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Properties of Divalent Cobalt and Nickel as Impurities in Silver Chloride Single Crystals*

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An experimental study of the optical spectra of single AgCl:Co and AgCl:Ni crystals and the EPR (electron paramagnetic resonance) spectra of oriented AgCl:Co crystals is described. Six optical absorption peaks due to Co and five due to Ni diffused into AgCl were found at 77°K in the 3500 to 26 000 Å range. The optical data are interpreted using the Tanabe and Sugano crystal field theory as due to divalent Co and Ni in an octahedral field. The crystal field theory parameters are $Dq=680\pm30$ cm^{-1}, $B=790\pm20$ cm^{-1}, and $C=3320\pm70$ cm^{-1} for Co^{++} and $Dq=670\pm5$ cm^{-1}, $B=805\pm7$ cm^{-1}, and $C=3130\pm50$ cm^{-1} for Ni^{++}. The EPR spectra of AgCl:Co samples oriented by the back-reflection x-ray technique were obtained at 77 and 2.1°K where the Co hyperfine structure was resolved. The EPR data are interpreted as due to divalent cobalt in two different centers both with octahedral symmetry distorted axially in a [100] direction. The spin Hamiltonian parameters for the two centers are $g_{\parallel}=5.38\pm0.03$, $g_{\perp}=3.87\pm0.02$, $A=(233\pm3)\times10^{-4}$ cm^{-1}, and $B=(89\pm2)\times10^{-4}$ cm^{-1} for the most prominent EPR lines and $g_{\parallel}=3.48\pm0.02$, $g_{\perp}=4.70\pm0.05$, $A=(55\pm10)\times10^{-4}$ cm^{-1}, and $B=(170\pm20)\times10^{-4}$ cm^{-1} for the weak lines. Thermal and optical bleaching experiments demonstrated the stability of the divalent state for Co and Ni in AgCl. Attempts to produce intrinsic centers by quenching AgCl from a Cl$_2$ anneal or by irradiation with blue light at 2.1 and 77°K did not produce measurable EPR or optical spectra.

I. INTRODUCTION

THIS paper reports an experimental study of the optical spectra of single AgCl:Co and AgCl:Ni crystals and the EPR (electron paramagnetic resonance) spectra of oriented AgCl:Co crystals. EPR has previously been used in studies of AgCl:Mn [1–4] and AgCl:Cu.[5–8] The purpose of the work reported here has been to establish the valence state, lattice position, and site symmetry of Co and Ni in AgCl. In part, this study has been motivated by a desire to understand the role of these impurities in the photographic process. There has also been a desire to make comparisons with studies of Co and Ni in alkali halide and magnesium oxide crystals in order to better understand the effect of the host lattice on the properties of these impurities.

The optical absorption was measured at 77°K over the 3500 to 26 000 Å range in single AgCl crystals which had been colored by diffusion using CoCl$_2$ or NiCl$_2$. The optical spectra are interpreted in terms of crystal field theory as due to divalent Co and Ni in a dominantly octahedral field. The determination of octahedral symmetry is consistent with the hypothesis that Co and Ni go into AgCl substitutionally for Ag. The EPR spectra of AgCl:Co samples oriented by the back reflection x-ray technique were studied at 77 and 2.1°K at 9.8 Gc/sec over the 500 to 6000 G range. Using the spin Hamiltonian formalism, the EPR data are interpreted as arising from divalent cobalt in two different centers both with octahedral symmetry distorted axially in a [100] direction. A number of models for centers with the observed symmetry are presented, but the data do not permit a definite assignment of models. In particular, the data are consistent with, but do not prove, the existence of a positive ion vacancy in the site along [100] nearest the Ag site occupied by the Co^{++}. Thermal and optical bleaching experiments are described which indicate the stability of the divalent state for Co and Ni in AgCl. Preliminary EPR studies of AgCl:Ni have not yielded reportable results. Unsuccessful attempts to produce intrinsic centers in AgCl with measurable EPR or optical spectra by quenching from a Cl$_2$ atmosphere anneal or by irradiation with blue light at 77 and 2.1°K are also discussed.

II. EXPERIMENTAL TECHNIQUES

The EPR spectrometer used in this work has been described by Ohlsen.[9,10] Because of the rather high dielectric constant of AgCl, the resonant frequency of an X-band cavity was lowered roughly 6% to the operating frequency of about 9.8 Gc/sec by a sample of dimensions 2 mm×8 mm×16 mm. The sample was placed against one of the side walls in the region of maximum microwave field, H_1, so that the dc magnetic field, H_0, was always perpendicular to H_1. A Model 14 Cary Recording Spectrophotometer[11] was used to measure optical densities from zero to two over the 2000 to 26 000 Å

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wavelength band. The reproducibility of the recorded spectra was found to be better than 0.01 O.D. unit.

The samples used in this work[12] were always cleaned immediately before annealing and diffusion experiments. Since AgCl is photosensitive, they were handled under red safelights[13] during the cleaning and all other operations. To clean the samples, they were first washed in reagent quality acetone for about two minutes and then etched in a reagent grade $Na_2S_2O_3\cdot 5H_2O$ solution (hypo) for about 1 min. Next, they were washed in reagent grade NaOCl (sodium hypochlorite) for about 1 min and afterwards etched in reagent grade concentrated hydrochloric acid for 1 min. Finally, they were rinsed in four or five changes of distilled water for 1 min each and then dried on filter paper. Glass tweezers were used to transfer the samples from one reagent to another. The hypo solution was made up of 200 g of $Na_2S_2O_3\cdot 5H_2O$ reagent crystals in 400 ml of distilled water.

One of the unfortunate properties of AgCl is that it does not cleave at room temperature. This defect is partially mitigated by the relative softness of the material which permits easy sawing. No lubricant was used in the sawing operation.

The samples were smoothed by hand lapping on a ground glass plate covered with a slurry of superfine abrasive and the previously described hypo. Afterwards, the samples were polished by rubbing on a felt cloth saturated with the reagent quality hypo solution. Since the etching rate of the hypo depends upon the orientation of the lattice with respect to the surface of the sample, large angle grain boundaries, if any existed, were well defined after the sample had been polished. Surfacing of samples was found to be the most practical way of determining if they were single crystals.

Tucker[5] reported the use of back reflection x-ray techniques in the orientation of single AgCl: Cu crystals. Especial care must be given to the preparation of the surface of the sample to be x rayed. Since silver chloride is relatively soft and plastic, the regular lattice structure is easily deformed at the surface. A deformed surface will give rise to Laue smudges on the x-ray photograph rather than well defined Laue spots. Often, a satisfactory surface for x-ray photography could be obtained using only the techniques already described. If necessary, the surface could be further improved for x-ray photography by agitating the sample in a beaker of the hypo solution for 2 to 5 min. This treatment etched the surface, yet there was no danger of mechanical deformation.

For the EPR work, the samples were oriented so that a [110] direction would be perpendicular to the applied field, H_0. With a sample so oriented, the magnetic field, rotatable about a vertical axis, could be made successively parallel to [100], [110], and [111] directions in the sample.

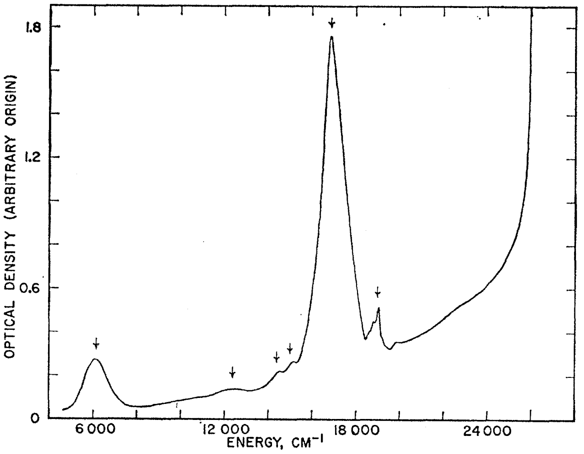

FIG. 1. Optical spectrum of divalent cobalt at liquid-nitrogen temperature. The arrows identify the six observed absorption peaks.

Cobalt and nickel as well as iron and chromium were successfully diffused into nominally pure AgCl samples. The techniques used in these diffusion experiments are described elsewhere.[14]

III. OBSERVATIONS

The observed optical spectrum of AgCl: Co at liquid nitrogen temperature is shown in Fig. 1 over the 3800 to 26 000 Å range. The data were taken after the sample had been annealed in distilled chlorine gas at a pressure of one atmosphere at 375°C for several hours and then allowed to cool to room temperature in about 10 min. The sample appeared blue in agreement with the observations of Moser, Nail, and Urbach.[15] These workers had added the cobalt impurity to the silver chloride in the melt. The spectrum shown in Fig. 1 bears a qualitative resemblance to the absorption spectrum of AgBr: Co reported by Moser and Urbach.[16] The most noticeable difference is that the main absorption peak occurs at about 15 900 cm^{-1} (6300 Å) in AgBr: Co whereas it is found at about 16 850 cm^{-1} in AgCl: Co. The AgCl: Co spectrum was also observed at room temperature, but better resolution of the optical absorption peaks was obtained at liquid nitrogen temperature. The fundamental absorption edge shifted toward shorter wavelengths as the temperature was lowered in agreement with the observations of Moser and Urbach[16] in nominally pure AgCl. Six optical absorption peaks which have been marked by arrows were seen with approximately the same relative intensities in a number of AgCl: Co samples and could be attributed to the cobalt impurity. Expressed in wave numbers these were at $19\,000\pm100$ cm^{-1}, $16\,850\pm100$ cm^{-1}, $15\,000\pm100$ cm^{-1}. $14\,400\pm75$ cm^{-1}, $12\,400\pm200$ cm^{-1}, and 6150 ± 50

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[12] Kindly provided by F. Moser and R. Gluck, Research Laboratories, Eastman Kodak Company.

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cm^{-1}. The approximate intensity ratio for these peaks was 15:150:10:10:5:20, respectively.[17] The peak at 19 000 cm^{-1} had some unresolved structure, but the other peaks appeared smooth. The sample thicknesses ranged from 2 to 8 mm in these optical experiments.

If too much cobalt was diffused in, the samples acquired a cloudy blue-white appearance. Presumably the cloudiness was due to scattering from precipitated $CoCl_2$ and occurred as the cobalt solubility limit in AgCl was exceeded.

Polycrystalline samples containing cobalt were surprisingly brittle and had to be handled with some gentleness. At room temperature these samples could be quite easily broken along large-angle grain boundaries.

Attempts were made to reduce the valence state of the cobalt by annealing AgCl:Co samples in various atmospheres. These experiments were prompted by the work of Moser, Nail, and Urbach[15] and Tucker[5] which showed that divalent copper in AgCl could be reduced to the monovalent state by an anneal in vacuum or in a helium, nitrogen, or air atmosphere. A sample containing cobalt was annealed in 1.1 atm of helium gas at 330°C for 90 min (nominally pure AgCl melts at 455°C). It was then allowed to cool to room temperature in about ten minutes, but the color of the sample was not visibly changed by this anneal. An optical absorption run at liquid nitrogen temperature also showed no measurable change in the optical absorption spectrum. These observations indicate that the valence state of cobalt in AgCl was not reduced by a helium atmosphere anneal.

A further attempt to reduce the valence state of the cobalt involved annealing a AgCl:Co sample in vacuum at 380°C for 14 h. Again, no visible change was produced in the optical absorption. An optical absorption run at room temperature over the 4000 to 6500 Å range also showed no measurable change in the spectrum.

An optical bleaching experiment at room temperature was performed with negative results on the AgCl:Co sample which had been annealed in vacuum. The sample was illuminated by light from a 300 W tungsten filament projector lamp for 30 min. During this experiment the lamp was about 5 cm from the sample and the light was filtered by a Corning 3–71 filter which cut out all light with a wavelength shorter than 4700 Å. No measurable decrease in the absorption peaks attributed to cobalt was noted. A decrease of 2% in the strong peak at 16 850 cm^{-1} would have been considered significant. This negative experiment is at variance with the work of Moser, Nail, and Urbach[15] who reported successful optical bleaching of the blue color attributed to cobalt.

A distinct color change from blue to gray-blue was produced by an air anneal at 380°C for 100 h. This change may correspond to the thermal bleaching effect noted by Moser, Nail, and Urbach.[15] The optical absorption of the gray-blue AgCl:Co sample was obtained at room temperature over the 4000 to 6500 Å range. Again, the peaks at 19 000 and 16 850 cm^{-1} were observed with no measurable change in intensity, but, in addition, there was a steady increase in the optical absorption with decreasing wavelength. The additional absorption appeared to be in the volume and not merely on the surface.

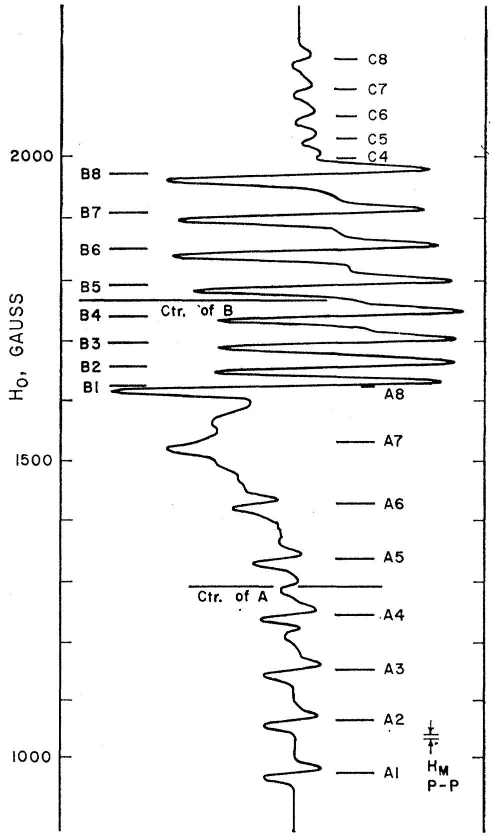

FIG. 2. EPR spectrum of divalent cobalt at liquid-helium temperature for $H_0 \parallel [100]$. The sample temperature is 2.1°K and the microwave frequency is 9.769 Gc/sec.

At liquid nitrogen temperature a single, broad EPR signal was observed for AgCl samples doped with cobalt. The g value of this resonance was measured as 4.09 ± 0.05 and the absorption derivative peak-to-peak width was about 300 G. No noteworthy change was observed in this signal as H_0 was made successively parallel to the [100], [110], and [111] directions.

However, at liquid helium temperatures the cobalt EPR signal was resolved into a series of octets. This anisotropic spectrum is shown in Fig. 2 for the case with H_0 parallel to the [100] direction. The absorption derivative peak-to-peak value of an individual line was about 15 G.

In Fig. 2, only five lines of the "*C*" octet can be seen. The other three lines are presumably obscured by the stronger absorption lines of the "*B*" octet. Three other weak lines could be discerned when H_0 was parallel to

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[17] In a private communication, F. Moser has reported additional peaks at 630 and 644 mμ in AgCl containing cobalt added in the melt.

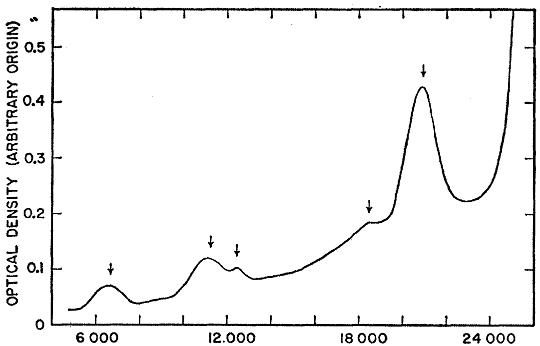

FIG. 3. Optical spectrum of divalent nickel at liquid-nitrogen temperature. The arrows identify the five observed absorption peaks.

the [100] direction. One fell on the low-field side of the "*A*4" line, one fell between "*A*4" and "*A*5," and one fell on the high-field side of "*A*5."

Whether a cobalt-doped sample was quenched from room to liquid nitrogen temperature in about 10 sec or cooled down in about 2 h did not affect the relative intensities of the EPR peaks shown in Fig. 2 in any noteworthy fashion. In particular, no isotropic octet was seen after the quench. Such an orientation-independent octet would have indicated the existence of cobalt ions with no associated positive ion vacancies.

Similarly, the cobalt EPR spectrum was not affected by the helium, air, or chlorine atmosphere anneals previously described. This statement is to be qualified by the usual reservations concerning EPR intensity measurements. The helium atmosphere anneal produced no EPR signal attributable to monovalent cobalt.

The relative intensities of the "*A*," "*B*," and "*C*" octets were found to be independent of the concentration of the cobalt impurity although the concentration was varied by more than a factor of five in the group of samples which were studied.

Qualitative observations were made of the EPR spectra of cobalt in oriented AgBr crystals. At 1.2°K the individual lines had an absorption derivative peak-to-peak width of about 30 G. Hence, the spectra were not as well resolved as those of AgCl:Co. In the AgBr:Co spectra, lines corresponding to the "*A*" and "*B*" octets of Fig. 2 were observed. No lines corresponding to the "*C*" octet were seen, but this could have been because of the poorer resolution.

The observed optical spectrum of nickel in AgCl at liquid nitrogen temperature is shown in Fig. 3 over the 3500 to 26 000 Å range. The data were taken after the sample had been annealed in distilled chlorine gas at a pressure of 1 atm at 395°C for many hours and then allowed to cool to room temperature in about 10 min. The sample appeared orange-red in agreement with the observations of Moser, Nail, and Urbach.[15] These workers had added the nickel impurity to the silver chloride in the melt.

Five optical absorption peaks were found and are identified with arrows in Fig. 3. Expressed in wave numbers these were at 20 920±40 cm^{-1}, 18 480±130 cm^{-1}, 12 470±70 cm^{-1}, 11 250±25 cm^{-1}, and 6680±40 cm^{-1}. The approximate intensity ratio for these peaks was 21:1:1:5:4, respectively. All of the peaks appeared to be without structure. The sample thickness was about 2 mm in these optical experiments.

In no case was sufficient nickel diffused into the samples to cause any cloudiness such as was sometimes observed in the AgCl:Co samples. Polycrystalline samples containing nickel had the same brittleness along large-angle grain boundaries as was noted previously for the samples containing cobalt. One of the AgCl:Ni samples fractured along a large-angle grain boundary when it was quenched to liquid nitrogen temperature in about 2 sec.

A sample containing nickel was annealed in 1.1 atm of helium gas at 325°C for 90 min and then allowed to cool to room temperature in about 10 min in an attempt to reduce the valence state of the nickel. Qualitatively, no change was seen from the spectrum observed after a chlorine anneal.

IV. DISCUSSION

A. Optical Spectra of AgCl:Co

In this section, the crystal field theory of Tanabe and Sugano[18] is used to establish that the hypothesis of octahedrally coordinated divalent cobalt is consistent with the AgCl:Co optical data. Arguments are then given to show that the cobalt ions responsible for the optical spectra occupy substitutional sites in the crystal. The failure of the thermal and optical bleaching experiments is interpreted as evidence for the stability of the divalent state for cobalt in AgCl.

The three parameters used by Tanabe and Sugano are Dq, B, and C, and they are regarded as empirical parameters to be determined from the data. The quantity Dq is the cubic crystal field parameter and is a measure of the interaction of the $3d$ electrons with the nearest neighbor ions. The quantities B and C are the Racah parameters[19] which characterize the electrostatic interaction within the $3d$ shell of the divalent cobalt ion.

The strong absorption peak at 16 850 cm^{-1} is assigned to the $\Gamma_4(^4F) \rightarrow \Gamma_4(^4P)$ transition since the spin multiplicity, S, is not changed. Transitions in which S changes are expected to be weaker. It is assumed that the fairly strong infrared absorption peak at 6150 cm^{-1} corresponds to the $\Gamma_4(^4F) \rightarrow \Gamma_5(^4F)$ transition. This transition is expected to be fairly strong since the representation of the initial state (Γ_4) is contained in the direct product of the representations of the electric dipole operator (Γ_4) and the final state (Γ_5). It is assumed that the absorption peak at 19 000 cm^{-1} cor-

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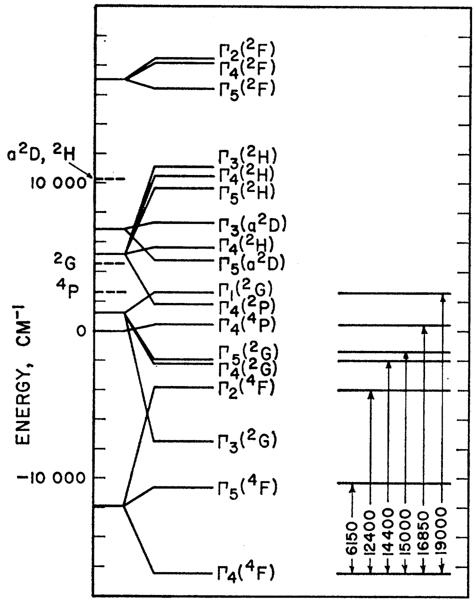

FIG. 4. Energy level diagram for divalent cobalt. The six observed optical transitions have been indicated on the right. In the center are the predicted levels computed using the energy matrices of Tanabe and Sugano with $Dq=680$, $B=790$, and $C=3320$ cm^{-1}. The solid lines on the left are the predicted levels using Tanabe and Sugano's matrices with $Dq=0$ cm^{-1}. The dashed lines on the left represent the free-ion energy levels. The $\Gamma_3(b^2D)$ and $\Gamma_5(b^2D)$ levels lie too high to be plotted on this diagram. The a^2D level lies within about 14 cm^{-1} of the ^2H level.

responds to the $\Gamma_4(^4F) \rightarrow \Gamma_1(^2G)$ transition. An argument based on group theory similar to that already given indicates that this transition is allowed. With these assignments, one obtains $Dq=680\pm30$ cm^{-1}, $B=790 \pm20$ cm^{-1}, and $C=3320\pm70$ cm^{-1}. These values of Dq, B, and C may be substituted into the energy matrices of Tanabe and Sugano in order to obtain the eigenvalues which are given in Fig. 4. It is felt that the agreement between the energy levels which have been computed from Tanabe and Sugano's matrices and those based on the observed absorption lines is fairly good and thus consistent with the hypothesis that the cobalt ions are in the divalent state and that they are octahedrally coordinated.

There are a number of arguments which indicate that the cobalt ions responsible for the optical spectra occupy substitutional sites. First, if the cobalt ion is in a substitutional site, its nearest neighbors will be six chlorine ions and these will produce the octahedral (sixfold cubic) symmetry suggested by the observed optical spectra. Second, the three crystal field parameters for AgCl:Co seem consistent with values found for divalent cobalt in other materials in which there is octahedral coordination with six nearest neighbor ions. For example, Pappalardo *et al.*,[20] have used $Dq=927$ cm^{-1}, $B=845$ cm^{-1}, and $C=3800$ cm^{-1} in MgO:Co; whereas in AgCl:Co the parameters $Dq=680\pm30$ cm^{-1}, $B=790 \pm20$ cm^{-1}, and $C=3320\pm70$ cm^{-1} have been found appropriate. McClure[21] presents a table of Dq values for iron group ions as a function of the six nearest neighbor ions which shows that Dq steadily decreases as one goes through the following sequence of nearest neighbor ions: NH_3, H_2O, Cl^-, and Br^-. Hence, Dq is expected to be smaller for AgBr:Co than for AgCl:Co. Such a prediction is consistent with the observation of Moser and Urbach[16] that the strongest absorption peak (presumably due to the $\Gamma_4(^4F) \rightarrow \Gamma_4(^4P)$ transition) falls at lower energy than the corresponding absorption peak in AgCl:Co. Third, if the assumption is made that the divalent cobalt ion occupies an interstitial site, one can reason that the optical spectra will be much different than what have actually been observed. Suppose the divalent cobalt ion is in such an interstitial position that it has four nearest neighbor silver ions with tetrahedral coordination and four equally near chlorine ions also with tetrahedral coordination. The Dq parameter would be positive if only the nearest neighbor silver ions were considered whereas it would be negative if only the nearest neighbor chlorine ions were considered. Hence, when the effects of all eight ions are considered simultaneously, it is expected that Dq will be rather small which would produce small crystal field splittings. In particular, the strong transition observed at 16 850 cm^{-1} would decrease in energy.

The failure of the thermal bleaching experiments to decrease the optical absorption peaks attributed to divalent cobalt in AgCl is evidence of the stability of the divalent state. The cause of the additional optical absorption after the air anneal is possibly oxygen. At any rate it is not explainable in terms of crystal field theory.

The negative optical bleaching experiments are at variance with the results of Moser, Nail, and Urbach.[15] Possibly their optical bleaching experiment was done to see if the Herschel effect is operative in cobalt-doped AgCl. The Herschel effect as discussed by Mott and Gurney[22] is the optical bleaching of photolytically darkened silver halide emulsions by strong red light. The optical bleaching of photolytically darkened AgCl crystals was studied by Hilsch and Pohl.[23] More recent investigations of the same phenomena have been made by Brown and Wainfan.[24,25] A study of the optical bleaching of photolytically darkened, copper-doped AgCl has been reported by Moser, Nail, and Urbach.[15] It is thought that the optical bleaching experiments reported by all these workers depend on the regression of the colloidal silver photoproduct. However, no evidence

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[22] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, 1948), 2nd ed., p. 243.

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

[24] F. C. Brown and N. Wainfan, Phys. Rev. **105**, 93 (1957).

[25] N. Wainfan, Phys. Rev. **105**, 100 (1957).

of any colloidal silver photoproduct has been observed in the optical absorption spectra of cobalt-doped AgCl. Hence, the failure of an optical bleaching experiment in AgCl:Co is not surprising.

B. EPR Spectra of AgCl:Co

The emphasis in this section is on the interpretation of the EPR spectra of AgCl:Co in terms of a spin Hamiltonian in order to establish the valence state and site symmetry of the cobalt ion. This interpretation does not depend on the discussion of the optical spectra, but it is consistent with the determination of the valence state and site symmetry which have already been made from the application of crystal field theory to the optical data. A number of models for centers which have the symmetry indicated by the EPR spectra are discussed, but a definite determination of which centers are actually responsible for the EPR spectra does not appear justified by the data.

The ground state, $\Gamma_4({}^4F)$, of divalent cobalt in an octahedral field has threefold orbital degeneracy and fourfold spin degeneracy. The combined action of spin-orbit coupling and an axial crystalline field is to split the ground state into six Kramers doublets. The lowest lying Kramers doublet has an effective spin $S'=\frac{1}{2}$. The spin Hamiltonian as developed by Abragam and Pryce[26] is

$$W=g_{\parallel}\beta H_zS'_z+g_{\perp}\beta(H_xS'_x+H_yS'_y)+AS'_zI_z+B(S'_xI_x+S'_yI_y) \quad (1)$$

plus higher order terms which turn out to be unimportant in the analysis of the observed divalent cobalt EPR spectrum in AgCl. Here β is the usual Bohr magneton. This spin Hamiltonian is applicable to the case of an EPR spectrum whose anisotropy has axial symmetry about the z axis. For divalent cobalt in AgCl, it is found that the z axis lies along a [100] or equivalent direction in the crystal.

For transitions between the lower and upper levels of a Kramers doublet, Bleaney[27] has found that

$$h\nu=g\beta H_0+Km+\frac{B^2}{4h\nu}\left[\frac{A^2+K^2}{K^2}\right][I(I+1)-m^2]+\frac{1}{2h\nu}\left[\frac{A^2-B^2}{K}\right]^2\left[\frac{g_{\parallel}g_{\perp}}{g^2}\right]^2\sin^2\theta\cos^2\theta m^2, \quad (2)$$

where

$$g=(g_{\parallel}^2\cos^2\theta+g_{\perp}^2\sin^2\theta)^{1/2} \quad (3)$$

and

$$K^2g^2=A^2g_{\parallel}^2\cos^2\theta+B^2g_{\perp}^2\sin^2\theta. \quad (4)$$

The nuclear spin, I, of Co^{59} (100% abundant) is $\frac{7}{2}$. Here, H_0 is the applied magnetic field, θ is the angle between the applied magnetic field and the axis of crystal field symmetry (in this case the [100] direction in the crystal), and ν is the microwave frequency. The four parameters, $g_{\parallel}$, $g_{\perp}$, A, and B can all be determined from the spectrum obtained when the applied magnetic field is parallel to a [100] direction.

It is found that (2)–(4) make a good fit with the experimental data (octets "A" and "B" of Fig. 2) if $g_{\parallel}=5.38\pm0.03$, $g_{\perp}=3.87\pm0.02$, $A=(233\pm3)\times10^{-4}$ cm^{-1}, and $B=(89\pm2)\times10^{-4}$ cm^{-1}.

For $H_0\|[100]$, the observed intensity ratio of the "B" to the "A" octet is about 4:1 although at this orientation there are only twice as many [100] symmetry axes at 90° to H_0 as at 0°. However, an intensity correction is necessary because the transition probability induced by H_1 is proportional to the (g value)^2 of the center in the direction of H_1. For example, the center responsible for the "A" octet ($\theta=0°$) has a g value of 3.87 in the H_1 direction. A small correction must also be made for the difference in the observed line widths of the individual lines of the "A" and "B" octets since the intensity of EPR lines on a derivative plot is inversely proportional to the square of their width. When these two corrections are made, good agreement is obtained with the 2:1 ratio expected for the intensity ratio of the "B" to the "A" octet.

So far, nothing has been said about the interpretation of the "C" octet in Fig. 2. Since this octet is small in intensity and three of its lines are obscured by the "B" octet, the interpretation of the "C" octet must be regarded as tentative. Studies of the EPR spectra as a function of angle indicate that the "C" octet corresponds to a divalent cobalt ion in an axially symmetric field which is in a [100] direction. However, it appears that $\theta=0°$ for the "C" octet. For if θ were 90° for the "C" octet, then this octet should again be seen when H_0 is made parallel to a [110] direction which it is not. The three weak lines seen in the vicinity of the "$A4$" and "$A5$" lines when $H_0\|[100]$ may be part of the octet corresponding to $\theta=90°$. Though these weak lines should again appear in the same place when H_0 is parallel to [110] they are not seen. They may be obscured in this case by more prominent lines. If the weak line observed on the low-field side of "$A4$" in Fig. 2 is the last line of the $\theta=90°$ octet, then $g_{\perp}=4.70\pm0.05$. In other words, it is suggested that the "C" octet corresponds to a divalent cobalt ion with [100] axial symmetry and a spin Hamiltonian having as its parameters $g_{\parallel}=3.48\pm0.02$ and $g_{\perp}=4.70\pm0.05$. Such values are consistent with the theoretical predictions of Abragam and Pryce.[28] A rough calculation based on the data in Fig. 2 gives $A=(55\pm10)\times10^{-4}$ cm^{-1} and $B=(170\pm20)\times10^{-4}$ cm^{-1} for the other parameters of the spin Hamiltonian corresponding to the weak EPR lines (including the "C" octet). The argument used to correct the intensities of

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the most prominent octets ("*A*" and "*B*" in Fig. 2) can also be applied to the intensities of the weak lines. The corrections turn out to be in the right direction for the identification which has been made for the "*C*" octet and the three weak lines seen in the vicintiy of "*A*4" and "*A*5."

The broadening of the EPR lines which produces the loss of resolution at liquid nitrogen temperature is probably the result of a very short spin-lattice relaxation time. The same observation has been made by Bleaney and Ingram[29] in their study of the hyperfine structure in the EPR spectrum of a diluted cobalt Tutton salt.

The values of the spin Hamiltonian reported here for the EPR spectra of AgCl:Co may be compared with the results of Low[30] for MgO:Co. He found only a single octet and this could be described by the following spin Hamiltonian parameters: $g=4.278$ and $A=97.8\times 10^{-4}$ cm^{-1}. Since the spectra were isotropic, this meant that there was no measurable distortion of the octahedral crystalline field. Hence, Low concluded that there was no measurable static Jahn-Teller effect[31] operative for divalent cobalt in MgO.

The main aim of this section has been to show that the most prominent EPR lines arise from centers with a [100] symmetry axis and that, tentatively, the weak lines arise from another center which also has a [100] symmetry axis. It is possible to construct a number of models for substitutional cobalt centers which have a [100] symmetry axis. The [100] distortion of the cubic crystalline field acting on the divalent cobalt ion may be due to a positive ion vacancy in a next-nearest cation site (one lattice constant removed) or to one which is two lattice constants away; it may be due to an impurity anion such as divalent oxygen in a nearest neighbor site; it may result from the Jahn-Teller effect. Although there are other more complicated models which will produce a [100] distortion, it is customary to assume that the simplest models are the ones which actually exist. Since there are no simple models for interstitial cobalt with a [100] crystal field distortion, one has an additional reason for believing the cobalt is substitutional.

The experiment of quenching a AgCl:Co sample from room to liquid nitrogen temperature in about ten seconds represented an attempt to produce divalent cobalt centers with no associated positive ion vacancies. Such centers might be expected to give an isotropic EPR spectrum. The experiment was suggested by Tucker's work[5] on AgCl:Cu which indicated that the formation of divalent copper centers with no associated positive ion vacancies was enhanced when the samples were cooled to liquid nitrogen temperature in about 2 min. When cooling times of several hours were used, he found the number of divalent copper centers with associated positive ion vacancies increased. On the other hand, Grossberg[2] found no evidence for manganese centers with no associated positive ion vacancies even when AgCl:Mn samples warmed to 60°C were plunged into liquid air.

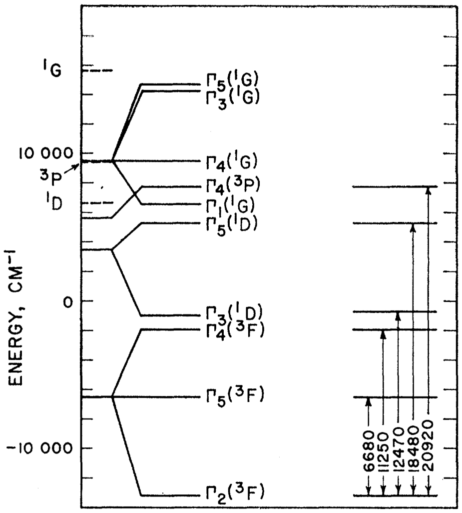

FIG. 5. Energy level diagram for divalent nickel. The five observed optical transitions have been indicated on the right. In the center are the predicted levels computed using the energy matrices of Tanabe and Sugano with $Dq=670$, $B=805$, and $C=3{,}130$ cm^{-1}. The solid lines on the left represent the predicted levels using Tanabe and Sugano's matrices with $Dq=0$ cm^{-1}. The dashed lines on the left represent the free-ion energy levels. The $\Gamma_1(^1S)$ level lies too high to be plotted on this diagram.

Based on considerations of charge neutrality and the conclusions of Tucker and Grossberg, it seems that a positive ion vacancy in a next-nearest cation site is the most probable model to explain one of the AgCl:Co centers (probably that one responsible for the *A* and *B* octets). The failure of the quenching experiment to change the AgCl:Co spectra is consistent with Grossberg's observation in AgCl:Mn.

The fact that the relative intensities of the "*A*," "*B*," and "*C*" octets were independent of the cobalt concentration indicates that neither of the observed centers involved an impurity anion such as divalent oxygen in a nearest neighbor site.

C. Optical Spectra of AgCl:Ni

The discussion of the AgCl:Ni optical spectra proceeds much like that already given for AgCl:Co. Here, the hypothesis of octahedrally coordinated divalent nickel is found to be consistent with the optical data. The fairly strong infrared absorption peak at 6680 cm^{-1} is assigned to the $\Gamma_2(^3F)\rightarrow\Gamma_5(^3F)$ transition (see Fig. 5) which is expected to be fairly strong since the direct product of the representation of the electric dipole operator (Γ_4) with the representation of the final state (Γ_5) contains the representation in the symmetry group of the initial state (Γ_2). Use of the energy matrices of Tanabe and Sugano[21] then gives $Dq=670\pm 5$ cm^{-1}. Next, it is assumed that the strong peak at 20 920

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cm^{-1} corresponds to the $\Gamma_2(^3F)\rightarrow\Gamma_4(^3P)$ transition. This transition is expected to be strong since the spin multiplicity, S, is not changed. Calculation then gives $B=805\pm7$ cm^{-1}. Lastly, it is assumed that the weak peak at 18 480 cm^{-1} corresponds to the $\Gamma_2(^3F)\rightarrow\Gamma_5(^1D)$ transition. One then finds $C=3130\pm50$ cm^{-1}. The three parameters have been substituted into Tanabe and Sugano's matrices to obtain the eigenvalues given in Fig. 5. It is believed that the agreement between the energy levels which have been computed from Tanabe and Sugano's matrices and those based on the observed absorption lines is good and thus consistent with the hypothesis that the nickel ions are in the divalent state and octahedrally coordinated. Strictly analogous arguments as were used in the discussion of the AgCl:Co optical spectra can be used to indicate that the nickel ions responsible for the AgCl:Ni optical spectra occupy substitutional sites. The failure of the bleaching experiments indicates the stability of the divalent state for nickel in AgCl.

V. SUMMARY AND CONCLUSIONS

This paper has described an experimental study of the optical spectra of AgCl:Co and AgCl:Ni single crystals and the EPR spectra of oriented AgCl:Co crystals. Tanabe and Sugano crystal field theory was used to interpret the optical spectra in terms of octahedrally coordinated divalent cobalt and nickel. Arguments were given for AgCl:Co which indicate that cobalt is substitutional for silver. Analogous arguments apply for AgCl:Ni. Unsuccessful thermal and optical bleaching experiments indicated the stability of the divalent state for cobalt and nickel in AgCl. Hence, it seems likely that the important role of nickel in electronic processes observed by Michel[32] results from its serving as a recombination center rather than as an electron trap. Although monovalent Co and Ni exist chemically, they fit poorly into the AgCl lattice because of their excess $4s$ electron. On the other hand, monovalent Cu, with its closed d shell, bears a strong resemblance to Ag$^+$, and hence can remain as a stable valence state in AgCl.

The divalent cobalt EPR spectra observed at liquid nitrogen temperature were successfully interpreted in terms of the spin Hamiltonian formalism as due to two different centers both with octahedral symmetry distorted axially in a [100] direction. Quenching experiments failed to produce an EPR spectrum characteristic of Co^{++} with no associated vacancy. Hence, Cu^{++}, with its $3d^9$ configuration, has a smaller binding energy for a vacancy than Co^{++} with its $3d^7$ configuration.

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APPENDIX. INTRINSIC CENTERS IN AgCl

This section describes several unsuccessful attempts to produce intrinsic centers in AgCl with measurable EPR or optical spectra. It is hoped that this section will be read with caution since the experiments which have been done are by no means exhaustive. Our attempts to produce intrinsic centers can be divided into two categories. One group of experiments aimed at producing V-type centers by quenching from a chlorine atmosphere anneal. The other group of experiments involved visible or uv illumination at low temperatures.

The quenching experiments were suggested by the work of Mollwo[33] who showed that by heating samples in a halogen atmosphere it was possible to introduce excess halogen into KBr and KI, but not into KCl. Quenching the samples increases the chances of freezing in excess halogen ions. In our experiments, nominally pure AgCl samples were annealed at 390°C in about 1 atm of distilled chlorine gas for 1 h. The Pyrex annealing tube was then broken and the sample was allowed to fall into a Dewar of liquid nitrogen. The sample was then transferred to the microwave cavity at liquid nitrogen temperature and EPR runs were made at liquid helium temperature. However, no resonances were seen. Also, there was no apparent coloration of the sample after quenching from a chlorine anneal. It must be admitted that during the 1 or 2 sec of the quench the sample was not in a chlorine atmosphere.

Perhaps, it is worthwhile to mention that the failure to color the samples by quenching from a chlorine atmosphere anneal is at variance with the work of Lehfeldt[34] who reported a yellow coloration after such a treatment. Seitz[35] has interpreted Lehfeldt's observations as evidence for V-type centers in AgCl. However, it may be that the yellow coloration reported by Lehfeldt could have been due to an impurity. Preliminary work has shown that AgCl:Tl appears yellowish at room temperature after a chlorine atmosphere anneal; before the anneal, the sample appeared colorless. Quite possibly there are other impurities which would make AgCl appear yellowish after a chlorine atmosphere anneal. The presence of impurities in the AgCl used in the 1930's by the Göttingen group is indicated by the fact that they observed volume photolysis in their purest samples. However, no visible volume photolysis is observed in the purest AgCl currently available.[15]

The group of experiments involving visible or uv illumination at low temperatures was suggested by the

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electrical glow curves reported by Van Heyningen and Brown.[36] These workers observed a number of current peaks during the warming of nominally pure AgCl samples which had been illuminated at liquid helium temperature. They attributed these current peaks to the thermal release of electrons from traps. Although some of the electron traps appeared to be caused by strains, the exact nature of the traps was not determined. Presumably some of the traps could be instrinsic and others could be caused by impurities. In our experiments, nominally pure AgCl samples were continuously illuminated with blue light from a Hg lamp as the samples were cooled from room to liquid nitrogen temperature in about 2 h and then quenched to helium temperature in less than 2 min. In other experiments, samples were continuously illuminated at liquid helium or nitrogen temperature for 10 to 30 min with either blue light from a Hg lamp or with white light from a tungsten filament lamp. No EPR signals were seen which could be attributed to the illumination. Also, there was no apparent coloration of the samples after these experiments. There exist at least two possible explanations for these failures. First, the electrical glow curve technique is several orders of magnitude more sensitive than EPR in the detection of electron traps. Second, there was no dc electric field applied during the illumination to help prevent electron-hole recombination.

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General Method for Determining Lattice Point Defect Configurations Including their Dependence on Electron Redistribution*

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A general method is proposed for determining the equilibrium configurations of single lattice point defects and complexes thereof. The equilibrium configuration of the lattice containing impurities, interstitials, and vacancies is determined by using a variational approach minimizing the energy of the crystal. The energy of the crystal is explicitly expressed in terms of the displacements of the ions. It is assumed that the energy of the system of ions, including the point defects, arises from two-body interactions. The energy of the system of valence or conduction electrons is derived in the general form from a Hamiltonian including the coupling between the distorted lattice and the electrons. The wave functions of the valence or conduction electrons are given by an integral equation derived from the Hartree-Fock equation. The explicit dependence of the wave functions on the displacements of the ions is obtained from the integral equation by using the Born approximation. Using these wave functions the energy of the considered system of electrons is explicitly expressed in terms of the displacements. To apply the method in practice the wave functions and the crystal energy need to be evaluated explicitly.

I. INTRODUCTION

MANY experiments[1–3] have been performed to study the effects of point defects in crystals. To be able to check theoretically the interpretation of these experiments it is necessary to determine the lattice distortion and changes in the distribution of the electrons associated with the various point defects and complexes thereof. In particular, it is of interest to determine the equilibrium configurations and formation energies of an interstitial, a vacancy, a close Frenkel pair (vacancy plus interstitial), a divacancy, and a di-interstitial. In all previous calculations[1–9] of point defect configurations the effect on the lattice distortion arising from the redistribution of the electrons has been neglected. The principal purpose of this paper is, therefore, to determine the lattice distortion by taking into account the coupling between the lattice and the electrons.

The crystal is represented by a system of ions (each ion consists of nucleus plus tighly bound electrons) arranged in a static lattice and valence or conduction electrons moving in a potential field produced by the electrons themselves and the ions. The lattice distortion

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