

Nuclear magnetic resonance of ^{133}Cs in a CsMnCl_3 single crystal

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1994 J. Phys.: Condens. Matter 6 10141

(<http://iopscience.iop.org/0953-8984/6/46/029>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.151

The article was downloaded on 12/05/2010 at 21:09

Please note that [terms and conditions apply](#).

Nuclear magnetic resonance of ^{133}Cs in a CsMnCl_3 single crystal

Ae Ran Lim[†], Sung Ho Choh[‡] and Se-Young Jeong[§]

[†] Department of Physics, Jeonju University, Chonju 560–759, South Korea

[‡] Department of Physics, Korea University, Seoul 136–701, South Korea

[§] Department of Physics, Pusan National University, Pusan 609-735, South Korea

Received 16 May 1994, in final form 17 August 1994

Abstract. The nuclear magnetic resonance of ^{133}Cs in a CsMnCl_3 single crystal grown by the Czochralski method has been investigated by employing a Bruker FT NMR spectrometer. The ^{133}Cs resonances of two different groups were recorded, that is the spectra of two groups with different intensity ratios associated with two physically inequivalent positions of caesium atoms in the unit cell. Various transitions belonging to two caesium spectra of different intensity ratios are analysed. The quadrupole coupling constant of Cs(I), giving weaker signals than the other, is 0.153 ± 0.014 MHz, and that of Cs(II) is 0.212 ± 0.014 MHz. The asymmetry 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.

1. Introduction

The CsMnCl_3 single crystal was reported to form a perovskite of space group $R\bar{3}m$ (a related crystal which belongs to the trigonal space group D_{3d}^5) at room temperature [1], and it was reported to be an antiferromagnetic phase transition with a weak ferromagnetic moment at $T_N = 67$ K [2]. Experimental investigations such as x-ray diffraction [3, 4], antiferromagnetic resonance [5], nuclear magnetic resonance (NMR) of ^{35}Cl [6] and optical properties [7] have been made for the CsMnCl_3 single crystal grown by the Bridgman method [8]. This crystal has excellent optical quality and has found increasing application in recent years as electro-optic modulators, acousto-optic deflectors and other devices for controlling laser beams [9].

Our present work reports the ^{133}Cs NMR in a CsMnCl_3 single crystal grown by the Czochralski method. The quadrupole coupling constant, the asymmetry parameter and the directions of the principal axes of the electric field gradient (EFG) tensor of ^{133}Cs ($I = \frac{7}{2}$) are determined at room temperature. This study appears to be the first ^{133}Cs NMR experiment on a CsMnCl_3 single crystal.

2. Crystal structure

The crystal structure of CsMnCl_3 is trigonal with the lattice parameters $a = 7.291$ Å and $c = 27.440$ Å (space group, $R\bar{3}m$) at room temperature [10]. This structure is essentially a hexagonal close-packed arrangement of caesium and chlorine ions. Since each Cs atom must be in contact with 12 Cl atoms, there are three possible positions of a layer in relation

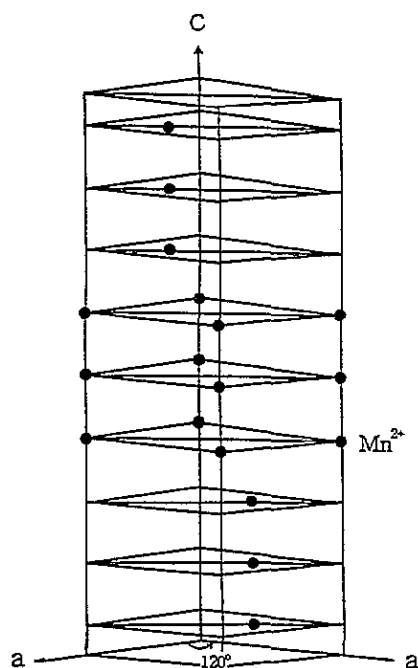


Figure 1. The positions of the magnetic ions (Mn^{2+}) in the hexagonal structure of $CsMnCl_3$.

to the framework of the unit cell; these correspond to types A, B and C. The structure of $CsMnCl_3$ is formed by a nine-layer stacking sequence ABABCBCAC... with a $CsCl_3$ composition. Mn cations fill the Cl_6 octahedra between the layers, yielding an arrangement closely related to the perovskite type. There are two kinds of site for the caesium ions (Cs^+) which occupy two physically inequivalent positions [4]. At room temperature, Cs(I) and Cs(II) in $CsMnCl_3$ have three and six atoms, respectively, per unit cell. The structure of $CsMnCl_3$ is shown in figure 1. The structure of $CsMnCl_3$ projected on the (100) plane is shown in figure 2. Figure 3 shows a perspective view of a $[Mn_3Cl_{12}]$ trimer unit in $CsMnCl_3$. The $MnCl_3$ trimer has three Cl atoms at the top and three Cl atoms at the bottom. The distances from the caesium and chlorine atoms to manganese atoms are given in table 1.

Table 1. The bond lengths of $CsMnCl_3$ at 300 K.

Bond type	Bond length (Å)
Cs(1)-Mn(2)	4.428
Cs(2)-Mn(2)	4.563
Cs(2)-Mn(1)	4.441
Cl(2)-Mn(1)	2.545
Cl(2)-Mn(2)	2.558
Cl(1)-Mn(2)	2.514

3. Experimental procedure

The $CsMnCl_3$ single crystals were grown by melting a mixture of $CsCl$ and $MnCl_2$ powder

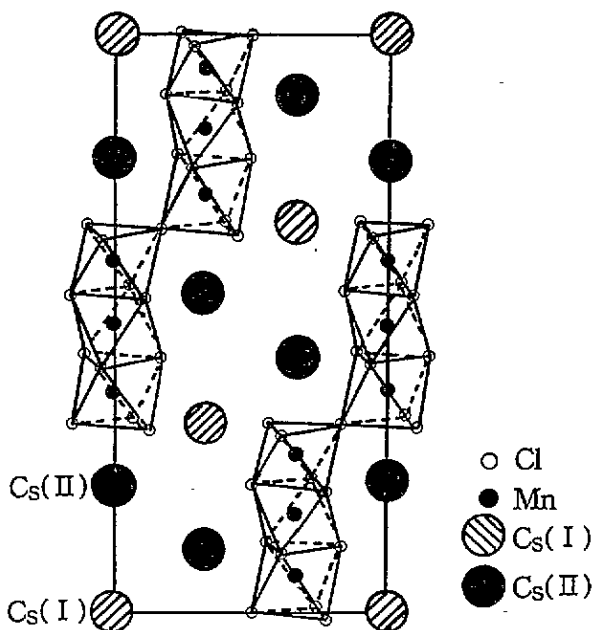


Figure 2. The structure of CsMnCl_3 projected on the (100) plane.

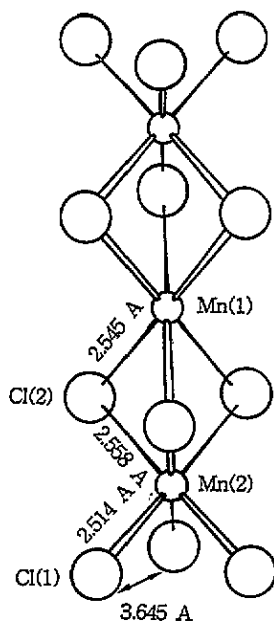


Figure 3. A perspective view of a $[\text{Mn}_3\text{Cl}_{12}]$ trimer unit in CsMnCl_3 .

by the Czochralski method [10]. This was slightly hygroscopic and pale magenta in colour. The orientation of the specimen was determined by the x-ray Laue method. The angular dependence of the NMR spectra was measured on the crystallographic a - c plane because the resonance spectra were angle independent in the hexagonal plane (a - a plane).

NMR signals of ^{133}Cs in the CsMnCl_3 single crystal, of size approximately $3 \times 3 \times 3$ mm, were measured using a Bruker MSL 200 FT NMR spectrometer at KBSC. The static magnetic field strength was 4.7 T and the central RF frequency was set at $\omega_0/2\pi = 26.2479$ MHz. The free induction decay of ^{133}Cs NMR was obtained with one pulse sequence, 512 scans and a repetition time of 1 s. A pulse length of $6 \mu\text{s}$ corresponding to a 90° pulse and a ring-down delay time of $10 \mu\text{s}$ were applied in order to remove the after-pulse effect and to adjust the phase of the signals.

4. Experimental results and analysis

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

$$H = H_Z + H_Q \quad (1)$$

where H_Z is the Zeeman term and H_Q describes the nuclear electric quadrupole interaction of the ^{133}Cs nucleus, which has a nuclear spin $I = \frac{7}{2}$ with 100% natural abundance. The Hamiltonian in the principal axes system of the EFG tensor is given by [11]

$$H = -\gamma\hbar B_0 \cdot (\mathbf{1} + \alpha) \cdot \mathbf{I} + \frac{e^2qQ}{4I(2I-1)} [3I_Z^2 - I(I+1) + \frac{1}{2}\eta(I_+^2 + I_-^2)] \quad (2)$$

where e^2qQ/h and η are the quadrupole coupling constant and the asymmetry parameter, respectively. α is the paramagnetic shift tensor. 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 points with the magnetic field applied along a general direction. All resonance spectra and the parameters are calculated by numerically diagonalizing the 8×8 matrix using a computer program to analyse the experimental data [12].

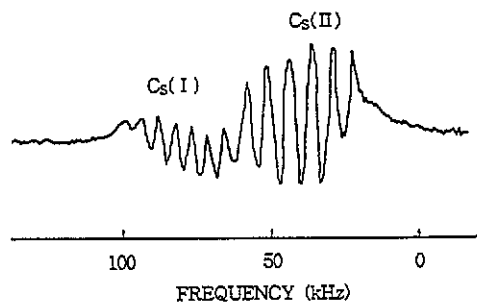


Figure 4. ^{133}Cs NMR spectra at two different Cs sites in the CsMnCl_3 structure. The zero point corresponds to the resonance frequency of 26.3479 MHz of the ^{133}Cs nucleus.

The seven-line structure is a result of the quadrupole interaction of the ^{133}Cs ($I = \frac{7}{2}$) nucleus. However, two different groups of Cs resonances were recorded as shown in figure 4. The zero point in figure 4 corresponds to the resonance frequency 26.2479 MHz of the ^{133}Cs nucleus. They consist of two groups 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 . The signals of these two groups, one weaker and the other stronger, represent the transition of ^{133}Cs NMR lines due to Cs(I) and Cs(II), respectively. The spectra showing an approximate intensity ratio of 1 to 2 are associated with two physically inequivalent positions of caesium atoms in the unit cell.

The rotation pattern of Cs(I), measured in the crystallographic a - c plane at room temperature, is shown in figure 5 by converting the resonance frequency into the resonance magnetic field. The maximum separation resulting from the quadrupole interaction was observed when the magnetic field was applied along the c axis of the crystal. The separations between adjacent 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 a - c plane. There was no angular dependence of Cs(II) in the a - a plane, similar to Cs(I). For both the Cs(I) and the Cs(II) groups, the satellite resonance lines show the angular dependence $3 \cos^2 \theta - 1$, where the polar angle θ is the direction of the magnetic field with respect to the c axis, whereas the central lines are angle independent. Therefore, the EFG tensors of Cs(I) and Cs(II) are both axially symmetric ($\eta = 0$) and the principal Z axis is parallel to the crystallographic c axis. The orientations of the principal axes of the EFG tensors coincide for the Cs(I) and Cs(II) sites.

Two different Cs resonance groups recorded with different magnitudes of the quadrupole splitting and paramagnetic shifts were analysed. Accordingly, the quadrupole parameters were determined by the least-squares fit using the experimental data in figure 5 for Cs(I), and corresponding data for Cs(II), respectively. The quadrupole coupling constants obtained for Cs(I) and Cs(II) are 0.153 ± 0.014 MHz and 0.212 ± 0.014 MHz, respectively. The experimental uncertainty of ± 0.014 MHz was caused mainly by reading the resonance position from the NMR spectra. The parameters analysed are summarized in table 2 together with the previously reported ^{35}Cl NMR.

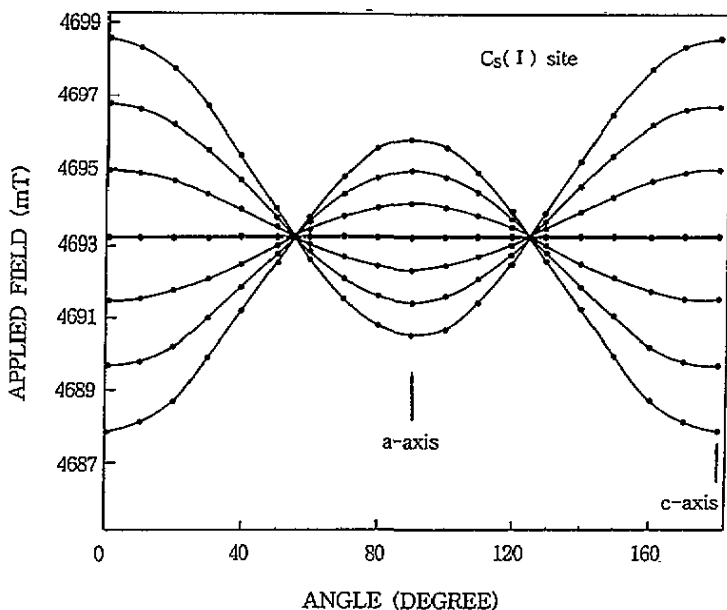


Figure 5. Rotation pattern of Cs(I) NMR measured in the a - c plane at room temperature.

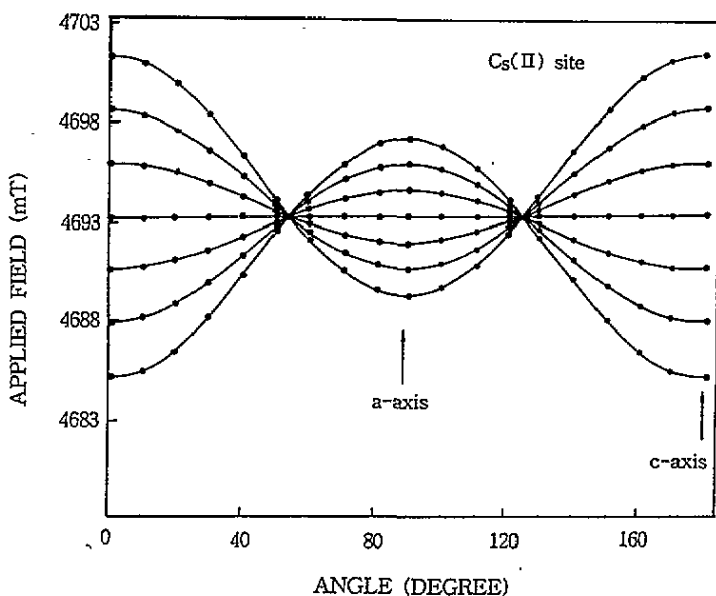


Figure 6. Rotation pattern of Cs(II) NMR measured in the a - c plane at room temperature.

We suggest that the central positions of the resonance points of the Cs(I) and Cs(II) nuclei may be different owing to different contributions of Mn^{2+} ions on the nuclei. The shift of lines from the ^{133}Cs signal obtained with the reference solution is related to the paramagnetic shift due to the Mn^{2+} ions in the CsMnCl_3 crystals.

Table 2. Quadrupole parameters of the NMR for CsMnCl₃ single crystals at room temperature.

Nucleus	e^2qQ/h (MHz)	η	Principal axes	Reference
Cs(I)	0.153 ± 0.014	0	$Z = c$	Present work
Cs(II)	0.212 ± 0.014	0	$Z = c$	
Cl(I)	5.2645 ± 0.0015	0.2683 ± 0.0004		[6]
Cl(II)	9.1835 ± 0.0015	0.0234 ± 0.0004		

5. Discussion and conclusions

The c axis of the CsMnCl₃ crystal has a three-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. Cs(I) and Cs(II) in the unit cell have three and six 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. From the NMR results, Cs(I) and Cs(II) sites are clearly distinguished. While the quadrupole coupling constants of Cs(I) and Cs(II) are 0.153 MHz and 0.212 MHz, respectively, those of Cl(I) and Cl(II) are 5.26 MHz and 9.18 MHz, respectively. Thus, the quadrupole coupling constant of ¹³³Cs nucleus is smaller than that of the ³⁵Cl nucleus in the CsMnCl₃ crystal. This is qualitatively consistent with the longer bond length of Cs–Mn (4.563 Å) than of the shorter Cl–Mn (2.557 Å) bond, even if one considers the difference between the quadrupole moments of ¹³³Cs and ³⁵Cl. Further studies on the temperature dependence near T_C and T_N are currently being conducted using the Cs NMR and Mn EPR technique.

Acknowledgment

The present studies were supported by the Basic Science Research Institute Program, Ministry of Education, 1994, under Project BSRI-94-2410.

References

- [1] Melamud M, Makovsky J and Shaked H 1971 *Phys. Rev. B* **3** 3873
- [2] Kedzie R W, Shane J R, Kestigian M and Croft W J 1965 *J. Appl. Phys.* **36** 1195
- [3] Goodyear J and Kennedy D J 1973 *Acta Crystallogr. B* **29** 744
- [4] Li T I, Stucky G D and McPherson G L 1973 *Acta. Crystallogr. B* **29** 1330
- [5] Andrienko A V and Prozorova L A 1980 *Sov. Phys.-JETP* **51** 1213
- [6] Rinneberg H and Hartmann H 1970 *J. Chem. Phys.* **52** 5814
- [7] Kampli U and Gudel H U 1984 *J. Phys. C: Solid State Phys.* **17** 4041
- [8] Kestigian M, Croft W J and Leipziger F D 1967 *J. Chem. Eng. Data* **12** 97
- [9] Mel'nikova S V, Anistratov A T and Beznosikov B V 1977 *Sov. Phys.-Solid State* **19** 1266
- [10] Jeong S and Haussuhl S 1992 *Z. Kristallogr.* **201** 93
- [11] Abragam A 1961 *The Principles of Nuclear Magnetism* (Oxford: Oxford University Press) ch VII
- [12] Lim A R, Choh S H and Jang M S 1992 *J. Phys.: Condens. Matter* **4** 1607