PHYSICAL REVIEW VOLUME 154, NUMBER 3 15 FEBRUARY 1967

Preferential Thermal Reorientation of V_K Centers in Potassium Chloride*

F. J. Keller,† R. B. Murray,‡ M. M. Abraham, and R. A. Weeks
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee

(Received 12 September 1966)

The thermally excited reorientation of V_K centers in KCl(Pb) has been studied using both optical and electron-spin-resonance techniques. Both methods of detection show that V_K centers reorient through 60° only; the probability of reorienting through 90° is effectively zero. This indicates that V_K centers reorient by jumping to first-nearest-neighbor sites. Further, the thermal activation energy (0.54 eV) measured in the optical-absorption experiments, when compared with a previous value determined elsewhere for the long-range diffusion of V_K centers, shows that this diffusive motion is probably by first-nearest-neighbor jumps only.

INTRODUCTION

The V_K center is considered to be a hole trapped in an otherwise perfect region of an alkali halide crystal. The hole is shared by two neighboring anions so that the center can be considered to be a $(\text{halogen})_2^-$ molecule ion.[1] For crystals having the NaCl structure, the molecular axis of a given center is along one of the six $\langle 110\rangle$ crystalline directions. The thermal motion of V_K centers is of interest since the moving entity is a hole and the motion takes place mainly in perfect regions of the crystal.

Since a V_K center must move in order to change its orientation, one can learn about the motion of these centers by studying the change in their orientations due to thermal activation. The population of centers in one or more of the $\langle 110\rangle$ directions can be enhanced at the expense of the others by exposing the crystal to plane-polarized light corresponding to V_K absorption bands.[2] This procedure is referred to as an optical orientation. By performing an optical orientation at low temperatures where the centers are thermally "frozen in" and then warming the crystal to a temperature where the centers move at a convenient rate, one can measure the rate at which the fractional population in each direction approaches the equilibrium value of $\frac{1}{6}$. The latter procedure is referred to as a thermal reorientation. In this paper, we report on measurements of the thermal reorientation of V_K centers in KCl(Pb), using both optical and electron-spin-resonance techniques.

KINETICS OF THERMAL REORIENTATION

The absorption cross section of the V_K center for plane-polarized light of a wavelength corresponding to one of its absorption bands can be expressed 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. This definition follows the nomenclature used by Delbecq, Hayes, and Yuster.[2] During this discussion we will sometimes make the simplifying assumption that $\pi_1=\pi_2=\pi$ since the electronic environments along π_1 and π_2 are relatively similar compared to that along σ. Delbecq *et al.* showed that the ultraviolet absorption bands for F_2^- in LiF, Cl_2^- in KCl, and Br_2^- in KBr are predominantly σ-polarized (i.e., $\sigma\gg\pi$). With reference to Fig. 1 the term "[011] light" shall be 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_k is the number of V_K centers per unit volume having orientation k. 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,

$$A_{100}=\alpha_{010}-\alpha_{001}\,,$$

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

These relations show that the optical anisotropies are zero if the centers are randomly oriented ($n_k=\frac{1}{6}N$ for all k, where N is the total number of V_K centers per unit volume). Exposing the crystal to $[0\bar{1}1]$ light of wavelength corresponding to a predominantly σ-

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* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

† Present address: Department of Physics, Clemson University, Clemson, South Carolina.

‡ Present address: Department of Physics, University of Delaware, Newark, Delaware.

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

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

polarized V_K absorption band orients the centers so that $n_2 > n_1$ and, hence, $A_{110} > 0$. This procedure shall be 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 $A_{100} > 0$.

The optical orientation results can be understood according to the following description (see Fig. 1): [0$\bar{1}$1] light interacts strongly with centers that have their molecular axes along [0$\bar{1}$1], i.e., having orientation 1, less so with centers having orientations 3, 4, 5, or 6, and only weakly interacts with centers having orientation 2. During an [0$\bar{1}$1] optical orientation, centers having orientation 1 are being pumped into an electronic excited state more often than centers having other orientations, and centers with orientation 2 are being disturbed least. Once a V_K center is in an electronic excited state it may then change its orientation (move to another site) before returning to the ground state. Evidently this is so even at temperatures as low as 5°K, since V_K centers can be oriented at these low temperatures.[3] The effect of bleaching with [0$\bar{1}$1] light is to preferentially pump centers out of orientations 1, 3, 4, 5, and 6 and into orientation 2. Note that [0$\bar{1}$1] light interacts equally with centers having orientations 3, 4, 5, and 6 so that $n_3 = n_4 = n_5 = n_6$. Similarly, during an [001] optical orientation $n_3 = n_4$ and $n_1 = n_2 = n_5 = n_6$.

Suppose the optical orientation is performed at a low enough temperature so that the centers are immobile in the electronic ground state and then the crystal is warmed in the dark to a temperature where the thermal reorientation is conveniently measurable. The centers will then change their orientations by thermal excitation and the number of centers in the various orientations will tend toward the equilibrium value of $\frac{1}{6}N$. From Fig. 1 it is evident that a V_K center might change its orientation by either 60° or 90° in wandering through the crystal. Let P_{90} be the probability per unit time that a V_K center reorients by thermal excitation through 90° (as direction 1 to 2), and let P_{60} be the probability per unit time that a V_K center reorients to any *one* of the equivalent 60° sites (as direction 1 to 3). The temperature dependences of P_{90} and P_{60} are expected to follow Arrhenius relations. The rate at which the population of centers in orientation 1 changes by thermal activation is given by

$$dn_1/dt = -n_1(P_{90}+4P_{60}) + n_2P_{90} + (n_3+n_4+n_5+n_6)P_{60}. \quad (4)$$

Similar expressions hold for the other orientations, giving a total of six differential equations. We have assumed that a negligible number of centers are lost because of recombination during the thermal reorientation, and our experiments show that this is an adequate assumption. Therefore, N can be considered to be constant throughout a thermal reorientation experiment, and the equation

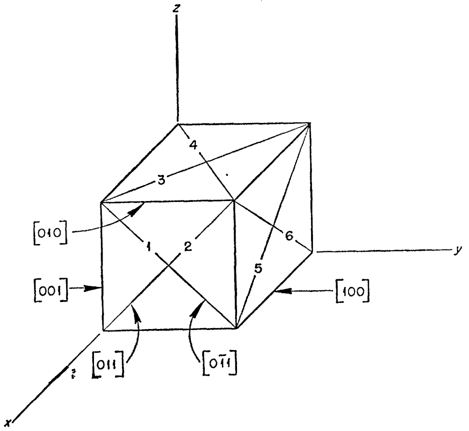

FIG. 1. Illustrating the six distinguishable orientations of V_K centers in alkali halide crystals having the NaCl structure.

$$N = \sum_{k=1}^{6} n_k$$

can be used in solving the differential equations. For the case of a thermal reorientation after an [0$\bar{1}$1] optical orientation

$$n_i(t) - \tfrac{1}{6}N = [n_i(0) - \tfrac{1}{6}N]\exp[-(2P_{90}+4P_{60})t] + 2[n_j(0) - \tfrac{1}{6}N]\{\exp[-(2P_{90}+4P_{60})t] - \exp(-6P_{60}t)\}, \quad (5)$$

and

$$n_j(t) - \tfrac{1}{6}N = [n_j(0) - \tfrac{1}{6}N]\exp(-6P_{60}t), \quad (6)$$

where $i = 1$ or 2, and $j = 3$, 4, 5, or 6. For the case of a thermal reorientation after an [001] optical orientation,

$$n_k(t) - \tfrac{1}{6}N = [n_k(0) - \tfrac{1}{6}N]\exp(-6P_{60}t), \quad (7)$$

where $k = 1$, 2, 3, 4, 5, or 6. The equations for the time dependence of the optical anisotropies are found from (2), (3), (5), and (7):

$$A_{110}(t) = A_{110}(0)\exp(-K_{110}t), \quad (8)$$

$$A_{100}(t) = A_{100}(0)\exp(-K_{100}t), \quad (9)$$

where

$$K_{110} = 2P_{90} + 4P_{60}, \quad (10)$$

and

$$K_{100} = 6P_{60}. \quad (11)$$

We note that optical measurements of either A_{110} or A_{100} give information on a difference in populations, whereas electron-spin-resonance (ESR) experiments give a direct measure of the relative number of centers in a given orientation. In order to describe the results of the ESR experiments, we wish to deal with a parameter proportional to $n_k - \frac{1}{6}N$, i.e., the difference between n_k and its equilibrium value. For later convenience we

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[3] R. B. Murray and F. J. Keller, Phys. Rev. **137**, A942 (1965).

normalize this parameter by defining

$$\eta_k=\frac{n_k-N\frac{1}{6}}{\frac{1}{6}N}=\frac{6n_k}{N}-1.$$

The case of interest in this work is the one after an $[0\bar{1}1]$ optical orientation where, from (5) and (6),

$$\eta_i(t)+2\eta_j(t)=[\eta_i(0)+2\eta_j(0)]\exp(-K_{110}t) \quad (12)$$

and

$$\eta_j(t)=\eta_j(0)\exp(-K_{100}t), \quad (13)$$

$i=1$ or 2, and $j=3$, 4, 5, or 6. We note from (12) and (13) that during a single ESR experiment at a fixed temperature both K_{110} and K_{100} are obtained. At least two optical experiments using first $\langle 110\rangle$ and then $\langle 100\rangle$ anisotropy measurements are required to obtain this same information.

A further quantity of interest that arises in the optical experiments is the sum of absorption coefficient, B_{110} or B_{100}, referred to as the "total absorption" and defined by

$$\begin{aligned}B_{110}&=\tfrac{1}{2}(\alpha_{011}+\alpha_{0\bar{1}1}),\\ B_{100}&=\tfrac{1}{2}(\alpha_{010}+\alpha_{001}),\end{aligned} \quad (14)$$

$$\begin{aligned}B_{110}=B_{100}=\sigma[\tfrac{1}{2}(n_1+n_2)+\tfrac{1}{4}(n_3+n_4+n_5+n_6)]\\ +\pi_1[\tfrac{1}{2}(n_1+n_2)+\tfrac{1}{4}(n_3+n_4+n_5+n_6)]\\ +\pi_2[\tfrac{1}{2}(n_3+n_4+n_5+n_6)].\end{aligned} \quad (15)$$

Although B_{110} and B_{100} are both given by (15), the subscript must be retained to indicate whether $\langle 110\rangle$ or $\langle 100\rangle$ anisotropy has been induced. This is because the values of B_{110} and B_{100} are numerically different for a given number of centers if they have been oriented with $[0\bar{1}1]$ light as compared to $[001]$ light. Let us consider an ideal case where $\sigma\gg\pi_1$ and π_2, and where the optical orientation has completely aligned the centers. $t=0$ refers to the beginning of the thermal reorientation and $t=\infty$ refers to the time when the centers are randomly distributed. (In practice $t=\infty$ corresponds to $t\gtrsim 2/P_{60}$.) We will distinguish between $N(0)$ and $N(\infty)$, so that, we can determine whether or not a significant number of centers are annihilated by recombination with electron excess centers during the thermal reorientation.

$$\begin{aligned}B_{110}(0)&=\tfrac{1}{2}\sigma N(0);\\ B_{100}(0)&=\tfrac{1}{4}\sigma N(0);\\ B_{100}(\infty)=B_{110}(\infty)&=B(\infty)=\tfrac{1}{3}\sigma N(\infty).\end{aligned}$$

If the number of centers remains constant during a thermal reorientation, $N(\infty)=N(0)$, then during a $\langle 110\rangle$-type experiment the total absorption will decrease from $\frac{1}{2}\sigma N$ to $\frac{1}{3}\sigma N$, and during a $\langle 100\rangle$-type experiment the total absorption will increase from $\frac{1}{4}\sigma N$ to $\frac{1}{3}\sigma N$. Actually we did not observe that the total absorption changed that much during our experiments because we did not attempt to align the centers to a maximum degree. (It can be shown that it is impossible to completely align the centers if either π_1 or π_2 is greater than zero.) However, we did note that, in general, the decrease in $B_{110}(t)$ and the increase in $B_{100}(t)$ were approximately in the ratio given above, indicating that almost no centers were being lost through recombination with electrons.

EXPERIMENTAL METHODS

The crystals used in these experiments were single crystals of KCl doped with Pb to act as an electron-trapping impurity. The samples used in the optical work were cleaved from a boule grown at this laboratory and contained about 300 ppm Pb. The samples were generally 1–2×10×15 mm^3. The ionizing radiation, the measuring light, and the orienting light passed through the samples along their shortest dimension. The sample used in the ESR work was cleaved from a boule purchsed from Harshaw and contained about 200 ppm Pb. This sample was 4×10×23 mm^3. The ionizing radiation and the orienting light passed through the sample along its shortest dimension in this case also. Before each experiment the samples were heated in air to 400°C for about 5 min and then cooled rapidly to room temperature in order to enhance the production of V_K centers.[4]

The cryostat used in these experiments is designed for variable temperatures and has been described previously.[5] The sample compartment and base were modified so that they could be used for either optical or ESR experiments.

A calibrated platinum-resistance thermometer was mounted in a drill hole in the sample compartment for use in the optical experiments. The temperatures quoted are probably within 0.1°K of the sample temperature. A copper-constantan thermocouple was connected to the exterior of the cavity in the ESR experiment. We believe that in this case the thermocouple did not give an accurate measure of the sample temperature. However, an accurate measure of the temperature was not needed in the ESR case. The thermocouple was used only to aid in maintaining the sample at a constant temperature. In both the optical and ESR experiments the samples were held to within ±0.1°K of the control temperature during the isothermal phase of the experiments according to the respective thermometers.

For the optical absorption experiments, V_K centers were induced by irradiating the samples with 1.7-MeV electrons from a Van de Graaff accelerator at a current density of the order of 10^{-2} μA cm^{-2} for a period of ~5 min. The electrons passed through a 0.008-in. aluminum window on the cryostat before penetrating the samples. The sample used in the ESR experiment was x irradiated for about 2 h from a 40-kV source

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[4] E. Sonder and W. A. Sibley, Phys. Rev. **140**, A539 (1965).

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

operated at 15 mA. The x rays passed through the mica-beryllium window of the tube and a 0.064-in. quartz window on the cryostat before penetrating the sample. The sample temperature during irradiation was approximately 78°K in both cases.

The optical absorption measurements were made on a Cary model-14 recording spectrophotometer. Monochromatic light (365 mμ) from the Cary was used to orient the centers for the optical experiments while a mercury lamp in conjunction with a color filter having maximum transmission at 433 mμ was used for this purpose in the ESR experiments. A Glan-Thompson calcite prism was used to polarize the light in both cases. A superheterodyne spectrometer of the Hirshon-Fraenkel design operating at ~10 Gc/sec was used in the ESR experiments.[6] The reflection-type rectangular cavity had a light pipe on the wall opposite the coupling iris with the crystal on the same wall as the opening to the light pipe. The entire cavity was maintained at approximately the same temperature as the sample. The spectrometer was operated at low power to avoid saturation effects.

EXPERIMENTAL RESULTS

A. Optical

After irradiation and optical orientation at ~78°K the samples were warmed rapidly to a control temperature where the optical anisotropy was measured isothermally. The anisotropy decreased exponentially with time in the temperature range investigated. Figure 2 shows the results of a typical experiment. Figure 3 is an Arrhenius plot of the rate constants derived from fitting the data to Eqs. (8) and (9). Letting

$$K_{110}=s_{110}\exp(-E_{110}/kT),$$

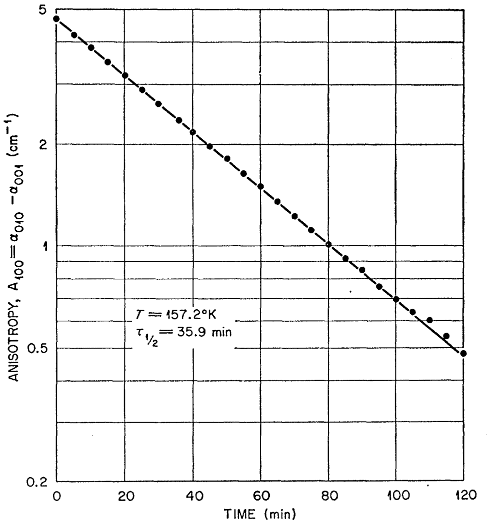

FIG. 2. ⟨100⟩ optical anisotropy versus time at 157.2°K.

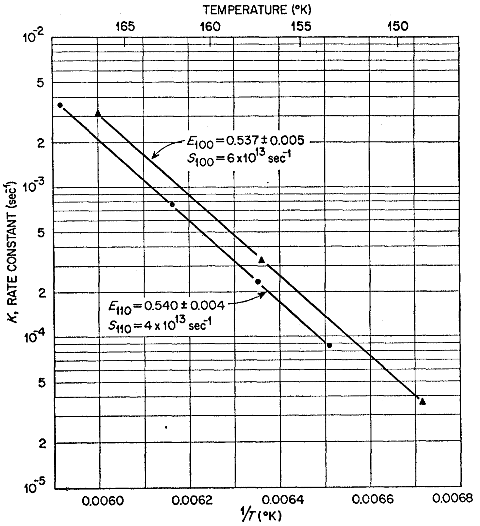

FIG. 3. Arrhenius plot for the loss of anisotropy of the 365-mμ V_K absorption band.

and

$$K_{100}=s_{100}\exp(-E_{100}/kT)$$

results in the values given in the figure. k is Boltzmann's constant and T is the temperature. The indicated uncertainties are the standard deviations obtained from the least-squares fit and pertain to random errors only. E_{110} is the same as E_{100} within experimental error. Using Eqs. (10) and (11) we find

$$\frac{K_{110}}{K_{100}}=\frac{2}{3}+\frac{1}{3}\frac{P_{90}}{P_{60}}.$$

From the data of Fig. 3

$$\frac{K_{110}}{K_{100}}=0.67\pm0.01.$$

Thus,

$$P_{90}=(0.01\pm0.03)P_{60}. \qquad (16)$$

Of course, both P_{90} and P_{60} are intrinsically positive quantities, so that, the ratio can have positive values only. From Eq. (16) P_{90} is effectively zero. Also,

$$P_{60}=1\times10^{13}\exp(-0.54/kT)\ \mathrm{sec}^{-1},$$

where kT is in units of eV.

B. Electron Spin Resonance

In order to substantiate our interpretation of the optical data we performed a thermal reorientation using ESR measurements. The ESR spectrum of V_K centers in KCl is well known.[1,7] We chose to make our measurements with the magnetic field parallel to one of the ⟨110⟩ directions, say [011] of Fig. 1. In this way we

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[6] J. M. Hirshon and G. E. Fraenkel, Rev. Sci. Instr. **26**, 34 (1955).

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

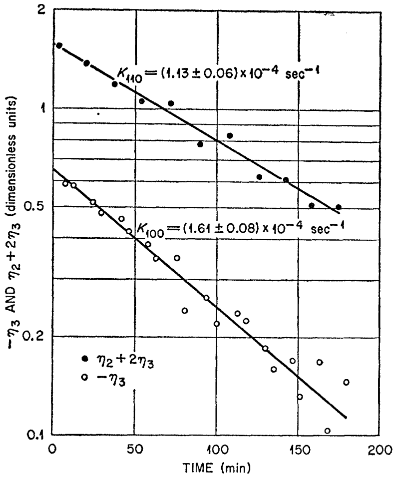

FIG. 4. Time dependence of $\eta_2+2\eta_3$ and $-\eta_3$.

could easily resolve several of the spectral lines due to centers in orientation 2 from those in orientations 3, 4, 5, and 6. Therefore, signals proportional to n_2 and n_3 were measured permitting a determination of η_2 and η_3 as a function of time. Using Eqs. (12) and (13) both K_{110} and K_{100} could be determined in the same experiment.

The sample was x irradiated and the resulting centers were oriented optically with [01̄1] light at 78°K so that $n_2>n_3=n_4=n_5=n_6>n_1$. The sample was then rapidly warmed to the control temperature. The first derivative of the absorption lines of the ESR spectrum was recorded continuously as the centers reoriented isothermally. The experimental values of $\eta_k(t)$ were determined from the amplitude of the ESR signal at time t as follows:

$$\eta_k(t)=\frac{S_k(t)}{S_k(\infty)}-1,$$

where $S_k(t)$ is the amplitude of the ESR signal for centers in the kth orientation at time t, and $S_k(\infty)$ is that when the centers are randomly oriented. Figure 4 shows a semilogarithmic plot of $\eta_2(t)+2\eta_3(t)$ and $-\eta_3(t)$ [$\eta_3(t)$ is intrinsically negative]. From Eqs. (12) and (13) we see that the slope derived from the former gives K_{110} and that from the latter gives K_{100}. From these data the relation between P_{90} and P_{60} is

$$P_{90}=(0.10\pm0.15)P_{60}. \tag{17}$$

Again, the uncertainty quoted is the standard deviation and was evaluated by the usual methods.[8] Equation (17) is in agreement with Eq. (16) within experimental uncertainty. We note that the results from the optical experiments are subject to a much smaller uncertainty than those from the ESR experiments.

DISCUSSION

Taking the results of both types of experiments together we conclude that $P_{90}\ll P_{60}$. This is in agreement with the conclusions of a previous paper on V_K centers in KI.[9] Therefore, when the hole thermally jumps from one site to another, the final site must be correlated to the initial site. This rules out long-range motion of more than several lattice spaces since, if such a motion occurred, then the final site would surely be independent of the initial one. (An exception to this last statement might be a long-range motion along the center's axis so that no reorientation is involved. We have previously shown[5] that such a motion probably does not occur in KI and will shortly indicate that the same thing may be said for KCl.) We note that in the lattice of possible V_K-center sites (midpoints between adjacent halide sites) the first-nearest-neighbor (nn) sites to a given reference site are oriented at 60° with respect to the reference site. The second nn sites are oriented at 90°, and the third nn sites are oriented at 60° with respect to the reference site. The closest sites having the same orientation as the reference site are fourth nn. Therefore, second nn jumps do not occur within the accuracy of our experiments. On this basis it is also quite reasonable to neglect third nn jumps also. Consequently, one may safely say that thermal reorientation occurs through first nn jumps only.

The above statement does not take into account all possibilities for the hole's motion, as we have indicated. Motion without reorientation (jump distance≥fourth nn jump distance) must also be considered. Neubert and Reffner have measured the activation energy for the long-range diffusion of V_K centers in KCl(Pb) to be 0.53 eV.[10] This is surely the same, within experimental error, as our measurement of 0.54 eV for reorientation. This suggests that diffusion and reorientation are caused by the same process. Since these experiments show that reorientation is the result of first nn jumps only it appears that motion without reorientation does not occur. Similar results for KI corroborate this interpretation for KCl.[5]

ACKNOWLEDGMENT

We wish to thank W. A. Sibley, who provided the samples for the optical experiments.

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[8] H. Margenau and G. M. Murphy, *The Mathematics of Physics and Chemistry* (D. Van Nostrand, Inc., Princeton, New Jersey, 1959).

[9] F. J. Keller and R. B. Murray, Phys. Rev. Letters **15**, 198 (1965).

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