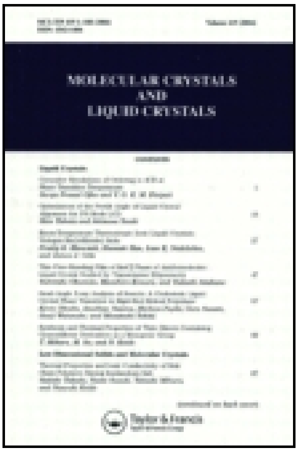

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Hyperfine Coupling and Magnetic Interaction of Layer-Structured Compound Ni(OD) 2 Studied by Solid-State High-Resolution Deuterium NMR

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Hyperfine Coupling and Magnetic Interaction of Layer-Structured Compound Ni(OD)$_2$ Studied by Solid-State High-Resolution Deuterium NMR

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Magnetic interaction and hyperfine coupling were investigated for Ni(OD)$_2$ as a reference of our series of studies of layer-structured Cu(II) assembled complexes. In crystal of Ni(OD)$_2$, Ni(II) ions with S = 1 are bridged by hydroxyl ions to form an equilateral planer triangular lattice. Hyperfine coupling constant of deuterium of hydroxyl ions was determined to be – 0.17 MHz from temperature dependence of isotropic shift of a magic angle spinning deuterium NMR spectrum. Ferromagnetic exchange interaction *J* in the layer was estimated to be + 3 K from the deuterium NMR shift by assuming Heisenberg model for planer triangular lattice. Present results indicated that magic angle spinning deuterium NMR is also useful to determine magnetic local structure and magnetic interaction of transition metal complexes with electron spins greater than S = 1/2.

Keywords: Ni(OD)$_2$, magnetic interactions, triangular lattice, hyperfine coupling constant, solid-state high-resolution deuterium NMR

INTRODUCTION

Magnetic local structures and magnetic interactions in Botallackite-type layer-structured Cu(II) complexes Cu$_2$(OD)$_3$X have been determined from isotropic shift of solid state high-resolution NMR of hydroxyl deuterium by use of high-speed magic angle spinning technique [1]. Principal character of magnetic lattice probed by isotropic deuterium NMR shift, which is caused by hyperfine coupling between hydroxyl deuterium and electron spin of Cu(II) ions, can be understood as a sum of one-dimensional Heisenberg ferro- and antiferromagnetic chains in the high temperature region [1]. Hydroxyl ions bridge Cu(II) ions to form a non-equilateral planer triangular lattice of Cu(II) ions with S = 1/2. As a reference of our series of NMR studies of magnetic local structures and magnetic interactions of assembled magnetic metal complexes, we studied hyperfine coupling constant of hydroxyl deuterium and magnetic interaction in a simple layer-structured compound $Ni(OD)_2$ with hexagonal symmetry in this paper.

In crystal of $Ni(OH)_2$, Ni(II) ions are bridged by hydroxyl ions to form equilateral triangular lattice as depicted in Fig. 1 [2]. It was reported that magnetic interaction in a layer is ferromagnetic while spins in adjacent layers are coupled antiferromagnetically [3]. This compound undergoes an antiferromagnetic phase transition at $T_N = 25.8$ K. The Néel temperature was reported from heat capacity measurements for specimen with a particle size between 0.1 and 3 μm [4]. The phase transition behavior was found to depend on the particle size [4,5].

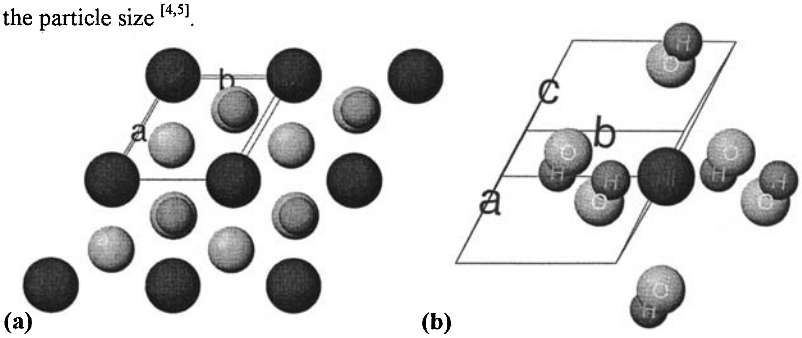

FIGURE 1 (a) Planer triangular lattice structure of Ni(II) ions of $Ni(OH)_2$. One hydroxyl ion bridges three Ni(II) ions. (b) Six equivalent oxygen atoms to form an octahedral coordination structure surround Ni(II) ion.

METHOD AND EXPERIMENT

Paramagnetic NMR shift of deuterium of hydroxyl ion must be an excellent probe for elucidating a local magnetic interaction in a Ni(II) layer, since a hydroxyl oxygen bridges three Ni(II) ions to form the layer. Magic angle spinning technique (MAS) averages the quadrupole interaction of deuteron and the dipole interaction between deuteron and electron spins to provide an isotropic shift of the D-NMR absorption line. In case of negligible zero field splitting, the observed isotropic shift in ppm consists of the Fermi contact term, the pseudo contact (dipole) term and the temperature independent diamagnetic term as follows,

$$\delta_{\text{iso}} = \delta_{\text{Fermi}} + \delta_{\text{Pseudo}} + \delta_{\text{dia}} \tag{1}$$

$$\delta_{\text{Fermi}} + \delta_{\text{Pseudo}} = \frac{\mu_{\text{B}}}{3k_{\text{B}}T} \cdot \frac{A_{\text{D}}}{\gamma_{\text{D}}/2\pi} S(S+1) \cdot F(J,T) . \tag{2}$$

The coefficient A_D is the hyperfine-coupling constant of the nucleus D in Hz [6], which consists of Fermi and pseudo contact terms. Since all Ni(II) ions are octahedrally coordinated by six crystallographically equivalent oxygen atoms with coordination distance of 2.120 Å, zero field splitting is small. And anisotropy of *g*-tensor is small. A function *F(J, T)* represents a term of exchange interaction among Ni(II) ions in a layer and is presented in discussion.

Deuterated compound $Ni(OD)_2$ was precipitated from heavy water solution of Ni(II) salt under basic condition at room temperature. Protonated one was prepared similarly from water solution. Powder X-ray diffraction pattern of the specimen is in excellent agreement with reported structure and particle size is not so small as to exhibit sharp X-ray diffraction lines shown in Fig. 2 [2, 5].

A D-MAS NMR spectrum was measured by a similar method described in ref. 8 at a resonance frequency of 46.1 MHz and at a magic angle spinning speed of 8 ~10 kHz on a Bruker DSX300 spectrometer between 194K and 300K. The thermometer of the MAS probe and an effect of spinning speed were carefully calibrated [8]. Uncertainty of the temperature measurement after the calibration was 4K. All D-NMR shifts were measured from the external second reference of CD_3OH (3.35 ppm). Direct current magnetic susceptibility was measured with a SQUID magnetometer (MPMS 5) at an external magnetic field of 1 T. Sample was cooled down to 6 K under zero-field and then magnetic susceptibility was measured up to 300 K.

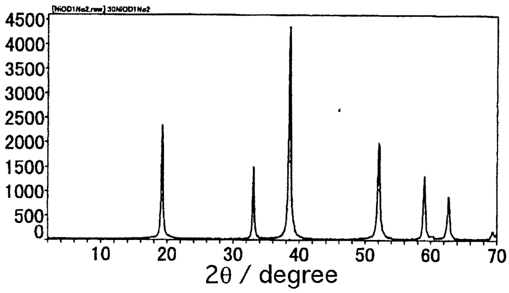

FIGURE 2 Powder X-ray diffraction of $Ni(OD)_2$ used for this study.

RESULTS AND DISCUSSION

A slope of inverse of magnetic susceptibility χ_A^{-1} as a function of temperature above 150 K gave a positive Weiss temperature of +24.9 K. This result indicates that a predominant ferromagnetic interaction exists as previously reported [3]. Plot of $\chi_A T$ as a function of temperature showed a maximum at 27.5 K. The temperature of maximum $\chi_A T$ is higher than Néel temperature T_N determined from heat capacity measurements as predicted by Fisher [4, 9].

Figure 3 (a) shows a full range spectrum of magic angle spinning deuterium NMR at spinning rate of 9 kHz at 300 K. There are many spinning side bands around isotropic shift at –37 ppm. The isotropic shift was distinguished by use of different spinning speeds as usual. The envelope of the spinning side bands corresponds to powder spectrum shape of hydroxyl deuterium. The spectrum shape is governed by quadrupole interaction of hydroxyl deuterium atom and anisotropic dipole interaction with axial symmetry between deuterium atom and electron spins of Ni(II) ions. Figure 3 (b) depicts a magnified spectrum of the isotropically shifted signal, which shows a single peak corresponding to the fact that all hydroxyl groups of $Ni(OD)_2$ are crystallographically equivalent. Half width at half maximum of the signal is 32 ppm which is larger than a typical value of 15 ppm for Cu(II) ion with $S = 1/2$ [1, 10].

The isotropic shift as a function of inverse temperature is shown in Fig. 3 (c). Slope of the plot is negative. This indicates that negative electron spin is

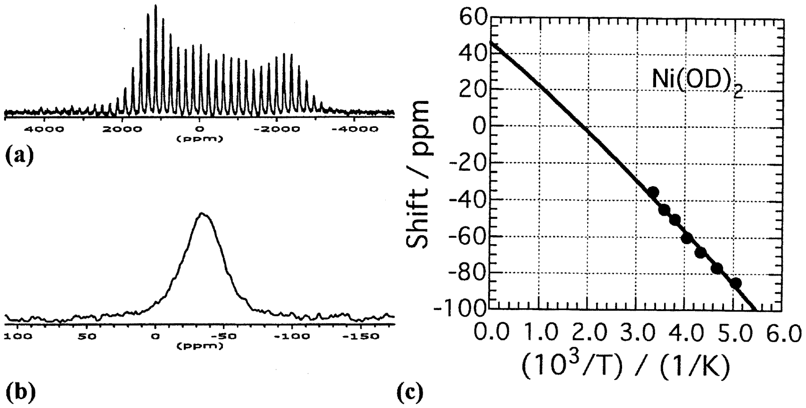

FIGURE 3 Magic angle spinning deuterium NMR of polycrystals of Ni(OD)$_2$. (a) Full range spectrum, (b) isotropically shifted signal and (c) temperature dependence of isotropic shift, where the solid curve is a fitting of Eqs. 1 – 3.

induced on hydroxyl deuterium atom due to positive electron spins of Ni(II) ions. The hyperfine-coupling constant A_D and exchange interaction J in the layer of Ni(II) ions can be determined from temperature dependence of isotropic shift of deuterium NMR shown in Fig. 3 (c). Since all hydroxyl deuterons are equivalent and experience the same hyperfine field for the present case of Ni(OD)$_2$, diamagnetic shift δ_{dia} in Eq. 1 can be estimated from extrapolation a linear plot of isotropic shift of the deuterium NMR spectrum as a function of bulk magnetic susceptibility measured at the same temperature. This procedure gave a slightly large value of diamagnetic shift $\delta_{dia} = +46$ ppm. Equations 1 and 2 were fitted to the temperature dependence of isotropic shift shown in Fig. 3 (c). In this calculation, we use high temperature expansion of susceptibility in powers of $v = (J/T)$ for $F(J,T)$ in Eq. 2 by assuming Heisenberg model of the ferromagnetic planer triangular lattice [7].

$$\begin{aligned}F(J,T) &= 1 + 8v + 49.33v^2 + 256v^3 + 1181.48v^4 + 5054.89v^5 \\ &\quad + 20630.80v^6 + 340894.42v^7 + 307123.12v^8\end{aligned} \qquad (3)$$

This fitting gave a ferromagnetic exchange interaction $J = +3$ K and hyperfine coupling constant $A_D = -0.17$ MHz. The derived value of $J = +3$ K is similar to ~ + 2.7 K estimated from molecular field theory [4].

This study demonstrated that high-speed magic angle spinning deuterium NMR is a powerful technique to elucidate the local magnetic interactions in magnetic metal assembled complexes with electron spins greater than S = 1/2.

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