Muon spin rotation in GdSr$_2$Cu$_2$RuO$_8$: implications


† Physikon Research Corporation, PO Box 1014, Lynden, Washington 98264, USA
‡ Physics Department, Arizona State University, Tempe, Arizona 85287-1504, USA
§ Physics Department, University of Notre Dame, Notre Dame, Indiana 46556, USA
|| Department of Physics, College of William and Mary, Williamsburg, Virginia 23187, USA
‡‡ Department of Physics, Virginia State University, Petersburg, Virginia 23806, USA
†† Department of Physics, Gonzaga University, Spokane, Washington 99258, USA
‡‡‡ Department of Physics, University of British Columbia, Vancouver BC V6T 1Z1, Canada
§§ Physics Department, Boston College, Chestnut Hill, Massachusetts 02167, USA

[Received 12 July 2002 and accepted 24 May 2003]

ABSTRACT

Muon spin rotation measurements are reported for GdSr$_2$Cu$_2$RuO$_8$, a material with an onset temperature for superconductivity of about 45 K (which is virtually the same for its superconducting sister compounds Sr$_2$YRu$_1$Cu$_n$O$_6$ and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$). The data indicate two magnetic ordering transitions, at about 15 K and about 130 K, in addition to the Gd ordering transition known to occur at about 2.6 K. We tentatively attribute the 130 K transition to Ru and the 15 K transition to Cu ordering, effectively ruling out any superconducting mechanism based on fluctuating magnetic moments, which are frozen below about 15 K. If there is only one mechanism of high-temperature superconductivity, then the three facts that (i) all three sister compounds have essentially the same onset $T_c$ for superconductivity and (ii) all three of these compounds contain SrO layers but (iii) only two of the three compounds, GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ (and not Sr$_2$YRu$_1$Cu$_n$O$_6$) contain cuprate planes imply that the superconducting layers of all three compounds must be the common SrO layers, and not the cuprate planes (which do not occur in Cu-doped Sr$_2$YRuO$_6$). Otherwise the coincidence of onset temperatures must be an accident, and there must be at least two mechanisms of high-$T_c$ superconductivity: one for doped Sr$_2$YRuO$_6$ and another for cuprate-plane superconductivity.
§1. **Introduction: Three Major Classes of Ruthenates**

Largely as a result of the pioneering studies of Wu and co-workers (Wu *et al.* 1996, 1999, 2000, Chen *et al.* 1997), the ruthenates have attracted considerable recent interest for their high-temperature superconductivity. There are three major classes of ruthenates (Dow *et al.* 2001) that are particularly interesting because elements of these different classes exhibit superconductivity at essentially the same rather high onset critical temperature $T_{c, \text{onset}}$ near 45 K. The members of these classes are as follows:

(i) non-superconducting $\text{Ba}_2\text{GdRuO}_6$ together with its superconducting homologues of the same class, $\text{Sr}_2\text{YRuO}_6$ and $\text{Sr}_2\text{HoRuO}_6$, all doped with Cu (Wu *et al.* 1996, 1999, 2000, Chen *et al.* 1997, Blackstead *et al.* 2000a, DeMarco *et al.* 2000, Harshman *et al.* 1999, 2000, 2001, Dow and Harshman 2002a);


(iii) superconducting $\text{Gd}_{2-x}\text{Ce}_x\text{Sr}_2\text{Cu}_2\text{RuO}_{10}$ and its rare-earth homologues (Bauernfeind *et al.* 1995a,b, 1996, Felner *et al.* 1997, Pringle *et al.* 1999, Fraser *et al.* 2000).

1.1. *Gd breaks pairs in $\text{Ba}_2\text{GdRu}_{1-y}\text{Cu}_y\text{O}_6$*

Although Cu-doped $\text{Ba}_2\text{GdRuO}_6$ does *not* superconduct, its only other homologues which have been fabricated to date, both without Gd, $\text{Sr}_2\text{YRuO}_6$ and $\text{Sr}_2\text{HoRuO}_6$, do superconduct when Cu doped (Wu *et al.* 1999). This suggests that any Gd variants of the $\text{Ba}_2$(rare-earth)$\text{RuO}_6$ or $\text{Sr}_2$(rare-earth)$\text{RuO}_6$ materials do not superconduct because of pair breaking by the $J \neq 0$ Gd (which is unsplit by the crystal field, because its orbital angular momentum is $L = 0$). Such pair breaking causes superconductivity to be absent from $\text{Ba}_2\text{Gd}(\text{Ru}_{1-y}\text{Cu}_y)\text{O}_6$, as is the case for $L = 0$ Gd and Cm in the (rare-earth)$_2$$_{2-x}\text{Ce}_x\text{CuO}_4$ compounds. (Neither $\text{Gd}_{2-x}\text{Ce}_x\text{CuO}_4$ nor Cm$_{2-x}\text{Th}_x\text{CuO}_4$ superconducts.) If, as we propose, Gd is a pair breaker, then the presence of Gd is why Cu-doped $\text{Ba}_2\text{GdRuO}_6$ does not superconduct, but Cu-doped $\text{Sr}_2\text{YRuO}_6$ (with $J = 0$ Y replacing Gd) does superconduct.

1.2. *GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$*

This takes us immediately to GdSr$_2$Cu$_2$RuO$_8$ and to the conclusion that its superconductivity does *not* occupy the cuprate planes adjacent to the pair-breaking Gd in this compound. (The crystal structure of GdSr$_2$Cu$_2$RuO$_8$ is depicted in figure 1.) Similarly, the superconducting condensate of Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ must *not* occupy either the CuO$_2$ layers or the O$_2$ layers adjacent to the Gd ions, because the range for pair breaking by Gd is about one nearest-neighbour distance, and the Gd would destroy the superconductivity. Consequently the superconductivity must be in the SrO layers more distant from the Gd (or possibly in the even more distant RuO$_2$ layers), with the virtual equality of onset critical temperatures for these two cuprate compounds and also for Cu-doped Sr$_2$YRuO$_6$, indicating that the SrO layers carry the superconducting hole condensate in all three classes of compounds.
The SrO layers, which control the superconducting condensation temperature $T_c$, are to be preferred for p-type superconductivity over the n-type Cu-doped YRuO$_4$ layers in Sr$_2$YRuO$_6$ and the RuO$_2$ layers in GdSr$_2$Cu$_2$RuO$_8$ and in Gd$_{2-\delta}$Ce$_{\delta}$Sr$_2$Cu$_2$RuO$_{10}$.

1.3. Same onset for superconductivity

What is even more interesting about these three classes of compounds is that the onset temperatures for superconductivity of the Gd$_{2-\delta}$Ce$_{\delta}$Sr$_2$Cu$_2$RuO$_{10}$ (Blackstead et al. 2000b), GdSr$_2$Cu$_2$RuO$_8$† (Blackstead et al. 2001a), and Cu-doped Sr$_2$YRuO$_6$ (Harshman et al. 2001) classes all appear to be about the same, near approximately 45 K. (Full superconductivity of Cu-doped Sr$_2$YRuO$_6$ actually sets in at a lower temperature, 23 K, and only after the Ru moments stop fluctuating and become static (Harshman et al. 2003), but the onset of superconductivity occurs near approximately 45 K, while the Ru moments still fluctuate somewhat, and at about the same temperatures in all these three classes of superconducting ruthenates (Blackstead et al. 2001a,b). The approximately 45 K onset of superconductivity due to holes in the SrO layers of Sr$_2$YRuO$_6$ is actually interfered with and degraded by the fluctuating magnetic field of Ru in the adjacent layers down to 23 K, at which temperature the fluctuations freeze out, and the superconductivity becomes complete.) Nevertheless, the common onset temperature, approximately 45 K, for the three classes of superconductors suggests that whatever superconducts must be the same in all three classes of ruthenate compounds. Consequently the superconductivity cannot originate primarily in the cuprate planes of any of these ruthenate compounds, because the class that includes Sr$_2$YRuO$_6$ has no cuprate planes and indeed has less than 1% defects of any kind. Since there are no cuprate planes in Sr$_2$YRuO$_6$, the superconductivity of the GdSr$_2$Cu$_2$RuO$_8$ and

†The highest value of the bulk critical temperature onset measured by standard methods is 35 K, obtained by Wang et al. (2003).
the Gd$_{2-\gamma}$Ce$_{\gamma}$Sr$_2$Cu$_2$RuO$_{10}$ compounds must not originate in the cuprate planes either, because all three compounds have nearly the same onset $T_c \approx 45$ K, indicating that the same p-type SrO layers present in all three compounds actually carry the superconducting hole condensate. To explore this interesting issue further, we have performed muon spin rotation ($\mu$SR) spectroscopy on GdSr$_2$Cu$_2$RuO$_8$.

§2. Experiment

Samples of GdSr$_2$Cu$_2$RuO$_8$ were prepared by the standard solid-state reaction method (Wu et al. 1996, Wang et al. 2003) and then structurally characterized using energy-dispersive X-ray analysis, high-resolution X-ray diffraction and neutron scattering (Chmaissem et al. 2000, Moudden et al. 1988). We were able to confirm the GdSr$_2$Cu$_2$RuO$_8$ stoichiometry and phase homogeneity. The standard time-differential $\mu^+\text{SR}$ technique was employed to study the sample on the M20 beam line of the TRIUMF accelerator (Schenck 1985, Cox 1987). Muons that did not strike the sample were eliminated by our veto system, thereby making it possible to observe any minority signal if present. However, the present data exhibited no evidence of such a minority signal.

We have also previously measured the Mössbauer spectrum of GdSr$_2$Cu$_2$RuO$_8$ using a different sample provided by J. L. Tallon (Blackstead et al. 2001a). Those data showed rather clearly that a majority of the Ru ions are in the Ru$^{5+}$ charge state.

2.1. Data and analysis

The $\mu$SR measurements discussed herein were taken in zero applied magnetic field. Since the data appeared to indicate only one component (namely only one magnetically distinguishable muon site), they were analysed assuming, firstly, an exponentially relaxing oscillating component plus, secondly, an exponentially relaxing tail component:

$$G_{zz}(t) = \frac{2A}{3} \exp(-\lambda_a t) \cos(2\pi \nu t + \phi) + \frac{A}{3} \exp(-\lambda_b t), \quad (1)$$

where $A$ is the initial total muon signal amplitude, $\lambda_a$ and $\lambda_b$ are the relaxation rates of the oscillating and tail components respectively, $\nu$ is the muon precession frequency and $\phi$ is the initial phase. The last term of equation (1) corresponds to the one-third component of the initial muon-spin polarization that is initially parallel to the internal local field, and exponential relaxations are used to model the effects of spin fluctuations.

\[†\] The only alternative to locating the superconductivity in the SrO layers in all three classes of superconductors, is to postulate that Cu-doped Sr$_2$YRuO$_6$ superconducts in its SrO layers, but that GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-\gamma}$Ce$_{\gamma}$Sr$_2$Cu$_2$RuO$_{10}$ superconduct in their cuprate-planes. However, this would imply, firstly, that the similar values of $T_c$,onset are accidental, secondly, that, although there do not at present exist any successful mechanisms of high-temperature superconductivity, at least two such mechanisms are needed (one for SrO superconductivity (as in Cu-doped Sr$_2$YRuO$_6$), and another for CuO$_2$-plane superconductivity (as in GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-\gamma}$Ce$_{\gamma}$Sr$_2$Cu$_2$RuO$_{10}$)) and, thirdly, that Ockham’s (1348) razor would be violated, to reject theories that postulate extra elements.

\[‡\] Moudden et al. (1988) found the same neutron reflections for NdBa$_2$Cu$_3$O$_{6.1}$ as Chmaissem et al. (2000) found for GdSr$_2$Cu$_2$RuO$_8$. Clearly both spectra can be interpreted as indicating that both the CuO$_2$ planes and the RuO$_2$ (or CuO chain) layers are ordered.
The frequency $\nu$ is shown as a function of temperature in figure 2. As is clear from that figure, there is a sharp rise with decreasing temperature at about 132 K, indicative of magnetic ordering. As the temperature is decreased below 130 K, the frequency $\nu$ is observed to increase monotonically until about 15 K, where $\lambda_a$ (figure 3) and to some extent $\nu$ show evidence of a transition. This transition indicates that either at least some of the magnetic moments associated with the 130 K transition undergo reordering as the temperature decreases to about 15 K or another magnetic species than that responsible for the 130 K feature is beginning to order near 15 K.

Figure 3 shows the $\mu$SR rate $\lambda_a$ in zero applied field for the oscillating component of the signal (see equation (1)) versus temperature. Note the peaks near 130 and 15 K.

The frequency $\nu$ is shown as a function of temperature in figure 2. As is clear from that figure, there is a sharp rise with decreasing temperature at about 132 K, indicative of magnetic ordering. As the temperature is decreased below 130 K, the frequency $\nu$ is observed to increase monotonically until about 15 K, where $\lambda_a$ (figure 3) and to some extent $\nu$ show evidence of a transition. This transition indicates that either at least some of the magnetic moments associated with the 130 K transition undergo reordering as the temperature decreases to about 15 K or another magnetic species than that responsible for the 130 K feature is beginning to order near 15 K.

Figure 3 shows the $\mu$SR rate $\lambda_a$ as a function of temperature. With decreasing temperature, we observe a precipitous rise in $\lambda_a$, beginning above 130 K, which stops at about 123 K. Reducing the temperature below about 120 K further reveals another rise in relaxation rate, which continues to rise through about 40 K, to a peak at about 15 K. The presence of two peaks in $\lambda_a(T)$ as the temperature varies suggests that two ions are ordering (perhaps Ru at about 130 K and Cu at about 15 K).
before the ionic system is fully ordered, with each peak corresponding to an ordering (or reordering) of magnetic moments. Earlier measurements (Bernhard et al. 1999, Blackstead et al. 2001a, b) have shown a third feature, due to Gd, ordering at 2.6 K. These facts indicate that the two peaks observed in figure 3 are due to the ordering of Cu and/or Ru ions.

In their original paper, Bernhard et al. (1999) assigned the 130 K peak to Ru ordering, suggested that the 15 K peak is a reordering of the Ru ions and indicated that Gd orders below about 2.6 K. Since there are three magnetic ions in this material, it seems relevant to discuss the possibility that Cu orders as well, which could occur at the 15 K peak. Other than this 15 K feature, our assignments agree with the original assignments of Bernhard et al. (1999), and we now believe that the differences between the work by Bernhard and our work are disappearing (C. Bernhard 2002, private communication).

Figure 4 gives the relaxation rate $\lambda_b$ of the (non-oscillatory) tail component, which is close to constant (within statistical uncertainties), except for a slight peak just below about 130 K; this reflects the same precursor disorder as seen in $\lambda_a(T)$ for the oscillating component.

§3. Interpretation

There are two ways that these data can be interpreted:

(i) assuming that the superconductivity is in the cuprate planes (Bernhard et al. 1999);
(ii) assuming that the superconducting hole condensate is in the SrO layers (Dow et al. 2000, 2001, Dow and Harshman 2002a).

We consider these two scenarios below.

3.1. Cuprate-plane interpretation and the need for two or more models

Interpretations of the data in terms of superconducting cuprate planes have been presented before for GdSr$_2$Cu$_2$RuO$_8$ (Moudden et al. 1988, Bauernfeind et al. 1995a,b, 1996, Bernhard et al. 1995, 1999, Fainstein et al. 1999, McLaughlin et al.

![Figure 4](image-url). The exponential relaxation rate $\lambda_b$ for the monotonically damped component of the signal (see equation (1)) versus temperature for the muons, taken in zero applied field.
1999, Pringle et al. 1999, Chmaissem et al. 2000, Fraser et al. 2000, Lynn et al. 2000, Nakamura et al. 2001, Blackstead et al. 2001a), and for Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ (Bauernfeind et al. 1995a,b, 1996, Pringle et al. 1999, Fraser et al. 2000), but not for Sr$_2$YRuO$_6$ doped with Cu on Ru sites (Dow et al. 2000, 2001, Dow and Harshman 2002b). That is because Sr$_2$YRuO$_6$ has no cuprate planes, and consequently the hypothesis of this paper, namely that the origin of the superconductivity is the same in Sr$_2$YRuO$_6$ (doped with Cu on Ru sites) as in GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$, cannot be correct if the superconductivity originates in the cuprate planes (which do not exist even at a 1% level in Sr$_2$YRuO$_6$). Therefore the superconductivity of Sr$_2$Y(Ru$_{1-x}$Cu$_x$)$_2$O$_6$ must have a different origin from that of the cuprate-plane superconductivity of the other two compounds, if cuprate-plane superconductivity exists in these two other materials. Consequently there must be at least two different kinds of high-temperature superconductivity if Cu-doped Sr$_2$YRuO$_6$, GdSr$_2$Cu$_2$RuO$_8$, and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ all superconduct, and if the cuprate planes of GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ are the loci of the superconductivity in those compounds. Indeed, if only one type of high-temperature superconductivity exists, then it is certainly not superconductivity in the cuprate planes.

In summary, the cuprate-plane interpretation is impeded by the fact that the Sr$_2$YRuO$_6$ compound has no cuprate planes (at least fewer than the number of defects and less than 1%) and so is not connected in any reasonable way to GdSr$_2$Cu$_2$RuO$_8$ or to Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$ if these two compounds are governed by a cuprate-plane model. Therefore the superconductivity of Sr$_2$Y(Ru$_{1-x}$Cu$_x$)$_2$O$_6$ must be unrelated to the superconductivity of these two Gd ruthenocuprates if the cuprate planes are responsible for the ruthenocuprate superconductivity.

Consequently, if we must preserve cuprate-plane superconductivity, then there must be at least two models of the high-temperature superconductivity: one for ruthenocuprates and another for ruthenates such as Sr$_2$YRuO$_6$. Few scientists will accept two models of high-temperature superconductivity easily, especially since we do not at present have a credible mechanism of even one. Furthermore, Ockham’s (1348) principle demands that we first search for one model of high-temperature superconductivity, and not two.

3.2. SrO interpretation

If Sr$_2$Y(Ru$_{1-x}$Cu$_x$)$_2$O$_6$ is in the same class of superconductors as GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-x}$Ce$_x$Sr$_2$Cu$_2$RuO$_{10}$, and if all three compounds feature the same mechanism of superconductivity (as the common onset temperature for the superconductivity of the three compounds suggests), then the holes associated with the superconductivity must be in the p-type SrO layers, because they are the only layers common to all three materials.

In this picture the Cu moments continue to fluctuate from high temperatures down to about 15 K, at which temperature they order, and they suppress the bulk superconductivity for all temperatures 15 K ≤ T ≤ 45 K. Below about 15 K, the Cu moment fluctuations are frozen out and ordered, and the superconductivity becomes complete. (This is similar to the situation in Sr$_2$YRuO$_6$ doped with Cu; the Ru librates and limits superconductivity for temperatures between about 23 K and about 45 K, but below 23 K the Ru librations are frozen out.)

The primary concern that many workers have about this SrO interpretation lacks a scientific basis; most workers believe that the superconductivity generally occurs in
the cuprate planes. However, now there is considerable evidence against the cuprate-plane viewpoint even in compounds as widely studied as PrBa$_2$Cu$_3$O$_7$. Experiments have shown that PrBa$_2$Cu$_3$O$_7$ superconducts when there is no Pr on Ba sites (Dow et al. 2000, Dow and Harshman 2002a) and that, with the cuprate planes essentially midway between Ba sites and Pr sites, placement of a Pr ion on a Ba site locally destroys the superconductivity, and this destruction is unrelated to the non-magnetic O ions in the BaO layer (Dow and Harshman 2002b). This behaviour of Pr$_{Ba}$ defects is incompatible with cuprate-plane superconductivity.

Furthermore, the four high-temperature superconductors first predicted and then observed to superconduct (Dow et al. 2001), PrBa$_2$Cu$_3$O$_7$, Pr$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$NbO$_{10}$, Gd$_{1.6}$Ce$_{0.4}$Sr$_2$Cu$_2$TiO$_{10}$ and Eu$_{1.5}$Ce$_{0.5}$Sr$_2$Cu$_2$TiO$_{10}$, are all consistent with the superconducting holes occupying the SrO layers, and not with those holes being in the cuprate planes.

§ 4. Exclusion of spin fluctuation models

Several workers who continue to subscribe to cuprate-plane-based superconductivity have also suggested that the superconductivity in some of the ruthenates (e.g. GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-\_}$Ce$_{\_}$Sr$_2$Cu$_2$RuO$_{10}$) is driven by spin fluctuations of the Cu moments in the CuO$_2$ layers (Moriya et al. 1991, Monthoux and Pines 1992). However, the μSR data presented here for GdSr$_2$Cu$_2$RuO$_8$ provide strong evidence that the Cu moments are ordered below about 15 K (and that the Ru moments are ordered below even higher temperatures), thereby ruling out the spin fluctuation mechanism of the superconductivity at the lowest temperatures $T \leq 15$ K. (In other contexts, spin fluctuations were ruled out earlier as a mechanism of high-temperature superconductivity (Howes et al. 1992, Blackstead and Dow 1998).)

§ 5. Conclusion

Our data show that superconducting GdSr$_2$Cu$_2$RuO$_8$ exhibits two transitions in its μSR behaviour down to 10 K: one due to a magnetic ion (presumably Ru at about 133 K), and another due to a second ion (presumably Cu at about 15 K). The (third) ordering (not shown), at 2.6 K, is clearly associated with Gd. The fact that both the Ru and the Cu moments are frozen below about 15 K effectively negates any superconductivity model which is dependent upon spin fluctuations for the pairing of quasiparticles. Moreover, when we interpret the data in the light of the fact that all three materials Sr$_2$YRu$_{1-\_}$Cu$_{\_}$O$_6$, GdSr$_2$Cu$_2$RuO$_8$ and Gd$_{2-\_}$Ce$_{\_}$Sr$_2$Cu$_2$RuO$_{10}$ superconduct with similar onset temperatures $T_c \approx 45$ K, the data of Sr$_2$YRu$_{1-\_}$Cu$_{\_}$O$_6$ force us to assign the superconductivity to the SrO layers in that compound, and consequently the superconductivity in all three materials must occupy the SrO layers, rather than the SrO layers of Sr$_2$YRu$_{1-\_}$Cu$_{\_}$O$_6$ and the cuprate planes of the last two (ruthenocuprate) materials.

Acknowledgements

D.R.H. and J.D.D. are grateful to the US Office of Naval Research (contract N00014-94-1-0147) for their support. D.R.N. and C.E.S. were supported in part by a grant from the US Air Force Office of Scientific Research. We thank Dr J. L. Tallon for graciously providing the sample on which we performed the Mössbauer experiments. Finally, we would like to thank the staff of the TRIUMF cyclotron facility in Vancouver, British Columbia, Canada, for technical assistance.
\section*{References}


Ockham, Sir William of, 1348, Non sunt multiplicanda entia praetor necessitatem.
Schenck, A., 1985, Muon Spin Rotation Spectroscopy (Bristol: Adam Hilger).