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1990 J. Phys.: Condens. Matter 2 3231

(http://iopscience.iop.org/0953-8984/2/14/007)

J. Phys.: Condens. Matter 2 (1990) 3231–3236. Printed in the UK

A structural phase transition in $YBa_2Cu_3O_7$ at high pressures

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Received 11 October 1989, in final form 21 November 1989

Abstract. We have performed detailed high-pressure studies up to 110 kbar to investigate the nature of the structural phase of $YBa_2Cu_3O_7$ using energy-dispersive diffraction techniques. We observed a reversible orthorhombic to tetragonal phase transition at between 70 and 80 kbar. During compression it is found that the c axis has the highest compressibility; thus c/a decreases. A possible explanation for the relationship between the variation of structure with pressure and the transition temperature is given.

1. Introduction

Since the discovery of the high-temperature superconducting ceramic oxides La_2CuO_4 (Bednorz and Müller 1986) and $YBa_2Cu_3O_7$ (Wu *et al* 1987) there have been an enormous number of studies designed to increase the critical temperature and to provide an understanding of the mechanism responsible for superconductivity. It has been confirmed that, in the latter material, a single phase $YBa_2Cu_3O_{9-x}$ ($x \simeq 2$) is responsible for the high transition temperature (Cava *et al* 1987).

It is well known that pressure has a positive effect on T_c in La–M–Cu–O (Chu *et al* 1987a, b, Dietrich *et al* 1987a, Kurisu *et al* 1987, Yamada *et al* 1989, Yomo *et al* 1987). But for $YBa_2Cu_3O_7$, some discrepancies have been found regarding the effect of pressure on T_c. Hor *et al* (1987) and Yoshida *et al* (1987) observed that pressure has a small positive effect on T_c comparable to that observed in La–M–Cu–O. Borges *et al* (1987) observed that pressure has a positive effect and T_c is enhanced at a rate of about 0.09 K kbar^{-1} for $YBa_2Cu_3O_x$ and 0.19 K kbar^{-1} for $YbBa_2Cu_3O_x$. Baszynski *et al* (1987) observed a large effect of pressure on T_c for $(Y_{1.2}Ba_{0.2})_4Cu_4O_{16-\varepsilon}$. They found that T_c increases at a rate of 1.5 K kbar^{-1} up to 3.4 kbar. Schirber *et al* (1987) also observed a small effect: a rate of enhancement of T_c of 0.07 K kbar^{-1}, for $YBa_2Cu_3O_7$ up to a pressure of 8 kbar. Chu *et al* (1988) observed that T_c is enhanced at a rate of 0.9 K kbar^{-1} for Eu–Ba–Cu–O with $T_c = 60$ K, while for Eu–Ba–Cu–O with $T_c = 90$ K, T_c increases at a rate of 0.16 K kbar^{-1}. Kurisu *et al* (1988) found that the rate of change of T_c with pressure is four times greater for the doped tetragonal $YBa_2(Cu_{1-x}M_x)_3O_{7-y}$ (M = Fe, Co, Ni and Zn) than for the corresponding orthorhombic phase for pressures up to 30 kbar.

In contast to these results, Murata *et al* (1987) and Koch *et al* (1988) found that pressure has a negative effect on T_c, with decreases with pressure of T_c of -0.25 K kbar^{-1}

0953-8984/90/143231 + 06 $03.50

and $-0.08\,\mathrm{K\,kbar^{-1}}$ respectively. Akahama *et al* (1987) also found that T_c decreases slightly with increasing pressure up to 17.5 kbar. Okai *et al* (1987) showed that for $Y_{0.4}Ba_{0.6}CuO_y$, T_c increases with pressure up to 100 kbar and then starts decreasing with further increase of the pressure.

Studies have been made to investigate the effect of pressure on the structure of $YBa_2Cu_3O_7$. Fietz *et al* (1987) applied pressure up to 120 kbar, but could not obtain any conclusive results. They proposed two models. In model I the orthorhombic phase persists throughout the pressure range, while in model II the orthorhombic phase transforms to a tetragonal phase at above 100 kbar. Takahashi *et al* (1987) did not record any phase transition up to 60 kbar, but a possibility of phase transition at higher pressure has been indicated; however, Dietrich *et al* (1987b) did not observe any phase transition up to 150 kbar. Jaya *et al* (1988) observed that the orthorhombic to tetragonal phase transition occurs above 70 kbar.

The effect of pressure on structure is therefore very unclear. A detailed knowledge of structural behaviour under pressure is crucial to interpret any results of the effect of pressure on transition temperature. The present study, therefore, reports a detailed investigation of the pressure dependence of the unit cell of $YBa_2Cu_3O_7$ using synchrotron-radiation-based energy-dispersive diffraction techniques.

2. Experimental methodology and results

2.1. Sample preparation

The $YBa_2Cu_3O_7$ sample was prepared by solid state reaction, as reported by Cava *et al* (1987). Powders of Y_2O_3, $BaCO_3$ and CuO were well mixed and ground in ethyl alcohol using a pestle and mortar. After drying, the mixture was heated at 950 °C for 16 hours in an alumina crucible under a flowing oxygen atmosphere. After the first heat treatment, the sample was cooled down to room temperature, reground and again annealed under oxygen at 950 °C for 12 hours. The laboratory powder x-ray diffraction pattern confirmed that a single phase had been prepared. At ambient pressures, the lattice parameters are $a = 3.8255$ Å, $b = 3.8841$ Å and $c = 11.6906$ Å, which are in excellent agreement with the neutron diffraction studies of Beech *et al* (1987). Since our interest in this study is regarding structural properties, the electrical behaviour of the material was not investigated.

2.2. Diffraction measurements

For high-pressure studies we employed energy-dispersive diffraction (EDD) techniques at the synchrotron radiation source (SRS) at the SERC Daresbury Laboratory, UK; this technique is suitable for such experiments when sample environments, e.g. high pressure, are needed, as both sample and detector are held at a fixed position throughout the experiment. The whole spectrum is obtained simultaneously using a solid state detector and multichannel analyser. Station (9.7) which is on the hard x-ray (Wiggler) line of the SRS was used. For generating high pressures, a diamond anvil cell (DAC) was employed. NaCl is used as an internal standard for pressure calibration (Decker 1971) and therefore a mixture of equal weights of $YBa_2Cu_3O_7$ and NaCl was filled into a 0.2 mm hole of a stainless steel gasket, and the gasket was then pressed between the diamond anvils. A mixture of methanol and ethanol (4:1) is used as the pressure-transmitting medium.

During the EDD experiment the detector was held at a fixed angle of $2\theta = 10.0°$. From the Bragg equation we can show a relationship between the energy of the radiation and the d-spacing, i.e. $d\,(\text{Å}) = 6.2/E \sin\theta$; where E is the energy of the x-ray photon in keV. From this relationship we can calculate the lattice parameters (Giessen and Gordon 1968). We have measured the effect of pressure on lattice parameters of $YBa_2Cu_3O_7$ from ambient pressure to 110 kbar at room temperature. Above 50 kbar, 014, 104 and 113 reflections start merging with each other, and in addition 114, 006 and 021 reflections also merge as shown in figure 1(*a*). Above 70 kbar these two sets of reflections are completely merged and each triplet becomes a single peak. A comparison of data at ambient pressure and 90 kbar is given in figure 1(*b*, *c*); this clearly indicates the occurrence of a phase transition. We should note that a number of reflections that remain non-degenerate in tetragonal symmetry (e.g. 104, 113 and 114, 006, 021) have merged in the high-pressure data due to the relatively low resolution of the energy-dispersive spectrum.

Refinement of the lattice parameters shows that above 80 kbar $a \simeq b$ (see figure 2(*a*)). Thus we observe that the orthorhombic symmetry changes to tetragonal between 70 and 80 kbar. The variation of lattice parameters with pressure is shown in figure 2(*a*, *b*). For the a axis the quantity $a_0^{-1}\,\mathrm{d}a/\mathrm{d}p = (1.33 \pm 0.41) \times 10^{-4}\,\text{kbar}^{-1}$ while for the b axis $b_0^{-1}\,\mathrm{d}b/\mathrm{d}p = (2.80 \pm 0.45) \times 10^{-4}\,\text{kbar}^{-1}$, and for the c axis $c_0^{-1}\,\mathrm{d}c/\mathrm{d}p = (3.89 \pm 0.55) \times 10^{-4}\,\text{kbar}^{-1}$.

The volume compressibility is found to be

$$v_0^{-1}\,\mathrm{d}v/\mathrm{d}p = (7.82 \pm 1.2) \times 10^{-4}\,\text{kbar}^{-1}$$

which remains linear throughout the pressure range (see figure 3). This shows that the orthorhombic to tetragonal transition is gradual. The large compressibility of the c axis results in a decrease in the c/a ratio, (figure 4) in contrast to the case for La_2CuO_4 which has an isotropic pressure effect (Akhtar *et al* 1988).

3. Discussion

The orthorhombic to tetragonal phase transition has been observed during high-temperature studies. Thus when the sample is heated above 750 °C it becomes tetragonal (Schuller *et al* 1987, Roth *et al* 1987, Gallagher *et al* 1987). During high-temperature studies it has been found that the tetragonal structure has no oxygen along the b axis and the tetragonal structure has a stoichiometry of $YBa_2Cu_3O_6$ (Izumi *et al* 1987, Santoro *et al* 1987). The Cu–O chains along the b axis do not exist in the tetragonal phase; they are thought to play an important role in superconductivity in this material (Santoro *et al* 1987).

We suggest that at high pressure when the orthorhombic to tetragonal transition occurs, the CuO_4 polyhedra which form the Cu–O chains along the b axis might be destroyed with CuO_6 octahedra being formed (Siegrist *et al* 1987). In this structure there are oxygen vacancies along the b axis and a random distribution of oxygen between sites $(\frac{1}{2}, 0, 0)$ and $(0, \frac{1}{2}, 0)$ leading to oxygen deficient octahedra about the copper atom. The resulting destruction of Cu–O chains might have a crucial effect on T_c under pressure. However, it is not possible to determine the atomic positions or stoichiometry by energy-dispersive diffraction of a powder sample, owing to the low resolution of the data. High-pressure monochromatic angle-dispersive or single-crystal studies of these materials would be desirable.

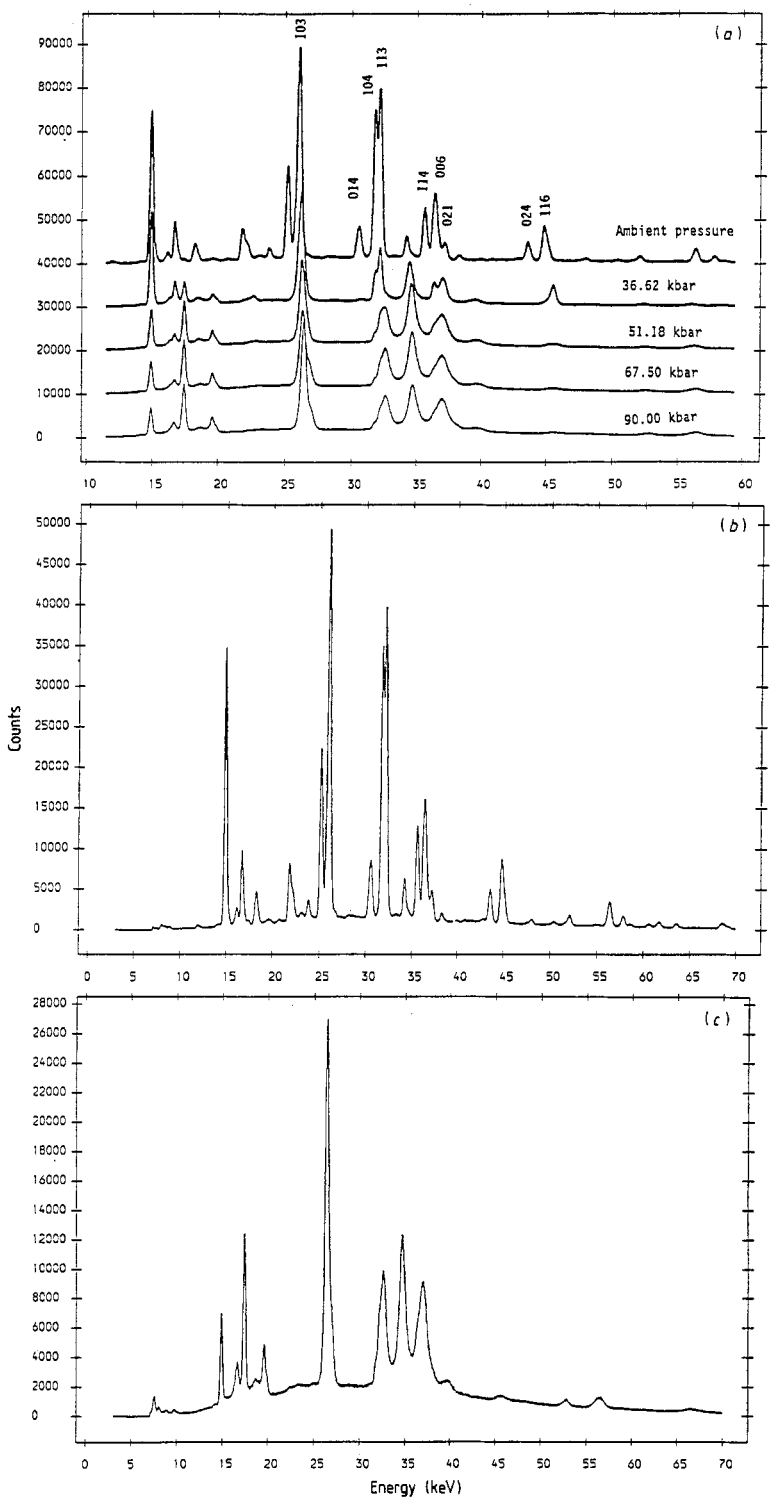

Figure 1. Energy-dispersive diffraction pattern of $YBa_2Cu_3O_7$ mixed with NaCl in a diamond anvil cell (*a*) at different pressures, (*b*) at ambient pressure, and (*c*) at 90 kbar. The Miller indices of some $YBa_2Cu_3O_7$ peaks are shown in (*a*).

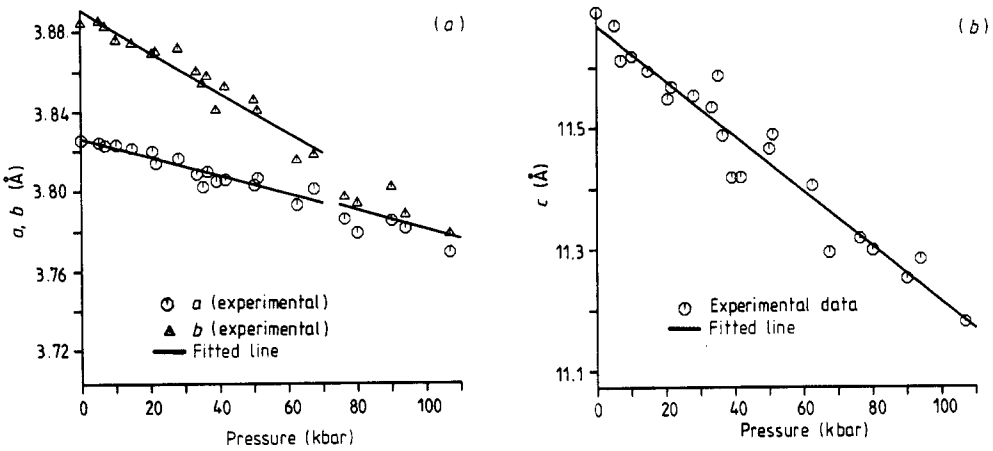

Figure 2. The effect of pressure on lattice parameters a, b (a) and c (b) for $YBa_2Cu_3O_7$.

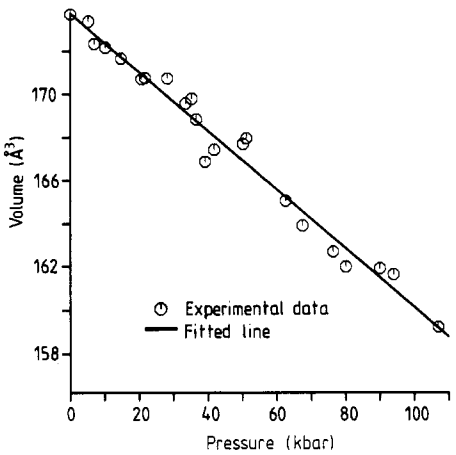

Figure 3. The variation of volume with pressure for $YBa_2Cu_3O_7$.

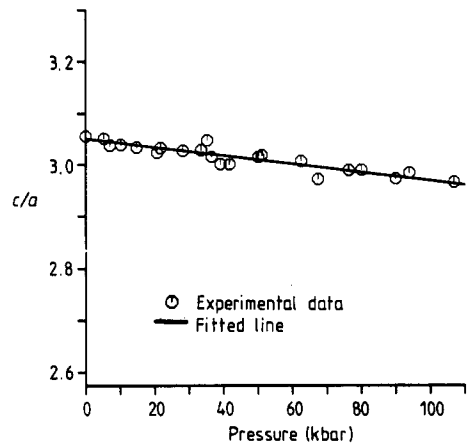

Figure 4. The effect of pressure on c/a for $YBa_2Cu_3O_7$.

Thus to conclude, we have studied the effect of pressure on $YBa_2Cu_3O_7$ up to 110 kbar. We have conclusively shown that there is a reversible orthohombic to tetragonal phase transition between 70 and 80 kbar, this transition being gradual. The large compressibility of the c axis results in a decrease in c/a ratio; a possible explanation for the relationship between the variation of structure with pressure and the transition temperature has been proposed.

Acknowledgments

We wish to express our thanks to S M Clark, K O'Reilly and D Hausermann for their assistance during the experimental work. We are also grateful to Dr A N Fitch for helpful discussions. MJA would like to thank the Ministry of Science and Technology of the Government of Pakistan for financial support, and Committee of Vice-Chancellors and Principals for an ORS award.

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