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Optical Absorption of Pure Silver Halides*

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The absorption spectra of pure silver bromide and silver chloride crystals grown from the melt have been measured in and near the so-called "absorption edge," where the absorption coefficient increases very rapidly with frequency. The temperature-dependence of the absorption edge has also been investigated. More limited data have been collected on the absorption spectra of mixed AgBr—AgCl and AgBr—AgI crystals.

The requirements for an accurate measurement of the absorption edge in pure materials are discussed briefly, and it is estimated that the room-temperature data reported here are accurate to somewhat better than 10%. These new data are combined with some published measurements in an effort to obtain absolute absorption spectra for silver chloride and silver bromide over a large range of absorption coefficients.

I. INTRODUCTION

ONLY limited data have been reported in the literature on the spectral absorption of silver bromide and silver chloride, both in the edge region and at higher absorptions. Several factors combine to make such measurements somewhat difficult.

The steepness of the absorption edges necessitates much care in the photometric measurements. In addition, it requires the preparation of a series of crystals covering a wide range of thicknesses, and having little volume and surface scattering. Finally, as will be seen in this paper, even slight traces of impurities may seriously modify the positions and shapes of the absorption edge, and hence crystals of very high purity must be used.

For silver bromide at room temperature in the spectral range 200–350 mμ, Hilsch and Pohl[1] and Fesefeldt and Gyulai[2] have published some data, but the absorption coefficients are given in relative values only, and some questionable assumptions are required in order to obtain the absolute values of the coefficients. Biltz[3] analyzed the Hilsch and Pohl data and also made some independent measurements of the absorption coefficient of silver bromide in the range 200–360 mμ. Although these measurements of Biltz are subject to all the difficulties inherent in measuring very thin and inhomogeneous films, Biltz estimated that his values were within a factor of two of the true values of the absorption coefficient of pure silver bromide crystals. In the spectral region 360–450 mμ, Slade and Toy[4] have published data which appear quite reliable. They are in good agreement with our own measurements in the range 400–450 mμ at room temperature. Some measurements at lower temperatures have also been reported by Toy and Harrison.[5] In these Laboratories, a study has been made of the shape and temperature-dependence of the silver bromide absorption edge. The results published[6] showed that for silver bromide the plot of the log absorption coefficient *versus* energy is approximately linear and that the numerical value of the slope in this plot approaches $1/kT$ (k=Boltzmann's constant, T=absolute temperature). This paper presents more accurate data taken at room temperature.

For the case of silver chloride, Hilsch and Pohl[1] and Fesefeldt and Gyulai[2] have published some data, and more recently, Gilleo[7] has published some measurements on the temperature-dependence of the absorption edge. A rather complete spectrum of silver chloride at room temperature in the range 220–400 mμ has been measured by Milliman.[8] Our own data cover the spectral range 380–435 mμ at room temperature. There is excellent agreement with Milliman in the wavelength range in which the data overlap.

II. MATERIALS

All our measurements were made on crystals prepared from the purest available AgCl and AgBr precipitates. The crystals were grown either as polycrystalline disks solidified slowly from the melt, as thin sheets crystallized between Vycor plates, or as large, cylindrical crystals grown by the modified Bridgman technique described elsewhere.[9] The thinnest samples were made by pressing the crystals, followed by annealing. By using these techniques, crystals ranging in thickness from several microns to several centimeters were obtained, enabling us to cover a large range of absorption coefficients.

III. EXPERIMENTAL REQUIREMENTS AND PROCEDURE

An accurate determination of the absorption coefficient of silver bromide and silver chloride in the edge

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[1] R. Hilsch and R. W. Pohl, Z. Physik **64**, 606–622 (1930).

[2] H. Fesefeldt and Z. Gyulai, Nachr. Ges. Wiss. Göttingen No. 3, 226 (1929).

[3] M. Biltz (private communication).

[4] R. E. Slade and F. C. Toy, Proc. Roy. Soc. (London) **A97**, 181–190 (1920).

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

[7] M. A. Gilleo, Phys. Rev. **91**, 534 (1953).

[8] P. D. Milliman, Cornell University, Ithaca, New York, master's thesis, 1954 (unpublished).

[9] Nail, Moser, Goddard, and Urbach (to be published).

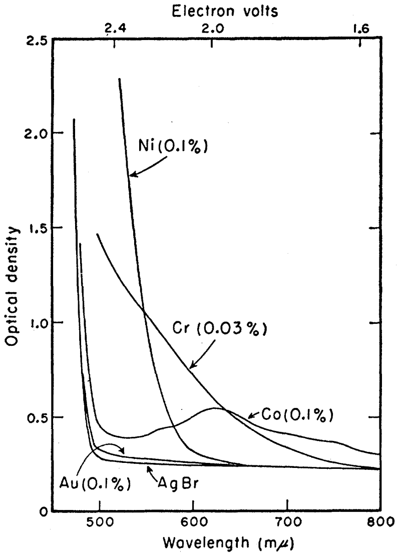

FIG. 1. Absorption spectra of AgBr crystals with various impurities. Impurity concentrations are nominal additions in mole percent. All samples are approximately 3 mm thick. Measurements made at 25°C.

region requires careful control of several factors because of the extreme steepness of the edge. In the edge region, a change of 1 A in wavelength causes about a 2% change in the absorption coefficient, k. Hence, a measurement of k, accurate to a few percent,requires an accuracy of wavelength measurement to 1 A. The steepness of the absorption edge also imposes a severe restriction on the band width that may be used in measuring the transmission of a sample. In general, measurement of an absorption edge with a finite band width gives incorrect values of the transmission, and hence of the quantities derived from it. In order to estimate the influence of the measuring band width, the error in k was calculated as a function of the steepness of the edge, the density being measured and the band width being used (Appendix 1). The calculation indicates that for silver chloride and silver bromide, in the steepest region of the edge, a band width of about 1 mμ or less must be used if an accuracy of a few percent is desired over a reasonable density range. Measurements made with varying band widths and with a monochromatic line source confirmed this conclusion.

The position and shape of the absorption edge of silver chloride and silver bromide are temperature sensitive (see Figs. 5 and 7). The edge shifts to longer wavelengths and flattens with increasing temperature. In the neighborhood of 25°C, the shift is about 2 A per degree Centigrade, or in terms of the absorption coefficient, k, about a 4% change in k per degree Centigrade. Therefore, strict control and measurement of temperature are necessary. At higher temperatures, this requirement becomes less stringent, since the edge flattens.

Certain cationic impurities appreciably alter the absorption spectrum of silver chloride and silver bromide if they are present in as small a concentration as several parts per million. Generally, this impurity absorption manifests itself as a long-wavelength absorp-

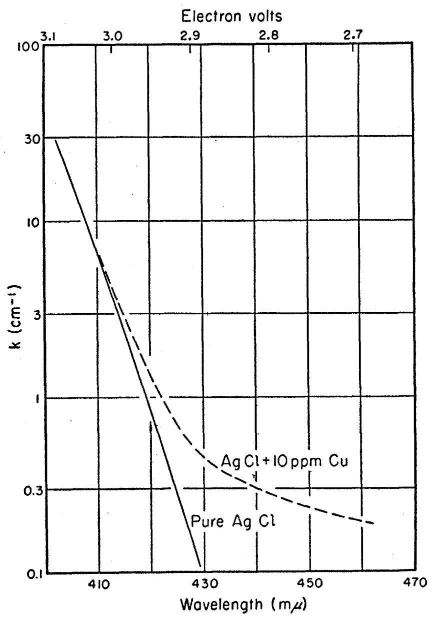

FIG. 2. Absorption spectrum of a AgCl crystal containing approximately 10 parts per million of copper impurity. Measurements made at 25°C.

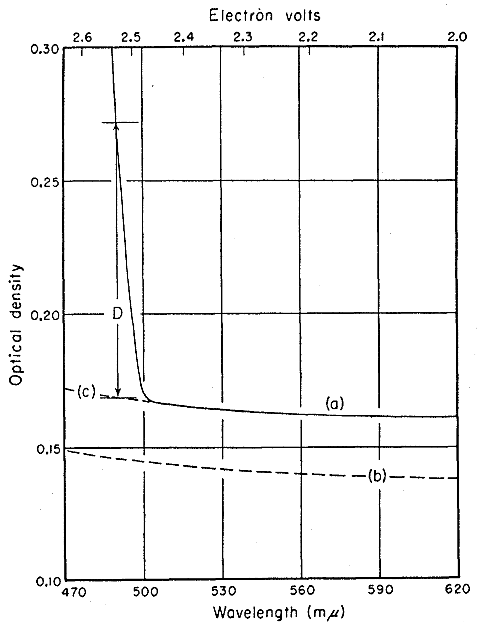

FIG. 3. Optical density as a function of wavelength for a 4.16 mm-thick AgBr crystal at 26°C. Curve (*a*) is the measured density; curve (*b*) represents the theoretical reflection losses; and curve (*c*) is the density attributed to nonabsorption losses. The absorption density is calculated by subtracting curve (*c*) from curve (*a*).

tion tail added to the main absorption edge. Figure 1 shows the effect of several metallic impurities added in comparatively large concentrations to a silver bromide melt before crystallization. Probably only a fraction of the nominal impurity content is effectively built into the crystals obtained from these melts, but the data may be regarded as indications of the strong effect of small concentrations of impurity on the long-wavelength absorption. More detailed data have been obtained on the absorption produced by copper in silver chloride. Figure 2 shows the absorption of a silver chloride crystal prepared by the Bridgman technique,[9] with 10 parts per million of cuprous chloride added to the starting precipitate. These results indicate that 1 part per million of copper added in this manner would probably produce a measurable long-wavelength absorption. If the crystal is prepared in a manner favoring the formation of cupric ions, for example, annealing in a chlorine atmosphere, the long-wavelength absorption is still larger, and extends to longer wavelengths. (Detailed data on the effects will be reported in later publications.)

Extreme care is therefore taken to avoid any contamination of the precipitate and of the final crystal. The excellent reproducibility of the absorption spectra of carefully prepared samples grown from different precipitates and by different methods indicates that these spectra are not affected by the absorption of residual impurities.

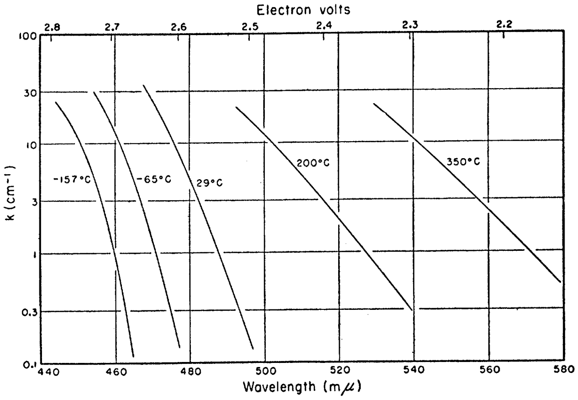

FIG. 5. Absorption spectra of AgBr crystals as a function of temperature in the range −157°C to 350°C.

The samples used in these measurements generally exhibit strain patterns when viewed between crossed Polaroid filters. However, similar measurements were made on carefully annealed samples, and on samples subjected to stresses resulting in a deformation of several percent, and in no case was a significant change in the optical absorption detected. The crystals received no exposure other than that used in the actual measurement. This measuring exposure was shown not to cause a detectable change in the absorption spectrum. Hence, the absorption spectra reported here are believed to represent those of unexposed crystals of a high degree of purity and perfection.

In determining absorption coefficients from our transmission measurements, it is necessary to take into account the light losses due to scattering at the surface and in the volume of the crystals, as well as the specular reflection losses at the surfaces. The manner in which this was done is shown for a typical measurement in Fig. 3. Curve (*a*) is the measured transmission density as a function of wavelength, (*b*) is the theoretical reflection loss calculated from a knowledge of the index of refraction, and (*c*) represents the density that was subtracted from the measured density to give the true absorption. Curve (*c*) is drawn as an extension of (*a*)

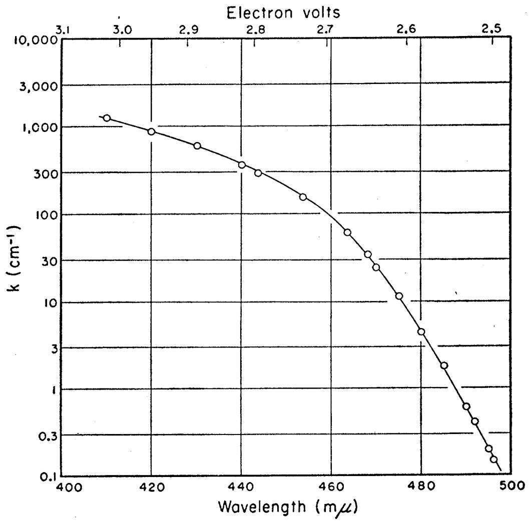

FIG. 4. Absorption spectrum of AgBr crystals at 29°C.

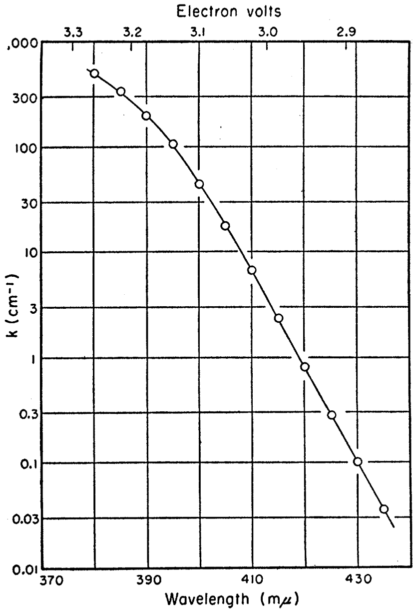

FIG. 6. Absorption spectrum of AgCl crystals at 26°C.

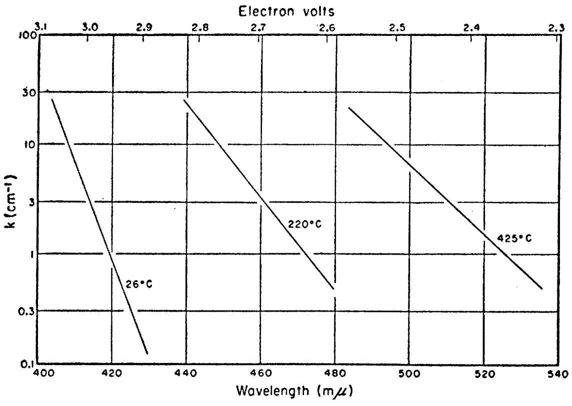

FIG. 7. Absorption spectra of AgCl crystals as a function of temperature in the range 26°C to 425°C.

and approximately parallel to (*b*). The short wavelength range over which the extrapolated curve (*c*) is used makes any large error unlikely. Confidence in this method of analysis is justified by the good agreement obtained in calculating *k* from crystals of different thicknesses and of widely varying optical qualities. Depending on the sample, the scatter correction varied greatly, but in the most favorable cases it was negligibly small. The absorption values derived from these samples agree well with those obtained on highly scattering samples. It should be emphasized that this method of analysis is practical only if a wide range of sample thicknesses, varying by small amounts, is readily available. The measurements reported here have been made with either a double-beam spectrophotometer designed and built in these Laboratories, or a Cary Recording Spectrophotometer. No absorption coefficients were calculated from densities greater than about 2.5, since at higher densities, wide slits, possible stray light, and the steep absorption edge of silver chloride and silver bromide combine to make such data unreliable.

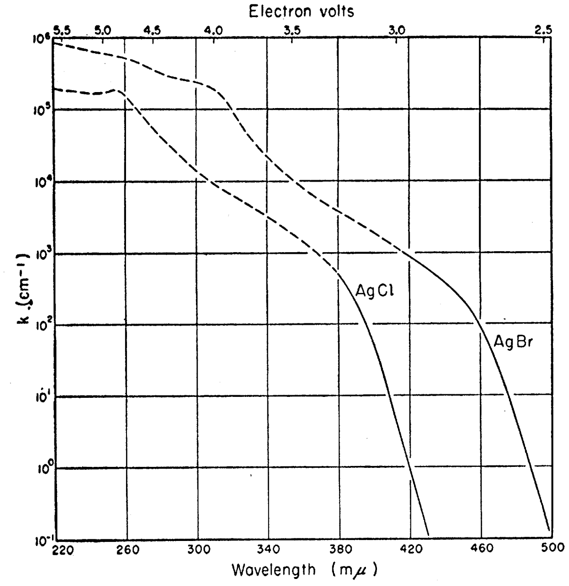

FIG. 9. Absorption spectra of AgCl and AgBr crystals at a temperature of about 25°C. The broken curves represent data compiled from other sources referred to in this publication.

For absorption measurements at elevated temperatures, the sample was mounted in an all-glass cell, which, in turn, was placed in a furnace having quartz windows through which the incident and the transmitted beams pass. The temperature was determined by a thermocouple embedded in the sample. For low-temperature measurements, the sample was held in a Dewar flask just above the surface of an acetone—dry ice mixture, or of liquid nitrogen. In all cases, careful insulation allowed completion of the experiment without objectionable temperature drift.

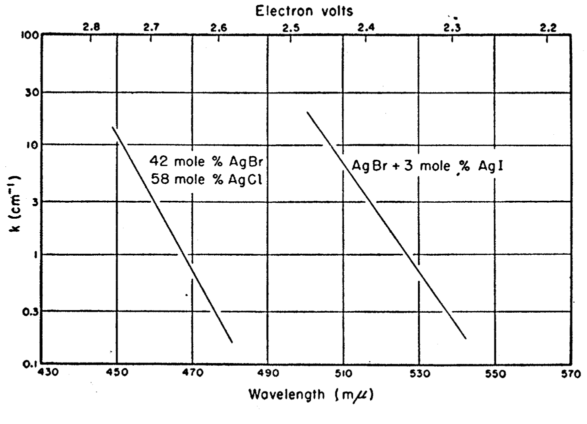

FIG. 8. Absorption spectra of mixed silver halide crystals at 25°C.

Figure 4 is the absorption spectrum of pure silver bromide crystals at a temperature of 29°C in the spectral range 410–500 mμ. It is estimated that the values are accurate for our materials to ±10%, and probably somewhat better. Figure 5 shows the temperature-dependence of the absorption edge of silver bromide from −157°C to 350°C. These data are not as reliable as the room-temperature values reported in Fig. 4.

The absorption spectrum of pure silver chloride crystals from 380–435 mμ at 26°C is shown in Fig. 6.

TABLE I. Absorption coefficient, *k* (cm^{-1}), of pure AgBr and AgCl crystals.

AgBr 29°C		AgCl 26°C	
λ (mμ)	*k* (cm^{-1})	λ (mμ)	*k* (cm^{-1})
500	7.0×10^{-2}	435	3.7×10^{-2}
490	6.3×10^{-1}	430	1.0×10^{-1}
480	4.7×10^{0}	420	8.1×10^{-1}
470	2.7×10^{1}	410	6.9×10^{0}
460	9.2×10^{1}	400	5.0×10^{1}
450	2.2×10^{2}	390	2.0×10^{2}
440	3.9×10^{2}	380	4.9×10^{2}
430	6.1×10^{2}		
420	9.0×10^{2}		
410	1.3×10^{3}		

For silver chloride, values in the absorption edge only have been measured, and, again, are accurate to ±10 percent. The temperature dependence of the absorption edge of silver chloride from 26°C to 425°C is given in Fig. 7. The room-temperature data on silver chloride and silver bromide are listed in Table I.

Some limited data have been obtained on the absorption spectra of mixed silver halide crystals, and Fig. 8 shows the spectrum of a mixed AgCl—AgBr crystal (58 mole percent AgCl—42 mole percent AgBr) and of a mixed AgBr—AgI crystal (97 mole percent AgBr—3 mole percent AgI). Both measurements were made at approximately 26°C.

In Fig. 9, an attempt has been made to summarize the available information on the absorption spectra, at room temperature, of pure silver chloride and silver bromide. In joining the various sets of data, consideration has been given to the authors' estimates of accuracy, and to the type of samples on which the measurements were made. Apart from our own data, however, it is difficult to estimate the accuracy of the values reported. The measurements of Slade and Toy[4] appear to be quite reliable. The short-wavelength data of Biltz[3] do not agree with those reported by Hilsch and Pohl.[1] Milliman[8] has made his measurements on carefully pressed and annealed sheets of silver chloride and has used a wide range of thicknesses. The internal consistency of his data implies that they are quite reliable. Our own results on pressed samples suggest that this treatment does not modify the observed optical absorption.

ACKNOWLEDGMENTS

This work was done in close collaboration with N. R. Nail, C. A. Duboc, and P. E. Goddard, of these Laboratories. We are grateful also to E. E. Richardson, of these Laboratories, who was helpful in applying the Cary Recording Spectrophotometer to our special needs.

APPENDIX 1

It is desired to estimate the error introduced into a determination of the absorption coefficient, k, as a result of using a finite band width in the measurement of the transmission.

The transmission, T, of a sample of thickness t, at a wavelength λ is given by

$$T=e^{-k(\lambda)t}, \tag{1}$$

where $k(\lambda)$ is the absorption coefficient at wavelength λ.

From (1), one gets for the fractional change in k, expressed as a function of T,

$$\Delta k/k=\Delta T/T\ln T. \tag{2}$$

In a small neighborhood of wavelength λ_0, the transmission at wavelength λ is approximately represented by

$$T(\lambda)=T_0+\alpha(\lambda-\lambda_0)+\beta(\lambda-\lambda_0)^2, \tag{3}$$

where α and β are constants determining the first and second derivatives of T with respect to λ.

If one now measures the transmission at λ_0 by use of a band width of $\Delta\lambda$ wavelength units centered at λ_0 and equal weight is given to all wavelengths, the value obtained will not be T_0, but rather T_0', where

$$T_0'=\frac{1}{\Delta\lambda}\cdot\int_{\lambda_0-\frac{1}{2}\Delta\lambda}^{\lambda_0+\frac{1}{2}\Delta\lambda}[T_0+\alpha(\lambda-\lambda_0)+\beta(\lambda-\lambda_0)^2]d\lambda. \tag{4}$$

This assumes, for a first approximation, that the incident energy is uniformly distributed over the region $\Delta\lambda$. The difference between the true transmission T_0 at λ_0, and the measured transmission T_0', denoted by ΔT, is

$$T_0'-T_0=\Delta T=\beta(\Delta\lambda)^2/12, \tag{5}$$

evaluating T_0' from (4). From (3), $d^2T/d\lambda^2=2\beta$ and therefore,

$$\frac{\Delta k}{k}=\frac{(d^2T/d\lambda^2)(\Delta\lambda)^2}{24T\ln T}. \tag{6}$$

Formula (6) is a general expression for the fractional error in k. By assuming a specific form for the transmission curve, $\Delta k/k$ may be calculated.

In the case of silver bromide and silver chloride, the absorption coefficient in the edge region is fairly well represented by

$$k=k_0e^{-c\lambda}, \tag{7}$$

where k_0 and c are constants.

Writing $T=\exp(-k_0te^{-c\lambda})$, and evaluating $d^2T/d\lambda^2$ and $\ln T$, one may substitute directly in the general expression (6) and obtain, for the case of silver bromide and silver chloride,

$$\frac{\Delta k}{k}=\frac{c^2(\Delta\lambda)^2}{24}[1-kt]. \tag{8}$$

Equation (8) expresses the fractional error in k as a function of the band width, $\Delta\lambda$, the slope of the exponential edge, c, and the density being measured, kt. For silver bromide and silver chloride, c is found experimentally to be about 2.1×10^6 cm^{-1}.

Equation (8) shows that for $kt>1$, Δk is negative, implying too low a measured value of k, and that for $kt<1$, $\Delta k/k$ approaches a positive limiting value of $c^2(\Delta\lambda)^2/24$. The error in k is proportional to the square of the measuring band width.

If one requires, for silver bromide and silver chloride, the error in k to be less than, say, 3% for densities up to 3.0, the band width, $\Delta\lambda$, as calculated from (8) must not exceed 1.7 mμ. A precision of 1% would require a band width of not more than 1 mμ. A band width of 5 mμ, however, would cause an error of 25 percent in k at the higher densities. Equation (8) is useful in estimating the errors in k due to use of a finite band width $\Delta\lambda$, when k is approximately known.