Antiferromagnetic Resonance of Hyperfine-Enhanced Nuclear Spins of ^{165}Ho in $Cs_2NaHoCl_6$

Haruhiko Suzuki and Yumiko Masuda[(a)]
Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan

and

Akira Tamaki
Research Institute for Science Measurement, Tohoku University, Sendai 980, Japan

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Hyperfine-enhanced nuclear antiferromagnetic resonance of ^{165}Ho ($I=\frac{7}{2}$) in $Cs_2NaHoCl_6$ was observed below $T_N \simeq 4.5$ mK following demagnetization cooling. Measurements were carried out at several frequencies by cw NMR with a low-field sweep. From the temperature dependence of the resonance field, the resonance frequency versus applied-field diagram at 0 K was obtained. This is the first observation of enhanced nuclear antiferromagnetic resonance.

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An antiferromagnetic ordering of the hyperfine-enhanced nuclear spins in $Cs_2NaHoCl_6$ takes place at about 4.5 mK.[1,2] The nuclear-spin ordering, produced by adiabatic demagnetized cooling of the specimen, was observed in magnetic susceptibility measurements.[1,2] For a full understanding of the antiferromagnetic state, measurement of the antiferromagnetic resonance (AF resonance) is essential. However, AF resonance in hyperfine-enhanced nuclear-spin systems is hard to observe, partly because the resonance frequency is rather high, i.e., in the range of ~ 10 to $\sim 10^2$ MHz, and partly because the rf measurement field itself warms up the nuclear spins so quickly. In the present paper we report the first observation of the AF resonance of ^{165}Ho nuclear spins in $Cs_2NaHoCl_6$, which have an enhanced nuclear magnetic moment.

The ionic crystal elpasolite $Cs_2NaHoCl_6$ is known to be a hyperfine-enhanced nuclear-spin system at low temperature.[1,3] The ground state of the $4f$ electrons of Ho^{3+} ($4f^{10}, {}^5I_8$) in the cubic compound $Cs_2NaHoCl_6$ is a Γ_3 doublet and the Γ_4 triplet is located at 10.3 cm^{-1}. Since a Γ_3 doublet is nonmagnetic, the compound shows Van Vleck paramagnetism at low temperature. When the nuclear spin of ^{165}Ho ($I=\frac{7}{2}$) in $Cs_2NaHoCl_6$ couples with the induced electronic moment through the magnetic hyperfine interaction, the nuclear spin has an enhanced magnetic moment. The gyromagnetic ratio of the enhanced nuclear spin was found to be $\gamma/2\pi = 1980$ MHz/T in a NMR experiment.[3] At lower temperature the crystal structure of $Cs_2NaHoCl_6$ distorts from cubic symmetry to a lower symmetry. Although the direct observations of the crystal distortion by x-ray measurement has not been performed, the crystal distortion has been confirmed in specific-heat[4] and NMR[5] experiments. In the distorted phase the Γ_3 doublet splits into two singlet levels which give the $\gamma_z/2\pi$ value of 4 GHz/T, as will be discussed later. By the demagnetization from the initial field, which was of the order of 1 T at about 30 mK, the enhanced nuclear spins were self-cooled and moved into the antiferromagnetic state, which was observed by measurement of the magnetic susceptibility[1] and the specific heat.[4] The Néel temperature was estimated to be $T_N \simeq 4.5$ mK. However, since the enhanced nuclear spin is almost thermally isolated at these low temperatures, it is very hard to determine the nuclear-spin temperature precisely. Therefore this problem will be discussed elsewhere. To determine the spin structure, a neutron-diffraction experiment has already been carried out, but unfortunately the expected magnetic diffraction peak could not be observed.[2]

In our present experiments an AF resonance of the enhanced Ho nuclear spin in $Cs_2NaHoCl_6$ was observed. The consequences of this result with respect to the magnetic spin structure and the internal field will be discussed. Our conclusion is that this measurement might be the first observation of the AF resonance in a hyperfine-enhanced nuclear-spin system.

A single crystal of $Cs_2NaHoCl_6$, roughly spherical in shape with a diameter of 12 mm, was used for our experiment. The crystal was attached to the mixing chamber of a ^{3}He-^{4}He dilution refrigerator with thin copper wires and Ge7031 varnish. The crystal was mounted with the $\langle 011 \rangle$ axis parallel to the direction of the applied field. The cw NMR measurement was made by our sweeping the magnetic field through resonance at some fixed rf frequencies. A synthesized signal generator fed a rf signal to a NMR coil wound around the crystal. This NMR coil and a long coaxial cable formed the *LC* circuit. The *Q* value of this circuit showed a high value at characteristic frequencies. We could adjust the characteristic frequency to some extent with a room-temperature variable capacitor. The modulation coil of the magnetic field was wound outside the vacuum jacket of the dilution refrigerator. The spin temperature of the specimen was determined by measurement of the susceptibility of the enhanced nuclear spin itself. The magnetic susceptibility was measured by use of a flow-level resonant circuit.[6] The measuring coil was wound just outside the NRM coil. Since the rf field of the NMR measurement disturbed the magnetic susceptibility measurement, the magnetic susceptibility was measured just before and after each magnetic field sweep of the NMR measurement.

By this method we succeeded in measuring the temperature dependence of the AF resonance field below T_N. By demagnetization from the initial temperature of about 30 mK and the initial field of larger than 0.5 T, the nuclear spins were cooled down below the ordering temperature T_N. Without the rf and modulation fields of the NMR measurement, the enhanced nuclear spins remained in the ordered state for more than half a day. However, with rf and modulation fields applied, the spins quickly warmed up to T_N within 1 h. Therefore, just three or four NMR measurements were carried out below T_N for each demagnetization.

Before measurement of the AF resonance, the NMR measurement of the paramagnetic state was carried out. Below 150 mK the resonance spectrum of ^{165}Ho nuclear spins splits into seven lines, supporting the crystal distortion at about 150 mK. When we decrease the temperature, the resonance line at the lowest resonance field, corresponding to the $|\frac{7}{2}\rangle$-$|\frac{5}{2}\rangle$ transition, increases in intensity. This result suggests that the ground state of the enhanced nuclear spin of ^{165}Ho is $I_z = \pm\frac{7}{2}$. This result is shown in Fig. 1.

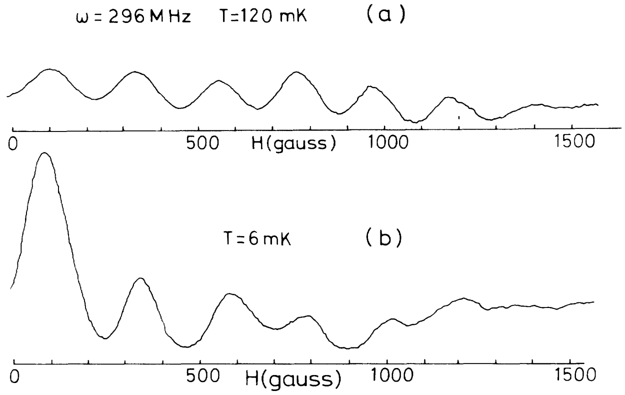

FIG. 1. (a) Quadrupole splitting spectrum at about 120 mK. (b) Resonance spectrum at about 6 mK, following demagnetization cooling. The intensity of the line at the lowest field increased the most.

It was difficult to determine the value of $\gamma/2\pi$ precisely. One reason may be the fact that the crystal was mounted such that the measuring direction was parallel to the $\langle 011\rangle$ axis, and the accuracy of the alignment of the crystal might not be so good at low temperatures. Furthermore, the splittings in the NMR spectra are not large compared with the line broadening and the adjacent lines overlap each other. However, by using the value of $\gamma/2\pi$ determined from the resonance line of the transition $|+\frac{1}{2}\rangle$-$|-\frac{1}{2}\rangle$, we determined the value of the coefficient of quadrupole interaction P/h to be 38.9 ± 0.5 MHz. In the antiferromagnetic state, the AF resonance can be observed as a shift of the resonance field from the paramagnetic resonance of the $|+\frac{7}{2}\rangle$-$|+\frac{5}{2}\rangle$ transition, $6P/h$.

When the relative motion between the induced electronic magnetic moment and the nuclear spin is considered, the theoretical treatment of the AF resonance of the hyperfine-enhanced nuclear spins is rather complicated.

Here we assume rigid coupling between the nuclear spin and the induced electronic magnetic moment. The resonance frequency ω can be analyzed by the following equation:

$$(\omega/\gamma)^2=(J_{zz}M_z+H_A)\{J_{zz}M_z-\tfrac{1}{2}(J_{xx}M_x+J_{yy}M_y)+H_A\}+H^2\pm[(J_{zz}M_z+H_A)(J_{xx}M_x-J_{yy}M_y)$$
$$+4H^2(J_{zz}M_z+H_A)\{J_{zz}M_z-\tfrac{1}{2}(J_{xx}M_x+J_{yy}M_y)+H_A\}]^{1/2}, \qquad (1)$$

where H_A is the anisotropy field and $J_{ij}M_j$ is the internal field along the i direction produced by the j component of the sublattice magnetization. Since we can assume $J_{ij}M_j$ $(i\neq j)=0$ in $Cs_2NaHoCl_6$ only, the $J_{ii}M_i$ terms appear in the equation.

We estimated the resonance frequency ω in Eq. (1). At high temperatures, a crystal of $Cs_2NaHoCl_6$ has the symmetry of the space group $Fm3m$ (O_h^5). On the other hand, magnetically the Ho ions lie on an fcc lattice. The two wave functions of the ground state $\Gamma_3^{(2)}$, the admixture $|8^s,4^s,0\rangle$ and the admixture $|6^s,2^s\rangle$ are labeled by $|E_1\rangle$ and $|E_2\rangle$, respectively. The three wave functions of the first excited state $\Gamma_4^{(2)}$ are the admixtures $|\pm7,\pm3,\mp1,\mp5\rangle$ and the admixture $|8^a,4^a,0\rangle$. Here $|8^s\rangle$ and $|8^a\rangle$ denote the symmetric and antisymmetric combinations $2^{-1/2}\{|+8\rangle\pm|-8\rangle\}$, respectively. The gyromagnetic ratio $\gamma/2\pi$ of the enhanced nuclear spin is $(\gamma-\gamma_I)h=2g_J\mu_BA_J\alpha$,where $\gamma_I/2\pi=9$ MHz T^{-1} is the gyromagnetic ratio of ^{165}Ho in the absence of any enhancement and $A_J/h=812$ MHz is the hyperfine coupling constant. $\alpha=\frac{1}{2}\sum|\langle\Gamma_4^{(2)}|J|\Gamma_3^{(2)}\rangle|^2/\Delta$, where Δ is the energy difference between $\Gamma_3^{(2)}$ and $\Gamma_4^{(2)}$ and we ignored the levels higher than $\Gamma_4^{(2)}$. Since $\sum|\langle\Gamma_4^{(2)}|J_z\times|E_2\rangle|^2/\Delta=0$, only the $|E_1\rangle$ level contributes to the enhancement of the nuclear moment. Therefore, in the distorted phase where only the $|E\rangle$ level is occupied, the value of $\gamma_z/2\pi$ is twice the value of $\gamma_z/2\pi\simeq2$ GHz/T in the cubic structure. In the distorted structure $\gamma/2\pi$

TABLE I. We show the calculated dipole fields in units of megahertz for the up-up down-down and up-down spin structures. The calculated resonance frequencies in zero field from Eq. (1) are also listed for these two spin structures.

	$J_{zz}M_z$ (MHz)	$J_{xx}M_x$ (MHz)	$J_{yy}M_y$ (MHz)	$\omega(0)$ (MHz)
Up-up down-down	39.2	−4.89	2.45	277.7,270.4
Up-down	26.4	−3.3	1.65	262.3,259.7

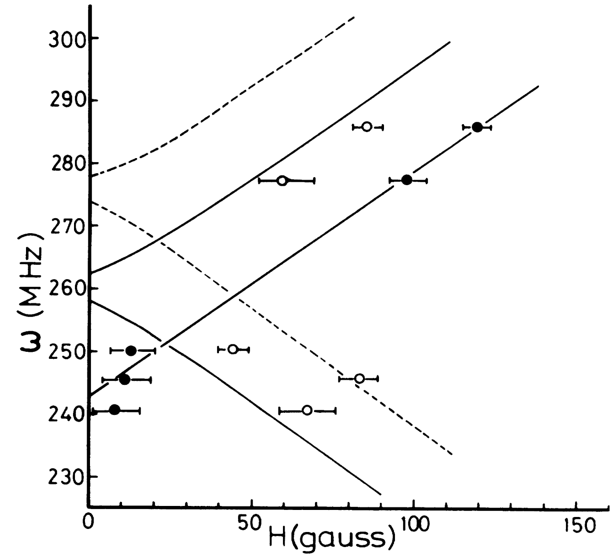

FIG. 3. Resonance field $\omega(0)$ at 0 K against applied field. Calculated curves are also shown. Calculations were made by use of Eq. (1) for the values listed in the table. The solid lines represent the up-down structure and the dashed lines, the up-down up-down structure.

gives us an anisotropic value. Since

$$|\langle\Gamma_4^{(2)}|J_{x,y}|E_1\rangle|^2=\tfrac{1}{4}\,|\langle\Gamma_4^{(2)}|J_z|E_1\rangle|^2,$$

the value of $\gamma_x/2\pi=\gamma_y/2\pi=1$ GHz/T can be expected. In Eq. (1), the anisotropy field H_A is mainly due to the nuclear electric quadrupole interaction. We used the value of $6P/h=233$ MHz. The anisotropy of the $\gamma/2\pi$ effects the resonance frequency through the JM term of the internal field. In the calculation to determine the internal field JM, we first assumed that only the dipole-dipole interaction between the enhanced nuclear spins exists. Because of the large anisotropic field of the nuclear quadrupole interaction, the nuclear spins are forced to align along the z axis of the distorted structure. We assumed the direction of the Q vector of the antiferromagnetic spin structure to lie along the x axis, and the calculated dipole fields are shown in Table I for both the up-down and up-up down-down structures. By using these values, we calculated the resonance frequencies for the case of vanishing field, $\omega(0)$. These results are also listed in Table I. In Fig. 2 a typical result for the temperature dependence of the resonance field is shown. Above the Néel temperature, the resonance fields take almost constant values. To obtain the value of the resonance field at $T=0$, the data were extrapolated to $T=0$. In this extrapolation the temperature dependence of the shift of the resonance field was fitted with the Brillouin function which is represented by the solid curve in the figure. In this way the resonance frequency ω versus the applied field diagram was obtained as shown in Fig. 3. At low temperature the resonance-field shift seems to vary linearly with $(T/T_N)^2$. In Fig. 4 we have also plotted $B(\omega)-B_0(\omega)$ against $(T/T_N)^2$, where $B_0(\omega)$ is the paramagnetic resonance field. Since our measured temperature was not so low, we will not discuss the temperature dependence of the spin-wave energy at present. When we fit the experimental points of the paramagnetic resonance by a straight line, 243 MHz was obtained as the zero-field value, as shown in Fig. 3. This value, however, is slightly larger than the value of 233 MHz ob-

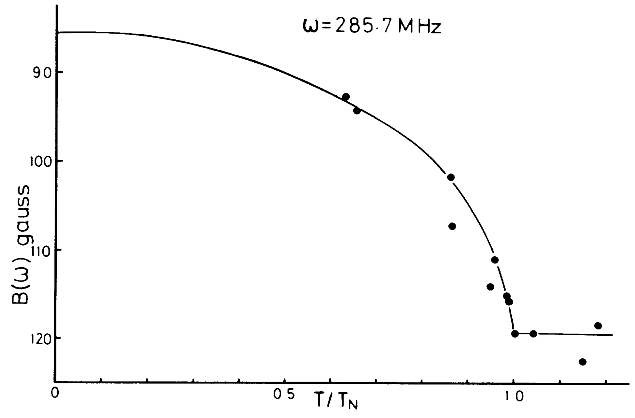

FIG. 2. Temperature dependence of the resonance field. The solid curve is the Brillouin function of $I=\frac{7}{2}$.

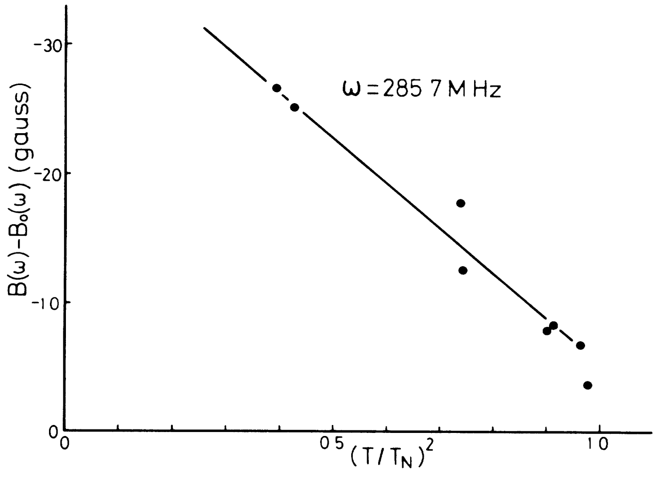

FIG. 4. Temperature dependence of the resonance field, plotted against $(T/T_N)^2$.

tained by measurement of the whole of the quadrupole splitting lines at higher temperatures. In Fig. 3 we have also plotted the field dependences calculated by using Eq. (1) for both the up-down and the up-up down-down spin structures. The higher branch can be explained well by the calculation for the up-down structure. The lower branch, however, seems not to be in such good agreement with the calculation. Since the error bars of these data are considerably larger, more detailed discussion cannot be made at present. From our experimental results we can conclude that the up-down spin structure seems to be preferred.

The curious point in our experiments is the intensity of the resonance spectrum. Below the Néel temperature, the intensity of the spectrum increased with increasing temperature. At the lowest temperature of our experiment, $T/T_N \simeq 0.65$, the intensity was less than half the value at the Néel temperature. For the linewidth, however, we found an almost constant value of about 130 Oe.

In conclusion, we can say that the first observation of the antiferromagnetic resonance of a hyperfine-enhanced nuclear-spin system was a success. The main features of our antiferromagnetic resonance can be understood by the electromagnetic quadrupole interaction and the dipole-dipole interaction between the enhanced nuclear spins.

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[a] Present address: Materials Research Laboratory, HOYA Corporation, Akishima, Tokyo 196, Japan.

[1] H. Suzuki, M. Miyamoto, Y. Masuda, and T. Ohtsuka, J. Low Temp. Phys. **48**, 297 (1982).

[2] H. Suzuki, Y. Masuda, and J. Arthur, J. Low Temp. Phys. **70**, 301 (1988).

[3] B. Bleaney, A. G. Stephen, P. J. A. Walker, and M. R. Wells, Proc. Roy. Soc. London A **376**, 235 (1981).

[4] H. Suzuki, Y. Masuda, M. Miyamoto, T. Ohtsuka, and P. J. Walker, J. Low Temp. Phys. **62**, 497 (1986).

[5] E. Bongers, H. B. Brom, E. J. Veenendaal, W. J. Huiskamp, and H. D. Amberger, Physica (Amsterdam) **115B**, 72 (1982).

[6] F. N. H. Robinson and K. V. Loftus, J. Phys. E **9**, 447 (1986).