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Incommensurate magnetic ground state revealed by resonant x-ray scattering in the frustrated spin system $Ca_3Co_2O_6$

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We have performed a resonant x-ray scattering study at the Co pre-*K* edge on a single crystal of $Ca_3Co_2O_6$. The measurements reveal an abrupt transition to a magnetically ordered state immediately below T_N=25 K, with a magnetic correlation length in excess of 5500 Å along the *c* axis chains. There is no evidence for modifications to the Co^{3+} spin state. A temperature dependent modulation in the magnetic order along the *c* axis and an unusual decrease in the magnetic correlation lengths on cooling are observed. The results are compatible with the onset of a partially disordered antiferromagnetic structure in $Ca_3Co_2O_6$.

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$Ca_3Co_2O_6$ provides us with an opportunity to study the phenomena of low-dimensional magnetism and topological magnetic frustration in a single compound. $Ca_3Co_2O_6$ consists of chains, made up of alternating face-sharing octahedral (Co I) and trigonal prismatic (Co II) CoO_6 polyhedra, running along the *c* axis and arranged in a triangular lattice in the *ab* plane.[1] The different Co environments leave the Co^{3+} ions on the Co I sites in a low-spin (S=0) state and those on the Co II sites in the high-spin (S=2) state.[2,3] Crystalline electric fields also lead to a very strong Ising-type anisotropy with the moments preferentially aligned along the *c* axis.[4,5] The magnetic exchange is ferromagnetic (FM) along the chains and antiferromagnetic (AF) in the buckled *ab* plane,[5,6] making this system a rare example where Ising ferromagnetic chains are antiferromagnetically coupled on a triangular lattice.

Specific heat and magnetization measurements show the onset of long range magnetic order at T_N=25 K.[6,7] AF interactions within the *ab* plane lead to a geometrical frustration of the magnetic structure and many degenerate spin configurations are possible, giving rise to highly susceptible dynamical states.[8] For this reason, despite several neutron diffraction studies,[6,9,10] the nature of the magnetic ground state is still not fully understood. An intriguing result of the neutron experiments is the observation of a decrease in the integrated intensity of the magnetic peaks on cooling. One model[11] describes the system below T_N as a "partially disordered antiferromagnet" (PDA), where two-thirds of the FM chains are antiferromagnetically coupled, while the remaining one-third are incoherent. Recent neutron diffraction measurements[12] have shown that the long range magnetic structure in $Ca_3Co_2O_6$ is PDA and not ferrimagnetic,[6] but that more complex models should be considered to fully describe the magnetic order.

Below $T_S \sim 8$ K, a frozen spin (FS) state appears, where the application of a magnetic field parallel to the chains leads to striking additional features; the appearance of hysteresis in the $M(H)$ curves together with a succession of magnetization steps with a roughly constant field spacing.[4,5,13] These irreversible steps are related to metastable states whose dynamics strongly depend on both the thermal and magnetic histories.[13] Magnetization data showed relaxation effects that are probably related to the frustration and the slow dynamics associated with spin reversals in the FM chains. The existence of the steps in the $M(H)$ curves could be due to the nearly degenerate energy of different arrangements of the Co magnetic moments in the triangular plane perpendicular to the chains.[5,14] An alternative mechanism analogous to quantum tunneling of magnetization in molecular magnets has been proposed, with a fragmentation of the FM chains into finite spin units.[15]

In this Rapid Communication, we present a resonant x-ray scattering (RXS) study of $Ca_3Co_2O_6$. The photon energy spectra measured on magnetic reflections are temperature independent indicating that there is no change in the Co electronic configuration below T_N nor a detectable change in the structural point symmetry at the Co sites. We observe a temperature dependent modulation in the FM order along the *c* axis. A counterintuitive decrease in the magnetic correlation lengths is observed on cooling. These results, compatible with both theoretical calculations for PDA systems and neutron diffraction measurements, open the way to different descriptions of the magnetic structure of this complex system.

Single crystals of $Ca_3Co_2O_6$ were grown by a flux method. The same single crystal $5\times2\times1$ mm^3 with the largest face perpendicular to the (110) direction was used for all the RXS experiments. Its high quality was confirmed by x-ray diffraction, energy dispersive x-ray, magnetization, and specific heat measurements. The RXS experiments were performed at the magnetic scattering beamline ID20 (Ref. 16) at the ESRF (Grenoble). The beamline optics were optimized at 7.7 keV close to the Co *K* edge.

Experiments were performed by using the natural (σ) incident synchrotron polarization, with the sample mounted in a displex cryostat. The diffractometer was operated in the vertical plane scattering mode with an azimuth setup to allow for a sample rotation about the scattering vector. The integrated intensity of the reflections was measured using a photon counting avalanche photodiode detector. The polarization of the reflected beam was linearly analyzed by rotating the scattering plane of a highly oriented $\langle 00L \rangle$ pyrolitic graphite plate.

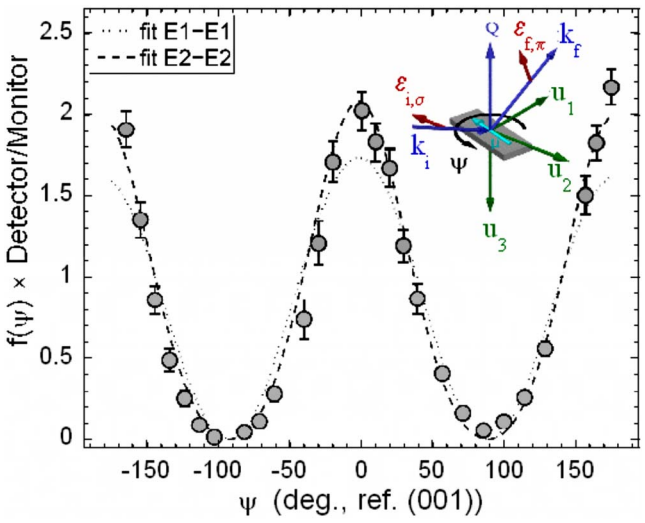

FIG. 1. (Color online) Azimuth scan on the (3 2 0) reflection collected in the σ-π channel at E=7.707 keV and T=4.2 K. Azimuth reference (0 0 1). The dotted line shows a purely $E1$-$E1$ fit and the dashed line is a fit including $E1$-$E1$ and $E2$-$E2$ contributions. The inset shows the geometry of the scattering and the fixed reference system u_1, u_2, and u_3 used.

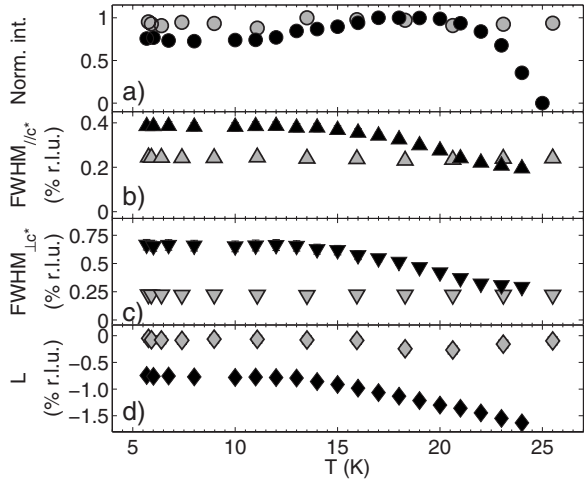

FIG. 2. Evolution of the (3 2 0) magnetic reflection (black symbols) versus T taken at ψ=0 and E=7.707 keV. Panels contain (a) the integrated intensity, (b) the FWHM along $\vec{c}$ (L scan), (c) the FWHM in the ab plane (HK scan), and (d) the evolution of the center position in the L direction. The T dependence of the corresponding parameters for the (3 3 0) charge peak (gray symbols) is shown for comparison.

The lattice parameters (a=9.062 Å and c=10.39 Å at T =30 K) were found to be in good agreement with neutron data.[1,6] The charge reflections have a full width at half maximum (FWHM) of less than 0.03° and show no changes in intensity, shape, or position. In nonresonant conditions, no extra charge reflections appear on cooling and no sign of a structural transition was detected down to T=2 K. Below T_N=25 K, antiferromagnetic reflections with $-h+k+l \neq 3n$ appear. These reflections were also observed with the neutrons and are generated by the onset of long range magnetic order,[6,9,10] which reduces the magnetic space group symmetry from $R\bar{3}c$ to $P3$.

In the rest of this Rapid Communication, we focus on the (3 2 0) reflection, as all the magnetic reflections measured provide the same physical information. Figure 1 shows the azimuth scan in resonant conditions (E=7.707 keV) collected in the rotated channel with respect to the (0 0 1) azimuthal reference direction at T=4.2 K. The fits to the data show that the elastic scattering amplitude is dominated by electric dipolar transitions,[17,18] with higher order contributions coming from quadrupolar electrical transitions. An analysis of the spherical multipoles that can contribute to the scattering in the case of the point group 3 is given in Ref. 18 Here, the reference system and the coordinates given in Ref. 17 are adopted. If just the dipolar contribution is considered, each magnetic ion's contribution to the scattering is zero in the unrotated $\sigma\sigma$ channel and is proportional to $\vec{k}\cdot\hat{z}$ in the rotated channel $\sigma\pi$, where $\vec{k}$ is the incident wave vector and $\hat{z}$, is a vector describing the magnetic moment. In the reference system sketched in the inset of Fig. 1, the magnetic structure factor is proportional to $z_1 \cos(\psi)\cos(\theta) - z_3 \sin(\theta)$, where $\hat{z}=(z_1,z_2,z_3)$ are the components of the magnetic moment along u_1, u_2, and u_3, θ is the Bragg angle, and ψ is the azimuth angle.

In our case, the proportionality coefficients, embedding both the magnitude of the magnetic moment and the matrix element between the ground state and the intermediate state, are considered as free parameters in the fit. Our data confirm the strong Ising character of the system. With the moment aligned along the c axis, z_3 is zero and the expected azimuthal dependency of the (3 2 0) reflection is given by the dotted line in Fig. 1. Allowing the magnetic moment to have an in-plane component does not improve the fit and contradicts a number of other observations. A significant improvement to the fit (dashed line in Fig. 1) is obtained by considering the quadrupolar $E2$-$E2$ channel. In the limit of a zero z_3 component, two quadrupolar higher order terms, proportional to

$$z_1^3 \cos^3(\psi)\cos^3(\theta) - z_1 \cos(\psi) z_2^2 \sin^2(\psi)\sin(2\theta)\sin(\theta)$$

and to

$$z_1 \cos(\psi)[z_1^2 \cos^2(\psi)\cos(\theta)\sin^2(\theta) + z_2^2 \sin^2(\psi)\cos(2\theta)\cos(\theta)],$$

contribute to the signal. The need to include higher rank tensors in the analysis is not surprising as the electronic d states are energetically localized in the preedge region.

The temperature dependence of several quantities characterizing the magnetic reflections measured at ψ=0 is reported in Fig. 2 (black symbols). As a comparison, the same quantities are presented for a charge reflection (gray symbols). The temperature dependence of the integrated intensity [Fig. 2(a)] is unusual. It shows a broad maximum at about 18 K and decreases (by up to 25% of the maximum value) on further cooling to 5 K, confirming the presence of an anomalous reduction in the magnetic scattering intensity seen in neutron diffraction studies.[6,9,10] However, whereas the neutron experiments measured a resolution limited magnetic

peak at all the temperatures, the much higher reciprocal space resolution of the x rays allows us to observe several features of the magnetic order.

The FWHMs of the (3 2 0) reflection measured along the *c* axis and in the *ab* plane are reported in Figs. 2(b) and 2(c), respectively. The inverse of the FWHM is directly related to the evolution of the magnetic correlation length and allows us to directly probe the dimensionality of the magnetic structure. The width of a magnetic reflection in an *L* scan [*HK* scan], i.e., the intensity as a function of the wave-vector offset along the (0 0 *l*) [(*h k* 0)] direction from the Bragg position, gives information on the magnetic correlation length along the *c* axis [in the *ab* plane]. Immediately below T_N, both the *L* and the *HK* scans produce magnetic peaks with a FWHM almost equal to those obtained in corresponding scans of charge reflections, which are, in turn, only slightly wider than the instrumental resolution. This is a proof that the transition to a metastable long range magnetically ordered state is very abrupt and that immediately below T_N there is a significant alignment of the magnetic moments both in the *ab* plane and along the *c* axis direction. Lower limits to the correlation lengths are $\simeq$5500 Å along the *c* axis and $\simeq$2500 Å in the *ab* plane.

Usually, the FWHMs of magnetic reflections in the vicinity of the Néel point are quite broad. On cooling, as the moment saturates and the thermal motion of the spins is reduced, the system normally becomes more correlated and the reflection widths decrease. Here, we observe an increase in the FWHM of the magnetic peaks on further cooling, with the values reaching a maximum at 12 K and then remaining almost constant down to base temperature. These data, therefore, provide direct experimental evidence that on cooling there is a reduction in the magnetic correlation length. Further evidence for the complex nature of the magnetic ground state is given by the results presented in Fig. 2(d). Clearly, the (3 2 0) magnetic peak is not centered at $L=0$ but moves as the temperature is changed. A similar change in the position with temperature in the *L* direction was observed for all the magnetic peaks examined, with either a positive or a negative shift with respect to the center of the Brillouin zone, whereas the *H* and *K* scans revealed no incommensurate behavior. As shown in Fig. 2(d), the lattice Bragg reflections do not change their *L* positions with *T*.

The movement of the magnetic reflections is a characteristic of the magnetic structure of the system, with the noninteger *L* values being a sign that the order along the *c* axis is not purely ferromagnetic. The modulation changes its periodicity in a continuous way from 700 Å at $T=23$ K to 1500 Å at $T=5$ K. The incommensurate structure and the reduction in intensity cannot be due to a modulation of the direction of the Co moment; the azimuth dependence of the (3 2 0) reflection at 20 and at 6 K are identical. There must, therefore, be a modulation in the magnitude and/or sign of the magnetic moment. A periodic repetition of low, intermediate, and high-spin states is quite improbable. More realistic is the hypothesis of a modulation of the magnetic order disorder in the FM spin chains.

Monte Carlo simulations[19] have revealed that the PDA structure is actually a metastable state: the disordering of one-third of the FM spin chains supposed in the PDA structure produces a frustration of the FM intrachain interaction. In other words, there is competition between the AF interchain coupling, which prefers to have one-third of the chains in an incoherent state, and the FM intrachain coupling, which requires that all the FM chains are ordered. The effect is a continuous interchange of the roles among the chains in the PDA structure as a function of time and space. Theoretical calculations reveal that these fluctuations can generate a time dependent randomly modulated PDA (RMP) structure.[20] Our data do not show an RMP phase, but a modulation with a well-defined periodicity. One should note that the Monte Carlo calculations do not include defects that might stabilize one particular structure and were performed by considering a FM intrachain coupling of the same order of magnitude as the AF nearest-neighbor interchain coupling. In $Ca_3Co_2O_6$, the FM coupling is much stronger than the AF coupling. We hypothesize that in this material, the modulation of the PDA structure is not random, but that a periodic repetition is stabilized. The continuous evolution of the propagation vector on cooling seems to indicate that the thermal energy above 12 K allows $Ca_3Co_2O_6$ to explore different metastable configurations characterized by a propagation vector closer and closer to (0 0 1), whereas below 12 K, the system is trapped, at least on the time scale of our observations, in one state.

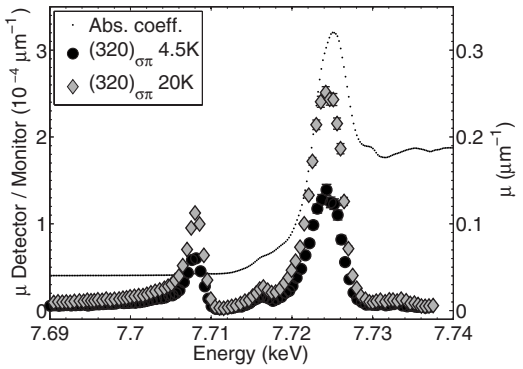

FIG. 3. Photon-energy dependence around the Co K-absorption edge of the intensity of the (3 2 0) magnetic reflection. Data were collected in the σ-π channel at $T=4.5$ (black circles) and 20 K (gray diamonds). Corrections for self-absorption have been applied. The absorption coefficient given by the fluorescence yield is shown by the dotted line.

One possible origin of the decrease in the intensity of the magnetic peaks is a reduction in the effective magnetic moment due to a transition of the Co I ion from a high spin ($S=2$) to an intermediate ($S=1$) spin state. Such a transition, however, should induce a change in the Co density of states that would be reflected in the energy spectra associated with the resonant magnetic reflection. To investigate this possibility, the incident photon energy dependence of the intensity of the (3 2 0) magnetic reflection was measured at $T=4.5$ and 20 K (Fig. 3). The spectra provide a direct access to the *p*-*d* empty density of states of the Co II site convoluted with the core-hole lifetime and the experimental resolution. They both exhibit a narrow preedge feature and two broader features between 7.71 and 7.73 keV. The main features of the spectra are in good agreement with Ref. 21 and provide experimental evidence of the mixing of the *p* and the *d* states over a

broad energy range. Such a hybridization results from the absence of the inversion symmetry at the Co II site, which is a condition not satisfied at a perfectly octahedral site. Therefore, a large dipolar contribution is present over the whole density of states, even though only the *d* states are magnetically active. The mainly dipolar character of the transition together with the experimentally measured large orbital moment [3] account for the unusually large enhancement observed over the nonresonant magnetic signal. Apart from a scaling factor related to the intensity decrease at low temperature, the two spectra are indistinguishable, ruling out a spin state transition. No change in the number or type of magnetic reflections is observed, which eliminates the possibility of a modification to the long range magnetic structure with a transfer of intensity to new reflections or different polarization channels.

The reduction in magnetic signal is due to a shift of intensity into a diffuse scattering as seen in our neutron diffraction data.[12] Our high resolution RXS measurements would not detect such a broad signal. The presence of an increasing volume of material with shorter range magnetic order (180 Å) is consistent with the picture of a metastable PDA structure presented above.

In conclusion, we report the experimental evidence for the modulated nature of the PDA order in $Ca_3Co_2O_6$, which is a feature that until now has only been predicted by theoretical calculations. Several characteristics of the experimental data suggest that $Ca_3Co_2O_6$ becomes more disordered as the temperature is reduced. The increased disorder is not due to an electronic change occurring at the Co site but is a cooperative phenomenon. At temperatures just below T_N, a weaker interchain exchange allows extended units of FM aligned magnetic moments to form along the *c* axis. On cooling, the AF in-plane coupling and the triangular geometry are incompatible with the FM order within the chains. This produces smaller spin units within the chains. The movement of the magnetic peak positions, as the system searches for an energetically favorable configuration slightly away from positions commensurate with the lattice, seems to support this interpretation. A reduction in the *T* dependence of the various parameters characterizing the magnetic state below 12 K reflects a slowdown in the evolution of the magnetic state as the system nears the FS state.

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