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Resonant X-ray scattering study of $Ca_3Co_2O_6$ ground state: Preliminary results of magnetic field effects

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ABSTRACT

We present resonant magnetic X-ray scattering (RMXS) measurements in an applied magnetic field on a single crystal of $Ca_3Co_2O_6$. We focus our attention on the transition from an incommensurate partially disordered antiferromagnetic state to a ferrimagnetic state: a lock-in and a divergence of the magnetic correlation length at the transition shed light on the nature of the ground state and on the *c*-axis vs. *in*-plane exchange couplings in this system.

1. Introduction

Magnetic frustration has been a subject of considerable interest over the last 50 years: the inability to simultaneously satisfy all pairwise interactions between spins can lead to the coexistence of a great number of nearly degenerates states, yielding a rich variety of exotic magnetic phases [1,2] characterized by peculiar dynamics. In particular, frustration due to competing magnetic interactions is known to be responsible for complex magnetic structures and unusual magnetic properties: for example non-collinear and incommensurate magnetic order have been found in systems such as fcc Fe, lanthanoides, multicomponent magnets (e.g. $LaMn_2Ge_2$) and Kagomé staircases.

$Ca_3Co_2O_6$ is another example of a magnetically frustrated material and has aroused great interest in the scientific community for its unconventional magnetic properties [3–6]. This compound consists of chains, made up of alternating face-sharing octahedral (CoI) and trigonal prismatic (CoII) CoO_6 polyhedra, running along the *c*-axis and arranged *in*-plane on a triangular lattice [7], as shown in Fig. 1. The different Co environments leave the Co^{3+} ions on the CoI sites in a low-spin ($S=0$) state, and those on the CoII sites in the high-spin ($S=2$) state [8,9]. Crystal field and spin–orbit coupling induce an Ising character, resulting in magnetic moments preferentially aligned along the *c*-axis [3,4], coupled by a strong ferromagnetic (FM) nearest neighbor interaction, (J1).

The *in*-plane structure has usually been described as a simple triangular lattice with an antiferromagnetic (AFM) interaction, (J2), the source of the geometrical frustration. Several theoretical and experimental studies have been carried out in order to determine the magnetic ground state of this material, principally taking into account two possible magnetic structures: (1) a ferrimagnetic (fM) structure, where two third of the chains have the spins up and one third spins down; (2) a partially disordered antiferromagnetic (PDA) structure, an exotic phase where one third of the chains have the spins up, one third spins down, and the remaining third contain spins that remain incoherent.

Recently, this issue was solved by resonant magnetic X-ray scattering (RMXS) and neutron diffraction investigations [10,11] showing that the real magnetic ground state of $Ca_3Co_2O_6$ is a modulated incommensurate PDA (iPDA) structure: a purely antiferromagnetic state. In each chain, the ordered magnetic moment is sinusoidally modulated along the *c*-axis. As no change in the charge distribution has been observed, the proposed sinusoidal wave seems to be related purely to magnetism. In this structure, we can expect a number of sites, having a large fraction of the effective magnetic moment, to be fluctuating quickly and therefore not contributing to the long range order.

This structure reflects the transfer of the frustration from the hexagonal planes to chains, through a helical exchange mechanism. This new picture is at odds with earlier planar models [12].

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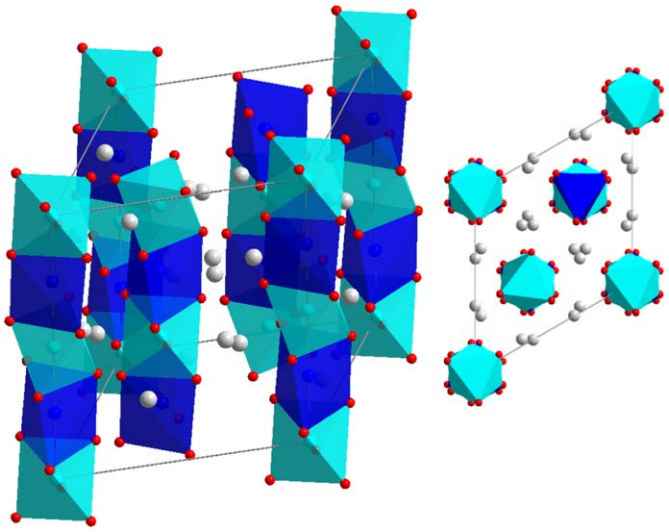

Fig. 1. $Ca_3Co_2O_6$ crystal structure. Left, 3D cartoon representation of a conventional cell. Co^{3+} stacked in octahedral (light blue) and trigonal prismatic (dark blue) polyhedra form chains running along the *c*-axis, shown vertically. Oxygen atoms are shown in red, calcium in light gray. Right, details of the triangular arrangement of Co^{3+} chains *in*-plane. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

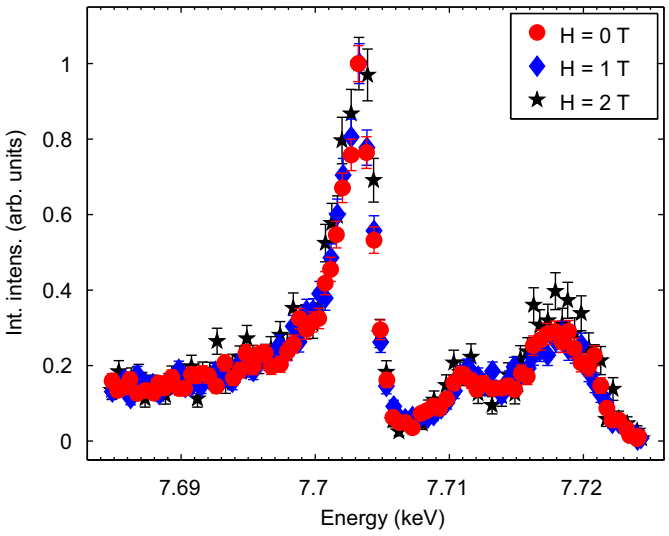

Fig. 2. Normalized energy scans at constant wave vector on the magnetic $(620)_{\pi\pi}$ reflection at various applied magnetic fields (no absorption correction). The data were collected at 5 K after having zFC the sample from 30 K.

Although the ground state is now better understood, a number of questions are still open and the most puzzling feature of this compound, i.e. the presence of equally spaced jumps in the magnetization when a magnetic field is applied, is still far from understood. These considerations are the motivation for studying the evolution of the magnetic ground state as a function of an applied magnetic field.

The number of the steps in the magnetization curve depends strongly on the sweep rate of the applied magnetic field and temperature [3,4,6]. Two steps are observed in the temperature range from 4 to 24 K, associated with transitions to an intermediate fM phase ($M \sim M_S/3$) and to a ferromagnetic phase, M_S being the saturation value of the magnetization [4,13]. At lower temperature ($T < 4$ K) the system exhibits irreversible properties and several (seven) steps are clearly visible with a roughly constant field spacing [3,4,6]. There have been several attempts to explain the origin of this peculiar magnetization behavior [4,12], including one invoking quantum tunneling of the magnetization [14].

Rough phase diagrams of $Ca_3Co_2O_6$, based on the magnetization measurements, are available in the literature [4,13]. A severe limitation of this data is that bulk magnetization measurements only probe the average properties of the magnetic structure, whereas techniques such as neutron scattering or RMXS can provide access to the microscopic details of the long range ordering. In this paper, we report on preliminary investigations performed by RMXS on a $Ca_3Co_2O_6$ single crystal in an external magnetic field.

2. Results and discussion

RMXS measurements under applied magnetic field were performed at the ID20 magnetic scattering beamline of the ESRF, Grenoble, France. The optics were optimized for energies around the Co K edge (~7.7 keV). A sample characterized by bulk magnetic measurements was mounted in a 10 T Oxford Instruments magnet [15] installed on a horizontal six circle diffractometer. The sample was oriented with the ab-plane coincident with the horizontal scattering plane, so that the direction of application of the magnetic field was parallel to the *c*-axis. A single crystal of pyrolitic graphite was used as a polarization filter in front of the detector.

No evidence for crystallographic distortions induced by magnetic field up to 10 T was detected from the *in*-plane charge reflections accessible in this geometry.

Fig. 2 shows energy scans collected at fixed wave vector for the magnetic reflection $(620)_{\pi\pi}$ at $T = 5$ K and different applied magnetic fields. The sample was zero field cooled (zFC) from 30 K to base temperature before the application of magnetic field. Above $B = 4$ T, in agreement with magnetization measurements, the sample becomes ferromagnetic and the (620) reflection vanishes.

In Fig. 2, the data collected at various magnetic fields have been normalized to each maximum (no absorption correction), highlighting the absence of any measurable variation in the magnetic density of states, both in the iPDA ($B = 0$ T) and the fM ($B = 1$ or 2 T) state within the available energy resolution (~1 eV).

Fig. 3 shows the field dependencies of the $(620)_{\pi\pi}$ magnetic reflection (top panel) and the $(520)_{\pi\pi}$ charge reflection (bottom panel) intensities at $T = 5$ K. Scans were performed along the *L*, reciprocal lattice direction; the magnetic field was increased after having zFC the sample from 30 K.

The magnetic peak position is incommensurate at zero field. At approximately $B = 0.4$ T the magnetic peak approaches $L = 0$, as shown in the top panel of Fig. 3. This corresponds to an incommensurate to commensurate transition and provides independent proof of the incommensurate nature of the iPDA state. In addition, the magnetic peak FWHM is not constant: the iPDA and fM states show comparable width, while a broadening marks the transition between the two. The system needs to decrease the coherence of the chains along the *c*-axis to reduce the energy necessary to relax the modulation, characteristic of the iPDA state, before reaching the fM state. However, even at $B = 0.4$ T the magnetic correlation length exceeds 100 unit cells. The long correlation length within the chain was unexpected and poses a severe constraint on the magnetic quantum tunneling model as it defines the unit responsible for the tunneling. Such a unit is considerably longer than the one needed to support the tunneling model, thing that must be kept in mind in any further development of this theoretical approach.

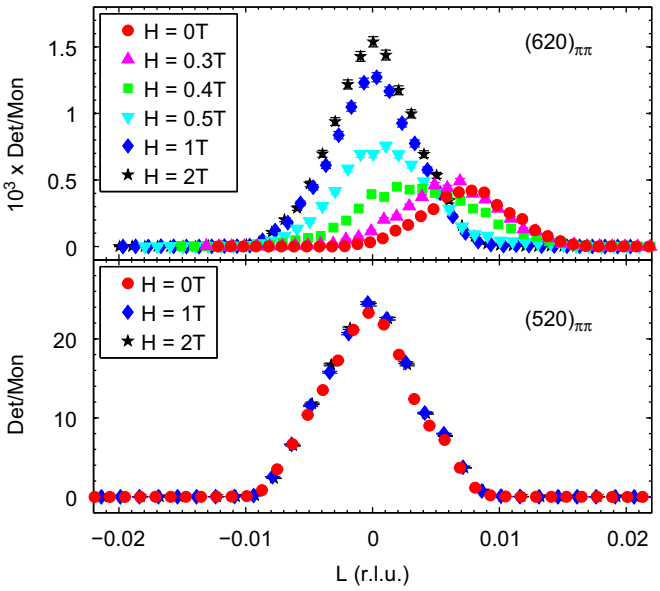

Fig. 3. Top (bottom) panel: L scan on magnetic $(620)_{\pi\pi}$ (charge $(520)_{\pi\pi}$) reflection, performed at 5 K in various applied magnetic fields.

Scans performed *in*-plane show practically no variation in either the reciprocal lattice position or the FWHM. This fact demonstrates the importance of the role played by geometry of the moments along the *c*-axis in determining the magnetic order in this compound and directly confirms the 3D nature of the coupling necessary to explain the existence of the ground state modulation [10].

Fig. 3, top panel, shows that there is an increase in magnetic intensity by a factor ~3.4 going from the iPDA to the fM structure (*in*-plane scans give the same result). The intensity variation across the iPDA to fM transition is very extended in field in comparison to the lock-in process. In our opinion, the change in intensity is due to the presence of short range ordered phases [11] which do not contribute to the iPDA signal, at least as seen by the high Q-resolution RMXS measurements. Once the system becomes fM, all the moments are forced to contribute to the magnetic intensity, with no room for incoherent spins within the system. This fact is also consistent with the anomalous decrease in the diffracted intensity at low temperature and zero magnetic field, as detected by several techniques [10,11,16–18]. For comparison, a charge reflection is reported in the bottom panel. No variation in intensity, position or FWHM is visible.

3. Conclusions

We have presented the first results of RMXS experiments performed under applied magnetic field on $Ca_3Co_2O_6$. No crystallographic distortion involving an *in*-plane modulation has been detected. Energy scans of typical magnetic peaks at 0 T and in a field sufficient to access the fM phase are identical, within in the sensitivity of the measurement, ruling out any spin state transition. Measurements performed as a function of the applied field on typical magnetic peaks, show a non-trivial evolution of the phase transition from the iPDA to the fM states. Along with an incommensurate to commensurate lock-in, a strong variation in the FWHM of the magnetic reflections across the lock-in transition stresses how costly it is for the system to exit the iPDA in terms of coherence length of the magnetic domains. The intensity gain in the fM phase highlights the fact that only a fraction of the total spin moments contribute to signal in the iPDA state. In future, we plan to directly probe the system in the region of the phase diagram where we observe the magnetization steps ($T<4$ K), in order to gain an insight into the magnetic transition mechanism bringing the system across each plateau, and to compare the data with the iPDA to fM transition investigated here.

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