PHYSICAL REVIEW B VOLUME 32, NUMBER 7 1 OCTOBER 1985

# Effect of superconducting electrons on the energy splitting of tunneling systems

Clare C. Yu and A. V. Granato
*Department of Physics, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801*
(Received 27 June 1985)

We consider the effect of superconducting electrons on the magnitude of the energy splitting of a tunneling system. A specific example is a hydrogen atom tunneling in niobium. We find that in this case the splitting is roughly 20% smaller in the normal state than in the superconducting state. This difference in the splitting should be observable in neutron scattering and ultrasonic measurements.

The interaction between tunneling centers and electrons has been studied in a variety of contexts such as metallic glasses,[1-3] NH (Ref. 4) and OH (Ref. 5) impurities in crystalline niobium and macroscopic quantum tunneling.[6] In metallic glasses the relaxation rate $T_1^{-1}$ of two-level systems (TLS) due to a Korringa-type process has been found to be four orders of magnitude larger than that due to phonon processes.[1] However, when the electrons are superconducting, $T_1^{-1}$ is strongly suppressed[2] as the number of quasiparticles available for scattering decreases. In this paper we examine the difference in the energy splitting of TLS when the electrons are normal and when they are superconducting. We shall show that the splitting is about 20% smaller in the normal state. Such changes are not observable in metallic glasses which have a broad distribution of level splittings. Consider, however, a hydrogen atom tunneling[7] in the vicinity of an oxygen defect[8] in $NbO_xH_y$ ($x,y \approx 10^{-4}$–$10^{-3}$). This provides a clean system in which these effects can be observed via neutron scattering[9,10] and ultrasonic measurements.[4,5,11,12]

For both neutron scattering and ultrasonic attenuation, as well as for other properties, there is a well-developed formalism for describing the results in terms of the parameters of the tunneling system. We start with the Hamiltonian:[2]

$$\begin{aligned} H &= H_0 + H_L + H' \ , \\ H_0 &= \sum_{k\sigma} \epsilon_k c_{k\sigma}^{\dagger} c_{k\sigma} + E_0 S_z \ , \\ H_L &= (\alpha S_x + \gamma S_z)\eta \ , \\ H' &= \frac{1}{N} \sum_{kk'} (V_{\parallel} S_z + V_{\perp} S_x) c_{k\sigma}^{\dagger} c_{k'\sigma} \ , \end{aligned} \tag{1}$$

where $E_0$ is the energy splitting of the TLS, $\mathbf{S} = \frac{1}{2}\boldsymbol{\sigma}$ is the pseudospin operator describing the two states of the system, $\boldsymbol{\sigma}$ are the Pauli matrices, $\eta$ is the elastic strain field, and $\eta$ and $\gamma$ are strain coupling coefficients. Since $\gamma$ just renormalizes $E_0$, we will set it to zero without loss of generality. $V_{\perp}$ and $V_{\parallel}$ describe the couplings between the electrons and the TLS, $c_{k\sigma}^{\dagger}$ and $c_{k\sigma}$ are the electron creation and annihilation operators, $N$ is the number of atoms, and $\epsilon_k$ are electron energies. Let us set aside the lattice contribution $H_L$ for a moment.

We now calculate the change in $E_0$ via perturbation theory in $H'$. This is the analog of the Knight shift in magnetic systems. Let us denote the zeroth-order energy levels by $E_{\pm}^{(0)} = \pm \frac{1}{2} E_0$. First-order perturbation theory gives $E_{\pm}^{(1)} = \pm V_{\parallel}$, i.e., the splitting $E$ is shifted by the same amount in both normal and superconducting states. We will ignore such terms. In the normal state second-order perturbation theory yields

$$E_{\pm}^{(2)} = \frac{V_{\perp}^2}{2N^2} \sum_{kk'} \frac{f_k(1-f_{k'})}{\pm E_0 + \epsilon_k - \epsilon_{k'}} \tag{2}$$

$$= \pm \tfrac{1}{2} (\rho V_{\perp})^2 E_0 \ln(E_0/\mu) + O(k_B T/E_0)^2 \ , \tag{3}$$

where $f_k$ is the Fermi function, $\rho$ is the density of states per atom at the Fermi surface, $\mu$ is the Fermi energy, and $T$ is the temperature. In the superconducting state we find

$$E_{\pm}^{(2)} = \tfrac{1}{2}(\rho V_{\perp})^2 \int_{\Delta}^{\infty} dE_k \int_{\Delta}^{\infty} dE_{k'} \, n(E_k) n(E_{k'}) \left[ 2(E_k E_{k'} - \Delta^2) \frac{f(E_k)[1-f(E_{k'})]}{\pm E_0 + E_k - E_{k'}} + (E_k E_{k'} + \Delta^2) \left[ \frac{f(E_k) f(E_{k'})}{\pm E_0 + E_k + E_{k'}} + \frac{[1-f(E_k)][1-f(E_{k'})]}{\pm E_0 - E_k - E_{k'}} \right] \right] , \tag{4}$$

where

$$n(E) = \theta(E^2 - \Delta^2)^{-1/2} \ ,$$

and

$$f(E) = (1 + e^{-\beta E})^{-1} \ ,$$

$\Delta$ is the BCS energy gap. The first term in brackets comes from considering virtual processes in which the intermediate state is related to the initial state by destroying one quasiparticle and creating another. In the second term two quasiparticles are destroyed, and in the third term two quasiparticles are created in going from the initial to the intermediate state. In the limit $\Delta \to 0$, (4) reduces to the normal state expression (2).

Let us estimate $\Delta E = E_+ - E_-$ in both the superconducting and normal states. We take $E_0 \approx 2$ K, $\Delta = 1.53$ meV,

 

$\mu = 5.32$ eV, and $(\rho V_\perp) \approx 0.15$. The values for $\Delta$ and $\mu$ are those for Nb. Our value for $\rho V_\perp$ is typical for metallic glasses[1] and agrees with the measured contribution to the resistivity due to hydrogen impurities in niobium.[13] Using these numbers, we obtain at $T=0$ $\Delta E_N \approx 1.5$ K and $\Delta E_{SC} \approx 1.9$ K, where the subscripts denote the normal and the superconducting state. The fact that $\Delta E_N$ is smaller than $\Delta E_{SC}$ is in keeping with the observation that the relaxation rate of the tunneling systems is higher in the normal state. Electrons scattering off the hydrogen assist in tunneling and soften the splitting. When the electrons are paired, this scattering is inhibited. As the superconducting gap goes to zero with increasing temperature, the number of quasiparticles increases and the superconducting splitting continuously approaches the value of the normal state splitting. We have numerically evaluated (2) at finite temperatures and found that $\Delta E_N$ does not change below 10 K within the error of the integral ($\approx \pm 40$ mK). It is hard to be more specific than this because the integral is somewhat sensitive to the cutoff. Between 10–50 K, $\Delta E_N$ appears to increase slightly by $\approx 150$ mK, though in this temperature range the effect of phonons should be taken into account more carefully.

For $H$ trapped by an oxygen atom in Nb, the spatial configuration of the tunneling complex has not yet been established, but inelastic neutron scattering and ultrasonic measurements can be described in terms of a TLS formalism. For neutron scattering the relationship between the inelastic scattering energy and $\Delta E$ is direct, but the measurements must be made on samples with very low OH concentration ($\approx 100$ ppm), so that the intensities are difficult to measure. In recent measurements of much improved sensitivity, there is evidence that changes in $\Delta E$ of this size have been seen.[14] For ultrasonic measurements the relationship between elastic constant changes and $\Delta E$ is indirect, but measurement sensitivities better than $10^{-6}$ can be achieved, so that the effects are easily detected even at low concentrations.

The relationship between the observed elastic constant change and the tunnel splitting depends upon the magnitude and distribution of strains acting on the TLS.[15–18] At high enough temperatures the measurements contain a "resonance" and a relaxation contribution to the elastic constants. The latter refers to the relaxation back to thermal equilibrium of the tunneling centers which have been perturbed by the sound wave. The former depends on the curvature of the energy levels as a function of strain, and does not necessarily refer to the absorption of a phonon with energy equal to the tunnel splitting. At low enough temperatures, only the resonance contribution remains. By making measurements in both the normal and superconducting states these contributions can be isolated, and the three parameters $\Delta E$, $\alpha$, and $\eta$ which completely specify the TLS states can be determined separately. This has been done[5] for the OH system in Nb, but not yet at low enough temperatures to determine $E_{SC} - E_N$. For a second system of hydrogen trapped by oxygen in niobium produced by quenching (perhaps $OH_2$), a change in the low-temperature resonance has been observed,[5] showing the existence of a change in the tunnel splitting. However, for this system the number of energy levels involved is not yet known, so that the magnitude of the tunnel splitting has not yet been determined. In what follows an outline of the formalism describing the relation between the elastic constant change and the tunnel splitting is given to define the optimum conditions for observing the effect. The result is that measurements should be made at low temperature in specimens containing low concentrations of oxygen and hydrogen.

A change in $\Delta E$ will cause a change $\delta C$ in the elastic constant, which, by definition, is given by

$$\delta C = \frac{\partial^2 F}{\partial \eta^2} , \tag{5}$$

where $F$ is the free energy. Taking $H_L$ into account, the total tunnel splitting $\Omega$ is given by

$$\Omega_0 = (\Delta E^2 + \alpha^2 \eta^2)^{1/2} . \tag{6}$$

The free energy is given by

$$F = k_B T f \ln Z , \tag{7}$$

where

$$Z = \sum_i \exp(-E_i/k_B T) ,$$

and the sum is over the energy levels at a single site. Here $f$ denotes the concentration of TLS. For $k_B T \ll \Delta E$, only the ground state $\Omega_- = -\frac{1}{2}(\Delta E^2 + \alpha^2 \eta^2)^{1/2}$ is populated, so that $F = f\Omega_-$ and

$$\frac{\delta C}{C} = -\frac{f\alpha^2}{2C} \frac{\Delta E^2}{(\Delta E^2 + \alpha^2 \eta^2)^{3/2}} . \tag{8}$$

Here $C$ is the $(C_{11} - C_{12})/2$ elastic constant. At finite temperatures Eq. (8) must be multiplied by $\tanh \Omega / 2k_B T$. Equation (8) shows how the elastic constant change depends upon the strains acting on the TLS.

There are two important limiting cases for strain distributions which might be expected. The first is one for which the same tunneling configuration appears throughout the sample and the local strain field dominates over random strain fields. In this case the distribution may be taken to be a delta function, and Eq. (8) gives the relation between $\delta C/C$ and the splitting (curve A in Fig. 1). In the other case only random strains act on the TLS and a Lorentzian distribution may be used:[19]

$$P(\eta) = \frac{1}{\pi} \frac{\eta_0}{\eta^2 + \eta_0^2} . \tag{9}$$

Let $x = \Delta E / \alpha \eta_0$. Then we obtain

$$\left\langle \frac{\delta C}{C} \right\rangle = -\frac{f\alpha A}{\pi C \eta_0} \left[ (1 + A^2) \tan^{-1}\left(\frac{1}{A}\right) - A \right], \quad x > 1$$

$$= \frac{f\alpha A'}{\pi C \eta_0} \left[ (A'^2 - 1) \tanh^{-1}\left(\frac{1}{A'}\right) - A' \right], \quad x < 1 , \tag{10}$$

where

$$A^2 = \frac{1}{x^2 - 1} ,$$

and $A'^2 = -A^2$. Curve B in Fig. 1 shows (8) averaged over $P(\eta)$. Here $\langle\ \rangle$ denotes an average over $P(\eta)$. For small strains ($\alpha \eta_0 \ll \Delta E$),

$$\left\langle \frac{\delta C}{C} \right\rangle \approx -\frac{\alpha^2 f}{2C\Delta E} \tag{11}$$

for both distributions. This is inversely proportional to $\Delta E$,

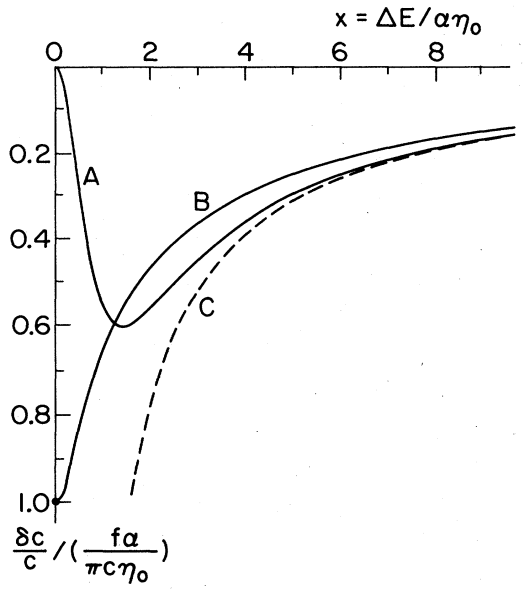


FIG. 1. Elastic constant change at zero temperature for a TLS as a function of the tunnel splitting. The elastic constant change $\langle \delta C/C \rangle$ is normalized by $f\alpha/\pi C\eta_0$, and the tunnel splitting $\Delta E$ is normalized by $\alpha\eta_0$. Curve A is for a delta-function strain distribution, curve B is for a Lorentzian distribution, and curve C is the small strain asymptote.

because decreasing the splitting increases the curvature (5) which determines the elastic constant. For large strains the change in the elastic constant goes to zero for a delta-function distribution, since the curvature becomes small, while for a Lorentzian distribution the change remains finite even for large $\eta_0$, since there are always some states with large curvature contributing. Since the strain $\eta$ is determined by the oxygen content, one sees from the above that optimum conditions for measurements are obtained when (a) $\alpha\eta_0 < \Delta E$ (low oxygen content), (b) the hydrogen concentration is comparable to the oxygen concentration $f_H \approx f_O$, and (c) the temperature is low ($k_B T \ll \Delta E$). This then suggests measurements in Nb samples with less than 100 ppm of oxygen at temperatures $\ll 2$ K.

For a moderate strain $\eta_0 \approx 10^{-3}$, Eq. (10) gives $\langle \delta C/C \rangle_N \approx -3.2\times10^{-4}$ in the normal state and $\langle \delta C/C \rangle_{SC} \approx -2.7\times10^{-4}$ in the superconducting state. We have taken $E_0 \approx 2$ K, $\alpha \approx 100$ meV, $C \approx 6.3$ eV/atom, and the concentration $f \approx 10^{-4}$. The change in the elastic constant is $\approx 5\times10^{-5}$. If the experiment is done at 10 MHz using an interferometric method in which an elastic constant change is detected as a frequency change with $\delta f/f = \delta C/2C$, this corresponds to a change of $\approx 250$ Hz which certainly should be observable. In the optimum case of small strain, Eq. (11) implies that the frequency change would be $\approx 660$ Hz. Thus, the presence of a moderate strain substantially reduces the frequency change, because it broadens the distribution of splittings. This implies that quantitative results require a measurement of the internal strain.

In conclusion, we have shown that tunnel splitting of a TLS is renormalized by electrons. In the case of a hydrogen atom tunneling in a niobium host, the splitting in the normal state is about 20% smaller than in the superconducting state. This should have observable consequences in neutron scattering and ultrasonic experiments.

We have enjoyed helpful discussions with M. C. Cross, E. Krasicka, and A. J. Leggett. This work was supported by National Science Foundation Grants No. DMR 83-16981 and No. DMR 84-09396.

[1]B. Golding, J. E. Graebner, A. B. Kane, and J. L. Black, Phys. Rev. Lett. **41**, 1487 (1978).
[2]J. L. Black and P. Fulde, Phys. Rev. Lett. **43**, 453 (1979).
[3]For a review, see J. L. Black, in *Glassy Metals I,* edited by H.-J. Guntherodt and H. Beck (Springer-Verlag, Berlin, 1981), p. 167.
[4]J. L. Wang, G. Weiss, H. Wipf, and A. Magerl, in *Phonon Scattering in Condensed Matter,* edited by W. Eisenmenger, K. Labmann, and S. Dottinger (Springer-Verlag, Berlin, 1984), p. 401.
[5]E. Drescher-Krasicka and A. V. Granato, in *Proceedings of the Conference on Internal Friction and Ultrasonic Attenuation in Solids* [J. Phys. (Paris) (to be published)]; Bull. Am. Phys. Soc. **29**, 239 (1984); **30**, 274 (1985).
[6]L. D. Chang and S. Chakravarty, Phys. Rev. B **31**, 154 (1985).
[7]G. J. Sellers, A. C. Anderson, and H. K. Birnbaum, Phys. Rev. B **10**, 2771 (1974).
[8]C. Morkel, H. Wipf, and K. Neumaier, Phys. Rev. Lett. **40**, 947 (1978).
[9]H. Wipf, A. Magerl, S. M. Shapiro, S. K. Satija, and W. Thomlinson, Phys. Rev. Lett. **46**, 947 (1981).
[10]A. Magerl, J. J. Rush, J. M. Rowe, D. Richter, and H. Wipf, Phys. Rev. B **27**, 927 (1983).
[11]D. B. Poker, G. G. Setser, A. V. Granato, and H. K. Birnbaum, Z. Phys. Chem. **116**, 39 (1979).
[12]G. Bellessa, J. Phys. (Paris) Lett. **44**, L387 (1983).
[13]R. Hanada, in *Proceedings of the Second International Congress on Hydrogen in Metals* (Pergamon, Oxford, 1978), Vol. 1, p. 1B6.
[14]A. Magerl (private communication).
[15]J. Jackle, Z. Phys. **257**, 212 (1972).
[16]J. Jackle, L. Piche, W. Arnold, and S. Hunklinger, J. Non-Cryst. Solids **20**, 305 (1970).
[17]A. V. Granato, in *Point Defect Interactions in Metals,* edited by J. J. Takamura, M. Doyama, and M. Kiritani (Univ. of Tokyo Press, Tokyo, 1982), p. 67.
[18]A. V. Granato, K. L. Hultman, and K. F. Huang, in *Proceedings of the Conference on Internal Friction and Ultrasonic Attentuation in Solids* [J. Phys. (Paris) (to be published)].
[19]A. M. Stoneham, Rev. Mod. Phys. **41**, 82 (1969).