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Specific heat and magnetization study on single crystals of the frustrated quasi-one-dimensional oxide $Ca_3Co_2O_6$

V. Hardy and S. Lambert
Laboratoire CRISMAT, UMR 6508, Boulevard du Maréchal Juin, 14050 Caen Cedex, France

M. R. Lees and D. McK. Paul
Department of Physics, University of Warwick, CV4 7AL, Coventry, United Kingdom

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Specific heat and magnetization measurements have been carried out under a range of magnetic fields on single crystals of $Ca_3Co_2O_6$. This compound is composed of Ising magnetic chains that are arranged on a triangular lattice. The intrachain and interchain couplings are ferromagnetic and antiferromagnetic, respectively. This situation gives rise to geometrical frustration, that bears some similarity to the classical problem of a two-dimensional Ising triangular antiferromagnet. This paper reports on the ordering process at low T and the possibility of one-dimensional features at high T.

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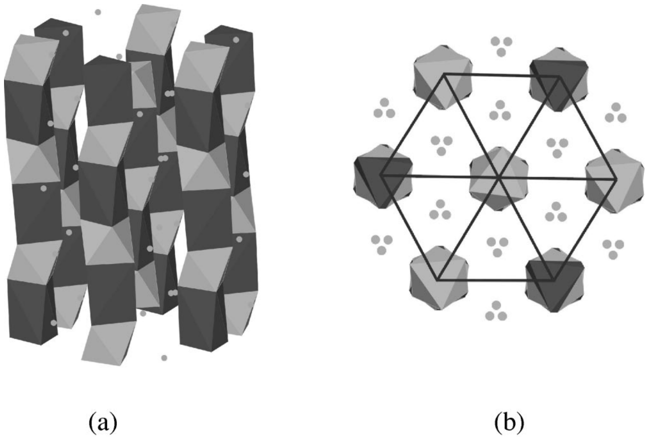
I. INTRODUCTION

$Ca_3Co_2O_6$ belongs to a large family of compounds of general formula A'_3ABO_6, with Ca, Sr, or Ba on the A' site, while the A and B sites can be occupied by a great variety of cations including many transition-metal elements.[1] The rhombohedral structure of these compounds consists of $[ABO_6]_\infty$ infinite chains running along the c axis of the corresponding hexagonal cell, with the A' cations located in between them (see Fig. 1). These chains are made of alternating, face-sharing AO_6 trigonal prisms and BO_6 octahedra. Each chain is surrounded by six equally spaced chains forming a triangular lattice in the *ab* plane. The intrachain A-B separation is quite small, whereas the interchain distance is approximately twice that distance (for example about 2.6 and 5.2 Å, respectively, in the case of $Ca_3Co_2O_6$).[2] Reinforcing this geometrical anisotropy, the oxygen atoms along the chains can efficiently mediate the intrachain coupling, whereas the A' cations play no role in the interchain coupling. Therefore, these compounds are expected to display pronounced one-dimensional (1D) magnetic character.

Amongst this family, $Ca_3Co_2O_6$ has attracted special interest in recent years due to its very peculiar magnetic properties.[3–6] According to the most recent studies,[5,6] both the cobalt ions in this compound are trivalent, but as they are subject to different crystalline electric fields (CEFs), the Co ions are in different spin states. As pointed out by Aasland *et al.*,[3] the CEF-induced splitting of the $3d$ orbitals produces a gap between a lower triplet and an upper doublet that is larger in an octahedral environment than in a prismatic one. As a consequence, the $3d^6$ configuration of Co^{3+} can produce a high-spin state $(S=2)$ on the prismatic site and a low-spin state $(S=0)$ on the octahedral site. Although indisputable evidence is still absent, this scenario is the most consistent with the neutron-diffraction data and the magnetic measurements that are available at the present time.[3–6] At high temperatures, it must be borne in mind that the situation may be complicated by a progressive transition from the low-spin state to the intermediate-spin state $(S=1)$ and/or the high-spin state.[6]

The previous studies on $Ca_3Co_2O_6$ have established several basic features about the Co-Co interactions in this compound: (i) a strong Ising character,[7] with the spins oriented along the chain axis; (ii) a ferromagnetic intrachain coupling; (iii) an antiferromagnetic (nearest-neighbor) interchain coupling. Such features, combined with the triangular arrangement of the chains on the *ab* plane, give rise to a prototypical situation of geometrical frustration. $Ca_3Co_2O_6$ is also reported to exhibit peculiar magnetic behavior, especially in $M(H)$ curves.[3–6] For instance, a sequence of irreversible metamagnetic transitions take place at very low T (<5 K), in the so-called frozen spin state, while there is a sharp ferrimagnetic-to-ferromagnetic transition at intermediate temperatures around 10 K. Complex phase diagrams have been proposed.[4,6] Some features of these phase diagrams are still the subject of controversy. One of the most debated issues deals with the ordering process under zero or low field.



(a) (b)

FIG. 1. Schematic drawings of the structure of A'_3ABO_6-type compounds. The dark and light polyhedra represent AO_6 trigonal prisms and BO_6 octahedra, respectively. The shaded circles denote A' atoms. (a) Perspective view showing the $[ABO_6]_\infty$ chains running along the hexagonal c axis. (b) Projection along the hexagonal c axis. Solid lines emphasize the triangular arrangement of the chains in the *ab* plane.

Kageyama *et al.*[4] have proposed a scenario similar to the one developed by Mekata *et al.*[8,9] for $CsCoCl_3$ (antiferromagnetic Ising chains, antiferromagnetically coupled on a triangular lattice).[10] Upon cooling, this model predicts an initial transition to a partially disordered antiferromagnetic (PDA) state, in which two-thirds of the chains are antiferromagnetically coupled while the last third remains incoherent,[11] followed by a second transition to a ferrimagnetic state at lower T. Whether this scenario is applicable to the case of $Ca_3Co_2O_6$ has recently been questioned.[6,12] To date no specific heat measurements have been performed on this compound, although such thermal data would be valuable in understanding the physics of this material.

In this paper, we report on specific heat measurements under an applied magnetic field, carried out on $Ca_3Co_2O_6$ single crystals. The magnetic field has allowed us to investigate the ordering process in the various magnetic states adopted by this material: disordered antiferromagnetic, ferrimagnetic, and ferromagnetic. Such a study had to be carried out on single crystals due to the highly anisotropic properties of this compound.[5,6] This paper is organized as follows. Section II is devoted to experimental details, and in particular details of the single-crystal alignment procedure and the subtraction of the lattice contribution to the specific heat. Section III reports the specific heat data under zero field and large magnetic fields, along with the corresponding magnetization measurements. The results are discussed in Sec. IV and our conclusions are presented in Sec. V.

II. EXPERIMENTAL DETAILS

Single crystals were grown using a flux method described previously.[6] This method yielded needlelike crystals—similar to those used for magnetic measurements in Ref. 6—along with other specimens that have an aspect ratio that is more suitable for specific heat measurements. These latter crystals have the shape of short hexagonal rods terminating in three diamondlike faces at each end. Their small size ($0.7\times0.7\times1\ \mathrm{mm}^3$) makes it difficult to get reliable specific heat data on only one crystal. We have used a set of four crystals with a total mass of 10.64 mg. Magnetic measurements carried out on each crystal verified the good homogeneity of this assembly.

All magnetic and specific heat measurements reported in this paper were recorded with the magnetic field along the c axis of the crystals. The crystals were aligned using the following procedure: (i) at 300 K, the four crystals were put into a small amount of Apiezon N grease (contained in a gelatine capsule, or on the measuring platform, for magnetization or specific heat, respectively); (ii) a magnetic field of 5 T is then applied. Owing to the substantial magnetic anisotropy persisting up to room temperature in this compound, the samples experience a torque which tends to align their c axis along the direction of the applied field. We checked that 5 T is large enough to rotate our crystals in Apiezon N at 300 K, a temperature at which this grease has a low viscosity; (iii) the samples are then slowly cooled under 5 T down to 150 K. This ensures the field alignment is maintained through the glass transition of Apiezon N grease that occurs around 230 K;[13] (iv) at 150 K, the grease is solid enough to hold the samples in position without a magnetic field, while the temperature is still above the magnetic transitions of the compound. The field is reduced to zero, and the cooling is resumed to prepare the samples in a zero-field-cooled (ZFC) state. The quality of the alignment obtained by this method was demonstrated by the sharpness of the ferrimagnetic-to-ferromagnetic transition and the magnetization values at the associated plateaus.

The specific heat measurements were carried out by a two-tau relaxation method (Physical Property Measurement System, Quantum Design) with magnetic fields up to 5 T and temperatures down to 2 K. A background signal (platform and grease) was recorded versus temperature under each field investigated. Magnetization measurements were carried out on the same set of crystals, by means of a superconducting quantum interference device magnetometer (Magnetic Property Measurement System, Quantum Design), with magnetic fields up to 5 T and temperatures down to 2 K.

In order to subtract the lattice contribution to heat capacity, a nonmagnetic isostructural compound was synthesized. A ceramic sample of Ca_4PtO_6 was prepared from a stoichiometric mixture of CaO and PtO_2. These starting materials were pelleterized in the form of bars and heated in a evacuated silica ampoule at 800 °C for 12 h. X-ray diffraction verified the single phase of the Ca_4PtO_6 compound, and confirmed that this material has the same rhombohedral structure as $Ca_3Co_2O_6$. In Ca_4PtO_6, the Ca^{2+} cations occupy the trigonal prisms, while the $Pt^{4+}(3d^6)$ on the octahedral sites are supposed to be in a low-spin state ($S=0$) due to a large CEF-induced gap. To check this point, magnetic measurements were performed between 2 and 300 K, leading to a susceptibility of the form $\chi=\chi_0+C/T$, with $C=0.001\,51\ \mathrm{emu\,K\,mol^{-1}}$. This Curie constant is about 0.05% of the value expected for high-spin Pt^{4+} ($S=2$), and 0.15% of the value expected for intermediate spin Pt^{4+} ($S=1$). This result ensures that the specific heat data of Ca_4PtO_6 (up to 300 K) do not contain a significant magnetic contribution from the electronic spins. Furthermore, the data down to 2 K for both compounds reveal no contribution from a Schottky term related to nuclear level splitting. Finally, one can also safely discard the presence of a significant electronic term in these compounds owing to their poor electrical conductivity.[6,14] One can thus consider that the specific heat of $Ca_3Co_2O_6$, in the range 2–300 K, is made up of two terms: $C(T)=C_L(T)+C_M(T)$, where C_L is the lattice contribution related to phonon excitations, while C_M is the magnetic term that we are interested in.

The contribution $C_L(T)$ of $Ca_3Co_2O_6$ can be derived from the total specific heat $C'(T)$ of Ca_4PtO_6, but the difference in molecular weight between the two compounds must be taken into account. There is no generally accepted method to do this, and some approximations have to be made. Within the framework of the Debye approach, the lattice contribution is determined only by the ratio θ/T, where θ is the Debye temperature, which depends on the structure and the mass of the constituent atoms.[15] Accordingly, the correction of mass amounts to the determination of the ratio $r=\theta/\theta'$, where θ and θ' are the Debye temperatures of $Ca_3Co_2O_6$ and Ca_4PtO_6, respectively. Since θ in the basic

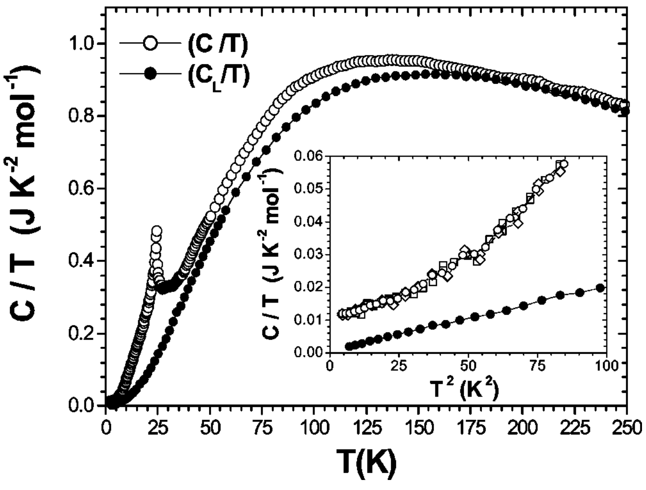


FIG. 2. Total specific heat (C) and lattice contribution (C_L) in $Ca_3Co_2O_6$ under zero field. The inset shows the low-T range in a C/T-vs-T^2 plot, with three separate runs for $C(T)$.

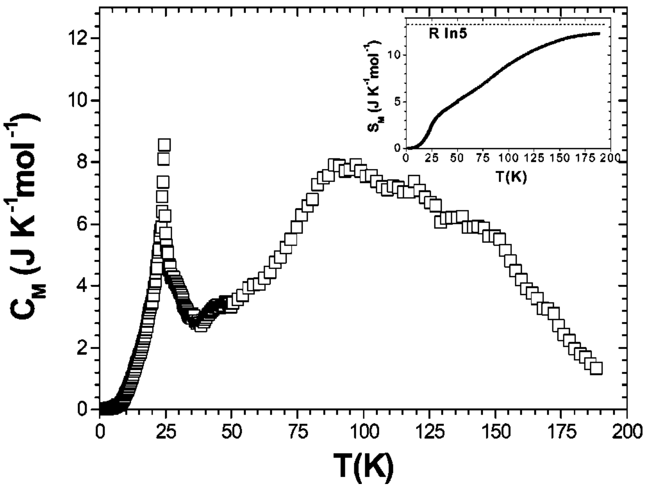


FIG. 3. Temperature dependence of the magnetic specific heat in zero field. The inset shows the calculated magnetic entropy as a function of temperature, along with the expected total value $R\ln 5$ (dashed line).

monoatomic model is inversely proportional to the square root of the mass, one can get a first estimate by using the molecular weights, leading to $r \simeq \sqrt{M(Ca_4PtO_6)/M(Ca_3Co_2O_6)} = 1.16$. A more sophisticated method based on the principle of corresponding states has been developed by Stout and Catalano.[16] This technique is based on the comparison of the specific heat data at high temperatures for the magnetic and the reference compounds. It has the great advantage of accounting for a temperature dependence in the parameter r, but, on the other hand, it requires an extrapolation of r in the low-T range (below about 190 K in our case) which introduces a significant uncertainty. Following the extrapolations proposed in Ref. 16, we found $r \sim 1.15$ at low T. In the present study, we also have the opportunity to derive an experimental estimate of r by analysing the low-temperature dependence of the specific heat data. Indeed, the lattice contribution is reduced to a term $\beta_3 T^3$ at low temperature, with $\beta_3 \propto (1/\theta)^3$. In a C/T-vs-T^2 plot, both the curves of $Ca_3Co_2O_6$ and Ca_4PtO_6 exhibit a linear regime at low T from which one can extract β_3 values leading to $r \simeq [\beta_3(Ca_4PtO_6)/\beta_3(Ca_3Co_2O_6)]^{1/3} = 1.13$.

In the analysis presented hereafter, we chose to retain this latter value, which appeared to us as the best compromise between simplicity and reliability. However, we will take the uncertainty on the r value into account when discussing the comparison of $C_M(T)$ with theoretical predictions (Sec. IV B). Since one can write $C_L(T) = C'(T/r)$ within the framework of the Debye model, the lattice contribution of $Ca_3Co_2O_6$ has been derived by multiplying the temperature values of the total specific heat data $C'(T)$ of Ca_4PtO_6 by $r = 1.13$.

III. RESULTS

Figure 2 shows the total specific heat versus temperature for $Ca_3Co_2O_6$ measured under zero field, along with the estimated lattice contribution obtained by using the procedure described above. The main feature is a prominent peak in the raw data around 25 K, indicative of a long-range ordering (LRO). It can also be observed that the total specific heat $C(T)$ tends to merge with the lattice contribution $C_L(T)$ at high T. The inset displays an enlargement of the low T portion of the data as a C/T-vs-T^2 plot. Three separate runs are shown together, which illustrate the good reproducibility of the $C(T)$ data. This plot also shows that the lattice term has a simple cubic temperature dependence ($C_L = \beta_3 T^3$), as expected for such contributions. We found $\beta_3 \simeq 3 \times 10^{-4}\ \mathrm{J\,K^{-4}\,mol^{-1}}$, leading to a Debye temperature $\theta \simeq 415$ K. Beside this lattice term, the specific heat of $Ca_3Co_2O_6$ exhibits a linear contribution γT ($\gamma \simeq 10\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$), and one can see the development of magnetic excitations above ~7 K.

Figure 3 shows the magnetic part of the specific heat, $C_M(T) = C(T) - C_L(T)$, under zero field. Beyond the sharp peak around 25 K,[17] there is a broad bump at higher temperatures. Because of increased scatter in the data at high T, which is further enhanced by the subtraction procedure, the curve has been cut above 200 K. The inset shows the temperature dependence of the magnetic entropy $S_M(T) = \int_0^T (C_M/T)dT$. The peak in $C_M(T)$ at 25 K yields a significant change in the rate of entropy variation around this temperature. It should be noted that the entropy at the LRO transition, $S_M(25\ \mathrm{K})$ is equal to 18% of the total magnetic entropy. This small value is consistent with the expected behavior in a 1D system.[18] One can also note that S_M at high T tends to saturate just below the expected value for one cobalt of spin 2 per formula unit ($R\ln 5$).

Before showing the specific heat results under magnetic field, let us consider the corresponding magnetization data. Figure 4 shows an enlargement of dc susceptibility curves for an applied field of 0.1, 2, and 5 T, and focuses on the region around the transition at 25 K. In both 2 and 5 T, one observes a small difference between the zero-field-cooling (ZFC) and field-cooling (FC) curves at very low T ($T < 5$ K), a behavior which is consistent with the large hysteresis displayed by the $M(H)$ curves in the same temperature range.[4–6] Above this irreversible regime, the low-T plateaus

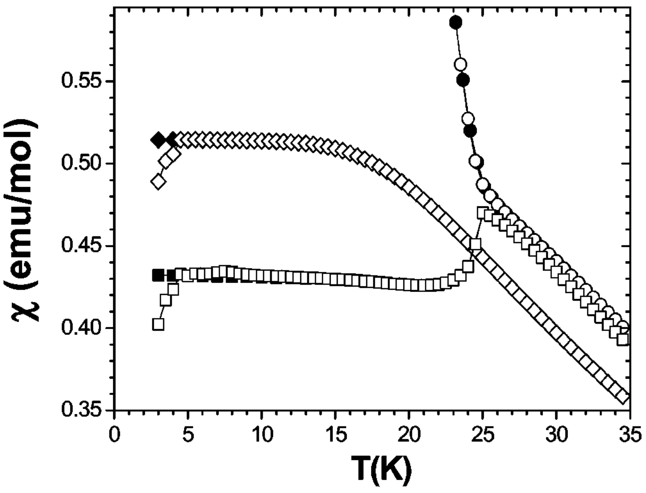


FIG. 4. Temperature dependence of the dc susceptibility under 0.1 T (circles), 2 T (squares), and 5 T (diamonds), in the ZFC (open symbols) and FC (closed symbols) modes. The field is applied along the *c* axis (direction of the chains and of the spins).

of the curves under 2 and 5 T correspond to magnetizations equal to $M_S/3$ and M_S, respectively, where M_S is the full spin polarization.[19] This is consistent with the ferrimagnetic and ferromagnetic natures of the low-*T* states in 2 and 5 T, respectively, that have been reported previously.[3–6] Let us now turn to the corresponding specific heat data recorded in 0, 2, and 5 T after ZFC. Even below 5 K, no significant hysteresis could be detected between the ZFC and the FC curves in the $C(T)$ data. Furthermore, we checked that there is no difference between the $C(T)$ curves recorded under 0 or 0.1 T. Figure 5 shows the $C_M(T)$ curves under field which were derived by subtracting $C_L(T)$ from the raw data.

The 2-T data exhibit a very large, lambdalike peak at 25 K. It must be emphasized that the height of this peak is much larger than that found under 0 T. In 5 T, there is only a smooth bump around 25 K. This is consistent with the expected behavior for a long-range ferromagnetic transition in a large field. In the low-*T* regime, one observes that the 2-T curve lies well below the data collected with no field applied. One can get a better insight into this low-*T* range by considering the temperature dependence of the magnetic entropy as displayed in Fig. 6(a). The curves for 0 and 2 T are close to each other below about 7 K and above T_N. In the intermediate range, the entropy in 0 T is much larger than in 2 T.

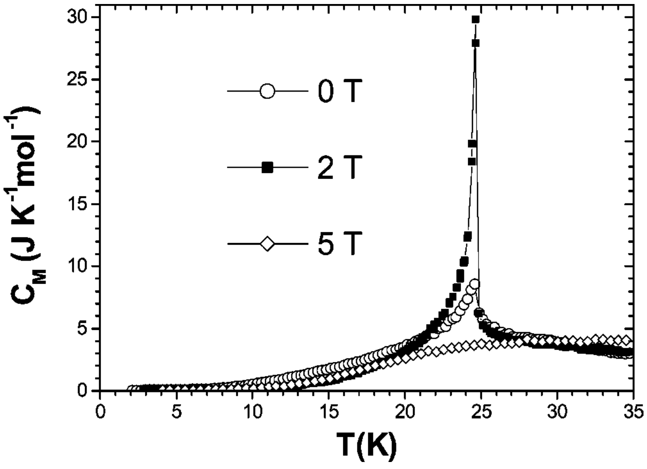


FIG. 5. Temperature dependence of the magnetic specific heat in 0 T (circles), 2 T (squares), and 5 T (diamonds). The field is applied along the *c* axis (direction of the chains and of the spins).

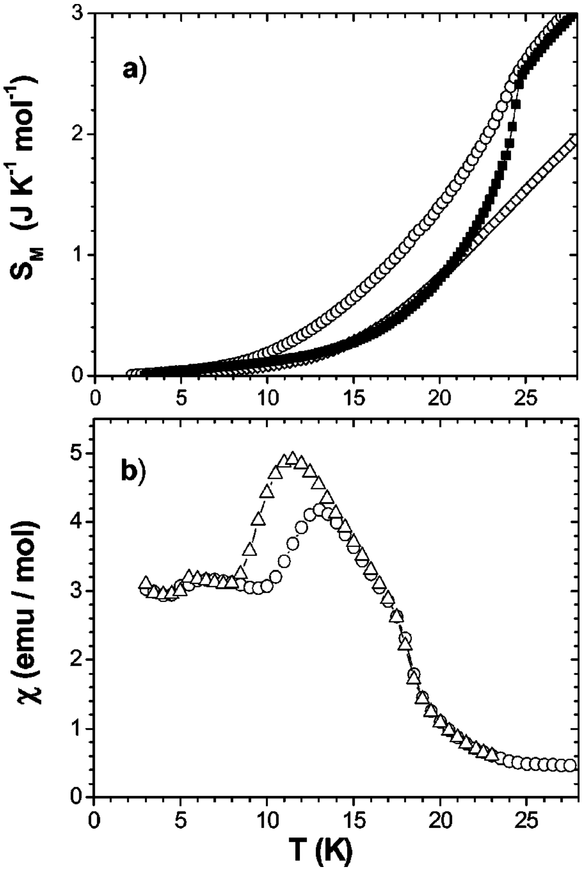


FIG. 6. (a) Temperature dependence of the magnetic entropy in 0 T (circles), 2 T (squares), and 5 T (diamonds). The field is applied along the *c* axis (direction of the chains and of the spins); (b) temperature dependence of the ZFC susceptibility under 0.1 T (applied along the *c* axis) for two values of waiting time after each temperature stabilization: 5 sec (circles) and 600 sec (triangles).

Figure 6(b) shows the ZFC susceptibility curves in the same temperature range, that were recorded under 0.1 T with a waiting time t_W after each temperature stabilization equal to either 5 or 600 sec. Although $\chi(T)$ starts increasing abruptly at T_N (see also Fig. 4), the maximum slope in the ZFC curves is actually found at ~18 K. In between 18 and 8 K, the ZFC curve exhibits a pronounced relaxation effect. Below 8 K, $\chi(T)$ becomes time independent and is roughly constant down to 2 K.

IV. DISCUSSION

A. Ordering process under low field

In the literature on $Ca_3Co_2O_6$, the existence of two critical temperatures at T_{C_1} ($\simeq$25 K) and T_{C_2} ($\simeq$10 K) has often been invoked: the first has been associated with a ferromagnetic intrachain transition, while the second is identified with an antiferromagnetic transition between the ferromagnetic chains. One of the main pieces of information provided directly by our specific heat investigations is the sharp peak observed at 25 K in the $C(T)$ data under zero field. This feature clearly demonstrates the occurrence of a collective magnetic transition. Since it is well known that such long-range ordering (LRO) cannot take place in one dimension, this feature cannot be ascribed to a ferromagnetic transition along the chains. The scenario described above is thus inconsistent with the specific heat data. We propose that there is a collective transition at $T_N \simeq 25$ K corresponding to an antiferromagnetic coupling between the chains. Note that this is consistent with the emergence of antiferromagnetic Bragg peaks around 25 K in neutron-diffraction data.[3] However, the entropy jump associated with this transition shows that the antiferromagnetic ordering is far from being complete. At the same time, the development of a long-range interchain ordering, even if it is partial, can reduce the magnetic fluctuations along the chains. This could explain why the antiferromagnetic ordering at T_N is accompanied by a sudden increase of the susceptibility.

The existence of a LRO transition at a rather high temperature in $Ca_3Co_2O_6$ emphasizes a clear departure from the pure Ising triangular antiferromagnet which has a totally frustrated ground state.[20–22] One of the most likely origins for such a lifting of degeneracy is the influence of next-nearest interchain interactions.[23] Some studies of $Ca_3Co_2O_6$ proposed a scenario involving a PDA (partially disordered antiferromagnetic) state,[4,5] which implies antiferromagnetic (AF) nearest-neighbor coupling and ferromagnetic (FM) next-nearest-neighbors coupling. In this model, the decrease of temperature first induces a transition at T_{N1} to a PDA state, followed at T_{N2} by a transition to a ferrimagnetic state.[8,9] This process is supposed to give rise to a smooth peak in specific heat at T_{N1} and a large one at T_{N2}. This is in contrast with our experimental results in $Ca_3Co_2O_6$, since we observed a sharp peak at the first transition, while no additional peak exists at lower temperatures. It should be noted, however, that even in the ABX_3 compounds ($A = $Cs, Rb, and $B = $Co) for which this model was developed, the specific heat data do not show clear support for the theoretical expectations.[24–26] It was argued that the transition to ferrimagnetism might be prevented by the establishment of a glassy phase at low temperatures.[27] In $Ca_3Co_2O_6$, this latter phase could be the frozen spin state which was found in magnetization studies.[4–6] Our specific heat measurements show that the transition to the frozen spin state ($T_{FS} \simeq 7$ K) is associated with a noticeable change of regime in a C/T-vs-T^2 plot (see inset of Fig. 2). In the low-T regime, the specific heat exhibits a linear term with $\gamma \simeq 10\ \mathrm{mJ\,K^{-2}\,mol^{-1}}$. Such a feature is usually found in spin glasses[28] and in other disordered magnetic systems such as mixed-valent manganites.[29,30] We can thus speculate that this linear contribution reflects the disorder that remains in the chain system of $Ca_3Co_2O_6$ at low T.

As for the shape of the peak at T_{N1}, it was found that it could vary considerably with the level of frustration.[27] Depending on the signs and respective values of the first, second, and third neighbor interactions in a 2D Ising triangular antiferromagnet, Monte Carlo simulations showed that a large variety of $C(T)$ curves can be expected, including a single large peak at T_{N1}. Our observations are thus consistent with such a generalized PDA scenario, while they seem to rule out the standard picture proposed earlier.[4,5]

The specific heat measurements provide us with information about the entropy variation in between T_{FS} and T_N. In an applied field of 2 T, $Ca_3Co_2O_6$ undergoes a transition from a disordered state (system of uncoupled chains) to a ferrimagnetic state. The specific heat data exhibit a very large, sharp peak at T_N, which is much more pronounced than under zero field. The magnetic entropies calculated at T_N, however, are found to be the same under both fields. Therefore the magnetic field only affects the way the entropy evolves below T_N. In an applied field of 2 T, the magnetic phase at low temperature is well ordered (ferrimagnetic state), so there is a sudden large release of entropy just around T_N. In contrast, the transition under zero field is more progressive. Although there is a noticeable change of entropy at T_N, it is much smaller than under 2 T, and the entropy is progressively reduced as the temperature is decreased further. The difference between the $S(T)$ curves under 0 and 2 T can give direct insight into the large magnetic disorder that persists far below T_N under zero field. Upon cooling below T_N, the slow decrease of entropy in zero field is interrupted by the spin freezing at $T_{FS} \simeq 7$ K. This is also the temperature at which the $S(T)$ curves at 0 and 2 T are found to merge onto each other.

Another aspect of this ordering process is revealed by magnetization data at low field, which showed that a pronounced relaxation effect takes place below T_N. This effect starts above T_{FS}, which is consistent with the fact that one cannot expect significant effects over short time scales (i.e., 600 sec) in a frozen spin state. This large relaxation effect [Fig. 6(b)] indicates that the magnetic disorder revealed by the specific heat measurements [Fig. 6(a)] evolves with time. This behavior is probably related to the frustration and the slow dynamics associated with spin reversals in ferromagnetic chains.[5,6]

B. Broad maximum at high temperature

Another striking feature of the magnetic contribution to the specific heat is the existence of a broad maximum at high temperatures, well above T_N. Actually, such a result is theoretically expected in a 1D magnetic compound, owing to the development of short-range ordering along the chains.[18] From an experimental point of view, however, there are not so many reports on such features, in particular for Ising systems. To our knowledge, the only clear report of such a broad maximum with Ising ferromagnetic chains dealt with $CoCl_2 \cdot 2NC_5H_5$.[31] The temperature of the maximum (T_{max}) in $C_M(T)$ as well as its height (C_{max}) are predicted to increase with the spin value.[18] This could explain why this broad maximum is so visible in our case while it is generally hidden by the LRO transition in Ising systems with smaller spin values. According to theoretical predictions for a Ising system with $S = 2$, one should expect $T_{max} \simeq 3.72J$ and $C_{max} \simeq 1.4R$, where J and R are the intrachain coupling and the gas constant, respectively.[18,32] In our case, C_{max} is found to be close to 8 rather than $1.4R \sim 12\ \mathrm{J\,K^{-1}\,mol^{-1}}$, but it should be noted that C_{max} is quite sensitive to the value of the r parameter used in the subtraction of the lattice contribution (e.g., one finds $C_{\mathrm{max}} \sim 11\ \mathrm{J\,K^{-1}\,mol^{-1}}$ for $r \sim 1.16$). In contrast, T_{max} is found to be essentially independent of the r value in the range 1.13–1.16. This characteristic temperature leads to $J \sim 22$ K, while Kageyama *et al.* reported $J \sim 15$ K from an analysis of the susceptibility at high T.[5] Taking into account that this latter analysis may also contain some uncertainties, one can consider that there is a reasonable overall agreement between the experimental $C_M(T)$ data and the theoretical expectations for short-range excitations in an $S=2$ Ising chain.

It must be emphasized that a totally different phenomenon may contribute to the existence of a broad peak in $C_M(T)$. The cobalt ions in the octahedral sites that are in low-spin (LS) state at low T could change their spin state to high or intermediate spin states (HS or IS) as T is increased. Such a phenomenon is currently the source of intensive debate[33–36] in the case of $\mathrm{LaCoO_3}$, which also contains LS $\mathrm{Co^{3+}}$ on octahedral sites at low T. Rather than a true spin state transition, an increase in temperature can induce a progressive thermal population of the IS and/or HS levels. Such a process will have a pronounced signature in $C_M(T)$, in the form of a Schottky anomaly.[15] Therefore a spin-state crossover, if it occurs, could contribute to the bump seen in specific heat at high T.[37] Accordingly, it is worth noting that the existence of such an additional phenomenon could affect to some extent the analysis of the bump in $C_M(T)$ in terms of pure short-range spin ordering. The interplay between the short-range spin ordering and a possible spin-state crossover must be very complex, and at the present time, it seems difficult to separate the two effects simply on the basis of specific heat and/or magnetization data. It is clear that more direct investigations of the Co spin states in $\mathrm{Ca_3Co_2O_6}$ are required to proceed further with this analysis.

V. CONCLUSION

Our specific heat investigations in $\mathrm{Ca_3Co_2O_6}$ have revealed several features that complement the previous magnetization studies. We have shown that there is a peak at $T_N \simeq 25$ K in $C_M(T)$ under an applied field of 0 and 2 T. This feature clearly demonstrates the occurrence of a long-range ordering associated with the antiferromagnetic interchain coupling. In 5 T, there is no longer a peak in the data, as expected for a ferromagnetic transition in a large magnetic field. In an applied field of 2 T, the ordered state is ferrimagnetic and the peak at T_N is found to be very pronounced. Under zero field, the peak at T_N is significantly reduced; the magnetic entropy displays a smooth, continuous evolution versus temperature below T_N, that is interrupted when entering the frozen spin state around $T_{\mathrm{FS}} \simeq 7$ K. One observes a pronounced crossover in the temperature dependence of $C_M(T)$ around T_{FS}. Below T_{FS}, the specific heat has a linear term (γT) that can be associated with frozen magnetic disorder. It must be emphasized that no additional peak was detected in $C_M(T)$ below T_N, which appears to rule out a ferrimagnetic transition as proposed by some PDA scenarios.[8,9]

Magnetization measurements revealed a noticeable time dependence in the intermediate temperature range between T_{FS} and T_N. The combination of our specific heat and magnetization results demonstrates that the magnetic state below T_N under zero field is still highly disordered and evolves continuously with both temperature and time. This feature probably derives from a combination of geometric frustration and the slow spin dynamics of ferromagnetic chains.

The magnetic heat capacity exhibits a broad maximum at high T which can be related to one-dimensional short-range ordering along the ferromagnetic chains. The fact that only a small fraction ($\simeq 0.18$) of the total magnetic entropy $[R\ln(2S+1)]$ is released up to T_N is consistent with the expectations for a 1D system. It is worth emphasizing that $\mathrm{Ca_3Co_2O_6}$ and a few other compounds of the same family[38] seem to be the only model systems for the case of Ising ferromagnetic chains, antiferromagnetically coupled on a triangular lattice.

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[1] K. E. Stitzer, J. Darriet, and H.-C. zur Loye, Curr. Opin. Solid State Mater. Sci. **5**, 535 (2001).

[2] H. Fjellvåg, E. Gulbrandsen, S. Aasland, A. Olsen, and B. Hauback, J. Solid State Chem. **124**, 190 (1996).

[3] S. Aasland, H. Fjellvåg, and B. Hauback, Solid State Commun. **101**, 187 (1997).

[4] H. Kageyama, K. Yoshimura, K. Kosuge, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **66**, 1607 (1997).

[5] H. Kageyama, K. Yoshimura, K. Kosuge, M. Azuma, M. Takano, H. Mitamura, and T. Goto, J. Phys. Soc. Jpn. **66**, 3996 (1997).

[6] A. Maignan, C. Michel, A. C. Masset, C. Martin, and B. Raveau, Eur. Phys. J. B **15**, 657 (2000).

[7] H. Kageyama, S. Kawasaki, K. Mibu, M. Takano, K. Yoshimura, and K. Kosuge, Phys. Rev. Lett. **79**, 3258 (1997).

[8] M. Mekata, J. Phys. Soc. Jpn. **42**, 76 (1977).

[9] M. Mekata and K. Adachi, J. Phys. Soc. Jpn. **44**, 806 (1978).

[10] M. F. Collins and O. A. Petrenko, Can. J. Phys. **75**, 605 (1997).

[11] The direction of the spins are undetermined both in the *ab* planes *and* along the length of the chain.

[12] S. Niitaka, K. Yoshimura, K. Kosuge, M. Nishi, and K. Kakurai, Phys. Rev. Lett. **87**, 177202 (2001).

[13] M. M. Kreitman, T. Ashworth, and M. Rechowicz, Cryogenics

12, 32 (1972).

[14] B. Raquet, M. N. Baibich, J. M. Broto, H. Rakoto, S. Lambert, and A. Maignan, Phys. Rev. B **65**, 104442 (2002).

[15] E. S. R. Gopal, *Specific Heat at Low Temperatures* (Plenum, New York, 1966).

[16] J. W. Stout and E. Catalano, J. Chem. Phys. **23**, 2013 (1955).

[17] The exact temperature of the peak was found to be 24.7 ± 0.1 K.

[18] L. J. de Jongh and A. R. Miedema, Adv. Phys. **23**, 1 (1974).

[19] From the high-field plateau of ferrimagnetic-to-ferromagnetic transitions around 10 K, we found $M_S \simeq 4.6\mu_B$/f.u. This value, that is slightly larger than those previously reported in the literature, is consistent with one cobalt of spin equal to two per formula unit, with a Landé factor close to 2.3.

[20] G. H. Wannier, Phys. Rev. **79**, 357 (1950).

[21] B. D. Metcalf, Phys. Lett. **46A**, 325 (1974).

[22] Y. Saito and K. Igeta, J. Phys. Soc. Jpn. **53**, 3060 (1984).

[23] Owing to the 3D character of the present situation, such next-nearest interactions could originate from the nearest-neighboring chains but involving magnetic cobalt shifted along the *c* axis.

[24] W. B. Yelon, D. E. Cox, and M. Eibschütz, Phys. Rev. B **12**, 5007 (1975).

[25] K. Amaya, H. Hori, I. Shiozaki, M. Date, M. Ishizuka, T. Sakakibara, T. Goto, N. Miura, H. Kikuchi, and Y. Ajiro, J. Phys. Soc. Jpn. **59**, 1810 (1990).

[26] J. Wang, D. P. Belanger, and B. D. Gaulin, Phys. Rev. B **49**, 12 299 (1994).

[27] T. Takagi and M. Mekata, J. Phys. Soc. Jpn. **64**, 4609 (1995).

[28] J. A. Mydosh, *Spin Glasses: An Experimental Introduction* (Taylor & Francis, London, 1993).

[29] L. Ghivelder, I. Abrego Castillo, M. A. Gusmão, J. A. Alonso, and L. F. Cohen, Phys. Rev. B **60**, 12 184 (1999).

[30] V. N. Smolyaninova, A. Biswas, X. Zhang, K. H. Kim, B.-G. Kim, S.-W. Cheong, and R. L. Greene, Phys. Rev. B **62**, R6093 (2000).

[31] K. Takeda, S. Matsukawa, and T. Haseda, J. Phys. Soc. Jpn. **30**, 1330 (1971).

[32] T. Obokata and T. Oguchi, J. Phys. Soc. Jpn. **25**, 322 (1968).

[33] J. B. Goodenough, J. Phys. Chem. Solids **6**, 287 (1958); R. R. Heikes, R. C. Miller, and R. Mazelsky, Physica (Amsterdam) **30**, 1600 (1964); M. A. Senaris-Rodrigues and J. B. Goodenough, J. Solid State Chem. **116**, 224 (1995); S. Stolen, F. Gronvold, H. Brinks, T. Atake, and H. Mori, Phys. Rev. B **55**, 14 103 (1997).

[34] S. Yamaguchi, Y. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B **53**, R2926 (1996).

[35] C. Zobel, M. Kriener, D. Bruns, J. Baier, M. Grüninger, T. Lorentz, P. Reutler, and A. Revcolevschi, Phys. Rev. B **66**, 020402(R) (2002).

[36] S. Noguchi, S. Kawamata, K. Okuda, H. Nojiri, and M. Motokawa, Phys. Rev. B **66**, 094404 (2002).

[37] Note that the gap values reported in the literature for $LaCoO_3$ (Refs. 34–36) can give rise to a Schottky anomaly in a temperature range consistent with the broad peak in $C_M(T)$ observed in our data.

[38] T. N. Nguyen and H.-C. zur Loye, J. Solid State Chem. **117**, 300 (1995); H. Kageyama, K. Yoshimura, and K. Kosuge, *ibid.* **140**, 14 (1998); S. Niitaka, H. Kageyama, M. Kato, K. Yoshimura, and K. Kosuge, *ibid.* **146**, 137 (1999).