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LETTER TO THE EDITOR

Superconductivity in a pyrochlore oxide, $Cd_2Re_2O_7$

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Abstract

We make the first report that a metallic pyrochlore oxide, $Cd_2Re_2O_7$, exhibits type II superconductivity at 1.1 K. The pyrochlore oxide is known to be a geometrically frustrated system, which includes a tetrahedral network of magnetic ions. A large number of compounds are classified in the family of pyrochlore oxides, and these compounds exhibit a wide variety of physical properties ranging from insulator through semiconductor and from bad metal to good metal. Until now, however, no superconductivity has been reported for frustrated pyrochlore oxides. The bulk superconductivity of this compound is confirmed by measurements of the resistivity and the alternating-current magnetic susceptibility. The upper critical field H_{c2}, which is extrapolated to 0 K, is estimated as about 0.8 T, using the resistivity measurements under an applied field. The plot of H_{c2} versus T indicates that the Cooper pairs are composed of rather heavy quasiparticles. This fact suggests that frustrated heavy electrons become superconducting in this compound.

Recently the subject of geometrical frustration in strongly correlated electron systems has attracted considerable interest. The ground states of these systems are expected to be highly degenerate. Such high degeneracies lead to thermodynamic instability at low temperatures. Lifting these degeneracies makes possible the production of exotic quantum ground states, such as the spin liquid, heavy fermions, and unconventional superconductivity.

The pyrochlore oxide, which has a general formula $A_2B_2O_6O'$, contains a tetrahedral network of A or B cations, leading to geometrical frustration. The A cations are eightfold coordinated with six O and two O′ anions and are located within distorted cubes, while the smaller B cations are sixfold coordinated and are located within distorted octahedra of which the six bond lengths from the central B cation to the corner O anion are equal. The corner-sharing

BO_6 octahedra compose a three-dimensional network as shown in figure 1(a). The sublattice of B cations composes a three-dimensional corner-shared tetrahedral network, namely, the pyrochlore lattice as shown in figure 1(b). If the A cations are non-magnetic and the B cations are magnetic, the B-spin magnetic couplings are strongly frustrated under a nearest-neighbour antiferromagnetic exchange interaction. For the case of localized electron spin moments, theoretical studies of the Heisenberg model on the pyrochlore lattice have suggested that the ground state of such an insulator would be long-range magnetic order [1], spin freezing [2], or the quantum spin liquid [3]. The geometrical frustration plays a crucial role even in the case of itinerant electrons in the pyrochlore lattice. Indeed, the metallic spinel oxide LiV_2O_4, which has a pyrochlore lattice of vanadium, has been reported to show heavy-fermion behaviour at low temperatures due to the geometrical frustration [4].

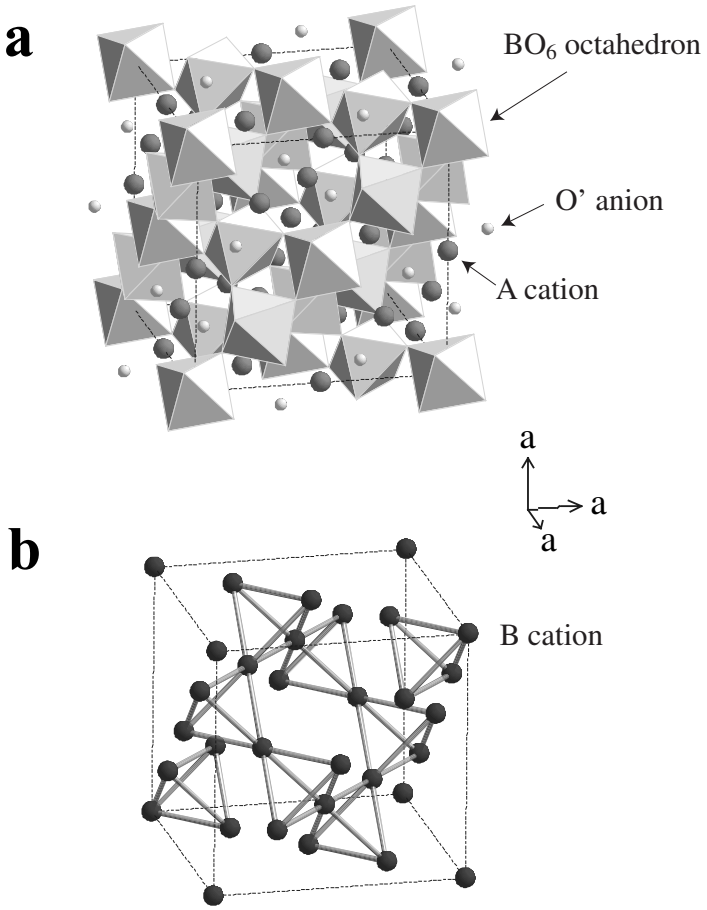

Figure 1. Crystal structure of pyrochlore oxide. (a) is drawn on a basis of the network of BO_6 octahedra. (b) shows the pyrochlore lattice of B cations.

A large number of compounds are classified in the family of pyrochlore oxides, and these compounds exhibit a wide variety of physical properties ranging from insulator through semiconductor and from bad metal to good metal [5]. Until now, however, no superconductivity has been reported for frustrated pyrochlore oxides. Here, we make the first report that a metallic cubic pyrochlore oxide, $Cd_2Re_2O_7$, exhibits type II superconductivity at 1.1 K.

Polycrystalline samples of $Cd_2Re_2O_7$ were prepared by solid-state reaction. A stoichiometric mixture of CdO, ReO_3, and Re metal was pelletized, and put into an alumina Tammann tube. The pellet in the Tammann tube was further inserted into an evacuated silica tube and preheated at 300 °C for several hours in order to avoid vaporization of the starting materials. Then, the pellet was heated at 1000 °C for several hours. The powder XRD pattern measured at room temperature was identified as that of the cubic pyrochlore structure with a lattice parameter $a = 10.221$ Å, which is consistent with the previous report [6].

The direct-current (d.c.) electrical resistivity of the sintered sample of $Cd_2Re_2O_7$ was measured using a standard four-probe technique in the temperature range of 0.3 to 300 K under an applied field from 0 to 2 T. Low-temperature measurements below 1.9 K were performed using a ^{3}He refrigerator. Figure 2 shows the temperature dependence of the d.c. electrical resistivity of $Cd_2Re_2O_7$ under zero applied field. The electrical resistivity shows a steep descent below $T^* \sim 200$ K. This anomaly at T^* was observed in the d.c. magnetic susceptibility measurement as well. The origin of this anomaly has not been identified. The electrical resistivity drops to zero sharply at the onset superconducting temperature $T_c = 1.1$ K, and shows effectively zero resistivity below 1.05 K. Changes of driving electric current density produced slight differences in the resistivity below 1.7 K, an effect which may be due to the superconductivity of a small amount of impurity rhenium metal ($T_c = 1.7$ K). The superconductivity transition at 1.1 K is not due to filamentary superconductivity of Re,

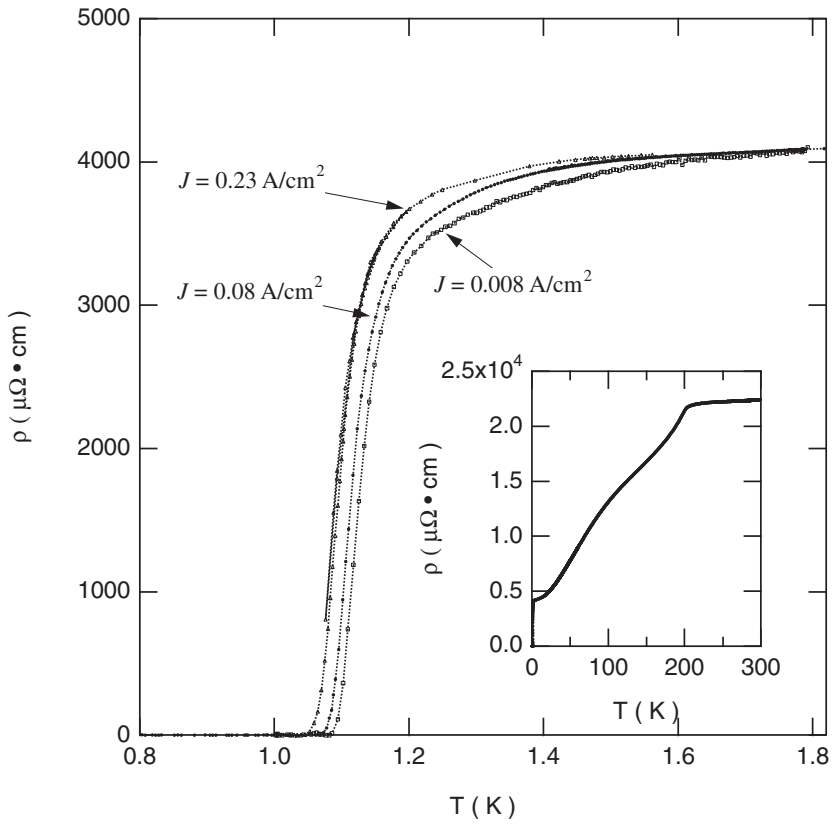

Figure 2. The temperature dependence of the d.c. electrical resistivity for $Cd_2Re_2O_7$ in the temperature range of 0.8 to 1.8 K. The inset shows the data in the range of 0.3 to 300 K.

since the observed critical field is much larger than the critical field of Re (0.02 T), as will be described below. The large residual resistivity of 4×10^{-3} Ω cm may suggest a low carrier density of this system. From band calculations, it is pointed out that the system has a very small density of states at the Fermi level, which is located within the 5d band and in the valley between the very flat bands of the rhenium 5d electrons [7]. However, the electronic specific heat coefficient has been found to be large, i.e., $\gamma = 13.3$ mJ K^{-2}/(Re mol) [8], indicating that heavy quasiparticles are formed due to the spin frustration in this compound.

The alternating-current (a.c.) magnetic susceptibility was measured by a mutual-inductance method at a magnetic field of 2×10^{-5} T in the temperature range of 0.3 to 1.8 K. As shown in figure 3, a strong diamagnetic signal (χ') has been observed below 1.06 K, which corresponds to the end-point transition temperature of the electrical resistivity measurement. The dissipative component χ'' shows only a small peak around T_c, indicating no weak superconducting link between superconducting grains. The superconducting volume fraction was estimated roughly as ∼50% at 0.3 K. From this experiment, a bulk superconducting state has been strongly confirmed in $Cd_2Re_2O_7$ below 1.1 K.

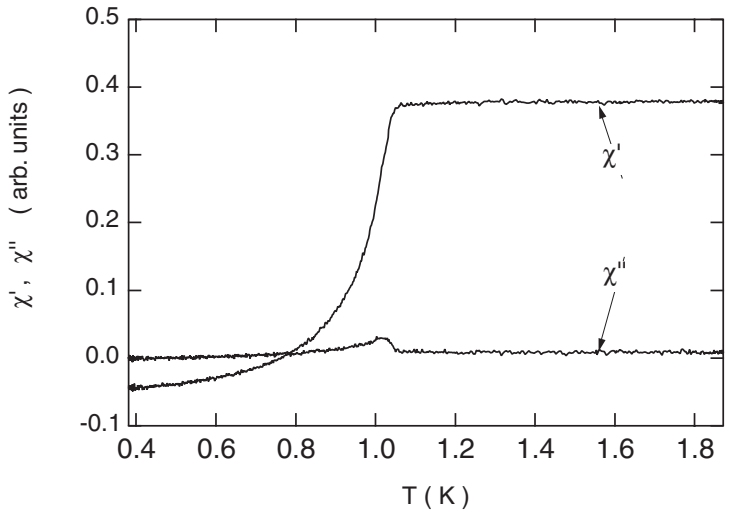

Figure 3. The temperature dependence of the a.c. magnetic susceptibility for $Cd_2Re_2O_7$. χ' and χ'' represent the real part and the imaginary part, respectively.

To estimate the superconducting critical field, the magnetic field dependence of T_c has been determined by resistivity measurements. As the magnetic field was applied, the sample maintained zero resistivity until the field reached H_{c2}. At H_{c2} the superconductivity was quenched abruptly as shown in figure 4. The value of the upper critical field, which is extrapolated to zero temperature in the plot of H_{c2} versus T (figure 4, inset) using the WHH model [9], is estimated as $H_{c2}(0) = 0.8$ T. The superconducting coherence length, ξ, is expressed as $\sqrt{\{\phi_0/[2\pi H_{c2}(T)]\}}$ (where ϕ_0 is the fluxoid quantum). The Pippard coherence length, $\xi_0 = \hbar v_F/[\pi \Delta(0)]$ (where v_F is the Fermi velocity, and $\Delta(0)$ is the superconducting energy gap at $T = 0$ K) was obtained as about 300 Å using the relation

$$\xi(T) = \frac{0.74\xi_0}{\sqrt{1 - T/T_c}}$$

for a clean superconductor. This compound is considered to be a clean superconductor, since

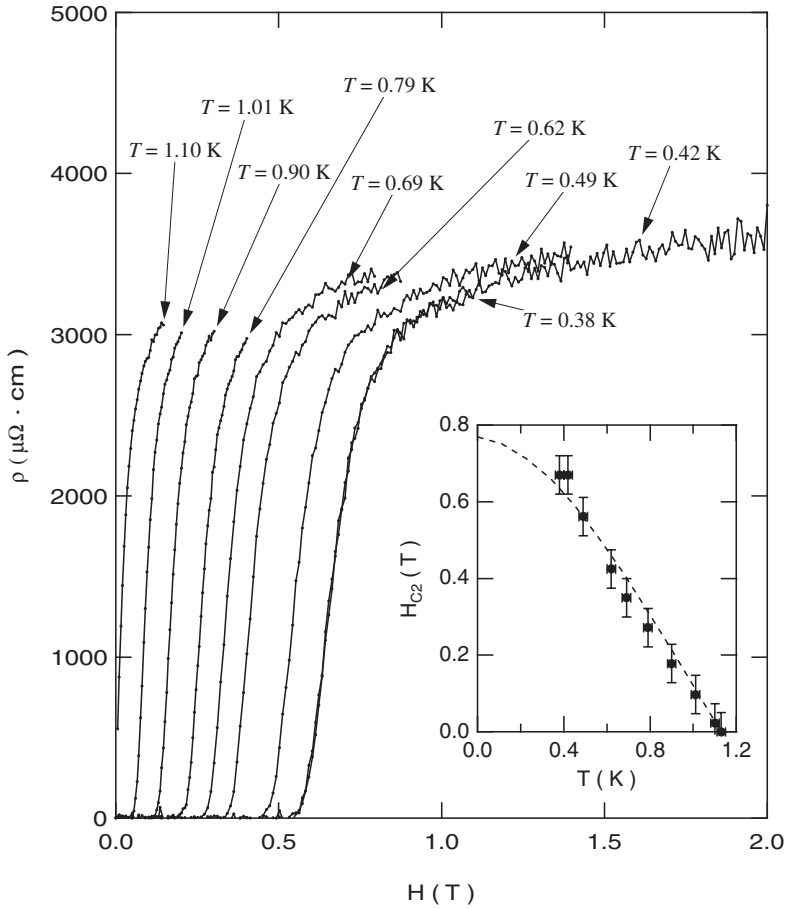

Figure 4. The magnetic field dependence of the resistivity for $Cd_2Re_2O_7$. The inset shows the plot of H_{c2} versus T.

the mean free path l is estimated as $\sim 4 \times 10^{-8}$ m $> \xi_0$, using the Drude relation

$$\rho = \frac{\hbar(3\pi^2)^{1/3}}{e^2 l} n^{-2/3}$$

with resistivity $\rho \sim 4 \times 10^{-5}$ Ω m and carrier concentration $n \sim 1 \times 10^{24}$ m^{-3} which is a typical value for metallic pyrochlore compounds. The observed large initial slope of H_{c2}, i.e.,

$$\left(\frac{1}{T_c}\frac{dH_{c2}}{dT}\right)_{T=T_c} \sim 1 \text{ T K}^{-2}$$

indicates that the Cooper pairs are composed of rather heavy quasiparticles, since $([1/T_c]\, dH_{c2}/dT)_{T=T_c}$ is proportional to the square of the effective mass m^{*2}, in agreement with the large γ-value. This fact suggests, indeed, that frustrated heavy electrons become superconducting in this compound.

Generally, superconductivity due to a magnetic interaction competes with magnetic frustration, since no particular magnetic excitation for a superconducting attractive channel exists due to the frustration. The present study gives the first example of coexistence of magnetic frustration and superconductivity.

At the final stage of preparation of this article, we have heard that Hanawa *et al* at the Institute of Solid State Physics in Japan have discovered the superconductivity of the same compound independently [10].

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