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Effective-mass theory for carriers in graded mixed semiconductors. II. Spin effects

Ludwik Leibler

Institut of Theoretical Physics, Warsaw University, 00-681 Warsaw, ul. Hoża 69, Poland

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An effective-mass-like equation is derived for carriers in mixed crystals with nonuniform composition in the presence of magnetic field. The spin-orbit interaction is taken into account. The effective magnetic moment of a carrier is shown to be position-dependent. Specific spin-dependent terms which appear in the effective Hamiltonian for graded mixed semiconductors are examined. It turns out that because of the spin-orbit coupling the knowledge of simple band parameters for homogeneous crystals is insufficient to describe the dynamics of carriers in graded mixed semiconductors. The general theory is illustrated by discussing the Γ_6 band in cubic crystals. The parameters describing the effective Hamiltonian for Γ_6 electrons are calculated in a three-band model. It is shown that spin and orbital motion can be strongly coupled due to inhomogeneity of composition.

I. INTRODUCTION

First attempts to describe the dynamics of carriers in mixed semiconductors with graded composition were based on the phenomenological assumption that a standard effective-mass equation holds but with position-dependent band-edge energy and effective mass.[1-4] Gora and Williams[5,6] have derived in the framework of the virtual-crystal approximation an effective-mass-like equation for the case of a graded-mixed semiconductor whose both components have cubic-lattice symmetry and a spherical nondegenerate band extremum at the Γ point. In a previous publication,[7] henceforth referred to as I, the effective-mass theory for the case of arbitrary lattice symmetry and more general band structure of the component crystals (degenerate and multivalley bands) has been presented, and limitations of the concept of position-dependent band parameters have been discussed. However, the range of applicability of the effective-mass equation derived in I was still limited because spin effects had not been included.

It is well known that in many semiconducting crystals relativistic corrections to the Schrödinger equation associated with electron spin are of great importance. For electronic states, the most significant is the spin-orbit interaction which couples the spin of a carrier and its orbital motion and, therefore, strongly influences the band structure and electron magnetic moment. Spin-orbit interaction leads to the whole class of important phenomena both in transport (see, e.g. Refs. 8 and 9) and optics (e.g., electric spin and combined resonances[10,11]).

Hence, in the present paper we examine the effective-mass theory for carriers in graded mixed semiconductors taking into account the spin-orbit interaction. We also generalize the derivation to account for the presence of external time-dependent electromagnetic field. In Sec. II we present the general effective-mass theory for carriers in mixed semiconductors with slowly varying composition for arbitrary lattice symmetry and general band structure and we discuss the assumptions under which this theory is valid. In Sec. III the applicability of the concept of position-dependent band parameters is discussed. Since in mixed crystals with nonuniform composition the crystal potential is not periodic (even in the virtual-crystal approximation) the spin-orbit interaction leads to specific properties of the effective Hamiltonian. First, the effective magnetic moment is position dependent. Secondly, an additional term proportional to kinetic momentum and to the gradient of composition appears. We would like to stress that because of the existence of this additional term the effective-mass equation for carriers in graded mixed semiconductors is not simply the standard one with only position-dependent band parameters, but is more involved. The effective-mass equation for an important case of conduction electrons from the Γ_6 band in cubic crystals is discussed in Sec. IV. The specific term in the effective-mass Hamiltonian for nonuniform mixed crystals mentioned above can be interpreted as representing an additional coupling of spin and orbital motion. With the use of a three-band model we calculate the parameters characterizing the effective Hamiltonian and we show that this coupling can be quite significant. Therefore, some specific effects connected both with electron spin and with nonhomogeneity of the crystal should be expected. In particular, it turns out that electric-dipole-excited spin resonance is strongly modified in mixed semiconductors with constant gradient of composition.[12]

It should be pointed out that the effective Hamiltonian derived in the present paper can be used not only in the treatment of mixed semiconductors with more or less constant gradient of composition, but also in the treatment of mixed semiconductors which, although macroscopically uniform, have long-range fluctuations of the composition.

II. EFFECTIVE-MASS THEORY

Many semiconducting alloys can be prepared with composition varying over a wide range. Typical examples are alloys whose two components have similar crystal structure, e.g., mixed crystals of II-VI or III-V compounds.

We consider a two-component graded mixed semiconductor $A_{1-f}B_f$ (A and B may denote elements or compounds) whose both component crystals have identical crystal structure and lattice constants. Let $f(\vec{r})$ denote the composition of the crystal in the neighborhood of point $\vec{r}$. We assume that the composition varies slowly, i.e., the fractional change of f over a unit cell is small. The atoms of the crystal are supposed to lie on periodic lattice sites. Our considerations are not restricted to any particular lattice symmetry.

Theoretical interpretation of the observed electronic structure of homogeneous mixed semiconductors is usually based on the virtual-crystal approximation.[13,14] The essence of this approximation lies in replacing the correct one-electron potential corresponding to the actual configuration of atoms of the alloy by its average over all possible random configurations. The smaller the difference between the component crystal potentials $V_A(\vec{r})$ and $V_B(\vec{r})$, the better the virtual-crystal approximation turns out to be. The generalization of the virtual-crystal concept to the case of the mixed semiconductor with slowly varying composition gives the one-electron potential[5]

$$\begin{aligned} V(\vec{r}) &= [1-f(\vec{r})]V_A(\vec{r}) + f(\vec{r})V_B(\vec{r}) \\ &= V_{f_0}(\vec{r}) + L(\vec{r})S(\vec{r}), \end{aligned} \tag{1}$$

where $S(\vec{r}) = V_B(\vec{r}) - V_A(\vec{r})$ and $L(\vec{r}) = f(\vec{r}) - f_0$. V_{f_0} denotes the one-electron periodic potential of a homogeneous mixed crystal with arbitrary chosen composition f_0 written in the virtual-crystal approximation

$$V_{f_0} = (1-f_0)V_A(\vec{r}) + f_0 V_B(\vec{r}) . \tag{2}$$

$L(\vec{r})$ characterizes the inhomogeneity of the crystal.

We consider the motion of a carrier in the graded mixed semiconductor in the presence of external time-dependent electric and magnetic fields. Since we are interested in the effects due to electron spin and magnetic moment we describe the motion of a carrier by the Pauli Hamiltonian with the spin-orbit interaction term

$$\begin{aligned} H = {} & \tfrac{1}{2}(P^2/m) + V(\vec{r}) + U(\vec{r},t) + \tfrac{1}{2}g_0\mu_B\vec{\sigma}\cdot\vec{B} \\ & + (\hbar/4m^2c^2)\,\vec{\sigma}\cdot[\nabla V(\vec{r}) \times \vec{P}] , \end{aligned} \tag{3}$$

where m and g_0 denote free-electron mass and g factor, respectively, $\mu_B = e\hbar/2mc$ is the Bohr magneton, $\vec{\sigma}$ is the Pauli matrices' vector, and $\vec{B}$ denotes the external magnetic field. The kinetic momentum operator is denoted by $\vec{P}$,

$$\vec{P} = \vec{p} - (q/c)\vec{A}(\vec{r},t) , \tag{4}$$

where $\vec{p} = -i\hbar\nabla$ is the canonical momentum operator and q is the charge of a carrier. $\vec{A}(\vec{r},t)$ denotes the vector potential of the external electromagnetic field. The scalar potential of this field equals $(1/q)U(\vec{r},t)$. The one-electron crystal potential $V(\vec{r})$ is given by Eq. (1). The Hamiltonian H given by Eq. (3) can be transformed into the following form:

$$\begin{aligned} H = {} & H_{f_0} - \frac{q}{2mc}(\vec{\pi}\cdot\vec{A} + \vec{A}\cdot\vec{\pi}) + \left(\frac{q}{c}\right)^2\vec{A}^2 + U \\ & + \tfrac{1}{2}g_0\mu_B\vec{\sigma}\cdot\vec{B} + LS + \frac{\hbar}{4m^2c^2}[\vec{\sigma}\times\nabla(LS)]\cdot\vec{P} , \end{aligned} \tag{5}$$

where the operator $\vec{\pi}$ is defined as

$$\vec{\pi} = \vec{p} + (\hbar/4mc^2)(\vec{\sigma}\times\nabla V_{f_0}) . \tag{6}$$

H_{f_0} denotes the Hamiltonian of a carrier in a homogeneous semiconductor with composition f_0 written in the virtual-crystal approximation

$$H_{f_0} = \frac{1}{2m}p^2 + V_{f_0}(\vec{r}) + \frac{\hbar}{4m^2c^2}[\vec{\sigma}\times\nabla V_{f_0}(\vec{r})]\cdot\vec{p} . \tag{7}$$

The usual procedure of finding the solutions of the Schrödinger equation of a carrier in the crystal, in the presence of external electromagnetic field, consists in replacing the effects of the periodic crystal potential by the effective dynamical parameters. Suppose the band structure of the homogeneous mixed crystal with composition f_0 is known, i.e., eigenenergies $E_n(\vec{K}, f_0)$ and eigenfunctions $\psi_{n\vec{K}}$ (Bloch functions) of the unperturbed Hamiltonian H_{f_0} are known (n labels the bands, $\vec{K}$ is the wave vector). Since the perturbation $H - H_{f_0}$ is neither periodic nor a slowly varying function of $\vec{r}$, the standard effective-mass method[15] is not applicable for solving the Schrödinger equation with Hamiltonian (5). However, it is possible to modify the effective-mass method and to apply it to the present problem in a way analogous to that described in I.

We consider the case of the mixed crystal described by H_{f_0} with a band with several equivalent d-fold degenerate extrema located at $\vec{K}_0^r$($r = 1, 2, \ldots, r'$, where r' is the number of extrema). For brevity, the location of the specific rth extremum within the Brillouin zone will be denoted by $\vec{K}_0$. We call ψ_n the Bloch functions at point $\vec{K}_0$. The complete orthonormal set of Kohn-Luttinger functions is defined in the following way[15]:

$$\varphi_{n\vec{k}} = \Omega^{-1/2} e^{i\vec{k}\cdot\vec{r}} \psi_n \,, \tag{8}$$

where $\vec{k} = \vec{K} - \vec{K}_0$, and Ω denotes the finite crystal volume (periodic boundary conditions are imposed).

The wave function $\Psi(\vec{r}, t)$ of the carrier in the graded mixed semiconductor can be expressed by a linear combination of Kohn-Luttinger functions $\varphi_{n\vec{k}}$,

$$\Psi(\vec{r}, t) = \sum_{n'} \sum_{\vec{k}'} A_{n'}(\vec{k}', t) \varphi_{n'\vec{k}'}(\vec{r}) \,. \tag{9}$$

Inserting Eq. (9) into the Schrödinger equation for the carrier in the graded mixed semiconductor, multiplying both sides of this equation by $\varphi^{\dagger}_{n\vec{k}}$ (Hermitian conjugate of the spinor $\varphi_{n\vec{k}}$) and integrating over the crystal volume, we obtain

$$\sum_{n'} \sum_{\vec{k}'} (n\vec{k} | H | n'\vec{k}') A_{n'}(\vec{k}', t) = i\hbar \frac{\partial A_n(\vec{k}, t)}{\partial t} \,. \tag{10}$$

The orthogonality relation for Kohn-Luttinger functions has been used to obtain right-hand side of Eq. (10).

We make the *Ansatz* so that the wave packet Ψ describing the carrier state in the crystal may be constructed with the help of only those Kohn-Luttinger functions that are characterized by wave vectors $\vec{K}$ lying near the band extremum $\vec{K}_0$. It means (see, e.g., I) that the only important terms in expansion (9) are those with $\vec{k}$ much smaller than the reciprocal-lattice vector $\vec{G}_{\vec{m}}$ (for any $\vec{m} \neq 0$). This assumption should be always verified after solving the Schrödinger equation by the effective-mass method.

As usual in the effective-mass theory we assume that external fields are slowly varying functions of $\vec{r}$, i.e., the fractional change of the scalar and vector potentials over a unit cell is small (see, e.g., Refs. 15 and 16). Moreover, we assume that also the composition $f(\vec{r})$ varies slowly within the crystal (see I). It means that in expansions of $U, \vec{A}$, and L in Fourier series the only important terms are those with wave vectors much smaller than the reciprocal-lattice vectors $\vec{G}_{\vec{m}}$ with $\vec{m} \neq 0$. Making use of these assumptions and of the periodicty of the function $S(\vec{r})$ (as in I), it is easy to calculate the matrix elements of the Hamiltonian H standing on the left-hand side of Eq. (10). It turns out that

$$\begin{aligned}(n\vec{k} | H | n'\vec{k}') \cong{}& E_n \delta_{nn'} \delta_{\vec{k}\vec{k}'} + \frac{1}{2m} \sum_{\vec{q}} \vec{\mathcal{P}}(\vec{k}, \vec{q}) \cdot \vec{\mathcal{P}}(\vec{q}, \vec{k}') \delta_{nn'} + \frac{1}{m} \vec{\pi}_{nn'} \cdot \vec{\mathcal{P}}(\vec{k}, \vec{k}') \\ &+ \tfrac{1}{2} g_0 \mu_B \vec{\sigma}_{nn'} \cdot \vec{B}_{\vec{k}-\vec{k}'} + U_{\vec{k}-\vec{k}'} \delta_{nn'} + s_{nn'} L_{\vec{k}-\vec{k}'} + i\hbar \vec{a}_{nn'} \cdot (\vec{k} - \vec{k}') L_{\vec{k}-\vec{k}'} \\ &+ \vec{b}_{nn'} \cdot \sum_{\vec{q}} \tfrac{1}{2} i\hbar \{ L_{\vec{k}-\vec{q}'} [(\vec{k} - \vec{q}) \times \vec{\mathcal{P}}(\vec{q}, \vec{k}')] - [\vec{\mathcal{P}}(\vec{k}, \vec{q}) \times (\vec{q} - \vec{k}')] L_{\vec{q}-\vec{k}'} \} \\ &+ \vec{c}_{nn'} \cdot \sum_{\vec{q}} \tfrac{1}{2} [L_{\vec{k}-\vec{q}} \vec{\mathcal{P}}(\vec{q}, \vec{k}') + \vec{\mathcal{P}}(\vec{k}, \vec{q}) L_{\vec{q}-\vec{k}'}] \,, \end{aligned} \tag{11}$$

where $E_n = E_n(\vec{K}_0, f_0)$ is the energy of the nth band at point $\vec{K}_0$ of the Brillouin zone in the homogeneous crystal with composition f_0. We have introduced the vector $\vec{\mathcal{P}}(\vec{k}, \vec{k}')$ which equals

$$\vec{\mathcal{P}}(\vec{k}, \vec{k}') = \hbar\vec{k} \delta_{\vec{k}\vec{k}'} - (q/c) \vec{A}_{\vec{k}-\vec{k}'} \,. \tag{12}$$

$\vec{B}_{\vec{q}}$, $U_{\vec{q}}$, $\vec{A}_{\vec{q}}$, and $L_{\vec{q}}$ denote the Fourier transforms of $B(\vec{r})$, $U(\vec{r})$, $\vec{A}(\vec{r})$, and $L(\vec{r})$, respectively. The Fourier transform of a function $h(\vec{r})$ is defined as follows:

$$h_{\vec{q}} = \Omega^{-1} \int_{\Omega} d^3r \exp(-i\vec{q} \cdot \vec{r}) h(\vec{r}) \,. \tag{13}$$

The coefficients of Eq. (11) $\vec{\sigma}_{nn'}$, $\vec{\pi}_{nn'}$, $\vec{a}_{nn'}$, $\vec{b}_{nn'}$, $\vec{c}_{nn'}$, and $s_{nn'}$ are equal to the matrix elements between the Kohn-Luttinger functions φ_{n0} and $\varphi_{n'0}$ of the operators $\vec{\sigma}$, $\vec{\pi}$, $\vec{a} = (1/4m^2c^2) S (\vec{p} \times \vec{\sigma})$, $\vec{b} = (1/4m^2c^2) S\vec{\sigma}$, $c = (\hbar/4m^2c^2)(\vec{\sigma} \times \nabla S)$, and $s = S + (\hbar/4m^2c^2)(\vec{\sigma} \times \nabla S) \cdot \vec{p}$, respectively.

It should be noted that nonhomogeneity of the crystal manifests itself in the Hamiltonian (11) in two different ways. First, the dependence of some terms on the Fourier transforms $L_{\vec{k}-\vec{k}'}$ leads to the additional coupling of functions with different wave vectors $\vec{k}$ and $\vec{k}'$ [when the composition is uniform $L(\vec{r}) = L = \text{const}$ and $L_{\vec{k}-\vec{k}'} = L \delta_{\vec{k}\vec{k}'}$]. Secondly, new terms characteristic to nonhomogeneous mixed crystals appear (terms with $\vec{a}_{nn'}$ and $\vec{b}_{nn'}$ vanishing when $L(\vec{r}) = \text{const}$).

Let us label by $\{j\}$ $(j = 1, 2, \ldots, d)$ the set of Bloch functions of the considered d-fold degenerate at point $\vec{K}_0$ extremum. The equations for coefficients $A_j(\vec{k}, t)$[Eq. (10)],

$$\begin{aligned} i\hbar \frac{\partial A_j(\vec{k}, t)}{\partial t} ={}& E_j A_j(\vec{k}, t) \\ &+ \sum_{n'} \sum_{\vec{k}'} (j\vec{k} | H' | n'\vec{k}') A_{n'}(\vec{k}', t) \,, \end{aligned} \tag{14}$$

are coupled with equations for $A_n(\vec{k}', t)$ with $n \notin \{j\}$ by interband matrix elements $(j\vec{k}|H'|n\vec{k}')$. From Eq. (11) we see that these matrix elements contain not only terms involving $\vec{\pi}_{jn}$, as is usually the case, but also terms which are specific for crystals with varying composition and which contain interband matrix elements s_{jn}, $\vec{a}_{jn}$, $\vec{b}_{jn}$, and $\vec{c}_{jn}$. The terms with $\vec{\pi}_{jn}$ are proportional to $\vec{\mathcal{P}}(\vec{k}, \vec{k}')$. Since the effective-mass theory holds only if important $\vec{\mathcal{P}}(\vec{k}, \vec{k}')$ are small (see Ref. 15), i.e., if

$$|\vec{\mathcal{P}}(\vec{k}, \vec{k}')\cdot\vec{\pi}_{jn}| \ll |E_j - E_n| , \tag{15}$$

these coupling terms can be regarded as small quantities of the first order in $\mathcal{P}$. As usual in the effective-mass approximation we shall treat Eq. (14) accurately up to terms quadratic in $\mathcal{P}$ but no further. The assumption (15) should be verified *a posteriori*, i.e., after the solution of the effective-mass equation is found. Roughly speaking, condition (15) means that a characteristic distance over which the envelope function of the wave packet changes appreciably (the Bohr radius for the impurity problem, the magnetic length for the problem of electron motion in magnetic field, etc.) should be much greater than the lattice constant.[15]

The specific coupling terms for mixed crystals are proportional to Fourier transforms $L_{\vec{k}-\vec{k}'}$ of the $L(\vec{r})$ function which characterizes the nonhomogeneity of composition. We assume that the overall change of the composition on a characteristic distance (e.g., the Bohr radius for impurity problem, the magnetic length for motion in an external magnetic field, the electron wavelength in transport problem) is small, i.e., the condition

$$|s_{jn}L_{\vec{k}-\vec{k}'}| \ll |E_j - E_n| \quad \text{for } n \notin \{j\} \tag{16}$$

is satisfied for $\vec{k}$ and $\vec{k}'$ important in expansion (9) (see I). [Analogous restrictions on L are connected with terms involving $\vec{a}_{jn}$ and $\vec{c}_{jn}$. However, these restrictions are weaker than (16) since the terms with $\vec{a}_{jn}$ and $\vec{c}_{jn}$ arise from relativistic corrections and, moreover, they are proportional to $\vec{\mathcal{P}}$ (or $\vec{k}$) which in turn is small.] We are interested in small changes of composition L, therefore we shall treat Eq. (14) accurately up to terms which are linear in L.

Hence, when conditions (15) and (16) are fulfilled, coupling terms in Eq. (14) $(j\vec{k}|H'|n\vec{k}')$ can be regarded as small quantities. We are able to remove these interband elements up to desired order by an appropriate canonical transformation e^T. When the frequency of the external electromagnetic field ω is sufficiently small so that

$$\hbar\omega \ll |E_j - E_n| \quad \text{for } n \notin \{j\},$$

the application of the canonical transformation gives the set of equations for coefficients

$$B_j(\vec{k}, t) = \sum_{n'} \sum_{\vec{k}'} (j\vec{k}|e^T|n'\vec{k}')A_{n'}(\vec{k}', t) , \tag{17}$$

in the form

$$i\hbar \frac{\partial B_j(\vec{k}, t)}{\partial t} = \sum_{n'} \sum_{\vec{k}'} (j\vec{k}|H_{\text{eff}}|n'\vec{k}')B_{n'}(\vec{k}', t) , \tag{18}$$

where

$$H_{\text{eff}} = e^{-T}He^{T} = H + [H, T] + (1/2!)[[H, T], T] + \cdots . \tag{19}$$

Since, as it has been discussed above, we treat Eq. (14) accurately up to terms which are linear in L and quadratic in $\mathcal{P}$ the canonical transformation e^T should remove nondiagonal terms of the order $\mathcal{P}$ and/or L. The method of finding the explicit form of such transformation has been described in I. After applying it the remaining nondiagonal terms in Eq. (18) $(j\vec{k}|H_{\text{eff}}|n'\vec{k}')(n' \notin \{j\})$ are at least of the order $\mathcal{P}^2$, $\mathcal{P}^2L$, or L^2 and will be neglected. Thus the set of equations for coefficients $B_j(\vec{k}, t)(j \in \{j\})$ is separated from equations for $B_{n'}(\vec{k}', t)$ with $n' \notin \{j\}$,

$$i\hbar \frac{\partial B_j(\vec{k}, t)}{\partial t} \cong \sum_{j'=1}^{d} \sum_{\vec{k}'} (j\vec{k}|H_{\text{eff}}|j'\vec{k}')B_{j'}(\vec{k}', t) . \tag{20}$$

The matrix elements $(j\vec{k}|H_{\text{eff}}|j'\vec{k}')$ can be calculated with the help of Eq. (19). For H_{eff} with the accuracy to terms of the third order in H', one obtains (see, e.g., Ref. 16)

$$\begin{aligned}
(j\vec{k}|H_{\text{eff}}|j'\vec{k}') \cong{}& (j\vec{k}|H|j'\vec{k}') - \sum_{n\notin\{j\}} \sum_{\vec{q}} \frac{(j\vec{k}|H'|n\vec{q})(n\vec{q}|H'|j'\vec{k}')}{E_n - E_j} \\
&- \tfrac{1}{2} \sum_{j''=1}^{d} \sum_{\vec{q}} \sum_{n\notin\{j\}} \sum_{\vec{q}'} \left(\frac{(j\vec{k}|H'|n\vec{q}')(n\vec{q}'|H'|j''\vec{q})(j''\vec{q}|H'|j'\vec{k}')}{(E_n - E_j)^2} \right. \\
&\left. + \frac{(j\vec{k}|H'|j''\vec{q})(j''\vec{q}|H'|n\vec{q}')(n\vec{q}'|H'|j'\vec{k}')}{(E_n - E_j)^2} \right) \\
&+ \sum_{n\notin\{j\}} \sum_{\vec{q}} \sum_{n'\notin\{j\}} \sum_{\vec{q}'} \frac{(j\vec{k}|H'|n\vec{q})(n\vec{q}|H'|n'\vec{q}')(n'\vec{q}'|H'|j'\vec{k}')}{(E_n - E_j)(E_{n'} - E_j)} .
\end{aligned} \tag{21}$$

The use of the third-order perturbation calculus guarantees that in expression (21) for H_{eff} all terms of the order $\mathcal{P}$, $\mathcal{P}^2$, L, $\mathcal{P}L$, and $\mathcal{P}^2L$ are taken into account. Since we are interested only in the effective-mass Hamiltonian which is rigorously valid up to terms linear in L, consequently, in calculating (21) we can drop terms of the order L^2 and higher as well as those of the order $\mathcal{P}^3$ (or k^3), $\mathcal{P}^3L$ (or k^3L), and higher.

Equation (21) together with Eq. (20) determines the set of effective-mass equations in $\vec{\mathrm{K}}$ space. To accomplish the transformation to $\vec{\mathrm{r}}$ space we define the envelope functions

$$F_j(\vec{\mathrm{r}},t)=\Omega^{-1/2}\sum_{\vec{\mathrm{k}}}B_j(\vec{\mathrm{k}},t)\exp\left[i\left(\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}+\frac{E_jt}{\hbar}\right)\right], \quad (22)$$

multiply both sides of Eq. (20) by $\Omega^{-1/2}\exp[i(\vec{\mathrm{k}}\cdot\vec{\mathrm{r}}+E_j\,t/\hbar)]$ and sum over all $\vec{\mathrm{k}}$. Making use of the fact that the function

$$\Delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}\,')=\Omega^{-1}\sum_{\vec{\mathrm{q}}}\exp[i\vec{\mathrm{q}}\cdot(\vec{\mathrm{r}}-\vec{\mathrm{r}}\,')]$$

may be treated as a δ function $\delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}\,')$(see, e.g., Ref. 15), i.e., for a slowly varying function of position $h(\vec{\mathrm{r}})$,

$$\int d^3r'\Delta(\vec{\mathrm{r}}-\vec{\mathrm{r}}\,')h(\vec{\mathrm{r}}\,')=h(\vec{\mathrm{r}}),$$

we obtain the set of equations for envelope functions $F_j(\vec{\mathrm{r}},t)$,

$$i\hbar\frac{\partial F_j(\vec{\mathrm{r}},t)}{\partial t}=\sum_{j'=1}^{d}\tilde{H}_{jj'}F_{j'}(\vec{\mathrm{r}},t). \quad (23)$$

$\tilde{H}_{jj'}$, the effective-mass Hamiltonian equals

$$\begin{aligned}\tilde{H}_{jj'}=&\tfrac{1}{2}D^{\alpha\beta}_{jj'}(f_0)\{P_\alpha,P_\beta\}+\vec{\mu}_{jj'}(f_0)\cdot\vec{\mathrm{B}}+U(\vec{\mathrm{r}},t)\delta_{jj'}+\tfrac{1}{4}\hbar^2(\Lambda^{\alpha\beta}_{jj'}+\Lambda^{\beta\alpha}_{jj'})(\partial_\alpha\partial_\beta U)\\&+\tfrac{1}{2}i\hbar(\Lambda^{\alpha\beta}_{jj'}-\Lambda^{\beta\alpha}_{jj'})\{P_\alpha,\partial_\beta U\}+s_{jj'}L(\vec{\mathrm{r}})+\hbar\vec{\mathrm{a}}_{jj'}\cdot\nabla L(\vec{\mathrm{r}})+\hbar\vec{\mathrm{b}}_{jj'}\cdot[\nabla L(\vec{\mathrm{r}})\times\vec{\mathrm{P}}]\\&+(\tfrac{1}{2}M^{\alpha\beta}_{jj'}+N^{\alpha\beta}_{jj'})P_\alpha P_\beta L(\vec{\mathrm{r}})+(\tfrac{1}{2}M^{\alpha\beta}_{j'j}+N^{\alpha\beta}_{j'j})^*L(\vec{\mathrm{r}})P_\beta P_\alpha+(\tfrac{1}{2}M^{\alpha\beta}_{jj'}+R^{\alpha\beta}_{jj'})P_\alpha L(\vec{\mathrm{r}})P_\beta\\&+(\tfrac{1}{2}M^{\alpha\beta}_{j'j}+R^{\alpha\beta}_{j'j})^*P_\beta L(\vec{\mathrm{r}})P_\alpha+\hbar W^{\alpha\beta}_{jj'}P_\alpha[\partial_\beta L(\vec{\mathrm{r}})]+\hbar(W^{\alpha\beta}_{j'j})^*[\partial_\beta L(\vec{\mathrm{r}})]P_\alpha.\end{aligned} \quad (24)$$

(The summation convention over repeated Greek indices is used.) $\{A,B\}$ denotes the anticommutator of operators A and B,

$$\{A,B\}=\tfrac{1}{2}(AB+BA).$$

The coefficients of the effective Hamiltonian $\tilde{H}_{jj'}$ [Eq. (24)], the Hermitian matrices $D^{\alpha\beta}_{jj'}(f_0)$, $\Lambda^{\alpha\beta}_{jj'}$, $M^{\alpha\beta}_{jj'}$, $N^{\alpha\beta}_{jj'}$, $R^{\alpha\beta}_{jj'}$, and $W^{\alpha\beta}_{jj'}$, and vector $\vec{\mu}_{jj'}(f_0)$ are built from the matrix elements of the operators $\vec{\pi}$, s, $\vec{\mathrm{a}}$, and $\vec{\mathrm{c}}$. Their explicit expressions are given in Appendix A.

For simplicity in writing Eq. (24) we restricted our considerations to the case when the location of the band extremum $\vec{\mathrm{K}}_0$ within the Brillouin zone does not depend on composition. In this case, apart from the usual relation,

$$\vec{\pi}_{jj'}=0 \quad \text{for } j,j'\in\{j\} \quad (25)$$

the following equations hold:

$$\sum_n\left(\frac{\vec{\pi}_{jn}s_{nj'}+s_{jn}\vec{\pi}_{nj'}}{E_n-E_j}\right)=0 \quad (26)$$

and

$$\vec{\mathrm{c}}_{jj'}=0. \quad (27)$$

Equations (25)–(27) result from the fact that if we put $L=\mathrm{const}$, $U=0$, and $\vec{\mathrm{A}}=0$, the band extremum should be at the point $\vec{\mathrm{K}}_0$, so in the effective Hamiltonian the terms linear in components of the kinetic momentum operator $\vec{\mathrm{P}}$ should identically vanish. The discussion of the case when the locations of band extrema within the Brillouin zone are different in the single-component crystals A and B (e.g., $\mathrm{Ge}_{1-f}\mathrm{Si}_f$ alloys), i.e., of the case when $\vec{\mathrm{K}}_0$ may depend on composition, presented in I (with spin-orbit interaction neglected and in the absence of magnetic field) can easily be generalized to the present problem.

We note that the specific terms characteristic for graded mixed semiconductors are involved in the effective Hamiltonian $\tilde{H}_{jj'}$ [Eq. (24)]. These are the terms containing the function $L(\vec{\mathrm{r}})$. Other terms occur also in usually considered one-component or homogeneous mixed crystals. The matrices $D_{jj'}(f_0)$ and $\Lambda_{jj'}$ and the vector $\vec{\mu}_{jj'}(f_0)$ characterize completely the dynamics of carriers in the mixed crystal $A_{1-f_0}B_{f_0}$ with the uniform composition f_0. $D_{jj'}(f_0)$ plays, as usual in the degenerate band case, the role of the reciprocal effective-mass tensor in the nondegenerate case. The vector $\vec{\mu}_{jj'}(f_0)$ determines the effective magnetic moment of the carrier. The term

$$\tfrac{1}{4}\hbar^2(\Lambda^{\alpha\beta}_{jj'}+\Lambda^{\beta\alpha}_{jj'})(\partial_\alpha\partial_\beta U)$$

adds to the potential energy U of the carrier. Usually it is much smaller than U (e.g., Ref. 15) and can be neglected. The term

$$\tfrac{1}{2}i\hbar(\Lambda^{\alpha\beta}_{jj'}-\Lambda^{\beta\alpha}_{jj'})\{P_\alpha,\partial_\beta U\}$$

depends on carrier kinetic momentum $\vec{\mathrm{P}}$. When the spin-orbit interaction is strong this term in the effective Hamiltonian leads to several particulary interesting effects, e.g., anomalous Hall effect, combined resonance. Since we are interested in effects due to carrier spin, we keep this term in further considerations.

Equation (23) is the set of effective-mass equations for the rth extremum of the band under consideration. The wave function $\Psi_r(\vec{r},t)$ is given by

$$\Psi_r(\vec{r},t) \cong \sum_{n'} \sum_{\vec{k}'} \sum_{j=1}^{d} \sum_{\vec{k}} B_j(\vec{k},t) \times (n'\vec{k}'\,|e^{-T}|\,j\vec{k})\varphi_{n'\vec{k}'}(\vec{r}) . \tag{28}$$

In the first approximation the leading term of Eq. (28) is

$$\Psi_r(\vec{r},t) \cong \sum_{j=1} F_j(\vec{r},t)\psi_j(\vec{r}) . \tag{29}$$

The solutions of Eq. (23) corresponding to different extrema give—with the help of Eq. (29)—independent solutions Ψ_r $(r=1,2,\ldots,r')$ of the equation of motion. For general dependence on $\vec{r}$ of $f(\vec{r})$, $U(\vec{r})$, and $\vec{A}(\vec{r})$ solutions of Eq. (23) corresponding to different extrema are different. The general electronic wave function is a linear combination of $\Psi_r(\vec{r},t)$.

III. LIMITATIONS OF THE CONCEPT OF POSITION-DEPENDENT BAND PARAMETERS

Many electron properties of semiconducting crystals can be determined starting from the effective-mass Hamiltonian. The effective Hamiltonian (24) derived in Sec. II is not in a convenient form to deal with, since it contains matrices $M_{jj'}$, $N_{jj'}$, $R_{jj'}$, and $W_{jj'}$ which do not seem to be directly measurable and cannot be evaluated unless the matrix elements of the operators $\vec{\pi}$, s, $\vec{a}$, and $\vec{c}$ are known. Thus, the essential question one asks is, whether Eq. (24) can be transformed into a form in which only the local values of some simple band parameters appear, such as the effective-mass tensor (the $D_{jj'}$ matrix), the effective magnetic moment, the energy of a band extremum. By local values, i.e., by values at point $\vec{r}_0$, we mean the values of band parameters of the homogeneous crystal with the uniform composition $f(\vec{r}_0)$. In order to answer this question we must know the way in which the band parameters change with composition in homogeneous mixed crystals. In Appendix B the band parameters, i.e., the energy of the band extremum $E_j(f)$, the $D_{jj'}(f)$ matrix, and the effective magnetic moment $\vec{\mu}_{jj'}(f)$ are expressed in terms of band parameters and some matrix elements of the crystal with composition f_0 for small $L=f-f_0$. It turns out that the expressions for $D_{jj'}(f)$ and $\vec{\mu}_{jj'}(f)$ [see Eqs. (B3) and (B4) in Appendix B] appear the same matrices $M_{jj'}$, $N_{jj'}$, and $R_{jj'}$ as in the effective Hamiltonian $\tilde{H}_{jj'}$ [Eq. (24)]. Therefore, making use of these relations we transform the effective Hamiltonian to the final form in which the local values of the band parameters occur

$$\begin{aligned}\tilde{H}_{jj'} ={}& E_j(f(\vec{r}))\delta_{jj'} + \hbar\vec{a}_{jj'}\cdot\nabla f(\vec{r}) + \tfrac{1}{4}\hbar^2(\Phi^{\alpha\beta}_{jj'} + \Phi^{\beta\alpha}_{jj'})[\partial_\alpha\partial_\beta f(\vec{r})] + U(\vec{r},t)\\ &+ \tfrac{1}{2}i\hbar(\Lambda^{\alpha\beta}_{jj'} - \Lambda^{\beta\alpha}_{jj'})\{P_\alpha, \partial_\beta U(\vec{r},t)\} + \tfrac{1}{2}\{D^{\alpha\beta}_{jj'}(f(\vec{r})),\{P_\alpha,P_\beta\}\} + \vec{\mu}_{jj'}(f(\vec{r}))\cdot\vec{B}\\ &+ \tfrac{1}{2}i\hbar(\Phi^{\alpha\beta}_{jj'} - \Phi^{\beta\alpha}_{jj'})\{P_\alpha, \partial_\beta f(\vec{r})\} + \hbar\vec{b}_{jj'}[\nabla f(\vec{r})\times\vec{P}] ,\end{aligned} \tag{30}$$

where

$$\Phi^{\alpha\beta}_{jj'} = M^{\alpha\beta}_{jj'} + 2R^{\alpha\beta}_{jj'} - 2iW^{\alpha\beta}_{jj'} . \tag{31}$$

Equation (30) gives the effective Hamiltonian describing the motion of a carrier moving in the graded mixed semiconductor. Comparing Hamiltonian (30) with the usual effective-mass Hamiltonian for a carrier moving in a homogeneous crystal [e.g., Eq. (B1) in Appendix B], we see two striking differences. First, the dynamical parameters characterizing the motion of a carrier D matrix, magnetic moment $\vec{\mu}$, depend on its actual position in the crystal. Second, the slowly varying fields acting on a carrier are not only given to be the external field (i.e., by U and $\vec{A}$), but depend on the variation of the composition f within the crystal. We would like to stress that the knowledge of simple band parameters in crystals with uniform composition does not determine entirely the effective Hamiltonian (30).

The kinetic energy of the carrier at point $\vec{r}$,

$$\tfrac{1}{2}\{D^{\alpha\beta}_{jj'}(f(\vec{r})),\{P_\alpha,P_\beta\}\} \tag{32}$$

is determined by the local value of the matrix $D_{jj'}$. The kinetic momentum operator P and the matrix $D_{jj'}(f(\vec{r}))$ do not commute. However, the kinetic energy operator (32) is Hermitian. It should be noted that the symmetrization of this term by the anticommutator is uniquely given in the present theory.

The potential energy is not entirely determined by the scalar potential of the electromagnetic field, as is the case in homogeneous crystals, but there is an additional term,

$$\epsilon_{jj'} = E_j(f(\vec{r}))\delta_{jj'} + \tfrac{1}{2}\hbar^2\Phi^{\alpha\beta}_{jj'}[\partial_\alpha\partial_\beta f(\vec{r})] + \vec{a}_{jj'}\cdot\nabla f(\vec{r}) , \tag{33}$$

which represents the interaction with a "quasielectric" field. This interaction depends on the band occupied by the carrier. The quasielectric field is not solely given by $E_j(f(\vec{r}))$, the variation of the energy of the band extremum with position (compare Refs. 1–3, 5 and 6). Therefore, the knowledge of the dependence of the energy of band edge on composition for homogeneous mixed crystals is not sufficient to describe completely the potential energy of the carrier in the graded mixed semiconductor.

The terms

$$\hbar \vec{b}_{jj'}(\nabla f \times \vec{P}) \tag{34}$$

and

$$\tfrac{1}{2} i\hbar(\Phi^{\alpha\beta}_{jj'} - \Phi^{\beta\alpha}_{jj'})\{P_\alpha, \partial_\beta f\} \tag{35}$$

describe the additional interactions characteristic for mixed crystals with nonhomogeneous composition. The first term (34) proportional to $\vec{b}_{jj'}$, is due to the spin-orbit interaction. When the spin-orbit interaction can be neglected in the carrier Hamiltonian (3), $\vec{b}_{jj'}$ vanishes identically. The second term (35) would be present in the low-lattice-symmetry case (see I) even if we neglect the spin-orbit interaction. This case has been discussed in detail in I, where the term (35) in the effective Hamiltonian has been interpreted as a "interaction with quasimagnetic field." However, this interpretation is not very fortunate since when the external magnetic field is applied (35) depends on kinetic momentum $\vec{P}$ instead of canonical momentum $\vec{p}$ and $(\frac{1}{2}\hbar)(\Phi^{\alpha\beta}_{jj'} - \Phi^{\beta\alpha}_{jj'})(\partial_\beta f)$ cannot be treated as a vector potential of this quasifield. The case when the term (35) occurs due to the spin-orbit interaction will be discussed below Sec. IV.

The term

$$\vec{\mu}_{jj'}(f(\vec{r}))\cdot\vec{B} \tag{36}$$

represents the interaction of the carrier effective magnetic moment with external magnetic field $\vec{B}$. The effective magnetic moment at point $\vec{r}$ is determined by the local composition $f(\vec{r})$.

When the spin-orbit interaction is neglected and when there is no magnetic field effective Hamiltonian (30) reduces to that obtained in I. When spin effects are neglected but a magnetic field is applied the effective Hamiltonian derived here is very similar to that derived in I, only the canonical momentum $\vec{p}$ is replaced by the kinetic momentum $\vec{P}$ (see Ref. 4). Note that the components of $\vec{P}$ do not commute, thus when the nonspherical band case is considered the anticommutator $\{P_\alpha, P_\beta\}$ appears in the kinetic energy term (32).

IV. ELECTRONS FROM Γ_6 BAND IN CUBIC CRYSTALS

The aim of the effective-mass theory is to describe the carrier dynamics with the help of a minimal number of empirical parameters which are introduced instead of an unknown crystal potential. As we have shown, the problem of calculating electronic states in a graded mixed semiconductor reduces to the problem of solving the set of effective-mass equations (23) with the effective Hamiltonian (30), which is characterized by the following parameters: position-dependent $D_{jj'}$ matrix and effective magnetic moment $\vec{\mu}_{jj'}$, matrices $\Lambda_{jj'}$ and $\Phi_{jj'}$, vectors $\vec{a}_{jj'}$ and $\vec{b}_{jj'}$, and the band-edge energy E_j. However, making use of the lattice symmetry, the number of independent parameters of Hamiltonian (30) can be reduced. This reduction is especially important in crystals with high lattice symmetry.

In this section we consider the conduction electrons in graded mixed semiconductors with cubic lattice (i.e., point group is T_d or O_h). We restrict our considerations to mixed crystals whose components have conduction band minimum at the Γ point ($\vec{K}_0 = 0$) and noninverted band structure, i.e., the conduction-band minimum has Γ_6 symmetry. This case is very important since many intensively studied semiconducting alloys have components with such a band structure (e.g., III-V compounds as InSb, GaAs, etc., II-VI compounds as CdTe, ZnSe, etc.). On the other hand, this case, although fairly simple, serves as a good illustration of unique features of dynamics of carriers in graded mixed crystals.

The effective Hamiltonian $\tilde{H}_c$ for a conduction electron is 2×2 matrix since Γ_6 representation is two dimensional. The effective-mass equations take a form

$$\tilde{H}_c F(\vec{r},t) = i\hbar \frac{\partial F(\vec{r},t)}{\partial t}, \tag{37}$$

where $F(\vec{r},t)$ denotes a spinor whose components are envelope functions $F_1(\vec{r},t)$ and $F_2(\vec{r},t)$. In order to reduce the number of parameters in $\tilde{H}_c$ given by Eq. (30), we shall use the method of invariants (see, e.g., Refs. 16 and 17). $\tilde{H}_c$ is a function of the kinetic momentum $\vec{P}$, the magnetic field $\vec{B}$, the scalar potential U, and its derivatives $\partial_\alpha U$, and also of the crystal composition f and its derivatives $\partial_\alpha f$ and $\partial_\alpha \partial_\beta f$. In general, every two-dimensional Hermitian matrix is a linear combination of four matrices—of three Pauli matrices $\sigma^\alpha_{jj'}$ ($\alpha = 1, 2, 3$) and of the unity matrix $\delta_{jj'}$. $\tilde{H}_c$ should be invariant under all transformations of the $T_d(O_h)$ group. The only invariant form of Eq. (30) in the considered case is

$$\tilde{H}_c = \tfrac{1}{2}\{m^{*-1}(f(\vec{r})), P^2\} + \tfrac{1}{2}g^*(f(\vec{r}))\,\mu_B\vec{\sigma}\cdot\vec{B} + U(\vec{r},t) - \hbar\lambda\vec{\sigma}\cdot(\vec{P}\times\nabla U) + E(f(\vec{r})) + \hbar^2 C\,\nabla^2 f(\vec{r}) - \hbar\Phi\vec{\sigma}\cdot(\vec{P}\times\nabla f)\,. \qquad (38)$$

$\tilde{H}_c$ contains the following parameters: the effective-mass m^* and the effective g factor g^* defined by relations

$$D^{\alpha\beta}_{jj'}(f) = [1/m^*(f)]\delta^{\alpha\beta}\delta_{jj'}\,, \qquad (39)$$

$$\mu^{\alpha}_{jj'}(f) = \tfrac{1}{2}g^*(f)\mu_B\sigma^{\alpha}_{jj'}\,, \qquad (40)$$

and the parameters λ, Φ, and C, given by

$$\lambda\sigma^{\alpha}_{jj'} = -\tfrac{1}{2}i\epsilon^{\alpha\beta\gamma}\Lambda^{\beta\gamma}_{jj'}\,, \qquad (41)$$

$$\Phi\sigma^{\alpha}_{jj'} = -\tfrac{1}{2}i\epsilon^{\alpha\beta\gamma}\Phi^{\beta\gamma}_{jj'} + b^{\alpha}_{jj'}\,, \qquad (42)$$

and

$$C\delta_{jj'} = \tfrac{1}{6}\Phi^{\alpha\beta}_{jj'}\delta_{\alpha\beta}\,, \qquad (43)$$

respectively.

It is worth stressing that the set of six parameters $m^*(f)$, $g^*(f)$, $E(f)$, λ, C, and Φ describes entirely the dynamics of conduction electrons from Γ_6 band.

We see that when effects of electron spin are not included, λ and Φ vanish and the Hamiltonian (38) takes the form postulated by Bastard *et al.* in Ref. 4. In such an approximation, the only effects of the gradient of composition are the appearence of a quasielectric field acting on electrons of the energy

$$\epsilon(\vec{r}) = E(f(\vec{r})) + C\nabla^2 f(\vec{r})\,, \qquad (44)$$

and the position dependence of the effective mass.

The existence of the quasielectric field is mainly connected with the dependence of the energy of the Γ_6 band minimum E on composition f. From Eq. (44) we note that when $\nabla^2 f$ does not vanish there is an additional term in potential energy, which cannot be determined if only $E(f)$ is known. On the other hand, $\epsilon(\vec{r})$ can be interpreted as a position-dependent band edge. Since the quasielectric field acts differently on electrons and holes, one may use the concept of position-dependent energy gap (when $\nabla^2 f = 0$). The variation of the energy gap with position leads to some specific effects as strong modification of photovoltaic[18-23] and photoelectromagnetic[19,23-25] effects and produces an anti-Stokes effect of the electric field dependence of luminescent spectra of electron-hole recombination.[22,26,27]

The position dependence of the effective-mass modifies both quantum electronic states and classical equations of motion.[2-7] In the presence of magnetic field the effective-mass gradient causes a mixing between different Landau states. This leads to strong modification of cyclotron resonance.[4] In terms of classical equations of motion, an additional force proportional to the kinetic energy and the effective-mass gradient

$$\{P^2/2[m^*(\vec{r})]^2\}\vec{\nabla}m^*(\vec{r}) \qquad (45)$$

appears making the equations strongly nonlinear. This leads to the second harmonic generation on free electrons for both optical frequency range[3,28-30] and low frequencies.[31]

When the electron spin is added to the picture, two additional terms specific for nonhomogeneous-mixed semiconductors appear in the Hamiltonian. The first term

$$\tfrac{1}{2}g^*(f(\vec{r}))\mu_B\vec{\sigma}\cdot\vec{B} \qquad (46)$$

describes the interaction of the spin magnetic moment with the external magnetic field. Even when the magnetic field $\vec{B}$ is uniform, the energy of the interaction (46) depends on position because of the inhomogeneity of composition and thus in classical equations of motion an additional force proportional to the gradient of g factor appears. This force adds to the force arising from the quasielectric field, but it is spin dependent. Such a force as well as those due to the quasielectric field and effective-mass gradient has no analog in homogeneous crystals. The g-factor gradient may be quite large in such crystals as $\mathrm{Hg}_{1-f}\mathrm{Cd}_f\mathrm{Te}$ in which by changing f from about 0.2 to 1.0, g^* changes from about 100 to 2.

The second spin-dependent term specific for crystals with graded composition

$$-\hbar\Phi\vec{\sigma}\cdot(\vec{P}\times\nabla f) \qquad (47)$$

is of particular interest since it couples the equations for envelope functions $F_1(\vec{r},t)$ and $F_2(\vec{r},t)$. It is interesting to note an analogy between the term (47) and the term

$$-\hbar\lambda\vec{\sigma}\cdot(\vec{P}\times\nabla U) = q\hbar\lambda\vec{E}\cdot(\vec{\sigma}\times\vec{P})\,, \qquad (48)$$

($\vec{E}$ denotes the external electric field) also present in one-component cubic crystals when the spin-orbit interaction is important (e.g., Refs. 9 and 10). The term (48) can be interpreted as describing the interaction with an electric field E of the electric dipole moment $q\hbar\lambda(\vec{\sigma}\times\vec{P})$, which the electron acquires because of spin-orbit coupling (see, e.q., Ref. 9). The term (48) is the only term responsible for coupling the equations for $F_1(\vec{r},t)$ and $F_2(\vec{r},t)$ in one-component crystals and it gives rise to interesting phenomena such as, for instance, electric-spin resonance or combined resonance (e.g., Refs. 10 and 11). The interaction (48) also influences the spin-dependent (anomalous) Hall effect (e.g., Ref. 9). In graded mixed semiconductors apart from term (48) the term (47) appears in the effective Hamiltonian. By analogy, one can say that (47) represents an interaction of the electron dipole moment mentioned above with some internal field

$$(\Phi/q\lambda)\nabla f\,, \tag{49}$$

arising because of the nonhomogeneity of the crystal composition. Such an additional coupling of spin and orbital motion strongly influences the electron energy levels in a uniform magnetic field.[12] It can be expected that the spin-dependent effects in graded mixed crystals, in particular the electric-dipole-excited spin resonance, whose measurement would give the value of the coupling constant Φ, are strongly modified.[12] Both terms (47) and (48) appear because the potential energy of electron is not a periodic function of position.

It should be pointed out that the parameter Φ cannot be obtained by experiments on homogeneous mixed semiconductors since Φ multiples the term proportional to the gradient of composition in the effective Hamiltonian (30). However, Φ may be calculated from Eq. (42) if some matrix elements of homogeneous crystals are known. We shall use a three-band model in order to estimate the parameter Φ and to compare terms (47) and (48) in narrow-gap crystals.

The effective Hamiltonian (38) for conduction electrons from Γ_6 band has been obtained taking into account (in perturbation calculus) all other bands. Let us consider the case of narrow-gap mixed semiconductors. Then, it is reasonable to calculate the parameters appearing in the Hamiltonian (38) using the three-band model which takes into account only two nearest valence bands: Γ_8 band and spin-orbit split Γ_7 band, and neglects the effect of other bands on electron dynamics. The three-band model turns out to be very useful for describing physical phenomena connected with electron spin as well as those due to external magnetic field.

As basis functions $\psi_n (n=1,2,\ldots,8)$ of Γ_6, Γ_8, and Γ_7 extrema, we take Bloch functions transforming according to respective representations of the T_d point group.[15] Using the symmetry properties of functions ψ_n it is easy to show that with accuracy to terms linear in $L=f-f_0$ the energy of Γ_6 band in the crystal with composition f is

$$E(f)=s_c(f-f_0)\,, \tag{50}$$

where s_c denotes the matrix element of $S=V_B-V_A$ between s-like functions and the energies of Γ_8 and Γ_7 bands maxima are equal

$$E_{\Gamma_8}(f)=-\epsilon_g+(s_v+\delta)(f-f_0) \tag{51}$$

and

$$E_{\Gamma_7}(f)=-\epsilon_g-\Delta+(s_v-2\delta)(f-f_0)\,, \tag{52}$$

respectively. ϵ_g and Δ denote, respectively, the $\Gamma_8-\Gamma_6$ energy gap and spin-orbit splitting of the crystal with composition f_0, and s_v and δ are equal to matrix elements

$$s_v=(X|S|X) \tag{53}$$

and

$$\delta=(-i\hbar/4m^2c^2)(X|(\nabla S\times\vec{p})_y|Z)\,, \tag{54}$$

respectively. X, Y, Z denote p-like functions. We have taken the energy of the Γ_6 band minimum for the crystal with composition f_0 to be equal to zero. From Eqs. (51) and (52) we see that the parameter δ characterizes the variation with composition of the spin-orbit splitting $\Delta(f)$ of Γ_8 and Γ_7 bands since

$$\Delta(f)=\Delta+3\delta(f-f_0)\,. \tag{55}$$

The explicit expressions for parameters of the effective Hamiltonian (38) in the three-band model are given in Appendix C. It turns out that both the effective mass and g factor are entirely determined by the dependence on composition of the energy of the band gaps $\Gamma_6-\Gamma_8$ and $\Gamma_6-\Gamma_7$ [see Eqs. (C1) and (C2)]. Thus, the knowledge of coefficients characterizing the variation of the energy gaps ($s_v+\delta-s_c$ for $\Gamma_8-\Gamma_6$ and $s_v-2\delta-s_c$ for $\Gamma_7-\Gamma_6$) is sufficient to describe the change of m^* and g^* with composition. The expression for the parameter

$$\Phi=\frac{\kappa^2}{3m^2}\left(\frac{S_v-2\delta}{(\epsilon_g+\Delta)^2}-\frac{S_v+\delta}{\epsilon_g^2}\right) \tag{56}$$

(κ denotes the matrix element of the operator $\hbar\partial_x$ between s-like function and X function) involves independently $s_v+\delta$ and $s_v-2\delta$, i.e., the coefficients characterizing the variation of the energy of valence-bands maxima with composition. Therefore Φ cannot be calculated unless these quantities are known. It should be noted that s_v, s_c, and δ are difficult to measure, since what can be usually given directly by experiment is the dependence of the energy gaps on composition and not of the energy of band extrema. On the other hand, the measurement of Φ would permit the calculation of the parameters s_v, s_c, and δ and so it would give important information on mixed crystals. The knowledge of these parameters is essential, for instance, for interpretation of transport experiments since they describe the disorder scattering (residual resistence).

With the help of Eq. (56) the spin-dependent terms (47) and (48) can be compared. As we have already discussed both terms represent the coupling of spin and orbital motion: the term (48) occurs also in homogeneous crystals whereas the term (47) is due to the inhomogeneity of the crystal composition. The ratio of these two terms equals

$$\Phi |\nabla f|/q\lambda |\vec{\mathrm{E}}| \,. \tag{57}$$

From Eq. (56) for Φ and Eq. (C3) in Appendix C for λ we see that when the spin-orbit splitting $\Delta(f)$ does not vary strongly with composition, i.e., when δ is small compared with s_v, which is very often a case

$$\Phi \cong s_v \lambda \,. \tag{58}$$

Therefore, the ratio of the terms (47) and (48), Eq. (57), is of the order of

$$s_v |\nabla f|/q|\vec{\mathrm{E}}| \,, \tag{59}$$

i.e., of the order of the ratio of the force acting on a hole due to the quasielectric field and the external electric field. A quasielectric field can be very strong (especially in an alloy of narrow-gap and wide-gap semiconductors), for instance, for $\mathrm{Hg}_{1-f}\mathrm{Cd}_f\mathrm{Te}$ for f changing from 0.25 to 1.0 on the distance of the order of 0.1 mm it can be of the order of 100 V/cm. Hence, we see that the coupling of spin and orbital motion due to the nonhomogeneity of the crystal composition can be very important even for relatively small gradient of composition.

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APPENDIX A: EXPRESSIONS FOR COEFFICIENTS IN EQ. (24)

The matrix $D^{\alpha\beta}_{jj'}(f_0)$ and the effective magnetic moment $\vec{\mu}_{jj'}(f_0)$ of a carrier in the homogeneous crystal with composition f_0 are given by the usual formulas (compare, e.g., Ref. 16)

$$D^{\alpha\beta}_{jj'}(f_0) = \frac{1}{m}\delta^{\alpha\beta}\delta_{jj'} + \sum_{n \notin \{j\}} \frac{\pi^{\alpha}_{jn}\pi^{\beta}_{nj'} + \pi^{\beta}_{jn}\pi^{\alpha}_{nj'}}{m^2(E_j - E_n)} \tag{A1}$$

and

$$\mu^{\alpha}_{jj'}(f_0) = \tfrac{1}{2}\mu_B\left(g_0\sigma^{\alpha}_{jj'} + (\mathrm{sgn}\, q)\frac{2i}{m}\epsilon^{\alpha\beta\gamma}\sum_{n \notin \{j\}} \frac{\pi^{\beta}_{jn}\pi^{\gamma}_{nj'}}{E_j - E_n}\right), \tag{A2}$$

where $\mathrm{sgn}\, q$ denotes the sign of the carrier charge; $\epsilon^{\alpha\beta\gamma}$ is the antisymmetric Levi-Civita tensor.

The matrices $M^{\alpha\beta}_{jj'}$, $N^{\alpha\beta}_{jj'}$, $R^{\alpha\beta}_{jj'}$, $W^{\alpha\beta}_{jj'}$, and $\Lambda^{\alpha\beta}_{jj'}$ are, respectively, equal to

$$M^{\alpha\beta}_{jj'} = \sum_{n \notin \{j\}} \frac{\pi^{\alpha}_{jn}c^{\beta}_{nj'}}{m(E_j - E_n}, \tag{A3}$$

$$N^{\alpha\beta}_{jj'} = \sum_{n \notin \{j\}}\sum_{n' \notin \{j\}} \frac{\pi^{\alpha}_{jn}\pi^{\beta}_{nn'}s_{n'j'}}{m^2(E_j - E_n)(E_j - E_{n'})} - \sum_{j''=1}^{d}\sum_{n \notin \{j\}} \frac{\pi^{\alpha}_{jn}\pi^{\beta}_{nj''}s_{j''j'}}{2m^2(E_j - E_n)^2}, \tag{A4}$$

$$R^{\alpha\beta}_{jj'} = \sum_{n \notin \{j\}}\sum_{n' \notin \{j\}} \frac{\pi^{\alpha}_{jn}s_{nn'}\pi^{\beta}_{n'j'}}{2m^2(E_j - E_n)(E_j - E_{n'})}, \tag{A5}$$

$$W^{\alpha\beta}_{jj'} = \sum_{n \notin \{j\}} \frac{\pi^{\alpha}_{jn}a^{\beta}_{nj'}}{m(E_j - E_n)}, \tag{A6}$$

$$\Lambda^{\alpha\beta}_{jj'} = \sum_{n \notin \{j\}} \frac{\pi^{\alpha}_{jn}\pi^{\beta}_{nj'}}{m^2(E_j - E_n)^2}. \tag{A7}$$

APPENDIX B: DEPENDENCE OF BAND PARAMETERS ON COMPOSITION

Let us consider a homogeneous mixed crystal with composition $f = f_0 + L$, where $L = \text{const} \neq 0$ does not depend on $\vec{r}$. In such an alloy the crystal potential in the virtual-crystal approximation is periodic, and the standard effective-mass theory gives the effective Hamiltonian in the form

$$\tilde{H}_{jj'}(f) = E_j(f)\delta_{jj'} + \tfrac{1}{2}D^{\alpha\beta}_{jj'}(f)\{P_\alpha, P_\beta\} + \vec{\mu}_{jj'}(f)\cdot\vec{\mathrm{B}} + U + \tfrac{1}{2}i\hbar(\Lambda^{\alpha\beta}_{jj'} - \Lambda^{\beta\alpha}_{jj'})\{P_\alpha, \partial_\beta U\}, \tag{B1}$$

where $E_j(f)$, $D_{jj'}(f)$, and $\vec{\mu}_{jj'}(f)$ denote the energy of the band extremum, the D matrix and the effective magnetic moment of a carrier in the virtual crystal with composition f. On the other hand, if we do not look for the electron wave function in the natural representation of Kohn-Luttinger functions corresponding to the virtual crystal with composition f, but we expand Ψ, as in Eq. (9), in Kohn-luttinger functions corresponding to the crystal with composition f_0, in order to get $\tilde{H}_{jj'}(f)$ (with accuracy to terms linear in L) we should simply put $L = \text{const}$ in Eq. (24). Comparison of these two forms of $\tilde{H}_{jj'}(f)$ gives the dependence of band parameters on composition

$$E_j(f) = s_{jj}(f - f_0)\,, \tag{B2}$$

$$D^{\alpha\beta}_{jj'}(f) = D^{\alpha\beta}_{jj'}(f_0) + 2(f - f_0)(\Xi^{\alpha\beta}_{jj'} + \Xi^{\beta\alpha}_{jj'})\,, \tag{B3}$$

$$\mu^{\alpha}_{jj'}(f) = \mu^{\alpha}_{jj'}(f_0) + \tfrac{1}{2}(i\hbar \mathrm{q}/\mathrm{c})\epsilon^{\alpha\beta\gamma} \times (f - f_0)(\Xi^{\beta\gamma}_{jj'} - \Xi^{\gamma\beta}_{jj'})\,, \tag{B4}$$

where

$$\Xi^{\alpha\beta}_{jj'} = M^{\alpha\beta}_{jj'} + N^{\alpha\beta}_{jj'} + R^{\alpha\beta}_{jj'}\,. \tag{B5}$$

In our approximation (accuracy up to terms linear in L) the dependence of $\Lambda_{jj'}^{\alpha\beta}$ on composition can be neglected.

APPENDIX C: EXPRESSIONS FOR PARAMETERS OF THE EFFECTIVE HAMILTONIAN IN THE THREE-BAND MODEL

Using the symmetry properties of the basis functions ψ_n ($n=1,2,\ldots,8$) and Eqs. (39)–(43), we obtain the parameters of the Hamiltonian (38) in the three-band model

$$\frac{1}{m^*(f)} \cong \frac{1}{m} + \frac{2\kappa^2}{3m}\left[\left(\frac{2}{\epsilon_g} + \frac{1}{\epsilon_g+\Delta}\right) + (f-f_0)\left(\frac{2(s_v+\delta-s_c)}{\epsilon_g^2} + \frac{s_v-2\delta-s_c}{(\epsilon_g+\Delta)^2}\right)\right], \quad \text{(C1)}$$

$$g^*(f) \cong g_0 - \frac{4\kappa^2}{3m^2}\left[\frac{1}{\epsilon_g} - \frac{1}{\epsilon_g+\Delta} + (f-f_0)\left(\frac{s_v+\delta-s_c}{\epsilon_g^2} - \frac{s_v-2\delta-s_c}{(\epsilon_g+\Delta)^2}\right)\right], \quad \text{(C2)}$$

$$\lambda \cong \frac{\kappa^2}{3m^2}\left(\frac{1}{\epsilon_g^2} - \frac{1}{(\epsilon_g+\Delta)^2}\right), \quad \text{(C3)}$$

$$C \cong \frac{\kappa^2}{6m^2}\left(\frac{2(s_v+\delta)}{\epsilon_g^2} + \frac{s_v-2\delta}{(\epsilon_g+\Delta)^2}\right), \quad \text{(C4)}$$

and

$$\Phi \cong \frac{\kappa^2}{3m^2}\left(\frac{s_v-2\delta}{(\epsilon_g+\Delta)^2} - \frac{s_v+\delta}{\epsilon_g^2}\right), \quad \text{(C5)}$$

where κ is the matrix element of the operator $\hbar\partial_x$ between s-like function and X function. (Note that $m\kappa$ corresponds to the usually used P-matrix element.[32]) For $f=f_0$, Eqs. (C1)–(C3) reduce to the well-known formulas for effective mass, g factor, and parameter λ (e.g., Ref. 9). In writing Eqs. (C1)–(C5) we made use of the fact that in calculating matrix elements of $\vec{\pi}$ the term arising from $(\hbar/4mc^2)(\vec{\sigma}\times\nabla V_{f_0})$ can be neglected.[32] We have also neglected matrix elements $\vec{a}_{nn'}$ and $\vec{c}_{nn'}$, which are small compared to κ/m (the ratio of these matrix elements and of κ/m is of the order of the ratio of the periodic potentials difference S to the free-electron rest energy mc^2).

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