Spectroscopy of multielectron centers in superconductors, at their surfaces, and in semiconductor-superconductor heterostructures

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(Submitted 31 January 1989)
Pis'ma Zh. Eksp. Teor. Fiz. **49**, No. 6, 337–340 (25 March 1989)

The effect of a superconducting condensate on the selection rules for electron transitions due to a violation of gradient invariance is analyzed.

1. Multicharge centers have traditionally been discussed in the theory of semiconductors, and recently they have also been discussed in connection with searches for nontrivial superconductivity mechanisms. In various scenarios, theories of high-temperature superconductivity are based on the idea of quasilocal electron pairs as centers with a negative correlation energy U.

In this letter we wish to call attention to another aspect of the behavior of multielectron centers, which is associated exclusively with the presence of a superconducting condensate—no matter why it appeared. In precisely the same way, the nature of the formation of the U centers (a bipolaron[1] or biexciton[2]) is important. The effects which we discuss here may be observed in deep-center spectroscopy in semiconductors, and they should be helpful in identifying the actual mechanism for high-temperature superconductivity.

2. A common feature of these systems is that the two-electron hybridization J of the states which are localized at the center and the band states must be taken into

 0021-3640/89/060384-05$01.00

account. This hybridization may be direct or associated with one-electron transitions which are correlated in time by virtue of an electron-electron coupling.

The model Hamiltonian of the problem is

$$\hat{H}=\hat{H}_{band}+\hat{H}_{loc}+\hat{H}_{int}, \tag{1}$$

where $\hat{H}_{\text{band}}$ is the Hamiltonian of the band electrons, which incorporates the possibility of a superconducting pairing of these electrons; $\hat{H}_{\text{loc}}$ is the Hamiltonian of the U center, given by

$$\hat{H}_{loc}=(\epsilon_0-\mu)(\hat{n}_\uparrow+\hat{n}_\downarrow)+U\hat{n}_\uparrow\hat{n}_\downarrow; \tag{2}$$

and $\hat{H}_{\text{int}}$ is the Hamiltonian of the effective two-electron hybridization, given by

$$\hat{H}_{int}=J\sum_{\mathbf{k},\mathbf{k}'} b_\uparrow^+ b_\downarrow^+ a_{\downarrow\mathbf{k}} a_{\uparrow\mathbf{k}'}+\text{c.c.} \tag{3}$$

Here ϵ_0 is the one-electron energy of the center, μ is the chemical potential, $b\uparrow$ and $a\uparrow$ are the intracenter and band operators which annihilate electrons with spin up, $\mathbf{k}$ is the quasimomentum, and $\hat{n}_{\uparrow(\downarrow)}=b^+_{\uparrow(\downarrow)}b_{\uparrow(\downarrow)}$ are the operators representing the number of electrons at a center.

If there is a finite density of a superconducting condensate of band electrons near the center, $\Psi(0)=\Sigma_{\mathbf{k},\mathbf{k}'}\langle a_{\mathbf{k}\uparrow}a_{\mathbf{k}'\downarrow}\rangle\neq 0$, the eigenfunctions $|\varphi_i\rangle$ and the eigenvalues E_i of the Hamiltonian of the pair, $\hat{H}_{\text{loc}}+\hat{H}_{\text{int}}$, can be determined accurately in the basis of intracenter states with a definite number of particles in the approximation of a self-consistent field in terms of the band states:

$$|0\rangle,\ |\uparrow\rangle=b_\uparrow^+|0\rangle,\ |\downarrow\rangle=b_\downarrow^+|0\rangle,\ |2\rangle=b_\downarrow^+b_\uparrow^+|0\rangle. \tag{4}$$

The corresponding expressions are

$$\begin{aligned}
&E_{\uparrow,\downarrow}\equiv E_1=\epsilon_0-\mu,\quad |\varphi_{\uparrow,\downarrow}\rangle=|\uparrow\rangle,|\downarrow\rangle\\
&E_\pm=\epsilon_0-\mu+(U/2)\pm[(\epsilon_0-\mu+(U/2))^2+\Delta^2]^{1/2},\ \Delta=J\Psi(0)\\
&|\varphi_+\rangle=u|2\rangle+v|0\rangle,\quad |\varphi_-\rangle=u|0\rangle-v|2\rangle\\
&u^2(v^2)=1/2\pm(\epsilon_0-\mu+U/2)/2[(\epsilon_0-\mu+U/2)^2+\Delta^2]^{1/2}.
\end{aligned} \tag{5}$$

According to these expressions, the appearance of a superconductivity does not alter the energy E_1 or the wave function $|\varphi_{\uparrow,\uparrow}\rangle$ of a singly filled U center, but it mixes the $|0\rangle$ and $|2\rangle$ states. If $\Delta\neq 0$, there will be $2u^2$ electrons in state $|\varphi_+\rangle$, and $2v^2$ in state $|\varphi_-\rangle$, while with $\Delta=0$ and $\mu<\epsilon_0+(U/2)$ the state $|\varphi_-\rangle$ corresponds to an empty center, and $|\varphi_+\rangle$ to a doubly filled center (if $\mu>\epsilon_0+U/2$, on the other hand, the state $|\varphi_+\rangle$ is empty). In the case $U<0$, according to (5), the state $|\varphi_-\rangle$ is always the ground state, so a center with a negative correlation energy stimulates the appearance of a superconducting condensate $\Psi(0)$ near itself.

3. The average number (n_i) of electrons at a center in the state $|\varphi_i\rangle$ $(i=\uparrow,\downarrow,+,-)$ can be calculated for an arbitrary temperature T by two methods: a) through a direct averaging,

$$n_i = W_i\langle\varphi_i|\hat{n}_\uparrow + \hat{n}_\downarrow|\varphi_i\rangle; \tag{6}$$

b) by means of the thermodynamic relation

$$n_i = -\frac{\partial\Omega}{\partial E_i}\frac{\partial E_i}{\partial\mu}. \tag{7}$$

Here $W_i = Z^{-1}\exp\{-E_i/T\}$ is the probability for the excitation of level i, $Z=\Sigma_i\exp\{-E_i/T\}$, and $\Omega = -T\ln Z$ is the thermodynamic potential. These methods of course lead to the same results if we incorporate the nontrivial (nonadditive) dependence of the energies $E_\pm$ on the chemical potential when we carry out the differentiation in (7).

4. As a result of the nonconservation of the numbers of particles in the states $|\varphi_\pm\rangle$ in the presence of a superconducting condensate, a change will occur in the selection rules for transitions associated with one-electron operators of the type $c_\uparrow^+ b_\uparrow, b_\uparrow^+ c_\uparrow, b_\uparrow^+ b_\uparrow$. Here $c_\uparrow$ is the operator which annihilates an electron in some (localized or band) highly excited state $|\alpha\rangle = c_\uparrow^+|0\rangle$ with an energy $E_\alpha = \epsilon_\alpha - \mu$. The transition amplitudes corresponding to these operators can be found easily with the help of (5):

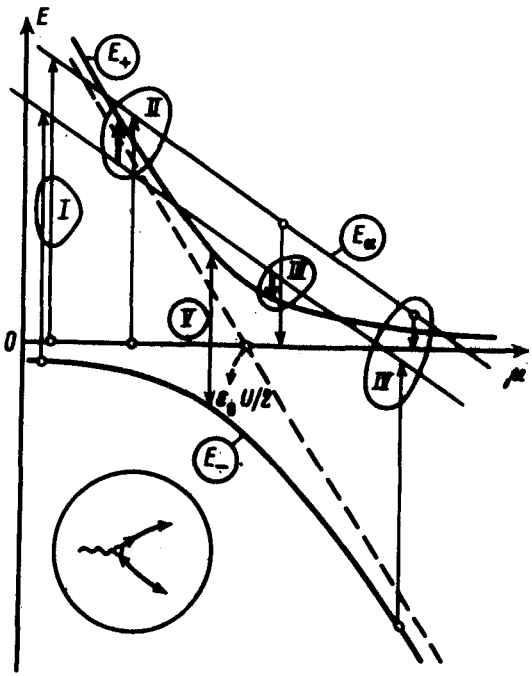
$$c_\uparrow^+\langle\varphi_\downarrow|b_\uparrow|\varphi_-\rangle = c_\uparrow^+\langle\varphi_+|b_\uparrow|\varphi_\uparrow\rangle = vc_\uparrow^+ \text{ and c.c.} \tag{8}$$

$$-\langle\varphi_+|b_\uparrow^+|\varphi_\downarrow\rangle c_\uparrow = \langle\varphi_\uparrow|b_\uparrow^+|\varphi_-\rangle c_\uparrow = uc_\uparrow \text{ and c.c.} \tag{9}$$

$$\langle\varphi_+|b_\uparrow^+ b_\uparrow|\varphi_-\rangle = -uv \text{ and c.c.} \tag{10}$$

If there is no condensate, then at small values of the Fermi level $(\mu<\epsilon_0+U/2)$, for which (with $U<0$) the ground state $|\varphi_-\rangle$ corresponds to empty centers $(n_-=0)$, transitions (8) are strictly forbidden $(v\equiv 0)$. At high values of the Fermi energy $(\mu>\epsilon_0+U/2)$ the ground state $|\varphi_-\rangle$ corresponds to doubly filled centers $(n_-=2)$, and transitions (9) are strictly forbidden $(u\equiv 0)$. Transitions of the type in (10) are always forbidden if $\Psi(0)\equiv 0$. If there is a condensate, on the other hand, all of transitions (8)–(10) will be allowed to an extent which increases with the density of the condensate.

Figure 1 shows a skeletal diagram corresponding to all these transitions, along with the dependence of the energies of the states $|\varphi_{\uparrow,\downarrow}\rangle, |\varphi_\pm\rangle$, and $|\alpha\rangle$ and that of the vacuum state $|0\rangle$ on the chemical potential μ. Also shown here (for $U<0$) are all of the additional transitions which arise in the system when there is a superconducting condensate. Transitions I and II correspond to processes (8), III and IV to (9), and V to (10). The conjugate (inverse) transitions differ from those shown in this figure in that the pairs of arrows are reversed. There is an absorption (or evolution) of energy in transitions I and II:



$$\left.\begin{aligned}\Omega(\mathrm{I}) &= E_\alpha + E_1 - E_- \approx \epsilon_\alpha + \epsilon_0 - 2\mu \\ \Omega(\mathrm{II}) &= E_\alpha + E_+ - E_1 \approx \epsilon_\alpha + \epsilon_0 + U - 2\mu\end{aligned}\right\} \begin{matrix}\Delta \to 0 \\ v \to 0\end{matrix}. \tag{11}$$

For transitions III and IV we have

$$\left.\begin{aligned}\Omega(\mathrm{IV}) &= E_+ - E_\alpha - E_1 \approx -\epsilon_\alpha - \epsilon_0 + 2\mu \\ \Omega(\mathrm{III}) &= E_1 - E_\alpha - E_- \approx -\epsilon_\alpha - \epsilon_0 - U + 2\mu\end{aligned}\right\} \begin{matrix}\Delta \to 0 \\ u \to 0\end{matrix} \tag{12}$$

and for transition V we have

$$\Omega(\mathrm{V}) = E_+ - E_- = 2[(\epsilon_0 - \mu + (U/2))^2 + \Delta^2]^{1/2}. \tag{13}$$

Energies of opposite sign correspond to the inverse transitions. All of transitions (11)–(13), which are forbidden in the absence of a superconductivity, depend explicitly on the chemical potential. This dependence indicates that these transitions are related to a creation of electron pairs from the condensate. The probability for such transitions is determined by the probability (W_i) for the excitation of level i, not by the number of electrons in it.

5. Transitions (11) and (12) can be seen in optical spectra if the nonzero dipole matrix elements between highly excited state $|\alpha\rangle$ and the states of the U center are nonzero. Transition V [see (13)] can also be observed in Raman scattering. Here it is

extremely pertinent to note the results of Ref. 3, where some new lines were observed in the cathodoluminescence spectrum of the superconducting phase of an yttrium-barium ceramic.

At a superconductor-insulator-superconductor tunnel junction, the presence of centers with a negative correlation energy U in the insulator should lead [according to (5)] to an increase in the transmission of the junction. Furthermore, additional resonances appear in the current-voltage characteristic of the junction because of transitions (11)–(13). A Josephson structure of this sort should also acquire some new Raman frequencies because of the tunneling of an electron through a U center in the insulator.

A promising possibility is to use a semiconductor-superconductor junction to study multielectron centers in semiconductors. Such a junction would make it possible not only to observe the new spectral lines corresponding to (11)–(13) but also to control their positions, through a variation of the chemical potential of the semiconductor by an external agent. The same comments apply to a study of the structure of dye molecules adsorbed on a superconductor.

The possibilities for observing transitions (11)–(13) are limited in terms of frequency by virtue of the spectral variation of the superconducting gap, $\Delta(\omega)$. We would ordinarily have $\Delta(\omega)\to 0$ at frequencies ω greater than the typical phonon frequencies. If, however, the superconductivity itself is due in large part to the presence of quasilocal electron pairs, the Éliashberg equations will contain—in addition to the ordinary exchange diagram—a Hartree part which does not depend on ω. A "pedestal" will thus be formed on the $\Delta(\omega)$ dependence. It is possible that specifically this superconductivity mechanism is operating in high-temperature superconductors. In such a case, a structure of the (high-temperature superconductor-semiconductor type would be the most promising for observing the effects which we have been discussing here.

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Translated by Dave Parsons