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Ultrasonic studies of the relation between two-level-tunneling systems, oxygen content, and superconducting transition temperature in $YBa_2Cu_3O_{7-\delta}$

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We have examined the behavior of two-level-tunneling systems (TLS's) in the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$ as a function of decreasing oxygen content, by measuring the temperature dependence of ultrasonic-velocity changes at low temperatures, $T \lesssim 1$ K. We find the density of states of the TLS decreases with decreasing oxygen content and varies exponentially with both T_c and oxygen content. We interpret these results in light of recent measurements on oxygen-vacancy ordering in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$.

Since the discovery of superconductivity in the $YBa_2Cu_3O_{7-\delta}$ system, there has been a great deal of interest in the dependence of the transition temperature T_c on the oxygen content, $7-\delta$. As δ increases from 0, T_c decreases from an initial value of ~93 to 60 K; for $0.3 < \delta < 0.4$, there is a plateau in T_c at approximately 60 K.[1] For $\delta > 0.4$, T_c decreases further from 60 K until at $\delta \sim 0.6$ there is a crystallographic transformation from orthorhombic to tetragonal structure—a phase which is semiconducting[2]—with a drop in T_c to 0 K. The structural effects of decreasing the oxygen content (increasing δ) have been studied by neutron diffraction,[2] electron microscopy,[3-8] and x-ray diffraction,[9] for example. These measurements indicate that when δ increases (by annealing the sample in an oxygen-deficient environment) the oxygen atoms are typically removed from the O(1) sites in the Cu-O chains along the b axis.[2]

Among the many questions, which are currently unanswered, are the presence and the role of low-energy excitations known as "two-level-tunneling systems" (TLS's).[10,11] Several reports of low-frequency sound-velocity measurements on the presence of TLS's in high-T_c superconductors have appeared in the literature,[12-15] and TLS's have been cited by several authors to account for the anomalously large term, linear in temperature, in the low-temperature specific heat.[16-19] Here we report measurements of the density of states of the TLS through ultrasonic velocity changes at low temperatures, $T < 1$ K, and probe the origin of the TLS by studying the dependence of the TLS density on oxygen content.

The TLS model[10,11] was originally developed to account for the disparity in low-temperature properties between amorphous materials and their crystalline counterparts. The model postulates there are two neighboring atomic configurations with nearly equivalent energies. These configurations are represented as the minima of an asymmetric double-well potential, with the atomic rearrangement corresponding to the tunneling of an entity between the two minima. With an appropriate coordinate transformation, these rearrangements correspond to the transition between two-energy states of splitting E; assuming an independent and uniform distribution of E, the model predicts, at low temperatures, a temperature dependence of the sound velocity of the form

$$\frac{\Delta v}{v} = \frac{v(T)-v(T')}{v(T')} = \mathcal{C} \ln\left(\frac{T}{T_0}\right), \tag{1}$$

where $\mathcal{C} = C = nM^2/(\rho v^2)$ for dielectric glasses and traditional BCS superconductors at temperatures well below T_c, and $\mathcal{C} = C/2 = nM^2/(2\rho v^2)$ for metallic glasses.[20-22] 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 and T' are arbitrary reference temperatures. In materials, either amorphous or crystalline, which contain TLS's, $\Delta v/v$ initially rises with increasing temperature according to Eq. (1), goes through a maximum, and then decreases with increasing temperature. This increase in $\Delta v/v$ is due to the resonant interactions between the applied ultrasonic wave and the TLS; the TLS relaxation interactions between phonons and/or electrons result in the decrease in $\Delta v/v$ and the maximum in $\Delta v/v$ occurs at temperatures where the contributions to $\Delta v/v$ from both processes become equal. This behavior constitutes a characteristic "signature" of TLS's.

While several reports on the presence of TLS's in high-T_c superconductors have appeared in the literature,[12-15] to our knowledge this paper is the first to investigate the dependence of the TLS on oxygen content δ in the $YBa_2Cu_3O_{7-\delta}$ system in the 5–20 MHz frequency range. Using 41° X cut (transverse wave) lithium niobate transducers and a pulse-echo system with phase-sensitive detection, we measured relative velocity changes with a sensitivity of 2×10^{-6}. Seven sintered power compact samples were prepared as described previously;[23] see Table I. The first sample (sample A), which showed a well-defined resistive transition at ~93 K (see Fig. 1 inset), was subsequently annealed for 6 h at 450 °C in N_2 to reduce the oxygen content and is listed as sample B; see Fig. 1. As seen in the inset of Fig. 1, the resistivity measurement following this treatment showed semiconducting

TABLE I. Experimental parameters for the seven superconducting $YBa_2Cu_3O_{7-\delta}$ samples: sample A (before annealing) and samples C–H, and the semiconducting sample B (after annealing) (sample A following the removal of oxygen).

Sample	Oxygen content $7-\delta$	δ	T_c (resistivity) (K)	Superconducting fraction (%)	Density ρ (g cm^{-3})	Sound velocity v_t (10^5 cm s^{-1})	Slope $\mathcal{C}$(10^{-5})	nM^2 (10^6 erg cm^{-3})
A	~7		~93		5.47	2.6	~2.4	~18
B			~0		5.45	2.2	...	...
C	~7		~93		4.42	2.1	~2.7	~16
D	~7		~93		5.40	2.1	~3.5	~17
E	~7		~92		5.35	2.1	~2.6	~18
F	6.97	0.03	~90	~95	4.59	2.3	~2	~10.5
G	6.85	0.15	~83	~92	4.84	2.4	~0.9	~5.2
H	6.42	0.42	≈60	~75	4.50	1.9	...	...

behavior down to 0.3 K. The oxygen content of three samples was determined by a temperature programmed reduction of the prepared samples.[24] By observing the weight loss corresponding to the decomposition of the $YBa_2Cu_3O_{7-\delta}$ compound, the oxygen content of the starting material can be determined. The samples in this series had oxygen contents of 6.97, 6.85, and 6.42. For the $\delta=0.03$ sample, from ac susceptibility measurements at 77 and 4.2 K, we estimate ~95% of the sample was superconducting. For the sample with $\delta=0.15$, we estimate 92% of the sample was superconducting. In the sample with $\delta=0.42$, we do not find a well-defined resistive transition; there is a sharp drop in the resistivity at ~60 K, but this occurs on a background which shows semiconducting behavior. ac susceptibility measurements show that approximately 75% of this sample is superconducting at 4.2 K.

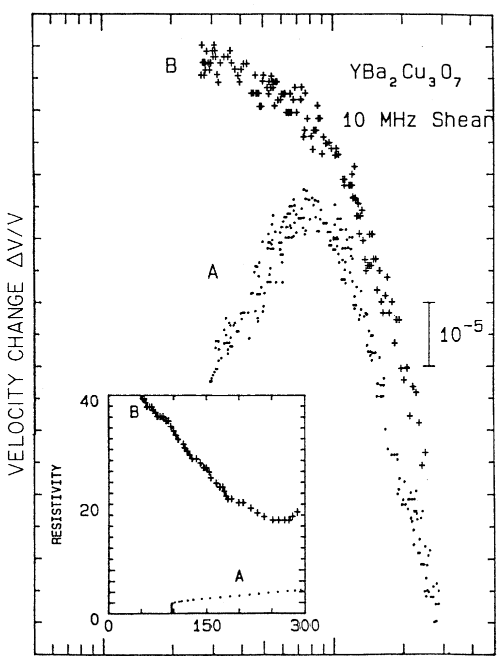

FIG. 1. The relative velocity changes for $YBa_2Cu_3O_{7-\delta}$ superconductor sample A (see curve *A* in the inset). Curve *A* shows the typical $\Delta v/v$ behavior of TLS, whereas the $\Delta v/v$ for the same sample after annealing, sample B, decreases in the same temperature region. This annealed sample does not show a resistive transition (see curve *B* in the inset). The scale for the resistivity measurements is 2×10^{-3} Ω cm/division.

Figure 1 shows the relative velocity change $\Delta v/v$ as probed with a 10-MHz shear wave in the $YBa_2Cu_3O_{7-\delta}$ sample A prior to annealing (see curve *A*). Clearly the velocity change increases logarithmically with temperature for $T<0.7$ K, passes through a maximum, and then decreases for increasing temperature. The slope of $\Delta v/v$ for $T<0.6$ K is $\mathcal{C}=2.4\times10^{-5}$. To obtain C and therefore nM^2 we need to determine whether the TLS relaxation is dominated by electrons as in metallic glasses, $\mathcal{C}=C/2$ or by phonons as in BCS superconductors for $T\ll T_c$, and in dielectric glasses where $\mathcal{C}=C$. We found[24] in the $YBa_2Cu_3O_{7-\delta}$ superconductors, a TLS relaxation dominated by electron-TLS interactions; therefore, we can calculate $nM^2=1.79\times10^7$ erg cm^{-3} for sample A (superconducting). As noted in Table I, we find similar results for the three samples: C, D, and E with similar transition temperatures. In contrast to these samples, sample A following the annealing, the semiconducting sample B, does not show any $\ln T$ increase in $\Delta v/v$ for $T>0.26$ K, the lowest temperature we could attain in our ^{3}He refrigerator. While we cannot state that the semiconducting sample does not contain any TLS's, it is clear that there is a connection between the observed $\Delta v/v$ behavior and the oxygen content of the sample.

To study this feature systematically, the low-temperature velocity changes were measured for the three samples with known oxygen content, $\delta=0.03$, 0.15, and 0.42. These results are shown in Fig. 2 with the resistivity measurements. As shown, $\Delta v/v$ for two samples with $\delta=0.03$ and 0.15, which have clearly defined resistive transitions at ~90 and ~83 K, respectively, show the characteristic $\ln T$ increase signature of TLS's. Unlike these two samples, within the temperature range covered, the sample with $\delta=0.42$ does not show the $\ln T$ increase resulting from the resonant TLS interactions, but only a monotonic decrease, similar to the $\Delta v/v$ curve for the semiconducting

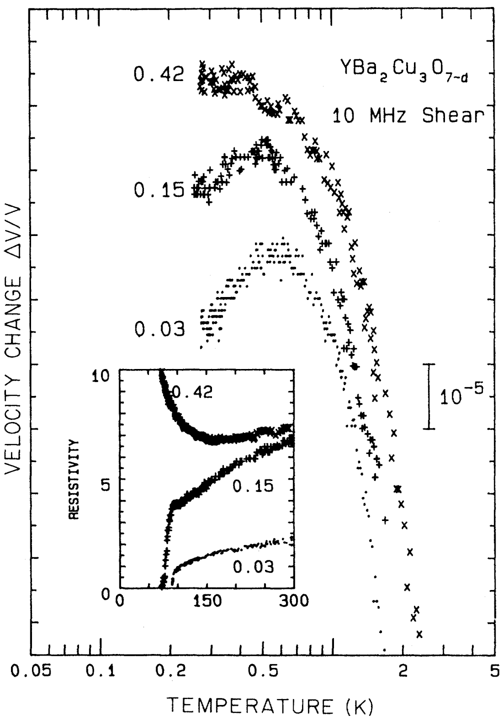

FIG. 2. The relative velocity changes as a function of $\ln T$ for three values of δ in the $YBa_2Cu_3O_{7-\delta}$ samples. Note that the two samples which show a well-defined resistive transition show the $\ln T$ increase in $\Delta v/v$. The resistivity scale is in 10^{-3} Ω cm/division.

sample B. Though there is some uncertainty to our measured slopes, it is interesting to note that the sample with $T_c \sim 93$ K, as measured by the midpoint of the resistivity drop, has a value of nM^2 almost twice that of the sample with $\delta = 0.03$, $T_c \simeq 90$ K, and approximately four times that of the sample with $\delta = 0.15$, $T_c \simeq 83$K. A plot of nM^2 as a function of T_c is shown in Fig. 3. A fit to the data leads to the following estimation: $nM^2 \sim 930 e^{0.116 T_c}$. Based on the known T_c versus oxygen content relation,[1] we can also plot the relation between nM^2 and oxygen content. We estimate the samples with $T_c \simeq 93$ K have oxygen contents of ~ 7; therefore, we have plotted the relation between nM^2 and oxygen content, $7-\delta$, in Fig. 4. This also has an exponential form: $nM^2 = 8.6 \times 10^{-18} e^{8(7-\delta)}$. Thus if these relations hold for larger values of δ and lower transition temperatures, a $T_c \sim 60$ K, or $\delta = 0.42$, would correspond to an nM^2 of 3.6×10^5 or $C \sim 10^{-6}$, ten times smaller than the slope observed in the sample with $\delta = 0.15$. This value of C would be below the resolution of our measurements. While we have shown that there is a relationship between T_c and TLS densities and oxygen content, it is difficult to determine if the TLS's are *intrinsic* to the superconducting state, or if they are only associated with the oxygen concentration. In what follows we analyze the possible origin of TLS's in $YBa_2Cu_3O_{7-\delta}$.

We note Golding *et al.*[12] have suggested that the most likely candidate for the TLS is oxygen, estimating that 1% of the oxygen can tunnel. This explanation requires that the density of states of TLS's and therefore nM^2 scale (at least approximately) with oxygen content. However, we observe a decrease in nM^2 of a factor of 2 (50) for a change in oxygen content from ~ 6.97 to ~ 6.85 (~ 6.42), thus no such scaling is found.

Here we propose that the TLS's are associated with oxygen vacancies. We note that even for samples with $T_c \sim 90$ K, Jorgensen *et al.*[2] found the occupancy of the O(1) sites on the Cu-O chain was only 0.7; therefore, even for small values of δ, there is a considerable number of oxygen vacancies on the Cu-O chain. However, a *direct* relation between oxygen vacancy content and TLS would require an *increase* in TLS, nM^2, for *decreasing* oxygen content (increasing δ), again contrary to our observations. Instead we consider the relation between TLS's and oxygen vacancy ordering. In several recent papers,[1-8] the ordering of oxygen vacancies along the Cu-O chains (b axis) has been discussed. Chaillout *et al.*[5] found in two samples with $\delta = 0.37$ and $\delta = 0.59$ well-defined ordering between oxygen vacancies. Werder *et al.*[4] have also found vacancy-ordered regions in single crystals of $YBa_2Cu_3O_{7-\delta}$ for $0.08 < \delta < 0.67$; for $\delta = 0.51$, they estimate vacancy correlation lengths of ~ 150 Å for the a and c axes, with the b-axis correlation length of ~ 200 Å. Chen *et al.*[3] found a similar b-axis correlation length for $\delta = 0.3$ but smaller correlation lengths in the a and c directions, ~ 20 and ~ 11 Å, respectively. In a series of papers,[5-8]

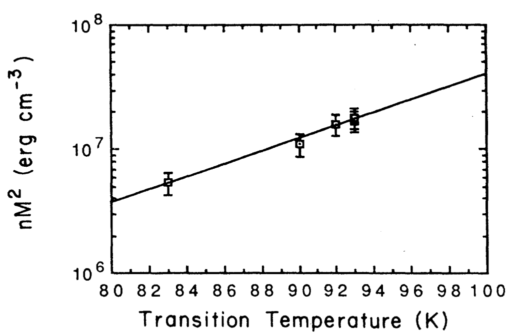

FIG. 3. nM^2, as determined by the slope of $\Delta v/v$, as a function of T_c, the temperature at the midpoint of the resistivity transition.

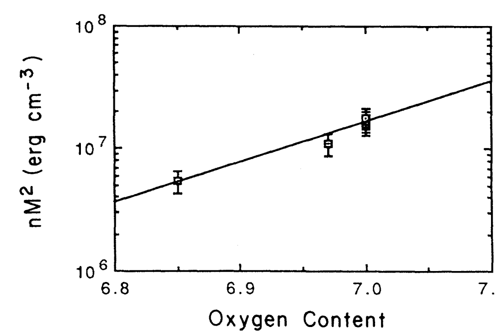

FIG. 4. nM^2, as determined by the slope of $\Delta v/v$, as a function of oxygen content, $7-\delta$.

Alario-Franco *et al.* have proposed four different crystal structures, depending on the oxygen concentration, for δ in the range of $0<\delta<1$, i.e., as the structure changes from orthorhombic to tetragonal. While they do not provide estimates of the vacancy correlation lengths, they conclude that when δ is small, the oxygen vacancies can be considered as isolated defects; however, for larger δ, the vacancies are abundant and order into "integral parts of the structure" and cannot be considered as isolated defects. We propose that the TLS's have their origin in the *disordered* oxygen vacancies on the Cu-O chains. As an increasing number of oxygen vacancies order, their contributions to TLS's is reduced and this model leads to the observed decrease in nM^2 as the vacancies order for increasing δ (increasing vacancy correlation lengths).

In conclusion, we have measured the ultrasonic velocity changes at low temperatures $T \lesssim 1$ K as a function of decreasing oxygen content (increasing δ) in a series of samples. We have also measured the effect of reducing the oxygen content on the density of states of TLS's, by measuring the velocity changes in a sample in the superconducting state (as prepared) and in the same sample, after annealing, when the resistivity exhibits typical semiconducting behavior. We have observed a strong relationship between the transition temperature and the density of states of the TLS's. Based on the reported oxygen vacancy ordering along the CuO chains with decreasing oxygen content, determined from reported x-ray diffraction and electron-diffraction experiments, we speculate that the TLS's have their origin in disordered oxygen vacancies. Therefore, the observed decrease in the TLS density of states, and a corresponding decrease in their density, with decreasing oxygen content is attributed to increasing vacancy ordering along the chains.

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