

Temperature and hydrostatic pressure effects on the exciton spectra of some lead and cadmium halides*

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The temperature and pressure shifts of the exciton peaks and positions on the optical absorption edges in thin films of PbBr_2 , PdCl_2 , PbF_2 , CdBr_2 , and CdI_2 in the region from 3.5 to 6.0 eV were measured in the temperature range -150 – 0°C and with hydrostatic pressures to 3500 atm. The electron-phonon contributions of the observed temperature shifts were calculated and found to be larger than the shift due to changing lattice parameters in all cases except CdI_2 . Similarities in the results for PbBr_2 and PbCl_2 suggest an s -like valence band, as is the case for PbI_2 . The cadmium-halide results suggest these two compounds have spectra arising from transitions of a closely related nature. The results indicate that the cationic exciton model is appropriate for these halides.

INTRODUCTION

There is considerable interest in the properties of partially ionic layered crystals. This paper presents some optical properties of the dihalides of cadmium and lead, which crystallize in the structure $X-M-X:X-M-X$, where X represents the halide layers and M the metal layers. These materials are of interest because of their low crystal symmetry and their layered structure, which generally produces "two-dimensional" excitons. They have potential application as photographic emulsions as well. Band-structure calculations are beginning to appear for some of the more stable and well-studied materials. Our study has been carried out to assist in better understanding these materials.

CdI_2 and usually PbI_2 crystallize in a hexagonal-close-packed structure (hcp), whereas PbCl_2 and PbBr_2 have orthorhombic structures. CdBr_2 arranges in the cubic-close-packed CdCl_2 structure. PbF_2 crystallizes in the fluoride structure, which is similar in its symmetry to the hcp structure.

These materials are polytypic. Since the iodide compounds are quite stable and have their fundamental absorption edge at the longest wavelengths, they have been most extensively studied. The typical CdI_2 polytype (4H) is one in which the halogen layer repeat distance is four, contrasted to two for the simple hcp structure. PbI_2 typically is found in the most simple polytype, 2H, or the hcp structure itself. Of the other compounds presented here only CdBr_2 , which has a typical halogen layer repeat distance of six in a rhombohedral structure (6R), has been typed.¹

Thin films of these materials give good polycrystalline diffraction patterns for thicknesses as low as 200 Å in the iodides, with the c axis perpendicular to the substrate. The films exhibit

a strong fundamental absorption edge in the visible or ultraviolet wavelength region, accompanied by several prominent exciton peaks in each case.¹

Paul² has shown that for group IV and III-V semiconductors, the pressure dependence of the interband gaps is governed primarily by the symmetries of the states involved and not by the nature of the atoms comprising the crystal. Evidence exists that this argument may be extended to more ionic materials.³ Thus structures arising from the same symmetry transition would be expected to have similar pressure shifts, whereas those arising from transitions of different symmetry would likely have different pressure coefficients. By measuring both temperature and the pressure shifts of the optical absorption from an interband transition it is possible to determine the portion of the observed temperature shift that is due to electron-phonon interactions. Application of hydrostatic pressure affects primarily only the lattice parameter, while a change in temperature affects the lattice parameter and the phonon vibrational population spectrum. These two effects may be separated by using the thermodynamic relationship

$$(\delta E/\delta T)_P = (\delta E/\delta T)_V - (\gamma/\kappa)(\delta E/\delta P)_T, \quad (1)$$

where γ is the isobaric thermal expansion coefficient and κ the isothermal compressibility. Grant *et al.*⁴ suggest that γ/κ be modified to $(\gamma_{\parallel} + 2\gamma_{\perp})/(\kappa_{\parallel} + 2\kappa_{\perp})$ for layered compounds, where the subscripts indicate directions along and perpendicular to the c axis. However these data are not available for the materials studied here.

EXPERIMENTAL

Thin-film samples were prepared by evaporation from molybdenum boats onto room-tempera-

ture fused quartz substrates at pressures of 1×10^{-5} Torr or less. Sample thicknesses varied from 300 to 3000 Å, but were typically about 600 Å. Thicknesses were determined by an interference technique using a separately prepared substrate held at the same distance from the boat as the sample substrate during evaporations. No determination of the polytype of the films was made. Films were handled in very subdued light after preparation, and tests of each material's stability to light and moisture were made prior to performing experiments on that material. Some films, especially of PbBr_2 , were found to be moisture sensitive, and appropriate precautions were taken with these films to prevent their deterioration while installing them in the cryostat used for the measurements. The spectra sharpened notably upon cooling, indicating that adhesion to the substrate and differential contraction were not problems.

Temperature runs were made using a conventional cryostat equipped with a copper-constantan thermocouple attached near the sample. The sample was mounted on a copper holder separated from the liquid-nitrogen reservoir by a neck wrapped with heating wire. This arrangement allowed the sample to be heated, using a Variac, to temperatures above liquid-nitrogen temperature in a well-controlled manner. Data for temperature shifts were generally taken from about -145 to 0°C . In some cases, when the shift began to deviate from linearity near 0°C , data from the lowest temperature to this point were used in determining the temperature coefficient.

For pressure measurements the sample was placed in a nickel-steel pressure cell equipped with two opposed synthetic sapphire windows held onto unsupported area-type pressure seals with low-temperature varnish.³ A tapered light path through these seals and the retaining nuts external to them allowed a 5-mm-diam light beam from the spectrophotometer to impinge on the sample. The cooled sample could then be subjected to hydrostatic helium gas pressures as high as 3500 atm with this system. To maintain the pressure seal as the sample cooled, the cell was generally pressurized to 1000 atm before cooling. To account for any changes in the spectra due to temperature changes during a pressure run, an equal number of data points were taken at ascending and descending pressures so that the observed shifts could accurately be ascribed to pressure effects.

The spectra were measured by a Cary 14 recording spectrophotometer. This instrument has a wavelength reproducibility of better than 1 Å, or 0.001 eV in the wavelength region encompass-

ing most of the spectra measured. This limitation, and not spectral resolution, was the ultimate experimental limitation in determining wavelength shifts accurately. Resolution affects the width of the exciton peaks and the sharpness of the absorption edges measured, but as we were concerned with small changes in the position of these spectra and not in their shape itself, resolution, as long as it remained at a constant value, did not materially affect our results. Peak positions were determined from the strip charts by bisecting the distance between points at several optical densities near the peak maxima and averaging these values. Positions to within 0.1 Å could generally be determined in this way by running the strip-chart drive at its maximum speed while running the wavelength drive at its slowest. For the edge positions the location of the edge at a given optical density comparable to that of the exciton's peak optical density was generally used. To indicate scatter as well as the linearity of the shifts, typical experimental results are shown in Figs. 1 and 2, measured with temperature and pressure, respectively. Determination of the slopes was made using a least-squares-fit linear-regression program on a programmable calculator.

Figure 3 displays typical absorption spectra for the materials studied. The spectrum for PbI_2 was presented in an earlier paper⁵ and is included here for purposes of comparison and discussion. The arrows shown on some of the spectra indicate the locations where the shifts of the absorption edge in these materials were typically taken both in temperature and pressure runs. (These positions are not always attributable to the absorption edge itself, as will be discussed later, but for ease of discussion they will be referred to as "edge" positions until more properly identified.) The spectra shown also serve to indicate our experimental limitations in optical density and incident photon energy. By using thinner films, the spectra could be extended somewhat to higher photon energies due to the accompanying decrease in optical density, but with an overall loss in the sharpness of the exciton structure. Optical densities ranged up to nearly 4 in pressure runs due to the restricted light path presented by the pressure cell and its cryostat as well as by the absorption coefficients of the samples themselves. Neutral density screens were placed in the reference beam in these instances to bring the optical density to below 2 so that spectra could be recorded. No changes in these screens were made during a given run.

Table I presents the results of our measurements. The value given for the shift with tem-

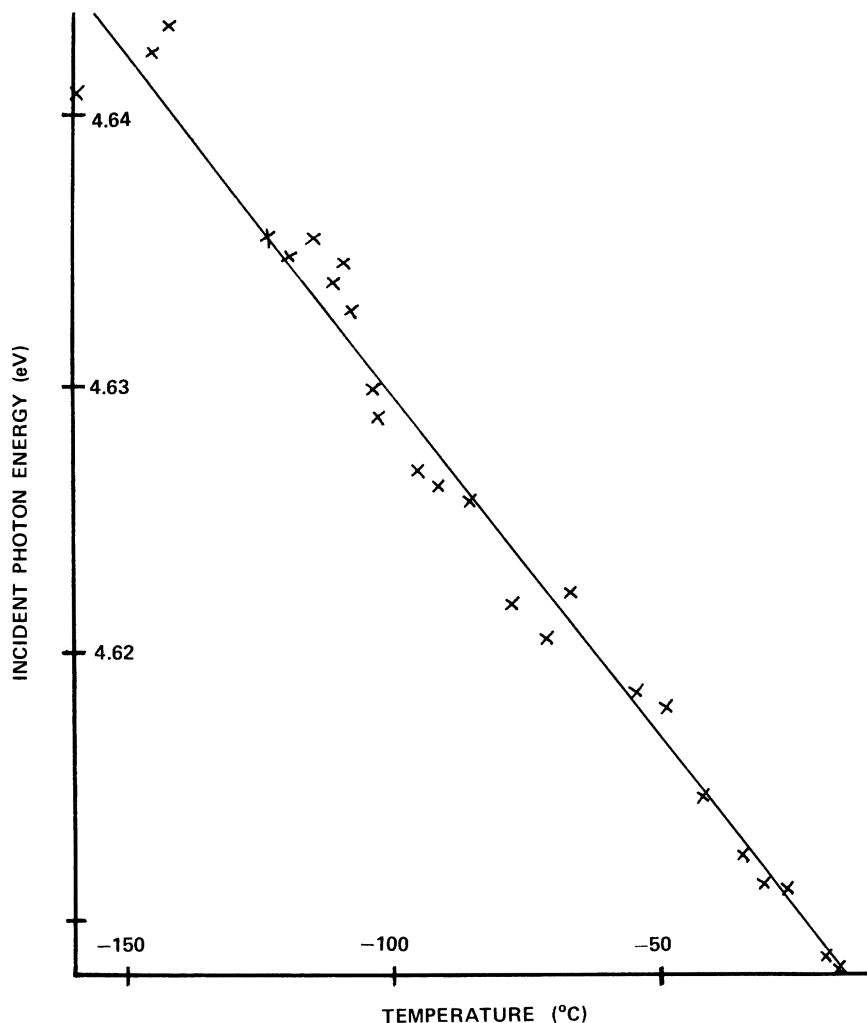


FIG. 1. Shift of the 4.6-eV exciton peak in PbCl_2 with temperature.

perature or pressure was arrived at from data collected from two or more samples of differing thicknesses. The values listed for the temperature and pressure coefficients are averaged values from all runs having acceptable fits to straight lines. The uncertainties listed in these columns include errors from all sources in the analysis of the data and indicate the range in which most values lay. For some materials values for γ and/or κ were not available. In these instances, calculations were made using available values for closely related materials. Negative values for a temperature or pressure coefficient indicate a shift to lower energy with increasing temperature or pressure, respectively. Negative temperature coefficients and positive pressure coefficients are thus typically expected. The value of $(\delta E/\delta T)_V$, the electron-phonon interaction term, is expected to be negative.^{8,9} The deformation potentials listed in the last column of Table I were obtained by converting the pressure

coefficients measured to deformation potentials using the relationship

$$\delta E/\delta(\ln V) = (1/\kappa)(\delta E/\delta P)_T. \quad (2)$$

For comparison, exciton deformation potentials in the cuprous halides range from -0.2 to -1.4 eV.¹⁰

DISCUSSION

Polytypism in layered compounds presents some difficulty in interpretation and comparison of data. For CdI_2 and PbI_2 , the two most extensively studied layered compounds discussed here, over 160 and 20 polytypes, respectively, have been reported.¹¹ Alterations in the optical spectra of thin films due to polytypism have not been systematically studied. For single crystals of PbI_2 variations in exciton peak positions due to polytypism were of the order of 20 \AA .¹² Exciton peak positions in our films did vary somewhat among sam-

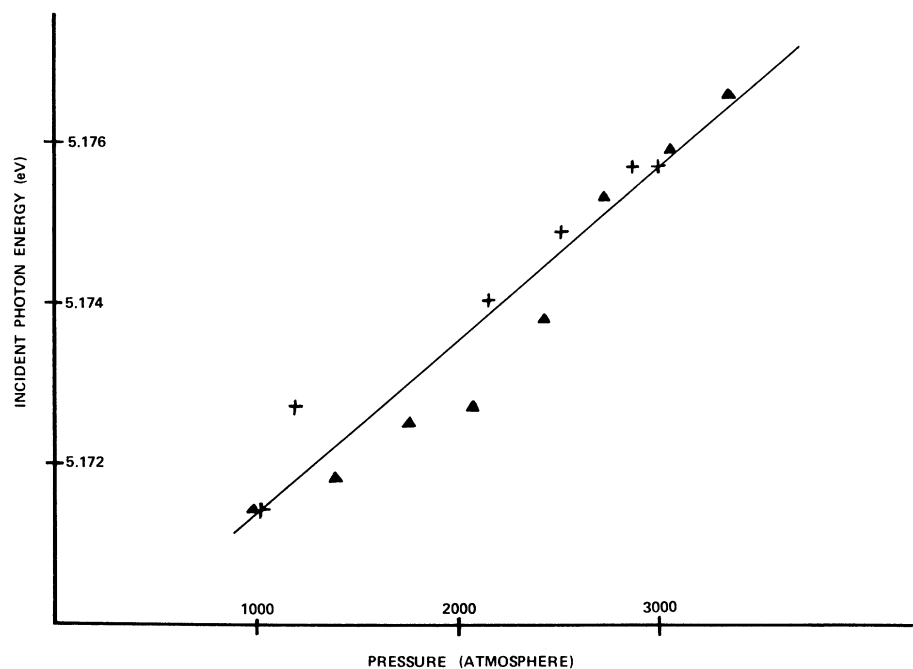


FIG. 2. Shift of the 5.2-eV exciton peak in CdBr_2 with pressure. Triangles are data taken at ascending pressure, crosses at descending pressure.

ples, but since other factors such as film thickness also affect the peak positions we could not ascribe these variations solely to differing polytypes.

In the temperature range we employed, no polytype conversion is expected.¹³ Application of localized stresses to ZnS crystals has induced a conversion to a higher polytype in that material,¹³ but no data are available on the effect of hydrostatic pressure on polytype conversion. Since our data for the pressure coefficients were obtained by cycling the pressure system from low to high, then back to low pressures again, any irreversible change in peak position of the order of 0.1 Å would have been detected. As this is substantially less than variation among polytypes reported above for crystals,¹² no pressure-induced polytype conversions were indicated by our data to 3500 atmospheres.

PbI_2

Since PbI_2 has been studied more extensively than all the other materials discussed in this paper, a summary of the findings for PbI_2 will provide a background and a basis for comparison. Referring to Fig. 3(d), the peaks at 2.5 and 3.4 eV in PbI_2 arise from a spin-orbit splitting of the p level in lead. That is, these peaks arise from $s-p$ transitions. This is the well-established cationic exciton model for PbI_2 . At higher energies a second pair of exciton peaks, caused by the

spin-orbit splitting of the halogen ion, is found.^{1,14,15} These peaks occurred at optical densities too great to be measured in our experiments. The broad peak at 3.1 eV is due to interband transitions. The large pressure shift of the 2.5-eV peak indicates that the valence band in PbI_2 is an admixture of Pb^{2+} states, since states of s -like symmetry shift faster under pressure than do p - or d -like states.² Studies of the absorption edge in PbI_2 indicate that it is direct, and the transition giving rise to the low-energy exciton doublet is well displaced from the Brillouin-zone center, reflecting the s -like symmetry of the valence band.^{1,14,16} Alloying experiments using Pb-CdI_2 crystals and reflectivity data have been interpreted as indicating a $\text{Pb } p$ -like conduction band for PbI_2 .¹⁷ Reliable band-structure calculations explaining the observed absorption spectrum recently have been presented.¹⁸ These indicate that the structure between 2.5 and 4.5 eV arises from transitions from the uppermost valence band to the three lowest-lying conduction bands. Absorption in the region 4.5 to 7.0 eV is due to transitions from the next-highest valence band to these same conduction bands. These transitions, since they arise from a p -like iodine valence band are of a mixed anionic-cationic nature.

PbBr_2

The absorption spectrum shown in Fig. 3(a) corresponds well with those obtained by Plekhanov¹⁵

and Malysheva and Plekhanov¹⁹ from absorption and reflectance measurements. Peaks at 4.0 and 4.8 eV and a weak absorption band at about 4.3 eV were typical features seen in the films. Liidya and Plekhanov²⁰ identify the peaks at 4.0 and 4.8 eV as arising from spin-orbit-split cationic excitons, identical to the PbI_2 case. They suggest that the shoulder at 4.3 eV is due to the second member of a hydrogenic exciton series beginning with the lower energy peak. This suggestion seems feasible from our observations since, even though for two-dimensional excitons the second

member is unusually weak, the low-energy exciton peak in PbBr_2 is exceptionally prominent.

What we describe in Table I as the edge, in reality, is the low-energy side of the third exciton in a series of four observed between 4 and 10 eV.¹⁹ Temperature coefficients for the second peak and the edge were not obtainable. The peak was not sufficiently prominent over a wide enough temperature range to determine its shift. The edge and second peak merged at temperatures above liquid-nitrogen temperature, causing whatever measurement of the edge shift made at a given optical density to be only approximate. Our values for the temperature and pressure shifts of the two peaks in PbBr_2 indicate that a transition quite different in symmetry from the one giving rise to the low-energy exciton pair in PbI_2 is involved here. Because the method for determining the shift of the edge is substantially less accurate than that used to determine peak positions, we cannot attach any great significance to the difference in the values of the pressure shift of the two peaks and the edge. That is, the entire spectrum of PbBr_2 from 4 to 6 eV likely shifts rigidly with pressure, and probably with temperature, indicating that the first three exciton peaks as well as the absorption edge on which they lie are related.

The comparatively small, and positive, pressure shift of the spectrum in PbBr_2 indicates that there is little *s*-like nature to the valence band in PbBr_2 , contrasted to the case of PbI_2 .^{2,10} Malysheva and Plekhanov¹⁹ suggest that the two higher energy exciton peaks may be anionic in nature because their separation of 4.0 eV corresponds to the free-bromine-ion spin-orbit-splitting energy. However, the similarity in the pressure shift of the low-energy side of the lower of these two excitons (lying near where our "edge" measurement was made) with those of the other two cationic excitons does not corroborate this suggestion. Plekhanov¹⁵ suggests that this third exciton in the lead halides arises from the *s* → *p* transition of the cationic exciton, which is more amenable to our results.

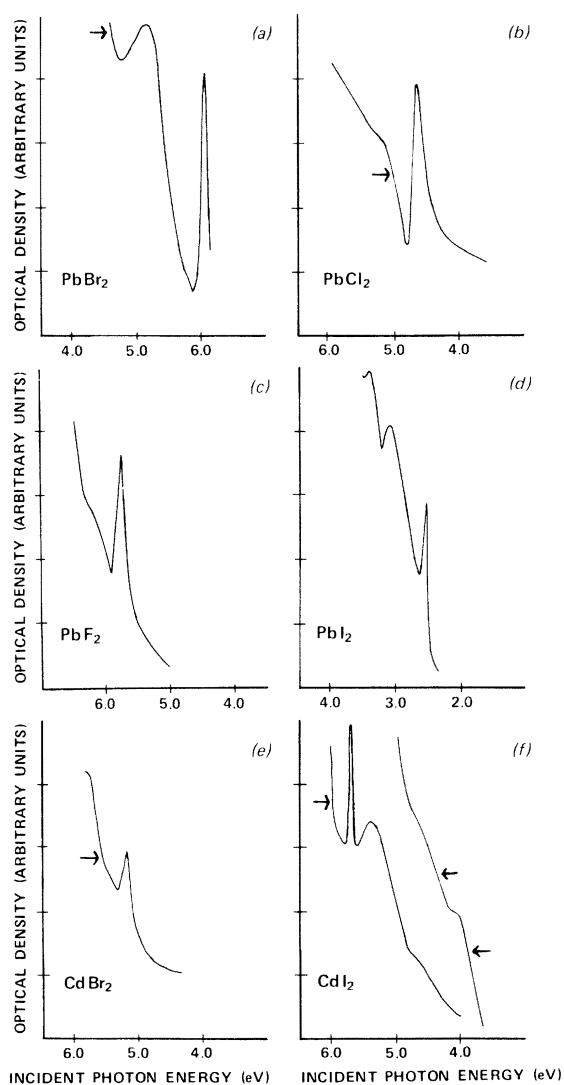


FIG. 3. Typical absorption spectra for the materials studied. Arrows on some spectra indicate locations where temperature and pressure shifts were also measured. The CdI_2 spectrum is a composite from films of differing thickness used to emphasize the various exciton peaks.

PbCl_2

Our PbCl_2 absorption spectrum [Fig. 3(b)] displays a sharp peak at 4.7 eV and a shoulder at about 5.2 eV. The 4.7-eV peak has been established as being due to a cationic exciton.^{20,21,22} The structure at 5.2 eV is also seen by Malysheva and Plekhanov,¹⁹ who attribute it to a splitting of the triplet state of the cationic exciton. Our "edge" is located at the low-energy side of the second exciton peak.^{19,20} The temperature coefficient of the

edge was clearly negative, but as the temperature increased the edge not only shifted, but also changed its slope somewhat, making an accurate determination of its shift impossible. Even had this slope change not occurred, any value taken at this point would be questionable since the optical density at this location is due to contributions from the second exciton peak and the structure at 5.2 eV as well as from the fundamental absorption edge itself. The pressure coefficients are at the extreme lower limit detectable by our equipment, but appear to be essentially zero for both the peak and the edge, that is, for both peaks of the low-energy exciton doublet.

Liidya and Plekhanov²⁰ suggest a band scheme for PbCl₂ that involves direct transitions at Γ for all observed excitons. The *p*-type conduction band, with its accompanying smaller pressure coefficient¹⁶ for this model is supported by our small values for the pressure coefficients.

PbF₂

The absorption spectrum for PbF₂ [Fig. 3(c)] is in good agreement with that of other workers.^{15, 19, 23} Here the first exciton peak occurs at 5.7 eV, with another hint of structure at 6.2 eV, which may again be a second member of a hydrogenic exciton series. The absorption edge above

this shoulder was at too short a wavelength to allow a determination of its temperature and pressure coefficients. The rather small temperature coefficient and large negative pressure coefficient (similar to those for the first exciton in PbI₂) are interesting and indicate that the symmetries of the states giving rise to the exciton and edge in PbF₂ are quite different from those in PbBr₂ and PbCl₂. The large pressure shift indicates that the valence band in PbF₂ may contain a substantial *s*-like component, as in PbI₂.¹⁶

CdBr₂

The absorption spectrum obtained [Fig. 3(e)] exhibits a sharp peak at 5.2 eV, with a hint of structure at 4.9 eV and perhaps at 5.4 eV, which is in general agreement with other spectra.^{1, 24} The pressure shift of the edge, once again, is the shift of the low-energy side of a second well-defined exciton peak that lies at 5.8 eV. If we again use the pressure shift of this edge to characterize roughly the shift of the second exciton peak, we see that the two peaks have approximately the same pressure shift, indicating that they arise from the same transition. A comparison of the combination of the temperature and pressure coefficients of the exciton peak in CdBr₂ with both quantities for the lowest energy exciton peaks

TABLE I. Summary of experimental results.

Sample	Structure ^a	$(\delta E/\delta T)_P$ (10 ⁻⁴ eV/K)	$(\delta E/\delta P)_T$ (10 ⁻⁶ eV/atm)	$(\gamma/\kappa)(\delta E/\delta P)_T$ (10 ⁻⁴ eV/K)	$(\delta E/\delta T)_V$ (10 ⁻⁴ eV/K)	$(1/\kappa)(\delta E/\delta P)_T$ (eV)
PbBr ₂	3.9-eV peak	-3.9 ± 0.3	+0.3 ± 0.2	0.1 ^b	-3.8	+0.9
	4.9-eV peak	< 0	+0.4 ± 0.2	+1.2
	Edge at 5.4 eV	< 0	+0.6 ± 0.2	+1.8
PbCl ₂	4.6-eV peak	-3.6 ± 0.4	0.0 ± 0.2	0.0	-3.6	0.0
	Edge at 5.0 eV	0	0.0 ± 0.2	
PbF ₂	5.7-eV peak	-1.2 ± 0.2	-8.1 ± 0.7	-2.1 ^c	-3.3	-2.4 ^e
PbI ₂	2.5-eV peak	-0.6 ± 0.2	-17.4 ± 0.5	-5.0	-5.6	-2.9
	3.1-eV peak	...	-5.7 ± 0.2	-0.9
	3.4-eV peak	...	-1.3 ± 0.3	-0.2
	Edge at 3.6 eV	-3.1	-7 ± 2	-2.5	-5.6	-1.2
CdBr ₂	5.2-eV peak	-3.0 ± 0.6	+2.0 ± 0.2	0.0 ^d	-3.0	+1 ^f
	Edge at 5.6 eV	-1.0 ± 0.4	+7 ± 1	0.0 ^d	-1.0	+3 ^f
CdI ₂	Edge at 4.0 eV	-4.0 ± 0.4	+5.5	+3.2	+0.2	+3.0
	Edge at 4.4 eV	-2.2 ± 0.2	+4 ± 1	+2.3	> 0	+2.2
	5.7-eV peak	-3.4 ± 0.1	+2.0 ± 0.1	+1.1	-2.3	+1.1
	Edge at 6.0 eV	-1.6 ± 0.2	+2 ± 1	+1.1	-0.4	+1.1

^a Peak positions vary somewhat from sample to sample due to changes in absorption coefficients with thickness and possibly to polytypism of samples.

^b The value of κ for PbCl₂ in Ref. 6 is used here since Zahner and Drickmer (Ref. 7) indicate that it should be similar to that of PbBr₂.

^c Reference 6. γ/κ ratio for PbCl₂ used.

^d Reference 6. γ/κ ratio for CdCl₂ used.

^e Reference 6. κ value for PbCl₂ used.

^f Reference 6. κ value for CdI₂ used.

for the other materials studied here shows a marked difference, again indicating different transitional symmetries.

CdI₂

Much more is known about CdI₂ than about any of the above-mentioned compounds except PbI₂, since its absorption spectrum lies farther into the visible. Figure 3(f) displays a typical CdI₂ absorption spectrum. The peaks at 4.0 eV and especially at 4.6 eV were generally not resolvable and disappeared completely at temperatures between liquid-nitrogen and room temperature. The two spectra in Figure 3(f) are typical of those obtained for CdI₂ films. Since a large range of optical densities was needed to study the complete exciton structure, thinner films were used for the higher energy peaks (left curve), while some thicker ones, (right curve) emphasized the detail near the onset of the absorption edge. Temperature shifts were measured at locations on the low-energy side of the first two poorly resolved peaks (marked by arrows) far enough away from the peak positions to eliminate any anomalous changes in the optical density caused by the peak blending into the spectrum as the temperature rose. Data taken in this manner yielded good fits to linear temperature shifts. Attempts to obtain sharper peaks at 4.0 and 4.6 eV were not successful. Best²⁴ finds that CdI₂ has a crystallization temperature of 335 K, higher than any of the other materials studied here. Annealing CdI₂ films after preparation, or evaporating onto a substrate at temperatures somewhat above crystallization temperature did not improve the definition of these peaks.

Our temperature coefficients for the region near the lowest energy exciton peak are somewhat lower than those reported by Grant *et al.*⁴ and Greenaway and Nitsche,¹⁵ which ranged from -5×10^{-4} to -5.7×10^{-4} eV/K. Our values for the well-resolved third exciton peak at 5.7 eV correspond quite well with other workers, who obtained values from -3×10^{-4} to -3.5×10^{-4} eV/K.^{4,14} Our value for the temperature shift of the highest energy exciton peak at 6.2 eV was determined from its low-energy side, and is somewhat lower than the values of from -4×10^{-4} to -5×10^{-4} eV/K reported by others for the peak.^{4,14} Thus, while our third exciton peak shift agrees well with others' values, using the shift of the low-energy side of an exciton peak or the shift of the absorption edge in this wavelength region seems to give an underestimate of the peak shift for the other peaks. This observation might suggest that the underlying absorption edge itself shifts less than do the exciton peaks

with temperature. However, measurements of shifts at the onset of the edge yield a value of from -12×10^{-4} to -15×10^{-4} eV/K,^{14,25} considerably more than any figure obtained for any of the excitons. The large discrepancy between the temperature shift of the edge itself and the considerably smaller values typically obtained in our work further supports our use of the shifts measured near the peaks as representative of the peak shifts themselves.

Greenaway and Harbeke²⁶ state that the different temperature coefficients of the 5.7- and 6.2-eV exciton peaks indicate that they are not a spin-orbit-split pair, but they do not present their values for these shifts. The similarity of our temperature and pressure shifts for these two peaks indicate, on the other hand, that they are clearly related.

Wright and Tubbs¹⁶ present a band-structure model based on photoconductivity and absorption measurements which suggests that an indirect edge produced by transitions near $k=0$ is responsible for the majority of the structure observed between 4.0 and 6.0 eV. The usual two pair of excitons are suggested, the lower energy halogen doublet at 4.0 and 4.6 eV appearing broadened due to indirect transition to the *s*-like conduction band, and the higher energy doublet at 5.7 and 6.2 eV sharpened due to a high density of states near the minimum of the upper *s*-like conduction band. The valence band is described as an admixture of Cd²⁺ *4d* and I⁻ *5p* states. The absorption hump appearing at 5.3 eV is an interband feature.^{16,26} Unlike those in PbI₂, the excitons in CdI₂ are found to be three-dimensional excitons produced by direct transitions not near $k=0$ in the Brillouin zone.^{1,26}

GENERAL COMMENTS

An examination of the data in Table I elicits several propositions. By comparing the temperature and pressure coefficients for PbBr₂ and PbCl₂ we see that the transitions giving rise to the observed low-energy exciton doublets in these materials are of similar or the same symmetry. This conclusion is especially meaningful as both materials are known to have the same crystal structure. For PbF₂ and PbI₂ such a definite suggestion cannot be made since the crystal structure for PbF₂ has not yet been determined. However it is clear upon examining the temperature and pressure coefficients of these two materials that the transitions producing the exciton peaks in these compounds that are observed in our spectra are quite different in symmetry from those of the other four materials presented in the table. The large negative pressure shift for PbF₂ suggests an *s*-like

valence band, as has been established for PbI_2 , and the similarity in the two coefficients for the two materials at least suggests that a transition involving bands of a similar nature gives rise to the observed excitons in both cases. This suggestion is particularly meaningful considering the similar crystal structures of those two compounds. The cadmium halides again form a pair whose temperature and pressure shifts are distinctly different from the other halides in Table I. Here we have moderate negative temperature shifts and moderate positive pressure shifts. The similarity of $(\delta E/\delta T)_P$ and $(\delta E/\delta P)_T$ for both cadmium salts suggests the influence of the cadmium ion in all of the spectra observed in this work, which is in keeping with a cationic exciton model for CdBr_2 as well as for CdI_2 .

The values of the electron-phonon term $(\delta E/\delta T)_V$ are strikingly similar for all but the iodides. The values for this term are all negative, as expected, and are the larger of the two changes occurring with a change in temperature for all halides studied except CdI_2 . The negative value is usual in ionic compounds.³ We see that for PbBr_2 , PbCl_2 , and CdBr_2 , the observed temperature

shifts are almost wholly due to changes in the phonon population and not in the lattice parameter, whereas for PbF_2 both terms have a significant contribution to the observed temperature shift. In PbI_2 the temperature shift results from the combination of two large terms of opposite sign, with the electron-phonon term again the larger of these two. This is the case for the lower two exciton peaks in CdI_2 also, whereas the two higher energy peaks in CdI_2 have a significantly different value of $(\delta E/\delta T)_V$ due to their smaller pressure shift.

Deformation potentials are often considered to be better for characterizing energy gaps than the pressure coefficient itself, and, while some observations can be made from our values of the deformation potentials, in too many cases the proper compressibilities are not available.

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¹M. R. Tubbs, Phys. Status Solidi B **49**, 11 (1972).

²W. Paul, J. Appl. Phys. **32**, 2082 (1961).

³A. D. Brothers and D. W. Lynch, Phys. Rev. **180**, 911 (1969).

⁴A. J. Grant, J. A. Wilson, and A. D. Yoffe, Philos. Mag. **25**, 625 (1972).

⁵J. B. Anthony and A. D. Brothers, Phys. Rev. B **7**, 1539 (1973).

⁶*Landolt-Bornstein Zahlenwerte und Funktionen*, 6th ed., edited by K. Schäfer and G. Beggerow (Springer, Berlin, 1971), Vol. II, Pt. I.

⁷J. C. Zahner and H. G. Drickmer, Phys. Chem. Solids **11**, 92 (1959).

⁸T. Muto and S. Oyama, Prog. Theor. Phys. **5**, 833 (1950).

⁹H. Y. Fan, Phys. Rev. **82**, 900 (1951).

¹⁰J. B. Anthony, A. D. Brothers, and D. W. Lynch, Phys. Rev. B **5**, 3189 (1972).

¹¹G. C. Trigunayat and G. K. Chadha, Phys. Status Solidi A **4**, 9 (1971).

¹²Ch. Gähwiller and G. Harbeke, Phys. Rev. **185**, 1141 (1969).

¹³G. C. Trigunayat, Phys. Status Solidi A **4**, 281 (1971).

¹⁴M. R. Tubbs, Phys. Chem. Solids **29**, 1191 (1968).

¹⁵V. Plekhanov, Phys. Status Solidi B **57**, K55 (1973).

¹⁶D. K. Wright and M. R. Tubbs, Phys. Status Solidi **37**, 551 (1970).

¹⁷G. Harbeke and E. Tosatti, Phys. Rev. Lett. **28**, 1567 (1972).

¹⁸I. Ch. Schlüter and M. Schlüter, Phys. Rev. B **9**, 1652 (1974).

¹⁹A. F. Malysheva and V. G. Plekhanov, Opt. Spectrosc. **34**, 527 (1973).

²⁰G. G. Liidya and V. G. Plekhanov, Opt. Spectrosc. **32**, 43 (1972).

²¹E. Ilmas, R. Kink, G. Liidya, and A. Malysheva, Trudy Inst. Fiz. Astron. Akad. Nauk. Estonian SSR **26**, 112 (1964).

²²G. Liidya, G. Dobrzanski, and V. Plekhanov, Trudy Inst. Fiz. Astron. Akad. Nauk. Estonian SSR **26**, 64 (1964).

²³A. Malysheva and V. Plekhanov, Eesti NSV Teaduste Akad. Toimetised. 22 Loide Fuusika Matemaatika Nr. 3 (1973).

²⁴K. J. Best, Phys. Kondens. Mater. **1**, 316 (1963).

²⁵D. L. Greenaway and R. Nitsche, Phys. Chem. Solids **26**, 1445 (1965).

²⁶D. L. Greenaway and G. Harbeke, J. Phys. Soc. Jpn. Suppl. **21**, 151 (1966).