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Superconductivity in the correlated pyrochlore $Cd_2Re_2O_7$

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We report the observation of superconductivity in high-quality $Cd_2Re_2O_7$ single crystals with room-temperature pyrochlore structure. Resistivity and ac susceptibility measurements establish an onset transition temperature $T_c^{onset}=1.47$ K with transition width $\Delta T_c=0.25$ K. In applied magnetic field, the resistive transition shows a type-II character, with an approximately linear temperature-dependence of the upper critical field H_{c2}. The bulk nature of the superconductivity is confirmed by the specific heat jump with $\Delta C=37.9$ mJ/mol-K. Using the γ value extracted from normal-state specific heat data, we obtain $\Delta C/\gamma T_c=1.29$, close to the weak coupling BCS value. In the normal state, a negative Hall coefficient below 100 K suggests electronlike conduction in this material. The resistivity exhibits a quadratic T dependence between 2 and 60 K, i.e., $\rho=\rho_0+AT^2$, indicative of Fermi-liquid behavior. The values of the Kadowaki-Woods ratio A/γ^2 and the Wilson ratio are comparable to that for strongly correlated materials.

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Interest in oxide superconductors has been greatly stimulated by the high critical temperatures (T_c) of the cuprates and the unconventional superconductivity in Sr_2RuO_4. These materials form in perovskitelike structures, where CuO_2 or RuO_2 layers play important roles in the occurrence of superconductivity. Oxide superconductors with nonperovskite structures are rare. In particular, while many oxides crystallize in a pyrochlore structure with the general formula $A_2B_2O_7$ (where *A* and *B* are cations), no superconductivity has been reported in the literature. At present, it is not clear why the pyrochlore structure is unfavorable for superconductivity. Previous studies indicate that the pyrochlores, like the spinels, are geometrically frustrated.[1] The effect of geometric frustration on the physical properties of spinel materials is drastic, resulting in, for instance, heavy-fermion behavior in LiV_2O_4.[2] To understand the role of geometrical frustration in pyrochlores, we have investigated transport, magnetic, and thermodynamic properties of $Cd_2Re_2O_7$, the only known pyrochlore superconductor discovered recently.[3]

Although $Cd_2Re_2O_7$ was synthesized in 1965,[4] its physical properties remained almost unstudied except for specific heat measurements below 20 K.[5] Careful measurements of electrical resistivity, Hall effect, specific heat, and magnetic susceptibility of $Cd_2Re_2O_7$ single crystals indicate that there are at least two phase transitions below room temperature: one near 200 K (Refs. 6 and 7) and another around 1.5 K. In this communication, we focus on the latter one. Both resistivity and ac susceptibility indicate a superconducting transition at $T_c=1.47$ K. The superconducting critical field, obtained from the resistive transition, reveals an approximately linear temperature dependence. Associated with the superconducting transition, the specific heat exhibits a peak with jump $\Delta C=37.9$ mJ/mol-K. Above T_c, the Hall coefficient is negative, reflecting electron dominated conduction. Both resistivity and Hall angle data exhibit a T^2 dependence when approaching T_c from high temperatures. The T^2 behavior of the resistivity and the values of the Kadowaki-Woods ratio A/γ^2 and the Wilson ratio suggest that the ground state of $Cd_2Re_2O_7$ is a correlated Fermi liquid.

Single crystals of $Cd_2Re_2O_7$ used in this study were grown using a vapor-transport method with details described elsewhere.[8] The Cd:Re ratio was confirmed using electron microprobe analysis, but no attempt was made to determine the oxygen content. A previous study on crystals prepared by the same method claimed an oxygen stoichiometry of 7.[4] The x-ray refinement results confirm the pyrochlore structure with unit cell parameter $a=10.2244(6)$ Å at room temperature. This value is in agreement with that obtained in Ref. 4. As pointed out in Ref. 7, there is a subtle structure change at low temperatures.

Figure 1 shows the temperature dependence of the ac susceptibility from a $Cd_2Re_2O_7$ single crystal, performed by using a mutual inductance technique at an applied field of $H\sim1$ Oe and a frequency of $f=1$ kHz. The real part, χ', reveals a large diamagnetic signal below 1.15 K, marking the superconducting transition. Below 0.75 K, χ' is flat, indicating that the superconducting transition is complete. We no-

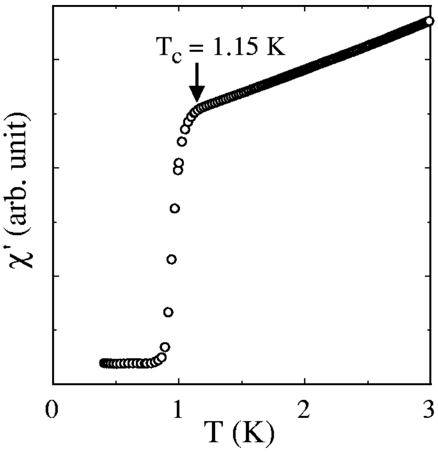

FIG. 1. Temperature dependence of the ac susceptibility (real part) of a $Cd_2Re_2O_7$ single crystal.

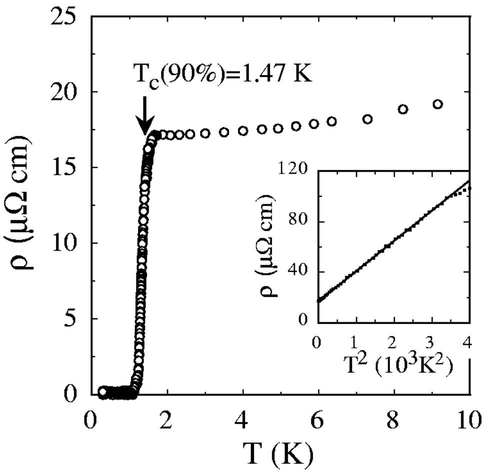

FIG. 2. Temperature dependence of the resistivity of $Cd_2Re_2O_7$. The superconducting transition is indicated. The inset shows the resistivity curve between 2 and 64 K plotted as ρ vs T^2. The solid line is a fit to experimental data between 2 and 60 K using $\rho=\rho_0+AT^2$.

ticed that χ' was not saturated down to 0.3 K in polycrystalline $Cd_2Re_2O_7$.[3]

Using a standard four-probe method, the dc electrical resistivity of $Cd_2Re_2O_7$ has been investigated. Shown in Fig. 2 is the temperature dependence of the electrical resistivity ρ between 0.3 and 10 K at zero magnetic field. Associated with the diamagnetic transition, ρ also departs from high-temperature behavior at 1.5 K and decreases abruptly to zero at 1.15 K, corresponding to the onset of diamagnetism. The resistivity varies from 10 to 90 % of the normal-state value ρ_N over a range of approximately 0.25 K.

Both resistivity and ac susceptibility measurements establish a superconducting transition with the onset transition temperature $T_c^{onset}=1.47$ K and a transition width $\Delta T_c=T_c(90\%)-T_c(10\%)=0.25$ K for our $Cd_2Re_2O_7$ single crystals, confirming the recent discovery.[3] As illustrated in the inset of Fig. 3, by applying a magnetic field H perpendicular to the current I $(H\perp I)$, the resistive transition shifts to lower temperatures. The transition width becomes wider with increasing H, a characteristic of type-II superconductivity. We may define a resistive transition temperature $T_c(H)$ which satisfies the condition that $\rho(T_c,H)$ equals to a fixed percentage p of the normal-state value ρ_N for each field H. The values of $T_c(H)$ for $p=10$, 50, and 90 % are shown in the main frame of Fig. 3, represented by the upper critical field $H_{c2}(T)$. In all cases, we find that $H_{c2}(T)$ depends more or less linearly on T with no sign of saturation down to 0.3 K (see the solid lines). The slope $dH_{c2}/dT|_{T=T_c}=-0.56$ T/K for $p=10\%$, -0.62 T/K for $p=50\%$, and -0.83 T/K for $p=90\%$. In the conventional BCS picture, H_{c2} is linear in T near T_{c0} and saturates in 0 K limit. Deviation may occur in the presence of strong impurity scattering.[9] In this case, the Werthamer-Helfand-Hohenberg (WHH) formula[10] is often used to describe the temperature dependence of H_{c2} with $H_{c2}(0)=-0.693\ T_c(dH_{c2}/dT)|_{T=T_c}$. The dashed lines in Fig. 3 are the results of fitting $H_{c2}(T)$ to the WHH formula, yielding $H_{c2}^{WHH}(0)=0.48$ T for $p=10\%$, 0.57 T for $p=50\%$, and 0.84 T for $p=90\%$. Note that at lower temperatures $H_{c2}(T)$ no longer follows the WHH expression, particularly for $p=10$ and 50 %. This suggests that the actual $H_{c2}(0)$ is larger than $H_{c2}^{WHH}(0)$. To find out whether $H_{c2}(T)$ continuously increases in a linear fashion or eventually saturates, resistivity measurements at lower temperatures and higher magnetic fields are in progress. Nevertheless, assuming $H_{c2}(0)=H_{c2}^{WHH}(0)$, we may estimate the superconducting coherence length ξ_{GL} using Ginzburg-Landau formula $\xi_{GL}=(\Phi_0/2\pi H_{c2})^{1/2}$, where $\Phi_0=2.07\times10^{-7}$ Oe cm^2. This results in the zero-temperature coherence length $\xi_{GL}(0)=263$ Å for $p=10\%$, 240 Å for $p=50\%$, and 198 Å for $p=90\%$.

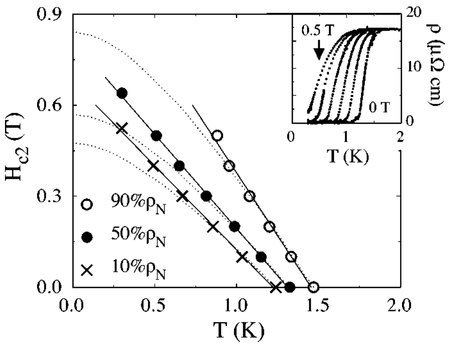

FIG. 3. Temperature dependence of the upper critical field H_{c2} deduced from the resistivity measured at 90% (open circles), 50% (solid circles), and 10% (cross) of the normal-state value ρ_N. The dash lines represent the WHH approach (see the text). The solid lines are the linear fit to experimental $H_{c2}(T)$. The inset shows the temperature dependence of resistivity at $H=0$, 0.1, 0.2, 0.3, 0.4, and 0.5 T.

Is $Cd_2Re_2O_7$ indeed a dirty superconductor? To address this issue, we need to compare the mean-free path l with Pippard coherence length $\xi_0=\hbar v_F/\pi\Delta(0)$, where v_F is the Fermi velocity and the zero-temperature energy gap $\Delta(0)=1.764\ k_BT_c$ according to the BCS theory. Information about l and ξ_0 may be obtained from Drude relation $l=\hbar(3\pi^2)^{1/3}/e^2\rho_0 n^{2/3}$ and $\xi_0=\hbar^2(3\pi^2 n)^{1/3}/1.764\pi m k_B T_c$, where m is the electron rest mass, n is the carrier density, and ρ_0 is the residual resistivity at 0 K at which the scattering is essentially from impurities. In analyzing the data above T_c, we found that the resistivity exhibits a quadratic temperature dependence over a wide temperature regime. Shown in the inset of Fig. 2 is the plot of ρ vs T^2 between 2 and 64 K. Note that ρ varies approximately linearly with T^2 below 60 K. By fitting the resistivity data between 2 and 60 K using a formula $\rho=\rho_0+AT^2$, we obtain the residual resistivity $\rho_0=17$ $\mu\Omega$ cm and constant $A=0.024$ $\mu\Omega$ cm/K^2. As illustrated in the inset of Fig. 2 by the solid line, the above formula fits the experimental data very well. This indicates the importance of the Umklapp process of the electron-electron scattering at low temperatures and is consistent with the formation of a Fermi-liquid state. The extrapolated residual resistivity of our crystals is approximately 235 times lower than that for polycrystals,[3] reflecting a much lower level of impurities in our single crystals. Interestingly, there

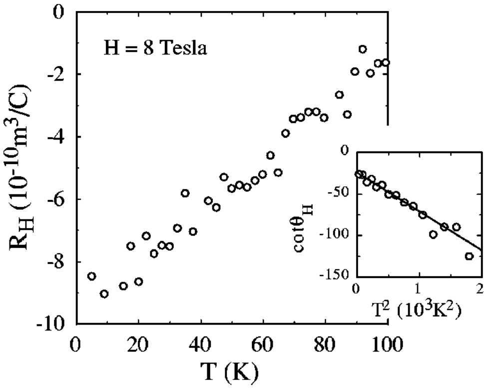

FIG. 4. Temperature dependence of Hall coefficient R_H between 5 and 100 K. The inset shows Hall angle cot θ_H vs T^2 (open circles). The solid line is the linear fit of experimental data between 2 and 40 K.

is little difference in T_c. We recall that the superconductivity in Sr_2RuO_4 is completely suppressed as ρ_0 exceeds $\sim 1\ \mu\Omega$ cm.[11] This suggests that the impurity effect on superconductivity in $Cd_2Re_2O_7$ is much weaker than in Sr_2RuO_4. To assess the carrier density n, we have performed Hall effect measurements. Using the standard four-point technique, the Hall component was derived from the antisymmetric part of the transverse resistivity under magnetic field reversal at a given temperature. As displayed in Fig. 4, the Hall coefficient R_H is T dependent and has negative sign below 100 K. This suggests that the Fermi surface of $Cd_2Re_2O_7$ may contain several sheets and electrons dominate the electrical conduction. Nevertheless, the T^2 behavior of the Hall angle cot θ_H (see the inset of Fig. 4) at low temperatures suggest that both longitudinal and transverse transport properties are controlled by the same scattering, unlike the high-T_c cuprate materials.[12] Using the simple Drude relation, we estimate $n=-1/eR_H \sim 7\times 10^{21}$ cm^{-3} for $T=5$ K. (We are aware that the simple Drude relation may not hold if the Fermi surface of $Cd_2Re_2O_7$ consists of multibands.) Inserting the estimated n and ρ_0, we obtain $l \sim 204$ Å and $\xi_0 \sim 6365$ Å. Since ξ_0 is much larger than l, $Cd_2Re_2O_7$ is in the dirty limit.

Given the values of l and ξ_0, we may also estimate the GL coherence length $\xi_{GL}(0)$ using $\xi_{GL}(0) \sim 0.855(\xi_0 l)^{1/2}$ for dirty superconductors.[13] This relation yields $\xi_{GL}(0) \sim 927$ Å, a few times larger than that obtained from $H_{c2}^{WHH}(0)$. There could be several reasons to cause the discrepancy. One possibility is that the slope $dH_{c2}/dT|_{T=T_c}$ is unexpectedly large, which results in large $H_{c2}^{WHH}(0)$ and consequently small $\xi_{GL}(0)$. As mentioned in Ref. 3, the large value of $dH_{c2}/dT|_{T=T_c}$ may imply that the Cooper pairs are composed of heavy quasiparticles since it is proportional to the effective mass m^*.[13] Given the fact that the effective electron mass is significantly enhanced due to geometric frustration in LiV_2O_4,[2] it is not surprising that such effect also plays a similar role in $Cd_2Re_2O_7$. Further evidence for heavy quasiparticles can be found from specific heat data.

The specific heat of $Cd_2Re_2O_7$ was measured using a relaxation calorimeter, where the contribution from the addenda has been carefully subtracted. Figure 5 shows the temperature dependence of specific heat between 0.4 and 2.0 K. Note that the specific heat reveals a pronounced peak associated with the superconducting transition, confirming the bulk nature of the superconductivity. At the midpoint of the transition $T_c^{mid}=0.99$ K, we determine the specific heat jump $\Delta C=37.9$ mJ/mol-K. In the weak coupling limit, ΔC is expected to approach $1.43\gamma T_c$,[13] where γ is the Sommerfeld coefficient and can be obtained from the normal-state specific heat. An expression of the form $C=\gamma T+\beta T^3$ is usually used to describe the specific heat data at temperatures well below the Debye temperature Θ_D, i.e., $T \ll \Theta_D$, where $\beta = N(12/5)\pi^4 R\Theta_D^{-3}$, $R=8.314$ J/mol-K and $N=11$ for $Cd_2Re_2O_7$. The T term comes from the electronic contribution (C_e) and the T^3 term arises from the lattice contribution (C_l). By plotting our specific heat data as C/T vs T^2 as shown in the inset of Fig. 5, a linearity is clearly seen below ~ 6.2 K. We fit the data between 1.2 and 6.2 K using the above formula and obtain $\gamma = 29.6$ mJ/mol-K^2 and $\Theta_D = 397$ K, slightly higher than those given in Ref. 5. This leads that $\Delta C/\gamma T_c^{mid}=1.29$, close to the weak coupling BCS result. In the framework of the BCS theory, the superconducting-state electronic specific heat $C_{es}(T)$ is expected to decay exponentially with T, i.e., $C_{es}=ae^{-b/T}$ (a and b are T independent constants). As can be seen in Fig. 5, the BCS formula (dashed line) describes our experimental data very well down to 0.4 K with $a=0.307$ J/mol-K and $b=1.52$ K. However, in the absence of the data at lower temperatures ($T \leqslant 0.3$ K), it is not clear whether or not $Cd_2Re_2O_7$ is a BCS-type superconductor.

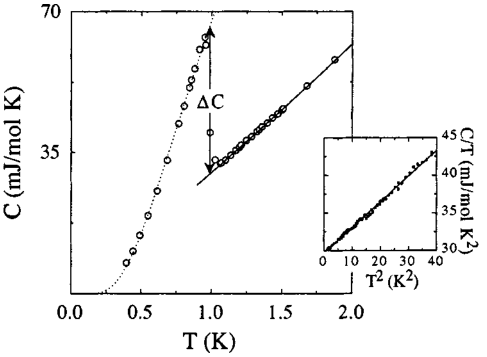

FIG. 5. Temperature dependence of the specific heat of $Cd_2Re_2O_7$ between 0.3 and 2.0 K. The dash line is the fit of experimental data to $C=ae^{-b/T}+\beta T^3$ using β value extracted from the normal-state specific heat data. The inset shows specific heat C versus temperature above T_c plotted as C/T against T^2. The solid lines (in both the inset and main panel) are the fit of experimental data to $C=\gamma T+\beta T^3$ between 1.2 and 6.2 K.

In comparison with other pyrochlores,[1,14,15] the γ value for $Cd_2Re_2O_7$ is large. A large electronic specific heat at low temperatures is usually observed in strongly correlated Fermi-liquid systems like heavy-fermion materials[2,16–18] and $Sr_{n+1}Ru_nO_{3n+1}$ series[19,20] due to an effective mass enhancement. It is known that for such systems, the Kadowaki-Woods ratio A/γ^2 is expected to approach the universal value $A/\gamma^2 = 1.0\times 10^{-5} \mu\Omega$ cm/(mJ/mol-K)^2.[16–18]

For $Cd_2Re_2O_7$, we obtain $A/\gamma^2 = 2.7\times 10^{-5} \mu\Omega$ cm/(mJ/mol-K)^2, very close to that found for the heavy fermion compound UBe_{13}. The consistency of A/γ^2 value with the universal description suggests that the electrons are strongly correlated in $Cd_2Re_2O_7$. In such a system, the Wilson ratio $R_W = \pi^2 k_B^2 \chi_{spin}/3\mu_B^2\gamma$ is expected to be greater than one, where χ_{spin} denotes the spin susceptibility, k_B is the Boltzmann's constant and μ_B is the Bohr magneton. According to our dc susceptibility data presented in Ref. 7, we estimate that $\chi_{spin} = 4.6\times 10^{-4}$ emu/mol at low temperatures. This gives that $R_W \sim 1.3$, well exceeding the unity value for a free electron system.

In summary, from transport and ac magnetic susceptibility measurements, we confirm the superconducting transition with $T_c^{onset} = 1.47$ K in $Cd_2Re_2O_7$ single crystals. The bulk nature of the superconductivity has been confirmed by the specific heat jump across T_c. The ratio $\Delta C/\gamma T_c^{mid}$ is close to the weak coupling BCS value. However, the almost linear temperature dependence of resistive critical field cannot be described by the WHH formula for a dirty superconductor. The T^2 dependence of the resistivity, the large values of $dH_{c2}/dT|_{T=T_c}$ and the Wilson ratio, and the value of A/γ^2, all suggest that the electrons in $Cd_2Re_2O_7$ are strongly correlated with the enhanced effective mass, resulting possibly from geometric frustration.

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