

Photochemistry of the V_1 Center*†

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A series of photochemical experiments on the color centers present in KBr and KCl after exposure to x rays at 80°K is discussed. These experiments are chemical in nature with the reactions being triggered through exposure to radiation of various wavelengths. It is shown that the only V center which has a large electron capture cross section is the V_K center and the cross section of the V_1 center is very small. It is also shown that the destruction of the V_1 center does not involve the annihilation of an electron or hole trapped at a crystal imperfection but apparently involves the addition of an interstitial to the F center, yielding as a product the undisturbed lattice. The implications of these observations as they relate to the structure of the V_1 center are discussed.

I. INTRODUCTION

CASLER, Pringsheim, and Yuster¹ discovered the V_1 optical absorption band in crystals of KBr and KCl which had been exposed to x rays at 80°K. Since then, a considerable effort has been made to determine the structure of the imperfection which gives rise to this absorption, but it is as yet not known. The work to be described here attempts to narrow the range of the possible structures through experiments which are essentially chemical in nature. The type of experiment to be discussed does not enable one to determine the detailed electronic structure of a color center such as has been possible for a number of defects with paramagnetic resonance but only allows one to conclude that a defect is chemically equivalent to some type of interstitial, vacancy, or impurity.

II. SUMMARY OF THE PROPERTIES OF THE V_1 CENTER

Teegarden and Maurer² were unable to find any photocurrents definitely attributable to the excitation of the V_1 center, and the quantum efficiencies for the destruction of V_1 centers by radiation absorbed in the spectral region of the V_1 band were observed to be rather small. The values for the bleaching efficiency were typically 0.05 center destroyed for each quantum absorbed at the initiation of the bleaching, but the efficiencies quickly fell to values near 0.01. Data to be presented here indicate that these values are not the correct ones but instead represent the influence of absorption bands which overlap that of the V_1 center.

Teegarden and Maurer also found that the V_1 center was converted into another center, the H center, when crystals which contained V_1 centers were irradiated with light absorbed by the V_1 band at temperatures at which

the H center is stable. The H center gives rise to an optical absorption band similar in shape to the V_1 band but one which maximizes at slightly higher energies.

Känzig and Woodruff³ have found a center through paramagnetic resonance whose concentration changes in response to optical irradiation and temperature variations in a manner similar to the concentration changes of the H center as evidenced by the variation in the size of its optical absorption band. The center found by Känzig and Woodruff can be described as a negative halogen molecule ion occupying the site of a single halogen ion. The axis of the molecule ion lies in one of the six $\langle 110 \rangle$ directions. It is very unlikely that the identification of the center of Känzig and Woodruff with the H center (as defined by the H optical absorption band) is incorrect.

The experiments of Teegarden and Maurer and those of Känzig and Woodruff together imply that the V_1 center converts into a type of interstitial defect when it is excited with 3- or 3.5-ev photons provided that the temperature is low enough to insure the stability of the H center. This result might suggest that the V_1 center is itself an interstitial of some kind.

Lambe and West⁴ investigated the symmetry properties of the V_1 center at 80°K by attempting to introduce dichroism in the V_1 absorption band. The method used involves bleaching the absorption band with polarized light and then measuring the absorption with polarized light. Lambe and West found, however, that the V_1 absorption could not be made dichroic and they thus concluded that the center has cubic symmetry. This conclusion may be invalid, however, since it has been found recently that some color centers reorient their axes even at liquid hydrogen temperatures under the influence of lattice vibrations.⁵

III. PROPERTIES OF THE OTHER CENTERS PRESENT WITH THE V_1

The other color centers formed with the V_1 center by exposing KCl or KBr to x rays at 80°K are the F ,

³ W. Känzig and T. O. Woodruff, *J. Phys. Chem. Solids* **9**, 70 (1958).

⁴ J. Lambe and E. J. West, *Phys. Rev.* **108**, 634 (1957).

⁵ W. Känzig (private communication).

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¹ R. Casler, P. Pringsheim, and P. H. Yuster, *J. Chem. Phys.* **18**, 887, 1564 (1950).

² K. Teegarden and R. Maurer, *Z. Physik* **138**, 284 (1954).

F' , α , V_2 , V_3 , V_4 , and V_7 . The structure of the F center is known to be an electron trapped at a halogen ion vacancy, primarily from paramagnetic resonance experiments. The structures of the F' and α centers have been inferred from photochemical experiments involving the F center, and there is very little doubt that these models are correct. The F' and α centers can be obtained from the F center by adding or subtracting electrons from an F center, respectively. Thus, the F' center consists of two electrons trapped at a halogen vacancy, and the α center is the halogen vacancy with no trapped charge carriers.

The V_K center is known from paramagnetic resonance to consist of a hole trapped by the lattice polarization set up by its own field.⁶ The electron deficiency is shared by two halogen ions forming a negative halogen molecule ion which occupies two halogen sites. This center has been called the self-trapped hole and the V center as well as the V_K center, but for brevity and avoidance of ambiguity the last notation will usually be used here. The optical absorption of the V_K center has been established through combined optical and paramagnetic resonance experiments.⁷

The structures of the remaining centers present in the crystal after exposure to x rays at 80°K are not known, but it will be seen that this does not seriously restrict the conclusions which can be drawn from the photochemical reactions which were studied.

IV. OBJECT OF THESE EXPERIMENTS

The experiments to be discussed here were designed to test the conclusion given above that the V_1 center involves an interstitial of some kind and to determine its charge. In these experiments, the V_1 center is destroyed through optical excitation, and the changes in the concentrations of the other types of color centers are observed. If these other changes involve only those centers whose structures are known, then, in principle, one can deduce the chemical structure of the V_1 center. This technique will obviously fail if any of the centers involved in the destruction of the V_1 do not produce absorption bands in the investigated regions of the spectrum.

V. EXPERIMENTAL APPARATUS AND PROCEDURE

In most of the experiments to be described here, the crystals were exposed to x rays at temperatures near the boiling point of liquid nitrogen. The cryostat used was similar to that described by Dutton and Maurer⁸ except that it had only one vessel. The crystal was mounted in the vacuum space and adhered to a copper block with high vacuum grease. The copper block was in good thermal contact with the liquid nitrogen

reservoir and the temperature was measured with a copper-constantan thermocouple cemented into the crystal. The pressure in the cryostat was maintained below 10^{-4} mm of Hg. The x-ray machine was a 50-kv, 20-ma industrial unit with a tungsten target, always operated at its maximum output, and the sample was placed about $1\frac{1}{2}$ in. from the exit window of the tube in nearly all of the experiments. No filtering other than two 50-mil beryllium windows was used.

Three spectrophotometers were used for the optical absorption measurements performed here. The majority of the data were taken with a Beckman model DU quartz spectrophotometer. The useful range of this instrument is from about 1 micron to 0.22 micron. The remaining data were taken with a Cary model 14R automatic recording spectrophotometer whose range for color-center research is from 1.8 to 0.185 microns.

A near infrared spectrophotometer was assembled from a Leiss double monochromator with LiF prisms, a global source, and a radiation thermocouple detector. The useful range of this instrument extended to about 5 microns. No color-center absorption at wavelengths longer than those of the F' absorption was found.

VI. RESULTS AND DISCUSSION

1. Centers Formed by X Rays at 80°K

The centers formed in KBr when it is exposed to x rays at 80°K are F , F' , α , V_K , V_1 , V_4 , and V_7 . Some of the studies were on KCl, but the effort was concentrated on KBr. The primary reason for this is that the α band could be studied in KBr but not in KCl with the equipment available. The centers formed in KCl at 80°K are F , F' , V_K , V_1 , and V_2 . Unless specified otherwise, the following results pertain to KBr.

2. Influence of Light with Wavelengths Corresponding to the V_1 Band

One of the principal difficulties of color-center research is that it is usually impossible to excite only one type of center at a time. As a consequence, the measured absorption spectra and the transformations which are observed to occur under the stimulation of monochromatic radiation are easily misinterpreted. When one irradiates a crystal of KBr or KCl with radiation which is absorbed in the peak of the V_1 band, not only the V_1 center is excited but also the V_K , the F' , and the F centers are excited. The excitation of F -center photo-currents by radiation lying at wavelengths shorter than the F band proper has been studied by Inchauspé⁹ and Robe.¹⁰ The quantum efficiency for the photoconductivity was found to be of the order of 0.01 electron freed per quantum incident on the crystal. This is comparable to the efficiencies reported by Teegarden and Maurer for the bleaching of the V_1 center.

Studies of the photoconductivity resulting from the

⁶ T. G. Castner and W. Känzig, *J. Phys. Chem. Solids* **3**, 178 (1957).

⁷ C. J. Delbecq, B. Smaller, and P. H. Yuster, *Phys. Rev.* **111**, 1235 (1958).

⁸ D. Dutton and R. J. Maurer, *Phys. Rev.* **90**, 126 (1953).

⁹ N. Inchauspé, *Phys. Rev.* **106**, 898 (1957).

¹⁰ J. K. Robe, thesis, University of Illinois, 1960 (unpublished).

excitation of the V_K center indicate that the distance the holes drift while in the untrapped state is very small.¹¹ As a consequence, it can probably be safely assumed that the excitation of the V_K center can be ignored in considering the consequences of exposure to radiation of the V_1 wavelength.

The efficiency for removing an electron from an F' center is 1 at all temperatures, but most of the curves found in the literature do not indicate quantitatively the amount of absorption the F' center has in the ultraviolet.

To determine the shape of the F' band, the F band of an additively colored crystal was partially bleached through optical excitation at the temperature at which the maximum number of F' centers could be formed, and the crystal was then quenched to liquid nitrogen temperature. The change in absorption produced by this process was measured, and by assuming that the F' band is smooth, the absorption in the vicinity of the F band was interpolated. The shapes of the F' , F , and K bands in KCl, obtained in this way, are shown in Figs. 1 and 2. Figure 1 shows that in KCl the F' band absorption at the V_1 wavelength is $\frac{1}{3}$ of that at the peak of the F' band. Since the optical density at the F' band maximum is typically about 0.050, that at the V_1 band is about 0.006.

3. Influence of Light with Wavelengths Corresponding to the F Band

If one cools a crystal of KCl or KBr containing only F centers to 80°K and then irradiates in the F -band

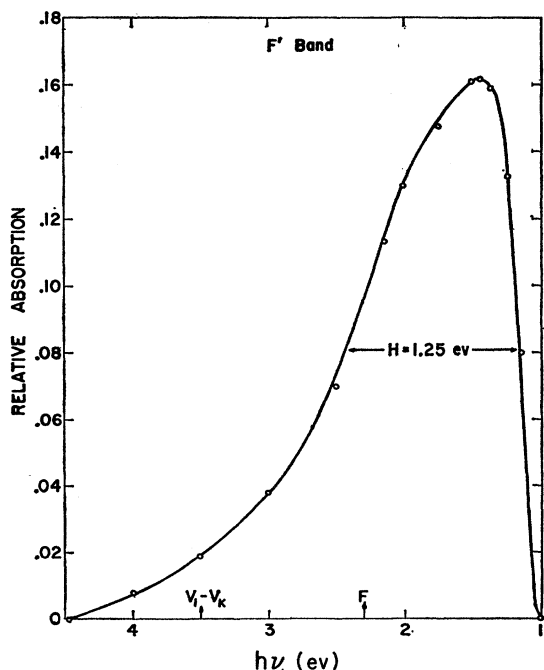


FIG. 1. The F' band in KCl at 80°K.

¹¹ C. J. Delbecq (private communication).

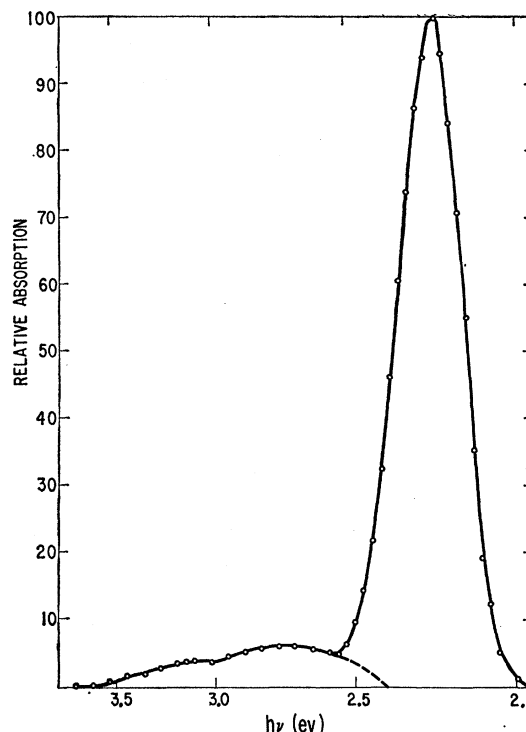


FIG. 2. The F and K bands in KCl at 80°K.

peak, the number of F' centers produced is very small, because the quantum efficiency for freeing electrons from F centers is very small, about 0.01, while that for freeing F' electrons is unity. In the steady state under F -band irradiation, one will destroy F' centers at the same rate as they are formed. Since the ease of freeing an electron from an F' center is much greater than from an F center, and since the electron capture cross section of the α center is relatively large at 80°K, the steady-state number of F' centers becomes rather small, perhaps 2% of the number of F centers.

These arguments do not pertain to the influence of radiation other than optical radiation absorbed in the F band, of course. In particular, the steady-state concentration of F' centers under x irradiation at 80°K is fairly large, a typical concentration of F' centers being $\frac{1}{5}$ the F concentration. If one exposes at 80°K a freshly x-irradiated crystal to radiation absorbed in the peak of the F band, it is found that the F band increases rather than decreases in intensity. Even though most of the light is absorbed by F centers, the smaller fraction of radiation absorbed by F' centers causes a greater number of transformations per quantum absorbed. The important point here is that if one wishes to study the influence of F irradiation independently of F' irradiation, this can be accomplished only by first removing the F' centers. This places a constraint on the operations which can be performed on the centers in the crystal.

4. Trapping of F' Photoelectrons

If one bleaches the F' band immediately after exposing KCl or KBr to x rays and measures the change in absorption, it is found that as the F' band disappears, the F band grows in size. Quantitative measurements of these changes indicated that the number of F centers formed is approximately equal to the number of F' centers destroyed. If the F' band in an additively colored crystal were bleached, twice as many F centers would be formed as F' centers were destroyed. One F center is left behind when one of the two F' electrons is removed from the vacancy and a second F center is formed when this electron is trapped at a halogen vacancy (α center). It would seem that in the case of an x-ray colored crystal, the electron which is removed from the F' center does not usually reach an α center before it is trapped elsewhere. In KBr, a measurement of the change in the α band caused by bleaching the F' band indicated that about $\frac{1}{10}$ of the released electrons are trapped in halogen vacancies.

The trap for the majority of the F' electrons was found by carefully subtracting the absorption found after bleaching F' from that found before (Fig. 3). It is seen that the V_K band is bleached by the electrons released from the F' centers.¹² Both the α and V_K have a charge of $+1$, but these results indicate that the electron capture cross section of the V_K is about 10 times as large as that of the α .

Only changes of the F' , F , α , and V_K bands have been found to result from F' bleaching. Assuming that there are no others, we can calculate the number of self-trapped holes destroyed in this process (this is 0.9 of the number of F' centers destroyed or 0.8 of the number of F centers formed). From the change in the V_K absorption, we can compute the oscillator strength of the V_K absorption band. The apparent oscillator strength is between 0.25 and 0.35. Since the V_K center absorbs only the component of the radiation which is polarized along one of the $\langle 110 \rangle$ directions, we must apply a correction factor to obtain the true oscillator strength. This factor is 3, so that the true oscillator strength of the V_K absorption is within 25% of unity.

5. Trapping of F Photoelectrons

If one irradiates in the F absorption band at 80°K after having first removed the F' centers, about 10% of the F band bleaches relatively quickly; but then the bleaching rate changes abruptly and becomes much smaller. The decrease occurring in the rapid bleach is about $\frac{1}{2}$ of the increase which had resulted from the bleaching of the F' band. The only other appreciable absorption change which occurs in the F bleaching is

a further destruction of V_K centers. The ratio of the number of V_K centers destroyed by F' bleaching to the number destroyed by the subsequent F bleaching is about 2 to 1.

The explanation for the observed behavior is probably as follows: Initially the number of F' centers is about $\frac{2}{3}$ the number of V_K centers. Bleaching F' releases enough electrons to annihilate about $\frac{2}{3}$ of the self-trapped holes. Subsequent irradiation in the F band releases more electrons which initially are trapped by V_K centers, but eventually the V_K centers are exhausted. A relatively small number of F' centers are then formed (because of the small quantum efficiency for bleaching an F center), but then no trap with an electron capture cross section of significant size is left except the α center. Removing an electron from one F center and trapping it at an α center does not change the crystal's color-center composition so that the optical absorption spectrum is unchanged. We can infer from this that the electron cross sections of the V_1 , V_4 , V_7 , and V_2 centers are very much smaller than that of the V_K . Prolonged bleaching in the F band (several hundred times as long as that required to destroy the V_K band) will show a measurable decay in the V_1 band, however. It was estimated that about 1 electron in 1000 is effective in destroying a V_1 center. No data were taken on the capture cross sections at temperatures higher than 80°K.

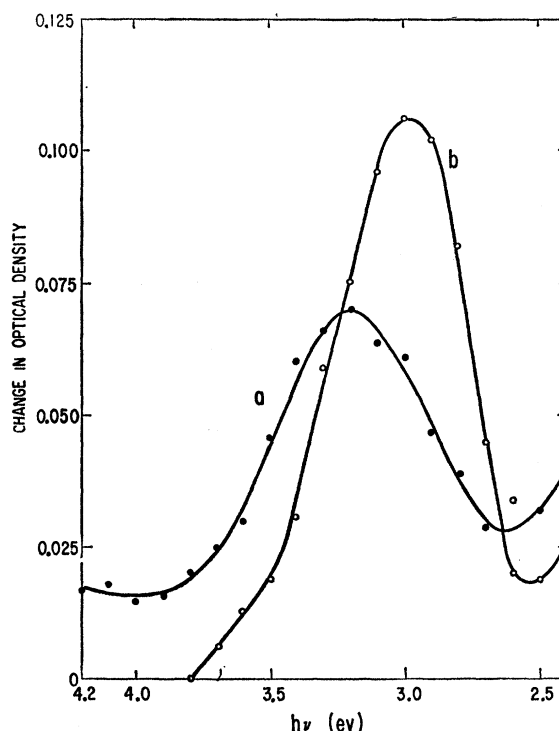


FIG. 3. (a) The change in optical density caused by optically bleaching the F' band. (b) The V_1 absorption alone (for comparison).

¹² The author wishes to thank C. J. Delbecq and P. H. Yuster for identifying the V_K absorption in KBr.

6. Quantum Efficiency for the Optical Destruction of the V_1 Band

It has already been mentioned that Teegarden and Maurer found initial quantum efficiencies of about 0.05 for bleaching the V_1 center, but these quickly fell to about 0.01 and remained roughly constant. They were probably observing the ultraviolet excitation of F' centers and the destruction of the V_K centers (whose existence was not known at the time) caused by the electrons released from the F' centers. The quantum efficiency for this last process is one, which is 20 times the initial value observed by Teegarden and Maurer. Typical optical densities at the maxima of the V_1+V_K band and the F' band are 0.12 and 0.05, respectively. It has already been remarked that the F' absorption in the V_1+V_K region is about $\frac{1}{8}$ of the maximum or 0.006 in the typical case. Since Teegarden and Maurer assumed the V_1 absorption (24%) instead of the F' (1.4%), they found a value 24/1.4 or 17 times smaller than the correct value. That is, they got about 0.06 instead of 1. As the number of F' centers decreased to zero, the absorption in the F' band fell to zero; but the absorption being used in the quantum efficiency calculation (that of the V_1 band) decreased only 20 or 30% (the contribution of the V_K band to the composite absorption of the V_1 and V_K centers). As a consequence, the apparent quantum efficiency decreased to a smaller value. The final value of 0.01 found by Teegarden and Maurer may be true value for the V_1 bleaching efficiency. There is still the possibility, however, that some of this bleaching was that of the V_K centers caused by the ultraviolet excitation of F centers. The incident quantum efficiencies for exciting F -center photocurrents in the ultraviolet are also of the order of 0.01.

The preceding results suggest that the optical bleaching of V_1 centers requires a rather intense light source if the destruction is to be accomplished in a reasonably short period of time. In particular, the radiation flux typically obtained from a monochromator is too weak to achieve the complete destruction except after very long irradiations. For this reason, some experiments were performed using the "white" light of an unfiltered tungsten lamp and some in which Corning glass color filters were used to restrict the radiation to comparatively broad bands.

7. Optical Bleaching of Color Centers at 80°K and Their Regeneration by X Rays

It was found that the "infrared number two" tungsten lamp in the Cary spectrophotometer could destroy all of the F' , V_K , and V_1 bands and the majority of the F and V_4 bands in a relatively short time (a few minutes). The α band grew under white light, presumably as a consequence of the bleaching of F centers. A brief second x irradiation of 2 minutes following this bleaching brought the F , F' , V_K , and V_4 bands back to

concentrations comparable to the original values which had required 10 minutes of exposure to x rays for their initial production. The F and V_4 bands probably grew more quickly after the white-light bleach than on the original x irradiation because the defects necessary for their production were still present after the bleaching. Thus, in the case of the F center, the bleaching light removed electrons from the halogen vacancies. These electrons destroyed the V_1 , V_4 , and V_K centers even though these processes are fairly inefficient. The halogen vacancies were not destroyed, however. The second exposure to x rays then produced electron hole pairs, the electrons were trapped at the halogen vacancies already present, and the F band quickly grew. The second x-ray exposure was contrasted from the first in that the x rays had to produce the vacancies in the first x raying. Since the vacancy production mechanism is almost certainly relatively inefficient, it probably limits the initial coloration rate.

The V_K band could grow more rapidly on the second exposure because the halogen vacancies which were present acted as effective electron traps, removed the electrons from the conduction band, and the holes thus left behind could become self-trapped without being subsequently annihilated by electrons. The fact that the V_4 band grew more rapidly on the second exposure to x rays suggests that the V_4 center is a hole which is trapped at a defect which is not destroyed through white-light bleaching. During the second period of irradiation with x rays, the defects retrap holes and V_4 centers are rapidly regenerated.

In contrast to the F , F' , V_K , and V_4 centers, the V_1 center was not formed any more rapidly on the second exposure than on the first. The reason for this is probably that the lattice imperfection which constitutes the core of the V_1 center is destroyed by the white light bleach. This suggests that the bleaching mechanism for the V_1 center is fundamentally different from that of the other centers. It is felt that this difference is probably a consequence of the V_1 center involving an interstitial type of defect. The bleaching process then effectively removed the interstitial from the lattice or at least placed it in a new position from which it could not easily re-form a V_1 center.

In order that less gross changes would result, the radiation from the tungsten lamp was filtered (glass filter C.S. 5-58) so that the radiation was strongly absorbed by only the V_1 center. To isolate the changes due to the V_1 bleaching from the other effects, all of the F' and V_K centers were removed in the manner previously described before irradiating in the V_1 band. Bleaching V_1 in this way destroyed a part of the F band but left the number of α centers essentially unchanged. Also, no other significant changes in absorption appeared.

If this V_1 bleaching process involved the removal of a hole from the V_1 center and the trapping of this hole at an F center (to account for the decrease in the F

band), then the number of empty halogen vacancies (α centers) would increase. If the bleaching occurred through the ultraviolet excitation of the F centers and the destruction of the V_1 centers by the electrons released from the F centers, then the α band would also grow. The lack of α -band growth in this experiment suggests the same conclusion as drawn in the preceding experiment: The destruction of V_1 centers involves the annihilation of point defects. In particular, the V_1 bleaching experiment seems to imply that V_1 and F centers are mutually annihilated.

8. Model for the V_1 Center

If we accept the conclusion that only V_1 and F centers are involved and nothing else is formed or destroyed, then a great deal is learned about the nature of the V_1 center. The apparent effect is that a V_1 center can, in some unknown way, be "added" to an F center so that the perfect lattice is restored. This would imply that the V_1 center is some form of the "complement" of the F center, the complement being defined as that ion, vacancy, electron, or combination of these which must be added to a center to produce an undisturbed lattice. The F center is an electron trapped in a halogen ion vacancy and, therefore, it is chemically equivalent to the absence of one neutral halogen atom. Thus, its complement is an interstitial halogen atom. The V_1 center is known to be distinct from the H center so the V_1 interstitial would have to be arranged in the lattice in a way different from the H -center interstitial.

This argument would break down if the product of the V_1 and F bleaching were not a perfect lattice but instead centers which have no observable absorption bands.

If the V_1 center were chemically equivalent to a positive interstitial halogen ion as proposed by Känzig and Woodruff,³ then the "addition" of V_1 and F centers would produce holes which would probably either form V_K centers or be trapped at other F centers, destroying them. Thus, in the latter possibility, two F centers would be destroyed and one α formed for each disappearing V_1 . The lack of growth of either the V_K or α bands tends to refute this hypothesis. If the V_1 involved a negative interstitial halogen ion, then an electron would be left over when the V_1 and F mutually annihilated each other. This electron would almost certainly be trapped by an α center resulting in a decrease in the α band, and the regeneration of the F center, which is not observed.

The H center may be considered to be a negative halogen molecule ion squeezed in between two other halogen ions in a halogen vacancy with the internuclear axis of the molecule ion lying along one of the six $\langle 110 \rangle$ directions. The V_1 center may consist of a halogen molecule ion placed in a halogen vacancy so that its symmetry axis lies along one of the four $\langle 111 \rangle$ axes. Simple geometric considerations indicate that there is

actually more room for the molecule ion in this position than in the H -center configuration, and it is conceivable that the V_1 molecule ion is free to move from one $\langle 111 \rangle$ orientation to another under thermal activation. This would explain the lack of dichroism in the V_1 absorption at 80°K. To explain the conversion under optical excitation from the V_1 center to the H center at low temperatures and the spontaneous conversion of the H center to the V_1 center at higher temperatures, we would have to conclude that the H -center configuration represents the lower electronic energy state (possibly because the hole is tightly bound to the inner pair of halogen ions and weakly bound to an additional pair of ions at either end of the inner pair), but it is unstable under the influence of lattice vibrations and gives way to the V_1 modification at higher temperatures. If the H center is the lower electronic state, however, one would expect the V_1 center to spontaneously convert into the H -center modification when the crystal temperature is lowered, and this has not been observed to occur.

The most serious objection to this model for the V_1 center is that despite an extensive search no paramagnetic resonance for the V_1 has been found and this model should be paramagnetic.

VII. SUMMARY

The salient points of the results presented here are the following:

1. Optically bleaching the F' band forms a number of F centers which is approximately equal to the number of F' centers destroyed. About 90% of the electrons released from the F' centers annihilate about $\frac{2}{3}$ of the self-trapped holes which are present and the other 10% are trapped at halogen vacancies to form F centers.
2. If one irradiates the crystal subsequent to bleaching F' with radiation which is absorbed in the F band, the remaining $\frac{1}{3}$ of the V_K band is destroyed by the electrons released from the F centers. In this way, a fraction (about 10%) of the F band is quickly destroyed; but when the V_K centers are exhausted, the bleaching rate of the F band becomes much smaller. About one electron in 1000 released from the F centers destroys a V_1 center.
3. The bleaching efficiencies previously reported for the V_1 band are probably incorrect and the true value is 0.01 or less.
4. The radiation from an incandescent lamp destroys all of the F' , V_K , and V_1 centers and most of the F and V_4 centers in a few minutes. A second exposure to x rays following this bleaching produces F , V_K , F' , and V_4 centers more rapidly than the initial exposure. In contrast to this, the growth rate of the V_1 band is not greater.
5. When the V_1 centers are excited with an intense light source, they are destroyed along with a fraction of the F centers but the size of the α band remains essentially unchanged.

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Abrupt-Kink Model of Dislocation Motion

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A new model of dislocation motion is presented. The behavior of a dislocation in the presence of an applied stress is described in terms of a redistribution of kinks along its length. In contrast with previous models, in which a kink is envisaged as a smooth step extending over many lattice constants, we suppose a kink to be abrupt. Consequently, kink diffusion is considered to be a thermally activated process. Transport equations are formulated which include the effects of generation, diffusion, and collision of kinks. General results obtained from these equations show that a dislocation does not behave like an extensible string in this model. Particular application to small harmonically-time-dependent stresses leads naturally to a new theory of the Bordoni anelastic peak. The characteristic relaxation time depends on line length as well as the attempt frequency and activation energy for

diffusion. As a result the decrease in the peak height and slight lowering of the peak temperature upon alloying or neutron irradiation are explained. Assuming an exponential distribution of line lengths, the results of the theory are used to evaluate the merit of different published values of the activation energy. Calculated attenuation peaks for different frequencies are shown to account for the experimentally observed large half-widths in pure cold-worked metals. The absence of a peak in well-annealed metals is explained if dislocations are then arranged parallel to the close-packed directions, thereby eliminating the kink density. The process by which cold-working annealed materials can give rise to kinks is discussed. Experiments are suggested which might further test the theory.

I. INTRODUCTION

IN this paper a new theory of dislocation motion is developed. The response of a dislocation to an applied stress is expressed in terms of a redistribution of kinks along its length. We consider here only dislocation loops which are firmly pinned. This first application of the model is shown to yield a new theory of the Bordoni anelastic peak, and provides a natural explanation of the shape of the peak and its behavior, both in magnitude and temperature, upon alloying, neutron irradiation, cold work, and annealing.

Although, in a general sense, some of the ideas contained within the model are not original with us, in detail we differ substantially from previous authors upon certain basic points. Accordingly in Sec. II we shall give an outline of the concepts which are later developed, expressed particularly from our point of view. In Sec. III we then formulate the mathematical problem and consider some of the general consequences of our treatment. Section IV is devoted to a study of internal friction and to a detailed discussion of the experimental properties of the Bordoni peak in terms of the theory we derive. Finally Sec. V contains a brief recapitulation of this research.

II. DESCRIPTION OF THE MODEL

The model is based upon the hypothesis that an isolated dislocation in a given slip plane would preferentially be oriented along a single close-packed crystal

direction. In real crystals, containing many dislocations, few can be expected to obtain this most favorable configuration. Because of their mutual interactions within the network and with other lattice imperfections, almost of necessity there will be many lying at some average inclination relative to a particular close-packed direction. We assume that at 0°K a possible steady state of a dislocation of this type is one in which, microscopically, equal segments are arranged parallel to the close-packed direction, each displaced laterally from its preceding neighbor by the same unit lattice vector, so that the average line direction is preserved.¹ This arrangement is illustrated schematically in Fig. 1. It is of course only one of many possible decompositions based upon our original premise and indeed we believe that others can also be important (see Sec. IV-3).

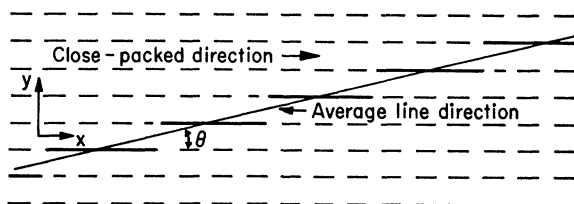


FIG. 1. A schematic illustration of the composition of a dislocation containing kinks. The dislocation segments are represented by the heavy lines.

¹ W. Shockley (private communication), quoted by W. T. Read, Jr., *Dislocations in Crystals* (McGraw-Hill Book Company, Inc., New York, 1953), p. 46.