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Magnetic interactions and magnon gap in the ferromagnetic superconductor $RuSr_2GdCu_2O_8$

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By means of *X*- and *Q*-band magnetic-resonance measurements we have investigated the magnetic interactions and derived the magnon gap in the ferromagnetic superconductor $RuSr_2GdCu_2O_8$. Two microwave absorptions are observed: first, a paramagnetic resonance of the Gd^{3+} ions, and second, appearing below the Curie temperature (T_{Curie}), a ferromagnetic resonance due to the ruthenium lattice. Located between the superconducting CuO_2 planes, the Gd ions serve as intrinsic probes of the internal magnetic fields near the Cu sites. Below T_{Curie} the Gd^{3+} signal shifts, evidencing the appearance of a homogeneous internal field, $H_{\text{Ru-Gd}} \sim 600$ Oe. We show that $H_{\text{Ru-Gd}}$ is due to a Ru-Gd ferromagnetic exchange interaction. The Ru ferromagnetic resonance indicates the existence of a magnon anisotropy gap $\omega/\gamma \gtrsim 4600$ Oe. We estimate the out-of-plane and in-plane anisotropy fields to be, respectively, $H_z \sim 110$ kOe and $H_x \sim 200$ Oe.
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An example of a superconductor where superconductivity and atomic ferromagnetism uniformly coexist in a microscopic scale has recently been reported in the hybrid ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ (Ru_{1212}).[1] In this compound, structurally similar to the high-T_c superconductor $GdBa_2Cu_3O_7$ (Gd_{123}), ferromagnetism associated with the Ru^{5+} ions develops below $T_{Curie} \sim 133$ K, while a superconducting onset is observed below $T_c \sim 46$ K without any apparent effect from the magnetic state. The interplay between superconductivity and magnetism has been an active subject of research for a long time. Cases have been reported where superconductivity coexists with antiferromagnetic long-range order as, e.g., in Gd_{123}, where Gd orders antiferromagnetically below ~ 2.3 K.[2] Reentrant systems also exist where the onset of ferromagnetism destroys the superconducting state as, e.g., in $ErRh_4B_4$.[3] The coexistence of ferromagnetic order and superconductivity, on the other hand, has been observed under some special conditions in the Chevrel phase compound $HoMo_6S_8$.[4] Several publications have recently appeared addressing the structural, magnetic and transport properties of Ru_{1212}.[1,5–7] Concerning the magnetic properties, dc magnetization and muon spin rotation experiments have been reported, providing evidence that the ferromagnetic phase is homogeneous on a microscopic scale, and that the magnetic order is not modified at the onset of superconductivity.[1,6] However, numerous questions are still open, in particular concerning the specific magnetic structure of the Ru moments and the internal fields sensed by the superconducting planes. These points are essential to understand the coexistence of superconductivity and ferromagnetism in Ru_{1212}, and to devise further pertinent experiments.

We present a magnetic-resonance study of Ru_{1212} polycrystalline samples in the temperature range 5–300 K that addresses these questions. Magnetic-resonance experiments have proved in the past to provide valuable data for understanding the complex magnetic properties of mixed paramagnetic-magnetically ordered systems similar in this sense to $RuSr_2GdCu_2O_8$. Such is the case for the rare-earth cuprates Gd_2CuO_4, where the paramagnetic Gd^{3+} ions coexist with a weak-ferromagnetically ordered Cu lattice.[8] Magnetic resonance is almost a natural technique to tackle the questions posed in Ru_{1212}, for the following reasons: first, the Gd ions constitute intrinsic probes of the internal magnetic field and its homogeneity developing below T_{Curie}. This holds also within the superconducting state. There is no uncertainty concerning the location of this ''internal probe,'' contrary to the case of muon spin rotation experiments.[6] In addition, by being situated between the two CuO_2 planes, Gd is an ideal probe of the Ru-Cu coupling. Second, the Ru ferromagnetic resonance is a direct measure of the magnon gap and of the anisotropy fields affecting the Ru spins.

Single phase Ru_{1212} samples were synthesized by solid-state reaction of stoichiometric powders of RuO_2, $SrCO_3$, Gd_2O_3, and CuO. Fabrication details can be found in Ref. 1. After proper annealing,[7] samples are obtained with $T_{Curie} = 133$ K and thermodynamic $T_c = 46$ K. Granularity lowers the zero resistance T_c to ~ 37 K. The crystal structure of Ru_{1212} is similar to that of Gd_{123}, but with Ru substituting the chain Cu of the conventional high-T_c superconductor, and both oxygen basal plane sites occupied.[7] The resulting structure can be viewed as two CuO_2 planes, separated by SrO_2 layers from the magnetic RuO_2 planes. The Gd ions are located *between* the two superconducting CuO_2 planes. Magnetic resonance measurements, at both the $X(\sim 9$ GHz) and $Q(\sim 35$ GHz) bands, were made between 5 and 300 K in a Bruker ESP-300 EPR spectrometer operating in the conventional absorption mode. Magnetic-field scans were performed in the range -50 – 15 000 Oe. In order to avoid spurious signals, care was taken not to saturate the cavity below T_{Curie}. For that purpose, and to assure good penetration of the microwaves into the sample, the Ru_{1212} ceramic

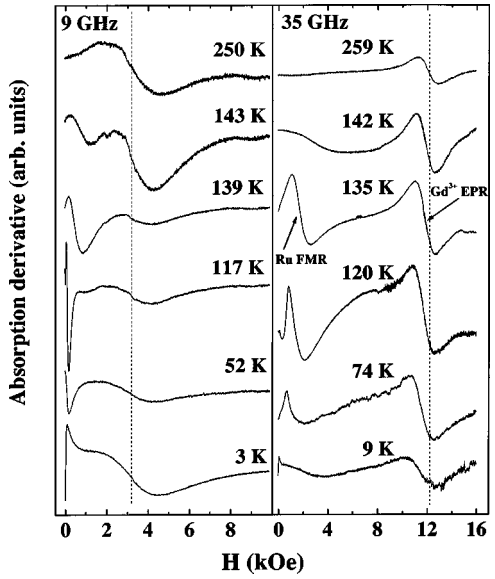

FIG. 1. Magnetic-resonance spectra at various temperatures from $T > T_{Curie} = 133$ K to $T < T_c = 37$ K, taken both at the X and Q bands. Note that derivatives of the absorption lines are displayed. Vertical dashed lines serve as indicators of the Gd^{3+} line shift.

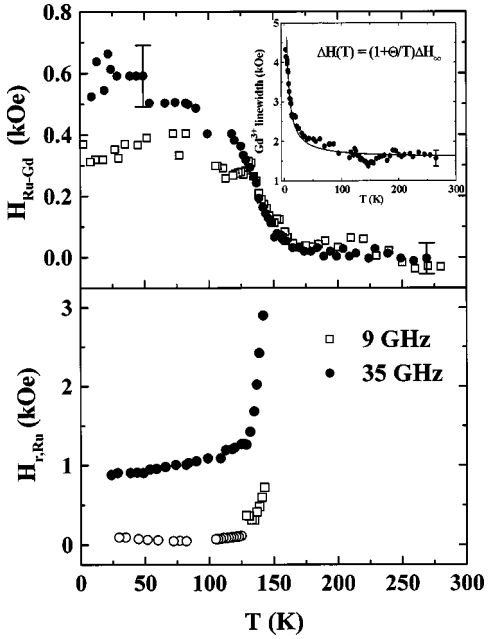

FIG. 2. Gd^{3+} (top) and Ru FMR (bottom) resonance fields as a function of temperature taken both at the X (open symbols) and the Q band (solid symbols). The X-band nonresonant FMR absorption is indicated with a different symbol. Inset: Temperature dependence of the Gd^{3+} ESR linewidth. The full curve is a fit with $\Delta H(T) = (1 + \theta/T)\Delta H_\infty$ (see text for details). The bars indicate experimental errors.

was thoroughly milled and mixed with a nonabsorbing KCl salt. No noticeable changes of the cavity coupling were registered in the whole set of experiments.

In Fig. 1 we present typical magnetic resonance spectra taken both at the X and Q bands, for various temperatures ranging from $T > T_{Curie}$ to $T < T_c$. Note that, as is customary, the derivatives of the absorption lines are shown. The following observations can be drawn from the spectra: (i) at all temperatures a relatively broad absorption ($\delta H \sim 2000$ Oe) is observed around $g = 2$ (3300 and 12 100 Oe at the X and Q bands, respectively). Here g is the gyromagnetic factor. This absorption is due to the electron paramagnetic resonance (EPR) of the Gd^{3+} ions. The linewidth is mostly determined by the large distribution of Gd-Gd dipolar fields.[8] (ii) Besides this broad EPR signal, a second absorption at lower fields develops around T_{Curie}. This second signal is a ferromagnetic resonance (FMR) absorption due to the ordered Ru ions.[12] (iii) Below T_{Curie}, the Gd^{3+} EPR shifts to lower fields. This shift reflects an internal field $H_{\text{Ru-Gd}}$ acting upon the Gd ions and due to the ordered Ru magnetic moments. (iv) The Ru FMR appears slightly above T_{Curie} as a relatively broad absorption and at a magnetic field that is frequency dependent. Then, with decreasing temperature, it narrows and strongly shifts to lower fields. For the X band this FMR signal rapidly approaches zero field and develops a line shape characteristic of a nonresonant absorption.[8] Finally, (v) there is no notable change of the Gd^{3+} ESR resonance field and linewidth at T_c. This is particularly clear for the Q band. The FMR, on the other hand, changes its line shape and a zero-field signal appears below T_c at the Q band. In what follows we will discuss in detail the five points outlined above.

The temperature dependence of the Gd^{3+} ESR internal field ($H_{\text{Ru-Gd}}$) and linewidth (ΔH), and of the Ru FMR field ($H_{r,\text{Ru}}$), are displayed in Fig. 2. As usual,[8] the internal field at the Gd sites is defined as $H_{\text{Ru-Gd}}(T) = H_{r,\text{Gd}}(300\ K) - H_{r,\text{Gd}}(T)$, where $H_{r,\text{Gd}}$ is the measured Gd^{3+} EPR resonance field. $H_{\text{Ru-Gd}}$ develops slightly above T_{Curie} due to the field induced long-range ferromagnetic order. In the phase-transition region, $H_{\text{Ru-Gd}}$ does not depend on the microwave frequency. This defines it as an ''internal field.'' The other possible origin of a resonance field variation, a g shift, is characterized instead by a shift proportional to the applied microwave frequency. At the lowest measured temperature, $H_{\text{Ru-Gd}}$ saturates around 600 Oe at the Q band. At the X band, for the values of applied field corresponding to the Gd^{3+} EPR resonance, the Ru magnetization is not completely saturated, as follows from the dc magnetization data.[6] This explains the somewhat smaller low-temperature value of $H_{\text{Ru-Gd}}$. We note that below T_c there is no notable variation of $H_{\text{Ru-Gd}}$, indicating that the magnetic order is not modified by the onset of superconductivity.[9] In addition, it also follows that the internal field is microscopically homogeneous in dimensions of a single unit cell within the whole sample. Separated ferromagnetic and superconducting phases would be characterized by regions with and without internal field $H_{\text{Ru-Gd}}$, respectively. Such a situation should be reflected in a line broadening with an onset at T_{Curie} or at T_c, depending on whether the separate phases correspond to different materials or to a partial reentrance induced by the superconducting onset, respectively. The measured linewidth (see the inset of Fig. 2), however, does not evidence any broadening specifically at these temperatures.[10] The monotonic increase of ΔH observed towards lower temperatures follows a $\Delta H(T) = (1 + \theta/T)\Delta H_\infty$ law, and can be understood as due to the Gd^{3+} antiferromagnetic ordering.[11] Here $\theta = 9$ K is the fitted Gd^{3+} Néel temperature, which can be larger than the ordering temperature in layered structures, and $\Delta H_\infty = 1500$ Oe is the high-temperature linewidth.

The above straightforward conclusions, concerning the homogeneity and coexistence of superconductivity and ferromagnetism in Ru_{1212}, agree with the muon spin rotation results reported in Refs. 1 and 6. In addition, a value is derived for the internal field existing at a precise location in the unit cell, i.e., at the Gd sites. We have considered two possible origins for $H_{\text{Ru-Gd}}$, that is, dipolar and exchange interactions between the ordered Ru and paramagnetic Gd moments. Two situations have to be evaluated for the case of dipolar fields: that the Ru magnetic moments ($\mu_{\text{Ru}} \sim 1\mu_B$ according to Ref. 6, where μ_B is the Bohr magneton) are normal or parallel to the RuO_2 planes. We obtain, respectively, $H_{dip,\perp} \sim 450$ Oe and $H_{dip,\parallel} \sim -225$ Oe. These values were calculated considering a fully ordered crystal, and should be an upper limit for a polycrystalline sample. In any case, they cannot account for the observed Gd^{3+} line shift. For the Ru moments parallel to the planes, in fact, it even leads to the wrong sign. It follows that $H_{\text{Ru-Gd}}$ must be due to a ferromagnetic exchange interaction, that is, due to an electronic wave function overlap, between the Ru and Gd magnetic moments: $F = -\lambda_{\text{Ru-Gd}} \mathbf{M}_{\text{Ru}} \cdot \mathbf{M}_{\text{Gd}} = -\mathbf{H}_{\text{Ru-Gd}} \cdot \mathbf{M}_{\text{Gd}}$. Here F is the free magnetic energy describing the interaction.[8] The Ru-Cu superexchange path is comparatively more direct and, in addition, the *d*-character Cu electronic levels are much more extended than the *f* Gd states. Considering that the Gd ions are located in between the two CuO_2 planes, this indicates that the exchange field connecting the Cu and Ru moments could be important. We note that, even in presence of a Ru-Cu magnetic interaction, the ferromagnetic order can be basically insensitive to the superconducting onset, as evidenced by the muon spin resonance[6] and Gd^{3+} EPR experiments. However, the reverse need not be true. In fact, this coupling could help to explain the origin of the relatively low T_c of Ru_{1212}, when compared with the structurally similar Gd_{123}, though it is believed that Ru_{1212} is strongly underdoped.[1]

We discuss next the Ru FMR observed at low fields in Fig. 1. The resonance fields, $H_{r,\text{Ru}}$, are displayed in the bottom frame of Fig. 2. This FMR corresponds to the $k=0$ Ru magnon excitations, which are tuned by the external field for resonant absorption at the applied microwave frequency. As for the Gd^{3+} EPR line shift, the FMR is seen to develop slightly above T_{Curie} due to the field-induced ordering of the Ru moments. At the higher temperatures, the lines are broad, indicating small magnon lifetimes characteristic of the short-range-order regime. With decreasing temperature the lines narrow, and $H_{r,\text{Ru}}$ rapidly decreases evidencing the buildup of a magnon gap proportional to the long-range-ordered magnetization. Just a few degrees below T_{Curie}, the *X*-band FMR develops into a non-resonant-type zero-field absorption, indicating that the microwave energy lies *below* the magnon gap. The *Q*-band absorption, on the other hand, is resonant in the full temperature range. $H^Q_{r,\text{Ru}}$ varies rapidly in the magnetic transition region, and then decreases slowly with decreasing temperature following the Ru magnetization saturation.[6] These data indicate that the magnon gap is somewhere between the *X*- and *Q*-band energies (40–150 μeV).

We describe the Ru ferromagnetic system both with an out-of-plane (H_z) and an in-plane (H_x) anisotropy field. As we will see below, this models well the above experimental observations. In addition, it agrees with the magnetic properties of $SrRuO_3$, which has similar RuO_2 planes and a ferromagnetic transition at 160 K.[13,15] H_z defines an easy magnetization plane, while H_x describes a given orientation within this plane. The FMR modes for such structure are textbook examples and can be found, e.g., in Ref. 12. They are given by

$$(\omega/\gamma)^2 = (H + H_x)(H + H_x + H_z), \tag{1}$$

for the external field H applied along H_x, and

$$(\omega/\gamma)^2 = (H - H_x)(H + H_z) \quad \text{for } H > H_x, \tag{2}$$

$$(\omega/\gamma)^2 = \frac{H_x + H_z}{H_x}(H_x^2 - H^2) \quad \text{for } H < H_x,$$

for H applied within the easy plane but normal to H_x. Here $\gamma = g\mu_B$. The expression for $H \| H_z$ is similar to Eq. (2), but H_z and H_x should be replaced by $-H_z$ and $H_x + H_z$, respectively. These FMR modes are shown in Fig. 3 as a function of the applied field. At $H=0$ an anisotropy magnon gap appears, $\omega_{gap}/\gamma = \sqrt{H_x(H_x + H_z)} \sim \sqrt{H_z H_x}$. This gap is proportional to the magnetization and thus increases below $T \sim T_{Curie}$ rendering an absorption nonresonant if it exceeds the incident frequency. For $H \| H_x$ the resonant frequency continuously increases with applied field. For $H \perp H_x$ within the easy plane, a ''nonsaturated'' region exists where the mode frequency decreases while the magnetization reorients with the applied field. The reorientation critical field corresponds to $H_c = H_x$ (or $H_c = H_x + H_z \sim H_z$ if $H \| H_z$). We note that such magnon softening is only observed for angles ex-

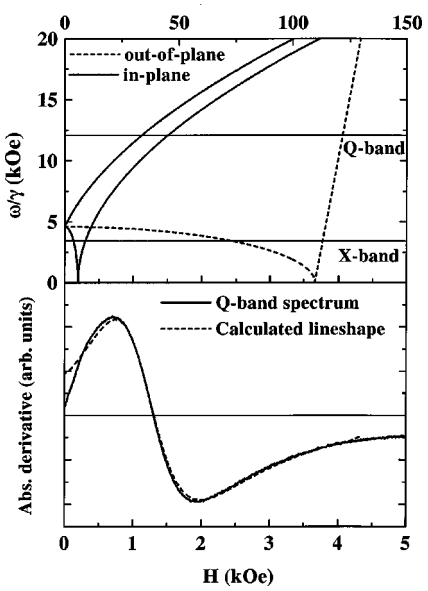

FIG. 3. Top: Resonance field modes for a ferromagnetic lattice with two anisotropy fields, out-of-plane $H_z = 110$ kOe, and in-plane $H_x = 200$ Oe. The continuous lines correspond to the in-plane parallel and perpendicular resonance modes (refer to the bottom *x* axis), while the dashed curve stands for $H \| H_z$ (top *x* axis). The crossing of the modes with the two horizontal solid lines are the fields where resonant absorptions are expected. Bottom: Calculated line shape obtained from an angle average of the resonance fields taken from the top frame (dashed curve). The continuous curve corresponds to the *Q*-band experimental data measured at 128 K.

tremely close to $H \perp H_x$, within a few degrees, and that zero gap occurs only when H is exactly normal to the easy axis.[8,12] Moreover, the perpendicular mode does not soften to zero if the coupling between the ferromagnetic and the paramagnetic excitations is considered.[8] In a polycrystalline sample all these angles have to be averaged. The resulting absorption displays a gap similar to the $H \| H_x$ case, but with a grain-disorder-induced line broadening of the order of $2H_c$. This picture qualitatively describes the main features of the FMR data, i.e., the decreasing resonant fields below T_{Curie}, and the nonresonant character of the *X*-band absorption.

The FMR mode curves in Fig. 3 were calculated using $H_z \sim 110$ kOe and $H_x \sim 200$ Oe. It follows from Eq. (1) that the magnon gap $\omega_{gap}/\gamma \sim 4600$ Oe, corresponding to a gap energy of about 50 μeV. These anisotropy fields have been estimated, for temperatures close to T_{Curie}, by analyzing the linewidth of the resonant absorptions at the two studied microwave frequencies. In fact, we can write a phenomenological expression for the absorption linewidth:[14] $\Delta H = a\omega/\gamma + b$, where the first term reflects an intrinsic relaxation mechanism and is proportional to the working frequency, and the second term, *b*, is only a function of the magnetization, that, in our case, accounts for the angular distribution of resonance fields. This expression agrees qualitatively with the experimental results in that, for all temperatures, the linewidths are considerably smaller at the *X* band as compared with the *Q* band. In the temperature region where resonant absorptions are observed at the two working frequencies, we can use the above expression for ΔH to derive *a* and *b*. This is only a crude order of magnitude approximation since, to be more precise, *b* depends indirectly on ω because the degree of magnetization saturation is not exactly the same for the two frequencies used in our experiments.[6] We obtain, at $T = 128$ K, the fitting parameters $a = 0.07$, and $b = 400$. If we assume that $b = 2H_x$, we get from the FMR equations $H_z \sim 110$ kOe. Just for an argument of consistency, we note that this value agrees with the out-of-plane anisotropy field found in $SrRuO_3$.[15]

In addition, as a further check, we can calculate with these anisotropy fields the absorption line shape. For that purpose, we have summed the angle average of Lorenztian absorptions with an intrinsic linewidth given by the parameter *a*. Such calculation is shown in Fig. 3, and compared with the experimental line. The agreement is excellent. We note first, that H_x is the most important parameter determining the linewidth in the angle average of the absorption lines. Second, the out-of-plane directions contribute to the asymmetry of the line shape, characterized by a larger tail at high magnetic fields. This is a simple consequence following from the relation $H_z \gg H_x$, which leads to larger resonance fields at higher out-of-plane angles.

Finally, we would like to briefly address the Ru FMR line shape change observed below T_c. Evidence seems to indicate that a shift and broadening of the low-field absorption develops below T_c. Though the data are preliminary and incomplete at present, we believe that this result might be indicating a self-energy change in the magnetic excitations, probably due to a dynamic screening by the superconducting carriers. Single crystal experiments would be important to establish this point.

In conclusion, we have shown that the Gd^{3+} EPR is an intrinsic probe of the internal fields in Ru_{1212}. These internal fields at the Gd sites amount to ~ 600 Oe, are microscopically homogeneous and do not change below the superconducting transition at T_c. This field was shown to be due to a Ru-Gd ferromagnetic exchange interaction, pointing to the need to take into account the electronic overlap between the magnetic (RuO_2) and superconducting (CuO_2) planes. It should be determined whether this fact is the origin of the (relatively) low T_c of Ru_{1212}, when compared with the structurally similar Gd_{123}. Finally, a ferromagnetic resonance due to the Ru magnetic moments is observed below T_{Curie} evidencing a magnon anisotropy gap $\omega_{gap}/\gamma \gtrsim 4600$ Oe. The FMR resonance fields and line shape indicate that the anisotropy fields are given by $H_z \sim 110$ kOe and $H_x \gtrsim 200$ Oe.

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[10] The small jump of $H_{\text{Ru-Gd}}$ observed at $T \sim 50$ K only for the *Q*band is not reproduced in different measurements, and its magnitude is within the experimental indetermination. Note, on the other hand, that a reentrance behavior should be reflected in an internal field *reduction.*

[11] There seems to be, on the contrary, a small Gd^{3+} ESR linewidth *reduction* around $T \sim T_{Curie}$ which might be evidencing some type of Ru-Gd magnetic coupling.

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