

It is to be observed, however, that a better theory, which allows for anisotropic scattering, gives $K = (m_l/m_t)(\tau_l/\tau_t)$, where τ_l and τ_t are the relaxation times for the two principal axes of energy ellipsoids.⁷

The comparison between theory and our experiments allows one to reach the following conclusions:

(a) There is good agreement between the experimental results and Eqs. (3), (4), and (5).

(b) When the electric current is in the (110) direction, the longitudinal coefficient M_{110}^{110} is smaller than the transverse one M_{110}^{010} . Then Eqs. (1), (2), and (3)

give

$$Z(K) < 2Y(K),$$

which is true for K smaller than 15.6.

(c) The ratio $M_{110}^{110}/M_{110}^{010}$ was calculated directly (curves *B2* and *C2*) and indirectly [curves *A1*, *A2*, *B1*, *B2*, *C1*, *C2*, and Eqs. (1) and (5)]. The values obtained range between 1.77 and 1.93; the average is 1.84. The corresponding K 's are between 7 and 11.4; the ratio 8.3 corresponds to the average 1.84. These values are smaller than the value 11.9 found by Goldberg and Davis.⁶ Our results, however, agree with theirs in showing that the ratio K in *n*-type germanium is smaller than ordinarily assumed (> 15) at about 300°K.

⁷ C. Herring and E. Vogt, Phys. Rev. **101**, 944 (1956).

Paramagnetic Resonance Investigation of Irradiated KCl Crystals Containing *U*-Centers*

C. J. DELBECQ, B. SMALLER, AND P. H. YUSTER
Argonne National Laboratory, Lemont, Illinois

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The effects of ultraviolet irradiation of KCl-KH and KCl-KD single crystals at 80°K and 300°K have been investigated using paramagnetic resonance and optical absorption techniques. KCl-KH crystals irradiated at 80°K have been found to exhibit, along with the usual *F*-center spin resonance, a resonance doublet with a splitting of 500 ± 10 gauss and a line width of 68 ± 5 gauss; the doublet is presumed to be due to hydrogen atoms in the crystal. This conclusion is substantiated by the fact that KCl-KD crystals, after a similar irradiation, exhibit a resonance triplet with a separation of outer components of 156 ± 10 gauss. Further results lead to the following conclusions: (1) that the hydrogen atoms produced by irradiation are located in interstitial positions in the lattice, (2) that these interstitial hydrogen atoms give rise to an optical absorption band (*U*₂-band) located at 236 mμ, (3) that a broad optical absorption band (*U*₁-band) extending to the long wavelength side of the *U*-band is due to interstitial hydride ions.

I. INTRODUCTION

IT has been known for some time that if an alkali halide crystal containing *U*-centers is exposed, at sufficiently high temperatures, to light absorbed by the *U*-centers, *F*-centers are formed.¹ Since a *U*-center is believed to be a hydride ion which has substitutionally replaced a halide ion in the lattice, the conversion of a *U*-center to an *F*-center must also produce a hydrogen atom. No experimental information is available regarding the state of the hydrogen atom thus produced. The present investigation was undertaken with the hope that paramagnetic resonance absorption measurements would yield information regarding the hydrogen atoms produced in the photodecomposition of *U*-centers. Parallel studies were also undertaken using optical absorption measurements in an attempt to obtain additional information.

*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ R. Hilsch and R. W. Pohl, Trans. Faraday Soc. **34**, 883 (1938); N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 157.

II. EXPERIMENTAL PROCEDURES

A. Paramagnetic Resonance Detection System

The paramagnetic resonance detection system used was a conventional microwave system utilizing a reflection cavity placed in a static magnetic field. The microwave generator used was a Sperry 2K39 or Varian V-58 operating at 9100 Mc/sec. The power level at the crystal detector was adjusted to optimum by a magic tee bridge with reactive balancing arm. An automatic frequency control locked the klystron frequency with the cavity resonance, compensating for both oscillator frequency drift and cavity resonance shifts. The cavity was constructed as part of a low-temperature Dewar system (Fig. 1) so that phenomena down to 80°K could be observed. The Dewar arrangement permitted easy exchange of samples, for the samples were placed in quartz tubes that could be lowered into the part of the Dewar extending into the cavity. No other adjustment was required other than possibly retuning the cavity. The tapered joint permitted removal of the entire Dewar assembly for cleaning or

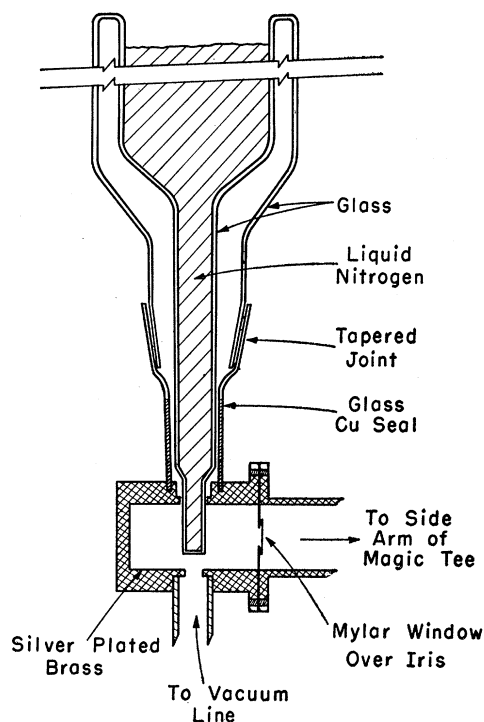


Fig. 1. Microwave cavity—Dewar assembly used in measuring paramagnetic resonance spectra at liquid nitrogen temperature.

use of the cavity with larger samples at room temperature. Adequate vacuum conditions in the Dewar assembly without loss of rf power were obtained by using a Mylar window at the cavity entrance iris. The design was restricted by the necessity of mounting the entire assembly in the one-inch gap provided by the magnet pole faces. A dual modulation system previously described,² operating at 25 cps and 2 kc/sec, was also incorporated into the design to achieve better signal-to-noise ratio for the crystal detector, along with a reduction in microphonics. The latter is achieved by selecting the spectral region of observation to be 2 kc/sec away from the carrier (i.e., 9100 Mc/sec \pm 2000 cycles/sec \pm 25 cycles/sec) rather than that in the immediate region of the carrier frequency (9100 Mc/sec \pm 25 cycles/sec). The 2 kc/sec coils were mounted directly into the sides of the cavity while the 25-cycle coils were mounted on the pole pieces of the magnet. The maximum field sweep for each coil was about 125 gauss, which was considered adequate. With this arrangement the noise level at the 1N23 detector during operation was about 2×10^{-8} volt and corresponded to a limiting detectability of 1,1-diphenyl-2-picrylhydrazyl of about 2×10^{12} spins at 80°K.

B. Preparation of Crystals

U-centers were introduced into potassium chloride in essentially the same manner as that described first by

² B. Smaller and E. Yasaitis, *Rev. Sci. Instr.* **24**, 991 (1953).

Rögener.³ Pure single crystals of potassium chloride were obtained from the Harshaw Chemical Company. Cleaved blocks (12 \times 12 \times 24 mm) from these single crystals, along with distilled potassium, were sealed off under vacuum in a Pyrex tube with a nickel liner. This tube was placed in a furnace, heated to 750°C for one hour, and then quenched with air down to room temperature. At this stage the crystals were estimated to contain over 2×10^{18} *F*-centers/cc. These additively colored blocks were then placed in Pyrex tubes and evacuated, $\frac{2}{3}$ atmosphere of H₂ was introduced, and the tubes were sealed off. These tubes were then heated at a temperature of 625°C for 24 hours at which time the crystals were essentially colorless to the eye. The crystals were quenched and removed from the tubes and were ready for use. Crystals prepared in this manner did not have a uniform distribution of *U*-centers. The outer parts of the crystal had the highest concentration and, since the samples used were never more than 3 mm thick, the outer 3 to 4 mm was cleaved off and used. These pieces had a concentration of about 2×10^{18} *U*-centers/cc. The concentration was so high that the peak optical absorption of the *U*-band was beyond measurement even on the thinnest crystals measured. The foregoing estimate of the concentration was made using the optical absorption of the *U*-band at wavelengths that could be measured.

Such KCl—KH crystals were cleaved into pieces approximately 3 \times 3 \times 12 mm for use in the magnetic resonance absorption experiments. The conversion of *U*-centers to *F*-centers at room temperature was accomplished by exposing the crystal to the "Mineralight"⁴ for about 5 minutes on each of the 3- \times 12-mm sides. The conversion of *U*-centers to *F*-centers at liquid nitrogen temperature was accomplished by exposing the crystal, which was immersed in a quartz Dewar containing liquid nitrogen, to the unfiltered light of a General Electric AH-4 mercury lamp⁵ for about 45 minutes on each side; subsequently this crystal was exposed for about 2 minutes on each side to the light of the AH-4 lamp filtered by a Corning 9863 filter.

The optical absorption measurements were taken on crystals which were from 0.25 to 0.60 mm thick. These crystals were mounted in a special Dewar⁶ so that experiments and measurements could be carried out at liquid nitrogen temperature. Optical absorption spectra were taken at 80°K in the range 206 to 800 μ using a Cary Recording Spectrophotometer.

³ H. Rögener, *Ann. Physik* **29**, 386 (1937).

⁴ A low-pressure mercury lamp manufactured by Ultraviolet Products, Inc., Los Angeles, California.

⁵ The outer Pyrex jacket of the AH-4 lamp had been removed, and the light was filtered by the inner quartz jacket only.

⁶ Casler, Pringsheim, and Yuster, *J. Chem. Phys.* **18**, 887 (1950).

III. EXPERIMENTAL RESULTS IN IRRADIATED CRYSTALS OF KCl-KH AND KCl-KD

A. Paramagnetic Resonance Absorption

Since both F -centers and hydrogen atoms might be stable products of the bleaching of U -centers, the primary aim of the paramagnetic resonance absorption measurements was to identify absorption lines which could be assigned to F -centers or hydrogen atoms. The paramagnetic resonance spectra of F -centers is well known,⁷ while that of free atomic hydrogen ($I=\frac{1}{2}$; $S=\frac{1}{2}$) would, for frequencies high in comparison with the hyperfine splitting constant of 1420 Mc/sec,⁸ be expected to consist of a doublet (separation 506 gauss) symmetrically situated with respect to the free electron spin resonance. The effect of the crystal environment might modify this separation.

A KCl-KH crystal was irradiated at room temperature with the "mineralight," immediately cooled and observed at 80°K. The F -center absorption was readily observed; however, the expected absorption due to hydrogen atoms was absent. There still remained the possibility that the separation of the hydrogen doublet in the crystal was comparable to or less than the F -center line width. However, the line width of the F -center absorption was equal to that of the F -center absorption in an additively colored crystal, and a search for a narrow doublet masked by the F -center absorption showed no fine structure.

Since at room temperature, any hydrogen atoms which are formed might diffuse to form hydrogen molecules and thus give no paramagnetic resonance absorption, KCl-KH crystals were irradiated at liquid nitrogen temperature where diffusion rates are much lower. Spin resonance spectra of such a crystal are shown in Fig. 2 where the line shapes represent the dispersion component of the susceptibility after dual phase-selective demodulation. The central peak in Fig. 2(a) is that of the F -center while the resonance lines on either side are presumed to be the doublet due to the presence of H^0 . That the F and H^0 species have a distinctive character was observed in their marked difference in relaxation time resulting in a different dependence on phase setting of the 2-kc selective amplifier. By adjusting the phase, the spectrum for each species can be preferentially suppressed. Thus in Fig. 2(b) the F -center resonance has been suppressed while in Fig. 2(c) that of the H^0 has been suppressed. At 80°K, the H^0 doublet splitting was found to be 500 ± 10 gauss; the line width was 68 ± 5 gauss, equal to that of the F -center line width at the same temperature.

To substantiate the association of the doublet structure with the presence of H^0 , similar experiments were performed using KCl-KD crystals. In the case of deuterium with $S=\frac{1}{2}$; $I=1$ and a hyperfine splitting constant of 327 Mc/sec,⁸ one might expect from D^0 a

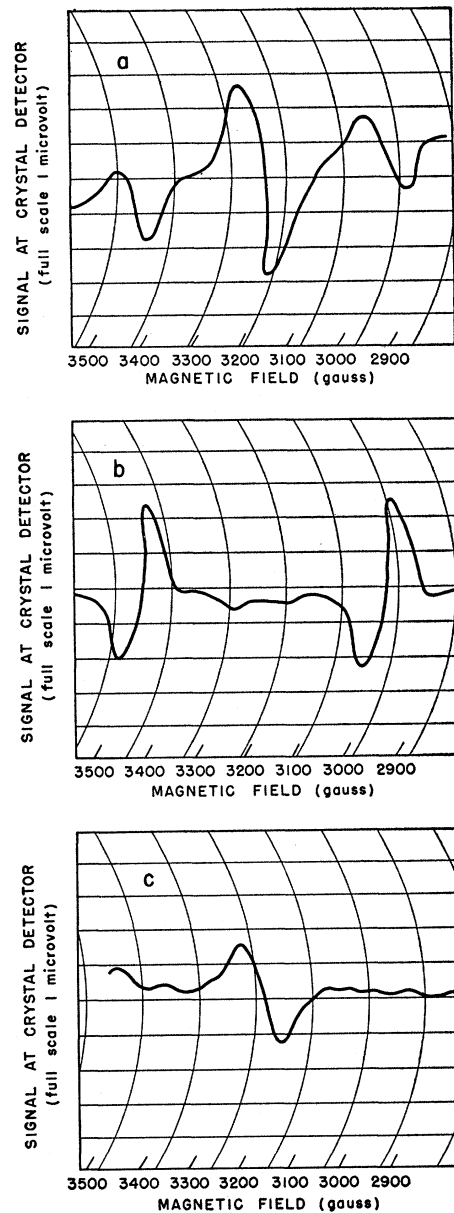


FIG. 2. Paramagnetic resonance spectrum, at 80°K, of a KCl-KH crystal after an irradiation, at 80°K, consisting of an exposure of 3 hours with the unfiltered AH-4 lamp followed by an exposure of 8 min with the AH-4 lamp filtered with a Corning 9863 filter. Effect of phase (ϕ) discrimination indicated. (a) $\phi = \phi_{\text{opt}}(F)$; (b) $\phi = \phi_{\text{opt}}(F) + \pi/2$, i.e., F -center resonance suppressed; (c) $\phi = \phi_{\text{opt}}(H^0) + \pi/2$, i.e., hydrogen atom resonance suppressed.

triplet with separation of 156 gauss between outer components. The resultant experimental patterns are shown in Figs. 3(a) and 3(b) where the proper phase selection has been used to suppress the D^0 or F patterns, respectively. As expected, the separation is 156 gauss, within experimental error. The increase in resolution due to phase selectivity is even more evident than in the case of the H^0 and F -center patterns.

⁷ Kip, Kittel, Levy and Portis, Phys. Rev. **91**, 1066 (1953).

⁸ P. Kusch, Phys. Rev. **100**, 1188 (1955).

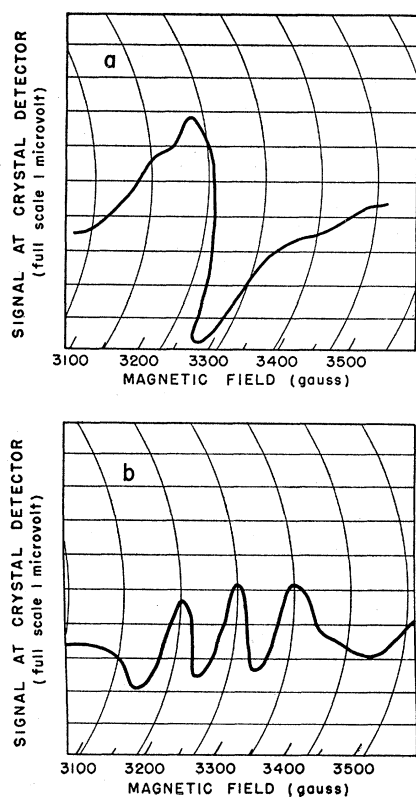


FIG. 3. Paramagnetic resonance spectrum, at 80°K, of a KCl-KD crystal after an irradiation, at 80°K, consisting of an exposure of 3 hours with the unfiltered AH-4 lamp followed by an exposure of 8 min with the AH-4 lamp filtered with a Corning 9863 filter. Effect of phase (ϕ) discrimination indicated. (a) $\phi = \phi_{\text{opt}}(\text{D}^0) + \pi/2$, i.e., deuterium atom resonance suppressed; (b) $\phi = \phi_{\text{opt}}(F) + \pi/2$, i.e., F -center resonance suppressed.

In order to obtain information regarding the stability of the hydrogen atoms with respect to temperature, annealing experiments were run. Samples were pulse-annealed for two minutes at the indicated temperatures and returned to the resonance detection system at 80°K for observation after each annealing. The maximum rate of disappearance of the hydrogen resonance occurs at about 108°K, as shown in Fig. 4. Similar results were obtained with KCl-KD crystals, the annealing curve showing, within experimental error, the same temperature dependence.

B. Optical Absorption

Along with the study of the paramagnetic resonance absorption spectra in KCl-KH and KCl-KD crystals after various irradiations, a parallel study of the optical absorption spectra of such crystals was made. When a single crystal of KCl-KH is irradiated at liquid nitrogen temperature with the light from an AH-4 mercury lamp of wavelength longer than 200 $m\mu$, the U -band (at 212 $m\mu$) is observed to decrease relatively rapidly and can be almost completely bleached [Fig. 5(a), (b), (c)]. As the U -band bleaches, a very broad

band, hereafter referred to as the U_1 -band, is formed which extends to the long wavelength side of the U -band. Upon prolonged irradiation, Fig. 5(c), the F -band (540 $m\mu$) and a band, hereafter referred to as the U_2 -band (236 $m\mu$), grow at about the same relative rates, but at rates much lower than the initial rate of disappearance of the U -band. If a crystal having the absorption spectrum of Fig. 5(c) is bleached with light (AH-4 lamp plus Corning 9863 filter) which is absorbed predominantly by the U_1 -band, the U_1 -band decreases somewhat and the F - and U_2 -bands increase proportionately and very rapidly, Fig. 5(d); continued bleaching affects the F - and U_2 -bands very little, but does cause a slow rise of the U -band. If however, a crystal having the absorption spectrum of Fig. 5(d) is bleached

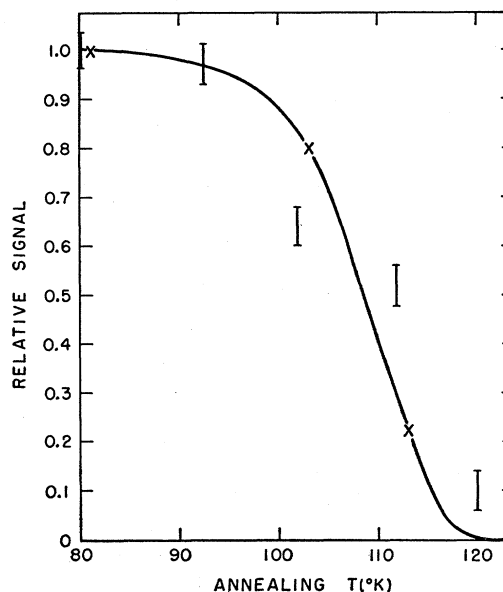


FIG. 4. Fraction of species remaining after annealing, I— as measured by intensity of hydrogen atom resonance, x—as measured by intensity of absorption of the U_2 -band, plotted as a function of annealing temperature. The measurements were made at 80°K.

at liquid nitrogen temperature with light of wavelength 540 $m\mu$, the F - and U_2 -bands are decreased proportionately and very rapidly by about 50%, Fig. 5(e), but subsequent bleaching with F -light causes little change in the absorption spectrum.

Irradiation of a KCl-KH crystal at liquid helium temperature with the light from an AH-4 mercury lamp of wavelength longer than 200 $m\mu$ produces changes in the absorption spectrum which are essentially the same as those obtained when the irradiation is carried out at liquid nitrogen temperature. In addition the rates of change are almost the same at the two temperatures. The only difference observed was that the ratio of the height of the U_2 -band to the height of the F -band appears to be slightly greater when the

irradiation is carried out at liquid helium temperature.

Upon warming a KCl-KH crystal, which has been treated to give an absorption spectrum similar to that in Fig. 5(d), it is found that the maximum rate of decay of the U_2 -band occurs at 108°K (Fig. 4). The U_1 -band was observed to disappear gradually in the temperature range 120–220°K with a maximum in the rate of disappearance occurring in the vicinity of 160°K. Very little change in the F -band occurred during the warmup to room temperature.

The behavior of KCl-KD crystals, with respect to the optical experiments described in the foregoing, is identical with the behavior of KCl-KH crystals except that the maximum rate of decay of the U_2 -band occurs at 113°K. This difference in temperature, which is thought to be greater than the experimental error in the temperature measurement, indicates that deuterium has a lower rate of diffusion at a given temperature than hydrogen, owing to the greater mass of the deuterium.⁹

IV. DISCUSSION OF RESULTS

Thomas¹⁰ has shown that, in KBr-KH crystals, irradiation at liquid nitrogen temperature in the U -band produces negative ion vacancies,^{11,12} decreases the U -band, forms very few F -centers, and produces an absorption band to the long wavelength side of the U -band.

Figure 5(b) shows that in KCl-KH crystals after short irradiations with the AH-4 lamp almost all the U -band is destroyed, very few F -centers are formed, and the broad U_1 -band is formed. A crystal which has been treated, such as that described in Fig. 5(b), is found to display no paramagnetic resonance signal, thus indicating no unpaired trapped electrons. If a U -center is accepted as being a hydride ion in a negative-ion vacancy, then at this stage the important decomposition products may be negative-ion vacancies,¹³ hydride ions not located in negative-ion vacancies, and hydrogen molecules and F' -centers or other electron-paired centers. Since optical absorption measurements show the absence of F' -centers and since no unknown absorption in the visible or near infrared is observed, it is assumed that the important products are negative-ion vacancies, and hydride ions. The most likely location for a hydride ion, not located in a negative-ion vacancy, would be an interstitial position,¹⁴ and, since the U_1 -band is the only band present of questioned origin, it is assumed to be due to these interstitial hydride ions.

⁹ It will be shown in the next section that the U_2 -band is the result of interstitial hydrogen or deuterium atoms.

¹⁰ H. Thomas, Ann. Physik 38, 601 (1940).

¹¹ Delbecq, Pringsheim, and Yuster, J. Chem. Phys. 40, 746 (1952).

¹² W. Martienssen, Z. Physik 131, 488 (1952).

¹³ Unfortunately it is not possible with our spectrophotometric equipment to observe far enough into the ultraviolet to observe the α -band in KCl. Nevertheless, its presence is assumed on the basis of the work of Thomas¹⁰ on KBr-KH.

¹⁴ F. Seitz, Revs. Modern Phys. 26, 90 (1954).

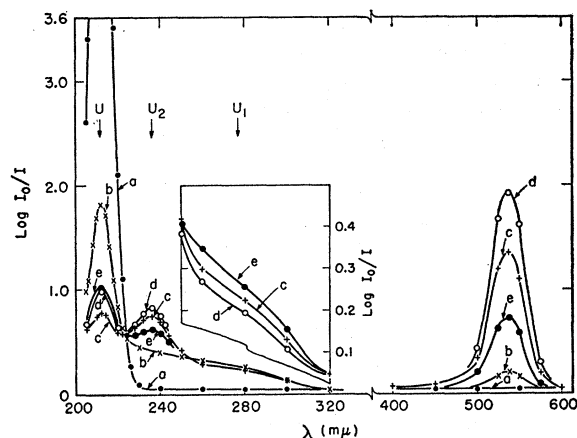


FIG. 5. Absorption spectra of a KCl-KH crystal, measured at 80°K, as a function of the following irradiations at 80°K: (a) no treatment, (b) 5-min irradiation with the unfiltered AH-4 lamp, (c) repeat for additional 15 min, (d) 1-min irradiation (in U_1 -band) with the AH-4 lamp filtered with a Corning 9863 filter, (e) 5-min irradiation (in F -band) with the AH-4 filtered with a Corning 3389 filter.

If a crystal having an absorption spectrum similar to that shown in Fig. 5(c) is now exposed to light absorbed in the U_1 -band and protected from F -light, the F -band absorption rises rapidly for a short time and the U_2 -band rises simultaneously. Upon continued irradiation no further change occurs in these two bands, but the interstitial hydride ions are now converted to U -centers at a slow rate. Further exposure to the unfiltered AH-4 lamp leads to an increase in intensity of the F - and U_2 -bands up to a point where the latter two tend to saturate. At this point it is estimated that the number of F -centers present is less than 20% of the number of U -centers originally present; however the concentration of F - and U_2 -centers is sufficiently high that their spin resonance absorption is readily detectable.

It has been found that the paramagnetic resonance absorption due to hydrogen atoms disappears at the same temperature, within experimental error, as that at which the U_2 -band disappears, from which it is concluded that the U_2 -band is due to the presence of hydrogen atoms in the crystal. The absorption process giving rise to the U_2 -band is thought not to take place within the hydrogen atom but rather to be the excitation of an adjacent halide ion in which the excited electron may be shared by the hydrogen and chlorine atoms. It has also been found that irradiation in the F -band decreases proportionately the height of the paramagnetic resonance signals due to the F -centers and hydrogen atoms and the optical density of the F - and U_2 -bands. These facts suggest that there are no other electron-excess or electron-deficient centers present and that F - and U_2 -centers are present in approximately equal numbers. The location of these hydrogen atoms in the crystal is indicated by the data presented in Fig. 5(d), (e). There it is seen that irradiation

tion in the F -band causes a decrease in the F - and U_2 -bands and an increase in the U_1 -band with a relatively small increase in the U -band. Thus, in the main, the electrons lost by the F -centers are captured by hydrogen atoms to form interstitial hydride ions (U_1 -centers), and it is concluded that the hydrogen atoms (U_2 -centers) are located at interstitial sites in the lattice. This conclusion concerning the location of the hydrogen atoms in the crystal is supported by observations on the inverse process—namely, irradiation in the U_1 -band causes a decrease in the U_1 -band and increases in the F - and U_2 -bands, Fig. 5(c), (d).

The paramagnetic resonance experiments show that under the proper conditions H atoms are stable products in the photodecomposition of U -centers. The pulse annealing experiments show that at quite low temperatures (above 100°K) the hydrogen atom is mobile and pairs its free electron. The facts, that (a) the F -band drops only slightly at about this same temperature, (b) the U -band rises only slightly, (c) F - and U_2 -centers are present in approximately equal numbers, and (d) all the hydrogen atoms disappear, indicate that the primary process responsible for the decrease in the number of hydrogen atoms is the formation of hydrogen molecules, while only a minor fraction of the hydrogen atoms are trapped at F -centers to form U -centers. At temperatures above 120°K, although hydrogen atoms

are probably formed as a product of the irradiation of the U -band, diffusion to form molecules is so rapid that no signal due to hydrogen atoms is observed.

Arguments based on the optical data show the hydrogen atoms to be in interstitial positions, while the separation of the hydrogen resonance doublet indicates that there is very little perturbation by surroundings in the crystal. Since an interstitial "hole" in KCl has a diameter of about 2.3 Å, it does not seem too unreasonable that the hydrogen atom in such a large hole is perturbed very little by the surroundings. The line width of the H^0 signal, equal to that of an F -center, may be, as in the case of the latter, the result of an electron whose wave function is determined by a central potential perturbed by a crystal lattice potential. The resultant wave function could yield a value of ψ^2 (the electron probability density) at the neighboring sites sufficient to account for the observed line width with only a slight deviation in its value at the hydrogen nucleus. The uncertainty in the doublet separation measurement may well contain this deviation from the free atom value.

ACKNOWLEDGMENT

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