temperature is decreased, should be feasible for cadmium. The change in the susceptibility being due to the fact that λ decreases rapidly with decreasing temperature in the region near T_c. It would also appear that resistance measurements on thin cadmium wires might give additional information on the penetration depth. In light of the large λ_0, wires with diameters in the 5 to 10 micron range should produce a readily measurable effect.

ACKNOWLEDGMENTS

The authors wish to express their gratitude to Mr. L. L. Wyman and Mr. R. E. Pollard of the Chemistry Metallurgy Division of the National Bureau of Standards, who separated the sub-44 micron spheres into suitable size groups by means of a Roller Air Elutriator. They also wish to express indebtedness to their colleagues of the Cryogenics Branch for their helpful suggestions and criticisms.

PHYSICAL REVIEW VOLUME 105, NUMBER 3 FEBRUARY 1, 1957

Optical Absorption by Silver Halides*

SIMPEI TUTIHASI
Institute of Optics, University of Rochester, Rochester, New York

(Received October 31, 1956)

The absorption spectra of silver chloride, silver bromide, and silver iodide films evaporated on quartz plates have been measured at room temperature and liquid nitrogen temperature. It has been found that the "exciton peaks," which have been believed to depend very little upon temperature, become sharper and shift toward the shorter wavelength side as the films are cooled down to liquid nitrogen temperature. Attempts are made to combine the present data with some published data to give absorption curves for silver chloride and silver bromide over a large range of absorption spectrum at room and low temperatures.

In the course of our attempts to produce V centers in silver halides by simultaneous evaporation of the silver halide and a halogen gas, we found it necessary to investigate absorption coefficients of evaporated thin films of pure silver halides at room and liquid nitrogen temperatures. It has been generally believed that the absorption bands of the silver halides depend very little upon temperature.[1] In particular, it has appeared that the absorption edge does not shift markedly upon cooling from room temperature, and that the small bumps on the absorption curves, frequently called the "exciton peaks," do not sharpen or grow more pronounced upon cooling. These beliefs have been the basis for various ideas and speculations regarding the energy band structure and absorption mechanisms in the silver halides. The results of our measurements are somewhat at variance with the older data.

Figure 1 shows the results for AgCl. Curve 1 gives the optical absorption coefficient *versus* wavelength for AgCl at room temperature. Curve 2 gives the optical absorption at −184°C and shows that the "exciton" band sharpens and shifts toward the shorter wavelength side at low temperature. These measurements are taken on a thin (210-mμ) AgCl film evaporated onto a quartz plate held at room temperature. Milliman[2] measured the optical absorption of AgCl at room temperature, using thin samples solidified from the melted materials; Curve 3 shows his result. It is noticed that Curve 1 is in fair agreement with Milliman's curve, Curve 3. Curve

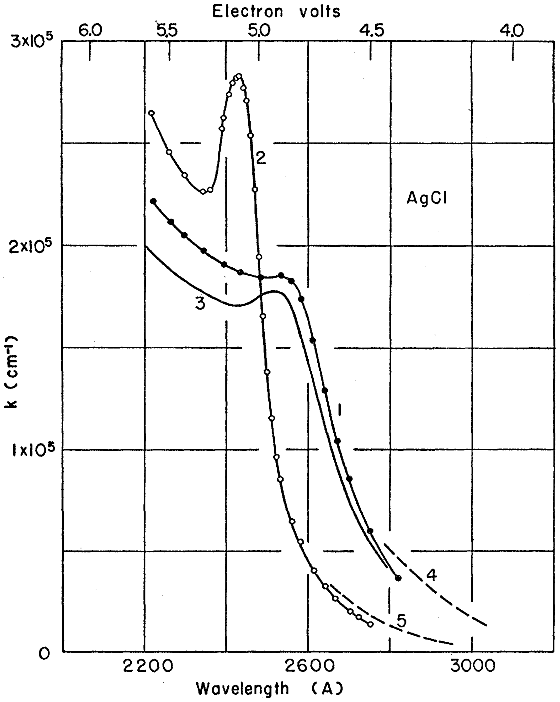

FIG. 1. The absorption spectrum of AgCl at room temperature and liquid nitrogen temperature. Curve 1 is the absorption curve at 26°C, and Curve 2 is at −184°C. The measurements were taken on a thin (210-mμ) evaporated film. Curve 3 shows the absorption curve measured by Milliman at room temperature on fused films. Curves 4 and 5 are data measured by Kaiser on an evaporated film of 510-mμ thickness at 27°C and at −183°C, respectively.

---

* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command.

[1] H. Fesefeldt, Z. Physik **64**, 741 (1930).

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

4 and Curve 5 are those reported by Kaiser[3] on somewhat thicker (510-mμ) evaporated film, the former showing the optical absorption at room temperature and the latter that at liquid nitrogen temperature.

Figure 2 shows the comparable results for AgBr. Curve 1 gives the optical absorption of AgBr at room temperature and Curve 2 gives the absorption at $-184°$C. Again sharpening and shifting toward the shorter wavelength side of the "exciton band(s)" can be noticed. One should notice the appearance of a discrete band at 2610 A in Curve 2. No absolute absorption data on AgBr have previously appeared, to our knowledge, in this spectral region, although Fesefeldt and Gyulai[4] measured optical density in thin films at room temperature. In their data (room temperature) the structure at 3150 A and 2750 A is somewhat more prominent.

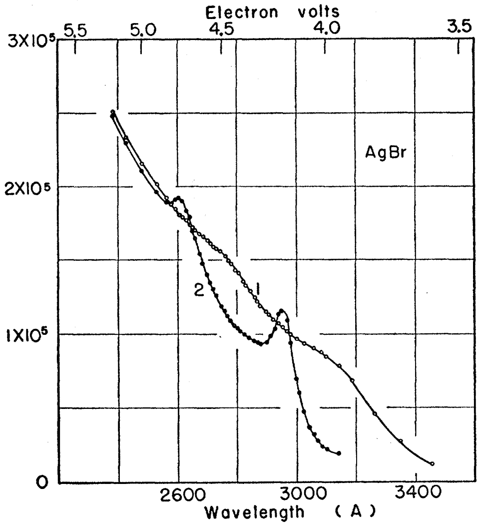

FIG. 2. The absorption spectrum of AgBr at room temperature and at liquid nitrogen temperature. Curve 1: at 23°C. Curve 2: at $-184°$C. The measurements were taken on an evaporated film (250 mμ thick).

Figure 3 shows the results for AgI. Curve 1 gives the optical absorption of AgI at room temperature. Curve 2 gives the optical absorption at $-184°$C. Curve 3 is the absorption curve at room temperature reported by Hilsch and Pohl[5] and is shown for reference. In AgI the first absorption peak at 4230 A shows very little temperature dependence and agrees with the assumption that this band is due to the forbidden transition ($d^{10}-d^9s$) in the Ag ion which becomes allowed because of the tetrahedral symmetry of the Ag ion site.[6] The second peak which occurs at about 3310 A appears to become sharper as the film is cooled to liquid nitrogen temperature.

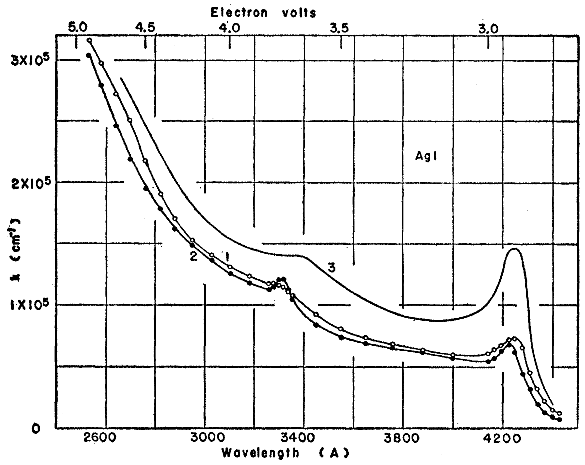

FIG. 3. The absorption spectrum of AgI at room temperature and liquid nitrogen temperature. Curve 1: at 22°C. Curve 2: at $-184°$C. The measurements were taken on two evaporated films, the thickness of which were 500 mμ and 215 mμ. Curve 3 is the absorption curve measured at room temperature by Hilsch and Pohl.

We also evaporated AgCl onto a quartz plate held at $-184°$C and measured the optical absorption, immediately after the evaporation, at $-184°$C. Curve 1 in Fig. 4 shows the result. Curve 2 in the same figure is the absorption curve obtained on the same film after it was warmed up to room temperature. The film was then again cooled down to liquid nitrogen temperature and

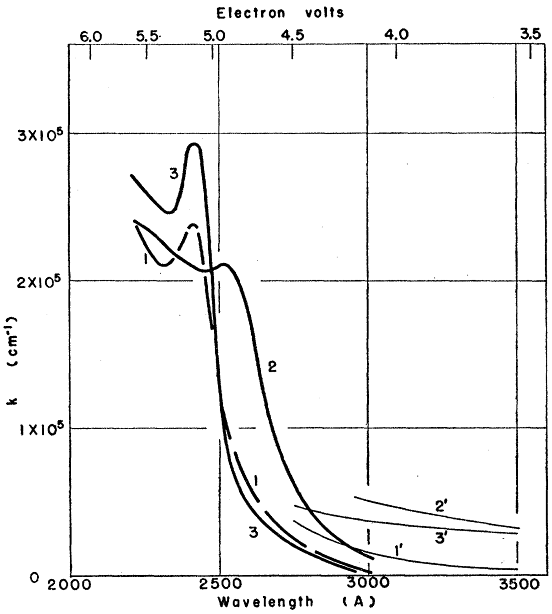

FIG. 4. Annealing effect on the absorption curve of AgCl film. Curve 1: a film of thickness 210 mμ was evaporated on a quartz plate held at $-184°$C, and the optical absorption was measured at $-184°$C immediately after the evaporation. Curve 2: the film was warmed up to 23°C, and the absorption was measured. Curve 3: the film was cooled back to $-184°$C, and the absorption was remeasured. Curves 1′, 2′, and 3′, reported by Kaiser on an evaporated film of 490 mμ, correspond to Curve 1, 2, and 3, respectively.

---

[3] W. Kaiser, Z. Physik **132**, 497 (1952).

[4] H. Fesefeldt and Z. Gyulai, Gött. Nachr. **3**, 226 (1929).

[5] R. Hilsch and R. W. Pohl, Z. Physik **48**, 384 (1928).

[6] F. Seitz, Revs. Modern Phys. **23**, 328 (1951).

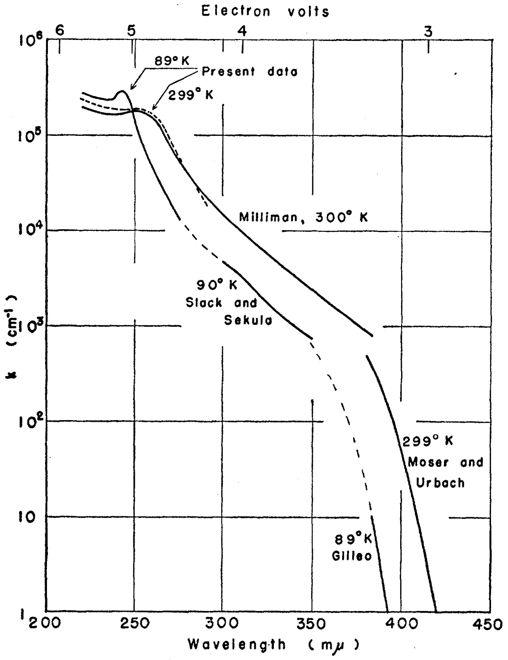

FIG. 5. The absorption spectrum of AgCl at room temperature and at liquid nitrogen temperature.

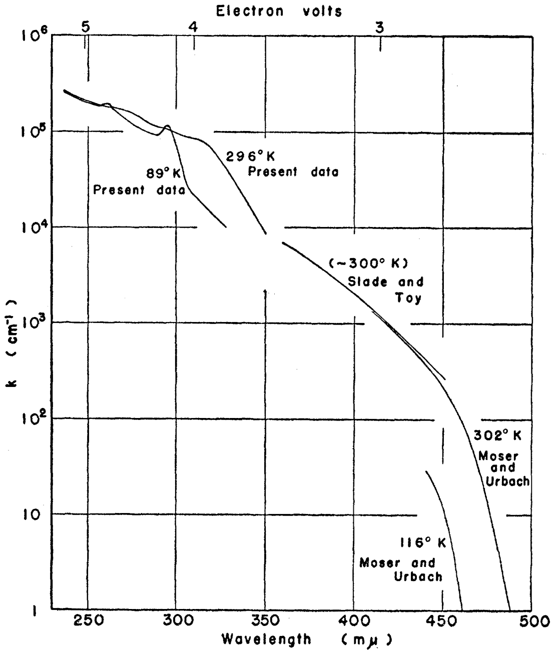

FIG. 6. The absorption spectrum of AgBr at room temperature and at low temperature.

the absorption was remeasured. The result is shown by Curve 3. Curve 3 shows an annealing effect as one might expect and the result is perfectly reproducible. This result is somewhat contrary to that reported by Kaiser,[3] who reported an irreversible increase in the optical absorption in the tail by annealing the film after evaporating it at liquid nitrogen temperature.

The thickness of the films in the above measurements are determined from the position of interference maxima in the transmission spectra. The data are corrected for the reflection loss which is calculated using the refractive indices for the sodium *D* line for silver halides and quartz. The calculated reflection loss is about 20% of the incident light or a density of 0.1 for all three silver halides. This value has been applied for the entire spectral region investigated, and may overestimate the absorption coefficient slightly in the region of high absorption.

In Fig. 5, data from various sources, covering a wide range of fundamental absorption spectrum of AgCl at room and low temperatures, are summarized. Both Milliman's[2] and Slack and Sekula's[7] data were taken on fused films, whereas the curves of Moser and Urbach[8] and of Gilleo[9] were measured on crystals. In Fig. 6, a similar attempt is made to give a composite picture of the absorption spectrum of AgBr at room and low temperatures, using data taken from various sources. The curve of Slade and Toy[10] was measured on fused films and those of Moser and Urbach[8] were taken on crystals.

The attempt to form *V* centers in silver halides has been unsuccessful. The simultaneous evaporation of a halogen gas with the silver halide has so far resulted only in an enhancement of the absorption tail; experiments are being continued.

---

[7] Slack and Sekula's curve was taken from J. A. Krumhansl, *Proceedings of the Conference on Photoconductivity*, Atlantic City, November 4–6, 1954 (John Wiley and Sons, Inc., New York, 1956), p. 450.

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

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

[10] R. E. Slade and F. C. Toy, Proc. Roy. Soc. (London) **A97**, 181 (1920). No comment on the temperature, at which their data were taken, is given in their paper. We assume that their data were taken at room temperature.