

Cesium NMR in a Paramagnetic CsMnCl₃ Single Crystal

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Nuclear magnetic resonance of ¹³³Cs in a CsMnCl₃ single crystal grown by the Czochralski method has been investigated by employing a Bruker FT NMR spectrometer. The ¹³³Cs resonance of two different groups were recorded. Various transitions belonging to two cesium spectra of a different intensity ratio are analyzed. The quadrupole coupling constant of Cs(I) is 0.15 ± 0.01 MHz, and that of Cs(II) is 0.21 ± 0.01 MHz. The anisotropy parameter is zero for both. The principal axes of the EFG tensors for these two sites are found to be the same. The Z axis, conventionally the largest component of the EFG tensor, is parallel to the crystallographic c-axis.

I. Introduction

The CsMnCl₃ single crystal was reported to form a perovskite R $\bar{3}m$ (a related crystal which belongs to the trigonal space group D_{3d}⁵) at room temperature [1]. There have been experimental investigations such as x-ray diffraction[2], antiferromagnetic resonance[3], nuclear magnetic resonance of ³⁵Cl[4], and optical properties[5] for the CsMnCl₃ single crystal grown by the Bridgman method[6]. This crystal has excellent optical quality and has found increasing application in recent years as the electro-optic modulators, acousto-optic deflectors, and other devices for controlling laser beams[7].

Our present work reports on ¹³³Cs nuclear magnetic resonance(NMR) in a CsMnCl₃ single crystal grown by the Czochralski method. The quadrupole coupling constant (e^2qQ/h), the asymmetry parameter(η), and the directions of the principal axes of the electric field gradient(EFG) tensor of ¹³³Cs(I = 7/2) are determined at room temperature.

II. Crystal Structure

The crystal structure of CsMnCl₃ is trigonal with lattice parameters of $a = 7.291 \text{ \AA}$ and $c = 27.440 \text{ \AA}$ (space group R $\bar{3}m$) at room temperature[8]. This structure is essentially a hexagonal close packed arrangement of cesium and chlorine ions. The structure

of CsMnCl₃ is formed by a nine-layer stacking sequence ABABCBCAC... with a CsCl₃ composition. Mn cations fill the Cl₆-octahedra between the layers, yielding an arrangement closely related to the perovskite type. There are two kinds of sites for the cesium (Cs⁺) ions which occupy two physically inequivalent positions[9]. At room temperature, the Cs (I) and Cs (II) in CsMnCl₃ have 3 and 6 atoms per unit cell, respectively. The structure of CsMnCl₃ is shown in figure 1. The structure of CsMnCl₃ pro-

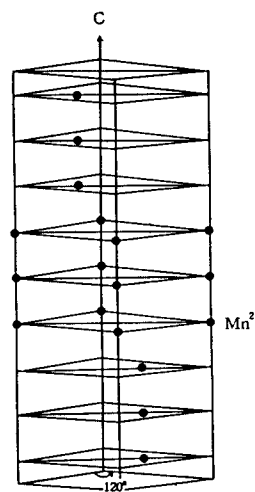


Fig. 1. Positions of magnetic ions (Mn²⁺) in the hexagonal structure of CsMnCl₃.

ected on the (100) plane are shown in figure 2.

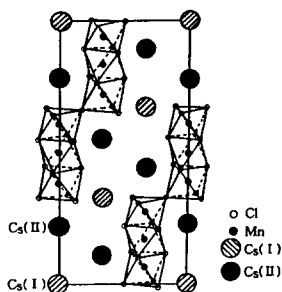


Fig. 2. The structure of CsMnCl₃ projected on the (100) plane.

Figure 3 shows a perspective view of a [Mn₃Cl₁₂] trimer unit in CsMnCl₃. The MnCl₃ trimer has three Cl atoms at the top and three Cl atoms at the bottom.

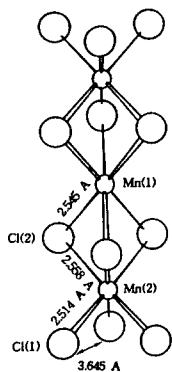


Fig. 3. A perspective view of a [Mn₃Cl₁₂] trimer unit in CsMnCl₃.

III. Experimental Aspects

The CsMnCl₃ single crystals were grown by melting a mixture of CsCl and MnCl₂ powder by the Czochralski method[8]. This was slightly hygroscopic and pale magenta in color. The orientation of the specimen was determined by the x-ray Laue method.

Nuclear magnetic resonance of ¹³³Cs in the CsMnCl₃ single crystal was measured using a Bruker

MSL 200 FT NMR spectrometer, operating at 4.7 T. The free induction decay of ¹³³Cs NMR was obtained with a one pulse sequence, 512 scans, and a repetition time of 1 sec. A pulse length of 6 μs and a ring-down delay time of 10 μs were applied in order to remove the after pulse effect and to adjust the phase of the signals.

IV. Theoretical Background of Nuclear Magnetic Resonance

The Hamiltonian for NMR to analyze the experimental results is the usual

$$H = H_Z + H_Q, \tag{1}$$

where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction of the ¹³³Cs nucleus, which has the nuclear spin $I = 7/2$ with 100 % natural abundance. The quadrupole Hamiltonian in the principal axes system of the EFG tensor is given by[10]

$$H_Q = e^2 q Q [3I_z^2 - I(I+1) + \eta(I_+^2 + I_-^2)/2] / 4I(2I-1), \tag{2}$$

where $e^2 q Q/h$ is the quadrupole coupling constant and η is the asymmetry parameter. Conventionally, the X, Y and Z axes are such that $|V_{XX}| \leq |V_{YY}| \leq |V_{ZZ}| = eq$; then $0 \leq \eta \leq 1$. The matrix form of the spin Hamiltonian of equation (1) is employed to calculate the resonance point with the magnetic field applied along a general direction. All resonance spectra and the parameters are calculated by numerically diagonalizing the 8 x 8 matrix using a computer program to analyze the experimental data[11].

V. Experimental Data and Analysis

The seven line structure is a result of the quadrupole interaction of the ¹³³Cs($I = 7/2$) nucleus. However, two different groups of the Cs resonances were recorded as shown in figure 4.

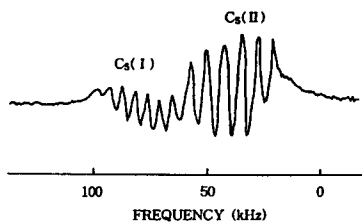


Fig. 4. ¹³³Cs NMR spectrum of two different groups in the CsMnCl₃ structure.

They consist of two groups displaced to the higher frequency side relative to the reference signal, obtained with the ¹³³Cs line in an aqueous solution of CsCl₃. Two groups, one weaker and the other stronger signals, represent the transition of ¹³³Cs NMR lines due to Cs(I) and Cs(II), respectively. The spectra consisting of two groups with an approximate intensity ratio of 1 to 2 are associated with two physically inequivalent positions of cesium atoms in the unit cell.

The rotation pattern of Cs(I) was measured in crystallographic ac-plane at room temperature, as shown in figure 5. The maximum separation result-

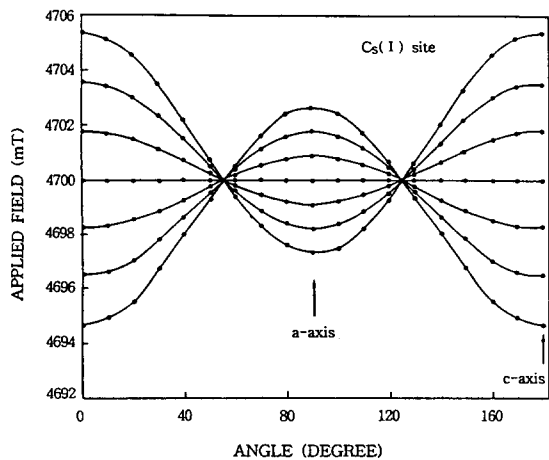


Fig. 5. Rotation pattern of Cs(I) NMR measured in the ac-plane at room temperature.

ting from the quadrupole interaction was observed when the magnetic field was applied along the c-axis of the crystal. The separations between ad-

acent lines are almost equal along this axis. The rotation pattern of Cs(II) was similar to that of Cs(I), as shown in figure 6 in the ac-plane. There

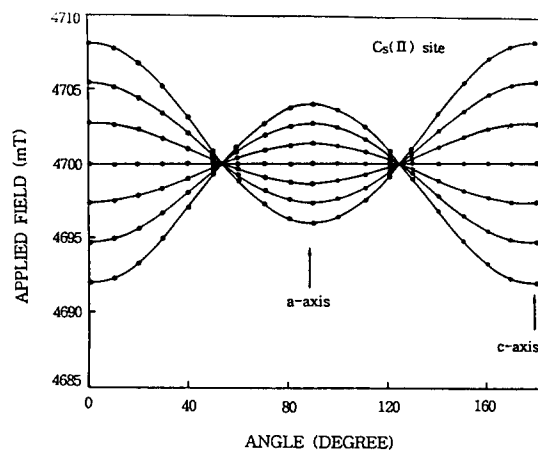


Fig. 6. Rotation pattern of Cs(II) NMR measured in the ac-plane at room temperature.

was no angular dependence of Cs(II) in the aa-plane, similar to Cs(I). For both of the Cs(I) and Cs(II) groups, the satellite resonance lines show the angular dependence of $3\cos^2\theta - 1$ with respect to the c-axis, whereas the central lines are angular independent. However, the rotation pattern in the aa-plane is angular independent for both Cs(I) and Cs(II). Therefore, the electric field gradient tensors of Cs(I) and Cs(II) are both axially symmetric ($\eta = 0$) and the principle Z-axis is parallel to the crystallographic c-axis. The orientations of the principal axes of the field gradient tensor coincide for the Cs(I) and Cs(II) sites.

Two different Cs resonance groups recorded with the different magnitude of the quadrupole splitting and paramagnetic shifts were analyzed. Accordingly, the quadrupole parameters were determined by the least squares fit using the experimental data of figure 5 for Cs(I), and corresponding data for Cs(II), respectively. The obtained quadrupole coupling constants of Cs(I) and Cs(II) are 0.15 ± 0.01 MHz and 0.21 ± 0.01 MHz, respectively. The experimental uncertainty of ± 0.01 MHz was cau-

sed mainly by reading the resonance position from the NMR spectra.

VI. Discussion and Conclusion

The c-axis of the CsMnCl₃ crystal has a 3-fold symmetry. Therefore, the asymmetry parameter of the Cs nucleus, $\eta = 0$ is consistent with the crystal structure. The maximum separation of the resonance line due to the quadrupole interaction was observed when the magnetic field was applied along the c-axis of the crystal. This direction is determined to be the Z axis of the EFG tensor. The Cs(I) and Cs(II) in the unit cell have 3 and 6 atoms, respectively. The Cs NMR intensity ratio of approximately 1 to 2 enabled us to designate Cs (I) and Cs (II) in the unit cell. We suggest that central positions of the resonance points of the Cs (I) and Cs (II) nuclei are different because due to the different contribution of Mn²⁺ ions on the nuclei. The shift of lines from the ¹³³Cs signal in the reference solution is related to the paramagnetic shift due to the Mn²⁺ ions in the CsMnCl₃ crystals.

Acknowledgement

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상자성체 CsMnCl₃ 단결정에서 ¹³³Cs 핵자기공명 연구

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Czochralski 방법에 의해 성장된 CsMnCl₃ 단결정에서 ¹³³Cs의 핵자기공명을 Bruker FT NMR 분광기를 이용하여 연구하였다. 두 개의 다른 무리의 ¹³³Cs 공명선이 관측되었다 : 서로 다른 intensity를 갖는 두 cesium 스펙트럼에 속하는 여러 transition이 분석되었다. Cs (I)의 핵 사중극 결합상수는 0.15 ± 0.01 MHz이고, Cs (II)는 0.21 ± 0.01 MHz이다. 비대칭인자는 두 경우에 대하여 영이고, 이들 두 경우의 EFG 텐서의 주축은 같았다. EFG 텐서의 가장 큰 성분을 만족하는 Z 축은 결정학적인 c축과 나란한 방향임을 알았다.