

# Study of Structural Phase Transitions in $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$ by Means of Single Crystal $^2\text{H}$ NMR

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The temperature and angular dependences of  $^2\text{H}$  NMR spectra were measured for single crystal of  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$ . At 283 K,  $(e^2Qq/h, \eta)$  of  $^2\text{H}$ , averaged by fast  $180^\circ$  flip of water molecules, were obtained as (128 kHz, 0.72), (123 kHz, 0.82) and (106 kHz, 0.80), corresponding to three unequal water molecules in  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ . At 338 K,  $(e^2Qq/h, \eta)$  averaged further by the fast reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis was obtained as (57 kHz, 0.01). In phase II, the jumping rate for the reorientation ( $k$ ) and the amplitude of the rotational modulation ( $\Delta\alpha$ ) of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  about the  $C_3$  axis were obtained from the simulation of  $^2\text{H}$  NMR spectra. The jumping rate at infinite temperature and the activation energy were estimated from the temperature dependence of  $k$  as  $k_0 = 9 \times 10^{17} \text{ s}^{-1}$  and  $E_a = 78 \text{ kJmol}^{-1}$ , respectively. The II-III phase transition was found to be related with the freeze of this motion.

**Key words:** Nuclear Quadrupole Interaction;  $^2\text{H}$  NMR; Incommensurate Phase; Rotational Modulation; Molecular Dynamics.

## Introduction

Most of the  $[\text{M}(\text{H}_2\text{O})_6][\text{SiF}_6]$  type crystals undergo structural phase transitions due to the orientational order-disorder of  $[\text{M}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{SiF}_6]^{2-}$  [1 - 11]. In particular,  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$  is known to exhibit successive phase transitions and to have five stable phases [1]. Denoting these phases as I, II, ..., V in order of decreasing temperature, phase II is an incommensurate phase. The crystal structure in phases II and IV has been investigated by diffraction methods [2 - 5]. The space group of phase IV is  $P2_1/c$  with  $Z = 2$ . The structure of phase II was specified as an arrangement of domains of different octahedra orientation with overall space group  $P\bar{3}$ , although an analysis based on a modulated structure was not performed. The modulated structure was found by ESR spectroscopy to be a vibrational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  expressed by a plane-wave nearly along the  $C_3$  axis [1]. A further transition at 343 K was observed in the incommensurate phase [1, 7 - 9].

This transition changed a modulational amplitude discontinuously. Recently we have studied the motion of  $\text{H}_2\text{O}$ ,  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  and  $[\text{SiF}_6]^{2-}$  by spectra and  $T_1$  of  $^1\text{H}$  and  $^{19}\text{F}$  NMR in the powder sample [9]. The phase transitions were found to be closely related with the motion of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ . However, information about the modulated structure was not obtained and is considered to be an acquired in an orientational sample. In the present work,  $^2\text{H}$  NMR spectra in a single crystal were measured to study the static and dynamic structures of  $\text{H}_2\text{O}$  and  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  in detail. The principal components and the direction cosines of the nuclear quadrupole interaction were obtained at 283 K (phase IV) and 338 K (phase II) from the angular dependence of the  $^2\text{H}$  NMR quadrupole splitting. From the spectral simulation in phase II, the rotational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  was shown to exist, and the jumping rate of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  was estimated. Moreover, the correlation between this motion and II-III transition was obtained.

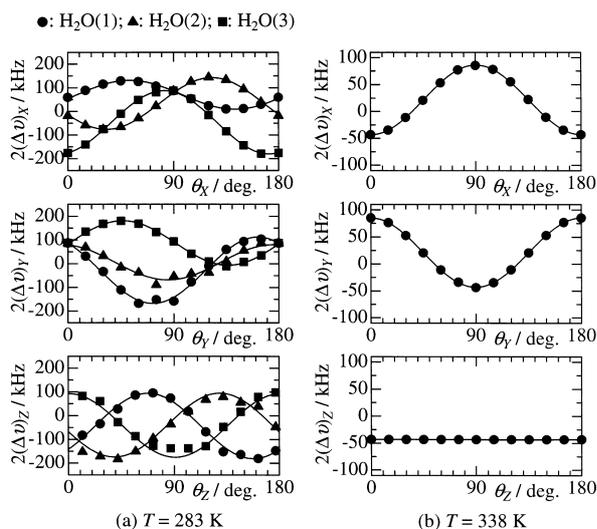


Fig. 1. Angular dependences of the  $^2\text{H}$  NMR quadrupole splitting,  $2(\Delta\nu)$ , around the  $X$ ,  $Y$ , and  $Z$  axes in  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$ . (a) and (b) show  $2(\Delta\nu)$  at 283 K (phase IV) and 338 K (phase II), respectively. The solid lines show the theoretical curves.

## Experimental

The deuterated sample was obtained by repeated recrystallization from heavy water. A single crystal of a transparent white prism elongated along the  $C_3$  axis was obtained. It was found that the crystal  $Z$  axis is along the  $C_3$  axis and the  $X$  and  $Y$  axes are perpendicular to the  $Z$  axis. The  $^2\text{H}$  NMR spectra were measured by a CMX-300 spectrometer at 45.826 MHz. The sample was mounted on an uniaxial goniometer so as to allow rotation about a chosen axis perpendicular to the external magnetic field. A quadrupole echo sequence ( $90_x^\circ - \tau - 90_y^\circ - \tau - \text{acq}$ ) was used. The  $90^\circ$  pulse width and  $\tau$  were 3.0 and 20  $\mu\text{s}$ , respectively.

## Results and Discussion

Figure 1(a) shows the angular dependences of the  $^2\text{H}$  NMR quadrupole splitting,  $2(\Delta\nu)$ , around the crystal  $X$ ,  $Y$ , and  $Z$  axes at 283 K (phase IV). Three  $2(\Delta\nu)$  which can be attributed to three unequal water molecules in  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  were observed for each rotation. It is found that the electric field gradient (EFG) tensors for two deuterons in a water molecule are averaged by the fast  $180^\circ$  flip of  $\text{H}_2\text{O}$  resulting in the same tensors [9, 12] and that inversion symmetry exists for  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  at this temperature [2]. The

Table 1. The principal components and the direction cosines of the EFG tensors of deuterons in  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$ .

$T / \text{K}$	$ e^2Qq_{ii} /h^{-1}$ / kHz	- Direction cosines -			
		$X$	$Y$	$Z$	
283	$\text{H}_2\text{O}(1)$	8	-0.0946	0.7270	0.6800
		120	-0.3627	0.6109	-0.7036
		128	-0.9270	-0.3132	0.2059
283	$\text{H}_2\text{O}(2)$	6	-0.5910	-0.4104	0.6943
		118	-0.3734	-0.6237	-0.6866
		124	0.7149	-0.6651	0.2154
283	$\text{H}_2\text{O}(3)$	1	0.6945	-0.1638	0.7005
		121	0.0684	0.9843	0.1622
		122	-0.7162	-0.0647	0.6948
338		29	0.9887	0.1492	-0.0011
		28	-0.1493	0.9887	-0.0053
		57	0.0003	0.0054	0.9999

fitting calculation for the rotation around the  $X$  axis was performed with the equation [13]

$$2(\Delta\nu)_X = \frac{3eQ}{4h} [V_{XX} + (V_{ZZ} - V_{YY}) \cos(2\theta_X) + 2V_{YZ} \sin(2\theta_X)], \quad (1)$$

where  $\theta_X$  is the angle between the  $Y$  axis and the external magnetic field  $B_0$ .  $V_{ij}$  ( $i, j = X, Y, Z$ ) are the components of the EFG tensor in the crystal fixed frame. The equations corresponding to the rotations around the  $Y$  and  $Z$  axis are obtained by cyclic permutation. All  $V_{ij}$  ( $i, j = X, Y, Z$ ) can be obtained by rotation around three orthogonal axes. Table 1 shows the principal values of the quadrupole interaction  $e^2Qq_{ii}/h$  ( $i = x, y, z$ ) and the direction cosines of the principal axes with respect to the crystal axes obtained by the diagonalization of the  $V_{ij}$  tensor. At 283 K, the deuteron quadrupole interaction parameters ( $e^2Qq/h, \eta$ ), averaged by the fast  $180^\circ$  flip of  $\text{H}_2\text{O}$ , were obtained as (128 kHz, 0.87), (124 kHz, 0.89) and (122 kHz, 0.98) for  $\text{H}_2\text{O}(1)$ ,  $\text{H}_2\text{O}(2)$  and  $\text{H}_2\text{O}(3)$ , respectively. Figure 1(b) shows the angular dependences of  $2(\Delta\nu)$  around the  $X$ ,  $Y$  and  $Z$  axes at 338 K (phase II). The  $Z$  axis is parallel to the  $C_3$  axis of the crystal in this phase. At this temperature only one  $2(\Delta\nu)$ , corresponding to the EFG tensor averaged further by the fast reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis, was observed for rotation about each crystal axis.  $e^2Qq_{ii}/h$  ( $i = x, y, z$ ) and the direction cosines with respect to the crystal axes at 338 K are also shown in Table 1. The EFG tensor, averaged

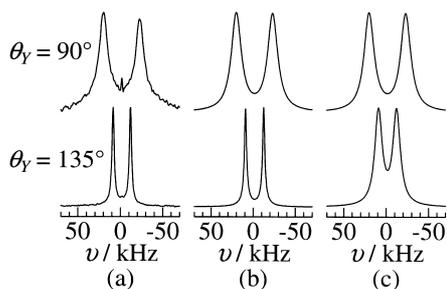


Fig. 2.  $^2\text{H}$  NMR spectra of  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$  at  $\theta_Y$  of  $90^\circ$  and  $135^\circ$ . (a) shows the observed spectra at 338 K. (b) and (c) show the simulated spectra with  $k = 7.7 \times 10^5 \text{ s}^{-1}$ . (b) takes account of the modulated structure ( $\Delta\alpha = 23^\circ$ ), but (c) does not ( $\Delta\alpha = 0^\circ$ ). All the spectra are normalized.

by the fast reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis, is axially symmetric ( $\eta_{\text{re}} = 0$ ) and has its principal  $z$  axis along the  $C_3$  axis [12, 14]. The quadrupole coupling constant  $e^2Qq_{\text{re}}/h$ , averaged by this reorientation is given by

$$\frac{e^2Qq_{\text{re}}}{h} = \frac{1}{2} \frac{e^2Qq}{h} (3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2\gamma), \quad (2)$$

where  $(e^2Qq/h, \eta)$  are the parameters of the non-averaged tensor.  $(\alpha, \beta, \gamma)$  are the Euler angles for the transformation from the molecular axes to the principal axes system of the non-averaged quadrupole tensor. Assuming that the molecular axes coincide with the crystal axes in phase IV and using  $(e^2Qq/h, \eta) = (128 \text{ kHz}, 0.87)$  and  $(\beta, \gamma) = (78.1^\circ, 226.0^\circ)$ , estimated from EFG tensor of the deuterons of  $\text{H}_2\text{O}(1)$  obtained at 283 K,  $e^2Qq_{\text{re}}/h$  was calculated as 58 kHz.  $(e^2Qq_{\text{re}}/h, \eta_{\text{re}})$  obtained at 338 K was (57 kHz, 0.01), and the principal  $z$  axis of the EFG tensor almost coincided with the  $C_3$  axis. Since the experimental results agreed with the theoretical prediction, the principal components and the direction cosines obtained at 283 and 383 K are considered to be reasonable.

Figure 2(a) shows  $^2\text{H}$  NMR spectra observed at 338 K. The simulation of the spectra in phase II was performed by considering the three-site jump of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  in the presence of the rotational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  ions along the  $C_3$  axis, as shown in Figure 3. The site frequency  $\omega_i$  is written by the second-order Wigner rotation matrix  $D_{nm}^{(2)*}(\Omega)$  as [9 - 11, 15 - 18]

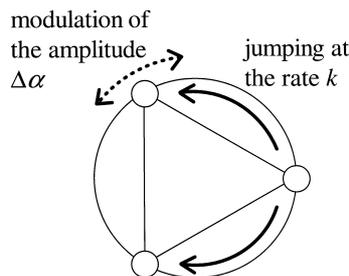


Fig. 3. Three-site jumping and rotational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  about the  $C_3$  axis. Three small circles show the water molecules on the top face of the  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  octahedron. The solid arrows show the possible jumps from a site. The dotted arrow shows the modulation expressed by (5).

$$\omega_i = \sqrt{\frac{3}{2}} \sum_{n,m=-2}^2 D_{0n}^{(2)*}(\psi, \theta, \phi) D_{nm}^{(2)*}(\alpha, \beta, \gamma) T_m^{(2)}, \quad (3)$$

$$T_0^{(2)} = \sqrt{\frac{3}{8}} \frac{e^2Qq}{\hbar}, \quad T_{\pm 2}^{(2)} = \frac{\eta e^2Qq}{4 \hbar}, \quad (4)$$

where  $(\psi, \theta, \phi)$  are the Euler angles for the transformation from the laboratory axes to the molecular axes. The rotational phase modulation can be given as [19 - 21]

$$\alpha = \alpha_0 + \Delta\alpha \cos \zeta(x) = \alpha_0 + \Delta\alpha \cos \zeta, \quad (5)$$

where  $\alpha_0$  is the initial phase.  $\Delta\alpha$  and  $\zeta(x)$  are the amplitude and the phase angle of the rotational modulation of the  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  ions.  $x$  is the coordinate along the modulation axis. A plane-wave modulation was assumed for  $\zeta(x)$  in the last step of (5). The values  $(e^2Qq/h, \eta) = (128 \text{ kHz}, 0.87)$  and  $(\beta, \gamma) = (78.1^\circ, 226.0^\circ)$  were used again. The frequencies of the three sites in the absence of the modulation were specified by  $\alpha_0 = 50^\circ, 170^\circ$  and  $290^\circ$ .  $(\theta, \phi)$  is  $(180^\circ, 90^\circ)$  and  $(180^\circ, 45^\circ)$  for  $\theta_Y$  of  $90^\circ$  and  $135^\circ$ , respectively. The quadrupole echo signal  $G(t, \zeta)$  is written as [9, 17, 18]

$$G(t, \zeta) = \mathbf{P} \cdot \exp[\hat{\mathbf{A}}t] \exp(\hat{\mathbf{A}}\tau) \exp(\hat{\mathbf{A}}^*\tau) \cdot \mathbf{1}, \quad (6)$$

$$\hat{\mathbf{A}} = \begin{pmatrix} i\omega_1 - 2k & k & k \\ k & i\omega_2 - 2k & k \\ k & k & i\omega_3 - 2k \end{pmatrix}. \quad (7)$$

Here,  $\mathbf{1}$  is a vector written by  $\mathbf{1} = (1, 1, 1)$ . A vector of site population was assumed as  $\mathbf{P} = (1/3, 1/3, 1/3)$ .

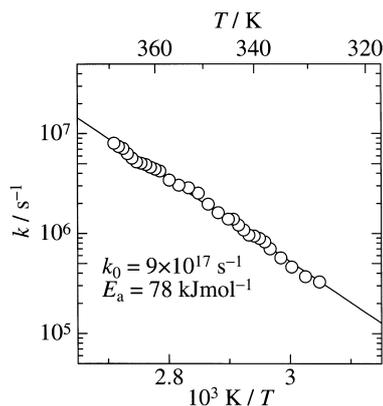


Fig. 4. Temperature dependence of the jumping rate ( $k$ ) for the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  in phase II.

The signal of the sample of the single crystal is given by

$$G(t) = \int_0^{2\pi} G(t, \zeta) d\zeta. \quad (8)$$

The spectrum was obtained by Fourier transform of  $G(t)$ . Figures 2(b) and 2(c) show the calculated spectra. At  $\theta_Y = 90^\circ$  ( $C_3 \perp B_0$ ) we could determine the jumping rate ( $k$ ) for the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis exactly, since the spectra were almost insensitive to the modulated structure. On the other hand, the spectra at  $\theta_Y = 135^\circ$  were sensitive to the modulation. The modulational amplitude ( $\Delta\alpha$ ) could be determined by the simulation of the spectra at  $\theta_Y = 135^\circ$  using  $k$  estimated from the simulation at  $\theta_Y = 90^\circ$ . In our model, the rotational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  influenced on the spectra at  $\theta_Y = 135^\circ$  not to produce the ‘edge singularities’ [19, 20] but to reduce the linewidth. This effect can be explained as follows: The signal for the different orientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  arising from the rotational modulation is added in (8), and the linewidth and the intensity of the spectrum transformed from each signal can be distinct owing to the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ . As a consequence, the resulting spectrum is dominated by the narrower and stronger spectrum if it exists. At 338 K,  $k$  and  $\Delta\alpha$  were estimated as  $7.7 \times 10^5 \text{ s}^{-1}$  and  $23^\circ$ , respectively. The temperature dependence of  $k$ , obtained by the spectral simulation in phase II, is shown in Figure 4. Assuming an Arrhenius relation,  $k$  is given by

$$k = k_0 \exp(-E_a/RT), \quad (9)$$

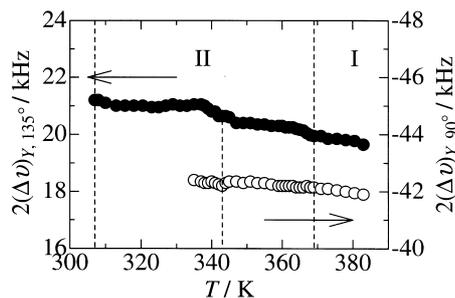


Fig. 5. Temperature dependences of the  $^2\text{H}$  NMR quadrupole splitting,  $2(\Delta\nu)$ , in phases I and II for  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$ .  $\circ$  and  $\bullet$  show  $2(\Delta\nu)$  at  $\theta_Y$  of  $90^\circ$  and  $135^\circ$ , respectively.

where  $k_0$  and  $E_a$  are the jumping rate at infinite temperature and the activation energy for the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis.  $k_0 = 9 \times 10^{17} \text{ s}^{-1}$  and  $E_a = 78 \text{ kJmol}^{-1}$  were obtained by fitting (9) to the temperature dependence of  $k$ . These values in the single crystal are different from those in the powder sample ( $k_0 = 3 \times 10^{15} \text{ s}^{-1}$  and  $E_a = 62 \text{ kJmol}^{-1}$ ), where the spectra were simulated by considering only the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  [9]. We believe that the former is better than the latter, because in this study the spectra were analyzed by separating the effect on the spectral shape of the motion of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  and that of the modulated structure.

Figure 5 shows the temperature dependences of the  $^2\text{H}$  NMR quadrupole splitting,  $2(\Delta\nu)$ , in phases I and II. Entering into phase II on heating, the spectrum changed suddenly. At  $\theta_Y = 90^\circ$  the spectrum was hardly observed below ca. 330 K in phase II because of the exchange broadening due to the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis. This shows that the II-III transition ( $T_c = 307 \text{ K}$ ) is closely related to the freeze of the motion of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ . Above ca. 330 K, the spectrum which consists of two peaks leading to one  $2(\Delta\nu)$  did appear, and motional narrowing occurred with increasing temperature. At  $\theta_Y = 135^\circ$  the peaks of the spectrum were so intense even at low temperatures that we could determine  $2(\Delta\nu)$ . This is because the spectrum at  $\theta_Y = 135^\circ$  is dominated by not only the reorientation but the modulated structure of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ , as described above. A change in  $2(\Delta\nu)$  due to the phase transition was observed at around 343 K. Since the change at  $\theta_Y = 135^\circ$  was larger than that at  $\theta_Y = 90^\circ$ , the transition at 343 K is predicted to be related with the rotational modulation

of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ . A large change in  $2(\Delta\nu)$  due to the I-II transition was not observed. This agrees with the normal-incommensurate transition being of second order.

### Conclusions

We analyzed the  $^2\text{H}$  NMR spectra in single crystal  $[\text{Mg}(\text{H}_2\text{O})_6][\text{SiF}_6]$  and found for the first time

the rotational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  along the  $C_3$  axis in phase II. Taking account of this modulation, the jumping rate for the reorientation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  around the  $C_3$  axis was estimated accurately. The II-III transition was found to be related closely with the freeze of this reorientation. The correlation between the transition at 343 K and the rotational modulation of  $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$  was predicted.

- [1] M. Suhara, T. Bandoh, T. Kitai, T. Kobayashi, and H. Katsuda, *Phase Transitions* **37**, 111 (1992).
- [2] S. Syoyama and K. Osaki, *Acta Cryst.* **B28**, 2626 (1972).
- [3] G. Jehano and F. Varret, *Acta Cryst.* **A31**, 857 (1975).
- [4] G. Chevrier and G. Jehano, *Acta Cryst.* **A35**, 912 (1979).
- [5] G. Chevrier, *J. Solid State Chem.* **99**, 276 (1992).
- [6] A. Kassiba, R. Hrabanski, D. Bonhomme, and A. Hader, *J. Phys.: Condens. Matter* **7**, 3339 (1995).
- [7] A. M. Ziatdinov, V. G. Kuryavyi, and R. L. Davidovich, *Sov. Phys. Solid State* **27**, 1288 (1985).
- [8] A. M. Ziatdinov, V. G. Kuryavyi, and R. L. Davidovich, *Sov. Phys. Solid State* **30**, 1833 (1988).
- [9] J. Kimura, T. Fukase, M. Mizuno, and M. Suhara, *Z. Naturforsch.* **53a**, 453 (1998).
- [10] T. Iijima, M. Mizuno, and M. Suhara, *Z. Naturforsch.* **55a**, 173 (2000).
- [11] M. Mizuno, T. Iijima, and M. Suhara, *J. Phys.: Condens. Matter* **12**, 7261 (2000).
- [12] T. G. Barnes, *Advances in Nuclear Quadrupole Resonance*, vol. 1, (ed. by J. A. S. Smith, Heyden, London 1974, p. 335).
- [13] G. M. Volkoff, *Can. J. Phys.* **31**, 820 (1953).
- [14] K. Schmidt-Rohr, and H. W. Spiess, *Multidimensional Solid-State NMR and Polymers*, (Academic Press: London 1994).
- [15] M. E. Rose, *Elementary Theory of Angular Momentum*, John Wiley, New York 1957).
- [16] R. R. Vold, *Nuclear Magnetic Resonance Probes of Molecular Dynamics*, (ed. by R. Tycko, Kluwer Academic Publishers 1994, p. 27).
- [17] M. S. Greenfield, A. D. Ronemus, R. L. Vold, R. R. Vold, P. D. Ellis, and T. E. Raidy, *J. Magn. Reson.* **72**, 89 (1987).
- [18] M. Mizuno, T. Iijima, K. Orii, and M. Suhara, *Z. Naturforsch.* **55a**, 178 (2000).
- [19] R. Blinc, *Phys. Rep.* **79**, 331 (1981).
- [20] R. Blinc, I. P. Aleksandrova, A. S. Chaves, F. Milia, V. Rutar, J. Seliger, B. Topic, and S. Zumer, *J. Phys. C: Solid State Phys.* **15**, 547 (1982).
- [21] M. Suhara and T. Kobayashi, *Phase Transitions* **27**, 51 (1990).