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*Institute of Crystallography, University of Lausanne, Dorigny (a) and
Laboratory of Solid State Physics, Swiss Federal Institute of Technology, Hönggerberg, Zürich (b)*

X-Ray Study of the Structural First-Order Phase Transition (Cmca-P4₂/ncm) in $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$

By

G. CHAPUIS (a), H. AREND (b), and R. KIND (b)

In honour of Prof. Dr. Dr. h. c. P. GÖRLICH's 70th birthday

$(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ is found to be isostructural at room temperature with $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ having the orthorhombic space group Cmca. A high temperature phase transition to a tetragonal phase could not be observed because of a decomposition slightly above 383 K. Two low temperature phase transitions are detected by means of DTA at about 283 and 173 K. The first one leads to the space group P4₂/ncm. A microscopic model for this phase transition is proposed.

Für die Raumtemperaturphase von $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ wird die mit $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ isostrukturelle, orthorhombische Raumgruppe Cmca gefunden. Eine Hochtemperaturumwandlung in eine tetragonale Phase konnte wegen thermischer Zersetzung oberhalb von 383 K nicht beobachtet werden. Mittels DTA werden zwei Tieftemperatur-Phasenumwandlungen bei ungefähr 283 und 173 K gefunden. Die erstere führt zu einer tetragonalen Modifikation mit der Raumgruppe P4₂/ncm. Ein mikroskopisches Modell dieser Phasenumwandlung wird vorgeschlagen.

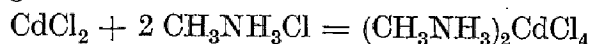
1. Introduction

The compounds $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$ with $\text{M} = \text{Cu}, \text{Mn}, \text{Fe}$, and $n = 1, 2, \dots$ crystallize in perovskite type layer structures exhibiting several interesting structural phase transitions in the paramagnetic phase. These phase transitions were studied in the past years especially for the simplest $n = 1$ compounds by means of differential thermal analysis (DTA), birefringence measurements, X-ray diffraction, neutron diffraction [1 to 3], group theoretical analysis [4] as well as by nuclear resonance techniques [5, 6]. These studies revealed a strange sequence of phase transitions starting from a high temperature tetragonal phase I4/mmm leading to an orthorhombic phase Cmca ($\text{M} = \text{Mn}, \text{Fe}$) or Pbca ($\text{M} = \text{Cu}$). At lower temperatures the structure changes again to tetragonal and afterwards to monoclinic. The two latter phases are not known in detail.

Since paramagnetic centres hinder NMR experiments considerably, especially in relaxation measurements, an examination of diamagnetic $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ is of particular interest. This substance was used already in a comparative specific heat study at low temperatures [7], but no structural data were given. The aim of the present study was to prove the isostructural nature of the Cd compound by an X-ray structure determination at room temperature, to determine its thermal stability and to scan by means of DTA and optical microscopy the occurrence of phase transitions. Since the scanning techniques yielded a first-order phase transition at 283 K the X-ray studies were extended also to this low-temperature phase.

2. Sample Preparation and Characterization

The starting substance for crystal growth was prepared by means of a double recrystallization of stoichiometric amounts of reagent grade $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ and $\text{CH}_3\text{NH}_3\text{Cl}$ according to the formula



from an aqueous solution. Within the accuracy of volumetric analysis, made both for the Cd and Cl content, the starting material corresponded to the ideal composition of the compound. Having thus established a congruent solubility we found its value to be at room temperature 0.01 mol per mol H_2O doubling approximately at 70 °C.

Crystals for X-ray work were grown by slow evaporation at room temperature, a method which made it possible to obtain untwinned samples. Larger, slightly twinned samples for microscopic observations were prepared by a temperature decrease technique.

The thermal stability of the substance was checked by means of thermogravimetry using, as well as in the following DTA measurements, the Mettler thermanalyser. Decomposition sets in around 383 K making physical investigations above this temperature practically impossible.

3. Scanning for Phase Transitions

Differential thermal analysis performed by means of the low temperature equipment of the thermoanalyser mentioned revealed in $(\text{CH}_3\text{NH}_3)_2\text{CdCl}_4$ two phase transitions occurring at about 173 and 283 K. The room temperature phase (twinned in large crystals) was found to be optically biaxial. Neither twinning nor the optical character changed up to the decomposition temperature with the exception of a slight apparent decrease in birefringence. Below 283 K the crystals changed to optically uniaxial in similar manner as observed already for the $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ compound [2].

4. X-Ray Measurements

The X-ray intensities of both structures were collected with an automatic four-circle diffractometer (Syntex —P2₁) up to $2\theta = 40^\circ$ using graphite monochromatized molybdenum radiation ($\lambda_{\text{MoK}\alpha} = 0.71069 \text{ \AA}$). For the data reduction and the crystal solving procedure we used the X-ray System [8] program package.

4.1 Structure of the room temperature phase

The room temperature phase at $(294 \pm 1) \text{ K}$ was found to be orthorhombic with lattice constants $a = 7.384 (2)$, $b = 19.22 (3)$, and $c = 7.483 (1) \text{ \AA}$. The space group is Cmca (no. 64) [9] and $Z = 4$. The data were corrected for absorption and at the end of the least-squares refining procedure an extinction correction was included. The final residual $R = \sum |\Delta F| / \sum |F_o|$ obtained was 0.029. The hydrogen atoms were located by means of a difference Fourier synthesis and are included in the structure factor calculation. Table 1 gives a list of the atomic coordinates and anisotropic temperature factors for the non-hydrogen atoms.¹⁾ No estimated standard deviations (e.s.d.) are given for the hydrogen parameters, as they were kept unchanged during the refinement. A projection of

¹⁾ A complete list of observed and calculated structure factors of both phases can be obtained on demand from one of the authors (G.Ch.).

Table 1

Atomic fractional coordinates and temperature factors for the room temperature phase Cmca. The temperature factors have the form $\exp(-T)$ where $T = 2\pi^2 u (2 \sin \theta / \lambda)^2$ for isotropic atoms and $T = 2\pi^2 \sum u_{ij} h_i h_j a_i^* a_j^*$ for anisotropic atoms; a_i^* are reciprocal lattice vectors and h_i are Miller indices. The u_{ij} are multiplied by a factor of 100.

atom	Wyckoff notation	point symmetry	x	y	z	u_{11} (u)	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Cd	a	2/m	0	0	0	2.27(3)	3.53(3)	2.27(3)	0	0	0.15(2)
Cl ₁	e	2	0.25	0.01516(9)	0.25	3.19(6)	7.6(1)	3.44(6)	0	-1.16(6)	0
Cl ₂	f	m	0	0.13070(9)	-0.0478(3)	9.6(2)	3.26(6)	5.02(8)	0	0	0.07(6)
N	f	m	0.5	0.1139(3)	-0.0216(7)	8.6(5)	4.0(3)	4.7(3)	0	0	-0.3(2)
C	f	m	0.5	0.1839(5)	0.044(1)	12(1)	5.1(5)	8.2(5)	0	0	-1.8(4)
H ₁	g	1	0.634	0.092	0.020	10					
H ₂	f	m	0.5	0.109	-0.139	10					
H ₃	g	1	0.628	0.206	-0.010	10					
H ₄	f	m	0.5	0.192	0.164	10					

Table 2

Atomic coordinates and temperature factors for the tetragonal low-temperature phase P4₃/nm. — For explanation of the symbols see

Table 1

atom	Wyckoff notation	point symmetry	x	y	z	$u_{11} = u_{22}$ (u)	u_{33}	u_{12}	$u_{13} = u_{23}$
Cd	d	2/m	0	0	0	1.65(1)	2.49(2)	0.10(1)	0.07(1)
Cl ₁	a	222	0.25	-0.25	0	2.38(4)	5.95(8)	0.80(5)	0
Cl ₂	e	mm	0.25	0.25	0.02327(7)	2.39(4)	3.92(7)	-0.70(6)	0
Cl ₃	i	m	-0.0390(1)	-0.0390	0.13109(5)	4.11(4)	2.45(4)	-0.52(4)	-0.03(3)
N	i	m	0.5188(4)	-0.0188	0.1142(2)	4.2(1)	3.1(2)	-0.4(2)	-0.2(1)
C	i	m	0.4671(7)	0.0329	0.1839(3)	7.1(3)	3.5(2)	-0.8(4)	-0.8(2)
H ₁	i	m	0.474(5)	0.026	0.077	7			
H ₂	j	1	0.505(5)	-0.119(6)	0.107(2)	6(1)			
H ₃ *)	j	1	0.553	0.053	0.071	7			
H ₄	i	m	0.526(5)	-0.026	0.210(3)	7			
H ₅	j	1	0.356(7)	0.007(6)	0.189(2)	11(2)			

*) Atom H₃ is not included in the struture factor calculation.

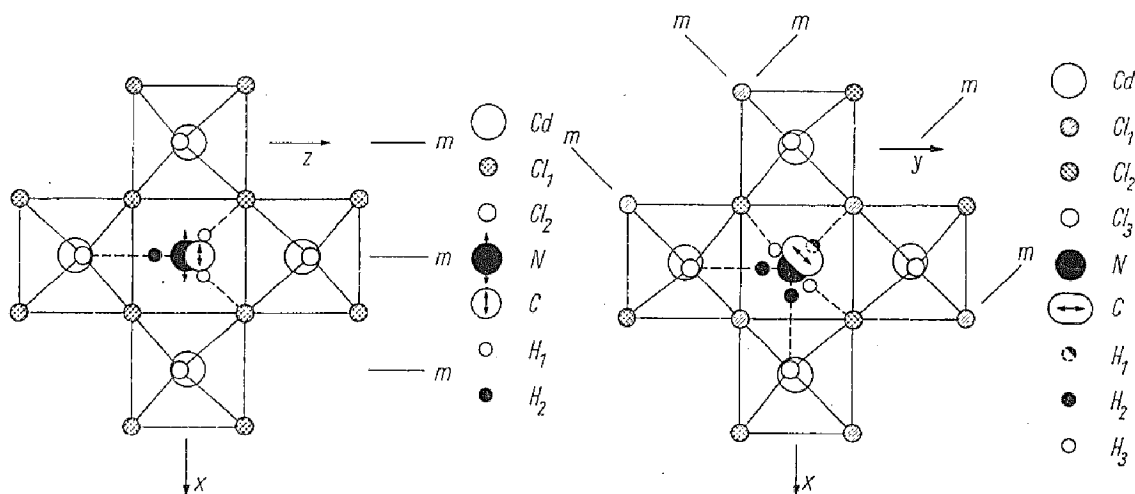


Fig. 1

Fig. 2

Fig. 1. Schematic projection on the layer plane of the essential features of the orthorhombic phase $Cmca$ (according to Table 1). The arrows at the N and C sites indicate the direction of their largest amplitudes. The CH_3NH_3 group is shown in the first potential well which corresponds to arrangement II. The second and the fourth potential wells which correspond to arrangement III can be obtained by a rotation about $\pm 90^\circ$ around the (long) b -axis

Fig. 2. Schematic projection on the layer plane of the essential features of the low-temperature tetragonal phase $P4_2/nm$ (according to Table 2). The arrow at the C site indicates the direction of the largest C amplitude. In arrangement I of the CH_3NH_3 groups only the protons H_1 and H_2 are contained. It could also be a superposition of the arrangements II and III of the orthorhombic phase which are responsible for the occurrence of H_3

the structure along the (long) b -axis showing one CH_3NH_3 group and the surrounding $CdCl_4$ octahedra is given in Fig. 1. The hydrogens of the methyl group are omitted for clarity.

4.2 Structure of the low-temperature phase

In this phase, the reflections were measured at a constant temperature of (234 ± 1) K. The structure was found to be tetragonal with the space group $P4_2/nm$ (No. 138, with the origin at the centre of symmetry). The lattice parameters are $a = b = 7.430$ (4), $c = 19.20$ (2) Å and $Z = 4$. (Note the reordering of the basis vectors to satisfy the space group convention.) The X-ray intensities were corrected for absorption and extinction in the same way as before. All hydrogen positions were found on a difference Fourier synthesis and the final residual was $R = 0.028$. Table 2 lists the parameters of the low-temperature phase. No e.s.d. are indicated for invariant or unrefined parameters. The hydrogen atom H_3 was found on a difference Fourier synthesis somewhat weaker than the remaining hydrogen atoms. This hydrogen did not converge during the refining procedure and was therefore not included in the structure factor calculation. Fig. 2 shows a projection of the tetragonal structure along the c -axis similar to Fig. 1.

5. Comparison of the Structures

Both structures can be described by two-dimensional layers stacked normal to the longest crystallographic axis with interlayer distances of approximately 9.60 Å. Each layer can be represented by a series of octahedra with Cd in the

centre and Cl in the corners; each octahedron is bonded to four others to form infinite two-dimensional layers as shown in Fig. 1 and 2. The NH_3 groups are located at the A-sites of the two-dimensional perovskite layer forming H bonds to chlorine atoms. The CH_3 groups are directed towards the adjacent layers linking these by van der Waals forces. The C-N bonds are located on mirror planes and are tilted relatively to the long axis with an angle of 20.13° in the room temperature phase and of 22.09° in the low-temperature phase.

In the orthorhombic phase the shortest hydrogen bond $\text{N}-\text{H}_2 \cdots \text{Cl}_2$ is $3.234(9) \text{ \AA}$ and lies approximately parallel to the layer on a mirror plane as shown in Fig. 1. The other two hydrogen bonds $\text{N}-\text{H}_1 \cdots \text{Cl}_1$ ($3.345(7) \text{ \AA}$) are symmetric and are connected to corner sharing atoms.

In the low-temperature phase the structure shows three crystallographically inequivalent Cl atoms as consequence of the splitting of the Cl_1 position of the room temperature phase. The NH_3 group lies also on a mirror plane parallel to the long axis but diagonally oriented to the layer axes (Fig. 2). There are three short $\text{N}-\text{H} \cdots \text{Cl}$ bonds of $3.305(4)$ and $3.320(3) \text{ \AA}$, respectively. Two of these bonds ($\text{N}-\text{H}_2 \cdots \text{Cl}_3$) are related by a mirror plane and lie nearly parallel to the layers; the third hydrogen bond ($\text{N}-\text{H}_1 \cdots \text{Cl}_2$) is connected to the corner sharing Cl atom above the Cd plane. There are two additional equivalent H bonds ($\text{N}-\text{H}_3 \cdots \text{Cl}_2$) with distances of $3.427(3) \text{ \AA}$ leading to chlorine atoms in the Cd plane. From the crystallographic point of view these five hydrogen bonds may be interpreted as a superposition of three different orientations of the methyl-ammonium group, the one described above (I) being the most probable one. The two additional orientations (II, III) are equivalent and correspond to the bonding scheme found in the orthorhombic phase with the three H bonds $\text{N}-\text{H}_1 \cdots \text{Cl}_2$, $\text{N}-\text{H}_3 \cdots \text{Cl}_1$ and $\text{N}-\text{H}_2 \cdots \text{Cl}_3$, the latter lying approximately parallel to the layer plane. From the anisotropic temperature factors, calculated by the structure refining procedure, the nitrogen shows a nearly isotropic behaviour, whereas the carbon exhibits large amplitudes perpendicular to the mirror plane.

These results show that the three orientations of the methyl-ammonium groups associated with the three bonding planes are related to a flipping of the C-N bond around a point located in the mirror plane. The flipping centre lies between carbon and nitrogen but closer to N.

6. Discussion

The structure determination of the orthorhombic phase proves that $(\text{CH}_3\text{NH}_3)_2 \cdot \text{CdCl}_4$ is isostructural with $(\text{CH}_3\text{NH}_3)_2\text{MnCl}_4$ and $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$. We assume that this is also the case for the tetragonal low-temperature phase since the deuterium NMR results obtained from $(\text{CH}_3\text{ND}_3)_2\text{MnCl}_4$ [6] are compatible with the space group $\text{P4}_2/\text{nem}$. The rare sequence of space groups with decreasing temperature: $\text{I4}/\text{mmm}$ ($Z = 2$), Cmca ($Z = 4$), and $\text{P4}_2/\text{nem}$ ($Z = 4$) can only be explained by changes in the motion of the CH_3NH_3 groups. In [5] a microscopic model of the phase transition $\text{I4}/\text{mmm}-\text{Cmca}$ is described for $(\text{CH}_3\text{NH}_3)_2 \cdot \text{MnCl}_4$ explaining the temperature dependence of the ^{35}Cl NQR frequencies of the two chemically inequivalent chlorine sites. This phase transition is due to a change in the CH_3NH_3 motion. NMR results [6] showed a fast rotation of the CH_3 radical as well as a fast jumpwise rotation of the NH_3 group around the molecular axis C-N. Since the C-N bond is tilted about 22° due to the formation

of N-H ... Cl bonds, the C-N bonds move on a conical surface between four equivalent potential wells above T_c becoming inequivalent below T_c . The potential wells are related only to the NH_3 group arrangements II and III for both phases I4/mmm and Cmca. This was derived from deuteron NMR measurements [6] which allowed the determination of the four possible NH_3 group orientations.

If the above model is correct, it should explain also our Cmca-P4₂/ncm transition. The motion of the CH_3NH_3 group in the orthorhombic phase at room temperature can be described by $W_1 \gg W_2 = W_4$, $W_3 \approx 0$, where the W_i denote the probability in time of finding the CH_3NH_3 group in the i -th potential well. Such a motion could well explain the anisotropy of the temperature factors found for the N and C atoms assuming a coupling between the x - and z -amplitudes.

At the phase transition a sudden change to $W_1 = W_2 = 1/2$, $W_3 = W_4 = 0$ occurs which leads to the five proton bridges shown in Fig. 2. Since the NH_3 group arrangement I does not exist in our model there is a slight discrepancy with X-ray results. With the information available we cannot decide whether the experimentally proved flipping of the C-N bond occurs between two or three stable positions. Although the maxima in the Fourier synthesis hint to the existence of arrangement I it must still be proved by an unambiguous measuring technique from which all possible C-N directions can be derived. For this reason a proton NMR study of $(\text{CH}_3\text{ND}_3)_2\text{CdCl}_4$ will follow in our laboratory.

An X-ray study of the structure below 173 K has been started simultaneously with an examination of other compounds in the $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{CdCl}_4$ series.

As a final remark we want to point out that the existence of isostructural Cd compounds in the family of two-dimensional perovskites of the formula $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)_2\text{MCl}_4$ opens new experimental possibilities for the study of their phase transitions and of the behaviour of alkyl-ammonium groups in solids.

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