Superconductivity and Magnetic Fluctuations in $Cd_2Re_2O_7$ via Cd Nuclear Magnetic Resonance and Re Nuclear Quadrupole Resonance

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We report Cd nuclear magnetic resonance (NMR) and Re nuclear quadrupole resonance (NQR) studies on $Cd_2Re_2O_7$, the first superconductor among pyrochlore oxides ($T_c \simeq 1$ K) . The Re NQR spectrum at zero magnetic field below 100 K rules out any magnetic or charge order. The spin-lattice relaxation rate below T_c exhibits a pronounced coherence peak and follows the weak-coupling BCS theory with nearly isotropic energy gap. The results of Cd NMR point to a moderate ferromagnetic enhancement at high temperatures followed by a rapid decrease of the density of states below the structural transition temperature of 200 K.

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The pyrochlore transition metal oxides with the chemical formula $A_2B_2O_7$ known for decades have recently attracted renewed interest. The A and B sublattices both form a network of corner-sharing tetrahedra known as the pyrochlore lattice. This geometry causes strong frustration of magnetic interactions when occupied by local moments, resulting in a large degeneracy of the low energy states and anomalous magnetic behavior [1]. Interplay between strong correlation and effects of lattice geometry in itinerant electron systems is a challenging issue. For example, large degeneracy inherent to the structure appears to be crucial also for the heavy-electron behavior of the spinel compound LiV_2O_4 [2], where V sites also form a pyrochlore lattice. Recent investigations of pyrochlores including $5d$ transition metal elements have led to the discovery of the superconductivity, for the first time among pyrochlore oxides, in $Cd_2Re_2O_7$ below $T_c \simeq 1$ K [3–5] and an unusual metal-insulator transition in $Cd_2Os_2O_7$ [6].

Besides superconductivity, $Cd_2Re_2O_7$ shows an unusual phase transition at 200 K [3,7,8]. Although complete structural determination below 200 K is yet to be done, x-ray studies proposed a second-order transition from the high-temperature (high-T) cubic $Fd\overline{3}m$ space group to the low-T cubic $F\overline{4}3m$ space group [7], accompanied by loss of the inversion symmetry at the Re and Cd sites. The transition also causes a large change of electronic properties [3,8]. The resistivity shows almost no T dependence near room temperature but drops abruptly below 200 K. The magnetic susceptibility also decreases steeply below 200 K, while at higher temperatures it shows only weak T dependence with a broad maximum near 300 K. Moreover, a kink in the resistivity near 120 K indicates an additional phase transition [7,9]. Results of band structure calculations [10,11] indicate that the material is a compensated semimetal with electron (hole) Fermi surfaces centered at the Γ (K) point, which are associated with the t_{2g} manifold of the Re-$5d$ bands. The electronic structure near the Fermi level is sensitive to structural distortion [11]. While it has been proposed that a structural transition may occur to remove large spin degeneracy of localized moments on a pyrochlore lattice [12], the relation between structure and electronic properties is largely unexplored for itinerant electron systems. In this Letter we describe the microscopic information on the magnetic and superconducting properties of $Cd_2Re_2O_7$ obtained from the nuclear magnetic resonance (NMR) at the Cd sites and the nuclear quadrupole resonance (NQR) at the Re sites.

The procedure of growing single crystals of $Cd_2Re_2O_7$ was described earlier [3]. For NQR measurements at zero magnetic field, a crystal was crushed into powder. NMR measurements were done for a single crystal in the external field of 10.47 T. Standard spin-echo pulse techniques were used, including inversion recovery to measure the spin-lattice relaxation rate.

We first discuss the low-temperature NQR results at the Re sites. The NQR spectra of ^{185}Re and ^{187}Re nuclei, both with spin $5/2$, have been obtained below 100 K. Measurements at higher temperatures were hampered by short spin-spin relaxation time. The spectra at 5 K are shown in Fig. 1 where the top and the bottom panels correspond

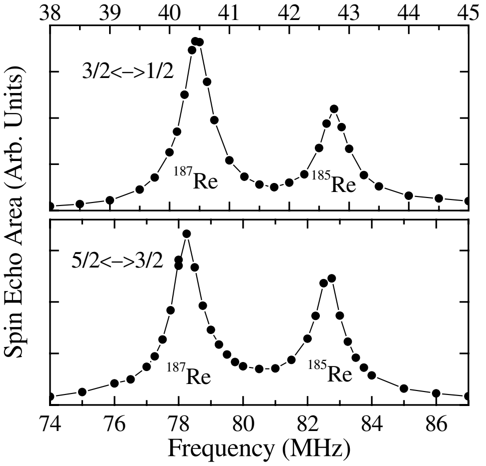

FIG. 1. The Re NQR spectra at 5 K. The top (bottom) panel corresponds to the $\pm 3/2 \leftrightarrow \pm 1/2$ ($\pm 5/2 \leftrightarrow \pm 3/2$)) transition.

to the $\pm 3/2 \leftrightarrow \pm 1/2$ and the $\pm 5/2 \leftrightarrow \pm 3/2$ transition, respectively. The NQR frequency of spin 5/2 nucleus can be expressed as [13] $\nu_{\pm 3/2, \pm 1/2} \approx \nu_Q[1 + (59/54)\eta^2]$ and $\nu_{\pm 5/2, \pm 3/2} \approx 2\nu_Q[1 - (11/54)\eta^2]$, with $\nu_Q = (3/20)V_{zz}eQ/h$. Here $Q = 2.6(2.8) \times 10^{24}$ cm^2 is the quadrupole moment of ^{187}Re (^{185}Re) nuclei, $V_{zz} = \partial^2 V/\partial z^2$ is the largest principal value of the electric field gradient (EFG) tensor at the nuclear position, V is the electrostatic potential, and $\eta = |V_{xx} - V_{yy}|/|V_{zz}|$ is the asymmetry parameter. Applying these expressions to the measured spectra one finds $\nu_Q = 39.3$ MHz at 5 K, gradually decreasing with temperature to 36.6 MHz at 100 K, and $\eta = 0.164 \pm 0.002$ without noticeable temperature dependence.

An important issue is whether there is any spin or charge order among Re-5d electrons at low temperatures. The Re nuclear resonance is extremely sensitive to such an order. The hyperfine coupling constant for the core polarization field due to 5d spin moments is typically -120 T/μ_B [14], leading to the Zeeman splitting of about 1 GHz/μ_B [15]. Regarding the charge distribution, one electron in the a_{1g} orbital with the $3z^2 - r^2$ symmetry (z is the trigonal $\langle 111 \rangle$ axis), for example, would cause the quadrupole splitting of a few hundred MHz [16]. Thus the observed sharp single line for each NQR transition of both Re isotopes completely rules out any magnetic order and nonuniform charge distribution of 5d electrons.

The Re sites possess a threefold rotation axis both in the high-T $Fd\overline{3}m$ structure or in the $F\overline{4}3m$ structure, the latter being proposed by x ray for the structure below 200 K [7]. Since EFG is a second rank symmetric tensor, it must be axially symmetric in these cases. Therefore, the nonzero value of η implies further lowering of symmetry at least in the temperature range below 100 K.

Figure 2 shows the spin-lattice relaxation rate $^{187}T_1^{-1}$ of ^{187}Re nuclei measured on the $\pm 5/2 \leftrightarrow \pm 3/2$ NQR transition at zero magnetic field as a function of inverse temperature. The relaxation was confirmed to be of magnetic (not quadrupolar) origin at several temperatures by observing that the variation of T_1^{-1} for two Re isotopes is proportional to the square of the nuclear gyromagnetic ratio. Above T_c in the region 1–1.5 K, $^{187}T_1^{-1}$ is practically linear in temperature, $^{187}(T_1T)^{-1} = 127$ (sec $\cdot$ K)$^{-1}$. Just below T_c, $^{187}T_1^{-1}$ increases sharply exhibiting a strong coherence peak [17] with a maximum of about 245 sec^{-1} at $\sim$0.88 K, which is twice as large as just above T_c. Below 0.8 K the relaxation rate decreases following an activated T dependence.

It is well known that a coherence peak in the T dependence of T_1^{-1} is easily depressed when magnitude of the superconducting gap varies substantially or the order parameter changes sign over the Fermi surface. Thus the observed well-pronounced coherence peak provides clear evidence for a nearly isotropic s-wave superconducting gap. The nodeless gap in this material has recently been inferred also from specific heat data [18] and μSR [19,20] measurements of the penetration depth. We have fitted the data to the BCS expression, considering distribution of the gap due to possible variation over the Fermi surface [21]. We assumed a uniform distribution of the gap between $\Delta - \delta$ and $\Delta + \delta$ and δ/Δ to be independent of temperature. The T dependence of Δ is assumed to follow the weak-coupling BCS theory. A good fit was obtained for $\delta/\Delta = 0.22$, $\Delta(T = 0) = 1.80$ K, and $T_c = 0.98$ K as shown by the solid line in Fig. 2. The ratio $\Delta(T = 0)/T_c = 1.84$ is close to the weak-coupling BCS value 1.75, justifying our analysis. The dashed lines in Fig. 2 indicate that the height of the coherence peak is sensitive to the distribution of the gap. The fitted value of δ/Δ puts the upper limit for the gap variation, since any damping of the quasiparticles will also suppress the coherence peak.

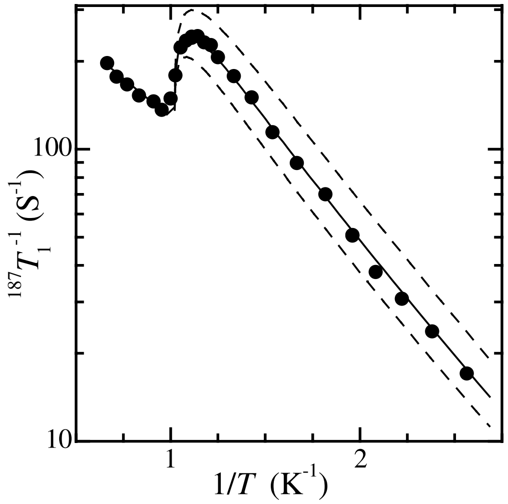

FIG. 2. ^{187}Re spin-lattice relaxation rate vs inverse temperature. The solid line is the fit to the weak-coupling BCS theory with $\delta/\Delta = 0.22$, $\Delta(T = 0) = 1.80$ K, and $T_c = 0.98$ K. The dashed lines represent the cases with $\delta/\Delta = 0.27$ or 0.17.

Let us now turn to the NMR results on the Cd sites. The Knight shift, K, and the spin-lattice relaxation rate, $^{111}T_1^{-1}$, were measured for ^{111}Cd nuclei (spin 1/2) using a single crystal. In the high-temperature $Fd\overline{3}m$ structure, threefold rotation symmetry at the Cd sites should give rise to the axially symmetric Knight shift, $K = K_{\text{iso}} + K_{\text{ax}}(1 - 3\cos^2\theta)$, where θ is the angle between the external field and the $\langle 111 \rangle$ direction. This angular dependence was indeed observed above 200 K. The structural transition causes small line splitting below 200 K. Detailed analysis of the NMR spectra, which will be presented elsewhere, revealed that the values of the isotropic (K_{iso}) and the axial (K_{ax}) parts of the shift can still be properly determined from the experimental spectra in the whole temperature range.

In Fig. 3a, K_{iso} is plotted against temperature (bottom axis) or magnetic susceptibility, χ (top axis). The axial part K_{ax} (not shown in the figure) is -0.042% at 300 K, much smaller than K_{iso}, and decreases only by 0.01%

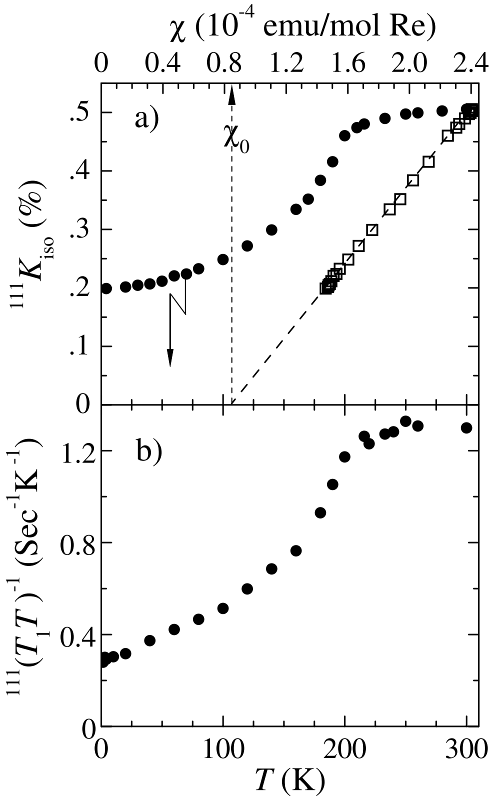

FIG. 3. (a) The isotropic part of the ^{111}Cd Knight shift vs temperature (circles—bottom axis) and vs magnetic susceptibility (squares—top axis). (b) Temperature dependence of $(T_1T)^{-1}$ at the ^{111}Cd sites.

upon cooling down to 4 K, indicating that the dominant hyperfine field comes from the Cd-s states hybridized with the Re-5d conduction bands. Similar to the magnetic susceptibility χ [3], $K_{\rm iso}$ decreases rapidly below 200 K. The shift is generally expressed as $K_{\rm iso} = K_0 + K_s(T)$, where the first term is the T-independent chemical shift and the second term is the T-dependent spin shift from conduction electrons. Likewise $\chi = \chi_0 + \chi_s(T)$, where the first term is the sum of the diamagnetic and the orbital (Van Vleck) susceptibility and the second term is the spin susceptibility. As shown in Fig. 3a, a linear relation was found between $K_{\rm iso}$ and χ in the whole temperature range, yielding the hyperfine coupling constant $A_{\rm hf} = N_A\mu_B K_s/\chi_s = 17.9\ {\rm T}/\mu_B$. Since the chemical shift of Cd in nonmagnetic and nonmetallic substances is typically 0.01% or less [22] and much smaller than the observed value of $K_{\rm iso}$, we assume $K_0 = 0$ in the following analysis. We then obtain $\chi_0 = 0.82 \times 10^{-4}$ emu/mole Re, leading to $\chi_s = 1.58 \times 10^{-4}$ emu/mole Re at 300 K. From the standard value for the diamagnetic susceptibility $\chi_{\rm dia} = -0.76 \times 10^{-4}$ emu/mole Re, the orbital susceptibility is estimated as $\chi_{\rm orb} = 1.58 \times 10^{-4}$ emu/mole Re.

In Fig. 3b, the T dependence of $^{111}(T_1T)^{-1}$ measured for $H \parallel [001]$ is shown. At some temperatures $^{111}T_1$ was measured for $H \parallel [110]$ and found to be isotropic. We found that $^{111}(T_1T)^{-1}$ also shows rapid reduction below 200 K, indicating that the phase transition at 200 K causes sudden loss of the density of states (DOS). For noninteracting electrons, when the spin shift and the spin-lattice relaxation are both due to the hyperfine field from s electrons, the *Korringa relation* is known to be satisfied, $T_1TK_s^2 = (\gamma_e/\gamma_n)^2(\hbar/4\pi k_B) \equiv S$, where γ_e and γ_n are, respectively, the electronic and nuclear gyromagnetic ratios. In the presence of interactions, the ratio

$$K_\alpha = S/(T_1TK_s^2) \tag{1}$$

provides a useful measure of magnetic correlation [23,24]. Since $(T_1T)^{-1}$ probes the dynamical susceptibility averaged over the Brillouin zone, it can be enhanced by either ferromagnetic (FM) or antiferromagnetic (AF) spin correlations, while only FM correlation strongly enhances the spin shift. Thus, generally speaking, the value of K_α being much smaller (larger) than unity is a signature for substantial FM (AF) correlation.

Filled circles in Fig. 4 show the T dependence of K_α. The value of $K_\alpha \sim 0.3$ above 200 K points to moderate FM enhancement. The sudden increase of K_α below 200 K can be accounted for by loss of DOS as explained below. However, there is a broad peak in K_α near 60 K, and K_α decreases at lower temperatures. Choice of nonzero values for K_0 does not change this behavior, which is already evident in Fig. 3 since $^{111}(T_1T)^{-1}$ keeps decreasing whereas $K(T)$ becomes nearly flat below 50 K.

In order to examine to what extent the behavior of K_α is explained by the T-dependent DOS, we utilize a simple RPA expression with a free-electron-like dispersion of the conduction band. This is certainly a gross simplification, since the specific feature of the multiple Fermi surfaces [10,11] and possible wave-vector dependence of the hyperfine matrix elements on the Fermi surface are both ignored. Therefore, the following analysis is presented only for qualitative discussion, even though the above simplification is partially supported by good proportionality between $K_{\rm iso}$ and χ. The Stoner enhancement factor of the spin susceptibility

$$1/(1-\alpha) = \chi_s/(2\mu_B^2\rho_0), \qquad \alpha = U\rho_0\,, \tag{2}$$

where ρ_0 is the DOS at the Fermi level and U denotes the Coulomb repulsion, is related to K_α by RPA as [23,24]

$$K_{\alpha,\rm RPA} = 2\int_0^1 \frac{(1-\alpha)^2 x\,dx}{[1-\alpha G(x)]^2}\,, \tag{3}$$

$G(x) = 0.5\{1 + (1-x^2)/(2x)\}\ln|(1+x)/(1-x)|$. Since K_α is nearly constant above 200 K, this equation determines $\alpha \sim 0.86$ near 250 K from the experimental data of K_α. Next we determine α or DOS as a function of temperature from the data of $\chi_s(T)$ by using Eq. (2), $\chi_s \propto \alpha/(1-\alpha)$. We then calculate $K_{\alpha,\rm RPA}$ using Eq. (3). The results are shown by filled circles in Fig. 4. One can see that from high temperatures down to $\sim$50 K the calculated and the experimental results agree reasonably well, supporting our assumption that the loss

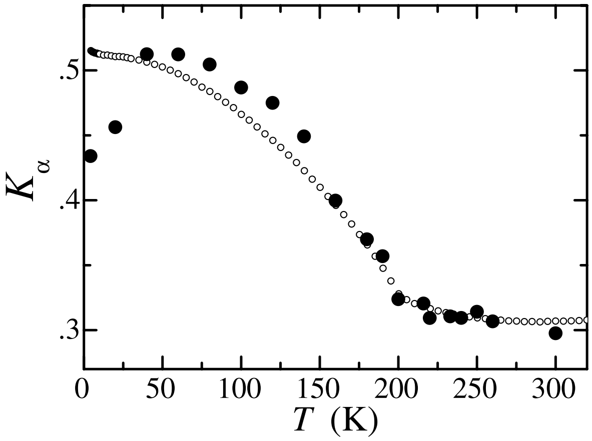

FIG. 4. Temperature dependence of K_α. Filled circles: experimental data of K_α obtained from ^{111}Cd $(T_1T)^{-1}$ and $K_{\rm spin} = K_{\rm iso}$ using Eq. (1). Open circles: $K_{\alpha,\rm RPA}$ calculated from Eqs. (2) and (3) and the data of χ_s from Ref. [3].

of DOS is the major cause for the reduction of both χ_s and $^{111}(T_1T)^{-1}$ below 200 K. However, they diverge below 40 K. The anomalous behavior at low temperatures implies that either ferromagnetic enhancement is restored or there is additional suppression only for the dynamical susceptibility.

We found that the ratio of $(T_1T)^{-1}$ at the Re and Cd sites at low temperatures is unexpectedly large. From the values of the hyperfine coupling, the nuclear gyromagnetic ratio and the reduction factor for the relaxation due to core polarization field [25], the expected ratio $^{187}T_1^{-1}/^{111}T_1^{-1}$ turned out to be about 17. Experimentally we obtain $^{187}T_1^{-1}/^{111}T_1^{-1} = 420$ at 5 K. Possible reasons for this may be the following: (i) Orbital hyperfine fields give a large contribution to $^{187}T_1^{-1}$. (ii) Spin fluctuations among $5d$ electrons enhance $^{187}T_1^{-1}$ but do not contribute to $^{111}T_1^{-1}$ due to possible cancellation of the hyperfine matrix elements. This is analogous to the form factor effects due to transferred hyperfine interaction in magnet with localized moments.

Finally, we comment on the large value of the T-linear coefficient of the specific heat $\gamma = 15$ mJ/K^2 mol Re above T_c [3,5]. Our estimate of χ_0 and the susceptibility data in Refs. [3,8] give $\chi_s = 7 \times 10^{-5}$ emu/mole Re at 5 K. We then obtain the Wilson ratio $R_W = 0.34$ [26]. Such a small value of R_W would normally imply strong electron-phonon coupling and appears to be incompatible with the weak-coupling superconductivity. An exotic possibility may be that the large γ is due to low lying excitations which do not contribute to χ_s, for example, orbital fluctuations.

In summary, Re NQR data below 100 K reveals no sign of magnetic or charge order in $\rm Cd_2Re_2O_7$. However, asymmetry of electric field gradient indicates that the Re sites do not possess the threefold rotation axis. The superconducting state, according to the temperature dependence of Re NQR spin-lattice relaxation rate, is apparently a weak-coupling BCS case with a nearly isotropic energy gap. The Cd NMR data show moderate ferromagnetic enhancement above 200 K. Rapid decrease of the spin susceptibility and $^{111}(T_1T)^{-1}$ below the structural phase transition at 200 K is accounted for by loss of the density of states down to 50 K. The shift and relaxation rate data at lower temperatures pose puzzles which remain to be clarified.

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