Resonant acceptor levels in zero-gap semiconductors under uniaxial stress

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(Received 30 June 1975)

The variation with uniaxial stress of acceptor binding energy, as well as the natural level width, are calculated by the resolvent method in the case of zero-gap structures. We have neglected the warping of the Γ_8 bands and assumed a short-range impurity potential. When the resonant level merges into the induced gap and becomes a perfectly localized state, an anomaly appears in the stress dependence of the binding energy. A phase-shift analysis of the problem is presented, which enables a complete discussion of the nature of the impurity levels in zero-gap semiconductors.

In a zero-gap semiconductor, the impurity levels interfere with a continuum of free states and are then not strictly localized.[1,2] It has been experimentally shown[3,4] that, in HgTe, the Hg vacancies give rise to an acceptor state with 2.2-meV binding energy. More recently, a model[4] was proposed which satisfactorily explains the existence of a quasilocalized acceptor state degenerate with the conduction band, but also shows that donor levels interfering with the heavy-hole valence band are always overdamped.

It is the purpose of this paper to extend this model to the case of a uniaxially stressed material in which, due to the breaking of cubic symmetry, a finite gap has been opened between the Γ_8 valence and conduction levels.

For stress parallel to the [111] direction, neglecting warping and the linear $\vec{k}$ term, the dispersion relations of the Γ_8 bands are[5]

$$\epsilon_{\pm}(\vec{k}) = \tfrac{1}{3}(L+2M)k^2 \pm \{[\tfrac{1}{3}(L-M)]^2k^4 + \Delta^2 + \Delta\tfrac{1}{3}(L-M)k^2(3\cos^2\theta - 1)\}^{1/2} . \tag{1}$$

In Eq. (1), the hydrostatic shift corresponding to a uniform motion of the bands has been omitted; 2Δ is the gap between the conduction (+sign) and the valence bands (−sign) at $k=0$, and θ is the angle between $\vec{k}$ and the [111] direction. In the following we shall restrict ourselves to the case $\Delta>0$, for which the valence and conduction bands are pulled apart.

In k space, the Dyson equation relating G_0 and G, the unperturbed and perturbed propagators, is written

$$G_{ij}(\vec{k},\vec{k}') = G^0_{ij}(k)\delta_{\vec{k}\vec{k}'} + \sum_{l,m}\int d^3k''\, G^0_{il}(\vec{k})\langle\vec{k}|V_{lm}|\vec{k}''\rangle\, G_{mj}(\vec{k}'',\vec{k}') , \tag{2}$$

where i, j refer to the basis of the four Bloch functions at $k=0$. In order to retain a simple algebra, we assume a short-range interaction, somewhat similar to the Slater-Koster potential,[6]

$$\langle\vec{k}|V_{lm}|\vec{k}'\rangle = V\delta_{lm}u(k)u(k') , \tag{3}$$

where $u(k)$ is an isotropic cutoff factor. In writing Eq. (3), we assume a potential which is slowly varying on an atomic distance a (as displayed by the absence of nondiagonal terms, $l\neq m$, that would couple the various orthogonal Bloch states at the center of the zone).

On the other hand, the potential is nearly local on the scale of the bound-state radius r_0, its range being that of u_k, which we assume to be $\ll r_0$ and $\gg a$. (The cut-off is needed in order to avoid spurious short-distance divergences. Qualitatively, it accounts for the finite bandwidth of the host material.)

To the extent that we are interested only in qualitative results on the damping and stress dependence of bound states, Eq. (3) may be viewed as a rough model, where V is adjusted to reproduce the correct zero-stress impurity level. In fact, the use of a short-range interaction is not unreasonable, in view of the large screening present in zero-gap materials. The main oversimplification is the assumption that V (i.e., screening) is stress-independent, which is at best approximately true.

The use of simple potential (3) allows us to take an exact account of the Γ_8 symmetry of the band

edge, i.e., of the intimate impurity coupling between conduction and valence bands, which is of primary importance in determining bound states.

The binding energy to the impurity is supposed to be much smaller than the bandwidth, so we can neglect the nonparabolicity of the band. Wherever the k sums converge naturally, we drop the cutoff factor u_k, the latter is retained only in divergent sums, where it essentially acts to renormalize the strength of the potential V.

Within these simplifications, the solution of Eq. (2) is straightforward. We define

$$\tilde{G}_{ij} = \sum_{\vec{k},\vec{k}'} G_{ij}(\vec{k},\vec{k}')u_{\vec{k}}u_{\vec{k}'} .$$

Equation (2) thus becomes a 4×4 matrix equation

$$(1 - V\underline{\tilde{G}}_0)\underline{\tilde{G}} = \underline{\tilde{G}}_0 . \tag{4}$$

Hereafter, the symbols $\underline{A}$ will define a 4×4 matrix A. Equation (4) is to be compared to the secular equation found by Mauger and Friedel.[7] In Ref. 7(b), the unperturbed propagator $G_0(k)$ was supposed to be diagonal; thus, for each k, the basis is chosen along the four eigenstates of $H(k)$. In this k-dependent basis, the matrix nature of the problem appears in the interaction $V_{kk'}$, instead of $G_0(k)$. Of course, the two approaches are up to that point completely equivalent. The difference appears in the choice of V. Mauger and Friedel take an arbitrary coupling matrix, depending on eventually three parameters. We instead show that the interaction depends only on one parameter V, a fact that is most easily seen in the Kohn-Luttinger representation where V is scalar. In this sense, our results may be viewed as a reduced form of the Mauger-Friedel approach, where the rotational structure of the conduction and valence bands is fully exploited.

In practice, the $\underline{\tilde{G}}_0$ and $\underline{\tilde{G}}$ matrices can now be expressed in terms of F, G, H, and I, defined by Bir and Pikus[5],

$$\underline{\tilde{G}}_0 = \begin{pmatrix} \langle\epsilon - G\rangle & \langle H\rangle & \langle I\rangle & 0 \\ \langle H^*\rangle & \langle\epsilon - F\rangle & 0 & \langle I\rangle \\ \langle I^*\rangle & 0 & \langle\epsilon - F\rangle & \langle -H\rangle \\ 0 & \langle I^*\rangle & \langle -H^*\rangle & \langle\epsilon - G\rangle \end{pmatrix} , \tag{5a}$$

$$\underline{\tilde{G}} = \frac{1}{S}\begin{pmatrix} R & \langle H\rangle & \langle I\rangle & 0 \\ \langle H^*\rangle & R & 0 & \langle I\rangle \\ \langle I^*\rangle & 0 & R & \langle -H\rangle \\ 0 & \langle I^*\rangle & \langle -H^*\rangle & R \end{pmatrix} , \tag{5b}$$

where

$$\langle X\rangle = \frac{1}{8\pi^3}\int \frac{d^3k\, u^2(k)X(k)}{(\epsilon - \epsilon_+)(\epsilon - \epsilon_-)} ,$$

$$R = (1 - V\langle\epsilon - F\rangle)\langle\epsilon - G\rangle + V(|\langle H\rangle|^2 + |\langle I\rangle|^2) , \tag{6a}$$

$$S = (1 - V\langle\epsilon - F\rangle)(1 - V\langle\epsilon - G\rangle) - V^2(|\langle H\rangle|^2 + |\langle I\rangle|^2) . \tag{6b}$$

From the identity $\langle F\rangle = \langle G\rangle$, all the diagonal elements of $\underline{\tilde{G}}$ are found to be equal. Bound states, if any, are given by the zeros of $S(\epsilon)$. Mathematics are considerably simplified if we assume an isotropic-band structure, characterized by the approximate dispersion relation

$$\epsilon_\pm = \tfrac{1}{3}(L + 2M)k^2 \pm \{\Delta^2 + [\tfrac{1}{3}(L - M)]^2k^4\}^{1/2} . \tag{7}$$

Equation (7) is exact in the stress-free case ($\Delta = 0$). In the presence of stress it yields the correct gap 2Δ at $k = 0$, and the exact effective masses at large values of k. On the other hand, the valence-band anisotropic camelback has been lost, and the dispersion relation of this band is now nonmonotonic for all the directions. With these approximations $\langle I\rangle = \langle H\rangle = 0$, and the $\underline{G}$ and $\underline{G}_0$ matrices reduce to scalars. The solution of Eq. (2) is then straightforward and yields

$$\tilde{G} = \tilde{G}_0/(1 - V\tilde{G}_0) ,$$

where

$$\tilde{G}_0 = \langle\epsilon - F\rangle .$$

More generally, one can calculate the density of states brought about by the impurity

$$\delta\rho(\epsilon) = -(1/\pi)\,\mathrm{Im}\,\mathrm{Tr}(\underline{G} - \underline{G}_0) , \tag{8}$$

where the trace involves summation over $\vec{k}$ and the four values of the angular momentum $\mathcal{M}_J$. From Eq. (2), we see that

$$\underline{G}(\vec{k},\vec{k}') - \underline{G}_0(k)\delta_{\vec{k}\vec{k}'} = Vu(k)u(k')\underline{G}_0(\vec{k})(1 - V\tilde{G}_0)^{-1}\underline{G}_0(\vec{k}') .$$

As $(\underline{G}_0)^2 = -(\partial/\partial\epsilon)\underline{G}_0$, we finally obtain

$$\delta\rho(\epsilon) = -\frac{4}{\pi}\frac{\partial}{\partial\epsilon}\,\mathrm{Im}\ln(1 - V\tilde{G}_0)$$

or

$$\delta\rho(\epsilon) = -\frac{4}{\pi}\frac{\partial}{\partial\epsilon}\,\delta(\epsilon) , \tag{9}$$

where $\delta(\epsilon) = \arg(1 - V\tilde{G}_0)$ is the s-waves phase shift produced by the potential.

A bound state will occur for an energy ϵ_0 such that $\delta(\epsilon_0) = \frac{1}{2}\pi$ and its width Γ will be given by

$$\Gamma = \frac{d\epsilon}{d\delta(\epsilon)}\bigg|_{\epsilon=\epsilon_0} = \frac{-\mathrm{Im}\tilde{G}_0(\epsilon_0)}{(d/d\epsilon)\mathrm{Re}\tilde{G}_0(\epsilon)|_{\epsilon=\epsilon_0}} . \tag{10}$$

1. Zero-stress case

Any root of $S(\epsilon)$ is necessarily fourfold degenerate. For instance, for a strong enough repul-

sion, we find a bound state with an energy $\epsilon_0 + i\Gamma_0$ given by[4]

$$-\frac{1}{V}+\frac{1}{V_c}=\beta m_v^{3/2}(\sqrt{\epsilon_0})\frac{\Gamma}{2\epsilon_0}=-\left(\frac{m_c}{m_v}\right)^{3/2}, \qquad (11)$$

where

$$\frac{1}{V_c}=\frac{m_v-m_c}{2\pi^2\hbar^2}\int_0^\infty u_k^2 dk \quad \text{and} \quad \beta=\frac{\sqrt{2}}{4\pi\hbar^3}.$$

In obtaining Eq. (11), we have used the following approximations:

$$\int_0^\infty \frac{u_k^2 k^2 dk}{\epsilon+\alpha k^2}\simeq\frac{1}{\alpha}\left(\int_0^\infty u_k^2\, dk-\epsilon\int_0^\infty\frac{dk}{\epsilon+\alpha k^2}\right). \qquad (12)$$

The cutoff, i.e., the finite bandwidth, only enters in the first term, which is ϵ independent, and acts only to correct the potential strength V. In fact, physical quantities such as the phase shift may be expressed in terms of ϵ_0, rather than V, according to

$$\begin{aligned}\delta(\epsilon,\epsilon_0)&=\arctan\frac{\pi}{2}\frac{t^{3/2}\sqrt{\epsilon}}{\sqrt{\epsilon}-\sqrt{\epsilon_0}}, \quad \epsilon>0,\\ \delta(\epsilon,\epsilon_0)&=-\arctan\frac{\pi}{2}\frac{\sqrt{-\epsilon}}{\sqrt{\epsilon_0}+t^{3/2}\sqrt{-\epsilon}}, \quad \epsilon<0,\end{aligned} \qquad (13)$$

where $t=m_c/m_v$. This result is only valid near $\epsilon=0$. Away from the origin, the cutoff ensures $\delta(+\infty)=\delta(-\infty)=0$. Such a feature applies in all cases, whether there exists a bound state or not; the strength of the coupling only enters in a scale of energy for the density of states.

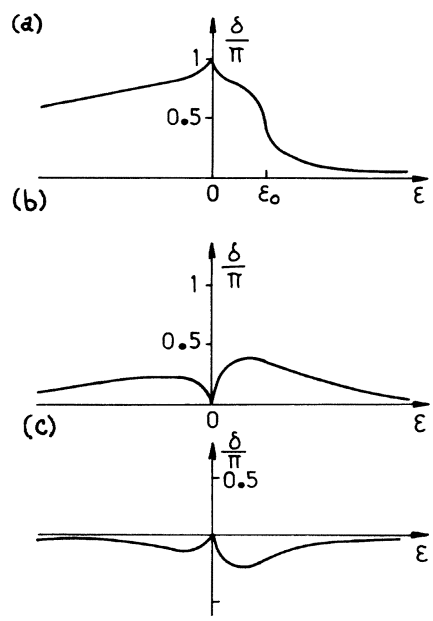

FIG. 1. Phase-shift energy dependence in the three cases discussed in the text: (a) $V>V_c$; (b) $0<V<V_c$; (c) $V<0$.

There are essentially three cases, which for $m_c/m_v \ll 1$ correspond to the following situations: (a) $V>V_c$, leading to a fairly sharp resonance in the conduction band, (b) $0<V<V_c$, corresponding to a non-resonant repulsion, and (c) $V<0$, where no resonance occurs.

The corresponding behavior of the phase shift is sketched in Fig. 1. Note that in case (a), the phase shift goes through $\frac{1}{2}\pi$ on both sides of the origin; however, the very high damping for $\epsilon<0$ completely kills the resonance.

Well-defined bound states only exist for $V>V_c$. They always correspond to acceptor states, since the resonance is taken away from the valence band. Indeed, the number of states drawn from the valence band to the impurity is

$$-\int_{-\infty}^0 \delta\rho(\epsilon)d\epsilon=+\frac{4}{\pi}\delta(0)=+4 \quad \text{in case (a)}.$$

These four states are precisely transferred into the resonant state for $\epsilon>0$.

2. *Finite stress*

The twofold solutions of Eq. (11), corresponding to four states because of the Kramers degeneracy, would split into two doublets if the dispersion relations we use were the exact ones. Within the approximation of Eq. (7), the two doublets remain degenerate, with an energy $\epsilon=x\epsilon_0$ which is the root of the equation

$$1=\frac{4t\sqrt{2}}{\pi}\int_0^\infty\frac{[x(1+t^2)/2t]z^2+(1-t)(D^2-x^2)}{z^4+2z^2x(1-t)+4t(D^2-x^2)}dz, \qquad (14)$$

where $D=\Delta/\epsilon_0$ and ϵ_0 has been defined in Eq. (8).

Figure 2 presents the $x(D)$ variation. When the acceptor level merges into the induced gap, i.e., when $x\leq D$, one observes a kink in the $x(D)$ dependence. This corresponds to a transition from a resonant state to a localized state which is obtained in numerical calculations by replacing in Eq. (14) a Cauchy principal part, when $x\geq D$ by a true definite integral when $x\leq D$. It should be stressed that this singularity reflects the singularity of Re $\tilde{G}_0$ itself and thus necessarily occurs.

For practically all stress values, the acceptor level follows the downward shift of the valence band. Only when it is inside the gap, but very close to the conduction band, is its position influenced by both bands. This result is a consequence of the large ratio between the two effective masses.

As long as $x\geq D$, the acceptor level has a finite width which can be calculated from Eq. (10). Fig-

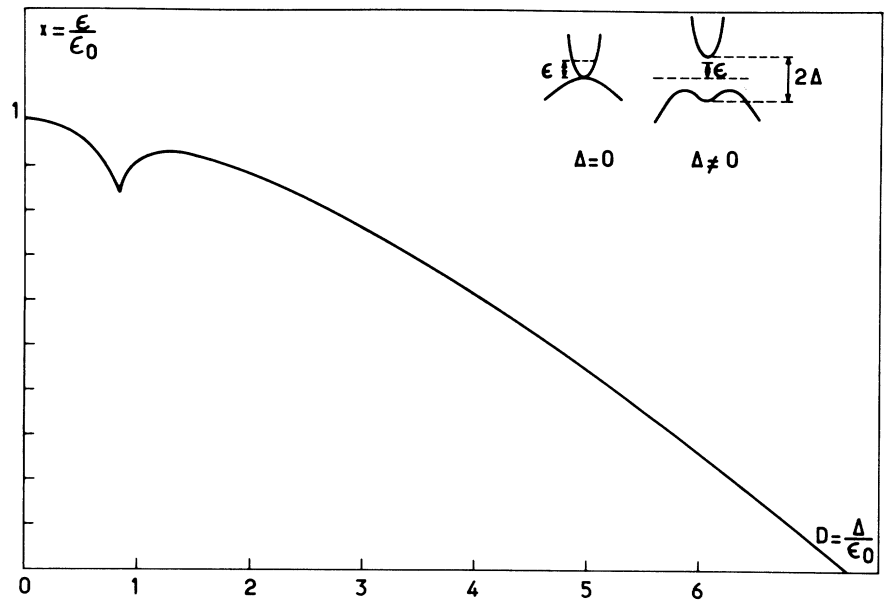

FIG. 2. Acceptor energy ϵ (in units ϵ_0) measured from the top of the valence band at zero stress, as a function of the applied stress. The binding energy $R^*(\Delta)$ with respect to the $k=0$ extremum of the valence band is such that $R^*(\Delta) = \Delta + \epsilon(\Delta)$.

ure 3 presents the variation of Γ/ϵ_0 with D. As expected, Γ/ϵ_0 goes to zero when D increases until the level merges into the gap where Γ is identically zero. This behavior is apparent in Eq. (10) as Γ is directly proportional to the conduction band density of states.

An interesting point is to observe that, even when the localized level is very close to the conduction band, it remains an acceptor state as shown by the phase shift variation sketched on Fig. 4; this state is always built from valence-band states.

The same kind of anomaly in the binding energy of acceptor states could be observed near the semimetal-semiconductor transition in $Hg_{1-x}Cd_xTe$ alloys. In the semiconductor configuration, near the transition point ($x \gtrsim 0.16$), the Γ_6 conduction band and the acceptor level belonging to the Γ_8 valence bands are degenerate.[3,7] From the previous discussion, this level depends mainly on

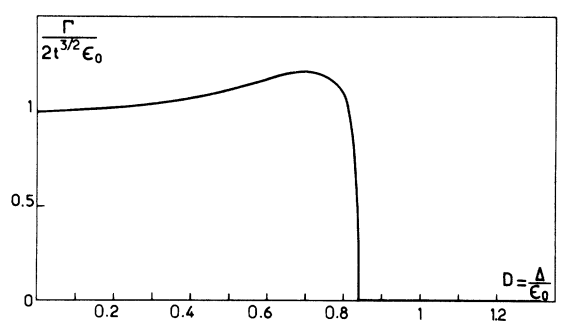

FIG. 3. Width of the acceptor level as a function of the stress.

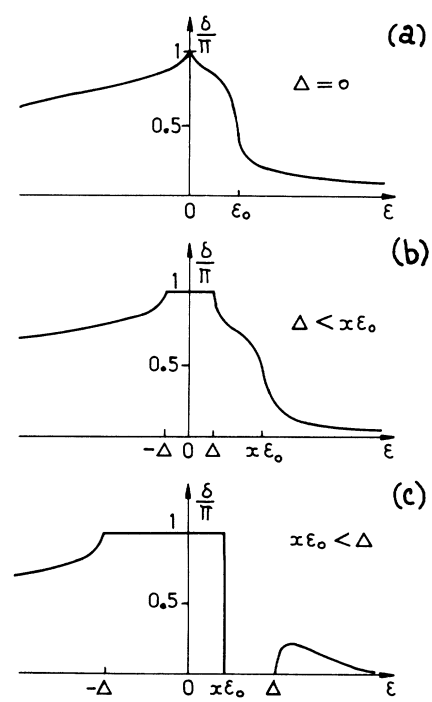

FIG. 4. Energy-dependence phase shift produced by an acceptor level with an energy $x\epsilon_0$ for different values of the stress: (a) $\Delta = 0$; (b) $\Delta < x\epsilon_0$; (c) $\Delta > x\epsilon_0$.

the valence-band position. By increasing x, or by applying a hydrostatic pressure the acceptor will fall inside the Γ_6-Γ_8 gap, and at this point its position will become influenced by all the bands, until the Γ_6-Γ_8 gap is large enough to stabilize the level at a rather fixed distance of the valence band.

ACKNOWLEDGMENTS

We gratefully thank A. Launay for considerable help in the numerical calculations and Dr. C. Rigaux for many stimulating discussions on this subject.

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