# Calculation of Defect States in Amorphous Selenium

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Self-consistent pseudopotential and tight-binding techniques are used to study glassy Se. Both onefold and threefold corrdinated defects give rise to nondegenerate, nonhydrogenic gap states. The former state arises from an interaction, unique to the chalcogenides, between a dangling bond and a neighboring lone pair. The latter state is surprisingly delocalized, involving interactions between many orbitals. It is shown that defect electronic configurations, and repulsive interatomic terms, are crucial to the calculation of total energies.

To explain the unusual properties[1-6] of amorphous chalcogenides, Anderson[7] recently proposed a model in which phonon coupling gives rise to a negative effective Hubbard energy $U_{eff}$. Street and Mott[8] then suggested that the negative $U_{eff}$ in chalcogenides arises from lattice distortions at dangling-bond sites, which are unstable towards formation of charged defect centers with entirely paired spins. Subsequently, Kastner, Adler, and Fritzsche[9] used simple chemical-bonding arguments to suggest that the lowest-energy neutral defect is a threefold-coordinated site (rather than a dangling bond) and to estimate the energies involved in the charge transfer reaction. They described the charged defects clearly as pairs of threefold and singly coordinated atoms (valence alternation pairs or VAP's), and focused attention on nearest-neighbor defect pairs (intimate valence alternation pairs or IVAP's) as the lowest-energy defects of all.

These simple models, however, cannot address with sufficient accuracy such important questions as the character, localization, and energy position of the defect states. It is not clear, for example, whether the threefold defect gives rise to a shallow donor level near the conduction-band edge, or a nonhydrogenic level deep inside the gap. In the former case, one might expect a Jahn-Teller distortion to weaken one of the three equivalent bonds. Moreover, it is not clear whether the defect-state wave functions are primarily localized on a single atom; this question plays an important role in the interpretation of the optically induced ESR spectra.[5]

To provide answers to such questions, we have developed an approach which makes use of flexible tight-binding techniques, while remaining grounded in a realistic self-consistent pseudopotential calculation. Using Se as a prototype, we have carried out the first realistic calculations on the electronic properties of bond coordination defects in amorphous glasses. We shall show below that, contrary to current modesl,[8,9] the defect bonding configurations naturally give rise to nondegenerate, nonhydrogenic states well within the gap, and thus no Jahn-Teller distortion is expected. Moreover, we find that the onefold defect state is highly localized, while the threefold defect state is spread out over many atoms. We also consider the defect states of the IVAP. Finally, we address the calculation of total energies for the defects, and point out that simple models based solely upon electronic energies must be amended to include repulsive interatomic terms. When we do so in an elementary way, we find that the neutral threefold and onefold defects are very close in energy, in contrast with earlier expectations.

We begin by performing self-consistent pseudopotential (SCPSP) calculations (described elsewhere[10]) on "superlattices" whose large unit cells contain defects. In Fig. 1, we show trigonal Se and two periodic structures containing defect pairs; note that Model $B$ represents the nearest-neighbor IVAP proposed by Kastner and Fritzsche.[11] We then parametrize a tight-binding Hamiltonian to fit the SCPSP results, and use this simpler Hamiltonian to solve more realistic defect structures. We include only nearest-neighbor interactions in the tight-binding Hamilton, but do not assume orthogonality of the orbitals. Surprisingly, it is essential to include self-energy shifts of about 1 eV at the defect sites. We find that these shifts are unique to the chalcogenides as will be described shortly.

In Figs. 2(a) and 2(b), we show the results of the SCPSP and tight-binding calculations for trigonal Se. The $s,p$ bonding, lone-pair, and $p$ antibonding bands are shown. Our tight-binding (TB) model cannot include explicit interchain interactions because the location of neighboring chains is indeterminate for most defect struc-
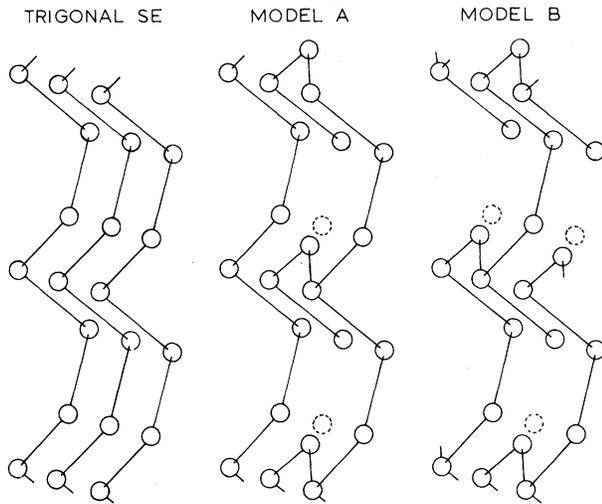
FIG. 1. Periodic structures to which SC PSP can be applied. Dotted circles represent unperturbed lattice positions.



FIG. 2. Theoretical electronic density of state for periodic structures. (a) SC PSP applied to trigonal Se. (b) Tight-binding fit for trigonal Se. (c) SC PSP applied to Model A. (d) Tight-binding fit for Model A.



FIG. 3. Tight-binding electronic density of states for nonperiodic defect structures. Dashed lines represent the gap edges. (a) Onefold defect. (b) Threefold defect. (c) IVAP. The structures are shown schematically.

tures. However, being of van der Waals character, they are expected to be weak. In any event, the fitting procedure includes these interactions implicitly and the agreement is satisfactory; all bands and gaps have approximately the correct widths. In fitting model $A$, Figs. 2(c) and 2(d), the only new TB parameters are the self-energy shifts on the defect sites, and these were obtained directly by taking diagonal matrix elements of the pseudo Hamiltonian between atomic orbitals. Going from trigonal Se to Model $A$, we find that the TB method reproduces the trends visible in the SCPSP: Two gaps and two sharp peaks appear in the $s$ band, sharp structure appears in the $p$ bands, and defect states intrude into the fundamental gap. Our tight-binding parameters will be reported in a longer paper.[12]

Figure 3(a) shows the tight-binding density of states for the neutral onefold (dangling bond) defect terminating a semi-infinite chain. We find two states in the gap, both of which are strongly localized on the nonbonding orbitals of the onefold site. The lower-energy nonbonding orbital is shifted into the gap as a result of the positive self-energy shift on the onefold site; the other lies parallel to the lone pair on the neighboring site and is therefore pushed higher still by the $\pi$ interaction between them.

In fact this $\pi$ interaction, unique to the chalcogenides, is doubly important; it is also responsible for the self-energy shift. If there were no self-energy defect state would be a $\pi$-antibonding

combination shared equally between orbitals on the last two atoms of the chain. The overall neutral defect has a hole in this state, so that the onefold site would carry a negative charge of about $0.5e$. The self-consistent process raises the self-energy of this site in order to achieve approximate neutrality; this is, in fact, the origin of the self-energy shift. Note that while we find self-energy shifts for onefold defects in chalcogenides, they are *not* to be expected for twofold defects in pnictides. In the latter case, the lone-pair orbital on the defect site has no neighboring lone pairs with which to interact, the hole remains localized on the defect site, and all sites are therefore neutral from the start.

In Fig. 3(b), we show the density of states for a neutral threefold defect. We find a single, localized, half-filled state in the gap, about half an eV below the conduction-band edge. This state arises from abnormally strong mixing of antibonding orbitals in the vicinity of the defect, and is a singlet with respect to the threefold symmetry. This state is fairly delocalized; its character is not much more than 15% on any one site. This delocalization stands in contrast to the strong localization of the onefold defect state. Bishop, Strom, and Taylor[5] attribute the observed optically induced ESR signal in Se to defect states localized primarily on a single nonbonding $p$ orbital; this fits in nicely with our results for the dangling-bond state. It is not clear, however, what sort of ESR spectrum would be expected from our threefold defect.

When the onefold and threefold defects become nearest neighbors, the corresponding gap states interact to give the spectrum for the IVAP shown in Fig. 3(c). The two states just above the valence-band edge remain strongly localized on the onefold site, and the state near the conduction-band edge remains delocalized over many atoms. For an overall neutral IVAP, the former states are filled at $T = 0$; in this configuration, the individual sites of the IVAP are neutral to within approximately $0.2e$. This is an interesting consequence of the self-energy shifts on the defect sites, without which the two defects would be oppositely charged.[11]

All our results quoted above have been obtained with bond lengths, bond angles, and dihedral angles matching those of the trigonal chain. One expects, however, that relaxations will occur in the vicinity of the defects. For example, work on surface relaxations[13] suggests that the onefold atom might draw closer to its neighbor; in this

case the midgap state on the onefold site would lie higher still. Also, we find that drastic dihedral-angle variations could move the defect states by several tenths of an eV. A more detailed study of relaxation effects is currently underway.

Having described the one-electron states, we turn to a discussion of the total energies of the various defect configurations. The total energy can be written

$$E_T = E_{BS} + U, \qquad (1)$$

where $E_{BS}$ is the sum of all the one-electron band-structure energies. We obtain this term by integrating the local density of states at the defect and neighboring sites. Thus it is not based simply upon atomic energy levels, but correctly includes localized states and resonance levels. The additional repulsive term $U$ includes the ion-ion repulsion and corrections for the overcounting of electron-electron and exchange-correlation terms in $E_{BS}$. The energy $U$ is difficult to treat exactly; to date, most discussions of defect energies in amorphous glasses have neglected it entirely. For the time being, we use a simple scheme, modeled upon Chadi's treatment[14] of surface relaxation, to give a rough estimate of the energies involved.

Chadi assumes that there is a repulsive energy $\Delta U$ associated with each nearest-neighbor bond in the material, and expands $\Delta U$ as a function of bond length. For our purposes, only the equilibrium (crystalline) value $\Delta U_0$ is required. The total energy for dissociating the solid into $Se_2$ molecules is known experimentally,[15] and the corresponding change in band-structure energy is calculated by treating $Se_2$ as a pair of nearest-neighbor onefold defects. By Eq. (1), $\Delta U_0$ is just the difference of these two, per broken bond. (The experimental energy for $Se_2$ is scaled to the crystal bond length from vibrational and rotational data on the diatomic molecule.[16,17])

Using this approach, we find the total energies of the neutral unrelaxed onefold defect, threefold defect, and IVAP to be 1.17, 1.56, and 1.22 eV, respectively, relative to the normally coordinated bulk. The VAP can gain 0.36 eV (Ref. 18) by transferring an electron from the threefold to the onefold defect level. This is much smaller than previous estimates[9] which assumed the electron transfer occurred between atomic levels. The VAP thus emerges with a total energy of 2.37 eV. Because we have not included relaxations, which can typically shift energies by half an eV, and because of our rough model for $\Delta U_0$, we cannot un-

ambiguously distinguish whether the threefold or the onefold defect lies lower in energy. However, we consider our calculation to be an improvement upon earlier arguments based solely on electronic energies, which suggested that the threefold site would be distinctly lower.[9] In summary, we wish to emphasize the importance of using defect electron levels, and including repulsive interatomic terms, in estimating defect energies.

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# Mean-Field Theory of Ferromagnetic Superconductors

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We present here a new mean-field theory of ferromagnetic superconductors in an external magnetic field. Simple models for the pure superconductor and the pure ferromagnet are chosen and the theory is considered in more detail. Phenomena predicted include both the destruction of superconductivity by the ferromagnetic order and the coexistence of ferromagnetism and superconductivity, as well as the magnetic field dependence of zero-temperature magnetization. Results obtained are in qualitative agreement with the experiments.

Considerable interest in the relationship between superconductivity and magnetism has been generated by the recent discoveries of magnetic transitions in superconducting alloys.[1-3] Destruction of superconductivity at the onset of long-range magnetic order raised many questions. The fundamental question of the coexistence of long-range magnetic order and superconductivity has been reopened, creating a stream of new experimental data.[4] Alloys analyzed were of the forms $MRh_4B_4$,[1] $M_x Mo_6Se_8$,[2] and $M_x Mo_6S_8$, where $M$ is a rare-earth element.[3] In $ErRh_4B_4$, for example, two transitions are observed[1]: At $T_{c1} \approx 8.7°K$ the compound becomes superconducting,