

Paramagnetic Resonance Study of Copper-Doped Silver Chloride*†

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This paper gives the results of paramagnetic resonance studies of copper in silver chloride crystals at temperatures between 77°K and room temperature. The crystals were treated in various ways by illumination or halogenation.

Resonances were observed in halogenated crystals which are interpreted as arising from Cu^{++} ions occupying sites which differ as to the presence and relative positions of associated vacancies. These spectra were observed to vary with temperature in a manner attributable to vacancy motion. The activation energy for this motion is estimated.

An estimate is made of the amount of Cu-Cl bonding through an approximate line-width analysis.

Speculations are offered as to the role of the copper ion in the photolytic process in silver chloride, and further experiments are suggested.

I. INTRODUCTION

THE study of copper-doped silver chloride has shown promise of shedding new light on the photographic process in silver chloride. Moser, Nail, and Urbach¹ have examined the optical properties of this system. They have studied three distinct states of the silver chloride-copper system. Crystals grown or annealed in air or vacuum are much more readily and extensively darkened upon illumination than are silver chloride crystals of high purity. Crystals in this photosensitive state, hereafter called state I, show a very slight yellow coloration and optical absorption measurements show a tail on the long wavelength side of the fundamental absorption attributed to a Cu^+ absorption band lying on the ultraviolet side of the fundamental absorption. Chlorinating the copper-doped crystals by annealing at about 400°C in a chlorine atmosphere produces state II of this system. The state II crystals are visibly darkened (yellowish-brown) and show little or no photolytic darkening upon illumination. The tail of the fundamental optical absorption in state II crystals extends well into the visible range in a manner consistent with the presence of a Cu^{++} band in the crystals. States I and II are readily and reversibly converted to one another by annealing in appropriate atmospheres. State II is not completely stable, but tends to decay to a third state, state III, in a non-reproducible fashion, apparently depending upon the amount of cold work suffered by the state II crystals after chlorination. The optical absorption spectrum of state III crystals lies between that of states I and II, and this state is not photolytically sensitive. State III can be completely converted to state II by mild heat

treatment in an inert atmosphere. State III is believed² to consist of a precipitate of cupric chloride in colloidal form in the silver chloride crystals.

The darkening of the photosensitive state I crystals proceeds initially with a high quantum efficiency,³ near unity. The saturation darkening in the colloid band is proportional to the amount of copper in the crystals. These facts imply that the copper ions play a fundamental role in the photochemical processes in silver chloride. The Kodak workers¹ propose that the Cu^+ ions in state I crystals act as efficient traps for photo-produced holes, allowing stable neutral silver to be formed in the lattice. Brown⁴ has speculated that the Cu^+ ions migrate to electrons trapped at sites that are relatively independent of the presence of the copper in the lattice. Neutral copper, Cu^0 , formed in this fashion might then nucleate the formation of silver specks in the crystal.

The present work reports a paramagnetic resonance study of copper-doped silver chloride crystals in each of the three states described above.

The experimental arrangements will be described in Sec. II and the experimental results stated in Sec. III. The interpretation of the observed spectra will be covered in Sec. IV. The pertinent results and conclusions will be summarized in Sec. V.

II. EXPERIMENTAL METHOD

An X-band microwave spectrometer of standard design was used in this research. The microwave power source used was a 2K25 klystron frequency-stabilized with a Pound dc stabilizer circuit.⁵ Reflected signals from the sample cavity were detected through a magic tee bridge with a Sperry 821 barretter. Field modulation and lock-in detection at 8 cps were used. The lock-in amplifier was a Liston-Becker model 14 dc amplifier,⁶

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¹ Moser, Nail, and Urbach, *J. Phys. Chem. Solids* **3**, 153 (1957).

² F. Urbach (private communication).

³ F. Moser (private communication).

⁴ F. Brown (private communication).

⁵ R. V. Pound, *Rev. Sci. Instr.* **17**, 490 (1946).

⁶ Liston-Becker Instrument Company, Inc., Stamford, Connecticut.

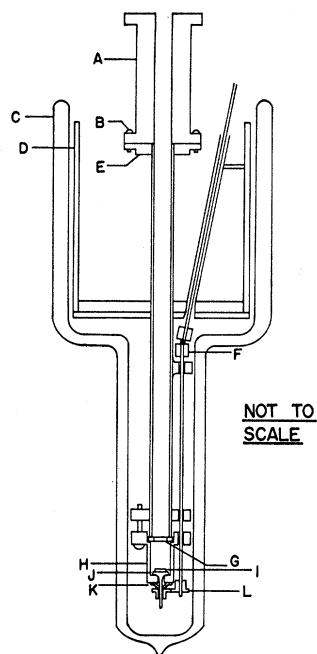


FIG. 1. The cryostat and cavity assembly. *A*—Lucite wave guide; *B*—nylon screws, *C*—Dewar flask, *D*—brass reservoir, *E*—choke flange, *F*—aluminum universal joint, *G*—iris, *H*—cavity, *I*—sample, *J*—Lucite pedestal, *K*—phosphor bronze washer, *L*—brass gears.

suitably modified. The derivative signals so obtained were recorded on a Varian G-10 strip chart recorder. The sensitivity of this spectrometer was such that a signal-to-noise ratio of unity could be obtained from a sample containing 5×10^{13} ions with $S = \frac{1}{2}$ and a line width of one gauss, with an unloaded cavity Q of 5000 and an integrating time constant of 2.5 seconds at the lock-in output.

The magnet employed in this work was an electromagnet designed and constructed by the University of Illinois Physics Department magnetic resonance group. It was powered from a high-voltage current-regulated supply of such design that the magnetic field could be varied continuously from 0 to greater than 10 000 gauss.

The liquid nitrogen cryostat and cavity design used in this work are shown in a cross section line sketch in Fig. 1. The cavity (labeled *H* in Fig. 1) is a half-wavelength rectangular cavity milled from a copper block and silver-plated. The iris (*G*) is an inductive type cut from $\frac{1}{32}$ -inch copper and silver-plated. It is butted between the end of the wave guide and the cavity by a screw and flange construction so as to make the wave guide, iris, and cavity system self aligning. The sample (*I*) is mounted on a Lucite pedestal which protrudes through a hole in the end wall of the cavity. This hole is of small enough diameter compared to its length so as to constitute a wave guide beyond cutoff. The pedestal is linked through a small brass gear train (*L*) to a shaft which runs, through a small aluminum universal joint (*F*), to the top of the cryostat. The sample mount is spring loaded with a bent phosphor bronze washer (*K*) between the cavity wall and gear hub. The sample and cavity are cooled by conduction up the wave guide to a reservoir (*D*) containing coolant.

The entire assembly fits inside a tailed Dewar flask (*C*) designed to fit the magnet gap. The connection from room temperature guide to the cryostat is made by a short piece of wave guide milled from Lucite (*A*) and painted with conducting silver paint.⁷ The Lucite section is fastened to a standard choke flange (*E*) with nylon screws to avoid cracking the Lucite due to thermal strains.

The samples used in this research were melt grown crystals of high-purity silver chloride⁸ which were doped with copper to a copper concentration of 18 parts per million by weight. They contained no more than one part per million of other heavy-metal impurity. They were oriented by using back-reflection x-ray photographs and cut with a carbide-tipped mill while still mounted on the goniometer.

III. RESULTS

State I crystals showed no resonance spectrum at 77°K or at room temperature. No resonance signal could be induced in these crystals by illumination at room temperature or at 77°K.

The chlorinated crystals, state II, showed a characteristic resonance spectrum at 77°K which depended upon the orientation of the crystal in the magnetic field. After cooling and subsequent warming, the resonance disappeared with time as state II decayed to state III. The resonance was fully restored by mild

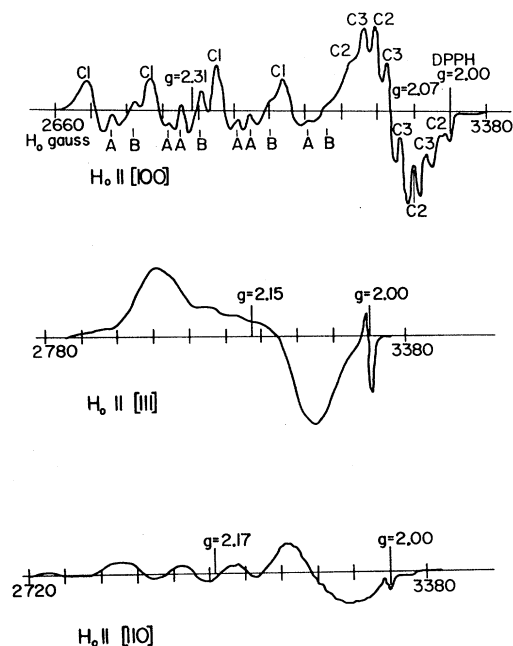


FIG. 2. Orientation dependence of spectrum (derivative of absorption) at 77°K.

⁷ Types SC-12 and SC-15 were used. Micro-circuits Company, New Buffalo, Michigan.

⁸ Nail, Moser, Goddard, and Urbach, *Rev. Sci. Instr.* **28**, 275 (1951).

heating of the state III crystals. The state II resonance spectrum showed a strong temperature dependence between 77°K and room temperature.

IV. INTERPRETATION

A. State II Low-Temperature Spectrum

The spectra observed in this experiment will be interpreted by using the reduced spin Hamiltonian of Abragam and Pryce.⁹ The low-temperature (derivative) spectrum is illustrated in Fig. 2 for three major orientations of the sample crystal in the magnetic field. The number and positions of lines in this spectrum can be accounted for approximately on the assumption that there are three different Cu⁺⁺ centers in these crystals. Figure 3 shows the effect of the rate of cooling of the

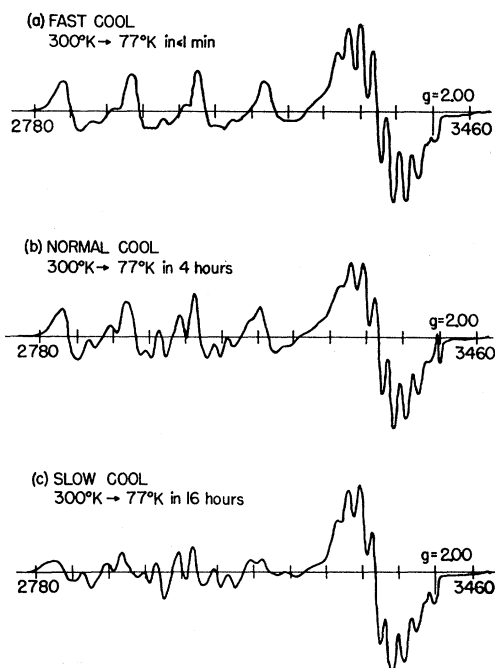


FIG. 3. Cooling rate dependence of [100] spectrum at 77°K.

sample on the [100] spectrum observed at 77°K. The change in relative intensities of the observed lines indicates that there is more than one Cu⁺⁺ center and the number of lines and their temperature dependence, illustrated in Figs. 4 and 5, indicates that there are probably three different kinds of Cu⁺⁺ centers. These centers will be referred to as types *A*, *B*, and *C*. The computed positions and approximate intensity ratios for the spectra from these three centers are shown, relative to the observed derivative spectrum, in Fig. 6 for the applied field along a [100] direction. These centers are treated as having approximately axially symmetric distortions of the basically cubic silver chloride crystalline field.

⁹ A. Abragam and M. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

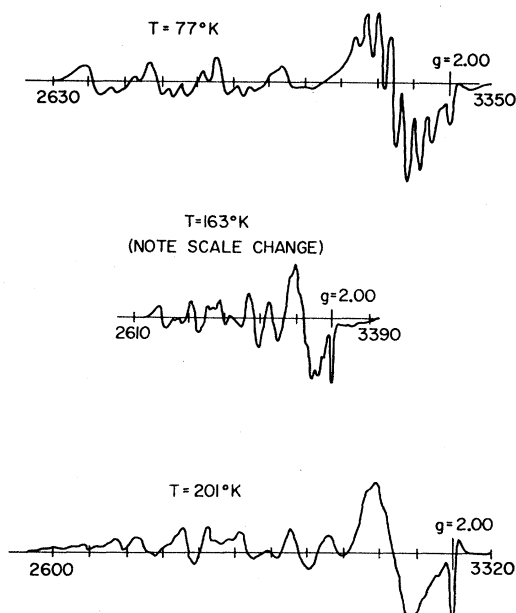


FIG. 4. Temperature dependence of [100] spectrum from 77°K to 200°K.

The spin Hamiltonian appropriate for an ion in a field having axial symmetry is,

$$H = g_{11}\mu_B H_z S_z + g_{\perp}\mu_B (H_x S_x + H_y S_y) + A I_z S_z + B(I_x S_x + I_y S_y) + Q'[I_z^2 - \frac{1}{3}I(I+1)]. \quad (1)$$

The subscripts in this expression refer to the axes of the crystalline field, where the *z* axis is the axis of the axial distortion.

Centers *B* and *C* have an axially symmetric distortion about cube edges, consequently, with the applied field

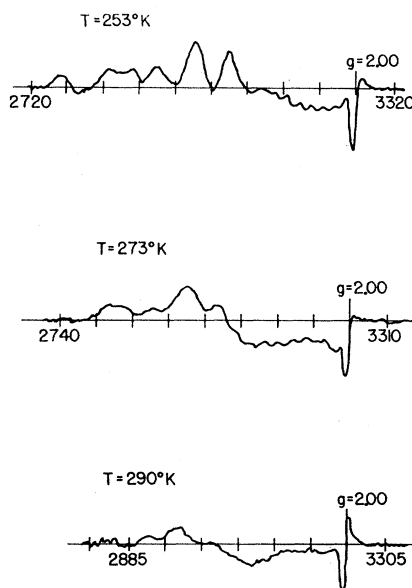


FIG. 5. Temperature dependence of [100] spectrum from 250°K to 290°K.

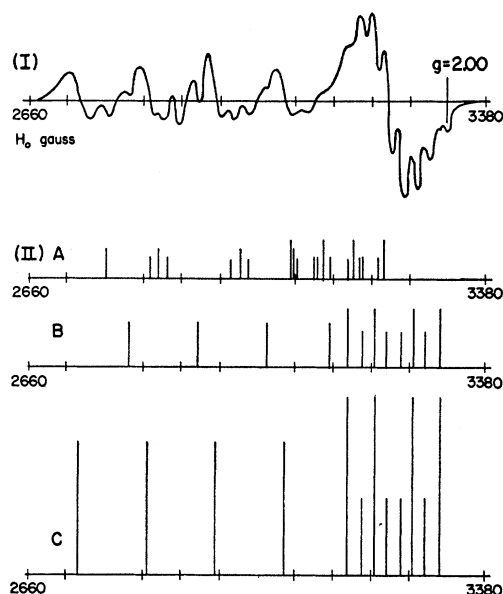


FIG. 6. (I) The observed $[100]$ spectrum at 77°K . (II) Relative positions and approximate intensity ratios of $[100]$ spectra from centers A , B , and C .

parallel to a $[100]$ crystal direction, one-third of these centers have their axes parallel to the applied field and two-thirds have their axes perpendicular to the applied field. Figure 7 shows a numerically integrated absorption spectrum for a $[100]$ crystal orientation. In this figure the broad peak on the high-field side has approximately twice the intensity of the four major peaks on the low-field side.

Center A has a distortion along cube face diagonals ($[110]$ and equivalent crystal axes). In this case the assumption of axial symmetry is especially poor since such a distortion must almost certainly result in orthorhombic symmetry of the crystalline field. The resolution of lines in this spectrum is so poor that departures from axial symmetry cannot easily be measured, therefore, only parallel and perpendicular parameters are quoted, even though they are insufficient to completely describe such a center.

The lines labeled $C1$ in Fig. 2 arise from the parallel spectrum of type C centers with a $[100]$ axis of symmetry. The perpendicular spectrum consists of eight partially resolved lines. The peaks labeled $C3$ in Fig. 2 arise from "forbidden" $\Delta M_I = \pm 2$ transitions,¹⁰ while

TABLE I. Summary of the spin Hamiltonian parameters for Cu^{++} centers in AgCl .

Center	Symmetry axis	g factors		Hyperfine splitting in gauss		Quadrupole interaction in gauss Q'
		g_{\parallel}	g_{\perp}	A	B	
A	(110)	2.00 ± 0.02	2.28 ± 0.02	10 ± 10	85 ± 5	20 ± 5
B	(100)	2.26 ± 0.02	2.07 ± 0.02	95 ± 5	45 ± 5	20 ± 5
C	(100)	2.30 ± 0.02	2.07 ± 0.02	105 ± 5	46 ± 5	20 ± 5

¹⁰ B. Bleaney, *Phil. Mag.* **42**, 441 (1951).

those labeled $C2$ are the normally allowed $\Delta M_I = 0$ hyperfine transitions.

The lines labeled B in Fig. 2 arise from the parallel spectrum of center B having the same symmetry as center C , but a slightly different magnitude of crystalline field. The perpendicular spectrum from this type of center almost coincides with that from the type C centers.

One-third of the type A centers with $[110]$ crystal field distortions should have the distortion axis perpendicular to the applied field for a $[100]$ crystal orientation. These centers give rise to the lines labeled A in Fig. 2. Two-thirds of these centers should be at 45° to the applied field. The lines from these centers

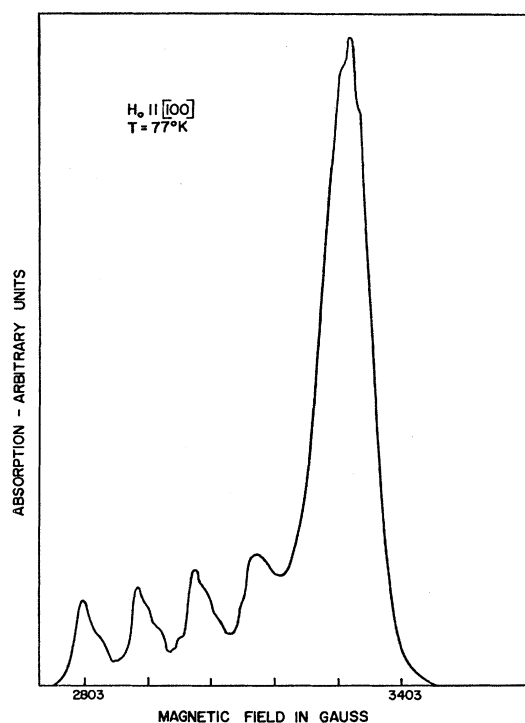


FIG. 7. $[100]$ absorption spectrum obtained by numerical integration.

are obscured by the perpendicular spectra of the B and C centers. This fact is believed to account for the apparent asymmetry of the broad peak in Fig. 7.

The determination of spin Hamiltonian parameters for these spectra is subject to considerable uncertainty due to the poor resolution of lines, plus an estimated instrumental error of about 2%. Table I summarizes the spin Hamiltonian parameters deduced for these centers.

The cooling rate effects and temperature dependence, which will be discussed below, indicate that these three types of centers can be accounted for on the assumption of differing degrees of association with bound vacancies. The type A center, with a distortion of the cubic

crystalline field along a [110] axis, is attributed to a Cu⁺⁺ ion with a bound vacancy in a nearest positive ion site. In type *B* there is a vacancy in a next-nearest positive-ion site, along a [100] direction. Type *C* has no bound vacancy near-by, but has a sizable Jahn-Teller¹¹ distortion along a cube edge of the surrounding octahedron of Cl⁻ ions.

At room temperature the degree of ion-vacancy association is slight. Ebert and Teltow¹² quote binding energies of about 0.2 electron volt for such complexes in silver chloride. Cooling the crystals rapidly to 77°K tends to quench in a distribution of ion-vacancy complexes characteristic of a higher temperature. Figure 3 shows that for the most rapid cooling rate the type *C* lines predominate, providing the basis for assigning these lines to copper ions without associated vacancies. As the cooling rate is made progressively slower, the *A* and *B* lines grow at the expense of the *C* lines.

The equilibrium number of bound ion-vacancy complexes at any temperature is determined by the binding energy of the complex. The time required to reach equilibrium when the temperature is changed is determined by the diffusion of vacancies under the influence of the potential due to the divalent ions. This problem is an extremely complicated one for which a satisfactory solution has not yet been found. Approximations to this problem can be solved indicating that the time required to reach equilibrium at 77°K is of the order of 10¹⁷ seconds, while the equilibrating time at 200°K is of the order of seconds.

The lines in the low-temperature [100] spectrum appear to be approximately Gaussian in shape, with a half-width of about 45 gauss. The dipolar interaction among paramagnetic ions at this concentration (1.8×10⁻⁵) would be only a fraction of a gauss. The shape of the lines, plus the fact that their width is relatively insensitive to temperature from 77°K to 150°K, makes it appear unlikely that the lines are lifetime limited by spin-lattice relaxation. The lines could be broadened by microcrystalline structure giving rise to a distribution of *g* factors and hyperfine splittings, but near the parallel or perpendicular axes the spectrum is insensitive to small angular displacements. The x-ray diffraction data used in orienting the crystal indicate that the dispersion of microcrystalline axes cannot be more than from 2 to 5 degrees. This much dispersion could be important in the [111] and [100] spectra. To account for the width of the lines in the [100] spectrum, it is necessary to assume that the wave function of the paramagnetic electron is distributed appreciably upon surrounding chlorine ions and that the observed lines represent the envelope of hyperfine lines due to interaction with the chlorine nuclei.

If one assumes the approximate wave function

$$\Phi = \psi_{Cu} + \left(\frac{p}{6}\right)^{\frac{1}{2}} \sum_{i=1}^6 \psi_{iCl}, \quad (2)$$

an rms width can be calculated.¹³ This calculation gives

$$\Delta H_{rms} = \left[\frac{5}{2} \left(\frac{1}{2} p A_{Cl}\right)^2 + 5 \left(\frac{1}{4} p B_{Cl}\right)^2 \right]^{\frac{1}{2}}, \quad (3)$$

when *H* is parallel to a [100] direction. If the assumption is made that the Cl hyperfine interaction arises primarily from *p* states, values of *A*_{Cl} and *B*_{Cl} can be inferred from the data of Castner and Känzig on the Cl₂⁻ molecule.¹⁴ These values are *A*_{Cl}=120 gauss, *B*_{Cl}=60 gauss. Using these values and assuming a Gaussian line shape, a value for *p* of 0.18 is obtained. This mechanism gives line widths of 30 gauss and 17 gauss, respectively, for the [110] and [111] spectra. The line widths in these spectra have to be at least 45 gauss to account for the lack of resolution; hence there is either a large *s*-function contribution to the Cl hyperfine interaction or the dispersion of microcrystalline axes in the crystal contributes appreciably to these widths.

B. The Temperature Dependence

As the state II crystals are warmed from 77°K, their resonance spectrum changes markedly. This temperature dependence can be described in two parts. In the range from 77°K to 200°K the lines from the *A* and *B* spectra, shown at 77°K in Fig. 6, change noticeably while the lines from the *C* spectrum remain relatively unchanged until the temperature reaches about 200°K. Above 200°K all of the observed lines are affected, the whole structure being nearly washed out at room temperature.

The low-temperature range (77°K to 200°K) is shown in Fig. 4. The first (low-field) line of the *A* spectrum and the first line of the *B* spectrum, both of which appear between the first two lines of the *C* spectrum at 77°K (Fig. 6), tend to move toward one another with increasing temperature until they become indistinguishable at 200°K. Others of the smaller *A* and *B* lines, which are distinguishable between the larger peaks of the *C* spectrum, appear to change in a similar manner. At 200°K all of the observed lines have started to broaden appreciably.

Above 200°K, as illustrated in Fig. 5, it is no longer possible to identify individual lines from the different centers as the whole pattern tends to coalesce toward some intermediate position.

The low-temperature change in the spectrum is attributed to a time variation of the crystalline field due to motion of the bound vacancies in centers *A* and *B*, where the vacancy moves from one bound configura-

¹¹ H. Jahn and E. Teller, Proc. Roy. Soc. (London) **A161**, 220 (1937).

¹² I. Ebert and J. Teltow, Ann. Physik **15**, 268 (1955).

¹³ Kip, Kittel, Levy, and Partis, Phys. Rev. **91**, 1066 (1953).

¹⁴ T. Castner and W. Känzig, J. Phys. Chem. Solids **3**, 178 (1957).

tion to another. The effect of this motion would be to change both the precession frequency and axis of quantization of the paramagnetic electron spin. The effects of this kind of motion on the observed spectrum could, in principle, be analyzed using Kaplan's theory of exchange broadening.¹⁵ This was not done since the data in this work were too crude to allow a complete analysis to be made. An estimate of the activation energy for this motion was made using the more elementary theory of Gutowsky, McCall, and Slichter¹⁶ as elaborated by Holm and Gutowsky.¹⁷ It was assumed that the motion of the vacancy, and hence the change in spin precession frequency, can be described by a rate equation of the form

$$1/\tau = \nu_0 \exp(-E/kT). \quad (4)$$

The correlation time, τ , was determined using the criterion $\tau\delta\omega = 10$, taken from the Holm and Gutowsky paper,¹⁷ where $\delta\omega$ is the separation in frequency of two adjacent lines. The frequency factor, ν_0 , was taken to be 10^{13} sec^{-1} as a typical lattice vibrational frequency. Using 200°K as the temperature at which the *A* and *B* spectra have coalesced, we get for the activation energy $E = 0.18$ electron volt. The activation energy for vacancy motion in silver chloride is 0.39 electron volt.¹⁸ It would not be surprising if the effect of the divalent ion were to relax the near neighbors in such a way as to considerably reduce the barrier to vacancy motion from one bound configuration to another. In this connection it should be noted that dielectric loss measurements on cadmium-doped silver chloride,¹⁹ show a peak at a frequency of 10^8 cps at a temperature between 100°K and 120°K , which has been attributed to this kind of motion of bound vacancies. The activation energy given above would imply a motional frequency of 10^8 cps at 91°K . Although this calculation is crude, it strongly suggests that the temperature effects seen here are due to vacancy motion. Watkins²⁰ has noted broadening effects in manganese-doped sodium chloride attributable to a similar sort of motion.

The changes in the spectrum in the high-temperature range (200°K to 290°K) are probably due to both a breaking up of complexes and a general motion of near-by ions as they oscillate between various possible Jahn-Teller distortions. The relatively low activation energy for vacancy diffusion in these crystals makes it possible that the high-temperature effects are due entirely to vacancy motion. It is also possible that the modulation of the hyperfine interaction due to motional effects can give an appreciable shortening of the spin-

lattice relaxation time, thus broadening the individual lines in this temperature range.

C. State III

Attempts to observe a Cu^{++} resonance in state III crystals were made with another apparatus, built by Newell and Castner,²¹ running at higher power and greater sensitivity than the spectrometer used for the bulk of this work. No resonance has been observed. This negative result does not necessarily contradict Urbach's hypothesis² that state III consists of precipitated colloidal cupric chloride in the silver chloride lattice. One would expect a line width in cupric chloride of approximately 100 to 200 gauss. It was estimated that for the concentration of copper in these crystals a line of 500 gauss breadth would have been detectable. The fact that no resonance was seen would require that there be some additional broadening mechanism in the cupric chloride phase. Likely possibilities would be random orientation of the colloids giving a distribution of *g* factors and hyperfine splittings, or an exchange interaction between centers of different orientations broadening the hyperfine structure lines.

D. Illumination Effects

If the Cu^{++} ions in state I crystals act as hole traps in sensitizing the crystals, then illumination of state I crystals should produce the Cu^{++} resonance spectrum. Several attempts were made to observe a resonance in this manner at both 77°K and room temperature. The most favorable conditions were achieved using the Newell and Castner spectrometer with a cavity and cryostat especially designed for admitting light into the cavity. After illuminating at 77°K , the crystals were allowed to warm up and no darkening was visible. They were then given the same illumination at room temperature and, in every case, saturation darkening was produced. According to Moser's data^{1,3}, this indicates that all the coppers were used up.

No resonance was observed in these experiments.

V. SUMMARY

The results of this investigation can be summarized as follows:

1. No paramagnetic resonance is observed in a copper-doped silver chloride crystal between room temperature and 77°K prior to halogenation of the crystal.
2. No resonance signal is observed in a copper-doped crystal upon illumination at room temperature or at 77°K .
3. After halogenation, a paramagnetic resonance signal having quite broad lines is observed in these crystals at 77°K . This spectrum is strongly temperature-dependent.

²¹ T. Castner (to be published).

¹⁵ J. Kaplan, *J. Chem. Phys.* **28**, 278 (1958).

¹⁶ Gutowsky, McCall, and Slichter, *J. Chem. Phys.* **21**, 279 (1953).

¹⁷ C. Holm and H. Gutowsky, *J. Chem. Phys.* **25**, 1228 (1956).

¹⁸ W. Compton and R. Maurer, *J. Phys. Chem. Solids* **1**, 191 (1956).

¹⁹ R. Breckenridge, *J. Chem. Phys.* **18**, 913 (1950).

²⁰ G. Watkins and R. Walker, *Bull. Am. Phys. Soc. Ser. II*, **1**, 324 (1956). Also G. Watkins, *Bull. Am. Phys. Soc. Ser. II*, **3**, 135 (1958).

4. The resonance signal can satisfactorily be ascribed to Cu^{++} ions.

5. At low temperatures there are three nonequivalent sites occupied by the Cu^{++} ions, all of which can be approximately described by assuming an axial distortion of a mainly cubic crystalline field.

6. The nature of the resonance signal is strongly temperature-dependent between 77°K and 290°K.

7. After halogenation the resonance signal diminishes with time in a nonreproducible fashion, but may be restored completely by giving the crystal a mild heat treatment in an inert atmosphere.

The major conclusions which can be drawn are as follows:

1. The action of light upon the copper-doped crystal does not form the Cu^{++} ion. The failure to produce the resonance upon illumination at room temperature might be explained by the formation of some sort of aggregated state due to diffusion of the Cu^{++} ions. Since the resonance was not detected upon illumination at 77°K, we can pretty well rule out an aggregation effect since ionic mobilities are extremely small at this temperature.

The possibility of the formation of neutral copper atoms upon illumination will bear further investigation. If the process whereby Cu^+ ions migrate to trapped photoelectrons to become Cu^0 atoms has any validity, it might be possible to detect a Cu^0 resonance by illuminating at temperatures between 77°K and room temperature where the ionic mobilities are appreciable, and then reducing the temperature to inhibit the formation of large colloids. It is possible that the spin-lattice relaxation time might be very short, requiring that the sample be cooled to temperatures in the liquid helium range.

It should be commented that at no time in this work were any resonances observed which might be attributable to trapped electrons. This fact is not too surprising since there is abundant evidence²¹ that the electron traps of importance to photolysis are located in highly strained regions of the crystal and we might expect rather broad lines due to a distribution of g factors and hyperfine splittings, or possibly lifetime-limited lines due to short lifetimes of the trapped states or short spin-lattice relaxation times. It would seem worth while to try illuminating crystals containing Cu^+ ions at liquid helium temperature to see if resonances are present due to trapped electrons.

2. The data on the halogenated crystals suggest several things. The line widths indicate a fairly large degree of covalent bonding between the Cu^{++} and Cl^- ions. The symmetry of the three types of Cu^{++} center observed suggests that at high temperatures there are few vacancies associated in complexes with the Cu^{++} ions, or else they are in a state of rapid motion about the ions, while at lower temperatures ion-vacancy complexes exist with the vacancy in either the nearest [110] or next-nearest [100] positive-ion site. The temperature dependence indicates that these vacancies can migrate around the ion with considerably lower energy of motion than for general motion of vacancies in the normal lattice. This energy must be somewhat smaller than the energy of association between the ion and the vacancy in order for its effect to have been detected. The manner in which the shape of the spectrum changes above 200°K could be due to a time dependence of the Jahn-Teller distortion in type-C centers, or could be due to the rapid motion of vacancies changing the crystalline field at the ion sites. Since the activation energy for the vacancy motion in silver chloride is only 0.39 electron volt, the latter possibility must get strong consideration and we cannot determine the exact origin of the high-temperature effects in our spectra.

3. The behavior of the signal in halogenated crystals as a function of time and mild heat treatment is consistent with Urbach's hypothesis of a precipitation of a CuCl_2 phase with cold work and a redissolving upon heating. The restoration of the signal upon heating to 150°C makes it seem unlikely that the valence state of the Cu^{++} ion is changed in this process.

VI. ACKNOWLEDGMENTS

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