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Thermal expansion of orthorhombic and tetragonal phases of the high T_c superconductors $RE_1Ba_2Cu_3O_y$ (RE = Y, Gd, Dy)

OM PRAKASH, ASHOK RAO, O PRAKASH* and P N DHEER
Department of Physics and Astrophysics, University of Delhi, Delhi 110007, India
*Materials Science Division, Indian Institute of Technology, Bombay 400076, India

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Abstract. Measurements of the coefficient of linear thermal expansion α have been carried out for the orthorhombic and tetragonal phases of $RE_1Ba_2Cu_3O_y$(RE = Y, Gd, Dy) compounds using a high resolution capacitance dilatometer in the temperature range 77–300 K. All the superconducting samples exhibit a jump $\Delta\alpha$ at their respective transition temperatures, T_c. Evidences of, sample-to-sample variation in α values and dependence of $\Delta\alpha$ on the sample preparation conditions, have been obtained. The non-superconducting samples, in general, exhibit lower values of α possibly because of lowering of oxygen content.

Keywords. Thermal expansion; high temperature superconductors; discontinuity in α; growth conditions; iodometric titration.

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1. Introduction

Thermal expansion of solids provides a useful experimental tool for the study of phase transitions and dynamics of lattice vibrations. A second order phase transition like the transition from normal to superconducting state is, for example, characterized by a discontinuity in the coefficient of thermal expansion α, at the transition temperature T_c. Early experiments on high-T_c superconductors failed to show any discontinuity in α [1–5] possibly because of the inadequate sensitivity of measuring technique. Later, more accurate measurements revealed a clear discontinuity $\Delta\alpha$ [6–12]. However, the reported values of $\Delta\alpha$ vary over a wide range. For example Meingast *et al* [10] found $\Delta\alpha = 4{\cdot}5 \times 10^{-8}(\mathrm{K})^{-1}$ whereas Schnelle *et al* [8] have reported $\Delta\alpha = 8 \times 10^{-8}(\mathrm{K})^{-1}$. Occasionally additional anomalies, such as a first order transition at a temperature above T_c [12, 13] and time dependent changes in the specimen dimensions [14] have also been reported. These anomalies are probably characteristic of the samples used and do not represent intrinsic property of the material. Sometimes anomalies have also been observed [3] which are probably due to the expansion of the sample mounting system. Om Prakash *et al* [15] have recently developed a dilatometer based on the three terminal capacitance technique in which there are no significant changes in the dimensions of the sample mounting system on heating the sample and thus, in principle, yields absolute measurements of α. In practice, however, a small correction term arises because of the expansion of the condenser plate mounted on the sample. This correction term can however, be

accurately determined experimentally. It was therefore interesting to carry out measurements on high T_c superconductors using this dilatometer. This paper reports results obtained on $RE_1Ba_2Cu_3O_y$ (where RE = Y, Gd, Dy) compounds. All the superconducting samples exhibit a jump $\Delta\alpha$ at their respective transition temperatures, T_c. However, none of the specimens has shown additional anomalies of the type mentioned above. Evidence has also been obtained that the values of $\Delta\alpha$ depend upon the conditions of specimen preparation. Measurements have also been carried out on non-superconducting (tetragonal phase) samples of each rare earth compound.

2. Experimental details

Specimens of each compound were prepared using the standard solid state reaction technique [16]. Appropriate amounts of RE_2O_3 (RE = Y, Gd, Dy), $BaCO_3$ and CuO (all > 99·9% pure) were thoroughly mixed and fired at 930°C in flowing oxygen for 24 h. The mixing and firing was repeated three times to ensure homogeneity. The powder was pressed into cylindrical rods using isostatic press. The rods were then sintered at 950°C in flowing oxygen for 48 h followed by slow cooling to 450°C. They were kept at 450°C for 72 h and then gradually cooled to room temperature. The specimens were examined by X-ray diffraction at room temperature using PW-1820 X-ray diffractometer. The X-ray diffraction analysis of all the samples confirm their being single phased. The X-ray diffraction patterns for typical superconducting specimens are shown in figure 1. Non-superconducting samples were obtained by rapid cooling from 950°C to liquid nitrogen temperature. The X-ray diffraction pattern confirmed the tetragonal structure of the non-superconducting samples.

The transition temperature T_c, width ΔT_c of the resistive transition, the susceptibility χ at 77 K and the oxygen content y have been measured for each specimen. T_c and ΔT_c were determined by measuring the temperature dependence of the electrical resistance in the range 77–300 K using the standard four-probe technique. χ was determined using the mutual inductance technique. The oxygen content of each sample was determined using the iodometric titration procedure suggested by Nazzal *et al* [17]. The procedure has the advantage that systematic errors including those associated with the calibration are eliminated. Reproducibility was checked by performing the titration twice for each sample. High purity argon gas was used to create an inert atmosphere. The accuracy in the determination of oxygen content was about $\pm 0{\cdot}03$.

Measurements of linear thermal expansion α were carried out in the temperature range 77–300 K using the three terminal capacitance dilatometer as developed by Om Prakash *et al* [15]. The apparatus has a sensitivity $\Delta l/l_0 \sim 10^{-8}$. The dilatometer was evacuated and filled with helium gas at low pressure. This was followed by cooling the specimen to liquid nitrogen temperature. After the specimen attained the bath temperature, the dilatometer was evacuated to a pressure of about 10^{-6} Torr. The specimen was heated to successively higher temperatures T. At each temperature it was made sure that the specimen was in thermal equilibrium and the changes $(l_T - l_{77})$ in the length of the specimen was measured by the usual three terminal capacitance technique. In the present set up we could control temperature within ± 5 mK. The performance of this dilatometer was first tested by the measurement of the linear thermal expansion of a copper rod and the results are reported elsewhere [15]. It may be mentioned that the results on copper are in good agreement with literature values. A copper-constantan thermocouple was used to measure the

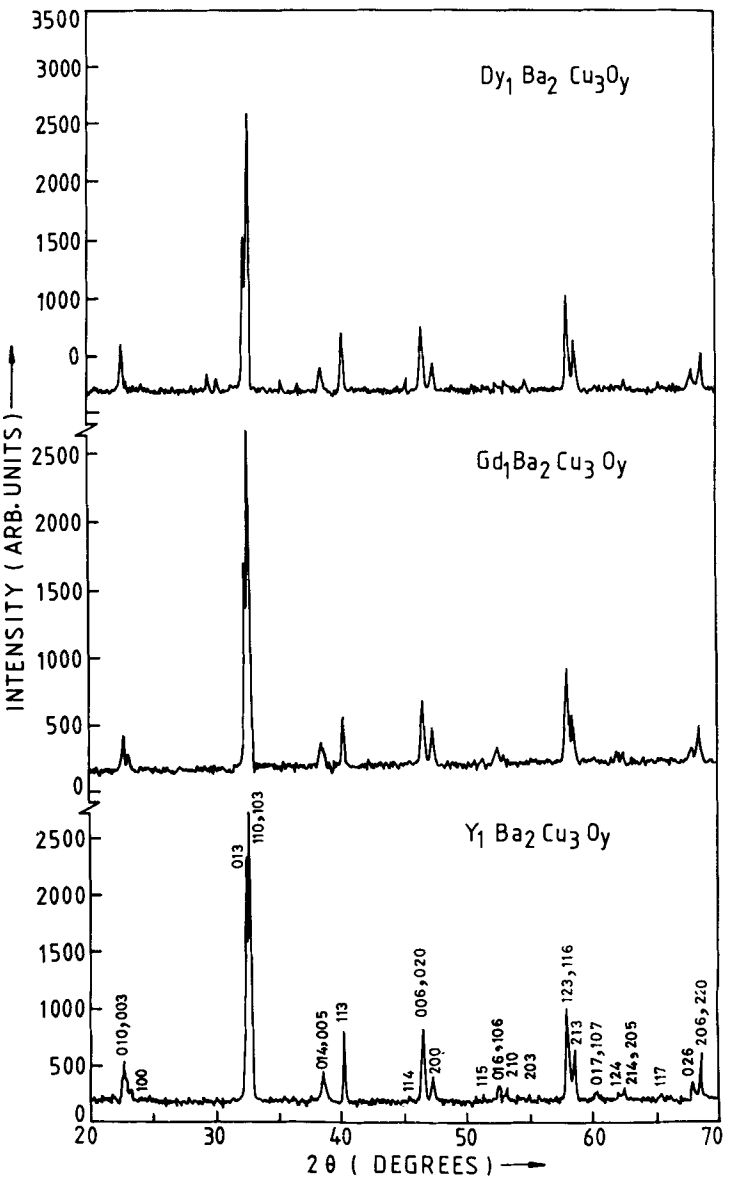

Figure 1. X-ray powder diffraction patterns for typical compounds at room temperature.

temperatures. A differential thermocouple was used to check if there were any temperature gradients along the sample. In the present investigation the temperature difference between the two ends of the specimen was always less than 5 mK.

3. Results and discussion

The observed temperature dependence of the thermal strain $(\Delta l/l_0) = (l_T - l_{77})/l_{77}$ for a typical specimen is shown in figure 2. The only anomaly seen is the change in the slope at the onset of the transition (around 91·8 K)—shown on an enlarged scale in

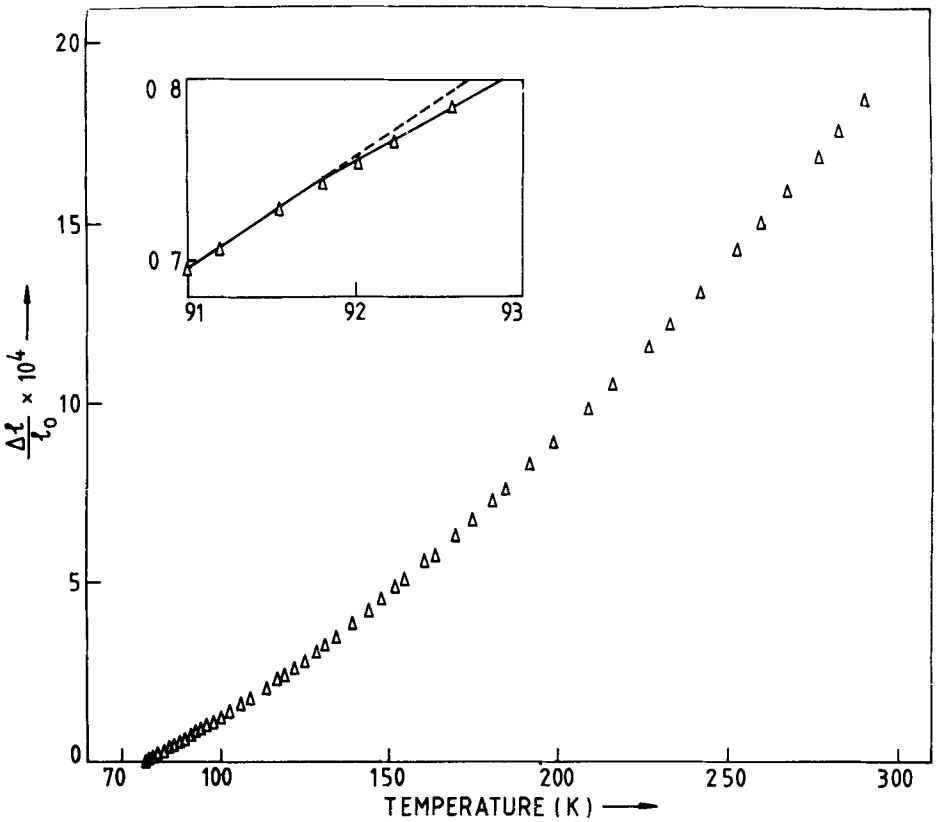

Figure 2. Thermal strain, $\Delta l/l_0$ for the sample Y_2, as a function of temperature.

the inset. The coefficient of linear thermal expansion α was determined by the following procedure. The $(\Delta l/l_0)$ data were fitted using two fifth order polynomials in temperature T—one below T_c and the other above T_c. At any temperature the thermal expansion coefficient α was obtained by differentiating the polynomial. The error in determination of α is estimated to be about $\pm 1{\cdot}5 \times 10^{-8}(\mathrm{K})^{-1}$. Figure 3 shows the behaviour of coefficient of linear thermal expansion $\alpha = (l_{T_1} - l_{T_2})/(T_1 - T_2)l_{77}$ in the temperature range $77 < T < 300$ K. Figure 4 shows the behaviour of α in the transition region for a typical sample. In conventional superconductors like Sn, the superconducting transition is very sharp—transition widths are usually of about 0·001 K in carefully prepared specimens. As a result a sharp discontinuity is observed in the thermal expansion coefficient at the transition temperature. In contrast, the superconducting transition in high T_c superconductors is quite broad (~ 1 K even in carefully prepared samples). Consequently the discontinuity in α is smeared and the experimental results instead of showing a sharp discontinuity in α at T_c, show a gradual change in α as the samples undergo transition from superconducting to normal state. These results, therefore, can at best be used to estimate the jump $\Delta\alpha$ in the coefficient of linear expansion α at the transition temperature T_c by extrapolating the portions of α vs T curves, below and above the transition temperature, to T_c as shown by solid lines in figure 4. The error in determination of $\Delta\alpha$ is estimated to be about $\pm 1{\cdot}5 \times 10^{-8}(\mathrm{K})^{-1}$. In order to ascertain that the values of $\Delta\alpha$ thus obtained

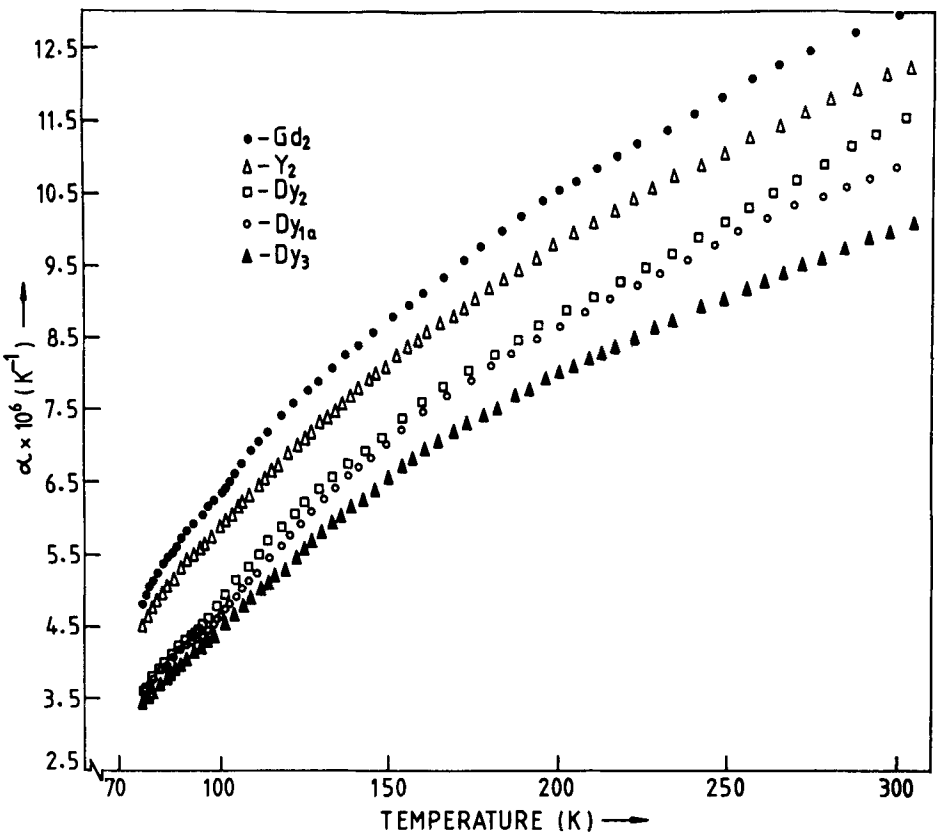

Figure 3. Temperature dependence of the linear thermal expansion coefficient α.

are indeed associated with the superconducting transition (and not due to any anomalies introduced by the extrapolation procedure), the same procedure was applied to the non-superconducting samples. It was found that in such samples the difference $\delta\alpha$ (at $T \approx 92$ K) in the two extrapolated values of α was always less than $1 \times 10^{-8}(\mathrm{K})^{-1}$ which is well within the experimental error. Some of the important parameters for all the specimens viz. the transition temperature T_c, oxygen content y, density ρ and the discontinuity $\Delta\alpha$ at T_c are depicted in table 1. Table 2 shows the α values for all the samples at three different temperatures.

It can be seen from figure 3 and table 2 that for all the superconducting compounds the behaviour of α is slightly specimen dependent. The reasons for this are not quite clear; it might probably be due to slight and unavoidable differences in the conditions of sample growth. Similar results have been reported earlier (see e.g. White *et al* [3]). For a given compound, α for superconducting phase has always been found to be greater than that for the non-superconducting phase. This could be due to the lower oxygen content of the non-superconducting sample. Olekhnovich *et al* [18] have indeed observed that in $Y_1Ba_2Cu_3O_y$ compounds, α decreases with decrease in the oxygen content y. It might also be mentioned that our values of α for Y and Dy compounds are in good agreement with those of White *et al* [3] and Schnelle *et al* [8]. Similarly α for Gd compounds agrees well with the results obtained by Kadowaki *et al* [6]. The present results, on the relative values of α for Y, Gd and Dy compounds, however, do not seem to agree with the results obtained by del Moral *et al* [4]. The

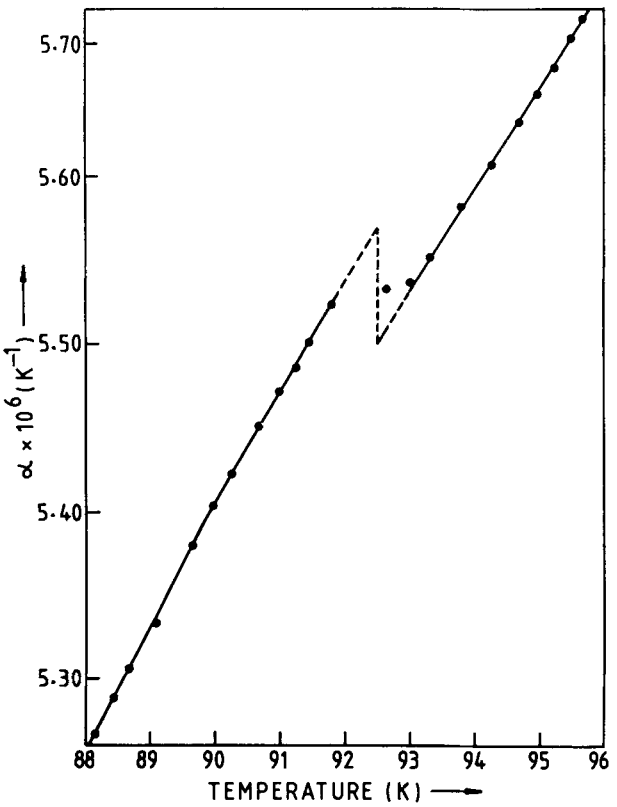

Figure 4. Behaviour of α in the vicinity of the transition temperature for the sample Y_2.

Table 1. The characteristic parameters of samples.

Sample	ρ gm/cm^3	y	T_c (K)	ΔT_c (K)	χ (at 77 K) (S.I. units)	$\Delta\alpha$ ($\times 10^{-8}$) (K)$^{-1}$
Y_1	5·23	6·93	92·0	1·4	−0·81	6·3
Y_2	5·54	6·92	92·4	1·0	−0·84	6·7
Y_3	5·54	6·43	not superconducting			
Gd_{11}	5·11	6·85	89·3	3·8	−0·78	3·1
Gd_1	5·11	6·93	90·6	1·2	−0·83	8·2
Gd_2	5·06	6·91	92·0	0·9	−0·85	8·7
Gd_3	5·06	6·39	not superconducting			
Dy_{11}	5·49	6·83	90·5	4·1	−0·73	7·2
Dy_1	5·49	6·92	92·0	1·1	−0·81	10·5
Dy_2	5·13	6·93	91·5	1·0	−0·84	11·4
Dy_3	5·13	6·45	not superconducting			

Table 2. The thermal expansion coefficient α of samples at various temperatures.

Sample	$\alpha(\times 10^{-6})\,(K)^{-1}$ 80 K	100 K	250 K
Y_1	4·78	5·92	11·2
Y_2	4·76	5·88	10·60
Y_3	4·66	5·75	10·32
Gd_{11}	4·96	6·13	11·47
Gd_1	5·00	6·20	11·68
Gd_2	5·13	6·38	11·92
Gd_3	4·90	6·12	10·88
Dy_{11}	3·72	4·62	9·60
Dy_1	3·76	4·68	9·91
Dy_2	3·82	4·87	10·15
Dy_3	3·60	4·50	9·05

present study shows α values to be highest for Gd compounds and lowest for Dy compounds. On the other hand del Moral *et al* [4] have observed highest values for Dy and lowest values for Y compounds.

It is clear from table 1 that the values of $\Delta\alpha$ obtained in the present investigation for various superconducting compounds are in reasonable agreement with those reported in the literature. The absence of quantitative agreement between the results of different investigations might be due to the slight differences in the specimen growth conditions especially the final heat treatment. Experimental evidences for such a dependence on the condition of heat treatment has been obtained both for Gd and Dy samples (Gd_{11} and Dy_{11}). Sample Gd_{11} kept during the initial preparation at 450 °C in flowing oxygen for 36 h showed a jump $\Delta\alpha = (3{\cdot}1 \pm 1{\cdot}5) \times 10^{-8}(K)^{-1}$. When the same sample was further annealed at 450 °C for another 36 h, the jump increased to $(8{\cdot}2 \pm 1{\cdot}5) \times 10^{-8}(K)^{-1}$. The absolute values of α obtained before and after additional annealing were however, nearly same. The oxygen content also increased only slightly viz. from $y = 6{\cdot}85$ to 6·93. ΔT_c however, showed a marked change; decreasing from 3·8 to 1·2 K. Similar results were obtained for Dy samples and are shown in table 1.

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