119Sn Mössbauer spectroscopy in the magnetic superconductor (Ru, Sn)Sr2GdCu2O8

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The 119Sn Mössbauer spectra for the (Ru1−xSnx)Sr2GdCu2O8 system, with nominal compositions x = 0.05−0.30, were measured from room temperature down to 4.2 K in samples exhibiting magnetic order followed by a resistive superconducting transition on cooling. Two contributions to the spectra are observed in the samples at room temperature: a doublet, dominating at low x, and a singlet, probably coming from the impurity phase SrSnO3. A part of the doublet evolves into a magnetic structure at low temperatures and is identified to sense the matrix properties. The isomer shift indicates that Sn enters into the RuO2 layers as Sn4+. The appearance of a magnetic phase, in the spectra, matches with the onset of the Ru-sublattice long-range order, as detected by susceptibility measurements. The area of this component exhibits a smooth decrease with the increase in the Sn content, which is well described by a random distribution in the (Ru, Sn)O2 layers. An average in-plane transferred hyperfine field of 4.29 T was sensed at 4.2 K for the sample with x = 0.05, gradually decreasing with an increase in x. This high value may be indicative of the emergence of a p-phase state for the superconducting order parameter across the magnetically ordered planes, with low pair-breaking effects.

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I. INTRODUCTION

The discovery of the hybrid ruthenocuprates RuSr2(Gd, Eu)Cu2O8 [Ru-(1212)],1,2 in which a ferromagneticlike order at TM ~ 133 K precedes a resistive superconducting transition at TC ~ 45 K, opened a new series of outstanding compounds which are particularly suitable to study the interplay between these two normally exclusive phenomena. The details about the long-range magnetic order of the Ru moments and how a ferromagnetic component emerges from an antiferromagnetic (AF) background are presently open questions. The appearance of bulk superconductivity at low temperatures was initially criticized3 and later turned out to be a problem of synthesizing processes. Muon spin rotation,4 heat capacity,5 and Meissner effect measurements5 strongly indicate that three-dimensional (3D) superconductivity and uniform long-range magnetic order at the RuO2 planes coexist in these oxides. Thermopower6 and Hall effect7 measurements are consistent with the behavior of conventional underdoped cuprates, while negative magnetoresistance is observed for T > TM. Thus changing the hole-underdoped character of the parent compound by an appropriate doping would be of interest to improve TC and to clarify the role of the magnetic interactions in the conduction mechanism. The choice of the doping cation should recognize that Ru, which was initially supposed to be formally pentavalent in the Ru-(1212) compounds, exhibits a Ru5+/Ru5+ mixed-valence state, as recently observed by 103Ru- (Ref. 9) and x-ray-absorption near-edge spectroscopy (XANES) (Ref. 10) measurements. Since attempts at Ca and Mn substitutions have failed,1,7 a more suitable series should be tried and Sn is very attractive, because it enters as Sn4+ in the conventional cuprates. Also, due to its diamagnetic nature, it would be easy to determine the occupation in the Ru sublattice via transferred hyperfine magnetic field measurements. At present, there are only a few papers on the Sn-doped Ru-(1212) system11,12 showing that both TM and TC can be properly tuned. For nominal compositions as large as x = 0.40 there was no evidence of overdoped behavior in the resistivity curves.11 This indicates that further studies about the actual valence of Sn and its limit of solubility are required. Also, conditions of sample preparation to yield pure-phase solid solutions need to be established. We report on 119Sn-Mössbauer spectroscopy measurements from room temperature (RT) down to 4.2 K in the (Ru1−xSnx)Sr2GdCu2O8 system, with nominal compositions x = 0.05, 0.10, 0.20, and 0.30, looking for clear evidence regarding the Sn location, its state of valence, and its effective concentration in the Ru-(1212) compound. It is also of interest to sense the in-plane magnetic field at the RuO2 layers, a relevant parameter for bulk superconductivity to occur in these compounds. Complementary x-ray diffraction (XRD), resistivity, and magnetic measurements are also presented in this paper.

II. EXPERIMENT

Polycrystalline samples of the (Ru1−xSnx)Sr2GdCu2O8 series with x = 0.0, 0.05, 0.10, 0.20, and 0.30 were prepared by conventional solid-state reaction with high-purity RuO2, SnO2, SrCO3, Gd2O3, and CuO powders (the undoped sample x = 0 was done as a reference). Enriched 119SnO2 (85%) was used for samples with x = 0.05 and 0.10. The initial mixture was decomposed at 960 °C in air for the synthesis. After milling and pressing procedures, the material...
was reacted in flowing nitrogen at 1010 °C for 12 h. Sintering was performed at 1050 °C for 4 days in flowing oxygen, followed by cooling at a rate of 45 °C/h. The room-temperature x-ray diffraction patterns were collected in an automatic Rygaku powder diffractometer in step-scanning mode (20° ≤ 2θ ≤ 80°). Bars of approximately 1 × 1 × 12 mm³ were cut. The dc resistivity (four-probe method) was measured from RT down to 4.2 K in a computer data-logger system, using a Keithley 224 high-precision current source and a Keithley 181 nanovoltmeter. Isothermal magnetization at 5 K up to 5 T and dc magnetic susceptibility measurements at 5 Oe were performed in a Quantum Design superconducting quantum interference device (SQUID) magnetometer. The Mössbauer spectra (MS) were collected from RT down to 4.2 K in transmission geometry using a conventional spectrometer in constant acceleration mode and a BaSnO₃ source, to which the obtained isomer shift (δ) values are referred. From a calibration spectrum using a Sn foil a linewidth (full width at half maximum) Γ = 1.14 mm/s was obtained.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns for the parent compound (a) and for the two extremes of the doped (Ru₁₋ₓSnₓ)Sr₂GdCu₂O₈ series, with x = 0.05 (b) and x = 0.30 (c). No spurious lines were observed for x = 0, 0.05, and 0.10. There was no evidence of the itinerant ferromagnet SrRuO₃ in any of the samples: however, the cubic nonmagnetic perovskite SrSnO₃ [intensity lines indicated by dots in Fig. 1(c)] was detected for the samples with x = 0.20 and 0.30.

The magnetic parameters are summarized in Table I. The coercive fields Hₘ, and the remanent moments μᵥ, as determined from the hysteresis loops at 5 K, decrease regularly with the increase in Sn content. Figure 2 shows the temperature dependence of the resistivity for the samples with x = 0.05 and 0.30. The onset superconducting transition temperatures Tₐ, taken as the maxima in the resistivity curves, were 33 and 11 K, respectively. Both values are lower than Tₐ for RuSr₂GdCu₂O₈ (45 K). We note that the normal-state resistivity is lower for x = 0.30. The inset in Fig. 2 shows the temperature dependence of the magnetic susceptibility for the sample with x = 0.05, with a magnetic transition temperature T_M = 123 K (maximum in the derivative). The relevant point from these results is that the superconducting transition is preserved even for high effective Sn concentrations in the Ru-(1212) matrix. This again is consistent with Sn substituting Ru, since superconductivity is strongly affected in conventional cuprates when Sn replaces Cu in the CuO₂ layers, reaching a complete suppression of Tₐ already for x = 0.03. Probably the long final sintering precludes cation intermixing between Ru and Sn with Cu. In summary, structural, magnetic, and resistivity measurements suggest that Sn occupies Ru sites.

Figure 3 shows the MS at RT obtained for the samples with x = 0.05, 0.10, 0.20, and 0.30. We analyzed our data with one symmetric doublet (site I) and a single line (site II). The results are summarized in Table II. The first point to consider is the origin of the singlet observed in the MS for the samples with nominal concentrations x = 0.05 and 0.10. The almost vanishing isomer shift with respect to the BaSnO₃ source suggests the presence of SnSnO₃. We believe that a small amount of this compound, undetectable from XRD experiments, but giving a sizable signal to the MS, is the origin of the singlet. The fact that for x = 0.20 and 0.30 the lines of SnSnO₃ become detectable in the diffraction patterns agrees with this idea. The rest of the Sn atoms is assumed to enter into the Ru-(1212) matrix, and the effective Sn content x_eff for the nominal concentrations x = 0.05, 0.10, 0.20, and 0.30 are x_eff = 0.045, 0.074, 0.10, and 0.14, respec-
tively. Here we have assumed that the Debye-Waller factors of the doublet and singlet are the same at RT. This assumption is supported by the fact that the absorption area ratio between the doublet and singlet does not change going from RT to 4.2 K (see below). The values of the quadrupole splittings ($\Delta E_q$) of the doublet for the Ru-$\text{I}_{2}\text{I}_{2}$ system are higher than for SnO$_2$ and similar to those obtained for Sn-doped conventional cuprates.

A set of MS was collected for the $x=0.05$ sample between RT and 4.2 K as can be seen in Fig. 4. The broadened spectrum obtained at 123 K is an indication that a transferred magnetic hyperfine field ($B_{hf}$) starts to appear at this temperature. On cooling below $T_M\approx 123$ K there is a continuous evolution towards a defined magnetic structure. This $T_M$ value corresponds to the one obtained from the bulk magnetic transition temperatures. This is a strong indication that the Sn nuclei are sensing the long-range order of the Ru moments.

Figure 5(a) shows the MS collected at 4.2 K for samples with different $x$ values. In order to fit these spectra three components were needed: (1) the singlet already present in the RT spectra, (2) a quadrupole doublet, and (3) a magnetically split spectrum. The latter was fitted with a magnetic hyperfine field distribution $P(B_{hf})$. The corresponding $P(B_{hf})$ distributions are shown in Fig. 5(b), with maximum

<table>
<thead>
<tr>
<th>$x$</th>
<th>$H_{cd}$ (Oe)</th>
<th>$\mu_s (\mu_B)$</th>
<th>$T_M$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>412(1)</td>
<td>0.98(1)</td>
<td>139(2)</td>
</tr>
<tr>
<td>0.05</td>
<td>123(2)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>254(1)</td>
<td>0.42(3)</td>
<td>109(3)</td>
</tr>
<tr>
<td>0.2</td>
<td>101(1)</td>
<td>0.28(2)</td>
<td>102(4)</td>
</tr>
<tr>
<td>0.3</td>
<td>85(1)</td>
<td>0.13(3)</td>
<td>106(4)</td>
</tr>
</tbody>
</table>

FIG. 2. Temperature dependence of the resistivity for the two extremes samples of the (Ru$_{1-x}$Sn$_x$)Sr$_2$GdCu$_2$O$_8$ series (nominal compositions). Inset: temperature dependence of the magnetic susceptibility for the sample with $x=0.05$.  

FIG. 3. Room-temperature $^{119}$Sn-Mössbauer spectra for the (Ru$_{1-x}$Sn$_x$)Sr$_2$GdCu$_2$O$_8$ system with nominal $x$ values. Fits were obtained using a singlet and a symmetric doublet. See Table II for results.

<table>
<thead>
<tr>
<th>$x$</th>
<th>Sites</th>
<th>$\delta$ (mm/s)</th>
<th>$\Delta E_q$ (mm/s)</th>
<th>$A$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>I</td>
<td>0.19(2)</td>
<td>1.21(5)</td>
<td>90</td>
</tr>
<tr>
<td>0.05</td>
<td>II</td>
<td>-0.02(2)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>0.10</td>
<td>I</td>
<td>0.16(3)</td>
<td>1.12(2)</td>
<td>74</td>
</tr>
<tr>
<td>0.10</td>
<td>II</td>
<td>0.00(2)</td>
<td></td>
<td>26</td>
</tr>
<tr>
<td>0.20</td>
<td>I</td>
<td>0.16(3)</td>
<td>1.11(2)</td>
<td>51</td>
</tr>
<tr>
<td>0.20</td>
<td>II</td>
<td>-0.01(2)</td>
<td></td>
<td>49</td>
</tr>
<tr>
<td>0.30</td>
<td>I</td>
<td>0.16(3)</td>
<td>0.98(4)</td>
<td>47</td>
</tr>
<tr>
<td>0.30</td>
<td>II</td>
<td>0.00(2)</td>
<td></td>
<td>53</td>
</tr>
</tbody>
</table>
near 4 T. No correlation was imposed between $\delta$ and $\Delta E_q$ with the hyperfine field $B_{hf}$ and the linewidths were kept as in the RT spectra. The local electric field gradient was assumed to be axially symmetric. Using the relation $D_{\text{eff}} = \Delta E_q(3 \cos^2 \Theta - 1)/2$, the average values for $D_{\text{eff}}$ as obtained from the field distribution fitting, and the $\Delta E_q$ values as obtained from the RT spectra, we calculate an average angle $\Theta_{av} \equiv 78^\circ \pm 10^\circ$. Therefore, we conclude that the ferromagnetic component of the canted antiferromagnetically ordered Ru moments is oriented along the $a, b$ plane (RuO$_2$ plane), as determined from previous neutron diffraction measurements.$^{14}$ And recent NMR studies on RuY-(1212) have also indicated that a magnetic ordering with a ferromagnetic component occurs in the RuO$_2$ plane.$^{15}$

Table III shows the results from these fits. From the $\delta$ values and relative absorption areas we conclude that the single line is the same as that observed at RT—namely, the impurity line due to SrSnO$_3$. Analogously, the magnetic spectrum and the doublet found at low temperatures develop from the doublet (site I) at RT. This is most evident from the sum of the relative absorption areas of the magnetic components (called site $I_m$) and nonmagnetic doublet (called site $I_{nm}$), which is in reasonable agreement with the relative absorption area of the doublet (site I) at RT (see Table II).

The two main mechanisms for a transferred hyperfine field at the nucleus of a diamagnetic probe are the following:$^{16}$ (1) transfer of spin density from the $d$ orbitals of the magnetic neighboring cations to the $s$ orbitals of the probing one through the covalent bonding with the oxygen atoms and (2) overlap of the polarized $2s$ and $2p$ electrons of the oxide with the core $s$ orbital of the diamagnetic atom. The observed $\langle B_{hf} \rangle$ values in our samples are comparable to the transferred fields at Sn sites in Sn:YBCO and Sn:LSOCO systems with nonoptimum hole doping. In those compounds,
this field has been associated with different degrees of stiffness of the Cu 3$d$-spin sublattice, such as a slow-down rate in the fluctuations$^{13}$ or the emergence of a glassy state,$^{17,18}$ or even the onset of long-range magnetic order.$^{19}$ In our samples, the transferred field at the Sn sites is due to the long-range-order of the neighboring Ru magnetic moments.

As already mentioned above, the sum of the relative areas of the magnetic and nonmagnetic component at 4.2 K is equal to the relative area of doublet (site I) at RT. Furthermore, both components (site I$_m$ and site I$_nm$) have the same isomer shift (see Table III). This indicates that the magnetic fraction and the fraction of the Sn species giving the nonmagnetic doublet have the same origin—namely, are due to Sn sites in the RuO$_2$ layer. While the magnetic fraction sees a transferred hyperfine field, the nonmagnetic doublet at $T = 4.2$ K comes from Sn sites in the RuO$_2$ layers, which do not sense a transferred hyperfine field. This certainly is the case for Sn sites with no Ru magnetic ions in the four in-plane nearest cation positions of the Ru-(1212) structure.$^{20}$ However, the probability of this neighborhood is extremely low for all samples and can not account for the effective areas observed for the nonmagnetic doublet. Effects leading to a net zero transferred field, such as spin fluctuations with frequencies larger than the inverse of the lifetime of the excited state of the $^{119}$Sn nucleus ($5.6 \times 10^7$ s$^{-1}$), should also be considered. Configurations with three or fewer Ru magnetic ions as nearest cation neighbors around a central Sn atom may exhibit such an effect. A calculation of the probability of finding specific nearest-neighbor configurations helps to clarify this point. If we assume that the Sn atoms distribute at random in the (Ru, Sn)O$_2$ planes, the probability of finding $n$ Sn atoms as nearest cation neighbors is given by $P(n) = P(4n)(1 - x_{eff})^{4-n}x_{eff}^n$, where $P(4n) = 4!/(4-n)!n!$. For $x_{eff} = 0.045$ we obtain $P(0) = 0.83$ and $P(1) = 0.15$: i.e., 98% of the total possible configurations correspond to $n = 0$ and 1 or to Sn atoms with four and three Ru ions as the nearest neighbors. These values match reasonably well with the effective absorption areas of the magnetic component (0.89) and the doublet at 4.2 K (0.11). According to our approach, these results suggest that the Sn atoms at the Ru sites with one Sn as the nearest neighbor are affected by fluctuation effects at 4.2 K. For the sample with $x_{eff} = 0.074$, the configurations with $n = 0$ and 1 still represent a large fraction of the total possible neighborhoods (96%) and a good agreement again is obtained between $P(0) = 0.73$ and $P(1) = 0.23$ and the effective areas of the magnetic component (0.78) and the doublet (0.22).

Actually, not only the number of Ru ions as the nearest-neighbor cations is relevant, but also how their spins are connected to the chain of exchange interactions. This fact becomes more relevant as the dilution of the spin system proceeds with increase in the Sn content, making the comparison between the $P(n)$ probabilities and the relative areas less direct. The decrease in the average transferred hyperfine field observed with the increase in $x_{eff}$ (see Fig. 6) reflects the gradual disruption of the exchange network.

The determination of the in-plane magnetic field just at the RuO$_2$ layers is quite relevant for theories on the coexistence of superconductivity (SC) and ferromagnetism (FM) in

![FIG. 6. Average magnetic hyperfine field ($B_{hf}$) transferred to the Sn sites at 4.2 K, as a function of the effective Sn concentration $x_{eff}$. The solid line is a guide to the eye.](image-url)
the ruthenocuprates. Since in these compounds the long-range magnetic order is established at $T_M \approx T_C$, SC onsets are well within the canted AF state leading to a weak ferromagnetism state. This situation has led to Fulde-Farrell-Larkin-Ovchinnikov- (FFLO-) type theories,\textsuperscript{21} where the SC and FM order parameters exhibit spatial variations to accommodate each other. According to nanoscale theory for SC-FM superlattices, the so called $\pi$-phase SC order parameter changes its phase by $\pi$ from one SC layer (CuO$_2$ planes in our case) to another, with a node at the FM intermediary one (RuO$_2$ planes). This will strongly decrease the pair-breaking effect expected from the magnetic order, allowing the onset of a bulk coherent SC state along $c$ axis.\textsuperscript{22} However, a $\pi$ phase has been predicted to occur only if the FM layer fulfills two requirements: (a) it must be extremely thin and (b) a certain critical high value of the magnetization in the layer must be exceeded.\textsuperscript{23} Similar results have been recently obtained for superconducting-antiferromagnetic interfaces, concerning the exchange field in the AF layer.\textsuperscript{24} Since the ruthenocuprates represent the first atomic-scale SC-FM or SC-AF system (ferromagnetic canting of a long-range AF order or ferrimagnetic order of Ru$^{4+}$ and Ru$^{5+}$ states), the first point is satisfactorily accomplished ($\sim 2$ Å for the RuO$_2$ layer). The second one seems to require a more careful consideration, because local fields of only $\sim 600-700$ Oe have been determined at the Gd site by electron spin resonance (ESR) (Ref. 25) and at the muon site in $\mu^+\text{SR}$ measurements\textsuperscript{4} (the so-called “apical site” of the structure, as in YBa$_2$Cu$_3$O$_{7-\delta}$). However, exchange fields may be relevant, and the magnetization at the RuO$_2$ layer might be considerably higher. Our extrapolated value of $\sim 4.9$ T at 4.2 K for the average field at the Sn sites gives an on-site estimation of the in-plane field in the RuO$_2$ layers, which can be considered as a lower limit, due to its transferred nature. Since Sn carries no atomic moment, the interpretation of this field is more straightforward than in the case for $^{57}$Fe-Mössbauer studies, where a comparison between the Ru-Fe-Mössbauer studies, where a comparison between the Ru-Fe and Ru-Ru exchange strengths is needed.\textsuperscript{26}

Since the strength of the SC coupling between the CuO$_2$ planes is not known, the threshold value for the in-plane field cannot be determined, but our results could indicate that $\pi$-phase formation may be favored in the Ru-(1212) system.

**IV. CONCLUSIONS**

$^{119}$Sn-Mössbauer spectra have been measured in the Sn:Ru-(1212) system. We have provided evidence indicating that Ru is substituted by Sn$^{4+}$ ions at the RuO$_2$ layers. Effective Sn concentrations as high as around 15 at.% were obtained. The Sn nuclei sense an in-plane transferred hyperfine field which is two orders of magnitude higher than the fields measured by other techniques at out-of-plane sites. Our indirect estimation of the in-plane field at the RuO$_2$ layers may be indicative of the emergence of a $\pi$-phase state for the superconducting order parameter across the magnetically ordered planes, with low pair-breaking effects. Spin fluctuations effects are proposed to account for a remaining doublet at low temperatures. No signature of distinct states of valence for the Ru ions was detected via the quadrupole interaction. The perpendicular orientation of the transferred field with respect to the $c$ axis confirms that a magnetic ordering with a ferromagnetic component exists in the RuO$_2$ planes.

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