PHYSICAL REVIEW B **86**, 214409 (2012)

Field-induced polar order at the Néel temperature of chromium in rare-earth orthochromites: Interplay of rare-earth and Cr magnetism

B. Rajeswaran,[1] D. I. Khomskii,[2] A. K. Zvezdin,[3,4] C. N. R. Rao,[1] and A. Sundaresan[1,*]
[1]*Chemistry and Physics of Materials Unit and International Centre for Materials Science, Jawaharlal Nehru Centre for Advanced Scientific Research, Jakkur P.O., Bangalore 560 064, India*
[2]*II. Physikalisches Institut, Universität zu Köln, ZülpicherStrasse 77, 50937 Köln, Germany*
[3]*A. M. Prokhorov General Physics Insitute of the Russian Academy of Science - Vavilova 38, Moscow, 119991, Russia*
[4]*Moscow Institute of Physics and Technology (State University) - Institutskii per. 9, Dolgoprudny, 141700, Russia*

(Received 3 January 2012; revised manuscript received 19 November 2012; published 10 December 2012)

We report field-induced switchable polarization ($P \sim 0.2$–$0.8\ \mu\text{C/cm}^2$) below the Néel temperature of chromium (${T_N}^{\text{Cr}}$) in weakly ferromagnetic rare-earth orthochromites, $R\text{CrO}_3$ (R = rare earth) but only when the rare-earth ion is magnetic. Intriguingly, the polarization in ErCrO_3 ($T_C = 133$ K) disappears at a spin-reorientation (Morin) transition ($T_{SR} \sim 22$ K) below which the weak ferromagnetism associated with the Cr sublattice also disappears, demonstrating the crucial role of weak ferromagnetism in inducing the polar order. Further, the polarization (P) is strongly influenced by an applied magnetic field, indicating a strong magnetoelectric effect. We suggest that the polar order occurs in $R\text{CrO}_3$, due to the combined effect of the poling field that breaks the symmetry and the exchange field on the R ion from the Cr sublattice that stabilizes the polar state. We propose that a similar mechanism could work in the isostructural rare-earth orthoferrites $R\text{FeO}_3$ as well.

DOI: 10.1103/PhysRevB.86.214409 PACS number(s): 75.85.+t, 75.25.Dk, 75.47.Lx, 77.80.−e

Magnetoelectric multiferroics constitute an emerging class of novel materials that combine coupled electric and magnetic dipole orders.[1–6] Interaction between the two order parameters leads to a magnetoelectric effect, which gives rise to magnetization on application of an electric field or to electric polarization on applying a magnetic field. Coupling between magnetic and ferroelectric order is generally strong in the so-called type-II materials where the ferroelectricity arises due to certain type of magnetic spin structures.[4] A cycloidal spin structure below the spiral magnetic ordering of Mn^{3+} ions in centrosymmetric orthorhombic (*Pbnm*) TbMnO_3[5,6] and collinear magnetic ordering with E-type magnetic structure in HoMnO_3[7] break the inversion symmetry, causing net electric polarization. It has been reported that the induced moment on the rare-earth ion enhances the ferroelectric polarization in DyMnO_3.[8] In cycloidal-spin induced ferroelectricity, the antisymmetric exchange Dzyaloshinskii-Moriya (DM) interaction ($S_i \times S_j$) plays a key role in producing the electric polarization.[9] Based on symmetry analysis of magnetoelectric interactions in rare-earth orthoferrites and orthochromites, it has been shown that the spontaneous electric polarization or magnetic-field-induced polarization can appear at the magnetic ordering temperature of rare-earth ions.[10] This effect was found experimentally in some rare-earth orthoferrites, $R\text{FeO}_3$ (R = Gd and Dy) where exchange striction between R and Fe moments has been suggested to be responsible for the origin of ferroelectricity.[11–13]

It has been reported recently that SmFeO_3, which belongs to the rare-earth orthoferrite family, exhibits ferroelectric features at the magnetic ordering temperature of iron (${T_N}^{\text{Fe}} = 670$ K).[14] This is surprising because rare-earth moments order at low temperatures (<10 K) and thus the exchange striction mechanism as discussed above may not directly account for the origin of polarization at such high temperatures. Also, the spin-current or the inverse DM interaction model for such a canted antiferromagnetic system suggests zero net polarization because local polarization cancels out due to the alternate arrangement of pairs of canted spins.[5,9] We believe that magnetic interactions between Sm^{3+} and canted moments of Fe^{3+} ions may play a crucial role in inducing ferroelectric behavior in this oxide. In fact, anisotropic interactions between R and Fe^{3+} ions were suggested to be responsible for the temperature-induced spin-reorientation in this as well as in many other rare-earth orthoferrites ($R\text{FeO}_3$).[15,16] This is consistent with the fact that such spin reorientation does not occur in orthoferrites with a nonmagnetic R ion, as in YFeO_3. Accordingly, the orthoferrites with a nonmagnetic R ion should not show ferroelectric polarization at the magnetic transition. However, the spin disorder at the Fe site in $\text{YFe}_{1-x}M_x\text{O}_3$ (M = Cr, Mn) can induce spin reorientation.[17–19]

Since the high Néel temperature of $R\text{FeO}_3$ (${T_N}^{\text{Fe}} = 620$–740 K) makes it difficult to carry out polarization measurements due to the high leakage current, we have chosen isostructural rare-earth orthochromites ($R\text{CrO}_3$) which exhibit similar magnetic properties with relatively lower T_N values (120–300 K). In this article, we report field-induced polar order below the Néel temperature of chromium in weakly ferromagnetic $R\text{CrO}_3$ containing magnetic R ions such as Sm, Gd, Tb, Tm, and Er, and no polar order when the R ion is nonmagnetic.

In the orthochromites with orthorhombic structure (*Pbnm*), the following three types of G-type antiferromagnetic configurations are observed: $\Gamma_1(A_x,G_y,C_z)$, $\Gamma_2(F_x,C_y,G_z)$, and $\Gamma_4(G_x,A_y,F_z)$ following the Bertaut notation.[20] The first configuration, as reported in ErCrO_3 below a spin-reorientation transition ($T_{SR} \sim 22$ K), does not allow weak ferromagnetism, but the second and third have weak ferromagnetism along the x and z directions, respectively.[21–25] When the R ion is nonmagnetic, the ground state remains weakly ferromagnetic with the magnetic spin configuration Γ_4. If the R ion is magnetic, the high-temperature magnetic structure can be Γ_4 or Γ_2 depending upon the R ion. At low temperatures, some $R\text{CrO}_3$ systems show a spin-reorientation transition below

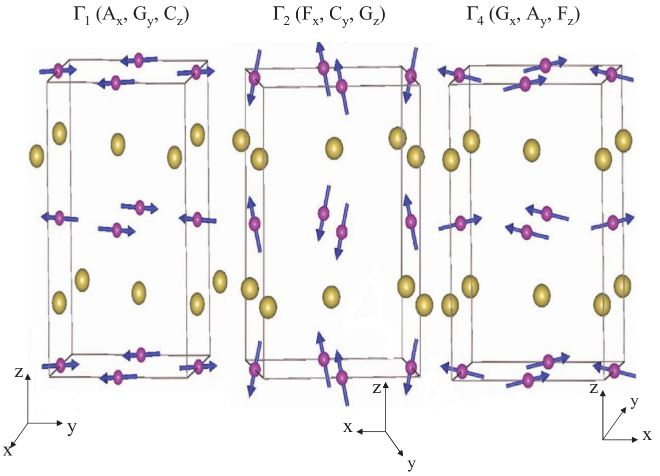

FIG. 1. (Color online) Spin structures in Γ_1, Γ_2, and Γ_4 with *Pbnm* symmetry showing absence of spin canting in Γ_1. The location of the *R* ion is marked by spheres without spin.

which the spin structure becomes Γ_2 or Γ_1.[21] All the three spin configurations (Γ_1, Γ_2, and Γ_4) are shown in Fig. 1.

Polycrystalline samples of RCrO$_3$ (R = Sm, Gd, Tb, Er, Tm, Lu, and Y) were prepared by the solid state reaction of stoichiometric quantities of R_2O_3 and Cr_2O_3 at 1673 K for 12 hours followed by several intermittent grinding and heating steps. Phase purity was confirmed by Rietveld refinement on the x-ray powder diffraction data collected with a Bruker D8 Advance diffractometer. Magnetic measurements were carried out with a vibrating sample magnetometer (VSM) in the physical property measurement system (PPMS) of Quantum Design, USA. Capacitance and pyroelectric measurements were carried out with LCR meter Agilent E4980A and 6517A Keithley electrometric resistance meter, respectively, using the multifunction probe in the PPMS. In the pyroelectric current measurement, first the sample was poled by applying electric fields of +1.43 and −1.43 kV/cm at a temperature greater than T_N, and then the sample was cooled down to low temperatures under the applied field. After shorting the circuit for a reasonably long duration, the current was measured using the electrometer while warming the sample to a temperature higher than T_N at a rate of 4 K/min. Upon integrating the pyrocurrent with respect to time and dividing it by the area of the sample, we obtain electric polarization, which can be plotted as a function of temperature. Positive-up and negative-down (PUND) and resistivity measurements were carried out by using a Radiant Technologies Inc. precision workstation.

In Fig. 2(a), we show the temperature dependence of magnetization of SmCrO$_3$ under field-cooled conditions with an applied field of 100 Oe. The observed behavior is characteristic of antiferromagnetic ordering of Cr moments ($T_N = 197$ K) with weak ferromagnetism. The drop in magnetization below 40 K is due to spin reorientation where the Cr-spin configuration changes from $\Gamma_4(G_x, A_y, F_z)$ to $\Gamma_2(F_x, C_y, G_z)$. Spin reorientation in orthoferrites and orthochromites is known to be brought about by anisotropic magnetic interactions between R^{3+} and Fe/Cr ions.[15,25] In Fig. 2(b), we show the temperature-dependent dielectric constant, $\varepsilon_r(T)$, of SmCrO$_3$ measured at 1 kHz. The dielectric constant is almost independent of temperature up to 170 K, above which it increases with a steep rise above 200 K which is associated with a large frequency-dependent Maxwell-Wagner relaxation.[19] Though we do not observe a dielectric anomaly in the vicinity of T_N, the derivative of $\varepsilon_r(T)$ shows (right inset) a clear anomaly at T_N indicating a magnetodielectric effect.[26] On the other hand, a clear anomaly in ε_r is seen at T_{SR} (left inset). It is seen from the insets that the frequency dependence of ε_r is large above 200 K but relative small at low temperatures. A similar anomaly in $d\varepsilon_r/dT$ is observed at T_N in Tb, Gd, and Tm orthochromites, which do not exhibit spin reorientation down to 15 K.[27]

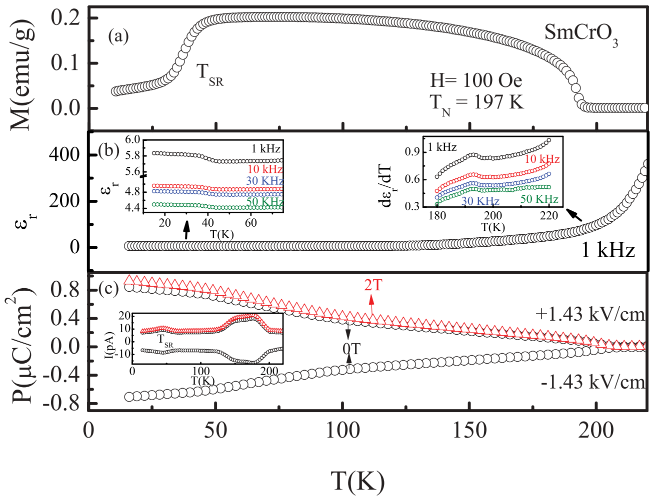

FIG. 2. (Color online) (a) Field-cooled magnetization of SmCrO$_3$ at 100 Oe with respect to temperature. (b) Dielectric constant with respect to temperature at 1 kHz. Insets show the frequency dependence of the dielectric constant and the first derivative of the dielectric constant in the vicinity T_{SR} and T_N, respectively. (c) Electric polarization (corrected for leakage) as a function of temperature, and the inset shows the corresponding pyroelectric current.

Figure 2(c) shows electric polarization of SmCrO$_3$ ($P \sim \pm0.80$ μC/cm^2 at $T = 15$ K for $E = \pm1.43$ kV/cm) and pyroelectric current peaks (inset) obtained from pyroelectric measurements, where it is to be noted that the polarization results are corrected for leakage current. This figure clearly demonstrates the development of the electric polarization in the vicinity of $T_N{}^{\mathrm{Cr}}$ and confirms that the polarization is switchable. Further, it shows a signature of spin reorientation in pyroelectric current and electric polarization. It is important to note that the observed polarization values are relatively higher than those reported in most of the magnetically induced ferroelectric materials.[2,26–30] This figure also demonstrates the effect of magnetic field on the polarization, where an increase of ~0.05 μ_C/cm^2 per tesla is observed at 15 K.

We also find electric polarization near $T_N = 167$ K for the canted antiferromagnetic GdCrO$_3$ ($P \sim \pm0.7$ μC/cm^2 at $T = 15$ K for $E = \pm2.25$ kV/cm) as shown in Fig. 3.[31,32] In the case of TbCrO$_3$, we observe electric polarization ($P \sim \pm0.5$ μC/cm^2 at $T = 15$ K for $E = \pm1.43$ kV/cm) in the vicinity of $T_N = 157$ K.[27] In TmCrO$_3$, in addition to electric polarization at $T_N = 127$ K ($P \sim \pm0.25$ μC/cm^2 at $T = 15$ K for $E = \pm1.43$ kV/cm), we also observe a

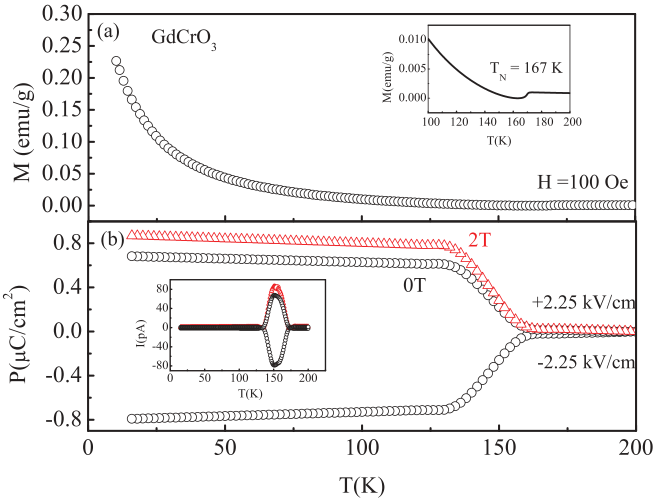

FIG. 3. (Color online) (a) Field-cooled magnetization of $GdCrO_3$ at 100 Oe with respect to temperature. (b) Electric polarization (corrected for leakage) as a function of temperature. The inset in (b) shows the pyroelectric current as a function of temperature with (red) and without the presence of magnetic field of 2 T (black).

temperature-induced magnetization reversal with a compensation temperature (T^*) of 25 K indicating that the Tm and canted Cr moments are coupled antiferromagnetically, similar to observations in $SmFeO_3$.[14,27]

In order to further confirm the intrinsic nature of the observed electric polarization, we have performed PUND measurements.[27,28] This method allow us to separate out the intrinsic contribution to pyrocurrent from that due to leakage currents, etc. Though the value of remnant polarization obtained by this method is small (0.01 $\mu C/cm^2$), probably due to the relatively small applied effective poling field, these measurements confirm that the polarization observed in orthochromites with magnetic rare-earth ions below T_N is intrinsic, and that these systems are indeed multiferroic. It is noteworthy that in the case of $LuCrO_3$ and $YCrO_3$ with nonmagnetic R ions no intrinsic electric polarization is observed.[27]

In addition to the magnetic R ion, we show that the weak ferromagnetism of the Cr sublattice is also essential for inducing polarization in these orthochromites. The compound $ErCrO_3$ undergoes antiferromagnetic ordering with a weak ferromagnetism at $T_N{}^{Cr} = 133$ K [Fig. 4(a)] and at low temperatures it exhibits a spin-reorientation (Morin) transition at $T_{SR} \sim 22$ K, below which the weak ferromagnetism disappears [Fig. 1(a)]. We observe dielectric anomalies both at T_N and at T_{SR} confirming the magnetoelectric coupling [Fig. 4(b)]. Interestingly, the electric polarization [Fig. 4(c)], measured following the procedure adapted for CuO,[33] disappears along with the weak ferromagnetism below T_{SR}, which demonstrates that the weak ferromagnetism of the Cr sublattice is essential for inducing electric polarization. However, the polarization below T_{SR} is revived by cooling the sample under an applied magnetic field (±2 T). The applied magnetic field suppresses the spin reorientation and thus the weak ferromagnetic state and the polarization remain down to the lowest temperature.

Most importantly, the electric polarization is influenced strongly by the applied magnetic field, indicating a strong coupling between spontaneous magnetization and polarization as shown in Fig. 5 for $GdCrO_3$. By applying a positive magnetic field, the polarization increases, whereas it decreases under negative applied field. It can be seen that the change in polarization is $\sim 0.1\ \mu C/cm^2$ per tesla.

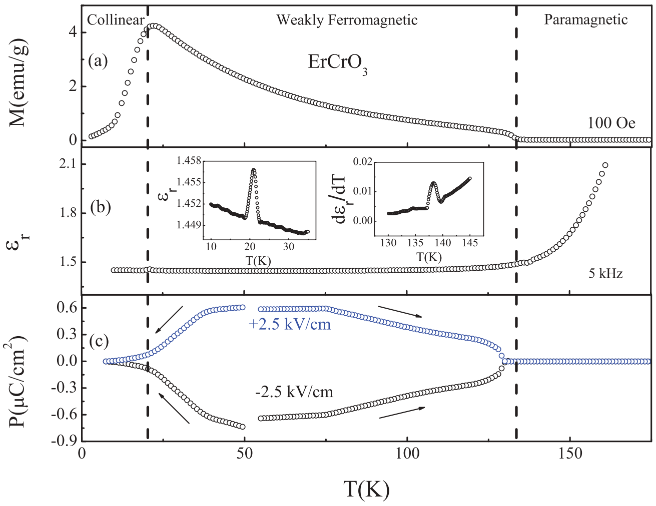

FIG. 4. (Color online) (a) Field cooled magnetization of $ErCrO_3$ at 100 Oe showing a spin reorientation transition from weakly ferromagnetic Γ_4 to collinear Γ_1 magnetic spin structure at ∼22 K. (b) Dielectric constant as a function of temperature at 5 kHz. Insets show the dielectric anomaly at both the T_{SR} and T_N temperature regions. (c) Ferroelectric polarization as a function of temperature measured following the procedure adapted for CuO in Ref. 33. It should be noted that the ferroelectricity disappears in the collinear phase.

Our experimental results clearly establish the presence of electric polarization ($P \sim 0.2$–$0.8\ \mu C/cm^2$) below the magnetic ordering temperature of Cr ions ($T_N{}^{Cr} = 120$–300 K) in $RCrO_3$ but only when the R ion is magnetic and the ordered Cr sublattice is weakly ferromagnetic. It is apparent that these phenomena could be observed in similar materials, for example, the isostructural orthoferrites $SmFeO_3$ with magnetic R ion. The experimental data on $SmFeO_3$ agree with our findings, and they show in addition that the polarization in

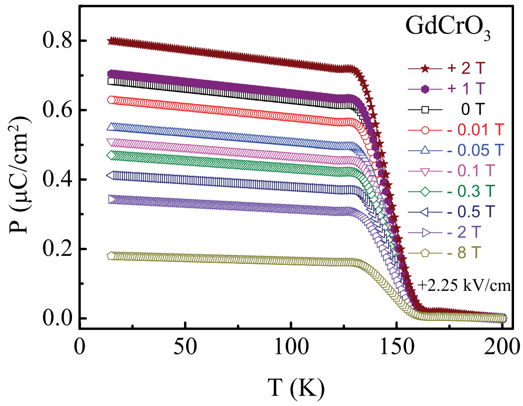

FIG. 5. (Color online) Effect of applied magnetic field on electric polarization in $GdCrO_3$. It can be seen that the polarization changes systematically with the strength and polarity of the applied magnetic field.

$SmFeO_3$, and most probably also in our systems, lies in the *ab* plane.[14]

Theoretical interpretation of our findings should, first of all, take into account symmetry restrictions imposed by the crystal structure. As argued, e.g., in Refs. 10 and 34 and especially stressed in Ref. 35, with full symmetry (*Pbnm*) no magnetic ordering of Cr (or Fe) in $R\mathrm{CrO}_3/R\mathrm{FeO}_3$ can in itself produce ferroelectric polarization. As demonstrated by our experimental results, the observed polarization should be connected with the interplay of magnetism between Cr and R. Spontaneous magnetization of R below its Néel temperature can in some cases give polarization.[10,12] But at higher temperatures ${T_N}^R < T < {T_N}^{\mathrm{Cr}}$ only induced magnetization on R ions due to their interaction with Cr could exist, and, with the full lattice symmetry intact, this induced magnetization also cannot lead to ferroelectricity.[36]

Thus, we are left with two options: (1) One can suspect that the actual lattice symmetry of orthochromites and orthoferrites is lower than the usually assumed *Pbnm* (or *Pnmc*), due to some tiny, as yet undetected distortion. In this case the Cr-R exchange field could in principle lead to nonzero polarization. The R ions in the *Pbnm* structure are not lying at the center of symmetry; their point group is Cs not D_{2h}. They lie in the mirror plane perpendicular to the c axis, but their coordinates in this *ab* plane are not fixed, and each R ion can be shifted so as to produce a local dipole. However, the *Pbnm* symmetry requires that such dipoles at other R ions be opposite, so that the sum of such dipoles in a unit cell is zero. Thus, there is no net ferroelectric polarization caused by orthorhombic distortions, but one can consider such perovskites as antiferroelectric. Consequently, also the contribution to such dipoles, e.g., due to exchange striction of R-Cr exchange, also sum up to zero. However, if the real symmetry of the lattice (and consequently the point symmetry of the R ion) would be lower, these contributions would not cancel and could give ferroelectric polarization below ${T_N}^{\mathrm{Cr}}$.

Another option, which we think is more plausible, is that the very process of measuring polarization, which involves the poling procedure, causes some small distortion of R ions and their surroundings, producing odd contributions to the crystal field of R and triggering "releasing" the exchange-striction mechanism. That is, we propose that the poling field reduces the symmetry, and the metastable state thus formed can survive after we release the poling field. The main part of polarization arises due to the R-Cr exchange striction, which strongly enhances the distortion initially caused by the poling field. Thus, the poling acts as a trigger, and the metastable "self-poled" state created below ${T_N}^{\mathrm{Cr}}$ is the state which displays a relatively large measured polarization. This picture agrees with the general experimental conclusions summarized above.

Now, the dominant contribution to the exchange striction comes from the isotropic Heisenberg-like R-Cr exchange. A purely antiferromagnetic G-type ordering of the Cr sublattice would not lead to a net nonzero striction, but if there exists weak ferromagnetism of Cr there would be nonzero striction of the same sign at every (magnetic) R ion, i.e., there would appear net polarization lying in the *ab* plane.

In principle, there may also appear effects due to an antisymmetric R-Cr interaction,[15] which could also contribute to polarization. The analysis of these terms should be done specifically for a particular system. But, in general, we expect that such contributions to polarization would be weaker, so that the main conclusions rationalized above generally hold.

In conclusion, we found that the field-induced metastable state with electric polar order appears at the magnetic ordering temperatures of Cr^{3+} ions in the weakly ferromagnetic rare-earth orthochromites ($R\mathrm{CrO}_3$, where R is a magnetic rare-earth ion), exhibiting a relatively large electric polarization $\sim$0.2–0.8 $\mu\mathrm{C/cm}^2$, starting at rather high temperatures ($\sim$120–250 K) corresponding to the Néel temperatures of the Cr subsystem. We propose that the multiferroic behaviour of these systems is caused by the interaction between magnetic rare earth and weak ferromagnetic Cr^{3+} ions following the breaking of symmetry by the effect of poling. The observation of a strong dependence of polarization with applied magnetic field along with their high Curie temperatures and large polarization suggest that these materials are potential candidates for device applications.

The authors are grateful to P. Mandal and Maxim Mostovoy for useful discussions and help. The work of D.Kh. was supported by the German programs SFB 608 and FOR 1346, and by the European project SOPRANO.

---

[*] sundaresan@jncasr.ac.in

[1] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) **442**, 759 (2006).
[2] S.-W. Cheong and M. V. Mostovoy, Nat. Mater. **6**, 13 (2007).
[3] C. N. R. Rao and C. R. Serrao, J. Mater. Chem. **17**, 4931 (2007).
[4] D. Khomskii, J. Magn. Magn. Mater. **306**, 1 (2006); Physics **2**, 20 (2009).
[5] T. Kimura, Annu. Rev. Mater. Res. **37**, 387 (2007).
[6] Y. Tokura and S. Seki, Adv. Mater. **22**, 1554 (2010).
[7] S. Picozzi, K. Yamauchi, B. Sanyal, I. A. Sergienko, and E. Dagotto, Phys. Rev. Lett. **99**, 227201 (2007).
[8] O. Prokhnenko, R. Feyerherm, E. Dudzik, S. Landsgesell, N. Aliouane, L. C. Chapon, and D. N. Argyriou, Phys. Rev. Lett. **98**, 057206 (2007).
[9] H. Katsura, N. Nagaosa, and A. V. Balatsky, Phys. Rev. Lett. **95**, 057205 (2005).
[10] A. K. Zvezdin and A. A. Mukhin, JETP Lett. **88**, 505 (2008).
[11] A. Stroppa, M. Marsman, G. Kresse, and Silvia Picozzi, New J. Phys. **12**, 093026 (2010).
[12] Y. Tokunaga, S. Iguchi, T. Arima, and Y. Tokura, Phys. Rev. Lett. **101**, 097205 (2008).
[13] Y. Tokunaga, N. Furukawa, H. Sakai, Y. Taguchi, T. Arima, and Y. Tokura, Nat. Mater. **8**, 558 (2009).
[14] J.-H. Lee, Y. K. Jeong, J. H. Park, M.-A. Oak, H. M. Jang, J. Y. Son, and J. F. Scott, Phys. Rev. Lett. **107**, 117201(2011).
[15] T. Yamaguchi, J. Phys. Chem. Solids **35**, 479 (1974).
[16] G. Gorodetsky and Lionel M. Levinson, Solid State Commun. **7**, 67 (1969).

[17] K. P. Belov, A. K. Zvezdin, A. M. Kadomtseva, and R. Z. Levitin, Sov. Phys. Usp. **19**, 574 (1976).

[18] N. Dasari, P. Mandal, A. Sundaresan, and N. S. Vidhyadhiraja, Europhys. Lett. **99**, 17008 (2012).

[19] P. Mandal, Venkata Srinu Bhadram, Y. Sundarayya, Chandrabhas Narayana, A. Sundaresan, and C. N. R. Rao, Phys. Rev. Lett. **107**, 137202 (2011).

[20] E. F. Bertaut, in *Magnetism III*, edited by G. T. Rado and H. Suhl (Academic, New York, 1968), p. 149.

[21] E. F. Bertaut, G. Bassi, G. Buisson, P. Burlet, J. Chappert, A. Delapalme, J. Mareschal, G. Roult, R. Aleonard, R. Pouthenet, and J. P. Rebouillat, J. Appl. Phys. **37**, 1038 (1966).

[22] G. Gorodetsky, B. Sharo, and S. Strikman, J. Appl. Phys. **39**, 1371 (1968).

[23] C. Veyret, J. B. Ayasse, J. Chaussy, J. Mareschal, and J. Sivardiere, J. Phys. (France) **31**, 607 (1970).

[24] M. Ebschutz, L. Holmes, J. P. Maita, and L. G. Van Uitert, Solid State Commun. **8**, 1815(1979).

[25] J. B. Goodenough, Rep. Prog. Phys. **67**, 1915 (2004).

[26] A. Maignan, C. Martin, K. Singh, Ch. Simon, O. I. Lebedev, and S. Turner, J. Solid State Chem. **195**, 41 (2012).

[27] See Supplemental Material at http://link.aps.org/supplemental/10.1103/PhysRevB.86.214409 for results on (i) PUND, (ii) dielectric constant, (iii) resistivity, (iv) magnetization, and (v) pyroelectric measurements in RCrO$_3$.

[28] S. M. Feng *et al.*, New J. Phys. **12**, 073006 (2010).

[29] M. Kenzelmann, A. B. Harris, S. Jonas, C. Broholm, J. Schefer, S. B. Kim, C. L. Zhang, S.-W. Cheong, O. P. Vajk, and J. W. Lynn, Phys. Rev. Lett. **95**, 087206 (2005).

[30] M. Mostovoy, Phys. Rev. Lett. **96**, 067601 (2006).

[31] K. Yoshii, J. Solid State Chem. **159**, 204 (2001).

[32] A. H. Cooke, D. M. Martin, and M. R. Wells, J. Phys. C **7**, 3133 (1974).

[33] T. Kimura, Y. Sekio, H. Nakamura, T. Siegrist, and A. P. Ramirez, Nat. Mater. **7**, 291 (2008).

[34] K. P. Belov, A. K. Zvezdin, A. M. Kadomtseva, and R. Z. Levitin, *Orientational Phase Transitions in Rare Earth Magnetic Materials* (Nauka, Moscow, 1985) (in Russian).

[35] R. D. Johnson, N. Terada, and P. G. Radaelli, Phys. Rev. Lett. **108**, 219701 (2012).

[36] The explanation proposed in Ref. 37 would not work: the authors introduced the term in energy $\sim P(M^2 - L^2)$, but this term is not invariant, because the polarization P changes sign under inversion, whereas the antiferromagnetic vector L and net magnetization M are even with respect to inversion.

[37] J. H. Lee, Y. K. Jeong, J. H. Park, M.-A. Oak, H. M. Jang, J. Y. Son, and J. F. Scott, Phys. Rev. Lett. **108**, 219702 (2012).