Eur. Phys. J. B **47**, 79–83 (2005)
DOI: 10.1140/epjb/e2005-00308-y

THE EUROPEAN PHYSICAL JOURNAL B

Single crystal neutron diffraction study of the magnetisation process in $Ca_3Co_2O_6$

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Received 27 April 2005 / Received in final form 24 June 2005
Published online 21 September 2005 –

Abstract. We have performed neutron diffraction measurements on a single crystal sample of $Ca_3Co_2O_6$ both in a zero field and in an applied magnetic field. The measurements have revealed details of the zero-field structure of this geometrically frustrated Ising-like spin-chain compound at low temperatures and have also allowed us to examine its magnetisation process. Transitions to the $M = M_{sat}/3$ ferrimagnetic state and fully polarised ferromagnetic state have been observed. The neutron scattering results are compared with the magnetisation data, where these transitions are accompanied by the appearance of several steps and plateaux.

PACS. 75.30.Kz Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.) – 75.50.Ee Antiferromagnetics – 75.60.Ej Magnetisation curves, hysteresis, Barkhausen and related effects

1 Introduction

A new family of spin-chain oxides of general chemical formula A'_3ABO_6 (where A′ is Ca or Sr, while A and B are transition metal elements) has recently attracted a lot of interest [1]. This intense activity is due not only to the variety of magnetic behaviour shown by these compounds, but also due to the very peculiar properties found in some of them. A point of crucial importance is that the one-dimensional chains of magnetic ions in these oxides are arranged on a triangular lattice. Since some of these compounds possess both a pronounced Ising-like character (with the spins parallel to the chains) and an antiferromagnetic interchain coupling, this combination gives rise to a situation of geometrical frustration leading to complex magnetic properties.

$Ca_3Co_2O_6$ is one of the most studied geometrically frustrated spin-chain compounds [2–6]. In contrast to the triangular Ising spin-chain antiferromagnets $CsCoCl_3$ and $CsCoBr_3$ [7], the intrachain coupling in $Ca_3Co_2O_6$ is ferromagnetic. This compound appears to be one of the few examples of a system where Ising ferromagnetic chains are positioned on a triangular lattice and coupled antiferromagnetically. The complex magnetic ordering expected in such a situation bears some similarities with the classical problem of 2D Ising triangular antiferromagnets.

$Ca_3Co_2O_6$ has a rhombohedral structure composed of Co_2O_6 infinite chains that run along the c-axis of the corresponding hexagonal cell, with the Ca cations located in between them. The chains are made of alternating, face-sharing CoO_6 trigonal prisms and CoO_6 octahedra. Each chain is surrounded by six equally spaced chains forming a triangular lattice in the ab plane (see Fig. 1). The intrachain Co-Co separation is ∼2.6 Å, while the interchain spacing is twice this distance. It is now generally accepted that the Co ions in the two different crystalline electric field environments are trivalent with an alternate high-spin $S = 2$ and low-spin $S = 0$ states along the chain, corresponding to the trigonal prisms and the octahedra, respectively. At $T_N \simeq 26$ K, there is long-range

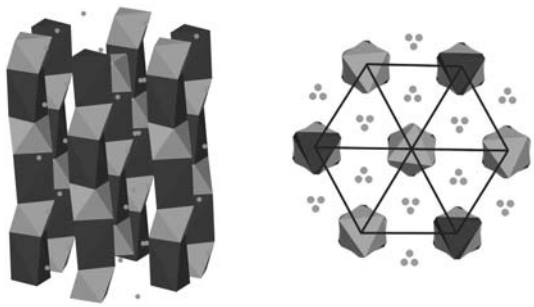

Fig. 1. Crystal structure of $Ca_3Co_2O_6$: a perspective view showing the chains of CoO_6 trigonal prisms and CoO_6 octahedra running along the hexagonal c-axis (left) and a projection along the c-axis (right). The calcium cations are shown as small circles located between the chains.

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spin ordering driven by the antiferromagnetic interchain coupling [2]. However, the development of this ordering is impeded by the geometrical frustration, which, it is suggested, leads to a complex "partially disordered antiferromagnetic" (PDA) state, as proposed by Kageyama et al. [3] in accordance with the theoretical model developed by Mekata [8,9].

The application of a magnetic field parallel to the c-axis (i.e. parallel to the chains and to the spins) leads to new and puzzling features [3,5,10]. When the field is increased at an intermediate temperature below T_N (e.g. 10 K), the magnetisation rapidly reaches a first plateau, before being switched to the saturation value ($M_{sat} \simeq 4.8\,\mu_B$/f.u.) above $H_C \simeq 3.6$ T. The magnetisation on the first plateau is equal to $M_{sat}/3$, a feature that has been ascribed to the onset of a ferrimagnetic state, consisting of ferromagnetic chains with two thirds of them having spins up and one third having spins down. As the temperature is decreased below 10 K, the hysteresis in the M vs. H curves becomes more pronounced, tending to occupy the whole field range, and new steps appear below H_C.

Below H_C, one can observe two additional "step" fields, $H_{S1} \simeq 1.2$ T and $H_{S2} \simeq 2.4$ T. The origin of these low temperature steps was recently discussed in terms of the possible occurrence of a Quantum Tunneling of the Magnetisation (QTM) in $Ca_3Co_2O_6$ [11].

The aim of the present work is to shed light on the magnetisation process in $Ca_3Co_2O_6$ by performing a direct investigation of the magnetic structure as a function of the field and temperature using the single-crystal neutron diffraction technique. To date, the two reported neutron diffraction studies of the magnetic structure of $Ca_3Co_2O_6$ have been limited to measurements on powder samples. A zero-field study by Aasland et al. [2] demonstrated the occurrence of long range ordering below $T_N \sim$ 24 K. Based on their neutron diffraction data the authors proposed a model for the magnetic structure of $Ca_3Co_2O_6$ which consists of ferrimagnetically ordered chains of alternating magnetic moments (of $(0.08 \pm 0.04)\,\mu_B$ and $(3.00 \pm 0.05)\,\mu_B$) on the Co sites. An investigation of the influence of an applied field on the intensity of the magnetic peaks has been reported by Kageyama et al. [4]. Unfortunately, their study was performed only above 4 K, a temperature for which the magnetisation steps below H_C are almost invisible. The single crystal study we report here has allowed us to investigate for the first time the step features under appropriate conditions.

2 Experimental details

Single crystal samples of $Ca_3Co_2O_6$ were grown using a flux method described previously [5]. The same crystals were used for measurements of specific heat, magnetisation and ac susceptibility as reported earlier [10–12]

Neutron diffraction measurements were performed using the PRISMA time-of-flight spectrometer at the ISIS pulsed neutron source. In diffraction mode, the spectrometer is particularly well suited for reciprocal space surveys due to the large Q coverage, good signal to noise ratio and the large flux of long wavelength neutrons delivered by the supermirror guide system. The scattered neutrons were recorded by sixteen ^{3}He gas detectors covering a scattering angle of 25°–40°, which provided a good neutron flux in the range 0.5 to 5.5 Å. By rotating the crystal about the vertical axis in steps of 8°, intensity maps were constructed covering large regions of scattering plane (see Fig. 2). Alternatively, much finer step-sizes (around 0.2°) were used to accumulate data sets which are sufficiently detailed to investigate the temperature or field dependence of the magnetic Bragg peaks.

The experiments were performed in the temperature interval from 2 to 35 K and in magnetic fields up to 7 T. A vertical magnetic field was applied along the c-axis, defining the scattering plane as $(hk0)$. The accuracy of the crystal alignment with respect to magnetic field was better than 1° [13]. The relatively small size of the crystal used (about 2 mg in mass) ensured that there was no need to make absorption or extinction corrections. All parts of the sample environment in the beam were made of aluminium, which gives rise to powder lines at Q = 2.70, 3.12 and 4.40 Å^{-1}. Standard data reduction procedures were applied to transform time of flight and angle information to reciprocal space, and to normalize the data to a vanadium run. The latter corrects for the wavelength-dependent flux profile for a pulsed source and detector efficiency.

3 Results and discussion

Examples of the maps of neutron scattering intensity collected at different temperatures and in different magnetic fields are shown in Figure 2. Some important observations can be made from inspection of these maps. First of all, the transition to a magnetically ordered phase is accompanied by the appearance of antiferromagnetic (AFM) Bragg peaks, such as (100), (200) and (120). No peaks were found with non-integer indices – all peaks can be indexed using the high-temperature hexagonal unit cell. This result agrees with the powder diffraction data [2] and suggests that under all conditions the length of the magnetic unit cell in the ab plane does not exceed the length of the nuclear cell. This means that the magnetic structure can be adequately described by considering only the three spins at the corners of a triangle. Secondly, the application of an external magnetic field does not change the number of magnetic peaks in the $(hk0)$ plane or their positions – it affects only their intensity. The intensity of the AFM peaks is enhanced by the application of the moderate fields (up to about $H_C \simeq 3.6$ T), while in the higher fields the AFM peaks disappear and ferromagnetic (FM) peaks become significantly more intense.

The temperature dependence of several AFM and FM peaks in zero field and on cooling in a field of 1.7 T is shown in Figure 3. In zero field, quite unusually for antiferromagnets, there is a pronounced drop in the intensity of these peaks at low temperature. It is important to notice that the observed decrease in intensity is not accompanied

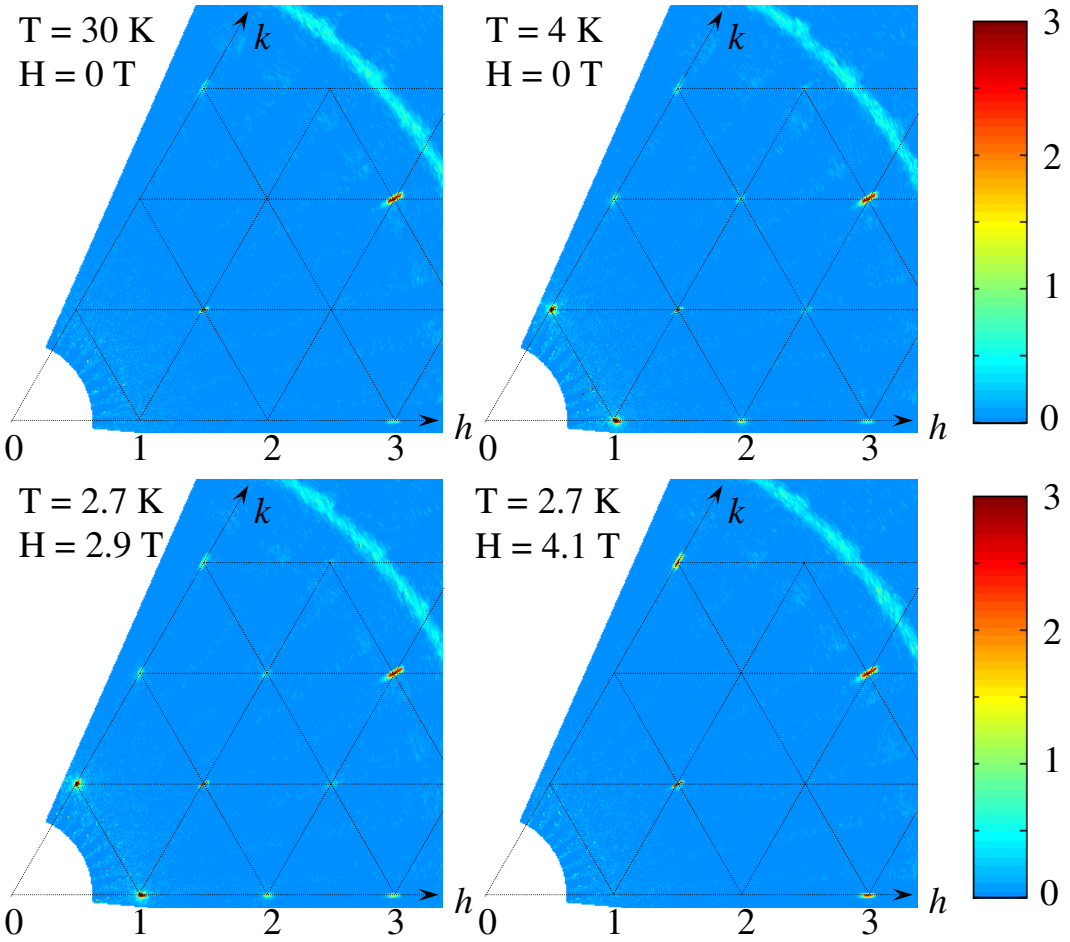

Fig. 2. Neutron scattering intensity of $Ca_3Co_2O_6$ in the $(hk0)$ plane. The data in the top panels are recorded in zero field at $T = 30$ K (left) and $T = 4$ K (right). The data in the bottom panels are recorded at $T = 2.7$ K in a field of 2.9 T (left) and 4.1 T (right).

by any change in the peak width, although for the chosen scattering angles the resolution of PRISMA is quite coarse and does not allow for a detailed analysis of the sample's magnetic correlation length. A similar puzzling decrease in the intensity of the (100) Bragg peak below 15 K has been observed in the powder diffraction studies [2,4]. In a field of 1.7 T, which corresponds to the ferrimagnetic state, the temperature dependence of the intensity looks much more conventional, as the intensity increases gradually with decreasing temperature (see Fig. 3).

For the AFM peaks such as (100) and (200), the ratio of the intensities for FC and ZFC samples at zero temperature is around 1.7. Simple calculations show that the ratio of the intensities for ferrimagnetic (Up-Up-Down) and PDA (Up-Down-Zero) arrangements of the Ising spin-chains on a triangular lattice should be 4/3. This observation suggests that the zero-field structure of $Ca_3Co_2O_6$ is not a simple PDA. A possible appearance of magnetic domains may need to be considered in order to explain a reduced intensity of the magnetic peaks in $Ca_3Co_2O_6$ at low temperature. Despite the existence of reasonably strong arguments in favour of Ising-like behaviour in $Ca_3Co_2O_6$, a small deviation of the spins from the c-axis cannot be

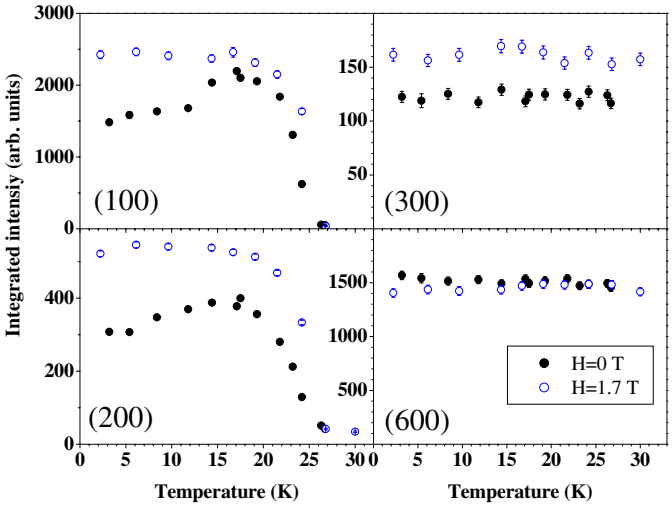

Fig. 3. Temperature dependencies of the integrated intensity of the AFM (100), (200) and FM (300), (600) reflections in zero magnetic field (solid symbols) and for FC in a field of 1.7 T (open symbols).

ruled out. Therefore a model describing magnetic domains may need to include the xy spin components.

It is also interesting to notice that for the (100) and (200) peaks the structure factors are the same in the PDA phase as well in the ferrimagnetic phase, therefore the ratio of intensities $I_{(100)}/I_{(200)}$ is determined only by the magnetic form-factor. Given that the momentum transfer is relatively low for these peaks, 0.8 Å and 1.6 Å respectively, their intensities should only differ by about 20% [14], while Figure 3 clearly shows that the peaks are significantly different both in zero field and in an applied magnetic field. Again magnetic domains are suspected in playing an important role in moderating the magnetic peaks intensity in $Ca_3Co_2O_6$. Magnetic disorder on a scale longer than that which could be detected by PRISMA may also contribute towards the unusually fast decline of magnetic intensity with increasing momentum transfer.

The temperature dependence of the neutron scattering intensity at the magnetic ordering vector (which is effectively an order parameter) should be compared with the observed temperature dependence of the order parameter in other Ising-like triangular magnets. However, as will become evident from the comparisons made below, no known materials have magnetic properties that closely resemble those of $Ca_3Co_2O_6$.

There are not many examples of 1D Ising ferromagnets on a triangular lattice. Those that exist mostly belong to the same A'_3ABO_6 (where A = Co and B = Ni, Ru, Ir, Rh) group or to the family of hexagonal magnets of the ABX_3 type.

Among the well studied ABX_3 family members, compounds where B is Co, A is Cs, Rb or Tl, X is Cl or Br are known to possess a pronounced Ising character [7]. The most intensely studied compounds of this type are $CsCoCl_3$ and $CsCoBr_3$, which along with $Ca_3Co_2O_6$ are profoundly one-dimensional in terms of their magnetic interactions. Unlike $Ca_3Co_2O_6$ the intrachain interaction in these materials is antiferromagnetic [9,15]. At first glance, the temperature dependence of the order parameter of the AFM compounds immediately below T_N (see Fig. 6 in [15] and Fig. 2 in [9]) is similar to that shown in Fig. 3, as on all the curves there is drop in intensity at lower temperature after the initial intensity rise just below the ordering temperature [16]. In order to explain this drop several partially ordered magnetic structures have been considered. The major difference to the data shown here is, however, that upon further cooling the AFM compounds regain the intensity and their low-temperature ground state become fully ordered. This clearly does not happen in $Ca_3Co_2O_6$, where the intensity of the AFM peaks at the lowest measured temperature is significantly reduced compared to the maximum intensity attained at around $T \sim 18$ K.

There is limited information available on the temperature dependence of the magnetic Bragg peaks in other Ca_3CoBO_6 compounds; all this information has been obtained using powder samples. In Ca_3CoRhO_6 the intensity of magnetic reflections is reported to rise monotonically below the ordering temperature [17], although a drop in intensity was observed at about 30 K for measurements

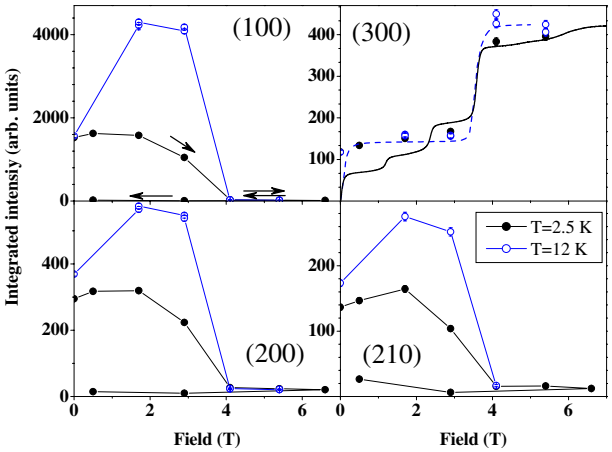

Fig. 4. Field dependencies of the integrated intensity of the AFM and FM reflections at $T = 2.5$ K (solid symbols) and $T = 12$ K (open symbols). For the AFM (100) peak the arrows indicate the sequence of magnetic fields at which the measurements were taken. On the upper-right panel along with the intensity of the FM (300) peak the magnetisation value is also shown by the solid ($T = 2.5$ K) and dashed ($T = 12$ K) lines.

in a field of 2 T [18,19]. This change has been attributed to a phase transition from the field-induced ferrimagnetic state to a frozen PDA state. There are no neutron scattering data for Ca_3CoIrO_6, Ca_3CoRuO_6 or Ca_3CoNiO_6.

Another comparison can be drawn with the low-temperature behaviour of $CoNb_2O_6$, a quasi-one-dimensional Ising magnet on an isosceles triangular lattice [20]. In this compound the FM zigzag chains formed along the c direction (with a tilt angle of about 31°) interact antiferromagnetically in the ab plane. The magnetic structure of $CoNb_2O_6$ in zero field is quite complicated; it is affected by the appearance of different types of magnetic domains. At intermediate temperature just below T_N the ground state of this system is an incommensurate structure, while at lowest temperatures it is replaced by a noncollinear AFM structure. However, no significant reduction of the AFM peaks at low temperature is reported for $CoNb_2O_6$. We therefore conclude that none of the well studied magnetic model systems, described above, match precisely the magnetic properties of $Ca_3Co_2O_6$.

Figure 4 shows the field dependence of the intensity of both the AFM and FM peaks measured at 2.5 K and 12 K. The intensity of both the FM and AFM peaks increases in the ferrimagnetic phase compared to zero field. The increase for the AFM peaks is much more pronounced at higher temperature. Upon entering the fully polarised phase above $H_C \simeq 3.6$ T the intensity of the FM peaks reaches a maximum and saturates, while the AFM peaks disappear completely. For reference, we have also included in Figure 4 the magnetisation data obtained at the same temperatures [10].

It is interesting to note that at 2.5 K in a field of 4.1 T (well above the transition field $H_C \simeq 3.6$ T) the intensities of the FM peaks such as (300) are not completely saturated, in accordance with the magnetisation data. At the same field, however, the intensities of all the

AFM peaks are practically zero. This observation suggests that before reaching the fully polarised phase in higher fields, $Ca_3Co_2O_6$ passes at low temperatures through a state where the AFM correlations between the spin chains are already removed, while the full FM alignment inside the chains is not yet reached.

In order to investigate the details of the magnetisation process around one of the "step" fields $H_{S2} \simeq 2.4$ T we have measured the intensity of both the FM and the AFM peaks at $T = 2.5$ K by increasing the applied field from 2.2 to 2.55 T and then back down to 2.0 T. The step-size for these measurements was 0.05 T. No significant variation of intensity was observed either for the FM or the AFM peaks, although given the experimental time-restrictions (typical counting time for this experiment was an hour per field) the accuracy of the integrated intensity was limited to several percent. Significantly longer counting times or larger samples would be required to investigate the possible occurrence of a QTM process in $Ca_3Co_2O_6$. It would also be necessary to follow more accurately the time dependence of magnetic peaks intensity, as the field-driven magnetisation steps in $Ca_3Co_2O_6$ crystals have been shown to have a pronounced time as well as temperature dependence [10]. For this reason a direct comparison of the curves shown in Figure 4 with the hysteresis loops observed by Hardy et al. [10] is not possible, although the absence or at least the significant reduction of the hysteresis at 12 K compared to 2.5 K does seem to agree with the magnetisation data.

4 Conclusions

We have measured neutron diffraction patterns of a single crystal of $Ca_3Co_2O_6$ at low temperatures in an applied magnetic field, $H \| c$. All the magnetic Bragg peaks observed in the $(hk0)$ scattering plane at all temperatures and fields have integer indices. In zero field, an unusual drop in intensity of the AFM peaks has been observed at low temperature. The measured ratio of the intensities of these peaks for FC and ZFC samples indicates that the zero-field structure of $Ca_3Co_2O_6$ is not a simple PDA. The field dependence of the intensity of the magnetic peaks generally agrees well with the magnetisation data, but in order to study the smaller steps seen in the magnetisation at the lowest temperature larger samples are required.

The authors thank Martyn Bull and the sample environment team at ISIS for assistance on PRISMA as well as Don McK. Paul for critical reading of the manuscript.

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