Pressure dependence of the magnetic ordering in M_2RuO_5 (M = Sm, Gd, and Tb)

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The antiferromagnetic ordering temperatures of Sm_2RuO_5 (T_N = 19.1 K) and Tb_2RuO_5 (T_N = 13.1 K) are depressed with increasing hydrostatic pressure to 0.6 GPa, but that of Gd_2RuO_5 (T_N = 9.8 K) shows no change with pressure. The depression of T_N is consistent with an increase in the crystalline electric field interaction strength accompanying a decreasing lattice constant. Based on the data for Gd_2RuO_5, the magnetic exchange interaction is constant in this pressure regime and Gd_2RuO_5, with negligible crystalline electric field interaction strength, serves as a control for these measurements. The data support the role of the Ru cations in promoting interactions among the lanthanide ions, yet Ru itself has a vanishingly small magnetic moment.

INTRODUCTION

We present here the results of magnetization as a function of pressure[1,2] for three magnetically ordered members of the lanthanide–transition-metal oxide series, M_2RuO_5—for M = Sm, Gd, and Tb.[3] M_2RuO_5 has a complex orthorhombic structure, having space group *Pnma*. The Ru are coupled via chains of corner-sharing RuO_5 square pyramids. There are two inequivalent seven-oxygen-coordinated M sites, and their polyhedra are edge sharing. Sm_2RuO_5, Gd_2RuO_5, and Tb_2RuO_5 order magnetically at T_N = 19.1, 9.8, and 13.1 K, respectively, very likely with a canted antiferromagnetic structure, based on very-low-field-cooled (FC) and zero-field-cooled (ZFC) temperature-dependent magnetization studies. A highly anomalous feature of M_2RuO_5 is a very large low-temperature linear contribution to the heat capacity.[3] This is normally associated with the electronic heat capacity, but it is unexpected in M_2RuO_5, all of which are insulators.

In M_2RuO_5 both the M and Ru ions can, in principle, support localized magnetic moments because of the unfilled $4f$ and $4d$ shells, respectively. In most metallic ruthenates, the $4d$ electrons drive both the low-temperature transport and magnetic properties, achieving magnetic ordering as high as 165 K (Ref. 4) in the Ruddlesden-Popper (RP) series ruthenates. Most are highly correlated electron materials with large electronic heat capacities.[5] In the RP systems, the Ru ion is in an octahedral cage of six nearest-neighbor oxygens, where the Ru $4d$ electrons are involved in bonding with the surrounding oxygen p orbitals. This leads to the familiar crystalline electric field (CEF) splitting of the $4d$ orbitals into the stationary states of doubly degenerate e_g and triply degenerate t_{2g} levels, the latter lying lowest in energy. For M_2RuO_5, however, five nearest-neighbor oxygens surround the Ru, forming RuO_5 square pyramids instead of RuO_6 octahedra. Defining the tip of the pyramid along the z direction, this alters the splitting so that the lowest-energy state is a doublet (d_{xz}, d_{yz}) followed by three progressively higher-energy singlets: d_{xy}, d_z^2, and d_x^2-d_y^2, respectively.

Thus, at temperatures low compared to the splitting, tetravalent Ru ($4d^4$) is expected to be in a $S = J = 0$ ground state, assuming the CEF quenches the orbital component of the angular momentum ($L = 0$) and accounting for double degeneracy associated with electronic spin.

By contrast, lanthanide magnetism is more ionically based than transition-metal magnetism, with highly localized unpaired $4f$ electrons providing the local moment and dominating the magnetic properties. The CEF from neighboring ions can partially and sometimes fully lift the $2J + 1$ degeneracy of the M Hund's rule ground state. Because the radial extent of the $4f$ electrons tends to be much smaller than that of the $4d$ electrons, the magnitude of the splitting ought to be significantly less than in the case of the $4d$ electrons.[6] The results of the work presented here emphasize the CEF effect on the magnetic properties of M_2RuO_5 and demonstrate how the CEF interaction *itself* is influenced by a uniform decrease in lattice constant. The results support the description that for M_2RuO_5 the Ru moment is small and that the excited states are sufficiently removed in energy from the ground state that they are not observably pressure dependent. There is clear evidence, however, that Ru mediates and promotes ordering among the M ions.[3]

EXPERIMENTAL PROCEDURE

Black polycrystalline M_2RuO_5 samples, all of which are insulators with room-temperature resistivities, $\rho \approx 100\ \Omega$ cm, were grown using the solid-state reaction procedures outlined elsewhere.[3]

The pressure-dependent magnetization measurements $M(H,T,P)$ were carried out in a manner described earlier,[1] but using an entirely new apparatus. A self-locking clamp device machined and then hardened from high-purity beryllium copper provides the hydrostatic pressure. The dimensions of the main body are 0.800″ in length by 0.437″ diameter, and the bore is 0.125″. A Teflon bucket located in the clamp body center is filled with the hydrostatic medium, 1:1 isoamyl alcohol and *n*-pentane, and it also contains a small disk of Pb, used as a superconducting manometer. Pressure is
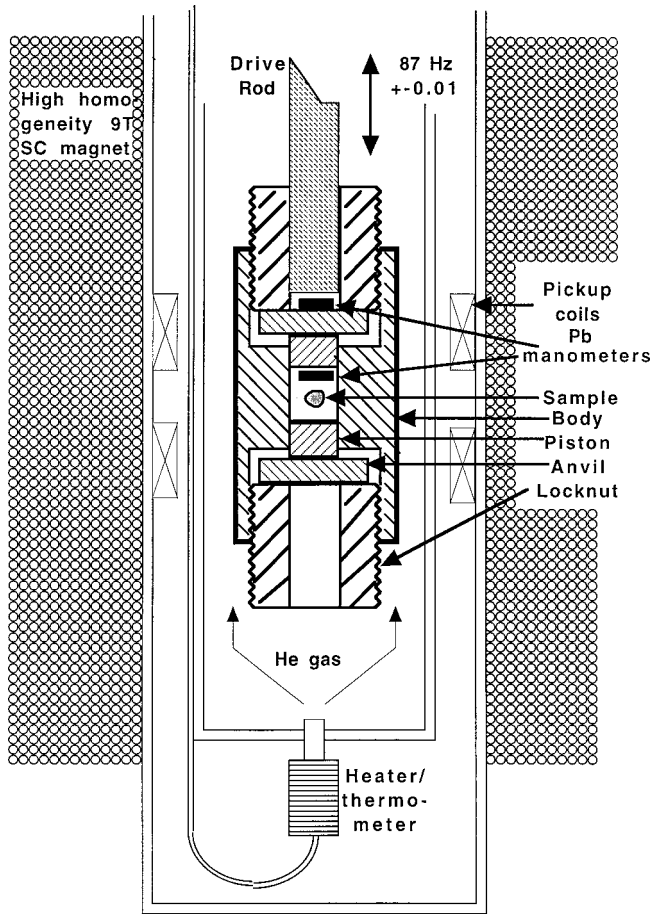
FIG. 1. Pressure-dependent magnetization apparatus showing a 9-T high-homogeneity superconducting magnet (0.01% over 1 in^3), the pressure clamp assembly which is attached to the drive rod of a vibrating sample magnetometer, and an outline of the variable-temperature gas-flow cryostat used for temperature regulation. The sample is located in a hydrostatic (isoamyl alcohol/n-pentane) pressure medium in a Teflon capsule at the center of the clamp along with one Pb superconducting manometer. The clamp body is 0.8″ long by 0.437″ OD and the bore is 0.125″. The clamp has a mass of about 13 gm, the sample typically about 10 mg. The entire sample moment is detected by the pickup coils, but only a small fraction of the clamp moment is detected due to the high-homogeneity field, which reduces eddy currents in the clamp, and canceling of the clamp moment due to its length and symmetry.

exerted using a hydraulic press and secured with lock nuts located at both ends of the symmetric clamp. The pressurized clamp attaches securely to the end of the drive rod of a vibrating-sample magnetometer (EG&G-4500), which is integrated with a 9-T high-homogeneity superconducting magnet. The general features of the high-pressure magnetization apparatus are seen in Fig. 1.

For this method of measurement, the mass of the sample is typically 10 mg or less, whereas the clamp has a mass of about 13 g. Although the magnetic moment of the entire clamp-sample complex is, in principle, detected by the series opposing pickup coils located inside the magnet, only a small fraction of the clamp moment is detected due to canceling of its moment because of its high symmetry and its
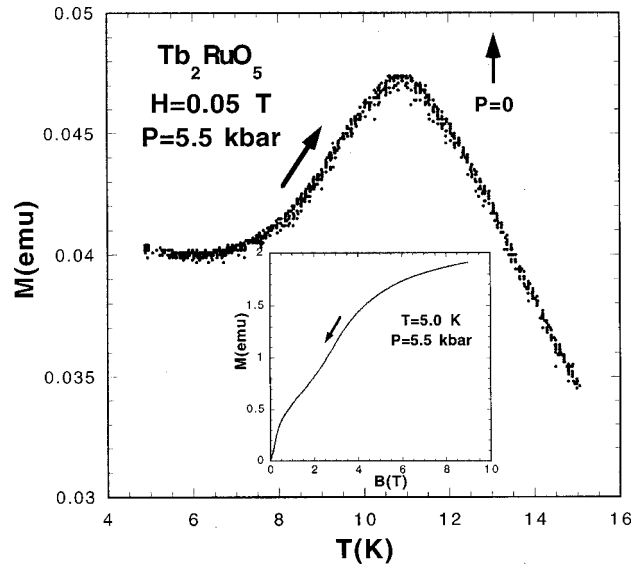

FIG. 2. Temperature dependence of the magnetic moment of Tb$_2$RuO$_5$ in an applied field of 0.05 T (500 G). The $\approx$10 mg sample is under 5.5 kbar hydrostatic pressure. The inset shows isothermal magnetization at 5.0 K of Tb$_2$RuO$_5$ under the same pressure. With this method, over 500 data points are taken during a field sweep of a few minutes. There was no discernible shift in the field-induced transitions as a function of pressure to within $\pm$0.02 T.

length. However, 100% of the sample moment is detected. At full field the clamp-only background is typically about 0.15 emu diamagnetic, and it is less than 0.01 emu for $B < 2$ T. Data are recorded continuously as a function of field for $0 < B < 9$ T or temperature for $2 < T < 300$ K.

Pressure was determined in these experiments by measuring the differential in the superconducting transition temperature T_c between a Pb disk located inside the high-pressure chamber and another Pb disk at the same temperature, but located at ambient pressure on the outside of the clamp[7] (see Fig. 1). The accuracy of the pressure determination using this method was about $\pm$0.2 kbar. The superconductivity of the Pb manometers is quenched and their magnetization undetectable for $T < T_c$ and in modest fields of no more than a few hundred gauss.

EXPERIMENTAL RESULTS

For M_2RuO$_5$, the FC and ZFC temperature-dependent magnetization $M(T)$ differs for $T < T_N$ in fields less than a few tesla, so all data reported here were taken ZFC, i.e., after warming the clamp to $T \gg T_N$ and then cooling in zero applied field to 5 K. The data were taken during extremely slow warming to ensure thermal equilibrium between clamp and thermometer, and T_N was arbitrarily assigned to the peak in $M(T)$. In Fig. 2 we show representative results for Tb$_2$RuO$_5$ using this procedure; the data shown are for $H = 0.05$ T and pressure of 5.5 kbar. The $P = 0$ peak in $M(T)$ measured using the identical protocol is also indicated in Fig. 2, so the pressure-induced reduction in T_N, $\Delta T_N = -2.2$ K, is readily apparent.

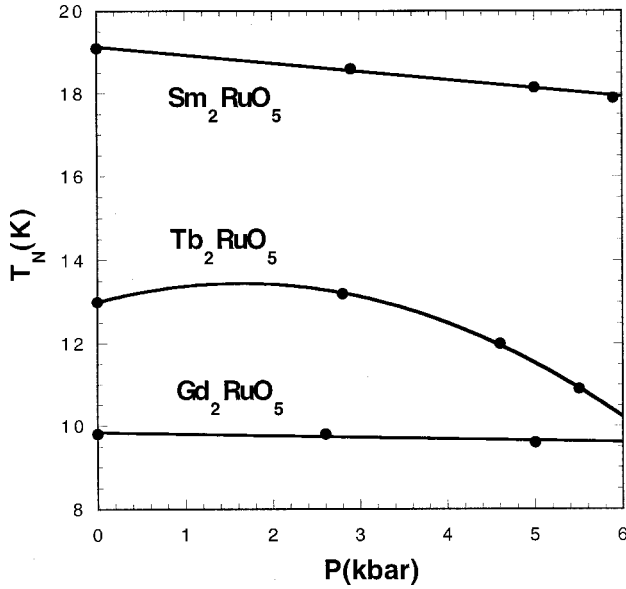The inset to Fig. 2 shows isothermal magnetization at T

FIG. 3. Pressure dependence of the antiferromagnetic ordering temperature of three M_2RuO_5 samples. The data are taken from temperature-dependent magnetization sweeps similar to that of Fig. 2.

$=5.0$ K, and at the same high pressure, $P=5.5$ kbar. More than 500 data points were collected in about 13 min. The two steplike features at $B=2.61$ and 3.19 T were also seen in ambient-pressure data, as well as the pulsed-field data measuring dM/dt reported in Ref. 3. They appear to be spin reorientation transitions associated with magnetic anisotropy, though in polycrystalline materials the spin reorientation directions cannot be determined with certainty. By carefully differentiating the $M(B)$ data for $P=0$ and $P=5.5$ kbar, we found no pressure-induced shift of these transitions to within ±0.02 T. If these anomalies were field-induced CEF-level crossings transitions, we might expect some shift with pressure along with T_N. Thus the evidence points instead to their origin as magnetic anisotropy and exchange-dominated spin reorientation transitions. Finally, there is no hysteresis observed in the transitions; nor is there hysteresis at $B=0$, supporting antiferromagnetic rather than ferromagnetic ordering in M_2RuO_5.

Figure 3 is a composite of all the pressure-dependent $T_N(P)$ measurements determined from ZFC $M(T)$ sweeps. Although there is a clear depression of T_N for Sm_2RuO_5 and Tb_2RuO_5 (the latter being nonlinear), there is none for Gd_2RuO_5, for which T_N appears to be independent of pressure.

DISCUSSION

The antiferromagnetic ordering temperature T_N for M_2RuO_5 is a function of the complex superexchange interaction, modified by the CEF interaction. For Gd_2RuO_5, however, the CEF interaction should be zero to first order because Gd^{3+} is an S-state ion ($4f^7$ configuration) with no orbital component to the total angular momentum. Thus we understand $dT_N/dP\approx0$ as due to vanishingly small CEF. In

addition, the data show that the superexchange responsible for M-M coupling is pressure insensitive, at least in this modest pressure range. Finally, these data show no pressure-induced changes in the Ru moment, already quite small as discussed above, even though the Ru evidently promotes M-M coupling and contributes to the large linear term in the specific heat.[3]

Pressure changes the CEF interaction in a generally predictable way[8,9] and can help explain the results shown in Fig. 3. The crystal field Hamiltonian for the M sites and pertinent to the M_2RuO_5 crystal structure includes a second-, fourth-, and sixth-order term in the expansion of the electrostatic potential for the surrounding seven oxygen atoms.

$$H_{CEF}=(A_2\langle r^2\rangle/a^3)O_2+(A_4\langle r^4\rangle/a^5)O_4+(B_6\langle r^6\rangle/a^7)O_6. \quad (1)$$

Here the coefficients A_n differ for the two inequivalent M sites, $\langle r^n\rangle$ represents the expectation value of the nth power of the orbital radii of $4f$ electrons, a is the rare-earth–oxygen ligand distance, and the O_n are linear combinations of Stevens operator equivalents.[10]

The coefficients A_n, as well as the composition of the operators O_n, depend on the precise placement of the oxygen atoms, and this problem is highly complex because of the very low M-site symmetry of the M_2RuO_5 lattice. However, we have modeled this problem by assuming that the M ion sits in the middle of a triangular prism with one additional oxygen, the seventh, equidistant to the others along a line perpendicular to one face of the prism. For Sm^{3+} ($J=5/2$), which has an odd number of f electrons, the CEF lifts the sixfold degeneracy, yielding three doublets, and for Tb^{3+} ($J=6$) the degeneracy is lifted entirely, yielding 13 singlets, Tb^{3+} being a non-Kramers ion.

Regardless of the exact level scheme, we can make some general predictions about the pressure dependence of W, which we define as scaling with the CEF interaction strength. This scaling energy will be proportional to the size of the parameters in Eq. (1):

$$W=\alpha/a^3+\beta/a^5+\gamma/a^7, \quad (2)$$

with α proportional to $A_2\langle r^2\rangle$, etc. For Gd_2RuO_5, as noted above, $W=0$. To find the pressure dependence of W, we differentiate $dW/dP=(dW/da)(da/dP)$, where da/dP is related to the isothermal compressibility, $\kappa(=-V^{-1}dV/dP)$ by $da/dP=-\kappa r/3$. Differentiating Eq. (2) with respect to a and making substitutions, we find, after rearrangement of some terms,

$$W^{-1}dW/dP=(\kappa/3)[3+2\beta/Wa^5+4\gamma/Wa^7]. \quad (3)$$

Borrowing from the parametrization of Lea, Leask, and Wolf[11] and redefining their use of x, we can relate the fourth- and sixth-order terms in Eq. (1) to the second-order term:

$$W_4(1-|x|)=\beta/a^5, \quad W_6(1-|y|)=\gamma/a^7, \quad (4)$$

$$\text{with}\,|x|,|y|\leqslant1.$$

Here W_4 and W_6 are the interaction strengths for the fourth- and sixth-order terms, respectively, if the second-order term

is zero and x and y weigh the relative strength of the fourth- and sixth-order terms. E.g., $x = \pm 1$ means the fourth-order term is null. We find

$$W^{-1}dW/dP = (\kappa/3)[3 + 2W_4(1 - |x|)/W$$
$$+ 4W_6(1 - |y|)/W]. \quad (5)$$

If, for example, the second-order term dominates, the relative pressure dependence is just κ, and if the CEF Hamiltonian were dominated by the sixth-order term, the result would be $7\kappa/3$. In any case pressure causes an *increase* in W.

The relationship between the ordering temperature and the CEF interaction strength is less straightforward. In general, we expect the coupling between M ions to be modified by the overall CEF interaction strength, i.e., $T_N \propto f(J_{\mathrm{ex}}/W)$,[12] so an increase in W would lead to a decrease in T_N, as observed for Sm_2RuO_5 and Tb_2RuO_5.

One closed-form example of T_C vs W is the ferromagnetic transition temperature of a CEF singlet ground-state system within the framework of the molecular field model. In this case it is assumed that only the first-excited CEF level contributes to the molecular field.[13] The relationship between T_C and W, which represents the singlet-triplet CEF splitting, is

$$W = T_C \ln\{1 + 3[1 - (M_0)^2]^{1/2}\}/\{1 - [1 - (M_0)^2]^{1/2}\}. \quad (6)$$

Here M_0 is a normalized quantity proportional to the magnetic moment at $T = 0$ K. The argument of the ln function increases rapidly as M_0 decreases, as expected for increasing pressure. This increase drives T_C down with increasing pres-sure as long as the increase in the ln function is more rapid than that of W. (This model would be more appropriate for Tb_2RuO_5 with a singlet ground state than for $Sm_2Ru_2O_5$.)

The nonlinearity of T_C vs P for Tb_2RuO_5 may be due to multiple mechanisms associated with the magnetic ordering. Sheng and Cooper[14] describe such nonlinearity for highly correlated electron systems. While Tb_2RuO_5 appears to be highly correlated from measurements of the large linear heat capacity coefficient, it is an insulating system and so the model may not be applicable. The results presented here are somewhat analogous to noncorrelated systems among the heavy rare earths such as antiferromagnetic $Tb_{1-x}Y_xSb$.[15]

In summary, the depression with increasing pressure of T_N for Sm_2RuO_5 and Tb_2RuO_5 can be attributed to an increase of the overall CEF interaction strength arising from decreasing lattice constants (increasing pressure). While this rule is not always followed,[9] it does give a satisfactory explanation for the observed results in the M_2RuO_5 system.

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