Optically Stimulated Orientation of V_k Centers in KCl†

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Previous studies in KI and KCl have shown that the thermally excited reorientation of V_k centers (in the dark) occurs by a jumping motion in which the V_k axis changes direction in a single jump by 60° but not by 90°. The experiments reported here were performed to determine whether such a preferred reorientation occurs in the electronic excited state of the V_k center following light absorption in the uv band, or whether the V_k center reorients randomly among sites having axes at 60° and 90° to the original site. This question is answered by two measurements of the optical anisotropy as a function of exposure time to linearly polarized light absorbed in the uv band of V_k centers in KCl:Pb at 78°K. Analysis of the experimental results indicates agreement with the case of random reorientation.

INTRODUCTION

THE V_k center, or self-trapped hole, is a well-known defect in alkali halide crystals having the NaCl structure.[1] This center consists of an X_2^- ion (X represents the appropriate halogen) whose symmetry axis is along one of the six $\langle 110 \rangle$ crystalline directions. The optical absorption bands of V_k centers in several alkali halides have been studied by Delbecq, Hayes, and Yuster.[2] They also demonstrated that V_k centers can be aligned along one of the six $\langle 110 \rangle$ directions by illuminating with linearly polarized light that is absorbed in one of the V_k absorption bands.

If V_k centers are aligned in a crystal at a low temperature and the crystal is then warmed, a thermally excited reorientation of V_k centers occurs and the population returns to the equilibrium distribution of $\frac{1}{6}$ of the total number in each of the $\langle 110 \rangle$ directions. The kinetics of this thermally excited reorientation has been studied[3,4] in KI and KCl, and it was found that V_k centers reorient by a jumping process in which, in a single jump, the V_k axis changes direction only by 60° but not by 90°. The geometry is shown in Fig. 1. The angle between direction 1 and any of directions 3, 4, 5 or 6 is 60°; direction 1 is, of course, at 90° to direction 2. Since a change in orientation of the axes of V_k centers occurs during alignment by absorption of linearly polarized light, the question arises as to whether an optically excited center changes the direction of its axis only by 60° in a single excitation (analogous to the thermally excited motion), or whether it reorients at random among sites at 60° and 90° to the original axis. This paper reports experiments designed to distinguish between these two cases for absorption of light in the uv band of V_k centers in KCl.

Previous work on the thermally excited motion[3,4] of V_k centers was performed by first orienting the centers optically at a low temperature (78°K), then warming the crystal to a higher fixed temperature, and making observations as the V_k centers reoriented to a random distribution. In the present work we study the kinetics of the optical orientation process by starting with an initial random distribution and making observations while the population of a particular direction increases at the expense of other directions.

KINETICS OF ORIENTATION

The work reported here is concerned only with the ultraviolet absorption band of V_k centers in KCl, a transition from the $^2\Sigma_u^+$ ground state to a $^2\Sigma_g^+$ excited state. Electric dipole transitions between pure $^2\Sigma_u^+$ and $^2\Sigma_g^+$ states are allowed for σ polarized light, i.e., light whose electric vector is parallel to the molecular axis. The polarization selection rule is not rigorously obeyed, as demonstrated by the fact that one does not achieve a complete orientation of the centers along one axis in an optical alignment experiment. We take into account the existence of (weak) transition moments perpendicular to the symmetry axis by writing the ab-

[1] J. H. Schulman and W. D. Compton, *Color Centers in Solids* (The MacMillan Company, New York, 1962).
[2] C. J. Delbecq, W. Hayes, and P. H. Yuster, Phys. Rev. **121**, 1043 (1961).
[3] F. J. Keller and R. B. Murray, Phys. Rev. Letters **15**, 198 (1965).
[4] F. J. Keller, R. B. Murray, M. M. Abraham, and R. A. Weeks, Phys. Rev. **154**, 812 (1967).
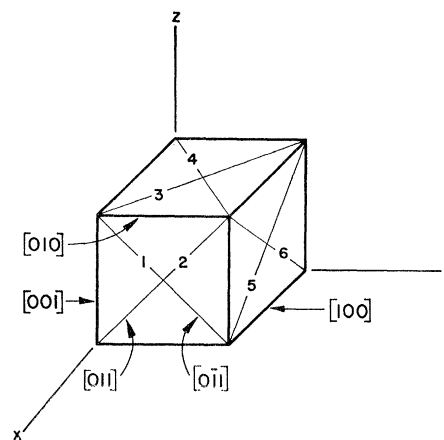

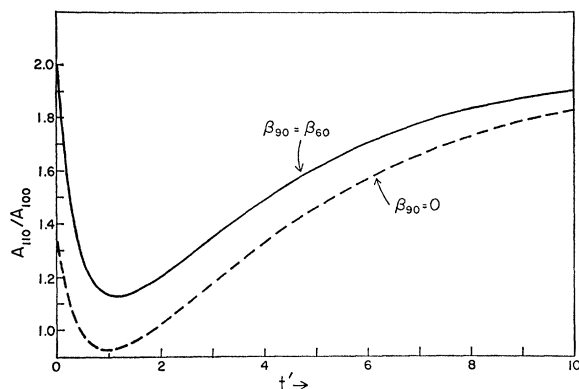FIG. 1. Showing the six distinguishable orientations of V_k centers in KCl.

FIG. 2. Calculated curves for the ratio A_{110}/A_{100} as a function of t', where t' is a dimensionless variable proportional to the bleaching time. For these curves $\pi_1/\sigma = \pi_2/\sigma = 0$.

sorption cross section for plane-polarized light as

$$\sigma \cos^2\theta + \pi_1 \cos^2\phi + \pi_2 \cos^2\gamma .$$

θ, ϕ, and γ are the angles between the electric vector of the light and the direction parallel to the molecular axis, perpendicular to the molecular axis along $\langle 110 \rangle$, and perpendicular to the molecular axis along $\langle 100 \rangle$, respectively. Delbecq et al.[2] showed that the ultraviolet absorption band for Cl_2^- in KCl is predominantly σ polarized, i.e., $\sigma \gg \pi_1$, π_2. With reference to Fig. 1, the term "[011] light" is used to indicate plane-polarized light that has its propagation vector parallel to [100] and its electric vector parallel to [011]. Similar definitions hold for [0$\bar{1}$1], [001], and [010] light, all of which have their propagation vectors parallel to [100]. The absorption coefficient for [011] light, α_{011}, is given by

$$\alpha_{011} = \sigma[n_2 + \tfrac{1}{4}(n_3 + n_4 + n_5 + n_6)]$$
$$+ \pi_1[n_1 + \tfrac{1}{4}(n_3 + n_4 + n_5 + n_6)]$$
$$+ \pi_2[\tfrac{1}{2}(n_3 + n_4 + n_5 + n_6)], \quad (1)$$

where n_j is the number of V_k centers per unit volume having orientation j. Similar expressions hold for $\alpha_{0\bar{1}1}$, α_{010}, and α_{001}. We define the $\langle 110 \rangle$ optical anisotropy A_{110} as

$$A_{110} = \alpha_{011} - \alpha_{0\bar{1}1}.$$

Therefore,

$$A_{110} = (\sigma - \pi_1)(n_2 - n_1). \quad (2)$$

Similarly,

$$A_{100} = \alpha_{010} - \alpha_{001},$$
$$A_{100} = [\tfrac{1}{2}(\sigma + \pi_1) - \pi_2][(n_3 + n_4) - (n_5 + n_6)]. \quad (3)$$

Exposing the crystal to [0$\bar{1}$1] light of wavelength corresponding to a predominantly σ polarized V_k absorption band orients the centers so that $n_2 > n_1$ and, hence $A_{110} > 0$. This procedure is referred to as an [0$\bar{1}$1] optical orientation. An [001] optical orientation rearranges the centers so that $(n_3 + n_4) > (n_5 + n_6)$ and $A_{100} > 0$.

Let I be the number of photons per unit area per unit time of nearly monochromatic linearly polarized light incident on the crystal, τ be the lifetime of V_k center in electronic excited state, $P_{90}{}^*$ be the probability that a center in an excited state will reorient through 90° per unit time, $P_{60}{}^*$ be the probability that a center in an excited state will reorient to one of the equivalent 60° sites per unit time, $\beta_{60} \equiv I\tau P_{60}{}^*$, $\beta_{90} \equiv I\tau P_{90}{}^*$, $\pi_3 \equiv \tfrac{1}{4}(\sigma + \pi_1) + \tfrac{1}{2}\pi_2$. Then for bleaching with [0$\bar{1}$1] light,

$$dn_1/dt = -n_1\sigma(\beta_{90} + 4\beta_{60}) + n_2\pi_1\beta_{90} + 4n_3\beta_{60}\pi_3, \quad (4)$$

$$dn_2/dt = -n_2\pi_1(\beta_{90} + 4\beta_{60}) + n_1\sigma\beta_{90} + 4n_3\beta_{60}\pi_3, \quad (5)$$

$$dn_3/dt = -2n_3\pi_3\beta_{60} + n_1\sigma\beta_{60} + n_2\pi_1\beta_{60}, \quad (6)$$

where Eqs. (4), (5), and (6) utilize the fact that

$$n_3 = n_4 = n_5 = n_6 \quad (7)$$

for a bleach with [0$\bar{1}$1] light. Similar equations in the time derivatives of n_4, n_5, and n_6 need not be written by virtue of Eq. (7).

In working with these equations, it is convenient to rewrite them in terms of the parameters β_{90}/β_{60}, π_1/σ, and π_2/σ. The latter two ratios are of order 10^{-2} as will be shown later, so that π_3/σ is approximately $\tfrac{1}{4}$. Defining a dimensionless variable $t' \equiv \beta_{60}\sigma t$, Eqs. (4), (5), and (6) become

$$\frac{dn_1}{dt'} = -\left(\frac{\beta_{90}}{\beta_{60}} + 4\right)n_1 + \frac{\pi_1}{\sigma}\frac{\beta_{90}}{\beta_{60}}n_2 + \frac{4\pi_3}{\sigma}n_3, \quad (4')$$

$$\frac{dn_2}{dt'} = \frac{\beta_{90}}{\beta_{60}}n_1 - \frac{\pi_1}{\sigma}\left(\frac{\beta_{90}}{\beta_{60}} + 4\right)n_2 + \frac{4\pi_3}{\sigma}n_3, \quad (5')$$

$$\frac{dn_3}{dt'} = n_1 + \frac{\pi_1}{\sigma}n_2 - \frac{2\pi_3}{\sigma}n_3. \quad (6')$$

The initial conditions are $n_i(0) = \tfrac{1}{6}N$, where N is the density of V_k centers and $i = 1 \cdots 6$. Equations (4'), (5'), and (6') constitute a system of coupled linear differential equations with constant coefficients, and can be solved by the method of Laplace transforms. Having found n_1 and n_2 as functions of t', we obtain $A_{110}(t')$ by Eq. (2). Knowing approximate values of π_1/σ and π_3/σ as indicated above, we can then plot $A_{110}(t')$ for the two cases $\beta_{90} = \beta_{60}$ (random reorientation), and $\beta_{90} = 0$ (analogous to thermal reorientation). The shape of the function $A_{110}(t')$ proves to be relatively insensitive to the ratio β_{90}/β_{60} (either 0 or 1); it is therefore not possible to decide between the two cases on the basis of a measurement of $A_{110}(t')$ alone. It is possible, however, to decide between the two cases by performing, in addition, a measurement of $A_{100}(t')$, as follows:

For bleaching with [001] light

$$n_3 = n_4, \quad n_1 = n_2 = n_5 = n_6, \quad (8)$$

$$dn_3/dt = -4n_3\pi_2\beta_{60} + 2n_5\beta_{60}(\sigma + \pi_1), \quad (9)$$

$$dn_5/dt = 2n_3\pi_2\beta_{60} - n_5\beta_{60}(\sigma + \pi_1). \quad (10)$$

Introducing $t' \equiv \beta_{60}\sigma t$

$$dn_3/dt' = -(4\pi_2/\sigma)n_3 + 2(1+\pi_1/\sigma)n_5, \qquad (9')$$

$$dn_5/dt' = (2\pi_2/\sigma)n_3 - (1+\pi_1/\sigma)n_5. \qquad (10')$$

The initial conditions are again $n_i(0) = N/6$. Equation (9') and (10') can be solved for $n_3(t')$ and $n_5(t')$, knowing approximate values of π_1/σ and π_2/σ, and $A_{100}(t')$ follows from Eqs. (3) and (8). We note that $A_{100}(t')$ does not involve the ratio β_{90}/β_{60}.

The ratio $A_{110}(t')/A_{100}(t')$ proves to be sensitive to the value of β_{90}/β_{60} and permits comparison with experiment. The ratio of course depends on the value of the parameters π_1/σ and π_2/σ. As an example, a plot of $A_{110}(t')/A_{100}(t')$ versus t' is shown in Fig. 2 for the case $\pi_1/\sigma = \pi_2/\sigma = 0$; the two curves correspond to $\beta_{90}/\beta_{60} = 1$ and 0.

For comparison with experiment we need to obtain π_1/σ and π_2/σ. A method for obtaining these parameters from optical alignment experiments has been worked out by Keller[5] as follows: After an infinitely long bleaching time with $[0\bar{1}1]$ light the V_k centers reach an equilibrium distribution that is governed by π_1/σ and π_2/σ. We designate the anisotropy at $t = \infty$ as $A_{110}{}^\infty$, and we introduce a quantity $B_{110} = \alpha_{011} + \alpha_{0\bar{1}1}$, i.e., B_{110} is the sum of the absorption coefficients. After a long bleach, B_{110} reaches its asymptotic value $B_{110}{}^\infty$. At $t = \infty$, $dn_i/dt = 0$ where $i = 1$–6, and this condition plus some arithmetic leads to

$$\frac{B_{110}{}^\infty}{A_{110}{}^\infty} = \left(\frac{\sigma}{\pi_1} + \frac{\pi_1}{\sigma} + 10\right) \Big/ \left(\frac{\sigma}{\pi_1} + \frac{\pi_1}{\sigma} - 2\right).$$

Both $B_{110}{}^\infty$ and $A_{110}{}^\infty$ can be measured, and this permits a determination of π_1/σ. A similar analysis for bleaching with $[001]$ light shows

$$\frac{B_{100}{}^\infty}{A_{100}{}^\infty} = \left(\frac{\pi_4}{\pi_2} + \frac{\pi_2}{\pi_4} + 4\right) \Big/ \left(\frac{\pi_4}{\pi_2} + \frac{\pi_2}{\pi_4} - 2\right),$$

where $\pi_4 \equiv \frac{1}{2}(\sigma + \pi_1)$. Knowledge of π_1/σ from the preceding analysis combined with a measurement of $B_{100}{}^\infty/A_{100}{}^\infty$ determines π_2/σ. It is not possible to determine π_1/σ and π_2/σ with great accuracy, primarily because of a broad absorption underlying the V_k band and extending to shorter wavelengths. The origin of this absorption is unknown, but is presumably due to another type of V center or to (Pb^{++}+electron) centers. Our best estimate from several experiments is

$$\pi_1/\sigma = 0.02 \pm 0.01, \quad \pi_2/\sigma = 0.04 \pm 0.02.$$

EXPERIMENT

A crystal of KCl(Pb) containing about 300 ppm Pb was supplied by W. A. Sibley, Oak Ridge National Laboratory. Samples were cleaved in the form of plate-

[5] F. J. Keller (private communication).

lets of approximate dimensions $2 \times 10 \times 15$ mm^3. Prior to a set of experiments, a platelet was annealed in air at 400°C for a few minutes and then quenched by placing it on a copper block at room temperature. The crystal was x rayed at 78°K, typically for a period of 30 min, using a tungsten target x-ray tube operated at 50 kV and 20 mA. X rays were filtered by the Be window of the x-ray tube and by a 0.020-in.-thick aluminum cryostat window. The peak optical density of the V_k absorption band was in all cases between 0.7 and 1.0. V_k centers were oriented with nearly monochromatic light at 425 mμ from a Cary Model 14R spectrophotometer. The bleaching wavelength was chosen to be at a low optical density so that the light intensity was nearly constant throughout the 2-mm thickness of the crystal. The bleaching light was linearly polarized with a Glan-Thompson prism. Measurements of the optical anisotropy were made in the Cary at 360 mμ by rotating the prism through 90°. All measurements were made at 78°K. The intensity of the Cary light source was monitored by an auxiliary photomultiplier looking at the lamp through a small aperture and an interference filter with peak transmission at 400 mμ. In a typical set of experiments the crystal was first oriented in the cryostat so that the electric vector of the bleaching light was along a particular direction, say $[0\bar{1}1]$. During bleaching the Cary slits were open to the full 3 mm; during measurement of the anisotropy the slits were about 0.02 mm. Following this measurement of the anisotropy the crystal was warmed to room temperature, rotated through 45° in the cryostat, and the above procedure repeated, taking care to introduce nearly the same number of V_k centers in the second case as in the first. A small correction (a few percent) was applied where necessary to account for the difference in V_k concentration at the beginning of the two bleaching runs.

A total of three sets of experiments were performed, giving three measurements of the anisotropy ratio A_{110}/A_{100} as a function of bleaching time. In one set of experiments the alignment was carried out first with $[0\bar{1}1]$ light; in two sets of experiments the alignment was performed first with $[001]$ light. The order in which the alignments were performed did not affect the results. A separate sample was prepared for each set of experiments; samples were not annealed between the two runs in one set of experiments.

The results of a typical set of experiments are shown in Fig. 3. The data of Fig. 3 are plotted as the ratio of anisotropies, A_{110}/A_{100}, in Fig. 4. It is seen in Fig. 4 that the measured ratio of anisotropies passes through a distinct minimum and has the general shape of the calculated curves of Fig. 2. In order to compare the measured ratio of anisotropies with the calculated functions for the determination of β_{90}/β_{60}, it is necessary to establish the relation between t' and t. This has been done empirically by fitting the time at which the minimum occurs in the measured functions to the value
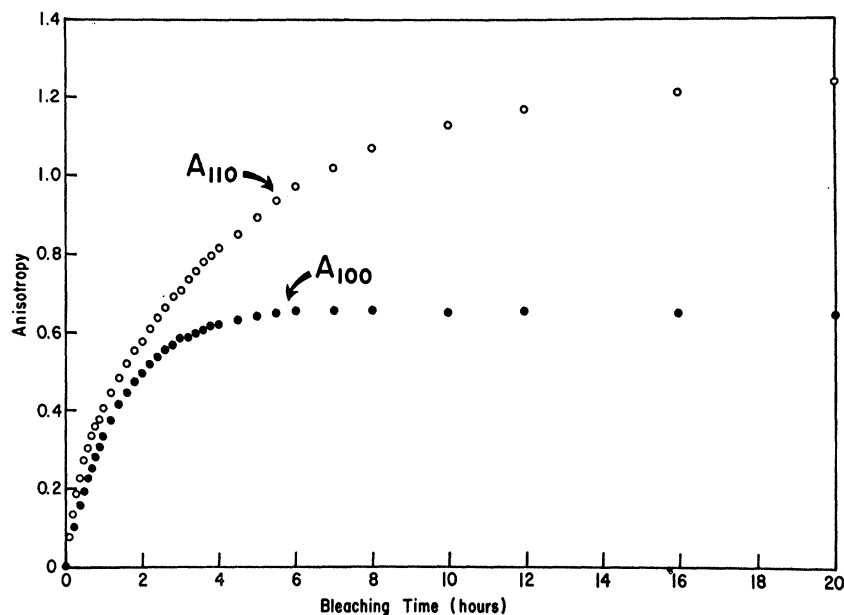
FIG. 3. Optical anisotropy in a crystal of KCl(Pb) at 78°K in a set of experiments, as a function of bleaching time. Anisotropy measured at 360 mμ, bleaching wavelength 425 mμ. The anisotropy represents the difference in optical density for two polarizer orientations.

of t' at the minimum in the calculated functions. The fitting of experimental data to the calculated curves therefore involves only one adjustable parameter.

To determine the ratio β_{90}/β_{60}, we compare the experimental ratio of anisotropies with calculated curves for the cases $\beta_{90}/\beta_{60}=1$ and 0. This comparison is meaningful only at early bleaching times (small t'), as the calculated functions are not expected to give an accurate description of the data after a long bleaching time. This fact arises from several contributions: (a) the calculated curves assume a constant number of V_k centers during the reorientation process. It is known, however, that some V_k centers are lost due to recombination with electron excess centers, primarily $(Pb^{++}+e^-)$ or F centers. Another process which can

occur is the trapping of a V_k center (without annihilation) at a defect, such that this V_k center can contribute to optical absorption but is not free to reorient. (b) The shape of the calculated curve at large t' depends sensitively on π_1/σ and π_2/σ, and these parameters are not accurately known. For these reasons we restrict comparison of experiment with calculated curves to early bleaching times. This comparison is shown in Fig. 5, in which we have plotted data from all three experiments; the time scale for the data points was established as indicated previously from the minimum in the measured curve, and constitutes the only adjustable parameter. The dashed curves of Fig. 5 are calculated functions for the case $\pi_1/\sigma=\pi_2/\sigma=0$. These curves represent the limiting case of complete σ polarization.
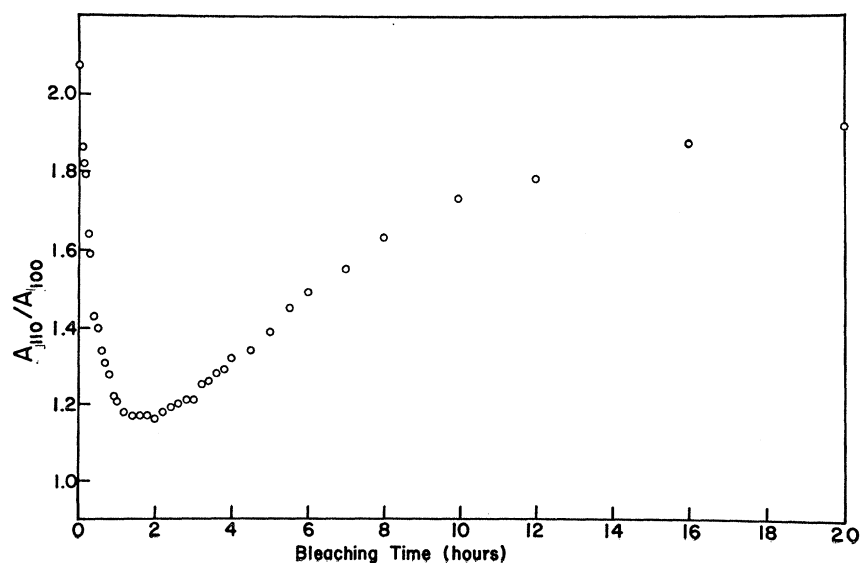

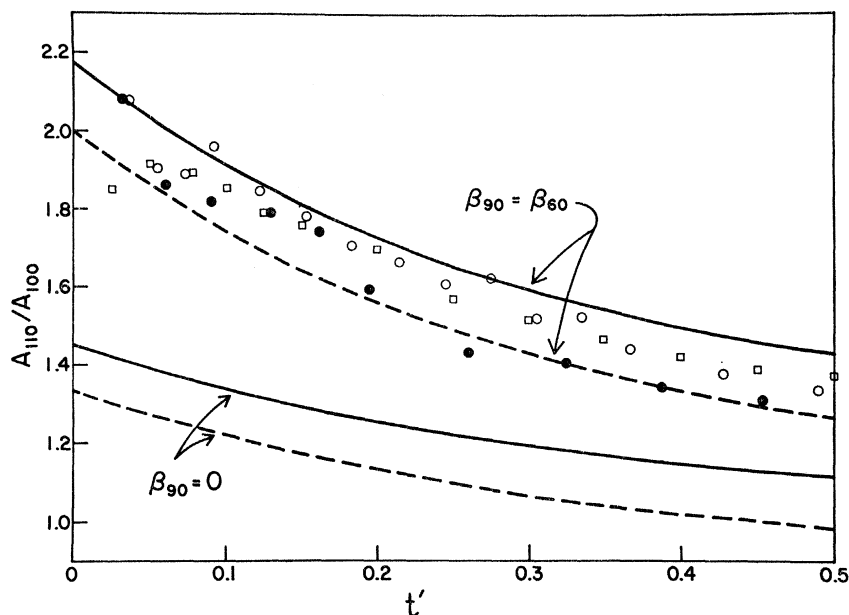FIG. 4. Ratio of anisotropies, A_{110}/A_{100}, from data of Fig. 3, as a function of bleaching time.

FIG. 5. Comparison of experimental data with calculated curves for the cases $\beta_{90}=\beta_{60}$ and $\beta_{90}=0$. Dashed curves correspond to $\pi_1/\sigma=\pi_2/\sigma=0$. Solid curves are for the case $\pi_1/\sigma=0.02$, $\pi_2/\sigma=0.04$. Experimental points are shown for three separate experiments.

The solid curves correspond to the case $\pi_1/\sigma=0.02$, $\pi_2/\sigma=0.04$, representing our estimate of these ratios as discussed previously. The ratios π_1/σ and π_2/σ are subject to a generous uncertainty. We have calculated curves for other values of π_1/σ and π_2/σ that are within the error of our analysis, and find that the solid and dashed curves shown in Fig. 5 constitute upper and lower bounds. For example, the case $\pi_1/\sigma=\pi_2/\sigma=0.03$ lies slightly above the dashed curves; the case $\pi_1/\sigma=0.01$, $\pi_2/\sigma=0.03$ is immediately below the solid curves.

DISCUSSION

The comparison of experimental data with the calculated curves in Fig. 5 strongly favors the case $\beta_{90}=\beta_{60}$, corresponding to a random reorientation. The present experiments therefore indicate a qualitative difference in the thermally excited motion of the V_k center as compared to motion in the electronic excited state. In the case of thermal excitation, there is a correlation between the initial and final orientation in a single jump, and this fact implies that one ion is common to both the initial and final states. In the case of reorientation in the electronic excited state, experiment shows that there is no correlation ($\beta_{90}=\beta_{60}$). This result seems quite reasonable in view of the fact that the excited state following absorption in the uv band is predicted to be an antibonding state, and would lead to dissociation of the free molecule ion. In the present case of the molecule ion in an alkali halide matrix, "dissociation" may correspond to a migration of the hole over several lattice distances, followed by reformation of a Cl_2^- ion. If this is the case the hole is shared by a completely different set of ions in the initial and final states. Alternatively, dissociation may occur by breakup of the Cl_2^- into a

Cl^- and a Cl^0 (each at an anion lattice site), and the Cl^0 subsequently forms a Cl_2^- with any one of its twelve adjacent Cl^- ions. The present experiments cannot distinguish between the suggested modes of dissociation. Either of these mechanisms of dissociation and reformation constitutes a motion of charge and would contribute to a photocurrent upon absorption of light by a V_k center. Such a photocurrent has in fact been observed by Delbecq[6] upon excitation in the infrared absorption band of Br_2^- in KBr.

In principle it would be possible to repeat the present experiments for the case of excitation in the 750-mμ absorption band. In practice there is a significant problem: The 750-mμ band is only weakly anisotropic indicating that the π cross sections contribute significantly, in contrast to their small contribution to the 365-mμ band. Since the theoretical curves depend on π_1/σ and π_2/σ and these ratios cannot be determined with high accuracy, it does not seem feasible to apply the present method to the 750-mμ band.

A measurement of the ratio β_{90}/β_{60} for the uv band in KCl, similar to the present work but utilizing the methods of electron paramagnetic resonance, has been reported by Bishop and Keller.[7] They concluded that $\beta_{90}=\beta_{60}$, in agreement with the results of the present work.

[6] C. J. Delbecq, J. Phys. Chem. Solids **22**, 323 (1961).
[7] T. P. Bishop and F. J. Keller, Bull. Am. Phys. Soc. **13**, 254 (1968).