

The result of the numerical sum in $S'_{2/3,2/3,1/2}$ is

$$\sum_{i=1}^3 \frac{n_i \hbar c_i}{\sinh \hbar_i \pi \alpha} = -0.574459 \times 10^{-4}. \quad (\text{A16})$$

To complete the numerical evaluation, we use the values of the other two sums computed in the calculation of *EFG* at the *A* layer site. The numerical result for a *B* or *C* layer site, $q_{2\text{-hcp}} = 0.4870 \times 10^{22} \text{ cm}^{-3}$, is nearly 10% lower than the *A* layer site value.

Electron Spin Resonance and Optical Studies on Copper-Doped AgCl

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(Received 3 June 1964)

Upon exposure at room temperature, large, strain-free AgCl crystals containing up to 10^{17} cuprous ions per cm^3 show a stable darkening (print-out) and an electron spin resonance (ESR) absorption which is characteristic of cupric ions. The intensity of the print-out band and of the ESR signal are proportional. Essentially all the cuprous ions are converted to cupric ions by prolonged exposure. For well-annealed crystals, the cupric ESR signal is stable below 180°C in exposed samples and stable below 280°C in halogenated samples, showing that the cuprous ion is a deep hole-trap at room temperature. When the samples are deliberately strained, there are rapid decays in the ESR signal at room temperature. Evidence from ESR suggests that such decays are related to coagulation of cupric ions. Exposure at -180°C converts some cuprous to cupric ions without associated vacancies. Total conversion of cuprous to cupric ions by exposure at room temperature is not obtained in samples containing higher copper concentrations. It is suggested that, at sufficiently high concentrations, cupric ions can compete with intrinsic electron traps, thereby limiting the maximum ESR signal and darkening produced by exposure to smaller values than those expected on the basis of studies of samples with low copper concentration.

I. INTRODUCTION

A NUMBER of studies of the optical,¹ electronic,^{2,3} and magnetic effects⁴⁻⁷ associated with low concentrations of copper ions in large AgCl crystals have been reported. The copper ion in the AgCl lattice can exist in either the cuprous (Cu^+) or the cupric (Cu^{2+}) valence state. These valence states are readily established by heating to about 400°C in nitrogen or chlorine atmospheres, respectively.⁸ It is found that the cupric ion produces a broad optical absorption in the visible region (Fig. 1), which is stable in well-annealed crystals but decays in days in strained samples. This decay seems to be produced by some sort of aggregation of the cupric ions. The original cupric absorption band can be restored by heating the sample to about 200°C ; this

treatment apparently redisperses the cupric ion.^{1,4} The cuprous ion adds a weak absorption "tail" to the fundamental absorption edge of AgCl (Fig. 1). Recent studies³ have clarified the positions of energy levels and the transitions involved in optical absorption and emission associated with the copper ions.

When exposed, pure AgCl crystals do not darken visibly in their volume. AgCl crystals containing cuprous ions darken or "print-out" efficiently at room temperature upon exposure to volume-absorbed light.¹ The absorption produced by exposure is a broad band with the peak near $570 \text{ m}\mu$ and is stable at room temperature. The strength of the exposure-induced band is initially proportional to the number of absorbed quanta. For concentrations of cuprous ion not exceeding $10^{17}/\text{cm}^3$, the maximum attainable absorption of the exposure-induced band is proportional to the copper concentration and occurs when the number of volume-absorbed quanta is approximately equal to the number of cuprous ions in the sample.⁸ Further exposure, even after a period of dark storage, does not produce significant additional darkening. This behavior is illustrated in Figs. 1 and 2. It was postulated that the cuprous ions act as deep hole-traps at room temperature, forming cupric ions, and that silver ions combine with trapped electrons to form metallic silver. The absorption produced by exposure is then due to the superposition of two absorption bands: one due to silver and one due to cupric ions.

¹ F. Moser, N. R. Nail, and F. Urbach, *Phys. Chem. Solids* **9**, 217 (1959).

² A. M. Gordon, *Phys. Rev.* **122**, 748 (1961).

³ R. S. Van Heyningen and F. Moser, *Bull. Am. Phys. Soc.* **8**, 230 (1963).

⁴ R. F. Tucker, *Phys. Rev.* **112**, 725 (1958).

⁵ I. S. Ciccarello, M. B. Palma-Vittorelli, and M. A. Palma, *Phil. Mag.* **5**, 723 (1960).

⁶ L. Bellomonte, M. B. Palma-Vittorelli, and M. A. Palma, *Phys. Rev. Letters* **9**, 84 (1962); *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963), Vol. 2, p. 790.

⁷ D. C. Burnham and F. Moser, *Bull. Am. Phys. Soc.* **8**, 231 (1963).

⁸ F. Moser, N. R. Nail, and F. Urbach, *Phys. Chem. Solids* **3**, 153 (1957).

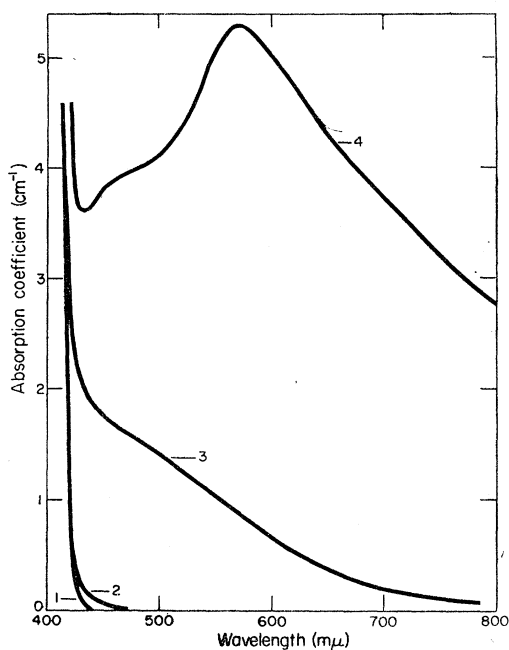


FIG. 1. Optical absorption spectrum at 23°C of a AgCl crystal containing 10^{17} copper ions per cm^3 in the region of weak absorption. (1) Pure AgCl unexposed; (2) AgCl+Cu²⁺ unexposed; (3) AgCl+Cu²⁺ unexposed; (4) AgCl+Cu²⁺, after saturation exposure to 436-m μ light of incident intensity 5×10^{15} quanta per cm^2 per sec. (Measurements made on a sample 6.2 mm thick.)

Electron spin resonance (ESR) studies of this system have been made by Tucker⁴ and by Ciccarello, Bellomonte, and co-workers.^{5,6} Tucker made a detailed study of the paramagnetic cupric ion obtained by halogenation of the samples (annealing samples at 400°C in chlorine). He found that under some conditions the cupric ion is associated with a silver-ion vacancy in the nearest or next-nearest-neighbor positions. Those cupric ions not associated with vacancies are subject to Jahn-Teller distortions. The ESR signal due to the cupric ion was stable in well-annealed crystals but, like the optical absorption associated with this ion, decayed in days in strained samples. This decay, as already noted, is attributed to the precipitation or coagulation of the cupric ions into larger aggregates.

Ciccarello *et al.*⁵ were the first to produce a cupric ESR signal by exposing cuprous-doped material, confirming that cupric ions were indeed formed by exposure. Using single crystals cut from thin sheet crystals⁹ which contained about 10^{19} cuprous ions/ cm^3 , they exposed the samples at room temperature to light from an unfiltered mercury lamp and then quenched them to liquid-oxygen temperature. The ESR signal they observed, although it agreed with that obtained by Tucker on halogenated samples, decayed rapidly at temperatures above -120°C . They concluded that the cuprous ion was a shallow trap for

photoholes at room temperature. They did not study the ESR spectrum of cupric ions formed by halogenation of the crystals.

Bellomonte, *et al.*⁶ extended the previous work by using sheet crystals⁹ containing somewhat lower concentrations of copper (about 10^{18} copper ions/ cm^3) and volume-absorbed light (436 m μ). They exposed the samples at room temperature, quenched them to -193°C for an ESR measurement, and measured the cupric ESR signal. After warming the crystal quickly to room temperature and waiting for a period of time, they again quenched the samples to -193°C for another ESR measurement. They found that the decay of the ESR signal as measured in this way was several orders of magnitude faster than the concurrent decay of the optical absorption of the print-out product. They interpreted their results by assuming that cuprous ions are shallow traps for photoholes at room temperature. The relative stability of the print-out absorption was explained by assuming that the photoholes were re-trapped at silver-ion vacancies generated during exposure and thus prevented from attacking the photolytic silver. They also found that the greater the initial exposure, the greater is the rate of decay of the ESR signal. Another result of interest is that, although a plot of darkening versus exposure time gave a curve similar to that of Moser, *et al.*,¹ allowing the sample to remain in the dark overnight and repeating the experiment resulted in a curve of similar shape whose *initial* value of the rapidly increasing darkening was near the saturation value reached the previous day (Fig. 3). This was repeated on three consecutive days. The initial *slope* was the same in successive experiments as it was in the first, and the "saturation" slope increased after each re-exposure. (The "saturation" slope is the final value of the darkening rate obtained during one day's ex-

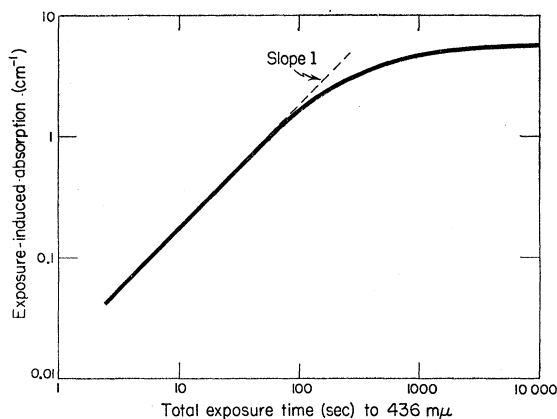


FIG. 2. Log-log plot of the exposure-induced absorption (measured at the peak of the band) as a function of exposure to 436-m μ light in a AgCl-Cu¹⁺ crystal. Copper concentration, thickness, and exposing intensity are the same as noted for the sample in Fig. 1. Note the initial proportionality between the total exposure and the induced absorption, and the marked saturation after about 1000 sec of exposure.

⁹ J. M. Hedges and J. W. Mitchell, *Phil. Mag.* 44, 357 (1953).

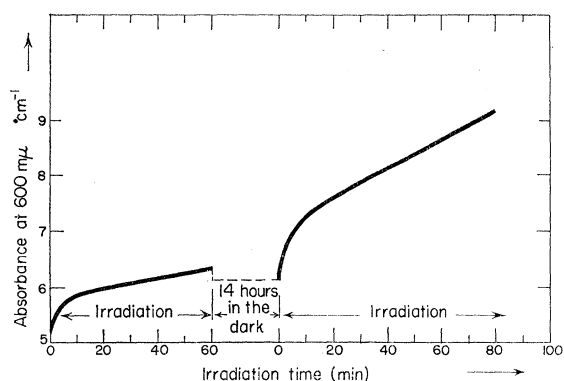


FIG. 3. (From Bellomonte, *et al.*, Ref. 6.) Exposure-induced absorption, measured at 600 $m\mu$ as a function of exposure to 436- $m\mu$ light, in a AgCl crystal containing about 2×10^{18} Cu^{+} ions/ cm^3 . Most of the ESR signal decays in the 14-h dark period. The third and fourth of a set of similar curves obtained by exposure, dark storage, and further exposure are shown. This explains the starting value of the absorbance. (Figure used with permission of Academic Press Inc., New York.)

periments.) These results are given by Bellomonte as evidence for the cyclic operation of the cuprous ion in its role as a shallow hole-trap.

The optical studies on large crystals and the ESR studies on halogenated crystals containing copper suggest that the cuprous ion acts as a deep hole-trap. On the other hand, the ESR studies on sheet crystals led Bellomonte to conclude that the photohole is not permanently trapped at the cuprous ion. If these conclusions are correct, they imply that there are fundamental differences in the properties of large crystals and sheet crystals, and further, that the stability of a hole localized at a cuprous ion is somehow related to whether the hole is injected chemically (by halogen) or optically (by exposure).

Therefore, it seemed desirable to carry out both the optical and the ESR studies on large crystals containing low concentrations of copper and in which the cupric ion was produced either by halogen treatment or by exposure. The present paper deals with such a study. As will be seen, the result can best be interpreted by assuming that the cuprous ion is a deep hole-trap in all cases. The work of Bellomonte, *et al.* can be interpreted in a way consistent with this conclusion.

II. EXPERIMENTAL METHODS

Unless otherwise indicated, the samples were cut from large boules grown from high-purity AgCl by the Bridgman technique¹⁰ and were about 1.5 by 2.5 by 18 mm. The results of spectrochemical analysis of portions of the boules used are found in the Appendix. The samples were polished by using slurries of abrasive or polishing powders and water. After the samples had been polished, they were etched for 15 min in concen-

trated HCl, rinsed well with distilled water, and annealed in nitrogen or chlorine atmospheres. The maximum annealing temperature (420°C) was maintained for several hours, after which the temperature was decreased at a rate of 12°/h. The ESR measurements were made with the Varian V-4502 equipment (X-band, 100-kc/sec field modulation). All optical measurements were made at room temperature with a Perkin-Elmer Spectracord Recording Spectrophotometer. Exposures were made at room temperature with the 436- $m\mu$ line from a 100-W mercury lamp.

III. RESULTS

A. Preliminary Results

Our preliminary experiments showed that it was possible to obtain an ESR signal at room temperature as a result of exposing, to 436- $m\mu$ radiation, AgCl samples containing about 1.5×10^{17} Cu ions/ cm^3 . This signal was a single line and was reasonably stable at room temperature. Later studies of the stability of this signal showed some variation in the rate of decay from as little as 3% during 16 h to as much as 3% in 30 min and 25% overnight. It was then established that the signal observed at room temperature was due to the cupric ion. This was accomplished by taking an oriented crystal of somewhat higher copper concentration (3×10^{18} Cu ions/ cm^3), annealing the sample in chlorine, and obtaining an ESR spectrum at $-170^\circ C$ which agreed with one obtained by Tucker⁴ [see his Fig. 3(c)]. The sample was then annealed in nitrogen, converting the cupric ion to the cuprous ion, and was exposed at room temperature. After cooling to $-170^\circ C$, the ESR spectrum was found to agree with that obtained after halogenation.

B. Correlations Between Optical and ESR Signals

The stability of the exposure-induced signal enabled us to take the time to make both optical and ESR measurements on the same sample, and we studied the correlation between the integrated value of the ESR signal and the "print-out density," that is, the density due to the darkening caused by exposure. Shown in Fig. 4 is one set of results for a sample containing, initially, about 1.5×10^{17} Cu^{+} ions per cm^3 . (Sample C-99-12.) The magnitude of the ESR signal is seen to be proportional to the print-out density measured at 550 $m\mu$, near the peak of the print-out band. This proportionality was found in all samples studied. Figure 4 also shows that the ESR signal obtained after a saturation exposure was about equal to that after halogenation. From this fact we conclude that in this sample essentially all the cuprous ions are converted to cupric ions by exposure.

The experiment was repeated on other samples (C-99-21) from the same boule but which contained a

¹⁰ N. R. Nail, F. Moser, P. E. Goddard, and F. Urbach, *Rev. Sci. Instr.* **28**, 275 (1957).

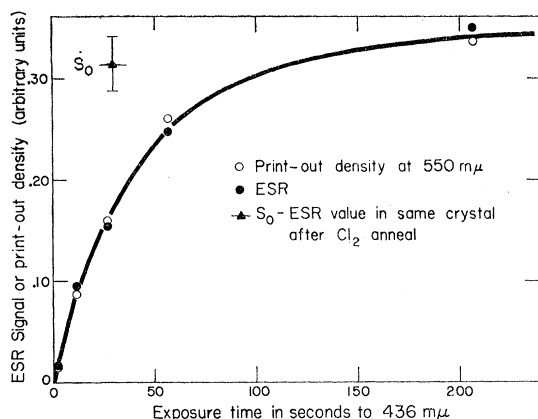


FIG. 4. Simultaneous growth of optical absorption and ESR signal with exposure to 436-m μ light. Exposure and measurement at room temperature. Crystal: AgCl— 1.5×10^{17} Cu $^{1+}$ /cm 3 (C-99-12). Thickness: 1.0 mm.

higher concentration of copper (about 4×10^{17} Cu ions/cm 3) and possibly differing amounts of other trace impurities. The proportionality between the ESR signal and the print-out density was observed, but the maximum ESR signal obtainable by exposure was considerably less than that after chlorination. This lack of agreement required clarification. It might have been due to a change in intensity of the exposing light, to the difference in copper concentration, or to the higher concentration of other impurity ions.

C. Effect of Exposing Intensity on ESR Signal

In order to investigate the effects of intensity, three samples of the higher copper concentration were annealed in nitrogen and exposed to 436-m μ light with intensities of 4.4×10^{15} , 0.73×10^{15} , and 0.18×10^{15} quanta/cm 2 -sec. The samples were about 1.5 mm thick. The optical darkening was followed as a function of exposure time, and when the darkening reached saturation levels, the magnitude of the ESR signal was measured. After an anneal in halogen, the ESR signal was again measured. In each case, the maximum ESR signal obtained by exposure was about 65% of that after halogenation, and no significant effects due to intensity variations could be found. In these samples, the print-out absorption band was less sharply peaked than usual.

D. Concentration Dependence on ESR Signal

To study the effect of concentration we studied a set of samples containing about 0.02, 0.2, and 3×10^{17} copper ions/cm 3 (C-50-11, C-81-10, and C-97-25, respectively). In this case, the samples used for the optical measurements were 5 to 10 mm thick. On using the procedure described in the last paragraph, it was found that at saturation exposure the approximate

TABLE I. Conversion of Cu $^{1+}$ to Cu $^{2+}$ by exposure.

| Cu $^{1+}$ concentration (ions/cm 3) | Fraction of Cu $^{1+}$ converted to Cu $^{2+}$ by "saturation" exposure |
|--|---|
| 0.02×10^{17} | 1.0 |
| 0.2×10^{17} | 0.9 |
| 1.5×10^{17} | 1.0 |
| 3×10^{17} | 0.75 |
| 4×10^{17} | 0.65 |

fractions of cuprous ions converted to the cupric state were 1, 0.9, and 0.75 for the three concentrations, respectively. These data, together with those of the previous two sections, are summarized in Table I. It is seen that the fraction converted falls well below unity when the concentration exceeds 2×10^{17} /cm 3 . It appears that the copper ions that have already been converted to the higher valence state by trapping of photoholes act as electron traps and at high concentration begin to compete effectively with those electron traps which cause silver formation. Luminescence studies 3 at low temperatures have shown that cupric ions can act as electron traps.

E. Stability of the Cu $^{2+}$ ESR Signal

As already noted in the Introduction, the stability of the ESR signal in halogenated samples is related to the state of strain and the temperature of the sample. To investigate this problem in more detail, we studied the changes in the ESR signal in both well-annealed and strained crystals. One sample was annealed in chlorine, and the stability of the ESR signal was studied over a period of approximately six days at room temperature. In this experiment, pains were taken to avoid straining the crystal, and the crystal remained in place in the spectrometer during this time. The results are plotted in Fig. 5, which shows that the ESR signal decays very little in a period of six days. Another sample of similar material containing about one-third the copper concentration was annealed in halogen and then strained by a 10% compression. It will be seen in Fig. 5 that this strain causes a high rate of decay.

In an annealed, unstrained, halogenated sample, the ESR signal is stable well above room temperature. An oriented sample containing about 3×10^{18} Cu $^{2+}$ ions/cm 3 was cooled to -170°C and the usual ESR spectrum was obtained. After the sample had been heated to 250°C for 15 min, it was cooled to -170°C in a few hours, and the same ESR spectrum was found. In annealed, unstrained, halogenated samples the decay time of the ESR signal becomes short only at temperatures above about 290°C . For example, at 25°C the decay time is measured in days, at 165°C there is less than 5% decay in the first hour, and at 340°C the ESR signal decays to half-strength in about 7 min. One might speculate that holes are released from cupric ions at

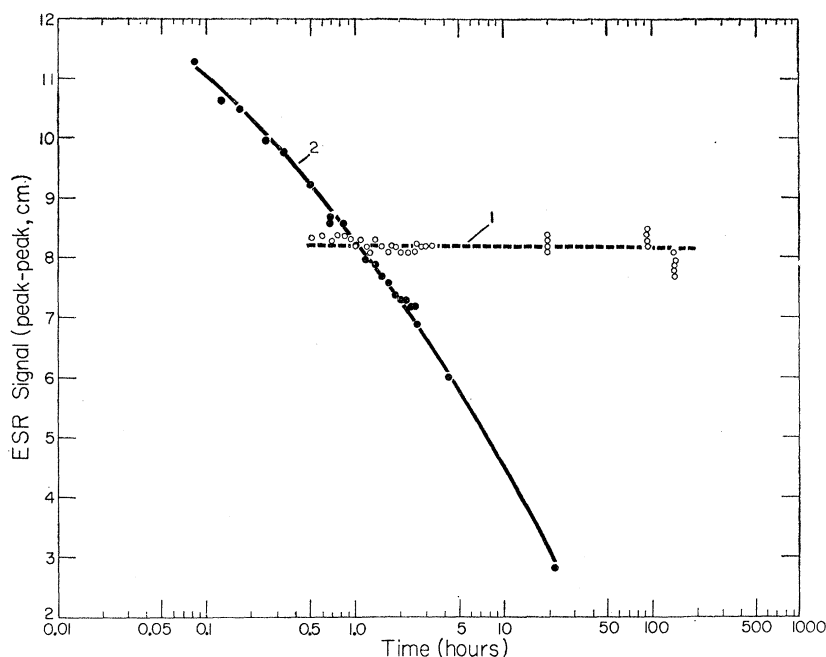


FIG. 5. ESR signal (peak to peak) in halogenated AgCl-Cu crystals as a function of time. Different spectrometer gains were used for the two samples. Curve 1: Annealed in chlorine atmosphere and removed at time=0 at room temperature. (Sample C-99-21 4×10^{17} Cu ions/cm³.) Curve 2: Annealed as above, but strained 10% in compression at time=0. (Sample C-99-12; 1.5×10^{17} Cu ions/cm³.)

lower temperatures but cannot escape through the surface of the crystal. However, the work of both Luckey¹¹ and Hanson,¹² who found that the conductivity of AgCl changes within seconds after the application or removal of halogen, rules out this possibility.

In Sec. III-A, we pointed out that the cupric signal obtained by exposure of annealed samples is stable at room temperature, decaying as little as 3% in the first 16 h. We also examined the stability of this *exposure-induced* ESR signal at elevated temperatures. Up to temperatures near 180°C, the decay rate is not markedly accelerated. At temperatures between 180 and 190°C, however, the cupric ESR signal decreased significantly in times of 5 min or so. Compressing a cuprous-doped exposed sample also brought about a decay rate much greater than that found in crystals handled in a more normal fashion. For example, one sample containing about 5×10^{17} Cu ions/cm³ was exposed to saturation and compressed in one dimension by about 15%. Forty minutes after straining, about half of the ESR signal before compression remained, and about one-third of the original signal was present after 140 min.

F. Aggregation and Redispersal of the Cu²⁺ Ion

As discussed earlier, changes in the optical and ESR properties have been attributed to a coagulation or precipitation of cupric ions. Some additional experimental evidence has now been obtained which supports this hypothesis. An oriented AgCl crystal containing

about 3×10^{18} Cu ions/cm³ was annealed in chlorine. Two weeks later, after normal handling and thermal straining in the course of other experiments, the ESR spectrum was recorded at a temperature near -170°C , the [100] direction being parallel to the external magnetic field. The results are shown in Fig. 6 and may be compared with Tucker's spectra,⁴ which arise from the cupric ion in the dispersed or substitutional form. Figure 6 shows an almost-complete intermingling of the lines arising from the vacancy-associated substitutional copper with those lines due to Jahn-Teller distortions parallel to the external magnetic field. In the spectrum of the dispersed cupric ion, all these lines would appear at field values less than that equivalent to the point marked 55 on Fig. 6. One explanation of this spectrum is that the cupric ions are found in a variety of crystalline environments, many of which are not those of a dispersed substitutional ion, and the precipitation hypothesis is consistent with the results obtained. It should be noted that Parasnis, Frank, and Mitchell¹³ conclude that cupric and silver ions occupy alternate positions in certain edge dislocations.

It has been found earlier^{1,4} that, by heating halogenated crystals containing precipitated cupric ions in an inert atmosphere to about 200°C for a few hours, one could redisperse the cupric ion and regenerate the optical and ESR signals. Using ESR techniques, we now find that heating to 130°C for several minutes is sufficient to redisperse these ions and to obtain samples which displayed ESR spectra at -180 and 25°C which

¹¹ G. W. Luckey and W. West, J. Chem. Phys. 24, 879 (1956).

¹² Roland C. Hanson and Frederick C. Brown, J. Appl. Phys. 31, 210 (1960).

¹³ A. S. Parasnis, F. C. Frank, and J. W. Mitchell, Phil. Mag. 8, 1503 (1963).

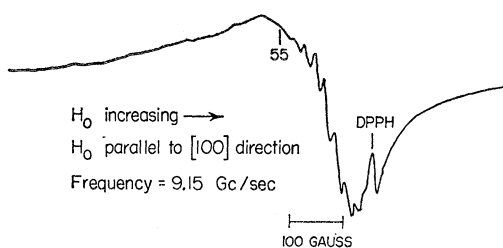


FIG. 6. ESR derivative spectrum of partially precipitated cupric ions in AgCl at $T = -170^\circ\text{C}$.

were like the freshly halogenated samples. The redispersal occurred in air and in an oxygen atmosphere.

G. Variation in Number of Spins

By using ESR techniques, the variation in the magnitude of the ESR signal was studied as a function of temperature. If the number of "spins" is constant as the temperature changes, the magnitude of the spin resonance signal obtained will vary with the inverse of the absolute temperature, in accordance with the Curie law. On this basis, it is concluded that the number of spins at 25°C is the same as that at -180°C .

H. Hole Trapping at -180°C

An oriented AgCl:Cu²⁺ crystal containing about 3×10^{18} Cu ions/cm³ was exposed to 405- and 436-m μ light at a temperature near -180°C , the purpose being to see if we could obtain the cupric ESR spectrum and, if so, to determine whether or not any vacancy association occurs at this temperature. The sample had been quenched to -196°C and warmed to room temperature several times so as to form dislocations which might act as electron traps. With the external magnetic field parallel to the [100] direction, an ESR spectrum was obtained which is the superposition of the cupric spectrum without vacancy association and a single line at a g value near 2.13. However, Tucker's C2 and C3 lines are missing. The single line is apparently due to a new center, and further detailed investigation is being made. However, it is clear that photoholes are trapped at cuprous ions at -180°C and that vacancies are not associated with the newly formed cupric ions when the sample is held at this temperature.

The optical effects of low-temperature exposure have not been investigated in crystals containing such high copper concentrations. Low-temperature exposure of crystals containing lower copper-ion concentrations ($\sim 10^{17}/\text{cm}^3$) have not given rise to an observable optical absorption. It seems probable that the concentration of cupric ions formed by exposure near -180°C , although detectable by ESR techniques, is below the optical detection limit of about $10^{15}/\text{cm}^3$. However, simultaneous studies of both optical absorption and ESR signal induced in AgCl-Cu crystals by low-temperature exposure have not been made.

I. Experiments with Sheet Crystals

Since Bellomonte, *et al.*⁶ used sheet crystals⁹ with a copper concentration of about 10^{18} Cu ions/cm³ and obtained results different from ours, we prepared similar crystals and studied their properties. They annealed their samples, exposed them, and quenched them to -196°C for their ESR measurements. We did not anneal our samples but kept them at room temperature for exposure and measurement. The general features reported by Bellomonte were also found in our sheet crystals.

IV. DISCUSSION

Our work confirms earlier work that the photoholes are trapped at cuprous ions to form cupric ions and shows for the first time that the ESR signal from such cupric ions is stable in carefully handled, well-annealed large crystals at temperatures below 180°C . When the holes are introduced into this system by a chlorine anneal, it is found that the cupric ESR signal is stable at temperatures below 280°C . These results show clearly that the cuprous ion is a deep hole-trap at room temperature. These results also indicate that the first step in thermal bleaching of darkened samples may be the thermal release of electrons from silver metal. However, one should not exclude the possibility that silver metal provides sinks for the small fraction of holes free at 180°C , preventing some of the normal retrapping of holes at cuprous ions and causing a decay of the cupric ESR signal.

The correlation between the print-out density and the magnitude of the spin-resonance signal confirms the role of the cuprous ion in trapping holes. In the case of low copper concentrations (less than 10^{17} Cu ions/cm³), essentially all the cuprous ions are converted to cupric ions by exposure. As for the hypothesized coagulation and redispersal of the cupric ion, new spin-resonance data indicate that this is a correct mechanism. Exposure of cuprous-doped AgCl at -180°C produced the cupric ion, without associated vacancies, and a new paramagnetic center which requires further investigation.

The results of Bellomonte, *et al.*⁶ can be interpreted in a way that is completely consistent with our conclusion that the cuprous ion is a deep hole-trap at room temperature. If one assumes that the disperse cupric ion has some cross section for electron capture, and that this cross section is greatly reduced when the cupric ion aggregates, then the decays and redarkenings observed by Bellomonte can be qualitatively explained in the following way.

At low cuprous-ion concentrations, prolonged exposure results in essentially complete conversion of the cupric ion. The conversion is complete because the total capture cross section of the cupric ions for electrons is still small compared to the electron capture

cross section of the centers which lead to silver formation. The observed ESR decay is then related to the aggregation of the cupric ions; such decay is accelerated by strains introduced by quenching. The optical absorption is less affected since it is dominated by the silver absorption. At higher cuprous-ion concentrations (of the order of $10^{18}/\text{cm}^3$ and up), however, prolonged exposure does not lead to complete conversion of the cuprous to the cupric ion, since the cupric ions formed by trapping of photoholes build up to a concentration where they effectively compete with other electron traps. The rate of darkening is markedly reduced by this process and reaches a constant much less than the initial value; the optical density approaches a "saturation" value. If now there is a period of dark storage during which the cupric ions aggregate (causing a loss in ESR signal but little loss in optical signal), then re-exposure leads to further formation of photoproduct, since cuprous ions are still available and the cupric ions formed by the first exposure have aggregated and no longer act as electron traps. As a result of prolonged re-exposure, the cupric-ion concentration again builds up to a point where it effectively competes for the photoelectrons, and the optical density approaches a saturation value higher than before. Such a process is consistent with Bellomonte's results, shown earlier in Fig. 3.

This argument implies that in high-concentration samples, each prolonged exposure converts only some small fraction of the copper. Earlier studies^{1,2} of samples containing only a few parts per million of copper by weight (in which saturation corresponds to total conversion of cuprous to cupric) showed that the saturation value of the absorption coefficient at the peak of the darkening curve is about $2 \text{ cm}^{-1} \text{ ppm}^{-1}$. One part per million (ppm) by weight is about 5.3×10^{16} Cu ions per cm^3 , and the 10^{-4} molar concentrations of CuCl in AgCl used by Bellomonte correspond to about 50 ppm of Cu by weight. Therefore, in samples containing this concentration the saturation corre-

sponding to total conversion would give an absorption constant of about 100 cm^{-1} . The maximum value shown in Fig. 3 is less than 10 cm^{-1} , which indicates that only about 10% of the cuprous ions are converted to the higher valence state.

Figure 3 also shows that the "saturation" slope increases with successive "redarthenings," from which we conclude that the formation of photoproduct at saturation becomes more efficient with each redarthening. One possible explanation is that as the silver aggregates grow larger, they increase the strains in the sample,¹⁴ which increase the rate of cupric-ion aggregation and decrease the concentration of disperse cupric ions which may be maintained in the lattice. The total effectiveness of the cupric ions as electron traps is decreased, and the saturation darkening proceeds with higher efficiency than before.

If silver-ion vacancies were indeed deep hole-traps at room temperature, as suggested by Bellomonte, one might expect to enhance the darkenability of AgCl crystals by incorporating divalent cations which would lead to higher concentrations of silver-ion vacancies. Silver chloride crystals containing divalent copper (prepared by halogenation of the crystal) are completely insensitive to light, as are crystals containing Cd^{2+} and Ni^{2+} .

ACKNOWLEDGMENTS

We should like to thank Dr. F. Urbach, whose interest and suggestions concerning this problem date over many years, and Dr. R. S. Van Heyningen, whose studies on the AgCl-Cu system led to many helpful discussions and ideas. Conversations with many others, including Professor F. C. Brown, Dr. R. F. Tucker, and Dr. T. R. Sliker provided stimulation along the way. Vernon Saunders helped us make the sheet crystals, and R. M. Gluck was of great help in growing the large crystals used in these studies.

APPENDIX

Spectrochemical analyses of AgCl crystals used in these studies are given in Table II. Impurity concentrations are given in parts per million (ppm) (weight of impurity to weight of silver chloride). Note: 1 ppm Cu is equivalent to 5.3×10^{16} atoms per cm^3 .

TABLE II. Impurity concentrations in AgCl samples.

| Element Detection limit (ppm) Sample No. | Cd 0.5 | Cr 0.5 | Co 0.1 | Cu 0.03 | Au 1.0 | Fe 0.05 | Pb 0.07 | Mn 0.05 | Ni 0.05 | Sn 0.05 | Zn 4.0 |
|---|-----------|-----------|-----------|---------------------|-----------|------------------|------------|------------|------------|------------|-----------|
| C-50-11 | a | a | a | 0.04 ^{b,c} | a | <0.07 | a | a | a | a | a |
| C-81-10 | a | a | a | 0.4 | a | 0.1 ^b | a | a | a | a | a |
| C-97-25 | a | a | a | 5 | a | <0.07 | a | a | a | a | a |
| C-99-21 | a | a | a | 8 | a | <0.07 | a | a | a | a | a |
| C-99-12 | a | a | a | 3 | a | <0.07 | a | a | a | a | a |

^a Not detected.

^b Approximate value.

^c Averaged for 6 samples.

¹⁴ D. A. Jones and J. W. Mitchell, *Phil. Mag.* 3, 1 (1958).