samples used in the present investigation will be required. It seems likely that very superior signals may be obtained using larger samples with smaller neutron irradiations. The signal may also be enhanced by use of an optimum rf modulation frequency with the sample at 4.2°K, or perhaps at 20°K.

ACKNOWLEDGMENTS

Jerald Lee of Ohio University assembled the ENDOR spectrometer and was chiefly responsible for its excellent performance. We wish to thank Professor J. C. Kemp of the University of Oregon for providing us with samples and for enthusiastic encouragement.

PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

Correlation of the Optical and Electron-Spin-Resonance Absorptions of the *H* Center in KCl†

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(Received 24 August 1966)

It has been shown that the optical *H* band and the ESR *H* spectrum arise from the same center, the *H* center, in KCl. Similar to the Cl_2^- (or V_K) center, the *H* center has two optical transitions: A strong and highly σ-polarized transition giving rise to an absorption band at 336 nm, and a much weaker transition, which is very weakly σ-polarized, giving rise to an absorption band at 522 nm. The disorientation temperature of the *H* center has been found to be (10.9±0.3)°K.

I. INTRODUCTION

IT was found by Duerig and Markham[1] that x-irradiation of 5°K produced an absorption band in KCl crystals, with a peak at 345 nm, which they called the *H* band. Compton and Klick,[2] through the use of polarized-light bleaching experiments, showed that the optical dipole moment of the transition responsible for the *H* band absorption lies along a $\langle 110\rangle$ direction. Känzig and Woodruff,[3] using electron spin resonance (ESR) techniques, found that after x-irradiation at 20°K a paramagnetic species was produced which involves an interstitial. The ESR spectrum indicates that this species consists of a Cl_2^- molecule ion located at a single negative ion site; the positive hole has additional interaction with two adjacent Cl^- ions and the complex, consisting of four collinear chlorine nuclei, has its axis along a $\langle 110\rangle$ direction. Känzig and Woodruff attributed this ESR signal to the presence of *H* centers in the crystal. Although there probably is little doubt that the center studied by Känzig and Woodruff is the *H* center and is associated with the *H* band studied by compton and Klick, there have at times been questions regarding this association.

Since the *H* center is of such fundamental importance in the study of color centers, the present work was undertaken to test directly whether the *H* band in KCl arises from an optical transition of the *H* center observed in the ESR spectrum, and at the same time to obtain more detailed information concerning its optical absorption spectrum, methods of production, and orientation properties.

II. EXPERIMENTAL PROCEDURE

A. Optical Measurements

The crystals used in these experiments were cleaved from large single crystals which were either grown in air by the Kyropoulos method or were purchased from the Harshaw Chemical Company. The crystals prepared in this laboratory were grown from melts containing a mixture of 0.1 to 1.0 g of NaCl with about 100 g of KCl. The cross sectional dimensions of the cleaved crystals were about 8×14 mm^2 while the thicknesses of the crystals varied from 1 to 12 mm. Color centers were produced by exposure to a 2000-Ci Co^{60} γ-ray source. Absorption spectra were obtained by using a Cary 14R recording spectrophotometer. Polarized light was produced through the use of either an Ahrens or Glan prism; the Glan prism permits measurement of optical absorption spectra down to about 220 nm since it has no absorbing cement and is limited only by the absorption of calcite itself. The source of bleaching light was an HBO-500 high pressure mercury arc lamp in conjunction with interference and sharp cutoff filters.

B. ESR Measurements

The crystals used in the electron spin resonance investigation were 3×3×20 mm^3 in size and were taken from the same source crystals used in the optical work. Color centers were produced by irradiation at 77°K

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

[1] W. H. Duerig and J. J. Markham, Phys. Rev. 88, 1043 (1952).

[2] W. D. Compton and C. C. Klick, Phys. Rev. 110, 349 (1958).

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

in the 2000-Ci Co^{60} γ source. Optical bleaching and excitation was done with a Bausch and Lomb SP-200 mercury arc light source using appropriate Corning and interference filters.

A superheterodyne spectrometer operating at X-band microwave frequencies was used for this work. Because of the saturation characteristics of the *H* center and other color centers in the alkali halides at liquid helium temperature, it was designed to work at low power levels. The lowest practical level was with 80 dB of attenuation, corresponding to about 10^{-9} W of microwave power incident upon the sample cavity. The frequency of the klystron was phase-locked to that of the sample cavity assuring that the absorption mode was being detected at all times.

The sample cavity was a cylindrical quartz cavity resonant at about 9.5 Gc/sec and operating in the TE_{011} mode. The cavity and the sample were immersed in liquid helium at all times and the sample could be lowered through the bottom of the cavity for the various optical bleaches. The Dewar was constructed with a three-wall tail and the light used for optical bleaching passed through two curved quartz windows as well as through the liquid helium before illuminating the sample.

The optical investigation of the *H* center in KCl showed that the temperature of the sample had to be kept below 10°K in order to prevent the thermal disorientation of the center. For this reason, all the spin resonance work was carried out at 4.2°K even though the long relaxation time of the *H* center at this temperature required that low powers be used. To avoid all traces of saturation, 85 dB of attenuation had to be used; however, it was not practical to work at such a low power because of the weak signal intensity and the difficulty in keeping the klystron frequency locked. As a compromise a slightly higher power level was used where, although some saturation was observed, the intensity ratios of the various lines were preserved and an acceptable signal to noise ratio was realized.

III. EXPERIMENTAL RESULTS AND DISCUSSION

A. Optical Measurements

It has been shown in this laboratory[4] that the concentration of V_1 centers in KCl can be enhanced greatly by the addition of Na^+ impurity. Teegarden and Maurer[5] have found that *H* centers can be formed by the optical destruction of V_1 centers at 4.2°K. If *H* centers are formed in this manner, some interfering centers can be eliminated. Consequently, most of the experiments reported here use KCl-NaCl crystals and involve the production of *H* centers by first producing V_1 centers and then converting these V_1 centers to *H* centers by optical means.

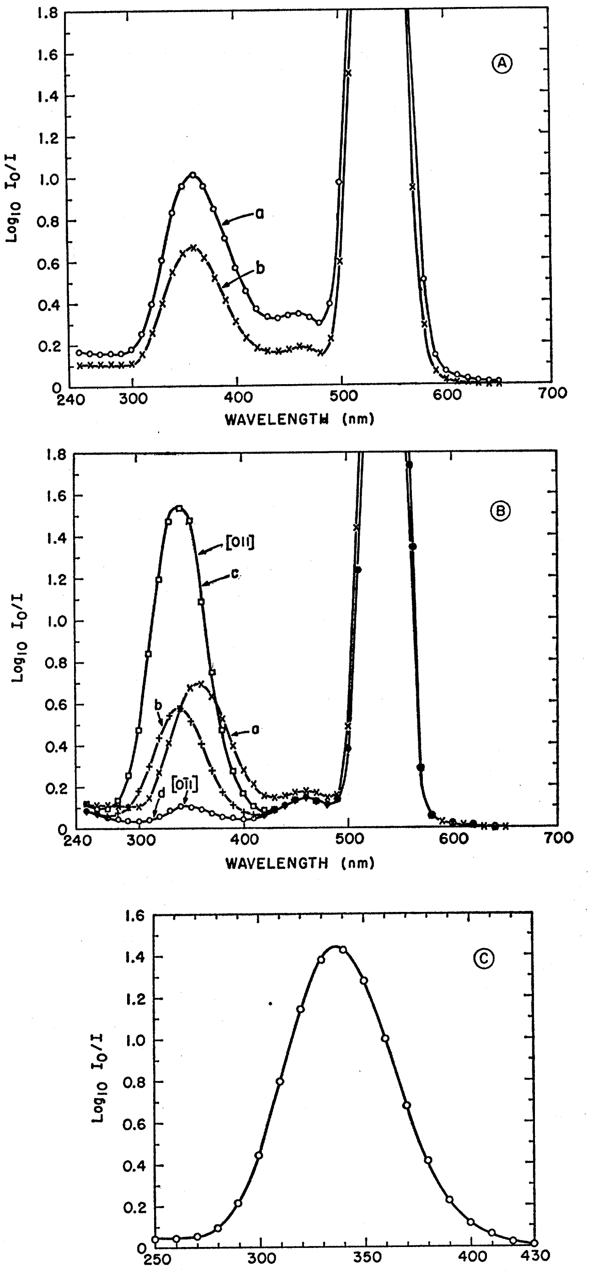

FIG. 1. The optical absorption introduced into a 1.2 mm thick crystal of KCl-NaCl after the following series of treatments, (A) (curve a) Exposure at 77°K to γ rays for 18 h. (curve b) Bleaching at 77°K with light of wavelength greater than 560 nm. (B) (curve a) Cooling to 5°K. (curve b) Bleaching at 5°K with unpolarized 405 nm light. (curves c and d) [011] and $[0\bar{1}1]$ absorption spectra, respectively, taken after bleaching with $[0\bar{1}1]$ polarized 305 nm light. (C) Anisotropic absorption spectrum of the *H* center obtained by subtracting curve c from curve d of Fig. 1(B).

Figure 1(A), curve a, shows the optical absorption introduced into a crystal of KCl-NaCl after an 18-h exposure at 77°K to γ rays. Since the irradiation was performed at 77°K no *H* centers are present in the

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[4] C. J. Delbecq, International Symposium on Color Centers in Alkali Halides, University of Illinois, 1965 (unpublished).

[5] K. J. Teegarden and R. J. Maurer, Z. Physik **138**, 284 (1954).

crystal; however, V_1, V_K, and F' centers are present. Since V_K centers would interfere in the determination of the anisotropic spectrum of the H center, they must be eliminated. Kingsley[6] has shown that Cl_2^- centers are destroyed rapidly if electrons are readily available in the conduction band. We have observed, in ESR experiments, that all of the V_K centers are destroyed by a brief irradiation into the F band. Figure 1(A), curve b, shows the remaining absorption after bleaching with light of wavelength greater than 560 nm. This treatment eliminates all F' and V_K centers while preserving a very large fraction of the V_1 centers. Figure 1(B), curve a, shows the spectrum, after cooling to 5°K, of the crystal which has received the above treatment. Figure 1(B), curve b, shows the absorption spectrum after destroying the V_1 band by exposure to nonpolarized 405 nm light. Curves *c* and *d* of Fig. 1(B) show the absorption spectra for $[011]$ and $[0\bar{1}1]$ polarized light after bleaching with $[0\bar{1}1]$ polarized 365 nm light. The $[0\bar{1}1]$ spectrum has dropped considerably in intensity from that in curve b while the $[011]$ spectrum has increased by almost a factor of three. These changes in intensity show that the distribution of H centers among the six $\langle 110\rangle$ directions has changed greatly. Since, as will be seen from the ESR results, the optical dipole moment of the transition responsible for the H center absorption in the ultraviolet lies along the molecular axis of the center, the population of centers aligned along all the remaining five $\langle 110\rangle$ directions has decreased considerably. Therefore, as in the case of the V_K center,[7,8] and as observed by Compton and Klick,[2] reorientation of the axes of these centers has taken place as a result of light excitation.

Since the above experiment shows that reorientation of the H center axis can take place upon excitation with light, it is clear that the methods used by us to produce H centers, i.e., by optical destruction of V_1 centers or photochemical treatment of OH^- containing crystals, do not yield a random distribution among the six $\langle 110\rangle$ directions. A beam of unpolarized light incident upon a (100) face of a crystal will have a tendency to remove centers oriented in the (100) plane and put them equally into (010) and (001) planes until an equilibrium, but not random, distribution is obtained. A random distribution can be obtained by warming the crystal above the disorientation temperature (Fig. 3) of the H center. However, in the experiments reported here, the fact that the starting distribution is not random is unimportant.

Figure 1(C) shows the anisotropic spectrum of the H center which was obtained by subtracting curve c from curve d of Fig. 1(B). This subtraction process eliminates any absorption which does not show anisotropy. From this spectrum we determine that the H band has a peak at 336 nm and a half-width of 0.66 eV.

The V_K center in KCl, which is a Cl_2^- molecule ion occupying two negative ion sites, has in addition to a strong anisotropic absorption in the ultraviolet, a very weak almost isotropic absorption in the near infrared. Since to a first approximation the H center is the same chemical species, i.e., a Cl_2^- in a single negative ion site, it also would be expected to possess a weak long wavelength absorption. Attempts were made to produce changes which would indicate the presence of such an absorption and also to observe the absorption directly. In the case of the V_K center, the long-wavelength absorption was first detected by destroying the ultraviolet anisotropy by excitation with infrared radiation of various wavelengths. Such an experiment has also been carried out on the H center and it too shows the presence of a weak almost isotropic long-wavelength absorption. If a crystal is treated in the manner described to obtain curves c and d of Fig. 1(B) and then exposed to light of wavelength longer than 580 nm, the anisotropy originally present in the crystal is destroyed. If the rate of disorientation is measured as a function of the wavelength of the disorienting radiation, it can be seen that the maximum in rate would occur for a wavelength which lies under the F-center absorption.

In order to observe the long-wavelength absorption of the H center, a technique first discovered by Kingsley[6] was used. He showed that if KCl-KOH crystals were irradiated at 4.2°K with light absorbed in the 205 nm OH^- absorption band, H centers were formed. The big advantage of crystals prepared in this manner over those that are γ-irradiated is that the F band is weak in the former case. We have found that by bleaching into the F band we can eliminate essentially all of the F centers and thus examine the properties of the long-wavelength absorption of the H center with very little interference from the F-center absorption.

A KCl crystal obtained from the Harshaw Chemical Company, containing an intense OH^- absorption band at 205 nm, was irradiated at 5°K with the full light of an AH-4 mercury lamp. This excitation results in the formation of H, F, U, U_1, U_2, α and other centers.

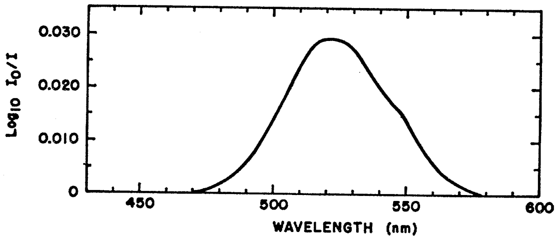

FIG. 2. Absorption spectrum showing the long wavelength H band.

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[6] J. D. Kingsley, U. S. Air Force Office of Scientific Research Technical Note No. 2, AFOSR-TN 60-635, University of Illinois, 1960 (unpublished).

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

[8] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).

Excitation in the *F* band at 5°K almost completely removes the *F* centers from the crystal. Figure 2 shows the absorption from about 450–600 nm in a crystal after irradiation with the mercury lamp and subsequent bleaching in the *F* band. At 5°K the *F* band peaks at 536 nm and since the band in Fig. 2 peaks at 522 nm it is clear that there is little *F* band remaining. However, the hump on the long wavelength side of the 522-nm band may be caused by a small residual *F* band. Excitation into the 522-nm band with polarized light produces a very small anisotropy in the 336-nm band and shows, in light of the ESR results to be presented, that the former transition has a slight amount of σ character. Excitation of a crystal, containing preferentially oriented *H* centers, with polarized light absorbed by the 522-nm band removes almost all of the anisotropy in the 336-nm band; consequently, it is clear that both the 336 and 522-nm absorptions arise from the same ground state and that excitation of either transition results, with fairly high probability, in a change in orientation of the center. Independent of the manner of production of *H* centers the anisotropic spectra obtained through the use of polarized light bleaching experiments are identical, within experimental error.

The axis of the *H* center is fixed in direction in the crystal at 5°K since the anisotropy which was shown in curves c and d of Fig. 1(B) remains unchanged over several hours if the crystal temperature is maintained at 5°K. However, if the crystal is warmed to a sufficiently high temperature, the thermal energy is adequate to cause the *H* centers to disorient so that a random population distribution among the six equivalent ⟨110⟩ directions is established and the anisotropy disappears.

Starting with a crystal having the absorption spectra shown in curves c and d of Fig. 1(B), the [0$\bar{1}$1] absorption at 336 nm was followed as a function of temperature. These data were obtained by warming at a rate of about $\frac{1}{2}$°K per min. and are plotted in Fig. 3. The disorientation temperature of the *H* center,[9] as determined from this curve and others like it, is 10.9±0.3°K. In the case of the V_K center, in which the Cl_2^- occupies two halide-ion lattice sites, a change in orientation of the molecule ion requires a displacement of the molecule ion in the lattice, and the mechanisms for disorientation and diffusion[7,10–12] are the same. However, in the case of the *H* center, a change in orientation can take place by a rotation, without translation, of the axis of the two central strongly bonded nuclei. This can occur by a breaking of the weak bonds between the two outer nuclei and the central nuclei and then re-establishing these weak bonds with another pair of nuclei after the rotation. The migration of the *H* center through the lattice results from the breaking of the strong bond between the two central nuclei and the formation of an interstitial halogen atom which, after some migration, can be retrapped to form an *H* center. Although the *H* center disorients at 10.9°K, its decay temperature is over 40°K. This decay of the *H* center is believed to result from its thermal instability as indicated by the fact that, in a KCl-NaCl crystal, as the *H* center decays the V_1 center is reformed.

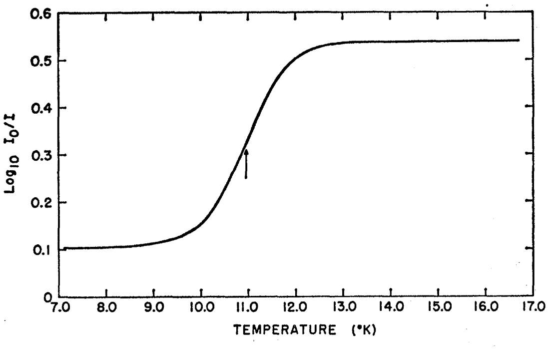

FIG. 3. Disorientation temperature of the *H* center. Starting with a crystal having the absorption spectra shown in curves c and d of Fig. 1(B), the [0$\bar{1}$1] absorption at 336 nm is followed as a function of temperature.

B. ESR Measurements

After an 18-h exposure of a KCl-NaCl crystal at 77°K to γ rays, the ESR spectrum at 4.2°K revealed the presence of Cl_2^- and *F* centers as well as O_2^- centers which were initially present in the crystal. Exposure of the crystal at 4.2°K to light of wavelength greater than 560 nm caused the complete removal of the Cl_2^- spectrum and no observable change in the remaining spectrum. Subsequent excitation of the crystal at 4.2°K with unpolarized 405 nm light incident on the (010) face of the crystal converted a very large fraction of the V_1 centers into *H* centers. The most prominent set of lines in the *H* center spectrum corresponds to the case where all four of the nuclei involved are Cl^{35}.

The two central nuclei and the two outer nuclei are equivalent, but the central and outer pairs of nuclei are inequivalent to each other. The principal hyperfine interaction of the two central nuclei, because Cl^{35} has spin $\frac{3}{2}$, yields a characteristic seven line intensity pattern 1:2:3:4:3:2:1. The additional interaction of the two outer nuclei yields a superhyperfine structure which splits each of the seven principal lines again into a 7-line pattern with intensity ratio 1:2:3:4:3:2:1. The spectrum is further complicated by the presence of

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[9] Concurrent to the present work, K. Bachmann and W. Känzig have determined the disorientation temperature of *H* centers to be between 10 and 11°K using mechanical stress. International Symposium on Color Centers in Alkali Halides, University of Illinois, 1965 (unpublished).

[10] C. J. Delbecq, W. Hayes, M. C. M. O'Brien, and P. H. Yuster, Proc. Roy. Soc. (London) **271**, 243 (1963).

[11] T. J. Neubert and J. A. Reffner, J. Chem. Phys. **36**, 2780 (1962).

[12] R. B. Murray and F. J. Keller, Phys. Rev. **150**, 670 (1966).

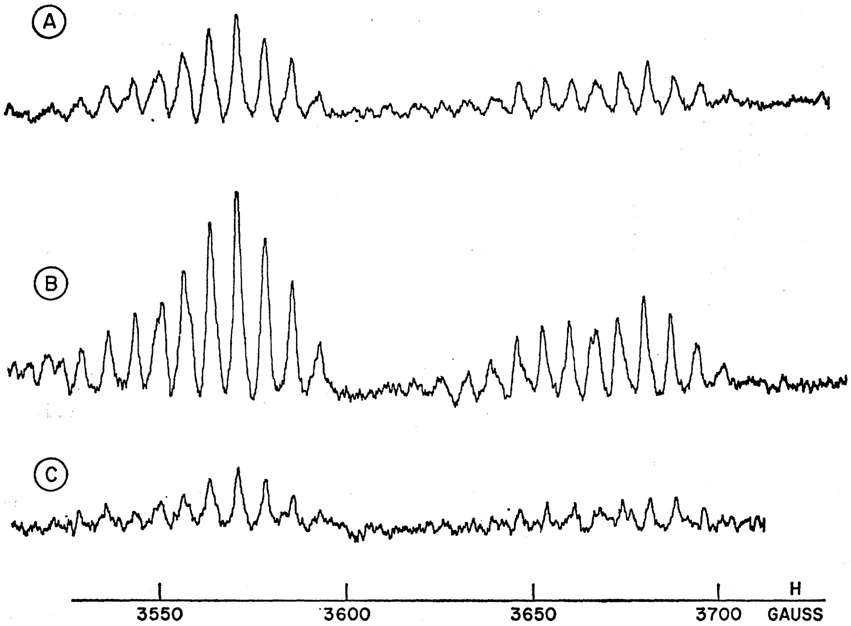

FIG. 4. The effect of reorientation on the intensity of the ESR spectrum of the *H* center at 4.2°K for the high field groups of lines of the $\theta=0°$ spectrum with *A*: $\mathbf{H}_0$ parallel to either the [011] or [0$\bar{1}$1] axis before reorientation, *B*: $\mathbf{H}_0$ parallel to the [011] axis after reorientation and *C*: $\mathbf{H}_0$ parallel to the [0$\bar{1}$1] axis after reorientation.

the species consisting of all the other possible combinations of the two chlorine isotopes. Furthermore, with the magnetic field along a ⟨110⟩ axis, there are three sets of spectra, arising from the anisotropy of the hyperfine interaction of the *H* center, which correspond to those centers whose molecular axes make angles of 0°, 60°, or 90° with respect to the magnetic field. The principal lines of two of these spectra are indicated in Fig. 5 which also shows the *F* center, the broad line at 3350 G, and two of the O_2^- impurity lines at 3228 G and 3450 G which distort the *H*-center pattern.

With the magnetic field parallel to a ⟨110⟩ axis of the crystal, the magnetic field position of the lines of the 0° spectrum can be adequately described by the expression:

$$\left(\frac{g_z}{g_0}\right)H=H_0+A(m_1+m_2)+A'(m_3+m_4)\,,$$

where $H_0=h\nu/g_0\beta$ and for the *H* center, the $m_i=\frac{3}{2}, \frac{1}{2}, \cdots, -\frac{3}{2}$. For the 0° spectrum we find that $g_z=2.0015\pm0.0007$, $A=109.1$ G, and $A'=7.0$ G. These values are in good agreement with those reported by Känzig and Woodruff.[3] There is no doubt, therefore, that the *H* center produced by the conversion of V_1 centers to *H* centers in KCl-NaCl is the same as that produced directly by x rays or γ rays when the crystal is irradiated at or below 20°K. The high field side of the ESR spectrum of the crystal at 4.2°K after this treatment is shown in Fig. 4(A). The external magnetic field is parallel to [011] and the outside groups of the 0° spectrum are shown; the spectrum taken with H_0 along [0$\bar{1}$1] is identical. The result of excitation of the crystal with an unpolarized beam of parallel light rays with the direction of propagation along the [011] axis is shown in Fig. 4(B). With the external magnetic field along [011] the 0° spectrum, Fig. 4(B), is seen to be twice as large as the initial intensity of the 0° spectrum, Fig. 4(A), and the 0° and 60° spectra, Fig. 5, are seen to have about the same intensity. The spectrum measured with the external magnetic field along [0$\bar{1}$1], Fig. 4(C), shows the 0° spectrum to be $\frac{2}{3}$ as intense as in the initial spectrum. From these results we conclude that the *H* center has an optical transition which gives rise to the *H* band at 336 nm, and that this transition is anisotropic and σ-polarized; i.e., the transition is permitted for light with electric vector parallel to the molecular axis.

The enhancement of the population of *H* centers in the [011] orientation and the depletion in the other ⟨110⟩ orientations are smaller than would be expected based on the anisotropy of the transition as measured in the optical experiment, Fig. 1(B). These results arise primarily from a change in the direction of propagation, [011], of the orienting light caused by reflection of the exciting light off the crystal and the Dewar walls, refraction at the crystal surfaces, and scattering of the light by the "snow" in the liquid helium.

Although it was not possible to determine accurately the disorientation temperature of *H* centers by ESR measurements with our experimental equipment, it was found that they disorient in the temperature range between 8° and 15°K. This temperature range is in good agreement with the disorientation temperature of 10.9°K determined from the optical absorption measurements.

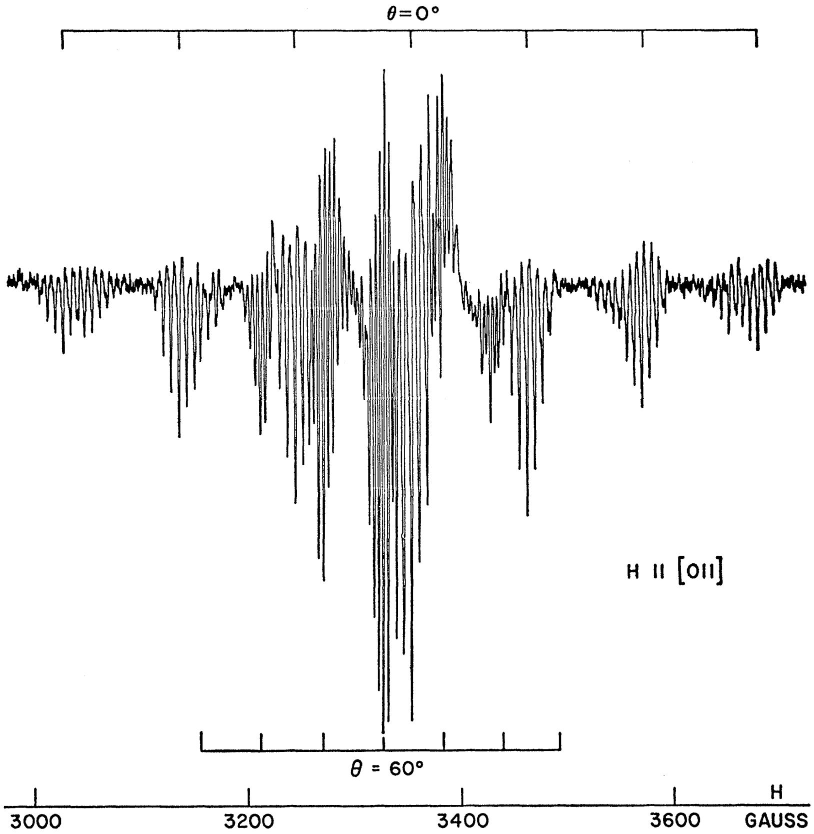

FIG. 5. The ESR spectrum of the *H* center after reorientation at 4.2°K with $\mathbf{H}_0$ parallel to the [011] axis. The principal lines of the 0° and 60° spectra are indicated.

IV. SUMMARY

High concentrations of V_1 centers have been produced in KCl crystals containing Na^+ impurity. These V_1 centers have been converted, at 5°K, into *H* centers by optical means. Polarized light bleaching experiments with *H* centers produced in this manner have been performed using both optical and electron spin resonance absorption techniques. The results of these experiments show that the *H* center has two absorption bands with peaks at 336 and 522 nm, and that the intense 336-nm band results from a transition which is highly σ-polarized while the transition responsible for the weak 522-nm band is only very slightly σ-polarized. The axis of the *H* center is fixed in a given $\langle 110\rangle$ direction in the crystal below 10°K, but if the temperature is raised above 11°K, thermal energy is sufficient to cause the axis of the center to change its orientation.

ACKNOWLEDGMENTS

We wish to thank John R. Gabriel for preliminary design and construction work on the ESR spectrometer. We also wish to thank Elson Hutchinson for growing the KCl-NaCl crystals used in these experiments.