Superconductivity in the Correlated Pyrochlore Cd$_2$Re$_2$O$_7$

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We report the observation of superconductivity in high-quality Cd$_2$Re$_2$O$_7$ single crystals with room-temperature pyrochlore structure. Resistivity and ac susceptibility measurements establish an onset transition temperature $T_{c}^{\text{onset}} = 1.47$ 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 $\gamma$ 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 electron-like conduction in this material. The resistivity exhibits a quadratic $T$-dependence between 2 and 60 K, indicative of Fermi-liquid behavior. The values of the Kadowaki-Woods ratio $A/\gamma^2$ 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$_2$RuO$_4$. These materials form in perovskite-like structures, where CuO$_2$ or RuO$_2$ layers play important roles in the occurrence of superconductivity. Oxide superconductors with non-perovskite 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 this 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$_2$O$_4$ [2]. To understand the role of geometrical frustration in pyrochlores, we have investigated transport, magnetic and thermodynamic properties of Cd$_2$Re$_2$O$_7$, the only-known pyrochlore superconductor discovered two weeks ago [3].

Although Cd$_2$Re$_2$O$_7$ was first 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$_2$Re$_2$O$_7$ single crystals indicate that there are at least two phase transitions below room temperature: one near 200 K [6, 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 $\Delta C = 37.9$ 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 $A/\gamma^2$ and the Wilson ratio suggest that the ground state of Cd$_2$Re$_2$O$_7$ is a correlated Fermi liquid.

Single crystals of Cd$_2$Re$_2$O$_7$ 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. [4], there is a subtle structure change at low temperatures.

Fig. 1 shows the temperature dependence of the ac susceptibility from a Cd$_2$Re$_2$O$_7$ single crystal, performed by using a mutual inductance technique at an applied field of $H \sim 1$ Oe and a frequency of $f = 1$ kHz. The real part, $\chi'$, reveals a large diamagnetic signal below 1.15 K, marking the superconducting transition. Below 0.75 K, $\chi'$ is flat, indicating that the superconducting transition is complete. We noticed that $\chi'$ was not saturated down to 0.3 K in polycrystalline Cd$_2$Re$_2$O$_7$ [3].

Using a standard four-probe method, the dc electrical resistivity of Cd$_2$Re$_2$O$_7$ has been investigated. Shown in Fig. 2 is the temperature dependence of the electrical resistivity $\rho$ between 0.3 and 10 K at zero magnetic field. Associated with the diamagnetic transition, $\rho$ also departs from high-temperature behavior at 1.5 K and

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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 $\rho_N$ over a range of approximately 0.25 K.

Both resistivity and ac susceptibility measurements establish a superconducting transition with the onset transition temperature $T_{c onset} = 1.47 \text{ K}$ and a transition width $\Delta T_c = T_c(90\%) - T_c(10\%) = 0.25 \text{ K}$ for our Cd$_2$Re$_2$O$_7$ single crystals, confirming the recent discovery. 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 $\rho_N$ 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 $dH_{c2}/dT\big|_{T=T_c}$ 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 $\rho_N$ over a range of approximately 0.25 K.

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

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

Note that $\rho$ 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 \[5\], reflecting a much lower level of impurities in our single crystals. Interestingly, there is little difference in $T_c$. We recall that the superconductivity in Sr$_2$RuO$_4$ is completely suppressed as $\rho_0$ exceeds $\sim 1 \mu\Omega$ cm \[6\]. This suggests that the impurity effect on superconductivity in Cd$_2$Re$_2$O$_7$ is much weaker than in Sr$_2$RuO$_4$. 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$_2$Re$_2$O$_7$ may contain several sheets and electrons dominate the electronic conduction. Nevertheless, the $T^2$ behavior of the Hall angle $\cot \theta_H$ (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$_2$Re$_2$O$_7$ consists of multibands.) Inserting the estimated $n$ and $\rho_0$, we obtain $l \sim 204$ Å and $\xi_0 \sim 6365$ Å. Since $\xi_0$ is much larger than $l$, Cd$_2$Re$_2$O$_7$ is in the dirty limit.

Given the values of $l$ and $\xi_0$, we may also estimate the GL coherence length $\xi_{GL}(0)$ using $\xi_{GL}(0) \sim 0.855(\xi_0)^{1/2}$ for dirty superconductors \[13\]. This relation yields $\xi_{GL}(0) \sim 927$ Å, a few times larger than that obtained from $H^{WH}_c(0)$. There could be several reasons to cause the discrepancy. One possibility is that the slope $dH_c^2/dT|_{T=T_c}$ is unexpectedly large, which results in large $H^{WH}_c(0)$ and consequently small $\xi_{GL}(0)$. As mentioned in Ref. \[3\], the large value of $dH_c^2/dT|_{T=T_c}$ may imply that the Cooper pairs are composed of heavy quasiparticles since it is proportional to the effective mass $m^*$ \[3\]. Given the fact that the effective electron mass is significantly enhanced due to geometric frustration in LiV$_2$O$_4$ \[3\], it is not surprising that such effect also plays a similar role in Cd$_2$Re$_2$O$_7$. Further evidence for heavy quasiparticles can be found from specific heat data.

The specific heat of Cd$_2$Re$_2$O$_7$ was measured using a relaxation calorimeter, where the contribution from the addenda has been carefully subtracted. Fig. 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, $\Delta C$ is expected to approach $1.43\gamma T_c^3$, where $\gamma$ 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 $\Theta_D$, i.e., $T \ll \Theta_D$, where $\beta = N(12/5)\pi^2 R\Theta_D^{-3}$, $R = 8.314$ J/mol-K and $N = 11$ for Cd$_2$Re$_2$O$_7$. 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 $\sim 6.2$ 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. \[3\]. This leads that $\Delta C/\gamma T_{c(mid)}^3 = 1.29$, 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., $C_{es} = a e^{-b/T}$ (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 ($T \leq 0.3$ K), it is not clear whether or not Cd$_2$Re$_2$O$_7$ is a BCS-type superconductor.

In comparison with other pyrochlores \[1, 14, 15\] the $\gamma$ value for Cd$_2$Re$_2$O$_7$ is large. A large electronic specific heat at low temperatures is usually observed in strongly correlated Fermi-liquid systems like heavy-fermion materials \[2, 4, 7, 15\] and Sr$_{n+1}$Ru$_n$O$_{3n+1}$ series \[13, 20\] due to an effective mass enhancement. It is known that for such systems, the Kadowaki-Woods ratio $A/\gamma^2$ is expected to approach the universal value $A/\gamma^2 = 1.0 \times 10^{-5}$ $\mu\Omega$ cm/(mJ/mol-K)$^2$ \[14, 16, 18\]. For Cd$_2$Re$_2$O$_7$, we ob-
tain \(A/\gamma^2 = 2.7 \times 10^{-5} \mu\Omega \text{ cm}/(\text{mJ/mol-K})^2\), very close to that found for the heavy fermion compound UBe\(_{13}\). The consistency of \(A/\gamma^2\) value with the universal description suggests that the electrons are strongly correlated in Cd\(_2\)Re\(_2\)O\(_7\). In such a system, the Wilson ratio \(R_W = \pi^2 k_B^2 \chi_{\text{spin}} / 3\mu_B^2 \gamma^3\) is expected to be greater than one, where \(\chi_{\text{spin}}\) denotes the spin susceptibility, \(k_B\) is the Boltzmann’s constant and \(\mu_B\) is the Bohr magneton. According to our dc susceptibility data presented in Ref. 7, we estimate that \(\chi_{\text{spin}} = 4.6 \times 10^{-4} \text{ 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 \(T_{\gamma\text{onset}} = 1.47\) K in Cd\(_2\)Re\(_2\)O\(_7\) single crystals. The bulk nature of the superconductivity has been confirmed by the specific heat jump across \(T_c\). The ratio \(\Delta C/\gamma T_c^{\text{mid}}\) 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 \(A/\gamma^2\), all suggest that the electrons in Cd\(_2\)Re\(_2\)O\(_7\) are strongly correlated with the enhanced effective mass, resulting possibly from geometric frustration.

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