Layer dependent antiferromagnetism in the Sr₄Ru₃O₁₀ ruthenate at the metamagnetic-like transition
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Abstract
We have investigated the nature of the metamagnetic-like transition in the triple layer ruthenate Sr₄Ru₃O₁₀ by means of neutron diffraction from single crystals. The magnetic structure of the compound is likely to be determined in a complex way by the two sublattices of inequivalent ruthenium ions. At T_c=105K the system has a sharp transition into a ferromagnetic state along the c-axis which is driven by the ruthenia in the central octahedra of the triple layers whereas the sublattice of the outer ruthenia tend to align in the ab plane achieving an antiferromagnetic order at the metamagnetic transition T*≈50K. Below T* the strong anisotropy along c prevails, the outer ruthenium align along the c-axis and the in-plane antiferromagnetic contribution disappears. This finding confirms the delicate balance between antiferro and ferromagnetic couplings in the (Sr,Ca)_n+1Ru_nO_{3n+1} family of compounds, and proves the layer dependence of the magnetic anisotropy in Sr₄Ru₃O₁₀.

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1. Introduction

The triple layer Sr₄Ru₃O₁₀ belongs to the Ruddlesden-Popper perovskite ruthenates (Sr,Ca)_n+1Ru_nO_{3n+1}, a family of 4d transition-metal oxides whose magnetic and electronic properties are sensitively dependent on the layer number n and on the structural distortions.

For instance, the single-layer Sr₂RuO₄ (n = 1) shows an unconventional superconducting state [1], whereas the ground state of the double-layer Sr₃Ru₂O₇ (n = 2) is a Fermi liquid close to a ferromagnetic instability [2]. The three-dimensional SrRuO₃ (n = ∞) is a ferromagnetic metal with a Curie temperature Tc = 160 K [3,4]. On the other hand, the calcium ruthenate Ca₂RuO₄ (n = 1) is an antiferromagnetic Mott insulator with a Neel temperature T_N ~ 110 K [5], while Ca₃Ru₂O₇ (n = 2) exhibits a quasi-two-dimensional metallic behavior and becomes antiferromagnetic below T_N ~ 56 K [6,7]. Last, CaRuO₃ is a paramagnetic metal [8,9].

The triple-layer Sr₄Ru₃O₁₀ has been attracting considerable interest because of its complex structure and its unusual magnetic behaviour. Susceptibility measurements show a paramagnetic-ferromagnetic transition at Tc = 105 K, below which the easy axis is along the c direction [10]; a minor transition is observed at around T*≈50K et it is referred to as the metamagnetic transition because below this temperature the magnetisation shows a sudden increase at a magnetic field of about 2 T. Intriguingly, while the metamagnetic transition is a well pronounced feature in the magnetic susceptibility [10,11], it does not appear in the specific heat curves [12]. Although several distinct scenarios have been proposed to account for the anomaly at T*, its intrinsic
character remains an open question. Many experimental techniques, including neutron scattering \[13,14\], Raman scattering \[15\] and resistivity \[16\] have been used to try to clarify the origin of T* and some contradictory pictures have been put forward. From Raman and resistivity experiments it has been inferred that the metamagnetism would arise from an antiferromagnetic (AF) component in the \(ab\) plane due to canting of all spins; conversely initial neutron diffraction experiments \[13,14\] discarded the possibility of an AF component. In our previous neutron study for instance, we focussed on the low temperature magnetic structure \((T=1.5\text{K})\) which was found to have a magnetic propagation vector \(\mathbf{K}=(0,0,0)\) with all magnetic moments ferromagnetically aligned along \(c\) \[14\]. The clear anomaly at \(T^*=50\text{K}\) that we observed in the temperature dependence of the Bragg peaks \[14\] was not interpreted in terms of an additional magnetic phase because of the absence of convincing magnetic signal in the \(ab\) plane within our experimental conditions. More recently, the hypothesis of a ferromagnetic component in the \(ab\)-plane at around \(T^*\) has been put forward by Zhu et al, based on the observation of a sizable neutron magnetic scattering in the \(ab\) plane \[17\]. However such a model does not fit entirely our previous experimental observations \[14\], in particular the lack of intensity of some specific reflections. On the basis of symmetry analysis and a few additional neutron measurements, we propose in this paper an alternative scenario in which the metamagnetic transition would stem from an antiferromagnetic ordering in the sublattice of the ruthenia in the outer octahedra of the triple layers, almost independently of the sublattice of the inner ruthenia which are predominantly ferromagnetic.

1. Results and discussion

The experiments were carried out at the Institut Laue Langevin in Grenoble on the crystal diffractometer D10 in normal beam configuration and equipped with a two-dimensional detector and a vertical cryomagnet. A wavelength of 2.36 Å was chosen in order to measure the magnetic reflections. The sample is the single crystal of dimensions \(\sim L_xL_yL_z=3\times2\times0.5\text{ mm}^3\) reported in Ref.14, it was grown with the floating zone technique as described elsewhere \[18\] and was oriented with the \([h,-h,0]\) direction along the vertical axis while the magnetic field was varied between 0 and 6 tesla. The crystal structure has a primitive space group \[10\] with a rather long \(c\) axis \(\sim 28\) Å. The magnetically active part of the unit cell consists of four blocks of three layers of ruthenia octahedrally coordinated with oxygens: two of such trilayers are centred in the basal plane, at \(z=0\) with the outer ruthenia (i.e. the ruthenia in the external octahedra of the trilayer) situated at the position \(\pm z_2\) along the \(c\) axis; the two other trilayers are located at \(z=0.5\) (with the outer ruthenia at \(\pm z_3\)). The inner ruthenia (i.e. the ruthenia in the central octahedra of the trilayers) are therefore at \(z_1=0\) and \(z_4=0.5\). As a result, each cell contains four formula units with a total of twelve ruthenia which are inequivalent for crystallographic and physical reasons; first they occupy four different Wyckoff sites, the two inner ruthenia (Ru_in) being in more symmetric sites with multiplicity 2 and the two outer ruthenia (Ru_out) having each multiplicity 4. Moreover at room temperature the outer octahedra are slightly elongated contrary to the inner ones which are regular octahedra \[10\]. Finally, the inner octahedra are more rotated than the external ones, with an angle of rotation above the critical angle for ferromagnetism \[19\]. As a consequence, the Ru_in are supposed to be more prone to ferromagnetism than the Ru_out. This is reflected in the value of the ferromagnetic moment along the \(z\)
axis on the two sites, which has been measured with neutron scattering at low temperature (1.5K) yielding 1.59 $\mu_B$ on the inner ruthenia and 0.92 $\mu_B$ on the outer ones [14]. The magnetic structure at T=1.5K is a ferromagnetic state with all ruthenia in the $\Gamma_4$ irreducible representation, with modes $F_z$ and $F_x$ on the inner and outer ruthenia respectively [14]. However, the magnetic structure at the metamagnetic temperature T*=50K is still not entirely clear. Given the diversity of the inner and outer ruthenia, it can be speculated that the different sites be responsible for the two observed transitions at $T_C=105$ K and at T*=50K. In a recent report [17], neutron scattering experiments have been able to ascertain the presence of a magnetic signal in the ab plane about T* based on the observation of additional intensity in the (002), (006) and (008) reflections. The hypothesis of a ferromagnetic axis slightly tilted in the ab-plane at around T* has been put forward to explain the occurrence of magnetism in the ab plane but no explanation has been provided for the absence of the (004) reflection. We believe instead that the lack of intensity in the (004) be an important key to solving the puzzle. Indeed, if the magnetic coupling in the ab plane was of ferromagnetic nature, then the magnetic contribution to the Bragg reflections would be comparable for the (004) and for the (002) reflection because for ferromagnetic modes in the ab plane the magnetic structure factor would be modulated with $l$ according to the periodic form $\cos[\pi z_2 + \pi z_3]\cos[\pi z_2 - \pi z_3]$. Our measurements (Figure 1) show however that this is not the case, on the contrary at around T* the reflection (002) is much more intense than the (004) which is in fact vanishing, and this difference is well beyond the attenuation of the magnetic scattering by the magnetic form factor at these two close scattering vectors [20].

We argue that an antiferromagnetic ordering of the type $A_zG_y$ on exclusively the outer ruthenia (corresponding to the irreducible representation $\Gamma_8$ [14]) can account for the large difference in the intensity of the two reflections. In the irreducible representation $\Gamma_8$ the inner ruthenia do not carry a magnetic moment whereas the outer ruthenia have a $A_zG_y$ ordering, i.e. an A mode along x, a G mode along y and zero moment along $z$: $M_x, +M_y, 0; -M_x, -M_y, 0; +M_x, -M_y, 0; -M_x, +M_y, 0$. The square magnetic structure factor for the (00l) reflections, (assuming that the ruthenia at $z_2$ and $z_3$ be in phase) would write:

$$|F(00l)|^2 = 16M_y^2 \cos^2[l \pi (z_2+z_3)] \sin^2[l \pi (z_2-z_3)]$$

where $M_y$ is the component along the b-axis of the moment on the outer ruthenia.

In this model the only magnetic reflection having a sizable intensity is the (002), which is indeed what we observe experimentally (Figure 1).

We have mainly focussed on the (00l) reflections because they are sensitive only to the components of the magnetic moments in the ab plane and do not probe the components along $z$. As a consequence, the additional intensity at T* adds to a signal which is purely nuclear. It is worth stressing that this additional intensity peaks at T* and vanishes as the temperature is lowered to T=1.5 K. This behaviour rules out the possibility of a canted structure [18] (ferromagnetic modes along $z$ but antiferromagnetically canted in the ab plane) at T=1.5K because the signal at T* does not persist down to 1.5K.
In Table 2 we compare the intensities of the main magnetic reflections as calculated with the program Fullprof [21] in the case of the only two candidate irreducible representations that contain in plane magnetism: the $\Gamma_2$ which involves also ferromagnetism in the $ab$ plane and the $\Gamma_8$ which has antiferromagnetism in the $ab$ plane but does not allow any contribution from the inner ruthenia. All the other irreducible representation had to be discarded since they yield calculated intensities $I(hkl)$ at odds with the experimental observations, for instance the $\Gamma_5$ would give $I(002)<I(004)$, whilst the $\Gamma_6$ and $\Gamma_7$ would yield vanishing intensities for all the (00$l$) reflections. The quality of our data which have been collected on a rather small crystal is not sufficient to solve quantitatively the magnetic structure at $T^*$, in particular to establish whether there is a canting i.e. a component along $z$, but we have nonetheless a clear indication that at $T^*$ an antiferromagnetic order sets in in the $ab$ plane being triggered either by temperature or some other effect. As previously reported [14, 15], in Sr$_4$Ru$_3$O$_{10}$ there is a clear correlation between magnetic and structural effects, in particular the metamagnetic transition occurs at a temperature $T^*$=50K for which the cell volume has a sharp minimum. Whilst the $a$ parameter has a monotonic dependence on temperature, the $c$-axis decreases down to 50K [14] and is clearly much more affected by temperature and or magnetism. Theoretical calculations have pointed out that in the regime of $c$-axis elongated, the spin–orbit coupling in the RuO$_6$ octahedra would tend to favour magnetic correlations along the $c$-direction, while for in-plane elongated octahedra the orbital occupation would cooperate with the spin–orbit for inducing local spin moments in the $ab$-plane [22,23].

### Table 1

**Intensities in arbitrary units of the main magnetic reflections in Sr$_4$Ru$_4$O$_{10}$ as calculated with the program Fullprof for the two models corresponding to the irreducible representations $\Gamma_2$ and $\Gamma_8$.** As already reported [14], the IrRep $\Gamma_8$ does not allow a magnetic moment on the inner ruthenia. Ru1 and Ru4 (Ru_in) but only on the outer ruthenia, Ru2 and Ru3 (Ru_out).

| I(hkl)/T | Ru1 | Ru2 | Ru3 | 002 | 004 | 006 | 008 | 110 | 111 |
|----------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| $\Gamma_2$ | $a_x$ | $f_y$ | $F_x$ | $C_y$ | 336 | 248 | 56 | 32 | 0 |
| $\Gamma_8$ | --- | $A_x$ | $G_y$ | | 339 | 10 | 18 | 5 | 0 | 12 |
Consistently, the temperature dependence of the (220) reflection (see Figure 2) shows a clear deep at around T*, indicating that the total M_z component of the magnetic moments is sensibly reduced at the temperature where the M_{xy} component is maximised and the c axis shorter.

On the basis of these considerations, one can envisage a scenario in which the two sublattices of inner and outer ruthenia act partly as independent players in determining the magnetic order in Sr4Ru3O10. At T_c=105K the sublattice of the inner ruthenia orders ferromagnetically along z whilst the outer ruthenia would tend to align antiferromagnetically in the ab plane. This ab antiferromagnetic ordering is achieved at T* where the c axis has a minimum [14] and the anisotropy along c is reduced. At around T* the irreducible representation \Gamma_4 (ferromagnetism along z) coexists thus with the \Gamma_8 describing an antiferromagnetic order of the type A_xG_y uniquely in the sublattice of the outer ruthenia. In other words, below T_C the antiferromagnetic and ferromagnetic interactions are in competition, with the inner ruthenia more constraint along z and the outer ruthenia more free to bend away from the easy axis. As the temperature is lowered to 2K, the c axis becomes longer and the stronger anisotropy along z forces all ruthenia to line up along c. Such a scenario is further supported by polarised neutron measurements [22] conducted with an external field applied in the ab plane. In the magnetisation maps [22], the outer ruthenia appear to be sensibly more magnetised at 65K than at 2K whereas the inner ruthenia stayed unchanged throughout the metamagnetic temperature T*. The (004) reflection is again a good test of what happens at T*: unlike the other reflections, it goes from a negative to a positive value throughout T* [22] which, in a regime of in plane polarisation, indicate a stronger anisotropy along c for T<T*.

Furthermore, with unpolarised neutrons we also see that if a magnetic field is applied in the ab plane (Figure 3) the magnetic moment in the (h,-h, l) plane, as probed by the (220) reflection, is almost unaffected by the field at low temperature (1.5K) whilst it is significantly reduced at 70K just above the metamagnetic transition T* suggesting that at this temperature some magnetic moments are intrinsically more prone to lean away from the c-axis and to bend into the ab plane.

Antiferomagnetic correlations at intermediate temperatures are not unusual in ruthenates. As an example, in the bilayered compound Sr3Ru2O7 magnetic fluctuations have been detected and shown to evolve from a ferromagnetic position to an incommensurate antiferromagnetic vector as the temperature decreases from 115K to 15 K [24]. Similarly in the superconducting single layer Sr2RuO4, antiferromagnetic fluctuations were likewise observed at low temperature at an incommensurate position in the [hh0] direction [25]. In the triple layer Sr3Ru3O10 the anomaly observed in the specific heat at T_c=105K [12] is an order of magnitude smaller than expected for a complete spin ordering corroborating a picture in which only the inner ruthenia contribute initially to the ferromagnetic transition whereas the outer ones tend to be antiferromagnetically ordered. There exists therefore a delicate balance between ferro and antiferromagnetic interactions in ruthenates, and this balance can be altered by temperature or external pressure. In Sr3Ru3O10 the application of a modest hydrostatic pressure for instance diminishes the c-axis ferromagnetism and induces basal plane antiferromagnetism as recently shown with resistivity measurements [16].
Unlike Sr$_3$Ru$_2$O$_7$, Sr$_4$Ru$_2$O$_{10}$ orders at a relatively high Curie temperature but the step observed in the ab magnetisation [10] in the triple-layer is reminiscent of a similar feature observed in the paramagnetic bilayered material Sr$_3$Ru$_2$O$_7$ [26] so that the presence of antiferromagnetic interactions and eventually long range order is a very plausible picture (Figures 4) and agrees with the anisotropic behaviour of the susceptibility which, below $T^*$, depends strongly on the direction of the applied field [10].

![Figure 1](image-url) The neutron intensity of the (002), (004), (006) Bragg reflections as a function of temperature, normalized to their respective values at $T=15$K. The curves were measured on the diffractometer D10 at ILL. The small size of the crystal explains the noise in the measured intensity of the weak magnetic signal of the (004) and (006) reflections.
Figure 2 The intensity of the Bragg reflections (220) as a function of temperature, as measured on the D10 diffractometer at ILL.

Figure 3 The intensity of the Bragg reflections (220) as a function of an \( ab \) applied magnetic field, as measured on the D10 diffractometer at ILL. The upper curve was taken below the metamagnetic transition at \( T^* \) and the lower curve above \( T^* \).

Figure 4a Magnetic structure at \( T=2 \)K [14]. Both sublattices of ruthenia, inner and outer, are in the \( \Gamma_4 \) irreducible representations for the magnetic modes. The \( c \) axis is the long one.

Figure 4b Proposed magnetic structure at \( T^*=50 \)K. The sublattice of inner ruthenia is in the \( \Gamma_4 \) irreducible representations. The outer ruthenia are in the \( \Gamma_8 \). In the inset, the cell volume as a function of temperature [14] shows a sharp minimum at the metamagnetic transition at \( T^*=50 \)K.

Conclusions

Using neutron diffraction we have made a further step in understanding the origin of the metamagnetic transition in the triple-layer ruthenate \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \). The two sublattices consisting of the inner and outer ruthenia of the trilayer seem to have a different temperature evolution around the metamagnetic temperature, in
particular the antiferromagnetic order appearing around $T^*$ would seem to be driven only by the outer ruthenia which order in the GxAy mode with the trilayers at the face centre in phase with the blocks located in the basal plane. The sublattice of the inner ruthenia does not contribute to the antiferromagnetic order but are ferromagnetically ordered along the $c$-axis.

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