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Effective-mass theory for carriers in graded mixed semiconductors*

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The applicability of the effective-mass method and of the concept of the position-dependent band parameters to the description of the motion of carriers in graded mixed semiconductors (i.e., quasiheterojunctions) is examined. Within the framework of the virtual-crystal approximation the effective-mass Hamiltonian is found and discussed for graded mixed crystals whose components have a degenerate band with several nonspherical extrema. The case in which the locations of the band extrema within the Brillouin zone are different in the single-component crystals is considered. It is shown that in the case of low lattice symmetry the knowledge of the effective-mass tensor and of the energy of the band edge for homogeneous mixed crystals is insufficient to describe the dynamics of carriers in graded mixed semiconductors.

I. INTRODUCTION

Properties of graded mixed semiconductors (quasiheterojunctions) have aroused substantial theoretical and experimental interest in recent years.[1-18] Several particularly interesting phenomena have been observed, e.g., strong modification of photovoltaic[1-5] and photoelectromagnetic[2,6-8] effects and an anti-Stokes effect of the electric field dependence of luminescent spectra of electron-hole recombinations.[5,9,10] Some nonlinear electric and optical effects in graded mixed crystals have recently been proposed and calculated.[11-14] For theoretical interpretation of the properties of mixed crystals with slowly varying composition, knowledge of the laws of motion of charge carriers is necessary.

The principal tool for solving the problem of the motion of carriers in pure crystals is the well-known effective-mass method, which also applies in the virtual-crystal approximation to the treatment of homogeneous alloys (e.g., of $A_{1-x}B_x$ and $A_{1-x}B_xC$ types). The essence of the virtual-crystal approximation lies in replacing the correct one-electron potential of the actual configuration of atoms of the alloy by its average over all possible random configurations.[19] For homogeneous alloys the virtual-crystal potential is equal to the weighted average of the components potentials; therefore, it is periodic. The basic characteristic feature of graded mixed semiconductors is the lack of spatial periodicity of the one-electron potential (even in the virtual-crystal approximation).

The first attempts to describe the dynamics of carriers in crystals with slowly varying composition were based on the phenomenological assumptions of a position-dependent energy gap[15] and of a position-dependent effective mass.[16] From the first assumption it follows that a carrier moves in a quasielectric force field the strength of which depends on the band it occupies.[15] The assumption of a position-dependent effective mass gives rise to an additional force proportional to the gradient of the carrier's effective mass.[16] In addition, a kind of quasimagnetic field appears when it is assumed that inhomogeneity resulting from the change of crystal composition produces a shift of the location of the band extremum within the Brillouin zone, and that a standard effective-mass equation also holds for this case.[15] The quantum effective-mass equations were formulated by Lax[12] for carriers in graded mixed crystals in the two-band model and in the presence of an external magnetic field. However, the effective-mass Hamiltonians given in this paper are not Hermitian.

Gora and Williams[17,18] generalized the concept of virtual crystal to the case of graded mixed semiconductors and derived an effective-mass equation using the Wannier representation. Their calculations were restricted to the case of graded mixed crystals whose components have a nondegenerate spherical band with an extremum at the Γ point. However, in this derivation the reduction of the set of coupled equations to one effective-mass equation was achieved by omitting the interband matrix elements of $S(\vec{r}) = V_B(\vec{r}) - V_A(\vec{r})$ (V_A and V_B are the one-electron potentials of components A and B, respectively). The omission of these elements leads to an incomplete expression for the change of the effective mass with composition (see discussion in Sec. III).

In general, in experimentally available graded mixed semiconductors the components do not have a simple band with an extremum at the Γ point. Therefore, the problem arises of finding the equation of motion of carriers for a more realistic band structure of the components. The purpose of the present paper is to examine the applicability of the effective-mass theory and to derive the effective-mass equation for carriers in graded mixed semiconductors whose components have degenerate nonspherical bands with several extrema. We also consider the case when the locations of band extrema within the Brillouin zone are different in single-component crystals A and B (e.g., Ge and Si). The Wannier method used in Refs. 17 and 18 is not convenient to use in this case. We use the Kohn-Luttinger representation, which enables us to treat the degenerate and multivalley bands. In Sec. II, starting from the one-electron virtual-crystal Hamiltonian, we derive an effective-mass equation for graded mixed crystals with arbitrary lattice symmetry. In Sec. III, this equation and its classical counterpart are discussed. We also consider the case of low lattice symmetry, which is of theoretical interest because in such a case the knowledge of the effective-mass tensor for a homogeneous alloy is insufficient to describe the dynamics of carriers in crystals with varying composition.

II. EFFECTIVE-MASS EQUATION

We consider a two-component graded mixed semiconductor and assume that both components A and B have identical crystal structure and lattice constants. Let $f(\vec{r})$ denote the composition of the crystal in the neighborhood of point $\vec{r}$, i.e., the ratio of the number of atoms of component A to the number of atoms of component B equals $(1-f)/f$. We assume that the composition $f(\vec{r})$ varies slowly, i.e., the fractional change of f over a unit cell is small [see discussion following Eq. (16)] and that f may be treated as a smooth function of $\vec{r}$. The atoms of the crystal are supposed to lie on periodic lattice sites. (Lattice symmetry is arbitrary.) The generalization of the concept of virtual-crystal approximation to the case of the crystal under consideration gives the one-electron Hamiltonian[17]

$$H = -(\hbar^2/2m)\Delta + [1 - f(\vec{r})]\,V_A(\vec{r}) + f(\vec{r})\,V_B(\vec{r}) + U(\vec{r})\,, \tag{1}$$

where m is the free-electron mass and $U(\vec{r})$ denotes the potential energy of the electron in an external field. As usual in the effective-mass theory, we assume that U is a slowly varying "gentle" potential (see, e.g., Ref. 20). The one-electron Hamiltonian [Eq. (1)] can be written in the form

$$H = H_{f_0} + L(\vec{r})S(\vec{r}) + U(\vec{r})\,, \tag{2}$$

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

$$H_{f_0} = -(\hbar^2/2m)\,\Delta + (1-f_0)\,V_A(\vec{r}) + f_0 V_B(\vec{r})\,. \tag{3}$$

We are attempting to find the solution of the Schrödinger equation

$$H\Psi(\vec{r},t) = i\hbar\,\frac{\partial\Psi(\vec{r},t)}{\partial t}\,, \tag{4}$$

assuming the band structure of the homogeneous mixed crystal described by the eigenvalues $E_n(\vec{K}, f_0)$ and eigenfunctions (Bloch functions) $\psi_{n\vec{K}}$ of the unperturbed Hamiltonian H_{f_0} to be known (n labels the band and $\vec{K}$ is the wave vector). Equation (4) cannot be solved with the help of the usual effective-mass theory since the perturbation potential $LS + U$ is not a slowly varying function of $\vec{r}$. However, it is possible to modify the effective-mass method and to apply it to the present problem making use of the spatial periodocity of $S(\vec{r})$.

We consider the case of mixed crystals with a degenerate band with several extrema located at $\vec{K}_0^r(f_0)$ ($r = 1, \ldots, r'$; where r' is the number of extrema). $\vec{K}_0^r$ may depend on the composition of the crystal, f_0, when the locations of extrema within the Brillouin zone are different in the single-component crystals A and B (e.g., $\mathrm{Ge}_{1-x}\mathrm{Si}_x$ crystals). For brevity $\vec{K}_0^r(f_0)$ will be denoted by $\vec{K}_0$, but it should be remembered that $\vec{K}_0$ is a function of f_0 and denotes a specified (rth) extremum.

We call $\psi_{n\vec{K}_0}$ the Bloch functions at point $\vec{K}_0$. When functions labeled by n and n' belong to the same degenerate band this is briefly denoted by $n = n'$ and when they belong to different bands by $n \neq n'$. We define the complete orthonormal set of Kohn-Luttinger functions,[20]

$$\varphi_{n\vec{k}} = \Omega^{-1/2}\,e^{i\vec{k}\cdot\vec{r}}\,\psi_{n\vec{K}_0}\,, \tag{5}$$

$$(n\vec{k}\,|\,n'\vec{k}') \equiv \int_\Omega \varphi^*_{n\vec{k}}\,\varphi_{n'\vec{k}'}\,d^3r = \delta_{nn'}\,\delta_{\vec{k},\vec{k}'}\,, \tag{6}$$

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

We express the wave function $\Psi(\vec{r},t)$ by a linear combination of Kohn-Luttinger functions $\varphi_{n\vec{k}}$,

$$\Psi(\vec{r},t) = \sum_{n'}\sum_{\vec{k}'} A_{n'}(\vec{k}',t)\,\varphi_{n'\vec{k}'}(\vec{r})\,. \tag{7}$$

Inserting Eq. (7) into Eq. (4), multiplying both sides of Eq. (4) by $\varphi^*_{n\vec{k}}$, and integrating over the crystal volume, we obtain

$$\sum_{n'}\sum_{\vec{k}'} (n\vec{k}\,|\,H_{f_0} + LS + U\,|\,n'\vec{k}')A_{n'}(\vec{k}',t) = i\hbar\,\frac{\partial A_n(\vec{k},t)}{\partial t}\,, \tag{8}$$

where Eq. (6) has been used to obtain the right-hand side of Eq. (8) and $(n\vec{k}|O|n'\vec{k}')$ denotes the matrix elements of operator O.

We make the Ansatz so that the wave packet Ψ describing the electron 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 $\vec{K}_0$. When $\vec{K}_0$ is located in the interior of the Brillouin zone, the points in $\vec{K}$ space that lie near $\vec{K}_0$ are described by the condition $|\vec{k}'| = |\vec{K}' - \vec{K}_0| \ll \vec{G}_{\vec{m}}$ $(\vec{m} \neq 0)$, where $\vec{G}_{\vec{m}}$ are reciprocal-lattice vectors. When $\vec{K}_0$ is located on the boundary of the Brillouin zone the same condition describes the points lying near $\vec{K}_0$ only if we choose as the region of $\vec{K}$ space over which the summation in Eqs. (5) and (8) is carried, not the Brillouin zone, but a region in whose interior $\vec{K}_0$ lies (such a region can always be chosen because of the periodicity of the reciprocal lattice). Thus our Ansatz means that the only important terms in expansion [Eq. (5)] are those with $\vec{k}'$ much smaller than the reciprocal-lattice vector $\vec{G}_{\vec{m}}$ (for any $\vec{m} \neq 0$). This assumption must always be verified after solving the Schrödinger equation by the effective-mass method.

Making use of Eq. (6) we obtain the matrix elements of the H_{f_0} appearing in Eq. (8),

$$(n\vec{k}|H_{f_0}|n'\vec{k}') = [(E_n + \hbar^2 k^2/2m)\delta_{nn'} + \hbar\vec{k}\cdot\vec{p}_{nn'}/m]\,\delta_{\vec{k},\vec{k}'}\,, \tag{9}$$

where $E_n = E_n(\vec{K}_0, f_0)$ and

$$\vec{p}_{nn'} = \frac{1}{\Omega}\int_\Omega d^3r\,\psi^*_{n\vec{K}_0}\vec{p}\,\psi_{n'\vec{K}_0}\,. \tag{10}$$

$\vec{p} = -i\hbar\nabla$ is the momentum operator. It should be noted that

$$\vec{p}_{jj'} = 0\,, \tag{11}$$

for j and j' belonging to the same degenerate band. From the assumption that U is a slowly varying potential, i.e., that the fractional change of U over a unit cell is small, and from the Ansatz that important $\vec{k}$ and $\vec{k}'$ are much smaller than any $\vec{G}_{\vec{m}}$ with $\vec{m} \neq 0$, it follows that[20]

$$(n\vec{k}|U|n'\vec{k}') \cong \delta_{nn'}\,\mathcal{U}(\vec{k} - \vec{k}')\,, \tag{12}$$

where

$$\mathcal{U}(\vec{q}) = \frac{1}{\Omega}\int_\Omega d^3r\,e^{-i\vec{q}\cdot\vec{r}}\,U(\vec{r}) \tag{13}$$

denotes the Fourier transform of $U(\vec{r})$.

The matrix elements of LS are given by

$$(n\vec{k}|LS|n'\vec{k}') = \frac{1}{\Omega}\int_\Omega d^3r\,e^{-i(\vec{k}-\vec{k}')\vec{r}}\,LS\psi^*_{n\vec{K}_0}\psi_{n'\vec{K}_0}$$

$$= \Omega\sum_{\vec{m}} b^{nn'}_{\vec{m}}\,\mathcal{L}(\vec{k} - \vec{k}' + \vec{G}_{\vec{m}})\,, \tag{14}$$

where

$$\mathcal{L}(\vec{q}) = \frac{1}{\Omega}\int_\Omega d^3r\,L(\vec{r})\,e^{-i\vec{q}\cdot\vec{r}} \tag{15}$$

is the Fourier transform of $L(\vec{r})$. The function $S\psi^*_{n\vec{K}_0}\psi_{n'\vec{K}_0}$, which has the lattice periodicity, has been expanded in the Fourier series

$$S\psi^*_{n\vec{K}_0}\psi_{n'\vec{K}_0} = \Omega\sum_{\vec{m}} b^{nn'}_{\vec{m}}\,e^{-i\vec{G}_{\vec{m}}\cdot\vec{r}}\,. \tag{16}$$

We assume that the fractional change of $L(\vec{r}) = f(\vec{r}) - f_0$ over a unit cell is small. Then, the main contribution to the sum (14) is due to terms with $|\vec{k} - \vec{k}' + \vec{G}_{\vec{m}}| \ll |\vec{G}_{\vec{m}'}|$ $(\vec{m}' \neq 0)$. Since we have assumed that important $\vec{k}$ and $\vec{k}'$ are small compared with any $\vec{G}_{\vec{m}}$ with $\vec{m} \neq 0$, the contribution of terms containing higher Fourier components to the sum (14) is much smaller than that of a term with $\vec{m} = 0$. Therefore, we assume that in expansion (14) all terms with $\vec{m} \neq 0$ can be neglected. [This is precisely what we mean when we assume that the composition $f(\vec{r})$ varies slowly in the crystal.] Thus,

$$(n\vec{k}|LS|n'\vec{k}') \cong \Omega b_0^{nn'}\,\mathcal{L}(\vec{k} - \vec{k}') = S_{nn'}\,\mathcal{L}(\vec{k} - \vec{k}')\,, \tag{17}$$

where $S_{nn'}$ is given by

$$S_{nn'} = \Omega b_0^{nn'} = \frac{1}{\Omega}\int_\Omega d^3r\,S\psi^*_{n\vec{K}_0}\psi_{n'\vec{K}_0}\,. \tag{18}$$

From Eqs. (9), (12), and (17) it follows that Eq. (8) can be written

$$i\hbar\frac{\partial A_n(\vec{k},t)}{\partial t} = \sum_{n'}\sum_{\vec{k}'} A_{n'}(\vec{k}',t) \times (n\vec{k}|H_0 + H_B^{\mathrm{D}} + H_S^{D} + U + H_B^{\mathrm{ND}} + H_S^{\mathrm{ND}}|n'\vec{k}')\,, \tag{19}$$

where

$$(n\vec{k}|H_0^{\mathrm{D}}|n'\vec{k}') = E_n\,\delta_{nn'}\,\delta_{\vec{k},\vec{k}'}\,, \tag{20}$$

$$(n\vec{k}|H_0^{\mathrm{D}}|n'\vec{k}') = (\hbar^2k^2/2m)\,\delta_{nn'}\,\delta_{\vec{k},\vec{k}'}\,, \tag{21}$$

$$(n\vec{k}|H_S^{\mathrm{D}}|n'\vec{k}') = \begin{cases} S_{nn'}\,\mathcal{L}(\vec{k} - \vec{k}') & \text{for } n = n' \\ 0 & \text{for } n \neq n'\,, \end{cases} \tag{22}$$

$$(n\vec{k}|H_S^{\mathrm{ND}}|n'\vec{k}') = \begin{cases} 0 & \text{for } n=n' \\ S_{nn'}\,\mathcal{L}(\vec{k}-\vec{k}') & \text{for } n\neq n', \end{cases} \tag{23}$$

$$(n\vec{k}|H_B^{\mathrm{ND}}|n'\vec{k}') = \begin{cases} 0 & \text{for } n=n' \\ \dfrac{\hbar\vec{k}\cdot\vec{p}_{nn'}}{m}\,\delta_{\vec{k},\vec{k}'} & \text{for } n\neq n' \end{cases} \tag{24}$$

It should be remembered that $n=n'$ means that functions labeled by n and n' belong to the same degenerate band. The subscripts B and S denote, respectively, Bloch terms and terms resulting from the gradient of the composition; the superscripts D and ND label diagonal and nondiagonal terms, respectively.

Equation (19) is coupled not only by the usual terms involving $\vec{p}_{nn'}$ (part H_B^{ND} of the Hamiltonian), but also by terms which are specific for crystals with varying composition and which contain interband matrix elements $S_{nn'}$ (part H_S^{ND} of the Hamiltonian). We construct a canonical transformation operator e^T in order to remove the nondiagonal terms. We label by $j=1,2,\ldots,s$ the functions of the specific s-fold degenerate band occupied by the charge carriers (e.g., the valence band for holes). Application of the canonical transformation gives the set of equations for

$$B_j(\vec{k},t) = \sum_{n'}\sum_{\vec{k}'}(j\vec{k}|e^{-T}|n'\vec{k}')A_{n'}(\vec{k}',t), \tag{25}$$

in the form

$$i\hbar\,\frac{\partial B_j(\vec{k},t)}{\partial t} = \sum_{n'}\sum_{\vec{k}'}(j\vec{k}|H_{\mathrm{eff}}|n'\vec{k}')B_{n'}(\vec{k}',t), \tag{26}$$

where

$$\begin{aligned} H_{\mathrm{eff}} &= e^{-T}He^{T} \\ &= H+[H,T]+(1/2!)[[H,T]T]+\cdots . \end{aligned} \tag{27}$$

Our transformation T contains three parts,

$$T = T_1+T_2+T_3 . \tag{28}$$

The first term T_1 removes the nondiagonal part H_B^{ND} of the Hamiltonian H, i.e.,

$$[H_0,T_1] = -H_B^{\mathrm{ND}}, \tag{29}$$

where T_1 is assumed to be small,

$$|\hbar\vec{k}\cdot\vec{p}_{ji}/m(E_i-E_j)| \ll 1 \quad (i\neq j), \tag{30}$$

for $\vec{k}$ important in Eq. (19). (This assumption must be verified after the solution of the effective-mass equation is found.)

The second term T_2 removes the nondiagonal part H_S^{ND} of the Hamiltonian H, i.e.,

$$[H_0,T_2] = -H_S^{\mathrm{ND}} . \tag{31}$$

Moreover, T_2 is assumed to be small and this gives the condition for $L(\vec{r})$,

$$|\mathcal{L}(\vec{k}-\vec{k}')S_{ij}/(E_i-E_j)| \ll 1 \quad (i\neq j) . \tag{32}$$

In particular, if the crystal is homogeneous, i.e., the composition $f=f_0+L$ does not depend on $\vec{r}$, the Fourier transform of L is $\mathcal{L}(\vec{k}-\vec{k}') = L\delta_{\vec{k},\vec{k}'}$, and the condition (32) means that L must be small enough to satisfy $LS_{ij}/|E_i-E_j| \ll 1$. For a crystal with a linearly varying composition, the quantity L in the last inequality must be replaced by the change of the crystal composition over a characteristic length (e.g., the extent of an impurity state for impurities in graded mixed semiconductors and the electron wavelength in the case of electron transport). Hence, in the case of graded mixed crystals the change of crystal composition over the characteristic length must be sufficiently small to satisfy Eq. (32).

By applying T_1 and T_2 one obtains new nondiagonal terms of the order

$$\vec{k}\cdot\vec{p}_{ij}\,\mathcal{L}(\vec{k}-\vec{k}')S_{i'j'}/|(E_i-E_j)(E_{i'}-E_{j'})|$$
$$(i\neq j,\ i'\neq j') .$$

In order to cancel them we introduce T_3, i.e.,

$$[H_0,T_3] = -\tfrac{1}{2}[H_B^{\mathrm{ND}},T_2] - \tfrac{1}{2}[H_S^{\mathrm{ND}},T_1] - [H_S^{\mathrm{D}}T_1] . \tag{33}$$

Therefore, our canonical transformation eliminates interband elements first order in k (p_{ij}) and/or $\mathcal{L}$ (S_{ij}). When the inequalities (30) and (32) are satisfied the interband terms of order k^2, $k^2\mathcal{L}$, $\mathcal{L}^2$ and higher as well as the intraband terms of order k^3, $k^3\mathcal{L}$, $\mathcal{L}^2$ and higher can be neglected in Eq. (26). Thus, Eq. (26) for the band under consideration decouples and is of the form

$$\begin{aligned} i\hbar\frac{\partial B_j(\vec{k},t)}{\partial t} \cong \sum_{j'=1}^{s}\sum_{\vec{k}'}&(j\vec{k}|H_{\mathrm{eff}}|j'\vec{k}') \\ &\times B_{j'}(\vec{k}',t), \end{aligned} \tag{34}$$

where from Eqs. (27)–(29), (31), and (33) it follows that

$$\begin{aligned} (j\vec{k}|H_{\mathrm{eff}}|j'\vec{k}') &\cong (j\vec{k}|H_0+H_B^{\mathrm{D}}+H_S^{\mathrm{D}}+U+\tfrac{1}{2}[H_B^{\mathrm{ND}},T] \\ &\quad+\tfrac{1}{2}[H_S^{\mathrm{ND}},T_1]+\tfrac{1}{12}[[H_B^{\mathrm{ND}},\boldsymbol{T}_2]\boldsymbol{T}_1] \\ &\quad+\tfrac{1}{12}[[H_S^{\mathrm{ND}},T_1]T_1]+\tfrac{1}{3}[[H_B^{\mathrm{ND}},T_1]T_2]|j'\vec{k}') . \end{aligned} \tag{35}$$

In writing Eq. (35) we have neglected the term $[U,T]$. In fact, for slowly varying potentials for which the effective-mass theory is applicable (see

Ref. 20), and for an L function fulfilling the condition (32), it can be verified that the contribution of $[U,T]$ to H_{eff} is negligible.

Making use of definitions (29), (31), and (33), and calculating the matrix elements in Eq. (35), we obtain the set of equations for $B_j(\vec{k},t)$ $(j=1,\ldots,s)$:

$$\sum_{j'=1}^{s}\sum_{\vec{k}'}\{E_j\delta_{jj'}\delta_{\vec{k},\vec{k}'}+\tfrac{1}{2}\hbar^2 D_{jj'}^{\alpha\beta}(f_0)k_\alpha k_\beta\delta_{\vec{k},\vec{k}'}+\tfrac{1}{2}\hbar^2[(P_{j'j}^{\alpha\beta})^*k'_\alpha k'_\beta+P_{jj'}^{\alpha\beta}k_\alpha k_\beta+2R_{jj'}^{\alpha\beta}k_\alpha k'_\beta]\mathfrak{L}(\vec{k}-\vec{k}')$$
$$+\hbar[J_{jj'}^{\alpha}k_\alpha+(J_{j'j}^{\alpha})^*k'_\alpha]\mathfrak{L}(\vec{k}-\vec{k}')+S_{jj'}\mathfrak{L}(\vec{k}-\vec{k}')+\quad(\vec{k}-\vec{k}')\delta_{jj'}\}B_{j'}(\vec{k}',t)=i\hbar\frac{\partial B_j(\vec{k},t)}{\partial t}. \tag{36}$$

(The summation convention over repeated Greek indices is used.) In Eq. (36) we use the following notation:

$$D_{jj'}^{\alpha\beta}(f_0)=\frac{1}{m}\delta_{jj'}\delta_{\alpha\beta}+\frac{1}{m^2}\sum_{i\neq j}\frac{p_{ji}^{\alpha}p_{ij'}^{\beta}+p_{ji}^{\beta}p_{ij'}^{\alpha}}{E_j-E_i}, \tag{37}$$

which plays as usual in degenerate-band theory the role of the reciprocal effective-mass tensor of nondegenerate-band theory. The matrix $D_{jj'}^{\alpha\beta}(f_0)$ characterizes the dynamics of carriers in the virtual crystal with composition f_0. The matrices $P_{jj'}^{\alpha\beta}$ and $R_{jj'}^{\alpha\beta}$ and the vector $J_{jj'}^{\alpha}$ are defined

$$P_{jj'}^{\alpha\beta}=\frac{1}{m^2}\sum_{i\neq j}\sum_{i'\neq j}\frac{(p_{ji}^{\alpha}p_{ii'}^{\beta}+p_{ji}^{\beta}p_{ii'}^{\alpha})S_{i'j'}}{(E_j-E_i)(E_j-E_{i'})}$$
$$-\frac{1}{2m^2}\sum_{i\neq j}\sum_{j''=1}^{s}\frac{(p_{ji}p_{ij''}+p_{ji}p_{ij''})S_{j''j'}}{(E_j-E_i)^2}, \tag{38}$$

$$R_{jj'}^{\alpha\beta}=\frac{1}{m^2}\sum_{i\neq j}\sum_{i'\neq j}\frac{p_{ji}^{\alpha}S_{ii'}p_{i'j'}^{\beta}}{(E_j-E_i)(E_j-E_{i'})}=(R_{j'j}^{\beta\alpha})^*, \tag{39}$$

$$J_{jj'}^{\alpha}=\frac{1}{m}\sum_{i\neq j}\frac{p_{ji}^{\alpha}S_{ij'}}{E_j-E_i}. \tag{40}$$

$(P_{jj'}^{\alpha\beta})^*$ and $(R_{jj'}^{\alpha\beta})^*$ are matrices complex conjugate to $P_{jj'}^{\alpha\beta}$ and $R_{jj'}^{\alpha\beta}$ respectively.

Equation (36) is the set of effective-mass-like equations in $\vec{K}$ space. To accomplish the transformation of this set to $\vec{r}$ space we define the envelope functions

$$F_j(\vec{r},t)=\Omega^{-1/2}\sum_{\vec{k}}B_j(\vec{k},t)\exp[i(\vec{k}\cdot\vec{r}+E_jt/\hbar)], \tag{41}$$

multiply both sides of Eq. (36) by $\Omega^{-1/2}\exp[i(\vec{k}\cdot\vec{r}+E_jt/\hbar)]$, and sum over all $\vec{k}$. We obtain the set of equations for the envelope functions $F_j(\vec{r},t)$,

$$\sum_{j'=1}^{s}\{-\tfrac{1}{2}\hbar^2[D_{jj'}^{\alpha\beta}(f_0)\partial_\alpha\partial_\beta+P_{jj'}^{\alpha\beta}\partial_\alpha\partial_\beta L(\vec{r})+(P_{j'j}^{\alpha\beta})^*L(\vec{r})\partial_\alpha\partial_\beta+R_{jj'}^{\alpha\beta}\partial_\alpha L(\vec{r})\partial_\beta+(R_{j'j}^{\alpha\beta})^*\partial_\beta L(\vec{r})\partial_\alpha]$$
$$+(\hbar/i)[J_{jj'}^{\alpha}\partial_\alpha L(\vec{r})+(J_{j'j}^{\alpha})^*L(\vec{r})\partial_\alpha]+S_{jj'}L(\vec{r})+U(\vec{r})\delta_{jj'}\}F_{j'}(\vec{r},t)=i\hbar\frac{\partial F_j(\vec{r},t)}{\partial t}. \tag{42}$$

In order to obtain Eq. (42) we have used the fact that the function

$$\Delta(\vec{r}-\vec{r}')=\frac{1}{\Omega}\sum_{\vec{q}}e^{i\vec{q}(\vec{r}-\vec{r}')}$$

may be treated as a delta function $\delta(\vec{r}-\vec{r}')$ (see, e.g., Ref. 20), i.e., for slowly varying functions of position $g(\vec{r})$,

$$\int d^3r'\,\Delta(\vec{r}-\vec{r}')g(\vec{r}')\cong g(\vec{r}).$$

Equation (42) is set of effective-mass equations for the rth extremum of the band under consideration. If we investigate the motion of charge carriers in this band (e.g., electrons in the conduction band) we get from Eq. (7) the leading term in the wave function

$$\Psi_r(\vec{r},t)\cong\sum_{j=1}^{s}F_j(\vec{r},t)\psi_{j\vec{K}_0}(\vec{r}). \tag{43}$$

The subscript r means that Ψ_r is a particular wave packet corresponding to the rth extremum. The solutions of Eq. (42) corresponding to different extrema give—with the help of Eq. (43)—independent solutions Ψ_r $(r=1,2,\ldots,r')$ of the equation of motion. For general $U(\vec{r})$ and $f(\vec{r})$ the solutions of Eq. (42) corresponding to different extrema are different. The general electronic wave function is a linear combination of $\Psi_r(\vec{r},t)$.

III. DISCUSSION

The set of effective-mass equations (42) is not in a convenient form since it contains matrices $\mathrm{P}_{jj'}$ and $R_{jj'}$ and a vector $\vec{J}_{jj'}$, which do not seem to be directly measurable and cannot be evaluated unless the matrix elements of the momentum and of $S(\vec{r})$ are known. Thus, one asks whether Eq. (42) 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 energy, and the location 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 constant composition $f(\vec{r}_0)$. In order to answer this question we must know the way in which the band parameters change with composition (for homogeneous mixed crystals).

Let us consider a homogeneous mixed crystal with composition $f = f_0 + L$, where $L = \text{const} \neq 0$ does not depend on $\vec{r}$, and let us put $U = 0$. In this case the crystal potential (in the virtual-crystal approximation) is periodic, and the standard set of effective-mass equations obtained with the use of Kohn-Luttinger functions corresponding to the virtual crystal of composition f is

$$E(\vec{k}', \vec{K}_0(f), f) B_j'(\vec{k}')$$
$$= \sum_{j'=1}^{s} B_j'(\vec{k}') [\tfrac{1}{2}\hbar^2 D_{jj'}(f) k_\alpha' k_\beta' + E_j(0, \vec{K}_0(f), f)\, \delta_{jj'}], \tag{44}$$

where $\vec{k}'$ is defined as $\vec{k}' = \vec{K} - \vec{K}_0(f)$, and $E_j(0, \vec{K}_0(f), f)$ and $D_{jj'}(f)$, respectively, denote the energy of the band extremum located at $\vec{K}_0(f)$, and the $D_{jj'}$ matrix [see Eq. (37)] for a virtual crystal with composition f. On the other hand, when we do not look for the electric wave function in this natural representation, but expand Ψ, as in Eq. (7), in Kohn-Luttinger functions corresponding to the virtual crystal with composition f_0, we obtain (for L small) a set of equations of the form

$$E(\vec{k}, \vec{K}_0(f_0), f) B_j(\vec{k}) = \sum_{j'=1}^{s} B_{j'}(\vec{k}) \{\tfrac{1}{2}\hbar^2 D_{jj'}^{\alpha\beta}(f_0) k_\alpha k_\beta + \tfrac{1}{2}\hbar^2 [\vec{P}_{jj'}^{\alpha\beta} + (P_{j'j}^{\alpha\beta})^*$$
$$+ R_{jj'}^{\alpha\beta} + (R_{j'j}^{\alpha\beta})^*] L k_\alpha k_\beta + \hbar [J_{jj'}^{\alpha} + (J_{j'j}^{\alpha})^*] L k_\alpha + S_{jj'} L + E_j(0, \vec{K}_0(f_0), f_0)\, \delta_{jj'}\}, \tag{45}$$

where $\vec{k} = \vec{K} - \vec{K}_0(f_0)$. This set can be also obtained from Eq. (36) by putting $L = \text{const.}$ and $U = 0$. Comparing Eqs. (44) and (45) gives

$$D_{jj'}^{\alpha\beta}(f) = D_{jj'}^{\alpha\beta}(f_0)$$
$$+ L[P_{jj'}^{\alpha\beta} + (P_{j'j}^{\alpha\beta})^* + R_{jj'}^{\alpha\beta} + (R_{j'j}^{\alpha\beta})^*], \tag{46}$$

$$[J_{jj'}^{\alpha} + (J_{j'j}^{\alpha})^*] L = \hbar D_{jj'}^{\alpha\beta}(f) \Delta K_\beta, \tag{47}$$

and

$$E_j(0, \vec{K}_0(f), f) = E_j(0, \vec{K}_0(f_0), f_0) + S_{jj} L . \tag{48}$$

$\Delta \vec{K} = \vec{K}_0(f) - \vec{K}_0(f_0)$ denotes the shift of the location of the band extremum within the Brillouin zone. In Eq. (48) we have used the fact [resulting from the symmetry of $S(\vec{r})$] that for the degenerate band (unless there is no accidental degeneracy)

$$S_{jj'} = S_{jj}\, \delta_{jj'} .$$

(S_{jj} are the same for each j.) Equations (46)–(48) give the relations between simple band parameters and the combination of matrices $P_{jj'}$ and $R_{jj'}$, the vector $\vec{J}_{jj'}$, and their complex conjugates.

Therefore, in the following discussion of the effective-mass equation for graded mixed crystals two cases must be considered, the high-symmetry case in which the matrices are real, and the low-symmetry case in which they are complex.

A. High-symmetry case

We deal first with the case in which the symmetry of the homogeneous crystal (of composition f_0) is sufficiently high to enable us to choose the eigenfunctions $\psi_{n\vec{K}_0}$ in such a way that all matrix elements of the momentum $\vec{p}$ and of $S(\vec{r})$ are real. Then, the matrices $P_{jj'}$ and $R_{jj'}$ and the vector $\vec{J}_{jj'}$ are real. An example of such a situation is the case when the inversion belongs to the wave-vector group $G_{\vec{K}_0}$.

Making use of relations (46)–(48) we can transform Eq. (42) into the form

$$\sum_{j'=1}^{s} [-\tfrac{1}{4}\hbar^2 \partial_\alpha \partial_\beta D_{jj'}^{\alpha\beta}(f(\vec{r})) - \tfrac{1}{4}\hbar^2 D_{jj'}^{\alpha\beta}(f(\vec{r})) \partial_\alpha \partial_\beta + \tfrac{1}{2}\{(\hbar/i)\partial_\alpha [D_{jj'}^{\alpha\beta}(f(\vec{r}))\, \hbar \Delta K_\beta] + (\hbar/i)[D_{jj'}^{\alpha\beta}(f(\vec{r}))\, \hbar \Delta K_\beta] \partial_\alpha\}$$
$$+ S_{jj}\delta_{jj'} + U\delta_{jj'} + \tfrac{1}{4}\hbar^2 (R_{jj'}^{\alpha\beta} + R_{jj'}^{\beta\alpha})(\partial_\alpha \partial_\beta L)] F_{j'}(\vec{r}, t) = i\hbar \frac{\partial F_j(\vec{r}, t)}{\partial t} . \tag{49}$$

Equations (49) are the set of effective-mass equations for carriers occupying the degenerate band, when the locations of the band extrema within the Brillouin zone shift with composition. This set resembles that describing the motion of carriers in pure crystals in the presence of a weak magnetic field. However, there is one principal difference, the $D_{jj'}$ matrix is position dependent. The role of the vector potential is played by the vector

$$\Phi_1(\vec{r}) = (c\hbar/e)\Delta\vec{K}_0$$
$$= -(c\hbar/e)[\vec{K}_0(f(\vec{r})) - \vec{K}_0(f_0)]. \tag{50}$$

From Eq. (47), it turns out that the vector potential does not vanish unless $\vec{J}_{jj'} + \vec{J}_{j'j}$ is equal to zero (e.g., as a result of the crystal symmetry). Thus, when a change in crystal composition produces a shift in the location of the band extremum within the Brillouin zone $(\vec{J}_{jj'} + \vec{J}_{j'j} \neq 0)$, a quasimagnetic field of strength

$$-(c\hbar/e)\,\mathrm{rot}\vec{K}_0(f(\vec{r}))$$

acts on the carrier. This quasimagnetic field acts differently on carriers occupying different band extrema. In the case of the nondegenerate band this field is the same as that introduced by means of the phenomenological assumption by Kroemer.[15]

Therefore, from the above consideration, it follows that the kinetic part of Eqs. (49) is determined only if the matrix $D_{jj'}$ and the location of the band extrema within the Brillouin zone are known for a homogeneous crystal. However, the potential energy [the last three terms in the left-hand side of Eq. (49)] is not solely determined by the change in the energy of the band extremum with composition [given by Eq. (48)] and by the potential energy of the external field because of the term $\frac{1}{4}\hbar^2(R^{\alpha\beta}_{jj'} + R^{\beta\alpha}_{jj'})(\partial_\alpha\partial_\beta L)$. This term, together with the term $L(\vec{r})S_{jj}\delta_{jj'}$, may be interpreted as resulting from a quasielectric field acting on the carrier apart from the external field.

When we consider the carriers occupying the nondegenerate band j we obtain the effective-mass Hamiltonian

$$H^* = \tfrac{1}{4}[p_\alpha p_\beta m^{*-1}_{j\alpha\beta}(f(\vec{r})) + m^{*-1}_{j\alpha\beta}(f(\vec{r}))p_\alpha p_\beta]$$
$$- e/2c)[p_\alpha m^{*-1}_{j\alpha\beta}(f(\vec{r}))\Phi_{1\beta}(\vec{r})$$
$$+ m^{*-1}_{j\alpha\beta}(f(\vec{r}))\Phi_{1\beta}(\vec{r})p_\alpha] + U(\vec{r}) + \epsilon_j(\vec{r}). \tag{51}$$

In Eq. (51) we use the definition of reciprocal effective-mass tensor,

$$m^{*-1}_{j\alpha\beta}(f) = D^{\alpha\beta}_{jj}(f), \tag{52}$$

and we introduce

$$\epsilon_j(\vec{r}) = S_{jj}L(\vec{r}) + \tfrac{1}{2}\hbar^2 R^{\alpha\beta}_{jj}[\partial_\alpha\partial_\beta L(\vec{r})]. \tag{53}$$

In the case considered by Gora and Williams,[17,18] i.e., that of alloys with an isotropic, nondegenerate band with extremum at the Γ point, our formulas give the Hamiltonian

$$H^* = \frac{1}{4}p^2\frac{1}{m_j^*(\vec{r})} + \frac{1}{4}\frac{1}{m_j^*(\vec{r})}p^2 + \epsilon_j(\vec{r}), \tag{54}$$

where

$$\frac{1}{m_j^*(\vec{r})} = \frac{1}{m_j^*(f_0)} + L\frac{2}{m^2}$$
$$\times\Bigg[\sum_{i\neq j}\sum_{i'\neq j}\left(\frac{p_{ji}p_{ii'}S_{i'j}}{(E_j - E_i)(E_j - E_{i'})}\right.$$
$$\left. + \frac{p_{ji}S_{ii'}p_{i'j}}{(E_j - E_i)(E_j - E_{i'})}\right)$$
$$- \frac{1}{2}\sum_{i\neq j}\frac{p_{ji}p_{ij}S_{jj}}{(E_j - E_i)^2}\Bigg]. \tag{55}$$

The form of Eq. (54) is very similar to that obtained in Refs. 17 and 18. However, formula (55) for the position dependence of the effective mass is different from that obtained by Gora and Williams, who neglected some interband matrix elements of S. Namely, in their expansion the second and the fourth terms on the right-hand side of Eq. (55) do not appear. Another difference is that $\epsilon_j(\vec{r})$ is not equal to $E_j(f(\vec{r})) - E_j(f_0)$, i.e., to the change in the energy of the band extremum, because of the term $\frac{1}{2}\hbar^2 R_{jj}(\nabla^2 L)$.

It should be pointed out that the method of canonical transformation used in this paper enables one to derive the effective Hamiltonian with accuracy to arbitrary powers of $L(\vec{r})$. In particular, the canonical transformation (28) gives the effective Hamiltonian, and therefore the effective mass and other band parameters, accurate to terms linear in L (all such terms are taken into account).

It should also be noted that the symmetrization of the kinetic term in the effective-mass Hamiltonian (54) is unique [the obtained Hamiltonian (42) is, of course, Hermitian], whereas in Ref. 18 it was obtained by an arbitrary procedure.

It is interesting to investigate the classical counterpart of the equation of motion of carriers in a graded mixed crystal. From the fact that the solution $F_j(\vec{r}, t)$ of the effective-mass equation describes the physical situation only if it is a slowly varying function of $\vec{r}$ and from Eq. (43) it can be shown that

$$\langle\vec{r}(t)\rangle \equiv \int_\Omega d^3r\,\Psi^*\vec{r}\Psi \cong \int_\Omega d^3r\,F_j^*\vec{r}F_j$$

and

$$\langle\vec{p}(t)\rangle \equiv \int_\Omega d^3r\,\Psi^*\vec{p}\Psi \cong \int_\Omega d^3r\,F_j^*\vec{p}F_j.$$

This means that the average values of position and momentum of the charge carrier described by the wave function $\Psi(\vec{r}, t)$ are equal to and vary in the same way as the mean values for a particle described by the effective-mass Hamiltonian H^* [given by Eq. (51)]. Therefore, in order to find the classical counterpart of the quantum equation of motion of the charge carrier we can investigate the particle described by H^* and find the classical limit of its motion. Using the Ehrenfest theorem and replacing the mean values $\langle \vec{r} \rangle$ and $\langle \vec{p} \rangle$ by $\vec{r}$ and $\vec{p}$ which describe the position and momentum of the classical particle, we obtain

$$\frac{dr_\alpha}{dt} = m^{*-1}_{j\alpha\beta}(f(\vec{r}))[p_\beta - (e/c)\Phi_{1\beta}(\vec{r})], \tag{56}$$

$$\frac{dp_\alpha}{dt} = -\tfrac{1}{2} p_\beta p_\gamma \partial_\alpha m^{*-1}_{j\beta\gamma}(f(\vec{r})) - \partial_\alpha \epsilon_j(\vec{r}) - \partial_\alpha U(\vec{r}) + (e/c) p_\beta \partial_\alpha (m^{*-1}_{j\beta\gamma} \Phi_{1\gamma}). \tag{57}$$

The first relation, which connects the velocity of the particle with its canonical momentum, shows that the momentum of the quasimagnetic field is $(e/c)\vec{\Phi}_1(\vec{r}) = \hbar \Delta \vec{k}_0(\vec{r})$. In Eq. (56) the position-dependent effective-mass tensor plays the role of the free mass in the ordinary relation between momentum and velocity. Equation (57) is analogous to Newton's law. It shows that apart from the usual force due to the external field $U(r)$ three additional forces, resulting from the position dependence of the composition of the crystal, act on a carrier. The first is proportional to the gradient of the effective mass tensor. The second can be interpreted as a force due to a quasielectric field. [$\epsilon_j(\vec{r})$ is the potential energy of the carrier in this field.] The third is the force acting on a particle moving in a weak magnetic field characterized by the vector potential $\vec{\Phi}_1(\vec{r})$. All these forces depend on the band the carrier occupies.

B. Low-symmetry case

We now deal with the case in which the crystal symmetry is low, so that the representations of the group of the wave vector $G_{\vec{k}_0}$ are not real and $P_{jj'}$, $R_{jj'}$, and $\vec{J}_{jj'}$ are complex (e.g., in trigonal Te and Se crystals). For simplicity we consider the case of a nondegenerate band with an extremum which does not shift within the Brillouin zone. From Eq. (42) we obtain

$$\{\tfrac{1}{4}[m^{*-1}_{j\alpha\beta}(f(\vec{r})) p_\alpha p_\beta + p_\alpha p_\beta m^{*-1}_{j\alpha\beta}(f(\vec{r}))] + \tfrac{1}{2}[p_\alpha \Phi_{2\alpha}(\vec{r}) + \Phi_{2\alpha}(\vec{r}) p_\alpha] + U(\vec{r}) + \epsilon_j(\vec{r})\} F_j(\vec{r}, t) = i\hbar \frac{\partial F_j(\vec{r}, t)}{\partial t}, \tag{58}$$

where

$$\Phi_{2\alpha} = \hbar \operatorname{Im}(P^{\alpha\beta}_{jj} - R^{\alpha\beta}_{jj})(\partial_\beta L). \tag{59}$$

Hence, in the low-symmetry case a new term $\frac{1}{2}(\vec{p}\vec{\Phi}_2 + \vec{\Phi}_2\vec{p})$ appears in the effective-mass Hamiltonian. This term resembles the part of Hamiltonian characteristic of the motion of a particle in a weak magnetic field. $\vec{\Phi}_2(\vec{r})$ may be interpreted as a vector proportional to the vector potential of the "quasimagnetic field." It should be pointed out that the origin and the nature of this field are completely different from those of the field introduced in the high-symmetry case, $\vec{\Phi}_1(\vec{r})$. The low-symmetry case is interesting, as can be seen from Eqs. (58) and (59), because the knowledge of the effective-mass tensor for a homogeneous crystal is insufficient to describe the dynamics of the carrier in a graded mixed crystal. For homogeneous crystals another band parameter, namely, the matrix $\hbar \operatorname{Im}(P^{\alpha\beta}_{jj} - R^{\alpha\beta}_{jj})$ must be known.

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