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Magnetic and transport properties of single-crystal Ca_2RuO_4: Relationship to superconducting Sr_2RuO_4

G. Cao, S. McCall, M. Shepard, and J. E. Crow
National High Magnetic Field Laboratory, Florida State University, Tallahasee, Florida 32310

R. P. Guertin*
Department of Physics, Tufts University, Medford, Massachusetts 02155

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Ca_2RuO_4, which has the single-layer tetragonal K_2NiF_4 structure, shows nonmetallic behavior for $T<300$ K unlike its isostructural counterpart, Sr_2RuO_4, which is metallic for all $T<1300$ K and which undergoes a superconducting transition temperature below $T=1.35$ K, possibly with p-wave spin pairing. Magnetization, electrical-resistivity, and heat-capacity data for single-crystal Ca_2RuO_4 are presented. An antiferromagnetic transition is identified at $T_N=110$ K in all samples studied. The easy axis for magnetization is parallel to the a or b axis (in the Ru-O plane). Isothermal magnetization studies in fields to 30 T show a spin reorientation transition for $B=3.5$ T at $T=105$ K and a metamagnetic transition for $T\ll T_N$ at about 9 T. The saturation magnetization even at 30 T, $M_{\mathrm{sat}}\approx 0.4\mu_B/\mathrm{Ru}$, is less than expected for the Ru $S=1$ moment ($M_{\mathrm{sat}}\approx 2.0\mu_B/\mathrm{Ru}$). The electrical resistivity, $\rho(T)$, increases with decreasing temperature by eight orders of magnitude for $70<T<300$ K and fits a variable-range hopping model including correlations. The magnetoresistivity below T_N shows some dependence on spin orientation. In contrast to all the other Sr and Ca-based ruthenates, Ca_2RuO_4 has a relatively small low-temperature electronic specific-heat coefficient ($\gamma=4$ mJ/mole K^2), and unlike them, Ca_2RuO_4 shows no anomaly in either $\rho(T)$ or $d\rho(T)/dT$ at T_N. Some magnetization results are presented for lightly Sr-doped Ca_2RuO_4. The data are contrasted with those of metallic Sr_2RuO_4 and discussed in terms of the weak spin disorder scattering in Ca_2RuO_4 compared to the very strong coupling in the other Sr- and Ca-based ruthenates. [S0163-1829(97)50230-X]

The discovery of superconductivity in single-crystal Sr_2RuO_4,[1] the first noncuprate based superconductor with a high T_c structure, has helped to spur an enhanced level of research in $4d$ and $5d$ metallic transition metal oxide systems, and in ruthenium-based oxides, in particular. The superconducting transition temperature of Sr_2RuO_4 is rather low [$T_c=1.35$ K (Ref. 2)], but it is significant because Sr_2RuO_4 is structurally similar to the first high-T_c superconductors and the superconducting phase is extant in only very highly pure undoped stoichiometric samples. Also unlike high-T_c cuprates, there seems to be no significant dependence of T_c on oxygen content,[3] though there is quite strong dependence on nonmagnetic impurity content,[2] a feature along with others such as the failure of the heat capacity to approach zero near $T=0$ K, that suggest the system may represent the long sought p-wave superconductivity.[4] Excellent Shubnikov–de Haas and de Haas–van Alphen results[5] on Sr_2RuO_4 have mapped the Fermi surface, as have a series of angle-resolved photoemission spectroscopy studies.[6] The normal-state electrical resistivity of Sr_2RuO_4 is rather extraordinary: The highest quality superconducting samples have resistivities just above T_c of about 1 $\mu\Omega$ cm yet increase to nearly eight times the estimated Ioffe-Regel limit[7] by 1300 °C, thus placing Sr_2RuO_4 in the category of ''bad metals.''[8]

Both Sr_2RuO_4 and Ca_2RuO_4 have the single-layered K_2NiF_4 structure, similar to the first (doped) high-T_c materials, e.g., $(La,Sr)_2CuO_4$, and this represents the $n=1$ (single layer) member of the alkaline earth-ruthenium Ruddlesden-Popper series,[9] $(Sr,Ca)_{n+1}Ru_nO_{3n+1}$ for $n=1$ to ∞. In all the ruthenates examined to date which show a temperature-dependent susceptibility, the Ru moment appears to have $S=1$, the low spin state, with the t_{2g} triplet ground state two-thirds filled ($4d^4$ Ru configuration). The low spin state is expected for a $4d$ system[10] because the larger radial extent of the $4d$ shell compared to the $3d$ shell should be more strongly affected by the crystal-field interaction of surrounding ions. This in turn should cause the t_{2g}-e_g splitting to be quite large, so filling of the lower-lying triplet t_{2g} should preceded filling of the much more highly excited doublet e_g level [excited perhaps by 3 eV (Ref. 11)].

In spite of a considerable body of work surrounding the nonconventional aspects of superconductivity in Sr_2RuO_4, there has been essentially no work forthcoming about the Ca isomorph to Sr_2RuO_4, namely Ca_2RuO_4. The work described here addresses this hiatus and presents magnetization, electrical resistivity, and heat-capacity results for single-crystal Ca_2RuO_4. In contrast to the Sr isomorph, Sr_2RuO_4, which remains metallic at least in the ab plane for $T_c<T<1300$ K,[2] the electrical resistivity of Ca_2RuO_4 is nonmetallic in the ab plane ($d\rho/dT<0$) for $70<T<300$ K, 70 K being the lowest temperature at which meaningful resistivity could be obtained. The system shows antiferromagnetism below $T_N=110$ K. Unlike the transport properties in all the other Sr- and Ca-based Ruddlesden-Popper ruthenates, which show strong changes in spin disorder scattering, neither the electrical resistivity of Ca_2RuO_4 nor its temperature derivative show any resistive anomaly at the magnetic ordering temperature.

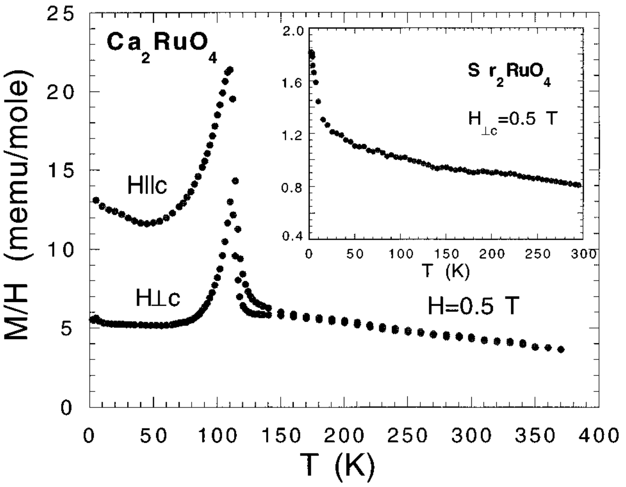

FIG. 1. Magnetic susceptibility along two principal directions for single-crystal Ca_2RuO_4. The inset shows the susceptibility of Sr_2RuO_4; note the much smaller susceptibility scale than for Ca_2RuO_4.

Single crystals of Ca_2RuO_4 were prepared by a self-flux technique described elsewhere.[12] All samples were measured in the as-grown state. Examination of sample surfaces by differential interference contrast microscopy showed uniformity of the surfaces without any mosaic features and quantitative analysis of the surfaces of the crystals carried out with energy dispersive x-ray scanning electron microscopy ascertained the composition. X-ray diffractometry confirmed the K_2NiF_4 structure, the lattice constants being $a=b=3.8163$ Å and $c=12.0250$ Å.

In order to determine the sensitivity of Ca_2RuO_4 single crystals to oxygen content, we attempted to increase the oxygen level by annealing some as-grown crystals in a flowing O_2 atmosphere. However, the single crystals did not survive the oxygen anneal, nor did they survive the opposite treatment, a flowing argon anneal, which was meant to reduce oxygen content. The high sensitivity of Ca_2RuO_4 to oxygen content is consistent with results of similar tests on $Ca_3Ru_2O_7$ ($n=2$ Ruddlesden-Popper member) and $CaRuO_3$. Sr-based ruthenates are less sensitive to oxygen or argon annealing, perhaps because the Sr ion is larger and forms more ideal, less distorted structures.

We show in Fig. 1 the magnetic susceptibility of a single-crystal Ca_2RuO_4 sample with the applied field ($H=0.5$ T) parallel and perpendicular to the [001] (c) axis. M vs H is linear for all T up to 0.5 T, so the data are the ''zero field'' limit of susceptibility. The inset of Fig. 1 displays the magnetic susceptibility of Sr_2RuO_4 for contrast; note the much smaller and less temperature-dependent susceptibility. The data of Fig. 1 show clear evidence for antiferromagnetic ordering. Maeno[13] also found antiferromagnetism below 110–150 K in polycrystalline materials. The value of the susceptiblity with $H\perp c$ is lower than for $H\| c$, suggesting the easy axis for antiferromagnetic order must lie in the ab plane of this highly anisotropic structure. This is consistent with the orientation of the spins for the $n=2$ counterpart to Ca_2RuO_4, namely antiferromagnetic ($T<56$ K), where [110] is identified as the easy axis.[12]

The transitions in Fig. 1, while having the general appearance associated with the onset of antiferromagnetism, are rather more sharply defined than those typical of antiferromagnets. For $T>110$ K, which we identify as the Néel temperature, T_N, the high-temperature susceptibility is unusual, nearly linear with increasing T, and it cannot be fit successfully to a modified Curie-Weiss law, $\chi=\chi_0+C/(T+\Theta)$, without unrealistically large moments and a large characteristic temperature, Θ. (The effective moment is about $4\mu_B$/Ru, much larger than $\approx 2.8\mu_B$/Ru expected for the Ru^{4+} $S=1$ configuration.) This unusual behavior is also seen in related materials (see Fig. 4 below) and we speculate it results from a large incipient structural distortion that occurs near T_N with precursive effects for $T>T_N$ that effect the Ru-O-Ru bond angle, which so sensitively determines the ordered moments as well as $4d$-$2p$ orbital overlap in other ruthenates.[10] The structural distortion near T_N was evident in early experiments: Single crystals were found to shatter after decreasing the temperature below about 100 K.

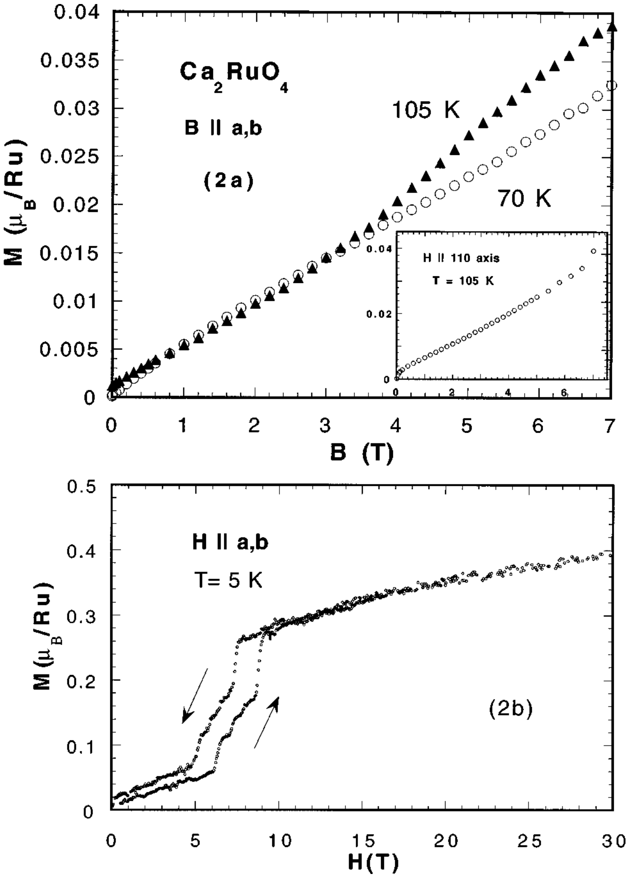

FIG. 2. (a) Magnetization vs applied field along the in-plane direction for two temperatures. The inset shows comparable data for the [110] direction. The break in M vs H at 3.5 T for $T=105$ K is probably a spin reorientation transition. (b) Very high field $M(H)$ showing a hysteretic metamagnetic transition at about 9 T. The magnetization by $H=30$ T is well below the value (≈ 1.4–$1.8\mu_B$/Ru) expected for the $S=1$ $4d^4$ configuration for Ru^{4+}.

Evidence for antiferromagnetic ordering below 110 K is also provided in Fig. 2(a) where we show the isothermal magnetization to $H=7$ T at two different temperatures. The break in $M(H)$ at about $H=3.5$ T for the $T=105$ K isotherm is characteristic of a spin reorientation transition, perhaps a spin flop transition, which occurs when the exchange energy competes with the anisotropy energy. This transition is not seen at lower temperatures (see $T = 70$ K isotherm) so it is possible the anisotropy gains the upper hand and prevents the spin reorientation from occurring. The inset shows similar data for $H \| [110]$, which is the easy axis for the analogous $Ca_3Ru_2O_7$ system in the nonmetallic antiferromagnetic phase, $T < 48$ K.[12] For the [110] orientation, the spin reorientation field appears to occur close to 7 T, supporting [100] or [010] as the easy axis.

The very high field magnetic isotherm data for $T = 5$ K in fields to 30 T are seen in Fig. 2(b). The results show a well-defined metamagneticlike transition at about 9 T. (Because of the reduced sensitivity of the vibrating sample magnetometer relative to the superconducting quantum interference device magnetometer, several individual single crystals were included in this measurement, oriented with $H \| a$ or b. This explains the somewhat ragged structure in M vs H because not all crystals could be oriented exactly parallel.) Metamagnetism at this low temperature supports strong anisotropy dominating over exchange. This transition is not unlike that observed at comparable temperatures for the related compound $Cu_3Ru_2O_7$, which shows a first-order Mott-like transition from a metallic to nonmetallic state at $T = 48$ K.[13]

The magnetization of Ca_2RuO_4 does not saturate even at 30 T, but attains only about 0.4 μ_B/Ru, well below the expected saturation value near 2.0μ_B/Ru for the $S = 1$ Ru moment with the $4d^4$ configuration. By contrast, ferromagnetic $SrRuO_3$, with $T_c = 165$ K saturates at about 1.65μ_B/Ru above 20 T at $T = 5$ K,[14] ferromagnetic $Sr_3Ru_2O_7$ at 1.4μ_B/Ru,[15] metamagnetic $Ca_3Ru_2O_7$ at 1.8μ_B/Ru,[13] and most recently we have measured magnetization up to 7 T in single-crystal $Sr_4Ru_3O_{10}$, an $n = 3$ Ruddlesden-Popper member, and found saturation at 1.65μ_B/Ru.[16] There may be several explanations for this anomalous behavior: First, a higher field metamagnetic transition may carry the moment to above 1μ_B/Ru, because even by $H = 100$ T, at the rate of increase $M(H)$ would attain less than 0.7μ_B/Ru so probably only with such a transition would $M(H)$ attain the high moment consistent with the other materials. Second, the spin-orbit coupling may be relatively strong; i.e., the orbital angular momentum may not be fully quenched, in which case the effective total angular momentum may be smaller, $J = |L - S|$ with $L \neq 0$. Finally, t_{2g} may not be the crystal-field ground state or well isolated from the e_g state in Ca_2RuO_4 unlike all the other Sr- and Ca-based ruthenates. We plan higher-field (pulsed field) measurements of $M(H)$ to search for higher-field spin reorientation transitions.

The temperature dependence of the electrical resistivity, $\rho(T)$, of Ca_2RuO_4 is shown in Fig. 3(a) for $70 < T < 300$ K. Unlike transport behavior in the other Sr- and Ca-based ruthenates, the resistivity shows nonmetallic behavior, i.e., $d\rho/dT < 0$, over the entire temperature range covered, with a decrease of eight orders of magnitude from $T = 70$ to 300 K. Data for $T < 70$ K could not be obtained due to saturation effects in the electrometer used to make the measurements. There is no anomaly in $\rho(T)$ at T_N [nor in $d\rho(T)/dT$ at T_N, see inset]. As noted above this is not typical of the other magnetically ordered Ruddlesden-Popper materials, where magnetic ordering is accompanied by clearly defined resistive anomalies. The superexchange, or other mechanism, which couples the Ru moments must not involve the conduction carriers.

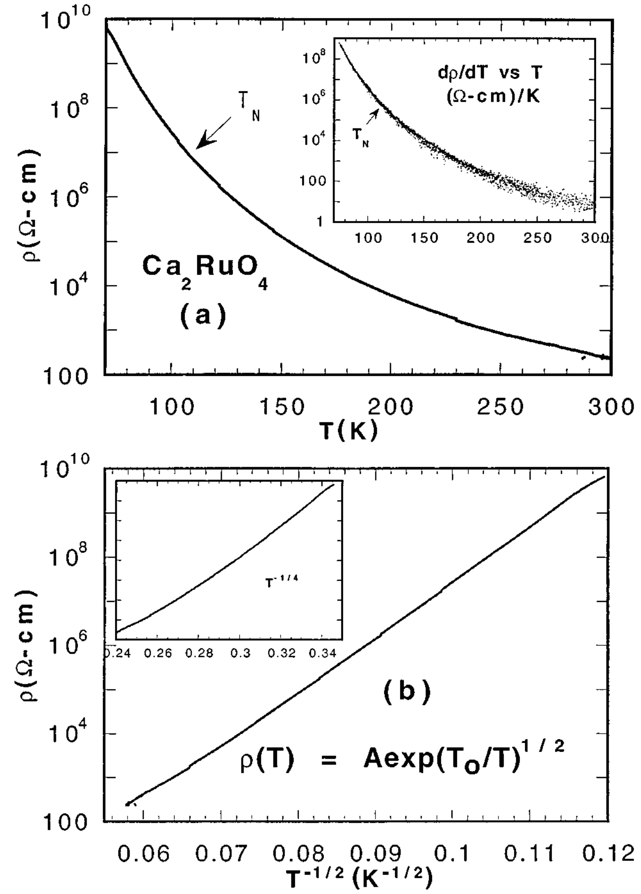

FIG. 3. (a) Electrical resistivity in the ab plane, $\rho(T)$, of single-crystal Ca_2RuO_4 showing semiconducting behavior. There is no anomaly at the antiferromagnetic transition, nor in $d\rho/dT$ (see inset). (b) Fit of the data to 3D variable-range hopping including correlations. The fit to the model neglecting correlations is less good (see inset). Fits to an activated resistance model were unsuccessful.

The $\rho(T)$ could not be fit successfully to an activation energy. However, the high-temperature data, $220 < T < 290$ K, fit an activation gap of about 200 meV, which agrees with the value determined in polycrystalline materials,[12] and the low-temperature data, $70 < T < 100$ K, fit a gap of about 110 meV. Variable-range hopping (VRH) conductivity fits were more successful, and in Fig. 3(b) we show the fit to $\rho_0 = A\ \exp(T_0/T)^{\beta}$, for $\beta = 1/2$.[10,17] This exponent is expected for three-dimensional (3D) hopping including correlations among the carriers and is appropriate for temperatures well below a metal-insulator transition. The $\beta = 1/4$ fit for VRH neglecting correlations is less good [see inset to Fig. 3(b)].

The magnetoresistance of Ca_2RuO_4 to 12 T was determined for several fixed temperatures for both the longitudinal ($H \| J$) and transverse ($H \perp J$) orientations. For $T > T_N$, $\rho(H) \approx H^2$ for both orientations, the transverse magnetoresistance increasing by about 6% at $T = 200$ K and 10% at $T = 120$ K by 12 T. For $T = 100$ K, which is slightly below T_N, the magnetoresistance was slightly negative (by 1%) to 6 T, then increasingly positive (by 5%) to 12 T. The slightly negative magnetoresistance probably reflects the magnetic ordering, though there is no evidence of magnetic ordering in either zero-field $\rho(T)$ or $d\rho/dT$ at T_N.

The heat capacity of Ca_2RuO_4 was measured for $1<T<20$ K and fit to C/T vs T^2. The intercept at $T=0$ K yielded an electronic heat-capacity coefficient, $\gamma=4$ mJ/mole K^2, much smaller than any of the other Sr- or Ca-based ruthenates ($\gamma=30$–70 mJ/mole K^2). However, the small value of γ is consistent with the low electrical conductivity at low temperatures, suggesting few carriers at the Fermi surface. This small γ contrasts with that of Sr_2RuO_4 (45 mJ/mol K^2), where ferromagnetic spin fluctuation enhancement of the heat capacity may also be what drives the suggested p-wave superconductivity.

Finally, we see in Fig. 4 the susceptibility vs temperature of two Sr-doped Ca_2RuO_4 single crystals, namely $(Ca_{1-x}Sr_x)_2RuO_4$ for $x=0.02$ and $x=0.04$. The peaks in the susceptibility are larger than for the $x=0$ sample with the same field and orientation, but broader, and T_N is shifted to lower temperatures. We intend to follow this trend more closely in the future by examining the $(Sr_{1-x}Ca_x)_2RuO_4$ system in more detail, matching previous studies for the $n=2$ (Ref. 18) and $n=\infty$ (Ref. 19) counterpart mixed systems.

The data presented here are shown for single-crystal Ca_2RuO_4. The contrast with paramagnetic metallic Sr_2RuO_4, which is isostructural with Ca_2RuO_4, is the most striking among the Sr and Ca ruthenate pairs studied to date.[18,19] This system dramatically reflects the extreme sensitivity of the physical properties to lattice constant. A key variable in this contrast may be the metal-oxide-metal bond angle, which is smaller in Ca compounds than in Sr compounds (Ref. 10, p. 231). We hope the rich array of physical properties displayed by these remarkable materials will precipitate further studies of the properties of $4d$ and $5d$ transition metal oxides, so long ignored in favor of their $3d$ counterparts.

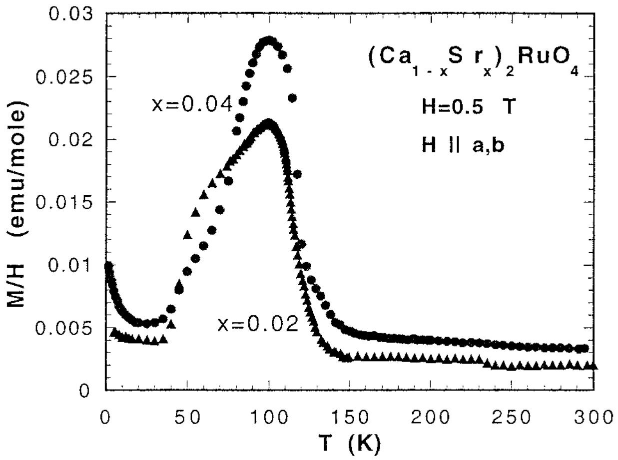

FIG. 4. Magnetic susceptibility with field along the ab plane for two lightly Sr-doped Ca_2RuO_4 single crystals.

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