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Destruction of the Mott insulating ground state of Ca_2RuO_4 by a structural transition

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We report a first-order phase transition at $T_M = 357$ K in single-crystal Ca_2RuO_4, an isomorph to the superconductor Sr_2RuO_4. The discontinuous decrease in electrical resistivity signals the near destruction of the Mott insulating phase and is triggered by a structural transition from the low-temperature orthorhombic to a high-temperature tetragonal phase. The magnetic susceptibility, which is temperature dependent but not Curie-like decreases abruptly at T_M and becomes less temperature dependent. Unlike most insulator to metal transitions, the system is not magnetically ordered in either phase, though the Mott insulator phase is antiferromagnetic below $T_N = 110$ K. [S0163-1829(99)52536-8]

The highly extended d shells of the $4d$ and $5d$ transition-metal cations in transition-metal oxides (TMO's) suggest *a priori* a weaker intra-atomic Coulomb interaction, U, relative to the $3d$ TMO's. Within the Mott-Hubbard model this alone would suggest metallic behavior, with $U/W < 1$, W being the bandwidth, proportional to the near-neighbor hopping probability. On the other hand, the extended d shells suggest a robust interaction between d orbitals and nearest-neighbor oxygen orbitals, and as a result some $4d$ and $5d$ TMO's have a tendency to form structures which are distortions of the more ideal generic structure, such as the K_2NiF_4 structure on which the subject of this report is based. In these cases the M-O-M bond angle may be considerably less than the ideal 180° and this generally implies insulating behavior because of a narrowing of the d-electron bandwidth.[1] Given the competition between these two effects, it is not surprising that some $4d$ and $5d$ TMO's verge on the interface between metal and insulator with $U/W \approx 1$. Owing to such a sensitive U/W ratio, small perturbations, such as slight alterations of crystal structure, dilute doping, etc., can readily tip the balance across the metal-nonmetal boundary, with resultant pronounced changes in physical properties. This feature has been well illustrated in recent studies on layered ruthenates and iridates.[2–4]

In this paper, we report a strongly first-order phase transition at ambient pressure from a low-temperature orthorhombic Mott insulating phase to a high-temperature tetragonal ''near'' metallic phase at $T_M = 357$ K in stoichiometric single-crystal Ca_2RuO_4. Much of the interest in Ca_2RuO_4 derives from it being isostructural with Sr_2RuO_4, the only noncuprate superconductor with a high T_c cuprate structure.[5] In contrast to spontaneous metal-insulator transitions which normally accompany a transition from low-temperature antiferromagnetism to paramagnetism [e.g., $T_M = 150$ K in V_2O_3 (Ref. 6) and $T_M = 48$ K in $Ca_3Ru_2O_7$ (Ref. 2)], Ca_2RuO_4 is paramagnetic on both sides of the transition, with well defined magnetic moments associated with the Ru ions. (Antiferromagnetic coupling exists only below $T_N = 110$ K.) We propose that the origin of the transition is an energy balancing tradeoff between the saving of elastic energy as the system transforms from a state of low to higher symmetry at the expense of electronic energies from a phase of high resistance, low entropy to a phase of lower resistance, higher entropy.

The results of x-ray diffraction (lattice parameters), electrical resistivity and magnetization are presented as a function of temperature for $70 < T < 600$ K in single-crystal Ca_2RuO_4,[3,8] which belongs to the layered Ruddlesden-Popper series with a single Ru-O layer in the unit cell. Our motivation for this study extends from prior work where the resistivity of Ca_2RuO_4 was found to decrease by an astonishing eight orders of magnitude (from 10^{10} to 100 Ω cm between $70 < T < 300$ K).[3] This suggested a rapid temperature-driven decrease in U/W, which could eventually lead to an insulator-to-metal transition at a more elevated temperature. The transition is also predicted by a simple extrapolation of the temperature-dependent neutron scattering studies of Braden *et al.*[9]

Based on reported studies on Ca_2RuO_4 to date, a few major features are known:[3,8,9] (1) It has a distorted K_2NiF_4 structure with large rotations and tilts of the RuO_6 octahedra compared to Sr_2RuO_4 due to the smaller ionic radius of Ca; (2) it appears to be a Mott insulator below $T = 300$ K with a narrow gap of about 0.2 eV, as determined from both transport[3] and optical measurements;[10] (3) it is antiferromagnetically ordered below $T_N = 110$ K; and (4) the magnetic moment ($\approx 0.4\,\mu_B$/Ru at 30 T) is low compared to the other Ca and Sr ruthenates[3] which have moments closer to the $2.0\,\mu_B$/Ru expected for the low spin ($S = 1$) state of the $Ru^{4+}(4d^4)$ configuration.

Single crystals of Ca_2RuO_4 were grown in Pt crucibles using a flux technique described elsewhere.[2] X-ray diffraction for $90 < T < 400$ K was performed on powdered single

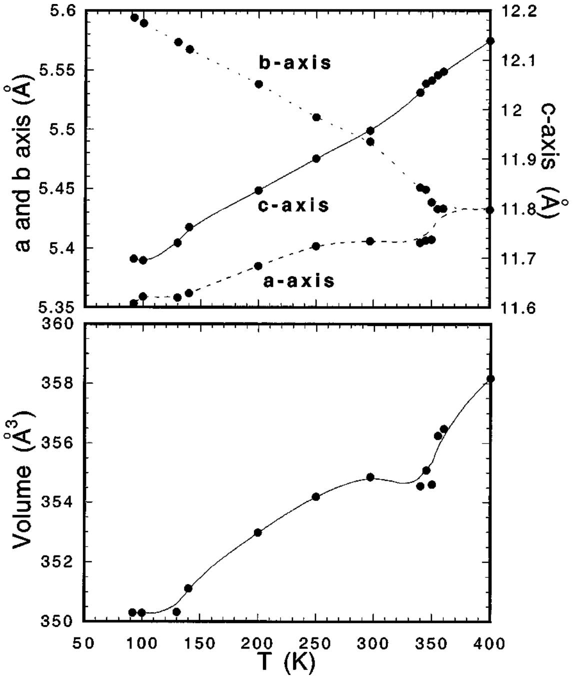

FIG. 1. Temperature dependence of lattice parameters for $90 < T < 400$ K for the powdered single-crystal Ca_2RuO_4.

crystals using Siemens $\Theta - 2\Theta$ and $\Theta - \Theta$ diffractometers with low- and high-temperature attachments. The metric refinement was carried out using 21 reflections. Resistivity was measured with a standard four probe technique and magnetization with a commercial superconducting quantum interference device magnetometer. All results of x-ray diffraction and energy dispersive x-ray (EDX) indicate that the crystals studied are pure, without any second phase.

Shown in Fig. 1(a) is the temperature dependence of the lattice parameters for $90 < T < 400$ K revealing a sharp transition near $T_M = 357$ K from a low-temperature orthorhombic phase to a high-temperature tetragonal phase. The results for $T < 300$ K agree reasonably well with those described in Ref. 9, which were derived from neutron measurements on polycrystalline Ca_2RuO_4 for $11 < T < 300$ K. The phase transition is well characterized by splittings of (l00) or (0k0) peaks in the temperature-dependent diffraction patterns. Below T_M, the *a* axis decreases whereas the *b* axis increases. As temperature decreases over the interval from 400 to 90 K, the *a* axis contracts by 1.5% and the *b* axis expands by 3%. The positive and negative thermal expansion coefficients derived from the temperature dependence of the lattice parameters not only indicate an increasingly strong orthorhombic distortion in the Ru-O plane but also are conspicuously large, i.e., one order of magnitude larger than those for other related compounds such as Sr_2IrO_4,[11] and $SrRuO_3$,[12] $CaRuO_3$,[12] and Sr_2RuO_4,[13] which do not undergo first-order phase transitions. The lattice volume is also substantially changed by 1.3% [see Fig. 1(b)]. It is therefore not surprising that such a drastic structural change is even macroscopically visible: The crystals shatter when heated through the transition temperature. (The shattering makes the resistivity measurements a difficult task: The measurements had to be performed on extremely small residual pieces of shattered crystals which are about $0.3 \times 0.3 \times 0.1\ \mathrm{mm}^3$.)

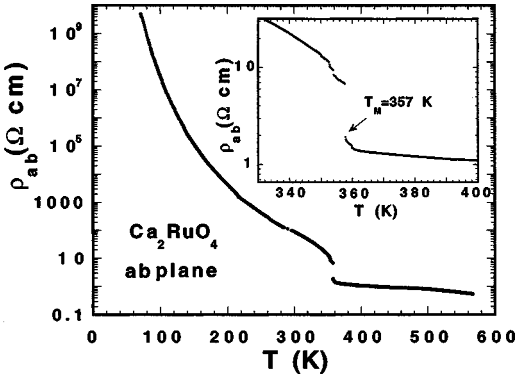

FIG. 2. Electrical resistivity $\rho(T)$ for the *ab* plane as a function of temperature for $70 < T < 600$ K. Inset: Detail of the abrupt jump in $\rho(T)$ near the transition at $T_M = 357$ K.

Although the sensitivity of our powder x-ray diffraction data is not sufficient to obtain a complete structural determination, the phase transition at $T = 357$ K is most likely caused by a rotation and tilt of the RuO_6 octahedra. According to the results in Ref. 9, the presence of the orthorhombic distortion below $T = 300$ K is due to a combination of a rotation of the RuO_6 octahedra around the *c* axis (11.8°) and a temperature-dependent tilt of the Ru-O basal planes (11.2°–12.7°). A similar structural phase transition due to basal plane tilting is also observed in isomorphic compounds La_2NiO_4 and La_2CuO_4 although the orthorhombic distortion is much less severe[14] and there is no corresponding impact on the electrical conductivity.

Figure 2 shows electrical resistivity, $\rho(T)$, in the *ab* plane as a function of temperature for $70 < T < 600$ K. (The resistivity results up to room temperature as well as those of the magnetic properties for $10 < T < 300$ K agree reasonably well with those of Ref. 8 for the ''*S*'' phase.) An abrupt transition from an insulating state to a nearly metallic state occurs at $T_M = 357$ K, simultaneous with the structural transition. The sudden decrease in ρ by a factor of 3.5 at the transition observed in several well-characterized crystals results in a pronounced discontinuity (see inset) indicating a robust first-order transition and unambiguously characterizes a discontinuous alteration in the *d*-band structure typical of a metal-insulator transition. Below the transition, $\rho(T)$ rises rapidly, increasing eight orders of magnitude over a relatively narrow temperature interval. More remarkably, $\rho(T)$ can be well fit for $70 < T < 300$ K to variable-range hopping or the Efros-Shklovskii mechanism given by $\rho(T) = A \exp(T_0/T)^{\nu}$ with $\nu = 1/2$. We note a discontinuity in $d\rho/dT$ at $T \approx 250$ K [though not in $\rho(T)$] in the *c*-axis resistivity of the isostructural system $(La_{1-x}Sr_x)_2CuO_4$ for $x \approx 0.10$, presumably due to a change in incoherent hopping.[15]

We note that the metallic state is not fully realized above the transition. For this system, the ''near'' metallic behavior may, in fact, be an artifact of the required method of measurement, i.e., the temperature must be *increased* from room temperature through T_M, and some microcracking of the sample occurs as evidenced by the inability to reproduce all the data upon lowering the temperature. In lightly La-doped samples, $(Ca_{1-x}La_x)_2RuO_4$ for $x < 0.05$ (unpublished data), where T_M is *below* room temperature, all samples show clear metallic behavior as temperature is reduced through T_M,

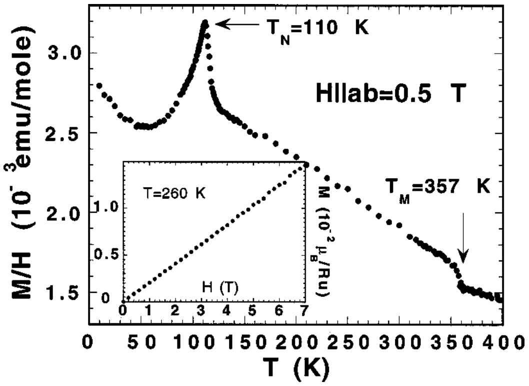

FIG. 3. Magnetic susceptibility defined as M/H for the *ab* plane as a function of temperature for $2<T<400\,\mathrm{K}$. Inset: Isothermal magnetization vs magnetic field up to 7 T at $T=260\,\mathrm{K}$.

which remains a first-order transition to an insulating phase. Then upon raising the temperature through T_M, ''near'' metallic behavior is observed. Such behavior is not limited to this system. ''Near'' metallic behavior is seen in $(V_{1-x}Cr_x)_2O_3$, for Cr concentrations very close to that which completely suppresses the metallic phase (Ref. 7, Fig. 6.3). Although due to different causes, ρ above the Verwey transition at $T=120\,\mathrm{K}$ in Fe_3O_4 is surprisingly similar to that observed in Fig. 2.[7,16] (See also Ref. 17, Sec. IV.)

Figure 3 shows the magnetic susceptibility defined as M/H vs temperature for the field along the *ab* plane, featuring the antiferromagnetic transition at $T_N=110\,\mathrm{K}$.[3,8] At $T=357\,\mathrm{K}$ there is a small yet well defined anomaly. While the shape might suggest the onset of ferromagnetism, there is neither hysteresis nor negative curvature of the isothermal magnetization normally expected for a ferromagnet for $T<357\,\mathrm{K}$ (see inset to Fig. 3), so the system remains paramagnetic through the structural/metal insulator transition.

It is puzzling that M/H vs T is effectively ''negative linear'' for $130<T<350\,\mathrm{K}$, clearly not Curie-Weiss (CW)-like. Nakatsuji, Ikeda, and Maeno observed a similar effect.[8] The sample volume changes extensively [+1.3%—see Fig. 1(b)] over this temperature interval. However, a simple increase in volume should reduce $\chi(T)$ slightly, retaining CW behavior.[18] We postulate, therefore, that the unstable lattice structure and the concomitant change in band structure is indirectly responsible for the anomalous behavior: The magnetic moment at individual sites is probably a strong function of bandwidth (hopping probability). This instability drives a strong temperature dependence of the M-O-M bond angle, which controls the bandwidth and indirectly the individual site moments. This is somewhat analogous to the case for paramagnetic a-Y(Fe) alloys[19] where temperature-dependent spin fluctuations link anomalous $\chi(T)$ with large volume changes.

The sharp peak in M/H at $T_N=110\,\mathrm{K}$ is attributed to an antiferromagnetic transition, but no corresponding change in ρ is discerned.[3] This is understandable because for an antiferromagnetic insulator the magnitude of the Hubbard gap is not greatly affected through T_N (Ref. 7, p. 137). The spin structure associated with this Neel phase is quite sensitive to impurity doping: 1% La doping for Ca, for instance, can effectively alter the spin configuration from antiferromagnetic to apparent ferromagnetic coupling, with a Curie temperature $T_C=135\,\mathrm{K}$.

While it cannot be totally ruled out that the abrupt change in resistivity at T_M merely reflects a massive change in incoherent hopping conductivity at a structural transition and hence not a true metal-insulator transition, the confluence of structural, transport, and magnetic anomalies at this first-order transition, coupled with the anomalous magnetization for $T<T_M$ suggests otherwise. In Ca_2RuO_4 the low-temperature phase, $T_N<T<T_M$, is characterized by a relatively small electronic gap in $N(E)$ ($\approx$0.2 eV) due to the rotation and tilt of the RuO_6 octahedra, which is known to minimize the total energy of the system. If the gain in elastic energy, E_E, is larger than the loss of the electronic coherence energy, then the system will be a paramagnetic Mott insulator at low temperatures. One expects the E_E gain to be reduced as the temperature is increased, and the associated rotation or tilt angle Θ will decrease. As a result, the electronic bandwidth $W\approx\cos(\Theta/2)$ will increase to the point that it will be more favorable for the system to transform to a metallic (correlated Fermi liquid) state. Thus, the thermally induced vibrations will reduce the overall distortion of the RuO_6 octahedra, and ultimately increase the electronic bandwidth and stabilize a paramagnetic metallic state at high temperatures. This structurally driven Mott transition can be straightforwardly modeled by extending the existing models to incorporate the relevant coupling to elastic degrees of freedom.

We emphasize that the transition at $T_M=357\,\mathrm{K}$ is not driven or even indirectly influenced by a magnetic ordering instability, which in the case of antiferromagnetism and the associated band splitting may help stabilize a low temperature insulator, as recognized early by Slater. Of course, at the lower temperatures one does expect exchange coupling between the localized magnetic moments in the insulator which will lead to an antiferromagnetically ordered state, and indeed such a Neel phase is observed below $T_N=110\,\mathrm{K}$. The opposite type of temperature-driven metal-insulator transition from high-temperature paramagnetic insulator to a lower temperature paramagnetic metal has been experimentally observed in $(V_{1-x}Cr_x)_2O_3$ for $x=0.51$.[6,7] The lower temperature metallic state is viewed as a highly correlated Fermi liquid characterized by a large effective mass m^* and a low coherence temperature $T^*\approx(m^*)^{-1}$. At temperatures $T>T^*$, a transition to a paramagnetic insulating state is predicted, where electrons become localized magnetic moments.

The dynamical mean field theory describing the above transition requires an electronic system with a fixed bandwidth, W and an on-site Coulomb repulsion U which is a function of temperature. In real systems the W can also be a strong function of temperature as described above. Consequently, in Ca_2RuO_4, where the sequence of phases is reversed, strong temperature dependence to the bandwidth may drive the transition. Evidence that the bandwidth has such temperature dependence comes from two sources: First, the M-O-M bond angle is a strong controller of bandwidth[1]—the smaller the angle, the narrower the band. For Ca_2RuO_4, the M-O-M bond angle at $T=11\,\mathrm{K}$ is only 151°, far from the ideal 180°. This angle increases with increasing temperature, as evidenced in Fig. 1, driving the system towards a more metallic phase. Second, we expect the localized paramagnetic moments to be a function of bond angle, and the anomalous (non-Curie) behavior for $T_N < T < T_M$ reflects this effect (see Fig. 3).

In conclusion, a structurally driven transition from a nearly metallic state to an insulating state is observed at $T = 357\,\mathrm{K}$. We have argued that the transition is Mott-like and not associated with a magnetic transition, and it is driven primarily by the coupled electronic elastic energies associated with the structural change. Generally, in a Mott insulator the gap depends only on the existence of moments and is not coupled to the crystal structure.[7] In contrast the simultaneous structural and electronic transition at $T = 357\,\mathrm{K}$ in Ca_2RuO_4 clearly points out that the transport properties are chiefly driven by changes in elastic energy. This transition is the most dramatic manifestation of the control exerted by the crystalline phase on the transport properties through bandwidth in Ca_2RuO_4.

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