

Effect of Fe substitution on the thermal expansion of the high T_c superconductor $Y_1Ba_2Cu_3O_y$

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Abstract. Thermal expansion measurements have been carried out on Fe substituted superconducting compounds $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ ($0 < x < 4\%$) using a high resolution dilatometer employing the three terminal capacitance technique. The experimental set up is sensitive enough to detect changes in α of less than $10^{-8} K^{-1}$. Results show that the jump $\Delta\alpha$ in the coefficient of linear thermal expansion at the superconducting transition temperature, T_c , increases almost linearly with Fe concentration. The normal state thermal expansion coefficient α first decreases, attains a minimum value around $x = 1\%$ and then increases for higher Fe concentrations. The oxygen content per unit formula is almost constant up to $x = 1\%$ and then increases rapidly with x . It has also been observed that the anomalous behaviour of α around 260K observed by Meingast *et al* [22] for Fe concentration $x = 5\%$ is due to inadequate annealing of the sample.

Keywords. Thermal expansion; high temperature superconductors; discontinuity in α ; iodometric titrations.

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1. Introduction

It is well-known that addition of magnetic impurity to a superconductor results in a dramatic reduction in the superconducting transition temperature due to the breaking-up of Cooper pairs because of the magnetic interactions [1]. This phenomenon is more complicated in high T_c superconductors since the addition of the impurity ions may also cause changes in the structure and the oxygen content of the unit cell. There are several reports of the effect of substitution for Cu in $Y_1Ba_2(Cu_{1-x}M_x)_3O_7$ ($M = Ti, V, Cr, Mn, Fe, Co, Ni, Zn, Al$ and Ga) [2–18]. The effect of substitution on the structural changes have been studied using X-ray diffraction [2–4] and neutron diffraction [2, 4, 6] where it is found that the substitution of Al, Co, Fe and Ga causes a structural change from orthorhombic to tetragonal for about 2–3% of substituent [2, 4]. Site occupancies have been investigated by using various methods such as neutron diffraction [2, 4, 6–13], EXAFS [10, 14, 15] and Mössbauer spectroscopy [4, 16–18]. There have been disagreements about the site preference of a particular substituent, but now there is a general agreement that Co, Ga substitute for Cu(I) site whereas Ni [11, 12] goes into the Cu(II) site. In case of Fe, for low concentrations Fe goes almost entirely to Cu(I) positions; for higher concentrations Cu(II) sites are also occupied. Experiments [19, 20] also show that doping by Fe, increases the pressure dependence, dT_c/dP of T_c . Zhernov and Chuklin [21] have suggested that this increase in dT_c/dP is due to the increase in the density

of states at the Fermi level. As a result the discontinuity $\Delta\alpha$, in the coefficient of thermal expansion α at the superconducting transition, should increase with increasing Fe concentration. Furthermore, because of the structural changes, the coefficient of thermal expansion in the normal state of $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ should also exhibit a dependence on x , the Fe concentration.

The only measurements on the thermal expansion of $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ compounds in the normal and superconducting state seem to have been carried out by Meingast *et al* [22]. Meingast *et al* have indeed found that $\Delta\alpha$, increases nearly by a factor of 4 as x is increased to 5%. The normal state value of α seems to decrease first and then increase with a minimum around $x = 1\%$. These variations in α , although well beyond the limits of experimental error, are quite comparable to the sample to sample variations [23, 24] generally observed in the thermal expansion measurements. It was therefore decided to carry out an independent study of the thermal expansion of $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ compounds to ascertain if the results obtained by Meingast *et al* truly reflect dependence of α on x or are only indicative of random sample to sample variations.

2. Experimental details

The samples were prepared by the conventional solid state reaction technique [25]. Appropriate amounts of Y_2O_3 , $BaCO_3$, CuO and Fe_2O_3 powders (all of purity 99.9%) were thoroughly mixed in an agate mortar and sintered in air at 930°C for 48 hr. This process was repeated three times in order to ensure homogeneous distribution of the substituted oxide. Finally the powder was reground and pressed into rectangular bars and annealed in flowing oxygen at 950°C for 48 hr. It was cooled slowly to 450°C and kept at this temperature in flowing oxygen for 72 hr, and then slowly cooled to room temperature. Typical XRD patterns shown in figure 1 indicate that the samples were single phased. The lattice parameters determined from the XRD patterns are given in table 1. It can be seen that the unit cell for all the samples is orthorhombic except for Fe = 4% which has a tetragonal structure. The transition temperature, T_c , and the transition width, ΔT_c , were determined by measuring the temperature dependence of resistance in the range 77–300 K using the standard four probe technique. The oxygen content of each sample was determined using an iodometric titration procedure suggested by Nazzari *et al* [26] with an accuracy of about ± 0.03 . These parameters along with the density, ρ , for each specimen are also given in table 1.

Measurements of linear thermal expansion were carried out using the three terminal capacitance dilatometer developed by Om Prakash *et al* [27]. One of the plates of a parallel plate capacitor is mounted on the sample. Heating the specimen changes the capacitance of this capacitor from which the change, Δl , in the length of the sample can be determined as a function of the temperature, T . The dilatometer design is such that there are no significant contributions to Δl from the specimen mounting system. The dilatometer thus essentially yields absolute values of α . Each sample was cooled to 77 K and then heated in steps of about 0.3 K to higher temperatures. At each temperature the capacitance of the parallel plate condenser was measured using a GR-1620 capacitance bridge in the three terminal configuration. The experimental arrangement is sensitive enough to detect changes of about $10^{-8}(\text{K})^{-1}$ in α .

Thermal expansion of $Y_1Ba_2Cu_3O_y$

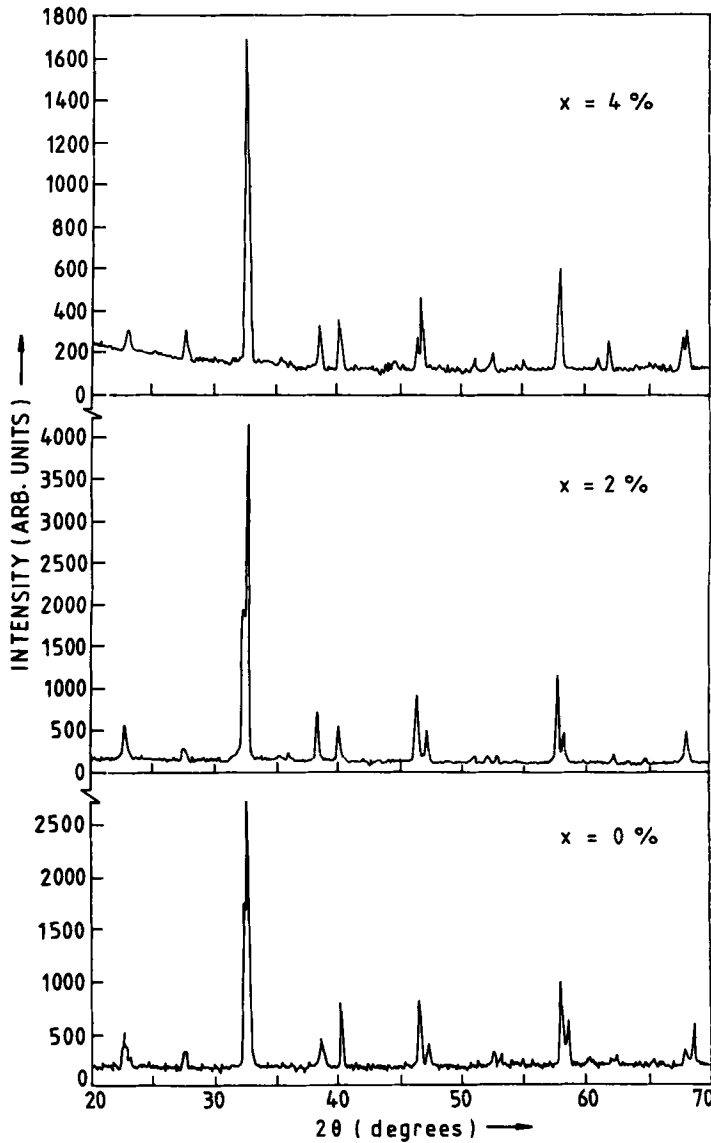


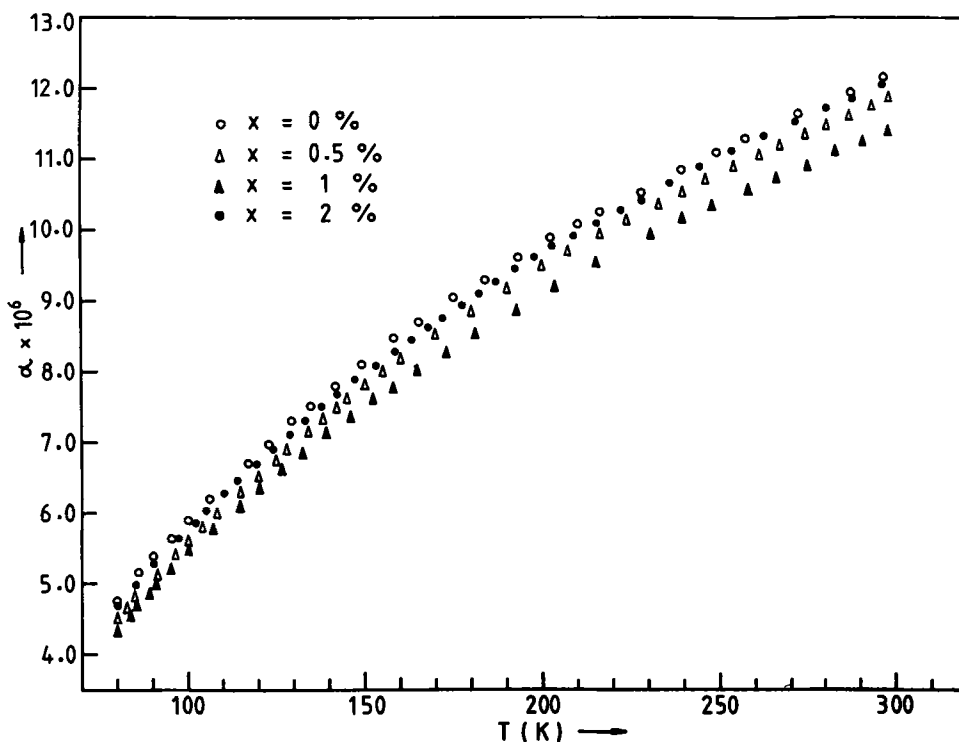
Figure 1. X-ray diffraction patterns for typical $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ compounds at room temperature.

3. Results and discussion

The temperature variation of the linear thermal expansion coefficient, α , in the temperature range $77\text{ K} < T < 300\text{ K}$ for various samples is shown in figure 2. Figure 3 shows the behaviour of α in the transition region. Because of the large transition width, the results do not show a sharp discontinuity in α ; instead α increases gradually as the specimen undergoes transition from normal to superconducting state. In order to estimate the discontinuity $\Delta\alpha$ for an ideal specimen, the following procedure, was adopted. Two polynomials in T one for $T < T_c$ and the other $T > T_c$ were fitted to

Table 1. Various parameters for the $Y_1Ba_2(Cu_{1-x}Fe_x)_3O_y$ compounds.

Lattice parameters							
x (%)	a (Å) (± 0.001)	b (Å) (± 0.001)	c (Å) (± 0.003)	T_c (K)	ΔT_c (K)	ρ (g/cm ³)	y (± 0.003)
0	3.823	3.888	11.681	91.3	1.4	5.32	6.93
0.5	3.824	3.886	11.682	90.5	1.6	5.27	6.94
0.75	3.826	3.886	11.681	89.5	1.8	5.30	6.93
1.0	3.827	3.884	11.683	89.2	2.0	5.35	6.92
1.25	3.826	3.884	11.683	88.6	2.2	5.31	6.96
1.5	3.828	3.881	11.680	87.9	2.9	5.28	6.99
2.0	3.830	3.879	11.679	86.9	3.1	5.33	7.02
4.0	3.865	3.864	11.675	—	—	5.37	7.06

**Figure 2.** Temperature dependence of linear thermal expansion coefficient α for various specimens.

the experimental data of $\Delta l/l_0$ as a function of temperature T (l_0 = length of the sample at 77 K). Differentiation of the polynomials, thus obtained gives α as a function of temperature. The jump in α at T_c , given by $\Delta\alpha$, was determined by extrapolating the two branches of α vs T curves thus obtained (solid lines in figure 3) to T_c . The variation of $\Delta\alpha$ with Fe concentration obtained by using the extrapolation procedure is shown in figure 4(a) along with the results obtained by Meingast *et al* [22]. It can

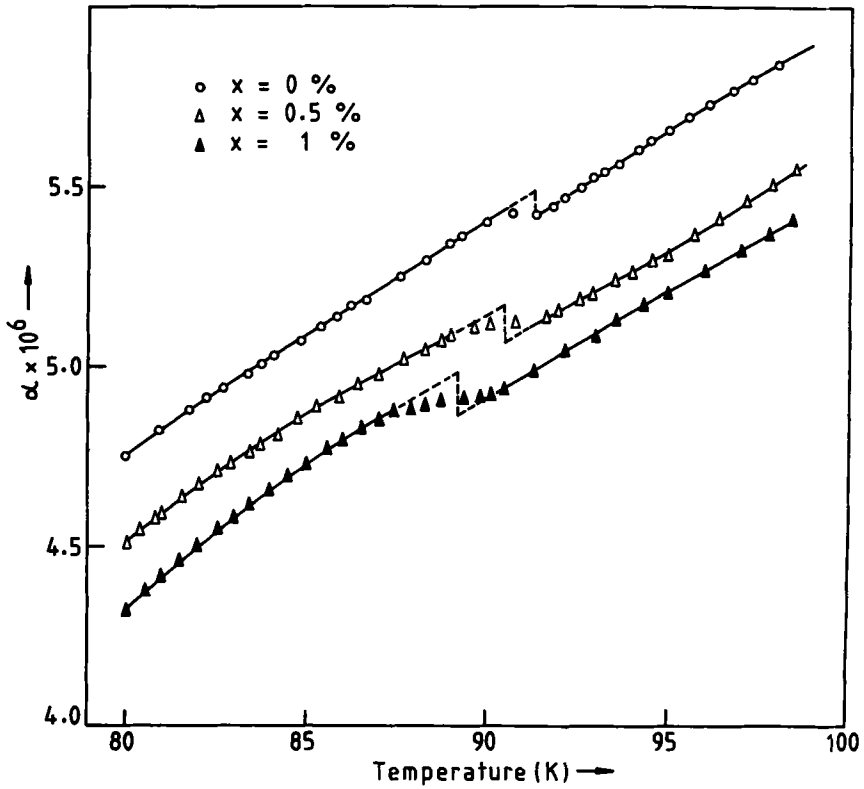


Figure 3. Behaviour of α in the vicinity of the transition temperature for some of the specimens.

be seen that the present results showing an almost linear dependence of $\Delta\alpha$ on x are in good agreement with those of Meingast *et al.* It might be mentioned that although T_c and oxygen content do not change appreciably (table 1) for Fe concentrations up to 1% there is almost a two-fold increase in $\Delta\alpha$.

Figure 4(b) shows the observed variation of the normal state α values (at $T = 95$ K) as a function of Fe concentration; the data of Meingast *et al.* are also shown for comparison. Although there is significant difference in the absolute values of α , the dependence on Fe concentration observed by us is almost identical to that of Meingast *et al.* As x is increased, α at first decreases, attaining a minimum value around $x = 1\%$ and then increases for further increase of x . Figure 4(c) shows the variation of oxygen content y of the unit cell with Fe concentration. The oxygen content y is almost independent of Fe concentration up to about 1% and then increases rapidly with x . It thus appears that the minimum value of α occurs at that value of x at which there is a rapid increase in the oxygen content of the unit cell.

Meingast *et al.* [22] have reported that in addition to the jump $\Delta\alpha$ at T_c , a specimen with high Fe concentration e.g. $x = 5\%$, showed additional anomalies e.g. a jump in α at $T = 250$ K, hysteresis in the temperature region $50 < T < 250$ K and non-reversible length changes at low temperatures ($T < 45$ K). They have also suggested that these anomalies are perhaps indicative of some structural transformation in the specimen and are characteristic features of a particular specimen. It is quite likely

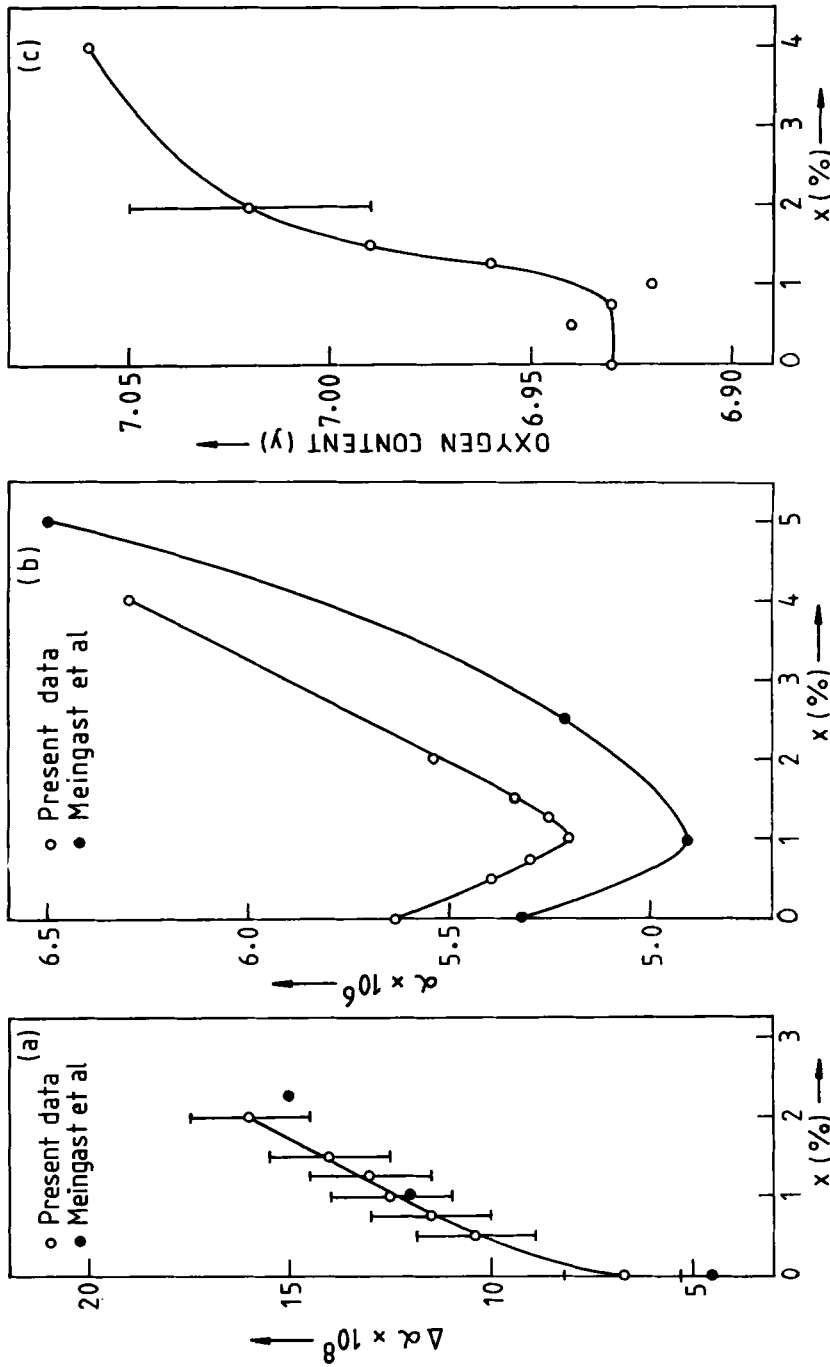


Figure 4. (a) The jump in the coefficient of thermal expansion as a function of Fe concentration, x . (b) Variation of the coefficient of linear thermal expansion in the normal state ($T=95\text{K}$) with Fe concentration. (c) Oxygen content variation with Fe concentration.

Thermal expansion of $Y_1Ba_2Cu_3O_x$,

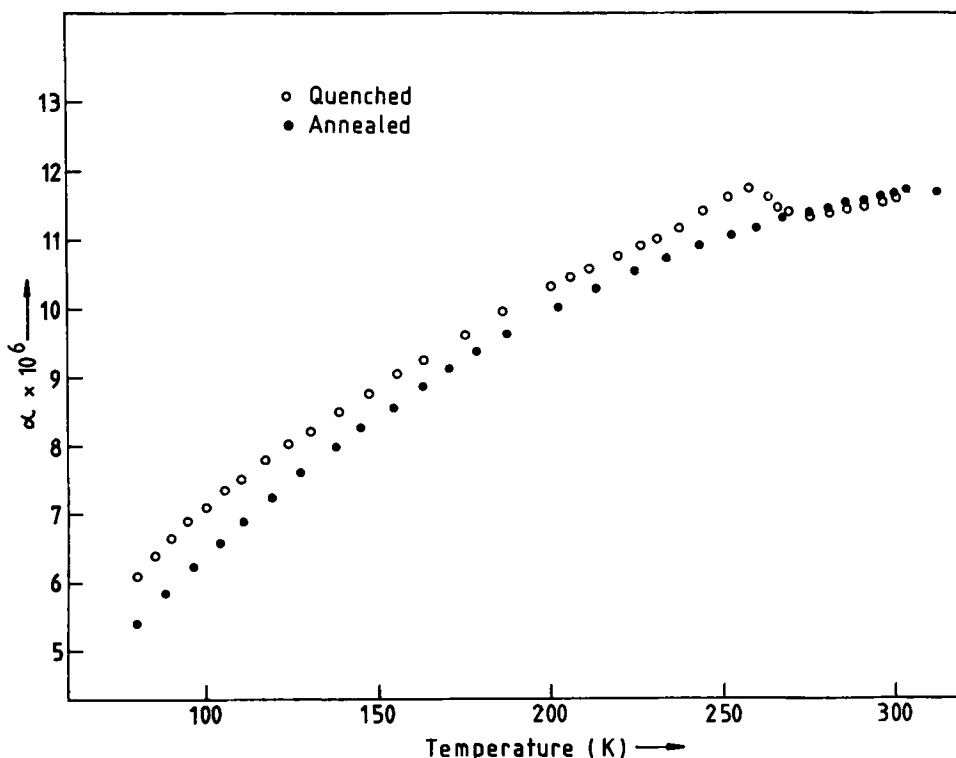


Figure 5. Thermal expansion coefficient vs temperature for the quenched and unquenched specimens with $x = 4\%$. The quenched specimen clearly shows an anomaly around 260 K.

that these anomalies arise because of internal strains or inhomogeneities in the specimen due to improper annealing. In order to understand the nature of the anomaly at $T = 250$ K the sample containing 4% Fe was deliberately quenched from 200°C to room temperature. The measurements of the thermal expansion were then repeated to this quenched sample. Figure 5 compares the observed temperature dependence of α for both the quenched and unquenched samples. It can be seen that the quenched sample shows an anomaly around 260 K similar to that observed by Meingast *et al*; the unquenched sample does not exhibit any such anomaly. In addition, in the temperature range $77 < T < 260$ K, the α values for the quenched sample are larger than those for the unquenched specimen. For $T > 260$ K the behaviour of both the samples is almost identical. These results do seem to suggest that presence of small strains in samples can markedly affect the temperature dependence of the linear thermal expansion coefficient and can also perhaps lead to the type of anomalies observed by Meingast *et al*. It may, however, be pointed out [28, 29] that there is strong evidence for phase instability of $Y_1Ba_2Cu_3O_{7-\delta}$ system at low temperature, particularly around $T = 200^\circ\text{C}$, where [29] ageing for an extended length of time leads to a decomposition into oxygen ordered orthorhombic and vacancy ordered tetragonal phases. It is quite likely that such phase decomposition also takes place in the Fe doped samples and so leads to the observed anomaly at $T = 260$ K. The sample in the present study was kept at $T = 200^\circ\text{C}$ for only ~ 8 h. The phase

decomposition during this ageing period is likely to be rather small. However, further investigations are needed before the nature of the anomaly at 260 K can be unambiguously understood.

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References

- [1] A A Abrikosov and L P Gorkov, *Sov. Phys. – JETP* **12**, 1243 (1960)
- [2] G Xiao, M Z Cieplak, D Musser, A Gavrin, F H Streitz, C L Chien, J J Rhyne and J A Gotaas, *Nature (London)* **332**, 238 (1988)
- [3] Y Maeno, T Tomita, M Kyogoku, S Awaji, Y Aoki, K Hoshino, A Minami and T Fujita, *Nature (London)* **328**, 512 (1987)
- [4] J M Tarascon, P Barboux, P F Miceli, L H Greene and G W Hull, *Phys. Rev.* **B37**, 7458 (1988)
- [5] Y Xu, R L Sabatini, A R Moodenbaugh, Y Zhu, S G Shyu, M Suenaga, K W Dennis and R W McCallum, *Physica C* **169**, 205 (1990)
- [6] P Bordet, J L Hodeau, P Strobel, M Marezio and A Santoro, *Solid State Commun.* **66**, 435 (1988)
- [7] A M Balagurov, G M Mironova, A Pajaczkowska and H Szymczak, *Physica C* **158**, 265 (1989)
- [8] G Roth, G Heger, B Renker, J Pannetier, V Caignaert, M Hervieu and B Raveau, *Z. Phys.* **B71**, 43 (1988)
- [9] R Sonntag, D Hohlwein, A Hoser, W Prandl, W Schäfer, R Kiemel, S Kemmler-Sack, S Losch, M Schlichenmaier and A W Hewat, *Physica C* **159**, 141 (1989)
- [10] H Maeda, A Koizumi, N Bamba, E Takayama-Murocmachi, F Izumi, H Asano, K Shimizu, H Moriwaki, H Maruyama, Y Kuroda and H Yamazaki, *Physica C* **157**, 483 (1989)
- [11] H Shaked, J Faber Jr, B W Veal, R L Hitterman and A P Paulikas, *Solid State Commun.* **75**, 445 (1990)
- [12] T Kajitani, K Kusaba, M Kikuchi, Y Syono and M Hirabayashi, *Jpn. J. Appl. Phys.* **27**, L354 (1988)
- [13] S Katano, T Matsumoto, A Matsushita, T Hatano and S Funahashi, *Phys. Rev.* **B41**, 2009 (1990)
- [14] F Bridges, J B Boyce, T Claeson, T H Geballe and J M Tarascon, *Phys. Rev.* **B39**, 11603 (1989)
- [15] M Qian, E A Stern, Y Ma and R Ingalls, *Phys. Rev.* **B39**, 9192 (1989)
- [16] A Simopoulos and D Niarchos, *Phys. Rev.* **B38**, 8931 (1988)
- [17] E R Bauminger, M Kowitz, I Felner and I Nowik, *Solid State Commun.* **65**, 123 (1988)
- [18] D Heckel, I Nowik, E R Bauminger and I Felner, *Phys. Rev.* **B42**, 2166 (1990)
- [19] M Kurisu, K Kumagai, Y Maeno and T Fujita, *Physica C* **152**, 339 (1988)
- [20] J G Huber, W J Liverman, Y Xu and A R Moodenbaugh, *Phys. Rev.* **B41**, 8757 (1990)
- [21] A P Zhernov and E P Chuklin, *Phys. Status. Solidi* **B173**, 691 (1992)
- [22] C Meingast, R Ahrens, B Blank, H Burkle, B Rudolf and H Wuhl, *Physica C* **173**, 309 (1991)
- [23] G K White, S J Collocott, R Driver, R B Roberts and A M Stewarts, *J. Phys.* **C21**, 631 (1988)
- [24] Om Prakash, Ashok Rao, O Prakash and P N Dheer, *Pramana – J. Phys.* **41**, 421 (1993)
- [25] S N Das, R Kapoor, S S Dubey and P N Dheer, *Physica* **B163** 245 (1990)

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- [26] A I Nazzal, V Y Lee, E M Engler, R D Jacowitz, Y Tokura and J B Torrance, *Physica C* **153-155**, 1367 (1988)
- [27] Om Prakash, Ashok Rao and P N Dheer, *Pramana - J. Phys.* **39**, 665 (1992)
- [28] A G Khachatryan and J W Morris Jr, *Phys. Rev. Lett.* **64**, 76 (1990)
- [29] T S Radhakrishnan, J Janaki, G V N Rao, S Kalavathi, V S Sastry, Y Hariharan, M P Janawadkar, K Govinda Rajan, P Parameswaran and O M Sreedharan, *Pramana - J. Phys.* **32**, L705 (1989)