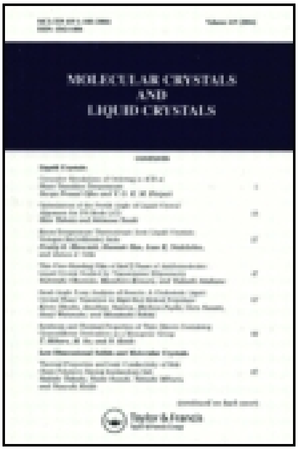

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Temperature and Pressure Induced Phase Transitions in the Perovskite-Type Layer Compound $(CH_3\text{-}NH_3)_2\ CdCl_4$

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TEMPERATURE AND PRESSURE INDUCED PHASE TRANSITIONS IN THE PEROVSKITE-TYPE LAYER COMPOUND $(CH_3NH_3)_2CdCl_4$

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Abstract The phase diagram of $(CH_3NH_3)_2CdCl_4$ has been established by means of a Raman scattering study under hydrostatic pressures ranging from 0 to 6 Kbars, and at different temperatures between 80 and 300 K. The phase sequence observed for this compound at ambient pressure is shown to be related not only to the reorientational dynamics of the $CH_3NH_3^+$ groups, but also to disordering processes involving the $CdCl_6$ octahedra. Increasing pressure causes the appearance of a new high pressure phase (HP). It is suggested that HP is an ordered phase and that its structure results from anti-phase slips of the perovskite layers.

INTRODUCTION

Bis-methylammonium cadmium tetrachloride, $(CH_3NH_3)_2CdCl_4$ (short MACC) belongs to the family of perovskite-type layer compounds. These compounds, with the general formula $(C_nH_{2n+1}NH_3)_2MX_4$ (where M = Mn,Cd, Fe,Cu,... and X = Cl, Br) exhibit a "two-dimensional" structure consisting of layers formed by corner-sharing MX_6 octahedra. The cavities between octahedra are occupied by the NH_3 heads of the alkylammonium groups which from hydrogen bonds with the halogen octahedra. Inter-layer bonding is mainly achieved by Van der Waals interactions between the alkyl ends.

These compounds received considerable interest recently because they can exhibit quasi two-dimensional magnetic properties[1] and also because they may serve as matrixes for chemical reactions occuring within the organic layers[2] ;

furthermore, they are also very attractive from the point of view of lattice dynamics, since most of these systems undergo numerous structural phase transitions[3]. This paper is devoted to a Raman scattering study of such transitions in MACC, for which the following phase sequence has been determined at ambient pressure[4,5] :

$$\underset{\text{(THT)}}{D_{4h}^{17}\ (Z=1)} \overset{484\ \text{K}}{\longleftrightarrow} \underset{\text{(ORT)}}{D_{2h}^{18}\ (Z=2)} \overset{279\ \text{K}}{\longleftrightarrow} \underset{\text{(TLT)}}{D_{4h}^{16}\ (Z=4)} \overset{163\ \text{K}}{\longleftrightarrow} \underset{\text{(MLT)}}{C_{2h}^{5}\ (Z=2)}$$

Z hereabove designates the number of formula units per primitive (Wigner-Seitz) unit-cell. This sequence of transitions has been extensively studied in recent years[3] and the mechanisms for the phase changes have been shown to be mainly related to the reorientational dynamics of the $CH_3NH_3^+$ groups coupled with different tilts of the $CdCl_6$ octahedra. Hence, in the THT, ORT and TLT phases, the $CH_3NH_3^+$ cations are in specifically disordered states of dynamic nature, whereas they are ordered in MLT. Hamann[6], from a high pressure infrared study of MACC, concluded that a new high pressure phase (HP) occurs at room temperature for $P > 14$ Kbars, but no conclusion could be given as to its structure.

In this paper, we shall report experimental results we have obtained recently by means of a low frequency Raman scattering study of MACC under hydrostatic pressures ranging from 0 to 6 Kbars and at various temperatures between 80 and 300 K. After having summarized our previous results obtained at ambient pressure[7,8,9], we shall discuss on a possible mechanism responsible for the occurence of the HP phase.

EXPERIMENTAL DETAILS

Single crystals of MACC measuring about 5 x 5 x 1 mm^3 were prepared at room temperature by slow evaporation of saturated aqueous solutions containing stoichiometric amounts of CH_3NH_3Cl and $CdCl_2$[10].

The Raman spectra were recorded on a Jobin-Yvon type Ramanor HG 2S double-monochromator spectrometer, coupled with a Spectra-Physics model 165 argon-ion laser. We used the 5145 Å emission line, with an incident power of about 400 mW.

The variable temperature high pressure cell used in this study was built in our laboratory ; it will be described in detail in a forthcoming paper[11].

RESULTS

The Raman spectra of MACC obtained at ambient pressure in the ORT, TLT and MLT phase have already been analysed[7,8,9]. It appears that the spectral features observed in these different structural modifications allow a determination of their respective domains of existence under high pressure. Also, the occurence of the new high pressure phase can be easily characterized on these spectra, and the P-T phase diagram of MACC, as established for the first-time from our data, is shown on figure 1. An experimental point previously obtained by Hamann[6] is also reported on this figure. As a matter of fact,this author concluded that MACC undergoes at $P \approx 14$ Kbars and at room temperature a phase change from ORT to a new high pressure phase ; in view of our data (limited up to 6 Kbars) the latter corresponds probably to the same HP phase as ours, so that the shape of the phase diagram has been extrapolated as indicated on figure 1 by the dashed lines. It clearly appears that the domains of existence of the TLT and MLT phases are limited at high pressures, whereas the ORT and HP phases are stable in wider pressure ranges. The THT phase occuring at high temperature[5] could not be studied with our high pressure cell.

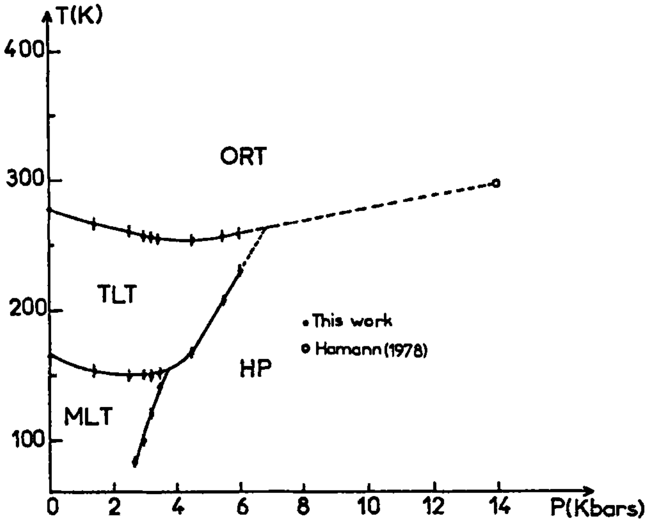

FIGURE 1 . The phase diagram of MACC.

The low frequency Raman spectra of MACC observed at different temperatures and at P = 3.5 Kbars are represented on figure 2, thus showing the sequence of transitions ORT ⟷ TLT ⟷ MLT ⟷ HP. Well defined polarization selections are obtained with MACC single crystals in the ORT, TLT and MLT phases, even at high pressures[11], but these selections are almost completely destroyed in the HP phase because of important crystal damage occuring at the MLT ⟷ HP and at the TLT ⟷ HP transitions ; this probably indicates that these transformations have a pronounced first order character. Also, these high pressure transitions are characterized by the presence of an underdamped soft-mode (figure 3a) lying between 8 and 15 cm^{-1} in the HP phase,

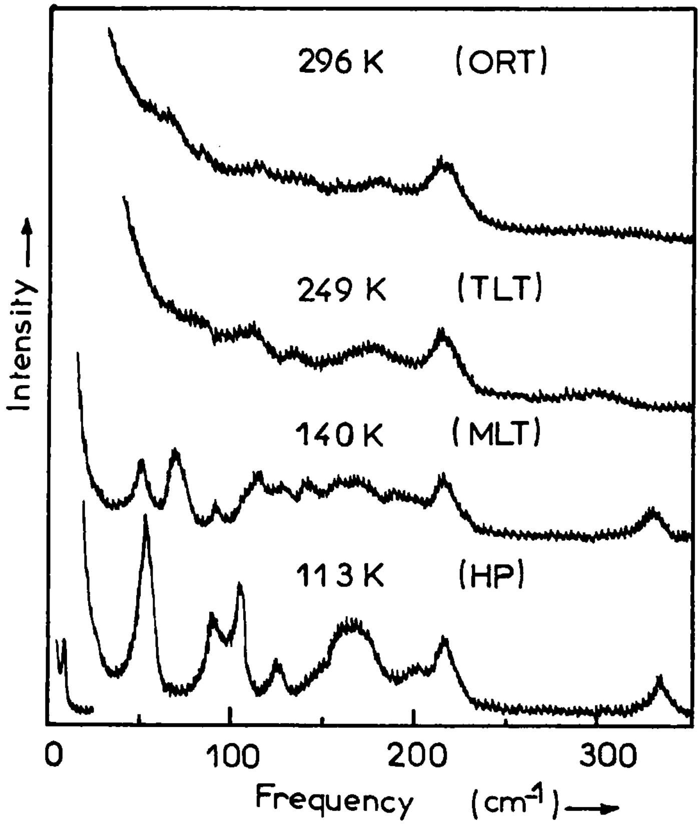

FIGURE 2 . The low frequency Raman spectra of MACC recorded at different temperatures and at P = 3.5 Kbars with the scattering geometry Z (XX) Y (Direction Z is collinear with the crystallographic axis perpendicular to the layer planes and X and Y to the crystallographic axes contained in these planes).

whose frequency, both temperature and pressure dependent, strongly decreases as the MLT or the TLT phase is approached

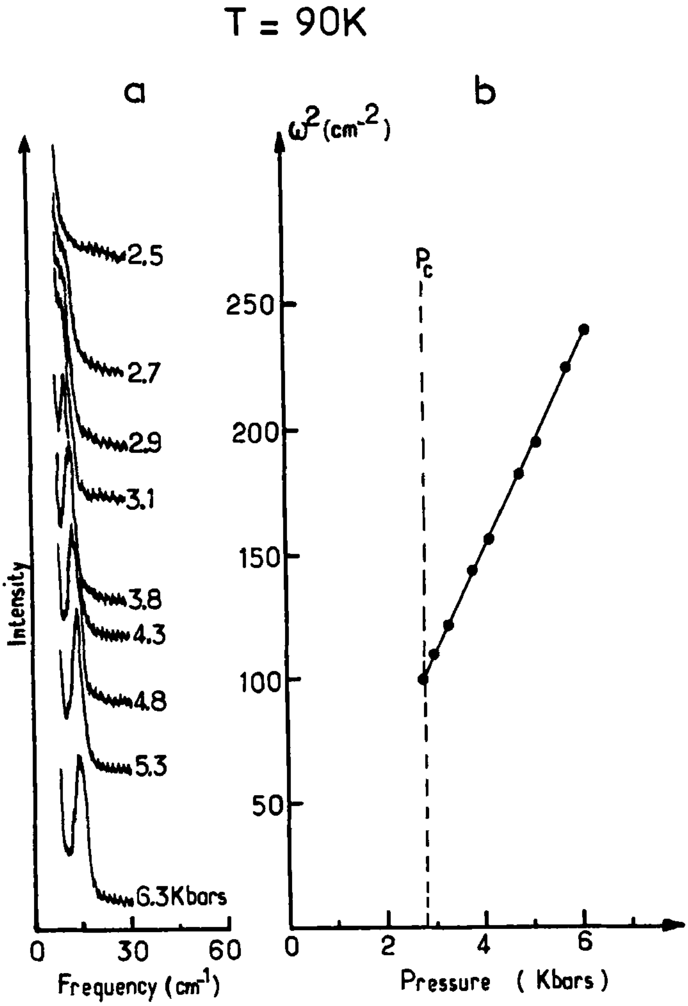

FIGURE 3 . a) Detail of the low frequency part of the Raman spectra through the HP ↔ MLT phase transition.

b) Pressure dependence of the soft mode frequency showing the Landau like behaviour $\omega^2 \propto (P-P_c)$.

from lower temperatures or from higher pressures. In particucular, we notice a Landau like behaviour for the frequency dependence of the soft-mode with pressure, at a fixed temperature (fig.3b). Note however the soft-mode frequency never reaches the value of zero at the transition temperatures and pressures, which is also consistent with a first-order character for the HP ⟷ MLT and the HP ⟷ TLT transitions. Nevertheless, the observation of a soft-mode clearly indicates that a displacive mechanism must be related to the occurence of the HP phase.

DISCUSSION

The phase sequence of MACC at ambient pressure

In previous studies on MACC[7,8,9], we gave already a complete assignment for the low frequency modes observed at ambient pressure and at different temperatures, through the domains of existence of the THT,ORT,TLT and MLT phases. Hence, on the bases of polarization selections observed with single crystal samples, comparisons with the spectra of isotopic derivatives $(CD_3NH_3)_2CdCl_4$ and $(CH_3ND_3)_2CdCl_4$ and group – theoretical considerations, we have interpreted the lattice vibrational spectra of MACC in terms of vibrations of the $CdCl_6$ octahedra and of "external" modes (rotatory and translatory vibrations) of the methylammonium groups. Low-lying diffusive or overdamped modes appearing on the α_{xx}, α_{yy} and α_{xy} spectra were shown to be a "finger-print" of the disordered ORT and TLT phases[9] (figure 4). These modes have been unambiguously assigned to "rotatory" vibrations of the rigid $CdCl_6$ octahedra and furthermore in the ORT phase, could not be accounted for by the $\vec{K} = 0$ selection rules derived from the time and space averaged structure determined by X-ray diffraction[4].

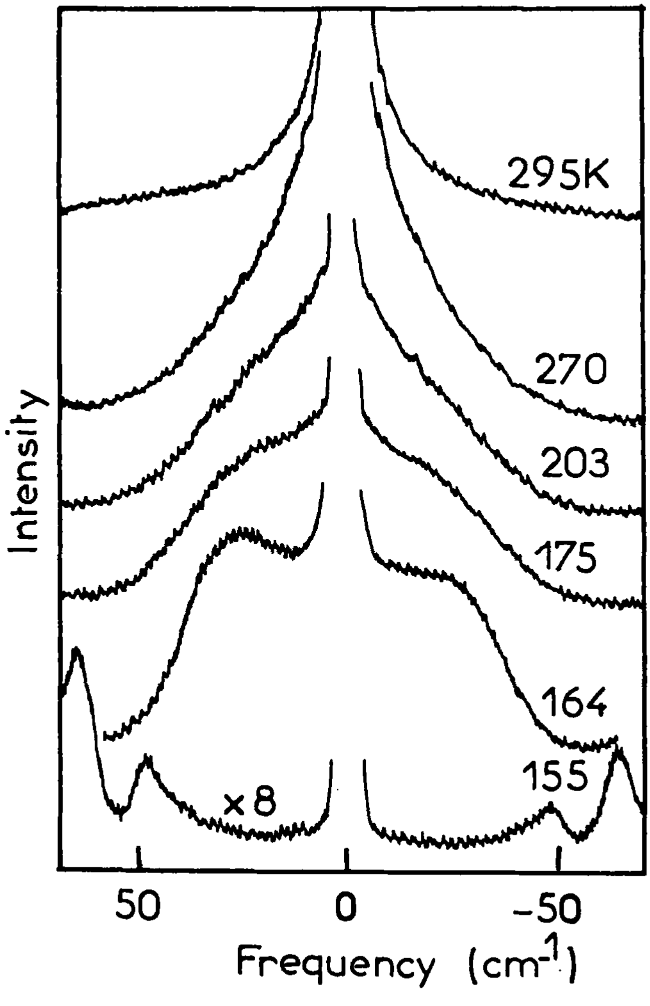

FIGURE 4 . Temperature evolution of the low-lying "Rayleigh-wings" observed on the Z(XX)Y spectrum of MACC at ambient pressure.

A new qualitative approach of the phase transitions mechanism has been proposed[9], based on the hypothesis that disorder involves not only the $CH_3NH_3^+$ groups but also the $CdCl_6$ octahedra. Then, the peculiar selection rules observed for the low-lying phonon modes involving $CdCl_6$ motions (figure 4) can be explained by the existence of local distorsions of the octahedra lattice, which reduce its instantaneous symmetry in a short range. Hence, these modes cannot be considered as the "symmetry breaking" or the "symmetry restoring" soft-modes associated to the order parameters relevant for the phase sequence[9], but rather must be interpreted as the "symmetry preserving" modes able to generate statistically the symmetry of the ORT and of the TLT phases. In a similar way, the "anomalous" selection rules also observed for the NH_3 torsional vibration of the organic cation are assigned to the existence of short-range correlations resulting from a coupling between the $CdCl_6$ and the $CH_3NH_3^+$ sub-lattices[9], due to the existence of NH...Cl hydrogen bonds.

Then we conclude that a realistic model for the description of the phase sequence observed at ambient pressure in MACC must take into account competing interactions existing between the $CdCl_6$ octahedra and the $CH_3NH_3^+$ sub-lattices.

The HP phase

The spectral changes observed at the TLT ⟷ HP phase transition show strong similarities with those noticed at the TLT ⟷ MLT transition[9], and in particular, we notice the complete disappearance of the broad low-frequency soft "Rayleigh-wing" characterizing disorder in the TLT structure (figure 4). This probably indicates that the HP phase, as MLT, has an ordered structure. On the other hand, the NH_3 torsional mode of the organic cation, situated at about 300 cm^{-1} in the ORT and the TLT phases[9] is abruptly shifted to higher frequency (330 cm^{-1}) in HP ; the same phenomenon was also noticed at the TLT ↔ MLT transition and was assigned[7] to a change of the $CH_3NH_3^+$ configuration from "orthorhombic" in TLT to "monoclinic" in MLT[4,5]. Hence, the $CH_3NH_3^+$ groups possibly adopt the so-called "monoclinic" configuration in HP too. There are however marked differences that appear between the spectra of the MLT and of the HP phases (figure 2), the most salient of which being observed in the frequency range around 70 cm^{-1} and in the very low frequency part of the spectra where a strong and narrow line is present at 8-15 cm^{-1} in the HP phase. As already mentioned it behaves as a soft-mode (figure 3) and appears to be a specific feature of the HP phase which has no equivalent in none of the structural modifications of the $(C_nH_{2n+1}NH_3)_2MCl_4$ compounds (with M = Mn and Cd and n = 1 to 3) actually studied by means of Raman spectroscopy[7,8,9,12,13,14]. Then, this feature must be related to a particular character of the HP structure and of course requires explanation ; however, in the absence of any structural data, the discussion developed hereafter must be considered essentially as speculation.

In view of our present knowledge of the lattice-dynamics in $(C_nH_{2n+1}NH_3)_2CdCl_4$ compounds[7,8,9,13,14], the low frequency soft-mode observed at 8-15 cm^{-1} in the HP phase of MACC cannot be assigned to an "external" vibration of the $CH_3NH_3^+$ groups, nor to a mode coming from the $CdCl_6$ octahedra, all of which being localized at much higher frequencies. Now if we refer to inelastic neutron scattering data obtained with $(CD_3ND_3)_2MnCl_4$[15] (the manganese homologue isostructural with MACC), obviously acoustical phonons only can account for the frequency of our soft-mode. This means we have to find a mechanism able to replace acoustical modes at zone-centre in the HP phase and to make them Raman active.

All acoustical branches inside the first Brillouin zone (defined with respect to the parent THT structure) exhibit phonon modes in the 8-15 cm^{-1} frequency range, compatible with our soft-mode[15]. Then numerous possibilities are offered ; note however that in any case, a mechanism involving such modes would lead to a modulated (incommensurate) phase and/or to a "lock-in" phase with a complex structure[16]. The spectra observed for the HP phase are rather simple, similar to those of the MLT phase (figure 2) and then, apparently, do not reflect very well such an eventuality.

Among the zone-boundary acoustical phonons, that of lowest frequency corresponds to the TA mode at point Z, the zone-boundary in the [001] direction[17], and lies at about 15 cm^{-1} [15], i.e. exactly in the frequency range of our soft-mode. This TA(Z) mode corresponds to anti-phase slips in the (a,b) plane of the octahedra layers against each other, and belongs to the Z_5^-/Eu irreducible representation in THT[18]. In the hypothesis that the HP phase derives from the parent THT phase by group to sub-group relations, as it is the case for all actually known structural modifications of MACC the assignment of the TA(Z) mode to the soft-mode for the transition to HP means that TA(Z) would be replaced at zone-centre and would be Raman active in HP as a totally symmetric mode. In other words, the order parameter for the phase transition to HP then corresponds to the Z_5^-/Eu representation in THT. Here again numerous possibilities are offered for the space-group of the HP phase, considering the kind of tilt adopted by the $CdCl_6$ octahedra in the layer planes, i.e. depending on what structure (THT,ORT,TLT,MLT or other) the HP phase derives from. All of them have minimum unit-cell volumes corresponding to Z = 2 or to Z = 4, and also lead to the loss of inversion symmetry for the Cd^{2+} sites.

To conclude, our data suggest that the mechanism for the occurence of the new HP phase of MACC is related to anti-phase slips of the perovskite layers. Note however that the possibility of a mechanism related to the occurence of an incommensurate phase at high pressure in MACC cannot be completely ruled out. Of course, diffraction measurements at high pressure are absolutely necessary to progress in the analysis of the structure of the HP phase.

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