Anomalous magnetic order in the magnetoelectric oxide NdCrTiO₅ revealed by impurity effects

Shunsuke Kori, Takuma Okamura, Ryuji Okazaki, and Ichiro Terasaki* Department of Physics, Nagoya University, Nagoya 464-8602, Japan

Yukio Yasui

Department of Physics, Meiji University, Kawasaki 214-8571, Japan (Received 26 March 2014; revised manuscript received 28 February 2015; published 6 April 2015)

We have prepared two sets of polycrystalline samples of $Nd_{1-x}Eu_xCrTiO_5$ and $NdCr_{1-y}Al_yTiO_5$, and have measured susceptibility, dielectric constant polarization, and specific heat below 30 K. In both sets, we find that the antiferromagnetic temperature systematically decreases with increasing impurity concentrations. This clearly indicates that not only Cr but also Nd is essential to the magnetic order in the title compound. Such a cooperative behavior of the 4*f* and 3*d* moments is quite unique in comparison with other complex oxides. A possible mechanism of the magnetic order and magnetoelectric response is discussed.

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I. INTRODUCTION

Magnetoelectric materials are materials that exhibit a finite coupling between polarization and magnetization, where polarization is proportional to magnetic field in the absence of electric field, and magnetization is proportional to electric field in the absence of magnetic field [1-3]. They have been long studied over a century since Pierre Curie suggested such possibilities. In the 60's [4-7], the magnetoelectric coupling constants have been measured experimentally and calculated theoretically in Cr₂O₃ and various complicated materials.

Recently the magnetoelectric effect has received renewed interest since the discovery of multiferroic materials exhibiting a huge response to external fields [8–10]. The term multiferroic originally stood for coexistence of ferromagnetic and ferroelectric orders, but now extends to coexistence of ferroelectric order and various magnetic orders. A critical difference from magnetoelectric materials is that multiferroic materials exhibit a finite polarization in the absence of external electric and magnetic fields. Noncollinear magnets are most extensively investigated as promising candidates for multiferroic materials because the inversion symmetry is often broken. Among them, some magnetic structures can allow the material to be polar to induce ferroelectricity.

In this respect, the magnetoelectric oxide NdCrTiO₅ is a controversial material. This oxide was first synthesized and identified in 1970 by Buisson [11]. The crystal structure is schematically drawn in Fig. 1. A Cr³⁺ ion is surrounded with six oxygen ions to form a CrO_6 octahedron, and a Ti⁴⁺ ion is surrounded with four oxygen ions to from a TiO₄ tetrahedron. The CrO_6 octahedra are connected along the c axis via the edge-shared network to make the CrO_6 chain structure. The TiO₄ tetrahedra bridge the gap between the two CrO₆ chains with corner-shared network. The Nd³⁺ ions are located in between the two TiO_4 tetrahedra. Buisson [11] also measured and analyzed the magnetic structure of this oxide at low temperature using neutron scattering and found that the magnetic moments on the Nd and Cr ions exhibit a long range order below 13 K. An important feature is that the magnetic order is noncollinear; the Nd moments antiferromagnetically align in the *ab* plane, while the Cr moments do along the *c* axis. Later Greenblatt *et al.* [12] found the magnetoelectric response below 21 K in this compound and revealed that the coupling constant is smaller than that of Cr_2O_3 [5,6]. Recently Hwang *et al.* [13] have reported an extensive study of magnetodielectrics of this oxide and have discussed whether this material is magnetoelectric or multiferroic. They have found a kink in the susceptibility and a peak in the specific heat at 21 K and have identified the antiferromagnetic temperature T_N to be 21 K. Since they did not observe any other peaks in the specific heat down to 2 K, the magnetic structure measured by Buisson is the only one ordered state. Vopson [14] has suggested multicaloric effect in this oxide, because the multicaloric effect works only when ferroelectric and magnetic orders set in at the same temperature.

A controversial issue in NdCrTiO₅ is whether the magnetic order at T_N is driven by only Cr moments or by both Cr and Nd moments. Greenblatt et al. [12] speculated that the Cr moments likely order first at T_N , because an interaction between the Nd moments is much weaker as is seen in the low ordering temperatures of Nd moments in NdFeO₃ (1 K) and NdCoO₃ (4 K). They further found a broad maximum in the susceptibility around 9 K, which they ascribed to the freezing of the Nd moments. Hwang et al. speculated similarly that the Nd moments follow the ordered Cr moments below 13 K. If so, the magnetoelectric effect should be due to the same mechanism in Cr₂O₃ with an antiferromagnetic structure similar to the Cr moments in NdCrTiO₅. In contrast, if the Nd moments order together with the Cr moments below T_N , some multiferroic order may happen from the noncollinear magnetic structure. Hwang et al. [13] have discussed this issue carefully and have finally concluded that NdCrTiO₅ is likely to be magnetoelectric but cannot exclude the possibility of multiferroic state. On the contrary, Saha et al. [15] have reported a small but finite polarization below 21 K in zero magnetic field and have claimed that NdCrTiO₅ is multiferroic.

In order to address this issue, we have studied the isovalent, nonmagnetic impurity effects on the magnetoelectric state of NdCrTiO₅. Here we show the magnetic susceptibility, dielectric constant, polarization, and specific heat of polycrystalline samples of Nd_{1-x}Eu_xCrTiO₅ and NdCr_{1-y}Al_yTiO₅, and we discuss the effects of disorder in the Nd and Cr sites on the

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^{*}terra@cc.nagoya-u.ac.jp



FIG. 1. (Color online) (a) The crystal structure of NdCrTiO₅. The edge-shared CrO₆ octahedra form a chain structure along the *c* axis, and the TiO₄ tetrahedra bridge the CrO₆ chains with a corner-shared oxygen network. Nd ions are located between the TiO₄ tetrahedra. (b) X-ray diffraction patterns of typical samples. Cu K_{α} is used as an x-ray source.

magnetoelectric properties. We have chosen Eu^{3+} and Al^{3+} as impurity, because they are nonmagnetic and isovalent to Nd^{3+} and Cr^{3+} . We find that both the substitutions suppress the magnetic order and concomitantly suppress the dielectric anomaly. This clearly reveals that both Nd and Cr are essential to the magnetic order, and the magnetic interaction between 3d and 4f determines T_{N} . This d-f interaction is quite unique in the title compound, for magnetic orders are driven predominantly by d-d interaction in most of the 3d transition metal oxides.

II. EXPERIMENTAL

Polycrystalline samples of $Nd_{1-x}Eu_xCrTiO_5$ with x = 0, 0.05, 0.1, 0.5, 0.7, 1.0 and $NdCr_{1-y}Al_yTiO_5$ with y = 0, 0.025,

0.05, 0.1 were made using solid-state reaction. Stoichiometric amounts of Nd_2O_3 , Eu_2O_3 , Cr_2O_3 , Al_2O_3 , and TiO_2 powders were mixed and heated in air at 1000 °C for 24 h. Then the powders were reground and pressed into pellets under 300 atm hydrostatic pressure and sintered in air at 1300 °C for 24 h.

The x-ray powder diffraction was taken with Cu K_{α} radiation at room temperature. The obtained patterns were identical to those reported in the previous literature [11], and no trace of impurity phases was detected as shown in Fig. 1(b). In addition, the observed diffraction patterns are in excellent agreement with the calculated patterns. Within experimental uncertainties, any change in the degree of Cr-Ti site disorder was not detected in all the samples.

The dielectric constant was measured in platy samples of $50.0 \text{ mm}^2 \times 0.350 \text{ mm}$ with the surfaces painted with silver paste above 2 K using an LCR meter (Agilent E4980A) at 100 kHz in a cryostat equipped with a superconducting magnet (Quantum Design PPMS). The polarization was evaluated from the pyroelectric current measured with an electrometer (Keithley 6517A) after polling in 5 kV/cm from 40 down to 5 K in Quantum Design PPMS. The magnetic susceptibility was measured with a superconducting quantum interference device magnetometer (Quantum Design MPMS) in a field-cooling process at 0.1 T above 4 K. The specific heat was measured in zero magnetic order, and dipole order were visualized with VESTA [16].

III. RESULTS AND DISCUSSION

Figure 2(a) shows the relative change in the dielectric constant at 7 T defined by

$$\Delta \varepsilon / \varepsilon_{25\mathrm{K}} = \frac{\varepsilon(T) - \varepsilon(25 \mathrm{K})}{\varepsilon(25 \mathrm{K})}$$

for NdCr_{1-y}Al_yTiO₅. Although the magnitude of $\Delta \varepsilon / \varepsilon_{25 \text{ K}}$ is as small as 10^{-3} , it clearly exhibits a sharp peak at 19.5 K for NdCrTiO₅ (y = 0), indicating a dielectric anomaly induced by external magnetic field. Our data well reproduce the dielectric response reported by Hwang *et al.* [13] and warrant the quality of our samples.

Let us have a look at the Al substitution effects. The substituted Al ions shift the dielectric peak to low temperatures and suppress the peak height together with broadening the width. Considering that the Al substitution does not vary the magnitude of the dielectric constant very much as shown in the inset, we conclude that the Al ions predominantly affect the magnetoelectric part of ε , and that the Cr ions are essential to the magnetoelectric response. We further note that the x-ray diffraction patterns in Fig. 1(b) are essentially identical between y = 0 and 0.1, and change in the crystal structure plays a secondary role in the decrease in the dielectric anomaly. The peak temperature lowers down to 12 K from y = 0 to 0.1, indicating that only 10% substitution of nonmagnetic elements reduces T_N by 50%. This is much more remarkable than the prediction of conventional dilution effect expressed by $T_N(y)/T_N(0) = 1 - y$.

We find that Nd-site substitution effects are much more unconventional than Cr-site substitution effects. Figure 2(b) shows $\Delta \varepsilon / \varepsilon_{25 \text{ K}}$ for Nd_{1-x}Eu_xCrTiO₅. As clearly shown in





FIG. 2. (Color online) Relative change in the dielectric constant from 25 K ($\Delta \varepsilon / \varepsilon_{25 \text{ K}}$) plotted as a function of temperature for (a) NdCr_{1-y}Al_yTiO₅ and (b) Nd_{1-x}Eu_xCrTiO₅. The absolute values of the dielectric constant at 25 K ($\varepsilon_{25 \text{ K}}$) are shown in the insets.

this figure, the substituted Eu ions rapidly suppress the peak height and lowers the peak temperature. These results strongly suggest that the Nd ions are as essential as the Cr ions to the magnetoelectric response in NdCrTiO₅. This is highly incompatible with the previous belief that only the Cr ions are responsible for the magnetic transition and thereby the magnetoelectric effect just below T_N . The x = 1 sample shows no dielectric anomaly above 2 K, which unambiguously proves that the Nd moments are indispensable to the magnetoelectric order. We should note here that the magnitude of ε does not vary within experimental uncertainties as shown in the inset of Fig. 2(b), and the Eu substitution mainly affects the magnetoelectric part of ε . Again, the x-ray diffraction patterns in Fig. 1(b) smoothly evolve from x = 0 to 1.0, and change in the crystal structure plays a secondary role in the decrease in the dielectric anomaly.

Figures 3(a) and 3(b) show the polarization *P* of NdCr_{1-y}Al_yTiO₅ and Nd_{1-x}Eu_xCrTiO₅, respectively, measured at 7 T. The data for x = 0 well reproduce the previously reported values. The polarization shows up below T_N and reaches 14 μ C/m² around 8 K. The temperature at which dP/dT takes a dip roughly equals the peak temperature in Fig. 2(a). The low-temperature polarization dramatically suppresses with the Al substitution as well, and scales with the peak temperature in Fig. 2(a). The relation of $P \propto T_N$ implies that the order parameter is rather homogeneously suppressed, and a mean-field approximation seems valid in the Al-substituted samples, although the transition becomes broad with increasing y. In contrast, the polarization of Nd_{0.5}Eu_{0.5}CrTiO₅ shown in Fig. 3(b) is negligibly small, but

FIG. 3. (Color online) Temperature dependence of the polarization *P* for (a) $NdCr_{1-y}Al_yTiO_5$ and (b) $Nd_{1-x}Eu_xCrTiO_5$.

the peak temperature remains as high as 16 K. We should note that the x = 0.05 sample has the same T_N but a smaller P in comparison with x = 0. These results suggest that the Eu substitution retains the magnetic order, but modifies the magnetic structure to diminish the polarization.

Thus far we have shown that the Nd and Cr ions are indispensable to the magnetoelectric response. However, ferroelectric response does not directly indicate magnetic order; many antiferromagnets are not ferroelectric. Accordingly there is a possibility that the Eu and Al substitutions retain the magnetic order but lose the ferroelectricity. In order to examine such possibilities, we carefully measured the susceptibility near the peak temperature. Figure 4(a) shows the temperature dependence of the magnetic susceptibility in 0.1 T for the prepared samples. NdCrTiO₅ exhibits a subtle slope change around 21 K, which is assigned to the antiferromagnetic temperature in the preceding work [13]. In order to clearly see the slope change, we plot the temperature derivative of the susceptibility in Figs. 4(b) and 4(c), in which the slope change is converted to a discontinuous step. We clearly define the transition temperature in the midpoint of the step and indicate by the arrows in Fig. 4(a). The transition temperatures thus obtained decrease with increasing x and y, which is in excellent agreement with the peak temperatures in Fig. 2. Since an Eu³⁺ ion has a nonmagnetic ground state of J = 0, the present result shows that the Cr³⁺ ions order with the help of magnetic moments in the rare-earth ions. One may notice that the steps in $d\chi/dT$ are sharper in Fig. 4(c) than in Fig. 4(b), which corresponds well with the width of the dielectric peak in Fig. 2. The steps in Fig. 4(c) are almost independent of x, which suggests that the volume fraction of the magnetic order is essentially unchanged with x.



FIG. 4. (Color online) (a) The magnetic susceptibility χ for the prepared samples at 0.1 T. Arrows indicate the magnetic transition temperature. The temperature derivative of the susceptibility for (b) NdCr_{1-y}Al_yTiO₅ and (c) Nd_{1-x}Eu_xCrTiO₅. For clarity, $d\chi/dT$ data are arbitrarily shifted along the vertical axis.

One can see a subtle anomaly in $d\chi/dT$ for x = 1 around 10 K. In order to examine whether this is intrinsic or not, we measured the specific heat of EuCrTiO₅ together with NdCrTiO₅. Figure 5 shows the specific heat of the two compounds plotted as a function of temperature. The data for NdCrTiO₅ quantitatively agree with those in the preceding work [13]. The specific heat of EuTiCrO₅ shows a much smaller value below 20 K, implying that the Eu ions do not carry entropy because of the J = 0 state. One can see a small but clear peak at 10 K, which coincides with the anomaly in $d\chi/dT$. This is most likely a magnetic order of Cr³⁺ ions. The entropy change across the transition temperature is tiny, and this subtle change indicates that most of the entropy on the Cr³⁺



FIG. 5. (Color online) Specific heat of NdCrTiO₅ and EuCrTiO₅ plotted as a function of temperature. The arrows indicates phase transition temperatures.



FIG. 6. (Color online) (a) The transition temperature for $Nd_{1-x}Eu_xCrTiO_5$ and $NdCr_{1-y}Al_yTiO_5$ plotted as functions of *x* and *y*. The filled circles and open triangles represent the peak temperatures determined from the dielectric constant at 7 T and the magnetic transition temperatures determined from the susceptibility at 0.1 T. The data for x = 1 (EuCrTiO₅) is taken from the anomaly in the susceptibility and the peak in the specific heat. The broken and solid lines are the prediction from conventional dilution effect for the Al-doped and Eu-doped cases, respectively. (b) The polarization *P* at 8 K plotted as a function of *x* and *y*. The broken line is the prediction from conventional dilution effect.

moments is already lost at much higher temperatures where they start to show a short range antiferromagnetic correlation along the c axis.

Figure 6 summarizes the substitution effects in NdCrTiO₅. In Fig. 6(a), the characteristic temperatures are plotted, where the filled circles and open triangles represent the peak temperatures determined from the dielectric constant and the transition temperatures determined from the susceptibility. The two sets of temperatures are in excellent agreement for all the samples, and this result evidences that there is only one transition temperature in this class of oxides. The transition temperature obtained from the susceptibility measured in 0.1 T is slightly higher than that from the dielectric constant measured in 7 T, which suggests that a high external field tends to suppress the antiferromagnetic order. We find that the transition temperatures decrease linearly with x and y. As was already discussed above, the slope for x is smaller than the slope for dilution effect shown by the broken line. As for the Eu-substituted samples, the data of 10 K for x = 1 suggest that dilution effect (the solid line) well agrees with the observed transition temperature. Figure 6(b) shows the polarization at 8 K plotted as a function of x and y. The decrease in the polarization is much more remarkable than is predicted by the simple dilution effect.



FIG. 7. (Color online) Arrangement of the spins and the electric dipoles in the Cr-Nd-Cr layer in the *ab* plane in NdCrTiO₅. (a) Spins (left) and electric dipoles (right) for zero magnetic field. The spin on the Cr³⁺ ion \vec{S}_{Cr} points perpendicular to the sheet, and the spin on the Nd³⁺ ion \vec{S}_{Nd} aligns along the *b* axis. The electric dipoles are calculated from $(\vec{S}_{Nd} \times \vec{S}_{Cr}) \times (\vec{R}_{Nd} - \vec{R}_{Cr})$. The arrow representing the electric dipole is plotted on the Nd-Cr bond. (b) Spins (left) and electric dipoles (right) for the magnetic field parallel to the *a* axis.

Now let us discuss a possible mechanism of the magnetic ordering in the title compound. As emphasized previously, the most remarkable feature of this oxide is that the Cr and Nd moments simultaneously align below the transition temperature, which strongly suggests existence of strong d-f interaction. One can notice this interaction by looking at the crystal structure carefully. The CrO₆ chains are far separated by the nonmagnetic TiO₄. Consequently, the Cr moments cannot develop coherence along the interchain direction at such a high temperature of 21 K without the help of magnetic rare-earth ions.

Next we will argue whether NdCrTiO₅ is magnetoelectric or multiferroic. Linear magnetoelectricity is most likely, because it is allowed from the magnetic point symmetry of (*mmm'*) [11]. Even in this case, the present study has revealed that it does not only come from the Cr^{3+} moments, but also from the Nd³⁺ moments. Although the symmetry of the magnetic order does not allow a ferroelectric order, it may cause an antiferrotype dipole order, i.e., another type of coexisting magnetic and dielectric orders.

Figure 7 shows a model of the electric dipoles predicted from the noncollinear arrangement of Nd³⁺ and Cr³⁺ spins. We focus on the magnetic structure of the three layers of CrO₆-Nd- CrO_6 in Fig. 1(a), where the Nd layer is sandwiched by the two Cr layers. In the absence of magnetic field, the Nd³⁺ spin \vec{S}_{Nd} aligns by canting at 12 deg from the b axis, but we approximate that they align along the b axis just for simplicity. The Cr spin \vec{S}_{Cr} aligns along the *c* axis, and the spin moment points perpendicular to the sheet. Then the electric dipole moment is calculated through $(\hat{S}_{Nd} \times \hat{S}_{Cr}) \times (\hat{R}_{Nd} - \hat{R}_{Cr})$ [8,9], which orders antiparallel to each other. Thus the net polarization is zero for H = 0. In contrast, in the presence of magnetic field parallel to the *a* axis, the spins cant to the magnetic field through the Zeeman effect. Concomitantly the electric dipoles are twisted, as shown in Fig. 7(b), and a finite net polarization appears. To examine this model, the anisotropy measurement using single crystalline samples is indispensable.

Finally we will make some comments related to the present work. (i) Our preliminary work on neutron diffraction reveals that the Nd and Cr moments follow the same temperature dependence below 16 K. This further consolidates our main claim of the present paper. (ii) We have found that GdCrTiO₅ shows a magnetodielectric anomaly around 10 K. Since Gd³⁺ has a large magnetic moment, the magnetism in the rare-earth site is a key in this class of oxides. (iii) Ti-site substitution plays a secondary role. We find that the solubility of Sn for the Ti site is only 5%, and within this solubility limit, the Ti substitution effect can be simply understood as conventional dilution effect.

IV. SUMMARY

In summary, we have prepared sets of polycrystalline samples of $Nd_{1-x}Eu_xCrTiO_5$ and $NdCr_{1-y}Al_yTiO_5$, and we have measured and analyzed the dielectric constant polarization and magnetic susceptibility. We find that both the Eu and Al substitutions suppress the magnetic transition, and that Nd and Cr moments are indispensable to the magnetic ordering. This naturally indicates a finite *d*-*f* interaction which is responsible for the noncollinear magnetic structure reported in this oxide.

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- E. Bertaut and M. Mercier, Mater. Res. Bull. 6, 907 (1971).
- [2] M. Fiebig, J. Phys. D 38, R123 (2005).
- [3] W. Eerenstein, N. D. Mathur, and J. F. Scott, Nature (London) 442, 759 (2006).
- [4] D. N. Astrov, Sov. Phys.-JETP 13, 729 (1961).

- [5] V. J. Folen, G. T. Rado, and E. W. Stalder, Phys. Rev. Lett. 6, 607 (1961).
- [6] G. T. Rado, Phys. Rev. Lett. 6, 609 (1961).
- [7] G. T. Rado and V. J. Folen, Phys. Rev. Lett. 7, 310 (1961).
- [8] T. Kimura, Ann. Rev. Mater. Res. 37, 387 (2007).

PHYSICAL REVIEW B 91, 144403 (2015)

- [9] S.-W. Cheong and M. Mostovoy, Nat. Mater. 6, 13 (2007).
- [10] J. F. Scott and R. Blinc, J. Phys.: Condens. Matter 23, 113202 (2011).
- [11] G. Buisson, J. Phys. Chem. Solids **31**, 1171 (1970).
- [12] M. Greenblatt, R. Hornreich, and B. Sharon, J. Solid State Chem. 10, 371 (1974).
- [13] J. Hwang, E. S. Choi, H. D. Zhou, J. Lu, and P. Schlottmann, Phys. Rev. B 85, 024415 (2012).
- [14] M. M. Vopson, Solid State Commun. 152, 2067 (2012).
- [15] J. Saha, G. Sharma, and S. Patnaik, J. Mag. Mag. Mater. 360, 34 (2014).
- [16] K. Momma and F. Izumi, J. Appl. Crystal. 44, 1272 (2011).