Ferromagnetic correlations and mixed Ru valence in the magnetic superconductor RuSr$_2$(Eu,Gd)Cu$_2$O$_8$

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We present a characterization through magnetization measurements as a function of field and temperature of the magnetic superconductor RuSr$_2$$RCu_2O_8$ (R=Eu or Gd). The effective magnetic moment was carefully determined from measurements up to 900 K. For both compounds we have obtained almost the same value, $\mu_{eff} \sim 3.15(4)\mu_\beta$. This value confirms recent x-ray absorption experiments where a mixed valence state (40% Ru^{4+}–60% Ru^{5+}) was proposed. We have found that the predominant interaction among Ru ions is ferromagnetic [$\Theta=100(3)$ K and $\Theta=87(3)$ K for the Eu and Gd compounds, respectively], but the high-field susceptibility curve displays the characteristics of an antiferromagnetic transition. The possible type of order of the Ru moments is discussed in view of these and previous experiments. We propose a type-I ordering (antiferromagnetically coupled ferromagnetic RuO$_2$ planes) and give reasons supporting this choice.

In the ruthenate cuprate RuSr$_2$$RCu_2O_8$, with R=Eu or Gd (so-called 1212) ferromagnetic order and superconductivity (two phenomena that are normally exclusive) can coexist on a microscopic scale.[1] The crystal structure of Ru1212 is formed by successive layers of RuO$_2$/SrO/CuO$_2$/R/CuO$_2$/SrO.[2] The Ru moments in these compounds order magnetically at around $T_M \sim 135$ K and dc magnetization, muon spin rotation,[2] electronic paramagnetic resonance (EPR) and ferromagnetic resonance (FMR) (Ref. 3) demonstrate that the development of the superconducting phase (associated with the CuO$_2$ planes) below $T_S \sim 45$ K does not produce any significant effect on the magnetic order.

The magnetic properties of these compounds are still not understood. The first measurements[2] in Gd1212 samples indicated ferromagnetic (FM) ordering of the Ru moments at $T_M = 133$ K. From low-temperature (5 K) and high-field (70 kOe) data the saturation moment of the Ru lattice was estimated to be $\mu_0(\text{Ru}) \sim 1\mu_\beta$. This value supported the idea that Ru was present as Ru^{5+} in its low-spin ($S=\frac{1}{2}$) state ($4d^3, t_{2g}^3, e_g^0$). Assuming complete orbital quenching a theoretical value of $\mu_0 = 2J = 1\mu_\beta$ is obtained (see Table I). Fixing the Curie-Weiss temperature at $\Theta = 133$ K, the high-temperature susceptibility data was fitted in Ref. 2 using a Curie-Weiss (Ru contribution) + Curie (Gd contribution) law. A Ru effective moment $\mu_{eff} = 1.05\mu_\beta$/Ru atom was thus obtained. Note that this value is considerably smaller than the theoretically expected $\mu_{eff} = 2\sqrt{J(J+1)} = 1.73\mu_\beta$ for $S=\frac{1}{2}$.

The first attempt to observe ferromagnetic order using neutron diffraction in ^{160}Gd enriched samples was unsuccessful.[4] Another group[5] found afterward extra peaks corresponding to a doubled unit cell ascribed to the antiferromagnetic (AF) ordering of the Ru moments in a G-type arrangement (neighboring spins are antiparallel in all three directions). The low-temperature sublattice saturation mo-

ment was found to be $\mu_0(\text{Ru}) = 1.18\mu_\beta$ in close agreement with magnetization data (where, however, FM alignment was assumed). The c axis was proposed as the direction of spin alignment at variance with muon spin rotation and FMR results that suggested in-plane orientation of the magnetic moments. Recent x-ray absorption near-edge structure (XANES) experiments[6] show that not all Ru ions are pentavalent, but there is a mixture of 60% Ru^{5+} and 40% Ru^{4+}, showing that a critical reinterpretation of the preliminary magnetic data was necessary.

In this work we present detailed magnetic measurements made in Eu and Gd 1212 samples. Eu has the advantage over Gd in that its lower magnetic moment permits an easier interpretation of the intrinsic Ru magnetism. Great care was taken in the subtraction of the magnetic contributions to the high-temperature magnetization not coming from the Ru ions. The high-field susceptibility was analyzed over a broad temperature range (5 K–900 K) allowing the precise determination of the Ru effective magnetic moment, the Curie-Weiss temperature, and the low-temperature saturation magnetization.

Details to obtain an impurity-free phase with $T_M \sim 135$ K and $T_S \sim 48$ K (Gd), $T_S \sim 33$ K (Eu) can be found in Ref. 1. Magnetic measurements were made in a Quantum Design Squid magnetometer in the temperature range 5 K–300 K and field range 0 Oe–50 kOe. Above room temperature and up to 900 K a home made Faraday balance was used.

To isolate the intrinsic magnetic behavior of the Ru ions the following contributions to the measured susceptibility should be considered: (i) paramagnetism of the RE ions. In the case of Gd^{3+} it is usually described using $\chi_{\text{Gd}^{3+}} = C_{\text{Gd}}/T$ with $C_{\text{Gd}} = 7.88$ emu K/mol Gd^{3+}. Eu^{3+} ions are also paramagnetic, but do not follow a Curie law. Because of the proximity of excited J multiplets to the $J=0$ ground state the susceptibility is usually described using the Van Vleck

TABLE I. Effective and saturation moment of low- and high-spin Ru^{4+} and Ru^{5+} ions.

	S	$\mu_{eff}=2\sqrt{J(J+1)}\,(\mu_\beta)$	$\mu_0=2J\,(\mu_\beta)$
$Ru^{5+}\,(3d^3)$	$\frac{1}{2}$	1.73	1
$Ru^{4+}\,(3d^4)$	1	2.83	2
$Ru^{5+}\,(3d^3)$	$\frac{3}{2}$	3.87	3
$Ru^{4+}\,(3d^4)$	2	4.90	4

formula.[7] At low temperatures the Van Vleck susceptibility is temperature independent and M vs H curves remain linear at 5 K with fields of 50 kOe. (ii) Core diamagnetism: This correction is specially important at high temperatures. We have used $\chi_{d1212}=-1.84\times10^{-4}$ emu/mol for the total diamagnetic contribution of the 1212 compounds.[8] (iii) Temperature-independent susceptibility: In the $YBa_2Cu_3O_{7-\delta}$ (123) family of compounds a Pauli-like contribution to the magnetic susceptibility coming from the conduction electrons is present. The magnitude of this term is $\chi_0\lesssim1\times10^{-3}$ emu/mol,[9] but its precise value depends on the doping of the CuO_2 planes. As this contribution is not coming from the RE magnetism it is expected to be of the same order for the Eu and the Gd compounds. We have found that in the case of Eu1212 the best way to isolate the Ru magnetism is to subtract the measured susceptibility of the structurally similar optimally doped $EuBa_2Cu_3O_{7-\delta}$ (Eu123) compound, corrected by the corresponding diamagnetic susceptibility. In this way there is no need for an estimation of χ_0.

In Fig. 1 we present magnetization vs field data below room temperature for the Eu1212 system. When $T<T_M$ a
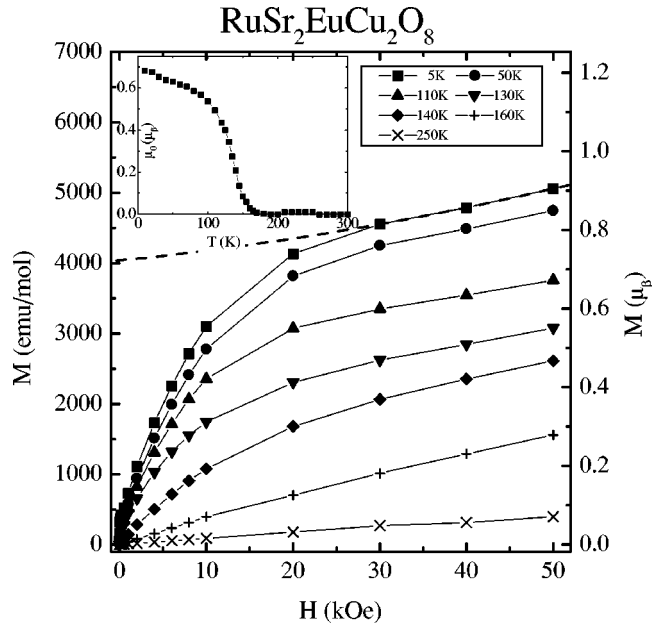

FIG. 1. Magnetization vs field for Eu1212 at several different temperatures. The extrapolated zero-field saturation moment μ_0 and the high-field differential susceptibility (shown in Fig. 2) were obtained from the linear regime above 30 kOe. In the inset the temperature variation of μ_0 is shown.
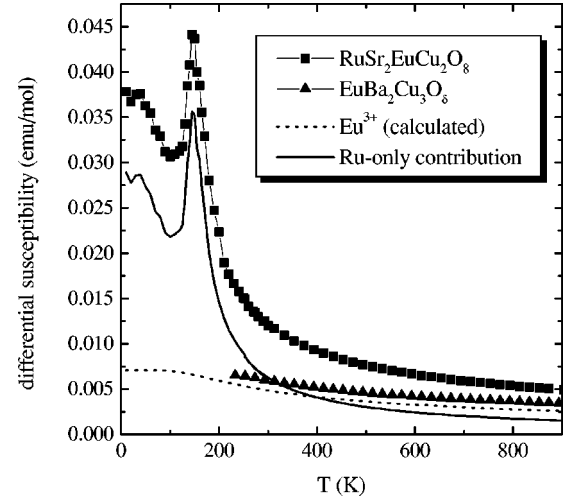

FIG. 2. Differential high-field susceptibility ($H\gtrsim30$ kOe) of Eu1212 and of Eu123. The Ru-only contribution is shown as a continuous line. The dashed curve is the calculated Van Vleck susceptibility of Eu^{3+} ions. Note that χ_{Eu1212} is larger than $\chi_{Eu^{3+}}$.

sharp increase in M is observed at low fields reaching a linear regime above 30 kOe. With our maximum available field (50 kOe) saturation of the magnetization is not achieved even at 5 K. From the extrapolation of the high-field linear behavior to $H=0$ Oe a saturation moment at 5 K of $\mu_0=0.7\mu_\beta$/Ru atom is estimated. The temperature dependence of μ_0 is plotted in the inset of Fig. 1. It is observed that μ_0 vanishes at ~160 K. Although the magnetic ordering temperature of this compound is $T_M\sim138$ K (determined from M vs T measurements at low applied fields) the magnetization vs field curves are linear only above 250 K, indicating the existence of short-range order well above T_M, consistent with the two-dimensional (2D) magnetic nature of Ru1212.

The measured high-field ($H>30$ kOe) differential susceptibility of Eu1212 and of Eu123 and the Ru-only contribution $[\chi_{Ru}=\chi_{measured}-\chi_{d1212}-(\chi_{Eu123}-\chi_{d123})]$ are shown in Fig. 2. For comparison the theoretical free ion Eu^{3+} Van Vleck susceptibility, $\chi_{Eu^{3+}}$, is also shown. We note that this contribution can be two to five times smaller than the Ru susceptibility depending on temperature. The only free parameter in the calculation of the Van Vleck susceptibility $[\chi(T=0\text{ K})\sim7.1\times10^{-3}$ emu/mol $Eu^{3+}]$ was taken from the measurements in Eu_2CuO_4.[7] The susceptibility of Eu123 (χ_{Eu123}) can be very well described as $\chi_{Eu123}=\chi_{Eu^{3+}}+\chi_0$ with $\chi_0=8.7\times10^{-4}$ emu/mol. Below 250 K this correction was used instead of performing the direct subtraction of χ_{Eu123}. The value of χ_0 is close to previously measured values in fully oxygenated, optimally doped samples,[9] but larger than the values found in underdoped samples. Optimal doping was also deduced from XANES measurements,[6] in contrast with thermopower and superconducting properties that are indicative of underdoped superconductors.[1,2] The temperature where the susceptibility is maximum is $T_{\chi_{max}}\sim145$ K, slightly higher than $T_M\sim138$ K. Note also that χ does not go to zero below the ordering temperature as would be expected for a usual ferromagnet.

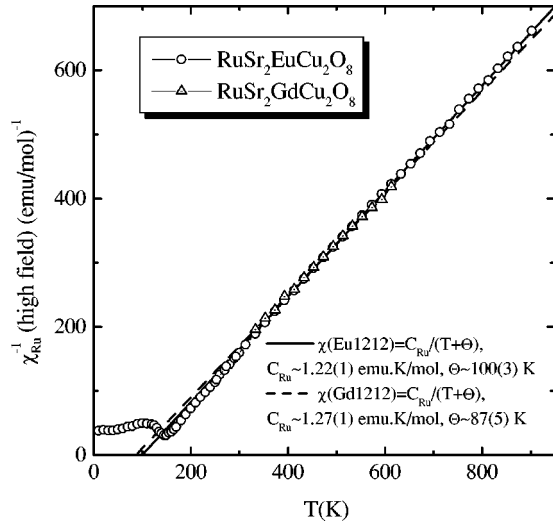We show in Fig. 3 the Ru contribution to the inverse

FIG. 3. Inverse magnetic susceptibility for Eu1212 and Gd 1212. The values shown correspond to the Ru contribution only. The curves are perfectly linear from 300 K up to 900 K.

susceptibility, χ_{Ru}^{-1}. Above 300 K and up to 900 K an almost perfect linear behavior is observed, $\chi_{Ru}^{-1} = (T - \Theta)/C_{Ru}$, with $C_{Ru} = 1.22(1)$ emu K/mol and $\Theta = 100(3)$ K giving an effective moment $\mu_{eff} = 3.12(3)\mu_\beta$. High-temperature data for the Gd compound are also presented in the same figure. In this case the Ru contribution was estimated as $\chi_{Ru} = \chi_{\text{measured}} - \chi_{d1212} - \chi_0 - \chi_{Gd}$, with χ_{d1212} and χ_0 the same as for Eu1212 and $\chi_{Gd} = C_{Gd^{3+}}/(T - \Theta_{Gd})$ with $C_{Gd^{3+}} = \mu_{eff}^2/8 = 4J(J+1)/8 = 7.9$ emu K/mol and $\Theta_{Gd} = -9$ K. As the direct determination of Θ_{Gd} from magnetic measurements is quite difficult, we decided to use the value obtained from the behavior of the Gd^{3+} linewidth in low-temperature EPR experiments.[3] The inverse susceptibility is also very linear and we have estimated $C_{Ru} = 1.26(1)$ emu K/mol [$\mu_{eff} = 3.17(4)\mu_\beta$] and $\Theta = 87(5)$ K. In determining χ_{Ru}^{-1} for Gd1212 the Gd contribution that has to be subtracted is considerably larger than that intrinsic to the Ru spins, leading to some uncertainty in the determination of C_{Ru} and Θ. In Eu1212, on the other hand, Eu^{3+} contributes a smaller part of the total magnetization (see Fig. 2). Thus, we conclude that within experimental error both compounds can be characterized by basically the same effective moment and Curie-Weiss temperature, indicating that the RE magnetism has only a minor effect on the ordering of the Ru moments. Finally, we note that for the correct determination of these values it is extremely important to perform a precise subtraction of all contributions other than Ru. In fact, since all the parameters are coupled, fixing Θ can lead to a wrong determination of μ_{eff} (as in Ref. 2), and not including χ_0 may lead to completely incorrect values of both μ_{eff} and Θ (which can even be negative if χ_0 is overlooked).

As previously mentioned there is evidence supporting both FM and AF ordering of the Ru moments. Ferromagnetic order is mainly supported by magnetization measurements that show: a zero-field extrapolated moment $\mu_0(5 \text{ K}) \gtrsim 0.7\mu_\beta$, a remanence of $\sim 15\% \mu_0$, a coercive field of ~ 450 Oe, and a positive Curie-Weiss temperature (Θ

~ 100 K for Eu1212 and $\Theta \sim 87$ K for Gd1212). Neutron diffraction experiments, on the other hand, are consistent with a G-type AF ordering of spins parallel to the c axis. They indicate the absence of a FM component, at least in zero field. When a magnetic field is applied the change of the neutron spectra is interpreted as due to a spin-flop-like transition occurring at $H_{sf} = 4$ kOe.[5] The presence of an absorption below T_M in FMR experiments indicates that there is a *net* FM component, but its magnitude cannot be determined from such experiments. In principle it could come either from a FM or from an unbalanced AF. Unbalanced AF can be of the canted type [weak ferromagnetism (WF)] or with unequal sublattices (ferrimagnetism). The small distortion of the oxygen octahedra[4,10] allowing a nonzero anisotropic superexchange and hence the presence of WF could explain[5] the nonvanishing Ru magnetization in this system. We note that the induced saturation moment is a large fraction of the theoretical value expected for Ru, implying a very large canting angle independent of whether Ru is low or high spin. Normally the spontaneous magnetization in WF is at most a few percent of the AF sublattice magnetization as in α $- \text{Fe}_2\text{O}_3$, Mn, and Co carbonates, orthoferrites, and the rare-earth cuprates.[11] If this system is indeed a WF it would be a very unusual one. Ferrimagnets are characterized by two AF coupled sublattices with different magnetic moments. There should be at least two different crystallographic sites (with different oxygen environment) where the magnetic ion can reside. This is not the case in the 1212 compounds where diffraction techniques confirmed the existence of only one site for Ru.[4,10]

The effective moment obtained in both the Eu and Gd compounds ($\mu_{eff} \sim 3.15\mu_\beta$) is not coincident with any of the theoretical values expected for a single valence state of the Ru ions, either high or low spin (see Table I). If mixed valence is assumed, the measured effective moment would be compatible with: (a) 55% Ru^{5+} ($S = \frac{1}{2}$) and 45% Ru^{4+} ($S = 2$) or (b) 31% Ru^{5+} ($S = \frac{3}{2}$) and 69% Ru^{4+} ($S = 1$). The former estimation is coincident with the values determined using XANES techniques.[6] However, it should be noted that Ru^{4+} is usually found in its low-spin state in perovskites with octahedral oxygen environment (SrRuO_3, $\text{Sr}_3\text{Ru}_2\text{O}_7$, and $\text{Sr}_4\text{Ru}_3\text{O}_{10}$) with high-spin Sr_2RuO_4 being the only exception[12] probably because of the relatively larger elongation of the RuO_6 octahedra along the c axis in this latter compound. In 1212 compounds the octahedra is actually compressed in this direction,[4,10] making the presence of high-spin Ru^{4+} unlikely. The effective moments in Ru^{4+} are very close to the spin-only theoretical value[12] in spite of the nonlocalized nature of the FM order.

Ru^{5+} has been extensively studied[13] in perovskites of the type $\text{Ru}(\text{Sr},\text{Ba},\text{Ca})_2(\text{RE},\text{Y})\text{O}_6$ where it is only present in the $S = \frac{3}{2}$ high-spin state. In contrast to Ru^{4+} compounds, $5+$ valence materials show some spread in the reported effective moment around the theoretical spin-only value. With the experimental data[13] of seven different compounds we obtained an average effective moment $\mu_{eff}(Ru^{5+}) = 4.03 \pm 0.42\mu_\beta$. Thus, option (b) should not be ruled out because it is the most probable spin configuration and, due to the wide range of μ_{eff} values found for Ru^{5+}, μ_{eff} can be tuned

to derive the observed 40% Ru^{4+}–60% Ru^{5+} valence percentage.[6] Also note that this percentage was estimated through x-ray absorption techniques comparing the 1212 spectrum with two high-spin compounds ($RuSr_2GdO_6$ and Sr_2RuO_4).[6] It is probable that slightly different values may be determined if the estimation is done with low-spin tetravalent materials as in Ref. 14.

Regarding the type of ordering of the Ru moments that was proposed from neutron-diffraction experiments it seems to be incompatible with magnetization measurements in several aspects: (i) We have found a *positive* Curie-Weiss constant smaller than the ordering temperature indicating that the predominant interaction among Ru ions is FM. The G-type structure, in fact, requires AF interactions. (ii) The low-temperature magnetization, which is close to the saturation value, is not consistent with a small canting of the AF alignment. (iii) EPR results show that there is a net magnetic field of ~ 600 Oe at the Gd site coming from the ordered array of Ru,[3] whereas a cancellation of the Gd-Ru interaction is predicted in a G-type-ordered AF. (iv) The proposed spin-flop transition that at 80 K occurs at $H_{sf} \sim 4$ kOe would imply a vanishingly small anisotropy.[15] The observed distortion of the RuO_6 octahedra, the strong 2D character of the RuO_2 planes, and the FMR results (where an easy plane anisotropy field $H_{AZ} \sim 110$ kOe was estimated) are again contradictory with this latter result.

However, the high-field susceptibility data (Fig. 2) give evidence of AF order. In addition, the fact that $\Theta < T_M$ implies that AF interactions may be present together with the main FM correlation. In a mean-field theory the maximum susceptibility, occurring close to T_M, is (Ref. 16) $\chi_{max} = C/(T_N - \Theta) \sim 0.032$ emu/mol, in close agreement with the experimental value of Fig. 2. The maximum susceptibility (χ_{max}) occurring above T_M, the nonvanishing χ below T_M, and $\chi(T=0 \text{ K}) \sim \frac{2}{3}\chi_{max}$ are also indicative of an AF-ordered material. Even the increase observed at low T (that does not come from paramagnetic impurities as was corroborated in M vs T experiments) is sometimes found in antiferromagnets and has been ascribed to the presence of spin waves and anisotropy.[15] Also, all Ru^{5+} compounds studied by Battle and Jones and co-workers present AF order.[13] However, none of these compounds presented G-type spin arrangement. All but one ($RuBa_2LaO_6$) order in a type-I (or type A) structure consisting of antiferromagnetically coupled FM RuO_2 planes with the Ru moments laying in plane. Due to the high bidimensionality of the 1212 system (the superexchange path in the c axis requires at least four atoms) the interplane exchange coupling, $H_{e\perp}$, is expected to be considerably smaller than the intraplane $H_{e\parallel}$. FMR experiments show that the easy plane anisotropy is very large (H_{AZ}

~ 110 kOe), but the in-plane easy axis anisotropy is small ($H_{AX} \sim 200$ Oe). With these results in mind the M vs H curves of Fig. 1 could be explained as the superposition of a magnetization component saturating at ~ 20 kOe and a linear component. The former contribution appears when the field is applied parallel to the planes. In this case total alignment of the spins with H is expected for $2H_{e\perp} \sim 20$ kOe. The spin-flop transition should hence occur at the critical field $H_{sf} \sim \sqrt{H_{e\perp}H_{AX}} \sim 1.4$ kOe. The expected and not observed sudden increase of M at H_{sf} is probably due to the polycrystalline nature of the sample and perhaps also due to a distribution of anisotropy and exchange fields. For fields larger than $2H_{e\perp}$ the linear behavior comes in this scenario from crystals with the c axis oriented parallel to the applied field. The expected saturation moment for a 50% Ru^{4+}–50% Ru^{5+} valence mixing would be around $2.5\mu_\beta$ according to Table I. A somewhat smaller value ($\mu_0 \sim 1.75\mu_\beta$) can be estimated from the experimental data.[12,13] However, if the 1212 system has as proposed a large easy-plane anisotropy, this value could only be reached for $H \sim \sqrt{H_{e\parallel}H_{AZ}} \sim 400$ kOe ($H_{e\parallel}$ was estimated from the measured T_M and mean-field theory).

We would like to point out that the existence of mixed Ru^{4+}/Ru^{5+} valence ($4d$ electrons with the same electronic configuration of $3d$ Mn^{3+}/Mn^{4+}) opens the possibility for the existence of double exchange. Although this mechanism was never observed in Ru perovskites before, very recent work[17] in LaSrMnO where Mn was partially replaced by Ru shows that the introduction of Ru ions, even in large quantities, affects only marginally the ferromagnetism, as opposed to the strong suppression of FM observed when other ions are used for replacement.

In summary, we have determined the effective magnetic moment of Eu and Gd1212 ruthenate cuprates. The values obtained are in agreement with the recently proposed mixed valence state for the Ru ions. We have also derived the Curie-Weiss temperature that implies that the most important correlations are ferromagnetic. The observed magnetic properties do not agree with the previously proposed type-G AF arrangement for the Ru moments. A type-I lattice seems to be more adequate to explain the experiments. A plausible explanation of the doubled unit cell proposed in neutron-diffraction experiments is still lacking. It is probable that, due to the mixed valence nature of this material, some kind of charge ordering is responsible for the observed behavior.

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