

Anomalous Thermoelectric Response in an Orbital-Ordered Oxide Near and Far from Equilibrium

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We report the thermoelectric transport properties in the orbital-ordered Mott insulating phase of Ca_2RuO_4 close to and far from equilibrium. Near equilibrium conditions where the temperature gradient is only applied to the sample, an insulating but non-monotonic temperature variation of the Seebeck coefficient is observed, which is accounted for in terms of a temperature-induced suppression of the orbital order. In non-equilibrium conditions where we have applied high electrical currents, we find that the Seebeck coefficient is anomalously increased in magnitude with increasing external current. The present result clearly demonstrates a non-thermal effect since the heating simply causes a decrease of the Seebeck coefficient, implying a non-trivial non-equilibrium effect such as a modification of the spin and orbital state in currents.

Understanding various phenomena arising from interplayed spin and orbital degrees of freedom in correlated electrons, such as high- T_c superconductivity and colossal magnetoresistance, is a central topic in contemporary condensed matter physics.¹⁾ Recently, it also becomes a challenging issue to explore how such an electronic state is changed in non-equilibrium situations,^{2,3)} which are realized under laser irradiations⁴⁾ or by applying high electric fields.⁵⁾ Intriguingly, the photo-induced or field-induced state might be essentially distinguished from thermally-excited one,⁶⁻⁹⁾ stimulating further investigation for an inherent non-equilibrium property of correlated electrons.

The Mott insulator Ca_2RuO_4 ^{10,11)} offers a unique playground to study the non-equilibrium effect on correlated electron systems. In equilibrium, this compound exhibits a first-order metal-insulator transition at $T_{\text{MI}} \simeq 360 \text{ K}$ ¹²⁾ and an antiferromagnetic transition at $T_N = 110 \text{ K}$. The optical conductivity,¹³⁾ resonant x-ray¹⁴⁾ and perturbed angular correlation¹⁵⁾ experiments have revealed that a ferro-type d_{xy} orbital ordering is realized below T_{MI} , as is expected from flattening of the RuO_6 octahedra at low temperatures,¹⁶⁻¹⁹⁾ while different orbital patterns are also suggested.²⁰⁻²²⁾ Recently, Nakamura *et al.* reported that this compound exhibits an electric-field-induced insulator-to-metal transition at $E_{\text{th}} \sim 40 \text{ V/cm}$ at room temperature,²³⁾ which is very low threshold field compared with that for Zener and avalanche breakdown.²⁴⁾ The subsequent experiment using a non-contact infrared thermometer has revealed that, although it does not reach the transition point, the nonlinear conduction indeed occurs in the isothermal environments below E_{th} ,²⁵⁾ indicating a novel non-equilibrium state in this system.

In this paper, we investigate how the non-equilibrium parameter affects the orbital ordering phase of Ca_2RuO_4 by means of thermoelectric transport measurement near and far from equilibrium. The Seebeck coefficient studied here is a powerful probe to clarify the electronic state^{26,27)} including the spin and orbital nature of correlated electrons.^{28,29)} First

we show the Seebeck coefficient measured without applying external currents. The temperature variation is found to be insulating but non-monotonic, which is qualitatively explained by the suppression of the orbital ordering with heating. In non-equilibrium, we have measured the Seebeck coefficient with applying currents, and find that the absolute value of the Seebeck coefficient is surprisingly increased with increasing currents. Since the heating leads to a decrease of the Seebeck coefficient, the present result clearly shows an inherent non-equilibrium effect, which we suggest to be attributed to a current-induced quenching of the spin and orbital degrees of freedom of the Ru $4d$ electrons.

The experiments were performed using Ca_2RuO_4 single crystals with typical sample dimensions of $2 \times 2 \times 0.2 \text{ mm}^3$ grown by a floating-zone method.³⁰⁾ Near equilibrium condition, the Seebeck coefficient was measured with a conventional steady-state method using a copper-constantan differential thermocouple from 360 down to 180 K in an electrical furnace and a liquid helium cryostat. In the present experiments, the sample temperature was kept below T_{MI} because it is highly probable that the crystal will be broken owing to the large structural change at T_{MI} .¹⁷⁾ The experimental setup in the non-equilibrium condition is schematically shown in Fig. 1(a). The temperature gradient ∇T ($\parallel ab$ planes) is controlled by using two Peltier modules, the gap of which was bridged with a sapphire plate. The sample is fixed on the sapphire using varnish and its temperature gradient is measured by a non-contact infrared thermography (InfReC R300, Nippon Avionics). This method is highly advantageous to directly measure the temperature without additional heat capacity and contact thermal resistance of conventional contact-type thermometers.²⁵⁾ The four electrical contacts were carefully made with a gold deposition technique to reduce the contact resistance.

In the present thermoelectric measurement in the external current I , the measured voltage V is expressed as

$$V = V_R + V_{\text{th}} + V_0 = R(I)I + S(I)\Delta T + V_0, \quad (1)$$

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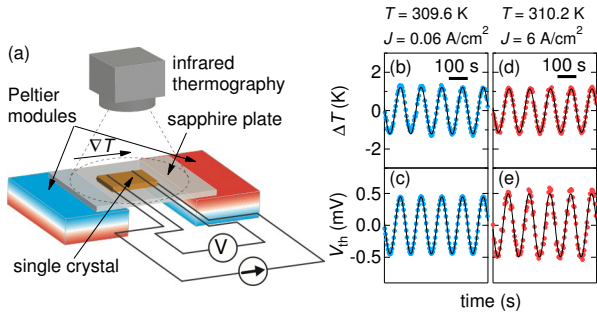


Fig. 1. (Color online). (a) Schematic figure of the experimental configuration for measurements of the Seebeck effect in non-equilibrium. The temperature gradient ∇T is controlled by using two Peltier modules, which are bridged with a sapphire plate. The single crystal is fixed on the sapphire and the temperature gradient is directly measured by an infrared thermography. The right panels display the time variations of (b,d) the temperature difference between the voltage contacts ΔT and (c,e) the thermoelectric voltage V_{th} for (b,c) low and (d,e) high current densities. The solid curves show the sinusoidal fitting results.

where $R(I)$ and $S(I)$ are current-dependent resistance and Seebeck coefficient, respectively, ΔT is the temperature difference between the voltage contacts, and V_0 is an extrinsic offset term. Since the resistive voltage V_R is much larger than the thermoelectric one V_{th} in currents, we used a double ac method as follows: By applying ac current with a rectangular waveform (2.5 Hz), we obtain $R = V_R/I = (V_+ - V_-)/2I$ and $V_{th} + V_0 = (V_+ + V_-)/2$, where V_+ (V_-) is the measured voltage with applying current for positive (negative) direction. We further vary the temperature difference with a slow sinusoidal waveform (0.01 Hz) as shown in Fig. 1(b,d). Correspondingly the thermoelectric voltage oscillates with the same waveform as seen in Fig. 1(c,e), in which the offset contribution is subtracted, and then $S(I)$ is calculated from the amplitudes in these oscillations.

We first discuss the thermoelectric transport near equilibrium. Figure 2(a) depicts the temperature dependence of the Seebeck coefficient measured with applying no external current. The Seebeck coefficient with positive sign decreases in magnitude with increasing temperature. We find that, above around 270 K, the Seebeck coefficient is more strongly suppressed than that expected from the non-degenerate formula $S(T) = \frac{k_B}{e} \frac{\Delta}{k_B T}$, where k_B is the Boltzmann constant, e is the elementary charge, and Δ is an energy gap measured from the valence-band top to the Fermi level. This anomaly is clearly seen in a plot of ST as a function of T shown in the upper right inset of Fig. 2(a), in which ST deviates from a constant value above 270 K.

To clarify an origin of the anomalous suppression of the Seebeck coefficient toward T_{MI} , we have measured the Hall effect because the Seebeck coefficient is often discussed in terms of the carrier concentration.²⁶⁾ The Hall resistivity ρ_{yx} exhibits a linear H dependence up to $\mu_0 H = 7$ T (not shown), and we obtain the carrier concentration $n = e^{-1} R_H^{-1}$. Note that the Hall coefficient $R_H = d\rho_{yx}/d(\mu_0 H)$ is positive, as is indicated from the positive Seebeck coefficient shown in Fig. 2(a). Here we plot S and $\ln n$ as a function of T^{-1} in Fig. 2(b) for comparison. In non-degenerate semiconductors, the Seebeck coefficient is related to n as $S(T) = \frac{k_B}{e} \frac{\Delta}{k_B T} = \frac{k_B}{e} \ln(\frac{N_V}{n})$, where

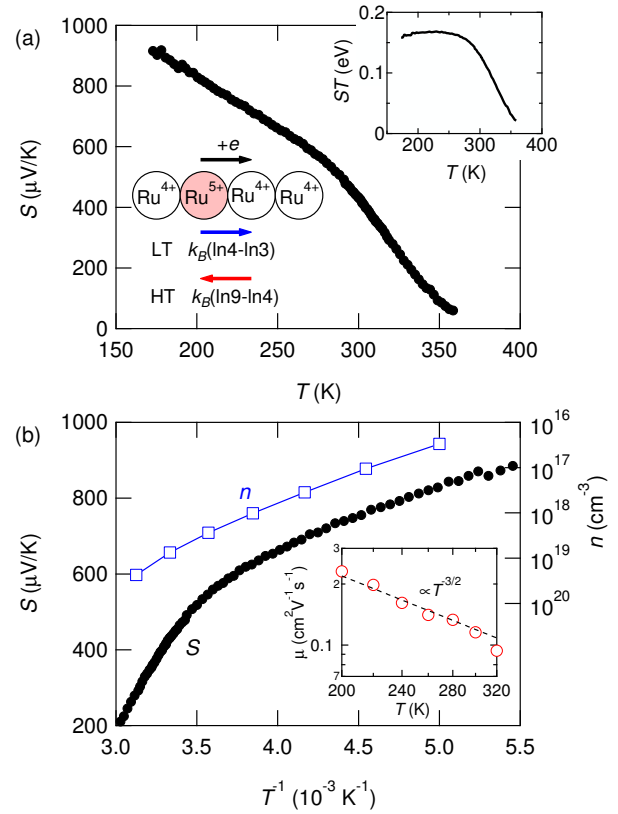


Fig. 2. (Color online). (a) The Seebeck coefficient S measured with applying no electrical current as a function of temperature T . The upper right inset shows ST as a function of T . The lower left inset is a schematic illustration of the carrier transport. At low temperatures the hole carries a positive entropy of $k_B \ln(4/3)$, while it flows with a negative entropy of $k_B \ln(4/9)$ at high temperatures. For details see text. (b) S (black circles, left axis) and the carrier concentration n (blue squares, right axis) as a function of T^{-1} . The inset is a log-log plot for the temperature variation of mobility μ . The dashed line represents a $T^{-3/2}$ dependence.

N_V is the effective density of states in the valence band. In the present case, while $S(T)$ is drastically suppressed and deviates from the T^{-1} dependence above around 270 K, $\ln n(T)$ varies almost linearly against T^{-1} even above 270 K. Thus this result shows that the anomalous temperature variation of the Seebeck coefficient does not stem from temperature variation of the carrier concentration. We note that the optical gap varies linearly with temperature as $\Delta(T) = \Delta_0 + aT$, where Δ_0 and a are temperature-independent constants, in the present temperature range.¹³⁾ Also, this is not the origin because in this case the formula is rewritten as $S(T) = \frac{k_B}{e} \frac{\Delta_0}{k_B T} + \frac{a}{e}$, which still shows a T^{-1} dependence.

Here we focus on the spin and orbital state in the orbital ordering phase, which affects the Seebeck coefficient through its degeneracy as discussed in several transition-metal oxides.^{31–33)} In a temperature range of $t \ll k_B T \ll U$, where t is the transfer energy (bandwidth) and U is the Coulomb interaction, the Seebeck coefficient is expressed as

$$S = -\frac{k_B}{e} \ln \left(\frac{g_{4+}}{g_{5+}} \frac{x}{1-x} \right), \quad (2)$$

known as an extended Heikes formula.²⁸⁾ Here g_{4+} and g_{5+} are the degeneracy of the electron configuration of Ru^{4+} and

Ru⁵⁺ sites, respectively, and $x = M/N_A$ (M is the number of Ru⁵⁺ sites and N_A is the total number of Ru sites) is the fraction of the Ru⁵⁺ ions, equal to the hole concentration per Ru site. Note that the measured temperature range of $T_N < T < T_{MI}$ may satisfy the temperature range valid for Eq. (2), since T_N can be scaled to t^2/U and T_{MI} to U . Also suggested that the Heikes formula still holds at low temperatures where $k_B T < t$.³⁴ Now $n = 10^{19} \text{ cm}^{-3}$ at $T \sim 310 \text{ K}$ corresponds to $x \approx 1 \times 10^{-3}$ holes per Ru atom, which is much less than unity. Thus Eq. (2) is reduced to

$$S = -\frac{k_B}{e} \ln x - \frac{k_B}{e} \ln \left(\frac{g_{4+}}{g_{5+}} \right). \quad (3)$$

The first term is positive and related to the hole concentration n . The second term, which shows the ratio of the entropy carried by a carrier to the charge, can take either positive or negative, depending on the degeneracy in the Ru sites.

The degeneracy of the Ru $4d$ electrons is summarized in Table I. Four and three $4d$ electrons in the t_{2g} manifolds lead to the spin magnitude (the spin degeneracy) of 1 ($g_{\text{spin}} = 3$) and $3/2$ ($g_{\text{spin}} = 4$) for Ru⁴⁺ and Ru⁵⁺ sites, respectively. Then we consider the orbital degeneracy g_{orbital} . For Ru⁴⁺ sites, at low temperatures (noted as LT in Table. I), the d_{xy} orbital is well ordered, meaning that the orbital degeneracy is completely quenched ($g_{\text{orbital}} = 1$). At high temperatures (HT), on the other hand, the d_{xy} orbital polarization is decreased with heating. This means that the orbital degeneracy *recovers* with increasing temperature toward T_{MI} and approaches to $g_{\text{orbital}} = 3$. Consequently, for Ru⁴⁺ sites, the total degeneracy $g_{\text{total}} = g_{\text{spin}} g_{\text{orbital}}$ increases from 3 to 9 with heating. For Ru⁵⁺ sites, g_{orbital} is always unity since three electrons occupy the lower Hubbard t_{2g} manifolds¹⁸) and then $g_{\text{total}} = 4$ holds in the entire temperature range. The degeneracy ratio of g_{4+}/g_{5+} thus varies from $3/4$ to $9/4$ with heating, and therefore the degeneracy term in Eq. (3) positively contributes to the Seebeck coefficient at low temperatures but negatively at high temperatures close to T_{MI} . This gives a qualitative explanation for the observed suppression of the Seebeck coefficient toward T_{MI} . Such a hole transport is schematically illustrated in the lower left inset of Fig. 2(a). It should be noted that the interference intensity in the resonant x-ray scattering technique, which represents the degree of d_{xy} orbital polarization, is reduced above around 220 K.¹⁴ This is close to the temperature above which the Seebeck coefficient deviates from the T^{-1} dependence in the present study.

We now examine the non-equilibrium current effect on the Seebeck coefficient. Figures 3(a) and 3(b) show temperature variations of the resistivity and the Seebeck coefficient measured with applying current density J using the setup shown in Fig. 1(a). The resistivity indeed decreases with increasing currents in the isothermal conditions, which has been suggested to be attributed to a current-induced energy-gap suppression.²⁵ There, the current acts as an injection of excess

quasiparticles, as proposed in non-equilibrium superconducting state³⁶) and charge ordering.³⁷) Note that the present field range is too small to drive the conventional Zener or avalanche breakdown phenomena.^{23,25}) Hot electron phenomenon, in which the electronic temperature $T_e \equiv \varepsilon_{\text{kin}}/k_B$ (ε_{kin} is the kinetic energy of electron) becomes larger than the lattice temperature T_l to produce the nonlinearity,²⁴) is also unlikely. In this compound, as shown in the inset of Fig. 2(b), the mobility $\mu = (ne\rho)^{-1}$ exhibits a $T^{-3/2}$ dependence, indicating that the acoustic phonon scattering is dominant. In this regime, the relaxation time depends on the energy as $\tau(\varepsilon) \propto \varepsilon^{-1/2}$. Thus an increase of T_e leads to a decrease of τ , and the conductivity decreases with increasing currents as observed in Si and Ge.³⁵) This model does not adapt the present result since the conductivity increases with currents in Ca₂RuO₄.

The most highlighted result is the current effect on the Seebeck coefficient shown in Fig. 3(b), because the Seebeck coefficient increases with currents, in total contrast to the thermal effect that reduces its magnitude. This is also distinguished from the results in other systems that exhibit the nonlinear conduction. In the charge-density-wave (CDW) materials, the sliding motion of depinned CDW causes a nonlinear conduction in fields.³⁸) There, both the resistivity and the Seebeck coefficient decrease with increasing fields,³⁹) in high contrast to the present study. Hot electron characterized by its large kinetic energy may enhance the Seebeck coefficient,⁴⁰) since the Seebeck coefficient measures the energy difference from the Fermi level to the electron energy as seen in its non-degenerate formula. The current-induced change in the Seebeck coefficient is given as $\Delta S \sim \frac{mJ^2}{e^3 n^2 T}$,⁴⁰) where m is the electron mass, yielding $\Delta S \sim 10^{-16} \text{ V/K}$ for Ca₂RuO₄ at $T = 300 \text{ K}$ and $J = 6 \text{ A/cm}^2$. This estimated value is much smaller than the change of $\sim 100 \mu\text{V/K}$ observed in the present study, again indicating that hot electron is not im-

Table I. Degeneracy of the electron configuration of the Ru sites.

	Ru ⁴⁺ (LT)	Ru ⁴⁺ (HT)	Ru ⁵⁺
g_{spin}	3	3	4
g_{orbital}	1	3	1
g_{total}	3	9	4

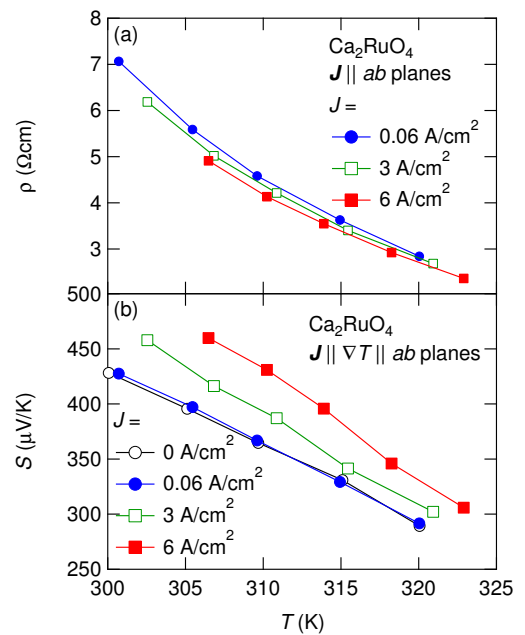


Fig. 3. (Color online). Temperature dependence of (a) the electrical resistivity ρ and (b) the Seebeck coefficient S measured with applying several current densities J .

portant in this system.

The present result of the Seebeck effect seems to be incompatible with the current-induced gap suppression suggested from the nonlinear resistivity measurement,²⁵⁾ since the gap reduction usually leads to the decrease of the Seebeck coefficient. Instead, we again consider the degeneracy of the Ru $4d$ electrons on the basis of the extended Heikes formula of Eq. (3). The first term is decreased when the energy gap is suppressed by currents, while the reduction is small due to the weak nonlinear conduction in this current range. We then focus on the second term. Now applying external current makes the system more metallic, indicating that the localized model for counting such a degeneracy becomes less effective with increasing currents. Therefore, in currents, the correlated hole with the degeneracy $g_{5+} = 4$ is regarded to flow among the itinerant Ru sites in which the spin and orbital degeneracy is quenched owing to the current-induced metallization. This picture is contrast to the conduction near equilibrium in which the hole flows among the localized Ru sites. In the itinerant model, the second term in Eq. (3) becomes a positive value of $+\frac{k_B}{e} \ln 4$. This is larger than the values near equilibrium, possibly contributing to the enhancement of the Seebeck coefficient far from equilibrium, while further microscopic investigation for clarifying the non-equilibrium spin and orbital state is required as a future study.

In summary, we report the anomalous thermoelectric transport in the orbital-ordered Mott insulating phase of Ca_2RuO_4 near and far from equilibrium. The Seebeck coefficient near equilibrium is qualitatively explained by the degeneracy of the spin and orbital state of Ru $4d$ electrons. Far from equilibrium, we find a non-trivial current-induced enhancement of the Seebeck coefficient in isothermal conditions, which is difficult to be explained by conventional mechanisms such as hot electron. We suggest a quenching of the spin and orbital degrees of freedom due to the current-induced metallization for understanding the observed non-equilibrium phenomena.

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