

Symmetry of the H Center in KCl and KBr

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H centers were produced in KCl and KBr by x-irradiation at temperatures near liquid helium. The symmetry of these centers was determined by observing the dichroism produced in the absorption band after bleaching with polarized H -band light. It was found that the optical dipole moment of the H center is parallel to $\langle 110 \rangle$. The polarized bleaching light tends to reorient the H centers as well as to bleach them. The oscillator strength of the H center was found to be greater than about 0.3 that of the F center in KCl and greater than about 0.5 that of the F center in KBr.

INTRODUCTION

A COMPARISON of the absorption spectrum of an alkali halide crystal before and after x-irradiation shows that strong absorptions are introduced into the crystal by the irradiation.¹ In most alkali halides the spectral absorption after x-raying is found to be appreciably simpler if the irradiation is made at temperatures well below room temperature. This is particularly true for irradiations near liquid-helium temperatures. Duerig and Markham² report that only two prominent absorption bands appear in KCl, KBr, and NaCl if these materials are irradiated and measured at 5°K. These are the F band and a band at shorter wavelength that they called the H band. Upon warming the crystal to 77°K, they found that the H band bleached, that the F band was reduced, and that the V_1 band appeared. Table I gives the spectral location of the F , H , and V_1 bands in these materials.

Markham, Platt, and Mador³ studied the low-temperature bleaching of centers formed by x-irradiation of KBr at 5°K. They found that both the F and H bands were bleached by optical irradiation into the F band at 5°K. Since no photoconductivity was expected from the F band at 5°K, it was suggested that the bleaching is caused by a tunneling of the electron from the excited F center to a neighboring H center.⁴ It was suggested, then, that the color centers are not uniformly distributed but are concentrated in certain regions of the crystal.

Teegarden and Maurer⁵ extended the study of the H center with particular reference to KCl. The H band in KCl was found (1) to bleach thermally at 57°K with a release of free charge, (2) to bleach optically with a quantum efficiency of about 0.01 with no observable photocurrent, and (3) to be produced at 35°K by optical irradiation in a V_1 band that had been produced by x-irradiation at 77°K.

Seitz⁶ tentatively proposed that the H center consists of a hole trapped at a positive- and negative-ion vacancy pair. Such a center should provide free holes upon warming. These free holes could either annihilate F centers or be trapped by free positive-ion vacancies to form V_1 centers during the warmup to 77°K.

Varley⁷ and more recently Saint-James⁸ have suggested that the H band arises from an interstitial halogen atom that has trapped a hole.

Because of the relative simplicity of the absorption curves after x-irradiation at these low temperatures, it was thought that further knowledge of the H center would be valuable in attempting to understand the coloration processes. This paper gives the results of a study of the bleaching of the H center that is induced by irradiation with polarized light absorbed by the center. The symmetry of the H center is deduced from these results and compared with the symmetry of the models proposed by Seitz, Varley, and Saint-James. This work utilized the optical properties of anisotropic color centers that was first used by Ueta⁹ in establishing the symmetry of the M center in KCl.

ANALYSIS OF POLARIZED BLEACHING EXPERIMENTS

The symmetry of a color center is determined by the distribution of lattice defects that compose the center. The highest symmetry that a center can have is that of the lattice. For such a center, in a NaCl-type lattice, the amount of energy that can be absorbed from a light beam by an electron or hole that is trapped by the

TABLE I.^a Spectral location of the F , H , and V_1 bands at temperatures below 30°K.

	F (m μ)	H (m μ)	V_1 (m μ)
KCl	540	345	356
KBr	602	380	410
NaCl	454	330	345

^a See reference 2.¹ See F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954), for a comprehensive review of this subject.² W. H. Duerig and J. J. Markham, *Phys. Rev.* **88**, 1043 (1952).³ Markham, Platt, and Mador, *Phys. Rev.* **92**, 597 (1953).⁴ N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, New York, 1940), p. 134; G. Glaser, *Nachr. Akad. Wiss. Göttingen, Math.-physik. Kl.* **3**, 31 (1937).⁵ K. Teegarden and R. Maurer, *Z. Physik* **138**, 284 (1954).⁶ F. Seitz, *Phys. Rev.* **89**, 1299 (1953); *Revs. Modern Phys.* **26**, 7 (1954).⁷ J. H. O. Varley, *J. Nuclear Energy* **1**, 130 (1954).⁸ D. Saint-James, *J. phys. radium* **17**, 907 (1956); *J. phys. radium* **18**, 260 (1956).⁹ M. Ueta, *J. Phys. Soc. Japan* **7**, 107 (1952).

TABLE II. Anisotropy produced by bleaching with polarized light.

Centers with optical dipole moments oriented parallel to	Bleached with [100] light Absorption measured with light polarized along		Bleached with [110] light Absorption measured with light polarized along	
	[100]	[010]	[110]	[1 $\bar{1}$ 0]
(100)	(O.D.) ₁₀₀ decreases	No change in (O.D.) ₀₁₀	$\Delta(\text{O.D.})_{110} = \Delta(\text{O.D.})_{1\bar{1}0}$	
(110)	The initial rate of decrease of (O.D.) ₁₀₀ is twice that of (O.D.) ₀₁₀		The initial rate of decrease of (O.D.) ₁₁₀ is five times that of (O.D.) _{1\bar{1}0}	
(111)	$\Delta(\text{O.D.})_{100} = \Delta(\text{O.D.})_{010}$		(O.D.) ₁₁₀ decreases	No change in (O.D.) _{1\bar{1}0}

defects will not depend upon the polarization of the light. The optical dipole moment associated with this transition will not have a preferred orientation relative to the lattice and the center will appear isotropic. The *F* center is an example of such an isotropic center.

If the arrangement of the defects composing the center is such that only certain orientations in the lattice are possible, then the symmetry of the center will be lower than that of the lattice. The dipole moment associated with an optical transition of a trapped electron or hole will have a preferred orientation relative to the lattice. Such a center will absorb light most strongly if the electric vector of the light is parallel to the center's optical dipole moment. The *M* center is an example of such an anisotropic center.

If an absorption band becomes anisotropic after irradiation with polarized light absorbed by the band, then the color center responsible for the absorption is anisotropic. The symmetry of the center can be determined by noting the manner in which the absorption band is bleached by light of various polarizations.

Table II presents a summary of the changes that would be introduced in an absorption band in a NaCl-type crystal by bleaching with polarized light, if the band results from centers whose dipole moments are parallel to (100), (110), or (111). The light is presumed to enter the [001] face of the crystal. If the crystal is bleached with light polarized along [100], the absorption is measured with light polarized along [100] and [010]. Similarly absorption is measured with [110] and [1 $\bar{1}$ 0] light after bleaching with [110] light. The notation (O.D.)₁₀₀ indicates that the optical density [=log₁₀(*I*₀/*I*), where *I*₀ is the intensity of incident light and *I* is the intensity of transmitted light] was measured with the light polarized along [100].

The symmetry of a simple anisotropic center can be determined, then, by comparing the results obtained from polarized bleaching of the absorption band with the information given in Table II.

EXPERIMENTAL PROCEDURE

Figure 1 is a block diagram of the apparatus. A Bausch and Lomb grating monochromator (*M*) was used with a regulated tungsten or regulated hydrogen discharge lamp (*L*). The crystal (*S*) was cooled to

temperatures near liquid helium in the cryostat (*C*) described by Russell and Klick.¹⁰ An 0.040-inch thick beryllium window (*B*) was rotated into position for x-raying and the quartz windows (*Q*) were rotated into position for the optical measurements. The signal from a 1P28 photomultiplier (*PM*) was amplified by a General Radio dc amplifier and electrometer and recorded. A Wollaston prism (*P*), that transmits to wavelengths longer than 230 mμ, was used to polarize the measuring and bleaching light.

The bleaching lamp, an *H*-4 mercury lamp or a tungsten lamp with appropriate filters to select the spectral region desired, was inserted in place of the photomultiplier. The x-ray tube (tungsten target) was operated at 50 kvp and 20 ma. The photomultiplier and prism were removed so that the x-ray tube could be placed close to the beryllium window.

Crystals of KBr were obtained from Harshaw Chemical Company, the KCl from Optovac Company, and the KCl(Tl) were grown in this laboratory by the Bridgman technique. The pure KCl crystals from Optovac Company were free from Tl impurities within the limits of detection of our absorption and excitation apparatus. Sample thicknesses varied between one and two mm.

The absorption measurements were made as follows. A transmission spectrum of the crystal before x-raying was taken as a measure of the light incident upon the crystal. The optical density after x-raying was computed as the logarithm of the ratio of the transmission prior to x-raying to the transmission after x-raying; the same procedure was followed for computing the optical density after bleaching.

Absorption spectra that were taken in this way required that the photomultiplier and prism be accurately relocated after each x-irradiation or bleaching

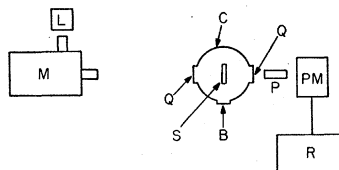


FIG. 1. Block diagram of the apparatus.

¹⁰ G. A. Russell and C. C. Klick, Phys. Rev. **101**, 1473 (1956).

and that the lamp brightness remain constant during various measurements. Variations in the alignment or lamp brightness manifest themselves as slight variations in the absorption background. These were insignificant in most cases.

RESULTS AND DISCUSSION

The absorption curves shown in Fig. 2 were obtained after a one hour x-irradiation at a temperature near liquid helium. Although the F and H bands are the most prominent, a small absorption band appears between them in KBr.¹¹ No information was obtained about the nature of this absorption.

Data on the anisotropic bleaching of the H band in KCl are shown in Figs. 3 and 4. The x-irradiations and bleaching were made near liquid-helium temperatures. Figure 3(A) was taken with light polarized along $[110]$ while 3(B) was taken with light polarized along $[1\bar{1}0]$. Curves 1 were taken after x-irradiation. Curves 2 were taken after the crystal had been bleached with 3.4-eV

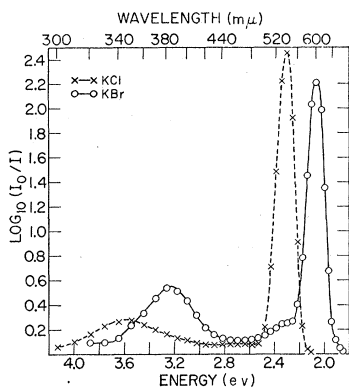


FIG. 2. Absorption spectrum of KCl and KBr. The crystals were x-irradiated and measured at temperatures near liquid helium.

(3650 Å) light polarized along $[110]$. It is seen that $(O.D.)_{110}$ decreased more than $(O.D.)_{1\bar{1}0}$.

Consider Fig. 4 where data are presented on the anisotropy induced by bleaching with light polarized along $[100]$. Figure 4(A) was measured with light polarized along $[100]$ while 4(B) was measured with light polarized along $[010]$. Curves 1 and 2 were taken after x-irradiation and bleaching, respectively. It is seen that $(O.D.)_{100}$ decreased more than $(O.D.)_{010}$.

A comparison of these data with Table II indicates that the centers giving rise to the H band in KCl behave as if they had optical dipole moments oriented parallel to $\langle 110 \rangle$.

The results obtained on KBr are more complicated. They are shown in Fig. 5. 5(A) and 5(B) were measured with light polarized along $[110]$ and $[1\bar{1}0]$, respectively. Curves 1 were taken after x-raying. Curves 2 were taken after a brief bleach with 3.4-eV light polarized along $[1\bar{1}0]$. The absorption measured with light polarized parallel to the bleaching light decreased

¹¹ Duerig and Markham (reference 2) observed this band and labeled it V_0 .

while the absorption measured with light polarized at right angles to the bleaching light increased markedly. Thus there were more centers that could absorb $[110]$ light after the bleach than there were before the bleach. The crystal was now bleached with light parallel to $[110]$. Curves 3 indicated that, although a general bleaching occurred for both polarization directions, $(O.D.)_{110}$ was now greater than $(O.D.)_{1\bar{1}0}$. This is the reverse of that shown in curves 2.

Curves 2 of Fig. 5 suggest that the H centers in KBr reorient under the action of the bleaching light.

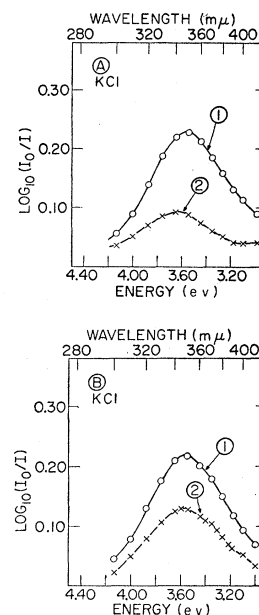
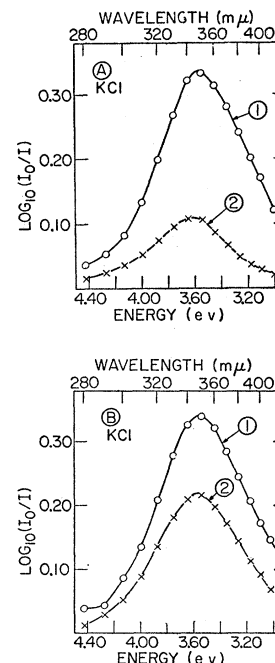


FIG. 3. Absorption spectrum of the H band in KCl. A—measured with light polarized along $[110]$, B—measured with light polarized along $[1\bar{1}0]$. Curve 1—after x-irradiation. Curves 2—after 55-min bleach with 3.4-eV light polarized along $[110]$. The x-irradiation and measurements were made at temperatures near liquid helium.

Figure 4: Absorption spectrum of the H band in KCl. Two subplots, A and B, show LOG10(I0/I) versus Wavelength (mμ) and Energy (eV). Subplot A shows curves 1 and 2 for light polarized along [100]. Subplot B shows curves 1 and 2 for light polarized along [010]. Both show a peak around 3.4 eV (3650 Å).

FIG. 4. Absorption spectrum of the H band in KCl. A—measured with light polarized along $[100]$, B—measured with light polarized along $[010]$. Curves 1—after x-irradiation. Curves 2—after 55-min bleach with 3.4-eV light polarized along $[100]$. The x-irradiation and measurements were made at temperatures near liquid helium.



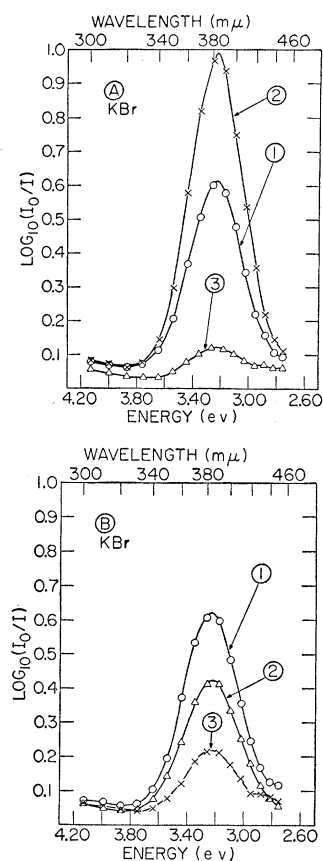


FIG. 5. Absorption spectrum of the H band in KBr. A—measured with light polarized along $[110]$. B—measured with light polarized along $[110]$. Curves 1—after x -irradiation. Curves 2—after 5-min bleach with 3.4-ev light polarized along $[110]$. Curves 3—after 10-min bleach with 3.4-ev light polarized along $[110]$. The x -irradiation and measurements were made at temperatures near liquid helium.

A comparison of the data of Fig. 5 with Table II indicates that the dipole moments cannot be parallel to $\langle 100 \rangle$, for anisotropy cannot be induced into dipoles oriented parallel to $[100]$ and $[010]$ by irradiating with $[110]$ light, even if the centers are reoriented by the light.

Another KBr crystal was strongly bleached with 3.4-ev light polarized along $[100]$. It was found that $(O.D.)_{100}$ was zero after the bleach while $(O.D.)_{010}$ had not changed. Thus, the optical dipole moments cannot be parallel to $\langle 111 \rangle$. A similar crystal was strongly bleached with 3.4-ev light polarized along $[110]$. After the bleach it was found that $(O.D.)_{110}$ was nearly zero while $(O.D.)_{1\bar{1}0}$ had increased slightly.

The above experimental results are consistent with the assumption that the optical dipole moments of the H centers in KBr are oriented parallel to $\langle 110 \rangle$ and that these centers can be made to reorient by the absorption of light.

No major reorientation of the dipoles was observed in KCl. However, a brief bleach with $[110]$ light produced a decrease in $(O.D.)_{110}$ that was appreciably greater than five times the decrease in $(O.D.)_{1\bar{1}0}$. This ratio should be five. A slight reorientation of the centers would result in a ratio greater than five. Thus, it seems likely that this process occurs in KCl, but to a much lesser degree than in KBr. As a result of the reorienta-

tion of the centers, the initial rates of decrease of the absorption that are given in Table II could not be experimentally verified.

It is concluded from the experimental results that the H centers in KCl and KBr have optical dipole moments oriented parallel to $\langle 110 \rangle$. The models proposed by Seitz,⁶ Varley,⁷ and Saint-James⁸ can now be compared with this observation.

The model suggested by Seitz has an axis of symmetry along $\langle 100 \rangle$ or $\langle 111 \rangle$ depending upon whether the vacancies are nearest neighbors or occupy sites along the body diagonal of the crystal. The optical dipole moment associated with these centers will likely have the direction of the symmetry axis. In neither case would the model agree with the experimental results.

The models by Varley and Saint-James would be expected to appear isotropic in the experimental arrangement used here.

It is evident from Figs. 3 and 4 that the H band in KCl changes shape somewhat under the action of the 3.4-ev bleaching light. The peak appears at slightly higher energies after the bleach than before. Such an effect is not evident in the KBr data. The shift in the H band in KCl could arise from a V_1 band that lies under the H band and which bleaches with a higher efficiency than does the H band.

It should be noted that the anisotropy that is produced in the H band in KCl and KBr does not result from the anisotropic bleaching of a V_1 band that may be under the H band. The work of Lambe and West¹² shows that the V_1 band cannot be anisotropically bleached with polarized light.

The F - and H -absorption bands that were produced by x -irradiation at temperatures near liquid helium are not represented by simple Gaussian curves. A plot of the data in the manner described by Russell and Klick¹⁰ shows that the F -band curves are broader on the high-energy side of the peak absorption while the H -band curves are broader on the low-energy side of the peak absorption.

As was reported by Markham, Platt, and Mador,³ irradiation with F light resulted in a simultaneous reduction of the F and H bands. If the bleaching results from a tunneling of the excited F -center electron to a nearby H center, then it is of interest to determine whether the nearness of the F and H centers produces nonisotropic F centers. This was tested by bleaching the F band in KBr with light polarized along $[110]$. No anisotropy was introduced into either the F or H bands, within the accuracy of the experiment. Likewise, no anisotropy was introduced into the F band when the H centers in KBr were reoriented (as shown in Fig. 5) by a brief bleach with 3.4-ev light.

The results of the simultaneous bleaching of the F and H bands with F light at temperatures near liquid helium can be used to determine the relative oscillator

¹² J. Lambe and E. J. West, Phys. Rev. **108**, 634 (1957).

strengths of the *F* and *H* centers. If one *H* center bleaches for each *F* center that bleaches, then the relative oscillator strength of the two centers is given by the ratio of the changes in area under the absorption curves. This ratio gives the minimum value of the oscillator strength of the *H* center, for some *F* centers may bleach without bleaching *H* centers. The half-widths of the absorption curves that were used in this calculation were taken from the present data and are given in Table III. Using these values, it was found that the *H*-center oscillator strength, f_H , was

$$f_H/f_F \geq 0.3 \pm 0.1 \text{ for KCl,}$$

and

$$f_H/f_F \geq 0.5 \pm 0.1 \text{ for KBr.}$$

Figure 6 is a plot of the optical density at the peak of the *F* and *H* bands as a function of x-ray time. After an hour of x-irradiation the crystal was bleached by a simultaneous irradiation into the *F* and *H* bands. This removed nearly all of the absorption. The crystal was now x-rayed for another 5 minutes. The *F* and *H* bands

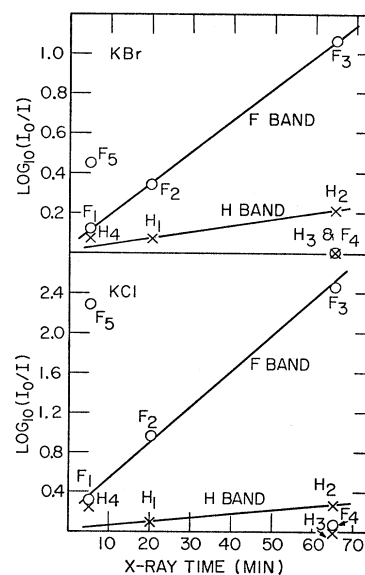
TABLE III. Half-widths of the *F* and *H* bands at temperatures near liquid helium.

	<i>F</i> band (ev)	<i>H</i> band (ev)
KCl	0.168	0.75
KBr	0.165	0.45

were substantially greater than after the original 5-minute x-irradiation. It appears that a substantial number of the defects produced by the x-rays are not removed by the bleaching light and that these are available for trapping electrons or holes during a subsequent x-irradiation.

The effect of thallium impurity upon the production of the *H* band was examined in KCl. No differences between the pure crystal and a crystal that contained less than 10 parts per million of Tl were noted after an hour of x-irradiation. However, an hour x-ray of a crystal containing about 1000 parts per million of Tl showed such a large absorption at somewhat lower energies that the *H* band was not resolvable. It is presumed that this large absorption is the same as has been reported by Yuster, Delbecq, and Smaller in KCl(Tl) after x-irradiation at liquid-nitrogen tempera-

FIG. 6. Optical density at the peak of the *F* and *H* bands as a function of x-irradiation time. Subscripts indicate the order in which the points were taken. H_3 and F_4 were taken after the crystal had been optically bleached. H_4 and F_5 were taken after the crystal was x-irradiated for another 5 min. The temperature was maintained near liquid helium.



ture,¹³ and which has been ascribed to the Cl_2^- molecule. Thus, the presence of the Tl impurity did not appreciably alter the *H* band.

CONCLUSIONS

The results of dichroic bleaching of the *H* band indicate that the center responsible for the absorption has an axis of symmetry parallel to $\langle 110 \rangle$. It has been suggested by Seitz⁶ that the *H* center consists of a hole trapped at a positive- and negative-ion vacancy pair, and by Varley⁷ and Saint-James⁸ that the center is a hole trapped by an interstitial chlorine atom. These models are inconsistent with the observed symmetry of the center. Although many models can be proposed that satisfy this symmetry, the present information does not allow one to choose among them. A specific model probably cannot be proposed until a search for the paramagnetic resonance of the center has been made.

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¹³ Yuster, Delbecq, and Smaller, Bull. Am. Phys. Soc. Ser. II, 2, 302 (1957).