Valence-Alternation Model for Localized Gap States in Lone-Pair Semiconductors*

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A model is presented for the structure and properties of active centers in lone-pair semiconductors, based on the possibility of unique bonding configurations which can arise from the presence of nonbonding orbitals. It is shown that the lowest-energy neutral center is unstable towards the creation of different positively and negatively charged centers, thus resulting in a negative effective correlation energy. These centers yield gap states which explain the unusual properties of lone-pair semiconductors.

Recent measurements of luminescence[1] and of photoinduced optical absorption and electron spin resonance[2] demonstrate the presence of gap states in chalcogenide materials. The absence of spin magnetism[3] before photoexcitation has made a chemical identification of the associated bonding configurations difficult. Anderson[4] has proposed a model to account for these properties based on the idea that in amorphous and vitreous materials the effective interaction between a pair of electrons in the same state can be attractive because of coupling to atomic motion. Street and Mott[5] have specialized this idea by assuming that a large density ($\sim 10^{18}$ cm^{-3}) of dangling bonds in such materials act both as acceptors and donors and that atomic motion sufficiently lowers the total energy to make the effective correlation energy negative, resulting in charged centers. These charged centers in turn give rise to states in the gap and explain the principal properties of chalcogenide glasses. The purposes of this Letter are to describe the bonding configurations that yield the relevant gap states, to show that a negative effective correlation energy is expected in crystalline as well as in disordered chalcogenides but not in tetrahedral materials, and to show that the presence of 10^{17}–10^{19} cm^{-3} centers is plausible.

Ovshinsky[6] suggested that interactions between lone-pair electrons[7] on different atoms and interactions with their local environment result in localized states in the gap of chalcogenide glasses. We utilize this concept to show that specific interactions between nonbonding orbitals give rise to unusual bonding configurations which we call *valence alternation pairs* (VAP's). These configurations result, for example, when two chalcogen atoms, each twofold coordinated in its ground state, form instead one positively charged threefold-coordinated atom and one negatively charged singly coordinated atom. The creation of such a VAP requires a relatively small energy, so that the density of VAP's in most glasses is relatively large.

The important bonding configurations for chalcogens are shown in Fig. 1. The energy of a non-

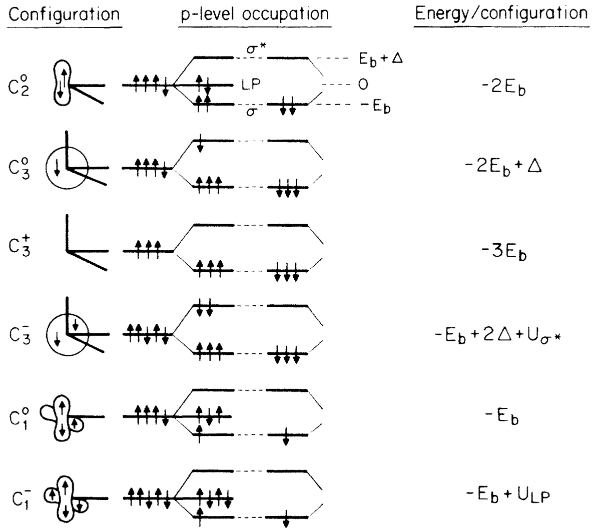

FIG. 1. Structure and energy of simple bonding configurations for group-VI elements in amorphous semiconductors. In configurations, straight lines represent bonding (σ) orbitals, lobes represent the lone-pair (LP) orbitals, and large circles represent the antibonding (σ*) orbitals. Arrows represent electrons with spin, at left on atom or ion or at right in bonding configuration. Energies are given using LP energy as zero.

bonding lone-pair (LP) orbital is taken to be zero. As a first approximation, we take the energy per electron of any σ orbital to be $-E_b$, independent of the nature of the bond. Since antibonding (σ^*) orbitals are always pushed up in energy more than σ orbitals are pushed down,[8] the energy of a σ^* orbital is $E_b+\Delta$, where $\Delta>0$. Finally, whenever an additional electron is placed on an atom, there is an increase in energy due to electronic correlation. The correlation energy is smaller if the electron is placed in a linear combination of σ^* orbitals (U_{σ^*}) than if it is placed in a single localized LP (U_{LP}) orbital. We expect that E_b is considerably larger than Δ, U_{σ^*}, and U_{LP}.

The lowest-energy configuration $C_2^{\,0}$ is the ordinary, neutral, twofold-coordinated chalcogen atom, which has an energy of $-2E_b$.[7] The threefold configuration $C_3^{\,0}$ and the single-coordinated $C_1^{\,0}$ have energies $-2E_b+\Delta$ and $-E_b$, respectively. $C_1^{\,0}$, the dangling bond of Ref. 5, costs a full bond energy E_b and is thus energetically unfavorable.[6] The lowest-energy *neutral* defect is rather $C_3^{\,0}$. However, we can show that $C_3^{\,0}$ is unstable. Consider first the charge-transfer reaction,

$$2C_3^{\,0}\rightarrow C_3^{\,+}+C_3^{\,-}. \tag{1}$$

As is clear from Fig. 1, this reaction costs an energy U_{σ^*}. Simply by breaking one of the three bonds, $C_3^{\,-}$ spontaneously becomes an ordinary $C_2^{\,0}$ converting a nearest-neighbor $C_2^{\,0}$ site into a singly coordinated chalcogen with the extra electron, $C_1^{\,-}$. This reaction

$$C_3^{\,-}+C_2^{\,0}\rightarrow C_2^{\,0}+C_1^{\,-}, \tag{2}$$

is exothermic if $2\Delta-(U_{\mathrm{LP}}-U_{\sigma^*})>0$. The system can thus lower its energy by transferring two σ and two σ^* electrons into the LP states of one singly coordinated and one twofold-coordinated chalcogen. The sum of Reactions (1) and (2) is

$$2C_3^{\,0}\rightarrow C_3^{\,+}+C_1^{\,-}. \tag{3}$$

Of course, the local-bonding picture of Fig. 1 gives only a rough estimate of the relative energies of localized states introduced by VAP's. Mixing between atomic states on the active center and its neighbors will alter the energies. In addition to the atomic rearrangements accompanying the above configuration changes, there are relaxation effects associated with a change in charge state of a given configuration, as proposed by Street and Mott.[5] Denoting these relaxation energies by W, the reaction energy of (3) becomes $U_{\mathrm{LP}}-2\Delta-W$ which should be negative for most chalcogenide materials.[9]

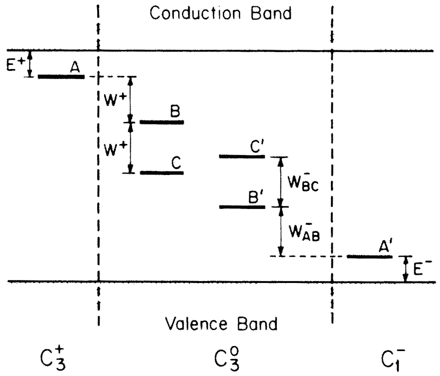

FIG. 2. Energy level diagram of Street-Mott model showing the corresponding valence-alternation states $C_3^{\,+}$, $C_3^{\,0}$, and $C_1^{\,-}$. The notations are those of Street and Mott (Ref. 5) except for an interchange of labels A' and C'.

Equation (3) is similar to Eq. (1) of Ref. 5 and yields gap states equivalent to those of Street and Mott. For clarity, they are sketched somewhat differently in Fig. 2. Under equilibrium conditions, the $C_3^{\,+}$ and $C_1^{\,-}$ centers occur in equal concentrations. Under optical excitation they give rise to the levels A and A', respectively. If a $C_3^{\,+}$ center captures an electron either from the conduction band (CB) or by photoexcitation from the valence band (VB), a $C_3^{\,0}$ center is formed with the level spectrum shown in the middle of Fig. 2. The $C_3^{\,0}$ center is amphoteric and acts either as a donor (levels B, C) or as an acceptor (levels B', C'). In a configurational-coordinate diagram, the levels B and B' would correspond to nonvertical (thermal) transitions, whereas C and C' would correspond to vertical (optical) transitions. Removal of an electron from the $C_3^{\,0}$ center, either thermally (B) or by an optical transition (C), restores $C_3^{\,+}$ and thus level A. The processes involved when $C_3^{\,0}$ acts as an acceptor are less obvious. Consider an electron placed on $C_3^{\,0}$ without a change in configurational-coordinate (optical transition to C' from either VB or CB); this produces a $C_3^{\,-}$ center. The correlation energy of the extra electron in the antibonding states of $C_3^{\,-}$ causes C' to lie above C. The $C_3^{\,-}$ center is unstable, however, as explained above. A bond change occurs according to (2) yielding a $C_1^{\,-}$ center with its level A'. The reverse reaction $C_1^{\,-}+\text{hole}\rightarrow C_3^{\,0}$ can again be thought of as occurring in two steps. First, a $C_1^{\,0}$ is formed, a configuration similar to a free radical. It lowers its energy by utilizing LP electrons on neighboring atoms for bonding. The extent of this bonding depends on the environment. The lowest-energy state is reached by bonding to a neighboring chalcogen and converting it to a C_3^{0}.[10]

We have shown that any one center can be in either one of the three states—C_3^{+}, C_3^{0}, and C_1^{-}—and that the C_3^{0} converts either into a C_3^{+} or a C_1^{-} center depending on whether the physical situation utilizes the C_3^{0} as a donor or as an acceptor. This remains valid when valence alternation involves a group-V atom whose normal coordination configuration is P_3^{0} (P stands for pnictide and C for chalcogen atom). In As_2Se_3 for instance, there is thus the additional possibility of utilizing the s-like LP's to form P_4^{0} configurations which then lower their energy in the reaction

$$2P_4^{0} \rightarrow P_4^{+} + C_1^{-}. \qquad (4)$$

Interconversion C_1^{-} + hole $= P_4^{0}$ then involves a change in bonding between a chalcogen and a pnictide atom. The simple energy relationships discussed above will be modified by the ionicity difference between constituent atoms and hybridization effects. It should be emphasized that W_{AB} in Fig. 2 involves a bond rearrangement in addition to atomic relaxation, whereas W^{+} is a simple relaxation energy. Thus, we expect $W_{AB}^{-} > W^{+}$ and B' not to be centered between A' and C'.

A consequence of the interconversion of these centers between say C_3^{+} and C_1^{-} is that their relative concentrations are shifted in space-charge regions or if the material contains other donors or acceptors falling above B or below B', respectively. Moreover, several neighbors are available for the interconversion steps. This leads to configurations falling into a narrow energy spectrum and the possibility of a motion of a given center by bond switching.

We now turn to the problem of estimating the energy $E_{\rm VAP}$ required to create a VAP. Two C_3^{0} centers are higher in energy than a VAP by the magnitude of the effective correlation energy, $U_{\rm eff}$, which is the separation between the levels B and B' in Fig. 2. (Experimentally, $U_{\rm eff} \sim -\frac{1}{2}E_g$, where E_g is the mobility gap.) According to the molecular energy diagram of Fig. 1 one needs 2Δ for creating $2C_3^{0}$ from $2C_2^{0}$. If there were no nearest-neighbor mixing, the two σ^* electrons of the two C_3^{0} would be near the middle of the conduction band (of width $E_{\rm CB}$), formed by the σ^* orbitals of the C_2^{0}. In the solid, this mixing allows the electrons to move down by an energy of about $\frac{1}{2}E_{\rm CB} + W^{+} + E^{+}$ per electron, to the levels B. Thus we obtain

$$E_{\rm VAP} = 2\Delta - 2(\tfrac{1}{2}E_{\rm CB} + W^{+} + E^{+}) - \tfrac{1}{2}E_g. \qquad (5)$$

Since $2(W^{+} + E^{+}) \simeq \frac{1}{2}E_g$ from Fig. 2, one finds that $E_{\rm VAP}$ can be quite small, provided that 2Δ is not much larger than $E_{\rm CB} + E_g$.

For Se, one has $E_{\rm CB} \simeq E_g \simeq 2$ eV and from pseudopotential calculations,[11] $2\Delta \simeq 3$ eV. We tend to believe that Δ is in fact somewhat larger because we assume that the Se VAP density of $n_{\rm VAP} \simeq 10^{16}$ cm^{-3} (as observed by ESR at low temperatures[2]) was frozen in at the glass transition temperature $T_g = 310$ K; then the relation $n_{\rm VAP} \simeq n \exp(-E_{\rm VAP}/2kT_g)$, where n is the atomic density of 3×10^{22} cm^{-3}, yields $E_{\rm VAP} \simeq 0.8$ eV. The observation[12] of threefold coordination in liquid Te confirms the possibility of relatively small values of $E_{\rm VAP}$ in some chalcogenides.

In materials with large dielectric constants, ϵ, and high T_g, the C_3^{+} and C_1^{-} centers are probably randomly distributed. However, in materials having low average covalent coordination, relatively small ϵ and low T_g, the Coulomb attraction between C_3^{+} and C_1^{-} makes it likely that there is a nonrandom distribution with an appreciable density of intimate valence alternation pairs (IVAP). For IVAP's the creation energy $E_{\rm VAP}$ is reduced by $M(\boldsymbol{R})$, the electrostatic energy of a pair with separation $\boldsymbol{R}$.

We believe that VAP's and/or IVAP's account for many of the unusual properties of chalcogenide materials as explained by Street and Mott in terms of their charged dangling-bond centers. Furthermore, the reversible photostructural changes commonly observed in these materials may be the result of photoinduced creation of an excess concentration of VAP's. Moreover, the degrees of freedom associated with bond switching and the chemical reactivity associated with photoexcited VAP's may also play an important role in processes such as photoinduced diffusion, crystallization, phase separation, and decomposition.

In conclusion, we emphasize that the dominant contribution to the negative effective correlation energy and thus the behavior of valence alternation centers is chemical in origin. Therefore, valence alternation plays an important role in crystalline (albeit with additional steric constraints) as well as vitreous or liquid chalcogenides. For group-V atoms, hybridization can also result in valence alternation and to a negative effective correlation energy. However, it is important to note that this process cannot occur for group-IV atoms, because they cannot be fivefold coordinated. Thus, our model accounts for the lack of spin pairing in tetrahedral materials.

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[10] Although it appears from Fig. 2 that relaxation is moving the filled level up in energy, the total energy is being reduced, since the two other lone-pair states are becoming bonding levels as $C_1{}^0$ transforms to $C_3{}^0$ (see Fig. 1).

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Postulated Electronic Phase Diagram of *n*-Type Semiconductors*

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A new type of phase diagram for the metal-insulator transition in n-type semiconductors and related systems is proposed. By starting from the Herzfeld criterion for the polarization instability, it is argued that an intermediate ferroelectric phase may arise. The ferroelectric and excitonic phases are shown to be complementary structures.

The metal-insulator phase transition (PT) in n-type doped semiconductors can be estimated by various criteria. Mott,[1] starting from the metallic side, argues that the PT occurs once the Thomas-Fermi screening length q_{TF} decreases so much that the screened potential assumes a bound state. The corresponding criterion is $q_{\mathrm{TF}} \times a_D = 1$, where a_D is the donor Bohr radius. It leads almost to the same numerical values for the critical donor concentration n_c as the criterion[2] $U/B = 1$ based on the Hubbard model with U the intra-atomic Coulomb repulsion and B the bandwidth of the uncorrelated problem. On the other hand, if the metal-insulator PT is approached from the insulating side, one expects, on account of the Clausius-Mossotti (CM) relation

$$(\epsilon - 1)/(\epsilon + 2) = (4\pi/3)n\alpha_D, \tag{1}$$

a polarization catastrophe (PC) to occur for $n \to n_c = 3/4\pi\alpha_D$, where α_D is the donor polarizability and ϵ is the dielectric constant. It has been suggested by Herzfeld[3] that the PC marks the onset of metallic behavior of the system. All three criteria lead almost to the same numerical values of n_c.[4] If one neglects anharmonic strain effects, it is also believed that the metal-insulator PT is of first order[5] as originally proposed by Mott.[1]

In the following we study the problem from the insulating side. It follows from a detailed discussion of the PC presented in this Letter that a PC can occur via a first- or second-order PT. Only in the latter case $\epsilon \to \infty$ as $n \to n_c^-$ and a ferroelectric phase results, whereas in a first-order PT, ϵ is discontinuous at n_c and a metallic or ferroelectric state may be reached.

Consider first the range of validity of Eq. (1). Starting from the dilute limit, localized donor orbitals are appropriate, as is also the use of a single-particle α_D. The ground-state properties of the system are then obtained via the dipole approximation[6]

$$\vec{p}_i = \alpha_D \vec{D}_z - \alpha_D \sum_{k \neq i} \overleftrightarrow{T}_{ik} \cdot \vec{P}_k. \tag{2}$$

Here $\vec{p}_i$ is the dipole moment induced on the ith donor by the external electric field $\vec{D}_z = \epsilon \vec{E}_z$, where $\vec{E}_z$ is the total macroscopic field in the dielectric. Note that the polarization surface charge densi-