Electron-electron interaction and weak localization effects in badly metallic $SrRuO_3$

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(Received 13 July 1999; revised manuscript received 14 August 2000; published 5 January 2001)

We report on the effect of light ion irradiation on the low-temperature electrical resistivity of ferromagnetic $SrRuO_3$ thin films. Fresh samples displayed a ferromagnetic transition at $T_c \sim 160$ K, good metallic behavior ($\rho(300\,\mathrm{K}) \sim 400\ \mu\Omega$ cm, $d\rho/dT > 0$) at room temperature, and the low-temperature upturn in the electrical resistivity commonly found in $SrRuO_3$. Badly metallic films, displaying high values of the electrical resistivity ($O(1000\ \mu\Omega$ cm)) and incipient nonmetallic behavior ($d\rho/dT < 0$) at low temperature, were obtained by He^+ irradiation. For high enough irradiation doses, these samples did not show magnetic order down to the base temperature of our experiments. The temperature dependence of the electrical conductivity of virgin and irradiated samples is discussed in terms of a weak localization contribution plus a large electron-electron interaction term. The magnitude of the e^--e^- contribution reflects the enhancement of strong electron correlations in $SrRuO_3$ due to disorder.

DOI: 10.1103/PhysRevB.63.052403 PACS number(s): 72.15.Rn, 71.30.+h

INTRODUCTION

Materials classified as ''bad metals'' have focused a great deal of interest during the past years. Among the remarkable properties of this class of systems, perhaps the most characteristic is their anomalous electrical resistivity, which takes extremely high values. Furthermore, the electrical resistivity does not seem to approach the saturation value above room temperature, as it is usually observed in other poorly conducting metals.[1,2] Many of the most interesting and exotic materials discovered during the last decade belong to this category. We will mention here high-temperature superconductors, fullerenes, and organic superconductors as examples of such materials. Thus, the term ''bad metals'' embraces strongly correlated electron systems in the limit $k_F l = O(1)$, i.e., materials for which the room-temperature resistivity value, well above the Ioffe-Regel limit for the metallic state, implies an electronic mean free path shorter than the interatomic spacing.[3] In this case, the Boltzmann theory of transport is not applicable, and deviations from metallic temperature dependence of the electrical resistivity are usually observed.[4]

$SrRuO_3$ is an orthorhombically distorted perovskite, the only example of ferromagnetism in a conducting $4d$ transition-metal oxide. This material has been classified as a badly metallic itinerant ferromagnet.[5,6] The actual nature of magnetism in this system is not fully understood yet.[7,8] Although it was usually considered as a typical example of itinerant ferromagnetism, several authors have pointed to experimental facts that cast some shadows on such a simple picture. The possibility of a significant contribution to ferromagnetism coming from localized moments has been proposed.[9] Klein *et al.* have shown that the itinerant model for $SrRuO_3$ is clearly an oversimplification. As a matter of fact, they have proposed that this system represents a whole class of badly metallic itinerant ferromagnets,[10] different of both good metals (Ni, Co, Fe) and very poor conductors as the perovskite manganites. The properties of these materials with $k_F l \leqslant O(1)$ are not well described within the present theoretical frames, not only because of the lack of a thorough theoretical study but also due to the scarce experimental information available.

In a previous work we have discussed the effects of irradiation damage on thin film samples of $SrRuO_3$.[11] Interestingly enough, ion damage destroys ferromagnetism, while for virgin films grown on the same substrate with different deposition conditions the Curie temperature remains essentially unchanged ($T_c \sim 160$ K). In this paper we present a study of the low-temperature resistivity of poorly conducting thin-film samples of $SrRuO_3$ obtained by ion irradiation, and virgin samples displaying a low-temperature upturn of the resistivity. The results will be discussed in terms of weak electron localization and electron-electron interaction in disordered systems.[12]

EXPERIMENT

The samples studied in this work were grown from a $SrRuO_3$ target on (100)-oriented MgO substrates. A high-pressure dc sputtering system was used, with pure oxygen (3.6 mbar) as discharge gas. Some of the samples were obtained by 80-keV He+ irradiation with doses up to $5 \times 10^{15}/\mathrm{cm}^2$ of virgin films showing metallic behavior in most of the experimental temperature ranges and ferromagnetic order below $T_c \sim 160$ K. The films studied in this work were around 1000 Å thick and presented values of the room temperature electrical resistivity in the range between 500 and 1000 $\mu\Omega$ cm, with negative values of $d\rho/dT$ at low temperatures, which indicates an incipient departure from metallic character. Structural characterization was performed by

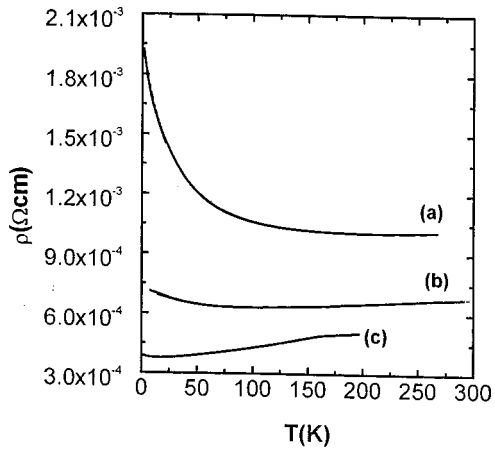

FIG. 1. Temperature dependence of the electrical resistivity of three $SrRuO_3$ thin films: (a) He^+ irradiated (nonmagnetic sample) with a dose $5\times10^{15}\,cm^{-2}$; (b) He^+ irradiated with a dose $3.5\times10^{15}\,cm^{-2}$; (c) virgin sample ($T_c\sim160\,K$).

x-ray diffraction (Siemens D5000) using Cu $K\alpha$ radiation. Scanning electron microscopy and high-resolution transmission electron microscopy experiments were conducted to characterize structural changes taking place as the effect of irradiation. dc electrical resistivity (ρ) was measured in the temperature range 1.5–300 K. For both samples $\rho(T)$ was measured with different values of applied magnetic field ranging between $H=0$ and 70 kOe.

RESULTS AND DISCUSSION

From the x-ray spectra we inferred that the films grew well textured, with the pseudocubic (001) direction perpendicular to the substrate. Increasing irradiation doses resulted in an enlargement of the pseudocubic *c*-lattice parameter.[11] Scanning electron microscopy observations revealed a granular structure with an average grain size of 0.5 μm. Surface topography and grain size were not affected by irradiation. Transmission electron microscopy experiments performed using cross-section geometry before and after irradiation showed that the intergrain structure was not changed due to the irradiation process either. A structural coherence length of 300 Å was obtained from the x-ray diffraction peaks using the Scherrer formula. This value was also not modified upon irradiation. This suggests that, like in other oxide perovskites,[13] defects created by irradiation consist mainly of point defects, most likely related to oxygen displacements, due to the small mass of oxygen compared to the other constituent elements. Lattice strains due to point defects could explain the expansion of the pseudocubic *c*-lattice parameter observed in the irradiated samples.

The electrical resistivity as a function of temperature of irradiated ((a) and (b)) and virgin ((c)) samples is depicted in Fig. 1. Our measurements reveal a clear ferromagnetic transition taking place at $T_c\sim160\,K$ for the virgin film. On the other hand, no signs of a magnetic transition are observed, down to the base temperature of our experiments, for sample (a), which was irradiated with the highest He^+ dose. In Figs. 2 and 3 the electrical *conductivities* (σ) of films (a) and (c)

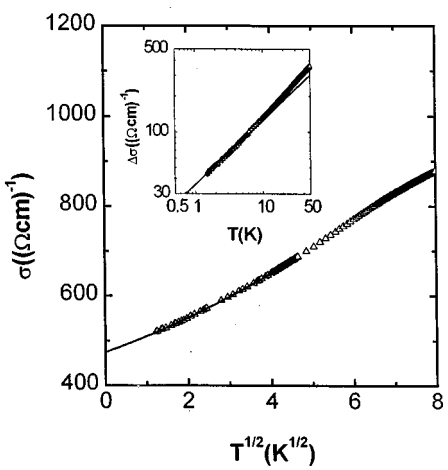

FIG. 2. Temperature dependence of the electrical conductivity of sample (a), plotted as σ vs $T^{1/2}$. Solid lines are fits to Eq. (1) with the parameters given in text. The inset shows the correction to the electrical conductivity ($\Delta\sigma=\sigma(T)-\sigma_0$) vs T as a log-log plot, which includes a solid line of slope $\frac{1}{2}$.

are presented as a function of $T^{1/2}$. The low-temperature dependence of σ can be described quite well by a model that considers the effects of electron-electron interaction and weak localization in three-dimensional (3D) systems.[4] In this case, σ takes the following form:

$$\sigma(T)=\sigma_0+mT^{1/2}+BT, \tag{1}$$

where the square root term accounts for the effect of the e^--e^- interaction[12,14] (the *Altshuler-Aronov* correction), and the linear term is the weak localization correction to the conductivity.[15] Our samples are still enough apart from the metal-insulator transition (MIT) to consider the alternative temperature exponent for the interaction correction ($\frac{1}{3}$) that other authors have predicted right at MIT (Ref. 16) or more sophisticated analysis proposed to avoid unphysical fitting of the low-temperature conductivity when approaching the in-

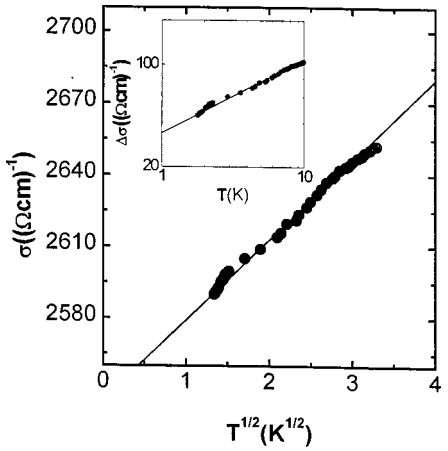

FIG. 3. Temperature dependence of the electrical conductivity of the virgin sample, plotted as σ vs $T^{1/2}$. Solid line is a fit to Eq. (1) with the parameters given in text. The inset shows the correction to the electrical conductivity ($\Delta\sigma=\sigma(T)-\sigma_0$) vs T as a log-log plot, with a solid line of slope $\frac{1}{2}$.

sulating regime.[17] We consider that the films are thick enough (1000 Å) as to discard effects coming from two-dimensional behavior. At least from the point of view of magnetic properties, the high Curie temperatures observed support this assumption. An excellent fit to the conductivity was obtained for the irradiated sample (a), in the temperature range $T \leqslant 20$ K, which rendered the following values for the three parameters: $\sigma_0 = 474.4 \pm 0.4$ $(\Omega\,\mathrm{cm})^{-1}$, $m = 33.0 \pm 0.3$ $(\Omega\,\mathrm{cm\,K}^{1/2})^{-1}$, $B = 2.76 \pm 0.05$ $(\Omega\,\mathrm{cm\,K})^{-1}$ (see Fig. 2). We want to point out that a similar analysis could be performed also for samples irradiated with lower doses, as, for example, sample (b). However, the relatively low T_c of these films (~90 K for sample (b)) makes fits to expression (1) less reliable due to the limited fitting range and the disturbing effect of the ferromagnetic transition taking place close to the low-temperature upturn in the resistivity. The results can be displayed in a more illustrative fashion as $\Delta\sigma$ vs T in a log-log scale (inset of Fig. 2), where $\Delta\sigma = \sigma - \sigma_0$ is the correction to the conductivity coming from interaction and localization effects. Note how the $T^{1/2}$ term is clearly dominant below $T \sim 20$ K for the irradiated sample (inset of Fig. 2). This behavior is similar to that observed in amorphous metallic glasses, like $Cu_{50}Zr_{50}$ and $Cu_{50}Ti_{50}$.[18,19] For other systems that display the effects of e^--e^- interaction on their electrical transport properties, as heavily doped semiconductors,[20] this $T^{1/2}$ term is usually dominant only below 1 K. This points to an enhanced e^--e^- interaction in irradiated $SrRuO_3$. In metallic glasses, for instance, the maximum value of $\Delta\sigma$ is about 1% of the residual conductivity σ_0, whereas in our irradiated sample it attains values even higher than 10%. The results of measurements performed with applied magnetic fields of 30 and 70 kOe (not shown) indicate a small (~1%) and negative magnetoresistivity. An analogous temperature dependence of the conductivity is observed, with fits to expression (1) that render coefficient values very similar to those of zero-field measurements. The magnitude and the sign of this magnetic field effect are reasonable if the correction to the electrical conductivity is dominated by the localization and interaction contributions.[3,12]

A similar temperature dependence of the conductivity is observed for the ferromagnetic fresh samples (see Fig. 3). These films display much better metallicity than the irradiated samples, as the lower value of the room-temperature resistivity and the overall shape of the $\rho(T)$ curve clearly indicate. Below $T \sim 20$ K the resistivity shows an upturn that reflects the effect of weak localization and e^--e^- interaction. These upturns are a ubiquitous low-temperature feature of $SrRuO_3$ thin films.[10] The lower relative value of these two contributions to the resistivity, the experimental uncertainty of the data around the lambda point of ^{4}He, and the restriction imposed by our base temperature limit of 1.5 K make a fit to Eq. (1) more difficult than in the other sample. This can be perceived in the higher relative errors in the three parameters of the fit, especially in the weak localization coefficient B: $\sigma_0 = 2545 \pm 4$ $(\Omega\,\mathrm{cm})^{-1}$, $m = 35.1 \pm 3.4$ $(\Omega\,\mathrm{cm\,K}^{1/2})^{-1}$, $B = -0.7 \pm 0.7$ $(\Omega\,\mathrm{cm\,K})^{-1}$. In spite of this, the low-temperature data ($T < 10$ K) also follows rather well a $T^{1/2}$ temperature dependence, as it is shown when we plot $\ln(\Delta\sigma)$ vs $\ln(T)$ (inset to Fig. 3). We want to point out that other virgin samples that display slightly better metallic properties show also similar upturns, but at temperatures too low for obtaining fits to expression (1) of comparable goodness to those presented above.

As it was pointed out in our previous work,[11] ion irradiation has a destructive effect on the ferromagnetic ordering in thin-film samples of $SrRuO_3$. The progressive depression of T_c with increasing He^+ dose correlates with an expansion of the pseudocubic lattice constant c. At the same time, significant changes have to occur at the Fermi level due both to (a) the decreasing overlap of the Ru orbitals and (b) the enhanced disorder. Both of them conspire to enhance both the localization term ($\sim 1/N(E_F)$) and the Altshuler-Aronov correction to the electrical conductivity.[3,4,12] Thus, the results presented in this work can be interpreted in terms of electron localization plus e^--e^- interaction *in both virgin and irradiated films*, because we observe quantum corrections to the conductivity for the $SrRuO_3$ films studied. The experimental values of the electrical resistivity indicate that the electronic mean-free path l is clearly approaching the limit $l \sim 1/k_F$. Using the values of Fermi energy E_F ($E_F = 3.5$ eV) and carrier concentration ($n = 2 \times 10^{22}/\mathrm{cm}^3$) previously reported for $SrRuO_3$ (Refs. 8 and 20–22), we estimate the room-temperature value of l to be about 3 A and $k_F l \sim 2.5$ for our more metallic sample ($\rho(300\,\mathrm{K}) \sim 400\ \mu\Omega$ cm). As we expect that ion irradiation must reduce the mean free path, we infer that $k_F l \leqslant O(1)$ for sample (a) ($\rho(300$ K) $\sim 1000\ \mu\Omega$ cm). As a matter of fact, irradiation doses in excess of $10^{15}\,\mathrm{cm}^{-2}$ correspond to more than one ion impact per unit cell on the surface. In principle, that would be consistent with a density of point defects resulting in mean free paths smaller than the interatomic distance. Considering the size of the pseudocubic lattice as a typical interatomic distance a we have estimated the resistivity corresponding to the Ioffe-Regel limit[3] ($\rho_{IR} = 3\hbar a/e^2$) for our samples to be around 500 $\mu\Omega$ cm. Our experimental results indicate that the change of regime of the high-temperature resistivity of our films from positive to negative values of $d\rho/dT$ in the whole temperature range takes place not far from this limit (around 700 $\mu\Omega$ cm). This observation is strongly reminiscent of the ''saturation'' and breakdown of Matthiessen's rule observed in $A15$ compounds and other disordered intermetallic materials, in this case for resistivity values about 150–200 $\mu\Omega$ cm (Ref. 4, 23, and 24). In the case of irradiated and virgin $SrRuO_3$ it is very likely that this ''saturation'' takes place at higher resistivity values due to the lower carrier density typical of conducting oxides.[25] Therefore, in our samples, the carriers seem to be suffering the effects of localization, although the films are still barely ''metallic.'' Our results suggest that ion irradiation produces an enhancement of disorder, which triggers a metal-insulator transition. This increasing degree of disorder is reflected in the localization and interaction effects at low temperature reported in this work. The large electron-electron interaction term in the conductivity, which can be observed even at relatively high temperature in the irradiated sample, appears as a consequence of the enhancement of e^--e^- interaction in poorly

conducting materials, and is an indication of the relevance of electron correaltions in $SrRuO_3$.

Our results show also that the resistivity minima observed even in the best conducting samples of $SrRuO_3$ are definitely correlated with nonmagnetic disorder. As the irradiation dose is increased, those resistivity minima move to higher temperatures, while magnetic order is dramatically weakened. The fact that we observe similar behavior for both magnetic and nonmagnetic samples makes a magnetic origin of the upturn in the electrical resistivity very unlikely. Alternative descriptions in terms of other mechanism, like the Kondo effect,[10] are not justified. Contrary to this, we believe that the low-temperature rise of the resistivity is a genuine reflection of the intrinsic tendency to become localized of the electron states in $SrRuO_3$. As we have already pointed out, the scenario is, to some extent, similar to that of amorphous metals, where localization and interaction effects are known to give rise to low-temperature corrections to the electrical conductivity and ''saturation'' effects in the high-temperature electrical resistivity.

CONCLUSIONS

The low-temperature electrical resistivity of irradiated and virgin thin-film samples of $SrRuO_3$ shows clear evidence of weak localization and electron interaction effects. This makes unlikely a magnetic origin for the low-temperature upturn observed in the electrical resistivity of both samples. The magnitude of the interaction term is evidence of the importance of electron correlations in this system. From our experimental results, we conclude that the crossover from *metallic* to an incipient *nonmetallic* behavior takes place for resistivity values close to the Ioffe-Regel limit, in agreement with an interpretation in terms of quantum interference effects.

ACKNOWLEDGMENTS

This work was supported by Comisión Asesora de la Investigación Científica y Técnica through Projects Nos. MAT94-0604C0102 and Acción Especial MAT 17/95. Z.S. acknowledges financial support from Agencia Española de Cooperación Internacional (AECI).

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[1] V. J. Emery and S. A. Kivelson, Phys. Rev. Lett. **74**, 3253 (1995).
[2] P. B. Allen, H. Berger, O. Chauvet, L. Forro, T. Jarlborg, A. Junod, B. Revaz, and G. Santi, Phys. Rev. B **53**, 4393 (1996).
[3] N. F. Mott, *Conduction in Non-Crystalline Materials* (Oxford University, 1993).
[4] P. A. Lee and T. V. Ramakrishnan, Rev. Mod. Phys. **57**, 287 (1985).
[5] J. J. Randall and R. Ward, J. Am. Chem. Soc. **81**, 2629 (1959).
[6] R. J. Bouchard and J. L. Gilson, Mater. Res. Bull. **7**, 837 (1972).
[7] S. C. Gausepohl, M. Lee, R. A. Rao, and C. B. Eom, Phys. Rev. B **54**, 8996 (1996).
[8] L. Klein, J. S. Dodge, C. H. Ahn, G. J. Snyder, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, Phys. Rev. Lett. **77**, 2774 (1996).
[9] Cho, Q. X. Jia, X. D. Wu, S. R. Foltyn, and M. P. Maley, Phys. Rev. B **54**, 37 (1996).
[10] L. Klein, J. S. Dodge, C. H. Ahn, J. W. Reiner, L. Miéville, T. H. Geballe, M. R. Beasley, and A. Kapitulnik, J. Phys.: Condens. Matter **8**, 10 111 (1996).
[11] Z. Sefrioui, D. Arias, M. A. Navacerrada, M. Varela, G. Loos, M. Lucia, J. Santamaría, F. Sánchez-Quesada, and M. A. López de la Torre, Appl. Phys. Lett. **73**, 3375 (1998).
[12] B. L. Altshuler and A. G. Aronov, in *Electron-Electron Interactions in Disordered Systems*, edited by M. Pollak and A. L. Efros (North-Holland, Amsterdam, 1984).
[13] J. M. Valles, Jr., A. E. White, K. T. Short, R. C. Dynes, J. P. Garno, A. F. J. Levi, M. Anzlowar, and K. Baldwin, Phys. Rev. B **39**, 11 599 (1989).
[14] B. L. Altshuler and A. G. Aronov, Solid State Commun. **30**, 115 (1979).
[15] L. P. Gorkov, A. I. Larkin, and D. Khmelnitskii, Pis'ma Zh. Eksp. Teor. Fiz **30**, 248 (1979) [JETP Lett. **30**, 228 (1979)].
[16] D. J. Newson and M. Pepper, J. Phys. C **19**, 3983 (1986).
[17] Möbius, C. Frenzel, R. Thielsch, R. Rosenbaum, C. J. Adkins, M. Schreiber, H.-D. Bauer, R. Grötzschel, V. Hoffmann, T. Krieg, N. Matz, H. Vinzelberg, and M. Witcomb, Phys. Rev. B **60**, 14 209 (1999).
[18] M. A. Howson and D. Grieg, J. Phys. F: Met. Phys. **13**, L155 (1983).
[19] J. S. Dugdale, Contemp. Phys. **28**, 547 (1987).
[20] F. Rosenbaum, K. Andres, G. A. Thomas, and P. A. Lee, Phys. Rev. Lett. **46**, 568 (1981).
[21] M. Shikano, T-K. Huang, Y. Inaguma, M. Itoh, and T. Nakamura, Solid State Commun. **98**, 115 (1994).
[22] Z. Sefrioui *et al.* (unpublished).
[23] Z. Fisk and G. W. Webb, Phys. Rev. Lett. **36**, 1084 (1976).
[24] R. C. Dynes, J. M. Rowell, and P. H. Schmidt, in *Ternary Superconductors*, edited by G. K. Shenoy, B. D. Dunlap, and F. Y. Fradin (North-Holland, Amsterdam, 1981), p. 169.
[25] A. J. Millis, Jun Hu, and S. Das Sarma, Phys. Rev. Lett. **82**, 2354 (1999).