Magnetic ordering in the superconducting weak ferromagnets $RuSr_2GdCu_2O_8$ and $RuSr_2EuCu_2O_8$

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Neutron powder-diffraction measurements for $RuSr_2GdCu_2O_8$ and $RuSr_2EuCu_2O_8$ show that both compounds, below their magnetic ordering temperatures of 133 and 120 K, respectively, have the same *G*-type antiferromagnetic structure in which Ru moments are antiparallel in all three crystallographic directions. The ferromagnetism in these compounds, which is clearly indicated by hysteresis loops, can be explained if the Ru moments are canted to give a net moment perpendicular to the *c* axis. In such a model, one would expect an induced ferromagnetic ordering of the magnetic Gd ions, which have large ($\sim 7\mu_B$) moments, as a result of the net field at the Gd site, while Eu, being nonmagnetic, would exhibit no such response. The dramatically larger hysteresis loops for $RuSr_2GdCu_2O_8$ compared to those for $RuSr_2EuCu_2O_8$ are consistent with this hypothesis.

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INTRODUCTION

The observation of coexisting ferromagnetism (below ~133 K) and superconductivity (T_c as high as 46 K) in $RuSr_2GdCu_2O_8$ (Ref. 1) has motivated studies to understand the nature of superconductivity and magnetism in this system. Because of the strong competition between superconductivity and ferromagnetic ordering, their coexistence is rare and typically involves some kind of spatial accommodation. Maple has written a nice review of the interplay between magnetism and superconductivity, in which heavy Fermion and Chevrel-phase compounds are the key examples.[2] The strongly competitive nature of ferromagnetism and superconductivity is typically manifest by the formation of long-wavelength oscillatory magnetic states at low temperature ($\leqslant 1$ K); with superconductivity being quenched at the ferromagnetic lock-in temperature.[3–5] In $HoMo_6S_8$, Burlet *et al.* explained the occurrence of ''partial superconductivity'' in a ferromagnetic state in terms of superconducting walls in a magnetically ordered lamellar domain structure.[6]

More recently, Felner *et al.*[7] reported the development of bulk superconductivity in a magnetically ordered phase in the compound $R_{1.4}Ce_{0.6}RuSr_2Cu_2O_{10}$ (R=Gd, Eu). These materials order magnetically at $T_N \approx 180$ and 122 K and enter a bulk superconducting state at $T_c \approx 42$ and 32 K, for R = Gd and Eu, respectively. Scanning tunneling microscopy measurements showed a superconducting gap structure at all locations in the samples, indicating that the materials were single phase. The existence of hysteresis loops showed that the magnetic ordering included weak ferromagnetism. The actual magnetic structure was not determined. In a subsequent paper, these authors argued that the development of diamagnetism at temperatures much below T_N, where weak ferromagnetism is fully developed, implied the existence of a spontaneous vortex phase in these materials.[8]

The related compound $RuSr_2GdCu_2O_8$, which displays similar magnetic ordering and superconducting transition temperatures ($T_N \approx 133$ K, T_c as high as 46 K) has been more extensively studied and is providing additional insight into this remarkable phenomenon. The magnetic ordering is seen in magnetization measurements and is concluded to involve ferromagnetism because of the existence of well-defined hysteresis loops.[1] Muon spin rotation (μSR) experiments show that the magnetic phase is homogeneous on a microscopic scale and that this phase accounts for most of the sample volume.[1] Electron spin resonance (ESR) measurements which probe the local field at the Gd site confirm the presence of a Ru-Gd ferromagnetic exchange interaction and a ferromagnetic resonance due to the ordered Ru magnetic moments below the magnetic ordering temperature.[9] Measurements of the high-field magnetization below T_N define a saturation magnetization of $1.05(5)\mu_B$/Ru, consistent with that expected for Ru^{5+} ($4d^3$) in its low spin state.[1] Evidence for bulk superconductivity has been somewhat controversial because the strength of the diamagnetic response depends on sample processing and full diamagnetism is only observed well below the onset temperature for superconductivity.[10,11] However, specific-heat measurements show that a bulk superconducting transition occurs.[12] The variation in the diamagnetic response has been explained in terms of a crossover from a spontaneous vortex phase to a Meissner state when the magnetization reaches $H_{C1}/4\pi$.

Neutron-diffraction measurements have been employed by our group[13] and that of Lynn *et al.*[14] to establish the microscopic nature of the magnetic ordering in $RuSr_2GdCu_2O_8$. The work of both groups was done with the same sample which was made from ^{160}Gd in order to avoid the very large absorption cross section of natural-abundance Gd. Ferromagnetic ordering would manifest itself as additional scattering below T_N at the positions of specific nuclear Bragg peaks; in particular, ordering with moments in the plane perpendicular to the *c* axis would be manifest as increased scattered intensity in the 001 Bragg peak, which has an accidentally small nuclear scattering cross section. In our study, we concluded that the ferromagnetically ordered moment (in the plane perpendicular to the *c* axis) could not be larger than $0.3\mu_B$.[13] Shortly thereafter, Lynn *et al.* using polarized neutrons were able to establish an upper limit of $0.1\mu_B$.[14] More importantly, Lynn *et al.* showed that the dominant spontaneous magnetic ordering was antiferromagnetic, with adjacent Ru spins aligned antiparallel in all three crystallographic directions and with an ordered moment of $1.18(6)\mu_B$, in reasonable agreement with the Ru moment deduced from the high-field saturation magnetization measurements.[1] As we will show in this paper, we were also able to see the same antiferromagnetic ordering in our unpolarized time-of-flight neutron-diffraction data, confirming the result of Lynn *et al.*

For these neutron-diffraction results to be consistent with the previous evidence for spontaneous ferromagnetism, the antiferromagnetically ordered Ru moments must be canted to give a small ferromagnetic moment in the plane perpendicular to the *c* axis. Recently, it was suggested[7] that it is the antisymmetric superexchange (Dzyaloshinsky-Moriya[15]) interaction that is responsible for the canting of the magnetic moments to produce weak ferromagnetism. The rules governing the existence of this interaction,[15] require that the horizontal mirror symmetry operator (i.e., in the plane perpendicular to the *c* axis) must be removed. The removal of this mirror would result from tilting of the Ru-centered oxygen octahedra about an axis in the plane perpendicular to the *c* axis. Synchrotron x-ray-diffraction experiments[16,17] suggest that small disordered tilts of this character might exist, but neutron-diffraction experiments,[13] which are more sensitive to oxygen-atom displacements see only ordered rotations around the *c* axis. The neutron-diffraction experiments do not confirm the existence of tilts around an axis perpendicular to the *c* axis.

From symmetry (Fig. 1), it is easy to see that the dipolar fields from the antiferromagnetic component in the Ru sublattice cancel at the sites of the Gd sublattice, and vice versa when the Gd sublattice orders with the same antiferromagnetic structure below 2.5 K, as shown by Lynn *et al.*[14] However, if the Ru moments are canted to give a ferromagnetic component, the resulting field at the Gd site is no longer zero and one has the possibility of an induced ferromagnetic moment at the Gd site. A similar situation arises if Ru moments are canted by application of an external magnetic field. Lynn *et al.*[14] report neutron-diffraction evidence for an induced moment at the Gd site in an applied field, consistent with this model.

Because Gd has a much larger moment ($\sim 7\mu_B$) than Ru ($\sim 1\mu_B$), the Gd has a strong effect on the magnetic properties in the proposed model. The canting of the Ru moments would be expected to induce a ferromagnetic moment at the Gd site which, in turn, will give rise (via the increased dipolar field) to increased canting of the Ru moments. Thus, the total ordered ferromagnetic moment would depend on the degree of ordering of both the Ru and Gd. Additional insight can be obtained by probing the magnetism in an isostructural system with a nonmagnetic ion at the Gd site. In such a system, one would expect, due to the lack of induced ferromagnetism in the rare-earth sublattice, a weaker field with less canting at the Ru site. In this paper, we compare bulk magnetization and neutron-diffraction measurements for $RuSr_2GdCu_2O_8$ and $RuSr_2EuCu_2O_8$—Eu being a nonmagnetic ion that can be used to form the same compound. As

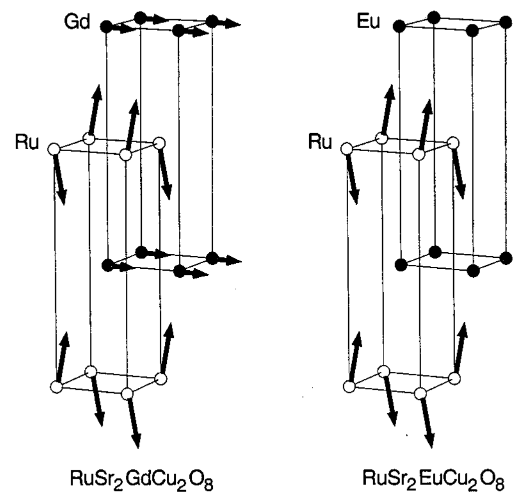

FIG. 1. Models for the magnetic structures of $RuSr_2GdCu_2O_8$ (left) and $RuSr_2EuCu_2O_8$ (right). In both cases, the dominant ordering of the Ru moments is *G*-type antiferromagnetic. The weak ferromagnetism, which leads to hysteresis loops in magnetization measurements, can be explained by canting of the Ru moments to produce a net ferromagnetic moment in the plane perpendicular to the *c* axis. This will induce a small component of ferromagnetic ordering at the Gd sites, because Gd also carries a moment, while there will be no induced ordering at the (nonmagnetic) Eu sites. The ferromagnetic moments shown on the Gd sites are the small, average, induced moments. Much higher fields would be required to fully order the Gd ferromagnetically.

expected, the measured hysteresis loops suggest a significantly smaller component of ferromagnetism for the Eu sample than for the Gd sample, while both systems exhibit the same antiferromagnetic ordering of Ru moments as probed by neutron diffraction; neither shows neutron-diffraction evidence for ferromagnetism at the limit of sensitivity of the measurement.

SYNTHESIS

A polycrystalline sample of $RuSr_2EuCu_2O_8$ was synthesized by solid-state reaction of a stoichiometric mixture of the oxides RuO_2, $^{153}Eu_2O_3$, CuO, and $SrCO_3$. After calcination in air at 900 °C, the material was ground, pressed into pellets and annealed in flowing Ar at 1010 °C. This step helps to minimize the amount of the $SrRuO_3$ impurity phase present in final material. Subsequently, the sample was annealed in flowing oxygen at increasing temperatures from 1030 to 1045 °C with frequent intermediate grindings and pelletization. The resulting material was fast cooled to room temperature. The weak superconducting response observed for this sample (evidenced by a downward inflection of the real part of the susceptibility at 15 K) is consistent with previous observations[1] that special annealing techniques may be required to produce pronounced superconducting behavior. The synthesis of the $RuSr_2GdCu_2O_8$ sample, using ^{160}Gd to avoid the large neutron absorption cross section of normal-abundance Gd, was described previously.[13]

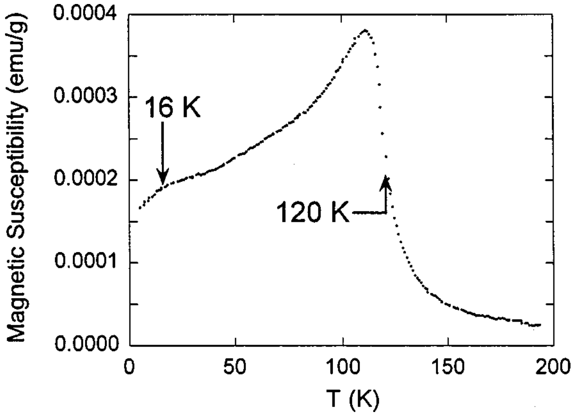

FIG. 2. Ac susceptibility data for $RuSr_2EuCu_2O_8$ showing the magnetic transition at 120 K.

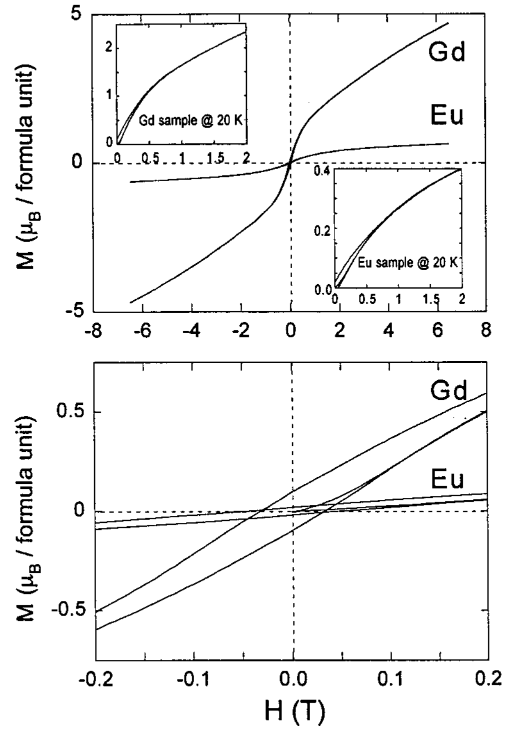

FIG. 3. Hysteresis loops for $RuSr_2GdCu_2O_8$ and $RuSr_2EuCu_2O_8$ measured at 20 K to a maximum applied field of 6.5 T, which is sufficient to achieve saturation. The remnant magnetizations are $0.10\mu_B$/formula unit and $0.02\mu_B$/formula unit for the Gd- and Eu-containing compounds, respectively. The integrated area of the loop for $RuSr_2GdCu_2O_8$ is about six times larger than that for $RuSr_2EuCu_2O_8$.

SUSCEPTIBILITY AND MAGNETIZATION

The ac susceptibility and dc magnetization were measured using a Quantum Design Physical Properties Measurement System. The ac susceptibility data were collected upon warming from a zero-field-cooled state, using an ac field of 1 Oe at 200 Hz (Fig. 2). For $RuSr_2EuCu_2O_8$, the real component of the ac susceptibility peaks at 116 K. The rapid change of the imaginary component of the ac susceptibility at 120 K marks the magnetic ordering transition. The temperature irreversibility of zero-field-cooled and field-cooled branches of the dc magnetization measured at small fields (of the order of 10 Oe) also develops below 120 K. Both measurements show that the temperature of the magnetic ordering for the Ru sublattice is lower than for $RuSr_2GdCu_2O_8$ where the same features of the magnetic characteristics have been observed at 133 K.[13] A similar behavior was reported for the related system $R_{1.4}Ce_{0.6}RuSr_2Cu_2O_{10-\delta}$ ($R = \mathrm{Eu, Gd}$).[7]

Hysteresis loops for $RuSr_2EuCu_2O_8$ were measured in the temperature range between 5 and 120 K with a maximum applied magnetic field of 6.5 T. The sample was warmed above 150 K after collecting data at each temperature. Figure 3 shows the M vs H data for $RuSr_2EuCu_2O_8$ compared with those for $RuSr_2GdCu_2O_8$. The two loops show about the same coercive field of ~250 Oe. This is expected in view of the identical crystal structures and magnetic interactions (of the Ru sublattice) and is indicative of similar morphology in the two samples. The remnant magnetizations M_r at 20 K are $0.10\mu_B$/formula unit and $0.02\mu_B$/formula unit for the Gd- and Eu-containing samples, respectively. Thus the remnant magnetization of $RuSr_2GdCu_2O_8$ is approximately five times larger than that of $RuSr_2EuCu_2O_8$. This result agrees with the recent measurements of Williams and Kramer[18] which show a factor of about four at 5 K. Since M_r is a measure of the spontaneous ferromagnetic moment, this shows that when (nonmagnetic) Eu is replaced by (magnetic) Gd, the low-temperature ferromagnetic moment M and the dipolar field, $H = 4\pi M$, are increased by a factor of 5. The ferromagnetic component of the magnetic moment of the Ru ion can be estimated from the M_r of the Eu compound [$M(\mathrm{Ru}) \approx 2M_r$] to be $0.034\mu_B$. The net (Ru and Gd) ferromagnetic component in the Gd compound is estimated to be $\sim 0.2\mu_B$, between the reported detection limits of the polarized ($\sim 0.1\mu_B$) (Ref. 14) and unpolarized ($0.3\mu_B$) (Ref. 13) neutron-diffraction experiments. The corresponding internal dipolar magnetic fields are 22 and 132 Oe in the Eu and Gd compounds, respectively. Assuming an upper critical field H_{C1} of a few tens of Oe, these internal fields are below and above H_{C1}, respectively. This result is of particular interest to the discussion of the spontaneous vortex phase.[8] It is also worth noting that in spite of this fundamental difference between the Eu and Gd compounds their superconducting behaviors are very similar.

NEUTRON DIFFRACTION

Time-of-flight neutron powder-diffraction data were collected using all detector banks of the Special Environment Powder Diffractometer at Argonne's Intense Pulsed Neutron Source.[19] The magnetic peaks are best seen in the 60° detector banks. To minimize the background, the samples were sealed in specially made thin-walled aluminum cans (4 cm long, 0.6 mm diameter, and 0.013 mm wall thickness) with helium exchange gas to ensure homogeneous cooling. Diffraction data were acquired at several temperatures between 300 and 12 K using a closed-cycle helium (Displex) refrigerator.

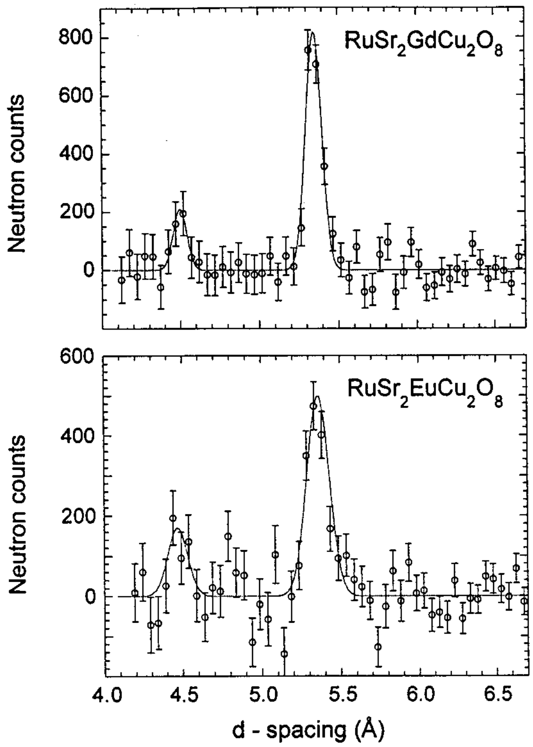

FIG. 4. Raw neutron powder-diffraction data, for the $\{1\ 0\ \frac{1}{2}\}$ and $\{1\ 0\ \frac{3}{2}\}$ magnetic peaks of $RuSr_2GdCu_2O_8$ and $RuSr_2EuCu_2O_8$. The data for $RuSr_2GdCu_2O_8$ are the sum of measurements at 12, 20, 40, 60, and 80 K minus the sum of data taken above T_N (properly normalized); the data for $RuSr_2EuCu_2O_8$ are the sum of measurements at 10, 30, 50, and 80 K minus the sum of data taken above T_N (properly normalized).

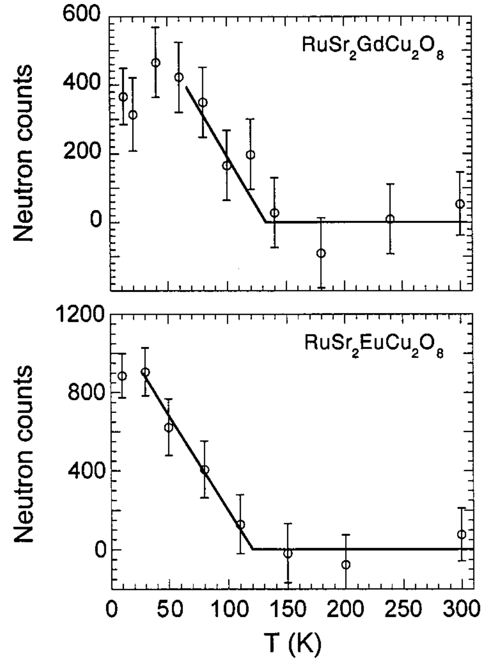

FIG. 5. Normalized integrated intensities for the $\{1\ 0\ \frac{1}{2}\}$ magnetic peaks of $RuSr_2GdCu_2O_8$ and $RuSr_2EuCu_2O_8$ as a function of temperature. The magnetic ordering temperatures deduced from these data agree with those from susceptibility data.

Figure 4 shows raw neutron powder-diffraction data from the 60° detector bank, below T_N, for the $\{1\ 0\ \frac{1}{2}\}$ and $\{1\ 0\ \frac{3}{2}\}$ (Ref. 20) magnetic peaks for $RuSr_2EuCu_2O_8$ and the same data for $RuSr_2GdCu_2O_8$ from our previous experiment.[13] The existence of these magnetic peaks shows that the basic magnetic structure for both compounds is *G* type, in which the Ru moments are aligned antiparallel in all three crystallographic directions. This is the same conclusion reached by Lynn *et al.* for $RuSr_2GdCu_2O_8$,[14] and is in agreement with a recent electronic structure calculation[21] which shows that antiferromagnetic ordering is energetically favored over ferromagnetic ordering. Magnetic reflections of higher index cannot be seen because of the rapidly decreasing form factor for Ru. This limitation prevents a direct investigation of whether the moments are canted.

Using the form factor of Mo^{3+} (a $4d^3$ ion whose form factor is expected to approximate that for Ru^{5+}, for which there are no data,[13,22]) we have obtained the ratio of the calculated integrated intensities, $I\{1\ 0\ \frac{1}{2}\}/I\{1\ 0\ \frac{3}{2}\}$. The expected ratio is 2.6 and 1.4 for antiferromagnetic ordering with the moments aligned along the *c* axis or perpendicular to the *c* axis, respectively. The observed ratio (Fig. 4) is 4.6(1.6) and 3.5(1.2) for the Gd and Eu compounds, respectively. In spite of the large statistical errors, this result shows convincingly that the antiferromagnetic moments are aligned along the *c* axis in both compounds.

The integrated neutron counts in the $\{1\ 0\ \frac{1}{2}\}$ peaks were obtained for each temperature by subtracting a fitted background and normalizing to the total upstream neutron monitor count. The results are plotted vs temperature in Fig. 5. For both compounds, the temperature dependence is in agreement with the magnetic ordering temperatures determined from ac susceptibility measurements (133 K for $RuSr_2GdCu_2O_8$ and 120 K for $RuSr_2EuCu_2O_8$). As was true in our previous study of $RuSr_2GdCu_2O_8$ and that of Lynn *et al.*,[14] we see no additional intensity in the {0 0 1} peak that would be characteristic of ferromagnetic ordering at T_N. This is to be expected because the limit of our sensitivity for the most favorable case where the ferromagnetic moments are aligned perpendicular to the *c* axis is about $0.3\mu_B$. For weak ferromagnetism, i.e., canted antiferromagnetism giving a moment perpendicular to the *c* axis (Fig. 1), with $\mu_\perp < 0.3\mu_B$, we would not expect to see measurable intensity in the {0 0 1} peak in this measurement.

CONCLUSIONS

We conclude from our neutron-diffraction measurements that $RuSr_2EuCu_2O_8$ ($\mu_{Eu} \approx 0$) and $RuSr_2GdCu_2O_8$ ($\mu_{Gd} \approx 7\mu_B$) both order below T_N in an antiferromagnetic structure of the *G* type with $\mu_{Ru} \approx 1\mu_B$ along the *c* axis. Thus the antiferromagnetic ordering of the Ru sublattice does not depend on whether the ions on the rare-earth sublattice are magnetic or nonmagnetic (this decoupling is due to symmetry). From hysteresis loop measurements, we conclude that both compounds are also weak ferromagnets. It is argued that the ferromagnetism in this system is due to canting of the Ru moments. Unlike the antiferromagnetism, the ferromagnetic component on the Ru sublattice couples to the rare-earth sublattice, yielding a total ferromagnetic component in the Gd compound which is five times larger than that in the Eu compound. A rough estimate of the dipolar magnetic fields (resulting from the ferromagnetic component) suggests that they are larger and smaller than H_{C1} in the Gd and Eu compounds, respectively. This situation is of interest in the study of spontaneous vortex phases.

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