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# Field-driven magnetisation steps in $\text{Ca}_3\text{Co}_2\text{O}_6$ : A single-crystal neutron-diffraction study

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**Abstract** – The behaviour of the spin chain compound  $\text{Ca}_3\text{Co}_2\text{O}_6$  in an applied magnetic field has been the subject of a detailed single-crystal neutron diffraction study. The low-temperature magnetisation process is shown to be accompanied by clearly visible steps in the intensity of the ferromagnetic and antiferromagnetic Bragg peaks. The field and temperature dependence of the long-range and the short-range components of magnetic order in  $\text{Ca}_3\text{Co}_2\text{O}_6$  have been studied. Detailed measurements have shown that the presence of the short-range correlations cannot account for the reduction in intensity of the antiferromagnetic peaks at low temperatures.

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**Introduction.** –  $\text{Ca}_3\text{Co}_2\text{O}_6$  is one of a family of low-dimensional magnetic systems  $A'_3\text{ABO}_6$ , where  $A'$  is Ca or Sr, while A and B are transition-metal elements [1]. It has a spin-chain structure [2] and undergoes a complex magnetic ordering below a Néel temperature of 25 K arising from the effects of geometrical frustration [3–7]. In zero field,  $\text{Ca}_3\text{Co}_2\text{O}_6$  was recently shown to have a sinusoidally modulated spin-density wave with a very long period propagating along the  $c$ -axis [8,9]. A series of low-temperature magnetisation steps [3,10,11], reminiscent of the quantum tunnelling observed in molecular magnets [12,13], has ensured continued experimental and theoretical interest in this system in recent years [14–21].

The crystal structure of  $\text{Ca}_3\text{Co}_2\text{O}_6$  (space group  $R\bar{3}c$ ) [2] shown in fig. 1 is highly anisotropic. Along the  $c$ -axis there are chains of alternating  $\text{CoO}_6$  trigonal prisms and  $\text{CoO}_6$  octahedra with a Co-Co spacing of 2.59 Å. In the  $ab$  plane the  $\text{CoO}_6$  chains are arranged in a triangular lattice with a separation of 5.24 Å [2]. Both the cobalt ions are trivalent with alternate high-spin  $S=2$  and low-spin  $S=0$  states corresponding to the  $\text{CoO}_6$  trigonal prisms and the octahedra, respectively [5,22–24]. The intrachain coupling is ferromagnetic (FM) while the interchain coupling is antiferromagnetic (AFM) [3–5].

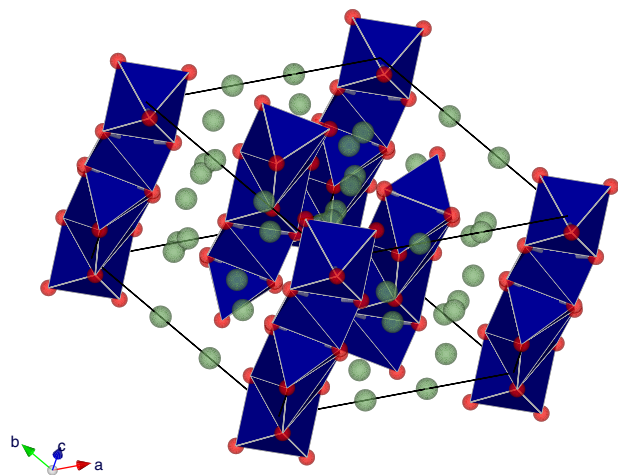


Fig. 1: (Colour on-line) The crystal structure of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in the hexagonal setting. The  $\text{CoO}_6$  polyhedra form spin chains along the  $c$ -axis with the calcium atoms positioned between them.

At low-temperatures ( $\leq 8$  K), a series of equally spaced steps emerge in the magnetisation when a magnetic field is applied along the  $c$ -axis [3]. Magnetisation steps have been observed at  $\sim 0$  T, 1.2 T, 2.4 T, 3.6 T, with possible steps at the higher fields of 4.8 T and 6 T [10,12]. When the temperature is increased to an intermediate value

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( $\approx 10$  K), only the 3.6 T step remains and the hysteresis in the magnetisation as a function of magnetic field is greatly reduced. At these temperatures, the magnetisation is saturated above 3.6 T with a value of  $M_{sat} \approx 5.1 \mu_B/f.u.$ , indicating complete ferromagnetic ordering. Below 3.6 T the value of the magnetisation is  $M_{sat}/3$ . This value is ascribed to two thirds of the chains having spin up and one third having spin down [10]. In a previous neutron diffraction study we have found a sharp change in the intensity of the magnetic Bragg peaks associated with the transition at 3.6 T. However, a small sample size and a low-flux instrument have prevented us from studying the transitions at any other fields [25]. In this letter, we report the first observation of all the metastable magnetisation plateaux in  $\text{Ca}_3\text{Co}_2\text{O}_6$  with a microscopic probe such as neutrons.

Another important aspect of the behaviour of  $\text{Ca}_3\text{Co}_2\text{O}_6$  is a coexistence of short-range and long-range magnetic correlations [9] and the associated decrease at low temperatures of the intensity of the main AFM Bragg peaks [5,6,25]. We therefore also report on the balance between the short-range and long-range magnetic components in  $\text{Ca}_3\text{Co}_2\text{O}_6$  in an applied magnetic field. We answer the question as to whether the magnetisation steps result in a change in the degree of magnetic disorder signified by a redistribution of intensity between the short and the long-range magnetic components, and assess the more general role of the short-range component in the behaviour of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in an applied magnetic field.

**Experimental details.** – An  $8 \times 2 \times 2 \text{ mm}^3$  single crystal grown using a flux method described previously [9] was used for the experiment. The high quality of the crystal was confirmed by X-ray diffraction, energy-dispersive X-ray, magnetisation, and specific-heat measurements. The neutron diffraction measurements were made on the high-flux single-crystal diffractometer D10 at the Institut Laue-Langevin in Grenoble, France.

The sample was mounted in a 6 T vertical cryomagnet and aligned to within  $1^\circ$  of the magnetic field with the field directed along the  $c$ -axis limiting the scattering to the  $(hk0)$  plane. The incident wavelength used was  $2.36 \text{ \AA}$  from a pyrolytic graphite (PG) (002) monochromator with the half-wavelength contamination suppressed by a PG filter. Measurements were made in the temperature range 2–30 K with the sample warmed well above the ordering temperature and cooled in zero field between runs to avoid possible hysteresis effects.

A vertically focussing PG analyser was used to give improved resolution for some of the measurements. The two-dimensional  $80 \times 80 \text{ mm}^2$  area detector was used for all the measurements except for those made with the energy analyser, where a single  $^3\text{He}$  detector was used.

The measurements were made in one of two modes. Either by measuring the peak intensity (summing up the counts in a small area of the detector surrounding the peak) while ramping the temperature or field, or by integrating rocking curves (labelled as  $\omega$  scans below) at

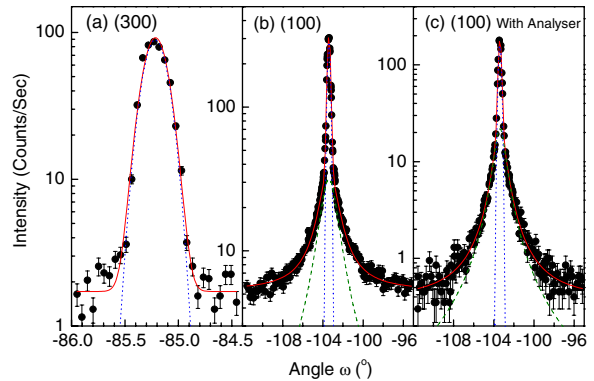


Fig. 2: (Colour on-line) Examples of the lineshapes of the FM (300) peak (a) and the AFM (100) peak ((b), (c)), measured at 2 K and in zero field. The profile shown in panel (c) was obtained with the use of a vertically focussing PG analyser. Solid lines are the fits consisting of two components, a main resolution-limited Gaussian component (dotted line) and a broad Lorentzian component (dashed line) as well as a flat background. The FM peak shown in panel (a) can be fitted with a single Gaussian and a flat background.

various fixed values of field/temperature. All the data have been normalised to the monitor time, typically 60 seconds per point in sweeping mode and 20 seconds per point for  $\omega$  scans.

The magnetic Bragg peaks observed in  $\text{Ca}_3\text{Co}_2\text{O}_6$  can be split into two groups, those appearing on top of nuclear peaks in an applied magnetic field and labelled as FM peaks, and the AFM peaks, such as (100), (200) and (120), whose intensity is zero above  $T_N$ . In order to compare the intensity of the FM peaks with both the bulk magnetisation and the intensity of the AFM reflections, the nuclear component of the FM peaks was measured in zero field at  $T > T_N$  and subtracted to give a purely magnetic intensity.

**Results and discussion.** – We start the discussion of the results by comparing the characteristic shapes of the FM and the AFM reflections. As illustrated in fig. 2a, the FM peaks, for example (300), can be adequately fitted with a single Gaussian. The width of these peaks (typical FWHM of  $\simeq 0.35^\circ$ ) is considered to be limited by the instrumental resolution.

On the other hand, the AFM peaks, such as (100), can best be fitted with a combination of a Gaussian and a Lorentzian component. The Gaussian component (FWHM of  $0.37^\circ$ ) is again resolution limited, while the Lorentzian component is indicative of the presence of magnetic disorder (see fig. 2b). This observation is in agreement with the previously reported coexistence of a short-range magnetic structure with the long-range order in zero field at 5 K [9]. The observed width of the Lorentzian component (typically  $1.9^\circ$ ) and the resulting estimate for the magnetic correlation length,  $D = 250 \text{ \AA}$  (see footnote <sup>1</sup>)

<sup>1</sup>The magnetic correlation length is estimated using  $D (\text{\AA}) = 2\pi/\text{FWHM} (\text{\AA}^{-1})$ .

are similar to the previously reported values ( $D = 180 \text{ \AA}$  was obtained in ref. [9]). It is possible that this small difference is due to the truncation of the data in the earlier measurement, where typically the scans were much shorter than the  $20^\circ$  scans shown in figs. 2b and c.

The AFM (100) peak was also measured using the PG energy analyser with a typical peak profile shown in fig. 2c. Apart from a narrowing of the Gaussian component due to the improved resolution down to  $0.34^\circ$  and a significant reduction in the background (from 5.3 to 0.4 counts per second) the shape of the peak remained largely unchanged. The ratio of the areas of the Lorentzian to the Gaussian components of the peak measured with and without the analyser are 0.7 and 0.9 respectively. This observation might suggest that the magnetic disorder is at least partially dynamic in nature. However, to draw any firm conclusions regarding the presence of magnetic excitations in  $\text{Ca}_3\text{Co}_2\text{O}_6$  and their influence on the short-range magnetic correlations, much more systematic measurements with greatly improved energy resolution are required.

In agreement with our previous neutron diffraction study [25], the application of a magnetic field did not result in the appearance of additional Bragg reflections. All the peaks were found at integer positions which means that they can be indexed using the nuclear unit cell. Figure 3 shows the field dependence of the integrated intensity of the FM (300) peak and the AFM (100) peak, measured at 2K with  $\omega$  scans. The magnetisation curve is also shown for comparison<sup>2</sup>. The equally spaced steps in intensity for both the FM and the AFM reflections match well with those seen in magnetisation measurements, with clear steps observed at 2.4 T, 3.6 T and 4.8 T, and a possible feature at 1.2 T. There is a small but distinctly nonzero intensity for the AFM reflection even above the transition at 3.6 T. This field value is sufficient to polarise fully the system only at higher temperatures, while at 2 K a much higher field is required.

Figure 3 also shows that the step-like behaviour is observed for both the Gaussian and the Lorentzian components of the AFM peak. Therefore the application of a magnetic field affects both the long-range and the short-range antiferromagnetic correlations in  $\text{Ca}_3\text{Co}_2\text{O}_6$ . The figure also shows that the steps at 1.2 and 2.4 T are not associated with a redistribution of intensity between the Gaussian and Lorentzian components, establishing that the degree of antiferromagnetic disorder does not change at these fields. Significantly, the AFM peak continues to have some intensity above 3.6 T, commonly believed to be the critical field at which there is a transition to the ferromagnetic state. The widths of both components of the AFM peak are found to be field independent until the transition at 3.6 T above which the width becomes resolution limited.

<sup>2</sup>The magnetisation curve of  $\text{Ca}_3\text{Co}_2\text{O}_6$  has been measured using a vibrating sample magnetometer according to the procedures previously described [11].

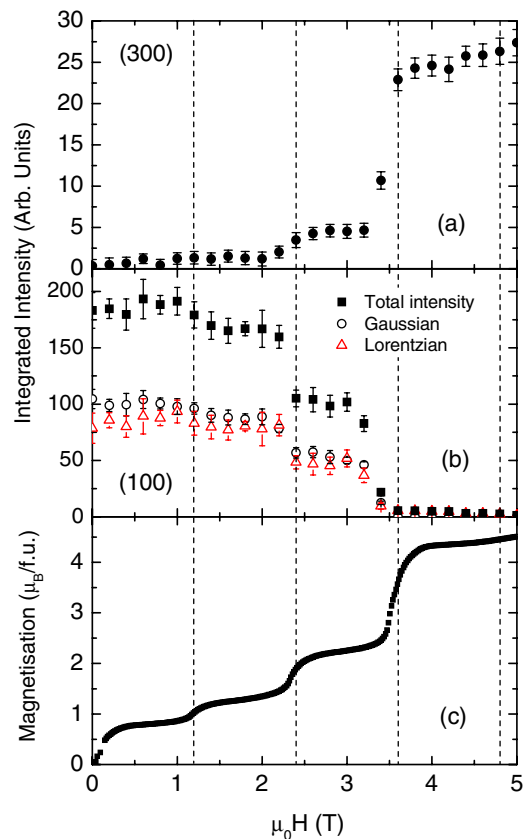


Fig. 3: (Colour on-line) Intensity of (a) the FM (300) reflection and (b) the AFM (100) reflection (split into Gaussian and Lorentzian components) as a function of an increasing applied magnetic field. The nuclear component of the FM peak (equating to 24.9 in the units used in the figure) has been subtracted. The equivalent magnetisation measurements are shown for comparison (c). The dashed lines are drawn at fields of 1.2, 2.4, 3.6 and 4.8 T. All the measurements were made at a temperature of 2 K.

The  $\omega$  scans performed at various temperatures have shown that the positions of magnetic peaks in the  $(hk0)$  scattering plane do not change noticeably as a function of applied field. It is therefore permissible to measure the field dependence of the intensity of the magnetic reflections without scanning through them. The results of such measurements are shown in fig. 4. The two different measurement methods give results that are in a good agreement with one other, as can be seen from the comparison between the field dependence of the intensity of an AFM peak (100) and a FM peak (300). A similar step-like behaviour of intensity was also seen for the FM (110) peak.

The field-ramping approach allowed much faster data collection, which is particularly important for  $\text{Ca}_3\text{Co}_2\text{O}_6$ , where the shape of the magnetisation curve is strongly dependent on the measurement time [11]. The large hysteresis seen in the magnetisation measurements at low temperatures has also been observed with neutron diffraction, and is shown in fig. 4. The most striking feature

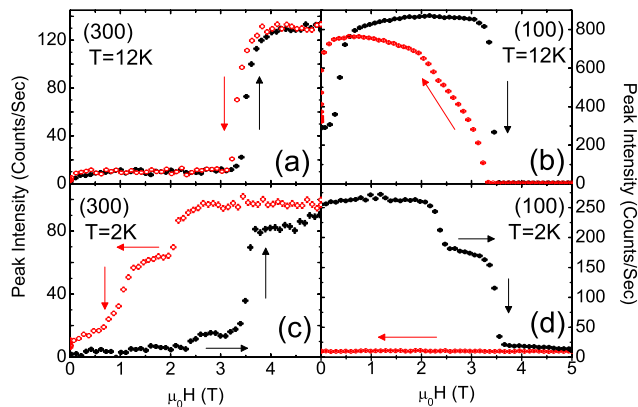


Fig. 4: (Colour on-line) The intensity of the FM peak (300) peak (left) and the AFM peak (100) (right) as a function of magnetic field at 12 K ((a), (b)) and 2 K ((c), (d)). The nuclear component of the FM peak (equating to 89 counts per second) has been subtracted. The solid symbols show the data taken while increasing the magnetic field and the open symbols show the data taken while decreasing the field. The magnetic-field ramp rate was 0.1 T/min for all the measurements.

observed at base temperature is that the intensity of the AFM reflection is very weak (nearly zero) for decreasing magnetic fields. Therefore at 2 K the ZFC magnetic state of  $\text{Ca}_3\text{Co}_2\text{O}_6$  is completely different from the magnetic state after the application and subsequent removal of an external magnetic field. This observation is only possible with a microscopic magnetic probe such as neutrons while all the previous bulk-properties measurements have failed to note such a difference in the magnetic state after the application/removal of a magnetic field. In order to restore the intensity of the AFM peaks the sample has to be warmed up to 30 K and then cooled in zero field.

At low temperature, the observed increase in the intensity of FM peaks close to 0 T is relatively small (see fig. 3a and fig. 4c). However, given the fact that the magnetic intensity of the FM peaks is proportional to magnetisation squared, the agreement between the neutron data and the magnetisation curve shown in fig. 3c is quantitatively good.

Unlike the FM peaks, the intensity of the (100) AFM peak shows significant hysteresis at 12 K in a wide range of applied fields (see fig. 4b). At this temperature there is also a rapid change in the intensity of the AFM reflection near zero field for the data taken in both ascending and descending magnetic fields, while at 2 K the intensity of this peak does not change appreciably for ascending fields and is close to zero for descending fields. The intensity curve for the AFM reflection taken while decreasing the field at 12 K suggests a transition at 2.4 T, which in magnetisation measurements [11] is also visible at temperatures as high as 10 K.

The intensities of the FM peaks were also measured in magnetic fields of 0.6 T, 1.8 T and 3 T as a function of temperature. These fields were chosen as they are the mid-points on the plateaux seen in the bulk magnetisation

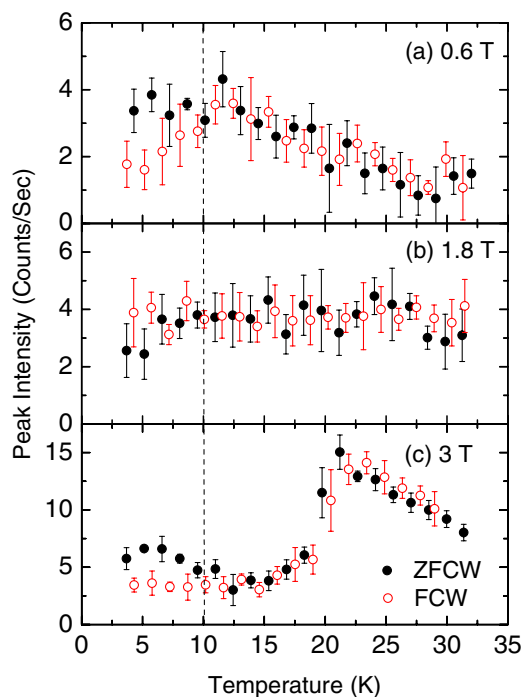


Fig. 5: (Colour on-line) Temperature dependence of the intensity of the FM (300) peak measured in three different fields, 0.6 T, 1.8 T and 3 T. The solid symbols show the data taken while warming the sample in field after zero-field-cooling (ZFCW) and the open symbols show the data taken in field while increasing the temperature after field-cooling (FCW). An irreversibility temperature is visible at around 10 K, where the intensities of the ZFCW and FCW diverge, marked by a dashed line on the figure. The temperature ramp rate was 0.3 K/min.

curve. The results are shown in fig. 5. In addition to the apparent transition to the saturated state at 20 K in a magnetic field of 3 T (see fig. 5c) another notable feature is the presence of an irreversibility temperature around 10 K. Below this temperature there is a pronounced difference between the zero-field-cooled and field-cooled data for 0.6 T and 3 T measurements, while in the intermediate field of 1.8 T the difference is barely visible. This observation should be linked with the magnetisation relaxation measurements [11], which revealed that at lower temperatures the magnetisation of  $\text{Ca}_3\text{Co}_2\text{O}_6$  has a pronounced time dependence and that the magnetisation could relax either upwards or downwards depending on the value of the applied field.

Recent investigations [9] have suggested that the origin of the anomalous dip in the intensity of the AFM peaks at low temperatures is due to an increase in the fraction of material exhibiting short-range correlations at the expense of the fraction of long-range-ordered material. We have repeated the zero-field measurements reported in ref. [9] in a field of 0.6 T, the results of which are shown in fig. 6. For a ZFC sample both the Gaussian and Lorentzian components are present at base temperature. On warming, the intensity of both components initially increases. There is a sharp dip in the Gaussian component at 8 K. However,



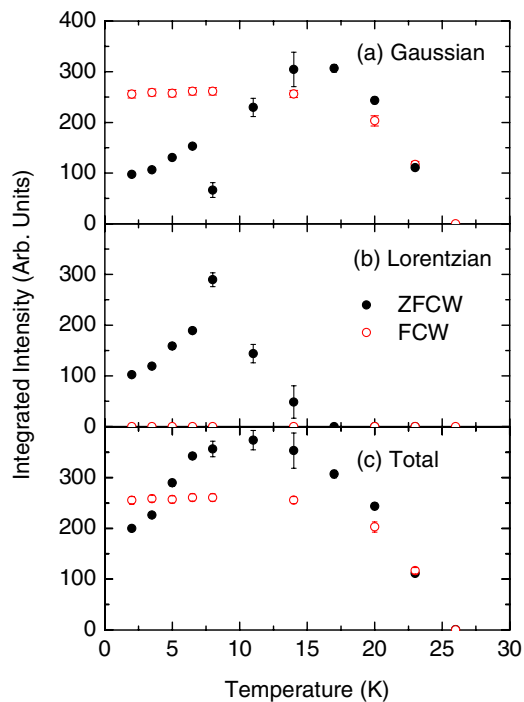


Fig. 6: (Colour on-line) The temperature dependence of the Gaussian and the Lorentzian components as well as of the total integrated intensity of the AFM (100) peak in a field of 0.6 T. The solid symbols show the data taken while warming the sample in field after zero-field-cooling (ZFCW) and the open symbols show the data taken in field while increasing the temperature after field-cooling (FCW).

above this temperature the Gaussian component continues to grow while the Lorentzian component diminishes rapidly. The sharp decrease of the Gaussian component at 8 K indicates that some additional magnetic restructuring is taking place at this temperature, as the fraction of material exhibiting short-range order is at a maximum. For a FC sample the peak shape is largely Gaussian and the short-range magnetic component is absent. At 2 K, the overall intensity of the FC data collected in 0.6 T is higher than the ZFC intensity at the same temperature. The total intensity of the AFM (100) peak for the FC sample decreases monotonically as the temperature is increased and the ZFC and FC data sets crossover below the irreversibility temperature before coming together again at temperatures close to  $T_N$ .

Similar measurements made in fields of 1.8 T and 3 T (not shown) gave comparable results for the behaviour of the short-range and long-range components of the magnetic order in  $\text{Ca}_3\text{Co}_2\text{O}_6$ .

From inspection of fig. 6 it is obvious that, for a ZFC sample, the total intensity of the main AFM peak at base temperature is significantly lower than at 12 K. Therefore, the presence of short-range correlations cannot fully account for the anomalous dip in the intensity of the AFM peaks at low temperatures as some intensity is still missing.

**Conclusions.** – The temperature and magnetic-field dependence of both the FM and the AFM reflections in  $\text{Ca}_3\text{Co}_2\text{O}_6$  have been studied using single-crystal neutron-diffraction. The use of a larger sample, and an instrument with a better resolution and a lower intrinsic background compared to previous measurements [25], have enabled the first observation of changes in the intensity of magnetic peaks at each of the values of applied magnetic field where a step is seen in the bulk magnetisation. Using a microscopic probe the temperature and field dependences of the FM peaks have been confirmed to mirror those previously reported in the bulk magnetisation data.

At low temperatures, the application of magnetic fields of up to 5 T does not lead to the complete disappearance of the intensity on the AFM peaks and the intensity of these peaks is not restored by the subsequent removal of the field. It is shown that the magnetic states for a ZFC sample and a sample that has previously been exposed to a high magnetic field are completely different on a microscopic level. Pronounced history dependence of the intensity of both the FM and the AFM peaks has also been observed.

The magnetic-field dependence of the short-range correlations in  $\text{Ca}_3\text{Co}_2\text{O}_6$ , which in this study are reflected in the line shape and intensity of the AFM peaks, has also been measured for the first time. Both long-range and short-range correlations decrease in a stepwise fashion as the magnetic field is increased. We have shown that there is no change in the degree of magnetic disorder at fields of 1.2 and 2.4 T, where the bulk magnetisation shows steps. We have also shown that the increase in volume of the material with short-range order cannot completely account for the loss in intensity from the AFM peaks seen as the temperature is reduced well below  $T_N$ , and an alternative explanation of the low-temperature intensity dip is still required.

In summary, we have made careful measurements of the microscopic magnetic behaviour of  $\text{Ca}_3\text{Co}_2\text{O}_6$  in an applied magnetic field. The authors hope the new detail provided by this study will guide the current theoretical efforts in pursuit of a full description of the magnetic order in  $\text{Ca}_3\text{Co}_2\text{O}_6$ .

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