

Effect of Sn, Nb, and La substitution on superconductivity and magnetic order in $\text{RuSr}_2\text{RCu}_2\text{O}_8$ ($R = \text{Eu, Gd}$)

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We report the results from a resistance, and magnetization study on $\text{Ru}_{1-x}\text{A}_x\text{Sr}_{2-z}\text{B}_z\text{RCu}_2\text{O}_8$ ($A = \text{Sn, Nb}$, $B = \text{La}$, $R = \text{Eu, Gd}$) where the parent compound has previously been reported to display superconductivity and predominately low field antiferromagnetic order. We show that, contrary to a study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$, there is no significant change in the superconducting transition temperature when Sn is substituted for Ru, implying that there is no significant Sn-induced charge transfer to the CuO_2 planes. Furthermore, increasing the Sn concentration has the effect of increasing the temperature where zero resistance and the onset of bulk ac diamagnetic shielding occurs, which we interpret in terms of a decreasing ferromagnetic component leading to an increase in the temperature where the spontaneous vortex phase occurs. Contrary to previous studies on the pure compounds, we find an initial negative dM/dB at low temperatures in magnetically ordered $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ for Sn concentrations at, and greater than, 0.1. The substitution of Ru by nuclei that have a larger (Nb^{5+}) or smaller (Sn^{4+}) valence results in a similar decrease in the magnetic ordering temperature and an increase in the average Ru valence. La substitution for Sr causes charge transfer to the CuO_2 planes and an increase in the magnetic ordering temperature that is not expected.

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INTRODUCTION

It has recently been reported that the ruthenate cuprate, $\text{RuSr}_2\text{RCu}_2\text{O}_8$ ($R = \text{Gd, Eu}$) displays superconductivity arising from the CuO_2 planes¹⁻⁵ and magnetic order arising from the RuO_2 layers.¹⁻⁶ These materials and the related ferromagnetic superconductors, $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10+\delta}$, were first discovered by Bauernfeind, Widder, and Braun.^{1,2} It was originally believed that $\text{RuSr}_2\text{RCu}_2\text{O}_8$ is ferromagnetic; however, powder neutron diffraction studies have shown that the low field magnetic order is predominately antiferromagnetic.^{3,4} The small ferromagnetic component, which orders at 132 K, is believed to be large enough to affect superconductivity unless there is some form of accommodation via a spatial modulation of the respective order parameters or a spontaneous vortex phase.^{7,8} This model was originally proposed for the ferromagnetic superconductor, $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10+\delta}$.⁹ In this model, there exists a spontaneous vortex phase for $T_{\text{SVP}} < T < T_c$, where the local field, B_{loc} , is greater than the lower critical field B_{cl} . For temperatures less than T_{SVP} , B_{cl} is greater than B_{loc} and hence the bulk diamagnetic transition occurs. However, it has been suggested that a bulk diamagnetic transition does not occur in $\text{RuSr}_2\text{RCu}_2\text{O}_8$ because the derivative of the initial change in magnetization with increasing applied magnetic field is positive.^{10,11} The application of the spontaneous

vortex phase model to $\text{RuSr}_2\text{RCu}_2\text{O}_8$ has been indirect^{7,8} and it is not known if changing the magnetic ordering temperature and the ferromagnetic component will lead to changes in the magnetization data that are consistent with the spontaneous vortex model.

Recent theoretical band structure calculations based on the experimentally observed structure have concluded that antiferromagnetic order is energetically favored over ferromagnetic order in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.¹² In particular, Nakamura *et al.* showed the importance of including the effect of the rotations of the RuO_6 octahedra. Previous calculations by Pickett, Weht, and Schick¹³ had concluded that the magnetic order was ferromagnetic but Pickett, Weht, and Schick had used the structure as determined by the analysis of the x-ray diffraction spectra where rotations of RuO_6 octahedra could not be observed. Unfortunately, the experimental data shows that the magnetic order is more complex than purely antiferromagnetic. For example, Takagiwa *et al.*¹⁴ have reported the existence of a significant low field ferromagnetic component in $\text{RuSr}_2\text{YCu}_2\text{O}_8$ [$\sim 0.28\mu_B/\text{Ru}$ (Ref. 14)], which is $\sim 24\%$ of the low field antiferromagnetic moment. They also reported a magnetic field induced transition to predominately high field ferromagnetic order, which has also reported in a study on $\text{RuSr}_2\text{EuCu}_2\text{O}_8$.¹⁵ Another problem in understanding the ruthenate cuprates is that $\text{RuSr}_2\text{RCu}_2\text{O}_8$ and $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10+\delta}$ have essentially the same rotations

of the RuO_6 octahedra, Ru-O-Ru and Ru-O-Cu bond lengths¹⁶ but the first compound displays a large antiferromagnetic component for low applied fields and a spin-flop transition with increasing applied field^{3,14,16} while the second compound is predominately ferromagnetic. This would appear to suggest that the different magnetic order observed in $\text{RuSr}_2\text{RCu}_2\text{O}_8$ and $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10+\delta}$ is not driven by structurally induced changes in the RuO_2 layer conduction band. $\text{RuSr}_2\text{RCu}_2\text{O}_8$ is also believed to have a mixed Ru valence (average value ~ 4.62) as determined by an x-ray absorption near edge spectroscopy (XANES) study.¹⁷ The observation of a mixed Ru valence is supported by nuclear magnetic resonance studies.^{18,19} As far as we are aware, this is the only ruthenate compound where a mixed Ru valence is observed. This can be contrasted with $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10+\delta}$, where the Ru valence is near 5.^{20,21}

The similar bond angle distortions and bond lengths in the SrRuO_3 substructure but different average Ru valences in $\text{RuSr}_2\text{RCu}_2\text{O}_8$ and $\text{RuSr}_2\text{R}_{2-x}\text{Ce}_x\text{Cu}_2\text{O}_{10+\delta}$ would appear to suggest that band filling effects are responsible for the different magnetically ordered states. This can be contrasted with the ruthenates where isoelectronic substitution for atoms not in the RuO_2 layers shows that the magnetic ordering temperature is correlated with the rotation angle of the RuO_6 octahedra and the Ru-O-Ru bond length,²² which is consistent with a theoretical study by Mazin and Singh.²³ Electronic doping via substitutions for atoms not in the RuO_2 layers can lead to a change in the rotation and tilting of the RuO_6 octahedra as well as electronic doping in the RuO_2 layers where the individual effects on the magnetic ordering temperature are not easy to separate. For example, Na^+ substitution for Sr^{2+} in SrRuO_3 leads to a decrease in the magnetic ordering temperature as well as a transition from an itinerant ferromagnetic metal to a ferromagnetic semiconductor.²⁴ Direct substitution for Ru by a nonmagnetic atom with the same valence will lead to a decrease in the magnetic ordering temperature via a dilution of the magnetic lattice and broken superexchange paths. However, it is also believed that changes in the rotation and tilting of the RuO_6 octahedra are also important.²⁵ A study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ showed that the magnetic ordering temperature decreased with increasing Sn concentration.²⁶ This was accompanied by a large change in the Ru-O-Ru bond angle distortion that is nearly half of that observed in $\text{Sr}_{1-x}\text{Ca}_x\text{RuO}_3$,²² which indicates that bond angle distortions and bond length changes also contribute to the decrease in the magnetic ordering temperature. The magnetization and resistance data were interpreted in terms of a fixed Ru valence of 4+ and charge transfer between the CuO_2 and RuO_2 layers. However, the $x=0$ and $x=0.1$ samples did not show zero resistance at a finite temperature and more recent measurements have found a mixed Ru valence in the pure compounds.¹⁷⁻¹⁹

It is apparent that further experimental research is required to enable a better understanding of the magnetic and superconducting order in the ruthenate cuprates. In this paper, we report the results from a resistance and magnetization

study on $\text{RuSr}_2\text{RCu}_2\text{O}_8$, where the superconducting and magnetic order were probed by substituting La for Sr, Sn for Ru, and Nb for Ru.

EXPERIMENTAL DETAILS

The $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$, $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$, $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$, and $\text{RuSr}_{1-z}\text{La}_z\text{EuCu}_2\text{O}_8$ ceramic samples were made from a stoichiometric mix of RuO_2 , SnO_2 , Nb_2O_5 , SrCO_3 , La_2O_3 , Eu_2O_3 , Gd_2O_3 , and CuO . The powder was first calcined in air at 960 °C for 12 h. The samples were then pressed into pellets and sintered at 1010 °C in N_2 gas for 10 h, 1050 °C in O_2 gas for 10 h, 1055 °C in O_2 gas for 10 h, and 1060 °C in O_2 gas for 10 h, 24 h, and 7 days. The samples were reground after sintering at each temperature. The initial sintering at 1010 °C was performed to suppress the formation of ferromagnetic SrRuO_3 . As found in a previous study,²² all $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ samples with $x>0$ showed evidence of SrSnO_3 in the x-ray diffraction spectra which could not be decreased by additional sintering. However, as we show later, the magnetic ordering temperatures are lower than those found in the previous study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ for similar Sn concentrations. Furthermore, all our pure and Sn substituted samples display a zero resistance at finite temperatures, which was not reported in the previous study. There was no evidence of impurity phases in the $\text{Ru}_{1-x}\text{Nb}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ and $\text{RuSr}_{1.9}\text{La}_{0.1}\text{EuCu}_2\text{O}_8$ x-ray diffraction spectra.

The ac and dc magnetization measurements were made using a SQUID magnetometer. The ac magnetization measurements were made with an ac field of 5 mT and a frequency of 1 kHz. The remanent magnetic field of the superconducting magnetic was ± 0.6 mT. The resistance measurements were made using the four terminal technique.

RESULTS AND ANALYSES

We show in Fig. 1 the normalized resistance data from $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ [Fig. 1(a)] with $x=0$ (solid curve) and $x=0.2$ (dashed curve) and $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ [Fig. 1(b)] with $x=0, 0.1$, and 0.3 (solid curves). Unlike the study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$,²⁶ we find that the resistance for $x=0$ and $x=0.2$ does reach zero at a finite temperature. Furthermore, the temperature where the resistance is zero, $T_c^R(0)$, systematically increases with increasing Sn concentration for both the $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ and $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ samples. It is possible that the samples used in the previous study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ (Ref. 26) were very disordered because it is known that annealing for an additional seven days leads to a $T_c^R(0)$ of ~ 35 K in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.^{27,28}

It has previously been shown that superconductivity in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ occurs at ~ 45 K and corresponds to the initial decrease in the resistance but the bulk diamagnetic transition occurs for temperatures below ~ 35 K.^{1,27,28} A similar effect was observed in $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ where superconductivity and the initial decrease in the resistance occur near 32 K while the transition into the bulk diamagnetic state occurs near 12 K.^{8,15} As mentioned earlier, this has been attributed

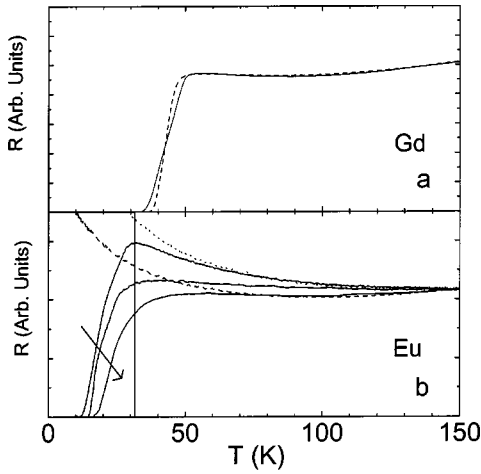


FIG. 1. Plot of the resistance against temperature for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ with (a) $R=\text{Gd}$ and $x=0$ (solid curve) and $x=0.2$ (dashed curve), (b) $R=\text{Eu}$ and $x=0, 0.1$, and 0.3 where the arrow indicates increasing Sn concentration and the solid line indicates the superconducting transition temperature in the pure compound reported in other studies. Also shown in (b) is the resistance data from $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (dashed curve) and $\text{RuSr}_{1.9}\text{La}_{0.1}\text{EuCu}_2\text{O}_8$ (dotted curve).

to the existence of a spontaneous vortex phase. The normal-state resistance data shows a semiconductorlike increase for temperatures less than ~ 100 K. It has recently been shown that this semiconductorlike increase is not intrinsic and is due to intergranular transport.⁸ Therefore, it is not appropriate to use the initial decrease in the resistance as the criterion to determine T_c . This is especially pertinent to the previous study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ where a semiconductorlike upturn was observed for all Sn concentrations and the peak in the resistance data was used to determine that T_c increased from 36 K to 48 K as the Sn concentration increased from 0 to 0.2.²⁶ However, it is apparent in Fig. 1 that there is no well-defined peak in the resistance data for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ with $x=0.3$ or $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ with $x=0.2$ that can be used to estimate T_c . It has previously been argued that T_c in the pure compound can also be estimated from the temperature where there is a significant increase in the derivative of the resistance.^{27,29} If we use a similar criteria to estimate T_c using the resistance data from our $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ samples, we obtain T_c values of 52 K and 49 K for $x=0$ and $x=0.2$, respectively. Thus, unlike the previous study on $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$, we find no significant change in T_c , as estimated from the resistance data, with increasing Sn concentration.

Also plotted in Fig. 1(b) is the normalized resistance from $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (dashed curve) and $\text{RuSr}_{1.9}\text{La}_{0.1}\text{EuCu}_2\text{O}_8$ (dotted curve), where it can be seen that both samples do not exhibit a metallic ground state at low temperatures. The disappearance of superconductivity when La is substituted for Sr or Nb is substituted for Ru is likely to be due to charge transfer to the CuO_2 planes and hence a decrease in the hole concentration on the CuO_2 planes. We first note that studies on the high temperature

superconducting cuprates have shown that there is a good correlation between T_c and the hole concentration, p , on the CuO_2 planes where superconductivity exists for $0.05 \leq p \leq 0.27$. In particular, it has been found that

$$T_c(p) = T_{c,\text{max}}[1 - 82.6(p - 0.16)^2], \quad (1)$$

where $T_{c,\text{max}}$ is the maximum T_c for each family of superconductors.³⁰ It should be noted that p is not the carrier concentration on the CuO_2 planes because the carrier concentration cannot be estimated in the usual way via the Hall coefficient owing to the strong dependence of the Hall coefficient on temperature. Rather, p derives from valence counting. For example, it is directly proportional to the Sr content in $\text{La}_{2-p}\text{Sr}_p\text{CuO}_4$. The effect of increasing (e.g., La^{3+} for Sr^{2+} in $\text{YBa}_2\text{Cu}_3\text{O}_7$) or decreasing (e.g., Ca^{2+} for Y^{3+} in $\text{YBa}_2\text{Cu}_3\text{O}_7$) the valence at one of the atomic sites can lead to a decrease or increase in p . Recent studies have shown that $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ is very underdoped where $p \sim 0.07$.^{27,31} Thus, substituting 0.1La^{3+} for Sr^{2+} could correspond to a maximum decrease in p to 0.02, which is in the insulator region. Similarly, applying the simple valence counting model to the substitution of Nb for Ru (average valence 4.62) shows that p could decrease to as low as -0.01 , assuming that there is no change in the Ru valence. We show later that there is a small Nb-induced increase in the average Ru valence to 4.77 that corresponds to a decrease in p to -0.05 , which is in the insulator region. Note that if there was charge transfer to the CuO_2 planes in the Sn-substituted samples this would cause an increase of the hole concentration from ~ 0.07 to ~ 0.16 for 0.3Sn substitution. According to Eq. (1), T_c should increase considerably. However, as mentioned above a significant change in T_c is not observed. This implies that there is no Sn-induced charge transfer to the CuO_2 planes and hence, in a simple valence counting model, Sn substitution should lead to an increase in the average Ru valence in the RuO_2 layers leading to an average Ru valence of up to 4.89 for $x=0.3$.

The onset of bulk ac diamagnetic shielding for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ can be seen in Fig. 2, where we plot the ac susceptibility. We use the ac susceptibility rather than dc susceptibility, because the remanent magnetization from the SQUID magnetometer superconducting magnet is close to the field where the bulk dc diamagnetic phase disappears in the pure samples. Furthermore, the small remanent field is sufficient to partially align the ferromagnetic component from the RuO_2 planes. It is clear that Sn substitution systematically increases the temperature where the transition into the bulk ac diamagnetic state commences. The real part of the ac susceptibility data also contains a contribution from the small ferromagnetic component, and hence the transition to the bulk diamagnetic state commences at a temperature greater than that where $\chi' = 0$ occurs. The onset of bulk ac diamagnetic shielding in $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ is clear in the inset to Fig. 2(b), where we plot the imaginary part of the ac susceptibility, χ'' . Thus, the bulk ac diamagnetic transition for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ commences at temperatures of 11, 16, and 20 K for $x=0, 0.1$, and 0.3 , respectively. We show below that there is also a Sn-induced decrease in the ferro-

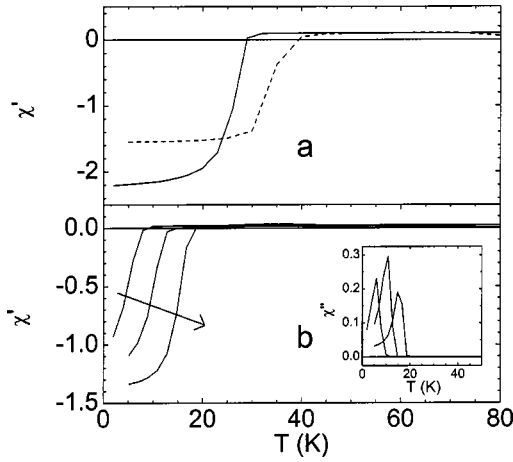


FIG. 2. Plot of χ' against temperature for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ with (a) $R=\text{Gd}$ and $x=0$ (solid curve) and $x=0.2$ (dashed curve), (b) $R=\text{Eu}$ and $x=0, 0.1$, and 0.3 where the arrow indicates increasing Sn concentration. The data have not been corrected for demagnetizing effects. Inset: Plot of the corresponding χ'' against temperature.

magnetic component of the magnetization and the low temperature and high field magnetization. Thus, within the spontaneous vortex phase model, the increase in the diamagnetic transition temperature can be attributed to a decrease in the local field arising from the ferromagnetic component in the RuO_2 layers.

Unlike previous studies on $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ and $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, we find that the dc magnetization initially decreases with increasing magnetic field at 2 K for Sn concentrations ≥ 0.1 . This is apparent in Fig. 3, where we plot the initial magnetization against the applied magnetic field at 2 K for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ with $x=0, 0.1$, and 0.3 . It can be seen in Figs. 4(a) and 4(b) that these samples are still magnetically ordered where the magnetic ordering temperature is above the superconducting ordering temperature. As

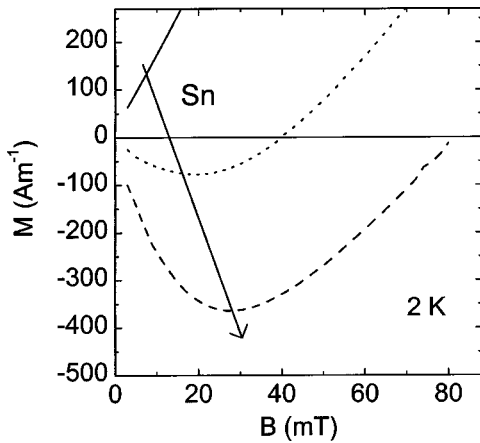


FIG. 3. Plot of the dc magnetization against applied magnetic field at 2 K for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ with $x=0$ (solid curve), 0.1 (dotted curve) and 0.3 (dashed curve). The data have not been corrected for demagnetizing effects. The arrow indicates increasing Sn concentration.

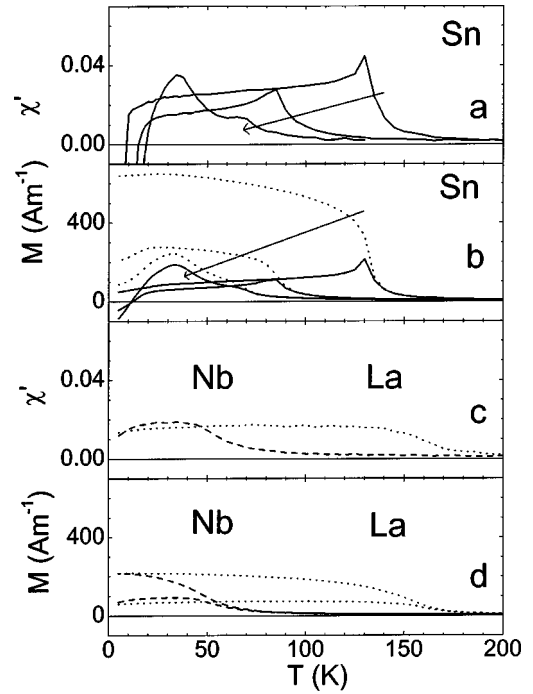


FIG. 4. (a) Plot of χ' against temperature for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ with $x=0, 0.1$, and 0.3 . The arrow indicates increasing Sn concentration. (b) Corresponding dc zero-field-cooled magnetization (solid curves) and field-cooled magnetization (dotted curves) for an applied magnetic field of 5 mT. (c) Plot of χ' against temperature for $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (dashed curve) and $\text{RuSr}_{1.9}\text{La}_{0.1}\text{EuCu}_2\text{O}_8$ (dotted curve). (d) Corresponding dc zero-field-cooled magnetization and field-cooled magnetization for an applied magnetic field of 5 mT. The data have not been corrected for demagnetizing effects. The upper curves correspond to the field cooled condition.

mentioned earlier, it has been argued that the absence of an initial negative dM/dB in magnetically ordered $\text{RuSr}_2\text{RCu}_2\text{O}_8$ implies the absence of a bulk diamagnetic transition in this compound.¹⁰

It is clear in Fig. 4 that Sn or Nb substitution for Ru significantly suppresses the magnetic ordering temperature, while La substitution for Sr results in a small increase in the magnetic ordering temperature. The peak in the ac and dc data for the pure compound is also observed in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ at the same temperature of 132 K (not shown). This peak is close to the magnetic ordering temperature defined as the temperature where dM/dT is a maximum negative value. The effect of Sn or Nb substitution is to broaden the peak observed in the ac data and in the zero-field-cooled magnetization data for small applied fields. However, this low field peak has disappeared in the La substituted sample. Note that the magnetization data for the $x=0.3$ Sn sample also has a small peak near 65 K, which indicates that there is an inhomogeneous Sn distribution. Despite repeated annealing, we were unable to reduce the magnitude of this small peak.

The low field peak at 132 K observed in the pure compound disappears for applied magnetic fields greater than ~ 0.25 T and the zero-field-cooled and field-cooled hysteresis

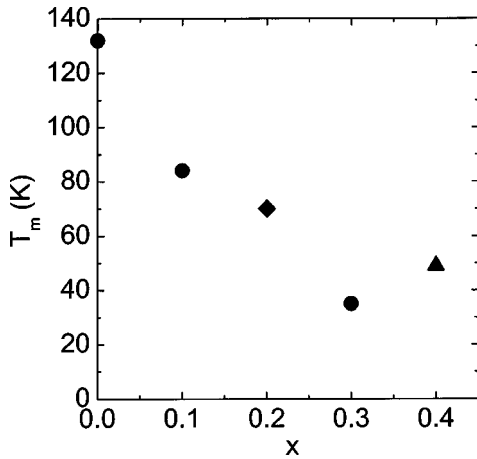


FIG. 5. The magnetic ordering temperature against x for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ (filled circles), $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ (filled diamond) and $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (filled up triangle).

behavior disappears for applied magnetic fields greater than 2 T. The hysteresis behavior has been attributed to the small ferromagnetic component.¹⁵ The appearance of bulk dc diamagnetic shielding at 5 mT for Sn substituted samples and $x \geq 0.1$ makes it difficult to use the low temperature field-cooled magnetization to estimate the ferromagnetic component, as has been done for the pure compound.¹⁵ However, it is evident in Fig. 4(b) that, in the absence of diamagnetic shielding, the low-temperature field-cooled magnetization from the $x=0.1$ sample is $\sim 44\%$ of that in the pure compound. We also note that the magnetic ordering temperature for the $x=0.3$ sample is close to the superconducting transition temperature, which indicates that spin fluctuations do not significantly affect the superconducting order in the CuO_2 planes.

The resulting magnetic ordering temperatures are plotted in Fig. 5, where it is apparent that Sn or Nb substitution for Ru cause a similar decrease in the magnetic ordering temperature. We note that the magnetic ordering temperature for our $x=0.3$ sample (35 K) is significantly less than that reported in $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ with a similar nominal Sn concentration [~ 87 K (Ref. 26)]. The origin of the similar decrease in the magnetic ordering temperatures is discussed later. The effect of La substitution for Sr is to increase the magnetic ordering temperature to 160 K, which is not expected when compared with similar substitutions in the ruthenates and assuming that there is no charge transfer to the RuO_2 layers. For example, in $\text{Sr}_{1-y}\text{Ca}_y\text{RuO}_3$, substituting Ca (ionic radii 0.112 nm) for the larger Sr (ionic radii 0.126 nm) results in an increase in the Ru-O-Ru bond angle distortion that affects the superexchange interaction and leads to a decrease in the magnetic ordering temperature.²² The La ionic radii (0.116 nm) is also less than that of Sr (0.126 nm) and hence it might be expected that La substitution for Sr in $\text{RuSr}_2\text{RCu}_2\text{O}_8$ should also lead to an increase in the Ru-O-Ru bond angle distortion and hence a decrease in the magnetic ordering temperature.

The effect of Sn, Nb, or La substitution on the magnetic field dependence of the magnetization in $\text{RuSr}_2\text{EuCu}_2\text{O}_8$ can

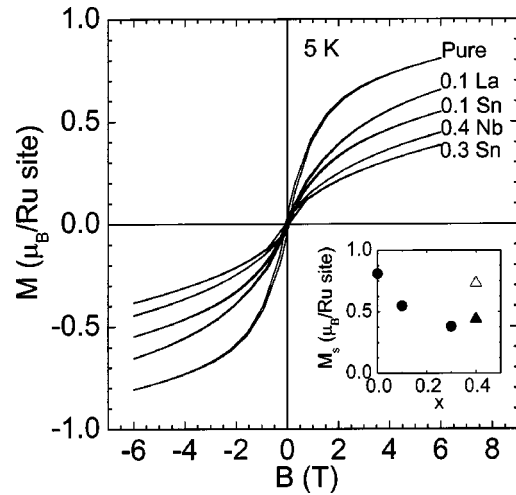


FIG. 6. Plot of the dc magnetization against applied magnetic field at 5 K for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ with $x=0, 0.1$, and 0.3 , $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ and $\text{RuSr}_{1.9}\text{La}_{0.1}\text{EuCu}_2\text{O}_8$. The initial increase in the magnetization has been removed for clarity. Lower right plot: Plot of the magnetization per Ru site at 5 K and 6 T for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{EuCu}_2\text{O}_8$ with $x=0, 0.1$, and 0.3 (filled circles) and $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (filled up triangle). Also shown is the magnetization per Ru atom for $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (open up triangle).

be seen in Fig. 6. The curves for $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ are not shown because they are significantly distorted by the large moment from Gd^{3+} , which magnetically orders near 2.5 K.³ The general feature of a gradual increase in the magnetization with increasing magnetic field is preserved irrespective of the substituted atom. In the case of the pure compound, the slow increase in the magnetization was attributed to a spin-flop transition¹⁵ that was also evident from neutron diffraction measurements.^{3,14} Unfortunately, there is no neutron diffraction data for the substituted samples; however, the similar general increase in the magnetization may suggest a similar spin-flop transition from a predominately antiferromagnetic low field state.

The remanent magnetization for the pure compound is $\sim 0.034\mu_B/\text{Ru site}$, which is slightly less than that found in a previous study ($\sim 0.05\mu_B/\text{Ru site}$ ¹⁵). It decreases to $\sim 0.015\mu_B/\text{Ru site}$ for 0.4Nb substitution for Ru and for 0.1La substitution for Sr. The remanent magnetization is $\sim 0.023\mu_B/\text{Ru site}$ and $0.026\mu_B/\text{Ru site}$ for the Sn substituted samples with $x=0.1$ and 0.3 , respectively, but these values are significantly affected by dc diamagnetic shielding. The effect of increasing Sn and Nb substitution for Ru, as well as La substitution for Sr is to decrease the high field magnetization, as can be seen in Fig. 6. This is more evident in the lower right inset to Fig. 6, where the magnetization is plotted at 6 T and per Ru site rather than per Ru atom (solid symbols). Correcting for the actual Ru concentration when Nb is substituted for Ru leads to a magnetization per Ru atom that is $\sim 86\%$ of that in the pure compound (open up triangle) and slightly higher than that from the La substituted sample ($\sim 0.66\mu_B/\text{Ru atom}$ or 80% of that from the pure compound). Unfortunately, the appearance of a Sn impurity

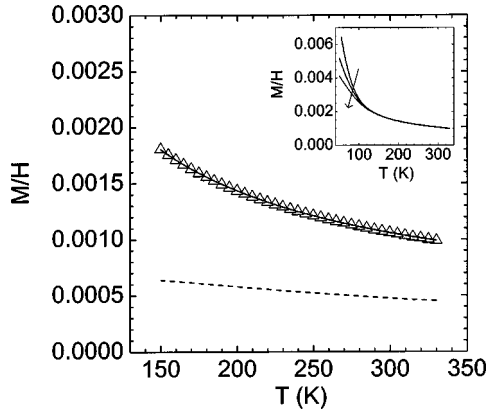


FIG. 7. Plot of M/H against temperature for $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ (filled up triangles) for an applied magnetic field of 1 T. The dashed curve is the calculated Eu^{3+} van Vleck paramagnetism contribution. The solid curve is a fit to the data as described in the text. Inset: Plot of M/H against temperature for $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ with applied magnetic fields of 1, 3, and 6 T. The arrow indicates increasing applied magnetic field.

phase means that the exact Sn fraction on the Ru sites is unknown and hence it is not possible to perform a similar calculation for the Sn substituted samples. However, it is clear that the magnetization at 6 T for $x=0.3$ is less than 70% of that from the pure compound. Thus, the low temperature, high field moment per Ru is decreased by direct substitution onto the Ru site or by substitution of La for Sr.

As mentioned earlier, there is no Sn-induced charge transfer to the CuO_2 planes and hence Sn substitution is expected to increase the average Ru valence. To determine if Nb substitution also changes the effective Ru valence, we estimate the moment per Ru atom above the magnetic ordering temperature in a manner similar to that of Butera *et al.*³² for the $\text{Ru}_{0.6}\text{Nb}_{0.4}\text{Sr}_2\text{EuCu}_2\text{O}_8$ sample using the data plotted in Fig. 7. Here we plot M/H for an applied magnetic field of 1 T (filled up triangles). We show in the inset that M/H is independent of field for $T > 130$ K, which is ~ 80 K above the magnetic ordering temperature. The temperature above which M/H is independent of field is significantly less than that found in $\text{RuSr}_2\text{EuCu}_2\text{O}_8$, where M/H is independent of field for temperatures above 200 K.¹⁵ This corresponds to ~ 70 K above the magnetic ordering temperature and provides additional evidence that the intrinsic magnetic ordering temperature is reduced rather than phase separation occurring. Therefore, we fit the data in Fig. 7 above 150 K, and in the region where M/H is independent of field, to

$$\chi = c/(T - \vartheta) + \chi_{\text{VV}} + \chi_0. \quad (2)$$

The first term is the Curie-Weiss term from the Ru moments with ϑ being the Curie-Weiss temperature and $c = \mu_0 \rho N_A (1-x) \mu_B^2 P_{\text{eff}}^2 / (M_r 3 k_B)$ where μ_0 is the vacuum permeability, ρ is the sample density, N_A is Avogadro's constant, μ_B is the Bohr magneton, M_r is the molecular weight, k_B is Boltzmann's constant, and P_{eff} is the Ru effective Bohr magneton number. For Ru^{4+} with a low spin t_{2g}^4 ground state, $P_{\text{eff}} = 2.83$ and for Ru^{5+} with a t_{2g}^3 ground state, P_{eff}

$= 3.87$. The second term in Eq. (1) is the van Vleck paramagnetism from Eu^{3+} . As in a previous study, we use the crystal field parameter of 303 cm^{-1} found in Eu_2CuO_4 .³³ This term is plotted in Fig. 7 (dashed curve). The final term in Eq. (2) contains the Pauli spin susceptibility from the CuO_2 planes, any temperature independent Stoner enhanced term from the RuO_2 layers and orbital and core terms. The contribution from the CuO_2 planes is small and less than 4×10^{-5} in the high temperature superconducting cuprates.³⁴ Therefore, we approximate the contribution from the CuO_2 planes as being temperature independent.

The resultant fit to Eq. (2) is plotted in Fig. 7. The fitting parameters are $\vartheta = 29$ K, $P_{\text{eff}} = 3.66$, and $\chi_0 = 12 \times 10^{-5}$. We find that ϑ is positive and ~ 21 K is less than the magnetic ordering temperature. A positive ϑ would appear to suggest ferromagnetic correlations. However, a positive ϑ was also observed in the pure compound ($\vartheta = 100$ K) even though neutron diffraction measurements have now shown that the low temperature ground state is predominately ferromagnetic.³⁴ A similar apparent contradiction was observed in CaRuO_3 , where a negative ϑ occurs that would appear to suggest antiferromagnetic correlations.³⁵ However, recent studies have shown that the correlations are ferromagnetic.³⁶ In the case of the $\text{Ru}_{1-x}\text{A}_x\text{Sr}_{2-z}\text{B}_z\text{RCu}_2\text{O}_8$ compounds these discrepancies between the paramagnetic Curie-Weiss temperature and the low field magnetic ground state are related to the fact that the low-temperature magnetic ground state strongly depends on the external magnetic field. For example, as mentioned above, $\text{RuSr}_2\text{RCu}_2\text{O}_8$ displays a large antiferromagnetic component for low applied fields and a spin-flop transition into a ferromagnetic state with increasing applied magnetic field.^{3,14,16}

The fitted value of P_{eff} implies an average Ru valence of ~ 4.77 , which is greater than that found in the pure compound [~ 4.62 (Ref. 17)] from the analysis of the XANES data. In a simple valence counting model, replacing Ru (average valence 4.62) with Nb^{5+} should lead to a decrease in the average Ru valence. Thus, similar to Sn substitution for Ru, we find that Nb^{5+} substitution also leads to an increase in the average Ru valence. Consequently, there is charge transfer to the CuO_2 planes, which is consistent with the absence of superconductivity.

χ_0 is larger than that found in the high-temperature superconducting cuprates, which indicates that there is a contribution from the RuO_2 planes. By comparison with SrRuO_3 , we expect the orbital and core terms to be small and hence χ_0 is dominated by the spin susceptibility in the RuO_2 planes. We note that χ_0 is less than that found in SrRuO_3 [$\sim 50 \times 10^{-5}$ (Ref. 25)], which has a significant Stoner enhancement.

Thus both Nb and Sn substitution for Ru lead to an increase in the average Ru valence as well as similar decreases in the magnetic ordering temperature. However, there is no evidence for a major change in the magnetic order or spin correlations from that observed in the pure compound. Rather, the major effect of Nb and Sn substitution is to dilute the magnetic lattice, leading to a decrease in the magnetic ordering temperature. There is also the added effect of the increase in the Ru-O-Ru bond angle distortions observed in $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$.²⁶ In the absence of neutron diffrac-

tion data, it would seem reasonable to speculate that there is an increase in the RuO_6 rotation angle induced by Nb substitution.

CONCLUSION

In conclusion, we find that Sn substitution for Ru in $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ results in a systematic increase in the temperature where the bulk ac diamagnetic transition commences. This can be accounted for within the spontaneous vortex phase interpretation, by a decrease in the local field from the ferromagnetic component in the RuO_2 planes. We also find that dM/dB is initially negative for magnetically ordered $\text{Ru}_{1-x}\text{Sn}_x\text{Sr}_2\text{RCu}_2\text{O}_8$ when $x \geq 0.1$, which is not observed in the pure compound. The appearance of an initially negative dM/dB for $x \geq 0.1$ may be related to the decrease in the magnitude of the ferromagnetic component. The absence of superconductivity when 0.1 La is substituted for Sr or 0.4 Nb is substituted for Ru is likely to be due to a decrease in the hole concentration on the CuO_2 planes. However, contrary to a previous report, we find no evidence for Sn-induced charge transfer to the CuO_2 layers. Substitution of Sn or Nb for Ru, which is believed to have an average valence of ~ 4.62 in the pure compound, leads to comparable decreases in the magnetic ordering temperature and an in-

crease in the average Ru valence. However, there is no evidence for a change in the nature of the magnetic correlations or magnetic order. The magnetic ordering temperature decreases primarily due to a spin dilution of the magnetic lattice as well as broken superexchange paths. There is also the additional effect of an increase in the Ru-O-Ru bond angle distortion in Sn-substituted $\text{RuSr}_2\text{RCu}_2\text{O}_8$ and it is possible that a similar decrease in the Ru-O-Ru bond angle distortion occurs in Nb-substituted $\text{RuSr}_2\text{RCu}_2\text{O}_8$. The small decrease in the low-temperature moment per Ru is likely to be a consequence of spin dilution and broken superexchange paths. La substitution for Sr leads to a small increase in the magnetic ordering temperature that, by comparison with ruthenate compounds, is not expected.

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