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# Bonds and band structure in $Ge_xSe_{1-x}$ compounds

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The electronic structure of $Ge_xSe_{1-x}$ compounds is studied in a tight-binding approximation for $0 \leq x \leq 1/3$. The starting point consists of a "molecular approximation." The widening of the molecular levels into bands is then analyzed. The band gaps are shown to depend only on the local order. Qualitative resuts about the *s* or *p* character of the different bands are derived. It is shown that the behavior of optical properties with respect to *x* is correctly predicted. Essential features that one should observe in photoemission spectra are also described.

## INTRODUCTION

The simplest description of the electronic structure of covalent and partially ionic tetrahedral semiconductors is provided by the tight-binding approximation.[1-7] It has allowed to prove that the existence of a gap in these systems is related to the local order. This result, which we shall refer to as Leman, Thorpe, and Weaire's theorem, has been established for the elements of column IV, the III-V, and the II-VI compounds. We intend here to generalize such a study to the case of the $Ge_xSe_{1-x}$ compounds. The increased complexity is due here to the selenium atoms, for which tetrahedral hybrids loose their interest.

A tight-binding treatment has been applied to the related case of $SiO_2$,[8] where oxygen atoms can roughly be considered to play the same rule as the selenium atoms in $GeSe_2$. This treatment starts from an idealized $\beta$ cristobalite structure which is known to be far from the real situation with respect to the bonding angles; nevertheless, it leads to results which are qualitatively similar to those of a more recent pseudopotential calculation.[9] The treatment that we propose here differs from that in Ref. 8 in the sense that we try to obtain general information concerning the gaps. We do this for the whole range of compositions $0 \leqslant x \leqslant 0.33$ and for arbitrary structure (crystalline or amorphous) respecting local tetrahedral coordination at the Ge sites.

We begin by recalling the experimental information concerning the local structure of these compounds. From this we define structural units and then the basic molecular orbitals. The situation for pure Ge and pure Se is used as a guide for building the correct hybrid orbitals pointing approximately towards the nearest neighbors. From these we can define bonding, antibonding, and lone-pair orbitals. This leads to a simple scheme for the chemical bond in these systems. We call it the "molecular model." We then include interactions between the eigenstates of this simplified model. This results in a widening of the molecular levels into bands as in tetrahedral solids.[10] It is for these bonds that we want to demonstrate generally the existence of gaps and we first do it for $GeSe_2$ and extend the proof to an arbitrary composition.

Finally, we apply these results to the prediction of optical properties which we compare to the experimental spectra.

## I. LOCAL STRUCTURE IN $Ge_xSe_{1-x}$ COMPOUNDS

The phase diagram of the Ge-Se system, described in Ref. 11, shows in the range of $x$ considered here, the existence of a crystalline compound $GeSe_2$. The detailed crystalline structure of $GeSe_2$ has been established recently.[12] It is built from distorted tetrahedra $GeSe_4$ in which a germanium atom is bonded to four selenium atoms, each selenium being shared between two tetrahedra. The unit cell contains 48 atoms distributed in two layers having each a width of 3.7 Å. The separation between the layers is 2.3 Å. Details are given in Fig. 1. The average nearest-neighbor distance Ge-Se is 2.36 Å. This is a typical example of a local 4-2 coordination.

An essential characteristic of the Ge-Se system is to allow the obtention of bulk amorphous $Ge_xSe_{1-x}$ compounds over a large range of $x$ ($0 \leqslant x \leqslant 0.45$). An important problem is to know the local structure of these compounds and its evolution as a function of $x$. This has been studied by many authors. The radial distribution function of amorphous $GeSe_2$ has been established in Ref. 13 by x-ray diffraction. The first two maxima are located

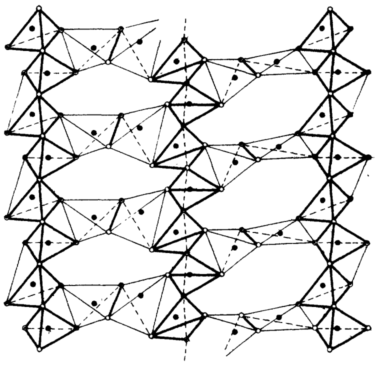


FIG. 1. Upper view of a crystalline $GeSe_2$ layer.

at 2.4 and 3.8 Å. The ratio of these distances is 1.58, quite close to the value 1.633, which corresponds to a perfect tetrahedral coordination. X-ray diffraction studies[14] as a function of $x$ show the existence of tetrahedral units $GeSe_4$. Radial distribution function measurements[15,16] show a great similarity with amorphous $GeSe_2$ for $0 \leq x \leq 0.40$ (same 4-2 coordination; nearest-neighbor distance varying between 2.3 and 2.4 Å). However, for $x > 0.40$, the results show an increasing distortion with respect to a tetrahedral environment. The study of x-ray absorption in these materials leads to similar conclusions. The chemical shift of the germanium x-ray absorption limit[17] shows that $GeSe_2$ presents a more covalent character than $GeO_2$ and $GeS_2$, and that the local coordination is effectively 4-2. X-ray-absorption-fine-structure (EXAFS) measurements[18] show that amorphous and crystalline $GeSe_2$ are quite similar. The nearest-neighbor distances are also quite close: 2.35 Å for the crystal, 2.38 Å for the amorphous system. Again the average coordination is found to be 4 for Ge, 2 for Se.

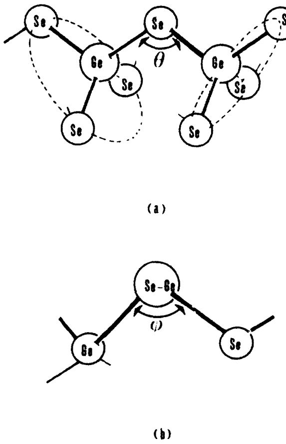


FIG. 2. Local structure in $GeSe_2$. (a) Tetrahedral environment around Ge sites. (b) $\varphi$ is the dihedral angle Ge-SeGe-Se.

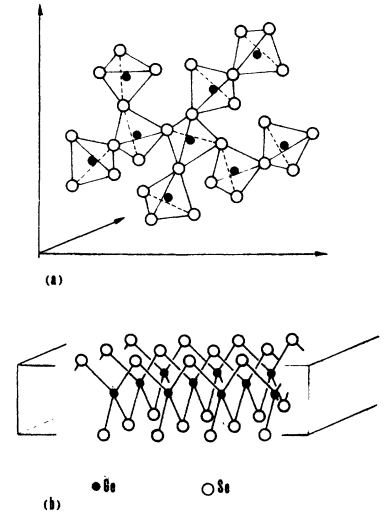


FIG. 3. Two possible crystalline arrays for $GeSe_2$. (a) Three dimensional. (b) Two dimensional (layer structure).

These informations on the local structure are confirmed by Raman diffusion experiments[11,19] which lead to other interesting conclusions: for $0 \leq x \leq 0.33$ there is a tendancy to a maximum dilution of the Ge atoms in Se (the Ge-Ge bonds are statistically forbidden; the Ge-Se-Ge sequences are as few as possible). In this range the number of Se-Se sequences decreases as a function of $x$ and vanishes for $x = \frac{1}{3}$. For $x \geq \frac{1}{3}$ the situation becomes gradually different[19,20] with the apparition of threefold coordinated Ge and Se atoms like in the GeSe crystal.

In the compounds with $0 \leq x \leq \frac{1}{3}$ the local structure can thus be defined with two parameters: the Ge-Se-Ge angle $\theta$ and the dihedral angle $\varphi$ (Fig. 2). There must be some "plasticity" for $\theta$ since in crystalline $GeSe_2$ it already takes eight values lying between 80° and 101° (Ref. 12) while the Ge tetrahedron remains almost undistorted. $\varphi$ completely defines the long-range order. The value of $\varphi$ certainly plays a central role in the lattice formation. For instance, one can build two completely different lattices for $GeSe_2$ which respect the local order: a simplified layer structure, or a completely random structure (Fig. 3).

## II. MOLECULAR APPROXIMATION

When applying the tight-binding approximation to covalent systems it is helpful to first define what is called a "molecular"[21,22] or "bond orbital"[21,23] approximation. Its interest comes from the fact that each band is derived mainly from one

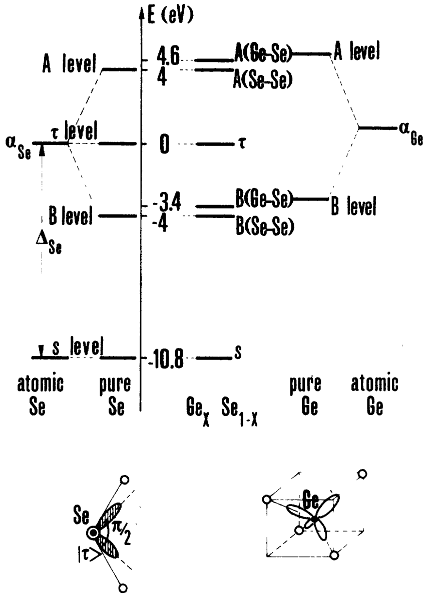


FIG. 4. Molecular levels and molecular orbitals in $Ge_xSe_{1-x}$.

type of localized orbital with bonding, antibonding, or lone-pair character. In this description which includes the most important terms of the Hamiltonian matrix, the band structure is obtained under the form of flat degenerate molecular levels. When further interactions are included these levels widen into bands.

To obtain some insight into the $Ge_xSe_{1-x}$ electronic structure problem it appears useful to recall what happens in pure Ge and trigonal Se, where the coordination numbers are the same as in $Ge_xSe_{1-x}$ compounds, i.e., 4 and 2, respectively. In pure germanium one has tetrahedral coordination and the molecular description is well known.[21-23] One builds four $sp^3$ hybrids (Fig. 4) pointing towards the nearest neighbors. One then associates pairs of $sp^3$ orbitals belonging to the same bond in bonding and antibonding combinations whose energies are

$$\alpha_{Ge}\pm\beta_{Ge}, \tag{1}$$

where $\alpha_{Ge}$ is the average $sp^3$ energy; $\beta_{Ge}$ is equal to the resonance integral between two $sp^3$ hybrids belonging to the same bond. The two molecular levels in (1) are degenerate and form a crude description of the valence and conduction band.

The description of Se is a little more elaborate. In view of the large $s$-$p$ promotion energy ($E_p - E_s \simeq 11$ eV) there is little $s$-$p$ hybridization and the bonding orbitals have mainly $p$ atomic character. The molecular model follows fairly simply from these considerations. If $\alpha_{Se}$ denotes the atomic $p$ energy and $\Delta_{Se}$ the $s$-$p$ promotion energy, one first finds a pure $s$ band at the energy $\alpha_{Se}-\Delta_{Se}$. For the $p$ states one can proceed in the following way: first consider a $|\tau\rangle$ state perpendicular to the plane joining an atom to its two nearest neighbors; then form two other orthogonal $p$ states in that plane symmetrical with respect to the bisectrice of the corresponding angle (Fig. 4). These orbitals approximately point towards the nearest neighbors (rigorously if this angle was $\frac{1}{2}\pi$). From these orbitals bonding and antibonding states are built, thus leading to the final set of molecular states, in order of increasing energy:

$$\begin{aligned}&\alpha_{Se}-\Delta_{Se}:\ \text{pure } s\,,\\ &\alpha_{Se}+\beta_{Se}:\ \text{pure } p \text{ bonding}\,,\\ &\alpha_{Se}:\ \text{pure } p\,,\\ &\alpha_{Se}-\beta_{Se}:\ \text{pure } p \text{ antibonding}\,.\end{aligned} \tag{2}$$

Here $\beta_{Se}$ is the resonance integral between two nearest-neighbor $p$ states pointing towards each other.

This simplified model of band formation correctly describes the nature of the subbands especially within the valence band and provides a quite simple basis[24,25] for the interpretation of photoemission spectra.

From these considerations we shall now derive a molecular model for the $Ge_xSe_{1-x}$ compounds. In view of the local environment, we shall define the atomic orbitals in the same way as in pure Ge and trigonal Se. For the germanium atoms we take the four $sp^3$ orbitals pointing towards the four nearest selenium atoms. For any selenium atom one has one $|s\rangle$ orbital, one $|\tau\rangle$ orbital and two equivalent $p$ orbitals pointing approximately towards the nearest neighbors. The $s$ and $\tau$ energies remain unchanged with respect to pure selenium. For the bonding and antibonding states one must consider two situations (Fig. 4): (a) Se-Se bonds: In this case, the bonding and antibonding states are identical to those of pure selenium. (b) Ge-Se bonds: There, in view of the small difference between $\alpha_{Ge}$ and $\alpha_{Se}$ the bond is slightly ionic, the bonding and antibonding levels being given by

$$E_{B,A}=\tfrac{1}{2}\alpha_{Ge}+\tfrac{1}{2}\alpha_{Se}\mp[(\tfrac{1}{2}\alpha_{Ge}-\tfrac{1}{2}\alpha_{Se})^2+\beta^2]^{1/2}. \tag{3}$$

Here $\beta$ is the resonance integral for the Ge-Se bond, which we take to be the average between $\beta_{Ge}$ and $\beta_{Se}$.

The next step in the study of band formation is to consider the interactions between orbitals belonging to the same molecular level. For the $s$ and $\tau$ states of Se atoms we restrict ourselves to nearest-neighbor interactions which we call $\beta_{ss}$ and $\beta_{\tau\tau}$. The other interactions which we take into account are between adjacent bonding orbitals and between adjacent antibonding orbitals. The formal results which we derive in Secs. III and IV only depend upon these assumptions. However, for a detailed numerical application we shall make the further simplifying assumption that when these orbitals are adjacent on a Ge atom their interactions are the same as in pure Ge (which we call $\Delta_B$ for bonding states and $\Delta_A$ for antibonding states); when this occurs on a Se atom they become equal to the pure Se values $\Delta'_B$ and $\Delta'_A$. This is a quite plausible assumption when one looks in detail at these matrix elements.

Let us now include the numerical values of the parameters describing all these interactions. For the intra-atomic terms we use the free atom values[26]

$$\alpha_{Ge} = -8.37 \text{ eV}, \quad \alpha_{Se} = -9.53 \text{ eV}, \quad \Delta_{Se} = 10.79 \text{ eV}. \tag{4}$$

For all other interactions we choose values that give a good overall agreement with existing experimental and theoretical informations in[27] pure Ge and pure Se.[24,25,28] We thus obtain

$$\begin{aligned} &\beta_{ss} = -1.5 \text{ eV}, \quad |\beta_{\tau\tau}| = 0.5 \text{ eV}, \quad \Delta_B = -1.5 \text{ eV}, \\ &\Delta'_B = +0.5 \text{ eV}, \quad \Delta_A = -0.5 \text{ eV}, \quad \Delta'_A = -0.5 \text{ eV}, \\ &\beta = \beta_{Ge} = \beta_{Se} = -4 \text{ eV}. \end{aligned} \tag{5}$$

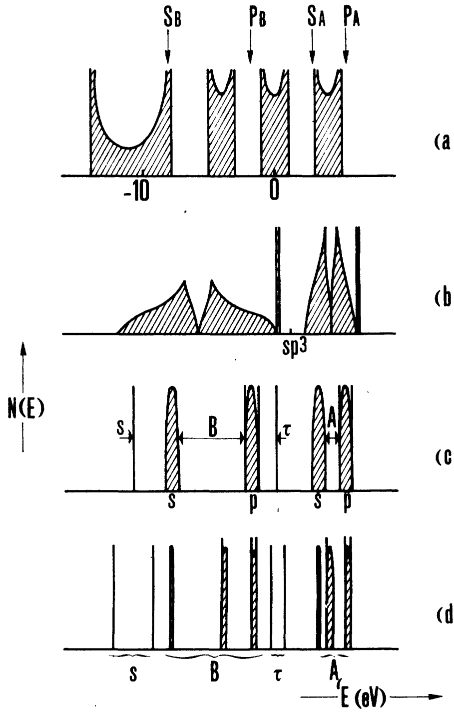


FIG. 5. Density of states of $Ge_xSe_{1-x}$. (a) Pure Se: the arrows indicate the localized levels introduced by Ge impurities. (b) Pure Ge. (c) $GeSe_2$. (d) $GeSe_4$.

For $\Delta'_B$ and $\Delta'_A$ the sign has been obtained from a detailed consideration of the matrix elements, within a nearest-neighbor approximation. The corresponding densities of states are reproduced on Figs. 5(a) and 5(b). They correctly describe the main structures of the valence bands. This is not so true for the shape of the conduction bands, especially in Ge, but nevertheless this model is capable of describing qualitatively the features of the optical properties.

The molecular levels of $Ge_xSe_{1-x}$ are thus found to be grouped in the following way (Fig. 4): in order of increasing energy; the $s$ states of Se atoms; the bonding states belonging either to Ge-Se or to Se-Se bonds; the $\tau$ states of Se atoms which might be called lone-pair states; and the antibonding states of Ge-Se or Se-Se bonds. We shall see in the following how the corresponding bands appear, first in $GeSe_2$, then in $Ge_xSe_{1-x}$.

## III. BAND FORMATION FOR $GeSe_2$

Here we shall consider how the interactions between the molecular states defined in Sec. II will widen degenerate levels of $GeSe_2$ into bands. For this we shall first treat separately groups of molecular levels: the $s$ states, the bonding states, the $\tau$ states, and the antibonding states. We shall then try to investigate the effect of interband coupling.

*a. s band.* It is derived from the $s$ atomic states of Fig. 4. In $GeSe_2$ a selenium atom has two germanium nearest neighbors. Thus a nearest-neighbor approximation leads to the conclusion that the $s$ band remains flat. Only interband coupling which we neglect for the moment can lead to a widening of this band.

*b. Bonding band.* It is due to intraband coupling between the bonding molecular states defined in Sec. II (combinations of a $sp^3$ orbital on Ge and a $p$ one on Se). Choosing the origin of energies at the bonding level defined by Eq. (3), one can write the interaction Hamiltonian in the form

$$h_B = \Delta_B \sum_{\substack{i,J,J' \\ J\neq J'}} |i,J\rangle\langle iJ'| + \Delta'_B \sum_{J} |iJ\rangle\langle i'J| . \tag{6}$$

Here $|i,J\rangle$ stands for the bonding orbital connecting the $i$th germanium atom to the $J$th selenium atom. Let us write an eigenstate $|\psi\rangle$ of this Hamiltonian as

$$|\psi\rangle = \sum_{i,J} a_{iJ} |iJ\rangle . \tag{7}$$

It is clear that one has the coupled equations

$$
\begin{aligned}
&(E+\Delta_B)a_{iJ}=\Delta_B S_i+\Delta_B' a_{i'J}\,,\\
&(E+\Delta_B)a_{i'J}=\Delta_B S_{i'}+\Delta_B' a_{iJ}\,,\\
&S_i=\sum_J a_{iJ}\,,\quad S_{i'}=\sum_J{}' a_{i'J}\,.
\end{aligned}
\tag{8}
$$

Here $E$ is the energy and the sums over $J$ defining $S_i$ and $S_{i'}$ are over the four nearest Se atoms.

From Eq. (8) one easily obtains

$$[(E+\Delta_B)^2-\Delta_B'^2]a_{iJ}=(E+\Delta_B)\Delta_B S_i+\Delta_B\Delta_B' S_{i'}\,, \tag{9}$$

which by summing over $J$ gives

$$
\begin{aligned}
&\epsilon S_i=\sum_{i'} S_{i'}\,,\\
&\epsilon=[(E-\Delta_B)^2-\Delta_B'^2-4\Delta_B^2]/\Delta_B\Delta_B'\,.
\end{aligned}
\tag{10}
$$

In Eq. (10) the sum is over the nearest neighbors $i'$ of the $i$th germanium atom in the germanium superlattice. $\epsilon$ are thus the eigenvalues of the connectivity matrix corresponding to this superlattice.

There is a first nontrivial type of solutions to Eq. (10) where all $S_i$ vanish. Using Eq. (9) for $a_{iJ}\neq 0$, one obtains

$$E=-\Delta_B\pm\Delta_B'\,. \tag{11}$$

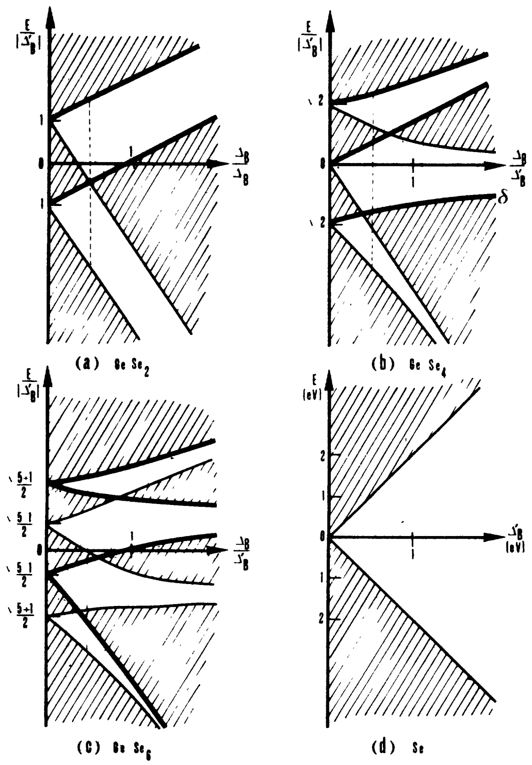


FIG. 6. Allowed energy ranges for the bonding states (shaded regions) assuming $\delta=0$.

This is the equation of degenerate flat bands which are characteristic of this Hamiltonian.

Again using Eq. (10) for $S_i\neq 0$, the other bands are found to be solutions of

$$(E-\Delta_B)^2=\Delta_B'^2+4\Delta_B^2+\Delta_B\Delta_B'\,. \tag{12}$$

For coordination number 4, one has $|\epsilon|<4$[2] which allows one to easily find all band limits. The results are given in Fig. 6. For $|\Delta_B/\Delta_B'|<\frac{1}{2}$ there is a forbidden gap separating two allowed bands, each containing two states per germanium atom, corresponding to one flat and one wide band. For $|\Delta_B/\Delta_B'|=\frac{1}{2}$ the gap vanishes. For $|\Delta_B/\Delta_B'|>\frac{1}{2}$ there is again a gap, but now the flat bands are both in the upper energy range so that the lowest band only contains one state per atom. These results are independent of the long-range order.

*c. $\tau$ band.* A $\tau$ orbital is chosen to be perpendicular to the plane joining a Se atom to its two nearest neighbors. In $GeSe_2$ there are two germanium atoms, so that in a nearest-neighbor approximation there can be no $\tau$-$\tau$ interactions and thus no widening of the band due to intraband coupling.

*d. Antibonding band.* The basis states are the antibonding combinations of the $sp^3$ germanium orbital and the $p$ selenium orbital (we choose the sign convention such that the + sign is attributed to the $sp^3$ orbital). We now take the origin of the energies at the antibonding level defined in Eq. (3). The Hamiltonian is thus exactly the same as Eq. (6), changing $\Delta_B, \Delta_B'$ into $\Delta_A, \Delta_A'$ and the bonding states into antibonding states. The formal treatment is exactly the same.

A final comment concerning the symmetry properties of the wave functions will be required for studying the optical properties. It concerns the $s$ or $p$ character of the wave function on the Ge atoms. Let us for instance consider the four bonding orbitals $|iJ\rangle$ connected to the $i$th atom. The sum of these has pure $s$ character on the Ge atom. Its coefficient in the total wave function is just $S_i$. The three other combinations have pure $p$ character and correspond to $S_i=0$. Now it is clear that the flat bands are pure $p$. The wide band which is bound by two flat bands is also practically $p$-like. Finally the isolated wide bands must thus be practically $s$-like. This can be analyzed in much detail from Eqs. (8), (9), and (10) and will be extended in another work.[29]

With the numerical values of Eq. (4) and Eq. (5) one obtains the density of states of Fig. 5(c). In order of increasing energy, we first find the $s$ states of the Se atoms. Then the bonding states form two bands, a lower $s$-like one containing one state per $GeSe_2$ unit, and an upper $p$-like one containing three states per unit. After these one finds the $\tau$ band, which remains flat in our model. All these bands are filled. The conduction band is thus formed of the antibonding states which also split into two subbands. It must be stressed that up to now we have not mixed molecular states of different natures, but this can be done by a perturbation approach as in[28] Se and will not change our qualitative conclusions.

## IV. EXTENSION TO ARBITRARY COMPOSITION

We extend here the results of Sec. III to other concentrations. We show that it is possible to transform the total Hamiltonian into an effective one which has the same form as (6). This again allows us to demonstrate the existence of forbidden energy gaps related to short-range order. However, for $Ge_xSe_{1-x}$ compounds it is necessary to consider systems of formula $GeSe_{2n}$ where chains of $n$ selenium atoms connect the germanium atoms. We find that the matrix elements occuring in the effective Hamiltonian are energy dependent, their form being more complicated as $n$ increases. We analyze $GeSe_4$, $GeSe_6$, and the small $x$ limit.

### A. $GeSe_4$ case

Again we look at the different bands separately.

*a. s band.* There are now two nearest selenium neighbors. $\beta_{ss}$ being the corresponding interaction, the $s$ level will split into two flat bands, one at $+\beta_{ss}$, the other one at $-\beta_{ss}$.

*b. Bonding band.* The situation is complicated by the fact that there are now two types of bonds, Se-Se and Ge-Se, which do not necessarily fall at the same energy [Fig. 4(a)] (we shall call $-\delta$ the Se-Se bonding level relative to the Ge-Se one). Denoting by $|0\rangle\,|1\rangle$ and $|2\rangle$ the bonding orbitals in the notations of Fig. 7, one can write the set of equations

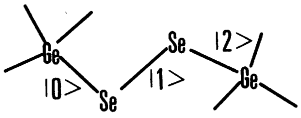
$$\begin{aligned}(E+\Delta_B)a_0&=\Delta_B S_0+\Delta'_B a_1\,,\\(E+\delta)a_1&=\Delta'_B(a_0+a_2)\,,\\(E+\Delta_B)a_2&=\Delta_B S_2+\Delta'_B a_1\,.\end{aligned}\tag{13}$$

Again we restrict ourselves to the interactions between adjacent bonding orbitals, $S_0$ and $S_1$ being sums of coefficients on the corresponding atoms.

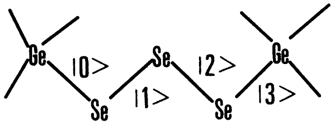
Let us now eliminate $a_1$ in (13). This leads to

$$\begin{aligned}&[E+\Delta_B-\Delta'^2_B/(E+\delta)]a_0=\Delta_B S_0+[\Delta'^2_B/(E+\delta)]a_2\,,\\&[E+\Delta_B-\Delta'^2_B/(E+\delta)]a_2=\Delta_B S_2+[\Delta'^2_B/(E+\delta)]a_0\,.\end{aligned}\tag{14}$$

This is strictly equivalent to Eqs. (8) except that there is a shift of the atomic level given by $\Delta'^2_B/(E+\delta)$, and an interaction $\Delta'_B$ replaced by $\Delta'^2_B/(E+\delta)$. An important point is that such terms are now energy dependent. However, all the above



(a) $GeSe_4$



(b) $GeSe_6$

FIG. 7. Structural units in $GeSe_4$ and $GeSe_6$.

arguments still apply and one has flat degenerate bands at the energies given by

$$E-\Delta'^2_B/(E+\delta)=-\Delta_B\pm\Delta'^2_B/(E+\delta)\,,\tag{15}$$

which has three distinct solutions.

Similarly, the other allowed energy bands must be such that $|\epsilon|\leq 4$, i.e., must satisfy the inequality

$$\left[\left(E-\Delta_B-\frac{\Delta'^2_B}{E+\delta}\right)^2-4\Delta_B^2-\left(\frac{\Delta'^2_B}{E+\delta}\right)^2\right]^2-16\left(\frac{\Delta_B\Delta'^2_B}{E+\delta}\right)^2\leq 0\,.\qquad 16)$$

In Fig. 6 we give the allowed energy ranges as a function of $\Delta_B/\Delta'_B$ for the simple case $\delta=0$.

*c. $\tau$ band.* The situation is similar to the $s$ band. However the $\tau\tau$ interactions are smaller than the $ss$ interactions so that the two levels are closer.

*d. Antibonding band.* There the situation is also analogous to that of the bonding band with simply a change in the definition of the parameters.

The main conclusion to draw from the comparison between $GeSe_2$ and $GeSe_4$ is that the number of subbands derived from each molecular level increases, some of the new forbidden gaps being related to the short-range order. This tendency will be confirmed when looking at $GeSe_6$.

### B. $GeSe_6$ case

There are now chains of three selenium atoms connecting the germanium atoms. The $s$ and $\tau$ bands now consist of three levels. The bonding and antibonding bands can be studied in a similar way. Let us summarize the case of the bonding band with the notations of Fig. 7

$$\begin{aligned}(E+\Delta_B)a_0&=\Delta_B S_0+\Delta'_B a_1\,,\\(E+\delta)a_1&=\Delta'_B a_0+\Delta'_B a_2\,,\\(E+\delta)a_2&=\Delta'_B a_3+\Delta'_B a_1\,,\\(E+\Delta_B)a_3&=\Delta_B S_3+\Delta'_B a_2\,.\end{aligned}\tag{17}$$

Eliminating $a_1$ and $a_2$ one obtains

$$\left[E+\Delta_B-\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}+\frac{1}{E+\delta+\Delta_B'}\right)\right]a_0 =\Delta_B S_0+\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}-\frac{1}{E+\delta+\Delta_B'}\right),$$

$$\left[E+\Delta_B-\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}+\frac{1}{E+\delta+\Delta_B'}\right)\right]a_3 =\Delta_B S_3+\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}-\frac{1}{E+\delta+\Delta_B'}\right). \tag{18}$$

Now there are four distinct flat bands at energies given by

$$E-\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}+\frac{1}{E+\delta+\Delta_B'}\right) =-\Delta_B\pm\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}-\frac{1}{E+\delta+\Delta_B'}\right), \tag{19}$$

whose solution is clearly analytical.

The allowed ranges of energy are given by the inequality

$$\left\{E-\Delta_B-\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}+\frac{1}{E+\delta+\Delta_B'}\right)-4\Delta_B^2 -\left[\frac{\Delta_B'^2}{2}\left(\frac{1}{E+\delta-\Delta_B'}-\frac{1}{E+\delta+\Delta_B'}\right)\right]^2\right\}^2 -16\left[\frac{\Delta_B}{2}\Delta_B'^2\left(\frac{1}{E+\delta-\Delta_B'}-\frac{1}{E+\delta+\Delta_B'}\right)\right]^2\leqslant 0. \tag{20}$$

The limiting energies are also analytical.

Again the allowed energy ranges have been drawn on Fig. 6 as a function of $\Delta_B/\Delta_B'$ for $\delta=0$. The number of subbands still increases when compared to $GeSe_2$ and $GeSe_4$.

### C. Small $x$ limit

One could extend these results to lower values of $x$ corresponding to $GeSe_8$, $GeSe_{10}$,... It is clear that the number of discrete states in the $s$ and $\tau$ bands will increase gradually. The number of subbands derived from the bonding and antibonding states will also increase. The Ge atoms will not interact and can be considered as isolated impurities. In this limit it is thus interesting to consider the case of pure selenium chains first and then the problem of one germanium atom connected to four semi-infinite selenium chains by its $sp^3$ hybrids.

The pure Se case leads to trivially simple results in our model. As we only consider intrachain interactions, all densities of states have a one-dimensional nature. The widths of the different bands are: $4|\beta_{ss}|$ for the $s$ band, $4\Delta_B'$ for the bonding band, $4|\beta_{\tau\tau}|$ for the $\tau$ band, and finally $4\Delta_A'$ for the antibonding band. They have been chosen in order to correctly reproduce existing densities of states.

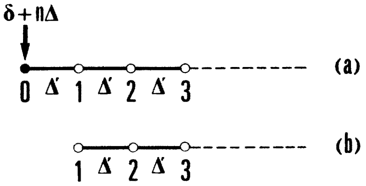


FIG. 8. Linear chains equivalent to the Ge impurity problem ($\Delta'$ stands for $\Delta_A'$ or $\Delta_B'$).

The problem of one Ge atom connected to four semi-infinite Se chains can be solved completely analytically. For this one must first build one $s$-like and three $p$-like combinations of the four bonding or antibonding orbitals which are connected to the Ge atom. Their energies are $E=\delta+n\Delta$ ($n=-3$ for $s$ states, $n=+1$ for $p$ states; $\Delta$ equals $\Delta_B$ or $\Delta_A$ and $\delta$ is the Ge-Se bonding or antibonding level relative to the Se-Se one). The problem then becomes equivalent to the linear chain pictured on Fig. 8(a). This can be solved using the Green's-function method and the Dyson's equation

$$G=g+gVG. \tag{21}$$

Here $g$ is the resolvent $(E-h)^{-1}$ corresponding to an unperturbed Hamiltonian $h$, $G$ the resolvent corresponding to a perturbed Hamiltonian $H$, $V$ being the perturbation. We want to calculate $G_{00}$ in the notation of Fig. 8(a). Let us first choose $H$ to be the total Hamiltonian, $V$ the potential connecting site 0 to site 1. From (21) one easily obtains[30]

$$G_{00}=1/(E-\delta-n\Delta-\Delta'^2 g_{11}). \tag{22}$$

Now $g_{11}$ can be determined from the solution of the semi-infinite pure Se chain alone [Fig. 8(b)]. If one applies the same technique to that case, noting the fact that cutting one atom from a semi-infinite Se chain leads to the same semi-infinite chain, one obtains

$$g_{11}=1/(E-\Delta'^2 g_{11}) =(E/2\Delta'^2)\{1\pm[1-(4\Delta'^2/E^2)]^{1/2}\}. \tag{23}$$

Injecting (23) in (22) finally leads to

$$G_{00}=1/\{\tfrac{1}{2}E-\delta-n\Delta\pm[(\tfrac{1}{2}E)^2-\Delta'^2]^{1/2}\}. \tag{24}$$

All eigenvalues of $H$ must be poles of $G_{00}$. They can either lie in the allowed energy range $|E|\leqslant 2|\Delta'|$ of the pure Se chain, or outside this range where they become localized states. These are thus given by the equation

$$\tfrac{1}{2}E - \delta - n\Delta = \pm\,[(\tfrac{1}{2}E)^2 - \Delta'^2]^{1/2}\,, \qquad (25)$$

which finally leads to

$$E = \delta + n\Delta + \Delta'^2/(n\Delta + \delta)\,. \qquad (26)$$

One can easily solve this equation in the four distinct situations we have to consider:

$$\Delta = \Delta_B,\quad \Delta' = \Delta'_B,\quad n = 3 \text{ or } -1\,,$$

$$\Delta = \Delta_A,\quad \Delta' = \Delta'_A,\quad n = 3 \text{ or } -1\,.$$

The corresponding localized states are shown on Fig. 5(a) with their symmetry labelling: $s_B, p_B, s_A, p_A$ ($s$-like or $p$-like, bonding or antibonding). Comparison of Figs. 5(a) and 5(d) clearly shows that these states are already apparent in the density of states of $GeSe_4$.

## V. DISCUSSION

We shall first summarize the results for the density of states as $x$ decreases from the value 0.33 corresponding to $GeSe_2$. We shall then discuss the optical properties and compare them to recent experimental data which have been obtained by one of us.[31,32] We also discuss the main features that should be observed in photoemission spectra.

The main results are the following: (a) $s$ and $\tau$ bands: these are narrow for $GeSe_2$ and widen as $x$ decreases with the apparition of a fine structure: two peaks for $GeSe_4$ ($x = 0.2$), three for $GeSe_6$ ($x = 0.14$), then tending towards a continuous distribution characteristic of pure Se. (b) bonding and antibonding bands: both split into two parts. The situation is analogous to the metallic range of the Leman, Thorpe, and Weaire Hamiltonian.[3,4] In $GeSe_2$ the lower subband contains one state per germanium atom while the upper one contains three of them. For decreasing $x$ one should tend towards the pure Se situation with Ge atoms contributing as impurities. These introduce localized states indicated by arrows on Fig. 5(a). This is practically the case for $GeSe_4$. The relative importance of these states is porportional to $x$.

We predict a fundamental energy gap equal to 2.6 eV for $GeSe_2$, 2.5 eV for $GeSe_4$, and decreasing continuously down to 2 eV as $x$ tends to zero. This is essentially due to the widening of the $\tau$ band as the number of selenium atoms in a chain increases. In the small $x$ limit the Ge localized $s$ antibonding states would tend to lower the gap with respect to 2 eV, but their relative importance is negligible. This tendency is confirmed experimentally, the gap decreasing from 2.5 eV for amorphous $GeSe_2$ (2.8 eV for the crystal) to about 2 eV for amorphous Se.

From our model it is also possible to predict the position of eventual peaks in optical absorption as well as their evolution with $x$. Let us first do this without considering the possible selection rules which we discuss later. For $GeSe_2$ there could be a first peak at 3 eV ($\tau \rightarrow s$ antibonding) of width 1 eV, then a second peak starting at 4 eV and ending at 6 eV ($p$ bonding $\rightarrow s$ antibonding; $\tau \rightarrow p$ antibonding). One should then gradually tend towards the Se situation where a first peak should occur between 2 and 6 eV ($\tau$ band $\rightarrow$ antibonding band) the second one starting at 6 eV up to 10 eV (bonding $\rightarrow$ antibonding). This is effectively the tendancy exhibited by the experimental reflectivity spectra.[31,32] For $GeSe_2$ the second peak begins at 4.5 eV while for pure Se it would start at more than 6 eV.

To obtain a more detailed information it becomes necessary to include the effect of selection rules. There is a strong selection rule in all $Ge_xSe_{1-x}$, namely that $s$-like states (on Ge atoms) can only make transitions to $p$-like states and vice versa. For this let us remember that all flat bands are pure $p$-like. For a wide band it is easy to see that when one of its extrema is degenerate with a flat band it is pure $p$ like. For a wide band it is easy to see that when one of its extrema is degenerate with a flat band it is pure $p$-like; if this is not the case it is pure $s$-like. This leads us to the following qualitative conclusion that when a wide band is bounded by: (a) two flat bands, it is mostly $p$-like; (b) only one flat band, it is $sp$-like; (c) no flat band, it is mostly $s$-like. This is coherent with Fig. 5(c).

Other loose selection rules can be obtained by considering what happens on selenium atoms. Let us consider only intra-atomic transitions. With this assumption there can be transitions only from the $s$ band to the $p$ antibonding band are from the $p$ bonding band to the $p$ antibonding band. No transitions from the $\tau$ band are allowed. This is confirmed by a more elaborate calculation taking nearest neighbors into account.[33] Thus to give an interpretation of the pure selenium experimental spectrum it is necessary to invoke a non-negligible coupling between the $\tau$ band and the bonding band, leading to a bonding population in the $\tau$ band. This is confirmed by a direct numerical calculation[33] and the chemical shift interpretation,[28] the bonding character of the $\tau$ band being of order 20%. The same considerations should hold true for the $Ge_xSe_{1-x}$ compounds.

In $GeSe_2$ the $\tau$ band will strongly couple with $p$-like bonding states. Thus the two absorption peaks (2.6–3.6 eV and 4–6 eV) will correspond respectively to transitions from the $\tau$ band and the $p$ bonding band to the $s$-like antibonding band. In $GeSe_4$ again the $\tau$ band will couple strongly to $p$-like bonding states. The first peak ($\tau \rightarrow s$-like antibond-

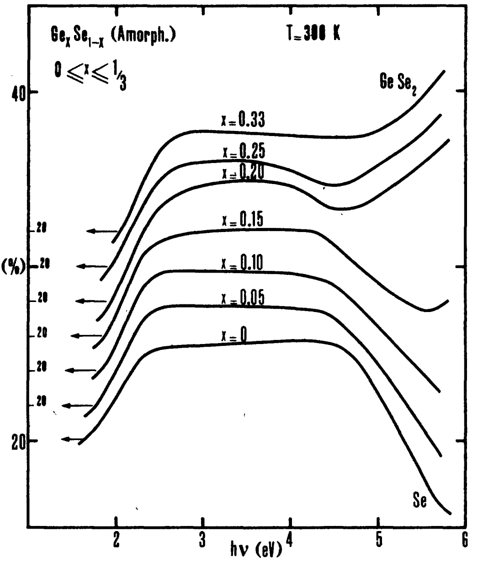


FIG. 9. Reflectivity spectra of amorphous $Ge_xSe_{1-x}$ $(0 \leqslant x \leqslant \frac{1}{3})$ at room temperature.

ing) will lie between 2.5 and 3.6 eV), a second weaker one ($\tau \rightarrow$ higher partly $s$-like antibonding) from 3.3 to 4.5 eV, another peak ($p$ bonding to lower $s$ antibonding) at about 4.8 eV, and so on.

It becomes clear that the essential difference in optical properties between the $Ge_xSe_{1-x}$ system and pure Se is due to the existence of the upper $p$-like bonding states and the lower $s$-like antibonding states. In the small $x$ limit the direct transition between them is equal to 4.6 eV [it is indicated on Fig. 5(a)]. This peak will then exist in all $Ge_xSe_{1-x}$ systems but its relative intensity will decrease as $x$ tends to zero. This evolution is confirmed by experiment (Fig. 9), except that the experimental values of the peaks are slightly higher than our predicted values.

Another experimental feature can be explained. This is the fact that the fundamental energy gap in crystalline $GeSe_2$ is 0.3 eV greater than in amorphous $GeSe_2$. This is probably due to the more important fluctuations in the interatomic distances and in the $\theta$ angle. These introduce a spreading of the parameters, especially $\beta$ and $\Delta'$, which will widen the allowed bands and thus reduce the gap (such a spreading already exists in the crystal but it should be more important in the amorphous phase).

## CONCLUSION

In this theoretical work we have studied the electronic structure of $Ge_xSe_{1-x}$ compounds. This was done in the composition range $0 \leqslant x \leqslant \frac{1}{3}$ using a simple tight-binding approximation. We have derived first a molecular model leading to flat degenerate bands. We have then included further interactions between the molecular states in order to describe the widening of these bands. We have demonstrated for $GeSe_2$, $GeSe_4$, and $GeSe_6$ the existence of gaps within the bands derived from the bonding states and the antibonding states, these gaps being related to the short-range order.

Finally, we have also considered the $x \rightarrow 0$ limit, treating analytically the problem of one germanium atom bonded to four semi-infinite selenium chains.

To compare our theoretical results to recent experimental informations concerning the optical properties of these compounds, we have determined our parameters from a consideration of pure Ge and pure Se separately. In this way we have been able to predict correctly the variations in optical properties as $x$ decreases: decrease of the gap and existence of two absorption peaks, the second one shifting to higher energies. Detailed predictions concerning the valence bands await experimental photoemission results to be confirmed.

We thus can safely conclude that this simple calculation leads to a correct description of the overall optical properties of these systems. At the time being it would be very interesting to perform photoemission studies in order to confirm the trends which we predict for the valence bands. All that one can say is that our predictions for the valence bands are qualitatively similar to the known situation for[8,9] $SiO_2$. A detailed comparison between $SiO_2$ and $GeSe_2$ together with a generalization of our results will be the subject of a forthcoming paper.

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