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DSC and Raman spectroscopy studies of high temperature structural phase transitions in $(C_3H_7NH_3)_2PbCl_4$ [1]

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Abstract

The Raman spectra (260–10 cm^{-1}) and differential scanning calorimetry of polycrystalline samples of $(C_3H_7NH_3)_2PbCl_4$ were investigated in the temperature range 300–450 K. This work shows three first-order phase transitions $I \rightarrow \gamma \rightarrow \beta \rightarrow \alpha$, respectively at 340 K ($\Delta H_1 = 3.73$ kJ mol^{-1}), 371 K ($\Delta H_2 = 0.22$ kJ mol^{-1}) and 406 K ($\Delta H_3 = 0.25$ kJ mol^{-1}). The thermal behaviour and crystal structure analogy with the Mn derivative suggest an incommensurability of the γ phase, embedded between two commensurate phases I and β, both belonging to the same space group. The phase transition $I \rightarrow \gamma$ is governed by an order–disorder mechanism involving mainly alkylammonium chains; the other transitions are driven by displacive mechanisms involving deformation of $PbCl_6$ octahedra. The highest temperature phase α seems to be a plastic phase.

INTRODUCTION

The compounds of general formula $(RNH_3)_2MX_4$ (R = alkyl; M = metal; X = Cl, Br) exhibit a perovskite bidimensional layered structure as encountered in K_2NiF_4 [1]. Their solid state polymorphisms are well known, including commensurate and incommensurate phases [2]. Previous studies have shown that the molecular dynamics responsible for these phase transitions involve either rotational jumps of NH_3 groups or conformational disorder of aliphatic chains [3–6]. In a recent work devoted to bis(*n*-propylammonium) tetrachloroplumbate ($(C_3H_7NH_3)_2PbCl_4$) we described two phase transitions, shown by means of Raman spectroscopy, between 80 and 300 K [3]. These results led us to complete this work by

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studying the thermal behaviour in a higher temperature range. Therefore our present work deals with this compound by both Raman spectroscopy and DSC measurements between 300 and 450 K, showing three new transitions. Their mechanism and also the existence of an incommensurate phase will be discussed.

EXPERIMENTAL

The title compound was synthesized by mixing $C_3H_7NH_3Cl$ and $PbCl_2$ in HCl solution with the stoichiometric ratio 1:2 [3,7]. Small crystals were dropped into a Pyrex vessel (3 mm diam.). The sealed vessel was introduced in an oven especially built in our laboratory (10–50 V a.c. supply). Raman spectra were recorded on a DILOR RTI 30 equipped with an argon ion laser (514.5 nm; Spectra Physics model 2000). A K-type thermocouple was fixed to the glass pipe on the opposite side to the incident beam.

Thermograms were recorded between 300 and 420 K (heat rate 10 K min^{-1}) on a differential scanning calorimeter (Perkin-Elmer DSC4). The sample was encapsulated in a 50 μl aluminium volatile sample pan (Perkin-Elmer model B014-3021). Apparatus calibration was effected with NBS benzoic acid. Curve analysis was performed with the Perkin-Elmer TADS program. Temperature transitions were determined by intercepting the baseline with the tangent to the left side of the peak (onset temperature in the TADS program).

DIFFERENTIAL SCANNING CALORIMETRY

The thermogram (Fig. 1) shows three endothermic peaks in the range 300–420 K, at 340, 371 and 406 K, respectively. In Table 1 are listed, for each transition, the transition temperature, the enthalpy change, the entropy change computed from the relation $\Delta S = \Delta H/T$ and the number Ω (equivalent position) deduced from the relation $\Delta S = R \ln \Omega$.

The results suggest that these phase transitions belong to the first-order type, after Ehrenfest [9]. By analogy with the nomenclature of Depmeier et al. [10,11] and of Kind and Muralt [12], the high temperature phases have been named γ, β, α; the phase I is that existing at 300 K.

A recent calorimetric study was undertaken by DSC on the same compound [15] but restricted to the domain 293–400 K. Only one transition has been observed at $T_c = 339.5$ K, $\Delta H_T = 3.25$ kJ mol^{-1}.

Analysis of results shows a transitional behaviour of this compound very similar to that of the manganese derivative $(C_3H_7NH_3)_2MnCl_4$ [10,11]. The latter exhibits three transitions: a first-order transition at 344 K ($\Delta H = 0.8$ kJ mol^{-1}, $\Delta S = 2.34$ J mol^{-1} K^{-1}, $\Omega = 1$) more energetic than the second first-order one observed at 396 K ($\Delta H = 0.25$ kJ mol^{-1}, $\Delta S =$

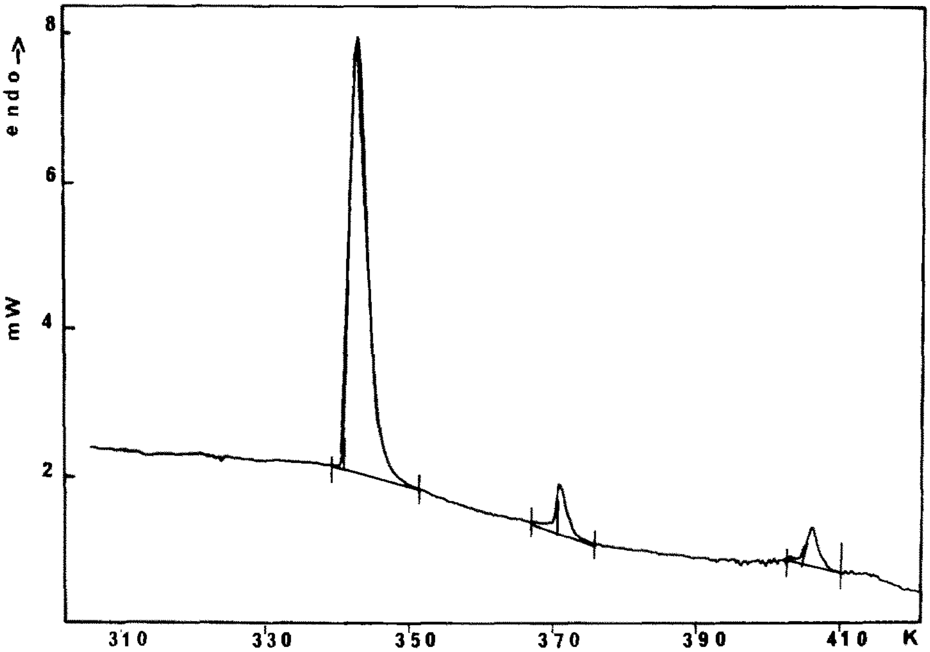

Fig. 1. Thermogram of $(C_3H_7NH_3)_2PbCl_4$ between 300 and 420 K. Heating rate 10 K min^{-1}.

0.63 J mol^{-1} K^{-1}, $\Omega = 1$) and the third one at 446 K, estimated to behave as a second-order type [10,11].

A great difference in transition enthalpies (or entropies) has been observed in mesogenic compounds of the type H_{2n+1}–C_n–O–C_6H_4–N–(O)–N–C_6H_4–O–C_n–H_{2n+1} ($n = 1$–7). These compounds exhibit a solid–solid phase transition preceding the appearance of the first mesophase, with an enthalpy variation depending mainly on the n parity (odd–even effect) [8], according to

even n: ΔH (solid II $\rightarrow$ solid I) $<$ ΔH (solid I $\rightarrow$ mesophase)
odd n: ΔH (solid II $\rightarrow$ solid I) $>$ ΔH (solid I $\rightarrow$ mesophase)

However, in these compounds, the transitions between mesogen phases or mesogen phase → isotropic liquid exhibit enthalpy values nearly identi-

TABLE 1

Thermodynamic results from DSC measurements

Transition	Temperature (K)	ΔH (kJ mol^{-1})	ΔS (J mol^{-1} K^{-1})	Ω
$I \rightarrow \gamma$	340	3.73	11	3.74
$\gamma \rightarrow \beta$	371	0.22	0.59	1.06
$\beta \rightarrow \alpha$	406	0.25	0.61	1.07

cal with and much weaker than (about one tenth) those of solid II → solid I or solid I → mesophase transitions. This previous study pointed out that the transition II → I generates a structural disorder (more or less important according to the n value) in the alkyl chain C_nH_{2n+1}.

From Table 1, the Ω number is about 4 for the first transition I → γ and very close to 1 for the other transitions $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$.

Our results suggest an order–disorder mechanism for the I → γ transition at 340 K: the alkylammonium cations may occupy equiprobably four equivalent positions. In contrast, the other transitions $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ occur without any static disorder change.

This mechanism differs notably from that described by Kind [2], who proposed a dynamic reorientational disorder of the propylammonium group among four equivalent positions, occurring only in the highest temperature transition $\beta \rightarrow \alpha$ (second-order transition) in the homologous compound $(C_3H_7NH_3)_2MnCl_4$. On the other hand, these thermodynamic results show the same behaviour as that observed in the homologous $(RNH_3)_2MX_4$ compounds; the first phase transition I → γ observed at 340 K remains the most important step towards the gradual crystal breakdown.

RAMAN SPECTROSCOPY

Raman spectra (Fig. 2) have been recorded at different temperatures corresponding to the phases observed by DSC, and only in the 260–10 cm^{-1} frequency range. This spectral domain includes the lattice modes which are the most sensitive to phase transitions and give rise to the most intense bands throughout the spectrum. Therefore, when a phase transition is occurring, the spectral evolution is directly connected with structural changes in the crystal. The frequencies of the observed modes are listed in Table 2.

Transition I → γ (340 K)

When the first transition is occurring, the Raman band at 183 cm^{-1}, previously assigned to a libration of the cationic chain [3], shifts to 188 cm^{-1} without noticeable broadening, whereas the feature below 150 cm^{-1} is broadened because of thermal motions. The wavenumbers of bands observed at 131, 112 and 75 cm^{-1} decrease by about 10 cm^{-1} with nearly the same relative intensities. The three bands between 47 and 34 cm^{-1} seem to be fused in a single broad band at about 40 cm^{-1}, but it is not easy to distinguish whether some modes are really vanishing or these bands are coalescing because they are strongly broadened. These latter bands were assigned to librations of $PbCl_6$ cages [3], and one can accept—under the second hypothesis—that the external modes in both phases I and γ keep the same shape, subsequently leading to a fairly similar packing of layers of

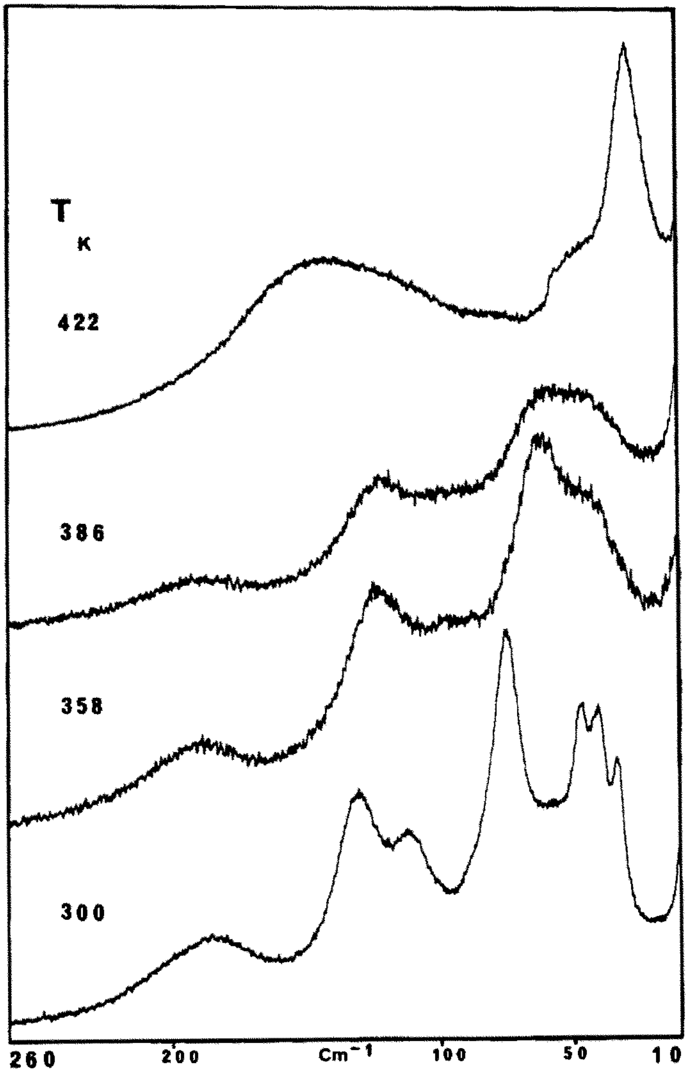

Fig. 2. Raman spectra at different temperatures of lattice vibrations in $(C_3H_7NH_3)_2PbCl_4$, corresponding to phases I (300 K)$\xrightarrow{340\,K}\gamma$ (358 K)$\xrightarrow{371\,K}\beta$ (386 K)$\xrightarrow{406\,K}\alpha$ (422 K).

$PbCl_6$ octahedra. Thus the decrease in the wavenumbers between 140 and 75 cm^{-1} would reflect the weakening of the N–H $\cdots$ Cl hydrogen bonds.

Transition $\gamma \to \beta$ *(371 K)*

The spectral alterations concern mainly the bands at about 60 and 40 cm^{-1}: firstly, their relative intensities are strongly decreasing towards those of the bands at 122 and 188 cm^{-1}, which remain almost unmodified.

TABLE 2

Raman spectral wavenumbers (cm^{-1}) at different temperatures [a]

Phase I $\xrightarrow{340\text{ K}}$	Phase $\gamma \xrightarrow{371\text{ K}}$	Phase $\beta \xrightarrow{406\text{ K}}$	Phase α	Assignment
10vw				
34m			29	R′ $PbCl_6$
41m	≈ 40	44		R′ $PbCl_6$
47m			45	R′ $PbCl_6$
63m				
75s	63	≈ 60	56	
84vw				R′ Alk–NH_3^+
112m	98	96	80	
131s	123	123	118	ν_5 $PbCl_6$
183m	188	188	143	R′ NH_3^+

[a] Key: vw, very weak; m, medium; s, strong.

Secondly, besides a strong broadening of these bands, the lowest frequency band (44 cm^{-1}) becomes nearly as intense as the other at 60 cm^{-1}. This result could be explained in terms of $PbCl_6$ octahedra distortions with the same plane chaining; the chlorine atoms shared by two octahedra would remain weakly perturbed, so that the vibration ν_5 (Cl–Pb–Cl) is not disturbed by the transition.

Transition $\beta \to \alpha$ (406 K)

The α phase spectrum is totally different from the previous ones. In particular, the band at 188 cm^{-1} vanishes while a very broad band appears at about 143 cm^{-1} and the band at 122 cm^{-1} becomes a shoulder at about 118 cm^{-1}. The band at 96 cm^{-1} shifts as a damped band at 80 cm^{-1}, while those previously observed at 60 and 44 cm^{-1} appear to shift to 56 and 45 cm^{-1}, respectively. However, the outstanding character of this new phase is the appearance of a very intense and sharp line at 29 cm^{-1}. This spectroscopic behaviour is close to that observed in "plastic phases" [13], in which there exists a dynamic rotational disorder. The very broad line at 140 cm^{-1} could be assigned to the almost free anharmonic rotation of the alkylammonium cation around its median axis (the lowest inertia moment). Finally, the band at 29 cm^{-1} could be assigned to the rotation of $PbCl_6$ octahedra around their axis perpendicular to the layer planes.

STRUCTURAL INFORMATION

The compound studied here, like its homologues with Mn [10,11,14,17] or with Cd [1] cations, exhibits a perovskite structure with bidimensional

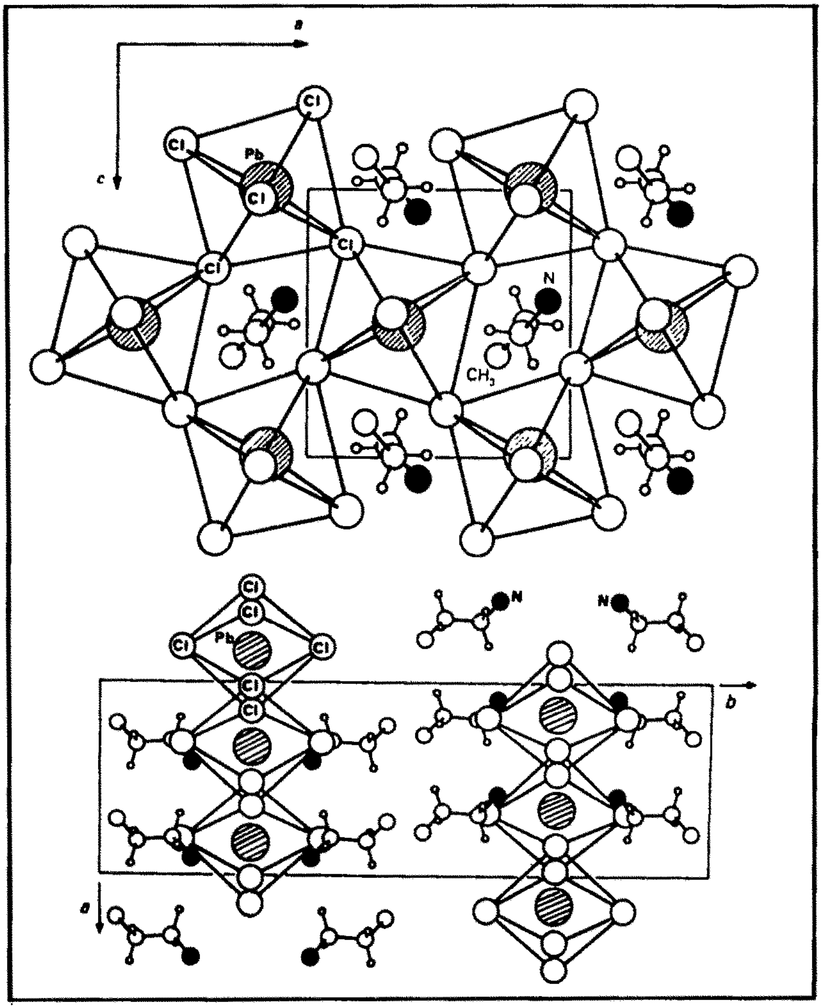

Fig. 3. Crystal structure of $(C_3H_7NH_3)_2PbCl_4$ at 300 K. Projections along the *b* axis and the *c* axis (based on ref. 7).

layers of corner-sharing $PbCl_6$ octahedra [3,7], alternating with aligned organic chains; NH_3 groups of propylammonium cations are connected with chlorine atoms by hydrogen bonds. The space group is Pnma-D_{2h}^{16}, with four formular entities in the unit cell [3,7] (Fig. 3).

The phase I of the homologous Mn or Cd compounds exhibits at 300 K an orthorhombic structure (space group Abma, $Z = 4$) [1,17]. Above 344 K, the Mn derivative shows an incommensurate γ phase [2,10,11]: the long molecular axes of the alkylammonium groups are tilted with respect to the normal of the (ab) plane; tilt angles, $MnCL_6$ layer and interlayer distances are modulated [2,16]. Above 396 K, the β phase structure is also orthorhombic, with the same space group Abma.

Therefore the incommensurate γ phase is embedded by two isotype phases I and β. The re-entrant character would appear as a coupling of the incommensurate order parameter with the interlayer distance, itself depending on temperature [16].

Despite the difference in the space group describing the $(C_3H_7NH_3)_2PbCl_4$ structure, the similarity of phase transitions with those of the Mn compound may allow the same temperature behaviour with an orthorhombic β phase. Under these conditions, the γ phase would exhibit a modulated character. However it seems difficult to assign particular Raman bands to specific modes of that incommensurate phase, e.g. amplitudon and phason [18]. Nevertheless, the weak band observed at 10 cm^{-1} in phase I would correspond to the pseudo-phason usually observed in the low-temperature phase.

The main alterations of the Raman bands at 131 and 47–34 cm^{-1}, which were assigned to motions of $PbCl_6$ octahedra (Table 2), occur during the first-order transition $I \rightarrow \gamma$, which has the most important ΔH (Table 1). Subsequently, during this latter transition, mainly perovskite lattice changes take place, and both the following transitions involve rather motions of rearrangement in organic chains: the first-order transition $\gamma \rightarrow \beta$ (371 K) would involve an essentially displacive mechanism in which the atoms occupy neighbouring and relatively ordered positions. The last transition $\beta \rightarrow \alpha$ should behave as a plastic phase owing to a reorientational disorder of $PbCl_6$ anions.

All these results must be supplemented and confirmed by X-ray structural studies of the different phases, particularly the γ phase, in order to confirm its incommensurate character.

CONCLUSION

This calorimetric and spectroscopic study of $(C_3H_7NH_3)_2PbCl_4$ has shown evidence of three first-order phase transitions above 300 K. The three phases have been characterized unambiguously by their Raman spectra, and their thermal behaviour allows us to compare them with the homologous Mn compound, for which, however, the last transition $\beta \rightarrow \alpha$ would belong to the second-order type.

The structural analogies between these two compounds lead us to consider the γ phase to be incommensurate and embedded by two commensurate phases, i.e. I and β, belonging to the same space group. The perovskite lattice changes occur mainly during the transition $I \rightarrow \gamma$ governed by an order–disorder mechanism involving organic chain cations which occupy statistically and equiprobably four positions. The following transitions $\gamma \rightarrow \beta$ and $\beta \rightarrow \alpha$ would be driven by a displacive mechanism. The last phase α would exhibit a "plastic phase" character.

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