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Ferromagnetism in $Sr_4Ru_3O_{10}$: Relationship to other layered metallic oxides

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Single crystals of $Sr_4Ru_3O_{10}$, the $n=3$ member of the Ruddlesden-Popper series $Sr_{n+1}Ru_nO_{3n+1}$, have been found to be ferromagnetic for $T<T_C=148$ K. Measurements of the magnetization for $2<T<350$ K, and in fields H to 30 T, electrical resistivity for $2<T<300$ K and $0<H<12$ T, and heat capacity for $2<T<20$ K reveal that the magnetic, transport, and thermal properties are consistent with those of $n=1$, 2, and ∞ members of the series. Low-field ($H=0.01$ T) magnetization shows a sharp ferromagnetic transition at T_C, and isothermal magnetization for $T\ll T_C$ reveals some hysteresis, but magnetic saturation occurs only for $H>16$ T. The easy axis for magnetization lies in the ab plane. The saturation value, $1.75\mu_B$/Ru is consistent with that expected for the low-spin state for the Ru $4d^4$ configuration. The resistivity shows a Fisher-Langer-type anomaly at T_C that is suppressed for fields of a few T. The heat capacity measures a large electronic component, $\gamma=110$ mJ/mole K^2, suggesting a highly correlated d band, but similar to the $n=1$, 2, and ∞ members of the series when normalized to the number of Ru-O layers in the repeated structure. The data are discussed in terms of the other members of the $Sr_{n+1}Ru_nO_{3n+1}$ series and of analogous properties for the Ca-based counterpart materials. [S0163-1829(97)50834-4]

Although it has been over forty years since the rather surprising discovery of ferromagnetism in the first $4d$ transition metal oxide, $SrRuO_3$,[1] it was not until the discovery in 1994 of superconductivity in high quality single crystals of the related compound, Sr_2RuO_4,[2] that interest was rekindled in the physical properties of the alkaline earth ruthenates. $SrRuO_3$ and Sr_2RuO_4 are end members of a series of materials conveniently classified by the repeated sequence of the number of their Ru-O layers, the Ruddlesden-Popper series.[3] They have the general structural formula $A_{n+1}B_nO_{3n+1}$ for $1\leqslant n\leqslant\infty$, where A is an alkali or alkaline earth and B is a $3d$, $4d$, or $5d$ transition metal and n the number of Ru-O layers in the sequence. The $n=\infty$ member, $SrRuO_3$, which has a distorted perovskite structure, is rather strongly ferromagnetic with a high Curie temperature ($T_C=165$ K), and the $n=1$ member, Sr_2RuO_4, is superconducting, albeit with a low transition temperature, $T_c=1.35$ K.[4] The superconducting phase of Sr_2RuO_4 is restricted to only fully stoichiometric, undoped, single crystals of very high quality, and Sr_2RuO_4 is the only noncuprate having the same structure of a high T_c material, e.g., like $(La,Sr)_2CuO_4$. These and other factors have driven theories positing nonconventional pairing mechanisms, including p-wave pairing for this material.[5] The similar compositions but dissimilar properties suggest that structure and dimensionality (which plays a major role in magnetocrystalline anisotropy) control the wide variation in physical properties.

Between the $n=1$ and $n=\infty$ limiting members of the Ruddlesden-Popper $Sr_{n+1}Ru_nO_{3n+1}$ series lie an infinite number of structures with increasing number of repeated Ru-O layers, n. We have reported recently on the $n=2$ member, $Sr_3Ru_2O_7$,[6] which shows ferromagnetism in well characterized single crystals, with $T_{C1}=105$ K and evidence for a lower temperature ($T_{C2}=66$ K) canted ferromagnetic spin reorientation phase. The saturation magnetic moment of $Sr_3Ru_2O_7$ is $1.4\mu_B$/Ru and is reached by a field of about 0.2 T for $T\ll T_C=105$ K. The saturation moment of $SrRuO_3$ reaches $1.65\mu_B$/Ru for $T\ll T_C$, but only above about 20 T.[7] (The latter number has been reported over the past forty years to vary from 0.8 to $2.0\mu B$/Ru, depending on the applied field and temperature. The value of $1.65\mu_B$/Ru was measured in the highest dc fields conveniently available and the measurements extended to 30 T. These values of the saturation moment are significant because Ru is presumed to have the ‘‘low spin’’ $S=1$ configuration of Ru $4d^4$ with octahedral symmetry, not the ‘‘high spin’’ $S=2$ configuration, which is expected for the $3d$ series, which has a more confined d-shell radial extent and lower crystal field splittings between the t_{2g} crystal field ground state and the excited e_g state.[8] The low spin saturation moment would approach $2.0\mu_B$/Ru, the high spin state, $4.0\mu_B$/Ru.

In this paper we report the ferromagnetism of $Sr_4Ru_3O_{10}$, the $n=3$ member of the Sr,Ru Ruddlesden-Popper series. The Curie temperature, $T_C=148$ K, lies predictably between that of the $n=2$ and $n=\infty$ members of the series, and the saturation moment, which is achieved only above about 16 T, reaches $1.75\mu_B$/Ru, higher than the others but consistent with the low spin, $S=1$, configuration. We also report on the electrical resistivity and its magnetic field dependence and on the specific heat at low temperatures. The samples were grown by the flux method. Nonstoichiometric quantities of $SrCO_3$, RuO_2, and $SrCl_3$, the self-flux, were mixed in platinum crucibles, heated to 1500 °C for 24 hours, cooled slowly to 1350 °C over several hours, then quickly quenched to room temperature to avoid twinning, which could occur because the sample structure is orthorhombic. X-ray diffraction

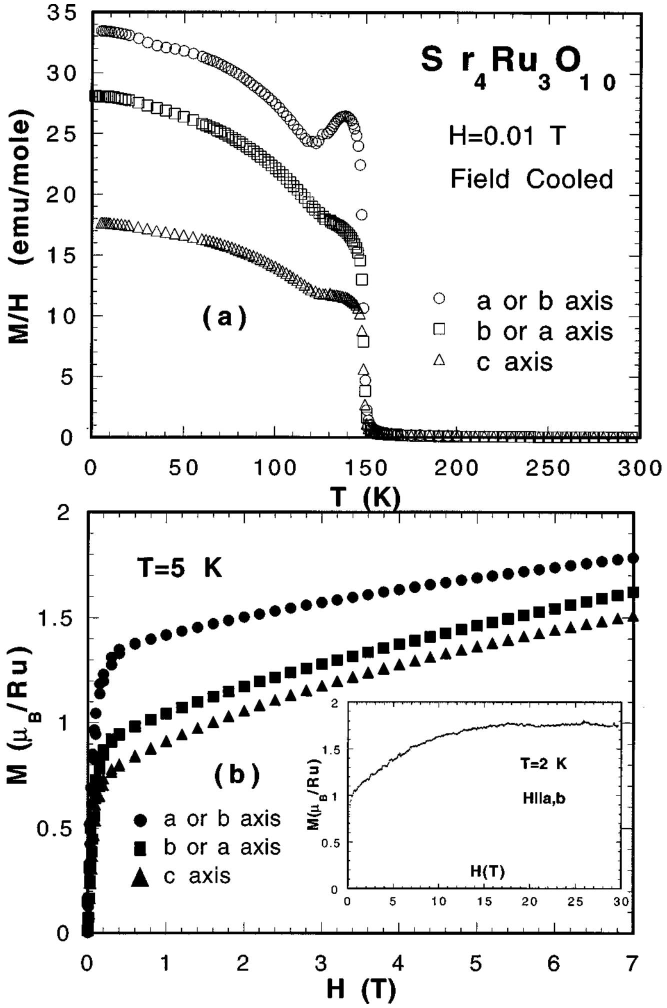

FIG. 1. Magnetization vs temperature at low fields for $Sr_4Ru_3O_{10}$ for the three principal crystallographic directions. The feature just below $T_C = 148$ K may be due to temperature dependence of the anisotropy field. The lower figure shows magnetization at $T = 5$ K to 7 T for the same three directions. The inset shows $M(H)$ at $T = 2$ K to 30 T, taken in high dc magnetic fields. Magnetic saturation occurs at $1.75\mu_B$/Ru for $H > 16$ T.

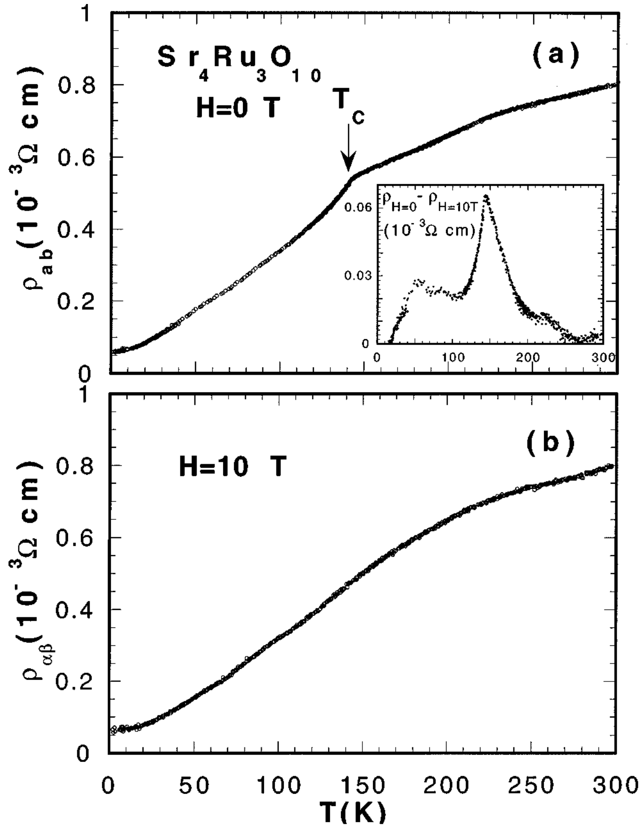

FIG. 2. Electrical resistivity vs temperature for $Sr_4Ru_3O_{10}$ showing a Fisher-Langer type anomaly at T_C. (b) shows the magnetoresistivity at $H = 10$ T, the anomaly at T_C is no longer seen. The inset shows the difference between the two figures, with a clear maximum near the Curie temperature.

measurements revealed a single crystal structure, with the lattice constants $a = 5.556$ A, $b = 5.524$ A and $c = 7.832$ A. Sample surfaces were examined under a differential interference contrast microscope, but no twinning of the materials was observed. A scanning electron microscope-EDX system determined the 4:3 ration of Sr:Ru to within 1%. Because there was no evidence for ferromagnetism near 165 K in low field magnetization measurements, we determine there is $<1\%$ contamination of the $n = \infty$ component in these single crystal samples, a contaminant which occurs at the several percentage range in polycrystalline, sintered samples of the Sr ruthenates.[9]

In Fig. 1 we show the temperature dependence of the low field magnetization of $Sr_4Ru_3O_{10}$ along the three principle crystallographic directions, taken with a Quantum Design MPMS superconducting quantum interference device magnetometer adapted to a 7 T superconducting magnet. The magnetization is linear in the 0.01 T field at all temperatures, so the data of Fig. 1(a) represent the magnetic susceptibility, $(dM/dH)_{H \rightarrow 0}$. The evidence for ferromagnetism at $T_C = 148$ K from this ''kink point'' method is clear for all three directions, and the largest moment values presumably indicate the easy axis lies in the ab plane, consistent with the easy axis for the $n = \infty$ member,[10] but not the $n = 2$ structure, where it was determined that the c axis is the easy axis for magnetization.[6] The rather sharp feature in the low field magnetization for $120 < T < T_C$ is reproducible from sample to sample and is probably a manifestation of the strong temperature dependence of the anisotropy field, which is expected near T_C. There may be a small spin reorientation (canting) below 120 K, but the evidence is not nearly as compelling as for the $n = 2$ system.[6]

Isothermal magnetization curves to 7 T were taken over a wide range of temperatures and data for $T = 5$ K are shown in the lower part of Fig. 1, again for the same three principal crystallographic directions. As was the case for $SrRuO_3$, a field of 7 T, even for $T \ll T_C$ is not sufficient to determine the saturation moment. Consequently, we measured $M(H)$ at $T = 2$ K in fields to 30 T, using a vibrating sample magnetometer, in the dc magnet facility of the National High Magnetic Field Laboratory. Several samples oriented with $H \| a$ or $H \| b$ were used to provide significant signal. The results are shown in the inset of Fig. 1. For $H > 16$ T the magnetization saturates and $M(H)$ attains a value of $1.75\mu_B$/Ru.

In Fig. 2 we show the electrical resistivity as a function of temperature, $\rho(T)$, taken with a standard four lead technique. The anomaly at $T_C = 148$ K is like that observed at

$T_C=165$ K for SrRuO$_3$ and is consistent with a Fisher-Langer anomaly associated with a decrease in spin disorder scattering below the transition temperature.[11] However, to our knowledge, no comprehensive treatment of the resistivity at magnetic ordering temperatures exists appropriate to ferromagnetism in the transition metal oxides. For example, there are no apparent *s* electrons at the Fermi surface based on photoemission studies and band structure calculations.[12] Furthermore, the magnetic scattering is largely *d* wave rather than Fisher-Langer s-f scattering. Finally, the magnetic moment of the *d* shell is diffuse, not necessarily well localized as treated in Fisher-Langer theory. (Diffuse neutron scattering of SrRuO$_3$ show that about 10% of the ''localized'' *d*-shell moment associated with the Ru moment piles up on the octahedral O sites through covalency.[13]) Nevertheless, the sudden decrease in $\rho(T)$ at T_C is consistent with removal of a spin disorder scattering channel. The longitudinal magnetoresistivity, $\rho(H,T)$ was measured for a few fields to 12 T. The results for $H=10$ T are shown in the lower part of Fig. 2 and show the decrease in $\rho(T)$ and elimination of the spin disorder resistivity anomaly with increasing field. The difference between the zero and high field negative resistivity is shown in the inset of Fig. 2. Note there is a sharp peak in $\rho_{H=0}-\rho_{H=10\ \mathrm{T}}$ near $T_C=148$ K.

Finally, measurements of the heat capacity, $C(T)$ for $2<T<20$ K were fit to C/T vs T^2, and the intercept of the curve (not shown) gives a value of the electronic density of states, $\gamma=110$ mJ/mole K^2. This value of γ is similar to those of the other members of the Sr,Ru Ruddlesden-Popper series when normalized to the number of Ru-O layers in the respective repeated sequence. These normalized values are shown in Fig. 3 (right-hand scale). While γ is not as large as observed for some very highly correlated electron systems such as heavy fermion materials ($\gamma\approx1000$ mJ/mole K^2 or higher), they show considerable enhancement over the values calculated from band structure calculations. For example $m^*\approx3m_e$ for SrRuO$_3$ (Ref. 14) and $m^*\gg1$ for Sr$_2$RuO$_4$.[15] The results underscore the nonconventional behavior and the tendency of the Sr ruthenates to be highly correlated electron materials with metallic conductivity.

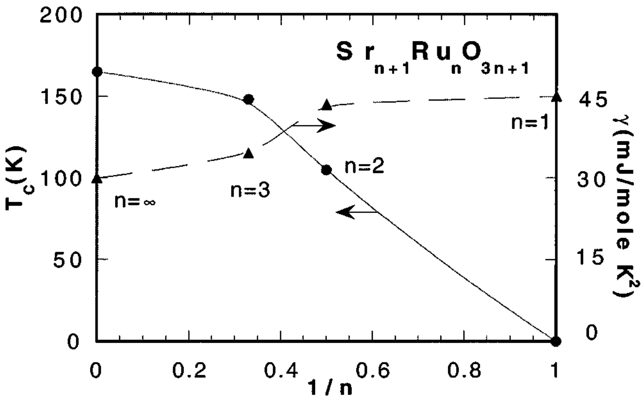

FIG. 3. Magnetic ordering temperature vs 1/*n* for four Sr-Ruddlesden-Popper metallic magnetic systems (left-hand scale). The symbol *n* represents the number of layers in a sequence and reflects decreasing anisotropy with increasing *n*. Also shown (right-hand scale) are values of the electronic heat capacity coefficient, γ, in mJ/mole K^2 normalized to the number of repeated Ru-O layers in the structure.

In Fig. 3 (left-hand scale) we also illustrate the magnetic ordering temperatures as a function of 1/*n* for all four members of the Sr, Ru Ruddlesden-Popper series examined to date. A clear trend to increasing ferromagnetic strength accompanies an increase in *n*, and a decrease in the magnetocrystalline anisotropy. This curve illustrates the importance of dimensionality in the strength of the magnetic interactions. It is noteworthy that a similar graph of antiferromagnetic ordering temperatures in the Ca counterparts to this series shows exactly the opposite trend: T_N, the Néel temperature, *decreases* from $T_N=110$ K to $T_N=0$ K from $n=1$ to $n=\infty$.[16]

We believe the result of the additional member of the Sr,Ru Ruddlesden-Popper series contributes additional information to our understanding of the role of dimensionality and structure on magnetic ordering and the associated transport properties in transition metal metallic oxides. Further work will go into fabricating high quality single crystals of the $n=3$ Ca counterpart of Sr$_4$Ru$_3$O$_{10}$, namely, Ca$_4$Ru$_3$O$_{10}$, which we believe should show a low temperature metallic paramagnetic to antiferromagnetic transition, T_N, perhaps accompanied by a transition from metallic to nonmetallic.

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