Conduction- and valence-band effective masses in spontaneously ordered $GaInP_2$

Yong Zhang and A. Mascarenhas
National Renewable Energy Laboratory, 1617 Cole Boulevard, Golden, Colorado 80401
(Received 21 December 1994)

An eight-band $\mathbf{k}\cdot\mathbf{p}$ model is developed for zinc-blende semiconductor alloys that exhibit spontaneous CuPt ordering. Energy dispersions and effective masses are calculated analytically for the conduction band and valence band as a function of the degree of ordering. All the effective-mass tensors are found to be diagonal and the energy dispersions are ellipsoidal to terms quadratic in the wave vector when the axis of quantization (the z direction) is chosen along the ordering direction. The change of effective masses is found to satisfy a sum rule when ordering is weak. Numerical results are given for the ordered $GaInP_2$ alloy. We find that, as the order parameter increases, along the ordering direction, $m_{\parallel}$ is unchanged for the heavy-hole band, increases for the light-hole band, and decreases for the spin-orbit split-off band. In the plane perpendicular to the ordering direction, $m_{\perp}$ for the heavy- and light-hole bands decreases, whereas it increases for the split-off band. For the conduction band, both $m_{\parallel}$ and $m_{\perp}$ decrease.

I. INTRODUCTION

Many semiconductor alloys have been found to form ordered structures spontaneously, from which interesting physical properties as well as potential device applications have emerged.[1] The $GaInP_2$ alloy is probably one of the most extensively studied systems. Theoretically, band structures of ordered semiconductors (very short-period superlattices) have been studied for many years. Most previous work has concentrated on the band edge states.[1-3] An interpolation method has been proposed for obtaining the electronic states of a partially ordered semiconductor from those of the fully disordered alloy and the perfectly ordered superlattice.[4] The conduction-band energy dispersion, as well as effective masses, of a partially ordered CuPt alloy have been calculated by a simplified theory.[5] In this theory, the effect of ordering on the conduction band was treated by a two-level model in which only the interaction between the conduction-band states near the Brillouin-zone center and states near the L point was considered. This theory predicted that the conduction-band effective mass always increases due to the ordering effect, as L-point effective masses are generally believed to be larger than that of the Γ point. On the other hand, experimentally, the conduction-band effective mass in a partially ordered $GaInP_2$ crystal has been found to be slightly reduced from its disordered value,[6] in contrast to the theory of Ref. 5. A possible reason for the disagreement is the omission of interaction with the valence band. Roughly speaking, due to the ordering-induced band-gap reduction, the conduction-band effective mass is expected to be reduced. Thus, to be able to predict the change of the conduction-band effective mass correctly, the contribution of the valence band has to be considered. Moreover, the changes of the valence-band effective masses due to ordering have not been studied yet, and are important in understanding various experimental results, such as magnetoluminescence,[7] the band structure of disorder-order-disorder systems,[8] and excitonic properties.

In this paper, we develop an eight-band (two conduction bands and six valence bands) $\mathbf{k}\cdot\mathbf{p}$ model for calculating the band structure and effective masses in a CuPt-ordered alloy. The effects of the folded bands[5] can be incorporated into the current results perturbatively if they are indeed significant, but are ignored in this paper. The theory is applied to the $GaInP_2$-type alloy, which has a relatively large band gap, so a renormalization procedure is employed to decouple the conduction and valence bands. Then both conduction- and valence-band Hamiltonians are solved analytically. All the effective-mass tensors are found to be diagonal, and the energy dispersions are ellipsoidal to terms quadratic in the wave vector when the axis of quantization is chosen along the ordering direction. The effective masses are calculated numerically as a function of the order parameter, and nonparabolicity of the valence-band dispersions is examined. This paper is organized as follows. In Sec. II, we give a brief discussion of the band-edge states. Section III is our major effort, where we present the electronic states at $\mathbf{k}\neq\mathbf{0}$. In Sec. IV, we discuss the physical processes involved in the results, and the possible effects of the folded bands. Section V is a summary of this work. An Appendix is attached which gives details of the derivations.

II. BAND-EDGE STATES OF ORDERED $GaInP_2$

The energy levels of a perfectly CuPt-ordered $GaInP_2$, $(GaP)_1/(InP)_1$ [111] superlattice have been obtained at the Brillouin-zone center by Wei and Zunger[2] from first-principles calculations. It was found that the results of the first-principles calculation for the valence-band maximum can be described by a perturbation model[9,2]

$$E_1=\Delta_{CF}/3 ,$$
$$E_{2,3}=-\tfrac{1}{2}(\Delta_0+\Delta_{CF}/3) \pm\tfrac{1}{2}[(\Delta_0+\Delta_{CF})^2-\tfrac{8}{3}\Delta_0\Delta_{CF}]^{1/2} , \quad (1)$$

where Δ_0 is the spin-orbit splitting of the disordered $GaInP_2$ and Δ_{CF} is the crystal-field splitting of the heavy- and light-hole bands in the absence of spin-orbit coupling. E_1 and $E_{2,3}$ represent the heavy-hole, light-hole, and split-off bands, respectively, with strong mixing among them due to CuPt ordering. The energy reference is the top of the valence band of the disordered $GaInP_2$, and the energy toward the conduction band is chosen to be positive. For perfectly ordered $GaInP_2$, by fitting the calculated results to Eq. (1), Δ_0 and Δ_{CF} were found to be 105 and 200 meV,[2] respectively. The corresponding band-gap reduction was found to be 320 meV.[2]

On the other hand, it has been shown that[3] purely from the point of view of symmetry, the Hamiltonian of ordered $GaInP_2$ has the same symmetry as that of a cubic crystal subjected to a [111] uniaxial stress. Thus, by employing the theory for strain,[10] the perturbation part of the Hamiltonian for CuPt-ordered $GaInP_2$ can be written more generally as follows:

$$h_c=a_c , \quad (2)$$
$$h_1=a_1+d_1[(L_xL_y+L_yL_x)+\text{c.p.}] , \quad (3)$$
$$h_2=a_2(\mathbf{L}\cdot\boldsymbol{\sigma})+d_2[(L_x\sigma_y+L_y\sigma_x)+\text{c.p.}] , \quad (4)$$

where $\mathbf{L}$ is the angular momentum operator, $\boldsymbol{\sigma}$ is the Pauli matrix vector, and c.p. denotes cyclic permutation with respect to the indices x, y, and z. The quantity a_c is a constant which represents the absolute shift of the conduction band, h_1 describes the variation of the valence band without changing spin-orbit coupling, and h_2 describes the change in spin-orbit coupling. The parameters a_i and d_i, in Eqs. (2)–(4) are functions of the ordering parameter η (Ref. 4) which varies from 0 (fully disordered) to 1 (perfectly ordered). According to the theory of Ref. 4, the leading term of the η dependence is η^2 for these parameters. The meanings of constants a_1, a_2, d_1, and d_2 can be seen clearly from the solutions of Eqs. (3) and (4) in a Luttinger-Kohn-type basis:[11]

$$e_1=a-d ,$$
$$e_{2,3}=\tfrac{1}{2}(a+a')-\tfrac{1}{2}(\Delta_0-d) \pm\tfrac{1}{2}[(\Delta_0+d+a-a')^2+8d'^2]^{1/2} , \quad (5)$$

where $a=a_1+a_2$, $a'=a_1-2a_2$, $d=d_1+2d_2$, and $d'=d_1-d_2$. Without considering the rhombohedral distortion (associated with quantities d_1 and d_2), the heavy- and light-hole bands are shifted by an amount $a=a_1+a_2$ and the split-off band is shifted by $a'=a_1-2a_2$, which is equivalent to increasing the spin-orbit splitting by $3a_2$. As in the case of the strain problem,[10] the change in spin-orbit coupling due to the ordering is small according to Wei and Zunger's calculation,[2] since Δ_0 in Eq. (1) is very close to the spin-orbit splitting of 103 meV obtained experimentally for the disordered $GaInP_2$.[12] Ignoring the small quantities a_2 and d_2, we can simplify Eq. (5) to

$$e_1=a_1-d_1$$
$$e_{2,3}=a_1-\tfrac{1}{2}(\Delta_0-d_1)\pm\tfrac{1}{2}[(\Delta_0+d_1)^2+8d_1^2]^{1/2} . \quad (6)$$

Except for a_1, Eq. (6) is the same as Eq. (1) with the substitution $d_1=-\Delta_{CF}/3$. The quantity a_1 represents a rigid shift of the valence band due to the interaction with other bands. The quantity d_1 describes the effect of rhombohedral distortion on the valence bands. If $\Delta_0 \gg d_1$, the heavy- and light-hole splitting can be shown as $e_{12}=e_1-e_2=2|d_1|$. In the first-principles calculation,[2] a_1 has been included in the band-gap reduction. The total change in band gap is $\Delta E_g=a_c-a_1+d_1$. Since many experimental results[12] have shown that the heavy-hole-like state e_1 is the topmost valence band, we know that $d_1<0$. As the band-gap reduction is larger than $|d_1|$, we know that $a_c-a_1<0$ as well. Thus, the total band-gap reduction is $|a_c-a_1|+|d_1|$. Furthermore, due to the repulsion from the folded L-point conduction band,[2] the conduction-band minimum of the ordered $GaInP_2$ is lower than that of the disordered alloy, that is $a_c<0$. However, the shift of the valence-band maximum is a_1-d_1, and the sign of this shift is yet undetermined either from experimental studies or theoretical calculations. If $a_1>0$, the shift is upward and we have a type-I band offset for disorder-order-disorder quantum-well structures; if $a_1<0$ and $|a_1|>|d_1|$, we have a type-II band offset.[8,7] Because of $d_1<0$, the ordering effect is equivalent to that of a [111] tensile stress in terms of symmetry.

Note that even though the parameters a_i and d_i in the Hamiltonians have a η^2 dependence, due to interband coupling, the energy level will not have a linear dependence on η^2 in general. For instance, $E_{2,3}$ given by Eq. (1) does not obey the η^2 dependence, as pointed out in Ref. 3. Thus the interpolation theory of Ref. 4 should only be applied to parameters in the Hamiltonians. As can be seen in Sec. III, the conduction-band and heavy-hole energy dispersions follow the η^2 dependence, which is due to weak interband coupling, so that the energy levels are proportional to a_i and d_i as a result of a first-order perturbation. On the other hand, the light-hole and split-off band dispersions show strong nonlinearity on η^2 due to strong interband coupling.

III. ENERGY DISPERSIONS AND EFFECTIVE MASSES OF ORDERED $GaInP_2$

The next step is to calculate the energy dispersions near $k=0$ and effective masses using a $\mathbf{k}\cdot\mathbf{p}$ perturbative approach. We will treat both disordered and ordered $GaInP_2$ in an eight-band model.

The $\mathbf{k}\cdot\mathbf{p}$ Hamiltonian for the disordered $GaInP_2$ can be directly taken from a previous publication by one of the authors (Zhang[13]) for zinc-blende structures, but the effect due to the lack of inversion symmetry has been ignored for simplicity as usual. The Hamiltonian has the following form:

$$H_{\rm dis}=\begin{bmatrix} H_c & H_{\mathbf{k}\cdot\mathbf{p}} \\ H^{+}_{\mathbf{k}\cdot\mathbf{p}} & H_v \end{bmatrix}, \tag{7}$$

where H_c and H_v are 2×2 (diagonal) and 6×6 matrices for the conduction and valence bands, respectively, with the interaction with the higher bands accounted for by renormalization. $H_{\mathbf{k}\cdot\mathbf{p}}$ describes the coupling between the conduction and valence bands. The matrix elements of Eq. (7) are given in the Appendix [Eqs. (A1) and (A2)]. For ordered $GaInP_2$, adding the matrix forms of Eqs. (2)–(4) to Eq. (7) as perturbations, the Hamiltonian is

$$H_{\rm ord}=H_{\rm dis}+\begin{bmatrix} h_c & 0 \\ 0 & h_v \end{bmatrix}, \tag{8}$$

where $h_v=h_1+h_2$. In Eq. (8), the change in the renormalization caused by the ordering-induced change in the coupling to the higher bands is not considered. $H_{\mathbf{k}\cdot\mathbf{p}}$ is assumed to be unchanged with the ordering because the ordering does not change the lattice constant (in the case of the strain, $H_{\mathbf{k}\cdot\mathbf{p}}$ does change[13]). For the explicit forms of the matrix elements see the Appendix [Eqs. (A3) and (A4)].

Considering the relatively large band gap ($E_g\sim2$ eV), we have renormalized the 8×8 Hamiltonian matrix to 2×2 for the conduction band and 6×6 for the valence band by using the same method which was applied to the strain problem in Ref. 13. The coupling between conduction band valence bands is considered to terms quadratic in wave vector $\mathbf{k}$. The renormalized 6×6 matrices are given in the Appendix [Eqs. (A5)–(A9)]. For the conduction band, the 2×2 matrix is diagonal, and the conduction-band dispersion is given as follows:

$$E_c(\mathbf{k})=a_c+\frac{\hbar^2}{2}\left\{\frac{k^2}{m_0^*}-\frac{2E_p}{3m_c}\left[\frac{2(a_c-a)}{E_g^2}+\frac{(a_c-a')}{E_d^2}\right]k^2+\frac{2E_p}{3m_e}\left[\frac{d}{E_g^2}+\frac{2d}{E_d^2}\right]\times(k_1k_2+k_1k_3+k_2k_3)\right\}, \tag{9}$$

where m_0^* is the conduction-band effective mass in units of the free-electron mass m_e, and E_g and $E_d=E_g+\Delta_0$ are band gaps, all for the disordered alloy. Explicitly,

$$\frac{m_e}{m_0^*}=1+\frac{E_p}{3}\left[\frac{2}{E_g}+\frac{1}{E_d}\right]+C, \tag{10}$$

where $E_p=2|p_{cv}|^2/m_e$, $p_{cv}=\langle S|p_x|X\rangle$ is the interband transition matrix element, and C is the contribution from coupling to other bands outside of the eight-band manifold. C is normally considered as a constant in $\mathbf{k}\cdot\mathbf{p}$ calculations, but it is more complicated when dealing with the ordering effect. In the perfectly ordered case, i.e., a [111] $(GaP)_1/(InP)_1$ superlattice, the dispersion curves of the disordered crystal along the [111] direction (from Γ point to L point) will be folded to a smaller Brillouin zone, and the L point will be folded to the Brillouin-zone center. Because of the zone-folding effect, the folded Λ_{6c} band could have a significant interaction with the first conduction band, and a repulsion between them is expected.[5,14] The interaction may change the conduction-band effective mass in two ways: one way is to reduce the effective mass through reducing the band gap,[6] which has been taken care of in Eq. (9); the other way, because the interaction with the folded band is $\mathbf{k}$ dependent in general, the interaction affects the dispersion near the zone center.[5,6] It is not trivial how to treat the second effect in the same framework of the normal $\mathbf{k}\cdot\mathbf{p}$ theory. However, the second effect can be treated separately, for instance, as was done in Ref. 5, and its contribution may be added to Eq. (9) if it is not negligible but can be treated perturbatively.[1] We will come back to this problem in Sec. IV. Here we will still treat C as a constant, as in Ref. 6.

Note that Eq. (9) is given in a coordinate system with the x, y, and z axes along the [100], [010], and [001] directions. By rotating the coordinate system to have z' along the ordering direction [111] and (x',y') in the plane perpendicular to the ordering direction (for instance, x' along $[11\bar{2}]$ and y' along $[\bar{1}10]$, we can simplify Eq. (9) to an ellipsoidal form:

$$E_c(\mathbf{q})=a_c+\frac{\hbar^2}{2m_{c\perp}}(q_1^2+q_2^2)+\frac{\hbar^2}{2m_{c\parallel}}q_3^2, \tag{11}$$

where $m_{c\parallel}$ and $m_{c\perp}$ are effective masses for wave vector $\mathbf{q}$ parallel and perpendicular to the ordering direction, respectively. The transformation between $\mathbf{k}$ and $\mathbf{q}$ can be found in an early paper by Luttinger,[15] where q_1, q_2, and q_3 are along x', y', and z', respectively. $m_{c\parallel}$ and $m_{c\perp}$ can be expressed as follows:

$$\frac{m_e}{m_{c\perp}^*}=1+\frac{E_p}{3}\left[\frac{2}{E_g}+\frac{1}{E_d}\right]+C+\frac{E_p}{3}\left[\frac{2a_0}{E_g^2}+\frac{a_0'}{E_d^2}\right]-\frac{E_p}{3}\left[\frac{d}{E_g^2}+\frac{2d'}{E_gE_d}\right], \tag{12}$$

$$\frac{m_e}{m_{c\parallel}^*}=1+\frac{E_p}{3}\left[\frac{2}{E_g}+\frac{1}{E_d}\right]+C+\frac{E_p}{3}\left[\frac{2a_0}{E_g^2}+\frac{a_0'}{E_d^2}\right]+\frac{2E_p}{3}\left[\frac{d}{E_g^2}+\frac{2d'}{E_gE_d}\right], \tag{13}$$

where $a_0=a-a_c>0$ and $a_0'=a'-a_c>0$. We see that the rhombohedral distortion of the valence states removes the degeneracy of the conduction band along the parallel and perpendicular directions. This effect was ignored in Ref. 6.

For the valance band, symbolic results for the energy dispersion curves have been obtained by solving the 6×6 matrix (see the Appendix), although it is very complicated. In general, all the valence bands have ellipsoidal dispersions to the order of terms quadratic in $\mathbf{q}$, as long as $\eta\neq0$. However, due to the strong interband coupling (Δ_0 is relatively small), significant nonparabolicity in the dispersions is expected for the valence bands, as will be discussed below. The energy levels to terms quadratic in

q can be written as

$$E_i(\mathbf{q})=e_i+\frac{\hbar^2}{2m_{i\perp}^*}(q_1^2+q_2^2)+\frac{\hbar^2}{2m_{i\parallel}^*}q_3^2 , \tag{14}$$

where $i=1$, 2, and 3, corresponding to the three levels of Eqs. (5) or (6). Here the positive direction of the hole energy has been changed to be downwards. The effective masses of the topmost band (heavy-hole-like) are very simple:

$$\frac{m_e}{m_{\mathrm{hh}\perp}^*}=\gamma_1+\gamma_3+\frac{(a_0-d)E_p}{2E_g^2} , \tag{15}$$

$$\frac{m_e}{m_{\mathrm{hh}\parallel}^*}=\gamma_1-2\gamma_3 , \tag{16}$$

The results for the other two bands are too cumbersome to present here. However, if we ignore the contribution from the change in coupling to the conduction band (which is relatively small for the light-hole and split-off bands, compared to the coupling between them), the results are much simpler (ignoring the contribution of h_2 as well):

$$\frac{m_e}{m_{\mathrm{lh}\perp}^*}=\alpha_1(\gamma_1-\gamma_3)-\alpha_2\gamma_1'+\alpha_3\gamma_3' , \tag{17}$$

$$\frac{m_e}{m_{\mathrm{lh}\parallel}^*}=\alpha_1(\gamma_1+2\gamma_3)-\alpha_2\gamma_1'-2\alpha_3\gamma_3' , \tag{18}$$

$$\frac{m_e}{m_{\mathrm{sh}\perp}^*}=\beta_1\gamma_1'-\beta_2\gamma_3'+\beta_3(\gamma_1-\gamma_3) , \tag{19}$$

$$\frac{m_e}{m_{\mathrm{sh}\parallel}^*}=\beta_1\gamma_1'+2\beta_2\gamma_3'+\beta_3(\gamma_1+2\gamma_3) , \tag{20}$$

with

$$\alpha_1=\frac{(2d_1x+2\Delta_0d_1+6d_1^2)}{x^2-(\Delta_0-3d_1)x} ,$$

$$\alpha_2=\frac{(\Delta_0-d_1)x-\Delta_0^2-3d_1^2}{x^2-(\Delta_0-3d_1)x} ,$$

$$\alpha_3=\frac{4\Delta_0d_1-4d_1x-12d_1^2}{x^2-(\Delta_0-3d_1)x} ,$$

$$\beta_1=\frac{\Delta_0^2+3d_1^2+(\Delta_0-d_1)x}{x^2+(\Delta_0-3d_1)x} ,$$

$$\beta_2=\frac{-4\Delta_0d_1-12d_1^2-4d_1x}{x^2+(\Delta_0-3d_1)x} ,$$

$$\beta_3=\frac{2\Delta_0d_1+12d_1^2-2d_1x}{x^2+(\Delta_0-3d_1)x} ,$$

where $x=[(\Delta_0+d_1)^2+8d_1^2]^{1/2}$. The parameters $\alpha_1,\alpha_2,\alpha_3$ and β_1,β_2,β_3 are so defined that they are all positive when $|d_1|<\Delta_0$. γ_1 and γ_3 are Luttinger parameters which appear in the 4×4 block for the heavy and light holes. γ_1', corresponding to γ_1, appears in the 2×2 block of the split-off band. γ_3', corresponding to γ_3, appears in the matrix elements between the 4×4 and 2×2 blocks (see the Appendix for their definitions). In Eqs. (17) and (18), γ_1'- and γ_3'-related terms are from the coupling to the split-off band, and in Eqs. (19) and (20) γ_3'-, γ_1-, and γ_3-related terms are from the coupling to the light-hole band. When $|d_1|\ll\Delta_0$, we have $\alpha_1\to1$, $\alpha_2\to0$, $\alpha_3\to-4d_1/\Delta_0$, $\beta_1\to1$, $\beta_2\to-4d_1/\Delta_0$, and $\beta_3\to0$, which are the results of the first-order perturbation in which only off-diagonal terms with γ_3' contribute to the coupling between the light-hole and split-off bands.

The effective masses can be calculated numerically from the derived symbolic formalisms as functions of two parameters: d_1 and a_0. However, when plotting experimental data ΔE_g versus d_1 [d_1 is obtained by solving Eq. (6) for e_{12}] for a set of samples with systematic variation in the ordering parameter,[12] we find a linear relationship between ΔE_g and d_1 (see Fig. 1), as expected by the theory.[4] The ratio $r=|\Delta E_g|/|d_1|$ is found to be 6.1 ± 0.4, which corresponds to $|\Delta E_g(1)|/\Delta_{\mathrm{CF}}(1)\approx2$ [the theoretical result is 1.6 (Ref. 2)]. Thus the effective masses can be plotted as a function of a single parameter d_1 by using $a_0=(r-1)|d_1|$. Figures 2(a)–2(d) show the eight effective masses as a function of the degree of ordering using parameters given in Table I. E_g, E_p, and m_0 are taken from Ref. 6, Δ_0 is taken from Ref. 12, γ_1 and γ_3 are the averaged values of GaP (Ref. 16) and InP.[17] For the valence band, the results both with and without the change in conduction-band–valence-band coupling are shown. As expected, the contribution of the conduction band is relatively small (maximum 20% in the perfectly ordered crystal).

We have mentioned that the energy dispersion curves are ellipsoidal to terms quadratic in q. However, strictly speaking, the effective-mass tensors are not always diagonal. We will now briefly discuss the anisotropy, as well as to what extent the parabolic dispersions are valid for each band.

For the heavy-hole-like band, to terms quadratic in q, its effective-mass tensor is exactly diagonal; for the other two valence bands, their effective-mass tensors have off-

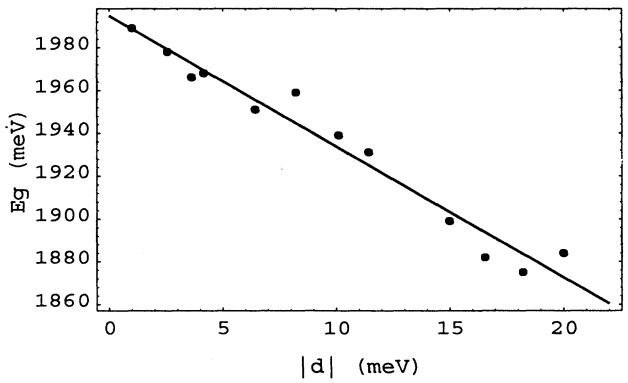

FIG. 1. Band gap E_g of partially ordered $GaInP_2$ as a function of the crystal-field splitting parameter d. Dots are experimental results of Ref. 12, and the line is a linear fit to the data.

TABLE I. Band-structure parameters for the disordered $GaInP_2$ alloy.

E_g (eV)	Δ (meV)	E_p (eV)	$m_0^*(m_e)$	γ_1	γ_2	γ_3
1.991	103	26	0.092	4.55	1.05	1.49

diagonal terms $1/m_{yz} \propto E_p d^2/(E_g^2 E_d)$ in the specific coordinate system we have used. However, they are negligibly small for ordered $GaInP_2$ (typically in the order of 10^{-4} of the diagonal terms). To terms higher order in $\mathbf{q}$, all the valence bands become slightly anisotropic in the (q_x, q_y) plane. The nonparabolicity is more significant in the (q_x, q_y) plane than along the q_z. Figures 3–5 show the computed dispersions, compared with the corresponding parabolic dispersions, for the three valence bands in a partially ordered $GaInP_2$ crystal with $|d| = 15$ meV (which is a typical case corresponding to a heavy-hole–light-hole splittings $e_{12} = 25$ meV or order parameter $\eta^2 = 0.23$). In general, the ordering effect makes the dispersions more isotropic, as we know that strong warping of the valence-band dispersion exists in the III-V semiconductors with zinc-blende structures.

IV. DISCUSSIONS

In this section, we will offer some general remarks about the effect of ordering on the effective masses within the $\mathbf{k}\cdot\mathbf{p}$ model. We will also briefly discuss the effect of the folded L bands on the effective masses.

First, we examine Eqs. (12) and (13) for the conduction-band masses. In both, the second to the last term corresponds to an isotropic reduction in band gap, thus reducing the effective mass of the conduction band; the last term in Eq. (12) or (13) is due to rhombohedral distortion, which increases the mass along the ordering direction and decreases the mass in the plane perpendicular to the ordering direction according to the sign of d_1 ($d \approx d' \approx d_1$).

For the valence-band masses, the situation is rather complicated, in general, because of strong interband coupling among the six bands. However, the results for the heavy-hole-like band, Eqs. (15) and (16), are rather simple. Because the ordering potential does not cause the

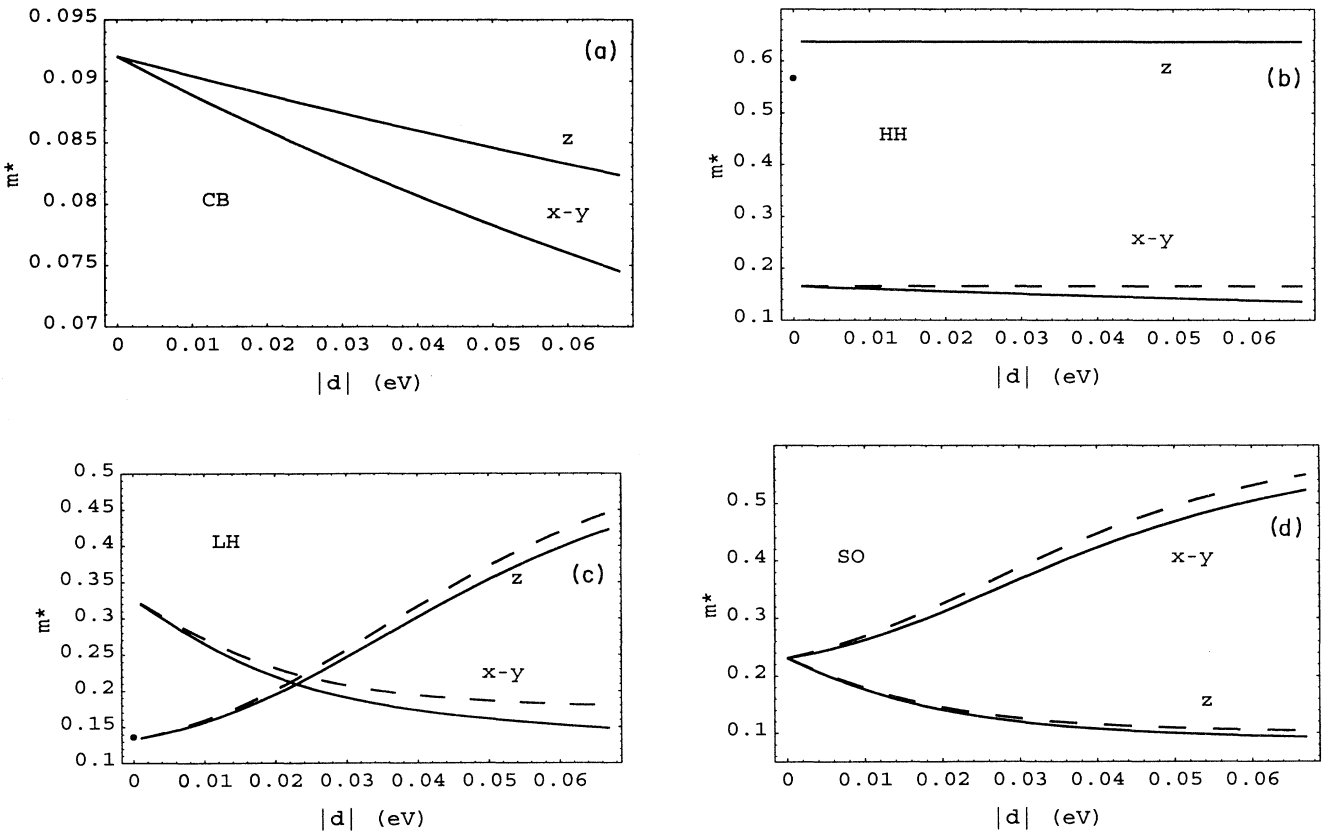

FIG. 2. Effective masses m^* as functions of the crystal-field splitting parmaeter d (a) for the conduction band, (b) for the heavy-hole band, (c) for the light-hole band, and (d) for the spin-orbit split-off band. z stands for the mass along the ordering direction, and x-y stands for the mass in the plane perpendicular to the ordering direction. The isolated dots in (b) and (c) are the in-plane masses in the disordered $GaInP_2$. Dashed lines in (b)–(d) are the results without the contribution of the ordering-induced change in the conduction-band-valence-band interaction.

heavy-hole states along the [111] direction with $k \neq 0$ to couple to either the conduction band or the other valence bands according to symmetry considerations, the effective mass $m_{\mathrm{hh}\parallel}$ does not change. For $m_{\mathrm{hh}\perp}$, the isotropic band-gap reduction tends to reduce the mass and the rhombohedral distortion to increase the mass, which is similar to the case of the in-plane mass of the conduction band. For the light-hole and split-off bands, to see the physical process more clearly, we consider the case of weak ordering, i.e., $d_1 \ll \Delta_0$. In this case, their masses can be given analytically without much difficulty:

$$\frac{m_e}{m^*_{\mathrm{lh}\perp}} = \gamma_1 - \gamma_3 - \frac{4d_1}{\Delta_0}\gamma'_3 + \frac{a_0 E_p}{6E_g^2} + \frac{d_1 E_p}{6}\left[\frac{1}{E_g^2} - \frac{2}{E_g E_d}\right] - \frac{2a_0 d_1 E_p}{3E_g E_d \Delta_0}, \tag{21}$$

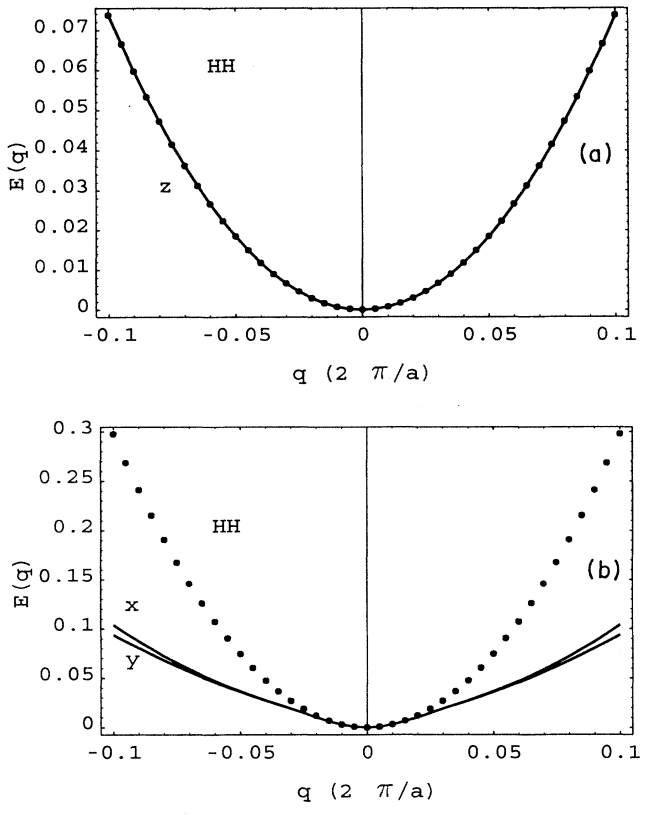

FIG. 3. Exact solutions (lines) and parabolic approximations (dots) for the energy dispersions in a partially ordered $GaInP_2$ with the crystal-field splitting parameter $|d| = 15$ meV, (a) for the heavy-hole band with the wave vector along the ordering direction, and (b) with the wave vector in the plane perpendiculae to the ordering direction. $a = 5.66$ Å is the lattice constant of the $GaInP_2$ alloy.

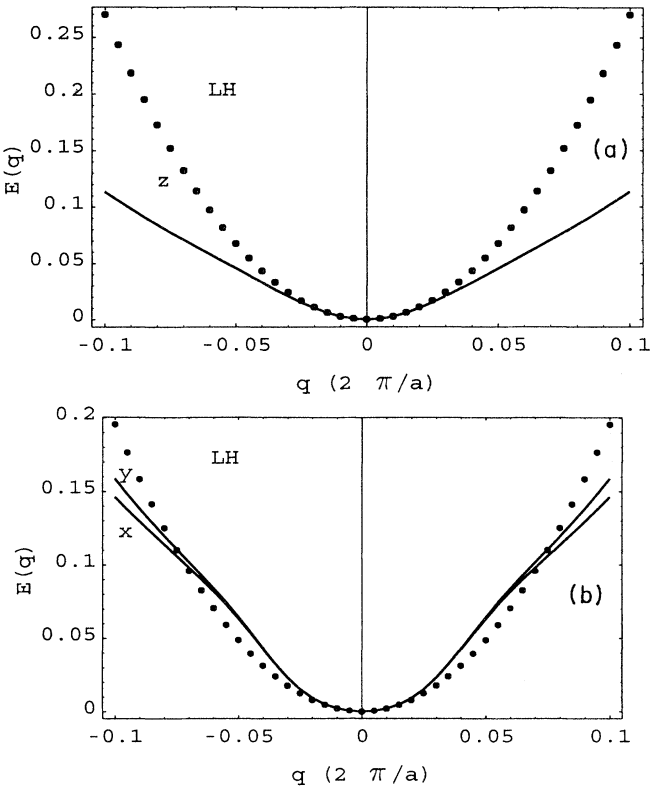

FIG. 4. Same as Fig. 3, but for the light-hole band.

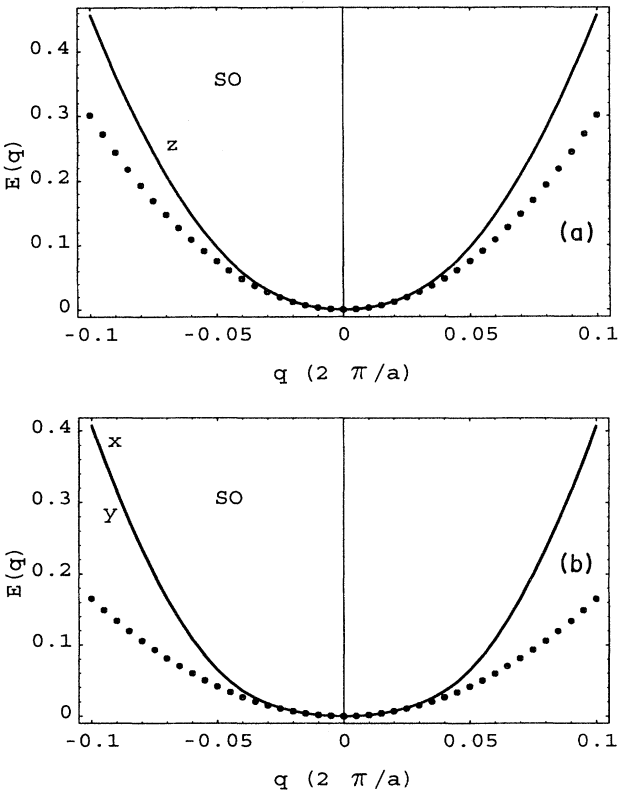

FIG. 5. Same as Fig. 3, but for the split-off band.

$$\frac{m_e}{m^*_{\mathrm{lh}\parallel}}=\gamma_1+2\gamma_3+\frac{8d_1}{\Delta_0}\gamma'_3+\frac{2a_0E_p}{3E_g^2}+\frac{2d_1E_p}{3}\left[\frac{1}{E_g^2}+\frac{1}{E_gE_d}\right]+\frac{4a_0d_1E_p}{3E_gE_d\Delta_0}\ , \tag{22}$$

$$\frac{m_e}{m^*_{\mathrm{sh}\perp}}=\gamma'_1+\frac{4d_1}{\Delta_0}\gamma'_3+\frac{a_0E_p}{3E_d^2}-\frac{d_1E_p}{3E_gE_d}+\frac{2a_0d_1E_p}{3E_gE_d\Delta_0}\ , \tag{23}$$

$$\frac{m_e}{m^*_{\mathrm{sh}\parallel}}=\gamma'_1-\frac{8d_1}{\Delta_0}\gamma'_3+\frac{a_0E_p}{3E_d^2}+\frac{2d_1E_p}{3E_gE_d}-\frac{4a_0d_1E_p}{3E_gE_d\Delta_0}\ . \tag{24}$$

From Eqs. (21)–(24), we can see that the isotropic band-gap reduction always reduces the effective masses, while the rhombohedral distortion tends to decrease $m_{\mathrm{lh}\perp}$ and $m_{\mathrm{sh}\parallel}$ and increase $m_{\mathrm{lh}\parallel}$ and $m_{\mathrm{sh}\perp}$. Since $\Delta_0 \ll E_g$, the major effect is from the direct coupling between the light-hole band and the split-off band, i.e., terms associated with γ'_3 in the above equations. Terms with $1/E_g^2$ or $1/E_d^2$ are related to self-coupling through the conduction band, and terms with $1/E_gE_d$ are the coupling of the light-hole and split-off bands via the conduction band. The last terms are the combined effect of direct and indirect coupling. The ordering-induced coupling can be understood simply as that, along the ordering direction, the light-hole and split-off bands repel each other; in the plane perpendicular to the ordering direction, they attract each other. Note that Eqs. (21)–(24) are not applicable when d_1 is comparable to Δ_0. If they were used for the strong ordering cases, the effective masses ($m_{\mathrm{lh}\parallel}$ and $m_{\mathrm{sh}\perp}$) would become infinite or negative. In fact, when $d_1 \ll \Delta_0$, the six-band model for the valence band can be renormalized to two blocks: a 4×4 block for the heavy- and light-hole bands and a 2×2 block for the split-off band. Equations (21)–(24) are then the solutions of the renormalized four- and two-band modes which treat the coupling between the light-hole and split-off bands perturbatively to the order of d_1/Δ_0. The results for the heavy-hole band are the same in both six- and four-band models, since the heavy-hole band does not couple to the split-off band.

The ordering-induced change in heavy- and light-hole in-plane masses can also be understood as the result of attraction between the two bands. As soon as the ordering effect sets in, i.e., from $\eta=0$ changing to $\eta=0^+$, the effective mass $m_{\mathrm{hh}\perp}$ decreases from an isotropic bulk value $[\gamma_1-(\gamma_2^2+3\gamma_3^2)^{1/2}]^{-1}$ to an isotropic value $(r_1+r_3)^{-1}$ due to coupling to the light hole. At the same time, the coupling makes the light-hole in-plane mass increase discontinuously from an isotropic bulk value $[\gamma_1+(\gamma_2^2+3\gamma_3^2)^{1/2}]^{-1}$ to an isotropic value $(\gamma_1-\gamma_3)^{-1}$. The discontinuity can be understood as arising from the fact that the treatment of the coupling between the heavy- and light-hole bands switches from degenerate perturbation to nondegenerate perturbation. Nevertheless, when η is very small, the effective masses obtained only reflect the second-order derivative of the energy dispersion curves at $k=0$ since, as one moves away from $k=0$, the dispersion curves are essentially the same as that of the disordered case.

Another interesting observation is a sum rule for the effective-mass change due to the ordering:

$$\delta\left[\frac{1}{m^*_{cj}}\right]=\sum_{\mathrm{VB}}\delta\left[\frac{1}{m^*_{vj}}\right]\ , \tag{25}$$

where $j=\parallel$ and $\perp$, when $d_1/\Delta_0 \ll 1$. This sum rule indicates that even though the $k\neq0$ states shift differently from the $k=0$ states, the change in the center of gravity of the eight bands is determined by the $k=0$ states. Note that the external coupling among the six values bands also satisfies a similar rule: the summation on the right-hand side of Eq. (25) equals zero if only internal coupling is considered. Also, in general, the effective-mass increase along the ordering direction will accompany a decrease of the in-plane effective mass, and vice versa.

Next, we will briefly discuss the effect of the folded bands with the wave vector along the ordering direction. Qualitatively, for the conduction band, the crossing of the folded part of the first conduction band and the first conduction band itself will tend to increase the conduction-band effective mass along the ordering direction, which gives an opposite effect to the coupling to the valence band. Experimentally, it has been found by cyclotron resonance that the conduction-band effective mass in partially ordered $GaInP_2$ is slightly smaller than the disordered one; m_c varying from $0.092\pm0.003m_e$ in a disordered $GaInP_2$ to $0.088\pm0.003m_e$ in an ordered one with a 56-meV band-gap reduction.[6] However, it was not realized that the conduction-band effective mass was anisotropic and that the magnetic field was not aligned selectively, and so the measured mass should be considered as an averaged value of the two directions. Assuming the same amount of band-gap reduction, we have $m_{c\parallel}=0.0905m_e$, $m_{c\perp}=0.0891m_e$, and an averaged value $m_c=\frac{1}{3}(1/m_{e\parallel}+2/m_{c\perp})^{-1}=0.0896m_e$. This example corresponds to $|d|=9.3$ meV in Fig. 2(a). According to the theory of Ref. 5, both $m_{c\parallel}$ and $m_{c\perp}$ would be larger than the disordered value m_0^* since $m_{L\parallel}$ and $m_{L\perp}$ (L-point effective masses) are larger than m_0^*, and the enhancement is rather significant. The experimental result seems to indicate that the effect of the folded band is relatively weak, as pointed out by Ref. 6. However, since the band-gap reduction of the sample used in Ref. 6 is relatively small, the result is not so conclusive. For the valence band along the ordering direction, the L points ($L_{5v}L_{6v}$) of the folded Λ_5 and Λ_6 bands lie below the split-off band. The repulsion between the valence band and the folded bands tends to increase all the effective masses of the six bands. However, due to a relatively large separation between the valence band and the folded L points, the corrections are expected to be small, especially for practically obtained partially ordered $GaInP_2$.

V. SUMMARY

In this paper, an eight-band $\mathbf{k}\cdot\mathbf{p}$ model has been used to calculate the energy dispersions and effective masses of the conduction and valence bands in ordered $GaInP_2$. The effective masses are given in analytic forms, thus the physical processes involved in the interband couplings

are clearly seen. To terms quadratic in wave vector **q**, the dispersions all have ellipsoidal forms with $m_{\parallel}$ (along the ordering direction) $\neq m_{\perp}$ (in the plane perpendicular to the ordering direction). The change in effective masses is found to satisfy a sum rule when ordering is weak. The numerical results for all the masses are shown as a function of the ordering parameter. The anisotropy and nonparabolicity of the energy dispersions are discussed. We find that, as the order parameter increases, $m_{\parallel}$ is unchanged for the heavy-hole band, increases for the light-hole band, and decreases for the spin-orbit split-off band; $m_{\perp}$ for the heavy and light-hole bands decreases, whereas it increases for the split-off band. For the conduction band, both $m_{\parallel}$ and $m_{\perp}$ decrease.

ACKNOWLEDGMENTS

We are very grateful to Dr. E. Jones, Dr. A. Zunger, Dr. S.-H. Wei, and Dr. A. Franceschetti for valuable discussions. This work was supported by the Office of Energy Research Material Science Division of the DOE under Contract No. DE-AC36-83CH10093.

APPENDIX

The Hamiltonian for the zinc-blende structures in the eight-band $\mathbf{k}\cdot\mathbf{p}$ approximation can be used for the disordered $GaInP_2$ alloy. Ignoring the effect due to the lack of inversion symmetry, we have the following Hamiltonian:[13]

$$H_{\rm dis}=\begin{pmatrix}
A_0 & 0 & \sqrt{3}V^+ & \sqrt{2}U^+ & -V & 0 & U & -\sqrt{2}V \\
0 & A_0 & 0 & -V^+ & \sqrt{2}U^+ & -\sqrt{3}V & -\sqrt{2}V^+ & U \\
\sqrt{3}V & 0 & -P+Q & S^+ & R^+ & 0 & -\frac{1}{\sqrt{2}}S^+ & \sqrt{2}R^+ \\
\sqrt{2}U & -V & S & -P-Q & 0 & -R^+ & \sqrt{2}Q & \sqrt{\frac{3}{2}}S^+ \\
-V^+ & \sqrt{2}U & R & 0 & -P-Q & S^+ & -\sqrt{\frac{3}{2}}S & \sqrt{2}Q \\
0 & -\sqrt{3}V^+ & 0 & -R & S & -P+Q & -\sqrt{2}R & -\frac{1}{\sqrt{2}}S \\
U^+ & -\sqrt{2}V & -\frac{1}{\sqrt{2}}S & \sqrt{2}Q & -\sqrt{\frac{3}{2}}S^+ & -\sqrt{2}R^+ & Z & 0 \\
-\sqrt{2}V^+ & U^+ & \sqrt{2}R & \sqrt{\frac{3}{2}}S & \sqrt{2}Q & -\frac{1}{\sqrt{2}}S^+ & 0 & Z
\end{pmatrix}, \tag{A1}$$

where

$$\begin{aligned}
A_0&=E_g+\hbar^2/2m_e(1+C)(k_1^2+k_2^2+k_3^2)\,,\\
P&=\gamma_{10}\hbar^2/2m_e(k_1^2+k_2^2+k_3^2)\,,\\
Q&=-\gamma_{20}\hbar^2/2m_e(k_1^2+k_2^2-2k_3^2)\,,\\
R&=-\sqrt{3}\hbar^2/2m_e[\gamma_{20}(k_1^2-k_2^2)-2i\gamma_{30}k_1k_2]\,,\\
S&=2\sqrt{3}\gamma_{30}\hbar^2/2m_ek_3(k_1-ik_2)\,,\\
Z&=-\Delta_0-\gamma_{10}\hbar^2/2m_e(k_1^2+k_2^2+k_3^2)\,,\\
V&=P_0/\sqrt{6}(k_2-ik_1)\,,\\
U&=iP_0/\sqrt{3}k_3\,,
\end{aligned} \tag{A2}$$

where E_g is the band gap; Δ_0 is the spin-orbit splitting; C is due to the coupling between the conduction band and the remote bands; γ_{10}, γ_{20}, and γ_{30} are so-called modified Luttinger parameters due to the coupling between the valence band and the remote bands; and $P_0=-i\hbar/m_e\langle S|p_X|X\rangle$. "†" stands for the complex conjugate.

The ordering-induced perturbation Hamiltonian is block diagonal. The 2×2 block for the conduction band is diago-

nal with an element a_c. The 6×6 block for the valence band (in a basis used by Ref. 13) can be written as follows:

$$h_v=\begin{pmatrix} -p+q & s^+ & r^+ & 0 & -\frac{1}{\sqrt{2}}s'^+ & \sqrt{2}r'^+ \\ s & -p-q & 0 & -r^+ & \sqrt{2}q' & \sqrt{\frac{3}{2}}s'^+ \\ r & 0 & -p-q & s^+ & -\sqrt{\frac{3}{2}}s' & \sqrt{2}q' \\ 0 & -r & s & -p+q & -\sqrt{2}r' & -\frac{1}{\sqrt{2}}s' \\ -\frac{1}{\sqrt{2}}s' & \sqrt{2}q' & -\sqrt{\frac{3}{2}}s'^+ & -\sqrt{2}r'^+ & z & 0 \\ \sqrt{2}r' & \sqrt{\frac{3}{2}}s' & \sqrt{2}q' & -\frac{1}{\sqrt{2}}s'^+ & 0 & z \end{pmatrix}, \tag{A3}$$

where

$$\begin{aligned} &p=-a\ , \\ &q=0\ , \\ &r=-id/\sqrt{3}\ , \\ &s=-d(1-i)/\sqrt{3}\ , \\ &z=a'\ , \\ &q'=0\ , \\ &r'=-id'/\sqrt{3}\ , \\ &s'=-d'(1-i)/\sqrt{3}\ . \end{aligned} \tag{A4}$$

Constants a, d a', and d' are defined in the main text.

After applying the renormalization procedure to the 8×8 Hamiltonian $H_{\rm ord}$ [Eq. (8)], we obtain a block-diagonal form with a 2×2 block for the conduction band and a 6×6 block for the valence band. The diagonal term in the 2×2 block is then the energy for the conduction-band states [Eq. (9)]. The 6×6 block can be written as

$$H_v^{\rm ord}=H_v^{\rm dis}+\bar{h}_v\ , \tag{A5}$$

where $H_v^{\rm dis}$ is the renormalized valence-band Hamiltonian in the absence of the ordering effect, and $\bar{h}v$ is the renormalized perturbation Hamiltonian for the valence band in which the coupling to the conduction band is included to the quadratic terms in $\mathbf{k}$. We have

$$H_v^{\rm dis}=\begin{pmatrix} -P+Q & S^+ & R^+ & 0 & -\frac{1}{\sqrt{2}}S'^+ & \sqrt{2}R'^+ \\ S & -P-Q & 0 & -R^+ & \sqrt{2}Q' & \sqrt{\frac{3}{2}}S'^+ \\ R & 0 & -P-Q & S^+ & -\sqrt{\frac{3}{2}}S' & \sqrt{2}Q' \\ 0 & -R & S & -P+Q & -\sqrt{2}R' & -\frac{1}{\sqrt{2}}S' \\ -\frac{1}{\sqrt{2}}S' & \sqrt{2}Q' & -\sqrt{\frac{3}{2}}S'^+ & -\sqrt{2}R'^+ & Z & 0 \\ \sqrt{2}R' & \sqrt{\frac{3}{2}}S' & \sqrt{2}Q' & -\frac{1}{\sqrt{2}}S'^+ & 0 & Z \end{pmatrix}, \tag{A6}$$

with

$$
\begin{aligned}
P&=\gamma_1\hbar^2/2m_e(k_1^2+k_2^2+k_3^2)\ ,\\
Q&=-\gamma_2\hbar^2/2m_e(k_1^2+k_2^2-2k_3^2)\ ,\\
R&=-\sqrt{3}\hbar^2/2m_e[\gamma_2(k_1^2-k_2^2)-2i\gamma_3k_1k_2]\ ,\\
S&=2\sqrt{3}\gamma_3\hbar^2/2m_ek_3(k_1-ik_2)\ ,\\
Z&=-\Delta_0-\gamma_1'\hbar^2/2m_e(k_1^2+k_2^2+k_3^2)\ ,\\
Q'&=-\gamma_2'\hbar^2/2m_e(k_1^2+k_2^2-2k_3^2)\ ,\\
R'&=-\sqrt{3}\hbar^2/2m_e[\gamma_2'(k_1^2-k_2^2)-2i\gamma_3'k_1k_2]\ ,\\
S'&=2\sqrt{3}\gamma_3'\hbar^2/2m_ek_3(k_1-ik_2)\ ,
\end{aligned}
\tag{A7}
$$

where $\gamma_1=\gamma_{10}+E_p/(3E_g)$, $\gamma_2=\gamma_{20}+E_p/(6E_g)$, $\gamma_3=\gamma_{30}+E_p/(6E_g)$, $\gamma_1'=\gamma_{10}+E_p/(3E_d)$, $\gamma_2'=\gamma_{20}+E_p/12\ (1/E_g+1/E_d)$, $\gamma_3'=\gamma_{30}+E_p/12\ (1/E_g+1/E_d)$, and $E_d=E_g+\Delta_0$.

We write $\bar{h}_v=h_v+\delta h_v$, then δh_v is the contribution from the conduction band:

$$
\delta h_v=\begin{bmatrix}
-p_c+q_c & s_c^+ & r_c^+ & 0 & -\frac{1}{\sqrt{2}}s_c'^+ & \sqrt{2}r_c'^+\\
s_c & -p_c-q_c & 0 & -r_c^+ & \sqrt{2}q_c'^+ & \sqrt{\frac{3}{2}}s_c'^+\\
r_c & 0 & -p_c-q_c & s_c^+ & -\sqrt{\frac{3}{2}}s_c' & \sqrt{2}q_c'\\
0 & -r_c & s_c & -p_c+q_c & -\sqrt{2}r_c' & -\frac{1}{\sqrt{2}}s_c'\\
-\frac{1}{\sqrt{2}}s_c' & \sqrt{2}q_c' & -\sqrt{\frac{3}{2}}s_c'^+ & -\sqrt{2}r_c'^+ & z_c & 0\\
\sqrt{2}r_c' & \sqrt{\frac{3}{2}}s_c' & \sqrt{2}q_c'^+ & -\frac{1}{\sqrt{2}}s_c'^+ & 0 & z_c
\end{bmatrix}\ ,
\tag{A8}
$$

where

$$
\begin{aligned}
p_c&=-\frac{(a_c-a)P_0^2}{3E_g^2}k^2+\frac{P_0^2}{3}\left[\frac{d}{E_g^2}+\frac{d'}{E_gE_d}\right](k_1k_2+k_1k_3+k_2k_3)\ ,\\
q_c&=\frac{(a_c-a)P_0^2}{6E_g^2}(k_1^2+k_2^2-2k_3^2)+\frac{P_0^2d'}{6E_gE_d}(k_1k_3+k_2k_3-2k_1k_2)\ ,\\
r_c&=-\frac{\sqrt{3}(a_c-a)P_0^2}{6E_g^2}(k_2+ik_1)^2+i\frac{\sqrt{3}P_0^2d}{9E_g^2}k^2+i\frac{\sqrt{3}P_0^2d'}{18E_gE_d}(k_1^2+k_2^2-2k_3^2)\\
&\quad-\frac{\sqrt{3}P_0^2d'}{6E_gE_d}[(k_1k_3-k_2k_3)-i(k_1k_3+k_2k_3)]\ .\\
s_c&=-\frac{\sqrt{3}(a_c-a)P_0^2}{3E_g^2}(k_1-ik_2)k_3+(1-i)\frac{\sqrt{3}P_0^2d}{9E_g^2}k^2+\frac{\sqrt{3}P_0^2d'}{18E_gE_d}[(k_1^2+k_3^2-2k_2^2)-i(k_2^2+k_3^2-2k_1^2)]\\
&\quad+\frac{\sqrt{3}P_0^2d'}{6E_gE_d}[(k_2k_3+k_1k_2)-i(k_1k_3+k_1k_2)]\ ,\\
z_c&=\frac{(a_c-a)P_0^2}{3E_d^2}k^2-\frac{2P_0^2d'}{3E_gE_d}(k_1k_2+k_1k_3+k_2k_3)\ ,\\
q_c'&=\frac{(2a_c-a-a')P_0^2}{12E_gE_d}(k_1^2+k_2^2-2k_3^2)+\frac{P_0^2}{12}\left[\frac{d}{E_gE_d}+\frac{d'}{E_g^2}\right](k_1k_3+k_2k_3-2k_1k_2)\\
&\quad+i\frac{P_0^2}{12}\left[\frac{d}{E_gE_d}-\frac{d'}{E_g^2}\right](k_1^2-k_2^2+k_1k_3-k_2k_3)\ ,
\end{aligned}
\tag{A9}
$$

$$r_c'=-\frac{\sqrt{3}(2a_c-a-a')P_0^2}{12E_gE_d}(k_2+ik_1)^2+i\frac{\sqrt{3}P_0^2d'}{18E_d^2}k^2+i\frac{\sqrt{3}P_0^2d'}{12E_g^2}(k_1^2+k_2^2)+i\frac{\sqrt{3}P_0^2d}{36E_gE_d}(k_1^2+k_2^2-2k_3^2)$$
$$+\frac{\sqrt{3}P_0^2}{12}\left[\frac{d'}{E_g^2}+\frac{d}{E_gE_d}\right][(-1+i)k_1k_3+(1+i)k_2k_3]\ ,$$
$$s_c'=-\frac{\sqrt{3}(2a_c-a-a')P_0^2}{6E_gE_d}(k_1-ik_2)k_3+(1-i)\frac{\sqrt{3}P_0^2d'}{18E_d^2}k^2+\frac{\sqrt{3}P_0^2d'}{6E_g^2}(k_1+k_2)(k_1-ik_2)$$
$$+\frac{\sqrt{3}P_0^2d}{18E_gE_d}[(1-i)(2k_3^2-k_1^2-k_2^2)+3k_3(k_2-ik_1)]\ .$$

Note that the hydrostatic terms in the above formulas are equivalent to changing Luttinger parameters in Eq. (A7) by $\delta\gamma_1=-[(a_c-a)E_p]/3E_g^2$, $\delta\gamma_2=\delta\gamma_3=-[(a_c-a)E_p]/6E_g^2$, $\delta\gamma_1'=-[(a_c-a)E_p]/3E_d^2$, and $\delta\gamma_2'=\delta\gamma_3'=-[(2a_c-a-a')E_p]/12E_gE_d$, respectively.

As we know that Hamiltonian Eq. (A5) has three double degenerate eigenvalues, it is possible to simplify the eigenvalue equation to a cubic equation, then solve it analytically. In fact, this approach has been conducted previously, but with certain simplifications.[18,19] Here we have obtained a cubic equation for the most general form, Eq. (A8), of the valence-band Hamiltonian:[20]

$$E^3+A_1(\mathbf{k})E^2+A_2(\mathbf{k})E+A_3(\mathbf{k})=0\ , \tag{A10}$$

with

$$A_1(\mathbf{k})=-2\mathbf{P}+\mathbf{Z}\ ,$$
$$A_2(\mathbf{k})=\mathbf{P}^2-\mathbf{Q}^2-2|\mathbf{Q}'|^2-|\mathbf{R}|^2-2|\mathbf{R}'|^2-|\mathbf{S}|^2-2|\mathbf{S}'|^2-2\mathbf{PZ}\ ,$$
$$A_3(\mathbf{k})=2(\mathbf{P}-\mathbf{Q})|\mathbf{Q}'|^2+2\mathbf{Q}'\mathbf{R}^\dagger\mathbf{R}'+2\mathbf{Q}'^\dagger\mathbf{R}\mathbf{R}'^\dagger+2(\mathbf{P}+\mathbf{Q})|\mathbf{R}'|^2-\mathbf{Q}'^\dagger\mathbf{S}^\dagger\mathbf{S}'-\mathbf{Q}'SS'^\dagger$$
$$+(2\mathbf{P}-\mathbf{Q})|\mathbf{S}'|^2+(\mathbf{P}^2-\mathbf{Q}^2-|\mathbf{R}|^2-|\mathbf{S}|^2)\mathbf{Z}+\sqrt{3}(\mathbf{R}'^\dagger\mathbf{S}\mathbf{S}'+\mathbf{R}'\mathbf{S}^\dagger\mathbf{S}'^\dagger)+\sqrt{3}(\mathbf{R}^\dagger\mathbf{S}'^2+\mathbf{R}\mathbf{S}'^{\dagger 2})/2\ ,$$

where $\mathbf{P}$, $\mathbf{Q}$, $\mathbf{R}$, $\mathbf{S}$, $\mathbf{Z}$, $\mathbf{Q}'$, $\mathbf{R}'$, and $\mathbf{S}'$ are the sums of the corresponding matrix elements in Eqs. (A6), (A3), and (A8): $\mathbf{P}=P+p+p_c$, $\mathbf{Q}=Q+q+q_c$, and so on. The three solutions of Eq. (A10) give heavy-hole, light-hole, and split-off bands, respectively:

$$E_1=2\sqrt[3]{u}\cos(v/3+2\pi/3)-A_1/3\ , \tag{A11}$$
$$E_2=2\sqrt[3]{u}\cos(v/3+4\pi/3)-A_1/3\ , \tag{A12}$$
$$E_3=2\sqrt[3]{u}\cos(v/3)-A_1/3\ , \tag{A13}$$

where $u=\sqrt{-w_1^3/27}$, $v=\arccos[-w_2/(2u)]$, $w_1=(3A_2-A_1^2)/3$, and $w_2=2A_1^3-A_1A_2/3+A_3$.

The effective-mass tensors can be obtained from series expansions of the above solutions. However, there is an easier way to get the effective-mass tensors through the following relationship:

$$\frac{1}{m_{ij}}=-\hbar^{-2}\frac{\left[\frac{\partial^2A_1}{\partial k_1\partial k_j}\right]_0E_0^2+\left[\frac{\partial^2A_2}{\partial k_i\partial k_j}\right]_0E_0+\left[\frac{\partial^2A_3}{\partial k_1\partial k_j}\right]_0}{3E_0^2+2A_1E_0+A_2}\ , \tag{A14}$$

where the derivatives are evaluated at $\mathbf{k}=\mathbf{0}$, and E_0 is the energy eigenvalue at $\mathbf{k}=\mathbf{0}$. Note that this method is not applicable when two bands are degenerate at $\mathbf{k}=\mathbf{0}$ but have different effective masses.

[1]A. Zunger and S. Mahajan, in *Handbook on Semiconductors*, 2nd ed., edited by S. Mahajan (Elsevier, Amsterdam, 1994), Vol. 3, Chap. 19, p. 1399.

[2]S.-H. Wei, D. B. Laks, and A. Zunger, Appl. Phys. Lett. **62**, 1937 (1993).

[3]S.-H. Wei and A. Zunger, Phys. Rev. B **49**, 14 337 (1994).

[4]D. B. Laks, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **69**, 3766 (1992).

[5]M. E. Raikh and E. V. Tsiper, Phys. Rev. B **49**, 2509 (1994).

[6]P. Emanuelsson, M. Drechsler, D. M. Hofmann, B. K. Meyer, M. Moser, and F. Scholz, Appl. Phys. Lett. **64**, 2849 (1994).

[7]E. D. Jones, D. M. Follstaedt, H. Lee, J. S. Nelson, R. P. Schneider, Jr., R. G. Alonso, G. S. Horner, J. Machol, and A. Masarenhas, in *Physics of Semiconductors—Proceedings of the 22nd International Conference (Vancouver, Canada, 1994)*, edited by D. J. Lockwood (World Scientific, Singapore, 1995),

p. 293.
[8]R. P. Schneider, Jr., E. D. Jones, and D. M. Follstaedt, Appl. Phys. Lett. **65**, 587 (1994).
[9]J. J. Hopfield, J. Phys. Chem. Solids **15**, 97 (1960).
[10]F. H. Pollak, in *Effects of Homogeneous Strain on the Electronic and Vibrational Levels in Semiconductors,* edited by R. K. Willardson and A. C. Beer, Semiconductors and Semimetals Vol. 32 (Academic, New York, 1990), Chap. 2, p. 17.
[11]J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[12]R. G. Alonso, A. Mascarenhas, G. S. Horner, K. A. Bertness, S. R. Kurtz, and J. M. Olson, Phys. Rev. B **48**, 11 833 (1993).
[13]Yong Zhang, Phys. Rev. B **49**, 14 352 (1994).
[14]S.-H. Wei and A. Zunger, Appl. Phys. Lett. **58**, 2684 (1991).
[15]J. M. Luttinger, Phys. Rev. **102**, 1030 (1956).
[16]*Semiconductors, Physics of Group IV Elements and IV-V Compounds,* edited by O. Madelung, M. Schulz, and H. Weiss, Landolt-Börnstein, New Series, Group III, Vol. 17, Pt. a (Springer-Verlag, Berlin, 1982).
[17]M. Cardona, N. E. Christensen, and G. Fasol, Phys. Rev. B **38**, 1806 (1988).
[18]J. von Borzeszkowski, Phys. Status Solidi B **61**, 607 (1974).
[19]C. Y.-P. Chao and S. L. Chuang, Phys. Rev. B **46**, 4110 (1992).
[20]Yong Zhang (unpublished). This is the most general form of the six-band $\mathbf{k}\cdot\mathbf{p}$ model for ordering along any direction or any arbitrary small homogeneous strain, although the explicit expressions for p, q, etc. are different for different cases.