

## Acceptor resonances in zero-gap and small-gap semiconductors

A. Mauger

*Laboratoire de Physique des Solides, Centre National de la Recherche Scientifique, 92190 Meudon-Bellevue, France*

J. Friedel

*Université de Paris-Sud, Laboratoire de Physique des Solides, 91405 Orsay, France*

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An extension of the Koster-Slater theory is performed to study the effect of a localized perturbing potential in zero-gap and small-gap semiconductors. According to this two-band model, the existence of resonant energies depends upon the ratio of the effective mass of the valence and conduction bands, respectively. Owing to the large value of this ratio, it is shown that donors do not lead to any quasisdiscrete level. On the contrary, acceptors lead to resonances in the conduction band, provided that the perturbing potential is strongly repulsive. We find that the interband coupling potential mainly results in a dependence of the location of the resonance upon the density of conduction-band states. Experiments performed on  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys are shown to be in good agreement with these theoretical results.

### I. INTRODUCTION

The problem of impurity states in semiconductors has been studied by many authors. In particular, Luttinger and Kohn<sup>1,2</sup> have developed an effective-mass formalism to write the Hamiltonian in the case of a strong spin-orbit coupling energy, for materials having the diamond or, in first approximation, the zinc-blende symmetry. Lipari and Baldereschi have neglected the small terms with no spherical symmetry, and having added to the Hamiltonian a Coulomb potential, they solved the eigenvalue problem in small-gap semiconductors.<sup>3</sup> Gel'mont and D'yakonov have solved the same problem by different calculation techniques, not only in small-gap,<sup>4</sup> but also in zero-gap semiconductors.<sup>5</sup> Nevertheless, the only attempt to take into account a highly localized central-cell coupling was performed by Liu and Brust.<sup>6</sup>

This paper deals with resonance conditions (location and width) of donors and acceptors in zero-gap or small-gap semiconductors, when the perturbing potential is entirely localized on the site of the impurity or defect. This potential is expected to be more appropriate than the Coulomb potential to describe those of the acceptor states evidenced in  $\text{HgTe}$  and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys<sup>7</sup> which are essentially induced by native defects (mercury vacancies).

In Sec. II, the scattering problem is solved by using the Green's-function formalism in the framework of a two-band model. We also discuss the existence of resonant states, their location and width. The outline of the theory is exactly the same as in Ref. 6. However, some of our results are quite different, because we take into account a strong interband coupling potential underestimated by

Liu and Brust. Section III deals with a discussion of some recent experimental results showing a typical illustration of our calculations.

### II. SCATTERING PROBLEM

This section is split up in four parts: In Sec. IIA we recall the basic equations previously set by Liu and Brust.<sup>6</sup> The existence and location of resonances are then investigated in Sec. IIB. The main features of the resonance, such as the width and the relaxation time of electrons in virtual bound states, are determined in IIC and IID, respectively.

#### A. Basic equations

We shall write the Hamiltonian  $H$  of the problem in a tight-binding approximation, and we shall only take into account the conduction band and the valence band. We must thus define a set of doubly degenerate Wannier function, i.e., two Wannier functions  $i_c$  and  $i_v$  per site  $i$  associated with the conduction- and valence-band states, respectively. We shall assume that these functions are localized on the site  $i$ . It will prove useful to define the basic projectors  $P_i$  which select both states at a given site  $i$ , and have then the property

$$P_i P_j = P_i \delta_{ij}, \quad (2.1)$$

where  $\delta_{ij}$  is the Kronecker symbol. For  $i=j$ , Eq. (2.1) is nothing but the definition of  $P_i$  as a projector, and for  $i \neq j$ , this expression results from the orthogonality of Wannier functions on different sites. Since we shall only consider the dilute limit in which the interactions between defects are neglected, we may consider a single scattering center, on site  $O$  for example. The

Hamiltonian then takes the form

$$H = H_0 + U. \quad (2.2)$$

Owing to the localized character of the perturbing potential  $U$  induced by the defect, we can write  $U = P_0 \underline{V} P_0$ .  $\underline{V}$  is a  $2 \times 2$  matrix which, in the Wannier representation, is defined by

$$V = \begin{pmatrix} V_{cc} & V_{cv} \\ V_{vc} & V_{vv} \end{pmatrix}. \quad (2.3)$$

$V_{cc}$  and  $V_{vv}$  are the intraband coupling energies of the conduction and valence bands, respectively;  $V_{cv}$  and  $V_{vc}$  are the interband coupling energies. Let  $G_0$  and  $G$  be the unperturbed and perturbed Green's functions of the problem:

$$G_0(E) = \frac{1}{E - H_0}, \quad (2.4)$$

$$G(E) = \frac{1}{E - H}.$$

According to the Eq. (2.2), the variation of the Green's function induced by the perturbing potential is given by the Dyson's equation

$$P_i(G - G_0)P_i = \frac{1}{\Delta} \begin{pmatrix} \langle i_c | G_{0c} | O_c \rangle & 0 \\ 0 & \langle i_v | G_{0v} | i_v \rangle \end{pmatrix} \begin{pmatrix} 1 - F_v V_{vv} & V_{cv} F_v \\ V_{vc} F_c & 1 - F_c V_{cc} \end{pmatrix} \begin{pmatrix} V_{cc} \langle O_c | G_{0c} | i_c \rangle & V_{cv} \langle O_v | G_{0v} | i_v \rangle \\ V_{vc} \langle O_c | G_{0c} | i_c \rangle & V_{vv} \langle O_v | G_{0v} | i_v \rangle \end{pmatrix}. \quad (2.9)$$

$\Delta$  is the following determinant:

$$\Delta = \begin{vmatrix} 1 - V_{cc} F_c & -V_{cv} F_v \\ -V_{vc} F_c & 1 - V_{vv} F_v \end{vmatrix}. \quad (2.10)$$

We can sum the diagonal elements of Eq. (2.9) to find the trace of  $\delta G = G - G_0$ :

$$\text{Tr} \delta G = \frac{1}{\Delta} \sum_i \{ [V_{cc} - (V_{vv} V_{cc} - V_{cv} V_{vc}) F_v] \langle O_c | G_{0c} | i_c \rangle \langle i_c | G_{0c} | O_c \rangle + [V_{vv} - (V_{vv} V_{cc} - V_{cv} V_{vc}) F_c] \langle O_v | G_{0v} | i_v \rangle \langle i_v | G_{0v} | O_v \rangle \}. \quad (2.11)$$

It should be noticed that, according to Eqs. (2.4) and (2.7),

$$\langle O_c | G_{0c}^2 | O_c \rangle = -\frac{\partial F_c}{\partial E}, \quad (2.12)$$

$$\langle O_v | G_{0v}^2 | O_v \rangle = -\frac{\partial F_v}{\partial E}.$$

Equation (2.11) thus takes the form

$$\text{Tr} \delta G = \frac{1}{\Delta} \frac{\partial \Delta}{\partial E}. \quad (2.13)$$

The change of density of states  $\delta n(E)$  induced by the perturbing potential is determined by the usual re-

$$G - G_0 = G_0 U G. \quad (2.5)$$

We shall define the  $2 \times 2$  matrix  $F$  by the formula  $P_0 G_0 P_0 = P_0 F P_0$  or

$$F = \begin{pmatrix} F_c & 0 \\ 0 & F_v \end{pmatrix}, \quad (2.6)$$

with

$$F_c = \langle O_c | G_{0c} | O_c \rangle, \quad (2.7)$$

$$F_v = \langle O_v | G_{0v} | O_v \rangle.$$

$G_{0c}$  and  $G_{0v}$  are the unperturbed Green's functions associated with the conduction and the valence bands, respectively. Taking Eq. (2.3) into account, the iterative solution of Eq. (2.5) is

$$G - G_0 = G_0 P_0 (1 + \underline{V} F + \underline{V} F \underline{V} F + \dots) \underline{V} P_0 G_0. \quad (2.8)$$

We notice that the sum in the brackets is a development of the matrix  $(1 - \underline{V} F)^{-1}$  which can be calculated from Eqs. (2.3) and (2.6). The projection of Eq. (2.8) on the subspace  $\{|i_c\rangle, |i_v\rangle\}$  is then

lation,

$$\delta n(E) = -\frac{1}{\pi} \text{Im Tr} \delta G, \quad (2.14)$$

Im and Re meaning the imaginary and real parts, respectively, Eqs. (2.13) and (2.14) imply

$$\delta n(E) = -\frac{1}{\pi} \text{Im} \left( \frac{(\partial \Delta / \partial E) (\text{Re} \Delta - i \text{Im} \Delta)}{(\text{Re} \Delta)^2 + (\text{Im} \Delta)^2} \right). \quad (2.15)$$

$\delta n(E)$  is quite small, except in the vicinity of the energy  $E_R$  which, provided it exists, is defined by

$$\text{Re} \Delta(E_R) = 0. \quad (2.16)$$

For energies  $E \simeq E_R$ , we can replace  $\text{Re} \Delta$  by 0 in

the numerator of Eq. (2.15), and by  $(E - E_R)\partial \times \text{Re}\Delta/\partial E$  in the denominator. We then obtain

$$\delta n(E) = \frac{1}{\pi} \frac{\Gamma}{(E - E_R)^2 + \Gamma^2} . \quad (2.17)$$

$\Gamma$  is the resonance half-width determined by

$$\Gamma = \left[ \frac{\text{Im}\Delta}{d \text{Re}\Delta/dE} \right]_{E=E_R} . \quad (2.18)$$

### B. Resonance conditions

We must now solve Eq. (2.16). According to Eq. (2.10)

$$\text{Re}\Delta = 1 - V_{cc}F_c^1 - V_{vv}F_v^1 + (V_{cc}V_{vv} - V_{cv}V_{vc})\text{Re}(F_cF_v) . \quad (2.19)$$

$F_c^1$  and  $F_v^1$  are defined by

$$F_{c,v}^1 = \text{Re}F_{c,v} . \quad (2.20)$$

Otherwise, the unperturbed Hamiltonian  $H_0$  is invariant under lattice translation, so that  $F_c$  and  $F_v$  do not depend on the choice of the site  $O$ . Hence  $F_{c,v} = (1/N)\text{Tr}G_{oc,v}$ ,  $N$  being the number of atoms in the crystal. We can then write

$$\text{Im}F_{c,v}(E) = -\pi g_{oc,v}(E) ; \quad (2.21)$$

$g_{oc}(E)$  and  $g_{ov}(E)$  are the density of states per atom of the conduction and valence bands, respectively. We now make a fundamental assumption different from that of Ref. 6, according to which the inter-band coupling energy induced by the perturbing potential is large, and has the same order of magnitude as the intraband coupling energy. In other words, we shall write

$$V_{cc} \simeq V_{vv} \simeq V_{cv} \simeq V_{vc} . \quad (2.22)$$

Let  $V_I$  be the value of these potentials. The resonance position is defined, according to Eqs. (2.16) and (2.19), by

$$V_I F^1(E_R) = 1 ,$$

$$F^1(E) = F_c^1(E) + F_v^1(E) . \quad (2.23)$$

Owing to the form of the potential defined in Eq. (2.22), we find that Eq. (2.23) is identical to the equation we would have obtained in a one-band model assuming that the conduction and valence bands are two half parts of a single band. Since the real and imaginary parts of the Green's functions are correlated by the usual Kramers-Kronig relations, we can write, according to Eq. (2.21),

$$F_c^1(E) = P \left( \int \frac{g_{oc}(E')}{E - E'} dE' \right) ,$$

$$F_v^1(E) = P \left( \int \frac{g_{ov}(E')}{E - E'} dE' \right) . \quad (2.24)$$

The symbol  $P$  means that only the principal part of the integrals is considered. This equation is of fundamental interest, and  $F_c^1$ ,  $F_v^1$ , and  $F^1(E)$  will be deduced from the knowledge of the density of states according to this formula.

In all zero-gap semiconductors, the hole mass  $m_p$  is much larger than the electron mass  $m_n$  at the bottom of the conduction band:

$$m_p/m_n \gg 1 . \quad (2.25)$$

Besides, at the first order of the tight-binding approximation, when we truncate the Hilbert space to take as a basis only the two Wannier functions associated with the conduction and valence bands,  $m_p$  is infinite.<sup>8</sup> We implicitly take account of the other bands by considering  $m_p$  finite and equal to the experimental value in order to determine  $g_{ov}(E)$ . In zero-gap semiconductors which crystallize in the zinc-blende structure, the conduction and valence bands are degenerate at the  $\Gamma_8$  point. The main features of the curve  $F^1(E)$  deduced from Eq. (2.24) are then reported in Fig. 1. All the curves  $F^1(E)$ ,  $F_v^1(E)$ , and  $F_c^1(E)$  exhibit a Van Hove anomaly at  $\Gamma_8$ . It follows that  $F_c^1(E)$  is minimum and  $F_v^1(E)$  is maximum at  $E(\Gamma_8)$ , with

$$F_v^1[E(\Gamma_8)] > 0 ,$$

$$F_c^1[E(\Gamma_8)] < 0 . \quad (2.26)$$

$E(\Gamma_8)$  is the energy of the  $\Gamma_8$  level. Because of Eq. (2.25), the Van Hove anomaly is much more important for  $F_v^1(E)$  than for  $F_c^1(E)$ :

$$F_v^1[E(\Gamma_8)] \gg |F_c^1[E(\Gamma_8)]| \quad (2.27)$$

The Eqs. (2.26) and (2.27) lead to

$$F^1(E) > 0 . \quad (2.28)$$

This last inequality is fulfilled over a range of energies equal to around one half-width of the peak of the curve  $F_v^1(E)$ , i.e., one half-width of the valence band.  $F^1(E)$  is thus positive at energies extending above  $\Gamma_8$  up to a few electronvolts and, in particular, in the whole range of energies of interest, i.e., in the vicinity of the  $\Gamma_8$  point.

According to Eq. (2.23), the energy of the resonance is the abscissa of the intersection point of the curve  $F^1(E)$  with a straight line parallel to the axis of energies, having an intercept  $y = 1/V_I$ . It follows from Eq. (2.28) that the problems of donor and acceptor states are quite different.

(i) For donors,  $V_I < 0$ , the straight line  $y = 1/V_I$  and the curve  $F^1(E)$  do not intersect at any point. The variation of the density of states due to the existence of donors is very small, and is a smooth function of energy. Since we do not have any resonance, the additional electrons provided by the donors are not in virtual bound states localized

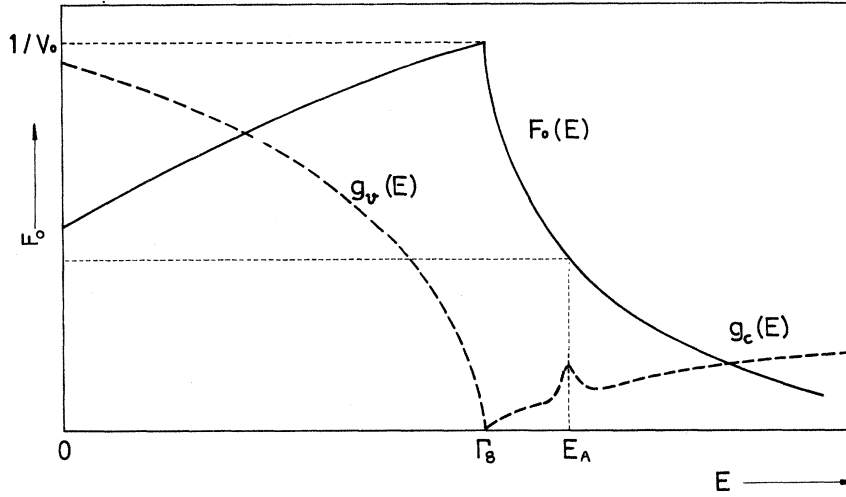


FIG. 1. Resonance conditions for impurity states in zero-gap semiconductors, illustrated by a virtual acceptor level  $E_A$ .

in the vicinity of the impurity sites, but in the extended states of the conduction band. All the donor states are thus ionized in such materials. These results agree with those deduced from the theory of Gel'mont and D'yakonov, who assumed that the perturbing potential was of the Coulomb form.<sup>5</sup> Note that our calculations imply that resonant donor states do not exist even in the case of a strong localized potential on the site of the defect. This situation would apparently correspond to HgSe, where extrinsic electrons usually attributed to Se vacancies are systematically observed.

(ii) For acceptor states, on the contrary,  $V_I > 0$ . We can then see in Fig. 1 that there exists a critical potential  $V_0$  defined by  $V_0 F^1[E(\Gamma_B)] = 1$ .

For strong potentials ( $V_I > V_0$ ), the straight line  $y = 1/V_I$  intersects the curve  $F^1(E)$  at an energy  $E_R = E_A$  inside the conduction band. A resonant, quasidiscrete level thus appears at this energy.

The weaker the potential  $V_I$ , the smaller the activation energy  $E_A$ , with  $E_A$  vanishing when  $V_I = V_0$ . If  $V_I < V_0$ , the acceptor states are inside the continuum of the valence-band states, and are not localized, since the straight line  $y = 1/V_I$  does not intersect the curve  $F^1(E)$ . For such weak potentials, not repulsive enough to generate acceptor states away from the valence band, the acceptors like donors exhibit a total ionization, at all temperatures.

In Sec. II C, we shall consider the case when the perturbing potential is strong enough to induce a resonant level

### C. Resonance width, virtual bound states

The resonance width is determined by Eq. (2.18). Since this resonance lies in the conduction band,  $g_{ov}(E) \approx 0$  for energies close to  $E_A$ . Equations (2.10) and (2.21) then lead to

$$(\text{Im}\Delta)_{E \approx E_A} = \pi g_{oc}(E) V_{cc} [1 - V_{vv} F_v^1(E)] + \pi g_{oc}(E) |V_{cv}|^2 F_v^1(E) \quad (2.29)$$

Equations (2.23) and (2.27) imply that, in first approximation,

$$1 - V_{vv} F_v^1(E_A) = 0. \quad (2.30)$$

This approximation may be used to obtain the order of magnitude of  $\Gamma$ . According to Eqs. (2.29) and (2.30), Eq. (2.18) takes the form

$$\Gamma = \pi g_{oc}(E_A) |V_{cv}|^2 F_v^1(E_A) \left/ \frac{d}{dE} \left[ \text{Re} \left( \frac{\Delta}{E_A} \right) \right] \right. \quad (2.31)$$

To determine the wave functions of electrons and holes in resonant states to the first order of perturbation, we shall notice that, to the order 0,

$$\Gamma = 0. \quad (2.32)$$

In other words, the acceptor states are bound. The spectral decomposition of the Green's operator can thus be written

$$G(E) = \sum_n \int \frac{|\psi_k^n\rangle \langle \psi_k^n|}{E - E_n(k)} d^3k + \frac{|\psi_L\rangle \langle \psi_L|}{E - E_A}; \quad (2.33)$$

$n$  indexes the conduction and valence bands,  $k$  is the wave vector,  $|\psi_k^n\rangle$  are the Bloch states, and  $|\psi_L\rangle$  is the localized acceptor state on site  $O$ .

Equation (2.33) shows that

$$|\langle O_v | \psi_L \rangle|^2 = \text{Res}(\langle O_v | G - G_0 | O_v \rangle)_{E = E_A}; \quad (2.34)$$

Res means the residue. Equation (2.9) with  $i = O$  implies that

$$\langle O_v | G - G_0 | O_v \rangle = (1/\Delta) [V_{vv} - (V_{cc} V_{vv} - V_{cv} V_{vc}) F_c] |F_v^1|^2. \quad (2.35)$$

According to Eq. (2.22),  $(V_{cc} V_{vv} - V_{cv} V_{vc}) F_c \approx 0$ .

Moreover, Eqs. (2.18) and (2.32) imply that  $\text{Im}\Delta = 0$ , and as a first approximation

$$\langle O_v | G - G_0 | O_v \rangle \simeq \left( \frac{V_{vv} |F_v^1|^2}{\text{Re}\Delta} \right)_{E=E_A}. \quad (2.36)$$

Taking Eqs. (2.30), (2.31), (2.34), and (2.36) into account, we can write

$$\Gamma = \pi g_{oc}(E_A) |V_{cv}|^2 |\langle O_v | \psi_L \rangle|^2. \quad (2.37)$$

It should be noticed that this is the same expression as the one obtained by Liu and Brust.<sup>6</sup>

#### D. Relaxation time of electrons located in the vicinity of a resonance

We shall call  $|k_c\rangle$  and  $|k_v\rangle$  the Bloch states of an electron in the conduction and valence bands,

$$\langle k_c | G | k_c \rangle = \frac{[E - E_c(k) - \Sigma_c(E)]^{-1}}{1 - (|V_{cv}|^2/N^2)[E - E_c(k) - \Sigma_c(E)][E - E_v(k) - \Sigma_v(E)]}. \quad (2.40)$$

In the dilute limit ( $N \rightarrow \infty$ ),  $\Sigma_{c,v} \propto N^{-1}$  and we can neglect the terms of higher orders,  $O(N^{-2})$ . Equation (2.40) may then be written

$$\langle k_c | G - G_0 | k_c \rangle = \frac{1}{E - E_c(k) - \Sigma_c(E)} - \frac{1}{E - E_c(k)}. \quad (2.41)$$

Otherwise, replacing  $|i\rangle$  by  $|k\rangle$  in Eq. (2.9), we obtain

$$\langle k_c | G - G_0 | k_c \rangle = |\langle k_c | G_{oc} | O_c \rangle|^2 \mathfrak{U} / \Delta, \quad (2.42)$$

with

$$\mathfrak{U} = V_{cc} - [V_{vv}V_{cc} - V_{cv}V_{vc}]F_v. \quad (2.43)$$

Owing to the translational invariance of the unperturbed Hamiltonian,  $G_{oc}$  is diagonal in  $k$  space. It then follows that

$$|\langle k_c | G_{oc} | O_c \rangle|^2 = |\langle k_c | G_{oc} | k_c \rangle|^2 |\langle k_c | O_c \rangle|^2. \quad (2.44)$$

Equations (2.39) and (2.42) thus lead to

$$\langle k_c | G - G_0 | k_c \rangle = \frac{\mathfrak{U}/N}{\Delta[E - E_c(k)]^2}. \quad (2.45)$$

The expression of  $\Sigma_c$  can be deduced from the identification of Eqs. (2.41) and (2.45), to the first order in  $N^{-1}$ :

$$\Sigma_c(E) = \frac{1}{N} \frac{\mathfrak{U}}{\Delta}. \quad (2.46)$$

$\mathfrak{U}$  is real in the range of energies of interest ( $E \simeq E_A$ ), and  $\text{Im}F_v = 0$  according to Eq. (2.21), since the resonance is located in the conduction band. Equation (2.29) then implies

respectively, with a wave vector  $k$ . In the representation  $\{|k_c\rangle, |k_v\rangle\}$ , the propagator  $G(E)$  is a  $2 \times 2$  matrix which may be written

$$G = \begin{pmatrix} E - E_c(k) - \Sigma_c(E) & \langle k_c | O_c \rangle V_{cv} \langle O_v | k_v \rangle \\ \langle k_v | O_v \rangle V_{vc} \langle O_c | k_c \rangle & E - E_v(k) - \Sigma_v(E) \end{pmatrix}^{-1}. \quad (2.38)$$

$\Sigma_c(E)$  and  $\Sigma_v(E)$  are the self-energies of the scattering problem for the conduction- and valence-band states.  $E_c(k)$  and  $E_v(k)$  are the dispersion relations of the two unperturbed bands. The normalization of  $|k_c\rangle$  and  $|k_v\rangle$  implies that

$$\langle O_c | k_c \rangle = \langle O_v | k_v \rangle = 1/\sqrt{N}. \quad (2.39)$$

We can then deduce from the Eq. (2.38)

$$\text{Im}\Sigma_c(E) = -\frac{1}{N} \frac{\pi g_{oc}(E)\mathfrak{U}^2}{(\text{Re}\Delta)^2 + \pi^2 g_{oc}^2(E)\mathfrak{U}^2}. \quad (2.47)$$

$\Sigma_c$  is not Hermitian, and we can define the relaxation time of the electrons  $\tau(E)$  by the usual formula,

$$\frac{1}{\tau(E)} = -2 \frac{\text{Im}\Sigma_c(E)}{\hbar}. \quad (2.48)$$

Until now we have assumed only one scattering center, localized on the site  $O$ . Since the interferences between the different scattered waves are negligible in the dilute limit, the value of  $1/\tau(E)$  determined above must be multiplied by the number of such scattering centers:

$$\frac{1}{\tau(E)} = \frac{2\pi X}{\hbar} \frac{g_{oc}(E)\mathfrak{U}^2}{(\text{Re}\Delta)^2 + \pi^2 \mathfrak{U}^2 g_{oc}^2(E)}, \quad (2.49)$$

where  $X$  is the concentration of scattering centers. This expression for  $\tau(E)$  is the same as the one deduced from the theory of correlations using double-time Green's functions.<sup>9</sup> The influence of the hole band on  $\tau(E)$  leads to a renormalization of the defect potential  $V_{cc}$  similar to the one defined by Riedinger and Gautier,<sup>10,11</sup> which may be related to virtual transitions between the conduction and valence bands. In our particular case, when the condition (2.22) is fulfilled,  $\mathfrak{U} \simeq V_I$ . In any case, according to Eq. (2.16), the electrons undergo a resonant scattering at  $E = E_A$ , and

$$\frac{1}{\tau(E_A)} = \frac{2X}{\pi \hbar} \frac{1}{g_{oc}(E_A)}. \quad (2.50)$$

III. APPLICATION TO HgTe AND Hg<sub>1-x</sub>Cd<sub>x</sub>Te MATERIALS

## A. Mercury vacancy

In this section, we confront the model with experimental results obtained on HgTe and on Hg<sub>1-x</sub>Cd<sub>x</sub>Te alloys. Mercury telluride is a semi-metallic II-VI compound which crystallizes in the zinc-blende structure. Its band scheme, similar to the one proposed for  $\alpha$ -Sn,<sup>12</sup> is depicted in Fig. 2. The lack of inversion symmetry makes possible the existence of an overlap  $\Delta E$  of the conduction and valence bands, which we shall neglect since it is quite small<sup>13</sup>:  $\Delta E \lesssim 1$  meV. Within this approximation, HgTe is a zero-gap semiconductor. A continuous range of Hg<sub>1-x</sub>Cd<sub>x</sub>Te alloys can be obtained by substitution of Cd atoms in place of Hg atoms, between the semimetal HgTe and the semiconductor CdTe. We shall neglect disorder effects like band tailing, for example, and we shall thus assign to these alloys the band structure reported in Fig. 2 and detailed in Ref. 13, deduced from those of HgTe and CdTe by a linear interpolation of band parameters between these two materials. We shall consider the compound HgTe and the alloy Hg<sub>1-x</sub>Cd<sub>x</sub>Te as simple crystals in which all the sites are equivalent, and we shall thus apply the model developed in Sec. II to investigate the acceptor states in these materials. Let the energy gap  $E_g$  be defined by  $E_g = E(\Gamma_6) - E(\Gamma_8)$ . The case  $E_g < 0$  corresponds to the semi-metallic (SM) configuration, while the case  $E_g > 0$  corresponds to the semiconductor (SC) configuration.

Three acceptor resonances have been exhibited in HgTe: The first has an activation energy<sup>7, 14</sup>  $E_{A0} \approx 0.7$  meV, and is assigned to Cu acceptor impurities.<sup>7</sup> The other two, denoted by A1 and A2 in Ref. 7, are due to stoichiometry defects. Their activation energies  $E_{A1} = 2.25$  meV and  $E_{A2} = 9.5$  meV in HgTe increase with composition  $x$ ,<sup>7</sup> or when a hydrostatic pressure  $P$  is applied.<sup>13</sup> The effects of an increase of  $x$  or  $P$  are the same, namely, an increase of  $E_g$ , leading to a deformation of the conduction band, the dispersion relation of which is given by<sup>8</sup>

$$E_c(k) = \frac{1}{2} \left[ -|E_g| + (E_g^2 + \frac{8}{3} k^2 P_K^2)^{1/2} \right], \quad (3.1)$$

where  $P_K$  is the Kane matrix element.

The two succeeding parts of this section are concerned with different aspects of the acceptor problem in these materials. In Sec IIIA, we analyze the main features of the resonance A1 which is assigned to mercury vacancies. Section IIIB deals with the mobility of electrons in virtual bound states due to Cu impurities.

As a first approximation, we shall assume that the mercury vacancy is described by a potential localized on the site of the defect, although it is rather localized on the broken bonds, i.e., on the neighbor sites. In this paragraph, we thus mean to determine the width and the position of the resonance and the strength of the potential  $V_I$  for the mercury vacancy, in the framework of the model developed in Sec. II. We also mean to compare our theoretical results with the experimental results described in a previous paper,<sup>13</sup> which have been deduced from measurements of transport properties of a Hg<sub>0.86</sub>Cd<sub>0.14</sub>Te alloy at 4.2°K for various pressures. At this low temperature, we have found that  $dE_g/dP \approx 8$  meV/kbar. This alloy was in the SM configuration at low pressures and underwent an SM-SC transition at  $P \approx 5.3$  kbars. At  $E_g \approx 0$ , it has been shown that, for this sample,

$$E_{A1} \approx E_F \approx 15 \text{ meV}, \quad \Gamma \approx 0.15 \text{ meV}, \quad (3.2)$$

where  $E_F$  is the Fermi energy. Owing to the high degeneracy of the electron gas, the concentration of electrons in the conduction band,  $n_e$ , is deduced from Eq. (3.1) and is related to  $E_F$  by the relation

$$n_e(E_F) = \frac{8}{3\sqrt{\pi}} \left( \frac{2\pi m_n k_0 T}{\hbar^2} \right)^{3/2} [E_F(1 + E_F/E_g)]^{3/2}; \quad (3.3)$$

$k_0$  is the Boltzmann constant, and  $m_n$  is the effective mass of the electrons at the bottom of the conduction band. The density of states at the Fermi

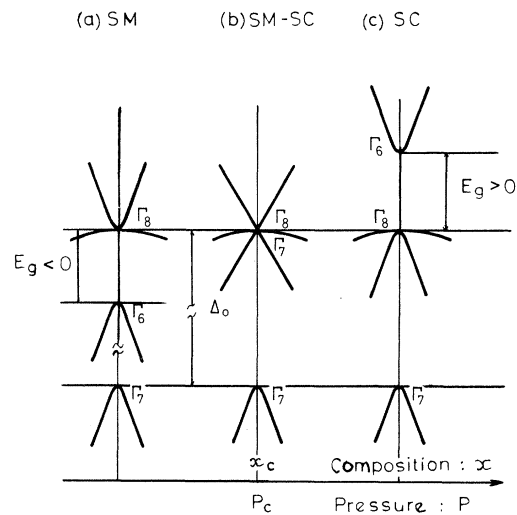


FIG. 2. Simplified band structure of Hg<sub>1-x</sub>Cd<sub>x</sub>Te alloys at the zero center versus composition  $x$  or pressure  $P$ , (a) in the semimetallic configuration, (b) at the semi-metal-semiconductor transition, and (c) in the semiconductor configuration.

energy  $g_{oc}(E_F)$  is

$$g_{oc}(E_F)dE_F = (1/\mathcal{N})dn_e(E_F). \quad (3.4)$$

$\mathcal{N}$  is the concentration of atoms in the crystal:  $\mathcal{N} \approx 10^{22} \text{ cm}^{-3}$ . At  $E_g = 0$ , Eq. (3.3) shows that  $n_e(E_F) \propto E_F^3$  so that Eqs. (2.37), (3.2), and (3.4) lead to

$$\Gamma = (3\pi n_e / E_{A1}) V_I^2. \quad (3.5)$$

Here, we have assumed that the probability that an electron in the state  $|\psi_L\rangle$  is located on the impurity site  $O$ , is  $|\langle O_v | \hat{\psi}_L \rangle|^2 \approx 1$ , which means that the resonance is quasidiscrete. Taking Eq. (3.2) into account, Eq. (3.5), in which  $n_e = 5 \times 10^{14} \text{ cm}^{-3}$  according to the results reported in Ref. 13, allows us to determine  $V_I$ :

$$V_I \approx 2.3 \text{ eV}. \quad (3.6)$$

The determination of the resonance position yet requires the knowledge of the density of states. We shall take for  $g_{ov}(E)$  the form suggested by Hubbard<sup>15</sup>:

$$g_{ov}(E) = (2/\pi w^2)(w^2 - E^2)^{1/2}, \quad |E| \leq w \\ = 0, \quad |E| \geq w \quad (3.7)$$

where  $w$  is the half-width of the valence band. In this equation, the origin of energies for the valence-band states is the middle of the band. The shape of  $g_{ov}(E)$  thus defined is semielliptic. It is then possible to find the analytic expression of the Hilbert transform of  $g_{ov}(E)$ :

$$F_v(E) = (2/w^2)[E - (E^2 - w^2)^{1/2}]. \quad (3.8)$$

If  $\epsilon$  is the energy of valence states with respect to  $E(\Gamma_8)$ , we can write  $E = w - \epsilon$ . The development of Eq. (3.8) to the first order in  $\epsilon$  shows that, in the framework of this model,  $g_{ov}(E)$  has a parabolic shape in the vicinity of the valence-band edge  $\Gamma_8$ , the heavy hole mass  $m_p$  being related to  $w$  by the relation

$$w = [\hbar^2(2\pi)^{2/3}/m_p] \mathcal{N}^{2/3}. \quad (3.9)$$

In  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  materials, a value of the reduced mass  $m_p/m_0 \approx 0.5$  accounts quite well for the transport properties,<sup>16</sup> while magneto-optical measurements performed on HgTe lead to<sup>17</sup>  $m_p/m_0 \approx 0.3$ ,  $m_0$  being the free-electron mass. We shall then assume  $m_p/m_0 = 0.4$ . Replacing the different quantities by their numerical value, we thus find

$$w \approx 4 \text{ eV}. \quad (3.10)$$

At the band edge,  $E = w$ , and Eq. (3.9) then becomes  $F_v[E(\Gamma_8)] = 2/w$ . According to Eqs. (3.6) and (3.10), we can conclude

$$F_v[E(\Gamma_8)] V_I \approx 1.1. \quad (3.11)$$

The expression of  $g_{ov}(E)$  in Eq. (3.7), chosen for mathematical convenience, accounts for the experimental density of valence-band states in the vicinity of the  $\Gamma_8$  point, i.e., in the range of energies from which the acceptor states are extracted. The Hubbard model is thus expected to determine  $F_v[E(\Gamma_8)]$  with a good accuracy. On the contrary, it is not possible to calculate  $F_c[E(\Gamma_8)]$  owing to the nonparabolicity and the large width of the conduction band. Nevertheless, an order of magnitude of this parameter may be obtained in HgTe. In effect, for this material, the resonance  $A1$  is located at  $E_{A1} \approx 2.25 \text{ meV}$  above the  $\Gamma_8$  point. As a first approximation, we may thus write  $E_{A1} \approx 0$ , and taking Eq. (3.11) into account, Eq. (2.23) leads us to assume

$$F_c^1[E(\Gamma_8)] V_I \approx -0.1. \quad (3.12)$$

This formula is only valid for HgTe, which has an energy gap<sup>17</sup>:  $E_g \approx -303 \text{ meV}$  at  $4.2^\circ\text{K}$ . We now study the variations of  $E_{A1}$  induced by variations of  $E_g$ .

In the semimetallic configurations, the density of conduction-band states decreases, in the vicinity of the  $\Gamma_8$  point, when  $E_g$  increases from  $-303 \text{ meV}$  to  $0$ , according to Eq. (3.1). It follows that  $F_c^1$  increases (i.e.,  $|F_c^1(E)|$  decreases) without, however, becoming positive in the range of energies which we consider (see Fig. 1). On the contrary, the shape of the heavy-hole valence band does not vary significantly with  $E_g$  since it is determined by interactions with the far-lying bands which do not stem from the  $\Gamma_6$  or  $\Gamma_8$  points,<sup>8</sup> and  $F_v^1(E)$  does not depend upon  $E_g$ . We can thus conclude that, according to Eq. (2.23),  $E_{A1}$  increases with  $E_g$ . This allows us to understand firstly the increase of  $E_{A1}$  with  $x$  (because  $dE_g/dx \approx 18 \text{ meV}/\%$  at low temperatures<sup>18</sup>), and secondly the increase of  $E_{A1}$  with  $P$  (because  $dE_g/dP \approx 8 \text{ meV/kbar}$  at  $4.2^\circ\text{K}$ ). From this, we deduce the plot of  $E_{A1}$  vs  $E_g$  shown in Fig. 3.

In both cases, the variations of  $E_{A1}$ , in the framework of our model, are the consequence of variations of  $E_g$ . In effect the value of  $E_g$  determines the density of states  $g_{oc}(E)$ , its Hilbert transform  $F_c(E)$ , and lastly  $E_{A1}$ . The curve  $E_{A1}$  vs  $E_g$  in Fig. 4 thus comprises the complete information about the location of this resonance in the SM configuration. The values of  $E_{A1}$  in the range  $-40 \leq E_g \leq +8 \text{ meV}$  are the values also reported in Fig. 3. The intermediate point at  $E_g \approx -92 \text{ meV}$  is deduced from the analysis of transport properties performed on a  $\text{Hg}_{0.89}\text{Cd}_{0.11}\text{Te}$  sample.<sup>19</sup> The other points are deduced from the data given in Ref. 7. The two parts of this curve,  $E_{A1}$  vs  $E_g$ , deduced from measurements of  $E_{A1}$  vs  $x$  on one hand and  $E_{A1}$  vs  $P$  on the other hand,

fit into each other, and the curve is continuous. This result agrees with the theoretical one, according to which  $E_g$  is the fundamental parameter.

In the semiconductor configuration, the increase of the energy gap leads to a dramatic decrease of the density of conduction-band states in the range of energies  $E(\Gamma_6) \leq E \leq E(\Gamma_6) + E_g$ . The activation energy  $E_{A1}$  is thus expected to increase, even more rapidly than in the SM configuration ( $dE_{A1}/dE_g > 0$ ). This result is corroborated by experiments (see Fig. 3). If  $F_v^1(E)$  did not depend on  $E$ , and if the increase of the energy gap only resulted in a shift of the conduction band with respect to the valence band, without any deformation, we should have  $dE_{A1}/dE_g = 1$ . Nevertheless, on one hand, according to Eq. (3.1), the density of states at the bottom of the conduction band  $\Gamma_6$  increases with  $E_g$ . On the other hand,  $F_v(E)$  decreases with  $E$  for  $E > E(\Gamma_6)$ . These two effects add together to slacken the increase of  $E_{A1}$  so that  $0 < dE_{A1}/dE_g < 1$ . In other words, the acceptor level moves up with respect to the valence-band edge  $\Gamma_6$ , but moves down in the conduction band, with respect to the  $\Gamma_6$  level. This result is corroborated by experiments, as can be seen in Fig. 5, illustrating the plot of  $E_{A1} - \epsilon E_g$  as a function of  $E_g$  in the range  $-40 \leq E_g \leq 10$  meV. The parameter  $\epsilon$  is defined by  $\epsilon = 0$  if  $E_g < 0$  and  $\epsilon = 1$  if  $E_g > 0$ , so that  $E_{A1} - \epsilon E_g$  is the energy of the ac-

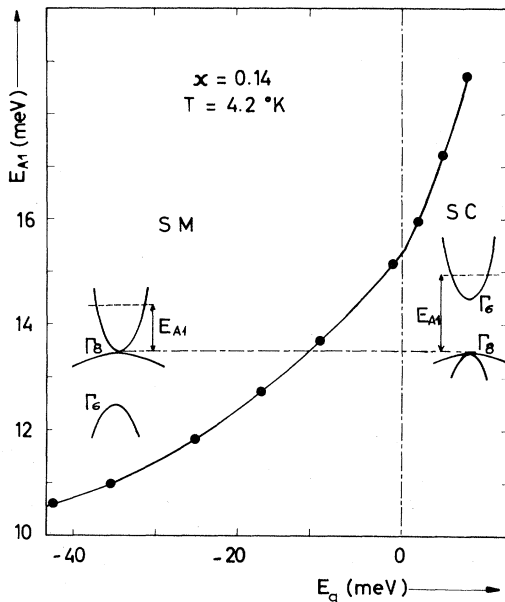


FIG. 3. Experimental variations of the activation energy  $E_{A1}$  of the resonance A1 as a function of the energy gap  $E_g$ . This curve has been deduced from the plot of the pressure-induced shift of this acceptor resonance in a  $\text{Hg}_{0.86}\text{Cd}_{0.14}\text{Te}$  alloy, reported in Ref. 13, using  $dE_g/dP = 8$  meV/Kbar at 4.2 K.

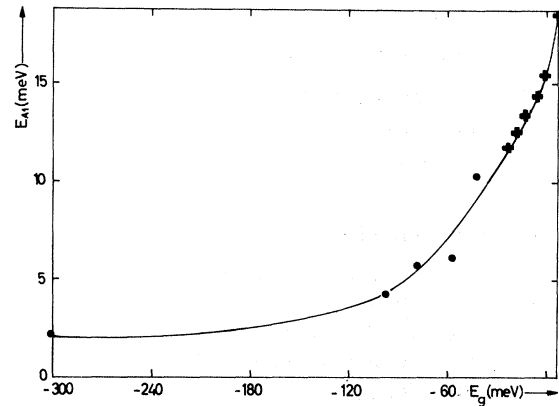


FIG. 4. Experimental variations of the activation energy  $E_{A1}$  of the resonance A1 as a function of the energy gap  $E_g$  in the semimetallic configuration for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys. The crosses are the data points reported in Fig. 3. The full circles are the data points given in Refs. 7 and 19.

ceptor level with respect to the bottom of the conduction band. Such a decrease of this energy in the SC configuration implies that there exists a well-defined value of  $E_g$ , beyond which the resonance falls into the gap, and then becomes the usual localized level. We now determine an order of magnitude of this energy gap by noticing that, in the limit of high values of  $E_g$ ,  $F_c^1(E_{A1})$  vanishes. In other words, the conduction band is shifted too far from the valence band to have any significant effect on the acceptor states, which are then bound to the valence band. Thus,  $E_{A1}$  does not increase further with  $E_g$  and remains equal to its extreme value  $E_{A1}^0$  determined by the use of Eq.

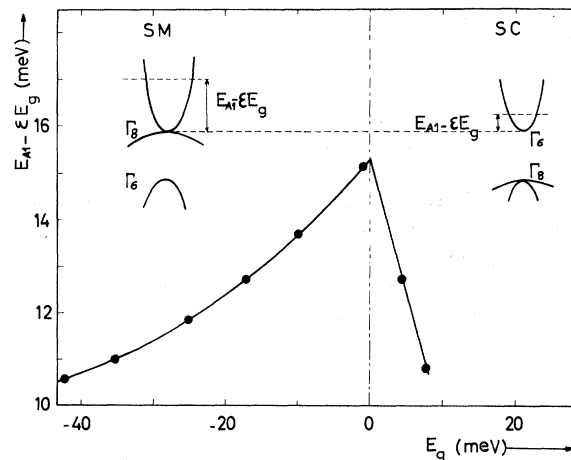


FIG. 5. Energy difference between the acceptor level A1 and the bottom of the conduction band as a function of the energy gap  $E_g$  for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys according to the results reported in Fig. 3.



(2.23), in which  $F_c^1 = 0$ :

$$V_I F_v^1(E_{A_1}^0) = 1. \quad (3.13)$$

The identification of Eqs. (3.13) and (3.8), in which  $E = E_{A_1} + w$  according to the choice of the origin of energies, leads to

$$E_{A_1}^0 = \frac{V_I}{w} \left(1 - \frac{w}{2V_I}\right)^2. \quad (3.14)$$

Assuming that  $V_I = 2.35$  eV and  $w = 4$  eV, according to Eqs. (3.6) and (3.10), we thus find

$$E_{A_1}^0 \approx 50 \text{ meV}. \quad (3.15)$$

This value is in fair agreement with the activation energy of an acceptor level determined by optical measurements in  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys having a large energy gap.<sup>20</sup> Moreover this high value allows us to understand that the resonance  $A_1$  still remains in the conduction band for an energy gap<sup>13</sup>  $E_g \approx +40$  meV. The acceptor level is thus expected to move down into the energy gap only when  $E_g \approx 50$  meV.

#### B. Mobility of electrons in Cu resonant states

According to Eq. (2.50), the relaxation time of electrons in virtual bound states is finite. Such electrons then have a finite mobility  $\mu_R$ , which has been found equal to<sup>13</sup>  $\mu_R \approx 9000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$  in HgTe when the resonant states were induced by Cu impurities. However, measurements of galvanomagnetic properties performed on  $\text{Hg}_{0.86}\text{Cd}_{0.14}\text{Te}$  showed that the mobility of the same electrons was much smaller in this material<sup>13</sup>:  $\mu_R \ll 2000 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ . All these results were obtained at zero pressure and  $T \leq 4.2^\circ\text{K}$ .

We intend in this paragraph to explain this large decrease of  $\mu_R$  with  $x$  (or  $E_g$ ). Since Cu is an acceptor impurity in substitution of Hg atoms, it is expected that the perturbing potential is mainly of the Coulomb form. We may thus use the theory of Gel'mont and D'yakonov according to which  $E_{A_0}$  does not significantly depend upon  $E_g$  (or the density of conduction states) in the range of energy-gap values considered. We can thus assume that  $E_{A_0}$  has almost the same value in HgTe and in  $\text{Hg}_{0.86}\text{Cd}_{0.14}\text{Te}$ . Equation (3.1) then shows that, at zero pressure and very low temperature,  $g_{oc}(E_{A_0})$  is 18 times smaller in the  $x=0.14$  sample than in HgTe. According to Eq. (2.50) the relaxation time, and consequently the mobility  $\mu_R$  of electrons in resonant states, is proportional to the density of conduction-band states  $g_{oc}(E_A)$ . Although established in the case of a localized potential in Sec. II, this result is still valid for a Coulomb perturbing potential.<sup>5</sup> The mobility  $\mu_R$  in the  $x=0.14$  sample is thus expected to be 18

times smaller than in the HgTe sample, i.e.,  $\mu_R \approx 500 \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ , which accounts for the small value expected.

#### IV. DISCUSSION

In this section, we intend giving physical interpretations of the results obtained in this paper.

Firstly, we have shown that donor levels do not exist in small-gap semiconductors, and we have emphasized that this is closely related to the relation  $m_p/m_n \gg 1$  in all small-gap semiconductors. To illustrate this feature, let us consider for a moment an imaginary material for which  $m_p/m_n \ll 1$ . Equation (2.28) must then be replaced by  $F^1(E) < 0$  in the vicinity of the band edges, Eq. (2.23) being unchanged. The discussion reported in Sec. II B then shows that resonant donor levels may exist, while acceptors never lead to quasi-discrete levels. This is just the opposite result to the one found for realistic small-gap materials with  $m_p/m_n \gg 1$ .

The nonexistence of donor levels is thus due not only to the narrowness of the energy gap, but also to the general features of the band parameters met in such materials. In particular, the first reason for the dissymmetry between the behaviors of acceptor and donor states is the dissymmetry between the conduction and valence bands expressed by the inequality  $m_p/m_n \gg 1$  between the band parameters  $m_p$  and  $m_n$ .

Such a behavior may be predicted without any calculation. In effect, the interference of a quasi-discrete level with the states of a band having the same symmetry leads to a strong mixing between the localized and extended states. The result is that the bound states become unlocalized. So, a perturbation can only produce a virtual bound state of a given symmetry near a band edge, if the wave functions of the band states at the same energy do not contain atomic orbitals of the same symmetry.<sup>21</sup>

Now in small-gap semiconductors, the strong interband coupling potential  $V_{cv}$  implies that the wave function of the localized states  $\psi_L$  is a mixing of orbitals with the symmetry of the conduction and valence bands. Nevertheless, in a range of energies around the band edge  $\Gamma_3$ , the number of valence states is much larger than the number of conduction states simply because  $m_p/m_n \gg 1$ . It follows that the component of  $\psi_L$  having the valence symmetry is predominant. So, the quasi-discrete levels are acceptor levels and may only exist at energies where the density of valence states vanishes, i.e., in the conduction band.

It should be noticed that this argument has been advanced without considering the shape of the po-

tential. This explains why this result is true not only for the localized potential considered in this paper, but also for a Coulomb potential.<sup>5</sup> Otherwise, not only the condition  $m_p/m_n \gg 1$ , but also the existence of the potential  $V_{cv}$ , has been required in the course of this argument.

In order to show in more details the fundamental importance of the potential  $V_{cv}$ , let us consider the results which we would have obtained in the framework of an unrealistic model with  $V_{cc} = V_{vv} = V_I$  and  $V_{cv} = V_{vc} = 0$  instead of the potential defined in Eq. (2.22). Equations (2.16) and (2.37) show that, in such a case, discrete donor levels lying in the valence band may exist. The problems of acceptor and donor levels then become quite similar and are reduced to the usual Koster-Slater problem in which one band is considered, i.e., the valence band for acceptor states and the conduction band for donor states. Such results are due to the oversimplified form of the unperturbed Hamiltonian chosen above, according to which the conduction and valence bands are orthogonal.

Comparing these results with those obtained in Secs. II and III, we can conclude that the second reason for the dissymmetry between the behaviors of donor and acceptor states is the existence of a strong potential  $V_{cv}$  which was underestimated by Liu and Brust.<sup>6</sup>

We have also found that even quasidecrete acceptor levels could not exist if the perturbing potential is weaker than a critical value  $V_0$ . Some elaboration is needed regarding this critical potential strength. According to Eq. (3.8),  $V_0 \approx 1/F_v(w) = 2/w$ . Taking Eq. (3.9) into account, we can write

$$V_0 = (\hbar^2/2m_p)^2 (2\pi)^{2/3} \gamma^{2/3}. \quad (4.1)$$

Let  $a$  be the lattice parameter. In the zinc-blende structure, the unit cell contains eight atoms, and  $\mathcal{X} = 8a^{-3}$ . Equation (4.1) then becomes

$$V_0 = \frac{\hbar^2 \pi^2}{2m_p a^2} \left[ \frac{2\sqrt{2} (2\pi)^{1/3}}{\pi} \right]^2. \quad (4.2)$$

The term in the brackets is equal to 1.7. Considering only the order of magnitude of  $V_0$ , we shall replace  $a/1.7$  by the distance  $b$  between nearest neighbors, so that

$$V_0 \approx \frac{\hbar^2 \pi^2}{8m_p (b/2)^2}. \quad (4.3)$$

Let us now consider the energy levels for the motion of a hole (i.e., a free particle with the mass  $m_p$ ) with angular momentum  $l=0$  in a centrally symmetric potential well:  $V(r) = -V_I$  for  $r < b/2$ ,  $V(r) = 0$  for  $r > b/2$ . The first of these levels with  $l=0$ ,  $-E_A$ , is at the same time the lowest of all energy levels, and corresponds to

the normal state of the hole. It is easily shown in quantum mechanics<sup>22</sup> that the minimum well depth to give the single negative level  $-E_A$  is exactly  $V_0$  defined by Eq. (4.3). If  $V_I > V_0$ ,  $E_A > 0$ , the normal state of the hole is a bound state, and  $E_A$  is a discrete acceptor level. If  $V_I = V_0$ , the hole in the well has a wave vector equal to  $\pi/b$  because of the boundary conditions at the edge of the well. The kinetic energy of the hole,  $E_h$ , is thus equal to  $V_0$  so that  $E_A = 0$ . If  $V_I < V_0$ , we find  $E_h > V_I$  so that the energy of the hole is  $E_h - V_I > 0$ : The hole cannot stay inside the well and is not localized.

We can thus conclude that the critical potential strength for the resonant acceptor states defined in Sec. II is none other than the critical strength for the existence of a bound state inside the localized potential well of width  $b$  equal to the intra-atomic length (when the interaction with the band states is switched off).

Let us now analyze our results concerning the location of the resonance  $A_1$ . It should be noticed that, according to Eqs. (3.11) and (3.13),  $1 \leq F_v^1(E_{A_1})V_I \leq 1.1$  or  $-0.1 \leq F_c^1(E_{A_1})V_I \leq 0$ . We have shown that the small variation of  $F_v^1(E_{A_1})$  equal to 10% is large enough to make  $E_{A_1}$  range from 2.25 to 50 meV. The reason is that  $F_v^1(E)$  is a smooth function of the energy (except for energies in the true vicinity of the  $\Gamma_8$  level). The resonance position must then be determined by Eq. (2.23) and not by Eq. (2.30), which is too crude an approximation to calculate  $E_{A_1}$ . In other words,  $E_{A_1}$  must be calculated in the framework of a model in which the conduction and valence bands are considered as two parts of a single band. This result shows that the concept of an acceptor resonance clamped to the valence band is deficient. In particular, even in the SC configuration for small energy gaps  $0 < E_g < 50$  meV,  $E_{A_1}$  increases with  $E_g$  when the conduction band moves off the valence one. This resonance is thus also partly attached to the conduction band (not entirely, since  $dE_{A_1}/dE_g < 1$ ). According to the model described in Sec. II, such a behavior of the resonance is assigned to a small-gap effect, since in such materials, virtual transitions between valence- and conduction-band states become important and widely affect the position of the resonance. According to Eq. (3.15), we can consider that the acceptor level is essentially attached to the valence band only for an energy gap  $E_g \geq 50$  meV. In effect,  $E_{A_1}$  is then determined by the Eq. (3.13). This is the usual equation which determines the location of an acceptor level in the single-band model of Koster and Slater,<sup>23</sup> the single band being the valence band.

In the unrealistic model characterized by  $V_{cv} = 0$ , the activation energy of the acceptor level is

determined by  $V_I F_v^1(E_A) = 1$  and is thus independent of both  $E_g$  and the density of states of the conduction band. This also illustrates that the large variations of the resonance energy  $E_{A1}$  vs  $E_g$  are mainly due to the virtual interband transitions induced by the potential  $V_{c,v}$  which couples the two bands. On the other hand, such transitions do not significantly affect the width of the resonance since the approximation which consists in replacing Eq. (2.23) by Eq. (2.30) does not lead to an error larger than 10%. This only means that the broadening of the acceptor level is mainly due to virtual transitions between the acceptor states and the extended states of the conduction band, which are also allowed by the potential  $V_{c,v}$  and are responsible for the finite mobility  $\mu_R$  of the electrons in the virtual bound states.

Finally, we are now able to give a more quantitative definition of the concept of "small gap" for the impurity problem. When  $E_g \gg 50$  meV,  $E_{A1}$  is in the energy gap, and  $F^1(E)$  goes through zero at an energy  $E_0$  which also moves down into the gap. This is induced by the increase of  $|F_c^1|$  and the decrease of  $F_v^1$  in the vicinity of the  $\Gamma_6$  point when  $E_g$  increases. But as soon as  $E_0 < E(\Gamma_6)$ , the discussion in Sec. II shows that discrete donor levels lying in the band gap may also exist. Thus, the semiconductors with  $E_g \gg 50$  meV cannot be considered as small-gap semiconductors when dealing with localized states.

## V. CONCLUSION

An over-all agreement has been obtained between the theoretical model developed in this paper and the experimental results otherwise obtained on HgTe and  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  materials. We have shown that localized potentials  $V_I$  strongly repulsive produce acceptor resonances in the conduction band. In particular, we have been led to take  $V_I = 2.3$  eV for the resonance named A1, and we have accounted for the shift of the resonance position when the energy gap  $E_g$  is in-

creased. In the semimetallic configuration, the activation energy  $E_{A1}$  depends upon  $E_g$ , owing to the dependence of the density of conduction-band states upon  $E_g$ . This effect is the consequence of our assumption according to which the interband coupling energy was strong (and of the same order as the intraband one). This assumption also implies that the acceptor level is not clamped to the valence band, but is also partly clamped to the conduction band, for an energy gap up to about 50 meV in the semiconductor configuration. This may explain why the resonance remains in the conduction band when  $0 < E_g \leq 40$  meV. All these features could not be understood in the framework of the model of Gel'mont and D'yakonov dealing with the scattering by a potential of a Coulomb form. This corroborates the assumption according to which this resonance is induced by a neutral native defect, namely, the mercury vacancy, as was suggested previously in our laboratory.<sup>7</sup>

Otherwise, taking into account the existence of an interband potential, the large ratio of the heavy-hole and electron effective masses results in a large dissymmetry between the acceptor and donor problems. It has been shown that any donor state does not lead to the existence of a quasiscrete level. This result is the same as the one given by the theory of Gel'mont and D'yakonov, and thus does not depend upon the detailed shape of the perturbing potential. In particular, donor states are not virtual bound states, so that electrons in donor states are unlocalized. In other words, these electrons are always in conduction-band states, leading to a total ionization of the donors at zero temperature.

Dealing with localized states, we were led to restrict the attribute small gap to semiconductors like those of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  alloys which have an energy gap  $E_g \approx 50$  meV.

On the contrary, when  $E_g \gg 50$  meV, the semiconductor is expected to have a classical behavior with both acceptor and donor levels lying in the band gap. In particular, the existence of donor levels in InSb is not surprising.

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