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Nuclear magnetic resonance of ^{23}Na in an NaMnCl_3 single crystal

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Abstract. The nuclear magnetic resonance of ^{23}Na ($I = \frac{3}{2}$) in an NaMnCl_3 single crystal grown by the Czochralski method has been investigated by employing a Bruker FT NMR spectrometer. From the experimental data, the quadrupole coupling constant $e^2qQ/h = 155 \pm 2$ kHz and asymmetry parameter $\eta = 0$ are determined at room temperature. The principal Z axis of the EFG tensor of the ^{23}Na , the largest component, is parallel to the crystallographic c axis. The temperature dependence of the quadrupole parameters is also investigated in the temperature range of 140–380 K. The quadrupole coupling constant of ^{23}Na is found to be linearly increasing as the temperature increases.

1. Introduction

The crystal structure of sodium manganese chloride (NaMnCl_3) is hexagonal with space group $R\bar{3}$ at room temperature [1]. It has been discovered that NaMnCl_3 is antiferromagnetic, with the Néel temperature $T_N = 7.1$ K [2, 3]. There have been experimental investigations such as x-ray diffraction [4], and investigation of the magnetic phase transition [5] for NaMnCl_3 single crystals grown by the Bridgman method. These crystals have excellent optical quality and have found increasing application in recent years as electro-optic modulators, acousto-optic deflectors, and other devices for controlling laser beams [6].

In this paper, we present the ^{23}Na nuclear magnetic resonance (NMR) in an NaMnCl_3 single crystal grown by the Czochralski method. The quadrupole coupling constant, the asymmetry parameter, and the direction of the principal axes of the electric field gradient (EFG) tensor of ^{23}Na ($I = \frac{3}{2}$) are determined at room temperature. Also, the temperature dependence of the quadrupole coupling constant has been analysed by means of experimental data obtained with a pulse NMR spectrometer. From the literature study of the NQR data base, this is the first ^{23}Na NMR measurement on an NaMnCl_3 single crystal.

2. Crystal structure

NaMnCl_3 is hexagonal with two formula units per unit cell. The lattice parameters of the hexagonal cell are $a = 6.591$ Å and $c = 18.627$ Å at room temperature [7]. The primitive cell of NaMnCl_3 contains two sodium ions as shown in figure 1. The structure of NaMnCl_3

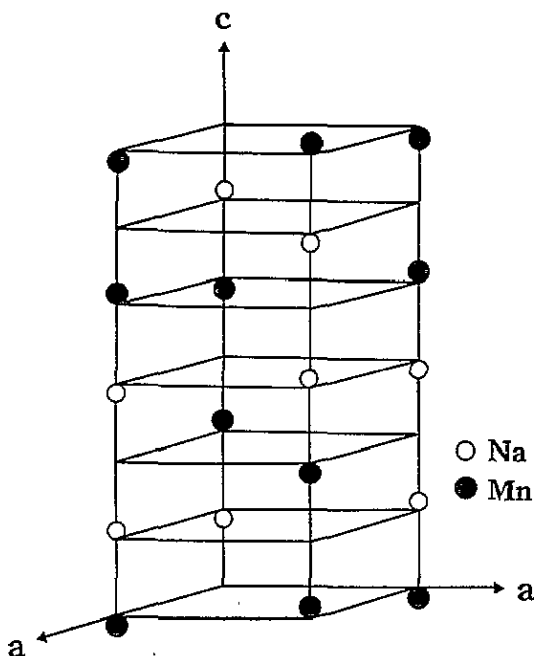


Figure 1. The hexagonal structure of NaMnCl_3 .

is formed by six close-packed layers of composition NaCl_3 in a ABCABC... stacking. Mn cations fill the Cl_6 octahedra between the layers, yielding an arrangement closely related to the perovskite type. Thus, its structure consists of alternating layers of 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 [4] (see figure 2).

3. Experimental procedure

The NaMnCl_3 single crystals were grown by melting a mixture of NaCl and MnCl_2 powder using the Czochralski method [8]. The crystals were extremely hygroscopic and pink in colour. The single crystals of NaMnCl_3 had to be kept under paraffin oil in order to avoid decomposition by moisture absorption. Furthermore, these crystals 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. The angular dependence of the NMR spectra was measured on the crystallographic ac plane because the resonance spectra in the hexagonal aa plane were angle independent.

Nuclear magnetic resonance signals of ^{23}Na in an NaMnCl_3 single crystal, with a size of approximately $3 \times 3 \times 3 \text{ mm}^3$, 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 $\omega_0/2\pi = 52.930 \text{ MHz}$. The NMR spectra of ^{23}Na were recorded with a sequence of one 90° pulse, 20 scans, and a repetition time of 10 s. A ring-down delay time of $7 \mu\text{s}$ was used to remove the effect of the pulse. This pulse sequence is shown in figure 3.

Temperature-dependent NMR measurements were made in the following way. Various temperatures were established by regulating the temperature of the nitrogen gas streaming

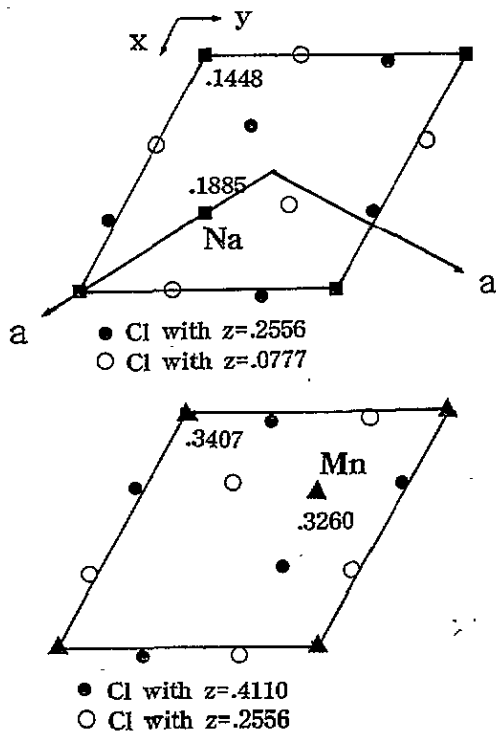


Figure 2. Projection along the *c* axis of the sodium and the manganese layer, respectively, and its nearest chlorine layers.

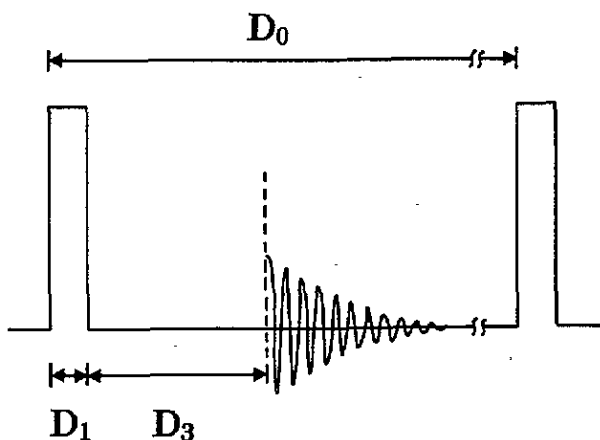


Figure 3. The pulse sequence. D_1 is the pulse length, D_0 the repetition time, and D_3 the ring-down delay time.

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.

4. Experimental results and analysis

The Hamiltonian for 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 ^{23}Na nucleus, which has the nuclear spin $I = \frac{3}{2}$ with 100% natural abundance. From the fact that the spacings between adjacent lines are equal, the first-order perturbation of H_Q with respect to H_Z is sufficient. The asymmetry parameter η is zero because the resonance points are independent of angle in the aa plane. Then, the Hamiltonian in the principal axis system of the EFG tensor is given by [9, 10]

$$H = -\gamma\hbar B_0 \cdot (1 + \alpha) \cdot I + e^2qQ[(3\cos^2\theta - 1)\{3I_z^2 - I(I + 1)\}/2]/4I(2I - 1) \quad (2)$$

where e^2qQ/h is the quadrupole coupling constant and α is the paramagnetic shift tensor. 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 the matrix using a computer program to analyse the experimental data [11].

The three-line structure is a result of the quadrupole interaction of the ^{23}Na ($I = \frac{3}{2}$) nucleus. A typical NMR spectrum of ^{23}Na is shown in figure 4, 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 ^{23}Na NMR. Only one set of NMR spectra of ^{23}Na is obtained even though there are two sodium nuclei per unit cell. This means that the two sites are crystallographically and magnetically equivalent. 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 4 corresponds to the resonance frequency 52.930 MHz of the ^{23}Na nucleus obtained with the ^{23}Na line in an aqueous solution of NaCl. The central signal relates to the crystal displaced to the higher-frequency side (paramagnetic shift) relative to the reference signal.

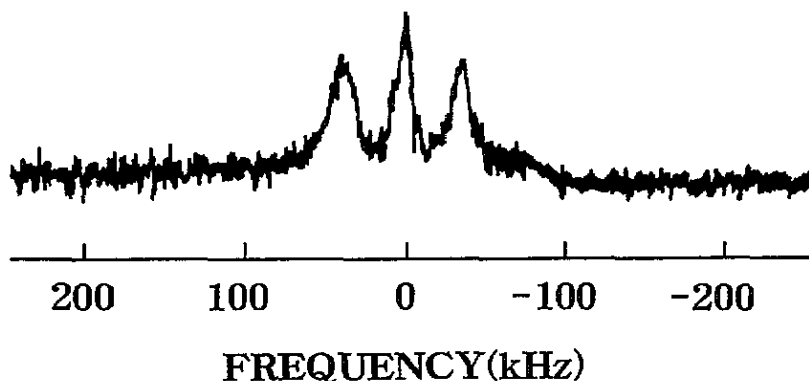


Figure 4. A typical NMR spectrum of ^{23}Na in an NaMnCl_3 crystal recorded with the pulse NMR spectrometer. The static magnetic field B_0 is parallel to the a axis. The zero point corresponds to the resonance frequency 52.930 MHz of the ^{23}Na nucleus.

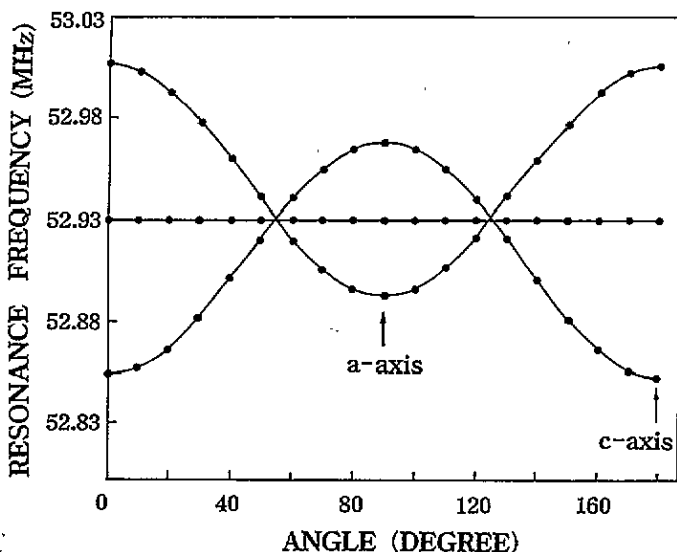


Figure 5. Rotation pattern of ²³Na NMR measured in the *ac* plane at room temperature. The circles are experimental data and the lines are calculations based on the best-fit parameters.

The rotation pattern of Na, measured in the crystallographic *ac* plane at room temperature, is shown in figure 5. The maximum separation resulting from the quadrupole interaction was observed when the magnetic field was applied along the *c* axis of the crystal. The satellite resonance lines show an angular dependence of $3 \cos^2 \theta - 1$, 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. However, the rotation pattern in the *aa* plane is angle independent. Therefore, the electric field gradient tensor of Na is axially symmetric ($\eta = 0$) and the principal *Z* axis is parallel to the crystallographic *c* axis. Accordingly, the quadrupole parameters are determined by least-squares fitting using the experimental data of figure 5; the quadrupole coupling constant is 155 ± 2 kHz at room temperature.

In order to examine the temperature dependence of e^2qQ/h for ²³Na in the NaMnCl₃ single crystal, the resonance spectra were measured at twelve different temperatures in the range of 140–380 K. NMR spectra as a function of temperature were measured only in the crystallographic *ac* plane. While the central transition stays constant, the splitting between the central and satellite lines is found to increase as the temperature increases. The temperature dependence of e^2qQ/h is shown in figure 6, where the experimental data may be fitted with a linear approximation of $e^2qQ/h = 155 + 0.117(T - T_r)$ kHz displayed with the solid line. Here, *T* (K) and *T_r* (K) are the temperature and room temperature (300 K), respectively.

Usually, e^2qQ/h decreases as a function of increasing temperature in many materials; i.e., the slope of e^2qQ/h against temperature is negative [12, 13]. However, the e^2qQ/h of ²³Na in NaMnCl₃ 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 LiNbO₃ and LiTaO₃ single crystals previously reported [14, 15].

The linear equation for e^2qQ/h as a function of temperature for ⁷Li in LiNbO₃ [14] and ⁷Li in LiTaO₃ [15] is represented by

$$e^2qQ/h = \alpha + \beta(T - T_r). \tag{3}$$

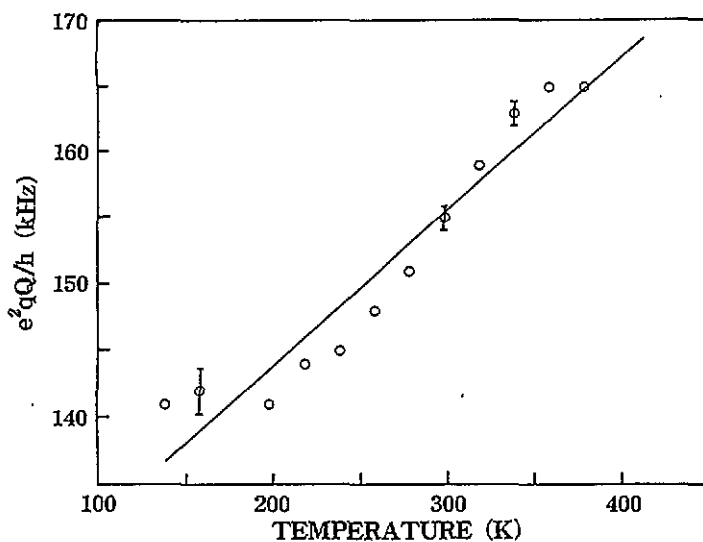


Figure 6. Temperature dependence of the nuclear quadrupole coupling constant for ^{23}Na in an NaMnCl_3 single crystal.

The value of β is 0.014 kHz K^{-1} for LiNbO_3 and 0.030 kHz K^{-1} 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 found to be 155 kHz and 0.117 kHz K^{-1} , 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 $R\bar{3}c$ for LiNbO_3 and LiTaO_3 at room temperature. However, the origin of this fast increasing trend of e^2qQ/h of ^{23}Na in NaMnCl_3 with increasing temperature is not properly understood.

We suggest that the central position of the resonance frequency of the Na nucleus in NaMnCl_3 may be different from the Na signal in an aqueous solution of NaCl due to contributions of Mn^{2+} ions. The shift of lines from the ^{23}Na signal obtained with the reference solution is related to the paramagnetic shift due to the Mn^{2+} ions in the NaMnCl_3 crystal.

5. Discussion and conclusion

The c axis of the NaMnCl_3 crystal has a threefold symmetry. Thus, the EFG tensor of ^{23}Na residing on this axis should be axially symmetric: $V_{XX} = V_{YY}$ and V_{ZZ} should point along the threefold c axis. From the NMR results, the EFG tensor of ^{23}Na is found to be axially symmetric ($\eta = 0$), 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 quadrupole coupling constant of ^{23}Na is 155 kHz at room temperature.

The quadrupole coupling constant of ^{23}Na in NaMnCl_3 increases as the temperature increases. The obtained 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. Further studies on the paramagnetic shift due to the transferred hyperfine interaction as a function of temperature are currently being conducted using Na NMR and magnetic susceptibility measurement.

Acknowledgment

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