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Speculations on the Properties of the Silver Halide Crystals

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The available experiments on the absorption spectra, photoelectric, and photolytic properties of the silver halide crystals are re-analyzed and interpreted. The conclusions drawn may be regarded in the nature of extensions of the Gurney-Mott theory of photolytic action. The principal speculative viewpoints are as follows:

1. The characteristic absorption spectra of the pure salts derive much of their structure from forbidden optical transitions associated with lattice distortion arising from dislocations. It is proposed that in materials prepared from the melt the dislocations are formed by condensation of lattice vacancies associated with about 0.1 percent of Schottky defects.
2. It is also concluded that some of the absorption structure is associated with "forbidden" $d^{10} \rightarrow d^9 s$ transitions in the silver ions.
3. It is proposed that the electron traps which are responsible for the early deposits of photolytic silver are incipient halogen-ion vacancies which have an effective charge $+e/2$. These vacancies occur at jogs in dislocation lines, where such lines pass from one slip plane to a parallel plane, and may be enhanced by plastic flow. Incipient positive-ion vacancies, having an effective charge $-e/2$, also occur and act as nuclei for forming halogen clusters whose absorption bands are hidden behind the fundamental band.
4. At room temperature, the photoelectrons may be trapped by interstitial silver ions before ending at incipient halogen-ion vacancies; however this process represents only a temporary delay since the entire silver atom may migrate to the dislocation.
5. It is suggested that the addition of sulfur to the silver halides plays a role in enhancing darkenability in three ways: (a) By forming precipitates which produce distortion that enhances the number of incipient vacancies; (b) by extending the absorption spectrum toward the red end of the spectrum; and (c) by increasing the equilibrium density of interstitial silver ions.
6. It is proposed that the luminescent radiation observed in pure silver halides by Farnell, Burton, and Hallama arises from transitions within the silver ion. The emitting ions are at dislocations in AgCl and AgBr.

A sequence of experiments is suggested.

I. INTRODUCTION

THE physical properties of silver chloride and bromide have been of outstanding interest for many decades. In spite of this, many of the most important characteristics[1] of the salts still seem highly enigmatic. The purpose of this paper is to attempt to throw additional light on the factors which determine the properties of the materials by advancing a series of somewhat speculative ideas concerning the electronic states of the constituents and the type of lattice disorder which occur.

The stimulus for this investigation originates in several sources: (1) Increased appreciation[2] of the fact that the imperfections of crystals form a tightly interlocking system of units and that the photographic properties of the alkali halides are probably influenced by a combination of the interactions of excitons, electrons and holes, dislocations and vacant lattice sites; (2) A series of recent papers by Mitchell,[3] Stasiw,[4] Teltow,[5] and Lawson[6] which have reopened the properties of the salts to consideration and have provided new

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[1] Surveys of the physical properties of the silver salts may be found in the following references: R. Hilsch and R. W. Pohl, Z. Physik **64**, 606 (1930); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, London, 1940), Chapter VII; and the review article by W. F. Berg, *Reports on Progress in Physics* II, 248 (1946–1947). See also the forthcoming book, edited by J. W. Mitchell, *Photographic Processes* (Butterworth Scientific Publications, London, 1950).

[2] An attempt to outline the interlocking nature of crystal imperfections has been made by the writer in a manuscript bearing the title "Imperfections in almost perfect crystals: a synthesis" prepared for the Pocono Conference on Almost Perfect Crystals (Sponsored by the National Research Council in 1950). This will be published in book form with the other papers of the conference.

[3] J. W. Mitchell, Phil. Mag. **40**, 249, 669 (1949).

[4] O. Stasiw and J. Teltow, Ann. Physik **40**, 181 (1940); Z. anorg. u. allgem. Chem. **257**, 109 (1949); Gött Nachr. **10**, 155 (1944). O. Stasiw, Z. Physik **127**, 522 (1950).

[5] J. Teltow, Ann. Physik **5**, 63, 71 (1949); Z. physik. Chem. **195**, 197, 213 (1950).

[6] A. W. Lawson, Phys. Rev. **78**, 185 (1950). At the time galley proof of this manuscript is being read (December, 1951), the investigations of Lawson and Kurnick on the influence of pressure, temperature, and divalent impurities on the electrolytic conductivity of silver bromide seem to indicate that below 300°C there is little question that Frenkel defects prevail, in agreement with other investigators. There is evidence to show, however, that Schottky defects may prevail above 300°C and that at the melting point there is of the order of 2.0 percent of Schottky defects. This work suggests that the energy required to form Schottky defects is slightly larger than that needed to form Frenkel defects; however the increase of lattice vibrational energy associated with the formation of Schottky defects is presumably greater than the increase associated with Frenkel defects, so that the former are favored above 300°C in spite of the somewhat larger energy. These conclusions, if substantiated by further work, are in accordance with the views expressed in the present manuscript in the sense that they imply the presence of a relatively high density of Schottky defects at the melting point (0.1 rather than 2.0 percent is assumed in the text) and hence the generation of a high density of dislocations when the crystal is cooled. Analyses bearing further on this point have been presented by K. Kobayashi, Science Rep. Tohuku University, I **34**, 112 (1950); Phys. Rev. **84**, 150 (1952); H. Kanzaki, Phys. Rev. **81**, 884 (1951). The experiments of R. Berry, Phys. Rev. **82**, 422 (1951) appear to contradict the conclusions of Lawson and Kurnick in the temperature range above 300°C, for he apparently finds that the expansion in lattice constant, as determined by x-ray diffraction, matches the linear expansion coefficient, as might be expected if no Schottky defects were formed. Actually, P. H. Miller has recently shown (as yet unpublished work) that the interpretation of x-ray data in the presence of high densities of lattice defects is fairly intricate and ambiguous, so that the issue apparently remains open.

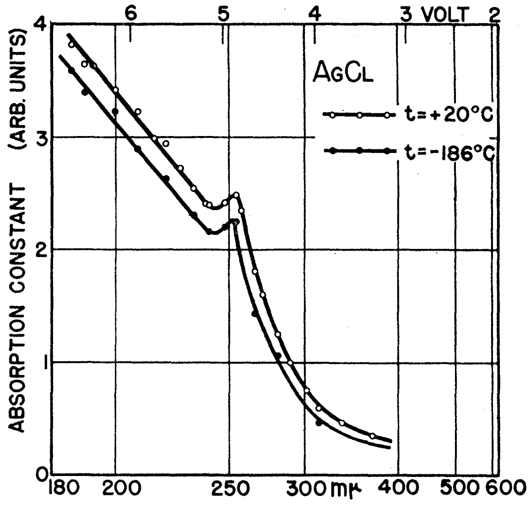

FIG. 1. The absorption spectrum of AgCl at room temperature and liquid-air temperature (after Fesefeldt). The measurements were made on evaporated films, probably of small particle size; however the qualitative features are characteristic of more crystalline materials. The extinction attains a value of the order of 10^5 cm^{-1} near 2500A.

experimental information. Stasiw and Teltow and Mitchell have proposed changes in parts of the Gurney-Mott[7] theory of production of the latent photographic image. In particular, they have proposed changes in the aspects which deal with the precise form of the latent image and the sensitivity specks, but have left the aspects which deal with the production and trapping of photoelectrons and with the migration of interstitial silver ions unchanged.

On the whole we shall not be concerned with the properties of silver halide emulsions as such, but will restrict attention to the bulk material. It is not possible at this time to state whether the properties of the halide grains in the emulsion are the same in all respects, other than those dealing with the increase in surface area, as those of the bulk material having identical chemical composition. For this reason we shall leave open the extent to which the views expressed here have an influence on the sensitivity of emulsions.

Since the thallium halides possess many properties in common with the silver halides, a fraction of the manuscript will be devoted to them for purposes of comparison and completeness.

II. ELECTRONIC ENERGY LEVELS; OPTICAL PROPERTIES

A. Absorption Bands

In analogy with the alkali halides,[8] it is reasonable to assume that the large peaks in optical absorption spectra[9] of the silver halides AgCl and AgBr (Figs. 1 and 2) are associated with the excitation and ionization of the halogen ions. Since the ionization energy of the silver atom is 7.54 ev, in contrast with the value of 5.12 ev for sodium, we should expect the excitation states in the silver salts to be about 2 ev lower, relative to the ground state, than in the corresponding sodium salts, which have the same structure and nearly equal lattice parameters (NaCl: 5.63A, AgCl: 5.54A; NaBr: 5.96A; AgBr: 5.76A). Thus, since the exciton levels of NaCl and NaBr are at 7.8 ev and 6.5 ev above the ground level, respectively, we should expect the levels to be at about 5.5 and 4.2 ev, respectively, for the corresponding silver salts. The separation between the exciton states and the ionization states having the same total wave number should be much less in the silver salts than in the alkali halides, for the indices of refraction of the former are much larger (2.071 and 2.225 for AgCl and AgBr, in contrast with 1.544 and 1.641 for the sodium

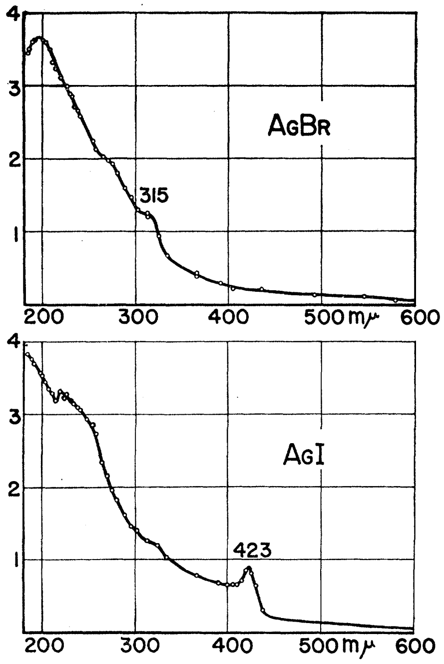

FIG. 2. Absorption curves similar to Fig. 1 for AgBr and AgI (after Fesefeldt and Gyulai). AgBr, like AgCl, possesses the NaCl lattice, whereas AgI has the zinc sulfide structure. The peak at 4230A in AgI is probably associated with the $d^{10}\rightarrow d^9s$ transition of the Ag^+ ion, which becomes allowed because of the tetrahedral symmetry of the Ag^+ site.

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[7] R. W. Gurney and N. F. Mott, Proc. Roy. Soc. (London) **A164**, 151 (1938); see also the references of footnote 1.

[8] The absorption spectrum in the exciton region of several alkali halides has been studied most completely by H. Fesefeldt, Z. Physik **64**, 623 (1930); see also R. Hilsch and R. W. Pohl, Z. Physik **59**, 812 (1930). L. Apker and E. Taft have repeated Fesefeldt's measurements for *KI* and have confirmed them to a high degree of accuracy (private communication). See also L. Apker and E. Taft, Phys. Rev. **79**, 964 (1950).

[9] The absorption spectra shown in Fig. 1 were obtained by H. Fesefeldt, Z. Physik **64**, 741 (1930). Evaporated films were used. Earlier work of a similar type shown in Figs. 2 and 5, was carried out by H. Fesefeldt and Z. Gyulai, Gött. Nachr. 226 (1929). The two results exhibit qualitative differences which presumably arise from the fact that the evaporated deposits were somewhat different and the grain structure influences the results. Absorption data have been obtained on more massive specimens of silver bromide by R. E. Slade and F. C. Toy, Proc. Roy. Soc. (London) **97A**, 181 (1920); see also K. Hecht, Z. Physik **77**, 235 (1932).

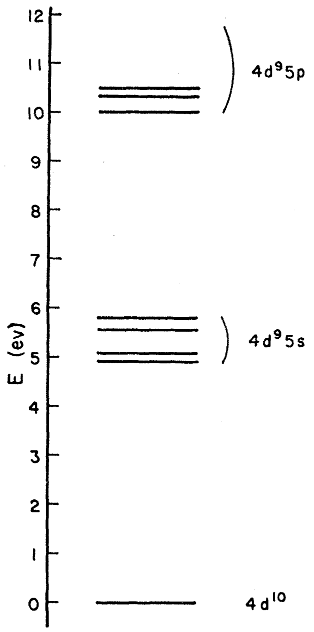

FIG. 3. The energy levels of the free Ag^+ ions. The energy scale is in electron volts. The transition from the $4d^{10}$ level to the $4d^95s$ is not an allowed dipole transition in the free ion because there is no change in parity. The ionization energy is 21.9 ev.

salts). If the Rydberg approximation[10] is employed to evaluate the energy of the lowest exciton state relative to the ionization continuum, one obtains values of 0.4 ev and 0.25 ev, respectively, for the chloride and bromide under the assumption that the masses of the electron and hole are equal.

It seems natural to identify the more or less prominent peaks at 2600A and 3200A (4.7 ev and 3.9 ev) in Figs. 1 and 2 for AgCl and AgBr with the exciton levels of the salts. On the other hand, it is evident that the absorption structure of the silver salts differs in essential qualitative details from that of the sodium salts. As was noted by the members of the Göttingen school, who first measured the spectra, the absorption bands of the silver salts (as those of many other halides of the elements having newly filled *d*-shells) possess long tails extending toward the visible part of the spectrum and depend very little upon temperature (Fig. 1), whereas those of the alkali halides are much sharper and become both narrower and higher as the temperature is lowered, as is to be expected from the simple theory of exciton structure.

B. Origin of Breadth

The origin of the great breadth of the exciton peak associated with the absorption spectrum of the heavy metal halides poses a problem of first-order importance. Regardless of how broad the spectrum of possible exciton states may be, we should expect that, in a perfect crystal, the selection rules on the wave number vector k_e of the exciton would be

$$\mathbf{k}_e = \mathbf{v} + \mathbf{K}, \qquad (1)$$

where $\mathbf{v}$ is the very small wave number vector of the light quantum and $\mathbf{K}$ is the principal vector in the wave number space of the lattice, which may be taken as zero if the reduced scheme of zones is employed. Thus (1) is essentially equivalent to the condition $\mathbf{k}_e = 0$, which singles out a very sharp transition. This condition may be relaxed if lattice vibrations are excited or absorbed during the transition, in which case one would expect the effect to vary as the square of the amplitude of the atomic oscillations, or linearly with temperature above the Debye temperature. It may also be relaxed if the absorption occurs near lattice imperfections which are not very sensitive to temperature. In the writer's opinion the observed breadth arises from the presence of a relatively high degree of lattice disorder in the crystals. Alternative possibilities will now be examined.

1. *"Forbidden" Transitions*

Adequate attention does not seem to have been given[11] to the fact that the silver halides possess a system of levels which are nearly coincident with the exciton levels and which would have the same parity as the ground state if the crystals were perfect. These levels are associated with the d^95s state[12] of the Ag^+ ion which lie about 5 ev (40,000 cm^{-1}) above the ground state in the free ion. One may expect the separation to be somewhat less in the crystal, for the electrons in the excited state are able to employ the crystalline field to advantage. A simple estimate shows that the excited state of the silver ions is relatively far from the conduction levels: The ionization energy of Ag^+ is 21.9 ev. Since the Madelung field at the position of the silver ion is between 8 and 9 ev, and since the conduction levels of the silver halides are probably between 3 and 4 ev below the external levels, it follows that the d^95s level is at least 4 ev below the conduction levels (Fig. 3).

It is difficult to estimate precisely the intensity of absorption to be expected as a result of direct optical transitions from the ground state to the d^95s levels. Such transitions can occur either as a result of quadrupole matrix components or as a result of a crystalline Stark effect associated with lattice vibrations which permits states of odd parity to be mixed with those of even parity. The second effect seems to be most important, as the case illustrated in Fig. 4 demonstrates. In this example, which is one of several studied by

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[10] See also, F. Seitz, Phys. Rev. **76**, 1376 (1949); F. Seitz and H. Fröhlich, Phys. Rev. **79**, 526 (1950); Mott and Gurney (reference 1).

[11] In an initial search of the literature, the only reference to a possibility of this kind that the writer could locate was a passing comment in the book by Mott and Gurney (see reference 1, p. 102) to the fact that the blue absorption band in cuprous oxide probably is the result of a $d^{10} \rightarrow d^9s$ transition in the cuprous ion. Subsequent to carrying out the analysis given in the text, the writer found that Krumhansl, of Cornell University, had suggested to his colleagues that the excited *d*-shell levels of Ag^+ may play an important role.

[12] See, for example, R. F. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill Book Company, Inc., New York, 1932).

Smakula,[13] MacMahon,[14] Forro,[15] and Hecht,[16] cuprous chloride has been added to NaCl and the absorption spectrum associated with the impurity has been observed[14] at both room temperature and at liquid air temperature. The cuprous ion, like the silver ion, possesses a low-lying set of levels of even parity, which begin at about 3 ev (22,000 cm^{-1}) and the peak shown in Fig. 4 is presumably associated with a transition of this type. It will be seen that the absorption peak *diminishes both in breadth and in height* as the temperature is lowered. Moreover the oscillator strength associated with the transition is only of the order of 10^{-3}.

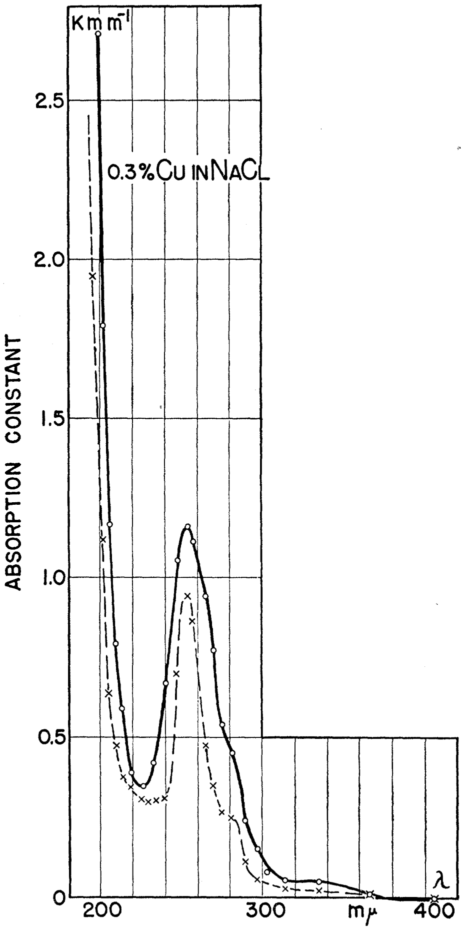

Fig. 4. The influence of temperature on the absorption spectrum of Cu$^+$ in NaCl (after MacMahon). The full curve corresponds to room temperature and the dotted curve to liquid air temperature. The cuprous ions presumably substitute for Na$^+$ so that they occupy positions of full cubic symmetry. Since the transition is of the $d^{10}\rightarrow d^9s$ type, the dipole transition is permitted only in so far as thermal oscillations provide a Stark perturbation of the states which adds wave functions of odd partity. Hence the height as well as the breadth of the absorption band diminishes with decreasing temperature. The oscillator strength associated with the transition is about 0.001 at room temperature.

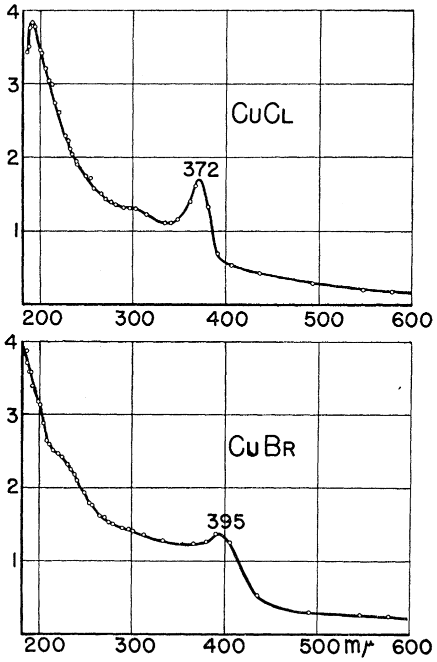

Fig. 5. The absorption spectra of CuCl and CuBr at room temperature (after Gyulai and Fesefeldt), given in relative units, as in Figs. 1 and 2. The wavelength scale is in units of 10^{-7} cm. The peaks at 3720A and 3950A are presumably $d^{10}\rightarrow d^9s$ transitions which become allowed because the ions occupy positions of tetrahedral symmetry, as in AgI.

We conclude that most of the transition probability at room temperature is associated with the admixture of a perturbing term of odd parity with the even wave functions as a result of thermal oscillations. The amount of admixture decreases with decreasing temperature.

The variation of the impurity absorption peak with temperature, shown in Fig. 4, is somewhat reminiscent of the variation of the entire absorption band of AgCl, shown in Fig. 1. This suggests that at least a portion of the absorption strength in the portion of the spectrum shown in Fig. 1 arises from "forbidden" transitions which are made possible by admixture of even and odd states through thermal vibration of the AgCl lattice.

Figure 5 shows the absorption spectra of CuCl and CuBr, obtained by Fesefeldt and Gyulai.[9] It will be seen that both spectra possess a relatively sharp absorption peak near 3800A (27,000 cm^{-1}). This peak is probably associated with a transition within the Cu$^+$ ion, for we should expect the exciton peaks to lie much farther toward the ultraviolet, in the vicinity of 2000A. In these cases the lattice has the sphalerite structure, instead of the NaCl structure, so that the ions are at positions of tetrahedral rather than cubic symmetry and the admixture of even and odd wave functions occurs without the need of thermal oscillations. Figure 2, also measured by Fesefeldt and Gyulai, shows that AgI, which crystallizes in the ZnS lattice, possesses a similar peak.

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[13] A. Smakula, Z. Physik **45**, 1 (1927).

[14] A. M. MacMahon, Z. Physik **52**, 336 (1928).

[15] M. Forro, Z. Physik **56**, 613 (1928); **58**, 613 (1929).

[16] K. Hecht, Z. Physik **77**, 235 (1932).

The magnitude of the absorption peaks at 2600A and 3200A in silver chloride and silver bromide (Fig. 1) appears to preclude the possibility that these peaks are to be associated directly with the forbidden transitions of Ag^+, for Lehfeldt[17] states that the extinction coefficient attains a value above 10^5 cm^{-1}, which can occur only if the oscillator strength is very close to unity.

To summarize, we seem led to the conclusion that the greater part of the absorption strength shown in Fig. 1 must be associated with excitation of the electrons on the halogen ion. This need not be true in the case of the thallous halides TlCl and TlBr which resemble the silver halides in many respects and have cubic (CsCl) structure, for the inner shell transition of Tl^+ is $6s^2 \rightarrow 6s6p$, which is allowed. In fact the thallous halides possess[9] several peaks which can be distinguished from the exciton peak only with difficulty.

It is not easy to see how the existence of excited states of primarily even parity could produce the broad tail of the fundamental absorption band in a perfect crystal. On the qualitative side, it is conceivable that, in the absence of selection rules forbidding the transition, the exciton could transfer its energy to a silver ion in a time of the order of 10^{-15} sec which would be the transition time under ideal circumstances. Such an effect would broaden the exciton peak by a large amount, of the order of one ev. However, the exciton state is odd, so that the transition is possible only through the small component of odd character in the excited state of Ag^+. One would expect such a transition to be delayed to 10^{-12} sec because the amplitude of the odd component of the wave function is of the order of 10^{-3}. The transition could occur more rapidly near imperfections, but one would have to suppose each atom is near an imperfection on the average to decrease the transition time to 10^{-15} sec.

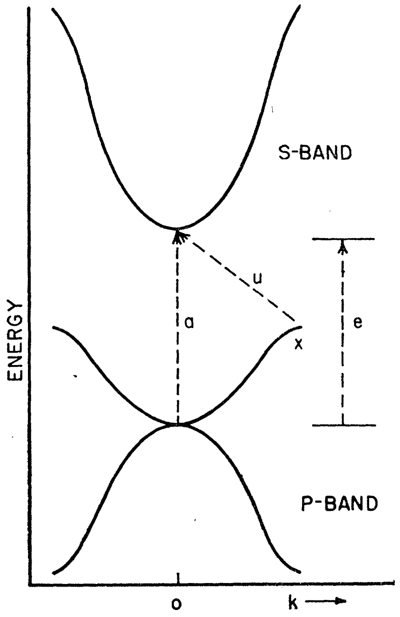

FIG. 6. Schematic energy *versus* wave number diagram showing a case in which forbidden transitions between the filled and occupied bands may have a lower energy than allowed exciton transitions. Energy is plotted vertically and wave number, k, horizontally. The p-band is filled and has segments which curve both upward and downward from the center of the zone at $k=0$. The s-band corresponds to the conduction states and is empty. Optically allowed transitions occur vertically in this type of reduced zone diagram. The transition a is the allowed jump of lowest energy between the bands, a free electron and free hole having zero wave number being produced. The vertical dotted arrow e on the right shows the lowest allowed exciton transition, in which the electron and hole are coupled. The slanting arrow u designates a forbidden transition having lower energy than e. The transition u, and similar forbidden transitions, may occur as a result of lattice distortion. The writer proposes that a system of bands of this type occurs in the silver halides, and that transitions of the type u occur even at low temperatures as a result of the distortion induced by dislocations.

The transition would also occur more rapidly in a perfect specimen of a salt such as TlCl in which the first excited states of the metallic ion are of odd parity. In this case, however, we would expect the exciton states for which the wave number vector $\mathbf{k}_e$ is zero (or a principal vector in wave number space) to be as sharply defined as in the alkali halides and to be composed of an appropriate linear combination of an exciton wave function in which the Cl^- ion is excited and of an exciton wave function in which the Tl^+ is excited. For in the absence of the halogen ions, the excited states of the thallium ions could be resolved into exciton bands with well-defined values of the wave number vector. When the halogens are present the two types of exciton wave may be combined to form new sets with well-defined values of $\mathbf{k}_e$, much as one combines states having different configurations in atomic spectra to obtain states of specified angular momentum.

2. *Decomposition of Excitons into Electrons and Holes*

It is possible that the energy of the lowest exciton state for which $\mathbf{k}_e$ is zero actually is higher than the energy of a state in which an electron and hole are free. As is indicated in Fig. 6, this situation can occur in a case in which the filled band of Bloch levels is very broad and in which the energy levels associated with this band curve upward with increasing $\mathbf{k}$ in at least one direction in space. $\mathbf{k}$ is here the wave number vector of the electron in the usual band picture based on the one-electron approximation. Could the transition indicated by the arrow $\mathbf{u}$ occur, it would require less energy than the transition $\mathbf{a}$. The energy of the exciton transition is indicated by the vector $\mathbf{e}$, it being supposed that the exciton energy is only slightly less than that associted with $\mathbf{a}$. The transition $\mathbf{u}$ cannot occur in the perfect crystal, for in this case the free electron would have zero wave number, whereas the hole would have a wave number associated with a boundary point on the zone for the case illustrated. The latter would be very large compared with the wave number of a light quantum having energy appropriate to induce the transition.

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[17] W. Lehfeldt, Gött. Nachr. 1, 171 (1935).

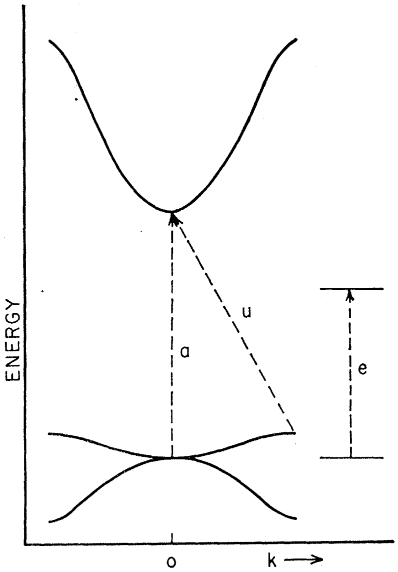

FIG. 7. Same as Fig. 6 for a case in which the filled band is sufficiently narrow that the forbidden transition u has greater energy than the exciton transition. The writer proposes that the alkali halides have energy spectra of this type.

Similarly, it is not possible for the transition **u** to occur in a perfect crystal by the production of an exciton, which then dissociates by spontaneous disintegration into an electron and hole in such a way that the former has zero wave number and the latter has wave number near the edge of the zone, unless an additional agent, such as a lattice vibrational wave or an imperfection enters to conserve wave number. One would expect the amplitude of the absorption peaks to vary more rapidly with temperature if the normal vibrational wave of the lattice were responsible.

It is conceivable that the exciton could become self-trapped in the lattice by producing a local distortion of atoms and that the electronic transition would occur during the process. Momentum could be absorbed by the lattice as a whole through the production of a spherical acoustical wave which emanates from the trapping site. One would expect the trapping procedure to require of the order of 10^{-13} sec, the time required for atomic motion. The corresponding breadth added to the exciton level would be only of the order of a few hundredths of an ev.

We seem compelled to conclude that the breadth of the absorption lines is associated with the presence of lattice imperfections which permit a violation of the selection rules involving the wave number vectors of the electrons and holes. This process is by no means new[18] in concept: It is well known that the irregularity in a metal associated with the existence of a surface[19] permits light quanta to eject photoelectrons without conservation of the wave number of the light quantum and of the electron. This surface photoelectric effect makes it possible for light quanta to eject any electron in the occupied band, provided sufficient energy is available.

One may reasonably ask whether the difference between the silver halides and alkali halides implies a fundamental difference in the degree of order in the two lattices. This question is difficult to answer with complete precision; however, it seems almost certain that the degree of imperfection is higher in the silver halides.

Consider first the possibility of a qualitative difference between the silver and alkali halides even if the lattice disorder is identical in the two cases. If the filled band of levels in the alkali halides[20] is quite narrow relative to that of the silver halides, and if the exciton level is appreciably below the ionization level (e.g., 2.6 ev in NaCl), the energy of the transition **u** may be larger than that of the exciton transition (Fig. 7). In this case the levels associated with the production of excitons of lowest energy (and $\mathbf{k}_e=0$) in the perfect crystal will not overlap those associated with the production of electrons and holes at irregular regions which are employed only to absorb momentum. Some of the higher exciton bands may overlap these levels, but not the first exciton band. In this event, which probably is one characteristic of the alkali halides, the first exciton peak will be relatively isolated and the band will be perturbed or distorted by imper-

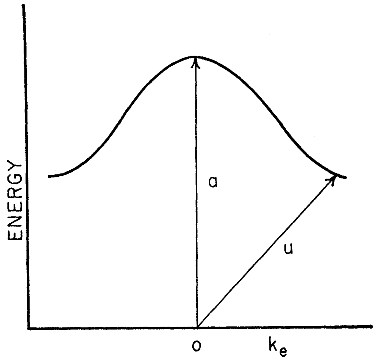

FIG. 8. Schematic diagram showing the energy *versus* wave number diagram for excitons in a case in which lattice distortion may have an important effect on the long wavelength edge of the exciton band. In this case the exciton surface bends downward so that the forbidden transition u has less energy than the allowed transition a which leads to an exciton of small wave number. It is not yet possible to say if this case occurs in practice.

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[18] Both K. F. Herzfeld, Z. physik Chem. **105**, 329 (1923) and Mott and Gurney, reference 1, p. 100 *et seq.*, have suggested that the tails are the result of irregularities in the lattice. More specifically Herzfeld has proposed that ions near internal cracks are responsible for the extra absorption. None of these investigators has apparently attempted to estimate the magnitude of the disorder.

[19] I. Tamm and S. Schubin, Z. Physik **68**, 97 (1931). See also more recent work by L. Apker and H. Huntington (to be published).

[20] Mott and Gurney (reference 1, p. 79) have estimated the breadth of the filled bands in the alkali halides with use of the x-ray emission bands and conclude that they are of the order of 2 ev or less, the maximum of 2.1 ev being achieved for LiF. The values for NaBr and CsI are under 1 ev. They also estimate that the breadth in AgBr is about 1.1 ev.

fections only to the extent to which the exciton levels themselves are distorted. Such distortion may occur because (a) free excitons for which $\mathbf{k}_s \neq 0$ have lower energy than those for which $\mathbf{k}_s = 0$ (Fig. 8) and are produced when imperfections allow relaxation of the rule $\mathbf{k}_e = 0$ and (b) excitons which are trapped at the imperfection are produced directly. If a fraction α of the atoms are near[21] the center of regions of distortion on the average, we would expect the fraction of the distorted area of the exciton absorption band, as determined, for example, by subtracting the exciton peak for a perfect crystal from that for an imperfect one, to be of the order α. On the other hand, suppose that the exciton peak overlaps a region of the energy spectrum associated with the ionization continuum, but which would not contribute to the absorption in the perfect crystal because of selection rules on wave number. In this case the background which is added to the exciton absorption curve is determined by the fraction α of distorted atoms and the ratio r of the oscillator strength associated with the ionization continuum and the exciton level. In order of magnitude, the fractional background area will be αr. Thus an exciton peak which has a low oscillator strength associated with it may be partly, or even completely, obliterated by the tail of the ionization bands.

The first exciton bands associated with the alkali halides appear[22] to have an oscillator strength of the order of 2 associated with them, so that they are very strong, as are the first few excited levels in free atoms. Several investigators, most notably Smakula,[23] have observed distortion in this band at the long-wavelength tail. The distortion depends upon impurity content and the previous history of the specimen. This distortion occurs in the region where the extinction coefficient is of the order of 10^2 cm^{-2}, in contrast with the peak value of 10^6 cm^{-1}. Moreover, the experiments show that photocurrents are not produced by irradiation in the tail of the fundamental band if the crystal has not been subject to previous irradiation, so that the distorted component presumably arises from the exciton levels themselves and corresponds to a value of α of the order of 10^{-4}, or possibly less in the most perfect specimens.

The full range of the absorption spectrum of the silver halides has not been explored. Thus it is not possible to state the extent to which the exciton peak shares the total oscillator strength. A value of 0.1, that is, about five percent that of the main portion of the band, seems to be a reasonable value. This component will diminish as the mean separation between the hole and electron in the exciton wave function increases. This separation will, in turn, increase with increasing dielectric constant. It is difficult to assess the fractional area to be associated with the background in the region of exciton absorption. A value of one-tenth of the exciton band is perhaps a reasonable lower limit. This is equivalent to stating that of the order of 0.1 percent of the strength associated with the ionization continuum extends into the region of the exciton band as a result of lattice distortion, or that about 0.1 percent of the atoms in the lattice are in distorted regions. The value appears to be much larger than that found in the alkali halides, by at least a factor of ten or more.

III. LATTICE DEFECTS IN THE SILVER SALTS

A. Density and Jump-Frequency of Defects

As a result of the work of Koch and Wagner,[24] Teltow,[5] Lawson,[6] Christy and Kurnick, and Berry[6] it appears to be well established that the predominant lattice defect in the chloride and bromide is of the Frenkel type, that is, consists of silver-ion vacancies and interstitial silver ions at least below 300°C. The nature of the defects above 300°C appears to be questionable. In any case the density of defects appears to be near one percent at the melting point. Teltow's equations give a value near or slightly below 2.0 percent; moreover Lawson and Kurnick estimate a similar value. The extrapolation of Teltow's results to room temperature leads to an equilibrium value between 10^{14} and 10^{15} defects per cc at 300°K and 10^{-7} per cc at 100°K in AgBr. The corresponding mobility of interstitial silver ions is $2.5 \cdot 10^{-4}$ cm^2/volt-sec, which corresponds to a jump frequency of about 7.10^9 sec^{-1}. The jump frequency at 100°K is about 10^4 sec^{-1}.

Measurements having accuracy comparable to Teltow's do not seem to be available for silver chloride; however the activation energies appear to be about twenty percent larger for the chloride than for the bromide. For example, the slope of the curve showing ionic conductivity at elevated temperatures, when plotted in the conventional way in which the logarithm of the conductivity is represented as a function of the reciprocal of the absolute temperature, is about twenty percent larger for the chloride than for the bromide. Use of this rule leads to a value of the density of Frenkel defects near 300°K that lies between 10^{12} and 10^{13} per cc.

It is doubtful if the imperfection which is responsible for the long tails of the fundamental band of the absorption spectrum, described in the previous sections can be the result either of the Frenkel defects which might exist at equilibrium at the temperature of measurement, or what is more to the point, the result of a "freezing-in" of the Frenkel disorder produced near the melting point. If the equilibrium density were

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[21] To avoid ambiguity, we shall distinguish between atoms which are *immediately* at a dislocation line and those which are *near* the line. The former lie about one atomic distance from the center of the dislocation; the latter lie in the region where the distortion produced by the dislocation is not negligible for whatever effect is being considered.

[22] J. Mayer, J. Chem. Phys. **1**, 270 (1933). Mayer has estimated the oscillator strength associated with the ultraviolet absorption band, most of which is concentrated in the exciton peaks.

[23] A. Smakula, Z. Physik **63**, 762 (1930); see also Mott and Gurney (reference 1), Fig. 33d, p. 101.

[24] E. Koch and C. Wagner, Z. physik Chem. **38B**, 295 (1938).

attained at each temperature, the magnitude would be far too small to explain the intensity of the tail at room temperature or below; in addition, the tail would be a very sensitive function of temperature. Actually, it is almost certain that the Frenkel defects achieve equilibrium in a very short time at any temperature near room temperature or above. We saw above that the jump frequency for interstitial silver ions at room temperature is about 10^9 sec^{-1}. Thus an interstitial silver ion would meet one of the 10^{14} or 10^{15} vacant silver-ion sites which exist in a time of the order of 0.1 sec. The activation energy for recombination should not be appreciably different from the value of about 2600 kg cal per mole (0.11 ev) for migration, which would have a negligible restraining influence on combination at room temperature or above. The time required to achieve equilibrium would be even faster at more elevated temperatures.

The attainment of equilibrium may take a long period of time at temperatures appreciably below room temperature. For example, near liquid air temperature, where the jump frequency of interstitial ions is about 10^4 sec^{-1}, the equilibrium density, estimated above to be about 10^{-7} per cc, could not be attained in a measurable time.

B. Schottky Defects

When an interstitial ion and a positive ion vacancy combine, the result removes the pair of imperfections entirely from the crystal, so that, with the exception of diffusion effects they may have induced, the crystal possesses no memory of the imperfection. The situation is quite different when Schottky defects prevail, that is, when the lattice contains matched pairs of positive and negative ion vacancies, as is the case in the alkali halides at elevated temperatures. In this case the recombination of a positive and a negative ion vacancy to form a stable pair does not remove the lattice imperfection from the crystal, but simply alters the form of the imperfection. It is true that the imperfection may be eliminated entirely by having the pairs diffuse to the surface; however, this is a very unlikely process compared to other processes, such as condensation at dislocations[25] or the formation of clusters.

For example, when the density of vacancies is 10^{16} per cc, a given vacancy will meet another after migrating about 10^6 atom distances along its trajectory, or after diffusing a radial distance of the order of 10^{-5} cm from its starting point, which is small compared to the dimensions of crystals of normal interest. Similarly, if the density of dislocation lines were even as low as 10^8 per cm, the vacancy would diffuse to such a line during the period of time in which it migrates a distance of 10^{-4} cm from its point of origin. Thus most vacancies will either join existing dislocations or will condense to form clusters within the crystal. The clusters may form in the perfect portions of the crystal, near dislocations, or possibly at other imperfections, if the lattice contains impurity aggregates or other sources of distortion. In either case the vacancies will leave a record upon the crystal. Apparently the most innocuous influence is that which would occur if they joined existing dislocations of the Taylor-Orowan type and, by simple addition to these, caused the dislocations to move from one slip plane to a parallel one, possibly adding at places where the dislocation jogs from one slip plane to another. In this case the influence of the vacancies would reduce to a simple change in the pattern of existing dislocations. Suppose, for example, the crystal contains 10^{19} vacancies per cc and 10^8 dislocation lines per cm^2. The dislocation lines may accommodate the vacancies by growing in a direction normal to the Burgers vector by about 10^3 atom distances. Or expressed in a different way, if the crystal contains 10^{13} general dislocation rings per cc having a diameter of 5000A, which is equivalent to a density of 10^8 lines per cm^2, the diameter of the rings would be less than doubled by the addition of the vacancies.

It is a remarkable fact[26] that the density of vacancies at the melting point in the alkali halides[27] and in the metals such as copper[26] is in the vicinity of 10^{18} to 10^{19} per cc, which is just sufficient to produce the density of dislocation rings which would be adequate to account for the normal mosaic structure of these materials. As the writer has suggested elsewhere[26] this coincidence seems to suggest that the vacancies present at the melting point eventually produce the dislocations responsible for the mosaic structure by condensation into dislocation rings when the solid is cooled. Such condensation is presumably nucleated at imperfections, which may be associated with a smaller number of "primary" dislocations.

It seems very likely that the vacancies aggregate into large dislocation-like clusters perhaps of the dimensions of the mosaic blocks ($\sim$5000A) whenever the crystal is well annealed. This means that they either join an existing dislocation pattern, if there are dislocations present in sufficient quantity to account for the mosaic structure, independent of those which might be created from vacancies, or that they form dislocations of the type which is required to interpret the mosaic structure.

Should the crystal be quenched very rapidly from temperatures near the melting point to temperatures at which small aggregates are immobile, they could form small clusters which are relatively stable.

The extent to which Schottky defects, namely, positive and negative ion vacancies, exist in equilibrium

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[25] For a review of the properties of dislocations, see for example the various articles in *Pittsburgh Symposium on the Plastic Deformation of Crystalline Solids*, edited by J. S. Koehler (published by Naval Research Laboratory, 1950). The nomenclature used in the present article is similar to that employed in the writer's article in the *Pittsburgh Symposium*.

[26] F. Seitz, Phys. Rev. **79**, 890 (1950).

[27] C. Wagner and P. Hantelmann, J. Chem. Phys. **18**, 72 (1950); H. Kelting and H. Witt, Z. Physik **126**, 697 (1949); H. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

in the silver halides is still entirely unknown. Jost and Nehlep[28] estimated the difference $\epsilon_s-\epsilon_f$ between the energy ϵ_s required to form a pair of separated positive and negative ion vacancies and the energy ϵ_f required to produce an interstitial silver ion and a positive ion vacancy. However their results did no more than show that the van der Waals energy in the silver halides is sufficiently great to give Frenkel defects preference over Schottky defects, in contrast with the situation for the alkali halides.

The writer would like to propose that the density of Schottky defects is of the order of 0.1 percent at the melting point in the silver halides and that the distortion which is responsible for the broad tails of the absorption bands of these crystals when they are prepared from the melt arises from the dislocation pattern produced by condensation of the pairs of vacancies corresponding to the Schottky defects. Crystalline deposits prepared by condensation of vapors should have a similar type of imperfection which arises from crystalline boundaries and other flaws which are frozen into the lattice. The ratio of Schottky to Frenkel defects assumed here would result automatically if the energy difference $\epsilon_s-\epsilon_f$ between the heats of formation of the two types of defect is of the order of or less than 10,000 cal per mole, or of the order of 0.4 ev per molecule. The corresponding density of Schottky defects in equilibrium at room temperature in AgBr would be of the order of 10^{11} per cc, that in AgCl of the order of 10^{9} per cc.

The densities of Schottky defects assumed here are about ten times higher than those observed[27] in NaCl and KCl at the melting points, for which the densities correspond to a mole fraction of almost exactly 10^{-4}. It will be assumed that this difference accounts for the fact that the absorption spectra of the alkali halides are relatively less distorted.

C. Relaxation of Selection Rules by Dislocations

This leads us to the interesting question of the extent to which dislocations permit a relaxation of the selection rules governing conservation of wave number during optical transitions in the crystal. In many calculations it is convenient to treat a dislocation line or ring as though the distortion were concentrated at the line or ring and as if one atom were disturbed in this region. Actually the distortion extends over many lattice distances, so that it is profitable to examine the distortion more carefully at this point.

The optical transition probability is governed[29] by the matrix components

$$\int \psi_{\mathbf{k}}'^{*} p \exp(i\mathbf{n}\cdot\mathbf{r})\psi_{\mathbf{k}'}' d\tau, \tag{2}$$

where $\psi_{\mathbf{k}}'$ is the initial wave function of the system, $\psi_{\mathbf{k}'}'$ is the final wave function, $\mathbf{p}$ is the momentum operator $\hbar\,\mathrm{grad}/i$, and $\mathbf{n}$ is the wave number vector of the light quantum. The integration extends over the volume of the crystal. If $\psi_{\mathbf{k}}'$ has the typical Bloch form for a perfect crystal, namely, $\chi_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})$, in which $\mathbf{k}$ is the wave number vector and $\chi_{\mathbf{k}}$ has the periodicity of the lattice, the matrix components vanish except when the selection rules

$$\mathbf{k}=\mathbf{k}'+\mathbf{n}+\mathbf{K},$$

in which $\mathbf{K}$ is one of the principal vectors in the reciprocal lattice, are obeyed. For simplicity, we shall assume that in the distorted crystal, which contains a dislocation, the perturbed wave functions can be written in the form,

$$\psi_{\mathbf{k}'}=\chi_{\mathbf{k}}(\mathbf{r}-\mathbf{R})\exp(i\mathbf{k}\cdot\mathbf{r}),$$

in which $\mathbf{R}$, the displacement vector associated with the strain pattern of the dislocation, is a function of position. This is equivalent to assuming that the modulation factor of the free electron wave function $\exp(i\mathbf{k}\cdot\mathbf{r})$ has the same value at a point $\mathbf{r}$ in the distorted crystal as it would have had at the point from which $\mathbf{r}$ was displaced by the strain field associated with the dislocation.

With this assumption (2) may be written

$$\begin{aligned}\hbar\int &\chi_{\mathbf{k}}^{*}(\mathbf{r}-\mathbf{R})\exp(-i\mathbf{k}\cdot\mathbf{r})\,\mathrm{grad}\\ &\times\{\exp[i(\mathbf{n}+\mathbf{k}')\cdot\mathbf{r}]\chi_{\mathbf{k}'}(\mathbf{r}-\mathbf{R})\}d\tau\\ &=(\hbar/i)\int\exp(i\mathbf{W}\cdot\mathbf{r})\chi_{\mathbf{k}}^{*}(\mathbf{r}-\mathbf{R})\\ &\times[i(\mathbf{n}+\mathbf{k}')\chi_{\mathbf{k}'}(\mathbf{r}-\mathbf{R})+\mathrm{grad}\chi_{\mathbf{k}'}(\mathbf{r}-\mathbf{R})]d\tau \qquad (3)\end{aligned}$$

in which $\mathbf{W}=\mathbf{n}+\mathbf{k}'-\mathbf{k}$. Next we shall divide the lattice into cells, using for example the distorted cells of the original lattice, and designate the position vector for a fiducial point in the ith cell by $\mathbf{r}_i$. The integral (3) may then be expressed in the form,

$$\begin{aligned}(\hbar/i)\textstyle\sum_i \exp(i\mathbf{W}\cdot\mathbf{r}_i)\displaystyle\int_i &\exp\{i\mathbf{W}\cdot(\mathbf{r}-\mathbf{r}_i)\chi_{\mathbf{k}}^{*}(\mathbf{r}-\mathbf{R})\}\\ &\times[i(\mathbf{n}+\mathbf{k}')\chi_{\mathbf{k}'}(\mathbf{r}-\mathbf{R})+\mathrm{grad}\chi_{\mathbf{k}'}(\mathbf{r}-\mathbf{R})]d\tau \qquad (4)\end{aligned}$$

where the integral $\int_i$ extends over the ith cell. We shall assume that the integrals over the cells have identical values, whence (4) can be written as

$$A\textstyle\sum_i \exp(i\mathbf{W}\cdot\mathbf{r}_i) \tag{5}$$

in which A is $(\hbar/i)\int_i$. This sum may be replaced by an integral in an approximation adequate for present purposes so that (5) becomes

$$(A/V_0)\int\exp[i\mathbf{W}\cdot(\mathbf{r}+\mathbf{R})]d\tau$$

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[28] W. Jost and G. Nehlep, Z. physik Chem. **32B**, 1 (1936).

[29] See, for example, F. Seitz, *Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 326.

in which V_0 is the volume of the cell and r_i is replaced by the continuous variable $\mathbf{r}+\mathbf{R}$.

Finally, if we restrict attention to values of $\mathbf{W}$ for which $\mathbf{W}\cdot\mathbf{R}$ is small compared with unity, this integral may be placed in the form,

$$(A/V_0)\int i\mathbf{W}\cdot\mathbf{R}\exp(i\mathbf{W}\cdot\mathbf{r})d\tau. \tag{6}$$

Two cases will be of interest to us: First that in which $\mathbf{R}$ is constant over a line of unit cells extending in the z-direction; and second the case in which there is a Taylor dislocation extending along the z-axis. Koehler[30] has evaluated the integral (6) for the second case in an example in which a pair of dislocations of opposite sign are present. He has obtained the following result for the square of the absolute value of the integral,

$$\int i\mathbf{W}\cdot\mathbf{R}\exp(i\mathbf{W}\cdot\mathbf{r})\Big|^2\Big/V_0^2=\frac{4|\delta(W_z)|^2\sin^2(W_y\rho/2)}{V_0^2}$$
$$\times d^2\left\{\frac{W_x^2}{W^4}+\left[\frac{m-2}{2(m-1)}\right]^2\frac{W_y^2}{W^4}+2\frac{W_x^2W_y^2}{W^6}\frac{m(m-2)}{(m-1)^2}\right\} \tag{7}$$

Here W_x, W_y, and W_z are the components of W; m is the reciprocal of Poisson's ratio; ρ is the spacing between the dislocations of opposite sign; d is the Burgers displacement associated with the dislocation; and $\delta(W_z)$ is a delta-function which enters because of the translational symmetry along the z axis.

The corresponding expression for a line of displaced cells which extend along the z axis and are displaced in the x direction is

$$\frac{d^2}{W_y^2V_0^2}16\sin^2\frac{W_xa_x}{2}\sin^2\frac{W_ya_y}{2}|\delta(W_z)|^2, \tag{8}$$

where d is the distance of displacement and a_x and a_y are the linear dimensions of the cell in the x and y directions, respectively.

We shall assume that $W_y\rho$ in (7) is large compared with unity and replace the $\sin^2$ term by $\frac{1}{2}$. In addition, we shall introduce another factor of $\frac{1}{2}$ in order to include the effect of only one dislocation. Moreover we shall replace W_x^2 and W_y^2 in both expressions by $W^2/3$. Finally, we shall assume that W_xa_x and W_ya_y in (8) are sufficiently small that the sine functions may be replaced by their arguments. The ratio of (8) to (7) is then

$$\frac{1}{W^4a_x^2a_y^2}\left[1+\frac{1}{12}\left(\frac{m-2}{m-1}\right)+\frac{2}{3}\frac{m(m-2)}{(m-1)^2}\right]. \tag{9}$$

It is evident from the nature of the approximations made, that this ratio should be of the order of magnitude unity when W lies near the boundary of the first Brillouin zone, that is, when Wa_x or Wa_y is near unity. In other words, the dislocation line acts much like a line of displaced atoms when one is considering selection rules in which the magnitide of the "forbidden" wave number is near a zone boundary.

On the other hand, Eq. (9) becomes very large compared with unity when W becomes small compared with the reciprocal of a_x or a_y. For example, the ratio is of the order of 100 or more if W is of the order of 0.3 times the distance to the zone boundary. It follows that a dislocation is much more effective in producing violations of the selection rules for optical transitions than a row of foreign atoms would be, particularly when consideration is given to transitions in which the lattice takes up momentum that is smaller than a principal vector of the reciprocal lattice by a factor of 0.1 or less. The extent to which this extra ability of the dislocation to broaden the lines will have a detectable influence depends upon the degree to which the absorption may be broadened by the slightly forbidden transitions corresponding to small values of W. This should be much greater in cases in which the energy functions in wave number space have a large curvature (Fig. 6) than in cases in which the curvature is small (Fig. 7).

Consider a case in which the crystal contains 10^{13} dislocation rings per cc, each having a diameter of the order of 2000 atom-distances. The total number of atoms lying in the immediate vicinity of the dislocation lines is then about 10^{17} per cc. These numbers seem to be reasonable values for the well-annealed silver halides if we assume that the dislocations are of the type responsible for normal mosaic structure and are formed by condensation of vacancies. We must assume that the dislocations have an effect in broadening the absorption bands that is of the order of 100 times larger than 10^{17} foreign atoms would have if we are to explain the long tails in the manner suggested in Sec. II. We saw there that the breadth resulting from broadening is similar to that which would be obtained from about 0.1 percent of foreign atoms, that is about 10^{19} per cc. A factor of this magnitude appears to be well within the range of possibility provided that forbidden transitions in which Wa_x or Wa_y is of the order of 0.3 have a significant broadening effect. This will be the case if, as in Fig. 6, the filled band is broad and has a branch which bends upward in the manner shown.

D. Spiral Prismatic Dislocations

The conclusion that dislocations arising from the condensation of vacant lattice sites are responsible for the distortion which produces the long tail of the fundamental absorption band, provided a magnification factor of 100 occurs, is not altered if the vacancies condense primarily in the form of spiral prismatic dislocations,[31] instead of in simple dislocation rings. For the

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[30] J. S. Koehler, Phys. Rev. **75**, 106 (1949). The sign of the third term in (7) is the reverse of that appearing in the original, which contained an error.

[31] F. Seitz, Phys. Rev. **75**, 723, 890, 1002, 1003 (1950). See also forthcoming paper in Phil. Mag. (Special Issue January, 1952).

pitch of the spiral dislocation would be of the order of 100 lattice spacings if, as the writer has proposed, they are responsible for the slip-lamellas observed by Heidenreich and Shockley.[32] Thus the individual turns of the spiral would be sufficiently far from one another so that each section would act essentially independently of the next in determining the distortion of interest for optical absorption.

IV. X-RAY EVIDENCE FOR LATTICE DISTORTION

A. Expected Influence

It is doubtful if the dislocation pattern which is assumed to occur in the silver halides would produce any x-ray diffraction effects that are substantially different from those observed in well-annealed metals. If one assumes that the energy required to form a vacancy in any one of the metals possessing a normal melting point is of the order of half the activation energy for self-diffusion, one concludes that there are about 10^{-3} vacancy per atom in the lattice at the melting point, as has been assumed for the silver halides. Hence, one would expect the silver halides and metals such as copper, aluminum, and zinc to possess about the same density of dislocations arising from this source.

The primary influence of the dislocations is to disturb the coherence of the lattice and thereby introduce mosaic boundaries, which have the effect of broadening the x-ray diffraction lines. If the views expressed here are correct, there should be a close similarity between the mosaic pattern in well-annealed metals and silver halides. Since the alkali halides presumably possess a somewhat smaller number of vacancies at the melting point, we might expect the density of dislocations arising from this source to be less. However the density of vacancies is probably only a factor of ten smaller in the alkali halides than in the silver halides, so that the difference may not be easy to detect.

B. Observations of Burgers and Co-Workers

Burgers and Hiok[33] found very strong diffuse bands in the Laue pattern obtained from silver chloride at and below room temperature. It is very probable that these bands are produced by thermal oscillations and hence have little to do with the distortion of interest to us. Nevertheless, it would be highly desirable to have additional experimental information on the structure of the x-ray diffraction lines of well-annealed silver halide crystals.

V. PHOTOCONDUCTIVITY IN THE SILVER HALIDES

A. Experimental Results

The silver halides, along with the thallous halides which resemble them closely, have been the objective of a number of highly informative experiments on photoconductivity. The principal results are the following:

1. Electrons are freed[34] by light quanta throughout the tail of the fundamental band and well into the fundamental region of most intense absorption, that is, where the extinction coefficient becomes of the order of 10^5 cm^{-1}. Hecht and Lehfeldt found no evidence for hole conductivity throughout this range. However as yet unpublished research carried out at Cornell University[35] by Moore shows that electron and hole currents of comparable magnitude can be obtained in AgCl at $-65°$ under proper circumstances. The Cornell measurements were made both on specimens bombarded with 10-kv electrons, several microamperes being employed, and on specimens irradiated with light in the range from 2537A to 4040A. Free lifetimes of the order of 10^{-6} sec were observed, which is in close agreement with those of Lehfeldt, if we combine Lehfeldt's measurements of the range per unit field with a value of the mobility[36] of the order of 400 cm^2/volt-sec. Lehfeldt usually employed between 10^7 and 10^{11} light quanta per cc in a measurement of the range. The results indicate that space charge effects were not serious for this level of illumination. On the other hand, electron bombardment with one microampere is equivalent to irradiation with nearly 10^{16} light quanta per second, which may have a pronounced influence on the range.

The photoconductive behavior of the silver and thallium halides is in striking contrast with that of the alkali halides which do not exhibit photoconductivity[37] in the tail of the fundamental band, at least for specimens not irradiated previously, although they become photoconductors when irradiated in the *F* band if colored either additively or by x-ray irradiation.

2. The quantum yield varies from 0.53 to 0.22 in AgCl and from 0.61 to 0.17 in AgBr as one passes from the outermost reaches of the tail to the vicinity of 2537A. The corresponding variation in TlBr is from 0.45 to 0.06, which is not radically different from the behavior of AgBr. The photoelectric yield appears to

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[32] R. Heidenreich and W. Shockley, *Report on a Conference on the Strength of Solids* (The Physical Society of London, 1948), p. 57.

[33] W. G. Burgers and Tan Koen Hiok, Physica **11**, 351 (1945); Nature **159**, 845 (1947).

[34] W. Flechsig, Z. Physik **46**, 788 (1928); Physik. Z., **32**, 843 (1931); K. Hecht, Z. Physik **77**, 234 (1932); W. Lehfeldt, Gött. Nachr. **1**, 171 (1935).

[35] After most of the present manuscript had been prepared, the writer learned of extensive measurements carried out at Cornell University under the supervision of Professors Smith, Sproull, and Krumhansl, and contained in the as yet unpublished theses of W. C. Caldwell, J. N. Nanda, A. R. Moore, and G. Warfield. A brief summary of this work is given at various points in the text and in Sec. IX. The writer is indebted to Professor Smith for the opportunity of reading these theses.

[36] Values of the mobilities of electrons in several salts have been estimated by R. Hofstadter, *Nucleonics 4*, No. 4, p. 2; No. 5, p. 29. The value of 400 cm^2 volt-sec quoted here could easily be too small by a factor of five, in which case the mean free time of the photoelectrons studied by Lehfeldt would be only about $2\cdot 10^{-7}$ sec.

[37] See, for example, the book by Mott and Gurney (footnote 1) for a review. Also F. Seitz, Revs. Modern Phys. **18**, 384 (1946); Phys. Rev. **79**, 239 (1950). The absence of photoconductivity was apparently studied most carefully by R. Hilsch and R. W. Pohl, Z. Physik **68**, 721 (1931). See also, A. Smakula, Z. Physik **59**, 603 (1929); **63**, 762 (1930).

be almost independent of temperature to temperatures as low as 80°K. In contrast, the photoelectric yield drops at low temperatures in the alkali halides if they are irradiated in the *F*-band.

3. The photoelectrons have very long ranges in the silver and thallous halides. Experiments of Lehfeldt at low temperatures (100°K) show that the density of traps is of the order of 10^{14} per cc or less in well-annealed single crystals, of one assumes the traps have a capture cross section of the order of $3\cdot10^{-15}$ cm^2. The range at low temperatures may be increased by irradiation, presumably because some of the traps become filled and are no longer able to act as traps. It is possible that the density of traps becomes very low after irradiation with about 10^{17} quanta, however space charge effects associated with the freeing of electrons apparently inhibit a precise determination of the internal fields, and hence of the range.

Haynes and Shockley[38] have determined the range of electrons at room temperature in silver chloride by observing the depth to which darkening occurs. They employed pulsed fields of 1 microsecond duration, in order to avoid the polarization associated with ionic conductivity at room temperature, and irradiated in such a way as to free between 10^{16} and 10^{17} electrons in an experiment. Their results, which yield an average range, show that the mean free life of a photoelectron in a well-annealed crystal is 9.5 microseconds. If we assume the trapping centers have a cross section of $3\cdot10^{-15}$ cm^2 and that the drift velocity of the electrons is 10^7 cm per sec, the density of traps is found to be about $3\cdot10^{12}$ per cc, which is about the same as the density of interstitial silver ions in AgCl, estimated in Sec. III.

The low density of traps in the silver halides at room temperature is in striking contrast with the alkali halides, which appear never to have less than 10^{15} traps per cc and may have considerably more, since *F*-centers act as traps. The range of electrons in a completely uncolored alkali halide crystal does not seem to be known.[39]

Haynes and Shockley have also measured the drift mobility of free electrons in silver chloride in the temperature range between 113°C and −26.5°C. This was done by determining the maximum distance which electrons produced by a pulsed light source drift when a field is applied for a specified time of the order of 1 microsecond. The distance which the electrons migrate is determined by measuring the depth to which darkening takes place when the surface normal to the applied field is illuminated. This depth is determined primarily by those electrons which remain completely free during the period of time during which the field is applied. Although the investigators do not say so, this appears to be true of an appreciable fraction of the electrons for the pulse times employed (between 1 and 6 microseconds) and over the entire range of temperature. The mobility μ_m measured in this way was found to vary relatively slowly with temperature, the dependence being given approximately by the relation $\mu_m = BT^{-\frac{3}{2}}$, in which $B = 2.54\times10^5$, when T is expressed in degrees centigrade, and the mobility is expressed in units of cm^2 per volt sec. The value of μ_m at 25°C was found to be 49.5 cm^2 per volt sec. An essentially identical value was obtained by determining the displacement of the electrons in a magnetic field.

It is interesting to note that Haynes and Shockley found that an appreciable fraction of the electrons have a mean free lifetime of 1 microsecond even at 113°C. This result suggests that $N_t\sigma_t v$ is not appreciably smaller than 10^6 sec^{-1} at this temperature, where N_t is the density of trapping centers, σ_t is the capture cross section for the traps, and v is the speed of the migrating electrons (about 10^7 cm per sec); or, it suggests that $N_t\sigma_t$ is not appreciably smaller than 0.1 cm^{-1}. Now, if the energy required to form Frenkel defects in silver chloride is $1.2\times29{,}000 = 35{,}000$ cal per mole, and, if there are 2.0 percent of defects at the melting point, the density should be about 10^{16} per cc at 113°C. Thus the experiments of Haynes and Shockley suggest that, if the density of interstitial silver ions is as high at 10^{16} per cc, the capture cross section cannot be appreciably larger than 10^{-17} cm^2; or, if the capture cross section actually is as large 10^{-15} cm, the density of the interstitial ions must be nearer to 10^{14} per cc. In any case, these experiments cast considerable doubt upon the suggestion made previously that the mean free life time of 9.5 microseconds observed at room temperature is determined by trapping at interstitial silver atoms.

4. Cold work has a pronounced influence on the range of photoelectrons, providing many new traps. Haynes and Shockley observed that the photoelectrons become trapped at the slip lines of the material, which is presumably the region where dislocations are generated and move.

5. Lehfeldt has found that the silver and thallium halides become electronic conductors in the dark at low temperatures if irradiated for a sufficiently long period of time. The current produced in this way is termed the secondary current. The effect, which can be induced by about 10^{13} absorbed light quanta, is presumably[40] associated with the build-up of space charge which generates a field at the cathode of sufficient intensity to draw electrons into the salt.

6. Lehfeldt has found that the space charge produced by irradiation under 80°K is very stable, for the secondary current varies reversibly with changes in temperature in this range. On the other hand, irreversible changes in the secondary current occur when the temperature is raised above liquid air temperature.

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[38] J. R. Haynes and W. Shockley, *Conference on the Strength of Solids* (see reference 32), p. 151; J. R. Haynes, Rev. Sci. Instr. **19** 51 (1949); J. R. Haynes and W. Shockley, Phys. Rev. **82**, 935 (1951).

[39] H. Witt [Z. Physik **128**, 442 (1950)] has determined the range of electrons in specimens of NaCl containing as few as 10^{15} *F*-centers per cc; see also G. Glaser, Gött. Nach. **3**, 31 (1937).

[40] N. F. Mott and R. W. Gurney (reference 1), p. 187.

B. Origin of Electrons; Absence of Holes

The fact that photocurrents are observed even at very low temperatures in the tail of the fundamental region and in the portion associated with exciton production supports the view that the electrons are released either as a result of the violation of the selection rules on wave number for a perfect crystal, or because excitons, which are produced in this region, wander to regions of imperfection and decompose in such a way as to yield free electrons, presumably because there are states of the dissociated exciton having lower energy than the exciton states generated with light quanta. It seems to be very difficult to decide between these two processes; perhaps both operate simultaneously.

The apparent inconsistency of measurements of hole conductivity seems to present a mystery at the present time, when contrasted with the apparent consistency of measurements of electron currents. The following explanations are possible:

(1) The electron range is very much greater in the specimens employed in the Göttingen work than in those employed at Cornell. Thus the hole component could be the same in both cases; however, it is masked by the larger electron currents in the first. This explanation seems to be implausible for the mean free life-time of the electrons is nearly the same in the specimens employed in the two laboratories.

(2) There is a much higher density of hole traps in the specimens employed at Göttingen, so that the holes have a very short range.

(3) The hole currents are observed only in the vicinity of $-65°$C, or at higher temperatures, and not in the range near liquid air temperatures employed by Lehfeldt.

It is difficult to decide between these alternatives on the basis of existing information. The fact that hole pulses are observed at all implies that the holes possess an appreciable mobility and hence have an effective mass comparable with that of the electrons. On the other hand, it is possible that the effective mass of the holes is sufficiently larger than that of the electrons that the former are more readily trapped, in spite of the fact that they are quite mobile in perfect regions of the lattice. For example, we should expect the strained regions about dislocations to provide places where a hole or an electron would be more stable than in the perfect lattice if zero point energy were negligible. The top of the filled band may be raised and the bottom of the empty band lowered in the compressive region on one side of a Taylor dislocation. It is possible that holes can be trapped in such regions at sufficiently low temperature whereas electrons cannot, either because the top of the filled band is raised relatively more than the bottom of the filled band is lowered, or because the hole has a sufficiently greater effective mass that it is able to form a discrete system of levels which are bound to the dislocation. We saw in the previous section that we may expect about 10^{17} atoms per cc to be at the center of a dislocation in the silver halides. The range of the holes would be exceedingly short if they could be trapped at such regions.

Similarly, it is difficult to understand why the "forbidden" transitions which occur in the tail of the fundamental band should yield free electrons more readily than free holes if the latter are mobile when free. Generally speaking, one would expect considerable symmetry in the production of carriers of both sign if they possess comparable mobilities.

Further experiments would be highly desirable.

C. Quantum Yield

The fact that the quantum yield for photoelectrons is less than unity at liquid air temperature and, actually, is of the order of a half or less can be explained in several ways:

1. Either free electrons and trapped holes or trapped electrons and free holes are produced at imperfect regions of the lattice (e.g., dislocations), having a probability of about 50 percent. The free holes possess a short range at $-200°$C and do not contribute to the photocurrent.
2. Only excitons are generated by the light quanta and have about equal probability of decomposing into free electrons and holes, of which only the former have a long range, and of losing energy in another way, such as by exciting the silver ions or the thallous ions, perhaps near dislocation where the transitions in Ag^+ are less forbidden than in the perfect crystal.
3. There is about equal chance of generating free pairs and excitons. The latter do not decompose but expend their energy in other ways.
4. The light quanta are absorbed both in the production of excitons and pairs and in stimulating the inner shells of the metallic ions, silver, and thallium. The energy absorbed in exciting inner shells is dissipated in a manner that does not yield photoelectrons, such as in the production of luminescent radiation or in radiationless return to the ground state.

None of these explanations seems to be entirely satisfactory. The first suggests that trapping sites for electrons should be very common—that is, as common as the distorted regions where forbidden transitions may occur. This is in contradiction with the observed long range of the photoelectrons.

The second explanation supposes that the entire tail of the fundamental band is associated with exciton production and is not primarily the result of broadening of the ionizing transitions. In this event it is necessary to assume that the lattice is much more highly distorted than any evidence indicates is feasible. (See Sec. III.) Moreover, it would be very surprising if the excitons possess nearly equal probability of disposing of their energy in two very different ways both in the silver halides in which the inner-shell transitions of the metal ion are forbidden and in the thallium halides, in which the transitions are allowed.

If the third explanation were correct, we might expect the fraction of transitions producing ionization to vary more rapidly than by the fivefold or tenfold factor that is observed as one passes from the tail of the fundamental band into the interior, where the absorption coefficient is about 10^5 times larger. The fourth explanation suffers both from this defect and the fact that the silver and thallous halides behave so nearly alike that it is difficult to believe that the inner-shell transitions play an important role in the primary absorption process.

On the whole, it appears that the diminution of the photoelectric yield from the value unity can best be explained at present by assuming that both pairs and excitons are generated in the tail of the fundamental band, that part of the energy transmitted to the excitons is lost without subsequent production of pairs, and that the fraction absorbed in the production of excitons increases as one goes into the ultraviolet region of the spectrum. The allowed excitation of the metallic ion may represent an additional competitive process in the thallous halides.

D. Trapping by Dislocations; Incipient Vacancies

It is very interesting to observe that the dislocations which are present in the well-annealed crystal do not act as good electron traps, although they may well act as good traps for holes. As mentioned in the previous discussion, we should expect as many as 10^{17} atoms per cc to be in the immediate vicinity of a dislocation line even in well-annealed material. The writer has pointed out in another connection[41] that in crystals having the NaCl structure a jog in a Taylor dislocation, where it passes from one slip plane to another, has a site which may be regarded as the locus of an "incipient" positive or negative ion vacancy. The type of incipient vacancy depends upon the point in the lattice at which the jog occurs. An incipient vacancy of this kind may act as an excellent trap for an electron or hole, at sufficiently low temperature. In fact the field in the immediate vicinity of such an incipient vacancy should be Coulomb-like with an effective charge of magnitude[42] $\pm e/2$, depending upon the sign of the vacancy. (See Fig. 9.) The long-range component of the field varies with distance r in the manner $\pm e/2\kappa_0 r^2$ where κ_0 is the static dielectric constant ($\kappa_0 = 12.3$ for AgCl and 13.1 for AgBr). The potential arising from this field should be of the order of ±0.2 ev at a distance of 2A from the center, that is about ten times larger in absolute value than kT at room temperature. The experiments carried out at liquid air temperature suggest that, while an electron can be trapped by incipient vacancies, it is not trapped by the average, unbroken region of the dislocation. On the other hand, a hole may be trapped at the average position and then may wander along the dislocation until it finds an incipient vacancy of the proper sign.

e/2 e/2

□ + − + − + − + − + − + □

FIG. 9. Simple demonstration of the fact that an incipient halogen ion vacancy has a charge of $e/2$ (courtesy of N. F. Mott, see footnote 42). The row of ions represents an extra strip on the edge of a Taylor dislocation in a crystal of the NaCl type, running in the (100) direction. The squares represent two incipient halogen ion vacancies at the points where the dislocation jogs. The row possesses an extra charge of $+e$, which may be regarded as being evenly divided between both end, and hence with the incipient vacancies.

One of the influences of annealing on the dislocation pattern should be to smooth the dislocations and reduce the number of jogs. On the other hand, the experiments of Gyulai[43] and others on the influence of plastic flow on the photographic properties of salts appear to show conclusively that cold-working not only increases the density of such jogs, but produces large numbers of free vacant lattice sites which condense into clusters during a period of rest after plastic flow. This viewpoint agrees very well with the observation of Haynes and Shockley[38] that plastic flow decreases the range of electrons, and that the electrons are captured near the slip lamellas. Presumably the negative ion vacancies, both incipient, and those in what ever clusters may form, act as traps.

E. Charge on Incipient Vacancies

In this connection, we may emphasize two additional points of interest for the silver halides:

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[41] F. Seitz, Phys. Rev. **79**, 239 (1950), in which Fig. 1 shows a dislocation containing a jog and the associated incipient-halogen ion vacancy.

[42] Both Mott and the writer have noted this property of the incipient vacancy independently. Mott has employed it to interpret unpublished measurements of Krumhansl on trapping energies determined with the use of phosphorescent "glow curves." These curves are obtained by measuring the intensity of luminescent radiation when specimens of silver chloride are warmed after being irradiated at low temperatures. The writer has employed the property in the manner described in the text. The fact that the charge on the incipient vacancy is $e/2$ may be seen in the following way. Imagine that the jog in the dislocation is shifted from one plane normal to the dislocation line to the next, so that the sign of the incipient vacancy is reversed. Suppose, for example, the jog is initially such that there is an incipient negative ion vacancy and that this is then filled with a negative ion. The long-range or Coulomb component of the field should change as by the addition of a charge $-e$. On the other hand, it should also have a sign that is the reverse of its initial value since the incipient negative ion vacancy is changed to an incipient positive ion vacancy. Hence the effective charge must have been $+e/2$ before the shift and must be $-e/2$ after it. Mott has pointed out that the same result can be obtained in the following simple manner (see Fig. 9). Imagine a dislocation which jogs from plane 1 to plane 2, runs for a distance in plane 2 and then jogs back to plane 1. Suppose that the incipient vacancies have the same sign at the two jogs. Then one may regard the additional segment of the dislocation in the range between jogs as a row of ions of alternative sign, the first and the last ions having the same sign. The entire row will have one unit extra of charge of the same sign as the first and last ions. Since the two ends behave symmetrically, both must have effective charges of one-half unit.

[43] See the paper of footnote 41 for an extensive set of references to this work.

1. When an incipient negative ion vacancy captures an electron, the resultant center has a net negative charge of $-e/2$. Hence, the center may attract a mobile interstitial positive ion, at sufficiently high temperatures, and form a center with a net charge $+e/2$, which is in an excellent position to capture another electron. If it does capture a second electron, a second interstitial positive ion may migrate to the region and "reset" the trap. We shall return to a discussion of this matter in the next section.

2. A row of negative ion vacancies distributed along the edge of the extra plane of an edge dislocation of the type discussed in reference 41, as well as in more general types, is indistinguishable from a row of interstitial positive ions which have condensed at the edge of the dislocation: The positive ions which separate the negative vacancies in the first case can be regarded as forming a row of interstitial ions. By the same reasoning, it follows that a row of F-centers, formed of halogen ion vacancies and electrons and distributed along the edge of a dislocation, is indistinguishable from a row of silver atoms distributed along the edge of the dislocation.

F. Recombination of Electrons and Holes

It is also interesting to consider the experimental observation that the holes which are produced along with free electrons are not effective traps for the electrons even after the former have become trapped. This is demonstrated by the fact that an appreciable number of the deep electron traps initially present can be diminished by extended irradiation at low temperatures, presumably because they become filled with electrons. For each deep trap of this type which disappears, a trapped hole must appear somewhere else in the lattice. There seem to be two possible types of explanation of this effect:

1. The hole becomes trapped at an incipient positive ion vacancy, perhaps after being trapped at a dislocation and wandering along the length of the dislocation until it finds the incipient vacancy. Since the resulting incipient V_1-center[44] formed in this way is positively charged, by an amount $+e/2$, it may attract a positive ion vacancy and become negatively charged by an amount $-e/2$. Hence it will repel an electron, although it may attract a second hole. This mechanism could operate at temperatures as low as liquid air temperature only if positive ion vacancies and interstitial silver ions are available and mobile. Although the density of such vacancies and ions must be negligibly small in the perfect regions of the crystal at such temperatures, it is not unreasonable to assume that there is a tenuous cloud in the immediate vicinity of the dislocation where the stress field may lower appreciably the energy required to form Frenkel defects. We shall return to this point in the next section.

2. The incipient V_1-centers occur for values of the configurational coordinates of the surrounding atoms which do not permit the electron and hole to combine. That is, the energy of the normal electronic state of the crystal, when the configurational coordinates have the value associated with an incipient V_1-center at equilibrium, is so high that recombination cannot occur unless a large activation energy is available. An explanation of this type apparently must be invoked to interpret the difficulty[44] incurred in the bleaching of V_3-centers in the alkali halides, which presumably are formed by aggregation of two V_1-centers.

The second explanation appears to be much less attractive than the first. For the incipient V_1-center will have a positive charge of $e/2$, and hence will attract the electron with a coulomb field, if it does not capture a mobile positive ion vacancy. Hence we should expect it to act as a moderately good trap for an electron at sufficiently low temperatures, even though an activation energy might be required to achieve the ground state by complete recombination of the electron and hole.

VI. PHOTOLYSIS IN THE PUREST SILVER HALIDES

A. Experimental Results

There is a very large lore relating to the photolytic darkening of pure massive specimens of the silver halides. We shall summarize what appear to be the most essential facts.

1. Photolytic darkening is produced[45] by light quanta having the same range of wavelengths as those which produce photocurrents.

2. The darkening arises from a broad band[45] which lies on the long wave side of the fundamental band and overlaps it in part. The breadth and shape of this band is almost independent of temperature, unlike the F-band of the alkali halides, although the magnitude and shape may be varied by changing the length of irradiation. Löhle has found that the peak shifts to the red with extended irradiation. We shall adopt the well-justified procedure of regarding the centers responsible for the band as silver atoms which are in states of aggregation to be discussed in more detail subsequently.

3. There appear to be two broad ranges of darkening of interest: (a) That in relatively early stages in which the centers responsible for the darkening contain only a few atoms of silver, in which the extinction[45,46] of light in the photolytic band is primarily a result of absorption, and in which the extinction coefficient is of the

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[44] For a discussion of the V-bands see the following papers: F. Seitz, Phys. Rev. **79**, 529 (1950); E. Burstein and J. J. Oberly, Phys. Rev. **79**, 903 (1950); Casler, Pringsheim and Yuster, J. Chem. Phys. **18**, 887 (1950); J. Alexander and E. E. Schneider, Nature **164**, 653 (1949); Dutton, Heller, and Maurer, Phys. Rev. **84**, 363 (1951).

[45] See the reviews noted in reference 1. The summary by R. Hilsch and R. W. Pohl, Z. Physik **64**, 606 (1930) contains important aspects of their research.

[46] F. Löhle, Gött. Nachr. **II**, 271 (1933).

order of 0.01 to 1 cm^{-1}, corresponding to between 10^{14} to 10^{16} centers per cc. This is the range in which the darkening centers resemble the F-centers of the alkali halides most nearly, although there are profound differences. (b) A range obtained by much more intense irradiation in which colloidal aggregates of silver are found. Apparently scattering of light is as important as absorption in this range. Burgers and Kooy[47] have demonstrated the presence of metallic silver in this range by x-ray diffraction. Haynes and Shockley[38] have examined the colloidal specks in this case in specimens of AgCl darkened at room temperature. The irradiation was continued sufficiently long that between 10^{16} and 10^{17} photoelectrons were released; moreover the darkening was localized in relatively narrow regions of the specimen so that the concentration of photoelectrons was relatively high. They found essentially spherical silver clumps of the order of 100A in diameter. We shall distinguish between the two ranges of darkening by designating them by the terms "molecular range" and "colloidal range," although there probably is no sharp dividing line between the two ranges. Nanda (Sec. IX) has confirmed Haynes and Shockley's measurements in the colloidal range.

4. The quantum efficiency for producing discoloration has been measured by Hilsch and Pohl[45] and is 0.4 and 0.33 for AgCl and AgBr, respectively, during the early stages of irradiation when less than 10^{15} light quanta have been absorbed per cc. The quantum efficiency falls later. The values of the quantum efficiency already given are derived on the assumption that the oscillator strength of the electrons in the absorption band is unity. It is not impossible that the oscillator strength actually is less than unity, as is true for F-centers in the alkali halides, and that nearly one trapped electron is formed for each of the photoelectrons released. It will be recalled that only about 0.5 photoelectron are produced per absorbed quantum in the silver (and thallium) halides.

5. During the molecular range, the bands may be bleached by irradiation with light in the region of wavelengths absorbed by the band; however if monochromatic radiation is used, only a portion of the band near the absorbed wavelength is bleached, that is, the optical transmission of the band is increased over a range of wavelengths near that absorbed. This behavior contrasts with that of the alkali halides in which the entire F-band may be bleached by irradiation in any part. Photoelectrons are released during the process. This experiment shows that, in the molecular range, the observed bands are the envelope obtained by superposition of a number of narrower bands, which cannot be resolved individually. Presumably each component band arises from a cluster of one or more silver atoms. The centers of the component bands differ either because they are identical centers in different environments, or because they are clusters containing different numbers of silver atoms, or because of both of these factors. The quantum efficiency for reversal of the darkening seems to be much less than unity. Reversal does not appear to be possible by light alone in the colloidal range.

6. There is no evidence for a band arising from the trapped holes, analogous to the V-bands[44] of the alkali halides. Presumably these are hidden behind the tail of the fundamental absorption band of the crystals and hence contribute to the tail.

7. There are many experiments[41] which show that mechanical working of the specimen greatly enhances darkening at room temperature. Perhaps the most careful experiments of this type were carried out by Löhle.[46] He observed that the darkening would saturate early in the molecular range unless the crystals had received sufficient handling to cold-work the specimens at least slightly. The quantum yield is much less than unity in the specimens which saturate early. Haynes and Shockley have shown that the darkening concentrates at the slip bands in specimens which have been deformed in such a way that the plastic flow can be localized moderately.

8. Löhle has also studied darkening at liquid air temperatures and has found the following important facts: (a) Absorption peaks which are exact duplicates in shape of those obtained at room temperature can be obtained under suitable conditions, however the area under the band of a given shape obtained at liquid air temperature is about 10 times larger than that under the band obtained at room temperature. In other words, the density of centers having a given relative distribution which can be obtained is about ten times higher at low temperatures than at high. (b) Cold-working is not sufficient to guarantee darkening at liquid-air temperature. It is also necessary to have a small amount of irradiation at room temperature prior to cooling the specimen. This prior irradiation need not be sufficient to produce perceptible darkening at room temperature.

B. Gurney-Mott Theory

The general basis of the Gurney-Mott theory[1] of darkening is now so well established that we need be concerned primarily with the nature of the trapping centers which occur in the specimens. We shall begin by restricting attention to the measurements at room temperature.

C. Importance of Plastic Flow

The importance of plastic flow indicates that the nuclei for the color centers of interest in photolysis occur at or near dislocations; moreover the presence of dislocations in the crystal is not sufficient; it is also necessary that they be placed in motion prior to darkening. As we saw in the preceding section, we may expect two changes to occur when dislocations are set in motion: (a) Lattice defects are generated so that there are clusters of positive and negative ion vacancies in the neighborhood of the dislocation immediately after cold-work.

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[47] W. G. Burgers and J. Kooy, Rec. trav. chim. **67**, 21 (1948).

(b) We may expect the course of the dislocations to be much less smooth, so that the number of incipient vacancies of both sign is much larger than in a well-annealed specimen. It is natural to suggest that either or both of these imperfections play an important role in providing trapping centers for the electrons and holes. Unless such traps are present in large numbers, the electrons and holes will recombine.

D. Trapping by Interstitial Ions

As was emphasized in the preceding section, the experiments of Haynes and Shockley on the range of electrons in well-annealed silver chloride, carried on in a band of temperature near room temperature, cast doubt on the view that the range of the free electrons may be determined by trapping at silver ions associated with the equilibrium density of Frenkel defects (between 10^{12} and 10^{13} per cc at room temperature). This hypothesis could be tested further by duplicating the experiment with pure silver bromide to see if the range is about two powers of ten smaller than in silver chloride. Even if the electrons are captured by interstitial silver ions, it is very likely that the resulting atoms would retain much of the mobility of the interstitial ion, for which the jump frequency is of the order of 10^9 sec^{-1} at room temperature. Hence the atom should migrate to a dislocation in a time of the order of a second or less. Thus unless it finds a good trapping site, it will carry the electron about until it meets a hole. Simpson[48] has suggested on theoretical grounds that the electron is not bound very tightly to an interstitial ion and will escape in a time less than a second. In this case the trapping by interstitial atoms might be unimportant for the photolytic darkening since the electron would wander from interstitial ion to interstitial ion until it finds a more stable trap.

In any case, it seems natural to assume that, in the plastically deformed material, the electron eventually is trapped near a dislocation and either at an incipient halogen ion vacancy or at a halogen ion vacancy associated with a cluster of Schottky defects. If, in the first case, it is not accompanied by an interstitial silver ion to which it is attached, the incipient F-center which results will have an effective charge $-e/2$ and will attract an interstitial ion, to yield a center with a charge $+e/2$. The extra ion may join the same row as the incompleted dislocation, thereby extending it. If the electron diffuses with an interstitial silver ion, to which it is attached, the silver ion will end in the same spot as if it had migrated later, so that the end results are identical in the two cases.

Should the electron be trapped at a halogen ion vacancy which is a member of a neutral cluster of vacancies, it will give the cluster a net charge of $-e$. Hence the cluster will attract an interstitial silver ion and become neutral again. The same end result would be achieved if the electron were first captured by an interstitial silver ion and the pair then diffused to the cluster as a neutral atom.

E. "Resetting" of Traps

It seems very important to emphasize that the unit formed by adding an electron and silver ion to the incipient F-center has a charge $+e/2$ and hence will repel holes, whereas that obtained by adding an electron and interstitial ion to a neutral cluster of vacancies will be neutral and hence may combine with a hole if the arrangement of configurational coordinates does not prevent this. In other words, we seem led to the conclusion that the incipient halogen ion vacancies are ideal traps for the electrons, and hence for forming aggregates of silver in the molecular range, since they may "reset" themselves after capturing an electron, in such a way as to repel holes and attract additional electrons.

F. Size of Molecular Clusters

If we grant that the first electrons which enter into the "molecular" clusters of silver observed in absorption measurements are trapped at incipient halogen ion vacancies, it is natural to ask if any part of the absorption peaks can be ascribed to single electrons at such centers, that is, to isolated incipient F-centers. This is a very difficult question to answer. We might expect isolated incipient F-centers to have absorption curves with peaks at different positions. For the dislocation may have jogs with many different geometries, depending upon the direction in which the dislocation is oriented relative to the lattice at the point of the jog and upon the configuration of other imperfections in the vicinity. Thus the incipient F-centers could have the characteristics of impurity atoms in glasses in the sense that a large variety of relatively stable positions are possible. Since large colloidal aggregates of silver may be produced, it is evident that aggregates of many sizes can occur and that isolated incipient F-centers would be present with greatest probability during the early stages of irradiation, perhaps at the stage studied by Löhle in which only 10^{14} centers are present per unit volume and in which the shape of the absorption band is relatively sensitive to cold work.

G. Fate of Holes

The fate of the holes at room temperature is somewhat more obscure. We may assume that they are captured either by positive ion vacancies or by dislocations. Silver ion vacancies in AgBr have a jump frequency of the order of 10^9 sec^{-1}. The jump frequency for a V_1-center, formed by adding a hole to a positive ion vacancy is probably almost as large. Hence, the V_1-centers that are formed in the first case, can migrate to dislocations and eventually join a jog in a dislocation where an incipient positive ion vacancy occurs. In the second case, the hole will migrate to a similar jog and

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[48] J. H. Simpson, Proc. Roy. Soc. (London) **197**, 269 (1949).

attract a positive ion vacancy. In analogy with the case of the electron trap formed by an incipient halogen ion vacancy, the incipient positive ion vacancy to which a hole and a positive ion vacancy have been added will have a net charge of $-e/2$ and hence will repel electrons, but attract holes. Thus the holes may build clusters of halogen atoms at such positions, just as the electrons build clusters of silver atoms at incipient halogen vacancies. Apparently the absorption bands associated with such clusters of halogen atoms are entirely masked by the tail of the fundamental band.

A large aggregate of *V*-centers would become the equivalent of a bubble of halogen gas and might make its presence felt through a change in the mechanical properties of the crystal.

H. Darkening at Low Temperatures

The experiments on darkening at low temperatures do not seem to be sufficient to give us a complete picture of the course of events. The need for cold-work appears, at least in part, to parallel the need at room temperature: Incipient vacancies are necessary as trapping centers if molecular or colloidal aggregates are to form. It is also possible that the clusters of vacancies formed during cold-work play a very useful role in furnishing interstitial silver ions and silver ion vacancies which may be added to the incipient vacancies when they have captured electrons or holes. The density of Frenkel defects must be negligibly small at liquid air temperatures in perfect regions of the crystal. However it is not unreasonable to suppose that the density of mobile defects is considerably higher in the immediate vicinity of a dislocation where the elastic stress field will lower the activation energy required to generate defects. Clusters of vacancies localized in regions will also contribute to this tenuous "gas" of lattice defects. In any case, it seems absolutely essential to assume that there is some residual mobility of ions in the vicinity of the trapping sites at liquid air temperatures, for otherwise the formation of molecular clusters of silver atoms beyond the incipient *F*-center, and presumably of halogen atoms, is very difficult to understand. Dislocations appear to have exactly those properties which are required to guarantee such mobility. It would be very interesting to know how large the clusters of silver which can be formed at liquid air temperatures are and if there is a limit to the size that is directly related to the amount of cold-work which has taken place.

As noted before in paragraph 8, Löhle found that prior irradiation at room temperature is essential for substantial darkening at liquid air temperatures in a short period of time. Presumably such irradiation forms a small number of clusters of silver atoms which contain a small number, perhaps only one, of silver atoms. We must conclude that unless such nuclei are present, further growth is essentially impossible. We shall defer a discussion of this point until we have commented further upon Lehfeldt's experiments on photoconductivity.

I. Relation between Darkening and Photoconductivity at Low Temperatures

Lehfeldt[34] found that the crystals which he employed in his photoconductive experiments could be darkened at room temperature, both molecular and colloidal aggregates being obtained. The radiation employed was confined to a narrow band of wavelengths about 500A wide, so that the specimen could be colored throughout its volume. Only a small fraction of the radiation, perhaps 1 percent, was absorbed in this process. We may conclude that his specimens had been given a critical amount of cold-work, although it is not clear how much this amount extends above the critical value. Interesting experiments carried on at low temperatures after various amounts of darkening are as follows:

1. If the crystal was not given prior irradiation at room temperature, the range of the photoelectrons at liquid air temperatures could be increased by a factor of twenty or more by continued exposure at low temperatures. In such exposure the total number of quanta incident on the crystal varied from a value below 10^{13} to a value near $5\cdot 10^{17}$, of which, as already mentioned, only a small fraction, perhaps one percent, was absorbed. This observation can be explained by assuming that the crystal contains of the order of 10^{15}, or possibly fewer, electron traps in the relatively perfect regions of the lattice, not near dislocations. These traps are exhausted during the irradiation because they capture electrons and obtain a negative charge. The negative charge cannot be neutralized by the migration of positive ions, for the density of Frenkel defects in perfect regions of the crystal is negligible at liquid-air temperature. Moreover, the negative charge presumably cannot be neutralized by holes because the latter have a far greater probability of being trapped at dislocations, where they eventually end at incipient positive ion vacancies and form units with a charge $-e/2$, which also repel electrons. Lehfeldt does not state whether his crystals darken at liquid air temperature under these conditions, but presumably they do not.
2. If the crystal is first irradiated with about $5\cdot 10^{17}$ light quanta at room temperature, so that molecular aggregates are presumably formed, a situation much like that outlined in paragraph 1 occurs during irradiation at liquid air temperature. The range is initially much smaller than in paragraph 1. However it can be increased to a value nearly as large as that described in paragraph 1 by extensive irradiation, of the order of 10^{20} incident light quanta being needed. It is not clear in these experiments to what extent the darkening was enhanced by the irradiation at low temperature, if it was enhanced. The explanation of this effect will be considered subsequently.
3. When the irradiation at room temperature is

carried out for a long period of time, sufficient for 10^{20} light quanta to be incident upon the crystal, so that colloidal particles of silver are presumably formed, as in the experiments of Haynes and Shockley, the range is very short and is not altered by long irradiation. It seems likely that in this case formation of large aggregates of silver causes an appreciable amount of cold-work in the neighborhood of the colloidal particles. In fact Mott[38] has suggested that the size of the colloidal particles in the silver halides is limited by the strain which they may impose on the surrounding medium. Thus the colloidal particle may be surrounded by a large volume which is relatively densely covered with dislocations which have been pushed out from the colloidal spot, and with the debris that is associated with motion of dislocation. This distorted region should provide many excellent electron traps. Incidentally, crystals possessing the NaCl structure should not permit prismatic slip[49] if the slip planes are of the (110) type and if the slip directions are (110) as is generally reported, for it is not possible to form prisms of (110) planes which have an axis in a (110)-type direction. If prismatic slip could occur, it might permit spheroidal precipitates to grow to any size since the stress would be relieved by such slip. Haynes and Shockley[38] have presented indirect evidence that slip may occur on (111) planes in AgCl. If this conclusion is valid and if the slip is in (110)-type directions, prismatic slip should be possible. It would be interesting to know if the size of particles formed by photolysis in the thallium halides is limited like that in the silver halides because prismatic slip definitely is possible in the thallium salts.

The experiments described in the foregoing paragraph 2, and Löhle's observation that irradiation at room temperature, prior to cooling to liquid air temperature, catalyzes darkening at liquid air temperature seem to be closely related. Molecular aggregates appear to be generated in both cases. Moreover, the experiments described in paragraph 3, which indicate that colloidal aggregates provide very effective traps (perhaps because of distortion they produce in the surrounding lattice) suggests that effects of a similar kind are produced in more moderate form even when the aggregates are of molecular size. Even small aggregates could cause appreciable plastic flow in the neighborhood of the incipient vacancies where we have postulated that they form.

VII. INFLUENCE OF FOREIGN ATOMS ON DARKENABILITY

There seems to be considerable consistent experimental information in the literature concerning the influence of foreign atoms on the electrical and photolytic properties of massive silver halides. We shall consider several cases:

1. In cases of additions of excess halogen, Lehfeldt[34] has impregnated his specimens of silver chloride with excessive halogen. The crystals were heated to 400°C in the presence of three atmospheres of chlorine. They displayed a homogeneous yellow color at room temperature. This can be removed by heating the specimen to 400°C in air. He found that the range of the photoelectrons was diminished to a very small value. The explanation of this effect appears to be very simple. The stoichiometric excess of chlorine enters the crystal by the outward migration of interstitial silver ions, which leave positive ion vacancies behind, and the inward migration of holes from the surface. The vacancies and holes combine at room temperature to form V-centers, probably of the V_2- and V_3-types since V_1-centers are not stable even in the alkali halides at room temperature. The photoelectrons are rapidly trapped by the V-centers, which are probably much more dense than any other trapping center, so the mean free life is small. Crystals containing excess halogen presumably do not show photolytic darkening.

One of the remarkable features of this observation is the fact that the V-centers produce visible discoloration when present in sufficient quantity that they alter the tail of the fundamental band. Further study of this question would be of value in determining the position of the V-bands. It would also be interesting to know if holes can be freed from the V-centers.

2. Teltow[5] has added a stoichiometric excess of silver to silver bromide by placing the specimen in contact with metallic silver at 400°C. The specimen becomes darkly colored presumably by the migration of electrons and interstitial silver ions into the lattice. There apprently are no systematic investigations of the properties of crystals colored in this way. It is possible that the silver precipitates in the form of colloidal aggregates at room temperature, similar to the aggregates formed by photolysis.[50]

3. Additions of the halides of divalent metals to the silver halides decrease[51] the sensitivity to light. The influence on photoconductivity does not seem to have been studied. Several factors may contribute to the loss of sensitivity. The divalent ions presumably substitute for silver ions and are accompanied by positive ion vacancies, which balance the excess charge. The divalent ions may capture electrons and form the analog of the Z_1-centers observed[52] in the alkali halides which contain divalent ions. In addition the positive ion vacancies may trap holes and form V-centers. In any event, the additional trapping centers may have the effect of keeping the electrons and holes away from the incipient vacancies. Instead they are attached to units which act as better catalysts for recombination in the

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[49] The term *prismatic slip* has been given by the writer to a simple type of punching observed by A. Smakula and M. W. Klein, J. Opt. Soc. Am. **39**, 445 (1949); see F. Seitz, Phys. Rev. **79**, 723 (1950).

[50] W. G. Burgers and J. N. Kooy, Rec. trav. chim. **67**, 16 (1948).

[51] K. Hecht, Z. Physik **77**, 235 (1932).

[52] H. Pick, Ann. Physik **35**, 73 (1939); Z. Physik **114**, 127 (1939); F. Seitz, Phys. Rev. **83**, 134 (1951).

sense that the Z_1-center and V_1-center are neutral and may capture a hole and an electron, respectively.[52a]

4. The influence of additions of Ag_2S has been studied extensively by Stasiw and Teltow.[4] This topic is of much interest since sulfur sensitizes the crystals so that they darken very easily. The effect has practical importance for photographic emulsions and has been the subject of considerable speculation by Stasiw, Teltow, and Mitchell.[3] Teltow[4] has proved, apparently beyond doubt, that at temperatures near the melting point the silver sulfide does not raise the electronic conductivity appreciably. Moreover, the sulfide ions are accompanied by compensating interstitial silver ions. The simplest interpretation to place upon the results is that near the melting point the sulfur is present as S^{--} ions in substitution for halogen ions and that the second electron is bound to the sulfur ion with an energy of at least 2 ev. Mitchell has suggested that the electron would be relatively unstable, so that the S^{--} ion would either prefer to have a halogen ion vacancy as a neighbor at low temperatures or might lose the electron and the halogen ion vacancy as a result of heating. The latter pair of particles could cluster as F-centers when the crystal is quenched. It is possible that the interstitial silver ion observed with the sulfide ion at elevated temperatures is transformed into a halogen ion vacancy at low temperatures and that the latter is then more tightly bound to the doubly charged sulfur ion than an interstitial silver ion would be. A dislocation could act as a catalyst for the conversion of an interstitial ion into a halogen ion vacancy. However there appears to be little doubt that the S^{--} can hold both its electrons at temperatures near the melting point.

The crystals of AgBr containing sulfur have a brown color, presumably because of a new absorption band which appears on the long wavelength side of the fundamental band and overlaps with it extensively. Stasiw and Teltow have attempted to separate this band from the fundamental band, but this separation is by no means unambiguous since the result depends upon the speed of quenching. It is possible that the tail of the fundamental band is extended as a result of lattice strains, induced by the sulfide ions, which permit further breakdown of selection rules for absorption. This would be particularly true if the sulfide is clustered into precipitates which distort the lattice. In fact this viewpoint seems to explain the fact that the extra absorption tail does not change when the crystal is irradiated with light absorbed in the tail. In this connection it may be remarked that the solubility of Ag_2S, obtained by extrapolating Teltow's measurements to room temperature, is of the order of 10^{-6} mole percent. Larger additions should aggregate near or above room temperature.

On the other hand, if we assume that the additional absorption is associated with the S^{--} ions, the exictation energy of the extra electron is found to be of the order of 2.5 or 3.0 ev in AgBr, which is in reasonable agreement with the idea that the ionization energy of the second electron in S^{--} is not less than 2 ev. Perhaps the sulfide ions absorb the photons and transfer the energy to the normal electrons, without becoming ionized.

For reasons which Mitchell has emphasized very clearly, it is surprising that the S^{--} ion succeeds in achieving such great stability in the silver halides. The sulfide ion occupies a position surrounded by positive ions, where the Madelung potential is of the order of -8.5 ev. Since the energy of attachment of the second electron to a free sulfur ion is about -5 ev, and since the energy of an electron at the bottom of the conduc-

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[52a] *Note added in proof:* Since the preceding was written, the book *Fundamental Mechanisms of Photographic Sensitivity* (Academic Press, Inc., New York, 1951), edited by J. W. Mitchell, has become available to the writer. Among the contributions to this symposium monograph which seem most relevant to the discussion of the present paper is that of W. West (page 99) which deals with measurements of photoconductivity in emulsions. This investigator has observed the enhancement of conductivity of somewhat typical silver bromide emulsions when illuminated by suitably chosen bands of light. The measurements are made at room temperature, under which conditions the natural electrolytic conductivity dominates the photoconductivity by a factor of about one thousand. West has been particularly interested in the influence of dye sensitizers upon the photoconductivity of emulsions and has shown that there is a close correlation with photographic sensitivity. However, what is more pertinent to the preceding discussion, he has also investigated the influence of additions of divalent ions of lead and cadmium upon the photoconductivity and has found that these additions *enhance* the photoconductivity even though they decrease the photographic sensitivity. This effect is sufficiently remarkable that it should be repeated with single crystals at low temperatures. Nevertheless, the effect seems to be sufficiently well established to merit discussion.

West has ascribed the increase in photoconductivity to a diminution of halogen-ion vacancies associated with Schottky defects because of the increase in density of positive-ion vacancies associated with the divalent metal ions. His view stems from Mitchell's suggestion that Schottky defects might dominate at room temperature and that the halogen-ion vacancies could provide the trapping centers for photoelectrons. West's view cannot be discarded at the present time, in spite of the fact that Frenkel defects predominate, for there is still a possibility that a small density of Schottky defects is present at room temperature and has an important influence on trapping. This view is supported by Simpson's work (see reference 48) which indicates that halogen-ion vacancies provide more stable traps for electrons than interstitial silver ions or substitutional Pb^{++} or Cd^{++} ions would.

It is also possible, however, that interstitial silver ions are the important trap, in spite of Simpson's calculations and the indications derived from the work of Haynes and Shockley that this is not true at 113°C in silver chloride (see Sec. V, A). In this event the increase in photoconductivity would be a result of the suppression of the density of interstitial ions by the positive-ion vacancies associated with the divalent metallic additions.

There remains the very interesting possibility that the divalent metallic additions concentrate at dislocations and interfere with the ability of dislocations to capture electrons. For example, it is possible that the incipient negative-ion vacancies are transformed, by union with divalent positive ions and the associated positive-ion vacancies, into a form which makes them very poor trapping sites.

It is evident that it would be exceedingly profitable to obtain information on the influence of divalent metallic impurities on the photoconductive properties of single crystals of the type investigated at Göttingen, Cornell, and the Bell Laboratories. Measurements at low temperatures would be particularly exciting, for the density of Schottky defects should be negligible both in pure crystals and in those containing divalent additions.

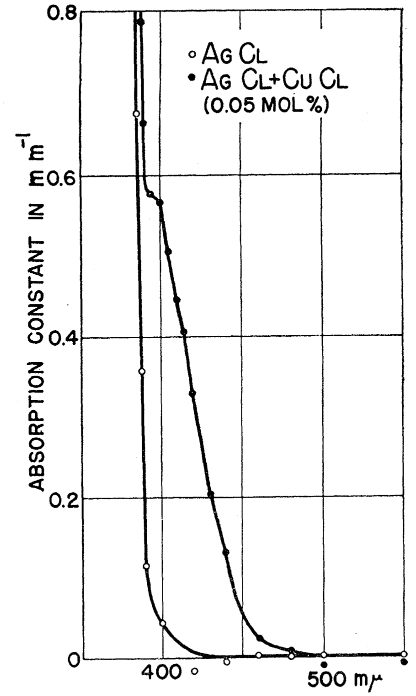

Fig. 10. The extension of the tail of the fundamental absorption band of AgCl produced by an addition of cuprous chloride (after Hecht). Curve *a* is obtained for pure silver chloride, whereas *b* is obtained for chloride containing a copper addition. Both curves are obtained at −186°C. The oscillator strength associated with the copper component is about 0.001. It should be noted (see reference 34) that the photoelectric yield associated with the tail arising from the copper shoulder has the same quantum efficiency as that associated with the tail in the pure crystal, as if the energy absorbed by the copper were transmitted to the electrons in distorted regions of the bulk material.

tion band in AgBr is probably between −2 and −3 ev, it would appear that the second electron on the sulfide ion in the halide lattice uses the local fields in the crystal very effectively to achieve stability.

5. In the case of monovalent additions, there is, scattered throughout the literature, a limited amount of information concerning the influence of various foreign monovalent ions on the properties of the silver halides. For example, Fig. 10 shows[34] the change in the tail of the absorption band of AgCl produced by the addition of 0.05 mole percent of cuprous chloride. It may be seen that an appreciable shoulder is added to the tail of the band. Hecht and Lehfeldt[34] have shown that the crystal is photoconducting for wavelengths lying in the region of the shoulder and that the quantum yield of electrons is almost exactly the same as in the pure salt. This suggests that the energy absorbed in the shoulder is treated by the crystal as any other energy which is absorbed in the outer regions of the tail. Perhaps the sulfide additions have a similar effect.

Teltow[5] has found that cuprous chloride decreases the density of interstitial ions, much like additions of divalent metallic ions, which are accompanied by positive ion vacancies. This effect has not yet received a satisfactory explanation.

VIII. LUMINESCENCE

A. Experimental Results

Farnell, Burton, and Hallama[53] have recently made a study of the luminescence of the purest silver halides available under a variety of conditions and have come to the following conclusions:

1. The pure salts luminesce at low temperatures. The "characteristic" luminescence appears in the chloride at 180°K, whereas the bromide must be cooled to somewhat lower temperatures. The iodide also exhibits luminescence at low temperatures.

2. The luminescent radiation is produced in any part of the tail of the fundamental absorption bands from 2480A into the visible region. The emitted radiation is identical in a given salt throughout this range.

3. In the case of the chloride, the emission spectrum consists of a broad band extending from 4350A to 5800A at 77°K. The bromide has a similar broad peak, shifted to the red. On the other hand, the iodide has a much narrower peak lying in the blue end of the spectrum. The position of this band depends upon the crystal structure, that is whether the lattice has the wurzite or the sphalerite form. The emission peaks for the chloride and bromide do not extend appreciably into the tail of the fundamental absorption bands, whereas that of the iodide overlaps the region where the absorption coefficient is of the order of 10^5 cm^{-1}.

4. Farnall, Burton, and Hallama studied the luminescent radiation observed at low temperatures and did not detect a phosphorescent component that could be observed with the naked eye. A faint component of this type has been observed by Moore, however (Sec. IX).

5. Crystals prepared in different ways exhibited the characteristic emission in such a manner as to leave little doubt that it is typical of the pure material. For example, in the case of the chloride the characteristic band was found in specimens which contain an excess of chlorine, in those which are partially reduced and in both powders and single crystals prepared by various types of precipitation procedures. Of particular interest are single crystals, of the order of 1 mm or more in linear dimensions, prepared by precipitation from ammonia solution, and silver chloride prepared by the interaction of metallic silver and chlorine gas. Specimens containing excess metal exhibit a red emission band superimposed on the characteristic emission band.

6. The emission spectrum is only slightly dependent upon temperature. The band for silver chloride shifts to the red in cooling from 145°K to 20°K and does not become markedly narrower.

7. Additional emission bands can be produced by

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[53] Farnell, Burton, and Hallama, Phil. Mag. 41, 157, 545 (1950).

adding suitable agents. In general large amounts, of the order of one percent, must be added to induce an appreciable effect or to alter the characteristic emission.

8. Observations by Moore at Cornell University (Sec. IX) show that the fluorescent efficiency is very low, of the order of 0.6 percent or less, so that the fluorescence probably cannot be ascribed to one of the primary processes governing the fate of absorbed energy.

B. Suggested Interpretation

The writer would like to propose that the emission spectra observed in the pure salts is a result of transitions within the Ag^+ ion between the d^9s and d^{10} levels. Farnall, Burton, and Hallama suggest that the spectra are the result of recombination of electrons and holes; however it seems very unlikely that it is the result of the typical recombination process since the efficiency is so low.

The observation that the emission bands in the chloride and bromide are broad and that they are not very sensitive to temperature suggests that the emitting silver ions are near imperfections, such as dislocations, in these salts. In fact it is possible that the transitions occur in a region where the excited silver ions are more stable than they would be in the more perfect parts of the lattice and where dipole emission becomes allowed because of perturbing fields. In contrast, the experiments suggest that the emission in the iodide occurs in more perfect regions. Since the iodide possesses tetrahedral coordination, dipole emission is permitted in the $d^9s \rightarrow d^{10}$ transition.

IX. ADDENDUM ON CORNELL WORK

After most of the forgoing manuscript was prepared, the writer was able to read detailed accounts[35] of as yet unpublished work of the group at Cornell University. A full report of this work must await publication. The most pertinent observations, related to the present paper, appear to be the following:

1. Caldwell has observed that the spectral sensitivity of photoconductivity in silver chloride is extended to the red end of the spectrum when silver specks are formed. In other words, he has found that appreciable photoconductivity is associated with illumination in the colloidal band. This band is found to terminate at about 0.9μ on the red side. If one assumes that this is the photoelectric threshold for ejection of electrons from the silver specks into the conduction band of AgCl, and that the surface dipole layer on the silver specks is the same as the value for a clean surface in a vacuum, for which the work function is 4.7 ev, one concludes that the bottom of the conduction band in AgCl is at -3.4 ev. This conclusion appears to focus additional attention on Mitchell's observation that the second electron on a substitutional S^{--} ion would not be very stable in a strictly ionic lattice. Since Teltow's experiments imply that the second electron actually is stable to the extent of 2 ev or more, we apprently must conclude that the sulfur ion employs the high polarizability of its neighbors to advantage.

2. Caldwell has found that irradiation with ultraviolet light at low temperatures invariably enhances photoconductivity for a given stimulating wavelength, in accordance with the view that the photoelectrons produced by the ultraviolet light fills traps which decrease the range. This is true even of the photocurrents generated by irradiation in the colloidal band.

3. Specimens of AgCl heated in chlorine become yellow in color. Moreover the photosensitivity in the region between 6000 and 8000A is diminished, as if light absorbed in this region were no longer effective in freeing electrons. The experiments on the influence of chlorine do not appear to be sufficiently complete to allow extensive conclusions to be drawn.

4. Both Nanda and Caldwell observed that the photoconductive response possesses a relatively sharp peak at about 3850A, the precise position of which is related to the history and origin of the specimen. Lehfeldt apparently did not observe a peak of this type, so that it may imply a difference in the composition of the crystals used in the two laboratories. Nanda studied the peak in a range of temperature between 20°C and -120°C. He found that it is followed by a drop and another broad rise as one goes farther into the ultraviolet.

5. Nanda investigated the absorption spectrum in the tail of the fundamental band and found, in agreement with the Göttingen investigators, that it is relatively insensitive to temperature, although the tail apparently does shift toward the ultraviolet as the temperature is decreased.

6. Nanda varied the temperature when the crystal was pulsed with 3900A radiation and found evidence that the photoconductive response of a crystal annealed in air attains a peak at about -40°C. Although the decrease of photoconductivity with increasing temperature is probably a real effect, it is possible that the drop found at low temperatures is a result of the shift of the absorption spectrum toward the ultraviolet with decreasing temperature. The fall of photoconductivity as one approaches room temperature may be related to the trapping effect of Frenkel defects, that is of the interstitial silver ions, which are transformed into mobile silver atoms. Crystals which have been annealed in a chlorine atmosphere show a smaller photoelectric response in the range below room temperature than those annealed in air.

7. Nanda studied the scattering of crystals exposed to light in the range where photolytic darkening occurs. The scattering was presumably a result of silver specks in the colloidal range. He did not find scattering specks when the crystal was irradiated near -100°C. He concluded that any specks formed are smaller than 30A, and presumably are molecular in size. The observation

of Haynes and Shockley that the scattering increases linearly with time of irradiation, as if the scattering particles attained a limiting size and increased linearly in number with time, was confirmed. The maximum radius was estimated to be 320A. It would be very valuable to have these measurements extended to the thallium halides.

8. Moore has examined the character of the fluorescence of AgCl in detail and has found that the fluorescent efficiency is very low under both pulsed optical and electron excitation. The efficiency for wavelengths between 3000 and 4040A is less than 0.01 percent, whereas that near 2500A is about 0.6 percent. The decay time of the fluorescence is less than $2\cdot10^{-7}$ sec. These results indicate that the fluorescent process is not a major link in the chain by which the energy transmitted to the crystal is dissipated. There is also a phosphorescent component that may be retained by cooling the crystal to liquid air temperature. Moore has demonstrated conclusively that there is so little correlation between the emission of luminescent radiation and the trapping of photoelectrons, that the radiation process cannot be ascribed principally to the recombination of electrons and trapping centers. This result is in agreement with the view expressed in Sec. VIII that the characteristic radiation is emitted by excited Ag^+ ions which lie in distorted regions and which receive their energy either directly from the exciting radiations or from other parts of the electronic system when the latter is excited.

9. Moore has observed hole currents at -65°C comparable to electron currents. These were produced both by bombardment with a pulsed electron beam having an energy that could be varied to 10 kv and with light in the range from 2537A to 4040A. The mean free time of the electrons and holes was comparable to the mean free time Lehfeldt found for electrons at -170°C, that is, of the order of 10^{-6} sec. From the time required for electrons to traverse the specimen, Moore has obtained a mobility $\mu_e=70$ cm^2 per volt-sec. Similarly, by a comparison of the decay of electron and hole pulses, he concludes that the hole mobility is about 40 cm^2 per volt-sec. Moore describes an electronic photocurrent produced by 4040A light which resemble Lehfeldt's very closely; the hole currents produced by light also resemble this. The fact that Moore observes hole currents, whereas Lehfeldt did not can be ascribed to any one of several factors: (a) Moore's investigations were carried out at -65°C whereas Lehfeldt's were at -170°C. (b) The specimens employed by the two investigators may have had different chemical composition and may have received different physical treatment. In any case, Moore's experiments show conclusively that the absence of hole currents in Lehfeldt's experiments does not arise from a low mobility of holes. The difference must lie either in a difference in the ease with which holes are freed, or in a difference in the manner in which electrons and holes are trapped.

10. Warfield studied the currents produced in silver chloride by electron bombardment at -100°C under conditions similar to those examined by Moore. However he used an electron beam which could be focused to a spot having a diameter of the order of 1 mm. The behavior of the induced current was critically dependent upon the particular spot which was bombarded. Some spots gave a very low yield; moreover the yield was very sensitive to time. Consistent observations could be made with a relatively defocused spot. The results obtained in this way are in general agreement with those previously described.

11. Nanda quotes a suggestion by Krumhansl that the excited states of the silver ion may play a role in determining the properties of the silver halides. In particular Krumhansl proposed that the absorption peak near 2500A may be associated with a transition to the first excited stage of Ag^+. For reasons given in the text, it seems more reasonable to the writer to assume that this peak is the exciton peak and that the excited states of Ag^+ play an important role in a secondary way.

X. SUGGESTED EXPERIMENTS

It is evident that the existing experimental information on the properties of the silver halides is not adequate to provide a very complete interpretation of the mechanisms responsible for their intricate behavior. It seems very likely that dislocations play an exceedingly important role in determining the properties which have been emphasized in the preceding pages. This situation is in striking contrast with that for the alkali halides, in which the influence of dislocations appears to occur in a much more subtle and indirect way. In fact it seems safe to say that the effect of dislocations is a primary one in the silver halides, whereas it is secondary in the alkali halides. As a result, it would appear to be very profitable to extend experimental investigation of the silver halides in the hope that such extension will enlarge our knowledge not only of this particular family of salts, but of the general manner in which dislocations may alter the properties of crystals.

The writer would like to propose the following experiments for consideration:

1. It would be interesting to determine the influence of cold-work and annealing on the optical absorption spectra of the silver halides, both in the tail and in the more central regions of the absorption spectrum. Measurements may be made in transmission in the region where the extinction coefficient is of the order of 1 cm^{-1} and by reflection of polarized light in the region where the extinction coefficient is decades larger. It would be particularly interesting to know if the absorption spectra are notably different in crystals grown from the melt and in those grown from ammonia solution.[53]

2. It would be valuable to have more accurate information on the density of lattice defects near room

temperature and near the melting point in the salts. In particular the more accurate measurements of Teltow on the bromide could be extended to the chloride and to the thallium salts.

3. Ionic currents exhibit[54] polarization effects at room temperature. Presumably these effects result from the fact that the interstitial silver ions migrate more rapidly than the silver ion vacancies. Measurements of such polarization effects and the associated relaxation may give direct information on the mobility of both carriers in the vicinity of room temperature.

4. It would be interesting to know if the ionic conductivity is altered by cold-work in the manner observed by Gyulai and Hartly[55] in the alkali halides. Experiments of this type would be particularly valuable at low temperatures where the mobility of the carriers diminishes.

5. The measurements of Burgers and Hiok[33] on the diffuse scattering pattern of silver chloride should be extended to very low temperatures to see if the effect diminishes in the manner to be expected if it is a result of lattice vibrations. There exists a small possibility that the bands are a result of permanent distortion. In any case, it would be valuable to have information on the breadth of the reflection spectra from specimens grown both from the melt and from solution[53] in order to see if there are substantial differences in the mosaic structure.

6. The experiments of Haynes and Shockley on the range of free electrons over a band of temperature should be extended to silver bromide for which the density of Frenkel defects is most accurately known, in order to see if there is a correlation between the range and the density of interstitial silver ions in well annealed specimens.

7. It would be valuable to have further experiments on the existence of hole conductivity under various means of excitation in order to see if the ambiguities which exist can be removed.

8. The photoconducting silver halides should provide good material on which to make Hall measurements at low temperatures, for the mobility should be of the order of several hundred. Such measurements would provide interesting values of the mobilities of electrons and possibly holes.

9. It would be valuable to know to what extent darkening can be produced at liquid-air and at liquid-hydrogen temperatures. Löhle's experiments indicate that prior irradiation at room temperature is necessary before darkening can take place at low temperatures. Can the same effect be obtained by irradiating at low temperatures, warming to room temperature in the dark for a period of time, and then cooling to low temperatures before continuing irradiation? Several variations of this procedure are possible and may give further insight into the mechanism of darkening.

10. Haynes and Shockley have found that the colloidal specks which appear in silver chloride have an upper limit in size in the neighborhood of 100A. It would be interesting to know if distinctly larger particles can be produced in the thallium halides, which permit prismatic slip.

11. Photoconductive experiments can be made on specimens which contain additions such as excess silver or halogen, divalent positive ions, or silver sulfide, in order to determine the influence of these agents upon the range of electrons (or holes) as well as upon darkening. Experiments with additions of divalent metals would be particularly valuable in view of West's observation that the photoconductivity of colloidal AgBr at room temperature is enhanced by the addition of lead and cadmium.

12. It would be important to know if sulfide ions diffuse more rapidly than or at the same rate as halide ions, particularly at temperatures in the neighborhood of 100°C or 200°C. Such information may furnish a clue concerning the extent to which halogen ion vacancies become associated with the sulfur ion as well as the ease with which coagulation of the sulfide occurs during quenching or annealing.

13. Similarly, it would be valuable to measure the density and lattice parameters of crystals containing the sulfide at room temperatures in order to obtain information concerning the aggregation of the sulfide and the association with halogen ion vacancies or interstitial silver ions. One would expect substantially different densities if the sulfide ions are accompanied by vacancies and if they are associated with interstitial ions.

14. Mitchell's hypothesis that the sulfide ion is present as S^- instead of as S^{--} could be tested by measuring the paramagnetic susceptibility of the quenched mixed salt in order to find evidence for paramagnetic S^-- and F-centers.

15. It is possible that the darkening process has a large effect on the plastic properties and tensile strength of the silver halides if the darkening products are formed in the vicinity of dislocations. It would be interesting to carry out a systematic investigation of the mechanical properties on specimens darkened in the colloidal range.

16. It would be valuable to study further the manner in which monochromatic light absorbed by the molecular silver aggregates produces local diminution of absorption. Is the width of the hole that is cut into the absorption band associated with molecular silver a function of temperature? It would also be interesting to study the range of the photoelectrons produced during such irradiation to see if it falls at low temperatures, as is the case for photoelectrons released from F-centers in the alkali halides. Moreover, does the range of the photoelectrons freed from the molecular aggregates depend upon the density of such aggregates?

17. There does not seem to be information available concerning the manner in which sulfur additions sensi-

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[54] See, for example, W. Lehfeldt, Z. Physik **85**, 717 (1933).

[55] Z. Gyulai and D. Hartly, Z. Physik **51**, 378 (1928).

tize the darkening of the silver halides at low temperature in the absence of prior irradiation at room temperature. Such measurements would be particularly valuable in view of Löhle's observation that such prior irradiation is very important at room temperature in pure halides.

18. It is a remarkable fact that there appear to be no absorption peaks in the colored alkali halides studied in detail to date which can be ascribed to *F*-centers near dislocations, analogous to the incipient *F*-centers which seem to be so important for the silver halides if the views expressed in this paper are correct. It is possible that the means normally employed to prepare colored specimens of the alkali halides preclude the observation of such bands. It is suggested that research on the alkali halides be extended to study specimens which have received moderate cold-work, without annealing, and which are darkened by ultraviolet light or x-rays to the level where they contain no more than 10^{15} color centers per cc. It is possible that effects analogous to those found in the silver halides will be observed.

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