



^{87}Rb NMR Quadrupole Coupling Constants and Asymmetry Parameters in RbMnCl_3

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Abstract: The ^{87}Rb quadrupole coupling constants (e^2qQ/h) and the asymmetry parameters (η) in RbMnCl_3 were determined from a nonlinear least-squares fit to the ^{87}Rb NMR powder spectra. The spectra were acquired in the temperature range from 260K to 330K. An important feature in this work is the determination of the quadrupole coupling constants and the asymmetry parameters for two physically nonequivalent Rb sites, Rb(I) and Rb(II), as a function of temperature. In addition, a structural phase transition at room temperature was conformed with the changes in the quadrupole coupling constant and the asymmetry parameter of Rb(II) site.

INTRODUCTION

RbMnCl_3 crystal has ferroelasticity and optical properties.¹ RbMnCl_3 with hexagonal (space group D_{6h}^4) structure at room temperature shows a structural phase transition to monoclinic (space group D_{2h}^2) structure below T_c ($= 272\text{K}$). The phase transition has been found by x-ray diffraction, DSC calorimetry, optical absorption studies, and etc.²⁻⁴ Single-crystal ^{87}Rb NMR spectroscopy was also used to conform the structural phase transition by the measurements of spin-lattice (T_1) and spin-spin (T_2) relaxation times for Rb(I) and Rb(II) sites.⁵

In this work, we present the quadrupole coupling constants and the asymmetry parameters for Rb(I) and Rb(II) sites as a function of the temperature. These results are used to explain the structural phase transition as changes in the electric field gradient tensors at Rb nuclei.

EXPERIMENTAL SECTION

RbMnCl_3 powder supplied by the Dielectric Crystal Bank was synthesized from a mixture of RbCl and MnCl_2 powder according to the method described by S. Jeong.⁶

Solid-state ⁸⁷Rb NMR powder pattern spectra for RbMnCl₃ were obtained at 65.573 MHz on a Varian Unity Inova 200 solid-state NMR spectrometer. over the temperature range of 260K–330K. The quadecho pulse sequence , 90_x-t₁-90_y-t₂-acq, was used;. The 90° ⁸⁷Rb pulse length was 0.8μs. The delays, t₁ and t₂, were 70μs and 16μs, respectively. The relaxation delay of 0.5s was used. Each spectrum was acquired from 8,000 to 10,000 free induction decays and an exponential line-broadening factor of 2,000Hz was applied. The ⁸⁷Rb NMR chemical shifts are referenced through external 1.0M aqueous solution of RbCl at 0ppm.

RESULTS AND DISCUSSION

Shown in Fig. 1 are the calculated ⁸⁷Rb NMR powder patterns at 4.7 T representing the characteristic line shapes for symmetric($\eta = 0$) and asymmetric($\eta = 1$) elec-

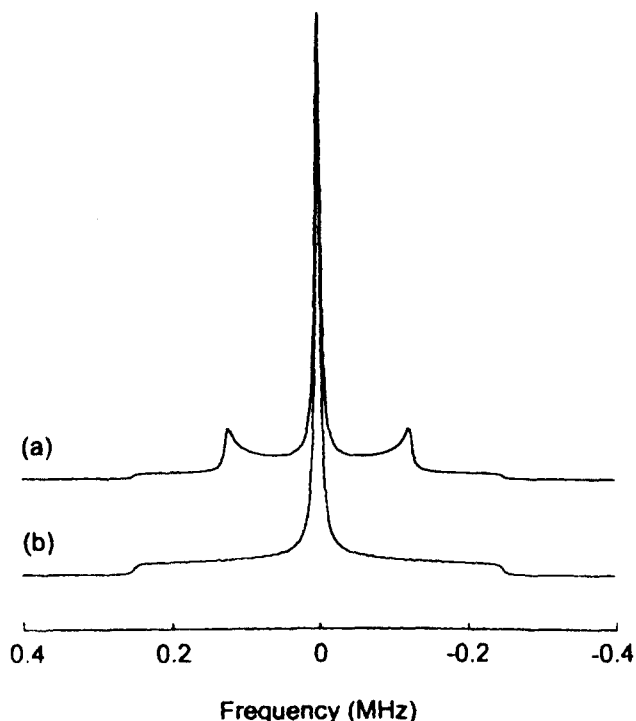


Fig. 1. Calculated ⁸⁷Rb NMR powder patterns for $e^2qQ/h = 0.5$ MHz with (a) symmetric($\eta = 0$) and (b) asymmetric($\eta = 1$) electric field gradient.

tric field gradients at ^{87}Rb nuclei, respectively. The calculations are based on the solution of the Zeeman and quadrupolar Hamiltonian. The solid-state NMR spectrum for quadrupole nucleus determined by the two measurable parameters, the quadrupole coupling constant (e^2qQ/h) and the asymmetry parameter (η), which describe the principal elements of the electric field gradient tensor.⁷ Important parameters used in these calculations are: $e^2qQ/h = 0.5$ MHz and $\eta = 0$ and 1. The calculations include the central ($+1/2 \leftrightarrow -1/2$) and two satellites ($+3/2 \leftrightarrow 1/2$, $-1/2 \leftrightarrow -3/2$) transitions.

Fig. 2 shows the experimental ^{87}Rb NMR powder patterns obtained at 260K, room temperature, and 330K for RbMnCl_3 and the best calculated fits. The fits are composed of two components, which implies the existence of two physically nonequivalent Rb sites, Rb(I) and Rb(II). According to the x-ray diffraction study at room temperature, RbMnCl_3 has hexagonal structure with two Rb(I) at the edges and four Rb(II) inside in the unit cell.⁸ Based on the relative peak intensity in ^{87}Rb NMR spectrum, Rb(I) and Rb(II) sites are assigned to upfield and downfield peak, respectively.

The Levenberg-Marquardt nonlinear least-squares algorithm⁹ was used in program to fit an experimental spectrum with a calculated line shape. The important fitting parameters include the ^{87}Rb NMR quadrupole coupling constant, the asymmetry parameter, and the relative peak intensity between Rb(I) and Rb(II) sites. The values of fitting parameters at 260K, room temperature, and 330K and previously reported values^{10,11} are listed in Table 1.

The interpretation of the ^{87}Rb quadrupole coupling constants and the asymmetry parameters for RbMnCl_3 provides three important aspects. First, we found that two physically nonequivalent Rb(I) and Rb(II) sites show the different magnitude and the shape of the electric field gradient at Rb nuclei. And, at room temperature, the quadrupole coupling constants and the asymmetry parameters are different from the values reported previously. The referenced values were obtained from RbMnCl_3 single crystals.^{10,11}

Second, the quadrupole coupling constants and the asymmetry parameters for Rb(I) site at 260K, room temperature, and 330K are almost the same, but not for Rb(II) site. It means that Rb(I) site is to nearly constant at three temperatures, whereas Rb(II) site is observed to exhibit temperature dependence. From this result we can conclude that a structural change at room temperature is due to Rb(II) site. This result conforms the fact that RbMnCl_3 undergoes a structural phase transition from the monoclinic to the hexagonal structure at T_c ($\approx 272\text{K}$). Herein, the phase transition of room temperature occurs at $\sim 20^\circ\text{C}$ higher than those obtained from various experimental measurements.

Finally, the relative peak intensities Rb(II)/Rb(I) irreversibly change from ~ 2 to ~ 1 at 330K. It implies that there may exist another structural change at 330K, which was not observed yet by experimental measurements. More extensive study for the change in the relative peak intensities is under way to be published.

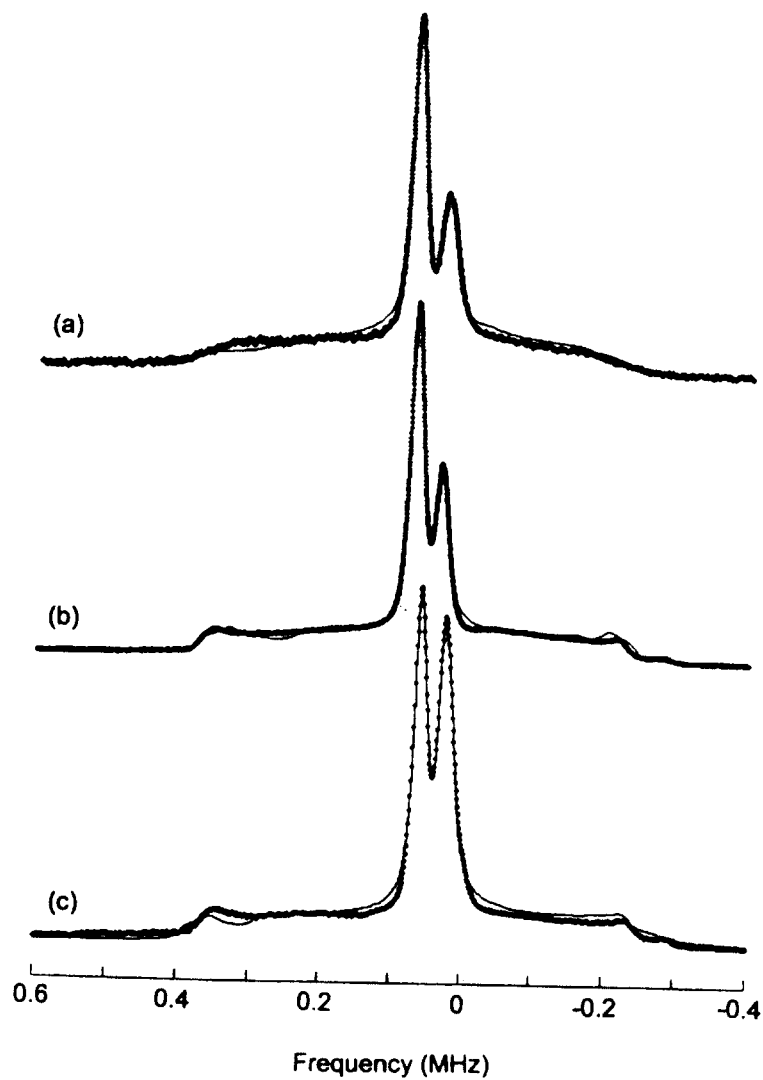


Fig. 2. Solid-state ⁸⁷Rb NMR powder patterns for RbMnCl₃, and the best fitted spectra. The spectra were obtained at (a) 260K, (b) room temperature, and (c) 330K.

Table 1. ^{87}Rb NMR Quadrupole Coupling Constants and the Asymmetry Parameters at 260K, room temperature, and 330K in RbMnCl_3 .

Temp.	Rb(I)		Rb(II)		Rb(II)/Rb(I)
	$e^2qQ/h(\text{MHz})$	η	$e^2qQ/h(\text{MHz})$	η	
260K	0.45(3)	1.0(2)	0.65(2)	1.0(2)	2.25(9)
room T.	0.43(4)	0.9(2)	1.16(9)	0.07(1)	2.00(7)
330K	0.52(2)	1.0(2)	1.27(2)	0.08(2)	1.06(5)

Temp.	Rb		ref.
	$e^2qQ/h(\text{MHz})$	η	
room T.	7.23(1)	0.30(2)	9
	1.2	0	10

CONCLUSIONS

^{87}Rb quadrupole coupling constants and the asymmetry parameters for Rb(I) and Rb(II) sites in RbMnCl_3 were determined from the nonlinear least-squares fit to the NMR powder patterns as a function of temperature. The result implies that the structural phase transition at room temperature occurs with the change in electric field gradient at Rb(II) site. In addition, an irreversible structural change at 310K does not accompany the change in quadrupole interaction but the relative peak intensity between two Rb sites.

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