Metal–insulator transition in $SrRuO_3$ induced by ion irradiation

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We have studied the effect of He^+ irradiation on the electrical resistivity and Curie temperature of ferromagnetic $SrRuO_3$ thin films. An evolution from metallic to insulating behavior is observed when He^+ ion fluence is increased, suggesting a metal–insulator transition. Damage by ion irradiation produces a strong decrease of the Curie temperature. On the other hand, no significant change in T_c (~160 K) takes place in fresh samples grown at different substrate temperatures. We discuss the possible correlation between structural changes induced by irradiation, which reflect in an increase of the pseudocubic lattice parameter, and the observed depression of T_c. © *1998 American Institute of Physics.* [S0003-6951(98)03349-X]

$SrRuO_3$ is an orthorhombically distorted perovskite (space group Pbnm), and the only example of ferromagnetic ordering (with a Curie temperature T_c, of 165 K) in conducting $4d$ transition-metal oxides.[1,2] This compound has a $4d^4$ low spin configuration ($S=1$) and is believed to have a narrow π^* band resulting from Ru t_{2g} and O $2p$ orbitals, which governs magnetic ordering.[3,4] The actual nature of magnetism in this material, usually considered as an example of pure itinerant magnetism,[5] is not fully understood yet. This system can be included in the group of the so-called ''bad metals,''[5,6] strongly correlated electron systems showing remarkable electrical and magnetic properties. A common feature of these materials is the high value of their room-temperature electrical resistivities, close to the theoretical limit for the metallic state (Ioffe–Regel limit). From the point of view of possible technological applications, both the crystallographic structure (pseudocubic perovskite) and lattice parameters of this material, close to those of (YBCO), make it a promising candidate for the fabrication of (SNS) Josephson junctions of high-T_c superconducting oxides.[7] In addition, its conducting character makes it a suitable material for electrodes in other types of devices based on perovskite oxides, as epitaxial conducting oxide–ferroelectric or superconduction–ferroelectric heterostructures.[8]

Structural distortions are known to play a central role in the magnetic properties of $SrRuO_3$. The absence of ferromagnetic ordering in the isostructural $CaRuO_3$ has been explained in terms of a stronger orthorhombical distortion in this compound which changes the sign of the magnetic interaction.[9] Both hydrostatic and chemical pressure resulting from the partial substitution of Sr^{2+} (0.62 A) by the bigger Ca^{2+} (1.06 A) give rise to a decrease of the Curie temperature, but the system remains metallic. This has been explained in terms of the magnetism of this compound being very sensitive to the Ru–Ru distance.[10] On the other hand, substitution of Ru by Ti up to 20% rapidly reduces the critical temperature and causes an increase of the resistivity which undergoes a crossover from metallic to semiconducting behavior at low temperatures. Once again, this has been proposed to occur as a result of local structural distortions arising from substitution of Ti atoms in Ru sites.[11]

In the case of thin films, structural defects can be introduced during growth by acting on parameters like substrate temperature. With increasing substrate temperature, the thermal energy supplied to the incoming atoms allows them to arrange at more stable positions, which produces a more ordered film growth. Alternatively, defects can be created after film growth by electron or ion irradiation. Ion irradiation is known to produce local displacements of oxygen atoms in YBCO causing significant changes in resistivity and T_c.[12] In this letter we present results on the effect of growth temperature and ion irradiation on the electrical and magnetic properties of dc-sputtered $SrRuO_3$ thin films. We show that by increasing the irradiation dose, it is possible to tune the Curie temperature in a continuous manner up to the vicinity of the metal–insulator transition.

Samples 1000 A thick were grown from a $SrRuO_3$ target on (100)-oriented MgO substrates using a high-pressure dc sputtering system. Pure oxygen (3.6 mbar) was used as the discharge gas. Substrate temperatures were changed in the range from 700 to 875 °C. The films grew well textured, with the pseudocubic (001) direction perpendicular to the substrate. Clear kinks were observed in the resistivity showing the presence of the ferromagnetic transition at $T_c \sim 160$ K, confirmed by magnetization measurements performed with a Quantum Design superconducting quantum interference device magnetometer. Samples were irradiated with 80 keV He^+ at room temperature and doses ranging between 10^{14} and 5×10^{15} cm^{-2} at an angle 7° away from the substrate normal to avoid channeling. The projected ion range for He^+ -implanted ions was calculated to be 3274 Å using the SRIM 96 software, which guarantees that ions go through the film into the substrate.

The structure analysis of $SrRuO_3$ thin films was performed by x-ray diffraction (Siemens D5000) using Cu $K\alpha$

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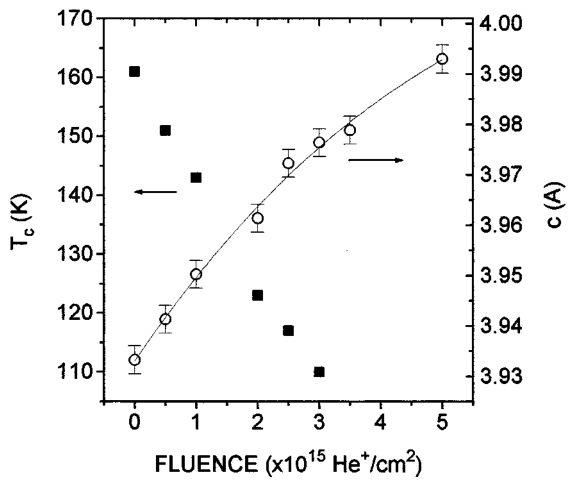

FIG. 1. Pseudocubic *c*-lattice parameter (open circles) and T_c (solid squares) vs 80 keV He-irradiation fluence. The solid line is a guide for the eye.

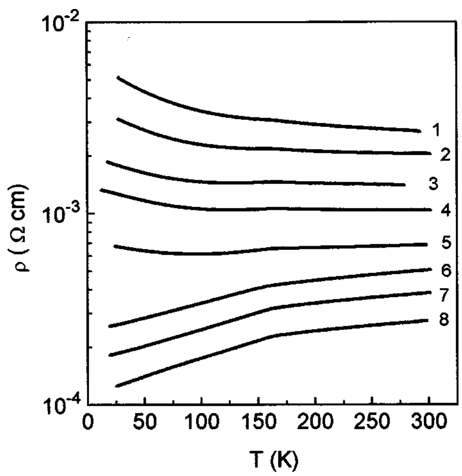

FIG. 3. Temperature dependence of the electrical resistivity of $SrRuO_3$ thin films grown at (1) 700, (2) 725, (3) 750, (4) 775, (5) 800, (6) 825, (7) 850, and (8) 875 °C.

radiation. Results on irradiated samples are shown in Fig. 1, which displays the evolution of the pseudocubic *c*-lattice parameter calculated from the angular position of the (00*l*) peaks as a function of dose. It is remarkable that the *c*-lattice parameter attains values as high as 3.99 A for the highest dose, similar to those recently reported as a result of energetic bombardment during growth for laser ablated films.[13]

Electrical resistivity characteristics as a function of temperature showed also significant changes for doses in excess of 10^{14} cm^{-2}. Figure 2 displays the electrical resistivity for various doses, showing how ion irradiation drives the samples to the vicinity of a metal–insulator transition. A decrease in the Curie temperature was observed for doses increasing up to 3×10^{15} cm^{-2} (Fig. 1).

At this point, it is worth comparing these results with those obtained on films grown at different substrate temperatures (Fig. 3). In this case, we observe similar effects on the electrical properties, i.e., an evolution of the system towards a nonmetallic state, but without any significant change either in the Curie temperature or in the lattice parameters (Fig. 4). This suggests that the Ru–O–Ru bond angles and Ru–Ru distance, and hence, the filling of the π^* band, remain unchanged. Thus, it seems that the effect of low-temperature growth in this material is only an enhancement of disorder, most likely due to a reduced crystalline quality related to the appearance of the high density of defects such as twins and domain boundaries, which reflect a decrease of the electronic mean-free path. The fact that the Curie temperature is found to be independent of the electrical properties indicates that the ferromagnetic interaction is not disturbed by the scattering mechanism responsible for carrier localization in these samples. This questions somewhat a *pure* itinerant model in this system.

It is tempting to conclude that irradiation induces structural effects that give rise to the changes both in the lattice parameters and the Curie temperature. The dependence of the Curie temperature on the lattice parameters points to a strain-induced depression of T_c, most likely due to distortion of the RuO_6 octahedra. As we have already pointed out, it is well known that the magnetic behavior of $SrRuO_3$ is very sensitive to the Ru–O–Ru distance and band angle: the magnetic properties of this compound are known to be determined by the filling and width of the narrow π^* conduction

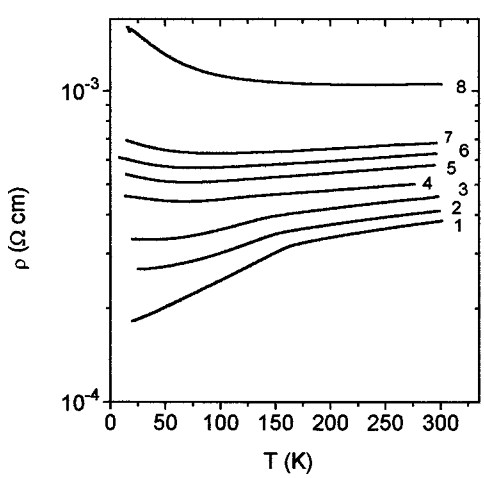

FIG. 2. Temperature dependence of the electrical resistivity of $SrRuO_3$ thin film grown at 850 °C, before (1) and after 80 keV He irradiation with doses: (2) $5\times10^{14}/cm^2$, (3) $1\times10^{15}/cm^2$, (4) $2\times10^{15}/cm^2$, (5) $2.5\times10^{15}/cm^2$, (6) $3\times10^{15}/cm^2$, (7) $3.5\times10^{15}/cm^2$, and (8) $5\times10^{15}/cm^2$.

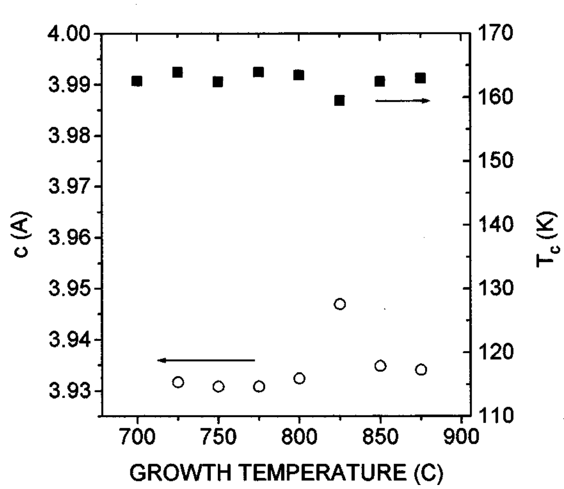

FIG. 4. Pseudocubic *c*-lattice parameter (open circles) and T_c (solid squares) as a function of growth temperature.

band resulting from the O2p–Ru4d overlapping orbitals. Irradiation could displace oxygen from its original sites to interstitial positions as discussed previously in other conducting perovskites.[12] This would have a twofold effect. First, vacancies would break the conduction path within the RuO_6 octahedra, responsible for the metallic properties, triggering a metal–insulator transition. And, as a second effect, Curie temperatures would decrease due to the disturbance of the Ru–O–Ru bonds and to the reduced overlap as a result of the enlarged c parameters. An explanation following the same line of reasoning has been proposed by Rao *et al.* to explain the $M-I$ transition in $CaRuO_3$.[14]

In summary, we have studied the evolution of $\rho(T)$ in thin films of $SrRuO_3$ grown on MgO when defects are systematically introduced by ion irradiation. We have observed that He^+ irradiation produces a controllable reduction of the Curie temperature, while we find a correlation between the pseudocubic lattice parameter and T_c. However, no significant change in T_c nor in the lattice parameters was observed in a series of films grown at different substrate temperatures. We conclude that irradiation produces a destructive effect on the ferromagnetism of $SrRuO_3$ thin films due to the distortion of RuO_6 octahedra. The results of magnetotransport measurements on these samples will help to understand how irradiation influences the electrical and magnetic properties of this system, and will be reported in due course.

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