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Degradation effects in the high-T_c superconductor $GdBa_2Cu_3O_{7-\delta}$

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Abstract. The curve of resistance against temperature for a $GdBa_2Cu_3O_{7-\delta}$ superconductor taken six weeks after preparation shows a degradation of its T_c with respect to the measurements taken just after preparation. Powder x-ray patterns show changes that could be attributed to disorder in the oxygen sites, possibly related to an incipient loss of oxygen rather than to a crystallographic phase transition.

The R–Ba–Cu–O system, with R ≡ Y or various rare earths (Escudero *et al* 1987a, Fisk *et al* 1987, McKinnon *et al* 1987, Hor *et al* 1987), forms a family of superconductors presenting an oxygen-deficient perovskite structure, with layered ordering of the yttrium (or rare-earth) and barium ions (Cava *et al* 1987, Steinfink *et al* 1987, Beyers *et al* 1987).

Recently, there have been several reports on the presence of a tetragonal-to-orthorhombic phase transition in the $YBa_2Cu_3O_{7-\delta}$ system that occurs close to 650 °C (Schuller *et al* 1987, Gallagher *et al* 1987, Swinnea and Steinfink 1987). Studies of the structural transformation of $YBa_2Cu_3O_x$ show a change in the oxygen stoichiometry, going from orthorhombic at $x = 7$ to tetragonal at $x = 6$. The change in the oxygen stoichiometry takes place in the Cu–O planes, which lie between the planes containing the barium ions. As the tetragonal phase has been found to be non-superconducting (Hatano *et al* 1987), these studies strongly confirm the vital role that the oxygen content in the Cu–O planes plays in superconductivity.

The facts mentioned above suggest that there is a high mobility of the oxygen atoms at high temperatures. One can expect that at room temperature there is still a strong diffusion of oxygen through vacant sites. Therefore, one could expect some degradation of the superconducting properties when the samples are kept in air at room temperature for several weeks. In fact, there have been reports of changes in the colour of La–Sr–Cu–O samples (Giapintzakis *et al* 1987) which may present a transformation from tetragonal to an unidentified complex phase. This is credible because there are structural transitions below room temperature in this system. This is not the case in the Y–Ba–Cu–O system, in which no crystallographic transformations below room temperature have been found, except possibly a new low-temperature orthorhombic phase (Nakazawa *et al* 1987). The 1:2:3 phase is fairly stable at room temperature in the yttrium system, since we have measured samples with $T_c = 90$ K just after preparation and 3 months later and we found no changes in T_c. There have been reports of degradation in the

1 : 2 : 3 yttrium system exposed to water vapour or humid air (Hyde *et al* 1987, Yan *et al* 1987), in which the proposal of oxygen diffusion enhanced by the presence of water is put forward in order to explain the inhibition of superconductivity.

All this information stresses the importance of investigating the stability of other compounds in the 1 : 2 : 3 superconducting phase and its relationship to their transition temperatures. In this paper we report in detail the degradation of T_c observed in a sample of Gd–Ba–Cu–O kept in air at room temperature for 6 weeks.

A sample with a nominal composition $GdBa_2Cu_3O_{7-\delta}$ was prepared and measured using the method reported elsewhere (Escudero *et al* 1987a, b).

Figure 1 shows the resistance against temperature characteristics of the sample measured just after preparation (curve A) and after 6 weeks (curve B). Before degradation the sample was metallic with a superconducting transition beginning at 93 K. After degradation the sample had a semiconductor-like behaviour, showing a sharp anomaly in resistance at exactly the same temperature as that of the onset of superconductivity before degradation. This drop is not complete, and the behaviour became semiconducting again until a sudden drop in resistance started at around 36 K.

In order to clarify the above results, we made x-ray powder diffraction measurements on the degraded sample using a diffractometer fitted to a secondary monochromator and Cu Kα radiation. As slow-scanned diffraction profiles of the sample before degradation were not available, a new sample was prepared with exactly the same procedure as that used for the degraded sample.

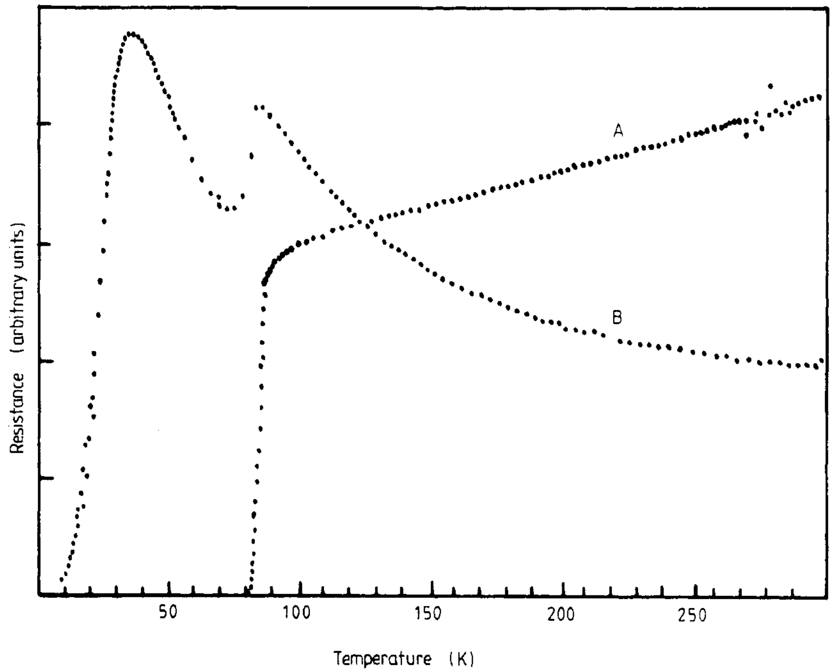

Figure 1. Temperature dependence of electrical resistance for a $GdBa_2Cu_3O_{7-\delta}$ sample: curve A, just after preparation; cuve B, after 6 weeks.

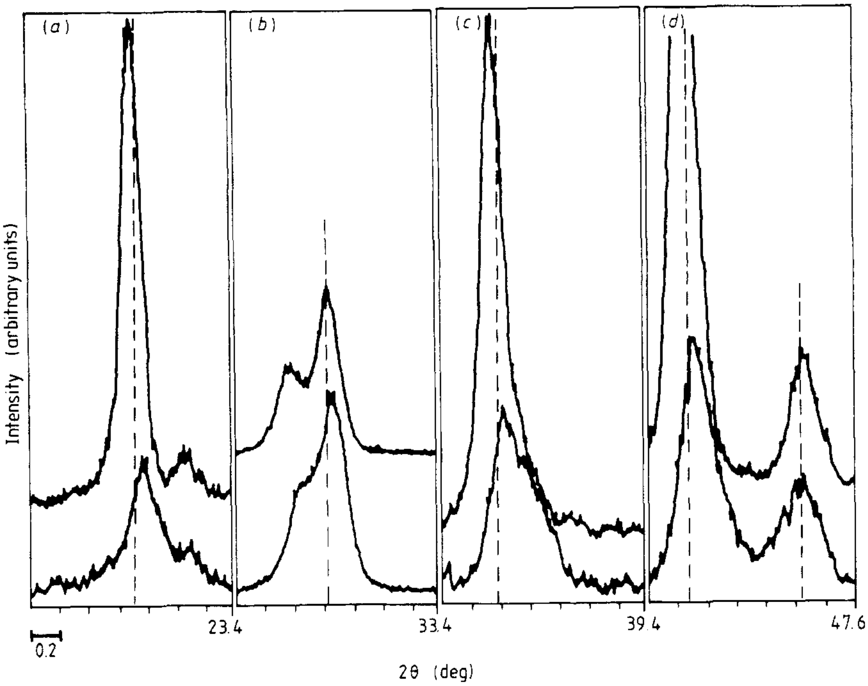

Figure 2. X-ray powder diffraction patterns: (*a*) new sample; (*b*) degraded sample.

Figures 2(*a*) and 2(*b*) show the diffraction patterns obtained from the new sample and from the degraded sample, respectively. The peaks in the diffraction pattern of the new sample correspond well to the orthorhombic 1 : 2 : 3 phase (Steinfink *et al* 1987). For the degraded sample, although the diffraction pattern reveals a basically orthorhombic structure, some small changes can be observed. These changes are presented in detail in figure 3, in which there are slow-scanned profiles taken from angular regions around selected key peaks, showing the profiles from the new sample in the upper parts of the figures and those from the degraded sample in the lower parts (the intensities are arbitrarily set in each case). Note that the shift of the peaks is almost zero, within experimental error. Furthermore, it should be noted that there is no sensible broadening of any peak after degradation. The only changes are in the relative intensities of the peaks.

Figure 3(*a*) corresponds to the doublet which arises from the degenerate reflection (003) + (010) and (100). Note that the degenerate peak is much more intense than (100) in the new sample, as in the perfectly orthorhombic structure. For the degraded sample the intensities of these two peaks are more similar. Figure 3(*b*) shows a doublet (on a highly reduced scale) which corresponds to the (013) reflection and a more intense degenerate peak from the (103) + (110) reflections. There is no obvious change in the relative intensities of these peaks, although there is a slight change in shape, suggesting that there is a leak of oscillator strength from the intense peak to the weak peak in the degraded sample. Figure 3(*c*) shows an unresolved doublet of the reflections (014) + (005) and (104). The change in the symmetry of this feature in the degraded

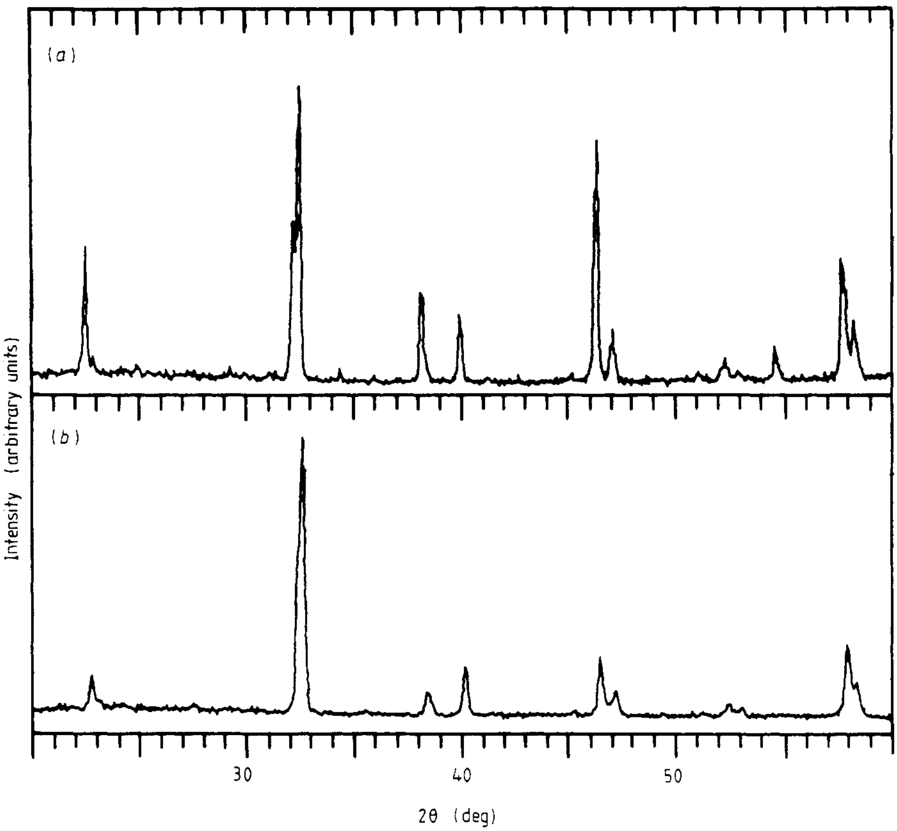

Figure 3. Slow-scanned diffraction patterns around selected peaks. The upper profiles correspond to the new sample and the lower profiles to the degraded sample. The arbitrary units of the intensity scale are different in each case.

sample suggests that a similar equalisation of intensities is occurring in these peaks, as in the former cases. Figure 3(*d*) shows the same phenomenon in the doublet due to the degenerate (020) + (006) and (200) reflections.

This information is sufficient to eliminate the possibility of having a tetragonal phase, or a second orthorhombic phase (Nakazawa *et al* 1987), with changes in the lattice parameter, which should show measurable shiftings and broadenings of the peaks. Furthermore, one could expect more peaks if one had a mixture of tetragonal and orthorhombic phases or, at least, a broadening of some of the peaks. None of these effects was observed.

The changes in the patterns can be explained by assuming that some of the perfect orthorhombic phase in a freshly prepared sample becomes disordered as it is exposed to air at room temperature for several weeks without change in the lattice parameters. This disorder consists of randomisation of the position of the oxygen atoms which form the Cu–O chains with respect to the crystallographic orientation *a* or *b*. If the length of the linear chains is reduced to a few cells, the orientations *a* or *b* lose their meaning, as far as x-rays are concerned. This picture is physically sound because, if there is an oxygen deficiency in some part of the crystal, the oxygen diffusion is enhanced and could help to form defects which, if numerous, lower the superconducting transition temperature.

There are phenomenological studies of the influence of oxygen ordering, and particularly twinning, on the superconducting properties of these oxides (Robledo and Varea 1988) which show a maximum transition temperature at a given concentration of oxygen, corresponding to the case when there are no vacancies in the barium planes. This theory is symmetrical for interchange of oxygen and vacancies. However, twinning and randomly arranged vacancies could both lower T_c.

The fact that one obtains a sharp variation in the resistivity of the degraded sample at exactly the same temperature as the sample without degradation (see figure 1) suggests that a certain amount of bulk material remains in the correct orthorhombic phase, while other parts of the sample, probably those close to the surface, lose oxygen at room temperature and the vacancies so created enhance the rearrangement of oxygen, causing degradation.

It has been pointed out (Raveau and Michel 1987) that defects in the oxygen arrangement can drastically affect the T_c of these materials. The present results support such ideas and emphasise the importance of changing the sample preparation procedure in order to eliminate these types of defect. One could imagine that 95 K is not the maximum T_c in the defect-free Y–Ba–Cu–O compound. Our studies are currently being extended to include longer periods of time and the effect of oxygenation in different high-T_c superconductors.

To summarise, the important points contained in this paper are as follows.

(i) Studies of the influence of the degradation of T_c in the 1:2:3 superconducting phase are exceedingly important, particularly those concerning the mobility of oxygen through the lattice.

(ii) It was shown that samples with gadolinium in the 1:2:3 phase present a degradation of T_c after a few weeks.

(iii) To date, no similar degradation has been detected in samples with yttrium.

(iv) The possibility that this degradation is due to a phase transformation was discarded.

(v) The x-ray patterns show that the effect of degradation is a systematic leak of oscillator strength from (hkl) to (khl) reflections. However, both patterns, with and without degradation, correspond well to the orthorhombic phase.

(vi) These results are explained by assuming a high mobility of oxygen at room temperature, enhanced by the presence of vacancies, thus facilitating oxygen disorder in the Cu–O planes. Possibly, gadolinium allows a higher mobility of oxygen in the structure than yttrium does.

(vii) Since the x-ray patterns show basically an orthorhombic symmetry for the structure of the bulk, we can infer that the degradation is just starting. This preliminary study should be continued for longer periods of time.

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