

Superconductivity in Magnetically Ordered Ru_{1-x}Ir_xSr₂GdCu₂O₈ Compounds

S. Andrade, F. C. Fonseca*, R. F. Jardim,

Instituto de Física, Universidade de São Paulo, CP 66318, 05315-970, São Paulo, SP, Brazil

I. Bossi, M. S. Torikachvili,

Department of Physics, San Diego State University, CA 92123-3344, San Diego, USA

A. H. Lacerda,

National High Magnetic Field Laboratory, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

and L. Ben-Dor

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem 91904, Israel

Received on 1st July, 2003.

We have performed a systematic study of the structural, transport, and magnetic properties of polycrystalline samples of the magnetic superconductors Ru_{1-x}Ir_xSr₂GdCu₂O₈; $x = 0, 0.02, 0.05, 0.10,$ and 0.15 . The samples were prepared by solid state reaction and sintered at $1060\text{ }^\circ\text{C}$ for 72 h under O₂ flow. X-ray diffraction analysis shows that all samples are nearly single phase and that the lattice parameters are independent of Ir content. Transport properties measurements revealed that the Ru substitution by Ir results in a decrease of $T_{c,onset}$ from $\sim 50\text{ K}$ ($x = 0$) to $\sim 30\text{ K}$ ($x = 0.10$). Further addition of Ir ($x > 0.10$) causes an evolution from metallic to non-metallic behavior of $\rho(T)$. We have also found that magnetic order develops in the undoped Ru-1212 materials near $T_M \sim 130\text{ K}$. This temperature decreases linearly with increasing Ir content at the rate of $\sim -1.6\text{ K / Ir at.}\%$, suggesting that Ir effectively substitutes Ru in the RuO planes. A subtle drop in $\rho(T)$ is observed close to T_M , probably due to the suppression of the spin-flip scattering. The magnetoresistivity measurements revealed that the temperature $T_{c,zero}$, in which $\rho(T) \sim 0$, decreases rapidly for low applied magnetic fields ($H < 2\text{ T}$), and that this drop becomes much less pronounced in higher magnetic fields ($2 \leq H \leq 18\text{ T}$). The appreciable broadening of $\rho(T)$ curves at low magnetic fields is reminiscent of the behavior in high- T_c materials showing granular behavior, as for example in Sm_{1.85}Ce_{0.15}CuO_{4-y}.

1 Introduction

A considerable research effort has been devoted recently to the understanding of the physical properties of the ruthenocuprate compounds with general composition RuSr₂LnCu₂O₈ and RuSr₂(Ln_{1+x}Ce_{1-x})Cu₂O₁₀ (Ln = Sm, Eu, and Gd). [1, 2] The interest in these materials was triggered by the observation of coexisting superconductivity (SC) and long-range magnetic order, including weak-ferromagnetism (wFM), at moderately high temperatures (T). [3, 4] The occurrence of long-range magnetic order has been determined by means of magnetic susceptibility, and muon spin relaxation, while details of the magnetic and crystal structure have been studied by neutron diffraction. [5] Heat capacity measurements and diamagnetic shielding fraction data indicate that SC is a bulk property, coexisting in a microscopic scale with magnetism in these materials. [6, 7] The crystal structure of the

RuSr₂LnCu₂O₈ compound (Ru-1212) is closely related to the one of the LnBa₂Cu₃O₇ (Ln-123), [1] in which the intermediate layer consists of vertex sharing RuO₆ octahedra replacing the CuO₄ squares of the Ln-123 structure. [4, 5] The coexistence of SC and FM can be sustained possibly because of the weak coupling between the Ru-O magnetically ordered layers and the SC Cu-O planes.

An important point concerning the superconducting and magnetic properties in these ruthenocuprates is the valence of the Ru ions. X-ray absorption near-edge structure spectroscopy in the Ru-1212 compounds yields 40-50% of Ru⁴⁺ and 60-50% of Ru⁵⁺. [8] In light of the proximity of the superconducting Cu-O and the magnetically ordered Ru-O layers, and taking into account that the superconducting transition temperature (T_c) is lower than the magnetic ordering temperature (T_M), it has been suggested that the onset of superconductivity is accompanied by a spontaneous vortex phase. [9]

*Present address: CCTM - Instituto de Pesquisas Energéticas e Nucleares, São Paulo, SP, Brazil

Another relevant feature of these superconductors is the strong dependence of parameters like the normal-state electrical resistivity (ρ), the superconducting transition temperature (T_c), and the width of the superconducting transition (ΔT_c) on the synthesis conditions. [6] Nevertheless, the onset of SC ($T_{c,onset}$) for the Ru-1212 $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ compound is usually ~ 45 K and the Curie temperature $T_M \sim 132$ K. [4]

The weak coupling that allows the coexistence of SC and FM is strongly affected by both high pressure and chemical substitutions. Thus, an approach to study the coexisting phenomena in these superconductors is via chemical substitution. Some results regarding different cation substitutions in Ru-1212 have already been reported. [6,10-14] However, only a fraction of them concern substitutions at the Ru site, in spite of their relevance, and given the currently unsolved configuration of spin and charge of Ru ions in Ru-1212 compounds. [11] Reported Ru substitutions include Sn^{+4} , Nb^{+5} , and Ta^{+5} . [10-16] More recently, Mo and Sb substitutions for Ru were performed on the Ru-1222 compounds and a competition of SC and magnetism was observed. [17, 18] These experiments probe the effect of the changes in ionic radius, valence, and magnetic character of the substituting ion. Both the superconducting and magnetic properties of Ru-1212 are affected by these substitutions. Carriers can be either introduced or removed from the CuO planes, depending on the valence of the substituting ion, modifying the transport properties relative to the parent compound. However, the majority of these substitutions resulted in changes in the structural parameters due to differences in the ionic radius.

In this work we have investigated the magnetic and transport properties of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ specimens in order to study the effect of the dilution of the magnetic Ru sublattice by substituting Ir for Ru. Since the ionic radii of Ir and Ru are close, it is reasonable to expect that partial substitutions of Ir for Ru can be made without appreciable structural changes.

2 Experimental

Polycrystalline samples of $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ ($0 \leq x \leq 0.15$) were prepared using a two-step solid state reaction procedure. [19] Initially, stoichiometric amounts of high-purity Ru, Ir, SrCO_3 , Gd_2O_3 were ground together and reacted in air at 1250°C for 12 h in order to obtain $\text{Sr}_2\text{GdRu}_{1-x}\text{Ir}_x\text{O}_6$ (Sr-2116) precursors. Then, CuO was added to the Sr-2116 powders and ground together extensively, followed by pelletizing and sintering at 1060°C for 72 h in flowing O_2 . The two-step route yielded samples with better quality than when the materials were prepared by direct solid state synthesis of all ingredients.

Ground samples were analyzed by X-ray powder diffraction (XRD) measurements at room temperature using $\text{Cu K}\alpha$ radiation in the $20 \leq 2\theta \leq 80^\circ$ interval with a 0.05° (2θ) step size.

Magnetization $M(T)$ measurements were performed using a SQUID magnetometer from Quantum Design. The values of $M(T)$ in the remanent field of the superconduct-

ing magnet (~ 1 Oe) were recorded in the T-range from 5 to 300 K, both with decreasing and increasing T. The temperature dependence of the ac magnetic susceptibility $\chi_{ac}(T)$ was measured at 155 Hz using an excitation field of 2 Oe.

Four-wire dc electrical resistivity $\rho(T)$ measurements were performed in the temperature range $2 \leq T \leq 300$ K and applied magnetic fields (H) to 18 T, utilizing a LR-700 Linear Research ac resistance bridge operating at 16 Hz. The high field measurements were carried out at the National High Magnetic Field Laboratory in Los Alamos.

3 Results and Discussion

The XRD analysis of the polycrystalline samples of $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ ($0 \leq x \leq 0.15$) revealed that all samples are nearly single-phase, while exhibiting very small fractions of SrRuO_3 ($< 2\%$) and Sr-2116 ($< 2\%$) impurity phases (Fig. 1). The impurity content shows no appreciable dependence on the Ir concentration. The diffraction patterns of the Ir-doped materials are nearly identical to that of the parent compound, and they were all indexed according to the $P4/mmm$ space group. [1]

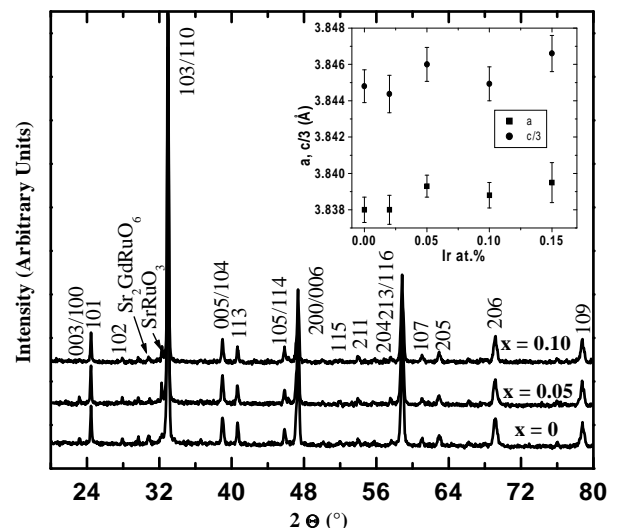


Figure 1. X-ray diffraction patterns for $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ polycrystalline samples for Ir content $x = 0, 0.05,$ and 0.10 . The main diffraction peaks of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ are indexed by the $[hkl]$ indexes and the arrows point to the main lines of the impurity phases. The inset shows the calculated lattice parameters a and c .

The lattice parameters for the pure Ru-1212 composition were calculated to be $a = b = 3.839$ (1) Å, and $c = 11.536$ (1) Å. These values were nearly unchanged due to Ir substitutions, as indicated in the inset of Fig. 1. The six-fold coordinated Ir^{+5} and Ir^{+4} (0.57 and 0.625 Å, respectively) have ionic radii values very close to the Ru^{+5} and Ru^{+4} (0.565 and 0.62 Å, respectively), which suggests that Ir can substitute for Ru in the Ru-1212 structure with no appreciable changes of the lattice parameters. [20]

Since the partial substitution of $\text{Ir}^{+5/+4}$ for $\text{Ru}^{+5/+4}$ is not accompanied by any significant change in lattice parameters, it can be seen as a dilution of the Ru magnetic sublattice.

tice. Its implications on both magnetic and transport properties of the Ru-1212 magnetic superconductors are discussed below.

The effect of Ir substitutions on the temperature dependence of the electrical resistivity $\rho(T)$ is displayed in Fig. 2. The $\rho(T)$ data show that the electrical resistivity $\rho(T)$ close to the onset of the critical temperature $T_{c,onset} \sim 50$ K is ~ 10 m Ω cm, a value within the range of other reported values for the pristine compound. [11-13] In addition, the commonly observed upturn in $\rho(T)$ close to $T_{c,onset}$ is hardly seen in lightly doped samples, which attests to the high quality of the samples. However, an upturn in the $x = 0.1$ sample close to $T_{c,onset}$ is quite noticeable. Also, the lightly Ir-doped materials have lower $\rho(T)$ values and a more pronounced metallic behavior, as gauged by the values of $d\rho/dT$ in the normal phase. The Ru substitution by Ir results in a decrease of $T_{c,onset}$ from ~ 50 K ($x = 0$) to ~ 30 K ($x = 0.10$). Further addition of Ir ($x > 0.10$) causes an evolution from metallic to non-metallic behavior of $\rho(T)$. However, the SC transition width ΔT_c was found to decrease with Ir addition from $\Delta T_c \sim 17$ K for the pristine compound to ~ 11 K for the $x = 0.10$ sample. The onset of magnetic ordering is accompanied by a subtle drop in $\rho(T)$ close to T_M , probably due to the suppression of the spin-flip scattering. This discontinuity can be determined from the maximum in the $d\rho(T, H = 0)/dT$ curves of the studied compounds, close to the magnetic ordering temperature T_M (see inset of Fig. 2).

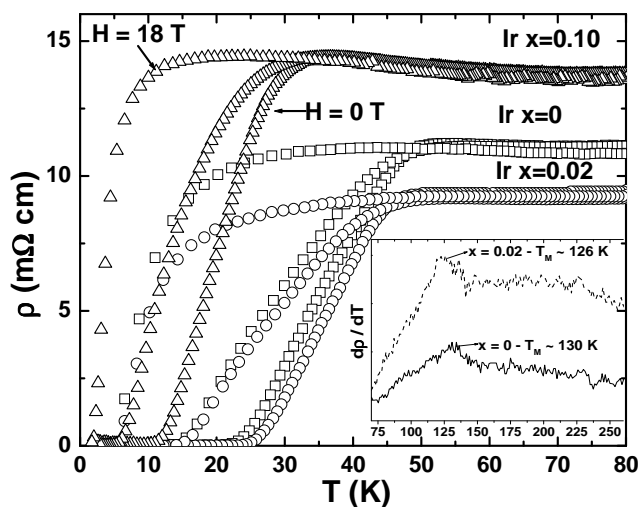


Figure 2. Temperature dependence of the electrical resistivity for $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ ($\text{Ir } x = 0, 0.02, \text{ and } 0.10$) polycrystalline samples in applied magnetic fields $H = 0, 1, \text{ and } 18$ T. The inset shows the derivatives of the $\rho(T)$ curves near T_c for $H = 0$.

The magnetoresistivity measurements revealed that all studied samples attained the zero-resistance state at $T > 2$ K up to the highest applied magnetic field of $H = 18$ T. From these curves one observes that the temperature $T_{c,zero}$, in which $\rho(T) \sim 0$ decreases rapidly for low applied magnetic fields ($H < 2$ T) and much more slowly thereafter ($2 \leq H \leq 18$ T). The appreciable broadening of $\rho(T)$ curves at low magnetic fields resembles features of granular superconductors, as for example in $\text{Sm}_{1.85}\text{Ce}_{0.15}\text{CuO}_{4-y}$. [21]

Using the magnetoresistivity data, we estimated the H_{c2}, T phase diagram of the Ir substituted Ru-1212 compounds (Fig. 3), by considering the same $T_{c,onset}$ for all H , and by taking the 50% drop of $\rho(T)$ as the criteria for the H_{c2} determination. The obtained results are shown in Fig. 3, which also exhibits the H_{c2} vs T data for the Ru-1222 for comparison. [22] The $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ curves show the same behavior with a steeper increase at low T in samples with high Ir content.

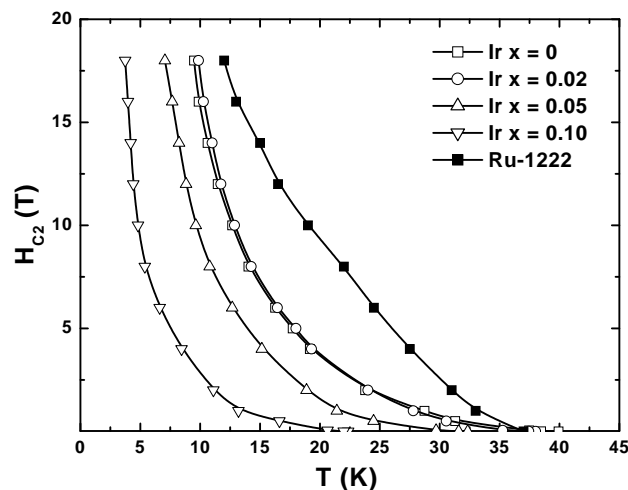


Figure 3. Temperature dependence of the upper critical field of the magnetic superconductor $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ ($x = 0, 0.02, 0.05, \text{ and } 0.10$) and Ru-1222 polycrystalline samples. [22] The solid lines are guides to the eye.

The observed features in the $\rho(T)$ data correlate well with the magnetization data. The temperature dependence of the magnetization taken in the remanent field of the superconducting magnet, which is of the order of 1 Oe, is displayed in Fig. 4. The first point to be discussed here is the low temperature $M(T)$ data. An offset in the diamagnetic transitions due to SC between the cooling and warming curves is clearly observed in samples with $x \leq 0.10$, while no diamagnetic values were found in samples of higher Ir content. Magnetization curves with applied magnetic field $H = 5$ Oe (not shown) were taken and revealed that the diamagnetic transition was suppressed in these fields. Even though such a small magnetic field can hinder the Meissner effect, the zero-resistance state is attained for applied magnetic fields H up to 18 T (see Fig. 2). Various reported magnetization curves of the Ru-based superconductors show the absence of the Meissner effect. These observations are consistent with the proposed spontaneous vortex phase (SVP) model, in which the magnetic moment of the RuO_2 layers generates an internal magnetic field that exceeds H_{c1} . [9] The ac magnetic susceptibility data at higher temperatures reveal that magnetic ordering develops at $T_M \sim 130$ K, as inferred from a peak in the in-phase component of $\chi_{ac}(T)$ data. The inset of Fig. 4 shows the in-phase $\chi_{ac}(T)$ component of the Ir-substituted samples. The magnitude of the magnetic moment decreases with the substitution of Ru, and the temperature T_M decreases linearly at a rate of ~ -1.60 K / Ir-at.%. This indicates that Ir is substituting at the Ru site. The positive upturn in the $M(T)$ below 15 K in the

cooling data is possibly due to the magnetization of the Gd-sublattice under field of the Ru-sublattice. Heat capacity measurements (not shown) revealed that the Gd sublattice ordering takes place at the same temperature $T_{Gd} \sim 2.5$ K for samples with Ir $x = 0$ and 0.10. These results further suggest that Ir substitutes for Ru in the Ru-O planes, resulting in a lower T_M , and in a smeared out magnetic transitions.

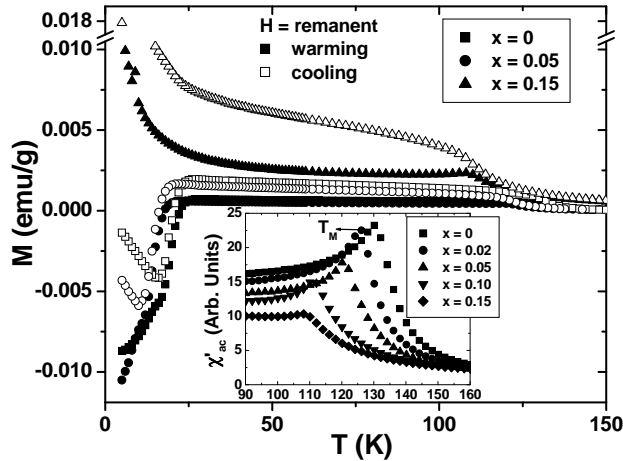


Figure 4. Temperature dependence of the magnetic susceptibility χ , measured during warming (full symbols) and cooling (open symbols) under the remanent field of the magnet for Ir $x = 0, 0.05$, and 0.15 samples. The inset shows the in-phase component of the $\chi_{ac}(T)$ for the Ir-substituted samples.

In summary, our results suggest that Ir substitutes for Ru in the $\text{Ru}_{1-x}\text{Ir}_x\text{Sr}_2\text{GdCu}_2\text{O}_8$ compounds. The main observed features due to the substitution of Ir for Ru in the structural, transport, and magnetic properties of the parent compound are: 1) no appreciable dependence on the lattice parameters; 2) the inducement of a more metallic behavior for lightly doped samples; 3) the decrease of both the superconducting transition temperature and the SC transition width; 4) the linear decrease of the magnetic ordering temperature; and 5) the suppression of superconductivity for $x > 0.15$. Since the lattice parameters are nearly independent of the Ir content, one can expect that the valence of the substituting Ir matches the valence of the replaced Ru. These isovalent substitutions can be accompanied by a dilution of the ordered magnetic moments, if substituting Ir is in a low spin state. However, the effect of these substitutions on T_c is still puzzling, and a more thorough investigation considering the band structure, and the pairing mechanism is in order.

This work was supported by the Brazilian agency FAPESP under Grants Nos. 99/10798-0, 01/01455-4, and 01/04231-0, and by the US National Science Foundation under Grants No. INT-9725929 (IB, MST, AHL) and DMR-0306165 (IB, MST). Work at the NHMFL was performed under the auspices of the NSF, the State of Florida, and the U.S. Department of Energy. RFJ is a CNPq fellow under Grant No. 304647/90-0.

References

- [1] L. Bauernfeind, W. Widder, and H. F. Braun, *Physica C* **254**, 151 (1995).
- [2] L. Bauernfeind, W. Widder, and H. F. Braun, *J. Low Temp. Phys.* **105**, 1605 (1996).
- [3] I. Felner, U. Asaf, Y. Levi, and O. Millo, *Phys. Rev. B* **55**, R3374 (1997).
- [4] C. Bernhard, J. L. Tallon, C. Niedermayer, T. Blasius, A. Golnik, E. Brücher, R. K. Kremer, D. R. Noakes, C. E. Stronach, and E. J. Ansaldo, *Phys. Rev. B* **59**, 14099 (1999).
- [5] J. W. Lynn, B. Keimer, C. Ulrich, C. Bernhard, and J. L. Tallon, *Phys. Rev. B* **61**, R14964 (2000).
- [6] C. Bernhard, J. L. Tallon, E. Brücher, and R. K. Kremer, *Phys. Rev. B* **61**, R14960 (2000).
- [7] J. L. Tallon, J. W. Loram, G. V. M. Williams, and C. Bernhard, *Phys. Rev. B* **61**, R6471 (2000).
- [8] R. S. Liu, L.-Y. Jang, H.-H. Hung, and J. L. Tallon, *Phys. Rev. B* **63**, 212507 (2001).
- [9] E. B. Sonin and I. Felner, *Phys. Rev. B* **57**, R14000-3 (1998).
- [10] P. W. Klamut, B. Dabrowski, S. M. Mini, M. Maxwell, J. Mais, I. Felner, U. Asaf, F. Ritter, A. Shengelaya, R. Khasanov, I. M. Savic, H. Keller, A. Wisniewski, R. Puzniak, I. M. Fita, C. Sulkowski, and M. Matusiak, *Physica C* **387**, 33 (2003).
- [11] J. E. McCrone, J. L. Tallon, J. R. Cooper, A. C. McLaughlin, J. P. Attfield, and C. Bernhard, *cond-mat/0302499v1*.
- [12] A. C. McLaughlin and J. P. Attfield, *Phys. Rev. B* **60**, 14605 (1999).
- [13] Z. Sun, S. Y. Li, Y. M. Xiong, and X. H. Chen, *Physica C* **349**, 289 (2001).
- [14] V. P. S. Awana, T. Kawashima, and E. Takayama-Muromachi, *Phys. Rev. B* **67**, 172502 (2003).
- [15] P. W. Klamut, B. Dabrowski, S. Kolesnik, M. Maxwell, and J. Mais, *Phys. Rev. B* **63**, 224512 (2001).
- [16] A. C. McLaughlin, V. Janowitz, J. A. McAllister, and J. P. Attfield, *Chem. Comm.* **14**, 1331 (2000).
- [17] L. Shi, G. Li, X. D. Zhang, S. J. Feng, and X.-G. Li, *Physica C* **383**, 450 (2003).
- [18] I. Felner and E. Galstyan, *cond-mat/0304552*.
- [19] T. P. Papageorgiou, T. Herrmannsdorfer, R. Dinnebier, T. Mai, T. Ernst, M. Wunschel, and H. F. Braun, *Physica C* **377**, 383 (2002).
- [20] R. D. Shannon, *Acta Cryst.* **A32**, 751 (1976).
- [21] R. F. Jardim, M. C. de Andrade, E. A. Early, M. B. Maple, and D. Stroud, *Physica C* **232**, 145 (1994).
- [22] M. T. Escote, V. A. Meza, R. F. Jardim, L. Ben-Dor, M. S. Torikachvili, and A. H. Lacerda, *Phys. Rev. B* **66**, 144503 (2002).