X-Ray Coloration of Alkali Halides*

D. L. DEXTER
Institute of Optics, University of Rochester, Rochester, New York, and Metallurgy Division, U. S. Naval Research Laboratory, Washington, D. C.
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Processes of importance in the coloration of solids by x-radiation are discussed on the basis of Seitz's hypothesis that vacancies are created at jogs on dislocations or at other imperfections. The interaction between F centers and dislocations is calculated, and it is shown that F centers located within about 50A of edge-type dislocations would experience measurable broadening and perhaps shifting of their absorption peaks, in contradiction of experiment. From the available energy in the form of point thermal pulses, it is shown that most vacancies freed from jogs or other sources probably make less than a thousand atomic jumps during x-irradiation at He temperatures and hence are unable to diffuse more than about 100A from their sources.

The tunneling of F-center electrons to positive-hole centers is calculated, and it is concluded that tunneling can occur with high probability over a distance of ~30A by an electron in its ground state, ~40A in its first excited state. Such tunneling is important in limiting local F- and V-center concentrations even at He temperature in the dark. Crystals achieving macroscopic concentrations of the order 10^{18} cm^{-3}, it is concluded, must contain very high densities of vacancy sources to be consistent with the requirements of both the large tunneling range and the small diffusion distance.

I. INTRODUCTION

IN the past year or so a number of speculations have been made regarding the role of dislocations in the formation of F centers by x-irradiation at He temperatures.[1,2] The general argument is as follows: An x-ray is absorbed by the crystal, thus giving rise to a single fast photoelectron of, let us say, 50-kev kinetic energy. Such an electron has insufficient momentum to displace a lattice ion from its normal site and consequently gives up its energy in the production of phonons, excitons, and free electrons and positive holes. The electrons and holes may subsequently combine with whatever few free vacancies exist at this low temperature, and thus color centers are readily produced from the positive- and negative-ion vacancies already present in the crystal. The excitons also can aid in the production of the color centers,[3] but none of these light particles (electrons, holes, and excitons) has sufficient momentum to increase by direct interaction the number of vacancies in the crystal. Further, the probability is negligibly small that a sufficient number of phonons will meet in a small region to contribute enough energy to produce a vacancy-interstitial pair.

It is generally believed from the work of Dutton and Maurer,[4] Duerig and Markham,[5] and others that more color centers are being produced at He temperatures than can be explained on the basis of vacancies initially present. Thus Seitz[2] has proposed a mechanism for the enhancement of darkenability by the intermediary of jogs[6] on edge-type dislocations: the ionic character of the alkali halides gives rise to effective charges on the jogs, or on their associated incipient vacancies; Mott and Seitz independently demonstrated that the magnitude of the effective charge is $e/2$.[7] Hence, according to Seitz, the free electrons and holes are attracted to the incipient negative- and positive-ion vacancies, respectively, and are trapped in localized energy states with the production of heat. Until recently it was assumed that the increased density of phonons made possible the escape of the incipient F and V centers by diffusion.[8] This interpretation was not entirely satisfactory because of the known low jump frequencies for diffusion[9] and because it is not at all evident that the energy of the system would be lowered by the escape of the centers. Seitz[2] has suggested a modification of this picture, namely, that many of the incipient vacancies occur as nearby positive-negative pairs because of the Coulomb attraction. Thus when an electron is trapped by the incipient negative-ion vacancy, the incipient F center has an effective charge of $-e/2$ and repels the nearby incipient positive-ion vacancy. The latter's

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[1] J. J. Markham, Phys. Rev. **88**, 500 (1952).
[2] F. Seitz, Phys. Rev. **89**, 1290 (1953).
[3] D. L. Dexter and W. R. Heller, Phys. Rev. **84**, 377 (1951).
[4] D. Dutton and R. J. Maurer, Phys. Rev. **90**, 126 (1953).
[5] W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

[6] Let the dislocation line lie along the Z direction in a cubic crystal, and let ZX represent the slip plane so that the YZ plane is parallel to the "extra plane" of atoms. If for $z>0$ the dislocation line is given by $x=y=0$, and if for $z<0$ the dislocation line is $x=0$, $y=\pm a$, where a is a crystal unit length, we say that a jog exists on the dislocation line at $z=0$. That is, a jog occurs at the terminus of an extra half line of atoms added to the extra half plane. F. R. N. Nabarro [Conference on the Strength of Solids (The Physical Society, London, 1948), p. 75] was apparently the first to recognize that diffusion of atoms to this jog could take place relatively easily for geometrical reasons. F. Seitz [Phys. Rev. **80**, 239 (1950)] has extended this concept with particular emphasis on the vacancies left behind by such diffusion and has given the name "incipient vacancy" to the immediate vicinity of the jog.
[7] F. Seitz, Revs. Modern Phys. **23**, 341 (1951).
[8] D. L. Dexter, Science **115**, 199 (1952); see, also, reference 1.
[9] See F. Seitz, Revs. Modern Phys. **18**, 384 (1946), for a review of the data on diffusion of vacancies. See also G. J. Dienes, J. Chem. Phys. **16**, 620 (1948), with regard to diffusion of vacancy pairs.

diffusion is aided by the liberation of heat when the electron is trapped. When the incipient positive-ion vacancy is filled by a positive ion, the jog moves over one lattice distance, that is, there is created in an adjacent site an incipient negative-ion vacancy. Thus at this stage there would be an incipient negative-ion vacancy and an incipient F center. The latter would subsequently trap a positive hole, presumably, and the point thermal spike following recombination would allow the diffusion away of the incipient negative-ion vacancy. Thus there would finally be, as initially, a positive-negative pair of incipient ion vacancies and in addition a positive-negative pair of free vacancies (not necessarily associated). Similar arguments may apply for the trapping of holes, but probably the specific processes are somewhat different. (For example, it is probable that the incipient negative-ion vacancy does not diffuse away when a positive hole is trapped, unless the incipient vacancies are very close together, since the activation energy for diffusion of the relatively large negative-ion is large.) By this process, according to Seitz, vacancies of both signs, both clustered and isolated, will come to exist in high concentrations near the dislocations. Other electrons and holes will be attracted to these vacancies to form F and V centers. The relative strength of the α band to that of the F band in crystals x-rayed at low temperatures and the high bleachability of such crystals are explained by the unusual closeness of the F and V centers to each other, since both are close to the dislocations.

It seems an inescapable conclusion that if additional vacancies are created during x-irradiation, they must be generated near imperfections such as dislocations. Qualitatively, then, one would expect that if dislocations interact appreciably with F centers, such interaction should be most important in crystals having been colored by irradiation at low temperatures, where diffusion frequencies are extremely low. In crystals heavily cold-worked at room temperature the dislocation concentrations are expected to be large, and appreciable broadening of the F band is observed. The crystals are so distorted that it is not clear how the observations can be quantitatively related to "good" crystals, but at least the existence of an interaction between F centers and dislocations is strongly indicated.

The purpose of this note is to investigate more quantitatively some of the processes believed to be important in the coloration of the alkali halides, in particular, the influence of dislocations on the position and width of the F band, the processes important for the diffusion of the free vacancies, and the extent to which tunneling of F-center electrons can be expected to occur.

II. INTERACTION OF F CENTERS WITH DISLOCATIONS

The lattice surrounding an imperfection is of course in a state of strain, and intuitively it is clear that the energy of the F band must be dependent on this distortion. One of the most effective imperfections for modifying the optical behavior of an F center we would expect to be an edge-type dislocation, since there is associated with it a long range strain pattern. Vacancies, interstitials, impurity atoms, and screw-type dislocations would have much less effect, and we shall ignore them in most of the following.

Surrounding an isolated edge dislocation in a medium of Poisson ratio ν, the density variation at a point P is given by

$$\frac{\Delta\rho}{\rho_0}=\frac{\lambda}{2\pi}\frac{1-2\nu}{1-\nu}\frac{\sin\omega}{r}, \tag{1}$$

where λ is the unit crystallographic slip distance, r the length of the position vector of P measured perpendicularly from the dislocation line, and ω the angle between this vector and the slip plane.[10] This equation is derived on the assumption of an isotropic, homogeneous continuum and is not expected to be valid within a few angstroms of the dislocation axis; it should be fairly accurate for r larger than, say, 5A.

Since the energy E of the optical transition corresponding to the F band is a function of the local density, we may expand it in a Taylor series, and obtain

$$E(\mathbf{r})=E_0(1+\gamma\Delta\rho(\mathbf{r})/\rho_0+\cdots). \tag{2}$$

The dimensionless constant γ can be calculated on the basis of specific models for the F center, and it may also be directly obtained from experiments on the pressure dependence of the F-band energy.[11] Burstein *et al.* find values of 0.87 for KI, 1.14 for KCl, and 1.73 for NaCl. Thus, combining Eqs. (1) and (2), we obtain for the energy of the absorption peak of the F center, as a function of its position with respect to the nearest dislocation, the value

$$E(\mathbf{r})=E_0\left(1+\frac{\gamma\lambda}{2\pi}\frac{1-2\nu}{1-\nu}\frac{\sin\omega}{r}\right). \tag{3}$$

This equation would perhaps be somewhat modified if the dislocation line were not straight. Let $n(\mathbf{r})$ represent the number density of F centers at position $\mathbf{r}$ from the nearest dislocation. Then the absorption coefficient is given as a function of energy E' by the expression

$$\mu(E')=\tau^{-1}\int d\tau n(\mathbf{r})\sigma(E'-E[\mathbf{r}]). \tag{4}$$

In this expression σ, the absorption cross section of an

[10] J. S. Koehler, Phys. Rev. **60**, 397 (1941).

[11] Burstein, Oberly, and Davisson, Phys. Rev. **85**, 729 (1952). The foregoing abstract will be written up in detail in the near future. The writer is indebted to Mr. Burstein for access to his data before publication. See also I. S. Jacobs, Fifth Annual Report to U. S. Office of Naval Research on High Pressure Research, Institute for the Study of Metals, the University of Chicago, July, 1952 (unpublished).

F center for light of energy E' is written as a function only of the difference between E' and E, the energy of maximum absorption. That is, it is assumed here that there is no change in the shape of the absorption cross section of a single center but only in the position of its midpoint. As Markham has pointed out,[1] the presence of a dislocation will probably modify somewhat the spectrum of lattice vibrations with which the given F center interacts, but this effect is assumed small here; Burstein and Jacobs observed no change in width of the F band with changing pressure.[11]

Let us evaluate Eq. (3) numerically for the case of KCl. Here $E_0=2.29$ ev, $\gamma=1.14$, $\lambda=4.44$A,[12] and $\nu=\frac{1}{3}$. Then we obtain

$$E(\mathbf{r})=2.29 \text{ ev}+0.92(\sin\omega/r) \text{ ev}, \qquad (5)$$

where r is measured in angstrom units. Thus an F center located 5A from the dislocation may have its peak absorption shifted by as much as ± 0.2 ev, and F centers within about 50A would experience easily measurable shifts.

In a well-annealed crystal additively colored at high temperatures, where the dislocation concentrations are no higher than 10^{10} per cm^2, and where the F centers are expected to be randomly distributed throughout the crystal, the fractional number of F centers within 50A of a dislocation line would be less than one percent, and the smearing associated with the dislocations would not be detectable. On the other hand, if every F center were within 50A of a dislocation line,[13] as one might expect in crystals colored by x-irradiation at He temperatures, the F band would be markedly changed, either broadened, or broadened and shifted. It would appear that the strain energy would be lower if the incipient vacancy exchanged places with an ion on the compression side of the slip plane than if it jumped to the low-density side. Thus it appears that the shift in the F band should be toward higher energy, but perhaps one cannot be certain. The writer has been able to think of no arguments in favor of diffusion preferentially along the slip plane, where $\sin\omega$, and, hence, the energy shift, are zero.

Experimentally no marked effect is observed. The F band produced by x-irradiation at 5°K and measured at this same temperature has the same mid-point as that produced at high temperatures and measured after cooling to 5°K; and, further, the width of the F band is if anything the *lower* in the sample irradiated at He temperatures.[5] Thus we are forced to the conclusion that the F centers are not predominantly located within 50A of edge-type dislocations in good crystals.

Clearly this could be true for either of two reasons: (1) vacancies are not produced at edge-type dislocations in the first place, or (2) the vacancies are able to diffuse much more than 50A away. Seitz has made two interesting comments to the writer in connection with (1). First, he has emphasized that in well-annealed single crystals the long-range elastic fields about edge-type dislocations are reduced as a result of their orientation in the formation of mosaic boundaries. This would decrease the distance over which the F-center dislocation interaction would be detectable. Second, he has cited recent unpublished calculations by Jean Dickey Apker indicating that the energy associated with screw dislocations is lower than that for edge dislocations in NaCl, so that one would expect the former to predominate in good crystals. Now the F-center interaction with screw dislocations would not be detectable for separations greater than a few angstroms, but of course a screw dislocation is not a suitable, low-energy source of vacancies. General dislocations combining the required properties can be readily imagined: for example, a short segment of edge type connecting greater lengths of screw-type dislocation would suffice as a source of vacancies, and, if the segment were sufficiently short, the elastic field at large distances would be greatly reduced. Collapsed vacancy disks of small linear dimensions would also appear to serve as a vacancy source without long-range elastic distortions which could be detected by a modification of the F band. Anticipating the results of the following analysis of possibility (2), we may expect that an interpretation along these lines is in fact correct.

The second possibility mentioned above involves the diffusion of negative-ion vacancies (or F centers). With activation energies for diffusion, W, of at least several tenths of an electron volt (1.1 ev for a negative-ion vacancy, 0.8 ev for a positive-ion vacancy, and 0.4 ev for a pair in KCl [9]), the jump frequencies at 5°K are vanishingly small with the equilibrium number of phonons. Some idea of the magnitude may be obtained from the value $\nu=\nu_0\exp(-W/kT)\sim 10^{-394}$ sec^{-1} for vacancy pairs in KCl. Markham[1] and Seitz[2] have pointed out that when an electron is trapped at an incipient vacancy much of the trapping energy will be released as a point thermal spike, and it is this thermal energy $E\sim 1$ ev which aids in the initial escape of the incipient vacancy. This energy will of course diffuse away as a cloud of phonons, and one may then estimate the excess thermal energy per atom at a distance from the center of the cloud. If the ionic density is n_0, the number of ions within a distance L is $(4/3)\pi L^3 n_0$, so that the energy per ion at distance L is less than $E/(4/3\pi L^3 n_0)$. At a distance 25A in KCl the latter has

[12] The slip planes in the alkali halides are presumably (110) planes with (110) as the slip direction. See F. Seitz, reference 6, for a description of this configuration.

[13] One may ask if it is physically possible to pack all of the centers into such a small volume as is represented by cylinders of 100-A diameter around each dislocation. If dislocation concentrations of 10^{10} cm^{-2} are present under these circumstances, the fractional volume within 50A of the lines is about one percent, so that a macroscopic F-center density of 10^{18} cm^{-3}, as observed by (reference 5) Duerig and Markham, would require local concentrations of 10^{20} cm^{-3}. Such a distribution is not obviously impossible, since macroscopic concentrations of this magnitude have been observed. [R. Hilsch (private communication), and R. Kaiser, Z. Physik **132**, 482 (1952). See also reference 3 and the papers by Apker and Taft cited there.]

a value $\sim 5\times 10^{-4}$ ev which is approximately equal to kT at 6°K. Thus the probability is negligibly small that the initial thermal spike can induce diffusion of vacancies or pairs to this distance.

A mechanism of much greater importance for the diffusion is the local heating produced by recombination of excitons and of free electrons with holes: consider the energy poured into the crystal during x-irradiation. If the tube is operated at 50 kv and 20 ma, if 0.2 percent of this energy is converted into x-radiation, and if the crystal is 4 cm from the target, the energy absorbed in the crystal is equal to $\sim 10^{17}$ ev/cm^2 sec. Thus, in 15 minutes of x-ray time, if the energy is absorbed in 0.1 mm,[5] the energy absorbed per cm^3 is about 10^{22} ev/cm^3. Now most of this energy eventually goes into the production of excitons and of free electrons and holes. If of the order of 10 ev is required for each exciton and electron-hole pair produced, there are about 10^{21} point thermal spikes per cm^3 in the 15-minute irradiation, arising from the recombination of the excitons and pairs. If 10^{18} F centers per cm^3 are produced by this exposure, about 10^4 ev or 10^3 thermal pulses accompany the creation of each F center. The above figures approximate the data in reference 5. Very similar values have been obtained by Maurer[14a] from the data of reference 4, by Harten, and by Martienssen.[14b] It seems noteworthy that such close agreement should be obtained by different workers on different crystals and with different experimental arrangements, for, if our present views are correct, the efficiency of F-center production should be distinctly structure-sensitive. Several remarks should be made in this connection. (a) First, the recombination of excitons and electron-hole pairs must occur extremely preferentially near imperfections; if the thermal pulses were randomly distributed with respect to the vacancies, then, since the fractional concentration of vacancies is less than 10^{-4}, a recombination would occur on a nearest neighbor of a vacancy less than once on the average. In this event the average vacancy would not be able to diffuse more than one or two atomic distances, and the F band so produced would certainly differ from that produced by additive coloration. It is reasonable that this preferential recombination near imperfections should be observed since phenomena involving "recombination centers" are common in luminescence and semiconductor investigations. (b) Secondly, the constancy of the production rate of F centers should be noted. It is remarkable that for several orders of magnitude change in F-center concentration the production rate is essentially unchanged. This observation could easily be interpreted on a picture involving F-center production at random points in a perfect lattice but in the present theory probably arises from a balancing of two phenomena, namely, the increasing fraction of thermal pulses located next to a vacancy where they can contribute to diffusion and the increasing probability of bleaching by tunneling as the concentration increases. (c) Finally, if we assume that recombinations occur exclusively on atoms adjacent to vacancies, and further assume that the associated thermal spike is sufficient to allow one atomic jump with high probability, we may obtain an estimate for the diffusion length perpendicular to the dislocation line of about 80A. This estimate is almost certainly too large but yet leads to a prediction of a measurable change in the F band, if long segments of edge-type dislocations were the source.

We have tacitly assumed above that diffusion occurs by isolated vacancies, whereas if vacancies of both signs are produced at the same or closely adjacent sources, the vacancies probably associate and diffuse together for part of their journey. This does not change the qualitative picture, except perhaps to improve the assumption that a thermal pulse induces one atomic jump. Eventually the vacancies must dissociate in order to form F and V centers.

Seitz[1,9] has discussed the solvent action of electrons and holes on pairs and clusters of vacancies and suggests that[1] "When a coupled pair of vacancies captures an electron, the positive-ion vacancy is, with the aid of the accompanying thermal spike, expelled for several lattice spacings even at helium temperatures, as a result of the electrostatic repulsion of the electron and the positive-ion vacancy. Hence the F center formed is essentially normal." The writer agrees with this conclusion, but would like to suggest that as a result of charge-dipole interactions the positive-ion vacancy is actually attracted to the F center, so that the thermal spike must overcome binding forces which are important at He temperatures. We may estimate the strength of the binding by computing the second-order perturbation energy associated with the interaction

$$V(\mathbf{R})=-e^2/(\kappa R)+e^2/\kappa|\mathbf{r}+\mathbf{R}|, \tag{6}$$

where $\mathbf{R}$ is the position vector of the negative-ion vacancy measured from the positive-ion vacancy and $\mathbf{r}$ is the position vector of the F-center electron measured from the negative-ion vacancy. The first term on the right side of Eq. (6) is the interaction energy between the vacancies, and the second is that between the positive-ion vacancy and the electron. In this expression κ is the static dielectric constant, 4.68 for KCl. Taking R along the X axis and expanding, we obtain

$$\Delta E=\frac{-e^2}{2R^4\kappa^2}\left\{2e^2\sum_n \frac{|\langle n|x|0\rangle|^2}{E_n-E_0}\right\}, \tag{7}$$

in terms of the dipole matrix elements between the

[14a] R. J. Maurer, (private communication).

[14b] H. U. Harten, Z. Physik **126**, 619 (1949); Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. **2a**, 15 (1950). W. Martienssen, Z. Physik **131**, 488 (1952); W. Martienssen and R. W. Pohl, Z. Physik **133**, 153 (1952); W. Martienssen, Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl. **2a**, 111 (1952). See also F. Seitz (submitted for publication to Revs. Modern Phys.) for a review of this work.

ground and excited states of the F center. The quantity in curly brackets is the polarizability of the F center, α_F, approximately 22×10^{-24} cm^3 in KCl. If the F center at **R** were replaced by a normal negative ion, the interaction energy would be $-e^2/(2R^4\kappa^2)\alpha_I$, where α_I is the polarizability of the halide ion, approximately 3.5×10^{-24} cm^3 for KCl. Thus the net reduction in the energy as a result of the nearness of the positive-ion vacancy to the F center is given by

$$U=\frac{-e^2}{2R^4\kappa^2}(\alpha_F-\alpha_I), \tag{8}$$

which becomes numerically equal to

$$U=-78(a_0/R)^4 \text{ ev}, \tag{9}$$

where a_0 is the Bohr radius. For R equal to the separation between nearest neighbors in KCl, 5.9 a_0, U has the value $U\sim-0.06$ ev, and the binding energy is probably of this order of magnitude. In the absence of thermal spikes, a binding energy this large would be important at He temperatures although not at nitrogen temperatures or above. When an electron is captured by a pair of vacancies, however, the point thermal spike accompanying lattice relaxation will usually be sufficient to overcome the attractive charge-dipole forces and will allow the escape of the positive-ion vacancy from the first shell about the F center.

It seems likely then that under the influence of the initial thermal spike when the electron is captured the positive-ion vacancy may jump from the nearest to one of the second nearest unlike lattice sites. Further diffusion must await the recombination of additional excitons and electron-hole pairs in the vicinity of the positive-ion vacancy. If the positive-ion vacancy traps a positive hole before making about a hundred jumps, the two centers will be annihilated by tunneling, as discussed in the next section. Thus there is a mechanism operating to keep the F centers "normal," and also, of course, the same mechanism tends to keep the efficiency of coloration low.

III. TUNNELING OF F-CENTER ELECTRONS

In view of the short diffusion lengths of vacancies at low temperatures and of observations on the relative strength of the α band and on the bleachability of the F band at low temperatures, it is of considerable interest to investigate the tunneling of an electron from an F center to a V center. The electron is bound to a negative-ion vacancy with a potential energy $U=-e^2/\kappa_0 r$ at large distances, where κ_0 is close to the high-frequency dielectric constant of the crystal. At distance R, let us say, there exists a V_1 center, and associated with it is a positive hole on one of the surrounding halide ions. If the electron should reach one of these ions, it would experience a strong attractive potential and would probably recombine with the hole, since the recombination energy is much larger than the binding energy to the vacancy. Thus we shall make use of a potential for the electron in the ground state which is constant within the negative-ion vacancy, varies as $-e/\kappa_0 r$ at larger distances, and drops abruptly by several volts at a distance $R-a\sqrt{2}$ from the negative ion vacancy, where a is the atomic spacing. Thus the "transmission coefficient" is given by

$$\exp\left(-2\int_{r_n}^{R-a\sqrt{2}}\{(2m/\hbar^2)[U_n(r)-E_n]\}^{\frac{1}{2}}dr\right),$$

reduced by the fractional solid angle subtended by the V center. In this expression r_n is the distance at which the kinetic energy becomes negative and E_n is the energy of the electron in the nth excited state. Multiplying by the electronic frequency $|E_n|/2\pi\hbar$, we obtain the recombination frequency

$$\nu_n(R)=-\frac{E_n}{8\pi\hbar}\frac{a^2}{(R-a\sqrt{2})^2}$$
$$\times\exp\left(-2\int_{r_n}^{R-a\sqrt{2}}\{(2m/\hbar^2)[U_n(r)-E_n]\}^{\frac{1}{2}}dr\right). \tag{10}$$

The potential energy is written with the subscript n to indicate that a different (larger) dielectric constant is to be used in the potential when the electron is in an excited state. This is a result of the relaxation of the surrounding lattice when the negative-ion vacancy no longer contains a large fraction of an electron charge. Equation (10) can be evaluated in closed form, and we find

$$\nu_n(R)=\frac{-E_n a^2}{8\pi\hbar(R-a\sqrt{2})^2}$$
$$\times\exp-2\left\{\frac{R-a\sqrt{2}}{a_0}\left(\frac{-2a_0}{\kappa_n(R-a\sqrt{2})}\frac{-2a_0E_n}{e^2}\right)^{\frac{1}{2}}\right.$$
$$\frac{-2}{\kappa_n(-2E_na_0/e^2)^{\frac{1}{2}}}$$
$$\left.\times\tanh^{-1}\left[1+\frac{e^2}{\kappa_nE_n(R-a\sqrt{2})}\right]^{\frac{1}{2}}\right\}. \tag{11}$$

Equation (11) has been evaluated with the results shown in Fig. 1. In the numerical computation we have used the values $a=3.14$A for KCl, $E_0=-2.9$ ev, and $E_1=-0.3$ ev for the energies of the ground and (relaxed) first excited states, and the values $e/2.5$ and $e/4.0$ for the effective nuclear charges of the negative-ion vacancy in these states.

From Fig. 1 we see that tunneling can occur in an hour to a distance of about 30A when the electron is in its ground state. Thus we conclude that at microscopic concentrations greater than $10^{24}/(4/3\pi30^3)=9\times10^{18}$

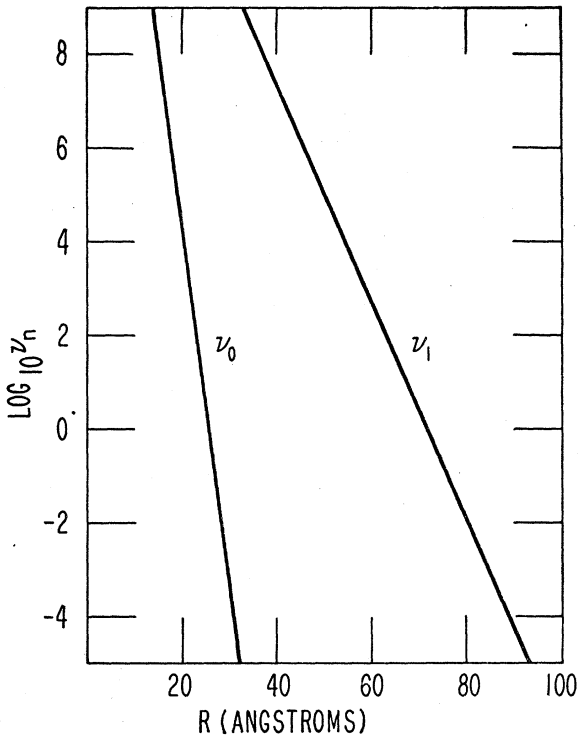

FIG. 1. Dependence of tunneling probability, in units of sec^{-1}, on the separation R between an F center and a hole-center in KCl. The two curves represent tunneling by an electron in the ground state (labeled ν_0) and in the first excited state (ν_1).

cm^{-3} many F and V centers would be destroyed by tunneling in the dark at low temperatures. Since macroscopic concentrations of the order of and greater than 10^{18} cm^{-3} have been observed,[5] it follows that the F and V centers must be distributed throughout much of the crystal. Because of the long tunneling range it is not difficult to understand why sizable α bands should be observed.

If we assume that screw dislocations can effectively act as vacancy sources through short segments of edge-type dislocation and take 80A as the diffusion length for the color centers, then, with local concentrations less than 10^{19} per cm^3, we require a dislocation density of 5×10^{10} line cm per cm^3. This corresponds to a degree of disorder to be expected in cold-worked crystals. If, on the other hand, we assume "point" vacancy sources, we obtain an upper limit for the diffusion length of about 100A and a maximum number of F centers per source of about 40. To explain observed macroscopic concentrations of 10^{18} per cm^3, then, we must imagine a source concentration greater than 2×10^{16} sources/cm^3. Such sources might be collapsed vacancy disks; and, computing the total periphery of these disks, we find an equivalent dislocation concentration of at least 8×10^{9} dislocation line cm/cm^3, a considerably higher value than we like to associate with good crystals. It should be emphasized that we are led to this unsatisfactory conclusion by the high efficiency of coloration, which makes the possible diffusion length small, and the large tunneling range, which prevents large interpenetrating concentrations of electron and hole centers. The combination of these two requirements argues for the existence of a high concentration of vacancy sources.

F-center concentrations in excess of 10^{19} cm^{-3} would perhaps not be inconsistent with the tunneling results if the hole centers should preferentially cluster either on an atomic or larger scale. The former is not observed as a growth of other V bands at the expense of V_1 bands at low temperatures, and there seems to be no direct evidence for the occurrence of the latter. However, it is likely that the F- and V_1-center distributions are not identical, but that the F centers are somewhat more dense and compact. This would be expected if the jump probability for negative-ion vacancies in the presence of a thermal pulse were less than unity. In this case the V_1 centers in the inner region occupied by F centers would be somewhat depleted, and qualitatively the distribution might be described as a spherical or cylindrical shell of V_1 centers surrounding a sphere or cylinder of F centers, depending on whether point or line sources are operative. A simple example suffices to show that the total number of color centers near each source may be considerably increased by such a configuration. Suppose that a region τ is uniformly occupied, instantaneously, by a concentration of 10^{20} per cm^3 of both F and V_1 centers. Subsequent tunneling will bleach both concentrations to about 10^{19} per cm^3 and leave 9×10^{19} α centers per cm^3. Now imagine that τ is occupied by 10^{20} per cm^3 of V_1 centers, and $\frac{1}{2}\tau$, contained within it, is filled by 2×10^{20} F centers per cm^3. After tunneling occurs, then, a volume $\tau/2$ will contain 10^{20} V_1 centers per cm^3, and the remaining region $\tau/2$ will contain 10^{20} F centers per cm^3 and 10^{20} α centers per cm^3.

A similar end result would be obtained if the recombination cross sections of positive- and negative-ion vacancies were different. It may be argued that positive ion vacancies easily trap positive holes because of their large effective mass and because of the relatively large interaction (between holes and the surroundings of a positive-ion vacancy) indicated by the extremely low thermal activation energy of V_1 centers. Thus the common recombination process may involve trapping of holes first, followed by annihilation of an electron and hole at the positive-ion vacancy. If this process occurs 80 percent of the time, the volume filled by V_1 centers will be 8 times as large as that filled by F centers, which will be characterized by a diffusion length $\lesssim$65A.

The tunneling range is appreciably larger when the F center is in an excited, bound state. However, it must be recalled that the electron is in an excited state for only a very short time so that this increased range becomes much less significant. One would expect an emission probability from an F center of about 10^{8} sec^{-1},

and since the luminescence efficiency is no more than a few percent,[15] the F center probably makes an internal, nonradiative transition in less than 10^{-9} sec. Thus the electron can probably tunnel a distance of about 35A while it remains in the excited state. If the intensity of the exciting light is such that an electron is raised to the first excited state about one hundred times per hour,[16] the average tunneling range is about 40A with a one-hour bleach. The figure 40A is to be compared with the comparable quantity 30A for an electron in the ground state. Thus one would expect appreciable bleaching of the F and V bands with F-band light at He temperatures for concentrations of the order 10^{18} cm^{-3}. Such bleaching has been observed by Markham and co-workers[16] and others. It is interesting to note in Fig. 11 of reference 16 that about half of the initial bleaching of KBr at nitrogen temperatures does not recover. This loss is presumably a result of the tunneling of F-center electrons to hole centers. Markham[16] has suggested that the recoverable part is associated with tunneling of F-center electrons to form F' centers. It should be remarked that the tunneling calculation above is independent of the specific process undergone by the electron after it passes the barrier, and hence one would expect probabilities for formation of F' centers by excited F centers comparable to those for annihilation of V centers at the same distance. Thus the fact that about half the bleaching is not recoverable might be an indication that the F-center and V-center distributions are locally about the same.

Note that the nonrecoverable diminution of the F band should be associated with a growth of the α band. Such a process should occur at He temperatures, where it could not easily be explained by thermal ionization of the F-center electron from its excited state. In the absence of data for KI on the temperature dependence of photoconductivity associated with the F band, it is not clear whether the tunneling mechanism is solely responsible for the growth of the α band observed by Pringsheim and co-workers at nitrogen temperatures.[17]

The statement is sometimes made that crystals x-rayed at higher temperatures bleach less easily than do those irradiated at low temperatures. It may be that this statement is correct only because the F-center concentration in the crystal colored at high temperature is lower than the concentration of centers in a crystal colored at low temperature. (The equilibrium concentration reached at high temperature where V centers are mobile might be depressed because diffusion by a few atomic spacings could result in annihilation by tunneling.) If the statement is true for crystals of the same macroscopic density, less than the final equilibrium value, it is likely that the coloration would be more uniform in the crystal irradiated at high temperature, and bleaching would be less probable. Another known effect is the absence of simple hole centers, i.e., V_1 centers, at high temperatures; if only two-hole centers were present, the effective concentration of hole traps would be reduced by almost a factor of two.

Dutton and Maurer[4] have measured the bursts of charge associated with thermal bleaching of the V_1 band in KCl and KBr and have correlated these currents with changes in the absorption due to F and V_1 centers. The characteristic temperatures are about -150°C. From the magnitude of the burst of charge and the number of V_1 centers destroyed, they conclude that the average distance of drift in the direction of the applied field is equal to 3×10^{-11} cm/(volt/cm) and 1×10^{-11} cm/(volt/cm) for KCl and KBr, respectively. These results are interpreted as indicative of thermal ionization of holes from the V_1 centers; from the temperatures of the current peaks the thermal ionization are estimated to be 0.26 ev and 0.23 ev for KCl and KBr.[4]

Maurer and Teegarden[18] have likewise investigated the photoconductivity in KCl and KBr upon irradiating in the V_1 band at -185°C and also the bleaching of the V_1 bands under these conditions. They find that the optical bleaching yield η_b is about 0.1 V_1 centers destroyed per photon absorbed, but that no appreciable photoconductivity is associated with the bleaching of the V_1 band. If η_h is the quantum yield for the ionization of V_1 centers to produce free holes and if w_h is the average range of the holes in the direction of a unit electric field, they find that $\eta_h w_h$ is probably less than about 10^{-14} cm/(volt/cm). If η_h should be as large as the bleaching yield, 0.1, the average range must be less than about 10^{-13} cm/(volt/cm). Such a hypothesis seems to be ruled out by: (1) the much larger range of holes, $10^{-11}-3\times10^{-11}$ cm/(volt/cm), thermally ionized at -150°C, and (2) the sizable photocurrents from holes optically ionized from V_2 and V_4 centers at -185°C.[18] Thus one is led to the conclusion that the quantum yield for the production of free holes is much less than the bleaching yield, and hence to the hypothesis that tunneling is responsible for the optical bleaching of the V_1 centers. The foregoing arguments have been presented by Maurer and Teegarden.[18]

We have not attempted a quantitative estimate of this tunneling range of holes because of too little knowledge of their energy levels. The personal opinion of the writer is that this range for holes in the ground state of V_1 centers would be less than for electrons in the ground state of F centers. Since nothing at all is known about the energy levels of excited V_1 centers, the difference in probabilities of tunneling of holes and electrons in excited states cannot be estimated even as

[15] C. C. Klick (to be published).

[16] This figure is obtained from the initial slope of the bleaching curve of Fig. 10, J. J. Markham, Preprint of Papers, J. Phys. Chem., Symposium of Impurity Phenomena, June 16–18, 1953 (unpublished).

[17] Delbecq, Pringsheim, and Yuster, J. Chem. Phys. **19**, 574 (1951).

[18] R. J. Maurer (private communication), and K. Teegarden, Report to National Science Foundation from the University of Illinois, August, 1953 (unpublished).

to sign. If the present interpretation based on tunneling should be correct for optical bleaching of V_1 centers, it would probably imply that the tunneling range of holes in excited states is larger than the tunneling range of electrons in the ground state, since, if not, the F and V centers would already have destroyed each other. The implication is not ironclad, however, since the thermal spike following absorption of a photon probably allows some diffusion of the center to positions of smaller separation from F centers.

A possible alternative to the interpretation of the thermal bleaching experiments of Dutton and Maurer,[4] namely, the thermal ionization of the V_1 centers, might be based on a tunneling process. For such a mechanism to be of significance, it would be necessary to assume that V_1 centers become mobile at about -150°C so that they diffuse to relatively small distances, say 25A, from F centers. At these separations tunneling by F-center electrons would occur with high probability, and, if an electric field were present, as in the experiments by Dutton and Maurer,[4] one would expect tunneling to occur preferentially opposite to the direction of the field, thus giving rise to a net current at the time of thermal bleaching. A current would also be expected in optical bleaching experiments for the same reason. If such a process should be responsible for thermal bleaching and the accompanying burst of charge, it would remove the current problem of the high ratio of the optical to the thermal ionization energy of V_1 centers. It is then of interest to examine the effect of an electric field upon the tunneling probability. In the presence of a field $\mathcal{E}$, another term, $-e\mathcal{E}\cdot\mathbf{r}$, must be added to the potential energy of the hole in Eq. (10). Since this term is small in comparison with the sum of the others over almost all of the range of interest, we may obtain the change in the tunneling probability in a simple way by expanding the square root and applying the mean value theorem. In this way we estimate the increased probability for tunneling in the direction of the field, which is larger by a factor of about

$$\{1+(2me^2/\hbar^2)^{\frac{1}{2}}\mathcal{E}R^2\langle(U_n-E_n)^{-\frac{1}{2}}\rangle_{\mathrm{Av}}\}$$

than the probability for tunneling in the opposite direction.

If the average energy difference U_n-E_n for holes in the excited states of V_1 centers is characterized by the value $\langle(U_n-E_n)^{-\frac{1}{2}}\rangle_{\mathrm{Av}}=(0.5\text{ ev})^{-\frac{1}{2}}$, then, for tunneling distances of the order of 30A, the above factor becomes $(1+6\times10^{-6}\mathcal{E})$, where $\mathcal{E}$ is expressed in volts/cm. Hence, the average net motion in the direction of the field is of the order 3×10^{-13} cm/(volt/cm). This is somewhat larger than the approximate upper limit fixed by Maurer and Teegarden[17] of 10^{-13} cm/ (volt/cm) in their optical bleaching experiments.

Tunneling almost certainly has nothing to do with thermal bleaching of V_1 centers even though it is probably responsible for optical bleaching. As we have just seen, the presence of an electric field gives rise to a preferred tunneling in the direction of the field such as to give the excited holes an average *schubweg* of about 3×10^{-13} cm/(volt/cm), about two orders of magnitude less than that observed by Dutton and Maurer[4] for KCl. In the thermal bleaching experiments where the electrons and holes are not in excited states, the average energy-difference term would be larger and the current would be still smaller. Hence, it does not seem possible to explain the thermal bursts of charge on the basis of tunneling, and thermal ionization of the V_1 centers appears essential to explain the observed currents, in agreement with the conclusions of Dutton and Maurer.

A further point that should be at least mentioned is the effect of thermal oscillation itself on tunneling probabilities, in the absence of diffusion. A quantitative account of the effect seems difficult, but qualitatively it is clear that thermal vibration of the lattice must instantaneously change the energy of the bound state of an electron or hole and thus would affect the tunneling probability. It is doubtful that such an effect would be important at -145°C.

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