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The Multidimensional Pseudo Spin Model and its Application to Phase Transitions in Layered Perovskites

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Pseudo spins with dimensionality larger than two may be used to describe disordered molecular, or ionomolecular, crystals in which the molecules have several equivalent orientations. We show that such models predict complex ordering schemes for these crystals, we describe the various problems related to the construction of these schemes and apply this technique in detail to the case of $NH_3(CH_2)_5NH_3CdCl_4$ and briefly to other similar layered perovskites.

1. INTRODUCTION

There are many examples of solids which display some orientational disorder in the high temperature phases of their crystalline state[1]. This orientational disorder, which can affect one or several sets of molecules (or ions) existing in the unit cell, has sometimes (Pauling model[2]) to be described by its orientational probability distribution function, a continuous function of the Euler angles, which defines the probability of finding a molecule with a given orientation. In other cases (Frenkel model[3]), there is only a discrete set of equiprobable orientations between which the molecule jumps from time to time, the residence time in a given orientation being much longer than the jump time from one orientation to another. When this discrete set is made up of two equiprobable orientations, lowering of the temperature leads to a phase transition below which one orientation has a probability larger than the other, the latter eventually going to zero at 0 K. The problem is thus equivalent to an Ising problem, i. e. may be treated with the help of a 1/2 pseudo spin formalism.

The situation becomes more complex when, in the high temperature phase, there are $n > 2$ equivalent orientations. In the Frenkel picture, this will happen in the following case. Let G_s be the symmetry group, of order g_s, of the site where the molecule resides, G_M the symmetry group, of order g_M, of the molecule and G_m the subgroup, of order g_m, common to G_s and G_M: $g_s/g_m = n$ is then the number of equivalent orientations. Lowering the temperature, one may find a phase transition below which $p \geq 2$ orientations are still equivalent, the n-p other orientations having occupation probabilities lower than the p equivalent ones. Such a phase cannot lead to an ordered crystal at $0 \leftrightarrow K$ and other phase transitions must take place in order to break completely the symmetry between these p orientations and to achieve a total ordering.

The description of this series of phase transitions, with a partial symmetry breaking at each step, requires a model in which n discrete occupation numbers must be considered at once: a specific generalization of the 1/2 pseudo spin model is thus needed in the present case. The purpose of this paper is to developp such a model and discuss its various aspects. In order to make them clear, this paper is organized as follows.

Section 2 gives a short account of the theoretical basis of this study and of several difficulties which may be encountered in the simple case when there is one disordered molecule per unit cell, and when all the possible phase transitions take place at the center of the Brillouin zone: we shall show that various ordering scenarios may take place, and also that the simple group theoretical arguments derived from the dimensionality of the order parameter may lead to prediction of scenarios with too many phase transitions. An example related to the case where $G_s = D_{4h}$ and $G_m = C_{2v}$ will be discussed in Section 3. A short outline of the new problems which may arise when the transition does not take place at the center of the Brillouin zone, or when the various disordered molecules belong to the same set, is given in Section 4. The long Section 5 describes the complex situation which actually takes place in $NH_3(CH_2)_5NH_3$ $CdCl_4$ (in short $2C_5Cd$) where the molecular cation $NH_3(CH_2)_5NH_3$ which is on a site with $G_s = D_{4h}$ may have this C_{2v} symmetry but may also, at a high temperature, have a lower C_2 symmetry. There, some of the transitions take place at the Brillouin zone boundary, but are, in fact, rather trivial generalizations of one of the scenarios described in Section 3. Paragraph 5-*a* describes the various phases existing in this crystal and gives evidence of the existence of two types of $NH_3(CH_2)_5NH_3$ cations in the substance; the corresponding model, with two pseudo spins of different dimensionalities, is given in 5-*b* while paragraphs 5-*c* and 5-*d* apply the theory of Sections 2 and 4 to the two sequences of transitions met here. The generalization of the present technique to other layered perovskites of similar types is briefly considered in the last section (Section 6) of this paper.

2. THEORY: THE SIMPLEST CASE APPROACH

In this paper, we shall be only interested in the second order (or slightly first order) transitions which satisfy the usual Landau criteria. In the present section we shall deal with the case where one considers only one disordered molecule per unit cell. This molecule is located on a site of symmetry G_s, and of order g_s, and a subgroup G_m of G_s exists (of order g_m) which transforms the disordered molecule into itself. This means that the molecule may have $n = g_s/g_m$ distinct, but equivalent, orientations that we shall label with index a, and we shall consider the variable θ_a^L which has the value 1 if the molecule in the cell L has orientation a and the value 0 otherwise. If one admits, in the Frenkel model, that only these n orientations are available, the θ_a^L satisfies the condition:

$$\sum_{a=1}^{a=n} \theta_a^L = 1 \qquad \forall L \tag{1}$$

Neglecting the influence of the motions of the molecular centers of mass (absence of orientation — translation coupling[4]) and considering, to simplify the problem, only pair interactions between the disordered molecules, the Hamiltonian of the system may be written as:

$$H = \frac{1}{2} \sum_{\substack{LL' \\ ab}} J_{ab}^{LL'} \, \theta_a^L \theta_b^{L'} \tag{2a}$$

$$J_{ab}^{LL} = 0 \qquad \forall a,b \tag{2b}$$

Using (2a) it is, at least in priciple, possible to compute the partition function, and the free energy of the system. In this section, we shall consider only phase transitions which take place at the center of the Brillouin zone; in a mean field approximation, to which we can restrict ourselves for the problems under study, this free energy, F, may, by definition, be expressed with the help of:

$$\overline{\theta_a} = \frac{1}{N} \sum_L \theta_a^L \tag{3a}$$

$$J_{ab} = \sum_{L'-L} J_{ab}^{LL'} \tag{3b}$$

and of $\beta = \frac{1}{k_B T}$ where k_B is the Boltzman constant. In practice, it is more convenient to express this free energy with the help of β and of linear combinations, Θ_j^α, of $\overline{\theta_a}$, which transform as irreducible representations of G_s. In the present notation, j labels an irreducible representation, α labels a partner coordinate if the dimension of j is larger than 1, and the transformation matrix U^{α}_{ja}, where:

$$\Theta^{\alpha}_j = \sum_a U^{\alpha}_{ja} \overline{\theta_a} \tag{4}$$

is a unitary matrix.

If j_o is the unity (or trivial) representation of G_s, (1) and (4) imply:

$$\Theta_{j_0} = \frac{1}{\sqrt{n}} \qquad \forall T \tag{5a}$$

The high temperature phase is easily described, using these notations, by:

$$\Theta_j^\alpha = \frac{1}{\sqrt{n}} \, \delta_{j\alpha, j_0} \tag{6a}$$

while the $T = 0$ ordered phase is more easily characterized by:

$$\overline{\theta}_a = \delta_{a,a_0} \tag{6b}$$

where a_o is one of the n possible orientations.

Due to (6a), it is convenient to make an expansion of $\overline{F}$ in increasing powers of Θ_j^α. One then obtains, using a straightforward procedure:

$$\overline{F} = \frac{1}{2} \sum_{j,\alpha} (kT - J_j^\alpha)\, \Theta_j^{\alpha^2} + \frac{1}{3!} \sum_{\{j_1,\alpha_1\}} J_{3 j_1 j_2 j_3}^{\alpha_1\alpha_2\alpha_3} (T)\, \Theta_{j_1}^{\alpha_1}\, \Theta_{j_2}^{\alpha_2}\, \Theta_{j_3}^{\alpha_3} +$$

$$+ \frac{1}{4!} \sum_{\{j_1,\alpha_1\}} J_{4\, j_1 j_2 j_3 j_4}^{\alpha_1\alpha_2\alpha_3\alpha_4} (T)\, \Theta_{j_1}^{\alpha_1}\, \Theta_{j_2}^{\alpha_2}\, \Theta_{j_3}^{\alpha_3}\, \Theta_{j_4}^{\alpha_4} + \ldots \tag{7}$$

In (7), the first term represents the lowest contribution in Θ_j^α to the entropy, the second is the mean field energy, where:

$$J_j^\alpha = \sum_{ab} U^{\alpha}{}_{j}{}^{a}\, J_{ab}\, U^{b}{}_{j}{}^{\alpha} \tag{8}$$

and the following terms arise from higher contributions in Θ_j^α to the entropy, each of these terms belonging to the unity representation j_o.

(7) has the usual form of a Landau type of free energy expansion, and one is thus able to perform a standard analysis of this free energy. There are, nevertheless, two aspects which are characteristic of the problem under study and thus deserve a special treatment.

a) $\overline{F}$ is a function of the $(n - 1)$ independent order parameters Θ_j^α, and the first transition, which will take place at Tc_1, will be driven by that j, α which corresopnds to the maximum J_j^α value, with $k_B\, Tc_1 = j_{j_1}^{\alpha_1}$. Just below Tc_1, the molecular site symmetry will correspond to the subgroup G_{s_1} of G_s which leaves Θ_j^α invariant. The other order parameters $\Theta_j^\alpha((j, \alpha) \neq ((j_1\, \alpha_1)\, U\, (jo)))$ are reducible representations of G_{s_1}, which, once reduced, do not belong, in general, to its unity representation, even if some of them (secondary order parameters — *c. f.* scenario 2 of the example of Section 3) belong to this trivial representation. Some order parameters are then not frozen at Tc_1, and one must, then, look for a second critical temperature Tc_2...

Consequently, for a system of pseudo spins with a dimensionality larger than 2, a more or less complex series of successive second order phase transitions exists, which will depend on the order through which the various order parameters will freeze. This aspect, which will be examplified by the three scenarios described in Section 3, is not specific to the case of one molecule per cell ,and a Brillouin zone center transition, as it will be discussed in Section 4, and in Section 5 for the specific case of $2C_5Cd$.

b) Conversely, the lowest temperature phase does not, necessarily, correspond to the freezing of all order parameters. Indeed, if the $T = 0$ situation corresponds to $\overline{\theta}_a = \delta_{a,a_0}$, in the same phase for finite temperature, and $b \neq a_o$, $\overline{\theta}_b$ is different from zero. It is possible that, in the sub group G_{s_p} of G_s obtained after p successive phase transitions, its various operations leave a_o invariant but transform b into b', b'',...; this implies that some order parameters are still equal to zero, as some orientations of the pseudo spin are still equivalent. There are then two possible scenarios.

— Either when $T \to 0$, $\overline{\theta}_{a_0} \to 1$ while all the $\overline{\theta}_b$ ($b \neq a_0$) $\to 0$. The lowest temperature phase, though completely ordered at $T = 0$, corresponds to zero values of some order parameters, even in the vicinity of $T = 0$.

— Or the thermal evolution of the free energy implies one (or several) additional symmetry breakings. These additional transitions may be of second order, and some (or all) additional order parameters may end up being non zero in the lowest temperature phase for $T \neq 0$.

It is not a priori possible to predict which possibility will actually take place without a precise study of F in each specific case. One must simply notice that the naive idea that all the order parameters must be frozen in the low temperature phase is incorrect in the case of pseudo spins with a dimensionality higher than 2: in other words, symmetry considerations based on the formal study of (7) without taking into account the physical problem underlying this expansion may lead to incorrect statements about the completly ordered phase. The example discussed in Section 3 will show the possibility of such situations.

3. A SIMPLE EXAMPLE

Let us discuss, in this section, an example which will serve as a preliminary to the study of $2C_5Cd$ performed in Section 5. We shall consider a crystal with molecular orientational disorder, described by the space group $P4/mmm$ (D^1_{4h}) with one disordered molecule located at the center of the cell. The factor group is isomorphous to group D_{4h}, and so is the site symmetry group G_s. Let us, furthermore, suppose that the isolated molecule has C_{2v} ($\equiv G_m$) symmetry, and that, in the crystal, one of its orientations is such that its twofold axis is along Ox, its two symmetry planes being σ_z and σ_y. The G_M and G_m are identical, $g_s/g_m = n = 4$, and the four distinct orientations correspond to the four directions ± Ox and ± Oy. We shall, in the following and in Section 5, adopt the convention that θ_1 corresponds to an occupation along $\vec{Ox}$, θ_2 to $\vec{Oy}$, θ_3 to $-\vec{Ox}$ and θ_4 to $-\vec{Oy}$. With the help of projection operators, it is easily found that the four $\overline{\Theta}_a$ generate the three irreducible representations A_{1g}, B_{1g} and E_u (doubly generate) of G_s with the unitary transformation matrix:

$$U^{j}_{\alpha^a} = \frac{1}{2} \left| \begin{array}{cccc} 1 & 1 & 1 & 1 \\ 1 & -1 & 1 & -1 \\ \sqrt{2} & 0 & -\sqrt{2} & 0 \\ 0 & \sqrt{2} & 0 & -\sqrt{2} \end{array} \right| \tag{9}$$

and we shall note the four symmetrized coordinates $\Theta_{A_{1g}}$, $\Theta_{B_{1g}}$, $\Theta^{1}_{E_u}$ and $\Theta^{2}_{E_u}$, respectively. The three last ones are possible order parameters and we shall now discuss the three possible scenarios which may take place when one considers only second order phase transitions related to the center of the Brillouin zone.

3-a) Scenario 1: $\Theta_{B_{1g}}$ as First Order Parameter

$\Theta_{B_{1g}}$ is the first order parameter to freeze. Below Tc_1, G_{s_1} is the point group D_{2h}, in which $\Theta^{1}_{E_u}$ induces the irreducible representations B_{3u} and $\Theta^{2}_{E_u}$

the representation B_{2u} which are still possible order parameters. Using the inverse matrix $U_{aj\alpha}$ of (9) one obtains $\overline{\theta}_1 = \overline{\theta}_3 \neq \overline{\theta}_2 = \overline{\theta}_4$. Such a phase cannot be ordered since the largest orientational probability is still degenerate between two sites, and a second transition must take place at $Tc_2 < Tc_1$. Let us suppose that it implies the order parameter B_{3u} of the D_{2h} phase ($\equiv E_u{}^1$ of the D_{4h} phase). Below Tc_2, one obtains a phase in which $G_{s_2} = C^x{}_{2v}$ and where $\Theta_{B_{2u}}$ ($\equiv \Theta^2_{E_u}$ of D_{4h}) induces the representations B_1 or B_2 (depending on the choice of axes) of $C^x{}_{2v}$. Such a phase is not ordered from the formal Landau theory point of view. Nevertheless, using again $U_{aj\alpha}$ one obtains $\overline{\theta}_1 \neq \overline{\theta}_3 \neq \overline{\theta}_2 = \overline{\theta}_4$. We are thus in the case of paragraph *2-b* where, decreasing the temperature below Tc_2:

- Either $\overline{\theta}_2 = \overline{\theta}_4$ and $\overline{\theta}_3$ go continuously to zero, without any further transition and the zero temperature phase will be $C^x{}_{2v}$.

- Or, at Tc_3, Θ_{B_1} of this C_{2v} phase ($\equiv \Theta^2_{E_u}$ of D_{4h}) also freezes, generating a $C_s{}^z$ phase in which the four $\overline{\theta}_a$ are all different at finite temperature.

This first scenario corresponds to the two aspects discussed in paragraphs *2-a* and *2-b*: a succession of two necessary transitions at Tc_1 and Tc_2, and a possible, but not compulsory, transition at Tc_3.

3-b) Scenario 2: $\Theta^1_{E_u}$ as First Order Parameter

Let us suppose now that $\Theta^1_{E_u}$ is the first order parameter to get frozen. Below Tc_1, G_{s1} is directly the $C^x{}_{2v}$ group (obtained at Tc_2 in the preceding scenario). The B_{1g} representation is found to induce also the trivial representation of $C^x{}_{2v}$ (*c. f. 3-a*) *i. e.* $\Theta_{B_{1g}}$ plays the role of a secondary order parameter mentioned in paragraph *2-a*, while $E_u{}^2$ induces again the B_1 representation of $C^x{}_{2v}$. The scenario will then be the same as in paragraph *3-a*, and would have also been the same (except for an $x \Longleftrightarrow y$ interchange) if one had considered $\Theta^2_{E_u}$ instead of $\Theta^1_{E_u}$.

3-c) Scenario 3: $\Theta^+_{E_u}$ as First Order Parameter

At Tc_1, $\Theta^1_{E_u}$ and $\Theta^2_{E_u}$ may freeze with the same amplitude. This implies using no longer these order parameters but rather their linear combinations:

$$\Theta^{\pm}_{E_u} = \frac{1}{\sqrt{2}} (\Theta^1_{E_u} \pm \Theta^2_{E_u}) \tag{10}$$

In this situation, the freezing of $\Theta^+_{E_u}$ leads to $G_{s1} = C^{110}_{2v}$, for which the polar axis is along the direction [110], and the representations $E_u{}^-$ and B_{1g} both induce the irreducible representation B_1 (or B_2) G_{s1}. Applying again $U_{aj\alpha}$ leads to $\overline{\theta}_1 = \overline{\theta}_2 \neq \overline{\theta}_3 = \overline{\theta}_4$: a second transition must then take place at Tc_2 leading to $G_{s_2} = C_s{}^z$. This last scenario is thus completely determined by the symmetry properties of (7) contrary to the preceding two cases.

3-d) Summary of the Scenarios and Remarks

The three preceding scenarios are summarized in Table I in which we have indicated by an arrow the involved order parameter, and all the induced representations, the non compulsory transitions being given in parentheses. All these scenarios are also represented, in the form of a tree, in Figure 1,

TABLE I

The three scenarios of Section 3
For each scenario, the successive site symmetries are indicated in the first line, below which appear the representations induced in these sites by the three pseudo spin representations. The order parameter involved in each transition is shown by an arrow

D_{4h}	D_{2h}	C^x_{2v}	(C^z_s)	D_{4h}	C^x_{2v}	(C^z_s)	D_{4h}	C^{110}_{2v}	C^z_s
B_{1g}	$\rightarrow A_g$	A_1	A'	B_{1g}	A_1	A'	B_{1g}	B_1	$\rightarrow A'$
E^1_u	B_{3u}	$\rightarrow A_1$	A'	E^1_u	$\rightarrow A_1$	A'	E^+_u	$\rightarrow A_1$	A'
E^2_u	B_{2u}	B_1	$\rightarrow A'$	E^2_u	B_1	$\rightarrow A'$	E^-_u	B_1	$\rightarrow A'$

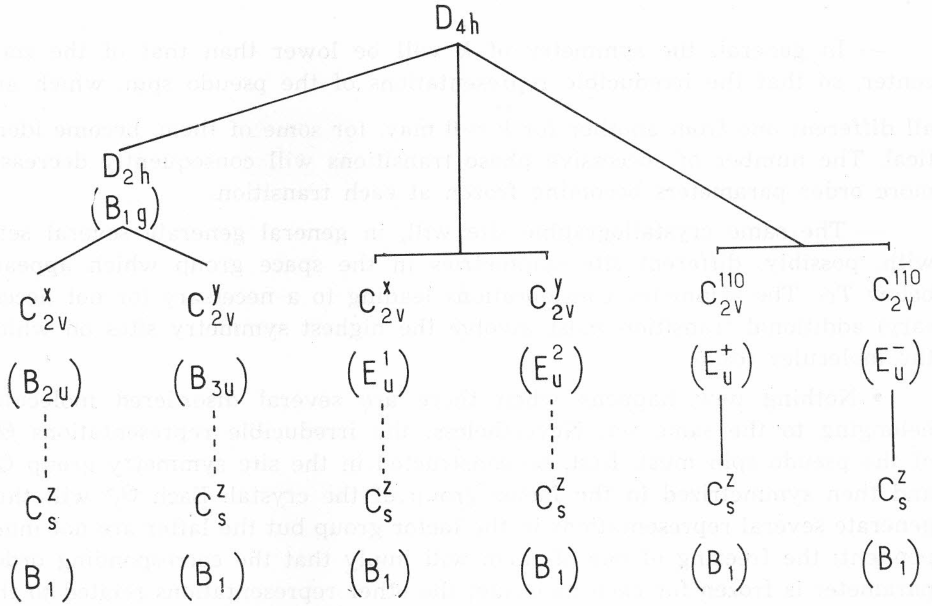

Figure 1. Representation of all the possible scenarios discussed in Section 3. The order parameter is given in parentheses, below the site symmetry found at the transition temperature. The full (resp. dotted) lines represent necessary (not compulsory) transitions.

in which the relevant order parameters appear in parentheses and where full (resp. dotted) lines represent necessary (resp. not compulsory) transitions.

The preceding example shows, on the one hand, the unusual complexity of this type of model, and on the other hand, that its treatment implies, at every step, a back and forth motion between the symmetrized and unsymmetrized variables in order to find out whether or not a transition is necessary.

4. GENERALIZATION TO MORE COMPLEX SITUATIONS

The problem treated in Section 2 may become more complex for two different reasons.

— The phase transition does not take place at the Brillouin zone center but at some other point of the zone.

— There are several disordered molecules, belonging to the same set *i. e.* related by symmetry operations of the space group of the high temperature phase, instead of one such molecule.

Both cases will appear together in the study of the phase transitions of $2C_5Cd$ conducted in Section 5, and it is thus useful to consider, beforehand, each case separately. None of them raises important new questions, and the general scheme exposed above remains essentially valid. Nevertheless, a few remarks have, to be made.

- In the case of transitions driven by $\vec{k} \neq 0$ wave vectors, two new aspects have to be considered.

— In general, the symmetry of $\vec{k}$ will be lower than that of the zone center, so that the irreducible representations of the pseudo spin, which are all different one from another for $\vec{k} = 0$ may, for some of them, become identical. The number of successive phase transitions will consequently decrease, more order parameters becoming frozen at each transition.

— The same crystallographic site will, in general generate several sets, with, possibly, different site symmetries in the space group which appears below Tc_1. The symmetry considerations leading to a necessary (or not necessary) additional transition must involve the highest symmetry sites on which the molecules reside.

- Nothing new happens when there are several disordered molecules belonging to the same set. Nevertheless, the irreducible representations Θ_j^α of the pseudo spin must, first, be constructed in the site symmetry group G_s, and then symmetrized in the factor group of the crystal. Each Θ_j^α will thus generate several representations in the factor group but the latter are not independent: the freezing of one of them will imply that the corresponding order parameter is frozen for each molecule; the other representations related to the same order parameter will not need to be further considered in the discussion of the necessary phase transitions. Such a case will appear in paragraph 5-c, in the case of the OHT ↔ ORT transition of $2C_5Cd$.

5. PHASE TRANSITIONS IN THE LAYERED PEROVSKITE $NH_3(CH_2)_5$ NH_3CdCl_4

As an example, let us consider now the case of pentylenediammonium cadmium tetrachloride, $NH_3(CH_2)_5NH_3$ $CdCl_4$; it will be shown that a pure order-disorder model based on multidimensional pseudo-spin variables is able to account for the sequence of transitions observed in this material.

5-a) — Experimental Results

$2C_5Cd$ belongs to the family of layered perovskites[5]. The structure consists of infinite sheets made of $CdCl_6$ octahedra sharing four corners (two-dimensional perovskite arrangement) (Figure 2); the cavities between the octahedra are occupied by the NH_3 polar heads of the diammonium groups. The pentylenediammonium chains are oriented perpendicular to the perovskite layers, and inter-layer bonding is achieved by means of NH . . . Cl hydrogen bonds at both ends of the chain.

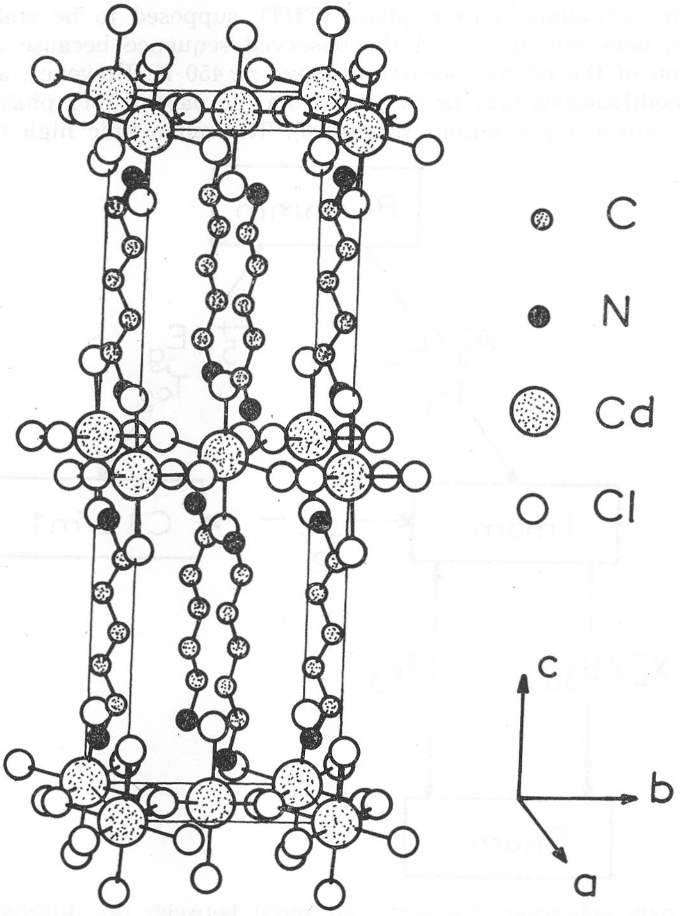

Figure 2. A schematic view of $NH_3(CH_2)_5NH_3CdCl_4$ in its hypothetical THT phase.

The parent phase belongs to the space-group $P4/mmm$ — D^1_{4h} [5,6,7] with $Z = 1$ formula unit per unit cell, and with orthogonal unit-vectors denoted by $\vec{t}_1$, $\vec{t}_2$ and $\vec{t}_3$ ($|\vec{t}_1| = |\vec{t}_2| \neq |\vec{t}_3|$): the $NH_3(CH_2)_5NH_3^{2+}$ groups are located on sites with D_{4h} ($\equiv G_s$) symmetry, which are not compatible with the molecular symmetry which may be considered to be C_{2v} for this »trans« conformation of the chain; this structure must then exhibit orientational disorder of the organic group in order to achieve, statistically, the D_{4h} site symmetry.

Recent experimental data[5-8] have shown that $2C_5Cd$ undergoes a number of temperature-induced structural phase transitions, according to the following sequence:

$$\begin{array}{ccccc} C2/m - C^3_{2h} & \underset{417\text{ K}}{\overset{407\text{ K}}{\rightleftarrows}} & \text{Imam} - D^{28}_{2h} & \overset{337\text{ K}}{\longleftrightarrow} & \text{Pnam} - D^{16}_{2h} \\ (Z = 1) & & (Z = 2) & & (Z = 4) \\ (\text{MHT}) & \text{1st order} & (\text{OHT}) & \text{2nd order} & (\text{ORT}) \end{array}$$

where Z refers to the number of formula units per primitive (Wigner-Seitz) unit-cell. The tetragonal parent phase (THT), supposed to be stable at high temperature, does not appear in the observed sequence because of chemical decomposition of the crystal occurring above ≈ 450 K. However, all observed structural modifications may be derived from the parent THT phase by means of group — sub group relations (Figure 3). The monoclinic high temperature

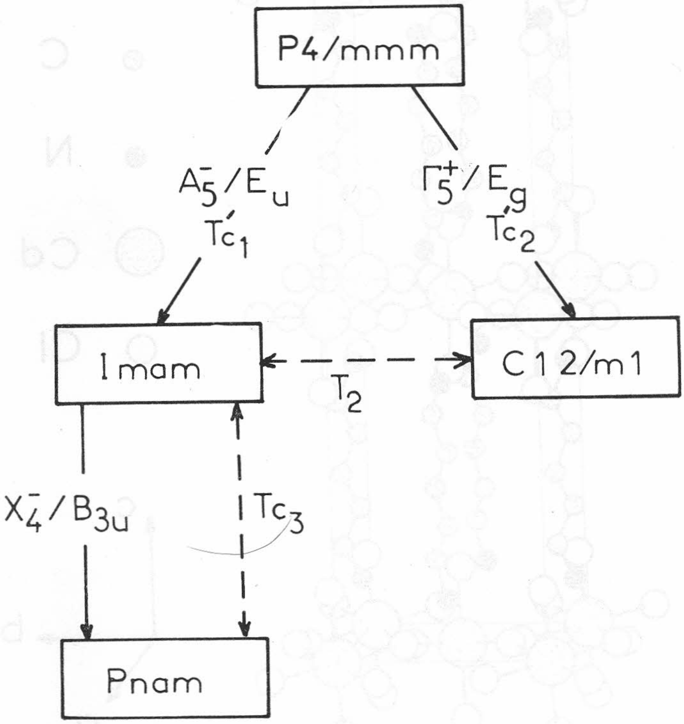

Figure 3. Group sub-group relations (full lines) between the different structural modifications of $2C_5Cd$. The observed phase transitions are indicated by the broken lines.

TABLE II

Symmetry relations between the different structural modifications of $2C_5Cd$

Phase	P4/mmm	C12/m1	Imam	Pnam
(a)	$\vec{a}_t = \vec{t}_1$ $\vec{b}_t = \vec{t}_2$ $\vec{c}_t = \vec{t}_3$	$\vec{a}_m \simeq \vec{t}_1 + \vec{t}_2$ $\vec{b}_m \simeq -\vec{t}_1 + \vec{t}_2$ $\vec{c}_m \simeq \vec{t}_3$ $\beta \neq 90°$	$\vec{a}_o \simeq \vec{t}_1 + \vec{t}_2$ $\vec{b}_o \simeq -\vec{t}_1 + \vec{t}_2$ $\vec{c}_o \simeq 2\vec{t}_3$	$\vec{a}_o \simeq \vec{t}_1 + \vec{t}_2$ $\vec{b}_o \simeq -\vec{t}_1 + \vec{t}_2$ $\vec{c}_o \simeq 2\vec{t}_3$
(b)	$\Gamma(0, 0, 0) \rightarrow$	$\Gamma(0, 0, 0)$		
	$\Gamma(0, 0, 0) \rightarrow$		$\Gamma(0, 0, 0) \rightarrow$	$\Gamma(0, 0, 0)$
	$A(\frac{\Pi}{a_t}, \frac{\Pi}{b_t}, \frac{\Pi}{c_t}) \rightarrow$		$\Gamma(0, 0, 0) \rightarrow$	$\Gamma(0, 0, 0)$
	$Z(0, 0, \frac{\Pi}{c_t}) \rightarrow$ $M(\frac{\Pi}{a_t}, \frac{\Pi}{b_t}, 0) \rightarrow$		$X(0, 0, \frac{\Pi}{c_o}) \rightarrow$	$\Gamma(0, 0, 0)$
(c)	$\Gamma_5^+/E^+_g \rightarrow$	Γ_1^+/A_g		
	Γ_4^+/B_{2g} - - →	Γ_1^+/A_g		
	$A_5^-/E_u^+ \rightarrow$		$\Gamma_1^+/A_g \rightarrow$	Γ_1^+/A_g
	Γ_4^+/B_{2g} - - →		Γ_1^+/A_g - - →	Γ_1^+/A_g
	$Z_3^+/B_{1g} \rightarrow$ $M_5^-/E_u \rightarrow$		$X_4^-/B_{3u} \rightarrow$	Γ_1^+/A_g

a) Parameters of the conventional crystallographic unit-cells[6].
b) Points of the Brillouin zone involved at the phase transitions[10].
c) Symmetry properties[10] of the primary (*full lines*) and secondary (*broken lines*) order parameters.

phase (MHT) on the one hand, and the orthorhombic phases (OHT and ORT) on the other hand, belong to two different branches of sub-groups. So, fictitious Landau-type transitions THT ↔ MHT and THT ↔ OHT may be considered. Table II gives the relationship between the conventional crystallographic

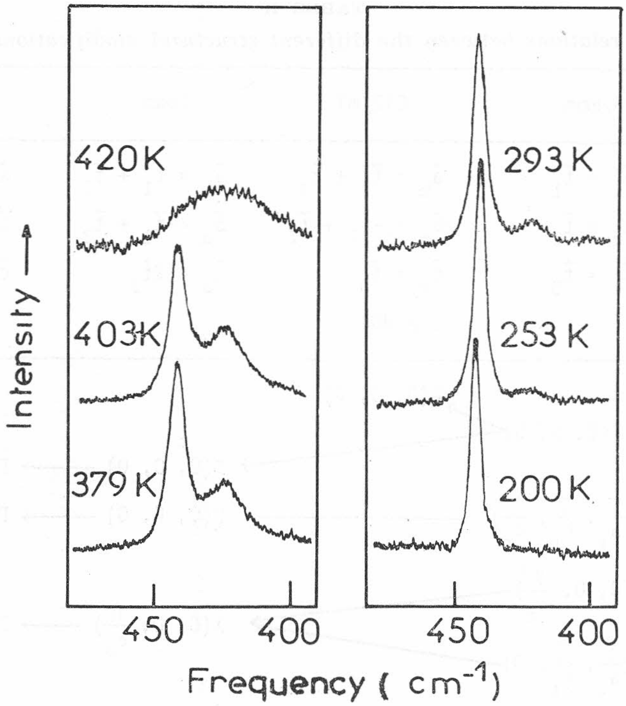

Figure 4. Evolution with temperature of the α_{zz} Raman spectrum of $2C_5Cd$ in the region of a CCC—CCN bending mode (after reference 6).

unit-cells of the different phases. Hence, the THT ↔ MHT transition corresponds to a lattice instability occurring at the zone-centre Γ point, and the THT ↔ OHT transition to an instability at the zone-boundary A point of the parent phase (Table II); as for the OHT ↔ ORT experimentally observed transition, it occurs at point X of the OHT phase, issued from the zone-boundary Z and M points of the parent THT Brillouin zone (Table II).

X-ray diffraction and Raman scattering experiments[6–8] have shown that orientational disorder of the pentylenediammonium chains is present in the MHT and OHT phases, whereas the ORT phase corresponds to an ordered structure at low temperature. In addition, conformational disorder of the chains is superimposed on the orientational disorder. This has been clearly proved by studying the Raman spectra of $2C_5Cd$ [7,8]: in the spectral range corresponding to the internal vibrational modes of the diammonium chains, the only features due to the »trans« conformation are observed at low temperatures, but a number of new lines assigned to another conformation progressively grow in intensity with increasing temperature. As an example, Figure 4 shows such a spectral evolution observed for the CCN—CCC bending modes (400—450 cm^{-1}), where a new line at 420 cm^{-1} begins to appear around $\approx$ 250 K and grows to the expense of the »trans« line at 440 cm^{-1}. These new lines have been assigned to a thermally activated »twisted« state of the chains[5–8] resulting from a rotation by $\approx 90^\circ$ of one of the NH_3 with respect to the other. From the temperature variation of the intensity ratio $I_{\text{»trans«}}/I_{\text{»twisted«}}$ of the Raman lines due to »trans« and »twisted« conformations (Figure 5), it has been shown[7] that the »trans« ↔ »twisted« equilibrium is well described by the relation:

$$\frac{p}{(1-p)} = A \cdot \exp\left(\frac{-\Delta H}{RT}\right) \tag{11}$$

where p and $(1-p)$ represent the relative proportions of »twisted« and »trans« forms, respectively, and where ΔH is the enthalpy of the reaction, A being a constant. The value of ΔH determined experimentally (Figure 5) is 4.1 ± 0.5 kcal/mol which is approximately one order of magnitude higher than the enthalpy corresponding to a »trans« ↔ »gauche« equilibrium in carbon chains; indeed, the »twisted« conformations can be expected to be much less stable than the »gauche« forms[5]. On the other hand, experimental data show that the »trans«↔ »twisted« equilibrium is not modified at the ORT ↔ OHT transition occurring in $2C_5Cd$ (Figure 5), whereas it is apparently shifted in favour of »twisted« chains at the OHT ↔ MHT transition (Figure 4). Finally, in the simple approximation where the twist angle between two neighbouring carbon atoms is constant along the chain axis[8], the »twisted« conformation belongs to the C_2 molecular point-group.

5-b) — *The Order-Disorder Model*

Let us first describe the structure of the fictitious parent THT phase in terms of a multidimensional pseudo-spin model; of course, we have to take into account the coexistence of »trans« and »twisted« states of the diammonium chains.

The structural data obtained in the OHT and ORT phases have shown that the »trans« chains in the crystal have the molecular C_{2v} symmetry, with the C_2 axis oriented parallel to the $\vec{t}_1$ or $\vec{t}_2$ directions and one symmetry plane perpendicular to $\vec{t}_3$ [8]. This refers to the case considered in Section 3 so that four eneregtically equivalent orientations for the »trans« chains will achieve statistically the D_{4h} site symmetry in the THT phase (Figure 4):

$$\overline{\theta_1} = \overline{\theta_2} = \overline{\theta_3} = \overline{\theta_4} = \frac{1}{4}(1-p) \tag{12}$$

The »twisted« chains belong to the C_2 point group and the C_2 axis in the crystal is oriented along the $(\vec{t}_1 + \vec{t}_2)$ or $(-\vec{t}_1 + \vec{t}_2)$ directions[8] Now, eight energetically equivalent orientations of the »twisted« chains are necessary to generate the D_{4h} site symmetry (Figure 6):

$$\overline{\theta_1}' = \overline{\theta_2}' = \ldots = \overline{\theta_8}' = \frac{1}{8}p \tag{13}$$

The symmetry properties of the pseudo-spin coordinates associated to the »trans« and »twisted« chains may be derived by means of the usual group-

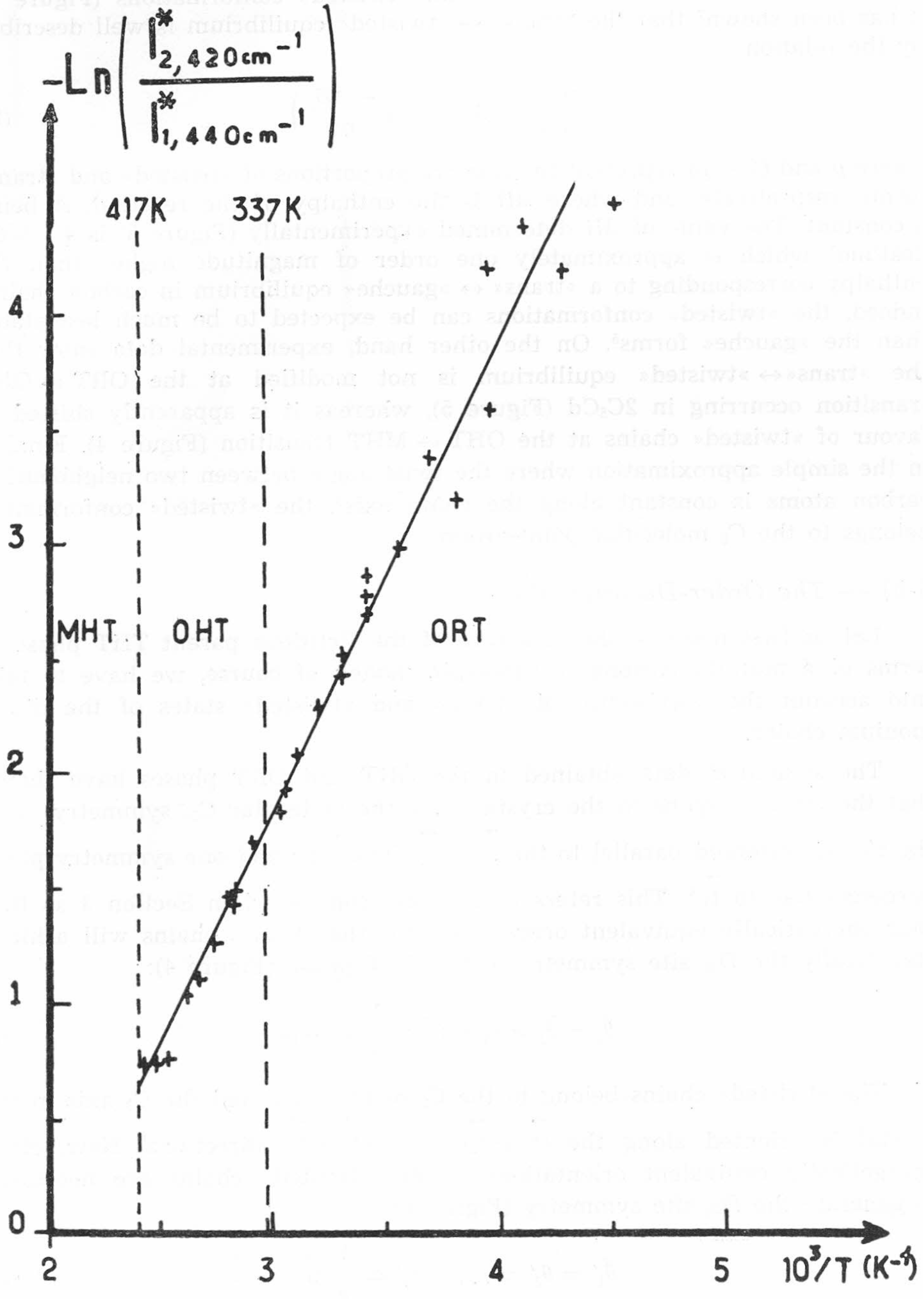

Figure 5. The temperature evolution of the intensity ratio $I_{420\ cm^{-1}}/I_{440\ cm^{-1}}$ of Raman lines due to »trans« (440 cm^{-1}) and »twisted« (420 cm^{-1}) chains (after reference 7).

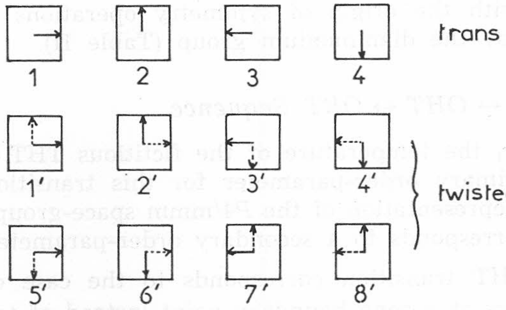

Figure 6. Schematic orientations of the four pseudo spins of the »trans« chains and of the eight pseudo spins of the »twisted« chains.

-theoretical methods. For the »trans« chains, four representations are found at $\vec{k} = 0$, with symmetry Γ_1^+/A_{1g}, Γ_3^+/B_{1g} and Γ_5^-/E_u (see Section 3), the transformation matrix of which is given by relation (9). The eight modes determined for the »twisted« chains of $\vec{k} = 0$ belong to the irreducible representations Γ_1^+/A_{1g}, Γ_4^+/B_{2g}, Γ_5^+/E_g, Γ_1^-/A_{1u}, Γ_4^-/B_{2u}, and Γ_5^-/E_u, with the transformation matrix given by:

$$\frac{1}{\sqrt{8}}\left|\begin{array}{rrrrrrrr} 1 & 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & -1 & -1 & -1 & -1 \\ 1 & -1 & -1 & 1 & 1 & -1 & -1 & 1 \\ 1 & -1 & -1 & 1 & -1 & 1 & 1 & -1 \\ 1 & -1 & 1 & -1 & -1 & 1 & -1 & 1 \\ 1 & -1 & 1 & -1 & 1 & -1 & 1 & -1 \\ 1 & 1 & -1 & -1 & -1 & -1 & 1 & 1 \\ 1 & 1 & -1 & -1 & 1 & 1 & -1 & -1 \end{array}\right| \qquad (14)$$

For the phase transitions studied here, it is necessary to consider not only the $\vec{k} = 0$ pseudo-spin representations but also the $\vec{k} \neq 0$ representations corresponding to high symmetry points in the THT Brillouin zone (Table II), and, to do this, one has to use the generalized method briefly discussed in Section 4. At this point, it is convenient to take the origin of the symmetry operations at the centre of mass of the diammonium chain; under this condition, the symmetry label of a given coordinate (for instance E_u) will be the same at all points of the Brillouin zone considered here (Γ_5^-/E_u, A_5^-/E_u, Z_5^-/E_u, M_5^-/E_u). Thus, four branches of pseudo-spin modes are determined for the »trans« chains and eight branches for the »twisted« chains, issued from the different $\vec{k} = 0$ representations (relations (9) and (14)). All branches, except for the A_{1g} ones, represent potential order-parameters for the transitions. However, it should be pointed out (see Section 4) that coordinates of a given branch are not independent; in other words, when freezing of an order-parameter occurs at a particular point of a branch, the whole branch is frozen and cannot induce any further phase transition.

Finally, we have determined the symmetry properties of the primary and secondary order parameters associated with the different phase transitions considered here, with the origin of symmetry operations taken in THT at the site occupied by the diammonium group (Table II).

5-c) — *The THT ↔ OHT ↔ ORT Sequence*

Let us call $T'c_1$ the temperature of the fictitious THT ↔ OHT transition (Figure 3). The primary order-parameter for this transition belongs to the A_5^-/E_u irreducible representation of the P4/mmm space-group while the representation Γ_4^+/B_{2g} corresponds to a secondary order-parameter (Table II).

The THT ↔ OHT transition corresponds to the case of paragraph *3-c*, except that it occurs at a zone boundary point instead of taking place at the zone-centre. The symmetrized coordinates of »*trans*« chains involved at this transition are (see relation (9)):

$$\Theta^1_{A_5^-} = \frac{1}{\sqrt{2}}(\overline{\theta}_1 - \overline{\theta}_3)$$

$$\Theta^2_{A_5^-} = \frac{1}{\sqrt{2}}(\overline{\theta}_2 - \overline{\theta}_4) \tag{15}$$

and the primary order-parameters are:

$$\Theta^{\pm}_{A_5^-} = \frac{1}{\sqrt{2}}(\Theta^1_{A_5^-} \pm \Theta^2_{A_5^-}) \tag{16}$$

$\Theta^{+}_{A_5^-}$ and $\Theta^{-}_{A_5^-}$ lead to the energetically equivalent Imam and Ibmm ferroelastic domains of the OHT phase, respectively. Then, the freezing of $\Theta^{+}_{A_5^-}$ (with $\Theta^{+}_{A_5^-} > 0$ for instance) induces an orientationally disordered state of the »trans« chains (Imam domains) described by:

$$\overline{\theta}_1 = \overline{\theta}_2 > \overline{\theta}_3 = \overline{\theta}_4 \qquad \text{with } \sum_a \overline{\theta}_a = (1-p) \tag{17}$$

Because of the cell-doubling occurring at the TMT ↔ OHT transition, the primitive OHT unit-cell contains two diammonium chains which still form one family set. Relation (17) describes an orientational disorder in which the »trans« chain at site (1) (origin of the symmetry operations) has a C_{2v} symmetry; the orientational disorder of the chain at site (2) is easily deduced by symmetry and is characterized by $\overline{\theta}_1 = \overline{\theta}_2 < \overline{\theta}_3 = \overline{\theta}_4$ with $\overline{\theta}_1$ at site (1) = $= \overline{\theta}_3$ at site (2) and *vice-versa.*

The freezing of $\Theta^{+}_{A_5^-}$ influences the pseudo spins corresponding to the »twisted« chains: it will freeze, in the same way, those Θ' representations which will belong to the unity representation at $\vec{k} = 0$ of the Imam space group. For these pseudo spins, we are in a case analogous to scenario n° 2) of Section 3 except for the fact that the secondary order parameter is Γ_4^+/B_{2g}. The revelant symmetrized coordinates involved at the TMT ↔ OHT transition are then (see relation (14)):

$$\Theta'^{1}_{A_5^-} = \frac{1}{\sqrt{8}} (\overline{\theta'}_1 + \overline{\theta'}_2 - \overline{\theta'}_3 - \overline{\theta'}_4 - \overline{\theta'}_5 - \overline{\theta'}_6 + \overline{\theta'}_7 + \overline{\theta'}_8)$$

$$\Theta'^{2}_{A_5^-} = \frac{1}{\sqrt{8}} (\overline{\theta'}_1 + \overline{\theta'}_2 - \overline{\theta'}_3 - \overline{\theta'}_4 + \overline{\theta'}_5 + \overline{\theta'}_6 - \overline{\theta'}_7 - \overline{\theta'}_8) \tag{18}$$

$$\Theta'_{B_{2g}} = \frac{1}{\sqrt{8}} (\overline{\theta'}_1 + \overline{\theta'}_2 + \overline{\theta'}_3 + \overline{\theta'}_4 - \overline{\theta'}_5 - \overline{\theta'}_6 - \overline{\theta'}_7 - \overline{\theta'}_8)$$

The freezing of $\Theta'^{+}_{A_5^-} = \frac{1}{\sqrt{2}} (\Theta'^{1}_{A_5^-} + \Theta'^{2}_{A_5^-})$ (primary order parameter) and of $\Theta'_{B_{2g}}$ (secondary order parameter), with for instance $\Theta'^{+}_{A_5^-} > 0$ and $\Theta'_{B_{2g}} > 0$, leads to a disordered state of the »twisted« chains in the OHT phase (site (1) in Imam domains) such as:

$$\overline{\theta'}_1 = \overline{\theta'}_2 > \overline{\theta'}_3 = \overline{\theta'}_4 > \overline{\theta'}_5 = \overline{\theta'}_6 = \overline{\theta'}_7 = \overline{\theta'}_8 \tag{19}$$

with $\sum_a \overline{\theta}_a' = p$.

For temperature $T \ll T'c_1$, one then obtains approximately:

$$\overline{\theta}_1 = \overline{\theta}_2 = \frac{1}{2}(1-p), \qquad \text{with } \overline{\theta}_3 = \overline{\theta}_4 \approx 0$$

$$\overline{\theta'}_1 = \overline{\theta'}_2 = \frac{1}{2} p, \qquad \text{with } \overline{\theta'}_3 = \ldots = \overline{\theta'}_8 \approx 0 \tag{20}$$

Relations (20) are in good agreement with the experimental data obtained in the OHT phase[7–8].

According to relations (11), and (20), the ground state of the OHT phase obtained at $T = 0$ still corresponds to a disordered state, such as $\overline{\theta}_1 = \overline{\theta}_2 = 1/2$ with all other $\overline{\theta}_a = 0$ and all $\overline{\theta}_a' = 0$; this justifies the existence of the OHT ↔ ORT transition, which is expected to lead to a completely ordered structure.

A group theory analysis[7] shows that the OHT ↔ ORT transition implies an order parameter belonging to the X_4^-/B_{3u} representation of the Imam space group. Such a representation may be generated by the pseudo spins representations of the »trans« chains which have not been frozen at $T'c_1$. Indeed, following the scenario n° 3 of Section 3, both the B_{1g} and E_u^- representations generate a B_1 representation in a site with C_{2v} symmetry, (sites (1) and (2)) which induces, in the D_{2h} factor group of Imam, the two representations B_{1g} and B_{3u}. More precisely, as indicated in Table II, only Z_3^+/B_{1g} and M_5^-/E_u^- induce X_4^-/B_{3u} in the Imam space group, Z_5^-/E_u^- and M_3^+/B_{1g} inducing X_3^+/B_{1g}. A phase transition involving X_4^-/B_{3u} must thus lead to a complete ordering of the »trans« chain pseudo spins, and the corresponding relevant coordinates are:

$$
\begin{aligned}
\Theta_{Z_3^+} &= \frac{1}{2}\,(\overline{\theta}_1 - \overline{\theta}_2 + \overline{\theta}_3 - \overline{\theta}_4) \\
\Theta^{-}_{M_5^-} &= \frac{1}{2}\,(\overline{\theta}_1 - \overline{\theta}_2 - \overline{\theta}_3 + \overline{\theta}_4)
\end{aligned}
\tag{21}
$$

According to relations (17) and (21), the orientational disorder present in the ORT phase at a finite temperature T will be given for the site (1) of $Pnam$ domains by:

$$
\begin{array}{ll}
& \overline{\theta}_1 > \overline{\theta}_2 > \overline{\theta}_3 > \overline{\theta}_4 \\
\text{or} & \qquad\qquad\qquad (\sum_{a} \overline{\theta}_a = (1 - p)) \\
& \overline{\theta}_1 > \overline{\theta}_2 > \overline{\theta}_3 > \overline{\theta}_4
\end{array}
\tag{22}
$$

depending on the relative amplitudes of $\Theta_{Z_3^+}$ and of $\Theta^{-}_{M_5^-}$. Each site has a C_s^z symmetry and the four molecules from a single family.

A similar analysis may be carried out for the »twisted« chain pseudo spins. Only the M_5^-/E_u representation freezes in at the transition, the representations A_{1u}, B_{2u} and E_g not being involved in the OHT ↔ ORT transition. One then obtains, using (19) and:

$$
\Theta'^{-}_{M_5^-} = \frac{1}{2}\,(-\overline{\theta'}_5 - \overline{\theta'}_6 + \overline{\theta'}_7 + \overline{\theta'}_8)
\tag{23}
$$

that, for the same site (1):

$$
\overline{\theta'}_1 = \overline{\theta'}_2 > \overline{\theta'}_3 = \overline{\theta'}_4 > \overline{\theta'}_7 = \overline{\theta'}_8 > \overline{\theta'}_5 = \overline{\theta'}_6\,(\sum_{a} \overline{\Theta'}_a = p)
\tag{24}
$$

which implies that, as expected, some disorder remains for the »twisted« chains in the $Pnam$ structure. Nevertheless, according to relation (11), $p \to 0$ when $T \to 0$, so that the ground state of the ORT phase corresponds to a completely ordered state containing »trans« chains only ($\overline{\theta}_1 = 1$ with all other $\overline{\theta}_a = 0$ and all $\overline{\theta}_a' = 0$); this is in agreement with the experimental data obtained in the ORT phase at low temperatures[6,7].

Thus, in spite of an apparent complexity due to the occurrence of phase transitions at $\vec{k} \neq 0$ and to the coexistence of »trans« and »twisted« states of the chains, the THT ↔ OHT ↔ ORT sequence of 2C$_5$Cd is formally equivalent to scenario n° 3 considered in Section 3, the results being indentical to those of that scenario for one given site, but different for the crystal symmetries due to cell multiplication at each transition. Furthermore, we see here that, as indicated in Section 4, the fact that a representation (here B_1) of the pseudo spin on a given site generates several different representations in the unit cell (B_{1g} and B_{3u} in Imam) does not modify the fact that B_1 is the proper order parameter: the freezing is complete in the Pnam phase when $T \to 0$.

5-d) — The THT ↔ MHT and MHT ↔ OHT Transitions

The primary order-parameter for the fictitious THT ↔ MHT transition belongs to the Γ_5^+/E_g irreducible representation of the $P4/mmm$ space-group, and the Γ_4^+/B_{2g} representation is associated with a secondary order parameter (Table II). None of the pseudo-spin coordinates attached to the »trans« chains correspond to these representations, so that the »trans« chains in MHT must stay in the same disordered state as in THT, *i. e.*

$$\overline{\theta}_1 = \overline{\theta}_2 = \overline{\theta}_3 = \overline{\theta}_4 = \frac{1}{4}(1-p) \tag{25}$$

In contrast, there are three relevant coordinates related to the »twisted« chains (relation (14)):

$$\begin{aligned} \Theta'^{1}_{E_g} &= \frac{1}{\sqrt{8}}(\overline{\theta'}_1 - \overline{\theta'}_2 - \overline{\theta'}_3 + \overline{\theta'}_4 + \overline{\theta'}_5 - \overline{\theta'}_6 - \overline{\theta'}_7 + \overline{\theta'}_8) \\ \Theta'^{2}_{E_g} &= \frac{1}{\sqrt{8}}(\overline{\theta'}_1 - \overline{\theta'}_2 - \overline{\theta'}_3 + \overline{\theta'}_4 - \overline{\theta'}_5 + \overline{\theta'}_6 + \overline{\theta'}_7 - \overline{\theta'}_8) \\ \Theta'_{B_{2g}} &= \frac{1}{\sqrt{8}}(\overline{\theta'}_1 + \overline{\theta'}_2 + \overline{\theta'}_3 + \overline{\theta'}_4 - \overline{\theta'}_5 - \overline{\theta'}_6 - \overline{\theta'}_7 - \overline{\theta'}_8) \end{aligned} \tag{26}$$

Then, the primary order parameters are (see paragraph *3-c*):

$$\Theta'^{+}_{E_g} = \frac{1}{\sqrt{2}}(\Theta'^{1}_{E_g} + \Theta'^{2}_{E_g}) \qquad C12/m1 \text{ domains}$$

$$\Theta'^{-}_{E_g} = \frac{1}{\sqrt{2}}(\Theta'^{1}_{E_g} - \Theta'^{2}_{E_g}) \qquad C2/m11 \text{ domains}$$

The freezing of the primary order parameter $\Theta'^{1}_{E_g}$ ($C12/m1$ domains) together with $\Theta'_{B_{2g}}$ (secondary order-parameter), with $\Theta'^{+}_{E_g} > 0$ and $\Theta'_{B_{2g}} >$ for instance, leads to a disordered state of the »twisted« chains in MHT such as:

$$\overline{\theta'}_1 = \overline{\theta'}_4 > \overline{\theta'}_2 = \overline{\theta'}_3 > \overline{\theta'}_5 = \overline{\theta'}_6 = \overline{\theta'}_7 = \overline{\theta'}_8 \; (\sum_a \overline{\theta'}_a = p) \tag{27}$$

From relations (25) and (27) it is clear that the MHT ground state cannot be ordered, so that a phase transition at $T < T'c_2$ (Figure 3) is necessary. Furthermore, the equilibrium value of the order parameter in the MHT phase, $\eta_0 = \overline{\theta'}_1 - 1/2\,(\overline{\theta'}_2 + \overline{\theta'}_5)$ is proportional to p. This means that $\eta \to 0$ when $T \to 0$ (relation (11)); in other words, the MHT phase is stabilized by the presence of »twisted« chains.

The MHT → OHT transition, occurring at $T_2 < T'c_2$ (Figure 3) corresponds to a shift from one branch of the sub-groups to another. Such a behaviour is well known in systems with competing order-parameters. The competing interactions in $2C_5Cd$ are due to the »trans« → »twisted« equilibrium. As shown previously, the increasing values of p with increasing temperature are a stabilizing factor for the MHT phase; so, as long as p is sufficiently low, the OHT (or ORT) phase is stable, while, above a threshold value of p, attained at T_2, the MHT phase becomes stable through a first-order phase transition.

Thus, the purely order-disorder model developed here is able to reproduce correctly the complex phase sequence observed in $2C_5Cd$. However, it cannot be considered as entirely realistic since we have ignored the deformations of the »perovskite« sub-lattice occurring at phase transitions[7–8], due to strong hydrogen bond interactions between the diammonium groups and the chlorine octahedra. Such interactions are probably responsible for the shift of the »trans« ↔ »twisted« equilibrium in favour of »twisted« chains observed at the OHT ↔ MHT transition[6], which our model is not able to reproduce. In other words, relation (11) is an oversimplified description of the »trans« ↔ »twisted« equilibrium in different structural modifications.

6. FURTHER EXAMPLES AND CONCLUDING REMARKS

It may be meaningful to consider now briefly the structural phase transitions occurring in the whole family of perovskite type layer compounds in view of the different scenarios predicted in Section 3.

We have established that the phase sequence of $2C_5Cd$ is governed by scenario n° 3, except for the occurrence of the MHT phase related to the existence of a conformational disorder of the chain. Most of the compounds of the »diammonium« series, with formula $NH_3(CH_2)_nNH_3MCl_4$ ($n = 3, 4, 5$ and $M = Mn$, Cd) exhibit phase sequences which would develop also according to scenario n° 3, were it not for »accidents« specific to each compound due to »non-Landau« (reconstructive) transitions[5]. For instance, in $2C_3Cd$ scenario n° 3 is interrupted, in a narrow temperature range, by the occurrence of a disordered phase (with probably Fmmm symmetry) resulting from a rotation by 45° of the pseudo-spin directions in the (*ab*) plane; in this case, the sequence of transitions is *P4*/mmm ↔ Imam ↔ Fmmm ↔ Pnam.

A common characteristic of crystals in the »diammonium« series is that they decompose before they reach the parent high temperature THT phase. This disadvantage no longer exists for a number of crystals of the »monoammonium« series $(C_nH_{2n+1}NH_3)_2MX_4$ [11]. In these cases, the parent THT phase is observed experimentally and belongs to the space-group *I4*/mmm ($Z = 1$). Now, in the expansion in terms of the pseudo spin coordinates, we must take into account the fact that the primitive unit-cell contains two alkylammonium groups (c. f. the generalized method presented in Section 4). These groups have C_s molecular symmetry and are located on sites with C_{4v} symmetry; so, $g_s/g_m = 4$ and a model similar to that considered for the trans chains of $2C_5Cd$ (Figure 2) is applicable.

The compound $(C_2H_5NH_3)_2$ $MnCl_4$ (C_2Mn for short) exhibits the following sequence of transitions:

$$\underset{(Z=1)}{I4/\mathrm{mmm}} \leftrightarrow \underset{(Z=2)}{Bmab} \leftrightarrow \underset{(Z=4)}{Pcab}$$

It can be shown that such a sequence exactly corresponds to scenario n° 3, with the occurrence of an intermediate disordered phase (*Bmab*), embedded between the parent phase (*I4*/mmm) and an ordered low temperature phase (*Pcab*). The cadmium homologue (C_2Cd) exhibits another phase transition at lower temperature *Pcab* ($Z = 4$) ↔ *P12*$_1$/a1 ($Z = 2$) due to the existence of competing order parameters; indeed, a phase sequence such as *I4*/mmm ↔ Bmam ↔ *P12*$_1$/a1 is another version of scenario n° 3.

The methyl compounds $(CH_3NH_3)_2MCl_4$ (M = Mn, Cd) have been widely studied, and they exhibit the same sequence of phase transitions[11]:

$$\begin{matrix} I4/\text{mmm} & \leftrightarrow & Bmab & \leftrightarrow & P4_2/\text{ncm} & \leftrightarrow & P12_1/\text{a}1 \\ (Z=1) & & (Z=2) & & (Z=4) & & (Z=2) \end{matrix}$$

In this case, the $CH_3NH_3^+$ group pseudo-spins are oriented at 45° with respect to the $\vec{t}_1$ and $\vec{t}_2$ directions. This means that the ground state of the *Bmab* phase is ordered; it can be shown easily that the transition *I4*/mmm ↔ ↔ *Bmab* now corresponds to scenario *n*° 2 and no further transition would be necessary to give an ordered phase. In fact, the *Bmab* ↔ *P4*$_2$/ncm phase change is associated to a shift from scenario *n*° 2 to scenario *n*° 3: indeed, in this case, the transition *I4*/mmm ↔ *P4*$_2$/ncm would correspond to the first step predicted by scenario *n*° 3. Finally, the low temperature transition *P4*$_2$/ncm ↔ *P12*$_1$/a1 is reconstructive, due to a change in the configuration of the $CH_3NH_3^+$ group in its cavity.

The few examples given above show clearly the potentialities of the multidimensional pseudo spin method: it allows for the prediction of ordering sequences, or scenarios, and has, thus, a predicting power, as well as it offers a possibility of classification of the various transitions which take place, *e. g.*, in the layered perovskites structures. Interestingly enough, in these materials, the transitions take place at various points of the Brillouin zone, but always at points of high symmetry. The various phase transitions are then, usually, either variations, at different points of the Brillouin zone, of one of the scenarios considered at the centre of the zone (*Γ* point) in Section 3, or first order transitions, representing (e. g., in $(CH_3NH_3)_2MnCl_4$) a shift from one scenario to another. The method presented here for ionomolecular crystals is clearly applicable to other systems, such as the plastic phases of some molecular crystals. For instance, molecules with general formula CX_4 (X = H, F, Cl, Br, CH_3...) with $G_M = Td$, display a crystalline high temperature disordered phase, which they form a *f.c.c.* Bravais lattice ($G_s = O_h$) while $G_m = D_{2d}$. Various low temperature phases have been reported for those crystals[12], with different metastable states. It is possible that similar studies could help clarifying this presently complex situation, as well as other similar ones.

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SAŽETAK

Multimedijski pseudospinski model i njegove primjene na fazne prijelaze u slojevitim perovskitima

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Pseudospinovi dimenzionalnosti veće od dva mogu se upotrijebiti u opisu nesređenih molekulskih, ili ionomolekulskih, kristala u kojima molekule imaju nekoliko ekvivalentnih orijentacija. Mi pokazujemo da takvi modeli predviđaju složene sheme sređivanja za te kristale, opisujemo različite probleme vezane uz konstrukciju takvih shema i detaljno primjenjujemo tu tehniku na slučaj $NH_3(CH_2)_5NH_3CdCl_4$, te skraćeno na druge slične slojevite perovskite.