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Crossover from incommensurate to commensurate magnetic orderings in $CoCr_2O_4$

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Abstract

The conical spin order of multiferroic $CoCr_2O_4$ has been studied by a neutron diffraction to investigate its magnetic phase transitions at temperatures below 40 K. Magnetic order of a spiral spin component with an incommensurate propagation vector of (0.63, 0.63, 0) was observed at 26 K, while at 14.5 K, the incommensurate conical spin order showed a transition into the fixed commensurate propagation vector of (2/3, 2/3, 0). In addition, two satellite peaks with propagation vectors of (0.035, 0, 0) and (0, 0.035, 0) from the commensurate vector were observed. The widths of these peaks indicate a long-range magnetic order. This new magnetic configuration below 14.5 K may lead to a new model of multiferroic behavior differing from the well-known spin–current model for magnetic ferroelectricity.

(Some figures in this article are in colour only in the electronic version)

Ferroelectricity and magnetism seem to be two competing physical phenomena and rarely coexist. Typically atomic displacements lead to ferroelectricity, whereas magnetism results from ordering of spins. Multiferroics, in which ferroelectricity and magnetic ordering coexist, are appealing for their physical interest and technological applications [1–6]. From the aspect of the technological applications, ferroelectricity and magnetic ordering are expected to be coupled with each other effectively, and one can therefore induce electrical polarization by a magnetic field or magnetization by an electric field. This is the so-called magnetoelectric effect. It may occur through the mechanisms of the magnetic or electric field induced phase transformation or by control of the multiferroic domain walls [1].

Some frustrated magnets such as $RMnO_3$ and RMn_2O_5 (R = Tb, Dy, and Ho) have been found to exhibit multiferroic features with a gigantic magnetoelectric coupling [2, 7]. In these frustrated magnets, the spontaneous electric polarization appears in certain antiferromagnetic phases with complicated spin structures. The magnetic transition temperature is higher than the ferroelectric one, suggesting that the ferroelectricity is induced by magnetic order. In addition, these magnets show anomalies in the temperature dependence of the dielectric constant. However, the underlying mechanism of the multiferroic properties in frustrated magnets remains controversial, because of the complexity of their magnetic structures. Multiferroicity has been recently observed in the spinel oxide of $CoCr_2O_4$, which exhibits net magnetization [1]. In contrast to the frustrated antiferromagnets of manganites, $CoCr_2O_4$ is the first example of a multiferroic with both a spontaneous magnetization and polarization of spin origin. The directions of the spontaneous polarization, the spin-spiral plane, and the propagation vector are perpendicular to each other in accord with the spin–current model for

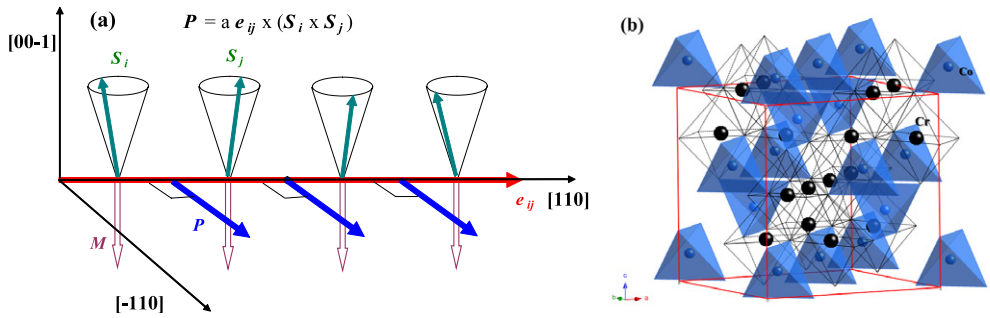

Figure 1. (a) The relations for these three vectors of the spin–current model for the magnetic ferroelectricity proposed by Katsura *et al* [7]. $\boldsymbol{P} = a\boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$, where $\boldsymbol{P}$ denotes the induced polarization, $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ are the canting spins at different i and j sites, $\boldsymbol{e}_{ij}$ is the vector connecting the two sites and a is the proportionality constant as determined by the spin exchange interaction and the spin–orbit interaction. The conical spin structure leads to the existence of the net magnetization $\boldsymbol{M}$, and explains the coexistence of the ferroelectricity and magnetization; (b) crystal structure of $CoCr_2O_4$. The Co^{2+} (blue spheres) occupy solid pyramid sites, the Cr^{3+} (black spheres) occupy open octahedral sites, and the red solid lines represent a unit cell. Oxygen atoms are left out for clarity.

magnetic ferroelectricity proposed by Katsura *et al* [8]. The relations between the three vectors of this model are presented schematically in figure 1(a) as $\boldsymbol{P} = a\boldsymbol{e}_{ij} \times (\boldsymbol{S}_i \times \boldsymbol{S}_j)$, where $\boldsymbol{P}$ denotes the induced polarization, $\boldsymbol{S}_i$ and $\boldsymbol{S}_j$ are the canting spins at different i and j sites, $\boldsymbol{e}_{ij}$ is the vector connecting the two sites, and a is the proportionality constant as determined by the spin exchange interaction and the spin–orbit interaction [1, 8]. The propagation of the spiral spins leads to spontaneous polarization with a direction perpendicular to the spiral propagation direction and the direction of spin rotation axis, while extending the spiral spins to the conical spin state, as shown in figure 1(a), the net magnetization $\boldsymbol{M}$ existing. This explains the coexistence of the ferroelectricity and magnetization.

$CoCr_2O_4$ has a spinel structure, with Co^{2+} and Cr^{3+} located in the centers of pyramids and octahedra respectively, as shown in the figure 1(b). The interactions and strong couplings between the magnetic ions on both Co^{2+} and Cr^{3+} sites lead to a complex magnetic phase diagram [9]. The system has a long-range ferromagnetic transition at $T_c \sim 93$ K. However, the reported magnetic phase diagrams at low temperatures contain some discrepancies. Menyuk *et al* found in their powder $CoCr_2O_4$ sample that the system has a short-range spiral magnetic order below 86 K, and a long-range spiral magnetic order below 31 K [10]. An incommensurate–commensurate transition of the propagation vector was observed by Plumier [11] and Funahashi *et al* [12]. More recently, Tomiyasu *et al* studied $CoCr_2O_4$ single crystals by neutron and magnetization measurements and revealed that the system develops incommensurate short-range order below 50 K. This short-range order persists to 8 K, with only a 3.1 nm correlation length at that temperature [13]. Yamasaki *et al* investigated the low temperature magnetic phase diagram of $CoCr_2O_4$ at lower temperature and found the compound undergoes a transition to a conical spin structure with an incommensurate propagation vector $Q \sim (0.63, 0.63, 0)$ at $T_N = 26$ K, and a lock-in transition occurring around 15 K [1]. In the present work, we report our studies of various magnetization states in $CoCr_2O_4$ single crystals by using a neutron diffraction method at temperatures between 40 and 5 K. An incommensurate magnetic state below 26 K, and a commensurate magnetic state with two modulated satellite peaks along the [100] and [010] directions below 14.5 K were observed.

The $CoCr_2O_4$ crystals were grown at Rutgers University, USA by using a vapor-transport method [14]. The details for crystal growth will be published elsewhere. The $CoCr_2O_4$ crystals were determined by synchrotron x-rays at NSRRC, Taiwan to be a cubic structure with lattice constant ~8.23 Å, and space group $Fd3m$. A large size crystal of $5 \times 5 \times 1$ mm^3 dimensions with the [111] orientation perpendicular to the plate was chosen for the experiments. High intensity neutron diffraction patterns were taken on the BT-9 triple-axis spectrometer at NIST, employing a pyrolytic graphite PG(002) monochromator crystal to select an incident wavelength of 2.359 Å, coarse collimation to increase the magnetic intensities, a PG filter, and a PG(002) analyzer crystal to discriminate against inelastic scattering. A closed-cycle cryostat was used to control the sample temperatures from 5 to 40 K. The sample was aligned along [110], in order to observe the variations of magnetic peaks around the $(h\ h\ 0)$ directions. The experiments were focused on the diffraction patterns around the $hkl = 220$ Bragg peak and its satellites.

Figure 2(a) shows the crossover spectra of neutron diffraction from incommensurate (higher temperatures) to commensurate (lower temperatures) along $(h\ h\ 0)$, which corresponds to the satellite reflection of the (220) reciprocal lattice point. At 26.5 K, the magnetic peak (phase-one) with incommensurate propagation vector $(\delta_1, \delta_1, 0)$, where $\delta_1 = 0.63$, was observed. This value decreases slightly within the experimental resolution when the temperature decreases. The intensity of the incommensurate peak increasing as the temperature decreases indicates the unsaturated magnetic configuration at the temperatures. The peak splits into a commensurate peak (phase-two) and two satellite peaks (not shown in the figure) below 14.5 K. The commensurate peak has the propagation vector $(2/3, 2/3, 0)$, and the propagation vectors of these two satellite peaks are $(2/3 - \delta_2, 2/3, 0)$ and $(2/3, 2/3 - \delta_2, 0)$, where $\delta_2 = 0.035$. This transition temperature 14.5 K is identical to the lock-in transition

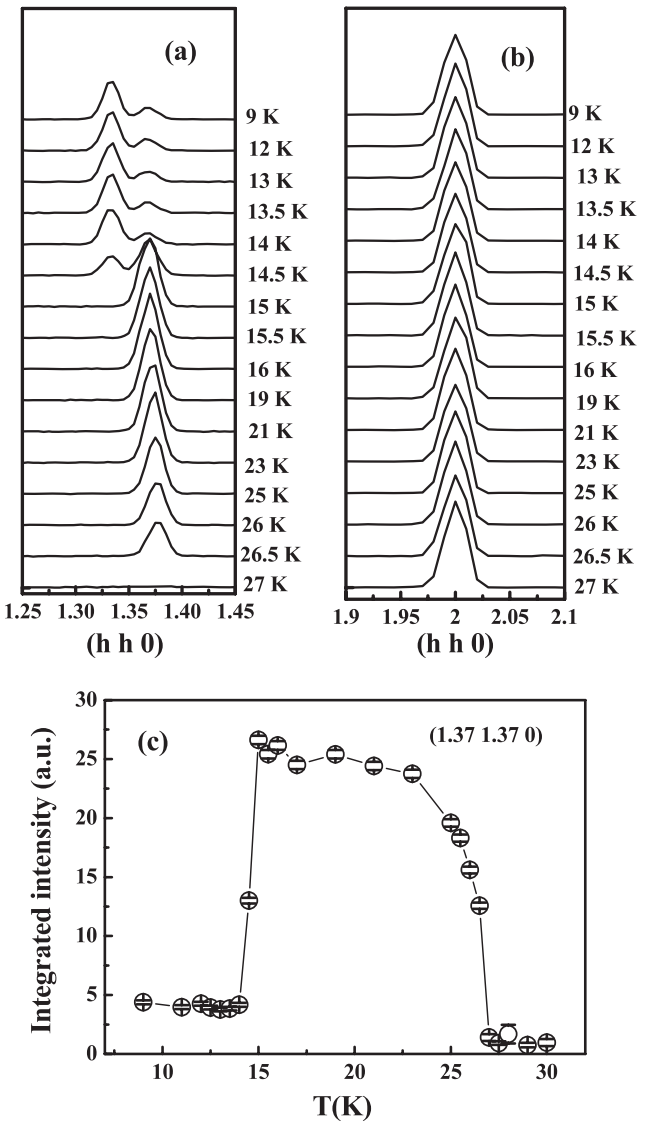

Figure 2. (a) Neutron diffraction spectra showing the crossover from incommensurate (higher temperatures) to commensurate (lower temperatures) phases. (b) Spectra of (220) from 9 K to 27 K. (c) The integrated intensities of phase one at (1.37, 1.37, 0) at different temperatures.

temperature reported by Yamasaki *et al* [1]. Choi *et al* has carried out a resonant magnetic soft x-ray scattering experiment on a $CoCr_2O_4$ crystal by tuning the photon energy at the Co L_3 edge, and exhibited that the incommensurate peak of the propagation vector $(\delta_1, \delta_1, 0)$ consists of two peaks with the Q value deviation only 0.005 from the center [15]. However, this resolution is below our experimental limits and was not observed in the present spectra. Figure 2(b) shows the spectra of the (220) Bragg peak from 9 to 27 K. The intensities and the positions of the (220) peaks in the temperature ranges are constant considering the resolution limits the experiments can achieve. The average value of the full width half maximum (FWHM) of the (220) peaks at different temperatures is $\delta Q \sim 0.0204 \pm 0.0001$ Å^{-1} ($\delta\theta \sim 0.22°$). There is no evidence in our experiments to reveal that the (220) peak is related to magnetism below 40 K. These results contrast with what had been observed by Tomiyasu's group [13], in which they claimed that the (220) peak includes intensities contribution from both nuclear and magnetic origins. The FWHM values for (1.37, 1.37, 0) peaks are 0.0203 ± 0.0002 Å^{-1} at 15 K, 0.0195 ± 0.0002 Å^{-1} at 21 K, and 0.0198 ± 0.0003 Å^{-1} at 26.5 K. The FWHM values for (1.33, 1.33, 0) peaks are 0.0180 ± 0.0003 Å^{-1} at 9 K, 0.0186 ± 0.0003 Å^{-1} at 12 K, and 0.0188 ± 0.0004 Å^{-1} at 14 K. The similar FWHM values for (220), (1.37, 1.37, 0), and (1.33, 1.33, 0) peaks in our results indicate that the magnetic correlation lengths do not change, which also does not agree with the results of Tomiyasu's work [13]. No lattice distortion was observed in our results.

The integrated intensities of phase-one at (1.37, 1.37, 0) for different temperatures are plotted, as in figure 2(c). The peak intensities were almost saturated below 23 K. Two magnetic transitions were clearly observed at 26.5 and 14.5 K. The transition occurring at 14.5 K is sharper than that of 26.5 K, which suggests that these two magnetic transitions may come from different ordering mechanisms. The magnetic ferroelectricity model proposed by Katsura in figure 1 explains our neutron diffraction results between 26 and 15 K, but the model does not explain well the results below the lock-in temperature of 14.5 K, for which the main propagation vectors are along [100] and [010] instead of [110]. The small residual intensities at the position of the (1.37, 1.37, 0) observed even down to 5 K indicates the first order transition at 14.5 K.

Figures 3(a) and (b) show the contour plots of the results around the positions of (2.67, 2.67, 0) at 5 K and 16 K respectively. At 16 K, the incommensurate peak is located at the position of (2.63, 2.63, 0); while at 5 K, a commensurate peak (2.67, 2.67, 0) together with two satellites corresponding to $(2.67 - \delta_2, 2.67, 0)$ and $(2.67, 2.67 - \delta_2, 0)$, are observed. These exhibit that the magnetic moments modulate along the (110) direction at 16 K; and the moments antiferro-coupling along the (110) direction together with the modulations along both a, and b axes at 5 K. The similar widths of these peaks suggest that those magnetic orderings are all of long range, which is different to the short-range ordering published by Tomiyasu's group [13]. The present data are not sufficient for us to solve the magnetic structures below the lock-in temperature 14.5 K.

Yamasaki's group had measured the polarization and magnetizations of $CoCr_2O_4$ well below the lock-in temperature [1]. Both polarization and magnetization curves do not change significantly at the lock-in temperature, which indicates that $CoCr_2O_4$ is still in the multiferroic state below the lock-in temperature. It suggests that another model, which is different to what has been proposed by Katsura *et al* [8] for multiferroics, may exist. Nevertheless, the recent electric polarization results reported by Choi *et al* indicate that the polarization has reversed direction at the lock-in transition temperature [15]. It is in contrast to the previous discovery by Yamasaki *et al* [1]. However, the relationship between this flipping and the change of the propagation vectors mentioned above is still unknown. Further detailed neutron diffraction experiments are necessary for figuring out all the

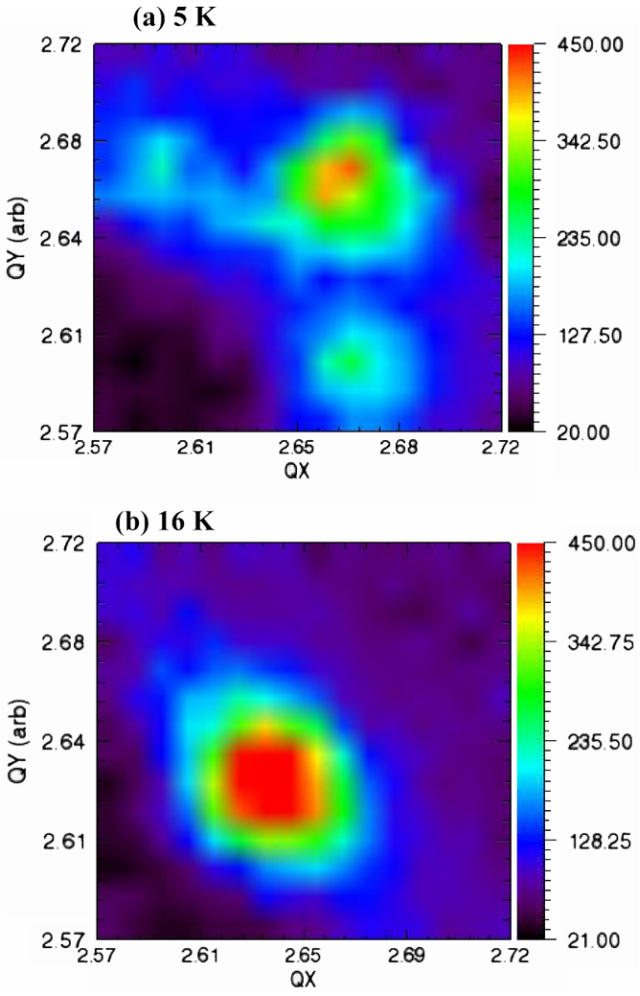

Figure 3. The contour plots of the results at (a) 5 K and (b) 16 K around the positions of (2.67, 2.67, 0).

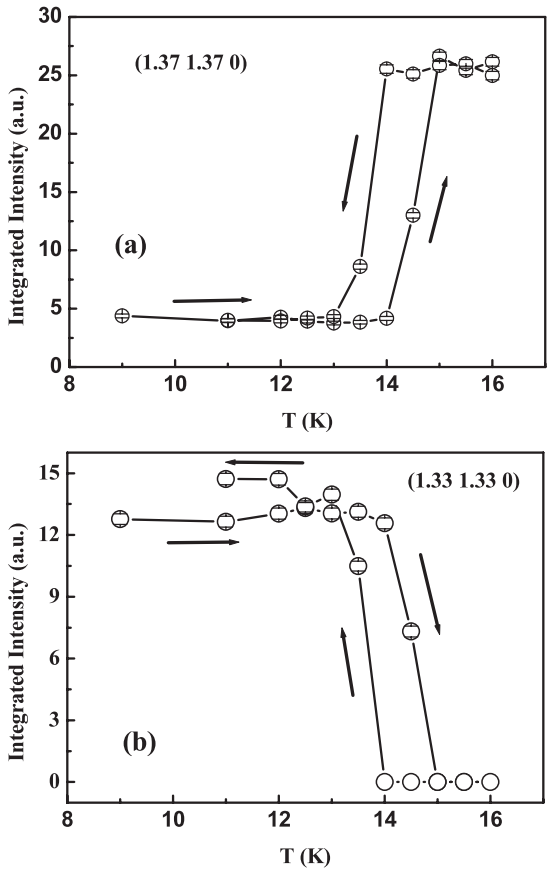

Figure 4. The hysteresis curves of the integrated peak intensities of (a) phase-one (1.37, 1.37, 0), and the (b) phase-two (1.33, 1.33, 0).

multiferroic models, and the magnetic structure below the lock-in temperature.

The hysteresis curves of the integrated peak intensities of phase-one at the (1.37, 1.37, 0) reciprocal lattice point, and phase-two at the (1.33, 1.33, 0) reciprocal lattice point are shown as figures 4(a) and (b) respectively. The integrated intensities of the former are larger than those of the latter due to the existence of satellite peaks (not shown in the figure) of (1.33, 1.33, 0). The loop widths of both hysteresis curves are very close to each other and are estimated as 1 K. It is also evident that the phase transition is of the first order, and these two magnetic peaks could be traced from the same magnetic moments in the specimen. Our results are similar to those of the resonant soft x-ray magnetic scattering at the Co L_3 edge performed by Choi *et al* [15]. Their results suggest that the magnetic peaks originate from Co^{2+}. With the better resolution of synchrotron x-rays, there is an indication that the propagation vectors of δ_1 and δ_2 in our work are increasing slightly and monotonically as the temperature decreases. The discrepancies on whether the spiral order is commensurate or incommensurate with the lattice periodicity, and the magnetic ordering is long-ranged and short-range in different groups work [10–13] are still in dispute. Dwight *et al* argued that the commensurate order results from the defects in the samples since only the incommensurate spiral order could be derived in theory [16]. However, how Cr^{3+} and Co^{2+} couple together, what are the magnetic structures of $CoCr_2O_4$ in different temperature ranges, what is the multiferroic model below the lock-in temperature, and what is the role of Cr^{3+} in the spin–current model are still unknown.

In conclusion, neutron diffraction experiments were carried out on a $CoCr_2O_4$ single crystal around the peak (220) to investigate the crossover magnetic orderings from incommensurate to commensurate. In the incommensurate ordering temperature range, the results are identical to Yamasaki's reports [1] on the multiferroic models. However, the short-range ordering claimed by Tomiyasu's group [13] was not observed in our experiments. In addition, commensurate magnetic ordering together with satellite modulated peaks with unknown magnetic structures below 14.5 K may demonstrate the existence of other possible models of the multiferroics. More detailed studies of this commensurate magnetic ordering are underway.

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