Weak ferromagnetism, metal-to-nonmetal transition, and negative differential resistivity in single-crystal Sr$_2$IrO$_4$

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Sr$_2$IrO$_4$ has the K$_2$NiF$_4$ structure and its Ir^{4+} ion ($5d^5$) is in a low spin configuration t_{2g}^5 with $S = \frac{1}{2}$. In this paper, we report results of our study on single-crystal Sr$_2$IrO$_4$. Magnetic susceptibility and isothermal magnetization display weak ferromagnetism below 240 K with an easy axis along the a axis and a spin reorientation transition in low magnetic fields. Both the effective paramagnetic moment μ_{eff} ($= 0.5\mu_B$) and the saturation moment μ_S($= 0.14\mu_B$) are found to be quite small, but the ratio of μ_{eff}/μ_S ($= 3.5$) qualitatively fits the Rhodes-Wohlfarth plot. Resistivity, $\rho(T)$, along two principal crystallographic directions is strongly anisotropic and shows a metallic behavior below 120 K. Sr$_2$IrO$_4$ exhibits strikingly nonlinear conductivity, i.e., a current-controlled negative differential resistivity for $2 \leq T < 300$ K. The origin of the nonohmic behavior may be associated with charge-density-wave depinning. Unlike other systems such as ruthenates Sr$_2$IrO$_4$ appears to show no correlation between conductivity and magnetism. [S0163-1829(98)51118-6]

One of the unique features of $4d$ and $5d$ transition metal oxides is the large spatial extent of d-electron orbitals. These extended orbitals enhance bonding interactions between transition metal and oxygen, leading to enhanced d-p hybridization, which, in turn, alter the metal-oxygen bonding length and angle and very often result in narrow d bands. This feature makes the $4d$ and $5d$ systems characteristically sensitive to intraband electron-electron or electron-phonon interactions, and, in most cases, leads to interesting phenomena. This point is well illustrated in this study as well as in recent studies on $4d$-based ruthenates, whose behavior represents a departure from $3d$-electron-based materials.[1,2]

Sr$_2$IrO$_4$ is a $5d$-based layered compound with the K$_2$NiF$_4$ structure similar to the first cuprate superconductor (La,Ba)$_2$CuO$_4$ and the noncuprate superconductor Sr$_2$RuO$_4$.[3–7] The space-group symmetry is found to be reduced to $I4_1/acd$ from $I4/mmm$ due to a rotation of the IrO$_6$ octahedra about the c axis by 11°.[4,5] As expected for most $4d$ and $5d$ compounds, the Ir^{4+} ions are presumed to be in the low spin state $^2T_{2g}$ with the degenerate d_{xz} and d_{yz} orbitals and an excited d_{xy} orbital (due to the elongated Ir-O bond along z direction) since crystal-field splittings are large and electron repulsion effects are small for extended orbitals. Thus the exchange terms favoring parallel spin configurations are negligible. With the half filled d_{xy} orbital, Sr$_2$IrO$_4$ is in the $S = \frac{1}{2}$ ground state.

Although Sr$_2$IrO$_4$ was first synthesized more than forty years ago, only recently have there been a handful of reported studies driven partially by an attempt to search for properties analogous to those in La$_2$CuO$_4$.[4] Based on these studies on *polycrystalline* Sr$_2$IrO$_4$,[4–7] there are two major features: (1) it is insulating; (2) it shows ferromagnetic ordering in the vicinity of 240 K with a nearly negligible ferromagnetic moment ($0.023\mu_B$/Ir) compared to $1\mu_B$ expected for $S = \frac{1}{2}$.

In this paper, we report results of magnetic and transport properties obtained from single-crystal Sr$_2$IrO$_4$. While our data show a magnetic ordering at $T_M = 240$ K consistent with that reported for polycrystalline samples, many unusual properties that are conspicuously absent in polycrystalline Sr$_2$IrO$_4$ have been observed: The system reveals nontrivial conducting behavior, i.e., the system undergoes a transition from a nonmetallic state ($d\rho/dT < 0$) at high temperatures to a metal-like state ($d\rho/dT > 0$) at low temperatures (ab-plane). $\rho(T)$ fits a three-dimensional variable range hopping model for $190 \leq T \leq 300$ K; furthermore, the resistivity is found to be strongly dependent on applied currents, indicating nonohmic behavior for $1.5 < T \leq 300$ K; the current-voltage characteristics exhibit current controlled negative differential resistivity (NDR) throughout the temperature range measured. This behavior is seen in both the a and c axes although the resistivity is highly anisotropic. A collective charge transport mode typical of the charge density wave (CDW) is suggested to account for such behavior. In addition, isothermal magnetization indicates an easy axis along the a axis and a sharp spin reorientation transition in low magnetic fields. Both the effective paramagnetic moment μ_{eff}($= 0.5\mu_B$) and the saturation moment μ_S ($= 0.14\mu_B$) are found to be substantially smaller than expected for a $S = \frac{1}{2}$ system, and the ratio of μ_{eff}/μ_S ($= 3.5$) qualitatively fits the Rhodes-Wohlfarth plot, implying an electronic state (Stoner model) intermediate between a ferromagnetic insulating state and a paramagnetic metallic state.

Single crystals were grown in Pt crucibles using flux techniques from off-stoichiometric quantities of IrO$_2$ or Ir, SrCO$_3$, and SrCl$_2$. Details are described elsewhere.[2] The resulting shapes of Sr$_2$IrO$_4$ tend to be platelike with an average size of the single crystals being $1 \times 1 \times 0.5$ mm^3 with the c axes along the shortest dimension. Results of EDX indicate that the ratio of Sr and Ir is 2:1 and uniformly distributed.
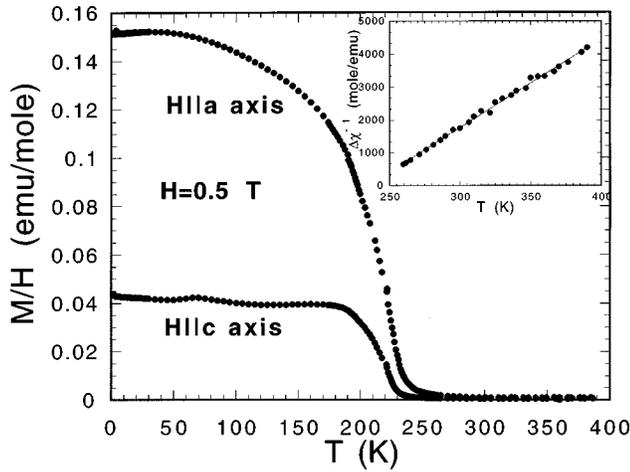
FIG. 1. Magnetic susceptibility M/H vs temperature at $H=0.5$ T for the two principle crystallographic directions. Inset: $\Delta\chi^{-1}$ vs temperature at $T>T_M$ where $\Delta\chi=\chi(T)-\chi_o$.

FIG. 2. Isothermal magnetization M vs magnetic field H at $T=5$ K for the two principle crystallographic directions. Inset: Isothermal magnetization $M(T=5$ K$)$ along the a axis vs magnetic field H for $-0.5\leqslant H\leqslant0.5$ T.

Results of x-ray-diffraction patterns from powdered Sr_2IrO_4 single crystals show no impurity peaks. The refinement of a tetragonal cell yielded $a=5.494$ A and $c=25.796$ A, consistent with those published.[4]

Shown in Fig. 1 is the temperature dependence of the magnetic susceptibility $\chi(T)$ of Sr_2IrO_4 along the two principal crystallographic directions in a field cooled sequence (FC) with $H=0.5$ T (for $T>T_M$, the magnetic ordering temperature, we determined that a field of 0.5 T was low enough to define ''zero field'' susceptibility). The evidence for weak ferromagnetism in the vicinity of $T_M=240$ K is obvious for both directions. The large anisotropy of the magnetic susceptibility clearly indicates that the easy axis is aligned with the a axis.

Fitting to a modified Curie-Weiss law for $T>T_M$ yields the following parameters (see the inset in Fig. 1): The temperature-independent susceptibility $\chi_o=8.8\times10^{-4}$ emu/mole, the Curie-Weiss temperature $\theta_{cw}=251$ K and effective paramagnetic moment $\mu_{eff}=0.50$ μ_B/Ir. θ_{cw} is comparable to the magnetic ordering temperature, and suggestive of a ferromagnetic spin coupling, but μ_{eff} is significantly lower than the Hund's-rule value $1.7\mu_B$/Ir for $S=\frac{1}{2}$. This reduction may indicate a strong hybridization between Ir ions and oxygen.[8] χ_o is relatively large compared to those for ordinary metals, but the low-temperature specific heat coefficient γ is found to be nearly zero (<0.2 mJ/mol K^2). This behavior is characteristic of the Stoner enhancement where χ_o is significantly enhanced, but γ has no equivalent enhancement. In oxides with a narrow band such as in $LaNiO_3$ and $LaCuO_3$, the exchange interaction is commonly enhanced by spin fluctuations and thus drives the paramagnetic state unstable, leading to a nearly ferromagnetic state. The magnetic properties observed in Sr_2IrO_4 appear to be consistent with this contention.

Shown in Fig. 2 is isothermal magnetization M at $T=5$ K in fields to 7 T for the two principal crystallographic directions. The large magnetic anisotropy between the directions is apparent, and the easy axis is evidently along the a axis consistent with Fig. 1. $M(H)$ at $H>0.5$ T appears to be nearly saturated below T_M, however, the saturation moment μ_S extrapolated is $0.14\mu_B$/Ir, only 14% of the expected spin-

only moment of $1\mu_B$/Ir which would be increased by any orbital contribution ($J=L+S$). There are a number of ways in which such a reduced moment may arise, including spin canting, as asserted in Ref. 4. However, Sr_2IrO_4 may be a band ferromagnet with low-density of charge carriers because the system appears itinerant ($\mu_{eff}/\mu_S>1$, and $d\rho/dT>0$ though the magnitude of ρ is large at low temperatures). If so, the density of states becomes spontaneously exchange split. As a result, there is an excess of electrons with spin up (majority-spin band) as compared to those with spin down (minority-spin band). The net overall magnetic moment then is largely determined by the exchange splitting of the $5d$ electrons and is necessarily nonintegral. The observed low moment reflects a small exchange splitting or unequal population of the two subbands. A larger t_{2g} band compared to a small exchange splitting may also result in a small polarization of d electrons. Yet it cannot be ruled out that the reduced moment may result from hybridization between Ir ions and oxygen which is presumably strong in $4d$ and $5d$ compounds such as Sr_2IrO_4. Measurements of magnetization up to 30 T are planned to search for possible high-field spin reorientations. A low-field spin reorientation is observed, and is clearly evidenced in the inset of Fig. 2 where $M(T=5$ K$)$ for the a axis vs H is plotted for $-0.5\leqslant H\leqslant0.5$ T. The mirror image, typical of a spin reorientation transition, illustrates the presence of such a transition at $H_{sr}=0.2$ T. This spin reorientation transition also takes place along the ''hard'' axis, the c axis, at a higher field (see Fig. 2). It is possible that such a transition in the weak ferromagnet is due to the strong electron-lattice coupling, i.e., the interplay between the magnetic energy and the elastic energy,[10] which is related to the change in volume at low temperatures reported in Ref. 4.

It is also remarkable that the ratio of μ_{eff}/μ_S ($=3.5$) qualitatively fits the Rhodes-Wohlfarth plot, μ_{eff}/μ_S vs T_C, yielding a corresponding T_C near 200 K.[9] This qualitative agreement indicates that spin fluctuations may be significant, and that Sr_2IrO_4 is in an intermediate region (which may be described by the Stoner model) between a ferromagnetic in-
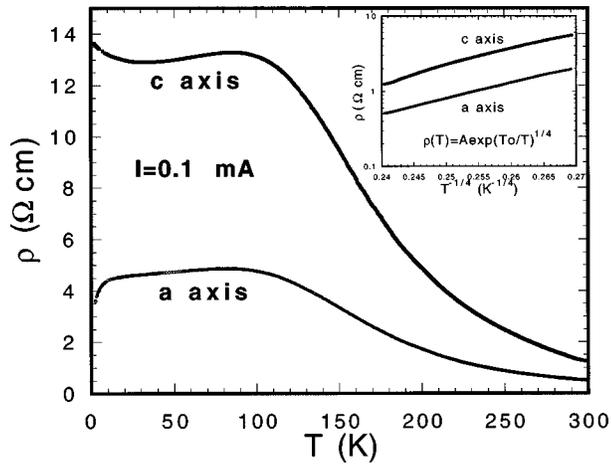
FIG. 3. Resistivity $\rho(T)$ vs temperature for the two principle crystallographic directions at $I=0.1$ mA. Inset: Fit of $\rho(T)$ to the $3d$ variable range hopping for $190 \leqslant T \leqslant 300$ K.

FIG. 4. Current I vs voltage V for various temperatures. Inset: $\rho(T)$ along the a axis vs temperature for various currents.

sulating state ($\mu_{\text{eff}}/\mu_S=1$) and a paramagnetic metallic state ($\mu_{\text{eff}}/\mu_S=$infinity). This point is supported by the following transport properties.

Shown in Fig. 3 is resistivity ρ at 0.1 mA as a function of temperature for the a and c axis. The anisotropy between the two directions is significant ($\rho_c/\rho_a=3$ and 5.6 for $T=295$ K and 2 K, respectively). In this compound, the Arrhenius law is not well obeyed, i.e., $\rho(T)$ could not be fit successfully to an activation energy. However, the temperature dependence of resistivity along the a axis is found to obey a law of the form $\rho=A \exp(T_o/T)^\nu$ with $\nu=\frac{1}{4}$ being slightly favored over $\nu=\frac{1}{2}$ for $190 \leqslant T \leqslant 300$ K (see the inset in Fig. 3; we note that the fitting range is relatively narrow). While both the $T^{-1/2}$ and $T^{-1/4}$ dependences are thought to be associated with the three-dimensional variable-range hopping (VRH) of carriers between states localized by disorder, the weaker temperature dependence $T^{-1/4}$ implies negligible long-range Coulomb repulsions between electrons in this temperature region. As T decreases, $\rho(T,\ a$ axis) shows a plateau, which is followed by a rapid drop below 20 K. The broad transition is possibly caused by a gradual change in disorder which dominates $\rho(T)$ in high temperatures (see the inset in Fig. 3) and becomes weaker at low temperatures, thus delocalizing more electrons. $\rho(T)$ along the c axis cannot be fit to any existing models at high temperatures (see the inset) and shows an even broader transition below 120 K. (At higher currents I, $\rho(T)$ along the c axis does as well show a down turn at $T<20$ K. This will be further discussed below.) No corresponding anomaly is discerned in $\rho(T)$ near $T_M=240$ K, suggesting a negligible contribution from spin scattering to the overall resistivity. Associated with this, magnetoresistivity in magnetic fields up to 12 T is found to be insignificant. Such a weak spin-charge coupling may not be unexpected considering the small saturation moment observed. This behavior is also found in the antiferromagnetic insulator Ca_2RuO_4 whose resistivity is well described by the VRH with $\nu=\frac{1}{2}$ (Ref. 11) although for most of the ruthenates, transport properties are intimately associated with magnetic properties.[2]

Another major feature in this system is the nonohmic behavior which exhibits current-controlled negative differential resistivity (NDR) for both the a and c axis directions. In the inset of Fig. 4, $\rho(T)$ for the a axis is shown for a few representative applied currents I. $\rho(T)$ is clearly current dependent and drastically decreases as I increases throughout the temperature range measured. For example, at $T=100$ K, the ratio of the decrease in $\rho(T)$, $[\rho(1 \text{ mA})-\rho(60 \text{ mA})]/\rho(1 \text{ mA})$ $=80\%$. It is noted that $\rho(T)$ shows a noisy yet well defined peak near 50 K for $I=40$ mA, signaling the existence of a metastable state near which the transition occurs, consistent with Fig. 4. The nonohmic behavior is apparently intrinsic, given the fact that the resistivity in low temperatures is still smaller than that at much higher temperatures [e.g., $\rho(10$ K$)<\rho(130$ K$)$]. Should it be a heating effect, $\rho(T)$, particularly at higher current, would be expected to show a plateau or an up turn rather than a sharp drop at low temperatures. The nonlinear characteristic persists up to room temperature and is more dramatically demonstrated in Fig. 4 where the dc I-V curves for the a axis are presented for various temperatures. As seen, the initial linear I-V response is followed by an apparent threshold voltage V_{th} above which the voltage across the sample V abruptly drops as I increases, resulting in the NDR. The I-V curve near V_{th} for all temperatures shows a hysteresis effect typical of the first-order transition. As the current increases further (much higher than 100 mA in this case), the ohmic behavior will be restored, giving rise to an I-V curve characterized by an ''S'' shape. The S-shaped effect is categorically different from the more commonly seen ''N''-shaped effect or the Gunn effect, which is referred to as voltage-controlled NDR and attributed to electrons transferred between multienergy valleys.[12]

It has been reported previously that the S-shaped effect is observed in some materials with a metal-insulation transition such as $CuIr_2S_{4-x}Se_x$.[13] This effect is, however, restricted only to the insulating phase, and is attributed to an electrothermal effect.[13] The similar I-V characteristic has been found earlier in a layered $Ca_3Ru_2O_7$.[14] Given the low dimensionality and the negligibly small γ which may be a reflection of a band gap associated with the CDW, the S effect observed here may be driven by collective dynamics in the presence of disorder commonly seen in the CDW state.[15] It is plausible that in this material the CDW is pinned to the un-

derlying lattice at $V < V_{th}$, and depinned and slides relative to the lattice, giving rise to the NDR at $V > V_{th}$. Accordingly, there may be a two-band model where the normal electrons and electrons in the CDW provide separate and independent channels for the conduction process.

Given the large extended $5d$ orbitals, the localized behavior observed seems to be surprising. However, in $4d$ or $5d$ systems close to the Mott transition borderline, the electronic properties depend in an extremely sensitive way on structural changes (e.g., the bond length or the bond angle) which, in turn, determines the band filling and the bandwidth. It is quite plausible that in Sr_2IrO_4 where the Ir-O-Ir angle is found to be severely distorted from the ideal angle of 180° to 157°,[4] the structural distortion causes narrowing of the t_{2g} bands which would otherwise be much wider. The distinct behavior displayed here largely deviates from that for the isostructural superconductors $(La,Ba)_2CuO_4$ and Sr_2RuO_4, and manifests the subtlety of electronic structures in the spatially extended $4d/5d$ electron systems.

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