PHYSICAL REVIEW B VOLUME 39, NUMBER 2 15 JANUARY 1989-I

Energy levels and charge distributions of nonideal dangling and floating bonds in amorphous Si

P. A. Fedders and A. E. Carlsson
Department of Physics, Washington University in Saint Louis, Campus Box 1105, St. Louis, Missouri 63130

(Received 20 June 1988)

Defect-state wave functions and energies are calculated for numerous configurations of nonideal dangling and floating bonds in *a*-Si with use of Bethe-lattice-terminated clusters and a tight-binding approach. The energy eigenvalue for the dangling bond is highly dependent on deviations from ideality while the wave-function amplitudes are much less so. Exactly the opposite holds for the floating bond. The experimental consequences of these calculations are discussed.

I. INTRODUCTION

A controversy has recently arisen over whether the defect, or *D*, levels[1] observed in the gap of amorphous Si (*a*-Si) are threefold-(under)coordinated "dangling bonds" or are fivefold-(over)coordinated "floating bonds." Until recently challenged,[2-4] the belief that the states were dangling bonds had been universal. The controversy persists,[5-11] at least in part, because total-energy calculations are not accurate enough to determine reliably which configuration has the lowest energy, and because present experiments[12,13] can be qualitatively interpreted to support either view.

The controversy has not been resolved by molecular-dynamics simulations for *a*-Si which have utilized empirical interatomic potential functions[14-18] as well as an *ab initio* treatment[19] of the electronic terms in the energy. All of these calculations have found fivefold defects; all but one[15] found threefold defects as well. While the *a*-Si growth process has certainly not yet been treated quantitatively, these calculations suggest that at least energetically there is no dominating preference for threefold over fivefold coordination. Recently we published[20] the results of tight-binding calculations on a nine-atom cluster terminated by Bethe lattices. These calculations showed that the energy eigenvalue of the defect state moved from about midgap to within 0.2 eV of the conduction band as the cluster evolved continuously from a configuration describing an ideal dangling bond to one describing an ideal floating bond. Similarly the maximum fraction of defect charge on any atom dropped from 70 to 15 %.

In this article we direct our attention to the energy eigenvalues and charge distributions of floating- and dangling-bond defect sites in *non*ideal configurations. One of the main goals of the calculations is to aid in the interpretation of the experimental magnetic resonance data regarding the charge distribution of these states. As we shall see, the combination of this data, the observed positions and widths of the electron levels, and the present results shed useful new light on the dangling- versus floating-bond controversy.

In a crystal, vacancies (the analogues of dangling bonds) and interstitials (the analogues of floating bonds) have well-defined positions in the otherwise perfect lattice with relatively small amounts of distortion or relaxation that are almost the same from defect to defect. Thus all defects of the same type are nearly identical. However, in *a*-Si even the fourfold-coordinated normal sites are not identical, let alone the defect sites. Typical bond-angle distortions in *a*-Si are 5°–10° and thus one should expect bond-angle distortions of at least that amount about any defect and quite possibly much more. That is, the dangling bond with its rather large volume devoid of any atoms and the floating bond with its extra bond do not fit effortlessly into the random network of fourfold-coordinated Si atoms. Thus one might expect substantial strain-induced distortions associated with the defect, over and above those associated with the perfect random network. For example, total-energy calculations for dangling bonds at (111) surfaces suggest deviations of 5% or more from the ideal angle.[20] The strain broadening of the defect state should be investigated independent of the dangling-floating bond controversy, because comparison of the broadening with the observed broadening provides a useful check on the model used. As will be seen, the energy eigenvalue of the dangling bond is highly dependent on local distortions while the energy eigenvalue of the floating bond is not.

In a simple sp^3 picture the hyperfine coupling constants A_{iso} and A_{aniso} are proportional to the square of the *s* or *p* part of the wave function, respectively, at a given site. The position of the electron-spin-resonance (ESR) hyperfine line is determined by A_{iso} and its width is usually determined by A_{aniso}. However, if A_{iso} varies from site to site, this will introduce an additional width to the ESR hyperfine line. Our calculations show that the wave function of the dangling-bond defect is relatively independent of strain but that the wave function of the floating-bond defect is considerably more strain dependent. This should lead to considerable strain broadening of the ESR hyperfine line for the floating bond, which is not observed in the experiment. Thus we conclude that floating bonds are not responsible for the observed ESR line. This line could, however, be due to either dangling bonds or configurations intermediate between dangling and floating bonds.

II. CALCULATION

In this paper we shall consider only fluctuations in the position of the neighbors nearest to the center of the defect. Since the wave functions of the defect tend to be localized on this group of atoms, the effects of second-neighbor fluctuations should be relatively minimal. Further, with a single exception at the end of the paper, we shall only consider bond-angle distortion and ignore bond-length variations. Since the elastic constant for bond-length changes is much greater than that for bond-angle changes, the bond-length variations are small and can usually be ignored; changes in the energy and wave function are substantial at bond-angle distortions typical of *a*-Si but are insubstantial at typical bond-length distortions.

As in our earlier work,[21] we use a basic cluster of a number of atoms and model the electronic states with a five-orbital sp^3s^* tight-binding Hamiltonian. A more critical discussion of this model is given in Sec. III. To terminate the cluster we attach Bethe lattices to each of the free bonds of the surface atoms, obtaining the appropriate one-electron Green's functions by standard techniques.[22] The nearest-neighbor couplings at the crystalline interatomic spacing ($d_0 = 2.35$ Å) are $h_{ss} = -2.075$ eV, $h_{sp} = 2.484$ eV, $h_{pp}^{\sigma} = 2.717$ eV, $h_{pp}^{\pi} = -0.715$ eV, and $h_{s^*p}^{\sigma} = 2.328$ eV. The single-site energies are $\varepsilon_p = 1.715$ eV, $\varepsilon_s = -4.2$ eV, and $\varepsilon_{s^*} = 6.68$ eV. These values are taken from previous studies[23] on crystalline Si. They reproduce the band structure of crystalline Si very well and predict a gap of 1.7 eV for *a*-Si. The interatomic couplings, as in Ref. 21 are assumed to decay as $h(r) \propto e^{1/ar-b}$ with $a = 2.243$ and $b = 3.600$, where r is measured in units of d_0. These parameters are such that the second-neighbor couplings are nonzero for the five atoms surrounding a central atom in the floating-bond case but vanish in the ideal crystal and for most dangling-bond configurations.

Our results are based upon the use of a tight-binding model with sp^3s^* orbitals on a finite cluster and the use of Bethe lattices to terminate the cluster. It is impossible to obtain accurate conduction-band structures with sp^3 models unless an inordinately large number of neighbor couplings is included. For the purpose of calculating defect-state energies, it is essential to obtain a reasonably accurate conduction-band density of states, since the defect-state energies are determined by the real part of the one-electron Green's function in the gap, which is in turn given in terms of the density of states by the Kramers-Kronig-type relations. Wave-function energies close to the conduction-band edge are particularly sensitive to the conduction-band density of states. Therefore, we have used the sp^3s^* model, since it gives a considerably improved description of the conduction-band density of states. Within the context of tight binding, the use of the Bethe lattice is comparable in accuracy to other termination procedures. In *a*-Si, the Bethe lattice yields an accurate gap[21] and a good density of states.[24] In most ways the defect cluster embedded in the Bethe lattice is the amorphous analogue of an impurity or an impurity complex embedded in a crystal. On the basis of studies of H defects,[25] we doubt that embedding the cluster in a large random network of fourfold-coordinated Si would yield appreciably different results. Although one would prefer to perform a first-principles calculation, tight-binding Green's-functions methods have been very successful in crystalline material[26–28] in obtaining deep-level energies and wave functions, distinguishing between deep and shallow impurities, and in treating impurity complexes[29,30] containing several atoms as well as surfaces and interfaces.[31,32] Typically, tight-binding calculations in crystalline semiconductors reproduce chemical trends of impurity states correctly and get absolute energies of these states (including vacancies) correct to a few tenths of an eV. Energy differences between states are considerably better. We expect the same sort of accuracy here.

III. RESULTS

The most general dangling-bond configuration with fixed bond lengths can be described by a central atom (atom 1) and three atoms (labeled 2–4) that are bonded to atom 1. Atoms 2–4 are all a distance d_0 from atom 1, these three atoms define a plane and a circle within that plane, and atom 1 lies directly above the origin of that circle. As shown in Fig. 1(a) we define the angle θ such that the angle between atom 1 and atoms 2, 3, and 4 is $90° + \theta$. The positions of atoms 2–4 on the circle are shown in Fig. 1(b) where angles ϕ_3 and ϕ_4 are defined. Thus the ideal dangling bond, which preserves the perfect tetrahedral symmetry, consists of the coordinates $\theta = 19.47°$, $\phi_3 = \phi_4 = 0°$. In general, distortions in all of the angles will occur.

We have investigated a large number of dangling-bond configurations, but two sets of distortions accurately epitomize the results. In the following, E is the energy eigenvalue of the defect wave function with respect to the

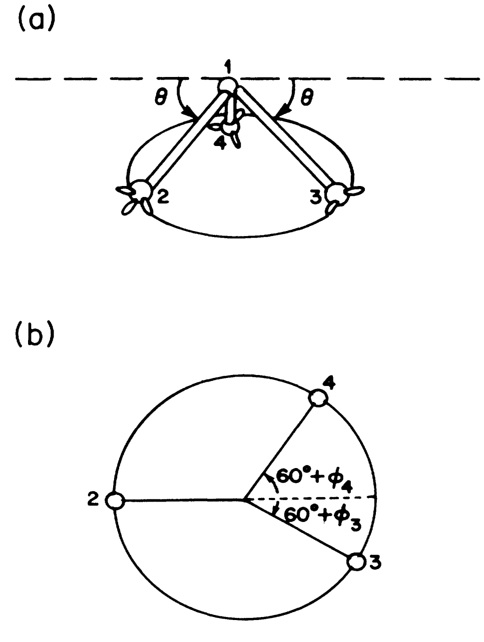

FIG. 1. The geometry of the most general angling bond. The angles θ, ϕ_3, and ϕ_4 yield a complete description.

conduction-band edge, Q is the fraction of the charge in the wave function on atom 1, and P is the fraction of the charge on atom 1 that is from the p orbitals. Most of the rest of Q is from the s orbitals with a small amount, unless otherwise noted, in the s^* orbitals. In Fig. 2 we have plotted E, Q, and P versus θ for $\phi_3=\phi_4=0°$. As can be seen, the eigenvalue moves rapidly towards the conduction band as θ is decreased and merges with the conduction band at $\theta \sim 4°$. Throughout most of the range $dE/d\theta \sim 0.057$ eV/deg. Thus E changes by more than half an eV over a 10° range. P and Q, on the other hand, depend on θ only weakly for θ near the ideal dangling-bond value of 19.47°. We believe that this weak dependence of P and Q on θ is due to the fact that the charge is mostly located on atom 1. In Fig. 3 the quantities E, P, and Q are plotted versus v_s $\phi_3=\phi_4=\phi$ for fixed $\theta=19.47°$. We note that E, Q, and P are almost completely independent of ϕ for $-10° < \phi < 20°$ and are relatively independent of ϕ for $\phi < 20°$. We have also studied the cluster for different ϕ_3 and ϕ_4 with various fixed values of θ and found that E, P, and Q depend only weakly on ϕ_3 and ϕ_4 as long as ϕ_3 and ϕ_4 are in the same range as above.

The above results for E can be understood in a simple fashion by considering the diagonal energy matrix elements in the sp^3 model. At $\theta=19.47°$ the dangling bond has mainly sp^3 character, but at $\theta=0°$ it has only p_z character, which gives a higher energy since $\varepsilon_p > \varepsilon_s$. In fact one can uniquely construct bond orbitals for bonds pointing in the three specified directions and obtain the direction and energy of the fourth or dangling bond. This also uniquely determines both the direction and the s, p_x, p_y, and p_z character of the dangling bond. An energy for this state can then be constructed from the amount of s and p character that it contains. Our detailed results are in agreement with this crude model in predicting energies that are quite θ dependent but only weakly ϕ_3 and ϕ_4 dependent. Further, we note that energy changes are first order in changes in θ but, from symmetry, are second order in changes in ϕ_3 and ϕ_4. Our simple model breaks down if $\phi_3+\phi_4$ exceeds 60°. In this extreme limit, all three atoms lie on the same half-circle in Fig. 1(b) and it is also the point where E, P, and Q change radically.

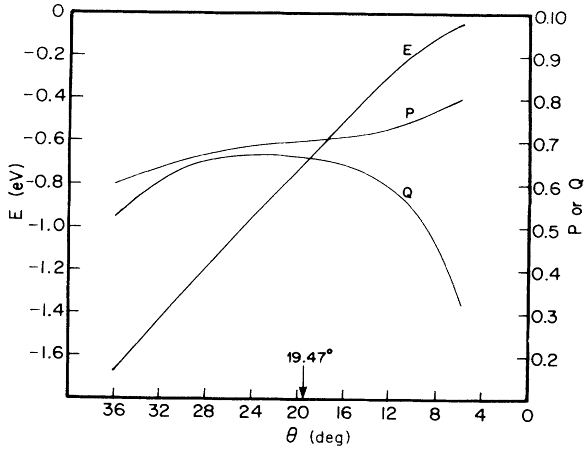

FIG. 2. The energy eigenvalue (E), the fraction (Q) of charge on atom 1, and the fraction (P) of charge on atom 1 that is from p states, for the dangling bond. The angles $\phi_3=\phi_4=0°$.

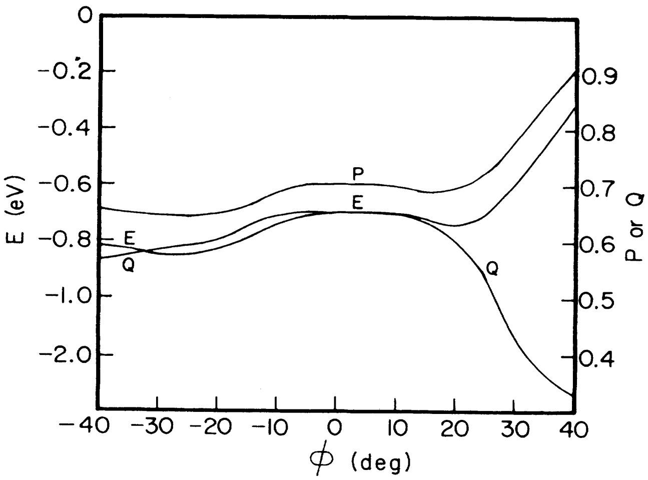

FIG. 3. The energy eigenvalue (E), the fraction (Q) of charge on atom 1, and the fraction (P) of charge on atom 1 that is from p states, for the dangling bond. Here $\theta=19.47°$ and $\phi_3=\phi_4=\phi$.

The first-order energy shift can be understood via a simple model including only the orbitals $|s,1\rangle$, $|p_x,1\rangle$, $|p_y,1\rangle$, and $|p_z,1\rangle$ on the defect site, and the components of the defect wave functions on the neighboring atoms directed at the defect atom, denoted $|h,2\rangle$, $|h,3\rangle$, and $|h,4\rangle$. For a first-order perturbation-theoretical analysis, only the ideal configuration wave function is needed. If we take the z axis to point along the dangling-bond direction, this wave function has the form

$$|\psi\rangle = \alpha_s|s,1\rangle + \alpha_p|p_z,1\rangle + \alpha_h(|h,2\rangle + |h,3\rangle + |h,4\rangle) + |\Delta\psi\rangle , \quad (1)$$

where $\Delta\psi$ denotes the contribution from the remaining orbitals. We can arbitrarily choose α_s to be positive: then $\alpha_p > 0$ since the wave function points in the $+z$ direction. Furthermore, we expect that $\alpha_h < 0$, since the dominant $|p_z,1\rangle$ orbital is negative below its azimuthal plane. Neglecting the $\Delta\psi$ terms, the only parts of the Hamiltonian which change to linear order in $\Delta\theta = 19.47° - \theta$ are the couplings between the $|p_z,1\rangle$ orbital and the three $|h,i\rangle$ orbitals. These couplings have the form

$$\langle p_z,1|H|h,i\rangle = -h_0\cos(90°+\theta), \quad h_0 > 0 .$$

Thus for small positive $\Delta\theta$ we have

$$\Delta E = -6h_0\alpha_p\alpha_h\sin(109.47°)\Delta\theta = -5.7h_0\alpha_p\alpha_h\,\Delta\theta . \quad (2)$$

For the parameters of our model, $\alpha_p=0.7$ and $\alpha_h=0.2$ are quite large, explaining the strong dependence of E on θ.

The number of variables needed to describe a general floating-bond state is much greater than for a dangling bond. We start with the same four atoms as before as well as the same definitions for θ, ϕ_3, and ϕ_4. Atoms 5 and 6 lie above and below the plane of the circle, respectively, at distances d_0 from atom 1. We define θ_5 and θ_6 to be the deviation of atoms 5 and 6, respectively, from the perpendicular vertical through atom 1, with azimuthal angles ϕ_5 and ϕ_6 with respect to the planar position of atom 2. There are two standard definitions for floating bonds. We have defined the highly symmetric "ideal" floating bond with $\theta=\theta_5=\theta_6=\phi_3=\phi_4=\phi_5=\phi_6=0°$ as shown in Fig. 4(a). On the other hand Pantelides has defined a "canonical" floating bond with $\theta=19.47°$ and $\theta_5=\theta_6=\phi_4=\phi_4=\phi_5=\phi_6=0°$. As shown in Fig. 4(b), this corresponds to a tetrahedrally coordinated Si atom with an extra atom attached directly opposite one of the original four atoms. We shall let Q_i denote the fraction of the defect-state charge on atom i and P_i denote the fraction of that charge that is from the p states.

Pantelides[3] stated that the central atom of the floating-bond configuration cannot contain any charge from the defect state, in a simple model. In fact, we have recently proved[21] that there is no such charge on the central atom of a floating bond in an sp^3 tight-binding model with only nearest-neighbor couplings and no rings. The proof is still valid if an s^* band is added, provided that the matrix elements of the s^* band have the same radial dependence as those of the s band. However, real Si does contain second-neighbor couplings and rings, and thus we expect a charge on the central atom. Since our calculations include second-neighbor interactions, we obtain a charge on the central atom.

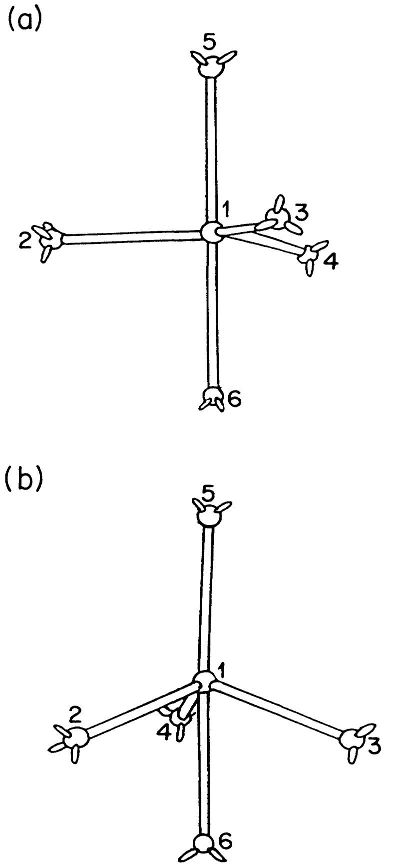

FIG. 4. (a) The "ideal" and (b) "canonical" floating-bond configurations.

Since the number of angles is much larger for the floating bond than for the dangling bond, we have not investigated all of the possibilities as completely. However, a few cases again epitomize the situation. First, consider a variation of θ with the rest of the angles fixed at 0°. In this case, atoms 2, 3, and 4 are equivalent so that $P_2=P_3=P_4$ and $Q_2=Q_3=Q_4$. The results are plotted in Fig. 5, and $P_1=0$ for all values of θ. We note that $dE/d\theta$ varies from 0 at $\theta=0°$ to 0.009 eV/deg at large values of θ. This is a much smaller variation than for the dangling bond. We believe that this relative insensitivity to changes in θ is due to the fact that the state lies very close to the conduction band and has a somewhat extended wave function. As such it has some resemblance to a shallow state, and the energy eigenvalues of such states are usually fairly insensitive to strains. We also note that all of the Q's are quite small for all values of θ, many of the P's and Q's vary quite rapidly with θ, and that the site with the largest amount of charge changes atoms twice. In Fig. 6 we have plotted the results versus $\phi=\phi_3=\phi_4$ varying with the rest of the angles set equal to 0°. E remains constant at -0.16 eV and none of the P's or Q's vary much and $P_1\sim0.0$, $P_2=P_3\sim0.07$, $P_4\sim0.07$, and $P_5=P_6\sim0.8$. Further studies show that variations of the P's, Q's, and E in Fig. 5 are typical for variation of θ, θ_5, or θ_6 while none of these quantities vary much as ϕ_3, ϕ_4, ϕ_5, or ϕ_6 change. The insensitivity of the floating-bond eigenvalue to θ can be understood via Eq. (2). In the

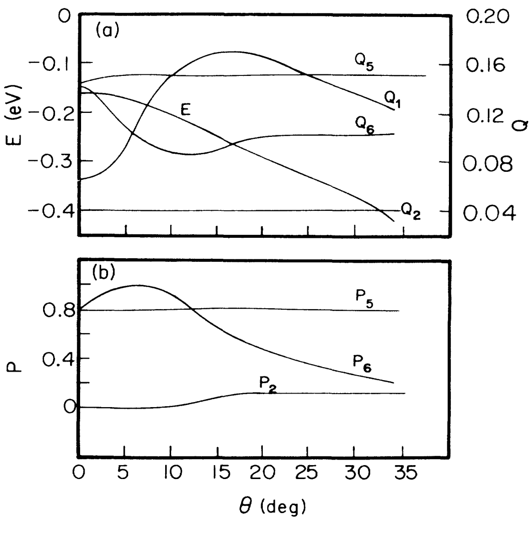

FIG. 5. (a) The energy (E) and charge fraction (Q_i) on atom i and (b) the fraction of charge (P_i) that comes from p states in the floating-bond configuration vs θ. Here $\theta_5=\theta_6=\phi_3=\phi_4=\psi_5=\psi_6=0°$. Note that $Q_2=Q_3=Q_4$ and $P_2=P_3=P_4$ while $P_1=0$.

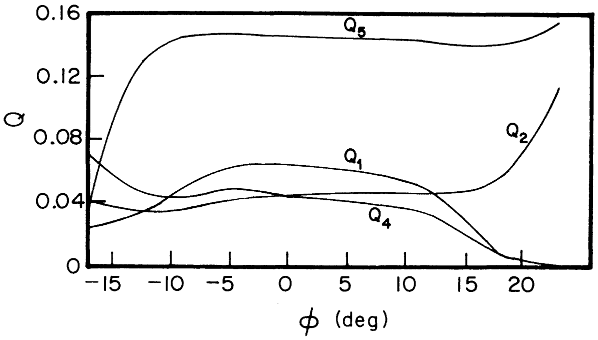

FIG. 6. The charge fractions (Q_i) on atom i for $\phi=\phi_3=\phi_4$ with the rest of the angles set equal to 0°.

floating-bond case $\alpha_p=0$ at $\theta=0°$ and α_p and α_h are very small for all values of θ.

Finally we note that floating bond is less localized than the dangling-bond state in that about half of its charge is situated on the central atom and its five nearest neighbors; is the state is localized at all, the localization length is probably 5 Å or greater. This, and its close proximity to the conduction-band edge, raise the possibility that it could be a part of the exponential band tails which are always present in amorphous Si.

IV. DISCUSSION

First consider the energy eigenvalue. The ideal dangling bond has an energy of -0.70 eV with respect to the conduction band, which is close to the experimental width of the D state. We find this state to be very strain dependent in that $dE/d\theta \simeq 0.057$ eV/deg. One might expect bond-angle distortions of at least 5°, which would yield $\Delta E = \pm 0.28$ eV. This is consistent with experiments, although the broadening of the D state could be due to other causes such as nearby impurities or phonons. On the other hand, the ideal floating bond has an energy eigenvalue of -0.16 eV, which is very close to the conduction-band edge. This is far from the observed position of the D state and one does not expect the tight-binding approximation to be in error by this much. In the canonical configuration, where the atoms get crowded quite closely together, the energy below the conduction band is still a very small 0.28 eV. These energies are much less strain dependent than the energy of the dangling bond.

Next we consider the amount of s and p charge density on the various atomic sites. We define q_s and q_p as the amount of s and p charge on a given site, where

$$\begin{aligned} q_s &= Q(1-P) , \\ q_p &= QP . \end{aligned} \tag{3}$$

As discussed in Sec. I, A_{iso}, and thus the position of a line in an ESR hyperfine experiment, is proportional to q_s. Furthermore, A_{aniso}, and thus the width of a line in a powder-averaged ESR hyperfine experiment, is proportional to q_p. The constants of proportionality cannot be accurately obtained from tight-binding theory. Of course, if one has a distribution of q_s's (or A_{iso}'s) this will also contribute to the linewidth. In fact, it is quite possible that this strain-broadening mechanism is more important than the broadening from A_{aniso}.

TABLE I. Values of q_s and q_p for the ideal (i) floating bond and the canonical (c) floating bond.

Atom number	$q_s(i)$	$q_p(i)$	$q_s(c)$	$q_p(c)$
1	0.063	0.00	0.157	0.000
2–4	0.043	0.00	0.039	0.005
5	0.028	0.12	0.025	0.123
6	0.028	0.12	0.044	0.044

For the ideal dangling bond, we find that $q_s=0.20$ and $q_p=0.45$. These numbers are close to those estimated by other investigators.[6,12] Whether these values are consistent with the experimental hyperfine data is a matter of contention, especially the value for q_p. Our main point here is that q_s varies very little with strain. That is, q_s changes by about 8% over a change of 5° in θ and about 17% over a change of 10° in θ. The ϕ_4 and ϕ_2 dependences are essentially zero. A linewidth of even 17% is consistent with the experimental hyperfine data of Biegelsen and Stutzmann.

The situation for the floating bond is far more involved because six different atoms can contribute to the ESR hyperfine line. In Biegelsen and Stutzmann's data on the natural (4.7%) abundance of Si, essentially only one atom in a cluster contributes to the signal and atoms whose q_s is less than half of the average q_s will not contribute to the signal because their contribution will be lost in the central peak. However, in the data from the enriched (93%) sample, nearly all of the atoms in a cluster should contribute to that defect's signal. Furthermore, there is no appreciable central peak.

For the ideal floating bond (see Table I) all of the q_s's are quite small and none of the atoms is dominant.

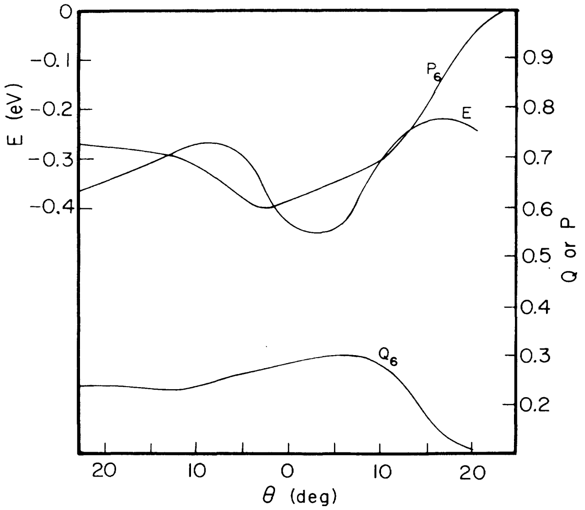

FIG. 7. The energy (E) and the charge fraction (Q_6) and fraction of charge (P_6) that comes from p states for an intermediate case between the dangling and floating bonds.

Furthermore, from their θ dependence, one could conclude that one should see a continuum hyperfine spectrum and not a well-defined line, as is observed. The situation is somewhat more favorable in the more asymmetric canonical configuration. In this case, atom 1 (the central atom) is at least slightly dominant. However, the sum of the q_s's from the other five atoms is greater than the q_s from atom 1. Given this situation and the θ dependencies of the q_s's, one would obtain a very broad line from variations in $A_{\rm iso}$ in an experiment on enriched material. This model cannot possibly be consistent with the experiments of Biegelsen and Stutzmann.

In an attempt to obtain results close to those envisioned by Pantelides, we have investigated one intermediate case between the dangling and floating bonds. In that case we take the bond length of atom 6 to be $1.15d_0$. In our model, the bond length of $1.15d_0$ corresponds to a coupling strength of 78% of the coupling strength at a nearest-neighbor distance d_0. It is the latter number which controls the properties of the state. The results are shown in Fig. 7. As expected, atom 6 is starting to become a dangling-bond atom. The energy eigenvalue has dropped and atom 6 has, by far, the most charge. However, even in this case, the angular dependence of q_s is too severe to be consistent with a spread in θ and the experimental data. Of course, as atom 6 pulls further away from atom 1, the defect cluster approaches the dangling-bond state. As expected from this and earlier work, E, P, and Q, as well as variations in these quantities with strain, are roughly linear functions of the coupling strength.

This work was supported in part by the National Science Foundation (NSF) Grant No. DMR-85-03083, by the U. S. Department of Energy Grant No. DE-FG02-84ER45130, and by the Solar Energy Institute, Golden, Colorado, under Subcontract No. XB-7-06055-1 of Contract No. DE-AC02-83CH10093.

---

[1] See, for example, the review articles in *Hydrogenated Amorphous Silicon,* Vol. 21 of *Semiconductors and Semimetals,* edited by J. I. Pankove (Academic, New York, 1984); *The Physics of Hydrogenated Amorphous Silicon II,* edited by J. D. Joannopoulos and G. Lucovsky (Springer-Verlag, Berlin, 1984).

[2] S. T. Pantelides, Phys. Rev. Lett. **57**, 2979 (1986).

[3] S. T. Pantelides, Phys. Rev. Lett. **58**, 1344 (1987).

[4] S. T. Pantelides, Phys. Rev. B **36**, 3479 (1987).

[5] P. A. Fedders and A. E. Carlsson, Phys. Rev. Lett. **58**, 1156 (1987).

[6] M. Stutzmann, Z. Phys. Chem. Neue Folge **151**, 211 (1987).

[7] J. C. Phillips, Phys. Rev. Lett. **58**, 2824 (1987).

[8] S. T. Pantelides, Phys. Rev. Lett. **58**, 2825 (1987).

[9] M. Stutzmann and D. Biegelsen, Phys. Rev. Lett. **60**, 1082 (1988).

[10] S. T. Pantelides, Phys. Rev. Lett. **60**, 1683 (1988).

[11] J. H. Stathis and S. T. Pantelides, Phys. Rev. B **37**, 6579 (1988).

[12] D. K. Biegelsen and M. Stutzmann, Phys. Rev. B **33**, 3006 (1986).

[13] H. Yokomichi, I. Hirabayashi, and K. Morigaki, Solid State Commun. **61**, 697 (1987).

[14] R. Biswas, G. S. Grest, and G. M. Soukoulis, Phys. Rev. B **36** 7437 (1987).

[15] M. D. Kluge and J. R. Ray, Phys. Rev. B **36**, 4234 (1987).

[16] W. D. Luedtke and U. Landman, Phys. Rev. B **37**, 4656 (1988).

[17] J. Q. Broughton and X. P. Li, Phys. Rev. B **35**, 9120 (1987).

[18] P. C. Kelires and J. Tersoff, Phys. Rev. Lett. **61**, 562 (1988).

[19] R. Car and M. Parrinello, Phys. Rev. Lett. **60**, 204 (1988).

[20] J. E. Northrup, J. Ihm, and M. L. Cohen, Phys. Rev. Lett. **43**, 1910 (1981).

[21] P. A. Fedders and A. E. Carlsson, Phys. Rev. B **37**, 8506 (1988).

[22] J. D. Joannopoulos, Phys. Rev. B **16**, 2764 (1977).

[23] P. Vogl, H. P. Hjalmarson, and J. D. Dow, J. Phys. Chem. Solids **44**, 365 (1983).

[24] D. J. Chadi, Phys. Rev. Lett. **41**, 1002 (1978); D. C. Allan and J. D. Joannopoulos, *ibid.* **44**, 43 (1980).

[25] D. C. Allan, Ph.D. thesis, Massachusetts Institute of Technology, 1982 (unpublished).

[26] H. P. Hjalmarson, P. Vogl, D. J. Wolford, and J. D. Dow, Phys. Rev. Lett. **44**, 810 (1980).

[27] P. Vogl, in *Festkörperprobleme,* Vol. XXI of *Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Braunschweig, 1981), p. 191.

[28] O. F. Sankey and J. D. Dow, Phys. Rev. B **27**, 7641 (1983).

[29] O. F. Sankey, H. P. Hjalmarson, J. D. Dow, D. J. Wolford, and B. G. Streetman, Phys. Rev. Lett. **45**, 1656 (1980).

[30] C. W. Myles and O. F. Sankey, Phys. Rev. B **29**, 6810 (1984).

[31] R. P. Beres, R. E. Allen, and J. D. Dow, Phys. Rev. B **26**, 5702 (1982).

[32] R. E. Allen and J. D. Dow, Phys. Rev. B **25**, 1423 (1982).