Effect of chemical and hydrostatic pressure on the cubic pyrochlore \( \text{Cd}_2\text{Ru}_2\text{O}_7 \)

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The cubic pyrochlore \( \text{Cd}_2\text{Ru}_2\text{O}_7 \) develops a metallic state below the antiferromagnetic transition at \( T_N \approx 90 \text{K} \), in contrast to the sharp transition to an insulating state below \( T_N \) of the 5d-analog \( \text{Cd}_2\text{Os}_2\text{O}_7 \). We have synthesized polycrystalline \( \text{Cd}_2\text{Ru}_2\text{O}_7 \) under high pressure, and investigated the responses of its electronic behavior to hydrostatic pressure and isovalent substitutions of \( \text{Ca}^{2+} \) for \( \text{Cd}^{2+} \). Three characteristic anomalies are identified in the electrical transport and magnetic properties of \( \text{Cd}_2\text{Ru}_2\text{O}_7 \), signaling an intimate correlation between charge and spin degrees of freedom. Interestingly, we found that the metallic state of \( \text{Cd}_2\text{Ru}_2\text{O}_7 \) below \( T_N \) is very fragile and can be suppressed by a small hydrostatic pressure of \( \leq 1 \text{GPa} \) or substitution of 5–10\% \( \text{Ca}^{2+} \) for \( \text{Cd}^{2+} \), resulting in a resistivity behavior similar to that of \( \text{Cd}_2\text{Os}_2\text{O}_7 \). In addition, the resultant insulating state below \( T_N \) is very robust against pressure, and the resistivity evolves gradually into two distinct activated regions under higher pressures. We constructed a temperature-pressure phase diagram for \( \text{Cd}_2\text{Ru}_2\text{O}_7 \) and discussed its peculiar metallic state in terms of the electronic itinerancy/localization dichotomy via side-by-side comparisons with the related compounds \( \text{A}_2\text{Ru}_2\text{O}_7 \) (\( \text{A} = \text{Ca}, \text{Hg} \)) and \( \text{Cd}_2\text{Os}_2\text{O}_7 \). Our results demonstrate that these cubic 4d/5d pyrochlore oxides offer an important paradigm for studying the exotic physics of correlated electrons on the border of (de)localization in the presence of strong geometrical frustration.

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I. INTRODUCTION

One challenging problem in strongly correlated electron systems is to understand the electronic behaviors near the localized to itinerant crossover, which lie at the heart of many exotic phenomena such as unconventional superconductivity, metal-insulator transition, and quantum criticality [1–3]. The Ru\(^{5+}\)-pyrochlore oxides \( \text{A}_2\text{Ru}_2\text{O}_7 \) (\( \text{A} = \text{Ca}, \text{Cd}, \text{Hg} \)) [4–7] with a divergent \( \text{A}^{2+} \) cation comprise such a system in which the Ru 4d electrons acquire the characteristics of both itinerancy and localization [8]. In particular, the magnetic Ru\(^{5+}\) (4d\(^3\)) ions that are situated on the vertices of a corner-shared tetrahedral lattice are subjected to strong geometrical frustration for antiferromagnetic (AF) interactions [8,9]. As such, the presence of both electronic dichotomy and strong geometrical frustration in these Ru\(^{5+}\)-pyrochlore oxides produces distinct ground states, which were found to vary sensitively as a function of the \( \text{A} \)-cation covalency on the order of \( \text{Ca} < \text{Cd} < \text{Hg} \) [8].

For \( \text{Ca}_2\text{Ru}_2\text{O}_7 \) with more ionic \( \text{Ca}^{2+} \), it forms a spin-glass magnetic state below \( T_f \approx 23 \text{K} \), as exemplified by the bifurcation of field-cooled (FC) and zero-field-cooled (ZFC) magnetic susceptibility [4,10]. The effective magnetic moment of \( \sim 0.36\mu_B/\text{Ru}^{5+} \) extracted from the Curie-Weiss fitting is one order lower than the expected value for localized \( S = 3/2 \). Although its resistivity in the whole temperature range takes relatively low values of 2–4 m\( \Omega \) cm typical for correlated metallic oxides, the observed semiconducting-like temperature dependence, \( d\rho/dT < 0 \), is contrary to a simple metallic behavior. No discernable anomaly was observed around \( T_f \) in resistivity. Muon-spin rotation (\( \mu \text{SR} \)) measurements have confirmed the presence of highly inhomogeneous local magnetism below \( T_f \) [8]. The observation of bad metallic behavior with a concurrent spin-frozen state in single-phase \( \text{Ca}_2\text{Ru}_2\text{O}_7 \) thus demonstrates an intrinsic dichotomy of Ru 4d electrons in a typical geometrously frustrated lattice.

When the \( \text{A} \) site is occupied by more covalent \( \text{Hg}^{2+} \), \( \text{Hg}_2\text{Ru}_2\text{O}_7 \) displays a metallic behavior, i.e., \( d\rho/dT > 0 \), around room temperature, and it undergoes a sharp metal-to-insulator transition at \( T_N = 107 \text{K} \) [6,7], which is accompanied by a long-range AF order and a first-order structural transition from cubic to monoclinic symmetry [11]. The low-temperature monoclinic structure has been determined as a stacking of kagome-like layers associated with a splitting of the Ru-Ru bond lengths, rendering more two-dimensional exchange interactions between the Ru ions [11]. The MIT was proposed to be a self-doping induced orbital-selective Mott transition, or to result from covalency-driven charge disproportionation [12,13].

For \( \text{Cd}_2\text{Ru}_2\text{O}_7 \) with intermediate \( \text{A}-\text{O} \) covalency, no structural transition was observed around \( T_N \approx 100 \text{K} \) [5]. Its magnetic susceptibility displays a drop at \( T_N \) similar to that of \( \text{Hg}_2\text{Ru}_2\text{O}_7 \), while the resistivity undergoes a gradual decrease and exhibits a metallic-like temperature dependence in the temperature range 60–100 K [6,7]. Such an AF metallic ground
state is rarely seen among the single-valent transition-metal oxides. For example, the 5d-analog Cd$_2$Os$_2$O$_7$ displays a continuous metal-to-insulator transition upon the development of AF order around $T_N = 225$ K [14]. More interestingly, recent first-principles calculations by Weng et al. have predicted multiple topological phase transitions induced by the “all-in, all-out” (AIAO) type AF order in Cd$_2$Ru$_2$O$_7$; the metalliclike state just below $T_N$ was ascribed to a Weyl semimetallic state due to the breaking of time-reversal symmetry [15]. Despite these unusual physical properties and potential topological states in Cd$_2$Ru$_2$O$_7$, only a few experimental studies have been performed on this interesting compound so far, presumably due to difficulties in stabilizing the high oxidation state of Ru$^{5+}$ [5]. To obtain a deeper understanding of the electronic behaviors of Cd$_2$Ru$_2$O$_7$, especially on the peculiar metalliclike state just below $T_N$, we performed a comprehensive study on the responses of its electronic behavior to external hydrostatic pressure and isovalent chemical substitutions of Ca$^{2+}$ for Cd$^{2+}$ on polycrystalline samples synthesized under high oxygen pressure. We found that the metalliclike state of Cd$_2$Ru$_2$O$_7$ below $T_N$ is very fragile and can be readily converted to an insulating phase by applying ~1 GPa hydrostatic pressure or replacing 5–10% Cd$^{2+}$ with Ca$^{2+}$. The resultant resistivity behavior is similar to that of Cd$_2$Os$_2$O$_7$. In addition, the insulating state is very robust against pressure, and the resistivity evolves gradually into two distinct activated regions under higher pressures. We have discussed the peculiar metalliclike state and its unusual responses to perturbations in terms of electronic dichotomy via side-by-side comparisons with the related compounds A$_x$Ru$_2$O$_7$ ($A = Ca, Hg$) and Cd$_2$Os$_2$O$_7$. Our results demonstrate that Cd$_2$Ru$_2$O$_7$ and related 4$d$/5$d$ cubic pyrochlore oxides offer an important paradigm for studying the exotic physics of correlated electrons on the border of (de)localization in the presence of strong geometrical frustration.

II. EXPERIMENT

All the polycrystalline Cd$_{1-x}$Ca$_x$Ru$_2$O$_7$ ($0 \leq x \leq 2.0$) samples used in the present study were prepared under high-pressure and high-temperature (HPHT) conditions with a Kawai-type multianvil module. These samples were obtained by sintering the stoichiometric mixture of CdO, CaO, and RuO$_2$ mixed with 20–30 wt.% KClO$_4$ in a sealed gold capsule at 4 GPa and 1000 °C for 30 min. Here, the KClO$_4$ was added as the oxygen source to create a high oxygen pressure within the sealed high-pressure compartment so as to stabilize the high oxidation Ru$^{5+}$ state in these samples. The resultant KCl was washed away with the deionized water after synthesis. To obtain dense pellets for various physical-property measurements, we have further treated the obtained powders with KClO$_4$ on both sides of sample under similar HPHT conditions. Details about the sample assembly and the procedure for HPHT synthesis can be found elsewhere [16].

Phase purity of the obtained samples was examined by powder x-ray diffraction (XRD) at room temperature with Cu $K\alpha$ radiation. Structural parameters were extracted from the XRD pattern via Rietveld refinement using the FULLPROF program. DC magnetic susceptibility was measured with a commercial Magnetic Property Measurement System (MPMS-III, Quantum Design) in the temperature range from 2 to 300 K under an external magnetic field of $\mu_0H = 1$ T. A Physical Property Measurement System (PPMS-9T, Quantum Design) was employed to measure the electrical resistivity with a standard four-probe method and the specific heat with the two-τ relaxation method in the temperature range from 2 to 300 K. A home-made setup was used to measure the thermopower with the steady-state method. X-ray photoemission spectra (XPS) were measured using an ESCALAB 250X spectrometer (Thermo-Fisher Scientific) employing monochromatic Al $K\alpha$ radiation (1486.6 eV) at room temperature. The spectra of the peaks of Ru $3d$ were recorded with an energy step of 0.1 eV. The binding energy (BE) of the XPS is calibrated with respect to the pure bulk Au $4f_{7/2}$(BE = 84.0 eV) and Cu $2p_{3/2}$(BE = 932.7 eV) lines. The BE is referenced to the Fermi level ($E_F$) calibrated by using pure bulk Ni as $E_F = 0$ eV.

High-pressure synchrotron XRD on Cd$_2$Ru$_2$O$_7$ was performed at room temperature with a symmetric diamond anvil cell of 300 μm culet at Beijing Synchrotron Radiation Facility with a wavelength of $\lambda = 0.6199$ Å. Neon gas was used as a pressure-transmitting medium, and the pressure values were calculated using the ruby fluorescence method. The temperature dependence of resistivity $\rho(T)$ under various hydrostatic pressures was measured with a self-clamped piston–cylinder cell (PCC) for $P < 2$ GPa [17] and a palm cubic anvil cell (CAC) in the pressure range $2 \leq P \leq 15$ GPa [18,19]. The pressure values in PCC was determined by monitoring the superconducting transition temperature of lead, and the pressure in CAC was estimated from the calibration curve based on the characteristic transitions of bismuth and lead at room temperature.

III. RESULTS AND DISCUSSION

A. Physical properties of Cd$_2$Ru$_2$O$_7$ at ambient pressure

The XRD pattern shown in Fig. 1 confirms that the obtained Cd$_2$Ru$_2$O$_7$ sample is nearly single phase with an ~1.9 wt.%
To further confirm the valence of Ru ions, we measured XPS at ambient pressure. As shown in Fig. 3(a), the temperature dependence of the Ru 3d orbital binding energy of 280.88 eV for Cd2Ru2O7 (281.68 eV) is very close to that of Hg2Ru2O7 [6]. As reported by Miyazaki et al. [8], the binding energy of the Ru 3d orbital binding energy of 281.3 eV for Cd2Ru2O7 (281.68 eV) is very close to that of Hg2Ru2O7 [6]. As shown in Fig. 2, the binding energy of the Ru 3d orbital binding energy of 281.3 eV for Cd2Ru2O7 (281.68 eV) is very close to that of Hg2Ru2O7 [6]. As reported by Miyazaki et al. [8], A2Ru5O7 (A = Ca, Cd, Hg) samples from different batches show a variation of $T_N$ in the range of 2–5 K. The variation can result from nonstoichiometry, which is determined by the synthesis parameters such as the percentage of oxidizer (e.g., KClO4), the reaction temperature and duration, the sealing condition of the noble-metal capsule, etc. Compared with previous reports, our syntheses were performed at a lower reaction pressure with a shorter duration. Nonetheless, we want to emphasize that the essential features of physical properties shown below are very similar to those reported previously [5,8], including the characteristic drop of $\chi(T)$ and $\rho(T)$ around $T_N$ shown in Fig. 3.

Above $T_N$, $\chi(T)$ does not follow the Curie-Weiss behavior but displays a broad hump centered around $T_0 \approx 200$ K. Such a feature has also been observed in previous studies [5,8] but received little attention. A similar feature in the paramagnetic magnetic susceptibility was also observed in the A-site ordered perovskite CaCu3Ru4O12 [22], implying the presence of enhanced spin fluctuations. In addition, a sudden drop of $\chi(T)$ at $T_s \approx 40$ K implies the presence of another magnetic...
transition within the antiferromagnetically ordered state. This transition has been reported by Miyazaki et al. [8] and was attributed to the reduction of Ru magnetic moment in light of the μSR measurements. Interestingly, our measurements of $\chi(T)$ in the thermal cycling evidenced a clear hysteresis around $T_s$, pointing to a first-order nature of this transition. Moreover, a tiny kink anomaly around 25 K can be also discerned in the $\chi(T)$ curves. Given the similar feature to the anomaly around $T_s$, the weak kink around 25 K might have a common origin due to the reduction of a portion of Ru magnetic moments. The upturn of $\chi(T)$ below 10 K should be attributed to some isolated magnetic impurities such as defects, vacancies, impurities, etc. To estimate the concentration of magnetic impurities, we have fitted the low-temperature tail of $\chi(T)$ in the temperature range 2–12 K with the modified Curie-Weiss law, i.e., $\chi = \chi_0 + C/(T + \theta_{CW})$, and the obtained effective moment $\mu_{eff} = (8C)^{1/2} = 0.10 \mu_B$. Assuming the magnetic impurities with a local spin $S = 1/2$, the concentration of impurity can be estimated as 0.34%.

Figure 3(b) shows the temperature dependence of resistivity $\rho(T)$ for Cd$_2$Ru$_2$O$_7$ showing three characteristic anomalies around the same temperatures as the $\chi(T)$ curves. Upon cooling down from room temperature, $\rho(T)$ increases gradually and exhibits a broad inflection point around $T_N$, below which $\rho(T)$ increases in a reduced rate. In light of the broad crossover of $\chi(T)$ around $T_N$, the decrease of $\rho(T)$ slope might be attributed to the reduced magnetic scattering due to the development of short-range AF correlations. This scenario is consistent with the fact that $\rho(T)$ undergoes a sudden drop at the long-range AF order, changing from the semiconducting-like $d\rho/dT < 0$ at $T > T_N$ to metallic-like $d\rho/dT > 0$ at $T < T_N$. The metallic-like state appears in a narrow temperature range and is replaced again by a semiconducting-like dependence at $T < T_{min} \sim T_s$. In light of the $\mu$SR measurements [8], the enhanced paramagnetic component below $T_s$ might be responsible for the reentrant semiconducting-like behavior at $T < T_{min}$. Unlike the first-order-like jump of $\chi(T)$, however, $\rho(T)$ changes smoothly around $T_{min}$. Although $\rho(T)$ seems to have an intimate correlation with the magnetic correlations, the $\rho(T)$ curves measured under $\mu_0 H = 0$ and 7 T overlap in the whole temperature range without discernable magnetoresistance. These results imply that the cubic pyrochlore Cd$_2$Ru$_2$O$_7$ is featured by a peculiar electronic band structure that is susceptible to AF order but is hard to alter by a finite magnetic field. In addition, the temperature dependences of $\rho(T)$ in the temperature regions of $T < T_{min}$ and $T > T_N$ do not follow a simple thermal activated behavior, and the magnitude of $\rho(T)$ in the whole temperature range is relatively small, i.e., 3.5–6 mΩ cm, which should fall within the range of bad metal as Ca$_2$Ru$_2$O$_7$ [4].

Figure 3(c) displays the specific heat divided by temperature $C/T$ at zero field. A broad $\lambda$-type anomaly around $T_N$ provides thermodynamic evidence for the long-range AF order as an intrinsic bulk phase transition rather than from magnetic impurities. However, thermodynamic signatures around $T_0$ and $T_s$ are absent in the specific heat, which suggests that these transitions are not of a cooperative type. The broad feature in both $\chi(T)$ and $\rho(T)$ around $T_N$ reflects a gradual crossover, while the reduction of magnetic moment around $T_N$ might not involve changes of the overall magnetic structure. A linear fitting to $C/T$ versus $T^2$ below 8 K yields a Sommerfeld coefficient $\gamma \approx 7.0(8)$ mJ mol$^{-1}$ K$^{-2}$, in accordance with a metallic ground state with a finite density of states at the Fermi level as reported earlier [23].

The correlated metallic behavior in Cd$_2$Ru$_2$O$_7$ is further probed by the thermopower $S(T)$ measurement. As shown in Fig. 3(d), $S(T)$ of Cd$_2$Ru$_2$O$_7$ is negative in the whole temperature range, signaling the dominant $n$-type charge carriers. $|S(T)|$ displays a broad maximum centered around $T_0$, but it shows no discernable anomaly around $T_N$ and $T_s$. The latter observations suggest that the changes of scattering rate rather than the density of electronic states at $T_N$ and $T_s$ should play an important role for producing the characteristic anomalies in $\rho(T)$. Since the thermopower is proportional to the energy derivative of $N(E_F)$, the relatively large value of $|S(T)| \sim 100 \mu$V/K at $T_0$ signals a quite narrow bandwidth in Cd$_2$Ru$_2$O$_7$. In contrast to $\rho(T)$, $S(T)$ points to a relatively wide range of metallic behavior, i.e., $d[S]/dT > 0$, at $T < T_0$.

These above characterizations show that the cubic pyrochlore Cd$_2$Ru$_2$O$_7$ has a peculiar correlated metallic state that is susceptible to magnetic correlations. The presence of geometrical frustration and strong paramagnetic scattering at $T > T_0$ renders a semiconducting-like behavior in both $\rho(T)$ and $S(T)$, while the development of short-range magnetic correlations below $T_0$ reduces partially the electron scattering and eventually gives rise to a metallic behavior in $\rho(T)$ below $T_N$ upon the formation of long-range AF order. It is the sudden enhancement of the paramagnetic component or the partial reduction of Ru magnetic moments below $T_s$ that causes the reentrant semiconducting-like behavior in $\rho(T)$ below $T_{min}$. Nevertheless, a considerable $N(E_F)$ is preserved considering the small resistivity, finite $\gamma$ value, and the metallic behavior $S(T)$ in a wide temperature range below $T_0$. Such an unusual AF metallic ground state is rarely seen among the single-valent transition-metal oxides, and we are thus motivated to investigate its responses to external physical pressure and isovalent chemical substitutions.

### B. Effect of high pressure on Cd$_2$Ru$_2$O$_7$

Figure 4(a) shows the $\rho(T)$ of Cd$_2$Ru$_2$O$_7$ under various hydrostatic pressures up to 1.6 GPa measured with a self-clamped piston cylinder cell (PCC). All $\rho(T)$ curves are insensitive to pressure at $T > T_N$ up to 1.58 GPa and exhibit only a slight reduction in the high-temperature region above $T_0$. Such a weak response to pressure of $\rho(T)$ at $T > T_N$ is expected considering the small external pressure in comparison with the large bulk modulus of $B_0 = 288$ GPa as determined below. In contrast, $\rho(T)$ below $T_N$ is significantly enhanced upon the application of external pressure, and the resistivity drop in the metallic-like region ($d\rho/dT > 0$) is suppressed quickly accompanied with a slight suppression of $T_N$. For $P > 0.56$ GPa, no metallic-like region can be observed, and $\rho(T)$ increases quickly upon cooling below $T_N$ following roughly three-dimensional variable range hopping (VRH) conduction [24], i.e., $\rho = \rho_0 \exp(T/T_0)^{-1/4}$. Fig. 4(b): further enhancement of $\rho(T)$ with pressure at $T < T_N$ becomes minute for $P > 1$ GPa. The observed significant enhancement of $\rho(T)$ at $T < T_N$ under such a small external pressure is against our expectation and signals the presence of peculiar electronic...
structures below $T_N$ that are susceptible to electron localization under compression. The distinct responses to external pressure of $\rho(T)$ at $T > T_N$ and $T < T_N$ imply that the electronic band structure might undergo a significant reconstruction upon the formation of AF order at $T_N$, which deserves in-depth studies both experimentally and theoretically.

To probe the electrical transport properties in a wider pressure range, we then measured $\rho(T)$ under various hydrostatic pressures from 2 to 15 GPa by using a cubic anvil cell apparatus. As shown in Fig. 5(a), the $\rho(T)$ curves above 2 GPa also show interesting evolutions. In agreement with the results obtained with PCC, $\rho(T)$ at 2 GPa displays a weak temperature dependence at the high-temperature region with a broad crossover around $T_0$, followed by a quick enhancement below $T_N \approx 70$ K. With further increasing pressure, $\rho(T)$ at both $T < T_N$ and $T > T_N$ decrease progressively except for the region near $T_N$, and the plateau region in between $T_N$ and $T_0$ shrinks gradually. For $P > 8$ GPa, the kink anomaly around $T_N$ can hardly be discerned from $\rho(T)$, and $T_0$ almost approaches $T_N$. As a result, the $\rho(T)$ curves at $P \geq 10$ GPa are featured by two distinct thermally activated regions. From the VRH plots in Fig. 5(b), it can be seen that pressure reduces the plateau region gradually between $T_N$ and $T_0$ so that the high-temperature activated region at $T > T_0$ is enlarged and moves closer until it connects smoothly to the low-temperature activation region. Despite the limited temperature range, the activation energy at $T > T_0$ seems to vary only slightly, whereas that at $T < T_N$ decreases progressively with pressure, as seen in Fig. 5(b). It is interesting to note that $T_N$ is insensitive to pressure in such a wide pressure range.

These high-pressure resistivity measurements enable us to uncover unusual responses to pressure of the electronic properties of cubic pyrochlore Cd$_2$Ru$_2$O$_7$. Figure 6 summarizes the temperature-pressure phase diagram superimposed by the contour plot of the resistivity curves. As can be seen, the metalliclike region confined in a very narrow temperature range $T_{\text{min}} < T < T_N$ is very fragile and is readily replaced by the AF insulating-like state below $T_N$ for $P \geq 0.6$ GPa. $T_N$ shows a very weak pressure dependence and seems to merge with $T_0$ at elevated pressures due to the shrinkage of the plateau region.

To check if these changes of electrical properties under pressure are correlated with some structural transition, we
performed high-pressure synchrotron XRD on Cd$_2$Ru$_2$O$_7$ up to 15.2 GPa at room temperature. As shown in Fig. 7(a), the cubic pyrochlore structure remains stable and no structural phase transformation is observed up to 15.2 GPa. We have fitted the XRD patterns with the LeBail method and plotted the obtained unit-cell constant $a$ and volume $V$ as a function of pressure in Fig. 7(b). The continuous reduction of $V(P)$ can be described well with the Birch-Murnaghan equation, which gives the bulk modulus $B_0 = 288(9)$ GPa and $V_0 = 1045.6(8)$ Å$^3$ with $B_1 = 4$ fixed. The large bulk modulus indicated that the cubic Cd$_2$Ru$_2$O$_7$ is highly incompressible, and thus the dramatic changes of electrical transport properties at $T < T_N$ below 1 GPa have to be associated with some peculiar electronic or magnetic states that are susceptible to change under small lattice compression.

C. Effect of Ca substitution in Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$

These unexpected high-pressure effects motivated us to check how the electronic properties of Cd$_2$Ru$_2$O$_7$ will evolve under a negative chemical pressure via substituting Ca$^{2+}$ for Cd$^{2+}$ in that the ionic radius of Ca$^{2+}$ (VIII: 1.12 Å) is slightly larger than that of Cd$^{2+}$ (VIII: 1.10 Å) [25]. Figure 8(a) displays the powder XRD patterns of the series of Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ ($0 \leq x \leq 2.0$), which are confirmed to form in the cubic pyrochlore structure. On the Ca-rich side, the XRD peaks with odd indices, such as (111) at $\sim 15^\circ$ and (311) at $\sim 29^\circ$, are getting stronger because the difference in scattering factor from the A-site cation and B-site Ru atom becomes bigger. As expected, the lattice constant $a$ increases gradually with $x$, Fig. 8(b), in accordance with the larger size of Ca$^{2+}$. Based on the extrapolation of $a(P)$ data shown in Fig. 7(b), substitutions of Ca$^{2+}$ for Cd$^{2+}$ in Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ correspond to the application of negative pressures of $-0.5$, $-1.0$, $-1.5$, $-3.0$, and $-4.3$ GPa for $x = 0.1$, $0.2$, $0.4$, $1.0$, and $2.0$, respectively. It should be noted that the obtained $a(x)$ does not follow exactly a linear behavior, or Vegard’s law, which is usually preserved only when the bonding character is comparable, e.g., Ca-O versus Sr-O. We believe that the deviation from Vegard’s law in the series of Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ is due to the very different bonding nature between Cd-O (with a strong covalent component) and Ca-O (mostly ionic). In this case, the partial substitution of Ca$^{2+}$ for Cd$^{2+}$ not only induces a steric effect, but also leads to additional contraction in Cd-rich samples due to the formation of more covalent bonding.
Figure 9 shows the temperature dependence of resistivity normalized at 300 K, $\rho(T)/\rho(300 \text{ K})$, for Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ ($0 \leq x \leq 2.0$) (a) and a plot of $\ln[\rho(T)/\rho(300 \text{ K})]$ vs $T^{-1/4}$ for the same data.

FIG. 9. (a) Temperature dependence of resistivity normalized at 300 K, $\rho(T)/\rho(300 \text{ K})$, for Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ ($0 \leq x \leq 2.0$) (b) a plot of $\ln[\rho(T)/\rho(300 \text{ K})]$ vs $T^{-1/4}$ for the same data.

The results of our experiment indicate that the metallicity of Cd$_2$Ru$_2$O$_7$ is accompanied by the development of AF order in the semiconducting-like state at $T_c$. As shown in Fig. 9(a), the $\rho(T)$ of Cd$_2$Ru$_2$O$_7$ increases upon cooling but does not follow any activated behavior; both the temperature dependence and the magnitude of $\rho(T)$ for our Cd$_2$Ru$_2$O$_7$ sample are consistent with those of single crystal reported by Munenaka et al. [4]. Interestingly, substitution of only 5–10% Ca for Cd destroys the metallic state of Cd$_2$Ru$_2$O$_7$ below $T_N$, and the $\rho(T)$ curves at $x = 0.1$ and 0.2 display a clear reflection point around 60 K followed by a quick increase upon further cooling, reminiscent of the $\rho(T)$ of Cd$_2$Ru$_2$O$_7$ at $P \approx 1 \text{ GPa}$ shown in Fig. 4(a). The presence of a gap opening around 60 K for $x = 0.1$ and 0.2 can be seen clearly in the VRH plot shown in Fig. 9(b). The observation of similar behavior in the Ca-doped Cd$_2$Ru$_2$O$_7$ with a negative chemical pressure is quite surprising, and further demonstrates the fragile nature of the semiconducting-like state of Cd$_2$Ru$_2$O$_7$ below $T_N$. Such an unexpected behavior exists in a narrow composition range and disappears upon further Ca doping for $x \geq 0.4$. As shown in Fig. 9(a), $\rho(T)$ for $0.4 \leq x < 2.0$ exhibits nearly identical behavior to that of Cd$_2$Ru$_2$O$_7$ in the whole temperature range.

To check if the gap opening around 60 K for $x = 0.1$ and 0.2 is associated with the formation of magnetic order, we measured the magnetic susceptibility $\chi(T)$ for the series of Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ under $\mu_0H = 1 \text{ T}$ in both ZFC and FC modes. As shown in Fig. 10(a), a peak anomaly and a splitting of ZFC and FC $\chi(T)$ curves are indeed observed around 40–50 K for $x = 0.1$ and 0.2, signaling the development of AF order or spin freezing. In the paramagnetic region, the $\chi(T)$ curves of $x = 0.1$ and 0.2 display a weak temperature dependence, Fig. 10(b), similar to Cd$_2$Ru$_2$O$_7$. Upon further Ca doping, the $\chi(T)$ exhibits a stronger temperature dependence, or a larger Curie-Weiss component, which can be seen more clearly in the $\chi^{-1}(T)$ curves of Fig. 10(b). The peak anomaly and the splitting of ZFC and FC curves around 30 K signal the formation of a spin-glass state as in Ca$_2$Ru$_2$O$_7$. From these results, we can see that the appearance of an insulating state is accompanied by the development of AF order in Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ ($x = 0.1$ and 0.2).

Figure 11 displays the temperature dependence of thermopower, $S(T)$, for the series of Cd$_{2-x}$Ca$_x$Ru$_2$O$_7$ showing dominant n-type charge carriers. Upon Ca doping, the broad maximum at $T_0 \approx 200 \text{ K}$ for Cd$_2$Ru$_2$O$_7$ vanishes and the $S(T)$ displays typical metallic behavior. For this isostructural single-valent system, the evolution of $|S|$ at a given temperature reflects the relative change of bandwidth; a broader bandwidth gives a smaller $|S|$. Therefore, the gradual reduction of $|S(T)|$ implies a broadening up of the conduction bands near the Fermi level derived mainly from the hybridized Ru 4$d$–O 2$p$ orbitals upon Ca doping. This is counterintuitive if one considers only the effect of negative chemical pressure. Instead, the covalency of the A cation (Ca < Cd) has to be invoked because...
the stronger covalency of Cd with oxygen can effectively reduce the hybridization between Ru 4d and O 2p orbitals via competing for the O 2p orbitals.

D. Discussion

The main finding of the present study is that the AF metallic-like state of Cd$_2$Ru$_2$O$_7$ in the temperature range ∼40–90 K is very fragile and can be readily converted to an insulating state by applying ∼1 GPa hydrostatic pressure or replacing 5–10% Cd with Ca. This finding is unexpected and thus underscores an instability of the electronic states near the localized to itinerant crossover for Cd$_2$Ru$_2$O$_7$. It is such an electronic dichotomy that causes the electrical properties to vary sensitively to both internal and external tuning parameters. This can be well illustrated by comparing the resistivity of Cd$_2$Ru$_2$O$_7$ with those of related isoelectronic pyrochlore compounds A$_2$Ru$_2$O$_7$ (A = Ca, Hg).

As shown in Fig. 12, the resistivity curves of these Ru$^{5+}$ pyrochlores at ambient pressure differ substantially, which has been ascribed to the different covalency of the non-magnetic A$^{2+}$ cation as mentioned in the Introduction [8]. The bad metallic behavior observed in Ca$_2$Ru$_2$O$_7$ should reflect the intrinsic electronic properties of Ru$^{5+}$ 4d$^3$ electrons with dual characters in the presence of strong geometrical frustration. The bandwidth of Ru 4d–O 2p derived bands near the Fermi level is relatively broad in Ca$_2$Ru$_2$O$_7$ according to the thermopower results shown in Fig. 11. When Ca$_{2+}$ is replaced by Hg$^{2+}$, the stronger covalency of Hg$^{2+}$ can effectively reduce the hybridization between the Ru 4d and O 2p orbitals via competence for the O 2p electrons. This will in turn reduce the bandwidth of Ru-O derived bands and strengthen the localized character of Ru 4d electrons in accordance with the μSR measurements [8]. As a result, long-range AF order takes place at $T_N = 107$ K accompanied with a sharp metal-to-insulator transition. For the intermediate Cd$_2$Ru$_2$O$_7$, the moderate covalency of Cd$^{2+}$ gives rise to electrical properties in between Ca$_2$Ru$_2$O$_7$ and Hg$_2$Ru$_2$O$_7$. Thus, the diverse electrical properties of A$_2$Ru$_2$O$_7$ at ambient pressure should arise from the delicate balance between the itinerant and localized characteristics of the Ru 4d electrons tuned by varying the covalency of the A-site cation.

In light of the tunability of Ru 4d electrons with dual characters, we can tentatively rationalize the observed AF insulating ground state for Cd$_2$Ru$_2$O$_7$ under moderate pressure or a small amount of Ca substitution. For the application of physical pressure, the compressed lattice might first strengthen the Ru 4d localized character, making it closer to Hg$_2$Ru$_2$O$_7$ and exhibiting an AF insulating ground state. But the Ru 4d–O 2p derived bands should also broaden up under lattice compression, and such a competing factor is responsible for the reduction of resistivity under higher pressures over 2 GPa, as observed in Fig. 5. In contrast to the application of hydrostatic pressure, the chemical substitutions of Ca$_{2+}$ for Cd$_{2+}$ inevitably introduce lattice disorders, which can usually reduce the Ru-O bandwidth and promote the charge localization. This might be responsible for the initial observation of an AF insulating ground state in Cd$_2$$_{2-x}$Ca$_x$Ru$_2$O$_7$ ($x = 0.1, 0.2$). But further Ca doping above $x = 0.4$ can overcome this factor and eventually favor a bad metallic behavior as observed in Ca$_2$Ru$_2$O$_7$.

As a 5d-analog of Cd$_2$Ru$_2$O$_7$, Cd$_2$Os$_2$O$_7$ displays a well-known, continuous metal-to-insulator transition around AF order at $T_N = 225$ K [14] as shown in Fig. 12. It is interesting to note that the resistivity of Cd$_2$Ru$_2$O$_7$ at 2 GPa and that of Cd$_{1.8}$Ca$_{0.2}$Ru$_2$O$_7$ resembles that of Cd$_2$Os$_2$O$_7$. Following the above-mentioned explanations, the reduction of the Ru-O
bandwidth makes Cd$_2$Ru$_2$O$_7$ also similar to Cd$_2$Os$_2$O$_7$. This is counterintuitive considering the reduced Coulombic repulsion of 5$d$ orbitals with a larger spatial extension. However, the enhanced spin-orbit coupling in the 5$d$ compound might renormalize the band structure and lead to narrower bandwidth in comparison with the 4$d$ counterpart. This has been well demonstrated in the perovskite iridates [26]. Although the spin-orbit coupling is expected to be reduced considerably in the 4$d$ compound, the delicate balance with crystal-field splitting and Hund’s coupling might influence the magnetic and transport properties. Thus, further theoretical investigations are needed in order to achieve a comprehensive understanding of these peculiar electronic behaviors near the localized to itinerant crossover.

IV. CONCLUSION

In summary, we have studied the effects of hydrostatic pressure and the isovalent substitution on the electrical transport properties of cubic pyrochlore Cd$_2$Ru$_2$O$_7$. Our results demonstrate that its peculiar metallic-like state below AF order at ambient pressure is very fragile and can be readily converted to an insulating state by applying ∼1 GPa hydrostatic pressure or replacing 5–10% Cd$^{2+}$ with Ca$^{2+}$. The resultant resistivity resembles that of 5$d$-analog Cd$_2$Os$_2$O$_7$. We have rationalized these unexpected observations in terms of the sensitive tunability of electronic itinerancy/localization dichotomy via side-by-side comparisons with the related compounds A$_2$Ru$_2$O$_7$ (A = Ca, Hg) and Cd$_2$Os$_2$O$_7$. These cubic 4$d$/5$d$ pyrochlore oxides offer an important paradigm for studying the exotic physics of correlated electrons on the border of (de)localization in the presence of strong geometrical frustration.

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