

# A new mechanism for impurity-level formation in semiconductors with strong electron correlations

S. G. Ovchinnikov

*L. V. Kirenskiĭ Institute of Physics, Siberian Branch of the Russian Academy of Sciences*

(Submitted 27 September 1991)

*Zh. Eksp. Teor. Fiz.* **102**, 534–540 (August 1992)

Within the framework of the generalized tight binding approximation incorporating strong electron correlations it is shown that deviations of the electron from an integral value can give rise to localized levels of the impurity type emerging inside the semiconductor gap despite the regularity of the lattice. The appearance of these levels is related to the contribution of excited many-electron states to the one-particle density of states.

## 1. INTRODUCTION

There is a broad class of compounds consisting of 3d-metals, rare-earth metals, and actinides that possess semiconducting properties owing to strong electron correlations. The best known examples are NiO, MnO, and the newly discovered compound  $\text{La}_2\text{CuO}_4$ . In the one-electron approach these compounds must be metals according to the Wilson criterion, since they have unfilled bands. Strong electron correlations lead to Mott–Hubbard band splitting, which results in a semiconductor gap emerging.<sup>1</sup> The size of the gap,  $E_g$ , is not necessarily determined by the Mott–Hubbard splitting  $U$ : depending on the positions of other bands (e.g., anion bands), various cases are possible, for instance, a gap with charge transfer.<sup>2</sup>

The problem of impurity levels in semiconductors with strong electron correlations has commanded attention for a long time.<sup>3</sup> Lately it became especially important in connection with the problem of formation of the electronic structure in high- $T_c$  superconductors. There are many indications that under doping, say, in the  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  system, not only is the Fermi level shifted into the valence band but deviations from the rigid-band model occur.<sup>4</sup>

In ordinary semiconductors, as is known, impurity levels appear because of fluctuations of the crystal potential in the vicinity of a defect. Below we will see that impurity levels can appear in the correlation semiconductors considered here in the absence of such fluctuations. We assume that the only quantity varying as a result of doping is the electron density  $\rho = N_e/N$ , where  $N$  is the number of atoms, that all the parameters of the Hamiltonian are fixed, and that impurities introduce no new terms into the Hamiltonian.

The physical reason why additional levels appear under doping is related to the way the one-particle spectrum forms in systems with strong correlations. A generalization of the tight binding approximation suitable for systems with strong correlations is discussed in Sec. 2. Sections 3 and 4 are devoted to a mechanism for impurity-level formation. Results are discussed in Sec. 5.

## 2. THE TIGHT BINDING APPROXIMATION IN THE MANY-ELECTRON APPROACH

For a meaningful description of strong electron correlations we incorporate all intracell interactions in the zeroth-

order Hamiltonian and include the interactions between cells in the perturbation Hamiltonian  $H_1$ :

$$H = H_0 + H_1, \quad (1)$$

$$H_0 = \sum_i H_0(i), \quad H_1 = \sum_{\langle i,j \rangle} H_1(i,j).$$

Let us suppose that we have succeeded in diagonalizing  $H_0(i)$ , that is, found for each number of electrons  $n$  in the cell the eigenfunctions  $|\Gamma\rangle \equiv |n, \gamma\rangle$  and the energies  $E_\gamma(n)$ , where  $\gamma$  stands for all the other quantum numbers. Then, in the representation of the Hubbard operator  $X_i^{\Gamma_1, \Gamma_2}$ , the Hamiltonian  $H_0$  can be written as

$$H_0(i) = \sum_{n, \gamma} [E_\gamma(n) - n\mu] X_i^{\Gamma, \Gamma}. \quad (2)$$

with  $\mu$  the chemical potential.

The creation of a one-particle Fermi excitation in the many-electron approach is associated with the transition of an  $n$ -electron state into an  $(n+1)$ -electron state.<sup>5,6</sup> A convenient parametrization suggested in Ref. 7 makes it possible to assign to each pair of states, the initial and the final, a root vector,  $(\Gamma_1, \Gamma_2) \rightarrow \alpha(\Gamma_1, \Gamma_2)$ . In this notation the spectrum of one-particle excitations in the zeroth approximation is determined by the energies:

$$\Omega_\alpha = E_{\Gamma_2}(n_i+1) - E_{\Gamma_1}(n_i). \quad (3)$$

A one-particle Fermi excitation is described by the annihilation and creation operators,

$$a_i = \sum_\alpha v(\alpha) X_i^\alpha, \quad a_i^+ = \sum_\alpha v^+(\alpha) X_i^{-\alpha},$$

where the matrix elements  $v(\alpha)$  are determined by the explicit form of the Hamiltonian  $H_0$ , while the nonzero matrix elements distinguish from the entire energy spectrum (3) the actual admissible excitations, which we call allowed resonances. Note that from commutation relations it follows that

$$\{a_i, a_i^\dagger\} = \sum_{\alpha} |v(\alpha)|^2 \bar{F}_i(\alpha) = 1, \quad \bar{F}_i(\alpha) = \{X_i^\alpha, X_i^{-\alpha}\}. \quad (4)$$

The number of remaining resonances in (3) with non-zero matrix elements is larger than the number of peaks in the one-particle density of states  $N(E)$ . The reason is that a number of resonances have a zero oscillator strength (a zero residue of the corresponding Green's function). Indeed, the one-particle Green's function is defined as

$$G_{ij} = \sum_{\alpha\beta} v(\alpha) v^*(\beta) D_{ij}^{\alpha\beta}, \quad D_{ij}^{\alpha\beta} = \langle\langle X_i^\alpha | X_j^{-\beta} \rangle\rangle,$$

and the zeroth-order Green's function is

$$G_i^{(0)}(\omega) = \sum_{\alpha} |v(\alpha)|^2 F(\alpha) (\omega - \Omega_{\alpha})^{-1}, \quad (5)$$

$$F(\alpha) = \langle \bar{F}_i(\alpha) \rangle = \langle X_i^{\Gamma_1, \Gamma_2} \rangle + \langle X_i^{\Gamma_2, \Gamma_1} \rangle.$$

Thus, for an oscillator strength to be finite the respective matrix element  $v(\alpha)$  must be nonzero and at least one of the states  $(\Gamma_1, \Gamma_2)$  must be filled. For this reason at absolute zero the allowed transitions between the excited states contribute nothing to  $N(E)$ .

Note that the total number of states is the same in the Fermi operators representation and Hubbard operators representation, which is easily seen if we take the Green's function (5) as an example:

$$\int -\frac{1}{\pi} \text{Sp Im } G(\omega + i\epsilon) d\omega = \sum_{\alpha} |v(\alpha)|^2 F(\alpha) = 1.$$

This sum rule is retained when we allow for intercell hopping, at least in the "Hubbard-I" approximation (the Hartree-Fock approximation in the diagrammatic technique<sup>7</sup>), which considers the band structure of one-particle excitations.

Intercell hopping can be written in the form

$$H_t = \sum_{ij} \sum_{\alpha\beta} T_{ij}^{\alpha\beta} X_i^\alpha X_j^{-\beta},$$

and the dispersion law in the "Hubbard-I" approximation has the form

$$\det[\delta_{\alpha\beta} (E - \Omega_{\alpha}) - F(\alpha) T^{\alpha\beta}(\mathbf{k})] = 0. \quad (6)$$

The matrix elements of  $T^{\alpha\beta}(\mathbf{k})$  determine not only the dispersion law but also the hybridization of the emerging bands. Equation (6) is valid far from the Mott-Hubbard transition point, that is, when  $\max\{T(\mathbf{k})\} \ll U$ .

### 3. THE BANDS IN AN UNDOPED SEMICONDUCTOR

The electron density in an undoped stoichiometric semiconductor is an integral number. Suppose, for the sake of simplicity, that  $\rho = 1$ . Then the important states are the vacuum state  $|0\rangle$ , one-particle states  $|1, \gamma\rangle$ , and two-particle states  $|2, \gamma\rangle$ ; at absolute zero ( $T = 0$ ) only the ground ( $n = 1$ ) state  $|1, 0\rangle$  is filled. The level diagram is depicted in

Fig. 1, where for simplicity only two excited states (for  $n = 1$  and for  $n = 2$ ) are shown. Since the only filled state is  $|1, 0\rangle$ , only three Fermi excitations have a nonzero residue at  $T = 0$ :

$$\begin{aligned} \Omega_0 &= E_0(1) - E_0(0), \\ \Omega_1 &= E_0(2) - E_0(1), \\ \Omega_2 &= E_1(2) - E_0(1). \end{aligned} \quad (7)$$

The density of states in the zeroth approximation is

$$N_0(E) = \sum_{i=0}^2 \delta(E - \Omega_i).$$

Of course, band dispersion "erodes" these delta functions, and the explicit form of  $N(E)$  is unimportant for the time being. Let  $E_v$  be the top of the valence band and  $E_c$  the bottom of the conduction band. The condition  $\max\{T(\mathbf{k})\} \ll U \sim \Omega_1 - \Omega_0$  guarantees that these bands do not overlap.

To calculate the position of the Fermi level we must allow for the spin structure of the states. At  $n = 1$  each level is twofold degenerate in spin, and at  $n = 2$  there are spin singlet states and spin triplet states. Hence,  $F(\alpha_0) = F(\alpha_1) = F(\alpha_2) = \langle X^{1,0\sigma;1,0\sigma} \rangle = 1/2$ .

As a result, even if we allow for twofold degeneracy in spin, the valence band contains not two states per cell, as would be the case for free electrons, but one state per cell. Hence, at  $\rho = 1$  the valence band is completely full and the conduction band is empty. The Fermi level is inside the gap.

### 4. VARIATION OF THE SPECTRUM UNDER DOPING

Let us now assume that the "number" of electrons  $\rho$  is  $1 + x$ . Since

$$\rho = \sum_{\tau} \langle X_i^{1\tau, 1\tau} \rangle + 2 \sum_{\tau} \langle X_i^{2\tau, 2\tau} \rangle, \quad (8)$$

at  $T = 0$  the filled levels are the ground level  $n = 1$ ,  $\langle X_i^{1,0;1,0} \rangle = 1 - x$  and the ground level  $n = 2$ ,  $\langle X_i^{2,0;2,0} \rangle = x$ . The new transition  $\Omega_3 = E_0(2) - E_1(1)$  now acquires a finite oscillator strength.

Calculation of the number of states in the doped case is more complicated and requires knowing the explicit form of the matrix elements of the allowed transitions. Hence, although the main statement of this paper is of a general nature, we consider a specific model, the two-band Hubbard model:

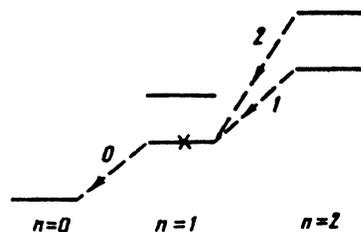


FIG. 1. The energy levels of states with different numbers of electrons  $n$ . The "x" stands for the filled level  $E_0(1)$ , the dashed arrows designate the processes of annihilation of a one-particle Fermi excitation, and 1, 2, and 3 at the arrows refer to the energies  $\Omega_{\alpha}$ .

$$H_0(i) = \sum_{\sigma} (\varepsilon_1 n_{1\sigma} + \varepsilon_2 n_{2\sigma}) + U_{1,1} n_{1\uparrow} n_{1\downarrow} + U_{2,2} n_{2\uparrow} n_{2\downarrow} + V n_{1\sigma} n_{2\sigma'} - JS_1 S_2 \quad (9)$$

where  $\varepsilon_1$  and  $\varepsilon_2$  are the energies of the first and second levels,  $n_{1\sigma}$  and  $n_{2\sigma}$  are the operators of the number of electrons with a spin projection  $\sigma$ ,  $U_{1,2}$  are the Coulomb parameters,  $V$  is the matrix element of the Coulomb interaction of electron on different orbits,  $J$  is the exchange integral, and  $S_1$  and  $S_2$  are the spin operators of the first and second levels.

The eigenstates of the cell are:

(a)  $n = 0$ , the vacuum state  $|0\rangle$ ;

(b)  $n = 1$ , two  $|\lambda\sigma\rangle$  doublets, where  $\lambda = 1, 2$  is the orbital index;

(c)  $n = 2$ , three singlets and one triplet:

$$|s, \lambda\rangle = a_{\lambda\uparrow}^+ a_{\lambda\downarrow}^+ |0\rangle, \quad |S, 0\rangle = 2^{-1/2} (a_{1\uparrow}^+ a_{2\downarrow}^+ - a_{1\downarrow}^+ a_{2\uparrow}^+) |0\rangle.$$

$$|t, 2\sigma\rangle = a_{1\sigma}^+ a_{2\sigma}^+ |0\rangle, \quad |t, 0\rangle = 2^{-1/2} (a_{1\uparrow}^+ a_{2\downarrow}^+ + a_{1\downarrow}^+ a_{2\uparrow}^+) |0\rangle; \quad (10)$$

(d)  $n = 3$ , two  $|3, \lambda\sigma\rangle$  doublets:

$$|3, 1\sigma\rangle = a_{1\sigma}^+ a_{2\downarrow}^+ a_{2\uparrow}^+ |0\rangle, \quad |3, 2\sigma\rangle = a_{1\uparrow}^+ a_{1\downarrow}^+ a_{2\sigma}^+ |0\rangle.$$

All the resonances with finite matrix elements for the operators  $a_{1\sigma}$  and  $a_{2\sigma}$  ( $\sigma = \pm 1/2$ ) are listed in Table I. The last columns contain the values of the root factors  $F_S$  and  $F_T$  for the cases of the singlet and triplet lower two-particle states, respectively. We assume that Hubbard repulsion fairly strong, so that the levels  $|s, 1\rangle$  and  $|s, 2\rangle$  always lie high.

Table I shows that doping introduces new resonances with finite oscillator strengths: these are the transitions 3, 10, and 14 for the singlet two-particle state and the transitions 6, 7, 11, 12, 15, and 16 for the triplet state. Figure 2 shows a simplified diagram of transitions, where the new resonances are labeled 3, 4, and 5 and distinguished by wavy lines. The large number of additional resonances in the triplet case is due to the spin degeneracy of the triplet.

Doping also results in the three-particle states contributing to the one-particle spectrum:

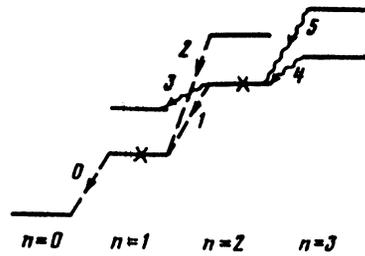


FIG. 2. The many-electron levels and the one-electron transitions between them that are essential in the doped cae. The wavy lines designate the new Fermi excitations  $\Omega_3$ ,  $\Omega_4$ , and  $\Omega_5$ .

$$\Omega_i = E_0(3) - E_0(2), \quad \Omega_3 = E_1(3) - E_0(2).$$

Using the data of Table I, we can easily verify the validity of the sum rule

$$\sum_{\sigma} \sum_{\alpha} (|v_1(\alpha)|^2 + |v_2(\alpha)|^2) F(\alpha) = 4$$

in both the undoped and doped cases.

Since

$$\Delta E = \Omega_1 - \Omega_3 = E_1(1) - E_0(1) > 0,$$

the level  $\Omega_3$  lies below  $\Omega_1$  and finds itself inside the gap if

$$E_b < \Omega_3 < E_c. \quad (11)$$

Since we have  $F(\alpha_3) \sim x$ , the number of states occupying this level is also of order  $x$ . Thus, in a regular system with an odd number of electrons there appears a level of the impurity type, and the dispersion of this level for  $x \ll 1$  is suppressed by the same factor  $F(\alpha_3) \sim x$ , as Eq. (6) shows. The same is true of the levels  $\Omega_4$  and  $\Omega_5$ .

If condition (11) is not met for one of the levels  $\Omega_i$  ( $i = 3, 4, 5$ ), the corresponding level winds up in a band and becomes a virtual level.

Figure 3 depicts the diagram of the density of states of a doped semiconductor for the case where condition (11) is

TABLE I. The allowed transitions, matrix elements, and root factors for the ground singlet ( $F_S$ ) and triplet ( $F_T$ ) two-particle states.

Number of resonance	Type of resonance	$v_1(\alpha)$	$v_2(\alpha)$	$F_S(\alpha)$	$F_T(\alpha)$
0	(0; 1 $\sigma$ )	1	0	(1-x)/2	(1-x)/2
1	(0; 2 $\sigma$ )	0	1	0	0
2	(1 - $\sigma$ ; S, 0)	0	$-\sigma V \sqrt{2}$	(1+x)/2	(1-x)/2
3	(2 - $\sigma$ ; S, 0)	$\sigma V \sqrt{2}$	0	x	0
4	(1, $\sigma$ ; T, 2 $\sigma$ )	0	1	(1-x)/2	$1/2 - x/6$
5	(1; - $\sigma$ ; T, 0)	0	$-1/V \sqrt{2}$	(1-x)/2	$1/2 - x/6$
6	(2, $\sigma$ ; T, 2 $\sigma$ )	1	0	0	$x/3$
7	(2, - $\sigma$ ; T, 0)	$1/V \sqrt{2}$	0	0	$x/3$
8	(1, - $\sigma$ ; S, 1)	$2\sigma$	0	(1-x)/2	(1-x)/2
9	(2, - $\sigma$ ; S, 2)	0	$2\sigma$	0	0
10	(S, 0; 3, 1, $\sigma$ )	0	$-1/V \sqrt{2}$	x	0
11	(T, -2 $\sigma$ ; 3, 1, - $\sigma$ )	0	$-2\sigma$	0	$x/3$
12	(T, 0; 3, 1, $\sigma$ )	0	$-\sigma V \sqrt{2}$	0	$x/3$
13	(S, 2; 3, 1, $\sigma$ )	1	0	0	0
14	(S, 0; 3, 2, $\sigma$ )	$1/V \sqrt{2}$	0	x	0
15	(T, -2 $\sigma$ ; 3, 2, - $\sigma$ )	$2\sigma$	0	0	$x/3$
16	(T, 0; 3, 2, $\sigma$ )	$\sigma V \sqrt{2}$	0	0	$x/3$
17	(S, 1; 3, 2, $\sigma$ )	0	1	0	0

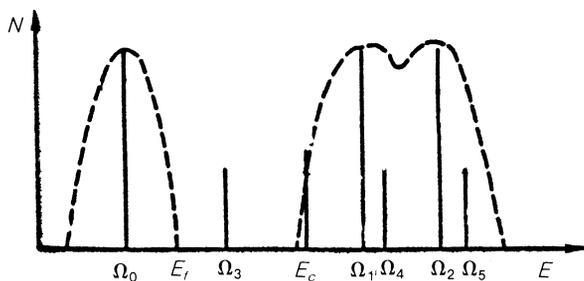


FIG. 3. The density of states of a doped semiconductor.

met for the level  $\Omega_3$ , while levels  $\Omega_4$  and  $\Omega_4$  fall in the empty conduction band. Let us find the position of the Fermi level, restricting our discussion for the sake of simplicity to the ground singlet two-particle state  $|s,0\rangle$ . The number of states (with spin taken into account) in the  $\Omega_0$  band (the valence band) is  $1 - x$ , and that on the  $\Omega_3$  level is  $x$ . Thus, as an impurity level the  $\Omega_3$  level does indeed split away states from the valence band, so that together they localize a single electron. The concentration  $\rho = 1 + x$  corresponds to  $x$  carriers in the next allowed band. For the singlet this is the band ( $1\sigma \rightarrow s0$ ) related to transitions between the ground one- and two-particle states. It contains  $(1 + x)/2$  states and proves to be partially filled with  $x$  electrons.

The reasoning is similar in the case of the ground triplet state of two holes. The resonances  $\Omega_6 = \Omega_7$  (in the notation of Table I) act as the impurity level, which holds  $x$  electrons. Additionally,  $x$  electrons partially fill the bottom of the conduction band formed in the triplet case by the transitions  $\Omega_4 = \Omega_5$ .

## 5. DISCUSSION

As  $x$  grows, when the impurity levels spread out into impurity bands, in the vicinity of the  $\Omega_3$  level a band forms that was absent in the undoped semiconductor. Since the  $\Omega_3$  band forms with the participation of the excited states  $E_\gamma$  (1) and the  $\Omega_0$  and  $\Omega_1$  bands with the participation of the ground state  $E_0$  (1), the symmetry of these bands may differ, that is,

in the presence of doping new states may be filled. The same feature has been discovered in superconducting copper oxides,<sup>8</sup> where the hybridized  $d_{x^2-y^2}-p_{x(y)}$  orbitals play the leading role in the undoped case, and the contribution of the  $d_{z^2}$ -states of copper manifests itself in the doped case.

Note that the formal approach taken in the present paper is similar to the way in which the Hubbard model is treated in the atomic limit. Nevertheless, in the Hubbard model no such mechanism for exhibiting the impurity levels exists, since the model allows only for a single state with  $n = 0$ ,  $n = 1$ , and  $n = 2$ . It is the presence of excited many-electron states and three-particles states in our transition that permits realizing this mechanism. This suggests that the Hubbard model is ill suited for describing highly correlated system with a nonintegral electron concentration.

The suggested mechanism for the appearance of new levels and bands with doping is, obviously, retained for other values of the electron concentration  $\rho$  close to an integral value. The physical reason for the appearance of new levels is the nonzero contribution from excited many-electron states, which is absent in the undoped case.

Of course, real substitution of one cation for another naturally introduces fluctuations into the crystal field, with the result that electrons scatter on these fluctuations. Hence, in calculating specific systems this mechanism must be taken into account along with the usual mechanism.

<sup>1</sup>N. F. Mott, *Metal-Insulator Transitions*, Taylor & Francis, London (1974).

<sup>2</sup>J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 410 (1985).

<sup>3</sup>V. N. Flyorov and K. A. Kikoin, *Preprint IAÉ-2986*, I. V. Kurchatov Institute of Atomic Energy, Moscow (1978) [in Russian].

<sup>4</sup>W. E. Pickett, *Rev. Mod. Phys.* **61**, 433 (1989).

<sup>5</sup>K. A. Kikoin and L. A. Maksimov, *Zh. Eksp. Teor. Phys.* **58**, 2184 (1970) [*Sov. Phys. JETP* **31**, 1179 (1970)].

<sup>6</sup>E. V. Kuz'min, G. A. Petrakovskii, and É. A. Zavadskii, *Physics of Magnetically Ordered Substances*, Nauka, Novosibirsk (1971) [in Russian].

<sup>7</sup>R. O. Zaitsev, *Zh. Eksp. Teor. Phys.* **68**, 207 (1975) [*Sov. Phys. JETP* **41**, 100 (1975)].

<sup>8</sup>A. Bianconi, M. de Santis, A. M. Flank *et al.*, *Physica (Utrecht) C* **153-155**, 1760 (1988).

Translated by Eugene Yankovsky