

approximately twice as large as the  $^3\text{He}$ -scattering contribution for the positive ion. However, we believe that there exists sufficient experimental evidence for excluding vortex-wave scattering as a dominant mechanism. Ostermeier and Glaberson<sup>15</sup> have measured ionic mobilities along vortex lines in pure  $^4\text{He}$  and found the drag force to be much less than that predicted by vortex-wave scattering at low temperatures. Further, the cross section for vortex-wave scattering is larger for the negative ion than for the positive ion, and vortex-wave scattering could not explain the difference in the mobilities for the two species along the condensed core.

Ohmi, Tsuneto, and Usui<sup>1</sup> have calculated a linear dispersion curve for small wave vectors for the  $l=0$  mode vortex waves of the condensed core. The lack of sufficient low-lying states should make this mode relatively unimportant in ionic scattering as compared to the  $l=-1$  mode.

In conclusion, we believe that the above-mentioned approach to the ion mobilities along vortex lines is correct although a more detailed and presumably complex calculation should be done in order to understand fully the microscopic structural change of the vortex line.

Ostermeier and Glaberson have independently calculated ionic mobilities along the condensed core using a different approach and different assumptions.<sup>16</sup> They also obtain good agreement with the positive ion data.

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## Localized States in the Gap of Amorphous Semiconductors

Stanford R. Ovshinsky

*Energy Conversion Devices, Inc., Troy, Michigan 48084*

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It is pointed out that the recent observation of localized holes and electrons at low temperatures after optical excitation of chalcogenide glasses by Bishop *et al.* is consistent with a model previously proposed for lone-pair amorphous semiconductors. The model uses the existence of these localized states to provide an explanation of how the conducting states are reached in threshold and memory switching.

Now that the initiation and maintenance of bias-induced switching in threshold-type,<sup>1</sup> chalcogenide-based, amorphous semiconductor materials have been definitively established as electronic processes,<sup>2-8</sup> there is one major remaining prob-

lem—the nature of the localized states in the gap of these materials. In this Comment I address this subject, with emphasis on their role in the switching transition.

The discovery of optically induced, localized,

paramagnetic states in chalcogenide glasses by Bishop, Strom, and Taylor<sup>9,10</sup> can be explained by utilizing a recently proposed model for the localized states in these glasses.<sup>11</sup> The model, which extends that of Mott<sup>12</sup> and Cohen, Fritzsche, and Ovshinsky<sup>13</sup> by identifying the nature and origin of localized states, is briefly the following. In lone-pair, amorphous, chalcogenide semiconductors,<sup>14</sup> of which the chalcogenide glasses are the chief example,<sup>15</sup> a spectrum of localized states tailing into the gap from the valence and conduction bands is introduced by the interaction of lone pairs with each other and with their local environment. Because the lone-pair orbitals are filled at equilibrium, these tail states are paired and thus diamagnetic. Excitation creates empty orbitals (holes) which are compensated by electronic or structural means.<sup>11,16</sup>

In noncompensated, tetrahedral, amorphous materials such as a germanium and silicon, an equilibrium density of dangling bonds should exist, and these should be reflected in paramagnetically detectable, singly occupied states. The experiments of Agarwal<sup>17</sup> confirm their existence in amorphous germanium.

However, while no paramagnetism is observed in the chalcogenide samples whose electron distribution is at equilibrium, Bishop, Strom, and Taylor<sup>9,10</sup> found ESR signals at low temperatures after excitation with sub-band-gap illumination. They interpret the spins as associated with holes localized on chalcogen atoms and electrons localized on arsenic atoms. The nonequilibrium state brought about by illumination produces, in addition, a broad optical absorption band below gap energies. This nonequilibrium state is stable for several hours at 6°K.

I believe that the explanation for this finding is related to the interaction of the lone-pair orbitals with the structural bonding configuration (matrix or "lattice"), so that when a lone-pair excitation takes place, a metastable, localized hole is created through the breaking up of the lone pair on the chalcogen atom. In order to understand the origin of the metastable hole, the question of the possibility of dangling bonds in these materials should be considered.

Street and Mott<sup>18</sup> recently proposed the existence of defect states arising from dangling bonds on the chalcogen atoms. As I have discussed,<sup>19</sup> such states are energetically unfavorable. Crosslinked chalcogenides are "ideal" glasses since they have the structural flexibility to intrinsically compensate dangling bonds. Such

compensation is uniquely associated with the nature of the lone-pair atom in most amorphous chalcogenide materials since it has a primary divalency based on any two of the  $p$  orbitals, and the remaining  $p$  orbitals have a spectrum of energetic interactions which are spin compensated as will be detailed later in this paper. Choices of these interactions are allowed by the amorphous state since they are dependent upon the *varying local environment* which provides three-dimensional orbital relationships found in no crystalline or nonchalcogenide amorphous material. The primary divalency provides for a maximum of these orbital interactions since the bends and twists of the resulting helical configurations place the remaining lone pairs in various bonding and nonbonding electronic interactions. While stabilizing the material, these provide for structural flexibility and the placement of a range of localized states in the gap. Such a polymeric structure leads to a strong interaction between the lone-pair localized states and their matrix environment. A change of charge and occupancy of the localized states acts upon the matrix just as the matrix helps position the localized states originally. This is unlike tetrahedral materials in which there is a great deal more structural rigidity since all four bonding positions must find mates or have some remain as dangling bonds or voids. It is this ability to have conformational changes which sets up the conditions for metastability since the presence or movement of lone-pair configurations has a profound effect in determining molecular shape.<sup>20</sup>

I think that at room temperature thermal fluctuations reduce the effect of stabilizing bonding distortions around the localized hole, and rapid recombination occurs. Thus, paramagnetism cannot be easily detected except under strong nonequilibrium conditions. However, at the temperature used by Bishop *et al.*, thermal bonding fluctuations are small and, therefore, local charge distributions associated with lone-pair interactions can be metastable. For example, excitation in the form of  $n$  to  $\pi^*$  or to  $\sigma^*$  transitions in such an environment can lead to a metastable, localized hole since the new electronic configuration interacts with the nearest-neighbor environment so that the nonequilibrium holes, electrons, or both are stabilized and prevented from recombination by atomic distortions created around the carriers. Structural relaxation processes ultimately re-establish the equilibrium electronic configurations, although these can take

hours or more at very low temperature. Either thermal or optical excitation (infrared) in the new absorption band restores equilibrium by exciting either electrons from the valence band into the metastable hole states or metastable electrons into the conduction band. This explains the photo-bleaching effect observed by Bishop *et al.* with low-energy photons.

The transient appearance of localized states associated with a disequilibrium of the carrier distribution should also occur at *room temperature* under proper excitation conditions. This has been the leitmotif of my work on switching in chalcogenide glasses.<sup>21</sup>

I now detail the model which is based upon an interaction between two different kinds of electronic configurations specific to amorphous chalcogenide materials.<sup>11,16</sup> The first is the arrangement of bonding electrons (ordinarily lying much lower in energy than the nonbonded lone pairs) which are responsible for the overall structural integrity of the material even when a very large density of lone-pair electrons is excited. This matrix is associated with the thermal fluctuations described. The second is the distribution of lone-pair electrons spread over a large energy range, but not primarily responsible for the cohesive energy of the material. It is among these nonbonded, lone-pair configurations that low-energy excitation processes play a role. In some cases to be described, some lone pairs have secondary structural effects. The various configurations, due to the variety of local environments afforded by the disordered state, have interesting and unique properties such as repulsive interactions of lone pairs with nearby filled orbitals, including other lone pairs, which spread the density of valence-band states into the gap; attractive interactions including the donation of the complete lone pair to an acceptor configuration—the dative bond and the additional coordination of the lone pair to nearest neighbors forming one- and three-electron bonds. These nearest neighbors can include other lone-pair atoms as well as the alloying elements and are attractive due to the charge configurations present, e.g., of either a dangling bond of the chalcogen or of the crosslinking atom. As a variation of these electronic configurations, I suggest that in some areas lone pairs can lose their electrons through their nearest-neighbor interactions and still be compensated through the replenishment of electrons coming from other nearby clusters of lone pairs so that there is a continuous mixing in

which the parentage of the electrons may be lost. The *p* orbitals, then, in both primary and secondary valency, pick off (compensate) any available, unsatisfied bond and the nonbonded lone pairs themselves, by their charge interactions, “buffer” the structural bonds. That is, the molecular bond shapes reflect their presence.

Therefore, in a lone-pair amorphous material, there are varying types of localized states, all dependent upon nearest-neighbor relationships which in some cases have an attractive effect, in others repulsive. Such a spectrum of states ranges from strong bonds to weak bonds, to varying charge configurations including inert lone-pair positions.<sup>22,23</sup> Even in the inert pair state, the lone pairs have steric effects since they help set up bond angles by their Coulombic interaction with nearest neighbors. In any case, whether strongly or weakly localized, the lone-pair configurations described are spin compensated.

The understanding of the nature of the localized states provides a basis to explain in principle the nondestructive, reversible breakdown, and the high resistance, as well as the highly conductive state, in amorphous switches. The density of these localized states is so great ( $10^{17} - 10^{19} \text{ eV}^{-1} \text{ cm}^{-3}$ ) that their field-induced excitation can lead to a sufficient concentration of free electrons to provide a metalliclike conducting state in what previously was a high-resistance, nonconducting material.<sup>1</sup> It is clear that, while switching is a bulk phenomenon, the redistribution of charge resulting from the availability and stability of a large density of localized holes and electrons, together with the excitation of a large concentration of free electrons, introduces the possibility of high-level injection processes.<sup>11</sup>

In memory-type materials, which are designed for bistability by reducing the composition of crosslinking group-IV and -V atoms, the excited lone-pair carriers interact with the structural bonds and the stabilizing distortions caused by excitation around the localized holes become nucleating centers for structural transformations.<sup>11,16,24</sup> Although the excitation processes in such materials are similar to those in threshold (unistable) switches in which structural change is prohibited by material design due to strong and heavy covalent crosslinking, structural rearrangements can occur because the memory class of materials contains much less crosslinking, weaker bonds, and more lone-pair interactions. They are, thus, much less structurally stable in the amorphous state, especially to electronic ex-

citations.<sup>25-27</sup>

Unlike an impurity in the lattice of a crystalline material or dangling bonds in some types of amorphous materials, the orbital configurations described in this model are only transiently exposed under nonequilibrium conditions. However, as discussed earlier, they are observable under conditions where thermal fluctuations are minimized and the distorted orbitals created by nearest-neighbor and lone-pair interactions are frozen in position sufficiently long enough to be detected. This explains the metastable conditions that can be observed. I suggest this is just what has been accomplished by the work of Bishop, Strom, and Taylor.<sup>9,10</sup>

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