

Magnetoelectric effect in NdCrTiO₅J. Hwang,^{1,2} E. S. Choi,² H. D. Zhou,² J. Lu,² and P. Schlottmann^{1,2}¹*Department of Physics, Florida State University, Tallahassee, Florida 32306-3016, USA*²*National High Magnetic Field Laboratory, Florida State University, Tallahassee, Florida 32310-3706, USA*

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We have measured the dielectric constant and the pyroelectric current of orthorhombic (space group *Pbam*) NdCrTiO₅ polycrystalline samples. The dielectric constant and the pyroelectric current show features associated with ferroelectric transitions at the antiferromagnetic transition temperature ($T_N = 21$ K). The effect of magnetic fields is to enhance the features almost linearly up to the maximum measured field (7 T) with a spontaneous polarization value of $\sim 3.5 \mu\text{C}/\text{m}^2$. Two possible scenarios, the linear magnetoelectric effect and multiferroicity (antiferromagnetism plus ferroelectricity), are discussed as possible explanations for the observations.

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I. INTRODUCTION

Multiferroicity,¹⁻⁴ when two or more ferroic orders coexist in a single phase of a material, has attracted renewed interest during the past decade. In particular, multiferroics with magnetic and ferroelectric (FE) orders have been under intense investigation, both experimentally and theoretically, due to their possible applications for memory devices. The common features of this type of multiferroics include dielectric anomalies and the emergence of spontaneous electric polarization at the magnetic ordering temperature, which are also strongly dependent on the strength and orientation of the magnetic field. In these materials, ferroelectricity is usually enabled via different types of exchange interactions, which break the spatial inversion symmetry of a paraelectric phase. On the other hand, magnetoelectric (ME) materials show strong magnetic-field-dependent polarization and dielectric anomalies.⁵ Consideration of magnetic symmetry and the thermodynamic potential can give a great deal of information about the ME effect. For example, both broken spatial- and time-inversion symmetries are required for a linear ME effect due to the linear potential term (EH) in the thermodynamic potential, while the spatial-inversion symmetry can be conserved for a quadratic term (EEH).

Two mechanisms have been proposed as the macroscopic driving force for the symmetry breaking in a multiferroic phase transition, namely, the spin-current model^{6,7} and magnetostriction.⁸ Within the spin-current model, the symmetry breaking is due to the Dzyaloshinskii-Moriya (DM) interaction,^{9,10} where the antisymmetric exchange allows an electric polarization, \vec{P} , proportional to $\vec{e}_{ij} \times \vec{S}_i \times \vec{S}_j$, where \vec{e}_{ij} is the unit vector connecting two sites of spin \vec{S}_i and \vec{S}_j . The spin current is more relevant to a system with spiral magnetic structure such as TbMnO₃,¹¹ DyMnO₃,¹² Ni₃V₈O₈,¹³ CuFeO₂,¹⁴ and other compounds.¹⁵ There are fewer examples to show multiferroicity with collinear magnetic structures. In Dy(Gd)FeO₃^{16,17} and Ca₃Co_{2-x}Mn_xO₆,¹⁸ the DM term vanishes from symmetry, and the magnetostriction mechanism was proposed to explain the multiferroicity. Another *Pbam* multiferroic RMn₂O₅ ($R = \text{Y, Ho, Tb, Er}$) has more complicated spin structures with orderings of different commensurability. Its origin of ferroelectricity has been ascribed to either the spin-current model^{19,20} or magnetostriction.^{20,21} Regardless of the apparently different underlying mechanism,

these types of multiferroics generally show large ME effect, which sometimes is linear ($P_i = \alpha_{ij}H_j$ or $M_i = \alpha_{ij}E_j$) depending on the magnetic and crystallographic symmetries.

The crystalline and magnetic structures of powder samples of NdCrTiO₅ were investigated via x-rays and neutron diffraction in 1970.²² The spins of the Cr and Nd ions were found to be antiferromagnetically ordered below 13 K with all magnetic ions participating in the magnetic order. The spins of the Cr ions are collinearly oriented along the *c* axis, while the Nd moments are ordered in the *ab* plane. Subsequently, the ME effect in NdCrTiO₅ was discovered.²³ NdCrTiO₅ was one of the first ME materials possessing two distinct magnetic sublattices, namely Cr³⁺ and Nd³⁺, known at that time. The ME susceptibility was measured²³ on a powder pellet sample showing a T_N of 20.5 K rather than 13 K.²² The magnetic point symmetry (*mmm'*) allows a linear ME effect.²⁴ Hence, under an applied electric field a magnetization is induced, $M_i = \alpha_{ij}E_j$, where α_{ij} showed a rapid increase at $T_N = 20.5$ K and a drop below 8 K.²³ The magnitude of α_{ij} observed was of the order of 1×10^{-5} CGS units, that is, smaller by one order of magnitude when compared to the well-known ME material Cr₂O₃.²⁵ In Ref. 23, it is argued that below T_N the magnetic moments of the Cr³⁺ ions order cooperatively and then induce the order of the Nd³⁺ ions by means of an exchange coupling, in contrast to a direct cooperative ordering of the Nd³⁺ spin subsystem.

Assuming that the antiferromagnetic (AFM) order in NdCrTiO₅ is driven by the Cr³⁺ spins, their collinear order would suggest that the mechanism giving rise to the ME is magnetostriction. However, if both magnetic sublattices participate in the buildup of the cooperative AFM order, then the order has to be considered noncollinear and the spin-current model would be applicable. The open question of the origin of the coexistence of AFM order and the ME effect motivated us to present a detailed study of the ME behavior of this compound.

In this work, we measure the electric response (dielectric constant, polarization) of NdCrTiO₅ under a magnetic field, which leads to observations of signatures of multiferroic and ME behavior such as a dielectric anomaly and spontaneously switchable polarization below T_N . For the measured magnetic field range up to 7 T, the saturated polarization (P_{sat}) increases with magnetic fields with a maximum $P_{\text{sat}} \sim 3.5 \mu\text{C}/\text{m}^2$. The observed ME annealing effect tends to point NdCrTiO₅ as ME

material rather than multiferroic material, but we cannot rule out the possibility that it is multiferroic.

II. EXPERIMENTAL

Polycrystalline NdCrTiO₅ was made by a solid-state reaction. A stoichiometric mixture of Nd₂O₃, Cr₂O₃, and TiO₂ was ground together and calcinated in air at 1000 °C for 24 h. The powder was then reground and pressed into pellets under 400 atm hydrostatic pressure and again calcinated in air at 1300 °C for another 24 h. The x-ray powder diffraction (XRD) patterns were recorded by a Huber imaging plate Guinier camera 670 with Cu $K_{\alpha 1}$ radiation (1.54059 Å) with a Ge monochromator. The dc magnetic susceptibility measurements were made with a Quantum Design superconducting interference device (SQUID) magnetometer with applied magnetic field of $H = 0.1$ T. The specific heat measurements were performed in a Quantum Design physical property measurement system (PPMS). A cylindrical sample was cut from the pressed pellet with dimensions of 16.0 mm² × 1.0 mm for the measurements of the electrical properties, and electrodes were painted with silver paste on the plane surfaces. The dielectric constant was measured using an Andeen-Hagerling AH-2700A capacitance bridge operating at a frequency of 10 kHz. The pyroelectric current was measured using a Keithley 6517A electrometer on warming after poling the crystal in an electric field while cooling down from above T_N . The sample was short-circuited for 15 min before warming to remove any residual charges. The spontaneous polarization was obtained by integration of the pyroelectric current with respect to time.

III. RESULTS

The room-temperature XRD pattern of NdCrTiO₅ shows a single phase with an orthorhombic, $Pbam$, structure. The lattice parameters are $a = 7.5812(2)$ Å, $b = 8.6803(2)$ Å, and $c = 5.8123(3)$ Å, similar to the previously reported data.²² The x-ray and neutron diffraction study²² identified that 95% of Cr³⁺ and 5% Ti⁴⁺ are distributed over the $4f$ sites (center of oxygen coordinated octahedral), 5%Cr³⁺ and 95% Ti⁴⁺ are distributed over the $4h$ sites (base center of a square pyramid), and Nd³⁺ ions are located at the $4g$ sites (see Fig. 1).

The dc magnetic susceptibility [see Fig. 2(a)] shows a slope change (kink) at 21 K. At the same temperature, the specific heat shows a λ shape peak, which indicates that this transition involves long-range magnetic order. This transition temperature is in good agreement with that previously reported from ME measurements.²³ The previously reported neutron diffraction study²² has identified the low-temperature phase ($T \leq 13$ K) as having AFM order. The magnetic moments of Cr³⁺ in the $4f$ sites [Cr ($4f$)] are pointing along the c axis, with alternating upward and downward orientations. The magnetic moments of Nd³⁺ and Cr³⁺ in the $4h$ sites [Cr ($4h$)] lie in the ab plane. The Cr ($4h$) moments are aligned along the b axis and antiferromagnetically correlated in that direction, while they are ferromagnetically correlated in the a direction. The Nd moments, on the other hand, order in a similar way except that they are tilted away from the b axis by 12 deg. The long-range order of the Nd moments is believed to follow the ordered Cr moments rather than being induced by a cooperative

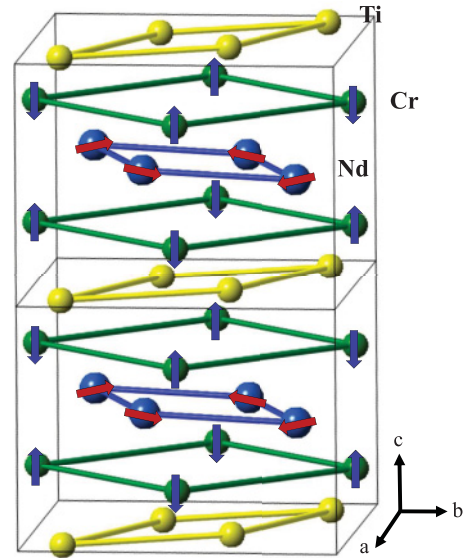


FIG. 1. (Color online) The crystallographic and magnetic structure of NdCrTiO₅ according to Ref. 22. Here we ignored the small interchange of sites found for Cr and Ti atoms (see text).

interaction of Nd³⁺ spin systems.^{23,26} The spin structure at temperatures well below T_N (ignoring the 5% of switched Ti and Cr ions between the $4h$ and $4f$ sites) and below the temperature of the magnetic susceptibility peak ($T = 11$ K) is depicted in Fig. 2. Note that the slope of the susceptibility

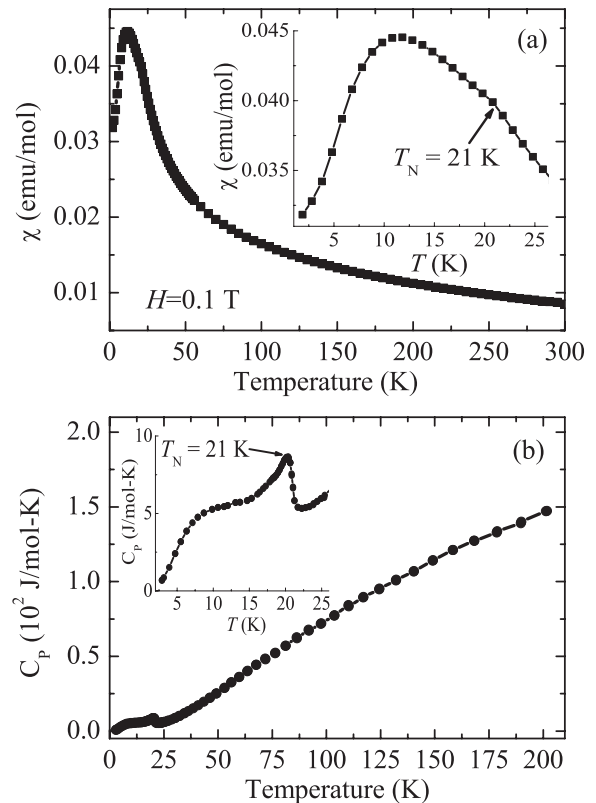


FIG. 2. Temperature dependence of (a) the magnetic susceptibility and (b) the specific heat of NdCrTiO₅. Each inset shows data over an extended temperature range around T_N . Note the kink in the susceptibility at 21 K.

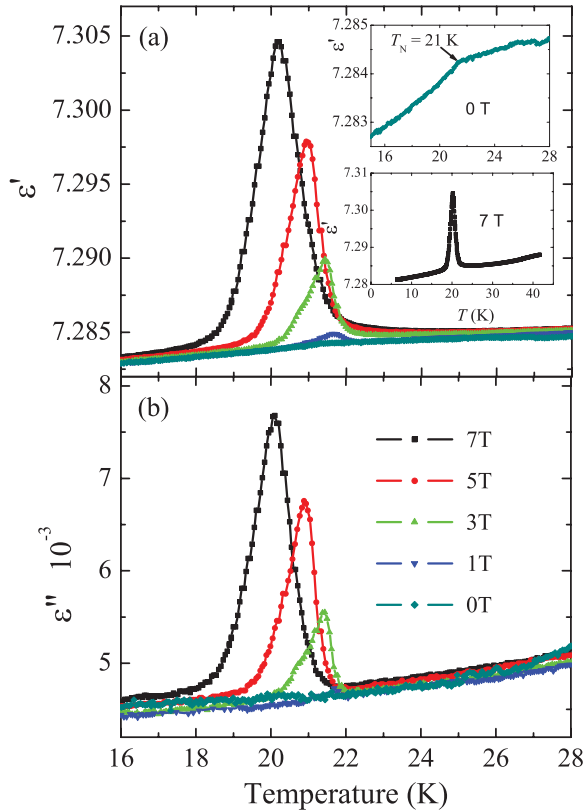


FIG. 3. (Color online) The temperature dependence of the real part (a) and the imaginary part (b) of the dielectric constant of NdCrTiO₅ at different applied magnetic fields. The upper inset of (a) shows the dielectric constant with zero magnetic field over an extended temperature range around T_N . Note the kink at the antiferromagnetic transition. The lower inset of (a) shows the dielectric constant down to 6.5 K at 7 T.

begins to change below 13 K, which is reported in Ref. 22 as the temperature below which the magnetic Bragg peaks were observed.

Figure 3 shows the dielectric constant measured for different applied magnetic fields. For $H = 0$ T, the real part of the dielectric constant (ϵ') shows a slope change around $T_N = 21$ K. When a magnetic field is applied, a peak is induced in ϵ' as shown in Fig. 3(a). Since T_N decreases with magnetic field in an antiferromagnet (the order is gradually suppressed), with increasing magnetic field, the position of the peak moves to lower temperatures. Since the spin symmetry is broken by the applied magnetic field, the peak becomes stronger with increasing field. We also notice that (i) the position of the peak in ϵ' shows no frequency dependence (not shown here) and (ii) the imaginary part of the dielectric constant, or the dissipation, also manifests a peak around a similar temperature as the peak of ϵ' with applied magnetic field. These two behaviors prove that the anomaly of ϵ' is really related to the phase transition. Hence, the observation of the anomaly of ϵ' around the AFM ordering transition at $T_N = 21$ K demonstrates the coupling between the magnetic and electric properties of NdCrTiO₅. We did not observe any anomaly associated with the broad peak in the magnetic susceptibility around $T = 11$ K.

Figure 4(a) shows the pyroelectric current measured for different magnetic fields and a fixed electric field. The

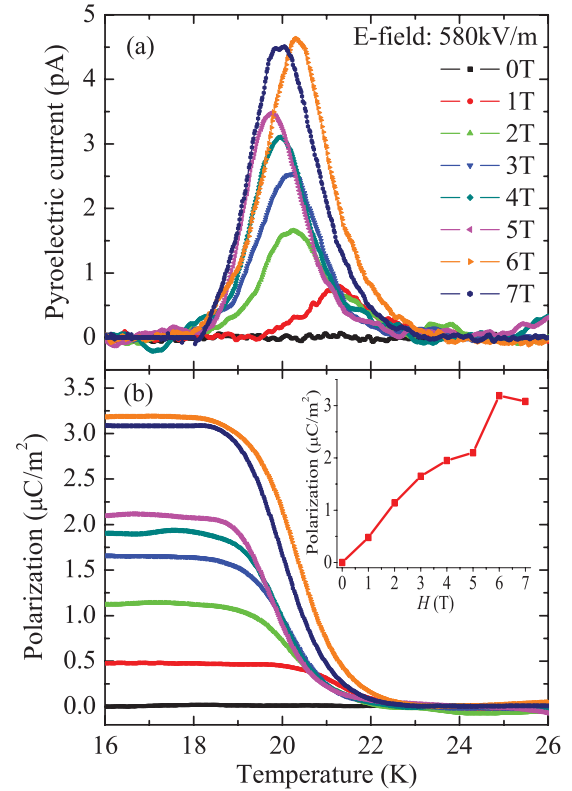


FIG. 4. (Color online) Temperature dependence of the pyroelectric current (a) and polarization (b) of NdCrTiO₅ for different applied magnetic fields for a fixed electric field of 580 kV/m ($E \perp H$). The inset of (b) shows the magnetic field dependence of the low T polarization.

magnetic fields were applied during both cooling and warming. In zero magnetic field, no pyroelectric current is observed. When a magnetic field is applied, a pyroelectric current arises in a temperature interval related to the phase transition. This broad peak of pyroelectric current starts at about 18 K, ends around 22 K, and becomes stronger with increasing applied magnetic field. Note that it is necessary to cool the sample through T_N with an applied electric field to observe a pyroelectric current. The spontaneous polarization is obtained by integration of the pyroelectric current with respect to time, shown in Fig. 4(b). With increasing applied magnetic field, the polarization monotonically increases and saturates around 3.2 $\mu\text{C}/\text{m}^2$ for H around 6–7 T. The pyroelectric current and the onset of polarization are then directly related to the magnetic phase transition. Note that again no change in the pyroelectric current was observed around $T = 11$ K, where the magnetic susceptibility has its maximum.

Figure 5 displays the pyroelectric current and its integrated polarization measured on a sample from a different batch for various applied electric fields under a fixed magnetic field $H = 6.7$ T. The peak of the pyroelectric current around T_N and its related polarization become stronger with increasing applied electric field. Moreover, the sign of the pyroelectric current and polarization switches simultaneously with the sign of the applied electric field. As shown by the solid and open circles in Fig. 5, a similar pyroelectric current of opposite sign is obtained and hence generates a polarization of the same

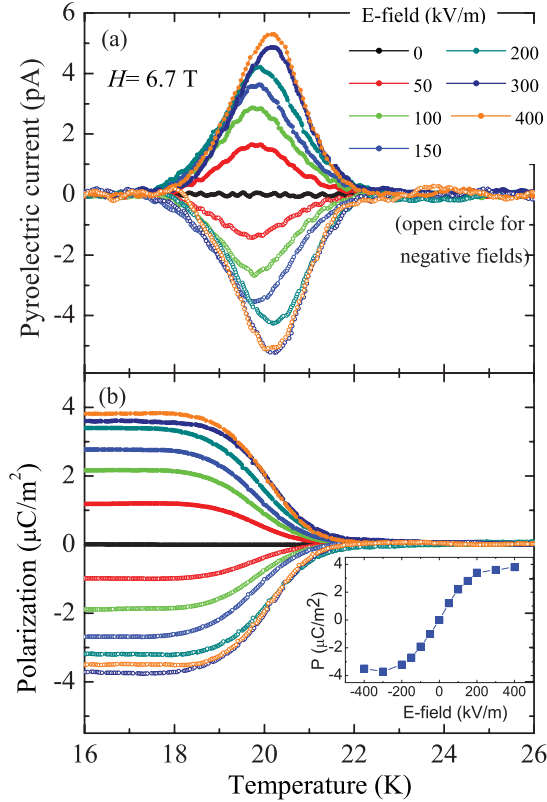


FIG. 5. (Color online) Temperature dependence of the pyroelectric current (a) and polarization (b) of NdCrTiO₅ at different electric fields and a magnetic field H of 6.7 T ($E \perp H$). The solid and open circles correspond to reversed poling electric fields. The inset shows the polarization as a function of poling electric fields.

magnitude. This is typical for ME annealing conditions, that is, poling with both H and E fields. The polarization increases linearly with applied electric fields up to 200 kV/m followed by saturation behavior at higher electric fields.

We studied the ME annealing effect more closely on another sample from the same batch measured in Fig. 5. For this study, we employed five different conditions of ME annealings, namely, four different conditions of positive or negative combinations of magnetic or electric fields and zero magnetic field cooling (ZMFC). As stated above, to observe polarization, the electric field is always applied during the annealing (cooling) process, as is the magnetic field during the pyroelectric current measurement (warming up). Figure 6 shows the pyroelectric current data from this study when the electric field is applied perpendicularly to the magnetic field. From this study, we found that the usual ME annealing condition (both magnetic and electric fields applied during cooling) is necessary to induce polarization. The polarization reversal is achieved by changing the polarity of the electric field but not the magnetic field. The same measurements were repeated after the sample was rotated by 90 deg so that the electric and the magnetic fields are parallel each other. The two different configurations ($E \perp H$ and $E \parallel H$) gave the same results but with 50% larger polarization value for the $E \perp H$ case.

IV. DISCUSSION

The maximum spontaneous polarization value ($3.5 \mu\text{C}/\text{m}$) is smaller by two orders of magnitude as compared to other well-known multiferroic materials with the same structure, for example, RMn_2O_5 (R : rare earth elements or Y). The polarization value is expected to be larger in NdCrTiO₅ when measured for a single crystal rather than for a polycrystalline sample but is likely to remain within the same order of magnitude. Considering the almost linear increase of the polarization with magnetic fields [see the inset of Fig. 4(b)], larger magnetic fields could also enhance the polarization. From the linear relation, we obtained ME coefficients $\alpha_{xy} = 1.5 \times 10^{-5}$ CGS units and $\alpha_{zz} = 0.7 \times 10^{-5}$ CGS units. These values are in the same order as those obtained from the ME susceptibility measurement.²³

Our findings, the dielectric constant anomaly and the polarization reversal, suggest two possible scenarios; (1) multiferroicity with a concurrent AFM/FE transition or (2) a linear ME effect with AFM fluctuation and domain effects. A high-resolution structural measurement or a polarization-electric field (PE) hysteresis experiment at low temperatures could discern the two scenarios, but neither of them is available to us at the moment. At room temperature, NdCrTiO₅ is orthorhombic ($Pbam$), a centrosymmetric structure at room temperature, which does not allow ferroelectricity via the DM interaction. Nevertheless, we cannot exclude the AFM/FE scenario without further definitive experiments. Hereafter, we discuss each scenario and its implications.

A. Multiferroicity with concurrent AFM/FE transition

In this case, the mechanism leading to FE transition is associated with the AFM phase transition. Due to the rather small magnitude of the polarization, the corresponding driving force inducing the symmetry breaking must be weak. To find the underlying mechanism, we examine the applicability of the spin-current model first. The origin of the downturn of the magnetic susceptibility below 11 K is not yet established. A possible plausible scenario is that the Nd³⁺ spins (the $J = \frac{9}{2}$ multiplet is split by crystalline fields to yield a Kramers ground doublet) gradually start to participate in the AFM order below 13 K, a temperature reported in Ref. 22 as the onset of some of the magnetic Bragg reflections. The onset of the order of the Cr³⁺ moments could not be determined in Ref. 22 and is seen as a very weak cusp in the magnetic susceptibility [see inset in Fig. 2(a)]. At T_N the fluctuations of the magnetic moments are rather weak compared to the thermal fluctuations at the transition. This picture agrees with the arguments presented in the earlier papers about this compound.^{22,23} Assuming that close to T_N only the Cr³⁺ moments order, then the magnetic structure is collinear, so that $\vec{S}_i \times \vec{S}_j$ terms are zero in the temperature interval around T_N . The spin current mechanism^{6,7} can then be excluded, leaving magnetostriction⁸ as the candidate to induce the FE transition.

The above arguments are based on the assumption that the Nd³⁺ and the Cr³⁺ ($4h$) moments are not participating in the magnetic order until lower temperatures. Should this not be the case, then spin cross-products between Cr ($4f$) and Nd sites are nonzero, and since the system lacks inversion symmetry,

the DM mechanism is active to produce a spin current. The strength of the spin current would depend on the magnitude of the magnetic order in the Nd sublattice. Such mechanism, however, seems to be absent in NdCrTiO₅, considering that no features of the dielectric constant and the polarization were observed around the Nd ordering temperature.

In order to explain the dielectric anomaly at zero field [see the inset of Fig. 3(a)] and the almost linear magnetic field dependence of the polarization, we turn to the Ginzburg-Landau expansion of the free energy in terms of the electric and magnetic fields.⁵ Differentiation with respect to the fields leads to the polarization and the magnetization,

$$P_i(\vec{E}, \vec{H}) = P_i^S + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \dots, \quad (1)$$

$$M_i(\vec{E}, \vec{H}) = M_i^S + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_j + \dots, \quad (2)$$

where \vec{P}^S and \vec{M}^S denote the spontaneous polarization and magnetization, whereas $\hat{\epsilon}$ and $\hat{\mu}$ are the electric and magnetic susceptibilities. The tensor $\hat{\alpha}$ represents the induction of polarization by a magnetic field or of magnetization by an electric field, which is known as the linear ME effect. For an AFM order, we have $\vec{P}^S = \vec{M}^S = 0$, so that in zero magnetic field an electric field can induce a finite magnetization, $M_i = \alpha_{ij} E_j$, and (vice versa) in zero electric field a magnetic field can induce a finite polarization, $P_i = \alpha_{ij} H_j$. We have mentioned this effect in the introduction.

In Fig. 4(b), we presented the polarization as a function of temperature for several fields. The magnetostriction, when the sample is driven through the Néel transition, induces strains and hence a local magnetization in the grains and their boundaries. The small displacements of the ions from their equilibrium position, the consequence of the magnetostriction, should change the polarizability of the sample and hence the dielectric constant. Also the local deviations from the ordered magnetization, δm_i , arising from the magnetostriction should generate local electric fields through the $\hat{\alpha}$ tensor, giving rise to a change in the dielectric constant at T_N . This effect is expected to be very weak in the absence of a magnetic field, but it is very sensitive to magnetic fields since all the local contributions δm_i align and become cooperative. This effect is restricted to the region around T_N . It is also expected that the zero magnetic field anomaly of ϵ' is stronger in a polycrystalline sample, due to the numerous grain boundaries, than in a single crystal. Its magnetic field dependence should, however, be stronger in a single crystal. The effect on the absorption (i.e., ϵ'') is expected to be much weaker than for ϵ' as indeed observed.

The pyroelectric current generated when the system is cooled through the Néel transition is also expected to be proportional to $\delta m_i E_j$. Hence, it is restricted to the region around T_N , grows with applied magnetic field approximately linearly, and is linear in the electric field. The saturation polarization is then almost linear in the applied H , in agreement with the observations. This is valid as long as the expression $P_i = \alpha_{ij} H_j$ is valid (i.e., the fields are not too large); otherwise higher order terms in the Ginzburg-Landau expansion would have to be taken into account.

A specific mechanism of how the magnetostriction exchange can lead to a broken inversion symmetry in NdCrTiO₅ below the Néel transition is not available yet. In other multiferroic materials with collinear spin structures, the

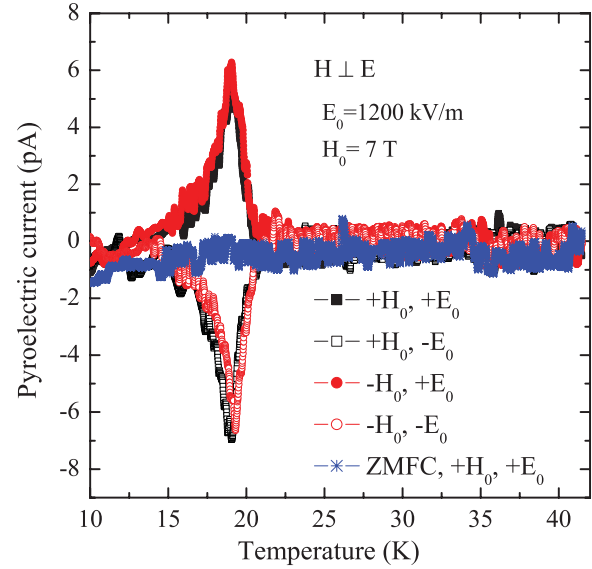


FIG. 6. (Color online) Temperature dependence of the pyroelectric current NdCrTiO₅ under different ME annealing conditions when the electric field is perpendicular to the magnetic field ($E \perp H$).

interactions between neighboring spins from different sites seem to play a crucial role. For example, there are ferromagnetically aligned Dy³⁺(Gd³⁺) and Fe³⁺ spin sheets in Dy(Gd)FeO₃^{16,17} and $\uparrow\uparrow\downarrow\downarrow$ order of Co²⁺ and Mn⁴⁺ Ising spins in Ca₃Co_{2-x}Mn_xO₆.¹⁸ This kind of spin arrangement is not clearly apparent for NdCrTiO₅ according to the available spin structure (see Fig. 1). Similar measurements on a single-crystal sample would give more insight into the preferred polarization direction and its magnetic field dependence.

B. Non-FE transition / linear ME effect

First of all, it should be noted that the linear ME effect and multiferroicity are not mutually exclusive; that is, they can occur in a single material as found in DyFeO₃.¹⁶ Experimentally, it is easier to observe the linear ME effect compared to proving ferroelectricity. We attempted PE hysteresis measurement on NdCrTiO₅ samples, but the experiment was inconclusive since we could not observe typical hysteresis behavior before the sample was damaged due to electrical breakdown.

There are characteristic behaviors observed in NdCrTiO₅ which favor the non-FE / linear ME effect scenario. For example, the ME annealing behavior shown in Fig. 6 is typical for powder ME material. It is well known that the ME annealing is necessary to observe the ME effect in AFM material; otherwise random AFM domains result in zero net polarization.²⁷⁻²⁹ The reversal of the polarization was found in other ME materials when the ME annealing was done with opposite polarity of the electric field.³⁰

Likewise, other experimental results can be also explained without evoking ferroelectricity, for example, the linear-field-dependent polarization and the larger ME coefficient for $E \perp H$. The observed dielectric anomaly around T_N is often found in other AFM systems, where spin fluctuations are ascribed to the anomaly.³¹ The recovery of the dielectric constant well below the transition and the increased anomaly

with the magnetic field can as well be qualitatively explained by this model.

However, we cannot completely exclude the possibility of multiferroicity. For example, it is also conceivable that the ME annealing is required for magnetic-field-induced FE transition. The poling process is to acquire a single domain state while the sample is cooled down through a transition (for example, paraelectric to ferroelectric); therefore, both magnetic and electric fields are necessary under the AFM/FE scenario as well. Between the two scenarios, however, we are inclined to the second one, the linear ME effect, rather than multiferroics. It is the simpler explanation and it is consistent with the small polarization.

In summary, we have observed a field-induced dielectric constant anomaly and electric polarization at the AFM state

of NdCrTiO₅. The polarization increases with magnetic fields and is reversible by changing the polarity of the poling electric field. We discussed multiferroicity and linear ME effect as a possible mechanism to explain the experimental results. While it is difficult to draw a definitive conclusion, the linear ME effect is more likely the cause considering the small polarization.

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