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Model of structural phase transitions in $(CH_3NH_3)_2CdCl_4$-type compounds

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A model has been proposed describing the structural phase transitions in $(CH_3NH_3)_2CdCl_4$ perovskite layer-type compounds as orientational order-disorder transitions of the CH_3NH_3 groups. Each CH_3NH_3 group has four possible equilibrium orientations in the cavities between the corner-sharing $CdCl_6$ octahedra and interacts with its nearest neighbors via two- and four-particle interactions. The four-particle interactions describe the fact that the energy of a given configuration of four CH_3NH_3 groups surrounding a $CdCl_6$ octahedron depends on the number of N-H···Cl bonds leading to the axial Cl sites of this octahedron, whereas the two-particle interactions describe the direct coupling between the CH_3 ends of the methylammonium groups as well as the indirect coupling via the N-H···Cl bonds leading to the equatorial Cl sites. In the absence of lattice distortions, the sequence of phase changes is: $I4/mmm \rightarrow Cmca \rightarrow P4_2/ncm \rightarrow Cmca$. Due to nonlinear coupling between the motion of the CH_3NH_3 groups and the rotation of the $CdCl_6$ octahedra, a monoclinic distortion of the lattice sets in as soon as the orthorhombic order parameter exceeds a critical value. For certain reasonable values of the coupling parameters one can thus reproduce the experimentally observed sequence of phase changes: $I4/mmm \rightarrow Cmca \rightarrow P4_2/ncm \rightarrow P2_1/b$.

I. INTRODUCTION

The structural order-disorder phase transitions in $(CH_3NH_3)_2CdCl_4$ and $(CH_3NH_3)_2MnCl_4$ have been investigated in the past three years by several experimental techniques[1-11] and the knowledge of the microscopic details is almost complete. The structure of these compounds consists of infinite sheets of MCl_6 octahedra sharing corners. Such an arrangement closely resembles a plane of the perovskite structure with the metallic ions (Cd, Mn) occupying the B sites, whereas the A sites in the cavities between the octahedra are occupied by the NH_3 groups of the methylammonium ions (Fig. 1). There are two chemically inequivalent chlorine sites, the bonding equatorial sites in the metal plane and the unbonding axial sites above and below the metal plane. The NH_3 groups are attached to the chlorine matrix by weak hydrogen bonds. Two bonding schemes were observed[4,5]: the "orthorhombic configuration" where two N-H···Cl hydrogen bonds lead to two out of the four equatorial $Cl_{(1)}$ sites and one hydrogen bond to one out of the four axial $Cl_{(2)}$ sites, and the "monoclinic configuration" where one bond leads to a $Cl_{(1)}$ site and two bonds lead to $Cl_{(2)}$ sites. Owing to these coupling schemes the C-N directions of the CH_3NH_3 groups are tilted with respect to the c axis (perpendicular to the octahedral sheets) by an angle of about 20°. Interlayer bonding is achieved by Van der Waals forces acting between the CH_3 groups of adjacent layers.

For each of the bonding schemes there are four possible orientations of the CH_3NH_3 groups in the

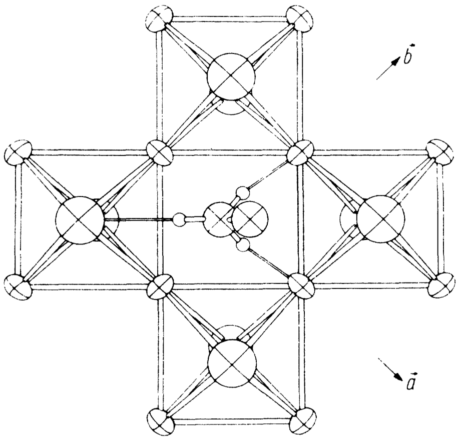

FIG. 1. Structure of one $(CH_3NH_3)_2CdCl_4$ layer in the THT phase in a projection along the c axis. Four Cl_6 octahedra are shown without the Cd atoms which have to be imagined in the centers of the octahedra. For simplicity the CH_3NH_3 group above the cavity is shown in one of the four possible orientations only. For the same reason the CH_3 protons and the CH_3NH_3 group below the cavity are not shown.

cavity. From the experimental investigations we know that the structural phase transitions in these and in related compounds[11,12] are order-disorder transitions of the NH_3CH_3 groups between the different possible orientations and coupling schemes. The MCl$_4$ planes play the part of stable but elastic matrices and do affect the phase transitions only indirectly by both linear and nonlinear coupling. The parent high-symmetry phase [tetragonal high-temperature (THT) phase] for $(CH_3NH_3)_2CdCl_4$ is the tetragonal space group $I4/mmm$. For this phase only the orthorhombic coupling scheme was observed[5,6] (Fig. 1). The occupation probabilities n_α ($\alpha = 1-4$) of the four different orientations of a CH_3NH_3 group in a given cavity are equal: $n_1 = n_2 = n_3 = n_4 = \frac{1}{4}$, i.e., the four potential wells corresponding to these orientations are equivalent.[3] On lowering the temperature below T_{c1} the potential wells become inequivalent so that the system undergoes a second-order phase transition to the orthorhombic (ORT) phase $Cmca$, where $n_1 > n_2 = n_4 > n_3$. For this phase also only the orthorhombic coupling scheme was observed. At T_{c2} a first-order phase transition leads to the tetragonal low-temperature (TLT) phase $P4_2/ncm$ which can be dedescribed in terms of the probabilities by $n_1 = n_2 > n_3 = n_4$ (Fig. 2). For this phase it was not possible to decide from the x-ray results[4] whether it consists only of orthorhombic configurations or of an admixture of orthorhombic and monoclinic coupling schemes. However, ^{14}N NMR investigations[9] and Raman study[13] gave strong hints that no new coupling scheme occurs at this phase transition. Although the transition is of first order[1-3] the Raman as well as the ir[14] spectrum is almost not affected, whereas below T_{c3} in the monoclinic (MLT) phase, where only a frozen-in monoclinic configuration exists, the spectra are completely different. The phase transition TLT-MLT is also of first order and shows besides a small hysteresis of 1 K an overlapping of the two phases in a region of 5 K.[15] The MLT phase cannot be described in terms of the probabilities n_α, but it can be understood as a distortion of a virtual orthorhombic ground state with $n_1 = 1$ and $n_2 = n_3 = n_4 = 0$ due to nonlinear coupling to the lattice (Fig. 3). The distorted configuration of Fig. 3 yields the real ground state shown on the right bottom of Fig. 2.

The aim of the present work was to investigate whether a simple model where the basic reorientable unit, i.e., the methylammonium group, moves among four potential wells, is capable of describing the observed phases in the correct sequence. Similarly we wanted to see whether the introduction of the coupling of methylammonium motion with the $CdCl_4$ lattice can account for the large lattice distortion in the real ground state which

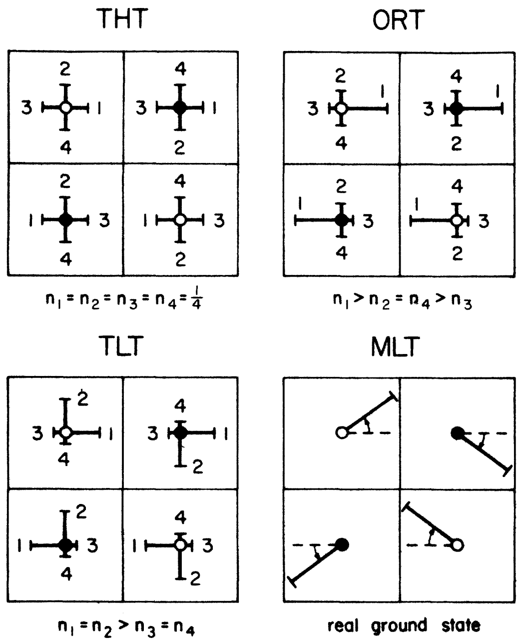

FIG. 2. Schematic representation of the four phases of $(CH_3NH_3)_2CdCl_4$ in the largest primitive unit cell of the system (TLT phase: $Z = 4$). The N-C directions of the four CH_3NH_3 groups between two adjacent layers are projected on the layer plane. The groups with closed circles are attached to cavities in the upper layer and the ones with open circles to cavities in the lower layer. The assignment of the four different orientations α of the groups ($\alpha = 1, 2, 3, 4$) is chosen in such a way that the probabilities n_α—which are represented by the length of the bars—do not depend on the site of the group in the unit cell for all the phases.

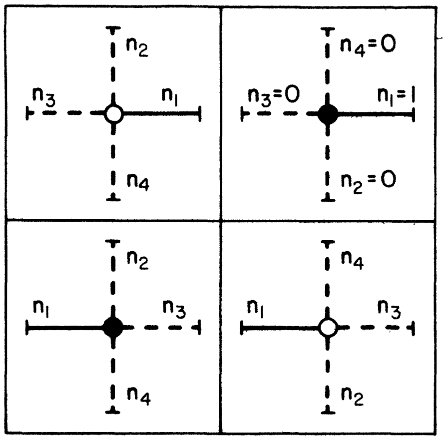

FIG. 3. Representation of the eigenvector ($n_1 = 1$, $n_2 = n_3 = n_4 = 0$) of the degenerated model ground state which corresponds to the frozen-in ORT domain shown in Fig. 2. The projection and assignment of the n_α are like those in Fig. 2. The THT, ORT, and TLT phases can be constructed by linear combinations of the four eigenvectors belonging to the orthorhombic model ground state.

is absent in the higher-temperature phases where the ordering is incomplete. For sake of simplicity we used the molecular-field approximation (MFA).

In Sec. II the free energy of such a system is calculated in the absence of lattice distortions. Several assumptions were made in order to keep the number of coupling constants as small as possible. In Sec. III the stability conditions of the THT phase are investigated, whereas in Secs. IV and V the self-consistency equations for the order parameters characterizing the ORT and TLT phases are derived. In Sec. VI the coupling to the lattice is taken into account and the real MLT ground state is obtained.

II. CALCULATION OF THE FREE ENERGY IN THE ABSENCE OF LATTICE DISTORTIONS

In deriving our model Hamiltonian the following assumptions were made:

(a) The structural phase transitions are mainly due to the interactions among the CH_3NH_3 groups. The MCl_4 layers within that approach are considered to be rigid matrices to which the NH_3 heads are linked. Any linear coupling between the CH_3NH_3 group motions and the phonons of the lattice just renormalizes the coupling constants. This linear coupling leads to a slight tilting of the $CdCl_6$ octahedra in the ORT and TLT phases, which however does not change the hydrogen bonding scheme and can be neglected in our treatment. Nonlinear coupling which has to be taken into account in the monoclinic phase is as well neglected in this first approach but will be treated in Sec. VI.

(b) Since the electronic structure of the Cl atoms depends strongly on the number of the attached N–H···Cl hydrogen bonds, the energy of a given configuration of CH_3NH_3 group orientations depends on this number. In all the phases, except for the distorted version of the MLT phase (real ground state), two hydrogen bonds are on the time average attached to a single equatorial $Cl_{(1)}$ site and only one N–H···Cl bond is attached to an axial $Cl_{(2)}$ site (Fig. 4).

(c) The first requirement (two bonds to any $Cl_{(1)}$ site) is always fulfilled when the two CH_3NH_3 groups belonging to the same cavity of a layer (one attached from above and the other from below) are related by a center of inversion $\bar{1}$ located in the middle of the cavity, i.e., the corresponding C-N bonds above and below the layer are parallel (Fig. 4). This center of inversion was found by means of the x-ray structure determinations[4,5] in all the phases. The energy of states which are at variance with this requirement is assumed to be so high that the occupation probabilities of these states are very low. These states are not taken into account in the present model Hamiltonian.

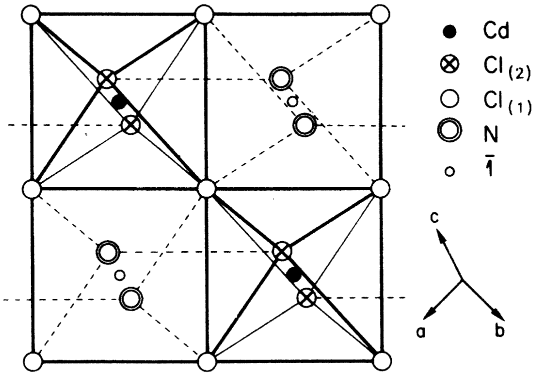

FIG. 4. Structure of one $(CH_3NH_3)_2CdCl_4$ layer in a projection along an axis which is tilted about 15° with respect to the c axis. For simplicity the CH_3 groups and the NH_3 protons are not shown. The dashed lines represent the N–H...Cl bonds. The configuration of the four NH_3 groups corresponds to the virtual orthorhombic ground state. In case of dynamic disorder of the groups one H bond is leading to an axial $Cl_{(2)}$ site and two H bonds to equatorial $Cl_{(2)}$ sites in the time average. If the two groups belonging to the same cavity are lined by a center of inversion $\bar{1}$ always two H bonds are attached to one $Cl_{(2)}$ site between successive jumps.

(d) To fulfill the second requirement (one bond to any $Cl_{(2)}$ site) the orientation of the $(CH_3NH_3)_2$ double groups in the four neighboring cavities of an octahedron must be correlated. Since each cavity has also four neighboring octahedra the effect of this short-range coupling extends through the whole lattice. This leads to four-particle interaction terms.

(e) Neglecting the four-particle interaction, the remaining states, i.e., all configurations of the $(CH_3NH_3)_2$ double groups differ very little in energy. The energy depends then only on two-particle interactions of the intralayer and interlayer type describing the direct coupling between the CH_3 ends of the methylammonium groups as well as the indirect coupling via the N–H···Cl bonds leading to the equational $Cl_{(1)}$ sites. For a MFA treatment it is, however, not necessary to distinguish between these interactions. Together with assumption (c) the model becomes three dimensional.

(f) In the parent THT phase the single-particle potential for CH_3NH_3 group motion has four equivalent potential wells. Any tunneling splittings of the energy levels are neglected. The undistorted model ground state shown in Fig. 3 is the one where the system is frozen in to one of the four single-particle potential wells, $n_1=1$, $n_2=n_3=n_4=0$. This corresponds to the frozen in orthorhombic phase. All higher phases are linear combinations of this ground state (Fig. 2). Lattice distortion of the virtual orthorhombic ground state results in the monoclinic MLT phase. These lattice distortions can be assigned to a nonlinear coupling between the CH_3NH_3 group motion and the phonons of the $CdCl_4$ lattice which becomes relevant at low temperatures. Such a coupling will be treated in Sec. VI.

For the description of the Hamiltonian we used the largest unit cell of the system, i.e., the one of the TLT phase with $Z=4$ so that all phase transitions can be described by instabilities at the Brillouin-zone center ($q=0$). The configuration of the system is given by the numbers $m_{i,\nu,\alpha}$ which can take the values of one or zero. The indices i, j stand for the ith or jth unit cell, the indices ν,κ ($\nu,\kappa=1,2,3,4$) denote the CH_3NH_3 groups in the unit cell, whereas the indices α,β ($\alpha,\beta=1,2,3,4$) describe the orientation of a given group. $m_{i,\nu,\alpha}=1$ when the νth group in the ith unit cell has the orientation α. Since each CH_3NH_3 group has to be in one of the four possible orientations we have

$$\sum_{\alpha=1}^{4} m_{i,\nu,\alpha}=1.$$

The CH_3NH_3 groups interact both via direct (two-particle) interactions as well as via indirect, lattice mediated four-particle interactions.

The Hamiltonian of the two-particle interactions in its most general form is

$$\mathcal{H}_2=\frac{1}{2}\sum_{i,j,\nu,\kappa,\alpha,\beta} a_{i,j,\nu,\kappa,\alpha,\beta}\, m_{i,\nu,\alpha} m_{j,\kappa,\beta} \qquad (1)$$

with the constraints

if $i=j$, then $\nu\neq\kappa$;

if $\nu=\kappa$, then $i\neq j$.

$a_{i,j,\nu,\kappa,\alpha,\beta}$ is the interaction energy between the νth group in the ith unit cell with orientation α and the κth group in the unit cell j with orientation β. Hamiltonian (1) includes interactions among groups of the same layer as well as interaction between groups of adjacent layers. In the molecular-field approximation the internal energy can be expressed as

$$U_2=\langle\mathcal{H}_2\rangle=\frac{1}{2}\sum_{i,j,\nu,\kappa,\alpha,\beta} a_{i,j,\nu,\kappa,\alpha,\beta} \times\langle m_{i,\nu,\alpha}\rangle\langle m_{j,\kappa,\beta}\rangle. \qquad (2)$$

The occupation probability $\langle m_{i,\nu,\alpha}\rangle$ does not depend on i because the chosen unit cell is the largest primitive cell observed in our system. The assignment of the orientations α is performed in such a way that $\langle m_{i,\nu,\alpha}\rangle$ does not depend on the position ν in the unit cell for all the phases (Figs. 2 and 3)

$$\langle m_{i,\nu,\alpha}\rangle=n_\alpha. \qquad (3)$$

The molecular-field approximation for the treatment of the structural phase transitions in $(CH_3NH_3)_2CdCl_4$ was used for sake of simplicity. This is justified also by the experimentally determined critical exponent β of the order parameter.[3] The value $\beta=\frac{1}{4}$ indicates a nearly tricritical transition with a mean-field exponent.

With the help of expression (3) we can rewrite the internal energy U_2 [Eq. (2)] as

$$U_2=\frac{1}{2}\sum_{\alpha,\beta} a'_{\alpha,\beta} n_\alpha n_\beta, \qquad (4)$$

where

$$a'_{\alpha,\beta}=\sum_{i,j,\nu,\kappa} a_{i,j,\nu,\kappa,\alpha,\beta}.$$

In view of the symmetry of the parent THT-phase expression (4) simplifies to

$$U_2=\frac{1}{2}a(n_1^2+n_2^2+n_3^2+n_4^2) +b(n_1n_2+n_2n_3+n_3n_4+n_4n_1)+c(n_1n_3+n_2n_4). \qquad (5)$$

The contribution to the internal energy of the four-particle interactions which correspond to the states described in assumption (d) can be taken into account in the following way (see Appendix A):

$$U_4=d(n_1n_2n_3n_4)+e(n_1n_2n_3+n_2n_3n_4+n_3n_4n_1+n_4n_1n_2), \qquad (6)$$

so that the total internal energy per one CH_3NH_3 group becomes $U=U_2+U_4$. The entropy S per one CH_3NH_3 group is in the same approximation given by

$$S=-k[n_1\ln(n_1)+n_2\ln(n_2)+n_3\ln(n_3)+n_4\ln(n_4)], \qquad (7)$$

and the corresponding free energy becomes $F=U-TS$, where T is the temperature. In view of the requirement $\sum_{\alpha=1}^{4}n_\alpha=1$ we have to minimize the expression

$$F^*=F-\lambda(n_1+n_2+n_3+n_4-1), \qquad (8)$$

where λ is the Lagrange multiplier. In equilibrium the first derivatives of F^* must vanish with respect to n_α:

$$\frac{\partial F^*}{\partial n_\alpha}=0,\quad \alpha=1,2,3,4, \qquad (9)$$

e.g.,

$$\frac{\partial F^*}{\partial n_1}=an_1+b(n_2+n_4)+cn_3+dn_2n_3n_4 +e(n_3n_4+n_2n_4+n_2n_3) +kT[\ln(n_1)+1]-\lambda=0, \qquad (10)$$

and all the eigenvalues of the matrix of the generalized inverse susceptibilities $\chi^{-1}_{\alpha\beta} = \partial^2 F^*/\partial n_\alpha \partial n_\beta$ have to be positive.

In Secs. III–VI only those solutions of Eq. (9) are discussed which have been observed in $(CH_3NH_3)_2CdCl_4$ and in the isomorphous manganese compound, respectively.

III. STABILITY CONDITIONS FOR THE DISORDERED THT PHASE

From Eqs. (6)–(8) and the definition $n_1 = n_2 = n_3 = n_4 = \frac{1}{4}$ of the tetragonal-high-temperature phase the matrix of the second derivatives of the free energy F can be obtained as

$$\frac{\partial^2 F}{\partial n_\alpha \partial n_\beta} = \begin{bmatrix} A & B & C & B \\ B & A & B & C \\ C & B & A & B \\ B & C & B & A \end{bmatrix}, \tag{11}$$

where $A = a + 4kT$, $B = b + \frac{1}{16}d + \frac{1}{2}e$, and $C = c + \frac{1}{16}d + \frac{1}{2}e$. The eigenvalues x_i of this matrix are given by

$$\begin{aligned} &[1,2]\colon\ x_1 = x_2 = A - C = a + 4kT - c - \tfrac{1}{16}d - \tfrac{1}{2}e,\\ &[3]\colon\ x_3 = A + C - 2B = a + 4kT + c - 2b - \tfrac{1}{16}d - \tfrac{1}{2}e,\\ &[4]\colon\ x_4 = A + C + 2B = a + 4kT + c + 2b + \tfrac{3}{16}d + \tfrac{3}{2}e, \end{aligned} \tag{12}$$

and the corresponding sets of eigenvectors—representing deviations from the THT equilibrium occupation probabilities—are denoted by [1], [2], [3], and [4]. The THT phase is stable as long as all these eigenvalues are positive. The two eigenvectors belonging to the doubly degenerated eigenvalue $x_{1,2}$ are

$$\begin{aligned} &[1]\colon\ \delta n_1 = -\delta n_3,\quad \delta n_2 = \delta n_4 = 0,\\ &\text{and}\\ &[2]\colon\ \delta n_2 = -\delta n_4,\quad \delta n_1 = \delta n_3 = 0. \end{aligned} \tag{13}$$

They are represented in Fig. 5(a).

Below the temperature T_1,

$$T_1 = (c - a + \tfrac{1}{16}d + \tfrac{1}{2}e)/4k, \tag{14}$$

the system becomes unstable with respect to the eigenvectors [1,2]. The corresponding order parameters η_1 and η_2 can be defined as

$$\eta_1 = 2n_1 - 2n_3,\quad \eta_2 = 2n_2 - 2n_4, \tag{15}$$

and can take on values between +1 and −1.

The eigenvector corresponding to the eigenvalue x_3 is given by

$$[3]\colon\ \delta n_1 = \delta n_3 = -\delta n_2 = -\delta n_4, \tag{16}$$

and is represented in Fig. 5(b). The instability with respect to this eigenvector occurs at T_3,

$$T_3 = (2b - c - a + \tfrac{1}{16}d + \tfrac{1}{2}e)/4k. \tag{17}$$

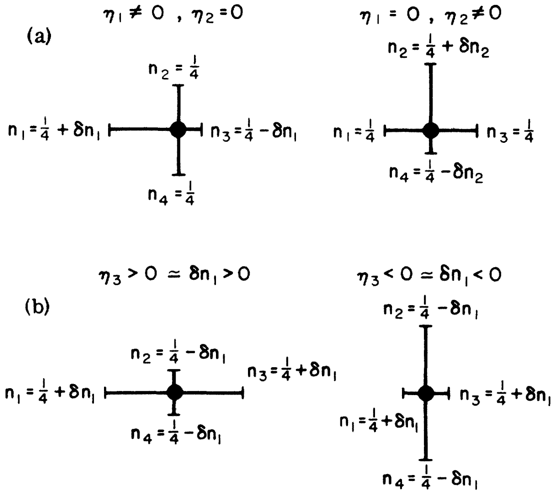

FIG. 5. (a) Schematic representation of the eigenvectors [1] (left) and [2] (right) according to Eq. (13) and the corresponding order parameters $\eta_1 = 2n_1 - 2n_3$ and $\eta_2 = 2n_2 - 2n_4$. (b) Schematic representation of the eigenvector [3] according to Eq. (16) and the corresponding order parameter $\eta_3 = 2n_1 + 2n_3 - 1$ which can be either positive (left) or negative (right).

The order parameter η_3 for this solution is defined as

$$\eta_3 = 2n_1 + 2n_3 - 1 = 1 - 2n_2 - 2n_4. \tag{18}$$

It also can take on values between +1 and −1. The eigenvector [4] is the trivial solution $\delta n_\alpha = 0$ and thus all possible phases must be linear combinations of the eigenvectors [1], [2], and [3]. The free energy of the THT phase is equal to

$$\begin{aligned} &F_{\text{THT}} = -kT\ln(4) + K,\\ &K = \tfrac{1}{8}a + \tfrac{1}{4}b + \tfrac{1}{8}c + \tfrac{1}{256}d + \tfrac{1}{16}e. \end{aligned} \tag{19}$$

This energy has to be compared with the free energy of the low-temperature phases.

IV. SELF-CONSISTENT EQUATION FOR THE ORDER PARAMETER OF THE TLT PHASE

By comparing Figs. 2 and 5 one can see that the TLT phase $n_1 = n_2 > n_3 = n_4$ is a frozen in linear combination of the eigenvectors [1] and [2] with $\eta_1 = \eta_2$. Rewriting the expression for the free energy by using Eqs. (14) and (15) and by introducing the reduced temperature t,

$$t = T/T_1, \tag{20}$$

and the new parameter

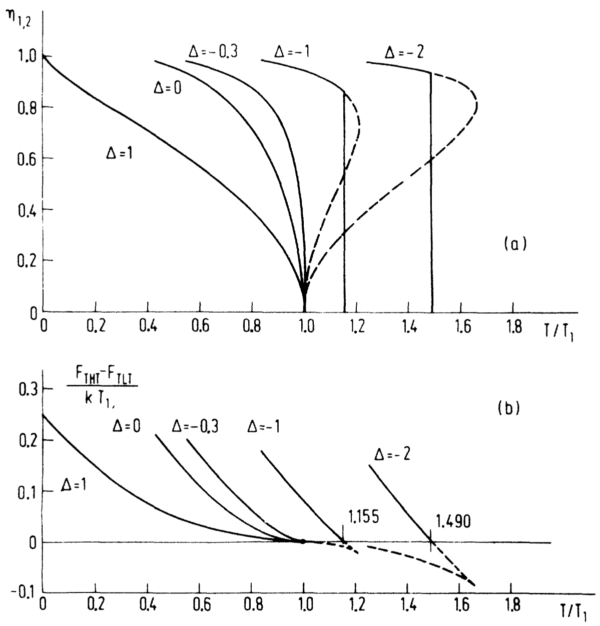

FIG. 6. (a) Solutions of the self-consistent equation (23) for the order parameter $\eta_{1,2}$ of the TLT phase for different values of the parameter Δ. $\eta_{1,2}$ is plotted as a function of the reduced temperature T/T_1. For $\Delta < -\frac{1}{3}$, the transition is of first order. (b) Comparison of the free energies of the THT and TLT phases for different values of Δ. $(F_{\text{THT}} - F_{\text{TLT}})/kT_1$ is plotted as a function of T/T_1. The free-energy differences for the metastable THT phase below the first-order transition are also shown.

$$\Delta = d/64kT_1, \tag{21}$$

one finds

$$F_{\text{TLT}} = \tfrac{1}{4}kT_1(-2\eta_{1,2}^2(1-\tfrac{1}{2}\Delta\eta_{1,2}^2) + 2t\{(1+\eta_{1,2})\ln[\tfrac{1}{4}(1+\eta_{1,2})] + (1-\eta_{1,2})\ln[\tfrac{1}{4}(1-\eta_{1,2})]\}) + K. \tag{22}$$

The self-consistent equation for $\eta_{1,2}$—resulting from the requirement that the $\partial F^*/\partial n_\alpha = 0$, $\alpha = 1,2,3,4$, which for this case is identical to $\partial F_{\text{TLT}}/\partial \eta_{1,2} = 0$—becomes

$$\eta_{1,2} = \tanh[(1/t)\eta_{1,2}(1-\Delta\eta_{1,2}^2)]. \tag{23}$$

In Fig. 6(a) the solution of Eq. (23) is shown for different values of the parameter Δ. For $\Delta = -\frac{1}{3}$ the phase transition from the THT phase to the TLT phase is tricritical, i.e., for $\Delta > -\frac{1}{3}$ the transition is of second order and for $\Delta < -\frac{1}{3}$ of first order, respectively. A comparison of the free energies $F_{\text{THT}} - F_{\text{TLT}}$ [Fig. 6(b)] yields the transition temperatures for the first-order transitions. For $\Delta \geq -\frac{1}{3}$ the transition temperature is $T_c = T_1$.

V. SELF-CONSISTENT EQUATIONS FOR THE ORDER PARAMETERS OF THE ORT PHASE

By again comparing Figs. 2 and 5 one can construct the ORT phase $n_1 > n_2 = n_4 > n_3$ by a linear combination of the frozen in eigenvector [1] with $\eta_1 > 0$, $\eta_2 = 0$ and the eigenvector [3] with $\eta_3 > 0$.

Changing the sign of η_1 leads to the antiphase domain $n_1 < n_2 = n_4 < n_3$ which can be obtained also by a shift in the direction of both orthorhombic layer axes by half a lattice constant. The 90° domains $n_2 > n_1 = n_3 > n_4$ which are observed also in $(CH_3NH_3)_2CdCl_4$ are a linear combination of the eigenvector [2] with $\eta_2 > 0$, $\eta_1 = 0$ and the eigenvector [3] with $\eta_3 < 0$. The combination of [1] and [3] with $\eta_3 < 0$ as well as the combination of [2] and [3] with $\eta_3 > 0$ have not been observed so far and in addition do not lead to the virtual orthorhombic ground state shown in Fig. 3. These combinations will not be considered in the following treatment. A phase corresponding to the pure eigenvector [3] was also not observed and will not be taken into account. This can be realized by choosing the parameters so that $T_1 > T_3$. By using Eqs. (14) and (16) this requirement leads to the inequality $c > b$.

Due to the fact that an increase of η_3 results in an increase of n_1 and n_3 by $\delta n_1 = \frac{1}{4}\eta_3$, the limits of η_1 are increased

$$-(1+\eta_3) \leq \eta_1 \leq (1+\eta_3), \tag{24}$$

and η_1 can thus take on values between +2 and −2. Any violation of inequality (24) implies a violation of the requirement $0 \leq n_\alpha \leq 1$. In the following only the domain $n_1 > n_2 = n_4 > n_3$ will be considered and instead of η_1 a normalized order parameter will be used

$$\eta = \tfrac{1}{2}\eta_1 = n_1 - n_3. \tag{25}$$

In order to simplify the following expressions two new parameters are introduced

$$\tau = T_3/T_1 \tag{26}$$

and

$$\delta = (d+4e)/64kT_1. \tag{27}$$

The free energy of the ORT phase then reads

$$F_{\text{ORT}} = kT_1(-\eta^2 - \tfrac{1}{2}\tau\eta_3^2 + \tfrac{1}{4}\Delta(\eta_3^4 - 4\eta^2\eta_3^2) + 2\delta\eta^2\eta_3 + \tfrac{1}{2}t\,\{2\ln(\tfrac{1}{2}) + [\tfrac{1}{2}(\eta_3+1)+\eta]\ln[\tfrac{1}{2}(\eta_3+1)+\eta] + [\tfrac{1}{2}(\eta_3+1)-\eta]\ln[\tfrac{1}{2}(\eta_3+1)-\eta] + (1-\eta_3)\ln[\tfrac{1}{2}(1-\eta_3)]\}) + K. \tag{28}$$

As one could expect from the symmetry of the ORT phase, the free energy is symmetric in η but not with respect to η_3. The requirement that in equilibrium all first derivatives with respect to the n_α must vanish, $\partial F^*/\partial n_\alpha = 0$, is equivalent to the requirement that both $\partial F/\partial\eta = 0$ and $\partial F/\partial\eta_3 = 0$:

$$\frac{\partial F}{\partial \eta} = kT_1\left\{-2\eta - 2\Delta\eta\eta_3^2 + \tfrac{1}{2}t\left[\ln\left(\frac{\eta_3+1}{2} + \eta\right) - \ln\left(\frac{\eta_3+1}{2} - \eta\right)\right]\right\} = 0, \tag{29}$$

$$\frac{\partial F}{\partial \eta_3} = kT_1\left\{-\tau\eta_3 + \Delta(\eta_3^3 - 2\eta^2\eta_3) + 2\delta\eta^2 + \tfrac{1}{4}t\left[\ln\left(\frac{\eta_3+1}{2} + \eta\right) + \ln\left(\frac{\eta_3+1}{2} - \eta\right) - 2\ln\left(\frac{1-\eta_3}{2}\right)\right]\right\} = 0. \tag{30}$$

We are thus left with only three parameters τ, δ, and Δ. Only those solutions of the coupled equations (29) and (30) are stable for which the determinant of the second derivatives of F with respect to η and η_3 is positive definite.

Let us first consider the simple case where only two particle interactions are taken into account, i.e., $\Delta = 0$ and $\delta = 0$. By some algebraic manipulations one obtains for the self-consistent equations

$$\eta = \sinh(2\eta/t)/[\cosh(2\eta/t) + \exp(-2\tau\eta_3/t)], \tag{31}$$

$$\eta_3 = [\cosh(2\eta/t) - \exp(-2\tau\eta_3/t)]/[\cosh(2\eta/t) + \exp(-2\tau\eta_3/t)]. \tag{32}$$

With the help of Eq. (32) it is possible to eliminate one of the parameters

$$\cosh(2\eta/t) = [(1+\eta_3)/(1-\eta_3)]\exp(-2\tau\eta_3/t), \tag{33}$$

and the equation for η_3 becomes

$$\frac{1+\eta_3}{1-\eta_3}\exp\left(-\frac{2\tau}{t}\eta_3\right) = \cosh\left(\frac{2\{1 - [(1-\eta_3)/(1+\eta_3)]^2\exp(4\tau\eta_3/t)\}^{1/2}}{t[1 + (1-\eta_3)/(1+\eta_3)]}\right). \tag{34}$$

Expanding Eq. (34) for small values of η_3 results in

$$\eta_3 = [3/(1-4\tau)](1-t). \tag{35}$$

Eliminating η_3 in Eq. (31) by Eq. (35) and expanding it for small values of η leads to

$$\eta = [3(1-\tau)/(1-4\tau)]^{1/2}(1-t)^{1/2} \tag{36}$$

up to first order terms in $(1-t)^{1/2}$. Since $\tau < 1$ $(T_3 < T_1)$, one sees from Eq. (36) that for (i) $\tau < \frac{1}{4}$, a real solution exists only for $t < 1$, i.e., the phase transition is of second order, whereas for (ii) $\tau > \frac{1}{4}$, a real solution exists for $t > 1$, i.e., the phase transition is of first order.

Introducing into Eq. (35) the conditions for the existence of real solutions of Eq. (36), one always finds $\eta_3 > 0$. This is consistent with the choice of the orthorhombic domain at the beginning of Sec. V.

In Figs. 7(a) and 7(b) the solutions of the coupled equations (29) and (30) are shown for different values of τ and $\Delta = \delta = 0$. The corresponding difference in the free energy with respect to the THT phase $F_{\mathrm{THT}} - F_{\mathrm{ORT}}$ and $F_{\mathrm{THT}} - F_{\mathrm{TLT}}$ are plotted in Fig. 6(c) as a function of reduced temperature. Comparing the free energies of the ORT and TLT phases one can see that for $\Delta = \delta = 0$ (i.e., only two-particle interactions are taken into account), the free energy of the ORT phase is lower than the one of the TLT phase for $0 \leq t \leq 1$. Thus, the ORT phase and not the TLT phase is stable below T_1. The computer calculations yield for the critical exponents β and β_3 of the two order parameters $[\eta \propto (T_1 - T)^{\beta}$, $\eta_3 \propto (T_1 - T)^{\beta_3}]$, $\beta = \frac{1}{2}$, $\beta_3 = 1$ for $\tau < \frac{1}{4}$ and $\beta = \frac{1}{4}$, $\beta_3 = \frac{1}{2}$ for $\tau = \frac{1}{4}$, respectively. They show also that the assumption made in Eq. (3) of Ref. 3

$$n_1 - n_3 = c(n_1 - \tfrac{1}{4}),$$

which was based on one order parameter only does not hold since the "constant" c varies from $c = 2$ at T_1 to $c = \frac{4}{3}$ for complete order $(n_1 = 1)$. In fact it is not possible to deduce the temperature dependence of η_3 from the macroscopic treatment[16] of the high-temperature phases only without the corresponding microscopic picture of all phase transitions occurring in this system. The order parameter used in Ref. 16 corresponds to our η.

To obtain the TLT phase one has to take into account in the free energy of the ORT phase [Eq. (28)], the previously neglected third-order term $2\delta\eta^2\eta_3$. The fourth-order term is always negative for positive values of Δ, since the calculations yielded $\eta_3 < \eta$ for all temperatures in the ORT phase. For example, if $\Delta = 0$, $\delta = 0.15$, and $\tau \leq 0.25$ the TLT phase is favored just below T_1 but a second phase transition to the ORT phase occurs at a temperature well below T_1, i.e., the phase sequence for this set of parameters is THT → TLT → ORT on lowering the temperature. The transition THT-TLT is of second order since $\Delta > -\frac{1}{3}$,

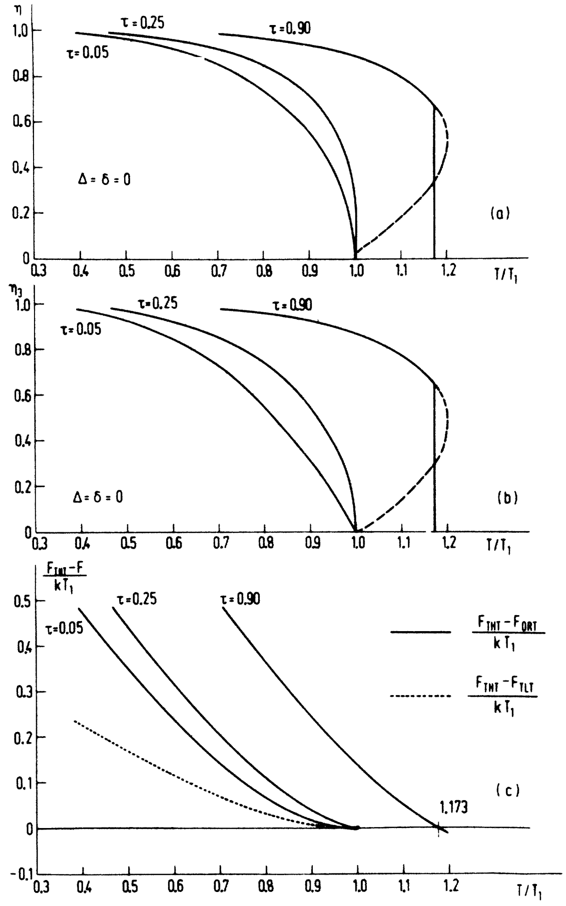

FIG. 7. Solution of the self-consistent equations (29) and (30) for the order parameters η and η_3 of the ORT phase for two-particle interactions only ($\Delta = \delta = 0$). The order parameters η (6a), η_3 (6b) and the differences in the free energies $(F_{\text{THT}} - F_{\text{ORT}})/kT_1$ and $(F_{\text{THT}} - F_{\text{TLT}})/kT_1$ (6c) are plotted vs the reduced temperature T/T_1 for different values of $\tau = T_3/T_1$. The free energy of the ORT phase is always lower than the free energy of the TLT phase so that the ORT phase is stable below T_c. Note that the critical exponents of the two order parameters are different $\beta_3 = 2\beta$ for $\tau \leq 0.25$.

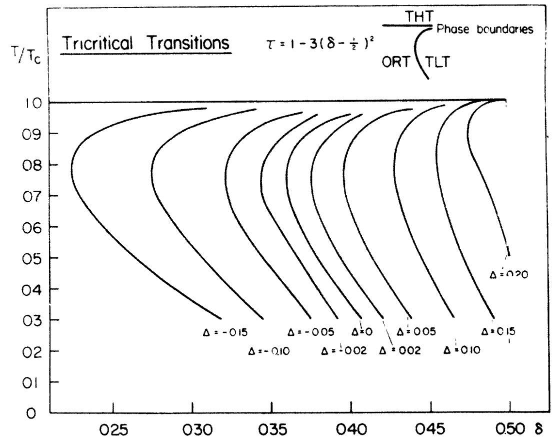

FIG. 8. Phase boundaries between the THT, ORT, and TLT phases for tricritical transitions at T_1 $[\tau = 1 - 3(\delta - \frac{1}{2})^2]$. The four-particle interaction is introduced by the parameters δ and Δ. The phase sequence THT-ORT-TLT-ORT is achieved only if δ exceeds a critical value which is strongly influenced by the value of the parameter Δ.

but the transition TLT-ORT is of first order because it is connected with a sudden change in the n_α. Let us recall that we are looking for a phase sequence THT-ORT-TLT-ORT with reduced transition temperatures $t_{c1} = 1$, $t_{c2} = 0.58$, $t_{c3} = 0.36$ for the case of $(CH_3NH_3)_2CdCl_4$ and $t_{c1} = 1$, $t_{c2} = 0.64$, $t_{c3} = 0.25$ for the case of $(CH_3NH_3)_2MnCl_4$, respectively.[2,4,5] The transitions at t_{c1} are of second order and in case of $(CH_3ND_3)_2MnCl_4$ the critical exponent β of the order parameter η was measured by means of deuteron magnetic resonance[12] to be $\beta = \frac{1}{4}$. This corresponds to a tricritical transition.

Let us first look for the condition for a tricritical transition from THT to ORT at $t = 1$ for $\delta \neq 0$ and $\Delta \neq 0$. By some algebraic manipulation of Eqs. (29) and (30) and by a similar expansion, as in the case $\delta = \Delta = 0$ for small η and η_3, one obtains the condition

$$\tau_t = 1 - 3(\delta - \tfrac{1}{2})^2, \qquad (37)$$

which contains the solution $\tau_t = \frac{1}{4}$ for $\delta = 0$ already obtained from Eq. (36). For $\tau \leq \tau_t$ the phase transition at $t = 1$ is of second order. For the tricritical transitions we are left with only two parameters δ and Δ. The computer calculations show that the correct phase sequence (THT-ORT-TLT-ORT) can be reached for $0.36 < \delta < 0.5$ if Δ is positive. For $\delta \geq 0.5$ the free energy of the TLT phase is always lower than the free energy of the ORT phase. In Fig. 8 the phase boundaries between the ORT and TLT phases are shown for different values of Δ. The phase boundary between the THT and the ORT phase is the line at $t = 1$. One can see that the observed transition temperatures t_{c2} and t_{c3} can not be reached by any set of the parameters δ and Δ. In addition to this the critical exponent β has a value of 0.25 only exactly at $t = 1$. At $t = 0.96$ where the experimental value is still 0.25, the calculated value is already $\beta = 0.34$. Since a molecular field approximation does usually not yield exact values of critical exponents we decided to fit only the transition temperatures to the experimental values by means of all three parameters τ, δ, and Δ.

The best fit was obtained for $\tau = 0.25$, $\Delta = 0.4$ and $\delta = 0.45$ for the Mn compound and $\tau = 0.30$, $\Delta = 0.4$, and $\delta = 0.45$ for the Cd compound, re-

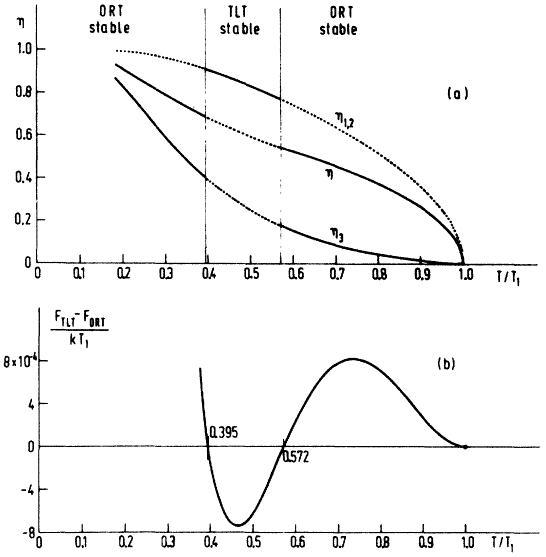

FIG. 9. Solution of the self-consistent equations for the order parameters η and η_3 of the ORT phase for the set of parameters τ, δ, Δ which yields approximately the transition temperatures observed in $(CH_3NH_3)_2CdCl_4$ ($\tau = 0.30$, $\Delta = 0.40$, $\delta = 0.45$). The order parameters η and η_3 of the ORT phase and $\eta_{1,2}$ of the TLT phase with $\Delta = 0.40$ (8a) and the difference in the free energies $(F_{TLT} - F_{ORT})/kT_1$ (8b) are plotted vs the reduced temperature $t = T/T_1$.

spectively. In Fig. 9(a) the order parameters η and η_3 are plotted versus reduced temperature t for the case of the Cd compound. The corresponding difference in the free energies of the ORT and TLT phases F_{ORT}-F_{TLT} is given in Fig. 9(b). For $\tau = 0.35$ and the same values of Δ and δ as used in Fig. 9 the system remains in the ORT phase for all the values of $t < 1$, i.e., an increase in τ lowers the value of t_{c2} and raises the value of t_{c3}. A similar behavior was observed experimentally by Knorr and Jahn[17] by application of hydrostatic pressure to a single crystal of $(CH_3NH_3)_2MnCl_4$. Hydrostatic pressure could thus act on the parameter $\tau = T_3/T_1$. From the obtained values of the parameters τ, δ, Δ one can calculate the coupling constants of Eqs. (5) and (6) as

$$a = -0.6kT_1, \quad b = 0, \quad c = 1.4kT_1,$$
$$d = 25.6kT_1, \quad e = 0.8kT_1.$$

The value $b = 0$ fixes just the energy scale for the two-particle interactions (a, b, c). Also a or c could be chosen to be zero which would just lead to a corresponding shift in the values of both remaining interaction constants. However, the values of d and e are not affected by such a shift in the energy scale.

VI. INTRODUCTION OF THE COUPLING TO THE LATTICE

Since any attempt to construct the THT, ORT, and TLT phases by linear combinations of the real monoclinic ground state failed,[5,9] we had to find a way leading from our orthorhombic model ground state to the monoclinic low-temperature MLT phase. The idea for the solution came just from a structural argument. If one considers a single sheet of $CdCl_4$ octahedra without any attached hydrogen bonds one can imagine that the restoring forces for bending of the sheet or for tilting of octahedra are very weak. Thus the restoring forces for these deformations in our crystals are mainly due to the $N-H\cdots Cl$ bonds. In view of the disorder in the orientations of the CH_3NH_3 groups there are enough $N-H\cdots Cl_{(2)}$ hydrogen bonds partly occupied in the THT, TLT, and ORT phases to provide for a restoring force against the tilting or rotation of the octahedra and to make the layers rather stiff. In the virtual orthorhombic ground state, however, there are no hydrogen bonds left which would restore a "monoclinic" tilting of octahedra, because n_2 and n_4 are zero. In fact the lattice can become unstable against "monoclinic" deformations as soon as n_2 $(= n_4)$ becomes smaller than a critical value, i.e., as soon as the order parameter η_3 exceeds a threshold value η_0. Now we introduce two new order parameters q_1 and q_2 corresponding to a tilting or small rotation of octahedra around an axis perpendicular to the layers. For $q_1 \neq 0$, $q_2 = 0$, the Cl octahedra with centers at 000 and $\frac{1}{2}0\frac{1}{2}$ are rotated in phase around the c axis, whereas for $q_2 \neq 0$, $q_1 = 0$ they are rotated in antiphase.[18] The free energy of the total system then becomes the sum of the order-disorder term F_n and a displacive term F_q due to lattice distortions:

$$F = F_n + F_q . \tag{38}$$

F_q must also contain the symmetry of the THT phase. Because of the change in the NH_3 coupling scheme the transition to the MLT phase is of first order even for a supposed direct transition from ORT to MLT. This leads to the following ansatz for F_q up to sixth-order terms:

$$\begin{aligned} F_q &= \tfrac{1}{2}f(\eta_0 - \eta_3)q_1^2 + \tfrac{1}{4}gq_1^4 + \tfrac{1}{6}hq_1^6 \\ &\quad + \tfrac{1}{2}f(\eta_0 + \eta_3)q_2^2 + \tfrac{1}{4}gq_2^4 + \tfrac{1}{6}hq_2^6 \\ &= \tfrac{1}{2}f(\eta_0 + 1 - 2n_1 - 2n_3)q_1^2 + \tfrac{1}{4}gq_1^4 + \tfrac{1}{6}hq_1^6 \\ &\quad + \tfrac{1}{2}f(\eta_0 + 1 - 2n_2 - 2n_4)q_2^2 + \tfrac{1}{4}gq_2^4 + \tfrac{1}{6}hq_2^6 . \end{aligned} \tag{39}$$

For a first-order transition, g must be negative, whereas f and h are positive. We can safely assume that the contribution of the displacements q_i can be neglected in the entropy compared with the order-disorder contributions. For both the

THT and TLT phases we have $n_1+n_3=n_2+n_4=\frac{1}{2}$ and F_q becomes

$$F_{q\ \mathrm{THT,TLT}}=\tfrac{1}{2}f\eta_0(q_1^2+q_2^2)+\tfrac{1}{4}g(q_1^4+q_2^4)+\tfrac{1}{6}h(q_1^6+q_2^6). \qquad (40)$$

For $\eta_0>0$ the minimum of F_q is obtained for $q_1=q_2=0$, i.e., $F=F_n$. For the ORT and MLT phases, we have

$$F_{\mathrm{ORT\text{-}MLT}}=F_n(\eta,\eta_3)+\tfrac{1}{2}f(\eta_0-\eta_3)q_1^2+\tfrac{1}{4}gq_1^4+\tfrac{1}{6}hq_1^6+\tfrac{1}{2}f(\eta_0+\eta_3)q_2^2+\tfrac{1}{4}gq_2^4+\tfrac{1}{6}hq_2^6. \qquad (41)$$

The first derivatives with respect to the order parameters become

$$\frac{\partial F}{\partial \eta}=\frac{\partial F_n}{\partial \eta}=0, \qquad (42)$$

$$\frac{\partial F}{\partial \eta_3}=\frac{\partial F_n}{\partial \eta_3}-\tfrac{1}{2}fq_1^2+\tfrac{1}{2}fq_2^2=0, \qquad (43)$$

$$\frac{\partial F}{\partial q_1}=f(\eta_0-\eta_3)q_1+gq_1^3+hq_1^5=0, \qquad (44)$$

$$\frac{\partial F}{\partial q_2}=f(\eta_0+\eta_3)q_2+gq_2^3+hq_2^5=0. \qquad (45)$$

If we choose the domain where $\eta_3>0$, the solutions of Eq. (44)—which correspond to stable minima in the free energy—are

$$q_1=0 \quad \text{for } \eta_3<\eta_0-\tfrac{3}{16}g^2/hf$$

and

$$q_1^2=(|g|/2h)\{1+[1-(4hf/g^2)(\eta_0-\eta_3)]^{1/2}\} \quad \text{for } \eta_3>\eta_0-\tfrac{3}{16}g^2/hf. \qquad (46)$$

These results correspond to the treatment of first-order phase transitions given in Ref. 19 if $\eta_0-\eta_3$ is replaced by $T-T_0$. From Eq. (45) we then obtain $q_2=0$ for all positive values of η_3. Equation (43) now reads

$$\frac{\partial F}{\partial \eta_3}=\frac{\partial F_n}{\partial \eta_3}=0 \quad \text{for } \eta_3<\eta_c=\eta_0-\frac{3}{16}\frac{g^2}{hf},$$

$$\frac{\partial F}{\partial \eta_3}=\frac{\partial F_n}{\partial \eta_3}-\frac{f|g|}{4h}\left[1+\left(1-\frac{4hf}{g^2}(\eta_0-\eta_3)\right)^{1/2}\right]=0 \quad \text{for } \eta_3>\eta_c. \qquad (47)$$

Thus neither t_{c1} nor t_{c2} are affected if we choose, e.g., $\eta_c=0.4$ and the parameter set used for the calculations of the curves shown in Fig. 9. Using expression (46) for q_1 the free energy of the MLT phase becomes

$$F_{\mathrm{MLT}}=F_{\mathrm{ORT}}+\tfrac{1}{4}(\eta_0-\eta_3)\frac{f|g|}{n}\times\left[1+\frac{2}{3}\left(1-\frac{4hf}{g^2}(\eta_0-\eta_3)\right)^{1/2}\right]-\frac{1}{24}\frac{|g|^3}{h^2}\left[1+\left(1-\frac{4hf}{g^2}(\eta_0-\eta_3)\right)^{1/2}\right]. \qquad (48)$$

For the special cases $\eta_3=\eta_c$ and $\eta_3=\eta_0$ one obtains $F_{\mathrm{MLT}}=F_{\mathrm{ORT}}$ and $F_{\mathrm{MLT}}=F_{\mathrm{ORT}}-\frac{1}{12}|g|^3/h^2$, respectively. The corresponding values of the order parameter are $q_1=0$, $\pm(\frac{3}{4}|g|/h)^{1/2}$ and $q_1=\pm(|g|/h)^{1/2}$. A direct transition from ORT to MLT would occur exactly at $\eta_3=\eta_c$, whereas the TLT-MLT transition occurs at a higher value of η_3 because $F_{\mathrm{TLT}}<F_{\mathrm{ORT}}$ and thus the MLT phase is metastable until F_{MLT} becomes smaller than F_{TLT}.

An estimate of the values η_c, f, g, and h can be obtained in the following way:

First q_1 is normalized so that $q_1=1$ for $\eta_3=1$. Since a strong first-order character of the transition is required, q_1 should take on a value near 1 but at least 0.75 for $\eta_3=\eta_c$. This is fulfilled for $g/h=-0.8$ and leads to $(4hf/g^2)(1-\eta_0)=1.25$ for the normalization of q_1. This yields $f(1-\eta_0)/g=-0.25$ from the multiplication of the two expressions. The phase transition should occur just above T_{c3} in order to have a transition TLT-MLT at approximately the same temperature. For the metastable ORT phase of the Cd compound just above T_{c3} the calculations of Sec. V yield $\eta_3=0.4$ and thus $\eta_c=\eta_0-\frac{3}{16}g^2/hf=0.4$. This leads to the following equation for η_0:

$$\eta_0-\tfrac{3}{5}(1-\eta_0)=0.4\rightarrow\eta_0=0.625,$$

and we get $f/g=-\frac{2}{3}$. Thus, the ratio $f:g:h$ is $\frac{2}{3}:-1:1.25$. An estimate of the values can be obtained from the difference in free energy $F_{\mathrm{ORT}}-F_{\mathrm{MLT}}=+\frac{1}{12}|g|^3/h^2=0.053\,|g|$ for $\eta_3=\eta_0$. This amount should be a considerable contribution to the total free energy in order to obtain also a discontinuous change in η and η_3 at the phase transition ($\eta\rightarrow1$, $\eta_3\rightarrow1$) via the coupled equations (29) and (47). In view of the free-energy values shown in Figs. 6 and 7, a range of $kT_1<|g|<10kT_1$ should be suitable for this purpose.

For $g=-kT_1$ the computer calculations yielded discontinuous changes of q_1 from 0 to 0.96, of η_3 from 0.4 to 0.84 and of η from 0.7 to 0.91 at the TLT→MLT transition (Fig. 10). The static rotation of the octahedra around the c axis about an angle of 5.6° favors the monoclinic bonding scheme of the NH_3 group.[5] This angle corresponds to $q_1=1$ The rotation angle of the real ground-state vector shown in Fig. 2 on the lower right-hand side does not depend linearly on q_1. For the undistorted lattice the angle between the monoclinic and the or-

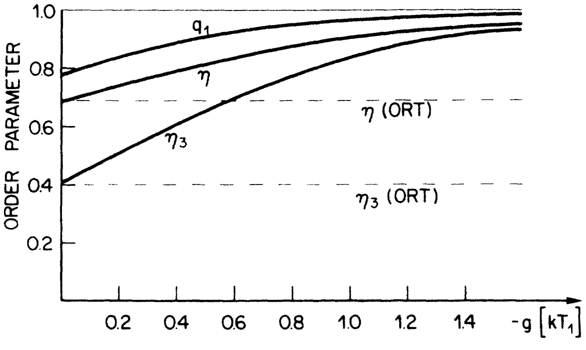

FIG. 10. Solution of the self-consistent equations (29) and (47) for the order parameters η, η_3, and q_1 of the MLT phase just below the transition temperature as a function of the coefficient g. The set of coefficients used for the calculations was $\tau=0.30$, $\Delta=0.40$, $\delta=0.45$, $\eta_0=0.625$, $f:g:h=\frac{2}{3}:-1:1.25$. The dashed lines correspond to the values of η and η_3 of the ORT phase for the same temperature.

thorhombic coupling schemes would be in this projection 45°. Due to the monoclinic distortion (q_1) this angle is reduced to 33°. Thus by nonlinear coupling between the CH_3NH_3-group motion and a tilting mode of octahedra we were able to introduce the real monoclinic ground state in our model.

VII. CONCLUSIONS

From the above results the following conclusions can be reached.

(i) The structural phase transitions in $(CH_3NH_3)_2CdCl_4$-type compounds can be basically described as order-disorder transitions of the CH_3NH_3 groups each of which has four possible equilibrium orientations in the cavities between the $CdCl_6$ octahedra.

(ii) In the absence of lattice distortions, the correct sequence of phase changes is

$$\text{THT} \rightarrow \text{ORT} \rightarrow \text{TLT} \rightarrow \text{ORT}.$$

This sequence is obtained only if four-particle interaction terms are added to the two-particle interactions.

The four-particle interactions describe the fact that the energy of a given configuration of four CH_3NH_3 groups surrounding a $CdCl_6$ octahedron depends on the number of N–H···Cl bonds leading to the axial $Cl_{(2)}$ sites of this octahedron, whereas the two-particle interactions describe the direct coupling between the CH_3 ends of the methylammonium groups as well as the indirect coupling via the N–H···Cl bonds leading to the equatorial $Cl_{(1)}$ sites.

(iii) Due to nonlinear coupling between the motion of the CH_3NH_3 groups and the tilting of the $CdCl_6$ octahedra, a monoclinic distortion of the lattice sets in as soon as the orthorhombic order parameter η_3 exceeds a critical value. In the high-temperature phases there are—in view of the disorder in the orientations of the CH_3NH_3 groups—enough N–H···$Cl_{(2)}$ hydrogen bonds partly occupied to make the layers stiff and to ensure the stability of the lattice against the "monoclinic" tilting of the octahedra. The orthorhombic ground state is, however, ordered and there are no N–H···$Cl_{(2)}$ bonds to restore the tilting of the octahedra. Thus it is unstable against a monoclinic tilting of the octahedra, and a corresponding change in the N–H···Cl bonding scheme. Very recently a group theoretical analysis was performed for the whole phase sequence in $(CH_3NH_3)_2CdCl_4$ in order to check the present order-disorder model.[18] It was shown that this model is in accordance with the symmetry of the lattice modes which condense at the transition points.

ACKNOWLEDGMENTS

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APPENDIX: FOUR-PARTICLE INTERACTION HAMILTONIAN

As already mentioned in Sec. II(d) the energy of a given configuration of four CH_3NH_3 groups surrounding one octahedron depends on the number of N–H···Cl bonds leading to the $Cl_{(2)}$ site of this octahedron. This number can take on the values

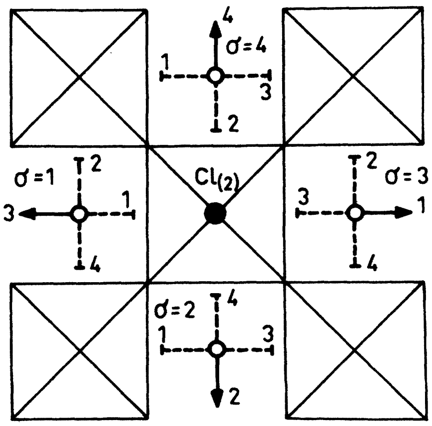

FIG. 11. Schematic representation of an arrangement of the four neighboring CH_3NH_3 groups of an octahedron where four N–H···Cl bonds are leading to the same $Cl_{(2)}$ site. The arrows indicate the N-C directions of the groups and are thus pointing to the opposite side of the N–H···$Cl_{(2)}$ bond (see Fig. 1).

0, 1, 2, 3, 4, and we can assign to the corresponding configurations of the four CH_3NH_3 groups the energies $E_0, E_1, \ldots, E_4$. The number $m_{\sigma,\alpha}$ ($\sigma = 1,2,3,4$; $\alpha = 1,2,3,4$) denotes whether the σth group is in the orientation α. With the assignments used in Fig. 11 the corresponding Hamiltonian $\mathcal{H}_4$ can be written

$$\begin{aligned}\mathcal{H}_4 = {} & E_4 m_{13}m_{22}m_{31}m_{44} + E_3[(1-m_{13})m_{22}m_{31}m_{44} + m_{13}(1-m_{22})m_{31}m_{44} + m_{13}m_{22}(1-m_{31})m_{44} + m_{13}m_{22}m_{31}(1-m_{44})] \\ & + E_2[(1-m_{13})(1-m_{22})m_{31}m_{44} + m_{13}(1-m_{22})(1-m_{31})m_{44} + m_{13}m_{22}(1-m_{31})(1-m_{44}) + (1-m_{13})m_{22}m_{31}(1-m_{44}) \\ & \quad + (1-m_{13})m_{22}(1-m_{31})m_{44} + m_{13}(1-m_{22})m_{31}(1-m_{44})] \\ & + E_1[(1-m_{13})(1-m_{22})(1-m_{31})m_{44} + m_{13}(1-m_{22})(1-m_{31})(1-m_{44}) + (1-m_{13})m_{22}(1-m_{31})(1-m_{44}) \\ & \quad + (1-m_{13})(1-m_{22})m_{31}(1-m_{44})] + E_0(1-m_{13})(1-m_{22})(1-m_{31})(1-m_{44}) .\end{aligned} \tag{A1}$$

In the molecular-field approximation we obtain from the relation $\langle m_{\sigma,\alpha}\rangle = n_\alpha$ [Eq. (3)], the expression for the internal energy

$$\langle \mathcal{H}_4\rangle = d(n_1n_2n_3n_4) + e(n_1n_2n_3 + n_2n_3n_4 + n_3n_4n_1 + n_4n_1n_2) + b'(n_1n_2 + n_2n_3 + n_3n_4 + n_4n_1) + c'(n_1n_3 + n_2n_4) + \text{const.}, \tag{A2}$$

where

$$d = E_4 - 4E_3 + 6E_2 - 4E_1 + E_0, \quad e = E_3 - 3E_2 + 3E_1 - E_0, \quad b' = c' = E_2 - 2E_1 + E_0. \tag{A3}$$

The coefficients b' and c' just renormalize the coefficients b and c of Eq. (5) so that the relevant part one has to add to the two-particle interaction energy U_2 is

$$U_4 = d(n_1n_2n_3n_4) + e(n_1n_2n_3 + n_2n_3n_4 + n_3n_4n_1 + n_4n_1n_2). \tag{A4}$$

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