Optical Detection of Magnetic Resonance for a Deep-Level Defect in Silicon

K. M. Lee, K. P. O'Donnell, J. Weber,[(a)] B. C. Cavenett,[(b)] and G. D. Watkins
Department of Physics, Sherman Fairchild Laboratory, Lehigh University, Bethlehem, Pennsylvania 18015

(Received 9 November 1981)

Optical detection of magnetic resonance is reported for the 0.97-eV luminescence in neutron-irradiated silicon. The resonance is of an excited triplet ($S = 1$) state of the defect, which is not the radiative state, known to be a singlet ($S = 0$). The spectrum is unusual in that it is characteristic of a statically distorted defect (from C_{3v} to C_{1h}), but with residual dynamic tunneling effects where random strain stabilizes mixtures of the *static* C_{1h} distortions. Vacancy-related models previously suggested for the defect are tentatively ruled out.

PACS numbers: 71.55.Fr, 61.80.-x, 76.70.Hb, 78.55.Ds

In this Letter, we report the first optical detection of magnetic resonance (ODMR) in crystalline silicon. It has been detected in a luminescence band, with zero-phonon transition at 0.97 eV,[1-9] which is one of the dominant bands produced by electron or neutron irradiation in high-purity silicon. There are several unique features observed in this study: (1) Magnetic resonance is not detected in the radiative excited singlet ($S = 0$) state but rather in a nonradiative excited triplet ($S = 1$) state of the defect. (2) The excited triplet state reveals an ODMR spectrum characteristic of a dynamic Jahn-Teller system in trigonal symmetry (C_{3v}), where random strain produces a "powder-pattern" mixing between the *static* distorted states of C_{1h} symmetry. To our knowledge this is the first magnetic resonance observation of this particular dynamic distortion limit. (3) Finally, this observation of intense well-resolved ODMR transitions for luminescent defects in silicon provides the first demonstration that this powerful technique can be applied to defect problems in this important material.

The 0.97-eV luminescence system (and associated absorption bands) has been the subject of numerous previous optical studies[1-10] and a great deal is known about it: The band is associated with a defect of monoclinic $I(C_{1h})$ symmetry with dipole transition moment perpendicular to its $\{110\}$ reflection plane.[3,7-9] Observation of a sharp local mode due to carbon and an isotope shift of the zero-phonon line due to silicon[8,9] reveals the presence of a single nearby carbon-atom impurity, but suggests that the electronic transition is between single-particle electronic states most strongly localized on a single silicon atom. Magneto-optic studies resolved no splittings of the 0.97-eV line up to 10 T which indicates a nonmagnetic singlet-to-singlet transition.[9,11] The microscopic identity of the defect has not been established, although several models have been suggested.[2,4-6,8-10]

For the present study, oriented single crystals of typical dimensions $4\times2\times0.5$ mm^3, with long axis parallel to a $\langle110\rangle$ direction, were cut from a wafer of (thermal) neutron-irradiated (5×10^{17} n/cm^2) n-type silicon and mounted in a 35-GHz TE_{011} microwave cavity having the form of concentric rings for easy optical access. The sample and cavity were immersed in pumped liquid helium ($T \lesssim 2$ K) and luminescence was excited by 100–300 mW of the 514-nm line of an argon ion

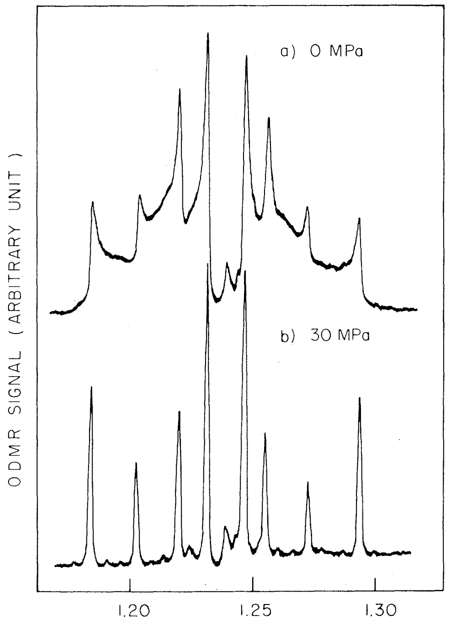


FIG. 1. (a) ODMR spectrum with $\vec{B}\parallel[011]$ at $T \cong 1.7$ K, $\nu = 35.0$ GHz. (b) Spectrum, same orientation, with compressional stress of 30 MPa, $\vec{T}\parallel[0\bar{1}1]$, showing ^{29}Si hyperfine satellites.

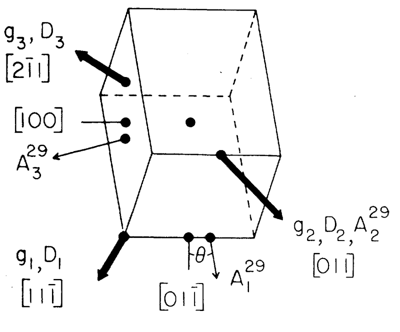
laser. Magnetic fields up to 3 T were supplied by a pair of superconducting Helmholtz coils. The 35-GHz microwaves (≃ 50 mW) were chopped at 1.25 kHz by a ferrite modulator and synchronous changes in the luminescence were detected by a cooled high-sensitivity intrinsic Ge detector (North Coast EO-817), lock-in detected, and recorded. Uniaxial compressional stress was applied to the crystal via a stainless steel rod coaxial with the TE_{011} cavity.

The ODMR spectrum for $\vec{B}\parallel[011]$ is shown in Fig. 1(a). We note that it resembles a "powder-pattern" spectrum with sharp singularities at the extrema. In Fig. 1(b), we show the spectrum when uniaxial compressional stress is applied, $\vec{T}\parallel[0\bar{1}1]$. The extrema sharpen up and the "powder-pattern" intensity between them disappears. Under stress, each of the sharpened stronger lines reveals satellites arising from hyperfine interaction with a single ^{29}Si nucleus (4.7% abundant, $I=\frac{1}{2}$). Angular dependence studies with $\vec{B}$ in the $\{0\bar{1}1\}$ plane reveal that the spectrum (the sharp lines under stress, or the extrema in the absence of stress) arises from a single anisotropic (C_{1h}) defect, $S=1$, with spin Hamiltonian

$$H=\mu_B\vec{B}\cdot\tilde{g}\cdot\vec{S}+\vec{S}\cdot\tilde{D}\cdot\vec{S}\cdot\tilde{A}\cdot\vec{I},$$

where the parameters for one of the twelve equivalent defect orientations are given in Fig. 2.

The spectral features in the absence of applied stress, Fig. 1(a), bear the characteristic signature of a dynamic Jahn-Teller system stabilized by internal strains.[12,13] In such a case, the "powder-pattern" shape results from the fact that strain can mix and stabilize any combination of the "pure" states represented by the singularities. In the present case, the "pure" states are the three equivalent C_{1h} static distorted states, which in the ODMR spectrum share a common $\langle 111\rangle$ axis (i.e., g_1, D_1). If the distortion is indeed of Jahn-Teller origin,[14] then this implies that the electronic state is ^3E for a defect in $\langle 111\rangle$ C_{3v} symmetry before distortion and that the Jahn-Teller coupling is to E modes of distortion. Except for the triplet spin state, this is a common, much studied dynamic Jahn-Teller system. Reynolds and Boatner[13] have classified the various regimes for this system as "dynamic" "quasidynamic," "quasistatic," and "static," depending upon the relative magnitudes of the random strain splitting $\bar{\delta}$, and the dynamic "tunneling" splitting 3Γ. The commonly observed cases have been in the dynamic and quasidynamic regimes, $\bar{\delta}/3\Gamma\lesssim 1$, or the static regime, $\bar{\delta}/3\Gamma\gg 1$. We believe ours is the first clean example of a system squarely in the "quasistatic" regime.



$g_1 = 2.006(5)$ $D_1 = \pm 270(1)$ $A_1^{29} = 105(10)$

$g_2 = 2.004(5)$ $D_2 = \mp 315(1)$ $A_2^{29} = 115(5)$

$g_3 = 2.00(1)$ $D_3 = \pm 45(2)$ $A_3^{29} = 86(10)$

$\theta = 15(20)^\circ$

FIG. 2. Spin-Hamiltonian parameters for one of the twelve equivalent defect orientations of the $S=1$ excited state. D and A values are expressed in the unit of 10^{-4} cm^{-1}.

This interpretation is confirmed by the change in the spectrum under externally applied uniaxial stress, Fig. 1(b). Here the stress-induced splittings exceed the tunneling splittings, stabilizing the static distortions and removing the impure mixtures. No stress alignment (as evidenced by changes in the relative amplitudes of the spectral components) was observed up to 100 MPa. This implies that the reorientation time between the static distortions exceeds the lifetime of the excited state. The near equivalence of the intensities of the $M=+1\rightleftarrows 0$ and $M=-1\rightleftarrows 0$ transitions shows further that the spin-lattice relaxation time in the excited state also exceeds the lifetime of the state.

Preliminary studies at elevated temperatures ($T\sim 30$ K) indicate the onset of thermally activated reorientation between the three C_{1h} distortions for each defect. The powder pattern disappears and a "motionally averaged" axial $\langle 111\rangle$ ODMR spectrum emerges at the average position of the three statically distorted C_{1h} spectra. ^{29}Si hyperfine satellites are also observed in this regime at the average position of the corresponding static C_{1h} ^{29}Si satellites. Their intensities relative to the corresponding central component remain the same as for the static spectrum, reflecting the 4.7% ^{29}Si abundance of a *single* silicon atom. This means that the *electronic spin density remains on the same silicon atom as the defect reorients from one distortion direction to the other.* This differs from the more frequently observed dynamic case at low temperatures for Jahn-Teller systems, where *electronic* hopping from one equivalent silicon site to another occurs (for instance, around a vacancy-related defect).[15] [In that case, the hyperfine interaction is motionally averaged between the 4.7%-abundant ^{29}Si nucleus ($I=\frac{1}{2}$) at one site and the major-abundance ^{28,30}Si ($I=0$) nuclei at the $N-1$ other equivalent sites. The motionally averaged hyperfine interaction is therefore reduced by $\sim 1/N$ and the satellite intensity increased by $\sim N$ because the averaged wave function is now spread equally over the N equivalent silicon sites.[15]]

The spectral dependence of the ODMR signal, determined by inserting a monochromator before the detector, confirms that the ODMR signal is associated only with the 0.97-eV luminescence system. In addition, a study of the dependence of the ODMR spectrum on the polarization of the emitted light reveals different relative amplitudes of the spectral components for each polarization. This demonstrates unambiguously that the triplet state being studied is an excited state of the same defect that is emitting the luminescence.

Since previous magneto-optic studies have shown that the luminescent state is a singlet, we are led to the following conclusion: Magnetic resonance is being observed in a nonradiative excited triplet state of the defect giving rise to the 0.97-eV luminescence. The C_{1h} distortion which exists in the ground and excited singlet states as evidenced by the previous luminescence and absorption studies[2,4,5,9] also exists in the excited triplet state, but in this case it is partially dynamic. Two possible models are demonstrated in Fig. 3. In Fig. 3(a), the triplet state is above the emitting singlet state and decays spin selectively (preferentially either $\Delta M=0$ or $\Delta M=\pm 1$) into the radiative state. ODMR transitions therefore cause an increase in the luminescence, as observed, by emptying the bottlenecked state. In Fig. 3(b), the triplet state is below the emitting state and decays nonradiatively to the ground state. ODMR transitions increase the ground-state population as the bottlenecked triplet state is depopulated, providing more defects for luminescence. This second model has been proposed for a previously studied organic molecular system.[16] Work is in progress to distinguish between these two possibilities.

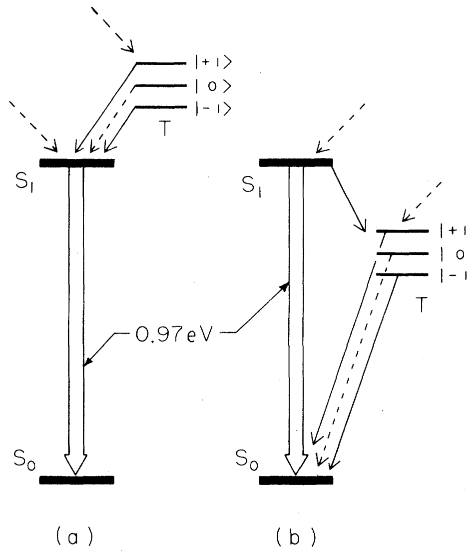


FIG. 3. Two models for triplet ODMR in the singlet-to-singlet luminescence. (a) The triplet state is above the radiative singlet state and ODMR $\Delta M = \pm 1$ transitions enhance the decay to the radiative state by emptying the bottlenecked triplet $|M\rangle$ state. (b) The triplet state is below the radiative state and ODMR enhanced radiationless decay to the ground state provides more defects in the ground state for excitation to the emitting state.

The ODMR studies therefore confirm in detail many of the features deduced from previous optical studies. These include the C_{1h} symmetry and the strong localization of the excited electronic state on a single silicon atom. In addition, the ODMR studies provide the important new information that as the defect reorients from one C_{1h} distortion to another, the excited electronic state remains localized on the same silicon site. We believe that this allows us to rule out the vacancy-related models suggested for the defect[2,5,8-10] where hopping from one equivalent silicon atom site to another around the vacancy would have been predicted. Two suggested interstitial-related models involving one[9] or two[4,6] carbon atoms remain possibilities.

We have also detected ODMR signals associated with other luminescent bands in silicon. [The weak ODMR lines in the central region of the spectrum of Fig. 1(b) arise from another luminescence system, with zero-phonon line at 1.019 eV. These ODMR signals dominate in samples where this luminescence is strong and are currently under study.] The prospects are therefore good that this technique may be generally applicable to many of the important deep-level defects in silicon.

Various aspects of this collaboration were made possible by partial support from a Ford Motor Company Research Grant, the Science Research Council (United Kingdom), and the University of Hull. The research was supported by the National Science Foundation under Grant No. DMR-77-11309.

---

[a] Permanent address: Physikalisches Institut (Teil 4) der Universität Stuttgart, Pfaffenwaldring 57, D-7000 Stuttgart 80, Federal Republic of Germany.

[b] Permanent address: Department of Physics, The University, Hull, England.

[1] A. V. Yukhnevich, Fiz. Tverd, Tela (Leningrad) 7, 322 (1965) [Sov. Phys. Solid State 7, 259 (1965)].

[2] C. E. Jones, E. S. Johnson, W. D. Compton, J. R. Noonan, and B. G. Streetman, J. Appl. Phys. 44, 5402 (1973).

[3] A. V. Yukhnevich and A. V. Mudryi, Fiz. Tekh. Poluprovodn. 7, 1215 (1973) [Sov. Phys. Semicond. 7, 815 (1973)].

[4] J. R. Noonan, C. G. Kirkpatrick, and B. G. Streetman, J. Appl. Phys. 47, 3010 (1976).

[5] V. D. Tkachev and A. V. Mudryi, in *Radiation Effects in Semiconductors 1976*, IOP Conference Series No. 31, edited by N. B. Urli and J. W. Corbett (Institute of Physics, London, 1977), p. 231.

[6] V. S. Konoplev, A. A. Gippius, and V. S. Vavilov, in Ref. 5, p. 244.

[7] C. P. Foy, M. C. do Carmo, G. Davies, and E. C. Lightowlers, J. Phys. C 14, L7 (1981).

[8] G. Davies and M. C. do Carmo, J. Phys. C 14, L687 (1981).

[9] K. Thunke, H. Klemisch, J. Weber, R. Sauer, Phys. Rev. B 24, 5874 (1981).

[10] A. R. Bean, R. C. Newman, and R. S. Smith, J. Phys. Chem. Solids 31, 739 (1970).

[11] G. Davies and M. Skolnick (private communication); K. R. Elliot (private communication).

[12] F. S. Ham, in *Electron Paramagnetic Resonance*, edited by S. Geschwind (Plenum, New York, 1972).

[13] L. A. Boatner, R. W. Reynolds, Y. Chen, and M. M. Abraham, Phys. Rev. B 16, 86 (1977).

[14] The distortion need not be of Jahn-Teller origin; the driving force may not arise from the electron degeneracy. An off-axis "hindered rotator" can display all of the same dynamic manifestations. It is not necessary therefore to make a distinction at this stage because the formalism that has been developed for the dynamic Jahn-Teller problem should be applicable to this case as well.

[15] G. D. Watkins and J. W. Corbett, Phys. Rev. 134, A1359 (1964).

[16] W. G. Van Dorp, T. J. Schaafsma, M. Soma, and J. H. Van der Waals, Chem. Phys. Lett. 21, 221 (1973).

Observation of Electron Paramagnetic Resonances at Multiples of the "Classical" Resonance Magnetic Field

B. Clerjaud and A. Gelineau
Laboratoire de Luminescence II, Université Pierre et Marie Curie, F-75230 Paris 05, France

(Received 21 October 1981)

Observation of electron paramagnetic resonance signals at multiples (up to 7) of the conventional magnetic resonance field are reported in the case of the system GaP:Cr$^+$ at low temperatures. These signals are shown to be due to multiphoton transitions. The physical reason for the observation of these resonances is a long relaxation time consistent with the physical nature of this paramagnetic center.

PACS numbers: 76.30.Fc, 76.20.+q

Resonant multiphoton absorption in magnetic resonances has been known to exist since the optical pumping experiments of Margerie and Brossel,[1] which have been interpreted by Winter.[2,3] In these experiments the amplitude $2H_1$ of the microwave magnetic field and the static magnetic field H were of the same order of magnitude. To our knowledge such resonances have never been reported in nuclear magnetic resonance nor in electron paramagnetic resonance (EPR). In this Letter, we report the observation of such multiphoton resonances in EPR experiments in which H_1/H is as low as 10^{-5}. We will show that these resonances can be observed because of the long re-