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TIGHT-BINDING CALCULATIONS OF THE VALENCE BANDS OF DIAMOND AND ZINCBLENDE CRYSTALS

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Tight-Binding Calculations of the Valence Bands of Diamond and Zincblende Crystals*

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Abstract

Using the tight-binding method, we have calculated the valence band structures and densities of states for C, Si, Ge, GaAs and ZnSe. We obtain very good agreement with other calculations when we include all nearest and one second nearest neighbor interactions. The effects of the various interactions on the density of states are discussed.

I. Introduction

The tight-binding approach to the problem of the electronic energy levels in solids is intuitively very appealing. The method provides a real space picture of the electronic interactions which give rise to the particular features of the energy band structure, density of states, etc. This is extremely useful in studies of how these features change when the electronic configuration is altered. The tight-binding method is most practical when only a few types of electronic interactions are dominant. In such a case an adequate description of the system of interest can be obtained by specifying a small number of interaction parameters. In this way a qualitative description of the valence bands can be obtained[1-6] for materials in the diamond, zincblende and other structures.

In this paper we show that a tight-binding method using a few interaction parameters gives accurate results for the valence bands of the diamond and zincblende crystals C, Si, Ge, GaAs, and ZnSe. The tight-binding method we use is equivalent to that of Slater and Koster.[6] It can also be regarded as a more complete version of the Weaire and Thorpe[2] model in which interactions between more distant directed orbitals are included.[7,8] It is necessary to include these extra interactions for a more complete description of the valence bands. In section II we give a brief review of the method and consider the effects of the various interactions on the density of states. We show that the inclusion of all the possible nearest neighbor interactions[9] between s and p-tight-binding states is not sufficient to broaden the "p-like" bands along all symmetry directions. The resulting error in the energies is about 1 eV and occurs mostly for states near the surface of the Brillouin zone. With the inclusion of only one second-nearest-neighbor interaction, the accuracy is greatly improved and the resulting valence band structures and densities of states exhibit all the structures obtained in other calculations.

The band structures, densities of states and interaction parameters for C, Si, Ge, GaAs and ZnSe are discussed in section III. The dependence of the energy levels, along several symmetry directions and at some symmetry points, on the interaction parameters are also given in section III. These expressions are useful for obtaining information about the interaction parameters.

II. Tight-Binding Method

In diamond and zincblende crystals, every atom is tetrahedrally coordinated and there are two atoms in the primitive cell. For each tight-binding basis function centered on these atoms, two Bloch functions can be constructed. For example for a tight-binding basis function $b(\underset{\sim}{r})$ we have the two Bloch functions

$$\psi_0(\underset{\sim}{k},\underset{\sim}{r}) = \frac{1}{\sqrt{N}} \sum_R e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}\, b_0(\underset{\sim}{r}-\underset{\sim}{R}) \ , \tag{1}$$

and

$$\psi_1(\underset{\sim}{k},\underset{\sim}{r}) = \frac{1}{\sqrt{N}} \sum_R e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}\, b_1(\underset{\sim}{r}-\underset{\sim}{R}-\underset{\sim}{\tau}) \tag{2}$$

where $\underset{\sim}{\tau}$ is the vector joining the two atoms in the primitive cell and the subscripts on b refer to the atoms in the primitive cell. In the diamond structure crystals we take $b_0(\underset{\sim}{r}) = b_1(\underset{\sim}{r})$, but in the zincblende crystals the two functions are different.

In order to have

$$\langle\psi_i(\underset{\sim}{k},\underset{\sim}{r})|\psi_j(\underset{\sim}{k},\underset{\sim}{r})\rangle = \delta_{ij} \quad i,j = 0,1 \tag{3}$$

we must require that the tight-binding functions on different atomic sites be orthonormal:

$$\langle b_0(\underset{\sim}{r}-\underset{\sim}{R}_m)|b_1(\underset{\sim}{r}-\underset{\sim}{R}_n-\underset{\sim}{\tau})\rangle = 0 \qquad (4)$$

$$\langle b_i(\underset{\sim}{r})|b_i(\underset{\sim}{r})\rangle = 1 \qquad (5)$$

These conditions can always be accomplished by a method due to Löwdin[6,10] without affecting the symmetry of the basis functions.

The basic problem of the tight-binding method is to find the matrix elements of the Hamiltonian between the various basis states. For example, if we place s-states on each atomic site and take only nearest-neighbor interactions, we find the following 2 × 2 matrix for the eigenvalues:

$$\begin{vmatrix} E_{s_0}-E(\underset{\sim}{k}) & V_{ss}g_0(\underset{\sim}{k}) \\ V_{ss}g_0^*(\underset{\sim}{k}) & E_{s_1}-E(\underset{\sim}{k}) \end{vmatrix} = 0 \ . \qquad (6)$$

The parameters E_{s_0} and E_{s_1} are the energies of the tight-binding s-states:

$$E_{s_0} = \langle s|H|s\rangle \ , \quad E_{s_1} = \langle s_1|H|s_1\rangle \ .$$

In diamond structure crystals $E_{s_0} = E_{s_1}$ and will be denoted simply by E_s. The parameter

$$V_{ss} = 4\langle s_0(\underset{\sim}{r})|H|s_1(\underset{\sim}{r}-\underset{\sim}{\tau})\rangle$$

measures the strength of the nearest neighbor interaction (the factor of 4 is used for convenience) and

$$g_0(\underset{\sim}{k}) = \frac{1}{4}\sum_{j=1}^{4} e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_j} \tag{7}$$

results from the phase difference between the atoms at the four corners of the tetrahedron defined by $\underset{\sim}{\tau}_1 = \frac{1}{4}(1,1,1)a$, $\underset{\sim}{\tau}_2 = \frac{1}{4}(1,\bar{1},\bar{1})a$, $\underset{\sim}{\tau}_3 = (\bar{1},1,\bar{1})a$ and $\underset{\sim}{\tau}_4 = \frac{1}{4}(\bar{1},\bar{1},1)a$ where a is the lattice constant. (To obtain g_0 we assign a phase factor $e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_j}$ to each orbital in Fig. 1. In this way the phase of the Bloch function changes by $e^{i\underset{\sim}{k}\cdot(\underset{\sim}{\tau}_j-\underset{\sim}{\tau}_i)} = e^{i\underset{\sim}{k}\cdot\underset{\sim}{R}}$ in going from atom i to j (i,j = 1,2,...,4), which is consistent with Eqs. 1-2.)

In a similar way, we can obtain the matrix elements of the interactions between the other orbitals. We will consider here only the case where we have only one set of s, p_x, p_y and p_z orbitals at each atomic site. We will denote these by s_0, x_0, y_0, z_0 or s_1, x_1, y_1, z_1 where the subscripts as before refer to the atoms in the primitive cell. The Hamiltonian matrix elements between an s and a p-state on the same atom or two different p-states on the same atom are zero because of symmetry in diamond and zincblende crystals. To describe the interaction of an s-state on one atom with the p-state of a nearest neighbor atom we need one parameter for the group IV crystals and two parameters for the zincblende crystals, where there are different s and p orbitals on the basis atoms. We will denote the interactions between s and p_x orbitals by $V_{s_0p}g_1$ and $V_{s_1p}g_1$ where

$$V_{s_0p} = 4\langle s_0(\underset{\sim}{r})|H|x_1(\underset{\sim}{r}-\underset{\sim}{\tau}_1)\rangle \tag{8}$$

$$V'_{s_1p} = -4\langle s_1(\underset{\sim}{r}-\underset{\sim}{\tau}_1)|H|x_0(\underset{\sim}{r})\rangle \qquad (9)$$

$$g_1(\underset{\sim}{k}) = \frac{1}{4}\left(e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_1}+e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_2}-e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_3}-e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_4}\right) . \qquad (10)$$

For the group IV crystals $V_{s_0p} = V_{s_1p}$ and will be denoted simply by V_{sp}. The minus sign in front of some of the phase factors result from the fact that the sign of the matrix elements $\langle s_0(\underset{\sim}{r})|H|x_1(\underset{\sim}{r}-\underset{\sim}{\tau}_j)\rangle$ and $\langle s_1(\underset{\sim}{r}-\underset{\sim}{\tau}_j)|H|x_0(\underset{\sim}{r})\rangle$ depend[6] on the sign of $(\underset{\sim}{\tau}_j)_x$. For $\underset{\sim}{\tau}_1$ and $\underset{\sim}{\tau}_2$ the sign is positive, for $\underset{\sim}{\tau}_3$ and $\underset{\sim}{\tau}_4$ it is negative. These differences in sign are incorporated into g_1. To obtain the matrix elements for the s-p_y and s-p_z interactions g_1 should be replaced by

$$g_2(\underset{\sim}{k}) = \frac{1}{4}\left(e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_1}-e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_2}+e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_3}-e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_4}\right) \qquad (11)$$

for s-p_y type interactions, and

$$g_3(\underset{\sim}{k}) = \frac{1}{4}\left(e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_1}-e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_2}-e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_3}+e^{i\underset{\sim}{k}\cdot\underset{\sim}{\tau}_4}\right) \qquad (12)$$

for s-p_z type interactions. The matrix elements between s, p and d basis functions have been derived in Ref. (6). The 8 × 8 secular matrix representing all possible nearest neighbor interactions between the tight-binding s and p orbitals centered on each atom in the crystal is:

$$
\begin{array}{cc|cccccccc|}
 & & 4 & 8 & 1 & 2 & 3 & 5 & 6 & 7 \\
 & & s_0 & s_1 & x_0 & y_0 & z_0 & x_1 & y_1 & z_1 \\
\hline
4 & s_0 & E_{s_0}-E(\underset{\sim}{k}) & V_{ss}g_0 & 0 & 0 & 0 & V_{s_0p}g_1 & V_{s_0p}g_2 & V_{s_0p}g_3 \\
8 & s_1 & V_{ss}g_0^{*} & E_{s_1}-E(\underset{\sim}{k}) & -V_{s_1p}g_1^{*} & \boxed{-V_{s_1p}g_2^{*}} & -V_{s_1p}g_3^{*} & 0 & 0 & 0 \\
1 & x_0 & 0 & \boxed{-V_{s_1p}g_1} & \boxed{E_{p_0}-E(\underset{\sim}{k})} & 0 & 0 & V_{xx}g_0 & \boxed{V_{xy}g_3} & \boxed{\overset{g_2}{V_{xy}g_1}} \\
2 & y_0 & 0 & \boxed{-V_{s_1p}g_2} & 0 & E_{p_0}-E(\underset{\sim}{k}) & 0 & \boxed{V_{xy}g_3} & V_{xx}g_0 & V_{xy}g_1 \\
3 & z_0 & 0 & -V_{s_1p}g_3 & 0 & 0 & E_{p_0}-E(\underset{\sim}{k}) & \overset{2}{V_{xy}g_1} & \boxed{V_{xy}\cancel{g_2}^{1}} & V_{xx}g_0 \\
5 & x_1 & V_{s_0p}g_1^{*} & 0 & V_{xx}g_0^{*} & V_{xy}g_3^{*} & V_{xy}g_1^{*} & E_{p_1}-E(\underset{\sim}{k}) & 0 & 0 \\
6 & y_1 & V_{s_0p}g_2^{*} & 0 & V_{xy}g_3^{*} & V_{xx}g_0^{*} & \boxed{V_{xy}g_2^{*}} & 0 & E_{p_1}-E(\underset{\sim}{k}) & 0 \\
7 & z_1 & V_{s_0p}g_3^{*} & 0 & V_{xy}g_1^{*} & \boxed{V_{xy}g_1^{*}} & V_{xx}g_0^{*} & 0 & 0 & E_{p_1}-E(\underset{\sim}{k})
\end{array} = 0.
\tag{13}
$$

g_3 1 2 g

down

8

$(2\pi, 0, 0)$

.25

1

$\cos k_1 = 0$
$\cos k_2, k_3 = 1$
$\sin k_1 = 1$
$k_2 k_3 = 0$

For diamond structure crystals $E_{s_0} = E_{s_1}$, $E_{p_0} = E_{p_1}$ and $V_{s_0p} = V_{s_1p}$ and from this point we will drop the subscripts for these crystals. The functions g_0, g_1, g_2 and g_3 which we have previously defined can also be expressed in the following way:

$$g_0(\underset{\sim}{k}) = \boxed{\cos\pi\frac{\overset{x}{k_1}}{2}}\,\boxed{\cos\pi\frac{\overset{y}{k_2}}{2}}\,\cos\pi\frac{\overset{z}{k_3}}{2} - i\sin\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2} \qquad (14)$$

$$g_1(\underset{\sim}{k}) = -\cos\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2} + i\sin\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2} \qquad (15)$$

$$\boxed{g_2(\underset{\sim}{k})} = -\sin\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2} + i\cos\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2} \qquad (16)$$

$$g_3(\underset{\sim}{k}) = -\sin\pi\frac{k_1}{2}\sin\pi\frac{k_2}{2}\cos\pi\frac{k_3}{2} + i\cos\pi\frac{k_1}{2}\cos\pi\frac{k_2}{2}\sin\pi\frac{k_3}{2} \qquad (17)$$

where $\boxed{\underset{\sim}{k} = \frac{2\pi}{a}(k_1, k_2, k_3)}$ $k_x\ k_y\ k_z$

For diamond structure crystals, the parameters appearing in (13) are related to those of Slater and Koster[6] by

$$\begin{aligned} E_s &= E_{s,s}(000), & E_p &= E_{x,x}(000) \\ V_{ss} &= 4E_{s,s}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}), & V_{xx} &= 4E_{x,x}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}) \\ V_{xy} &= 4E_{x,y}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}), & V_{sp} &= 4V_{s,x}(\tfrac{1}{2}\,\tfrac{1}{2}\,\tfrac{1}{2}) \ . \end{aligned} \qquad (18)$$

Before describing the total interaction between s and p states, it is interesting to look at each one separately. If we set the s-p interaction parameters V_{s_0p} and V_{s_1p} equal to zero the 8 × 8 matrix (13) decouples into a 2 × 2 (Eq. 6) and a 6 × 6 matrix. The energy eigenvalues of the 2 × 2 matrix which describes the s-states is given by

$(\frac{1}{4}\ \frac{1}{4}\ \frac{1}{4})$

$(0, \frac{1}{2}, \frac{1}{2})$

K $e^{ika/2}$ 2π

$\underline{e^{ika/4}}$

$$E(\underset{\sim}{k}) = E_s \pm V_{ss}|g_0(\underset{\sim}{k})| \tag{19}$$

for diamond structure crystals. Although this expression is very simple it nevertheless provides a very good description of the lowest valence band in these crystals. Specifying the width of the band (which is about 3.5-4.0 eV in Si and Ge) determines the band structure to within a few tenths of an eV throughout the Brillouin zone. The largest errors (compared to calculations based on the empirical pseudopotential method (EPM)) occur along the Λ direction and along the Z direction which runs between the symmetry points $X = \frac{2\pi}{a}(1,0,0)$ and $W = \frac{2\pi}{a}(1,\frac{1}{2},0)$ of the Brillouin zone. Along this direction the two bands are degenerate (by symmetry) and have no dispersion. The second valence band in the group IV crystals is p-like at Γ and (19) does not therefore provide a valid description for this band. The band structure and density of states associated with the tight-binding s-like bands is shown in Fig. 2. The dip in the density of states occurs near the line X → W in the Brillouin zone. For $V_{ss} < 0$ the lower energy band is bonding at Γ and the higher band is antibonding. For $V_{ss} > 0$ the order of the bonding-antibonding states is reversed. For the zincblende crystals (6) gives

$$E = \frac{E_{s_0}+E_{s_1}}{2} \pm \sqrt{\left(\frac{E_{s_0}-E_{s_1}}{2}\right)^2 + V_{ss}^2\, g_0 g_0^*} \tag{20}$$

whereas as a result of inversion symmetry the two bands were degenerate at X in the diamond structure crystals, a gap of magnitude $|E_{s_0}-E_{s_1}|$ opens up at X for the zincblende crystals. The maximum of the first band and the minimum of the second still occur at X. But unlike the case of the group IV crystals the bands approach X with zero slope and this results in a sharp peak in the density of states (not shown) for states near X. Except for this structure the s-band density of states in the group IV and zincblende crystals are very similar to each other. The band structure and density of states associated with the six p-states of the group IV crystals is shown in Fig. 3 for $V_{xx} = 0$, $V_{xy} = 6.8$ and $E_p = 0$. The sharp rise and fall of the curve near threshold occurs at Σ_1^{min} and is very similar to the Σ_1^{min} edge observed in the density of states of a number of diamond and zincblende crystals.[11-13] As in the case of the s-bands there is no dispersion along the line joining the points X and W of the Brillouin zone and the dip in the density of states corresponds to these states. The overall shape of the curves for the s and p-states are similar in the region near the density of states minimum. For the zincblende crystals the band structure and density of states for the p-states is similar to that of Fig. 3. The maximum of the lower three bands and the minimum of the upper three bands occur at X and are separated by a gap. The zero slope of the bands at X gives rise, as in the case of the s-states, to a sharp structure in the density of states (not shown). Except for this structure the densities of states of the p-bands in the group IV and the zincblende crystals are very similar as may be expected.

Sometimes it is more convenient (e.g.: surface calculations: Ref. 7) to use tight-binding orbitals directed along the bond directions. The parameters which appear in this approach can be easily related to s and p interaction parameters: This can be done by taking the Hamiltonian matrix elements between the following directed orbitals (see Fig. 3).

$$\phi_1 = \frac{1}{2}(s_0+x_0+y_0+z_0) \qquad \phi_5 = \frac{1}{2}(s_1+x_1+y_1-z_1) \tag{21}$$

$$\phi_2 = \frac{1}{2}(s_0+x_0-y_0-z_0) \qquad \phi_6 = \frac{1}{2}(s_1+x_1-y_1+z_1) \tag{22}$$

$$\phi_3 = \frac{1}{2}(s_0-x_0+y_0-z_0) \qquad \phi_7 = \frac{1}{2}(s_1-x_1+y_1+z_1) \tag{23}$$

$$\phi_4 = \frac{1}{2}(s_0-x_0-y_0+z_0) \qquad \phi_8 = \frac{1}{2}(s_1-x_1-y_1-z_1) \tag{24}$$

The results for diamond structure crystals in Hirabayashi's[7] notation are:

$$\gamma_1 = \langle\phi_i|H|\phi_i\rangle = \frac{1}{4}(E_s+3E_p) \tag{25}$$

$$\gamma_2 = \langle\phi_1|H|\phi_2\rangle = \frac{1}{4}[E_s-E_p] \tag{26}$$

$$\gamma_3 = \langle\phi_1|H|\phi_8\rangle = \frac{1}{16}[V_{ss}-3V_{xx}-6V_{xy}-6V_{sp}] \tag{27}$$

$$\gamma_4 = \langle\phi_2|H|\phi_8\rangle = \frac{1}{16}[V_{ss}+V_{xx}+2V_{xy}-2V_{sp}] \tag{28}$$

$$\gamma_5 = \langle\phi_2|H|\phi_5\rangle = \frac{1}{16}[V_{ss}+V_{xx}-2V_{xy}+2V_{sp}] \tag{29}$$

$$\gamma_6 = \langle\phi_2|H|\phi_7\rangle = \frac{1}{16}[V_{ss}-3V_{xx}+2V_{xy}+2V_{sp}] \tag{30}$$

The parameter γ_1 appears in the diagonal matrix elements and can be taken equal to zero. The parameters γ_2 and γ_3 are the same as the parameters V_1 and V_2 of Weaire and Thorpe [2] and from Fig. 4 it can be expected that they represent the most important interactions. The properties of a model Hamiltonian based only on these two types of interactions has been studied in detail by Weaire and Thorpe[2,14] and has been employed in a number of calculations involving crystalline polytypes of Si and Ge.[3] These calculations show that the two parameter model gives a relatively good description of the lower "s-like" valence bands but gives a poor description of the higher p-like bands which appear as delta functions in the density of states. The inclusion of the other interactions broadens the delta functions[8] and gives a better description of the valence bands.

For zincblende crystals we need three extra parameters to describe the overlaps corresponding to nearest-neighbor s-p interactions. The interaction parameters are:

$$\alpha_1 = \langle\phi_1|H|\phi_1\rangle = \tfrac{1}{4}(E_{s_0}+3E_{p_0}) \tag{31}$$

$$\beta_1 = \langle\phi_8|H|\phi_8\rangle = \tfrac{1}{4}(E_{s_1}+3E_{p_1}) \tag{32}$$

$$\alpha_2 = \langle\phi_1|H|\phi_2\rangle = \tfrac{1}{4}(E_{s_0}-E_{p_0}) \tag{33}$$

$$\beta_2 = \langle\phi_7|H|\phi_8\rangle = \tfrac{1}{4}(E_{s_1}-E_{p_1}) \tag{34}$$

$$\alpha_3 = \beta_3 = \langle\phi_1|H|\phi_8\rangle = \tfrac{1}{16}[V_{ss}-3V_{xx}-6V_{xy}-3V_{s_0p}-3V_{s_1p}] \tag{35}$$

$$\alpha_4 = \langle\phi_2|H|\phi_8\rangle = \tfrac{1}{16}[V_{ss}+V_{xx}+2V_{xy}-3V_{s_0p}+V_{s_1p}] \tag{36}$$

$$\beta_4 = \langle\phi_1|H|\phi_5\rangle = \tfrac{1}{16}[V_{ss}+V_{xx}+2V_{xy}+V_{s_0p}-3V_{s_1p}] \tag{37}$$

$$\alpha_5 = \langle\phi_2|H|\phi_5\rangle = \tfrac{1}{16}[V_{ss}+V_{xx}-2V_{xy}+V_{s_0p}+V_{s_1p}] \tag{38}$$

$$\alpha_6 = \langle\phi_2|H|\phi_7\rangle = \tfrac{1}{16}[V_{ss}-3V_{xx}+2V_{xy}+V_{s_0p}+V_{s_1p}] \tag{39}$$

The fact that the interactions represented by α_4 and β_4 are different is caused by the lack of inversion symmetry.

It can be shown that independent of the choice of the interaction parameters $\gamma_1,\ldots,\gamma_6$ (diamond structures) and $\alpha_1,\ldots,\alpha_9$ (zincblendes), the bands have no dispersion along the symmetry direction Z which goes through the points $X = \frac{2\pi}{a}(1,0,0)$ and $W = \frac{2\pi}{a}(1,\frac{1}{2},0)$ of the Brillouin zone. Other calculations such as those based on the empirical pseudopotential method (EPM) show[11] however a dispersion of about one eV between X and W for the upper two valence bands. This dispersion is reflected in the density of states where each of these points gives rise to a characteristic and well resolved peak. To obtain this result in the tight-binding calculation it is necessary to include at least one second nearest-neighbor interaction. Figures 5 show the density of states of a crystal such as Ge with and without second nearest neighbor interactions. For the nearest-neighbor calculation the parameters used were (in eV): $(E_p-E_s) = 8.41$, $V_{ss} = -6.78$, $V_{xx} = 2.62$, $V_{xy} = 6.82$ and $V_{sp} = 5.31$. The second nearest neighbor interaction we have used (in Fig. 7) arises from the overlap of a p_x orbital at the origin with a p_x orbital separated by a lattice vector of the type $(0,\pm\frac{1}{2},\pm\frac{1}{2})a$. Its effect is to change the diagonal matrix elements to $<x_i|H|x_i> \rightarrow E_p + U_{xx} \cos k_2 \cos k_3$, etc. for diamond structure crystals. The interaction U_{xx} is denoted by $4E_{xx}(011)$ in Ref. 6. The interaction parameters when both nearest and second nearest interactions were used (Fig. 5) are: $(E_p-E_s) = 8.41$, $V_{ss} = -6.78$, $V_{xx} = 1.62$, $V_{xy} = 6.82$, $V_{sp} = 5.31$ and $U_{xx} = -1.0$ (eV). The resulting density of states in Fig. 5 shows the separate structures arising from the points X and W. These structures coalesce into a single peak when U_{xx} is set equal to zero. It should be pointed out here that not all second nearest neighbor interactions are useful in broadening the bands along Z. Interactions between two s-states or between s and p states separated by a primitive lattice vector have no effect on the dispersion along Z which is affected mainly by second-nearest neighbor interactions between p-states, the largest[6] one being U_{xx}.

III. Results for C, Si, Ge, GaAs and ZnSe

Since there is not sufficient information on the valence bands of C we have used only nearest-neighbor interactions in our calculations on C. The parameters were obtained by fitting to the results of a variational calculation[15] and they are shown in Tables I. The energy eigenvalues are compared to other calculations in Table II and the resulting band structures and densities of states are shown in Fig. 6. Table II shows good agreement between the simple tight-binding calculation and the variational[15] calculations for the valence bands of C. The results are also very similar to those obtained from an APW[16] calculation. The conduction bands are not well reproduced by the simple tight-binding method except at Γ where the splittings were fitted.

For Si and Ge we have used one second nearest neighbor interaction in addition to the nearest neighbor interactions in the calculations. The nature of these interactions was discussed in Sec. II. The interaction parameters for Si and Ge are listed in Table I and the eigenvalues at some symmetry points in the Brillouin zone are compared to the EPM[17,18] values in Table II. The corresponding band structures and densities of states are shown in Figs. 7-8 and compared to those obtained from recent EPM calculations[17,18] involving non-local (angular momentum dependent) potentials. The agreement in all cases is within a few tenths of an eV for the valence bands but for the conduction bands the method is not as successful. For the sake of completeness we give in Tables III and IV the interaction parameters for C, Si, and Ge if only nearest neighbor interactions are used. These tables show that the strength of nearly every interatomic interaction decreases as we go from C to Si to Ge.

In the case of the zincblende crystals GaAs and ZnSe we have only used nearest neighbor interactions for convenience.

A second nearest neighbor interaction between the Ga or Zn p-states similar to the one used for Si and Ge is, however, necessary to broaden the upper two valence bands. The band structures and densities of states for GaAs and ZnSe are shown in Figs. 9-10 and compared to nonlocal (angular momentum dependent) EPM calculations.[19,20] The interaction parameters are listed in Tables V and VI. The largest error in the band structures occur for the states denoted by Σ_1^{min}. The tight-binding results are actually much closer to older EPM calculations which used local pseudopotentials resulting in upper valence bands which are narrower. Ultraviolet and X-ray photoemission spectra however reveal a larger width for these bands than those indicated by local pseudopotentials and this has been one reason for the use of nonlocal pseudopotentials. The energy eigenvalues at some symmetry points in the Brillouin zone are given in Table VII and compared to the EPM values. For more accurate conduction bands second nearest neighbor interactions, especially those between s and p states, need to be included.

The tight-binding method allows a simple calculation of the s and p character of the valence bands and it is interesting to see how close to ideal sp^3 they are. We have therefore computed the average s and p components of the wavefunctions for the valence bands. We find the top two valence bands to be completely p-like in character in all five crystals. The differences in the s-p characters occur

$k = \frac{2\pi}{a}(1,0,0) \quad \left(\frac{\pi}{2},0,0\right) \quad 3\pi$

$[.5] \; (\pi,0,0)$

mainly for the first two valence bands and these are shown in Table VIII. The average of the s and p-electrons in the four valence bands of C, Si and Ge are, C: 1.25s, 2.75p; Si: 1.4s, 2.6p and Ge: 1.5s, 2.5p. The ratio of the number of s to p electrons is 0.45 for C, 0.54 for Si and 0.6 for Ge. Carbon is therefore as expected the closest to the ideal ratio of 0.333. In GaAs and ZnSe the first valence band is s-like around As and Se. The second valence band is mainly s-like around Ga and Zn and p-like around As and Se.

In the simple model of Weaire and Thorpe[2] in which only two interaction parameters (equivalent to γ_2 and γ_3) are used the bonding and antibonding p states give rise to two δ-functions, each of weight two, in the density of states. The delta functions correspond to doubly degenerate bands which are flat throughout the Brillouin zone. The addition of extra interactions obviously broadens these bands and the δ-functions. It is interesting to see which interactions are most important in producing this broadening of the bands. In the s-p interaction picture, it can be shown that if we set $V_{xx} = V_{xy}$ then we immediately obtain, for both diamond and zincblende crystals, two sets of bands which are doubly degenerate and flat throughout the Brillouin zone independent of the magnitude of the other nearest neighbor interactions. In the directed-orbital representation Eqs. (39)-(30), and Eqs. (38)-(37) show that $V_{xx} = V_{xy}$ corresponds to $\gamma_5 = \gamma_6$ (diamond structures) or $\alpha_5 = \alpha_6$ (zincblendes). Therefore independent of the other interactions between the orbitals if $\gamma_5 = \gamma_6$ or $\alpha_5 = \alpha_6$ we will have flat p bands in the entire Brillouin zone. The broadening of the p bands can be expected to be related to $V_{xx}-V_{xy}$. In fact if we take second nearest neighbor interactions to be zero then in diamond structure crystals the width of the doubly degenerate valence bands is exactly equal to $|V_{xx}-V_{xy}|$ or $4|\gamma_5-\gamma_6|$ with the top of the bands at Γ and the bottom at X. It is obviously not a good approximation to take $V_{xx} = V_{xy}$ or $\gamma_5 = \gamma_6$. In fact we expect the interaction V_{xy} to be stronger than V_{xx} because the overlap between the orbitals x_0, y_1 is larger than the overlap between the orbitals x_0 and x_1. This is born out in Tables I, III, and V.

In order to calculate the interaction parameters we used the dependence of the energy gaps at a few points in the Brillouin zone on the potentials. Along some symmetry directions and at some symmetry points the dependence of the energies on the potentials can be obtained in closed form. Here we list some of these relations a number of which were first obtained in Ref. (6).

For the diamond structure crystals we have:

$$E(\Gamma_1) = E_s + V_{ss}$$

$$E(\Gamma_{2'}) = E_s - V_{ss}$$

$$E(\Gamma_{25'}) = \cancel{E_s} + (\cancel{E_p}-\cancel{E_s}) + \cancel{U_{xx}} - \underline{V_{xx}}$$

$$E(\Gamma_{15}) = E_s + (E_p-E_s) + U_{xx} + V_{xx}$$

At L the doubly degenerate eigenvalues are given by

$$E(L_{3'}) = E_s + (E_p - E_s) \pm \tfrac{1}{2}(V_{xx} + V_{xy})$$

and the four non-degenerate states are:

$$E(L) = E_s + \left(\frac{E_p - E_s}{2}\right) \pm \tfrac{1}{4}(V_{ss} - V_{xx} + 2V_{xy})$$

$$\pm \frac{1}{2}\sqrt{\left[\frac{V_{ss} + V_{xx} - 2V_{xy}}{2} \mp (E_p - E_s)\right]^2 + 3V_{sp}^{\,2}}$$

(There is a slight error in Ref. (6) for this expression, i.e., V_{ss} outside the square root is replaced by V_{sp}.) At X the energy of the doubly degenerate roots are given by

$$E(X_4) = E_s + (E_p - E_s) - U_{xx} \pm V_{xy}$$

$$E(X_1) = E_s + \frac{E_p - E_s + U_{xx}}{2} \pm \frac{1}{2}\sqrt{(E_p - E_s + U_{xx})^2 + (2V_{sp})^2} \; .$$

When U_{xx} is set equal to zero the energy of the bands for $\underset{\sim}{k} = \frac{2\pi}{a}(1,k,0)$ are equal to the energies at X. Along the symmetry direction $\Lambda = \frac{2\pi}{a}(k,k,k)$ only the energy of the doubly degenerate bands can be obtained in closed form:

$$E(\Lambda_3) = E_p + U_{xx}\cos^2\pi k \pm |V_{xx}g_0 - V_{xy}g_1|$$

$$= E_p + U_{xx}\cos^2\pi k$$

$$\pm\sqrt{\left(V_{xx}\cos^3\pi\frac{k}{2} + V_{xy}\sin^2\pi\frac{k}{2}\cos\pi\frac{k}{2}\right)^2 + \left(V_{xx}\sin^3\pi\frac{k}{2} + V_{xy}\cos^2\pi\frac{k}{2}\sin\pi\frac{k}{2}\right)^2} \; .$$

Along the symmetry direction $\Delta = \frac{2\pi}{a}(k,0,0)$, the singly degenerate eigenvalues are given by

$$E(k) = E_s + \frac{E_p - E_s + U_{xx} \pm (V_{ss} + V_{xx}) \cos\pi \frac{k}{2}}{2}$$

$$\pm \frac{1}{2} \sqrt{(E_p - E_s + U_{xx} \pm (V_{xx} - V_{ss}) \cos\pi \frac{k}{2})^2 + (2V_{sp} \sin\pi \frac{k}{2})^2} \ .$$

The doubly degenerate eigenvalues along Δ are given by

$$E = E_s + (E_p - E_s) + U_{xx} \cos\pi k \pm \sqrt{(V_{xx} \cos\pi \frac{k}{2})^2 + (V_{xy} \sin\pi \frac{k}{2})^2}$$

Along the symmetry direction $\Sigma = \frac{2}{a}(k,k,0)$, the energy of the fourth valence band is given by

$$E(k) = E_s + (E_p - E_s) + U_{xx} \cos\pi k - (V_{xx} \cos^2\pi k + V_{xy} \sin^2\pi k) \ .$$

Changing the sign of V_{xx} and V_{xy} gives the result for one of the conduction bands.

The tight binding expressions sometimes give equalities between energies at different points in the Brillouin zone, e.g. $E_4(\frac{1}{2},\frac{1}{2},\frac{1}{2}) = E_4(\frac{1}{2},\frac{1}{2},0) = E_p - \frac{1}{2}(V_{xx} + V_{xy})$, where the subscripts refer to the band index. This equality holds only when a few parameters are used and as it stands it is incompatible with the results of EPM calculations[16,17] which show a difference of 0.1-0.2 eV between the two states. The interaction parameters can be determined by using the following eigenvalues $E(\Gamma_1)$, $E(\Gamma_{25'})$, $E(\Gamma_{15})$, $E(\Gamma_{2'})$, $E(X_1)$, $E(X_4)$, and $E(L_1)-E(L_{2'})$.

For the zincblende crystals the eigenvalues at the symmetry points Γ, X and L are given by

$$E(\Gamma_1) = \frac{E_{s0} + E_{s1}}{2} \pm \sqrt{\left(\frac{E_{s0} - E_{s1}}{2}\right)^2 + V_{ss}^2}$$

$$E(\Gamma_{15}) = \frac{E_{p0}+E_{p1}}{2} \pm \sqrt{\left(\frac{E_{p0}-E_{p1}}{\quad}\right)^2 + V_{xx}^2} \quad \text{(triply degenerate)}$$

$$E(X_1) = \frac{E_{s_0}+E_{p1}}{2} \pm \sqrt{\left(\frac{E_{s_0}-E_{p1}}{2}\right)^2 + V_{s_0p}^2}$$

$$E(X_3) = \frac{E_{s_1}+E_{p0}}{2} \pm \sqrt{\left(\frac{E_{s_1}-E_{p0}}{2}\right)^2 + V_{s_1p}^2}$$

$$E(X_5) = \frac{E_{p0}+E_{p1}}{2} \pm \sqrt{\left(\frac{E_{p0}-E_{p1}}{2}\right)^2 + V_{xy}^2}$$

$$E(L_3) = \frac{E_{p0}+E_{p1}}{2} \pm \frac{1}{2} \sqrt{\left(\frac{E_{p0}-E_{p1}}{2}\right)^2 + (V_{xx}+V_{xy})^2}$$

The energies of the bands for $\underset{\sim}{k} = \frac{2\pi}{a}(1,k,0)$ is equal to the energies at X when only the nearest neighbor interactions listed above are used.

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Table Captions

Table I. Tight-binding interaction parameters (in eV) for C, Si and Ge. The parameter U_{xx} represent a second nearest neighbor interaction. The parameter E_s determines the zero of energy and is arbitrary.

Table II. Comparison of the energy eigenvalues of C, Si and Ge at some symmetry points in the Brillouin zone. The energies in (eV) are measured relative to the top of the valence bands at $\Gamma_{25'}$.

Table III. Interaction parameters (in eV) appropriate for C, Si and Ge when second nearest neighbor interactions are ignored. The parameter E_s is arbitrary.

Table IV. Interaction parameters (in eV) between directed orbitals for C, Si and Ge. These parameters are related to those in Table III through the equations given in Sec. II. The parameter γ_1 can be chosen arbitrarily.

Table V. Interaction parameters (in eV) for GaAs and ZnSe. The four intra-atomic parameters E_{s_0}, E_{s_1}, E_{p_0} and E_{p_1} give information only on the relative energy differences between the tight-binding s and p functions. The subscripts 0 and 1 refer to As (or Se) and Ga (or Zn) respectively.

Table VI. Tight-binding parameters (in eV) between directed orbitals for GaAs and ZnSe. These parameters are related to those in Table V through the relations given in Sec. II.

Table VII. Comparison of the energy eigenvalues of GaAs and ZnSe at some symmetry points in the Brillouin zone. The energies in (eV) are measured relative to the top of the valence bands at Γ_{15}.

Table VIII. The average s and p characters for the valence bands of C, Si, Ge, GaAs and ZnSe.

Table I

	E_s	(E_p-E_s)	V_{ss}	V_{sp}	V_{xx}	V_{xy}	U_{xx}
C	--	7.40	-15.2	10.25	3.0	8.30	--
Si	--	7.20	-8.13	5.88	1.71	7.51	-1.46
Ge	--	8.41	-6.78	5.31	1.62	6.82	-1.0

$\frac{x}{.77}$

.61 Ge

.85 Si

.82
.62

1.22
1.17

.19

$\frac{x}{10.2}$
$\frac{x}{7.7} = .2$

.16

.20

Table II

State	C		Si		Ge	
	Tight-Binding	DVM[a]	Tight-Binding	EPM[b]	Tight-Binding	EPM[c]
$\Gamma_{25'}$	0	0	0	0	0	0
Γ_1	-19.6	-19.6	-12.16	-12.16	-12.57	-12.57
Γ_{15}	6.0	6.0	3.42	3.42	3.24	3.24
$\Gamma_{2'}$	10.8	10.8	4.10	4.10	0.99	0.99
$L_{2'}$	-15.2	-14.5	-9.44	9.57	-10.30	-10.30
L_1	-9.8	-11.7	-7.11	-6.98	-7.52	-7.52
$L_{3'}$	-2.6	-2.4	-1.44	-1.23	-1.60	-1.44
X_1	-11.6	-11.6	-7.70	-7.70	-8.60	-8.56
X_4	-5.3	-5.3	-2.87	-2.87	-3.20	-3.20
$\Sigma(0.5,0.5,0)$	-2.35	--	-3.84	-3.74	-3.80	-3.80
$\Sigma(0.7,0.7,0)$	-1.83	--	-4.32	-4.46	-4.29	-4.29

a. Ref. 15.

b. Ref. 17.

c. Ref. 18.

Table III

	E_s	(E_p-E_s)	V_{ss}	V_{sp}	V_{xx}	V_{xy}
C	--	7.40	-15.2	10.25	3.0	8.3
Si	--	7.20	-8.13	5.88	3.17	7.51
Ge	--	8.41	-6.78	5.31	2.62	6.82

Table IV

	γ_1	γ_2	γ_3	γ_4	γ_5	γ_6
C	--	-1.85	-8.47	-1.01	-0.52	0.81
Si	--	-1.80	-6.13	-0.11	-0.51	0.57
Ge	--	-2.10	-5.46	-0.07	-0.45	0.60

Table V

	E_{s_0}	E_{s_1}	E_{p_0}	E_{p_1}	V_{ss}	V_{s_0p}	V_{s_1p}	V_{xx}	V_{xy}
GaAs	-6.01	-4.79	0.19	4.59	-7.00	7.28	3.70	0.93	4.72
ZnSe	-8.92	-0.28	0.12	7.42	-6.14	5.47	4.73	0.96	4.38

Table VI

	α_1	β_1	α_2	β_2	$\alpha_3=\beta_3$	α_4	β_4	α_5	α_6
GaAs	-1.36	2.25	-1.55	-2.35	-4.44	-0.92	-0.03	-0.28	0.66
ZnSe	-2.14	5.57	-2.26	-1.93	-4.12	-0.51	-0.32	-0.23	0.62

Table VII

State	Tight-binding	EPM[a]	Tight-binding	EPM[b]
Γ_{15v}	0	0	0	0
Γ_{1v}	-12.4	-12.4	-12.1	-12.1
Γ_{1c}	1.6	1.6	2.9	2.9
Γ_{15c}	4.8	4.8	7.5	7.5
L_{1v}	-10.7	-10.5	-11.0	-10.9
L_{2v}	-6.2	-6.7	-4.7	-4.9
L_{3v}	-1.2	-1.2	-0.75	-0.75
L_{1c}	1.7	1.6	3.9	4.1
L_{3c}	6.0	4.8	8.3	7.9
X_{1v}	-9.7	-9.7	-10.6	-10.6
X_{3v}	-6.8	-6.8	-4.8	-4.8
X_{5v}	-2.8	-2.8	-1.9	-1.9
X_{1c}	2.2	2.2	4.7	4.7
Σ_1^{min}	-3.1	-4.1	-2.1	-3.2

a. Ref. 19.

b. Ref. 20.

Table VIII

	Band 1 s,p	Band 2 s,p	Bands 3,4 s,p
C	0.84,0.16	0.39,0.61	~0,1
Si	0.9,0.1	0.45,0.55	~0,1
Ge	0.9,0.1	0.57,0.43	~0,1
GaAs	0.88,0.12	0.61,0.39	~0,1
ZnSe	0.94,0.06	0.42,0.58	~0,1

Figure Captions

Fig. 1. Tight-binding s-orbitals on a tetrahedron.

Fig. 2. Band structure and density of states of s-states for diamond structure crystals.

Fig. 3. Band structure and density of states of p-states for diamond structure crystals.

Fig. 4. Directed sp^3 orbitals on two adjacent tetrahedrons. The different possible interactions of the orbitals on the nearest neighbor atoms are given in Sec. II.

Fig. 5. The density of states of Ge with and without second nearest neighbor interaction. The second nearest neighbor interaction splits the energies at X and W and gives rise to extra structure in the density of states.

Fig. 6. Band structure and density of states of diamond.

Fig. 7. Tight-binding band structure and density of states of Si as compared to the results obtained from empirical pseudopotential calculations. (Ref. 17)

Fig. 8. Tight-binding band structure and density of states of Ge as compared to the results obtained from empirical pseudopotential calculations. (Ref. 18)

Fig. 9. Tight-binding band structure and density of states of GaAs compared to the results of EPM calculations. (Ref. 19)

Fig. 10. Tight-binding band structure and density of states of ZnSe compared to the results of EPM calculations. (Ref. 20)

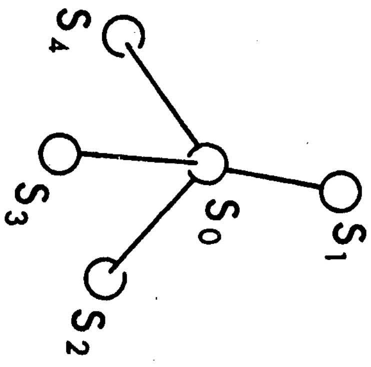
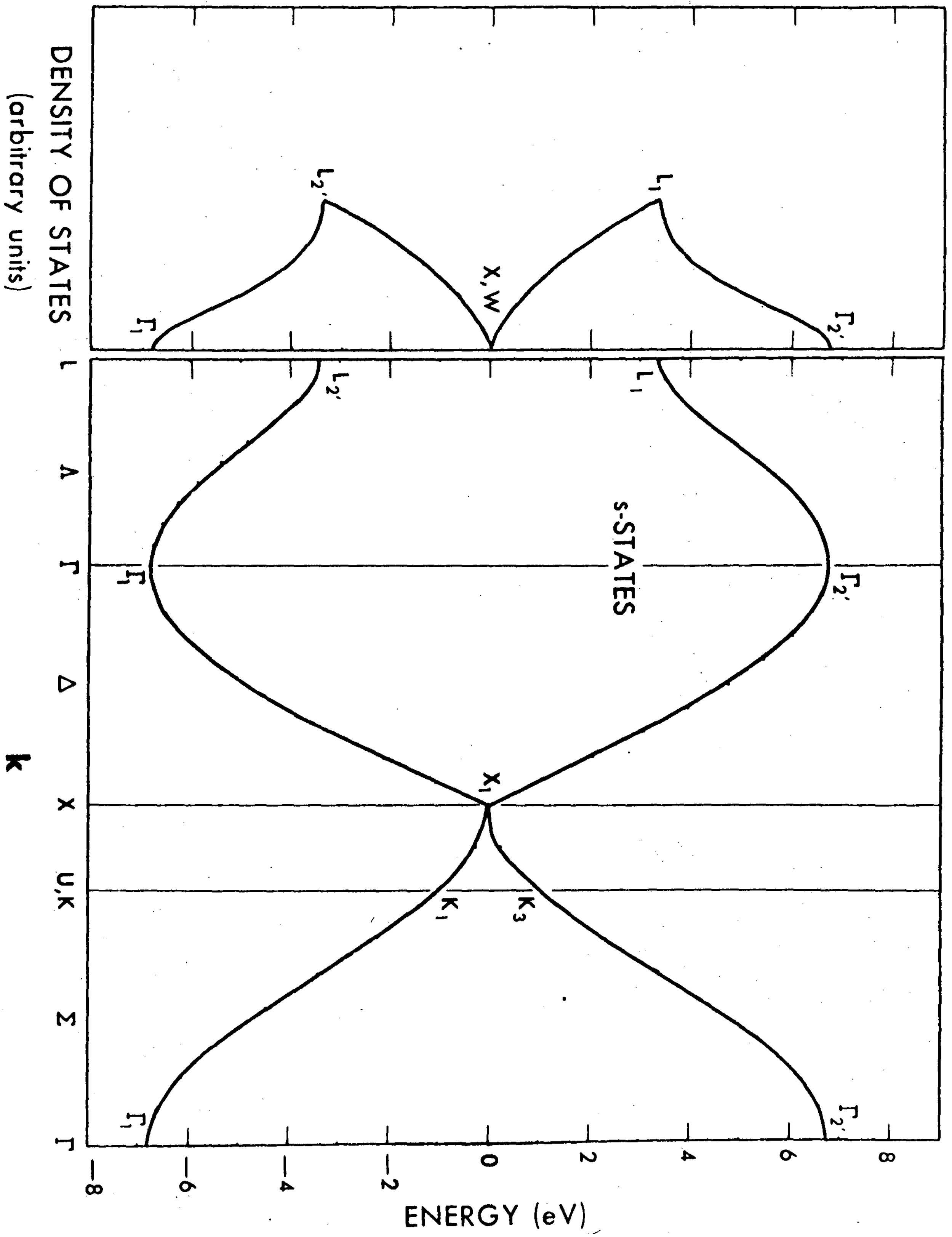


Fig. 1


DENSITY OF STATES
(arbitrary units)
L₁
L₂'
X, W
Γ₁
Γ₂'
s-STATES
L
Λ
Γ
Δ
X
U,K
Σ
k
X₁
K₁
K₃
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−6
−4
−2
0
2
4
6
8
ENERGY (eV)

Fig. 2

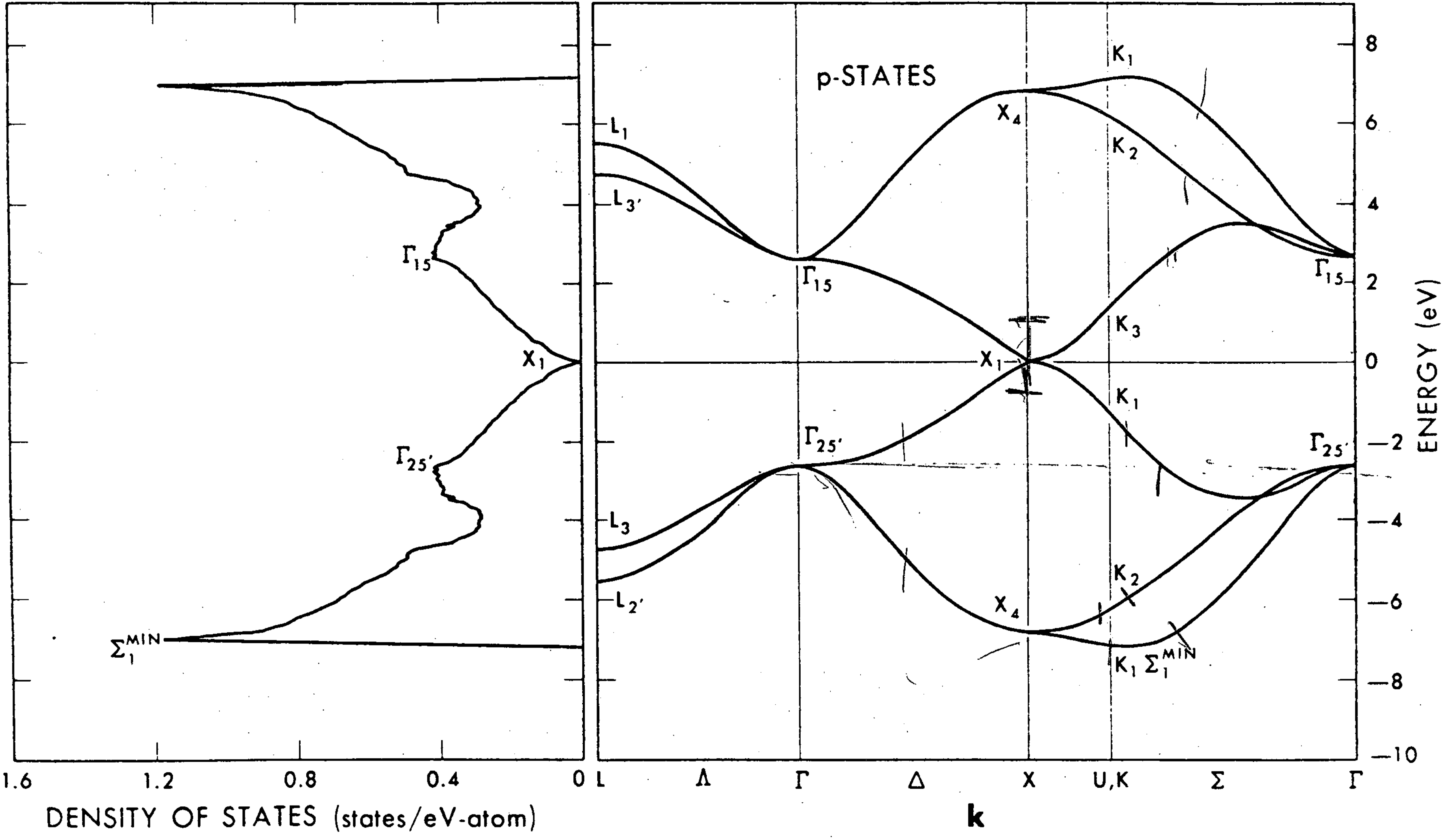
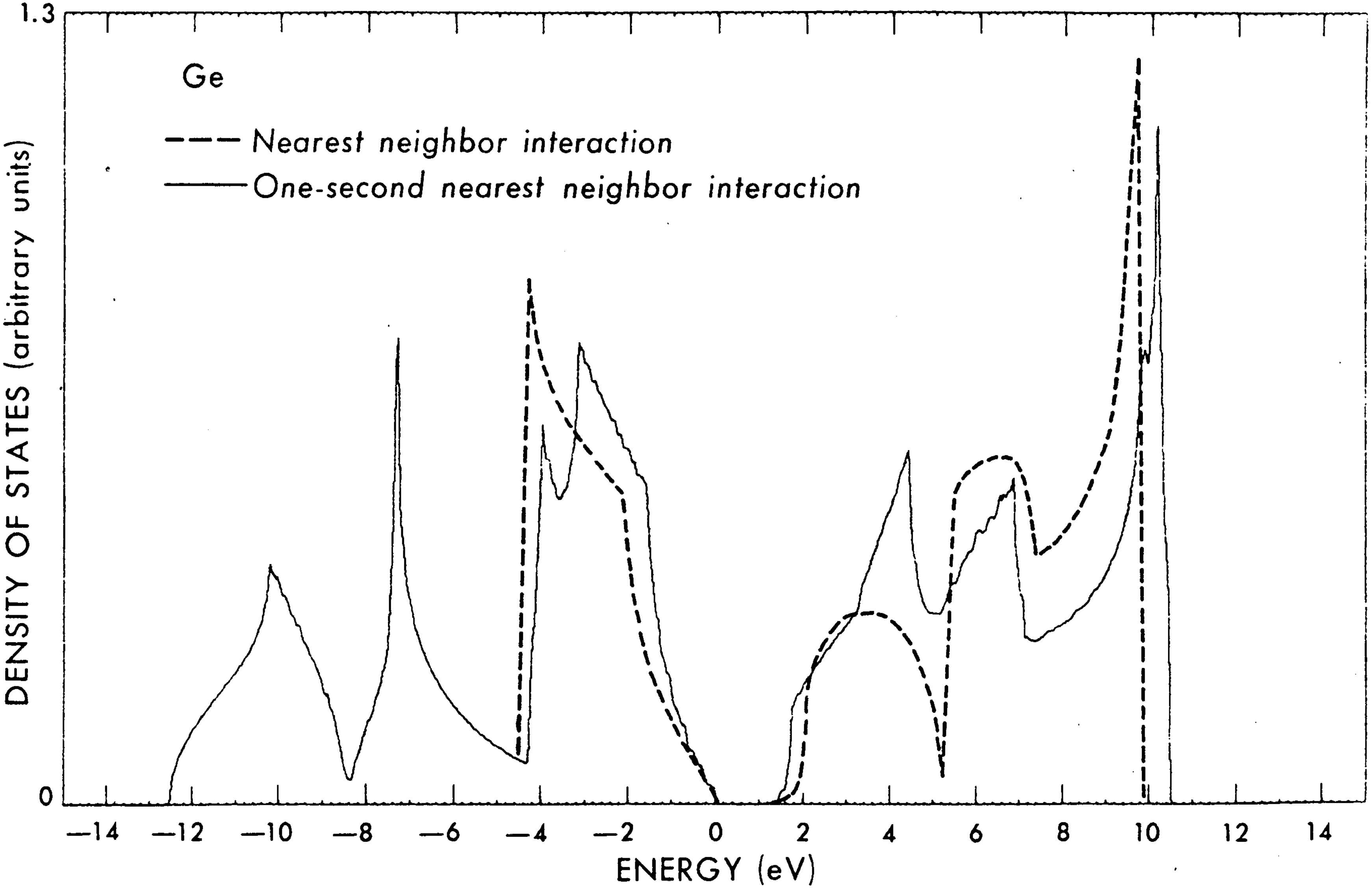

p-STATES
1.6
1.2
0.8
0.4
0
DENSITY OF STATES (states/eV-atom)
Σ_1^{MIN}
$\Gamma_{25'}$
X_1
Γ_{15}
L
Λ
Γ
Δ
X
U,K
Σ
Γ
k
L_1
$L_{3'}$
L_3
$L_{2'}$
Γ_{15}
$\Gamma_{25'}$
X_4
X_1
X_4
K_1
K_2
K_3
K_1
K_2
K_1
Σ_1^{MIN}
Γ_{15}
$\Gamma_{25'}$
8
6
4
2
0
−2
−4
−6
−8
−10
ENERGY (eV)

Fig. 3


1.3
Ge
Nearest neighbor interaction
One-second nearest neighbor interaction
DENSITY OF STATES (arbitrary units)
0
—14
—12
—10
—8
—6
—4
—2
0
2
4
6
8
10
12
14
ENERGY (eV)

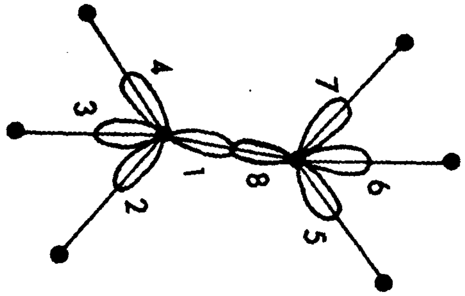


Fig. 4

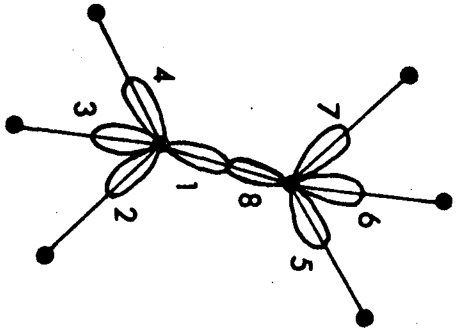
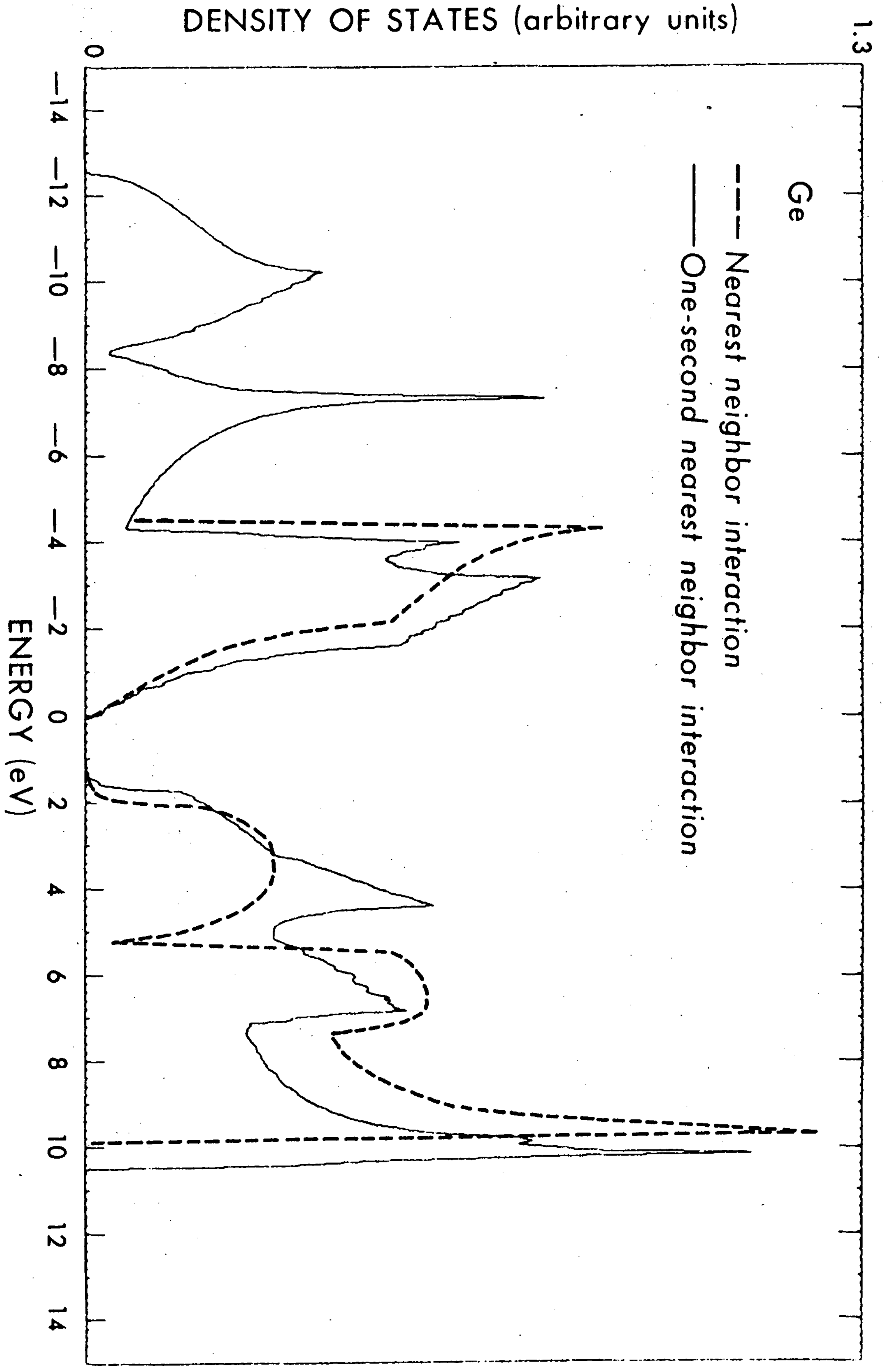


Fig. 4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0
1.3
Ge
Nearest neighbor interaction
One-second nearest neighbor interaction
ENERGY (eV)
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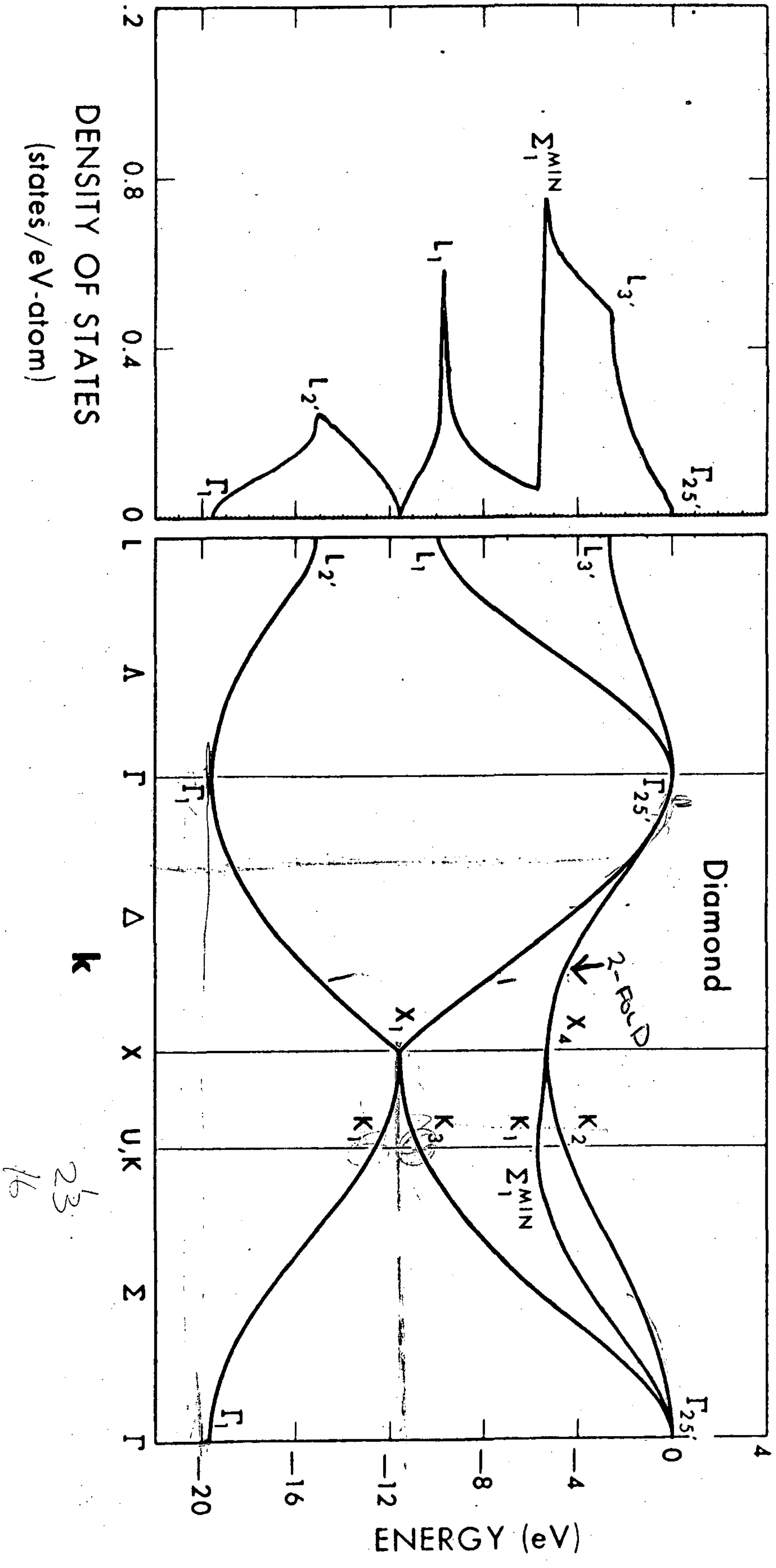
−10
−8
−6
−4
−2
0
2
4
6
8
10
12
14

Fig. 5


DENSITY OF STATES
(states/eV-atom)
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0.8
0.4
0
Σ_1^{MIN}
L_1
$L_{3'}$
$L_{2'}$
Γ_1
$\Gamma_{25'}$
Diamond
2-FOLD
X_1
X_4
K_1
K_3
K_2
L
Λ
Γ
Δ
X
U,K
Σ
k
4
0
−4
−8
−12
−16
−20
ENERGY (eV)

23
16

Fig. 6

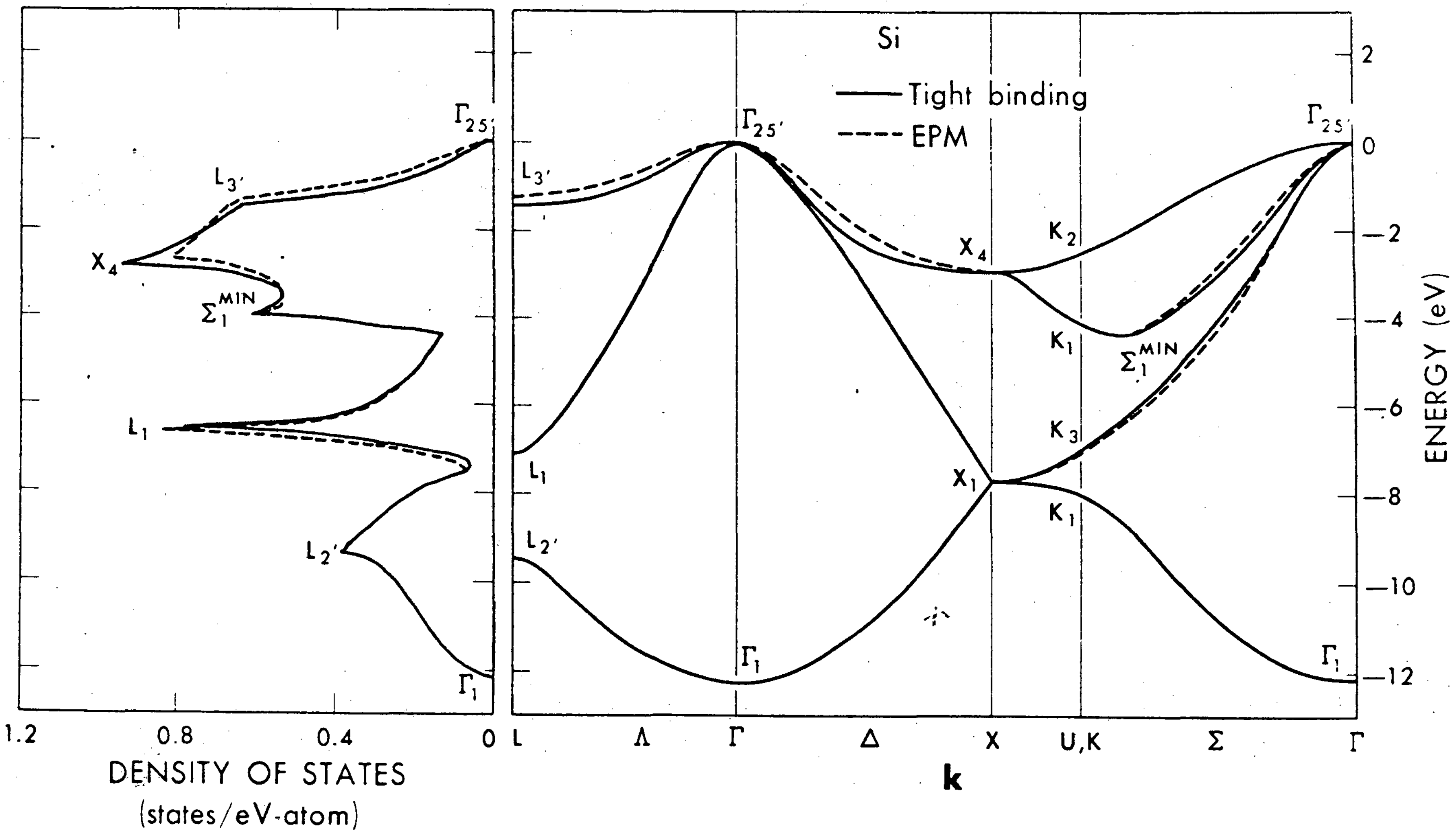
Si
Tight binding
EPM
$\Gamma_{25'}$
$L_{3'}$
X_4
Σ_1^{MIN}
L_1
$L_{2'}$
Γ_1
K_2
K_1
K_3
X_1
1.2
0.8
0.4
0
DENSITY OF STATES
(states/eV-atom)
L
Λ
Γ
Δ
X
U,K
Σ
k
2
0
−2
−4
−6
−8
−10
−12
ENERGY (eV)

Fig. 1

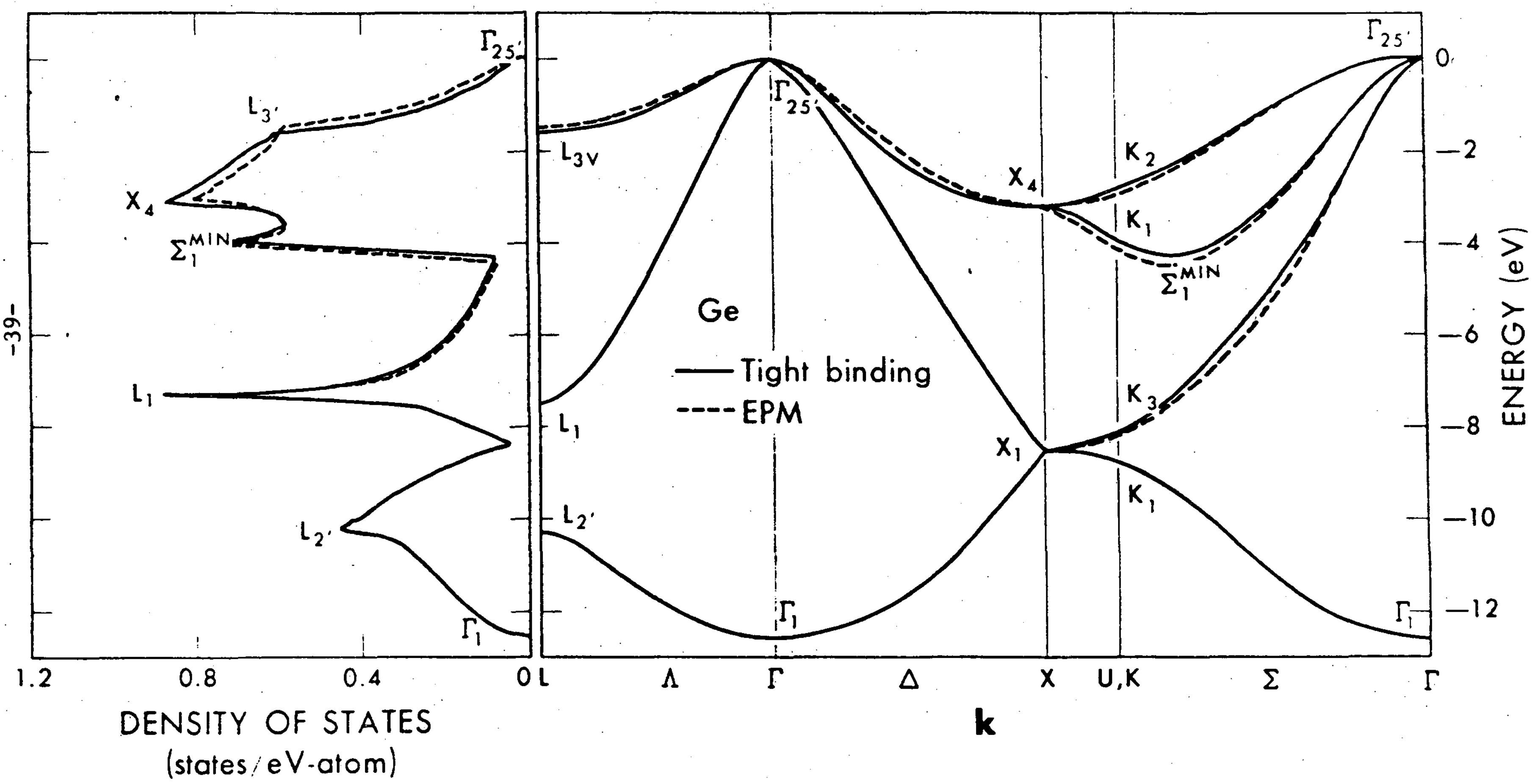
Ge
Tight binding
EPM
$\Gamma_{25'}$
$L_{3'}$
X_4
Σ_1^{MIN}
L_1
$L_{2'}$
Γ_1
L_{3v}
L_1
$L_{2'}$
$\Gamma_{25'}$
Γ_1
X_4
X_1
K_2
K_1
Σ_1^{MIN}
K_3
K_1
$\Gamma_{25'}$
Γ_1
0
−2
−4
−6
−8
−10
−12
ENERGY (eV)
1.2
0.8
0.4
0
DENSITY OF STATES
(states/eV-atom)
L
Λ
Γ
Δ
X
U,K
Σ
Γ
k

Fig. 8

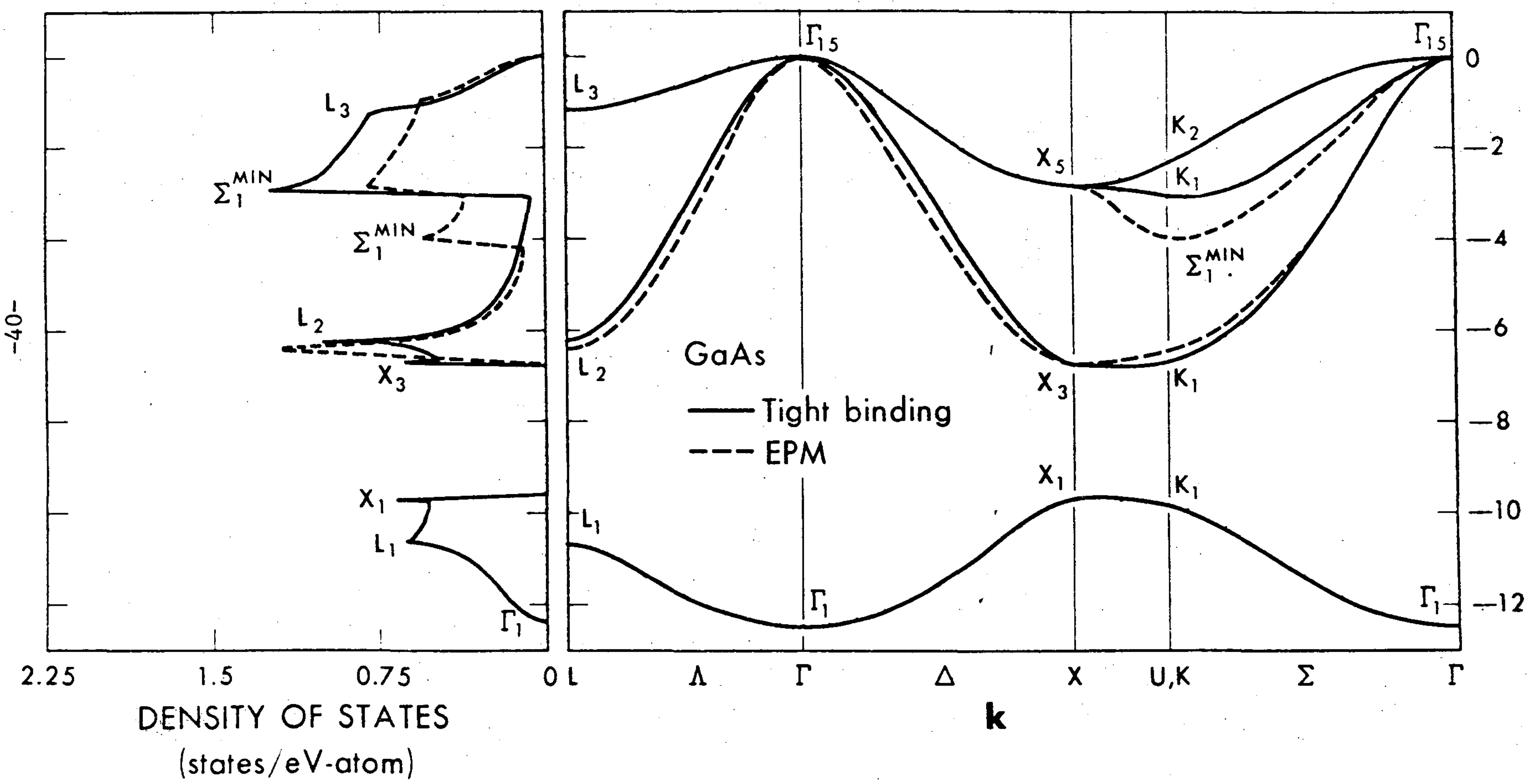
L3
Σ1 MIN
Σ1 MIN
L2
X3
X1
L1
Γ1
2.25
1.5
0.75
0
DENSITY OF STATES
(states/eV-atom)
Γ15
L3
X5
K2
K1
Σ1 MIN
L2
X3
K1
GaAs
Tight binding
EPM
X1
K1
L1
Γ1
Γ1
Γ15
0
−2
−4
−6
−8
−10
−12
ENERGY (eV)
L
Λ
Γ
Δ
X
U,K
Σ
Γ
k

fig. 9

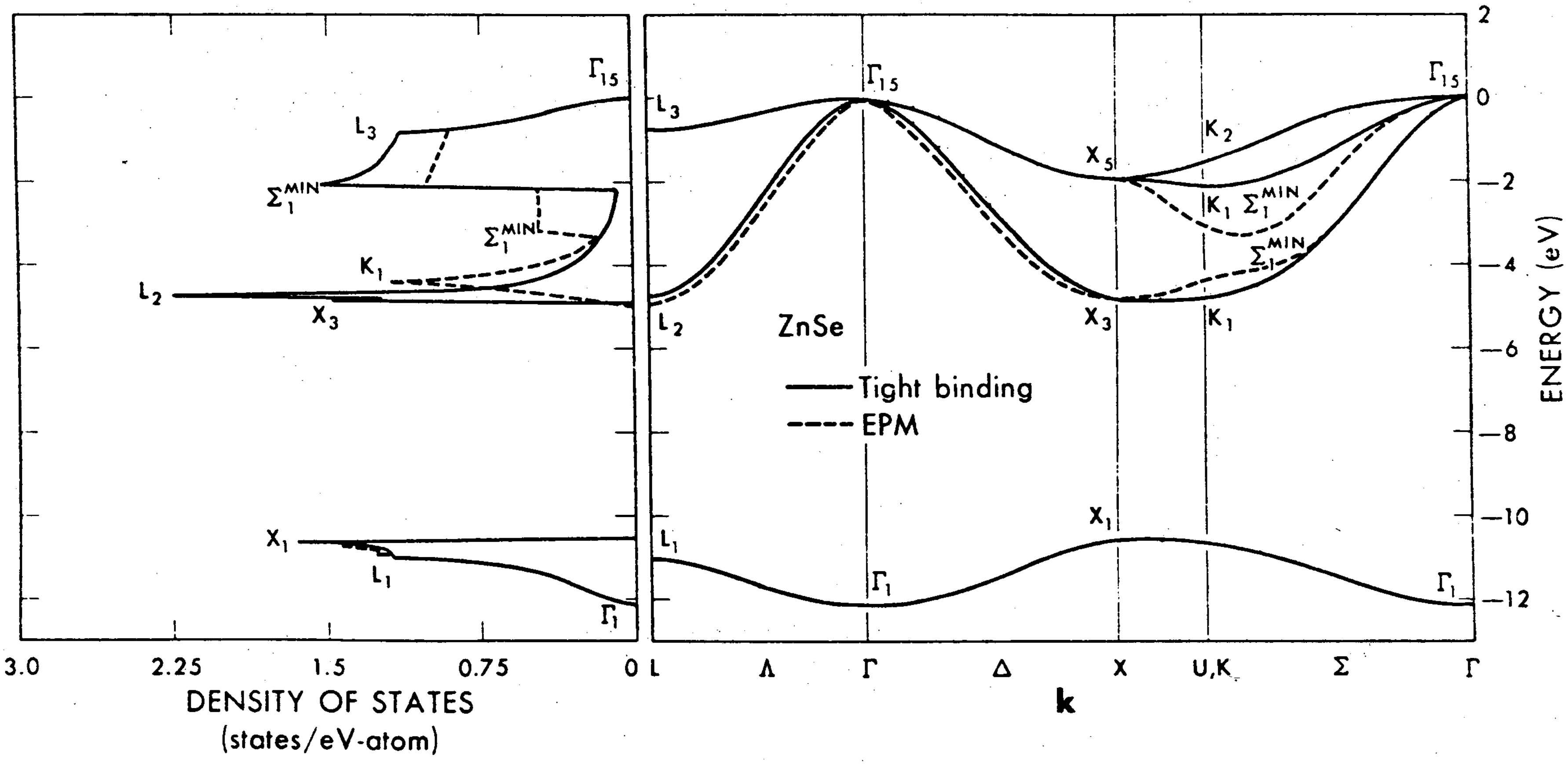
ZnSe
Tight binding
EPM
Γ_{15}
L_3
Σ_1^{MIN}
K_1
L_2
X_3
X_1
L_1
Γ_1
X_5
K_2
ENERGY (eV)
2
0
−2
−4
−6
−8
−10
−12
3.0
2.25
1.5
0.75
0
DENSITY OF STATES
(states/eV-atom)
L
Λ
Γ
Δ
X
U,K
Σ
Γ
k

Fig.10

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