# Magnetic phase transition in superconducting $Sr_2YRu_{0.95}Cu_{0.05}O_6$ observed by the $^{99}$Ru Mössbauer effect

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$^{99}$Ru Mössbauer effect measurements at 4.2, 23, 30, and 40 K show that the hyperfine magnetic field vanishes near 30 K, lower than the superconducting onset temperature of 45 K in $Sr_2YRu_{0.95}Cu_{0.05}O_6$. The data confirm that superconductivity and homogeneous magnetic order coexist. The hyperfine magnetic field measured at 4.2 K is 58.5(0.8) T. The well-resolved set of 18 lines in the 4.2 K measurement enabled a determination of a new value, $-0.293(0.005)$ nm, for the nuclear magnetic moment of the 3/2 state of $^{99}$Ru. The isomer shift in this compound was measured to be 0.13(0.01) mm/s and it is consistent with a $+5$ charge state of Ru.

## INTRODUCTION

$Sr_2YRuO_6$, when doped with several percent Cu on the Ru site, contains both antiferromagnetic dopant copper for $T<86$ K and antiferromagnetic Ru for $T<23$ K despite being superconducting for all temperatures below $T_C \approx 45$ K.[1–4] The Ru orders ferromagnetically in each basal (*a-b*) plane, but the magnetization alternates in direction, producing an antiferromagnetic structure (see Fig. 1). As a consequence of this order, the magnetic field vanishes in the SrO layer.[4] This coexistence of superconductivity and antiferromagnetism in a material which has only two layers, $YRuO_4$ magnetic planes doped with Cu, and SrO layers, presents a new theoretical challenge. Either conventional ideas hold and the superconductivity resides in the nonmagnetic SrO layers, or else the superconductivity arises in the ferromagnetic $YRu_{1-u}Cu_uO_4$ layers, which are stacked antiferromagnetically.

In this paper, we report $^{99}$Ru Mössbauer effect (ME) measurements of $Sr_2YRu_{1-u}Cu_uO_6$ which (i) show that a hyperfine magnetic field, $B=58.5(0.8)$ T, was measured at the Ru nucleus, (ii) determine a more precise magnetic moment for the 3/2 state of $^{99}$Ru, (iii) demonstrate that Ru has $+5$ charge, and (iv) show that the hyperfine magnetic field disappears above $T \approx 30$ K.

## EXPERIMENT

The compound was synthesized by a solid-state reaction as described elsewhere.[1,2] X-ray and neutron diffraction[5] measurements showed that this material was single phase. A resistance versus temperature measurement showed that this sample possesses a phase transition to superconductivity, with an onset temperature at $T_C \approx 45$ K. In addition, a magnetic transition occurred in this and similar samples with Cu contents up to 0.15, at $T \approx 23$ K to $T \approx 30$ K, all in a dc magnetic field of 25 Oe.[4]

The $^{99}$Ru ME measurements were performed with a 2 mCi $^{99}$Rh source produced by bombardment of a target containing $^{100}$Ru and $^{101}$Ru by 30 MeV protons. The ME measurements were performed in a cryostat with transmission geometry, as previously described.[6] The absorber was a 1 cm diameter pellet with a mass of 540 mg ($=120$ mg of Ru/cm$^2$). The velocity calibration was determined by the four

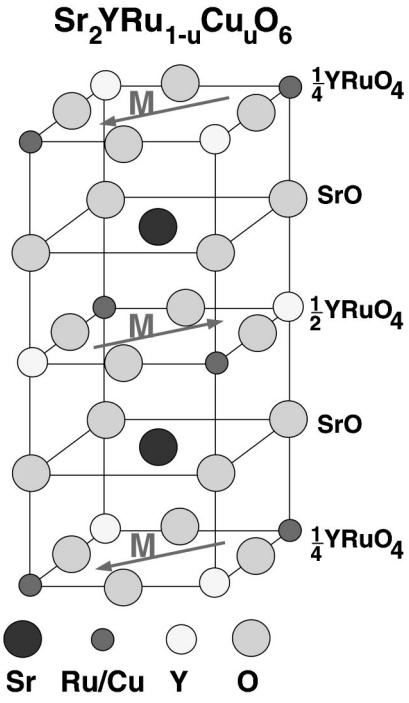


FIG. 1. Structure of $Sr_2YRu_{1-u}Cu_uO_6$; here 1/4 of the unit cell is illustrated. Arrows in the $YRuO_4$ layers indicate that the ferromagnetic magnetization lies in the basal plane, but alternates in direction, as in Ref. 17. This produces an antiferromagnetic structure, and a vanishing magnetic field in the nonmagnetic SrO layers.

 

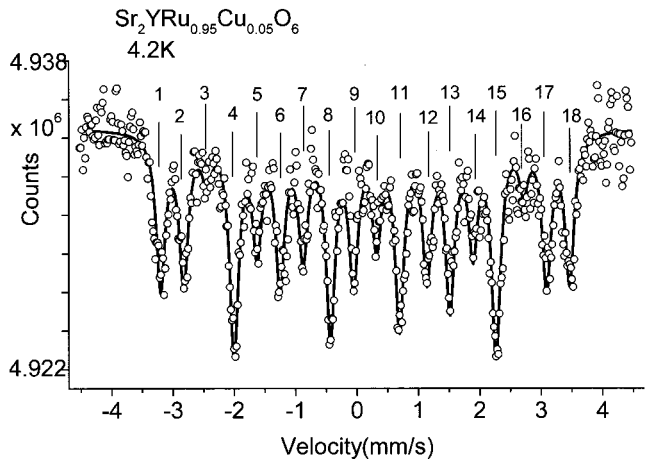


FIG. 2. Transmission ME spectrum showing the number of counts versus velocity for the source, $^{99}$Rh(Ru), and absorber, $Sr_2YRu_{0.95}Cu_{0.05}O_6$, at 4.2 K. The ME lines in the spectrum are numbered 1–18 and are labeled by vertical lines. The open circles represent the data and the black line represents the superposition of 18 Lorentzian lines on the data.

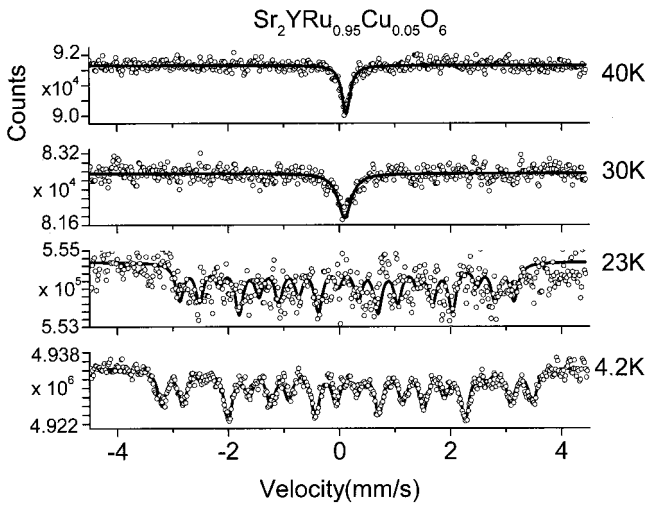


FIG. 3. Transmission ME spectrum showing the number of counts versus velocity for the source, $^{99}$Rh(Ru), and absorber, $Sr_2YRu_{0.95}Cu_{0.05}O_6$, at 4.2, 23, 30, and 40 K. The open circles represent the data and the black line represents the superposition of 18 Lorentzian lines on the data in the spectra for $T=4.2$ and 23 K. For $T=30$ and 40 K, the data were fit with a single line.

inner lines of a $^{57}$Co(Rh) source versus iron foil measurement, while the zero velocity was determined by a $^{99}$Rh(Ru) versus ruthenium powder experiment. The source and the absorber were kept at nearly the same temperature by helium exchange gas in the sample chamber. The temperature was varied by coupling a Lakeshore diode temperature controller to a nichrome wire-wrapped absorber holder, and this controlled the temperature with an error of 0.1 K.

## RESULTS

Figure 2 illustrates the spectrum of $^{99}$Rh(Ru) versus $Sr_2YRu_{0.95}Cu_{0.05}O_6$ plotted as a function of velocity at 4.2 K. This spectrum shows a magnetic hyperfine interaction that contains 18 lines, which results from the mixed multipole character of the 3/2 to 5/2 ($E2/M1$) transition.[7] The spectrum was fit with 0.180 mm/s full width at half maximum (FWHM) Lorentzian lines, which are broader than the natural linewidth, but which are still narrow experimental lines. The linewidth of the $^{99}$Rh(Ru) source is broader than the natural linewidth, because of the hexagonal structure of Ru metal.[8] The lines are well resolved from one another, and the areas were found to follow approximately the areas predicted by the Clebsch-Gordan coefficients for these transitions.[7] The spacing of most of the 18 lines, shown in Fig. 2, was equal to 0.38 mm/s (with an uncertainty less than 0.01 mm/s) except for the spacing between lines 3–4, 7–8, 11–12, and 15–16. These spacings were equal to 0.45 mm/s (with an uncertainty less than 0.01 mm/s) and scale with the spacings found by Kistner in the $^{99}$Ru ME of $Ru_{0.023}Fe_{0.977}$.[7] These spacings are due to a pure magnetic hyperfine splitting and therefore, the spacings of the lines show that there is no measurable electric quadrupole interaction (EQ). The splitting parameters deduced from the spectrum are $g_0B=1.584(0.020)$ mm/s and $g_1B=1.206(0.014)$ mm/s, for the ground state (5/2) and the first excited state (3/2), respectively. The $g$ value for a nuclear state, $I$, is the nuclear magnetic moment for that state, $\mu$, divided by $I$, $g=\mu/I$. The hyperfine magnetic field, 58.5(0.8) T, was determined by using the energy splitting of the ground state magnetic moment, $-0.641(0.005)$ nm, rather than the excited state magnetic moment, $-0.284(0.006)$ nm,[9] because the magnetic moment of the ground state is more precise. This is the largest hyperfine magnetic field ever reported as measured by the $^{99}$Ru ME, and clearly shows all of the 18 lines.

The narrow and sharp lines in Fig. 2 show the quality of the spectrum. This means that in the sample there is only one site for the Ru ion, and that all the Ru ions are experiencing the same hyperfine magnetic field. Therefore, both the sample and the magnetic order are homogeneous.

The value of the hyperfine magnetic field determined by using the ground state (5/2) nuclear magnetic moment enabled the determination of a new value for the excited (3/2) ME state nuclear magnetic moment. It was found that the value should be slightly larger at $-0.293(0.005)$ nm compared with $-0.284(0.006)$ nm by using $B=58.5(0.8)$ T and $g_1B=1.206(0.014)$ mm/s. This revised nuclear magnetic moment is consistent with the data reported in 1966 by Kistner.[7]

Figure 3 shows the spectra resulting from measurements at 4.2, 23, 30, and 40 K on the same sample. The spectrum at 23 K is not well resolved, but the data indicate that the spectrum is still magnetically split and has a hyperfine magnetic field of 53(3) T. The spectrum at 30 K consists of a single line, which is broader than the experimental linewidth (0.18 mm/s). This breadth results from a hyperfine magnetic field of about 1 T. In contrast, the linewidth at 40 K is equal to the experimental linewidth, and indicates a vanishing hyperfine magnetic field. The change from the 18-line spectrum observed at 4.2 K to a single line spectrum above 30 K indicates that a phase transition occurs near 30 K, which is completely consistent with earlier[1–4] observations at $\approx$23 K to $\approx$30 K. The isomer shift (IS) for all the measurements is $+0.13(0.01)$ mm/s.

## DISCUSSION

The interpretation of the hyperfine magnetic field in $Sr_2YRu_{0.95}Cu_{0.05}O_6$, which has a double perovskite

structure,[10] follows from the Fermi contact interaction, which describes the hyperfine magnetic field at the nucleus to be $B=(8\pi/3)\mu_B g(\rho(0)\uparrow-\rho(0)\downarrow)$, where spin up density, $\rho(0)\uparrow$, and spin down density, $\rho(0)\downarrow$, refer to the spin orientations of the polarized *s* electron density.[11] The hyperfine magnetic field, assumed to be negative, is caused by the interaction between *d* and *s* electrons in the Ru compound, and this results in a negative net electron polarization.[11] It has been argued that in $SrRuO_3$ (which has a perovskite structure) with $B=33$ T, that the spin of the electrons is $S=1$.[12] The charge state of Ru in $SrRuO_3$ is +4, not +5 as here. Therefore, in $Sr_2YRu_{0.95}Cu_{0.05}O_6$, where $B=58.5$ T, it is clear that $S>1$.

The isomer shift results from an interaction[11] which involves the density of *s* electrons over the nuclear volume. This density is influenced by 4*d* electrons, which can shield or antishield *s* electrons from the nucleus. This change, brought about by the *d* electrons, is related to the charge state of Ru. The isomer shifts for other perovskites are $SrRuO_3$ (−0.33 mm/s),[13] $CaRuO_3$ (−0.30 mm/s),[14] and $Sr_2RuO_4$ (−0.25 mm/s).[6] $BaRuO_3$ is hexagonal, but it contains Ru-O octahedra and has an IS of −0.18 mm/s.[14] The foregoing isomer shifts indicate a +4 charge state for Ru. The $Ba_5Ru_2MO_9$ (where $M=$ In, Fe, Ni, Co) (Refs. 15 and 16) compounds, which have a hexagonal barium titanate type structure with $RuO_6$ octahedra, exhibit a $^{99}$Ru IS of approximately 0.0 mm/s. In these compounds, Ru has a higher charge state than +4. In addition, the hyperfine magnetic field in $SrRuO_3$ is 33 T (Ref. 13) due to the two polarized 4*d* electrons on the Ru ion. Since the IS (+0.13 mm/s) in $Sr_2YRu_{0.95}Cu_{0.05}O_6$ is much greater than for any of the compounds shown above, and the hyperfine magnetic field is 58.5(0.8) T as compared to 33.0(0.4) T for $SrRuO_3$, it is concluded that $S=3/2$ due to three polarized 4*d* electrons with a charge state for Ru of +5.

The constancy of the spacing of the lines in the spectrum shown in Fig. 2, indicates that there is no measurable EQ interaction. Therefore, the oxygen ions surrounding the Ru ion are symmetric, and the Ru-O octahedron is not significantly distorted.

## CONCLUSIONS

In this paper we report the largest hyperfine magnetic field, 58.5(0.8) T, measured at a Ru nucleus in the superconducting compound $Sr_2YRu_{0.95}Cu_{0.05}O_6$, and a more precise magnetic moment for the 3/2 state of $^{99}$Ru. The IS has been determined to be +0.13(0.01) mm/s and this, together with the magnitude of the hyperfine magnetic field, indicates a +5 charge state for Ru in this compound. The phase transition in the Ru sublattice of this compound occurs around 30 K. The absence of an EQ interaction indicates undistorted oxygen octahedra around Ru. The data show a unique spectrum corresponding to only one type of Ru site, which indicates a homogeneous magnetic character for the sample. This means that magnetism coexists with superconductivity in this sample.

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