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Elastic properties of polycrystalline $(La, Sr)_2CuO_4$ and $YBa_2Cu_3O_{7-\delta}$ doped with iron

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The elastic modulus of polycrystalline $(La, Sr)_2CuO_4$ and $YBa_2Cu_3O_{7-\delta}$ with copper replaced by iron has been measured in the temperature range from room temperature to 4.2 K using the cube resonance method. For the former system, 0.5% Cu is displaced by iron and the content of strontium is varied. The incorporation of iron gives rise to an apparent coexistence of magnetic order and superconducting order in samples $La_{2-x}Sr_x(Cu, Fe)O_4$ with $x = 0.15$ and 0.3, which is reflected in the temperature dependence of Young's modulus. For samples with $x = 0$ and 0.05, an anomalous behaviour of Young's modulus, which is thought to correspond to orthorhombic–monoclinic transition, is observed. For the $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ system, softening and a thermal hysteresis loop are observed in the temperature dependence of shear modulus of the sample with $y = 0$. The softening also appears in the temperature variation of Young's modulus. The degree of softening becomes smaller as the iron content which displaces copper is increased. These phenomena are discussed on the basis of the microstructure of the samples and the change of crystal structure with the iron content.

1. Introduction

Since the discovery of superconductivity in the La–Ba–Cu–O system by Bednortz and Müller [1], intense efforts have been made to determine the mechanism responsible for the high critical temperature of copper-containing oxide superconductors. The temperature dependence of elastic modulus for copper-containing oxide superconductors has been investigated extensively because it gives us useful information about phase transitions. For the $(La, Sr)_2CuO_4$ system, sound velocities and elastic modulus of the superconducting phases such as $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.86}Sr_{0.14}CuO_4$ were measured and softening of sound velocities and elastic modulus to a large extent was found in the temperature region much higher than T_c [2–4]. This softening was attributed to Peierls-like instability [2].

The temperature dependence of the elastic modulus of $YBa_2Cu_3O_{7-\delta}$ superconductor has also been examined by many investigators to discuss the relation between the behaviour of phonons and superconducting transition, as well as to reveal any phase transformations which may occur in several temperature regions. For example, an anomalous stiffening of Young's modulus was observed just below T_c for both single crystalline and polycrystalline $YBa_2Cu_3O_7$ [5, 6]. Datta *et al.* [5] explained this phenomenon in terms of a re-entrant softening model. Hoen *et al.* [6] stated that the anomalous stiffening is partly attributable to orthorhombic strain arising from a structural phase transition near T_c.

Another interesting feature in the temperature variation of elastic modulus of $YBa_2Cu_3O_{7-\delta}$ is the fact that a thermal hysteresis appears in the temperature dependence of the elastic modulus of polycrystalline $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 0$. Several investigators ascribed these phenomena to the microstructure of polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples [7–9]. As described in detail below, according to Wang *et al.* [9], the softening and the thermal hysteresis are brought about by the difference between the thermal expansion constant of the lattice in grains and that in grain boundaries; the crystal structure is orthorhombic in grains and is tetragonal in grain boundaries. Because the displacement of copper by iron in $YBa_2Cu_3O_{7-\delta}$ leads to a change of crystal structure from orthorhombic to tetragonal [10] as well as a decrease in the critical temperature [11], it is of interest to examine whether or not the softening and the thermal hysteresis manifest themselves in the polycrystalline $YBa_2(Cu, Fe)_3O_{7-\delta}$ system.

For the $(La, Sr)_2CuO_4$ system, the variation of magnetic transition temperature with strontium content was examined using Mössbauer spectroscopy for samples with 0.5% Cu replaced by iron [12]. The existing magnetically ordered phase is antiferromagnetic in $La_2(Cu, Fe)O_4$ and is spin glass in $La_{2-x}Sr_x(Cu, Fe)O_4$ with $x = 0.03$–0.07, and some magnetic order coexists with a superconducting state in $La_{2-x}Sr_x(Cu, Fe)O_4$ with $x > 0.07$. The superconducting transition temperature decreases from 37 K to 20 K with the incorporation of 0.5% Fe in the sample with $x = 0.15$. It is expected that these properties are reflected in the temperature dependence of elastic modulus. In the present study, the elastic moduli of polycrystalline $(La, Sr)_2(Cu, Fe)O_4$ and $YBa_2(Cu,$

$Fe)_3O_{7-\delta}$ prepared by the conventional solid state reaction were measured at room temperature to 4.2 K, and the effect of incorporation of iron on the temperature dependence of elastic modulus was discussed.

2. Experimental procedure

2.1. Sample preparation

The $La_{2-x}Sr_x(Cu, Fe)O_4$ system was prepared from reagent-grade La_2O_3, $SrCO_3$, CuO and Fe_2O_3. The molar ratio of copper to iron was kept 0.995:0.005 and x was varied from 0–0.3. Mixtures of these materials were calcined in alumina crucible at 900 °C for 5–10 h in air. The resultant powders were heated again at 1100 °C for 20 h in air. The powders thus obtained were pressed into a pellet under a hydrostatic pressure of 10 MPa. After the specimen was sintered at 1100 °C for 10 h in air, it was cooled to room temperature at a rate of about 30 °C h^{-1} in the furnace.

Polycrystalline $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ specimens were prepared using reagent-grade Y_2O_3, $BaCO_3$, CuO and Fe_2O_3 as starting materials. They were mixed thoroughly so as to make compositions of $y = 0$, 0.035 and 0.085, and submitted to first calcination at 880 °C for 15–20 h in air. The resultant specimen was reground thoroughly and calcined at 920 °C for 5–10 h in air. The powders thus obtained were pressed into a pellet under a hydrostatic pressure of 10 MPa and sintered at 950 °C for 12 h in air. The specimen was cooled slowly in the furnace and kept at 480 °C for 5 h in air. Then, it was cooled to room temperature.

The identification of crystalline phases was performed by means of X-ray diffraction measurements with CuK_α radiation. All the specimens were confirmed to be single-phase materials. The density of the specimen was determined at room temperature by Archimedes' method.

2.2. Measurements of elastic modulus

The specimen thus obtained was cut into a cube of $3 \times 3 \times 3$ mm^3, and submitted to measurements of elastic modulus using the cube resonance method at various temperatures from room temperature to 4.2 K. The specimen was placed in a cryostat and cooled with liquid helium. The temperature was determined by using an Au–Fe (0.07%)/chromel thermocouple placed close to the specimen. The cubic specimen in the cryostat was held between two transducers made from $BaTiO_3$ which are in contact with the opposite corners of the specimen. The resonant spectrum was obtained by searching the resonant frequencies which correspond to several modes of free oscillation of the specimen. The sound velocities and the elastic moduli were determined by analysing the resonant spectrum with the aid of a computer. For the calculation of the sound velocities and the elastic moduli, a variation of the edge length of the specimen with temperature due to thermal expansion was not taken into account because it was found that the thermal expansion had little influence on the values of the elastic modulus for the present materials [3, 13]. The apparatus for the measurements and the method of the analyses were described in detail elsewhere [14, 15]. For $YBa_2Cu_3O_{7-\delta}$, the measurements were performed on cooling and warming runs. The cooling and warming rates were about 2.5 and 0.5 K min^{-1}, respectively.

3. Results

3.1. (La, Sr)$_2$(Cu, Fe)O$_4$ system

The temperature dependence of Young's modulus of $La_2(Cu, Fe)O_4$, $La_{1.95}Sr_{0.05}(Cu, Fe)O_4$, $La_{1.85}Sr_{0.15}$ (Cu, Fe)O_4 and $La_{1.7}Sr_{0.3}(Cu, Fe)O_4$ with Fe/(Cu + Fe) = 0.005 is shown in Figs 1–4, respectively. The value of Young's modulus divided by that at room temperature is shown as the ordinate in these figures. All the experimental data were obtained on a warming run. For $La_2(Cu, Fe)O_4$, the Young's modulus increases with a decrease of temperature from 300 K to about 200 K, and then decreases with a further decrease in temperature. From about 120 K, the decrease in Young's modulus becomes more rapid. The Young's modulus first increases from 63–49 K, and then decreases again to 17 K. For $La_{1.95}Sr_{0.05}$(Cu, Fe)O_4, Young's modulus decreases with decreasing

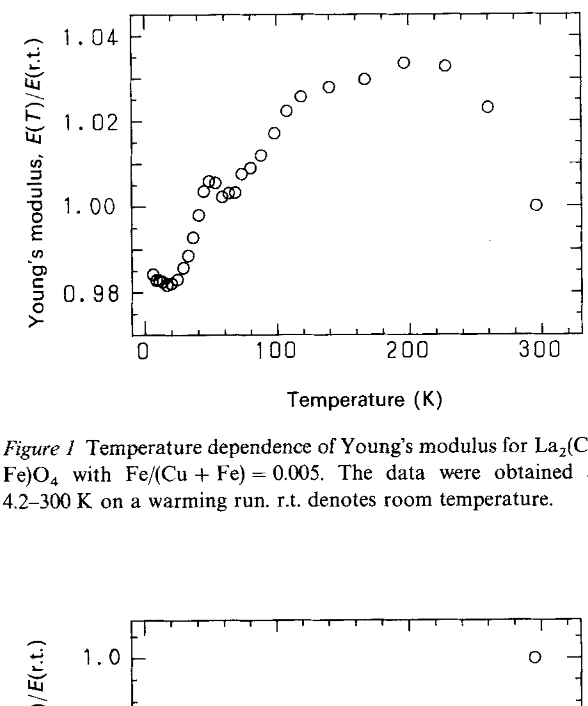

Figure 1 Temperature dependence of Young's modulus for La_2(Cu, Fe)O_4 with Fe/(Cu + Fe) = 0.005. The data were obtained at 4.2–300 K on a warming run. r.t. denotes room temperature.

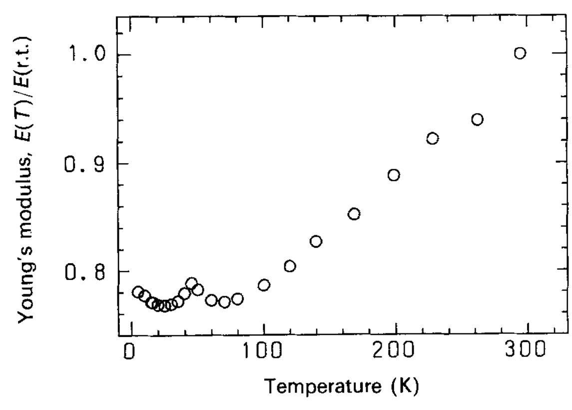

Figure 2 Temperature dependence of Young's modulus for $La_{1.95}Sr_{0.05}$(Cu, Fe)O_4 with Fe/(Cu + Fe) = 0.005.

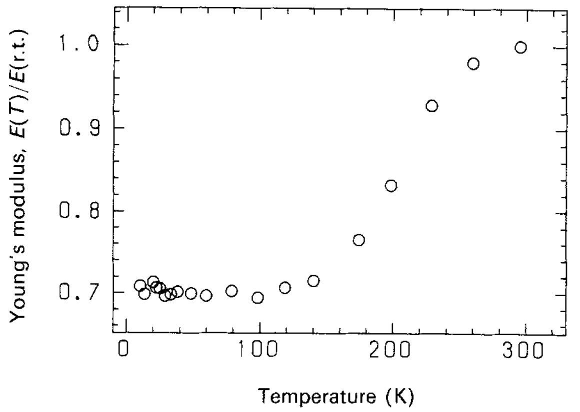

Figure 3 Temperature dependence of Young's modulus for $La_{1.85}Sr_{0.15}(Cu, Fe)O_4$ with Fe/(Cu + Fe) = 0.005.

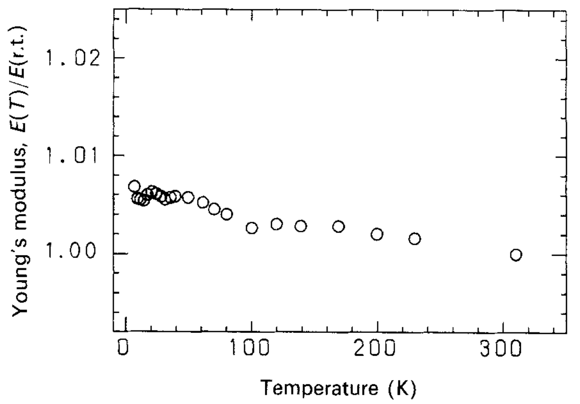

Figure 4 Temperature dependence of Young's modulus for $La_{1.7}Sr_{0.3}(Cu, Fe)O_4$ with Fe/(Cu + Fe) = 0.005.

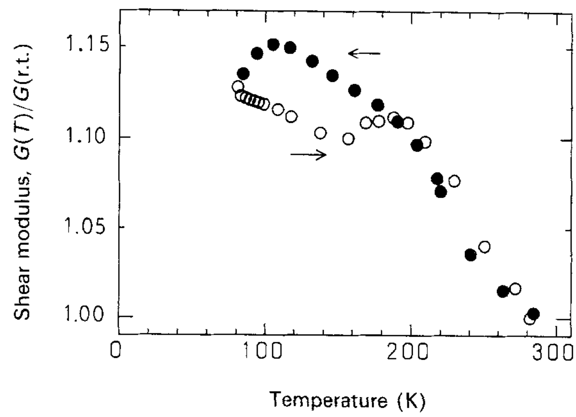

Figure 5 Temperature dependence of shear modulus for $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 0$. The sample is a polycrystal prepared by the solid state reaction. The temperature range where the shear modulus was measured was 300–80 K. The measurements were made on cooling and warming runs. (●) Cooling runs, (○) warming runs.

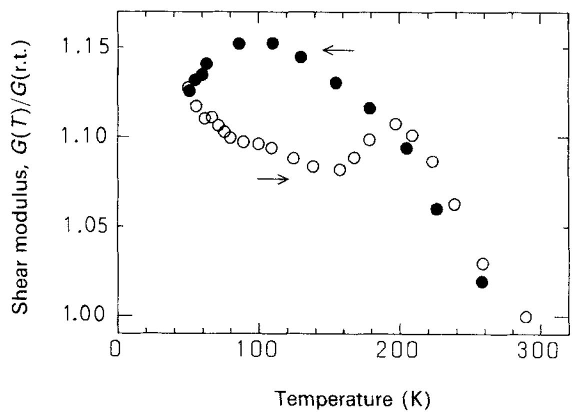

Figure 6 Temperature dependence of shear modulus for $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 0$. The temperature range where the shear modulus was measured was 300–50 K. (●) Cooling runs, (○) warming runs.

temperature from 300–70 K, then increases from 70–45 K and decreases again to 24 K. For $La_{1.85}Sr_{0.15}(Cu, Fe)O_4$, the Young's modulus largely decreases with decreasing temperature from 300–100 K; the extent of the decrease is about 30%. Although the Young's modulus varies little below 100 K, a close look at Fig. 3 reveals that softening of Young's modulus occurs at 38–28 K and at 20–13 K. For $La_{1.7}Sr_{0.3}(Cu, Fe)O_4$, Young's modulus tends to increase monotonically as temperature decreases from 300–4.2 K. However, softening of Young's modulus is visible at 38–30 K and at 21–14 K.

3.2. $YBa_2(Cu, Fe)_3O_{7-\delta}$ system

Fig. 5 shows the temperature dependence of shear modulus of $YBa_2Cu_3O_{7-\delta}$ at 300–80 K. The figure shows the variations of the shear modulus on cooling and warming runs. A large thermal hysteresis loop and softening of the shear modulus are seen around the temperature range 80–190 K. Fig. 6 shows the temperature dependence of shear modulus of $YBa_2Cu_3O_{7-\delta}$ at 300–50 K. A large thermal hysteresis is again seen around the temperature range 50–190 K in this figure. Similar phenomena were observed in the temperature range 4.2–300 K as indicated in Fig. 7 which shows a small hysteresis loop at 33–56 K in addition to the large thermal hysteresis loop at 56–180 K.

Fig. 8 shows the temperature dependence of Young's modulus of $YBa_2Cu_3O_{7-\delta}$ at 300–4.2 K. The data were obtained on the warming run. The variation of Young's modulus with temperature is very similar to that of the shear modulus shown in Fig. 7. In addition to softening of the Young's modulus to a large extent at 171–128 K and at 42–33 K, a softening to a very small degree is observed around 100 K. Fig. 9 shows the temperature dependence of Young's modulus of $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.035$ at 300–4.2 K. The degree of softening is smaller when compared with that for $YBa_2Cu_3O_{7-\delta}$ shown in Fig. 8. Fig. 9 exhibits that softening of Young's modulus to a small extent takes place at 96–76 K and at 34–19 K. Fig. 10 shows the temperature dependence of Young's modulus of $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.085$ at 300–4.2 K. Although Young's modulus tends to increase with a decrease in temperature, softening to a small extent is observed at 48–29 K.

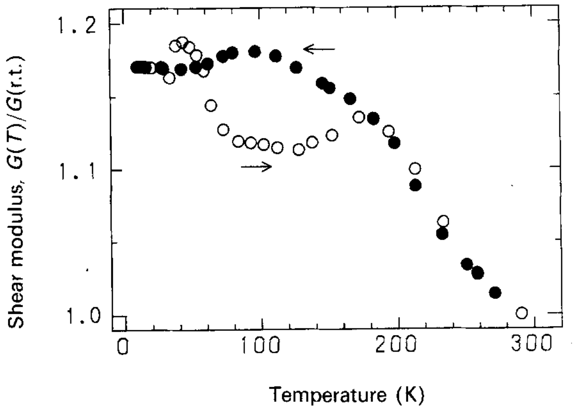

Figure 7 Temperature dependence of shear modulus for $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 0$. The temperature range where the shear modulus was measured was 300–4.2 K. (●) Cooling runs, (○) warming runs.

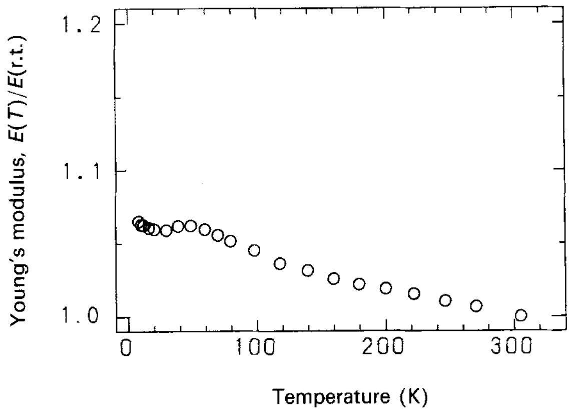

Figure 10 Temperature dependence of Young's modulus for $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.085$. The data were obtained at 4.2–300 K on a warming run.

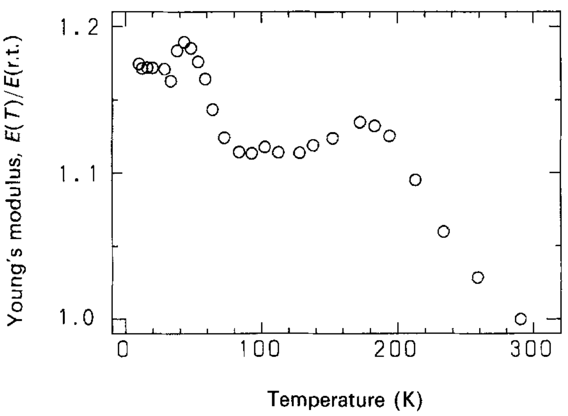

Figure 8 Temperature dependence of Young's modulus for $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 0$. The data were obtained at 4.2–300 K on a warming run.

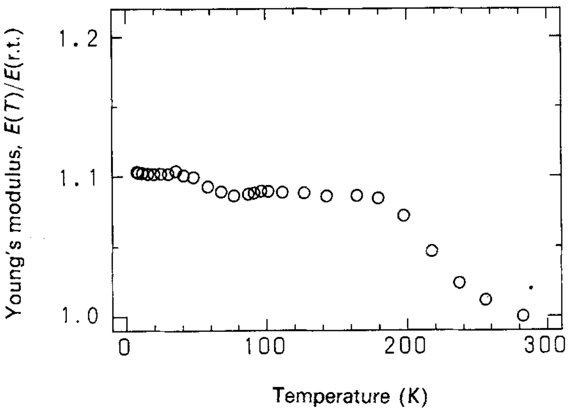

Figure 9 Temperature dependence of Young's modulus for $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.035$. The data were obtained at 4.2–300 K on a warming run.

4. Discussion

4.1. (La, Sr)$_2$(Cu, Fe)O_4 system

Among the samples examined in the present study, $La_{1.85}Sr_{0.15}$(Cu, Fe)O_4 and $La_{1.7}Sr_{0.3}$(Cu, Fe)O_4 with Fe/(Cu + Fe) = 0.005 exhibit superconductivity with a critical temperature of about 20 K for both samples [12]. The temperature dependence of Young's modulus for these samples, which is shown in Figs 3 and 4, is very similar to that for samples which have the same composition but do not contain iron. The explanation on the behaviour of the elastic modulus for samples without iron [2–4] is applicable to the present samples containing iron. Namely, for the $La_{1.85}Sr_{0.15}$(Cu, Fe)O_4 sample, the decrease of Young's modulus with decreasing temperature from 300–100 K may be attributable to the Peierls-like instability, and the normal behaviour of Young's modulus in the $La_{1.7}Sr_{0.3}$(Cu, Fe)O_4 is due to a small fraction of superconducting phase in the sample, as demonstrated by the magnetic susceptibility measurements [16]. The effect of the incorporation of iron in these samples is to decrease the critical temperature and to bring about a magnetic transition, as mentioned above. The critical temperature and the magnetic transition temperatures are about 20 and 7 K, respectively, for these two samples [12]. The softening of Young's modulus to a small degree, seen around 30 and 15 K in Figs 3 and 4, reflects these phase transitions, respectively. The fact that the temperature at which the softening of Young's modulus occurs is slightly higher than the transition temperature is not surprising, because such a phenomenon has been generally observed for many crystalline compounds. For example, in a polycrystalline α-Fe_2O_3, an anomalous behaviour of elastic modulus appears at about 20 K above the Morin transition [17].

The sample La_2(Cu, Fe)O_4 with Fe/(Cu + Fe) = 0.005 is antiferromagnetic with a Néel temperature of 240 K [12]. The softening of Young's modulus around 200 K, as shown in Fig. 1, reflects this phase transition. The structural phase transition between tetragonal and orthorhombic states also occurs at 533 K in La_2CuO_4 [18]. The same transition takes place at 300 K in $La_{1.95}Sr_{0.05}CuO_4$ [19]. It is thought that because of this structural phase transition, the gradual decrease of Young's modulus with a decrease of temperature is observed in a wide temperature range in La_2(Cu, Fe)O_4 and $La_{1.95}Sr_{0.05}$(Cu, Fe)O_4.

In other words, an increase in spontaneous strain of the lattice with a decrease of temperature causes the softening of the Young's modulus.

Figs 1 and 2 also indicate that a certain anomalous behaviour of Young's modulus occurs around 50 K in $La_2(Cu, Fe)O_4$ and $La_{1.95}Sr_{0.05}(Cu, Fe)O_4$ which are not superconducting materials. Considering that such an anomaly is not observed in the superconducting $La_{1.85}Sr_{0.15}(Cu, Fe)O_4$ and $La_{1.7}Sr_{0.3}(Cu, Fe)O_4$, this anomaly is thought to be related to the stability of the superconducting phase in this system. As mentioned above, La_2CuO_4 is orthorhombic below 533 K. According to the theoretical calculations by Kasowski *et al.* [20], orthorhombic La_2CuO_4 is metallic at any temperature and should be superconducting. However, many previous experiments indicate that La_2CuO_4 does not show a superconducting transition. Kasowski *et al.* [20] proposed that the orthorhombic La_2CuO_4 is transformed into a polymorph with lower symmetry, such as a monoclinic phase, at low temperatures, which interrupts the occurrence of superconducting transition in La_2CuO_4. They also showed theoretically that a band gap appeared in the monoclinic La_2CuO_4, leading to a semiconducting character. This suggestion was demonstrated by Skelton *et al.* [21]. By carrying out X-ray diffraction analyses at various temperatures, they revealed that the main phase in La_2CuO_4 at 11.5 K was monoclinic. They also determined the phase transition temperature to be about 37 K on the warming run. Based on these theoretical and experimental results, it is concluded that the anomalous behaviour in Young's modulus observed around 50 K is due to the orthorhombic–monoclinic transition.

4.2. $YBa_2(Cu, Fe)_3O_{7-\delta}$ system

For $YBa_2Cu_3O_{7-\delta}$, the softening and thermal hysteresis are observed in the temperature dependence of shear and Young's moduli as shown in Figs 5 and 6. Similar phenomena were reported by several investigators. For instance, Ledbetter and Kim [13] found that the bulk modulus of polycrystalline $YBa_2Cu_3O_{7-\delta}$ prepared by the usual solid state reaction, exhibited a hysteresis loop around the temperature range between 70 and 240 K. When the sample was cooled from room temperature, the bulk modulus increased until the temperature reached 160 K where the bulk modulus experienced a maximum, then decreased, and increased again below 70 K. On the other hand, when the sample was warmed from 5 K, the bulk modulus continued to decrease until 170 K, then increased until the temperature became 240 K, from which it decreased through the path that was drawn in the cooling process. Ledbetter and Kim [13] attributed this phenomenon to a phase transition accompanying thermal hysteresis; the phase transition took place between 160 and 70 K in the cooling process, while it occurred between 170 and 240 K in the warming process. Zhao *et al.* [22] reported a similar thermal hysteresis in the temperature dependence of sound velocity for polycrystalline $YBa_2Cu_3O_{7-\delta}$ prepared by a sinter-forging process. Their samples were composed of platelet grains with the *c*-axis of the crystal perpendicular to the plate surface. They stated that the hysteresis might reflect a gradual first-order like structural phase transition.

On the other hand, Ewert *et al.* [7] carried out ultrasonic velocity measurements on polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples with different microstructures, and found that the thermal hysteresis in the temperature dependence of sound velocity was observed only for the coarse-grained sample. In the fine-grained sample, neither thermal hysteresis nor softening of the sound velocity was observed. They attributed the different behaviour of the elastic properties to the different microstructures of the polycrystalline samples. A similar result was obtained by Burenkov *et al.* [8]. They considered that the anomaly in elastic properties results from thermoelastic stresses which arise from an anisotropy of thermal expansion coefficients of the coarse grains. Recently, Wang *et al.* [9] suggested a similar mechanism of thermal hysteresis based on the microstructure. They stated that in the coarse-grained sample, grain boundaries exist which possess oxygen defects. As a result, the crystal structure in the grain boundaries is orthorhombic, although that in the grains is tetragonal, as expected from the composition. When such a sample is cooled, a distortion energy arises in the regions between a grain and a grain boundary because of the different thermal expansion coefficients between grain and grain boundary due to the different crystal structures, and the distortion energy increases with decreasing temperature. When this distortion energy becomes equal to the connecting energy between grains, defects of pore size arise around the grain boundary, leading to the softening of elastic modulus. They supposed that such defects cannot disappear until the lattice parameters recover their original values, which leads to the thermal hysteresis. Very recently, Ikuhara [23] carried out electron diffraction analyses at various temperatures on polycrystalline $YBa_2Cu_3O_{6.9}$ prepared by the conventional solid state reaction, and discovered that the temperature dependence of the *c*-axis exhibited an anomalous behaviour. The length of the *c*-axis decreased with a decrease of temperature from 300 K to about 170 K as naturally expected, but it increased from about 170 K to 80 K. Below around 80 K, the dimension of the *c*-axis is almost independent of temperature. These temperatures, (170 and 80 K) are in a good agreement with the temperatures at which the elastic modulus manifests an anomalous behaviour [7–9, 13, 22]. On the basis of these experimental results, the origin of the thermal hysteresis loop and the softening of the elastic modulus may be explained as follows. As suggested by Wang *et al.* [9], the coarse-grained sample contains grain boundaries which possess a composition nearly equal to $YBa_2Cu_3O_6$, and the thermal stress or the distortion energy arises in the interconnecting regions on the cooling run. Before the release of the distortion energy with the creation of defects of pore size, the lattice parameter of the orthorhombic $YBa_2Cu_3O_{7-\delta}$ in the grains is elongated because of the tensile stress caused by the grain boundaries. As a result, softening of the elastic modulus and expansion of the *c*-axis occur at about 170 K.

On further cooling the thermal stress increases and causes the creation of defects of pore size, accompanied by a release of the distortion energy. Once such defects are created, the temperature dependence of the elastic modulus, as well as the lattice parameter, becomes normal. This phenomenon occurs around 70 K. When the sample is warmed from a temperature at which the pore-size defects are not created but softening of the elastic modulus does occur, such as 80 K, the elastic modulus first decreases with an increase in temperature, because the tensile stress remains on the surface of the grains. Such a stress disappears as the lattice constant dimension of the grain and the grain boundary become equal to each other with increasing temperature. Consequently, the elastic modulus approaches the original value obtained on the cooling run at some temperatures: in the present case, this is around 190 K. Thus, the thermal hysteresis loop appears.

According to the present idea, mentioned above, it is expected that neither the softening nor the hysteresis will appear in the temperature dependence of the elastic modulus for coarse-grained $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 1$. Indeed, no softening of elastic modulus was observed for $YBa_2Cu_3O_{6.3}$ prepared by the conventional solid state reaction [24]. Further, a displacement of copper by iron may decrease the degree of softening and thermal hysteresis, because the crystal structure changes from orthorhombic to tetragonal with the replacement of copper by iron. The variation of the temperature dependence of Young's modulus with the iron content for $YBa_2(Cu, Fe)_3O_{7-\delta}$ is shown in Figs 8–10. It is seen from these figures that the degree of softening decreases as the iron content increases. It is inferred that in $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.085$, the crystal structure is orthorhombic in both grains and grain boundaries, and hence the temperature dependence of the lattice constant in the grain is similar to that in the grain boundary, leading to no thermal stress during the cooling process. Consequently, the temperature dependence of Young's modulus manifests normal behaviour.

Figs 7 and 8 show that the softening of shear and Young's moduli also occurs at 42–33 K. To our knowledge, such a softening of the elastic modulus in this temperature region has not yet been observed. The origin of this softening and the reason why a similar softening has not been observed by other investigators may be explained as follows. As seen in Figs 5–7, the temperature at which softening of the shear modulus begins to occur on the cooling run is about 100 K, which is lower by 60–100 K than temperatures reported by other investigators [7–9, 13, 22]. Presumably, this is due to the faster cooling rate in the present measurements. In other words, the cooling rate is so fast in the present case that the expansion of the lattice parameter in grains due to the tensile stress applied by the grain boundaries cannot occur at high temperatures. As a result, the temperature at which softening begins to occur becomes lower, as 100 K. In addition, as shown in Fig. 7, the shear modulus varies little below 50 K. Hence, a release of the distortion energy with the creation of pore-size defects does not occur, even at 4.2 K in the present sample. It is plausible that the residual distortion energy is released on the warming run. As described above, after the release of the distortion energy, the elastic modulus of the sample behaves normally, that is, increases with decreasing temperature. It is thought that in the present sample, the release of the distortion energy takes place around 33 K on the warming run, which causes an abrupt increase in the elastic modulus because of the abrupt decrease in the lattice parameter.

A small softening of Young's modulus is seen around 100 K on the warming run in Fig. 8. This corresponds to the superconducting transition. The superconducting transition temperature is decreased as the iron content increases in the $YBa_2(Cu, Fe)_3O_{7-\delta}$ system [11]. In contrast, the magnetic transition temperature increases with increasing iron content, as demonstrated by Mössbauer measurements [11]. For $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.035$, the superconducting transition temperature and the magnetic transition temperature are about 70 and 10 K, respectively. These transitions are reflected in the softening of Young's modulus at 96–76 K and at 34–19 K, respectively, as shown in Fig. 9. In $YBa_2(Cu_{1-y}Fe_y)_3O_{7-\delta}$ with $y = 0.085$, it is thought that the softening at 48–29 K shown in Fig. 10 corresponds to the magnetic transition. According to the phase diagram presented by Tamaki *et al.* [11], the magnetic transition temperature lies between 20 and 30 K, although its exact value has not been determined.

5. Conclusion

By using the cube resonance method, measurements of elastic modulus were performed for polycrystalline samples of $(La, Sr)_2CuO_4$ and $YBa_2Cu_3O_{7-\delta}$ doped with iron at 300–4.2 K. For $La_{1.85}Sr_{0.15}(Cu, Fe)O_4$ and $La_{1.7}Sr_{0.3}(Cu, Fe)O_4$ with Fe/(Cu + Fe) = 0.005, a softening of Young's modulus which corresponds to the superconducting and magnetic transitions was observed. Apart from the occurrence of softening due to the magnetic transition, the temperature dependence of Young's modulus is very similar to the dependence reported previously for $La_{1.85}Sr_{0.15}CuO_4$ and $La_{1.7}Sr_{0.3}CuO_4$ without iron. For $La_2(Cu, Fe)O_4$ and $La_{1.95}Sr_{0.05}(Cu, Fe)O_4$ with Fe/(Cu + Fe) = 0.005, an anomalous behaviour of Young's modulus was observed around 50 K. It is thought that this anomaly is due to orthorhombic–monoclinic transition.

A thermal hysteresis loop and softening were observed in the temperature variation of the shear modulus for $YBa_2Cu_3O_{7-\delta}$. A similar softening was also seen in the temperature dependence of Young's modulus on the warming run. The extent of this softening of Young's modulus was decreased as the iron content, which replaced copper, was increased. In other words, the change of crystal structure from orthorhombic to tetragonal phases accompanied by the replacement of copper by iron made the softening of Young's modulus disappear. These observations are coincident with the suggestion that the thermal hysteresis and the softening of the elastic modulus in $YBa_2Cu_3O_{7-\delta}$ arise from the thermal stress in the interconnecting region between grain and grain boundary which is brought about by the different dependence of lattice parameter on temperature in the grain than in the grain boundary.

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