 4 demonstrates that both P_{avg} and dielectric permittivity decreases with increasing magnetic field and is proportional of square of magnetic field for less than 10 T. On the basis of symmetry analysis it is proposed that in this material, polarization may appear only under magnetic field.[15] On the contrary we have observed electric polarization without any external magnetic field.

On the basis of symmetry analysis two different explanations can be proposed for the observation of ferroelectricity in $\alpha - CaCr_2O_4$ below $T_N = 43$ K, which are consistent with the orthorhombic symmetry $2221'$ assumed for this phase by Chapon *et al.*[15] in the absence of applied electric field and a vanishingly small value of polarization ($P <$ 1 $\mu C/m^2$) found under applied electric field of 630 kV/m. The preceding authors show that two magnetic incommensurate bidimensional complex order-parameters (η_1, η_1^*) and (η_2, η_2^*) are associated with the transition at T_N. The lowest symmetry phase induced by their coupling (Fig. 6 in Ref. 15) is a polar phase of monoclinic symmetry $21'$, which allows a spontaneous polarization P_y. One can therefore assume that a large poling electric field destabilizes the nonpolar $2221'$ phase and induces a crossover to the ferroelectric phase.

Using the symmetries of the order-parameters, i.e., from the corresponding irreducible representations, one can work out the dielectric contribution to the Landau-free energy, given by Eq. (1) in Ref. 15. It reads

$$F_D = \frac{P_y^2}{2\varepsilon_{yy}^0} + \delta P_y\left(\eta_1^2\eta_2^{*2} - \eta_1^{*2}\eta_2^2\right),$$

where δ is a coupling constant and ε_{yy}^0 is the dielectric permittivity in the paramagnetic phase. Minimizing F_D with

respect to P_y and putting $\eta_1 = \rho_1 e^{i\varphi_1}, \eta_1^* = \rho_1 e^{-i\varphi_1}, \eta_2 = \rho_2 e^{i\varphi_2}, \eta_2^* = \rho_2 e^{-i\varphi_2}$, one gets the equilibrium polarization below T_N:

$$P_y^e = -\delta\varepsilon_{yy}^0 \rho_1^2 \rho_2^2 \sin 2(\varphi_1 - \varphi_2), \quad (1)$$

where $\varphi_1 - \varphi_2$ is the dephasing between the coupled order-parameters, which is arbitrary in the ferroelectric phase.[15] Thus, P_y varies as the *fourth-degree* of the order-parameter amplitude Eq. (1) and should exhibit a vanishingly small value below the first-order transition at T_N, as observed experimentally.

Another possible explanation of the emergence of a weak polarization below T_N consists of assuming that the high electric field *decouples* the two order-parameters and *locks* the incommensurate magnetic wave-vector $\vec{k} = (0,0.3317,0)$ to the closest commensurate value $\vec{k} = (0, \frac{1}{3}, 0)$. Taking into account the corresponding symmetries of the irreducible representations, denoted Δ_1 and Δ_2 in Ref. 15, one can show that the same transition free-energy is associated with (η_1, η_1^*) or (η_2, η_2^*), which is

$$F = \frac{\alpha}{2}\rho^2 + \frac{\beta}{4}\rho^4 + \frac{\gamma_1}{6}\rho^6 + \frac{\gamma_2}{6}\rho^6 \cos 6\varphi, \quad (2)$$

where $\rho = \rho_1$ or ρ_2, and $\varphi = \varphi_1$ or φ_2. Minimizing F with respect to ρ and φ yields the following results for the decoupled order-parameters:

(1) The (η_1, η_1^*) order-parameter, transforming as Δ_1, induces three possible stable commensurate phases having the respective magnetic symmetries $P2_1/b$ for $\cos 6\varphi = 1$, $Pma2$ for $\cos 6\varphi = -1$, and Pm for $\cos 6\varphi \neq \pm 1$, involving a three-fold multiplication of the b-lattice parameter. In the orthorhombic $Pma2$ the polarization is along the z axis, varying as

$$P_z^e = -\delta\varepsilon_{zz}^0 \rho^3 \sin 3\varphi, \quad (3)$$

whereas in the monoclinic Pm phase the polarization is located in the (y, z) plane with the same cubic dependence on the order-parameter given by Eq. (3) for the P_y and P_z components, which corresponds to a weak value of the induced polarization.

(2) The (η_2, η_2^*) order-parameter, transforming as Δ_2, gives rise to three possible commensurate phases having the symmetries $P2/b(\cos 6\varphi = 1), Pmn2_1(\cos 6\varphi = -1)$ or $Pb(\cos 6\varphi \neq \pm 1)$ with the same three-fold multiplication of the paramagnetic unit cell along b. The polarization in the $Pmn2_1$ phases is along the x axis whereas it is in the (x, y) plane for the Pb phase, with a similar dependence on ρ and φ given by Eq. (3).

The different interpretations given for the electric field-induced polarization in $\alpha - CaCr_2O_4$ correspond to different orientations for the polarization and to different (incommensurate or commensurate) structures for the polar phase. Dielectric and high resolution structural analysis on single crystal is essential to confirm the most suitable direction for ferroelectricity. However, since no lock-in transition was observed in Ref. 15, first interpretation in terms of polar phase of monoclinic symmetry $21'$ is the most probable.

IV. CONCLUDING REMARKS

The multiferroicity in α-$CaCr_2O_4$ polycrystalline sample has been investigated. Our results show the spin-induced ferroelectricity in the incommensurate helical magnetic phase. These results also confirm that the transition at T_N is of first order. Magnetoelectric and magnetodielectric coupling exists and follows quadratic dependence of magnetic field, which is the classical dependence of such phase. In magnetic multiferroic materials the polarization represents a secondary effect (order-parameter) induced by the primary antiferromagnetic ordering. Because of the incommensurate character of the multiferroic phases, which correspond to grey point-group preserving time-reversal symmetry, there is no magnetoelectric effect induced by an electric field. In $\alpha - CaCr_2O_4$ the observed polarization results from a more complex mechanism: the applied electric field destabilizes the magnetic nonpolar phase (discussed in Ref. 15), which is replaced by a more stable polar phase. Therefore, although the applied electric field triggers the onset of the polarization by destabilizing the ground state of the system, the observed polarization is not "electric field-induced" since it simply results from the symmetry of the more stable new phase. The similar properties could be expected for other related materials which opens the avenue to find new multiferroics materials.

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