crystals be colored. The blue color could be bleached by heating the crystals in a vacuum at 300°C with the concurrent deposition of a Cd mirror on the cooler glass walls. Changes observed in the Sm^{+3} fluorescence after coloration are consistent with the idea that the local symmetry about the rare earth ion is changed due to the absence of the nearby interstitial fluoride ion in the colored crystal.

In addition to Sm-doped CdF_2, free-carrier absorption has also been observed in material doped with Tb and Dy. With CdF_2:Eu^{+3} the electrons are trapped in the $4f$ Eu states, giving rise to a Eu^{+2} absorption band in the near ultraviolet. Although free-carrier absorption has been observed in several other binary compounds (e.g., in[6] ZnO and[7] CdS), CdF_2 is the first material with a 6-ev band gap to show these effects.

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SUPERCONDUCTIVE TUNNELING*

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Experiments[1-3] involving the tunneling of electrons between superconducting films covered by a thin (~20 Å) oxide layer and either normal or superconducting metals have shown that the tunneling current between, e.g., normal and superconducting metals is directly proportional to $\rho_S(E)$, the superconducting density of states as predicted by the BCS theory,[4]

$$\rho_s(E)=\rho_n(E)\times[E/(E^2-\Delta^2)^{1/2}], \quad |E|>\Delta$$
$$=0, \quad |E|<\Delta. \qquad (1)$$

Several attempts have been made to explain this result. Bardeen[5] has obtained the formula for the tunneling rate from state a to state b,

$$R_{ab}=(2\pi/\hbar)|T_{ab}|^2\rho(E_b)f_a(1-f_b). \qquad (2)$$

Here f_a and f_b are the occupation numbers of states a and b, respectively. Bardeen has used the Gor'kov[6,7] formalism to argue that the matrix element T_{ab}, which usually contains energy-dependent coherence factors, should be constant. In order to obtain this result, assumptions must be made about the number of particles in a quasiparticle state.[8]

Other treatments[9] have used the two-fluid model[10] in analogy with semiconductors. Harrison[11] has emphasized the fundamental problem of the two-fluid picture, i.e., according to the WKB treatment of quasi-particle tunneling,

$$|T_{ab}|^2\sim V_aV_b|I_{ab}|^2, \qquad (3)$$

where I_{ab} is the exponential tunneling integral and V_a and V_b the velocity of the quasi-particle in the states a and b. Because $V_b\sim[\rho(E_b)]^{-1}$, the single-particle $\rho(E_b)$ cancels from (2), leaving the transition rate independent of $\rho(E_b)=\rho_S(E)$.

Here we present a Hamiltonian treatment of the tunneling process from normal metal to superconductor:

$$H=H_n+H_s+H_T, \qquad (4)$$

where H_n and H_S are the exact Hamiltonians for the normal metal and the superconductor. The coupling term H_T transfers electrons from the normal metal to the superconductor and vice versa.

We choose representations such that

$$H_n=\sum_{k\sigma}\epsilon_k a_{k\sigma}^{\dagger}a_{k\sigma}, \qquad (5)$$

$$H_S = U + \sum_q E_q(\alpha_q^\dagger \alpha_q + \beta_q^\dagger \beta_q) + H_2 + H_{\text{int}}, \tag{6}$$

$$H_T = \sum_{kq\sigma} [T_{kq} a_{k\sigma}^\dagger a_{q\sigma} + T_{qk} a_{q\sigma}^\dagger a_{k\sigma}]. \tag{7}$$

Here k represents states in the normal metal and q in the superconductor; ϵ_k is the normal electron energy measured from the Fermi level and a is an electron destruction operator;

$$E_q = (\epsilon_q^2 + \Delta^2)^{1/2} \tag{8}$$

is the superconducting quasi-particle energy and the α's and β's, the quasi-particle operators, are related to the normal electron operators by the Bogoliubov[12] transformation:

$$\alpha_q = u_q a_{q\uparrow} - v_q a_{-q\downarrow}^\dagger, \tag{9}$$

$$\beta_q = u_q a_{-q\downarrow} + v_q a_{q\uparrow}^\dagger, \tag{10}$$

where $-q$ indicates the state that is the time-reversal conjugate of q. The first two terms in H_S are the thermodynamic Hamiltonian; H_2 represents terms of the form $\alpha^\dagger\beta^\dagger$ and $\beta\alpha$, and H_{int} is the quasi-particle interaction Hamiltonian which consists of a series of terms containing four quasi-particle operators. Finally, (7) contains the matrix elements T_{kq} given essentially by (3) which relate normal electrons on both sides of the oxide layer. These electrons are described by wave functions with decaying exponential tails in the oxide layer; T_{kq} is obtained from the overlap integral of these tails.

We determine the tunneling current by the artifice of calculating $\langle \dot{N}_S \rangle$, the average value of the rate of change of the number of superconducting electrons. To insure that some terms in H_S that lead to fluctuations in N_S do not give spurious contributions, we require

$$\langle \dot{N}_S \rangle = -\langle \dot{N}_n \rangle. \tag{11}$$

This condition is automatically satisfied by starting from the exact equation of motion for N_S:

$$i\hbar \dot{N}_S = [N_S, H] = [N_S, H_T]. \tag{12}$$

Equation (12) follows from (6) because we have employed the complete superconductive Hamiltonian H_S, which conserves the number of electrons and therefore commutes with N_S.

From (12) and (7), and making use of (9) and (10), we obtain

$$i\hbar\langle \dot{N}_S \rangle = \sum_{kq} \{T_{qk}[u_q \langle \alpha_q^\dagger a_{k\uparrow}\rangle + v_q \langle \beta_q a_{k\uparrow}\rangle] + \text{similar terms}\}. \tag{13}$$

To compute the expectation value of operators like $\alpha_q^\dagger a_{k\uparrow}$, we must derive their exact equation of motion by commuting them with H. We then introduce the Hartree-Fock approximation by replacing the expectation value of terms, such as $\langle \alpha_1^\dagger \beta_2^\dagger \beta_3 a_{k\uparrow}\rangle$ obtained by commuting $\alpha_q^\dagger a_{k\uparrow}$ with H_{int}, by the factorized products

$$\langle \alpha_1^\dagger \beta_2^\dagger \rangle \langle \beta_3 a_{k\uparrow}\rangle - \langle \beta_2^\dagger \beta_3 \rangle \langle \alpha_1^\dagger a_{k\uparrow}\rangle,$$

evaluated to zeroth order in T_{kq}. This procedure is equivalent to the use of a BCS reduced Hamiltonian containing renormalized E_q, u_q, and v_q, but with all number-nonconserving terms removed from the equations of motion, and yields

$$\langle \dot{N}_S \rangle = \frac{2\pi}{\hbar} \sum_{kq} |T_{kq}|^2 \{u_q^2 [f_k - g_q] \delta(E_q - \epsilon_k) + v_q^2 [f_k - (1 - g_q)] \delta(E_q + \epsilon_k)\}, \tag{14}$$

where g_q is the occupation number of the quasi-particle state q.

We observe that there are two channels, q and q', such that

$$u_q^2 + u_{q'}^2 = 1 \text{ if } q < q_F,\ q' > q_F,\ E_q = E_{q'}; \tag{15}$$

and similarly for v_q^2. Making the voltage difference explicit, replacing the sums in (14) by an integration over energy, and inserting (15), we obtain

$$\langle \dot{N}_S \rangle \propto \int_{-\infty}^{\infty} |T|^2 [f_n(\epsilon - eV) - f_S(\epsilon)] \rho_n(\epsilon - eV) \rho_S(\epsilon) d\epsilon, \tag{16}$$

where f_n is the Fermi factor for the normal metal,

$$f_S(\epsilon) = g(\epsilon) \text{ for } \epsilon > 0$$
$$= 1 - g(-\epsilon) \text{ for } \epsilon < 0, \tag{17}$$

and $\rho_S(\epsilon)$ is even in ϵ. It is evident from (16) that the tunneling current depends only on the density of states of the superconductor in precisely the way found experimentally. All coherence factors add to give unity because of (15). Because we have started[13] with the exact H_S, including H_2 and H_{int}, there are no terms in Eq. (14)

of the form $u_q v_q$. These would have appeared as interference terms $u_q u_{q'}$ between the channels q and q' of Eq. (15).

It is interesting to compare our result, which depends essentially on using the complete H_S, with the microscopic derivation[7] of the Landau-Ginzburg equations, which in effect uses only the first two terms of (6). The latter equations treat long-wavelength spatial variations, where the fluctuations in the number of particles can be neglected. For the tunneling problem, fluctuations must be treated exactly in order to obtain agreement with experiment.

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DOUBLE NUCLEAR RESONANCE AND NUCLEAR RELAXATION

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Following the discovery of the electron nuclear double resonance (ENDOR) effect,[1] several techniques for performing double-resonance experiments have been proposed, each with an area of applicability dependent on the mechanism. The present Letter describes a double-resonance technique which we have investigated recently.

The effect is a double nuclear resonance observable in materials wherein nuclear spin-lattice relaxation occurs through paramagnetic impurities. The technique uses Zeeman transitions of the distant nuclei to detect hyperfine transitions associated with nuclei at the paramagnetic impurities.

A more detailed operational description is as follows. The nuclear magnetic resonance of the host lattice (e.g., Al^{27} in ruby) is monitored. An auxiliary radio-frequency field is used to excite hyperfine transitions associated with the paramagnetic impurity (e.g., Cr^{53} hyperfine transitions in ruby). The monitored signal decreases when the auxiliary signal strikes the hyperfine resonance.

In addition to observing the Cr^{53} hyperfine spectrum in ruby[2] using the Al^{27} nuclei as detectors (Fig. 1), we have also observed the hyperfine spectrum associated with defects in x-irradiated crystalline succinic acid[3] using the protons of the host lattice as detectors (Fig. 2). The existence of this effect in ruby was mentioned previously,[4] but recent experiments show that the effect is much larger than anticipated, and the mechanism quite different from ENDOR.

The experiments were performed at liquid helium temperature. The nuclear magnetic resonance (NMR) spectrum was observed either by a conventional marginal oscillator or by an rf bridge. The NMR observation coil was wound directly on