

Temperature Dependence of Elastic Properties  
of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  Superconductor

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The elastic properties were investigated for the high  $T_c$  superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from the liquid-nitrogen temperature to room temperature. Sound velocities and elastic moduli increased with decreasing temperature down to about  $T_{\text{onset}}$  (95 K), below which they decreased with decreasing temperature. The Debye temperature was also calculated to be 350 K.

After the epoch-making discovery of a new class of high-temperature superconducting materials by Bednorz and Müller,<sup>1)</sup> the best 90 K superconductors have been found in the Y-Ba-Cu-O system and their electrical, magnetic, and thermal properties near the transition temperature ( $T_c$ ) have been reported.<sup>2,3)</sup> However, no reliable data have been reported so far on their sound velocities and elastic moduli, except those of longitudinal velocity,<sup>4)</sup> while a number of data exist for metallic superconductors, such as tin, which show the change in elastic moduli in the order of a few parts per million at  $T_c$ .<sup>5)</sup> Since the superconductivity for the Y-Ba-Cu-O system is considered to be associated with the Jahn-Teller effect, it is expected that the lattice-vibrational properties, such as sound velocities and elastic moduli, would change at  $T_c$  more than those of metallic superconductors.

In this letter, the values of sound velocities and elastic moduli of the superconducting polycrystalline  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  from the liquid-nitrogen temperature to room temperature are reported with an emphasis on the change around  $T_c$ . The Debye temperature is also calculated from these data.

The sample investigated was prepared from the batch composition corresponding to  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  by mixing  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{BaCO}_3$  (99%), and  $\text{CuO}$  (99.9%) powders. The batch was well mixed, and then calcined in a platinum crucible at 850 °C for 10 h. The product was then ground, and calcined again at 900 °C in air for 3 h. The well calcined product was ground, compacted at 98 MPa by a hydrostatic press. The compact was sintered at 950 °C for 20 h and then annealed at 350 °C for 10 h in air. The XRD pattern at room temperature, shown in Fig. 1, revealed that only the orthorhombic perovskite phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  existed in the product. The annealed specimen was cut into a cube of edge length about 4 mm required for the elastic modulus measurement. The isotropy of the sample was assured by measuring the XRD patterns of different faces.

The cubic resonance method was used to determine the sound velocities and elastic moduli at various temperatures from 80 K to 300 K. The specimen was placed in a cryostat and its temperature was measured by a Chromel-Alumel thermocouple

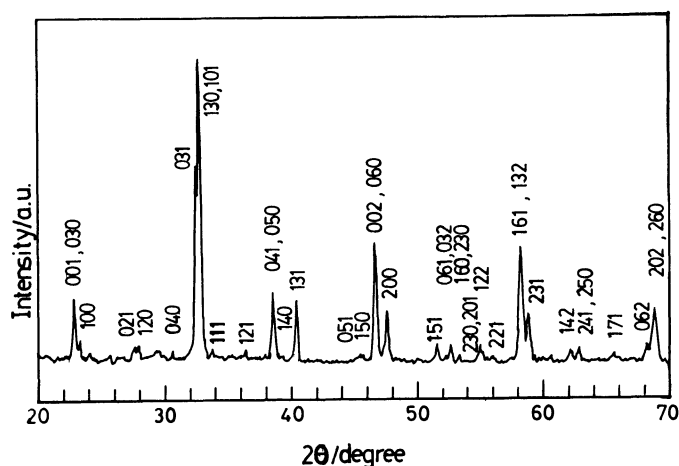


Fig.1. X-Ray diffraction pattern at room temperature for the specimen (showing an orthorhombic perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ).

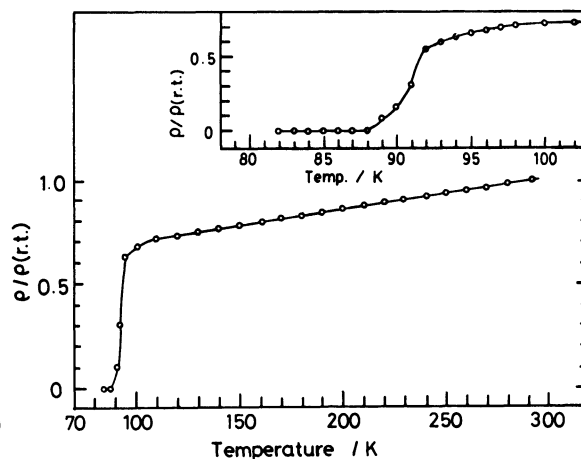


Fig.2. Temperature dependence of resistivity for an orthorhombic perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

Table 1. Elastic properties at room temperature for a polycrystalline orthorhombic perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

Density /g cm <sup>-3</sup>	Vs /km s <sup>-1</sup>	Vp	Poisson's ratio	Shear modulus /GPa	Bulk modulus /GPa	Young's modulus /GPa
5.992	2.372	4.086	0.246	33.72	55.08	84.01

placed close to the specimen. Two piezoelectric transducers ( $\text{BaTiO}_3$ ) were in contact with the opposite corners of the cubic specimen. In order to avoid electric current through the specimen, two electrodes of the transducers contacting with the specimen were grounded. The measuring procedure of this method and the analysis of resonant spectra were described in detail elsewhere.<sup>6)</sup> The sound velocities and Poisson's ratio were determined from a series of resonance frequencies of the free oscillations of the cubic specimen and its length, and the shear modulus, bulk modulus, and Young's modulus were calculated from the sound velocities and density. The density was measured at room temperature by the Archimedes method. The elastic properties and density at room temperature for the present sample were given in Table 1. The thermal expansion was also measured as a function of temperature on the same sample in order to calculate the density at low temperatures.

The dc electrical resistivity was measured by means of the four-point probe method in the same cryostat used for measuring elastic moduli. The temperature dependence of resistivity for the present  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  sample is shown in Fig. 2. The resistivity decreased gradually with decreasing temperature down to about 100 K, and then decreased sharply at about 92 K, reaching to zero at 88 K ( $=T_c$ ). The Meissner effect was also observed at the liquid-nitrogen temperature. From these results it was concluded that the present sample

exhibited superconductivity below 88 K.

The temperature dependence of elastic moduli for the present superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  are shown in Fig. 3. Figures 4 and 5 show the changes in sound velocities and elastic moduli near  $T_c$ , respectively. Clearly, the sound velocity and elastic moduli increased with decreasing temperature as in the case of normal solids down to 96 K, below which they decreased with decreasing temperature. Such an abnormal decrease in sound velocity and elastic moduli disappeared when the sample was annealed again at 950 °C for 6 h and quenched rapidly. The quenched sample had only the tetragonal perovskite phase of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and showed no superconductivity and its elastic moduli increased almost linearly with decreasing temperature down to 82 K. Thus, it is concluded that the deviation of sound velocities or elastic moduli from the linearity in Fig.4 or 5 is related to the superconducting transition of the sample.

Figure 5 exhibits that the elastic moduli start to decrease at near the onset temperature of superconductivity. The decrease in elastic moduli with decreasing temperature is anomalous, but it can be found often in association with phase transformation or magnetic transition. For example, the Young's modulus becomes maximum at the Curie point for the ferromagnetic materials, and this change in Young's modulus with temperature was explained by the domain wall-stress interaction.<sup>7)</sup> Although it might be possible that the change of the phonon mode of the superconducting phase may affect the elastic properties, it is necessary to have more profound evidences for this.

The Debye temperature is important to discuss the superconducting mechanism involving phonons. Since the present sample contained about 6% porosity, the sound velocities have to be adjusted to those for the one with theoretical density in order to calculate the Debye temperature. According to the previous study on the effect of porosity on the sound velocity of ceramics, almost a linear relationship exists between the sound velocity and density when the porosity is low.<sup>8)</sup> Thus, the  $V_s$  and  $V_p$  for the sample of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  with theoretical density of  $6.36 \text{ g cm}^{-3}$  were estimated to be 2.52 and  $4.34 \text{ km s}^{-1}$ , yielding the Debye temperature of 350 K.

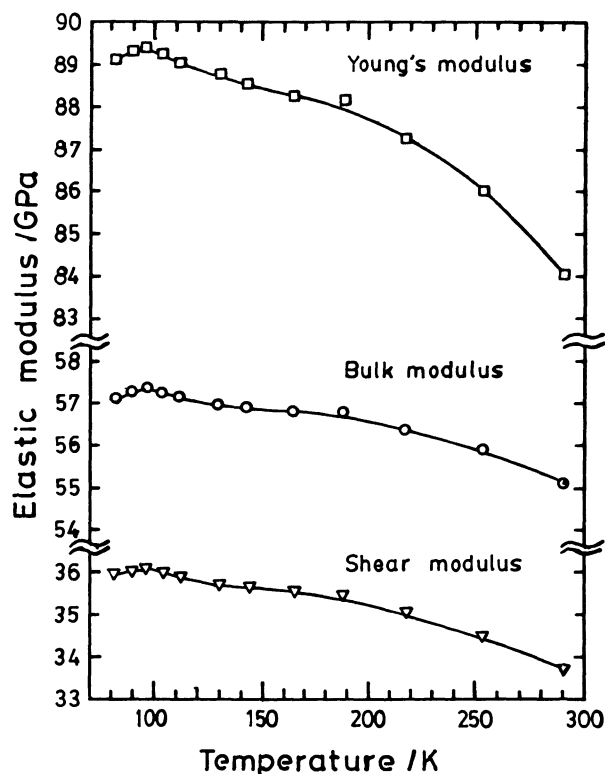


Fig.3. Temperature dependence of elastic moduli for an orthorhombic perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

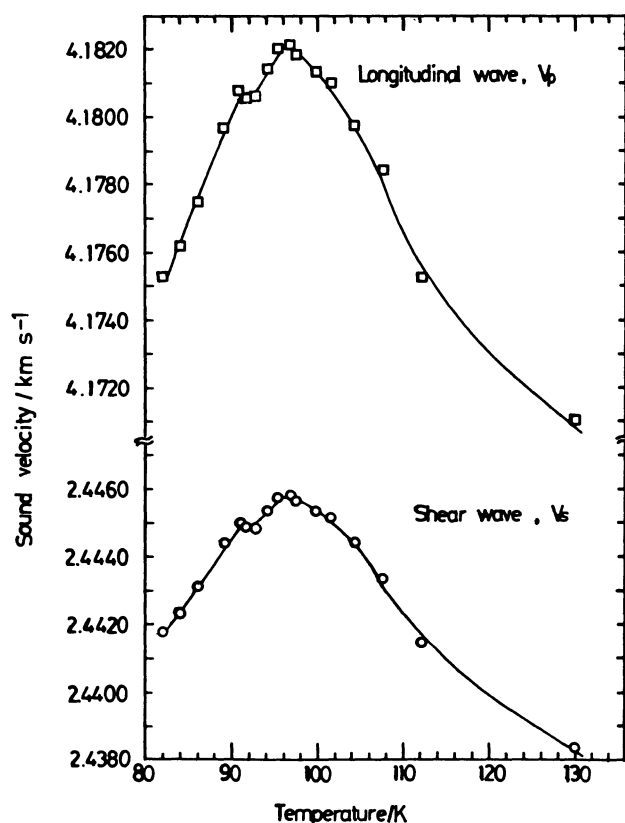


Fig.4. Temperature dependence of sound velocities for an orthorhombic perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

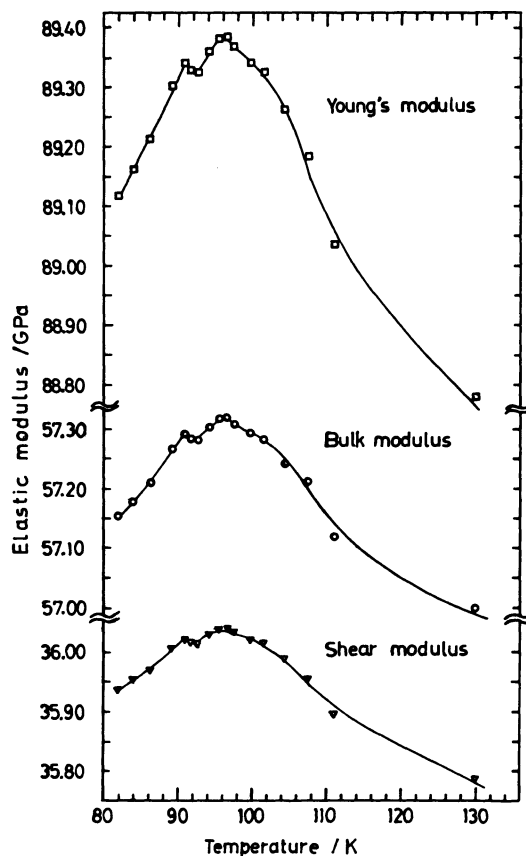


Fig.5. Temperature dependence of elastic moduli for an orthorhombic perovskite  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ .

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