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Research Article

Nb Substitution Effects on Superconducting Properties of $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$

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In order to gain further insight into the role of substitution of Ru by Nb on superconductivity, polycrystalline samples of $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ ($0.0 \le x \le 1.0$) have been synthesized by solid-state reaction method. Substitution of Nb at the Ru site in the system takes place isostructurally in the tetragonal structure (space group $I4/mmm$) with full solubility ($x = 1.0$). Superconductivity exists for all compositions. Resistivity measurements in function of temperature from 0 to 300 K were done using the four-probe technique. It is found that the substitution of Ru^{5+} for Nb^{5+} depresses the superconductivity of samples from $T_c = 29$ K for $x = 0.0$ to $T_c = 5$ K for $x = 1.0$ (where T_c is the critical temperature, when resistivity becomes equal to zero). In the normal state, the dependence of resistivity with temperature, for compositions with $x = 0.0$ and 0.2, shows a metallic behavior, while for compositions between $x = 0.4$ and $x = 1$ it shows a semiconducting behavior. In that way, the density of charge carriers is reduced with niobium doping, leading to the semiconducting behavior. The resistive transition to the superconducting state of all samples is found to be affected by granularity. Samples undergo double superconducting transition.

1. Introduction

In 1996, the possible coexistence of superconductivity and weak ferromagnetism in both $RuSr_2RE_{2-x}Ce_xCu_2O_{10}$ (Ru-1222) [1–6] and $RuSr_2RECu_2O_8$ (Ru-1212) [7–9] layered cuprate systems, where RE = Eu, Gd, or Sm, has triggered a large number of studies of the properties of these superconducting ferromagnets, since these two phenomena are usually considered to be mutually exclusive [10]. All ruthenocuprates have tetragonal symmetry and similar planar structure, with the RuO_2 planes responsible for the magnetic ordering and CuO_2 planes responsible for the superconductivity. Between the two CuO_2 planes there is a rare earth RE layer or a $RE_{2-x}Ce_xO_2$ block for Ru-1212 and Ru-1222, respectively [11]. The Ru-1222 compound has a complicated magnetic behavior. The material has been found to be paramagnetic at room temperature, but as it is cooled down, it undergoes antiferromagnetic transition, followed by spin glass behavior [12] and a ferromagnetic transition. The superconductivity sets in below T_c = 15–50 K for Ru-1212 and 25–50 K for Ru-1222, depending strongly on oxygen concentration and sample preparation [13].

At present, most physicists adhere to the view that the mechanism for high temperature superconductivity (HTSC) in cuprate metal oxide compounds originates in the interaction of degenerate charge carriers (holes) in the conducting layers of CuO_2 with fluctuations in the spin density, which are associated with antiferromagnetic ordering of the half-integral spins of Cu^{2+} ions in the crystal lattice sites of the cuprate metal oxide compounds [14].

It is possible to control relevant parameters that affect the superconducting properties of the sample by studying chemically altered compounds, with proper chemical substitutions, and thus it is possible to obtain a better understanding on the mechanisms of superconductivity. Specially, substitutions in the Ru site can be used to investigate superconductivity,

for example, Mo [15], Co [16], Sn [17], Sb [18], and Pb [19] substitutions affect the carrier density in the CuO_2 planes. Nb substitution for Ru is more interesting because Nb is a nonmagnetic ion, and both Nb and Ru ions have valence close to 5^+, and changes in the carrier density should be smaller than in previous examples.

In order to gain further insight into the role of substitution of Ru by Nb on superconductivity, we synthesized doped $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ compounds [20], which correspond to the optimum Ce concentration [21] for the emergence of the SC state. This is an appropriate isostructural system to conduct a systematic study on how the critical temperature varies.

2. Materials and Methods

We have polycrystalline samples of composition $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0) which were synthesized through a solid state reaction route from stoichiometric amounts of high purity powders (≥99.9%) of RuO_2, Nb_2O_5, Sr_2CO_3, Eu_2O_3, CeO_2, and CuO. Calcinations were carried out on the mixed powders at 1000°C, 1020°C, and 1040°C each for 24 h, with intermediate grindings. The samples were pressed into pellets and then synthesized at 1075°C during 96 h in flowing oxygen and subsequently cooled slowly to room temperature. All samples were prepared simultaneously under the same conditions. X-ray diffraction (XRD) patterns were obtained with Cu-Kα radiation in a PANalytical X'pert PRO MDP diffractometer with X'Celerator detector at room temperature. Rietveld refinement of the structure was carried out using the FullProf program [22]. Resistivity measurements were made in the temperature range of 2–300 K using the four-probe technique. Nonlinear ac susceptibility measurements with ac fields of 1, 5, and 10 Oe and frequency varying from 127 to 10,000 Hz in the temperature range of 2–200 K were done in a commercial Quantum Design's Physical Property Measurement System (PPMS).

3. Results and Discussion

Figure 1 presents the XRD patterns for all the studied compositions, $Ru_{1-x}Nb_x$-1222. The Rietveld analysis shows that the main phase is the Ru-1222 with some impurity of Sr_2RuEuO_6 (Sr-2116).

The lattice parameters which are used for $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$, $0.0 \le x \le 1.0$ samples obtained from the refinement of the crystal structure are presented in Figure 2. This result indicates that a, b, and c lattice parameters tend to increase on increasing the Nb doping content, consistent with the larger ionic size of Nb^{+5}, 0.64 Å compared to that of Ru^{+5}, 0.565 Å. This behavior is in agreement with previous studies data for $Ru_{1-x}Nb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_z$ [23].

Figure 3 presents the temperature dependence of the electrical resistivity normalized to the maximum value for $Ru_{1-x}Nb_x$-1222. The resistivity of compositions $x = 0.0$ and $x =$

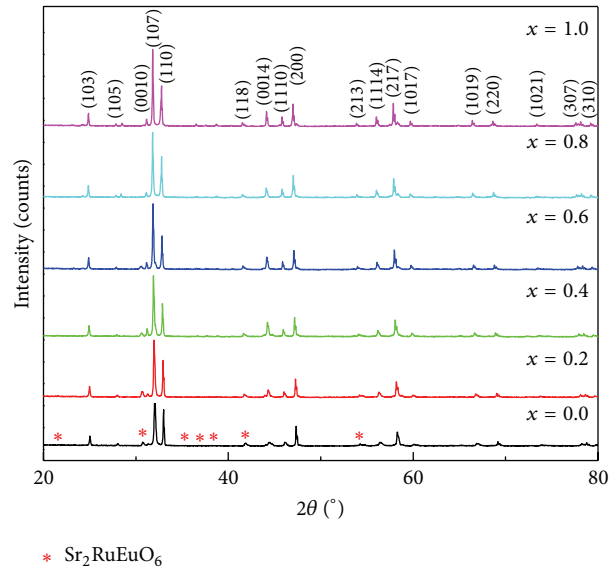

Figure 1: XRD patterns of the $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system (x = 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0).

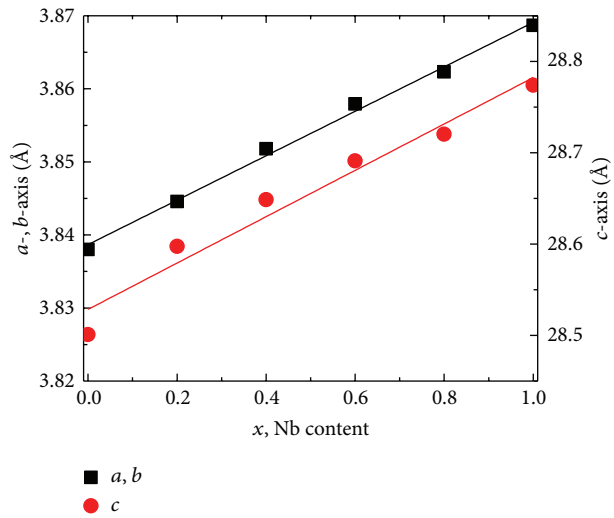

Figure 2: Dependence of a, b, and c lattice parameters on Nb doping content for $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system.

0.2 showed a slight metallic-like behavior with temperature in the normal state, with onset of the superconducting transition at 44 K and 40.4 K, respectively, and reached zero resistivity at 29 and 28 K, respectively. In general, the drop to zero is relatively broad, suggesting that the sample doping may be inhomogeneous. For the compositions from x = 0.4 to x = 1.0 samples, the resistivity reveals a semiconducting behavior with temperature in the normal state. That is expected if niobium with valence 5^+ replaces ruthenium with valence smaller than 5^+. In that way, the density of charge carriers is reduced with niobium doping, leading to the semiconducting behavior. In fact, it is well known that ruthenium ions present an average valence smaller than 5^+, as indicated in previous studies [24]. The superconducting

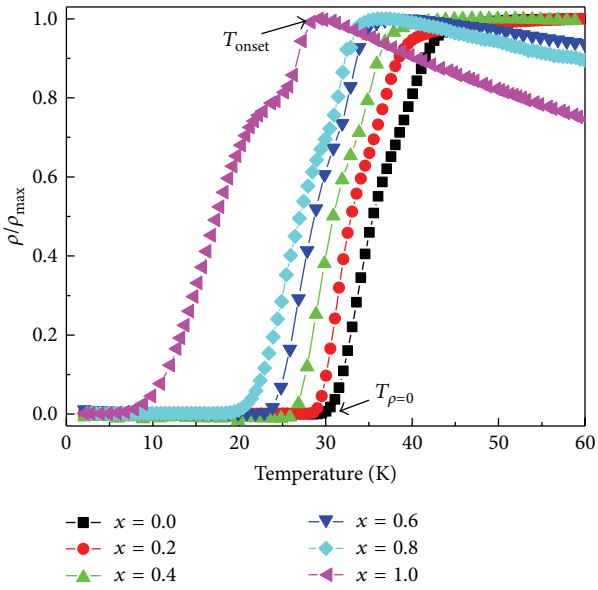

FIGURE 3: Electrical resistivity normalized to the maximum value as a function of temperature for $Ru_{1-x}Nb_x$-1222.

transition is significantly affected by Nb substitution in the RuO_2 layer in the $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system: the zero resistivity transition is depressed from $T_c = 29$ K for $x = 0.0$ to $T_c = 5$ K for $x = 1.0$. These results are in contrast with the $Ru_{1-x}Nb_xSr_2Gd_{1.4}Ce_{0.6}Cu_2O_z$ system [21] in which the superconducting transition temperature is not significantly affected by Nb substitution for Ru.

$Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$, $0.0 \le x \le 1.0$ samples undergo double superconducting transition, as can be seen in the first derivative of the resistivity in Figure 4. This double transition is attributed to the granularity of these polycrystalline samples [25, 26], arising from the weak-Josephson intergrain coupling. The structurally more perfect material inside the grain has a higher transition temperature, T_{c1}, while the structurally less perfect material at the grain boundaries has a lower transition temperature, T_{c2}. A similar double transition behavior has been observed for $RuSr_2Eu_{1.5}Ce_{0.5}Cu_2O_{10}$ which contains Ru-1212 as an impurity phase. In this case, T_{c1} is attributed to the bulk superconductivity of the dominant Ru-1222 phase, and T_{c2} to the secondary Ru-1212 phase [27].

The separation of the peaks into intragranular and intergranular in the first derivative of the resistivity versus temperature using the Matlab program was carried out, as seen in Figure 4. For $x = 0.0$, the area that corresponds to the intragranular peak is 42.17%, while the area corresponding to the intergranular peak is 57.83%. In general, the area that corresponds to the intragranular peak diminishes as the Nb content increases. SEM observation exhibits (not shown here) pronounced granularity with grain size between 2 and 5 μm and pronounced grain boundaries and large intergranular regions.

Figure 5 shows the dependence of critical temperatures: T_{onset}, T_{c1}, T_{c2}, and T_c ($\rho = 0$) with Nb content. The critical

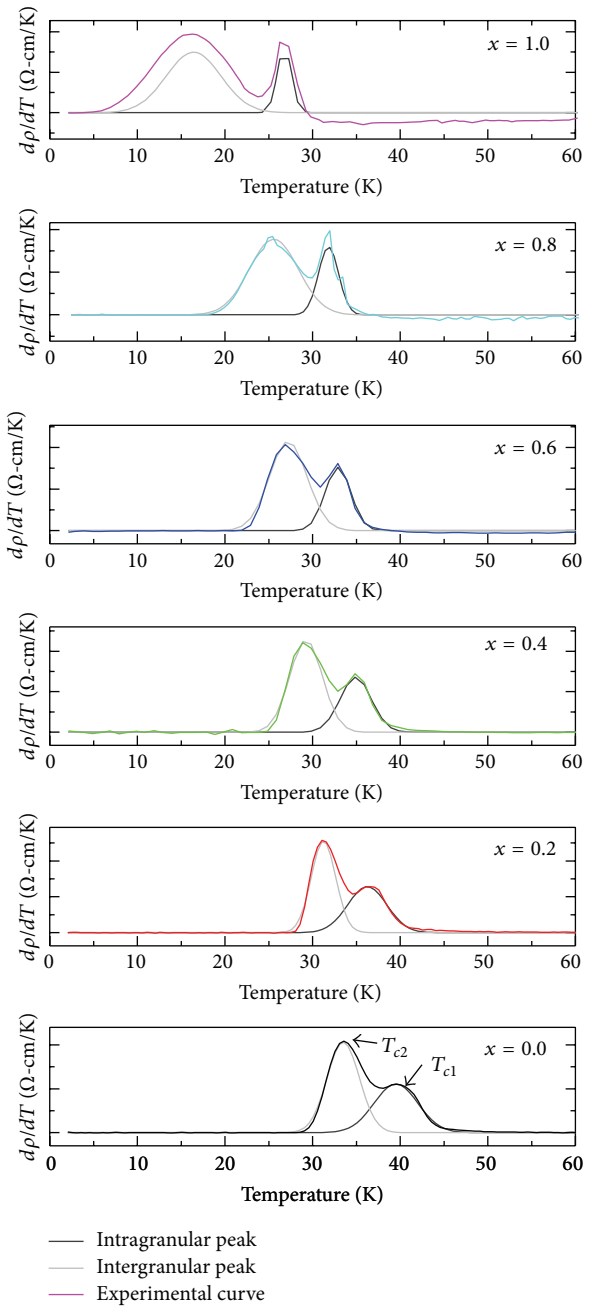

FIGURE 4: First derivative of the resistivity as a function of temperature for $Ru_{1-x}Nb_x$-1222 ($x = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0). Also it is shown the deconvolution of the derivative curves into two Gaussian peaks corresponding to temperatures T_{c1} and T_{c2}.

temperatures vary in a monotonous way with the Nb content, and they are depressed with increasing Nb content that varies almost linearly with x up to $x = 0.8$ when this dependence is more abrupt.

Figure 6 shows the real component of the ac susceptibility for compositions $x = 0.0$ and 1.0. For $x = 0.0$, the compound is paramagnetic at high temperatures, and the susceptibility begins to separate from the zero value at about 180 K, which approximately coincides with the irreversibility temperature

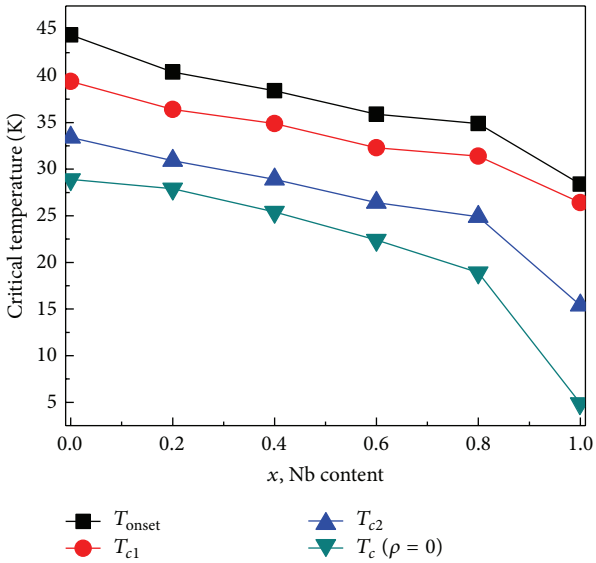

FIGURE 5: Dependence of the critical temperatures on niobium doping content.

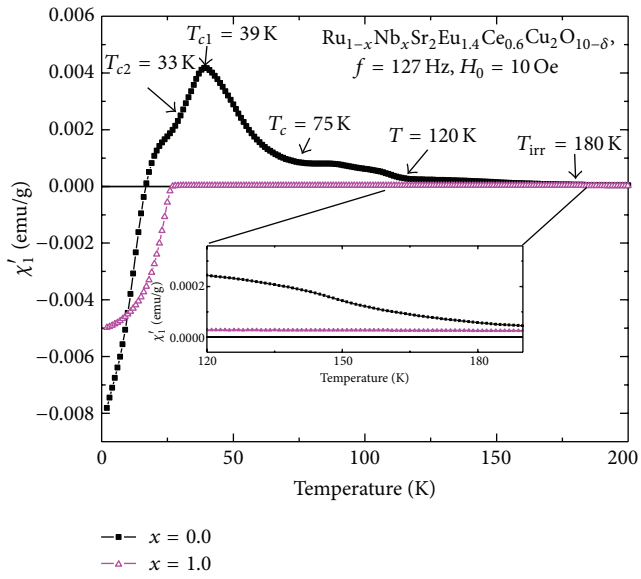

FIGURE 6: Real part of the first harmonic of ac susceptibility (χ_1') as a function of temperature, measured at 127 Hz and an ac applied field of 10 Oe for $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ system.

determined by field cooling and zero field cooling curves (not shown here). Thereafter, two magnetic transitions were observed: the first begins at about 120 K and the second at about 75 K. The nature of those magnetic transitions is controversial and they have had different interpretations [12, 28]. The susceptibility maximum at about 39 K coincides with the intragrain superconducting transition temperature (T_{c1}) determined by resistivity measurement. A shoulder at still lower temperatures is associated with the intergrain superconducting transition (T_{c2}), whose temperature coincides with the intergrain superconducting transition temperature determined by resistivity measurement. The intra- and intergrain superconducting transitions occur at positive values of susceptibility because the strong ferromagnetic component initially exceeds the negative component of the superconductor diamagnetism. All the other intermediate compositions show similar behavior with the susceptibility values decreasing with the increase of the Nb content. The sample with composition $x = 1.0$ has a different behavior: the sample remains paramagnetic from high temperature to the superconducting transition, where the susceptibility takes directly negative values because it has not any competing ferromagnetic component. It can also be observed that the superconducting transition for the composition $x = 1.0$ occurs at a temperature lower than that for the other compositions containing Ru.

4. Conclusions

It was found that the replacement of Ru by Nb in $Ru_{1-x}Nb_xSr_2Eu_{1.4}Ce_{0.6}Cu_2O_{10-\delta}$ reduces the superconducting transition (temperature when zero resistivity is reached) from, $T_c = 29$ K for $x = 0.0$ to $T_c = 5$ K for $x = 1.0$.

In the normal state, compositions $x = 0.0$ and 0.2 showed metallic behavior, while semiconducting behavior for $x = 0.4$ to 1.0; this because the charge carrier density is reduced by Nb doping.

Coexistence of superconductivity and magnetism appears for all samples that contain Ru, while the concentration $x = 1.0$ (when Ru is completely substituted by Nb) presents only superconductivity. Superconducting transition for the composition $x = 1.0$ occurs at a temperature lower than that for the other compositions containing Ru.

The transition from normal to superconducting state is affected by the granularity of the samples, which have double transition to reach the resistivity equal to 0 due to weak coupling between grains.

The magnetic response is reduced as the Nb content is increased, indicating the dilution of the magnetic Ru^{5+} ions.

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