Spin-Driven Ferroelectricity in Triangular Lattice Antiferromagnets $A\mathrm{CrO}_2$ (A = Cu, Ag, Li, or Na)

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The correlation between the dielectric and magnetic properties is investigated on the triangular-lattice antiferromagnets $A\mathrm{CrO}_2$ (A = Cu, Ag, Li, or Na) with a 120-degree spiral structure. For the A = Cu and Ag compounds with a delafossite structure, the ferroelectric polarization emerges with a spiral-spin order, implying strong coupling between ferroelectricity and the spiral-spin structure. For the A = Li and Na compounds with an ordered rock salt structure, on the other hand, no spontaneous polarization is discerned, while the clear anomaly in the dielectric constant can be observed upon the transition to the spiral-spin ordered state. This feature can be ascribed to the possible antiferroelectric state induced by the alternate stacking of the Cr-spin sheet with opposite vector spin chirality.

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The correlation between magnetic and dielectric properties has been pursued for a long time in condensed matter physics [1]. Toward the enhanced magneto-electric coupling, the materials, termed multiferroics, with both dielectric and magnetic order have been extensively explored [2], yet the attempts were not fully successful: Even with the multiferroic order, the compounds occasionally undergo magnetic and dielectric phase transitions at much different temperatures, resulting in the merely weak coupling between the both orders. In the family of helimagnetic ferroelectrics as recently discovered, however, the ferroelectricity emerges concomitantly with the magnetic order, and hence the magnetic (electric) control of the dielectric (magnetic) properties becomes possible [3]. These multiferroics commonly show the magnetic frustration, which is a source of complex spin orders such as the helimagnetic structure.

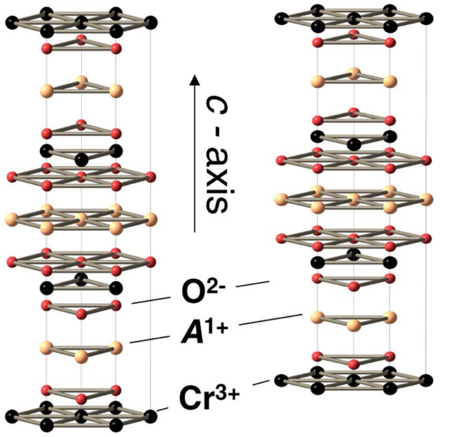
As for the mechanism of coupling between the ferroelectricity and the magnetic order, a successful scheme has recently been given for the case of the transverse spiral-spin order, in which the spin-spiral plane contains the propagation vector of spin modulation. According to the spin-current model or the inverse Dzyaloshinskii-Moriya (D-M) model [4], the electric polarization $\mathbf{P}_{ij}$ produced between the mutually canted magnetic moments ($\mathbf{S}_i$ and $\mathbf{S}_j$) on the neighboring sites i and j is given as

$$\mathbf{P}_{ij} = A_0 \mathbf{e}_{ij} \times (\mathbf{S}_i \times \mathbf{S}_j). \tag{1}$$

Here, $\mathbf{e}_{ij}$ is the unit vector along the direction from the site i to j, and A_0 a coupling constant related to the spin-orbit and spin-exchange interactions. This model can explain, at least qualitatively, the ferroelectricity which is concomitant with the spiral-spin order, for example, in $R\mathrm{MnO}_3$ (R = Tb and Dy) [5,6], $\mathrm{Ni_3V_2O_8}$ [7], $\mathrm{CoCr_2O_4}$ [8], $\mathrm{LiCu_2O_2}$ [9,10], etc.

In contrast to the above cases, still left unclear is the microscopic origin of magneto-electric coupling for triangular-lattice antiferromagnet, the most typical example of geometrically frustrated spin systems. With classical Heisenberg spins, this system generally favors the 120° spiral-spin structure at the ground state. Depending on the sign of anisotropy term $\mathcal{H}' = D\sum(S_i^z)^2$, the spin spiral is confined in the plane parallel ($D > 0$: easy-plane type) or perpendicular ($D < 0$: easy-axis type) to the triangular-lattice plane [11]. In neither case can the spin-current model predict ferroelectricity. Nevertheless, the appearance of polarization in the 120° magnetic phase has recently been reported for $\mathrm{RbFe(MoO_4)_2}$ with the easy-plane anisotropy [12]. The symmetry analysis allows the presence of polarization, yet leaving its microscopic origin still unclear.

$A\mathrm{CrO}_2$ (A = Cu, Ag, Li, or Na) as investigated in this study is viewed as another prototype of triangular-lattice antiferromagnets. Each element forms the triangular lattice and stacks along the c-axis in the sequence Cr-O-A-O-Cr. $\mathrm{CuCrO_2}$ and $\mathrm{AgCrO_2}$ crystallize into the delafossite structure [Fig. 1(a)], while $\mathrm{LiCrO_2}$ and $\mathrm{NaCrO_2}$ into the ordered rock salt structure [Fig. 1(b)]. Both belong to the space group $R\bar{3}m$, and only a difference is in the stacking pattern of O-A-O layers; the delafossite structure has the straight stacking, while the ordered rock salt structure does the zigzag one. In both cases, the rhombohedral ($ABCABC\ldots$) stacking is realized among Cr layers, although the distance between them is much shorter in the latter case [13]. The magnetic properties are dominated by Cr^{3+} ion with $S = 3/2$ spin, which is surrounded by the octahedron of O^{2-}. Because of the geometrical frustration of the antiferromagnetic interaction, the 120° spin structure is realized at the ground state. Former neutron diffraction studies have shown that these systems have the easy-axis anisotropy along the c-axis [14,15]. In this Letter, we



(a) Delafossite (b) Ordered Rock Salt

FIG. 1 (color online). Crystal structure of $A\mathrm{CrO_2}$: (a) delafossite structure (A = Cu or Ag) and (b) ordered rock salt structure (A = Li or Na).

report the discovery of the ferroelectricity and possible antiferroelectricity driven by the 120° spin structure with easy-axis anisotropy. Considering also the case for $\mathrm{RbFe(MoO_4)_2}$ with the easy-plane anisotropy [12], we can predict that a broad range of trigonal materials with the 120° spin structure can be multiferroic, irrespective of their magnetic anisotropy.

Powder specimen of $\mathrm{CuCrO_2}$, $\mathrm{AgCrO_2}$, $\mathrm{LiCrO_2}$, and $\mathrm{NaCrO_2}$ were prepared by solid state reaction from the stoichiometric mixture of CuO, Ag, $\mathrm{Li_2CO_3}$, $\mathrm{Na_2CO_3}$, and $\mathrm{Cr_2O_3}$. They were heated at 1000 °C for 24 hours in air, at 900 °C for 48 hours in $\mathrm{O_2}$, at 1200 °C for 24 hours in air, and at 1100 °C for 30 hours in Ar, respectively. Powder x-ray diffraction measurements showed no detectable impurity, except a trace of Ag in $\mathrm{AgCrO_2}$ specimen and of $\mathrm{Cr_2O_3}$ in $\mathrm{NaCrO_2}$ specimen [16]. They were pressed into rods, sintered with additional heating, and cut into thin plates. As the electrodes, silver paste was painted on the widest end faces. Dielectric constant was measured at 100 kHz using an LCR meter. To deduce the electric polarization, we measured the pyroelectric current with a constant rate of temperature sweep (2 K/ min~20 K/ min) or magnetic field sweep (100 Oe/ sec) and integrated it with time. To align the polarization in the specimen, the poling electric field was applied in the cooling process and removed just before the measurements of pyroelectric current. Heat capacity was measured by the thermal relaxation method. Magnetization was measured with a SQUID magnetometer.

Figures 2(a)–2(c) show the temperature dependence of magnetic susceptibility, dielectric constant, and electric polarization for $\mathrm{CuCrO_2}$. The susceptibility shows a clear kink at T_N ~24 K. A former powder neutron diffraction study suggests the 120° spin structure with spiral plane including the c-axis below T_N [14]. At T_N, the dielectric constant also shows a sharp anomaly, and the spontaneous electric polarization begins to develop. With the opposite poling electric field, the polarization direction can be reversed. These indicate the ferroelectric nature of the ground state, coupled with the spiral magnetic order.

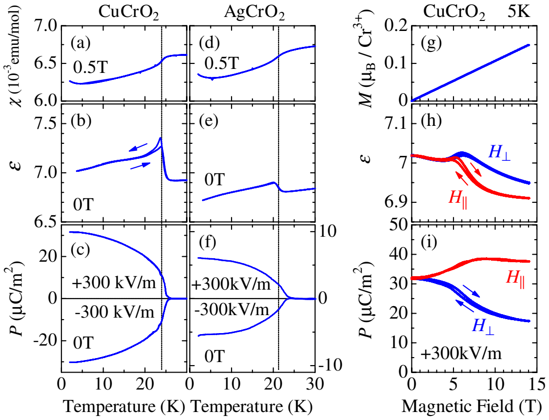


FIG. 2 (color online). Temperature dependence of magnetic susceptibility χ, dielectric constant ε, and electric polarization P for (a)–(c) $\mathrm{CuCrO_2}$ and (d)–(f) $\mathrm{AgCrO_2}$ with delafossite structure. (g)–(i) Magnetic field dependence of magnetization M, dielectric constant, and electric polarization for $\mathrm{CuCrO_2}$. For (i), electric poling was performed at 0T. In (c), (f), and (i), the magnitude and sign of poling electric field are also indicated. $H_\parallel$ and $H_\perp$ indicate the magnetic field parallel and perpendicular to the direction of electric field.

Figure 3(a) indicates the symmetry elements in the $A\mathrm{CrO_2}$ system with space group $R\bar{3}m$. Because of the ambiguity of spin structure, hereafter we examine two types of 120° magnetic order with spin spiral either in the (110) plane [Fig. 3(b)] or in the (1$\bar{1}$0) plane [Fig. 3(c)]. The former case can be considered as the proper screw magnetic structure, whose spins rotate in the plane perpendicular to the modulation vector. Recently, Arima theoretically investigated this situation with the delafossite crystal structure in the light of the possible spin-driven ferroelectricity [17]. In the following, we follow his view in the present specific triangular-lattice system. With the (110) spin-spiral plane, only a $2'$ symmetry element, i.e., the twofold rotation axis along the [110] direction with time reversal operation, remains unbroken. Thus, the symmetry allows only $\mathbf{P}$ perpendicular to the spin-spiral plane (along the [110] direction). As for the microscopic origin of $\mathbf{P}$, any 120° spin structure gives the same $\mathbf{S}_i \cdot \mathbf{S}_j$ for all bonds in the regular triangular lattice, and hence the conventional magnetostriction cannot cause the net polarization with centrosymmetric crystal structure. Another candidate, the spin-current model or the inverse D-M mechanism, also fails to explain the emergence of ferroelectricity. Recently, Jia *et al.* pointed out that the spin-orbit interaction brings about some modification on the d-p hybridization between ligand and 3d magnetic ions, which can cause the polarization along the bond direction [18,19]. Although this term oscillates in the crystal and usually cannot cause the macroscopic polarization, some components along the modulation vector are proven not to be canceled out in

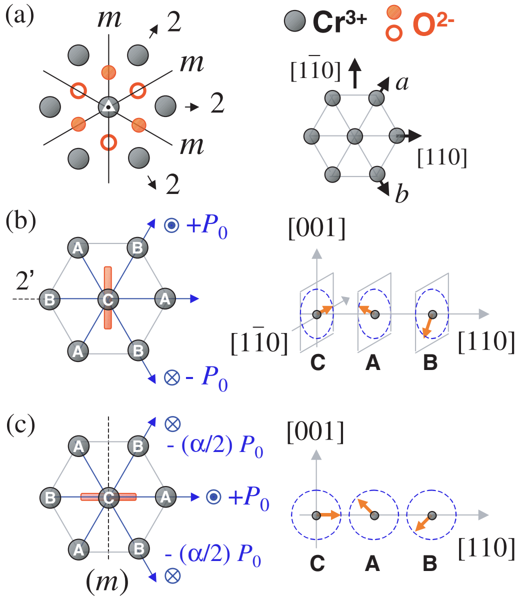


FIG. 3 (color online). (a) Symmetry elements in the ACrO$_2$ system with space group $R\bar{3}m$: twofold rotation axis (2), reflection mirror (m), and threefold rotation axis along the c-axis with inversion center (triangle with small circle). O^{2-} site above (below) the Cr^{3+} layer is indicated as closed (open) circle. (b), (c) Symmetry elements compatible with the 120° spin structure with (b) (110) spiral plane or (c) (1$\bar{1}$0) spiral plane. The thick bars (orange online, left panel) indicate the spin-spiral plane. Electric polarization expected from the spin-current model along each chain is also indicated, such as $\pm P_0$ and $-(\alpha/2)P_0$ (see text).

the delafossite system with the proper screw spin structure [17]. In CuFe$_{1-x}$Al$_x$O$_2$ with the same crystal structure and the proper screw spin configuration (with the incommensurate wave number, $q \sim 0.22$), the emergence of the polarization along the modulation vector has recently been confirmed [20–22]. The same mechanism of the polarization is also anticipated in CuCrO$_2$. In the case of (1$\bar{1}$0) spiral plane [Fig. 3(c)], on the other hand, only a reflection mirror can survive or disappear depending on the spin direction. Therefore, from the symmetry, polarization is allowed in any direction. The spin-current model predicts the polarization $(1-\alpha)P_0$ along the c-axis, where α represents the difference of coupling constant A_0 in Eq. (1) between the spin chains along [110] and [100] (or [010]). Given the isotropic coupling constant ($\alpha = 1$), the polarization should vanish, and hence other microscopic origin would be required. Note that the symmetry analysis in Figs. 3(b) and 3(c) is valid even under the lattice distortion associated with the magnetic order as observed in CuFe$_{1-x}$Al$_x$O$_2$, since the magnetostriction always reflects the symmetry of magnetic structure. The similar argument as above is applicable for other centrosymmetric trigonal systems.

In Figs. 2(g)–2(i), magnetic field (H) dependence of magnetization, dielectric constant, and electric polarization for CuCrO$_2$ are indicated. The magnetization increases linearly with H up to 14 T. For dielectric properties, we performed measurements both under magnetic field parallel ($H_\parallel$) or perpendicular ($H_\perp$) to the direction of electric field. After the poling process at 0 T, electric polarization is enhanced with $H_\parallel$ and suppressed with $H_\perp$. The **P** value recovers when magnetic field is removed. In dielectric constant, corresponding anisotropic behavior between $H_\parallel$ and $H_\perp$ is observed above 6 T. These large magneto-electric effects ensure the spin-driven ferroelectricity in this system. The threefold symmetry allows the existence of three equivalent magnetic domains. The large H-dependence of dielectric properties may be caused by the rotation and/or the volume change of the domains.

The isostructural material AgCrO$_2$ also shows the similar ferroelectricity driven by the magnetic order. Figures 2(d)–2(f) indicate the temperature profiles of the same physical quantities for AgCrO$_2$. The kink in magnetic susceptibility is observed at $T_N \sim 21$ K. Again, the anomaly in dielectric constant and the emergence of the ferroelectric polarization **P** are observed at T_N although the **P** value is reduced as compared with CuCrO$_2$. A former powder neutron diffraction study has proposed a slightly modulated 120° spin structure for the magnetic ground state below T_N, and the shorter correlation length and the larger spin fluctuation than in CuCrO$_2$ have been reported [23]. Although the detail of magnetic structure, such as the direction of spin-spiral plane, has not been determined yet, the smaller spontaneous polarization value in AgCrO$_2$ ($\sim$1/5 of that for CuCrO$_2$) is consistent with these features. Since dielectric constant ε reflects the fluctuation of polarization (ΔP) in the form of $\varepsilon - \varepsilon_\infty \propto \langle|\Delta P|^2\rangle/k_B T$, the weaker anomaly in ε must come from the smaller polarization.

In addition to the above delafossite crystals, we have also investigated LiCrO$_2$ and NaCrO$_2$ composed of the similar CrO$_2$ sheets but with ordered rock salt structure [Fig. 1(b)]. The magnetic structure of LiCrO$_2$ has been investigated by the polarized neutron diffraction study on the single crystal [15], and below T_N ~60 K [24], the proper screw type 120° spin structure [Fig. 3(b)] was reported to give the best fit. For NaCrO$_2$, only a powder neutron diffraction study was performed [25] and $T_N \sim$ 40 K has been reported [26]. Figures 4(a)–4(f) indicate the temperature profiles of heat capacity, dielectric constant, and electric polarization for LiCrO$_2$ and NaCrO$_2$. Although the anomaly in magnetic susceptibility is not clear [26], the heat capacity manifests the magnetic phase transitions, as seen in Figs. 4(a) and 4(d), in accord with the former neutron diffraction studies. At T_N, dielectric constant shows a strong cusplike anomaly as in the two compounds with delafossite structure. Since dielectric constant is denoted as the fluctuation of electric polarization, the dielectric peak at T_N means the generation of the local electric dipole moments around the magnetic order temperature. This confirms the local correlation between the electric dipole and the magnetic structure also in this

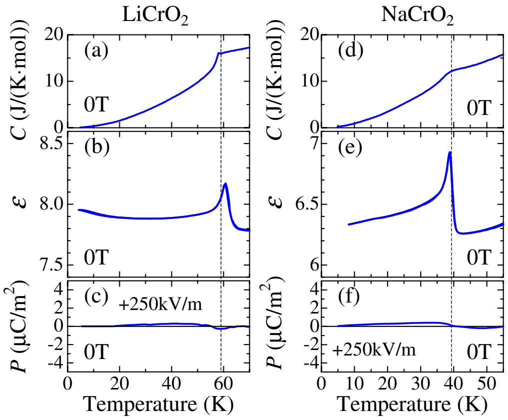


FIG. 4 (color online). Temperature profiles of specific heat capacity C, dielectric constant ε, and electric polarization P for (a)–(c) LiCrO$_2$ and (d)–(f) NaCrO$_2$ with ordered rock salt structure.

system. However, unlike the case for delafossites of CuCrO$_2$ and AgCrO$_2$, the macroscopic polarization can hardly be observed for LiCrO$_2$ or NaCrO$_2$. One of the possible interpretations for the absence of $\mathbf{P}$ but the presence of sharp ε-peak is the antiferroelectric order of electric dipoles. When ferroelectricity is induced by the spiral-spin structure, the symmetry requires coupling between spin helicity (vector spin chirality as represented $\mathbf{S}_i \times \mathbf{S}_j$) and the sign of polarization. In fact, this relationship is confirmed by the recent polarized neutron scattering studies on several multiferroics (such as TbMnO$_3$ [27], CuFe$_{1-x}$Al$_x$O$_2$ [22], and LiCu$_2$O$_2$ [10]). For LiCrO$_2$, on the basis of the two magnetic modulation vectors $\mathbf{q}_1 = (1/3, 1/3, 0)$ and $\mathbf{q}_2 = (-2/3, 1/3, 1/2)$, alternate stacking of Cr^{3+} layer with the opposite vector spin chirality was suggested [15]. Considering the spin-polarization coupling in CuCrO$_2$ and AgCrO$_2$, such an antiferro-chiral order in LiCrO$_2$ is naturally expected to induce the antiferroelectric state. For CuCrO$_2$ and AgCrO$_2$, by contrast, the $\mathbf{q}_2$ peaks, which characterize the alternate stacking of opposite chirality layers, have not been observed in neutron diffraction profiles [14,23] in accord with the emergence of ferroelectricity in these compounds. At this stage, the origin of interaction that favors such antiferro-chiral spin order is an open question since the interlayer magnetic interaction should always favor the ferroic coupling of the vector spin chirality. The antiferroic coupling may possibly be ascribed to the interlayer electrostatic and/or spin-lattice interaction. For example, the intralayer polarization is governed by the spin chirality, yet could cause the lattice distortion that is dependent on the stacking form of the CrO$_2$ planes. The different stacking pattern of O-A-O layers and the shorter distance between Cr^{3+} layers in the ordered rock salt structure, which is anticipated to cause stronger interplane interaction and higher T_{N} [13], may be related to the antiferroic order of spin chirality.

In summary, we have investigated the correlation between the dielectric and magnetic properties of triangular-lattice antiferromagnet ACrO$_2$ showing the 120° spin structure with the easy-axis anisotropy. For the $A =$ Cu and Ag compounds with delafossite structure, appearance of electric polarization is concurrent with the magnetic order, implying the strong magneto-electric coupling in this system. For the $A =$ Li and Na compounds with ordered rock salt structure, by contrast, no polarization but only anomalies in dielectric constant were observed at T_{N}. Considering the results of the former neutron scattering study, this can be interpreted as the antiferroelectric state due to the alternate stacking of magnetic layers with opposite vector spin chirality. Combine the present results with the recent report for RbFe(MoO$_4$)$_2$ with the easy-plane anisotropy [12], a broad range of trigonal materials with the 120° spin structure can be multiferroic, irrespective of their magnetic anisotropy.

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