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On the Landau theory of structural phase transitions in layered perovskites \((\text{CH}_3\text{NH}_3)_2\text{MCl}_4(M = \text{Mn, Cd, Fe})\): comparison with experiments

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Résumé. — La séquence de transitions de phase \(\text{I}4/\text{mmm} \leftrightarrow \text{Abma} \leftrightarrow \text{P}4_2/\text{ncm}\) (THT \(\leftrightarrow\) ORT \(\leftrightarrow\) TLT), qui est une caractéristique commune des composés \((\text{CH}_3\text{NH}_3)_2\text{MCl}_4\) \((M = \text{Mn, Cd, Fe})\), est examinée sur la base de la théorie de Landau, en comparaison avec les résultats expérimentaux disponibles. Une attention particulière est portée sur le comportement «anormal» de la constante élastique \(c_{66}\). D’après le modèle microscopique de type champ moyen, développé antérieurement par Blinc, Zeks et Kind, et à partir de considérations classiques de théorie des groupes, il apparaît que l’énergie libre de Landau doit être développée à l’ordre huit pour obtenir une description cohérente de l’ensemble des données expérimentales.

Abstract. — The phase sequence \(\text{I}4/\text{mmm} \leftrightarrow \text{Abma} \leftrightarrow \text{P}4_2/\text{ncm}\) (THT \(\leftrightarrow\) ORT \(\leftrightarrow\) TLT), which is a common feature in \((\text{CH}_3\text{NH}_3)_2\text{MCl}_4\) compounds \((M = \text{Mn, Cd, Fe})\), is discussed on the basis of Landau theory, in comparison with available experimental results. Much attention is paid to the «anomalous» behaviour of the \(c_{66}\) elastic constant. After the microscopic model of mean-field type, developed previously by Blinc, Zeks and Kind, and from classical group theoretical considerations, it turns out that a Landau free-energy expansion up to the eighth-order is necessary to obtain a coherent description of all experimental data.

1. Introduction.

During the last fifteen years, much attention has been paid to the structural phase transitions occurring in perovskite-type layer compounds with formula \((\text{CH}_3\text{NH}_3)_2\text{MCl}_4\) (MAM Cl for short, with \(M = \text{Mn, Cd, Fe}\) [1, 2] and cited Ref.). The structure of these materials consists of double-layers of methylammonium groups (MA) sandwiched between perovskite-type layers made of corner-sharing \(\text{MCl}_6\) octahedra. All structural modifications found in these systems derive from a tetragonal high temperature parent phase (THT), with space-group

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I4/mmm and \( Z = 1 \) formula unit in the primitive unit-cell of the body-centred multiprimitive cell. In this phase, the MA groups are statistically distributed between four energetically equivalent orientations, so as to reconcile the four-fold site symmetry with the three-fold molecular symmetry [3-7]. Then, the phase transitions are governed essentially by ordering processes of the MA groups, coupled with rotations of the \( \text{MCI}_6 \) octahedra within the perovskite layers; the following phase sequence has been established, in the order of decreasing temperature:

\[
\begin{align*}
\text{I4/mmm} & \leftrightarrow \text{Abma} \leftrightarrow \text{P4}_2/\text{ncm} \leftrightarrow \text{P2}_1/\text{b} \\
(Z = 1) & \quad (Z = 2) \quad (Z = 4) \quad (Z = 2) \\
\text{THT} & \quad \text{ORT} \quad \text{TLT} \quad \text{MLT}.
\end{align*}
\]

The THT \( \leftrightarrow \) ORT transition is of second-order, while all other structural changes correspond to first-order transitions; also, in MA\( \text{MnCl} \) and MA\( \text{CdCl} \), all structural modifications exhibit orientational disorder of the MA groups, of dynamic nature, excepted the monoclinic low temperature phase (MLT) which is ordered [1-7]. In the case of MA\( \text{FeCl} \), the MLT phase has never been observed though experiments have been carried out down to liquid helium temperature, so that the phase sequence is reduced to THT \( \leftrightarrow \) ORT \( \leftrightarrow \) TLT [8]; thus, it can be thought that the ordered state of MA\( \text{FeCl} \) corresponds to the TLT phase.

Due to the ferroelastic character of the phase transitions in MAMCl compounds, numerous ultrasonic or Brillouin scattering experiments have been performed in order to analyze the behaviour of the elastic constants through the phase sequence [9-13]. All experimental data agree with an unexpected behaviour of the elastic constant \( c_{66} \) in the TLT phase, exhibiting almost complete softening when the TLT \( \leftrightarrow \) ORT transition temperature is approached from below (Fig. 1). Different approaches using Landau theory have been made to explain this «anomalous» behaviour of \( c_{66} \) [10, 13, 14]. In particular, the importance of an hypothetical orthorhombic low temperature phase (OLT) with space-group Pccn and \( Z = 4 \) has been stressed [10]; note that this phase has never been observed experimentally, but its existence can be predicted on simple group-theoretical grounds [6, 7, 10]. Moreover, different formulations for the Landau free-energy expansion as adopted by some authors have been the subject of controversy [10, 14-16].

The aim of the present paper is to reconsider this problem; we shall restrict ourselves to the THT \( \leftrightarrow \) ORT \( \leftrightarrow \) TLT sequence, which is a common feature for all three compounds (\( M = \text{Mn, Cd, Fe} \)). First, some basic aspects of Landau theory when applied to these systems

![Fig. 1. Schematized representation of the temperature dependence of the \( c_{66} \) elastic constant in MAMCl compounds with \( M = \text{Mn, Cd, Fe} \) (composed from Ref. [9-13]).](image-url)
will be recalled, as well as the essential results derived from a microscopic model by Blinc, Zeks and Kind [6, 7] (hereafter referred to as B.Z.K. model) which actually provides the best description of the transition mechanisms. Then, different formulations already proposed for the free-energy expansion [10, 13, 14] will be discussed in view of experimental results, and it will be stressed the need for a complex development of the thermodynamic potential including terms up to eighth-order.

2. Basic considerations and the B.Z.K. model.

2.1 GROUP THEORY. — From the only point of view of group theory, the phase sequence in MAMCl compounds can be explained by successive freezings of a two-dimensional order parameter at the zone boundary point X (D\textsubscript{2h} symmetry) of the THT Brillouin zone [17-20].

The star of the wave vector at point X contains two arms \((k_X = 00 \frac{1}{2} \frac{1}{2} 00)\) and the two-dimensional order parameter \((\eta_1, \eta_2)\) transforms according to the small representations \(X_2^+ / B_{2g}\) for \(\eta_1\) at X and \(X_2^+ / B_{3g}\) for \(\eta_2\) at \(\bar{X}\) (here we use the notation of Bradley and Cracknell [21]). Regardless of the stability conditions, four different phases can be expected owing to the symmetry properties of the order parameter components (Tab. I):

<table>
<thead>
<tr>
<th>(\eta_1)</th>
<th>(\eta_2)</th>
<th>(\eta_3)</th>
<th>(\xi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(X_2^+)</td>
<td>(X_2^+)</td>
<td>(\Gamma_4^+)</td>
<td>(Z_3)</td>
</tr>
<tr>
<td>(\Gamma_1^+)</td>
<td>(\Gamma_3^+)</td>
<td>(\Gamma_3^+)</td>
<td>(\Gamma_1^+)</td>
</tr>
</tbody>
</table>

Table I. — The symmetry properties of the primary \((\eta_1, \eta_2)\) and secondary \((\eta_3, \xi)\) order parameters in the different phases of MAMCl compounds (the notations of Bradley and Cracknell [21] are used).

i) the THT phase (I4/mmm) is described by the trivial solution \(\eta_1 = \eta_2 = 0\);
ii) the ORT phase corresponds to solutions such as \(\eta_1 \neq 0, \eta_2 = 0\) or equivalently by \(\eta_1 = 0, \eta_2 \neq 0\) (ferroelastic domains Abma/Bmab);
iii) the TLT phase (P4\(_2\)/ncm) is described by \(\eta_1 + \eta_2 \neq 0, \eta_1 - \eta_2 = 0\), or equivalently by \(\eta_1 + \eta_2 = 0, \eta_1 - \eta_2 \neq 0\) (antiphase domains);
iv) finally, the OLT phase (Pcn) corresponds to the general solutions where \(\eta_1 \neq 0, \eta_2 \neq 0\) with \(\eta_1 \neq \eta_2\). Note that Pcn is the common maximal sub-group of the Abma (Bmab) and P4\(_2\)/ncm space groups.

Still on the only basis of group-theoretical considerations, secondary order parameters can also be introduced, designated as \(\eta_3(\Gamma_4^+/B_{2g})\) and \(\xi(Z_3^+/B_{1g})\) [13, 17-20]; then, the THT phase is further characterized by \(\eta_3 = \xi = 0\), the ORT phase by \(\eta_3 \neq 0, \xi = 0\), the TLT phase by \(\eta_3 = 0, \xi \neq 0\) and the OLT phase by \(\eta_3 \neq 0, \xi \neq 0\) (Tab. I).

2.2 LANDAU THEORY. — Following the method developed by Gufan [22], see also Ref. [23], we introduce the full rational basis of invariants for the image of the primary order parameter \((C_4\nu\nu\nu, \text{in our case})\); we do not introduce here the secondary order parameters. Then, the Landau free-energy developed up to the eighth-order writes [23]:

\[
F = A_1 I_1 + A_2 I_1^2 + A_3 I_1^3 + A_4 I_1^4 + B_1 I_2 + B_2 I_2^2 + C_{12} I_1 I_2 + C_{112} I_1^2 I_2
\]  

(1)
where:

\[ I_1 = \eta_1^2 + \eta_2^2 = \rho^2 \]
\[ I_2 = (\eta_1^2 - \eta_2^2)^2 - 4 \eta_1^2 \eta_2^2 = \rho^4 \cos 4 \varphi \]

with \( \eta_1 = \rho \cos \varphi \) and \( \eta_2 = \rho \sin \varphi \).

In order to make things clear in the following, let us first come back to some basic results obtained when the expansion (1) is truncated to the fourth or to the sixth order terms in \( \eta_i \) (\( i = 1, 2 \)). In the case of a fourth-order development, i.e. when \( A_3 = A_4 = B_2 = C_{12} = C_{112} = 0 \), the range of stability is limited on the \( B_1 \) axis to values \( -A_2 < B_1 < A_2 \) with \( A_2 > 0 \) (Fig. 2); also, the OLT phase is never stable and the ORT \( \Leftrightarrow \) TLT transition is not possible as long as \( B_1 = \) constant, as usually taken. When adding the sixth-order terms, i.e. when \( A_4 = B_2 = C_{112} = 0 \) in (1), the range of stability is extended on the \( B_1 \) axis beyond the points \( B_1 = -A_2 \) and \( B_1 = A_2 \) which now become tricritical points; note that one should always have \( A_2 > 0 \) to account for a second-order THT \( \Leftrightarrow \) ORT transition (Fig. 3). In addition, the first-order ORT \( \Leftrightarrow \) TLT transition line is distorted, so that this transition is now possible at constant \( B_1 \), and sequences such as THT \( \Leftrightarrow \) ORT \( \Leftrightarrow \) TLT or THT \( \Leftrightarrow \) TLT \( \Leftrightarrow \) ORT can be predicted, depending on the sign of \( C_{12} \) (Fig. 3); note again that the OLT phase never appears. Finally, a number of situations encountered with the full

Fig. 2. — Phase diagram as determined from the potential (1), with \( A_3 = A_4 = B_2 = C_{12} = C_{112} = 0 \) \( (A_2 > 0) \). Dashed and continuous lines are respectively lines of second and first-order transitions. Hatched areas correspond to regions of instability.

Fig. 3. — Phase diagrams as determined from the potential (1), with \( A_4 = B_2 = C_{112} = 0 \). a) \( A_2 > 0, C_{12} > 0 \). b) \( A_2 > 0, C_{12} < 0 \). Dashed and continuous lines are respectively lines of second and first-order transitions.
development up to the eighth-order, with $A_2 > 0$, are represented in figure 4 [23]. The OLT phase now appears as a stable state; indeed, the eighth-order expansion provides three different (eighth-order) invariants, $I^4_1, I^2_2$ and $I^1_I I_2$, able to make the discrimination between the three expected low symmetry phases, ORT, TLT and OLT.

Fig. 4. — Phase diagrams as determined from the potential (1) (after Ref. [23]). a) $A_2 > 0$, $\Delta = 4 A_2 B_2 - C_{12}^2 > 0$, $C_{12} > 0$. b) $A_2 > 0$, $\Delta > 0$, $C_{12} < 0$. Dashed and continuous lines are respectively lines of second and first-order transitions.

2.3 THE B.Z.K. MODEL. — This model consists in a mean-field treatment of the ordering process of the MA groups in MAMnCl and MACdCl in a rigid network of octahedra [6, 7]. According to the structural data [3-5], these groups are supposed to be statistically distributed between four energetically equivalent orientations directed along [110], [110], [110] and [110] in the THT unit-cell (« orthorhombic » configuration [3, 4]). Let us call $\bar{\theta}_i (i = 1$ to $4$) the mean occupation probabilities of the MA group in each of its possible orientations; then, in the THT phase one has:

$$\bar{\theta}_1 = \bar{\theta}_2 = \bar{\theta}_3 = \bar{\theta}_4 = \frac{1}{4}.$$  (2)

This model leads to the definition of symmetry breaking multidimensional pseudo-spin coordinates [6, 7, 24]:

$$\begin{align*}
\Theta_1 &= \frac{1}{\sqrt{2}} (\bar{\theta}_1 - \bar{\theta}_3) \\
\Theta_2 &= \frac{1}{\sqrt{2}} (\bar{\theta}_2 - \bar{\theta}_4) \\
\Theta_3 &= \frac{1}{2} (\bar{\theta}_1 - \bar{\theta}_2 + \bar{\theta}_3 - \bar{\theta}_4)
\end{align*}$$  (3)

with

$$\sum \bar{\theta}_i = 1.$$  

In the $C_{4v}$ point group of the MA site, these coordinates belong to the $E(\Theta_1, \Theta_2)$ and $B_2(\Theta_3)$ representations, and they can generate in the I4/mmm space-group the $X^{a}_2 (\Theta_1)$,
secondary order axes around coordinates. The pseudo-spin transforming which the transition bilinearly. It has the parameter (\(\eta_1, \eta_2\)) and \(\eta_3\) order parameters, respectively (Tab. I). It is worth noting that none of the pseudo-spin coordinate (3) is able to generate the \(Z_3^+\) representation corresponding to \(\xi\) (Tab. I).

The mean field B.Z.K. treatment, including four-particles interactions is able to reproduce the phase sequence as observed in MAMnCl and MACdCl, excepted that the authors could not get rid of the existence of the OLT phase appearing as an intermediate state stable between ORT and TLT (Fig. 4), even though its domain of stability could be limited to a very narrow temperature range, by using a convenient set of coefficients [7]. It is also important to notice that, in the frame of this model, the ordered state (ground state) expected to occur as \(T \Rightarrow 0\) \((\bar{\theta}_1 = 1, \bar{\theta}_2 = \bar{\theta}_3 = \bar{\theta}_4 = 0)\) corresponds either to the ORT \((\theta_1 \neq 0, \theta_2 = 0\) and \(\theta_3 \neq 0)\) or to OLT phase \((\theta_1 \neq 0, \theta_2 \neq 0, \theta_3 \neq 0)\); so, an additional compulsory transition should occur leading either to the ORT or to OLT phase as an ultimate step. Instead of this, the ordered MLT phase takes place at low temperature; the transition to MLT is driven by an additional order parameter with \(X^+_3\), \(\bar{X}^+_3\) symmetry [7, 20] and exhibits some reconstructive character due to a change of the MA configuration from «orthorhombic» to «monoclinic» [4]. This transition will not be further considered.

Incoherent quasi-elastic neutron scattering experiments with MAMnCl [25] have been interpreted on the basis of the B.Z.K. model. It turned out that \(\theta_1\) and \(\theta_2\) (primary order parameter) are indeed of major importance in the transition mechanism, but that \(\theta_3\) (secondary order parameter) is almost negligible since, within experimental errors, one always has \(\bar{\theta}_2 = \bar{\theta}_4 = \frac{1}{4}\) in the ORT phase. In the TLT phase, one has \(\theta_1 = \theta_2 \neq 0\) and \(\theta_3 = 0\), as expected [25]:

The Raman scattering experiments performed with MAMnCl and MACdCl [20] have shown that coupling exists between the pseudo-spin coordinates and the rotary modes of the \(\text{MCI}_6\) octahedra. Because of the corner-shared octahedra arrangement, these rotatory modes are necessarily zone-boundary modes of the THT phase; in particular, octahedra rotations around axes contained in the layer planes have the \(X^+_3\) and \(\bar{X}^+_3\) symmetry, and so can be bilinearly coupled with \(\theta_1\) and \(\theta_2\), respectively. In contrast, there is no octahedra rotation transforming as the zone-centre \(\Gamma^+_4\) representation, so that direct coupling between octahedra rotation and \(\theta_3\) is forbidden by symmetry. Structural data [3-5], show that the \(\text{MCI}_6\) octahedra behave essentially as rigid bodies (the \(\Gamma^+_4\) octahedra distortion is small) and this certainly explains the fact that \(\theta_3\) is almost negligible. On the other hand, there is no lattice mode in the THT phase transforming as \(Z^+_3\), as it was already the case for the pseudo-spin coordinates. Thus, in the frame of the B.Z.K. model, the secondary order parameter \(\xi\) (Tab. I) has no physical meaning.

For the sake of completeness, let us point out that the ultimate step (ordered state) of the phase sequence in MAFeCl is the TLT phase. A modified version of the B.Z.K. model, in which the MA orientations lie along the \([100], [\overline{1}00], [010]\) and \([0\overline{1}0]\) directions «monoclinic» configurations [3, 4] is able to account for an ordered TLT ground state. Indeed pseudo-spin coordinates of the same form as (3) can be constructed, but now \(\theta_3\) belongs to the \(B_1(C_{4v})\) representation instead of \(B_2\); it follows that \(\theta_3\) can be associated with the secondary order parameter \(\xi(Z^+_3)\) which is the relevant one in TLT (Tab. I).
3. Discussion.

We intend in this section to reconsider the formulations of the Landau free-energy as previously introduced by different authors [10, 13, 14] in order to explain the peculiar behaviour of the $c_{66}$ elastic constant in the TLT phase; it will be shown that such a behaviour (Fig. 1) can be fully understood with the help of a eighth-order expansion.

First, let us recall that coupling terms of the form $e_6(\eta_1^2 - \eta_2^2)$ are allowed by symmetry (improper ferroelastic), where $e_6$ designates the $e_{xy}$ component of the strain tensor with $\Gamma_4^+$ symmetry in the THT phase. Thus, using a fourth-order expansion of the free-energy, a step like variation of the corresponding $c_{66}$ elastic constant is expected to occur at the transition temperature, with no additional temperature dependence [26], which is in contrast with the experimental results (Fig. 1). Of course, one may think about the influence of order parameter fluctuations but, at least in the TLT phase, there is no significant difference between the data obtained for $c_{66}$ by means of ultrasonic measurements at 5 MHz [12] and the Brillouin scattering ones obtained in the GHz range [13]. Obviously, additional terms should be introduced in the free energy expansion provided that their physical sense is in accordance with the basic statements presented in section 2.

3.1 Goto et al.'s FORMULATION. — Goto et al. have observed for the first-time the «anomalous» behaviour of $c_{66}$ in the TLT phase of MAMnCl and MACdCl, by means of ultrasonic measurements [9, 10]. They have considered the following expansion for the Landau-free-energy [10]:

$$F = a(\eta_1^2 + \eta_2^2) + \frac{1}{2} b (\eta_1^4 + \eta_2^4) + c \eta_1^2 \eta_2^2 + d \eta_2^2 +
+f \eta_3^4 - g \eta_3(\eta_1^2 - \eta_2^2) + \frac{1}{2} c_0 e^2 - h e \eta_3 - k e (\eta_1^2 - \eta_2^2). \quad (4)$$

In this expression, $\eta_1$, $\eta_2$ and $\eta_3$ are the same as defined in section 2, $e$ stands for $e_6$ and $c_0$ for $c_{66}^0$ (the «bare» $c_{66}$ elastic constant). As usual, the authors have put $a = a_0(T - T_1)$. The bi-linear coupling term $e \eta_3$ is able to account for a softening of $c_{66}$ provided that the $\eta_3$ order parameter fluctuation mode also softens. Since $c_{66}$ exhibits a strong softening in the TLT phase with increasing temperatures (Fig. 1), an unusual temperature dependence of the $d$ coefficient has been introduced, such as $d = d_0(T_3 - T)$ [10]. There are many problems with such a potential:

i) Because of the unusual temperature dependence of the $d$ coefficient, the parent THT phase cannot be stable above $T_3$, as stated already by Ishibashi and Suzuki [14].

ii) The secondary order parameter $\eta_3$ plays a prominent role in (4), since it is introduced as a full order parameter with its own (unusual) temperature dependence. Now, on the basis of experimental results [25], it has been stressed in section 2 that $\eta_3(\Theta_3)$ is almost negligible.

iii) The authors assertion [10] according to which the introduction of $\eta_3$ is the only way to explain the soft-mode with $\Gamma_4^+$ symmetry as observed on the Raman spectra of the TLT phase [20] is not correct. As shown in table I, such a mode can merely be assigned to the $(\eta_1 - \eta_2)$ component of the primary order parameter fluctuation mode, even though bi-linear coupling with an octahedra rotatory mode may occur (see Sect. 2).

3.2 Yoshihara et al.'s FORMULATION. — Brillouin scattering experiments on MAFeCl [13] have complemented previous ultrasonic results [12]; in particular, the behaviour of $c_{66}$ in the TLT phase has been confirmed, and for the first time, data have been obtained in
the ORT phase, as schematized in figure 1. Then, Yoshihara et al. have proposed the following free-energy expansion [13]:

\[
G = \frac{1}{2} \alpha(T) (\eta_1^2 + \eta_2^2) + \frac{1}{4} \beta (\eta_1^2 + \eta_2^2)^2 + \frac{1}{2} \gamma \eta_1^2 \eta_2^2 + \\
+ \frac{1}{2} c_{66}^0 \xi^2 + \frac{1}{2} a \xi^2 + A \epsilon_6 (\eta_1^2 - \eta_2^2) + B \xi \eta_1 \eta_2. \tag{5}
\]

Again, \(\eta_1, \eta_2\) and \(\xi\) as introduced in (5) are the same as defined in section 2; as usual, the authors have put \(\alpha(T) = \alpha_0(T - T_0)\). This is a fourth order expansion of the free energy and, as established in section 2, the ORT \(\Leftrightarrow\) TLT transition is not possible if the fourth-order coefficients are temperature independent. So, a temperature dependence of one of these coefficients is indirectly introduced by taking \(a = a_0(T - T_1)\) [13]. Indeed, after minimization of \(G\) with respect to \(\epsilon_6\) and \(\xi\), the renormalized fourth-order coefficients of the « effective » potential write [13]:

\[
\beta' = \beta - \frac{2A^2}{c_{66}^0} \tag{6}
\]

\[
\gamma' = \left( \gamma + \frac{4A^2}{c_{66}^0} \right) \left( \frac{T - T_2}{T - T_1} \right) \tag{7}
\]

with

\[
T_2 = T_1 + \left( \frac{B^2}{\gamma a_0} \right) \frac{c_{66}^0}{c_{66}^0 + \frac{4A^2}{\gamma}} > T_1. \tag{8}
\]

Then, the stability conditions for the ORT phase give in particular:

\[
\beta' > 0, \quad \gamma' > 0 \tag{9}
\]

and those for the TLT phase:

\[
\beta' > 0, \quad -2 \beta' < \gamma' < 0. \tag{10}
\]

Thus, \(T_2\) represents the actual ORT \(\Leftrightarrow\) TLT transition temperature at which \(\gamma'\) changes of sign and \(c_{66}^0\) (TLT) goes exactly to zero [13]. The additional temperature dependence of \(c_{66}^0\) on both sides of the THT \(\Leftrightarrow\) ORT transition temperature (Fig. 1) are assigned to critical fluctuations [13].

There are again problems with the potential (5):

i) According to (7), \(\gamma'\) changes of sign at \(T_2\) (ORT \(\Leftrightarrow\) TLT transition) but also it diverges at \(T_1\). This results in negative susceptibilities for the order parameter fluctuation modes as \(T \to T_1\). Indeed, because of (10), the potential (5) is not bound (the crystal is instable) in a range of temperature \(T_1 < T < T_1\) where:

\[
T_1 = T_1 + \frac{B^2}{2 a_0 \left( \beta + \frac{1}{2} \gamma \right)} < T_2 \tag{11}
\]

and in the absence of \(\xi^4\) terms, the potential (5) is also instable below \(T_1\) because \(a < 0\).

ii) As stated in section 2, the order parameter \(\xi\) can be a relevant one in MAFeCl, but has no physical sense in the case of MAMnCl or MACdCl. Clearly, \(\xi\) is not a determining
parameter, since the behaviour of the $c_{66}$ elastic constant is quite the same in all three compounds.

3.3 Ishibashi and Suzuki's Formulation. — In a critical examination of Goto et al.'s formulation (4), Ishibashi and Suzuki [14] have stressed the importance of sixth-order terms, in order to explain the temperature dependence of $c_{66}$ in both the ORT and TLT phases; the following thermodynamic potential is considered [14]:

$$f = \frac{\alpha}{2} (q_1^2 + q_2^2) + \frac{\beta}{4} (q_1^4 + q_2^4) + \frac{\gamma}{2} q_1^2 q_2^2 + \frac{c_0}{2} u^2 + \xi u (q_1^2 - q_2^2) + \frac{\eta}{6} (q_1^2 - q_2^2)^2 (q_1^2 + q_2^2). \quad (12)$$

In this expression, $q_1$ and $q_2$ stand for $\eta_1$ and $\eta_2$ (as defined in Sect. 2), respectively; $c_0$ stands for $c_{66}$ and $u$ for $e_6$. For convenience, the authors have introduced in (12) only one sixth-order invariant out of the two allowed ones. It should be pointed out that an algebraic error is contained in this paper: the equation of state for the TLT phase should read $\alpha + \frac{1}{2} (\beta + \gamma) q_T^2 = 0$ instead of $\alpha + (\beta + \gamma) q_T^2 = 0$ [14], so that the simulated curves for the behaviour of $q_T^2$ and $c_{66}(TLT)$, as well as the calculated phase diagram, are biased. Nevertheless, as stated in section 2, a sixth-order expansion is indeed able to reproduce the observed THT $\leftrightarrow$ ORT $\leftrightarrow$ TLT sequence, and to introduce a temperature dependence of $c_{66}(ORT)$ and $c_{66}(TLT)$ [14]; we shall come back on the implications of such a potential with the help of a more general formulation presented just below.

3.4 The Complete Eighth-order Development. — In order to make things clear and directly comparable with section 2, we have developed the thermodynamic potential as:

$$\Delta \phi = \Delta \phi (\eta) + \Delta \phi (e) + \Delta \phi (\eta, e) \quad (13)$$

where

$$\Delta \phi (\eta) = A_1 (\eta_1^2 + \eta_2^2) + (A_2 + B_1) (\eta_1^4 + \eta_2^4) + (2 A_2 - 6 B_1) \eta_1^2 \eta_2^2$$

$$+ (A_3 + C_{12}) (\eta_1^6 + \eta_2^6) + (3 A_3 - 5 C_{12}) (\eta_1^2 \eta_2^4 + \eta_1^4 \eta_2^2)$$

$$+ (A_4 + B_2 + C_{112}) (\eta_1^8 + \eta_2^8) + (6 A_4 + 38 B_2 - 10 C_{112}) \eta_1^4 \eta_2^4$$

$$+ (4 A_4 - 12 B_2 - 4 C_{112}) (\eta_1^2 \eta_2^6 + \eta_1^6 \eta_2^2) \quad (14)$$

$$\Delta \phi (e) = \frac{1}{2} c_{11}^0 (e_1^2 + e_2^2) + \frac{1}{2} c_{33}^0 (e_3^2 + e_5^2) + \frac{1}{2} c_{44}^0 (e_4^2 + e_6^2)$$

$$+ \frac{1}{2} c_{66}^0 e_5^2 + c_{12}^0 e_1 e_2 + c_{13}^0 (e_1 e_3 + e_2 e_3) \quad (15)$$

$$\Delta \phi (\eta, e) = g e_6 (\eta_1^2 - \eta_2^2) + h (e_1 + e_2) (\eta_1^2 + \eta_2^2) + k e_5 (\eta_1^2 + \eta_2^2) + \cdots \quad (16)$$

The expression (14) is nothing else than (1) (see Sect. 2) developed as a function of $\eta_1$ and $\eta_2$. The full expression of the elastic energy in a form adapted to the symmetry of the THT phase is given by (15), where the $e_i$'s ($i = 1$ to 6) are the components of the strain tensor and the $c_{ij}^0$'s are the associated elastic constants; (16) contains the coupling terms of lowest order between strain and order parameter components. All coefficients are supposed to be temperature independent, excepted $A_1$ which is written under the form $A_1 = a_1 (T - T_0)$. As shown in the preceding sections, the secondary order parameters $\eta_3$ or $\xi$ are not the relevant
ones in the bahaviour of $c_{66}$, so that they have been omitted in (13). Also, strictly speaking, the primary order parameter $(\eta_1, \eta_2)$ consists in linear combinations of pseudo-spin an octahedra rotation coordinates (see Sect. 2.3); for the sake of transparency, we do not come into such details (coupled pseudo-spin-phonon mechanism) and we consider the order parameter as a whole.

Minimizing $\Delta \phi$ (13) with respect to the $e_i$’s leads to an “effective” potential of the form:

$$\tilde{\phi} = A_1 \rho^2 + \left[ A_2 - a_2 + \left( B_1 - \frac{1}{2} b_1 \right) \cos 4 \varphi - \frac{1}{2} b_1 \right] \rho^4 +$$

$$+ (A_3 + C_{12} \cos 4 \varphi) \rho^6 + (A_4 + B_2 \cos^2 4 \varphi + C_{112} \cos 4 \varphi) \rho^8$$  \hspace{0.5cm} (17)

where:

$$a_2 = h \lambda_1 + \frac{1}{2} k \lambda_3$$

$$\lambda_1 = \frac{h c_{33}^0 - k c_{13}^0}{(c_{11}^0 + c_{12}^0) c_{33}^0 - 2 c_{13}^0}$$

$$\lambda_3 = \frac{k (c_{11}^0 + c_{12}^0) - 2 h c_{13}^0}{(c_{11}^0 + c_{12}^0) c_{33}^0 - 2 c_{13}^0}$$

$$b_1 = \frac{g^2}{2 c_{66}^0}.$$  

It should be noticed that (13) is reduced to a form similar to (12) when $a_2 = 0$ ($h = k = 0$), $A_3 = C_{12} \neq 0$ and $A_4 = B_2 = C_{112} = 0$. After straightforward but lengthy calculations, expressions can be established for the equations of state of the different phases, and for the temperature dependencies of the order parameter susceptibilities and of the elastic constants. In particular, in the THT phase $(T > T_0)$, it comes:

$$\rho_{\text{THT}} = 0$$

$$(X_{11}^0)^{-1} = (X_{22}^0)^{-1} = 2 \lambda_1 \cdot (X_2^0, \tilde{X}_4^0) \text{ mode}$$  \hspace{0.5cm} (19)

$$(X_{12}^0)^{-1} = (X_{31}^0)^{-1} = 0$$  \hspace{0.5cm} (20)

$$c_{66}(\text{THT}) = c_{66}^0.$$  \hspace{0.5cm} (21)

For the ORT phase $(T < T_0, \varphi = n \pi/2)$, one obtains:

$$A_1 + 2(A_2 + B_1 - a_2 - b_1) \rho^2_{\text{ORT}} + 3(A_3 + C_{12}) \rho^4_{\text{ORT}} + 4(A_4 + B_2 + C_{112}) \rho^6_{\text{ORT}} = 0$$  \hspace{0.5cm} (22)

$$(X_{11}^e)^{-1} = 8[(A_2 + B_1) \rho^2_{\text{ORT}} + 3(A_3 + C_{12}) \rho^4_{\text{ORT}} +$$

$$+ 6(A_4 + B_2 + C_{112}) \rho^6_{\text{ORT}}]: \Gamma_1^+ \text{ mode}$$  \hspace{0.5cm} (23)

$$(X_{22}^e)^{-1} = 8[(b_1 - 2 B_1) \rho^2_{\text{ORT}} - 2 C_{12} \rho^4_{\text{ORT}} - 2(2 B_2 + C_{112}) \rho^6_{\text{ORT}}]: \Gamma_3^+ \text{ mode}$$  \hspace{0.5cm} (24)

$$(X_{12}^e)^{-1} = (X_{31}^e)^{-1} = 0$$  \hspace{0.5cm} (25)

$$c_{66}(\text{ORT}) = c_{66}^0 \left[ 1 - \frac{b_1}{A_2 + B_1 + 3(A_3 + C_{12}) \rho^2_{\text{ORT}} + 6(A_4 + B_2 + C_{112}) \rho^4_{\text{ORT}}} \right].$$  \hspace{0.5cm} (26)
For the TLT phase \((T < T_0, \phi = (2 n + 1) \pi/4)\), one has:

\[
A_1 + 2(A_2 - B_1 - a_2) \rho^2_{\text{TLT}} + 3(A_3 - C_{12}) \rho^4_{\text{TLT}} + 4(A_4 + B_2 - C_{112}) \rho^6_{\text{TLT}} = 0
\]

\[
(X^\phi_{11})^{-1} + (X^\phi_{12})^{-1} = 8[(A_2 - B_1) \rho^2_{\text{TLT}} + 3(A_3 - C_{12}) \rho^4_{\text{TLT}} +
+ 6(A_4 + B_2 - C_{112}) \rho^6_{\text{TLT}}] \cdot \Gamma_1^+ \text{ mode}
\]

\[
(X^\phi_{11})^{-1} - (X^\phi_{12})^{-1} = 16[B_1 \rho^2_{\text{TLT}} + C_{12} \rho^4_{\text{TLT}} - (2B_2 - C_{112}) \rho^6_{\text{TLT}}] \cdot \Gamma_3^+ \text{ mode}
\]

\[
c_{66}(\text{TLT}) = c_{66}^0 \left[1 - \frac{b_1}{2B_1 + 2C_{12} \rho^2_{\text{TLT}} - 2(2B_2 - C_{112}) \rho^4_{\text{TLT}}} \right].
\]

In the OLT phase \([T < T_0, n\pi/2 < \phi < (2 n + 1) \pi/4]\), the equivalent expressions that could be obtained would be very complex because now both \(\rho\) and \(\phi\) are temperature dependent. Such expressions will not be given here, since the OLT phase has never been observed experimentally.

Attempts to fit the behaviour of the \(c_{66}\) elastic constant with the help of the expressions reported above would not be very meaningful, given the large number of free parameters that cannot be evaluated independently from other data (for instance, the temperature dependencies of the order parameter and of the susceptibilities in all phases are not still available). Nevertheless, one can at least discuss on the general trends predicted according to these equations.

Thus, in order to make the junction with section 3.3, we shall first consider a sixth-order expansion \((A_4 = B_2 = C_{112} = 0)\) with \(a_2 = 0\) and \(A_3 = C_{12} \neq 0\) [14]. We have represented in figure 5 the order parameter \(\rho^2\), the inverse susceptibilities \((X^\phi_{ij})^{-1}\) and the \(c_{66}\) elastic constant as a function of \(A_1 = a_1(T - T_0)\), for arbitrary sets of parameters that make possible the THT \(\leftrightarrow\) ORT \(\leftrightarrow\) TLT sequence to take place, with a second order THT \(\leftrightarrow\) ORT transition. The corresponding phase diagram is represented in figure 6.

The ORT \(\leftrightarrow\) TLT transition is related to a softening of the \(Y_3^\phi\) (ORT) mode and of the \(c_{66}(\text{TLT})\) elastic constant, but this softening is not complete at the transition temperature (first-order transition). Thus, at least qualitatively, the sixth-order expansion is already able to reproduce the behaviour of \(c_{66}(\text{ORT})\) and \(c_{66}(\text{TLT})\) (Fig. 1), with a convenient choice of the coefficients [14]. There are however fundamental limitations with such a potential:

i) In figure 6, we have represented the stability limits of the ORT and TLT phases, i.e. the lines where the \(Y_3^\phi\) (ORT) mode frequency (line 1) and where \(c_{66}(\text{TLT})\) (line 2) extrapolate to zero. The first-order ORT \(\leftrightarrow\) TLT transition line lies in between; it corresponds to points where the minimum value of \(\Delta\phi\) (ORT) is equal to that of \(\Delta\phi\) (TLT) (see relation (17)). It can be demonstrated that lines 1 and 2 can never come upon, excepted at the triple point THT-ORT-TLT (Fig. 6). Thus, it becomes evident that the exact cancellation of \(c_{66}(\text{TLT})\) on the ORT \(\leftrightarrow\) TLT transition line prevents the ORT phase to appear in the phase sequence (as far as \(B_1\) is constant).

ii) As stated in section 2, the ordered ground state expected for MAMnCl and MACdCl as \(T \rightarrow 0\) is the ORT or OLT phase; obviously, the sixth-order potential is not able to account for this implication of the B.Z.K. model.

iii) The concomitant softening of the \(Y_3^\phi\) (ORT) mode and of the \(c_{66}(\text{TLT})\) elastic constant \((\Gamma_3^+\)\) represents premonitory effects for the occurrence of the OLT phase (Tab. 1), which can never be stable.

Thus, let us now examine the influence of eighth-order terms. As seen from relations (24)
Fig. 5.— Temperature dependence of the order parameter, of the susceptibilities and of the $c_{66}$ elastic constant, calculated from relations (18) to (30). The following values of the coefficients have been chosen: $A_2 = 0$, $A_2 = A_3 = C_{12} = b_1 = 1$, $A_4 = B_2 = C_{112} = 0$ and (a) $B_1 = 0$, (b) $B_1 = 0.25$, (c) $B_1 = 0.5$. 
and (30), these terms can be destabilizing ones for both the ORT and TLT phases (and so become stabilizing ones for the OLT phase) provided that:

\begin{align}
2 B_2 + C_{112} & > 0 \quad (31) \\
2 B_2 - C_{112} & > 0 . \quad (32)
\end{align}

On the other hand, positive values of the discriminant \( \Delta = 4 A_2 B_2 - C_{112}^2 (A_2 > 0) \) [23] prevents the ORT \( \Leftrightarrow \) TLT transition to occur, since OLT will be always stable between ORT and TLT (Fig. 4). Thus, interesting features can be observed in the phase diagram in the intermediate case where \( \Delta < 0 \) (\( A_2 > 0 \)) and where relations (31) and (32) are fulfilled (note that one always has \( \Delta < 0 \) in the case of a sixth-order expansion (\( B_2 = 0 \))). As a matter of fact, the lines 1 and 2 now can come across, leading to the existence of a multicritical (triple) point at the junction of two second-order transition lines (ORT \( \Leftrightarrow \) OLT and TLT \( \Leftrightarrow \) OLT) and of a first-order one (ORT \( \Leftrightarrow \) TLT) (Fig. 7). Increasing values of \( \Delta \) make this triple point to move towards the other THT-ORT-TLT triple point, and this latter becomes a four-phase point for positive values of \( \Delta \) (Fig. 4).

Now, the behaviour of the \( c_{66} \) elastic constant in both the ORT and TLT phases can be fully understood with the help of a thermodynamic path crossing the first-order ORT \( \Leftrightarrow \) TLT transition line very close to the ORT-TLT-OLT triple point, i.e. at the limit of stability of the OLT phase (Fig. 7). In figure 8, we have represented the behaviour of quantities of interest (see relations (18) to (30)) in such a situation. Marked differences can be noticed when compared to figure 5; in particular, \( c_{66} \) (TLT) goes exactly to zero at the triple point, whereas the ORT phase may be stable in a wide temperature range, as expected. At this stage, we have not tried to go further in the adjustment of calculated curves for \( c_{66} \) to the observed ones (Fig. 1), for reasons already mentioned. Let us note however that introduction of the \( a_2 \) coefficient resulting from the coupling with the volume strain (\( h \neq 0, k \neq 0 \)) will just renormalize \( A_2 \), but that a higher-order coupling term of the form \( e_2^L(\eta_1^2 + \eta_2^2) \) (which has been neglected in (16)) may be of some help for such adjustments, since it leads to an additional upward or downward temperature dependence of \( c_{66} \) (ORT) and \( c_{66} \) (TLT), depending on the sign of the corresponding coupling coefficient. Also, it should be pointed

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Fig. 6. — The phase diagram corresponding to the thermodynamic potential (13)-(17) with the following values for the coefficients: \( a_2 = 0, A_2 = A_3 = C_{112} = b_1 = 1, A_4 = B_2 = C_{112} = 0 \). Dashed and continuous lines are respectively lines of second and first-order transitions. The dotted lines correspond to the limit of stability of the ORT phase (1) and of the TLT phase (2).
Fig. 7. — The phase diagram corresponding to the thermodynamic potential (13)-(17) with the following values for the coefficients: \( a_2 = 0, A_2 = A_3 = C_{12} = b_1 = 1, A_4 = 1, B_2 = -C_{112} = 0.125 \). Dashed and continuous lines are respectively lines of second and first-order transitions. The dotted-dashed line is the inferred thermodynamic path for the MAMCI systems.

Fig. 8. — Temperature dependence of the order parameter, of the susceptibilities and of the \( c_{66} \) elastic constant, calculated from relations (18) to (30). The following values of the coefficients have been chosen: \( a_2 = 0, A_2 = A_3 = C_{12} = b_1 = 1, B_1 = 0.25, A_4 = 1, B_2 = -C_{112} = 0.125 \).

It is found that Landau theory will never account for a temperature dependence of \( c_{66}(\text{THT}) \) (see relation (21)) as observed experimentally (Fig. 1); thus, dynamical critical fluctuations have to be introduced [10, 13, 26] for a complete description of experimental data around the THT \( \leftrightarrow \) ORT transition.

Finally, it can be predicted from relations (30) and (32) that \( c_{66}(\text{TLT}) \) will cancel again at much lower temperatures (where eighth-order terms become important), so that the complete phase diagram will include a further transition to the reentrant OLT phase. Depending on the value of \( B_1 < \frac{1}{2} b_1 \) (Fig. 7), the complete phase sequences predicted by the eighth-order expansion are either THT \( \leftrightarrow \) ORT \( \leftrightarrow \) TLT \( \leftrightarrow \) OLT or THT \( \leftrightarrow \) ORT \( \leftrightarrow \) OLT \( \leftrightarrow \) TLT \( \leftrightarrow \) OLT, which is formally in agreement with the B.Z.K. model [7].


From the above discussion, it clearly appears that experimental data obtained on MAMCl systems cannot be accounted for in a satisfactory way by means of a fourth-order expansion of the Landau free-energy, including secondary order parameters [10, 13]; an expansion up to the eighth-order in the primary order parameter is necessary, even though a sixth-order expansion provides already interesting information on the behaviour of the \( c_{66} \) elastic constant [14].
In fact, the Raman scattering spectra of MAMnCl and MACdCl obtained several years ago [20] have been tentatively interpreted in terms of OLT phase « clusters » present in both ORT and TLT phases (short range ordering phenomena). This tentative interpretation finds some support in the present analysis, since the ORT ⇔ TLT transition probably takes place in the close vicinity of a multicritical ORT-TLT-OLT triple point.

A major difficulty encountered in the interpretation of experimental data is the non-observation of the OLT phase in MAMCl systems, whereas most of previous analyses (and also the present one) have stressed the importance of premonitory effects connected to fictitious ORT ⇔ OLT or TLT ⇔ OLT transitions [7, 10, 20]. Of course, many attempts have been made to stabilize the OLT phase. In particular, high pressure measurements with MAFeCl have been unsuccessful [12]; in the case of MAMnCl and MACdCl, a new high pressure phase has been evidenced, but the mechanism as established for the high pressure phase transition has nothing to do with the occurrence of the OLT phase [27, 28].

Now, judging from the value of $c_{66}(\text{TLT})$ at the ORT ⇔ TLT transition temperature [9, 13], one can evaluate qualitatively the nearness of the ORT-TLT-OLT triple point; it turns out that the smaller is the ionic radius of M$^{2+}$, the closer the triple point would be the ORT ⇔ TLT transition ($r_{\text{Fe}^{2+}} < r_{\text{Mn}^{2+}} < r_{\text{Cd}^{2+}}$). So, after such empirical considerations, it might be thought that MAMCl compounds with smaller M$^{2+}$ cations will give some chance to observe the OLT phase. As a matter of fact, MAMCl compounds with M = Cu$^{2+}$, Co$^{2+}$, Zn$^{2+}$ have been investigated. In MACuCl, a strong Jahn-Teller distortion of the CuCl$_6$ octahedra takes place, and the sequence of transitions is quite different from that considered here [29]. On the other hand, MAZnCl (and probably also Co$^{2+}$ compounds) belong to the A$_2$BX$_4$ family of crystals with β-K$_2$SO$_4$ structure, i.e. with tetrahedrally coordinated M$^{2+}$ cations [30]; the same holds true for MACdBr [31]. Moreover, changing the MA group by n-alkylammonium cations C$_n$H$_{2n+1}$NH$_3^+$ ($n = 2$, 3...) also changes the phase sequence [1, 2].

Thus, apparently, the THT ⇔ ORT ⇔ TLT sequence is the unique fact of MAMCl compounds with M = Mn, Fe, Cd and, unfortunately, we are still left with the non-existence of the OLT phase.

**Note added in proof:**
Just as this paper was accepted for publication, I learned from one of the referees that a similar discussion has been already developed, in the context of the copper oxides superconductors La$_{2-x}$Ba$_x$CuO$_4$, by Axe J. D., Moudden A. H., Hohlwein D., Cox D. E., Mohanty K. M., Moodenbaugh A. R. and Youwen Xu, *Phys. Rev. Lett.* 62 (1989) 2751.

References


