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On the ferroelectric phase transition in (CH₃)₄ NCDBr₃ (TMCB)

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Résumé. — La transition de phase ferroélectrique de (CH₃)₄ NCDBr₃ (TMCB) à ~ 156 K est étudiée par diffraction des rayons X ; on montre que le groupe d’espace de la phase paraélectrique est P63/m, avec des paramètres de maille a, a, c, et que celui de la phase ferroélectrique est P61 (ou P65) avec pour paramètres a, a, 3c. La transition est analysée à l’aide de la théorie de Landau. En particulier, le changement de symétrie observé implique l’existence d’invariants d’ordre trois (transition du premier ordre). Un développement classique de l’énergie libre de Landau, incluant les termes de couplage avec les composantes du vecteur polarisation (ferroélectrique impropre) rend compte d’une manière satisfaisante de la dépendance en température de la polarisation spontanée et des susceptibilités diélectriques, mesurées précédemment.

Abstract. — The ferroelectric phase transition in (CH₃)₄ NCDBr₃ (TMCB) at ~ 156 K is studied by X-ray diffraction measurements; it is shown that the space group of the paraelectric phase is P63/m, with lattice parameters a, a, c, and that of the ferroelectric phase is P61 (or P65) with lattice parameters a, a, 3c. The transition is analyzed in the framework of the Landau theory. In particular, the observed symmetry change implies the presence of cubic invariants (first-order transition). A classical Landau type expansion of the free-energy, including coupling terms with the polarization vector components (improper ferroelectric) is able to account satisfactorily for the temperature dependence of the spontaneous polarization and dielectric susceptibilities which have been previously measured.

The crystals with formula (CH₃)₄ NMX₃ (M = Mn, Cd; X = Cl, Br) are hexagonal at room temperature, with space-group P6₃/m and Z = 2 formula units per unit-cell [1-4]. The structure is made of infinite linear chains of face-sharing MX₆ octahedra and the space between the chains is occupied by the tetramethylammonium groups (TMA) exhibiting an orientational disorder of dynamic nature [5, 6]. The chlorides (CH₃)₄ NMnCl₃ (TMMC) and (CH₃)₄ NCDCl₃ (TMCC) undergo a number of structural phase transitions, governed essentially by the reorientational dynamics of the TMA, and leading to different non-polar ordered phases with monoclinic symmetry, stable at low temperatures ([5-10] and cited references). The controversial case of (CH₃)₄ NMnBr₃
(TMMB) [4, 11, 12] has been solved in favour of a monoclinic low temperature phase [12], which is probably also non-polar.

In this series of compounds, \( (\text{CH}_3)_4 \text{NCdBr}_3 \) (TMCB) exhibits a particular behaviour, since recently the low temperature phase has been found to be ferroelectric [13]. A first-order phase transition from \( \text{P6}_3/m \) to the polar phase occurs around 156 K; it is characterized by a marked lambda-shaped anomaly of the dielectric constant along the \( e \) direction (polar axis) [13, 14], whereas a very small discontinuous change of the dielectric constant along \( a \) is observed [13] (Fig.1). In addition, the ferroelectric phase is optically uniaxial, which means that it has a hexagonal or trigonal symmetry, with point group other than \( 6/m \) [14].

![Fig. 1. — Schematic representation of the temperature dependence of (a) the spontaneous polarization \( P_z \) and of (b) the dielectric constant along the \( a \) and \( c \) directions (frequency 100 kHz, on cooling). Data points are taken from [13]; note that a similar curve for \( \varepsilon_c \) has been obtained in [14].](image)

In this short paper we present X-ray diffraction measurements made on TMCB at low temperatures allowing an unambiguous determination of the space-group of the ferroelectric phase. Then, the phase transition will be described in the framework of Landau theory.

Single crystals of TMCB have been prepared from saturated aqueous solutions, as described previously [3]. Small needles, elongated along the \( c \) direction, with dimensions of about 0.12 x 0.4 x 0.8 mm\(^3\) have been selected for X-ray diffraction measurements, after examination through a polarizing microscope.

The phase transition is first evidenced on powder photographs obtained with a Guinier-Simon camera, operating between 80 and 300 K; it is characterized by small discontinuities in the thermal evolution of a number of reflection lines, and by the appearance of new reflections in the low temperature phase. The data are consistent with the occurrence of a weak first-order transition around 160 K, as found already [13, 14].

Single crystal Weissenberg and precession photographs of TMCB at room temperature confirm the space-group \( \text{P6}_3/m \) with lattice parameters \( a = 9.432(4)\text{Å} \) and \( c = 7.003(4)\text{Å} \) [3]. Bragg
photographs at 110 K (ferroelectric phase), with crystal rotating around the c axis, clearly show a triplication of the lattice parameter along c, as evidenced by the presence of superstructure reflections along c* which were absent at room temperature. A similar result has been obtained already with TMCC at low temperature [7, 8].

With TMCB, the Weissenberg photographs of the (hk0) and (hk1) planes at 110 K show that the hexagonal symmetry is conserved, with no change of the lattice period along a and b. This is now in contrast with TMMC and TMCC where superstructure reflections have been observed at low temperature in those planes, together with a splitting of the main reflections due to a monoclinic distortion [8]. In the low temperature phase of TMCB, the only systematic absence of reflection is observed for the [00l] row line (reflection condition l = 6n) on precession photographs of the (h0l) plane.

Thus, the space-group for the low temperature phase can be either P61 (or equivalently P65) or P6122 (P6522). Since P6122 is not a polar group, the space group of the ferroelectric phase of TMCB is then unambiguously determined as P61 (P65). Note that the polar axis of P61 lies along the c direction, as observed experimentally [13]; also, P61 is a sub-group of P63/m (paraelectric phase), which is not the case for P6122.

It should be also pointed out that Raman scattering experiments with TMCB [15] show that the doubly degenerate lattice modes with E₂g symmetry in the paraelectric phase are not split in the ferroelectric phase, as expected for an uniaxial structure [14] such as P61. Again, this is in contrast with TMMC and TMCC, where the corresponding E₂g modes showed a doublet structure at low temperatures owing to the monoclinic symmetry of the ordered phases [9].

The hexagonal unit-cell of the ferroelectric phase, with lattice parameters such as a, a, 3c determines a lattice instability occurring at a point \( \Delta(0, 0, \alpha) \) inside the hexagonal Brillouin zone of the paraelectric phase \( (a, a, \alpha) \) [16]; the triplication along c is obtained for the particular value \( \alpha = 1/3 \). In the P63/m space-group, the wave-vector group for all points \( \Delta \) lying on the \( \Gamma - A \) line is \( C_6 \) [16], of which the four little representations are denoted as \( \Delta_1/A_1, \Delta_2/B \) (one-dimensional) and \( \Delta_3/E_1, \Delta_4/E_2 \) (these are short-hand notations for the complex conjugate physically degenerate \( E_1(1), E_2(2) \) and \( E_2(1), E_2(2) \) representations [16]). Following classical group theoretical procedures [17], we have performed a systematic search for all sub-groups of P63/m issued from point \( \Delta(0, 0, 1/3) \). It turns out that P61 (or P65) is induced by \( \Delta_3/E_1 \). Now, the full representation \( \Delta_3/E_1 \uparrow P63/m \) is of dimension four since there are two arms in the star of the wave-vector at point \( \Delta \) [16]; it follows that the order parameter has four components \( q_1, q_2, q_3 \) and \( q_4 \) such as \( q_1 = q_2^* \) and \( q_2 = q_3 \).

The P61 space-group corresponds to such solutions as \( q_1 \neq 0, q_4 \neq 0, q_2 = q_3 = 0 \) and P65 to equivalent solutions where \( q_2 \neq 0, q_3 \neq 0, q_1 = q_4 = 0 \). The symmetric and anti-symmetric powers of the representation \( \Delta_3/E_1 \uparrow P63/m \) (with \( \alpha = 1/3 \)) give in particular:

\[
[\Delta_3/E_1]^2 = A_g + E_{2g} + A_u + \Delta_1/A(2/3) + \Delta_4/E_2(2/3)
\]

\[
[\Delta_3/E_1]^2 = A_g + A_u + E_{2u} + \Delta_1/A(2/3)
\]

\[
[\Delta_3/E_1]^3 = 2A_g + E_{2g} + 2A_u + E_{2u} + 2\Delta_2/B(1/3) + 2\Delta_3/E_1(1/3)
\]

According to (2), there is a Lifschitz invariant since the anti-symmetric square contains the vector representation \( A_u(z) \); on the other hand, the relation (3) determines the presence of two cubic invariants \( 2A_g \).

After these group-theoretical considerations, the Landau free-energy expansion is fully determined. First, we put:

\[
\begin{align*}
q_1 &= e^{i\phi} q \\
q_2 &= e^{i\phi} q' \\
q_4 &= e^{-i\phi} q \\
q_3 &= e^{-i\phi} q'
\end{align*}
\]
where \( \omega = \varphi \pm n \pi / 3 \) (n integer), but for convenience we shall consider a real form expansion using order parameters \( \eta_i \) (i = 1 to 4) defined as:

\[
\begin{align*}
\eta_1 &= q \cos \varphi \\
\eta_2 &= q' \cos \omega \\
\eta_4 &= q \sin \varphi \\
\eta_3 &= q' \sin \omega
\end{align*}
\]

Then, the Landau free-energy developed up to the fourth order writes:

\[
\Delta \Phi = a(T) \left( \eta_1^2 + \eta_2^2 + \eta_3^2 + \eta_4^2 \right) + 2b \left( \eta_1^3 + \eta_2^3 - 3\eta_1\eta_2^2 - 3\eta_2\eta_3^2 \right)
+ 2b' \left( \eta_3^2 + \eta_4^2 - 3\eta_1^2\eta_4 - 3\eta_2^2\eta_3 \right)
+ c \left[ (\eta_1^2 + \eta_4^2)^2 + (\eta_2^2 + \eta_3^2)^2 \right]
+ d \left( \eta_1^2 + \eta_4^2 \right) \left( \eta_2^2 + \eta_3^2 \right)
+ \frac{1}{2}\chi_0^{-1}(\|)P_z^2 + \frac{1}{2}\chi_0^{-1}(\perp)(P_x^2 + P_y^2)
+ g(\eta_1^2 - \eta_2^2 - \eta_3^2 + \eta_4^2)P_z + h(\eta_1^2 + \eta_2^2 + \eta_3^2 + \eta_4^2)(P_x^2 + P_y^2) + \ldots
\]

In this expression \( \chi_0(\|) \) and \( \chi_0(\perp) \) are the free dielectric susceptibilities parallel and perpendicular to the \( c \) axis, respectively, and \( P_x, P_y \) (E\(_{1a}\) symmetry) and \( P_z \) (A\(_{1u}\) symmetry) are the three components of the polarization vector; for convenience, only coupling terms of lowest order between the \( \eta_i \) and \( P_j \) components have been included. Coupling terms with the strain tensor components have been omitted, since the transition is non-ferroelastic; also, the Lifschitz invariant and other gradient terms have been omitted, since according to calorimetric, dielectric [13, 14] and Raman scattering [15] experiments, there is no hint of existence of an intermediate (possibly incommensurate) phase. As usual we put:

\[
a(T) = a(T - T_0)
\]

all other coefficients being supposed temperature independent (improper ferroelectric transition [18]).

So, the effective potential for the ferroelectric phase P\(_{61}\) (\( q \neq 0, \ q' = 0 \)) can be written as:

\[
\tilde{\Delta} \Phi = a(T)q^2 + 2(b \cos 3\varphi - b' \sin 3\varphi)q^3 + cq^4
+ \frac{1}{2}\chi_0^{-1}(\|)P_z^2 + \frac{1}{2}\chi_0^{-1}(\perp)(P_x^2 + P_y^2)
+ gq^2P_z + hq^2(P_x^2 + P_y^2)
\]

Of course, a similar expression can be obtained for energetically equivalent P\(_{65}\) domains (\( q = 0, \ q' \neq 0 \)).

Minimizing \( \Delta \Phi \) with respect to \( \varphi \) yields:

\[
\tan 3\varphi = -\frac{b'}{b}
\]

and the minimization equations

\[
\frac{\partial \tilde{\Delta} \Phi}{\partial P_j} = 0 \quad (j = x, y, z)
\]

give:

\[
\begin{align*}
P_x &= P_y = 0 \\
P_z &= -g\chi_0(\|)q^2
\end{align*}
\]
Then, the transition temperature \( T_c \) is given by:
\[
T_c = T_0 + \frac{b^2 + b'^2}{a c'}
\]
and the equilibrium value of the order parameter by:
\[
q(T) = \begin{cases} 
0 & \text{for } T > T_c \\
\frac{3q_c}{4} \left\{ 1 + \left[ 1 - \frac{8}{9} \frac{(T - T_0)}{(T_c - T_0)} \right]^{1/2} \right\} & \text{for } T < T_c
\end{cases}
\]
where:
\[
c' = c - \frac{1}{2} g^2 \chi_0(||)
\]
and where \( q_c \) is the jump value of \( q(T) \) at \( T_c \) (first-order transition):
\[
q_c = -\frac{b}{c' \cos 3\varphi}
\]

Now, in the paraelectric phase \( (T > T_c) \) the static dielectric susceptibilities are:
\[
\begin{align*}
\chi_p(||) &= \chi_0(||) \\
\chi_p(\perp) &= \chi_0(\perp)
\end{align*}
\]
and in the \( P6_1 \) ferroelectric phase \( (T < T_c) \), it comes \([18,19]\):
\[
\begin{align*}
\chi^{-1}_f(||) &= \chi_0^{-1}(||) - 4g^2 q(T)^2 \left( \chi_{11} \cos^2 \varphi + \chi_{44} \sin^2 \varphi \right) \\
&\quad + 2\chi_{14} \sin \varphi \cos \varphi \\
\chi^{-1}_f(\perp) &= \chi_0^{-1}(\perp) + 2hq(T)^2
\end{align*}
\]
where the \( \chi_{ij} \)'s are the “high frequency” susceptibilities of the order parameters \([19]\) given by:
\[
\chi^{-1}_{ij} = \frac{\partial^2 \Delta \Phi}{\partial \eta_i \partial \eta_j} \quad (i, j = 1 \text{ to } 4)
\]
i.e.:
\[
\begin{align*}
\chi_{11}^{-1} &= 2a(T) + 12(b \cos \varphi - b' \sin \varphi)q(T) + 4 \left( 2c \cos^2 \varphi + c' \right) q(T)^2 \\
\chi_{44}^{-1} &= 2a(T) - 12(b \cos \varphi - b' \sin \varphi)q(T) + 4 \left( 2c \sin^2 \varphi + c' \right) q(T)^2 \\
\chi_{14}^{-1} &= \chi_{41}^{-1} = -12(b \sin \varphi + b' \cos \varphi)q(T) + 8c(\sin \varphi \cos \varphi)q(T)^2
\end{align*}
\]
In figure 2, we have represented a numerical simulation of the characteristic quantities given by the relations \((11), (13), (16)\) and \((17)\), with coefficients chosen so as to reproduce qualitatively the experimental results \([13,14]\). So, the general trends observed for the temperature dependence of the spontaneous polarization \( P_z \) and dielectric susceptibility \( \chi(\perp) \) \([13]\) can be simulated in a satisfactory manner. As for \( \chi(||) \), a lambda-shaped anomaly as observed in TMCB \([13,14]\) indeed
can be reproduced, but the experimental data exhibit an additional downward variation that makes $\chi_{f}(||)$ to reach values lower than $\chi_{0}(||)$ at low temperature [13, 14] (Fig.1). Obviously, such an observation cannot be accounted for (Fig.2) with only a coupling term of the form $q^{2}P_{z}$ (8) [18], but as shown from (3), higher order coupling terms of the form $q^{3}P_{z}$ are allowed by symmetry, since $[\Delta_{3}/E_{1}]^{3}$ contains $2A_{6}(z)$; also, a coupling term of the form $q^{2}P_{z}^{2}$ can always be added. Clearly, this latter term is able to introduce an additional downward variation of $\chi_{f}(||)$ provided that the coupling coefficient is positive [18], as shown here for $\chi_{f}(\perp)$ (Fig. 2). Note however that introducing such terms as $q^{3}P_{z}$ and $q^{2}P_{z}^{2}$ in (6) is equivalent to consider an effective potential for the ferroelectric phase developed up to the sixth order in $q$ including cubic terms (already present) and fifth order terms, which is not very easy to apprehend.

![Diagram](image)

**Fig. 2.** — Numerical simulation for the temperature dependence of (a) the order parameter $q$ and the spontaneous polarization $P_{z}$ and of (b) the dielectric susceptibilities $\chi(||)$ and $\chi(\perp)$, according to the model potential (6). The following coefficients have been chosen: $T_{c} = 156$ K, $T_{0} = 119$ K, $\eta_{c} = 2.43$, $c' = 1$, $\chi_{0}(||) = 7.5$, $\chi_{0}(\perp) = 4.75$, $g = 0.18$, $h = 0.0006$; for convenience we put $\varphi = 0$.

Thus, we conclude that the phase transition $P6_{3}/m \leftrightarrow P6_{1}$ ($P6_{5}$) of TMCB at $\sim 156$ K is improper ferroelectric; it is of first order because of the existence of third order invariants and it can be accounted for in a satisfactory way with a classical Landau free-energy expansion, as far as the static properties are concerned. The dynamical aspects of this phase transition will be considered in a forthcoming paper, devoted to a Raman scattering study [15].
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