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Anomalous low dimensional system: Study of magnetism and electrical conductivity in $Na_2Ru_4O_{9-\delta}$

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The magnetic susceptibility $\chi_\parallel(H\parallel b)$, $\chi_\perp(H\perp b)$ $(2\leqslant T\leqslant 700\ \mathrm{K})$ and electrical resistivity $\rho(T)$ $(2\leqslant T\leqslant 300\ \mathrm{K})$ of single crystal $Na_2Ru_4O_{9-\delta}$ $(\delta\geqslant 0)$ with various oxygen content were measured. The crystal structure of this compound is monoclinic with single, double, and triple chains along the b axis. The most striking feature of this compound is the drastically large anisotropy reflected in the resistivity which exhibits metallic behavior along chains and semiconducting behavior perpendicular to the chains. The resistivity ratio for these two directions $(\rho_\perp/\rho_\parallel)$ is larger than 10^5. This ratio is exceptionally large, indicating that the anisotropy of the bandwidth is substantial. It is remarkable that, after reduction of oxygen content in the system, the magnetic susceptibility undergoes a drastic change, whereas the electrical resistivity along the conducting chains is altered only slightly. It is argued that the different sensitivity to oxygen content reflected in magnetic and transport properties may be attributed to the complexity of the crystal structure. The striking observations presented here may suggest a one-dimensional system that possesses unique physical properties. © *1996 American Institute of Physics.* [S0021-8979(96)36008-6]

INTRODUCTION

The discovery of superconductivity in the cuprates has led to a resurgence of interest in the $3d$ transition-metal oxides. However, physical properties of the $4d$ and $5d$ metal oxides, though recently drawing moderate attention, remain largely unexplored. One class of these oxides is the ruthenium oxides which exhibit a rich variety of unusual magnetic behavior while also possessing rather high electrical conductivity. While exploring magnetic and electrical properties, looking, in part, for superconductivity in the oxides, we have found that $Na_2Ru_4O_9$ displays an anomalously large anisotropy in conductivity with metallic behavior in one direction and semiconducting behavior in others. In addition, the magnetic susceptibility parallel to the chains $\chi_\parallel$ has a maximum in the vicinity of 70 K with significant anisotropy in $\chi_\parallel$ and $\chi_\perp$ below the maximum. It is remarkable that, after reduction of oxygen content in the system, the maximum completely disappears, and $\chi(T)$ is radically changed, whereas the electrical resistivity along the b axis is altered only slightly.

EXPERIMENTAL

The crystal structure of $Na_2Ru_4O_9$ shown in Fig. 1[1] is monoclinic with $a=23.180$, $b=2.832$, $c=10.990$ A, $\beta=104.50°$, and space group $C2/m$.[1,2] The Ru_4O_9 network is formed by single, double, and triple chains of RuO_6 octahedra sharing edges. These chains share oxygen on the corner of the RuO_6 octahedra and run parallel to the shortest axis (b axis). The sodium ions are inserted in three different sites in the tunnels.[1] This compound is very stable in air. Additionally, the results of x-ray powder diffraction indicate that $Na_2Ru_4O_9$ can accommodate a relatively large oxygen deficiency without a breakdown of its crystal structure, however, the monoclinic structure appears to be unstable with small oxygen overdoping.

The starting materials were Na_2CO_3 and RuO_2 with purity of 99.9%. The single crystals of $Na_2Ru_4O_9$ were then grown out of a Na-rich flux, yielding needle-shaped crystals with the largest dimension along the b axis. The size of the average crystals is of $1.0\times 10\times 0.5\ \mathrm{mm}^3$. Deoxygenated $Na_2Ru_4O_{9-\delta}$ $(\delta>0)$ crystals were obtained by sealing as-grown crystals in evacuated quartz tubes which were then heated at 400–550 °C for 100 h. The crystal structure and lattice parameters obtained from powder x-ray diffraction patterns of both as-grown and deoxygenated single crystals were in excellent agreement with published data.[2] Scanning electron microscopy (SEM) and energy dispersive x-ray (EDX) were also performed on the single crystals, confirming that the crystals were of high quality. The electrical resistivity was measured using four standard probe techniques, and the magnetic susceptibility was measured using a superconducting quantum interference device (SQUID) magnetometer.

RESULTS AND DISCUSSION

Shown in Fig. 2 is the magnetic susceptibility $\chi_\parallel(H\parallel b)$ and $\chi_\perp(H\perp b)$ vs temperature for an as-grown crystal $Na_2Ru_4O_9$. A broad maximum occurs at 70 K. The orientation dependence of χ below the maximum seems to be attributed to the anisotropy of sublattice magnetization and would suggest an antiferromagnet. However, no anomaly in the vicinity of 70 K in specific heat is seen, implying that the maximum observed may not be associated with long range order. The low temperature Curie tail is somehow sample dependent, and probably an extrinsic effect. The magnetic susceptibility $\chi(T)$ well above the peak $(100\ \mathrm{K}<T<300\ \mathrm{K})$ indicates an extremely narrow electronic band and can be described by a modified Curie–Weiss law, i.e., $\chi=\chi_0+C/(T+\theta)$, where χ_0 is a temperature independent contribution to $\chi(T)$, C is the Curie constant, and θ is the Curie–Weiss temperature. Fitting $\chi(T)$ for $100\leqslant T\leqslant 300$ K to the Curie–Weiss law leads to the values of $\chi_0=7.92\times 10^{-4}$ and 1.06×10^{-3} emu/mol for $\chi_\parallel$ and $\chi_\perp$, respectively. These values are unusually large when compared to those typically reported for ordinary metals (10^{-5} emu/mol). Such large values of χ_0, when taken as a measure of

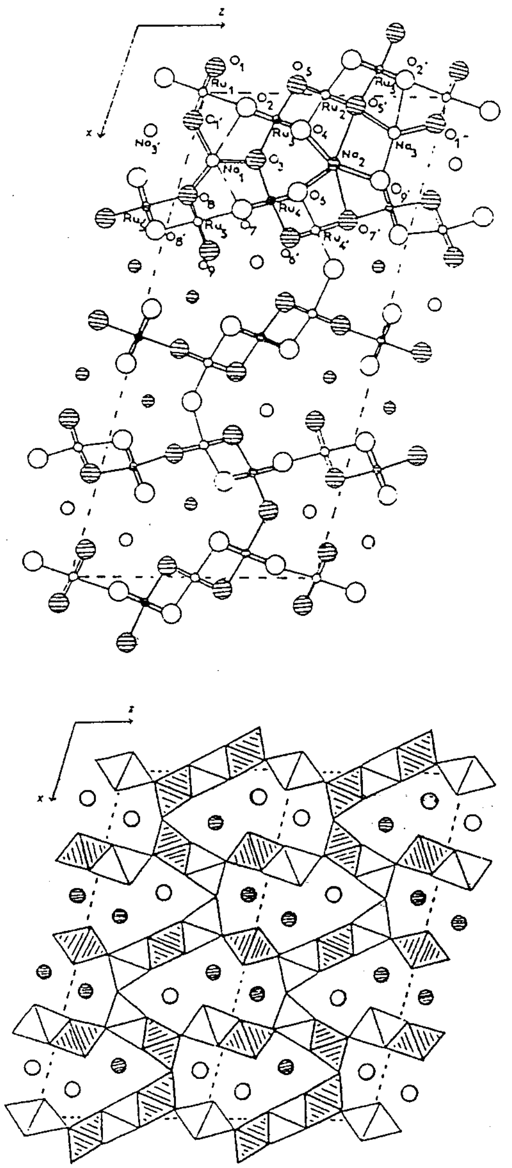

FIG. 1. Crystal structure of $Na_2Ru_4O_9$ (Ref. 1). Note: The b axis, i.e., the multichain direction, is perpendicular to the paper.

the density of states at the Fermi level, represent either a highly correlated spin state or strong electron–electron correlation.

The valence state of Ru for $Na_2Ru_4O_9$ is Ru^{4+} $(4d^4)$ which is in the low-spin state with $S=1$. Were the charges localized, the material would be an insulator. $Na_2Ru_4O_9$ is a metallic conductor along the b axis which will be described later, and remains metallic below the maximum. The effective magnetic moment obtained from χ is 1.67 μ_B for both $\chi_\parallel$ and $\chi_\perp$, which is only 58% of the Hund's rule value (2.83 μ_B), assuming quenching of orbital contribution.

The resistivity $\rho_\parallel(T)$ for the as-grown $Na_2Ru_4O_9$ single crystal measured with electrical current running along the b axis is shown in Fig. 3. While showing metallic behavior, $\rho_\parallel(T)$ decreases with a slightly negative curvature from 0.54 to 0.24 mΩ cm as temperature decreases from 300 to 40 K. No unusual structure is apparent in $\rho_\parallel(T)$ in the vicinity of

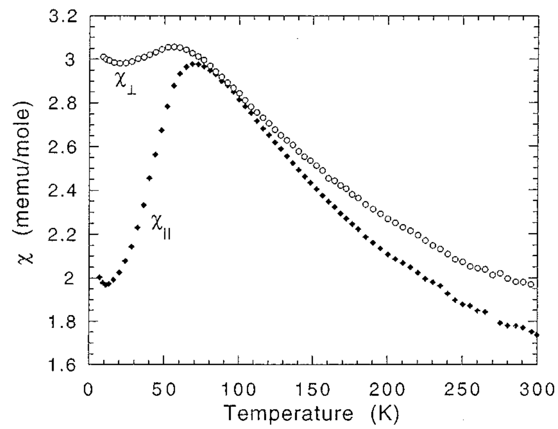

FIG. 2. The magnetic susceptibility $\chi(T)$ vs temperature for the as-grown single crystal $Na_2Ru_4O_9$.

the maximum observed in $\chi(T)$. Near 40 K, however, a slightly sharper drop is developed. For $T<30$ K, $\rho(T)$ is well described by $\rho(T)=A+BT^2$. The resistivity characterized by the T^2 dependence is reflective of spin fluctuations which apparently dominate the scattering process in this temperature region.

The most striking feature of the conductivity in this compound, however, is the drastically large anisotropy reflected in the resistivity. Also shown in Fig. 3 is the resistivity perpendicular to the b axis, i.e., the chain direction. Yet, like $\rho_\parallel(T)$, in the vicinity of 40 K, $\rho_\perp(T)$ displays a slight but well defined slope change which, again, may be associated with the reduction of spin scattering. The most noteworthy feature is the extremely large anisotropy, i.e., the ratio of $\rho_\perp(T)/\rho_\parallel(T)$ at $T=280$ and 2 K is about 2×10^5 and 7×10^5, respectively. Evidently, the resistivity with such a severe anisotropy suggests that the nature of electron scattering processes governing the conductivity in these two directions must be completely different. Although the anisotropy in conductivity is commonly seen in many compounds and alloys such as high T_c materials, the ratio of the resistivity for the conducting direction and the less conducting direc-

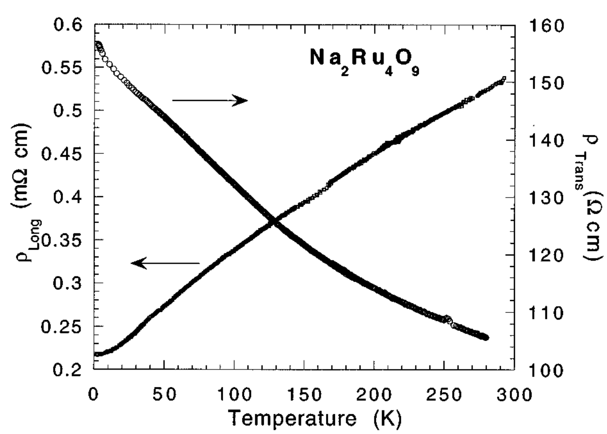

FIG. 3. $\rho_\parallel(T)$ and $\rho_\perp(T)$ vs T for the as-grown single crystal $Na_2Ru_4O_9$.

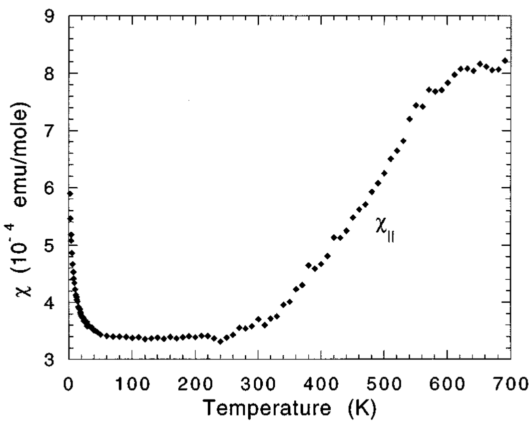

FIG. 4. The magnetic susceptibility $\chi(T)$ vs temperature for the deoxygenated single crystal $Na_2Ru_4O_{9-\delta}$ ($\delta > 0$).

tion is typically much smaller, e.g., $\rho_c/\rho_{ab} = 20-100$ for $YBa_2Cu_3O_7$.

The unusual behavior of $Na_2Ru_4O_{9-\delta}$ becomes even more interesting after comparing magnetic and transport properties observed in crystals which were deoxygenated. Shown in Fig. 4 is magnetic susceptibility $\chi_{\parallel}$ for $Na_2Ru_4O_{9-\delta}$ with $\delta > 0$ vs temperature for $2 \leqslant T \leqslant 700$ K. The great fascination of this data is that the system undergoes a drastic change in magnetic spin interactions due to reduction of oxygen content. The low temperature up-turn in $\chi_{\parallel}$ may reflect a small impurity phase. However, the unusual temperature dependence at higher temperatures is quite interesting. For $60 \leqslant T \leqslant 270$ K, $\chi(T)$ is essentially independent of temperature, and then develops a rapid up-turn near 270 K which is followed by a saturation occurring in the vicinity of $T = 600$ K. The origin of such behavior is not yet clear. However, it cannot be ruled out that oxygen deficient $Na_2Ru_4O_{9-\delta}$ ($\delta > 0$) may be involved in one-dimensional spin interactions which leads to an energy gap opening below 270 K. In fact, the behavior displayed by $\chi(T)$ mimics those of known low dimensional systems, such as Y_2BaNiO_5,[3] $CuGeO_3$,[4] $SrCu_2O_3$,[5] etc.

On the other hand, the electrical resistivity $\rho(T)$ for the deoxygenated sample changes only slightly with an increase in linearity down to 40 K and a mild decrease in magnitude. Yet, above 40 K, $\rho(T)$ shows, to the first order approximation, the linear-T behavior with the slope $d\rho/dT = 1.16 \times 10^{-6}$ (Ω cm K^{-1}). Interestingly, this linear-T behavior, though with the faster slope (10^{-7} Ω cm K^{-1} for $YBa_2Cu_3O_7$, for instance), is reminiscent to that observed in optimally doped high T_c superconductors when $T > T_c$. The linear-T dependence in $\rho(T)$ is thought to be non-Fermi liquid behavior. Below 30 K, the temperature dependence of $\rho(T)$ evolves the T^2 behavior, which is also seen in the as-grown sample. Fitting $\rho(T)$ to $A + BT^2$ for $0 < T < 30$ K yields $A = 2.2 \times 10^{-4}$, 2.0×10^{-4} (Ω cm) and $B = 3.2 \times 10^{-8}$, 2.0×10^{-8} (Ω cm K^{-2}) for the as-grown and deoxygenated samples, respectively. While A, which is due to the impurity scattering, remains essentially unchanged, B for the deoxygenated sample is almost 40% smaller than that for the as-grown sample. However, the change in the conductivity is by no means significant when compared to that in magnetism.

Nevertheless, it becomes clear that $Na_2Ru_4O_{9-\delta}$ ($\delta \geqslant 0$) is indeed unique in that it shows a wide range of unusual properties that may be attributed to one-dimensional behavior. The most striking feature of this compound is the drastically large anisotropy reflected in resistivity which exhibits metallic behavior along one direction and semiconducting behavior along others. The resistivity ratio for these two directions $\rho_{\perp}/\rho_{\parallel}$ is larger than 10^5. This result doubtlessly suggests that the bandwidth in this material is highly anisotropic. Consistently, the magnetic susceptibility also suggests occurrence of low dimensional behavior with a maximum in the vicinity of 70 K. It is remarkable that, after reduction of oxygen content in the system, the magnetic susceptibility undergoes a drastic change in spin interactions, whereas the electrical resistivity along the b axis alters only slightly with an increase in linearity. The striking observations reported here require more careful study including measurements of the oxygen deficiency in the deoxygenated samples. These and other studies are being pursued.

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