STRUCTURAL PHASE TRANSITION IN THE CRYSTAL OF $CH_3 NH_3 Cd Br_3$
Pseudospin description using group theory

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RESUME

Le cristal de $CH_3NH_3CdBr_3$ présente une transition de phase de type ordre désordre vers 170K , entre une structure hexagonale (Z=2) et une structure orthorhombique complexe (Z=96) . Un modèle de pseudo spins à six dimensions est développé dans un essai de description du mécanisme de cette transition de phase . Les coordonnées de pseudo spins , associées au désordre orientationnel des groupes méthylammonium dans la phase hexagonale , sont déterminées à différents points de la zone de Brillouin . Des processus de couplage entre ces coordonnées sont capables de fournir des solutions possibles , compatibles avec la structure en" projection" , qui contient Z = 12 unités formulaires ; ces solutions constituent des hypothèses de travail pour la détermination de la structure de la maille complexe de basse température .

ABSTRACT

The crystal of $CH_3 NH_3 CdBr_3$ exhibits an order disorder phase transition at 170 K from an hexagonal (Z = 2) to a complex orthorhombic (Z = 96) structure . A six dimensional pseudo-spin model is tentatively used to describe the mechanism of this phase transition. Pseudo-spin coordinates, associated to the orientational disorder of the methylammonium groups in the hexagonal phase, are determined at different points of the brillouin zone. Coupling processes between these coordinates are able to provide possible solutions for the structure of the "projection" unit cell with Z = 12 , that could be taken as starting hypotheses for the structure determination of the complex unit cell of the low temperature phase.

I-INTRODUCTION

There are many examples of solids which display some orientational disorder in the high temperature phases of their crystalline state (réf.1). In a number of cases, this orientational disorder, which can affect several sets of molecules (or polyatomic ions), can be described in the framework of the Frenkel model (réf.2), where 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 an another. Such a situation generally occurs when the molecules reside on sites with higher symmetry than their own symmetry. The Frenkel picture for orientational disorder, when justified by experimental results, provides us with the definition of pseudo-spin coordinates attached to the different orientations of the molecule, which can be handled with the help of classical group theoretical methods (see e.g. (réf.3);(réf.4)). The "freezing" of one or several coordinates depending on the dimension of the pseudo-spin produces phases transitions to orientationally ordered phases, and so, the pseudo-spin variables act as order parameters (O.P.'S) for such transitions (réf.4).

The crystal of $CH_3NH_3CdBr_3$ (MACB) belongs to this class of materials ; it has been the subject of experimental studies by means of X- ray diffraction (réf.5);(réf.6) and Raman scattering measurements (réf.6). The phase of MACB ,stable at room temperature, is hexagonal, with space group $P6_3/mmc$ (D^4_{6h}) and Z = 2 formula units per unit cell ; the lattice parameters are defined as a_{hex}, c_{hex}. The structure consists of infinite chains made of face sharing $CdBr_6$ octahedra, running parallel to the $\vec{c}$ (hexad) axis (réf.5). The methylammonium (MA) groups, situated in the space between chains, occupy sites with $\bar{6}$ m 2 (D_{3h}) symmetry of order g_S = 12. Now, the molecular point group of the free MA group is 3 m (C_{3v}) of order g_M = 6, but, because of a tilt of the C-N bond with respect to the $\vec{c}$ direction (réf.5), its instantaneous position conserves a mirror m (σ_v) as a unique symmetry element, thus defining the point group m(C_s) of order g_m = 2 (réf.5);(réf.6); note that C_s is a common subgroup of both D_{3h} and C_{3v} point groups . Then, the number of equivalent orientations accessible to the MA group, i.e.the dimension of the pseudo-spin, is merely given by the ratio g_S/g_m = 6 (réf.4);(réf.6). A schematic representation of orientational disorder of the MA group in hexagonal MACB is shown in figure 1.

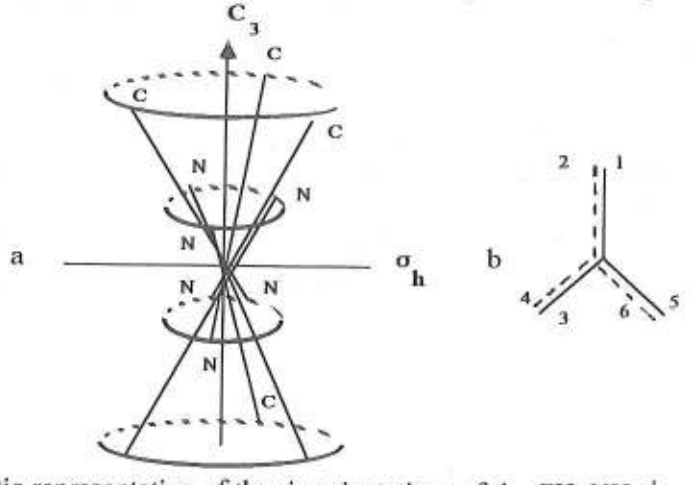

Figure 1 : Schématic representation of the six orientations of the $CH_3NH_3^+$ groups of MACB in the hexagonal phase , generating statistically a site with D_{3h} symmetry . a:Projection along direction perpendicular to c .b:Projection along c direction . Full lines : MA group oriented "up"(1,3,5) . Broken lines:MA group oriented "down" (2,4,6) .

A phase transition occurring at $T_c \approx 170$ K in MACB has been reported ; it is certainly of order-disorder type, connected with the reorientational dynamics of the MA groups (réf.6). Though this transition has found of first order, the Raman spectra recorded in the low temperature phase show that an important residual disorder is still present just below the transition temperature and then, the system gets progressively ordered by lowering the temperature. Under these conditions, it seems justified to consider the pseudo-spin variables acting as (O.P.'S), in the framework of Landau theory. Now, the symmetry of the temperature ordered phase of MACB, as determined by X-ray diffraction, is orthorhombic with a complex unit-cell involving not less than Z = 96 formula units (réf.6). Clearly, it would not be very meaningful to try to handle such a

complex system, especially in the absence of space group determination ; fortunately, as established in (réf.6) , a simplified representation of the structure at low temperature is provided by a "projection"unit-cell, which is still orthorhombic, and with lattice parameters such as $a_p \approx a_{hex}$, $b_p \approx \sqrt{3}\, a_{hex}$ and $c_p \approx 3\, c_{hex}$. This " projection unit cell is obtained by ignoring the spontaneous atomic displacements occurring along the $\vec{c}$ axis and contains Z = 12 formula units ; as a result, only a trebling of the lattice parameter along $\vec{c}$ and a doubling of one lattice parameter contained in the hexagonal plane are taken into account (réf.6).

In this paper, we will attempt to describe the phase transition of MACB on the basis of the six dimensional pseudo-spin model such as defined in figure 1. To do this, we shall refer to previous results obtained with related crystal of general formula $(CH_3)_4 NMX_3$ (M : Mn, Cd ; X : Cl, Br). As a matter of fact, all these systems exhibit an hexagonal chain like structure similar to that of MACB, but with disordered tetramethylammonium groups in place of the MA groups. The crystals of $(CH_3)_4 NMnCl_3$ (TMMC), $(CH_3)_4 NCd Cl_3$ (TMCC) and $(CH_3)_4 NCd Br_3$ (TMCB) have been widely studied as for their structural phase transitions (see e.g.(réf.7);(réf.8);(réf.9);(réf.10) and references cited therein), of which the mechanisms have also been discussed in terms of pseudo spin models.

Our discussion will be essentially focussed on the orthorhombic "projection" unit-cell of MACB (réf.6). First, it should be pointed out that the direct phase transition from the hexagonal (Z=2) to the orthorhombic ("projection") unit-cell (Z =12) may be described by a lattice instability occurring at point $U(0, \frac{1}{2}, \frac{1}{3})$ of the hexagonal Brillouin zone (réf.11) ; moreover , in the same time, points $M(0, \frac{1}{2}, 0)$ and $\Delta(0, 0, \frac{1}{3})$ are also replaced at zone centres in the orthorhombic phase, whereas point $\Gamma(0, 0, 0)$ is of course a zone centre in both phases .Thus, we could define a primary (O.P.) at the point U, knowning that secondary (O.P.'S) at points Γ, M or Δ may also be relevant ones in the transition mechanism . However, such a procedure prevents any intermediate phase to take place, with e.g. Z = 2, Z = 4 or Z = 6 . In fact, lattice instabilities occurring at points Γ and M have been clearly evidenced with TMMC and TMCC (réf.7), and another one occurring at point Δ has been observed with TMCB (réf.10) ; in addition, a complex ordered phase with Z = 12, similar to the "projection" unit cell of MACB, takes place at low temperature in the phase diagram of TMCC (réf.7);(réf.8). Thus , we shall postulate that all systems, including MACB, pertain to the same "generalized" phase diagram, which means that we assume that in all crystals the phase transitions are governed by similar mechanisms, so that intermediate with Z = 2 , Z = 4 or Z = 6 (such as those found with TMMC,TMCC and TMCB) "virtually" exist in the case of MACB. So, in this context, (O.P.'S)at points Γ, M and Δ are considered as primary ones and consequently, the "projection" unit cell with Z = 12 can be generated by means of non-linear coupling between (O.P'.S) at point M and Δ ; under these conditions, because of redundancy, there is no need to consider another (O.P.) at point U. It

should be noted that, from the sole point of view of group theory, these two procedures ((O.P.) at point U and coupled (O.P'.S) at points M and Δ) are absolutely equivalent as for the symmetry properties of the resulting "projection" unit-cell, but of course, they differ in the description of the physical mechanisms involved at the phase transitions ; the last one seems to us more realistic, as mentioned just above.

This paper is organized as follows :

- In section II, we first develop the implications of the pseudo-spin model when applied to one site only.

- Then, in section III, the collective aspects of the pseudo-spin variables are presented at those points of interest in the Brillouin zone, namely points Γ (0,0,0), M (0, $\frac{1}{2}$, 0) and Δ(0, 0, $\frac{1}{3}$).

- The coupling between (O.P.'S) at points M and Δ, which is necessary to obtain the "projection" unit-cell, is discussed afterwards in section IV.

- Finally, the possible mechanisms for the occurrence of the actual low temperature phase with Z = 96 are tentatively proposed in section V.

II–PSEUDO SPIN COORDINATES AT ONE SITE

As stated already in section I, a six dimensional pseudo spin spanned by the mean occupation probabilities n_i (i= 1 to 6) of the MA group over its different orientations, is necessary to generate statistically the D_{3h} site symmetry. Thus, in the disordered hexagonal room temperature phase one has :

$$\sum_i n_i = 1 \text{ with } n_i = \frac{1}{6} \quad (i = 1 \text{ to } 6) \qquad (1)$$

Here, we have adopted notations such as i = 1, 3, 5 refer to orientations "up" and i = 2, 4, 6 to orientations "down" (figure1) .

Whatever the space group of the low temperature phase, the ordering of the MA group on each site is the primary process, so that, in the D_{3h} site symmetry, the six n_i variables generate a six dimensional reducible representation which decomposes as

$$R_{site} = A_1' + A_2'' + E' + E'' \qquad (2)$$

The symmetry adapted combinations of n_i transforming as irreducible representations (I.R.'S) of D_{3h} are easily obtained by means of the projection operators technique, thus giving :

$$A_1' : q_1 = n_1 + n_2 + n_3 + n_4 + n_5 + n_6$$

$$A_2'' : q_2 = n_1 + n_3 + n_5 - n_2 - n_4 - n_6$$

$$E' : \begin{cases} q_3 = 2\,n_1 - n_3 - n_5 + 2n_2 - n_4 - n_6 \\ q_4 = n_3 - n_5 + n_4 - n_6 \end{cases} \qquad (3)$$

$$E'' : \begin{cases} q_5 = 2\,n_1 - n_3 - n_5 - 2n_2 + n_4 + n_6 \\ q_6 = n_3 - n_5 - n_4 + n_6 \end{cases}$$

Figure 2 shows a schematic representation of the ground states derived from the different q_i. It should be noticed that the coordinate q_1 is invariant by all the symmetry elements of D_{3h} (totally symetric A_1' (I.R.)), while all other coordinates q_2 to q_6 break this symmetry. For instance q_2 is invariant under the elements of C_{3v} point group, and leads to a partially ordered ground state where the MA group occupy the orientations "up" ($q_2>0$) or the orientations "down" ($q_2<0$). Similarly, the other coordinates q_i ($i\neq 1, 2$) describe also partially ordered ground states of the MA group (figure2). Now, we are looking for an ordered ground state in the low temperature phase, where the MA group occupies only one of its six possible orientations. Obviously, this is possible only if non linear coupling exists between coordinates belonging to different (I.R.'S) ; for instance coupling between $q_3>0$ and $q_2>0$ leads to the ordered state where $n_1 = 1$ with n_i ($i\neq 1$) = 0. The possibilities to obtain ordered ground states are couplings between q_2 and q_5 or between q_3 and q_5. This coupling procedure, which is a necessary condition to obtain directly an ordered ground state, will be a leitmotiv when considering the pseudo spin coordinates at the different points of interest (Γ,Δ,M) in the Brillouin zone (see section III and IV).

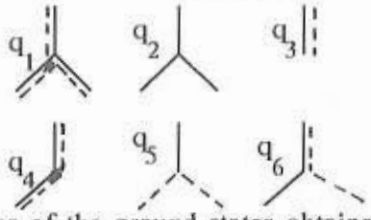

Figure 2:Schematic representations of the ground states obtained from the site pseudo spin coordinates q_i (see relations (3)) .

It should be noticed that the coordinates q_4 (q_6), of the same site symmetry as q_3 (q_5) may also be involved in the ordering process, but in the absence of q_3 (q_5) . As will be shown in section III, orthogonal combinations of site coordinates, such as (q_3+3q_4) and (q_3-q_4) on the one hand and ($q_5+ 3q_6$) and (q_5-q_6) on the other hand, must be used as (O.P.'S), when prescribed by the (I.R.'S) at some points in the Brillouin zone.

III - PSEUDO SPINS COORDINATES AT POINTS Γ, M , AND Δ

First, it should be pointed out that the hexagonal unit cell contains two MA groups on D_{3h} sites, related to each other by an inversion centre ; thus, we shall consider coordinates denoted by q_i at site 1 ($\frac{2}{3}$, $\frac{1}{3}$, $\frac{1}{4}$) and by q_i' at site 2 ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{3}{4}$). Of course q_i' are of same form as the q_i, given by relations (3), excepted that the mean occupation probabilities ($\Sigma_i' = 1$) now refer to the MA group at site 2. It follows that each coordinate q_i, when symmetrized in the D_{6h} factor group of the crystal will generate two (I.R.'S), each one being related to a branch of pseudo spins in the Brillouin zone (dispersion like curves). These two representation are not physically independent : the freezing of one of them will imply that the corresponding q_i(or combination of q_i) is frozen for each MA group at any site in the crystal, and that the other branch related to the same q_i (or to the

same combinaison of q_i) will not need to be further considered as an (O.P.) in the ordering process (réf.4).

In the following, the site coordinates q_i and q'_i will be labelled by a supscript N(q_i^N , q'^N_i with N = 1 to 6). As a matter of fact, we are looking for a "projection " unit cell containing Z = 12 formula units so that, for the description of the pseudo spin coordinates in this system, we need at least six adjacent hexagonal unit cells with label N.

III-1- Pseudo spin coordinates at zone centre : Point Γ(0,0,0)

The reducible representation R_Γ corresponding to the symmetry breaking pseudo spin coordinates of the MA group of the unit cell is :

$$R_\Gamma = \Gamma_4^+ / B_{2g} + \Gamma_5^+ / E_{1g} + \Gamma_6^+ / E_{2g} + \Gamma_2^- / A_{2u} + \Gamma_5^- / E_{1u} + \Gamma_6^- / E_{2u} \quad (4)$$

The corresponding pseudo spin coordinates are given in table I (the supscrits N have been omitted, since at point Γ all unit-cells are in phase) and the subgroups obtained when these coordinates act as primary (O.P.) are given in table II ; they are in agreement with previous group theoretical investigations of the subgroups of $P6_3/mmc$ (réf.12);(réf.13) . As pointed out already in section II , ordered ground states can not be obtained with the help of one coordinate alone ; however, there exist a number of subgroups that can correspond to an ordered ground state, thanks to the possibility of quadratic linear coupling between a two dimensional primary (O.P.) such as (q_3,q'_3), (q_4,q'_4) or (q_5,q'_5), (q_6,q'_6) and a secondary one dimensional (O.P.) (q_2,q'_2).

This is indicated in the last two columns of table II. Also, a number of subgroups reported in table II are underlined : they correspond to space groups which belong to the orthorhombic system or are super groups of orthorhombic space groups, so that they can induce a "projection "unit cell with orthorhombic symmetry (such as the one we are looking for) by means of group subgroup relations.

TABLE I : Pseudo spin coordinates of physical interest determined at zone centre (point Γ(000)).

$Q(B_{2g},\Gamma) = q_2 - q'_2$
$Q(E_{1g},1,\Gamma) = q_5 - q'_5$
$Q(E_{1g},2,\Gamma) = q_6 - q'_6$
$Q(E_{2g},1,\Gamma) = q_3 + q'_3$
$Q(E_{2g},2,\Gamma) = q_4 + q'_4$
$Q(A_{2u},\Gamma) = q_2 + q'_2$
$Q(E_{1u},1,\Gamma) = q_3 - q'_3$
$Q(E_{1u},2,\Gamma) = q_4 - q'_4$
$Q(E_{2u},2,\Gamma) = q_5 + q'_5$
$Q(E_{2u},2,\Gamma) = q_6 + q'_6$

TABLE II : Subgroups of P63/mmc generated by the pseudo spin coordinates at zone centre . O.stands for "orderd" and D.O . for "disordered".

I.R	PSEUDO-SPIN COORDINATES	SUBGROUPS	SECONDARY O.P	GROUND STATE
Γ_4^+/B_{2g}	$Q(B2g,\Gamma) \neq 0$	$P\bar{3}\,m1$	none	D.O
Γ_5^+/E_{1g}	$Q(E_{1g},1,\Gamma)\neq0$ $Q(E_{1g},2,\Gamma)=0$	$C1\frac{2}{m}1$	$Q(B_{2g},\Gamma)$	O.
	$Q(E_{1g},1,\Gamma)=0$ $Q(E_{1g},2,\Gamma)\neq0$	$C\frac{2}{c}11$	none	D.O
	$Q(E_{1g},1,\Gamma)\neq0$ $Q(E_{1g},2,\Gamma)\neq0$	$P\bar{1}$	$Q(B_{2g},\Gamma)$	O.
Γ_6^+/E_{2g}	$Q(E_{2g},1,\Gamma)\neq0$ $Q(E_{2g},2,\Gamma)=0$	Ccmm	none	D.O
	$Q(E_{2g},1,\Gamma)=0$ $Q(E_{2g},2,\Gamma)\neq0$	$P11\frac{2_1}{m}$	none	D.O
	$Q(E_{2g},1,\Gamma)\neq0$ $Q(E_{2g},2,\Gamma)\neq0$			
Γ_2^-/A_{2u}	$Q(A_{2u},\Gamma)\neq0$	$P6_3mc$	none	D.O
Γ_5^-/E_{1u}	$Q(E_{1u},1,\Gamma)\neq0$ $Q(E_{1u},2,\Gamma)=0$	C2mm	none	D.O
		Cc2m	none	D.O
	$Q(E_{1u},1,\Gamma)=0$ $Q(E_{1u},2,\Gamma)\neq0$	P11m	none	D.O
	$Q(E_{1u},1,\Gamma)\neq0$ $Q(E_{1u},2,\Gamma)\neq0$			
Γ_6^-/E_{2u}	$Q(E_{2u},1,\Gamma)\neq0$ $Q(E_{2u},2,\Gamma)=0$	$Ccm2_1$	$Q(A_{2u},\Gamma)$	O.
		$C222_1$	none	D.O
	$Q(E_{2u},1,\Gamma)=0$ $Q(E_{2u},2,\Gamma)\neq0$	$P112_1$	$Q(A_{2u},\Gamma)$	O.
	$Q(E_{2u},1,\Gamma)\neq0$ $Q(E_{2u},2,\Gamma)\neq0$			

III-2- Pseudo spin coordinates at point M $(0,\frac{1}{2},0)$

The reducible representation spanned by the pseudo spins of physical interest at point M of the hexagonal Brillouin zone is determined as :

$$R_M = M_1^+ / A_g + 2M_2^+ / B_{2g} + M_3^+ / B_{1g} + M_4^+ / B_{3g} + M_1^- / A_u + M_2^- / B_{2u} + 2M_3^- / B_{1u} + M_4^- / B_{3u} \qquad (5)$$

The symmetry adapted combinations of the site pseudo spin coordinates, q_i^N and q'^N_i, are easily obtained by means of the operator projection techniques . Now, it should be noticed that the star of the wave vector at point M contains three arms $(0,\frac{1}{2},0)$, $(\frac{1}{2},0,0)$, $(\frac{1}{2},\frac{1}{2},0)$ (réf.11) , so that the full (I.R.'S) of the space group at point M are three dimensional, thus corresponding to a three dimensional (O.P.) (η_1,η_2,η_3) . However, as shown in (réf.6), the "projection" unit cell corresponds to such a solution where one point M only is involved (for instance $(0,\frac{1}{2},0)$; therefore, we are only interested by the solutions of the form $(\eta,0,0)$ where η corresponds to the pseudo spin coordinates at point $M(0,\frac{1}{2},0)$. Under these conditions, all subgroups obtained belong to the mmm (D_{2h}) class (réf.12);(réf.13).

It should be pointed out that the Γ_6^+ / E_{2g} (I.R.) corresponds to the $(e_1\text{-}e_2)$ and e_6 components of the elastic strain tensor, so that, in all cases, $(e_1\text{-}e_2)$ which generates subgroups with the mmm class (réf.14), acts as a secondary (O.P.) ; as a result, the coordinate $Q(E_{2g},1,\Gamma)$ (see table I) which can be bilinearly coupled with $(e_1\text{-}e_2)$ may also be involved in the ordering process. Then, a number of subgroups can exhibit ordered ground states. As an example, the disordered ground state generated by the primary (O.P.) :

$$Q_1(B_{2g},M) = q_2^1 + q'^1_2 - q_2^2 - q'^2_2$$

is shown in figure 3, together with the ordered state obtained when coupling with the secondary (O.P.) $Q(E_{2g},1,\Gamma)$ is taken in to account.

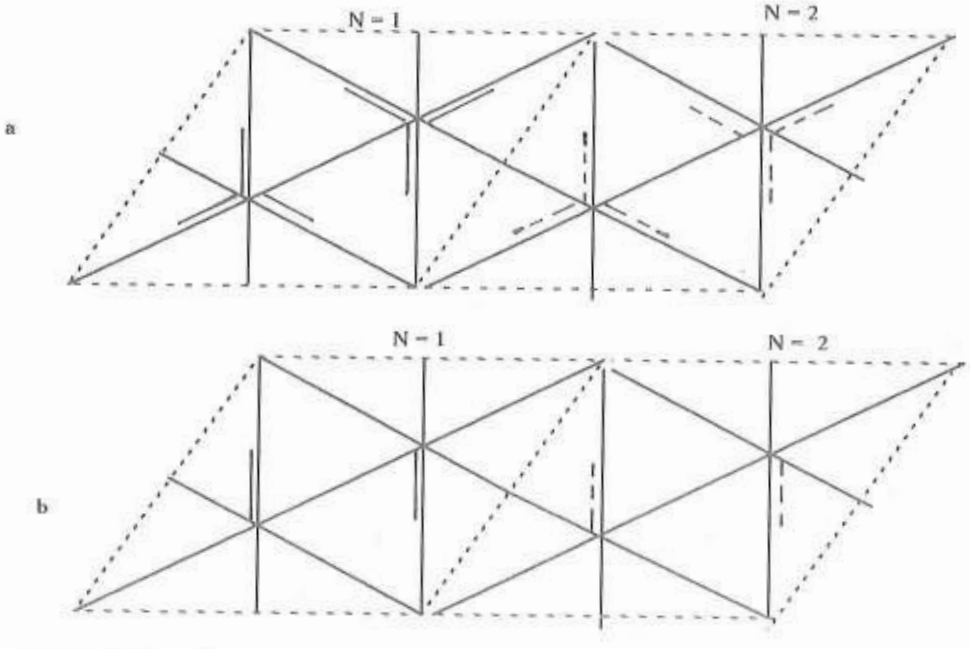

Figure 3 : Schematic representation of :
a: The disordered ground state induced by the pseudo spin coordinate $Q(B_{2g},M)$.

b: The ordered ground state obtained when introducing a coupling with $Q(E_{2g},1,\Gamma)$ acting as a secondary (O.P.) . The space group so obtained is Pnmn .

III-3- Pseudo spin coordinates at point $\Delta(0, 0, \frac{1}{3})$

The reducible representation spanned by the pseudo spin coordinates at any point $\Delta(0,0,\alpha)$ situated on the Γ-A line (réf.11) is :

$$R_\Delta = \Delta_1/A_1 + \Delta_3/B_2 + 2\Delta_5/E_2 + 2\Delta_6/E_1 \qquad (6)$$

There are two arms in the star of the wave vector at point Δ, namely $k(00\alpha)$ and $-k(00-\alpha)$, so that the full (I.R.) Δ_1 and Δ_3 are of dimension two and Δ_5 and Δ_6 of dimension four (complex conjugate representations related to k and -k).The triplication of the "projection" unit cell along the $\vec{c}$ direction is obtained for the particular value $\alpha = \frac{1}{3}$, so that two points $\Delta(0,0,\frac{1}{3})$ and $(0,0,-\frac{1}{3})$ are replaced at zone centre in the "projection" unit cell.

It should be noticed that for all subgroups, the ground state is disordered , even in case where coupling with a secondary (O.P.) at zone centre is possible. As an example, we take the $P6_122$ subgroup (réf.11);(réf.12) ,which is obtained by considering the (I.R.) Δ_6/E_1 with an (O.P.) of the form $(\rho,0,0,-\rho)$. This means that the pseudo spin coordiantes are choosen as follows:

$$Q_1(E_1,1,\Delta) = -\,Q_1(E_1,4,\Delta) \neq 0 \text{ and } Q_1(E_1,2,\Delta) = Q_1(E_1,3,\Delta) = 0$$

where :

$$Q_1(E_1,1,\Delta) = (q_3^1 + 3q_4^1) - 2(q'^1_3 + 3q'^1_4) + (q_3^3 + 3q_4^3) + (q'^3_3 + 3q'^3_4) - 2(q_3^5 + 3q_4^5) + (q'^5_3 + 3q'^5_4)$$

$$Q_1(E_1,2,\Delta) = -(q_3^1 - q_4^1) + 2(q'^1_3 - q'^1_4) - (q_3^3 - q_4^3) - (q'^3_3 - q'^3_4) + 2(q_3^5 - q_4^5) - (q'^5_3 - q'^5_4)$$

$$Q_1(E_1,3,\Delta) = (q_3^1 + 3q_4^1) - (q_3^3 + 3q_4^3) + (q'^3_3 + 3q'^3_4) - (q'^5_3 + 3q'^5_4)$$

$$Q_1(E_1,4,\Delta) = (q_3^1 - q_4^1) + (q_3^3 - q_4^3) - (q'^3_3 - q'^3_4) + (q'^5_3 - q'^5_4)$$

The ground state obtained in such a way is schematized in figure 4, where a residual disorder is evidenced together with the trebling of the unit cell along the $\vec{c}$ direction.

IV-COUPLING OF PSEUDO SPIN COORDINATES AT POINTS M AND Δ : THE " PROJECTION "STRUCTURE

In order to describe the "projection" structure with a unit cell triplicated in the $\vec{c}$ direction and doubled in the hexagonal plane, it is necessary to couple an (O.P.) (η) at point M with an (O.P.) (ρ) at point Δ ; the coupling terms of lowest order are biquadratic, i.e. of the form $\eta^2\rho^2$. The subgroups so obtained are generated by the direct product of (I.R.'S) (R.R) at point M and Δ and then correspond to the intersection of space groups generated independently by these representations.

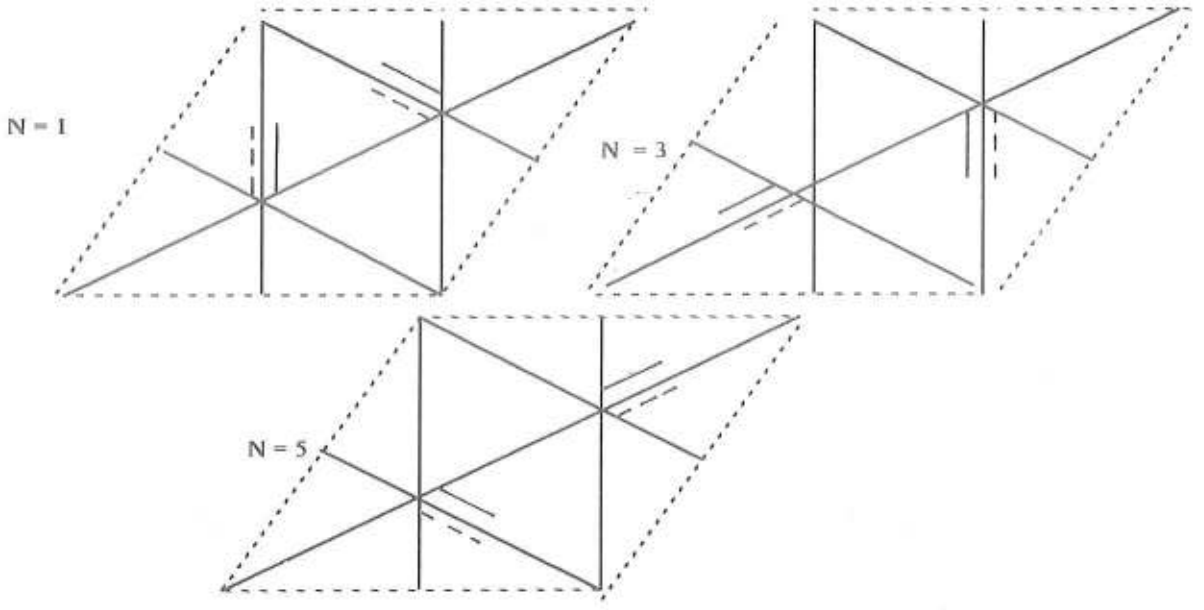

Figure 4 : Schematic representation of the disordered ground state obtained for the P 6_122 space group .

In a pure order disorder description, i.e. when all pseudo spin coordinates at points M and Δ are considered as (O.P.'S), there are 32 (R.R) combinations of the form ($\Gamma_i(M)$ + $\Gamma_j(\Delta)$)(see relations (5) and (6)), which lead to a total number of 176 different solutions, of which 89 belong to the orthorhombic system . Obviously, it would not be meaningful to go further in this analysis , unless a drastic choice can be made. Indeed, this choice is dictated by the experimental results obtained by means of X-ray diffraction (réf.6) ; as a matter of fact, it is clear from the atomic scattering factors that most of the X-ray intensity diffracted by the crystal of MACB comes from the $CdBr_6$ octahedra chains. This means, in particular, that super structure reflections responsible for the "projection" structure are due to $CdBr_6$ chain displacements that can couple with pseudo spin coordinates of the MA groups, provided that these displacements are polarized in the hexagonal (x,y) plane ; this coupling process has been clearly established in the cases of related crystals of TMMC and TMCC (réf.7);(réf.8);(réf.9). As shown already in crystals of this family, low-lying chain motions such as acoustic modes or octahedra chain rotations always assist the ordering processes of the organic groups (réf.7);(réf.8);(réf.9);(réf.15);(réf.16);(réf.17), and thus provide a more realistic description of the phase transition mechanisms.

Chain rotation polarized in the (x,y) plane with Γ_2^+ / A_{2g} symmetry at zone centre, is reponsible for the $P6_3/mmc \rightarrow P6_3/m$ phase transition observed with TMMC and TMCC (réf.7);(réf.9). At point M, this mode has the M_3^+ / B_{1g} symmetry and is responsible for the

orthorhombic room temperature phase observed in $(CH_3)_3 NHCdCl_3$ (TrMCC) with space group Pnam (Pbnm) (réf.15);(réf.16); thus , this mode can be linearly coupled with the $Q(B_{1g},M)$ pseudo spin coordinate of the same symmetry. At point Δ, the chain rotation has the Δ_2/A_2 symmetry, and so can not be directly coupled with any pseudo spin coordinate (see relation 6). As for the acoustic modes, those polarized along z ($\vec{c}$ direction) must be ignored in the description of the "projection" structure, as mentioned already. The remaining ones, polarized in the hexagonal (x,y) plane, have the M_2^- / B_{2u} and M_4^- / B_{3u} symmetries at point M. To our knowledge there is no example of lattice instability coming from such modes in this family of crystals ; thus, these (I.R.'S) will not be further considered . At point $\Delta(0, 0, \frac{1}{3})$, the transverse acoustic TA (x,y) mode is of the same symmetry as that of the primary (O.P.) responsible for the $P6_3/m \rightarrow P6_1$ phase transition observed in TMCB (réf.10) ; in hexagonal MACB, the corresponding symmetry for TA(x,y) at point Δ is Δ_6/E_1, which is indeed of the same symmetry as that of a number of pseudo spin coordinates (see relation (6)).

Thus , provided that such semi-empirical considerations also hold true in MACB, we are just left with the (R.R) (M_3^+ / B_{1g}+ Δ_6/E_1) ; of course, this procedure reduces considerably the number of possible solutions for the "projection" structure. These solutions are reported in table III and among them, only five belong to the orthorhombic system. It should be pointed out that all orthorhombic space groups so obtained correspond to a disordered (D.O.) ground state (table III), even in cases where coupling with a secondary (O.P.) at zone centre is possible. So, we conclude that an additional mechanism has to be found, in order to account for the ordered state as observed in the complex low temperature phase of MACB.

V- CONCLUDING REMARKS

The attempt to describe the order-disorder phase transition in MACB with the help of a model of multidimensional pseudo spins clearly show the unusal complexity of this type of approach (réf.4) ; as a matter of fact, at every step of the treatment, a back and forth motion between symmetrized and unsymmetrized (site) variables is necessary to find out whether or not the obtained ground state is an ordered one. After reasonable considerations (coupling of pseudo spins with particular phonon modes) we have selected five different possibilities for the orthorhombic space group of the "projection " structure (table III) ; all of them correspond to a disordered ground state. To find out how the system can get completely ordered in the complex orthorhombic unit cell (Z = 96) observed at low temperature (réf.6), two lines of arguments can be developed :

1) Because of the cell volume muliplication in the hexagonal plane with respect to the projection structure, pseudo spin coordinates at points situated inside the hexagonal Brillouin zone

(instead of the zone boundary point M) could be involved ; this process is indeed possible, but the corresponding model becomes unworkable, in practice. We shall not go further in this direction.

2) The projection structure itself can get ordered (provided that it remains orthorhombic) thanks to an additional primary (O.P.) at zone centre which was not considered in section IV . Indeed, the pseudo spin coordinate of the same symmetry as that of zone centre atomic displacements along z (ferroelectric optical mode) has been ignored, namely $Q(A_{2u},\Gamma)$ (table I). Introduction of this additional (O.P.) will further reduce the point symmetry of the projection structure excepted for the $Pna2_1$ solution (table III), but this latter is still disordered after the action of $Q(A_{2u}, \Gamma)$. In fact, the only interesting solution is Pnma (mmm class) : figure 5a shows a schematic representation of the disordered ground state obtained from the coupling of $Q(B_{1g}, M)$ with $Q_1(E_1, 1,\Delta)$. In this structure all MA groups at each site are equally distributed between two orientations (one "up" and one "down") and it becomes evident , from examination of the form of $Q(A_{2u},\Gamma)$ that a completely ordered ground state can be obtained, with space group $Pna2_1$ (figure 5 b). According to this process, this is actually the only way to find out an orthorhombic ordered projection structure with Z = 12.

TABLE III : Subgroups of $P6_3/mmc$ generated by the coupling of pseudo spin coordinates with symmetry M_3^+/B_{1g} and Δ_6/E_1. For all underlined orthorhombic space groups, the ground state is disordered (D.O).

R.R	Order parameter	Subgroups
$M_3^+/B_{1g}+\Delta_6/E_1$	$(\eta,0,0,\rho,0,0,0)$ $(\eta,0,0,0,\rho,0,0)$ $(\eta,0,0,0,0,\rho,0)$ $(\eta,0,0,0,0,0,\rho)$ $(\eta,0,0,\rho,0,0,-\rho)$ $(\eta,0,0,\rho,0,0,\rho)$ $(\eta,0,0,\rho_1,\rho_2,-\rho_1)$ $(\eta,0,0,\rho_1,\rho_2,\rho_1)$	Pnam $P11\frac{2_1}{m}$ $Pna2_1$ $P2_12_12_1$ $P2_12_12_1$ $P2_12_12_1$ $P112_1$ $P112_1$

So we are still left with the cell volume multiplication (Z = 96) observed experimentally (réf.6). This could be achieved by means of the condensation of transverse acoustic TA (z) modes at particular points situated inside the hexagonal Brillouin zone on the reciprocal $(\vec{a}^*, \vec{b}^*, 0)$ plane (réf.11) ; in this respect, the points $\Sigma\,(0, \frac{1}{4}, 0)$ responsible for the doubling of b_p and $T(\frac{1}{4}, -\frac{1}{8}, 0)$ responsible for the quadrupling of a_p (réf.6) are good candidates. The reason for such a complex

process is not clear ; one may think however that it could be related to the presence of NH...Br hydrogen bonds in MACB, introducing very specific interactions between the MA groups and the octahedra chains. As a matter of fact, complex unit cells with Z up to 18 have also been observed in the related hydrogen-bonded system TrMCC (réf.17).

We would like to point out that, according to the present analysis, the ordering process in MACB involves at least three coupled primary (O.P'.S). Examples of phase transitions involving two coupled (O. P. 'S) are known and have been analysed in the frame of Landau theory (réf.18), but such a complex situation as found in MACB has never been established before. The difficulty, here, is that phase transition occurs in only one step, whereas intermediate states such as reported in section III could eventually take place. Attempts to characterize such intermediate states have been made by means of high pressure (up to 6kbar) Raman scattering experiments at different temperatures (between 80 and 300 K) ; all we could see with MACB is always the existence of only one phase transition with a very slight increase of the transition temperature with increasing pressure.

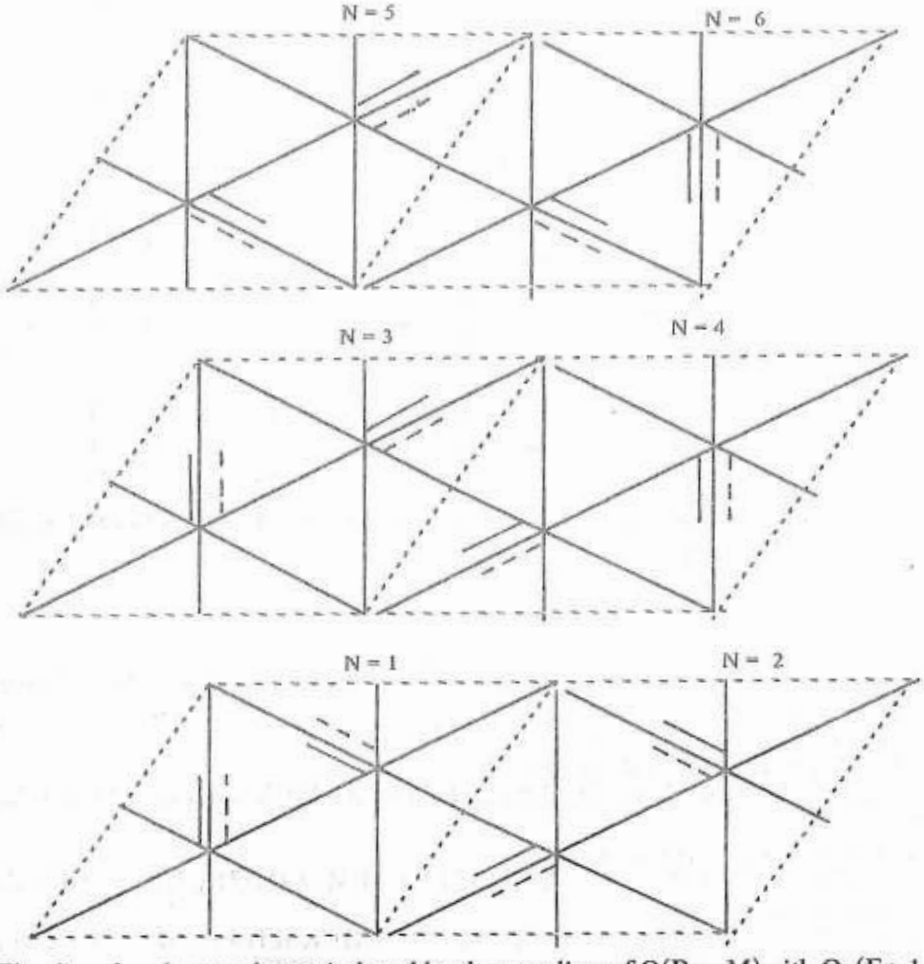

Figure 5 a: The disordered ground state induced by the coupling of $Q(B_{1g},M)$ with $Q_1(E_1,1,\Delta)$. The space group so obtained is Pnam .

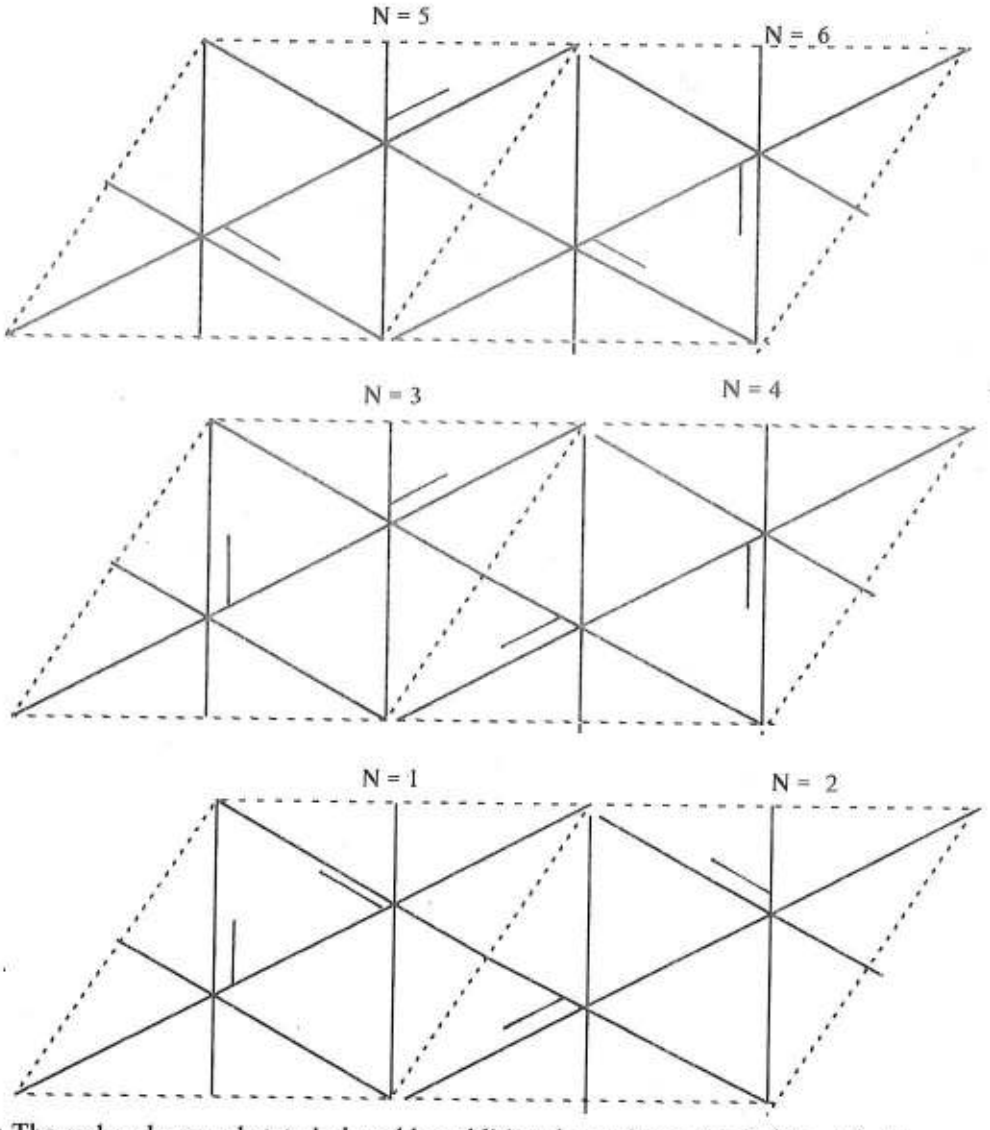

Figure 5b : The ordered ground state induced by additional coupling with Q (A_{2u},Γ). The space group so obtained is Pnam .

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