

Electrical properties of $\text{Cd}_2\text{Re}_2\text{O}_7$ under pressureN. Barišić,¹ L. Forró,¹ D. Mandrus,² R. Jin,³ J. He,³ and P. Fazekas^{4,1}¹*IPMC, Faculté Science de Base, EPFL, CH-1015 Lausanne, Switzerland*²*Condensed Matter Sciences Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831, USA*³*Department of Physics and Astronomy, The University of Tennessee, Knoxville, Tennessee 37996, USA*⁴*Research Institute for Solid State Physics and Optics, Budapest 114, P.O.B. 49, H-1525 Hungary*

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We examine the resistivity and thermopower of single crystal specimens of the pyrochlore oxide $\text{Cd}_2\text{Re}_2\text{O}_7$ at pressures up to 2 GPa. Thermopower proves to be a sensitive tool in the study of the phase diagram of $\text{Cd}_2\text{Re}_2\text{O}_7$. The 200 K metal-to-metal phase transition is accompanied by a strong increase of the absolute value of the thermopower. A weaker anomaly allows us to identify a second phase transition at 125 K. Following the temperature dependence of this anomaly, we obtain the corresponding phase boundary up to 1.2 GPa, and argue that it must drop to $T=0$ before p reaches 1.8 GPa. There is a wide temperature range where the electrical properties are fairly sensitive to pressure, indicating the strong coupling of the electronic degrees of freedom to the lattice.

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I. INTRODUCTION

d - and f -electron systems show a variety of Mott phenomena.^{1,2} The occurrence of Mott transitions is readily understood in stoichiometric $3d$ transition metal compounds since for these systems, the electron–electron interaction (measured by an effective Hubbard U) is comparable to the bandwidth W . In contrast, $4d$ and, quite in particular, $5d$ transition metal compounds are supposed to be less correlated because of their relatively wide d -bands. For example, the $5d$ oxide ReO_3 is a good metal with wide d -bands.

There are, however, at least a few $5d$ compounds which show cooperative behavior with no obvious interpretation in terms of independent electron theory. The Mott localization aspects of the low-temperature behavior of 1T-TaS_2 are long known.³ Recently, the interest turned towards pyrochlore oxides.⁴ $\text{Y}_2\text{Ir}_2\text{O}_7$ is characterized as a Mott insulator.⁵ $\text{Cd}_2\text{Os}_2\text{O}_7$ undergoes a metal–insulator transition at 220 K. The phenomenon is well described as a BCS-type mean field transition which clearly involves the ordering of an electronic degree of freedom on the background of a rigid lattice.^{6,7} This led to the proposal of a Slater transition of the spins.⁶ Let us note, however, that the supposed spin-densitylike order parameter is experimentally not yet identified, and it would be no simple matter to postulate it because of the frustrated nature of the pyrochlore lattice.⁸ Furthermore, whatever the nature of the order parameter, there is a basic difficulty: according to band theory, the Fermi surface of $\text{Cd}_2\text{Os}_2\text{O}_7$ does not seem to be nested,⁹ and it is difficult to see how a small-amplitude order can immediately open gaps all over the Fermi surface. This alone suffices to show that for $\text{Cd}_2\text{Os}_2\text{O}_7$, correlation effects are important. We may also infer that $\text{Cd}_2\text{Re}_2\text{O}_7$, which differs from $\text{Cd}_2\text{Os}_2\text{O}_7$ only in having one $5d$ -electron/site less, is also a correlated system.

We may immediately observe that geometrical frustration tends to amplify correlation effects: For 1T-TaS_2 , the triangular lattice of Ta ions, while for $\text{Cd}_2\text{Os}_2\text{O}_7$ and $\text{Cd}_2\text{Re}_2\text{O}_7$,

the even more frustrated pyrochlore lattice of the $5d$ sites is playing an important role.^{17,18} The concept of frustration is not quite straightforward for itinerant systems, but one can argue that it involves the suppression of kinetic energy by destructive interference, and the resulting enhanced importance of interaction effects. Weak coupling density wave phases tend to be eliminated and instead, local correlation effects like mass enhancement and the opening of a spin gap dominate.^{10,11}

Models based on the degenerate t_{2g} subband are directly relevant for the Re and Os pyrochlore oxides. Experience with Mott-localized spin–orbital systems suggests that the spin and orbital degrees of freedom play similar roles, and this should hold for correlated itinerant systems as well. A RPA treatment of the t_{2g} pyrochlore Hubbard model demonstrates the close competition between spin and orbital instabilities.¹² The interplay of spin and orbital fluctuations yields a novel scenario of mass enhancement.¹³

The importance of correlation effects is judged by checking to which extent band structure calculations account for the observed properties. The LDA electronic structure of the high-temperature (cubic) phases of $\text{Cd}_2\text{Os}_2\text{O}_7$ and $\text{Cd}_2\text{Re}_2\text{O}_7$ has been determined.^{9,14} For $\text{Cd}_2\text{Re}_2\text{O}_7$, there is a discrepancy between the LDA result and the measured specific heat coefficient γ . Two calculations give somewhat different results: Singh *et al.*⁹ imply that $m^*/m \approx 2.4$ is not unexpected for a superconductor (it could be due to electron–phonon coupling), while Harima¹⁴ finds $m^*/m > 5$, and concludes that $\text{Cd}_2\text{Re}_2\text{O}_7$ is a strongly correlated system. Optical data indicating an even higher $m^*/m \approx 20$ add to the weight of evidence that electron correlation is important in $\text{Cd}_2\text{Re}_2\text{O}_7$,¹⁵ but the origin of the discrepancy between the specific heat and optical estimates for the mass enhancement factor remains unclear. Sakai *et al.*¹⁶ interpret susceptibility and NMR data as indicating localized moment character, which is synonymous with local correlations.¹⁹

Here we present the results of electrical resistivity and thermopower measurements on $\text{Cd}_2\text{Re}_2\text{O}_7$ in the pressure range 0–2 GPa. Our basic finding is that there is a wide

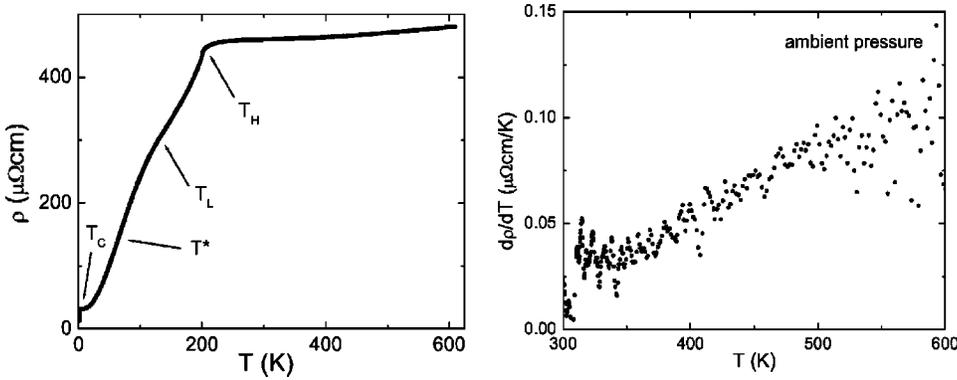


FIG. 1. (Left) The temperature dependence of the resistivity of $\text{Cd}_2\text{Re}_2\text{O}_7$ at ambient pressure. T_H , T_L , and T_c signify phase transitions, while T^* marks the position of the crossover to a low- T power law regime (see the text). (Right) Plotting $d\rho/dT$ vs T shows that the high temperature resistivity is not linear in T .

range of temperature (roughly $60 \text{ K} < T < 200 \text{ K}$) where the electronic state of the material is “soft,” which is shown by the strong pressure dependence of the thermopower S (and to a lesser extent also of the resistivity ρ). The existence, and extreme pressure sensitivity, of the so-called second phase transition of $\text{Cd}_2\text{Re}_2\text{O}_7$,²⁰ is only one aspect of this behavior. We display a phase diagram based on thermopower anomalies, including data on the pressure dependence of the second structural transition. Measuring thermopower under pressure is currently the only way to learn about the shape of that phase boundary.

II. THE PHASES OF $\text{Cd}_2\text{Re}_2\text{O}_7$

$\text{Cd}_2\text{Re}_2\text{O}_7$ has attracted interest by being the only $5d$ pyrochlore which becomes superconducting at $T_c = 1-2 \text{ K}$.²² However, we discuss normal metallic phases only.

The contrasting behavior of $\text{Cd}_2\text{Re}_2\text{O}_7$ and $\text{Cd}_2\text{Os}_2\text{O}_7$ is intriguing. At room temperature T_{RT} both are bad metals with similar values of the nearly temperature independent resistivity corresponding roughly to a mean free path of the order of the lattice constant. Band structure calculation^{9,14} shows they are $5d$ semimetals with the Fermi level position corresponding to a $1/3$ -, and $1/2$ -, filled t_{2g} subband, respectively. We know of no feature of the density of states, or the Fermi surface, which would obviously account for the fact that $\text{Cd}_2\text{Os}_2\text{O}_7$ becomes an insulator at 220 K , while at almost the same transition temperature $T_H = 200 \text{ K}$, $\text{Cd}_2\text{Re}_2\text{O}_7$ becomes a better metal. In the notation T_H , the subscript H stands for “higher,” for $\text{Cd}_2\text{Re}_2\text{O}_7$ has also a “lower” transition temperature T_L which will be discussed later.

We illustrate the character of the phase transitions of $\text{Cd}_2\text{Re}_2\text{O}_7$ by the results of our measurements of the temperature dependence of the resistivity at ambient pressure (Fig. 1, left). We note that none of the previous measurements were carried out up to 600 K . The extended temperature scale makes the fundamental change in the character of $\text{Cd}_2\text{Re}_2\text{O}_7$ at $T_H = 200 \text{ K}$ clear. The high- T phase is a bad metal, with a resistivity which at first seems to saturate at $\sim 500 \mu\Omega \text{ cm}$, but then picks up again.

Decreasing the temperature through $T_H = 200 \text{ K}$, the system becomes a good metal. The low- T normal state resistivity²³ extrapolates to $30 \mu\Omega \text{ cm}$. The resistivity change around $T_H = 200 \text{ K}$ could be compatible either with a change in the scattering mechanism, or a change in carrier

concentration, or a combination of both. Whether a phase transition occurs, has to be decided from other measurements.

Closer examination of the resistivity vs T plot reveals that the slope passes through a maximum, a minimum, and reaches a maximum again at T_H , thus plotting $d\rho/dT$ vs T readily offers the possibility of identifying characteristic temperatures as either extrema, or zeroes, of the derivative. This holds at all pressures (Fig. 2, top). The high-temperature peak belongs to the bad-metal-to-good-metal transition at T_H . It was mentioned in Ref. 24 that the low-temperature hump at $T^* \approx 60 \text{ K}$ is also significant; however, it does not belong to a phase transition. Rather, it is a crossover temperature where the low- T $\rho(T)$ begins to follow a power-law

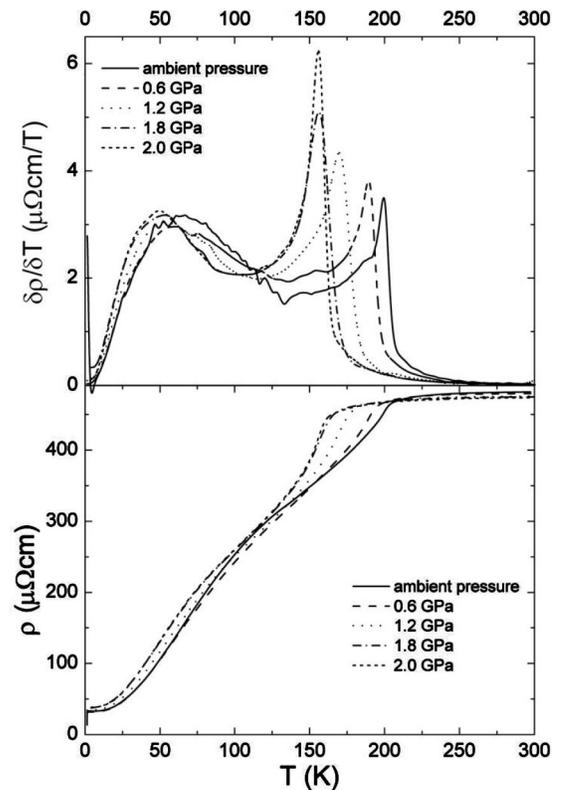


FIG. 2. (Bottom) The temperature dependence of the resistivity of $\text{Cd}_2\text{Re}_2\text{O}_7$ for several pressures. The sharp downturn occurs at T_H . (Top) The temperature dependence of the derivative of the resistivity $\partial\rho/\partial T$ for several pressures.

behavior whose form will be discussed later. It is clear that other features (e.g., the minimum of $d\rho/dT$) might have been selected. However, the status of such “characteristic temperatures” is somewhat uncertain, and we need further evidence to show that the properties of the system undergo substantial changes at any of these points.

The continuous bad-metal-to-good-metal transition of $\text{Cd}_2\text{Re}_2\text{O}_7$ at $T_H=200$ K is clearly seen in resistivity, susceptibility, and specific heat measurements. There is no magnetic ordering.²⁵ X-ray scattering finds new Bragg peaks, with an accompanying anomaly in the intensity of fundamental reflections. Though at first it was tentatively described as a cubic-to-cubic phase transition, there is now evidence that the symmetry is lowered to tetragonal. However, the deviation from the cubic structure is quite small, only about 0.05%.^{19,26}

Evidence that a second phase transition occurs at ambient pressure at $T_L \approx 120$ K (“L” stands for “lower”), was presented by Hiroi *et al.*²⁰ They present a magnified image of the ρ vs T plot which reveals a minute hysteresis loop of a few K width in this region. The transition has little effect on the resistivity, no known signature in the susceptibility, and the specific heat shows merely an anomaly which is two orders of magnitude weaker than the one associated with the 200 K transition. Clearer evidence comes from magnetoresistivity measurements which show that, after $\Delta\rho$ essentially vanishes by the time T reaches 100 K, it reappears and becomes quite anisotropic from 120 K onwards. Thus $\text{Cd}_2\text{Re}_2\text{O}_7$ has two good metallic phases in addition to the bad metal above $T_H=200$ K. The first thermopower data²⁷ are compatible with this scenario.

Whatever the nature of the second phase transition, it is very weak. X-ray diffraction shows an anomaly in the temperature dependence of the fundamental reflections.²⁰ A recent refinement¹⁹ yielded the suggestive picture of distorted tetrahedra with three unequal Re–Re distances on each triangular plaquette. The order of the bonds allows to define a bond chirality parameter for each triangle; the low- T structure of $\text{Cd}_2\text{Re}_2\text{O}_7$ can be thought of as “ferrochiral.” Thus the 120 K transition involves a change of symmetry, but it is, strictly speaking, not symmetry breaking: it does not belong to a symmetry lowering (i.e., choosing a subgroup of the original symmetry group) from the $T > 120$ K phase, but to replacing one symmetry element with another. This symmetry characterization is compatible with the idea that the transition at T_L is of first order.²¹

It is not clear what really happens at either the T_H or the T_L phase transition; in particular, whether there is an electronic order parameter coupled to the obvious structural ones. Though the symmetry changes are marked, they are realized by quite minute²⁸ distortions of the high- T cubic structure; thus though both phase transitions are literally structural transitions, it is not obvious that the structural change is enough to explain the drastic changes in electrical properties. In other words, we still have to search for the concomitant change of the many-electron state, which might well be the primary phenomenon. X-ray study indicates that the temperature dependence of the new Bragg peaks is anomalously slow,²⁶ which would be compatible with the

idea that the structural order parameter is secondary, induced by some underlying electronic order parameter. Re NQR and Cd NMR reveal that the local environment of the Re site loses trigonal symmetry at T_H , and that the character of orbital fluctuations changes at T_L .^{25,29} All the evidence points to significant rearrangement of the t_{2g} subbands, with consequent changes in their occupation, starting from T_H , and continuing well below T_L . We envisage an itinerant version of orbital ordering transitions.³⁰

Extending the measurements to higher pressures brings further insight. Hiroi *et al.*^{31,32} measured the resistivity under the pressure of 1.5 GPa, and at five high-pressure values between 3 and 8 GPa. 3.5 GPa suffices to suppress the major structural transition at T_H . The weak transition at T_L seems more sensitive to pressure. A single data point published in the less known Ref. 33 indicates that T_L is suppressed to zero somewhere beyond 2 GPa. Mapping out the boundary between the two good metallic phases is an outstanding issue.

Here we present new data about the resistivity ρ and thermopower S of good-quality single crystal specimens of $\text{Cd}_2\text{Re}_2\text{O}_7$ under pressure. For resistivity, we have more pressure values up to 2 GPa than in previous works, and at ambient pressure, we have extended the measurement to 600 K. Our thermopower data reveal the highly anomalous nature of the “good metallic” phases of $\text{Cd}_2\text{Re}_2\text{O}_7$. At ambient pressure, our thermopower vs T curve has a much better resolved anomaly at the lower phase transition than the recently published,²⁷ allowing us to identify it as a secondary minimum. We performed the first measurements of thermopower under pressure, and present a pressure–temperature phase diagram based on them, including new results on $T_L(p)$. We find a distinctive feature of the intermediate temperature range $T^* < T < T_H$: it is where electrical properties are remarkably sensitive to pressure. It stands to reason that this is a regime of continuing rearrangement of $5d$ subbands where the electron–lattice interaction is particularly important. In contrast, the low-temperature ($T < T^*$) good metal, and the high-temperature ($T > T_H$) bad metal, are essentially pressure-insensitive.

III. RESULTS AND DISCUSSION

A. Sample preparation and characterization

$\text{Cd}_2\text{Re}_2\text{O}_7$ single crystals were grown using vapor transport. Appropriate amounts of source materials Cd (99.9999%) and Re_2O_7 (99.99%) (both from Johnson Matthey) were sealed in an evacuated quartz tube, heated at 966 °C for 3–5 days, cooled down to 600 °C at a rate of 1–5 °C/min; then dwelt for 1–3 days before being quenched in the air. The long dwell time at 600 °C and large temperature gradient were found crucial to produce large crystals, while the cooling rate is less important. The final products appeared as purple, shiny polyhedrons, mostly formed on the cold end of the quartz tube, with dimensions from 1 mm to 1 cm on edge.

von Laue photography roughly proves the single crystallinity of the final products. However, close examination on the synchrotron x-ray powder diffraction revealed a small

portion ($\sim 2.85\%$ in weight) of ReO_2 inclusion in crystals of some specific growths. The integrated energy disperse x-ray (EDX) spectroscopy and scanning electron microscope (SEM), with an effective resolution of 1 micron, also detected the ellipsoidlike ReO_2 inclusions randomly distributed in the bulk, with nonuniform size and nonpreferred orientation. Since the formation of a detectable amount of inclusion is reasonably inferred under certain conditions in vapor transport, empirical measures regarding starting materials and growth temperature were thereafter applied. We also used magnetization and dc resistivity measurements for sample characterization. The T -dependence of the susceptibility shows a Curie-type tail below 50 K for specimens with inclusions, and the absence of a Curie tail for samples without detectable inclusions. The $T > 50$ K part of the curves was not exactly coincident but quite close. Assuming Re^{4+} ions (i.e., ReO_2 inclusions), the measured Curie constant can be used to deduce the inclusion fraction, confirming the EDX and SEM estimates. Inclusions do affect electrical properties: we found that the resistivity is significantly lowered (from $510 \Omega \text{ cm}$ to $406 \Omega \text{ cm}$ at 300 K, and from $84 \Omega \text{ cm}$ to $17 \Omega \text{ cm}$ at 2 K), when going from a sample with 2.85% inclusion to one with nominal 0%. We selected a 3 mm^3 inclusion-free sample for our measurements.

As for stoichiometry, x-ray photoelectron spectroscopy found a oxygen-rich layer formed on the top surface. The electronic probe microanalysis (EPMA) proves the homogeneity of the specimen was satisfactory, i.e., $\text{Cd:Re} = 1.00 \pm 0.01$ while the oxygen content shows definite deficiency from stoichiometry, ranging at least from 6.770 ± 0.18 to 6.990 ± 0.19 . The large deviations from an average value mostly happen at the surface part of the specimen, and simultaneously to all three elements.

The powder neutron scattering on optimally grown 114Cd(98.5% richness)-substituted $\text{Cd}_2\text{Re}_2\text{O}_7$ clearly indicates an oxygen occupancy of 0.860 ± 0.03 on the O2 site (with Rp-factor 6.7%) and no vacancy at other sites. On the same specimen, EMPA gave an agreeable $0.6.770 \pm 0.18$ within experimental error. We conclude that all of our specimens have the composition $\text{Cd}_2\text{Re}_2\text{O}_{6.86}$.

B. Resistivity and thermopower under pressure

For electrical measurements, the crystal was cut in smaller pieces of rectangular parallelepiped shape with the dimensions $1.5 \times 0.25 \times 0.025 \text{ mm}$. After placing four contacts on the sample, it was mounted on a homemade thermopower sample holder, which fits into a clamped pressure cell. Small metallic heaters installed at both ends of the sample generated the temperature gradient measured with a Chromel–Constantan differential thermocouple. The pressure medium used in this study was kerosene, and the maximum pressure was 2 GPa. The pressure was measured using a calibrated InSb pressure gauge.

The temperature dependence of the ambient-pressure resistivity of a single-crystal specimen of $\text{Cd}_2\text{Re}_2\text{O}_7$ was shown in Fig. 1(left). We stress that previous measurements did not extend up to 600 K. Right above the $T > T_H$ transi-

tion, the resistivity appears to have saturated, but the extended scale shows up a further increase with temperature. It strikes the eye that the high- T resistivity is not linear in T ; this is also brought out by the enlargement of the high- T part of the derivative plot (Fig. 1, right). The shape of the ρ vs T curve deviates from what one would expect from the phonon mechanism, and we ascribe it to interorbital (or intersubband) scattering.

We refer also to the $d\rho/dT$ derivative plots shown in Fig. 2(top). The continuous metal-to-metal transition at $T_H = 200 \text{ K}$ is marked by a strong peak of the derivative which is known to correlate with the susceptibility and specific heat anomalies.²⁴ The overall $T < T_H$ behavior is similar to that known from previous measurements. The derivative plot $d\rho/dT$ vs T shows three characteristic temperatures. The large peak on the high- T side could serve to define T_H , but we prefer the definition from the derivative of the thermopower. The broad, nearly pressure-independent hump at $T^* \approx 60 \text{ K}$ marks the boundary between two regimes within the same low-temperature phase. There is also a recognizable minimum between these two maxima; at $p = 1 \text{ atm}$, it is a rather sharp feature at $\sim 130 \text{ K}$, and happens to lie near the second transition temperature T_L which we identify from thermopower data. However, we discard the possibility of identifying T_L from this anomaly. The reason is that a minimum in $d\rho/dT$ continues to show up at all pressures, while there are good reasons to think that the second phase transition is completely suppressed before p reaches 1.8 GPa.

The residual resistivity is $30 \mu\Omega \text{ cm}$, similar to the value given in Ref. 31, but about a factor of 2 higher than the value quoted in Refs. 20 and 27. The cooling/heating rate in our measurements was $\approx 0.6 \text{ K/min}$, six times faster than in the measurements of Hiroi *et al.*²⁰ This might be the reason why we did not see hysteresis in either resistivity or thermopower, though we have a fairly dense set of data points with little scatter in the relevant range of T . Nevertheless, we agree with the suggestion that the second phase transition is weakly first order.

We carried out measurements at pressures of $p = 1 \text{ atm}$, 0.6, 1.2, 1.8, and 2 GPa. The T -dependence of the resistivity ρ for different pressures (up to 300 K) is shown in Fig. 2 (bottom), the derivative curves in Fig. 2 (top), while the thermopower S is shown in Fig. 3.

The thermopower is negative at all temperatures/pressures. The T_H phase transition has, at any pressure, an even more spectacular signature in the thermopower than in other quantities measured before. It is associated with a steep decrease of S , which continues until at $T^* \approx 60 \text{ K}$, S reaches a minimum at which $|S|$ is about a factor of 10 higher than at $T = T_H$. Below T^* , S tends to zero in an approximately pressure-independent manner. Our thermopower data allow identifying three distinct regimes of temperature: (i) both ρ and S are essentially pressure-independent up to T^* ; (ii) the thermopower is quite sensitive to pressure at $T^* < T < T_H$; (iii) S and ρ are again essentially pressure-independent in the high-temperature ($T > T_H$) regime. Regime (ii) is the same where x-ray studies indicate an anomalously slow

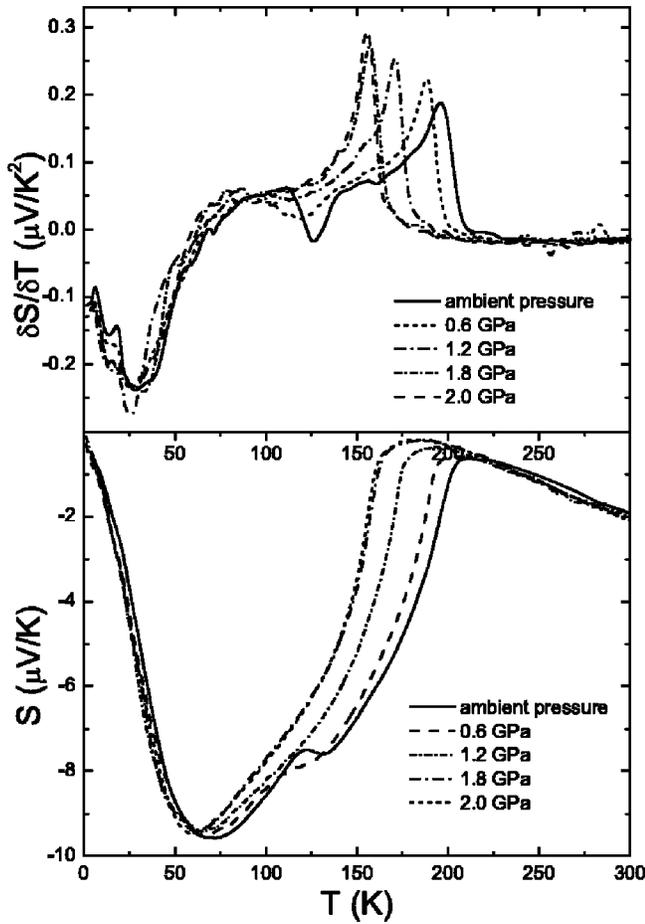


FIG. 3. (Bottom) The temperature dependence of the thermopower S for several pressures. (Top) The temperature dependence of the derivative of the thermopower $\delta S/\delta T$ for several pressures.

T -dependence of the structural order parameter. The second phase transition, whenever found, sits in the middle of (ii).

The overall value of the thermopower is rather small: $|S|$ never exceeds $10 \mu\text{V}/\text{K}$. Some $5d$ elements have higher thermopower than this, and one might have expected that the narrower d -bands of our oxide give rise to a larger thermopower. However, T -dependent partial cancellation between holelike and electronlike contributions may explain the observations. The degree of cancellation is smaller in the $T < T_H$ phases; this may be compatible with the disappearance of the heavy hole pocket found in the high-temperature (cubic phase) band structure.^{9,32} It may also explain why we do not find the straightforward metallic behavior $S \propto T$ at $T > T_H$; in fact, the regime $200 \text{ K} < T < 300 \text{ K}$ is better described by $S \propto T^2$.

Some features are more clearly seen in the derivative plot dS/dT (Fig. 3, top). The T_H transition is well defined by the cusp of dS/dT . This is the definition we use in plotting the corresponding phase boundary (Fig. 7). This may seem arbitrary, but we may bring the following argument: Loosely thinking of the thermopower as a measure of the electronic entropy, finding an anomaly in dS/dT is like finding an anomaly in the specific heat. In any case, the peak

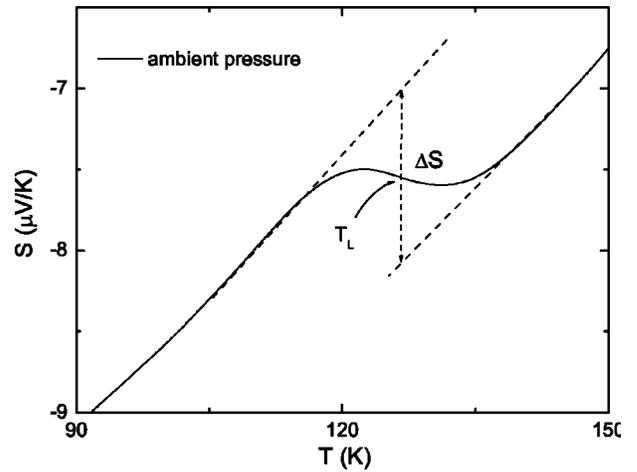


FIG. 4. We interpret the S -shaped thermopower anomaly as a smoothed-out discontinuity.

positions of dS/dT and $d\rho/dT$ are lying pretty close.³⁴ It is remarkable that the dS/dT peak gets sharper under pressure. (A similar observation was made about the ρ vs T curves in Ref. 31.)

The second phase transition shows up in the S vs T plot (Fig. 3). At ambient pressure, there is a sizable dip in S at about 120 K, followed by a secondary minimum at ≈ 130 K. Let us observe that if we imagine the S -anomaly sharpened

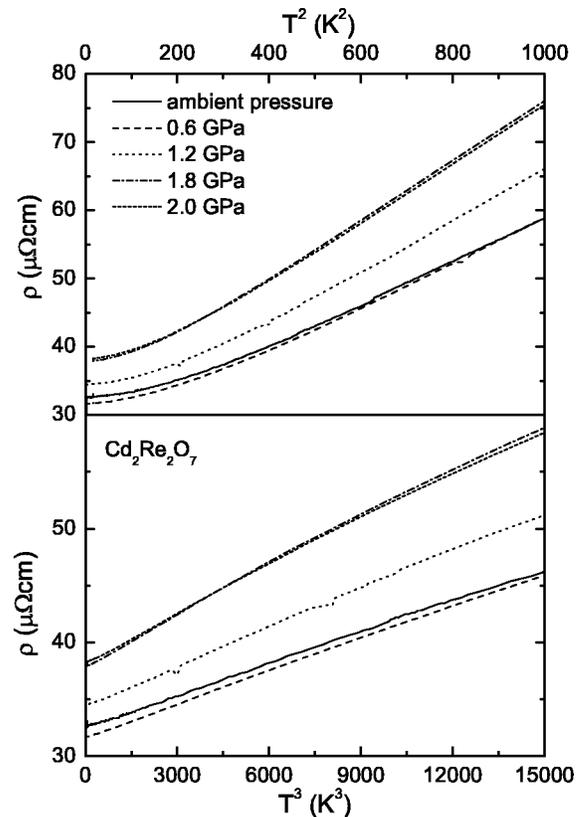
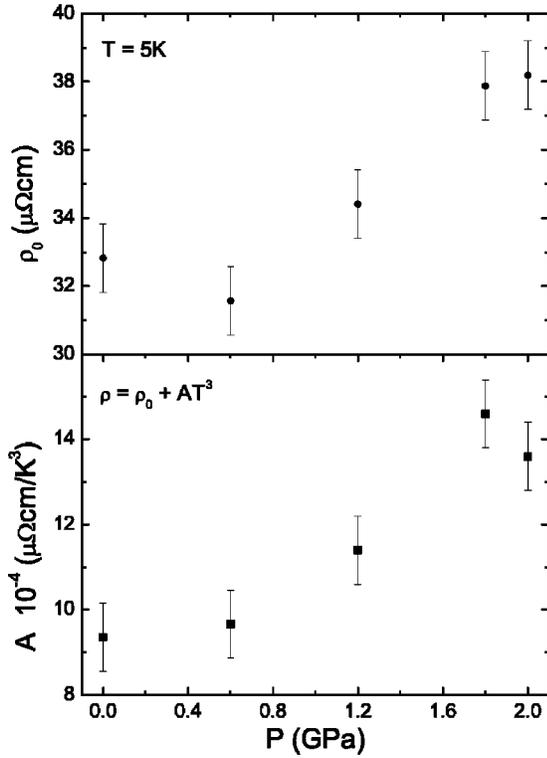


FIG. 5. (Top) The resistivity in the range 1–30 K, plotted as a function of T^2 . (Bottom) The resistivity in the range 1–25 K, plotted as a function of T^3 .

FIG. 6. The pressure dependence of ρ_0 and A_3 .

(the bump and the dip getting closer, without reducing their amplitudes), it would be consistent with a discontinuity³⁵ of $\Delta S \approx -1 \mu\text{V/K}$ (Fig. 4). It suggests that we center the phase transition at the point of inflection between the bump and the dip, in other words at the local minimum of dS/dT . This would be consistent with regarding the thermopower anomaly as the sign of a smeared-out (and very weak) first order transition, confirming Hiroi *et al.*²⁰ We note that a thermopower discontinuity is associated with some first order electronic transitions, such as the valence transition of YbInCu_4 .³⁶

The phase transitions shift under pressure: T_H drops to 156 K under 2 GPa [this is a less steep decrease than that seen in Ref. 31, where $T_H(2 \text{ GPa}) \approx 130 \text{ K}$. This reflects a difference in sample quality, a point to which we return later]. We already commented on the apparently increasing sharpness of the transition. The T_L transition gets suppressed rather fast under pressure. At 0.6 GPa the dip-and-bump complex seems just to have shrunk to a point of inflection: the local minimum of dS/dT reaches 0 at 115 K (Fig. 3, top). At 1.2 GPa there is not even a point of inflection, but we still risk identifying the bottom of a valley in dS/dT at $\approx 105 \text{ K}$. The thermopower curves are perfectly smooth in the region $T^* < T < T_H$ at higher pressures, thus the second phase transition certainly vanishes somewhere below 1.8 GPa.

Now we return to our resistivity data. The $T > T_H$ resistivity is large, essentially pressure-independent, and increases slowly with T , indicating the presence of a strong scattering mechanism specific to the pyrochlore structure.

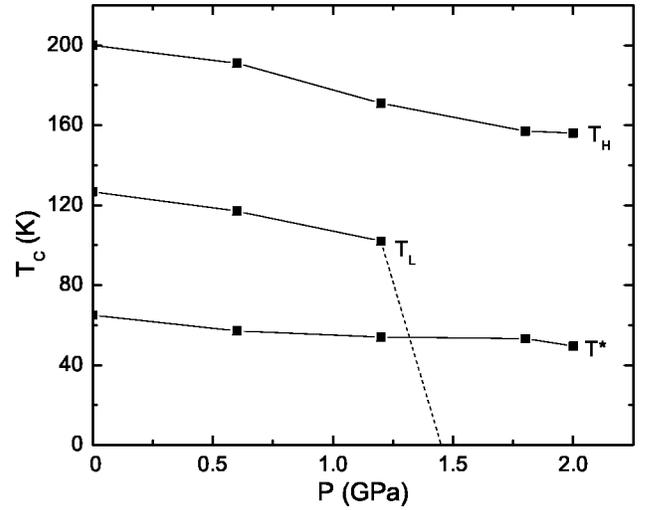


FIG. 7. The T - p phase diagram derived from thermopower and resistivity measurements. Definitions: T_H from the peak in dS/dT ; T_L from the minimum of dS/dT ; T^* is the position of the low- T broad maximum of ρ .

The high-temperature phase is cubic, thus the restoration of the orbital degree of freedom gives an extra scattering mechanism.

The observed lack of a magnetic field dependence of the thermopower also indicates that spin disorder scattering is not important in $\text{Cd}_2\text{Re}_2\text{O}_7$.²⁷

Below T_H the resistivity begins to decrease sharply, following a roughly linear T -dependence down to about 50 K, below which it bends over into a seemingly power-law regime which has been fitted either with T^2 or with T^3 dependencies.^{22,27,31} $\rho = \rho_0 + A_2^* T^2$ with an enhanced value $A_2^*/A_2 \propto (m^*/m)^2$ would be considered typical of strongly correlated systems, and it would be expected to show up here, since the specific heat shows enhancement. However, we found that the T^2 law would give an acceptable fit only in a narrow range of T , and even then at low pressures only (Fig. 5, top). In agreement with previous work,²² we find that a $\rho = \rho_0 + A_3 T^3$ fit works better (Fig. 5, bottom). The T^3 -law is to be ascribed to electron-phonon rather than to electron-electron scattering. We did not attempt to fit with a combination of T^2 - and T^3 -like terms. Undoubtedly one would find a T^2 contribution, but certainly not so large as to satisfy the Kadowaki-Woods relation.

The pressure dependence of ρ_0 and A_3 is given in Fig. 6. A moderate increase in A is compatible with increased electron-phonon interaction in a compressed lattice. We call attention to the fact that the pressure dependence of ρ_0 is quite weak, even at 2 GPa we find less than 40 $\mu\Omega \text{ cm}$. This is to be contrasted with the results of Hiroi *et al.*³¹ who find an approximately sixfold increase in ρ_0 at 1.5 GPa, and a twofold increase in A_2^* . The authors of Ref. 31 would probably agree that correlation, as manifested in A_2^* , is weak at ambient pressure, but argue that its role is increasing at higher pressures. Our pressure range is limited to 2 GPa, but within this range, we do not detect a tendency towards heavy fermion behavior. Obviously, there is sample dependence in

the observed behavior; we think that the weak pressure dependence of ρ_0 is an indication of the good quality of our samples.

The difficulty in deciding what happens to the electronic structure below 200 K may partly arise from trying to reduce everything to a single number, the enhancement factor of the effective density of states $z^{-1} = \mathcal{N}^*(\epsilon_F)/\mathcal{N}(\epsilon_F)$. This would appear as the enhancement factor of the thermal effective mass $z^{-1} = m^*/m = \gamma^*/\gamma$, the spin susceptibility, and the plasma frequency.¹⁵ Much of the previous discussion relied on the idea that the structural transitions open pseudogaps in the spaghetti of t_{2g} subbands, and consequently $\mathcal{N}^*(\epsilon_F)$ is reduced.²⁴ This seems to agree with the reduction in susceptibility,¹⁶ but makes it difficult to understand why the conductivity is substantially increased. One may argue²⁴ that heavy carriers got eliminated, which at $T > 200$ K did not contribute to conductivity but rather acted as scatterers. Removing narrow subbands from the vicinity of ϵ_F would mean that $\mathcal{N}(\epsilon_F)$ is reduced. The temperature dependence of χ , the Knight shift and $(TT_1)^{-1}$ measured by ^{111}Cd NMR are well described by assuming a reduced $\mathcal{N}(\epsilon_F)$.²⁵

Our thermopower measurements do not allow us to infer $\mathcal{N}(\epsilon_F)$. Using the simplest picture of a correlated one-band model³⁷ the thermopower $S \propto -(k_B/|e|)z^{-1} \times (\mathcal{N}'(\epsilon_F)/\mathcal{N}(\epsilon_F))$ measures the band asymmetry about ϵ_F rather than the density of states. Our data are thus indicative of a strongly increasing asymmetry below 200 K. We may envisage a heavy subband gradually crossing out from the vicinity of ϵ_F , which gives a strong contribution to $\mathcal{N}'(\epsilon_F)$.

A pressure–temperature phase diagram based on plotting the characteristic temperatures T_H , T_L , and T^* is shown in Fig. 7. The last data point for T_L at 1.2 GPa is, as we have seen, rather tentative; in any case, T_L is suppressed fast. This is in general agreement with a previous observation,³³ but our critical pressure for T_L is rather lower. In contrast, our T_H vs pressure curve would lie above that found by Hiroi *et al.*³¹ T^* is always defined by the peak position of the broad maximum of dp/dT . It is rather pressure-independent, and approximately coincides with the low- T minimum of S . We do not think it associated with a phase transition but it is nevertheless significant since it marks the crossover from a stable good metallic state into a fluctuating intermediate- T state. We may think of it as the coherence temperature of the low- T electronic structure.

Since we did not find the third normal metallic phase at 1.8 GPa, we drew a dashed line to show that T_L should drop to zero somewhere between 1.2 and 1.8 GPa. In principle, a line of first-order transitions could terminate at a critical point at some finite temperature, but the recent finding of a symmetry change at T_L rules this out;¹⁹ the phase boundary has to continue down to $T=0$.

Finally, let us return to the question whether we find $\text{Cd}_2\text{Re}_2\text{O}_7$ a system with significant correlation effects. The answer is yes. Let us recall, though, that it is foremost the high- T ($T > 200$ K) phase of $\text{Cd}_2\text{Re}_2\text{O}_7$, which is assumed to be strongly correlated. This view is supported by a recent

observation³² that stabilizing the cubic phase under very high pressure ($p > 3.5$ GPa) gives rise to substantially larger m^*/m than the value inferred for the low-pressure good metallic phases. Large mass enhancement is tantamount to the system having high entropy at relatively low temperatures. There are two ways to let the entropy vanish as $T \rightarrow 0$: either by sustaining heavy fermion behavior to low T s, or by letting ordering transitions intervene.³⁸ Apparently, the first scenario is realized in $\text{Cd}_2\text{Re}_2\text{O}_7$ at high pressures, while the second at low-to-medium pressures. The 200 K and 125 K transitions reduce the apparent mass enhancement by suppressing short-range fluctuations, first of all orbital fluctuations. As far as thermopower can be thought of as giving a measure of electronic entropy, we can invoke our Fig. 3: suppression of T_H under pressure means the smooth continuation of the fluctuating electronic state of the cubic phase to lower temperatures.

IV. CONCLUSION

We presented resistivity and thermopower measurements on single crystal samples of $\text{Cd}_2\text{Re}_2\text{O}_7$ under five different pressure values up to 2 GPa, and used the data to analyze the phase diagram in the T – p plane. The pressure dependence of the thermopower shows that the wide temperature interval between the upper structural transition (at ambient pressure $T_H = 200$ K) and the coherence temperature $T^* \approx 60$ K is a regime of continuing rearrangement of the electronic structure. The cubic-to-tetragonal transition at 200 K does not immediately lead to a stable low-temperature phase, but rather to a state with electronic and structural ambiguity. A particular manifestation of this behavior is the appearance of a second structural phase transition which is, however, confined to relatively low pressures (< 1.8 GPa), while the overall features of the system remain the same at higher pressures.

Our results indicate that both coupling to the lattice, and the strongly temperature dependent redistribution of the electrons over the t_{2g} orbital states (or alternatively the t_{2g} subbands) are important for understanding the behavior of this frustrated itinerant system.

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- ¹N.F. Mott, *Metal-Insulator Transitions* (Taylor & Francis, London, 1974).
- ²P. Fazekas, *Lecture Notes on Electron Correlation and Magnetism* (World Scientific, Singapore, 1999).
- ³P. Fazekas and E. Tosatti, *Philos. Mag. B* **39**, 229 (1979).
- ⁴In the $A_2B_2O_7$ structure, both the A and B sublattices can be envisaged as a network of corner sharing tetrahedra, which is nowadays referred to as the pyrochlore lattice.
- ⁵H. Fukazawa and Y. Maeno, *J. Phys. Soc. Jpn.* **71**, 2578 (2002).
- ⁶D. Mandrus, J.R. Thompson, R. Gaál, L. Forró, J.C. Bryan, B.C. Chakoumakos, L.M. Woods, B.C. Sales, R.S. Fishman, and V. Keppens, *Phys. Rev. B* **63**, 195104 (2001).
- ⁷W.J. Padilla, D. Mandrus, and D.N. Basov, *Phys. Rev. B* **66**, 035120 (2002).
- ⁸C. Pinettes, B. Canals, and C. Lacroix, *Phys. Rev. B* **66**, 024422 (2002).
- ⁹D.J. Singh, P. Blaha, K. Schwarz, and J.O. Sofo, *Phys. Rev. B* **65**, 155109 (2002).
- ¹⁰S. Fujimoto, *Phys. Rev. B* **64**, 085102 (2001).
- ¹¹H. Kontani and K. Ueda, *Phys. Rev. Lett.* **80**, 5619 (1998).
- ¹²H. Tsunetsugu, *J. Phys. Soc. Jpn.* **71**, 1844 (2002).
- ¹³Y. Yamashita and K. Ueda, *Phys. Rev. B* **67**, 195107 (2003).
- ¹⁴H. Harima, *J. Phys. Chem. Solids* **63**, 1035 (2002).
- ¹⁵N.L. Wang, J.J. McGuire, T. Timusk, R. Jin, J. He, and D. Mandrus, *Phys. Rev. B* **66**, 014534 (2002).
- ¹⁶H. Sakai, H. Kato, S. Kambe, R.E. Walstedt, H. Ohno, M. Kato, K. Yoshimura, and H. Matsuhata, *Phys. Rev. B* **66**, 100509(R) (2002).
- ¹⁷H. Tsunetsugu, *Phys. Rev. B* **65**, 024415 (2001).
- ¹⁸Y. Yamashita and K. Ueda, *Phys. Rev. Lett.* **85**, 4960 (2000).
- ¹⁹J. Yamaura and Z. Hiroi, *J. Phys. Soc. Jpn.* **71**, 2598 (2002).
- ²⁰Z. Hiroi, J. Yamaura, Y. Muraoka, and M. Hanawa, *J. Phys. Soc. Jpn.* **71**, 1634 (2002).
- ²¹I.A. Sergienko and S.H. Curnoe, cond-mat/0301029.
- ²²M. Hanawa, Y. Muraoka, T. Tayama, T. Sakakibara, J. Yamaura, and Z. Hiroi, *Phys. Rev. Lett.* **87**, 187001 (2001); R. Jin, J. He, S. McCall, C.S. Alexander, F. Drymiotis, and D. Mandrus, *Phys. Rev. B* **64**, 180503(R) (2001); H. Sakai, K. Yoshimura, H. Ohno, H. Kato, S. Kambe, R.E. Walstedt, T.D. Matsuda, Y. Haga, and Y. Onuki, *J. Phys.: Condens. Matter* **13**, L785 (2001).
- ²³Figure 1 also shows the superconducting transition at $T_c \approx 1$ K which is not discussed in the present paper.
- ²⁴R. Jin, J. He, J.R. Thompson, M.F. Chisholm, B.C. Sales, and D. Mandrus, *J. Phys.: Condens. Matter* **14**, L117 (2002).
- ²⁵O. Vyaselev, K. Arai, K. Kobayashi, J. Yamazaki, K. Kodama, M. Takigawa, M. Hanawa, and Z. Hiroi, *Phys. Rev. Lett.* **89**, 017001 (2002).
- ²⁶J.P. Castellán, B.D. Gaulin, J. van Duijn, M.J. Lewis, M.D. Lumsden, R. Jin, J. He, S.E. Nagler, and D. Mandrus, *Phys. Rev. B* **66**, 134528 (2002).
- ²⁷D. Huo, A. Mitsuda, Y. Isikawa, J. Sakurai, H. Sakai, H. Ohno, M. Kato, K. Yoshimura, S. Kambe, and R.E. Walstedt, *J. Phys.: Condens. Matter* **14**, L257 (2002).
- ²⁸Strictly speaking, we know only that the overall changes in unit cell dimensions are very small. It may turn out that individual intracell atomic motions are relatively large, which would allow that the phase transitions are primarily structurally driven. We take a different view.
- ²⁹K. Arai, K. Kobayashi, K. Kodama, O. Vyaselev, M. Takigawa, M. Hanawa, and Z. Hiroi, *J. Phys.: Condens. Matter* **14**, L461 (2002).
- ³⁰The lattice responds to the change in the electronic state, thus the transitions may be called band-Jahn-Teller transitions. When speaking of orbital order, we imply that the phenomenon is driven by electron-electron interactions, and it would occur even in a rigid lattice.
- ³¹Z. Hiroi, T. Yamauchi, T. Yamada, M. Hanawa, Y. Ohishi, O. Shimomura, M. Abliz, M. Hedo, and Y. Uwatoko, *J. Phys. Soc. Jpn.* **71**, 1553 (2002).
- ³²Z. Hiroi, M. Hanawa, Y. Muraoka, and H. Harima, *J. Phys. Soc. Jpn.* **72**, 21 (2003).
- ³³Z. Hiroi and M. Takigawa, *Solid State Phys. (in Japanese)* **37**, 253 (2002).
- ³⁴We checked that the peak positions of $d\rho/dT$ and dS/dT are quite close-lying, thus our choice of identifying T_H from thermopower is not in conflict with resistivity data.
- ³⁵Using the naive Thomson recipe of equating thermopower with electronic entropy, we would arrive at the fairly small entropy discontinuity 0.08 J/K(mol). This would be in qualitative agreement with the finding by Hiroi *et al.* (Ref. 20).
- ³⁶M. Očko, D. Drobac, J.L. Sarrao, and Z. Fisk, *Phys. Rev. B* **64**, 085103 (2001).
- ³⁷J. Merino and R.H. McKenzie, *Phys. Rev. B* **61**, 7996 (2000).
- ³⁸C.M. Varma, *Comments Solid State Phys.* **11**, 221 (1985).