

Application of local-spin-density approximation to *a*-Si and tetrahedral *a*-C

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We discuss the application of the local-spin-density approximation (LSDA) and provide criteria to gauge the reliability of supercell models of *a*-Si:H and tetrahedral amorphous carbon (*ta*-C). We identify models of *a*-Si:H that exhibit a localization on dangling bond consistent with electron-spin-resonance (ESR) experiments and show that a LSDA level description of the electron states is essential to describe these states. We offer an *ab initio* calculation of a well-isolated floating bond state and show that neither the charge nor spin is well localized. Finally, we suggest the origin of the ESR signal in *ta*-C is π -bonded pairs at the Fermi level. [S0163-1829(99)08639-5]

I. INTRODUCTION

In this paper, we describe significant insights concerning supercell models of amorphous Si (*a*-Si) and tetrahedral amorphous carbon (*ta*-C), which accrue from the use of a local-spin-density approximation (LSDA) level *ab initio* study rather than the local-density approximation (LDA), which is the common choice for these materials. We use the SIESTA (Ref. 1) implementation of local-orbital LSDA. This is a very fast and highly accurate local basis *ab initio* molecular-dynamics (MD) code with excellent flexibility in the basis (we use up to double zeta with polarization functions in this work). We will show that an LSDA description of electron states in *a*-Si:H and tetrahedral amorphous carbon (*ta*-C) leads to a better link between electron-spin-resonance (ESR) experiments and structural models and as such enables an improved understanding of the “physical realism” of proposed structural models. In *ta*-C, we are able to infer the likely origin of the ESR signal, but an LSDA-level description is required to accomplish this.

Some vexing inconsistencies that our work bears on are: (1) ESR experiments show that over 50% of the spin density of dangling bonds is located on the one central atom of the dangling bonds^{2,3} while *ab initio* LDA calculations yield a charge localization⁴ of 10–15% on one atom in supercells with only one defect⁵ and far less on supercell models with many defects. This includes many supercell samples that we and others have constructed and is independent of whether one uses an *ab initio* code or orthogonal tight binding. (2) *ta*-C samples exhibit a substantial ESR signal⁶ although theoretical work shows that threefold coordinated C atoms are virtually all in π -bonded pairs or π -bonded chains of an even length,⁷ which are believed not to yield an ESR signal. Further, the π -bonded pairs are quite numerous so that one

would expect strong delocalization through hybridization (it is correctly argued in Ref. 6 that π states can be localized in *ta*-C). (3) Most investigators exhibit a pair-correlation function as evidence that a given supercell sample of *a*-Si is a realistic one. Often such supercells contain as many as 15–20% defects (which lead to states in the gap) and therefore can have a barely identifiable optical gap. This seems to be a universal feature of models that are formed from MD quenches from the liquid.⁸ The inconsistency between the models (a “poor” gap, filled with many states) and experiment (defect densities of order 10^{-4}) is important, since a qualitative change in the character of the defect states results (due to banding between nearly resonant defect states—essentially impurity band formation). (4) We also add specific new results about the venerable controversy on the floating bond⁹ (fivefold coordinated site) in *a*-Si. While the *a*-Si community generally believes that floating bonds are rare or nonexistent, many MD investigators see them routinely in their supercells.

II. METHODOLOGY

Our calculations were performed within the local-spin-density approximation of density-functional theory¹⁰ (DFT), using the SIESTA program.^{1,11} We used the parametrization of Perdew and Zunger¹² for the exchange-correlation functional and norm-conserving Troullier-Martins pseudopotentials¹³ in the Kleinman-Bylander factorized form.¹⁴ To describe the valence electrons, we use an atomic orbitals basis set consisting of finite-range numerical pseudoatomic wave functions in the line of Sankey and Niklewski.¹⁵ The finite range of the orbitals is defined by an orbital confinement energy of 0.02 Ry.¹⁶ In all calculations we used a single- ζ basis set with polarization orbitals on all the atoms. This means a

basis of one s , three p , and five d orbitals for C and Si, and one s and three p orbitals for H. Convergence tests were performed by using a double- ζ basis with polarization functions and found that doubling the basis has much less effect than including the polarization functions. Due to the large sizes of the supercells studied here, only the Γ point was used to sample the Brillouin zone in all the calculations. All calculations were performed with spin polarization, which turns out to be vital for defect states. As one relevant test of the code, we computed the energy of H in a bond centered position in crystalline Si and obtained an answer within a few hundredths of an eV of a generally accepted answer from a very accurate plane-wave calculation.¹⁷

Our study in this paper is based on three supercell models. Model I (Ref. 18) starts as a model of a -Si:H containing 142 atoms (122 Si atoms and 20 H atoms) which is stable, has no geometrical or spectral (electronic) defects, and has a good pair-correlation function. There are four isolated (as opposed to clustered) Si-H bonds, and these hydrogens can be singly removed in order to study isolated dangling bonds. In this work, we avoid the complexities of dangling bonds in an H cluster. Model II is an a -Si model of 63 Si atoms¹⁹ including two dangling bonds and two quasilocated states in the gap that are formed by badly strained pieces of the supercell. This cell thus has a concentration of over 6% defects, which is very high compared to experiment, though far better than most models obtained from MD quenches from the melt. The last model is a supercell of 64 atoms of ta -C obtained from a very well-converged self-consistent plane-wave calculation²⁰ and which contains no “defects.” That is, the threefold coordinated sites (dangling bonds or sp^2 sites) are all paired. The models can all be doped with B or P by replacing Si or C atoms to move the Fermi level.

In the following analysis, we shall use $q(\epsilon, i)$ to denote the fraction of the charge for eigenvalue ϵ that is localized on orbitals pertaining to atom i , according to Mulliken population analysis. When summed over all i , the sum of the charge is one for each eigenvalue. Another measure of localization is defined by $Q_2(\epsilon) = [\sum_i q^2(\epsilon, i)]^{1/2}$ where the sum is over all N sites of the supercell. Note that $Q_2(\epsilon)$ is unity for a state that is totally localized on one site and is $1/N$ for a state that has its weight equally distributed on all N sites.

III. RESULTS

A. LSDA results for amorphous silicon

1. Isolated floating bond in the LSDA

Four dangling-bond configurations were obtained from model I by quenching with at least nine orbitals on the Si atoms (in “quantum chemistry” nomenclature, this is a single- ζ basis with polarization orbitals). In a test case, when we quenched with only sp^3 (single- ζ basis) the dangling bond relaxed to a fivefold coordinated defect or a floating bond. The resulting floating bond configuration was stable when it was relaxed again including polarization functions. Some time ago this was discussed in the literature,⁹ and they are quite common in many MD quenches from the melt. It was argued that the floating bond was very delocalized compared to the dangling bond,²² and this was used as an argument that the floating bond was not the primary midgap de-

fect in a -Si and produced a level located near the conduction-band edge. However, that calculation was based on orthogonal tight binding and the Bethe lattice. Now, we believe for the first time, we have a good supercell with one floating bond that is the only defect in a supercell of a reasonable number (141) atoms. Our results support the earlier tight-binding work in both the spin polarization and position of the eigenvalue: the most spin polarization on any of the six atoms making up the floating bond defect (the central atom and five neighbors) is 0.208, and the total polarization on all six is 0.555. The energy difference between the two states with opposite spin $\Delta\epsilon$ is only 0.11 eV. To finish the comparison, Q_2 and the maximum $q(\epsilon, i)$ are both 0.08. We wish to emphasize the trend that as the state becomes less localized the spin polarization (and charge localization) decreases dramatically. Also, since LSDA places the floating bond state well above midgap, it argues against the floating bond as being the $g = 2.0055$ defect. However, it does *not* prove that the floating bond does not exist, and perhaps it contributes to the conduction-band tail.

2. LSDA versus LDA

Next we consider 63 Si atom model II, which was created before we had an alloy code so that it contains no hydrogen. This cell¹⁹ has one dangling bond, one floating bond, and two strain defects. The strain defects consist of a collection of a few atoms with very strained bond angles but contain only fourfold coordinated Si atoms. They also give a state in the gap. Since the cell has an even number of electrons, and the defect states are strongly hybridized, the calculation yielded no spin polarization (either net or local). In order to produce a net polarization, it was necessary to dope the cell (by replacing an Si atom with B or P) in order to move the Fermi level to a defect state. However, because of the large (4 out of 63) number of defects, the defects levels are well hybridized, and there is no one-to-one correspondence between geometrical and spectral defects. In this case there was no significant spin polarization on any of the atoms related to the defects (although there is a net spin, distributed through the cell). There was a 10% polarization of the dopant atom, and this was not observed with better supercells. In addition, of course, there was no significant charge localization anywhere. This lack of any significant polarization on any one site is independent of whether one starts the self-consistent iterations by placing the spin polarization on a single site or not. Earlier we had thought that strain defects would lead to an ESR signal. We still believe that this *may* be true but only if the defects are not clustered too close together. This points out the fact that defects hybridize, even in supercells containing hundreds of atoms.²³ This can drastically reduce both the spin density and charge localization.

ESR hyperfine experiments^{2,3} show that the (spin) localization on the central dangling-bond atom is between 50% and 80%, with a dominant p -orbital component in that single atom. Our results for this are shown in Table I, and while the agreement is not perfect, it is reasonable. Because of the ambiguities of assigning charge or spin to specific atoms, the correct polarization should probably contain part of the spin density assigned to the three neighbors. On the other hand, the charge localization given by $q(\epsilon, i)$ and $Q_2(\epsilon)$ are completely misleading. Simply put, “most experiments, and cer-

TABLE I. Properties of the isolated dangling bonds in the “good” *a*-Si:H supercell. *P*1 stands for the spin polarization on the central atom of the dangling bond and *P*4 for the polarization of the central atom and its three neighbors. $\Delta\varepsilon$ is the shift of the relevant single-particle eigenvalue between spin-polarization states in eV. $Q_2(\varepsilon)$ is defined by the equation above while $q(\varepsilon, i)$ is the fraction of a charge on the site *i* associated with the energy eigenvalue ε .

	Cell 1	Cell 2	Cell 3	Cell 4
<i>P</i> 1	0.515	0.404	0.499	0.414
<i>P</i> 4	0.584	0.484	0.569	0.495
$\Delta\varepsilon$	0.31	0.24	0.30	0.25
$Q_2(\varepsilon)$	0.15	0.14	0.14	0.15
$q(\varepsilon, i)$	0.17	0.16	0.16	0.16

tainly ESR hyperfine experiments measure spin polarization and not charge localization.” The LSDA results indicate clearly that the degree of localization of the spin is not the same as the localization of the defect electronic state. Apparently, it costs substantial energy to localize a charge but not nearly as much to localize the spin density. Thus, a spin-polarized computer code appears to be vital in assessing whether the dangling bond or bonds in a supercell model are realistic.²¹

The difference between the localization of the spin and charge is a somewhat unexpected and important result, at least to the extent that there are qualitative differences in these quantities. In this paper we take the attitude that this is essentially an “empirical” finding, and we intend to study the distinction fully elsewhere.

B. LSDA results for tetrahedral amorphous carbon

Finally, we consider a supercell of 64 C atoms in a *ta*-C configuration (with 18 threefold and 46 fourfold coordinated C atoms). In this supercell model all “defects” (threefold coordinated or *sp*² C atoms) are paired.⁷ Thus there are no defects in the usual sense of the word. Nevertheless, when

we doped this model with B replacing a C atom, a spin polarization was observed from a pair of π -bonded (threefold coordinated) C atoms whose energy was at the Fermi level. That is, the threefold coordinated nearest-neighbor C atoms had spin polarizations of 0.341 and 0.368, respectively. This very definitely implies that paired π -bonded atoms will produce an ESR signal. However, the π -bonded pair must produce a level that is at the Fermi surface, which presumably would be a rather small fraction of all π -bonded pairs. On the other hand, the charge localization as measured by Q_2 was only 0.14.

IV. CONCLUSIONS

The following conclusion should be gleaned from our work. (1) A credible supercell model of *a*-Si:H should have very few defects, which implies a gap with few defect states. The pair-correlation function appears to have little relevance to the electronic properties of the supercell. (2) Spin polarization appears to be necessary in order to assess how good a supercell model is if the supercell contains any defects at all. Spin polarization should not be confused with charge localization. Just because a defect has a large spin polarization does not imply the existence of a corresponding charge localization. (3) A *ta*-C model with no isolated dangling bonds can still produce an ESR signal from π -bonded pairs. (4) An accurate *ab initio* calculation shows that the floating bond localization is much weaker than the dangling-bond defect. This does not show that floating bonds do not exist but does make the case rather conclusively that (if they do exist) they are not responsible for the spin localized states observed near midgap (they would be associated rather with the conduction-band tail).

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