Improved High-T_c Superconductors

R. N. Bhargava, S. P. Herko, and W. N. Osborne
Philips Laboratories, North American Philips Corporation, Briarcliff Manor, New York 10510

(Received 14 August 1987)

We report an experimental observation of an increased T_c up to 159 K with temperature cycling in Y-Ba-Cu-O and Y-Ba-Cu-O:F samples. This increase in T_c is tentatively associated with a structural phase transition or ordering occurring at a well-defined temperature close to 239 K. We have used the presence of this phase ordering to achieve improved-T_c material and tentatively attribute it to a two-dimensional to one-dimensional structural change.

PACS numbers: 74.10.+v, 74.70.Ya

The discovery of high-T_c superconductors by Bednorz and Müller[1] has triggered an onslaught of research activity to achieve higher-T_c materials. To date, the reliable and reproducible T_c for zero resistance is about 95 K,[2,3] and the physical reasons for the existence of this high T_c are not clearly understood. Higher T_c's such as 160 K,[4] 240 K,[5] and beyond[6] have been observed in the system $\mathrm{YBa_2Cu_3O_{7-\delta}}$. In all of these reports, reproducibility of the observation is lacking. In particular, after temperature cycling, typically from T_c to room temperature and above, the higher-T_c phase disappears and the material reverts back to a lower T_c value.[4,6]

We have studied the variation of T_c as a function of temperature cycling in Y-Ba-Cu-O and Y-Ba-Cu-O:F samples. It is observed that temperature cycling through a well-controlled procedure improves the T_c^+ from 95 to 130 K and beyond. T_c^+ is defined as the 90% point of onset of the superconducting transition. This temperature cycling involves our raising the temperature of the sample to a superconducting-phase healing temperature (T_{SPH}) and subsequently cooling the sample to determine T_c^+. Upon cycling of the sample several times to T_{SPH}, the T_c^+ of 95 K increases in a stepwise manner to a higher temperature, typically up to 130 K. In one of the samples, we have raised the T_c^+ up to 159 K. The degree of improvement that can be achieved depends also on the sample preparation process.

The samples were prepared from the appropriate mixtures of $\mathrm{Y_2O_3}$, $\mathrm{BaCO_3}$, CuO, and $\mathrm{BaF_2}$. The mixtures were pulverized, placed in a high-purity alumina crucible, and fired in air at 950 °C for up to 32 h. Under 13.6-kbar pressure, the resultant sintered, porous material was pressed into 1.0-cm pellets, 0.2 cm thick. Most of the pellets were fired for up to 64 h in oxygen at 950 °C. The furnace was then cooled to room temperature at 10 °C/min. By means of x-ray diffraction, the presence of the $\mathrm{YBa_2Cu_3O_{7-y}}$ phase was confirmed.

The resistivity measurements were done with the four-point probe technique. The magnetic susceptibility was measured with a system described elsewhere.[7] The key parameter was the temperature measurement and its cycling. Care was taken to measure the sample temperature within ± 0.1 K. This temperature was measured by a calibrated Si diode and represents the exterior temperature of the sample.

The room-temperature resistivity of sample B (Fig. 1) was about 1.2×10^{-2} Ω cm. Between 300 and 100 K, R decreased monotonically with decreasing T and did not extrapolate to zero at $T=0$. At $T=T_c(0)$, the resistivity was about 4.0×10^{-7} Ω cm, a change of about 4 orders of magnitude in resistivity with only a <1 K change in temperature. $T_c(0)$ is simply referred to as the temperature where the measured voltage falls below 10^{-8} V (instrument sensitivity) at a current of 10 mA flowing through the sample; it is no longer possible to ascertain reliable values of R below this temperature. In these resistivity measurements, the reversal of current direction did not change the R vs T curve. Additionally, when voltage and current contacts were interchanged no discernible change in the R vs T curve was observed. In all samples, the I-V characteristics were linear, and in very-low-resistive samples ($\rho \simeq 10^{-4}$ Ω cm), the extrapolated value of R was zero for $T=0$.

To determine T_c^+ from resistivity measurements, the samples were periodically cooled and heated. In this process, when the heating cycle was stopped close to 240

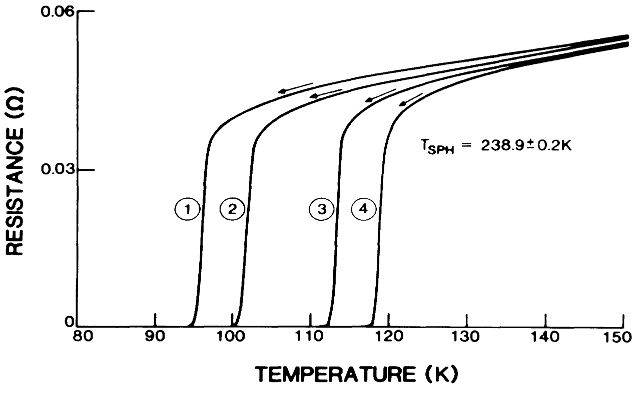

FIG. 1. Improvement in T_c^+ as a result of repeated cycling of sample B to a temperature $T_{\mathrm{SPH}} = 238.9 \pm 0.2$ K. In this case T_c^+ improved from 95 to 120 K.

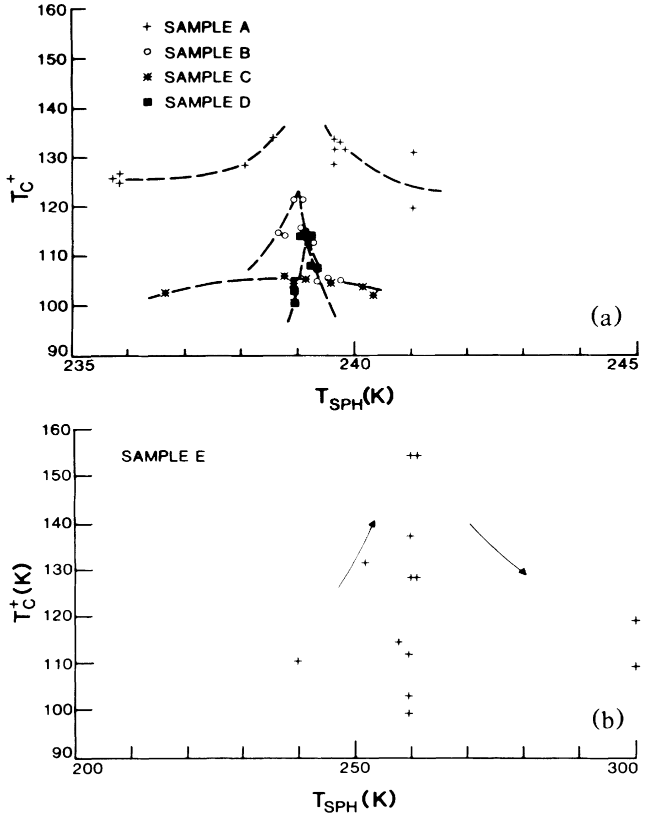

FIG. 2. Variation of T_c^+ as a function of $T_{\rm SPH}$ for five different samples. (a) Variation in T_c^+ for cycling at $T_{\rm SPH} = 239$ K for Y-Ba-Cu-O and Y-Ba-Cu-O:F samples. Samples A and B contained 0.67 mole fraction fluorine. Sample C had traces of F and no F was added to sample D. (b) T_c^+ vs $T_{\rm SPH}$ for sample E in which 2.0 mole fraction F was added. The data points at $T_{\rm SPH} = 260$ K show the improvement in T_c^+ up to 159 K as a function of cycling. The arrows depict the trends.

K, a pattern of improved T_c^+ was observed. The pattern of improved T_c^+ is shown in Fig. 1. In this case, the sample was cooled from room temperature to 77 K and then the temperature was raised to 238.9 ± 0.2 K. The observed pattern for this sample was that T_c^+ improved in a stepwise manner over several runs until it reached a value close to 130 K. Beyond this, the value did not change in spite of continued cycling. If, however, in the process of heating, the temperature was raised beyond 240 K, a sudden decrease in the value of T_c^+ was immediately observed. Thus, beyond $T_{\rm SPH}^{\rm max} = 238.9 \pm 0.2$ K, the healing process decayed rapidly. The resultant data for different samples are shown in Fig. 2(a). In this figure, data are plotted for four different samples. Samples A and B were prepared with 0.67 mole fraction of fluorine in the reactant mixture, while sample C had only traces of fluorine. Sample D was not doped with fluorine. Raising the temperature to exactly $T_{\rm SPH}$ without overshooting is the key factor in maximizing T_c^+. The measurements of $T_{\rm SPH}^{\rm max}$ taken for several samples reveal that the peak value of T_c^+ occurs in a very narrow range of $T_{\rm SPH}$, possibly less than ± 0.1 K. For example, in sample B, a drop of $\simeq 10$ K was observed in T_c^+ for an excursion of ± 0.5 K from the peak of the curve. This sharp transition at $T_{\rm SPH}$ observed in these samples probably reflects an unusual phase transition or ordering occurring in these materials. The tentative explanation for this is discussed later. All samples do not show the same degree of improvement. So far, samples with higher fluorine concentration have shown the most improvement. In Fig. 2(b), the observed change in T_c^+ vs $T_{\rm SPH}$ is plotted for another sample (E). The mole fraction of fluorine in the starting material was 2.0. In this sample an improved T_c^+ of 159 K was observed for $T_{\rm SPH}^{\rm max}$ of 260 ± 1.0 K. After two days of cycling, the T_c^+ of the sample degraded back to 95 K.

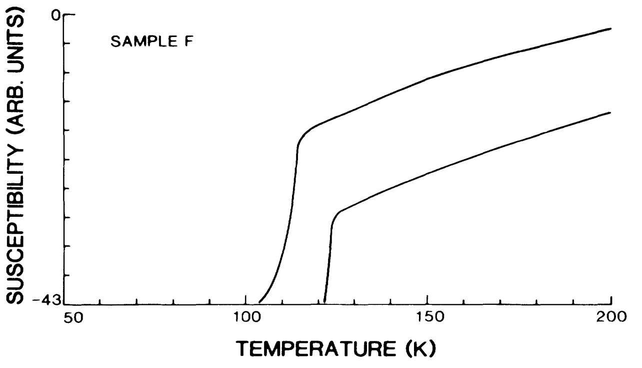

FIG. 3. Improvement in T_c^+ in the magnetic susceptibility observed after temperature cycling in sample F containing 2.0 mole fraction of F. Because of the limited accuracy in the magnetic-susceptibility measurements, $T_{\rm SPH}$ was determined to be 239.0 ± 2.0 K.

Magnetic-susceptibility measurements were also performed with temperature cycling and results are shown in Fig. 3. The healing effect was observed at 239.0 ± 2.0 K confirming the resistivity measurements in sample F.

In Fig. 4 the width of the transition ΔT_c, as measured from the 90% point (T_c^+) to the 50% point (T_c^m), is plotted as a function of increased T_c^+. We observe that ΔT_c varies from about 0.7 K for T_c^+ at 95 K to > 2.0 K for T_c^+ at 130 K. This same trend was followed by samples showing higher T_c. In the process of temperature cycling we observed that there is a hysteresis between the onset of $T_c(0)\downarrow$ when the sample is cooled and that of $T_c(0)\uparrow$ when the sample is heated. However, these hysteresis measurements do not show any consistent pattern, possibly because of the fact that the measured temperature is the exterior temperature of the sample which does not correspond precisely to the interior temperature of the sample.

In most of the samples studied we have observed an

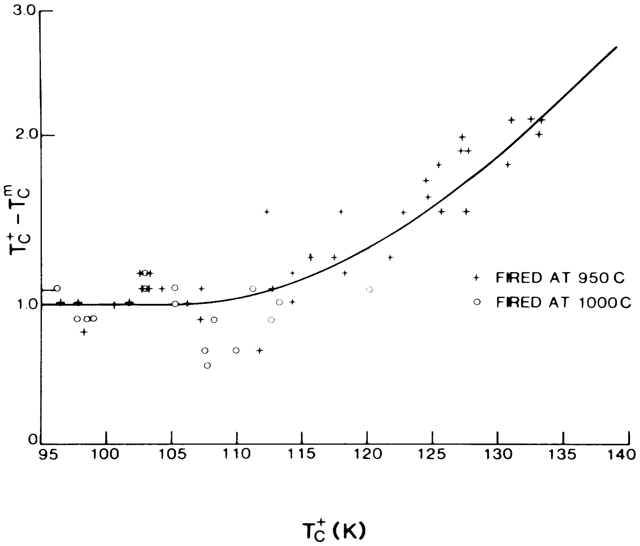

FIG. 4. Variation of the width ΔT_c ($T_c^+ - T_c^m$) as a function of improved T_c^+. ΔT_c seems to increase as T_c^+ is improved through temperature cycling.

enhanced T_c^+ after cycling the sample to $T_{\rm SPH}$. To determine how reliable the process is, and how well one can maintain this enhanced T_c^+ over longer periods of time, continues to be an active research endeavor. Experiments done to date demonstrate that the higher-T_c phase is indeed stable over several days. In samples that are cycled beyond $T_{\rm SPH}$, the higher T_c^+ reverts back to a normal $T_c^+ \simeq 95$ K. Even after repeating cycling of this type, the higher T_c^+ can be regained by careful cycling to $T_{\rm SPH}$. This effect of increased T_c^+ when cycled up to $T_{\rm SPH}$ has been observed in several samples, but the value of the final T_c varies from 103 to 159 K for different samples. It appears that a higher $T_{\rm SPH}$ is associated with a higher final T_c^+.

In the experiments described above and summarized in Fig. 2, we find that there exists a temperature $T_{\rm SPH}^{\rm max}$ in the Y-Ba-Cu-O and Y-Ba-Cu-O:F systems which corresponds to a maximum value of T_c^+. The observed $T_{\rm SPH}^{\rm max}$ of 239 K is almost the same temperature which Chen *et al.*[5] estimated from the reverse Josephson effect. We believe that this unique temperature of 240 K observed by Chen *et al.* and by us reflects a change in the structure or corresponds to a phase instability that results in a higher T_c, and most probably is not related to a T_c of 240 K as reported by Chen *et al.*

A search for structural phase transitions and instabilities which may be associated with a change in the electrical resistivity was reported for the La-Ba-Cu-O system.[8] With the use of high-resolution neutron diffraction, the presence of the tetragonal to the orthorhombic phase transition at 180 K with anomalous structural instabilities was reported.[8] In our case we are stabilizing a phase instability directly through temperature cycling. We have tried to look for phase instabilities at higher temperatures but have not observed any beyond 260 K. If the observation that higher $T_{\rm SPH}^{\rm max}$ is associated with higher T_c is indeed valid, then further investigation may reveal a higher $T_{\rm SPH}^{\rm max}$ that is associated with a T_c closer to 300 K. Furthermore, the physical understanding of the relationship between structural change or ordering at $T_{\rm SPH}^{\rm max}$ and T_c can lead to a clearer picture of the role of structural phase transitions in higher-T_c material.

From these observations, we feel that at $T_{\rm SPH}^{\rm max}$ a structural ordering or metastable phase transition occurs. We propose that at this temperature, a high-T_c phase is formed or stabilized and "frozen in" when the temperature is lowered. A possible explanation for this phase change may involve rearrangement of chainlike Cu—O bonds in the Y-Ba-Cu-O system. The cycling to $T_{\rm SPH}^{\rm max}$ changes the delicate equilibrium between 2D Cu-O planes and 1D Cu-O chains. Structural changes, between the one-dimensional Cu-O chains and two-dimensional Cu-O planes, brought about by Sr doping in Y-Ba-Cu-O, has been recently reported by Veal *et al.*[9] They concluded that Sr substitution onto Ba sites leads to a depression of T_c due to a change in the equilibrium between the 2D and 1D Cu-O structures.

In conclusion, we have reported an experimental observation of an increased T_c up to 159 K with temperature cycling in Y-Ba-Cu-O and Y-Ba-Cu-O:F samples. This increase in T_c is tentatively associated with a structural phase transition or ordering occurring at a well-defined temperature $T_{\rm SPH}^{\rm max}$. In these materials, when $T_c \gg 95$ K, instabilities associated with superconducting were reported by others[5] and usually disappeared after temperature cycling. However, in our case, we have used the existence of phase instability to achieve improved-T_c material. We tentatively associate this phase transition with a two-dimensional to one-dimensional structural change or ordering.

---

[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).

[2] M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, Phys. Rev. Lett. **58**, 908 (1987).

[3] H. Takagi, S. Vchida, K. Kishio, K. Kitazawa, K. Fueki, and S. Tanaka, Jpn. J. Appl. Phys., Pt. 2 **26**, L320 (1987); R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, Phys. Rev. Lett. **58**, 676 (1987).

[4] S. R. Ovshinsky, R. T. Young, D. D. Allred, G. DeMaggio, and G. A. van der Leeden, Phys. Rev. Lett. **58**, 2579 (1987).

[5] J. T. Chen, L. E. Wenger, C. J. McEwan, and E. M. Logothetis, Phys. Rev. Lett. **58**, 1972 (1987).

[6] Several reports of T_c close to room temperature have ap-

peared in the popular press. Consistent scientific data are lacking, probably as a result of the lack of reproducibility of these results.

[7] S. P. Henko, unpublished; see also R. Bhargava, Phys. Rev. **156**, 785 (1967).

[8] D. Mck. Paul, G. Balakrishnan, N. R. Bernhoeft, W. I. F. David, and W. T. A. Harrison, Phys. Rev. Lett. **58**, 1976 (1987).

[9] B. W. Veal, W. K. Kwok, A. Uinezawa, G. W. Crabtree, J. D. Jorgensen, J. W. Downey, L. J. Nowicki, A. W. Mitchell, A. P. Paulikas, and C. H. Sowers, Appl. Phys. Lett. **51**, 279 (1987).