Observation of a Structurally-Driven Mott Transition in Single Crystal Ca_2RuO_4

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We report a first-order structurally-driven Mott transition at T=357 K in single crystal Ca_2RuO_4, an isomorph to the superconductor Sr_2RuO_4. A discontinuous jump in electrical resistivity with a concomitant change in magnetic moment is triggered by a pronounced structural transition from a high temperature tetragonal phase to a low temperature orthorhombic phase. We argue that the elastic energy associated with the reduction of the crystal symmetry coupled with the electronic delocalization energy represent primary forces that drive the observed Mott transition.

The d-shell of the 4d and 5d-transition metal cations in transition metal oxides (TMO) are more extended than their more thoroughly studied 3d counterparts. On the one hand this suggests a robust electron-phonon interaction between the d-electrons and the lattice which in the extreme could lead to structural phase transitions. Transitions to lower symmetry with decreasing temperature suggest a distortion of the $180°$ M-O-M bond angle, which generally implies insulating behavior because of a narrowing of the d-electron bandwidth, W. On the other hand, the extended d-shells also suggest *a priori* a weaker intra-atomic Coulomb interaction, U, relative to the 3d's. Within the context of the Mott-Hubbard model this alone would suggest metallic behavior, with U/W<1, W being proportional to the inter-atomic hopping transition probability. Given the competition between these two effects, it is not surprising that some 4d and 5d systems verge on the interface between metal and insulator with U/W~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 borderline, and promote pronounced changes in physical properties. This feature has been well illustrated in recent studies on layered ruthenates and iridates [1-3].

In this paper, we report a structurally-driven transition from a high temperature paramagnetic "near" metallic phase to a well defined low temperature insulating phase at T=357 K and ambient pressure in stoichiometric single crystal Ca_2RuO_4, a compound isostructural with the superconductor Sr_2RuO_4 [4]. In contrast to the temperature-driven metal-insulator transition which is intimately associated with an antiferromagnetic phase and presumably triggered by the extra entropy of correlated metallic electrons relative to that of a magnetically ordered insulator (e.g. at 150 K in V_2O_3 [5] and at 48 K in $Ca_3Ru_2O_7$ [1]), the transition at T=357 K in Ca_2RuO_4 is believed to be primarily driven by the elastic energy associated with a structural transition. We propose that when the gain in the elastic energy $E_{elastic}$ is larger than the loss of the coherence energy, E_{FL}, near the Fermi surface, the system then undergoes an abrupt first-order transition from a paramagnetic "near-metal" to a paramagnetic insulator as temperature is decreased.

Ca$_2$RuO$_4$ is a newly discovered compound [2,6] belonging to the layered Ruddlesden-Popper series with a single Ru-O layer in the unit cell. There have been a handful of reported studies on this compound stimulated partially by the discovery of superconductivity in the Sr isomorph, Sr$_2$RuO$_4$ [2,6-8]. Based on these studies, a few major features have been revealed: (1) It has the K$_2$NiF$_4$ structure with severe distortions compared to Sr$_2$RuO$_4$ due to the small ionic radius of Ca (i.e., a rotation and tilt of the RuO$_6$ octahedra) [2,6,7]; (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 and optical measurements [2,6,8]; (3) it is antiferromagnetically ordered below T=110 K with a low magnetic moment (~0.4 μ$_B$/Ru at 30 tesla)[2]. All these studies, however, were carried out below room temperature, and there has been no work forthcoming on physical properties at higher temperatures, namely, T>300 K. We have noticed from our previous study that the resistivity of Ca$_2$RuO$_4$ rapidly decreases by an astonishing eight orders of magnitude (from 10^{10} to 100 Ω cm) from T=70 K to 300 K [2], suggesting a rapid temperature-driven decrease in U/W which may eventually lead to a possible insulator to metal transition at a more elevated temperature. With this premise, we have extended our study to a higher temperature regime (70<T<800 K). In this paper, we address the high temperature behavior and present the results of x-ray diffraction (lattice parameters), electrical resistivity, and magnetization as a function of temperature for single crystal Ca$_2$RuO$_4$. We make reference to theories of the temperature-driven Mott transition where W is assumed to be temperature independent, and propose that the elastic energy associated with the structural phase transition is the driving force for the nearly metal-insulator transition observed in Ca$_2$RuO$_4$.

Single crystals of Ca$_2$RuO$_4$ were grown in Pt crucibles using a flux technique described elsewhere [1]. X-ray diffraction for 90<T<400 K was performed on powdered single crystals using Siemens θ−2θ and θ−θ diffractometers with low and high temperature attachments. The metric refinement was carried out using 21 reflections. Resistivity for both low and high temperatures was measured with a standard four probe technique and magnetization with a commercial SQUID magnetometer. All results of x-ray diffraction and EDX indicate that the crystals studied are pure

without any second phase that may otherwise be present in polycrystalline samples.

Shown in Fig.1 is the temperature dependence of the lattice parameters for 90<T<400 K taken from x-ray diffraction studies. The major feature observed here is a sharp transition occurring in the vicinity of T=357 K from a high temperature tetragonal phase to a low temperature orthorhombic phase. This phase transition is well characterized by splittings of (l00) or (0k0) peaks in the temperature-dependent diffraction patterns. As will be discussed later, it is this pronounced structural transition that drastically narrows the d-band width W with decreasing temperature, and thus leads to an abrupt transition to an insulating phase. Below T=357 K, the a-axis gets shorter whereas the b-axis becomes longer as temperature decreases, or specifically, the thermal expansion of the basal plane for the measured temperature interval (90<T<400 K) is 1.5% for the a-axis and -3% for the b-axis (see Fig.1a). The positive and negative thermal expansion coefficients 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 [9], and $SrRuO_3$[10], $CaRuO_3$ [10] and Sr_2RuO_4 [11], where no first order phase transition is discerned. The lattice volume is also substantially changed by 1.3% (see Fig.1b). It is therefore not surprising that such a drastic structural change is even macroscopically visible: the crystals shatter violently when they were cooled 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 approximately 0.3x0.3x0.1 mm^3). It is also noted that in the vicinity of T=120 K all lattice parameters except for the b-axis tend to be saturated. Given the Neel temperature at T=110 K (see Fig.3 and Ref.2), the saturation suggests an occurrence of the Invar effect which has been recently observed below the ferromagnetic ordering temperature T_C=165 K in $SrRuO_3$ as well [10]. The results presented here reasonably agree with those for the S-Ca_2RuO_4 phase described in Ref.7 where results of recent neutron measurements on polycrystalline Ca_2RuO_4 below T=300 K are reported. Although the resolution of our powder x-ray diffraction data is not sufficient to obtain a complete structural determination, the phase transition at

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T=357 K is most likely to be caused by a rotation and/or tilt of the RuO_6 octahedra. According to the results in Ref. 7, 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°). Similarly, a 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 [12] and has no corresponding impact on the electrical conductivity.
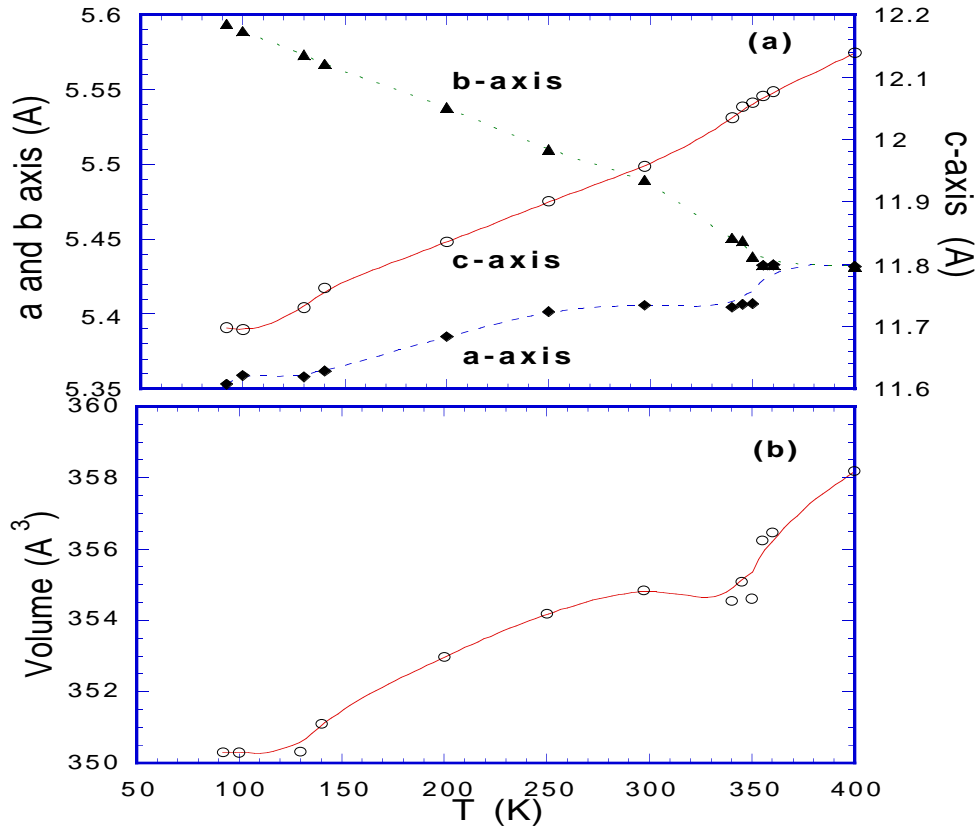

Fig.1. Temperature dependence of lattice parameters for 90<T<400 K for the powdered single crystal Ca_2RuO_4.

Fig.2 shows electrical resistivity ρ for the ab-plane as a function of temperature for 70<T<600 K. An abrupt transition from a nearly metallic state to an insulating state occurs at T=357 K, the structural phase transition temperature displayed in Fig.1. A sudden increase in ρ near the transition, observed in several well-characterized crystals, results in a pronounced discontinuity (see inset), indicating a robust first-order transition which is structurally-driven. We note that the metallic state is not fully realized above the transition. This may be attributed to disorder or randomness associated with the crystal structure that could create random potentials, thus localizing some electronic states (Although due to different cause, ρ near the transition is surprisingly similar to the Verwey transition at T=120 K in Fe_3O_4 [13,14].) The abrupt jump in ρ ($\Delta\rho$[=5 Ω cm]$/\Delta T|_{T=357.7 \ K}$[=0.11 K]=45.5 Ω cm/K) and drastic change in $d\rho/dT$ unambiguously characterize a discontinuous alteration in the d-band structure typical of a metal-insulator transition. In fact, the nearly zero slope of ρ ($d\rho/dT\sim0$) above the transition implies that Ca_2RuO_4 is indeed on the verge of the gap opening, demonstrating how close Ca_2RuO_4 is to the Mott transition borderline. Results of a recent optical conductivity study on Ca_2RuO_4 give a optical gap of 0.2 eV at T=300 K, a narrow gap characteristic of Mott systems such as V_2O_3 in the insulating phase [7].
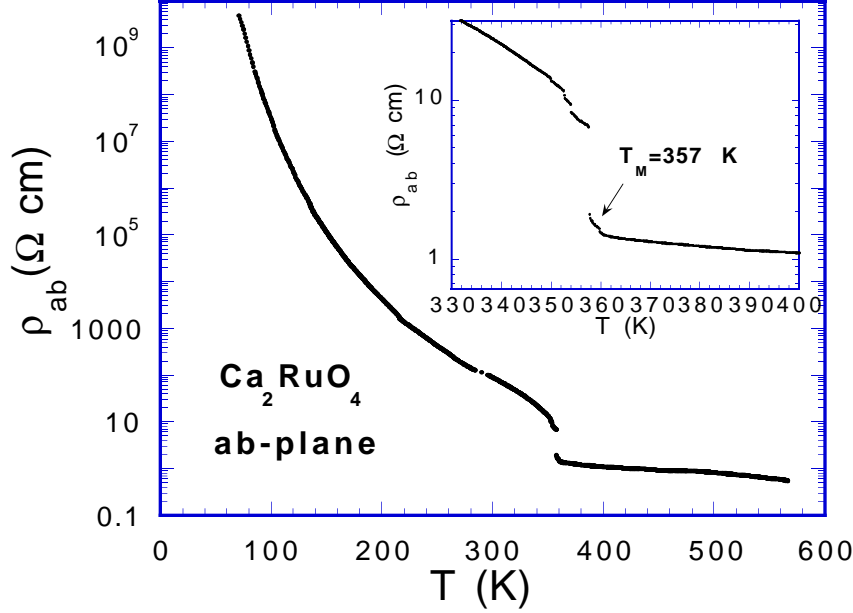
Fig.2. Electrical resistivity ρ for the ab-plane as a function of temperature for $70<T<600$ K. Inset: Detail of the abrupt jump in ρ near the transition T=357 K.

Below the transition, ρ rises rapidly, covering eight orders of magnitude over a relatively narrow temperature interval. More remarkably, ρ can be well fit for $70<T<300$ K to variable-range hopping or the Efros-Shklovskii mechanism given by $\rho(T)=A\exp(T_o/T)^\nu$ with $\nu=1/2$. We have already reported this part of the data, i.e., the results of ρ below T=300 K [2]. Without further elaborating the discussions here, we point out that the VRH conductivity with $\nu=1/2$ is generally limited to low temperatures far from the metal-insulator transition, where the overlap between wave functions is small, i.e., $k_BT<<\Delta E$ (ΔE is the soft Coulomb gap near E_F). The successful fit to $\nu=1/2$ rather than $\nu=1/4$ at such a high temperature range is anomalous, suggesting that there may be more subtle mechanisms at work connected with the energy dependence of the density of states, $N(\varepsilon)$. The $\nu^{1/2}$ behavior of ρ results from $N(\varepsilon)\sim\varepsilon^2$ near the Fermi surface ε_F. The $\nu=1/2$ behavior is well

preserved when the system is doped with Sr up to 4 % but breaks down when doped with even 1% La.

Fig.3 shows the magnetic susceptibility defined as M/H vs. temperature for the field along the ab-plane. At T=357 K, there is a weak, yet well defined, anomaly. Its shape would suggest a ferromagnetic transition, however neither hysteresis nor a curvature in isothermal magnetization (see the inset) normally expected for a ferromagnet is observed for 110<T<357 K. Although there are a few possibilities to account for the behavior, the linear and non-hysteretic dependence of M vs. H at T=260 K shown in the inset indicates a paramagnetic state. The anomaly is more likely to be due to the structure change discussed above. It is however puzzling that the almost linear magnetic susceptibility for 130<T<350 K does not seem to follow the Curie-Weiss law. This may imply an enhanced paramagnet and could be attributed to the severe volume and stuctural changes over this temperature interval. Since the M-O-M bond angle is changing drastically, the amount of d-electrons weight that represents the "localized" moment may be changing as well, therefore the actual moment/Ru could be T-dependent.
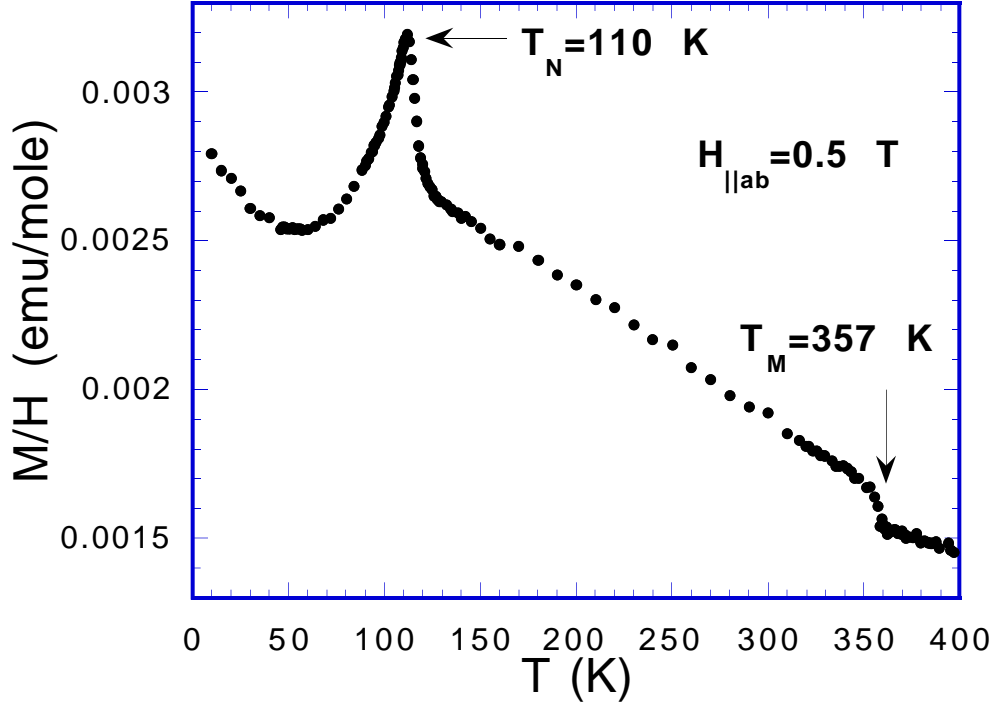
Fig.3. Magnetic susceptibility defined as M/H for the ab-plane as a function of temperature for 2<T<400 K. Inset: Isothermal magnetization vs. magnetic field up to 7 T at T=260 K.

As reported earlier [2], there is a sharp peak occurring at T=110 K which is attributed to an antiferromagnetic transition, and no corresponding change in ρ is discerned. This may not be completely unexpected since for an antiferromagnetic insulator the magnitude of the Hubbard gap is not greatly affected when temperature goes through the Neel temperature [13]. It is also remarkable that the spin structure associated with this Neel state 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=125 K. The sensitivity of the spin configuration to the impurity doping reflects the subtlety of the magnetic structure which, again, may be related to the instability of the distorted crystal structure.

A temperature-driven metal-insulator transition from high temperature paramagnetic insulator (PMI) to a paramagnetic metal

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(PMM) has been experimentally observed in $(V_{1-x}Cr_x)_2O_3$ (the Cr induced "re-entrant" transition at higher temperatures, e.g., T_M=380 K for x=0.51) [5,13] as well as in a number of other strongly correlated compounds. Theoretically, the origin of this transition has been interpreted based on early ideas of Brinkmann and Rice, and its more recent elaboration based on slave-boson and dynamical mean-field approaches. In this picture, the low temperature metallic state is viewed as a highly correlated Fermi liquid characterized by a large effective mass m* and a low coherence temperature $T^* \sim (m^*)^{-1}$. At temperatures $T > T^*$, a transition to a paramagnetic insulating state has been predicted, where electrons become localized magnetic moments, liberating an appreciable amount of spin entropy (per electron) $S_{spin} \sim k_B \ln(3)$. This entropy gain overwhelms the energy loss $E_{FL} \sim T^*$ due to the destruction of the coherent Fermi liquid and serves as a driving force for this transition. Since the PMM and PMI phases cannot be distinguished on symmetry grounds, one generally expects this to be a robust first order transition, as indeed observed in experiments.

The PMI to PMM transition that we have observed in Ca_2RuO_4 seems to have little in common with the temperature-driven Mott transition described above because the phases are reversed. However, the above picture has an electronic system with a fixed bandwidth W and an on-site Coulomb repulsion U as a function of temperature. In real systems the bandwidth W can also be a strong function of temperature, so that the proposed theoretical picture has to be modified. A well known example of such situations can be found in "strong" ferromagnets such as CrO_2, where the electronic bandwidth can be considerably reduced in the high temperature paramagnetic phase due to the double-exchange coupling of conduction electrons to local magnetic moments. This may explain why this material can be an excellent metal at low temperatures, but an extremely "bad metal" in the high temperature paramagnetic phase.

We propose a similar basic mechanism that can account for the behavior observed in Ca_2RuO_4, but the net results can be diametrically opposite. In Ca_2RuO_4, as described above, the low temperature phase is characterized by a relatively small electronic gap in $N(\varepsilon)$ due to the rotation and tilt of the RuO_6 octahedra, which is

known to minimize the elastic energy $E_{elastic}$. If the gain in elastic energy $E_{elastic}$ is larger than the loss of the coherence energy E_{FL}, then the system will be a paramagnetic Mott insulator at low temperatures. On the other hand, one expects the elastic energy 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 $W \sim \cos(\theta/2)$ will increase to the point that it will be more favorable for the system to transition to a metallic (correlated Fermi liquid) state and gain a coherence energy E_{FL}. 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. Preliminary calculations indicate that the expected PMI to PMM transition can follow, the detailed results will be presented elsewhere. It is to be emphasized that this transition is therefore a "pure" Mott transition, i.e. not driven or even directly influenced by a magnetic ordering instability, which in the case of itinerant antiferromagnets may help stabilize a low-temperature insulator. Of course, at the lower temperatures one does expects a superexchange coupling between the localized magnetic moments in the insulator which will lead to an antiferromagnetically ordered state, inducing a second PMI to AFI transition as the temperature is lowered. As shown in Fig. 3, such a Neel state is indeed observed below T_N=110 K.

In conclusion, a structurally-driven transition from a nearly metallic state to an insulating state is observed at T=357 K. We have argued that the transition is Mott-like in nature, and is driven primarily by the coupled electronic elastic energies associated with the structural change. Generally, in a Mott insulator the gap, given by $U-0.5(B_1+B_2)$ (with B_1 and B_2 being the lower and upper Hubbard subbandwidths, respectively), depends only on the existence of moments and is not coupled to the crystal structure [13]. In contrast, the simultaneous structural and electronic transition at T=357 K in Ca_2RuO_4 clearly points out that the transport properties are chiefly driven by changes in elastic energy. The metal-insulator transition has been one of the most intriguing questions of transition metal oxides because it always underlines the interplay between spin,

charge and orbital degrees of freedom and, most important of all, there seems to be no quantitatively satisfactory theory that can adequately describe the complex interactions taking place in metal oxides when U/W~1. We hope that Ca_2RuO_4 can serve as one of a few rare model materials for the pursuit of solutions to this time-honored question.

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