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## Lattice dynamics and structural phase transitions in the chain compounds TMMC and TMCC: III. Landau theory

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**Abstract.** A phenomenological model is developed in the framework of Landau theory, in order to account for the structural phase transitions occurring in TMMC and TMCC. This model includes pseudo-spin coordinates attached to the orientation of tetramethylammonium groups that describe order–disorder processes, coupling terms with rotatory and translatory modes of the octahedra chains leading to displacive contributions and coupling terms with the strain components that account for the ferroelastic behaviour. Thus, the phase transitions between phases I', I, II and III are described in a satisfactory way, when compared with the experimental data. It is shown that the complex structure of phase IV must be seen as the result of a 'lock-in' transition from a hypothetical incommensurate phase.

### 1. Introduction

The experimental results reported in the preceding papers (I and II) of this series [1, 2] made it possible to interpret the mechanisms of the structural phase transitions occurring in the crystals of  $(\text{CH}_3)_4\text{NMnCl}_3$  (TMMC) and  $(\text{CH}_3)_4\text{NCdCl}_3$  (TMCC). These mechanisms are of complex nature, since they generally involve order–disorder processes due to the reorientational dynamics of the  $(\text{CH}_3)_4\text{N}^+$  (TMA) groups, coupled to displacive contributions coming from rotations or translations of the  $\text{MCl}_3$  octahedra chains. In addition, coupling should exist between strain components and the order parameter, when the transitions are ferroelastic.

In the present paper (III), which is the last one of this series, we intend to give a coherent description of all phase transitions in these systems, through a phenomenological model developed in the framework of Landau theory.

The first step (section 2) will consist of the determination of the general formulation of a thermodynamic potential able to account for the existence of the parent phase I' ( $P6_3/mmc$ ,  $Z = 2$ ) and of the subgroup related phases I ( $P6_3/m$ ,  $Z = 2$ ), II ( $P2_1/b$ ,  $Z = 4$ ) and III ( $P2_1/m$ ,  $Z = 2$ ); at this stage, phase IV ( $P2_1/b$ ,  $Z = 12$ ) will be ignored.

In section 3, the I'  $\leftrightarrow$  I phase transition will be considered in detail. Then section 4 will be devoted to the phase sequences occurring between phases I, II and III.

**Table 1.** Symmetry properties of the order parameters in the different structural modifications I'(P6<sub>3</sub>/mmc, Z = 2), I(P6<sub>3</sub>/m, Z = 2), II(P2<sub>1</sub>/b, Z = 4) and III(P2<sub>1</sub>/m, Z = 2). The notations of Bradley and Cracknell [3] are used. The origin of symmetry operations is taken on the metallic M = Mn, Cd cation.

Order parameters	Phase			
	I'	I	II	III
$\rho$	$\Gamma_2^+ / A_{2g}$	$\Gamma_1^- / A_g$	$\Gamma_1^+ / A_g$	$\Gamma_1^+ / A_g$
$\eta_1$	$\Gamma_6^+ / E_{2g}$	$\Gamma_5^+ / E_{2g}$	$\Gamma_1^+ / A_g$	$\Gamma_1^+ / A_g$
$\eta_2$	$\Gamma_6^+ / E_{2g}$	$\Gamma_6^+ / E_{2g}$	$\Gamma_1^+ / A_g$	$\Gamma_1^+ / A_g$
$\xi_1$	$M_3^- / B_{1u}$	$M_1^- / A_u$	$\Gamma_1^+ / A_g$	$B_1^- / A_u$
$\xi_2$	$M_3^- / B_{1u}$	$M_1^- / A_u$	$Y_1^+ / A_g$	$A_1^- / A_u$
$\xi_3$	$M_3^- / B_{1u}$	$M_1^- / A_u$	$Y_1^- / A_u$	$Y_1^- / A_u$

Expressions that are able to account for the behaviour of the elastic constants and of soft modes will be established and compared with the experimental data. Finally, the particular problems associated with the occurrence of the complex phase IV will be discussed in section 5.

## 2. General formulation of the free energy

As established in paper II [2], three different order parameters, let us say  $\rho$ ,  $\eta$  and  $\xi$ , are necessary to describe the sequences of transitions occurring between phases I', I, II and III. Table 1 summarizes the symmetry properties [3] of these order parameters in the different structural modifications;  $\rho$  is one-dimensional, ( $\Gamma_2^+ / A_{2g}$ ),  $\eta$  is two-dimensional since it belongs to the doubly degenerate  $\Gamma_6^+ / E_{2g}$  representation, and  $\xi$  is three-dimensional since there are three arms in the star of the wavevector at point M ( $0 \frac{1}{2} 0$ ) [3].

Then, from classical group-theoretical procedure, the Landau free energy of the system can be developed up to the fourth order as a function of  $\rho$ ,  $\eta$  and  $\xi$  as follows:

$$\Delta\Phi(\rho, \eta, \xi) = \frac{1}{2}A_1\rho^2 + \frac{1}{4}C_1\rho^4 + \frac{1}{2}A_2\eta^2 - \frac{1}{3}B_2\eta^3 + \frac{1}{4}C_2\eta^4 + \frac{1}{2}A_2\xi^2 + \frac{1}{4}C_3\xi^4 - \frac{1}{3}D\rho\eta^3 + \frac{1}{2}E\rho^2\eta^2 + F\xi^2\eta + \frac{1}{2}G\xi^2\eta^2 + \frac{1}{2}H\rho^2\xi^2 + \dots \quad (1)$$

This is a 'reduced' formulation, which does not explicitly take into account the different components of  $\eta$  ( $\eta_1, \eta_2$ ) and  $\xi$  ( $\xi_1, \xi_2, \xi_3$ ). For instance, the third-order invariant of  $\eta$  appears because  $[\Gamma_6^+ / E_{2g}]^3 = A_{1g} + A_{2g} + E_{2g}$ , leading to an invariant ( $A_{1g}$ ) of the form [4]  $\eta_1^3 - 3\eta_1^2\eta_2 - 3\eta_1\eta_2^2 + \eta_2^3$ , denoted by  $\eta^3$  in 'reduced' form, etc. All coupling terms between  $\rho, \eta, \xi$  up to the fourth order have been included.

The different phases observed with TMMC and TMCC correspond to solutions such as [2]:

- |       |               |               |              |           |
|-------|---------------|---------------|--------------|-----------|
| (i)   | $\rho = 0$    | $\eta = 0$    | $\xi = 0$    | phase I'  |
| (ii)  | $\rho \neq 0$ | $\eta = 0$    | $\xi = 0$    | phase I   |
| (iii) | $\rho \neq 0$ | $\eta \neq 0$ | $\xi = 0$    | phase III |
| (iv)  | $\rho \neq 0$ | $\eta \neq 0$ | $\xi \neq 0$ | phase II. |

### 3. The transition I' ↔ I

This is, of course, the simplest case, since it concerns only the one-dimensional order parameter  $\rho$ . As shown in paper II [2], the I' ↔ I phase transition involves a displacive mechanism due to octahedra chain rotation coupled to order–disorder processes of the TMA. Thus, the order parameter  $\rho$  is a linear combination of a pseudo-spin coordinate (attached to the TMA reorientations) and of the chain rotation coordinate with the same symmetry. So, a pseudo-spin phonon coupling formalism is certainly the best way to describe the phase transition mechanism. Unfortunately, we have no information on the pseudo-spin dynamics (collective excitation). All we know is that the characteristic frequency for individual TMA reorientations lies in the range  $10^{11}$  to  $0.5 \times 10^{12} \text{ s}^{-1}$  [5], which is significantly lower than the frequency of the chain rotatory mode, observed around  $(2 \text{ to } 3) \times 10^{12} \text{ s}^{-1}$ . Also, it should be noticed that this latter frequency is far from being zero at the transition temperature, and that its softening observed in phase I is rather small (see figure 4 in paper II [2]).

After these remarks, we shall use an oversimplified procedure in which the pseudo-spin coordinate is considered as the primary order parameter, the chain rotatory mode being treated separately according to a harmonic potential slightly perturbed by anharmonic coupling terms with the pseudo-spin coordinate. This means that the pseudo-spin frequency is supposed to be always much lower than the chain rotation frequency. Hence, we define  $\rho$  as a linear combination of the two  $A_{2g}$  pseudo-spin coordinates derived from model (1) and (2) [1, 2]:

$$\begin{aligned}\Theta'_{A_{2g}}^{(1)} &= \frac{1}{2}(\bar{\theta}_1 + \bar{\theta}_2 - \bar{\theta}'_1 - \bar{\theta}'_2) \\ \Theta'_{A_{2g}}^{(2)} &= (1/\sqrt{6})(\bar{\theta}_3 + \bar{\theta}_4 + \bar{\theta}_5 - \bar{\theta}'_3 - \bar{\theta}'_4 - \bar{\theta}'_5).\end{aligned}\quad (2)$$

In order to account for the behaviour of the elastic constants, the elastic energy is introduced in the Landau free-energy expansion, together with the coupling terms between the strain components and the order parameter. So, the effective free energy is developed as

$$\Delta\Phi = \Delta\Phi(\rho) + \Delta\Phi(e) + \Delta\Phi(\rho, e) \quad (3)$$

where

$$\Delta\Phi(\rho) = \frac{1}{2}a(T - T_1)\rho^2 + \frac{1}{4}C\rho^4 + \dots \quad (4)$$

$$\begin{aligned}\Delta\Phi(e) &= \frac{1}{2}C_{11}^0(e_1^2 + e_2^2) + \frac{1}{2}C_{33}^0e_3^2 + \frac{1}{2}C_{44}^0(e_4^2 + e_5^2) \\ &\quad + \frac{1}{2}C_{66}^0e_6^2 + C_{12}^0e_1e_2 + C_{13}^0(e_1 + e_2)e_3\end{aligned}\quad (5)$$

$$\Delta\Phi(\rho, e) = f(e_1 + e_2)\rho^2 + ge_3\rho^2 + \dots \quad (6)$$

In expression (4),  $T_1$  is the actual temperature for the second order I' ↔ I transformation. The  $e_i$  appearing in relation (5) are the strain tensor components and the  $C_{ij}^0$  are the 'bare' elastic constants, adapted to the hexagonal symmetry of the system [2, 6]; note that  $C_{66}^0 = \frac{1}{2}(C_{11}^0 - C_{12}^0)$ .

The minimisation equations of  $\Delta\Phi$  with respect to  $e_i$  ( $i = 1$  to 6) lead to the relations

$$e_1 = e_2 = (gC_{13}^0 - fC_{33}^0)/[(C_{11}^0 - C_{12}^0)C_{33}^0 - 2C_{13}^{02}]\rho^2 \quad (7)$$

$$e_3 = [2fC_{13}^0 - g(C_{11}^0 + C_{12}^0)]/[(C_{11}^0 - C_{12}^0)C_{33}^0 - 2C_{13}^{02}]\rho^2 \quad (8)$$

$$e_4 = e_5 = e_6 = 0. \quad (9)$$

By putting (7), (8) and (9) back into (3) one obtains

$$\Delta\Phi[\rho, e(\rho)] = \frac{1}{2}a(T - T_1)\rho^2 + \frac{1}{4}(C + C')\rho^4 \quad (10)$$

where

$$C' = -[4f^2C_{33}^0 + 2g^2(C_{11}^0 + C_{12}^0) - 8fgC_{13}^0]/[(C_{11}^0 + C_{12}^0)C_{33}^0 - 2C_{33}^0{}^2]$$

so that the equilibrium value of the order parameter is given by

$$\begin{aligned} \rho &= 0 && \text{in phase I}' (T > T_1) \\ \rho^2 &= a(T_1 - T)/(C + C') && \text{in phase I} (T < T_1). \end{aligned} \quad (11)$$

From relations (2) and (11), it follows that the orientational disorder of the TMA at a finite temperature  $T < T_1$  is described by

$$\begin{aligned} \bar{\theta}_1 &= \bar{\theta}_2 > \bar{\theta}'_1 = \bar{\theta}'_2 \\ \bar{\theta}_3 &= \bar{\theta}_4 = \bar{\theta}_5 > \bar{\theta}'_3 = \bar{\theta}'_4 = \bar{\theta}'_5 \end{aligned} \quad (12)$$

with

$$\begin{aligned} \sum_{i=1,2} (\bar{\theta}_i + \bar{\theta}'_i) &= p_1 \\ \sum_{i=3,4,5} (\bar{\theta}_i + \bar{\theta}'_i) &= p_2 \end{aligned}$$

$p_1$  and  $p_2$  being the relative weights of model (1) and model (2), respectively ( $p_1 + p_2 = 1$ ) [1, 2]. Then, the phase I ground state, obtained when  $T \rightarrow 0$ , corresponds to  $\bar{\theta}'_i \rightarrow 0$  ( $i = 1$  to 5), i.e.

$$\begin{aligned} \bar{\theta}_1 &= \bar{\theta}_2 = \frac{1}{2}p_1 \\ \bar{\theta}_3 &= \bar{\theta}_4 = \bar{\theta}_5 = \frac{1}{3}p_2. \end{aligned} \quad (13)$$

This is actually the approximation adopted for the structure determination of TMCC in phase I [1].

The adiabatic elastic constants are now given by the general relation [7]

$$C_{ij} = C_{ij}^e - (\partial^2 \Delta\Phi / \partial e_i \partial \rho) \chi_\rho^e (\partial^2 \Delta\Phi / \partial \rho \partial e_j) \quad (14)$$

where  $C_{ij}^e$  are the elastic constants determined at constant order parameter ( $\rho$ ) and  $\chi_\rho^e$  is the susceptibility of the order parameter determined at constant strain. In phase I', from (14) one finds for all elastic constants

$$C_{ij} = C_{ij}^0 \quad (15)$$

and in phase I

$$C_{11} = C_{22} = C_{11}^0 - 2f^2/C = \tilde{C}_{11}^0 \quad (16)$$

$$C_{33} = C_{33}^0 - 2g^2/C = \tilde{C}_{33}^0 \quad (17)$$

$$C_{12} = C_{12}^0 - 2f^2/C = \tilde{C}_{12}^0 \quad (18)$$

$$C_{13} = C_{13}^0 - 2fg/C = \tilde{C}_{13}^0 \quad (19)$$

and

$$C_{ij} = C_{ij}^0 \quad \text{for } ij = 44, 55, 66. \quad (20)$$

The step-like variation of  $C_{11}$  observed at  $T_1$  (see figure 8 in paper II [2]; see also [8, 9]) is in agreement with relations (15) and (16). There is, however, an additional quasi-linear variation with temperature, due to the thermal expansion of the crystal. As for  $C_{33}$  [8, 9], the anomaly predicted at  $T_1$  by relations (15) and (17) is much less pronounced than for  $C_{11}$ , and this can be explained with the present model. As a matter of fact, the order parameter corresponds to TMA reorientations around the  $c$  axis. These motions can induce some deformation in the hexagonal plane ( $e_1, e_2$ ), but not in the direction parallel to  $c$  ( $e_3$ ) since they have no component along  $c$ . Because of this anisotropy, it can be stated that the coupling coefficients are very different ( $g \ll f$ ), which can explain the experimental results.

Let us now write the chain rotatory mode potential as

$$\Phi(R, \rho) = \frac{1}{2}M\omega_E^2 R^2 + hR\rho + \frac{1}{2}kR^2\rho^2. \quad (21)$$

$R$  represents the mean value of the chain rotation coordinate;  $\omega_E$  is the harmonic frequency and  $M$  is the reduced mass of the oscillator. The bilinear coupling term  $hR\rho$  leads to a proportionality relation between  $R$  and the order parameter  $\rho$ , and so introduces a displacive contribution coming from chain rotation. This term also leads to a renormalisation of the transition temperature  $T_1$ , which can be neglected as long as  $M\omega_E^2 \gg A_1 = a(T - T_1)$  (this is the basic assumption of our approximate treatment). Then, the frequency of the chain rotatory mode is obtained from  $\chi_R^0$ , i.e. the susceptibility determined at constant order parameter, which gives

$$\begin{aligned} T > T_1 & \quad \omega_R^2 = \omega_E^2 \\ T < T_1 & \quad \omega_R^2 = \omega_E^2 + ka(T_1 - T)/MC'. \end{aligned} \quad (22)$$

The relations (22) account for the non-zero value of the soft-mode frequency at  $T_1$  and predict a linear variation with temperature of  $\omega_R^2$  below  $T_1$  (see figure 4 in paper II [2]). This linear variation is approximately verified in phase I, the saturation effect observed well below  $T_1$  probably being related to the influence of sixth-order terms, which have been neglected in (3).

#### 4. The I $\leftrightarrow$ II and I $\leftrightarrow$ III phase transitions

The free-energy expansion (1) is unworkable, in practice, for the description of phases II and III where the equilibrium values of  $\xi$  and/or  $\eta$  are non-zero. So, we have simplified the problem by considering that the I'  $\leftrightarrow$  I phase transition is disconnected from the

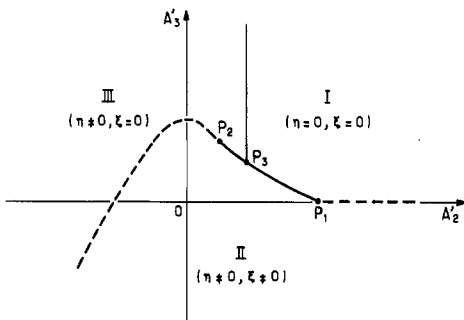


Figure 1. The phase diagram corresponding to the potential (23), with  $B_2' > 0$ ,  $C_2 > 0$ ,  $C_3 > 0$ ,  $F < 0$  and  $G > 0$  (from [10]): —, first-order transition lines; - - -, second-order transition lines.

other, since it occurs at a much higher temperature. Then, the equilibrium value of the order parameter  $\rho$  will be almost saturated in the temperature range of the I  $\leftrightarrow$  II and I  $\leftrightarrow$  III transitions. In other words, we shall consider the phase I ground state. Hence, the effective free energy is obtained by putting  $\rho = \rho_0 = \text{constant}$  in (1), which gives

$$\begin{aligned} \Delta\Phi(\eta, \xi) = & \Delta\Phi_0 + \frac{1}{2}A'_2\eta^2 - \frac{1}{3}B'_2\eta^3 + \frac{1}{4}C_2\eta^4 \\ & + \frac{1}{2}A'_3\xi^2 + \frac{1}{4}C_3\xi^4 + F\eta\xi^2 + \frac{1}{2}G\xi^2\eta^2 + \dots \end{aligned} \quad (23)$$

where

$$\Delta\Phi_0 = \frac{1}{2}A_1\rho_0^2 + \frac{1}{4}\rho_0^4 = \text{constant}$$

$$A'_2 = A_2 + E\rho_0^2$$

$$B'_2 = B_2 + D\rho_0$$

$$A'_3 = A_3 + E\rho_0^2.$$

The minimisation equations can now be written as

$$\eta(A'_2 - B'_2\eta + C_2\eta^2 + G\xi) + F\xi^2 = 0$$

$$\xi(A'_3 + C_3\xi^2 + 2F\eta + G\eta^2) = 0.$$

The stability conditions of a potential of this form have already been studied by Gufan and Torgashev [10]; figure 1 shows the corresponding phase diagram, as established by these authors from numerical simulations. It is worth noting that all transitions occurring around the triple point  $P_3$  between phases I, II and III are of first order, as observed experimentally [2]. In the 'trigger' case [2], i.e. when  $A'_2 = f(T)$  and  $A'_3 = \text{constant}$ , the I  $\leftrightarrow$  II transition is necessarily of first order, which is indeed verified in TMMC. Furthermore, because of the  $\eta^3$  term, the I  $\leftrightarrow$  III transition is always of first order, as observed in both TMMC and TMCC. It should be noticed that the potential (23) produces a 're-entrant' phase III (figure 1). However, this 're-entrant' character disappears when neglecting the biquadratic coupling term  $\frac{1}{2}G\eta^2\xi^2$  [11]. In fact, it has been found experimentally that phase II is 're-entrant' and not phase III (see figure 1 in [1] or [2]), and clearly the potential (23) is not able to account for this observation. It should be recalled that, at this stage of the discussion, we are still ignoring the existence of phase IV, and of course this simplification prevents any realistic description of the observed phase diagram.

#### 4.1. The pure order-disorder model

Starting from the phase I ground state, as described by the relations (13), it has been shown in paper II [2] of this series that the driving order parameter for both the I  $\leftrightarrow$  II and I  $\leftrightarrow$  III phase transitions are the two pseudo-spin coordinates with  $E_{2g}$  symmetry, issued from the model (2):

$$\begin{aligned} \Theta_{E_{2g}}^{(2)} &= (1/\sqrt{6})(2\bar{\theta}_3 - \bar{\theta}_4 - \bar{\theta}_5) \\ \Theta_{E_{2g}}^{(3)} &= (1/\sqrt{2})(\bar{\theta}_4 - \bar{\theta}_5). \end{aligned} \quad (24)$$

These coordinates account for ordering processes of the TMA in phases II and III, the

additional unit-cell doubling occurring in phase II being explained by a trigger-type mechanism [2] (see section 4.2).

Thus, it is meaningful, as a first step, to discuss the implications of such an order-disorder model. At this point, phases II and III (ordered phases) will not be distinguished. The representations  $\Gamma_5^+$ ,  $\Gamma_6^+/E_{2g}$  (table 1) are complex conjugate, so that the two components  $\eta_1$  and  $\eta_2$  of the order parameter  $\eta$  are such as  $\eta_1 = \eta_2^*$ . Then we have

$$\begin{aligned}\eta_1 &= \Theta_{E_{2g}}^{(2)} + i\Theta_{E_{2g}}^{(3)} \\ \eta_2 &= \Theta_{E_{2g}}^{(2)} - i\Theta_{E_{2g}}^{(3)}.\end{aligned}\quad (25)$$

According to classical group-theoretical procedure, the free energy expanded as a function of  $\eta_1$  and  $\eta_2$  [12, 13] is

$$\Delta\Phi(\eta) = \alpha(T)\eta_1\eta_2 + \beta(\eta_1^3 + \eta_2^3) + i\beta'(\eta_1^3 - \eta_2^3) + \gamma\eta_1^2\eta_2^2 + \dots \quad (26)$$

where

$$\begin{aligned}\alpha(T) &= \alpha^0(T - T_0) \\ \eta_1 &= e^{i\varphi}\eta \quad \eta_2 = e^{-i\varphi}\eta.\end{aligned}$$

Minimising  $\Delta\Phi(\eta)$  with respect to  $\varphi$  leads to the relation

$$\tan 3\varphi = -\beta'/\beta \quad (27)$$

and the first-order transition to the ordered phase occurs at a temperature  $T_c$  such that

$$T_c = T_0 + (\beta^2 + \beta'^2)/\alpha^0\gamma. \quad (28)$$

In the ordered phase ( $T < T_c$ ), the equilibrium value of the order parameter is

$$\eta(T) = (3\eta_c/4)[1 + (1 - \frac{8}{3}(T - T_0)/(T_c - T_0))^{1/2}] \quad (29)$$

where  $\eta_c$  is the jump of  $\eta$  at  $T_c$  given by

$$\eta_c = -\beta/(\gamma \cos 3\varphi). \quad (30)$$

Thus, from the relations (25), (26) and (29), the orientational disorder of the TMA at a finite temperature  $T < T_c$  is described by

$$\bar{\theta}_3 > \bar{\theta}_4 > \bar{\theta}_5 \quad \text{with} \quad \bar{\theta}_3 + \bar{\theta}_4 + \bar{\theta}_5 = p_2.$$

On the other hand, one always has

$$\bar{\theta}_1 = \bar{\theta}_2 \quad \text{with} \quad \bar{\theta}_1 + \bar{\theta}_2 = p_1$$

since the order parameter  $\eta$  does not contain any pseudo-spin coordinate issued from model (1) [2]. Such a complex situation has been encountered in the structure determination of TMMC (phase II), just below  $T_c$  [1].

Now, in both phases II and III, we are looking for a completely ordered state of the TMA at  $T = 0$ , corresponding to  $p_1 = 0$  and  $\bar{\theta}_3 = p_2 = 1$ . Obviously, this cannot be achieved with the help of the  $E_{2g}$  order parameter (25), which belongs to model (2) only. So, one has to consider an additional coordinate:

$$\Theta_{A_g} = (1/\sqrt{30})[-3(\bar{\theta}_1 + \bar{\theta}_2) + 2(\bar{\theta}_3 + \bar{\theta}_4 + \bar{\theta}_5)] \quad (31)$$

in order to account for the conversion of the TMA from the model (1) orientations ( $\bar{\theta}_1$ ,  $\bar{\theta}_2$ ) into those of model (2) ( $\bar{\theta}_3$ ,  $\bar{\theta}_4$ ,  $\bar{\theta}_5$ ). This coordinate (31) is totally symmetric in both



the disordered and ordered phases, and so has non-zero spontaneous values on both sides of the transition. As a consequence, it cannot be treated as a usual order parameter. Nevertheless,  $\Theta_A$  (31) is able to account for the complete conversion to model (2) ( $p_1 = 0, p_2 = 1$ ) at  $T = T_0$ , owing to thermally activated processes expected between energetically inequivalent orientations, as determined in phase I ( $\theta_1 = \bar{\theta}_2 \neq \bar{\theta}_3 = \bar{\theta}_4 = \bar{\theta}_5$  from the symmetry properties of the crystal).

Additional information on the dynamics of the TMA reorientation through the phase transition is necessary to test the validity of such a complex model, based on structural data [1].

#### 4.2. Complete development of the free energy

In order to account for the behaviour of the elastic constants, on the one hand, and for the unit-cell doubling occurring in phase II, on the other hand, one has to introduce in (26) the elastic energy, the order parameter  $\xi$  and the coupling terms between these quantities and the order parameter  $\eta$ . The complete form of the free energy becomes

$$\Delta\Phi(\eta, e, \xi) = \Delta\Phi(\eta) + \Delta\Phi(e) + \Delta\Phi(\eta, e) + \Delta\Phi(\eta, \xi) \quad (32)$$

where

$$\Delta\Phi(\eta) = \alpha_1(T)\eta_1\eta_2 + \beta_1(\eta_1^3 + \eta_2^3) + i\beta_1'(\eta_1^3 - \eta_2^3) + \gamma_1\eta_1^2\eta_2^2 + \dots \quad (33)$$

$$\begin{aligned} \Delta\Phi(e) = & \frac{1}{2}\bar{C}_{11}^0(e_1^2 + e_2^2) + \frac{1}{2}\bar{C}_{33}^0e_3^2 + \frac{1}{2}\bar{C}_{44}^0(e_4^2 + e_5^2) \\ & + \frac{1}{2}\bar{C}_{66}^0e_6^2 + \bar{C}_{12}^0e_1e_2 + \bar{C}_{13}^0(e_1 + e_2)e_3 \end{aligned} \quad (34)$$

$$\begin{aligned} \Delta\Phi(\eta, e) = & (a_1\eta_1 + a_2\eta_2)(e_1 - e_2) + (b_1\eta_1 + b_2\eta_2)e_6 + d_1(e_1 + e_2)\eta_1\eta_2 \\ & + d_2e_3\eta_1\eta_2 + \dots \end{aligned} \quad (35)$$

$$\Delta\Phi(\xi) = \alpha_2(\xi_1^2 + \xi_2^2 + \xi_3^2) + \gamma_2(\xi_1^4 + \xi_2^4 + \xi_3^4) + \delta_2(\xi_1^2\xi_2^2 + \xi_1^2 + \xi_3^2 + \xi_2^2 + \xi_3^2) + \dots \quad (36)$$

$$\Delta\Phi(\eta, \xi) = l_1(\xi_1^2 - \xi_2^2 e^{-i\pi/3} - \xi_3^2 e^{i\pi/3})\eta_1 + l_2(\xi_1^2 - \xi_2^2 e^{i\pi/3} - \xi_3^2 e^{-i\pi/3})\eta_2 + \dots \quad (37)$$

The  $\bar{C}_{ij}^0$  appearing in (34) are the renormalized 'bare' elastic constants of phase I given by the relations (16) to (19). For the sake of simplification, coupling terms of the form  $\eta^2 e^2$  have been neglected in (35) as well as coupling terms of the form  $\eta^2 \xi^2$  in (37).  $\xi_1, \xi_2$  and  $\xi_3$  are the three components of the order parameter  $\xi$ , corresponding respectively to the three arms of the wavevector at point M ( $0 \frac{1}{2} 0$ ) (table 1). Note that phase II corresponds to solutions such that [4]

$$\xi_1 \neq 0 \quad \text{with} \quad \xi_2 = \xi_3 = 0 \quad (38)$$

since only one point M is replaced at the zone centre in this phase. Because the  $\Gamma_5^+, \Gamma_6^+ / E_{2g}$  representations are complex conjugate, the coefficients introduced in  $\Delta\Phi$  are such that

$$\begin{aligned} a_1 b_2 + a_2 b_1 &= 0 \\ a_1 &= \pm i b_1 = a_2^* = \pm i b_2^* \\ l_1 &= l_2^* \end{aligned} \quad (39)$$

so that we take

$$\begin{aligned}\eta_1 &= e^{i\varphi} \eta & \eta_2 &= e^{-i\varphi} \eta \\ a_1 &= e^{i\psi} a & a_2 &= e^{-i\psi} a \\ l_1 &= e^{i\omega} l & l_2 &= e^{-i\omega} l.\end{aligned}\quad (40)$$

Finally, because of the ‘trigger’ character of the I  $\leftrightarrow$  II transition, as evidenced from ultrasonic measurements with TMMC [2], we put

$$\begin{aligned}\alpha_1(T) &= \alpha_1^0(T - T_0) \\ \alpha_2 &= \text{constant}.\end{aligned}\quad (41)$$

Note also that one always has [6]

$$C_{66}^0 = \frac{1}{2}(\tilde{C}_{11}^0 - \tilde{C}_{12}^0) = \frac{1}{2}(C_{11}^0 - C_{12}^0).\quad (42)$$

Then, minimizing  $\Delta\Phi$  (32) with respect to the  $e_i$  leads to the relations

$$\begin{aligned}e_1 + e_2 &= \frac{2d_2\tilde{C}_{13}^0 - 2d_1\tilde{C}_{33}^0}{\tilde{C}_{33}^0(\tilde{C}_{11}^0 + \tilde{C}_{12}^0) - 2(\tilde{C}_{13}^0)^2} \eta_1 \eta_2 \\ e_1 - e_2 &= -2(\alpha_1 \eta_1 + \alpha_2 \eta_2)/(\tilde{C}_{11}^0 - \tilde{C}_{12}^0) \\ e_4 = e_5 &= 0 & e_6 &= -(b_1 \eta_1 + b_2 \eta_2)/C_{66}^0.\end{aligned}\quad (43)$$

The relations (43), combined with (39), (40) and (42), give

$$e_6/(e_1 - e_2) = \tan(\varphi + \psi)\quad (44)$$

and

$$\eta = \frac{C_{66}^0}{2a \cos(\varphi + \psi)} |e_1 - e_2| = \frac{C_{66}^0}{2a \sin(\varphi + \psi)} |e_6|.\quad (45)$$

So, the effective free energy deduced from (32) and from the preceding relations can be written as

$$\begin{aligned}\Delta\Phi[\eta, e(\eta), \xi_1] &= \alpha_1^0(T - T_1)\eta^2 + 2(\beta_1 \cos 3\varphi - \beta_1' \sin 3\varphi)\eta^3 \\ &+ \gamma_1' \eta^4 + \alpha_2 \xi_1^2 + \gamma_2 \xi_1^4 + 2l \cos(\varphi + \omega)\eta \xi_1^2\end{aligned}\quad (46)$$

where

$$T_1 = T_0 + 2a^2/\alpha_1^0 C_{66}^0$$

and

$$\gamma_1' = \gamma_1 - [2d_1^2 \tilde{C}_{33}^0 + d_2^2(\tilde{C}_{11}^0 + \tilde{C}_{12}^0) - 4d_1 d_2 \tilde{C}_{13}^0]/2[\tilde{C}_{33}^0(\tilde{C}_{11}^0 + \tilde{C}_{12}^0) - 2(\tilde{C}_{13}^0)^2].$$

The expression (46) is indeed of the same form as (23) except for the biquadratic coupling term  $\eta^2 \xi^2$ , which has been neglected.

At this point, it is worth noting that Levola and Kleemann [13] and then Levola and Laiho [8] have already worked up a free-energy expansion such as

$$\Delta\Phi(\eta, e) = \Delta\Phi(\eta)(33) + \Delta\Phi(e)(34) + \Delta\Phi(\eta, e)(35)$$

and they have used this thermodynamic potential for the description of the I  $\leftrightarrow$  II transition of TMMC. By no means is this potential able to account for a multiplication of

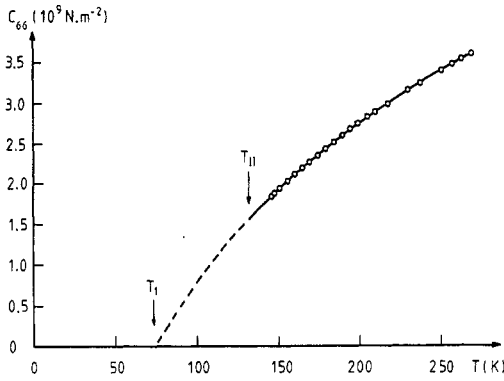


Figure 2. The temperature dependence of  $C_{66}$  in TMMC. Circles are experimental points from [2], and the full curve is the best fit from relation (50).

the unit-cell volume [1], since the order parameter  $\eta$  is at zone centre. In addition, the expression of  $T_1$  given by these authors [13]

$$T_1 = T_0 - 5a^2/4\alpha_1^0 C_{66}^0$$

is incorrect; as will appear clearly in the following,  $T_1$  cannot be lower than  $T_0$ .

Now, from the preceding development, expressions can be easily established to discuss the behaviour of the parameters of interest in this study.

4.2.1. Phase I ( $\eta = 0, \xi = 0$ ). Expressions for the elastic constants are established from the general relation [7]:

$$C_{ij} = C_{ij}^\eta - \sum_{kl} \frac{\partial^2 \Delta \Phi}{\partial e_i \partial \eta_k} \chi_{kl}^e \frac{\partial^2 \Delta \Phi}{\partial \eta_l \partial e_j} \quad (k, l = 1, 2)$$

namely

$$C_{11} = C_{22} = \bar{C}_{11}^0 - 2a^2/\alpha_1^0(T - T_0) \tag{47}$$

$$C_{33} = \bar{C}_{33}^0 \tag{48}$$

$$C_{44} = C_{55} = C_{44}^0 \tag{49}$$

$$C_{66} = C_{66}^0 - 2a^2/\alpha_1^0(T - T_0) \tag{50}$$

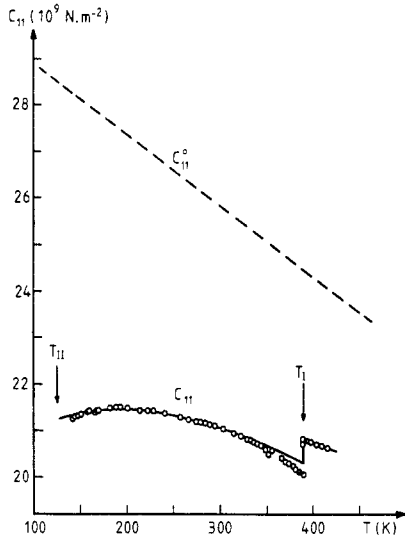
$$C_{12} = \bar{C}_{12}^0 + 2a^2/\alpha_1^0(T - T_0) \tag{51}$$

$$C_{13} = \bar{C}_{13}^0. \tag{52}$$

Figure 2 shows the best fit for the temperature dependence of  $C_{66}$  in phase I of TMMC [2], obtained from (50). The agreement is quite satisfactory with the following values of the parameters:

$$\begin{aligned} C_{66}^0 &= 8.18 \times 10^9 \text{ N m}^{-2} \\ 2a^2/\alpha_1^0 &= 2.03 \times 10^{12} \text{ K N m}^{-2} \\ T_0 &= -175 \text{ K}. \end{aligned} \tag{53}$$

It follows that  $C_{66}$  diverges at  $T_0$ ; meanwhile, it extrapolates to zero at  $T_1 = 74 \text{ K}$ , which is much lower than the actual transition temperature  $T_{II} = 126 \text{ K}$ , as expected for a first-



**Figure 3.** The temperature dependence of  $C_{11}$  in TMMC. Circles are experimental points from [2], and the full curve is the best fit from relations (15), (16) and (47). The broken line corresponds to the equation  $C_{11}^0 = (30.493 - 0.01533 T) \times 10^9 \text{ N m}^{-2}$  adjusted to account for the influence of thermal expansion.

order ‘pseudo-proper’ ferroelastic transition. The difference

$$T_1 - T_0 = 2a^2/\alpha_1^0 C_{66}^0$$

characterizes the strength of ferroelastic coupling. In the case of TMMC, this coupling is extremely strong ( $T_1 - T_0 = 249 \text{ K}$ ). For a comparison, note that the corresponding  $T_1 - T_0$  values observed in the displacive ‘pseudo-proper’ ferroelastic  $\text{Na}_5\text{Al}_3\text{F}_{14}$  [14],  $\text{LaP}_5\text{O}_{14}$  [15] and  $\text{BiVO}_4$  [16] are respectively 27, 160 and 230 K. In the case of ammonium oxalate (order-disorder transition),  $T_1 - T_0$  equals 143 K [17, 18].

The best fit for the temperature dependence of  $C_{11}$  [2] is shown in figure 3; according to (47) and (50), the same parameters as those found for  $C_{66}$  (53) have been taken. Also, the step-like variation of  $C_{11}$  at  $T_1$ , according to (15) and (16), is introduced in the fitting procedure. Finally, a linear variation of  $C_{11}^0$  with temperature has been adjusted, in order to account for anharmonic effects due to thermal expansion. The agreement is again satisfactory (figure 3). There is however an additional temperature dependence of  $C_{11}$  just below  $T_1$ , probably coming from coupling terms of the form  $e^2\rho^2$  (see for instance [14]), which have been neglected in (3).

Except for a quasi-linear variation with temperature due to thermal expansion,  $C_{33}$  remains essentially constant in phase I [8, 9], as expected from (48).

**4.2.2. Phase III ( $\eta \neq 0$ ,  $\xi = 0$ ).** As shown in section 4.1, the temperature value for the first-order I  $\leftrightarrow$  III transition is given by

$$T_{\text{III}} = T_1 + (\beta_1^2 + \beta_1'^2)/\alpha_1^0\gamma_1'. \quad (54)$$

This gives the equation of the I  $\leftrightarrow$  III transition line in figure 1. The equilibrium value of the order parameter is

$$\eta_{\text{III}} = (3\eta_c/4)[1 + (1 - \frac{8}{3}(T - T_1)/(T_{\text{III}} - T_1)^{1/2})] \quad (55)$$

where

$$\eta_c = -\beta_1/(\gamma_1' \cos 3\varphi). \quad (56)$$

Again, expressions for the elastic constants in phase III can be easily established, but unfortunately there are no available experimental data [9] to compare with.

4.2.3. *Phase II* ( $\eta \neq 0$ ,  $\xi_1 \neq 0$ ,  $\xi_2 = \xi_3 = 0$ ). The minimization equation  $\partial \Delta \Phi / \partial \xi_1 = 0$  gives the relation between  $\eta$  and  $\xi_1$  as

$$\xi_1^2 = [-\alpha_2 - 2l \cos(\varphi + \omega)\eta] / 2\gamma_2 \quad (57)$$

so that the condition  $\xi_1^2 > 0$  (with  $\gamma_2 > 0$ ) yields the two conditions

$$\begin{aligned} \eta &> -\alpha_2 / [2l \cos(\varphi + \omega)] > 0 \\ \eta &< -\alpha_2 / [2l \cos(\varphi + \omega)] < 0 \end{aligned} \quad (58)$$

owing to the two different types of equivalent domains determined from the sign of the coefficient  $\beta_1 / \cos 3\varphi$ . In particular, in the case ( $\eta > 0$ ) where

$$\eta_c = -\beta_1 / (\gamma_1' \cos 3\varphi) > -\alpha_2 / [2l \cos(\varphi + \omega)] > 0 \quad (59)$$

phase III will never be stable and the direct transition  $I \leftrightarrow II$ , of the 'trigger' type, will occur. This is actually our interpretation of the zero-pressure  $I \leftrightarrow II$  transition of TMMC at  $T_{II} = 126$  K. The value of  $\eta_c = -\alpha_2 / [2l \cos(\varphi + \omega)]$  determines the coordinates of the triple point  $P_3$  (figure 1). Thus, the change from  $I \leftrightarrow II$  to  $I \leftrightarrow III$  transition as observed with TMMC at high pressure (see figure 1 in paper II [2]) can be accounted for by a pressure dependence of the coefficients, that makes the 'trigger' condition (59) not valid beyond  $P_3$ .

By putting (57) back into (46), the effective free energy for phase II is rewritten as

$$\begin{aligned} \Delta \Phi[\eta, e(\eta), \xi_1(\eta)] &= -\alpha_2^2 / 4\gamma_2 - (\alpha_2 l \cos(\varphi + \omega) / \gamma_2) \eta \\ &+ [\alpha_1^0 (T - T_1) - l^2 \cos(\varphi + \omega) / \gamma_2] \eta^2 \\ &+ 2(\beta_1 \cos 3\varphi - \beta_1' \sin 3\varphi) \eta^3 + \gamma_1' \eta^4 \end{aligned} \quad (60)$$

and the minimization equation is

$$\begin{aligned} -\alpha_2 l \cos(\varphi + \omega) / \gamma_2 + 2[\alpha_1^0 (T - T_1) - l^2 \cos(\varphi + \omega) / \gamma_2] \eta \\ + 6(\beta_1 \cos 3\varphi - \beta_1' \sin 3\varphi) \eta^2 + 4\gamma_1' \eta^3 = 0. \end{aligned} \quad (61)$$

Then, the solution ( $\eta_{II}$ ) of (61) minimizing (60) does not have a simple algebraic form. In order to discuss more easily the temperature dependence of  $\eta_{II}$ , it can be shown [19] that an upper limit of  $\eta_{II}$  is obtained by neglecting the constant term  $-\alpha_2 l \cos(\varphi + \omega) / \gamma_2$  in (61), which gives

$$\eta_{II}^{\dagger} = \frac{3\eta_c}{4} \left\{ 1 + \left[ 1 + \frac{8}{9} \left( \frac{T - T_1}{T_{III} - T_1} + \frac{l^2 \gamma_1' \cos^2(\varphi + \omega) \cos^2 3\varphi}{\beta_1^2 \gamma_2} \right) \right]^{1/2} \right\}. \quad (62)$$

On the other hand, a lower limit of  $\eta_{II}$  is given by  $\eta_{III}$  (55). Thus, we have

$$\eta_{II}^{\dagger} > \eta_{II} > \eta_{III}. \quad (63)$$

In the 'trigger' case, the  $I \leftrightarrow II$  transition occurs at a temperature  $T_{II} > T_{III}$  (figure 1). Also, an upper limit of  $T_{II}$  is obtained from  $\eta_{II}^{\dagger}$ , i.e.

$$T_{II}^{\dagger} = T_{III} + l^2 \cos^2(\varphi + \omega) / \alpha_1^0 \gamma_2 \quad (64)$$

so that

$$T_{\text{II}}^+ > T_{\text{II}} > T_{\text{III}}. \quad (65)$$

In the limiting case where  $\alpha_2 = 0$ , one has  $\eta_{\text{II}} = \eta_{\text{II}}^+$  and consequently  $T_{\text{II}} = T_{\text{II}}^+$ ; this determines the coordinates of the tricritical point  $P_1$  (figure 1).

From  $(a, b)$  birefringence measurements, Levola and Kleemann [13] have been able to determine the temperature dependence of  $\eta_{\text{II}}$ , through the I  $\leftrightarrow$  II transition of TMMC. The data can be well reproduced with the help of relation (55) [13]. However, the value of  $T_1$  determined with such a procedure ( $T_1 = 119.8$  K) is considerably higher than ours ( $T_1 = 74$  K) determined rigorously from the temperature dependence of  $C_{66}$  in phase I (figure 2). As pointed out just above, relations such as (55) or (62) are approximate. In fact, if such laws in  $T^{1/2}$  are able to reproduce the temperature dependence of  $\eta_{\text{II}}$  [19], the physical meaning of the coefficients deduced from these expressions are not so simple.

Now it is not meaningful to give here the expressions established for the elastic constants in phase II, though some of these have been measured [8]. As a matter of fact, these relations are not of practical use because of their complexity.

Finally, it has been established that the order parameter  $\xi$  contains the chain translation coordinate  $\tau_{\text{A}}(\text{M})$  and the pseudo-spin coordinate  $\Theta_{\text{M}\Gamma}^{(1)}$  issued from model (1) [2]. Again, a pseudo-spin–phonon coupling formalism is probably the most appropriate to describe the resulting excitations [20]. Nevertheless, in the rough approximation where  $\Theta_{\text{M}\Gamma}^{(1)}$  is neglected, the frequency of the  $\tau_{\text{A}}(\text{M})$  mode with  $\text{A}_g$  symmetry in phase II is obtained directly from  $\chi^e(\xi_1)$ , i.e.

$$M\omega_{\text{A}_g}^2 = -4\alpha_2 - 8l \cos(\varphi + \omega)\eta_{\text{II}}. \quad (66)$$

Qualitatively, the experimental results (see figure 7 in paper II [2]) agree with relation (66), as long as the temperature dependence of  $\eta_{\text{II}}$  can be approximated by a law in  $T^{1/2}$  [8].

## 5. Phase IV

Phase IV is characterized by a doubling of the hexagonal unit cell along  $\mathbf{b}$  and a trebling of the lattice period along  $\mathbf{c}$  (see paper I [1]). Thus, phase IV results from an additional lattice instability occurring at point U ( $0\frac{1}{2}\alpha$ ), situated at the surface of the hexagonal Brillouin zone [3]. The trebling along  $\mathbf{c}$  is obtained for the particular value  $\alpha = \frac{1}{3}$ .

The two representations of the wavevector at point U, denoted as  $\text{U}_1/\text{A}$  and  $\text{U}_2/\text{B}$  [3], are of dimension 6, owing to the six arms in the star of this wavevector. It can be shown [21] that both representations  $\text{U}_1/\text{A}$  and  $\text{U}_2/\text{B}$  can induce the phase IV space group  $P2_1/b(Z = 12)$  [1], when  $\alpha = \frac{1}{3}$ . Let us call  $\xi'$  the order parameter for phase IV that belongs either to  $\text{U}_1/\text{A}$  or  $\text{U}_2/\text{B}$ ; the six components  $\xi'_1, \xi'_2, \dots, \xi'_6$  are such that

$$\xi'_1 = \xi'_2^* \quad \xi'_3 = \xi'_4^* \quad \xi'_5 = \xi'_6^* \quad (67)$$

and phase IV ( $\alpha = \frac{1}{3}$ ) corresponds to solutions [21] such as

$$\xi'_1 = \pm \xi'_2 \neq 0 \quad \xi'_3 = \xi'_4 = \xi'_5 = \xi'_6 = 0. \quad (68)$$

It is important to notice that the antisymmetric squares  $\{\text{U}_1/\text{A}\}^2 \equiv \{\text{U}_2/\text{B}\}^2$  contain the vector component representation  $\Gamma_1^-/\text{A}_u(z)$  of the  $P6_3/m$  space group [21], which

determines the presence of a Lifschitz invariant in the free-energy expansion. Thus, the thermodynamic potential including the coupling terms between  $\xi'$  and the primary order parameter  $\eta$  is of the form

$$\Delta\Phi(\xi') = \int f(z) dz \quad (69)$$

with

$$\begin{aligned} f(z) = & \alpha'_2(\xi'_1\xi'_2 + \xi'_3\xi'_4 + \xi'_5\xi'_6) + \gamma'_2(\xi'^2_1\xi'^2_2 + \xi'^2_3\xi'^2_4 + \xi'^2_5\xi'^2_6) \\ & + \delta'_2(\xi'_1\xi'_2\xi'_3\xi'_4 + \xi'_1\xi'_2\xi'_5\xi'_6 + \xi'_3\xi'_4\xi'_5\xi'_6) \\ & + i\epsilon'_2 \left( \xi'_1 \frac{\partial \xi'_2}{\partial z} - \xi'_2 \frac{\partial \xi'_1}{\partial z} + \xi'_3 \frac{\partial \xi'_4}{\partial z} - \xi'_4 \frac{\partial \xi'_3}{\partial z} + \xi'_5 \frac{\partial \xi'_6}{\partial z} - \xi'_6 \frac{\partial \xi'_5}{\partial z} \right) \\ & + \lambda'_2 \left( \frac{\partial \xi'_1}{\partial z} \frac{\partial \xi'_2}{\partial z} + \frac{\partial \xi'_3}{\partial z} \frac{\partial \xi'_4}{\partial z} + \frac{\partial \xi'_5}{\partial z} \frac{\partial \xi'_6}{\partial z} \right) + \dots \end{aligned} \quad (70)$$

and

$$\begin{aligned} \Delta\Phi(\eta, \xi') = & l'_1(\xi'_1\xi'_2 - \xi'_3\xi'_4 e^{-i\pi/3} - \xi'_5\xi'_6 e^{i\pi/3})\eta_1 \\ & + l'_2(\xi'_1\xi'_2 - \xi'_3\xi'_4 e^{i\pi/3} - \xi'_5\xi'_6 e^{-i\pi/3})\eta_2 + \dots \end{aligned} \quad (71)$$

Now, it is not an easy task to discuss the stability conditions of a potential including three coupled order parameters, such as given by adding (69) and (71) to (32), even when limiting the problem to solutions corresponding to (38) and (68). However, it is yet possible to take out some general ideas.

The Lifschitz invariant  $\xi'_i \partial \xi'_j / \partial z - \xi'_j \partial \xi'_i / \partial z$  in (70) is able to stabilise an incommensurate phase with a modulation vector along  $c^*$ , whereas the terms  $(\partial \xi'_i / \partial z)(\partial \xi'_j / \partial z)$  stabilise a commensurate phase resulting from a 'lock-in' transition where this modulation vector takes on a rational value [22]. So, phase IV must be seen as the result of a 'lock-in' transition from a hypothetical incommensurate phase, at the particular value  $\alpha = \frac{1}{3}$ . Note that the existence of an incommensurate phase is not a necessary condition, since the direct transition (of first order) from a normal phase (I, II or III) to the commensurate phase IV is also possible.

It should also be pointed out that the expressions (69) and (71) are reduced to the forms of (36) and (37), respectively, if the 'lock-in' occurred at  $\alpha = 0$  (point M  $(0 \frac{1}{2} 0)$ ). Thus, phase II, as well, could be seen as the result of a 'lock-in' transition. If such were the case, one has just to replace (36) and (37) by (69) and (71), respectively, in (32), so as to account for all transitions occurring between phases I, II, III and IV.

Additional information concerning the structure of phase IV can be obtained from group-theoretical considerations. In the case where phase IV is induced by the  $U_1/A$  representation, the atomic displacements responsible for the modulation (amplitudon) are longitudinal, i.e. they are polarised along  $c$ . Then, the resulting structure for the octahedra chains in phase IV would correspond to 'accordion'-like distortions. In the case where phase IV is induced by  $U_2/B$ , the atomic displacements are transverse, resulting in 'undulation'-like distortions of the octahedra chains. In fact, x-ray diffuse scattering experiments performed in phase I with TMMC and TMCC (see paper I [1]) have been interpreted in terms of 'accordion' motions of the chains, which could resemble in a short range the structure of phase IV if induced by  $U_1/A$ . Finally, the pseudo-spin coordinates issued from the model (2) are well suited to account for the trebling of the

unit cell along  $c$ , since TMA can adopt alternately one out of the three possible orientations provided by this model.

## 6. Conclusions

The structural phase transitions occurring in the chain compounds TMMC and TMCC have been studied in detail by means of different and complementary techniques. The mechanisms for the phase transitions in these materials are very complex, since in most cases they involve order–disorder processes due to reorientations of the TMA groups, coupled with displacive contributions coming from octahedra chain rotation or translation. In spite of this complexity, a rational description of the transition mechanisms has been made possible, using phenomenological models developed in the framework of Landau theory.

As far as the order–disorder processes of the TMA are concerned, we have adopted a Frenkel-type description, in which the TMA can perform jump motions between discrete orientations. This results in the definition of pseudo-spin coordinates. We have stressed the importance of model (2) corresponding in phase I to three energetically orientations in the mirror plane perpendicular to the sixfold screw axis. Indeed, this model provides the primary order parameter for both the  $I \leftrightarrow II$  and  $I \leftrightarrow III$  phase transitions. However, according to structural data, a model (1) is also present, corresponding to two mirror-related orientations of the TMA. Then, the ordering processes are already of a complex nature, due to the necessary conversion of the TMA from model (1) orientations to those of model (2) at low temperature, which is probably achieved by means of thermally activated processes (the two models are mutually exclusive by symmetry).

In order to account for the displacive mechanisms, coupling between the pseudo-spin coordinates (primary order parameters) and atomic displacements in the octahedra chains (rotatory and translatory modes) has been introduced in the free-energy expansion. Moreover, due to the ferroelastic behaviour of these materials, the elastic energy and coupling terms of the order parameters with the strain components are also introduced. All together, this results in a complex formulation of the Landau free energy, including three coupled order parameters, so as to account for the existence of the parent phase  $I'$  and of phases I, II and III. The problem has been solved by assuming that the  $I' \leftrightarrow I$  transition occurring at high temperature is disconnected from the other. Then expressions are derived for the temperature dependence of elastic constants and soft-mode frequencies that qualitatively fit the experimental data. In particular, both transitions  $I \leftrightarrow II$  and  $I \leftrightarrow III$  are ‘pseudo-proper’ ferroelastic, driven by a pseudo-spin coordinate (order–disorder process), phase II being stabilised by an additional displacive contribution, of ‘trigger’ type.

Finally, it is shown that the complex structure of phase IV must be seen as the result of a ‘lock-in’ transition from a hypothetical incommensurate phase. The existence (or non-existence) of an incommensurate phase in TMMC and/or TMCC is an important question still open to discussion.

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