Superconducting T_c Enhancement Due to Excitonic Negative-U Centers: A Monte Carlo Study

H.-B. Schüttler,[a] M. Jarrell, and D. J. Scalapino
Department of Physics, University of California, Santa Barbara, Santa Barbara, California 93106
(Received 17 November 1986)

The enhancement of superconductivity by a small concentration of excitonic negative-U centers is studied by a new method which combines diagrammatic perturbation theory and Monte Carlo simulation. Results are given which show how the impurity parameters should be selected in order to obtain the maximum increase in the superconducting transition temperature T_c.

PACS numbers: 74.20.Fg

The enhancement of T_c as a result of negative-U bipolaron centers[1] has been examined by use of various perturbative techniques.[2,3] Here we present a new approach to this problem which combines Monte Carlo simulation techniques with the usual diagrammatic formulation. It allows us to treat a strongly interacting dynamical impurity system exactly, in principle, and relate the properties of the impurity model directly to experimentally observable quantities. Specifically, we report results for dT_c/dc produced by a small concentration, c, of exciton-mediated negative-U centers[4] in a superconducting host. The negative-U impurity we consider is a double-valence-fluctuating molecule[1] which is hybridized with the conduction-electron band. Such a center has two low-lying, degenerate or nearly degenerate configurations differing by two electrons, and its Hamiltonian can be written as

$$H=\sum_{p,\sigma}\frac{V}{N}(d_\sigma^\dagger c_{p\sigma}+c_{p\sigma}^\dagger d_\sigma)+\lambda\sigma_x(n_{d\uparrow}+n_{d\downarrow}-1)+\frac{\Omega}{2}\sigma_z+\varepsilon_d(n_{d\uparrow}+n_{d\downarrow}). \tag{1}$$

Here $c_{p\sigma}^\dagger$ and $c_{p\sigma}$ are Fermion creation and destruction operators for the conduction-band electrons, and $d_\sigma^\dagger$ and d_σ are those for the impurity orbital with $n_{d\sigma}=d_\sigma^\dagger d_\sigma$. Pauli operators σ_x and σ_z characterize the excitonic degrees of freedom. The first term in H hybridizes the impurity orbital to the conduction band, and the second term couples d-electrons to the two-level excitonic system which has an excitation energy Ω set by the third term in H.

In the absence of hybridization, the single-impurity ground-state energy depends on the occupation $n_d=n_{d\uparrow}+n_{d\downarrow}$ of the impurity orbital:

$$E_0(n_d)=\varepsilon_d n_d-[(\Omega/2)^2+(n_d-1)^2\lambda^2]^{1/2}. \tag{2}$$

If $\varepsilon_d=0$, the zero and doubly occupied $(d\uparrow,d\downarrow)$ states are degenerate with energy $E_0(0)=-[(\Omega/2)^2+\lambda^2)]^{1/2}$, while the singly occupied state has $E_0(1)=E_0(0)+U$ with

$$U=[(\Omega/2)^2+\lambda^2)]^{1/2}-\Omega/2. \tag{3}$$

In this case, electron-pair fluctuations between the conduction band and the impurity center can favor superconductivity. Such fluctuations arise from the hybridization which transfers conduction electrons onto the negative-U centers where they are coupled by the attractive exciton-mediated interaction.

To determine the effect of the impurities on the transition temperature of an intrinsically superconducting host, we follow the basic approach introduced by Abrikosov and Gor'kov.[5,6] For small impurity concentrations, c, the change in T_c is given by

$$dT_c/dc\,|_{c=0}=[T_c/\rho(0)](\chi_e+\chi_i). \tag{4}$$

Here T_c is the transition temperature of the superconductor in the absence of impurities and $\rho(0)$ is the single-spin electron density of states per site at the Fermi energy. χ_e and χ_i correspond to the "elastic" and "inelastic" contributions shown in Figs. 1(a) and 1(b), respectively, and can be expressed in terms of d-electron Green's functions for a *single* impurity evaluated at

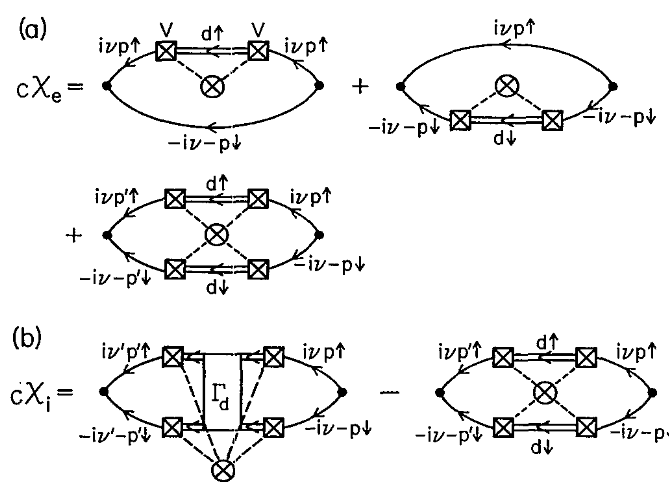

FIG. 1. (a) Elastic and (b) inelastic contributions to the superconducting susceptibilities entering into Eq. (4), expanded to first order in c.

$T = T_c$.

$$\chi_e = -T_c \sum_{i\nu}{}' \nu^{-2} [\Delta | \mathrm{Im} G_d(i\nu) | - \Delta^2 | G_d(i\nu) |^2], \tag{5}$$

$$\chi_i = \Delta^2 T_c^3 \sum_{i\nu, i\nu'}{}' | \nu\nu' |^{-1} [\Gamma_d(i\nu', i\nu) - \delta_{\nu\nu'} | G_d(i\nu) |^2 / T_c^2], \tag{6}$$

with

$$G_d(i\nu) = -\int_0^\beta d\tau e^{i\nu\tau} \langle d_s(\tau) d_s^\dagger(0) \rangle \tag{7}$$

and

$$\Gamma_d(i\nu', i\nu) \equiv \int_0^\beta d\tau_1 \cdots d\tau_4 \exp[i\nu'(\tau_1 - \tau_2) - i\nu(\tau_3 - \tau_4)] \langle T_\tau d_\uparrow(\tau_1) d_\downarrow(\tau_2) d_\downarrow^\dagger(\tau_4) d_\uparrow^\dagger(\tau_3) \rangle. \tag{8}$$

Here ν and ν' denote odd Matsubara frequencies, and $\beta \equiv 1/T_c$ is the inverse superconducting transition temperature of the metal in the absence of the impurities. We have assumed that the exciton frequency Ω is large compared to ω_D and that the summations in Eqs. (4) and (5) are cut off so that $T_c \sum' \nu^{-1} = \ln(2\gamma\omega_D/\pi T_c)$.

To obtain $G_d(i\nu)$ and $\Gamma_d(i\nu', i\nu)$ we have carried out a Monte Carlo simulation for the one-impurity problem.[7] Here the Hamiltonian H is broken up into three pieces, $H = H_1 + H_2 + H_3$, containing respectively the conduction band and the hybridization ($\equiv H_1$), the σ_z-terms of the two-level system ($\equiv H_2$), and the remaining parts ($\equiv H_3$). The complete sets of states inserted in the corresponding Lth order Trotter approximation for $\exp(-\beta H)$ are chosen to be eigenstates of σ_x. Upon tracing out the fermion degrees of freedom, one is then left with an effective action for the corresponding τ-dependent pseudospin configuration $\{\sigma(\tau_1) \cdots \sigma(\tau_L)\}$ where $\tau_l = l\Delta\tau$ and $\Delta\tau = \beta/L$. For most of our runs $\Delta\tau = \beta/L = 0.25$. A typical run consisted of 2000 (warm-up) updating sweeps, followed by 2000 measurement sweeps. Each measurement was preceded by at least ten further updates of the basic pseudospin configuration. For a typical chain length of $L = 80$, such a run took several hours on the University of California, Santa Barbara, ST-100 array processor. By sampling all measured quantities after every 200 measurements, we have estimated the statistical error of our results for G_d and Γ_d to be typically a few percent. To test for systematic breakup errors, due to the finite $\Delta\tau$, runs were repeated with $\Delta\tau = 0.125$. The systematic $\Delta\tau$ errors for $G_d(i\nu)$ were less than a few percent, but these errors in $\Gamma(i\nu', i\nu)$ were typically of order 5% and could be as large as 10–15% for the largest coupling strengths λ which were studied. We consider this to be the major source of error in our final results for dT_c/dc presented below. In Fig. 2 we show some results comparing results obtained using $\Delta\tau = 0.25$ and $\Delta\tau = 0.125$.

In analyzing the dependence of dT_c/dc on the parameters characterizing the excitonic impurity we will measure all energies in units of the exciton frequency Ω. In these units we take $\omega_D = 0.25$, and $\rho(0) = 0.1$ corresponding to a conduction-electron bandwidth of order 10. In Fig. 2 we show dT_c/dc vs λ for various T_c values of the pure host. Here the hybridization V is such that the impurity resonant width $\Delta = \pi\rho(0) | V |^2 = 1$. We see that a minimum λ coupling is required to achieve a positive value of dT_c/dc. This reflects the fact that conduction electrons which tunnel onto an impurity d orbital leave the attractive electron-phonon pairing interaction of the host while occupying the impurity. Formally, this effect arises from the elastic contribution of χ_e in (4) which is negative and nonzero even when $\lambda = 0$, whereas the inelastic contribution $\chi_i \geq 0$ vanishes when $\lambda = 0$. Thus the impurity must have a critical pairing attraction just to maintain the T_c of the host. As the host T_c increases, this critical value of λ increases as shown in Fig. 2. For $T_c = 0.05$, the dT_c/dc variation exhibits a broad maximum for $\lambda \sim 4$. For $T_c = 0.025$, we believe, this maximum is pushed to larger values of λ. Large values of λ give rise to an effective reduction in the hybridization, which, as we will discuss, is near its optimum value when $\Delta = \Omega$.

The effect on dT_c/dc of changing the hybridization strength which we will measure in terms of the resonance width Δ is shown in Fig. 3. Here the pure host $T_c = 0.05$,

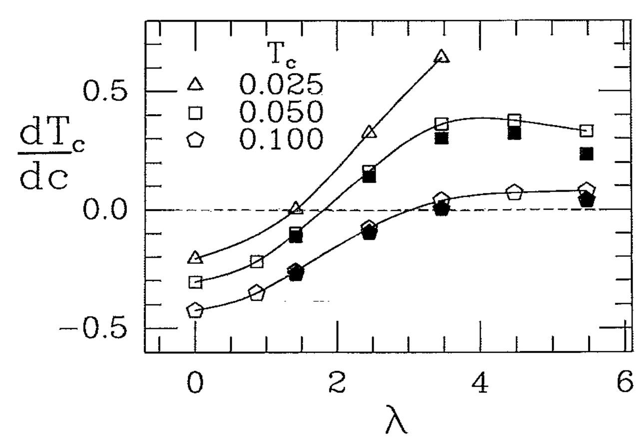

FIG. 2. dT_c/dc vs λ for different values of the host T_c. Here $\varepsilon_d = 0.0$, $\omega_d = 0.25$, and $\Delta = 1$. The open symbols indicate data obtained with $\Delta\tau = 0.25$ and the closed symbols are for $\Delta\tau = 0.125$. Here, and in all the figures, energy is measured in units of Ω.

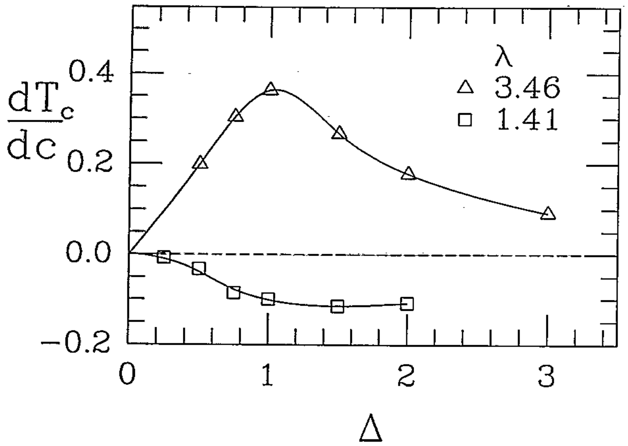

FIG. 3. dT_c/dc vs Δ for $T_c=0.05$, $\omega_D=0.25$, and $\lambda=3.46$ and 1.41 with $\Delta\tau=0.25$.

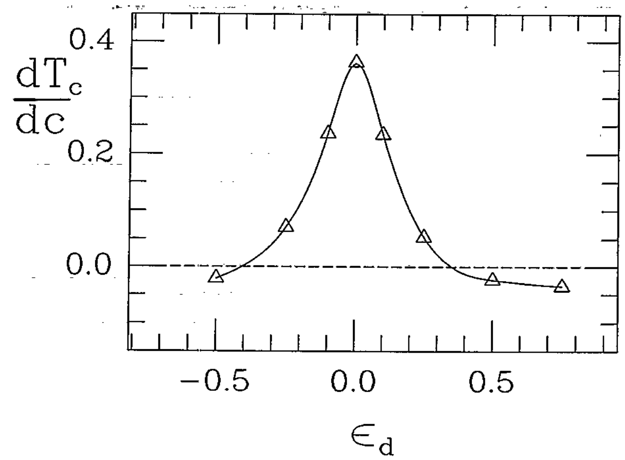

FIG. 4. dT_c/dc vs ε_d for $\lambda=3.46$, $\omega_D=0.25$, and $T_c=0.05$. Superconductivity is clearly favored when the double-valence-fluctuating impurity has degenerate empty and paired ground-state configurations.

and λ values of 1.41 and 3.46, corresponding to $U(\lambda)$ values of 1 and 3, respectively, were taken.[8] From Fig. 2 we see that when $\lambda=1.41$, dT_c/dc is negative while for $\lambda=3.46$, dT_c/dc is positive. In the latter case, dT_c/dc exhibits a maximum when the impurity hybridization resonance width is of the order of the exciton energy. At weak hybridization, the conduction electrons are seldom on the impurity while at too strong a hybridization they remain there for too short a time to allow the exciton mechanism to be effective.

In Fig. 4, we have explored what happens when the degeneracy between the empty and paired states of the double-valence-fluctuating center is lifted by having $\varepsilon_d \neq 0$. For $\varepsilon_d > 0$, the energy of the empty state $E_0(0) < E_0(2)$, so that as ε_d is increased it becomes energetically more difficult for a conduction-electron pair to tunnel into the unoccupied impurity. For $\varepsilon_d < 0$, on the other hand, $E_0(2) < E_0(0)$ and the centers are mostly doubly occupied since it is energetically unfavorable for the d-electron pairs to tunnel into the conduction band. A similar ε_d dependence has been suggested for impurity models with instantaneous[3] or phonon-mediated[2] negative-U properties.

In conclusion, we have applied quantum Monte Carlo techniques to study the effects of a small concentration of excitonic impurities on T_c. Combining standard many-body analysis with results from a Monte Carlo simulation we have avoided the lack of adequate approximations for treating a strongly interacting dynamic local mode embedded in a Fermi sea. We have shown that excitonic impurities can enhance T_c if their parameters are tuned such that (1) there is a near degeneracy between the empty and doubly occupied states of the impurity; (2) the hybridization is such that the resonance width Δ is of order of the exciton energy Ω; (3) the coupling λ has an optimal value which is determined by the competition between the enhancement of the on-site attraction and the reduction of the effective hybridization overlap as λ increases. This corresponds to a situation in which the energy $E_0(1)$ of the one-electron occupied impurity state lies several resonant linewidths above $E_0(0)$ and $E_0(2)$ (e.g., $U \gtrsim 4$). Finally, the enhancement of T_c can be significant. For example, consider a 1% impurity concentration in a system with $\omega_D=100$ K. Then for $T_c=0.05\Omega$ corresponding to $T_c=20$ K, we have for $dT_c/dc \cong 0.4\Omega$ a $\Delta T_c=(0.4)(400)(0.01)=1.6$ K.

We would like to thank E. Loh, Jr., R. L. Sugar, and D. Toussaint for helpful discussions. This work was supported by the National Science Foundation under Grant No. DMR-83-20481. We are grateful to E. I. du Pont de Nemours and Company and the Xerox Corporation for their support.

[a]Present address: Material Science Division, Argonne National Laboratory, Argonne, IL 60439.

[1]P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

[2]E. Simanek, Solid State Commun. **32**, 731 (1979).

[3]C. S. Ting, D. N. Talwar, and K. L. Ngai, Phys. Rev. Lett. **45**, 1213 (1980).

[4]J. E. Hirsch and D. J. Scalapino, Phys. Rev. B **32**, 5639 (1985).

[5]A. A. Abrikosov and L. P. Gor'kov, Zh. Eksp. Teor. Fiz. **39**, 1781 (1960) [Sov. Phys. JETP **12**, 1243 (1961)].

[6]See also A. Sakurai, Phys. Rev. B **17**, 1195 (1978); T. Matsuura, S. Ichinose, and Y. Nagaoka, Prog. Theor. Phys. **57**, 713 (1977).

[7]J. E. Hirsch and R. M. Fye, Phys. Rev. Lett. **56**, 2521 (1986).

[8]The excitation energy U, Eq. (3), is likely to be a more accessible experimental quantity than λ.