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Raman spectroscopy of new lead iodide intercalation compounds

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Abstract. PbI_2 crystals have been intercalated with ammonia, methylamine (CH_3NH_2), ethylamine ($\text{C}_2\text{H}_5\text{NH}_2$), and butylamine ($\text{C}_4\text{H}_9\text{NH}_2$) for the first time. Raman spectra of these materials, and also of PbI_2 intercalated with nonylamine ($\text{C}_9\text{H}_{19}\text{NH}_2$) were obtained using an excitation wavelength of 514.531 nm. For comparison a study of the interaction of CdI_2 with the same molecules is included. Raman spectroscopy in the range $10\text{--}500\text{ cm}^{-1}$ demonstrated the occurrence of a polytypic phase transition from 1T to 3T on intercalation of PbI_2 and also that intercalation results in the breaking up of the crystal into many small crystallites. The existence of strong Pb–N interactions was demonstrated by both infrared and Raman spectroscopy.

1. Introduction

Intercalation has been a topic of considerable interest in recent years. The host materials studies have most often been transition metal dichalcogenides and graphite. However, PbI_2 can be intercalated by organic molecules and there have been a number of recent studies of this [1–5]. We have chosen to investigate the intercalation of PbI_2 by NH_3 and alkyl amines. In this paper we present Raman spectra of these materials which provide important evidence for a polytypic phase transition from 1T to 3T on intercalation of PbI_2 , and also for the formation of small crystallites during the intercalation process. Additional results concerned CdI_2 are included. Raman and infrared spectroscopy demonstrate the existence of strong metal–nitrogen interactions in most of these materials.

We have carried out other extensive studies of these intercalation systems: the optical absorption and ESR spectra of these materials are presented along with stoichiometric determinations [8] and we explain these on the basis of a model involving quantum confinement and small crystallite formation. This model is also consistent with results presented in this paper.

2. Materials and methods

Pristine PbI_2 is a direct gap semiconductor having a hexagonal layered structure. The pristine crystals used were of 1T polytype of PbI_2 . This was identified by x-ray diffraction of single crystals. (This polytype is often referred to as 2H following a different notation; the 1T structure is identical in stacking to that of 1T transition metal dichalcogenides.) The

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Raman spectrum of the 1T polytype has A_{1g} at 96 cm^{-1} and E_g at 72 cm^{-1} [6, 7, 10]. At the incident wavelength of 514.5315 nm used however, the laser is resonant with the band gap of PbI_2 at 2.45 eV or 507 nm. This results in a breakdown of the Raman selection rules so that the longitudinal optic A_{2u} and E_u modes at 113 and 106 cm^{-1} are Raman active. An overtone of this, and possibly of the A_{1g} modes, occurs at 220 cm^{-1} . The Raman spectrum of a PbI_2 crystal of 1T polytype at 80 K is shown (figure 1). The peaks at 43 and 177 cm^{-1} are probably due to multiphonon interactions (i.e. they correspond to sum and difference combinations of two or more phonons). Apart from these this spectrum agrees well with previous published spectra of PbI_2 [6, 7, 10].

Crystals of 1T PbI_2 were mounted on a cryostat and exposed at room temperature to dry ammonia and amines in the vapour phase. The Raman spectra were monitored during the formation of the resulting new intercalation complexes. CdI_2 crystals of 1T hexagonal layered structure (often referred to as 4H polytype) were treated in the same way for comparison. The polytype was identified by the Raman spectrum (figure 2).

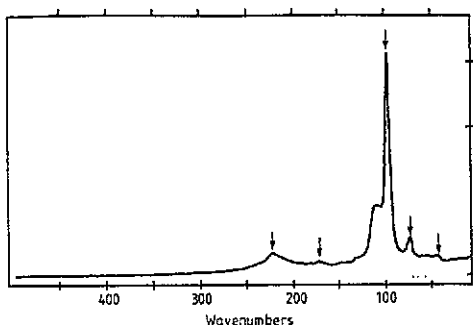


Figure 1. Raman spectrum of 1T PbI_2 at 80 K.

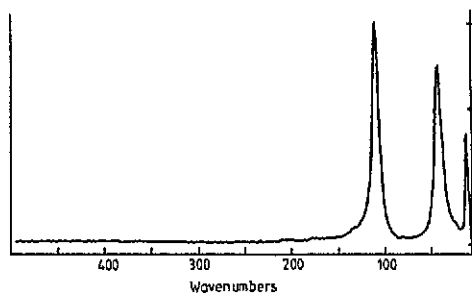


Figure 2. Raman spectrum of 2T CdI_2 at 300 K.

All measurements were carried out using a 50 mW argon ion laser and a DILOR OMARS-89 Raman spectrometer. Raman spectra in the range of $10\text{--}500\text{ cm}^{-1}$ were obtained at room and liquid nitrogen temperatures before and after intercalation. Methods used in an attempt to deintercalate the crystals entirely were the evacuation of the intercalated sample for 1–2 days to a pressure of 10^{-5} mbar, and also the simultaneous heating of the samples to approximately 350 K during the evacuation process. Further Raman spectra were then recorded.

Near-infrared (NIR) absorption measurements were carried out on a Nicolet FTIR spectrometer (range $4000\text{ to }400\text{ cm}^{-1}$). Films of PbI_2 and CdI_2 were deposited on ZnSe windows which were mounted on a cold finger cryostat equipped with two ZnSe windows for infrared transmission. *In situ* measurements were made during intercalation by ammonia; the experiments were repeated using PbI_2 crystals of thickness of the order of $4\text{ }\mu\text{m}$ in the unintercalated form (this is the thickness appropriate for NIR measurements). The intercalation was carried out as described above for the Raman measurements.

3. Results

PbI_2 crystals became intercalated by ammonia or amines after a few hours' exposure at room temperature in the cryostat. The effects of this were a dramatic *c*-axis swelling of the

crystal, and a slow colour change from bright yellow through dull yellow and pale yellow to white. On one occasion a shiny yellow PbI_2 crystal of dimensions $1 \times 1 \times 0.1 \text{ mm}^3$ was transformed into a $2 \times 2 \times 10 \text{ mm}^3$ pillar of opaque white flakes stacked above one another! Many of the layers had become completely detached.

Figure 3 shows a typical Raman spectrum of ammonia-intercalated PbI_2 at 80 K. At 300 K the spectrum is similar but poorly resolved. The photon spectrum of ammonia-intercalated PbI_2 appears to be complex and entirely different from that of the pristine material. The most surprising feature is the appearance of a number of sharp low-frequency Raman lines below 72 cm^{-1} . The original modes of PbI_2 vanish except a weak mode near 96 cm^{-1} which remains.

On using thicker crystals or short intercalation times, the spectrum shown in figure 4 was obtained from ammonia-intercalated PbI_2 at 80 K. Spectra similar to figure 4, but less clearly resolved, were obtained from thinner crystals of PbI_2 after 1 hour in ammonia gas at room temperature. As intercalation proceeded, a spectrum similar to figure 3 was then obtained (but again less well resolved). If the crystals were cooled at this point to 80 K, the spectrum was again obtained. This implies that figure 4 represents an earlier step in the intercalation process than figure 3. (An unavoidable side-effect of the cooling of the samples to 80 K is that the intercalant vapour surrounding them condenses onto the cold finger. The drop in pressure inevitably causes a certain amount of deintercalation.) After a day's exposure to ammonia the spectrum shown in figure 5 was obtained. This consists simply of two broad modes near 163 and 297 cm^{-1} . Once the crystal has reached this stage it is not possible to obtain again the spectrum of pure PbI_2 indicating that a chemical reaction has probably occurred; this final step is irreversible. In contrast after a few hours in NH_3 , corresponding to figure 3, the original spectrum of pristine PbI_2 (figure 1) can be fully recovered showing the complete reversibility of the intercalation of PbI_2 with ammonia.

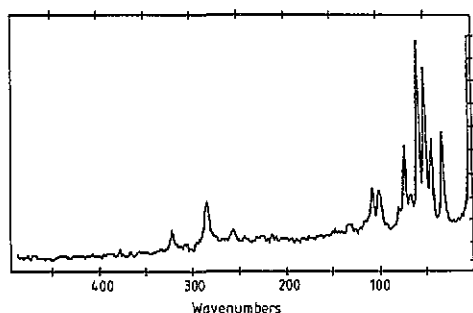


Figure 3. Raman spectrum of NH_3 -intercalated PbI_2 at 80 K.

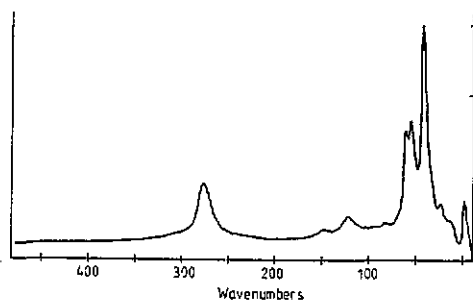


Figure 4. Raman spectrum of PbI_2 at intermediate stage of intercalation by NH_3 .

Table 1 compares the Raman frequencies in 1T, 2T, and 3T PbI_2 , and in the intercalation complexes. It also includes the rotational Raman modes of ammonia, the amines, and the modes of solid ammonia I (this work, [9–12, 14–16]).

When PbI_2 was exposed to CH_3NH_2 at a vapour pressure of 180 mbar the crystal swelled and changed colour from dark yellow to pale yellow and finally to white over a period of about 1 hour. The Raman spectrum of the white intercalate is shown in figure 6 at 80 K. When the crystal was pale yellow, the same Raman spectrum was obtained. It was possible to completely deintercalate the crystal of methylamine by simultaneously heating

Table 1. Raman active modes in the range 10–500 cm^{-1} in PbI_2 polytypes, in PbI_2 intercalated by NH_3 or by alkylamines, and in these organic molecules.

1T	Pristine PbI_2 , 300 K		PbI_2 Intercalated by						NH_3		Aggregate		Gaseous amines at 300 K				
	2T	3T	NH_3	CH_3NH_2	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_4\text{H}_9\text{NH}_2$	$\text{C}_9\text{H}_{19}\text{NH}_2$	Rotation	Solid I	Aggregate	CH_3NH_2	$\text{C}_2\text{H}_5\text{NH}_2$	$\text{C}_4\text{H}_9\text{NH}_2$	$\text{C}_9\text{H}_{19}\text{NH}_2$	[11]	[12]	[13]
	[7]	[7]	*80 K	80 K	80 K	80 K	(Gas)	80 K	[10]								
	14	12			14.5					16							
	29	29	33	24	29	28	26			28							
			39							33							
	47	46	44	45	45	46	43	40	45								
		50	52	52	52			60	50								
			59						66								
73	(E_g)72	71	72	75	68	63	65										
	74	73	76			74											
		80					81	80									
96	(A_{1g})96	94	100	101			99	99(8)	93								
107	(E_g)106	109						119									
113	(A_{2g})113	113	109	109	109	109		139									
			257			158											
220 (overtone)			285	275	205	205	270										
			322	322			315										
										403							
											218						
											248						
												270					
												350					
												400					
												436,484					
												500					

* Includes modes shown in figures 3 and 4 combined.

the samples to 350 K and evacuating them to 10^{-5} mbar, and recover a Raman spectrum identical to that of the pristine material.

The Raman spectrum of methylamine-intercalated PbI_2 is also given in table 1. This table also shows the remarkably similar results obtained for ethylamine and for nonylamine. Throughout, we examined the polarization dependence of the Raman spectra of the intercalated samples, but none was detected. Slightly different patterns in the Raman spectra were observed in the case of butylamine (table 1).

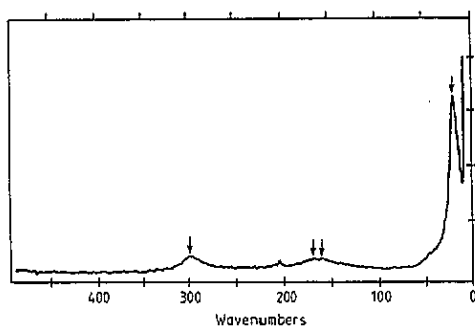


Figure 5. Raman spectrum of PbI_2 after 24 hours' exposure to NH_3 .

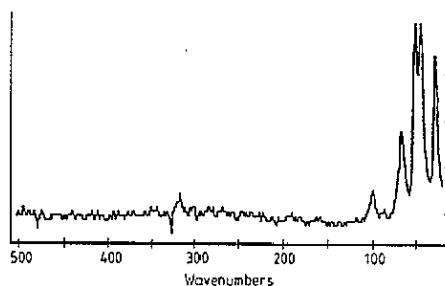


Figure 6. Raman spectrum of PbI_2 intercalated by CH_3NH_2 at 80 K.

CdI_2 crystals swelled after about 1 hour in 400 mbar ammonia gas at room temperature and became opaque and white, losing their crystallinity. Typical Raman spectra taken at 300 K are shown in figure 7. Table 2 shows the Raman modes of CdI_2 before and after exposure to NH_3 . The change in CdI_2 is clearly quite different from that occurring in PbI_2 . At first, the A_{1g} mode in CdI_2 remained prominent in the Raman spectrum of the ammoniated material, whereas the E_g mode softened by 13 cm^{-1} (not shown). The rigid layer mode at 16 cm^{-1} also disappeared. Finally, both A_{1g} and E_g modes vanished and additional modes appeared at 160 and 322 cm^{-1} (figure 7). This state of the sample was stable for at least 2 days since the Raman spectrum did not alter throughout this time. It was impossible to extract NH_3 from such crystals by simultaneous heating and pumping; the reaction was irreversible, and the original Raman spectrum could not be recovered.

The behaviour of 2T CdI_2 crystals on exposure to the amines is very similar to that described previously for exposure to ammonia. The Raman spectra however appear more complex. The frequencies are listed in table 2. Sequential Raman spectra obtained during the reaction of methylamine or ethylamine with CdI_2 , showed the gradual disappearance of the rigid layer mode and also of both A_{1g} and E_g modes. On (presumably) complete reaction these modes disappeared and new broad modes appear near 157 and 313 cm^{-1} which apparently correspond to those at 160 and 322 cm^{-1} in CdI_2 after complete reaction with ammonia; in both cases the final spectrum was simple. A similar type of spectrum was in fact found for PbI_2 (figure 5) after long exposure to ammonia.

After reaction with butylamine, CdI_2 displayed a rather different Raman spectrum with modes at 40, 108 and 129 cm^{-1} . It is worth noting that the Raman spectra of butylamine-intercalated PbI_2 were also rather different from those of methylamine- or ethylamine-intercalated PbI_2 .

Typical NIR spectra of ammonia-intercalated PbI_2 and of CdI_2 complexed with ammonia in the range of $3600\text{--}3000\text{ cm}^{-1}$ are shown in figures 8 and 9. Figure 10 shows the IR spectra of solid and gaseous ammonia for comparison.

Table 2. Raman active modes in the range 10–500 cm^{-1} of CdI_2 and of its complexes with NH_3 and with alkylamines.

CdI_2	Mode	CdI_2 Complexed with NH_3		CdI_2 Complexed with $\text{C}_2\text{H}_5\text{NH}_2$		CdI_2 Complexed with CH_3NH_2			$\text{C}_4\text{H}_9\text{NH}_2$	CdI_2	
		80 K	300 K	Final stage 300 K	Crystal edge 300 K	Crystal face 300 K	Early stage 300 K	[1]			[2]
300 K	16				22	23	18	17	20		
	Rigid lattice										
	E_g^3										
55	E_g	33	37		45	46	46	47	46		
85	A_{2u}	46			85	83	87	80	80	40	75
114	A_{1g}	112	113		97	97	948	113		108	
138	E_u				116	116	114				
		170	160	160	158	156	156	157	157	129	175
					222	224	224				210
						268					222
						297					
					482	482	482	315	315	313	

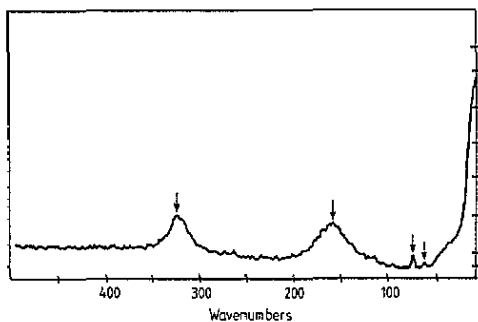


Figure 7. Raman spectrum of CdI_2 complexed with NH_3 at 300 K.

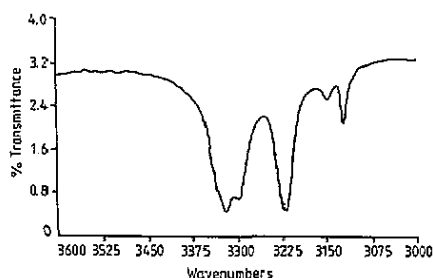


Figure 8. IR spectrum of NH_3 -intercalated PbI_2 at 80 K.

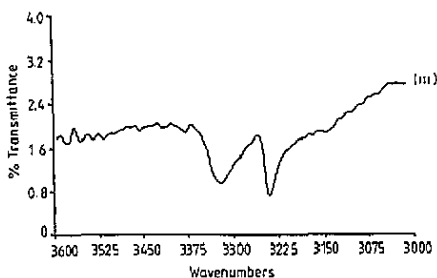


Figure 9. IR spectrum of CdI_2 complexed with NH_3 at 80 K.

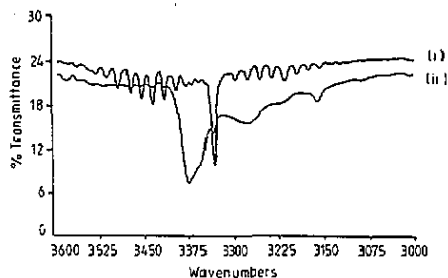


Figure 10. IR spectra of (i) gaseous and (ii) solid NH_3 .

4. Discussion

It is clear from the Raman spectra that a significant structural change occurs on intercalation of PbI_2 . The Raman spectra of PbI_2 intercalated by methylamine, ethylamine, and nonylamine are very similar. Those of ammonia-intercalated PbI_2 differ slightly, as there are some additional modes. The great similarity between the Raman spectra of PbI_2 intercalated by these different molecules shows that the low-wavenumber phonons are associated with the PbI_2 lattice alone. In fact, these new phonon modes are precisely those of the 3T (6H) polytype (table 1). The modes between 71 and 76 cm^{-1} correspond to the E_g mode of the 3T polytype. Those in the range 98–101 cm^{-1} result from A_{1g} . Referring to table 1, the modes of ammonia/amine intercalated PbI_2 in the ranges 24–33 cm^{-1} , 43–46 cm^{-1} , and 63–67 cm^{-1} , are also attributable to a 3T structure of PbI_2 . It should be noted that the phonons of the 3T polytype in PbI_2 are expected to be very similar to those of the 3R (either trigonal prismatic or octahedral) polytype, so from Raman evidence 3T and 3R cannot be distinguished. The 3T polytype has a stacking sequence AcB CbA BaC ..., whereas 3R has AbA BcB CaC (in its trigonal prismatic form) and AbC CaB BcA (in its octahedral form). Polytypism in PbI_2 is discussed in detail in [14]. The polytype 3R is not found naturally in PbI_2 , but could be induced by intercalation. Transition to 3R (trigonal prismatic coordination) is unlikely.

It is actually extremely easy for the 1T structure to undergo a phase transition to a 3T or 3R (octahedral) structure. In fact, pristine crystals of PbI_2 often contain a mixture of an

(n)T and a (3) n R polytype (where n are integers > 1). This is due to the occurrence of a Shockley dislocation $a/\sqrt{3}$ [010], see [17]. The Raman spectra clearly indicated that prior to intercalation these crystals were 1T polytype at the surface. Heat can induce a transition from 1T to 2T, but not to 3T or 3R. The transition to 3T or 3R (octahedral coordination) can be taken to be entirely the result of intercalation. If after intercalation the stacking were 3T, the ammonia would occupy octahedral sites in the Van der Waals gap. If however, the transition were to 3R (octahedral), the ammonia could occupy trigonal prismatic sites in the Van der Waals gap (figure 11). Stacking in 3T and 3R (octahedral) polytypes and possible intercalation sites for ammonia are identical to the structures of K_2ZrS_2 [18].

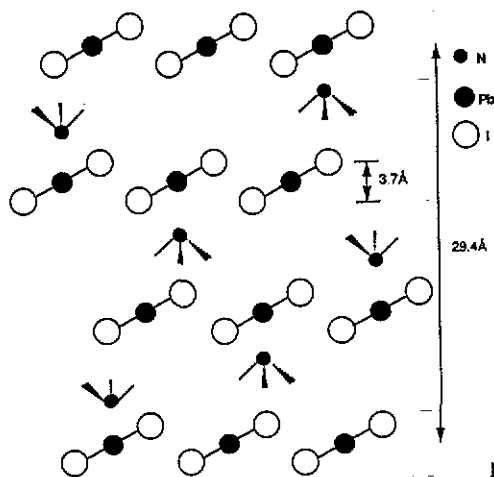


Figure 11. Proposed structure of intercalate $PbI_2(NH_3)_2$.

Thus a polytypic transition has been shown to occur as a result of intercalation of PbI_2 by NH_3 or by alkyl amines. This is a manifestation of the sliding of the layers relative to each other to form a more stable configuration. Such a transition from 1T to 3R (octahedral coordination) is known to occur in 1T TaS_2 during intercalation by hydrazine [10]. A similar structural transformation occurs in ZrS_2 during intercalation by lithium. In $Li_x ZrS_2$, when $x = 0.25$, a structural change from 1T to 3T occurs [20]. This is thought to be the result of the weaker Coulomb repulsion between the metal atoms in the 3T structure in which all the adjacent metal atoms are staggered (AcB[a]CbA[c]BaC[b]AcB...), as opposed to the 1T structure (AcB[c]AcB...) in which the metal atoms are directly above each other aligned along the c -axis.

Amine-intercalation of PbI_2 can result in the formation of a superlattice in the plane of the layers (referred to hereafter as the ab plane) [21]. The effect on Raman spectra of the formation of a superlattice in the ab plane as a result of the intercalation of transition metal dichalcogenides (TMD) by organic molecules has been investigated e.g. for ethylenediamine (EDA) intercalation of 1T and 2H TaS_2 [22]. 1T TaS_2 has the same structure as 1T PbI_2 . However, unlike PbI_2 , 1T TaS_2 undergoes periodic lattice distortions with which charge density waves are associated (PLD-CDWs), in which the lattice spontaneously distorts to a structure of lower energy. EDA intercalation suppressed the CDW distortion producing a complex Raman spectrum. Clearly CDWs are not involved in PbI_2 , but if the intercalants were to form a superlattice in the ab plane, thus applying a modulating potential commensurate with the host lattice periodicity, such low-frequency modes might be expected to appear. The precise frequencies would of course depend on the multiplicity of the superlattice and

it would be a great coincidence if these modes coincided with those of the 3T polytype of PbI_2 .

Incidentally, it has been shown that the longer-period polytypes of PbI_2 have lower-energy bandgaps than the 1T polytype [23]. Although the value for the 3T polytype is not given, the fact that the bandgap of the 6T polytype is 1.65 eV compared with 2.5 eV in 1T PbI_2 suggests that that of 3T PbI_2 is likely to be near 2 eV. This makes the giant optical absorption edge shift of 2.0 eV [8] accompanying intercalation of PbI_2 by ammonia even more dramatic if it is accompanied by conversion to a lower bandgap polytype.

Once the absorption edge shift has taken place, the incident laser light is no longer resonant with the absorption edge at 2.4 eV. It is owing to this initial resonance that the E_u and A_{2u} phonons of PbI_2 at 106 and 113 cm^{-1} are seen in figure 1. However, in figure 1 these modes are superposed over the A_{1g} peak. After intercalation, the intensity of the E_u and A_{2u} phonons will be much reduced, since the Raman selection rules now hold. However, in figure 3, this frequency range can now be examined against a zero background, so two small peaks are still visible at 106 and 113 cm^{-1} .

At 300 K, the Raman spectrum of ammonia-intercalated PbI_2 was often masked by the rotational Raman lines of ammonia in the cryostat. At 80 K one may eliminate the rotational modes of gaseous ammonia, but there may still be contributions to the phonon spectrum from

- (i) vibrations and rotations of ammonia in the Van der Waals gap of PbI_2 ;
- (ii) solid ammonia condensed on the crystal surface.

In fact, most of the ammonia condensed on the steel cold finger rather than on the crystal itself, and in any case the observed Raman frequencies did not correspond to those of solid ammonia I. Thus at 80 K most of the observed modes are phonons in ammonia-intercalated PbI_2 . The observed additional low-wavenumber modes at 39, 59, and 80 cm^{-1} are the rotational modes of the intercalant ammonia molecules. These modes are at very similar wavenumbers to those of the free molecules. One might expect a change in the moment of inertia of the ammonia molecule on intercalation, causing an alteration in the energy spacing of the rotational modes; however this was not apparent.

In the intermediate stage of intercalation of PbI_2 by ammonia, the Raman peaks are quite broad, owing to a high degree of disorder in the structure (figure 4.) However, once the intercalation process has been completed, a more ordered structure is obtained, resulting in the very narrow Raman peaks of figure 3, is obtained.

Since the crystals were irradiated by a laser at low power (50 mW) we are confident that the surface of the crystal is at the same temperature as that of the cold finger. It is observed that the Raman spectrum of the crystal does not change as the laser power is varied and maintained at a low level. The laser power used was the maximum that could be tolerated (in order to maximize the signal-to-noise ratio) without causing damage to the sample.

The Raman spectrum of 3T PbI_2 [10] shows that the A_{1g} and E_g Raman peaks are much more intense than the new low-wavenumber phonons associated with the 3T stacking. In contrast, the intensity of the low-wavenumber phonons in the ammonia (and amine) intercalates of PbI_2 is very high in comparison to that of the A_{1g} mode at 96 cm^{-1} .

The Raman spectrum of the aggregate of PbI_2 obtained from a colloidal suspension in acetonitrile (table 1, [13]) is very similar to that of ammonia-intercalated PbI_2 (figure 3). The colloidal suspension [13] consisted of very small PbI_2 crystallites. In the crystallites the spatial extent of the layered structure is greatly reduced and there is a very high proportion of surface and edge atoms, so rigid layer modes would be likely to be reduced in intensity relative to new modes [13]. The high pressure Raman spectrum of the acetone aggregate

[13] showed that the application of pressure causes partial recovery of the spectrum of pristine PbI_2 . It is likely that what was occurring here was in fact deintercalation and that molecules such as acetonitrile may also become intercalated. This is discussed in detail in [8]. The Raman spectrum of figure 3 probably corresponds to a structure containing a series of ordered domains, arranged in a mosaical pattern, similar to the compact array of small crystallites studied in [13].

The normal behaviour of TMD intercalates contrasts greatly with the behaviour of PbI_2 intercalates. For example 2H TaS_2 (which does not undergo PLD-CDW distortions) has a Raman spectrum consisting of A_{1g} at 400 cm^{-1} and E_{2g} at 280 cm^{-1} ; on intercalation by EDA the E_{2g} mode shifts 20 cm^{-1} to higher energy as a result of enhanced interlayer interactions. The A_{1g} mode shifts only slightly probably because of the anisotropy of the long-range force.

It should be noted that after prolonged exposure of PbI_2 to ammonia, a different Raman spectrum was irreversibly obtained (figure 5). This suggests that a post-intercalation reaction occurs in which a new structure forms.

The Raman spectra of CdI_2 complexed with ammonia or amines are sufficiently similar to each other to indicate that a common process seems to be occurring. This has been termed complex formation owing to the irreversible nature of the optical changes occurring during the process [8]. During the reaction with ammonia, the A_{1g} modes in 2T CdI_2 becomes weak in intensity and finally disappears. The folding of the Brillouin zone in 2T CdI_2 is certainly disrupted by the additional of ammonia/amines because the rigid-layer mode at 16 cm^{-1} disappears in the later stages of the reaction. However, in the case of ammonia there is initially a pronounced shift of the E_g mode of 13 cm^{-1} to lower energy implying that there has been a decrease in interlayer forces as a result of the reaction and indeed that the layer structure is retained in the initial stages of complex formation. Since the Raman spectrum of figure 7 is eventually obtained the layered structure is clearly lost after an hour in NH_3 . The Raman spectra of the CdI_2 systems showed no evidence of low-wavenumber phonons.

The two Raman spectra (table 2) recorded using light face-scattered respectively from the edge and centre of a CdI_2 crystal during its reaction with ethylamine provide information about the kinetics of this interaction. These imply that the amine is penetrating the crystal from its edge and the diffusing through the crystal layers, disrupting the layer structure in the process.

In fact, CdI_2 is known to form three complexes with ammonia: $\{\text{Cd}(\text{NH}_3)_4(\text{I}_2)_2\}$, $\{\text{Cd}(\text{NH}_3)_4\text{I}_4\}$ [21] and $\{\text{Cd}(\text{NH}_3)_6\text{I}_2\}$ [25]. Raman spectra of the hexamine compound only have been reported [26, 27]. Comparison of figure 7 with [24] shows that the data are very similar. It appears [27] that the broad mode at 322 cm^{-1} is an A_{1g} type mode arising from Cd-N stretch; the mode at 160 cm^{-1} is a T_{2g} mode arising from N-Cd-N bend; that at 112 cm^{-1} is T_{1g} arising from NH_3 ; and that at 35 cm^{-1} is G_{25} . The assignment is based on the cell of a FCC structure $\{\text{Cd}(\text{NH}_3)_6\text{I}_2\}$. Since complexes of ammonia with CdI_2 can form, with coordination numbers of 4 or 6, it is quite possible that similar complexes of amines with CdI_2 exist. The modes appearing are probably of similar origin to those of CdI_2 complexed with ammonia. For example, in CdI_2 complexed with methylamine, the modes at 157 and 313 cm^{-1} are T_{2g} of N-Cd-N bending and A_{1g} of Cd-N stretch. (The notation assumes that the space group for the methylamine complex is the same as for the ammonia complex.) In the ethylamine complex, the modes at 156 , 224 and 482 cm^{-1} can be assigned to T_{2g} of N-Cd-N bending, E_{1g} of Cd-N stretch, and A_{1g} of Cd-N stretch respectively.

Most of the results presented above feature the appearance of new modes in the range

150 to 500 cm^{-1} . From a comparison of the reported Raman spectra of the pure amines with those of the intercalated metal halides presented here it is clear that the modes near 270 cm^{-1} in the latter are in fact torsional modes of the amine NH_2 group; in ammonia a corresponding mode occurs at 284 cm^{-1} .

We assign the modes at 322 cm^{-1} in NH_3 - or CH_3NH_2 -intercalated PbI_2 , and 315 cm^{-1} in $C_9H_{19}NH_2$ -intercalated PbI_2 to Pb-N bonds. As mentioned above, that at 322 cm^{-1} in CdI_2 complexed with NH_3 has already been assigned to Cd-N stretching in $\{Cd(NH_3)_6I_2\}$. A large number of infrared and Raman frequencies for ammine complexes of metal halides have been published [28]. The metal-nitrogen stretching frequencies in all these are in the range 243 to 545 cm^{-1} . Raman and IR spectra of ethylenediamine complexes with zinc, cadmium or mercury chloride have shown metal-nitrogen bond stretching modes between 400 and 450 cm^{-1} [29]. (Note that only the energy range above 150 cm^{-1} is covered by [28] and [29].)

This indicates that in ammonia-intercalated PbI_2 a strong Pb-N interaction exists which requires close proximity of the two atoms such that the ammonia molecules are orientated with their C_3 axes perpendicular to the layers with the N atoms closest to the layers.

The near infrared spectra of ammonia-intercalated PbI_2 at 80 K (figure 8) show the modes of intercalated ammonia only since we found that PbI_2 itself has no absorptions in this range. A pronounced softening of the symmetric (ν_1) (from 3333 to 3220 cm^{-1}) and of the antisymmetric (ν_3) (from 3414 to 3321 cm^{-1}) modes occurs on intercalation. (In NH_3 gas the ν_3 mode is normally obscured by the P band of the ν_1 mode. In the intercalant NH_3 at 80 K these rotations are frozen out and ν_3 becomes visible.) Such softening of the N-H stretching modes is usually considered indicative of hydrogen bonding. However, the H-N-H torsional mode would then be expected to harden, and in fact it softens from 628 to 617 cm^{-1} (not shown). Hydrogen bonding is precluded by the orientation of the NH_3 molecules between the layers. However, the Pb-N bonding (which was also detected by Raman spectroscopy) can equally well account for the observed softening of the N-H stretching modes.

The characteristic strong broad absorptions of NH_4^+ ions in the range 3000-3030 cm^{-1} are not observed; hence it is shown that protonation of ammonia does not occur on intercalation of PbI_2 by ammonia. NH_4^+ absorptions were also absent in the spectra of CdI_2 complexed by ammonia. Protonation of ammonia would result in the evolution of N_2 and H_2 which were not detected in hydrazine intercalation of PbI_2 [30] or during the preparation of the ESR samples of ammoniated PbI_2 which involves immersing PbI_2 in liquid ammonia [8]. In contrast, ammonia-intercalated TiS_2 and NbS_2 contain both neutral and protonated ammonia molecules. In PbI_2 , protonation of the intercalant molecule only occurs if one attempts to prepare the intercalate in acid solution [31].

It was shown from the weight-gain experiments [8] that the fully intercalated form of PbI_2 has the stoichiometry $PbI_2(NH_3)_2$ [32]. The complete reversibility of the intercalation process in both films and crystals has been demonstrated by x-ray diffraction [32] and by both optical absorption and Raman spectroscopy and shows that the intercalation compound retains the original layered structure of PbI_2 . The Raman spectra show that PbI_2 becomes broken up into small crystallites on intercalation and that although the layered structure in these crystallites is preserved, the stacking in them is now either 3T or 3R (octahedral).

On the basis of the above the structure of the intercalation compounds of PbI_2 and ammonia, or rather the microstructure of the small intercalated crystallites of stoichiometry $PbI_2(NH_3)_2$, is proposed. By comparison with ammonia intercalates of transition metal dichalcogenides such as TaS_2 , TiS_2 and NbS_2 , and from geometrical arguments, a c -axis expansion of 3 Å per layer of intercalated ammonia molecules is expected.

Attempts have been made to obtain x-ray diffraction patterns of both single crystal and powdered samples of ammonia-intercalated PbI_2 . However, we have not been able to obtain a diffraction pattern of sufficient quality to deduce lattice constants, and it is not clear what is the precise cause of the degradation of the x-ray diffraction patterns. For reasons not yet understood, any disorder in the samples appeared to affect the x-ray diffraction far more seriously than the Raman spectra.

On the basis of the Raman spectra and stoichiometric analysis [8] we suggest the structure shown in figure 11 for the intercalation compound $\text{PbI}_2(\text{NH}_3)_2$.

References

- [1] Ghorayeb A M, Coleman C C and Yoffe A D 1984 *J. Phys. C: Solid State Phys.* **17** L715
- [2] Rybalka A I and Miloslavskii V K 1976 *Opt. Spectrosc.* **41** 252
- [3] Koshkin V M, Kukul V V, Milner A P, Zabrodskii Y R and Katrunov K A 1977 *Sov. Phys.—Solid State* **19** 1608
- [4] Katrunov K A, Koshkin V M, Milner A P and Shevchenko S I 1978 *Sov. J. Low Temp. Phys.* **4** 260
- [5] Al-Jishi R, Coleman C C, Treece R and Goldwhite H 1989 *Phys. Rev. B* **39** 4862
- [6] Sears W and Morrison J A 1979 *Phys. Rev. B* **19** 2305
- [7] Sears W, Klein M L and Morrison J A 1979 *J. Phys. C: Solid State Phys.* **40** 503
- [8] Warren R F and Liang W Y 1993 *J. Phys.: Condens. Matter* submitted
- [9] Herzberg G 1964 *Molecular Spectra and Molecular Structure: II Infrared and Raman Spectra of Polyatomic Molecules* (New York: Van Nostrand)
- [10] Khilji M Y, Sherman W F and Wilkinson G R 1982 *J. Raman Spectrosc.* **13** 127
- [11] Reding F and Hornig D 1951 *J. Chem. Phys.* **19** 1926
- [12] Binbreck O S and Anderson A 1972 *Chem. Phys. Lett.* **15** 421
- [13] Sandroff C J, Hwang D M and Chung W M 1986 *Phys. Rev. B* **33** 5953
- [14] Wolff H and Ludwig H 1972 *J. Chem. Phys.* **56** 5278
- [15] Hamada Y *et al* 1983 *J. Mol. Spectrosc.* **102** 123
- [16] Teixeira-Dias J J C *et al* 1986 *Spectrochim. Acta A* **42** 589
- [17] Hanoka J I and Vand V 1968 *J. Appl. Phys.* **39** 5288
- [18] Lévy F A (ed) 1979 *Intercalated Layer Materials* (Dordrecht: Reidel)
- [19] Acrivos J V 1979 *Intercalated Layer Materials* vol 6, ed F Lévy (Dordrecht: Reidel) ch 2
- [20] McKinnon W R, Dahn J R and Lévy-Clement C 1984 *Solid State Commun.* **50** 101
- [21] Katrunov K A, Koshkin V M and Kulakov V M 1982 *Ukr. Fiz. Zh.* **27** 226
- [22] Hangyo M, Nakashima S and Mitsuishi A 1983 *Ferroelectrics* **52** 151
- [23] Rao M and Srivastava O N 1980 *Solid State Commun.* **35** 801
- [24] Von Tebbe K F and Plewa M, 1982 *Z. Anorg. (Allg.) Chem.* **489** 111
- [25] Wyckoff R W G 1965 *Crystal Structure* 2nd edn (New York: Interscience)
- [26] Bates A R, Ferris L T H and Jenkins T E 1979 *J. Phys. C: Solid State Phys.* **12** 2945
- [27] Jenkins T E, Ferris L T H, Bates A R and Gillard R D 1977 *J. Phys. C: Solid State Phys.* **10** L521
- [28] Nakamoto K 1978 *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (New York: Wiley) pp 197–206
- [29] Krishnan K and Plane R 1966 *Inorg. Chem.* **5** 853
- [30] Ghorayeb A M 1985 *PhD Thesis*
- [31] Ishihara T, Takahashi J and Goto T 1989 *Solid State Commun.* **69** 933
- [32] Warren R F 1989 *PhD Thesis*