

Hyperfine Interactions of the P_b Center at the $\text{SiO}_2/\text{Si}(111)$ Interface

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Multiple-scattering $X\alpha$ results are reported which show that spin polarization must be included to obtain a detailed understanding of the hyperfine spectra of the Si dangling-bond P_b defect at the $\text{SiO}_2/\text{Si}(111)$ interface. The largest superhyperfine interaction is found to be produced not by the trivalent Si atom's nearest neighbors as has been commonly assumed, but by three second-nearest neighbors located behind the defect in bulk c -Si. Our P_b -center results support the threefold-coordinated Si model for this defect; they also suggest a straightforward interpretation of recent ESR data on the dominant paramagnetic center in a -Si:H.

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The P_b center at the $\text{SiO}_2/\text{Si}(111)$ interface is among the most important and thoroughly characterized intrinsic defects in metal-oxide-semiconductor devices.¹⁻³ Definitive data on the nature and environment of this defect have come from ESR experiments.⁴⁻⁸ The measured g tensor and hyperfine interactions have been used to identify the P_b center as a Si atom backbonded to three c -Si atoms, with a dangling bond pointing in the Si-substrate $\langle 111 \rangle$ direction. These results have also been used as benchmarks for discussing other possibly threefold-coordinated Si defects, such as the D center in hydrogenated amorphous Si (a -Si:H).⁹

Sophisticated modern magnetic-resonance techniques have been applied to the P_b center, but theoretical analysis of the experimental data has so far been confined to parametrized models that do not allow direct calculation of the hyperfine tensors. The most widely used such interpretative tool is the localized hybrid-orbital model.^{8,10} Although this model neglects core and valence spin polarizations, it has been notably successful in associating the principal axes of defect g and hyperfine tensors with local coordinate axes and identifying large local bond-angle changes (rehybridizations) at Si dangling-bond atoms. We show below, however, that spin-polarization effects play an essential role in an understanding of the superhyperfine spectra of the P_b center. The importance of spin polarization has long been recognized in other contexts, such as proton hyperfine interactions in organic π radicals¹¹ and Fermi-contact couplings at transition-metal nuclei.¹² More recently these effects have also been found to be important in the description of transition-metal impurities in silicon.¹³ Nevertheless, the importance of spin polarization has not been appreciated sufficiently for the intrinsic defects in silicon and silica. Our results show that when polarizations are included, the threefold-coordinated Si model for the P_b center accounts in detail for the hyperfine and superhyperfine spectra of the defect. These results therefore provide strong evidence in favor of this model of the P_b center. Our calculations also suggest that differences between the P_b - and D -center hyperfine data can be naturally

reconciled without abandoning a threefold-coordinated Si model for the D center.

Our conclusions are based on all-electron, self-consistent, spin-unrestricted, multiple-scattering $X\alpha$ (MS- $X\alpha$)¹⁴⁻¹⁶ results on cluster models of the P_b center. The calculated hyperfine tensors include both valence and core polarizations and take into account changes in the atomic orbitals caused by perturbations from the host environment. The MS- $X\alpha$ method is particularly suitable for such a study. It is rapid computationally, so that large model clusters can be examined. Also, density-functional methods such as MS- $X\alpha$ lead to generally good accuracy in the values of properties depending on the spin density (e.g., as in recent discrete-variation method- $X\alpha$ calculations for the isotropic proton hyperfine coupling constants in organic π radicals).¹⁷

The largest cluster model used in these studies is shown in Fig. 1. This 73-atom, 563-electron $\text{Si}_6\text{O}_{18}\text{H}_6/\text{Si}_{22}\text{H}_{21}$ cluster has C_{3v} symmetry about the z axis. The $\text{Si}(111)$ substrate is modeled by a Si_{22} fragment with all bond lengths and bond angles held at their bulk c -Si values¹⁸ except at the threefold coordinated Si atom, Si' . Hydrogen atoms saturate the unsatisfied Si bonds at the exposed surfaces of the Si_{22} fragment to sweep them out of the gap into the valence regions. These H saturators are positioned along c -Si bond directions but the Si-H bond lengths are set equal to 1.48 Å, the experimental bond distance in SiH_4 .¹⁹

The silica side of the interface is modeled by a puckered, ditrigonal ring of six SiO_4 tetrahedra. Such rings are common in the naturally occurring phases of silica.^{20,21} By adjustment of the dihedral angles of these rings they can be fitted neatly onto a hexagon of $\text{Si}(111)$ surface atoms with very little strain in the connecting Si-O-Si bonds. The local bonding around Si on the oxide side of the cluster is kept regular and tetrahedral, with Si-O bond lengths fixed at the α -quartz value, 1.61 Å.²² The spread of Si-O-Si angles in the cluster is 139° - 151° —a very reasonable range.²³ This silica cap is terminated by six O-H groups; all Si-O-H bond angles are assumed the same as the Si-O-Si bond an-

gle in α -quartz with the O–H bond distance the same as in H_2O .²⁴

The most important unresolved structural question concerning the P_b center is what value to use for the vertical reconstruction $\Delta z_{\text{Si}'}$ of Si' from its tetrahedral position along the z direction. Self-consistent semiempirical^{25,26} and *ab initio*^{26–28} total-energy minimizations agree that $\Delta z_{\text{Si}'}$ should be negative in the ESR-active neutral charge state, but the calculated values appear sensitive to the sizes of both the model cluster and the basis set. Here we consider calculations at two geometries: $\Delta z_{\text{Si}'} = 0 \text{ \AA}$, which serves as a well-defined benchmark, and $\Delta z_{\text{Si}'} = -0.09877 \text{ \AA}$, a representative reconstructed value.²⁹ All other cluster atoms are held fixed.

The basis set used in our calculations includes angular functions up to $l=4$ on the outer MS- $X\alpha$ sphere, $l=2$ on all Si, $l=1$ on O, and $l=0$ on H. This constitutes a polarization basis on Si, and a minimum angular basis on O and H. The α values used are the atomic α_{HF} from the tabulation of Schwarz,³⁰ with the exception of H, where the spin-polarized value was used.³¹ The α for the intersphere and outer-sphere regions in the MS- $X\alpha$ method were valence-electron weighted averages over the atoms in the cluster. The results were checked to verify that they were not sensitive to the particular choice of the muffin-tin parameters.

The MS- $X\alpha$ wave function for our P_b -center cluster model is a spin-polarized, single-determinantal wave function constructed from molecular spin orbitals $\phi_{\mu}^{\alpha,\beta}$. Once this wave function is obtained self-consistently, the isotropic, a^N , and anisotropic, A_{ij}^N , hyperfine interactions for a nuclear center N are computed directly from

$$a^N = \frac{8}{3} \pi g_e \beta g_N \beta_N \left\{ \sum_{\mu}^{\text{occ}} \langle \phi_{\mu}^{\alpha} | \delta^3(\mathbf{r}_N) | \phi_{\mu}^{\alpha} \rangle - \sum_{\mu}^{\text{occ}} \langle \phi_{\mu}^{\beta} | \delta^3(\mathbf{r}_N) | \phi_{\mu}^{\beta} \rangle \right\}$$

and

$$A_{ij}^N = g_e \beta g_N \beta_N \left\{ \sum_{\mu}^{\text{occ}} \langle \phi_{\mu}^{\alpha} | \frac{3r_{Ni}r_{Nj} - \delta_{ij}r_N^2}{r_N^5} | \phi_{\mu}^{\alpha} \rangle - \sum_{\mu}^{\text{occ}} \langle \phi_{\mu}^{\beta} | \frac{3r_{Ni}r_{Nj} - \delta_{ij}r_N^2}{r_N^5} | \phi_{\mu}^{\beta} \rangle \right\},$$

where g_N is the nuclear magnetogyric ratio $g_N = \mu_N/I_N$, β and β_N are the Bohr and the nuclear magnetons, and g_e is the free-electron g value.

Models holding Si' at the tetrahedral position were first studied both with and without the SiO_2 cap, to measure the effects of the oxide on the hyperfine spectra of the P_b center. When the cap is removed, the Si_{s2} atoms are saturated by H atoms as for the rest of the cluster. The full cluster calculation showed that very little of the Si' defect orbital, $\phi_{\text{Si}'}^g$, delocalizes along the surface onto the six Si_{s2} second-nearest neighbors or into more distant regions of the cluster. Because of the very small amount of $\phi_{\text{Si}'}^g$ amplitude and spin density in the silica cap and the Si_{s2} atoms bonded to it, the cap has only a small effect on the hyperfine interactions (cf. the unrelaxed $\text{Si}_6\text{O}_{18}\text{H}_6/\text{Si}_{22}\text{H}_{21}$ and unrelaxed $\text{Si}_{22}\text{H}_{27}$ columns in Table I). In view of this result, we have used only the smaller cluster for the relaxed Si' calculations.

As Table I shows, we find that the unrelaxed clusters

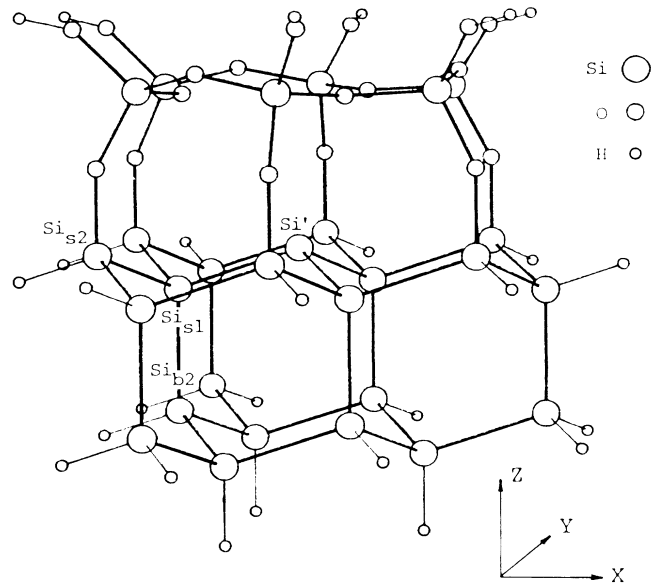


FIG. 1. Ball-and-stick model of the $\text{Si}_6\text{O}_{18}\text{H}_6/\text{Si}_{22}\text{H}_{21}$ P_b defect cluster showing the labeling scheme used in the text. The sphere radii are in the same ratios as the MS- $X\alpha$ radii but are greatly reduced in size for clarity.

produce hyperfine couplings at Si' which are too large compared with experiment. This is what we should expect: As Si' relaxes downward toward the plane of its three nearest neighbors Si_{s1} , the Si' s character of the defect orbital is diminished and the isotropic hyperfine coupling becomes smaller. With the relaxed value of $\Delta z_{\text{Si}'}$, our calculated $a^{\text{Si}'}$ is reduced from -152.7 to -128.6 G while $A_{zz}^{\text{Si}'}$ is not greatly affected by the relaxation (-57.8 to -59.2 G). These relaxed values are in very good agreement with experiment—closer agreement would be fortuitous, given the uncertainty in $\Delta z_{\text{Si}'}$ and the muffin-tin approximations inherent in the MS- $X\alpha$ method.

As expected, after Si' , $\phi_{\text{Si}'}^g$ has its largest amplitude on the nearest neighbors, Si_{s1} . Nevertheless, as reported in Table I, we find a very small hyperfine coupling at these sites. This result—although unanticipated in the P_b literature—is consistent with well-understood spin-

TABLE I. Model P_b -center hyperfine tensors (gauss).^a

		Unrelaxed Si ₆ O ₁₈ H ₆ /Si ₂₂ H ₂₁	Unrelaxed Si ₂₂ H ₂₇	Relaxed Si ₂₂ H ₂₇	Expt. ^d
Si'	a	-151.94	-152.73	-128.62	(±)113 ± 7 ^e
	\mathbf{A}_{zz}	-65.57	-57.96	-59.16	(±)44 ± 13 ^e
Si _{s1}	a	0.45	-0.17	1.24	
	$\mathbf{A}_{x'x'}$	-2.33	-2.38	-1.64	
	η^b	0.19	0.08	0.09	
	θ^c	42.1°	33.2°	33.6°	
Si _{b2}	a	-9.67	-8.31	-9.84	} ± 15 ^{e,f}
	$\mathbf{A}_{z'z'}$	-3.36	-3.04	-3.12	
	η^b	0.03	0.03	0.03	
	θ^c	-3.5°	-2.3°	-1.6°	

^aCalculated values of a are converted to gauss by use of $a[\text{G}] = 285.522g_N \langle \delta^3(\mathbf{r}_N) \rangle_{\alpha-\beta} [\text{a.u.}]$ for nucleus N : $g_{^{29}\text{Si}} = -1.11052$ (Ref. 32). The conversion factor for the anisotropic \mathbf{A} tensor is smaller by a factor of $8\pi/3$. The principal axes of \mathbf{A} coincide with local coordinate axes only for Si'. For other atoms the principal component of \mathbf{A} is labeled by the coordinate axis with which it makes the smallest angle (primed subscripts).

^bThe asymmetry parameter $\eta = (A_{11} - A_{22})/A_{33}$, where A_{ii} denotes the principal-axis values in order of increasing magnitude. For an axial tensor $A_{11} = A_{22} = -\frac{1}{2}A_{33}$, and $\eta = 0$.

^cCounterclockwise rotation angle about the axis out of the paper in Fig. 1 (the $-y$ axis) required to bring the local coordinate axes into coincidence with the principal axes of \mathbf{A} .

^dReference 8.

^eThe sign of the hyperfine interaction is not directly measured by the experiments.

^fEstimated from the figure in Ref. 8 (field along the $\langle 111 \rangle$ direction).

polarization effects in the AH_3 radicals. When A lies in the plane of the H atoms, as in CH_3 , the defect orbital is pure p -like and a negative spin density is induced at the protons by polarization effects. As A is raised into a more pyramidal conformation, as in SiH_3 , positive spin density is built in at the protons by direct overlap so that the net spin density at the nucleus can pass through zero and become positive. For Si, which has a negative value of $g_{^{29}\text{Si}}$, this corresponds to $a > 0$ on Si_{s1} in the planar geometry and $a < 0$ for highly pyramidal geometries. At values of $\Delta z_{\text{Si}'}$ corresponding to moderately pyramidal conformations the nearest-neighbor isotropic hyperfine coupling is close to zero. The situation in the P_b center is slightly more complex than this analysis implies, but we see by comparing the unrelaxed and relaxed Si₂₂H₂₇ results in Table I that the net trend is the same as for a simple AH_3 system.

Because of the opposing effects of direct spin delocalization and induced exchange polarization, the nearest neighbors of Si' cannot be the source of the large P_b superhyperfine interaction that Brower observes ($\approx \pm 15$ G).⁸ It is the three second-nearest neighbors labeled Si_{b2} in Fig. 1 that actually produce this interaction.³³ All other atoms in the cluster are found to have much smaller hyperfine couplings (< 3 G) which should be buried under the wings of the central ESR line. As reported in Table I, $a^{\text{Si}_{b2}}$ is -9.8 G: When the field is in the z direction this is reinforced by the principal component of the dipolar tensor \mathbf{A} (-3.1 G), giving a net interaction of -13 G, close to the experimentally ob-

served coupling.

Subsequent to the completion of the theoretical calculations reported here, the superhyperfine ESR spectrum of the P_b center in SIMOX (separation by implantation of oxygen) material has been examined in detail by Carlos.³⁴ The magnitude of the isotropic coupling and the size and orientation of the principal anisotropic component in our theoretical Si_{b2} tensor all agree well with these new experimental results. This good agreement of our model calculations with experiment provides strong evidence that the P_b center is in fact a threefold-coordinated silicon, with the Si dangling bond pointing into an SiO₂ microvoid; there is no need to invoke an overcoordinated O atom³⁵ to explain in detail the ²⁹Si hyperfine spectra of this defect.

Our findings for the P_b center are also important in the interpretation of recent ESR hyperfine data of Biegelsen and Stutzmann for the D center in a -Si:H.⁹ They found that the magnitude of the primary isotropic hyperfine interaction of the D defect is only ≈ 70 G, much smaller than the corresponding value in the P_b center. This discrepancy has recently been used to question the standard identification of the D center as a simple Si dangling bond.³⁵ However, we see from the $a^{\text{Si}'}$ results in Table I that a large range of isotropic hyperfine coupling will be covered as the trivalent silicon atom is relaxed toward the plane of its nearest neighbors. The most reasonable explanation of the smaller coupling constant at Si' in the D center is simply that a more nearly planar reconstruction at Si' is favored in the less

constrained amorphous material than in the tetrahedral *c*-Si lattice. Strong support for this view is provided by the molecular radical Si[Si(CH₃)₃]₃. The experimental magnitude of the major isotropic coupling in that radical is 65 G,³⁶ very close to the *D*-center value of 70 G. These results then suggest that this difference between the *P_b*- and *D*-center hyperfine data can be understood within the undercoordinated-dangling-bond model, without our proposing alternative (overcoordinated) structures for the *D* center.³⁵

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