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Elastic anomaly of $YBa_2Cu_3O_{7-x}$ superconductors containing different oxygen contents

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Four samples of $YBa_2Cu_3O_{7-x}$ with different values of x were prepared and characterized, and their elastic properties from 80 K to room temperature were investigated. It was found that an anomalous softening of the elastic moduli G, K, and E at temperatures slightly higher than T_c appeared only on the specimens with the superconducting orthorhombic phase. As the value of x became small and the transition width ΔT_c became narrower, the softening became remarkable. The elastic constants also showed a thermal hysteresis at low temperatures. Relationships between this behaviour and proposed structural and domain changes are discussed.

1. Introduction

The high values of T_c of $YBa_2Cu_3O_{7-x}$ and other oxide superconductors [1, 2] strongly suggest that a new pairing mechanism instead of the Bardeen, Cooper and Schrieffer theory of superconductivity (BCS) plays an important role in their superconducting phenomenon. The measurements of the temperature dependences of the elastic moduli and sound velocities of these superconductors provide useful information both on the nature of electron–lattice interaction and on the peculiarities of the crystalline structure of these compounds. The previous studies on elastic response have shown many intriguing features such as anomalous hardening [3–5] or softening [6–8] of the elastic moduli at temperatures close to the superconducting transition. Although such anomalies near T_c have been related to the lattice or electronic properties, or to the microstructure of the samples, the real reasons for them have not yet been understood. The elastic constants were measured between 80 K and room temperature for the $YBa_2Cu_3O_{7-x}$ superconductors with different oxygen contents and the effect of oxygen content on the elastic softening was investigated.

2. Experimental details

The sample was prepared by utilizing the solid state reaction of a powder mixture of Y_2O_3, $BaCO_3$ and CuO, and following the process illustrated in Fig. 1. In order to prepare samples with different oxygen contents, they were annealed in oxygen or inert atmosphere at various temperatures. The X-ray diffraction patterns of the samples showed that they were monophasic. The lattice parameters of the samples were calculated from these patterns and their densities were measured at room temperature by Archimedes' method. The oxygen contents in the samples were estimated from the cell parameters and unit cell volumes based on the published data [9–11] and the results are shown in Table I. Although x varied depending on the literature used, the difference was not high ($\pm$ 0.1).

The temperature dependence of d.c. resistivity for the samples was measured using the four point probe method in order to obtain the onset and offset temperatures of the superconductive transition. Only sample 4 was a semiconductor.

The sound velocities and elastic moduli were determined as functions of temperature from 80 K to 300 K by means of the cubic resonance method. The specimen was placed in a cryostat and its temperature was measured by a Chromel–Alumel thermocouple placed close to the specimen. Two piezoelectric transducers ($BaTiO_3$) were in contact with the opposite corners of the cubic specimen, the edge length of which was 3–4 mm. The measuring procedure of this method and the analysis of resonant spectra are described in detail elsewhere [12]. The sound velocities, V_s and V_p, and the Poisson's ratio were determined from a series of resonant frequencies of the free oscillations of the cubic specimen and its length, and the shear modulus, G, bulk modulus, K, and Young's modulus, E, were calculated from the sound velocities and density.

3. Results and discussion

The temperature dependences of G, K, and E from 80 K to room temperature are shown in Figs 2, 3 and 4, respectively. In these Figures, the values relative to those at 290 K were plotted against temperature instead of the absolute elastic values, in order to obtain the effect of oxygen content on the elastic anomaly, since the absolute values are easily influenced by microcracks or porosity [13]. As for the thermal expansion, the mean coefficient of $1.3 \times 10^{-5}\ K^{-1}$ was

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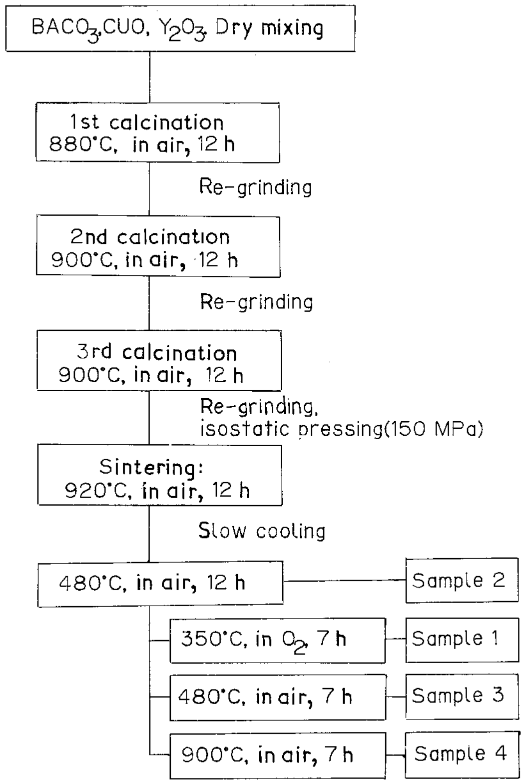

Figure 1 Scheme of the sample preparation.

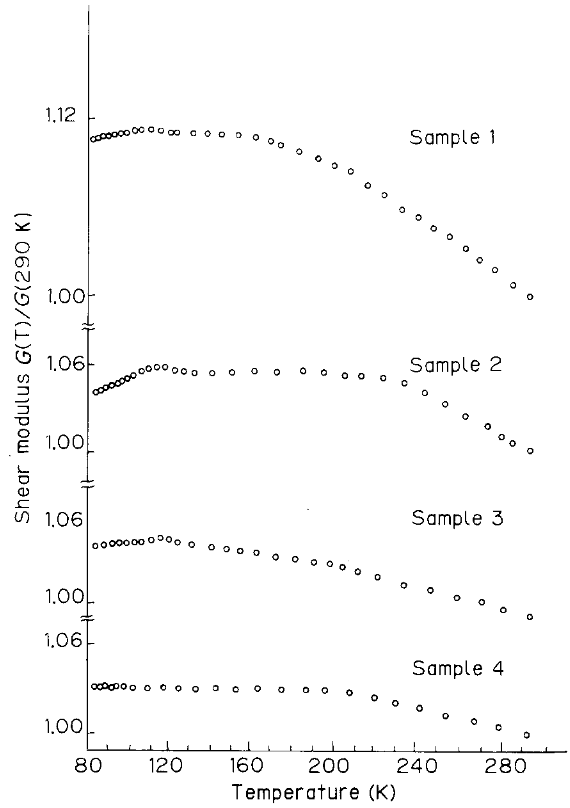

Figure 2 Temperature dependence of the shear moduli, G.

used [14, 15]. All the data shown in these figures were taken on the cooling run. The values taken on the heating run were slightly lower. The presence of such thermal hysteresis has been also reported by other authors [16 ,17].

From Figs 2–4, it can be seen that each sample shows a different temperature dependence on the elastic moduli. Among them, the behaviour of the shear moduli is a typical one. Above 200 K, a gradual increase of stiffening with lowering temperature was observed, as expected for usual solids. As the oxygen content of the specimen increased and the unit cell volume decreased from sample 4 to sample 1, the slopes of the curves against temperature became steeper, and then the softening appeared in all the samples except for sample 4. In order to see such a softening more clearly, the low temperature data were replotted on an expanded scale in Fig. 5. All the samples showing the superconducting behaviour gave the anomalous behaviour of softening in the range of 105–120 K and the onset temperature was lower for the sample having a narrow transition range from the onset to the offset of the superconductive transition temperature. The deviations of elastic constants from those of a stable crystalline state have been observed on a number of compounds near their phase transformation, usually before the transformation takes place. It appears also in a polycrystalline specimen of haematite at about 20 K above the Morin transition temperature where only the spin states or magnetic domains change without accompanying any crystallographic phase transformation [18].

The question as to whether a structural change occurs in $YBa_2Cu_3O_{7-x}$ superconductors near T_c has not yet been solved. Khachaturyan and Morris [19] proposed the decomposition of the orthorhombic oxide into a mixture of two phases by means of the principles of thermodynamics. This gets some support

TABLE I Characterization of the samples used in this study

	Sample 1	Sample 2	Sample 3	Sample 4
Density (g/cm^3)	5.85	5.65	5.80	5.72
Cell parameters (nm)	$a = 0.3812 \pm 0.0002$	$a = 0.3822 \pm 0.0002$	$a = 0.3840 \pm 0.0002$	$a = b$
	$b = 0.3892 \pm 0.0002$	$b = 0.3895 \pm 0.0002$	$b = 0.3874 \pm 0.0002$	$b = 0.3861 \pm 0.0002$
	$c = 1.1682 \pm 0.0002$	$c = 1.1706 \pm 0.0002$	$c = 1.1735 \pm 0.0002$	$c = 1.1795 \pm 0.0002$
Unit cell volume (A3)	173.3	174.3	174.6	175.8
x	0.1–0.2	0.3–0.4	0.5–0.6	0.7–0.8
T_c (K)	onset = 94 ± 05	onset = 94 ± 05	onset = 87 ± 05	semiconductor
	offset = 88 ± 05	offset = 81 ± 05	offset = *	

x was estimated from the relations given in References 9–11.
* Lower than liquid nitrogen temperature.

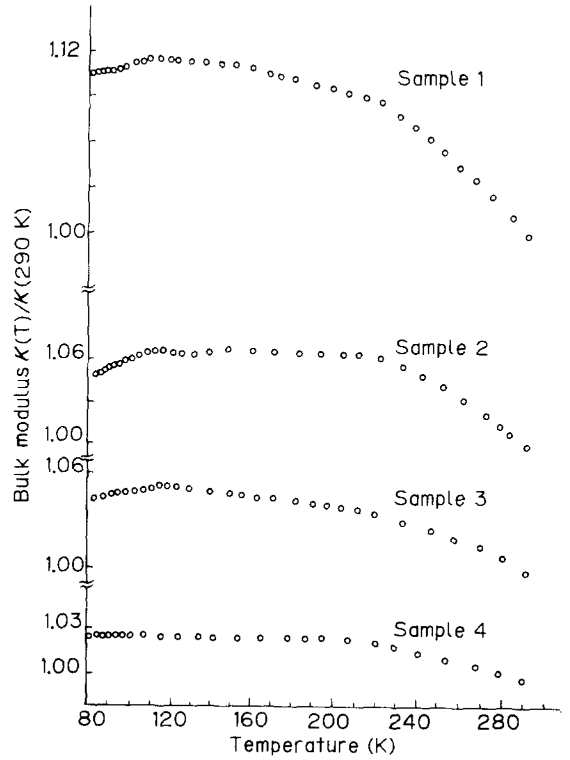

Figure 3 Temperature dependence of bulk moduli.

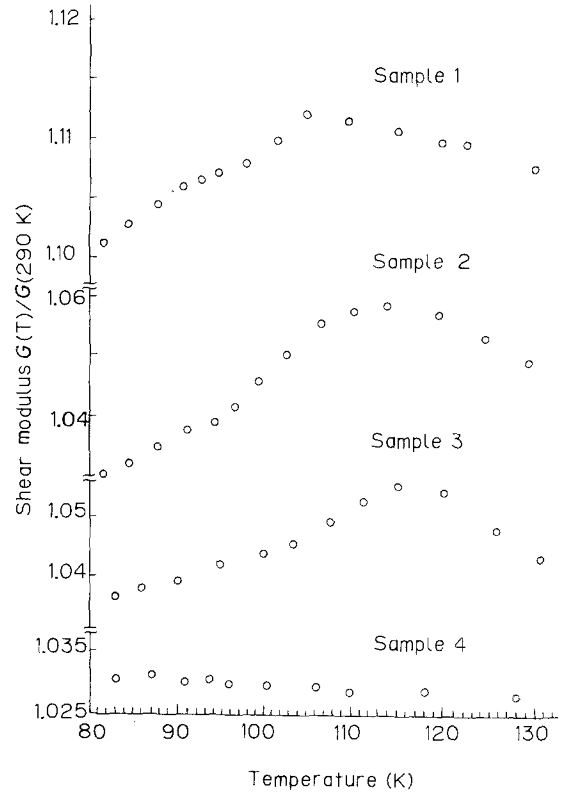

Figure 5 Temperature dependence of shear moduli at low temperatures, plotted on an expanded scale.

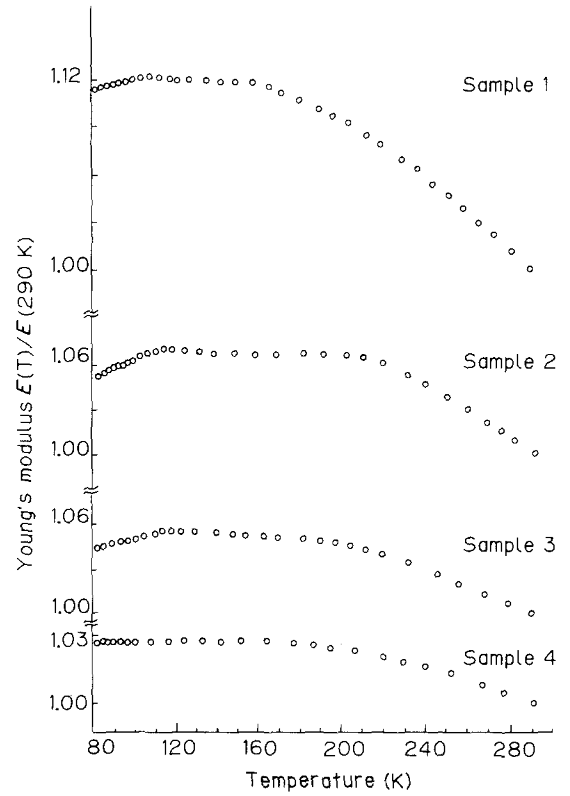

Figure 4 Temperature dependence of Young's moduli.

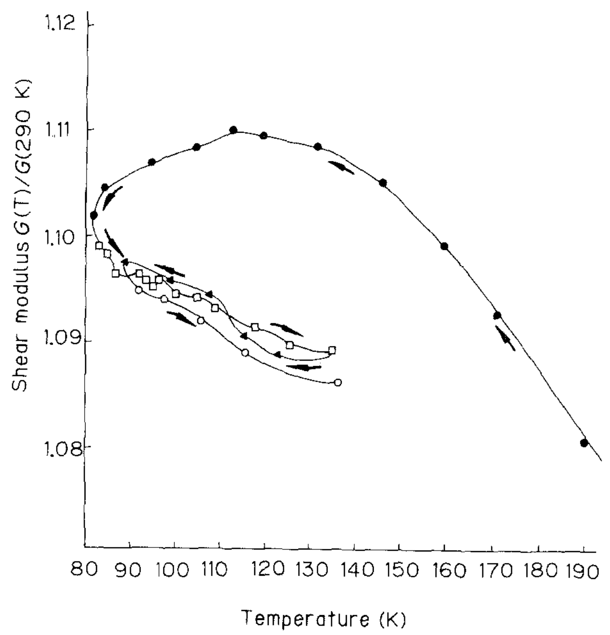

Figure 6 Temperature dependence of shear moduli for sample 1, on cooling and heating run. Lines are only a guide for the eye. (●—●—●) 1st cooling run (curve 1); (□—□—□) 1st heating run; (◀—◀—◀) 2nd cooling run (curve 2); (○—○—○) 2nd heating run.

by X-ray diffraction studies of single crystal [20]. On the other hand, the twin boundary dynamics and ferroelastic domain switching have been reported by Schmid *et al.* [21], using polarized light microscopy and by Smith and Wolleben [22], who observed the spontaneous refining of twinnings by means of transmission electron microscopy studies.

This anomalous change of elastic constants showed a thermal hysteresis. As shown in Fig. 6, the softening behaviour was observed clearly on Sample 1 during the first cooling run (curve 1) but not on the subsequent thermal cycling between 80 K and 130 K. However, when the sample was heated to room temperature and then cooled again, curve 1 was reproduced. This phenomenon shows that the change in crystal structure or boundary domain responsible for the elastic anomaly is not realized in this temperature range, although the sample does not show superconductive behaviour any more. A broad phase transition seems to occur over a wide temperature range as suggested by Ledbetter and Kim [17]. In order to clarify this phenomenon, the further measurement of the elastic properties at low temperatures in a magnetic field is now being undertaken.

4. Conclusions

The elastic properties of $YBa_2Cu_3O_{7-x}$ with different values of x from 80 K to room temperature were investigated. An anomalous softening of the elastic constants G, K, and E at temperatures 15–30 K higher than T_c appeared only on the specimens with the orthorhombic superconducting phase, but not in the semiconducting sample. The onset temperature of this softening behaviour seemed to be higher with increasing x. Thermal hysteresis of the elastic moduli was also observed in this range of temperatures. It is suggested that in this case they are associated with structural or boundary domain changes of the more oxidized orthorhombic samples at temperatures close to the superconducting transition temperature.

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