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Effect of heat treatment procedures on site preferences of Fe in $YBa_2Cu_3O_{7-D}$

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Abstract. Mössbauer spectra of $YBa_2Cu_{2\cdot85}Fe_{0\cdot15}O_{7-d}$ prepared using different heat treatment procedures have been obtained. The transition temperature varies from 23 to 53 K, depending on the procedure adopted for preparation. Associated with this are changes in the lattice structure. Mössbauer spectra reveal population of the four components and their relation to the decrease in the transition temperatures.

Keywords. Heat-treatment; site preferences.

1. Introduction

The reduction in the superconducting transition temperature (T_c) of $YBa_2Cu_3O_{7-d}$ can be due to a variety of reasons. The change of d from 0 to 1 results in the destruction of superconductivity. Alternatively, substitution of cations in the 123 superconductor with other ions reduces T_c. When Y is substituted by other rare earth elements (except Pr, Ce and Tb), magnetic or non-magnetic, there is no appreciable change in T_c, but when Cu is replaced by other transition metal ions, magnetic or non-magnetic, T_c reduces. Also, the change in T_c shows large dependence on the heat-treatment procedure used to make the oxide.

In the present study, we use Mössbauer spectroscopy, resistivity and DC susceptibility to investigate the cause of the reduction in T_c. Mössbauer spectroscopy can not only distinguish the two sites (Cu_1 and Cu_2) but also differentiate the different environments of the Cu_1 sites. Earlier studies have shown the presence of four components (Boolchand *et al* 1988; Bhargava *et al* 1988) in the Mössbauer spectra. These correspond to Cu_2 and the three different oxygen configurations around the Cu_1 sites. We keep the concentration of the dopant fixed and vary the heat-treatment procedure to vary the T_c and relate it to the variation in the relative population of the four sites to see if a certain configuration is more favourable to superconductivity than others.

2. Experimental

We prepared samples of composition $YBa_2Cu_{3-x}Fe_xO_{7-d}$, $x = 0\cdot15$, using the heat treatment procedures which can affect the oxygen ion concentration as well as their locations in the lattice, but cannot alter the distribution of the Fe ions. Y_2O_3, $Ba(NO_3)_2$, CuO and Fe_2O_3 (enriched in ^{57}Fe) were intimately mixed under ether. The dried powder was calcined at 950°C for several hours with intermediate grindings

Table 1. Lattice parameters of $YBa_2Cu_{2.85}Fe_{0.15}O_7$.

Sample No.	a(Å)	b(Å)	c(Å)	T_a (°C)	R deg./h	T_c (K)
1	3·8678	3·8684	11·6291	350	30	22·5
2	3·8439	3·8871	11·6470	450	50	52·7
3	3·8494	3·8670	11·6458	550	50	41·5
4	3·8601	3·8823	11·6381	550	25	64·35

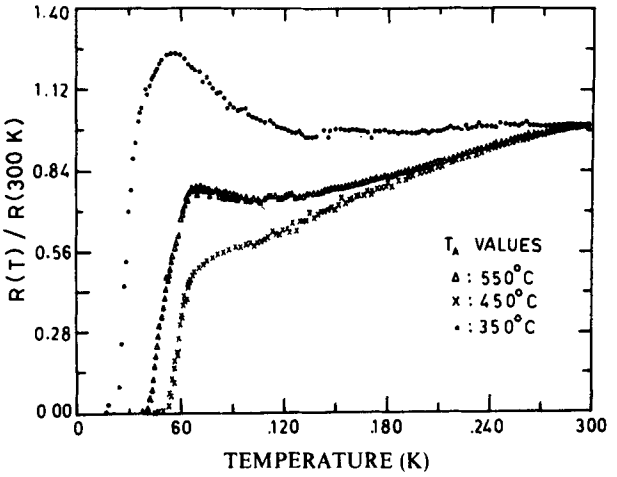

Figure 1. Resistivity of the samples obtained using the cooling rate of 50°C/h.

are pressings. It was sintered in flowing oxygen at 950°C for 17 h, cooled at rate $R°$ per hour to temperature T_a and kept there for 17 h and again cooled to 150°C with rate R per hour. T_a is referred to as the annealing temperature in the discussion below. The sample made with $T_a = 350$°C and $R = 50$°/h was further heated in argon atmosphere at 550 or 750°C for ≈ 24 h cooled at 100°C/h. X-ray analyses show all the oxides to be of single phase. The lattice parameters of the superconducting samples are given in table 1, along with T_a and R.

Resistivity was measured using the four-probe method. In the normal state, when R is 50°C/h, the oxide is metallic when T_a is 450°C and semiconducting when T_a is 350°C (figure 1). When the rate is slow (25°C/h), it is metallic when T_a is 450 or 550°C, but semiconducting when T_a is 350°C. On the other hand, when the cooling rate is high, the oxide is semiconducting even at $T_a = 450$°C.

DC susceptibility (χ) in the non-superconducting state was measured in the temperature from T_c to 300 K using magnetic field of 6 kOe. The temperature dependences were fitted to

$$\chi = \chi_0 + (C/(T-\theta))$$

using the least squares method. The results are summarized in table 2. The temperature dependences of $(\chi - \chi_0)^{-1}$ are shown in figure 2. To deduce the moment on iron, it is assumed that the Cu ions carry no moment. The negative values of θ show finite

Table 2. Results of DC susceptibility measurements. R = 50°/h.

T_a (°C)	$C \times 10^4$ emu/g	θ (K)	$\chi_0 \times 10^6$ emu/g	μ/Fe atom. (Bohr magneton)
550	5·46	−6·64	11·6	4·39
450	5·00	−4·90	6·9	4·21
350	5·62	−5·95	2·9	4·46

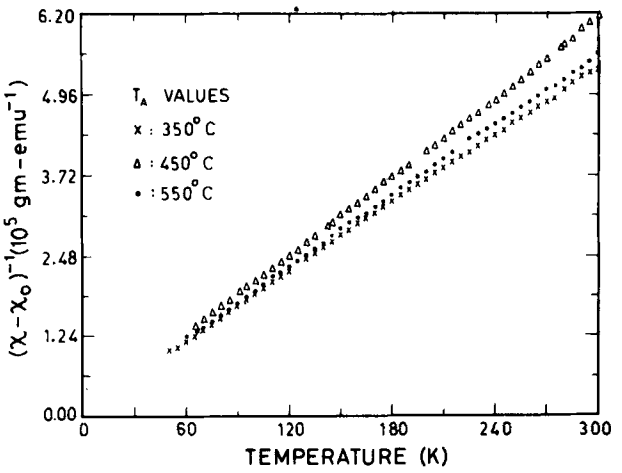

Figure 2. Temperature dependences of $(\chi - \chi_0)^{-1}$ of the samples obtained with the cooling rate of 50°C/h.

antiferromagnetic correlations between Fe ions which increase as T_c lowers. μ_{Fe} increases as the metallic nature of the oxide decreases.

Mössbauer spectra have been obtained using ^{57}Co in Rh source (figure 3). The paramagnetic spectra have been fitted to four symmetric doublets. The linewidths are kept the same for all the lines. Different spectra differ mainly in the relative intensities of the component spectra. The results are given in table 3. There is systematic variation in the relative intensities of the four component spectra with T_a. This is shown in figure 4. We find that the results obtained from Ar-annealed sample (obtained by heating in Ar at 750°C) also lie on these curves. It appears that the desorption of oxygen at this temperature does not affect the redistribution of relative intensities due to variation in T_a.

3. Discussion

There are four inequivalent sites occupied by Fe, viz the pyramidal Cu_2 site and the three inequivalent Cu_1 sites, which differ in the number and the symmetry of the oxygen ions in their immediate neighbourhood. We believe that component 1 corresponds to Fe at Cu_2 site, and components 2 and 4 correspond to Fe and Cu_1 sites with oxygen at O(1) sites present and vacant, respectively. The component 3

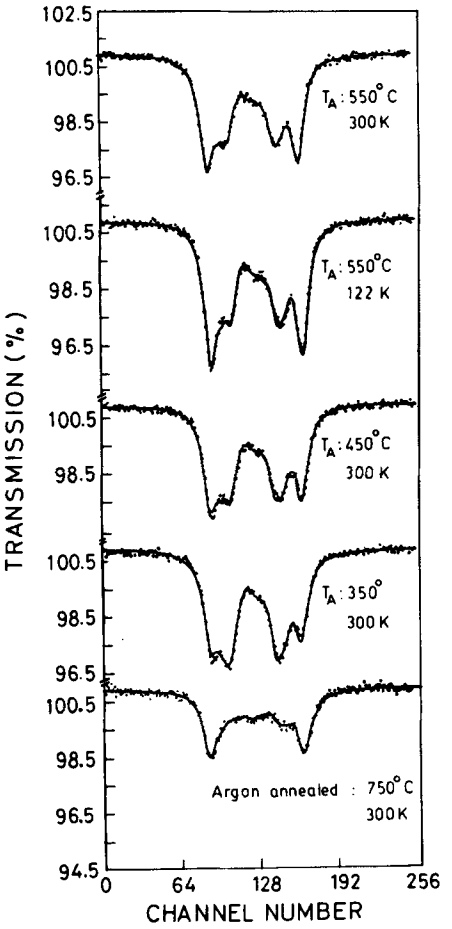

Figure 3. Mössbauer spectra of samples prepared with the cooling rate of 50°C/h.

Table 3. Result of analyses of paramagnetic spectra of $YBa_2Cu_{3-x}Fe_xO_7$.

	Component 1			Component 2			Component 3			Component 4		
T_a (°C)	IS mm/s	QS mm/s	RI %	IS mm/s	QS mm/s	RI %	IS mm/s	QS mm/s	RI %	IS mm/s	QS mm/s	RI %
550	0·27	0·20	7·4	0·22	0·94	25·0	0·21	1·34	19·3	0·26	1·95	48·3
450	0·26	0·16	6·8	0·20	0·95	30·6	0·19	1·35	21·1	0·26	1·97	41·5
350	0·27	0·13	5·1	0·19	0·97	37·9	0·19	1·36	21·8	0·255	1·95	35·3
750*	0·27	0·24	13·2	0·29	0·93	15·5	0·21	1·43	12·8	0·29	2·02	58·5
550*	0·12	0·29	6·6	0·32	0·82	8·5	0·20	1·48	9·0	0·28	2·01	75·9

$R = 50°$/h. *Annealing in argon atmosphere the sample obtained with $R = 50°$/h and $T_a = 350°C$

may correspond to Cu_1 site with any of the other oxygen configurations possible, e.g. an oxygen along *a* axis in addition to oxygen at both the O(1) sites or at one of the O(1) sites. For the present discussion, the exact assignment of the components to the specific oxygen configurations is not essential.

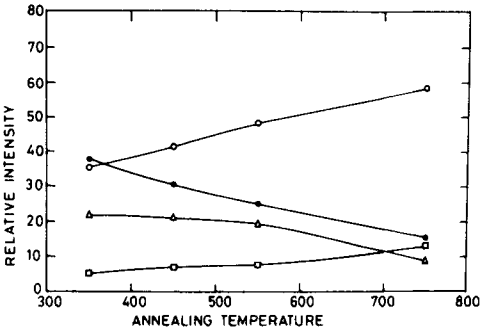

Figure 4. Dependences of the relative intensities on T_a of the samples prepared with the cooling rate of 50°C/h.

In figure 4 is shown the variation in the relative intensities of the four components with T_a when the rate of cooling is 50°/h. I_2 decreases and I_4 increases as T_a increases. The variation in I_3 and I_1 is regular and finite though small. However, T_c does not decrease (or increase) with T_a similarly. Thus, a relationship between the population of any particular configuration and T_c is not found. Consequently, the decrease in the transition temperature due to doping with Fe does not appear to be due to preferential population of any particular oxygen configuration in the lattice. Other factors which are related to the changes in T_c are as follows. T_c is found to increase with $(b-a)/a$, and decrease with increase in the lattice parameter c. Furthermore, T_c is found to decrease as the metallic nature of the oxide decreases.

References

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