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A nuclear magnetic resonance study of tetramethylammonium cadmium chloride (TMCC)

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Abstract. The structural phase transition at 118 K was investigated in TMACdCl₃ (TMCC) crystals by means of 35 Cl NMR spectroscopy. For a rotation around different crystallographic axes the angular dependencies of 35 Cl NMR spectra are given. The three observed lines and their angular variation show the hexagonal symmetry of the crystal in the room-temperature phase. The principal axes and principal values of the electric field gradient (EFG) tensors have been evaluated for this phase applying the Volkoff formalism. The direction of the largest principal value coincides with the projection of the Cd–Cl bond direction into the (001) plane. Below the phase transition temperature in the ferroelastic phase a splitting of each NMR line into three pairs was observed. The line splitting into three pairs is explained by the loss of the hexagonal symmetry and by the coexistence of three different domains. The three different tensors of the EFG were calculated for the inequivalent chlorine atom positions.

1. Introduction

The crystal of $(CH_3)_4NCdCl_3$ (TMCC) belongs to the large family of compounds of the type $(CH_3)_4NMX_3$ with the bivalent metals M = Mn, Ni, Cd, Cu, V and the halogen atoms X = Cl, Br. Crystals of this family containing transition metals are extensively studied [1–10] because of their magnetic behaviour. This is in particular valid for the compound $(CH_3)_4NMnCl_3$ (usually abbreviated as TMMC) which is well known as a quasi-one-dimensional antiferromagnetic crystal [7–10]. A similar quasi-one-dimensional behaviour is also suggested for the diamagnetic crystal TMCC. In the structure of this crystal one can distinguish infinite linear chains of the type $(-M-Cl_3-M-Cl_3-)$ which are separated by tetramethylammonium (TMA) cations. The ordering of the TMA cations plays a great role in the structural phase transitions.

All compounds of this family undergo structural phase transitions leading to different ordered low-temperature phases, which are expected to be ferroelastic in the case of TMMC and TMCC. A ferroelectric phase was found in the case of $(CH_3)_4NCdBr_3$ (TMCB) [4, 6, 11–13]. The crystals of TMCC possess a hexagonal structure at room temperature with the space group $P6_3/m$ and with Z = 2 formula units per unit cell. TMCC undergoes two structural phase transitions at 118 K and 104 K [2–3, 5, 11, 14, 15]. For the phase below 118 K a symmetry with the space group $P2_1/m$ (Z = 2) was proposed. At a temperature of 115 K the lattice parameters were found to be a = 9.33 Å, b = 8.76 Å, and c = 6.67 Å and 120.5° for the monoclinic angle [11]. A space group $P2_1/b$ with Z = 12 formula units

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was determined for the phase below 104 K. Here the lattice parameters were a = 8.84 Å, b = 18.41 Å and c = 20.0 Å with the same monoclinic angle [11]. Recently, a ferroelastic domain structure was found to appear at 118 K in TMCC. However, the appearance of this domain structure which is observed along the direction perpendicular to the sixfold axis of the room-temperature phase is in contradiction to the symmetry proposed from x-ray measurements ($P2_1/m$, Z = 2) [11]. Neutron diffraction studies [17] on deuterated crystal samples showed some forbidden (001) reflections which are also in contradiction to the symmetry proposed in [11].

The mechanism of the phase transitions is regarded to be of order–disorder type related to the ordering of $[(CH_3)_4N]^+$ cations coupled to the displacive contributions originating from rotations or translations of the MCl₃ chains [11]. Various methods were applied (among them dielectric measurements and ¹H NMR studies) in order to characterize the phase transitions. However, in spite of numerous experimental data, the mechanism of phase transitions and the properties of the crystals are not fully explained, especially there are no data related to the changes of the structure of the linear chains (-M–Cl₃–M–Cl₃–) in the phase below 118 K which might explain the obvious discrepancies inferred from the previous results [11].

To obtain more information about structural changes and other properties near the phase transitions in TMCC, ³⁵Cl NMR investigations on single crystals are carried out. These measurements are known to be very sensitive to small structural and dynamical changes and, thus, they are suitable to probe both local and collective phenomena. Systematic studies will be undertaken to recognize the microscopic properties of the crystal lattice and especially the role of the one-dimensional chains in the phase transition. The first step of our studies is to derive the information on the electric field gradient (EFG) tensors in the room-temperature phase which is of fundamental importance for further studies of the phase transitions. For this purpose it seems to be advantageous to prove the symmetry properties when the single crystal orientations with respect to the external magnetic fields for which small structural changes lead to measurable effects in the ³⁵Cl NMR rotation patterns. In this frame it will be shown that the NMR studies enable detailed conclusions about structural changes below the first phase transition which may answer the questions mentioned above.

2. Experiment

Polycrystalline samples of TMCC were obtained from aqueous solutions containing stoichiometric quantities of $(CH_3)_4NCl$ and $CdCl_2 \cdot 2.5 H_2O$. After recrystallization a saturated solution of TMCC was prepared and a single crystal of this compound was grown at a temperature of 305 K by using the slow-evaporation method. A part of a crystal with good optical quality was used in order to prepare two single-crystal samples for the NMR measurements. They allow rotations around the hexagonal crystallographic axis *c* and around the *a* axis. The ³⁵Cl NMR measurements were run at magnetic fields of 7.05 T and 11.7 T and the corresponding resonance frequencies of 29.4 MHz and 48.99 MHz, respectively, using MSL300 and MSL500 spectrometers (Bruker Analytik GmbH).

3. Results

3.1. Measurements in the high-temperature phase at 300 K

In order to determine the electric field gradient tensors at the chlorine sites in the roomtemperature phase and to prove the crystal structure and the symmetry proposed by Braud et al [11] in this way, ³⁵Cl NMR measurements were performed rotating the single crystals around two different crystallographic axes. These two rotational patterns were sufficient to derive unambiguously the structural information. A typical NMR spectrum is given in figure 1 which shows three central transition lines. Because of the rather large quadrupole coupling constants for the ³⁵Cl nuclei in these crystals (with quadrupole frequencies of about 13 MHz), satellite transitions were not investigated here. The number of the central lines in figure 1 is consistent with the crystal symmetry proposed: at room temperature the crystal possesses two formula units (Z = 2) per unit cell each with six chlorine atoms. Due to the existence of an inversion centre, only three different central lines are to be expected. The angular dependence of rotation around the crystallographic axes a and c are shown in figure 2(a) and 2(b). According to the known structure, a rotation around the hexagonal c axis clearly shows the 60° symmetry in the spectra (figure 2(a)). In the case of the rotation around the *a* axis, for one of the three resonance lines only a slight angular variation is seen which is consistent with the fact that two chlorine atoms are placed close to this axis of rotation. The typical angular dependence in figure 2(b), measured for the other chlorine atoms, clearly proves the 180° symmetry.



Figure 1. Room-temperature 35 Cl NMR spectrum of TMCC showing the three central transition lines (*c* axis perpendicular and *a* axis aligned to the magnetic field).

For the interpretation of the angular dependence an orthogonal crystallographic frame a, b^*, c is introduced where the third orthogonal axis is defined according to $b^* = [c \times a]$. This crystallographic frame is chosen in a way that its origin is placed at the site of a Cd atom. In order to simplify the determination of the EFG tensors at the chlorine sites, a Cartesian crystallographic axis frame (CAF: x, y, z) is applied in such a way that the z axis is parallel to the hexagonal c axis. The x direction of the Cartesian crystallographic axis frame is parallel to the crystallographic a axis.

The elements of the EFG tensor in the CAF may be determined from the angular dependence of the central transitions by means of the well known Volkoff formula [18] in



Figure 2. Angular dependence of quadrupolar splitting of the 35 Cl NMR central lines of TMCC at room temperature: (a) rotation about the *c* axis perpendicular to the magnetic field; (b) rotation about the *a* axis perpendicular to the magnetic field.

second order of the perturbation theory. For a rotation around the c(z) axis the splitting Δv of the central line is given by the following formulae, where the tensor elements V_{ij} refer to the CAF:

$$\begin{split} \Delta \nu &= \frac{1}{\nu_L} [n_z + p_z \cos(2\theta_z) + r_z \sin(2\theta_z) + u_z \cos(4\theta_z) + v_z \sin(4\theta_z)] \\ n_z &= \frac{1}{192} \{ (9V_{zz}^2 - 14[\frac{1}{4}(V_{xx} - V_{yy})^2 + V_{xy}^2] - 8(V_{zy}^2 + V_{zx}^2) \} \\ p_z &= \frac{1}{32} [V_{zz}(V_{xx} - V_{yy}) + 4(V_{zy}^2 - V_{zx}^2)] \\ r_z &= \frac{1}{16} [-V_{zz}V_{xy} + 4V_{zy}V_{zx}] \\ u_z &= \frac{3}{32} [\frac{1}{4}(V_{xx} - V_{yy})^2 - V_{xy}^2] \\ v_z &= \frac{3}{32} (V_{yy} - V_{xx})V_{xy}. \end{split}$$

The angle θ_{τ} will be defined below. In this procedure the fact is taken into account that one principal axis of the EFG tensor should be parallel to the hexagonal axis c(z). Hence, in the CAF the tensor should contain only the non-vanishing values V_{xx} , V_{yy} , V_{zz} and the element V_{xy} . In a rather simple way this allows the determination of the tensor in the principal axis frame (PAF: X, Y, Z) for which one axis is parallel to the z axis of the CAF. Because of the 60° symmetry seen in the spectra for a rotation around the c(z) axis (figure 2(a)), the tensors of the three chlorine atoms should have identical principal elements and deviate only in the elements V_{xy} . The ascription of the crystallographic axes to the angular dependence is better understood if the rotation pattern for the a(x) rotation is inspected (figure 2(b)). From these curves it may be easily seen that all chlorine atoms possess the same line splitting if the crystallographic c(z) axis is oriented parallel to B_0 . Through this position the value $\theta_x = 0$ is defined as the angle between the crystallographic c(z) direction and the direction of B_0 . Because of the 180° symmetry visible from figure 2(b), the orientation c (z) perpendicular to B_0 ($\theta_x = 90^\circ$, $a \perp B_0$, $c \perp B_0$) may be easily determined, which gives us the possibility to assign this special orientation also to figure 2(a) (angle $\theta_z = 90^\circ$ for $a \perp B_0$, $c \perp B_0$) for one of the three chlorine sites (denoted here by $Cl_{(1)}$). Note that the orientation $\theta_z = 90^\circ$ in figure 2(a) slightly deviates from the maximum of the line splitting by an angle of about 6.8° . The maximum corresponds to an orientation where the projection of the Cd–Cl bond direction into the (x, y) plane for this chlorine site is perpendicular to the direction of the field B_0 .

For instance, the EFG tensor for the $Cl_{(1)}$ site in the CAF is given by

$$\mathbf{V} = \begin{bmatrix} 13.18 & 2.52 & 0\\ 2.52 & -7.55 & 0\\ 0 & 0 & -5.63 \end{bmatrix}$$

from which we derive the principal values of the tensor to be $V_{XX} = -7.85$ MHz, $V_{YY} = -5.63$ MHz and $V_{ZZ} = 13.48$ MHz with the usual convention $V_{ZZ} \ge V_{YY} \ge V_{XX}$. In the principal axis frame (PAF: X, Y, Z) of the EFG tensor, the Z axis with the largest principal value is parallel to the projection of the Cd–Cl bond direction into the plane of the Cd atoms and the direction X of the smallest principal value is parallel to the hexagonal axis. In the CAF the matrix of the unit vectors is given by

$$\mathbf{E} = \begin{bmatrix} 0.119 & 0 & 0.993 \\ 0.993 & 0 & -0.119 \\ 0 & 1 & 0 \end{bmatrix}.$$

In agreement with these unit vectors, the Eulerian angles for the transformation from the CAF to the PAF are $\alpha = 6.8^{\circ}$, $\beta = 90^{\circ}$, $\gamma = 90^{\circ}$, from which again the angle of 6.8° results between the projection of the Cd–Cl bond direction for the Cl₍₁₎ sites and the crystallographic a axis (see figure 3). The angle α very well agrees with the results of the x-ray structural analysis [2, 11, 12]. The values for the other angles ($\beta = \gamma = 90^{\circ}$) reflect the fact that the principal axes X, Y, Z have been chosen according to the convention for the elements V_{ii} as introduced above. An analogous assignment is applied for the other chlorine sites (Cl₍₂₎, Cl₍₃₎) where only the changes in the orientation according to the sixfold symmetry around the c axis have to be taken into account. From the crystallographic data [12] one finds that the projection of one of the Cd–Cl₍₁₎ bond directions into the plane of the Cd nuclei perpendicular to the hexagonal axis is given by the unit vector

$$\overrightarrow{\mathrm{Cd-Cl}}_{(1)} = \begin{pmatrix} 0.118\\ 0.993\\ 0 \end{pmatrix}.$$

The same analysis was repeated at a temperature of about 120 K which is about 2 K above the phase transition temperature into the ferroelastic phase. As expected, the same angular dependences appear and the 60° symmetry is again clearly seen. However, the principal values are slightly changed ($V_{XX} = -7.77$ MHz, $V_{YY} = -5.93$ MHz and $V_{ZZ} = 13.70$ MHz) and the three chlorine atoms in the (x, y) plane are rotated around the hexagonal axis c by an angle of about 2°. These changes reflect the usual temperature effects on the quadrupole frequencies which are not of interest for the further discussion.



Figure 3. Projection of the chlorine atoms into the (x, y) plane in the room-temperature phase.

3.2. Measurements in the ferroelastic phase at 113 K

According to a first-order behaviour steplike changes occur in the spectra at the phase transition temperature. As in the high-temperature phase, the rotational patterns were measured rotating the crystals around the crystallographic a and c axes. As seen in the figures 4(a) and 4(b), in both cases the number of lines is increased by a factor of six. For the further discussion it is of great importance that, in principle, the main features



Figure 4. Angular dependence of quadrupolar splitting of the 35 Cl NMR central lines of TMCC at the temperature of 113 K: (a) rotation about the *c* axis perpendicular to the magnetic field; (b) rotation about the *a* axis perpendicular to the magnetic field.

of the rotational patterns are kept. Thus, in the case of the *a* rotation three groups of lines appear which show approximately the same angular dependence as found for the three different types of chlorine $Cl_{(i)}$ (i = 1, 2, 3) in the high-temperature phase. In particular, the behaviour of the chlorine atoms assigned above as chlorine of type $Cl_{(1)}$ allows us in a rather simple way to understand the changes. For this reason it is useful to consider at first the frequency changes for the rotation around the high-temperature *a* axis which shows six different lines. Each line has only a relatively small angular dependence which again reveals that the projections of the Cd–Cl₍₁₎ bond directions into the high-temperature (x, y) plane exhibit small deviations from the crystallographic *a* axis. Obviously, three pairs of lines exist with approximately the same splitting of 4° between each of them. For the further discussion we have to take into account that the inversion centre cannot be lost with this phase transition due to the fact that below 118 K no spontaneous polarization appears. Hence, to each chlorine atom of type $Cl_{(1)}$ another identical one exists which is related by a 180° rotation around the now twofold axis *c* (see figure 4(a)).

Now we have to combine these clear results from the orientationally selective measurements for rotations around the a axis with the spectra run for the c rotation in order to come to an unambiguous interpretation of the results. However, since we are limited to the influence of second-order quadrupole effects on the central lines (due to large value of the quadrupole frequency with V_{ZZ} close to 15 MHz for the different sites), the new tensors in the CAF cannot be derived in a simple analytical way. Thus, the interpretation is performed by a fitting procedure in strong analogy with the treatment for the high-temperature phase as described above.

At first the different pairs of lines obtained in case of a rotation around the crystallographic c axis (defined for the high-temperature phase) were fitted taking into account changes in the tensor elements V_{xx} , V_{yy} , V_{zz} and V_{xy} . This procedure is simplified by the fact that the shift of the angles with respect to the high-temperature phase, at which the maxima and minima in the rotation patterns appear, can be simply used in order to estimate the tilting angles regarding the high-temperature c axes (i.e. from the changes in the off-diagonal elements V_{xy}). Furthermore, the magnitude of the splitting is changed for each pair in a typical way which allows an estimation of the changes in the diagonal tensor elements V_{ii} used for the fitting process. Subsequently, the fitting procedure is extended to the patterns for the rotation around a where again only the NMR lines for the chlorine atoms of type $Cl_{(1)}$ were taken into account at first. Finally, we obtained three pairs of tensors for the $Cl_{(1)}$ atoms in the CAF (x, y, z) which were denoted by K1, K2, L1, L2, M1 and M2 (see the assignment of the curves in figure 4(a) and 4(b)) and which are given in MHz by the elements in table 1.

Tensor	V_{xx}	V_{yy}	V_{zz}	V_{xy}	V_{xz}	V_{yz}
K1	14.64	-8.03	-6.61	2.83	0.38	-0.21
K2	14.92	-8.32	-6.60	1.22	0.36	-0.23
L1	12.83	-7.32	-5.51	5.43	0.32	-0.02
L2	13.49	-7.98	-5.51	3.94	0.32	-0.04
M1	11.67	-7.05	-4.62	4.37	0.38	-0.08
M2	12.24	-7.62	-4.62	2.85	0.43	-0.12
Error	± 0.02					

Table 1. Tensor elements for the six EFG tensors for $Cl_{(1)}$.

The usual procedure then leads to the following principal values, eigenvectors and Eulerian angles with the same conventions as introduced above:

Pair K.

Principal values: [-8.41, -6.58, 14.99] and [-8.41, -6.57, 14.98] matrices of eigenvectors:

	┌ -0.123	0.001	ך 0.992	$\Gamma - 0.054$	-0.009	ך 0.998
$E_{(K1)} =$	0.982	-0.141	0.122	$E_{(K2)} = 0.989$	-0.136	0.052
	L 0.140	0.990	0.016	L 0.136	0.991	0.016

Eulerian angles:

 $(\alpha = 7^{\circ}, \beta = 89.1^{\circ}, \gamma = 90.6^{\circ})$ and $(\alpha = 3.0^{\circ}, \beta = 89.1^{\circ}, \gamma = 90.6^{\circ})$, respectively. *Pair L.*

Principal values: [-8.69, -5.51, 14.20] and [-8.68, -5.51, 14.19], matrices of eigenvectors:

	$\Gamma - 0.245$	-0.007	ך 0.969	$\Gamma - 0.175$	-0.010	ך 0.984
$E_{(L1)} =$	0.969	-0.033	0.244	$E_{(L2)} = 0.984$	-0.032	0.175
	L 0.031	0.999	0.055	0.030	0.995	0.016

Eulerian angles:

 $(\alpha = 14.2^{\circ}, \beta = 89.1^{\circ}, \gamma = 90.3^{\circ})$ and $(\alpha = 10.7^{\circ}, \beta = 89.1^{\circ}, \gamma = 90.2^{\circ})$, respectively. *Pair M*.

Principal values: [-8.03, -4.62, 12.65] and [-8.03, -4.62, 12.65] matrices of eigenvectors:

$$\mathbf{E}_{(M1)} = \begin{bmatrix} -0.217 & -0.010 & 0.976\\ 0.975 & -0.050 & 0.216\\ 0.047 & 0.999 & 0.020 \end{bmatrix} \qquad \mathbf{E}_{(M2)} = \begin{bmatrix} -0.140 & -0.016 & 0.990\\ 0.989 & -0.055 & 0.139\\ 0.052 & 0.998 & 0.024 \end{bmatrix}$$

Eulerian angles:

 $(\alpha = 12.5^{\circ}, \beta = 88.8^{\circ}, \gamma = 91.7^{\circ})$ and $(\alpha = 8.0^{\circ}, \beta = 88.6^{\circ}, \gamma = 91.8^{\circ})$, respectively.

Instead of the angles $\alpha = 6.81^{\circ}$ found for the chlorine atoms of type $Cl_{(1)}$ in the hightemperature phase, different values between about 4° and 14° are calculated but it is interesting to note that the angles for each pair of lines differ by a value of about 4° within the limits of experimental accuracy. Furthermore, the angles β and γ for each pair of lines are approximately the same. Slight deviations are observed from pair to pair which are clearly indicated by the obvious differences in the spectra (figure 4(a)). In an analogous way also the simulations of the angular dependence for the crystal rotation around the crystallographic axis *a* for the chlorine atoms $Cl_{(2)}$ and $Cl_{(3)}$ were performed. The results are shown in figure 4(b).

4. Conclusions

The experimental results obtained in this work can be used to explain the structural changes which occur at the phase transitions and, thus, have to be analysed in comparison with the x-ray structural investigations [2, 11]. In the room-temperature phase the number of lines and angular variation of the line splitting is in complete agreement with the hexagonal symmetry of the crystal. Due to the inversional symmetry, the six chlorine atoms lead to three equivalent resonance lines which differ only with respect to 120° symmetry easily derived from the spectra measured for the *c* rotation. That means there exist three equivalent EFG tensors with identical principal values.



Figure 5. Projection of the chlorine atoms into the (x, y) plane in the ferroelastic phase (measurement at 113 K): (a) one domain type; (b) the three types of domain characteristic of the ferroelastic phase.

principal axes which have been determined show that the axis with the greatest principal value is along the projection of the Cd–Cl bond direction into the (x, y) plane.

The fact that below the phase transition temperature at 113 K each NMR line is split into three pairs can be explained in the following way: first of all we have to take into account that the three types of chlorine atom, i.e. six chlorine atoms where each two are equivalent in accordance with the existence of an inversion centre (cf the x-ray study in [11]), are no longer structurally identical. The result is also confirmed by NQR measurements [19]. This interpretation is in agreement with the loss of the hexagonal symmetry below the phase transition at 118 K according to the symmetry group $P2_1/m$ as proposed in [2, 11, 20]. However, in this way the doubling of the lines in the three pairs observed cannot be explained as will be discussed later. A simple explanation, for instance, of the existence of three different line pairs in the orientationally selective measurements (i.e. the rotation around the crystallographic *a* axis) is possible if it is assumed that below $T_c \approx 118$ K three ferroelastic domains appear (which differ by angles of 120°). In each domain we have three structurally different chlorine atoms of the same kind. This situation leads to the appearance



Figure 6. Low-temperature ³⁵Cl NMR spectrum of TMCC showing the three pairs of central transition lines. Both lines in a pair have the same relative intensity. For this spectrum the axis *a* is perpendicular to the magnetic field and the axis *c* inclined at $\theta_a \approx 110^\circ$ with the magnetic field.

of the three pairs each of which belongs to another domain. The three pairs are easily seen in the case of the orientationally selective measurements. This interpretation is in particular reflected by the measurements for a rotation around the crystallographic *c* axis from which the 120° domains may be inferred. From these measurements it can be derived that the angles between the projections of the Cd–Cl bond directions into the (x, y) plane for the different chlorine atoms deviate from 120°, i.e. values of 112°, 123° and 125° were found, the differences between which are clearly beyond the limits of experimental error (figure 5).

The explanations given so far do not explain, however, the appearance of the pairs of the three lines with the additional splittings corresponding to small rotations with difference angles of $|\Delta \alpha| \approx 4^{\circ}$. Different explanations are possible which up until now do not lead to unambiguous conclusions. It might be possible that this line splitting reflects a doubling of the unit cell along the *a* or *b* crystal direction. This interpretation would be especially suggested by the fact that for TMMnC (C = chlorine) a symmetry group $P2_1/b$ with Z = 4occurs in the corresponding temperature range [11]. A unit cell with Z = 4 has also been also found for the bromine crystal TMMnB [14]. However, for the present crystal this suggestion would not be consistent with recent results of XRD studies which came to our attention during the revision of this paper [21]. Another explanation would in particular reflect the finding that a nearly equal splitting of $|\Delta \alpha| \approx 4^{\circ}$ is observed in all pairs. Since the sign of $\Delta \alpha$ cannot be determined in these measurements, positive or negative changes are not excluded. This situation could reflect the existence of a more complicated domain structure where instead of each 120° domain two different domains with an additional separation of $\pm |\Delta \alpha|$ would appear. According to the recent XRD measurements already mentioned [21] also this interpretation seems to be not appropriate. Further measurements on TMCC at

various temperatures are still in progress in order to obtain a consistent interpretation of the structural changes below the first phase transition.

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