Proposed Mechanism for the Conversion of *U*-Centers to *F*-Centers below 90°K*

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Experiments with KCl-KH single crystals suggest the following mechanism for the production of *F*-centers from *U*-centers at temperatures below 90°K. The thermal spike, produced after excitation of a *U*-center, is sufficiently energetic to eject the hydride ion into an interstitial position. Excitation of an interstitial hydride ion (U_1-center) may result in the transfer of the excited electron via a tunneling process to a negative-ion vacancy (α-center) forming an *F*-center and an interstitial hydrogen atom. Excitation of an *F*-center may reverse the latter process, also via a tunneling process. The tunneling probabilities for these processes vary with the tunneling distance, and experimental results indicate the existence of four distance intervals, about an α center, each interval being characterized by the tunneling processes which can occur.

THE preceding paper[1] presented data which established the nature of the U_1- and U_2-centers observed in irradiated KCl-KH crystals. The present paper will use these same data in making speculations concerning the mechanism for the conversion of *U*-centers to *F*-centers at temperatures below 90°K. It was shown[1] that irradiation, at 80°K, of a KCl-KH crystal in the *U*-band destroys *U*-centers, and that the hydride ion which is ejected from the *U*-center to an interstitial position gives rise to the U_1-band. Seitz[2] has suggested that the excited hydride ion prefers an interstitial to a substitutional position, and consequently leaves the negative ion vacancy; on the other hand it is possible that the thermal spike produced after excitation of the hydride ion is sufficient to eject the hydride ion from its substitutional position. If we define

$\square \equiv$ negative-ion vacancy (α-center),
$[e] \equiv$ an electron trapped at a negative-ion vacancy (*F*-center),
$[H^-] \equiv$ hydride ion substituted for a halide ion in the lattice (*U*-center),
$H_i^- \equiv$ interstital hydride ion (U_1-center),
and
$H_i^0 \equiv$ interstitial hydrogen atom (U_2-center),

then the destruction of *U*-centers, by light absorbed in the *U*-band, to form α and U_1-centers may be represented by

$$[H^-] \xrightarrow{h\nu(U)} H_i^- + \square .$$

At 80°K, *F*-centers are formed as a result of excitation of U_1-centers; it is proposed that this process is the main source of *F*-centers. Absorption of light by an interstitial hydride ion could yield a hydrogen atom (U_2-center) and a conduction electron; subsequent capture of this electron by a negative ion vacancy would produce an *F*-center. However, irradiation in the U_1-band yields *F*- and U_2-centers for only a short time and causes a small drop in the U_1-band, continued irradiation causes a slow conversion of U_1-centers to *U*-centers. At this stage there is a great excess of negative ion vacancies, and if electrons were in the conduction band it seems probable that *F*-centers could be formed easily. It might be argued that the back reaction $e + H_i^0 \rightarrow H_i^-$ has a much higher probability than $e + \square \rightarrow [e]$ and therefore prevents further *F*-center formation. However, further treatment with the unfiltered AH-4 lamp increases the concentration of both F- and U_2-centers without appreciably changing the concentration of negative-ion vacancies. It seems likely therefore that this explanation is not valid and that absorption by the hydride ion does not result in an electron being released into the conduction band.

Another possibility is that the absorption of light by the interstitial hydride ion raises an electron to a bound excited state from which it can tunnel to a negative-ion vacancy to form an *F*-center and a U_2-center. However it would have to be proposed, in order to fit the experimental facts, that stable *F*-centers and U_2-centers would result only in cases in which the U_1-center and the α-center were separated by more than some minimum distance; when the U_1-center and the α-center are separated by distances smaller than this minimum distance, the above tunneling process may be considered to occur but the reverse process in which the electron at the α-center tunnels back to the U_2-center is highly probable and effectively prevents the formation of *F*-centers and U_2-centers. This conversion, by a tunneling process, of α- and U_1-centers to *F*- and U_2-centers by excitation in the U_1-band may be represented by

$$\square + H_i^- \underset{\rho}{\overset{h\nu(U_1),\,\rho}{\rightleftarrows}} H_i^0 + [e],$$

where ρ indicates that the occurrence of the reaction depends on the distance of separation of the reactants. Thus in Fig. 1, where the α-center is located at the origin and ρ is the distance between the α- and U_1-centers, tunneling from the excited U_1-center to the α-center occurs when the U_1-center is in regions *A*, *B*, and *C* but not in *D*; however, in region *A* the reverse tunneling

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[1] Delbecq, Smaller, and Yuster, preceding paper [Phys. Rev. **103**, 599 (1956)].
[2] F. Seitz, Revs. Modern Phys. **26**, 90 (1954).

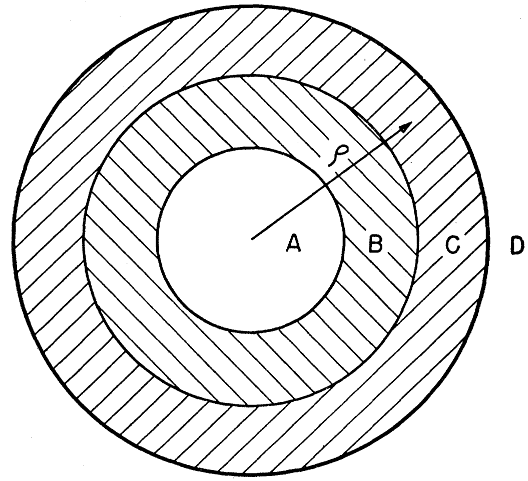

FIG. 1. Stability regions for U_1-centers in the vicinity of α centers, and U_2-centers in the vicinity of F-centers.

process takes place and no F-center is formed, whereas in regions B and C a stable F-center is formed. In the case of an F-center excited by F-light, the electron is presumed to tunnel to a U_2-center located in region B but not to one located at greater distances. This reaction may be represented by the expression

$$H_i^0+[e]\xrightarrow{h\nu(F),\,\rho}H_i^-+\square.$$

The fact that F-centers bleach by absorption of light in the F-band at liquid helium temperature substantiates the proposal that a similar bleach at liquid nitrogen temperature takes place by a tunneling process.

The experimental facts[1] can be explained as follows: (1) Irradiation of KCl-KH crystals with the unfiltered AH-4 lamp bleaches the U-band by exciting the U-center, the hydride ion being ejected into an interstitial position with high probability to give a U_1-center. Light absorbed by the U_1-center raises the electron to an excited state from which it can tunnel to an α-center and, provided the separation is greater than the minimum distance (regions B and C, Fig. 1), will give an F-center and U_2-center. However some of these F-centers can be bleached with F-light since an electron in an excited state of an F-center can tunnel to give a U_1-center and an α-center if a U_2-center is sufficiently close (region B, Fig. 1). The thermal spikes produced after excitation of U_1-centers and capture of electrons by U_2-centers are believed to be sufficient to cause diffusion of U_2- and U_1-centers interstitially through the lattice. Thus during exposure to the unfiltered light of the AH-4 lamp there is a continual flux between U-, U_1-, α-, F-, and U_2-centers. (2) Irradiation (with AH-4 lamp and 9863 filter) in the U_1-band immediately converts U_1-centers to F- and U_2-centers in the case in which the separation of the U_1- and α centers is greater than the minimum distance (regions B and C, Fig. 1). Further irradiation slowly converts U_1-centers to U-centers, by causing diffusion of U_1-centers until captured by α centers, but changes the concentration of F- and U_2-centers very little. This lack of increase in the concentration of F- and U_2-centers as the concentration of the U_1-centers decreases indicates that during irradiation very few U_1-centers migrate such that their separation from α centers permits the formation of F- and U_2-centers. Thus we conclude that there are very few U_1-centers which are separated from α centers by distances so large that tunneling from the excited U_1-center to the α center cannot occur (region D, Fig. 1); and further, that in the case of the large majority of U_1-centers which are too close to α centers to form F- and U_2-centers (region A, Fig. 1) the direction of migration of the U_1-center upon excitation with light is predominantly toward the α center,[3] and ultimately U-centers are reformed. (3) Irradiation of a crystal, which had been exposed at 80°K to the unfiltered AH-4 lamp followed by a short exposure to the AH-4 lamp plus a Corning 9863 filter, with light absorbed in the F-band causes a bleaching of a large fraction of the F-centers, namely those for which a U_2-center lies in region B, Fig. 1; if the crystal had been exposed to the unfiltered light of the AH-4 lamp for only a short time, only about one-fifth of the F-centers remain after bleaching with F-light, and if it had been exposed for a long time to the unfiltered light of the AH-4 lamp about one-half of the F-centers remain. The different stabilities of the F-centers could be accounted for by "V-centers" (in this case involving H atoms, not Cl atoms) of different stability; however, since the shape of the U_2-band does not change with irradiation and the U_2-band seems to account for all of the "V-centers" this possibility has been discarded. The changing stability of the F-centers is interpreted as indicating that irradiation with the unfiltered AH-4 lamp causes a net motion of U_1-centers away from the α centers until the separation is such that tunneling from the excited U_1-center to the α-center will occur but tunneling from the excited F-center to the U_2-center will not occur (region C, Fig. 1). Thus as the irradiation time increases the fraction of stable F- and U_2-centers increases.

[3] (I.e., the attraction between the U_1- and α centers is large at these distances and random motion does not occur.)