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Anisotropic pressure dependence of the superconducting transition in $YBa_2Cu_3O_{7-\delta}$ single crystals

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The anisotropic nature of the superconducting transition and its pressure dependence in $YBa_2Cu_3O_{7-\delta}$ single crystals are shown. This anisotropy may bear a close relation to the double transition often mentioned in the literature. A transition-temperature minimum around 1–3 kbar of pressure is clearly revealed. The origin of the minimum still needs to be clarified.

Many experiments have been reported on the pressure dependence of the superconducting transition in $YBa_2Cu_3O_{7-\delta}$,[1–7] but very few were measured on single crystals.[6] The conclusion that could be drawn from these experiments is limited by the broadening of the transition under pressure and rather poor repeatability from sample to sample. In this paper we report careful measurements on $YBa_2Cu_3O_{7-\delta}$ single crystals. Our results show that the anisotropic nature of the pressure dependence of the superconducting transition in the material and the double transition often mentioned in the literature[8–10] are closely related to the crystal anisotropy. In the meantime, a transition-temperature minimum in the 1–3 kbar range was unambiguously revealed.

The $YBa_2Cu_3O_{7-\delta}$ single crystals were grown by solid-state reactions in air with appropriate amounts of thoroughly ground and well-mixed $BaCO_3$, Y_2O_3, and CuO. The material was heated to 960 °C and kept at that temperature for 9 d. The temperature was then decreased and maintained at 800 °C for 3 d. With a speed of 6 °C/h, the material underwent a tetragonal-orthorhombic transition between ~780 and ~620 °C. It was kept at 600 °C for 20 h before cooling to room temperature at a speed of 10 °C/h. The resultant regular rectangular crystals had shiny faces but were rather small, having a general size of about $0.15\times0.15\times0.03\ \mathrm{mm}^3$. ac susceptibility measurements at zero pressure resulted in a superconducting transition width of 0.5–1.5 K around 92 K. In the liquid N_2, the crystal showed a very good levitation nature in the magnetic field. The hydrostatic pressure was achieved by using the self-clamp technique described elsewhere.[11] The superconducting transition was measured by a modified ac bridge working at ~5 MHz. Both the sample arm and the compensation arm were located in the pressure cell and tuned separately to resonant states, which greatly improved the sensitivity of the measurements. Using this setup and an ac magnetic field of less than 2 mG, we were able to trace the superconducting transition of our small crystals with a signal-to-noise ratio of better than 30–40. To follow the detailed change of the transition temperature the copper-constantan thermopower was carefully calibrated for every pressure.

Four $YBa_2Cu_3O_{7-\delta}$ single crystals have been measured. All give consistent results. The transitions at three different pressures for sample 1 with the *ab* plane aligned along the ac field H are shown in Fig. 1. Two superconducting transitions can clearly be seen at lower pressures. Such a double transition was observed earlier by specific heat,[8,9] thermopower,[10] as well as resistivity[8,12,13] measurements, and attributed to two different phases,[13] a steplike distribution of the oxygen content,[14] the percolation nature of the transition,[9] and T_c enhancement at the surface shell.[10] These explanations do not seem to fit to our results, showing that the two transitions progressively combine into a single one when pressure goes up (Fig. 1). Such a combination implies that the two transitions may be intrinsically intercorrelated. This inference is supported by the following experiment: For one sample at 7 kbar, we measured the superconducting transition in several thermal cycles between 80 and ~160 K. We observed T_c enhancement in the second run but

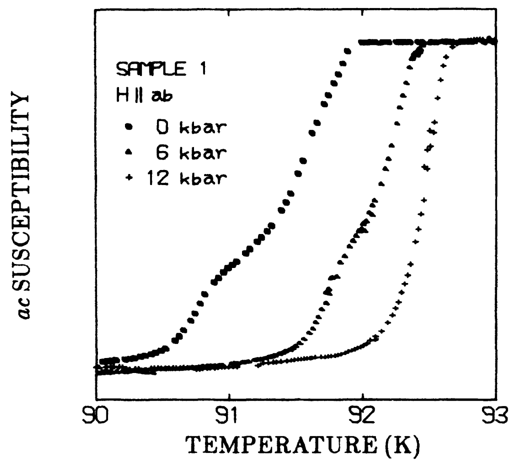

FIG. 1. The superconducting transition of $YBa_2Cu_3O_{7-\delta}$ single crystal at three different pressures. Note the disappearance of the double transition at 12 kbar.

no marked further change was detected in subsequent measurements, indicating some metastable nature of the crystal. However, the two transitions increased synchronously (Fig. 2). We also measured the pressure dependence of the transition with the crystal's *c* axis parallel to *H*. The double transition character is much less typical (Fig. 3). Since the diamagnetic current is a combined contribution of the twin bodies and the twin boundaries when the *c* axis is parallel to *H*, and is the combined contribution of the *ab* plane and the *c* axis when $H \| ab$ plane, all the experimental results lead to the close correlation of the double transition with the anisotropic nature of the crystal. This is consistent with the measurements of thermopower,[10] where the amplitude of the lower transition was always higher when the temperature gradient was along the *c* axis, and the opposite was true when the measurement was along the *ab* plane.

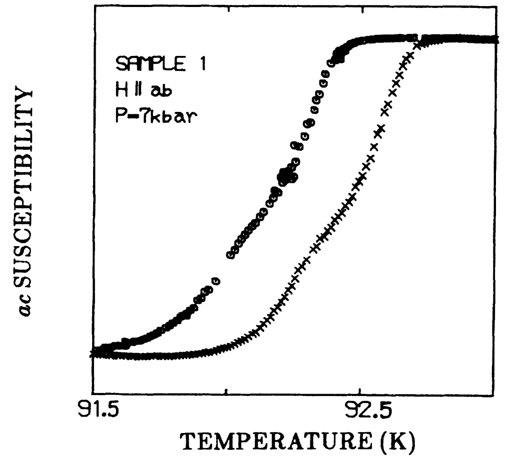

FIG. 2. The metastable nature of the transition. In the second run of the thermal cycle between 80 and 160 K the double transition synchronously shifts to a higher temperature. (○) First run; (×) second run.

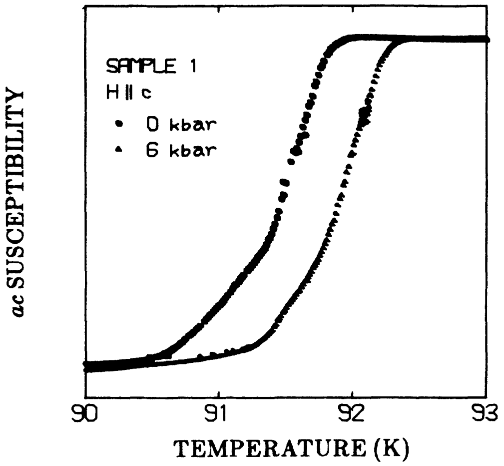

FIG. 3. The transition at two pressures when the field is parallel to the *c* axis.

Thanks to the narrowness of the transition of our samples and their even narrower transition under pressure, proving that there was no pressure-induced inhomogeneity in such small crystals, we were able to follow the pressure-induced changes of the two transitions separately, with much less ambiguity than in previous measurements. A typical result is shown in Fig. 4 where T_{HO}, T_{HF}, T_{LO}, T_{LF} represent the onset and finishing of the upper and lower transitions, respectively, as defined in the inset of the figure. If we neglect the anomaly below ~4 kbar, the slope of the upper transition, dT_H/dp, falls in the range 0.06–0.08 K/kbar, while dT_L/dp falls in the range 0.1–0.14 K/kbar. The ratio of dT_H/dp to dT_L/dp for the same sample was about 0.6–0.7, in good agreement with the anisotropy of compressibility of the crystal.[15,16]

To check the validity of our inference that T_H is linked with the *ab* plane and that T_L is linked with the *c* axis,

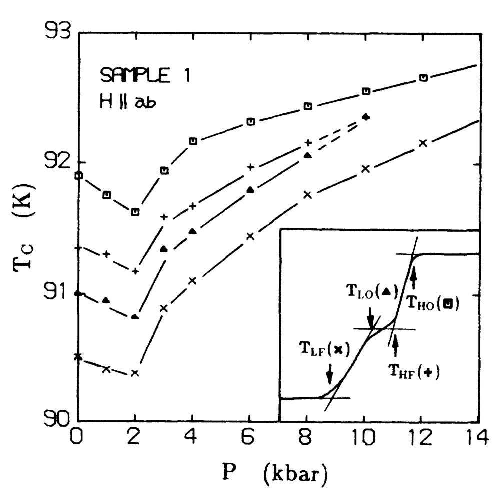

FIG. 4. The pressure dependence of the upper and lower transitions.

we try to relate them to the lattice parameters *b* (or *a*) and *c*, respectively. The pressure influences the superconducting transition either by changing the band structure or the band filling, both of which result in a shift of the density of states and the dynamical properties of electrons at the Fermi surface, or by changing the interaction leading to a superconducting pairing. As there was the interesting result that T_c for the new oxide superconductors was proportional to ω_p^2 (ω_p is the plasma frequency),[17] in the first approximation we may assume that the pairing interaction remains little affected under pressure. The authors of Ref. 17 also argued that the T_c change in $YBa_2Cu_3O_{7-\delta}$ with increasing δ can be interpreted as a consequence in renormalization of the change of the effective bandwidth by taking into account the electron-electron correlation.[18] If we accept their interpretation, the only factor left that influences T_c should be the bandwidth or, equivalently, the transfer integral *t*. For a half-filled band in a tight-binding approximation we have $T_c \propto \omega_p^2 \propto t$. Many experiments prove that the Cu-O planes are responsible for the superconductivity in $YBa_2Cu_3O_{7-\delta}$.[19] We may think of the puckered Cu-O planes as quasi-two-dimensional superconductors. This is consistent with the very short coherence length in the *c* direction. Then T_H can be supposed to only depend on the transfer along the *ab* plane, $T_H \propto t_{ab}$. If, arbitrarily, we choose the dependence of $t_{ab} \propto b^{-1}e^{-b}$, and take the bulk elastic modulus to be 1700 kbar,[15] considering the anisotropy of the compressibility along the *b* (or *a*) direction and along the *c* axis to be ~0.6:1, as given by ultrasonic measurements,[16] we may plot T_{HM} against t_{ab} as shown in Fig. 5(a), here T_{HM} represents the midpoint of the upper transition. The transition along the *c* axis T_L should depend on both the two-dimensional (2D) bandwidth t_{ab} and the coupling between the quasi-two-dimensional superconducting layers.[20] In the simplest form we assume that the coupling is inversely proportional to the lattice parameter *c*. Then we have $T_L \propto c^{-1}t_{ab}$. The result is shown in Fig. 5(b). Ignoring the anomaly at lower pressure we see a surprising agreement between the experimental data and our picture, in spite of the oversimplification of the model. Notice that the variation range of T_c is greatly enlarged in the figures. The selected function of t_{ab} resembles the interaction integral of the hydrogenlike atoms[21] instead of that expected from the O 2*p* and Cu 3*d* overlap, which should give a more rapid change.[22] However, the puzzle is not so serious if we take into account the renormalization due to the Coulomb repulsion, which should slow down the *b* dependence of t_{ab}. We have shown here the important coincidence of the anisotropy nature of the crystal with the difference in the pressure dependence of T_H and T_L.[23] It is interesting to note that from the preceding model T_c is proportional to *t* rather than t^2 as required in the resonating-valence-bond (RVB) theory.[24]

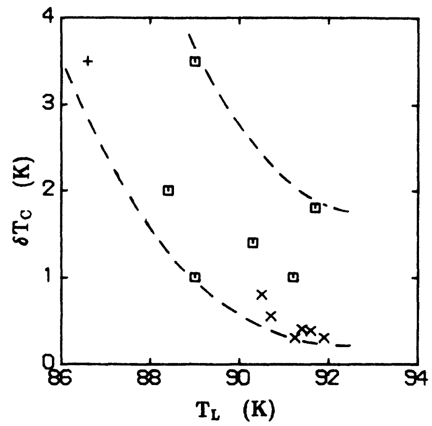

FIG. 6. The relation of the separation of the double transition, $\delta T_c = T_H - T_L$, with T_L showing the tendency to saturate, which should reflect the intrinsic anisotropic nature of the crystal. (+), taken from the specific-heat measurements (Ref. 9); (□), taken from the thermopower measurements (Ref. 10); (×), the present results.

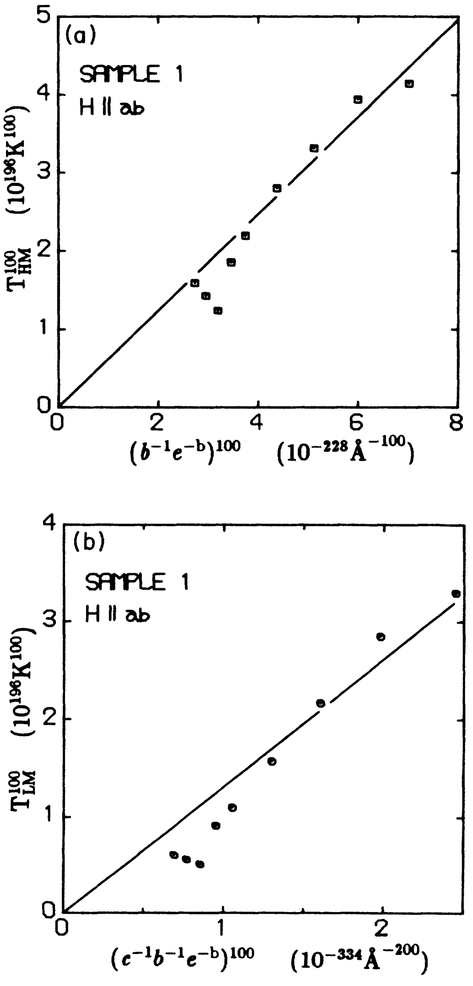

FIG. 5. (a) The dependence of T_H on the transfer integral t_{ab}, t_{ab} is selected to be of the form $t_{ab} \propto b^{-1}e^{-b}$. (b) The data show that T_L depends on both t_{ab} and *c*.

There were several experiments showing that the lower transition is governed by weak links. The magnetic field[14] or the measuring current[12] easily move the transi-

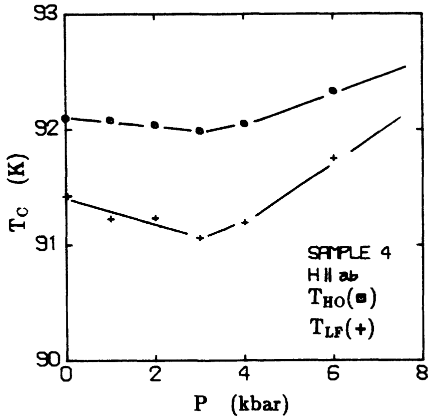

FIG. 7. The transition minimum around 3 kbar.

tion to lower temperatures. The results are consistent with the picture that superconductivity along the *c* axis is weakly coupled. The repeatable closeness of T_H and T_L, the dependence of T_L on *c*, and the almost equal steepness of the two transitions, show the intrinsic and coherent nature of these weak links.[25] However, these coherent weak links can be frustrated by the incoherent defects caused by oxygen deficiency or nonstoichiometry, which broaden and shift the transition to lower temperatures. The existence of the incoherent defects may be used to account for the derivation of the experimental data from the linear relation of T_L versus $c^{-1}t_{ab}$ at lower pressures. We could see the asymptotic approach from extrinsic to intrinsic anisotropy of the superconducting transition when we plotted the separation between the two transitions δT_c against the lower transition T_L, as shown in Fig. 6, where the data are taken from different measurements. The data show that the intrinsic separation might be somewhere below ~0.3 K for very good samples. So one needs every transition to be very narrow to make the double transition visible. If our picture is true, i.e., the more rapid increase of T_L originates from the intrinsically weakly coupled superconductivity along the *c* axis, the pressure dependence of T_H and T_L should be locked together above the combination pressure. It would be interesting to extend the experiments to a higher pressure to see if this inference is correct.

Now we turn to the anomaly at lower pressures. All of the four measured samples show a T_c minimum around 1–3 kbar. Figure 7 presents the results for sample 4. The negative slope of dT_c/dp near zero pressure was not expected from the thermodynamical consideration, taking into account the fact that at T_c the jump of the thermal expansion from the normal to superconducting state is positive.[26] This T_c minimum was also observed earlier for a ceramic sample.[27] The origin is not clear yet. However, since sometimes we saw a reversible dependence in pressure runs, and sometimes the T_c minimum disappeared with releasing pressure, we guess that the minimum is related in some way to the metastable nature of the crystal—maybe the crystal is still in some strained state after the tetragonal-orthorhombic transformation—in spite of that, part of the deformation energy is released by the formation of twins. It would be interesting to mention the following estimation: suppose the relative deformation of *a* and *b* to be ~0.5% during the tetragonal-orthorhombic transition, take bulk modulus to be 1700 kbar, and the anisotropy of elastic modulus along the *ab* plane and the *c* axis to be 1:0.6, we get a deformation stress of about 3 kbar. Further work is needed to clarify whether this is only fortuitous or if it reflects some essence of the T_c minimum.

In summary, we have shown for the first time the intrinsic anisotropic nature of the superconducting transition and its pressure dependence in $YBa_2Cu_3O_{7-\delta}$ single crystals. The pressure dependence of T_c is not monotonic, showing a minimum around 1–3 kbar whose origin still needs to be clarified.

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[23] Actually, the data might better fit the relation $T_H \propto t_{ab} \propto b^{-1}$ and $T_L \propto c^{-1} t_{ab} \propto c^{-1} b^{-1}$. But in this case, to make the relation hold, we should accept the bulk modulus to be ~ 400 kbar, too low to agree with structural analysis. However, the coincidence of the behavior of T_H and T_L with the elastic anisotropy still holds in this case.

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