**99Ru Mössbauer effect measurements in superconducting and magnetic RuSr$_2$GdCu$_2$O$_8$**

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$^{99}$Ru Mössbauer effect measurements have been carried out at a temperature of 4.2 K on a sample RuSr$_2$GdCu$_2$O$_8$ with a Néel temperature of $T_N=132$ K and superconducting transition temperature $T_c=45$ K. The hyperfine magnetic field was determined to be 59.1(1.0) T at 4.2 K and the isomer shift was measured to be $+0.05(0.02)$ mm/s, determining a valence state for the single Ru site to be close to +5. The Mössbauer measurements also show an electric quadrupole interaction $eQV_{zz}$ of 0.37(0.04) mm/s. These results differ from the NMR results in RuSr$_2$GdCu$_2$O$_8$ and RuSr$_2$YC$_2$O$_8$, where two different hyperfine magnetic fields ($\sim$60 T, $\sim$29 T) and charge states (+5, +4) were found for Ru.

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**INTRODUCTION**

The study of RuSr$_2$GdCu$_2$O$_8$ has become interesting because of the coexistence of superconductivity and magnetism in this material.$^{1,2}$ RuSr$_2$GdCu$_2$O$_8$ is a 1212-type layered cuprate with an average structure that is tetragonal. dc magnetization measurements$^3$ show that magnetic order sets in at 132 K and superconductivity below $T_c=46$ K, depending on sample preparation. Muon spin-resonance$^5$ measurements show that the dominant magnetic ordering is antiferromagnetic. The antiferromagnetism resides on the Ru magnetic moments while the Gd moments remain paramagnetic down to very low temperatures, both moments lying parallel to the $c$ axis.$^4$ At the same time, this material exhibits weak ferromagnetism with a spin-flip transition at 0.4 T or lower.$^5$

The $^{99}$Ru Mössbauer effect (ME) is a useful technique$^6$ for the study of this compound because Ru is a natural constituent of the compound and the ME probes the local electronic structure of Ru sites. The isomer shift (IS) enables determination of the charge state of Ru through systematic studies. Information on the magnetic hyperfine interaction enables a determination of the magnetic status of the Ru ions, and the electric quadrupole hyperfine interaction is determined by the effect of distortions of the crystal symmetry about the Ru ion.

The ME measurements presented here show that there is only one Ru site with a hyperfine magnetic field of 59.1 (1.0) T at Ru. The IS is $+0.05(0.02)$ mm/s, consistent with a valence state for Ru close to the +5 charge state. There is also an electric-field gradient across the Ru nucleus as determined by the electric quadrupole hyperfine interaction (EQI) (EQI = $eQV_{zz}$) of 0.37(0.04) mm/s.

**RESULTS**

The transmission Mössbauer spectrum of $^{99}$Rh(Ru) versus the Gd 1212 compound is shown in Fig. 1. The spectrum shows a hyperfine magnetic interaction that contains 18 lines arising from the mixed multipole ($E_2/M_1$) transition of the ME state.$^9$ In Fig. 1 it is evident that the lines are not evenly spaced in the spectrum. The spacing of these lines can be compared with the $^{99}$Ru Mössbauer experiment in Sr$_2$Ru$_{0.95}$Cu$_{0.05}$YO$_6$, where the data$^{10}$ show that the spectrum is purely magnetic, giving nearly evenly spaced lines. This shows that the RuSr$_2$GdCu$_2$O$_8$ spectrum also contains a hyperfine EQI.

The spectrum is analyzed using the Hamiltonian$^{11-13}$ for the two levels that includes hyperfine magnetic and electric quadrupole interactions:

$$H_a = \mu_a \cdot H_{hf} + \sum_{i,j=x,y,z} q_{ij} \frac{Q_a}{Q_0} \frac{1}{6I_a(2I_a-1)} \left\{ \frac{3}{2} (I_a P_{ji} + I_{ai} P_{ij}) - I_a(I_a+1) \delta_{ij} \right\}$$

$$q_{ij} = e Q_0 \frac{\partial^2 V}{\partial x_i \partial x_j} = e Q_0 V_{ij},$$
where $H_{hf}$ is the hyperfine magnetic field and $I_u$ are the angular momenta for the ground and excited states. The $V_{ij}$ are the elements of the electric-field gradient tensor at the Ru nucleus, where $Q_0$ is 1 b so that the $q_{ij}$ have dimensions of energy. The $\mu_{\alpha}'s$ and $Q_\alpha'$s are the magnetic dipole and electric quadrupole moments of the ground and excited states.\textsuperscript{14}

In this spectrum the relative magnitudes of the lines in the spectrum are determined by the Clebsch-Gordan coefficients, the magnitude of the reduced matrix elements for the magnetic dipole and electric quadrupole operators, and by the angle average over the orientations of the crystallites that make up the powder sample, which are assumed not to be polarized. The ratio between the reduced matrix elements for the magnetic dipole and electric quadrupole transitions is fixed ($\delta^2=2.43$).\textsuperscript{9}

The linewidth, represented as a Lorentzian with a full width at half maximum (FWHM), was varied with the result that 0.18 mm/sec optimized the fit to the data.\textsuperscript{10} The electric quadrupole interaction, the isomer shift, and the hyperfine magnetic field at the nucleus are considered as fitting parameters. In addition the calculated spectrum is multiplied by a scaling parameter to fit the data. The best fit in the principal axis system of the electric-field gradient tensor is determined by calculating a $\chi^2$ fit for the parameters.

The best fit is given by $H_{hf}=59.1(1.0)$ T, where the angle $\theta$ between $H_{hf}$ and $V_{zz}$ is found to be zero. The IS is found to be +0.05(0.02) mm/sec. It is found that for the EQI, $eQV_{zz}=0.37(0.04)$ mm/sec. However, the fit for the data is equally good for a range of $V_{zz}$ values, where $V_{xx}+V_{yy}+V_{zz}=0$. Consequently, we are unable to determine values for $V_{xx}$ and $V_{yy}$ separately and are, therefore, unable to report a value of $\eta=[V_{xx}-V_{yy}]/V_{zz}$.

**DISCUSSION**

The analysis of the data for SrRu$_2$GdCu$_2$O$_8$ leads to the conclusion that $H_{hf}$ is along a crystal axis, which is consistent with the results of neutron scattering by Chmaissem \textit{et al.}\textsuperscript{4} and Lynn \textit{et al.}\textsuperscript{4} They determined that the Ru magnetic moments were ordered antiferromagnetically along the $c$ axis.\textsuperscript{4} Therefore, we identify our $z$ axis with the crystal $c$ axis.

The charge state of the Ru atoms is also probed by the IS. The IS, $+0.05(0.02)$ mm/s, is consistent with a charge state close to $+5$ for Ru.\textsuperscript{10,4} From the point of view of local coordination around the Ru site, SrRuO$_3$,\textsuperscript{15} Sr$_2$Ru$_{0.95}$YCu$_{0.05}$O$_6$,\textsuperscript{10} Na$_3$RuO$_4$,\textsuperscript{16} and RuSr$_2$GdCu$_2$O$_8$ are similar in structure and this provides a basis for comparison of the hyperfine magnetic fields in these compounds. The hyperfine magnetic field at $^{99}$Ru in SrRuO$_3$ is 33 T. The magnetic order in this compound is ferromagnetic. The IS for $^{99}$Ru in SrRuO$_3$ is $-0.33$ mm/s ($S=1$), which is consistent with a $+4$ charge state for Ru. The hyperfine magnetic fields measured at the $^{99}$Ru in Sr$_2$YRu$_{0.95}$Cu$_{0.05}$O$_6$ and Na$_3$RuO$_4$ are 59 T with an IS ($0.13, 0.11$ mm/s) corresponding to $+5$ ($S=+\frac{3}{2}$). Therefore, we conclude that in Gd 1212, $S=+\frac{3}{2}$.

Clearly there cannot be two static charge states in the ME spectrum of RuSr$_2$GdCu$_2$O$_8$ because this would produce two distinct sites, each with a different IS, one corresponding to $+4$ and the other to $+5$. Such an arrangement would produce two different hyperfine fields, one for each IS. This is not observed. The FWHM linewidths (0.18 mm/s) are narrow and we observe only a single spectrum with no superposition of subspectra. Our finding that there is only one Ru site is in apparent disagreement with the conclusions of Tokunaga \textit{et al.}\textsuperscript{17} and Kumagai \textit{et al.}\textsuperscript{18} who found that there are two Ru sites based on their NMR experiments on RuSr$_2$YC$_2$O$_8$ and RuSr$_2$GdCu$_2$O$_8$. Both NMR and Mossbauer measurements measure the high-field site while NMR also measures the low-field site. In their NMR experiments, the low-field site, $~29$ T, has a Ru charge state of $+4$ while the high field, $~60$ T, has a charge state of $+5$. Perhaps, this difference is due to the NMR measurement that samples both the interdomain (domain wall) and intradomain-wall sites.

The EQI, $eQV_{zz}=0.37(0.04)$ mm/s, $\nu_Q=27(3)$ MHz, result, determined by evaluating the exact Hamiltonian,
shifts the lines in the ME spectrum from the purely magnetic case and makes the spacing nonuniform. The ME value for the angle between the $H_{hf}$ and the $V_{zz}$ is zero. The ME result agrees with the neutron-diffraction data but differs from the NMR (Refs. 17 and 18) results determined by perturbation theory, in that their angle is nearly 90°. The NMR EQI which suggests the RuO$_6$ octahedra in Gd$_{1212}$.

It is known that RuSr$_2$GdCu$_2$O$_8$ is superconducting at 4.2 K and so superconductivity and large magnetic fields coexist, supporting our previous results.7,8 This compound can be considered a member of the high-$T_c$ family of compounds with perovskite structure and layered cuprate planes. In many of these compounds antiferromagnetism and superconductivity exist in close proximity in the phase diagram. This suggests a magnetic mechanism for superconductivity. The present result that 60-T magnetic fields are present in the Ru planes while CuO layers are superconducting lends further support to this idea.

CONCLUSIONS

A unique site has been determined for Ru in RuSr$_2$GdCu$_2$O$_8$, where $H_{hf}=59.1(1.0)$ T, $eQV_{zz}=0.37(0.04)$ mm/s, with a Ru ion state of nearly +5. The values of the $H_{hf}$, $eQV_{zz}$, and the Ru ion state are consistent with the values found for different samples reported earlier7,8 and with the ME value reported in a recent report by Kruk et al.19 but different from the previously mentioned results from NMR in both RuSr$_2$GdCu$_2$O$_8$ and RuSr$_2$YCu$_2$O$_8$.

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