Spin Handedness of Conical-spiral Magnetic Order in Multiferroic $CoCr_2O_4$

The coexistence of magnetism and ferroelectricity with cross coupling, termed multiferroicity, rarely occurs. The discovery of gigantic magnetoelectric coupling in frustrated magnets has revived interest in their multiferroic behavior. We have studied the magnetic ordering in multiferroic $CoCr_2O_4$, which has ferrimagnetic conical-spiral magnetic order, by Co L_3-edge resonant magnetic X-ray scattering and discussed the evolution of the wave vector of magnetic ordering about the temperatures of multiferroic transitions, i.e., spiral magnetic transition temperature T_S (27 K) and magnetic lock-in transition temperature T_L (14 K). We proffer scattering evidence of multiferroicity and a pathway for understanding the intricate coupling between magnetism and ferroelectricity in magnets with spin spirals, the presence of multiple spiral sub-lattices in $CoCr_2O_4$.

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Magnetism, in which the ordering of spins comes into play, has kindled great scientific minds. Ferroelectricity is an electric version of magnetism, associated with the polar arrangement of charges. Technologically, materials exhibiting the coexistence of magnetism and ferroelectricity, termed multiferroicity, are attractive because they offer the possibility of realizing mutual control of electric and magnetic properties. The key phenomenon behind such mutual control lies in the capability of what to induce either magnetization by an electric field or electric polarization by a magnetic field, known as the magnetoelectric effect, an important phenomenon that has received much attention. In recently discovered multiferroics, electric polarization **P** is spontaneously induced in certain antiferromagnetic phases. However, unlike in old examples of multiferroics, the magnetic phases involved are complicated. The inversion symmetry in these phases is broken, implying that the magnetic order couples to odd orders of **P**.

Two distinct scenarios have been proposed for understanding multiferroicity. One involves the exchange striction via the symmetric spin coupling $\mathbf{S}_n \cdot \mathbf{S}_{n+1}$, in which n is a site index. The other scenario involves spin-orbit coupling through the antisymmetric superexchange interaction $\mathbf{S}_n \times \mathbf{S}_{n+1}$ resulting from the inverse Dzyaloshinskii-Moriya interaction or spin current. To fully understand the multiferroicity of frustrated magnets, one has to examine the magnetic phase transition in the vicinity of the onset of ferroelectric transition. Neutron scattering is the best tool for revealing the magnetic structures of multiferroics. As complementary to neutron scattering, resonant L-edge X-ray scattering is sensitive to the magnetic structure of transition-metal d electrons, allowing us to obtain magnetic orders with high sensitivity.

$CoCr_2O_4$ is the first observed multiferroic compound exhibiting the coexistence of spontaneous electric polarization and magnetization. Figure 1 (a) shows the schematic view of the composition of $CoCr_2O_4$ with conical spin structures. It is a normal cubic spinel with magnetic Co^{2+} ions occupying the tetrahedral A

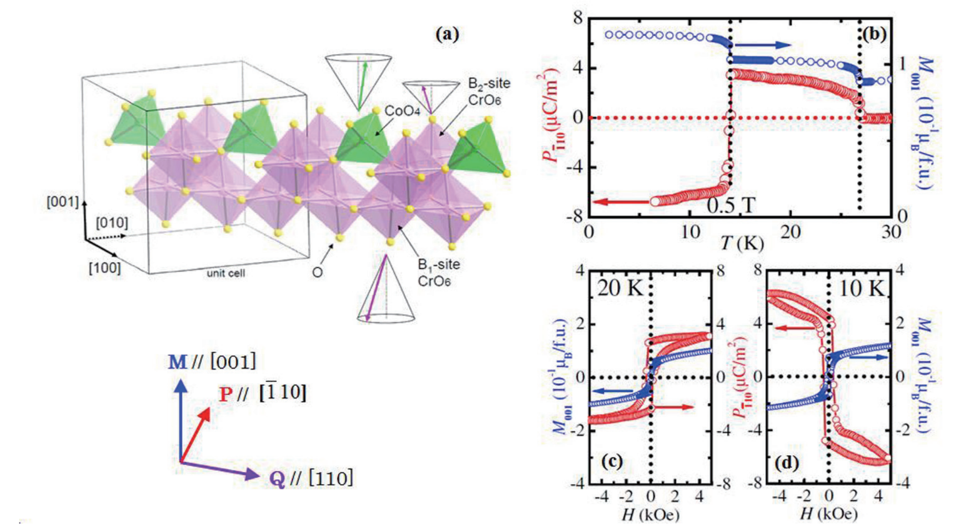

Fig. 1: (a) Schematic view of A-site CoO_4 tetrahedron and B-site CrO_6 octahedron along the [110] direction in $CoCr_2O_4$ with conical spin structures. The black box is the unit cell of the spinel structure. The magnetization easy axis is [001] and the spin spirals are in the *ab* plane with a propagation vector **Q** along [110]. The arrows on the conical surfaces indicate the spin directions on the corresponding Co and Cr sites. (b) Temperature dependence of electric polarization **P** along the [$\bar{1}$10] direction, and **M** along the [001] direction below 30 K. **P** suddenly switches its sign when cooling across 14 K without changing the signs of **M** and **Q**. (c) and (d) H dependence of **M** and **P** at 20 K and 10 K, respectively. The reversal of all **M** and **P** is achieved by H reversal. (Y. J. Choi *et al.*, Phys. Rev. Lett. **102**, 067601, 2009.)

sites and Cr^{3+} ions occupying the octahedral B sites. A ferromagnetic transition occurs at Curie temperature T_C of 93 K, followed by an antiferromagnetic (AF) transition at T_N of 26 K. Below T_C, two magnetically different Cr^{2+} ions on the B1 and B2 sites couple antiferromagnetically, and the spontaneous magnetization appears along the [001] or equivalent directions. Neutron measurements suggest a ferrimagnetic spiral for the ground state. Co^{2+} and Cr^{3+} ions in the AF phase form a transverse conical spin structure with the propagation vector **Q** along the [110] or equivalent directions, and the spin spirals are in the *ab* plane. In such domains, **Q** is in the + or – [110] direction, and the complex conical-spiral ferrimagnetic spin order of $CoCr_2O_4$ has a spontaneous magnetization **M** along the ± [001] direction. The spiral components give rise to ferroelectricity, where the spontaneous electric polarization $\mathbf{P} \propto \mathbf{e}_{12} \times (\mathbf{S}_1 \times \mathbf{S}_2)$ for a pair of spins, $\mathbf{S}_1$ and $\mathbf{S}_2$, with a relative displacement $\mathbf{e}_{12}$. Neutron results also suggest that, during cooling, the compound undergoes a lock-in transition at $T \sim 15$ K from an incommensurate conical spin state to a commensurate one.

Measurements of the T dependence of electric polarization by Y. J. Choi *et al.* revealed that the onset of ferroelectricity along the [$\bar{1}$10] direction matches the spiral magnetic ordering transition at T_S = 27 K. When the temperature is cooled across 14 K without changing the signs of **M, P** suddenly reverses its direction at 14 K as shown in Fig. 1 (b). However, when magnetic field H, and therefore **M**, is reversed at a fixed T, **P** is reversed as shown in Figs. 1 (c) and (d). This correlation between **M** and **P** was attributed to the Bloch domain wall motion involved in reversing **M**. Such an essentially uniform rotation of the spin state characterizing the wall, taking **M** to -**M**, can be seen to take a **Q** domain to a -**Q** domain. To understand the unexpected evolution of the interrelation between the polarization **P** and the magnetization **M**, one has to know the temperature dependence of the spiral wave vector **Q** in $CoCr_2O_4$.

For spin spirals $\mathbf{S}_j = \mathbf{S}^a\cos(\mathbf{Q} \cdot \mathbf{r}_j) + \mathbf{S}^b\sin(\mathbf{Q} \cdot \mathbf{r}_j)$ lying in the *ab* plane with a wave vector Q and position vectors $\mathbf{r}_j$, the scattering intensity $I(\mathbf{q}, \mathbf{Q})$ of circularly polarized X-rays can be expressed as

$$I_0[\delta(\mathbf{q} + \mathbf{Q}) + \delta(\mathbf{q} - \mathbf{Q})] + \Delta I_0[\delta(\mathbf{q} + \mathbf{Q}) - \delta(\mathbf{q} - \mathbf{Q})],$$

in which I_0 is the scattering intensity of unpolarized X-rays, and ΔI_0 is the additional intensity arising from the helicity of the X-ray. One can view the sign reversal of spin handedness as the sign reversal of **Q**; $I(\mathbf{q}, \mathbf{Q})$ differs for opposite spin handedness by $2\Delta I_0$ as a result of the interference between the scattered waves from the two components of spins, similarly to the polarized neutron results of Yamasaki *et al.* for $TbMnO_3$ (Phys. Rev. Lett. **98**, 147204, (2007)). We have directly observed this sign change of **Q** upon the reversal of magnetic field H using circularly polarized resonant magnetic X-ray scattering. With photon energy tuned at the Co L_3 edge, the scattering results reveal that there is an abrupt change in magnetic modulations at the lock-in transition temperature $T_L \sim 14$ K. Unlike earlier neutron results, two incommensurate magnetic modulations $\mathbf{Q}_+$ and $\mathbf{Q}_-$ at 15 K, which is above T_L, were observed; for T below T_L, one commensurate modulation, $\mathbf{Q}_C$=(2/3,2/3,0), and two incommensurate ones, **Q'**+ and **Q'**-, were observed, with the separation along [1$\bar{1}$0] being much larger than that between $\mathbf{Q}_+$ and $\mathbf{Q}_-$, as shown in the contour plots of Fig. 2 (a). The three vectors are approximately equal in direction; similarly, the vectors $\mathbf{Q}_+$ and $\mathbf{Q}_-$ are approximately equal. Figures 2 (b), (d), and (e) show that the scattering intensity measured with circularly polarized light indeed changes upon the flip of magnetization along [001], disclosing the expected reversal of **Q** with *H* reversal. Figure 2 (c) illustration shows conical-spiral spins above and below the 14 K transition where +**M** and -**M** correspond to +**Q** and -**Q** respectively. Interestingly, the scattering results also reveal that the sign of the ±**Q** of the largest peak at each *T* ($\mathbf{Q}_C$ and $\mathbf{Q}_-$) remains unchanged as *T* changes across T_L. The *H* dependences of the intensities of these peaks show no reverse. Thus, for single-**Q** approximation, this is evidence of the sign invariance of **Q** across T_L.

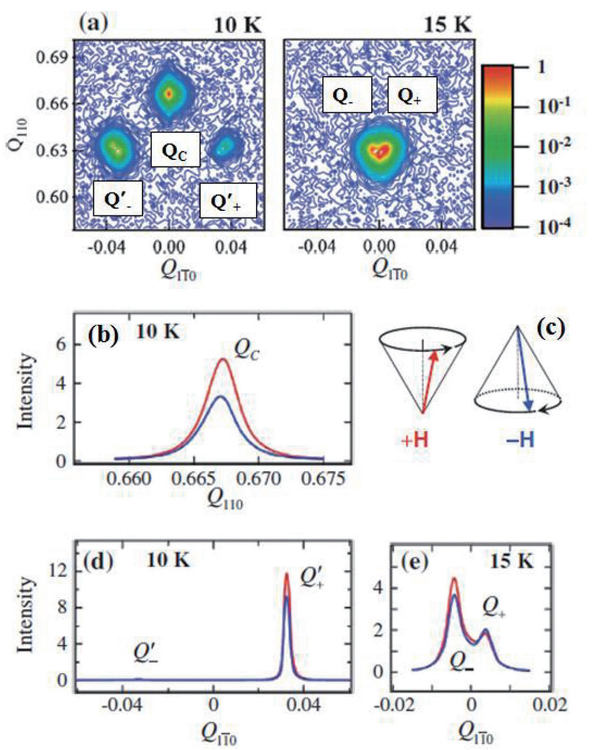

Fig. 2: (a) Contour plots of the Co-L_3 edge magnetic X-ray scattering intensity in the plane defined by Q_{110} and $Q_{1\bar{1}0}$, recorded at temperatures above and below 14 K with a photon energy of 778.4 eV. The **E** vector of incident soft X-rays was parallel to the [001] axis, i.e., the σ polarization. The contour plots are shown on a logarithmic scale with its order of magnitude expressed in rainbow color. (b), (d), and (e) Scattering intensities of **Q** scans along [110] and [1$\bar{1}$0] under +**M** (red) and –**M** (blue) with circularly polarized soft X-rays. (c) Depiction of conical spiral spins where ±**M** go with ±**Q** above and below 14 K, respectively.

Since in a multiferroic with a spiral magnetic order with only one magnetic sublattice, the switching of **P** results from a sign change of **Q**, a plausible interpretation for the switch in the sign of **P** across 14 K without sign change of **Q** and **M** is found in a "ferrielectric"-type scenario. Now, Co^{2+} has a more-than-half-filled *d* shell, while Cr^{3+} has a less-than-half-filled shell, suggesting that Co-Cr and Cr-Cr bonds have the opposite sign of spin-orbit interaction, resulting in the opposite directions of electric dipole moments, $P_{Co\text{-}Cr}$ and $P_{Cr\text{-}Cr}$ from the different bonds. Furthermore, the bond charges that give rise to the dipole moments are interionic overlap charge densities, and are therefore very sensitive to small changes in interionic distances expected to occur through the first order phase transition at T_L. Then, it is conceivable that the delicately balanced net polarization can change its sign at T_L without a change in sgn(**Q**). Directions of each contribution from $P_{Co\text{-}Cr}$ and $P_{Cr\text{-}Cr}$ do not change, but their magnitudes do.

Our results demonstrate that spontaneous electric polarization induced by the noncollinear spin order shows a discontinuous jump with a change in sign across the magnetic lock-in transition temperature (T_L = 14 K); furthermore the sign change occurs while keeping fixed the spin rotation direction, i.e., spiral handedness. This differs from the usual behaviour wherein for a simple spiral, change in the sign of **P** requires the handedness to change sign, and we give a possible mechanism for such unusual behaviour, the multiple spiral sublattices.

Experimental Station

Soft X-ray Scattering end station

Publications

1. Y. J. Choi, J. Okamoto, D. J. Huang, K. S. Chao, H. J. Lin, C. T. Chen, M. V. Veenendaal, T. A. Kaplan, and S.-W. Cheong, Phys. Rev. Lett. **102**, 067601 (2009).
2. D. J. Huang, J. Okamoto, S. W. Huang, and C. Y. Mou, J. Phys. Soc. Jpn. **79**, 011009 (2010).

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