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Optical effects of methylated hydrazine intercalation in lead iodide

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Hydrazine and methylhydrazine were intercalated into polycrystalline thin films of lead iodide. Optical-band-edge shifts decreased with increasing methylation. This suggests a model whereby the polarization of the intercalate lowers and flattens the valence-band energy thereby increasing the fundamental band-gap energy.

I. INTRODUCTION

Intercalation is the process whereby a guest (intercalate) is inserted uniformly into the gaps of a layered-structure host lattice. This has been shown to occur in graphite,[1,2] sheet silicates,[3] transition-metal dichalcogenides (TMDC),[4,5] and in heavy-metal iodides (HMI).[6,7] Detailed studies on graphite and TMDC intercalation indicate charge transfer as the chief mechanism in the intercalation process. This results in band filling and dramatic changes in the electrical properties of the host material. However, the intercalation of HMI does not appear to involve the charge-transfer mechanism to any significant degree, as evidenced by the lack of a Drude edge in the infrared optical adsorption. Rather, there is a dramatic shift of the optical band edge to higher energies.

The structure of the HMI is similar to that of the TMDC, both being of the CdI_2 type. However, there is more of an ionic nature to the bonding between the heavy-metal layer and the iodide layer on either side of it in the HMI than between the metal and the chalcogenide layers in the TMDC. Hence, it is anticipated that the van der Waals forces holding the iodide layers together are weaker in the HMI than in the TMDC due to the greater negative charge on the iodine atoms. On the other hand, the electronic structure of the HMI is more like graphite than that of the TMDC. The conduction band in PbI_2 corresponds to lead p_z states similar to the carbon p_z states in graphite. The valence band is an admixture of iodine s and p states and lead s states. The dispersion of the valence band is due to the interlayer coupling. The conduction band of the TMDC has a d character, while the valence band of the TMDC is formed from the p orbitals of the chalcogenide atoms. Charge transfer in intercalation in the TMDC fills up portions of the conduction band, thereby changing its electrical properties.

Intercalation by hydrazine causes an increase in the optical-band-edge energy in PbI_2 of 1 eV and in BiI_3 of more than 3 eV. We have found that for PbI_2, intercalation with methylhydrazine causes an increase in the optical-band-edge energy of 0.6 eV.

II. EXPERIMENTAL PROCEDURE AND RESULTS

Polycrystalline thin films of lead iodide were made by standard evaporation techniques. The films were deposited on glass, sapphire, and quartz substrates. They were determined to be 700±35 Å thick by means of a deposition monitor oscillator, step interference patterns, and Rutherford backscattering. Films of this thickness are known to be composed of platelets oriented with their c axis perpendicular to the substrate.[8] The substrate with the film comprised one window of a two-window sample chamber. This chamber was attached to a vacuum line which could admit controlled pressures of the intercalate to the sample. The chamber was also placed in a spectrometer system to allow *in situ* optical measurements of the transmission. The starting hydrazines were more than 98% pure. They were dried over KOH pellets for 12 h before they were admitted to the vacuum system and taken through three freezer thaw cycles under vacuum. They were then stored in the vacuum system in a side flask. The purities of the hydrazines were checked by comparing their vapor pressures and NMR spectra against standards. The pressure of the hydrazine admitted to the sample chamber was measured by an oil manometer during transfer. Spectra of the host lead iodide films were taken after 10 h of pumping at 10^{-5} Torr, after exposure to the intercalate, and after reevacuating the chamber by pumping on it. In general, HMI are subject to photodecomposition and photosublimation at elevated temperatures.[9] Since intercalation can disrupt pinning bonds,[10] our intercalation tends to make the lead iodide more photosensitive as expected. Hence, it was necessary that care be taken to reduce the sample's exposure to light during preparation.

The thin polycrystalline films of lead iodide were exposed to a range of pressures from 1 to 20 Torr of hydrazine and methylhydrazine. It was observed that when the pressure of the intercalate was below some low threshold pressure there was no optical change observed in the films. This threshold was 2.0 Torr for hydrazine and 2.5 Torr for methylhydrazine. The time to affect the shift of the optical band edge due to intercalation was of the order of minutes at these threshold pressures for both intercalates but was less than a second above the threshold. The shift in the optical band edge was reversible upon pumping for both intercalates between the low-pressure threshold and an upper-limit pressure. The upper-limit pressure was 12.0 Torr for hydrazine and 11.0 Torr for methylhydrazine. Above the upper-limit pressure the films tended to break apart and decompose.

Optical spectra of lead iodide before intercalation, during intercalation, and after deintercalation by pumping are shown in Fig. 1. The figure shows curves for the optical transmission of the pure host material and of samples intercalated with hydrazine and methylhydrazine. The spectra for both hydrazine and methylhydrazine intercalation were taken at 5.5 Torr and the deintercalation spectrum was taken after pumping for 4 h. Transmission and reflection spectra for the host material yield standard results as obtained by others resulting in a value for the absorption coefficient of 10^5 cm^{-1} at the band edge.[8,11] Electroabsorption in the thin films has confirmed that this is a direct-band-gap material.[12] Although the well-known band-edge exciton[8] of lead iodide can be seen in the large scale of Fig. 1, it is not apparent in the intercalated film. This is not surprising when one compares the 30-meV exciton energy to the 1-eV band-edge shift.

III. DISCUSSION

As a first approximation to understanding the effect of intercalation on the fundamental energy gap of lead iodide, we consider the following simple one-dimensional model. Each lead or iodine layer is treated as an entity with energy E_{Pb} and E_{I}, respectively. The matrix element of the Hamiltonian between the adjacent lead and iodine layers is denoted by V_1, whereas that between nearest-neighbor iodine layers is denoted by V_2. Denoting the lattice constant of this one-dimensional system by c, and using the fact that the distance between adjacent lead and iodine layers is approximately $c/4$, the Hamiltonian matrix becomes

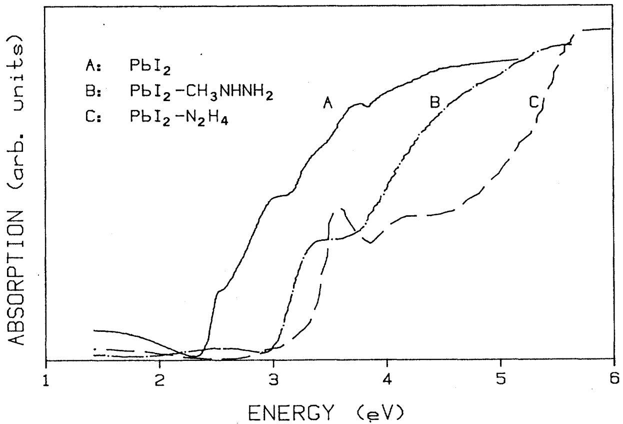

FIG. 1. Optical adsorption plotted as a function of the energy of incident photons. Results are shown for pure lead iodide, and for hydrazine- and methylhydrazine-intercalated lead iodide.

$$H=\begin{bmatrix} E_{\mathrm{I}} & V_1 & V_2(1+e^{-ikc}) \\ V_1 & E_{\mathrm{Pb}} & V_1 \\ V_2(1+e^{ikc}) & V_1 & E_{\mathrm{I}} \end{bmatrix} . \tag{1}$$

Diagonalizing H at the A point of the Brillouin zone (which corresponds to a wave vector $k=\pi/c$), we find that while one of the energy values is E_{I}, the other two are given by

$$E_{\pm}=\tfrac{1}{2}(E_{\mathrm{Pb}}+E_{\mathrm{I}})\pm|(E_{\mathrm{Pb}}-E_{\mathrm{I}})^2+8V_1^2|^{1/2} , \tag{2}$$

the positive sign corresponding to the energy level of the highest valence band in lead iodide. Similar values can be calculated at the Γ point of the Brillouin zone, for which $k=0$. Upon calculating the corresponding eigenvectors at Γ and A, we can identify these three energy valence bands with three valence bands obtained by an elaborate band-structure calculation by Schlüter and Schlüter[13] and by Robertson.[14] This identification allows us to determine all the parameters in the Hamiltonian matrix. If we set the energy of the highest valence band at A equal to zero, we find

$$E_{\mathrm{Pb}}=-2.15 \text{ eV},\quad E_{\mathrm{I}}=-3.30 \text{ eV} ,$$
$$V_1=-1.9 \text{ eV},\quad V_2=-0.75 \text{ eV} .$$

Upon intercalation with hydrazine molecules, the coupling between neighboring iodine layers belonging to different unit cells is appreciably reduced, causing a flattening of the valence band along ΓA. The energy level of the lowest conduction band at A is unaffected by intercalation, since the wave function there is made up mainly of Pb orbitals. On the other hand, the wave function at A of the upper valence band has about a 60% contribution from the p_z orbital of the iodines and a 40% contribution from the Pb s orbital.

If the only effect of the intercalation is to flatten the upper valence band, then we can calculate the increase in the energy gap within our one-dimensional model. This turns out to be 0.25 eV, which is significantly lower than the observed shift of 1 eV.

To understand this large shift, we consider the effect of intercalation on the $5p_z$ electron of the iodine atom, because it is that p_z orbital which contributes significantly to the energy level at A of the upper valence band. The dipole moment of the hydrazine molecule N_2H_4 can be thought of as the vector sum of two dipole mements, each given by the dipole moment of NH_2. The direction of the N—N bond in the N_2H_4 molecules between the iodine layers is governed by two competing effects. To minimize the increase in length of the c axis one could expect the N—N bond to be parallel to the iodine layers. On the other hand, to lower the electrostatic energy one expects the N—N bond to be tilted by about 20° in order to make one of the two NH_2 dipoles close to one iodine layer, while the other NH_2 dipole would be closer to the other iodine layer in the neighboring unit cell. Thus, it is likely that the N—N bond will be tilted a little bit away from the horizontal direction.

We consider a simplified model in which the effect of intercalation on the $5p_z$ electron of iodine is a perturbation due to the electrostatic attraction between the electron and a NH_2 dipole. Furthermore, we shall represent the NH_2 by a point dipole, of dipole moment p. First-order perturbation theory yields for the change in energy of the $5p_z$ electron

$$\Delta E_{\mathrm{I}}=\frac{ep}{4\pi\epsilon_0}\left\langle\Psi\left|\frac{b-r\cos\theta}{(b^2+r^2-2br\cos\theta)^{3/2}}\right|\Psi\right\rangle , \tag{3}$$

where $\mathbf{r}$ is the electron position vector relative to the iodine nucleus, θ is the angle between this vector and the line joining the nucleus to the dipole, b is the corresponding distance, and $|\Psi\rangle$ is the state describing the $5p_z$ electron. In our one-electron approximation, we have

$$\langle \mathbf{r}|\Psi\rangle=R(r)Y_{lm}(\theta,\phi) , \tag{4}$$

where $Y_{lm}(\theta,\phi)$ are the well-known spherical harmonics. Although the above form of the wave function is correct only for hydrogenlike atoms, it is still appropriate to use in our simplified model. Evaluation of the above integral yields

$$\Delta E_{\mathrm{I}}=\frac{3ep}{8\pi\epsilon_0 b^2}\left[\frac{1}{6}-\frac{4}{5b^2}\langle r^2\rangle\right] , \tag{5}$$

where $\langle r^2\rangle$ is approximately 5 Å^2. Assuming that $b=3.5$ Å and $p=10^{-29}$ C m, we find that $\Delta E_{\mathrm{I}}=-0.5$ eV. We also note that the state of the $5p_z$ electron is changed by the perturbation from $|\Psi\rangle$ to $|\Psi'\rangle$ such that

$$|\Psi'\rangle=|\Psi\rangle+\sum_k\frac{\langle k|H|\Psi\rangle}{E_{\mathrm{I}}-E_k}|k\rangle , \tag{6}$$

where the sum is over all unoccupied states of the iodine atom. The average value of the coordinate z in the unperturbed state vanishes, but in the perturbed state it is

$$\langle z\rangle=2\sum_k\frac{\langle k|H'|\Psi\rangle\langle\Psi|z|k\rangle}{E_{\mathrm{I}}-E_k} . \tag{7}$$

Most of the contribution to $\langle z\rangle$ comes from the $|k\rangle=6s$ state since this is closest in energy to the unperturbed state, the energy difference being about 1.5 eV. Evaluation of the above expression gives $\langle z\rangle=0.6$ Å. Consequently, this induced polarization of the iodine atom causes an increase in separation between the iodine $5p_z$ electronic cloud and the nearest-neighbor lead atoms. This in turn reduces the coupling between these atoms. Assuming that the interaction matrix element is inversely proportional to the square of the distance between atoms, we get a 20% reduction in the coupling between the lead and iodine atoms. In our model this leads to a 20% reduction in V_1. According to Eq. (2), this reduction in V_1 combined with the lowering of E_{I} causes a lowering by about 1 eV of the value of the energy level at A of the upper valence band.

IV. CONCLUSIONS

The simple model of hydrazine as point dipoles interacting electrostatically with the one-dimensional representation of lead iodide does produce a quite close agreement between the predicted shift of the absorption band edge and that observed experimentally.

Other standard theoretical models are not successful in explaining our unusual optical data. The HMI have a large negative pressure coefficient and one would expect that an increase of the van der Waals gap due to the physical presence of the intercalate would increase the fundamental band gap. If the band-edge shifts were due simply to an increase of the c axis of the unit cell by increasing the van der Waals gap, then an increase of the size of the intercalate should increase the effect. This is not what we observe. Similarly, if the band-edge shift were due simply to reducing the interlayer coupling caused by the presence of the intercalate, then the only effect would be a flattening of the valence band which, as we have shown, does not provide a sufficient change. Furthermore, our model implies that the usual rigid band model commonly used in graphite and TMDC is not applicable here. The change in the optical spectrum tends to support this.

The experimental result for methylhydrazine intercalation into lead iodide is that there is a smaller band-edge shift observed than for hydrazine intercalation: 0.6 eV versus 1.0 eV. The experimental dipole moments for the two hydrazines are in the same order; that of methylhydrazine is 5.6×10^{-30} C m while the dipole moment of hydrazine[15] is 6.14×10^{-30} C m. The dipole moment is unlikely to be the only significant factor in the phenomena we have observed. It is to be expected that factors such as size, polarizability, and polarity all play a part not only in the final state of the lead iodide intercalate system, but also in the mechanism of intercalation. It seems reasonable that a methylated hydrazine might not attach to and migrate into the quite ionic lead iodide lattice as readily as the parent hydrazine molecule. However, the model proposed here does account for the relative optical effects for two closely related compounds, and does provide a reasonable basis for the extension of both the experimental work and the theoretical analysis.

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