X-ray and Raman studies of the re-entrant phase and phase transitions in the perovskite-type layer compound bis(n-propylammonium) lead tetrabromide

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Abstract. Bis(n-propylammonium) lead tetrabromide (($C_3H_7NH_3$)$_2$PbBr$_4$) is a new member of the family of perovskite-type layer compounds. It exhibits two structural phase transitions according to the phase sequence: φ (172 K)→ ϵ (283 K)→ δ. These transitions are characterized by x-ray diffraction and Raman scattering. The ϵ-phase is embedded between two isomorphic phases φ and δ; the latter exhibits monoclinic cell symmetry, and the space group is $P2_1/a$ ($Z = 2$). The room-temperature phase δ is disordered. φ is the most ordered phase. The $\epsilon \rightarrow \varphi$ transition is characterized by a noticeable decrease in the interlayer distance and a distortion of the PbBr$_6$ octahedra. This transitional behaviour will be discussed and compared with those found in the literature for homologous compounds; the re-entrant phenomenon and other points of similarity suggest for instance an incommensurate structure for the ϵ-phase.

1. Introduction

The perovskite-type layer compounds with the general formula ($C_nH_{2n+1}NH_3$)$_2$MX$_4$ (C_nMX$_4$ for short) (M $\equiv$ metal; X $\equiv$ Cl, Br) are known to crystallize in a two-dimensional structure, built up from MX$_6$ corner-sharing octahedra layers; the cavities between the octahedra contain NH$_3$ groups which form NH...X hydrogen bonds with the halogen sublattice (figure 1(a)) (Depmeier 1981, Meresse and Daoud 1989, Chapuis 1978). In recent years this family of compounds have attracted much interest because they exhibit numerous structural phase transitions (Mokhlisse et al 1985, Couzi et al 1977, Abid et al 1990, 1993a, b, Romain et al 1992).

In the series of compounds with $n = 3$, previous investigations have been made for C_3MnCl$_4$, C_3CuCl$_4$ and C_3PbCl$_4$ and show complex transitional behaviour with the presence of incommensurate phases: for C_3MnCl$_4$, δ (344 K) $\rightarrow$ γ (396 K) $\rightarrow$ β (446 K) $\rightarrow$ α (Depmeier et al 1977, Depmeier 1981); for C_3CuCl$_4$, δ (378 K) $\rightarrow$ γ (423 K) $\rightarrow$ β (436 K) $\rightarrow$ α (Doudin and Chapuis 1990a, b, Doudin and Heine 1990); for C_3PbCl$_4$, δ (340 K) $\rightarrow$ γ (371 K) $\rightarrow$ β (406 K) $\rightarrow$ α (Romain et al 1992). In the three compounds, the γ-phases are believed to be incommensurate; the long molecular axis of organic chains are tilted with respect to the normal of MCl$_6$ layers plane. Tilt angles, MCl$_6$ layers and interlayer distance are modulated (figure 1(b)).

The incommensurate γ-phases are embedded between two isomorphic phases β and δ. This re-entrant behaviour was explained by a coupling of the incommensurate order parameter with the interlayer distance, which itself depended on temperature (Muralt et al 1982, Muralt 1986). On the other hand, three low-temperature modulated phases denoted
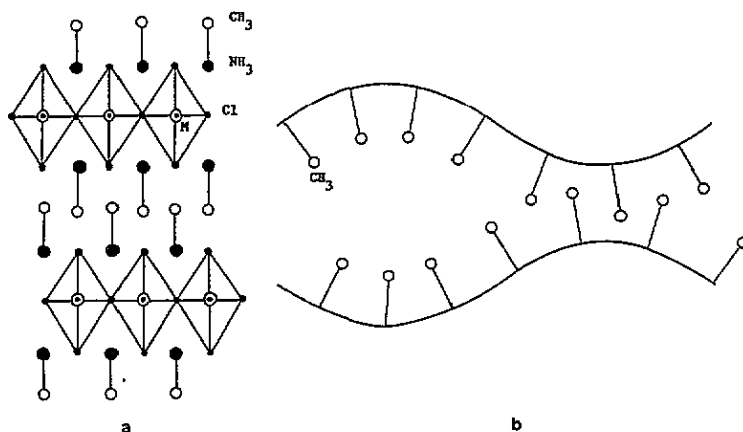
Figure 1. Schematic structure of the $(C_nH_{2n+1}NH_3)_2MX_4$ compounds: (*a*) in the hypothetical tetragonal structure; (*b*) in the modulated γ- and ϵ-phases.

ϵ have been demonstrated in C_3CdCl_4, C_3MnCl_4 and C_3PbCl_4: C_3MnCl_4 ζ (115 K) $\rightarrow$ ϵ (183 K) $\rightarrow$ δ (Depmeier *et al* 1977); C_3CdCl_4 φ (150 K) $\rightarrow$ ϵ (175 K) $\rightarrow$ δ (Doudin and Chapuis 1988); C_3PbCl_4 IV (35 K) $\rightarrow$ ϵ (III) (91 K) $\rightarrow$ (II) (170 K) $\rightarrow$ δ (I) (Abid *et al* 1992). In the case of C_3PbCl_4 the ϵ-phase also has a re-entrant character.

Recently, numerous qualitative and microscopic explanations have been proposed for the occurrence of γ and ϵ modulated structures (Muralt *et al* 1982, Muralt 1986, Doudin and Chapuis 1990a, b, Doudin and Heine 1990, Abid *et al* 1993a, b). In the high-temperature phases α and β, the organic chains exhibit orientational and conformational disorder; the commensurate $\rightarrow$ incommensurate transition ($\beta \rightarrow \gamma$) is due to the freezing of the organic chain motions and to the interpenetration of successive layers (figure 1(*b*)). The $\gamma \rightarrow \delta$ re-entrant transition is accompanied by an important decrease in the interlayer distance (of about 6%), whereas the in-plane parameters show no significant changes (only about 1%) (Depmeier 1981, Doudin and Chapuis 1990a, b, Doudin and Heine 1990, Muralt *et al* 1982, Muralt 1986). The large decrease in the interlayer distance has been explained as a result of the interpenetration of successive organic strata.

In order to learn more about the transitional behaviour of this family of compounds, we have undertaken experimental studies on a new bromide derivative, C_3PbBr_4. In this paper we intend to characterize the structural phases and phase transitions by means of x-ray diffraction and Raman spectroscopy. The results will be compared with those found in the literature for homologous compounds.

2. Experimental details

The title compound was synthesized by mixing $C_3H_7NH_3Br$ and $PbBr_2$ in HBr solution with the stoichiometric ratio 1:2. Raman spectra were recorded on a Dilor RTI 30 spectrometer equipped with an argon ion laser (514.5 nm). The low-temperature measurements were performed with a Dilor liquid-nitrogen cryostat, and a thermocouple was used to estimate the sample temperature. X-ray powder diffraction experiments as a function of temperature have been performed with a Huber G. 645 Guinier diffractometer equipped with a closed-cycle cryostat. Cu Kα radiation was used.

3. Results and discussion

3.1. Structural information on the room-temperature phase δ

The structural determination of the room-temperature phase of C_3PbBr_4 is in progress (Chanh, Daoud and Abid 1994), although some structural information should be mentioned here for x-ray powder investigations. At 300 K, the title compound crystallizes in perovskite-type layered structure with space group $P2_1/a$ ($Z = 2$), the main characteristic of this structure is a strong spontaneous distortion of the $PbBr_6$ octahedra. The values of the cell parameters obtained from single-crystal investigations were refined through the 21 reflections observed in the powder diffractogram (table 1), and the following values obtained: $a = 8.064(6)$ Å, $b = 8.237(8)$ Å, $c = 13.502(7)$ Å and $\beta = 111.08(4)°$. The parameter c is related to the interlayer distance, and a and b are parallel to the plane of the layers.

Table 1. Indexation of the powder diagram (21 observed reflections) in the monoclinic room-temperature phase δ, at 300 K.

Number	d_{cal} (Å)	d_{obs} (Å)	hkl	I/I_{max} (%)
1	12.598	12.593	001	50
2	6.299	6.301	002	20
3	5.669	5.667	$11\bar{1}$	100
4	5.555	5.551	110	85
5	4.854	4.856	$11\bar{2}$	25
6	4.647	4.649	111	9
7	4.199	4.201	003	75
8	4.118	4.120	020	80
9	4.023	4.021	$20\bar{1}$	71
10	3.906	3.904	$20\bar{2}$	11
11	3.761	3.763	200	16
12	3.615	3.617	$21\bar{1}$	14
13	3.148	3.146	$20\bar{3}$	60
14	3.004	3.003	$20\bar{4}$	10
15	2.923	2.924	122	90
16	2.878	2.879	$22\bar{1}$	16
17	2.834	2.832	$22\bar{2}$	14
18	2.814	2.817	202	12
19	2.698	2.696	$10\bar{5}$	6
20	2.604	2.604	$12\bar{4}$	41
21	2.590	2.592	$13\bar{1}$	22

The homologous compounds C_3MCl_4 ($M \equiv$ Cd, Cu, Mn or Pb), cited above exhibit orthorhombic room-temperature phases (δ) (see the corresponding references) and the monoclinic ordered phases occur only at low temperatures. C_3PbBr_4 is therefore the first member of this family of compounds which exhibits a monoclinic cell symmetry at 300 K. This may be related to the spontaneous distortion of $PbBr_6$ octahedra. In addition, it has been previously established (Depmeier 1979) that the normalized difference (ND) $(b-a)/a$ between the in-layer parameters characterizes the MX_6 octahedra distortion and the strength of hydrogen bonds; the higher the ND the more the MX_6 octahedra are distorted the stronger the NH...X hydrogen bonds and the more ordered the crystal.

If we compare the ND in C_3PbCl_4 with that in C_3PbBr_4, we obtain, for C_3PbBr_4, ND (300 K) = 2.14% (present work) and, for C_3PbCl_4, ND (300 K) = 1.74% (Meresse and Daoud 1989); it can be seen that the $PbBr_6$ octahedra are more distorted than $PbCl_6$ octahedra, but the Raman study shows, as expected, that NH...Cl hydrogen bonds are stronger than NH...Br bonds.

3.2. X-ray study of phase transitions

Preliminary DTA experiments have been performed between 300 and 400 K and no transitions have been detected in this temperature interval. The present work is thus restricted to the low-temperature range (80–300 K).
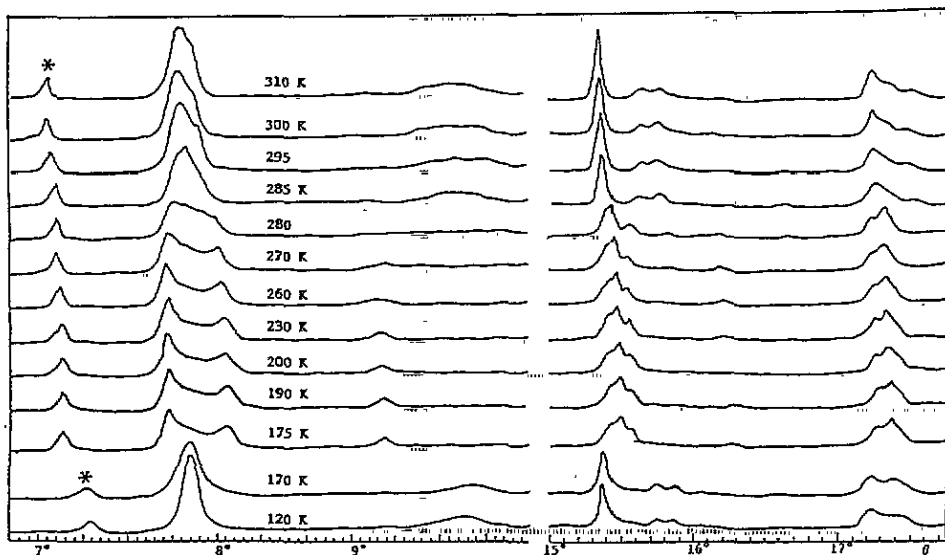

Figure 2. X-ray powder diffractograms of C_3PbBr_4 at different temperatures. Only the θ intervals which are sensitive for phase transitions are selected.

X-ray powder diffractograms of C_3PbBr_4 have been recorded at different temperatures between 80 and 300 K. In figure 2 we have selected the θ intervals which show significant changes with temperature variation; two phase transitions have been shown according to the phase sequence

$$\varphi \ (172 \ K) \rightarrow \epsilon \ (282 \ K) \rightarrow \delta.$$
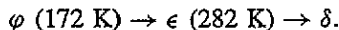
Both $\delta \rightarrow \epsilon$ and $\epsilon \rightarrow \varphi$ transitions are characterized by discontinuous evolution of the powder data (figure 2); indeed, large changes occur in narrow temperature intervals (of about 5 K) around $T_1 = 282$ K and $T_2 = 172$ K. This suggests a first-order character for both transitions. The most interesting feature in this crystallographic evolution is the re-entrant character of the intermediate phase ϵ. Indeed, in δ- and φ-phases, the powder data are almost identical and differ only in the shift of the (001) reflections (e.g. 002 in figure 2) corresponding to the interlayer distance and by overlapping of (11$\bar{1}$) and (110) reflections (figure 2). Under these hypotheses we have indexed the φ-phase powder data in

the same space group $P2_1/a$ ($Z = 2$); the lattice parameters at 150 K have been determined after least-squares refinement and the choice of the space group has been confirmed, the retained values of the parameters are $a = 7.841(3)$ Å, $b = 8.083(6)$ Å, $c = 12.673(4)$ Å, $\beta = 109.32(4)°$ and ND $= (b - a)/a = 3.09\%$.

Two main changes with respect to the δ-phase should be mentioned: on the one hand, the parameter c related to the interlayer distance decreases noticeably; on the other hand, the increase in the ND characterizes the distortion of the $PbBr_6$ octahedra and indicates that in the φ-phase the NH bond...Br hydrogen bonds become stronger.

In the absence of single-crystal investigations at low temperatures, no well defined space group has been found for the intermediate ϵ-phase, although some points of similarity with homologous compounds could be informative. As we have already established, the ϵ-phase is embedded between two isomorphic phases δ and φ; this re-entrant phenomenon is the main common characteristic of the high-temperature modulated phases in C_3CuCl_4, C_3MnCl_4 and C_3PbCl_4 and it has been interpreted as a coupling of the incommensurate order parameter with the interlayer distance which itself depends on temperature (Muralt *et al* 1982, 1986). In addition, when comparing the powder data on the δ- and φ- phases, it should be noted that only the (001) reflections show a large shift; the other reflections show no significant changes. This corresponds to a decrease in the interlayer distance: $\Delta d = d_{001}(\delta) - d_{001}(\varphi) = 0.60$ Å. The same behaviour has been demonstrated in C_3CuCl_4 and C_3MnCl_4 with the same order of magnitude for Δd: for C_3CuCl_4, $\Delta d = d_\beta(435$ K$) - d_\delta(370$ K$) = 0.55$ Å (Doudin and Chapuis 1990a, b, Doudin and Heine 1990); for C_3MnCl_4, $\Delta d = d_\beta(400$ K$) - d_\delta(340$ K$) = 0.62$ Å (Depmeier 1981). This unusual decrease in the interlayer distance has been explained as a result of the interpenetration of successive organic strata (Depmeier 1981, Doudin and Chapuis 1990a, b, Doudin and Heine 1990). Despite the difference in the space group describing C_3PbBr_4, these points of similarity in the transitional behaviour suggest for instance an incommensurate structure for the ϵ-phase.

3.3. Raman study of phase transitions

In order to gain more information on the crystal dynamics, on the degree of disorder in different phases and on the mechanisms involved in the transitions, we have undertaken a Raman study between 80 and 300 K. This study is restricted to the low-frequency range (5– 200 cm^{-1}), because it includes lattice modes and some internal modes which are the most sensitive for crystal changes and phase transitions. The spectral evolution with temperature variation is shown in figure 3. The two transitions are again clearly characterized. In the limit of temperature accuracy, the transition temperatures are close to those found by x-ray diffraction.

3.3.1. Assignment. The frequencies of the observed modes in different phases are listed in table 2. We shall not give a detailed assignment here, but we intend as far as possible to distinguish between the bands corresponding to $PbBr_6$ octahedra motions and those associated with organic cations; to this end we have compared the Raman spectra of C_3PbBr_4 at 120 K with those of C_3PbCl_4 (Abid *et al* 1992) and C_3CdCl_4 (Mokhlisse *et al* 1985).

The Raman lines observed near 87 and 104 cm^{-1} are associated with translational motions of the organic chains, and the large band at 129 cm^{-1} corresponds to the torsional motion of CH_3 group. The narrow frequency range between 30 and 60 cm^{-1} includes librational motions of both organic and inorganic ions and it is not easy to give a detailed assignment.
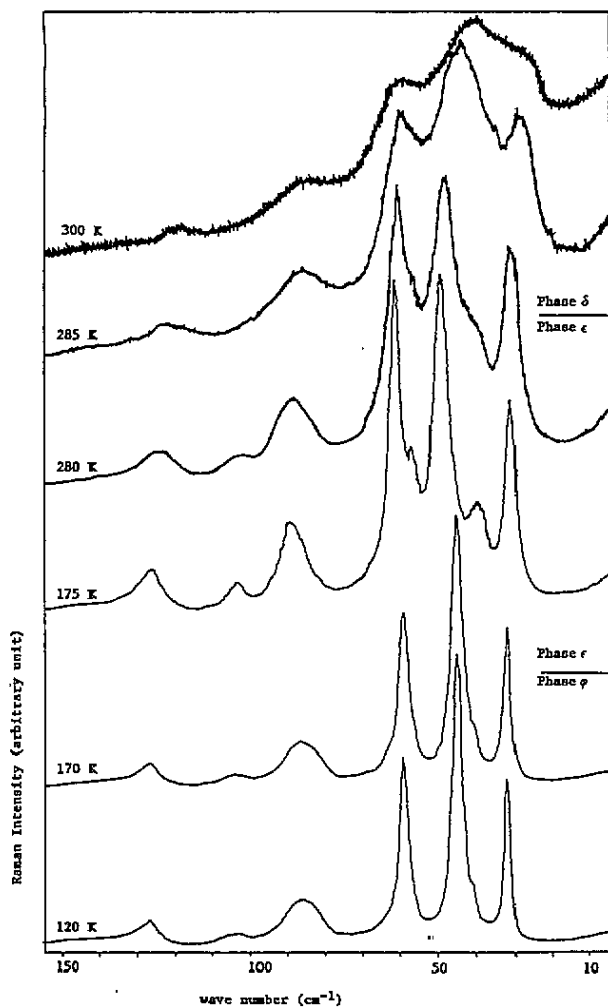
Figure 3. Low-frequency Raman spectra of polycrystalline samples of C_3PbBr_4 at different temperatures between 120 and 300 K.

Table 2. Raman spectra wavenumbers (5–250 cm^{-1}) at different temperatures

Wavenumber (cm^{-1})			
φ-phase (120 K)	ϵ-phase (220 K)	δ-phase (300 K)	Assignment
34	31	29	
42	40		
47	48	44	R$'$ PbBr$_6$ and R$'$ chains
	58		
62	60	61	
87	89	86	T$'$ chains
104	104		T$'$ chains
129	125	120	CH$_3$ torsion

3.3.2. $\varphi \rightarrow \epsilon$ transition (172 K).
The $\varphi \rightarrow \epsilon$ transition is characterized by the following spectral changes.

(a) The shoulder at 42 cm^{-1} shifts to 40 cm^{-1} and increases in intensity.

(b) A new Raman line appears at 58 cm^{-1}.

(c) The band at 62 cm^{-1} decreases in intensity with respect to that at 47 cm^{-1}.

(d) The weak band at 105 cm^{-1} assigned to cation translation becomes well resolved and increases in intensity.

All these changes occur in a narrow temperature interval and confirm the first-order character of this transition.

The lower-temperature phase φ is characterized by a well resolved spectra, with relatively narrow bands as is expected for fully ordered crystals; the broadening of most Raman bands across the transition characterizes the beginning of a disordering process.

The appearance of the new lines at 40 and 58 cm^{-1} is not necessarily due to a doubling of the unit cell such as that evidenced for the order–disorder transitions in CCdCl$_4$ and CMnCl$_4$ (Couzi *et al* 1977), but it may be explained by a removal of degeneracy due to the lattice distortion; similar behaviour has been observed for numerous substances which exhibit incommensurate phases, e.g. C$_3$CdCl$_4$ (Mokhlisse *et al* 1985), Na$_2$CO$_3$ (Meekes *et al* 1986), K$_2$SeO$_4$ (Iisumi *et al* 1977), Rb$_2$ZnBr$_4$ (Poulet and Pick 1986) and pyrrol (Lautie and Romain 1990).
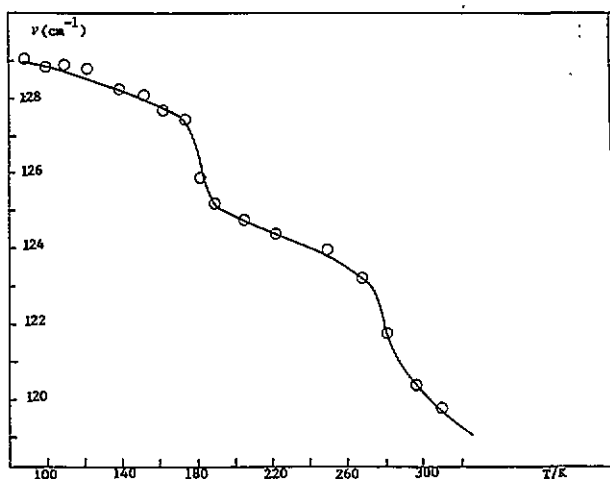

Figure 4. Frequency of NH$_3$ torsional motion versus temperature.

3.3.3. $\epsilon \rightarrow \delta$ transition (283 K). When the temperature is increased across the $\epsilon \rightarrow \delta$ transition, the Raman spectra show the opposite evolution with a noticeable broadening of all observed bands, indeed, the shoulders at 40 and 58 cm^{-1} overlap again with the lines at 47 and 62 cm^{-1}, respectively, and the lines at 62 and 105 cm^{-1} decrease in intensity. In addition the Raman line assigned to the CH$_3$ torsion mode shows an unusual shift from 129 to 120 cm^{-1} (figure 4), a fact which may be related to the increase in the interlayer distance and therefore to the changes in van der Waals interaction between successive organic strata; this interpretation is consistent with previous results inferred from crystallographic data. On the other hand both δ- and φ-phases are characterized by similar Raman spectra, since they exhibit the same number of Raman lines at almost the same frequencies and with the same relative intensities. This confirms the re-entrant character of the ϵ-phase already evidenced by x-ray diffraction. Although these spectra differ noticeably in the broadness of

most of the observed bands, this indicates that the room-temperature δ-phase is disordered with respect to the lower-temperature φ-phase. It should also be noted that the spectrum at 300 K (figure 3) shows a high degree of disorder similar to that observed in the high-temperature β- and γ-phases of the homologous compound C_3PbCl_4 (Romain *et al* 1992). As the hydrogen bonds are believed to be responsible for the disordering process in this family of compounds, this may be explained by the weakness of the NH bond–Br hydrogen bonds with respect to the NH bond–Cl bonds.

4. Conclusion

The title compound undergoes two structural phase transitions:

$$\varphi \ (172 \ \text{K}) \rightarrow \epsilon \ (282 \ \text{K}) \rightarrow \delta.$$
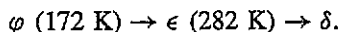
The ϵ-phase appears as an intermediate ordered phase embedded between two isomorphic phases δ and φ. The latter phases differ only in the degree of disorder and the interlayer distance. In addition, the x-ray powder data and the low-frequency Raman spectra show an unusual lowering of the symmetry in the ϵ-phase. This transitional behaviour is consistent with those shown by the homologous compounds C_3MCl_4, ($M \equiv Mn$, Cu or Pb) and suggests for instance an incommensurate structure for the ϵ-phase. The last point remains to be confirmed by x-ray diffraction or neutron scattering experiments on single crystals.

Acknowledgment

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