Magnetism, structure, and superconductivity of Cd$_2$Re$_2$O$_7$ pyrochlore: Cd and Re NMR.

Institute for Solid State Physics, University of Tokyo 5–1–5 Kashiwanoha, Kashiwa, Chiba 277–8581, Japan

Abstract
We present Cd and Re NMR results on Cd$_2$Re$_2$O$_7$, the first and as yet the only superconductor ($T_c \approx 1$ K) among pyrochlore oxides. Re spin-lattice relaxation rate below $T_c$ exhibits a pronounced coherence peak and follows the weak-coupling BCS with nearly isotropic energy gap. Cd NMR points to moderate ferromagnetic enhancement at high temperatures followed by rapid decrease of the density of states below 200 K, and to strong suppression of spin fluctuations below $\sim 75$ K. Cd and Re NMR spectra reveal two structural phase transitions, one at 200 K and another at 120 K. Re NQR rules out any magnetic or charge order.

Key words: NMR, NQR, oxides, phase transitions

1. Introduction
Materials with a pyrochlore structure, i.e. network of corner-sharing tetrahedra, have recently yielded a lot of novel phenomena whose common source is geometrical frustrations of electron-electron interactions. Studies of pyrochlores including 5$d$ transition metal elements have led to the discovery of the superconductivity, for the first time among pyrochlore oxides, in Cd$_2$Re$_2$O$_7$ below $T_c \approx 1$ K [1]. Besides superconductivity, the phase diagram of Cd$_2$Re$_2$O$_7$ includes two structural phase transitions of unknown origin, one (second order) at $T_{s1}=200$ K and another (first order) at $T_{s2}=120$ K [1,2]. The upper transition is also associated with strong changes in magnetic and transport properties: the susceptibility, $\chi$ and resistivity, $\rho$, both relatively flat above $T_{s1}$, sharply decrease below $T_{s1}$ [1]. At $T_{s2}$ only a small hump in $\rho$ vs $T$ curve is visible, without any effect on $\chi$. In this proceeding we review our extensive study of the properties of Cd$_2$Re$_2$O$_7$ by means of NMR, undertaken to clarify its electronic phase diagram.

2. Results and discussion
Structure. The structure of Cd$_2$Re$_2$O$_7$ above $T_{s1}$ is cubic $Fd\bar{3}m$. Within this symmetry, both Cd and Re tetrahedra have three-fold symmetry axes coinciding with (111). This in turn provides axial symmetry of hyperfine and quadrupole tensors. Angular dependence of $\chi$ and resistivity, is fully compatible with $Fd\bar{3}m$ above $T_{s1}$. Specifically, for the arbitrary direction of the external field $H$ the spectrum counts 4 peaks according to the number of (111) axes. Below $T_{s1}$ the number of Cd NMR peaks triples indicating the loss of axial symmetry. The model to describe this evolution of the spectrum implies: (i) breaking of the axial asymmetry of the hyperfine tensor and (ii) tilt of its principal $z$-axis by $\varphi$ from (111), as shown in the diagram in Fig. 1. Symmetry considerations also require the 3(C3) point operation around (111), which results in 3 domains for each site, with hyperfine tensors having $z_0$, $z_1$, and $z_2$ principal axes arranged in the way shown in Fig. 1.

Analysis of angular patterns of Cd spectra using the above model has shown the following [3]: (1) From $T_{s1}$ down to $T_{s2}$, the tilt of principal $z$-axis of Cd hyperfine...
yielding frequencies are well reproduced in the calculation, direction (see diagram in Fig. 1). At lower parameter, 4.2 and 160 K [4] have revealed a non-zero asymmetry between two tetragonal structures.

Re NMR spectra (Re spin 5/2) measured between 4.2 and 160 K [4] have revealed a non-zero asymmetry parameter, $\eta$, of the Re quadrupole tensor, as well as a discontinuous change of $\eta$ at 120 K. As in the case of Cd, this indicates the absence of the 3-fold axis, hence the symmetry is non-cubic. Discontinuity around 120 K evidences the first-order transition.

To better understand the geometry of Re quadrupole tensor, Re NMR has been done at 4.2 K. Field-sweep spectra have been taken with external field parallel to [001], [111], and [110] directions of the crystal. The low-field half of the spectrum for $H \parallel [001]$ measured at 84.2 MHz, is shown in Fig. 1.

The same model as for Cd hyperfine tensor, outlined in the diagram in Fig. 1, has been used to analyze Re NMR spectra. The spin-5/2 Zeeman-quadrupole interactions Hamiltonian has been numerically diagonalized to reproduce the spectra. The asymmetry parameter $\eta=0.162$ and the quadrupole frequencies, $\nu_{Q}=39.37$ MHz for $^{187}\text{Re}$ and $\nu_{Q}=42.4$ MHz for $^{185}\text{Re}$, determined in the zero-field NQR measurements [4], were used for the calculation. The magnetic shift of Re has been neglected at this stage because its estimated value, $\sim 1\%$, is comparable to the line width and is much smaller than the quadrupole shift. The only adjustable parameter therefore has been $\varphi_{Re}$, the tilt of the $z$-axis of Re quadrupole tensor from (111) direction (see diagram in Fig. 1).

Re NMR spectra for different field orientations and frequencies are well reproduced in the calculation, yielding $\varphi_{Re} \approx 87^\circ$. This indicates the dramatic distortion of Re environment at 4.2 K (above 200 K the $Fd\bar{3}m$ symmetry presumes $\varphi_{Re}=0$). Re NMR measurements at higher temperatures are in progress.

Magnetism. Re NQR (spin 5/2) spectrum below 160 K [4] consists of sharp resonance peaks, ruling out any magnetic or charge order. Cd NMR has shown moderate ferromagnetic enhancement above 200K [5], with Stoner factor of $\sim 7$. This conclusion has been drawn from quantitative comparison between the spin contribution to the Knight shift $K_{s}$ and the spin-lattice relaxation rate $(T_{1}/T)^{-1}$. Rapid decrease of $K_{s}$ and $(T_{1}/T)^{-1}$ below $T_{c}$ down to $\sim 75$ K can be described within RPA by loss of the density of states. At lower temperatures the drop in $(T_{1}/T)^{-1}$ becomes excessive implying some extra mechanism damping the spin fluctuations.

Superconductivity. The spin-lattice relaxation rate $T_{1}^{-1}$ of $^{187}\text{Re}$ has been measured at zero magnetic field between 0.4 and 1.5 K [5]. Just below $T_{c} \approx 1$ K, $T_{1}^{-1}$ increases sharply exhibiting a strong coherence peak. The observed well-pronounced coherence peak provides a clear evidence for nearly isotropic $s$-wave superconducting gap. Below 0.8 K the relaxation rate decreases following an activated $T$-dependence. The fit to the data with the classic BCS expression for the spin-lattice relaxation rate gives the superconducting gap $\Delta(T = 0)/T_{c}=1.84$, close to the weak coupling BCS value 1.75.

Acknowledgements

This work is supported by the Grant–in–Aid for Scientific Research, No. 12–00037 and No. 10034027 from the JSPS, and No. 12046219, Priority Area on Novel Quantum Phenomena in Transition Metal Oxides (from the Ministry of Education, Culture, Sports, Science and Technology Japan. The research activity of O.V. in Japan is supported by the JSPS.

References