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Electron Paramagnetic Resonance Optical and Absorption Studies of the $V_1(\mathrm{Li}^+)$ Center in KCl:Li$^+$ †

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An interstitial chlorine atom created by x or γ irradiation at low temperatures can be stabilized by a Li$^+$ ion in KCl and form a $V_1(\mathrm{Li}^+)$ center, which is a bent (~ 8°) Cl_2^- molecule ion occupying a single negative-ion vacancy next to a substitutional Li$^+$. The two chlorine nuclei are inequivalent, and the internuclear axis is tipped 26° away from ⟨001⟩ in a {110} plane. The angular variation of the electron paramagnetic resonance (EPR) linewidth indicates a further weak hyperfine (hf) interaction with two other chlorine nuclei. One deduces that the nuclear configuration of the $V_1(\mathrm{Li}^+)$ center has the shape of a nonplanar Y, this in contrast to the H and $V_1(\mathrm{Na}^+)$ centers in KCl, whose nuclear configurations are either linear or almost linear. The symmetry of the $V_1(\mathrm{Li}^+)$ center is consistent with the well-known ⟨111⟩ off-center position of the Li$^+$ ion. The optical absorption bands of $V_1(\mathrm{Li}^+)$ are situated at 293, 354, and 618 nm and they are σ polarized. Optical anisotropy can be produced in these bands with ⟨110⟩-polarized light, and a disorientation temperature $T_D = 23.5$ °K is found.

I. INTRODUCTION

X or γ irradiation of alkali halide crystals at low temperatures results in the formation of three fundamental paramagnetic centers which have been studied very profitably with electron paramagnetic resonance (EPR) and electron-nuclear double resonance (ENDOR) techniques: (a) the well-known F center[1] which is an electron trapped by a negative-ion vacancy, (b) the self-trapped hole or V_K center[2,3] which is a positive hole stabilized and shared by two adjoining substitutional halogen ions as a ⟨110⟩-oriented X_2^- halogen molecule ion, and (c) the H center[4,5] which is an interstitial halogen atom stabilized as a ⟨110⟩-oriented[6] X_2^- halogen molecule ion occupying one negative-ion vacancy. These fundamental paramagnetic centers can interact with impurities and form a variety of other centers which are interesting in themselves and whose study often sheds light on some properties of the fundamental centers.

An important class of impurities are the foreign alkali ions. F centers for which one of the surrounding alkali ions is replaced by a foreign alkali ion have been studied extensively and are called F_A centers.[7] V_K centers stabilized to a higher temperature by a foreign alkali ion have been observed and are called V_{KA} centers.[8,9] In a recent paper[10] it was established that a center in KCl, known for a long time as the V_1 center, is an H

center associated with a Na^+ impurity. This center will be called the $V_1(Na^+)$ center in this paper, although $H_A(Na^+)$ might be a more generic notation. It was found[10,11] that because of the presence of the Na^+ impurity the $V_1(Na^+)$ Cl_2^- internuclear axis made a 5.7° angle with a $\langle 110\rangle$ direction in a $\{001\}$ plane. In the course of this $V_1(Na^+)$ study, the KCl : Li^+ system was also investigated. It was observed[12,13] that the Li^+ ion can also trap an interstitial halogen atom, and in this paper we present the results of an EPR and optical absorption study of the $V_1(Li^+)$ [or $H_A(Li^+)$] center. It will be shown that the geometry of the $V_1(Li^+)$ center is quite different from that of the $V_1(Na^+)$ center, and that this geometry is consistent with the well-established $\langle 111\rangle$ off-center position of the Li^+ impurity.[14-16]

II. EXPERIMENTAL

The crystals used in these measurements were grown in air by the Kyropoulos method. To the KCl melt were added between 0.1 and 1.0 wt% of LiCl. Neutron activation analysis of a KCl : Li^+ (0.1 wt% LiCl) crystal, grown from reagent grade KCl powder, showed the following impurity concentrations: 5.9×10^{-3} mole % of Li^+, 1.0×10^{-3} mole % of Na^+ and 5.6×10^{-3} mole % of Br^-. Analysis of the KCl : Li^+ (1.0 wt%) gave: 83×10^{-3} mole % of Li^+, 1.0×10^{-3} mole % of Na^+, and 5.6×10^{-3} mole % of Br^-.

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. Most of the irradiations were done at 77 K, and some at 192 K, the temperature of dry ice. The length of the irradiation was usually a few hours. The experimental details of the optical absorption and electron-spin resonance measurements have been given in Ref. 10.

III. EPR RESULTS

The $V_1(Li^+)$ center is produced at 77 K by x or γ irradiation of a KCl : Li^+ crystal. Besides the $V_1(Li^+)$ center, V_K, F, and F' centers are also produced. If the KCl material from which the crystal was grown contained Na^+ as an impurity, as is often the case, the irradiation produces also $V_1(Na^+)$ centers.[10] These can be eliminated by warming the crystal above −150 °C, the decay temperature of $V_1(Na^+)$. The positively charged V_K centers are also quickly eliminated through recombination with electrons created by a short optical excitation of the F and F' bands. The $V_1(Li^+)$ centers are practically unaffected by this treatment. Because of its high thermal stability, the $V_1(Li^+)$ center can also be created at the temperature of dry ice (−81 °C). F and F' centers are again present, but V_K and $V_1(Na^+)$ are not formed since they are not stable at this temperature. However, the $V_{KA}(Li^+)$ center,[9] i.e., a V_K center stabilized next to a substitutional Li^+ ion, is produced. Like the V_K center, the $V_{KA}(Li^+)$ center is positively charged, and is also easily and preferentially eliminated by a short optical excitation of the F and F' centers. Before they were destroyed, however, the V_K- or $V_{KA}(Li^+)$-center EPR spectra were often used to orient the crystal accurately with respect to the external magnetic field.

The $V_1(Li^+)$ EPR spectrum is most strongly observed around 22 K with a microwave power level of ~100 mW, and the spectra for three special orientations of the magnetic field $\vec{H}$ are shown in Fig. 1. However, in contrast to the H and $V_1(Na^+)$ centers, there is no difficulty in observing the $V_1(Li^+)$ EPR spectrum at lower temperatures. The $V_1(Na^+)$ is strongly saturated and unobservable in absorption at 4.2 K even at the lowest power levels[10] (~85 dB below 125 mW). The H center is observable in absorption at 4.2 K, but shows saturation at −65 dB.[5] However, the $V_1(Li^+)$ center is easily observable in absorption at 4.2 K and at 2 K with power levels as high as −35 dB. This orders-of-magnitude difference in relaxation behavior between the $V_1(Li^+)$ and $V_1(Na^+)$ centers is very striking and has not yet been explained.

The $\vec{H} \parallel [001]$ spectrum of $V_1(Li^+)$ in Fig. 1 shows clearly a seven-line hyperfine (hf) structure with a hf separation which is characteristic of a Cl_2^- species.[2] The chlorine isotopes (^{35}Cl, 75% abundant, and ^{37}Cl, 25% abundant) all have nuclear spin $\frac{3}{2}$, and so hf interaction with, e.g., two ^{35}Cl nuclei in a Cl_2^- species should give a hf spectrum of

TABLE I. Classification of the EPR spectra of the $V_1(Li^+)$ center whose internuclear axis κ makes a 26° angle with $\langle 001\rangle$ in a $\{110\}$ plane, for three special orientations of the magnetic field $\vec{H}$ with respect to the crystal axes.

Direction of $\vec{H}$	Angle θ between $\vec{H}$ and κ	Degeneracy
$\langle 001\rangle$	26°	4
	71.9°	8
$\langle 111\rangle$	28.7°	3
	58.7°	6
	80.7°	3
$\langle 110\rangle$	31.3°	4
	64.0°	2
	65.4°	4
	90°	2

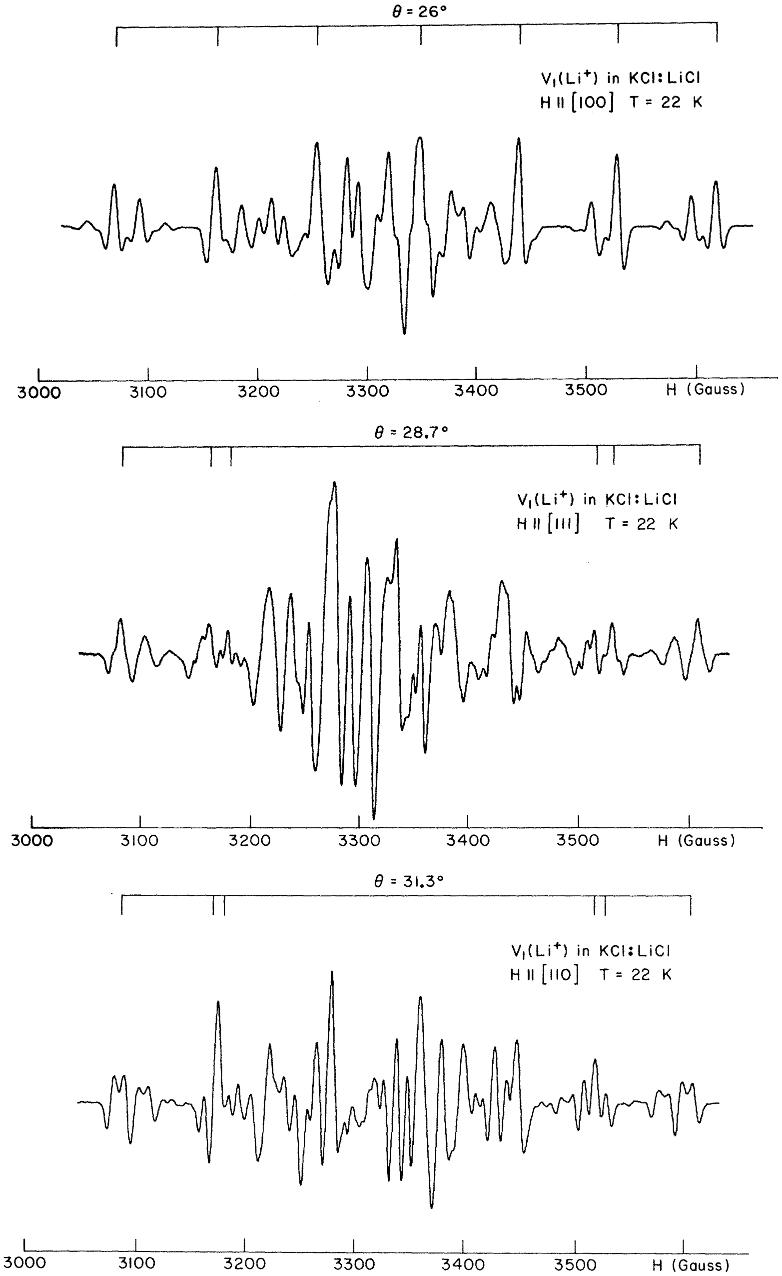

FIG. 1. EPR spectra recorded at 22 K and at about 9.402 GHz of the $V_1(\mathrm{Li}^+)$ center in KCl:Li⁺ (~ 50 × 10^{-3} mole % of Li⁺) for three special orientations of the magnetic field $\vec{H}$. The crystal was irradiated at 77 K and the V_K centers had been bleached out optically. The second derivative of the absorption is presented.

seven lines whose intensities would be 1 : 2 : 3 : 4 : 3 : 2 : 1 if the two nuclei were equivalent. An angular variation study in the {001} and {110} planes shows that the molecular axis lies in a {110} plane and that the total hf splitting reaches a maximum when $\alpha = 26° \pm 1°$, where α is the angle measured from a ⟨001⟩ direction in a {110} plane. Table I shows the classification for three special orientations of the magnetic field $\vec{H}$ of a center whose symmetry axis makes an angle of 26° with a ⟨001⟩ direction in a {110} plane. Some lines of some of the spectra that are readily recognized are indicated in Fig. 1. A closer inspection of the $\theta = 26°$ spectrum observed when $\vec{H} \parallel [001]$ reveals that the seven strong hf lines (arising from the $^{35}\mathrm{Cl}$-$^{35}\mathrm{Cl}^-$ combination, which we will consider exclusively) do not have the 1 : 2 : 3 : 4 : 3 : 2 : 1 intensity ratios, but rather 1 : 1. 6 : 2. 1: · · · :2. 1 : 1. 6 : 1. Furthermore, in the $\theta = 28.7°$ spectrum observed when $\vec{H} \parallel [111]$, the degenerate lines are clearly split. These observations can only be explained if it is accepted that (a) the two Cl nuclei, labeled 1 and

2, of the Cl_2^- species are inequivalent, i.e., the hf interaction is somewhat different for each nucleus, and (b) the 1-2 molecular bond is bent. The latter means that the symmetry axes of the hf tensors of the two nuclei do not coincide with each other but make angles δ and $-\delta'$ with the internuclear axis 1-2. This implies that the maximum hf interaction with nucleus 1 will occur for an angle α_1 which is different from α_2, the angle for which the hf interaction with nucleus 2 reaches a maximum. The total bending $|\delta+\delta'|$ is given by $|\alpha_1-\alpha_2|$. In principle, α_1 and α_2 could be determined by a careful quantitative angular variation study in a $\{110\}$ plane by observing for which angles K_1 and K_2, the first-order hf separations as defined in (2), reach their respective maximum. Such a procedure was adopted in the case of the $V_1(Na^+)$ center in KCl[10,11] to determine the sense and the magnitude of the bending. However, the large linewidths and the large number of overlapping spectra make such measurements very difficult for the $V_1(Li^+)$ center. Therefore, the magnitude and sense of the bending were determined by the quantitative analysis of the EPR spectra described below.

The spin Hamiltonian used to describe the $V_1(Li^+)$ center was taken as

$$\frac{\mathcal{H}}{g_0\beta}=\frac{1}{g_0}\,\vec{H}\cdot\overleftrightarrow{g}\cdot\vec{S}+\sum_{i=1}^{2}\vec{S}\cdot\overleftrightarrow{A}_i\cdot\vec{I}_i\ , \qquad (1)$$

in which the principal axes of the $\overleftrightarrow{g}_1$, $\overleftrightarrow{A}_1$, and $\overleftrightarrow{A}_2$ tensors do not coincide with each other or with the straight internuclear axis 1-2. Note that in principle the straight internuclear axis 1-2 does not coincide with the direction defined by the maximum of the gross hf interaction, since nuclei 1 and 2 are not equivalent. However, it is found that $\overleftrightarrow{A}_1$ and $\overleftrightarrow{A}_2$ are comparable in size and, therefore, comparable in angular variation and so it is a good approximation to identify $\alpha=26°$ with the direction of the internuclear axis 1-2.

Not enough lines could be measured with enough precision to determine quadrupole effects, and a quadrupole term was not included in (1). For the same reason, axial symmetry was assumed for both the $\overleftrightarrow{g}$ and $\overleftrightarrow{A}_i$ tensors. A second-order perturbation solution[17] was used in fitting (1) to the experimental spectra. The angular variations of the g factor and the first-order hf separation are given by

$$\begin{aligned} g^2(\theta_g)&=g_\parallel^2\cos^2\theta_g+g_\perp^2\sin^2\theta_g\ ,\\ K_i^2(\theta_i)\,g^2(\theta_i)&=A^2_{\parallel,i}\,g_\parallel^2\cos^2\theta_i+A^2_{\perp,i}\,g_\perp^2\sin^2\theta_i\ , \end{aligned} \qquad (2)$$

where θ_g and θ_i are measured from the principal axis of the $\overleftrightarrow{g}$ tensor and the principal axis of the $\overleftrightarrow{A}_i$ tensor, respectively.

Analysis of the $\theta=0°$ spectrum ($\alpha=26°$), gives $K_1(\delta)=106.2\pm0.5$ G and $K_2(-\delta')=96.2\pm0.5$ G. Since K_1 and K_2 are not much different from each other it is a good approximation to take $\delta\cong\delta'$. The analysis to be given below shows indeed that $\delta\cong\delta'=4°$. So A_{z1} and A_{z2} were determined to a sufficient degree of accuracy by $A_{z1}=K_1(4°)/\cos 4°=106.5$ G and $A_{z2}=K_2(-4°)/\cos 4°=96.5$ G. The total bending angle $\delta+\delta'$ was determined from the $\theta=26°$ ($\vec{H}\parallel[001]$), and the $\theta=28.7°$ ($\vec{H}\parallel[111]$) spectra. The $\theta=26°$ spectrum yields $K_1(26°+\delta)=93.4\pm0.5$ G and $K_2(26°-\delta')=90.4\pm0.5$ G, and the $\theta=28.7°$ spectrum yields $K_1(28.7°-\delta)=95.8\pm1$ G and $K_2(28.7°+\delta')=80.1\pm1$ G. The values of δ and δ' are then obtained by requiring that $K_1(26°+\delta)$ and $K_1(28.7°-\delta)$, and similarly $K_2(26°-\delta')$ and $K_2(28.7°+\delta')$, should extrapolate to, respectively, the same $A_{\perp1}$ and $A_{\perp2}$ value, using (2). One finds that $A_{\perp1}\cong A_{\perp2}\cong 10$ G, and $\delta\cong\delta'=4°\pm1°$, which means that the total bending of the molecular bond is about 8°. Similarly, the orientation of the g-tensor principal axis is obtained by determining ϵ, so that $g(26°+\epsilon)=2.0085\pm0.0010$ (from $\vec{H}\parallel[001]$) and $g(28.7°-\epsilon)=2.0080\pm0.0010$ (from $\vec{H}\parallel[111]$) extrapolate to the same $g_\perp$ value. It is found that $\epsilon=2°\pm1°$ which means that the g-tensor symmetry axis does not coincide with the internuclear axis, but is tilted, as it should be, in the direction of the symmetry axis of the hf tensor which has the largest magnitude, i.e., $\overleftrightarrow{A}_1$. The analysis of the $\theta=31.3°$ spectrum observed when $\vec{H}\parallel[110]$ is in general agreement with the previous results.

The H- and $V_1(Na^+)$-center EPR spectra show resolved superhyperfine structure (shf)[4,10] originating from hf interaction with two other chlorine nuclei, labeled 3 and 4, requiring the addition of a term

$$\sum_{i=3,4}\vec{S}\cdot\overleftrightarrow{A}_i\cdot\vec{I}_i$$

to the spin Hamiltonian (1). We believe that a similar thing is also true for the $V_1(Li^+)$ center because careful measurements reveal that the linewidth and line shape show an angular dependence. The widths ΔH (between the extrema of the first derivative) are obtained as follows:

$$\begin{aligned} &\Delta H(26°)=7.5\pm0.5\ \text{G},\quad (\vec{H}\,\|\,[001])\\ &\Delta H(28.7°)=11.7\pm0.5\ \text{G},\quad (\vec{H}\,\|\,[111])\\ &\Delta H(0°)=9.5\pm0.5\ \text{G},\quad (\vec{H}\,\|\,[001]+26° \text{ in } (1\bar{1}0) \text{ plane}) \qquad (3)\\ &\Delta H(31.3°)=15.4\pm0.5\ \text{G},\quad (\vec{H}\,\|\,[011])\ . \end{aligned}$$

A few examples of the first-derivative experimen-

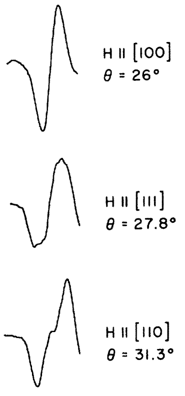

FIG. 2. The first derivative EPR line shapes of the $V_1(\mathrm{Li}^+)$ center at 22 K for a few orientations of the magnetic field $\vec{H}$. The lowest field lines are presented.

tal line shapes, some of which show a hint of unresolved shf structure, are shown in Fig. 2. The 0° line shape is qualitatively similar to the 28.7° line shape. One crucial experiment was performed which shows clearly where the unresolved shf does *not* come from. A KCl crystal was grown with isotopically enriched LiCl: 99.3% of ^{6}Li. The ^{6}Li isotope, which is normally 7.4% abundant, has a nuclear moment $\mu = 0.821\,92$ and a nuclear spin $I = 1$, as compared to $\mu = 3.2560$ and $I = \frac{3}{2}$ for ^{7}Li, which is normally 92.6% abundant. If a large fraction of the linewidth originated from hf interaction with the nearby Li nucleus, then the $V_1(^6\mathrm{Li}^+)$-center lines should be appreciably narrower than the $V_1(^7\mathrm{Li}^+)$-center lines. The experiment with the KCl : ^{6}Li$^+$ crystal showed not the slightest change in linewidth and line shape compared to KCl : ^{7}Li. Consequently, the contribution of the Li nuclear moment to the $V_1(\mathrm{Li}^+)$-center linewidth is negligible. It is also unlikely that the unresolved shf structure originates from interaction with the K$^+$ nuclei, not only because they have a low nuclear moment ($\mu = 0.3909$, $I = \frac{3}{2}$ for the 93.1% abundant ^{39}K) but also because no resolved K-nucleus hf effects have been observed in other centers such as H, $V_1(\mathrm{Na}^+)$, or V_K. We conclude that the unresolved structure is caused by hf interaction with one or more chlorine nuclei, just as in the cases of H and $V_1(\mathrm{Na}^+)$.

It is immediately clear from the linewidth results (3), that the symmetry axis or axes of this unresolved shf structure do not coincide with the symmetry axes of the hf tensors of chlorine nuclei 1, 2, or the g tensor. Furthermore, the line shapes of the $\theta = 0°$, 26°, and 28.7° spectra, which are all measured in the same (110) plane, show a sharp center, while the $\theta = 31.3°$ spectrum, not measured in the same plane, shows a flattened center (see Fig. 2). A flattened line is indicative of an unresolved set of lines which have equal intensity.[18] Such a line shape could originate from a four-line hf pattern of a single chlorine nucleus, or from a $4 \times 4 = 16$ line pattern of two *strongly* inequivalent Cl nuclei. Lines that have sharp centers originate from a symmetric set of lines of unequal but monotonically changing intensities. For instance, a line with a sharp center might result from the unresolved 1 : 2 : 3 : 4 : 3 : 2 : 1 hf pattern of two equivalent Cl nuclei. It is clear that we have gone about as far as we can in extracting information from the shape and angular variation of the linewidth, and we need some further information in order to decide where the unresolved shf structure comes from. The discussion of the $V_1(\mathrm{Li}^+)$-center model to be given in Sec. VI strongly indicates, however, that the shf originates from two symmetrically placed Cl nuclei, labeled 3 and 4, which are positioned in such a way with respect to the basic Cl_2^- molecule ion (with nuclei 1 and 2) that the shape of the center is that of a nonplanar Y (see Fig. 3), and the hf symmetry axes 2-3 and 2-4 are roughly perpendicular to one another. Such a geometry is consistent with the observed linewidth angular dependence. The 1-2 internuclear axis of the basic Cl_2^- lies in the $(1\bar{1}0)$ plane. 26° from [001], and for all orientations of the magnetic field in this $(1\bar{1}0)$ plane Cl nuclei 3 and 4 are completely equivalent. The $\theta = 0°$, 26°, and 28.7° spectra correspond to this situation, and as we just discussed, their line shapes are consistent with interaction with two equivalent nuclei. For the 31.3° spectrum observed when $\vec{H} \parallel [011]$, Cl nuclei 3 and 4 are strongly inequivalent since their hf symmetry axes are nearly perpendicular, and this again is consistent with the observed line shape.

With this specific geometry of the $V_1(\mathrm{Li}^+)$ center in mind, and making use of a line-shape atlas,[18] the linewidth results can be analysed. By trying to fit the linewidths (3) to an angular variation of the type (2) and keeping in mind that for $\Delta H(31.3°)$ the two Cl nuclei 3 and 4 are strongly inequivalent, one can very roughly determine the orientation of the $\overleftrightarrow{A}_3$ and $\overleftrightarrow{A}_4$ symmetry axes 2-3 and 2-4. The direction cosines with respect to, respectively,

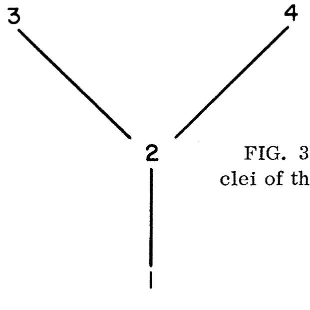

FIG. 3. Configuration of Cl nuclei of the $V_1(\mathrm{Li}^+)$ center.

[100], [010], and [001] are, very roughly,

$$\text{for 2-3:}\quad [0.912; -0.154; 0.380]\ ,$$
$$\text{and for 2-4:}\quad [-0.154; 0.912; 0.380]\ . \tag{4}$$

The angles between 2-3 (or 2-4) and [001], the internuclear axis 1-2 (whose direction cosines are [0.3100; 0.3100; 0.8988]) and [111] are, respectively, ~68°, ~55°, and ~49°, and the angle between 2-3 and 2-4 is ~90°. The angle between 2-3 and [011] is ~80°, and between 2-4 and [011] it is ~24°. The analysis finally leads to the values

$$A_{\parallel 3} = A_{\parallel 4} = 4.2 \pm 0.3\ \text{G}\ ,$$

$$A_{\perp 3} = A_{\perp 4} = 1.4 \pm 0.5\ \text{G}\ ,$$

and a reduced linewidth

$$\Delta H = 3.5 \pm 1\ \text{G}\ .$$

The spin-resonance results are summarized in Table II, and the results for the H and $V_1(\text{Na}^+)$ centers[10] are included for comparison. On the whole the $V_1(\text{Li}^+)$ parameters are somewhat less precise than those of $V_1(\text{Na}^+)$ and H. Definite trends are observed in Table II. The perpendicular g shift $\Delta g_\perp = \frac{1}{2}(\Delta g_x + \Delta g_y)$, in which $\Delta g_x = g_x - g_0$, etc., increases going from H to $V_1(\text{Na}^+)$ to $V_1(\text{Li}^+)$. Since these three centers are all essentially Cl_2^- molecule ions (we ignore bending, inequivalence of the nuclei, and the effect of ions 3 and 4), the $g_\perp$ value is to first order given by[2,19]

$$g_\perp \cong g_0 + 2\lambda/E\ ,$$

in which $g_0 = 2.0023$ is the free-electron g value, $\lambda > 0$ the spin-orbit coupling constant of the molecule ion, and E the energy between the $^2\Sigma_g^+$ ground state and the $^2\Pi_g$ excited state of Cl_2^-. Because of the r^{-3} dependence of the spin-orbit interaction near each nucleus, the value of λ is probably not strongly dependent upon the internuclear separation r_e. For the same change Δr_e, the value of E changes probably more than λ, and so the increase in $\Delta g_\perp$ is very likely caused by a decrease of E going from H to $V_1(\text{Na}^+)$ to $V_1(\text{Li}^+)$. The calculations of Wahl and Gilbert[20] indicated that E decreases with increasing internuclear distance. The increase in $\Delta g_\perp$ could, therefore, be indicative of a slight increase in Cl_2^- internuclear distance, going from H to $V_1(\text{Na}^+)$ to $V_1(\text{Li}^+)$. A similar conclusion is drawn from the change in the average hf separation: It decreases from H to $V_1(\text{Na}^+)$ to

TABLE II. Spin-Hamiltonian parameters of the $V_1(\text{Li}^+)$, $V_1(\text{Na}^+)$, and H centers in KCl at, respectively, $T = 22$, 35, and 25 K. The hyperfine (hf) parameters A (corresponding to the ^{35}Cl nucleus) and the linewidth ΔH (between the extrema of the first derivative) are given in G. δ is the total bending of the Cl_2^- molecular bond.

Center	g_z	g_x	g_y	$A_{\parallel 1,2}$	$A_{\perp 1,2}$	$A_{\parallel 3,4}$	$A_{\perp 3,4}$	ΔH	δ
$V_1(\text{Li}^+)$	2.0020^{a} ± 0.0004	2.031 ± 0.002		$A_{\parallel,1}{}^{\text{b}} = 106.5$ ± 0.5 $A_{\parallel,2}{}^{\text{b}} = 96.5$ ± 0.5	$A_{\perp,1} = 10$ ± 10 $A_{\perp,2} = 10$ ± 10	$A_{\parallel,3}{}^{\text{c}} \equiv A_{\parallel,4}{}^{\text{c}}$ $= 4.2$ ± 0.5	$A_{\perp,3} = A_{\perp,4}$ $= 1.4$ ± 0.3	3.5^{d} ± 1	8° ±2°
$V_1(\text{Na}^+)$	2.0018^{e} ± 0.0003	2.024 ± 0.001	2.027 ± 0.001	$A_{\parallel,1}{}^{\text{f}} = 109.1$ ± 0.1 $A_{\parallel,2}{}^{\text{f}} = 101.1$ ± 0.1	$A_{\perp,1} = 14$ ± 4 $A_{\perp,2} = 14$ ± 4	$A_{\parallel,3}{}^{\text{g}} = 13.7$ ± 0.1 $A_{\parallel,4}{}^{\text{g}} = 3.1$ ± 0.1	$A_{\perp,3} = 4.6$ ± 0.5 $A_{\perp,4} = 1.3$ ± 0.5	1.8 ± 0.1	4.5° ±1.°
H^{h}	2.0018^{i} ± 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	$A_{\perp,3} \equiv A_{\perp,4}$ $= 2.7$ ± 0.1	1.2 ± 0.1	0°

[a] For $V_1(\text{Li}^+)$: $z \parallel [\langle 001\rangle + 28° \pm 1°$ in a $\{110\}$ plane].

[b] The symmetry axes of $\overleftrightarrow{A}_1$ and $\overleftrightarrow{A}_2$ of $V_1(\text{Li}^+)$ make, respectively, a 30° ± 1° and 22° ± 1° angle with $\langle 001\rangle$ in a $\{110\}$ plane. The gross total hf separation reaches a maximum for $\alpha = 26° \pm 1°$.

[c] The symmetry axes of $\overleftrightarrow{A}_3$ and $\overleftrightarrow{A}_4$ do not coincide and are roughly perpendicular to one another. Approximate direction cosines are given by Eq. (4) in the text.

[d] This is the reduced $V_1(\text{Li}^+)$ linewidth (see text).

[e] For $V_1(\text{Na}^+)$: $z \parallel [\langle 110\rangle + 5.7°$ in a $\{001\}$ plane], $x \parallel \langle 001\rangle$.

[f] The symmetry axes of $\overleftrightarrow{A}_1$ and $\overleftrightarrow{A}_2$ of $V_1(\text{Na}^+)$ make, respectively, a $3.5° \pm 0.6°$ and $8.0° \pm 0.6°$ angle with $\langle 110\rangle$ in a $\{001\}$ plane.

[g] For the analysis it was assumed that the $\overleftrightarrow{A}_3$ and $\overleftrightarrow{A}_4$ symmetry axes of $V_1(\text{Na}^+)$ coincide with each other and with the g-tensor axis z (Ref. 10).

[h] For the quadrupole term $\Sigma_{L=1}^{z} P I_{zi}^2$ one finds for the H center: $P = -5.7 \pm 2$ G.

[i] For the H center: $z \parallel [110]$, $x \parallel [001]$, and $y \parallel [1\bar{1}0]$ and the symmetry axes of the $\overleftrightarrow{g}$ and the four $\overleftrightarrow{A}$ tensors coincide.

$V_1(\mathrm{Li}^+)$. A comparison with the hf calculation of Jette, Gilbert and Das[21] on Cl_2^- again indicates that such a trend can be correlated with a small increase in internuclear distance in going from H to $V_1(\mathrm{Na}^+)$ to $V_1(\mathrm{Li}^+)$. The behavior of the optical transitions, which will be discussed in Sec. IV, leads to identical conclusions.

The hf interaction is roughly 10% larger for nucleus 1 than for nucleus 2, which indicates that the unpaired electron density is at most 10% larger at and around nucleus 1 than at and around nucleus 2. This means also that the total electron density around nucleus 1 is smaller than the total electron density around nucleus 2.

Finally, the reduced linewidth of $V_1(\mathrm{Li}^+)$ is larger than the linewidth of $V_1(\mathrm{Na}^+)$ and H. If the $^7\mathrm{Li}^+$ nucleus contributed considerably to this reduced linewidth, then, as we discussed before, the reduced linewidth of the $V_1(^6\mathrm{Li}^+)$ center should be considerably smaller and this should be reflected in the unreduced line shape. Since experimentally no difference is observed between the $V_1(^7\mathrm{Li}^+)$ and $V_1(^6\mathrm{Li}^+)$ linewidths and line shapes, one concludes that the reduced linewidth is also caused primarily by unresolved hf interaction with Cl nuclei rather than with the Li^+ nucleus. This conclusion for the $V_1(\mathrm{Li}^+)$ center makes one wonder whether the larger linewidth for the $V_1(\mathrm{Na}^+)$ center[10] (1.8 G) compared to the H center (1.1 G) is really explained by the larger nuclear moment of $^{23}\mathrm{Na}^+$ ($\mu = 2.2161$, $I = \frac{3}{2}$) compared to $^{39}\mathrm{K}^+$ ($\mu = 0.390\,94$, $I = \frac{3}{2}$). An ENDOR investigation of these centers could further clarify this point.

IV. OPTICAL ABSORPTION MEASUREMENTS

The H and $V_1(\mathrm{Na}^+)$ centers, which are both to a first approximation Cl_2^- molecule ions, have two absorption bands[5,10]: a strong one in the uv and a weaker one in the red [e.g., respectively, 357 and 560 nm for $V_1(\mathrm{Na}^+)$]. Since the $V_1(\mathrm{Li}^+)$ center is also basically a Cl_2^- molecule ion, it too should possess two analogous absorption bands. In terms of the free Cl_2^- molecule ion, whose valence electron configuration and ground state is

$$(\sigma_g^2\pi_u^4\pi_g^4\sigma_u^1),\quad {}^2\Sigma_u^+ \quad , \tag{5}$$

these two transitions are identified with

$${}^2\Sigma_u^+ \to (\sigma_g^1\pi_u^4\pi_g^4\sigma_u^2),\quad {}^2\Sigma_g^+$$

and $^2\Sigma_u^+ \to (\sigma_g^2\pi_u^4\pi_g^3\sigma_u^2)$, $^2\Pi_g$, respectively.

Even though the $V_1(\mathrm{Na}^+)$ and $V_1(\mathrm{Li}^+)$ centers do not have inversion symmetry (actually both only have m symmetry), it is convenient to use the free-molecule-ion nomenclature to indicate the molecular states.

These two transitions are indeed observed for

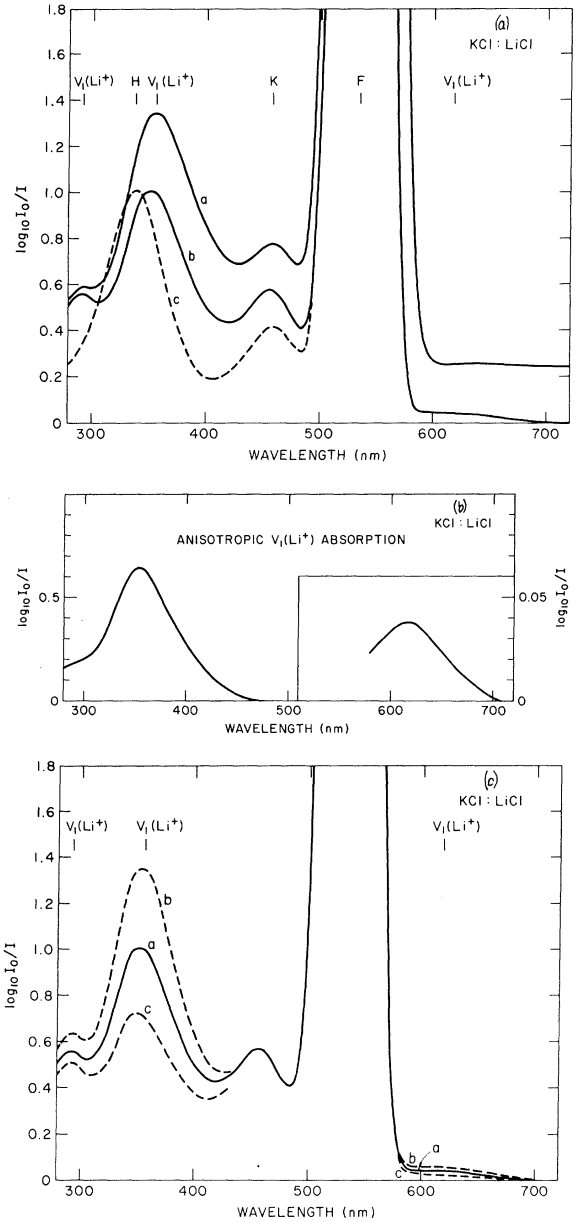

FIG. 4. (a) Optical absorption measurements on a 10-mm-thick KCl:Li^+ crystal ($\sim 50\times10^{-3}$ mole % of Li^+): curve a irradiated for 4 h with γ rays of a 2000 Ci^{60}Co source at the temperature of dry ice (-81 °C), warmed up to -60 °C and measured at 77 K; curve b after an optical bleach into the F and F' bands and measured at 4.2 K; curve c H-center absorption obtained by prolonged excitation in the long-wavelength tail of the $V_1(\mathrm{Li}^+)$ center absorption with nonpolarized 405-nm light at 4.2 K.

(b) Anisotropic optical absorption measurements at 4.2 K on a KCl : Li^+ crystal: curve a, same curve as curve b of (a); curve b after a [110]-polarized light excitation in the 618-nm band of $V_1(\mathrm{Li}^+)$ and measured along [110]; curve c measured along [110].

(c) Anisotropic optical absorption of the $V_1(\mathrm{Li}^+)$ center, obtained by subtracting curve c from curve b in (b).

the $V_1(\text{Li}^+)$ center, and Fig. 4 shows a sequence of optical absorption measurements. Curve a in Fig. 4(a) shows the absorption of a KCl: Li$^+$ crystal irradiated with γ rays at the temperature of dry ice (− 81 °C) and measured at 77 K after a warmup to about − 60 °C. One observes the strong F band, the very broad F' band, and an absorption in the 300–400-nm region which is mainly a superposition of the $V_{KA}(\text{Li}^+)$ and $V_1(\text{Li}^+)$ absorption bands. As a result of this high irradiation temperature, no $V_1(\text{Na}^+)$ absorption at 357 nm nor V_K at 367 nm is present [another convenient irradiation temperature which avoids the formation of $V_1(\text{Na}^+)$ is the boiling temperature of Freon 14: − 128 °C]. The crystal is subsequently irradiated for a few minutes with light in the F' band and the long-wavelength tail of the F band (HBO-500 lamp + Corning filter No. 3480). All F' centers and a fraction of the F centers disappear together with part of the absorption in the 300–400-nm region. This is shown by curve b in Fig. 4(a), which was measured at 4.2 K after this treatment. What has disappeared in this region is primarily the total $V_{KA}(\text{Li}^+)$ absorption. The $V_{KA}(\text{Li}^+)$ centers are positively charged and they therefore attract the electrons released from the F and F' centers. The remaining absorption at 354 nm represents primarily the $^2\Sigma_u^+ \to {}^2\Sigma_g^+$ uv absorption from the $V_1(\text{Li}^+)$ center. Continued excitation of the F center hardly affects this absorption band. This behavior under F-center excitation, which is also observed in the EPR experiments, parallels that of the H and $V_1(\text{Na}^+)$ centers, indicating that, like these centers, the $V_1(\text{Li}^+)$ is also a neutral center. The same curve b in Fig. 4(a) also shows a weak absorption around 618 nm which, it turns out, represents the $^2\Sigma_w^+ \to {}^2\Pi_g$ absorption band of $V_1(\text{Li}^+)$.

Optical anisotropy can be produced in both bands at 4.2 K with ⟨110⟩-polarized light. The polarization character of both bands is the same, i.e., if after excitation with [110]-polarized light in either one of these bands, the absorption is measured with the electric vector along the [110] direction, one observes that both absorption bands have decreased. On the other hand, both absorption bands have increased when measured along the perpendicular [1$\bar{1}$0] direction. Since by analogy with the H^5 and V_K^3 centers, the $^2\Sigma_u^+ \to {}^2\Sigma_g^+$ uv transition at 354 nm is undoubtedly σ polarized, one concludes that the $^2\Sigma_u^+ \to {}^2\Pi_g$ at 618 nm is also σ polarized.

It is observed, however, that in orienting the $V_1(\text{Li}^+)$ centers with light in the 354-nm band, oriented H centers are formed quite efficiently, because this excitation has a high probability of dissociating the Cl_2^- molecule ion of the $V_1(\text{Li}^+)$ center. The interstitial chlorine atom Cl_i^0 thus produced is stabilized as an H center a few lattice spacings away. Apart from a shift of the absorption peak to shorter wavelengths (the H-center absorption is situated at 335 nm), the presence of H centers is indicated unambiguously by the fact that part of the produced anisotropy disappears at 10.9 K, which is the characteristic disorientation temperature of the H center.[5,22] This optical $V_1(\text{Li}^+) \to H$-center conversion was furthermore verified in the EPR experiments. Curve c in Fig. 4(a) actually shows the H-center absorption, obtained by prolonged excitation with nonpolarized light (405 nm) in the long-wavelength tail of the $V_1(\text{Li}^+)$-center absorption band. If the crystal is subsequently warmed up above the decay temperature of the H centers (~42 K), $V_1(\text{Li}^+)$ centers are reformed.

However, large anisotropies are also produced by irradiating with ⟨110⟩-polarized light in the 618-nm $V_1(\text{Li}^+)$ band. In this case there is no evidence, neither from the optical absorption nor from the EPR measurements, that H centers are formed. Therefore, this transition was used in determining the anisotropic absorption spectrum of the $V_1(\text{Li}^+)$ center.

These measurements are shown in Fig. 4(b). Curve a [which is the same as curve b in Fig. 4(a)], represents the absorption before polarized-light excitation. Curves b and c represent the absorption measured with the electric vector along, respectively, the [1$\bar{1}$0] and [110] directions after excitation with [110]-polarized light in the 618-nm band (HBO-500 lamp + Corning filter No. 2418). The difference between curves b and c represents the anisotropic absorption spectrum of the $V_1(\text{Li}^+)$ center and it is plotted in Fig. 4(c), from which one determines that the relative intensity of the 354- to the 618-nm peak is ~35: 1, compared to ~70: 1 for $V_1(\text{Na}^+)$ (Ref. 10) and ~100: 1 for H (Ref. 5).

Besides these two bands one observes clearly an anisotropic absorption at about 293 nm in Fig. 4 whose intensity is about one-fourth that of the 354-nm band. This peak stands out a little more in the gross absorption spectrum [Figs. 4(a) and (b)] than in the anisotropic absorption spectrum [Fig. 4(c)], indicating that the strength of the σ character is smaller for the 293- than for the 354-nm peak. All the measurements performed so far point to the fact that this 293-nm transition belongs to the $V_1(\text{Li}^+)$ center. Apart from the polarized-light measurements one also finds that the 293- and 354-nm peaks decay at the same temperature (− 35 °C), and in the optical $V_1(\text{Li}^+)$ to H conversion [see Fig. 4(a)] the 293- and 354-nm peaks disappear together. Furthermore, for the $V_1(\text{Li}^+)$ center in KBr: Li$^+$ two corresponding optical transitions are observed (see Sec. V). The possible origin of this 293-nm band will be discussed in

TABLE III. Results of the optical absorption measurements on the $V_1(\mathrm{Li}^+)$, $V_1(\mathrm{Na}^+)$, and H centers in KCl.

Center	Peak position (nm)	Half-width (eV)	Relative intensity	Disorientation temp. (°K)	Decay temp. (°K)
$V_1(\mathrm{Li}^+)$	618^a	0.30	1	23.5	240
	354^b	0.70	35		
	293^c	0.7	9		
$V_1(\mathrm{Na}^+)^d$	560^a	0.32	1	16.8	120
	357^b	0.65	70		
H^d	522^a	0.25	1	10.9	42
	338^b	0.66	100		

[a] This transition corresponds to the ${}^2\Sigma_u^+ \rightarrow {}^2\Pi_g$ transition of the free Cl_2^- molecule ion.

[b] This transition corresponds to the ${}^2\Sigma_u^+ \rightarrow {}^2\Sigma_g^+$ transition of the free Cl_2^- molecule ion.

[c] It is proposed that this band represents a charge-transfer transition from the Cl_2^- to the Li^+ ion (see text).

[d] From Ref. 10.

Sec. VI.

The optical anisotropy produced at 4.2 K with ⟨110⟩-polarized light persists indefinitely at this temperature, but when the crystal is warmed up slowly (~0.5 K/min) one observes that above ~21 K the anisotropy begins to disappear. If the excitation was done in the 618-nm band in order to avoid H-center formation, and if the $V_1(\mathrm{Na}^+)$ centers, if present originally, were eliminated beforehand through a warmup above − 150 °C, then there is no change in the anisotropy between 4.2 and 21 K. At 23.5 K, half of the anisotropy has disappeared, and this temperature is defined as the disorientation temperature T_D. This T_D is very characteristic for the $V_1(\mathrm{Li}^+)$ center and can be used to identify it. An experiment in a ${}^6\mathrm{Li}^+$-enriched KCl crystal showed that within the accuracy of the measurements (~1°) the T_D of $V_1({}^6\mathrm{Li}^+)$ was the same as for $V_1({}^7\mathrm{Li}^+)$.[23]

The results of the optical measurements are summarized in Table III. This table also includes the decay temperatures of these centers. Both the optical and EPR measurements gave the same temperature. As can be seen, the thermal stability of the interstitial chlorine atom Cl_i^0 increases substantially in going from H to $V_1(\mathrm{Na}^+)$ to $V_1(\mathrm{Li}^+)$. The decay of the $V_1(\mathrm{Li}^+)$ center gives rise to the creation of a strong absorption band at 234 nm.

Table III also shows that the energies of the optical transitions, especially the red transitions, decrease going from H to $V_1(\mathrm{Na}^+)$ to $V_1(\mathrm{Li}^+)$. Such behavior may indicate that there is a slight increase in the Cl_2^- internuclear distance going from H to $V_1(\mathrm{Na}^+)$ to $V_1(\mathrm{Li}^+)$. These observations agree with those obtained from the EPR measurements in Sec. III.

V. $V_1(\mathrm{Li}^+)$ CENTER IN KBr:Li$^+$

A preliminary EPR experiment on a KBr crystal containing small amounts of Li^+, showed that the $V_1(\mathrm{Li}^+)$ center can be produced by x or γ irradiation at 77 K and that qualitatively it has the same symmetry as the $V_1(\mathrm{Li}^+)$ center in KCl. At 4.2 K the gross hf interacton reaches a maximum when the magnetic field makes a 27° ± 1° angle with ⟨001⟩ in a {110} plane, but the spectrum was not analyzed further. Optical absorption measurements indicated that the uv absorption bands of the $V_1(\mathrm{Li}^+)$ center in KBr are situated at 438 and 380 nm. These absorption bands are very likely analogous to, respectively, the 354- and 293-nm bands of $V_1(\mathrm{Li}^+)$ in KCl. The $V_1(\mathrm{Li}^+)$ center in KBr decays thermally at − 55 °C, and a strong absorption band at 304 nm is produced.[24]

VI. STRUCTURE OF $V_1(\mathrm{Li}^+)$ CENTER AND DISCUSSION

The model for the $V_1(\mathrm{Li}^+)$ center must agree with the following observations which were discussed in Secs. I–V: (a) The center comprises a Cl_2^- molecule ion which makes a 26° angle with ⟨001⟩ in a {110} plane, (b) the center is very likely associated with a Li^+ ion since it is only produced in Li^+-doped KCl, (c) the center is electrically neutral, (d) decomposition of $V_1(\mathrm{Li}^+)$ centers through optical excitation in the 354-nm uv absorption results in the formation of H centers, and (e) H centers which migrate through the crystal above 42 K can be converted back to $V_1(\mathrm{Li}^+)$ centers.

Since the H center is essentially an interstitial chlorine atom Cl_i^0 stabilized as a Cl_2^- molecule ion in a single negative-ion vacancy, these observations strongly indicate that the $V_1(\mathrm{Li}^+)$ center is an interstitial chlorine atom stabilized to a higher temperature by being trapped next to a substitutional Li^+ ion as a Cl_2^- molecule ion in a single negative-ion vacancy. In short, the $V_1(\mathrm{Li}^+)$ center can be considered as being an H center trapped and stabilized next to a substitutional Li^+ impurity, just as the $V_1(\mathrm{Na}^+)$ center is an H center stabilized by a substitutional Na^+ ion.[10]

The difference in geometry between $V_1(\mathrm{Na}^+)$ and $V_1(\mathrm{Li}^+)$ is immediately obvious: For $V_1(\mathrm{Li}^+)$, the Cl_2^- internuclear axis makes a 26° angle with a ⟨001⟩ direction in a {110} plane, whereas for $V_1(\mathrm{Na}^+)$, the internuclear axis makes a 5.7° angle with a ⟨110⟩ direction in a {001} plane.[10]

The difference in symmetry between $V_1(\mathrm{Li}^+)$ and $V_1(\mathrm{Na}^+)$ can be correlated with the difference in behavior of the Na^+ and Li^+ ions in KCl. The Na^+ impurity ion (radius: 0.96 Å) replaces the K^+ ion (radius: 1.33 Å) exactly, i.e., it sits at the center of the site vacated by the K^+ ion. This is not so for the Li^+ ion. Its small size (radius: 0.61 Å)

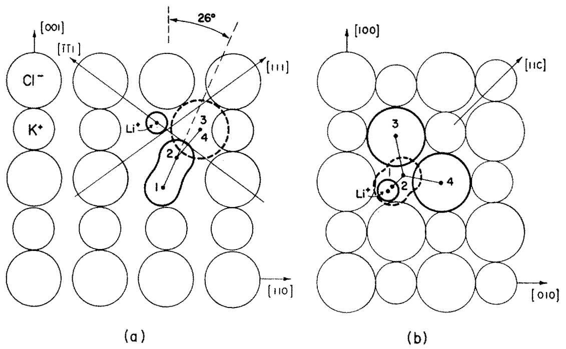

FIG. 5. Schemative representation of the $V_1(Li^+)$ center as seen from two sides: (a) in a {110} plane; (b) along a ⟨001⟩ direction. No attempt has been made to represent the lattice distortions around the center.

is one of the reasons (but not the only one[16]) why it occupies an equilibrium position off the center of the K^+ vacancy along one of the four ⟨111⟩ orientations of the lattice. This is now well established both experimentally and theoretically.[14-16]

The proposed model for the $V_1(Li^+)$ center which fits all observations is shown schematically from two sides in Fig. 5. No attempt has been made to represent the distortions of the lattice around this center. The Cl_2^- occupying a single negative-ion vacancy and making a 26° angle with the [001] direction in the (1$\bar{1}$0) plane is shown. The Li^+ ion is shown displaced along a ⟨111⟩ direction, but of course, after it has trapped and stabilized the interstitial Cl_i^0 atom it may be positioned either above or below the [$\bar{1}\bar{1}$1] line in the (1$\bar{1}$0) plane, drawn in Fig. 5; the latter possibility seems the most likely one. Since the Li^+ ion is both small and displaced, the Cl_2^- molecule ion is probably displaced a bit toward the Li^+ ion. This then would result in the Cl_2^- being closer to the two Cl^- ions labeled 3 and 4 in Fig. 5, than to any other Cl^- ion of the surroundings. Therefore, it is most likely that the nuclei of Cl^- ions 3 and 4 are the ones responsible for the unresolved shf structure of the $V_1(Li^+)$ EPR lines, and in the EPR analysis in Sec. III we have made use of this conclusion. The nuclear configuration of the $V_1(Li^+)$ center is, therefore, quite different from those of the H and $V_1(Na^+)$ centers. In the latter two cases the configuration (see Fig. 6) was linear or almost linear,[10] e.g.,

3-1-2-4 or 3-2-1-4.

For $V_1(Li^+)$ the nuclear configuration has the shape of a nonplanar Y, as in Fig. 3. From the evidence supplied by the EPR measurements (mainly the inequivalence of nuclei 1 and 2 together with the sense of the bending of the 1-2 molecular bond) it does not seem possible to decide, with a simple qualitative argument, what the relative positions of nuclei 1 and 2 are with respect to ions 3 and 4 (or for that matter, with respect to the Li^+ ion). The choice in Fig. 5 is an arbitrary one.

The difference in geometry between the $V_1(Li^+)$ and $V_1(Na^+)$ centers in KCl is not confined to the interstitial Cl_i^0 atom. Interstitial Br_i^0 and I_i^0 atoms in KCl are also trapped differently by the Li^+ and Na^+ ions.[12] Interstitial Br_i^0 and I_i^0 stabilized next to a Li^+ in, respectively, KCl: Li^+ : Br^-, and KCl: Li^+: I^-, manifest themselves as $BrCl^-$ and ICl^- molecule ions occupying a single negative-ion vacancy next to a Li^+ ion and their internuclear axes make both about a 23° angle with ⟨001⟩ in a {110} plane.[25] We call these centers $V_1(Li^+)$-type [or $H_A(Li^+)$-type] $BrCl^-$ and ICl^- centers. On the other hand, the Br_i^0 and I_i^0 interstitial atoms stabilized by Na^+ in KCl: Na^+: Br^- and KCl:Na^+: I^- manifest themselves as ⟨110⟩-oriented symmetric (i.e., of the type XYX^{--}) and almost linear $BrCl_2^{--}$ and ICl_2^{--} molecule ions in which the Br and I occupy an interstitial position next to the substitutional Na^+ ion, and between the two equivalent and substitutional chlorines. These observations lend further support to the conclusion that the characteristic geometry of the $V_1(Li^+)$-type centers is determined primarily by the off-center properties of the Li^+ ion as such in KCl.[26]

However, we have observed the $V_1(Li^+)$ center in KBr, but it has also been established experimentally that the Li^+ ion in KBr does not occupy a ⟨111⟩ (or other direction) off-center position.[15] A theoretical analysis of the KBr: Li^+ system has confirmed this latter observation,[16] but these calculations have also indicated that a very small change in the KBr lattice parameter will probably result in a ⟨111⟩ off-center position of the Li^+ ion in KBr. It is, therefore, probably more accurate to say that the characteristic $V_1(Li^+)$-center sym-

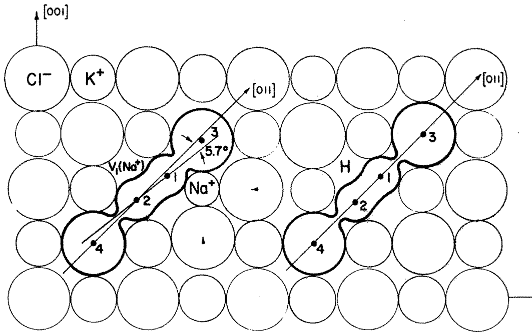

FIG. 6. Schematic models of the $V_1(Na^+)$ and H centers.

metry will occur when interstitial halogen atoms are trapped by impurity alkali ions which are either incipiently, or in fact $\langle 111 \rangle$ off center. Clearly, the investigation of other systems such as RbCl doped with Li^+, Na^+, or K^+ would be quite interesting. The possibility that some impurity alkali ion in some alkali halide may give rise, at sufficiently low temperatures, to both a $V_1(\mathrm{Na}^+)$ and a $V_1(\mathrm{Li}^+)$ geometry-type center cannot *a priori* be excluded. In such a case, one would expect that at higher temperatures one geometry would be transformed into the other.

For both the $V_1(\mathrm{Li}^+)$ and $V_1(\mathrm{Na}^+)$ centers in KCl, the interstitials are trapped by impurity alkali ions which are smaller than the alkali ion of the host lattice. The interstitial flourine atom trapped by a Na^+ ion in Na^+-doped LiF, whose ENDOR spectrum was analyzed by Dakss and Mieher,[27] is obviously different in this respect: the Na^+ has a larger size than the Li^+ ion of the host crystal. The F_2^- molecule ion of this center is accurately aligned along $\langle 110 \rangle$, whereas the F_2^- of the H center in LiF is $\langle 111 \rangle$ oriented.[6] In this respect, it would be interesting to investigate the V_1 centers (if they can indeed be created) in systems such as $\mathrm{KCl}:\mathrm{Rb}^+$ or $\mathrm{NaCl}:\mathrm{K}^+$, etc., in order to determine whether or not these types of V_1 centers exhibit the same geometry.

Finally, the existence of the 293-nm transition for the $V_1(\mathrm{Li}^+)$ center is quite interesting and should be investigated more thoroughly. It cannot be correlated with an excitation within the valence configuration (5) of the free Cl_2^- molecule ion. The transition corresponding to $^2\Sigma_u^+ \to {}^2\Pi_u$ is, in principle, allowed for $V_1(\mathrm{Li}^+)$ because of the low symmetry of this center. However, this transition should fall on the long-wavelength side of the 354-nm absorption band and furthermore it is very unlikely that the difference in charge distribution around the two chlorine nuclei (at most 10% according to the hf parameters) and the small bending of the molecular bond would make this transition a strong one. Rather, it is proposed that the 293-nm absorption band represents a charge-transfer transition, i.e., a transition in which the σ_u electron from the Cl_2^- is excited and transferred to the neighboring Li^+ ion. An alternative but possibly a less likely explanation, involves the transition of an electron from a Cl^- neighbor (essentially a valence-band electron) to the σ_u orbital of the Cl_2^-. However, since the Li^+ ion is not directly involved here, one would also expect to observe a similar transition at a comparable energy for the $V_1(\mathrm{Na}^+)$ and for the H center in KCl. Such transitions have not been reported for these centers in KCl,[5,10,28] and so the first mechanism for the 293-nm transition is favored.

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Host-Sensitized Energy Transfer in Molecular Crystals[†]

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The time evolution of the fluorescence intensities of tetracene-doped anthracene and anthracene-doped napthalene crystals was investigated for various concentrations of activators and different methods of excitation. Singlet exciton diffusion, generally invoked to explain energy transfer in these systems, cannot explain the observed time dependence, which indicates that energy transfer is more efficient at short times than at long times. Such a variation of energy-transfer efficiency is characteristic of long-range resonant interaction, but the predictions of the normal mathematical formulation of this theory also disagree with the results. A combined theory of long-range interaction and exciton diffusion can be made to fit the data only with a critical energy-transfer distance R_0, which is much greater than that determined from spectral considerations and a diffusion coefficient D, which is much smaller than that measured by other techniques.

I. INTRODUCTION

Energy transfer between an anthracene-host crystal and tetracene-impurity molecules was first observed about 35 yr ago.[1] Since that time, an extensive amount of work has been done in studying energy transfer in tetracene-doped anthracene and similar systems and the results of these investigations are summarized in several review articles.[2–7] In most of the recent investigations, energy transfer in these systems is attributed to singlet exciton diffusion where the transfer of energy is considered to be short-range process occurring between an excited host molecule and a nearest-neighbor impurity.[8–10] The singlet exciton diffusion coefficient D has been measured by several techniques and is reported to be on the order of 10^{-3} cm^2 sec^{-1} for anthracene crystals[10–13] and on the order of 10^{-4} cm^2 sec^{-1} for napthalene crystals.[14]

We recently reported experimental results on the time evolution of anthracene and tetracene fluorescence intensities in tetracene-doped anthracene crystals.[15,16] The usual mathematical formulation of singlet exciton diffusion theory cannot explain the observed time dependence. The results indicate that energy transfer is more efficient at short times than at long times, which is characteristic of long-range resonant interaction. It was found that the best fit to the data is obtained using a combined theory of diffusion plus long-range interaction. This theory yields a value for the diffusion