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Electron-Paramagnetic-Resonance Detection of Optically Induced Divacancy Alignment in Silicon

C. A. J. Ammerlaan
Natuurkundig Laboratorium, Universiteit van Amsterdam, Amsterdam, The Netherlands

and

G. D. Watkins
General Electric Corporate Research and Development, P. O. Box 8, Schenectady, New York 12301

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An EPR study was made of the divacancy in silicon, produced by 1.5-MeV electron irradiation at room temperature, under illumination with polarized light. A light-induced alignment of divacancies among the various Jahn-Teller distortion directions in the lattice is observed for the singly positively charged state, as monitored directly in the corresponding EPR spectrum. Optical bands at 1.8 and 3.9 μ, which have been previously correlated with the positive divacancy, are found to have no alignment effect. Instead a band at ~ 2.15 μ, not previously reported, is found to have the maximum alignment efficiency. The transition-dipole-moment direction for this band is determined with respect to the defect axes.

I. DIVACANCY PROPERTIES

The divacancy V_2 in irradiated silicon has been extensively investigated by electron paramagnetic resonance,[1-4] infrared absorption,[5-10] and photoconductivity.[10-13] From the EPR experiments it was deduced that there are four equivalent atomic orientations for the divacancy, corresponding to the four $\langle 111 \rangle$ nearest-neighbor vacancy-vacancy directions in the silicon lattice. Each of these exists in one of three different electronic configurations, which are linked with small Jahn-Teller distortions of the lattice surrounding the divacancy. The defect has the symmetry of the point group $2/m(C_{2h})$. A model of the divacancy consistent with the results of EPR studies is shown in Fig. 1. One-electron molecular-orbital wave functions, obtained by linear combination of atomic orbitals (LCAO), and the corresponding energy levels are given in Fig. 2. The divacancy is a paramagnetic center for both the singly positively and the singly negatively charged states. The former state occurs for a Fermi level below $E_v + 0.25$ eV. In this charge state there is only one electron in the $b + b' - \lambda_1(a + d + a' + d')$ bonding orbital. The corresponding EPR spectrum is named[3] $G6$.

Three optical absorption bands in the infrared, at 1.8, 3.3, and 3.9 μ, respectively, have been attributed to the divacancy.[7] This correlation is mainly based on the explanation by the divacancy model of the response of these bands to uniaxial stress, and on the annealing properties. The absorption bands are only observable for restricted ranges of the Fermi level within the gap, i. e., for certain charge states of the divacancy. From these arguments Cheng *et al.*[7] originally concluded that the 3.3-μ band arises from V_2^{2-}, the 3.9-μ band from V_2^{+}, and the 1.8-μ band from V_2^{+}, V_2^{0}, and V_2^{-}. The allowed electric dipole transitions are indicated in the LCAO energy-level scheme depicted in Fig. 2. For all three bands the transition dipole moments were deduced to lie in the XY plane. The 1.8-μ band was tentatively identified as the transition labeled α. In subsequent work Cheng and Vajda[9] used polarized light and observed a light-induced dichroism of the 1.8- and 3.3-μ bands. The kinetics of the recovery were studied for each band and it was found that neither could be directly correlated with the Jahn-Teller reorientation kinetics previously studied in uniaxial stress studies for the EPR observable states V_2^{+} and V_2^{-}. Although this remains consistent with the identification of

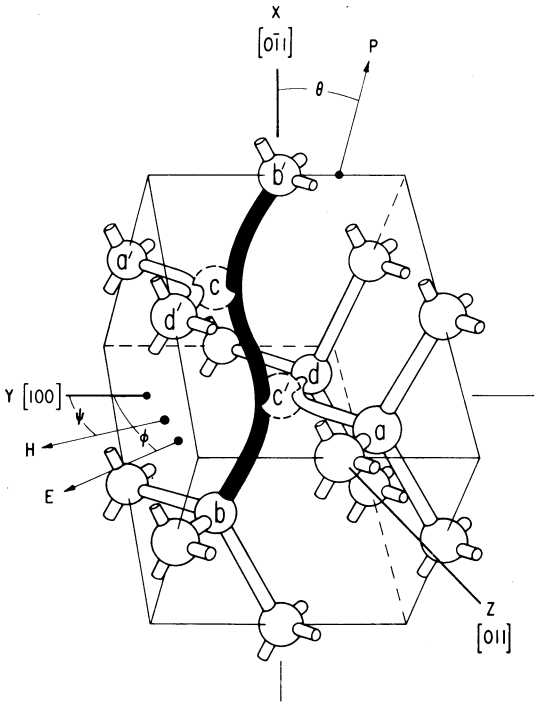

FIG. 1. Model of the divacancy, showing the crystallographic axes and the XYZ coordinate system of the defect. $\vec{P}$ is the transition dipole moment. $\vec{H}$ denotes the magnetic field direction as varied in the EPR experiments. $\vec{E}$ is the direction of the electric field vector of the polarized light.

the 3.3-μ band with V_2^{2-}, this forced Cheng and Vajda to conclude that the 1.8-μ band arises only from V_2^0. No effect of illumination with polarized light was observed at all for the 3.9-μ band.

Actually, then, no *direct* correlation exists between the optical properties attributed to the divacancy and the particular charge states observable in EPR: The 3.3-μ and 1.8-μ bands are presently assigned to the nonobservable EPR states V_2^{2-} and V_2^0. The 3.9-μ band, although assigned to V_2^+, has not been correlated via its low-temperature reorientation kinetics to the EPR because it shows no optically induced dichroism. A direct correlation is highly desirable since these absorption bands, or the associated photoconductivity, are often assumed to be monitors of the divacancy.[14–17]

In this paper, we describe an experiment to determine the optical properties of the positively charged divacancy V_2^+. The effect of linearly polarized light is studied by detecting changes in its EPR spectrum directly.

II. PRESENT EXPERIMENT

A. Experimental Procedure

A vacuum-floating-zone p-type silicon sample, boron doped to a resistivity of 0.3 Ω cm, was irradiated at room temperature by 1.5-MeV electrons. The total dose, divided equally on two opposite sides, was 1.06×10^{18} electrons/cm^2. The sample was still low-resistivity p type after the irradiation. This assures that divacancies are present only in the positively charged state V_2^+, which is observable in EPR. Complications due to optical absorptions associated with other charge states of the defect are avoided in this way. The sample, approximately $20\times2\times2$ mm^3 in size, was mounted with its long dimension, the crystallographic [0$\bar{1}$1] direction, along the axis of a cylindrical TE011 cavity. Samples were illuminated on the top—the (0$\bar{1}$1) face—with polarized and monochromatic light in the wavelength range 1.2–3.6 μ. Most of the studies were in the range 1.2–2.4 μ, and for these the light was channeled to the specimen through a long quartz rod extending from a small hole in the cavity top to outside the cryostat. The light was linearly polarized with its electric vector $\vec{E}$ in the (0$\bar{1}$1) plane by passing through an HR-2 Polaroid filter mounted on the end of the quartz rod directly above the sample. By rotating the rod, the electric vector $\vec{E}$ could be rotated in the (0$\bar{1}$1) plane. For studies beyond 2.4 μ, a hollow polished stainless-steel light pipe was used with no polarizer. Here the fact that light is inherently polarized in the plane perpendicular to the propagation direction was utilized.

The monochromator was a Jarrell-Ash $\frac{1}{4}$-m instrument fitted with a 295-line/mm grating. With input and exit slits of 5 and 11 mm respectively, the resolution was ~0.15 μ. For the studies at < 2.4 μ, a 600-W tungsten source was used with quartz optics. Beyond 2.4 μ, the source was a globar with mirror optics. Calibration of the intensity of the light reaching the sample was obtained with a thermocouple detector placed at the exit of the light pipes.

In the EPR studies, the static magnetic field $\vec{H}$ was rotated in the (0$\bar{1}$1) plane. All measurements were carried out at 20.4 K in a balanced bolometer homodyne spectrometer operating at 14 GHz.

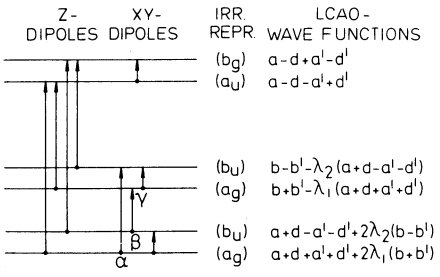

FIG. 2. Electron energy-level scheme of the divacancy as shown in Fig. 1, with LCAO wave functions and allowed electric dipole transitions indicated.

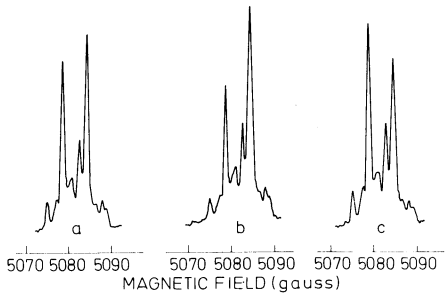

FIG. 3. EPR spectrum of the positively charged divacancy V_2^+ for $\vec{H} \| [011]$; (a) the spectrum before illumination, (b) after illumination with polarized light, $\vec{E} \| [100]$, $\lambda = 2.2\ \mu$, (c) after illumination with polarized light, $\vec{E} \| [011]$, $\lambda = 2.2\ \mu$.

B. Experimental Results

An illustration of the effect of illumination with polarized light of suitable wavelength on the divacancy is given in Fig. 3. It is seen in this figure that by illuminating with $\vec{E} \| [100]$ light, the amplitude of the low-field resonance has decreased, whereas $\vec{E} \| [011]$ light strengthens this resonance. The high-field resonance, on the other hand, behaves oppositively, with the middle resonance being nearly unaffected by the light. Since each resonance component corresponds to a different orientation of the divacancy, it is apparent that partial alignment of the defects is being produced via the polarized light.

In order to analyze the alignment produced it is first necessary to identify each component in the EPR spectrum in terms of the specific defect orientation from which it originates. For this, we reproduce in Fig. 4 the spectrum variation vs magnetic field orientation as given in Ref. 3. The labels given in the figure identify the defect orientation according to the following recipe, as previously outlined in that reference: Referring to Fig. 1, one of the vacancies is considered to be located at c' (the center of the unit cell of the figure). The first letter in the label denotes the position of the other vacancy, and the second letter denotes the site (and its primed partner) that lies in the horizontal reflection plane of the C_{2h} defect. (The second letter and its primed partner therefore denote the sites on which the unpaired electron orbital is primarily located.) The defect orientation in Fig. 1 therefore corresponds to orientation cb.

The effect of illumination on the EPR spectra was measured for $\vec{H}$ in the principal crystallographic directions [100], [211], [111], and [011]. Referring to Fig. 4, it is apparent that from these data one can deduce the effect of polarized light on all of the divacancy orientations which can be separately seen in the EPR spectra, i. e., on the orientations ad, da, $ab+ac$, $ba+ca$, $bc+cb$, $bd+cd$, and $db+dc$. A systematic study was made in this manner of the dependence of the divacancy alignment on the wavelength λ of the incident light. This was done by measuring both the *rate* of divacancy reorientation under the influence of the light (which should be proportional to the absorption coefficient of any absorption band involved) and the saturation value of the alignment after prolonged illumination. Results are shown in Fig. 5. Below $\lambda = 1.9\ \mu$ the time constant could not be measured because the alignment was too small to be followed. We note that no alignment at all is observed at $\lambda = 1.7\ \mu$, which is at the maximum of the 1.8-μ band at low temperature. A few additional measurements were made at longer wavelengths. For these, the alignment was first erased by illumination with light $\lesssim 1.5\ \mu$. The rate of alignment growth was then monitored with monochromatic light introduced through the hollow stainless-steel light pipe as described earlier. The inherent polarization of the light perpendicular to its propagation direction was sufficient to produce easily measurable alignment effects. The rate of alignment $1/\tau I$ was found to decrease continuously as the wavelength increased. At $3.6\ \mu$, within the 3.9-μ band, the rate was so slow as to be undetectable ($< 15\%$ of the rate at $2.4\ \mu$).

Therefore, the absorption bands which have been correlated with the divacancy, at $\lambda = 1.8\ \mu$ and $\lambda = 3.9\ \mu$, are not reproduced in the present experiment. Instead a band at $\lambda \sim 2.15\ \mu$ appears to be observed. At the maximum of this new band the angular dependence of the alignment effect was studied. Figure 6 shows the variation of the population of the various divacancy orientations when the direction of the electric field $\vec{E}$ of the polarized light is varied in the $(0\bar{1}1)$ plane. In Fig. 6, and throughout the paper, "unity" population for a

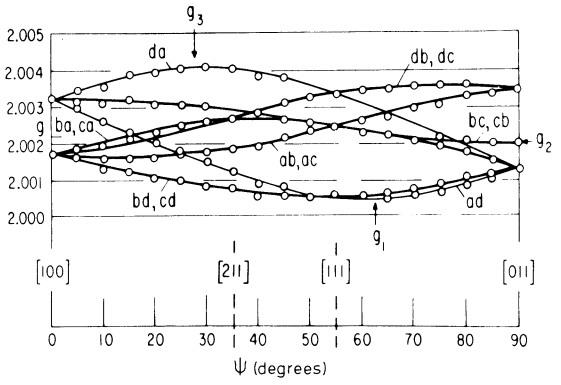

FIG. 4. G6 EPR spectrum for the positively charged divacancy V_2^+ vs orientation of the magnetic field $\vec{H}$ in the $(0\bar{1}1)$ plane (from Ref. 3). The labels denote the defect orientation (see text).

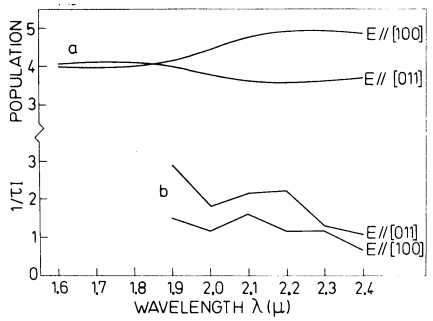

FIG. 5. (a) Saturation population and (b) alignment rate $1/\tau I$ (τ is the time constant, I the light intensity) vs wavelength λ for the incident light polarized along [100] or [011] for the group of divacancy orientations *ad*, *da*, *bc*, and *cb*, as monitored by the low-field resonance for $\vec{H} \parallel [100]$.

specific defect orientation corresponds to its normal equilibrium population, i. e., zero alignment.

C. Analysis of Angular Dependence

To explain the reorientation mechanism the following model is invoked. By absorbing a photon the divacancy is excited into a higher electronic state. The Jahn-Teller deformation corresponding to this temporary electronic configuration may be different from that in the ground state. Therefore upon deexcitation there is a certain probability for the divacancy to assume a ground state different from the original one. Thus, absorption of a photon by a divacancy may lead to loss of its initial orientation. This effect will be dominated by those divacancies which have the highest probability for excitation, i. e., by those divacancies which have their transition dipole moments closest to the electric field vector.

A model based on this mechanism, considering only exchange between divacancies differing in their Jahn-Teller distortions and keeping their vacancy-vacancy axes unchanged, is shown schematically in Fig. 7. The excitation probabilities contain angular-dependent parts which, for the defect orientation ij, are given by the quantity M_{ij}^2, which is the square of the cosine of the angle between the transition dipole moment $\vec{P}_{ij}$ and the electric field vector $\vec{E}$ of the polarized light,

$$M_{ij}^2 = \cos^2(\vec{E}, \vec{P}_{ij}).$$

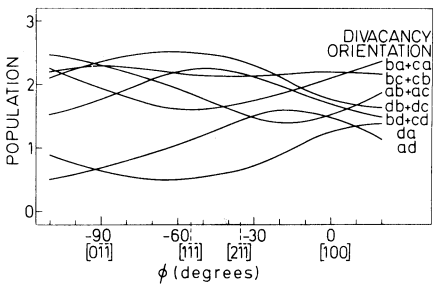

FIG. 6. Population of the various divacancy orientations after illumination with polarized light with $\vec{E}$ in the $(0\bar{1}1)$ plane, for a wavelength $\lambda = 2.15\ \mu$.

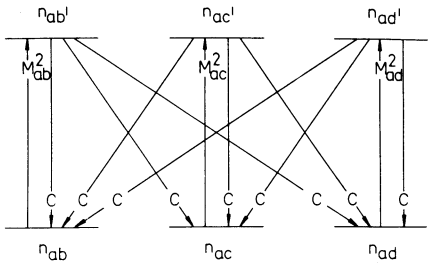

FIG. 7. Schematic of the model for reorientation within the Jahn-Teller triplet consisting of the divacancy orientations *ab*, *ac*, and *ad*.

The direction of the transition dipole moment with respect to the axes of the particular divacancy orientation is defined by the angle θ in Fig. 1. $\vec{E}$ is rotated in the $(0\bar{1}1)$ plane, its angle with respect to the [100] crystallographic direction being given by ϕ. In the model it is assumed that deexcitation occurs with equal probability to the ground state of any member of the Jahn-Teller triplet to which the original orientation belonged. Formulas for the steady-state populations n_{ad}, etc., which can be worked out straightforwardly on the basis of this model, are

$$n_{ad} = 3M_{ab}^2 M_{ac}^2/(M_{ab}^2 M_{ac}^2 + M_{ac}^2 M_{ad}^2 + M_{ad}^2 M_{ab}^2),$$

with cyclic permutations of *ab*, *ac*, and *ad* for n_{ab} and n_{ac}. Here,

$$M_{ab} = M_{ac} = (\tfrac{1}{2}\sqrt{2}\ \cos\theta\ \cos\phi + \tfrac{1}{2}\sqrt{2}\ \sin\theta\ \sin\phi - \tfrac{1}{2}\cos\theta\ \sin\phi),$$

$$M_{ad} = \sin(\theta + \phi).$$

Similar expressions hold for the other three Jahn-Teller triplets.

We find that the general features of the alignment and its angular dependence can be accounted for satisfactorily by this model. The degree of alignment observed, however, is always less than the model predicts. We attribute this in large part to incomplete polarization of the light resulting from divergence of the beam direction, scattering within the sample and on the cavity walls, etc.

A comparison between the experimental data as given in Fig. 6 and the model shows that the transition dipole moment must be in the XY plane of the divacancy (Fig. 1). A best fit is obtained for the angle

$$\theta = +15^\circ \pm 5^\circ.$$

This angle and its sign are determined unambiguously directly from the amplitudes of the *ad* and *da* spectral components. For these specific defect orientations, the XY plane is the $(0\bar{1}1)$ plane in which the $\vec{E}$ vector of the light is polarized. Their angular dependence therefore reveals θ directly. In Fig. 8 the prediction of the model and the actual experimental population of the *da* divacancy orientation is illustrated.

The angle θ and the XY components of the transition dipole moment are related by the goniometric expression $\tan\theta = -\langle f|y|i\rangle / \langle f|x|i\rangle$, with $|i\rangle$ and $|f\rangle$ representing the initial and final state before and after the optical excitation, respectively. In terms of the one-electron LCAO-level scheme (Fig. 2), it appears that only the three transitions, labeled α, β, and γ, have the required XY-type transition dipole moment and in addition connect an occupied with an empty level. These, therefore, should be considered for a possible identification with the 2.15-μ band. By substituting the relevant initial and final LCAO wave functions as shown in Fig. 2, a rough estimate for the value of θ for the three transitions can be made. Ignoring overlap between the orbitals on the different atom sites, we obtain

$$\tan\theta \approx (3\lambda_2+\lambda_1)/(3\lambda_1-\lambda_2)\sqrt{2} \quad \text{for transition } \alpha$$

$$\approx (3\lambda_1+\lambda_2)/(3\lambda_2-\lambda_1)\sqrt{2} \quad \text{for transition } \beta$$

$$\approx (1-6\lambda_1\lambda_2)/(3+2\lambda_1\lambda_2)\sqrt{2} \quad \text{for transition } \gamma.$$

A rough estimate, in turn, of the values of λ_1 and λ_2 can be obtained from η_j^2, the percentage of the EPR wave function at each atom site j neighboring the divacancy, deduced from hyperfine interactions and tabulated in Table I of Ref. 3. We take $\lambda_1^2 = \eta_a^2/\eta_b^2 \sim 0.06$ from the $G6$ spectrum for V_2^+ and $\lambda_2^2 = \eta_a^2/\eta_b^2 \sim 0.11$ from the $G7$ spectrum for V_2^-.[18] Assuming λ_1 and λ_2 of the same sign,[19] the result is

$$\theta \approx +65^\circ \quad \text{for transition } \alpha$$

$$\approx +45^\circ \quad \text{for transition } \beta$$

$$\approx +7^\circ \quad \text{for transition } \gamma.$$

This clearly is a very rough estimate. We have ignored the contribution of the more extended parts of the wave functions. Also our treatment of the localized parts clearly involves considerable oversimplification, which may or may not be justified. However, with these reservations, this may still serve as a guide as to what to expect. Positive angles seem to be indicated in agreement with the value $\theta = +15^\circ \pm 5^\circ$ determined for the 2.15-μ band. The observed magnitude agrees somewhat better with transition γ, but this may not be significant.

III. DISCUSSION

For the observation of light-induced divacancy reorientation several requirements have to be met. If the reorientation model proposed in Sec. II is a realistic one, then these requirements will include the following three.

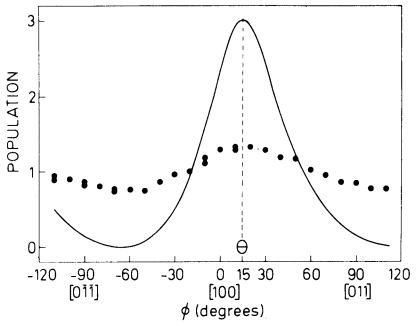

FIG. 8. Angular dependence of the number of divacancies in the orientation *da*. The solid line is calculated by the model for $\theta = +15°$; the dots represent the experimental behavior, $\lambda = 2.15\ \mu$.

(i) The transition probability for the excitation should be different for the various divacancy orientations. This is clearly so for the transitions between the localized molecular-orbital states visualized in Fig. 2.

(ii) The Jahn-Teller deformation in the excited state should be substantially different from that in the ground state.

(iii) There should not be a rapid spontaneous redistribution of orientations in the ground state. For the positively charged divacancy we know this condition to be fulfilled, since the time constant for thermally activated redistribution is as long as 2×10^5 sec at $T = 20.4$ K.[3]

No V_2^+ alignment due to polarized light in the 1.8-μ band was observed in this experiment. On the other hand, from the results of Cheng and Vajda,[9] we know that the defect giving rise to the 1.8-μ band is aligned by polarized 1.8-μ light. Our results therefore confirm directly that the 1.8-μ band does not arise from the positively charged state of the divacancy, as deduced by Cheng and Vajda.

No V_2^+ alignment was observed with polarized light in the 3.9-μ band either. This is consistent with the experimental observation of Cheng and Vajda[9] that no dichroism is induced into the band by polarized light. This, in turn, means that if the 3.9-μ band is associated with V_2^+, one of the three requirements above is not satisfied. We know that a well-defined dipole-moment direction exists for the 3.9-μ band [condition (i)] from studies involving stress-induced dichroism in both absorption[7] and photoconductivity.[11,13] Therefore, the failure would have to be in condition (ii). This is, of course, possible, and is roughly equivalent to the arguments given by Cheng and Vajda.

However, a serious question should be raised at

this point as to whether the 3.9-μ band really is associated with V_2^+ at all. Cheng and Vajda also state that dichroism is not induced into the 3.9-μ band by polarized light anywhere in the 1–5-μ region. Our present results definitely establish that light in a broad region around 2.15 μ achieves significant alignment of V_2^+. If the 3.9-μ band also arises from V_2^+, it should therefore display dichroism when the defect is aligned with 2.15-μ light. Perhaps, this could have been missed in the experiments of Cheng and Vajda. In any event, this represents a simple positive experiment that could be performed which should answer this important question directly.

The evidence that has been cited for identification of the 3.9-μ band (as well as the 1.8- and 3.3-μ bands) with the divacancy is certainly substantial. However, it is instructive to point out that, with only a few exceptions,[13] optical studies on these bands have been done on samples that have been irradiated either with very high-energy electron (~ 46 MeV) or with fast neutrons. EPR studies, on the other hand, have been performed mostly on lower-energy-electron-irradiated material. The possibiltiy cannot be ruled out that some of these optical bands may be associated with more complex defects which still bear a superficial resemblance to the simple divacancy. One minor point in this regard is the observation that the 3.3-, 1.8-, and 3.9-μ bands were deduced to have[7] $\theta \approx -15°$. Here we have argued that a positive value is more to be expected for the divacancy, as is observed for the 2.15-μ band.

Finally, let us ask if any evidence exists for a band at 2.15-μ in optical studies. One possibility is in photoconductivity studies by Cheng.[13] He reported a broad band in this region which displayed different stress-induced dichroism from that of the 3.9-μ band. From low-temperature stress studies he tentatively concluded that the defect had $\langle 111 \rangle$ symmetry. This is not consistent with the identification as the divacancy, but perhaps the symmetry determination could be in error. He also observed no dichroism induced after 160 °C stress which should have produced vacancy-vacancy alignment. Superficially this also argues against identification with the divacancy. However, it is interesting to note that for $\theta \sim +15°$ negligible quenched-in dichroism should be observed for the divacancy (see Fig. 17 of Ref. 7), for the degree of vacancy-vacancy alignment in these experiments.

We have also observed alignment with polarized light for V_2^-, as monitored by the $G7$ EPR spectrum at 14 K in neutron-irradiated n-type silicon. Here the phenomena appear more complex and systematic studies have not as yet been made. Some of the complexity here is probably associated with the possible simultaneous presence of divacancies in several charge states in the neutron-irradiated sample. Work is being continued on this problem.

ACKNOWLEDGMENTS

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[17] H. J. Stein, F. L. Vook, D. K. Brice, J. A. Borders, and S. T. Picreaux, Radiation Effects 6, 19 (1970).
[18] The $G7$ spectrum arises from an unpaired electron in the b_u orbital (Fig. 2), giving an estimate of λ_2.
[19] The hyperfine interaction does not give the sign. Simple molecular arguments can be made to say that both are positive. There are pitfalls, however, in such arguments, particularly when embedded in a solid, and this could be in error.