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Optical Properties of AgCl, AgBr, TlCl, and TlBr under Hydrostatic Pressure*

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The pressure shifts of the optical absorption edges in four thallium and silver halides at 10°K were determined to be, in units of 10^{-6} eV/atm, -1.5 (AgCl), -1.9 (AgBr), -18 (TlCl), and -16 (TlBr). The pressure shifts of the first exciton peaks in thin evaporated films of these salts were measured at 80°K. In the same units these are 6.2 (AgCl), 6.4 and 5.6 (AgBr doublet), -13.9 (TlCl), and -13.4 (TlBr). The similarity of the pressure coefficients of the absorption edge in the two silver halides is evidence that the same indirect transition is responsible for the edge in both salts, presumably $L_{3'}\rightarrow\Gamma_1$. The deformation potentials for the first direct exciton in the silver halides are approximately the same as those for the corresponding transitions in KBr and KI. The similarity of the pressure coefficients of the absorption edge and exciton peaks in the thallium salts is evidence that the absorption edge in these salts is the tail of the first direct exciton peak. The "anomalous" red shift upon cooling of the absorption edge and exciton peak in the thallium halides is shown to be the effect of thermal contraction.

INTRODUCTION

CONSIDERABLE experimental information has been obtained about the nature of the valence-band maxima and conduction-band minima in AgCl and AgBr.[1] Similar information is becoming available for TlCl. The band structures of AgCl and AgBr have been calculated[2,3] and, as Seitz[4] predicted, the valence bands are complicated because of the mixing of Ag$^+$ $4d$ states with halogen-ion p states. (See Figs. 1 and 2.) Valence-band maxima lie along Σ, along Δ, and at L. The difficulty of choosing a potential and properly treating spin-orbit effects makes theoretical prediction of the ordering of these maxima uncertain. Brown and

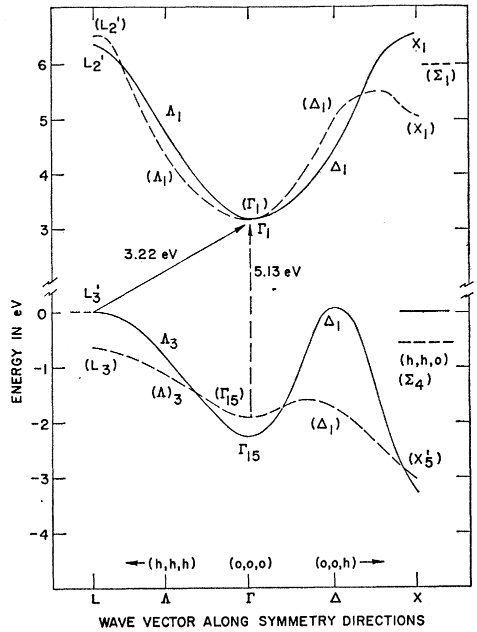

FIG. 1. Calculated band structure of AgCl. Solid lines, Bassani *et al.* (Ref. 2); dashed lines, Scop (Ref. 3). The potentials were adjusted differently in the two calculations. Bassani *et al.* forced the indirect band gap (3.22 eV) to agree with experiment, while Scop required agreement at the direct band gap (5.13 eV). In this figure the two calculated band structures were made to agree at Γ_1. The differences in symmetry notation at L are discussed in Ref. 2.

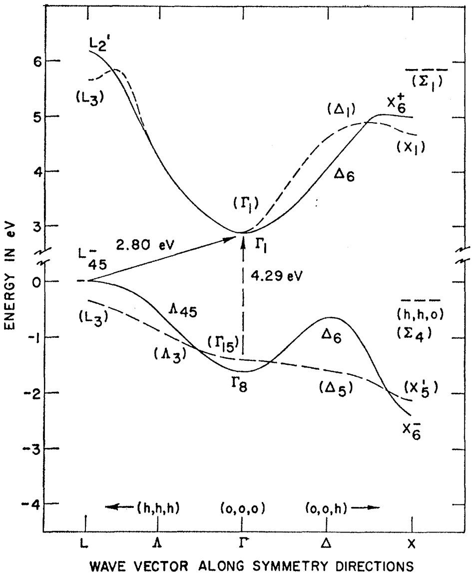

FIG. 2. Calculated band structure of AgBr. Solid lines, Bassani *et al.* (Ref. 2); dashed lines, Scop (Ref. 3). The potentials were adjusted differently in the two calculations. Bassani *et al.* forced the indirect band gap (2.80 eV) to agree with experiment, while Scop required agreement at the direct band gap (4.29 eV). In this figure the two calculated band structures were made to agree at Γ_1. The differences in symmetry notation at L are discussed in Ref. 2.

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* Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 2322.

[1] F. C. Brown, J. Phys. Chem. **66**, 2368 (1962), and several more recent references listed below.

[2] F. Bassani, R. S. Knox, and W. B. Fowler, Phys. Rev. **137**, A1217 (1965).

[3] P. M. Scop, Phys. Rev. **139**, A934 (1965).

[4] F. Seitz, Rev. Mod. Phys. **23**, 328 (1951).

co-workers[1,5,6] have measured carefully the absorption edge as a function of temperature in AgCl and AgBr. In AgCl they find that the edge arises from four indirect transitions, for some of which they determined the energy of the phonon involved. Bassani *et al.*[2] used a rough phonon dispersion curve for AgCl and a symmetry analysis of the phonons to show that two of these transitions probably originate at spin-orbit-split maxima at L and a third from a maximum along Σ. The conduction-band minimum is at Γ in both AgCl and AgBr.[1,7,8] The indirect transitions in AgBr could not be identified with a particular valence-band maximum. Recently, Ascarelli[9] showed that the indirect transition in AgBr arises from a valence-band maximum along Λ, probably at L. He also suggested[10] an alternative interpretation for the absorption edge in AgCl. Between 1 and 2 eV above the absorption edge, there is an exciton peak in AgCl and a pair of peaks in AgBr[11,12] which probably arise from direct transitions at Γ, the splitting in AgBr being due to spin-orbit splitting in the valence band, although this is not completely clear.[2]

The band structures of TlCl and TlBr have not been calculated. The Tl^+ $5d$ levels should lie deep enough so that the valence band arises predominantly from halogen p states or Tl^+ $6s$ states, or both. It should thus be simpler than that in the silver halides. Recent magnetoresistance measurements[13] indicate that the valence-band maximum in TlCl is at Γ, while cyclotron resonance measurements[8,14] show that TlCl has a conduction-band minimum at Γ. Although indirect transitions are unlikely, TlCl and TlBr have long absorption edges,[15] which are in many respects like those of the silver halides. These salts also have exciton peaks at photon energies above the absorption edge.[11,15–17] An unusual feature of the absorption edge and the lowest-energy exciton peaks in TlCl and TlBr is that they shift to lower energy as the crystal is cooled.

A study of the pressure shift of the absorption-edge and exciton peaks in these two pairs of compounds was undertaken for several reasons. Paul[18] has shown that in the group-IV and III-V semiconductors the shifts of interband energy gaps with pressure depend primarily on the symmetries of the states involved, and not on the nature of the atoms in the crystal, as long as the crystal symmetry is constant. [Melz[19] has shown that $a^2(\partial E/\partial \ln V)_T$ is a better parameter than $(\partial E/\partial P)_T$ for characterizing a transition in the above semiconductors, where a is the lattice parameter and V the volume.] The idea that it is primarily the symmetry of the states involved in a transition that causes $(\partial E/\partial P)_T$ to have a particular value probably can be extended to other solids, including more ionic solids, although this has yet to be proved. In AgBr and AgCl we can compare $(\partial E/\partial P)_T$ values for the indirect transitions. If they are nearly the same, as they seem to be, then most of the absorption edge in AgCl probably arises from $L \rightarrow \Gamma$ transitions, since this is the transition giving the absorption edge in AgBr.[9] The direct exciton peaks should have the same values of $(\partial E/\partial P)_T$ in both silver salts, but the values probably should not be the same as those for the indirect band gap. In TlCl and TlBr, where direct transitions are expected, one expects the direct exciton peak and the absorption edge to have very similar values of $(\partial E/\partial P)_T$, although these cannot be compared with those found in the silver halides because the crystal structures differ.

A second reason for measuring pressure coefficients of interband transitions is to determine how much of the temperature coefficients of the transitions arises from thermal expansion and how much from electron-lattice interaction. This can be done by evaluating the terms

$$\left(\frac{\partial E}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_V - \frac{\beta}{K}\left(\frac{\partial E}{\partial P}\right)_T. \qquad (1)$$

β is the volume isobaric thermal-expansion coefficient and K the isothermal compressibility. The first term on the right arises from the electron-lattice interaction, and is the only part of Eq. (1) that cannot be measured directly. The second term on the right is the part of the temperature coefficient of the energy level or energy gap E that arises from thermal expansion. It is of particular interest to evaluate Eq. (1) for TlCl and TlBr, because $(\partial E/\partial T)_V$ is expected to be negative,[20,21] while $(\partial E/\partial T)_p$ is measured to be positive.[15] $(\partial E/\partial P)_T$ can have either sign. Finally, measurements of $(\partial E/\partial P)_T$ are useful for future comparison of the results of band-structure calculations.

EXPERIMENTAL

A hydrostatic pressure system using He gas as the pressure fluid supplied pressures of up to 3500 atm to the pressure cell. The cell used unsupported area

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[5] F. C. Brown, T. Masumi, and H. H. Tippins, J. Phys. Chem. Solids **22**, 101 (1961).

[6] B. L. Joesten and F. C. Brown, Phys. Rev. **148**, 919 (1966).

[7] G. Ascarelli and F. C. Brown, Phys. Rev. Letters **9**, 209 (1962).

[8] J. W. Hodby, J. A. Borders, F. C. Brown, and S. Foner, Phys. Rev. Letters **19**, 952 (1967).

[9] G. Ascarelli, Phys. Rev. Letters **20**, 44 (1968).

[10] G. Ascarelli, Phys. Letters **26A**, 269 (1968).

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[13] Y. Makita, K. Kobayashi, and M. Kanada, J. Phys. Soc. Japan **23**, 1180 (1967).

[14] H. Tamara and T. Masumi, J. Phys. Soc. Japan **23**, 1173 (1967).

[15] H. Zinngrebe, Z. Physik **154**, 495 (1959).

[16] S. Tutihasi, J. Phys. Chem. Solids **12**, 344 (1960).

[17] I. Lefkowitz, R. P. Lowndes, and A. D. Jaffe, J. Phys. Chem. Solids **26**, 1171 (1965).

[18] W. Paul, J. Appl. Phys. **32**, 2082 (1961).

[19] P. J. Melz, J. Phys. Chem. Solids **28**, 1441 (1967).

[20] T. Muto and S. Oyama, Progr. Theoret. Phys. (Kyoto) **5**, 833 (1950).

[21] H. Y. Fan, Phys. Rev. **82**, 900 (1951).

pressure seals, with the optical path provided by sapphire windows varnished to the sealing plugs with General Electric 7031 low-temperature varnish.[22] The cell was housed in a cryostat.

When liquid He was transferred into the inner chamber of the cryostat, the cell reached a temperature of 10°K in less than an hour. Because He is a solid at 10°K and 3000 atm, the cell was warmed to 30–40°K to melt the He, then recooled to 10°K by a second liquid-He transfer after the pressure in the cell had been changed. The exciton spectra in the thin films were sufficiently sharp at 80°K, so that liquid-helium temperatures were required only for the single-crystal absorption-edge measurements, for which it was necessary to remove the phonon absorption component to obtain a well-defined edge.

The single-crystal silver halides were obtained from Dr. Van Heyningen of the Eastman Kodak Research Laboratory. These yielded spectra in excellent agreement with other data.[5] AgBr from commercial sources had additional temperature-independent broad structure on the absorption edge. The thallium-halide single crystals were obtained from the Harshaw Chemical Company.

In preliminary tests, thin films of AgCl and TlCl were evaporated onto various substrates: sapphire, quartz, NaCl, and LiF. Upon cooling to 80°K, a sharp exciton peak was found only in films on quartz. Differential contraction badly strained the films on the other substrates, while the films apparently did not adhere strongly enough to the quartz to be strained when the films were cooled. All thin-film data reported for both silver and thallium halides were taken on films made by evaporating reagent-grade salts onto quartz substrates. Films closest to 1000 Å thickness were generally used. The film thicknesses were measured with a Varian multiple-beam interferometer.

Since all the halides studied are light-sensitive to varying degrees, handling of the crystals and films was done under light from Kodak Wratten 1A filters. The films of AgBr deteriorated somewhat upon storage.

The spectra were measured on a Cary 14R spectrophotometer. The slowest possible scan speed and the fastest chart speed were used to maximize the readout accuracy. Typical resolution for the thin films was 4 Å, while in all cases the resolution obtained when the pressure and temperature shifts of the absorption edges were measured was better than 4 Å. Background optical densities were high, due to the high refractive indices of the samples and the constricted optical path through the pressure cell.

The temperature shifts of the absorption edges in the thallium-halide single crystals and thin films were measured in a cryostat with a helium exchange gas chamber surrounding the sample. A gold (0.03% iron) versus copper thermocouple was used to determine the temperature of the sample.[23]

RESULTS

Pressure Dependence of Single-Crystal Absorption Edges

Figure 3 displays the results obtained when the absorption edge of a crystal of AgBr was measured at 10°K at two pressures. α is the absorption coefficient. For α greater than 4.5 cm^{-1}, the points lie on a straight line which connects them to the zero absorption points when extrapolated. The portions of the spectra above these extrapolated lines are redrawn along the baseline of the graph. The horizontal distance between the two straight lines gives the pressure shift of the onset of the crystal's absorption edge, -1.9×10^{-6} eV/atm, the negative sign indicating a shift to lower energy with increasing pressure.

The data in Fig. 4 display the shape of the AgCl absorption edge at two pressures. The pressure shift was found to be -1.5×10^{-6} eV/atm at the onset of the absorption edge. Note that here, rather than an enhancement of the edge over a straight line extrapolated from the high absorption coefficient, there is a marked dropoff near the beginning of the absorption edge.

The data in Figs. 3 and 4 were compared with those of Brown *et al.*[1,5,6] who have studied extensively the optical absorption of these salts. Brown plotted curves obtained from the spectra of several crystals of widely varied thicknesses, so that the present data correspond to only the lower values of $(\alpha h\nu)^{1/2}$ which he plots. The spectrum for the AgBr absorption edge at 4.2°K from Brown (Ref. 1, Fig. 8, p. 2372) and the spectrum from the present work (Fig. 3, 0 atm) were compared graphi-

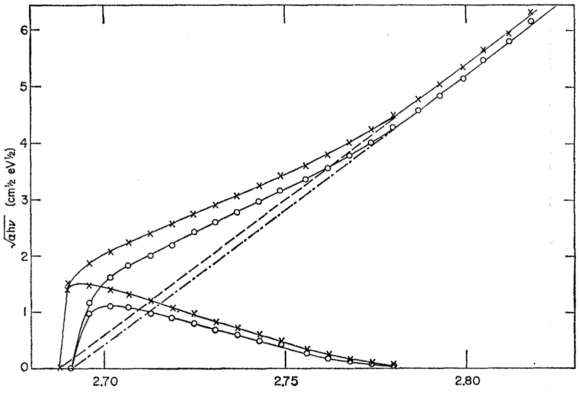

FIG. 3. Absorption edge of a single crystal of AgBr at 10°K. ○, zero atm; ×, 2100 atm. The lower curves are the result of subtracting the extrapolated straight lines from the actual edges.

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[22] D. B. Fitchen, Rev. Sci. Instr. 34, 673 (1963).

[23] D. K. Finnemore, J. E. Ostenson, and T. F. Stromberg, Rev. Sci. Instr. 36, 1369 (1965).

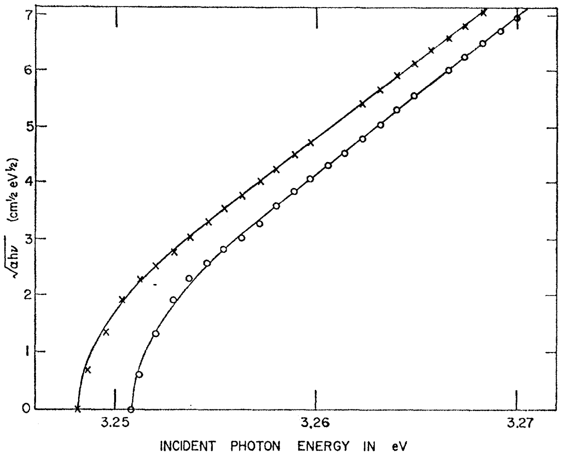

FIG. 4. Absorption edge of a single crystal of AgCl at 10°C. ○, zero atm; ×, 1830 atm.

cally. The values obtained for the onset of the absorption edge were 2.690 and 2.688 eV, respectively. This difference of 0.002 eV was the maximum discrepancy between the two spectra at any point.

When the curve in Fig. 4 (0 atm) was compared to that of Brown *et al.* (Ref. 1, Fig. 9, p. 2373) for the AgCl absorption edge, it was found to possess the same general shape and slope. Although the curve from this work lay generally 0.004 eV to lower energies than Brown's curve at 4.2°K, part of this small discrepancy is attributable to the higher temperature of the sample in this experiment, 10°K. Brown also detected, at optical densities less than 0.01 in a 2.08-mm-thick crystal, a nearly horizontal foot extending about 0.005 eV to lower energy on the absorption edge. This was not seen in this work because of the very small absorption level, as well as the somewhat poorer resolution than Brown had.

The two spectra for TlBr (Fig. 5) appear more like those for AgBr than those for TlCl. The value of the pressure shift of the onset of the absorption edge was found to be -18×10^{-6} eV/atm. An enhancement of the extrapolated line found here is of the general shape of that found for AgBr but smaller.

Figure 6 shows the absorption edge for a single crystal of TlCl at two pressures. The value of the pressure shift of the absorption edge as measured at the onset of absorption is -16×10^{-6} eV/atm. The shoulders near the beginning of the edges do not appear to be similar to those in TlBr and AgBr. A straight-line extrapolation from high α falls to the high-energy side of the horizontal intercept of the curves rather than nearly through the data points at the horizontal intercepts.

In Fig. 7, a comparison of the absorption edges of the four single-crystal samples is made. The plots are the zero-atmosphere runs of the four preceding figures, whose horizontal intercepts have been shifted such that all the absorption edges begin at the incident photon energy E_0. The slopes are more characteristic of the halogen ion than of the cation, crystal structure, or type of transition, at least in the limited range of α plotted.

Plots of $(\alpha h\nu)^{1/2}$ versus $h\nu$ should exhibit characteristic structure,[24,25] including straight line segments if the lowest-energy interband transition is an indirect (phonon-assisted) symmetry-allowed transition, as seems to be the case in the silver halides.[1,5] Plots were made of $(\alpha h\nu)^n$ versus $h\nu$, where $n=\frac{1}{3}, \frac{2}{3}, 2$, corresponding to indirect-forbidden, direct-forbidden, and direct-allowed transitions, respectively, as well as α versus $h\nu$, but none exhibited as straight a section as the plots

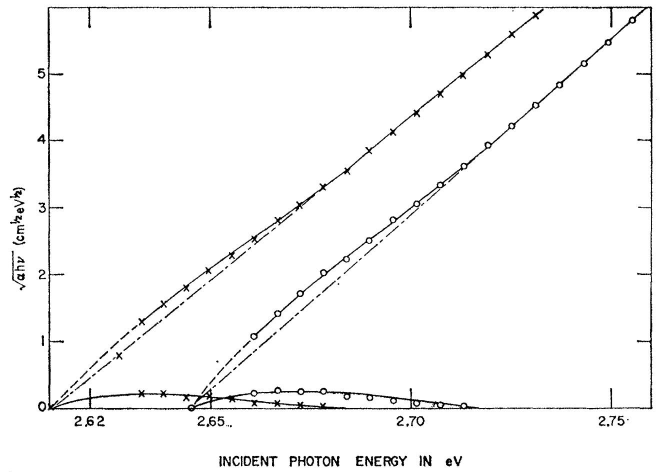

FIG. 5. Absorption edge of a single crystal of TlBr at 10°K. ○, zero atm; ×, 1890 atm. The lower curves are a result of subtracting the extrapolated straight lines from the actual edges.

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[24] See, for example, T. P. McLean, in *Polarons and Excitons,* edited by C. G. Kuper and G. D. Whitfield (Plenum Press, Inc., New York, 1962) p. 367.

[25] R. J. Elliot, Phys. Rev. **108**, 1384 (1957).

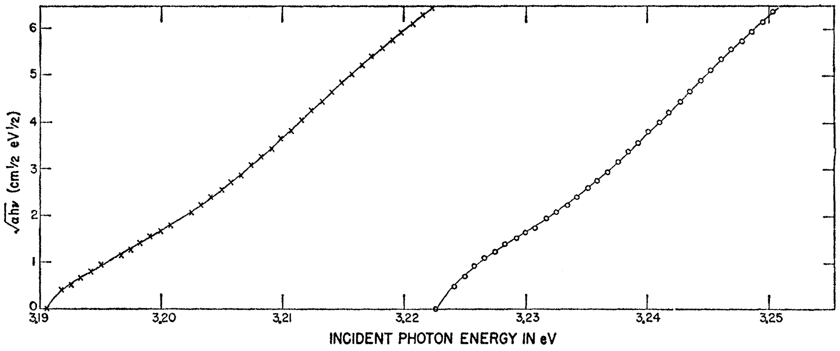

FIG. 6. Absorption edge of a single crystal of TlCl at 10°K. ○, zero atm; ×, 1970 atm.

TABLE I. Pressure and temperature derivatives of absorption edge and first-exciton peak.

Quantity	Units	AgCl	AgBr	TlCl	TlBr
$(\partial E/\partial P)_T$, absorption edge	10^{-6} eV/atm	-1.5	-1.9	-18	-16
$(\partial E/\partial P)_T$, exciton peak	10^{-6} eV/atm	6.2	6.4 5.6	-13.9	-13.4
$(\partial E/\partial T)_P$, absorption edge	10^{-4} eV/K°	-8.7[a]	-7.8[a]	...	...
$(\partial E/\partial T)_P$, exciton peak	10^{-4} eV/K°	...	...	0–1	0–1
Exciton peak position at 80°K, 1 atmosphere[b]	eV	5.138	4.292 4.786	3.468	3.073

[a] Figs. 6 and 7 of Ref. 1.

[b] These values are approximate. The peak positions cannot be obtained without careful subtraction of background absorption, even in the thallium salts where little background absorption is expected. In this work we found that the positions of the peaks in the data depended on the thickness of the films. Moreover, differences between positions of exciton peaks in thin films and in thin slices of single crystals have been found (Ref. 17).

displayed in Figs. 3–6. Another possibility for the functional dependence of the ordinate was suggested by Urbach.[26] According to Urbach's rule,[27] the optical absorption increases exponentially with energy near the absorption edge. The data comprising Figs. 5 and 6 were plotted in this manner and fit a straight line well. The pressure shifts, as determined from the horizontal displacement of these lines with pressure, were essentially the same for TlCl and for TlBr as for those obtained from the $\alpha h\nu$ plots.

Pressure Shifts of Exciton Peaks

Two exciton peaks were observed in AgBr films and one each in films of AgCl, TlCl, and TlBr, all at 80°K. At room temperature no peaks could be resolved. Plots of the photon energy at the peak versus pressure were straight lines whose slopes are reported in Table I, along with $(\partial E/\partial P)_T$ values for the absorption edges in these compounds.

Temperature Dependence of Absorption Edges and Exciton Peaks

Brown and co-workers[1,5] have measured the temperature dependence of the indirect energy gap in AgCl and AgBr. At high temperatures, $(\partial E/\partial T)_p$ becomes constant, and these constant values are reported in Table I. Attempts to determine $(\partial E/\partial T)_p$ for the exciton peak in AgCl were not successful. There was little shift (~0.02 eV) between 4 and 80°K, while above 80°K the peak was too poorly resolved even to allow us to see if E versus T was linear. We estimate, on the basis of 60–80°K data, that $(\partial E/\partial T)_P = (-6\pm 2) \times 10^{-4}$ eV(K°)$^{-1}$ for the AgCl exciton peak, but because of the large uncertainty this is not reported in Table I.

The exciton peaks in TlCl and TlBr were measured over the temperature range 4.2–300°K. Above about

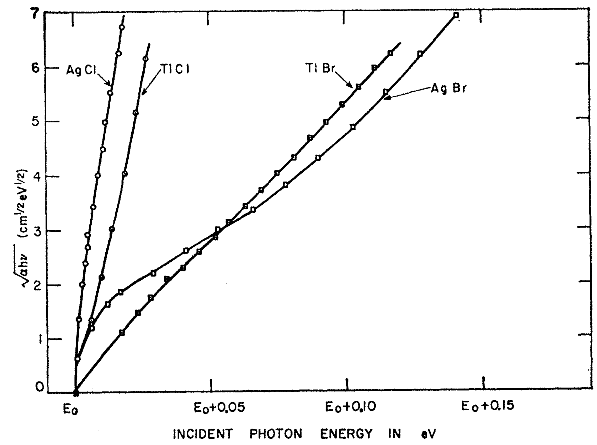

FIG. 7. Comparison of the absorption edges at 10°K of single crystals of AgCl, AgBr, TlCl, and TlBr. The curves have been shifted horizontally to have a common origin.

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[26] F. Urbach, Phys. Rev. 92, 1324 (1953).

[27] For a list of references relating to Urbach's rule fits in various crystals, see T. Tomiki, J. Phys. Soc. Japan 23, 1280 (1967), and references therein.

100°K, $(\partial E/\partial T)_P$ was positive but no linear region could be ascertained, partly because at higher temperatures the errors in locating the peak became large. We estimate that $(\partial E/\partial T)_P$ at high temperatures is positive, but not larger than 1×10^{-4} eV/K° in both thallium salts. At temperatures below 100°K the peak seems to shift toward higher energies. This unusual reversal in sign of $(\partial E/\partial T)_P$ was first noticed by Zinngrebe.[15] It may not be a genuine effect, for it may originate from strains in the films. The temperature dependences of the absorption edges of TlCl and TlBr single crystals were measured also, with results similar to those of Zinngrebe,[15] but as we shall show later these cannot be interpreted and thus not listed.

DISCUSSION

The spectra in Fig. 3, then, may be interpreted as follows. The onset of the indirect absorption edge is at $E_G-B+k\theta$. B is the indirect exciton binding energy and $k\theta$ is a phonon energy. (The phonon absorption term is negligible at 10°K). The enhancement of the edge due to the electron-hole Coulomb interaction extends to energies higher than the onset of the edge by several times B, the exciton binding energy.[25] The region of enhancement of the absorption will be pressure-dependent. It is reasonable to describe the indirect excitons in silver halides as Wannier excitons. The $n=1$ exciton has

$$B=\frac{1\ \mathrm{Ry}}{\epsilon^2}\left(\frac{\mu^*}{m_0}\right), \tag{2}$$

where ϵ is a dielectric constant, μ^* a reduced effective mass, and m_0 the free-electron mass. ϵ may range from the optical dielectric constant to the static dielectric constant.[28] For small μ^* and large static dielectric constant, the static dielectric constant is more appropriate. From Jones's work,[29] it is known that the dielectric constant decreases with increasing pressure. Assuming a Wannier exciton, $B(P)$ is proportional to $\epsilon(P)^{-2}$. This means that the exciton binding energy increases with increasing pressure. For the pressure range given in Fig. 3, this increase would be about 5%. The measured increase of the energy range where the absorption is enhanced is about 4%. The use of $\mu^*/m_0=0.5$ for AgCl and 0.3 for AgBr gives $B=0.045$ and 0.027 eV, respectively. The straight lines should intersect the axis 0.045 eV above the onset of absorption in Fig. 3 (or 0.023 eV [10]), but this doesn't seem to be the case. The explanation is probably found in the limited accuracy of the data at higher α values, making extrapolation difficult, and limited accuracy at very small values of α, as well.

The AgCl absorption edges displayed in Fig. 4 do not exhibit the same enhancement that the AgBr curves exhibit. The reason for this is probably the complexity of the AgCl edge compared to the AgBr edge. Brown *et al.*[1,5] have observed four humps near the onset of the absorption edge in AgCl, generally only 0.02–0.03 eV apart. Bassani *et al.*[2] feel that these are due to several transitions from L and possibly a transition from Σ ("several" because of spin-orbit effects not considered in Figs. 1 and 2). Each of these transitions would have a spectrum similar to that seen in the AgBr edge, but a combination of the four spectra, displaced only a few hundredths of an eV from one another, could produce edges which look like those in Fig. 4 (but see also Ref. 10).

The fact that $(\partial E/\partial P)_T$ is about the same for the absorption edge in AgCl and AgBr strongly suggests that the symmetry of the transition is the same in both salts. Since Ascarelli's data[9] on AgBr show that the valence-band maxima are along Λ, and both band-structure calculations yield maxima along Λ at L, the same $L-\Gamma$ transition seems to be responsible for the very *onset* of the edge in AgCl too.

The exciton peak in AgCl and both exciton peaks in AgBr all have about the same value of $(\partial E/\partial P)_T$, again strongly suggesting that the transitions all have the same symmetry, presumably $\Gamma_{15}-\Gamma_1$, with spin-orbit splitting in the valence band accounting for the doublet in AgBr. To get the shift of the band gap at Γ, we must correct for the pressure dependence of the direct exciton binding energy. Presumably a Wannier model can be used (although $n=2$ direct excitons haven't been detected), but now the effective mass of the hole will be different from its value in the indirect exciton. (Polaron effects[9] may be also different.) The altered reduced mass may make a dielectric constant smaller than the static one more appropriate, but we use the static value, because the pressure dependence of an effective dielectric constant is not a clear-cut concept. We used 0.5 for μ^*/m_0 in both AgCl and AgBr. This gives $B=0.045$ eV in both crystals, which places the interband gap at the center of the dip on the high-energy side of the exciton peak. By using Jones's values for the pressure dependence of the static dielectric constant, we get $(\partial B/\partial P)_T$. Using this with the exciton peak pressure coefficient, we find $\partial E/\partial P=5.1\times10^{-6}$ eV/atm and $(-4.5\text{ to }5.3)\times10^{-6}$ eV/atm for the $\Gamma_{15}-\Gamma_1$ gap in AgCl and AgBr, respectively. This interpretation of the experimental result assumes no dynamic screening effects of the type discussed by Fowler.[30]

The results of Slykhouse and Drickamer[31] may be interpreted in the light of the data taken in this work. They measured the pressure shift of the absorption edge in the silver halides to very high pressures. In the pressure range used in this work, their values for

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[28] H. Haken, J. Phys. Chem. Solids **8**, 166 (1959).

[29] B. W. Jones, Phil. Mag. **16**, 1085 (1967).

[30] W. B. Fowler, Phys. Rev. **151**, 657 (1966).

[31] T. E. Slykhouse and H. G. Drickamer, J. Phys. Chem. Solids **7**, 207 (1958).

the edge shifts were -3×10^{-7} eV/atm and -8×10^{-7} eV/atm for AgBr and AgCl, respectively. These values are both only a fraction of the values of the shifts observed in this work at the onset of the absorption edge, but this can be readily explained, since their measurements were not made at the onset of the edge. The further into the absorption edge the measurements are made, the more effect the pressure shift of the low-energy tail of the direct exciton, which is of opposite sign, will have on the net pressure shift of the edge.

The data for the thallium salts are also enlightening. The large negative pressure shifts of the absorption edges are close to the large negative pressure shifts of the exciton peaks (Table I). It is reasonable to conclude from this information that the absorption edge measured in the single crystals is the low absorption coefficient tail of the exciton band seen in the thin films.

In this case, the plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ is not justified theoretically, but the Urbach-rule plot, appropriate for alkali-halide absorption edges[27] of the type ascribed to TlCl and TlBr, gives the same value of $(\partial E/\partial P)_T$ for the absorption edges. By applying corrections for the pressure dependence of the exciton binding energy, using the Wannier model with $\mu^*/m_0=0.5$ and Samara's[32] values for the pressure dependence of the static dielectric constant, we obtain direct interband-gap pressure shifts that nearly coincide with the exciton peak shifts. The assumption that the Wannier exciton model can be used here is even more justifiable than its use for the silver salts, since the dielectric constants for the thallium salts are much larger.

The pressure shift of the exciton peak does not agree exactly with that of the onset of the absorption edge for both thallium halides. It is likely that pressure affects the half-width of the exciton band slightly, so that a point many halfwidths below the peak, namely, near the onset of the absorption edge in single crystals, would be likely to have a slightly different pressure shift than the exciton peak.

The pressure shifts which Zahner and Drickamer[33] obtain for the thallium halides are both about -15×10^{-6} eV/atm for pressures below 5000 atm. This is quite close to the values obtained in this work, which is reasonable since the edge seen in single crystals is a simple direct edge. The pressure shift of the edge should be essentially the same at any point on the edge.

The slope of the absorption edge in TlCl and TlBr shifts rapidly with increasing temperature, a consequence of the increased thermal broadening of the direct exciton. Zinngrebe[15] has carefully studied this effect in TlCl. He found that at temperatures above 150°K, the onset of the absorption edge shifts rapidly to longer wavelengths, while the exciton peak as measured in thin films shifts to the red at a much slower rate. He suggested that the much greater temperature shift of the edge is due to higher-temperature transitions occurring near the foot of the absorption edge, but it is more likely that the shift is a combination of the shift of the exciton peak and the broadening of the peak. We do not report our measurements of the absorption edge in TlCl and TlBr because they cannot give us $(\partial E/\partial T)_p$, being a result of such a combination of effects.

By using $\mu^*/m_0=0.5$ and the static dielectric constant, we get $B=0.0074$ and 0.0067 eV for TlCl and TlBr. (Lefkowitz *et al.*[17] find experimentally that $B=0.085$ eV in TlBr, by observing three exciton peaks in a Wannier series in single crystals.) This puts the band-gap energy just to the high-energy side of the exciton peak. From the temperature dependence of the dielectric constant[32] we can estimate the temperature dependence of the band gap in TlCl and TlBr. For TlCl it shows a sign reversal at about 160°K. This curious feature, if genuine, is difficult to explain; the temperature dependence of the reflectivity peak near the exciton absorption peak should be measured in single crystals to clear up this point.

The results for the thallium halides are consistent. They all imply a direct edge which is the low absorption coefficient tail of the direct exciton band seen in the thin films. These results are consistent with recent data. Makita *et al.*[13] found that the valence band in TlCl is spherical and located at zero wave vector, while Tamura and Masumi,[14] and Hodby *et al.*[8] have measured the cyclotron resonance of TlCl single crystals and found that these measurements indicate a simple conduction band with its minimum at zero wave vector. Further indication that the exciton peak and the absorption edge seen in single crystals are mainfestations of the same direct transition in the thallium halides is the similarity in their temperature dependences.

The temperature dependence and pressure shifts of the absorption edges and exciton peaks can be used to determine the quantity $(\partial E/\partial T)_v$ using Eq. (1). Since the absorption edge and excitons are optical manifestations of the crystal as a whole, the bulk values of β and K should be appropriate. The temperature shifts are taken at or near room temperature, and the value of $(\partial E/\partial P)_T$ at 80°K is assumed to be the same or only slightly smaller than its value at room temperature. Table II summarizes the results of substitution into this equation (Refs. 34, 35, and 36). Note that in every case $(\partial E/\partial T)_v$ is negative, as expected.[20,21] The "anomalous" positive value of $(\partial E/\partial T)_p$ for TlCl and

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TABLE II. Exciton transition parameters.

Crystal	Transition	$\frac{\beta}{K}$ atm/K°	$(\partial E/\partial P)_T$ 10^{-6} eV/atm	$\frac{\beta}{K}(-\partial E/\partial P)_T$ 10^{-4} eV/K°	$(\partial E/\partial T)_P$ 10^{-4} eV/K°	$(\partial E/\partial T)_V$ 10^{-4} eV/K°
AgCl	indirect edge	39.2[a]	-1.9	-0.74	-8.7	-9.5
AgBr	indirect edge	44.5[b]	-1.5	-0.67	-7.8	-8.5
TlCl	exciton peak	37.0[a]	-13.4	-4.96	$\leq +1$	-4 to -5
TlBr	exciton peak	34.0[a]	-13.9	-4.72	$\leq +1$	-4 to -5

[a] Reference 34.
[b] References 35 and 36.

TlBr is seen to arise from the sign and magnitude of the contribution of thermal expansion to $(\partial E/\partial T)_p$.

Deformation potentials for the direct excitons can be calculated from our data and compared with those found for alkali-halide excitons[37] (see Table III). There is roughly the same value of this parameter for the excitons at Γ in the first four salts listed, all having the NaCl structure. The excitons in the two thallium salts, presumably at Γ, have a positive deformation potential. This transition is symmetry-allowed in TlCl, according to recent two-photon absorption measurements,[38] as is the corresponding transition in alkali and silver halides. Onodera[39] has calculated the band structure of CsI and we[40] have measured the deformation potential for the exciton associated with the $\Gamma_{15} \rightarrow \Gamma_1$ transition, -2.10 eV. The band edges in CsI are primarily I^- $5p$ functions (Γ_{15}) and Cs^+ $6p$ functions (Γ_1). The thallium-halide deformation potentials for the lowest exciton disagree in sign with that for CsI. Probably one or both band edges differ in symmetry or in atomic wave-function character. The valence-band maximum may be primarily halogen p functions or Tl^+ $6s$ functions. It has been suggested that the latter is likely, for the halogen "spin-orbit doublet" is not in the first exciton spectra of these salts. The conduction-band edge may be primarily Tl^+ $6p$ functions.

TABLE III. Deformation potentials for direct exciton peaks.

Salt	Peak energy (eV)	Deformation potential (eV)
AgCl	5.1	-2.70
AgBr	4.3	-2.31
	4.8	-2.64
KBr[a]	6.8	-2.15
	7.3	-2.08
KI[a]	5.8	-2.80
TlCl	3.5	$+3.24$
TlBr	3.1	$+2.98$

[a] Reference 38.

Note added in proof. Two recent papers deal with the subject discussed above. Aust[41] measured pressure shifts of the spectra of AgCl and AgBr. The values he obtained for $(\partial E/\partial P)_T$ of the exciton peaks in both salts, 5×10^{-6} eV/atm, are in good accord with ours, while his pressure shifts of the absorption edges, -0.9×10^{-6} eV/atm for AgCl and -0.5×10^{-6} eV/atm for AgBr, are smaller than ours. Bachrach and Brown[42] show how strain-sensitive the exciton peak in the thallium halides really is. Thus, the odd behavior of $(\partial E/\partial T)_P$ for the excitons in TlCl and TlBr, reported above, probably resulted from thermal strains. Values of $(\partial E/\partial T)_P$ should be obtained on films made according to Ref. 42 before the last two columns of Table II can be considered reliable.

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