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LETTER TO THE EDITOR

Structural transition in the pyrochlore superconductor $\text{Cd}_2\text{Re}_2\text{O}_7$ observed by Re nuclear quadrupole resonance

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Abstract

We report results of nuclear quadrupole resonance (NQR) experiments on the Re sites in the pyrochlore superconductor $\text{Cd}_2\text{Re}_2\text{O}_7$. A discontinuous change of the NQR spectrum was observed near $T_{s2} = 120$ K, confirming the first-order structural transition in addition to the already known second-order transition at $T_{s1} = 200$ K. The spin–lattice relaxation rate at the Re sites shows a steep increase above T_{s2} , in contrast to the reported results for the Cd sites, suggesting changes of orbital fluctuations.

The peculiar geometry of the pyrochlore lattice, a network of corner-sharing tetrahedra, has been a subject of recent active research. This structure is found, for example, in the cubic Laves phase, in the spinel compounds, and in the pyrochlore oxides. The pyrochlore oxides with the cubic $Fd\bar{3}m$ space group have the chemical formula $\text{A}_2\text{B}_2\text{O}_7$, where the A and B sites form identical pyrochlore lattices. When these sites are occupied by localized magnetic moments with nearest-neighbour antiferromagnetic interactions, strong geometrical frustrations inhibit conventional Néel order, leading to a large degeneracy of the ground states and residual entropy at low temperatures. Recent theoretical [1–4] and experimental [5, 6] studies suggest that such degeneracy may be lifted either by deformation of the crystal lattice or by secondary non-frustrating exchange interactions, which select a unique ground state. Geometrical effects in itinerant-electron systems, are not as well understood as in the case of insulator magnets. However, recent discoveries of heavy-electron behaviour in the cubic spinel compound LiV_2O_4 [7], an unusual metal–insulator transition in $\text{Cd}_2\text{Os}_2\text{O}_7$ [8], and

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superconductivity in $\text{Cd}_2\text{Re}_2\text{O}_7$ with $T_c \sim 1$ K [9, 10] have provided new opportunities to look into the role of lattice geometry in various electronic phases.

According to the band-structure calculations [11, 12], $\text{Cd}_2\text{Re}_2\text{O}_7$ is a compensated semi-metal with electron (hole) Fermi surfaces centred at the $\Gamma(\text{K})$ point derived from the t_{2g} manifold of the Re 5d bands. Although the superconductivity in $\text{Cd}_2\text{Re}_2\text{O}_7$ appears to be conventional [13–15], it shows an unusual second-order structural phase transition at $T_{s1} = 200$ K, as revealed by a pronounced λ -type peak of the specific heat [16, 17], an anomaly of the lattice constant, and the appearance of new x-ray Bragg peaks [18] that are forbidden in the high-temperature $Fd\bar{3}m$ space group. Recent high-resolution x-ray results [19] suggest a tetragonal distortion below T_{s1} , although structural determination has not been completed. The magnetic susceptibility [9, 16], the Knight shift, and the nuclear spin–lattice relaxation rate ($1/T_1$) [13] at the Cd sites all show sudden reduction below T_{s1} , indicating that the structural change causes significant loss of the density of states (DOS). Thus the transition is characteristic of a Peierls transition or a band Jahn–Teller distortion. More recently, Hiroi *et al* [17] found another (first-order) phase transition near $T_{s2} = 120$ K. The structural change, however, is seemingly very small and only minor anomalies at T_{s2} were observed in transport and thermodynamic properties. Nevertheless, it is intriguing that both T_{s1} and T_{s2} decrease with pressure and the superconducting T_c reaches the maximum when T_{s2} approaches zero [20]. These results raise the interesting possibility that the superconductivity may be affected by the successive structural transitions, which are driven by instabilities to remove the high degeneracy of the electronic states inherent to the pyrochlore structure.

Nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) are excellent microscopic probes for both the structure and the electronic properties. The previous NQR measurements [13] at $^{185,187}\text{Re}$ nuclei in $\text{Cd}_2\text{Re}_2\text{O}_7$ have established weak-coupling BSC behaviour with a nearly isotropic gap in the superconducting state as well as the lack of threefold rotation symmetry at the Re sites, pointing to a non-cubic structure below 100 K. In this letter, we report the results of Re NQR measurements in a wider temperature range up to 160 K, which show pronounced anomalies at T_{s2} .

The procedure for growing the single crystals of $\text{Cd}_2\text{Re}_2\text{O}_7$ was described earlier [9]. A single crystal was crushed into powder for NQR measurements to achieve better penetration of the high-frequency magnetic field. The same sample was used in the previous NQR measurements [13]. Re NQR spectra were obtained by measuring the intensity of the spin-echo signal at discrete frequencies. The spin–lattice relaxation rate ($1/T_1$) was measured by the inversion–recovery method. The spin-echo decay rate was determined from the variation of the spin-echo intensity as a function of separation time between $\pi/2$ and π pulses.

Since both of the two isotopes of Re, ^{187}Re and ^{185}Re , have spin 5/2, two NQR lines are expected for each isotope at the following frequencies [21]:

$$\nu_1 \approx \nu_Q(1 + \frac{59}{54}\eta^2), \quad \nu_2 \approx 2\nu_Q(1 - \frac{11}{54}\eta^2), \quad (1)$$

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 Re sites, V is the electrostatic potential, and $\eta = |V_{xx} - V_{yy}|/|V_{zz}|$ is the asymmetry parameter. The above expression, valid for small η , can be used to determine the values of ν_Q and η from the observed NQR frequencies. When EFG is axially symmetric, i.e. $\eta = 0$, ν_1 (ν_2) corresponds to the transition $I_z = \pm 3/2 \leftrightarrow \pm 1/2$ ($I_z = \pm 5/2 \leftrightarrow \pm 3/2$), where z is the symmetry axis of the EFG.

The NQR spectra for the higher-frequency (ν_2) transition are shown in figure 1. Sharp spectra with well resolved peaks for the two isotopes are observed in the temperature range below 100 and above 130 K. However, the spectrum at 120 K is significantly broader and can be

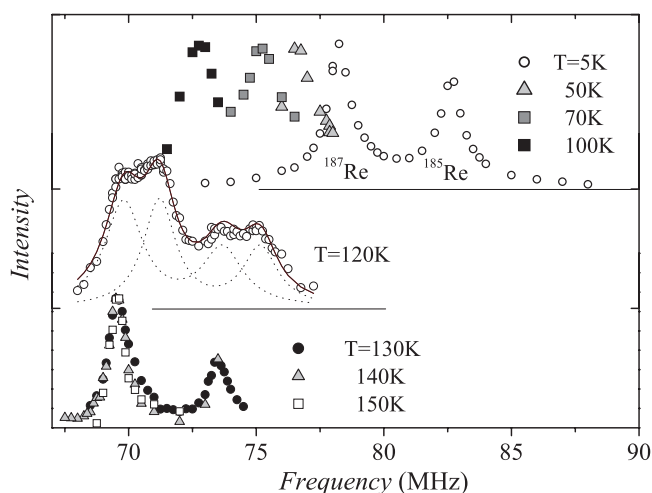


Figure 1. $^{187,185}\text{Re}$ NQR spectra for the higher-frequency (ν_2) transition at different temperatures. For $T = 50, 70,$ and 100 K, only the ^{187}Re spectra near the peak are shown. The spectrum at $T = 120$ K can be fitted to a superposition (solid curve) of two components (dotted curves) for each isotope, indicating coexistence of two phases.

decomposed into two peaks for each isotope (the dashed curves in figure 1). Below 100 K, the peak shifts to higher frequency with decreasing temperature, while above 130 K it stays almost unchanged. From these spectra and similar spectra for the lower-frequency (ν_1) transition, the values of η and ν_Q for ^{187}Re are determined as a function of temperature. The results are shown in figure 2. Both ν_Q and η show a clear discontinuous jump near 120 K, confirming the first-order structural transition reported earlier by Hiroi *et al* [17]. In the rest of the letter, three distinct structural phases, below $T_{s2} = 120$ K, between T_{s2} and $T_{s1} = 200$ K, and above T_{s1} , are called the low- T , intermediate, and high- T phases, respectively. The asymmetry parameter η stays nearly constant in the low- T phase but significantly varies with temperature in the intermediate phase. On the other hand, ν_Q decreases rapidly with temperature in the low- T phase but changes little in the intermediate phase. The NQR spectrum at 120 K is now understood as a result of coexistence of two phases at this temperature.

The high- T phase has the undistorted cubic pyrochlore structure ($Fd\bar{3}m$ space group), in which the Re sites possess a threefold rotation axis. Therefore the EFG must be axially symmetric ($\eta = 0$) above T_{s1} . As η is decreasing rapidly with temperature in the intermediate phase, it is reasonable to expect η to approach zero continuously at $T_{s1} = 200$ K. The non-zero values of η also lead us to conclude that both the intermediate and the low- T phases have non-cubic structures, since any cubic subgroup of $Fd\bar{3}m$ has a threefold axis at the Re sites. Yet a single set of sharp NQR lines indicates that there are still only one type of Re sites in the distorted structures and completely rules out any magnetic order or charge disproportion in both the intermediate and the low- T phases.

Our conclusions are consistent with the recent x-ray results [19] suggesting a tetragonal distortion below T_{s1} . It is remarkable, however, that the deviation from the cubic symmetry is so pronounced in the NQR measurements in spite of the extremely small tetragonal splitting of the lattice parameter ($<0.05\%$) observed by x-ray investigation. In describing the pyrochlore structure as an fcc Bravais lattice with a tetrahedral unit cell, there are two possible choices for the tetrahedral unit, A and B, which are related by inversion with respect to a site. As discussed by Tchernyshyov *et al* [2], possible lattice distortions with the crystal momentum

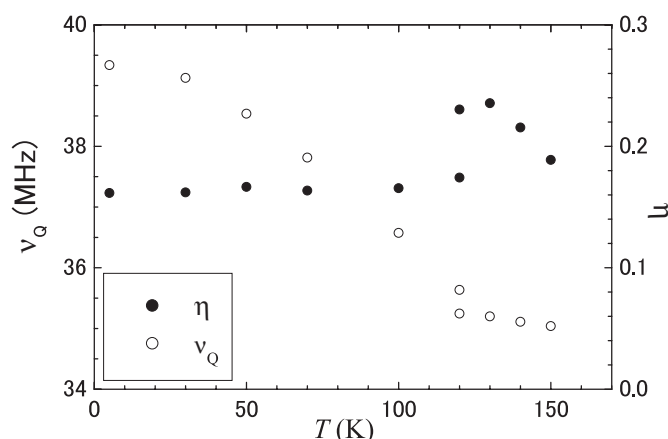


Figure 2. Temperature dependences of η (solid dots) and ν_Q (open circles) obtained from the peak positions of the spectra in figure 1 and similar spectra for the lower-frequency transition, using equation (1). The two data points at $T = 120$ K correspond to the two peaks of the NQR spectrum.

$q = 0$ are classified as either *even* or *odd* with respect to the inversion. For *even* modes, the two tetrahedral units distort in the same way, while for *odd* modes, the distortions for A and B tetrahedra are staggered. In the latter case, the lattice parameter will not change appreciably, since an equal number of A and B tetrahedra are contained in a cubic unit cell. Thus the puzzle of the apparent discrepancy between the pronounced local distortion observed by means of NQR and the small change in the lattice parameter can be reconciled if the distortions are *odd* in the intermediate and the low- T phases. We also observed discontinuous evolution of the Cd NMR spectrum with thermal hysteresis near 120 K, which will be reported on elsewhere [22].

We now turn to the results on the spin–lattice relaxation rate $1/T_1$. The temperature dependence of $(T_1 T)^{-1}$ for ^{187}Re nuclei is shown in figure 3(a) by solid dots. The results on $(T_1 T)^{-1}$ for ^{111}Cd nuclei reported in [13] are also included in the same figure (triangles). Remarkably, the Re and Cd sites show different T -dependences of $(T_1 T)^{-1}$. The relaxation rate at the Cd sites is due to the Fermi contact hyperfine field from the conduction electron spin [13]. At the Re sites, on the other hand, hyperfine fields not only from conduction electron spin but also due to orbital currents associated with the 5d (t_{2g}) states contribute to $1/T_1$ [23]. Therefore, it appears most natural to ascribe the different T -dependences to the orbital contribution to $(T_1 T)_{\text{Re}}^{-1}$. Indeed if we subtract an appropriately chosen T -independent orbital contribution ($70 \text{ s}^{-1} \text{ K}^{-1}$) from the measured value of $(T_1 T)^{-1}$, the remaining part, shown by the open circles in figure 3(a) after rescaling, follows the same T -dependence as $(T_1 T)_{\text{Cd}}^{-1}$ below $T_{s2} = 120$ K.

Above T_{s2} , however, they diverge; $(T_1 T)_{\text{Re}}^{-1}$ increases with temperature more rapidly than $(T_1 T)_{\text{Cd}}^{-1}$. The steep increase of $(T_1 T)_{\text{Re}}^{-1}$ above T_{s2} is also probably due to orbital contributions, but this is still not definite. By analogy with the Jahn–Teller effects for the localized orbitals, the decrease of DOS below T_{s1} implies that the large orbital degeneracy at the Fermi level inherent to the highly symmetric structure of the high- T phase is reduced due to structural distortion in the intermediate phase. Thus we expect the orbital fluctuations to grow with increasing temperature in the intermediate phase. The orbital (Van Vleck) susceptibility, on the other hand, remains nearly constant, judging from the good proportionality between the magnetic susceptibility and the Knight shift at the Cd sites over the whole temperature range [13]. This is reasonable since all the states in the 5d bands, not only those near the Fermi level, are relevant

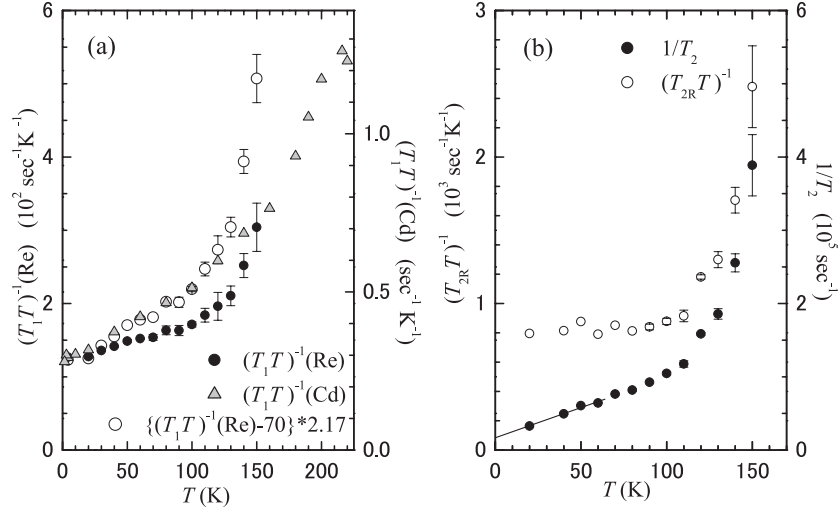


Figure 3. Nuclear relaxation rate results. (a) The temperature dependence of $(T_1 T)^{-1}$ for the ^{187}Re nuclei (solid dots, left-hand scale) is compared with the reported $(T_1 T)^{-1}$ results for the ^{111}Cd nuclei [13] (triangles, right-hand scale). On choosing the orbital contribution appropriately ($70 \text{ s}^{-1} \text{ K}^{-1}$) and subtracting it from the measured $(T_1 T)^{-1}$, the remaining part shows the same temperature dependence of $(T_1 T)^{-1}$ as the Cd sites, as shown by open circles. (b) The temperature dependence of $1/T_2$ for the ^{187}Re nuclei (solid dots, right-hand scale) and $(T_{2R} T)^{-1}$ (open circles, left-hand scale).

to the orbital susceptibility. One should keep in mind, though, that $\text{Cd}_2\text{Re}_2\text{O}_7$ is a compensated semi-metal, at least in the high- T phase, with multiple Fermi surfaces [12]. In such cases, the spin-lattice relaxation rate due to spin fluctuations is the sum of distinct intraband and interband contributions, which may have different T -dependences and contribute to the Re and Cd sites with different weights. Thus the different behaviours at the Re and Cd sites may be partly due to such band-structure effects.

The T -dependence of the spin-echo decay rate ($1/T_2$) is shown in figure 3(b) (solid dots). The measured $1/T_2$ is the sum of two contributions: $1/T_{2n}$ due to the nuclear spin-spin coupling and $1/T_{2R}$ from the spin-lattice relaxation processes (Redfield contribution). Assuming that $1/T_{2n}$ is independent of temperature, we obtain $1/T_{2n} = 1.5 \times 10^4 \text{ s}^{-1}$ by extrapolating the low-temperature data for $1/T_2$ linearly to $T = 0$ (solid curve). Then $(T_{2R} T)^{-1}$ (open circles) shows a similar T -dependence to $(T_1 T)^{-1}$, as expected. The rapid increase of $1/T_2$ with temperature prevented measurements at higher temperatures.

It is remarkable that in contrast to the NQR spectra, the $(T_1 T)^{-1}$ at both sites, as well as the magnetic susceptibility, show rather smooth variation at T_{s2} . Apparently the discontinuous structural change at T_{s2} does not alter the DOS or gross features of the Fermi surface. Thus what drives the transition at T_{s2} still remains a puzzle.

In summary, we have observed pronounced discontinuous change of the Re NQR spectrum near $T_{s2} = 120 \text{ K}$, confirming the first-order structural transition in $\text{Cd}_2\text{Re}_2\text{O}_7$. A staggered type of tetragonal distortion is suggested for the intermediate and low- T phases. Distinct temperature dependences of $(T_1 T)^{-1}$ for the Re and the Cd sites, particularly in the intermediate phase, indicate T -dependent change of the orbital fluctuations due to structural distortion. The intimate relation between the successive structural transitions and the electronic properties is a fascinating feature of $\text{Cd}_2\text{Re}_2\text{O}_7$, which deserves further microscopic investigation.

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