

From Mott insulator to ferromagnetic metal: A pressure study of Ca_2RuO_4

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We show that the pressure-temperature phase diagram of the Mott insulator Ca_2RuO_4 features a metal-insulator transition at 0.5 GPa: at 300 K from paramagnetic insulator to paramagnetic quasi-two-dimensional metal, and at $T \leq 12$ K from antiferromagnetic insulator to ferromagnetic, highly anisotropic, three-dimensional metal. We compare the metallic state to that of the structurally related p -wave superconductor Sr_2RuO_4 , and discuss the importance of structural distortions, which are expected to couple strongly to pressure.

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The Mott transition from the metallic to the insulating state, driven by a Coulomb interaction, is one of the most dramatic and fundamental many-body effects in condensed-matter physics. In recent years there has been a resurgence of interest in the Mott transition due on the one hand to the discovery of materials such as the high- T_c cuprates and the manganites in which the metal-insulator transition plays an essential role,¹ and on the other to insights gained from theoretical developments such as the dynamical mean-field theory² and the recognition of the importance of orbital ordering at the metal-insulator transition.¹

The system $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ has recently been investigated in detail and shown to have a metal-insulator transition at 0 K at $x \sim 0.2$.³ This is a layered perovskite system, isostructural to the cuprate $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, with one end member, Sr_2RuO_4 , being a highly anisotropic metal with an unconventional (probably p -wave) superconducting ground state,^{4,5} while the other, Ca_2RuO_4 , is an antiferromagnetic (AF) insulator for $T < 113$ K, a paramagnetic (PM) insulator for $113 \text{ K} < T < 360 \text{ K}$, and a “bad metal” for $T > 360 \text{ K}$.^{3,6} This system is of great interest for the following reasons.

First, the overwhelming majority of work on the metal-insulator transition has been done on $3d$ transition-metal compounds (mainly oxides) such as V_2O_3 .¹ $3d$ orbitals are comparatively compact and close to the ionic core, giving rise naturally to small bandwidths W , and large Coulomb repulsion U between $3d$ electrons on the same site. In contrast, $4d$ metal-insulator systems are rare, but they should offer a different viewpoint because the more extended $4d$ orbitals will tend to have larger effective correlation energy U/W , but greater susceptibility to orbital ordering via structural distortions around the $4d$ site. Indeed the phase diagram

of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ shows a series of structural transitions that are intimately related to changes in the electronic state.⁷

Second, although the cuprates show superconductivity in close proximity to a Mott insulating state, a clear connection between the metal-insulator transition and superconductivity has not been made experimentally, and there are many unresolved issues associated with the physics of the cuprates near the Mott insulating state. As a quasi-two-dimensional (Q2D) system bridging the gap between a Mott insulator and an unconventional superconductor, the $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ system promises to shed light on this question.

Finally, detailed understanding of how p -wave superconductivity arises in Sr_2RuO_4 is lacking. p -wave superconductivity is assumed to be mediated by magnetic fluctuations at low q , normally associated with proximity to a ferromagnetic (FM) state at 0 K (i.e., to a FM quantum critical point), but Sr_2RuO_4 does not itself appear to be close to FM order. The doped system, however, at $x \sim 0.5$ is on the verge of FM order at 0 K,⁷ although long-range FM order does not develop for any value of x .

Pressure is generally to be preferred to chemical doping to tune the properties of materials because pressure does not introduce disorder. Disorder can be extremely hostile to unconventional superconducting states⁸ and it also introduces enormous complications in studying the Mott transition. In this paper we show that application of very modest pressures to pure Ca_2RuO_4 transforms it from an insulator to a highly anisotropic metal with a FM metallic ground state, and we follow the evolution of this ground state as a function of pressure. Our results shed light on the nature of ferromagnetism in the layered ruthenates, and open up a $4d$ system for the study of the metal-insulator transition in the absence of disorder.

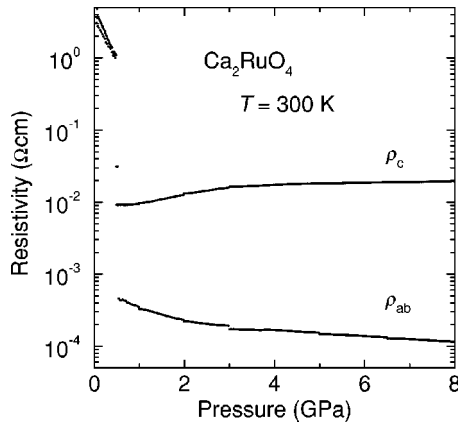


FIG. 1. Pressure variation of ρ_{ab} and ρ_c at 300 K. The insulator-metal transition occurs at 0.5 GPa, where ρ_{ab} and ρ_c fall by approximately four and two orders of magnitude, respectively.

We used single-crystal Ca_2RuO_4 with an essentially stoichiometric oxygen content.⁷ Resistivity under pressure P was measured by a standard four-probe method, with a ring contact geometry for the c -axis resistivity ρ_c . The electrodes were made by a silver evaporation technique. The typical sample size was $0.15 \times 0.5 \times 0.04 \text{ mm}^3$ for in-plane resistivity ρ_{ab} , and $0.35 \times 0.35 \times 0.04 \text{ mm}^3$ for ρ_c . Pressures up to 8 GPa were generated in a cubic anvil device with an equal volume mixture of Fluorinert FC70 and FC77 (3M Company, St. Paul, MN) as a pressure-transmitting medium. In this device quasihydrostaticity can be generated by isotropic movement of six anvil tops even after the fluid medium vitrifies at low temperature and high pressure.

Figure 1 shows ρ_{ab} and ρ_c at 300 K as a function of pressure up to 8 GPa. Both ρ_{ab} and ρ_c drop discontinuously at 0.5 GPa, indicating an insulator-metal transition. The discontinuity indicates that the transition is of first order and is thus most likely accompanied by a structural change.⁹

In the insulating state both ρ_{ab} and ρ_c decrease isotropically and monotonically with increasing pressure. Following the discontinuous drop at 0.5 GPa, however, while ρ_{ab} continues to fall, ρ_c begins to increase. The anisotropy ratio, $\rho_c/\rho_{ab} \sim 2$ in the insulating phase, jumps to about 100 in the metallic phase. Thus, the Q2D nature of the metallic state is comparable with high- T_c systems or Sr_2RuO_4 .

Figure 2 shows ρ_{ab} and ρ_c as a function of temperature at several fixed pressures. At ambient pressure, both ρ_{ab} and ρ_c show an activation-type increase. In contrast, above 0.5 GPa Ca_2RuO_4 shows a Q2D metallic nature for temperatures above ~ 25 K. That is, $\rho_{ab}(T)$ shows metallic ($d\rho_{ab}/dT > 0$) conduction whereas ρ_c has a negative slope indicating nonmetallic conduction. The anisotropy ratio rises to ~ 1000 at 25 K. The nonmetallic behavior of ρ_c down to 25 K in pressurized Ca_2RuO_4 is in sharp contrast with the metallic ρ_c seen below 130 K in Sr_2RuO_4 . The rise in ρ_c with increasing pressure at 300 K also contrasts with simple ideas of metallic conduction, in which the bandwidth would increase with pressure, but the same effect is seen in Sr_2RuO_4 at $T > 130$ K,¹⁰ so this seems to be a signature of incoherent c -axis transport in the ruthenates. We infer that above 25 K the c -axis conduction in metallic Ca_2RuO_4 is mainly de-

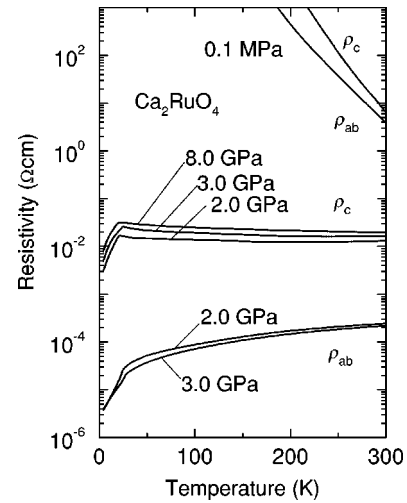


FIG. 2. Temperature variation of ρ_{ab} and ρ_c at fixed pressure P . For $P > 0.5$ GPa, $\rho_{ab}(T)$ is metallic while $\rho_c(T)$ above $T^* \sim 25$ K exhibits nonmetallic temperature dependence.

scribed by a tunneling mechanism as in the high T_c 's.

As the temperature falls below ~ 25 K, $\rho_c(T)$ peaks and then decreases rapidly, indicating a change from two-dimensional to three-dimensional metallic conduction. At the temperature T^* corresponding to the kink in the $\rho_c(T)$ curves, $\rho_{ab}(T)$ also exhibits an abrupt change in slope, falling rapidly to a residual resistivity of $\sim 3 \mu\Omega \text{ cm}$. This is a very low resistivity for an oxide metal, indicating that our samples are of high quality, but still somewhat higher than required to observe superconductivity in Sr_2RuO_4 .⁸ The behavior near 25 K is reminiscent of a phase transition. In order to clarify this point, the field (H) and temperature (T) dependence of the magnetization have thus been measured under pressures of 0.1 MPa, 0.2, 0.5, 0.7, and 0.8 GPa using a piston-cylinder Be-Cu clamp cell with a commercial superconducting quantum interference device magnetometer (Quantum Design, model MPMS).¹¹ We have used several rectangular pieces of sample with total masses of 12.5 mg for $H_{\perp c}$ and 6 mg for $H_{\parallel c}$.

Figure 3 shows magnetization (M) curves at 2 K with $H_{\perp c}$. FM ordering is indicated by the hysteresis in the M - H curves at 0.7 GPa, a pressure at which the system is metallic in the corresponding resistivity measurements. In contrast, no hysteresis is observed in the M - H curves at 0.1 MPa and 0.2 GPa where Ca_2RuO_4 is in the AF insulating phase. The remnant magnetization is $0.09 \mu_B$ at 0.7 GPa, growing to $0.125 \mu_B$ at 0.8 GPa,¹² while the coercive force of $H_c \sim 50$ mT, which is defined as the field necessary to restore zero magnetization, increases only weakly.

The volume fraction of the AF insulating phase ought to decrease with pressure above 0.5 GPa, so the remnant magnetization originates from the metallic phase. Moreover the small moment compared with the saturated moment $2\mu_B$ of a localized Ru^{4+} ion implies itinerant magnetism. The shape of the hysteresis curve, which indicates a typical soft ferromagnet, is different from that for the canted AF case seen, for example, in the AF insulating phase of Ca_2RuO_4 with excess oxygen.⁷ We have also observed a similar shape of

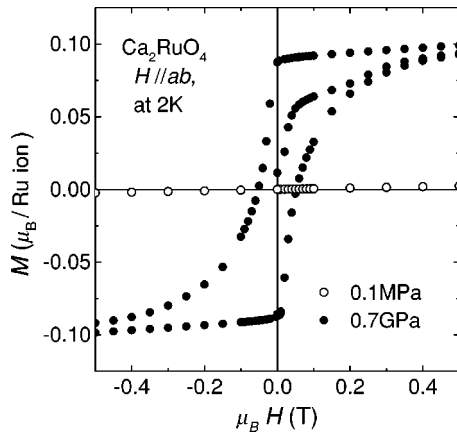


FIG. 3. Magnetization curves for $P=0.7$ GPa and 0.1 MPa, measured at 2 K. Hysteresis indicating FM ordering is observed at 0.7 GPa, but not at 0.1 MPa. The remnant M_r is $0.09\mu_B$ at 0.7 GPa while the coercive force is $\mu_B H_c \sim 50$ mT.

hysteresis loop with $H_{\parallel c}$ at 0.8 GPa where the remnant magnetization is $0.08\mu_B$ and the coercive force of H_c is ~ 50 mT. Comparing the hysteresis measured in $H_{\parallel c}$, we do not find anisotropy typical of antiferromagnetism. We therefore deduce that Ca_2RuO_4 in the pressure-induced metallic phase is an itinerant ferromagnet at low T , although neutron scattering should be done to confirm this.

Figure 4 summarizes the pressure dependence of T_N and T_C obtained from our $M(T)$ curves, and of T^* obtained from resistivity. T_N is almost independent of pressure up to 0.5 GPa, where it abruptly vanishes and is replaced by FM order below ~ 12 K. The FM T_C then rises with increasing pressure, becoming comparable to T^* near 1 GPa. Thus, the remarkable drop in $\rho(T)$ at T^* is most probably due to reduced magnetic scattering at a FM ordering transition. T^* continues to rise, reaching 25 K at ~ 5 GPa, then it decreases gradually. Extrapolation of the T^* vs P curve suggests that the FM order may be completely suppressed at ~ 15 GPa.

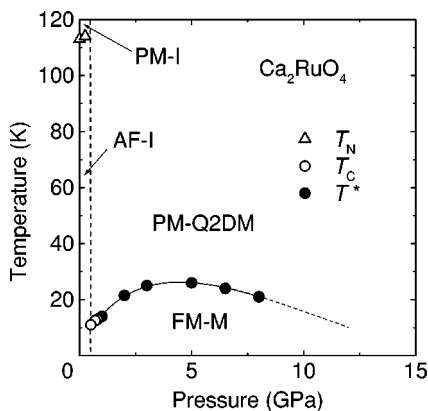


FIG. 4. The characteristic temperatures T_N (AF ordering), T_C (FM ordering), and T^* (cusp in the resistivity) plotted against pressure. The phases are labeled PM-I (paramagnetic insulator), AF-I (antiferromagnetic insulator), PM-Q2DM (paramagnetic quasi-two-dimensional metal), and FM-M (ferromagnetic metal). Solid and dotted lines are guides to the eye.

From ~ 360 to 113 K the 0.5-GPa transition is from a PM insulator to a PM-Q2D metal. The PM insulating phase with thermally activated conductivity is important because it shows that Ca_2RuO_4 is a many-body insulator, as opposed to being a band insulator with fully opened gaps on the Fermi surface due to AF order. It is also instructive to contrast the PM metallic state with the metallic phase of the manganites, which are always FM and can only be reached by doping. This reflects the difference in on-site repulsion U in $3d$ and $4d$ systems. Mn has a large U , so the Mn ion in the manganites is in a high-spin configuration, and the strong Hund's rule coupling requires that the spin of a conduction electron in an e_g orbital must be parallel to the localized t_{2g} spins both on the ion from which it is hopping and the one to which it is hopping (so-called "double exchange.") In the ruthenates, in contrast, lower U produces a low-spin configuration, and there is no constraint on the spin direction of the hopping electron in the metallic state.

It is tempting to interpret the phase diagram of Ca_2RuO_4 as a classic Mott transition to a metal with a FM ground state.^{13,14} But this might be too simple. Analogy with $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ shows that the physics is not simply driven by changes in U/W , but also the orbital degeneracy of the $\text{Ru}^{4+}t_{2g}$ levels may abruptly change due to structural transitions. These have been well characterized by neutron and x-ray scattering.^{3,15} Pure Sr_2RuO_4 is tetragonal, but at the Ca-rich end the structure is distorted by rotations of the oxygen octahedra about the c axis, tilts about an in-plane axis, and large variations in the degree of "flattening" of the octahedra along the c axis. In pure Ca_2RuO_4 the $T > 360$ K metallic phase is $L\text{-Pbca}$, with a smaller volume and weaker tilt and flattening distortions than the $T < 360$ K insulating $S\text{-Pbca}$ phase. Pressure should stabilize the low volume phase, so we expect the structural transition associated with the first-order insulator-metal transition to be from $L\text{-Pbca}$ to $S\text{-Pbca}$.⁹ Fang and Terakura¹⁶ have performed electronic structure calculations that take account of the distortions. They find that flattening, which lowers the d_{xy} orbital relative to the d_{xz} and d_{yz} orbitals, favors an insulating AF ground state; the tilt stabilizes AF correlations in the metallic state, while rotations favor ferromagnetism. Thus the insulator-metal transition and AF order may couple separately to pressure, the former caused by suppression of flattening, the latter by reduced tilting.

We now turn to a discussion of the FM metallic state above the insulator-metal transition. According to band-structure calculations FM order in layered ruthenates is a reflection of rotational distortions,^{16,17} which develop FM coupling by enlarging the density of states at the Fermi energy via band narrowing. This idea is supported by the large FM correlations in $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ with $x=0.5$, in which the octahedra are rotated but not tilted.¹⁸ More generally,²⁰ ruthenates show a tendency to ferromagnetism due to an unusually large admixture at the Fermi surface of the oxygen p orbitals, which can gain exchange energy from FM order. It will be very interesting to have electronic structure calculations on metallic Ca_2RuO_4 , once the crystal structure is known accurately in the high-pressure phase. It will also be

interesting to compare the properties of the itinerant-FM Q2D metal with theoretical predictions.²¹

Finally, the large range of temperatures for which pressurized Ca_2RuO_4 exhibits a nonmetallic ρ_c is of interest. In $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, for $0.5 < x < 1.5$ where the octahedra are rotated but not tilted, nonmetallic $\rho_c(T)$ is also seen over a wide temperature range, while Sr_2RuO_4 , having nonrotated octahedra, exhibits metallic ρ_c below 130 K. We therefore suspect that the rotational distortion affects not only the magnetic properties but also the two dimensionality in the electronic transport in the metallic phase.

In conclusion, high-purity Ca_2RuO_4 is a $4d$ system that at 0.5 GPa has a transition from a Mott insulating state to a

metal with a FM ground state. The P - T phase diagram of this system is unique and quite different from that of the doped system.^{3,19} Furthermore, our results suggest the existence of a FM quantum critical point at pressures above 10 GPa. We thus have strong interest in measurements at higher pressures as a crucial test of the connection between the p -wave superconductivity of Sr_2RuO_4 , and the ferromagnetism of metallic Ca_2RuO_4 .

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