A Review of Intercalation in Heavy Metal Iodides

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This review outlines the work to date concerning the mysteries of both the large optical effects and the bonding mechanisms involved with intercalation in heavy metal iodide systems. Such a system exhibits unusual shifts of the optical band edge to higher energies upon intercalation. The shift depends on which host−guest combination is used. Several models have been developed to describe this system. The bonding mechanism for this system is not clear because some data appear to support a model based on a polarization interaction between the guest and host material whereas other data support a charge transfer or quantum confinement model. There appear to be several different systems being formed by intercalation of the same substances that have different stoichiometry. This riddle may be solved by investigations of the particular methods of intercalation.

Introduction

Studies of intercalation have led to substantial advances in our understanding of the chemistry of layered materials and their intercalates. There is a great deal of controversy concerning intercalation in the heavy metal iodide system stemming in part from conflicting evidence concerning the bonding mechanisms proposed to govern the intercalation of the heavy metal iodide systems. In considering the bonding mechanisms, we find that some data point to polarization effects, some to electron transfer, some to localization effects, some to band modulation, and some to hydrogen bonding. In addition, the heavy metal iodides display an unusually large shift in the optical band gap upon intercalation. The intercalated heavy metal iodide systems also have several possible important uses. Being wide band gap semiconductors, they have potential as photo detectors or solar cells in the visible range.[1] Furthermore, these host materials exhibit an interesting photographic imaging mechanism that is heat sensitized and requires no chemical processing.[2−5] Because this effect can be produced in thin films, it is possible to obtain higher resolution than the usual photographic films. It is of some interest to optimize these properties.

Layer structure compounds are characterized by strong bonding, often ionic, within layers of the material. However, these compounds have weak bonding, usually van der Waals' bonding, between the layers. The van der Waals' gaps are known as galleries. Common layer structure compounds are graphite, transition-metal dichalcogenides, and layered silicates, and such compounds display a spatial repetition of single planes, triple planes, and as many as seven planes, respectively. Heavy metal iodides have a plane of hexagonally packed heavy metal atoms sandwiched between two planes of hexagonally packed iodine atoms. Each layer of such a triple-plane sandwich has an I−HM−I sequence where I represents the iodine atoms and HM represents the heavy metal atoms. Such triple-plane sandwiches are stacked one on the other throughout the lattice. Figure 1a shows a diagram of a heavy metal iodide layer structure compound. The vertical repeat distance in this figure gives the *c*-lattice parameter. There are three inequivalent sites in such a hexagonal lattice. Figure 1b shows a plane perpendicular to the *c*-axis and hence a plane containing the *a*-axis. The inequivalent sites, labeled as A, B, and C, are also shown. If we denote an iodine site by a capital letter and a heavy metal site by a small letter, then the stacking across the sandwich can be either AbA or AbC. Which sandwich appears above which sandwich can lead to many different polytypes with different repeat distances. There have been several different methods of describing the sandwich-stacking sequences in the literature of heavy metal iodides. If we designate a gallery by closed brackets, [ ], then the three simplest polytypes have an arrangement of sandwiches corresponding to AbC[ ]AbC, AbA[ ]CbC[ ]AbA, and AbA[ ]BcB[ ]AbA. The various polytypes are usually denoted by a number followed by a capital letter; that is, T, H, or R standing for trigonal, hexagonal, or rhombohedral symmetry, respectively. The majority of publications denote the first polytype as 2H because there are two anion sheets per unit cell between successive equivalent heavy metal atoms. However, other publications denote this same polytype as 1T because there is one sandwich (composed of two-half sandwiches) per unit cell. The coordination of the heavy metal atom by the surrounding iodine atoms in a sandwich is trigonal prismatic, hence, the 1T designation. There are a few publications that denote the first polytype as 4H, presumably because there are four layers in a unit cell including the first and last layer. We will follow the notation of the majority of publications and call the first polytype 2H. Following this procedure we will denote both the second and third

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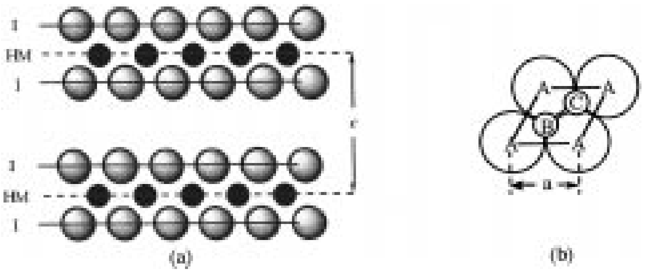

Figure 1. Packing scheme of heavy metal iodides. The layer structure is shown in (a) and the inequivalent packing sites in the nesting structure are identified in (b).

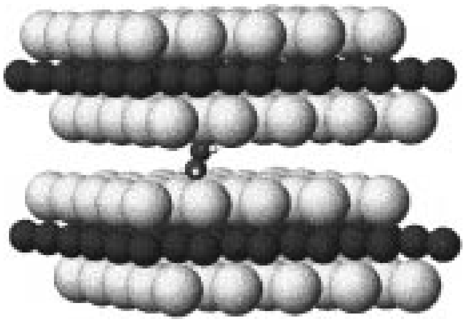

Figure 2. Cache representation of a hydrazine molecule intercalated in a gallery between PbI_2 layers. Only one hydrazine molecule is pictured for the sake of clarity.

polytypes as 4H because they both display the same space group.

Layer materials often show strong two-dimensional (2D) properties that can appear in electrical, optical, and mechanical responses.[6] Such properties can be drastically affected by the process of intercalation.[7−10] Intercalation is the introduction of foreign atoms, ions, or molecules (guests) into the galleries between the layer sandwiches of the layer structure (host) material. Figure 2 shows a model of a hydrazine molecule intercalated into a gallery of a lead iodide host crystal. During intercalation, the gallery spacing between the layer sandwiches is changed, usually increasing upon introduction of the guest. However, the atomic spacing within each layer is, for the most part, unchanged. The amount of guest per van der Waals' gap is generally uniform throughout the material. However, staging can occur, where the guests appear in alternate galleries or even with a higher periodicity, indicating a long-range ordering. Intercalation is reversible; most of the guest can be removed from the host, leaving both the host and guest with their original properties. This deintercalation can be accomplished by physical processes such as by pumping or heating. Extensive intercalation studies have been carried out over the past couple of decades on the well-known layered materials graphite, transition-metal dichalcogenides, and layered silicates.[11−19] Some intercalated compounds can be changed from an insulator to a semiconductor or to a superconductor depending on the relationships between the host and guest materials. Intercalated materials have appeared in a range of applications, such as batteries and lubricants. In addition, there is much theoretical interest concerning these systems because they could provide further information on 2D superconductivity, fast ion conduction, 2D magnetism, and charge density waves.

Most heavy metal iodide intercalation work has been carried out using PbI_2 as the host material, partially as a matter of convenience because many of the other heavy metal iodides are air sensitive. Most of the heavy metal iodide hosts have the same physical structure and symmetry. Electronically, the bonding is primarily due to the 6p electrons of the metal. The lower conduction band is composed mainly of cation p-states, whereas the upper valence band is a mixture of anion s-states and cation p_z-states. Cadmium iodide, although having the same physical structure and electronic bonding as lead iodide, has a somewhat different electronic configuration, which allows the investigator to separate guest size effects from the electronic effects more easily. However, CdI_2 has the widest optical band gap of the heavy metal iodides and requires vacuum ultraviolet (UV) spectroscopy to obtain information on the band structure. This property makes it difficult to measure the unusual optical changes involved with intercalation of these hosts. The structure of BiI_3 is similar to the CdI_2 structure except that in BiI_3 only two-thirds of the cation sites are occupied. This results in the bismuth atoms exhibiting a honeycomblike arrangement. Each bismuth atom or bismuth void is octahedrally coordinated by the surrounding iodine atoms. The most common polytype of BiI_3 has a unit cell extending over three layers of two molecules each. The BiI_3 lattice may be viewed as a $\sqrt{3}$ x $\sqrt{3}$ superlattice of the lead iodide lattice. The electronic bonding for BiI_3 involves the same s- and p-state configurations as that for lead iodide. Although most of the heavy metal iodide intercalation has been carried out using PbI_2 as a host, there are some comparable results using CdI_2 and BiI_3.

Heavy metal iodide host materials, such as PbI_2, CdI_2, and BiI_3, have several interesting features that make them attractive for intercalation studies. Interesting problems involve structure and bonding. For comparison, the dichalcogenides have the CdI_2-type structure with the cation at either an octahedral site or a trigonal prismatic site. Both structures show hexagonal symmetry within the layers. For graphite, three of the four electrons are hybridized to form σ bonds, the remaining p electron forming a delocalized π bond. Although the physical structure of the heavy metal iodides is similar to that of the transition metal dichalcogenides, their electronic structure is similar to that of the graphite system.[20,21] In general, the heavy metal iodide hosts have a stronger, more ionic bonding within the layers and weaker van der Waals bonding between successive triple layer sandwiches than do other layer structure host materials. All the aforementioned properties make the heavy metal iodides an interesting system with which to test the bonding mechanisms involved in intercalation.

Developments

Major work in heavy metal iodide intercalation has been carried out in numerous laboratories. The intercalation of heavy metal iodides with nitrogen-donor molecules has been investigated by a number of analytic techniques, including Raman, infrared (IR) and optical spectroscopy, powder X-ray diffraction (PXRD), luminescence, calorimetry, electron-spon resonance (ESR), and nuclear quadrupole resonance spectroscopy (NQR), photolysis, and gravimetric and many other methods. There are four main methods of synthesis for the preparation of possible heavy metal iodide intercalation systems. These can be summarized as (1) vapor diffusion by exposure of the host crystal to low vapor pressures of the guest material, (2) solution crystallization by growth of the guest−host crystal from solution containing both the host and guest, (3) solution diffusion by exposure of the host crystal to a liquid form of the guest material, and (4) gel diffusion by diffusion of reacting precursors through a gel medium. The first two methods produce the most consistent results. Numerous guests and series of guests have been applied to the heavy metal iodide system.

Considering the number of investigations of this system, the question arises as to why there is so much controversy concerning the bonding mechanisms. In some cases, different investigations of the same guest−host compound can favor different models. This ambiguity we believe is due to different conditions in the synthesis that may, in fact, produce different intercalated species. An added confusion to the data is that some investigations may have produced complexes as well as intercalation compounds. Hence, it is difficult to correlate the results of these investigations. The best model for the bonding in this system may display aspects of several of the proposed models. Next we present some of the major results followed by a comparison and overall analysis.

Early interest was sparked by the observation by Rybalka and Miloslavski in 1976 of reversible bleaching of lead iodide films upon exposure to pyridine vapor.[22] The continuous optical absorption spectrum observed for the lead iodide film changed to one containing two relatively narrow bands at 3.31 and 3.90 eV. These bands were not the result of complex formation, because these bands are not observed upon dissolving lead iodide in pyridine. The increase in the *c* lattice spacing by a factor of >2 was determined by a micro-interferometer. Reversal of the effect occurred upon exposure to air. The workers interpreted their observations as resulting from intercalation of the pyridine between the layers of the PbI_2 structure.

Powder X-ray diffraction and optical studies of PbI_2 and BiI_3 treated with bases such as quinoline, aniline, nonylamine, decylamine, and dimethylcetylamine were reported by Katrunov et al. shortly after this work.[23] The samples were obtained by solution crystallization. Intercalation produced an increase of the *c*-axis parameter The magnitude of this increase correlated with the Lewis base size or multiples of it. In addition, there were increases in the *a*-axis that were integer multiples of the pure lead iodide *a*-axis although the *a*-axis parameter of the pure PbI_2 was not detected in the intercalated compound. The investigators contended that this change in lattice periodicity would split the energy bands. The split bands could then be filled by an assumed electron transfer, resulting in a wider band gap and higher conductivity, although this latter effect was not confirmed. It is not clear why this periodicity should occur in the first place. This band modulation model is one of the five models put forward to explain heavy metal iodide intercalation. An increase in the *a* parameter is usually an indication of a strong interaction between the guest and host lattice and is more characteristic of complex formation than an intercalation process. Again, intercalation caused bleaching of the lower energy band, and produced a spectrum with sharper features that were ascribed to the possible splitting of the valence and conduction bands by the ordered intercalated molecules.

Other work has been performed on samples that were prepared by dissolving lead iodide in the intercalating substance and then precipitating crystalline or microcrystalline material from these solutions. Samples prepared in this fashion have been shown by Mil'ner et al. to contain a layered structure as demonstrated by the identical PXRD patterns obtained on samples prepared by the interaction of PbI_2 powder with piperidine vapor and the solution crystallization method.[24] It is not clear if this result is also true for the other guests tested. Intercalation of PbI_2 and BiI_3 with piperidine produced an increase of the *c* parameter with no increase of the *a* parameter. Possible stoichiometry was obtained by dividing the expanded *c* parameter by the length of the guest molecule.

Ziger et al.[24b] produced PbI_2 and BiI_3 crystals intercalated with piperidine by gel growth. Most of these crystals show various perovskite structures depending on the concentration of piperidine.[24b] Further support of layered intercalated structures being produced from solutions comes from a single-crystal XRD study carried out by Calabrese et al.[25] This study was performed on crystals obtained from solutions of lead iodide and an intercalating alkylammonium salt. The resulting XRD studies show the characteristic layered structure of heavy metal iodide compounds with the guest residing between the layers, although many of their compounds exhibited a perovskite structure.[25] The fact that samples of PbI_2 intercalated with Lewis base molecules can be prepared in this fashion speaks for the stability of the layered structure of these compounds. However, the stoichiometry of the intercalation products prepared using these methods cannot be controlled because multiple products have been obtained.[24a]

Specific heat determinations of PbI_2 intercalated with aniline, piperidine, and pyridine carried out by Gurevich et al.[26] indicated a 1:1 stoichiometry between PbI_2 and piperidine. In addition, the results supported the notion that the guests indeed reside between the layers and perturb the specific heat in a manner that depends on the interactions of the guest molecules with the PbI_2 layers.[26] The authors suggest that the presence of these particular guest molecules reduces the 2D character of the layered structure by adding stronger interactions between the layers.

Vibrational spectroscopic studies carried out by Zabrodski et al.[27] on the aniline−PbI_2 system indicated that hydrogen bonding occurs between the aniline guest molecules, and at 223 K, the aniline molecules undergo a phase transition that changes the hydrogen-bonding mode. These studies led to a model where the plane of the benzene ring of the aniline lies more or less parallel to the PbI_2 layers.[27] Although this model is in agreement with the crystallographic data and density determination of the intercalated material, later research by other groups tends to indicate that, in fact, the benzene ring is perpendicular to the layers.

Nuclear quadrupole resonance studies of the ^{127}I nucleus in these systems were used by Lyfar and Ryabchenko to investigate the nature of the intercalation process.[28] Intercalation led to changes in the NQR frequencies, the temperature dependence of the NQR frequencies, and spin−lattice relaxation rates and appearance of the asymmetry parameter, q, and nonequivalent positions of nuclei. The piperidine system shows less quasi-2D character in the spin−phonon interaction, whereas when aniline is the guest, there is significantly higher 2D character. This result disagrees with the previously noted specific heat studies. Piperidine apparently gives more three-dimensional (3D) character to the lead iodide host by a stronger interaction between the layers. This effect should produce a narrowing of the optical band gap and hence a shift to lower energies of the fundamental absorption edge, at least for the lead iodide−piperidine system. This shift was not observed.

Intercalation affects the photosensitivity of the host; the main products of the photolysis in PbI_2 are metallic lead, iodine, and the guest. The quantum efficiency of the process is dependent on the concentration or pressure of the guest molecules. Studies of this process were carried out by Koshkin et al.[29] for PbI_2 intercalated with NH_3 (4 NH_3 per PbI_2) and $H_2N(CH_2)_2OH$. Photolysis of the 2:1 guest:host is much less efficient than of the 1:1 guest:host.[29] In further studies by Gurina and Savchenko,[30] a plot of the logarithm of the photolytic rate constants for a series of p-substituted anilines intercalated in PbI_2 versus the Hammett constants gave $\rho = 0.63$ ($r = 0.981$), confirming a charge-transfer process between the N atom and a Pb atom upon photolysis. This charge transfer is not necessarily associated with the guest bonding. In addition, the N−H stretching frequencies shift to lower energy upon intercalation again yielding a linear Hammett-type correlation. This frequency change is in accord with charge transfer or Lewis base interaction between the guest and the lead iodide.

In 1984, Ghorayeb et al.[31] established that intercalation of hydrazine, H_2NNH_2, occurs in PbI_2, and BiI_3. Intercalation was achieved by exposing the host thin films or crystals to low pressure of gaseous hydrazine. This procedure avoided the problems of complex formation and disruption of the host lattice due to excess guest concentration during intercalation The shift in the band edge for PbI_2 was 1 eV to higher energies; for BiI_3, >3 eV to higher energies. The absorption edge became both steeper and sharper, which is indicative of an increase in the density of states. A model was presented that was based on flattening of the valence band through the reduction of the interlayer coupling terms. This flattening effectively widens the energy gap. Further optical data produced no evidence of a Drude edge, which was taken as evidence that there was little or no electron transfer producing free charge carriers in the intercalation process. Intercalation of this guest was reversible. The uptake of guest material was rapid, being complete in less than a second, whereas its removal from the host was only slowly effected by pumping over several weeks. This result indicated that the intercalated state was a stable one.

Al-Jishi et al.[32] extended the hydrazine guest studies to intercalation of methylhydrazine, CH_3NHNH_2, into thin films of lead iodide. Below threshold pressures of 2.0 Torr for hydrazine and 2.5 Torr for methylhydrazine, no intercalation occurred. Above pressures of ~12.0 Torr for hydrazine and 11.0 Torr for methylhydrazine, there was substantial degradation of the lead iodide films. Weight gain and X-ray data showed that upon intercalation, the hydrazine guest resided perpendicular to the host layers and there was no significant change of the a-axis of the host. The band edge shift of 1.0 eV noted for hydrazine was reduced to 0.6 eV for methylhydrazine. To explain these data, a new polarization interaction model was developed. A common model for intercalation compounds involves the rigid band model where the intercalation process is determined by a small amount of electron transfer between the guest and the host. This sharing fills some of the states in the host, raising the Fermi energy and thereby changing the electronic properties of the host. For the heavy metal iodides, a simple flattening of the valence band due to expansion of the c-axis cannot account for the shift in the optical band gap energy. The new model assumes a 1D interaction between the dipole moment of the guest and the $5p_z$ orbital of the iodine. This interaction appreciably increases the binding energy of the iodine electron. Additionally, the iodine outer electron cloud is physically displaced toward the dipole. Such a deformation of the iodide electron cloud reduces the interaction between the lead and iodine electron within a layer. The change in the electron cloud in turn leads to a decrease in energy of the valence band and hence a further increase in the fundamental energy gap. This model accounted semiquantitatively for the observed changes in the band gap.[32]

In 1991, Mehrotra et al.[33] intercalated aniline C_6H_5-NH_2 into lead iodide thin films. They used optical absorption to determine a band edge shift of 0.5 eV to higher energies upon intercalation. Raman spectroscopy confirmed the presence of the aniline molecule in the intercalated samples. The amine molecule was effectively unchanged in the intercalation process. Rutherford backscattering spectroscopy confirmed the stoichiometry of the pure host samples. X-ray analysis indicated an increase of the c-axis by 3.03 Å upon intercalation. A decrease of the full width half-maximum (fwhm) of the X-ray lines upon intercalation indicated an increase of the size of the crystal platelets by ~70%. The PXRD data indicate that the aniline axis was perpendicular to the host layers. Application of the dipole polarization model to their data tended to confirm the correctness of this model. In the case of aniline, however, it appears that the electron cloud displacement is not as great as with the hydrazine hence reducing the polarization effects on the lead−iodine coupling. The fact that aniline intercalates whereas benzene does not intercalate indicates that the dipole moment of the aniline or hydrogen bonding by the N−H bond is a necessary requirement for intercalation.

In 1993, Warren and Liang[34] reported the results of a study by Raman, ESR, and IR spectroscopy of the intercalation of ammonia, methylamine (CH_3NH_2), ethylamine ($C_2H_5NH_2$), butylamine ($C_4H_9NH_2$), and nonlyamine ($C_9H_{19}NH_2$) into both PbI_2 and CdI_2 for both room-temperature and liquid nitrogen temperature. Care had to be taken to prevent deintercalation due to pressure drops when the samples were cooled. All of the guests that were used did indeed intercalate with the lead iodide. Samples were prepared by vapor diffusion and it was noted that there were two or three forms produced depending on the pressure of the vapor. Low pressure produced the band shift common for the heavy metal iodide system, higher pressures resulted in even wider band gap shifts, and the highest pressures produced complexes, breakup into microcrystals, or exfoliation of the layer structure. This result is similar to the effects noted in the hydrazine work of Al-Jishi[32] et al. Warren and Liang[34] noted a larger range of intercalating vapor pressures for the amines than Al-Jishi et al.[32] did for the hydrazines. Upon intercalation, the lead iodide changed from a 2H polytype to a 6H polytype, as determined by the Raman data. This shift in polytype is due to the sliding of the layers relative to each other to form a more stable configuration. Such a change in polytype is similar to a polytype conversion that occurs in TaS_2 intercalated with hydrazine and ZrS_2 intercalated with lithium, although it had not been observed in the heavy metal iodides before.[8] In the 6H polytype, the ammonia molecule intercalated into lead iodide can reside in either an octahedral site or a trigonal prismatic site. Pure lead iodide of 6H polytype has a lower band gap of 1.65 eV than the pure lead iodide of 2H polytype. This difference means that the lead iodide 6H polytype has an increase of the optical band edge of ~2 eV upon intercalation with ammonia as compared with the pure lead iodide. This change in band gap is twice that seen in intercalation with hydrazine. The butylamine guest produced a different final structure than the other guests. The same guests tended to break up the CdI_2 crystals, but this may have been due to the guest pressures used. However, in both lead iodide and cadmium iodide, there are indications of a strong N−metal interaction, suggesting that the nitrogen atom is close to a layer. This suggestion appears to preclude hydrogen bonding in this system. A new model dependent on exciton localization was proposed. In this model, nanocrystals are formed, which are then intercalated by the guests resulting in practically isolated layers. Excitons trapped in these layers at Pb^{2+} sites next to the N−H bonds would have energy levels corresponding to particles in a box. The normal conduction band would then be broken up into box states. As the box size changes with the addition of further guest molecules, the box states shift up in energy, accounting for the enhanced exciton line generally seen around 3.2 eV. According to this model, as guest concentration increases, the first exciton disappears to be replaced by yet a higher energy state, thus giving the appearance of a higher energy shift of the band gap.

In 1996, Coleman et al.[35] reported intercalation of hydrazine and some methylated hydrazines into both thin films and crystalline samples of lead iodide. Weight gain measurements were made of the reversible intercalation of hydrazine, methylhydrazine, and 1,2-dimethylhydrazine [$CH_3(H)NN(H)CH_3$]. The first two compounds were taken up to the extent of ~1 molecule of guest per formula unit of PbI_2. The dimethylated compound was only taken up to the extent of about half a molecule per formula unit of PbI_2. The PXRD data were informative about the implications of this weight gain result. The minor changes in *a* values coupled with the substantial changes in *c* values support the intercalation model for these host−guest interactions. The changes in the *c* value for hydrazine of 5.81 Å and for methylhydrazine of 7.16 Å, taken with the packing suggested by the weight gain data, are consistent with accommodation of these guest molecules approximately perpendicular to the iodide layers and along the *c* axis. The result for 1,2-dimethylhydrazine is very interesting. The change in *c* value of 14.09 Å suggests strongly that staging is occurring in this process, with the guest being accepted into every second vacant gap between iodide layers; the stoichiometric result of uptake of only 0.58 guest per PbI_2 supports this interpretation. Staging is a well-described phenomenon in other intercalating systems; its observation in heavy metal iodides is novel. Coleman et al.[35] interpreted the optical changes seen for these three hydrazines in part, at least, to the polarization model. The observed band edge shifts increase with increasing dipole moment of the guest. The point dipole model used to interpret these data is obviously an oversimplification. It is noteworthy that such a simple model does at least rationalize the trends in optical data.

Summary

Table 1 summarizes the results of the investigations just described. The table lists a number of investigations of PbI_2 intercalation in alphabetical order of the guest used. In comparing these data it is clear that something is still missing. Although the data within various groups seem self-consistent, there are a number of conflicting results. In the earlier studies, the investigators were not alert to the possibility of complex formation nor were they aware of the effects of guest concentration on the resulting intercalation. Despite these problems, progress was still made in the attempts to model the intercalation process.

Various models have been proposed to explain the giant band edge shift to high energies observed in PbI_2 after intercalation. These are

1. band stabilization model of Ghorayeb et al.;[31]
2. polarization interaction of Al-Jishi et al.;[32]
3. superlattice and conduction band splitting of Katrunov et al.;[23]
4. quantum size effect of Koshkin et al.;[24d] and
5. exciton localization of Warren & Liang.[34]

Ghorayeb et al.[31] suggested the driving force for intercalation in PbI_2 and BiI_3 is the reduction in interlayer interactions during intercalation. This reduction would flatten the valence band and hence increase the band gap. However, this reduction was not enough to account for the larger band edge shifts. The strong feature present at ~3.2 in many heavy metal iodide intercalates was partially attributed to the increase in the density of states consequent to the change in band structure.

Al-Jishi et al.[32] extended this idea by including the electrostatic interaction between the iodine p_z orbitals and the dipoles associated with the guest molecules using first-order perturbation theory. Again, charge transfer is not a prerequisite for the applicability of this

Table 1. Summary of Guests, Experimental Methods, and Results and Related Parameters from Intercalation Studies of PbI_2

guest	preparation method	stoichiometry guest:PbI_2	a (Å)	c (Å)	Δc	ΔE_g (eV)	pK_b (l)	$\mu/10^{30}$ Cm	ref
1,2-dimethylhydrazine	vapor diffusion	0.58:1[a]	4.77	21.08	14.10	0.13		4.50	35
ammonia	vapor diffusion	2:1				2.00	4.75	4.90	34
ammonia	vapor diffusion	4:1[b]				0.19	4.75	4.90	29
aniline	solution crystallization	0.33:1[c]	18.40	20.50	13.52	0.40	9.37	5.10	23
aniline	vapor diffusion	n/r[d]	4.78	10.00	3.02	0.50	9.37		36
aniline	solution	0.125:1[c]	18.80	20.50	13.52		9.37		24(c)
butylamine	vapor diffusion					0.50	3.23		34
decylamine	solution crystallization	0.11:1[c]	27.60	73.40	66.42	0.25	3.36		23
decylamine	solution crystallization	0.11:1[c]	36.80	73.44	66.46	0.25	3.36		24(c)
dimethylcetylamine	solution crystallization	n/r	32.20	61.00	54.02	0.22			23
ethanolamine	solution diffusion	1:1[a]				−0.36	4.5		30
ethanolamine	solution diffusion	2:1[a]				0.52	4.5		30
ethylamine	vapor diffusion					0.52	3.193	4.07	34
hydrazine	vapor diffusion	1.09:1[a]	4.78	12.80	5.82	1.00	6.05	6.14	35
methylamine	vapor diffusion					0.58	3.343		34
methylhydrazine	vapor diffusion	1.09:1[a]	4.96	14.15	7.17	0.60		5.60	35
nonylamine	solution crystallization	n/r	23.00	62.00	55.02	0.30	3.36		23
piperidine	solution diffusion	1:1[c]	4.59	14.16	7.18	0.15	2.877		24(c)
pyridine	vapor diffusion	n/r				0.80	8.75	7.31	22
quinoline	solution crystallization	n/r	18.40	29.90	22.92	0.44	9.1	7.64	23
quinoline	solution crystallization	1:4[c]	18.40	29.88	22.90	0.40	9.1		24(c)
none (Host PbI_2)			4.56	6.98					

[a] Weight gain measurements. [b] X-ray methods. [c] Thermogravimetric determination. [d] n/r, Not reported.

model. The simplified band structure calculation allowed a calculation of the increased band gap that corresponded to the data. This calculation was later confirmed by Mehrotra et al.[33] with their intercalation of aniline. Further work by Coleman et al.[34] demonstrated that the band edge shift, change in the c axis, and corresponding modification of the band structure varied directly with the dipole moment of the guest as predicted by this theory.

The conduction band splitting model of Katrunov et al.[23] is based on the assumption that charge is transferred from the guest to the host material. This model only accounts for the small absorption shifts of 0.2 to 0.45 eV. The transfer of charge is thought to be from the N lone pair of pyridine as deduced from N−H frequency shifts during potolysis.[29] The authors proposed that a superlattice structure is formed by the guest collecting only at points separated by a specific multiple of the fundamental a lattice spacing. This spacing of the guests modulates the lattice, causing the valence and conduction bands to split into small sub-bands. The filling of sub-bands would produce a wider band gap but would also produce metallic behavior within the sub-bands that is not observed. Just why the guest should be stacked at the particular points chosen is not clear. The stoichiometric data shown in Table 1 for their results imply that the intercalation was not completed; the changes in the a-axis may imply complex formation instead of intercalation. Comparing their structural data of solution grown crystals for aniline with that of vapor diffusion samples of Mehrotra et al.[33] shows a large difference. This difference may be due either to the growth methods or to the amount of aniline included in the compound.

A quantum size effect model was developed by Koshkin et al.[29] associated with a superlattice in the layer plane. The energy gaps are then determined by the superlattice spacing. This model relies on the application of a superlattice potential applied as a result of a guest-to-host charge transfer. The superlattice periodic potential forms a series of quasi-2D wells with linear dimensions of the superlattice a-spacing. The model is similar to that of Sandroff and Farrow[36] except the electron is confined to a superlattice unit cell instead of a colloidal particle. An increase in the energy of the ground state will cause an identical increase in the energy of the absorption edge. Provided that the electron effective mass remains constant (which is unlikely if there is a band structure change), there will be a linear relationship between the position of the absorption edge and the inverse square of the superlattice spacing. The authors mention the case of piperidine intercalation in which there evidently was no superlattice and no modulating potential either, in other words, there would be no charge transfer and no band shift contrary to observation. Their luminescence data confirm there is no charged ion present in the piperidine intercalate.

The model of Warren and Liang[34] is a combination of charge transfer and quantum confinement. In this case, some of the charge from the N lone pair is transferred to the cation, which then traps an exciton in a unit cell of the intercalated lattice. This model does not require a superlattice. The prominent peak around 3.2 eV is taken to be the lowest level for the trapped exciton. This peak then disappears when the next level is occupied. For this model to produce observable results, the lattice must break up into nanocrystals of the order of the size of the unit cell. Although there is some evidence for this, particularly in CdI_2 intercalated with amines, other data by Mehrotra et al.[33] indicate that there is an increase of the size of the crystallites making up a thin film upon intercalation with aniline. Single-crystal data during both intercalation and deintercalation of Gurevich et al.[26] also contradict this assumption. Sandroff et al.[36] demonstrated a quantum size effect in PbI_2 and BiI_3 monolayered crystallites formed by evaporation of colloids of a heavy metal iodide in acetonitrile. The resulting single-layer crystallites showed a TEM (transmission electron microscopy) trinomial distribution. However, this distribution could not be fitted to the three peaks observed in the absorption spectrum, leaving in doubt whether these layers were intercalated by the acetonitrile.

The discrepancies between the various bonding models may, in part, be due to the production of different forms of the intercalation systems. Interaction of PbI_2 with various molecules may result in several different structures according to the concentration of the guest molecules and the pH of the solution. Exposure of the host to too high a pressure of the guest vapor or guest liquid can lead to decomposition of the host or the formation of complexes. Many earlier workers have not taken this into account, which is the reason for the apparent contradiction of the X-ray and optical absorption spectra obtained for the various compounds. Under certain conditions, an entirely new band structure may form.

The observations made so far on intercalation in heavy metal iodides and reviewed in this article indicate that there remains a fertile field for future investigations. It would be worthwhile to reinvestigate some of the earlier work in light of recent developments. Active monitoring of changes taking place during intercalation could pinpoint just when the system undergoes intercalation and when possible complexes are being produced. There is a question as to whether the polarization model or the localization model for this system actually changes the higher energy bands of the host material. The answer to this question can be determined by an investigation of the upper energy bands by UV spectroscopy. Resolution of this structure could well distinguish between the predictions of the various models. The strong exciting structure of the heavy metal iodide systems may have significant third-order optical nonlinearity that is worth pursuing in the search for "smart" materials. In terms of host materials, the study of bismuth iodide has sparse guest data. There are many other layered iodides. Work has begun on germanium(II) iodide, GeI_2.[37] Other candidates for study include the paramagnetic FeI_2 and a number of other transition metal halides.[38] Guest materials, in addition to ammonia, amines, and hydrazines, could clearly include other donors such as nitriles (RCN), isonitriles (RNC), and cyanamides (RR″NCN). Although it is tempting to invoke the phrase of the great organic chemist, Moses Gomberg, discoverer of the stable triarylmethyl radicals at the beginning of the twentieth century, and reserve further development of this field to ourselves, that is not the way of science in the late twentieth century. There is plenty of work for many hands in this fascinating new area, and it is fair to say that our understanding of intercalation processes in heavy metal halides is just at its beginning.

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