multiplet. The numerous site symmetries have been observed[3,4] in several *different* $0 \rightarrow J$ transitions. In this connection, the optical Zeeman effect appears to be more versatile than ESR. Not only is the optical Zeeman method not restricted to a paramagnetic ground level, it also has the benefit of information from *several* J-levels, instead of only one as in the case of ESR.

In earlier work[8,11,12] on compensated lattices in KCl:M^{2+} and closely related systems, such as CaF_2:M^{3+} in which the F^- interstitial is the compensation, the prevailing assumption was that the impurity cation was either in close association with the compensation resulting in the removal of the inversion center of the impurity site or that the impurity cation is essentially in a cubic site beyond any significant influence of the distant compensation. On the other hand, the unique existence of the nn $C_{2v}(1,1,0)$ sites was postulated[10] in the interpretation of the $Sm^{2+}4f^6 \rightarrow 4f^45d^1$ absorption bands in alkali halides. In view of the present work, neither of the above two assumptions appears to be valid. According to the predicted distributions, "cubic" sites corresponding to large R_l values are highly improbable. None were observed spectroscopically.[3,4] The unique presence of the $C_{2v}(1,1,0)$ sites is in direct contradiction with the predicted distributions as well as the spectroscopic observation, particularly those of Watkins's in which the $C_{4v}(2,0,0)$ sites are seen to be predominant.

The above calculations apply only in the case of low temperatures (<500°) and high dilutions. In KCl:Sm^{2+} samples containing 10^{20} Sm^{2+} ions per cm^{-3}, a group of new lines appear in the ${}^5D_0 \rightarrow {}^7F_4$ transition energy region.[13] They probably arise from the association of Sm^{2+}: vacancy pairs through attractive dipolar forces. These lines were not observed in samples containing 10^{18} centers per cm^3. Similar problems are involved in the CaF_2:M^{3+} systems for which a number of site symmetries have been well established.[14] Clearly, the procedure outlined above can be readily applied to the CaF_2:M^{3+} systems.

---

[11] W. Hayes, G. D. Jones, and J. W. Twidell, Proc. Phys. Soc. (London) **81**, 371 (1962).

[12] F. K. Fong and M. A. Hiller, J. Phys. Chem. **71**, 2854 (1967); F. K. Fong, *ibid.* **41**, 2291 (1964).

[13] F. K. Fong, R. H. Heist, C. R. Chilver, J. C. Bellows, and R. L. Ford, J. Luminescence (to be published).

[14] C. W. Rector, B. C. Pandy, and H. W. Moos, J. Chem. Phys. **45**, 171 (1966).

PHYSICAL REVIEW VOLUME 187, NUMBER 3 15 NOVEMBER 1969

ESR and Optical-Absorption Study of the V_1 Center in KCl: NaCl†

Charles J. Delbecq, Elson Hutchinson, Dirk Schoemaker,
Edward L. Yasaitis, and Philip H. Yuster
Argonne National Laboratory, Argonne, Illinois 60439

(Received 19 June 1969)

The results of optical experiments show that the V_1 center in KCl has a strong transition at 357 nm and a weak transition at 560 nm. Both transitions have the same polarization and the transition moments are oriented approximately along ⟨110⟩. The optical measurements show further that the V_1 center disorients in the neighborhood of 17 K, and suggest that it consists of an H center trapped in the immediate vicinity of a substitutional Na^+. These optical measurements have been correlated with the anisotropic ESR spectrum of the V_1 center, which is best observed at 35 K. It is found that the V_1-center ESR spectrum is similar to that of an H center; however, the four nuclei of the Cl_4^{3-} molecule ion are all inequivalent, and the internuclear axis of the two central nuclei lies in a {100} plane and is tipped (5.7°±0.3°) away from the ⟨110⟩ direction. Furthermore, the central molecular bond is bent by about 3.5°. The ESR spectra reveal that the V_1 center is an H center trapped by a substitutional Na^+ impurity. The Na^+ lies in the {100} plane containing the Cl_4^{3-} molecule ion and is in a nearest-neighbor position to the central nuclei of the molecule ion. The reorientation of V_1 centers is sufficiently rapid to result in lifetime broadening of the ESR lines above 35 K, and at 50 K the ESR spectrum shows a collapsing of certain four-line groups into single lines, which indicates that a restricted interstitial jump is occurring. At 80 K, the V_1 ESR spectrum averages into an isotropic line at $g = 2.020$, with a linewidth of 100 G.

I. INTRODUCTION

The V_1 absorption band in KCl, situated at about 357 nm, and created at 77 K by x or γ irradiation, was first reported by Casler, Pringsheim, and Yuster.[1] Many models have since been proposed for the corresponding V_1 center. Seitz[2,3] first proposed that it was the antimorph of the F center, a positive hole trapped at a positive ion vacancy. Varley[4] concluded that the V_1 center consisted of an interstitial chlorine atom and four surrounding substitutional chloride ions

---

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

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

[2] F. Seitz, Rev. Mod. Phys. **18**, 384 (1946).

[3] F. Seitz, Phys. Rev. **79**, 529(L) (1950).

[4] J. H. O. Varley, Atomic Energy Research Establishment, Harwell, England, Report No. AERE-M/R-1508, 1954 (unpublished).

in a tetrahedral array. Känzig and Woodruff,[5] in their study of the H center, suggested that the V_1 center consisted of a neutral Cl_2 molecule located at a site normally occupied by a chloride ion. Cape[6] proposed that it was Cl_3^{2-} in a triangular configuration with one chlorine nucleus in a positive ion vacancy. Seitz[7] made a second proposal which he felt agreed with most of the experimental data available, i.e., that the V_1 center is an interstitial chloride ion. Delbecq and Yuster[8,9] suggested that the V_1 center is an H center with a sodium ion impurity as a nearest neighbor.

From time to time in the past ten years research has been carried out in our laboratory to determine the exact nature of the V_1 center. This work will be presented in chronological order with experiments and arguments to show that most of the models proposed for the V_1 center do not agree with experiment. Finally, it will be shown that the model proposed by Delbecq and Yuster from purely optical experiments has now been confirmed with the measurement of the anisotropic ESR spectrum of the V_1 center.[10,11]

II. EXPERIMENTAL PROCEDURE

The crystals used in these experiments were cleaved from large single crystals which were either grown in our laboratory in air by the Kyropoulos method, were purchased from the Harshaw Chemical Co., or were obtained from Oak Ridge National Laboratory. The crystals produced in this laboratory were grown from melts containing a mixture of 0.01 to 1.0 g of NaCl and 100 g KCl, or from nominally pure KCl. For the one crystal with added OH^- impurity, the melt consisted of 0.030 g of KOH, 0.30 g of NaCl, and 100 g of KCl. The crystal obtained from Charles Butler at Oak Ridge National Laboratory had been grown from KCl which was specially purified at Oak Ridge. The sodium content of the crystals used in these measurements was determined by neutron activation analysis. These analyses are reported in ppm by weight of Na^+. Color centers were produced by exposure of the crystal to a 2000-Ci ^{60}Co γ-ray source or by exposure to x rays from a Machlett tube with a tungsten target operated at 50 kV and 50 mA and filtered through a 1-mm fused silica plate. Absorption spectra were obtained by using a Cary 14 R recording spectrophotometer. Polarized light was produced by means of an Ahrens or Glan calcite prism. Optical excitation of the crystal was accomplished by exposure to light from an HBO-500 high-pressure mercruy arc lamp filtered by appropriate interference and/or Corning glass filters. In the optical experiments, the temperature was measured with either a carbon resistor or a copper-constantan thermocouple. The estimated error on these temperatures is ±0.3 K.

Several ESR spectrometers were employed in the course of this investigation. For measurements at and above 77 K, a Varian V-4500 spectrometer equipped with a variable temperature cavity and employing 100-kHz field modulation was used. For measurement at 4.2 K the same superheterodyne spectrometer was used as for the H-center investigation.[12] For the measurements at 20.4 K, a specially constructed homodyne spectrometer using 100-kHz field modulation was employed. The sample was immersed in liquid hydrogen in the unsilvered narrow tail (o.d. 15 mm) of a quartz Dewar, which could be inserted in a cylindrical cavity operating in the TE_{011} mode. The sample could be irradiated with light through slits in the cavity wall. For the variable-temperature ESR measurements between 4.2 and 80 K, basically the same homodyne spectrometer was used, but now in conjunction with an Andonian variable temperature Dewar. [Double-field modulation was used (100 kHz and 40 Hz); therefore the second derivative of the ESR absorption is exhibited.] The innermost chamber of this Dewar, which can be entered from the top for sample insertion, was cooled by evaporating liquid helium at the bottom. Liquid helium is transported into this innermost chamber through a small capillary tube connected to the helium container. The flow of helium can be controlled from the top of the Dewar by a valve. The cavity was a cylindrical quartz cavity working in the TE_{011} mode and was coupled to a straight section of X-band waveguide. The samples, which were approximately $3\times3\times14$ mm^3, were loaded under liquid nitrogen into thin-walled quartz tubes which slid over a second long quartz tube. This combination containing the sample was then quickly transferred to the cooled cavity in the Dewar through the top and through the length of the waveguide. The long quartz tube was also used as a light pipe and allowed irradiation of the sample with light while in the cavity. On the cavity were placed a carbon resistor, a platinum resistor and a heating coil. These were connected to a Cryogenics Research TC101 temperature controller and allowed us to vary the temperature and control it to better than 0.1 K. We estimate that the measured temperatures in the ESR experiments are accurate to ±1 K.

III. EXPERIMENTAL OPTICAL RESULTS

The first experiments to determine the symmetry of the V_1 center were performed by Lambe and West[13]

---

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

[6] J. A. Cape, Phys. Rev. **122**, 18 (1961).

[7] F. Seitz, Phys. Rev. Letters **7**, 282 (1961).

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

[9] P. H. Yuster, Bull. Am. Phys. Soc. **12**, 550 (1967).

[10] D. Schoemaker, C. J. Delbecq, and P. H. Yuster, Bull. Am. Phys. Soc. **14**, 325 (1969).

[11] F. J. Keller and F. W. Patten, Bull. Am. Phys. Soc. **14**, 325 (1969).

[12] C. Delbecq, J. Kolopus, E. Yasaitis, and P. Yuster, Phys. Rev. **154**, 866 (1967).

[13] J. Lambe and E. J. West, Phys. Rev. **108**, 634 (1957).

and Delbecq, Smaller, and Yuster.[14] They were not able to produce any anisotropy at 77 K in the V_1 absorption by bleaching with polarized light. This result was not inconsistent with the first model of the V_1 center proposed by Seitz, a positive hole trapped at a positive ion vacancy and shared equally by the six surrounding chloride ions. Such a center would not be expected to show anisotropy. However, even a center that has an anisotropic optical transition will not show an absorption anisotropy after excitation with polarized light if the axis of the center is not fixed in orientation in the lattice for a time comparable to the measurement time of the experiment. One must, therefore, be sure that the experiment is performed at a temperature which is low enough to insure that the axis of the center is fixed in the crystal.

The next experiments were, therefore, performed at ~5 K.[15,16] At this temperature it was observed that an anisotropy could be produced in the V_1 absorption. The conclusion drawn from the experiments was that the optical dipole moment of the transition lay along $\langle 110\rangle$, or within several degrees of that direction. Because of the rather slow change in $\cos^2\theta$ around zero degrees, the optical method for determining the direction of the optical dipole moment of the transition is not very precise.

Previous to the production of anisotropy in the V_1 center, some of the properties of a very important electron-deficient center, the H center, had been determined. Compton and Klick[17] showed that at 4.2 K, the optical dipole moment of the ultraviolet transition of the H center in KCl lies along $\langle 110\rangle$; Känzig and Woodruff[5] determined its structure with the use of ESR techniques. The model which Känzig and Woodruff proposed is a Cl_2^- located in a single negative ion site. While the unpaired electron spends essentially all its time on the two central nuclei in the V_K center,[18] in the H center the unpaired electron spends about 10% of its time on the two chlorines adjacent to the central Cl_2^- and lying along its axis, a $\langle 110\rangle$ direction.

Teegarden and Maurer[19] showed with optical experiments at 5 K that if the V_1 center is excited with ultraviolet light, then H centers are formed. Känzig and Woodruff[5] confirmed this result with ESR. They did not observe any ESR to be associated with the V_1 center and assumed it was diamagnetic. The model which they proposed was very similar to the H center but instead of a Cl_2^- in a negative ion site, they suggested the V_1 center is a neutral Cl_2 in a negative ion site. In both centers an interstitial chlorine atom is present.

In addition, they suggested that the following reaction is responsible for the optical conversion of the V_1 center to the H center:

$$Cl_2(s,i)+e\rightarrow Cl_2^-(s,i)\,, \tag{1}$$

where s and i indicate a species located on a substitutional or interstitial site, respectively. The electrons in this reaction were believed to come from F' centers through light excitation in the wavelength region of the V_1 band (300–400 nm). To check this hypothesis we exposed a crystal at 77 K containing V_1 centers, F centers, and F' centers to light of wavelength longer than 750 nm, which eliminates all F' centers. No appreciable change in the V_1 band was observed. Then the crystal was cooled to 5 K and exposed to light absorbed by the ultraviolet V_1 band. The decomposition of the V_1 center proceeds just as easily without F' centers as it does when they are present. It can also be shown that F centers are not a source of electrons in this reaction by carefully observing the change in the F band which accompanies the change in the V_1 band; there are far fewer F centers destroyed than V_1 centers. In addition it was found that bleaching of the F' or F bands at 5 K did not result in the conversion of V_1 into H centers. Thus, although the anisotropic bleaching experiments at 5 K on the V_1 center are not inconsistent with the model of Känzig and Woodruff, reaction (1) is not responsible for the conversion of V_1 centers to H centers. There are at least two other ways that V_1 may be converted to H by optical means if one assumes that the V_1 center is a Cl_2 located at a single negative-ion site:

$$Cl_2(s,i)\overset{h\nu}{\rightarrow}Cl^0(s)+Cl^0(i)\,, \tag{2a}$$

with the products undergoing the reactions

$$Cl^0(s)+Cl^-(s)\rightarrow Cl_2^-(s,s)\,, \tag{2b}$$

$$Cl^0(i)+Cl^-(s)\rightarrow Cl_2^-(s,i)\,, \tag{2c}$$

and

$$Cl_2(s,i)\overset{h\nu}{\rightarrow}2Cl^0(i)+\ominus \tag{3a}$$

followed by

$$2Cl^0(i)+2Cl^-(s)\rightarrow 2Cl_2^-(s,i)\,. \tag{3b}$$

If the conversion of V_1 to H proceeds by reactions (2), according to (2b) one V_K center should be formed for each V_1 center destroyed. Using ESR we have looked for the formation of V_K centers during this conversion and have found none.

If reactions (3) occur, a negative-ion vacancy ($\ominus$, α center) should be formed for each V_1 destroyed. A search for the formation of the negative-ion vacancy, which absorbs at 1780 A, was made during the conversion of V_1 to H and none was found. Cape,[6] working independently, also observed this result. We therefore

---

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

[15] C. J. Delbecq and P. H. Yuster, in Proceedings of the International Symposium on Color Centers in Alkali Halides, Stuttgart, Germany, 1962 (unpublished).

[16] P. H. Yuster and C. J. Delbecq, Bull. Am. Phys. Soc. **8**, 541 (1963).

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

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

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

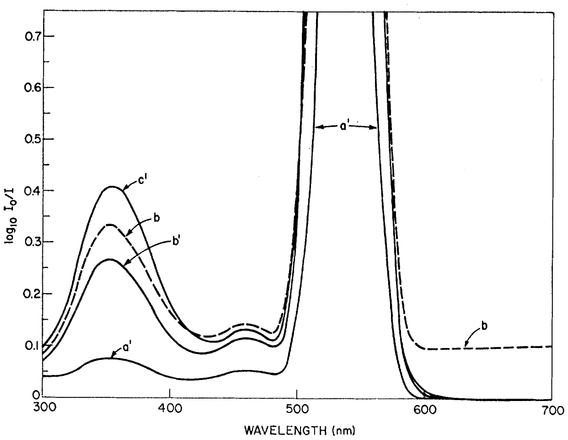

FIG. 1. V_1-band formation in KCl crystals containing different concentrations of Na^+. All crystals were 4.1 mm thick and were irradiated at 77 K with a 2000 Ci ^{60}Co source for 4 h. Curve (b) absorption introduced into KCl+5.8-ppm Na^+ after above treatment. All crystals were subsequently exposed to HBO-500 +Corning filter No. 2540 for 1 min, then to HBO-500+Corning filter No. 3480 for 1 min. The primed curves indicate that the crystals had optical treatment after γ irradiation. Curve (a'), KCl+0.2-ppm Na^+ (Oak Ridge crystal), curve (b'), KCl+5.8-ppm Na^+, curve (c'), KCl+15.2-ppm Na^+. All measurements were performed at 77 K.

conclude that neither reactions (2) nor (3) occur appreciably. These results, taken together with the previously described results, suggest that the model of Känzig and Woodruff is incorrect.

It became apparent after a sufficient amount of data was accumulated in our laboratory that the concentration of V_1 centers which could be produced in KCl varied from one batch of crystals to the next. These results suggested that impurities play an important role in the formation of the V_1 center. One possible impurity is the sodium ion and, therefore, a study was made of the intensity of the V_1 band produced by radiation as a function of sodium ion concentration. Figure 1 shows some of the results of this study. In the purest crystals we could obtain from Oak Ridge National Laboratory very few, if any, V_1 centers are formed. {We were unable to determine whether the absorption from 300–400 nm [Fig. 1(a')] which was produced in the Oak Ridge crystal was caused by the presence of V_1 centers; the concentration was too small for identification purposes.} One of the crystals studied (Fig. 1, curves *b* and *b'*) was grown from Analytical Reagent Grade KCl, and although no NaCl was added in the growth of the crystal, it contained 5.8 ppm of Na^+. "Pure" KCl contains varying amounts of Na^+ depending upon its source. Analysis of some of the crystals used in our past studies revealed that those crystals which showed appreciable V_1-band formation also showed an appreciable concentration of Na^+. Conversely, those crystals in which we could obtain only low concentrations of V_1 centers had very low Na^+ concentrations. These results indicate that Na^+ impurity in KCl plays an important role in the formation of V_1 centers.

Further experimental work on crystals containing up to 150 ppm of Na^+ showed very little increase in the concentration of V_1 centers over that obtained in the 15.2-ppm Na^+ crystal if the radiation dose was the same as that given the crystals described in Fig. 1. If we anticipate a conclusion to be drawn in later paragraphs of this paper, that the V_1 center is an H center trapped at a sodium ion, we can understand why such low concentrations of Na^+ are so efficient in producing V_1 centers; the efficiency appears to be related to the long range that an interstitial chlorine atom has before it is captured by an Na^+ to form a V_1 center. The long range is very likely a result of the neutral character of the diffusing chlorine atom and the relatively low concentration of species that can annihilate the atom.

The results shown in Fig. 1 (curves a', b', and c') were obtained on crystals which were treated in the following manner so that other centers which have absorption bands in the region of the V_1 band were eliminated: After exposure at 77 K to γ rays the crystals contain, in addition to V_1 centers, F, F', and V_K centers as well as some as yet unidentified rather weak absorption in the region 200–280 nm. F, F', and V_K centers all have transitions in the same region of the optical spectrum as the V_1 center. F' centers were eliminated first by excitation with light of wavelength longer than 750 nm. At the same time, a large number of V_K centers are destroyed because of the recombination of the electrons from the F' centers and the holes of the V_K centers. This reaction is very efficient because the V_K center is charged positively relative to the lattice, and attracts the electron. The next step involves excitation of the crystal with light having wavelengths longer than 570 nm; only a short (1–2 min) exposure to the HBO-500 high-pressure mercury arc lamp plus Corning No. 3480 filter is sufficient to destroy all of the V_K centers and a small fraction of the F centers. This fact has been confirmed using ESR techniques to monitor the concentration of the V_K centers. In this series of optical excitations, only a small fraction of the V_1 centers is destroyed. Further excitation in the long-wavelength tail of the F band causes only a very slow reduction in the height of the V_1 band. From the above results we conclude that the V_1 center probably is not positively charged relative to the lattice and therefore does not attract electrons as the V_K center does. In our study of the anisotropic optical absorption of the V_1 center, all *x*-ray- and γ-ray-irradiated crystals were treated in the above manner before excitation with polarized light. Since it has been shown that the V_K center has a $\langle 110 \rangle$ allowed transition with the absorption peak at 367 nm, it is important to remove these centers so that the V_K absorption cannot interfere with the V_1 absorption.

There are further problems in obtaining the anisotropic spectrum of the V_1 center even if all other absorptions in this region of the spectrum could be removed. Excitation with light absorbed in the 357-nm band of the V_1 center produces H centers. These H centers have a $\langle 110 \rangle$ allowed transition with an absorption maximum at 338 nm, which will interfere with the V_1 spectrum. We have found, however, that the V_1 center has a very weak $\langle 110 \rangle$ polarized transition at 560 nm. Excitation of this long-wavelength transition with polarized light does produce preferential orientation of V_1 centers and causes very little, if any, decomposition into H centers. Consequently, excitation with long-wavelength polarized light ($\lambda > 600$ nm) enables us to obtain the anisotropic absorption of the V_1 center with very little interference from other ansiotropic centers.

The anisotropic optical-absorption spectrum is one of the properties of the V_1 center which we use to characterize it. Another, more sensitive, property is the disorientation temperature of the center. The anisotropy in the optical absorption is produced at 5 K and persists as the crystal is warmed until, in the neighborhood of 16 K, it begins to disappear. Figure 2 shows such a measurement of the recovery of the absorption in the $[0\bar{1}1]$ direction, after excitation with $[01\bar{1}]$ light at 5 K, as the crystal is warmed slowly (0.5 K/min). The temperature at which half the anisotropy in this direction is recovered, 16.8 K, is defined by us as the disorientation temperature of the V_1 center. This temperature, for a given rate of heating, is very characteristic of the center and is the same, within experimental error, for all $\langle 110 \rangle$ disorientation experiments on the V_1 center which we have run; this includes all experiments before we knew that the Na^+ ion plays an important role in the V_1 center.

Since the H center involves an interstitial chlorine atom and the H center can be produced so easily from V_1 centers by relatively low-energy (e.g., 400 nm) optical excitation, it seems reasonable to assume that the V_1 center also contains an interstitial chlorine atom. Further proof that an interstitial is involved in the V_1 center is found in some experiments which we have performed on the conversion of V_1 centers to FCl^-. FCl^- contains an interstitial,[20] and in crystals containing both F^- and Na^+ ions, both the thermal decay at 113 K and the optical decomposition of V_1 at 77 K lead to an increase in the concentration of FCl^-. These facts can easily be explained if it is assumed that the decomposition of the V_1 center yields an interstitial chlorine atom which diffuses until it is captured by a substitutional F^- ion and becomes FCl^-. Although the results discussed to this point indicate that the V_1 center involves an interstitial and that a sodium ion is somehow involved in the formation of the V_1 center, it has not been shown that the Na^+ is an integral part of the center. The presence of the Na^+ could, for example, allow easier production of interstitials. We have, however, performed optical experiments which show that the Na^+ is part of the V_1 center.

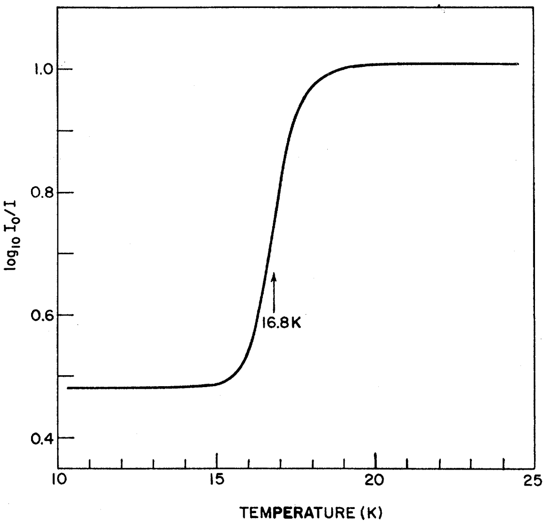

FIG. 2. Disorientation of the V_1 center. Recovery of the $[0\bar{1}1]$ absorption at 357 nm, after excitation with $[01\bar{1}]$ light, while warming the crystal at 0.5 K/min. The anisotropy was produced at 5 K by excitation with light of wavelength longer than 600 nm.

Kingsley[21] showed that H centers could be generated in a KCl:KOH crystal if it is exposed at 5 K to light absorbed by the OH^- impurity at 205 nm. Cape[6] expanded this work and studied the conversion of H centers to V_1 centers by thermal annealing, and the regeneration of H centers by optical excitation of the V_1 centers. Our experiments indicate that the efficiency of formation of H centers by optical excitation of OH^- is independent of the Na^+ concentration. Consequently, we conclude that Na^+ ions are not involved in the formation of interstitials (which eventually produce H centers) by optical excitation of OH^-. When these crystals which contain H centers and little Na^+ are warmed, very few V_1 centers are formed; the H centers are destroyed thermally without the production of V_1 centers. However, when a crystal containing H centers and an appreciable concentration of Na^+ is warmed, about 80% of the H centers can be converted to V_1 centers. Since interstitials are produced with an efficiency which is independent of the Na^+ concentration, yet the V_1 center is formed only when Na^+ is present, we conclude that the Na^+ is an integral part of the V_1 center.

Figure 3(A) shows the absorption introduced into a KCl crystal containing both OH^- and Na^+ impurities after exposure at 5 K to the unfiltered light of an AH4 medium-pressure mercury arc lamp for 80 min. A large H band at 338 nm, a very small F band, and some absorption at about 310 nm of unknown origin are produced. The F band can be almost completely

---

[20] J. W. Wilkins and J. R. Gabriel, Phys. Rev. **132**, 1950 (1963).

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

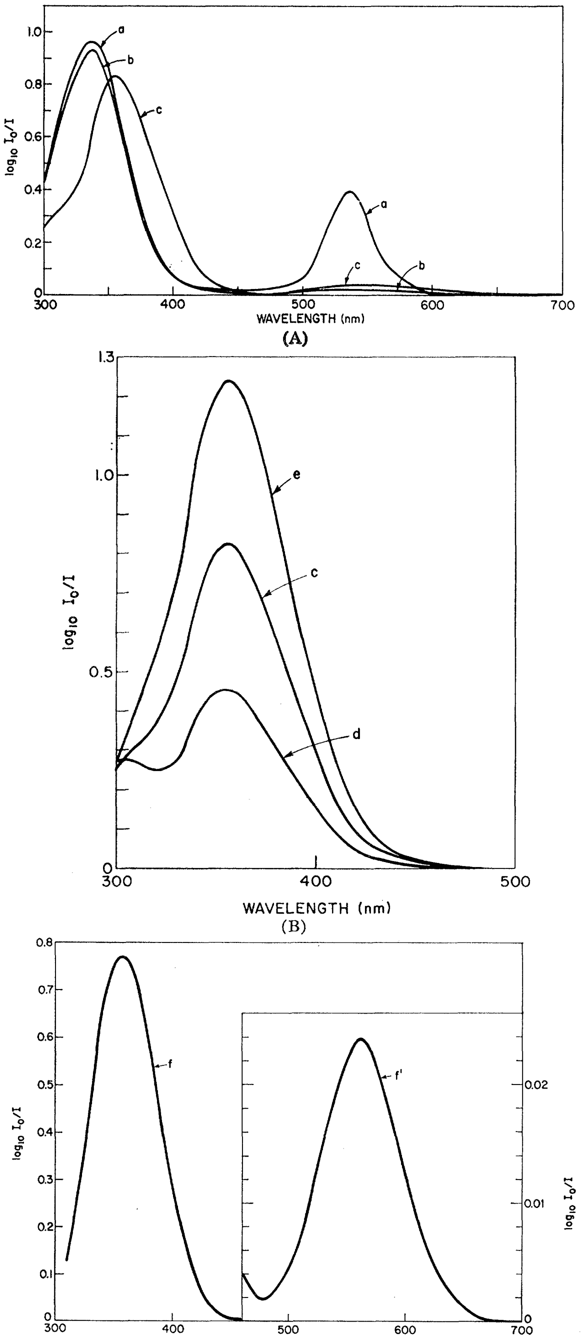

FIG. 3. (A): (a) Absorption introduced into a KCl:KOH:NaCl crystal at 5 K by exposure to the unfiltered light of an AH-4 mercury arc lamp for 80 min; (b) bleached at 5 K with HBO-500+Corning filter No. 3389 for 5 min; (c) warmed to 50 K for 10 min, then cooled to 5 K and remeasured. (B): (c) Remeasure curve (c) of (A) at 5 K with [011] and [0$\bar{1}$1] polarized light. Excite at 5 K with [0$\bar{1}$1] polarized light from HBO-500+Corning filter No. 3480 for 20 min and remeasure with [0$\bar{1}$1] light (d) and [011] light (e). (C): Anisotropic spectrum of V_1 center obtained by subtracting curve (d) of (B) from curve (e) of (B). The ordinate associated with curve (f′) is expanded by a factor of 25. This long-wavelength band was not plotted in (B) because of its low intensity.

eliminated by excitation with light of wavelength longer than 410 nm. (Cape[6] also reported that the F band was very low in KCl:KOH crystals after proper treatment. However, the F band was apparently never low enough so that he could observe the weak absorptions of the H or V_1 center in that region of the spectrum.) One also observes in this figure the very weak secondary band of the H center at 522 nm. After having warmed to about 50 K, the V_1 band at 357 nm has formed and a change has occurred in the absorption spectrum between 500 and 700 nm. This change is caused by the disappearance of the 522-nm H band and the formation of the secondary V_1 band at 560 nm. Figure 3(B) shows the change in the [011] and [0$\bar{1}$1] absorption after exposure to [0$\bar{1}$1] light of wavelength longer than 570 nm. Figure 3(C) is the anisotropic spectrum of the V_1 center obtained by subtracting curve d of Fig. 3(B) from curve e of Fig. 3(B). There are considerable similarities between this curve for the V_1 center and the curves for the V_K center and the H center. These similarities suggest that in all of these centers one is dealing with the same basic chemical species, namely Cl_2^-. Table I gives a comparison of some properties of H and V_1 centers as determined by optical techniques.

In summary, the results of all the experiments described in this section can be understood if we assume that the V_1 center consists of an H center trapped in the immediate neighborhood of an Na^+ ion in the KCl lattice. This is the model for the V_1 center which has been proposed by Delbecq and Yuster.[8,9] (Dakss and Mieher have reported a somewhat similar center in LiF.[22])

IV. EXPERIMENTAL ESR RESULTS

A. Detection of the Spectra

The results presented in Sec. III indicated that the V_1 center consists of an H center trapped in the immediate neighborhood of an Na^+ ion. If this model is correct, one would expect the center to be paramagnetic. Therefore, in order to test the proposed model, an intensive search was made to determine if there is an ESR spectrum associated with the V_1 center. Since the H center ESR spectrum can be observed at 20.4 K [5] and at 4.2 K,[12] although the microwave power must be drastically reduced to avoid saturation at this latter temperature, it was felt that a careful search at these temperatures might show the V_1 ESR spectrum, in spite of previous unsuccessful searches.[5,8,9]

A careful investigation of an x-irradiated KCl:NaCl crystal at 4.2 K, with the same superheterodyne spectrometer as used in the H-center investigation, failed to yield the V_1 ESR spectrum, though there was evidence that a very strongly saturated signal was present in the crystal. Measurements at 20.4 K with

---

[22] M. L. Dakss and R. L. Mieher, Phys. Rev. Letters **18**, 1056 (1967).

TABLE I. Characteristics of the H and V_1 centers.

	Optical absorption bands				
	Peak position (nm)	Half-width (eV)	Relative intensity	Polarization[a]	Disorientation temperature (K)
H center	338	0.66	~100	σ(s)	10.9
	522	~0.25	1	σ(w)	
V_1 center	357	0.65	70[b]	σ(s)[c]	16.8
	560	0.32	1[b]	σ(m)[c]	

[a] (s), (m), and (w) indicate strong, medium, and weak degrees of polarization, respectively.

[b] These numbers were obtained from the anisotropic spectrum of Fig. 3(C).

[c] Since the ESR spectrum of the V_1 center saturates so strongly, we are unable to make ESR measurements at sufficiently low temperatures to observe preferentially oriented V_1 centers. Consequently, we cannot use ESR techniques to determine the sense of polarization of the optical transitions. Our experiments only show that the two optical transitions of the V_1 center have the same polarization. By analogy with centers H and V_K, it is assumed that the transitions are σ-polarized.

both a superheterodyne and a homodyne spectrometer yielded very weak, and therefore unusable, ESR signals. Since the V_1 center, in contrast to the H center, is stable at relatively high temperatures (V_1 decays at 113 K and H at 39 K), a careful search was also made at 80 K using the Varian spectrometer. Figure 4 shows that at this temperature a strong line at $g=2.020$ with a width of 100 G is observed; it is not saturated even when the full available microwave power (125 mW) is used. This line has the same thermal-decay properties as the optical V_1 band.[14] Furthermore, since the V_1 center is believed to be a perturbed H center, and since the observed isotropic g value is close to the average of the g components of the H center, it is concluded that this isotropic line represents the motionally averaged V_1 ESR spectrum.

Since the ESR spectra of a number of interstitial-containing centers had been readily observed,[23–25] the difficulty in observing the anisotropic V_1 ESR spectrum at 4.2 and 20.4 K was attributed to the unusually long relaxation time of the V_1 center. It seemed likely that at some temperature between 20.4 and 80 K, the anisotropic V_1 spectrum would be observed since the relaxation lifetime of the center would be expected to decrease as the temperature is increased.

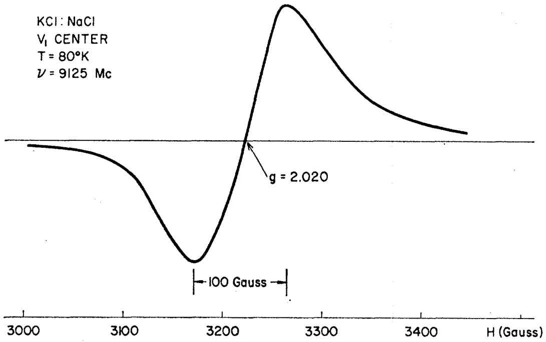

FIG. 4. Motionally averaged isotropic V_1-center ESR spectrum in KCl+150-ppm Na$^+$ at 80 K. The first derivative of the absorption is presented. This figure was redrawn from the experimental spectrum and corrected for some baseline shift.

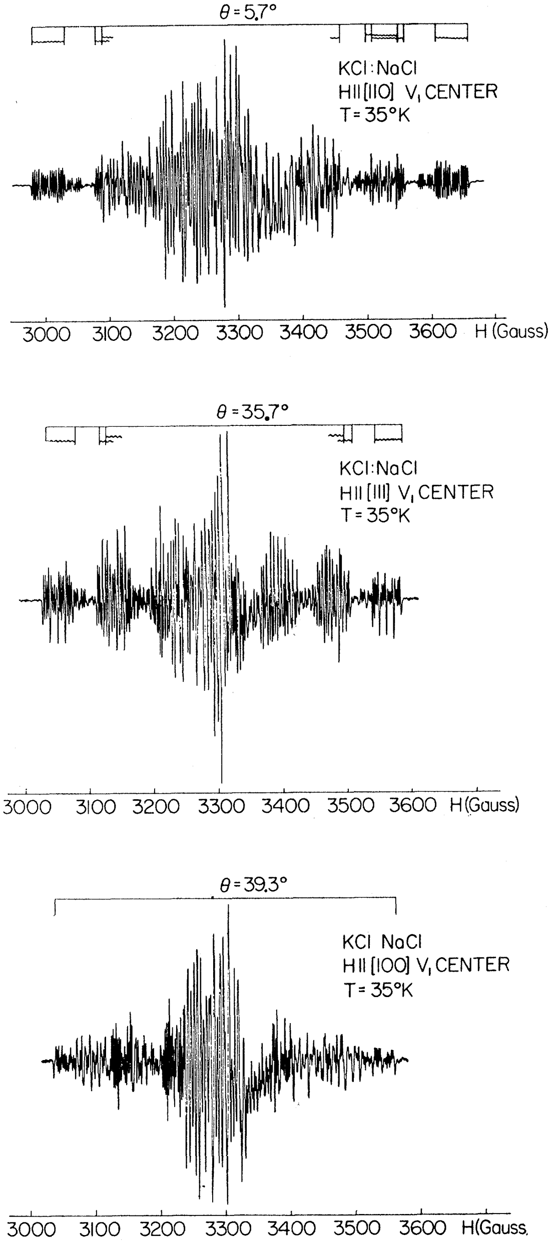

FIG. 5. Anisotropic V_1 center ESR spectra in KCl+150-ppm Na$^+$ for three special orientations of the magnetic field **H**, observed at 35 K. The second derivative of the absorption is presented, and the spectra were obtained after optically bleaching the V_K centers.

The final search, using a homodyne spectrometer with an Andonian variable temperature Dewar, readily yielded the anisotropic V_1 ESR spectrum which is shown in Fig. 5. It was found that the optimum temperature for measurement of the well-resolved aniso-

---

[23] D. Schoemaker, Phys. Rev. **149**, 693 (1966).

[24] J. L. Kolopus, C. J. Delbecq, D. Schoemaker, and P. H. Yuster, Bull. Am. Phys. Soc. **12**, 467 (1967).

[25] D. Schoemaker, Bull. Am. Phys. Soc. **12**, 410 (1967).

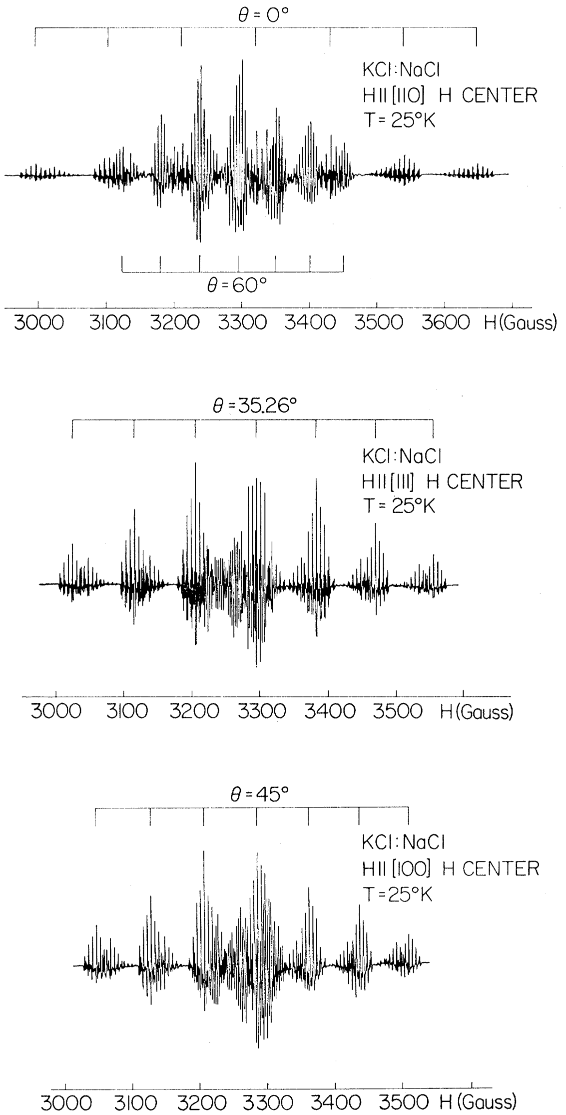

FIG. 6. H-center ESR spectra in KCl+150-ppm Na^+ for three special orientations of the magnetic field **H**. The second derivative of the absorption is presented. These H centers were obtained by optical conversion from V_1 centers by excitation with 405-nm light.

tropic ESR spectrum of the V_1 center is about 35 K using a microwave power of about 1.5 mW; above this temperature the lines begin to broaden.

B. Qualitative Analysis

The anisotropic ESR spectra of the V_1 center are shown in Fig. 5 for three special orientations of the magnetic field **H** with respect to the crystal axes. These spectra were recorded after optically bleaching the V_K centers by exciting the F' and F centers. Before the bleach, these V_K centers, which have single well-resolved lines, were often used to align the crystal accurately with respect to the magnetic field. A qualitative analysis of the V_1 spectra is facilitated by comparing it with the H-center ESR spectra which are shown in Fig. 6. Since the H-center ESR spectra have been analyzed extensively by Känzig and Woodruff,[5] only the more important features will be discussed. It will also be convenient to refer to the models of the V_1 and H centers which are given in Figs. 7(a) and 7(b). In drawing the model of the V_1 center in Fig. 7(a), a specific choice for the configuration of the nuclei 1, 2, 3, and 4 with respect to each other and with respect to the Na^+ was made. It should be stressed, however, that the nuclear configuration cannot be unambiguously derived from the ESR results. In fact, there are other possible configurations and they will be discussed later on.

Figure 6 shows that basically the H-center spectrum consists of seven groups of lines; the groups have relative intensities 1:2:3:4:3:2:1. This "seven-line" feature is readily explained by assuming that the unpaired electron of the H center interacts strongly with two equivalent chlorine nuclei of spin $\frac{3}{2}$ in a Cl_2^- molecule ion [nuclei 1 and 2 in Fig. 7(b)]. There are two chlorine isotopes, namely ^{35}Cl, 75% abundant with nuclear moment $\mu = 0.82091$, and ^{37}Cl, 25% abundant with $\mu = 0.68330$. Consequently there are three isotopically distinct Cl_2^- species, namely $^{35}Cl^{35}Cl^-$, $^{35}Cl^{37}Cl^-$, and $^{37}Cl^{37}Cl^-$, which have relative abundances of 9:6:1. These isotope effects are resolved for the H center, but are even more easily seen in the ESR spectra of the V_K-type Cl_2^- center which was analyzed by Castner and Känzig.[18] For instance, the highest or lowest field groups of lines of the Cl_2^- spectrum consist of three lines which experimentally are close to the 9:6:1 ratios. However, as can be seen in Fig. 6, in the case of the H center each of these basic Cl_2^- lines is further split into superhyperfine structure of seven lines with intensity ratios 1:2:3:4:3:2:1. This splitting is explained by assuming that the unpaired electron of the H center, in addition to its strong interaction with nuclei 1 and 2, also interacts weakly with two other equivalent chlorine nuclei [3 and 4 in Fig. 7(b)]; a

TABLE II. Classification of the V_1 and H centers for three important orientations of the static magnetic field **H** with respect to the crystal axes. θ and φ are measured from z and x, respectively.

Direction of **H**	Angle (θ; φ) H center	Angle (θ; φ) V_1 center	Degeneracy or relative intensity H center	Degeneracy or relative intensity V_1 center
⟨110⟩	(0°; φ)	(5.7°; 90°)	1	2
	(60°; 35.3°)	(56.8°; 32.3°)	4	4
		(63.4°; 37.7°)		4
	(90°; 90°)	(84.3°; 90°)	1	2
⟨001⟩	(45°; 90°)	(39.3°; 90°)	4	4
		(50.7°; 90°)		4
	(90°; 0°)	(90°; 0°)	2	4
⟨111⟩	(35.3°; 0°)	(35.7°; 8.0°)	3	6
	(90°; 54.7°)	(85.4°; 54.6°)	3	6

close inspection of this superhyperfine structure shows that all chlorine isotope effects are also resolved. One can look upon an H center as being a $\mathrm{Cl_4}^{3-}$ molecule ion with $3^2=9$ different isotopic molecular species. An analysis of the angular variation of the H center spectrum shows that this $\mathrm{Cl_4}^{3-}$ is linear and oriented precisely along a $\langle 110\rangle$ direction of the crystal. Table II shows the types and degeneracies of spectra that should be observed for three special orientations of the external magnetic field $\mathbf{H}$. Some of the readily identified spectra are indicated in Fig. 6.

Turning now to the V_1 ESR spectra of Fig. 5, one notices that there are again seven groups of lines (see, e.g., $\mathbf{H}\|\langle 111\rangle$), with about the same hyperfine separation as for the H center. These two facts indicate that the unpaired electron of the V_1 center also interacts strongly with two chlorine nuclei of a $\mathrm{Cl_2}^-$ species, but in contrast to the H-center spectra, these seven groups do not show the 1:2:3:4:3:2:1 intensity ratios. Rather the groups have about equal intensities. One must conclude that chlorine nuclei 1 and 2 in Fig. 7(a) are somewhat inequivalent, i.e., the hyperfine interaction is slightly different (according to analysis less than 8%) for the two nuclei. This has the result that a line that has a degeneracy n in the case of the H center is split into n lines of equal intensity for the V_1 center. Thus the central $\mathrm{Cl_2}^-$ of the V_1 center is better represented by writing $\mathrm{Cl(1)Cl(2)^-}$, where 1 and 2 are identified with the larger and smaller hyperfine interactions, respectively. The inequivalence of these two nuclei, which gives information concerning the possible locations of the $\mathrm{Na^+}$ in the V_1 center, arises principally from the asymmetric strain field surrounding the molecule ion. This local strain field is caused by the small $\mathrm{Na^+}$ ion in the KCl lattice.

Each of the basic seven V_1 "lines" shows a superhyperfine structure of 16 lines of roughly equal intensity. Of course the 1:2:3:4:3:2:1 superhyperfine structure of the H center is also a 16-line pattern, but with degeneracies brought about by the equivalence of nuclei 3 and 4. This 16-line superhyperfine structure of the V_1 center is most easily seen for the lowest and the highest field lines of the spectra (see Figs. 5 and 8). The experimental spectra clearly divide these lines into four groups of four each. This superhyperfine structure is explained by assuming that the unpaired electron of the V_1 center interacts weakly with two other nuclei with nuclear spin $\frac{3}{2}$ [3 and 4 in Fig. 7(a)] and that the interaction with nucleus 3 is about four times larger than the interaction with nucleus 4. The V_1 center can also be considered to be a $\mathrm{Cl_4}^{3-}$ molecule ion, but in contrast to the H center, all four chlorine nuclei are inequivalent. In the case of the H center, there are nine different isotopic combinations possible for the molecular species $\mathrm{Cl_4}^{3-}$, but, because of the inequivalence of all the nuclear positions in the V_1 center [for example, $^{35}\mathrm{Cl(1)}^{37}\mathrm{Cl(2)}\neq{}^{37}\mathrm{Cl(1)}^{35}\mathrm{Cl(2)}$], there are $4^2=16$ combinations. In contrast to the H center, the isotope effects of nuclei 3 and 4 are not resolved in the superhyperfine pattern since the smallest superhyperfine splitting is not much larger than the linewidth (1.8 G). The presence of these isotope effects is shown qualitatively, however, by the fact that the 16 superhyperfine lines of a given set do not have exactly the same widths and intensities. Figure 8 gives an expanded part of the two high-field line groups of the $\theta=5.7°$ V_1 spectrum. The highest group, arising from the $^{35}\mathrm{Cl(1)}^{35}\mathrm{Cl(2)}$ combination and showing 16 superhyperfine lines, is compared with the calculated but nonresolved lines of the four different isotopic combinations of the (3,4) nuclei.

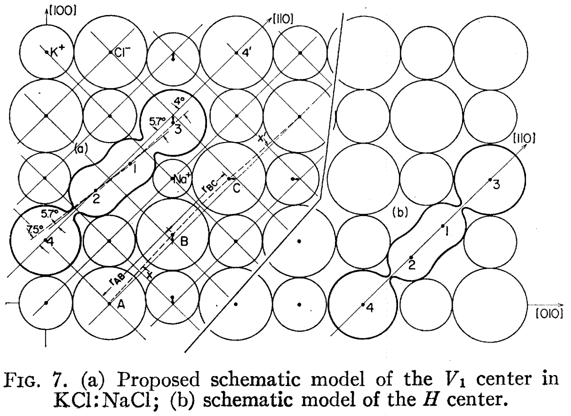

Fig. 7. (a) Proposed schematic model of the V_1 center in KCl:NaCl; (b) schematic model of the H center.

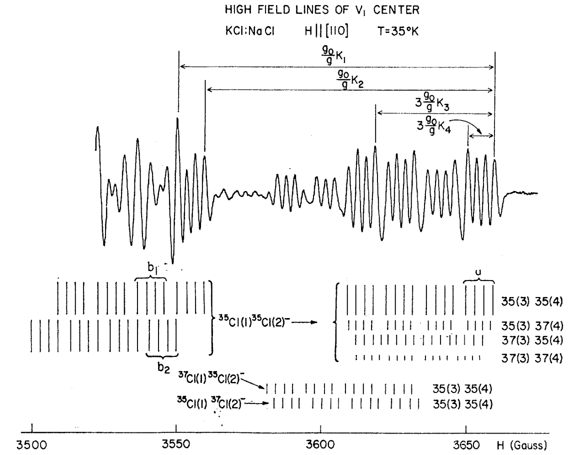

Fig. 8. Detail of the high-field side of the $\theta=5.7°$ ESR spectrum of the V_1 center, compared with the calculated positions of the lines. Only for the highest group are all isotopic combinations shown.

The spectra arising from combinations $^{35}\mathrm{Cl(1)}^{37}\mathrm{Cl(2)}$ and $^{37}\mathrm{Cl(1)}^{35}\mathrm{Cl(2)}$ (see lowest part of Fig. 8) are partly resolved experimentally. Only the lower-field half of the highest-line groups of these combinations is visible just to the left of the highest $^{35}\mathrm{Cl(1)}^{35}\mathrm{Cl(2)}$ line group; the upper half is buried under the $^{35}\mathrm{Cl(1)}^{35}\mathrm{Cl(2)}$ line group. This superhyperfine structure associated with $^{35}\mathrm{Cl(1)}$-$^{37}\mathrm{Cl(2)}$ and $^{37}\mathrm{Cl(1)}^{35}\mathrm{Cl(2)}$ would also consist of 16 lines of about equal intensities if there were no inequivalence

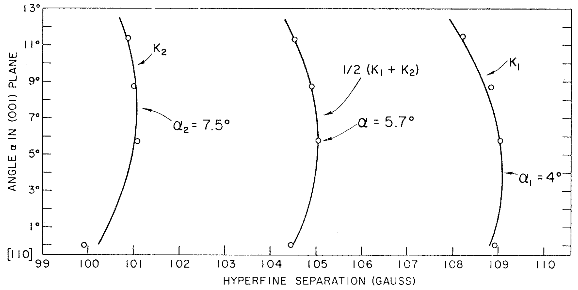

FIG. 9. Angular variation of the first-order hyperfine separations K_1, K_2, and $\frac{1}{2}(K_1+K_2)$. Circles: experimental points; solid line: calculated angular variation.

of the 1 and 2 nuclei. But the experimental spectrum shows something like four groups (only two are visible) of three lines, flanked by smaller lines. Such a pattern is the consequence of the fact that $^{37}\mathrm{Cl}(1)^{35}\mathrm{Cl}(2) \neq {}^{37}\mathrm{Cl}(2)^{35}\mathrm{Cl}(1)$. The experimental spectra suggest that the two resulting 16-line patterns are displaced with respect to each other by an amount of the order of the smallest superhyperfine splitting. (Only the ^{35}Cl isotopic combinations of nuclei 3 and 4 are reconstructed at the bottom of Fig. 8.) Actually, a simple calculation shows that this displacement is given by $\frac{3}{2}K_1(1-\alpha)(1-\beta)$ in which $\alpha = K_2/K_1$ [K_1 and K_2 are the first-order hyperfine separations for ^{35}Cl as given in (6)] and $\beta = \mu(^{35}\mathrm{Cl})/\mu(^{37}\mathrm{Cl})$. For $\theta = 5.7°$, $\alpha = 99.9/109.0 = 0.917$, $\beta = 1.201$, $K_1 = 109.0$, and the calculated displacement is 2.7 G.

Figure 8 also shows some of the second group of lines of the $^{35}\mathrm{Cl}(1)^{35}\mathrm{Cl}(2)$ combination; one of these lines is separated by $(g_0/g)K_2$ from the highest-field line of the spectrum. In the case of the H center, this group had intensity 2 with respect to the highest-field group, but for the V_1 center the inequivalence of nuclei 1 and 2 splits this group into two equally intense groups, each group consisting of 16 lines. The splitting is such that the highest-field superhyperfine line of one group falls on top of the fourth-highest-field superhyperfine line of the second group. A similar effect is observed in the low-field part of the spectrum (see Fig. 5) which is virtually identical to the high-field part. This identification allows an immediate quantitative determination of the inequivalence of nuclei 1 and 2, i.e., of K_1 and K_2. There is another and very important difference between the H and V_1 centers: an angular variation study shows that the V_1 center is not oriented along a ⟨110⟩ direction. Turning the magnetic field **H** away from ⟨110⟩ in the {100} plane shows that the V_1 spectrum, which corresponds to the nondegenerate $\theta = 0°$ spectrum of the H center, splits into two spectra of equal intensity. The total hyperfine splitting, which is determined primarily by K_1+K_2, of one of these spectra goes through a maximum when the external magnetic field makes an angle of $\alpha = 5.7° \pm 0.3°$ with the ⟨110⟩ direction. An angular variation in a {110} plane about a ⟨110⟩ direction does not remove the degeneracy; the total hyperfine separation merely decreases. These facts show that the V_1 center lies in a {100} plane and is tipped 5.7° away from a ⟨110⟩ direction. This tipping of the molecule will be further discussed in the following section. For an arbitrary orientation of **H**, there are 12 possible orientations of the V_1 center with respect to the magnetic field. Table II gives types and degeneracies of spectra of V_1 centers for three special orientations of the magnetic field **H**. Some of the spectra that are readily recognized are indicated in the experimental spectra of Fig. 5.

C. Quantitative Analysis

The purpose of a quantitative analysis of an ESR spectrum is to determine the magnitudes of the components of the g, hyperfine, and quadrupole tensors, and to establish the direction of the principal axes of these tensors with respect to each other and with respect to the crystallographic directions. In the case of the H or V_K centers the determination of the principal tensor axes is a trivial matter; the high symmetry (D_{2h}) makes it evident that the axes of these three tensors coincide with each other and with the molecular and crystallographic symmetry axes.

The situation is not as simple for the V_1 center. The symmetry of the center is low, namely, C_{1h}, i.e., it has only reflection symmetry through the {100} plane containing the V_1 center. This low symmetry is, as we will discuss later on, clearly caused by the presence of the Na$^+$ impurity ion in the immediate vicinity of the V_1 center.

This low symmetry would be expected to cause bending of the three molecular bonds in the V_1 center. In principle, the bending of these bonds manifests itself in the fact that the symmetry axes of the four hyperfine tensors do not coincide with each other or with the g-tensor axes. As is the case for the H center, the V_1 center should also show quadrupole effects. Again, because of the low symmetry of the V_1 center, the main axes of the quadrupole tensor do not necessarily coincide with those of the corresponding hyperfine tensors, but they are probably very close. Consequently, the spin Hamiltonian used to analyze the V_1 center was taken as

$$\frac{\mathcal{H}}{g_0\beta} = \frac{1}{g_0}\mathbf{H}\cdot\mathbf{g}\cdot\mathbf{S} + \sum_{i=1}^{4} \mathbf{S}\cdot\mathbf{A}_i\cdot\mathbf{I}_i + \sum_{i=1}^{4} \mathbf{I}_i\cdot\mathbf{P}_i\cdot\mathbf{I}_i, \quad (4)$$

where, in principle, the symmetry axes of the $\mathbf{g}$, $\mathbf{A}_i$, and $\mathbf{P}_i$ tensors are different from each other and from the internuclear axis. Not enough lines could be measured with enough precision to determine either the quadrupole effects or the orthorhombic character of the hyperfine tensors $\mathbf{A}_i$. The angular variation of the g tensor is given by

$$g^2(\theta_g,\varphi_g) = g_z^2\cos^2\theta_g + g_x^2\sin^2\theta_g\cos^2\varphi_g + g_y^2\sin^2\theta_g\sin^2\varphi_g, \quad (5)$$

TABLE III. Spin-Hamiltonian parameters of the V_1 center (at $T=35K$) and the H center (at $T=25K$) in KCl:NaCl. The hyperfine parameters (in gauss) correspond to the ^{35}Cl nucleus. ΔH is the linewidth between the extrema of the first derivative.

Center	g_z [a] $[110]+\alpha_g$	g_x $[001]$	g_y [a] $[1\bar{1}0]+\alpha_g$	$A_{\parallel,i}$ [b] $[110]+\alpha_i$	$A_{\perp,i}$	$A_{\parallel,i}$ [c] $[110]+\alpha_i$	$A_{\perp,i}$	P	ΔH
V_1	2.0018 ±0.0003	2.024 ±0.001	2.027 ±0.001	$A_{\parallel,1}=+109.1$ ±0.1	$A_{\perp,1}=+14$ ±4	$A_{\parallel,3}=+13.7$ ±0.1	$\lvert A_{\perp,3}\rvert=4.6$ ±0.5	···	1.8 ±0.1
				$A_{\parallel,2}=+101.1$ ±0.1	$A_{\perp,2}=+14$ ±4	$A_{\parallel,4}=+3.1$ ±0.1	$\lvert A_{\perp,4}\rvert=1.3$ ±0.5	···	
H[d]	2.0018 ±0.0002	2.0221 ±0.0005	2.0227 ±0.0005	$A_{\parallel,1}\equiv A_{\parallel,2}$ $=+108.6$ ±0.1	$A_{\perp,1}\equiv A_{\perp,2}$ $=+16.0$ ±1.5	$A_{\parallel,3}\equiv A_{\parallel,4}$ $=+7.4$ ±0.1	$\lvert A_{\perp,3}\rvert\equiv\lvert A_{\perp,4}\rvert$ $=2.7$ ±0.1	$P_1\equiv P_2$ $=-5.7$ ±2	1.2 ±0.1

[a] $\alpha_g=5.7°\pm0.3°$ in (001) plane.
[b] $\alpha_i\approx4.0°$, $\alpha_2\approx7.5°$ in (001) plane.
[c] For the analysis it was assumed that $\alpha_3=\alpha_4=\alpha_g=5.7°$ in (001) plane.
[d] For the H center $\alpha_i\equiv\alpha_2\equiv\alpha_3\equiv\alpha_4\equiv\alpha_g\equiv0°$.

where θ_g and φ_g are measured with respect to the g-tensor principal axis. The angular variation of the first-order hyperfine separation is given by

$$K_i^2(\theta_i)g^2(\theta_i)=A_{\parallel,i}^2g_{\parallel}^2\cos^2\theta_i+A_{\perp,i}^2g_{\perp}^2\sin^2\theta_i, \quad (6)$$

where θ_i is measured with respect to the principal symmetry axis z_i of $\mathbf{A}_i$; we have ignored the fact that the symmetry axes of $\mathbf{g}$ and $\mathbf{A}_i$ are not identical. One way to find the various hyperfine symmetry axes is to see for which angle a particular hyperfine interaction reaches a maximum. The hyperfine interactions with nuclei 1 and 2 are comparable and so are their angular variations. Since the hyperfine interactions with nuclei 1 and 2 are very much larger than with nuclei 3 and 4, the former are the predominant factors in determining the 5.7° tipping angle. (Note that the $\alpha=5.7°$ tipping angle does not necessarily define the orientation of the internuclear axis 1-2, with respect to $\langle110\rangle$. This would only be the case if the hyperfine interactions with nuclei 1 and 2 were identical. Since K_1 and K_2 for the V_1 center are not very much different, it appears to be a good approximation to identify $\alpha=5.7°$ with the tipping angle of the internuclear axis, z.) Therefore, we expect that the hyperfine axes for nuclei 1 and 2 either coincide with each other, in which case they coincide with the internuclear axis and there is no bending of the central molecular bond, or they are tipped approximately symmetrically with respect to the internuclear axis and the central molecular bond is bent. The latter is confirmed experimentally. An angular variation study in a $\{100\}$ plane about a $\langle110\rangle$ direction reveals that K_1 (see Figs. 8 and 9) reaches a maximum for $\alpha_1\approx4.0°$, while K_2 reaches a maximum for $\alpha_2\approx7.5°$, where α_1 and α_2 are angles between a $\langle110\rangle$ direction and the magnetic field direction in a $\{100\}$ plane. The bending of the central molecular bond (1-2) is given by $\alpha_2-\alpha_1\approx3.5°$. Very likely, a comparable bending exists for the (2-3) and (1-4) molecular bonds, but the angular variation of the superhyperfine structure could not be determined with enough precision to determine the magnitudes or the senses of the bending of these two bonds. In the actual analysis, these bond directions were taken to coincide with the internuclear axis.

Neglecting the small influence of nuclei 3 and 4, the g-tensor symmetry axis of the V_1 center lies between the hyperfine tensor axes of nuclei 1 and 2; it does not coincide with the internuclear axis since nuclei 1 and 2 are inequivalent, but is tipped in the direction of the symmetry axis of the hyperfine tensor that has the larger magnitude. In general, the principal g-tensor axis of a molecule coincides with the internuclear axis only if the molecule and the surrounding lattice has a symmetry plane of reflection perpendicular to the internuclear axis. Such is the case, e.g., for the V_F-type centers.[26,27]

For the actual analysis of the spectra, a combination of the solutions of the X_2^- and XY^- spin Hamiltonians was used.[23,27] $A_{\parallel,1}$ and $A_{\parallel,2}$ were obtained from the $\alpha=4.0°$ and $\alpha=7.5°$ spectra, respectively, and g_z, $A_{\parallel,3}$ and $A_{\parallel,4}$ were obtained from the $\alpha=5.7°$ spectrum. It was assumed that the positions of the superhyperfine lines were determined solely by the combination ^{35}Cl(3)^{35}Cl(4). Analysis of the $\theta=35.7°$ spectrum observed when $\mathbf{H}\parallel\langle111\rangle$ (θ is the angle between the internuclear axis and $\mathbf{H}$) yields $K_1(35.5°)$, $K_2(36.0°)$, $K_3(35.7°)$, $K_4(35.7°)$, and $g(35.7°)$. Extrapolation to $\theta=90°$ using expressions (5) and (6) yields $A_{\perp,1}$, $A_{\perp,2}$, $A_{\perp,3}$, $A_{\perp,4}$, and g_x where $x\parallel\langle100\rangle$. For the $\theta=39.3°$ spectrum observed when $H\parallel\langle100\rangle$, only the lowest and highest lines could be unambiguously identified. These data are sufficient to determine $g(39.3°)$, since the second-order shifts can be calculated. Extrapolation to $\theta=90°$ yields g_y, where y is the third orthogonal direction. The results of the analysis are given in Table III. This table also contains the parameters for H centers which were produced by optical destruction of the V_1 centers; the measurements were done at 25 K. Spin Hamiltonian (4) was used to analyze the H-center spectra with $\mathbf{A}_1\equiv\mathbf{A}_2$ and $\mathbf{A}_3\equiv\mathbf{A}_4$ and axial symmetry for the quadrupole term; a sufficient number of lines could be measured with enough precision to determine the quadrupole parameter.

The g shifts of the V_1 center are comparable, though somewhat larger than those of the H center, and the

---

[26] W. Känzig, J. Phys. Chem. Solids **17**, 80 (1960).
[27] D. Schoemaker, Phys. Rev. **174**, 1060 (1968).

orthorhombic character of the V_1 g tensor is somewhat more pronounced. The average hyperfine interaction, $\frac{1}{2}[K_1+K_2]$, of the V_1 center is a few percent smaller than for the H center. By analogy with the results for the V_K center,[23] it is proposed that the signs of $A_{\parallel,1}$, $A_{\parallel,2}$, $A_{\perp,1}$, and $A_{\perp,2}$ for both the H and V_1 centers are positive. Also $A_{\parallel,3}$ and $A_{\parallel,4}$ should have positive signs since, like $A_{\parallel,1}$ and $A_{\parallel,2}$, they are the sum of an isotropic Fermi part and a dipole-dipole part, both of which have positive signs. The signs, however, of $A_{\perp,3}$ and $A_{\perp,4}$ are not known. Using a procedure such as the one adopted by Schoemaker,[23] the hyperfine results could, in principle, be used to obtain a more quantitative idea of the charge distribution within the molecule, and more specifically about the difference in charge distributions around nucleus 1 and nucleus 2 in the V_1 center. However, for such an analysis, $A_{\perp,1}$ and $A_{\perp,2}$ of V_1 should be known to a higher accuracy than given in Table III. The present accuracy only allows us to conclude that the unpaired electron density on nucleus 1 is $(5\pm5)\%$ larger than on nucleus 2.

The value of $A_{\parallel,1}\equiv A_{\parallel,2}=+108.6$ G for the H center at 25 K is different from the values $+108.8$ G at 20.4 K [5] and 109.1 G at 4.2 K.[12] These differences are outside experimental error, and demonstrate what seems to be a general property of the X_2^- and XY^- molecule ion centers, namely, that the hyperfine interactions of a given molecule decrease with increasing temperature.

The linewidth of the V_1 center resonance is 1.8 G (between the extrema of the first derivative), considerably larger than the 0.8 G linewidth of the H center[5] at 20.4 K. A prime contribution to this increased linewidth is believed to be the neighboring ^{23}Na$^+$ nucleus which has the same nuclear spin $(\frac{3}{2})$, but a much larger nuclear moment $(\mu=2.2161)$ than the ^{39}K and ^{41}K nuclei $(\mu=0.39094$ and $\mu=0.21488$, respectively). This conclusion is supported by other results in KCl which show that the linewidths of the V_{KA}(Na$^+$) and V_{KA}(Li$^+$) centers are about twice the linewidth of the V_K center (for ^{7}Li, $\mu=3.256$).

V. DISCUSSION

A. Model of the V_1 Center

We have concluded that the V_1 center consists of an H center trapped near a single Na$^+$. The fact that the defect is a single Na$^+$ is indicated by the results of Fig. 1 which show that V_1 centers can be formed at very low Na$^+$ concentrations. There is a strong correlation between the height of the V_1 band and the intensity of the ESR spectra, which we have identified as the V_1 ESR spectra, typified by those shown in Figs. 4 and 5; no V_1 center ESR spectra can be detected in the pure Oak Ridge crystal, while the relative concentrations of V_1 centers observed with ESR techniques in the Na$^+$ containing crystals are the same as those observed in the optical experiments. The optical conversion of V_1 centers into H centers and the subsequent recovery of V_1 centers by thermal annealing can be followed using the intensity of the ESR signal of each center to determine its concentration. Because of overlapping lines and saturation problems in measuring the ESR spectra, and a loss of about 20–30% of the centers in the above conversion cycle, we cannot state positively that optical decomposition of one V_1 center yields one H center. However, the results do show that at the start of the conversion of V_1 centers to H centers, where the destruction of centers is minimal, the number of H centers formed is proportional to the number of V_1 centers destroyed; it is also very likely that the proportionality constant is equal to one. The above results indicate that the V_1 optical-absorption band and the ESR spectra shown in Figs. 4 and 5 both arise from the same center, the V_1 center. The ESR experiments confirm the conclusion drawn from the optical experiments, i.e., the V_1 center is an H center trapped by an Na$^+$ ion.

Figure 7(a) shows a two-dimensional representation of a KCl lattice containing a substitutional sodium ion. The diagonal lines indicate the $\langle 110\rangle$ directions of the undistorted lattice and would pass through the centers of rows of Cl$^-$ or K$^+$ ions in a perfect KCl lattice. The sodium ion is appreciably smaller than a potassium ion, so that the ions in the neighborhood of a sodium ion would be expected to be displaced from their normal lattice positions. The ion positions about an Na$^+$ ion were obtained by assuming that the ions behave as hard spheres with fixed radii; although this is only an approximation to the true situation, we will use it for our qualitative discussion. The nearest-neighbor Cl$^-$ ions, for example B and C, surrounding the Na$^+$ are displaced toward the Na$^+$ by a distance appreciably larger than that of the Cl$^-$ ions equivalent to the one labeled A; consequently a line $(X---X')$ connecting the centers of these Cl$^-$ ions is curved toward the Na$^+$ and does not coincide with the $[110]$ direction. The drawing also indicates that the separation between ions B and C is less than that between A and B, i.e., $r_{\mathrm{BC}}<{}_{\mathrm{AB}}$.

The presence of the Na$^+$ in the V_1 center strongly affects the properties of the Cl$_4^{3-}$ molecule ion; however, the spin resonance shows that, aside from some line broadening, there is very little interaction between the unpaired electron and the sodium nucleus, i.e., the Na$^+$ is not a part of the molecule. We conclude therefore that the influence of the Na$^+$ arises primarily from the fact that it is appreciably smaller than the K$^+$ it replaced, which results in nuclear displacements of ions in the neighborhood. These nuclear displacements affect the properties of the H center by (1) changing internuclear distances within the molecule, (2) changing distances between a particular nucleus in the molecule and the nuclei of ions outside the molecule, and (3) bending the molecule. While we have been unable to conclude from the optical experiments where the Na$^+$

is located in the V_1 center, the anisotropic ESR spectra do give considerable information on this point. Since the four chlorine nuclei of the V_1 center are inequivalent, any model suggested for the V_1 center must account for this inequivalence. In addition, the ESR results show that the four chlorine nuclei of the V_1 center lie in a $\{100\}$ plane; therefore, the perturbing Na^+ must be located so as to preserve this plane of reflection symmetry, i.e., the Na^+ must lie in the $\{100\}$ plane. If we limit the choice of Na^+ positions to those six nearest neighbors surrounding the interstitial, only those four positions that lie in the same $\{100\}$ plane as the Cl_4^{3-} satisfy these conditions. The fact that the axis of the V_1 center is tipped 5.7° away from $\langle 110\rangle$ suggests a fairly large perturbation and leads to the conclusion that the Na^+ is in a nearest-neighbor position to the interstitial. We, therefore, believe that the V_1 center is an H center with a Na^+ ion as a *nearest* neighbor to the interstitial and lying in the same $\{100\}$ plane as the H center, as shown schematically in Fig. 7(a). The tipping of the internuclear axis, and probably the bending of the bond of the central part of the molecule, are considered to arise in large part from the bending of the line of centers, $X---X'$, of the chloride ions in the vicinity of the Na^+.

There are three bonds in the Cl_4^{3-} molecule (H center) in a perfect KCl crystal: a strong bond between the two central nuclei 1 and 2, and two bonds of equal strength, but weaker than the central bond, between nuclei 1 and 3 and nuclei 2 and 4, Fig. 7(b). If one moves nucleus 3 toward the center of the molecule and pulls nucleus 4 away from the center, the strength of the outer bonds will be expected to increase and decrease, respectively. Therefore it does seem reasonable that, since $r_{BC}<r_{AB}$, the bond between 1 and 3 will be stronger than the bond between 2 and 4, Fig. 7(a). In first approximation, this movement of nuclei 3 and 4 increases the density of the unpaired electron on nuclei 2 and 3 and decreases it on 1 and 4. There very likely will be a further redistribution of the unpaired electron between 1 and 2, but qualitative considerations do not allow us to say whether it will be enough so that nucleus 1 will have a higher unpaired electron density than nucleus 2. However, analysis of the ESR spectra shows that the nucleus with the largest hyperfine interaction has a hyperfine tensor axis which makes an angle of $\sim 4°$ with $\langle 110\rangle$; therefore, on the basis of our model, in which it is assumed that the tipping and the bending follow the curvature of the line of centers $X---X'$, it is nucleus 1 which has the largest hyperfine interaction. The angles that the internuclear axis and the principal axes of the hyperfine tensors of the two central nuclei make with [110] are shown.

From the model of the V_1 center we see that there are 24 equivalent orientations of the center in the lattice. There are six possible sites about each Na^+ on which the two central nuclei can be located [i.e., six possible orientations of the Na^+ interstitial axis (the Na^+ interstitial axis is defined as the line connecting the Na^+ and the site occupied by nuclei 1 and 2 of the V_1 center)], and four possible orientations of the molecule ion on each site. However, only 12 of these 24 possible orientations are distinguishable in the experiments we performed.

B. Disorientation of the V_1 Center

Since the V_1 center can be considered to be a perturbed H center, it is advantageous first to discuss the disorientation and migration of the H center. In a KCl crystal containing preferentially oriented H centers, the associated optical anisotropy is observed to disappear near 11 K; at this temperature, a reorientation of the axis of the H center takes place, and the population distribution among the six equivalent $\langle 110\rangle$ directions becomes random. The fact that there is no loss in the number of H centers at 11 K indicates that the reorientation process does not involve a migration of the H center through the crystal; i.e., during this reorientation the molecule ion remains centered on the same lattice site. The reorientation process can be thought of as a breaking of the bonds between nuclei 1 and 3 and nuclei 2 and 4 coupled with a rotation of the central $Cl(1)Cl(2)^-$ and followed by reformation of a Cl_4^{3-} ion; the central nuclei 1 and 2 always remain the same but the outer nuclei 3 and 4 change with each reorientation. Bachmann and Känzig[28] have studied the kinetics of the reorientation of H centers and find that the most probable jump is one which changes the direction of the axis of the center by 60°. However, since two successive 60° jumps can produce a change of 90°, all six $\langle 110\rangle$ orientations can be reached. It is observed that there is a loss in the number of H centers near 39 K, from which it is concluded that at this temperature the H center can migrate through the crystal until it encounters a defect with which it can react.

At 39 K the center is believed to spend essentially all its time as the well-defined H center we have described and only a very small fraction of its time in transit, i.e., changing orientations or lattice sites between these successive well-defined states. At this temperature, we estimate the lifetime of the interstitial on a given site to be about 10^{-3} sec, and the lifetime of an H center in a particular orientation on a specific lattice site to be about 10^{-9} sec. Thus, the H center jumps many times among the six orientations associated with a given site before it undergoes a translational jump to a different site.

The exact mechanism by which the translational jump of the interstitial atom takes place at 39 K is not known. Since the H center has a crowdion-like configuration, diffusion might be expected to occur along its molecular axis. This jump, which is most likely

---

[28] K. Bachmann and W. Känzig, Physik Kondensierten Materie **7**, 284 (1968).

limited to the next lattice site along the ⟨110⟩ direction, seems favored energetically since (1) the four nuclei of the *H* center are crowded into the space occupied normally by three chloride ions, so that the distance the interstitial has to move is smaller than for any other jump, and (2) the inner nuclei of the *H* center are bonded to the outer nuclei, which should lower the energy required for the interstitial to jump in the axial direction, and would also tend to preserve the orientation. The combination of this crowdion-like interstitial jump and the rapid change in orientation of the molecule while on a particular site results in a random migration of the *H* center in the lattice.

The V_1 center has optical transitions which are anisotropic and, at a sufficiently low temperature, excitation of one of these transitions with plane polarized light in general changes the population distribution among the possible orientations of the V_1 center and thus gives rise to an optical anisotropy. This change in the population distribution might arise in two ways. The excitation could (1) leave the interstitial at its original site and simply change the distribution among the four possible orientations associated with that site, and/or (2) change the distribution of the interstitials among the six possible sites about the Na^+. Process (1) can be described as breaking the two outer bonds, between nuclei 1 and 3 and 2 and 4, and reforming a new Cl_4^{3-} after rotation of the central Cl_2^- through the appropriate angle. In this manner the four orientations associated with a given Na^+ interstitial axis are available. Process (2) includes breaking all the bonds of the original Cl_4^{3-}, moving the interstitial to another of the nearest-neighbor sites to the Na^+ and reforming a Cl_4^{3-} in any of the four directions consistent with the orientation of the Na^+ interstitial axis. Thus process (2) can change the V_1 center axis to any of the other 11 orientations while process (1) can only change the axis to any of the other three available to it. Since excitation of the violet transition of the V_1 center with polarized light yields some *H* centers, and thus shows interstitial motion, it is reasonable to expect both kinds of changes in the population distribution.

If, in the present context, the V_1 center can be considered to be simply a slightly perturbed *H* center, one would expect to be able to observe two disorientation temperatures for the V_1 center; the low-temperature disorientation would arise from jumping of the molecule among the four orientations available with the interstitial remaining on a fixed site (this process would remove a large fraction of the anisotropy), and the high-temperature disorientation would arise from jumping of the interstitial among the six sites about the Na^+. Our experiments have shown only one disorientation temperature, 17 K, which can be definitely attributed to the V_1 center. Since we have found no higher disorientation temperature, caused by the jumping of the interstitial about the Na^+ ion, we conclude that the disorientation processes of the V_1 center cannot be approached from the point of view that the V_1 center is a *slightly* perturbed *H* center.

On the other hand, if the perturbation of the *H* center were sufficiently large, it is possible that the rates of jumping of the two kinds of disorientation would be approximately the same in this temperature region, or that the rate of the interstitial jump might be higher. In considering these latter possibilities we will take into account the following elementary processes which might occur in the disorientation of the V_1 center:

(a) The pyramidal jump, in which the interstitial remains on a specific halide ion site and the molecule ion jumps among the four orientations associated with that site. These four orientations form a pyramid. (The sodium ion is assumed always to remain fixed in the lattice.) This process will remove a large fraction, but not all, of the anisotropy;

(b) The unrestricted interstitial jump, in which the interstitial jumps with a high probability, by a series of one or more elementary kinds of jumps, to any of the six possible sites about the sodium ion. (The probabiltiy of each kind of jump need not be equal.) It is assumed that this interstitial jumping will remove all anisotropy.

In view of our earlier discussion of the migration of the *H* center and the similarity between the *H* and V_1 centers, it seems probable that a special case of the crowdion-like interstitial jump of the *H* center will be energetically favored over process (b) for the V_1 center. Since the internuclear distance between nuclei 1 and 3 is less than that between nuclei 2 and 4 [Fig. 7(a)], the activation energy for nucleus 1 to jump to the 3 site, so that nuclei 1 and 3 form the central Cl_2^- and the orientation of the V_1 center changes by $2\times5.7° = 11.4°$, is expected to be appreciably lower than the activation energy for any other interstitial jump; therefore, we will consider as the most probable elememtary disorientation process involving an interstitial jump:

(c) The restricted interstitial jump between two possible V_1 orientations such that the change in orientation is just 11.4°. This process alone will not remove all anisotropy; however, this process plus process (a) will remove all anisotropy. The change in anisotropy (or optical density) to be expected from process (c) is small.

Our experiments indicate that no V_1 center anisotropy remains after the disorientation occurs at 16.8 K. A very large fraction, if not all, of the V_1 center anisotropy disappears at 16.8 K, and a very small amount of anisotropy disappears near 13.5 K; this latter may not arise from the V_1 center. Thus, we conclude that the pyramidal jump of the V_1 center takes place at 16.8 K and the restricted interstitial jump of the V_1 center takes place at about 16.8 or 13.5 K. As yet no detailed experiments have been carried out at a fixed temperature in an effort to ascertain if two processes (with somewhat different rates) are occurring in the neighborhood of 16.8 K.

C. Reorientation Effects

From Fig. 2 it is seen that the reorientation of the axis of the V_1 center is thermally activated. Without specifying the reorientation mechanism we can write the following to first approximation:

$$R = se^{-E/kT}, \tag{7}$$

where R is the rate of reorientation, s is a frequency factor, and E is the activation energy for the reorientation process. Although s probably varies somewhat with temperature, we will assume for our rough calculations that it is constant and equal to 10^{13}/sec. From the disorientation rate at 17 K we determine that $R \cong 10^{-2}$ jumps/sec and calculate from (7) that $E = 0.050$ eV. The rate formula then becomes

$$R = 1/\tau = 10^{13} e^{-0.050/kT}, \tag{8}$$

where τ is the mean lifetime in a given orientation. From Eq. (8) it is seen that as the temperature is raised, the lifetimes of the states involved in the ESR transitions are decreasing rapidly, since the hyperfine interaction is very anisotropic. The initial lifetime broadening will occur according to

$$\Delta\epsilon \times \tau \cong h/2\pi, \tag{9}$$

where $\Delta\epsilon$ is the width of the hyperfine level. The corresponding linewidth can be written as

$$\Delta H \cong 5.68 \times 10^{-8} R, \tag{10}$$

where ΔH is the ESR linewidth in gauss at $g = 2$ and R is the rate in Eq. (8).

Any line observed in the V_1 ESR spectrum, as in the V_K ESR spectrum, is an inhomogeneously broadened line, and is an envelope of many individual lines or spin packets.[29] These individual spin packets are lifetime broadened by the reorientation of the V_1 center, and as a result the envelope line broadens too. This broadening of the envelope should become noticeable when the individual spin-packet width becomes of the order of a few percent of the envelope width, i.e., $\sim$0.1 G in the case of the V_1 center. From (8) and (10) one calculates that the packet linewidth should be 0.1 G at 38 K. This calculation is in agreement with the experimental observations, since broadening of the envelope line does become noticeable at temperatures above 36 K. Since the observed ESR lines are inhomogeneously broadened and overlap each other somewhat, only qualitative arguments will be used to explain the behavior of the V_1 spectrum as a function of temperature.

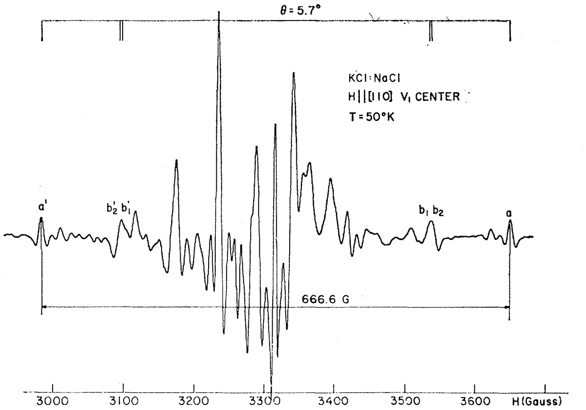

FIG. 10. V_1-center ESR spectrum for $\mathbf{H}\|[110]$ obtained at 50 K, showing the narrowing of the a, b_1, and b_2 4-line groups of Fig. 8, into single lines. The other 4-line groups have broadened practically beyond detection.

In order to understand the behavior of the $\theta = 5.7°$ ESR spectrum in the neighborhood of 50 K, it is necessary to have a closer look at the reorientation mechanism resulting from the restricted interstitial jump discussed in the preceding section. This jump leaves nuclei 1, 2, and 3 as members of the V_1 center (the roles of 2 and 3 are interchanged) while nucleus 4′, Fig. 7(a), takes the place of nucleus 4. If it is assumed that the orientation of the electron spin and orientations of the spins of nuclei 1, 2, and 3 are maintained during this jump, and if we consider only one Cl isotope, we may represent the jump as

$$4(m)2(\alpha)1(\beta)3(\gamma) \rightarrow 3(\alpha)1(\beta)2(\gamma)4'(m'),$$

where m and m' each indicate any of the four possible nuclear orientations (m or $m' = +\frac{3}{2}, +\frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$), while α, β, and γ indicate the specific nuclear orientations that are maintained during the jump. The four lines arising from the hyperfine interaction with nucleus 4 or 4′ will be called the 4-line manifold. Two important general cases must be distinguished in the restricted interstitital jump:

Case A:

$$\alpha = \gamma \text{ (including } \alpha = \beta)$$

and

Case B:

$$\alpha \neq \gamma \text{ (including } \alpha = \beta \text{ or } \beta = \gamma).$$

If a jump of the V_1 center corresponding to case A occurs, any component of a 4-line manifold may be converted to any of the components of the *same* 4-line manifold; for the twofold degenerate $\theta = 5.7°$ spectrum, when $\mathbf{H}\|\langle 110\rangle$, these two 4-line manifolds coincide. (The same is true for the $\theta = 35.7°$ spectrum observed when $\mathbf{H}\|\langle 111\rangle$.) Some of the 4-line manifolds corresponding to case A which are easily identified and originate from $^{35}\mathrm{Cl}_4{}^{3-}$ are indicated in Figs. 8 and 10 as a, a', b_1, b_1', b_2, and b_2'. Manifold a corresponds to $\alpha = \beta = \gamma = -\frac{3}{2}$; manifold b_2 corresponds to $\alpha = \gamma = -\frac{1}{2}$,

---

[29] T. G. Castner, Phys. Rev. **115**, 1506 (1959).

[30] H. S. Gutowsky and A. Saika, J. Chem. Phys. **21**, 1688 (1953).

$\beta=-\frac{3}{2}$ and manifold b_1 corresponds to $\alpha=\gamma=-\frac{3}{2}$, $\beta=-\frac{1}{2}$.

The situation here is analogous to the one treated by Gutowsky and Saika,[30] who studied the effect on the proton NMR spectrum of rapid chemical exchange of a proton between two or three chemical species. In case A, "resonance" occurs among the four components of a 4-line manifold, and following Gutowsky and Saika, the four lines will start to collapse into a single line when

$$4\tau 3\delta\omega \leq 1\,, \tag{11}$$

in which $3\delta\omega$ corresponds to the total $3K_4\sim 9$ G hyperfine separation of a 4-line manifold expressed in angular frequency units, and τ is the mean lifetime in a given orientation between jumps. The factor 4 arises because the probability of a jump from any component of a given 4-line manifold to any component of the same manifold is identical and equal to $\frac{1}{4}$. The equality in (11) gives a lower limit of reorientation rate for which collapsing into a single but still broad line will occur; in this case $R\sim 10^9$ Hz. The ESR spectrum at 50 K, shown in Fig. 10, demonstrates that such collapsing for $\theta=5.7°$ has partly taken place for the a, a', b_1, b_1', b_2, and b_2' manifolds. The separation between a and a', from the data determined at 35 K, should be $3(K_1+K_2)+3K_3=667.8$ G. Experimentally, one finds 666.6 G. The difference is attributed primarily to the temperature dependence of the hyperfine interaction.

If case B occurs, there is a jump from any given component of a 4-line manifold to any component of another 4-line manifold and these manifolds are separated by at least K_2. Thus the lines of these 4-line manifolds at 50 K will broaden beyond recognition, as is also observed in Fig. 10. Because each pyramidal jump involves a new set of nuclei 3 and 4 and a change in orientation of the V_1 center axis, there will, in general, be a change from one 4-line manifold to another 4-line manifold; this pyramidal jump can only cause lifetime broadening and cannot produce collapsing of the 4-line manifold into a single line. We have not been able to think of any other reorientation process that can lead to the unique collapsing of the 4-line manifold. The fact that such a collapsing of a 4-line manifold is observed at all at 50 K indicates that in this temperature range the restricted interstitial jump occurs not only as a well-defined process, but also with a rate that must necessarily be many times faster than the pyramidal jump or any other motion.

The estimated rate of about 10^9 jumps/sec for the restricted interstitial jump at 50 K would give a linewidth of about 56 G for ordinary lifetime broadening. Thus the rate accounts for the broadening beyond recognition of the lines associated with case B, and at the same time accounts for the collapse of a 4-line manifold into a single line for those manifolds associated with case A. The observed width of the collapsed 4-line manifolds at 50 K is about 8 G between the extrema of the first derivative. This width is at least partly determined by the lifetime broadening brought about by the pyramidal jump. If this 8-G linewidth is completely associated with the pyramidal-jump lieftime broadening, one finds from (10) that the reorientation rate at 50 K is about 1.4×10^8 jumps/sec, which is about seven times slower than the rate of the restricted interstitial jump.

The reorientation and lifetime broadening effects also occur in the case of the H center. A study of the disorientation kinetics has revealed that there is only one reorientation mechanism, namely, a succession of 60° jumps of the molecular axis.[28] The disorientation temperature of the H center is 11 K. The measured linewidth at 20.4 K is 0.8 G. Broadening of the envelope line is observed to occur above 22 K, and at 25 K the measured linewidth is 1.2 G. The reorientation geometry of the successive 60° jumps is unrestricted and completely cubic, and every jump involves a new set of nuclei 3 and 4. What is more important however, is the fact that for no orientation of the external field $\mathbf{H}$, is the angle between $\mathbf{H}$ and the molecular axis 1-2 conserved during a series of 60° jumps. Therefore, the lines broaden according to (10), as is observed, but a collapse of the superhyperfine structure, similar to that of the V_1 center (see Fig. 10), cannot occur.

The ESR spectra at 50 K show that the restricted interstitial jump occurs at a much faster rate than the pyramidal jump. Both of these mechanisms must be in operation at 17 K where all the optical anisotropy disappears, since the restricted interstitial jump cannot remove all the anisotropy. There appear to be two choices available to explain the optical anisotropy results near 17 K and the behavior of the ESR spectrum at 50 K. The first choice is to assume that the rate of the restricted interstitial jump is greater than the rate of the pyramidal jump near the disorientation temperature, 17 K. If so, one could associate the onset of the restricted interstitial jump with the small change in anisotropy at 13 K, and the pyramidal jump with the change in anisotropy at 17 K. We are, however, not certain that the change at 13 K is to be associated with the V_1 center. A second choice is to assume that the rates for disorientation for the restricted interstitial jump and the pyramidal jump are approximately equal at 17 K, but that the rate of the former is much greater than that of the latter at 50 K because the activation energies and frequency factors are different. We are unable to make a choice between these two alternatives from the experimental data.

On raising the temperature beyond 50 K, the lines a, a', b_1, b_1', b_2, b_2', etc., broaden because of the increased frequency of the pyramidal motion. Finally, at temperatures above 77 K, an isotropic line emerges, with $g=2.020\pm 0.002$ (Fig. 4). The line is neither Gaussian nor Lorentzian, though closer to the former, and the asymmetry on the high-field side of the line is at least partly caused by the *F*-center resonance which could not be completely suppressed. It is estimated that at 80 K the reorientation rate is about 7000 MHz, which is more than an order of magnitude larger than the hyperfine interaction with the central nuclei (~300 MHz). It is, therefore, not unexpected that a motionally averaged V_1 ESR spectrum appears at these high temperatures.

As a result of the combined motions of processes (a) and (c) of Sec. V B, one may consider that the interstitial Cl^0 atom continually jumps about the Na^+ and breaks and reestablishes molecular bonds with the six substitutional Cl^- ions surrounding the Na^+ impurity. At 80 K the frequency of these processes is much larger than the total hyperfine interaction, and the V_1 center behaves essentially as a $Cl_7{}^{6-}$ molecule when observed in ESR. Six of the seven Cl nuclei are equivalent, but in principle, the seventh (i.e., the interstitial) is not. However, since an almost Gaussian line is observed, it is probably not a bad first approximation to consider all seven nuclei as equivalent. Hyperfine interaction with seven equivalent Cl nuclei which have nuclear spin $\frac{3}{2}$ (we ignore isotope effects) results in a 22-line spectrum whose relative intensities are:

$$1:7:28:84:203:413:728:1128:1554:1918:2128:2128:\text{etc.}, \ldots \quad (12)$$

An estimate of the splitting between these lines is obtained as follows. The isotropic hyperfine interaction with the two nuclei of the basic Cl_2^- molecule ion is $A=\frac{1}{3}(A_{\parallel}+2A_{\perp})=40$ G, ignoring inequivalence effects and assuming that $A_{\perp}>0$, as is the case for the $Cl_2^-(V_K)$ center.[23] The isotropic hyperfine splitting for the $Cl_7{}^{6-}$ molecule is, therefore, probably of the order of $(2/7)\times 40=11$ G. With this separation, (12) defines an isotropic line about 100 G wide, provided the width of the individual lines is comparable to or larger than the 11-G separation. Such large individual linewidths seem reasonable since the superhyperfine interaction of the anisotropic V_1 ESR spectrum, which at least partly originates in the next shell of Cl^- ions, is sufficiently large to result in such large linewidths after motional averaging. Finally, the isotropic *g* factor is very nearly equal to the average of the *g* factors of the anisotropic spectra, $\frac{1}{3}(g_x+g_y+g_z)=2.018$.

ACKNOWLEDGMENTS

We wish to thank K. Orlandini and F. Lawless for performing the neutron-activation analyses and Charles Butler of Oak Ridge National Laboratory for supplying us with a specially purified single crystal of KCl.

We also wish to thank James L. Kolopus for early attempts to observe the anisotropic ESR spectrum of the V_1 center at 4.2 and 20.4 K.