# Anisotropic giant magnetoresistance near the Mott transition in pressurized $Ca_2RuO_4$

Fumihiko Nakamura, Ryuji Nakai, Tetsuo Takemoto, Mariko Sakaki, and Takashi Suzuki
*Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8530, Japan*

Patricia Lebre Alireza
*Cavendish Laboratory, University of Cambridge, JJ Thomson Avenue, CB3 OHE Cambridge, United Kingdom*

Satoru Nakatsuji
*Institute for Solid State Physics, University of Tokyo, Kashiwa 277-8581, Japan*

Yoshiteru Maeno
*Department of Physics, Kyoto University, Kyoto 606-8502, Japan*
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We have observed an anisotropic and giant magnetoresistance (MR) in the 4*d*-electron Mott transition system of $Ca_2RuO_4$. On the border of the Mott transition (~2 GPa), the MR effect at ~10 T reaches ~ −55% at $T_C$ for longitudinal and ~+120% at low temperatures for the transverse effects. The negative MR is most likely interpreted as a reduction in a ferromagnetic (FM) fluctuation at $T_C$. In contrast, the large positive effect is actually rare and is characteristic of the mixed state where the FM metallic islands are flecked with the insulating phases. We discuss the reason of the peculiar MR from the viewpoint of the "anisotropic magnetism," the "tunnel MR," and the "orbital physics."

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To explore novel quantum phenomena such as unconventional superconductivity (SC), itinerant magnetism, and large magnetoresistance (MR) effect, is one of the most important and interesting subjects in condensed matter physics.[1] It is known that transition-metal compounds in the vicinity of a Mott transition exhibit a rich variety of quantum phenomena caused by strong coupling with orbital degrees of freedom, charge and spin.[2] As seen in the discovery of anomalous metal such as the high-$T_C$ cuprates and the manganites, there has been a growing interest in the Mott transition, which is known as a dramatic and fundamental many-body effect in itself. Most of the previous work on the Mott transition has been confined to 3*d* transition-metal systems. In particular, there has been growing recognition of a large decrease of MR so-called the colossal magnetoresistance.[3]

In contrast, 4*d* metal-nonmetal systems are actually rare since 4*d* orbitals are generally more extended than 3*d* ones, giving rise naturally to wide bandwidths *W*. Moreover, the orbital angular momentum of 4*d* electron is not entirely quenched.[4] That is, the magnetic and electronic properties are more sensitive to coupling with spin, charge and the orbital degrees of freedom. We thus expect a peculiar Mott transition in 4*d* transition-metal systems. Much attention has been paid for a Mott transition system in ruthenates with perovskite-type structure. In particular, single-layered ruthenates ($Ru^{4+}$ $4d^4$) display versatile quantum phenomena, ranging from an antiferromagnetic (AFM) Mott insulator to a ferromagnetic (FM) metal, as well as SC. As well known, $Sr_2RuO_4$ shows the spin-triplet SC.[5] In contrast, $Ca_2RuO_4$ (CRO), which has a larger $U/W$ than $Sr_2RuO_4$, is a Mott insulator with an AFM ground state.[6] The solid solution system $Ca_{2-x}Sr_xRuO_4$ shows a complex phase diagram with a peculiar Mott transition.[7] Isoelectric substitution of Sr by Ca is, thus, an effective and convenient method to control $U/W$ over a wide range through tuning the $RuO_6$-octahedral distortions of flattening, tilt and rotation.[8] In particular, the Mott-type nonmetal-metal transition is accompanied by a first-order structural transition from S-Pbca with flatted octahedron (Ru-O distance along *c* is shorter than that perpendicular to *c*) into L-Pbca with nonflatted one (Ru-O distance perpendicular to *c* is longer than that along *c*). That is, the nonmetal-metal transition is strongly related to expanding the Ru-O distance along *c*.

In contrast, pressure, *P*, phase diagram is quite unique and different from that of the substituted system. We reported that pressurization of CRO transforms it from an AFM insulator to a quasi-two-dimensional metal with a FM ground state.[9,10] The intrinsic FM ground state thus appears only in the pressurized system. Our magnetization measurements[10] indicate that the FM has several features of an itinerant magnetism:[11] first, $M_{rem} \sim 0.35\mu_B$ at 1.5 GPa is much smaller than the saturated moment of 2 $\mu_B$ of localized $Ru^{4+}$ ion, second, magnetization is not easily saturated with applied magnetic fields up to 5 T, and lastly, a ratio of $p_{eff}/M_{rem} \sim 5$ is much larger than the 1 of localized systems.

Here, noteworthy is that there exists a mixed state in the pressure range $0.5 < P < \sim 2$ GPa where the FM shows itinerant nature in spite of nonmetallic *T* dependence of resistivity.[10] Indeed, two characteristic changes in $\rho_{ab}(T)$ were observed in CRO pressurized from 0.8 to ~2 GPa. First, the metallic $\rho_{ab}$ ($d\rho_{ab}/dT > 0$) jumps discontinuously and then turns into nonmetallic one ($d\rho_{ab}/dT < 0$). With pressurization, the metal-nonmetal transition temperature ($T_{MIT}$) is suppressed, and is killed above ~2 GPa. Second, CRO pressurized above 0.8 GPa shows a drop in $\rho_{ab}(T)$ at around $T_C$ determined by magnetization measurement. Such a drop in $\rho_{ab}(T)$ at $T_C$ is most likely understood as magnetic scattering reduced by a FM ordering. Moreover, our high-*P* diffraction study[12] indicates that the structural phase separa-

 

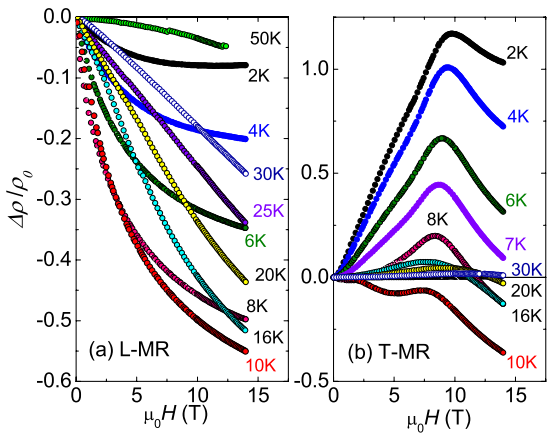


FIG. 1. (Color online) The longitudinal (a) and the transverse (b) MR up to 14 T at 1.9 GPa and several fixed $T$. The L-MR is negative in the whole temperature and field ranges we measured. The T-MR shows a positive MR reaching ~+120% at ~9.5 T and 2 K.

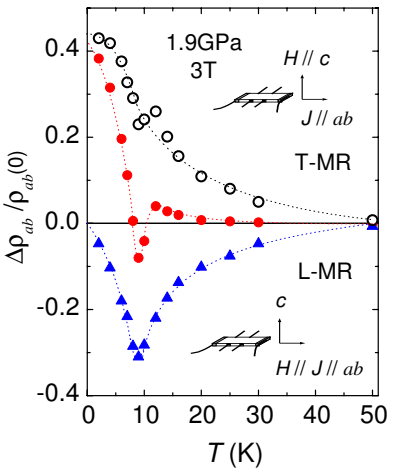


FIG. 2. (Color online) Anisotropic MR at 3 T and 1.9 GPa plotted against $T$, where (blue) triangle is the L-MR, (red) closed circle is the T-MR, open circle is reminder of subtraction of L-MR from T-MR. The dotted lines are guides to the eyes.

tion of L- and S-Pbca has been observed in the vicinity of the Mott transition at ~0.5 GPa.

Single-crystals $Ca_2RuO_4$ with an essentially stoichiometric oxygen content[6] were grown by a floating-zone method. Resistivity was measured by a standard four-probe method under $P$ up to 4 GPa and fields up to 14 T by using a physical properties measurement system (Quantum Design, model PPMS) equipped with a homemade nonmagnetic clamp-piston-cylinder cell. Our $P$ cell uses a compound design with the MP35N alloy inner cylinder and outer sleeve. Pressures were generated with Daphne oil 7243 (Idemitsu Kosan Co., Ltd.) as a $P$-transmitting medium.[13]

We have measured in-plane magnetoresistance MR $\{\Delta\rho_{ab}/\rho_{ab}=[\rho_{ab}(\mu_0 H)-\rho_{ab}(0)]/\rho_{ab}(0)\}$ up to 14 T for CRO pressurized at 1.9 GPa. The longitudinal (L-MR: $J\|\mu_0 H\perp c$) and the transverse MR (T-MR: $J\perp\mu_0 H\|c$) at several fixed temperatures between 50 and 2 K are plotted against magnetic fields in Figs. 1(a) and 1(b), respectively. Application of $\mu_0 H$ up to 14 T enlarges the L-MR negatively and monotonically over the whole $T$ range we measured. On heating from 2 K, the amplitude of the negative L-MR continues to rise from −7% at 2 K and 14 T, reaching a maximum of −55% at 10 K of $T_C$, then it turns to decrease. Moreover, the negative L-MR curve turns from concave to convex one in the vicinity of $T_C\sim 10$ K. It can, thus, be seen that the negative MR effect becomes remarkable at $T_C$.

On the contrary, the $\mu_0 H$ variation in the T-MR is mainly positive but relatively complicated $\mu_0 H$ and $T$ variations. At 2 K, the T-MR rises positively and monotonically, peaking at the maximum of ~+120% in 9.7 T, and then it turns to reduce. We note that the value of ~+120% at 2 K and 1.9 GPa is the largest effect in the $T$ and $P$ ranges we measured. Such a large MR is actually rare among positive than negative effect. With $T$, however, the amplitude of the positive T-MR reduces, and then the sign turns from positive to negative in the vicinity of $T_C$. Above 30 K the amplitude becomes quite small, similar to the L-MR. The characteristic peaks were observed at fields of 9.7, 9.4, 8.9, 8.6, 8.4, and 7.4 T for $T$=2, 4, 6, 7, 8, and 10 K, respectively. Thus, the peak decreases gradually and vanishes suddenly above 10 K of $T_C$. Thus, the peak nature is most probably related to the FM ordering.

In order to display the complicated MR nature intelligibly, the changes of L- and T-MR at 3 T are plotted as a function of $T$ in Fig. 2. With reducing $T$ from 50 K, the L-MR enlarges negatively, reaching a peak of ~−30% in the vicinity of $T_C\sim 10$ K, then it decreases rapidly toward zero at absolute zero. Qualitatively similar $\mu_0 H$ and $T$ variations in L-MR can be seen in a typical FM metal such as nickel in the vicinity of $T_C$.[14,15] This behavior is interpreted in terms of a change in the FM spin fluctuation, which is suppressed in the vicinity of $T_C$ with magnetic fields. We can, therefore, understand the observed nature of L-MR as a typical FM behavior near $T_C$.

In contrast, the T-MR nature, especially $T$ dependence, remains puzzling. On cooling from 50 K, the T-MR increasing positively and weakly dips suddenly into the negative value of ~−8% on the border of $T_C$. Below $T_C$ it rises again toward ~−40% at 2 K.

On the analogy of MR of nickel, the negative dip at $\sim T_C$ appears naturally in both T- and L-MR.[14,15] That is, the dip in the T-MR is most likely due to the same origin as seen in the L-MR. It is generally known that a resistance caused by magnetic scattering obeys the Matthiessen rule; therefore, the T-MR excluding the FM fluctuation effect is obtained after subtraction of the L-MR from the observed T-MR as is shown in Fig. 2 (open circle). We can understand the transverse effect is composed of two independent contributions: the one due to magnetic scattering near $T_C$ and intrinsically positive one.

To obtain further information of the positive effect, we examined the influence of $\mu_0 H\|c$ on the $\rho_{ab}(T)$. Figure 3 shows $\rho_{ab}(T)$ curves in several fixed $\mu_0 H\|c$ at 0.8 GPa. The $\rho_{ab}(T)$ curves show nonmetallic increase below $T_{MIT}$ ~230 K. The zero field $\rho_{ab}(T)$ curve peaks at $T_C\sim 10$ K, then it decreases monotonically as indicating a metal-like dependence. On the contrary, application of $\mu_0 H\|c$ induces a low-$T$ upturn (10 T), and then it kills the metallic decrease (14 T).

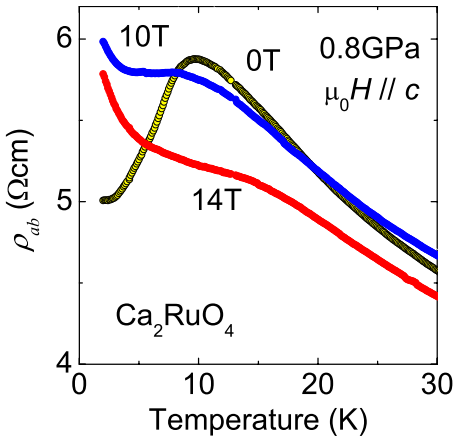


FIG. 3. (Color online) $T$-variation of $\rho_{ab}$ at 0.8 GPa in several fixed $\mu_0 H$ along $c$. The low-$T$ drop in $\rho_{ab}(T)$ is suppressed by applying $\mu_0 H \| c \geq 10$ T.

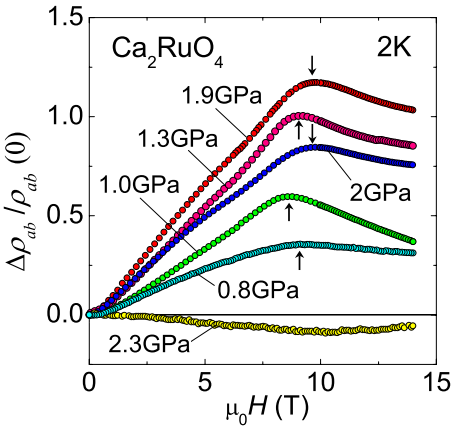


FIG. 4. (Color online) At 2 K the $\rho_{ab}(\mu_0 H \| c)$ (T-MR) measured in several fixed pressures. The T-MR curves below 2.3 GPa peaks at the characteristic fields, which are indicated by allows, are 9.1, 8.7, 9.2, 9.6, and 9.7 T at 0.8, 1, 1.3, 1.8, and 2 GPa, respectively.

Let us consider the reason why application of $\mu_0 H \| c$ only causes the characteristic changes in the resistivity. We infer that the characteristic MR nature is due to a change in the magnetization, namely, the magnetic scattering. Indeed, the characteristic MR has mainly been observed in the FM state only.

Recently we show that the FM moment is strongly anisotropic; that is, the $c$ axis is the hard direction.[11] A comparison of the anisotropic magnetization processes at 2 K and 1.8 GPa gives us $\mu_0 H_A \sim 9.5$ T of the anisotropy field, at which the direction of the spin orientation is forced from the $a$ to the $c$ axis by applying $\mu_0 H \| c$.[16] Here we note that $\mu_0 H_A \sim 9.5$ T corresponds to the peak field of the T-MR. Indeed, a change in MR at $\mu_0 H_A$ has often been reported as a characteristic nature of a ferromagnet. That is, a rotation of FM moment is known as a factor for a change in MR.[17]

In our T-MR case, the current and fields are applied perpendicular and parallel to the hard direction of the $c$ axis, respectively. With applying $\mu_0 H \| c$, the angle between the magnetized and the current directions initially increases, then it becomes a right angle above $\mu_0 H_A$. At $\mu_0 H_A$, such a change in magnetization is naturally reflected in the T-MR. In contrast, the L-MR shows no characteristic change because the application of $\mu_0 H \perp c$ induces no characteristic change in the FM moment. It, thus, can be seen that the anisotropic MR is interpreted in terms of anisotropic magnetization, namely, spin flop induced by fields applied to the hard direction of $c$.

However, there remains a question why the T-MR shows positive and giant MR effect. We can fully expect that our finding of the positive and giant MR effect is interpreted in terms of the tunnel MR effect although there is no direct evidence to confirm this so far. It is known that the tunnel MR effect, which can often cause a large and positive MR, occurs in magnetic tunnel junctions consisting of ferromagnet isolated by thin insulators. Electron tunnelling between the isolated FM islands can occur in the case that the insulating layer is thin enough. Moreover, an angle dependence of MR is known as a characteristic behavior of the tunnel MR.

In the pressurized CRO, the FM metallic phase is induced and enlarged by pressurizing above 0.5 GPa, then it is dominant above 1.5 GPa. Indeed, the linear extrapolation of pressuring the S-Pbca volume fraction vs $P$ suggests that the S-Pbca insulating phase is almost killed by $P \gtrsim 1.5$ GPa. Moreover, pressurization above $\sim$1.5 GPa kills $T_N$ and makes it possible to reach the remnant FM moment as a bulk system (the FM moment is almost constant above $\sim$1.6 GPa), as indicated by our magnetization[10] and $\mu$SR studies.[18] However, the resistivity still shows a nonmetallic $T$ dependence even above $\sim$1.5 GPa. These mean that there exist many of the FM metallic islands separated by the thin insulating layers in the mixed state. Moreover, we can fully expect that the magnetic tunnel junctions are naturally formed in the mixed state.

As shown in Fig. 4, with pressurizing above 0.5 GPa the positive and giant MR effect is initially enlarged, reaching a maximum value of $\sim$+120% at 1.9 GPa, then reduces rapidly and vanishes in the metallic state above $\sim$2.3 GPa. Thus, the positive MR effect is characteristic of in the mixed state. We, therefore, infer that the positive MR is due to the tunnel MR effect, namely the tunnel junctions consisting of the FM metallic islands (L-Pbca) isolated each other by the thin insulating layers (S-Pbca). The tunnel MR effect is actually a strong candidate for the mechanism of the peculiar MR in the mixed state, but it is not enough for full understanding of our observed MR effect.

As another factor enlarging MR, we should discuss the "orbital physics," which is proposed to understand the peculiar properties of Ru214 in the vicinity of Mott transition, specially the "orbital-selective Mott transition."[4,7,19] We focus on two evidences indicating importance of strong coupling with spin, charge, and the orbital degrees of freedom. First, we pay attention to the value of $\mu_0 H_A$, which is known as an indication of spin-orbit coupling. $\mu_0 H_A \sim 9.5$ T is one of the largest values as a $d$ electron ferromagnet. Even for a typical anisotropic ferromagnet of Co with $\mu_0 H_A \sim 1$ T, the orbital angular momentum plays a key role to understand the strong magnetic anisotropy. Thus, importance of the "orbital physics" is demonstrated by the strongly anisotropic ferromagnetism of the pressurized CRO.

Second, we note that the large negative MR is not limited in the mixed state. The negative L-MR reaching $\gtrsim -50\%$ have been observed in the paramagnetic region above $T_C$ and the metallic state above 2.3 GPa. It is known that MR in 3*d* FM metals shows the qualitatively similar $T$ and $\mu_0 H$ dependences, especially negative dip in the vicinity of $T_C$ although the amplitude of MR is a few percent at the most.[14] The amplitude of the MR in CRO is too large to explain in terms of simple magnetic scattering as is the case with 3*d* FM metals. We deduce that the orbital physics, namely strong spin-orbit coupling, amplifies the MR due to magnetic scattering.

We summarize several attractive findings in an anisotropic and giant MR effect in the $P$ induced Mott transition system of CRO as follows: first, the $T$ variation in both T-MR and L-MR shows a negative dip near $T_C$. The dip nature is qualitatively understood as a change in magnetic fluctuation as is also seen in typical FM metals. Second, concern has been paid to the positive T-MR peaking at $\mu_0 H_A \sim 9.5$ T and reaching $\sim +120\%$. Such a giant positive effect, which is actually rare in bulk system, is characteristic of the mixed state; therefore, this is due to the magnetic tunnelling between the FM islands isolated by the thin insulating layers. Lastly, we propose the importance of the orbital physics as another key factor for amplifying the MR effect. Indeed, this is clearly indicated by the largeness of the anisotropy field of 9.5 T.

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