Specific heat investigation of the magnetic ordering in two frustrated spin-chain oxides: $Ca_3Co_2O_6$ and Ca_3CoRhO_6

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Abstract
Specific heat measurements were carried out on the closely related spin-chain oxides $Ca_3Co_2O_6$ and Ca_3CoRhO_6. Both compounds consist of Ising magnetic chains that are arranged on a triangular lattice. The spin coupling along and between the chains is ferromagnetic and antiferromagnetic, respectively. Geometrical frustration is expected from the combination of these magnetic features. The present study reports that the specific heat data of these compounds exhibit similarities in the spin-freezing process at low T, whereas striking differences exist in the antiferromagnetic interchain ordering at higher T. These results are discussed in connection with previous magnetization and neutron diffraction data.

1. Introduction

Low dimensionality and frustration in magnetism continue to attract a lot of interest, since both features are known to yield exotic properties. Compounds of the family A'_3ABO_6 (where A' is Ca or Sr, while A and B are transition metal elements) contain magnetic chains that are arranged on a triangular lattice [1]. Some of these compounds possess an Ising-like character and an antiferromagnetic interchain coupling, giving rise to geometrical frustration. The two such compounds that have received most attention in recent years are $Ca_3Co_2O_6$ [2–5] and Ca_3CoRhO_6 [6–10]. It is worth emphasizing that the intrachain coupling in these compounds is ferromagnetic, in contrast to the case of the triangular Ising spin-chain antiferromagnets $CsCoCl_3$ and $CsCoBr_3$, which have been intensively studied since the 1970s [11].

The members of the A'_3ABO_6 family mentioned above seem to be the first examples of systems with Ising ferromagnetic chains that are antiferromagnetically coupled on a triangular lattice. Complex magnetic ordering can be expected in such a situation, bearing some similarities with the classical problem of 2D Ising triangular antiferromagnets [12]. The next-nearest interactions are known to be able to lift, at least partially, the ground state

degeneracy related to geometrical frustration, allowing some degree of magnetic ordering to occur [13]. As in the earlier studies on $CsCoCl_3$ and $CsCoBr_3$, the existence of a partially disordered antiferromagnetic (PDA) [14] state has been reported for both $Ca_3Co_2O_6$ [3] and Ca_3CoRhO_6 [7, 8]. In the PDA state, two thirds of the chains consist of antiferromagnetically coupled ferromagnetic chains, while the remaining third remain incoherent (disordered chains with zero net magnetization). Note that such a state is very similar to the IOP1 phase found in more recent theoretical work using the three-dimensional generalized six-state clock model [15].

The similarities between the magnetic properties of $Ca_3Co_2O_6$ and Ca_3CoRhO_6 have led to the suggestion that both compounds have similar phase diagrams with the same succession of magnetic states under zero field [3, 7]: a paramagnetic state without order between the chains at high T, a PDA state at intermediate temperature, and a frozen spin (FS) state at low T. Recently, the existence of a PDA state in the case of $Ca_3Co_2O_6$ was questioned [5, 8], while it was supported by neutron diffraction data for the case of Ca_3CoRhO_6 [8]. Furthermore, the distinction made between the PDA state and the FS state was questioned on the basis of magnetic relaxation measurements [10]. To date, there have been no reports of specific heat studies on these compounds. The aim of the present paper is to investigate by specific heat measurements the magnetic ordering process in $Ca_3Co_2O_6$ and Ca_3CoRhO_6, in order to gain a deeper insight into the similarities and differences that exist between these two materials.

2. Experimental details

Ceramic samples of $Ca_3Co_2O_6$ and Ca_3CoRhO_6 were prepared by standard solid state reaction in air. Stoichiometric proportions of CaO, $CoO_{1.38}$ and RhO_2 were intimately ground and heated at $900\,°C$ for a few days with intermediate grindings. Then the powder was pressed in the form of bars and heated for one week at high temperature. This sintering temperature was equal to 1000 and $1100\,°C$ for $Ca_3Co_2O_6$ and Ca_3CoRhO_6, respectively. X-ray analysis confirmed the purity of these samples and showed that both compounds crystallize in the space group $R\bar{3}c$. The cell parameters derived from x-ray powder diffraction at room temperature are $a = 0.907$ nm and $c = 1.038$ nm in $Ca_3Co_2O_6$, while they are $a = 0.919$ nm and $c = 1.071$ nm in Ca_3CoRhO_6. These values are consistent with previously published results for these compounds [2, 6].

In the A'_3ABO_6 family, the A cation is on a trigonal prismatic site, while B is on an octahedral site (see figure 1). Owing to their different crystalline electric field (CEF) environments, the former site favours high spin states, whereas the latter favours low spin states [2]. In Ca_3CoRhO_6, the Co atoms occupy the prismatic sites and the Rh atoms the octahedral sites [6]. The valence state of the transition elements in these compounds is still subject to controversy. In $Ca_3Co_2O_6$, the most likely configuration involves Co^{3+} on both sites, giving rise to $S = 2$ on the prismatic sites and $S = 0$ on the octahedral sites, owing to the CEF effects mentioned above [2–5]. In Ca_3CoRhO_6, the reciprocal susceptibility at high T suggests that one is dealing with Co^{2+} and Rh^{4+}, leading to an alternation between $S = 3/2$ and $1/2$ [6]. Nevertheless, recent neutron diffraction results at low T, as well as electronic band structure calculations, have reported that both transition metal elements of Ca_3CoRhO_6 should be in a trivalent state, giving rise to the same alternation of $S = 0$ and 2 along the chains, as for $Ca_3Co_2O_6$ [8, 16]. All the configurations discussed above are consistent with the fact that the measured saturation magnetization M_S in both compounds is found to be close to $4\,\mu_B/fu$ [2, 7].

A ceramic sample of Ca_3CaPtO_6 was used as a non-magnetic reference in the specific heat analysis. It has been prepared from a stoichiometric mixture of CaO and PtO_2 that was
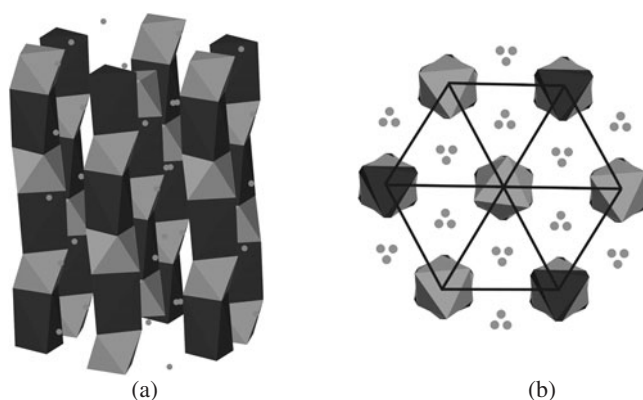
Figure 1. Schematic drawings of the structure of A'_3ABO_6-type compounds. The dark and light polyhedra represent AO_6 trigonal prisms and BO_6 octahedra, respectively. The shaded circles denote A' atoms. (a) Perspective view showing the $[ABO_6]_\infty$ chains running along the hexagonal c-axis. (b) Projection along the hexagonal c-axis. Solid lines emphasize the triangular arrangement of the chains in the ab plane.

pelletized in the form of bars and heated in a evacuated silica ampoule at 800 °C for 12 h. In Ca_3CaPtO_6, Pt^{4+} has a $3d^6$ configuration which is supposed to yield a low spin state ($S = 0$) on the octahedral site. Magnetic measurements confirmed that less than 0.15% of the platinum ions in this compound are magnetic.

The specific heat measurements were carried out by a two-tau relaxation method (PPMS, Quantum Design). In order to determine the magnetic contribution to the specific heat (C_M) in each compound, their lattice contributions were derived from the data of Ca_3CaPtO_6 by using an appropriate mass correction. We followed the procedure described by Bouvier *et al* [17] that is based on a rescaling of the Debye temperature. This method is quantitatively correct only at low temperature (below about 50 K in our case). At higher temperatures, one can still be confident in the overall temperature dependence of the magnetic contribution to the specific heat, but the uncertainty in the C_M values increases with T. The magnetization measurements were carried out by means of a SQUID magnetometer (MPMS, Quantum Design).

3. Results and discussion

Figure 2 shows the susceptibility curves for $Ca_3Co_2O_6$ and Ca_3CoRhO_6 in an applied field of 0.1 T that were recorded in the zero field cooled (ZFC) and field cooled cooling (FCC) modes. The high temperature regimes lead to positive Curie–Weiss temperatures, indicative of ferromagnetic intrachain coupling, in agreement with the literature [2, 6]. These Curie–Weiss temperatures were found to be equal to 30 K [2, 3] and 150 K [6] in $Ca_3Co_2O_6$ and Ca_3CoRhO_6, respectively, which indicates that the intrachain coupling J is significantly larger in the latter compound. Figure 2 shows that, for both compounds, χ undergoes a pronounced upturn below a characteristic temperature that is close to 25 and 90 K, for $Ca_3Co_2O_6$ and Ca_3CoRhO_6, respectively. Since long-range ordering does not exist in one-dimension [18], such features cannot simply be attributed to intrachain ferromagnetic transitions. They are connected to the interchain (antiferromagnetic) ordering, in accordance with the emergence of magnetic Bragg peaks found below $T_N = 26$ and 89.9 K, in $Ca_3Co_2O_6$ [2] and Ca_3CoRhO_6 [7], respectively. This shift in T_N indicates that the interchain coupling J' is also larger for Ca_3CoRhO_6 than for $Ca_3Co_2O_6$. A part of the apparent difference in the shape of $\chi(T)$ between $Ca_3Co_2O_6$
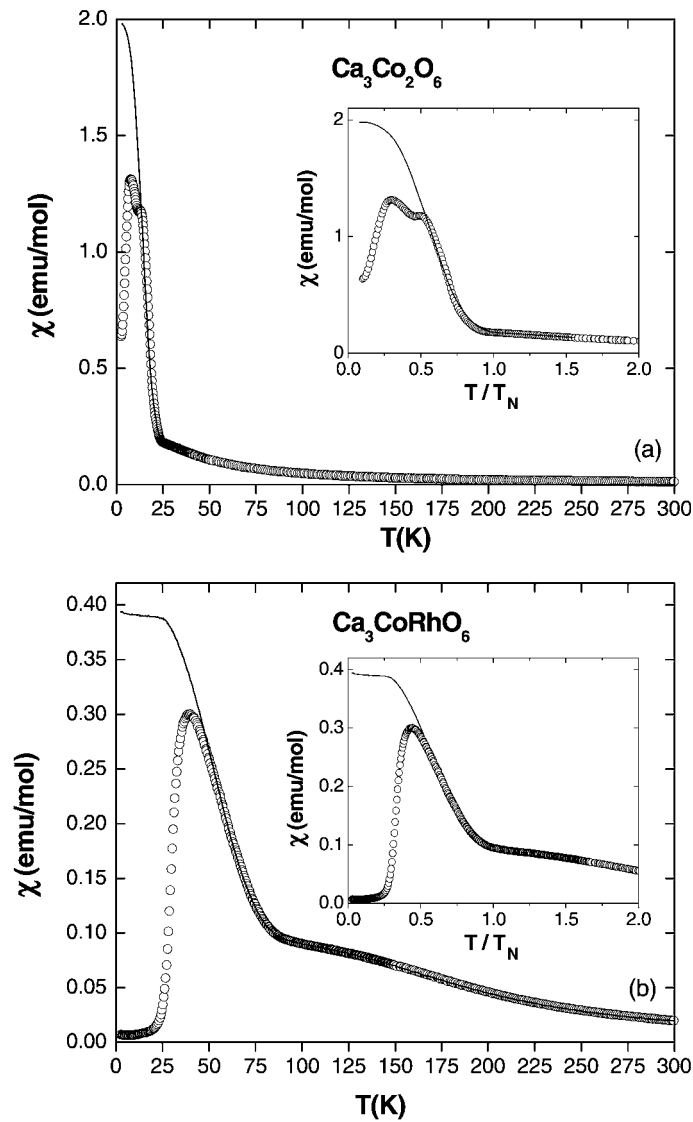
Figure 2. Magnetic susceptibility under 0.1 T in (a) $Ca_3Co_2O_6$ and (b) Ca_3CoRhO_6. The circles and the solid curves correspond to the ZFC and FCC modes, respectively. The insets show enlargements of these curves in reduced temperature scales, T/T_N, with T_N equal to 26 and 90 K in $Ca_3Co_2O_6$ and Ca_3CoRhO_6, respectively.

and Ca_3CoRhO_6 is simply a matter of temperature range. As shown in the insets of figure 2, the data for both compounds look quite similar after rescaling by T_N. In particular, it should be noted that the ZFC and FCC curves for $Ca_3Co_2O_6$ and Ca_3CoRhO_6 all flatten at very low temperatures. This low T regime, that is seen in both compounds, has been ascribed to the onset of an FS state [3] (more specifically a frozen PDA state [7] in the case of Ca_3CoRhO_6).

Beyond these similarities, figure 2 also displays several differences between the two compounds. First of all, the magnetic transitions take place at much higher temperatures in Ca_3CoRhO_6 than in $Ca_3Co_2O_6$, and the susceptibility values are significantly lower in
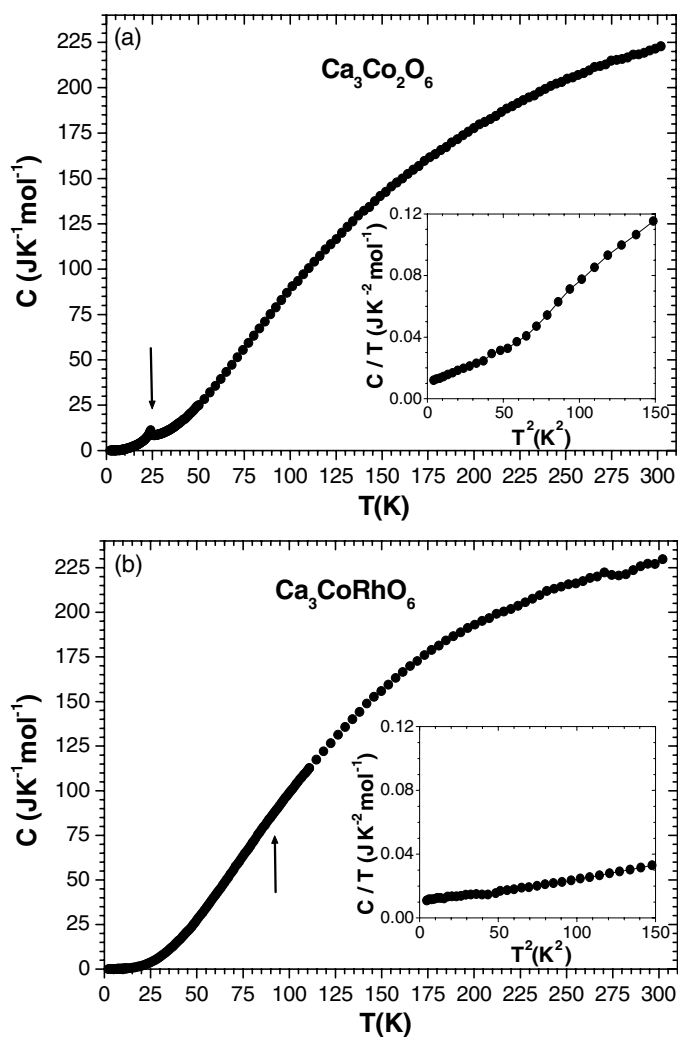
Figure 3. Specific heat under zero field in (a) $Ca_3Co_2O_6$ and (b) Ca_3CoRhO_6. The arrows denote the temperatures of the upturns in $\chi(T)$. The insets display the very low T regimes ($T < 12$ K) in C/T versus T^2 plots.

the former case. The rounding of $\chi(T)$ above T_N is also found to be more pronounced in Ca_3CoRhO_6 than in $Ca_3Co_2O_6$. It should be noted that such a rounding probably originates from fluctuations related to the antiferromagnetic interchain coupling. The second main difference concerns the shape of the ZFC curve which displays a double peak structure in the case of $Ca_3Co_2O_6$[3]. This particular behaviour—which is connected with a marked time dependence [4, 5] of the magnetization in this intermediate temperature range—will be discussed elsewhere.

Figure 3 shows the $C(T)$ curves recorded under zero field in $Ca_3Co_2O_6$ and Ca_3CoRhO_6. This data set points to a fundamental difference between the two compounds: while both compounds exhibit a sudden increase of $\chi(T)$ accompanied by the appearance of Bragg peaks

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[3] Such a feature can also be observed on the susceptibility curves of [2, 3] and [5].

below a characteristic temperature T_N (about 26 and 90 K in $Ca_3Co_2O_6$ and Ca_3CoRhO_6, respectively), *there is a specific heat peak associated with this transition in* $Ca_3Co_2O_6$ *but not in* Ca_3CoRhO_6. Owing to an antiferromagnetic coupling between Ising spin-chains that are arranged on a triangular lattice, the magnetic ordering is expected to be impeded by geometrical frustration effects in these compounds. However, next-nearest-neighbour (nnn) interactions can weaken such frustration effects, allowing the establishment of a long-range ordering [19]. In Ca_3CoRhO_6, a recent neutron diffraction study claimed that the magnetic ordering below $T_N \simeq 90$ K was a true PDA state [8]. This state is expected in the presence of a weak ferromagnetic nnn interaction [14]. It should be noted that a peak in $C(T)$ at the transition from the paramagnetic to the PDA state has never been observed in $CsCoCl_3$, despite the fact that this compound is supposed to be a prototypical example of a material exhibiting such a transition [14]. It should be also emphasized, however, that Monte Carlo simulations in the case of pure 2D Ising triangular antiferromagnets demonstrated that the transitions to partially ordered states can have very different signatures in the $C(T)$ data (including prominent peaks) depending on the values of the nnn interactions [19].

Since the partially ordered state below T_N is still poorly understood in the case of $Ca_3Co_2O_6$, one cannot rule out the possibility that the existence of a peak in $C(T)$ for this compound and not for Ca_3CoRhO_6 results from a totally different nature of the ordering process in these two compounds. Nevertheless, this would be surprising given their structural similarity, and it seems more reasonable to expect that the ordering process is qualitatively similar in both materials. In this case, the absence of a peak in specific heat for Ca_3CoRhO_6 should simply be ascribed to a more progressive character of the magnetic transition below T_N. We note that such a continuous character of the transition in Ca_3CoRhO_6 is consistent with the $\chi(T)$ curve that exhibits a smoother upturn below T_N as compared to that observed in $Ca_3Co_2O_6$ (see figure 2)[4]. Similarly, the increase in the amplitude of the antiferromagnetic Bragg peak (100) below T_N appears to be smoother in Ca_3CoRhO_6 than in $Ca_3Co_2O_6$ (see [2] and [7]). In $Ca_3Co_2O_6$, the amplitude of this Bragg peak reaches its maximum value well above half T_N [2], in contrast with the case of Ca_3CoRhO_6 [7]. At this stage, the question of why the magnetic transition is more progressive in Ca_3CoRhO_6 remains. In spite of their structural and electronic similarities, we have already noted that the two compounds clearly differ by their values of the intrachain coupling J, interchain coupling J', and critical temperature T_N (this last parameter being essentially determined by the two previous ones). In a situation of geometrical frustration, as in our case, it is worth noticing that the entropic effects, which tend to impede the ordering process, should be enhanced in the case of Ca_3CoRhO_6 because of the higher T range of the transition. This could spread out the entropy change at T_N so much that no peak would be detected in the $C(T)$ curve. In other respects, the large variations in J and J' that are observed between $Ca_3Co_2O_6$ and Ca_3CoRhO_6 suggest that the nnn interactions may also be different in these two compounds. According to [19], a difference between $Ca_3Co_2O_6$ and Ca_3CoRhO_6 about the values of these latter parameters could play a role in the difference that is observed in the signature of the ordering process in $C(T)$.

Let us now consider the insets of figure 3 that focus on the low temperature regime. A spin-freezing has been reported to occur in both compounds at low T [3, 7]. In addition to the divergence between the ZFC and FC curves, the spin-freezing leads to a large hysteresis in the $M(H)$ curves. This latter phenomenon was reported to take place below ~8 and ~30 K in $Ca_3Co_2O_6$ [4, 5] and Ca_3CoRhO_6 [6], respectively. The C/T versus T^2 plot of $Ca_3Co_2O_6$ shows a clear change of regime below ~8 K that can be associated with this crossover to the FS state. Because of the low crossover temperature in $Ca_3Co_2O_6$, this feature is directly visible

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[4] Note that this difference remains perceptible in the insets of figure 2 with reduced temperature scales.
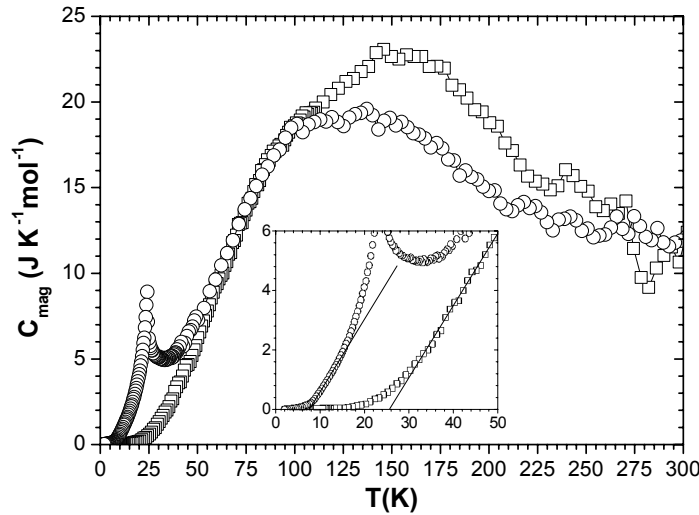
Figure 4. Magnetic contribution to specific heat under zero field, in $Ca_3Co_2O_6$ (circles) and Ca_3CoRhO_6 (squares). The inset is an enlargement of the low T range, with straight lines emphasizing the crossovers found around 8 and 25 K in $Ca_3Co_2O_6$ and Ca_3CoRhO_6, respectively.

in the total specific heat, contrary to the case of Ca_3CoRhO_6 for which the lattice contribution must be removed (see below). Furthermore, the C/T versus T^2 plots in the insets of figure 3 demonstrate the existence of a linear term γT at low temperature, with approximately the same value $\gamma \simeq 10$ mJ K^{-2} mol^{-1} in both compounds. Such a linear term in specific heat is consistent with the magnetic disorder expected in these FS states.

Figure 4 displays the magnetic specific heat of $Ca_3Co_2O_6$ and Ca_3CoRhO_6 in zero field. Apart from the 3D ordering peak in $Ca_3Co_2O_6$, both curves contain a broad maximum at intermediate temperature. Even if the subtraction of the lattice contribution leads to more uncertain values as T is increased, this uncertainty will not remove these features. Such broad maxima are probably related to the development of short-range correlations along the chains, as theoretically expected in 1D systems [18] and experimentally observed in various Ising spin-chain compounds [20]. Figure 4 also reveals that $C_M(T)$ for Ca_3CoRhO_6 exhibits a change in temperature dependence around 25 K. Below $\sim$20 K, $C_M(T)$ takes very small values and then increases rapidly with temperature above $\sim$30 K (see inset of figure 4). This change of regime correlates very well with the sudden increase in the ZFC curve around 25 K which was attributed to the transition from a PDA to an F-PDA state (see figure 2(b)). In $Ca_3Co_2O_6$, there is also a quite good agreement between the large increase in the ZFC curve at low T (centred around 6 K) and the change of regime in $C_M(T)$ around 8 K (see inset of figure 4). The data for both compounds indicate that the crossover to the FS state has a clear signature in the specific heat. On a simple level, one may expect the freezing of the spin configuration to lead to a marked decrease in the value of the specific heat. It must be noted that, for both compounds, the change of regime associated with the crossover between the PDA and F-PDA states is rather gradual.

The application of a magnetic field can profoundly affect the magnetic state in $Ca_3Co_2O_6$ and Ca_3CoRhO_6. On the basis of magnetization measurements [2–5, 7], a ferrimagnetic phase has been reported to occur in both compounds under intermediate fields (e.g. 2 T). In $Ca_3Co_2O_6$, the existence of such a phase is well supported by the plateau found at one third of the saturated magnetization in $M(H)$ curves [2–5]. For Ca_3CoRhO_6, the signature of this

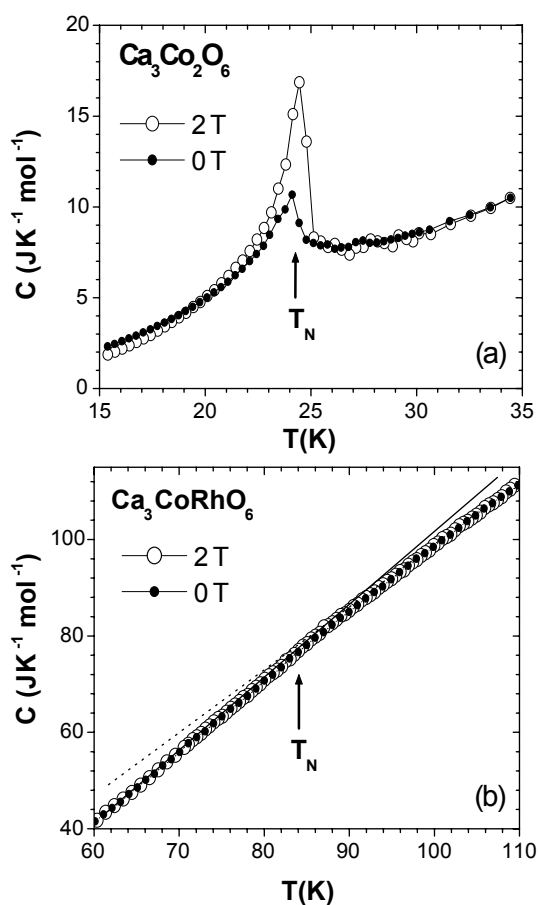**Figure 5.** Temperature dependence of the specific heat of (a) $Ca_3Co_2O_6$ and (b) Ca_3CoRhO_6, around the interchain magnetic ordering (T_N), under 0 and 2 T (solid and empty circles, respectively). The solid and dashed lines in (b) are linear fittings to $C(T)$ below and above 87 K, respectively.

ferrimagnetic transition in magnetization measurements is less clear [7], although a neutron diffraction study claimed the existence of a ferrimagnetic state in a field of 2 T [8]. Figure 5 displays enlargements of $C(T)$ around T_N in 0 and 2 T for both compounds[5]. In $Ca_3Co_2O_6$, one finds a peak in $C(T)$ at 2 T which is even more pronounced than the peak seen in zero field. This is consistent with the fact that the low T phase of the transition is better ordered in 2 T (ferrimagnetism) than in 0 T (disordered antiferromagnetism). In contrast, for Ca_3CoRhO_6 the curves in 0 and 2 T are found to be perfectly superimposed on each other[6]. It must be emphasized that the absence of a peak in $C(T)$ at 2 T for Ca_3CoRhO_6 calls into question the existence of a ferrimagnetic state in this compound. At least, this result eliminates the possibility that there is a simple paramagnetic-to-ferrimagnetic phase transition under field, as is found in $Ca_3Co_2O_6$.

Although there is no peak in 2 or 0 T fields in Ca_3CoRhO_6, one can detect a change in the slope of $C(T)$ around T_N, as illustrated in figure 5(b). This crossover takes place at around

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[5] No noticeable difference could be detected between ZFC and FC measurements under 2 T.

[6] Other $C(T)$ curves recorded under various fields up to 5 T led to the same result.

87 K. This value corresponds well to the kink in $\chi(T)$, and so may be correlated with the beginning of the magnetic ordering. A comparison of figures 5(a) and (b) clearly points to a much smoother magnetic interchain ordering in Ca_3CoRhO_6 than in $Ca_3Co_2O_6$, whatever the field value.

4. Conclusion

Specific heat measurements were carried out for the first time on $Ca_3Co_2O_6$ and Ca_3CoRhO_6, the two most studied members of a new family of spin-chain oxides. Both compounds exhibit peculiar magnetic properties that are related to a specific combination of features: Ising chains arranged on a triangular lattice, with a ferromagnetic intrachain coupling and an antiferromagnetic interchain coupling. Previous magnetization and neutron diffraction studies have shown that the properties of both compounds are similar in many points, as expected from their related magnetic chain structure, but some differences have also been reported [2–10].

The present specific heat study sheds new light on the comparison between these two compounds:

(i) $Ca_3Co_2O_6$ exhibits a peak in $C(T)$ at the beginning of the interchain ordering, while there is no such peak in the case of Ca_3CoRhO_6.
(ii) The crossover to the FS states is visible in the specific heat of both $Ca_3Co_2O_6$ and Ca_3CoRhO_6, below about 8 and 25 K, respectively. The specific heat in these FS states is characterized by a linear term of amplitude close to 10 mJ K^{-2} mol^{-1}.
(iii) In contrast to the situation for $Ca_3Co_2O_6$, the specific heat data for Ca_3CoRhO_6 is not consistent with a clear ferrimagnetic-to-paramagnetic transition around T_N in intermediate fields (e.g. 2 T).

Despite their structural similarity, $Ca_3Co_2O_6$ and Ca_3CoRhO_6 have significantly different intrachain and interchain coupling constants, which take larger values in the latter compound. The origin of such variations between $Ca_3Co_2O_6$ and Ca_3CoRhO_6, as well as their connection with the differences observed in the specific heat and magnetization features of these compounds, remains an open question at the present time.

Acknowledgments

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