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LETTER TO THE EDITOR

Fluctuation effects on the physical properties of $\text{Cd}_2\text{Re}_2\text{O}_7$ near 200 K

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Abstract

Experimental investigation of the resistivity ρ , susceptibility χ , specific heat C_p and Hall coefficient R_H of the pyrochlore $\text{Cd}_2\text{Re}_2\text{O}_7$ reveals the presence of a continuous phase transition of uncertain origin with critical temperature $T^* = 200$ K. Electron and x-ray diffraction measurements indicate that a commensurate structural transformation accompanies the changes in the electronic properties, implying that lattice as well as electronic degrees of freedom are involved in the transition. Remarkable scaling relationships between ρ , χ and C_p are observed, indicating that fluctuations are crucial in the transition regime. Both spin and ionic density fluctuation scenarios are considered.

Pyrochlores containing second- and third-row transition metals such as Ru, Os and Re have attracted considerable interest lately because they display novel collective phenomena [1–5]. In the case of $\text{Cd}_2\text{Os}_2\text{O}_7$, for example, the observed continuous metal–insulator transition was interpreted both in terms of a Slater transition [2], and as a transition to an excitonic insulating state [5]. Recently, superconductivity was discovered in $\text{Cd}_2\text{Re}_2\text{O}_7$ [3, 4] making it the only known superconductor based on the pyrochlore structure. Although superconductivity in $\text{Cd}_2\text{Re}_2\text{O}_7$ continues to attract interest, the normal-state properties of this material are also intriguing. In this letter, we present a study of the resistivity ρ , magnetic susceptibility χ , specific heat C_p and Hall coefficient R_H of $\text{Cd}_2\text{Re}_2\text{O}_7$ single crystals over a wide temperature range. We find that all quantities exhibit anomalies near a characteristic temperature $T^* = 200$ K, due to the onset of a continuous phase transition. Electron diffraction results, which show commensurate superlattice spots below 200 K, indicate that the lattice plays an important role in the transition. Quantitative analysis of the experimental data leads to the discovery of remarkable scaling relationships between $d(\rho T)/dT$, $d(\chi T)/dT$ and C_p in the transition regime. These scaling relationships imply that critical fluctuations associated with the phase transition dominate both the electronic transport and thermodynamic properties of $\text{Cd}_2\text{Re}_2\text{O}_7$ near 200 K.

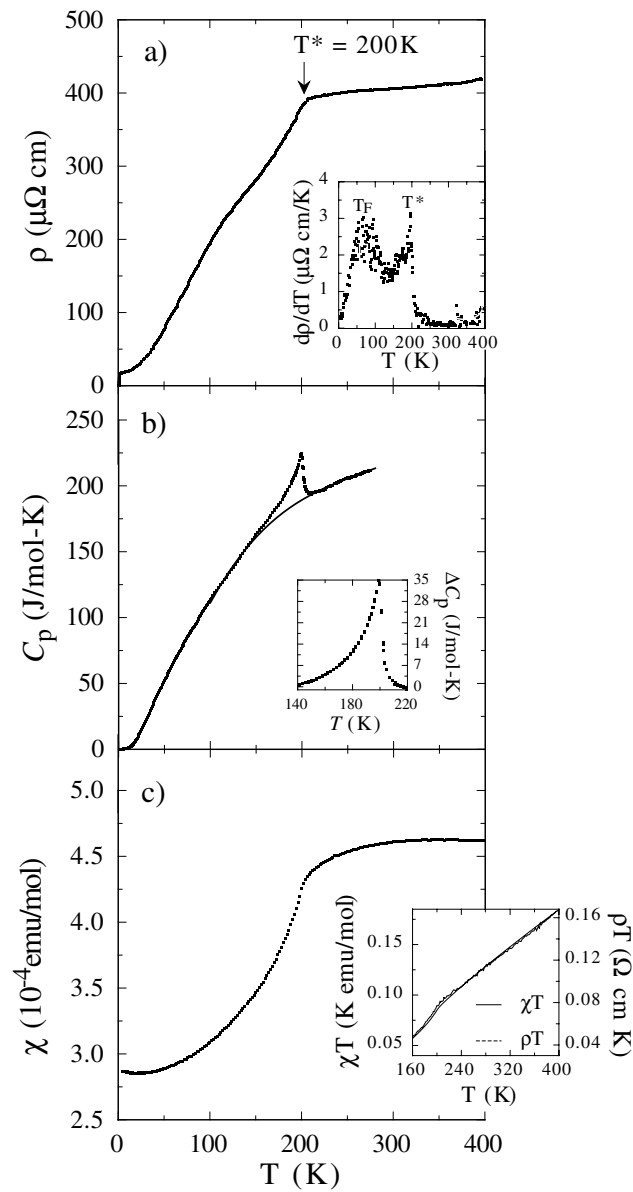


Figure 1. (a) Temperature dependence of the electrical resistivity of $\text{Cd}_2\text{Re}_2\text{O}_7$ between 1.5 and 400 K. The inset shows the temperature derivative of resistivity $d\rho/dT$ versus T . (b) Specific heat versus temperature from 2 to 280 K. The inset shows the temperature dependence of the anomalous component of the specific heat ΔC_p associated with the transition. (c) Magnetic susceptibility of $\text{Cd}_2\text{Re}_2\text{O}_7$ obtained in an applied field of 1 T. The inset shows the temperature dependence of χT (solid curve) and ρT (dashed curve) between 160 and 400 K.

The synthesis and initial characterization of the $\text{Cd}_2\text{Re}_2\text{O}_7$ crystals used in this work was reported in [4, 6]. Shown in the main frame of figure 1(a) is the temperature dependence of the dc electrical resistivity ρ between 1.5 and 400 K, measured using a standard four-probe technique. In general, ρ increases with increasing temperature, indicating the itinerant nature

of the electrons. However, it appears that $\rho(T)$ behaves differently in different temperature regimes. By plotting the data as $d\rho/dT$ versus T in the inset of figure 1(a), two peaks are clearly visible: one occurs at $T_F \sim 60$ K, the other at $T^* \sim 200$ K. Below 60 K, the resistivity has been found to exhibit a quadratic temperature dependence [4], suggesting that the ground state of $\text{Cd}_2\text{Re}_2\text{O}_7$ is a moderately correlated Fermi liquid. The sharp peak at 200 K, caused by a kink in $\rho(T)$, signifies a phase transition. Above T^* , $d\rho/dT$ is positive but small, displaying a slight increase with increasing temperature. Similar high-temperature behaviour was also observed in the related material $\text{Cd}_2\text{Os}_2\text{O}_7$ [2]. It should be mentioned that no thermal hysteresis was observed in the resistivity of $\text{Cd}_2\text{Re}_2\text{O}_7$, consistent with a continuous phase transition occurring at 200 K.

Although the metallic behaviour ($d\rho/dT \geq 0$) of $\text{Cd}_2\text{Re}_2\text{O}_7$ was first reported in 1965 [7], the kink in resistivity was not observed in these early measurements. Quantitatively, we obtain $\rho(300 \text{ K}) = 406 \mu\Omega \text{ cm}$ and a residual resistivity $\rho_{\text{res}} = 17 \mu\Omega \text{ cm}$ [4], much lower than those given in [7]. This suggests that scattering by defects may smear out the resistivity anomaly at 200 K, so that this important feature becomes visible only in samples made from very pure starting materials.

The specific heat C_p of $\text{Cd}_2\text{Re}_2\text{O}_7$ was measured using a commercial heat pulse calorimeter from quantum design. As can be seen in figure 1(b), C_p reveals an anomaly peaked at T^* . No latent heat or thermal hysteresis was observed in the specific heat, consistent with a continuous phase transition. To estimate the magnitude and shape of the specific heat anomaly, a smooth polynomial was fitted to the data from $100 \text{ K} \leq T \leq 140 \text{ K}$ and $220 \text{ K} \leq T \leq 280 \text{ K}$ (see the dashed curve in figure 1(b)). This results in a specific heat jump of $\Delta C_p(T^*) = 34.0 \text{ J mol}^{-1} \text{ K}^{-1}$ (see the inset of figure 1(b)) and entropy $S = 3.77 \text{ J mol}^{-1} \text{ K}^{-1}$ by integrating $\Delta C_p/T$ from 140 to 220 K.

The dc magnetic susceptibility χ of $\text{Cd}_2\text{Re}_2\text{O}_7$ was measured using a SQUID magnetometer from Quantum Design. Figure 1(c) displays the temperature dependence of χ at 1 T between 2 and 400 K. Measurements performed between 0.1 and 2 T yield identical results. No thermal hysteresis is noticeable within the experimental resolution. Like the resistivity, the susceptibility also reveals a kink at T^* , below which χ decreases rapidly and tends to saturate below ~ 30 K.

In an itinerant electron system, a smooth increase of the magnetic susceptibility with temperature may suggest the presence of spin fluctuations [8]. In this case, the electron scattering is expected to be dominated by short-range spin fluctuations as well [9]. For $\text{Cd}_2\text{Re}_2\text{O}_7$, the extremely weak temperature dependence of ρ above the transition indicates that the mean free path of the carriers has saturated, very likely on the order of an interatomic spacing. To further examine the role of spin fluctuations in the electrical transport of $\text{Cd}_2\text{Re}_2\text{O}_7$, we replot the resistivity and susceptibility as χT versus T and ρT versus T respectively in the inset of figure 1(c). It is remarkable that two sets of data are coincident between 160 and 400 K, with no adjustable parameters involved in this procedure. It is possible, therefore, that the electrical transport, at least in the scaling region, is governed by magnetic scattering due to spin fluctuations, with the fluctuations becoming longer ranged and slower below the transition, resulting in increased electrical conductivity. However, as we discuss below, it is also possible to argue that ionic density fluctuations are dominating the electronic scattering, although in this case the scaling of the resistivity and susceptibility over a broad temperature range becomes more difficult to understand.

The effects of spin fluctuations have been studied mainly in systems that magnetically order. Near the magnetic critical point, the temperature derivatives of the magnetic resistivity and susceptibility are expected to vary like the magnetic specific heat; i.e., $d\rho/dT$, $d(\chi T)/dT$ and ΔC_p are expected to scale as a function of temperature [9, 10]. In the case of $\text{Cd}_2\text{Re}_2\text{O}_7$ we

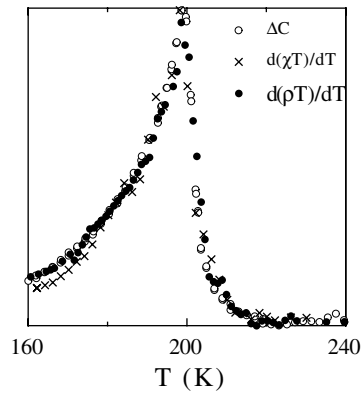


Figure 2. Temperature dependence of ΔC_p (open circles), $d(\chi T)/dT$ (crosses) and $d(\rho T)/dT$ (solid circles) between 160 and 240 K.

find that although $d\rho/dT$ scales reasonably well with ΔC_p , a much better scaling relationship was observed by comparing $d(\rho T)/dT$ with ΔC_p . In figure 2, we plot the temperature dependence of $d(\rho T)/dT$ (solid circles), $d(\chi T)/dT$ (crosses) and ΔC_p (open circles). Remarkably, all curves match well between 160 and 240 K with no adjustable parameters except an overall normalization for each quantity. This scaling behaviour clearly demonstrates that the anomalies observed in the specific heat, resistivity and magnetic susceptibility are intimately related and have a common origin.

Does the transition at 200 K involve magnetic order? The abrupt decrease of magnetic susceptibility below 200 K is certainly consistent with this idea, although Re compounds that display magnetic order are rare. In $\text{Cd}_2\text{Re}_2\text{O}_7$, the formal oxidation state of the Re ions is 5+ with two electrons accommodated in t_{2g} manifold. Hund's rules favour parallel spins within each manifold, and lead to spin $S = 1$. If the transition is accompanied by magnetic ordering, Re ions are expected to eliminate $2R \ln(2S+1) = 18.3 \text{ J mol}^{-1} \text{ K}^{-1}$ of entropy. This is clearly much larger than the observed value of $3.77 \text{ J mol}^{-1} \text{ K}^{-1}$ and suggests that the transition does not involve long-range magnetic order, at least of localized moments.

To gain further insight into the scattering mechanisms operative in $\text{Cd}_2\text{Re}_2\text{O}_7$, Hall measurements were performed. The Hall coefficient R_H was derived from the antisymmetric part of the transverse resistivity under magnetic field reversal at a fixed temperature. Figure 3 presents the temperature dependence of R_H at 8 T between 10 and 300 K. It is interesting to note that R_H also reveals a cusp at 200 K, above which R_H is positive and decreases with increasing temperature. Conversely, R_H decreases with decreasing temperature below 200 K and changes sign from positive to negative near 125 K. This is consistent with band structure calculations that predict both electron and hole sheets at the Fermi surface of $\text{Cd}_2\text{Re}_2\text{O}_7$ [5]. The observation of the cusp-shaped $R_H(T)$ suggests that the Hall contribution is also affected by the transition at 200 K. For comparison, we replot $d(\chi T)/dT$ versus T in figure 3. Unlike the resistivity, R_H does not scale well with $d(\chi T)/dT$ above 200 K. Nevertheless, it is worth noting that both R_H and $d(\chi T)/dT$ vary in the same manner below 200 K down to 60 K. This suggests that the scattering due to fluctuations remains effective at temperatures well below the critical point.

The scaling relation between $d(\chi T)/dT$ and ΔC_p is not unique for magnetic systems. For example, it was also observed in the blue bronze $\text{K}_{0.3}\text{MoO}_3$ near the charge density wave (CDW) transition [11]. Theoretically, Chandra [12] argued that ionic density fluctuations

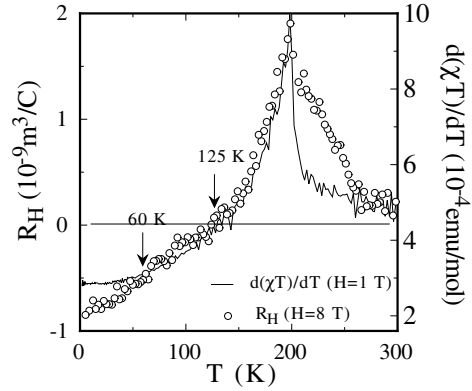


Figure 3. Temperature dependence of Hall coefficient R_H (open circles). For comparison, $d(\chi T)/dT(T)$ is also plotted (curve).

near the Peierls transition temperature could lead to a variation in the density of states (DOS) at the Fermi level, and consequently result in scaling behaviour between $d\chi/dT$ and ΔC_p . A CDW transition involves a (typically incommensurate) periodic structural distortion, and the opening of an energy gap at the Fermi level. For $\text{Cd}_2\text{Re}_2\text{O}_7$, both x-ray and electron diffraction indicate that there is indeed a structural change below T^* . Figure 4 presents [001] zone-axis electron diffraction patterns obtained at 300, 200 and 108 K. At room temperature, the Bragg spots in the diffraction pattern are consistent with the known cubic $Fd\bar{3}m$ space group of $\text{Cd}_2\text{Re}_2\text{O}_7$. Upon cooling from room temperature, sharp commensurate superlattice reflections at $hkl : h, (k, l) = 2n$ become visible below 200 K, where n is an integer. These spots become more intense with decreasing temperature. This result is also seen using x-ray powder diffraction [13] and rotating anode measurements [14]. A detailed analysis of the low-temperature structure will be presented elsewhere [13].

In the ionic-density-fluctuation scenario, the rapid decrease of magnetic susceptibility below 200 K results from a reduction in the DOS at the Fermi energy and consequent reduction of the Pauli paramagnetic contribution to the susceptibility. There are several possibilities for the detailed nature of this sort of transition. One possibility is that a portion of the Fermi surface develops a gap, possibly due to a CDW instability. Band structure calculations, however, show no evidence of Fermi surface nesting in $\text{Cd}_2\text{Re}_2\text{O}_7$ [5, 15]. Another possibility involves a cooperative Jahn–Teller transition similar to that observed in A-15 superconductors [16]. In A-15s the structural transition is cubic to tetragonal and it is believed that the tetragonal distortion splits a sharp peak in the DOS into two smaller peaks with the Fermi energy residing in the valley between the peaks. In $\text{Cd}_2\text{Re}_2\text{O}_7$ the low-temperature structure is also likely to be tetragonal [13] so similar physics could be driving the transition. Yet another possibility involves charge ordering of the Re ions. This possibility is supported by the fact that Re^{5+} is an uncommon oxidation state for Re.

We can estimate the fraction of states at the Fermi energy that are lost during the transition by considering the drop in susceptibility. The measured susceptibility is expected to contain a paramagnetic (Pauli) contribution from spin (χ_{spin}) and a core diamagnetic contribution (χ_{core}). The core contribution can be obtained from standard tables with $\chi_{\text{core}} = -1.72 \times 10^{-4} \text{ emu mol}^{-1}$ for $\text{Cd}_2\text{Re}_2\text{O}_7$. Thus, we estimate $\chi_{\text{spin}}(2 \text{ K}) = 4.59 \times 10^{-4} \text{ emu mol}^{-1}$ and $\chi_{\text{spin}}(400 \text{ K}) = 6.34 \times 10^{-4} \text{ emu mol}^{-1}$. This analysis implies that about $\sim 28\%$ of the states at the Fermi energy are lost during the transition.

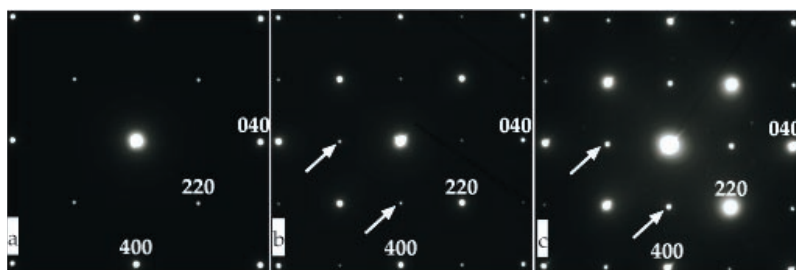


Figure 4. [001] zone-axis electron diffraction patterns of $\text{Cd}_2\text{Re}_2\text{O}_7$ at (a) 300 K, (b) 200 K and (c) 108 K. The arrows indicate the (2, 0, 0) superlattice spots as discussed in the text.

We can also evaluate the change in the DOS at the Fermi energy by considering the specific heat anomaly. The entropy of the itinerant electrons at 200 K is $\gamma \Delta T = (29.6 \text{ mJ mol}^{-1} \text{ K}^{-2}) (200 \text{ K}) = 5.92 \text{ J mol}^{-1} \text{ K}^{-1}$. The entropy eliminated during the transition is $3.77 \text{ J mol}^{-1} \text{ K}^{-1}$. If we assume that the specific heat anomaly is purely electronic, we find that approximately $3.77 / (5.92 + 3.77)$ or 39% of the states at the Fermi energy are lost. This fraction is higher than that estimated from the magnetic susceptibility. The discrepancy may be due to the assumption $S_{\text{el}} = S$, which is not fulfilled if the lattice contribution is significant.

While the variation of the susceptibility and specific heat is qualitatively consistent with the picture of a reduced DOS or partially gapped Fermi-surface, it is difficult to explain why a reduction in the DOS would result in the increased conductivity observed below the transition. Although better metallic behaviour has been previously observed in the presence of gap due to a CDW transition [17], a negative $d\rho/dT$ was observed in the critical regime. This feature is not seen in $\text{Cd}_2\text{Re}_2\text{O}_7$. One possibility is that the removed portion of Fermi surface is unimportant for the electrical transport. According to Rice and Scott [18], if the portion of Fermi surface removed by the transition is the saddle point where the Fermi velocity is very small and the DOS is high, the saddle points act as scattering sinks in high-temperature phase, and their removal can increase the conductivity. However, this theory was developed for layered materials with two-dimensional character and its application to a three-dimensional system such as $\text{Cd}_2\text{Re}_2\text{O}_7$ may be problematic. In any case, our Hall measurements indicate that the electronic structure has been affected by the transition, which leads to the sign change of R_{H} .

In summary, the normal state of $\text{Cd}_2\text{Re}_2\text{O}_7$ exhibits many intriguing properties. Thermodynamic and transport measurements indicate that a continuous phase transition of uncertain origin occurs at $T^* \sim 200 \text{ K}$. Both x-ray and electron diffraction measurements reveal commensurate superlattice reflections below T^* , indicating that lattice degrees of freedom play an important role in the transition. Remarkable scaling relationships exist between ρ , χ and C_p . These scaling relationships imply that critical fluctuations associated with the phase transition dominate both the electronic transport and thermodynamic properties of $\text{Cd}_2\text{Re}_2\text{O}_7$ near 200 K. Scenarios involving both spin and ionic density fluctuations are considered in the evaluation of the data. Although the observed structural transition suggests that ionic density fluctuations are likely to be important, a scaling relationship between ρ and χ over a wide temperature range suggests that spin fluctuations may be playing a role as well.

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