

York, 1969).

<sup>8</sup>On repeated wave equations, see, e.g., W. Nowacki, *Z. Angew. Math. Mech.* **51**, T1 (1971).

<sup>9</sup>See Ref. 2 and Ref. 5, p. 54.

<sup>10</sup>One of the authors discussed the electromagnetic analogy for the field of moving dislocations [S. Minagawa, *Phys. Status Solidi (b)* **47**, 197 (1971)].

## Bonding Bands, Lone-Pair Bands, and Impurity States in Chalcogenide Semiconductors\*

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(Received 29 November 1971)

The origin of electronic states in two classes of semiconductors is explored: (i) semiconductors containing group-VI elements in twofold coordination, and (ii) tetrahedral semiconductors. In the first case the valence band arises from the unshared electron pair (lone pair) of the group-VI atom. We examine the effects of compositional variation on the distribution of states in amorphous semiconductors. It is predicted that an Anderson transition will occur in the band of lone-pair states when a group-VI element is added to a tetrahedral amorphous semiconductor.

This Letter points out the special role played by unshared electron pairs<sup>1</sup> in semiconductors which contain group-VI elements in twofold coordination. Examples of such semiconductors are the elements S, Se, and Te, IV-VI compounds ( $\text{GeTe}_2$ ,  $\text{GeSe}_2$ , etc.), and V-VI compounds ( $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{Se}_3$ , etc.), as well as many crystalline and glassy chalcogenide alloys. In contrast to the tetrahedral semiconductors (Si, Ge, III-V compounds, etc.) in which the bonding band forms the valence band and the antibonding band forms the conduction band, the situation is quite different in the chalcogenide semiconductors. If a chalcogen is a major constituent, the valence band in these materials is formed by the unshared-electron states.

In the following, the origin of states in Ge will be contrasted with that of states in Se. The electronic states of a solid may be considered, to first order, to be a broadened superposition of the molecular orbital states of the constituent bonds. Thus, Ge in fourfold coordination has hybridized  $sp^3$  orbitals which are split into bonding ( $\sigma$ ) and antibonding ( $\sigma^*$ ) states. In the solid these molecular states are broadened into bands. Thus, in tetrahedral semiconductors the bonding band forms the valence band and the antibonding band forms the conduction band [see Fig. 1(a)]. In Se, on the other hand, the  $s$  states lie well below the  $p$  states and need not be considered. Because only two of the three  $p$  states can be utilized for bonding, one normally finds Se in twofold coordination. This leaves one nonbonding

electron pair. The situation is sketched in Fig. 1(b). In the solid these unshared or lone-pair (LP) electrons form a band near the original  $p$ -state energy. The  $\sigma$  and  $\sigma^*$  bands are split symmetrically with respect to this reference energy. Both the  $\sigma$  and LP bands are occupied. Thus, the bonding band is no longer the valence band; this role is played by the LP band. Mooser and Pearson<sup>2</sup> correctly identified the valence band in Se with the nonbonding  $p$  states. They used a molecular-orbital description to relate the semiconducting properties of many materials to their short-range order.

It is instructive to analyze the consequences of forming a dangling bond in the two classes of semiconductors. In both cases a filled state is

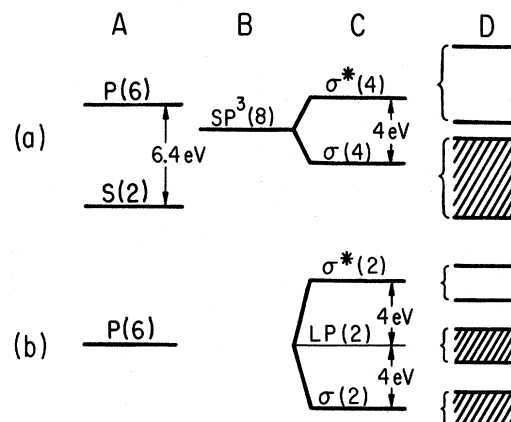


FIG. 1. Bonding in (a) Ge and (b) Se. (A) atomic states, (B) hybridized states, (C) molecular states, (D) broadening of states into bands in the solid.

pulled out of the  $\sigma$  band and an unoccupied state from the  $\sigma^*$  band. In the tetrahedral materials these produce localized states in the gap. Considering Coulomb interaction and correlation, one estimates that a donor is formed near the gap center and an acceptor above it. In the chalcogenide materials the LP band lies in the energy region between the  $\sigma$  and  $\sigma^*$  bands. The occupied state from  $\sigma$  falls into the LP band; the unoccupied state probably forms an acceptor above the LP band. It is also possible, particularly at a high concentration of dangling bonds, that the unoccupied state lies within the LP band. This case was considered by Cutler<sup>3</sup> to explain the transport properties of liquid Te-Tl alloys.

Keeping in mind the bonding discussed above, we can understand the effect of alloying group-IV, -V, and -VI elements into a chalcogenide material such as Se. One must distinguish crystalline from vitreous materials when one considers the effect of alloying on the distribution of states. In crystals the long-range order demands a unique coordination. In vitreous materials, on the other hand, the coordination environment can adjust to satisfy the valence requirements of each atom. Let us assume an ideal vitreous state in which this adjustment is perfect. An alloy of Se with another element contains various bonds. For example a Se-As alloy contains Se-Se, Se-As, and As-As bonds. The  $\sigma$ - $\sigma^*$  energy separation will be different for each bond. LP states are associated only with group-VI atoms. The  $\sigma$ - $\sigma^*$  as well as the LP- $\sigma^*$  splittings can be estimated from the optical-absorption spectra. Figure 2 shows the  $\epsilon_2$  spectra for amorphous and crystalline Ge and Se. The single broad peak in Ge is caused by  $\sigma$ - $\sigma^*$  transitions. In Se we attribute the broad maxi-

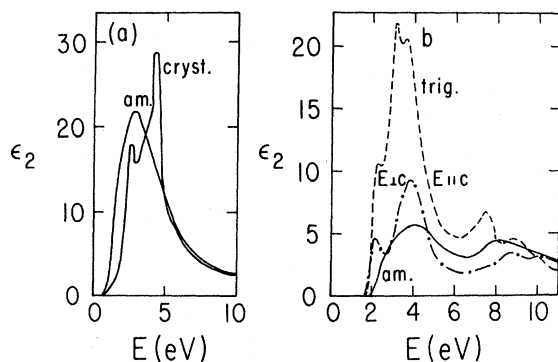


FIG. 2. Imaginary part of the dielectric constant versus photon energy for crystalline and amorphous (a) Ge (Ref. 8) and (b) Se (Refs. 5, 9, 10).

mum at 4 eV to LP- $\sigma^*$  and the second peak at 8 eV to  $\sigma$ - $\sigma^*$  transitions. The two broad maxima in  $\epsilon_2$  appear to be characteristic of chalcogenide semiconductors. They have been observed in Te,<sup>4,5</sup> As<sub>2</sub>Se<sub>3</sub>,<sup>6</sup> and As<sub>2</sub>S<sub>3</sub>.<sup>7</sup> The molecular state energies estimated from such  $\epsilon_2$  spectra<sup>5-11</sup> are sketched for a number of bonds in Fig. 3. The center energy of a particular  $\sigma$ - $\sigma^*$  bond must be shifted with respect to the LP state of Se by the difference in ionization energies. In lieu of experimental values for ionization energies for the various elements alloyed with Se, atomic ionization energies were used.<sup>12</sup>

It appears from Fig. 3 that weak bonds (e.g., As-As) create localized  $\sigma^*$  states in the band gap of Se. These are not acceptors, however, because of Coulomb interaction. If the density of weak bonds becomes large enough, the  $\sigma^*$  states will become delocalized. The conduction-band edge will then move to lower energy. This is a Mott delocalization<sup>13</sup> because it is due to Coulomb repulsion and correlation.

Considering, now, admixtures of group-VI elements to group-IV amorphous materials such as Ge, we observe from Fig. 3 that the LP states of Se and Te fall near the gap of Ge. It is probably possible to choose a tetrahedral host and a group-VI additive so that the LP states fall in the gap. These lone-pair states will be localized at low concentration. However, when their concentration exceeds a critical value, they become delocalized and we expect an Anderson transition<sup>14</sup> to occur. The LP band arising from these overlapping LP states is fully occupied unless an electron gets trapped into a lower-lying state. If

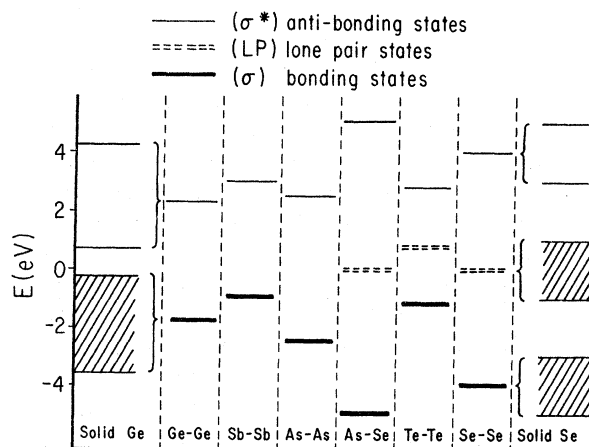


FIG. 3. Molecular states of various bonds estimated as discussed in the text. Energy bands of solid Ge and Se are sketched for comparison.

holes are created in this manner, we do not expect semimetallic conduction but rather conduction which requires thermal activation because of the Coulomb interaction between the holes and the trapped electrons.

Since most vitreous semiconducting alloys contain a group-VI element as a major constituent, the valence band is the LP band of that group-VI element. The tailing of the valence band is enhanced by adding different group-VI elements to the alloy. In addition, LP electrons adjacent to electropositive atoms will have higher energies than those near electronegative atoms. Therefore, addition of electropositive elements to the alloy may raise the energy of some LP states sufficiently to further broaden the valence-band tail. The conduction-band tail broadens as the number of different bonds in the alloy is increased. Therefore, we do not expect the tailing of the two bands to be symmetric.<sup>15</sup>

The addition of a highly electropositive atom like Cu to amorphous  $As_2Se_3$ , for instance, causes an increase in As-As bonds because strongly bonded copper selenide is formed. As discussed above, this will tend to lower the energy of the conduction-band edge. Considering electronegativity differences one might understand in this way the effect of other impurities on amorphous semiconductors.

In tetrahedral amorphous semiconductors weak bonds should have little effect on the conduction properties. In chalcogenide materials, however, weak bonds create localized antibonding states in the gap. The bonding states, on the other hand, fall below the valence band.

It is interesting to note that in chalcogenide material the number of states in the conduction band depends only on the number of bonds just as in tetrahedral materials. The number of states in the valence band, in contrast, can be considerably smaller. This number is equal to that of lone-pair states which in turn is twice the number of chalcogenide atoms. As the number of

chalcogenide atoms is decreased below a critical value these LP states cease to be the valence band. An Anderson transition occurs at this critical value.

Since the LP band determines the conduction properties, these materials might appropriately be called *lone-pair semiconductors*.

I am grateful to my thesis advisor, H. Fritzsche, for his inspiration and helpful suggestions.

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\*Work supported by the U. S. Air Force Office of Scientific Research, under Contract No. F 44620-71-C-0025.

†Fannie and John Hertz Foundation Fellow.

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