Exciton Absorption and Photoconductivity in Mercurous Halides

S. K. Deb

Central Research Division, American Cyanamid Company, Stamford, Connecticut 06904

The optical absorption spectra of thin films of Hg_2F_2, Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2 were measured in the wavelength range 190–750 mμ at 77°K and 300°K. With the exception of Hg_2F_2, sharp exciton peaks were observed in the spectra of all these halides, both near the fundamental absorption edge and at higher energies. The multiplicity and positions of the exciton peaks are characteristic of the Mott-Wannier (delocalized) type of excitons. Absorption peaks due to the splitting of the halogen doublet were also observed. The photocurrent spectrum of Hg_2I_2 shows close resemblance to the corresponding absorption spectrum.

I. INTRODUCTION

The optical absorption spectra of several metal halides have been studied considerably in recent years.[1-8] In many of these materials, sharp absorption bands have been observed near the fundamental absorption edge which have been interpreted as due to the formation of excitons. In general, two types of excitons are found: (a) The small-radius (tight-binding) excitons are typically observed in alkali halides,[3,4] and (b) the large radius or Mott-Wannier (delocalized) excitons which form well-defined hydrogenic series are typical of metal halides such as TlCl,[5] CuI,[2] PbI$_2$,[6-8] CdI$_2$,[9] SbI$_3$,[10] BiI$_3$,[11] etc.

In contrast to other metal halides of the M-X type which have alternating M and X atoms in the crystal, the crystal structure of mercurous halides consists of alternating linear units, X-Hg-Hg-X. The behavior of mercury is unique in that it forms a stable diatomic molecule $^+$Hg-Hg$^+$ and predominantly ionic compounds.[12] In addition to its structural peculiarities, mercurous halides are photosensitive, and their physical properties correspond in many respects to silver halides. However, little is known about the optical and electrical properties of these materials.

The absorption spectra of single-crystal and thin-film Hg_2I_2 were measured at room temperature by Turyanitsa *et al.*[13] They observed absorption peaks in the visible and ultraviolet, but no hydrogenic series was detected. Recently, Flannagan,[14] while studying the photographic properties of mercurous halides, measured the optical absorption of thin coatings of these materials in a gelatin binder and found straight absorption edges with no structure.

We have measured the absorption spectrum and photoconductivity of vacuum-evaporated thin films of mercurous halides at 77 and 300°K and found several absorption peaks near the fundamental absorption edge which can be represented by a hydrogenic series. The results also show additional absorption peaks on the high-energy side of the absorption edge. Some of these are attributed to transitions involving a split valence band.

II. EXPERIMENTAL

Thin films of mercurous halides, required for optical measurements in the regions of high absorption coefficients, are difficult to prepare. Mercurous halides sublime readily in vacuum at temperatures considerably below their melting points, but they do not adhere to glass or quartz substrates maintained at room temperature or above. However, we found that good quality films could be obtained on quartz substrates at room temperature if the depositions were carried out at pressures between 0.02 and 0.1 Torr. Therefore, during our optical measurements at low temperature we maintained a partial pressure of dry argon of 0.02 Torr in the cryostat. For each material studied, films of different thicknesses in the range 0.05–1 μ were prepared on quartz substrates by thermal evaporation from a tantalum boat of analytical grade material. The thicknesses of the films were monitored during deposition by means of a quartz crystal oscillator.

The optical absorption spectra in the temperature range 77–300°K were obtained using a Perkin-Elmer Model 450 spectrophotometer and a metal cryostat. The optical absorption was measured in terms of the quantity $\log_{10}(I_0/I)$, where I_0 is the intensity of the incident light and I is the intensity of the transmitted light. The data were corrected for the reflection loss. Photoconductivity was measured by the dc method described previously[15]; the current was measured with a Keithly 610B electrometer. Monochromatic light, used for irradiating the sample, was obtained from a 1000-W xenon lamp source, through a Jarrell Ash grating monochromator. Evaporated gold was used as the electrode material. The refractive index of the film was measured by the Brewster angle method.

III. RESULTS

A. Optical Absorption

Figures 1(a)–1(d) show the optical-absorption spectra of thin films of the mercurous halides deposited on quartz substrates. The results at room temperature are
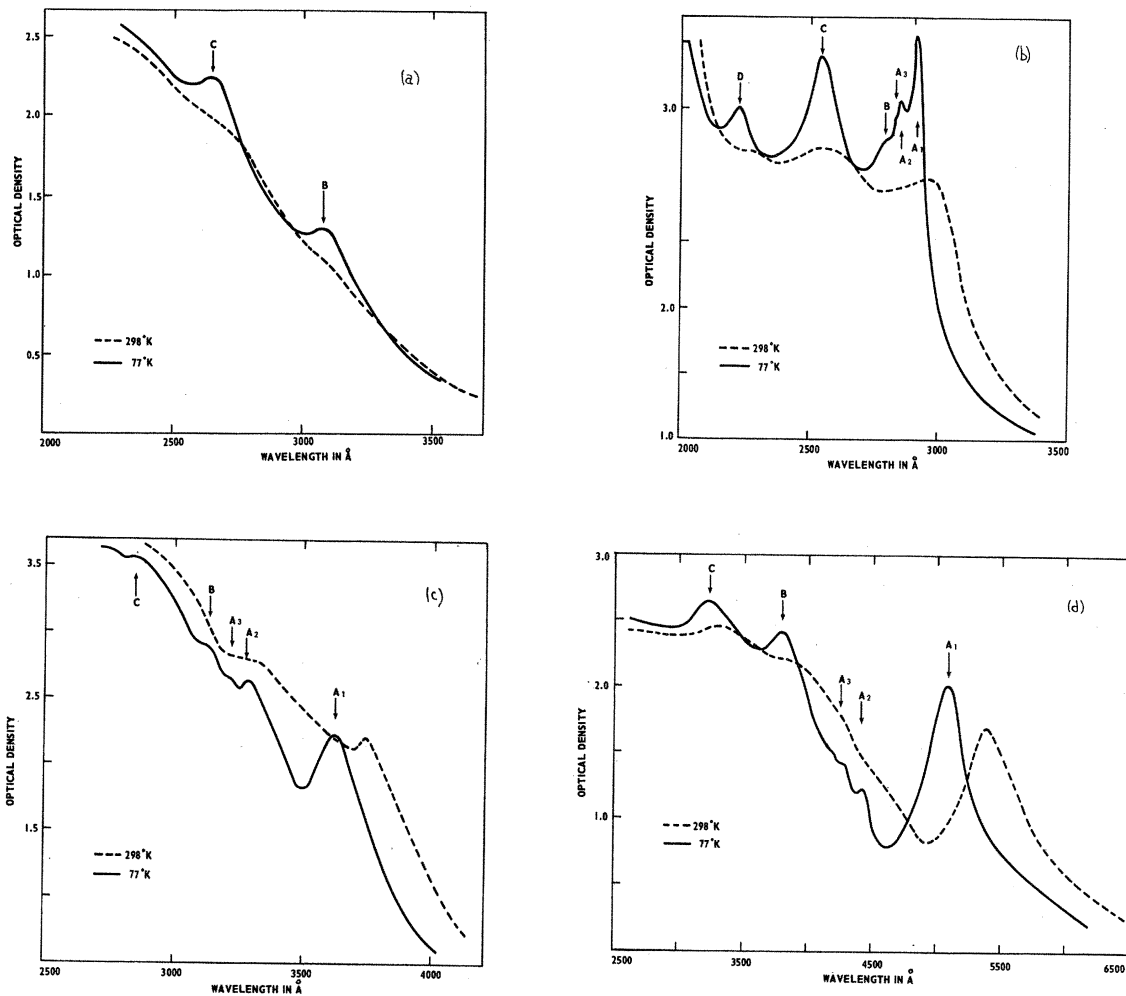
FIG. 1. Absorption spectra of thin films of the mercurous halides deposited on quartz substrates: (a) Hg_2F_2; (b) Hg_2Cl_2; (c) Hg_2Br_2; (d) Hg_2I_2.

shown as dashed lines, those at liquid-nitrogen temperature as continuous lines. In every case the structure in the absorption spectrum becomes more pronounced at lower temperature owing to narrowing of the peaks. Most of the peaks shift to higher energies at lower temperatures. The wavelength positions of the absorption peaks at 77 and 298°K together with the high-frequency dielectric constants and exciton orbital radii are given in Table I. High-frequency dielectric constants (ϵ_0) were computed from the measured values of the refractive index by the relation $\epsilon_0 = n^2$.

The variation of the absorption coefficient with incident photon energy at 77°K is shown in Fig. 2. This follows Urbach's exponential rule[16]

$$\alpha = \alpha_0 \exp[-\sigma(h\nu_0 - h\nu)/kT],$$

with the parameter σ between 0.02 and 0.06. The absorption edges shift to higher energies by 5.0×10^{-5},

7.5×10^{-4}, 6.5×10^{-4}, and 6.0×10^{-4} eV/°K for Hg_2F_2, Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2, respectively.

The oscillator strength of the strongest band A_1 at 77°K was calculated by the method of integral absorption,[2] according to which the oscillator strength is given by the expression

$$f = (nmc^2/\pi N e^2) \int \alpha d\nu,$$

where n is the refractive index value at the frequency of the band, e and m are the charge and mass of the free electron, N is the number of atoms per unit volume, c is the velocity of light, α is the absorption coefficient, and $d\nu$ is the half-width in the absorption. The integral of this equation was solved graphically by plotting absorption coefficient against wave number. Assuming the band A_1 to be symmetrical, the oscillator strengths were found to be 0.09 for Hg_2Cl_2, 0.10 for Hg_2Br_2, and 0.41 for Hg_2I_2. Similar calculation could not be made

TABLE I. Summary of peak positions, exciton orbital radii, and high-frequency dielectric constants (ϵ_0).

Compound	Estimated band gap in eV	Absorption bands	Position in eV at 298°K	Position in eV at 77°K	Exciton orbital radii in Å	High-frequency dielectric constant (ϵ_0)
Hg_2F_2	···	B	···	4.03	···	4.20
		C	···	4.70	···	
Hg_2Cl_2	4.39	$A_1(n=1)$	···	4.26	11	4.80
		$A_2(n=2)$	···	4.35	44	
		$A_3(n=3)$	···	4.37	99	
		B	···	4.39		
		C	4.86	4.88		
		D	5.47	5.57		
Hg_2Br_2	3.91	$A_1(n=1)$	3.31	3.42	24	6.3
		$A_2(n=2)$	3.76	3.78	96	
		$A_3(n=3)$	···	3.85	216	
		B	···	3.91		
Hg_2I_2	2.94	$A_3(n=1)$	2.30	2.43	19	7.3
		$A_2(n=2)$	2.69	2.80	76	
		$A_3(n=3)$	···	2.90	171	
		B	3.26	3.26		
		C	3.76	3.78		

for the other absorption bands A_2, A_3, B, and C because of the uncertainty in determining the background absorption.

B. Photoconduction

Thin films and pressed pellets of mercurous halides exhibit photoconduction when irradiated with light within the fundamental absorption edge. In all cases except Hg_2I_2, the photocurrent was too weak to make detailed spectral measurements. The measurement of the spectral distribution of photocurrent was therefore done only in thin films of Hg_2I_2. All measurements of the photocurrent were made on the sample at room temperature at a partial pressure of dry nitrogen of 0.2 Torr. The dark conductivities of the samples at room temperature were 8.0×10^{-11}, 5×10^{-11}, 2×10^{-8}, and 3.3×10^{-12} Ω^{-1} cm^{-1} for Hg_2F_2, Hg_2Cl_2, Hg_2Br_2, and Hg_2I_2, respectively. Figure 3 shows the spectral distribution of photocurrent in the film of Hg_2I_2 at room temperature. The photocurrent spectrum shows peaks at 2950, 3180, 3900, 4260, 4500, 4700 Å, and a shoulder at 3500 Å. The threshold wavelength for photocurrent occurs at 5500 Å.

The variation in photocurrent with exciting light in-

tensity at wavelengths 4800 and 3800 Å shows that the current is linearly proportional to intensity at 3800 Å and is proportional to the square root of intensity at 4800 Å.

IV. DISCUSSION

The absorption spectra of thin films of mercurous halides show several characteristic absorption peaks. With the exception of Hg_2F_2, the mercurous halides have a strong absorption band (A_1) followed by several other peaks superimposed on the continuous absorption. Since the absorption coefficient in the neighborhood of the first absorption peak A_1 is very high ($\alpha > 10^5$ cm^{-1}) it is assumed that the absorption in this region is due to direct allowed band-to-band transition at the center of the Brillouin zone. The strong temperature dependence of the bands A_1, A_2, and A_3 suggests that these transitions are due to the formation of excitons. The observed structure near the first absorption peak A_1 can be represented by a hydrogenic series according to the equation

$$E_n = E_0 - E_{ex}/n^2,$$

where $n = 1, 2, 3, \cdots$, and E_{ex}, the exciton binding en-

TABLE II. $\partial E(\frac{3}{2}, \frac{1}{2})$ splitting in some metal halides.

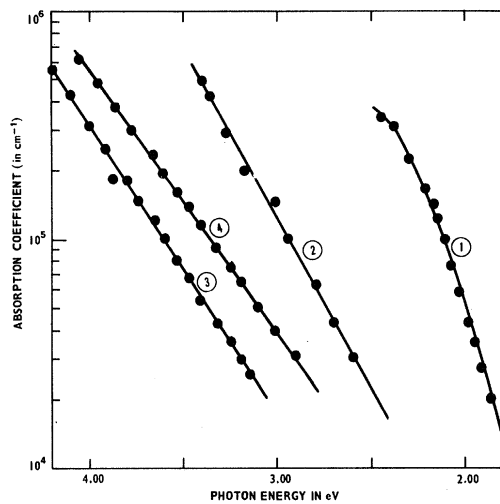|	Chlorides	Bromides	Iodides	Ref.
∂E in eV observed	0.06–0.13	0.30–0.52	0.15–1.17	2, 10, 11
∂E in eV theoretical	0.103	0.432	0.889	17
∂E in eV observed in Hg_2X_2	0.13	0.46	0.84	This work

FIG. 2. Variation of the absorption coefficient with incident photon energy at 77°K: (a) Hg_2I_2; (b) Hg_2Br_2; (c) Hg_2Cl_2; (d) Hg_2F_2.

ergy, is equal to $R\mu/\epsilon_0^2 m$, R is the Rydberg constant, μ is the reduced effective mass of the exciton, and ϵ is the high-frequency dielectric constant. The first strong band A_1 is therefore interpreted as due to the formation of a Mott-Wannier delocalized exciton with $n=1$, and the bands A_2 and A_3 correspond to quantum states $n=2$ and $n=3$, respectively. The observed peaks at 100°K may then be represented by the following equations:

In Hg_2Cl_2, $E_n = 4.39 - 0.13/n^2$ eV,

Hg_2Br_2, $E_n = 3.91 - 0.49/n^2$ eV,

Hg_2I_2, $E_n = 2.94 - 0.51/n^2$ eV $(n = 1, 2,$ and $3)$.

Similar delocalized excitons have been observed in a number of other metal halides.[5–11] The exciton binding energies (0.13–0.51 eV) are comparable to those observed in other metal halides.

The exciton orbital radii r_e were calculated from the formula

$$r_e{}^{(n)} = E_0 m n^2 / 2\mu,$$

where ϵ_0 is the high-frequency dielectric constant, μ is the exciton reduced effective mass, and n is an integer. The results of such calculations at 100°K are given in Table I.

On the high-energy side of the first exciton series (bands A_1, A_2, and A_3), the absorption coefficient increases steadily, and superimposed on it is the absorption maximum B which probably arises from transitions

from a split valence band. It seems reasonable to assume that the valence band in mercurous halides is formed from the np orbitals of the halogen ions and, therefore, should split into two levels $(J = \frac{3}{2}, \frac{1}{2})$ by spin-orbit interactions. The minimum energy separation of this halogen doublet $(\frac{3}{2}, \frac{1}{2})$ has been calculated by Knox and Inchauspé,[17] and the results of their calculation together with the experimentally observed splitting in the absorption spectra of various metal halides are given in Table II. It is apparent from Table II that the energy separations in mercurous halides are close to the theoretical values.

On the higher-energy side of the halogen doublets there are two more absorption peaks, C and D, which are quite pronounced in the chloride and iodide. In the absence of any band-structure calculation, it is difficult to interpret these bands. However, these peaks could be due either to exciton transition at different symmetry points in the Brillouin zone or to Van Hove singularities in the interband density of states. The strong temperature dependence of these bands suggests the formation of excitons. The energy separation of 0.51 eV between the two peaks C and D in Hg_2I_2 could be due to spin-orbit splitting of the valence band.

The spectral distribution of photocurrent shows several maxima which correspond to the absorption peaks. The absence of any photocurrent peak associated with the first exciton peak at A_1 shows that its binding energy (0.64 eV) is so large compared to kT that no appreciable dissociation of the exciton occurs to produce free carriers. Strong photocurrent peaks are observed in the wavelength regions corresponding to exciton transitions involving quantum numbers $n=2$ and 3. The photocurrent in this wavelength region varies as the square root of intensity, indicating that
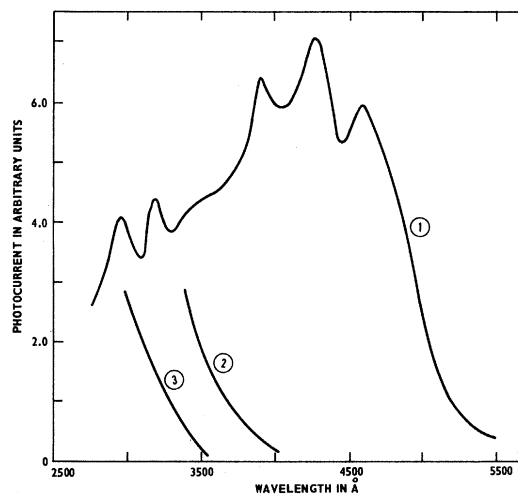

FIG. 3. Spectral distribution of photocurrent in the mercurous halides at 300°K: (1) Hg_2I_2; (2) Hg_2Br_2; (3) Hg_2Cl_2.

the free carriers are produced by the bimolecular dissociation of excitons. The linear dependence of photocurrent on intensity at wavelengths below 3800 Å is perhaps due to direct transitions across the band gap.

[1] J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1966), Vol. 18, p. 55.
[2] S. Nikitine, in *Progress in Semiconductors*, edited by A. F. Gibson (Wiley, New York, 1962), Vol. 6, p. 269.
[3] R. S. Knox, Solid State Phys. Suppl. **5**, (1963).
[4] J. E. Eby, K. J. Teegarden, and D. B. Dutton, Phys. Rev. **116**, 1099 (1959).
[5] K. Teegarden and G. Baldini, Phys. Rev. **155**, 896 (1967).
[6] I. Lefkowitz, R. P. Lowndes, and A. D. Yoffe, J. Phys. Chem. Solids **26**, 1171 (1965).
[7] S. Nikitine, Phil. Mag. **4**, 1 (1959).
[8] M. R. Tubbs and A. J. Forty, J. Phys. Chem. Solids **26**, 711 (1965).

[9] S. Brahms, Phys. Letters **19**, 272 (1965).
[10] B. L. Evans, Proc. Roy. Soc. (London) **A276**, 136 (1963).
[11] B. L. Evans, Proc. Roy. Soc. (London) **A289**, 275 (1965).
[12] N. V. Sidgwick, *Chemical Elements and Their Compounds* (Clarendon Press, Oxford, England, 1962), Vol. I, p. 289.
[13] I. D. Turyanitsa, D. V. Chepur, and B. M. Koperles, Izv. Akad. Nauk SSSR Ser. Fiz.-Mat. **4**, 60 (1961).
[14] G. N. Flannagan, Photo. Sci. Eng. **13**, 335 (1969).
[15] S. K. Deb, Trans. Faraday Soc. **59**, 1614 (1963).
[16] F. Urbach, Phys. Rev. **93**, 1324 (1953).
[17] R. S. Knox and N. Inchauspé, Phys. Rev. **116**, 1093 (1959).

Electromodulation of the Optical Properties of Thallium-Activated Potassium Bromide

U. Giorgianni, V. Grasso, and G. Saitta
Istituto di Fisica dell'Universita' di Messina, Messina, Italy
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The absorption spectrum of KBr:Tl crystals has been investigated using an ac electric field (2×10^4 V/cm, rms). The change of the absorption coefficient, versus photon energy, supports the validity of Henry, Schnatterly, and Slichter's theory concerning the zeroth-moment conservation. It is also shown that the absorption intensity of the B band is supplied, almost entirely, by the A band.

INTRODUCTION

The absorption spectrum associated with the thallium activator has stimulated the interest of many investigators.[1-3] When metal impurity ions with the $(s)^2$ outermost electron configuration, such as Tl^+, In^+, Sn^{++}, etc., are added in an alkali halide, one can observe three absorption bands which are called A, B, and C in order of increasing energy. In KBr:Tl their spectral positions at room temperature are 4.74, 5.55, and 5.87 eV, respectively. Seitz[4] has suggested a model in which he assumed that thallium is present in an alkali halide in the form of monovalent thallous ion, since this form of thallium ion is most stable at the high temperatures at which the crystals are grown. In addition, he assumed that the Tl^+ ion replaces an alkali ion of the lattice, and that the Tl^+ ions are dispersed at random through the lattice when the concentration of Tl^+ in the crystal is small. The C band was attributed to the completely allowed transition $^1S_0 \rightarrow {}^1P_1$ ($^1A_{1g} \rightarrow {}^1T_{1u}$) of high oscillator strength, and the A band to the spin-forbidden transition $^1S_0 \rightarrow {}^3P_1$ ($^1A_{1g} \rightarrow {}^3T_{1u}$), while the B band was attributed to the spin- and symmetry-forbidden transition $^1S_0 \rightarrow {}^3P_2$ ($^1A_{1g} \rightarrow {}^3T_{2u}$) as

supported by the observed temperature dependence of oscillator strength. Yuster and Delbecq[5] found the triplet structure in the C band of potassium iodide–thallium phosphors, attributing such a structure to the vibration-induced removal of the triple degeneracy of the $^1P_1$ state. Since then, several authors[2,6-9] observed the structures in the A and C bands of various alkali halide phosphors, revealing that the C band consists of three components and the A band has the doublet structure. Toyozawa and Inoue[10] have considered the possibility that the dynamical Jahn-Teller effect might be important in the case of Tl^+-type centers, and together with Cho[11] were able to reproduce theoretically the triplet structure of the C band; the calculations were made in the six-dimensional configuration coordinate space on the basis of the classical Frank-Condon approximation.

In previous papers[12,13] we confirmed experimentally both in absorption and emission that the A band shows a triplet structure and we also found an oscillator strength decrease. The present work was undertaken for the purpose of obtaining more information about A-band oscillator strength, extending measurements to B- and C-band spectral regions.