

## Impurity-induced narrow bands of continuous electronic states in doped semiconductors

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Impurity-induced modification of the density of electronic states in transition-metal-doped semiconductors is studied. The model Hamiltonian includes potential scattering of band electrons by impurity atoms randomly distributed in the host lattice, and hybridization between initial band states and  $d$  orbitals. The bare levels of the atoms are located in the band gap. By applying multiple-scattering theory, configuration-averaged Green functions over the impurity ensemble are calculated by using the Matsubara method in the short-range potential approximation. We demonstrate that for the defined attractive impurity potentials the potential scattering results in band tail formation. A narrow high-density band of free states within the gap have been found. The band is caused by the hybridization that induces the following virtual electron transitions over the impurity ensemble: an initial impurity site  $\rightarrow$  a band state  $\rightarrow$  another site  $\rightarrow$  a band state, etc. It is essential that the main high-density peak of the localized states lies within this band.

### I. INTRODUCTION

The density of states (DOS) of doped semiconductors is of considerable interest from the viewpoints of both theory and experiment. Recently, the widths and energy positions of impurity bands have been determined by band-structure calculations of hypothetical impurity superlattices<sup>1</sup> or by applying multiple-scattering theories with the use of the developed methods of calculations of the perturbation expansion of the configuration-averaged Green's functions.<sup>2-10</sup>

Usually, in the theory of impurity bands at impurity densities below the Mott value, band formation is associated with the potential component of impurity perturbations. Within this approach, the model Hamiltonian, in which the perturbation is presented by potential scattering of band electrons by an impurity ensemble, is used.<sup>1-3,7-10</sup> In the low-density limit, the DOS of impurity bands reveals sharp cutoffs and the absence of band tails in the approximation of a nonfluctuating impurity density.<sup>7,8,10</sup> The band tails can be obtained by the optimum fluctuation method.<sup>4,6,9</sup>

The theory of deep localized levels in crystal semiconductors doped by  $3d$  elements is based on the single-impurity Hamiltonian, in which the approximation of the self-consistent field both for band states and for perturbations, induced by the impurity, is used (see Refs. 11-14 and references therein). First of all, the theory assumes that the impurity bare  $d$  levels lie within the band gap or in the vicinity. Along with the potential scattering of band electrons, the resonance scattering is taken into account.<sup>12</sup> The latter is caused by hybridization between the initial band states of the semiconductor and the impurity  $d$  orbitals. It is assumed that the exact Green's function for the single-impurity atom in the host lattice allows one to determine both the spectrum of localized states and properties of band electrons at low impurity densities.<sup>12,14</sup>

In this paper, we study the impurity-induced modification of the DOS in a doped semiconductor by using a model Hamiltonian which includes both the resonance and the potential scattering of band electrons by an ensemble of the impurity atoms randomly distributed over equivalent sites in the host lattice. The resonance scattering may result in a mechanism of forming deep bands of continuous electronic states within the band gap even at low densities of the identical impurity atoms.

Let the single-impurity atom have a bare level lying within the band gap of the semiconductor. The resonance scattering, which can be described by the last term in the Hamiltonian (1) at a certain  $j$ , results in virtual electron transitions between the level and the initial band states.

For the impurity ensemble, delocalization of impurity electrons is caused by the following virtual electron transitions: an initial impurity site  $\rightarrow$  a band state  $\rightarrow$  another site  $\rightarrow$  a band state, etc. At such a macroscopic transfer of an electron the energy conservation law of the system is fulfilled. This ensemble effect must result in energy regions of the Green's-function poles within the band gap.

### II. MODEL HAMILTONIAN

We use the approximation of a single nondegenerate level  $\varepsilon_0$  of the impurity atom and consider only a single band of the semiconductor. We restrict ourselves to nonmagnetic solutions for which strong on-site correlation for the impurity atoms can be reduced to the renormalization of  $\varepsilon_0$  in the Hartree-Fock approximation.<sup>11-13</sup> Then the Hamiltonian is

$$H = \sum_{\mathbf{k}} \varepsilon_{\mathbf{k}} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} + \sum_j \varepsilon_0 d_j^{\dagger} d_j + \sum_{j, \mathbf{k}, \mathbf{k}_1} W_{\mathbf{k}\mathbf{k}_1 j} a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}_1} + \sum_{j, \mathbf{k}} \{ V_{\mathbf{k}j} a_{\mathbf{k}}^{\dagger} d_j + V_{j\mathbf{k}} d_j^{\dagger} a_{\mathbf{k}} \} \quad (1)$$

where  $a_{\mathbf{k}}$  and  $d_j$  are the usual annihilation operators (the spin index is omitted, but will be taken into account for the DOS);  $\mathbf{k}$  is the wave vector of an electron in the band state with the energy  $\varepsilon_{\mathbf{k}}$ ;  $j$  is the impurity atom number;  $W_{\mathbf{k}\mathbf{k}_j}$  describes the potential scattering of band electrons by the  $j$ th impurity atom; and  $V_{\mathbf{k}j}$  is the matrix element of the hybridization.

Considering only the neutral impurity in the host lattice, and using the short-range potential approximation,<sup>12</sup> these matrix elements can be presented in the form

$$W_{\mathbf{k}\mathbf{k}_j} = U_p \Omega^{-1} \psi_{\mathbf{k}}^*(\mathbf{R}_j) \psi_{\mathbf{k}_1}(\mathbf{R}_j), \quad (2)$$

$$V_{\mathbf{k}j} = U_h \Omega^{-1/2} \psi_{\mathbf{k}}^*(\mathbf{R}_j), \quad (3)$$

where  $\psi_{\mathbf{k}}(\mathbf{R}_j)$  is the value of the Bloch wave function  $\psi_{\mathbf{k}}(\mathbf{R}) = u(\mathbf{R}) \exp(i\mathbf{k}\mathbf{R})$  at the  $j$ th site with the radius-vector  $\mathbf{R}_j$ ;  $U_p$  and  $U_h$  are the constants determined by the impurity potential; and  $\Omega$  is the semiconductor

volume.  $U_p < 0$  corresponds to the attractive impurity potential.

### III. GENERAL EXPRESSIONS FOR DIAGONAL MATRIX ELEMENTS OF SELF-ENERGY OPERATOR

It is known that the properties of interest are described by the single-electron Green's function  $G(\varepsilon)$ , where  $\varepsilon$  is the energy of quasiparticles.<sup>2,7</sup> The diagonal elements  $G$  are represented in the form:

$$\begin{aligned} G_{\mathbf{k}\mathbf{k}}(\varepsilon) &= [G_{\mathbf{k}\mathbf{k}}^{(0)-1}(\varepsilon) - \Sigma_{\mathbf{k}\mathbf{k}}(\varepsilon)]^{-1}, \\ G_{jj}(\varepsilon) &= [G_{dd}^{(0)-1}(\varepsilon) - \Sigma_{jj}(\varepsilon)]^{-1}, \end{aligned} \quad (4)$$

where  $\Sigma(\varepsilon)$  is the self-energy part;  $G_{\mathbf{k}\mathbf{k}}^{(0)}(\varepsilon) = (\varepsilon - \varepsilon_{\mathbf{k}})^{-1}$ ;  $G_{dd}^{(0)}(\varepsilon) = (\varepsilon - \varepsilon_0)^{-1}$ ; and  $\varepsilon = \varepsilon + 0^+$ .

From (1)–(4), the following is obtained for  $\Sigma_{\mathbf{k}\mathbf{k}}$ :

$$\begin{aligned} \Sigma_{\mathbf{k}\mathbf{k}}(\varepsilon) &= Z\Omega^{-1} \sum_j |\psi_{\mathbf{k}}(\mathbf{R}_j)|^2 + Z^2\Omega^{-2} \sum_{j,j_1, \mathbf{k}_1 \neq \mathbf{k}} \psi_{\mathbf{k}}^*(\mathbf{R}_j) \psi_{\mathbf{k}_1}(\mathbf{R}_j) G_{\mathbf{k}_1\mathbf{k}_1}^{(0)} \psi_{\mathbf{k}_1}^*(\mathbf{R}_{j_1}) \psi_{\mathbf{k}}(\mathbf{R}_{j_1}) \\ &\quad + Z^3\Omega^{-3} \sum_{j_i, \mathbf{k}_i \neq \mathbf{k}} \psi_{\mathbf{k}}^*(\mathbf{R}_j) \psi_{\mathbf{k}_1}(\mathbf{R}_j) G_{\mathbf{k}_1\mathbf{k}_1}^{(0)} \psi_{\mathbf{k}_1}^*(\mathbf{R}_{j_1}) \psi_{\mathbf{k}_2}(\mathbf{R}_{j_1}) G_{\mathbf{k}_2\mathbf{k}_2}^{(0)} \psi_{\mathbf{k}_2}^*(\mathbf{R}_{j_2}) \psi_{\mathbf{k}}(\mathbf{R}_{j_2}) + \dots \end{aligned} \quad (5)$$

Here  $Z(\varepsilon) = U_p + U_h^2 G_{dd}^{(0)}(\varepsilon)$ .

In the same way  $\Sigma_{jj}$  can be expressed in the form

$$\Sigma_{jj} = \frac{U_h^2 F(\varepsilon)}{1 - U_p F(\varepsilon)}, \quad (6)$$

where

$$\begin{aligned} F(\varepsilon) &= \Omega^{-1} \sum_{\mathbf{k}} D_{\mathbf{k}} |\psi_{\mathbf{k}}(\mathbf{R}_j)|^2 + Z\Omega^{-2} \sum_{j_1 \neq j, \mathbf{k}, \mathbf{k}_1 \neq \mathbf{k}} D_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{R}_j) \psi_{\mathbf{k}}^*(\mathbf{R}_{j_1}) D_{\mathbf{k}_1} \psi_{\mathbf{k}_1}(\mathbf{R}_{j_1}) \psi_{\mathbf{k}_1}^*(\mathbf{R}_j) \\ &\quad + Z^2\Omega^{-3} \sum_{j_i \neq j, \mathbf{k}_i \neq \mathbf{k}_{i-1}} D_{\mathbf{k}} \psi_{\mathbf{k}}(\mathbf{R}_j) \psi_{\mathbf{k}_1}^*(\mathbf{R}_{j_1}) D_{\mathbf{k}_1} \psi_{\mathbf{k}_1}(\mathbf{R}_{j_1}) \psi_{\mathbf{k}_1}^*(\mathbf{R}_{j_2}) D_{\mathbf{k}_2} \psi_{\mathbf{k}_2}(\mathbf{R}_{j_2}) \psi_{\mathbf{k}_2}^*(\mathbf{R}_j) + \dots \end{aligned} \quad (7)$$

and

$$D_{\mathbf{k}}(\varepsilon) = S_{\mathbf{k}} G_{\mathbf{k}\mathbf{k}}^{(0)}, \quad S_{\mathbf{k}}(\varepsilon) = \left[ 1 - G_{\mathbf{k}\mathbf{k}}^{(0)} Z(\varepsilon) \sum_{j_1 \neq j} |\psi_{\mathbf{k}}(\mathbf{R}_{j_1})|^2 \right]^{-1}. \quad (8)$$

If the identical impurity atoms randomly occupy either equivalent host-lattice sites or interstitial ones in the semiconductor,  $u(\mathbf{R}_j)$  does not depend on  $j$ . In the process of summing over  $j$  in (5) and (7), one must take the average of the obtained result over the random distribution of the impurities. It turns out to be necessary to evaluate moments of the following type:

$$M_s(\mathbf{k}_1, \mathbf{k}_2, \dots, \mathbf{k}_s) = \left\langle \sum_{\{n_1\}} \sum_{\{n_2\}} \dots \sum_{\{n_s\}} \exp \left[ -i \sum_m \mathbf{k}_m \mathbf{R}_{n_m} \right] \right\rangle_{\text{av}},$$

where  $\langle \rangle_{\text{av}}$  is the average taken over all the possible configurations of the impurities. The configuration-averaged self-energies (5) and (7) have been calculated by using the Matsubara method.<sup>2,7</sup> Here omitting simple but bulky calculations, we arrive at

$$\begin{aligned} \Sigma_{\mathbf{k}\mathbf{k}}(\varepsilon) &= \frac{Z(\varepsilon) N_{\text{im}} |u_{\mathbf{k}}|^2}{1 - Z(\varepsilon) \sum'_{\mathbf{k}_1 \neq \mathbf{k}} |u_{\mathbf{k}_1}|^2 G_{\mathbf{k}_1\mathbf{k}_1}^{(0)}} \left[ 1 - Zc \sum'_{\mathbf{k}_2 \neq \mathbf{k}} |u_{\mathbf{k}_2}|^2 G_{\mathbf{k}_2\mathbf{k}_2}^{(0)} + 2Z^2 c^2 \left[ \sum'_{\mathbf{k}_2 \neq \mathbf{k}} |u_{\mathbf{k}_2}|^2 G_{\mathbf{k}_2\mathbf{k}_2}^{(0)} \right]^2 \right. \\ &\quad \left. - Z^2 c N_{\text{im}} \sum'_{\mathbf{k}_2 \neq \mathbf{k}} |u_{\mathbf{k}_2}|^4 G_{\mathbf{k}_2\mathbf{k}_2}^{(0)2} + \dots \right] \end{aligned} \quad (9)$$

and

$$F(\varepsilon) = \sum_{\mathbf{k}} S_{\mathbf{k}} |u_{\mathbf{k}}|^2 G_{\mathbf{k}\mathbf{k}}^{(0)} \left[ 1 + Z^2 N_{\text{im}} (1-c) S_{\mathbf{k}} |u_{\mathbf{k}}|^2 G_{\mathbf{k}\mathbf{k}}^{(0)} \sum_{\mathbf{k}_1 \neq \mathbf{k}} S_{\mathbf{k}_1} |u_{\mathbf{k}_1}|^2 G_{\mathbf{k}_1 \mathbf{k}_1}^{(0)} \right. \\ \left. + Z^3 N_{\text{im}} (1-3c+2c^2) S_{\mathbf{k}} |u_{\mathbf{k}}|^2 G_{\mathbf{k}\mathbf{k}}^{(0)} \left[ \sum_{\mathbf{k}_1 \neq \mathbf{k}} S_{\mathbf{k}_1} |u_{\mathbf{k}_1}|^2 G_{\mathbf{k}_1 \mathbf{k}_1}^{(0)} \right]^2 + \dots \right]. \quad (10)$$

Here  $\sum_{\mathbf{k}} \rightarrow \int d\mathbf{k} / (2\pi)^3$ ;  $S_{\mathbf{k}}(\varepsilon, N_{\text{im}}) = [1 - G_{\mathbf{k}\mathbf{k}}^{(0)} Z(\varepsilon) N_{\text{im}} |u_{\mathbf{k}}|^2]^{-1}$ ; and  $c = N_{\text{im}} / N_s$ , where  $N_s$  is the density of the host-lattice sites.

Nowadays the most important region of  $c$  is  $\sim n \times 10^{-2}$  for transition-metal-doped semiconductors. Thus in real situations the values of  $c \ll 1$ . From (9) and (10) one can write the condition imposed on the impurity concentration, at which one can restrict oneself only to the first term of the series for both  $\Sigma_{\mathbf{k}\mathbf{k}}$  and  $F(\varepsilon)$ . The latter, with the use of (6), allows us to obtain the self-energy  $\Sigma_{jj}$ . Of course, the exact Green's function for the Hamiltonian (1) must satisfy Levinson's theorem, that can be written as

$$\text{Im} \int d\varepsilon \text{Tr}[G(\varepsilon) - G^{(0)}(\varepsilon)] = 0. \quad (11)$$

The theorem means conservation of the total number of electronic states for the Hamiltonian (1) as compared with the unperturbed one.

To verify the validity of the first term approximation for the series (9) and (10) and, respectively, for the obtained diagonal elements of  $G^{(1)}(\varepsilon)$ , we have checked the condition

$$\gamma = \frac{1}{N_{\text{im}}} \text{Im} \int d\varepsilon \text{Tr}[G^{(1)}(\varepsilon) - G^{(0)}(\varepsilon)] \ll 1.$$

#### IV. CALCULATION RESULTS AND DISCUSSION

To model the impurity-induced modification of the DOS, we have chosen the semielliptical model of the symmetric band (the conduction band, for definiteness) with width  $2D_b$ , total number of states per spin  $N_t/2$  and the unperturbed DOS per spin

$$\rho_{\text{ext}}^{(0)}(\varepsilon) = \begin{cases} \frac{N_t}{\pi D_b^2} [D_b^2 - \varepsilon^2]^{1/2} & \text{for } |\varepsilon| \leq D_b \\ 0 & \text{for } |\varepsilon| > D_b. \end{cases} \quad (12)$$

$$\rho_{\text{loc}}(\omega) = N_{\text{im}} \begin{cases} \frac{1}{\pi} \frac{\text{Im} \Sigma_{dd}^{(1)}(\omega)}{(\omega - \varepsilon_0 - \text{Re} \Sigma_{dd}^{(1)})^2 + (\text{Im} \Sigma_{dd}^{(1)})^2}, & |\omega^*| \leq D_b \\ \sum_m (A'(\omega_m))^{-1} \delta(\omega - \omega_m), & |\omega^*| > D_b, \end{cases} \quad (17)$$

where the prime denotes differentiation; the values  $\omega_m$  are roots of

Further  $u_{\mathbf{k}}$  is taken to be independent of  $\mathbf{k}$ . Using (12) and replacing the sum over  $\mathbf{k}$  by an integral over  $\varepsilon_{\mathbf{k}}$ , the self-energies are given by

$$\Sigma_{\mathbf{k}\mathbf{k}}^{(1)}(\omega) = \frac{N_{\text{im}} Z(\omega) u_{\mathbf{k}}^2}{1 - \pi Z(\omega) u_{\mathbf{k}}^2 [\beta^{(0)}(\omega) - i\rho^{(0)}(\omega)]}, \quad (13)$$

and, with account of (6),

$$\Sigma_{dd}^{(1)}(\omega) = \frac{\pi U_h^2 u_{\mathbf{k}}^2 [\beta^{(0)}(\omega^*) - i\rho^{(0)}(\omega^*)]}{1 - \pi U_p u^2 [\beta^{(0)}(\omega^*) - i\rho^{(0)}(\omega^*)]}, \quad (14)$$

where  $\omega^* = \omega - u_{\mathbf{k}}^2 N_{\text{im}} Z(\omega)$  and

$$\beta^{(0)}(\omega) = \frac{N_t}{\pi D_b^2} \begin{cases} \omega, & |\omega| \leq D_b \\ \omega - \text{sgn}(\omega) [\omega^2 - D_b^2]^{1/2}, & |\omega| > D_b. \end{cases} \quad (15)$$

In the general case, poles of both  $G_{\mathbf{k}\mathbf{k}}^{(1)}$  and  $G_{dd}^{(1)}$  lie in the energy region of the initial conduction band as well as the gap region.

Finally, the DOS of extended electronic states per spin,

$$\rho_{\text{ext}}(\omega) = -\frac{1}{\pi} \sum_{\mathbf{k}} G_{\mathbf{k}\mathbf{k}}^{(1)}(\omega),$$

is given by

$$\rho_{\text{ext}}(\omega) = \frac{2N_t}{\pi D_b} \text{Im} \left\{ t \left[ 1 - \left( \frac{1+t}{t} \right)^{1/2} \right] \right\}, \quad (16)$$

where

$$t = \frac{-\omega - D_b + \Sigma_{\mathbf{k}\mathbf{k}}^{(1)}}{2D_b}$$

and the sign of  $\text{Im}(1+t/t)^{1/2} \geq 0$  must be taken.

For localized electronic states, the DOS per spin,

$$\rho_{\text{loc}} = -\frac{1}{\pi} N_{\text{im}} \text{Im} G_{dd}^{(1)}(\omega),$$

is expressed as

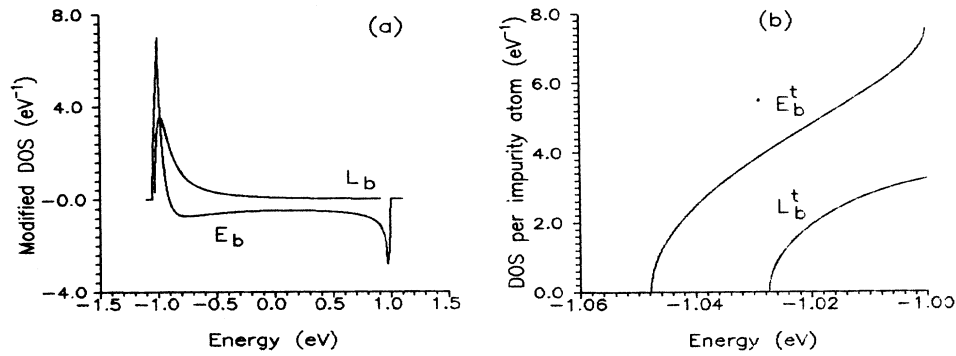


FIG. 1. (a) The change of the DOS per impurity atom for the band states ( $E_b$ ) and the normalized DOS for the localized states ( $L_b$ ). (b) Formation of the band tails in the gap region. Curve  $E_b^t$  presents  $E_b$  states, and curve  $L_b^t$  presents  $L_b$  states beyond the band bottom at  $-1$  eV. The parameters are  $N_i=0.06 \text{ \AA}^{-3}$ ,  $D_b=1.0$  eV,  $\varepsilon_0=-2.0$  eV,  $N_{im}=0.04 \times N_i$ ,  $U_p \times N_i=-3.0$  eV, and  $U_h \times N_i^{1/2}=1.5$  eV.

$$A(\omega)=\omega-\varepsilon_0-\text{Re}\Sigma_{dd}^{(1)}(\omega)=0. \quad (18)$$

To show clearly the impurity effect for extended states in the band region, below we have plotted the change of the DOS per impurity atom:

$$\Delta\rho_{\text{ext}}(\varepsilon)=2\frac{\rho_{\text{ext}}-\rho_{\text{ext}}^{(0)}}{N_{im}},$$

where the spin index is taken into account, and  $\rho_{\text{ext}}$  is given by (16).

Both for extended states in the gap region and for localized states, it is convenient to normalize the DOS to the impurity concentration  $N_{im}$ :

$$\rho_{\text{ext}}(\varepsilon)=2\frac{\rho_{\text{ext}}}{N_{im}}, \quad \rho_{\text{loc}}(\varepsilon)=2\frac{\rho_{\text{loc}}}{N_{im}}.$$

At first, we have analyzed the impurity-modified DOS of the doped semiconductor in the case when both the potential scattering  $U_p$  and the hybridization  $U_h$  are present. The calculation results in the two energy regions are shown in Figs. 1 and 2. Curve  $E_b$  in Fig. 1(a) demonstrates the change of the DOS per impurity atom for the band states. The energy dependence of the change is very sensitive to values of the constants  $U_p$  and  $U_h$ , as will be seen below. The main feature that is common for various parameter sets is that the change of total number of extended states per impurity atom

$$\Delta N_{\text{ext}}^b = \int_{-D_b}^{D_b} d\varepsilon \Delta\rho_{\text{ext}}^b$$

is negative in the band region. For the presented result,  $\Delta N(E_b)=-1.017$ . The curve  $L_b$  in Fig. 1(a) shows the normalized DOS for localized states. The effect of the advent of the localized states in the band is well known, and takes place at any nonzero  $U_h$ , even for the single-impurity Anderson's Hamiltonian.<sup>11,12</sup> The total number of these states per impurity atom  $N(L_b)=0.813$  in the band region.

As follows from Fig. 1(a), both  $E_b$  and  $L_b$  curves are beyond the initial band bottom at  $-1$  eV in the gap region. It is shown in more detail in Fig. 1(b), which demonstrates formation of the band tail, i.e., the states splitting off from the initial band and adjacent to it. The width of the tail is  $\approx 48$  meV. The total number of states per impurity atom is equal to 0.205 for curve  $E_b^t$  and  $6.38 \times 10^{-2}$  for curve  $L_b^t$ .

The band tail arises only at negative potential scattering constants. Varying the value of  $U_p$  at other parameters, we find that tail formation takes place at  $U_p N_i \leq -2.30$  eV. With increasing  $|U_p|$  the  $L_b^t$  tail of the localized states becomes deeper within the gap, and the total number of these states increases as well. Simultaneously the  $E_b^t$  tail tends to break away from the conduction band. This breaking away takes place at  $U_p N_i = -3.35$  eV. After that, the  $E_b^t$  states form the sharp band, the energy position of which becomes deeper in the gap with further increase of  $|U_p|$ .

An interesting situation occurs for states deep in the gap below bare  $d$  levels, as is shown in Fig. 2. There are two  $\delta$ -function distributions for localized states. The first, labeled  $D_0$ , corresponds to the simple pole of  $G_{dd}^{(1)}$

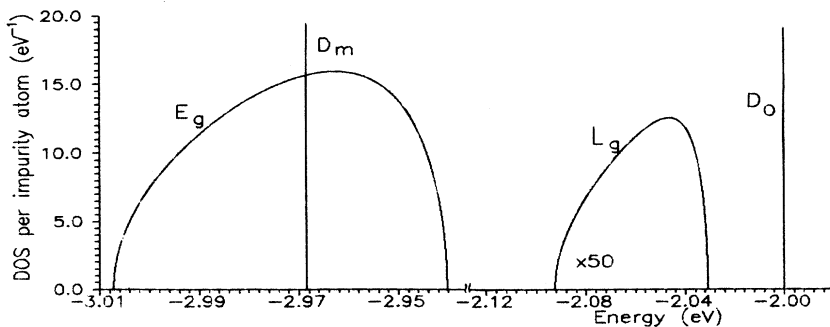


FIG. 2. Impurity-induced DOS per impurity atom deep in the gap region. Localized states are labeled by  $D_0$ ,  $D_m$ , and  $L_g$ . The band of extended states ( $E_g$ ) is caused by hybridization. The parameters are the same as in Fig. 1.

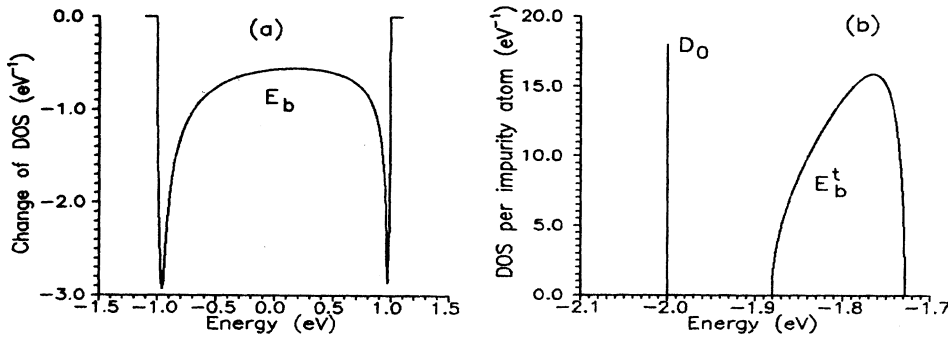


FIG. 3. The effect of the potential scattering on the DOS. (a) The change of the DOS per impurity atom for the band states ( $E_b$ ). (b) Formation of impurity band ( $E_b^t$ ) deep in the gap;  $D_0$  is formed by the bare levels of impurities. All other parameters but  $U_p$  are the same as at Fig. 1,  $U_h = 0$ .

that is equal to the bare atomic level  $\epsilon_0$ . One can easily verify it from (17), and obtain that for  $U_p \neq 0$  the pole amplitude is equal to

$$(A'(\epsilon_0))^{-1} = \frac{1}{1 + \frac{N_t}{2N_{im}}}$$

Because of  $N_t \gg N_{im}$ , the number of states is relatively small,  $N(D_0) = 0.148$ .

The second simple pole of  $G_{dd}^{(1)}$  labeled by  $D_m$  in Fig. 2, lies within the high-density band of extended states  $E_g$ . This position of the pole within the  $E_g$  band is a common feature for various parameter sets, as will be shown below. The total number of these localized states per impurity atom is  $N(D_m) = 1.027$ .

The formation of the  $E_g$  band occurs only at nonzero matrix elements of the hybridization, i.e., at  $U_h \neq 0$  within our approximation. The band is caused by the virtual electron transitions over the random ensemble of impurity: an initial impurity site  $\rightarrow$  a band state  $\rightarrow$  another site  $\rightarrow$  a band state, etc. The bandwidth is  $\Delta_g \approx 67$  meV, and the total number of these states per impurity atom is  $N(E_g) = 0.814$ . From the data one can estimate the average DOS in this band:

$$\langle \rho_{\text{ext}} \rangle = N_{im} \frac{N_h^g}{\Delta_g^g} \approx 0.3 \times 10^{23} \text{ cm}^{-3} \text{ eV}^{-1}$$

Hence the band is a narrow high-density one. Both the position and DOS of the band are strongly influenced by the potential scattering constant  $U_p$ .

The modified DOS includes the  $L_g$  band of localized states near the bare  $d$  level, as also is shown in Fig. 2.

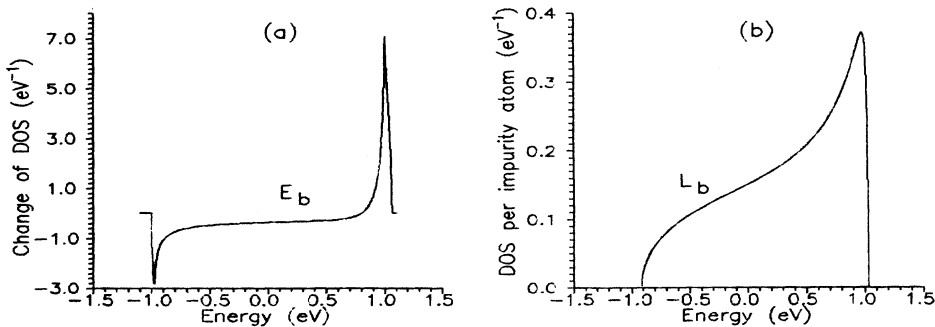


FIG. 4. The effect of hybridization on the DOS in the band region. (a) The change of the DOS per impurity atom for band states ( $E_b$ ). (b) The normalized DOS for localized states ( $L_b$ ). The band tail that exists is formed both by  $E_b$  and  $L_b$  states above the band top at 1 eV. All other parameters but  $U_p$  are the same as at Fig. 1,  $U_p = 0$ .

The band occurs only at nonzero matrix elements of the hybridization, and takes place at the potential scattering constant  $U_p = 0$ . Typically, the number of these states per impurity atom is relatively small:  $N(L_g) = 1.124 \times 10^{-2}$ .

Note that for the results presented in Figs. 1 and 2, the condition of conservation of the total number of electronic states (Levinson's theorem) fulfills with accuracy  $\gamma = 5.8 \times 10^{-4}$ .

The effect of changing the DOS due only to the potential scattering of band electrons by the impurity ensemble is shown in Fig. 3. Here  $U_h = 0$ , but the other parameters are the same as for the results presented in Figs. 1 and 2. The change in the DOS for the band states [Fig. 3(a)] differs from the result shown in Fig. 1(a). However, the change of the total number of band states per impurity atom is negative, and equal to  $\Delta N(E_b) = -1.770$ . This impurity-induced modification is caused by splitting off states from the initial band. These states form the impurity band, labeled  $E_b^t$  in Fig. 3(b), within the gap. Thus, in the absence of hybridization, the potential scattering can result in a deep impurity band formation. The energy position of this band becomes deeper in the gap with increasing  $|U_p|$ . This case agrees with the results.<sup>7</sup> The total number of these states per impurity atom is  $N(E_b^t) = -\Delta N(E_b)$ . For the results presented in Fig. 3, the condition of conservation of the total number of electronic states fulfills with accuracy  $\gamma = 2.7 \times 10^{-5}$ .

In Figs. 4 and 5 we show the impurity-induced modification of the DOS due to the hybridization only. The accuracy of the calculations was  $\gamma = 2.3 \times 10^{-5}$ . For the band states [curve  $E_b$  in Fig. 4(a)] the DOS decreases near the band bottom at  $-1$  eV, whereas it increases near

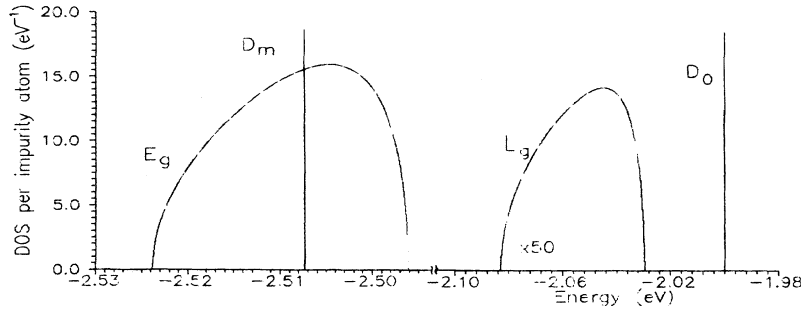


FIG. 5. The effect of hybridization on the DOS deep in the gap. The high-concentration  $D_m$  peak of localized states lies within the high-density  $E_g$  band on extended states. The parameters are the same as in Fig. 4.

the band top at 1 eV as compared with the initial one. The change of the total number of band states per impurity atom is negative. For the presented result,  $\Delta N(E_b) = -0.332$ . Curve  $L_b$  in Fig. 4(b) shows the normalized DOS for localized states in this region. The total number of these states per impurity atom is  $N(L_b) = 0.331$ . Note that in this case the band tail takes place beyond the band top in the gap region. The tail is formed by both  $E_b$  and  $L_b$  states.

The impurity-induced DOS for deep states below the band bottom is shown in Fig. 5. The total number of the localized states  $D_0$  with  $\delta$ -function distribution is the same as for the result in Fig. 2. Below the  $\epsilon_0$  level the band  $L_g$  of localized states with the total number of the states per impurity atom  $N(L_g) = 1.14 \times 10^{-2}$  is located. A gap of  $\approx 0.41$  eV separates this band from the high-density  $E_g$  band of extended states. The band is caused by the hybridization between the initial band states and  $d$  orbitals of the random ensemble of the impurity. The width of the band  $E_g$  is  $\Delta_g \approx 28$  meV, and the total number of these states per impurity atom is  $N(E_g) = 0.332$ . From the data one can estimate the average DOS in this band:  $\langle \rho_{\text{ext}} \rangle \approx 0.3 \times 10^{23} \text{ cm}^{-3} \text{ eV}^{-1}$ . The main  $\delta$ -function distribution  $D_m$  lies within the high-density  $E_g$  band. The total number of these localized states  $N(D_m) = 1.509$ .

Examining the variation of both  $D_m$  and  $E_g$  energy positions, as the impurity concentration  $N_{\text{im}}$  changes [Fig. 6(a)], we notice that the main high-concentration  $\delta$ -like peak of the localized states lies always within the high-density band of extended states. The value of  $\gamma$  is never in excess of  $8.4 \times 10^{-3}$ , corresponding to the case of the

impurity concentration  $N_{\text{im}} = 0.09$  and the potential scattering constant  $U_p = 0$ . As is shown in Fig. 6(b), the average DOS of the band  $E_g$  depends weakly on both  $N_{\text{im}}$  and  $U_p$ , whereas the concentration of the localized states  $D_m$  increases with increasing impurity concentration.

## V. CONCLUSION

Within the model considered we have shown that the parts played by the potential scattering and the resonance scattering of band electrons in the random ensemble of the impurity atoms in the modification of the DOS for transition-metal-doped semiconductors are essentially different. The potential scattering is important for the formation of the band tail, i.e., for the states splitting off from the initial band and adjacent to it. The band tail arises at the negative values of the scattering constant  $U_p$ , which are defined by Eqs. (16) and (17) and correspond to attractive potentials.

We have shown that the resonance scattering that is caused by the hybridization induces delocalization of impurity electrons due to virtual electron transitions over the impurity ensemble: an initial impurity site  $\rightarrow$  a band state  $\rightarrow$  another site  $\rightarrow$  a band state, etc., and brings about a mechanism of deep band formation. This narrow high-density band of extended states is located in the band gap below the impurity level. It is essential that the main high-concentration peak of the localized states lies within this band.

We believe that the position of localized states  $D_m$ , a high number of which are located within the high-density band of extended states  $E_g$  in the gap region, is the key to

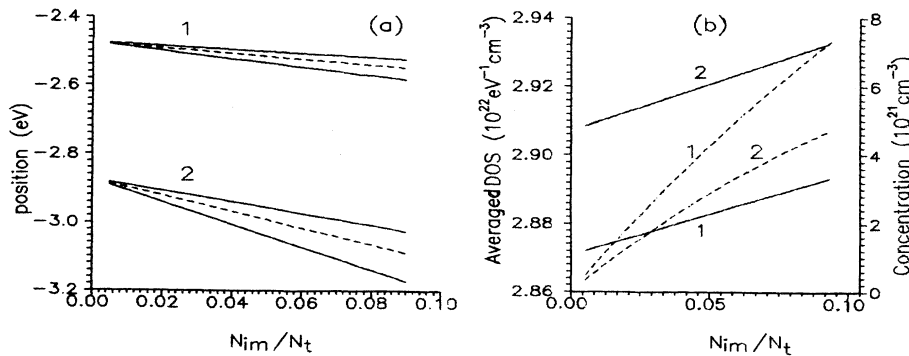


FIG. 6. (a)  $D_m$  peak position (dashed line), and  $E_g$  band—bottom and top—as a function of  $N_{\text{im}}$ . (b) The average DOS in the  $E_g$  band, and the concentration of  $D_m$  states (dashed line) as a function of  $N_{\text{im}}$ . Two cases are shown: (1)  $U_h \times N_i^{1/2} = 1.5$  eV,  $U_p = 0$ ; and (2)  $U_h \times N_i^{1/2} = 1.5$  eV,  $U_p \times N_t = -3.0$  eV. The other parameters are  $N_i = 0.06 \text{ \AA}^{-3}$ ,  $D_b = 1.0$  eV, and  $\epsilon_0 = -2.0$  eV.

understanding how the impurity involves the metal-insulator transitions for transition-metal-doped semiconductors. Considering the case of one electron per impurity atom, one finds, for the nonmagnetic solution presented in Figs. 1 and 2 and 4 and 5, that the Fermi energy of the system is equal to the simple pole for the  $D_m$  states, which are partially populated. As the position of the states is within the  $E_g$  band (see Figs. 2, 5, and 6), the Fermi level also lies in the band of extended states. Hence the solution, when it is realized, should corre-

spond to a paramagnetic metal state of the system. The phase transitions induced by the collective effect of the random ensemble of the impurity will be the subject of our forthcoming paper.

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