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## Magnetic behaviour of $\text{La}_7\text{Ru}_3\text{O}_{18}$

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### Abstract

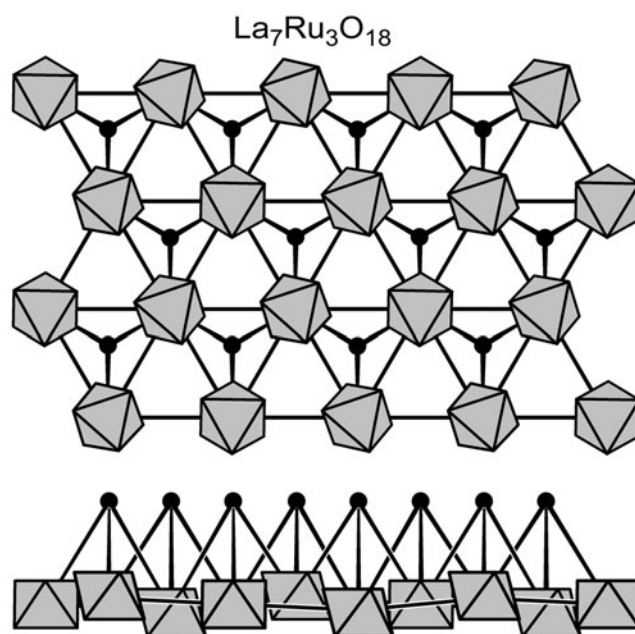
Rhombohedral  $\text{La}_7\text{Ru}_3\text{O}_{18}$  can be considered to be nearly geometrically frustrated due to its close structural similarity to the strongly geometrically frustrated compound  $\text{La}_{4.87}\text{Ru}_2\text{O}_{12}$ . The magnetic ordering of  $\text{La}_7\text{Ru}_3\text{O}_{18}$  was explored using a combination of dc and ac magnetic susceptibility measurements. The magnetic phase diagram shows two different ordering regimes. A low-field magnetic phase occurs at applied fields of 0–3 T and temperatures below 10 K, while a high-field phase is found at fields of 3–5 T and temperatures below 9 K.

### 1. Introduction

The long-range ordering of a compound with antiferromagnetic interactions between spins can be hindered by certain geometric arrangements of the magnetic ions [1]. This phenomenon of geometric frustration is known to occur for a number of different structures with magnetic ions patterned in specific highly symmetric arrangements in two or three dimensions. For two-dimensional structure types, both triangular and Kagomé lattices of magnetic atoms can lead to geometric frustration. Good examples of frustration due to triangular lattices can be found in delafossite-type compounds such as  $\text{LiCrO}_2$  [2] and  $\text{NaTiO}_2$  [3], while frustration has been extensively studied in Kagomé lattice compounds such as  $\text{SrCr}_8\text{Ga}_4\text{O}_{12}$  [4] which crystallize in the magnetoplumbite structure. Although a greater degree of lattice complexity has been observed for three-dimensional geometrically frustrated antiferromagnets, the basic building blocks of these 3D lattices are triangles and tetrahedra. Some compounds that are frustrated because of their three-dimensional lattice are the garnet  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  [5], the spinel  $\text{ZnCr}_2\text{O}_4$  [6], the FCC compound  $\text{K}_2\text{IrCl}_6$  [7], and the pyrochlore  $\text{Dy}_2\text{Ti}_2\text{O}_7$  [8].

$\text{La}_7\text{Ru}_3\text{O}_{18}$  has a rhombohedral structure closely related to that of monoclinic  $\text{La}_{4.87}\text{Ru}_2\text{O}_{12}$ , a compound previously reported to be a strongly geometrically frustrated

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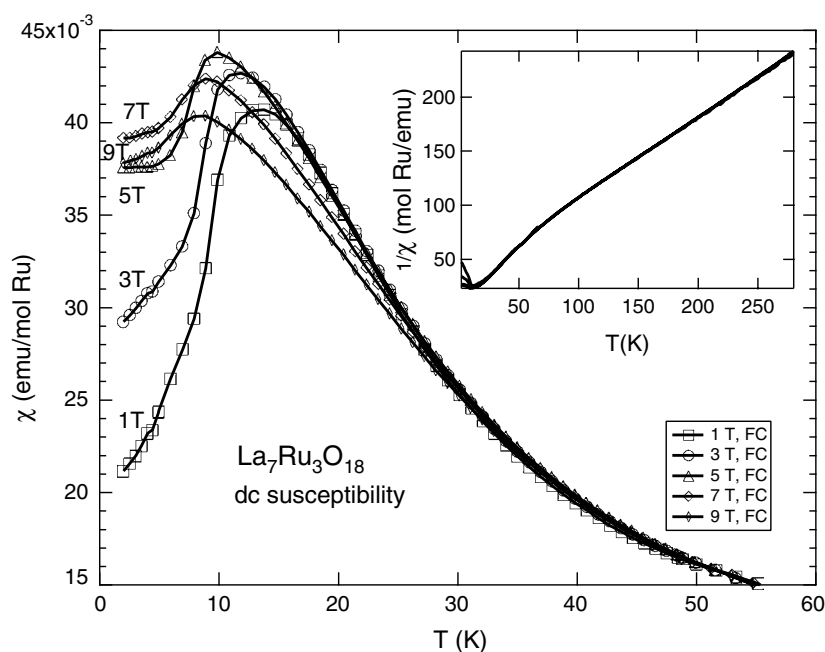
**Figure 1.** Top: view perpendicular to a plane of  $\text{RuO}_6$  octahedra (grey) showing the triangular arrangement of Ru atoms in two dimensions. Ru atoms are at the centre of the  $\text{RuO}_6$  octahedra while O atoms are at the vertices. Ru atoms in the next higher plane (shown in black) cap the  $\text{RuO}_6$  octahedra, giving rise to a tetrahedral arrangement of Ru sites in three dimensions. Bottom: in-plane view, highlighting the tetrahedral arrangement.

antiferromagnet [9]. Despite the structural similarities,  $\text{La}_7\text{Ru}_3\text{O}_{18}$  is at most only moderately frustrated, with a frustration index of  $f = -\theta/T_N \approx 6$ . Ru atoms in the  $ab$  plane of both compounds are patterned in a triangular lattice. Each in-plane triangle of Ru atoms is capped by a fourth Ru atom in a neighbouring plane, giving rise to a tetrahedral arrangement of Ru atoms in three dimensions, as illustrated in figure 1. There are three distinct Ru sites in the crystal structure.  $\text{La}_7\text{Ru}_3\text{O}_{18}$  was previously found to have a moment of  $3.49 \mu_B$ , and a Curie–Weiss constant of  $-58$  K, which indicates medium strength antiferromagnetic interactions between spins [9]. In the course of that initial investigation of  $\text{La}_7\text{Ru}_3\text{O}_{18}$ , behaviour more complex than that expected for a simple antiferromagnet was observed. Here we report a more detailed study of the magnetic behaviour of  $\text{La}_7\text{Ru}_3\text{O}_{18}$ , and show that it has an unusual magnetic phase diagram at low temperatures.

## 2. Experimental details

Starting materials were dried  $\text{La}_2\text{O}_3$  (99.99%, Alfa) and  $\text{RuO}_2$  (99.9%, Cerac).  $\text{La}_7\text{Ru}_3\text{O}_{18}$  was made by mixing  $\text{La}_2\text{O}_3$  and  $\text{RuO}_2$  in the stoichiometric ratio or with a slight Ru excess. The powders were placed in dense alumina crucibles and heated at 775, 850, and 875 °C for at least two days each with multiple intermediate grindings. Samples were then annealed for about two weeks at 875 °C with multiple regrindings until judged to be single phase by powder x-ray diffraction.

Both ac and dc magnetic susceptibility measurements were performed on the Physical Property Measurement System (PPMS, Quantum design). Field cooled (FC) measurements were carried out by applying the field, cooling the sample, and then measuring the temperature



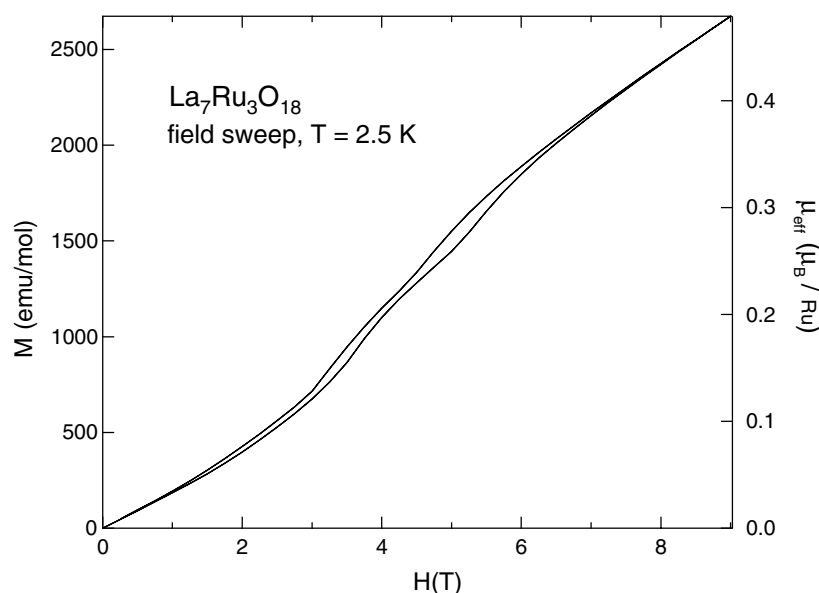
**Figure 2.** Magnetic susceptibility ( $\chi_{\text{dc}} = M/H$ ) at low temperatures. Inset shows linearity and field-independence of  $1/\chi_{\text{dc}}$  at higher temperatures. Data for  $H = 1, 3, 5, 7,$  and  $9$  T are superimposed.

dependence of the magnetic susceptibility upon heating. Field sweeps were done by ramping the field from 9 to  $-9$  to 9 T. The ac susceptibility measurements were done at a frequency of 10 kHz with an amplitude of 12 Oe. All ac susceptibility measurements made in the presence of a constant dc field were done with field cooling.

### 3. Results and discussion

$\text{La}_7\text{Ru}_3\text{O}_{18}$  obeys the Curie–Weiss behaviour at temperatures above 60 K for all applied fields studied (0–9 T), as seen in the inset to figure 2. There is no difference between the FC and zero-FC data (not shown), indicating that the low-temperature drop in the magnetic susceptibility (figure 2, main panel) represents a transition to a long-range ordered antiferromagnetic ground state rather than a spin glass ground state. Although the manner in which the field was applied does not affect the data, the magnitude of the field does. The maximum in the absolute susceptibility ( $\chi_{\text{dc}} = M/H$ ) is at 14 K at an applied field of 1 T, and drops to 9 K as the applied field is increased to 9 T. Furthermore, the magnitude of the low-temperature dc susceptibility ( $\chi_{\text{dc}} = M/H$ ) increases with increasing applied field in the range of  $0 < H < 7$  T. For antiferromagnets, increasing the applied field has no effect on  $\chi_{\text{dc}}$  until sufficiently high fields are reached, leading to saturation of the spins and causing  $\chi_{\text{dc}}$  to decrease with further increases in  $H$ . Since there is no simple explanation for the field behaviour of  $\chi_{\text{dc}}$ , it seems that  $\text{La}_7\text{Ru}_3\text{O}_{18}$  may have multiple types of magnetic ordering.

In order to better understand the atypical field behaviour of the low-temperature susceptibility, field sweep measurements were made at a variety of temperatures. Below 15 K, two distinct features were present in these  $M$  versus  $H$  loops, and at 5 K and below, hysteresis was observed.  $M$  versus  $H$  data collected at 2.5 K is shown in figure 3, with



**Figure 3.** Field dependence of magnetization at  $T = 2.5$  K showing the two distinct regions of hysteresis. Only the data for  $H > 0$  are shown.

hysteresis clearly visible in both the low-field ( $\sim 3$  T) and high-field ( $\sim 5$  T) regimes. It is therefore apparent that two distinct magnetic phase transitions can be induced in  $\text{La}_7\text{Ru}_3\text{O}_{18}$  by applying a magnetic field.

The two features in the  $M$  versus  $H$  data can be more clearly resolved by plotting the differential susceptibility,  $dM/dH$ , shown in figure 4. The two maxima in the derivative plots mark the location of the low-field and high-field magnetic phase transitions. The positive and negative field portions of the plots very accurately mirror each other, confirming the quality of the data. The close proximity of the low-field and high-field transitions at 7.5 K make it impossible to precisely locate the centre of the low-field transition. In the lowest temperatures (2.5 and 5 K), the location of both transitions depends on the measurement history. At these temperatures, there is an upper and a lower phase boundary for both the high-field and the low-field transition due to the observed hysteresis.

A second, complementary means of observing the magnetic phase boundaries is measurement of the ac susceptibility,  $\chi_{ac}$ . Measurements of  $\chi_{ac}$  can scan temperature while keeping the applied field fixed, while  $M$  versus  $H$  scans fix the temperature and vary the field. Unlike the  $dM/dH$  plots, the  $\chi_{ac}$  data can accurately map the phase boundaries near the zero-field transition temperature. The results of the ac susceptibility measurements on  $\text{La}_7\text{Ru}_3\text{O}_{18}$  are shown in figure 5.

Peaks are observed in two temperature ranges in the  $\chi_{ac}$  scans. Figure 5 shows the higher temperature peak. It can be seen that the shape of this peak changes from broad and asymmetric to sharp and more symmetric as the field is increased from 0 to 5 T. Above 5 T the intensity of the peak rapidly decreases. It can be seen that a low-temperature peak is present for the 3 T data. A low-temperature peak is found only within a narrow window ( $\sim 0.25$  T) of applied fields near 3 T (data not shown). The location of the peak shifts to lower temperatures with increasing field. The very low temperature of this second ac transition ( $< 4$  K) prevented a detailed determination of the low-temperature phase boundary, although one data point could be plotted in the overall magnetic phase diagram.

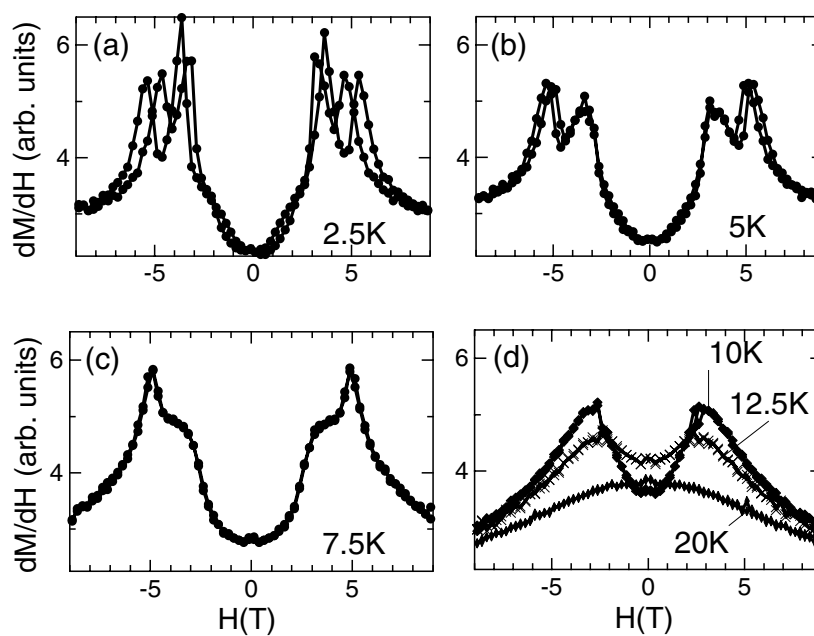


Figure 4. Field dependence of  $dM/dH$  at (a) 2.5 K; (b) 5 K; (c) 7.5 K; (d) 10, 12.5, and 20 K.

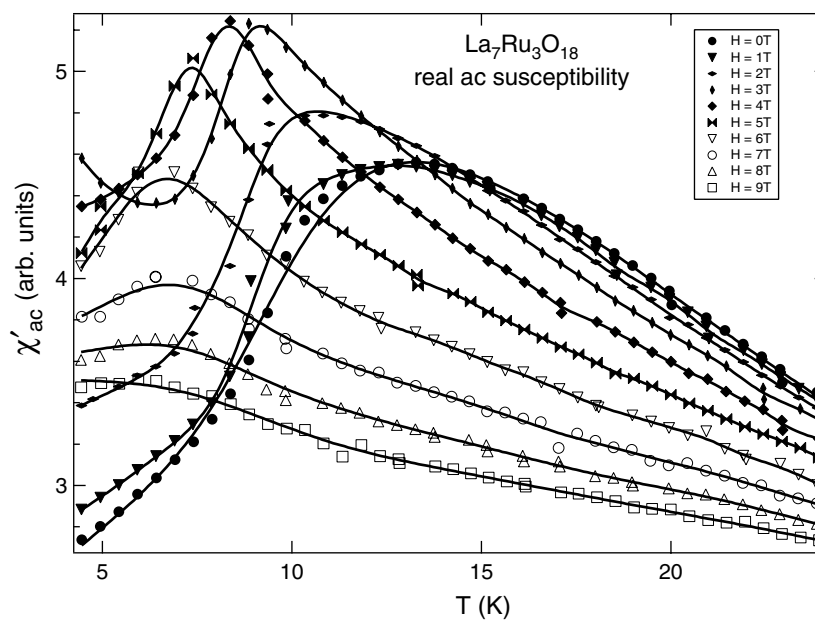
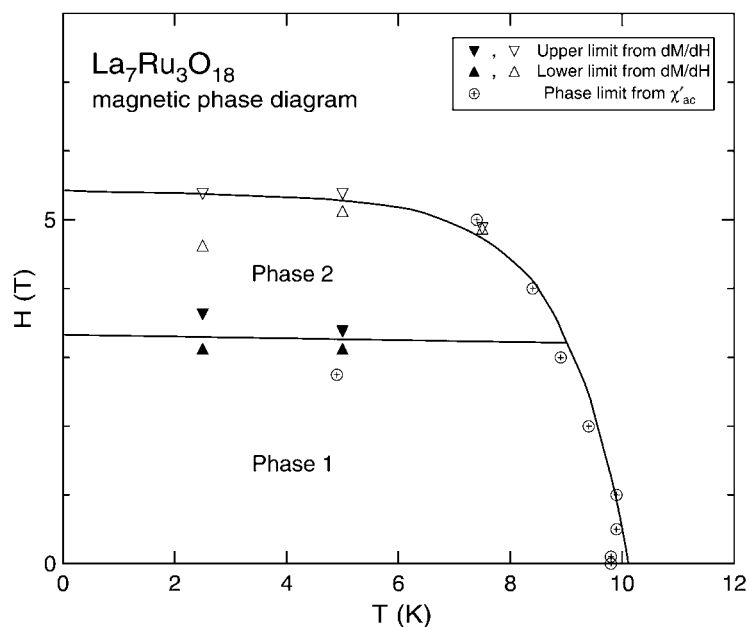


Figure 5. The real portion of the ac susceptibility ( $\chi'_{ac}$ ) of  $\text{La}_7\text{Ru}_3\text{O}_{18}$ . Solid curves are a guide to the eye.

Combining the  $dM/dH$  and the  $\chi_{ac}$  data allows the magnetic phase diagram of  $\text{La}_7\text{Ru}_3\text{O}_{18}$  to be drawn (figure 6). Two definite magnetic phases are labelled in the diagram. The  $dM/dH$  data clearly define the horizontal field boundaries between the different phases, while the



**Figure 6.** Magnetic phase diagram of La<sub>7</sub>Ru<sub>3</sub>O<sub>18</sub>. Solid lines are a guide to the eye.

ac susceptibility data provide the best measure of the transition temperatures of the phases. We note that for ac susceptibility measurements with applied fields of  $\leq 2$  T, the transition temperature was taken to be the point of maximum slope in  $\chi_{ac}$  versus  $T$  rather than the peak maximum due to the broad shape of the peak at low fields. Even though the highest field ( $H \geq 6$  T) measurements of  $\chi_{ac}$  still show a peak maximum, these points were not plotted on the phase diagram due to the broader and weaker character of the peaks. Similarly, the peaks observed in  $dM/dH$  plots for  $T \geq 10$  K were no longer sharp and were not plotted in the phase diagram. The observation of weak features outside the plotted limits of the magnetic phase diagram reflects the difficulty of defining sharp boundaries for magnetic phase transitions, which often involve continuous and gradual spin rearrangements in addition to exhibiting short-range correlations at temperatures just above the onset of long-range order.

#### 4. Conclusions

Since both the low-field (3 T) and high-field transition (5 T) involve a jump in the magnetization due to the increasing magnetic field, these transitions should involve spin reorientation, with spins moving from an axis defined by the crystal fields or the antiferromagnetic interactions to an axis defined by the magnetic field. From previously published structural data [9], it is known that there are two different types of layers in La<sub>7</sub>Ru<sub>3</sub>O<sub>18</sub>. The thicker layer has a 2.67:1 La:Ru ratio while the thinner layer has a 2:1 La:Ru ratio and has two inequivalent Ru sites. The different crystal environments may give rise to crystals fields of different strengths on the different Ru spins, with the effect that different magnetic field strengths are necessary to dislodge the spins from the crystal field in each type of Ru site. It should be noted that since  $\mu gH/k$  is 18 K for an applied field of 9 T, the energy scale of the applied field exceeds that of the antiferromagnetic ordering ( $T_N \sim 10$  K), where  $\mu$  is the moment of  $S = 3/2$  Ru. The  $g$ -factor  $\cong 2$ ,  $H$  is the applied field, and  $k$  is the Boltzmann constant. Even though our data is

from a powder sample, it is unlikely that the two transitions represent two different orientations of the grains in our powder since no evidence of preferred orientation was observed in previous structural studies [9]. Although it is interesting to speculate on the nature of the different magnetic phases, it is difficult to make definite conclusions about the precise nature of the magnetic ordering in the absence of neutron diffraction data or single crystal magnetization measurements.

### Acknowledgments

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