Impurity-induced transition to a Mott insulator in Sr$_3$Ru$_2$O$_7$

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The electrical, magnetic, and structural properties of Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ (0 ≤ x ≤ 0.2) are investigated. The parent compound Sr$_3$Ru$_2$O$_7$ is a paramagnetic metal, critically close to magnetic order. We have found that, with a Ru-site doping by only a few percent of Mn, the ground state is switched from a paramagnetic metal to an antiferromagnetic insulator. Optical conductivity measurements show the opening of a gap as large as 0.1 eV, indicating that the metal-to-insulator transition is driven by the electron correlation. The complex low-temperature antiferromagnetic spin arrangement, reminiscent of those observed in some nickelates and manganites, suggests a long range orbital order.

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The Ruddelson-Popper-type Sr$_{n+1}$Ru$_n$O$_{3n+1}$ series show metallic properties, as well as exotic superconductivity and spin/orbital order. SrRuO$_3$ (n = ∞, perovskite) and Sr$_3$Ru$_2$O$_{10}$ (n = 3) are itinerant ferromagnets with Curie temperatures ($T_C$) around 160 K and 100 K respectively. In contrast, the single-layered Sr$_2$RuO$_4$ (n = 1) and double-layered Sr$_2$Ru$_2$O$_7$ (n = 2) do not show ferromagnetism (FM). Sr$_2$RuO$_4$ is a well known superconductor, which displays the unconventional spin-triplet pairing. Sr$_3$Ru$_2$O$_7$ (Ru$^{4+}$, 4d$^4$) is essentially paramagnetic although there is some controversy in the literature related to the presence of ferromagnetic SrRuO$_3$ and Sr$_3$Ru$_2$O$_7$ impurities. A metamagnetic transition is observed at low temperatures in large magnetic fields, indicating the presence of quantum criticality. Another signature of this phase competition is found in hydrostatic pressure experiments or Sr-site doping by Ca, which stabilizes the antiferromagnetic (AFM) state. In the case of Ca$_3$Ru$_2$O$_7$, which has a lattice structure closely related to that of Sr$_3$Ru$_2$O$_7$, the AFM ordering is observed at low temperature (~56 K). The system remains metallic below this temperature, but near 48 K, a first-order-like transition to a less conductive state is observed.

In this article, we investigate the effects of the Ru-site doping by Mn of Sr$_3$Ru$_2$O$_7$. A metal-to-insulator transition is observed as the Mn content increases. Optical conductivity measurements reveal the opening of a Mott-like gap. Neutron diffraction experiments show that the low temperature insulating state is associated with a novel antiferromagnetic spin arrangement, which suggests some complex orbital order. Interestingly, while there are many observations of insulator-to-metal transitions upon tuning of one-electron bandwidth or bandwidth filling by doping, there are few reports of the opposite, i.e. of the formation of a Mott-like insulating state upon addition of impurities in a metal. One example of such impurity doping effects is found in the Mott insulator V$_2$O$_3$. As V$^{3+}$ is replaced by Ti$^{3+}/4^{+}$, the system becomes metallic by modification of the band filling and/or bandwidth. However, the replacement of V$^{3+}$ by Cr$^{3+}$ instead strengthens the electron correlation (via modification of the lattice and hence the bandwidth), so that the metal-to-insulator transition occurs at higher temperatures than in the undoped compound. In the present case of Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$, the effect of the impurity doping is even more dramatic. A few percents of Mn yield a drastic phase change, turning the paramagnetic metal Sr$_3$Ru$_2$O$_7$ (x = 0) into an antiferromagnetic Mott insulator (x > 0.025).

Single crystals of Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ (x = 0, 0.005, 0.025, 0.05, 0.075, 0.1, and 0.2) were grown by the floating zone method. The Mn composition x was checked by inductively coupled plasma (ICP) analysis. X-ray diffraction and SQUID magnetometry reveal minor impurities of Sr$_2$RuO$_4$ and traces of the ferrimagnetic Sr$_4$Ru$_3$O$_{10}$. The crystals easily cleave along shiny ab-planes. The in-plane resistivity $\rho$ of the crystals was measured as a function of the temperature $T$ using a standard four-probe method on a PPMS6000 system. The temperature was recorded using a relaxation method from $T$ = 0.6 K to 100 K with the same measurement system. X-ray and neutron diffraction data were collected at selected temperatures with setups using closed cycle helium refrigerators, for the crystal with x = 0.05: The x-ray data was recorded on a Rigaku SPD curved imaging plate system by using Si(111)-double-crystal monochromated synchrotron radiation x-ray ($\lambda$ = 0.688 Å) at the beam.
line BL-1A of the Photon Factory, High-Energy Accelerator Research Organization (KEK), Japan. The cell parameters were calculated from the diffraction peaks of the x-ray oscillation photographs of the single crystal assuming a tetragonal (I4/mmm) symmetry in the whole temperature region.

The powder neutron diffraction patterns were collected using a time-of-flight (TOF) diffractometer Vega, KEK, Japan. The single crystal was pulverized for this purpose. The obtained powders were sealed with helium gas in a vanadium cell with a diameter of 9.2 mm. TOF diffraction patterns for a wide d-range (1 - 20 Å) were obtained at a 30-degree scattering bank. The optical conductivity spectra \( \sigma(\omega) \) of the crystal with \( x = 0.1 \) were measured at different temperatures. Near-normal-incidence reflectivity spectra \( R(\omega) \) were collected in the 0.05 - 3 eV energy range. Kramers-Kronig analysis was performed to derive \( \sigma(\omega) \) from the measured \( R(\omega) \).

![FIG. 1: (color online) Temperature T dependence of the resistivity \( \rho \) of \( \text{Sr}_3(\text{Ru}_{1−x}\text{Mn}_x)\text{O}_7 \) for different Mn doping \( x \). The electrical current was fed in the ab-plane, and in the experiments shown in the upper inset, a magnetic field of \( \mu_0 H = 9T \) was applied along the c-axis of the crystal with \( x = 0.05 \). The resistivity was recorded on cooling and heating, as indicated by the arrows. The lower inset shows the weaker effect of such a substitution in the case of single crystals of \( \text{Sr}_2(\text{Ru}_{1−x}\text{Mn}_x)\text{O}_4 \) (from Ref. 17) for comparison; this effect is as well weak in the case of \( \text{Sr}(\text{Ru}_{1−x}\text{Mn}_x)\text{O}_3 \) (see Ref. 18) for similar amounts of Mn.](image1)

The dramatic effect of the Mn doping on the electrical properties of \( \text{Sr}_3(\text{Ru}_{1−x}\text{Mn}_x)\text{O}_7 \) is shown in Fig. 1. While all the samples are metallic at room temperature, only the crystals with \( x \leq 0.025 \) remain metallic at low temperatures. In the low-temperature metallic regime, the residual resistivity increases with \( x \), indicating that Mn impurities act as scatterers. The crystals with \( x > 0.025 \) in contrast show a sharp increase in resistivity at low temperatures. These resistivity jumps are accompanied by an insulating behavior at lower temperatures. The resistivity is discernibly affected by the application of a magnetic field, as seen in the upper inset for \( x = 0.05 \). The resistivity increase due to the metal-insulator transition is shifted to lower temperature with an applied magnetic field. This suggests the antiferromagnetic nature of the lower-lying insulating state.

The optical conductivity \( \sigma(\omega) \) spectra are shown in Fig. 2 for the crystal with \( x = 0.1 \) at different temperatures. Above \( T = 80 \) K, the optical conductivity spectra show a broad peak in the mid-infrared region (\( \sim 0.2 \) eV), which is typical of the incoherent metallic state \([11]\) in the vicinity of the Mott transition \([10]\). While \( \sigma(\omega) \) shows a minimal temperature variation above \( 80 \) K, the spectral weight in the low energy region is steeply suppressed below \( T = 70 \) K, forming a gap-like structure. As a measure of the spectral weight, we utilize the effective number of electrons, defined as \( N_{eff}(\omega) = (2m_0)/(\pi\hbar^2N) \int_0^\infty \sigma(\omega')d\omega' \) \([11]\), where \( m_0 \) is the free electron mass and \( N \) is the number of Ru ions per unit volume. The different \( \sigma(\omega) \) curves shown in Fig. 2 define an isosbestic point (equal-absorption point, across which the spectral weights are transferred) near 0.24 eV, the typical energy scale of the Mott gap \([11]\). Thus, by

![FIG. 2: (color online) Optical conductivity \( \sigma(\omega) \) of \( \text{Sr}_3(\text{Ru}_{0.9}\text{Mn}_{0.1})\text{O}_7 \) \( (x=0.1) \) at selected temperatures. The sharp peaks near 0.08 eV correspond to optical phonons coupled with the electronic excitations. The inset shows the low-energy spectral weight \( N_{eff} \) (effective number of electrons) plotted as a function of the temperature, obtained by integration of \( \sigma(\omega) \) between 0.07 eV and 0.24 eV.](image2)
integrating \( \sigma(\omega) \) in the 0.07 eV < \( \hbar \omega \) < 0.24 eV energy range, we could estimate the low-energy spectral weight, as \( N_{\text{eff}}(0.07 \text{ eV} < \hbar \omega < 0.24 \text{ eV}) = N_{\text{eff}}(0.24 \text{ eV}) - N_{\text{eff}}(0.07 \text{ eV}) \). As seen in the temperature variation of \( N_{\text{eff}}(0.07 \text{ eV} < \hbar \omega < 0.24 \text{ eV}) \) shown in the inset of Fig. 3, the formation of a gap occurs between \( T = 60 \) and 80 K, in the vicinity of the resistivity-jump temperature (near \( T = 78 \text{ K} \) for the crystal with \( x = 0.1 \), see Fig. 4). The Mn impurities increase the disorder. However, this large energy-scale (\( \sim 0.2 \text{ eV} \)) gap formation cannot be explained by disorder-induced localization effects \( 13 \), as the typical energy scale of the Anderson localization is much smaller (\( < 10^{-2} \text{eV} \)). It is worth noting that such a large energy gap formation is observed in the optical spectra of \( \text{Ca}_2\text{RuO}_4 \) \( 14 \) and other Mott insulators \( 11 \).

![Graph](image)

**FIG. 3:** (color online) Temperature dependence of different physical properties of \( \text{Sr}_3(\text{Ru}_{0.95}\text{Mn}_{0.05})_2\text{O}_7 \) (\( x = 0.05 \)). Upper panel: heat capacity \( C \) plotted as \( C/T \) (left axis); the resistivity (\( \rho \)) data from Fig. 1 is added for comparison (right axis). The inset of this panel shows the corresponding data for the crystals with \( x = 0.075 \) and \( x = 0.1 \). Middle panel: intensity of the \( (1/4,1/4,0) \) and \( (1/4,3/4,0) \) magnetic peaks observed in neutrons diffractograms, as shown in the inset. Lower panel: tetragonal \( a \)– and \( c \)-axis lattice parameters obtained from x-ray diffraction.

We now investigate the magnetic and structural properties of the insulating state of the crystals with \( x \geq 0.05 \). We display in Fig. 3 the temperature dependence of various physical properties of the system. The low-temperature heat capacity \( C \) data of the crystals with \( x \geq 0.05 \) (plotted as \( C/T \)) shown in the upper panel and inset of Fig. 3 could be fitted with the contributions of conduction electrons (the \( T \)-linear coefficient \( \gamma \) shows a weak sample dependence and amounts to \( 50 \pm 5 \text{ mJ/mol/K}^2 \)) and phonon modes (the \( T^3 \)-linear coefficient \( \beta \sim 1 \pm 0.2 \text{ mJ/mol/K}^3 \)). The fit is slightly improved introducing a \( T^2 \)-linear contribution, which may reflect a magnetic contribution to the heat capacity. More importantly, for the crystals with \( x = 0.05 \) (main frame), and \( x > 0.05 \) (inset), a peak is observed in the heat capacity in the vicinity of the resistivity jump temperature. In comparison, the heat capacity of the undoped compound (which remains a metal down to the lowest temperature) show no anomaly\( 8 \). By integrating the data of the Mn-doped crystals after subtraction of a certain baseline, an entropy change associated with the transition \( \Delta S \sim 0.45 \pm 0.05 \text{ R} \) could be estimated, implying the relevance of the spin entropy. This is confirmed by neutron diffraction experiments. As shown in the middle panel of Fig. 3, the magnetic peaks corresponding to AFM ordering show up below the metal-to-insulator transition temperature.

Furthermore, x-ray diffraction measurements show that around the same temperature the \( c \)-axis lattice parameter decreases, as seen in the lower panel of Fig. 3 for \( x = 0.05 \). This may indicate that the RuO\(_6\) octahedra are compressed along the \( c \)-axis, in a Jahn-Teller like fashion, or that the buckling of the octahedra occurs. The electrical and magnetic properties of ruthenates are usually associated with the \( 4d \) orbitals of Ru, and their hybridization with the \( 2p \) orbitals of oxygen. In \( \text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7 \), Ru\(^{4+}\) is in the \( S = 1 \) low spin state, so that the \( e_g \) levels are empty, and only the \( t_{2g} \) orbitals \( d_{xy} \), \( d_{yz} \), and \( d_{zx} \) are partially filled. Structural modifications such as distortions of the RuO\(_6\) octahedra yield changes in the relative energy of the \( t_{2g} \) orbitals \( 15 \), and hence in the magnetic interaction. The high-temperature metallic state of \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) was related to the predominant role of the \( d_{xy} \) orbitals \( 6 \). The low-temperature insulating state was then associated to the increased contribution of the \( d_{yz} \) and \( d_{zx} \) orbitals promoted by lattice changes. However, the contraction of the \( c \)-axis observed by x-ray diffraction in \( \text{Ca}_3\text{Ru}_2\text{O}_7 \), \( 16 \), and in our \( \text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7 \) (c.f. Fig. 3) amounts merely to \( \sim 0.1 \% \), which is one order of magnitude lower than observed in systems with ferroic \( d_{xy} \) orbital ordering such as \( \text{Ca}_2\text{RuO}_4 \) \( 14 \).

The measurement of the temperature dependence of various physical properties of \( \text{Sr}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7 \) enables us to draw the schematic electronic phase diagram shown in Fig. 4, which defines the phase boundary between the paramagnetic metal (PM) and the antiferromagnetic insulator (AFI). Antiferromagnetic peaks appear in neutron diffractograms at the metal-to-insulator transition.
FIG. 4: (color online) Electronic phase diagram showing the phase boundary between the paramagnetic metal (PM) and antiferromagnetic insulator (AFI) regions. The boundary is plotted using transport data from Fig. 1. A schematic view of the most probable magnetic arrangement in the ab-plane is shown in the inset using the neutron diffraction data collected for $x = 0.05$ (another possible AFM structure is the same up-up-down-down arrangement with spins parallel to the c-axis).

transition temperatures (no additional peaks appear in the high-Q region, nor $(n/2 1/4 0)$ peaks). The most probable magnetic arrangement in the ab-plane is an up-up-down-down arrangement (with spins in the ab-plane or parallel to the c-axis) with the magnetic wave vector of $(1/4 1/4 0)$, although this has to be confirmed by a thorough diffraction study. This spin arrangement is reminiscent of the zigzag chains of the E-type structure observed at low temperatures in manganites with significant GdFeO$_3$-type distortion such as HoMnO$_3$, as well as in (Nd/Pr)NiO$_3$ nickelates. In RMnO$_3$ (R being a rare earth ion), the amount of GdFeO$_3$-type distortion determines the strength of the superexchange interaction between Mn next-nearest-neighbors. For small R ions, like Ho, the large superexchange interaction, coupled to the orbital order, yields the spin frustration and the appearance of the E-type antiferromagnetic state. Hence the complex magnetic structure of Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ with $x > 0.025$ may reflect some long-range order in the orbital sector. The c-axis contraction observed in the vicinity of the resistivity jumps is similar to that observed in Ca$_3$Ru$_2$O$_7$, as well as in Ca$_2-x$Sr$_x$RuO$_4$ ($0.2 < x < 0.5$, so called “Phase II”) which displays a complex orbital order. However, the low temperature insulating AFM state of Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ ($x \geq 0.05$) does not result from such structural distortions as in the less conductive/two-dimensional metallic state of Ca$_3$Ru$_2$O$_7$ or Ca-rich (Sr,Ca)$_3$Ru$_2$O$_7$ but from the local modification of the orbital states induced by the Mn impurities.

In summary, the physical properties of single crystals of the Sr$_3$(Ru$_{1-x}$Mn$_x$)$_2$O$_7$ ($0 \leq x \leq 0.2$) system have been investigated. A metal-to-insulator transition, associated with the formation of a large charge gap ($\sim 0.1$ eV), is observed as the Mn concentration $x$ increases. The closely correlated temperature-dependence of various physical quantities suggests a tight coupling of the lattice, orbital and spin degrees of freedom. Interestingly, the low-temperature insulating state shows a complex antiferromagnetic spin structure, which suggests some long-range order in $t_{2g}$ orbital sector. The results illustrate how the impurity doping (substituting only a few percents of Ru) allows the phase control of the multicritical layered ruthenates. We thank Professors T. Ishigaki and T. Kamiyama for their help with the neutron diffraction measurements.

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