Structural and electronic properties of pyrochlore-type $A_2Re_2O_7$ (A = Ca, Cd, and Pb)

Kenya Ohgushi,[1,2] Jun-ichi Yamaura,[1] Masaki Ichihara,[1,3] Yoko Kiuchi,[1] Takashi Tayama,[1,4] Toshiro Sakakibara,[1] Hirotada Gotou,[1] Takehiko Yagi,[1] and Yutaka Ueda[1,2]

[1]*Institute for Solid State Physics, University of Tokyo, Kashiwanoha, Kashiwa, Chiba 277-8581, Japan*

[2]*JST, TRIP, Sanbancho, Chiyoda, Tokyo 102-0075, Japan*

[3]*Hosei University, Kajino-chou, Koganei, Tokyo 184-8584, Japan*

[4]*Department of Physics, University of Toyama, Toyama, Toyama 930-8555, Japan*

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$Cd_2Re_2O_7$ exhibits a unique structural transition characterized by a loss of the inversion symmetry in a metal. Here, we report on structural and electronic properties for $A_2Re_2O_7$ (A = Ca and Pb), and S-substituted $Cd_2Re_2O_7$. On the basis of material characteristics, we show that the covalency of particular bonds stabilizes the low-temperature phase without the inversion symmetry. We also observed an incoherent charge transport with a weakly temperature-dependent resistivity on the verge of structural transition. This phenomenon is argued in terms of the polaron formation.

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I. INTRODUCTION

Occasionally, the inversion symmetry in a solid is spontaneously broken. The most famous example of this phenomenon is ferroelectrics. It is by now common knowledge that the covalency plays a crucial role in stabilizing the ferroelectricity. This was first revealed by first-principles calculations for perovskite-type titanium oxides.[1] Later on, this was confirmed by the charge-density distributions visualized by powder x-ray diffraction experiments using maximum entropy methods (MEM).[2] The mechanism of room-temperature (T) ferroelectricity in $PbTiO_3$, which is in marked contrast to the ferroelectric phase below 85 K in $CdTiO_3$, is ascribed to the stronger covalency of the Pb-O bonds than Cd-O bonds.[3]

In contrast to the insulating nature of ferroelectrics, there is a class of materials categorized as a metallic state without the inversion symmetry, which is sometimes called a noncentrosymmetric metal or a polar metal.[4] Since itinerant electrons screen the electric field, the physics does not exactly parallel that of ferroelectrics. For example, the primary order parameter characterizing the phase is no longer the ferroelectric polarization, but rather a quantity related to the loss of the inversion center, e.g., a second-rank pseudotensor.[5,6] Moreover, instead of dielectric properties, transport properties are the focus of discussion. In the inversion-broken metal, any electronic states near the Fermi energy can no longer be classified according to the parity. This parity mixing of the Wannier function gives rise to intriguing transport phenomena such as the inverse Faraday effect.[7] Concerning the phase stability, there is no study which unravels the role of the covalency.

The pyrochlore-type compounds $A_2B_2X_6X'$ with cubic $Fd\bar{3}m$ (Fig. 1) have been extensively studied owing to fascinating phenomena arising from a geometrical frustration. In addition, they are also a good playground for investigating the physics relevant to the inversion symmetry. $Cd_2Nb_2O_7$ undergoes a ferroelectric transition at 200 K.[8] Interestingly, the transition temperature rises markedly upon the substitution of S into the X' site, and reaches ∼555 K in $Cd_2Nb_2O_6S$.[9] This can be understood as the stability of the ferroelectric phase is promoted by the covalent Cd-S bonds.

$Cd_2Re_2O_7$ with the $(5d)^2$ electronic configuration is not only the first superconductor in the pyrochlore-type compounds,[10–12] but also the first material to exhibit a structural transition of the type argued in the seminal work by Anderson and Blount in 1965.[6,13] This material undergoes a second-order structural transition at the transition temperature (T_s) of 200 K to noncentrosymmetric tetragonal $I\bar{4}m2$.[14] Since the lattice change is extremely small [$(a-c)/a \sim 0.05\%$],[15] there has been difficulty in determining the precise crystal structure parameters in the low-T phase,[16] however, the loss of the inversion symmetry is clearly indicated by the appearance of the second harmonic generation signal: When light is shined on the sample, the reflected light includes a component with twice the frequency of the incident light.[5] The Landau theory indicates that this transition is characterized by doubly degenerate E_u soft phonons above T_s;[6] these phonons are split into a B_1 Goldstone mode and a massive A_1 mode below T_s, which are observed in the Raman spectra.[17] There is evidence that charge and lattice degrees of freedom are mutually coupled. The electrical resistivity, which exhibits an anomalously weak T variation in the $Fd\bar{3}m$ phase, dramatically decreases below T_s.[10] Nevertheless, it subsequently turned out that photoemission spectroscopy detects less than a 5% change in the density of states across the transition.[18–20] Hence, it is still unclear how the charge and lattice degrees of freedom interact with each other. In this paper, we report on the structural and electronic properties of $A_2Re_2O_7$ (A = Ca and Pb),[21,22] and S-substituted $Cd_2Re_2O_7$. On the basis of material characteristics, we clearly show that the covalency is a key factor stabilizing the noncentrosymmetric phase. We also found a one-to-one correspondence in the resistivity: incoherent behavior in the centrosymmetric phase and coherent behavior in the noncentrosymmetric phase. We then discuss anomalous charge dynamics in the centrosymmetric phase in terms of the polaron formation.

II. EXPERIMENTAL

Single crystals of $Ca_2Re_2O_7$ were synthesized using the flux method under 4 GPa at 973 K in a cubic-anvil-type

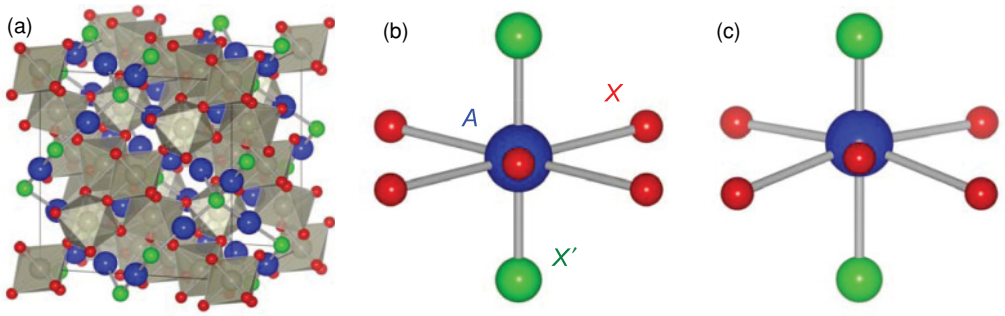

FIG. 1. (Color online) (a) Crystal structure of a pyrochlore compound $A_2B_2X_6X'$, which is composed of two interpenetrating units: an A_2X' network and corner-shared BX_6 octahedra. (b) Coordination environment of A atom in $Fd\bar{3}m$, which is surrounded by six X atoms and two X' atoms. (c) Coordination environment of A atom in $F\bar{4}3m$. Note that A atom is shifted toward one X' atom, resulting in two inequivalent A-X' bonds.

high-pressure apparatus. The starting materials were CaO, ReO_3, $CaCl_2$, and $Ca(OH)_2$ with a molar ratio of 1.1 : 1.0 : 0.13 : 0.19, and a Pt capsule was used as a container. Single crystals of $Pb_2Re_2O_7$ were grown using the solid-state reaction method. PbO and ReO_2 with a 1 : 1 molar ratio were heated at 953–973 K for 24 h in an alumina crucible inside an evacuated quartz tube. Single crystals of $Cd_2Re_2O_{7-x}S_x$ were synthesized by the chemical vapor transport method.[10] The chemical compositions were determined by combining iodometric titration, inductively coupled plasma atomic emission spectrometry, and energy-dispersive x-ray spectroscopy equipped with a scanning electron microscope. The actual compositions are $Ca_{1.53}Re_2O_{6.61}$, $Pb_{1.83}Re_2O_{6.70}$, and $Cd_{2.00}Re_2O_{6.81}S_{0.19}$. The low-$T$ crystal structure of A = Pb was examined by using a 200-kV electron beam, and oscillation photographs were taken by an imaging-plate-type Weissenberg camera. The magnetic properties of the collected crystals were investigated using a Faraday force capacitive magnetometer for 70–2000 mK,[23] and a superconducting quantum interference device (SQUID) magnetometer for 5–400 K. The specific heat was measured by the relaxation method.

III. STRUCTURAL PROPERTIES

Figure 2(a) represents the specific heat (C) for $A_2Re_2O_7$ (A = Ca, Cd, and Pb). The λ-type anomaly observed at 200 K in A = Cd is indiscernible in A = Ca, suggesting that the inversion symmetry is preserved down to the lowest T measured. On the contrary, C for A = Pb shows a broad peak at ∼295 K. We estimate the entropy associated with this transition to be S = 2.1 J K^{-1} mol^{-1} by subtracting the smooth background, which is determined by fitting the data at 170–210 and 350–380 K with a polynomial function of the third order. This value is of the same order of magnitude as S = 3.5–3.77 J K^{-1} mol^{-1} for A = Cd.[24,25] In the low-T phase of A = Pb, we observed $2l$ 0 0 reflections, which become allowed in noncentrosymmetric $F\bar{4}3m$, in the transmission electron microscope image [Fig. 3(a)] and the single-crystalline x-ray diffraction profile [Fig. 3(b)]; this is in agreement with results for A = Cd.[15,16] Considering that tetragonal splitting is not observed in the powder x-ray diffraction profile (data not shown), we conclude that the structural transition to cubic $F\bar{4}3m$ occurs in A = Pb.[26] The unit-cell volume shows a monotonic T dependence below T_s in A = Pb [Fig. 2(b)]; a negative thermal expansion in A = Cd (Ref. 27) might be related to slight tetragonal distortions. As shown in the left-hand inset of Fig. 2(a), T_s for $Cd_2Re_2O_{6.81}S_{0.19}$ is ∼225 K, indicating a marked increase in T_s due to the S substitution.

The variation in T_s points to a crucial role of the covalency.[28] The covalency of a chemical bond (f_c) can be quantitatively estimated by the formula $f_c = \exp(-\Delta\chi_P^2/4)$, where $\Delta\chi_P$ is the difference of the Pauling electronegativity (χ_P) between the cation and anion.[29] χ_P for atoms relevant to this study are χ_P(Ca) = 1.00, χ_P(Cd) = 1.69, χ_P(Pb) = 2.33, χ_P(O) = 3.44, and χ_P(S) = 2.58. We here introduce two quantities, $f_c(X,X')$ and $f_c(X')$: The A-X and A-X' bonds are equally treated in $f_c(X,X')$, whereas only the A-X' bonds are concerned in $f_c(X')$. As can be seen from Fig. 4, these quantities have a positive correlation with T_s, indicating that the noncentrosymmetric phase is quite stable in a more covalent crystal. To be underlined here is that the data point for $Cd_2Re_2O_{6.81}S_{0.19}$ is located differently depending on whether T_s is plotted against $f_c(X,X')$ (open circle) or $f_c(X')$ (closed circle). This is because S^{2-} ions with a large ionic radius are selectively incorporated into the X' site. When drawing lines between two data points for x = 0 and 0.19 in A = Cd and extrapolating them toward more covalent regions, we notice that the data point for A = Pb is more close to the line measured by $f_c(X')$ rather than $f_c(X,X')$.[30] This hints that A-X' bonds have a stronger impact on the structural transition than A-X bonds. This is plausible, since the A-X' bond is shorter than the A-X bond by 17% [Fig. 1(b)].

How the covalent A-X' bonds break the inversion symmetry is well interpreted for A = Pb. Pb^{2+} ions with a stereochemical active lone pair ($6s^2$ electrons) prefer a distorted metal coordination with two types of covalent A-X' bonds of different bond lengths [Fig. 1(c)] instead of the more symmetrical metal coordination surrounded equally by two X' atoms [Fig. 1(b)]. This local breakdown of inversion symmetry spreads over the global lattice, because the A site is the inversion center in $Fd\bar{3}m$. Indeed, the metal coordination shown in Fig. 1(c) is

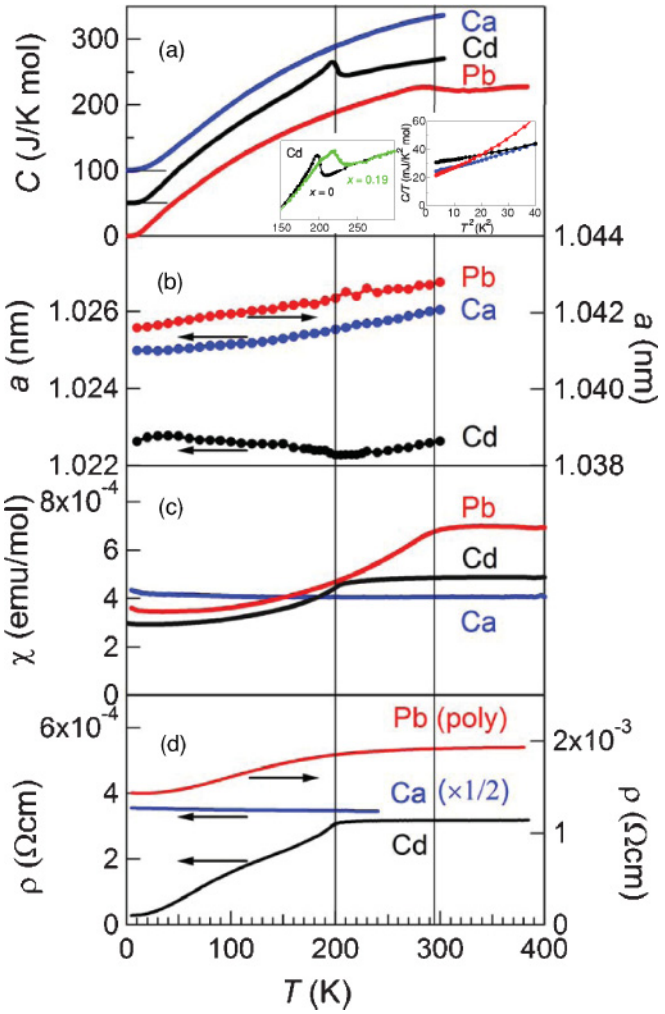

FIG. 2. (Color online) Structural and electronic properties of $A_2Re_2O_{7-x}S_x$ pyrochlores. The main panels show the data for $A = Ca$, Cd, and Pb with $x = 0$. The vertical solid lines located at 200 and 295 K correspond to the structural transition temperature for $A = Cd$ and Pb, respectively. (a) The temperature (T) dependence of the specific heat (C). Note that there are offsets for $A = Ca$ and Cd. The right-hand inset is C divided by T as a function of T^2 for $A = Ca$, Cd, and Pb. The left-hand inset shows the magnified view of C for $A = Cd$ with $x = 0$ and 0.19. (b) The T dependence of the lattice constant (a). The data for $A = Cd$ are taken from the literature (Ref. 27), where the small tetragonality is ignored. (c) Magnetic susceptibility (χ) at 5 T. (d) The T dependence of the resistivity (ρ). Note that the data for Ca are divided by 2 for clarity. The data for $A = Pb$ are for polycrystalline pellets, leading to the relatively large residual resistance.

the same expected for $F\bar{4}3m$. This view can be extended to $A = Cd$, where the strong Cd-O(S) hybridization leads to a large Cd polarizability.

Our result proving the importance of covalency is consistent with reported structural data for other metallic pyrochlore-type oxides. Among approximately ten known compounds with $B = Ru$, Os, and Ir, the inversion symmetry is broken at room temperature in $Pb_2Ru_2O_7$ and $Pb_2Ir_2O_7$ with $F\bar{4}3m$;[31–33] this can be well understood by the prominent Pb-O covalency. On the other hand, the absence of a noncentrosymmetric phase in $Pb_2Os_2O_7$ (Ref. 34) raises the possibility that the B-site related bonds are also responsible for the loss of inversion symmetry. In order to clarify this issue, a fine crystal structure refinement utilizing MEM as well as systematic band-structure calculations are necessary. We also note that the present conclusion is applicable only to the pyrochlore-type compounds. The impact of the covalency on the loss of inversion symmetry should be investigated for metals with other structures in the future.

IV. ELECTRONIC PROPERTIES

We focus on the thermodynamic properties of itinerant electrons. The magnetic susceptibility (χ), which is the sum of the spin susceptibility (χ_s) and orbital susceptibility (χ_0), shows T-independent Pauli paramagnetic behavior above T_s [Fig. 2(c)]. In the framework of the Fermi-liquid theory, the spin susceptibility is expressed as $\chi_s = 2\mu_B^2 D^*(E_F)/(1 + F_0^a)$, where μ_B is the Bohr magneton, $D^*(E_F)$ is the quasiparticle density of states at the Fermi energy (E_F), and F_0^a is the Landau parameter related to ferromagnetic instabilities (Stoner enhancement).[35] The large variation in χ with a change of A atoms [$\chi(Pb) > \chi(Cd) > \chi(Ca)$] is likely originating from an off-stoichiometry of the nominal Re valence, which is determined by iodometric titration method to be 5.08+ for $A = Ca$, 5.00+ for $A = Cd$, and 4.87+ for $A = Pb$, and a resultant distinguishable $D^*(E_F)$. χ for $A = Pb$ shows a dramatic decrease across the structural transition. There are two ideas for explaining this phenomenon in $A = Cd$: the loss of $D^*(E_F)$,[36] and the suppression of ferromagnetic fluctuations (change in F_0^a).[20] It is hard to judge which scenario is more plausible from the present data.

The C/T vs T^2 plot [right-hand inset of Fig. 2(a)] shows the linear dependence at $T < 4.5$ K for $A = Ca$, at $T < 5.0$ K for $A = Cd$, and at $T < 3.0$ K for $A = Pb$. The reason why the deviation is pronounced in $A = Pb$ is probably related to a low-lying optical phonon. For simplicity, we here fit the data below 5 K with the function $C = \gamma T + \beta T^3$, where the γ and β terms correspond to electron and lattice contributions, respectively. The results are $\gamma = 23.1$ mJ/K^2 mol and $\beta = 0.47$ mJ/K^4 mol for $A = Ca$, $\gamma = 30.0$ mJ/K^2 mol and $\beta = 0.32$ mJ/K^4 mol for $A = Cd$ (being consistent with Ref. 10), and $\gamma = 18.8$ mJ/K^2 mol and $\beta = 0.88$ mJ/K^4 mol for $A = Pb$. The β coefficient is related to the Debye temperature θ_D as $\beta = (12\pi^4/5)NR/\theta_D^3$, where N is the number of atoms per unit cell and R is the gas constant. Calculated results are $\theta_D = 346$ K for $A = Ca$, $\theta_D = 406$ K for $A = Cd$, and $\theta_D = 285$ K for $A = Pb$. Note that these values are extracted for the ground state, and therefore reflect the centrosymmetric (noncentrosymmetric) phase for $A = Ca$ ($A = Cd$ and Pb). The fairly large γ values indicate a substantial enhancement of the quasiparticle mass in both centrosymmetric and noncentrosymmetric phases; this has been revealed by the optical spectroscopy for $A = Cd$.[37] The Wilson ratio $R_W = \pi^2 k_B^2 \chi_s/(3\mu_B^2\gamma)$ (k_B being the Boltzmann constant) is computed by assuming $\chi_0 = 1.64 \times 10^{-4}$ emu/mol; χ_0 is the sum of the diamagnetic and the Van Vleck susceptibility, and this value was obtained by the nuclear magnetic resonance for $A = Cd$.[36] They are $R_W = 0.85$ for $A = Ca$, $R_W = 0.32$ for $A = Cd$ (being consistent with Ref. 36), and $R_W = 0.76$

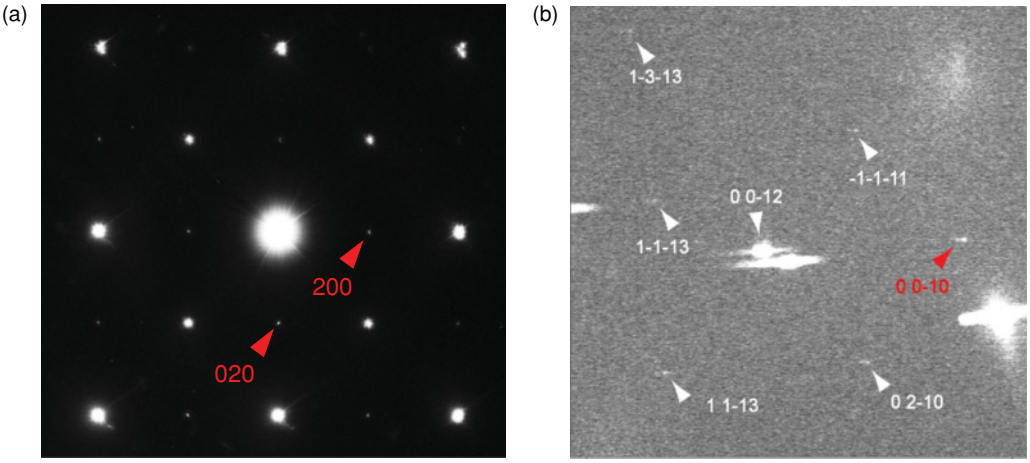

FIG. 3. (Color online) (a) Transmission electron microscope diffraction image for $Pb_2Re_2O_7$ at 103 K, where the incident electron beam is along the 001 axis. The $2l$ 0 0 reflections are forbidden in $Fd\bar{3}m$, but are allowed in $F\bar{4}3m$. (b) Oscillating photograph for $Pb_2Re_2O_7$ at 150 K, showing the 0 0 −10 reflection.

for $A =$ Pb, indicating that electron correlation effect are not prominent in both centrosymmetric and noncentrosymmetric phases. Hence, the quasiparticle mass is likely enhanced by the electron-phonon coupling. The larger β for $A =$ Pb than $A =$ Cd is attributable to the larger atomic number of Pb. However, this tendency does not hold for $A =$ Ca with a relatively large β, hinting at the downward energy shift in the phonon spectrum. One possible reason is that the compound is close to the structural transition, and there are soft phonons associated with it.

Next, we discuss the transport properties. Figure 2(d) represents the T variations in the electrical resistivity (ρ). Surprisingly, ρ for $A =$ Ca shows almost no T dependence with the value of 7×10^{-4} Ω cm over all the T range measured.[38] On the other hand, ρ for $A =$ Pb exhibits an incoherent-coherent crossover at ∼250 K, although this feature is blurred by the polycrystalline nature. By taking account of ρ for $A =$ Cd together, we can summarize ρ of rhenium pyrochlores as follows: incoherent behavior characterized by a nearly T independence in the centrosymmetric phase, and coherent behavior characterized by a dramatic decrease with decreasing T in the noncentrosymmetric phase.

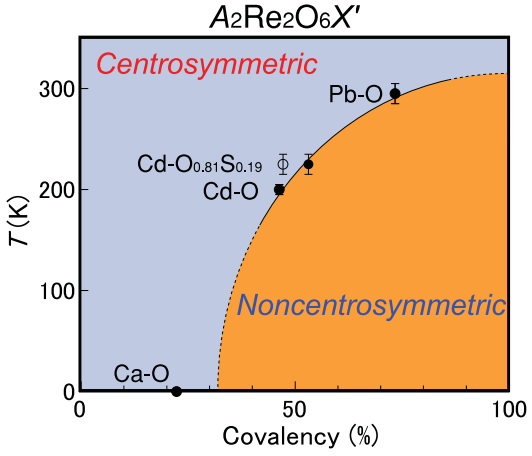

FIG. 4. (Color online) A proposed phase diagram for $A_2Re_2O_{7-x}S_x$. Structural transition temperature is plotted against the covalency of the A-X and A-X' bonds, $f_c(X,X')$ and $f_c(X')$ (see text for details). There are two data points for $Cd_2Re_2O_{6.81}S_{0.19}$, depending on whether the abscissa axis is $f_c(X,X')$ (open circle) or $f_c(X')$ (closed circle).

The incoherent charge dynamics in the centrosymmetric phase are truly remarkable, since a metal categorized into the Fermi liquid usually exhibits a $\rho \propto T^2$ behavior. We stress here that this anomalous feature is commonly observed in $A =$ Ca and Cd, indicating that the phenomenon is less sensitive to the Re valence, the randomness induced by deficiencies, and the delicate Fermi-surface topology. Instead, it is more likely that electrons moving in a certain fluctuating medium give rise to the exotic transport. Two possibilities are considered. One scenario is that electrons couple with magnetic fluctuations conduct incoherently.[39] Such a possibility is theoretically pursued when there are two competing interactions (the double-exchange and superexchange interactions) on the pyrochlore lattice.[40] However, there is no sign of phase competition in the present system. A more plausible mechanism is polaron formation. If the soft phonon relevant to the structural transition is responsible for this, the effective mass of quasiparticles increases with decreasing T owing to the downward energy shift of the phonon energy, leading to incoherent charge transport. The presence of the low-lying phonon suggested by the relatively large β seemingly supports this idea. However, to identify this mechanism, further studies are needed, since it is known that electrons interacting with classical phonons also have the weakly T-dependent ρ behavior.[41]

Despite an apparently conventional T dependence of ρ in the noncentrosymmetric phase, there still remains a nontrivial interplay between the electrons and lattice. This manifests itself through group-theoretical arguments. The noncentrosymmetric phases of $A =$ Cd and Pb have $I\bar{4}m2$ and $F\bar{4}3m$, respectively; the latest study clarified that the ferroelectric phase of $Cd_2Nb_2O_7$ possesses $Imm2$.[42] Among these space

groups, only $Imm2$ allows an appearance of the ferroelectric polarization, and there is a suggestive subgroup-supergroup relationship, $F\bar{4}3m \supset I\bar{4}m2 \supset Imm2$. These evoke a consideration that mobile electrons in a noncentrosymmetric metal screen the hypothetical ferroelectric polarizations, rendering the space group more symmetrical. Such a novel interplay is expected to affect the transport properties. As the order parameter gradually develops with decreasing T, Re $5d$ bands are reconstructed to follow the crystal structure change; the resultant ρ change might already be discernible in our data as large variations as a function of T [Fig. 2(d)]. We note that the redistribution of charges upon the ferroelectric transition is discerned in the insulating $PbTiO_3$;[2] we expect that such phenomenon is more pronounced in itinerant systems.

Finally, we briefly comment on the ground state for $A =$ Ca and Pb. Our magnetization measurements under 100 Oe (data not shown) indicate the absence of superconductivity down to 70 mK in both compounds, being in a stark contrast to $A =$ Cd with the superconducting transition temperature of 1 K.[10–12] We do not know the definite explanation for this at present; however, we speculate that the pair breaking effect of the cation deficiencies in $A =$ Ca and Pb, and/or the additional structural transition at 120 K in $A =$ Cd (Ref. 24) bears this difference.

V. CONCLUSIONS

We have systematically investigated structural and electronic properties for rhenium pyrochlores. The noncentrosymmetric phase is stabilized by the covalency of A-X' bonds. We observed an anomalous transport characterized by a temperature-independent resistivity on the verge of structural transition associated with the inversion symmetry. A possible explanation for it is the polaron formation with the soft phonons.

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