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Temperature-pressure phase diagram
do deuterated tetramethylammonium tetrachlorozincate

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Résumé. — Le diagramme de phase P-T du tétraméthylammonium-tétrachlorozincate deutéré a été obtenu par mesure du vecteur d'onde de la modulation k = (k, 0, 0) en fonction de la pression hydrostatique dans le domaine 0 à 1.8 kbar et de la température dans le domaine — 5 à + 36 °C. Ce diagramme constitue une illustration de l'escalier du diable : il contient différentes marches commensurables k = 1/3, 2/5 dans la phase ferroélectrique, 3/7 et 1/2.

Du côté des hautes températures, il est possible de suivre un chemin continu allant de 0,41 à 0,333 sans accrochage et sans hystérésis du vecteur d'onde et de l'intensité du satellite. A température plus basse, l'accrochage se produit sur la valeur 2/5, laquelle sépare deux phases incommensurables : l'une pour k > 0,4 et l'autre pour k < 0,4. Dans cette région l'escalier du diable est complet, avec par exemple la séquence 0,424, 0,4, 0,333 et le comportement irréversible.

Dans un modèle phénoménologique, les commensurabilités sont obtenues par l'introduction dans l'énergie libre des invariants du paramètre d'ordre principal, des termes de couplage avec un paramètre d'ordre secondaire. La phase polaire de dTMATC-Zn étant de multiplicité élevée et pour abaisser l'ordre de la contribution à l'énergie libre, le couplage est assuré par l'intermédiaire d'un paramètre d'ordre secondaire attaché à la distortion de vecteur d'onde 3 k ou 2 k. Les deux distorsions se confondent en une seule pour k = 0,4. L'un des couplages est sensé prévaloir pour k > 0,4 et l'autre pour k < 0,4. La symétrie du paramètre d'ordre passe alors de $\Sigma_2$ à $\Sigma_3$.

Abstract. — The pressure temperature phase diagram has been obtained in the deuterated TMATC-Zn by measuring the modulation wave vector in the range 0 to 1.8 kbar and — 5 to 36 °C. This diagram is a nice illustration of the devil's staircase. It exhibits various commensurate stairs with k = 1/3, 2/5 in the ferroelectric phase, 3/7 and 1/2.

At high temperatures lock-in occurs at 2/5. This phase separates two incommensurate phases, one with k > 0.4 and one with k < 0.4. There the devil's staircase is incomplete, hysteresis appears at the lock-in transitions. At low P and T the devil's staircase is complete and behaviour irreversible.

In a phenomenological theory, commensurability is induced by setting the proper terms in the free energy expansion. Together with invariant powers of the principal order parameter, there are coupling terms involving a secondary order parameter. Direct coupling of the POP with polarization leads to a contribution of order $2n$ for a commensurate phase of order $1/n$. In order to reduce this order, coupling is examined through a secondary order parameter depending on the distortion of wave vector 3 k or 2 k. These two distortions coincide for k = 0.4. One coupling term is dominant when k > 0.4, the other one when k < 0.4. The SOP then changes its symmetry from $\Sigma_2$ to $\Sigma_3$.

1. Introduction.

At atmospheric pressure, hydrogenated tetramethylammonium tetrachlorozincate is known to belong to the improper ferroelectric class of materials of $K_2SeO_4$ type [1, 2]. In TMATC-Zn a continuous phase transition occurs at about 25 °C, characterized by a satellite peak with wave vector close to 0.42 $a^*$(from Pnma high temperature space group) [3, 4]. Lock-in appears toward 10 °C and the ferroelectric phase with polarisation parallel to the b axis has a cell length of 5 $a_0$.

Ferroelectricity has been widely studied in structurally isomorphous compounds such as TMATC-X, $X = Co, Fe, Mn$ [5-7]. In these last two compounds, ferroelectricity is pressure-induced and as long as...
we are only concerned with ferroelectric properties, a single model would apply to all the dielectric diagrams [6].

In TMATC-Zn the H-D isotopic substitution seems at first sight to profoundly alter the transition sequence [8] : under normal pressure no ferroelectric phase is observed and the variation of the modulation wave vector with temperature is sample dependent as suggested by figure 1. After a plateau the wave vector locks in to the commensurate value $3/7 a^*$. By decreasing the temperature, the next phase is dependent on the specimen : $k$ generally jumps to $1/3$ but with some specimens there is in addition a $k = 1/2$ phase between the commensurate phases $3/7$ and $1/3$.

It has been suggested that the $2 a_0$ cell could be due to a uniaxial stress [9]. So the effect of pressure was investigated and ferroelectricity found in dTMATC-Zn, the ferroelectric phase having a fivefold cell length as do the other compounds of the tetrachlorate family.

In this paper we report on the effects of temperature and hydrostatic pressure on the modulation in a dTMATC-Zn crystal. The same crystal was used as in our previous study in which the phase with $k = 1/2$ was present at atmospheric pressure.

In the first part we give experimental results. The experiments were made easier by the knowledge of the dielectric $P, T$ diagram [10]. It allowed us to save a great deal of experimental time. Then we discuss a phenomenological theory applied to improper ferroelectric transitions. The discussion stems from two important published papers : the first one from Iizumi et al. [11] explains the existence of the threefold cell phase in $K_2SeO_4$ by coupling the primary order parameter to the macroscopic polarization. The latter from Mashiyama [12], more elaborate, is an extension of the preceding to the fivefold cell case by means of an adequate secondary order parameter.

2. Experimental settings.

The neutron experiment has been performed on the triple axis spectrometer IN2 at the LL.L. high flux reactor. Thermal neutrons of 5 meV were selected by using a PG(002) as a monochromator. Horizontal collimations were $60'-40'-40'-40'$ and $(a^*, b^*)$ was chosen as scattering plane.

Pressure was applied by means of a helium gas system. The sample cemented to the rod has been mounted in an aluminium alloy pressure cell and immersed into a cryostat. Pressure was measured with a manganin sensor in the intensifier unit. Temperature was estimated by a platinium resistor and monitored with a silicon diode. Technical details are described in reference [13].

To avoid shock damage, pressure has been limited to 1.8 kbar and measured within an accuracy of 20 bar. As some components of the pressure cell impose the high temperature limit 40 °C, temperature has been kept in the range $-2°C + 36°C$ and even if the silicon diode temperature stability was within 1 K, we believe the sample temperature was more stable due to the great heat capacity of the whole cell.

3. Experimental results.

Constant $T$ lines have been scanned in the $T-P$ domain mentioned above. Figure 2 shows the variation of the modulation wave vector along some isothermal lines.

At 36 °C the disordered-incommensurate transition appears at about 970 bar with $k = 0.408$. $k$ decreases as the pressure increases and no lock-in is observed while passing through the rational value $2/5$; at this temperature, the threefold cell phase is not reached at $P = 1.8$ kbar. No pressure hysteresis is observed when going back in the paraelectric phase.

Fig. 1. — Three modulation curves obtained with three deuterated samples of d-TMATC-Zn. Curve 1 is from our first neutron study, curve 2 from an X-ray analysis on a small crystal and curve 3 is given by Gesi from a neutron study.
For $25^\circ C < T < 33^\circ C$, isothermal lines have a plateau at $2/5$. This commensurate phase divides the incommensurate one in two parts: $\text{incA}$ for $k > 2/5$ and $\text{incB}$ for $1/3 < k < 2/5$. A pressure hysteresis is observed at each of the commensurate values $1/3$ and $2/5$ and mainly in the second incommensurate phase B. In this temperature range it has been experimentally possible to go back in the paraelectric phase by decreasing the pressure.

For $T < 25^\circ C$ too much time would have been required to restore the prototypic phase by increasing the pressure along the $P = 0$ isobaric line: the disordered phase is no longer encountered. From $15^\circ C$ to $25^\circ C$ the wave vector behaviour is grossly as above. At $20^\circ C$, hysteresis first appears at the threefold-incommensurate transition and $k$ seems to lock at 0.388; at $15^\circ C$ incB disappears, $k$ jumps from $1/3$ to $2/5$ and there is a global pressure-hysteresis in the phase incA: the two paths $k(P \uparrow)$ and $k(P \downarrow)$ have no point in common in phase incA.

Below $11^\circ C$, phase incA begins with a short plateau with $k = 0.424$ and phase incB disappears. The transition sequence is $k = 0.424$, incA, 2/5, 1/3; hysteresis is global in the incommensurate range.

For $T < 9^\circ C$ the modulation curve is a series of plateaux. Satellites of both phases are simultaneously observed at the first order transitions, as shown in figure 3 and the coexistence lasts over 40 to 60 bar. In this region and particularly below $1.5^\circ C$ where the $2a_0$ phase appears, hysteresis spreads out the steps of the devil's staircase.

This phase diagram achieves the two limits of the devil's staircase with a complete part at low temperatures and an incomplete one above $18^\circ C$. In order to go on with this description of experimental results, we add a perspective view of the devil's hill in figure 7. The 3/7 commensurate phase is sandwiched by quasi-commensurate phases $k = 0.424$ and $k = 0.430$.

To conclude this survey, we have drawn some isobaric curves on figure 5, constructed from the isothermal lines. Temperature and pressure are expected to play equivalent rôles. Above 1.3 kbar, $k$ decreases toward 1/3 and no lock-in is observed on the commensurate value 2/5. Of course this lock-in is not expected for pressures superior to 1.6 kbar as $k_0$ is less than 2/5. In the range 0.4 kbar to 1.3 kbar, $k$ makes a step at 2/5. Under 0.6 kbar the modulation curves present a plateau the $k$ value of which continuously varies between 0.412 and 0.417 according to the isobar observed. Under 0.3 kbar isobaric lines look like the one obtained in our previous neutron experiment.
In connection with the above mentioned experiment, we ought to note the following important differences related to the distortion in the modulated phases. In our first neutron study, odd order satellites were observed up to the seventh order. These satellites were regarded as contributions of the distortion harmonics. In the present study, $2k$ largely dominates the higher order perturbation over the whole phase diagram. Moreover we do not know if the narrowing of the $2a_0$ phase is a real effect or if it is due to hysteresis: the $P = 0$ isobar has not been scanned in this second experiment.

Figure 6 gives the variation of the first order satellites intensity with pressure at various temperatures. It can be seen that the intensity varies linearly with $P$. Since our previous experiment has indicated the intensity varies linearly with $T$, we can represent the satellite intensity with the following

$$I_k(T, P) = aT + bP$$

$a$ and $b$ being $T$- and $P$-independent i.e. the slopes of the various $I_k(P)$ curves are temperature-independent as shown in figure 6.

4. Discussion.

The discussion will conform to the following plan:

First we introduce the pressure parameter in the simplest phenomenological theory, taking into account the orthorhombic symmetry of the paraelectric phase, which is adapted to the rest of the discussion. Secondly we give a summary of the paper of Mashiyama [12] applied to the transition sequence of hTMATC-Zn and occasionally to some isothermal or isobaric curves of the dTMATC-Zn diagram. Thirdly we introduce commensurabilities in the free energy density expansion of the crystal and restrict the discussion to the case of two order parameters: one primary order parameter (POP) with two complex conjugate components and one secondary order parameter (SOP) with two components. We have not considered additional parameters since the minimization condition would lead to calculations which are hardly tractable.

Hydrostatic pressure contribution to the free energy.

Given a system with a one component order parameter $q$ submitted to a second order phase transition, the free energy density can be written up to the sixth order as:

$$F = a q^2/2 + bq^4/4 + cq^6/6$$

(1)

$b, c > 0$. When the continuous transition is realized by decreasing temperature or increasing pressure, $a$ can be written as:

$$a = \alpha(T - T_0) + \beta(P_0 - P) \quad \alpha, \beta > 0.$$
Table I. — Irreducible representations of D\(_2\) class and compatibilities between \(\Gamma, \Sigma, X\) points in the Brillouin zone. First column is the decomposition at \(\Gamma\) point of the translation-rotation representation. Third column in spectroscopic notation.

<table>
<thead>
<tr>
<th>(\Gamma)</th>
<th>(\Sigma)</th>
<th>(X)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\Gamma_1)</td>
<td>(A_{1u})</td>
<td>(\Sigma_1)</td>
</tr>
<tr>
<td>(\Gamma_2)</td>
<td>(A_{1u})</td>
<td>(X_1)</td>
</tr>
<tr>
<td>(\Gamma_3)</td>
<td>(B_{3g})</td>
<td>(\Sigma_2)</td>
</tr>
<tr>
<td>(\Gamma_4)</td>
<td>(B_{3u})</td>
<td>(X_2)</td>
</tr>
<tr>
<td>(\Gamma_5)</td>
<td>(B_{2g})</td>
<td>(\Sigma_3)</td>
</tr>
<tr>
<td>(\Gamma_6)</td>
<td>(B_{2u})</td>
<td>(X_3)</td>
</tr>
<tr>
<td>(\Gamma_7)</td>
<td>(B_{1g})</td>
<td>(\Sigma_4)</td>
</tr>
<tr>
<td>(\Gamma_8)</td>
<td>(B_{1u})</td>
<td>(X_4)</td>
</tr>
</tbody>
</table>

Notice that the origin is fixed on the inversion centre: the set given here differs from that of Masuyama but the physical content is not altered.

Simple application of Birman's criterion leads to table III summarizing the different ferroic species accessible from the \(\Sigma\) point in the Brillouin zone; this table is divided into two parts according to the \(p\) parity where \(k = p/q\), \(k\) being the wave vector of the superstructure reflections in the low temperature phases (\(p\) and \(q\) integers).

Only \(C_{2y}(Y), D_2, C_{2b}(x)\) and \(C_{2h}(z)\) species are examined which correspond to low symmetry phases existing in the dTMATC-Zn sequence. The first one is ferroelectric, the last two are ferroelastic.

In the free energy model of Mashiyama, the POP has \(\Sigma_1\) symmetry, the SOP belongs to \(\Sigma_2\). The free energy density consists of invariant terms of the

Table II. — Representatives of \(Pnma\) elements at the \(\Sigma\) point in the various irreducible representations \(\Sigma_q\). Origin is on the inversion centre.

| \((E|0)\) | \((2x|a + b + c)\) | \((2y|b)\) | \((2z|c + d)\) | \((I|0)\) | \((\sigma_1|b + c + d)\) | \((\sigma_2|a + d)\) | \((\sigma_3|b)\) |
|---------|---------|---------|---------|---------|---------|---------|---------|
| \(\Sigma_1\) | \(1\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) |
| \(\Sigma_2\) | \(1\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) |
| \(\Sigma_3\) | \(1\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) |
| \(\Sigma_4\) | \(1\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) | \(0\) |

\(E|a\) :
\[
\begin{pmatrix}
\varepsilon & 0 \\
\varepsilon^{*2} & 0
\end{pmatrix}
\]
\(E|b\) :
\[
\begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\]
\(E|c\) :
\[
\begin{pmatrix}
1 & 0 \\
0 & 1
\end{pmatrix}
\]

\(\varepsilon = \exp (3\pi\delta)\)

\(k_a = 6\pi\delta^*\)

Table III. — Ferroic species and spatial subgroups induced by \(\Sigma_q\), according to the parity of \(p\) in the \(p/q\) superstructure.

<table>
<thead>
<tr>
<th>(p/q)</th>
<th>Species</th>
<th>(\Sigma_1)</th>
<th>(\Sigma_2)</th>
<th>(\Sigma_3)</th>
<th>(\Sigma_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>odd (p)</td>
<td>(C_{2y}(Y))</td>
<td>(n 2_1 m)</td>
<td>(n 2_1 a)</td>
<td>(n 2_1 a)</td>
<td>(n 2_1 m)</td>
</tr>
<tr>
<td>(D_2)</td>
<td>(2 2_1 2_1)</td>
<td>(2 2_1 2_1)</td>
<td>(2 2_1 2_1)</td>
<td>(2 2_1 2_1)</td>
<td></td>
</tr>
<tr>
<td>(C_{2b}(X))</td>
<td>(\frac{2}{n})</td>
<td>(\frac{2}{n})</td>
<td>(\frac{2}{n})</td>
<td>(\frac{2}{n})</td>
<td></td>
</tr>
<tr>
<td>(C_{2b}(Z))</td>
<td>(11 \frac{2}{m})</td>
<td>(11 \frac{2}{a})</td>
<td>(11 \frac{2}{a})</td>
<td>(11 \frac{2}{m})</td>
<td></td>
</tr>
<tr>
<td>even (p)</td>
<td>(C_{2y}(Y))</td>
<td>(n 2_1 a)</td>
<td>(n 2_1 a)</td>
<td>(n 2_1 a)</td>
<td>(n 2_1 a)</td>
</tr>
<tr>
<td>(D_2)</td>
<td>(2 2_1 2_1)</td>
<td>(2 2_1 2_1)</td>
<td>(2 2_1 2_1)</td>
<td>(2 2_1 2_1)</td>
<td></td>
</tr>
<tr>
<td>(C_{2b}(X))</td>
<td>(\frac{2}{n})</td>
<td>(\frac{2}{n})</td>
<td>(\frac{2}{n})</td>
<td>(\frac{2}{n})</td>
<td></td>
</tr>
<tr>
<td>(C_{2b}(Z))</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
POP up to the tenth order of elastic energies of the different ferroic species,
where $R_k,$ is the SOP and $P_k$ the polarization (notice the change in the strain parameters indices in the Pmcn$\rightarrow$Pnma transition) and finally of coupling terms between the POP and the SOP and between the POP and the macroscopic quantities arising at each phase transition (among them $S$ has not received a physical meaning):

$$F_1 = \sum_k \left\{ \alpha_2 Q_k Q_k^2/2 + \alpha_4 Q_k^2 Q_k^2/4 + \alpha_6 Q_k^3 Q_k^3/6 + \alpha_8 Q_k^4 Q_k^4/8 + \alpha_{10} Q_k^5 Q_k^5/10 \right\}$$ (1)

of elastic energies of the different ferroic species,

$$F_2 = \sum_k \alpha_2^m R_k^m R_k^m/2 + \sum_k \alpha_2^m P_k^m P_k^m/2 + c_4 \alpha_2^m/2 + c_6 \alpha_2^m/2 + dS^2/2$$ (2)

where $R_k$ is the SOP and $P_k$ the polarization (notice the change in the strain parameters indices in the Pmcn$\rightarrow$Pnma transition) and finally of coupling terms between the POP and the SOP and between the POP and the macroscopic quantities arising at each phase transition (among them $S$ has not received a physical meaning):

$$F_3 = \sum_k \beta_4 Q_k Q_k^4(Q_{k/3}^4 + Q_{1/3}^4) + \sum_k \beta_2(Q_k^2 R_{k/3}^2 + Q_{1/3}^2 R_{1/3}^2) + \sum_k \beta_3(Q_k^2 R_{k/3}^2 P_{k/3}^2 + Q_{1/3}^2 R_{1/3}^2 P_{1/3}^2) + \beta_4(Q_{1/3}^2 + Q_{1/3}^4) x_k - i\beta_3(Q_{1/3}^4 - Q_{1/3}^4) S - i\beta_3(Q_0 - Q_0^4) x_0.$$ (3)

To the leading order the POP has a classical behaviour, the wave vector $k(T)$ presents a parabolic variation near the transition temperature $T_0$ and decreases as long as all $\gamma$ are positive ($\gamma$ are the coefficients of quadratic terms in the expansions of $x_2$, $x_2’$ and $x_2^2$ versus $k$; Mashiyama chooses a parabolic dependence).

$k - k$ degeneracy as $k \rightarrow 0$ (or $3k - 1 \rightarrow 0$) leads to the lock in energy for the three-fold phase and the first coupling term in $F_3$ drives $k$ towards the commensurate value 1/3.

**How to introduce commensurabilities.**

This section is divided into three parts; we summarize here their characteristic features: details are given in an appendix.

A : In the first part we select the area of the $T$-$P$ diagram where the model free energy of Mashiyama works well. Even in the soft mode concept there is no requirement of a parabolic variation of $x_2^2(k)$ and $x_2^3(k)$, so we choose

$$x_2' = c + \gamma k^k \text{ with } k' = 3 |k| - 1$$

and

$$x_2'' = c^{-1} + \gamma k^k \text{ with } k'' = 5 |k| - 2.$$ (4)

Symmetries of the different parameters are $Q_k \in \sum_4$, $R_k \in \sum_4$, $P_k \in \sum_4$.

Some changes related to the 3 $a_0$ phases are noticed in the appendix. Near $T_0$, $q^2 \propto T$ and $k \propto q^2 \propto T^2$.

B : We associate the SOP with the distortion of the wave vector $2k$. The choice of the fundamental invariants leads to the following symmetries as long as the POP $Q_k$ belongs to $\sum_4$: $R_k \in \sum_4$, $P_k \in \sum_4$.

Close to $T_0$, $q^2 \propto T$ and $k \propto q^2$. The $\beta_2$ coefficient in $\beta_2(Q_k^2 R_{3k-1}^2)$ depends implicitly on $T$ and $P$.

Transition sequences are $a_0$-incomm-$a_0$-$3a_0$ or $a_0$-incomm-$3a_0$ allowing to the original value $k_0$. These sequences and $k$ variations are those in the middle pressure range isotherms.

C : To follow the line adopted we propose a free energy for the $7a_0$ phase. The free energy does not contain any invariant power of the POP corresponding to that lock in; invariant terms appear through a coupling to the POP $R$ and $P$, but now $P$ is no longer a polarization. Symmetries are $Q_k \in \sum_4$, $R_k \in \sum_3$ and $P_k \in \sum_3$.

5. Conclusion

We have proposed a discussion of the phase diagram based on a classical phenomenological theory. The main drawback of such a model is that it involves powers of the POP up to a high order for a $(p/n)$ a cell phase. The advantage of the model of Mashiyama is that it provides the symmetries of the OP by means of their coupling terms and eventually predicts the symmetries of the low temperature phases.

Due to the lack of information about dynamics of TMATC-Zn we make the assumption that the POP keeps its $\sum_4$ symmetry over the whole $T$-$P$ plane. Actually, M. Iizumi and K. Gesi [15] have seen a slight softening at $k \approx 0.33$ of the transverse acoustic mode which symmetry is compatible with $\sum_4$.

The most important feature of our discussion is the crossover in the first coupling term between the POP $Q_k$ and the SOP $R_k$. With $Q_k$ belonging to the IR of $\sum_4$, $R_k$ belongs to $\sum_4$ at high $T$ (coupling term $Q_k^2 R_{3k-1}$) and to $\sum_3$ at low $T$ (coupling term $Q_k^2 R_{3k-1}$). Mashiyama uses the first term as $k$ decreases toward 0.33 and we introduce the second term as $k$ goes to 1/2.

We believe such a model can only lead to qualitative agreement, if any, and we have not tried to fit any pressure dependence of the parameters $\gamma_4$ and $\beta_2'$. We therefore sorted out terms at our convenience to deal with two or three of them at a time, by setting abruptly $\beta_2'$ to zero. Doing this, we have introduced commensurabilities into our system.
It is tempting to consider \( R_k \) as a SOP of the second kind associated with a distortion at \( k' \). In the diffraction pattern, satellites are observed at \( k_n = nk + t m \). These peaks may be diffraction harmonics or fundamental diffraction by a harmonic of the distortion. This last point of view has been adopted in our previous study [8], though we cannot leave out the possibility of multiple reflections. Although multiple reflections are highly improbable at 5 meV, third and fifth order satellites have been observed in one part of the diagram, second order satellites in another part.

The SOP \( R_k \) would then be associated in one region with a distortion at \( 3k - 1 \) and in another region with a distortion at \( 2k - 1 \). These distortions match in a single one exactly when \( k = \frac{2}{5} \). Below \( k = \frac{2}{5} \) the coupling \( Q^2 R \) concerns the commensurate value \( 1/3 \) while above \( Q^2 R \) is related to the rational value \( 1/2 \). With this point of view, the symmetry change is a phase transition as it modifies the extinction rules of a superspace group.

The reduced phase diagram proposed by Gesi [16] allowed to extrapolate the devil’s hill presented in figure 7 beyond the experimental scanned region. This diagram may be completed by an islet \( a_0 \). This phase appears in the dTMATC-Zn Crystal and in TMATC-Fe as well [17].

The \( 2a_0 \) phase is subject to some controversy. Authors have suggested that this phase appears under uniaxial \( X_n \) stress. We ought to say that in our first neutron study, when we saw this \( 2a_0 \) phase for the first time, the crystal was wrapped in an aluminium foil and not directly glued to the goniometer head as in the present study. In the former case, the \( 2a_0 \) phase was about 5 K wide and called intrinsic. In the latter study, being cemented to the sample holder the crystal is subjected to external hydrostatic pressure and also to a uniaxial stress due to different thermal expansions of crystal and holder. At 0 bar this \( 2a_0 \) phase is reduced to a domain of 1 K width, but this may be due only to hysteresis.

Bounded to an \( X_n \) shear stress, equilibrium in the \( 2a_0 \) phase is written, with respect to \( x_6 \) deformation

\[
X_n = \frac{\partial F}{\partial x_n} = c_6 x_6 - 2 \beta_5 q^2
\]

and the contribution to the free energy is \( x_6^2 / 2 c_6 - 2 \beta_5 q^4 / c_6 \). So \( F \) is enhanced by the quantity \( x_6^2 / 2 c_6 \) which appears only in the ferroelastic \( C_{2h}(z) \) variety.

In conclusion we will make two remarks. So far we have completely neglected impurities or stacking faults in the crystal. They are subjected to the modulation potential and competition between their pair interaction and interaction with the lattice potential may produce hysteresis or discommensurations. From the devil’s staircase point of view, the approach of S. Aubry [18] or F. Axel [19] is advantageous, but these studies treat one-dimensional models.

**Appendix.**

\( A : \) We consider the area in the \( T\cdot P \) diagram where \( T > 20 \) °C and \( P > 0.7 \) kbar. The free energy density is written

\[
F = F_1 + F_2 + F_3, \quad F_1 \text{ and } F_2 \text{ are given by (1) and (2)}
\]

\[
F_3 = \sum_{\sigma} \beta_3(Q_6^2 R_{3k-1} P_5 P_{5k-2} + Q_6^{12} R_{5k-1} P_{5k-2}) + \beta_4(Q_6^3 + Q_6^{13}) + \beta_5(Q_6^4 + Q_6^{14}) x_6 - i \beta_5(Q_6^3 - Q_6^{13}) S.
\]

The POP \( Q_4 \) belongs to \( \sum_{\sigma} \) SOP \( R_k \) to \( \sum_{\sigma} \) and polarization \( P_k \) to \( \sum_{\sigma} \). The sum \( \sum_{\sigma} \) runs over the star of \( k \) vectors and coefficients \( \sigma \) take into account the \( k \) interchange when satisfying translational invariance. The strain components \( x_4 \) and \( x_6 \) belong respectively to \( \Gamma_4 \) and \( \Gamma_3 \), and \( S \) to \( \Gamma_2 \), the \( \Gamma \) being the IR of \( \Sigma_{2h} \) point group at the zone centre.

The transition sequence is para \(-\) incomm- \( 5a_0 \) - \( 3a_0 \) - \( a_0 \) - \( 3a_0 \) with space groups Pnma.

The free energy density \( F_1 \) in the decomposition \( F = F_1 + F_2 + F_3 \) involves invariant terms of the POP up to the tenth order for the \( \Sigma_{2h} \) class with \( k \) incommensurate. When \( k \) takes the commensurable values \( 1/3 \) or \( 2/5 \) additional invariants are respectively \( (Q_6^6 + Q_6^{16}) \) and \( Q_6^{13} (Q_6^{16} + Q_6^{16}) \) for \( C_2 \) and \( \Sigma_2 \) crystalline classes, \( (Q_6^{10} + Q_6^{16}) \) for \( C_2 \) class.
Mashiyama has discussed the influence of the tenth order term and wrote the eighth order term as $Q_k Q_\ast (Q_{1/3}^6 + Q_{1/3}^{10})$ i.e. like a coupling term between the POP and harmonics of its commensurate value when $k = 1/3$. Mashiyama's analysis is unchanged until we reach the $3a_0$ phases. With $Q_{1/3} = q \exp(i\phi)$ the free energy is:

$$F = \alpha_2 (1/3) q^2 + \alpha_4 q^4/2 + \alpha_6 q^6/3 + \alpha_8 q^8/4 + \alpha_{10} q^{10}/5 + c_4 x_2^2/2 + dS^2/2 +$$

$$+ 2 \beta_6 q^8 \cos 6 \psi + 2 \beta_4 x_4 q^3 \cos 3 \psi + 2 \beta_5 q^3 \sin 3 \psi + 2 \beta_6 q^6 \cos 6 \psi .$$

Minimization with respect to $\psi$ leads to the two known solutions $S = 0 \cos 3 \psi = -1$ and $x_4 = 0 \sin 3 \psi = -1$ and to the free energies

$$F_{IV} = \alpha_2 q^2 + \alpha_4 q^4/2 + (\alpha_6 - 6 \beta_6/c_4 + 6 \beta_6) q^6/3 + (\alpha_8 + 8 \beta_8) q^8/4 + \alpha_{10} q^{10}/5$$

$$F_{VI} = \alpha_2 q^2 + \alpha_4 q^4/2 + (\alpha_6 - 6 \beta_6/d - 6 \beta_6) q^6/3 + (\alpha_8 - 8 \beta_8) q^8/4 + \alpha_{10} q^{10}/5 .$$

Phase IV is stabilized at low $q$ when $\beta_6/d + \beta_6 < \beta_4/c_4 - \beta_6$ and phase VI appears at higher $q$ with the aid of the eighth order term.

As the POP participates in all the phase transitions, we have to scale its saturation value at the lowest transition $\rightarrow 21/2 \rightarrow 1/2$.

$k$ is given by $k - k_0 = -\gamma_0(\alpha_2/\beta_2/\Delta) q^4/2 \gamma_0$ with $\Delta = \alpha_2^2 - \beta_2^2 q^4$ and $\gamma_0$ in $\alpha_2 = T + P + \gamma_0(k - k_0)^2$.

The predictions of Mashiyama's model are the following:

- If $k_0 > 0.4$, then $k$ decreases and locks to the commensurate value 0.4, the transition being of the first order. Then we may have a transition to an incommensurate phase B or to the $3a_0$ phase depending on the $c_4$ value.

- If $k_0 < 0.4$, $k$ decreases monotonically to $k = 1/3$ with probably a jump.

- If $k_0 \approx 0.4$ but slightly larger, the calculation predicts a lock-in but fluctuations of the POP may remove the small 0.4 step.

This model appears quite satisfactory in a qualitative way. Mashiyama gives a set of numerical values which produces a good quantitative agreement. Figure 8a shows the variations of $K$ and $q^2$ for three $k_0$ values with $\gamma_0 = \gamma_1 = 1$, $c_4 = 0.17$, $\beta_4 = 0.25$, and other coefficients as in [12].

B : At the opposite side of the diagram is a $k = 1/2$ locked phase. This $3a_0$ phase is distinctly observed in the Mn compound as well [14]. In this Mn salt, $P 12_1/1$ symmetry is attributed to that phase while in our Zn salt it appears to be of $C_{2h}(z)$ symmetry. This fact is related to the splitting observed in another crystal of the (0, 2, 0) Bragg peak along the direction of the modulation. The existence of such domains in the paraelectric phase seems to be a relic of the twofold cell phase.

With the SOP $R_k, k' = 2k - 1$, the free energy is written $F = F_1 + F_2 + F_3 + F_4$ given by $I, F_2$ by expression II with the substitution $k' = 3k - 1 \rightarrow k' = 2k - 1$. Coupling terms appear in $F_3$.

$$F_3 = \sum_k \left\{ \beta_2 (Q_k^2 R_{1k-1} + Q_k^{12} R_{2k-1}) + \beta_4 Q_k^4 R_{3k-1} - P_{3k-1} Q_k^3 - Q_k^4 R_{3k-1} - P_{3k-1} \right\} +$$

$$+ \beta_6 Q_k^3 (Q_k^2 + Q_k^{13}) x_4 + \beta_8 (Q_k^2 + Q_k^{16}) x_6 - i \beta_3 (Q_k^{1/3} - Q_k^{1/3}) S + \beta_2 Q_1 / 2 Q_1^{1/2} x_6 .$$

$Q_k, Q_k'$ belongs to the IR $R_k, R_k'$ to $S_3$ and $P_k, P_k'$ to $S_3$.

$F_1$ has to be treated with care when the $S_3$ point goes to the $X$ point in the Brillouin zone : when $k = 1/2$ there is only one arm in the star of $k$ vectors and the following quantities are additional invariant powers of the POP for the $C_{2h}(z)$ variety

$$(Q_k^4 + Q_k^{14}), Q_k^{1/2}, Q_k^{1/2} (Q_k^4 + Q_k^{14}), (Q_k^8 + Q_k^{18}), Q_k^{1/2} Q_k^{1/2} (Q_k^4 + Q_k^{14}) \ldots$$

- In the incommensurate phase, there are few changes with respect to Mashiyama's model. We get

$$R_k = -\alpha_2^2 \beta_2 q^2/\Delta \quad P_k = -\beta_2 q^3 R_k/x_4^2 \quad q = |Q_k| \quad \Delta = \alpha_2^2 - \beta_2^2 q^6$$

and $F$ reads

$$F = \alpha_2 q^2 + (\alpha_4 - 2 \alpha_2^2 \beta_2^2/\Delta) q^4/2 + \alpha_6 q^6/3 + \alpha_8 q^8/4 + \alpha_{10} q^{10}/5 \quad (4) \quad \partial F/\partial q = 0 \text{ and } \partial F/\partial k = 0$$

give the equilibrium values of $q$ and $k$:

$$q^2 = -\alpha_2 (1 + \alpha_6 \alpha_2/\alpha_4) \alpha_4 \quad k - k_0 = -\gamma_0(\alpha_2^2 \beta_2^2/\Delta) q^2/2 \gamma_0 \quad \text{with} \quad \alpha_4 = \alpha_4 - 2 \alpha_2^2 \beta_2^2/\Delta .$$

- In the commensurate phase $k = 2/5$ with $Q_{2/5} = q \exp(i\phi)$ and $R_{1/5} = r \exp(i\theta)$ while $P = P_o$, $F$ writes

$$F = \alpha_2 q^2 + \alpha_4 q^4/2 + \alpha_6 q^6/3 + \alpha_8 q^8/4 + \alpha_{10} q^{10}/5 + \alpha_2^2 r^2/2 + \alpha_2^2 P_o^2/2 + 2 \beta_2 q^2 r \cos (2 \psi - \theta) +$$

$$+ 2 \beta_2 q^3 r P_o \cos (3 \psi + \theta)$$
with $\beta_2$ and $\beta_3 > 0$, $\cos (2 \psi - \theta) = \cos (3 \psi + \theta) = -1$ minimizes $F$. Now $\alpha_2 = \alpha_4 (2/5, \ T + \hat{P})$ 
$A = x_2^2 (2/5) \ a x_2^2 (2/5) - 2 \beta_2^2 q^6$.

To get the $a^3/3$ phases, we have to set $\beta_3 (T, P) = 0$. As the coupling term between the POP $Q_k$ and SOP $R_k$, vanishes, $R_k = P_k^* = 0$. Free energy is:

$$F = F_1(k = 1/3) + \sum \beta_8 Q_k Q_k^0 (Q_k^0 + Q_k^1) + c_4 x_4^2/2 + dS^2/2 + \beta_4 (Q_k^3 + Q_k^1) x_4 -$$

$$- i\beta_5 S(Q_k^1 - Q_k^3) + \beta_6 (Q_k^0 + Q_k^1).$$

Setting $Q_{1/3} = q \exp(i\psi)$ and minimizing with regard to $\psi$, $x_4$ and $S$ we get the two known solutions [12]:

$\cos 3 \psi = -1 S = 0 x_4 = 2 \beta_4 q^3/c_4$ and $\sin 3 \psi = -1 x_4 = 0 S = 2 \beta_6 q^3/d$, leading respectively to phases IV and VI of P 2/m 11 and P 2 1 2 1 symmetries.

The $2 \alpha_0$ case is a little more difficult $F_2$ reduces to $c_6 x_6^2/2$ and $F_3$ to $P_{1/2} Q_{1/2} x_6$. $F_1$ gathers the various invariant powers of $Q_k$ with $k = 1/2$.

$$F_1 = x_2 Q_{1/2} Q_{1/2}^2 + x_4 Q_{1/2}^2 Q_{1/2}^2/4 + x_4 (Q_{1/2}^4 + Q_{1/2}^2) + x_6 Q_{1/2}^2 Q_{1/2}^2/6 + \beta_4 P_{1/2} Q_{1/2}(Q_{1/2}^2 + Q_{1/2}) +$$

$$+ x_4 Q_{1/2}^2 Q_{1/2}^{1/2}/8 + x_6 Q_{1/2}^2 Q_{1/2}^2/12 + \beta_4 Q_{1/2}^2 Q_{1/2}^2/12 + \cdots$$

Setting $Q_{1/2} = q \exp(i\psi)$ we get for that part of $F$ depending on $\psi$:

$$F_\psi = 2 \alpha_4 q^4 \cos (4 \psi) + 2 \alpha_6 q^4 \cos (4 \psi) + 2 \alpha_4 q^4 \cos (8 \psi) + 2 \alpha_6 q^4 \cos (4 \psi)$$

which is minimized only by $\sin (4 \psi) = 0$.

The equilibrium condition for $x_6$ is $x_6 = - \beta_2 q^4/c_6$ and the free energy density is

$$F = \alpha_2 q^2 + (\alpha_4/4 + 2 \alpha_2 - \beta_2^2/2 c_6) q^4 + (\alpha_6/6 + 2 \alpha_6) q^6 + (\alpha_6/8 + 2 \alpha_6 + 2 \alpha_6) q^8 \cdots$$

$F$ is lowered by $k$ degeneracy at the X point and the coupling to strain, whereas additional terms increase $F$.

Figure 8b is a plot of $k$ and $q^2$ with the coefficients previously given except $\beta_2 = 0.25$ $\beta_3 = 3 \alpha_4 = 1.15$ : the $2 \alpha_0$ phase is never stabilized against the $3 \alpha_0$ phase so the transition sequences are para-incomm-5 $\alpha_0$-3 $\alpha_0$ or para-incomm-3 $\alpha_0$.

C : We attempt here to write a free energy for the $7 \alpha_0$ phase. Actually we do not know the space group symmetry of this phase but all we need is the point group. If this phase is ferroelastic one then $F_3$ includes the corresponding elastic energy and $F_3$ contains invariant coupling terms like $x_2 Q_{1/7}^2$. Minimization leads to $x_2 \propto q^2$ and the contribution to the free energy is proportional to $q^{14}$. This term is likely to be small and will be neglected. Invariant terms like $(Q_{1/7}^3 + Q_{7/7}^3)$, $n$ even, will be discarded for the same reason.

One way to take into account this commensurability is to replace the polarization $P_{k^*} k^* = 5 k - 2$ by the SOP $P_k^* k^* = 7 k - 3$. The coupling terms in $F_3$ constructed with $Q$, $R$ and $P$ are:

$$F_3 = \sum_k \left\{ \beta_2 (Q_k^2 R_{1k}^2 + Q_k^1 R_{1k}^2 + R_{1k}^1 - P_{1k}^1 - Q_{1k}^1 R_{1k}^2 + Q_{1k}^1 R_{1k}^2) \right\}$$

the rest of $F$ being unchanged.

In the incommensurate phase, there are slight changes with respect to B. $A = \alpha_2 \alpha_2^* - \beta_2^2 q^{10}$.

In the $7 \alpha_0$ commensurate phase, $k^*$ goes to zero as does $P_{k^*}$.

$$F = F_1(k = 3/7) + \sum_k \left\{ \alpha_2 R_{1k}^1 R_{1k}^1 - \beta_2 (Q_k^2 R_{1k}^2 + Q_k^1 R_{1k}^2) \right\}$$

with $2 k - 1 = -1/7$. 
Setting $Q_k = q \exp(i\psi)$, $R_k = r \exp(i\theta)$ the equilibrium condition reads

$$F = \alpha_2 q^2 + (\alpha_4 - 2\beta_2^2/\alpha_2') q^4/2 + \alpha_6 q^6/3 + \alpha_8 q^8/4 + \cdots$$

The phase $2a_0$ is discussed as in B and the $3a_0$ phase is obtained by setting $\beta_2(T, P) = 0$. The origin of the lock-in energy is not trivial: compare expression IV for $F$ in B with $a_n(k)$ and $F$ here above with $a_n(k = 3/7)$.

Figure 8c shows the result of a calculation with $c_4 = 0.215$ and $c_4 = 0.17$. For the last $c_4$ value $F(1/2)$ is always larger than $F(1/3)$.

References