Control of the electronic states of Ca$_2$RuO$_4$ by uniaxial pressure

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Abstract. We study the uniaxial pressure effect on the Mott insulator Ca$_2$RuO$_4$. It is known that the crystal structure is a crucial parameter to determine the electronic states in this system. We revealed that a metal-insulator (M-I) transition is induced by the uniaxial pressure along the ab-plane at room temperature and the metallic state is sustained under cooling down to 5 K. In contrast, such a transition to a metallic state is not observed by the uniaxial pressure along the c-axis. Our experimental results suggest that the elongation of the RuO$_6$ octahedra along the c-axis can trigger the M-I transition.

1. Introduction

Recently, there has been growing interest in the varieties of the electronic states in the layered perovskite ruthenates. It is known that the single-layered ruthenate Sr$_2$RuO$_4$ with the 4d conduction electrons exhibits spin-triplet superconductivity below 1.5 K [1]. Moreover, the isovalent substitution of Sr with Ca changes a quasi-2D superconductor (Sr$_2$RuO$_4$) into a Mott insulator with an antiferromagnetic order (Ca$_2$RuO$_4$). Both Sr$_2$RuO$_4$ and Ca$_2$RuO$_4$ have the layered perovskite structure containing RuO$_6$ octahedra. In Ca$_2$RuO$_4$, the RuO$_6$ octahedra are flattened along c-axis, in addition to tilted and rotated. Previous experimental results suggest that these distortions of RuO$_6$ octahedra are strongly related to the electronic states. For example, the M-I transition is induced either by hydrostatic pressure of 0.5 GPa, by substitution of Sr for Ca, or by an electric field [2, 3, 4]; all of these M-I transitions are accompanied by structural transitions: RuO$_6$ octahedra in the crystal are elongated along the c-axis in the metallic state, while they are flattened in the insulating state [5, 6]. Application of uniaxial pressure is expected to be a useful method of controlling the electronic states because RuO$_6$ distortions, especially its flattening and stretching can be more effectively controlled by uniaxial pressure than hydrostatic pressure.

In addition, it was recently revealed that Ca$_2$RuO$_4$ exhibits superconductivity under hydrostatic pressure of about 10 GPa [7]. This superconductivity in Ca$_2$RuO$_4$ might be spin-triplet as well, because the ferromagnetic phase is located next to the superconducting phase. It is very interesting to investigate whether we can induce superconductivity by applying uniaxial pressure as well.
2. Experimental

For uniaxial pressure application, we use a piston-cylinder type pressure cell with spring washers. By making use of the fact that the cylinder is made of insulating plastic, we utilize the pistons made of CuBe as electrodes. Thus, the present results are obtained with a quasi-four-wire method. For the measurement at room temperature, we applied a DC current of 0.1–1.0 mA and the current direction is reverted in order to cancel the thermoelectric voltage. For the measurement of the temperature dependence, we adopted an AC method with AC current of 0.01–0.5 mA and 7 Hz. We used single crystals of Ca$_2$RuO$_4$ grown by a floating zone method. In order to apply pressure homogeneously with the ab-plane, the two planes perpendicular to the pressure are polished to be parallel to each other. The side surfaces of a crystal are covered by Stycast 1266 to prevent the crystal from being cleaved by pressure. In addition, the top surfaces are covered by indium to realize good electrical conductivity between the sample and piston. In contrast, for pressure along the c-axis, the side and top surfaces of a crystal was not covered by anything.

3. Results and Discussion

We present the uniaxial pressure dependence of the resistance at room temperature for $P \parallel ab$ in Fig. 1 and $P \parallel c$ in Fig. 2. For $P \parallel ab$, we observed a sharp drop of the in-plane resistance $R_{ab}$ by three orders of magnitude at around 1.5 GPa. We measured its temperature dependence at 1.8 GPa down to 4 K and found it to be metallic as shown in Fig. 3. We conclude that the resistance drop at around 1.5 GPa reflects a M-I transition, on the basis of the following two considerations. First, our sample would be insulating below 1.4 GPa because the estimated resistivity value at room temperature is consistent with those of insulating samples [2, 8]. Second, inspection under microscope as well as the increase of the resistance after releasing $P \parallel ab$ exclude the possibility of formation of metallic path by indium. We note that the initial drop of resistance from 0 GPa to 0.2 GPa is attributed to an improvement of the contact resistance between the sample and the piston, and thus this is not intrinsic.

![Figure 1](image1.png)  \hspace{1cm} ![Figure 2](image2.png)

**Figure 1.** Uniaxial pressure dependence of the resistance at room temperature for $P \parallel ab$.

**Figure 2.** Uniaxial pressure dependence of the resistance at room temperature for $P \parallel c$.

In contrast, for $P \parallel c$ we did not observe any sharp drop of the c-axis resistance $R_c$ as shown in Fig. 2. In addition, metallic temperature dependence of $R_c$ was not observed in the present pressure range up to 2.5 GPa as shown in Fig. 4. We note that in the insulating state the resistance value $R_{ab}$ for $P \parallel ab$ (Fig. 1) is greater than $R_c$ for $P \parallel c$. This is mainly due to the difference in sample size and shape, not to the difference in contact resistance.
Let us comment on the possibility that the sample is in a two-dimensional (2D) metallic state, in which only the in-plane transport is metallic. Indeed, in the hydrostatic pressure experiments, it was reported that the c-axis resistivity $\rho_c$ exhibits a non-metallic temperature dependence even in the metallic phase [2]. However, in Ref. [2], the M-I transition was clearly observed in the pressure dependence of $\rho_c$ at room temperature and the non-metallic behavior of $\rho_c(T)$ in the 2D metallic state was rather weak. Thus, our findings, a rapid non-metallic increase of $R_c(T)$ and the absence of a sharp drop of $R_c(P \parallel c)$, suggest that the sample is still insulating for all directions.

The variation between 300 K and 100 K is fitted well with activation-type insulating behavior as shown in Fig. 4,

$$R_c = R_0 \exp \left( \frac{\Delta}{2k_B T} \right)$$

(1)
giving $\Delta \approx 600$ K. This gap size is substantially smaller than that obtained from in-plane resistivity at ambient pressure, $\Delta \approx 4500$ K [8]. The resistance below 100 K cannot be fitted with the activation-type behavior, eq. (1), and exhibits a much weaker divergence.

Naively, it is expected that $P \parallel ab$ releases the flattening of the RuO$_6$ octahedra along c-axis and induces the M-I transition, whereas $P \parallel c$ enhances the flattening and does not induce M-I transition. Aside from the tendency of gap closing even for $P \parallel c$, the present observation agrees with this general expectation. Thus our results provide a clear demonstration that one can control the electronic states of Ca$_2$RuO$_4$ using uniaxial pressure.

The pressure value at which the M-I transition occurs under $P \parallel ab$ is greater than the one under hydrostatic pressure [2]. There are two possible reasons. One is that the distortion within the ab-plane is isotropic under hydrostatic pressure while it is anisotropic under uniaxial pressure. Thus, for example, if uniaxial pressure is along the a-axis, RuO$_6$ is elongated along the b-axis, as well as along the c-axis, and this in-plane elongation may suppress the M-I transition. The second possible reason is that the pressure value may not be estimated accurately; presence of stycast and indium may have led to an over-estimation of the pressure value.

In the future, investigation of the in-plane anisotropy of the uniaxial pressure effect, namely the difference between $P \parallel (100)$ along the in-plane Ru-O bonding and $P \parallel (110)$...
is worth studying. Such different pressure directions may cause quantitatively different in-plane distortions. (Here we use the notation for the tetragonal I4/mmm lattice.) Of course, clarification of the ground state characteristics under such uniaxial pressures is also important.

4. Conclusion
We revealed that M-I transition of the Mott insulator Ca$_2$RuO$_4$ occurs under the in-plane uniaxial pressure of 1.5 GPa, and does not occur under uniaxial pressure along the $c$-axis of at least up to 2.5 GPa. These observations suggest that the elongation of RuO$_6$ octahedra along the $c$-axis is a trigger of this M-I transition.

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