

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 m μ 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 m μ , a standard tungsten lamp was employed, and below 360 m μ , 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 m μ . 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.

Sample	Impurity (ppm)					
	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

* 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; Okamoto¹ 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 10² 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

¹⁹ R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, *J. Opt. Soc. Am.* **47**, 1015 (1957).

²⁰ J. Malinowski, *J. Phot. Sci.* **8**, 69 (1960).