Deuteron Magnetic Resonance (DMR) – Study on $CD_3NH_3HgCl_3$

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Deuteron magnetic resonance (DMR) spectroscopie was performed on a single crystal of $CD_3NH_3HgCl_3$. The electric field gradient tensors of the independent $CD_3NH_3^+$-groups were determined by quadrupole perturbed NMR. NMR-NQR-rotation patterns were recorded in the ferro- ($T = 295$ K) and paraelectric ($T = 342$ K) phases. In the ferroelectric phase a precessional motion of the $CD_3NH_3^+$-group was detected. The angle $\chi(T)$ between the axis of the molecule and the precession-axis increases with temperature. In the paraelectric phase the precession of methylammonium is superimposed by an anisotropic 90°-flipping motion. The flipping planes are parallel to the polar axis.

Introduction

Monomethylammonium trichloromercurate (II) is ferroelectric at room temperature and undergoes a ferro-/paraelectric phase transition at $T = 334(2)$ K [1]. The crystal structure analysis by X-ray and neutron diffraction [2] revealed trigonal symmetry with space group $P3_2$ and details on the hydrogen positions. The paraelectric phase has monoclinic symmetry (space group C2). The ferroelectric phase is characterized by domains which are related by three twofold pseudoaxes perpendicular to the threefold one. These pseudoaxes invert the direction of the $CH_3NH_3^+$-dipoles in related domains whereas the Hg-Cl-coordination is preserved. In the paraelectric phase, carbon and nitrogen cannot be distinguished due to thermal motion [2].

As these results of the structure determination suggest a correlation between ferroelectricity and the reorientation of the polar $CH_3NH_3^+$-group we decided to examine the structural phase transition by spectroscopic methods.

We report here on the results of a deuteron resonance (DMR)-study. Complementary results of inelastic neutron time of flight scattering (INS) and far infrared (FIR) measurements are reported elsewhere [3].

Experimental

A single crystal of $CD_3NH_3HgCl_3$ with dimensions $4.5 \times 7.5 \times 9.1$ mm was obtained from a solution of a stoichiometric mixture of CD_3NH_3Cl (MERCK) and $HgCl_2$ in methanole. The crystal growth was based on thermal convection and the solubility dependence of a solution exposed to a heat gradient. Pseudocubic faces $(0-11)_{cf}$, $(101)_{cf}$ and $(-111)_{cf}$ are formed. Here the subscript cf denotes the ferroelectric crystal system ($P3_2$).

The measurements have been performed on a pulsed NMR-NQR-spectrometer at the Laboratorium für Festkörperphysik at the ETH Zürich. The spectrometer consists of a 7 Tesla wide bore superconducting magnet (Spectrospin) with a self built gas flow cryostat for a temperature range of 10–400 K. The probe head is equipped for crystal rotation around an axis perpendicular to the external magnetic field B_0, which coincides with the axis of the RF-coil. The crystal was irradiated by 90° RF-pulses in the middle of the deuteron NMR-spectrum at 46.051 MHz. The free induction decay (FID) was recorded and accumulated in quadrature in a two channel 1024 point analyzer.

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Table 1. Relations between magnetic (M) and crystal-directions (Cf = ferro-, Cp = paraelectric System).

M	Cf	Cp
[001]	[0 – 11]	[–20 – 1]
[100]	[2 – 10]	[010]

The sampling time per point was set to 1 μs, which leads to 1 kHz intervals in the frequency space. After appropriate base line and time lag corrections the DMR-spectrum was obtained by a complex Fourier transform of the FID. For the analysis only the power spectrum was used.

In order to obtain the DMR-rotation pattern, the crystal was rotated around its $[0-11]_{cf}$ axis in subsequent steps of 5° between $\beta = 0$ and $\beta = 180°$, where β is the angle of rotation. For each of these orientations the DMR-spectrum was recorded and the corresponding signal positions were used for the rotation patterns, see e.g. Figs. 1 and 4. Rotation patterns were measured for the temperatures $T = 80$ K, 150 K, and 295 K (ferroelectric) and $T = 342$ K (paraelectric). Furthermore, the maximum line splitting was measured for a given orientation ($\beta = 35°$) for various temperatures between 80 K and 342 K.

For the analysis of the rotation patterns one has to introduce three different coordinate systems, the system of the crystallographic axes (C), the system of the magnetic field (M) and the system of the principal electrical field gradient (EFG) tensor axes (E). There are two crystal systems, one for the trigonal ferroelectric phase (Cf) and one for the monoclinic paraelectric phase (Cp). Due to the small deviations of the monoclinic angle $\beta_{cp} = 90.49(5)°$ [2] from orthogonality all transformations between the three systems are simple rotations. The magnetic system (M) is defined by the rotation axis $[001]_M$ and the intersection of the $(001)_M$-plane with the $(001)_{cf}$-plane, which is assigned to be the $[100]_M$-direction. The relation between the magnetic system and the two crystal systems is shown in Table 1.

Theoretical

From pure NQR-spectroscopy [4] only information on the magnitude (eq) and the asymmetry parameter (η) of an electric field gradient (EFG)-tensor can be derived (except for a nucleus with spin $I = 3/2$). In order to obtain the full information, e.g. the orientation of the principal EFG-tensor axes, an external magnetic field B_0 has to be used to remove the degeneracy of the eigenstates of the hamiltonian. Since the corresponding splitting of the transition frequencies is strongly anisotropic, one has to use a single crystal and measure one or two rotation patterns depending on whether the crystal symmetry is high enough. If the complete EFG-tensor is known in crystal coordinates one can determine the site symmetry. A detailed description of the theory is given by Kind [5]. We shall outline here some considerations.

If a nucleus on a general crystal site has a quadrupole moment, any point-symmetry element except an inversion center can be detected in a single rotation pattern. The NMR-NQR-pattern is also invariant against a translation symmetry operation. This rotation pattern depends only on the relative orientation of the EFG-tensor coordinate system "E" to the magnetic field coordinate system "M" and on the sign of rotation. The crystal coordinate system "C" is used to relate the EFG and the magnetic field directions. The hamiltonian for a nuclear spin $I = 1$ may be written

$$H_0 = H_Z + H_Q.$$

H_Z = nuclear Zeeman hamiltonian,
H_Q = nuclear quadrupole hamiltonian,
where H_Z and H_Q are three by three matrices.

The transition frequencies between the NQ-shifted eigenstates can be expressed for the high field case ($H_Z \gg H_Q$) by first order perturbation theory [5]:

$$\begin{aligned} \Delta\nu = &+ \nu_Q/2 \cdot [3\cos^2\alpha \cdot \cos^2(\beta-\beta_0) - 1] \\ &+ \eta[\sin(2\gamma)\ \sin(2\ (\beta-\beta_0)) \cdot \sin\alpha \\ &+ \cos(2\gamma) \cdot \sin^2(\beta-\beta_0) \\ &- \sin^2\alpha \cdot \cos^2(\beta-\beta_0)], \end{aligned} \tag{1}$$

$$\nu_Q(I=1) = 3e^2Q\,q/4h. \tag{1 a}$$

eq = V_{zz} = magnitude of the EFG-tensor,
eQ = nuclear quadrupole moment,
h = Planck's constant.

The angles α, γ, β_0 describe the relative orientation between the E, M, and C coordinate systems.

Time averaging of EFG-tensors

Due to the strong covalent bonding of the deuterons in the CD_3-groups the static NQ-coupling constant of the deuterons does not greatly depend on the crystal lattice in which the groups are embedded, nor on the temperature. For a CD_3NO_2-group the deuteron NQ-constant was measured to be $e^2qQ/h = 173$ kHz with the principal z-axis parallel to the C-D-bond [6]. It is, however, well known that CD_3-groups rotate quickly around the C-N-axis down to very low temperatures. This rotation leads to a single time averaged EFG-tensor with its principal z-axis parallel to the C-N-bond, and an asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz} = 0$. The reduced quadrupole coupling constant is given by

$$\overline{(e^2qQ/h)} = e^2qQ/2h\,(3\cos^2\theta - 1). \qquad (2)$$

With $\theta = 109.5°$ (tetrahedral angle) one obtains $\overline{(e^2qQ/h)} = 57.67$ kHz or $\overline{\nu_Q} = 43.25$ kHz. Any further reduction of this value can be achieved only by additionally superimposed motions of the whole $CD_3NH_3^+$-group. Since the CD_3-rotation is very fast compared to any other superimposed motion, one can treat the above calculated time average like a single EFG-tensor at the carbon site. A possible motion of the $CD_3NH_3^+$ dumb bell is a precession with a temperature dependent opening angle $\chi(T)$. This leads to

$$\overline{\overline{\nu_Q}}(T) = \overline{\nu_Q} \cdot (3/2 \cdot \cos^2\chi(T) - 1/2). \qquad (2\,a)$$

The principal z-axis of the averaged EFG-tensor is pointing along the precession axis, and again we have $\eta = 0$. This direction can be obtained accurately from an NMR-NQR-rotation pattern [5]. Similarly one can calculate $\chi(T)$ from the temperature dependence of $\overline{\overline{\nu_Q}}(T)$.

Another possible motion is a flipping motion around an axis perpendicular to the C-N-bond. In order to obtain the time averaged EFG-tensor of such a motion one has to write down the EFG-tensors of the two stable orientations in the EFG-tensor coordinate system (subscript "E"). Here we use a coordinate system where the flip axis correspond to $[100]_E$ and the bisectrix of the two stable orientations to $[001]_E$, respectively. In this system an EFG-tensor with a given eq and $\eta = 0$ and its principal z-axis in the $(100)_E$-plane is given by

$$\overline{V} = \overline{eq}\begin{pmatrix} -1/2 & 0 & 0 \\ 0 & 1/4 - 3/4 \cdot \cos 2\phi & 3/4 \cdot \sin 2\phi \\ 0 & 3/4 \cdot \sin 2\phi & 1/4 + 3/4 \cdot \cos 2\phi \end{pmatrix}, \qquad (3)$$

where ϕ is the angle between the $[001]_E$-direction and the principal z-axis of the EFG-tensor. The flipping motion can than be described as jumps of the z-axis from $+\phi$ to $-\phi$ and vice versa. This leads to a diagonal EFG-tensor in the time average if the two orientations are equivalent,

$$\overline{\overline{V}} = \overline{eq}\begin{pmatrix} -1/2 & 0 & 0 \\ 0 & 1/4 - 3/4 \cdot \cos 2\phi & 0 \\ 0 & 0 & 1/4 + 3/4 \cdot \cos 2\phi \end{pmatrix}. \qquad (3\,a)$$

The principal axes of this time averaged EFG-tensor are thus identical with the axes of the E-coordinate system. For $35° < \phi < 55°$ the $[100]_E$ direction is the new direction of the principal z-axis, and for $\phi = 45°$ (flipping angle 90°) the asymmetry parameter η becomes zero.

The same result is obtained for a free rotation of the group around the $[100]_E$ direction. An opening angle $\chi = 90°$ in the precession would lead to the same eq and $\eta = 0$, but there the direction of the principal z-axis remains fixed to the precession axis. Thus from a determination of the EFG-tensor axes one can distinguish between these two cases of motion. As we shall see below, both kinds of motion occur in our crystal.

Results

The patterns at $T = 295$ K and $T = 150$ K are similar but the frequency splitting increases for the latter. At $T = 80°$ the number of lines increased remarkably but no detailed evaluation is possible due to the lack of structural information [2]. FIR-measurements [3], however, give some evidence to a possible phase transition at $T = 120$ K.

In the ferroelectric phase at $T = 295$ K the inversion of the domain is obtained through a twofold pseudo-axis perpendicular to the threefold one. Therefore the site symmetry "32" is applied to the DMR-rotation (Fig. 1), which presents a 180° periodicity and a mirror plane at $\beta = 90°$. This latter value leads to $\eta = 0°$, (1). Therefore, (1), orientation angles $\alpha^{(i)}$ and $\beta_0^{(i,j)}$ ($i = 1, 2, 3, j = 1, 2$) must be determined from the rotation pattern. The $i = 1$, 2, or 3 indicate the $CH_3NH_3^+$-groups in the unit cell, and $j = 1$, 2 represent the two oppositely oriented sets of domains. The angles $\alpha^{(i)}$ and $\beta_0^{(i,j)}$ ($i = 1, j = 1, 2$) were first extracted from two sets of DMR-frequencies unambiguously resolved (Figure 1). The frequency split $+\Delta\nu$ has a maximum, (1), at

$$\beta(+\Delta\nu_{\max}) = \beta_0^{(1,1)}$$

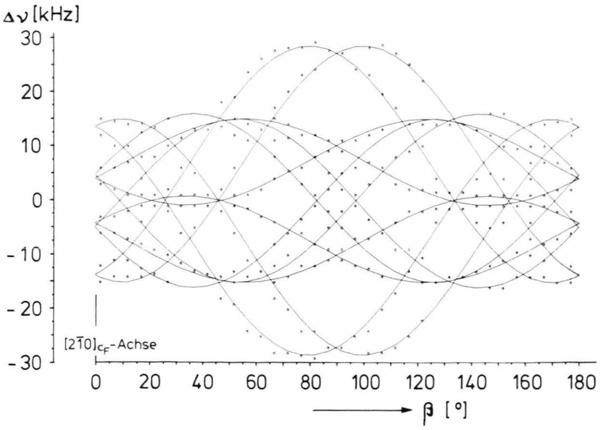

Fig. 1. DMR-rotation pattern of $CD_3NH_3HgCl_3$ at $T = 295$ K.

Table 2. Orientation angles $\alpha^{(i)}$ and $\beta_0^{(i,j)}$ of $\overline{\overline{V_{zz}}}$ of the EFG-tensor, (1), for the DMR-rotation pattern of $CD_3NH_3HgCl_3$ at $T = 295$ K.

i	$\alpha^{(i)}$	$\beta_0^{(i,1)}$	$\beta_0^{(i,2)}$
1	10.5	80.	100.
2	53.3	30.6	149.4
3	33.8	34.5	145.5

and a minimum at

$$\beta(+\Delta\nu_{\min}) = \beta_0^{(1,1)} + \pi/2,$$

The corresponding frequencies allow a determination of $\alpha^{(1)}$, (1),

$$\alpha^{(1)} = \operatorname{arcos}\left\{+\sqrt{(1-\Delta\nu_{\max}/\Delta\nu_{\min})/3}\right\}.$$

The angle $\beta_0^{(1,2)}$ is derived from the application of the pseudo twofold axis to the $\beta_0^{(1,1)}$,

$$\beta_0^{(1,2)} = -\beta_0^{(1,1)}.$$

The pseudo twofold axis appears in the rotation pattern (Fig. 1) at $\beta = 0$. It is therefore recognised as the $[2-10]_{cf}$-axis. The $\alpha^{(i)}$ and $\beta_0^{(i,j)}$ ($i = 2, 3$; $j = 1, 2$) were obtained from the application of the threefold symmetry around the $[001]_{cf}$-direction $\alpha^{(1)}$ and $\beta_0^{(1,j)}$. Table 2 summarizes the calculated angles. The results of the resonance splitting at $\beta = 35°$ revealed different quadrupolar constants $\overline{\overline{\nu_Q}}(T)$ for different temperatures. The frequencies decreased continuously from 120 K up to 333 K. This decrease may be explained by a second time averaging process which is due to a precession of the $CD_3NH_3^+$-group around an average $\overline{C-N}$ direction with increasing precession angle $\chi(T)$ which was calculated by

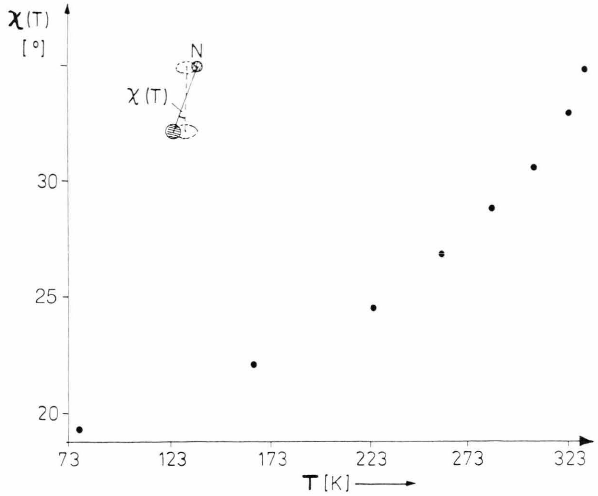

Fig. 2. Precession angle $\chi(T)$ for the $CD_3NH_3^+$-groups in $CD_3NH_3HgCl_3$.

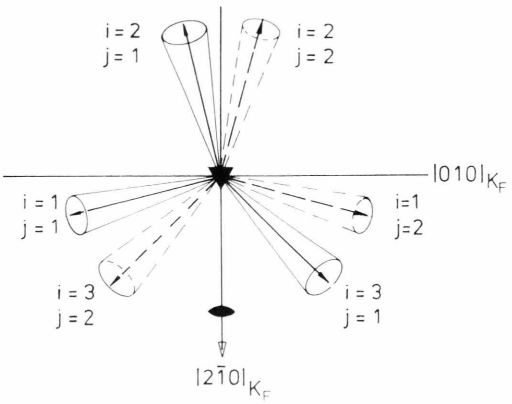

Fig. 3. Averaged $\overline{\overline{V_{zz}}}$-directions of the EFG-tensors of the $CD_3NH_3^+$-groups in $CD_3NH_3HgCl_3$ at $T = 295$ K, projected on the $(001)_{cf}$-plane (precession cones are indicated). —— projection from $[001]_{cf}$, – – – projection from $[00\text{-}1]_{cf}$.

$$\overline{\overline{\nu_Q}}(T) = \overline{\nu_Q}(CD_3)/2 \cdot (3\cos^2\chi(T) - 1)$$

with $\overline{\nu_Q}(CD_3) = 43.25$ kHz.

The temperature dependence of the precession angle is shown in Figure 2.

The $\overline{\overline{V_{zz}}}$-directions of the six different EFG-tensors derived from $\alpha^{(i)}$, $\beta_0^{(i,j)}$ ($i = 1, 2, 3$; $j = 1, 2$) at $T = 295$ K (Table 2) are shown in Figure 3. The full and dashed

Table 3. Orientation angles of $\overline{\overline{V}}_{zz}$ of the EFG-tensor of $CD_3NH_3^+$ in $CD_3NH_3HgCl_3$ at $T = 342$ K.

i	$\alpha^{(i)}$	$\beta_0^{(i,1)}$	$\beta_0^{(i,2)}$
1/fl	23.	8.	172.
2/fl	51.	63.	117.
3/fl	37.	30.	150.
2/st	16.	0.	180.

Table 4. Deuteron-quadrupolar constant $\overline{\overline{\nu_Q}}$ for the $CD_3NH_3^+$-group in $CD_3NH_3HgCl_3$ at different temperatures.

T(K)	$\overline{\overline{\nu_Q}}$ (kHz)	Motional state
120	37	precession around the C–N-axis (precession angle $\chi(T = 120\ \text{K}) = 22^\circ$)
295	30	precession around the C–N-axis (precession angle $\chi(T = 295\ \text{K}) = 30^\circ$)
342	14	90°-flipping in its plane with the polar $[001]_{cf}$-axis + (for the quasistatic group) precession around the C–N-axis (precession angle $\chi(T = 342\ \text{K}) = 43^\circ$)

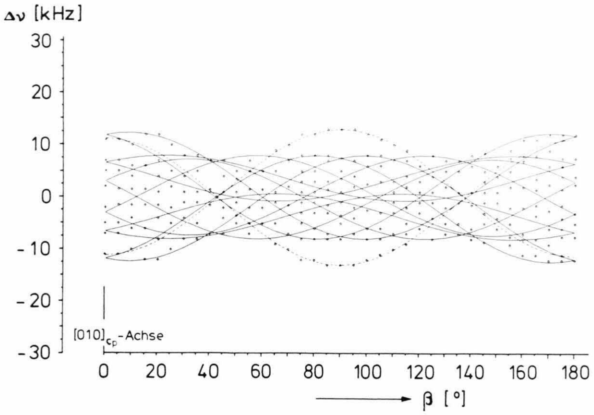

Fig. 4. DMR-rotation pattern of $CD_3NH_3HgCl_3$ at $T = 342$ K.

lines represent the two ferroelectric domains related by the twofold $[2\text{–}10]_{cf}$-axis. The cones describe the precessions of the whole $CD_3NH_3^+$-groups at room temperature. The screw symmetry of the $CD_3NH_3^+$-groups could not be detected due to the translational invariance of the DMR-frequencies.

For $T = 333$ K a remarkable change in the frequency splitting was observed. The DMR-rotation pattern for the paraelectric phase at $T = 342$ K (symmetry C2) is given in Figure 4. The discontinuous reduction of $\overline{\overline{\nu_Q}}$ at the phase transition temperature $T_c = 334(2)$ K and the absence of an asymmetry ($\eta(T = 342\ \text{K}) = 0$) may only be explained by a 90°-flipping motion of the whole $CD_3NH_3^+$-group. This assumption is supported by the results of the structure determination [2] and the inelastic neutron scattering [3], which revealed that $CD_3NH_3^+$ exhibits a motion about an axis perpendicular to C–N. The angle between the averaged $\overline{\text{C–N}}$-direction in the ferroelectric phase [2] and the $[001]_{cf}$-(respectively $[00\text{-}1]_{cf}$) direction is about 45° for every $CD_3NH_3^+$-group.

The orientation angles of the time averaged $\overline{\overline{V}}_{zz}$-directions according to the flipping motion $\alpha^{(i/\mathrm{fl})}$ and $\beta_0^{(i/\mathrm{fl},j)}$ (i/fl = 1, 2, 3; $j = 1$) are calculated from the EFG-tensor directions of the ferroelectric phase (Figure 3). This terminates the flipping plane for every $CD_3NH_3^+$-group in between its N–C- and the $[001]_{cf}$-direction. The orientation angles are used to fit the full lines in Fig. 4 to the measured resonance frequencies (dots). The quadrupolar constant $\overline{\overline{\nu_Q}}$ represents the fit parameter.

The dashed lines describe the quasistatic groups i/st, $i = 2$ with $\beta_0^{(2/\mathrm{st},2)} = \beta_0^{(2/\mathrm{st},2)} = \pi$. These groups have a preferred orientation between flipping and precession motion which is long enough to produce an NQR-splitting for both motional states. The orientation angles of the time averaged $\overline{\overline{V}}_{zz}$-directions of these two groups according to the precession motion are described by $\alpha^{(2/\mathrm{st})}$ and $\beta_0^{(2/\mathrm{st},j)}$ ($j = 1, 2$) (Table 3), which are calculated from N–C positions of the X-ray structure determination of the paraelectric phase [2]. The fit parameter $\overline{\overline{\nu_Q}}(2/\mathrm{st})$ leads to a precession angle of $\chi(2/\mathrm{st}) = 43^\circ$ for the $CD_3NH_3^+$-group in the quasistatic orientation. The rotation pattern confirms the twofold symmetry of the paraelectric phase around the $[010]_{cp}$-direction (Table 1).

Discussion and Summary

The CD_3-group rotates around the C–N axis in the temperature range $120 < T < 333$ K, resulting in an averaged EFG-tensor for each $CD_3NH_3^+$. The entire group itself has an additional precession of its C–N-axis around an average $\overline{\text{C–N}}$-axis with increasing precession angle $\chi(T)$. At $T = 333$ K the precession angle ($\chi(T = 333\ \text{K}) = 43^\circ$) approaches the angle between the $[001]_{cf}$- and the averaged C–N-direction (45°) [2].

Thus the precession turns over into a 90°-flipping motion in a plane parallel to the polar direction $[001]_{cf}$ of the ferroelectric structure. Therefore the charged $CD_3NH_3^+$-groups change their orientation at the ferro-/paraelectric phase transition at $T = 333$ K dynamically, whereas in the ferroelectric phase the methylammonium groups have different directions in opposite domains. This confirms the assumption that the orientation of $CD_3NH_3^+$ is responsible for the ferroelectricity in $CD_3NH_3HgCl_3$.

In the paraelectric phase also a component with precessional motion is still present. This leads to the assumption that the flipping $CD_3NH_3^+$ is not strictly reduced to a smooth plane but undergoes a much more complex motion.

The remarkable shifts in the Hg-Cl-frame, which are detected with X-ray structure determination of the paraelectric phase [2], seem to be introduced by the increased motions of the methylammonium groups.

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