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Effects of Temperature and Hydrostatic Pressure on the Exciton Spectrum of Lead Iodide

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The effects of changes in hydrostatic pressure between 1000 and 3500 atm and temperature changes between 90 and 300 K on the fundamental optical-absorption edge and the first three exciton peaks in lead iodide were studied. Values of the deformation potential for these structures were calculated. Arguments that the excitons are centered about the cation are presented.

Studies of the optical properties of lead iodide have attracted much interest over the past fifteen years. We present here measurements of the effects of hydrostatic pressure and temperature changes on the fundamental absorption edge and the exciton spectrum of lead iodide. It is hoped that from this information, and from the conclusions we draw from it, the nature of the excitons and of the band structure of lead iodide will be better understood.

Samples used in our investigation were thin films ranging in thickness from 700 to 3000 Å which were evaporated onto fused-quartz substrates at a pressure of about 5×10^{-6} Torr and at a rate of about 100 Å/sec. The absorption peaks sharpened significantly upon cooling the sample, indicating that adhesion to the substrate was not a major problem. For the pressure runs the films were placed in the high-pressure cell[1] immediately after their removal from the evaporator. This was done in subdued light to minimize possible photodecomposition of the films. The cell was mounted in the cryostat, pressurized to about 1000 atm, and immediately cooled with liquid nitrogen, reaching an equilibrium temperature of about 90 K. Pressures to 3500 atm could be achieved with this system. The temperature dependence was measured in a cryostat capable of spanning the range from liquid-nitrogen temperature to room temperature in a well-controlled fashion by using a sample holder equipped with a heating coil and a chromel-alumel thermocouple attached near the sample. For both the pressure and the temperature runs three peaks were recorded on a Cary 14 recording spectrophotometer operating at its slowest scan speed, and the average peak maximum for those three runs was recorded. The data were plotted as peak position in electron volts versus pressure in atmospheres, or temperature in degrees kelvin. In each case the data were fitted to a straight line by a least-squares linear-regression analysis.

A typical absorption spectrum showing three prominent exciton peaks[2-4] and the onset of the absorption edge is shown in Fig. 1. The exact peak positions varied somewhat from sample to sample, especially the higher-energy exciton peaks. The lowest-energy peak appeared as a doublet.[5] No systematic variations in the results occurred as a function of film thickness. Sample-to-sample variations in the results were on the order of a few percent, being largest for the 3.32-eV peak, which was the most poorly resolved. Figure 2 shows data for a typical pressure run for the lowest-energy exciton peak. A summary of the results and calculations made from these results appears in Table I. The negative signs indicate a shift to lower energies with increasing temperature or pressure.

Lead iodide belongs to a family of compounds having a hcp layer-type structure. In this structure the layers are composed of planes of lead ions sandwiched between planes of iodide ions. The bonding between the lead and iodine planes is partially ionic, though Dugan and Henisch[8] and Kleim and Raga[9] have reported the ionic character to be

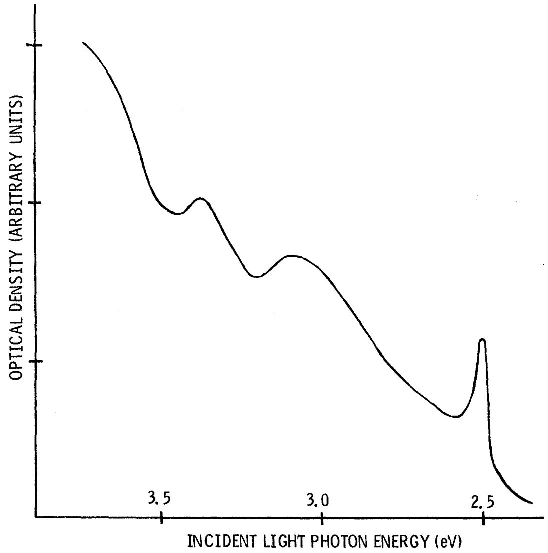

FIG. 1. Typical absorption spectrum of a lead iodide thin film used in these experiments.

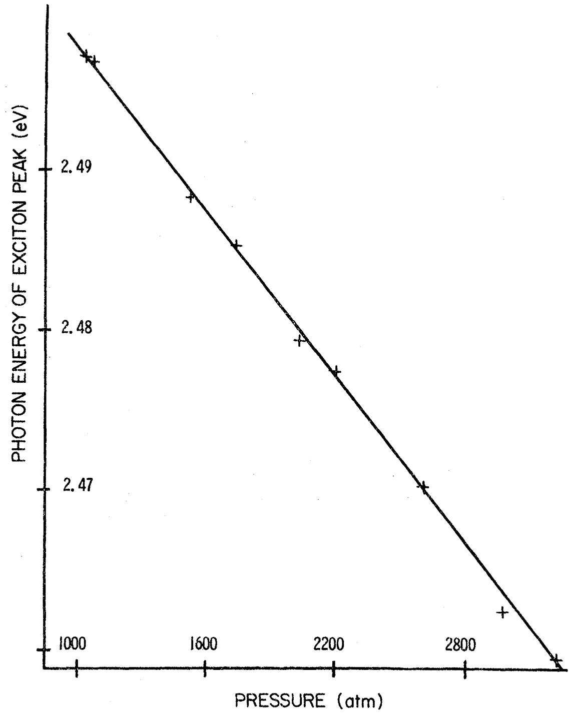

FIG. 2. Typical data for the lowest-energy—exciton-peak shift with pressure.

much less than once thought.

The absorption spectrum of lead iodide in the visible-wavelength region consists of a sharp peak at the fundamental absorption edge, followed by some weak structures that are sample dependent.[2,10] The first peak has been variously classified as a localized exciton,[2] the first of a series of delocalized excitons,[11] and a two-dimensional exciton.[12] Early models for the localized exciton placed it entirely on the iodide ion.[2] Since the iodide ion has a spin-orbit splitting of about 0.8 eV, an exciton is expected at about 0.8 eV higher in energy than the first peak. But this places it on the continuum of the first exciton, which would broaden the spectrum. Higher-energy structure may represent simply peaks in the joint density of states or matrix element, but electroreflectance data[3] indicate that they are excitons, as originally suggested by Tubbs.[2]

Keim and Raga[9] have concluded that the strong peak at 2.5 eV is associated with the band gap. This is substantiated here by the similarity in our values of $(\partial E/\partial T)_V$ for this peak and for the fundamental absorption edge. Our value of $(\partial E/\partial P)_T$ for the lowest-energy exciton peak is in close agreement with that obtained by Zahner and Drickhamer[13] and Grant and Joffe.[14] Grant and Joffe's[14] value of $(\partial E/\partial T)_V$ differs substantially from ours because of their use of Tubbs's[15] value for $(\partial E/\partial T)_P$, which was calculated using the slope obtained from measurements of the peak position at liquid-nitrogen temperature and at room temperature only. The value of the temperature shift of the absorption edge agrees very closely with that of Dugan and Henisch[16] for a single-crystal sample having a comparable absorption coefficient. They point out a moderate dependence on absorption coefficient of the value of $(\partial E/\partial P)_T$ for the edge, which probably accounts for the discrepancy between our results and those of Tubbs.[2] This discrepancy is expected since the edge at low optical density is simply the tail of the exciton and shifts bodily with the peak as the temperature is changed, but also broadens. The broadening contributes to the observed shift of the edge. Our values for $(\partial E/\partial P)_T$ for the edge were taken as far above the onset of absorption as the spectrophotometer could operate to minimize this dependence.

Without an established band structure it is difficult to speculate on these data, except to note that the very small value of $(\partial E/\partial P)_T$ for the 3.32-eV peak may indicate that the transitions are well localized on one of the ions; that is, it has some "charge-transfer" character. The wide variation in $(\partial E/\partial P)_T$ for each of the first three excitons indicated that the interpretation of the optical spectrum of lead iodide as due to two overlapping Wannier exciton series originating from a split upper valence band[17] may not be correct. Harbeke and Tosatti[18] recently concluded that the first two exciton peaks belong to the same Wannier series, which also makes the large variation in their pressure coefficients difficult to explain. Until a detailed exciton model is shown to be appropriate, one cannot correct the measured values of $(\partial E/\partial P)_T$

TABLE I. Summary of results for lead iodide.

Approximate position at 1 atm (eV)	$(\partial E/\partial P)_T$ (10^{-6} eV/atm)	$(\partial E/\partial T)_T$ (10^{-4} eV/atm)	$(\partial E/\partial T)_V$ (10^{-4} eV/atm)	Deformation potential[a] $(-1/\kappa)(\partial E/\partial P)_T$ (eV)
2.51	−17.4	−0.53	−5.5	4.8
3.08	−5.7	...	...	1.5
3.32	−1.3	...	...	0.4
3.6 (edge)	−8.8	−3.1	−5.6	...

[a] The values $\kappa = -3.73\times 10^{-6}$ atm (see Ref. 6) and $\beta = 108\times 10^{-6}$ K (see Ref. 7) were used to calculate this term.

for the effect of pressure on the exciton binding energy, an effect which can be appreciable if $(\partial E/\partial P)_T$ is small. Thus deformation potentials for band gaps cannot yet be determined from our data.

The temperature shifts, measured between 140 and 270 K, were analyzed using the relationship

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\beta}{\kappa}\left(\frac{\partial E}{\partial P}\right)_T ,$$

where E is a transition energy, β is the volume thermal expansion coefficient, and κ is the isothermal compressibility. The temperature shift of an absorption peak or edge arises from two effects—the electron-phonon term, the first term on the right-hand side, and the effect of thermal expansion alone, which is the second term on the right-hand side. Our calculations (see Table I) thus indicate that the observed temperature shift is influenced considerably by electron-phonon interaction for both the lowest-energy exciton peak and the absorption edge.

Preliminary experiments on cadmium iodide have shown the exciton peak at 4.05 eV to have a pressure shift of $+5.5\times10^{-6}$ eV/ atm and the absorption-edge shift to be $+4.8\times10^{-6}$ eV/atm. The difference in the sign of the pressure shift of the lowest-energy exciton peaks in lead iodide and cadmium iodide, as well as the large negative value for $(\partial E/\partial P)_T$ of the lowest-energy exciton peak in lead iodide, supports the theory of the "cationic" character of the excitons in these materials.

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High-Resolution Reflection Spectra of Alkali Halides in the Far Ultraviolet

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The reflectivity spectra of KCl and KBr have been measured at room temperature in the photon energy range 13.5–20.5 eV using a helium discharge source. Care has been taken to ensure high instrumental resolution so that several new structures have been revealed which previously were recorded only at low temperatures. The current interpretation which ascribes them to interband transitions from the valence-band to high-energy conduction-band states has been found to be not completely satisfactory. The possibility of double excitations—a conduction electron plus a surface plasmon—has been analyzed.

I. INTRODUCTION

The optical properties of the alkali halides have been extensively studied up to 12 eV and great progress has been made since the early work of Hilsch and Pohl[1] in 1930. The improvement of the spectroscopic techniques allowed the reflection and absorption spectra of many alkali halides to be measured with great accuracy, high resolution, and at very low temperatures.[2,3] The observed structures