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COMMENTS AND ADDENDA

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Optical Reorientation of V_K Centers in KI[†]

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Reorientation of V_K centers in KI during optical excitation in the 3.10- and 1.55-eV absorption bands has been examined. The results obtained by anisotropic-bleaching techniques are consistent with the probable antibonding nature of both excited states. Similar work performed previously in KCl is cited.

Optically stimulated reorientation of V_K centers in KCl upon excitation to the 3.39-eV excited state has been studied by Murray and Bethers.[1,2] Thermally stimulated reorientation in the electronic ground state has been examined in the same system[3] and in KI.[4] The work reported here extends the previous work with an investigation of optically stimulated reorientation of the center in the 3.10- and 1.55-eV excited states in KI. The information gained in these experiments provides a key to the bonding nature of the electronic excited states of the V_K center. The primary results of the previous work are as follows: (i) Thermally stimulated reorientation in the ground state occurs almost exclusively in both KCl and KI by 60° rather than by 90° jumps (see Fig. 1, Ref. 4), while reorientation stimulated by optical bleaching in the 3.39-eV band in KCl causes reorientation with equal probability for a 60° or a 90° jump; (ii) the probability of reorientation under optical stimulation in the 3.39-eV band of KCl is temperature independent.

The V_K center may be regarded as a diatomic molecular ion X_2^- (where X is a halogen) embedded in the alkali-halide lattice. The electronic excited states of the center are identified with specific molecular states by this model.[5] The primary optical absorptions are due to transitions from the ground $^2\Sigma_u^+$ state to a $^2\Sigma_g^+$ (near ultraviolet) or to a $^2\Pi_g$ (near infrared) excited state. In KI these transitions occur at 3.10 and 1.55 eV, respectively. Each state has associated with it a curve of effective potential energy versus configuration coordinate, in this case the halogen internuclear separation. The state is bonding if this curve has a minimum; if there is no minimum, the state is antibonding. Figure 1 shows possible potential-energy curves for a V_K center in two different orientations. Crossing the center line of Fig. 1 corresponds to dissociation of the original molecular ion. The molecular ion which subsequently forms can have an orientation which differs from that of the original by 0°, 60°, or 90°. The "0° reorientation" is not observable by the techniques used here and is treated as no reorientation at all. Excitation to the bonding state IV can be followed

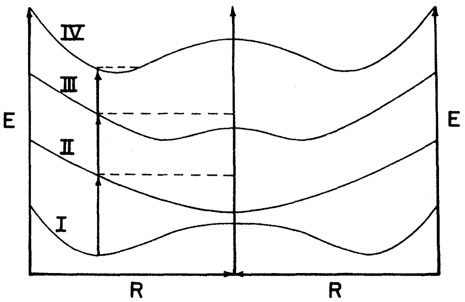

FIG. 1. Schematic configuration coordinate diagram of V_K center for two orientations. I, ground state; II, antibonding state; III and IV, bonding states.

by reorientation only if an additional thermal energy is available. The reorientation probability for this state will be temperature dependent and of the form $e^{-\delta E/kT}$, where δE is a characteristic thermal-activation energy. Excitation to state III (also bonding) or to II (antibonding) may lead directly to reorientation without thermal activation. The reorientation probability in these states will be independent of temperature.

Because there are two different types of reorientation, 60° and 90° jumps (see Fig. 1, Refs. 1 or 2), there may be two distinct activation energies, δE_{60} and δE_{90}, for reorientation from state IV. Using the nomenclature of Ref. 1, we may have $P^*_{60} \neq P^*_{90}$ in such a state. (V_K reorientation can actually occur by 60°, 90°, or 120° jumps. However, 60° and 120° reorientation are indistinguishable optically and we include both in our 60° probabilities. Three types of reorientation are treated by some authors.[6]) For reorientation without thermal activation (II or III), the reorientation is random and $P^*_{60} = P^*_{90}$. We conclude that an excited state which is shown experimentally to have $P^*_{60} \neq P^*_{90}$ or to have a reorientation probability exhibiting an $e^{-\delta E/kT}$ temperature dependence must be bonding. On the other hand, if experiment shows that $P^*_{60} = P^*_{90}$ and P^* is temperature independent, then the excited state is of type II or III.

Theoretically calculated potential-energy curves for the excited states of the V_K center are presently available only for the alkali fluorides and chlorides.[7,8] In these systems the ${}^3\Sigma_g^+$ excited state is calculated to be antibonding while the ${}^2\Pi_g$ state is weakly bonding. Although no calculations have been made for KI we expect the same qualitative behavior for the ${}^2\Sigma_g^+$ excited state. In the ${}^2\Pi_g$ state the binding energy is very small and decreases with increasing mass of the halogen atom. Therefore we expect that for iodine, the heaviest of the halogen series, the binding energy may vanish completely, suggesting probable antibonding behavior in this state also.

The results of Murray and Bethers for the 3.39-eV state of KCl are consistent with the prediction that this state be antibonding. The new work reported here is likewise consistent with the expectations outlined above.

TABLE I. Absorption cross-section ratios.

Band (eV)	π_1/σ (measured)	π_2/σ (measured)	A_{110}/A_{100} $(t\rightarrow 0)$ $P^*_{90}=P^*_{60}$ (calc.)	$P^*_{90}=0$ (calc.)
		KI		
3.10	0.11 ± 0.05	0.10 ± 0.10	1.88	1.25
1.55	0.08 ± 0.01	0.09 ± 0.01	2.04	1.36
		KCl[a]		
3.39	0.02 ± 0.01			

[a] Reference 1.

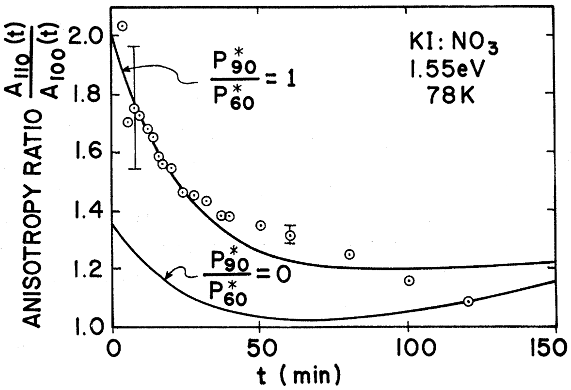

FIG. 2. Anisotropy-ratio curve, 1.55-eV excited state. Both experimental points and calculated (solid) curves are shown.

EXPERIMENTAL

The experimental procedure using anisotropic optical bleaching has been described previously.[1,2] Crystals of KI : Tl$^+$ and KI : NO$_2^-$, NO$_3^-$, each with a nominal 0.1-mol% doping, were used. V_K centers were produced by electron or x-ray bombardment at liquid-nitrogen temperature. Optical excitation was done at 410 nm (3.10-eV band) and at 800 nm (1.55-eV). Three distinct types of experiment were performed.

The first experiments were long bleaches with polarized light by which the optical-absorption cross-section ratios defined in Ref. 1, π_1/σ and π_2/σ, were measured. The measured ratios were used in the numerical solution of the differential equations describing the time evolution of the V_K-center distribution among the possible orientations during bleaching with polarized light.[1]

Second, the relative probabilities for 60° and 90° jumps were determined. It can be shown that[1]

$$\lim_{t\rightarrow 0} \frac{A_{110}}{A_{100}} = \frac{1}{6}\,\frac{(1-\pi_1/\sigma)^2}{(\frac{1}{2}[1+\pi_1/\sigma]-\pi_2/\sigma)^2}\left(\frac{P^*_{90}}{P^*_{60}}+2\right) , \tag{1}$$

where the anisotropies A are defined by

$$A = \mathrm{OD}_{(\perp)} - \mathrm{OD}_{(\parallel)} ,$$

and the optical densities OD are measured with light polarized perpendicular and parallel to the polarization axis of the bleaching light. The anisotropy is measured as a function of bleaching time t. A_{110} results from an experiment in which the bleaching light is linearly polarized with the electric vector along a $\langle 110\rangle$ axis; A_{100}, from a bleach along a $\langle 100\rangle$ axis. The ratio of these quantities in the limit $t\rightarrow 0$ was examined to determine which

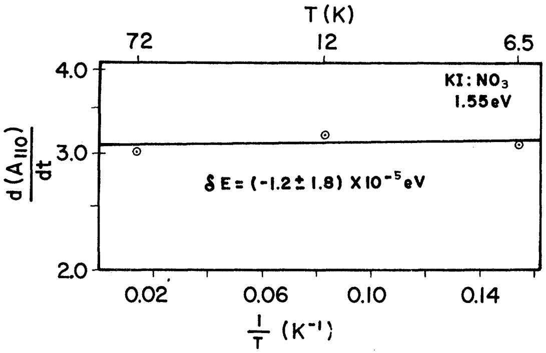

FIG. 3. Temperature dependence of initial slope of $A_{110}(t)$ for the 1.55-eV excited state. Straight line determined by least-squares fit has slope $-\delta E/k$.

of the two cases provided the best fit to the data: $P^*_{90} = P^*_{60}$ or $P^*_{90} = 0$.

The final experiments measured the temperature dependence of the reorientation probability. Theory shows that[2]

$$\lim_{t \to 0} \frac{dA_{110}}{dt} \propto P^* \propto e^{-\delta E/kT} \quad .$$

Thus a logarithmic plot of the early-time slope of A_{110} vs $1/T$ will be a straight line with slope $-\delta E/k$.

RESULTS AND DISCUSSION

The measured cross-section ratios for KI and for the 3.39-eV absorption band of KCl are listed in Table I. The increase in π character of the high-energy transition from Cl_2^- to I_2^- is attributable to increased spin-orbit coupling. The large error limits for the 3.10-eV band in KI are due to possible systematic error introduced by isotropic absorptions underlying the band in the samples studied; the deviation reported for the 1.55-eV band is based on random error and represents 1 standard deviation.

The calculated intercepts of the anisotropy-ratio curves from Eq. (1) are also given in the table. Figure 2 shows representative data for the 1.55-eV absorption. In addition, calculated curves for the two limiting cases are shown. The experimental $t \to 0$ limit clearly favors the case $P^*_{90} = P^*_{60}$ and the fit of the data to the calculated curve is good at early time where the theory is expected to be accurate. Increased discrepancies at longer times are attributed to the loss of centers by optical bleaching, a factor neglected in the theory. Similar results from the 3.10-eV band indicate that $P^*_{90} = P^*_{60}$ in this excited state also.

An example of the temperature-dependence measurements is shown in Fig. 3 for the 1.55-eV band. The activation energy here is of the order of 10^{-5} eV. (The measured activation energy itself is negative but this is compensated by the large uncertainty.) The mean energies from all experiments were as follows:

3.10 eV: $\delta E = (8 \pm 8) \times 10^{-5}$ eV;

1.55 eV: $\delta E = (4 \pm 7) \times 10^{-5}$ eV.

We interpret these results as indicating zero thermal-activation energy, that is, temperature-independent reorientation in both states.

The present results for both the 3.10- and 1.55-eV excited states of the V_K center in KI are (i) $P^*_{90} = P^*_{60}$ and (ii) $\delta E \approx 0$. These are consistent with antibonding behavior which we have reason to expect. Similarly, results for the 3.39-eV band in KCl are consistent with the calculated antibonding behavior in this state.

It seems likely that the ${}^2\Sigma_g^+$ excited state of the V_K center in all of the alkali halides will be antibonding. However, the nature of the ${}^2\Pi_g$ state is less clear, particularly for the lighter ions. The extension of measurement of this type to the ${}^2\Pi_g$ state of additional alkali halides would be desirable. Experimental determination of the ratio of anisotropies may well be frustrated by the decreasing anisotropy of this band with decreasing ion mass; however, it should be possible to determine the temperature dependence for the lighter ions.

Temperature-independent reorientation is not universal among anisotropic color centers as is demonstrated by work with both the F_A center[9] and the M center.[10] Anisotropic bleaching experiments have shown that reorientation from certain excited states of these systems is temperature dependent, with thermal-activation energies of the order of 0.1 and 0.04 eV, respectively.

In summary, the experimental evidence presented shows no contradiction of the reasonable assumption of antibonding behavior in the 3.10- and 1.55-eV excited states of the V_K center in KI.

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E_1 Transition in Ge: Two Dimensional or Three Dimensional?

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The recent interpretation of the two-dimensional M_0 critical-point nature of the E_1 and $E_1+\Delta_1$ transitions in Ge by Koeppen, Handler, and Jasperson, as determined from electroreflectance (ER) measurements, is reexamined using the low-field limit of the theory to be consistent with experimental conditions. We show that their interpretation was obtained by applying an inadequately broadened high-field theoretical line shape to a low-field spectrum, and is therefore not valid. The two-dimensional appearance of this spectrum is an indication of the presence of the electron-hole interaction as well as quasidegenerate M_0 and M_1 critical points in the band structure. Some aspects of ER spectral-line-shape interpretations are discussed.

In a recent publication,[1] Koeppen, Handler, and Jasperson (KHJ) analyzed their room-temperature surface-barrier electroreflectance (ER) data for the E_1 and $E_1+\Delta_1$ transitions of Ge and concluded that the Brillouin-zone regions centered about the $\langle 111\rangle$ symmetry directions, which give rise to these spectral features, could be represented as two-dimensional ($2D$) M_0 critical points in a one-electron parabolic-band approximation. While this model[2-4] has been highly successful in approximating contributions of these regions to long-wavelength phenomena such as piezobirefringence[4] and nonlinear optical susceptibilities,[5] this result was surprising in the context of ER spectra, whose third-derivative nature[6-8] should be sensitive to deviations of the actual band structure from the idealized model. This had been demonstrated previously[6] for low-temperature ER spectra taken for Ge in the heterojunction configuration,[9] where it was found that the E_1 and $E_1+\Delta_1$ transitions are probably best described as a broad three-dimensional ($3D$) M_1 singularity with a $3D$ M_0 contribution coming from the region near L.[6] In this comment, we examine these (low-field) ER data using low-field theoretical ER line shapes[7,10,11] obtained from simple parabolic bands, and demonstrate that KHJ reached an incorrect conclusion by using the Franz–Keldysh, high-field line shapes to fit experimental structure taken under low-field conditions. The subsidiary oscillations present in the high-field theory make it extremely difficult to distinguish between a single parabolic critical point and overlapping structures due to several degenerate critical points.

The experimental spectrum obtained by KHJ at a surface field $\mathcal{E}_s=81\ \text{kV cm}^{-1}$ and analyzed in detail in Ref. 1 is virtually identical with those determined by linearized-third-derivative spectroscopy under similar experimental conditions but measured rigorously in the low-field limit.[12] This is expected: the low-field region is defined by[7] $|\hbar\Omega| < \frac{1}{3}\Gamma$, where Γ is the phenomenological broadening energy and

$$(\hbar\Omega)^3=e^2\vec{\mathcal{E}}^2\hbar^2/8\mu_{\parallel}, \tag{1}$$

where $\vec{\mathcal{E}}$ is the electric field and $\mu_{\parallel}$ is the interband reduced mass in the field direction. Using values discussed later ($\Gamma=59$ meV, $\mu_{\parallel}=\frac{3}{2}\mu_t=0.073m_e$ [13]), we find from Eq. (1) that low-field spectra should be obtained for $\mathcal{E}\lesssim 77\ \text{kV cm}^{-1}$. Therefore we shall use only the low-field theory, taking advantage of the simplicity of the formalism.

In the low-field limit, the field-induced change in the dielectric function in the one-electron approximation $\Delta\epsilon^0$ for a parabolic $2D$ M_0 critical point is[7,10]

$$\Delta\epsilon^0_{2D,M_0}=\frac{4e^2C_0^2\mu_tK_g}{3\pi E^2m^2}\,\frac{(\hbar\Omega)^3}{(E+i\Gamma-E_g)^3}, \tag{2}$$

where E_g is the critical-point energy, K_g is the length of the two-dimensional region in momentum space, and $C_0^2=|\hat{\xi}\cdot\vec{\mathrm{P}}_{cv}|^2$, where $\hat{\xi}$ is the polarization vector of the incident radiation and $\vec{\mathrm{P}}$ is the momentum matrix element. The corresponding expression for a parabolic $3D$ M_1 critical point is

$$\Delta\epsilon^0_{3D,M_1}=-\frac{e^2C_0^2\mu_t(2|\mu_l|/\hbar^2)^{1/2}}{2E^2m^2}\,\frac{(\hbar\Omega)^3}{(E+i\Gamma-E_g)^{5/2}}, \tag{3}$$