The temperature dependence of ^{133}Cs nuclear magnetic resonance in a CsMnCl$_3$·2H$_2$O single crystal

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Abstract. The nuclear magnetic resonance of ^{133}Cs in a CsMnCl$_3$·2H$_2$O single crystal grown by the slow evaporation method has been investigated by employing a Bruker FT NMR spectrometer. The rotation patterns of the ^{133}Cs NMR spectra were obtained in three mutually perpendicular planes under an applied magnetic field of 4.7 T. From the experimental data, the nuclear quadrupole coupling constant $e^2qQ/h = 321.3 \pm 0.1$ kHz and asymmetry parameter $\eta = 0.301 \pm 0.002$ are determined at room temperature. The principal axes X, Y, and Z of the EFG tensor for the Cs ion are found to lie along the crystallographic $(c+45°)$-, $(b+45°)$-, and a-axes, respectively. The measurement was extended to the temperature range of 120–320 K. The temperature dependence of the quadrupole parameters is roughly explained with a single torsional frequency of the Cs–Cl bond in terms of the simple Bayer theory.

1. Introduction

The structure of CsMnCl$_3$·2H$_2$O crystal has been determined by Jensen *et al* [1] to be orthorhombic at room temperature. It has been proposed that the chains of Mn^{2+} ions order antiferromagnetically well above the Néel point, 4.8 K, in this crystal [2, 3]. There have been experimental investigations such as studies of x-ray diffraction [1], magnetic susceptibility measurements [2], and studies of the mobility of water via ^{1}H nuclear magnetic resonance [4] for the CsMnCl$_3$·2H$_2$O single crystal.

In this paper, we present the results of a ^{133}Cs nuclear magnetic resonance (NMR) study of a CsMnCl$_3$·2H$_2$O single crystal grown by the slow evaporation method. The quadrupole coupling constant, e^2qQ/h, the asymmetry parameter, η, and the direction of the principal axes of the electric field gradient (EFG) tensor of ^{133}Cs ($I = 7/2$) are determined at room temperature. Also, the temperature dependence of the quadrupole coupling constant and asymmetry parameter have been analysed by means of experimental data obtained with a pulse NMR spectrometer. This temperature dependence of ^{133}Cs NMR in a CsMnCl$_2$· 2H$_2$O single crystal is a new result.

2. Crystal structure

The crystal structure of CsMnCl$_3$·2H$_2$O is orthorhombic, characterized by the space group *Pcca* (D$_{2h}^8$). The unit cell contains four formula units and has the dimensions $a = 9.060$ Å, $b = 7.285$ Å, and $c = 11.455$ Å [1]. A projection of the structure onto the (001) plane is shown in figure 1. The magnetic Mn^{2+} ions are arranged in chains along the a-axis. Each
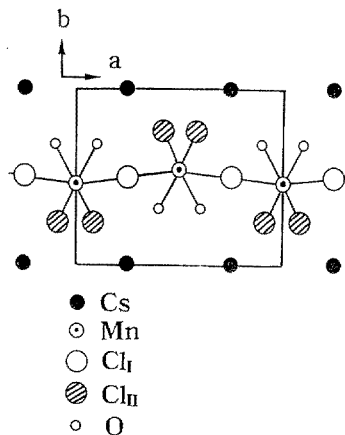
Figure 1. The structure of CsMnCl₃·2H₂O crystal projected onto the (001) plane.

Mn^{2+} ion is surrounded by an octahedral coordination consisting of four Cl^- ions and two O^{2-} ions. The two chlorines, which are designated as Cl_I, are shared by adjacent octahedra, while those designated as Cl_{II} belong to only one octahedron [5].

3. Experimental procedure

The single crystals of CsMnCl₃·2H₂O were grown by slow evaporation of a stoichiometric aqueous solution of CsCl and MnCl₂·4H₂O. The colour of the crystal is pink at room temperature. The optical axis (*c*-axis) was identified with a polarizing microscope, and the orientation of the crystallographic *a*- and *b*-axes was determined by the x-ray Laue method.

Nuclear magnetic resonance signals of ^{133}Cs in a CsMnCl₃·2H₂O single crystal were measured using a Bruker MSL 200 FT NMR spectrometer at the Korea Basic Science Institute in Seoul. The static magnetic field was 4.7 T and the central rf frequency was set at $\omega_0/2\pi = 26.2479$ MHz. The NMR spectra of ^{133}Cs were recorded with a sequence of one 90° pulse, 20 scans, and a repetition time of 3 s. A ring-down delay time of 11 μs was used to remove the effect of the pulse.

Temperature-dependent NMR measurements were made in the following way. Various temperatures were established by regulating the temperature of the nitrogen gas streaming past the sample. A heater element immersed in liquid nitrogen inside the Dewar boiled off the nitrogen gas which, in turn, was transferred to the cavity Dewar through the transfer arm. A second heater element, located at the transfer arm, was used to heat the gas for precise temperature regulation. At the sample coil insert, the nitrogen gas from the transfer arm was directed to flow past the sample. The temperature of the gas was monitored by a thermocouple inserted into the bottom of the sample coil. The thermocouple element was positioned as close as possible to the sample without affecting the signal detection adversely [6].

4. Experimental results and analysis

The NMR spectra can be analysed via the Hamiltonian [6, 7]

$$H = -\gamma\hbar B_0 \cdot I + [e^2 qQ/4I(2I-1)]\{3I_Z^2 - I(I+1) + \eta(I_X^2 - I_Y^2)\} \quad (1)$$

where e^2qQ/h is the quadrupole coupling constant, and η is the asymmetry parameter. The matrix form of the spin Hamiltonian of equation (1) is employed to calculate the resonance fields with the magnetic field applied along a general direction. All of the resonance spectra and the parameters are calculated by numerically diagonalizing the 8×8 matrix using a computer program to analyse the experimental data. The computer program used also included the Eulerian transfomation of the magnetic field vector with respect to the coordinate system made up of the principal axes of the EFG tensor. The Eulerian angles Φ, Θ, Ψ are for a transformation of the crystal system (a, b, c) into the EFG system (X, Y, Z).
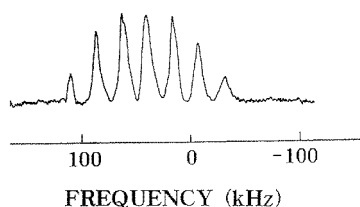

Figure 2. A typical NMR spectrum of ^{133}Cs for a CsMnCl$_3$·2H$_2$O crystal recorded with the pulse NMR spectrometer. The static magnetic field B_0 is parallel to the a-axis. The zero point corresponds to the resonance frequency 26.2479 MHz of the ^{133}Cs nucleus.

The seven-line structure is a result of the quadrupole interaction of the ^{133}Cs ($I = 7/2$) nucleus. A typical NMR spectrum of ^{133}Cs is shown in figure 2, where the signals were obtained with the magnetic field applied along the crystallographic a-axis. It is a Fourier transform of the free-induction decay for the ^{133}Cs NMR; the zero point in figure 2 corresponds to the resonance frequency 26.2479 MHz of the ^{133}Cs nucleus. It consists of signals displaced to the higher-frequency side (paramagnetic shift) relative to the reference signal, obtained with the ^{133}Cs line in an aqueous solution of CsCl.
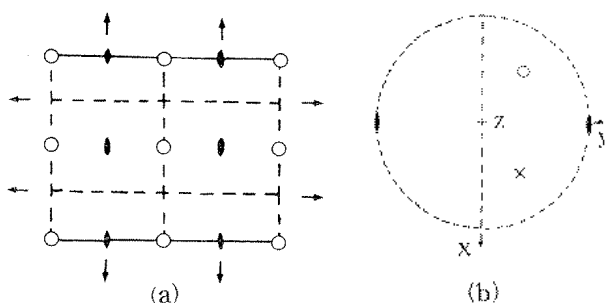

Figure 3. (a) A diagram of the symmetry element for *Pcca*. (b) The stereographic projection for the symbol 2.

Even though there are four caesium nuclei per unit cell, only one set of NMR spectra of ^{133}Cs is obtained. A diagram of the symmetry elements and of the general position for *Pcca* is shown in figure 3(a). The following position (Wyckoff notation and point symmetry) is occupied: 4Cs(c, 2). The local symmetry at the Cs site in CsMnCl$_3$·2H$_2$O has a twofold symmetry [8]. The stereographic projection for the symbol 2 is shown in figure 3(b). The symbol 2 signifies that the principal axis is a diad axis of rotation. With an initial pole of a general face (*hkl*) represented as a dot, we obtain by the operation of a diad axis another dot

so situated in the stereographic projection that the two points are at equal distances from the centre of projection and the line joining them passes through the centre. The general form therefore has two faces. The crystal will show faces in pairs, related to each other by a diad axis [9]. This means that four caesium sites are crystallographically and magnetically equivalent. Therefore, only one set of the NMR spectra of ^{133}Cs is obtained even though there are four caesium nuclei per unit cell.
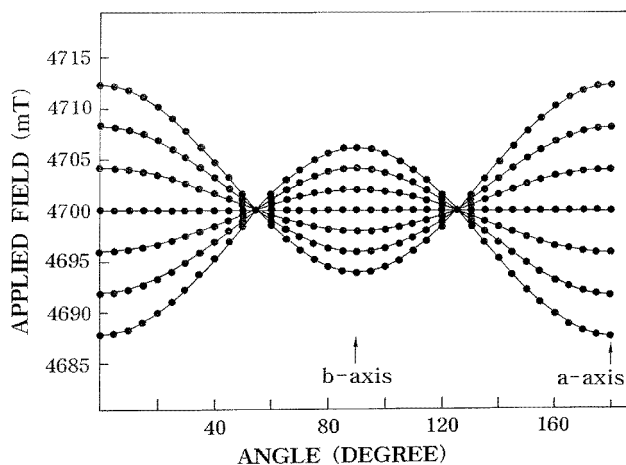

Figure 4. The rotation pattern of ^{133}Cs NMR measured in the *ab*-plane at room temperature. The circles show experimental data and the lines show calculations based on the best-fit parameters.
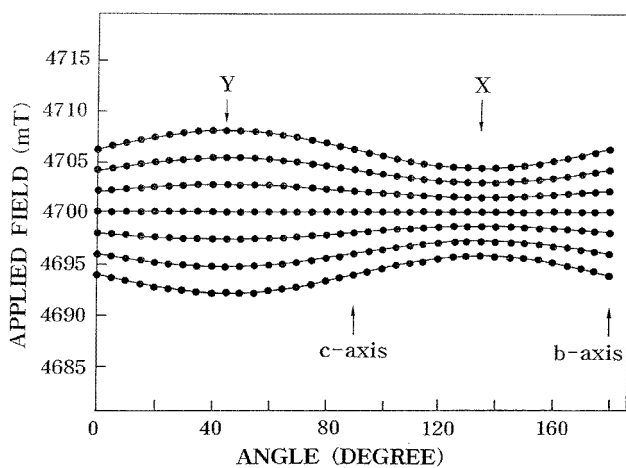
Figure 5. The rotation pattern of ^{133}Cs NMR measured in the *bc*-plane at room temperature. The circles show experimental data and the lines show calculations based on the best-fit parameters.

In general, rotation patterns in three mutually perpendicular directions are required to determine the quadrupole interaction completely. The rotation patterns of ^{133}Cs NMR spectra measured in the crystallographic planes at room temperature are displayed in figures 4, 5 and 6; they were obtained by converting the resonance frequency into the resonance

Figure 6. The rotation pattern of ^{133}Cs NMR measured in the *ca*-plane at room temperature. The circles show experimental data and the lines show calculations based on the best-fit parameters.
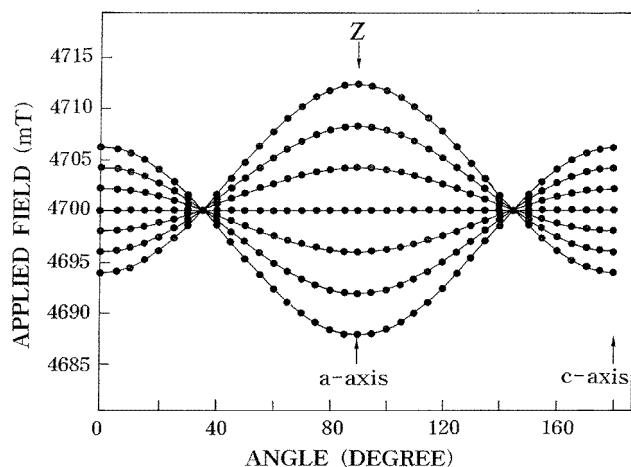
magnetic field. From the fact that the resonance field of the central line is almost constant and the spacings between adjacent lines are equal, the first-order perturbation of H_Q with respect to H_Z may be sufficient for analysis [10], where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction. In figure 5, the satellite resonance lines did not show the maximum separation for $0°$ and $180°$ or the minimum separation for $90°$. From these experimental results, we know that the principal axes of the Cs ion are not consistent with the crystallographic axes.

Table 1. The direction cosine of the principal axis direction of the EFG tensor for ^{133}Cs in a $CsMnCl_3 \cdot 2H_2O$ single crystal at room temperature.

	l_a	l_b	l_c
V_{ZZ}	0	0	1
V_{XX}	0.7071	−0.7071	0
V_{YY}	0.7071	0.7071	0

Table 2. Quadrupole parameters of ^{133}Cs in a $CsMnCl_3 \cdot 2H_2O$ single crystal at room temperature.

e^2qQ/h (kHz)	η	Principal axes	References
321.3 ± 0.1	0.301 ± 0.002	$X = c + 45°$	Present work
		$Y = b + 45°$	
		$Z = a$	
334.3 ± 0.15	0.293 ± 0.006	$X = c$	Bug *et al* [4]

The parameters were determined by a least-squares fit to the experimental data. The nuclear quadrupole coupling constant and asymmetry parameter of ^{133}Cs in a $CsMnCl_3 \cdot 2H_2O$ crystal are obtained as 321.3 ± 0.1 kHz and 0.301 ± 0.002 at room temperature. The direction of the principal EFG tensor of the caesium nucleus at 300 K is

shown in table 1. Here, l_a, l_b, and l_c are the direction cosines relative to the crystallographic a-, b-, and c-axes of CsMnCl$_3$·2H$_2$O, respectively. These results are consistent with the Eulerian angles $\Phi = 133.8°$, $\Theta = 90°$, and $\Psi = 90°$ of the earlier report [4]. However, the principal X-axis determined from our experimental data is different from that in the earlier report. The parameters analysed for the ^{133}Cs nucleus are summarized in table 2 together with those from the earlier report.
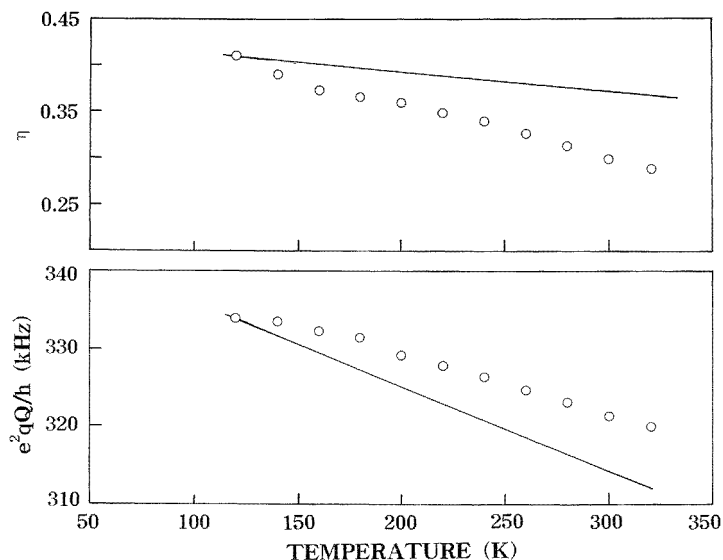

Figure 7. The temperature dependence of the nuclear quadrupole coupling constant, e^2qQ/h, and the asymmetry parameter, η, for ^{133}Cs in a CsMnCl$_3$·2H$_2$O single crystal. Measurements are indicated by the points. The solid lines are the predictions based on the theory of Bayer and of Wang.

In order to examine the temperature dependence of e^2qQ/h and η for ^{133}Cs in the CsMnCl$_3$·2H$_2$O single crystal, the resonance spectra were measured at eleven different temperatures in the range 120–320 K. ^{133}Cs NMR spectra as a function of temperature were measured in three mutually perpendicular crystallographic planes. While the central transition stays constant, the splitting between the central and satellite lines is found to decrease as the temperature increases. The temperature dependences of e^2qQ/h and η are shown in figure 7. The parameters were found to decrease almost linearly as a function of increasing temperature in this study.

A simple model given by Bayer [11] and Wang [12], which ascribes the temperature dependence to a torsional oscillation of the Cs–Cl ion in CsMnCl$_3$·2H$_2$O, was adopted in this study in an effort to comprehend the temperature dependence of e^2qQ/h and η for ^{133}Cs. The temperature dependence of e^2qQ/h and η may be explained with a single torsional mode about the X-axis of the EFG tensor. If the terms of second order in the angular displacement are retained, then the following equations hold [13]:

$$q' = q[1 - (3 + \eta)\langle\theta_X{}^2\rangle/2]$$
$$\eta' = \{\eta - (3 + \eta)\langle\theta_X{}^2\rangle/2\}/\{1 - (3 + \eta)\langle\theta_X{}^2\rangle/2\} \tag{2}$$

where unprimed and primed quantities are for the rigid and the motional molecules,

respectively. As the torsional motion is quantized, $\langle \theta_i^2 \rangle$ is related to the temperature by

$$I_i \omega_i^2 \langle \theta_i^2 \rangle = \hbar \omega_i [1/2 + 1/\{\exp(\hbar \omega_i / kT) - 1\}] \tag{3}$$

where ω_i ($i = X, Y, Z$) is the torsional angular frequency, I_i is the corresponding moment of inertia, and T is the temperature. In this torsional motion about the X-axis, both e^2qQ/h and η decrease with the increasing temperature. The solid line in figure 7 is the prediction of e^2qQ/h and η for ^{133}Cs with $I_X = 1.81 \times 10^{-44}$ kg m^2 and $\omega_X = 2.61 \times 10^{12}$ rad s^{-1}. Therefore, Bayer and Wang's theory can explain our data in the temperature range 120–320 K.

5. Discussion and conclusion

From the experimental data, the nuclear quadrupole coupling constant and asymmetry parameter of ^{133}Cs in a $CsMnCl_3 \cdot 2H_2O$ single crystal are obtained at room temperature: 321.3 ± 0.1 kHz and 0.301 ± 0.002. The principal axes X, Y, and Z of the EFG tensor for the Cs ion are found to lie along the crystallographic $(c + 45°)$-, $(b + 45°)$-, and a-axes, respectively. The temperature dependence of the nuclear quadrupole coupling constant and asymmetry parameter are found to be decreasing with the increasing temperature in the temperature range 120–320 K. The temperature dependence of e^2qQ/h and η is roughly explained by a single torsional frequency $\omega_X = 2.61 \times 10^{12}$ rad s^{-1} of the Cs–Cl ion by means of the simple Bayer theory.

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