parison of theory and absorption spectra that the $^1S_0$ curve of W I is fairly accurate. The observed emission spectra are in much less satisfactory agreement with those computed using the $^3P_1$ curve W I; nor is it possible to derive one-dimensional configuration coordinate curves which include all the experimental data on absorption and emission in a self-consistent manner. This may indicate either the presence of unsuspected complications in the absorption or emission properties of KCl:Tl, or it may indicate the limitations in the use of a one-dimensional configuration coordinate curve model for the center. The excitation spectra also casts some doubt as to the validity of the assumptions made by Johnson and Williams in obtaining the $^1P_1$ configuration coordinate curve from experimental data. It appears that the experimental results could also be interpreted as indicating the presence of two thallium centers in slightly different environments. It is probable that more certain conclusions concerning this state will arise from a detailed investigation of the 1960 A absorption band and the emission spectra associated with it.

ACKNOWLEDGMENTS

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Optical and Electrical Properties of Silver Chloride*

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Simultaneous measurements of absorption, fluorescence, and photoconductivity have been investigated for AgCl as functions of exciting radiation and temperature. Excitation in the range of 250 to 400 millimicrons with temperatures from −180°C to room temperature were employed. Frequency-sensitive apparatus was used throughout the measurements with the light beam chopped at 37.5 cps. An ac electrometer circuit was employed to measure currents in the range 10^{-16} to 10^{-11} ampere.

The temperature dependence of the absorption edge has been extended to lower temperatures and the coefficient of absorption observed to be an exponential function of wavelength. It was also observed to be an exponential function of $1/T$°K in the range 387 to 400 millimicrons. The fluorescence of AgCl at −175°C was 482 millimicrons for an exciting wavelength in the region of 270 millimicrons. A second weaker fluorescence peak of undetermined wavelength was observed at temperatures in the neighborhood of −150°C for an exciting radiation of 390 millimicrons. Photocurrents proportional to the intensity of the exciting radiation were observed in the saturation current region for low applied voltages. Photoconductivity was observed in each of two different regions of the temperature range and wavelength range of exciting radiation employed. There were large photocurrents for wavelengths of exciting radiation less than 270 millimicrons in the temperature region of −175°C and smaller photocurrents at temperatures of −55°C for exciting radiation of 398 millimicrons. The spectral distribution of photoconductivity was also investigated.

I. INTRODUCTION

RECENT investigations[1,2] on the properties of AgCl have made evident the importance of measurements on crystals at shorter wavelengths and lower temperatures. Limited studies of AgCl have previously been reported, both in the edge region and at higher absorptions.[3–5] Many factors enter to make such measurements difficult. The steepness of the absorption edge requires crystals covering a wide range of thicknesses. In absorption measurements, fluorescence at low temperatures must be corrected for along with any fluorescence of the supporting quartz materials for thin samples. However, photoconductivity measurements impose the requirement that thick crystals be used in order that as much light be absorbed as possible.

It appears to be necessary to study simultaneously these properties of AgCl before an interpretation of the electronic processes can be attempted.

II. EXPERIMENTAL

A. Materials

The samples used in these experiments ranged in thickness from 0.55 cm to 5×10^{-4} cm. Two single crystals,[6,7] 0.23 cm and 0.55 cm thick, were used in the low-absorption region. Also AgCl, 0.1 cm thick, ob-

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[†] Present address: General Electric Company, APED, San Jose, California.

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

[2] F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956).

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

[4] W. Lehfeldt, Nachr. Ges. Wiss. Göttingen **1**, 171 (1935).

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

[6] Obtained from J. W. Davisson, Naval Research Laboratories, Washington, D. C.

[7] Obtained from F. C. Brown, University of Illinois, Urbana, Illinois.

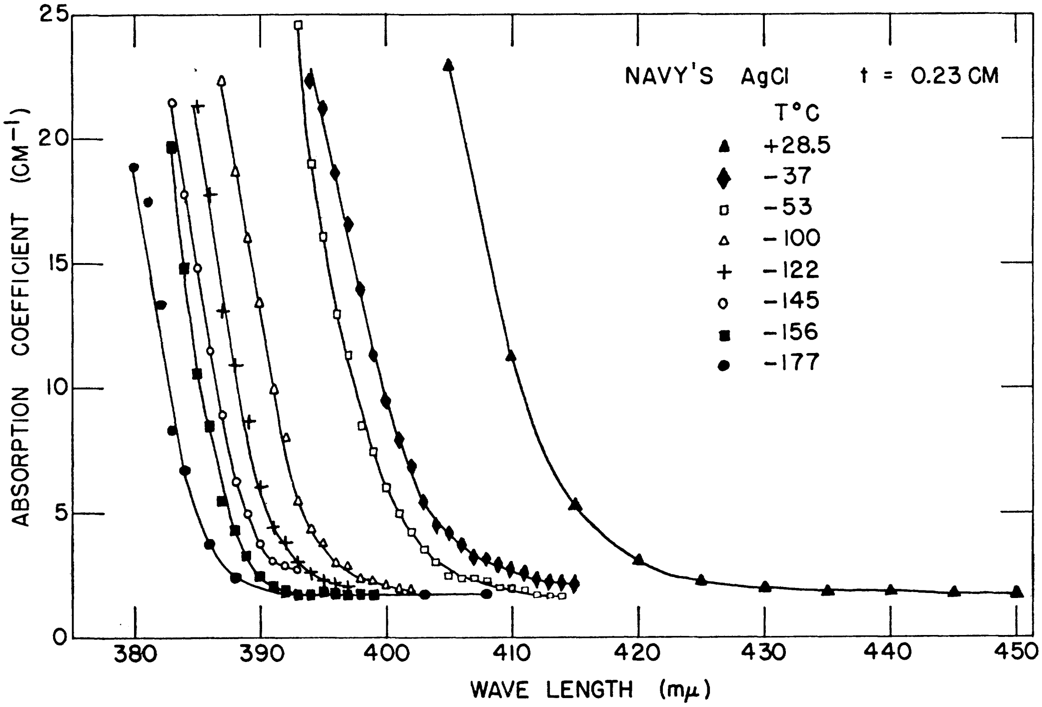

FIG. 1. Absorption spectra of AgCl as a function of temperature in the range −177°C to 28.5°C. Crystal thickness, 0.23 cm.

tained from the Harshaw Chemical Company, was used. This material, when etched, shows a surface structure which is not visible under polarized light before etching. In addition, single crystals were grown from chemically pure AgCl by the Kyropoulos technique.

The thin single crystals were grown between optically polished fused quartz plates from these materials. All crystals were supported on cp magnesium oxide powder and annealed in air[8] by heating in the dark to 400°C for three hours, and then were cooled to room temperature over a period of three days. After this treatment they

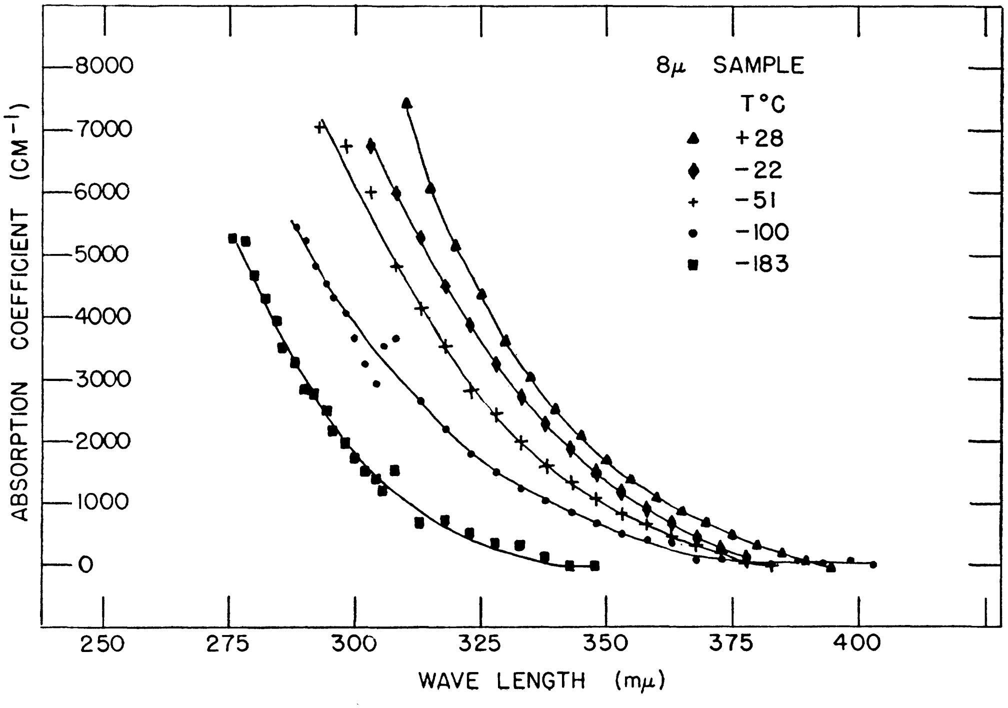

FIG. 2. Absorption spectra of AgCl as a function of temperature in the range −183°C to 28°C. Crystal thickness, 8 microns.

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[8] J. R. Haynes, Rev. Sci. Instr. 19, 51 (1948).

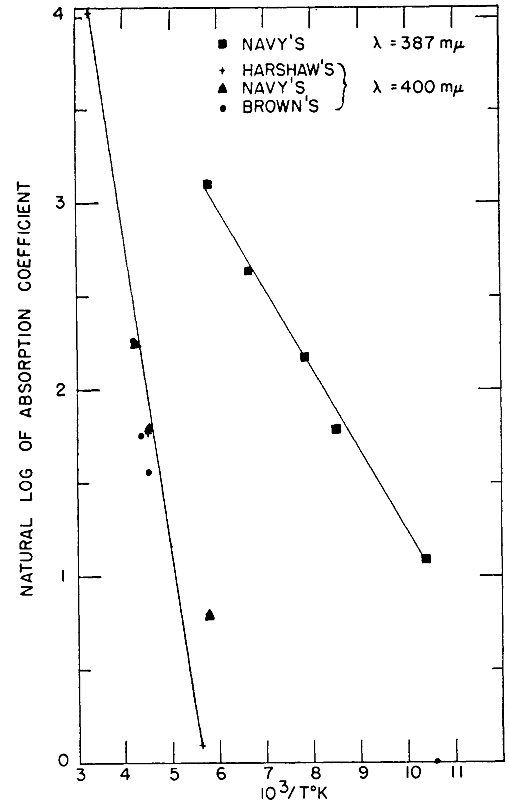

FIG. 3. Natural log of absorption coefficient *vs* $10^3/T$°K for two different wavelengths.

were etched, washed, and air dried. Subsequently, two coats of silver conducting paint[9] were applied to opposite edges of the crystals to serve as electrodes. The crystals, during manipulations, were exposed only to dim red light except during the period of actual investigation and the measuring exposure was found not to cause a detectable change in the crystals. When ready for use, a crystal was mounted in the crystal holder behind a slit system with its thin dimension perpendicular to the light beam, and silver electrodes were placed lightly against the painted electrodes. The crystal was then put in a double-wall crystal chamber which was flushed with dry nitrogen before the chamber was sealed. The crystals were cooled slowly to prevent strains and to allow any remaining moisture in the crystal chamber to be condensed in the lower chamber of the cryostat.

B. Apparatus

The crystal was maintained in a dry atmosphere rather than in vacuum and a circulating stream of dry nitrogen flowed past the crystal and through a large copper tube submerged in the cooling bath. The temperature of the crystal chamber was controlled by a platinum resistance thermometer sensing element above the crystal and a thyratron-operated controlling circuit with a heating element below the crystal. A copper-constantan thermocouple[10] placed in the crystal holder recorded the actual temperature of the crystal.

The continuum from a hydrogen discharge tube and a mercury arc served as light sources. The exciting radiation was passed through a Bausch and Lomb Grating monochromator and the beam was given a square wave modulation in intensity of 37.5 cps. Measurement of initial intensity incident on the crystal simultaneously with the measurement of the transmitted light through the crystal was afforded by a quartz beam splitter. The two resulting beams were measured by 1P28 phototubes whose output was amplified by frequency-sensitive amplifiers.[11] Calibrated neutral density screens were placed in the initial intensity beam during the course of an experiment to correct for differences in sensitivity of the two phototubes due to differences in the intensity of the beams. Filters were placed in front of the transmitted intensity phototube to remove the fluorescent light emitted by AgCl and quartz. Initial intensity measurements were corrected for these filters along with the corrections for

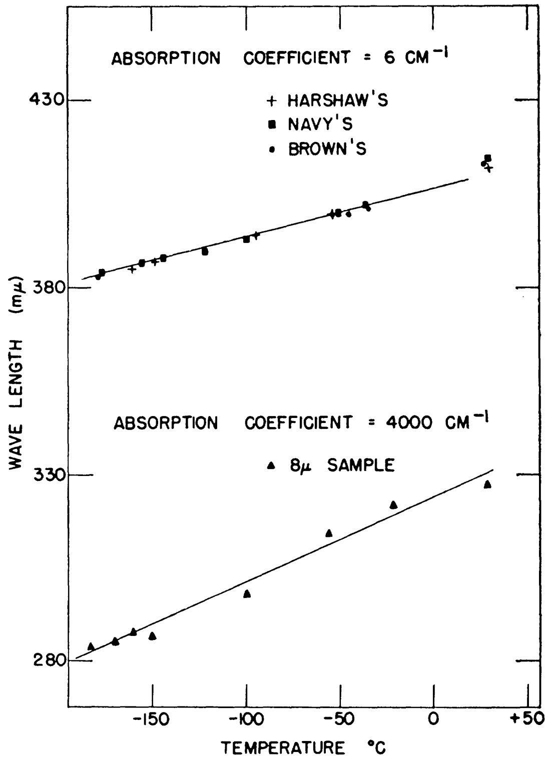

FIG. 4. Wavelength *vs* temperature for constant absorption coefficient.

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[9] Type SC-12 Silver conducting paint, Micro Circuits Company, New Buffalo, Michigan.

[10] Calibrated by the National Bureau of Standards, Washington, D. C.

[11] J. M. Sturtevant, Rev. Sci. Instr. 18, 124 (1947).

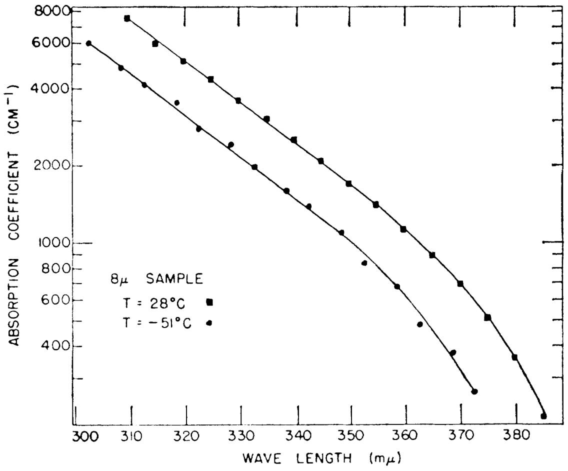

FIG. 5. Exponential dependence of absorption coefficient with wavelength for the temperature range −51°C to 28°C.

differences in intensity incident on the two phototubes without a crystal in place.

The fluorescent light emitted by the crystal at right angles to the incident light passed through double quartz windows in the cryostat wall, and was analyzed by a glass prism spectrometer. This light was measured by a 1P21 phototube whose output was amplified by a frequency-sensitive amplifier.[11]

The intensity falling upon the crystal is modulated and the current in the crystal varies, therefore, according to the modulation frequency. An ac electrometer circuit was developed to measure currents in the range of 10^{-16} to 10^{-11} ampere. The output of this circuit was amplified by a frequency-sensitive amplifier.[11] All data were taken with a positive voltage of 420 v applied to the crystal. A negative voltage of equal magnitude was applied between each reading. The number of photons per second incident on the crystal was determined by a 1P28 phototube and the published spectral sensitivity curve.

III. EXPERIMENTAL RESULTS

A. Absorption Coefficients

Characteristic absorption coefficient *vs* wavelength curves are given in Figs. 1 and 2. In each of these figures the absorption curve for the respective sample as measured at room temperature with a Beckman ultraviolet spectrophotometer is also shown. The absorption coefficient measured at low temperatures was normalized to the value measured at room temperature at 450 millimicrons. The difference between the two methods of measurement was about 15%, which is approximately the same error obtained for the absorption coefficient when measured on two different Beckman spectrophotometers.

The index of refraction for AgCl at 500 millimicrons is 2.096.[12] This value was used to apply a constant correction for reflections at the air AgCl interface. Similar corrections were applied to the thin samples crystallized between fused quartz plates to account for reflections at the air-quartz interface and the quartz-AgCl interface. The final correction took account of the absorption of the fused quartz plates as determined on the Beckman spectrophotometer.

The optical modes of vibration may be expected to set up fluctuating electric fields in the lattice which will perturb the band edges. The thermal excitation of these modes will vary exponentially with temperature and hence the absorption coefficient will be given by $\alpha=\alpha_0 e^{-\epsilon/T}$. For a wavelength of 400 millimicrons we obtain (Fig. 3) from the slope of the lines $\epsilon=1.7\times10^{-3}$ °K, while at 387 millimicrons $\epsilon=0.44\times10^{-3}$ °K. For wavelengths shorter than these the absorption coefficient does not appear to vary exponentially with $1/T$ °K.

Gilleo[5] found that the wavelength at which a given absorption coefficient is reached approaches a constant value asymptotically. In the present investigation this was not observed, as is shown in Fig. 4 for two widely differing absorption coefficients.

Moser and Urbach[2] investigated the variation of the absorption coefficient with wavelength and observed that it is an exponential function for wavelengths greater than 395 millimicrons. In the range 350 to

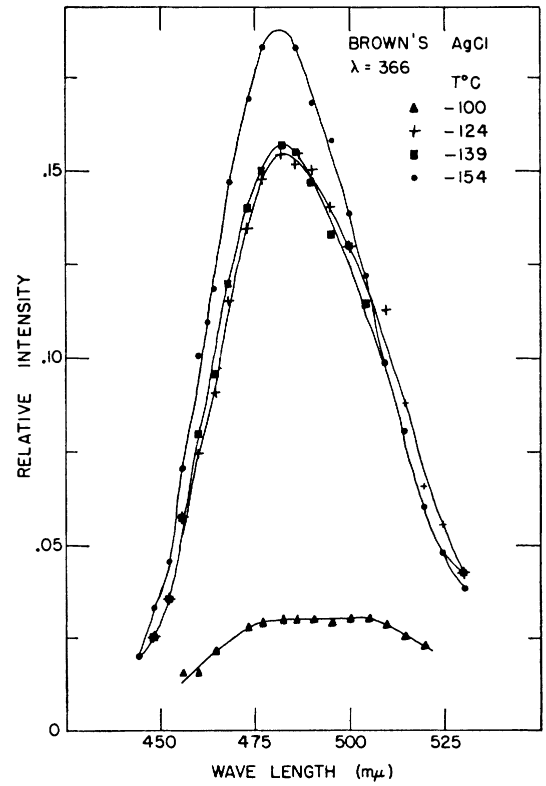

FIG. 6. Fluorescence spectra for the temperature range −154°C to −100°C with 366-millimicron excitation.

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[12] Tilton, Plyler, and Stephens, J. Opt. Soc. Am. 40, 540 (1950).

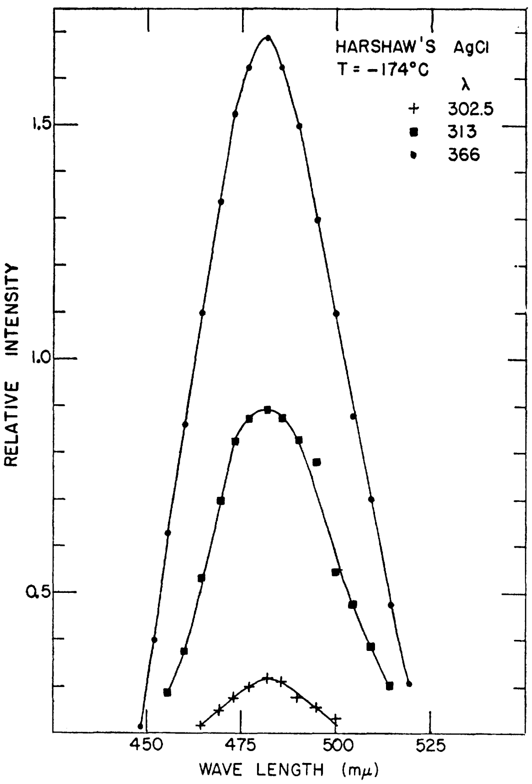

FIG. 7. Fluorescence spectra at constant temperature for an exciting wavelength range 302 to 366 millimicrons.

395 millimicrons this no longer holds, but in the range 300 to 350 millimicrons the absorption coefficient was observed to vary exponentially with wavelength again. Thus if the formula $\alpha = \alpha_0 e^{-c\lambda}$ holds well in the absorption edge, then we obtain (Fig. 5) at a temperature of 28°C, $c = 380$ cm^{-1}, while at a temperature of -51°C, $c = 220$ cm^{-1}.

B. Fluorescence Measurements

The intensity of the fluorescent light emitted by a crystal, for a constant wavelength of exciting radiation, decreases with increasing temperature (Fig. 6). At -100°C only weak fluorescence is observed. At a constant temperature the fluorescence increases with decreasing wavelength (Fig. 7). The fluorescence has a maximum at 482 millimicrons. The slit width is different in each of these figures. In these curves the fluorescence spectrum was corrected for the spectral sensitivity of the phototube and for the number of photons per second incident on the crystal.

The intensity of the fluorescent light emitted by the crystal changes not only with temperature but with the wavelength of the exciting radiation incident on the crystal (Figs. 8 and 9). For wavelengths longer than 400 millimicrons the incident radiation is scattered strongly (see Fig. 9). At wavelengths shorter than 400 millimicrons two bands of fluorescence appear, one in the region of 350-400 millimicrons and a second in the region 250–300 millimicrons. Below 250 millimicrons there are indications that the fluorescence again increases. However, this must be verified. At temperatures above -100°C there is possibly only weak fluorescence for exciting wavelengths greater than 250 millimicrons. The relative intensity in Figs. 8 and 9 is the emitted intensity corrected for the spectral distribution of the source.

C. Photoconductivity

Photocurrents in the saturation region were measured with 420 v applied to painted electrodes separated by 1.2 cm. The photocurrents in these measurements were proportional to the light intensity throughout the experiments. The photocurrents were of the order of 10^{-14} ampere for an intensity of monochromatic light at the crystal of the order of 10^{10} photons per second. With indium contacts evaporated on a crystal[13] greatly reduced currents were measured, probably due to an InCl barrier formed between In and AgCl.

Bands of photoconductivity were observed in two different regions of the temperature and wavelength range investigated (see Figs. 10 and 11). In the neigh-

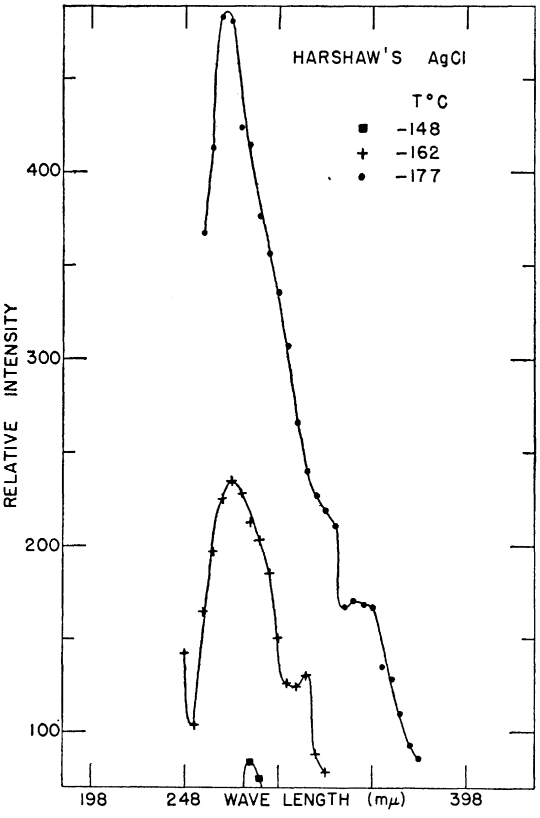

FIG. 8. Fluorescence *vs* exciting wavelength in the temperature range -148°C to -177°C.

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[13] R. W. Smith, Phys. Rev. **97**, 1525 (1955).

borhood of −55°C the photocurrent rises abruptly at about 410 millimicrons and drops rapidly for wavelengths shorter than 395 millimicrons. No photocurrents were observed for wavelengths shorter than 300 millimicrons or longer than 420 millimicrons in this temperature region.

Marked changes take place when photocurrents are measured at low temperatures. Although the current is erratic, which may be due to trapping and polarization, the general trend of Fig. 11 is interesting. The curve of fluorescence *vs* wavelength of incident light exhibits a maximum at about 270 millimicrons and from Fig. 11 there appears to be a corresponding rise in the photocurrent in this region, reaching higher values than at any other wavelength or temperature. In the region of 390 millimicrons there is another peak of lower magnitude in the photocurrent curve which corresponds to a second fluorscence maximum in the same region, also of lower magnitude. In the vicinity of −55°C the photoconductivity and fluorescence vanish in the 270-millimicron region, while the photocurrents and a possible weak fluorescence persist in the 390-millimicron region.

The spectral distribution of photoconductivity generally exhibits a maximum in the region of the absorption edge. As one approaches the absorption edge from the long-wavelength side, photoconductivity rises rapidly as the absorption edge is reached, goes through a maximum at some moderate value of absorption, and falls again while the absorption coefficient is still rising.

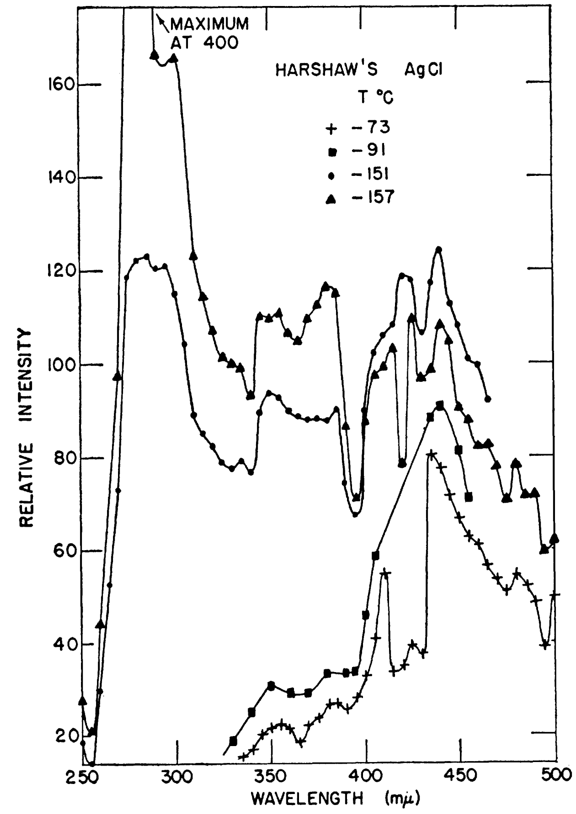

FIG. 9. Fluorescence *vs* exciting wavelength in the temperature range −73°C to −157°C.

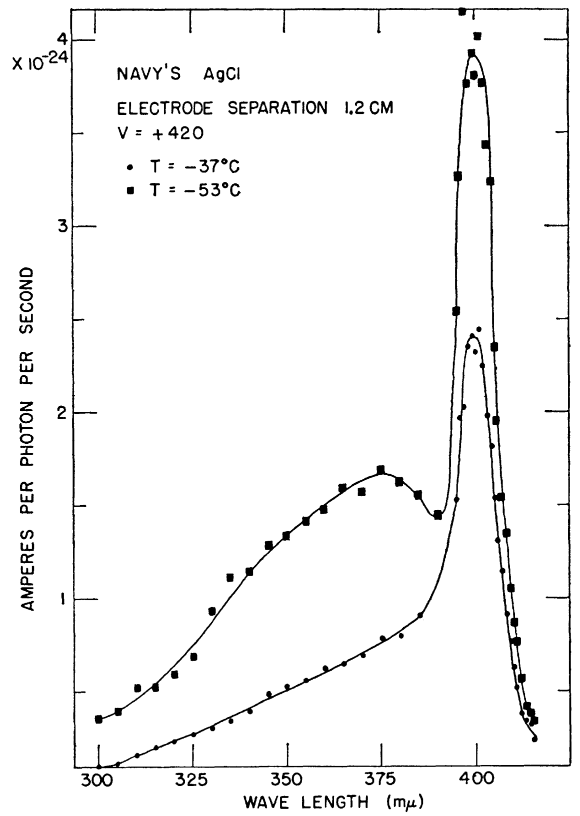

FIG. 10. Photocurrent *vs* exciting wavelength for the 398-millimicron band.

Recently this has been explained[14] by taking into account the recombination of carriers at the surface of the photoconductors. If the surface recombination rate is high, compared with that in the volume of the photoconductor, the equilibrium concentration of charge carriers will be less when these are generated close to the surface than when they are distributed through the volume of the material.

A comparison of the predictions of this theory with experiment has been carried out for photocurrents measured at two different temperatures (Fig. 12). Z is the product of the absorption coefficient and the thickness of the crystal. λ is proportional to the thickness of the crystal, while ξ is proportional to the ratio of surface to volume recombination rates. The experimental photoconductivity was normalized to 1.0 at its peak. Included are the theoretical curves for $\lambda=1$ and $\xi=10$ in one case and $\xi=100$ in the other, which give the best fit. The general shapes of the observed photoconductivity spectral distribution curves are in reasonable agreement with those predicted by the theory,

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[14] H. B. DeVore, Phys. Rev. **102**, 86 (1956).

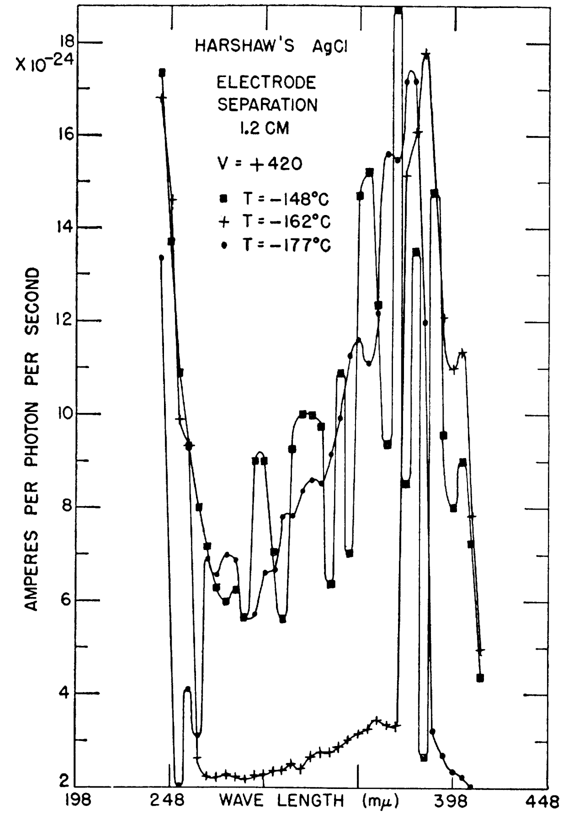

FIG. 11. 270- and 398-millimicron photosensitive bands in the temperature range −148°C to −177°C.

although photoconductivity was not measured over a large enough range of absorption coefficients to make any extensive comparison. However, no consideration of the variation of photoconductivity with temperature was taken into account in the theory. Disagreement may arise from the assumption that every photon absorbed creates a pair of charge carriers. This means that only band-to-band transitions occur. However, it appears that in AgCl other types of transitions may arise, not all of which give rise to photoconductivity.

IV. DISCUSSION

The results in this investigation can be interpreted from a consideration of the absorption curve. With decreasing temperatures the absorption coefficient becomes smaller for a constant wavelength. Absorption in the 398-millimicron band is possible for temperatures in the −55°C region. When the temperature decreases, the absorption in this region decreases and consequently the photoconductivity and any small fluorescence should also decrease. This may be viewed as a transition from the valence states to an intermediate level. In the neighborhood of −175°C there are weak photocurrents in the 398-millimicron region and larger photocurrents in the 270-millimicron region, which corresponds to the relative maximum on the absorption curve.[1] At these wavelengths the electrons are excited from the valence band to a second level of higher energy than the level observed with 398-millimicron radiation.

However, the second level may not be the bottom of the conduction band. Because the absorption curve rises to larger values below 240 millimicrons and hence must reach another maximum, it is felt that the second band does not represent the bottom of the conduction band but a second level between the valence and conduction bands.

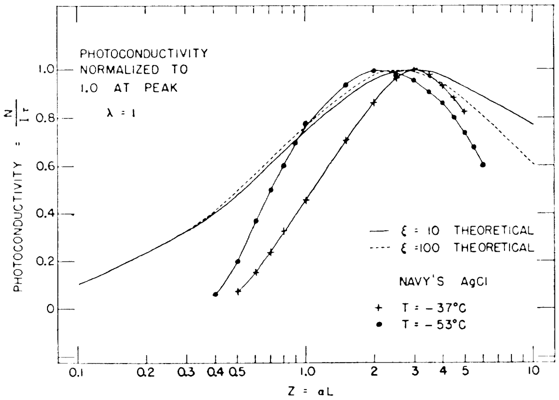

FIG. 12. Spectral distribution of photoconductivity.

Further investigations at wavelengths less than 270 millimicrons are required before the width of the forbidden region can be fixed.

V. ACKNOWLEDGMENT

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