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Magnetic resonance of Cu and of Gd in insulating $GdSr_2Cu_2NbO_8$ and in superconducting $GdSr_2Cu_2RuO_8$

J. D. Dow[1], *H. A. Blackstead*[+], *Z. F. Ren*[*], *D. Z. Wang*[*]

Department of Physics, Arizona State University, Tempe, Arizona 85287-1504 U.S.A.

[+]*Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556 U.S.A.*

[*]*Physics Department, Boston College, Chestnut Hill, MA 02167 U.S.A.*

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Weak-ferromagnetic (or anti-ferromagnetic) resonance of Cu and electron spin resonance (ESR) of Gd are observed both in insulating $GdSr_2Cu_2NbO_8$ and in superconducting $GdSr_2Cu_2RuO_8$. The Cu resonance implies that the CuO_2 planes are magnetic and indicates that the superconducting layer of $GdSr_2Cu_2RuO_8$ is SrO (not CuO_2), as in its related superconducting compound without cuprate-planes, doped Sr_2YRuO_6.

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1. Introduction. $GdSr_2Cu_2NbO_8$ is an especially interesting material because it is an insulator that does *not* superconduct, although a compound of similar structure exhibits high-temperature superconductivity, $GdSr_2Cu_2RuO_8$ [1 – 7]. In an attempt to determine which facts about electronic structure are essential to high-temperature superconductivity, we compare magnetic resonance measurements of superconducting $GdSr_2Cu_2RuO_8$ with similar measurements of non-superconducting $GdSr_2Cu_2NbO_8$.

One might have expected $GdSr_2Cu_2NbO_8$ and $GdSr_2Cu_2RuO_8$ to behave the same, because both materials have essentially the same crystal structure (Fig.1) and differ only in that the Ru ion, which is primarily in the Ru^{+5} charge-state, replaces Nb^{+5} [4]. (The Mössbauer data indicate that a minority of the Ru ions may be in the Ru^{+4} charge state [6].) However $GdSr_2Cu_2NbO_8$ does not superconduct, and is a charge-balanced insulator, although $GdSr_2Cu_2RuO_8$ does superconduct, with an onset transition temperature for superconductivity of order 45 K. (See Figs.2 and 3 and compare them with Fig.2 of Ref. [6].) This difference between Nb and Ru materials appears to be attributable completely to the different electronic bands and their electron-occupations in the two materials. Nb^{+5} has completely filled $4s$ and $4p$ shells (and an empty $4d$ shell), and Ru^{+5} has three $4d$ electrons outside its full $4s$ and $4p$ shells. (Ru^{+4} has four $4d$ electrons outside its $4s$ and $4p$ shells.) Clearly the electronic structures of the Nb and Ru ions must play important roles in determining why $GdSr_2Cu_2NbO_8$ does not superconduct, while $GdSr_2Cu_2RuO_8$ does superconduct.

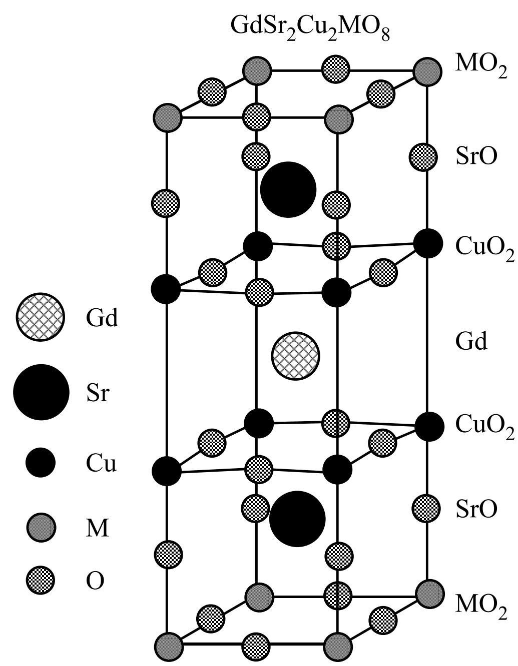

Fig.1. Crystal structure of $GdSr_2Cu_2MO_8$, for M=Ru or Nb

2. Nb bands are occupied. We propose that the reason for the difference between $GdSr_2Cu_2RuO_8$ on the one hand, and $GdSr_2Cu_2NbO_8$ on the other, is that the Ru bands are broader and partially filled with electrons, while the corresponding Nb bands are narrower, are fully occupied, and lie completely below the Fermi surface.

3. Gd ESR and Cu WFMR or AFMR. The measurements discussed below were all performed with a custom spectrometer which has the following three fea-

[1]e-mail: catsc@cox.net

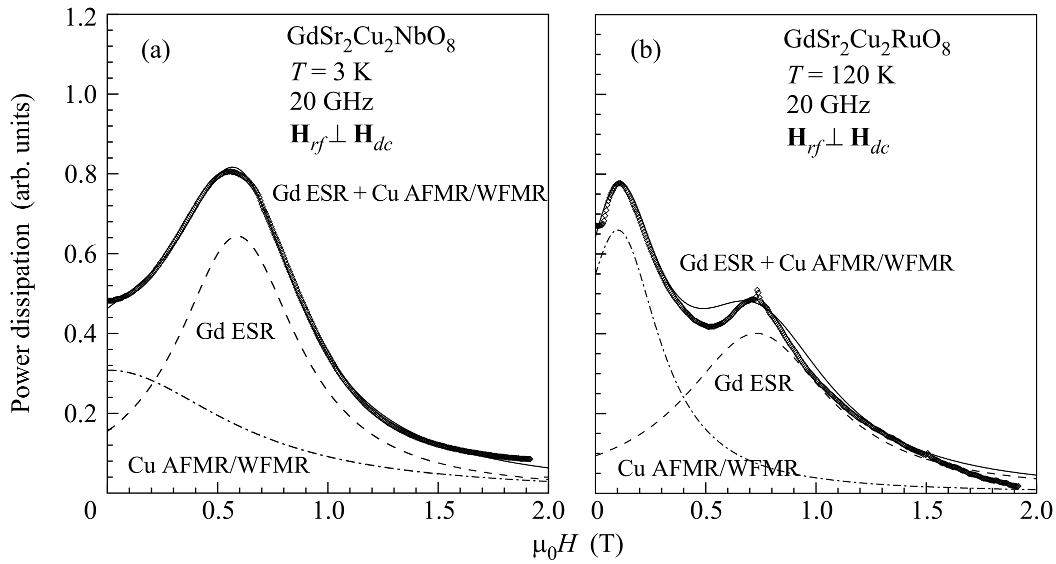

Fig.2. Power dissipation (in arbitrary units) (a) in $GdSr_2Cu_2NbO_8$ and (b) in $GdSr_2Cu_2RuO_8$ versus applied magnetic field $\mu_0 H$ in Tesla for $\mathbf{H}_{rf} \perp \mathbf{H}_{dc}$. The data are the heavy line. The dashed curve, which shows the electron spin resonance of Gd, and the dashed-dotted curve which shows the Cu weak-ferromagnetic resonance (or anti-ferromagnetic resonance) add up to the composite fit (thin solid line). The data were taken at 20 GHz and at a temperature of 3 K for $GdSr_2Cu_2NbO_8$ and 120 K (well above T_c) for $GdSr_2Cu_2RuO_8$. We attribute the broad low-field signals to Cu; one of these, for $GdSr_2Cu_2RuO_8$, has been assigned to Ru by other authors [2]

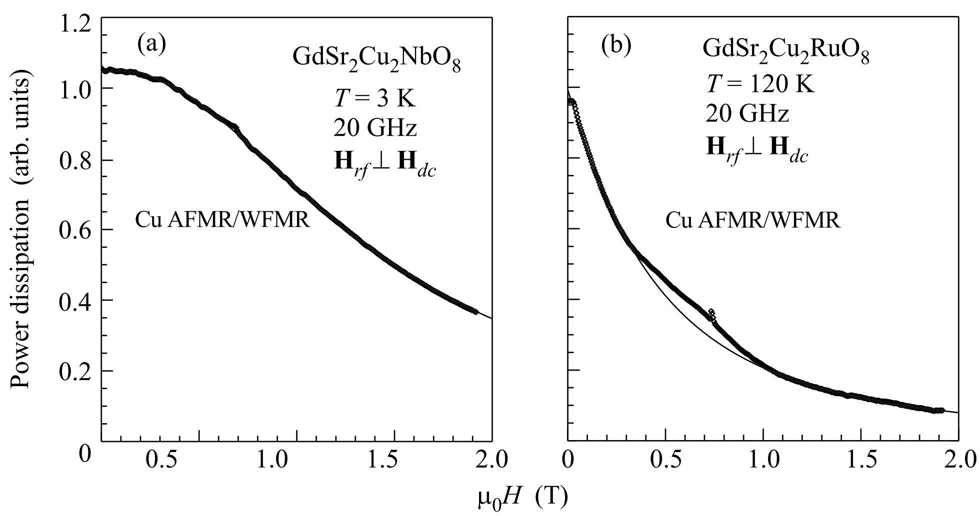

Fig.3. The power dissipation (in arbitrary units) of (a) $GdSr_2Cu_2NbO_8$ and (b) $GdSr_2Cu_2RuO_8$ versus applied magnetic field $\mu_0 H$ in Tesla, for the radio frequency field parallel to the *dc* field, $\mathbf{H}_{rf} \| \mathbf{H}_{dc}$. The data and the Lorentzian fits are given by the heavy and the solid lines. The microwave frequency is 20 GHz, and the temperature is 3 K for $GdSr_2Cu_2NbO_8$ and 120 K for $GdSr_2Cu_2RuO_8$ (above the superconducting transition temperature). The weak broad feature near 0.7 T is due to Gd moments which evidently see a net field that is not precisely parallel to the applied field. The Cu signals observed in this configuration are more intense than the corresponding Gd ESR signals (Fig.2)

tures: (i) The applied magnetic field $\mathbf{H}_{dc}$ (also denoted $\mathbf{H}$) can be rotated to be either parallel or perpendicular to the rf field $\mathbf{H}_{rf}$ in the microwave cavity; (ii) The spectrometer does not utilize field modulation, and so direct dissipation rather than its derivative is measured; (iii) The microwave cavity resonates in a TE_{101} mode, and for these experiments the sample is at the bottom-center of the cavity.

Electron spin resonance (ESR) of Gd produces a $g = 2$ spectral peak in both $GdSr_2Cu_2NbO_8$ and in $GdSr_2Cu_2RuO_8$ for $\mathbf{H}_{rf} \perp \mathbf{H}_{dc}$ (dashed lines of Fig.2), but not for $\mathbf{H}_{rf} \| \mathbf{H}_{dc}$ because of the ESR selection rules.

Non-superconducting $GdSr_2Cu_2NbO_8$ and superconducting $GdSr_2Cu_2RuO_8$ both also exhibit two weak-ferromagnetic resonances (WFMR) or anti-ferromagnetic resonances (AFMR) at low fields $\mathbf{H}_{dc}$ (both for $\mathbf{H}_{rf} \| \mathbf{H}_{dc}$ and for $\mathbf{H}_{rf} \perp \mathbf{H}_{dc}$ [8]), as shown in Figs.2 and 3. The magnon energy gaps at $\mathbf{H}_{dc}=0$ may exceed the microwave photon energies $\hbar\omega$, in which case we see only the "tails" of the resonant modes. (See Fig.3b.) These weak-ferromagnetic (or anti-ferromagnetic) resonance features are prominent and similar in $GdSr_2Cu_2NbO_8$ and in $GdSr_2Cu_2RuO_8$, but our method of measurement does not determine whether the modes are WFMR or AFMR.

For $GdSr_2Cu_2NbO_8$ we assign the low-field weak-ferromagnetic (or anti-ferromagnetic) resonance modes to Cu, because non-magnetic Nb (being Nb^{+5}) and non-magnetic Sr cannot resonate, leaving Cu as the only possible choice. (The separation of the signals in Fig.2 was accomplished by non-linear least squares fitting of two Lorentzian lineshapes to the data. In Fig.3 only one Lorentzian was employed.)

For $GdSr_2Cu_2RuO_8$, similar data for the weak-ferromagnetic (or anti-ferromagnetic) modes are given in Figs.2b (dashed-dotted line) and 3b (thin solid line) for a temperature (120 K) well above the superconducting transition temperature. We also attribute the broad low-field lines to Cu weak-ferromagnetism (or anti-ferromagnetism) due to their similarity to the data from the $GdSr_2Cu_2NbO_8$ sample, and the fact that no resonance signal of any kind has been detected in several materials with either Ru^{+5} or Ru^{+4}. Fainstein et al. [2] have observed resonances at 142 K and 143 K, more than 9 K above the Ru transition temperature (133 K), and we have seen such resonances at several temperatures up to 180 K. These observations rule out Ru as the source, leaving only Cu as a candidate for the observed resonances.

The Cu signals are robust: the integrated intensities for both $GdSr_2Cu_2RuO_8$ and $GdSr_2Cu_2NbO_8$ with parallel rf and dc fields in Fig.3, exceed those of the paramagnetic Gd in perpendicular rf and dc fields (Fig.2). In Fig.3b there is evidence that the Gd moments "see" a local field which is not precisely parallel to the applied field. The composite fits to the data of Figs.2 and 3 are denoted by thin solid lines, and are in good general agreement with the data.

The authors of Ref. [2] have evidently assigned the low-field resonance of Fig.2b incorrectly to *ferromagnetic* Ru. Other evidence supporting the assignment of our "Cu resonance" in $GdSr_2Cu_2RuO_8$ to Cu rather than to Ru is given by $YBa_2Cu_3O_7$ data [9, 11, 12]: When Co is partially substituted for Cu in the chains of $YBa_2Cu_3O_7$, it causes the cuprate-planes to order magnetically. The same effect may be expected to occur (and does) when $YBa_2Cu_3O_7$ is transmuted first to hypothetical $GdSr_2Cu_3O_7$ and then to $GdSr_2Cu_2RuO_8$ by replacing all of its CuO chains with magnetic RuO_2 layers. Ru in $GdSr_2Cu_2RuO_8$ orders at ≈ 133 K, and the cuprate-planes order at an even higher temperature (> 180 K).

We have other data which support the assignment of the weak-ferromagnetic (or anti-ferromagnetic) resonances in $GdSr_2Cu_2RuO_8$ to Cu rather than to Ru: one compound, $PrSr_2Cu_2TaO_8$ (which does not superconduct), but which exhibits resonances apparently due to Cu, features the same resonances we assign to Cu in $GdSr_2Cu_2NbO_8$ (neither material superconducts).

4. Cu resonances in similar materials. Additional evidence for the $\mathbf{H}_{dc} \| \mathbf{H}_{rf}$ resonance being associated with Cu comes from (a) the closely related compounds (rare-earth)$_{2-z}Ce_zSr_2Cu_2RuO_{10}$, (b) a comparison of $GdSr_2Cu_2RuO_8$ with $SrRuO_3$, and (c) Ba_2GdRuO_6, either undoped or doped with Cu on Ru sites.

4a. $Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$.
$Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$ and $Eu_{2-z}Ce_zSr_2Cu_2RuO_{10}$ both begin superconducting around $\sim$45 K, and also have resonances similar to the one we have identified as associated with Cu in $GdSr_2Cu_2RuO_8$. $Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$ has the same layers as $GdSr_2Cu_2RuO_8$ plus two $Gd_{1-z/2}Ce_{z/2}$ layers and one O_2 layer (the three of which replace one Gd-layer between two staggered half-cells of $GdSr_2Cu_2RuO_8$). The three layers of this $Gd_{2-z}Ce_zO_2$ partial structure (which is additional to half of $GdSr_2Cu_2RuO_8$ minus Gd) should not superconduct, because (i) the O_2 oxygen ions are too close to the Gd (and so should have any Cooper pairs associated with them broken by the Gd), and (ii) neither $Gd_{2-z}Ce_zCuO_4$ itself nor the combination of O_2, two $Gd_{1-z/2}Ce_{z/2}$ layers, and the adjacent cuprate-plane superconducts (because $Gd_{2-z}Ce_zCuO_4$ does not superconduct). Consequently the superconducting layers in $Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$ are undoubtedly the same layers as those that superconduct in $GdSr_2Cu_2RuO_8$ (the SrO layers).

4b. *Comparison of* $GdSr_2Cu_2RuO_8$ *with* $SrRuO_3$. It is instructive to compare $GdSr_2Cu_2RuO_8$ with $SrRuO_3$, a non-superconducting ferromagnet which orders magnetically near 160 K, and exhibits no radio frequency response whatsoever at the frequencies employed in our measurements. This is pertinent because the sequence of layers /SrO/RuO_2/SrO/ of $SrRuO_3$ is precisely the stacking sequence found in superconducting $GdSr_2Cu_2RuO_8$. The small difference in the magnetic ordering temperatures of $GdSr_2Cu_2RuO_8$ (133 K) and $SrRuO_3$ (160 K) indicates a significant similarity of the magnetic properties of the two compounds. Hence the lack of a magnetic resonance in $SrRuO_3$ implies that the observed resonances in $GdSr_2Cu_2RuO_8$ and $Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$ are due to Cu, rather than due instead to Ru.

4c. Ba_2GdRuO_6 *undoped and doped with* Cu. Ba_2GdRuO_6, whether doped with Cu or not [10], does not superconduct, although its homologous compound without pair-breaking Gd, Sr_2YRuO_6, does superconduct beginning at $\sim$ 49 K [6, 10, 13–15] when doped with Cu. (With decreasing temperature the superconductivity of Cu-doped Sr_2YRuO_6 becomes complete at $\sim$ 23 K.) Ba_2GdRuO_6 exhibits a $g = 2$ exchange-narrowed paramagnetic Gd resonance over a wide range of temperatures, from room temperature down to the $\sim$ 48 K Ru-ordering temperature.

Cu doping of Ba_2GdRuO_6 results in an additional weak-ferromagnetic (or anti-ferromagnetic) low-field resonance, detectable from below the ~86 K Cu ordering temperature to the lowest temperatures [10]. Clearly this low-field resonance is associated with Cu. No Ru resonance was detected.

Hence, the only reasonable interpretation of these many facts is that Cu, not Ru, is responsible for the observed low-field weak-ferromagnetic resonance (or anti-ferromagnetic resonance) in $GdSr_2Cu_2RuO_8$.

5. Summary. Therefore the two materials, $GdSr_2Cu_2MO_8$, with M=Ru and with M=Nb, (i) each exhibit two modes of Cu weak-ferromagnetic resonance (or anti-ferromagnetic resonance); (ii) each show a strong Gd electron spin resonance; and (iii) each exhibit a charge of approximately +5 on the ion M, which is not itself the determining factor for why the one material superconducts and the other does not. Thus, the three or four outer-shell electrons of Ru play a decisive role in determining the electronic structure and metallic character of the superconducting material.

$GdSr_2Cu_2RuO_8$ has four chemical layers that are candidates for superconductivity: (i) RuO_2, (ii) Gd, (iii) CuO_2, and (iv) SrO. (i) The RuO_2 layer can be eliminated from consideration because Ru is a magnetic ion and because no comparable magnetically ordered layer is known to superconduct at temperatures as high as $\sim$ 45 K. (ii) The Gd layer itself clearly does not superconduct (especially p-type). (iii) The cuprate-planes can be ruled out because Gd has $L = 0$ and $J \neq 0$, which indicates that the Gd energy levels are unsplit by the crystal fields: Gd should break Cooper pairs in the adjacent (cuprate) planes, as it does in $Gd_{2-z}Ce_zCuO_4$ and in the BaO layers of Cu-doped Ba_2GdRuO_6 [10, 16]. Moreover, the Cu ions themselves are magnetically ordered and exhibit weak-ferromagnetism (or anti-ferromagnetism), ruling out their participation in superconductivity, according to most theories. (iv) That leaves the SrO layers which are sufficiently remote from the pair-breaking Gd to superconduct in $GdSr_2Cu_2RuO_8$, as the SrO layers do in Cu-doped Sr_2YRuO_6, which has no cuprate-planes [17].

Similar arguments can be extended to $Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$, which also begins to superconduct at around $\sim$ 45 K, and has almost the same layers as $GdSr_2Cu_2RuO_8$, with two $Gd_{1-z/2}Ce_{z/2}$ layers and one O_2 layer (the three of which replace one Gd-layer) between two staggered half-cells of $GdSr_2Cu_2RuO_8$ (without its Gd).

From this perspective, it comes as no surprise that the three ruthenate compounds, doped-Sr_2YRuO_6, $GdSr_2Cu_2RuO_8$, and $Gd_{2-z}Ce_zSr_2Cu_2RuO_{10}$, all *begin* to superconduct around ~45 K, even though full superconductivity sets in at lower temperatures for some of the compounds, (i.e., 23 K for Cu-doped Sr_2YRuO_6).

The cuprate-plane Cu is not expected to be both weak-ferromagnetic (or anti-ferromagnetic) and superconducting, and so these data are inconsistent with a spin-fluctuation model [10].

The same Cu resonance occurs in both systems, $GdSr_2Cu_2NbO_8$ and $GdSr_2Cu_2RuO_8$, which implies that it is caused by Cu, not by Ru.

To our knowledge, no one has explained why $GdSr_2Cu_2RuO_8$ superconducts at $\sim$ 45 K, instead of at $\sim$ 90 K, as observed for $GdBa_2Cu_3O_7$. In our view, the reduction of T_c from $\sim$ 90 K for $GdBa_2Cu_3O_7$ to $\sim$ 45 K for $GdSr_2Cu_2RuO_8$ is due to pair-breaking in the SrO layers by the adjacent Ru, as observed in Sr_2YRuO_6 (doped with Cu) [16] — and so is further evidence against the superconductivity occupying the cuprate-planes.

6. Conclusions. We have looked at two structures, the first of which is $GdSr_2Cu_2RuO_8$ in which Ru can be replaced by Nb, and the second of which is Ba_2GdRuO_6, into which we have substituted Cu on Ru sites. We have found that the low-field resonances in $GdSr_2Cu_2RuO_8$ occur independent of replacement of Ru by Nb. Therefore, we have assigned these resonances to Cu. Our previous magnetic resonance studies of $Ba_2GdRu_{1-u}Cu_uO_6$ have shown that Ru^{+5} contributed no resonant response, and that the low-field resonance observed was associated with Cu.

The evidence is conclusive: the magnetic sublattice responsible for the low-field resonance is the one containing Cu. Hence the cuprate-planes should not superconduct (according to most theories), and the SrO layers must superconduct.

We conclude that (1) the $RSr_2Cu_2RuO_8$ materials superconduct for R=Gd (and for R=Eu or Y) because the superconducting SrO layers are remote from the pair-breaking rare-earth ion Gd; (2) the $R_{2-z}Ce_zSr_2Cu_2RuO_{10}$ sister materials superconduct for R=Gd (and R=Eu), for similar reasons; (3) the material Ba_2GdRuO_6, whether undoped or doped with Cu on Ru sites, does not superconduct because Gd, having $L = 0$ and $J \neq 0$, breaks Cooper pairs in its adjacent BaO layers; and (4) Cu-doped Sr_2YRuO_6 does superconduct in its SrO layers, because Y, unlike Gd which has $J \neq 0$, is not a Cooper pair-breaker.

The superconducting materials, (i) doped-Sr_2YRuO_6, (ii) (rare-earth)$Sr_2Cu_2RuO_8$, and (iii) (rare-earth)$_{2-z}Ce_zSr_2Cu_2RuO_{10}$, are simply explained as superconductors whose SrO layers all superconduct with (onset) T_c near $\sim$ 45 K, while Cu-doped Ba_2GdRuO_6 does not superconduct because of Gd pair-breaking. Materials such as $GdSr_2Cu_2NbO_8$ do not superconduct, but are insulators because their Nb electrons occupy filled orbitals and filled bands below the Fermi energy.

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