Temperature Dependence of ^{23}Na NMR in a $NaMnCl_3$ Single Crystal

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(Received 29 April 1995, in final form 30 June 1995)

The temperature dependence of ^{23}Na nuclear magnetic resonance in a $NaMnCl_3$ single crystal grown by the Czochralski method has been investigated by employing a Bruker FT NMR spectrometer operating at 4.7 T. The quadrupole coupling constant of ^{23}Na in $NaMnCl_3$ increases as the temperature increases. The temperature dependence of e^2qQ/h may be fitted with a linear equation of the form $e^2qQ/h = 155 + 0.117\ (T - T_r)$ kHz for the temperature range of 140-380 K.

Ⅰ. Introduction

The crystal structure of sodium manganese chloride, $NaMnCl_3$, is hexagonal with space group $R\bar{3}$ at room temperature[1]. There have been experimental investigations such as x-ray diffraction[2], magnetic phase transition[3] for the $NaMnCl_3$ single crystal grown by the Bridgman method. A magnetic phase transition from the antiferromagnetic to the paramagnetic state occurs in temperature of $T_N = 7.1\ K$[4, 5]. 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[6].

In this paper, we study the temperature dependence of ^{23}Na nuclear magnetic resonance (NMR) in a $NaMnCl_3$ single crystal grown by the Czochralski method. This is a continuation of our NMR work on ^{23}Na at room temperature[7]. The temperature dependence of the quadrupole coupling constant of ^{23}Na ($I = 3/2$) in a $NaMnCl_3$ single crystal has been analyzed by means of experimental data obtained with a pulse NMR spectrometer. This study appears to be the first on temperature dependence of e^2qQ/h of ^{23}Na in $NaMnCl_3$ single crystal.

Ⅱ. Crystal Structure

$NaMnCl_3$ is hexagonal with two formula units per unit cell. The lattice parameters of the hexagonal cell are $a = 6.591$ A and $c = 18.627$ A at room temperature[8]. The structure of $NaMnCl_3$ consists of alternating layers of the Mn^{2+} and Na^+ ions, separated by layers of Cl^- ions. The sodium and manganese ions are surrounded by six chlorine ions located at the corners of slightly distorted octahedra[2]. The chlorine ions are surrounded by two sodium and two manganese ions. The primitive cell of $NaMnCl_3$ contains two sodium ions as shown in figure 1.

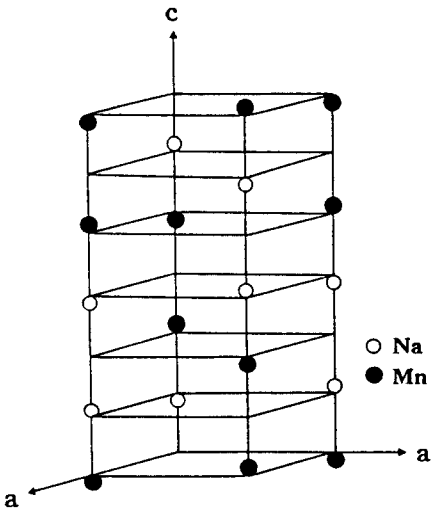

Fig. 1. The hexagonal structure of $NaMnCl_3$.

Ⅲ. Experimental Procedure

The $NaMnCl_3$ single crystals were grown by

melting a mixture of NaCl and $MnCl_2$ powder by the Czochralski method[9]. This was extremely hygroscopic and pink in color. The single crystal of $NaMnCl_3$ had to be kept under paraffin oil in order to avoid decomposition by the moisture absorption. Furthermore, this crystal had to be handled with special care due to easy cleavage along (001). The orientation of the specimen was determined by the x-ray Laue method.

Nuclear magnetic resonance signals of ^{23}Na in the $NaMnCl_3$ single crystal were measured using a Bruker MSL 200 FT NMR spectrometer at KBSC in Seoul Branch. The static magnetic field was 4.7 T and the central rf frequency was set at $\omega_0/2\pi = 52.930$ MHz. The NMR spectra of ^{23}Na were recorded with a sequence of one 90° pulse, 20 scans, and a repetition time of 10 sec. The pulse length of 7 μs was used to remove the effect of the pulse. This pulse sequence is shown in figure 2. NMR measurement method on the temperature dependence are mentioned in the previously paper[10].

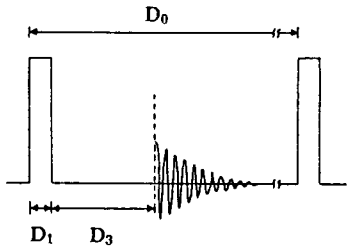

Fig. 2. The pulse sequence. D_1 is the pulse length, D_0 the repetition time, and D_3 the ring-down delay time.

Ⅳ. Experimental Results

In order to examine the temperature dependence of e^2qQ/h for ^{23}Na in the $NaMnCl_3$ single crystal, the resonance spectra were measured at twelve different temperatures in the range of 140-380 K. A typical NMR spectra of ^{23}Na is shown in figure 3, where the signals were obtained with the magnetic field applied along the crystallographic a-axis. The three line structure is a result of the quadrupole interaction of the ^{23}Na ($I = 3/2$) nucleus. It is a Fourier transform of the free-induction decay for the ^{23}Na NMR. The central transition is stronger than the satellite lines, and the separations between adjacent lines are almost equal. The zero point of the X axis in figure 3 corresponds to the resonance frequency 52.930 MHz of the ^{23}Na nucleus obtained with the ^{23}Na line in an acqueous solution of NaCl.

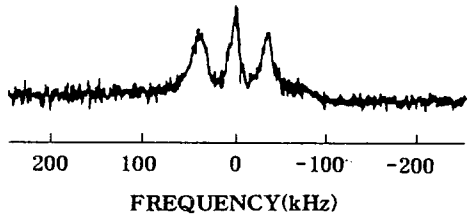

Fig. 3. A typical NMR spectrum of ^{23}Na in a $NaMnCl_3$ single crystal recorded with the pulse NMR spectrometer. The static magnetic field B_0 is parallel to the a-axis. The zero point corresponds to the resonance frequency 52.930 MHz of the ^{23}Na nucleus.

The NMR spectra as a function of temperature were measured in the crystallographic ac-plane for Na site, because the resonance spectra are independent of the direction of magnetic field in the hexagonal(aa-plane) plane. While the central transition stays constant, the splitting between the central and satellite lines is found to increases as the temperature increases.

Ⅴ. Analysis and Discussion

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 ^{23}Na nucleus, which has the nuclear spin $I = 3/2$ with 100 % natural abundance. The Hamiltonian in the principal axes system of the EFG tensor is given by[11]

$$H = -\gamma h B_o \cdot I + e^2qQ\,[3I_z^2 - I(I+1) + {}^1/_2\,\eta(I_+^2 + I_-^2)]\,/4I(2I-1), \qquad (2)$$

where e^2qQ/h and η are the quadrupole coupling constant and the asymmetry parameter, respectively. 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 (2) 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 of 4×4 matrix using a computer program to analyze the experimental data[12].

The nuclear quadrupole coupling constant are determined by the least squares fit using the experimental data. 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[7]. The temperature dependence of e^2qQ/h is shown in figure 4, where the experimental data may be fitted a linear equation of $e^2qQ/h = 155 + 0.117\,(T - T_r)$ kHz representing by the solid line. Here, T (K) and $T_r(K)$ are the temperature and room temperature (300 K), respectively.

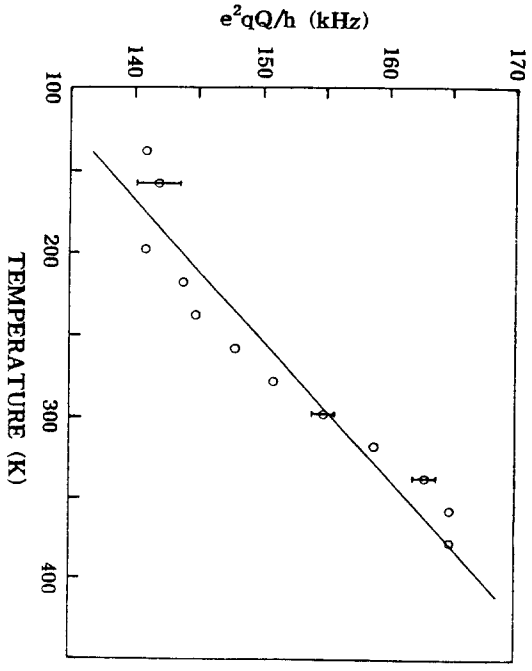

Fig. 4. Temperature dependence of the nuclear quadrupole coupling constant for ^{23}Na in a $NaMnCl_3$ single crystal.

Usually, e^2qQ/h decreases as a function of increasing temperature in many materials ; i. e., the slope of e^2qQ/h vs. temperature is negative[13, 14]. However, the e^2qQ/h of ^{23}Na in $NaMnCl_3$ increases as the temperature increases, in contrast to the general decreasing trend. This trend is similar to the temperature dependence of the ^7Li NMR in $LiNbO_3$ and $LiTaO_3$ single crystals previously reported [15, 16]. The temperature dependence in $NaMnCl_3$ may be explained as follows. It seems that the distance between sodium and the nearest chlorine ions (r) is becoming shorter with increasing temperature. Then, as far as the nearest chlorine ions are concerned, the electric field gradient at the Na nucleus may increase because the EFG is inversely proportional to r^3.

The linear equation for e^2qQ/h as a function of temperature for ^7Li in $LiNbO_3$[15] and ^7Li in $LiTaO_3$[16] is represented by

$$e^2qQ/h = \alpha + \beta\,(T - T_r) \qquad (3)$$

The value of β is 0.014 kHz/K for $LiNbO_3$ and 0.030 kHz/K for $LiTaO_3$. In the temperature range of 140-380 K, the values of α and β for Na in $NaMnCl_3$ single crystal are obtained to be 155 kHz and 0.117 kHz/K, respectively. The value of β for ^{23}Na in $NaMnCl_3$ is found to be much larger than that of ^7Li in $LiNbO_3$ and $LiTaO_3$. They have similar crystal structures ; the space group of $NaMnCl_3$ is $R\bar{3}$, and it is $R3c$ for $LiNbO_3$ and $LiTaO_3$, at room temperature.

Ⅵ. Conclusion

The temperature dependence of the nuclear

quadrupole coupling constant of ^{23}Na in a $NaMnCl_3$ single crystal was measured by employing a pulse NMR spectrometer. The quadrupole coupling constant of ^{23}Na in $NaMnCl_3$ increases as the temperature incrcreases. The obtained nuclear quadrupole coupling constant as a function of temperature could be fitted by a linear equation of $e^2qQ/h = 155 + 0.117\ (T - T_r)\ kHz$ in the temperature range of 140-380 K. This means that there is no apparent phase transition in this temperature range.

Acknowledgement

This work was supported by the Basic Science Research Institute Program, Ministry of Education, 1995, Project No. BSRI-95-2410, and in part by the Korea Science and Engineering Foundation (KOSEF) through the Research Center for Dielectric and Advanced Matter Physics (RCDAMP) at Pusan National University(1994-97).

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$NaMnCl_3$ 단결정에서 ^{23}Na 핵자기공명의 온도 의존성

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(1995년 4월 29일 받음, 1995년 6월 30일 최종수정본 받음)

Czochralski 방법에 의해 성장된 $NaMnCl_3$ 단결정에서 ^{23}Na의 핵자기공명의 온도 의존성이 Bruker FT NMR 분광기를 이용하여 연구하였다. $NaMnCl_3$에서 ^{23}Na의 핵 사중극 결합상수는 온도가 증가함에 따라 증가하였다. 140-380 K의 온도 범위에서 e^2qQ/h의 온도 의존성은 $e^2qQ/h = 155 + 0.117\ (T - T_r)\ kHz$의 직선방정식으로 나타낼 수 있었다.