Electron and Phonon Interactions with Two-Level-Tunneling Systems in the High-T_c Superconductor $YBa_2Cu_3O_{7-\delta}$ and in Niobium

M. J. McKenna, A. Hikata, J. Takeuchi,[a] and C. Elbaum
Metals Research Laboratory and Department of Physics, Brown University, Providence, Rhode Island 02912

R. Kershaw and A. Wold
Division of Engineering and Department of Chemistry, Brown University, Providence, Rhode Island 02912

(Received 23 January 1989)

We have measured ultrasonic velocity changes with temperature ($T \leq 1$ K) to study the interactions of two-level-tunneling systems (TLS) with electrons and with phonons in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ and in a niobium compact. In $YBa_2Cu_3O_{7-\delta}$, at $T \ll T_c$, TLS relaxation is dominated by conduction electrons, as in *normal* metallic glasses. In niobium, at $T \ll T_c$, this relaxation is dominated by phonons, as in other disordered, *conventional* superconductors. We also review recent specific-heat measurements in light of these results.

PACS numbers: 74.65.+n, 74.70.Mq

Although various properties of high-transition-temperature (high-T_c) superconductors, such as $YBa_2Cu_3O_{7-\delta}$, have been extensively documented in the last two years, many experimental and theoretical questions remain open. Among these questions are the existence of normal electrons at temperatures well below T_c, whether a term linear in temperature in the low-temperature specific heat is intrinsic or extrinsic, and the presence of excitations known as two-level-tunneling systems (TLS).[1,2] Here we report new experimental results on ultrasonic velocity measurements at frequencies up to 25 MHz, in a sintered $YBa_2Cu_3O_{7-\delta}$ compact and in a niobium compact, at temperatures below 1 K. These results provide information on electrons[3] and on phonons in the solid through their interactions with TLS.[4] In particular, we compare the behavior of TLS in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ with those in niobium, a "conventional" BCS superconductor, in both cases for $T \ll T_c$. Since we focus on the use of the TLS as a probe, in what follows we limit the discussion of their properties to interactions with phonons and electrons.

The TLS model,[1,2] originally proposed to explain the various characteristics unique to amorphous materials at low temperatures, postulates that there are two neighboring atomic configurations, with nearly equivalent energies. These two configurations can be represented as the minima of an asymmetric double-well potential, leading to two energy states with splitting E. The model predicts a temperature dependence of the sound velocity, at low temperatures, of the form

$$\Delta v/v = \mathcal{C} \ln(T/T_0) , \tag{1}$$

where $\mathcal{C} = C = nM^2/\rho v^2$ for dielectric glasses and traditional superconducting glasses at temperatures well below T_c, and $\mathcal{C} = C/2 = nM^2/2\rho v^2$ for metallic glasses.[5-7] Here n is the density of states of the TLS (in energy), M is the coupling parameter between phonons and the TLS, ρ is the mass density of the material, v is the sound velocity, and T_0 is an arbitrary reference temperature. In materials, either amorphous or crystalline, which contain TLS, $\Delta v/v$ initially rises with increasing temperature according to Eq. (1), goes through a maximum, and then decreases with increasing temperature. This behavior constitutes a characteristic "signature" of TLS.

The model allows one to determine the dominant relaxation mechanism for the TLS from the temperature dependence of the maximum in $\Delta v/v$ as a function of ultrasonic frequency.[6-8] In dielectric glasses, where the relaxation of TLS occurs via phonons, T_m is determined by the condition $\omega\tau_m \simeq 1$. Here ω is the angular frequency of the ultrasonic wave and τ_m is the fastest relaxation time of the TLS due to phonons at a given temperature,

$$\tau_m^{-1} = \left[\frac{M_l^2}{v_l^5} + \frac{2M_t^2}{v_t^5} \right] \frac{E^3}{2\pi\rho\hbar^4} \coth\left[\frac{E}{2kT}\right] , \tag{2}$$

where E is the energy of the TLS. Replacing E by $2.8kT$, the dominant thermal phonon energy at a temperature T, we obtain $\tau_m^{-1} \propto T^3$. Thus at the maximum of $\Delta v/v$, $T_m \propto \omega^{1/3}$ and T_m shifts to higher temperatures with increasing ω. In metals, T_m is determined by the condition $\tau_{\text{el}} \simeq \tau_m$, where τ_{el} is the relaxation time of the TLS due to interactions with conduction electrons,

$$\tau_{\text{el}}^{-1} = \frac{\pi(\rho_e V_\perp)^2 E}{4\hbar} \coth\left[\frac{E}{2kT}\right] . \tag{3}$$

Here $\rho_e V_\perp$ is the electron-TLS coupling coefficient, where ρ_e is the electronic density of states at the Fermi surface, and $V_\perp$ is the potential seen by the electrons for the different TLS configurations. At low temperatures, $\tau_{\text{el}} \ll \tau_m$ and the electronic relaxation of TLS dominates. As the temperature increases, τ_m decreases and starts to dominate for $\tau_m < \tau_{\text{el}}$. The crossover between the two regimes coincides with the maximum in $\Delta v/v$ in metallic glasses and T_m is independent of the ultrasonic frequency ω. For traditional superconducting metallic glasses at $T \ll T_c$, ρ_e is modified at the Fermi level because of the superconducting gap $\Delta_s(T)$. This leads to a modified TLS-conduction-electron relaxation rate,[5]

$$\tau_s^{-1} = \frac{\pi(\rho_e V_\perp)^2}{\hbar} \frac{k_B T}{e^{\Delta_s/k_B T}+1} \qquad (4)$$

for the condition $E \ll \Delta_s$. This electronic relaxation rate will decrease rapidly for temperatures below T_c, and for $T \ll T_c$, the phonon-TLS interaction will dominate the relaxation process and $T_m \propto \omega^{1/3}$. Experimentally, these frequency dependences are well established for dielectric, metallic, and conventional superconducting amorphous materials.[6-8]

Several reports on the presence of TLS in high-T_c superconductors have already appeared in the literature,[9-12] though in all these cases, measurements of internal friction and elastic modulus changes were made in the frequency range of 2-10 kHz using the vibrating-reed technique. To our knowledge, this paper is the first report of the TLS behavior in high-T_c superconductors in the frequency range of 5-25 MHz, and in niobium powder compact at any frequency. Measurements were performed using transverse-wave lithium-niobate transducers in a pulse-echo system with phase-sensitive detection[13]; the sensitivity in $\Delta v/v$ is 2×10^{-6}. The velocity measurements were done in a ^{3}He evaporation refrigerator in the temperature range of 0.26 to 5 K.

Two $YBa_2Cu_3O_{7-\delta}$ sintered powder samples were prepared by the conventional methods,[14] one with an oxygen content of 6.97 ($\delta=0.03$), and the other with an oxygen content of 6.85 ($\delta=0.15$). The oxygen content of these materials was determined by the method of temperature programmed reduction (TPR), using a Cahn system 113 thermal balance. A flowing atmosphere of 85% Ar and 15% H_2 (60 ml/min) was used. This was purified by passing it through a hot copper column to remove oxygen and then through P_2O_5 to remove water. The samples were heated at 50 °C/h up to 1000 °C until no further decrease in weight was observed. The sample with $\delta=0.03$ has an apparent density of 4.59 $\mathrm{g\,cm^{-3}}$ and a transverse sound velocity of 2.3×10^5 cm/s. A well-defined resistive transition was found at ~90 K and ac susceptibility measurements at 4.2 and 77 K found that approximately 95% of the sample was superconducting. The sample with $\delta=0.15$ showed a well-defined resistive transition at ~82 K, a density of 4.84 $\mathrm{g\,cm^{-3}}$, a transverse sound velocity of 2.41×10^5 cm/s, and a superconducting fraction of approximately 92%.

The niobium powder for the compact was obtained from CERAC, Inc.; it has a particle size of less than 44 μm and a purity of 99.8%. The powder was compacted in a die and plunger with a stress of 1.4 GPa. Its apparent density was 8.14 $\mathrm{g\,cm^{-3}}$ and the transverse sound velocity at 77 K was 1.95×10^5 cm/s. A resistivity measurement of a sister compact shows a superconducting transition at approximately 7.5 K.

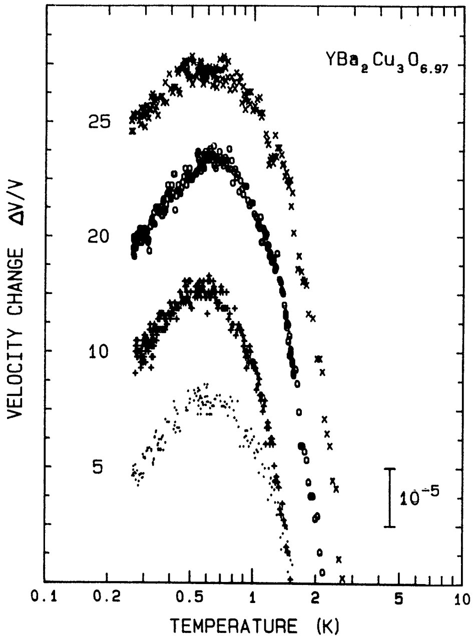

FIG. 1. Examples of the relative velocity changes for the high-T_c superconductor $YBa_2Cu_3O_{6.97}$, $\delta=0.03$, for ultrasonic frequencies of 5, 10, 20, and 25 MHz.

Figure 1 shows the relative velocity change $\Delta v/v$ in the $YBa_2Cu_3O_{6.97}$ sample as a function of temperature, for the ultrasonic frequencies 5, 10, 20, and 25 MHz. For each of the frequencies, the velocity change increases logarithmically with temperature up to 0.6 K, due to the resonant interaction between the ultrasonic wave and the TLS, passes through a maximum, and then decreases due to the TLS relaxation processes. Note that the temperature T_m of the maximum of $\Delta v/v$ is independent of frequency.

In Fig. 2(a) we present the frequency dependence of T_m for the $\Delta v/v$ curves for the $YBa_2Cu_3O_{6.97}$ sample shown in Fig. 1. Clearly the position of T_m did not shift with frequency, within the experimental uncertainty. It is clear that the behavior of the TLS at these temperatures is characteristic of the relaxation found in metals (particularly in metallic glasses), where the relaxation is dominated by TLS-electron interactions. Similar results are found for the superconductor with $\delta=0.15$ [see Fig. 2(b)]. We note that our maximum of 0.6 K for the $YBa_2Cu_3O_{6.97}$ sample is close to the data of Golding *et al.*[9] ($T_m \approx 0.4$ K) on $YBa_2Cu_3O_7$, despite a frequency difference of 2 kHz to 20 MHz. For phonon-dominated relaxation, $T_m \propto \omega^{1/3}$, this frequency difference of 10^4 would predict a shift in the maximum in $\Delta v/v$ from 0.4 K for $\omega \simeq 2$ kHz to 8.6 K for $\omega \simeq 20$ MHz. A similar lack of a frequency dependence of T_m was observed in PdSi-Cu metallic glass for an even larger frequency range, 1 kHz to 960 MHz.[6,8] In contrast to the high-T_c samples, the $\Delta v/v$ behavior for the niobium compact displays a phonon-dominated TLS relaxation process. The $\Delta v/v$

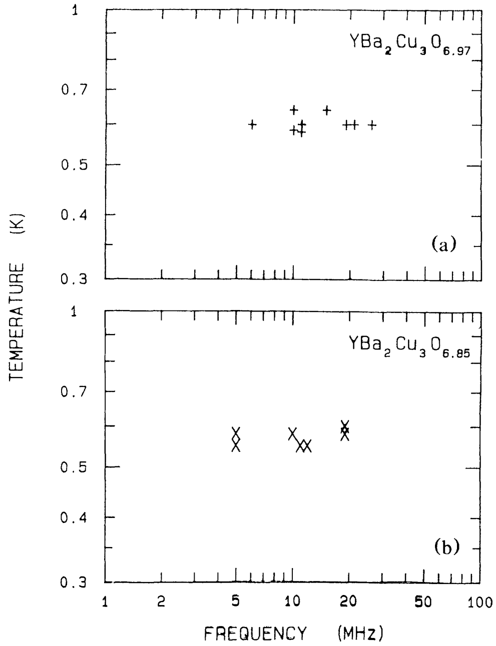

FIG. 2. The frequency dependence for all our measurements of the temperature T_m of the maximum of $\Delta v/v$ in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ with (a) $\delta=0.03$ and (b) $\delta=0.15$.

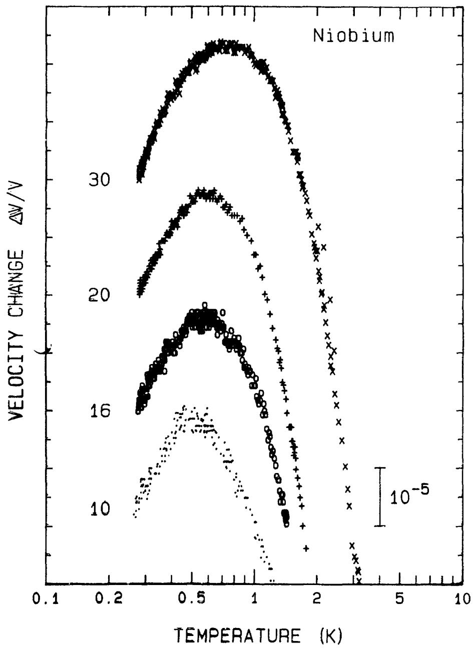

FIG. 3. Examples of the relative velocity changes as a function of temperature for the niobium compact at frequencies of 10, 16, 20, and 30 MHz.

curves for frequencies of 10, 16, 20, and 30 MHz are shown in Fig. 3. The corresponding frequency dependence of T_m ($T_m \propto \omega^{1/3}$) is shown in Fig. 4. It is evident that at these temperatures ($T \approx 0.7$ K) the relaxation process of the TLS is dominated by phonons. (With $\Delta_s \approx 3.8 k_B T_c$ for niobium[15] and $T_c \approx 7.5$ K, we estimate that the electron density at this temperature is reduced by a factor of 10^{21} from that in the normal state.) Thus we have a clear distinction between the high-T_c $YBa_2Cu_3O_{7-\delta}$ superconductors, which exhibit a TLS relaxation characteristic of the conduction-electron–dominated TLS relaxation at temperatures $T \ll T_c$ and the niobium compact, a "traditional" BCS type-II superconductor, where the TLS relaxation is dominated by phonons for $T \ll T_c$.

In the $YBa_2Cu_3O_{7-\delta}$ superconductors, the origin of the often observed large term in the specific heat with a linear temperature dependence, γT, is still unknown. Several authors have attributed this term to the presence of impurity phases, such as $BaCuO_{2+x}$, rare-earth impurities, or TLS. Under the TLS model, $\gamma_{TLS} = (\pi^2/6) n k_B^2$. If the TLS relaxation is dominated by phonons, one can calculate the value of the coupling parameter M from the condition $\omega\tau_m \simeq 1$ at the maximum of $\Delta v/v$. Golding *et al.* used this assumption to calculate M and obtained $\gamma_{TLS} = 1.4$ mJ/(mole K^2).[9] Because the maximum in $\Delta v/v$ in our superconducting $YBa_2Cu_3O_{7-\delta}$ samples is clearly governed by the condition $\tau_{el} \simeq \tau_m$, we cannot calculate M using the same method. With our observed slope of $\Delta v/v$ as a function of $\ln T$, $C \simeq 4 \times 10^5$, we calculate $nM^2 \simeq 10^7$ erg cm^{-3} for $YBa_2Cu_3O_{6.97}$. We can express the contribution to the linear term in the specific heat as a function of M [$\gamma_{TLS} M^2 \simeq 1.54 \times 10^{-6}$ J/(mole K^2), for M expressed in eV] and place estimates on this contribution by using reported values for M. From specific-heat measurements and $\Delta v/v$ measurements for rapidly quenched crystalline $Nb_{20}Zr_{80}$ (Ref. 16) $M \approx 0.4$ eV, for $Pd_{0.3}Zr_{0.7}$, $M \approx 0.1$ eV,[17,18] and for $Pd_{0.775}Si_{0.165}Cu_{0.060}$, $M \approx 0.4$ eV.[19] Thus γ_{TLS} ranges from ~10 μJ/(mole K^2) to ~0.15 mJ/(mole K^2); well below the reported γ for $YBa_2Cu_3O_{7-\delta}$, 5 to 9 mJ/(mole K^2).[20–23] These large values are attributed to the presence of the $BaCuO_{2+x}$ impurity phase.[20–22] Collo-

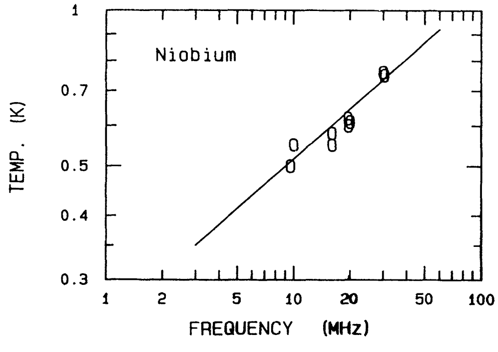

FIG. 4. The frequency dependence of all our measurements of the temperature T_m of the maximum of $\Delta v/v$ in the niobium powder compact.

cott *et al.*[20] claim to have determined a γ of ≈ 1.5 mJ/(mole K^2) intrinsic to the superconducting state, by studying a sample before and after the removal of oxygen by annealing[24]; they attribute this term to a resonant-valence-bond state or a bipolaronic superconducting state, or to the presence of TLS. Eckert *et al.*[22] have also observed a possible intrinsic γ of 1-3 mJ/(mole K^2). A γ_{TLS} of 1-3 mJ/(mole K^2) would require M, with nM^2 as determined by our measurements, to be in the range of 0.02 to 0.04 eV, far smaller than the typical values reported for metallic glasses and highly disordered alloys. So it is unlikely that TLS can account for this "intrinsic" γT term in the specific heat.

Our results on the behavior of TLS in $YBa_2Cu_3O_{7-\delta}$ indicate the presence of conduction electrons at $T \ll T_c$ ($T \leq 0.6$ K). The question arises whether a corresponding term in the electronic specific heat should be observed. We note that the electron density in the *normal* state of $YBa_2Cu_3O_{7-\delta}$ is estimated to be a factor of $\sim 10^2$ lower than that of a typical metal. Even if we assume that these electrons do not condense and remain normal, the electronic specific heat $\gamma_e T$ at $T \ll T_c$ would be below the resolution of the measurements reported so far.

In conclusion, we have used the behavior of TLS in the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ and in a conventional superconductor, compacted niobium powder, as a probe of TLS interactions with electrons and with phonons. This was accomplished by measuring the temperature dependence of the ultrasonic velocity below 1 K. The measurements indicate that in $YBa_2Cu_3O_{7-\delta}$ the TLS relax by interacting with conduction electrons, while in the niobium compact this relaxation occurs via phonons, as in other amorphous and highly disordered *conventional* superconductors. The results are consistent, therefore, with the presence of an appreciable density of conduction electrons in $YBa_2Cu_3O_{7-\delta}$ at $T \ll T_c$ ($T \leq 1$ K). We also note that these electrons would contribute a specific-heat term of a magnitude which is below the resolution of such measurements published to date. Our results, therefore, support the theoretical models which allow for the presence of conduction electrons in high-T_c superconductors for $T \ll T_c$. Finally, assuming a TLS-ultrasonic-wave coupling M typical of other materials, we find that the density of states of TLS in $YBa_2Cu_3O_{7-\delta}$ is not sufficient to account for the "linear" specific-heat term reported by several researchers.

This research was supported by the National Science Foundation in part through the Materials Research Laboratory at Brown University.

---

[a] Permanent address: Department of Physics, Shimane University, Matsue, Japan.

[1] P. W. Anderson, B. I. Halperin, and C. M. Varma, Philos. Mag. **25**, 1 (1972).

[2] W. A. Phillips, J. Low Temp. Phys. **7**, 351 (1972).

[3] We use the term *electrons* throughout to designate charge carriers, without making a distinction between electrons and holes.

[4] In order to achieve a close match to the structure of the sintered $YBa_2Cu_3O_{7-\delta}$ samples, we have used a compact of a niobium powder. The origin of TLS in $YBa_2Cu_3O_{7-\delta}$ and in the niobium compact is discussed in a separate paper (to be published).

[5] J. L. Black and P. Fulde, Phys. Rev. Lett. **43**, 453 (1979).

[6] See the review article by S. Hunklinger and A. K. Raychaudhuri, in *Progress in Low Temperature Physics,* edited by D. F. Brewer (Elsevier, Amsterdam, 1986), Vol. 9, pp. 265-344.

[7] H. v. Löhneysen, Phys. Rep. **79**, 161 (1981).

[8] A. K. Raychaudhuri and S. Hunklinger, Z. Phys. B **57**, 310 (1982).

[9] B. Golding, N. O. Birge, W. H. Haemmerle, J. Cava, and E. Reitman, Phys. Rev. B **36**, 5606 (1988).

[10] P. Esquinazi, J. Luzuriago, C. Duran, D. A. Esparza, and C. D. D'Ovidio, Phys. Rev. B **36**, 2316 (1987).

[11] P. Esquinazi, C. Duran, C. Fainstein, and M. Nunez Requeiro, Phys. Rev. B **37**, 545 (1988).

[12] M. A. Izbizky, M. Nunez Requeiro, P. Esquinazi, C. Duran, and C. Fainstein, Phys. Lett. A **129**, 71 (1988).

[13] For a brief description, see A. Hikata, M. McKenna, and C. Elbaum, Appl. Phys. Lett. **50**, 478 (1987). A more detailed description may be found in G. Cibuzar, thesis, Brown University, 1985 (unpublished).

[14] S. Davison, K. Smith, R. Kershaw, K. Dwight, and A. Wold, Mater. Res. Bull. **22**, 1659 (1987).

[15] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1976), 5th ed., p. 367.

[16] N. Thomas, W. Arnold, E. Gmelin, K. Guckelsberger, G. Weiss, and H. v. Löhneysen, J. Phys. (Paris), Colloq. **41**, C8-751 (1980).

[17] J. Graebner, B. Golding, R. J. Schutz, F. S. L. Hsu, and H. S. Chen, Phys. Rev. Lett. **39**, 1480 (1977).

[18] G. Weiss, S. Hunklinger, and H. v. Löhneysen, Physica (Amsterdam) **109-110B**, 1946 (1982).

[19] B. Golding, J. Graebner, A. B. Kane, and J. L. Black, Phys. Rev. Lett. **41**, 1487 (1978).

[20] S. J. Collocott, R. Driver, H. K. Welsh, and C. Andrikidis, Physica (Amsterdam) **152C**, 401 (1988).

[21] T. Sasaki, O. Nakatsu, N. Kobayashi, A. Tokiwa, M. Kikuchi, A. Liu, K. Hiraga, Y. Syono, and Y. Muto, Physica (Amsterdam) **156C**, 395 (1988).

[22] D. Eckert, A. Junod, A. Bezinge, T. Graf, and J. Muller, J. Low Temp. Phys. **73**, 241 (1988).

[23] S. von Molnar, A. Torresen, D. Kaiser, F. Holtzberg, and T. Penney, Phys. Rev. B **37**, 3762 (1988).

[24] Sasaki *et al.* (Ref. 21) feel this difference is due to possible annealing effects on the contribution to γ from the $BaCuO_{2+x}$ impurity phase.