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Effect of Pressure upon the Optical Absorption Spectra of Silver Chloride and Silver Bromide

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The effect of quasihydrostatic pressure up to 50 kbar upon the optical absorption spectrum of AgCl and AgBr at 295°K was measured in the spectral region 500–220 mμ. At 50 kbar the absorption edge of AgCl (AgBr) shifted to the red 350 cm^{-1} (200 cm^{-1}), whereas the direct exciton absorption exhibited a blue shift of 1900 cm^{-1} (1950 cm^{-1}); an isostatic point was observed at 25 800 cm^{-1} (21 700 cm^{-1}). The shift of the direct exciton absorption was the same for both halides when expressed in terms of the fractional volume change of the solid. The data are discussed in terms of pressure-induced changes in the structure of the conduction and valence bands. The energy of the conduction-band minimum was found to be a linear function of the unit-cell volume for volumes ranging from 193 Å^3 (AgBr at 0 kbar) to 155 Å^3 (AgCl at 50 kbar).

I. INTRODUCTION

NUMEROUS workers have investigated the optical absorption of AgCl and AgBr. The room-temperature absorption spectra of the two halides, as determined by Okamoto,[1] are shown in Fig. 1. The absorption coefficient α varies over several orders of magnitude, reaching a maximum of almost 10^6 cm^{-1} in the ultraviolet. Generally, the spectra have been characterized by two principal regions—the relatively intense absorption in the ultraviolet and the low-level absorption tail ($\alpha < 10^3$ cm^{-1}) which extends into the visible at room temperature. The region of strong absorption has been studied at room temperature and at low temperatures[1–3] and shows a marked resemblance to that of the alkali halides.[4] The first strong absorption peak observed at low temperature has been assigned to the formation of a direct exciton. With increasing temperature, the peak becomes less intense and shifts to lower energies; at room temperature, AgCl still has a distinct peak, whereas AgBr shows only a broad shoulder. The absorption edge, which distinguishes the silver halide spectra from those of the alkali halides, has been studied extensively and several review articles are available.[5–8] It has been attributed to indirect phonon-assisted transitions involving a valence-band maximum located away from the center of the Brillouin zone.[5,9,10] Experimental evidence for this interpretation was obtained by Brown *et al.*,[10] who observed structure in the absorption edge at 4.2°K.

Recently, band-structure calculations for the silver halides have been made by Bassani, Knox, and Fowler,[11] who used the tight-binding method, and by Scop,[12] who used the augmented-plane-wave method. Both calculations showed a complex valence band in which mixing of the Ag^+ $4d$ states and the halide p states produced valence-band maxima away from the center of the Brillouin zone. In agreement with magnetoresistance and cyclotron-resonance measurements,[13,14] the conduction band was found to be of nearly standard form.

Most of the optical absorption data on the silver halides taken at high pressure have dealt with the edge. Drickamer *et al.*[15,16] measured the combined effects of pressure and temperature to 160 kbar and 325°C. At room temperature, they observed a red shift which decreased in magnitude at higher temperatures; above 250°C, a blue shift was observed. Fiala[17] found that at −180°C the absorption edge of AgBr single crystals shifted to the blue for uniaxial, elastic deformations, whereas it shifted to the red, in agreement with the shift observed by Slykhouse and Drickamer,[15] for plastic deformations produced by uniaxial stresses between 0.5 and 3 kbar. Vacek[18] observed a red shift of the direct exciton peak (0.03 eV for AgCl) for pressures to 19.6 bar at 113°K. In the present work three regions of the AgBr and AgCl spectra, as indicated in Fig. 1, were investigated. Absorption spectra were taken at room temperature for pressures up to 50 kbar.

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II. EXPERIMENTAL

The high-pressure optical cell used in this work was similar to that developed by Drickamer *et al.*[19] and utilized NaCl for the windows and for the pressure-transmitting fluid. Room-temperature spectral measurements could be made down to 220 mμ at quasi-hydrostatic pressures up to 50 kbar. The pressure calibration was based upon the known phase transformations in KBr (18.0 kbar), Bi (I–II, 25.4 kbar), Bi (II–III, 26.8 kbar), and Te (42 kbar). It was found to be parallel to the calculated, linear force over area calibration, but was offset somewhat, owing to frictional forces resulting from the use of a seal ring.

The spectra were recorded with a modified Beckman DU single-beam spectrometer and quartz condensing optics. The wavelength calibration was made with a National Bureau of Standards holmium-doped glass plate and with several Hg emission lines. In the wavelength region above 360 mμ, a standard tungsten lamp was employed, and below 360 mμ, a 1-kW Hanovia hydrogen discharge tube with a sapphire window was used. The maximum monochromator slit width employed was 0.2 mm, corresponding to a spectral slit width of 9 Å at 254 mμ. Light transmitted through the optical cell was detected by a selected RCA 1P28 photomultiplier tube. Mechanical chopping of the incident light beam at 13 cps permitted phase-sensitive amplification of the photomultiplier signal. Amplifier time constants of either 0.04 or 0.8 sec were used. The spectral region of interest was scanned automatically from longer to shorter wavelengths, each spectrum taking approximately 15 min to complete.

The silver halides were prepared by the method of Malinowski.[20] Analysis by flame spectrophotometry showed the heavy-metal impurities listed in Table I.

TABLE I. Analysis of impurities in silver halide samples.

	Impurity (ppm)					
Sample	Cu	Fe	Pb	Mn	Ni	Cr
AgCl	<0.03	<0.07	<0.2	<0.03	a	a
AgBr	a	0.1	a	a	a	a

a Not detected.

Sheet samples were prepared by pressing the silver halide between microscope slides to the desired thickness. No observable heavy-metal contamination was introduced into the samples by this procedure. The sheet samples were not annealed before use; Okamoto[1] found that annealing made no measurable difference in the absorption coefficient over the range 0.3–100 cm^{-1}. Evaporated layer samples, 700 and 1000 Å thick, were prepared on two different substrates, 2-mil Aclar thermoplastic film manufactured by Allied Chemical Corporation and NaCl single crystals. The NaCl single crystals were cylinders ($\frac{1}{8}$ in. in diam$\times\frac{1}{8}$ in.), machined to fit the sample chamber of the high-pressure optical cell. They were cleaved in half along a (100) plane, and the cleaved face of one of the half-pellets was coated. The depositions were made from a graphite boat at a pressure of 5×10^{-5} Torr, and the substrates were at room temperature. X-ray diffraction measurements indicated that the evaporated silver halide grains were oriented with the (200) planes parallel to the substrate and that the crystallite size was greater than 1000 Å. The AgBr evaporated layers exhibited a large amount of light scattering, apparently caused by recrystallization of the halide grains. All samples were prepared and handled under red light and were stored *in vacuo* at room temperature until they were used.

In the loading procedure the silver halide samples were positioned inside the cylindrical sample chamber of the optical cell, perpendicular to the incoming light beam. Sheet samples were placed between Aclar protective coverings before being loaded between two machined NaCl half-pellets. Evaporated layer samples on the Aclar substrate were protected with an uncoated Aclar sheet, and samples deposited on the NaCl substrate were loaded both with and without the Aclar protective covering. To prevent extrusion of NaCl around the piston at high pressures, a hardened, stainless-steel seal ring was used. Prior to the taking of the high-pressure spectra, the sample chamber was fused at 15 kbar to improve the optical transmission of the cell. Spectral measurements generally were taken with increasing pressures; however, all the data reported here were shown to be reversible.

III. OBSERVATIONS

The qualitative features of the data obtained for both AgCl and AgBr were the same; therefore, the results for the two halides will be presented together. Three spectral regions were investigated for each compound. These regions are numbered in Fig. 1(a) and 1(b) according to the order in which the data will be presented.

A. Absorption Edge

The absorption in region 1, which is attributed to phonon-assisted indirect transitions, has an absorption coefficient less than 10^2 cm^{-1}, and because of the low value of α the purity of the silver halide samples was critical. Figure 2 shows the effect of pressure upon the absorption edge of a 0.03-cm-thick AgCl sheet sample. At constant optical density D, the edge shifted to lower energies with increasing pressure. This reversible red shift was approximately linear with pressure, had a maximum value of 350 cm^{-1} at 50 kbar and was constant for values of the atmospheric edge location, ν_0, below 25 000 cm^{-1}. The shifts for three separate runs, calculated for a ν_0 value of 24 950 cm^{-1}, are shown in Fig. 3

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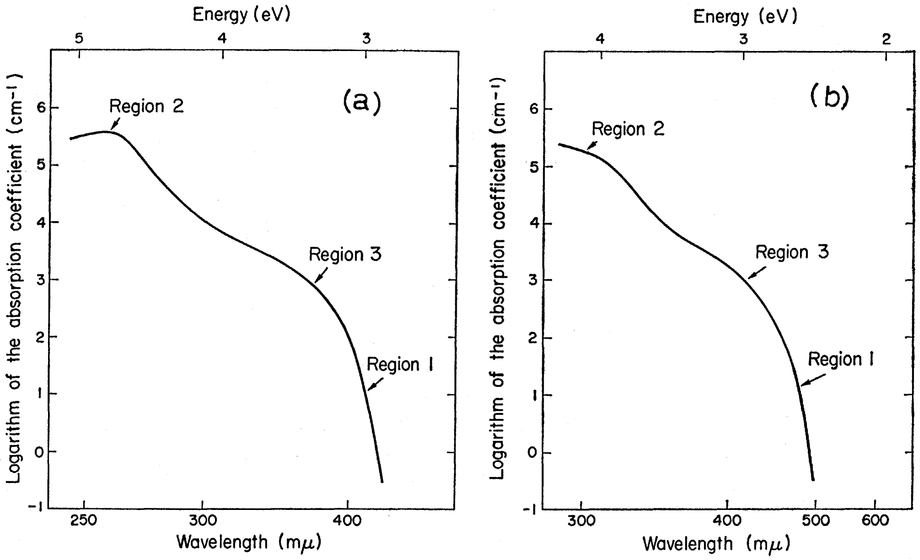

FIG. 1. Optical absorption of silver halides at 300°K after Okamoto. (Ref. 1). (a) AgCl, (b) AgBr. The base of the logarithms is 10.

and are in good agreement with the data of Slykhouse and Drickamer.[15] The scatter of the data shown in this figure was typical.

The observations for AgBr are illustrated in Figs. 4 and 5. The red shift had a maximum value of 180 cm^{-1} at 50 kbar and was constant for values of ν_0 below 21 000 cm^{-1}. The reversibility of the data may be noted for the 20-kbar spectra in Fig. 4.

B. Direct Exciton Absorption

Since the direct exciton absorption (region 2 in Fig. 1) is intense ($\alpha > 10^5\ \mathrm{cm}^{-1}$), the purity of the evaporated silver halide samples was less critical. Although the first exciton peak in the silver halides broadens and shifts to lower energies with increasing temperature, AgCl still shows a broad absorption maximum around 250 mμ at room temperature. Figure 6 shows this peak at several pressures up to 48 kbar. The curves have been arbitrarily positioned along the ordinate in order to separate them. The optical density at the peak was approximately 1.0, and, although there was some random variation in the maximum value, no reproducible change was observed. The peak exhibited a large shift to higher energies with increasing pressure, which is shown more clearly in Fig. 7 where the data from several runs are correlated. At 50 kbar a reversible blue shift of almost 2000 cm^{-1} was observed. The location of the exciton peak was dependent upon the substrate; spectra taken on a Cary 14R Spectrophotometer with large-area evaporated layers showed the

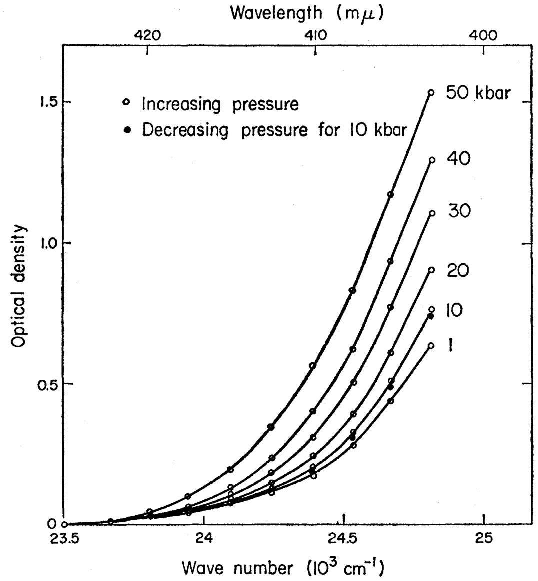

FIG. 2. Absorption edge of 0.03-cm-thick AgCl sheet at various pressures.

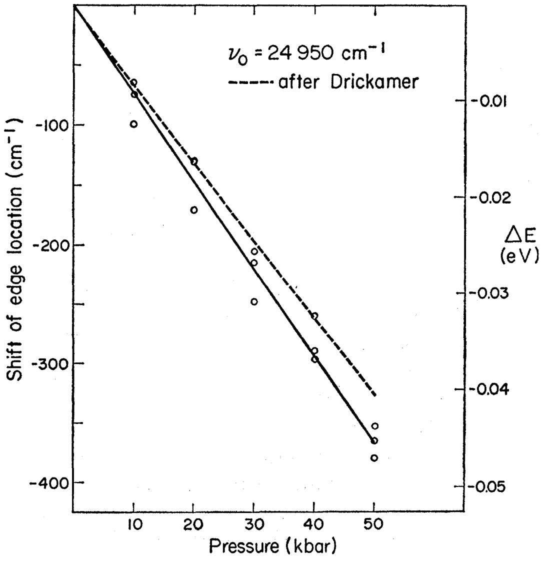

FIG. 3. Pressure dependence of the absorption edge of **AgCl**

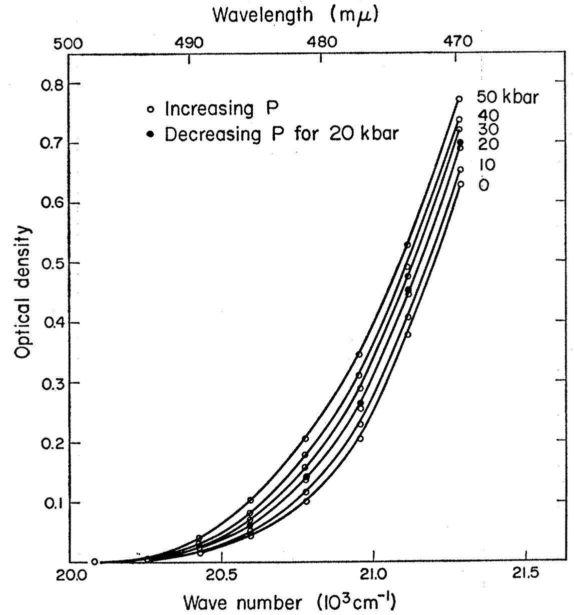

FIG. 4. Absorption edge of 0.04-cm-thick AgBr sheet at various pressures.

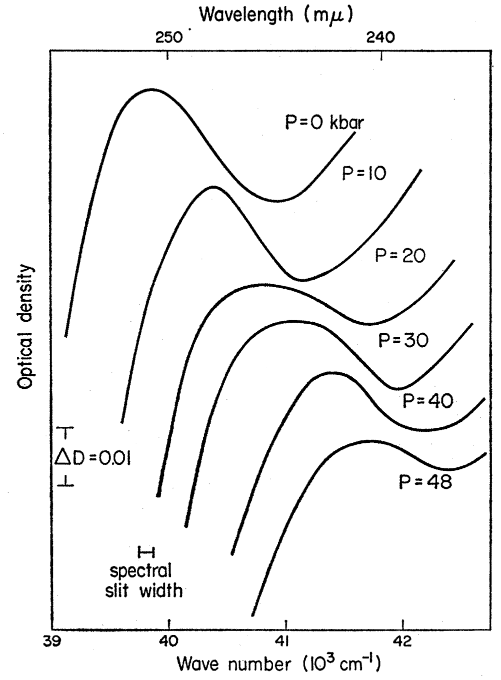

FIG. 6. Exciton peak in AgCl at various pressures. The curves have been arbitrarily positioned along the ordinate. The optical density of the peaks is approximately 1.0.

atmospheric pressure peak location at 39 730 and 39 370 cm^{-1} for the NaCl and Aclar substrates, respectively.

At room temperature the exciton absorption in AgBr is identified only by a shoulder in the absorption spectrum around 310 mμ. Figure 8 shows the exciton absorption spectra for various pressures up to 46 kbar. The large blue shift with increasing pressure was approximately the same magnitude as that observed for AgCl. The reversibility of the data is illustrated for the 20-kbar spectra. The AgBr exciton absorption was independent of the substrate, and no reproducible change in absorption intensity with pressure was observed. The spectra in Fig. 8 have been corrected for light scattering from the evaporated AgBr layer. In the region of sample transparency (ν less than 29 500 cm^{-1})

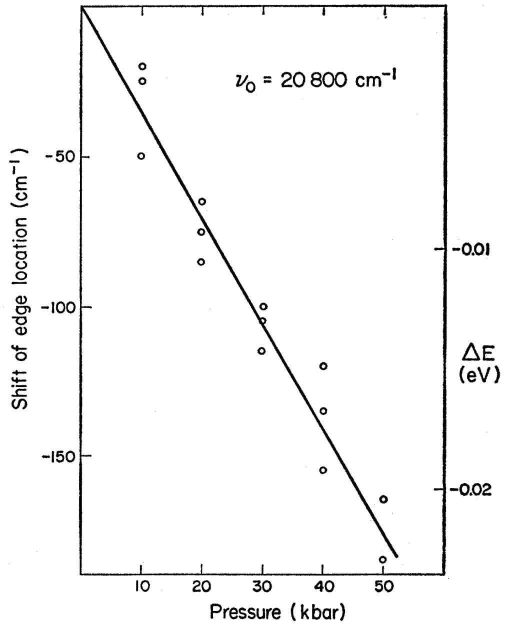

FIG. 5. Pressure dependence of the absorption edge of AgBr.

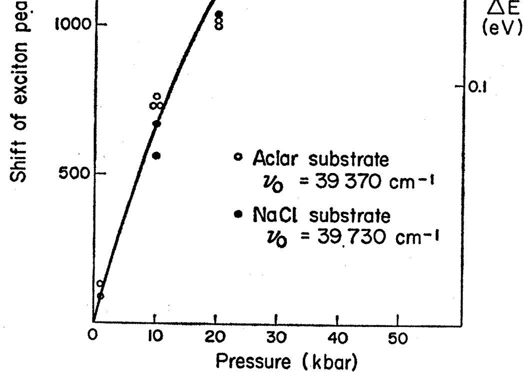

FIG. 7. Pressure dependence of the exciton peak location of AgCl.

there was a linear increase in the measured density with increasing wave number. This density, which was due to light scattering, was extrapolated to the spectral region of sample absorption and was subtracted from the measured density values.

Since a distinct peak was not present in AgBr, it was necessary to find another quantity to characterize the exciton absorption. In Fig. 8 it is seen that the spectra have nearly linear regions on both sides of the exciton shoulder. The wave number at which these two linear sections intersected was used to characterize each spectrum; the intersection for the atmospheric spectrum is shown in the figure. The characteristic intersection may be shown to be independent of sample thickness and of light scattering, as long as the density due to scattering is linearly proportional to the wave number. In Fig. 9 the variation of the characteristic intersection with pressure is shown for several runs. The blue shift was almost 2000 cm^{-1} in 50 kbar, and the rate of the shift decreased at higher pressures. The spectrum of a 1000 Å AgBr coating on Aclar did not change when it was measured repeatedly at atmospheric pressure, indicating that no gross photolytic effects would be expected in taking several spectra at high pressure.

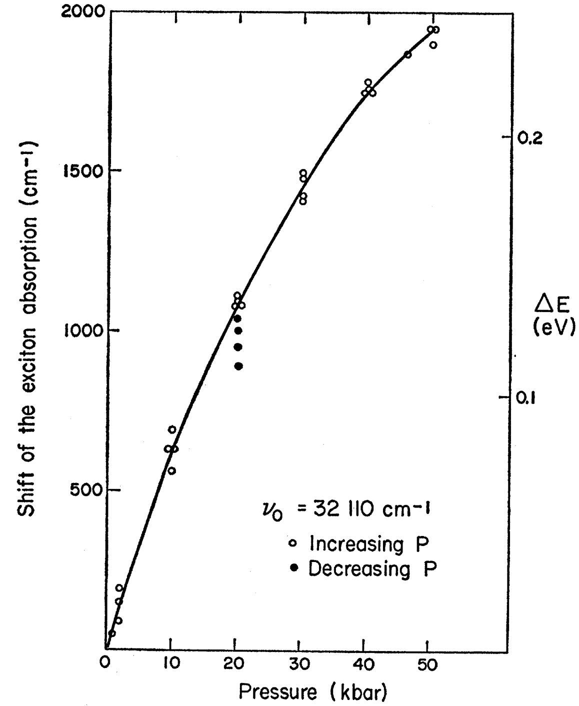

FIG. 9. Pressure dependence of the exciton absorption of AgBr.

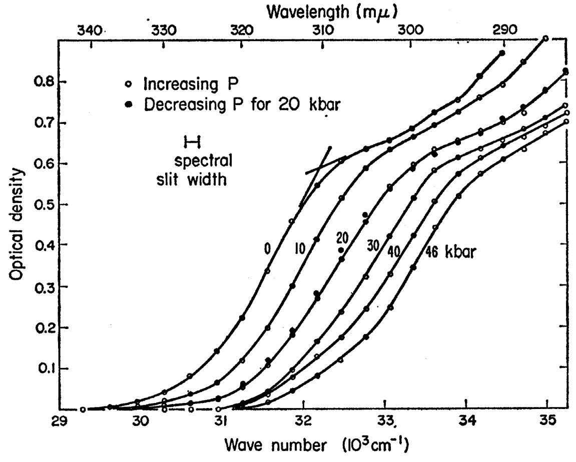

FIG. 8. Exciton absorption of AgBr at various pressures.

C. Intermediate Region

Since the exciton absorption showed a large blue shift and the edge showed a red shift with pressure, a region of the AgCl and AgBr spectra (region 3 of Fig. 1) existed where there was no pressure-induced shift. Figure 10 shows the effect of pressure upon a 0.0013-cm-thick, unannealed AgCl sheet. Both the red shift of the low-intensity edge and the blue shift at higher energies were observed. The isostatic point occurred at 25 800 cm^{-1}. The atmospheric-pressure spectrum obtained with thin sheet samples in the optical cell was not reproducible and was omitted from Fig. 10. In Fig. 11 the linear shift of the edge with pressure, dE/dP, is plotted for various locations on the 10-kbar spectrum. The graph includes data from both regions 1 and 3 of the AgCl spectrum [see Fig. 1(a)]. The red shift of the low-intensity edge was approximately -9×10^{-4} eV/kbar, in agreement with Slykhouse and Drickamer,[15] and was constant over a wide range of ν_0. The largest measured blue shift of 1.5×10^{-3} eV/kbar may be compared to the shift of the direct exciton peak, 5×10^{-3} eV/kbar.

The effect of pressure upon the intermediate region of a 0.025-cm AgBr sheet sample is shown in Fig. 12. The atmospheric pressure spectrum was reproducible, in contrast to the AgCl data, probably due to the thicker sample load. The isostatic point occurred at 21 700 cm^{-1} and is also shown in Fig. 13, in which dE/dP is plotted for various locations on the 0-kbar spectrum. The red

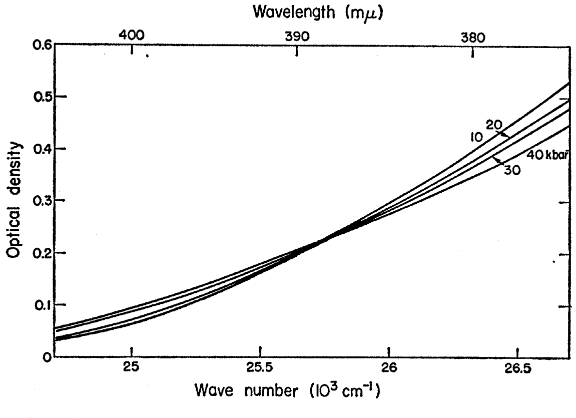

FIG. 10. Intermediate-region spectrum of 0.0013-cm-thick AgCl sheet at various pressures.

shift of the low-intensity edge was -5×10^{-4} eV/kbar and was constant for values of ν_0 less than 21 000 cm^{-1}. The largest measured blue shift was 1.6×10^{-3} eV/kbar, compared to 5×10^{-3} eV/kbar which was observed for the direct exciton absorption. It should be noted in Fig. 13 that the agreement with the AgBr data of Slykhouse and Drickamer[15] was poor.

IV. DISCUSSION

The pressure-induced changes in the optical-absorption spectra of AgCl and AgBr can be explained in terms of changes in the structure of the conduction and valence bands. The recent band-structure calculations for the silver halides[11,12] permit a firmer interpretation of these pressure effects. Since the pressure data and the calculated band structures for AgCl and AgBr are qualitatively the same, it is sufficient to consider only AgCl in detail, with the understanding that the qualitative explanations are valid for AgBr. The quantitative differences between the two halides will be considered separately.

The calculated band structure for AgCl showed a complex valence band with relative maxima at L_3', Δ_1, and Σ_4, resulting from mixing of the Ag$^+$ $4d$ and Cl$^-$ $3p$ states. Figure 14 shows a portion of the band structure calculated by Bassani, Knox, and Fowler, as reported by Peterson.[21] The exciton peak was assigned to the formation of an exciton betwen the Γ_{15} and Γ_1 states. The peaks observed by Brown *et al.*[10] in the absorption tail were assigned to indirect phonon-assisted transitions, probably involving the L_3' valence state.

The opposite pressure effects observed for the absorption edge and the region of intense absorption (red and blue shifts, respectively) provide additional experimental evidence for the presence of two different types of transitions, consistent with the present interpretation of the band structure.

Since the optical-absorption measurements in this work were made at room temperature, the absorption edge included transitions from various valence states. For simplicity, only the L_3' state will be considered in discussing the indirect transitions. In addition, spin-orbit splitting will be neglected, and it will be assumed that the effect of pressure upon the exciton binding energy is small. The solid arrows in Fig. 14 indicate the indirect and direct transitions at atmospheric pressure. The dotted curves and arrows show the proposed band structure and transitions at 50 kbar. Relative to Γ_{15}, the Γ_1 conduction-band minimum has been raised by 1900 cm^{-1} (0.24 eV) and the L_3' valence-band maximum has been raised by 2250 cm^{-1} (0.28 eV). The energy of the $\Gamma_{15}\rightarrow\Gamma_1$ transition has increased by 1900 cm^{-1}, whereas the $\Gamma_3'\rightarrow\Gamma_1$ transition energy has experienced a net decrease of 350 cm^{-1}, as observed experimentally. Although the Γ_{15} state might shift in energy at 50 kbar, the present data measured only changes with respect to this particular state. In AgBr at 50 kbar the energies of the Γ_1 and Γ_3' states relative to Γ_{15} were raised 1950 cm^{-1} (0.24 eV) and 2150 cm^{-1} (0.26 eV), respectively, so that the direct exciton energy increased by 1950 cm^{-1} and the $\Gamma_3'\rightarrow\Gamma_1$ transition energy decreased by 200 cm^{-1}.

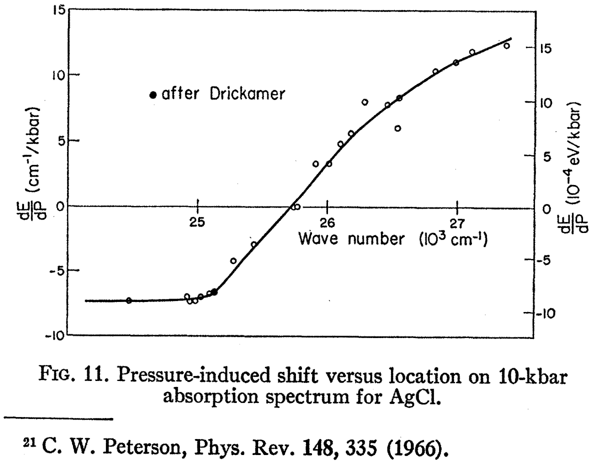

FIG. 11. Pressure-induced shift versus location on 10-kbar absorption spectrum for AgCl.

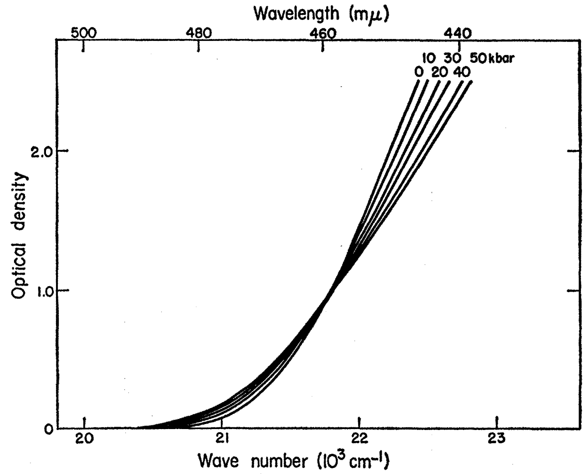

FIG. 12. Intermediate-region spectrum of 0.025-cm-thick AgBr sheet at various pressures.

The relative increase in energy of the L_3' state at

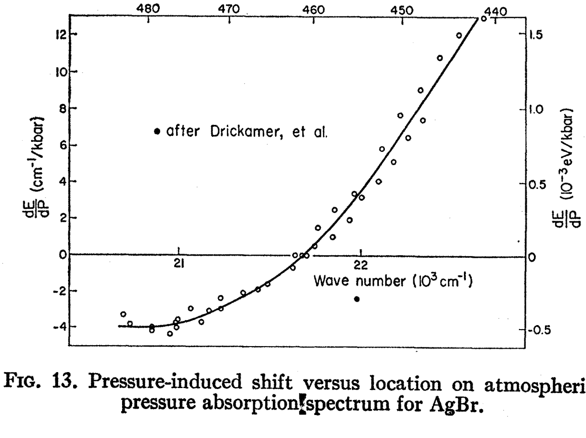

FIG. 13. Pressure-induced shift versus location on atmospheric-pressure absorption spectrum for AgBr.

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[21] C. W. Peterson, Phys. Rev. 148, 335 (1966).

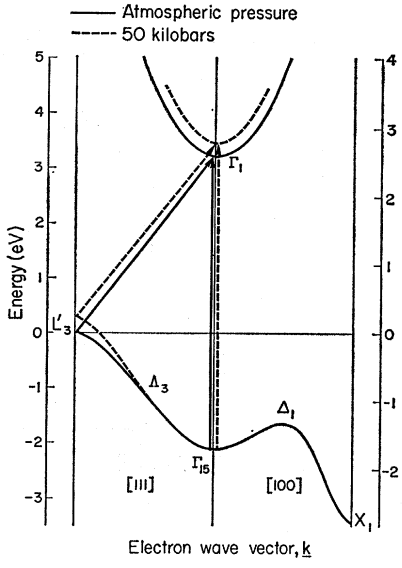

FIG. 14. Effect of pressure upon the band structure of AgCl: solid line, atmospheric pressure; dashed line, 50 kbar.

higher pressures can be explained through increased quantum-mechanical mixing of the Cl^- $3p$ and Ag^+ $4d$ states. These states, which overlap each other extensively, also lie close together in energy. It is the coupling term which produces the valence-band maximum at L'_3.[11,12] At the higher pressures the overlap of the p and d wave functions should increase as the interatomic distances are decreased. The resulting increased p-d coupling should raise the valence-band maximum at L_3' even further with respect to the Γ_{15} energy.

The increase in the energy of Γ_1 relative to the Γ_{15} energy at higher pressures can also be explained by the increased interaction between neighboring atoms. Scop[12] found that the lowest-lying conduction band in AgCl arose from s-like ionic functions corresponding to the Ag^+ $5s$ states and the valence-band state at Γ_{15} arose from Cl^- $3p$ wave functions. With increasing pressure the interatomic separation is decreased, and the repulsive forces are increased. If it is assumed that there is little quantum-mechanical mixing of states at either Γ_1 or Γ_{15}, the increase in the electron-electron repulsion of the conduction state should be greater than the increase in the corresponding term of the Γ_{15} state because of the greater radial extent and correspondingly greater interaction of the conduction-band wave functions. Thus, a pressure-induced blue shift of the direct exciton absorption would be predicted.

In order to explain the data, it is necessary for the pressure-induced energy shift of the L_3' state to be greater than that of the Γ_1 conduction state (in 50 kbar a difference of 350 cm^{-1} for AgCl and 200 cm^{-1} for AgBr). The distance between atomic centers of the various electronic states involved should be of direct relevance. The wave functions determining the p-d coupling are associated with neighboring Ag and Cl ions which are separated by $\frac{1}{2}a$ (a is the lattice constant), whereas the wave functions forming the conduction band are associated with neighboring Ag ions which are separated by a larger distance, $a/\sqrt{2}$. Although the quantitative dependence of the L_3' and Γ_1 states upon increased overlap of the contributing ionic wave functions would not be expected to be the same, the larger shift of the L_3' state is consistent with its smaller interaction distance.

The intermediate region in AgCl is located on a shoulder of the absorption spectrum [region 3, Fig. 1(a)]. At the isostatic point the absorption coefficient is not affected by increasing pressure. The valence states involved in the transitions at the isostatic point lie along Λ_3 near L_3' (see Fig. 14). With increasing pressure the energy shift of these states is equal to the shift of the conduction band. Since the isostatic point (25 800 cm^{-1}) lies close to the energy gap for indirect transitions, the pressure-induced increase in the p-d coupling term must fall off rapidly for values of **k** away from the zone boundary. At $\mathbf{k}=0$ the mixing term is zero.[11,12]

A comparison of the AgCl and AgBr data should reveal some of the differences between the interatomic forces within the two materials. A more meaningful comparison can be made if the fractional volume change of the halide is used instead of the applied pressure. Bridgman's[22] measurements showed that below 20 kbar the compressibilities of AgCl and AgBr were essentially identical, whereas above 20 kbar AgBr was significantly more compressible, as would be expected for the larger Br ion. By using Bridgman's data, the shift of the exciton absorption for both AgCl and AgBr can be plotted as a function of the fractional volume decrease, as shown in Fig. 15. It is seen that the dependence of the exciton absorption upon the fractional volume

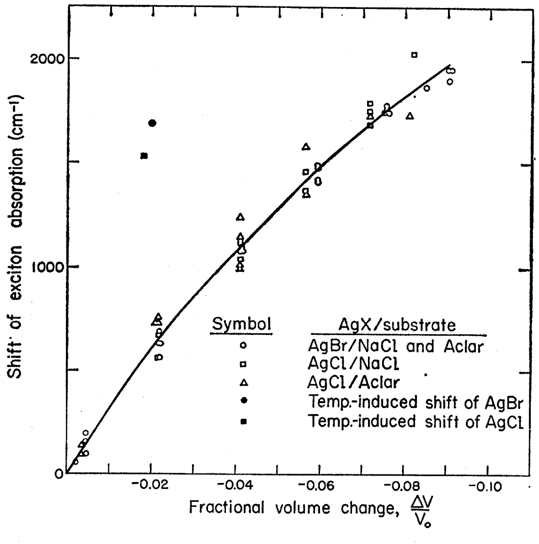

FIG. 15. Shift of exciton absorption as a function of fractional volume change for AgCl and AgBr.

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[22] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 74, 21 (1940).

change was the same for both halides and was inpendent of the substrate. Thus, the shift of the conduction-band minimum, Γ_1, with respect to Γ_{15} was the same for the two materials.

The temperature shift of the exciton absorption in going from room temperature to $-180°C$ may be calculated for both AgCl and AgBr from Okamoto's data.[1] At $-180°C$ Lawn[23] found the lattice parameter of AgCl (AgBr) to be 5.516 Å (5.736 Å) compared to the room-temperature value of 5.550 Å (5.775 Å), which corresponds to a fractional volume change of -0.018 (-0.020). The points giving the temperature shifts are shown in Fig. 15. There is no correlation between the temperature-induced shifts and the pressure-induced shifts of the exciton absorption when only lattice contraction is considered. One possible explanation is the decrease in phonon broadening of the peak at low temperatures. This decrease could result in a shift of the peak to higher energies which is essentially independent of the lattice contraction, resulting in a blue shift which is larger than would be predicted from the pressure data.

The measured red shifts of the absorption edge ($L'_3 \rightarrow \Gamma_1$) were different for AgCl and AgBr; for a fractional volume change of -0.085 the values were 350 and 180 cm^{-1}, respectively. Since the energy shift of the $\Gamma_{15} \rightarrow \Gamma_1$ transition was the same for the two halides, the observed difference for the $L'_3 \rightarrow \Gamma_1$ transition must be due to a difference in the shift of L'_3 with respect to Γ_{15}. The pressure-induced change in the energy of L'_3 with respect to that of Γ_{15} is an indication of the strength of the *p-d* interaction at L_3'. For a fractional volume decrease of 0.085 the changes were 2250 and 2080 cm^{-1} for AgCl and AgBr, respectively, indicating a larger *p-d* interaction for AgCl. The calculated band structures, which reflect experimental measurements at atmospheric pressure, show the larger *p-d* interaction for AgCl; the energy difference between the L_3' and Γ_{15} states, a qualitative measure of the *p-d* interaction, was 2.17 eV for AgCl and 1.55 eV for AgBr. The cause of the smaller interaction term for AgBr can be traced to the lower electron affinity of Br (3.49 eV) with respect to Cl (3.72 eV). Starting with the free-ion eigenvalues, Knox, Bassani, and Fowler[24] showed the evolution of the $3p$ and $4d$ bands at Γ for AgCl. Their calculation indicated that the energy of the $3p$ band was slightly above that of the $4d$ band. The lower electron affinity of Br would increase the energy separation of the p and d bands for AgBr, with a concomitant decrease in the *p-d* interaction for points in the Brillouin zone away from Γ. Although the difference in the pressure-induced shifts of the L_3' state was consistent with the calculated band structures, a calculation of the predicted shifts, based upon the lattice parameters of the compressed halides, would be of interest.

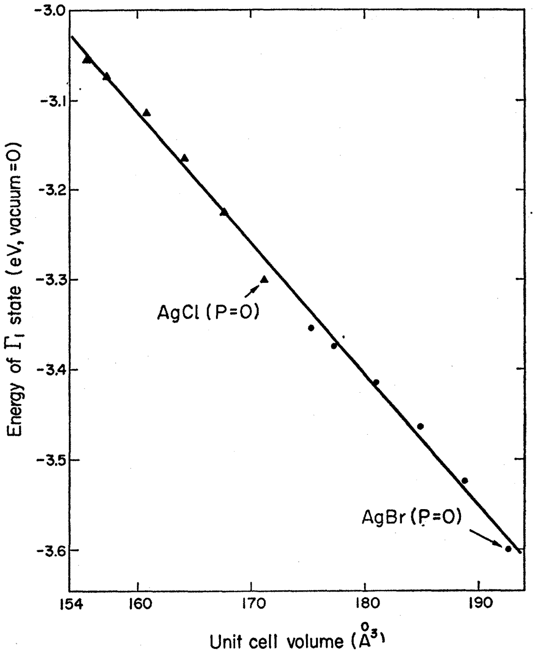

FIG. 16. Energy of the conduction-band minimum versus the unit-cell volume for AgCl and AgBr.

Figure 16 shows the energy of the Γ_1 conduction-band minimum of AgCl and AgBr as a function of the unit-cell volume. The atmospheric-pressure and room-temperature values of the energy of the Γ_1 state were calculated from the difference between the photoelectric threshold ($L_3' \rightarrow$vacuum) and the absorption edge ($L_3' \rightarrow \Gamma_1$). Reported values of the photoelectric threshold[21,25–27] were 6.2 eV for AgCl and 6.1 eV for AgBr, with uncertainties of the order of 0.1 eV. By using the absorption edge data of Moser and Urbach,[28] the energy of the Γ_1 state was found to be 3.3 and 3.6 eV for AgCl and AgBr, respectively. If it is assumed that the energy of the Γ_{15} state was unaffected by pressures up to 50 kbar, then the observed pressure-induced shifts of the $\Gamma_{15} \rightarrow \Gamma_1$ exciton transitions were entirely due to shifts of the Γ_1 state to higher energies. On this assumption the energy of the Γ_1 state with respect to vacuum was plotted as a function of unit-cell volume in Fig. 16. The unit-cell volumes were obtained from the atmospheric-pressure measurements of Lawn[23] and the compressibilities reported by Bridgman.[22]

From Fig. 16 it is seen that the energy of the conduction-band minimum is nearly a linear function of the unit-cell volume for volumes from 155 to 193 Å^3 (a 25% variation) and shows no dependence upon the particular halogen ion in the lattice. Since both silver halides have the NaCl structure (O_h^5), the conduction-band mini-

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mum varies linearly with the cube of the Ag ion separation. The independence of the energy of the Γ_1 state with respect to the halide ion indicates that the conduction states are centered on the Ag ions, in agreement with the calculations of Scop,[12] who found that the conduction band was formed principally from Ag^+ 5*s* states.

The correlation shown in Fig. 16 may be used to predict the energy of the Γ_1 state for other silver halide crystals which have the NaCl structure. If the absorption edge of the crystal is known, then the photoelectric threshold may be predicted also. By using a lattice constant of 4.92 Å, the conduction-band minimum of AgF is estimated to be at -2.5 eV. This value must be viewed in the light of the anomalous behavior often observed for fluorides. Since AgCl and AgBr form solid solutions in all proportions, the conduction-band minimum and the photoelectric threshold of mixed crystals may be estimated by using the published data for the lattice parameter[29] and for the absorption edge.[8,30] For a mixed crystal with 42% AgBr the absorption edge and lattice constant at room temperature are 2.64 eV and 5.68 Å. From Fig. 16 the energy of the Γ_1 state and the photoelectric threshold are estimated to be -3.45 and 6.1 eV, respectively. Similar estimates may be made for iodobromide and iodochloride mixed crystals and for the high-pressure phase of AgI ,which has the NaCl structure.[31–33] It would be of interest to see if the photoelectric threshold of the mixed crystals containing AgI is correlated by Fig. 16, since the absorption edge of these crystals is highly sensitive to small amounts of iodide ion.[8]

For both AgCl and AgBr Balchan and Drickamer[16] observed a blue shift of the absorption edge at temperatures above 250°C. Their observation may be explained in terms of the band-structure changes in the intermediate region (region 3, Fig. 1). For all temperatures, their shifts were calculated from the same ν_0 value—25 200 cm^{-1} for AgCl and 22 000 cm^{-1} for AgBr. At higher temperatures, it is known [1,30] that the edge shifts to the red; at 250°C, a shift of 0.2 eV (1600 cm^{-1}) was observed. Thus, the data obtained at high temperature did not correspond to the observed room-temperature transitions but to transitions involving valence states possibly 0.2 eV farther away from the valence-band maximum at L_3'. Since the *p-d* coupling term and pressure-induced energy increase of the valence state with respect to Γ_{15} decrease for values of **k** away from L_3', a pressure-induced blue shift at high temperatures is possible (i.e., the shift to higher energies of the valence band is less than the shift of the conduction band).

No explanation was found for the discrepancy between the present work and that of Slykhouse and Drickamer[15] concerning the AgBr absorption edge (see Fig. 13). One pertinent observation is that at the ν_0 value used by them, AgBr has a large absorption coefficient (150 cm^{-1}) which, at room temperature and atmospheric pressure, corresponds to the shoulder region of the AgBr spectrum [region 3, Fig. 1(b)]. It was in this shoulder region that the isostatic point was found both for AgBr and for AgCl.

The phonon spectrum in the silver halides should be affected by an increase in pressure, with a resulting effect on the indirect transitions in the absorption edge. However, at room temperature these effects should be overshadowed by the changes in the band structure.

At present no adequate explanation for the effect of the substrate upon the exciton peak location in AgCl is available. The peak locations for the Aclar and NaCl substrates differed by 360 cm^{-1}; however, no measurable difference was observed for the AgBr layers. It is difficult to attribute the difference to impurities, since the absorption coefficient of the AgCl is so large in this spectral region ($>10^5$ cm^{-1}).

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