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Effect of ordering on the energy spectrum of narrow-gap III-V alloys: Possibility of the transition into the gapless state

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The energy spectrum of a narrow-gap ordered alloy is calculated using the three-band Kane model. It is shown that when the energy gap, reduced by ordering, becomes negative, the transition to a gapless, rather than a semimetallic, state occurs. In order to study the effects beyond the Kane model, the exact equation for the energy spectrum including the finite hole mass and the band warp is derived. The stability of a gapless state with respect to these higher-band corrections is demonstrated.

The phenomenon of long-range ordering has been observed in nearly all ternary and some quaternary semiconductor alloys.[1] Ordering displays itself in alloys grown by metal-organic chemical vapor deposition within some range of growth conditions.[1] In the case of CuPt-type ordering the cation (or anion) sublattice represents a set of alternating {111}-type atomic planes, preferentially occupied by the different cations (anions).

By doubling the unit cell along the axis, perpendicular to the planes, ordering reduces the symmetry of the crystal and thereby modifies the energy spectrum of the material. The most significant manifestations of the ordering-induced change in the energy spectrum are a substantial reduction of the band gap and a splitting of the valence band, both revealing themselves in the photoluminescence[2,3] and electroreflectance[4] experiments.

Experimentally observed values of the band-gap reduction δE are about 100–150 meV,[5] while the valence-band splitting is usually smaller and was reported to be about 10–20 meV.[2] Values of the band-gap reduction and valence-band splitting for a variety of perfectly ordered alloys have been calculated numerically by Wei and Zunger.[6] Qualitatively the band-gap lowering is caused by the ordering-induced zone folding and consequent level-level repulsion of the states of the Γ and L minima.[6] Due to this repulsion, the bottom of the conduction band moves down. The top of the valence band also splits and is repelled upward as a whole. This is illustrated by the schematic band diagram shown in Fig. 1. The energy distance W_c between the lowest Γ and L conduction-band minima is usually much smaller than the corresponding value for the valence band W_v. In this case the total band-gap reduction can be ascribed to the shift of the conduction band only, which is given by the simple formula for the two-level repulsion.[7]

$$\delta E_c = \left[\left[\frac{W_c}{2} \right]^2 + V_c^2 \right]^{1/2} - \frac{W_c}{2} . \tag{1}$$

Here V_c is the absolute value of the matrix element of the ordering-induced perturbation, taken between the Γ- and L-minima Bloch functions. Note that V_c is proportional to the degree of ordering.

The intriguing question is what will happen with the spectrum in the case when the value of the band-gap reduction is close to or even larger than the band gap of the random alloy. The numerical calculations of band-gap reduction performed in Ref. 6 show this situation to be plausible for some narrow-band alloys. According to their results, the completely ordered $\mathrm{InGaSb_2}$ should have E_g as low as 0.09 eV instead of $E_g^0 = 0.4$ eV (Ref. 8) for the random alloy. The situation is even more drastic for $\mathrm{In_2AsSb}$, which has $E_g^0 = 0.1$ eV in the disordered phase. The position of the Γ_{1c} minimum in the completely ordered compound was predicted to lie lower than the top of the valence band, so that $E_g = -0.28$ eV.[6]

It is remarkable that a simple estimate, based on Eq. (1), is in very good agreement with these results. Namely, we can estimate the value of the band-gap reduction in the completely ordered $\mathrm{InGaSb_2}$ and $\mathrm{In_2AsSb}$ from that known for the "analogous" materials—$\mathrm{InGaAs_2}$ and $\mathrm{Ga_2AsSb}$, respectively. Indeed, $\mathrm{InGaSb_2}$ and $\mathrm{InGaAs_2}$ differ in anions. Ordering involves the atoms in the cation sublattice. One can then expect the value of the matrix element V_c not to change significantly as Sb is replaced by As. The same applies to the pair $\mathrm{In_2AsSb}$-$\mathrm{Ga_2AsSb}$. These materials differ in cations while the ordering occurs in the anion sublattice. Taking for W_c the average values of the Γ-L distance at $x=0$ and 1, $W_c = 0.7$ eV for $\mathrm{InGaAs_2}$ and $W_c = 0.35$ eV for

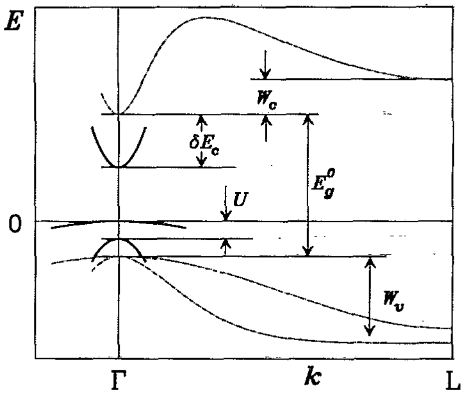

FIG. 1. Schematic illustration of the ordering-induced modification of the energy spectrum of an alloy. Dashed lines show the initial spectrum in the disordered phase; solid lines refer to ordered phase.

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Ga_2AsSb,[8] we find from Eq. (1) the matrix elements V_c for these alloys to be $V_c=\sqrt{\delta E_c(\delta E_c+W_c)}=0.57$ and 0.71 eV, respectively [here we have used the values $\delta E_c=0.32$ eV for $InGaAs_2$ and $\delta E_c=0.56$ eV for Ga_2AsSb (Ref. 6)]. Substituting these values and the values $W_c=0.8$ eV for $InGaSb_2$ and $W_c=1.1$ eV for In_2AsSb (Ref. 8) again into Eq. (1) we obtain $E_g\approx E_g^0-\delta E_c=0.10$ and -0.25 eV for $InGaSb_2$ and In_2AsSb.

The purpose of this paper is to calculate the spectrum of electrons and holes in narrow-gap ordered semiconductors. We demonstrate that when the energy gap becomes small enough to be comparable with the value of the valence-band splitting, the spectrum undergoes a drastic transformation and becomes strongly anisotropic and nonparabolic.

In the case when $\delta E > E_g^0$ it might be expected that the conduction and the valence bands will overlap and one will have a semimetal. We will show, however, that this case corresponds not to a semimetal but to a gapless semiconductor with quite unusual spectra for electrons and holes.

In order to calculate the spectrum we use perturbation theory, assuming the ordering-induced changes in the band structure to be small compared to the typical interband energy distances. Generally, the calculation of the energy spectrum requires all the extrema in the Γ and L points to be taken into account. However, since the energy gap and the valence-band splitting are both much smaller than the energy distances to all other extrema, we can restrict our consideration to three bands only: the conduction band and the heavy- and light-hole valence bands. In other words, we will study the effect of ordering on the energy spectrum in the framework of the standard three-band Kane model with the usual basis[9]

$$s_{\uparrow,\downarrow}=|S\uparrow\downarrow\rangle;\quad h_{\uparrow,\downarrow}=\sqrt{\tfrac{1}{2}}|(X\pm iY)\uparrow\downarrow\rangle\ ,$$

$$l_{\uparrow,\downarrow}=-\sqrt{\tfrac{2}{3}}|Z\uparrow\downarrow\rangle\pm\sqrt{\tfrac{1}{6}}|(X\pm iY)\downarrow\uparrow\rangle\ ,$$

where X, Y, Z, and S denote the periodic Bloch functions of p- and s-type, respectively.

Let us first consider the problem in the spherical approximation, neglecting the effects caused by the cubic symmetry of the crystal. The role of these effects will be studied below. Within the spherical approximation the ordering-induced perturbation has an axial symmetry. Thus we can choose the z axis along the direction of ordering. The perturbation will then be diagonal in the basis of the momentum eigenfunctions. Moreover, six diagonal matrix elements are, obviously, equal in pairs: $(s_\uparrow\delta\hat{\mathcal{H}}s_\uparrow)\equiv(s_\downarrow\delta\hat{\mathcal{H}}s_\downarrow)$, etc., so that the effect of ordering is characterized only by three independent matrix elements, which describe the shifts of the three-band extrema at $\mathbf{k}=0$. If we measure the energy from the top of the shifted heavy-hole band, only two ordering-induced matrix elements will appear in the Hamiltonian $\hat{\mathcal{H}}$ so that the corresponding matrix takes the form

$$\begin{array}{cccccc}
s_\uparrow & s_\downarrow & h_\uparrow & l_\uparrow & l_\downarrow & h_\downarrow \\
\hline
E_g & 0 & Pk_+ & -\sqrt{\tfrac{2}{3}}Pk_z & -\frac{1}{\sqrt{3}}Pk_- & 0 \\
0 & E_g & 0 & \frac{1}{\sqrt{3}}Pk_+ & -\sqrt{\tfrac{2}{3}}Pk_z & Pk_- \\
Pk_- & 0 & 0 & 0 & 0 & 0 \\
-\sqrt{\tfrac{2}{3}}Pk_z & \frac{1}{\sqrt{3}}Pk_- & 0 & -U & 0 & 0 \\
-\frac{1}{\sqrt{3}}Pk_+ & -\sqrt{\tfrac{2}{3}}Pk_z & 0 & 0 & -U & 0 \\
0 & Pk_+ & 0 & 0 & 0 & 0
\end{array} \qquad (2)$$

where $k_\pm=(k_x\pm ik_y)/\sqrt{2}$ and P is the Kane matrix element. In addition to the standard Kane matrix (see, e.g., Ref. 9) the matrix (2) contains the elements $(l_\alpha\hat{\mathcal{H}}l_\alpha)=-U$, which are responsible for the ordering-induced splitting of the valence band. The parameter E_g stands for the exact position of the conduction-band edge, shifted down by ordering. Note, that as the spherical Kane approximation is adopted, the form (2) of the Hamiltonian results from the *symmetry requirements only*.

The matrix (2) determines three doubly degenerate branches of the energy spectrum which are the solutions of the cubic equation

$$E\{(E-E_g)(E+U)-\tfrac{2}{3}P^2k^2\}=\tfrac{1}{2}UP^2k^2\sin^2\theta\ . \qquad (3)$$

Here θ is the angle between $\mathbf{k}$ and the ordering axis.

The solutions of Eq. (3) for different relations between E_g and U and for three directions of the wave vector $\mathbf{k}$ are shown in Fig. 2. For $\mathbf{k}=0$ the energy positions of the extrema of the branches 1, 2, and 3 are E_g, 0, and $-U$, respectively. At $\theta=0$ ($\mathbf{k}$ is parallel to the ordering axis) branch 1, which for positive E_g corresponds to the conduction band, crosses the heavy-hole branch 2 as E_g becomes negative. The intersection takes place at $k=\pm k_0$, where

$$k_0=\sqrt{3U|E_g|/2P^2}\ . \qquad (4)$$

With the further increase of $|E_g|$, branch 1 meets the light-hole branch 3 and the inversion of the branches occur (see Fig. 2). From the evolution of the spectrum at $\theta=0$ it might seem that the case of negative E_g corresponds to a semimetal. However, it is seen from Fig. 2 that the gap in the spectrum opens at finite θ. The crucial point is that in the absence of doping the Fermi-level position is $E_F=0$, i.e., the Fermi level coincides with the energy at which branches 1 and 2 cross each other at $\theta=0$. This is a consequence of the fact that the number of states with energies $E<0$ is just equal to the number of states in the valence band of the disordered alloy. Thus we conclude that the energy spectrum at $E_g<0$ corresponds to the *gapless semiconductor* with the conduction band having the almost flat bottom originating from the states of branch 2. On the contrary, the spectrum of the valence band includes part of the former branch 1.

The flat region in the conduction band implies that the longitudinal (in the direction of ordering) mass is infinitely large. The transverse mass is finite and is determined by the parameter E_g in a way which is usual for the Kane model: $m^c_\perp=\hbar^2|E_g|/P^2$. For the small energies $|E|\ll U$, $|E_g|$, Eq. (3) can be simplified. Then we get the analytic form of the energy spectrum of the conduction and the upper valence bands,

$$E_{1,2}(\mathbf{k})\approx\frac{U_0(k^2-k_0^2)}{2k_0^2}\left\{1\pm\left[1+\frac{3Uk^2\sin^2\theta}{U_0(k^2-k_0^2)}\right]^{1/2}\right\}, \tag{5}$$

where $U_0=U|E_g|/(U+|E_g|)$.

The density of states in the conduction band, $g(E)$, calculated with the use of Eq. (3), has the form

$$g(E)=\frac{4\sqrt{2U}\,|E_g|^{3/2}}{\pi^2\sqrt{3}P^3}\left[1+\frac{9U+|E_g|}{3U|E_g|}E\right]. \tag{6}$$

We see that the density of states remains finite when E goes to zero: $g(0)=8k_0m^c_\perp/3\pi^2\hbar^2$ as is the case in two-dimensional systems. Indeed, an infinite longitudinal mass makes the spectrum effectively two dimensional. In fact, the finite value of $g(0)$ is an artifact of the Kane model. When the dispersion of the heavy-hole band is taken into account, the density of states vanishes at $E=0$. However, Eq. (3) gives the correct behavior of the density of states in the wide range of energies $\hbar^2k_0^2/2m_h<E\ll\min(U,|E_g|)$, m_h being the heavy-hole mass in the absence of ordering.

We have mentioned above that the spectrum of electrons and holes becomes strongly anisotropic and nonparabolic even in the case when E_g is positive. Indeed, the values of the longitudinal and transverse effective masses in the conduction band as obtained from Eq. (3) for $E_g>0$ are given by

$$m^c_{1\parallel}=\frac{3\hbar^2(E_g+U)}{4P^2},\quad m^c_{1\perp}=\frac{3\hbar^2(E_g+U)E_g}{4P^2(E_g+\frac{3}{4}U)}. \tag{7}$$

When E_g becomes small, $m^c_\perp$ goes to zero, while $m^c_\parallel$ remains constant. This results in the strong anisotropy $m^c_\parallel/m^c_\perp\approx3U/4E_g\gg1$ for $E_g\ll U$.

As follows from Eq. (3) the longitudinal effective mass of a heavy hole remains infinite in the ordered phase. However, the transverse mass becomes finite due to ordering: $m^h_\perp=\hbar^2E_g/P^2$. Note, however, that the parabolic spectrum $E=-\hbar^2k_\perp^2/2m^h_\perp$ applies only in the narrow region, $k_\perp^2\ll6UE_g^2/P^2(3U+|E_g|)$, which is more narrow, the smaller the ordering is.

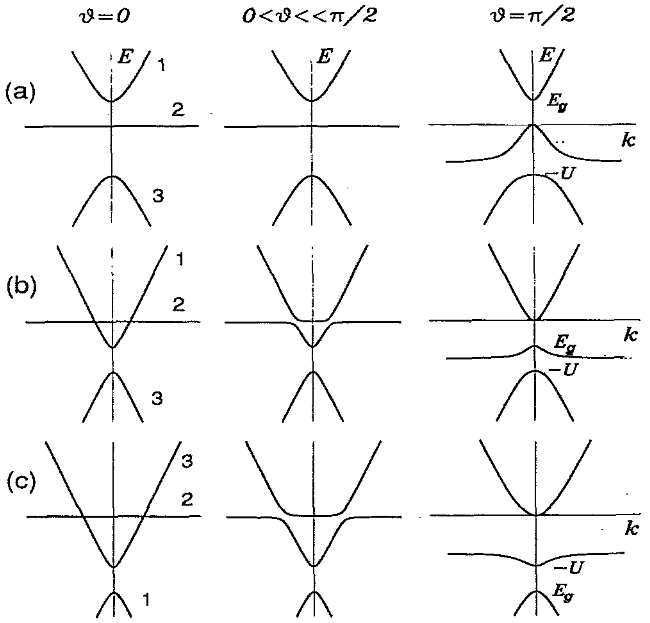

FIG. 2. Evolution of the spectrum with the increase of the ordering parameter, calculated in the frame of the spherically symmetric Kane approximation for three values of the angle between $\mathbf{k}$ and the ordering axis: $\theta=0$, 0.1π, and $\pi/2$, at (a) $E_g=0.5U$, (b) $E_g=-0.5U$, and (c) $E_g=-1.5U$. 1, 2, and 3 label the eigenenergy solutions in the representative directions and for the representative degrees of ordering.

The next important question is whether the prediction about the gapless state at $E_g<0$ survives when the finite mass of the heavy hole and the band warp, caused by the cubic symmetry of the crystal, are taken into account. Indeed, it might happen that small terms, responsible for these effects, can modify the spectrum in such a way that the conduction and valence bands overlap within some narrow energy interval, thus leading to a semimetal. In the latter case the sample would contain a finite and equal amount of free electrons and holes at zero temperature. On the contrary, in the absence of the overlap the concentration of free carriers would fall off as a power law with decreasing temperature. To get the answer to this question we have derived the complete equation which includes all higher-band corrections, which in turn cause the finite heavy-hole mass and warp.

We derive the complete Hamiltonian following the method used in Ref. 10. It is more convenient to write the generalized Hamiltonian in the cubic axes of the crystal. The Hamiltonian consists of three parts. First, the standard Kane Hamiltonian, which takes into account three bands exactly, has in our new representation the same form (2), because of its spherical symmetry. The higher-band corrections are known to give the Luttinger-like 4×4 block based on p functions.[9,11] They also renormalize the band gap and give small quadratic corrections to the diagonal (s-s) matrix elements. Finally, the matrix of the ordering-induced perturbation enters into the Hamiltonian after rotation of its diagonal form to the new axes. As a result we obtain

$$\begin{array}{cccccc}
s_{\uparrow} & s_{\downarrow} & h_{\uparrow} & l_{\uparrow} & l_{\downarrow} & h_{\downarrow} \\
\hline
E_g+\tilde{\gamma}_0k^2 & 0 & Pk_+ & -\sqrt{\frac{2}{3}}Pk_z & -\frac{1}{\sqrt{3}}Pk_- & 0 \\
0 & E_g+\tilde{\gamma}_0k^2 & 0 & \frac{1}{\sqrt{3}}Pk_+ & -\sqrt{\frac{2}{3}}Pk_z & Pk_- \\
Pk_- & 0 & F_h & B & C & 0 \\
-\sqrt{\frac{2}{3}}Pk_z & \frac{1}{\sqrt{3}}Pk_- & B^* & F_l & 0 & -C \\
-\frac{1}{\sqrt{3}}Pk_+ & -\sqrt{\frac{2}{3}}Pk_z & C^* & 0 & F_l & B \\
0 & Pk_+ & 0 & -C^* & B^* & F_h
\end{array} \tag{8}$$

where the parameters F_h F_l, B, and C include the ordering-induced terms and are given by

$$\begin{aligned}
F_{h,l} &= -(\tilde{\gamma}_1 \mp 2\tilde{\gamma}_2)k_z^2-(\tilde{\gamma}_1 \pm \tilde{\gamma}_2)(k_x^2+k_y^2) \, , \\
B &= 2\sqrt{3}\tilde{\gamma}_3k_z(k_x-ik_y)+(1-i)U/2\sqrt{3} \, , \\
C &= \sqrt{3}\{\tilde{\gamma}_2(k_x^2-k_y^2)-2i\tilde{\gamma}_3k_xk_y\}-iU/2\sqrt{3} \, .
\end{aligned} \tag{9}$$

Note that in the new axes the ordering-induced terms are nondiagonal.

In (8) and (9) we have introduced the notation $\tilde{\gamma}_i=(\hbar^2/2m_0)\gamma_i$, m_0 being the free-electron mass. Four dimensionless parameters γ_i are defined as

$$\gamma_0=\frac{m_0}{m_e}-\frac{4m_0P^2}{3\hbar^2E_g^0}, \quad \gamma_\alpha=\gamma_\alpha^0-\nu_\alpha\frac{m_0P^2}{3\hbar^2E_g^0} \, , \tag{10}$$

where $\alpha=1,2,3$, $\nu_1=2$, $\nu_{2,3}=1$; γ_α^0 are the standard Luttinger parameters.[12] As defined, the parameters γ_1, γ_2, and γ_3 are the higher-band corrections to γ_1^0, γ_2^0, and γ_3^0, respectively. The value γ_0 characterizes the higher-band contribution to the electron effective mass.

Note, that contrary to the Hamiltonian (2), the generalized Hamiltonian (8) is written for the particular type of ordering, namely, CuPt-type, when the ordering axis is directed along (111). The Hamiltonian (8) still does not contain small terms, connected with the absence of the inversion symmetry. In the crystalline III-V materials the twofold Kramers's degeneracy of the branches of the spectrum is lifted due to the absence of the inversion symmetry. The corresponding terms in the Hamiltonian are of the relativistic (spin-orbit) origin. They give rise to the small correction, $\pm\alpha k^3$, to the energy spectrum *in the absence of ordering.*[11] This splitting is especially small at small k. In the presence of ordering the top of the valence band is shifted to the point $k=k_0$, where the relativistic terms could be more important. Their magnitude in the region $k \sim k_0$ can be estimated as αk_0^3. Taking $U=|E_g|=100$ meV and the value of α from Ref. 13, $\alpha=40$ eV Å^3 (for GaAs) we obtain $\alpha k_0^3 \approx 0.07$ meV. We see that the correction is small and, thus, the terms caused by the absence of the inversion symmetry can be omitted.

Three doubly degenerate branches of the eigenvalues of the Hamiltonian (8) are the solutions of the following cubic equation:

$$\begin{aligned}
&[E+(\tilde{\gamma}_1-2\tilde{\gamma}_3)k^2]\left\{(E-E_g-\tilde{\gamma}_0k^2)[E+U+(\tilde{\gamma}_1+2\tilde{\gamma}_3)k^2]-\frac{2P^2}{3}k^2\right\} \\
&\quad +k^2\sin^2\theta\left\{k^2(\tilde{\gamma}_2-\tilde{\gamma}_3)f(\theta,\varphi)\left[(\tilde{\gamma}_2+\tilde{\gamma}_3)(E-E_g-\tilde{\gamma}_0k^2)-\frac{P^2}{3}\right]+\frac{3U}{2}\left[2\tilde{\gamma}_3(E-E_g-\tilde{\gamma}_0k^2)-\frac{P^2}{3}\right]\right\}=0 \, .
\end{aligned} \tag{11}$$

Here θ and φ are, respectively, the polar and the azimuthal angles of the wave vector $\mathbf{k}$. The angle φ is measured from the $(11\bar{2})$ direction, perpendicular to the (111) ordering axis. The function $f(\theta,\varphi)$ is defined as $f(\theta,\varphi)=7\sin^2\theta+2\sqrt{2}\sin 2\theta\cos 3\varphi-8$. Equation (11) differs from that derived in Ref. 12 by additional terms, proportional to U, which are caused by ordering. On the other hand, in the Kane limit ($\tilde{\gamma}_i=0$) Eq. (11) reduces to Eq. (3).

It is seen that at $\theta=0$ the heavy-hole branch $E=-(\tilde{\gamma}_1-2\tilde{\gamma}_3)k^2$ still does not interact with the other two branches. For stability of the gapless state the term with $\sin^2\theta$, which is responsible for the opening of the gap at nonzero θ, should be negative. It can be seen that this is the case in Eq. (11). Indeed, at the typical value $k=k_0$ the main terms are those proportional to P^2. The term proportional to U is always negative. The only possibility for the gap not to open at $\theta \neq 0$ occurs if the term proportional to $(\tilde{\gamma}_2-\tilde{\gamma}_3)$ is positive and compensates the second term. The corresponding condition for that is $(\gamma_2-\gamma_3)>m_0P^2/4|E_g|\hbar^2$. It is easy to see that this condition is not met for any realistic values of parameters. Indeed, the parameters $\gamma_{2,3}$ are of the order of unity, while the right-hand side is of the order of $m_0/m_e \sim 10^2$–10^3 for narrow-gap materials.

In conclusion we have demonstrated that ordering in narrow-gap semiconductors leads to a radical change in the energy spectrum, making it strongly anisotropic and nonparabolic (as in the case of $InGaSb_2$) and even causing the transition into a gapless state (as in the case of In_2AsSb).

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