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Photolytic Darkening and Electronic Range in AgCl†

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Photolytic darkening and electron range were investigated for a series of silver chloride crystals cut from a single boule which was grown in vacuum by the Bridgman technique. The effect of annealing atmosphere on both the initial darkening rate and electron range is discussed. Darkening produced by absorption of light in the tail of the fundamental band is shown to have a volume and a surface component. The volume darkening produced in a vacuum-annealed crystal is capable of absorbing but not scattering light. The darkened crystal can be bleached selectively with high efficiency by exposure to light near the peak of the induced absorption band. Difficulty is found with interpreting the results entirely in terms of a classical theory for light absorption by colloidal particles suspended in a dielectric medium. Crystals annealed in air darken quite differently then vacuum-annealed samples and crystals heated in chlorine show little sensitivity to light. Somewhat smaller but regular differences in low-temperature electron range were found for the various crystals heat treated in different annealing atmospheres.

I. INTRODUCTION

THE darkening of large crystals of AgCl upon exposure to light in the long-wavelength tail of the fundamental absorption band was first studied by Hilsch and Pohl[1] and by Löhle.[2,3] Throughout the work on photolysis in the silver halides there has been increasing realization of the importance of sample purity, stoichiometry, and condition of strain. Löhle, for example, concluded that in the case of very pure crystals a certain amount of previous handling is necessary for stabilization of the photochemical reaction products. At room temperature well-annealed and especially pure crystals darken slowly. Similarly, the electronic properties of AgCl have been shown to depend on the way in which the samples are handled.[4] Identical electron ranges result only when crystals are cut from adjacent regions of the same boule and prepared in a standard fashion by heat treatment in air at around 400°C.

The present experiments on both the rate of darkening and low-temperature electronic range were carried out in an effort to learn more about the darkening process, which is imperfectly understood, and to discover if there are any noticeable effects produced by the atmosphere surrounding the crystal during heat treatment. Crystals were annealed in air, vacuum, or chlorine in an attempt to control stoichiometry. On statistical grounds it can be shown[5] that the exact composition of any crystalline compound must be dependent upon the partial pressures of the components in equilibrium with the crystal phase. Shottky and Wagner[6] were the first to show this in the case of small deviations from stoichiometry. Silver chloride is a substance in which defects in the metal component predominate and consist mainly of interstitial silver ions and silver ion vacancies. For these defects the theory predicts either an excess or deficiency of silver for a crystal in equilibrium with chlorine gas depending upon the partial pressure of the gas.[7] Moreover, equilibrium between the halogen gas and the crystal apparently sets in rapidly at high temperature as shown by Koch and Wagner from a study of tarnishing reactions[8] and more recently by Luckey[9] for the case of bromine and AgBr.

In the present investigation marked differences in the initial rate of darkening were found for vacuum or air anneal, and crystals treated in chlorine showed little or no darkening within their volume. Somewhat smaller but regular differences in electronic range were found between the samples.

II. SAMPLE PREPARATION

All measurements were made on sections cut from a crystal grown by the Bridgman technique in a cylindrical platinum crucible measuring 1.5 cm in diameter by 10 cm long. Apparatus used previously[4] was modified so that the crucible and contents were contained in a vacuum of 5×10^{-4} mm or better. The rate of lowering was 1.5 mm/hr and at no time was the warm or molten AgCl exposed to the atmosphere. Raw material for charging the crucible was cut from unrolled crystal supplied by the Harshaw Chemical Company. After solidification of the melt and slow cooling to room temperature, the crystal was melted out of the crucible in vacuum and sections 1 through 8, each about 4 mm thick, were cut as needed from the boule starting at the

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

[2] F. Löhle, Nachr. Ges. Wiss. Göttiningen **II**, 271 (1933).

[3] Photolysis in the silver halides is discussed by F. Seitz, Revs. Modern Phys. **23**, 328, 342 (1951).

[4] F. C. Brown, Phys. Rev. **97**, 355 (1955).

[5] R. H. Fowler and E. A. Guggenheim, *Statistical Thermodynamics* (Cambridge University Press, Cambridge, 1939), pp. 545–553.

[6] W. Shottky and C. Wagner, Z. physik. Chem. **B11**, 163 (1930).

[7] L. G. Rees, *Chemistry of the Defect Solid State* (Methuen and Company, Ltd., London, 1954).

[8] W. Koch and C. Wagner, Z. physik. Chem. **B38**, 295 (1937).

[9] G. W. Luckey, Phys. Rev. **98**, 1558 (A) (1955); G. W. Luckey and W. West, J. Chem. Phys. **24**, 879 (1956).

lower end. About 0.010 inch of material was removed from all surfaces exposed to the steel cutting saw by means of a tungsten carbide surfacing tool. Kerosene was used as a coolant during the cutting operation, but the slices mounted in beeswax were surfaced by using the carbide tool without a lubricant. This was found to leave a reasonably good optical surface which could be improved by lapping very lightly on dry filter paper. Then the samples were immersed in petroleum ether, water, nitric acid, and finally rinsed in distilled water. The use of sodium thiosulfate or other etches was avoided before or after the casting of the crystal to eliminate the possibility of contamination by sulfur. Inspection under red polarized light showed that the samples were moderately strained before heat treatment. Large-angle grain boundaries separated the cylindrical disks into two or sometimes three single-crystal regions. The AgCl was exposed only to darkroom red light previous to making the darkening runs.

Following the treatment described above, the samples were annealed at 400°C in vacuum, air, or chlorine as indicated in Table I. The annealing was carried out in the central region of a well-insulated horizontal tube furnace which was turned on after establishing the desired annealing atmosphere. Samples number 1 and 2 held at 400°C for three hours then cooled uniformly to room temperature at the slow rate of 12°/hr. Crystals 3 through 8 were cooled exponentially at a maximum initial rate of 100°/hr by turning off the furnace. Observation between crossed polaroids showed that strains did not result from this faster rate of cooling and earlier crystal counter work established that electron ranges resulted which were similar to those obtained with the slower, linear cooling rate. In the case of the vacuum and chlorine anneal the crystals rested on a flat quartz plate at the end of a sealed-off quartz tube which projected into the furnace. Pumping to high vacuum was achieved by a glass-metal oil diffusion pump which was adequately trapped. With the exception of crystal 1, the annealing in chlorine or vacuum was accomplished by resting the samples directly on the quartz flat. In the case of the vacuum anneal of number 1, the quartz dust was sprinkled on the flat with results identical to the other vacuum anneals. AgCl does not stick to clean quartz or Pyrex glass when heated in vacuum or chlorine. However, when heated in the air the AgCl was found to adhere very strongly to the glass or quartz; therefore, precautions must be taken. The air anneals were carried out, as for the older crystal counter work, by imbedding the samples in special reagent-grade magnesium oxide in a stainless-steel-lined copper box.

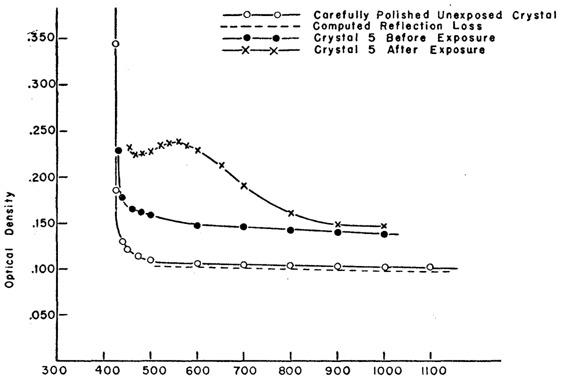

FIG. 1. Optical density *vs* wavelength for sample 5, thickness 0.509 cm, surfaced as explained in the text. The solid dots are before exposure and the crosses after exposure to 416-millimicron radiation (1.95×10^{16} absorbed quanta/cm^2). The open circles show the optical density of an unexposed crystal, thickness 0.65 cm, which was carefully polished using solvents.

In the case of the chlorine anneals, precautions were taken to remove air or other contaminants from the system. An all-glass manifold connected with the tube containing the sample was pumped to less than 10^{-5} mm pressure. Then the manifold was isolated from the pumps and gauges by turning off a large glass stopcock. Matheson chlorine, 99.5% purity, was admitted to the manifold and condensed in a side tube using liquid nitrogen. The stopcock was then opened briefly to pump off the small amount of noncondensible gases before warming the side arm containing most of the chlorine. This served to purify the gas and also permitted condensation of all the chlorine in the side arm if required in later operations. This degassing operation always preceded the warming of the furnace and the heat treatment indicated in Table I.

TABLE I. Annealing treatment and darkening rate.

Sample	Atmosphere during anneal	Duration of anneal[a] hours	Appearance after cooling[b]	Darkening rate[c] Δ(o.d.)
1	vacuum	7.0	dark	0.060
2	air, 760 mm	7.0	light	0.015
3	vacuum	9.0	dark	0.075
4	air, 760 mm	15.0	light	0.007
5*a*	chlorine, 760 mm	5.5		
	$+p(Cl_2)$ at 77°K[d]	9.0	light	0.086
5*b*	anneal as 5*a* +vacuum	9.0	dark	0.129
6	chlorine, $p(Cl_2)$ at 77°K	6.5	dark	0.072
7	chlorine, 760 mm	5.0	light	<0.002
8	chlorine, 250 mm slowly cooled to 120°C quenched in vacuum	6.0	light	0.005

[a] Samples 3–7 were held at 400°C for the times indicated, and were then quenched exponentially at an initial rate of 100° per hour. Samples 1, 2, and 8 were held at 400°C for 2 to 3 hours, and were then slowly cooled at 12° per hour. The numbers shown are the times above 350°C.

[b] Those indicated as "dark" appeared slightly dark under red light after removal from the annealing oven. Although these samples were heat-treated in the absence of light, a small amount of decomposition took place.

[c] The change in optical density, measured at 580 mμ, upon exposure to 416 mμ radiation for five minutes (1.96×10^{16} absorbed quanta/cm^2).

[d] While the crystal was at 400°C, the chlorine was condensed out in a side tube at liquid nitrogen temperature.

Some information concerning the purity of the AgCl was had from a routine spectrographic analysis[10] of sample number one. Iron was found present to an amount between 0.001% and 0.10% by weight. Much smaller amounts of Ca, Cu, Hg, Mg, Mn, Na, Pb, and Si were detected. The analysis was not capable of revealing the presence of sulfur or oxygen in the crystals. The ionic conductivity of sample two was measured from 20°C to 350°C by means of an ac bridge.[11] When plotted in the conventional way, $\log\sigma$ *versus* $1/T$, the results agreed qualitatively with the data of Lehfeldt.[12] The slope of the curve in the intrinsic region yielded an activation energy of 0.90 electron volt. The "knee" of the curve, separating intrinsic and structure sensitive conductivity, occurred in the vicinity of 150°C which would indicate a concentration of iron more nearly 0.001% than the higher figure mentioned above.

III. OPTICAL MEASUREMENTS

In making the measurements on photolytic darkening a modified Beckman model DU spectrophotometer was used both as a monochromator to expose the crystals and in its normal function to determine optical density. The modifications in the instrument were of a mechanical nature to permit the exposure of several small areas on each crystal slice and to allow for accurate, reproducible, positioning of samples. These changes resulted in a reproducibility of ±0.002 in optical density over the range most used in this work.

Darkening was produced in the crystals by light of 416 mμ wavelength. This wavelength is absorbed strongly enough so that only 40% of the incident light will pass through the 4-mm samples. For the exposures at a nominal 416 mμ, an exit slit width of 2 mm was used in order to keep exposure times down to a reasonable level. As a consequence of this wide slit opening, the emerging light beam had a half-width of 20 mμ. The intensity of the emerging light beam was measured using a General Electric vacuum thermocouple of the type found in the type DW-60 radiation meter and a Leeds and Northrup model 2284B voltage galvanometer. In turn, the thermocouple was calibrated against a standard lamp obtained from the National Bureau of Standards in the manner recommended by the Bureau. The photon flux at 416 mμ was about 1.1×10^{14} quanta per square centimeter per second. Although the absolute value of the incident intensity is uncertain to 20%, the relative uncertainty in the exposures on any given crystal is no more than 2%.

Several trials were made to show that variability was not being introduced by straining the crystals during handling. For example, the darkening experiments were made after the electronic measurements for all the samples discussed here and it was shown that this procedure had little effect on the subsequent rate of darkening.

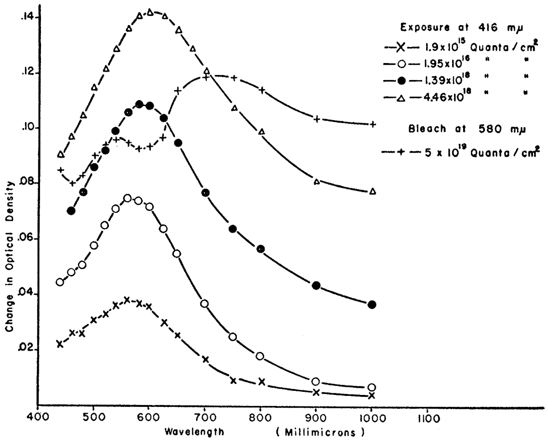

FIG. 2. Darkening results for sample 3, characteristic of crystals annealed in vacuum. Plotted are the changes in optical density produced by the absorption of various amounts of 416-mμ radiation.

Sample 1 was investigated at four spots across its surface and the initial darkening rates were found to be uniform across the crystal. In addition, to eliminate the possibility of a large anneal-induced surface nonuniformity, crystals 1 and 2 had their surfaces machined a few thousandths just before the optical measurements and crystals 3 and 4 were left with the surface as obtained from the anneal. Matching heat treatments yielded similar results.

One of the difficult technical problems associated with this investigation was the attempt to produce surfaces with reproducible optical properties. Since exactly similar optical surfaces were not achieved, the change in optical density rather than the total optical density is compared for the various crystals. In Fig. 1 may be seen the difference in apparent optical density between a carefully polished sample[4] and a sample whose surface has been milled by using a round-nosed tungsten carbide bit mounted in a fly cutter as mentioned in Sec. II.

The darkening produced by exposure at room temperature to various amounts of 416-mμ radiation is shown in Figs. 2 through 4 where we have plotted the change in optical density against wavelength. Figure 2, which is drawn for crystal 3, is representative of the results for a vacuum anneal. A rapid initial darkening occurs with a distinct peak at about 580 millimicrons. On the other hand, air-annealed crystals showed a slower initial darkening with a less well defined absorption peak as illustrated by Fig. 3. Crystals heated in an atmosphere of chlorine showed little or no initial darkening and the peak formed after long exposure was very small as indicated by Fig. 4.

In order to further illustrate the darkening behavior of a rapidly darkening crystal, the results obtained for the vacuum anneal of number 3 were plotted with the

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[10] New England Spectrochemical Laboratories, Ipswich, Massachusetts.

[11] W. D. Compton, thesis, University of Illinois, 1955 (unpublished).

[12] W. Lehfeldt, Z. Physik 85, 717 (1933).

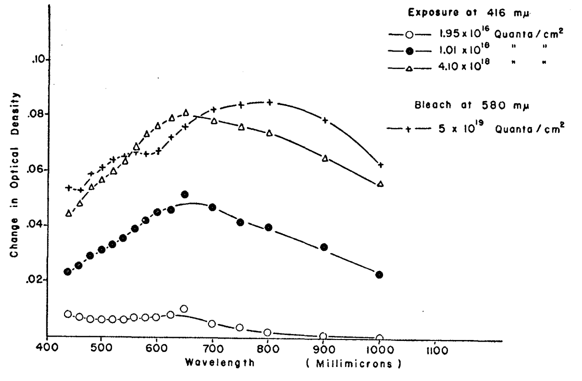

FIG. 3. Darkening results for crystal 4, typical of air-annealed samples.

change in optical density as ordinate and the exposure in quanta absorbed per cm² as abscissa. This semi-logarithmic plot may be seen in Fig. 5 with curves presented for several wavelengths. The saturation of the absorption peak near 580 mμ may be clearly seen. It is also to be noticed that the plateau for the peak breaks upward at the same time that the tail of the absorption curve begins to rise.‡

During the early part of the darkening of a rapidly darkening crystal, up to about 10^{17} absorbed quanta per cm², the darkened region can be seen as a purplish spot spread through the volume as observed in transmitted light. The spot cannot be seen by scattered light. If the same crystal is further exposed to 416-millimicron radiation, the additional darkening which occurs appears to be localized on the surface. This surface layer, visible in scattered light, can be completely removed by taking a 0.001-inch cut across the surface of the crystal leaving the volume darkening which is visible in transmitted light only. In examining Figs. 2, 3, and 4 it is important to note that by the time about 2×10^{16} quanta are absorbed, the absorption peak due to silver in the volume of the crystal appears to be completely formed. Thereafter, further long exposure causes the entire curve to rise at the same rate and this is due mainly to the production of darkening on the surfaces.[13] It is the volume part of the darkening which will be most interesting to us in the discussion to follow.

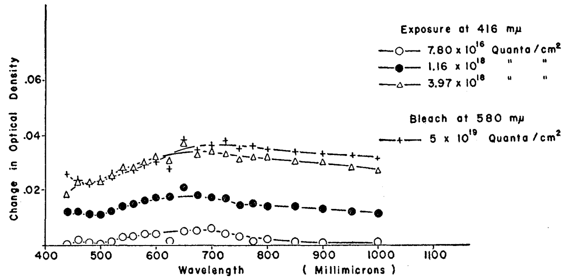

FIG. 4. Darkening results for crystal 7 which was heat-treated and cooled in an atmosphere of chlorine The small darkening shown was localized very close to the surface

An effort was made to detect any wavelength-dependent scattered light from illumination of the darkened portion of a vacuum-annealed crystal. The unexposed part of sample number 6 was given a second long anneal in vacuum then darkened by light of 416 mμ. After absorption of 4.2×10^{16} quanta/cm² the extinction, characteristic of volume darkening, shown in curve (a) of Fig. 6 was produced. The crystal was mounted in a special holder in a Model DU spectrophotometer having a photomultiplier attachment. By means of collimating holes and a small mirror, light from the monochromator was allowed to strike the crystal in the normal fashion to produce and measure the darkening, or conversely the darkened region was illuminated from below with a beam parallel to the face exposed to the photomultiplier. By moving the crystal, light scattered in a direction 90° to the incident beam could be compared for a darkened and an undarkened adjacent region of the crystal. It was estimated that scattered light amounting to less than 0.001% of the incident beam could easily be detected. No wavelength-dependent scattering was observable from the darkened volume of the crystal.

Hilsch and Pohl[1] reported that selective bleaching of the adsorption band could be produced by illumination within the band itself. To test this our crystals, darkened in both the volume and on the surface (absorption of about 4×10^{18} quanta per cm²), were illuminated with 580-mμ light near the absorption maxima. The results shown in Fig. 2 for a vacuum-annealed crystal indicate a strong bleaching effect at the wavelength of the incident light. An air-annealed sample, Fig. 3, bleached only slightly and in the case of the chlorinated sample, Fig. 4, there is practically no bleaching effect.

The bleaching curves of Fig. 2 and Fig. 3 were produced by long exposure to 580-mμ light having a spectral half-width of about 60 mμ. Bleaching under more controlled conditions is shown in Fig. 6, where, as mentioned above, volume darkening only is produced by absorption of 4.2×10^{16} quanta per cm² at 416 mμ. See curve (a), Fig. 6. Now further absorption of approximately the same number of quanta at 580 millimicrons (in the spectral band shown) resulted in curve (b), Fig. 6. On the other hand, if the bleaching is carried out at 520 mμ instead of 580, absorption of 4.2×10^{16} quanta per cm² produces the somewhat smaller effect shown by curve (c). Note that the bleaching at 580 mμ is highly efficient. Extended illumination at 580 mμ (over a wider 60-millimicron

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‡ Curves of this general shape have been reported by N. Nail *et al.*, Phys. Rev. 98, 1557(A) (1955). They give evidence that the first rise and plateau are due to volume darkening and depend strongly on crystal purity.

[13] Production of silver on the surface is responsible for the second upward turn of the curves in Fig. 5. This was pointed out in a private correspondence by G. W. Luckey of the Eastman Kodak Laboratories.

bandwidth) is capable of bleaching almost the entire absorption band. Repeated exposure to 416-mμ light will again produce darkening.

IV. ELECTRON RANGE

Before the darkening experiments and directly after the heat treatment, the samples were inserted in the crystal counter apparatus described previously in conjunction with a measurement of electron mobility.[4] They were slowly cooled to 86°K where the ionic conductivity is frozen out and a collecting voltage of 3500 volts can be applied. The pulse-height response of the crystals to Co^{60} gamma rays, of energies 1.1 and 1.3 Mev, was used as an indication of electron range. Analysis of the pulse-height distribution was made by observation of a large number of superimposed pulses recorded by photographing an oscilloscope screen. Carrier range in these samples was considerably less than in the mobility work referred to above, probably due to the presence of impurity. Electrons drift on the average only a fraction of the way through the thickness of the crystals.

TABLE II. Electronic properties of the crystals annealed as shown in Table I. Crystal counter data at 86°K.

Sample	Thickness, d cm	Saturation, ψ^a	Schubweg, w cm	Trapping time, T^b mμsec	Trap density, N^c cm^{-3}
1	0.356	0.14	0.050	18.7	4.5×10^{15}
2	0.351	0.33	0.120	67	1.3×10^{15}
3	0.378	0.14	0.053	21	4.0×10^{15}
4	0.399	0.38	0.160	67	1.3×10^{15}
5a	0.509	0.05	0.024	13	6.4×10^{15}
5b	0.509	0.19	0.097	52	1.6×10^{15}
6	0.368				
7	0.353	0.23	0.081	30	2.8×10^{15}
8	0.421	0.23	0.097	43	1.9×10^{15}

[a] For an applied potential of 3469 v.
[b] From $T=w/\mu E$ and for mobility $\mu=274$ cm²/v sec.
[c] Computing the thermal velocity as discussed in the text and taking the trapping cross section $\sigma=10^{-15}$ cm².

Cobalt-60 gamma rays produce ionization in AgCl predominantly by Compton effect with a maximum energy of the recoil electron in the vicinity of 0.94 Mev. A fraction of the scattered gamma ray energy will be absorbed within the crystal, so one expects an energy loss distribution with a peak in the neighborhood of 1.0 Mev. The charge, Q, induced on the electrodes of the crystal by an absorption of energy E is given by $Q=(Ee/\epsilon)\psi$, where e is the electronic charge, $\epsilon=7.5$ electron volts, the energy per electron-hole pair,[4] and ψ is the degree of saturation of the crystal counter. This latter quantity is given, for a volume release of ionization, by

$$\psi=\frac{w}{d}\left[1-\frac{w}{d}(1-e^{-d/w})\right],$$

where w is the mean range or "schubweg" and d the crystal thickness.[14] Except for crystals 2 and 4, ψ was taken as approximately equal to w/d since $w \ll d$. A sharply peaked pulse-height distribution showed this to be a reasonable procedure. In the case of air-annealed samples 2 and 4, the distribution was noticeably broader, ψ was of the order 0.35, and w/d was estimated from the more exact expression given above. The charge, Q in coulombs, was found from the peak of the observed pulse-height distribution. Table II gives the values of ψ and of w computed from Q.

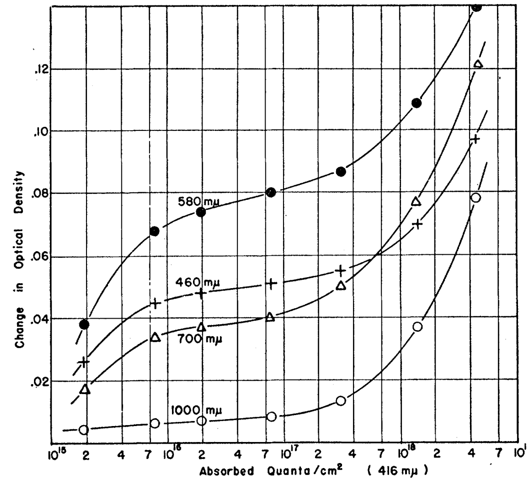

FIG. 5. Change in optical density *vs* exposure for vacuum-annealed crystal 3. The rise in the curves at about 10^{18} absorbed quanta/cm² is due to the production of silver near the surface.

Since electron mobility, μ, is equal to 274 cm²/volt sec at 86°K in AgCl, the mean time before trapping, T, can be found by using the relation $w=\mu ET$, where E is the electric field. By computing the thermal velocity of

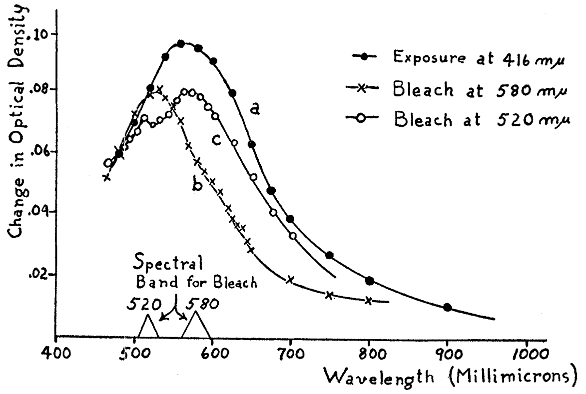

FIG. 6. Bleaching of the volume component of darkening in sample 6 (vacuum-annealed following the treatment indicated in Table I). Curve (a) shows the darkening produced by absorption of 4.2×10^{16} quanta/cm². Further absorption of the same number of quanta at 580 mμ produces curve (b). On the other hand, absorption of 4.2×10^{16} quanta/cm² at 520 mμ produces the curve (c).

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[14] N. F. Mott and R. W. Gurney, *Electronic Process in Ionic Crystals* (Oxford University Press, London, 1940).

TABLE III. Quantum efficiency, assuming the Mie theory, for the production of silver, sample 3, thickness 0.378 cm.

Absorbed quanta/cm² N_0	Absorption constant, 570 mμ k(mm^{-1})	Silver atoms/cm²[a] N_1	Efficiency N_1/N_0
1.90×10^{15}	0.022	1.64×10^{15}	0.86
7.60×10^{15}	0.068	3.08×10^{15}	0.41
1.95×10^{16}	0.045	3.36×10^{15}	0.17
1.39×10^{18}	0.066	4.90×10^{15}	0.0035

[a] Estimated from the Mie theory, assuming spherical particles of silver 600 A in diameter.

the conduction electrons[15] and assuming a cross section for trapping, one can compare the number, N, of traps per cm³. The results are presented in Table II.

We assume above that only electrons are mobile at low temperatures in these crystals. This was shown to be the case for air-annealed samples prepared by remelting Harshaw AgCl.[4] The assumption was tested in the present investigation for the samples having larger values of ψ. Beta rays which stop in a crystal near one electrode used to release ionization, and the pulse-height response observed for both polarities of collecting voltage. Hole ranges as large as the electron ranges were certainly not observed, and because of the small pulse heights, the drift of positive holes was not clearly demonstrated in any of the samples.

V. DISCUSSION

The absorption curves which we obtained in the case of rapidly darkening crystals, see Fig. 2, closely resemble those obtained by Löhle, although he was able to measure somewhat lower levels of darkening. Let us try to interpret them in terms of an optical absorption theory which assumes spherical particles of silver imbedded in a dielectric continuum. A simple theory, applicable when the particle size is small compared to the wavelength of light, is outlined by Pohl.[16] For AgCl it predicts an absorption maximum near 500 mμ whose magnitude, k(mm^{-1}), is proportional to the concentration by volume of silver. When the particle size is larger than about 80 A in diameter, the more complex theory of Mie[17] should be applied. This latter theory shows that, with increasing particle size, the efficiency for producing extinction decreases and the position of the maximum shifts toward longer wavelengths. Rohloff[18] has recently published curves for AgCl using the Mie theory. From these it is seen that our bands which have a maximum at 570 millimicrons correspond most nearly to the curve for 600 A diameter. It should be noted that this seems to be stable particle size in our crystals—the peak of the observed bands shift only slightly to longer wavelengths upon extended exposure.

Rohloff's curves are for a concentration of 2.3×10^{17} atoms per cm³ and the absorption coefficient at the maximum of the 600 A curve is about 1.2 mm^{-1}. An estimate of the number of atoms of colloidal silver formed per cm³ in our samples can be had by multiplying the above concentration by the ratio of absorption constants. We correct for crystal thickness to find the number of atoms formed per cm² of exposed area and finally divide by the number of absorbed quanta to determine a quantum efficiency for production of photolytic silver assuming the Mie theory. Results for crystal 3 are shown in Table III where it is assumed that the particles are all of 600 A size. As the number of absorbed quanta becomes larger the computed efficiency decreases to very low values as can also be seen from Fig. 5. One notes that the initial darkening occurs with a quantum efficiency as high as 0.86 and that a marked saturation in darkening rate takes place between 10^{15} and 10^{16} absorbed quanta. Average absorption coefficients were used in Table III, but similar results occur when the exponential absorption of the radiation which produced the darkening is taken into account.

If the Mie theory is applicable and the collodial silver particles are assumed to be spheres as large as 600 A in diameter, they each contain a very large number of silver atoms, roughly 10^{12}. Table III shows that during the early darkening the observed band would be due to about 4×10^{15} atoms per cm³, which means that the silver particles are initially in very low concentration and widely separated in the crystal. On this basis, there would be, in fact, only 10^3 to 10^4 of these large silver particles per cm³. If these large particle sizes actually exist, they are produced by a process of aggregation which is highly efficient. Furthermore, we did not observe any appreciable time delay in their production at room temperature. Löhle[2] also looked for, but did not find a delay between illumination and production of the colloidal aggregates.

There are further difficulties with the above analysis based entirely on the classical Mie theory. First, and perhaps most convincing, the classical theory predicts that for particles as large as 600 A an appreciable part of the extinction arises due to light scattering. The scattered light would have a wavelength dependence similar to the absorption curves.[19] Attempts to observe this light scattered from a volume-darkened crystal, both visually and by sensitive photometric means, failed. In addition, the bleaching described in section III occurred with remarkably high efficiency. One has difficulty in imagining a bleaching mechanism for large silver aggregates which is so efficient.

It is evident from the bleaching results that we are not dealing with a single band (or particle size) but a superposition of two or more absorption bands. One can effect a partial separation of the components by bleaching at 580 mμ. Curve (b), Fig. 6, shows a peak

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[15] For this purpose we use the expression $\frac{1}{2}m^*v^2=(3/2)kT$ and take $m^*\simeq0.27m$, where m is the free-electron mass.

[16] R. W. Pohl, *Optik und Atomphysik* (Springer-Verlag, Berlin, 1954), p. 206.

[17] G. Mie, Ann. Physik **25**, 377 (1908).

[18] E. Rohloff, Z. Physik **132**, 643 (1952); see Fig. 1.

[19] F. Seitz, Revs. Modern Phys. **26**, 7 (1954); see p. 37.

more nearly characteristic of the smallest particle size predicted by the dispersion theory. The band or bands near 520 mμ seem to be more stable than the longer wavelength component. There is further evidence for this form the results of heating a darkened crystal to 150°C for 10 min and then quenching. The curve peaked at 580 mμ is observed to shift toward 500 mμ. It is possible that extinction near 500 mμ is due to small aggregates, whereas the longer wavelength bands arise from a different kind of center also molecularly dispersed throughout the crystal. The classical theory alone does not seem adequate to explain the observed behavior.

Heat-treating in air causes a marked reduction in the amount of darkening produced during the first 5 min of exposure (absorption of 1.96×10^{16} quanta/cm^2). It also seems to allow a somewhat longer electron range than in the case of a vacuum anneal. Comparing crystals number 2 and 4 with 1 and 3 we see that long electronic range appears to be associated with low darkenability. However, the differences in optical behavior are considerably greater than the differences in low-temperature electronic range, and one takes note of crystal 5*b*, which was reannealed for 9 hours in vacuum after exposure to chlorine at 400°C. Here the darkening rate is high as well as the electronic range.

It should be kept in mind that impurities, chiefly iron, were present in our samples to not less than 5×10^{17} atoms/cc. Also, the darkening proceeded with high efficiency only in the vacuum-annealed samples. The saturation level of optical density may well be associated with impurity content and with a state of the crystal achieved during the heat treatment. An important requirement for high efficiency in the production of photolytic silver is that recombination between holes and electrons be delayed until silver ions can neutralize the charge of electrons trapped at sensitivity centers. It is thus necessary to consider that there are scattered throughout the crystal a sufficient number of hole traps which are not also recombination centers. Such is the case for AgCl containing copper—the hole traps being copper in the cuprous state.[20] Traps for holes may well be the important factor in determining the initial darkening rate in our crystals. This is certainly one explanation for the low sensitivity of crystals 7 and 8 heat-treated in the presence of chlorine. The simplest mechanism by which chlorine can enter the crystal is by an outward migration of interstitial silver ions and an inward migration of holes and silver ion vacancies. It is unlikely that we introduce enough chlorine to influence greatly the concentration of interstitial silver ions, which is determined in the structure-sensitive room temperature region by vacancies associated with multivalent impurities. Instead excess holes in the chlorinated crystals fill hole traps and therefore exert a sensitive influence on the darkening.

The amount of chlorine added depends on the equilibrium temperature and upon the halogen pressure.[21] Crystal 8 should have less of an excess than 7 but it still shows little or no darkening. Crystal number 6, which was annealed at the very low vapor pressure of chlorine gas above solid chlorine at 77°K, behaved in all respects like a vacuum-annealed sample. It appeared slightly dark after anneal, indicating a small amount of decomposition which was the case with all the samples treated in vacuum. Presumably the Cl_2 pressure established for number 6 was below that required for stoichiometric composition at 400°C.

We conclude that annealing atmosphere exerts a strong influence on both the optical behavior and the electronic properties of AgCl. Further experiments are indicated which take impurity concentration and crystal composition into account.

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[20] F. Urbach, Research Laboratories, Eastman Kodak Company Rochester, New York (private discussion). The authors are aware of the work on the optical properties of the silver halides being carried out at the Kodak Laboratories. See, for example, F. Moser and F. Urbach, Phys. Rev. **102**, 1519 (1956) and articles to be published.

[21] C. Wagner, Z. physik. Chem. **B32**, 447 (1936).