TEMPERATURE AND PRESSURE BEHAVIOUR OF PEROVSKITE-TYPE BIDIMENSIONAL MOLECULAR COMPOSITES

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INTRODUCTION

Crystal structure determinations and structural phase transitions in perovskite-type layer compounds have gained much interest in recent years. Many studies have been published on the substances with formula $(C_nH_{2n+1}NH_3)_2 MCl_4$ (with M=Cd, Mn, Cu...) referred to as the "monoammonium" series (see for instance [Kind R. 1980; Mokhlisse R., Couzi M., Chanh N.B., Haget Y., Hauw C. and Meresse A. 1985; Chanh N.B., Hauw C., Meresse A., Rey-Lafon M. and Ricard L. 1985; White M.A. 1984; Hagemann H. and Bill H. 1985; Schenk K.J. and Chapuis G., 1988; Chanh N.B., Housty J.R., Meresse A., Ricard L. and Rey-Lafon M., 1989] and references cited therein). The alkyl-ammonium chains are located in between perovskite layers made of corner-sharing MCl_6 octahedra. The NH_3 groups form NH...Cl hydrogen bonds with the octahedra, and the interlayer bonding is achieved by means of long-range Coulombic forces as well as by van der Waals contacts between the CH_3 ends. The structural changes in these compounds are the result of reorientational motions of alkylammonium chains coupled to tilts of octahedra occurring in the perovskite layers. Structural phase transitions have also been reported in compounds with the general formula $NH_3(CH_2)_n NH_3 MCl_4$ belonging to the so-called "diammonium" series (Kind R., Plesko S., Gunter P., Ross J. and Fonsek J., 1981). The link between adjacent octahedral planes is now performed by alkylene chains bearing NH_3 groups on both ends. Several structure determinations in this series have been performed: n=2 and M=Cu, Mn (Birell G.B. and Zaslow B. 1972; Tichy K. Benes J., Hälg W. and Arend H., 1978), n=3 and M=Mn, Fe, Cd (Willett R.D. and Riedel E.F.,

1975; Willett R.D. 1977), n=4 and M=Mn (Tichy K., Benes J., Kind R. and Arend H., 1980, n=5 and M=Cd (Négrier P., Chanh N.B., Courseille C., Hauw C., Meresse A. and Couzi M., 1987). The case of M=Cd appears to be of special interest since it exhibits an unusual phase sequence where the phase stable at highest temperature is that of lowest symmetry. On the other hand, the evolution of the structure as a function of temperature has pointed out a negative thermal expansion in the direction perpendicular to the perovskite plane. This fact has been interpreted by the appearance of "twisted" conformation of the organic chain leading to a shortening of the chain length when the temperature increases. The twisted chains are already evidenced on the compound n=4 and M=Mn from a neutron diffraction structural determination (Tichy K. et al., 1980) and from an incoherent quasi elastic neutron scattering (Guillaume F., Sourisseau C., Lucazeau G. and Dianoux A.J. 1987). More recently, it has been demonstrated that these compounds may serve as matrices for chemical reactions occuring within the organic layers, when the organic parts present insaturated molecules (Tieke B., 1983; Day P. and Ledsham R. D., 1982; Tieke B. and Chapuis G., 1984, 1987). For example, the butadiene derivatives are able to undergo a stereospecific 1,4- addition reaction (polymerization) if exposed to UV or γ irradiation (Tieke et al., 1987).

On the other hand, these materials are known in the fields of dielectrics, optics and magnetism. They have the same layer-type perovskite structure as the well-known high Tc superconductor $La_{2-x}Sr_xCuO_4$.

In the present paper, general and specific aspects of these materials will be summarized (synthesis, crystallographic structural arrangements, thermal phase transitions, pressure effects, order-disorder behaviour...) in order to get out the interests and the properties of these bidimensional organic-inorganic molecular composites. Some particular examples will be given to show a specific property for each case.

I. Experimental

I.1. *Synthesis*

In general, the compounds have been prepared following the method proposed by Kind and Ross (1976). By mixing alcoholic solutions of n-alkylammonium chloride (prepared by HCl on the corresponding amine) and the adequate metal halogenide, according to the reaction:

$$2 (C_nH_{2n+1}NH_3Cl) + MX_2 \rightarrow (C_nH_{2n+1}NH_3)_2 MX_4$$

The reaction gives good results when n ≤ 6, i.e. single crystals may be obtained easily. For n ≥ 6, the reaction leads often to powder materials. In many cases, the quality of the crystals may be improved by several recrystallizations in alcoholic solutions. Another difficulty consists in the twinning phenomena which appear to be frequent for this type of structure. Nevertheless, complementary data can be obtained for these single crystal diffraction patterns and corroborate the powder diffraction results for the complete diffraction characterization.

I.2. *Diffraction techniques*

Single crystal and powder samples are investigated by usual diffraction apparatus. For thermal evolution, powder X-ray analysis has been performed by a Guinier-Lenné camera or a Guinier-Simon camera: this technique allows to point out the structural changes of the product where the temperature varies in the range of 100K-500K. These results will be used for single crystal investigations (crystal structure determinations) at given fixed temperatures. Experiments with pressure have been performed on powder samples using neutron diffraction (Couzi M., Chanh N.B., Meresse A., Négrier P., Papoular R.J. and Millet R., 1989).

I.3. *Differential Scanning Calorimetry DSC)*

These investigations allow the determination of the accurate transition temperature and the corresponding enthalpy changes. The C_p measurements can be also obtained. This information is very precious in order to indicate the type of the transition (first order, second order, glassy transition...). They can be also used to interpret the order-disorder in the structure through the entropy changes from the ordered structure (low temperature) to the disordered ones (high temperature).

I.4. *Spectroscopic investigations (IR, Raman, Brillouin...)*

These investigations are very fruitful to give informations on the dynamics and on the geometry of the chains and changes with the temperature or the pressure. As an example, in the case of the compound NH_3-$(CH_2)_5$-NH_3CdCl_4 (Négrier P. et al., 1987), Raman results allow one to point out the existence of a "twisted" conformation of the organic chain in addition to the chains presenting an "all-trans" conformation. The equilibrium "twist-all trans" chains depend on the temperature.

II. Crystal structures – phase transitions

The schematic crystal structures of the series $(C_nH_{2n+1}NH_3)_2 MX_4$ and $NH_3\text{-}(CH_2)_n\text{-}NH_3MX_4$ are given respectively in figure 1a and 1b. These structures have a strongly bidimensional character. They are constituted by and alternative succession of inorganic layers MX_4 (of perovskite type) and organic layers $C_nH_{2n+1}NH_3$ or $NH_{3\_}(CH_2)_{n\_}NH_3)$, the bonding between these alternative layers is assumed by hydrogen bonds N-H...X type. The lattice energies of these compounds are so very anisotropic: very strong in the directions parallel to the perovskite layer (ionic or covalent character) and weak in the direction perpendicular to the layer (Van der Waals contacts). The figure 2 gives the details of the bonding between inorganic layer (octahedra MX_6) and the nitrogen atom (head of the organic chain). It can be seen that there are two possibilities for this bonding. First, when two hydrogen atoms are connected to two axial halogen atoms of the octahedra
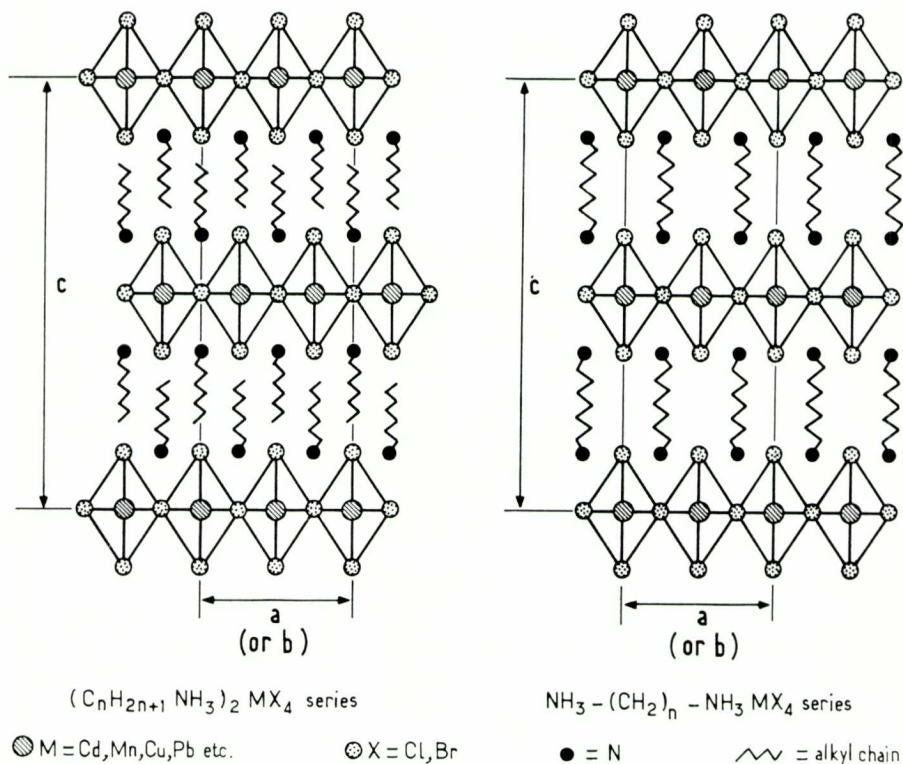

$(C_nH_{2n+1}NH_3)_2 MX_4$ series

$NH_3 - (CH_2)_n - NH_3 MX_4$ series

⊘ M = Cd,Mn,Cu,Pb etc.   ⊛ X = Cl,Br   ● = N   ∿ = alkyl chain

Fig. 1. Schematic representation of structural arrangement in the bidimensional perovskite-type molecular composites.

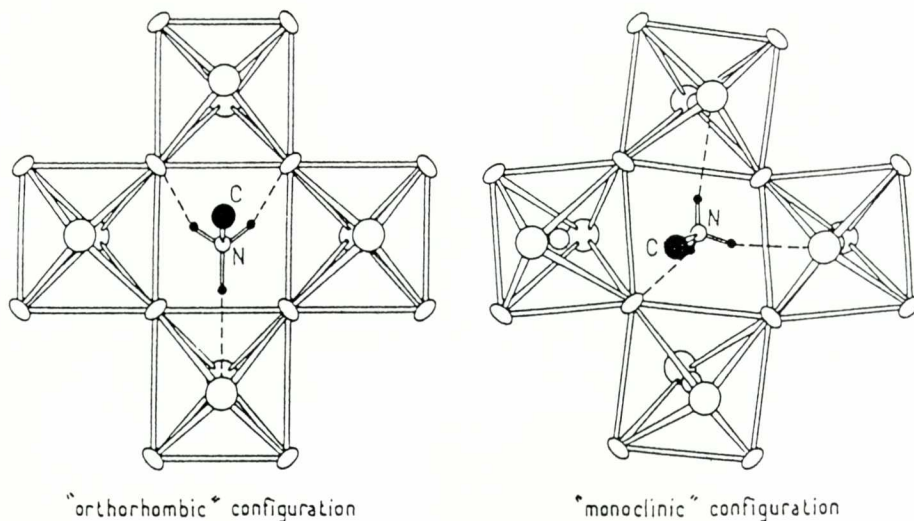"orthorhombic" configuration   "monoclinic" configuration

Fig. 2. Hydrogen bonding region showing the two types of linking between the organic chain and the inorganic perovskite layer.

and the third hydrogen atom to an equatorial halogen atom, this possibility is called "monoclinic" configuration; when two hydrogen atoms are connected to two equatorial halogen atoms and the third hydrogen atom to an axial halogen atom, this possibility is called "orthorhombic" configuration.

The hydrogen bonds N-H...X which connect the organic chain to the perovskite layer can be easily annealed by a thermal effect: during an increasing temperature process, it is demonstrated that the rigid organic chain can be reorientationally disordered by a rotation by steps of 90 degrees along their long axis. At higher temperature, in addition to this reorientational disorder, appear the conformational disorders leading to gauche or/and twisted conformations.

Crystallographically, the existence of twisted conformations of the organic chain has been confirmed in the case of the derivative NH_3-$(CH_2)_5$-NH_3CdCl_4 (Négrier P. et al, 1987, 1989). The crystal parameters present a negative thermal expansion in the crystal direction parallel to the chain axis (figure 3).

The phase sequence in this compound is unusual: the high temperature phase has the lowest symmetry (monoclinic)

	337 K		417 K	
orthorhombic	↔	orthorhombic	↔	monoclinic
Pnma	(2nd order)	Imma	407 K	(B2/m, powder results)

whereas the low temperature phases have a higher one (orthorhombic). Crystal structure determinations of the two orthorhombic phases have shown the presence of the twisted conformation besides the "all-trans" conformation: figure 4 gives the schematic representation of these confor-
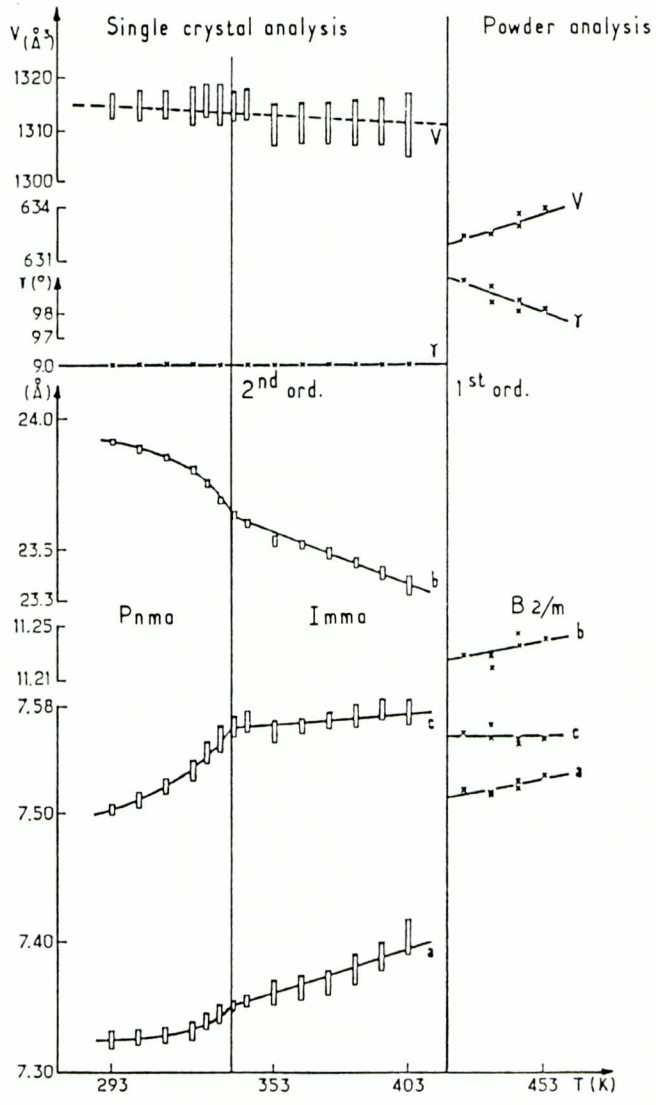

Fig. 3. Lattice parameters evolutions with the temperature and through the two phase transitions at 337K and 417K.

mations. The twisted chains correspond to states where the lower NH_3 has the orientation $N(1)$ and the upper NH_3 has the orientation $N(12)$ (or vice versa). The torsion angle 2φ of the twisted chains can be identified as the angle of rotation of the all-trans chains between these two limit positions: the best agreement in the refinement of the structure is obtained for a proportion of 0.45 ± 0.05 of twisted chains in the Imma phase and the value of φ equal to 45 degrees. The proportion of twisted chains increases with temperature and the high temperature monoclinic phase contains "twisted" chains only.

Another type of structural disorder can affect some particular derivatives of the series: the mineral perovskite layers are not always perfectly ordered in the direction perpendicular to their plane and the structure presents a
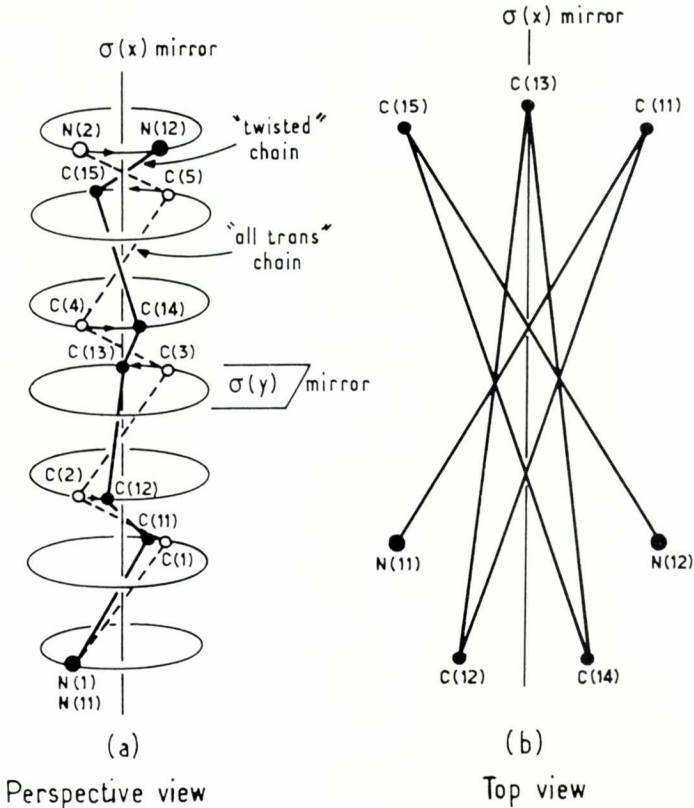

Fig. 4. Schematic representation of a "twisted" chain introduced in the high temperature phase (the "trans" chain is represented by a dashed line). a) perspective view, b) projection onto the ac plane.

bidimensional disorder. The existence of this kind of planar disorder can be pointed out by diffuse diffusion scattering experiments. It consists of fixed crystal diffusion exposures (film techniques) using monochromatized X-ray radiation (Denoyer F., Comes R., Lambert M. and Guinier A., 1974). A planar disorder implies the presence of diffuse streaks, perpendicular to direct perovskite planes: these streaks have been evidenced by this technique in the case of $(CH_3 NH_3)_2 CdCl_4$ (Mokhlisse R., Chanh N.B., Couzi M., Haget Y., Hauw C. and Meresse A., 1984) and $NH_3 - (CH_2)_5 - NH_3$ $CdCl_4$ (Négrier P. et al, 1989). As an example, figure 5 shows the presence of these diffuse streaks, perpendicular to the perovskite layers, obtained with fixed single crystal exposures (Mo λ radiation) of $NH_3 - (CH_2)_5 - NH_3$ $CdCl_4$. The diffuse intensities along the streaks are modulated. These modulations have been calculated using the "shape factor" of an idealized perovskite layer which yields three types of diffuse row lines (namely for $h \pm k = 4n$, $h \pm k = 4n + 2$ and $h \pm k = 2n$). The comparison between calculated and experimental diffuse streaks is satisfactory.


III. THERMAL CHARACTERIZATION AND THERMODYNAMIC APPROACH

Structural phase transitions in these compounds have been also investigated by thermal analysis and numerous publications related to this approach can be noted in the literature (Cp measurements, enthalpies and entropies of transition...) (Chanh N.B. et al, 1985; Chhor K., Abello L., Pommier C. and Sourisseau C., 1988; Van Oort M.J.M. and White A.M., 1985; Landi E. and Vacatello M., 1975). A thermodynamical analysis can be made to interpret the order-disorder changes of the organic chains. It is based on the entropy changes through the successive phase transitions which extend between the low temperature ordered phase to the high temperature total disordered one.

A first approach consists in considering that, in the organic chain, four consecutive atoms are involved in the definition of a torsion angle (knee). Two configurations can be obtained: a trans configuration and a gauche configuration. If p is the total number of knees, the variation of the configuration entropy change is $\Delta S_{conf}^{chains} = p R \, Log \, 2$ where R = Boltzmann constant. A second approach has been proposed by Kind et al. Kind R. Plesko S., Arend H., Blinc R., Zeks B., Selinger S., Lozar B., Slak J., Levstik A., Filipic C., Zagar V., Lahajnan G., Milia F. and Chapuis G. (1979), taking as model the melting of n-paraffin series. These authors propose $\Delta S_{conf}^{chains} = 0.9 \, (n-2)R$. A synthesis approach can be made in the cadmium derivatives series $(C_nH_{2n+1}NH_3)_2 CdCl_4$. In the table 1 values of $\Delta S_{exp}^{(ord \to disord)} = \Sigma \Delta S_{exp}$ and ΔS_{calc} obtained with the two above models have been reported. The
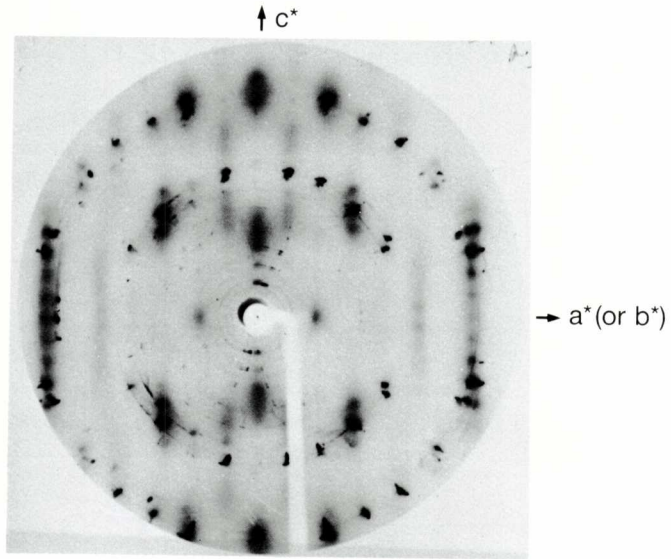
(a)
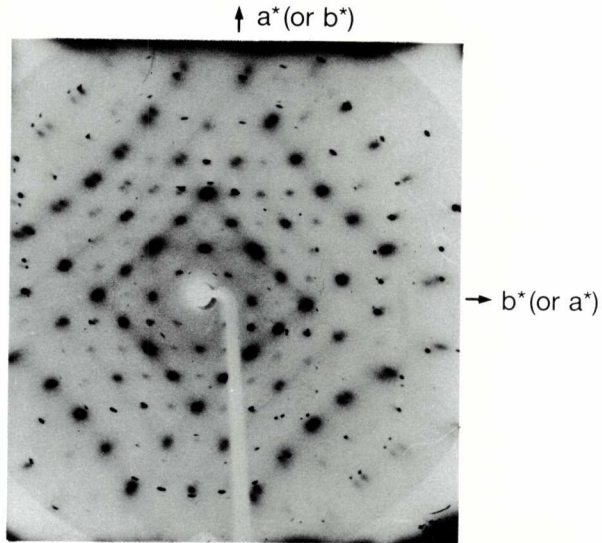
(b)

Fig. 5. Diffuse X-ray scattering patterns observed at room temperature with NH_3-$(CH_2)_5$-NH_3 $CdCl_4$ single crystal. a) the reciprocal a^*c^* (or b^*c^*) plane: b) the reciprocal a^*b^* plane.

comparison point out that the first approach is more valid for shorter chains and the second model for longer chains in the $(C_nH_{2n+1}NH_3)_2 CdCl_4$ series.

Table 1. Thermodynamical analysis of the order-disorder of organic chains in the $(C_nH_{2n+1}NH_3)_2 CdCl_4$ series.

Compound (n)	Nb of knees	ΔS_{exp} ord-disorder	ΔS_{calc} (*) model 1 - (**) model 2
8	12	8.6 ± 0.7 R	9.66 R (*) 10.80 R (**)
10	16	13.2 ± 0.8 R	12.50 R (*) 14.40 R (**)
12	20	14.6 ± 0.8 R	15.24 R (*) 18.00 R (**)
16	28	27.3 ± 1.6 R	20.79 R (*) 26.20 R (**)

IV. SPECTROSCOPIC INVESTIGATION

Spectroscopic analysis is also used to investigate the conformational disorder of the organic chains. In particular, in the diammonium series $NH_3 - (CH_2)_n - NH_3 MX_4$, the existence of a "twisted" conformation has been evidenced by both crystallographic and Raman spectroscopic (Négrier P. et al, 1987) approaches. Figure 6 shows the relative evolution of the "twisted" chains and "all - trans" chains when the temperature increases. The enthalpy corresponding to the transformation "all - trans" $\rightleftarrows$ "twist" chains can be determined from spectroscopic results. Table 2 gives the results concerning some derivatives, for different values of n: it is clear that this energy becomes higher when the length of the organic chains becomes shorter.

Table 2. Values of "twist" - "all - trans" enthalpy conversion (Négrier P. et al., 1989 and references cited therein)

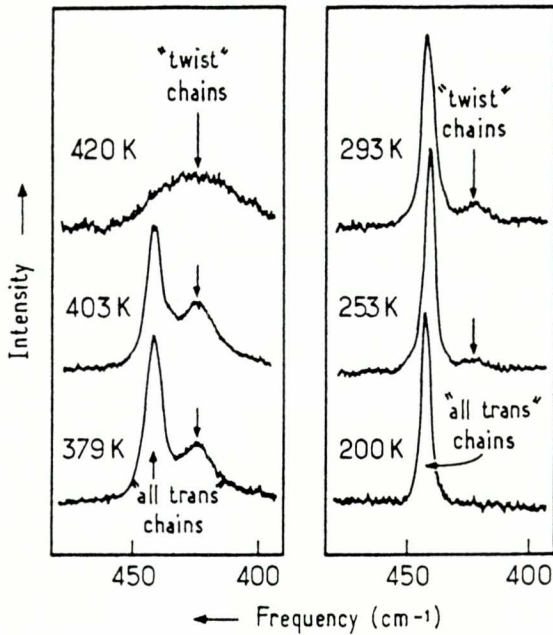| Compound	ΔH (KJ. mole-1)
$NH_3 - (CH_2)_5 - NH_3 CdCl_4$	17.1 ± 2
$NH_3 - (CH_2)_5 - NH_3 MnCl_4$	$\cong 16.7$
$NH_3 - (CH_2)_4 - NH_3 MnCl_4$	$\cong 21.7$
$NH_3 - (CH_2)_3 - NH_3 CdCl_4$	$\cong 24.2$

Fig. 6. Evolution with temperature of the α_{zz} Raman spectrum of NH_3-$(CH_2)_5$-NH_3 $CdCl_4$ in the region of CCN-CCC bonding vibration.

V. MOLECULAR COMPOSITES WITH INSATURATED ORGANIC PARTS

Since a few years, the layer perovskite-type mixed structures gained considerable interest as templates for solid state reactions (Tieke B., 1983; Tieke B. et al, 1984, 1987; Day P., 1982). It has been found that the derivatives with organic part having double or triple bonds can be the site of photoreacions as polymerization. The solid state polymerization of monomers preoriented in a crystal lattice or in a host matrix (here, the perovskite layers) represents a suitable method to obtain highly ordered polymers with a stereoregular arrangement of the substituents. An example of such reactions is the photochemical (2+2) cycloaddition of butadiene monomers in inclusion perovskite layers, initiated by UV, γ radiation. It has been shown (Tieke B. et al, 1984) that the 1,4 disubstituted butadiene derivatives can be polymerized in the crystalline state in the following way:
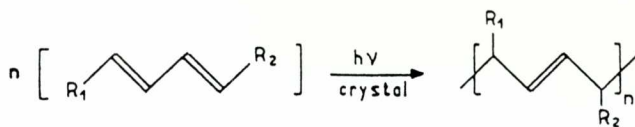
The schematic representation of the solid state polymerization in pe-
rovskite layered structure proposed by Tiene et al. is given in figure 7.

In our laboratory, several insaturated perovskite layered composites
have been studied. The chosen organic molecules have been:

– 1-4 diaminocinnamic acid - $CdCl_4$ (one double bond in the organic
part)

– sorbylamine - $CdCl_4$ (two double bonds in the organic part)

– propargylamine - $CdCl_4$ (one triple bond in the organic part)

The results show the compatibility and the incompatibility of a chemi-
cal addition with the crystalline structure arrangement. It is clear that these
materials can present very interesting physical or chemical properties, es-
sentially due to the low dimensional structure arrangement of the matrix
(anisotropic properties such as electric conductivity, optical behaviour
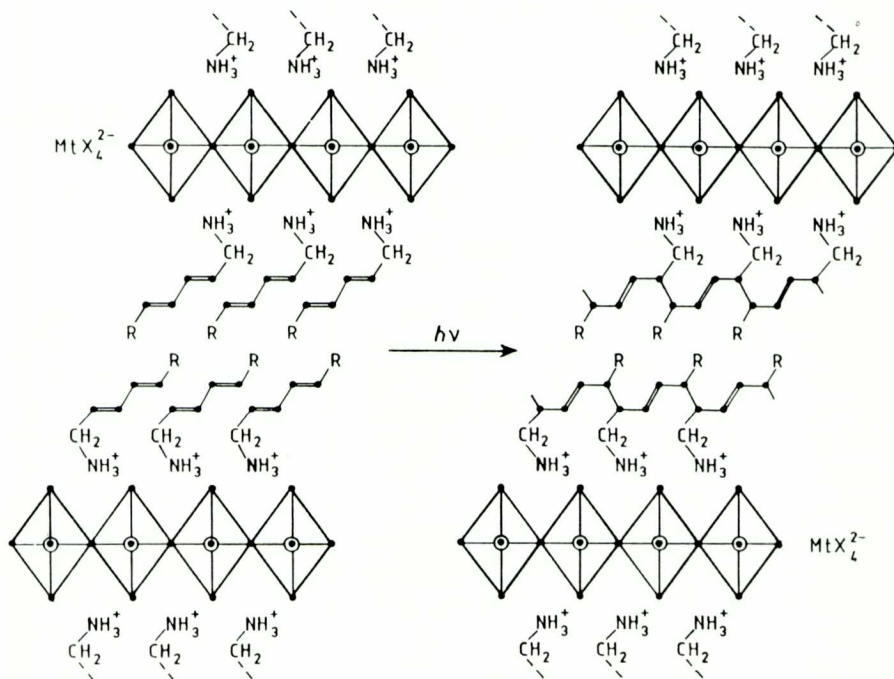etc.).

Fig. 7. Schematic representation of the butadiene polymerization in layer perovskites (after
Tieke et al, 1984, 1987).

SUMMARY

Inorganic-organic bidimensional complexes of the series of $(R - NH_3)_2 MX_4$ or/and $R - (CH_2)_n - R' MX_4$ (where R, R' = saturated or unsaturated organic part; MX_4 = mineral part with M = Cu, Mn, Cd, Fe, Pb... and X = Cl, Br) have gained many interest in last years. Various experimental and theoretical approaches (diffraction technique, calorimetric analyses, optical and dielectrics measurements, spectroscopy IR, Raman, group theory...) are used to investigate the temperature and pressure behaviour of these derivates (crystal structure determinations, phase transitions, phase diagrams...). The phase changes are mainly governed by the dynamics and the conformational disorders of the organic chains. On the other hand, the disorders of the perovskyte layers can be evidenced by diffuse diffusion experiments. The case of unsaturated organic part is particularly interesting: under irradiations (X, UV, γ...), it is possible to initiate the photo-reactivity in this part leading to the formation of stereoregular polymers (bidimensional arrangement).

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