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Mössbauer Spectroscopic Study of Superconducting Y-Ba-Cu(Fe)-O Ceramics and Gamma-Ray Irradiation Effect

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Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics (x=0.003, 0.008, and 0.017) measured at room temperature show a superposition of three quadrupole doublets. An outermost doublet (δ=0—0.04 mm s^{-1}, Δ=1.94—1.98 mm s^{-1}) is ascribed to high-spin Fe^{4+} ions present at substitutional sites of Cu^{2+} ions (Cu(2) site). An intermediate doublet (δ=−0.03—0.02 mm s^{-1}, Δ=1.12—1.17 mm s^{-1}) is ascribed to intermediate-spin Fe^{3+} ions present at substitutional sites of Cu^{3+} ions (Cu(1) site). An innermost doublet is ascribed to Fe^{3+} ions (high spin) with tetrahedral symmetry, present along the b-axis. A decrease in T_c from 72 to 60 K, observed when iron content (x) is increased from 0.008 to 0.017, is explained by a lowered layer structure composed of "dimpled" CuO_4 planes, owing to a displacement of O(4) oxygen atoms sharing CuO_5 tetragonal pyramids and CuO_4 square planars. One-dimensional chains composed of CuO_4 square planars proved to be primarily affected by γ-ray irradiation, whereas no change of T_c was observed. Low-temperature Mössbauer measurements revealed that "partial Debye temperatures" are 330 and 740 K for the chains and layer structure, respectively.

Since Bednorz and Müller exhibited a possibility of high-T_c superconductivity in oxide ceramics,[1] Ln–Ba–Cu–O ceramics, where Ln indicates lanthanide elements, have attracted much attention. Important findings of superconducting Y–Ba–Cu–O ceramics by Wu et al.[2] and Hikami et al.[3,4] suggested several practical applications at higher temperatures than so-called "liquid nitrogen temperature," e.g., fiber and thin film.[5–9] In addition to the applications and studies of physical properties (e.g. T_c and J_c), structure of Y–Ba–Cu–O superconductors has been studied by several groups. Using an electron probe microanalyzer (EPMA), Iwata et al.[10] elucidated that black-colored phase having a composition of Y:Ba:Cu=1:2:3 causes the superconductivity. Crystal structure of high-T_c $YBa_2Cu_3O_{7-\delta}$ was studied by Hazen et al.[11] and LePage et al.[12] by means of powder X-ray diffraction. As a result, it was revealed that orthorhombic (*Pmmm*) phase and tetragonal (*P4/mmm*) phase are present in $YBa_2Cu_3O_{7-\delta}$ ceramics. Powder neutron diffraction study combined with Rietveld analysis revealed that an orthorhombic (*Pmmm*) phase is concerned with the superconductivity in $YBa_2Cu_3O_{7-\delta}$ ceramics.[13–16] Beno et al.[13] elucidated that the orthorhombic phase is composed of distorted CuO_5 tetragonal pyramids, constituting "dimpled" CuO_4 layers in the a-b planes, and CuO_4 square planars constituting one-dimensional fence-like chains in the b-c planes. It was reported that the distorted CuO_5 tetragonal pyramids also constitute semiconducting $YBa_2Cu_3O_{7-\delta}$ ceramics (δ>0.5).[13] Most of the copper atoms in "dimpled" CuO_4 layers (denoted by Cu(2)) were reported to be divalent,[14] being in contrast to Cu^{3+} ions constituting one-dimensional CuO_4 square planars in the b-c planes.[15] Jorgensen et al.[14] revealed that Cu^{3+} ions in CuO_4 square planar chains (Cu(1)) play an important role in the conduction mechanism and that a depression of superconductivity is due to a loss of Cu^{3+} ions and/or a disordering of the one-dimensional chains. Similar conclusion has been drawn by Izumi et al.[16,17] in neutron diffraction studies.

^{57}Fe-Mössbauer spectroscopy has been utilized for a structural study of superconducting $GdBa_2Cu_3O_{7-\delta}$,[18,19] $YBa_2Cu_3O_{7-\delta}$,[20–27] and $EuBa_2Cu_3O_{7-\delta}$[28,29] ceramics. In a Mössbauer study of $GdBa_2(Cu_{0.94}Fe_{0.06})_3O_{7-\delta}$ ceramic at room temperature,[18,19] the spectrum was analyzed into two types of quadrupole doublets with isomer shifts (δ) of −0.12 and −0.17 mm s^{-1} and quadrupole splittings (Δ) of 1.97 and 1.05 mm s^{-1}, respectively. The former doublet peak with larger quadrupole splitting was ascribed to the Fe^{3+} ions present at substitutional sites of Cu^{2+} ions at Cu(1) site, whereas the latter peak was ascribed to the absorption due to Fe^{3+} ions present at substitutional sites of Cu^{3+} ions at Cu(2) site. In these studies,[18,19] a homogeneous single phase was recognized by X-ray diffraction method when the substitution of iron for copper was less than 15% in the $GdBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics. Furthermore, a Mössbauer spectrum proved to show a magnetic splitting at 4.2 K when the substitution of iron for copper was greater than 3%. A peak assignment similar to the case of $GdBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$[18,19] ceramics was made for $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics by the same research group.[20] They indicated that T_c is decreased with increasing iron content and that a superconductivity disappears when x is greater than 0.15. Isomer shift of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramic ($x=0.06$) also proved to be located around 0 mm s^{-1} with respect to a stainless steel.[20] On the other hand, quite a reverse assignment was made by several groups.[21,22,24,25,28] Nasu et al.[21] indicated that an asymmetric outermost doublet peak corresponds to high-spin Fe^{3+} ions ($S=5/2$) present at substitutional sites of Cu^{2+} ions (Cu(2) site), and that an intermediate doublet peak corresponds to intermediate-spin Fe^{3+} ions ($S=3/2$) present at substitutional sites of Cu^{3+} ions (Cu(1) site). An innermost weak doublet ($\delta=0.27$ mm s^{-1} and $\Delta=0.52$ mm s^{-1}) was ascribed to octahedral Fe^{3+} ions of high spin state.[21] Takano and Takeda[22] showed that both the outermost and intermediate doublet peaks correspond to intermediate-spin Fe^{3+} ions ($S=3/2$).

Structural information obtained by Mössbauer spectroscopy seems to be very useful because it is directly concerned with the mechanism of superconductivity in these ceramics. The present ^{57}Fe-Mössbauer study was carried out in order to elucidate a local (short-range) structure in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ superconductors and also a long-range structure in connection with lattice dynamics of lower-dimensional chain and layer structures composed of copper (Cu^{2+} or Cu^{3+}) and oxygen atoms. Mössbauer measurements of ^{60}Co-γ ray (ca. 10^8 R) irradiated $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ superconductor were also performed in order to elucidate a sensitivity to gamma rays in connection with a short- or long-range structure.

Experimental

Superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics, in which x was chosen to be 0.003, 0.008, and 0.017, were prepared from Y_2O_3, $BaCO_3$, CuO, and $^{57}Fe_2O_3$ (^{57}Fe=96.03%), of a guaranteed reagent grade. Each of the mixtures containing weighed quantities of these reagents was ground in an agate mortar and dehydrated at 110 °C for 1 h on an electric heater. Each mixture in an alumina crucible was then heated at 900 °C for 5 h in an electric muffle furnace. After being cooled to room temperature, the mixture was pressed into a pellet with a diameter of 6 mm, under a hydrostatic pressure of 200 kg cm^{-2}. Superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics were prepared by sintering each pellet at 900 °C for 35 h. After the sintering, temperature in the electric muffle furnace was cooled down to 200 °C with a rate of 70 °C h^{-1}. All the procedures were performed in ambient atmosphere. The $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics prepared in this way are black in color. Mössbauer measurements were performed on pulverized samples by using a metallic iron foil enriched with ^{57}Fe as a reference of isomer shift. The iron foil was also used for calibrating the velocity of spectrometer. Cobalt-57 (10 mCi) diffused into a sheet of palladium foil was used as a Mössbauer source. Gamma-Ray irradiation was performed at the Cobalt-60 Irradiation Facilities of Kyushu University at an ambient temperature. During the Mössbauer measurements and ^{60}Co-γ ray irradiations ranging from 10^6 to 10^8 R, each sample was placed in a polyethylene bag filled with dry nitrogen gas in order to prevent it from absorbing atmospheric moisture. DC resistivity measurements were performed by a four-terminal method. Magnetic susceptibility was measured between room temperature and 78 K. DTA measurements were performed between room temperature and 800 °C with a heating rate of 5 °C min^{-1}. In DTA measurements, powder of α-Al_2O_3 was used as a standard material.

Results and Discussion

Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics ($x=0.017$, 0.008, and 0.003) are demonstrated in Fig. 1. Each Mössbauer spectrum shows a superposition of three quadrupole doublet peaks; an outermost peak with a quadrupole splitting of 1.94—1.98 mm s^{-1} (doublet (a)), an intermediate peak with a quadrupole splitting of 1.12—1.17 mm s^{-1} (doublet (b)), and an innermost peak with a quadrupole splitting of 0.46—0.56 mm s^{-1} (doublet (c)). The isomer shift of doublets (a) and (b) are located at 0—0.04 and −0.03—0.02 mm s^{-1}, respectively. The isomer shift of doublet (c) is 0.27—0.29 mm s^{-1}. It should be noted that the linewidth of doublet (b) is 0.46—0.49 mm s^{-1}, whereas the linewidth of doublets (a) and (c) is in a range of 0.28—0.30 mm s^{-1}. The latter values are characteristic of the absorption due to iron in crystalline compounds. On the other hand, the large linewidth (0.46—0.49 mm s^{-1}) of doublet (b) indicates distributed bond lengths and bond angles between iron and oxygen atoms, as observed in several Mössbauer studies of inorganic glasses.[30-38] This suggests a non-crystalline character of steric configuration around the iron concerned with doublet (b). The isomer shift of doublet (b) (−0.03—0.02 mm s^{-1}) indicates a much increased s-electron density at iron nucleus compared with that of high-spin Fe^{3+} ions.[30-38] Therefore, doublet (b) is ascribed to the absorption due to either

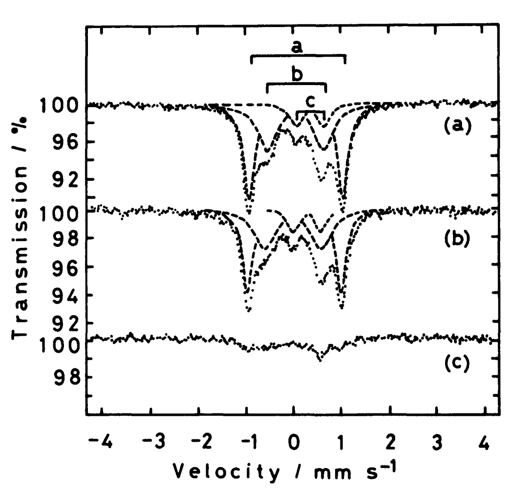

Fig. 1. Mössbauer spectra of superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics measured at room temperature. (a): $x=0.017$, (b): $x=0.008$, and (c): $x=0.003$.

high-spin Fe^{4+} ions or intermediate-spin Fe^{3+} ions ($S=3/2$).[39,40] If we take account of the small interatomic distance between Cu(1) and oxygen (O(1))[14,15] and therefore a strong ligand field at the copper (and also iron) site, we can speculate that iron is present at substitutional sites of Cu(1) in the form of intermediate-spin Fe^{3+} ($S=3/2$). In connection with this, Takano and Takeda[22] demonstrated a magnetically split peak at 1.5 K, which was assigned to Fe^{3+} ions of $S=3/2$, having an internal magnetic field (H_{int}) of about 33 T. A large linewidth of doublet (b) (0.46—0.49 mm s^{-1}), which is 30—75% greater than that of doublets (a) and (c), will reflect a decreased chain structure composed of CuO_4 chains in the b-c planes when Cu^{3+} (and small amounts of Cu^{2+}) ions are replaced by Fe^{3+} ions. In addition to the substitution of Fe^{3+} ions for Cu^{3+} (and also Cu^{2+}) ions, which preferentially conform CuO_4 square planars, incorporation of iron into $YBa_2Cu_3O_{7-\delta}$ ceramics will result in a formation of Fe^{3+}-oxygen polyhedra such as FeO_4 tetrahedra and FeO_6 octahedra. This will be discussed later.

Doublet (a) having a large quadrupole splitting is ascribed to Fe^{4+} ions present at substitutional sites of Cu^{2+} (and small amounts of Cu^{3+}) ions constituting CuO_5 tetragonal pyramids along the a-b planes. A bond length between copper (and also iron) present at Cu(2) site and an axial oxygen atom (O(4)), present at the apex of each pyramid, seems to be too longer[14,15] to form an intermediate spin state. Furthermore, isomer shift of high-spin Fe^{3+} ions present in tetragonal pyramids, having a coordination number 5, will be located around 0.4 mm s^{-1} with respect to metallic iron, i.e., between the isomer shift values of octahedra and tetrahedra.[30—40] A small isomer shift obtained for doublet (a) (0—0.04 mm s^{-1}) is explained by a decreased shielding effect of 4s-electron density by 3d-electrons when Fe^{3+} ($3d^5$) is oxidized to Fe^{4+} ($3d^4$). It seems that two-dimensional layers composed of "dimpled" CuO_4 planes constituting CuO_5 tetragonal pyramids along the a-b plane[13—17] will be less affected than one-dimensional chains composed of CuO_4 square planars (b-c plane), when Cu^{3+} and Cu^{2+} ions are replaced by Fe^{3+} and Fe^{4+} ions, respectively.

Doublet (c) having an isomer shift of 0.27—0.29 mm s^{-1} and a quadrupole splitting of 0.46—0.56 mm s^{-1} is ascribed to the absorption due to tetrahedral Fe^{3+} ions ($S=5/2$), because the isomer shift is characteristic of high-spin Fe^{3+} species with tetrahedral symmetry.[30—40] Magnetically-split Mössbauer spectra of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics ($x=0.010$—0.067) observed at low temperatures, having an internal magnetic field (H_{int}) of about 49 T,[22,24,27] are consistent with the peak assignment described in this paper. In those papers, however, the magnetic peak was ascribed to octahedral Fe^{3+} ions.[22,24,27] It is generally known that H_{int} for octahedral Fe^{3+} species is greater than that of tetrahedral Fe^{3+} species, e.g. an H_{int} value of α-Fe_2O_3 at the corresponding temperature is about 54 T.[39] It seems that the FeO_4 tetrahedra are preferentially formed along the b-axis, because one-dimensional chain structure composed of CuO_4 square planars will be more favorable for the formation of FeO_4 tetrahedra than two-dimensional layer structure composed of CuO_5 tetragonal pyramids. The formation of FeO_4 tetrahedra along the b-axis will reduce a regular atomic arrangement, and some oxygen atoms will be located between one-dimensional chains composed of CuO_4 square planars. This will cause an increased unit cell length (lattice parameter a) along the a-axis, as reported by Maeno et al.[26] and Zhou et al.[27] If one-dimensional chains in the b-c planes carry supercurrent,[14—17,23] formation of FeO_4 tetrahedra along the b-axis will directly suppress the superconduction. As a result, a decrease in T_c will be observed. On the other hand, if two-dimensional layers in the a-b planes carry the supercurrent,[25,26] we have to consider a different mechanism concerning the decrease in T_c brought about by the formation of FeO_4 tetrahedra along the b-axis.

A decrease in T_c caused by increased iron content of superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics is shown in Fig. 2. By increasing iron content (x) from 0.008 (Fig. 2a) to 0.017 (Fig. 2b), it proved that T_c decreases from 72 to 60 K. These T_c's are lower than that of original $YBa_2Cu_3O_{7-\delta}$ ceramics (80 K) without iron.[2] Paramagnetic to diamagnetic transition around T_c is observed in $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ superconductor ($x=0.008$), as shown in Fig. 3. Temperature dependency of the magnetic susceptibility (χ) shows a good agreement with that of electrical resistivity shown in Fig. 2a. The formation of FeO_4 tetrahedra along the b-axis will lower the layer structure composed of "dimpled" CuO_4 planes (Cu(2) site), owing to a displacement of O(4) oxygen atoms sharing CuO_5 tetragonal pyramids and CuO_4 square planars. Therefore, if the superconduction is concerned with the a-b planes (Cu(2) site), displacement of O(4) oxygen will be the primary reason for the decrease in T_c. This is

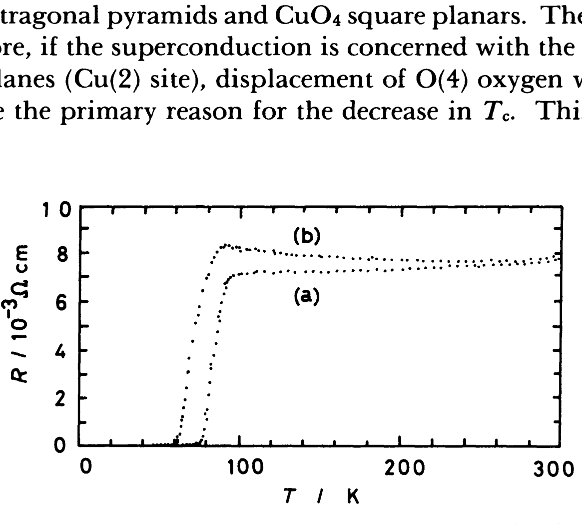

Fig. 2. Temperature dependency of electrical resistivity (R) of superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics. (a): $x=0.008$, (b): $x=0.017$.

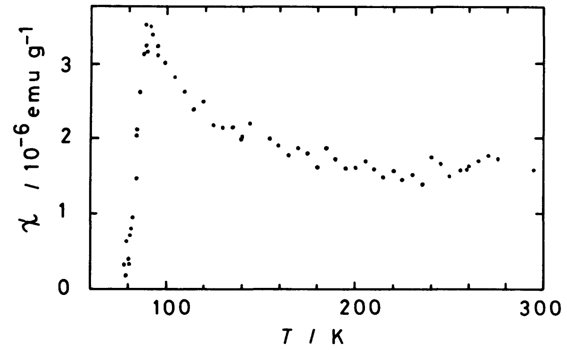

Fig. 3. Temperature dependency of magnetic susceptibility (χ) of superconducting $YBa_2(Cu_{0.992}Fe_{0.008})_3O_{7-\delta}$ ceramic.

also the case for the decrease in T_c observed in original $YBa_2Cu_3O_{7-\delta}$ ceramics when an oxygen content is decreased. Takano and Takeda,[22] reported that a relative absorption area corresponding to Cu(1) and Cu(2) sites depends on the oxygen content. This means that a decrease in T_c is not directly concerned with a relative occupation ratio of iron between Cu(1) and Cu(2) sites. Regarding the absorption and evolution of oxygen atoms, DTA measurements of superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramics (x=0.008 and 0.003) revealed a single and wide exothermic peak ranging from room temperature to about 680 °C (x=0.008) and 660 °C (x=0.003), followed by a continuous endothermic peak at the higher temperatures. The exothermic peak having a maximum at about 430 °C indicates a continuous oxygen absorption in this temperature range. At temperatures higher than 660—680 °C, evolution of oxygen will become frequent, indicating a phase transition from orthorhombic to tetragonal at the temperatures.

Mössbauer parameters of superconducting $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ ceramic (x=0.017) irradiated with ^{60}Co-γ rays are summarized in Table 1. Mössbauer spectra and most of the parameters except an absorption area proved to be independent of the irradiation. Experimental error of the isomer shift is estimated to be ±0.01 mm s^{-1} and that of quadrupole splitting and linewidth is ±0.02 mm s^{-1}. These results indicate that a local structure and a chemical bond around iron are scarcely affected by the ^{60}Co-γ ray irradiations. Actually, no change of T_c was observed after the γ-ray irradiation of 10^8 R. This is quite in contrast to the result of several oxide glasses,[31,33] in which a quantitative reduction of Fe^{3+} to Fe^{2+} or a change of isomer shift and/or quadrupole splitting was observed when irradiated with γ-rays$\geqq 10^6$ R. These experimental results demonstrate that $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ and also $YBa_2Cu_3O_{7-\delta}$ ceramics are highly resistant to γ-rays so far as a local structure is concerned. On the other hand, Table 1 indicates a dose-dependent change of relative absorption area. This is illustrated in Fig. 4, where plots in parentheses refer to the values before irradiation. We can understand from Fig. 4 that absorption area of doublet (b) decreases by the irradiation at the expense of absorption areas of doublets (a) and (c). This suggests a decrease in the recoil-free fraction f of Fe^{3+} ions present at substitutional sites of Cu(1) in one-dimensional chains. The reduced recoil-free fraction f will be closely concerned with the one-dimensional chain structure. This will be discussed later based on low-temperature Mössbauer measurements.

Table 1. Mössbauer Parameters of $YBa_2(Cu_{0.983}Fe_{0.017})_3O_{7-\delta}$ Ceramic Irradiated with ^{60}Co-γ Rays

Dose/R	δ[a]	Δ[b]	Γ[c]	A[d]
	mm s^{-1}	mm s^{-1}	mm s^{-1}	%
0	0.04	1.95	0.28	48.6
	0.02	1.17	0.46	39.1
	0.27	0.46	0.31	12.3
1×10^6	0.05	1.96	0.30	50.5
	0.03	1.17	0.47	36.3
	0.28	0.48	0.32	13.2
6×10^6	0.05	1.98	0.29	50.8
	0.03	1.16	0.39	36.7
	0.29	0.49	0.34	12.5
1×10^7	0.05	1.96	0.29	53.5
	0.03	1.16	0.39	30.6
	0.27	0.47	0.34	15.9
1×10^8	0.04	1.96	0.29	51.7
	0.03	1.15	0.50	30.8
	0.31	0.50	0.42	17.5

a) Isomer shift. b) Quadrupole splitting. c) Linewidth. d) Absorption area.

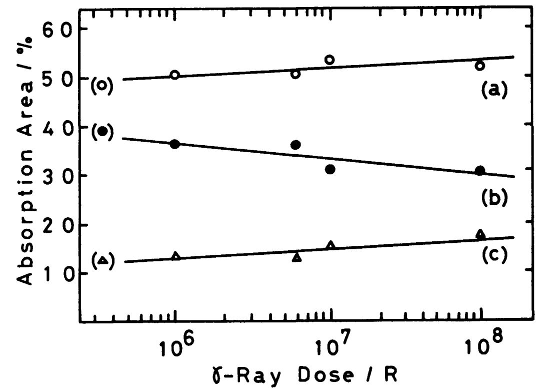

Fig. 4. Gamma-Ray dose dependency of relative absorption area (A) for superconducting $YBa_2(Cu_{0.983}Fe_{0.017})_3O_{7-\delta}$ ceramic. (a): doublet (a), (b): doublet (b), (c): doublet (c).

Mössbauer measurements of a superconducting $YBa_2(Cu_{0.992}Fe_{0.008})_3O_{7-\delta}$ ceramic were carried out at several temperatures ranging from room temperature to 78 K. As a result, no apparent spectral change was observed in any case. Temperature dependency of isomer shifts for the three doublets (a, b, and c) is shown in Fig. 5. It is obvious from Fig. 5 that all the isomer

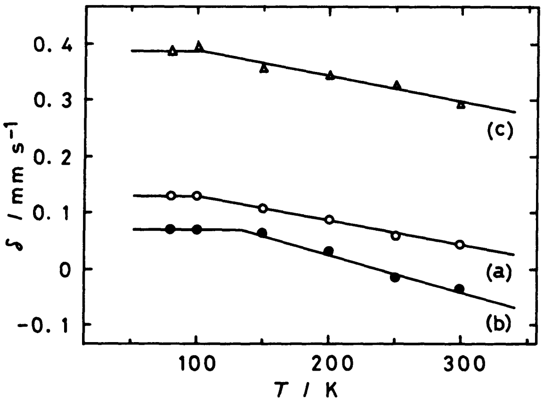

Fig. 5. Temperature dependency of isomer shift (δ). (a): doublet (a), (b): doublet (b), (c): doublet (c).

shift values are increased at lower temperatures owing to a decreased second-order Doppler effect. This suggests a decreased degree of atomic vibrations at iron and also copper sites, because a second-order Doppler shift is correlated with a mean square velocity of atomic vibration ($\langle v^2 \rangle$).[39] It can be known from Fig. 5 that a slope of doublet (b) is a little steeper than that of doublets (a) and (c). This means that a chemical bond between Fe^{3+} ion, present at substitutional sites of Cu(1) in one-dimensional chains, and four oxygen atoms is more affected by the lattice vibrations than two-dimensional Cu(2) sites or FeO_4 tetrahedra. In case of FeO_4 tetrahedra present along the b-axis, an atomic arrangement can be viewed to be three-dimensional because some oxygen atoms are located between two $Cu(1)O_4$ square planar chains, as described above. The experimental results shown in Fig. 5 are consistent with the result shown in Fig. 4. Another feature of Fig. 5 is that isomer shift is almost constant at 78 and 100 K. This result suggests that vibrational mode is changed at the onset of superconduction. The constant isomer shift values obtained at 78 and 100 K (and also at 150 K in case of doublet (b)) seem to suggest a retained amplitude (mean square velocity $\langle v^2 \rangle$) of lattice vibration, although we have only a few measuring points for each doublet peak. The present experimental results (Fig. 5) are consistent with the temperature dependencies of linewidth and absorption area shown in Figs. 7 and 8, respectively.

Figure 6 shows a temperature dependency of quadrupole splitting for each doublet peak. From Fig. 6, we can deduce on the average unchanged atomic configuration around Fe^{3+} or Fe^{4+} (and also Cu^{3+} or Cu^{2+}) ions and also unchanged 3d-electron configuration. In contrast to the quadrupole splitting values plotted in Fig. 6, linewidth (FWHM) of doublet (b) shows a significant decrease with increasing temperature (Fig. 7). The decrease in linewidth at higher temperatures is ascribed to a motional narrowing, which seems to be more frequent in case of one-dimensional chains composed of CuO_4 square planars. A slight decrease in linewidth is observed in case of two-dimensional "dimpled" CuO_4 layers (doublet (a)). Figure 7 also indicates that a linewidth of doublet (c), corresponding to FeO_4 tetrahedra, is independent of the temperature.

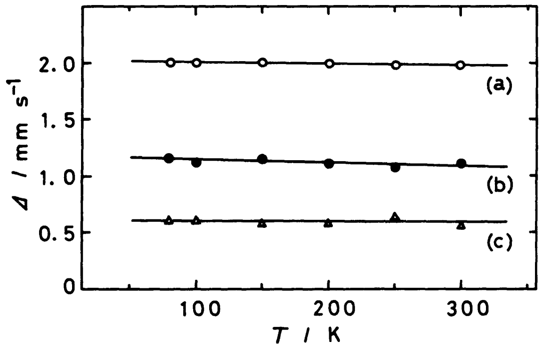

Fig. 6. Temperature dependency of quadrupole splitting (Δ). (a): doublet (a), (b): doublet (b), (c): doublet (c).

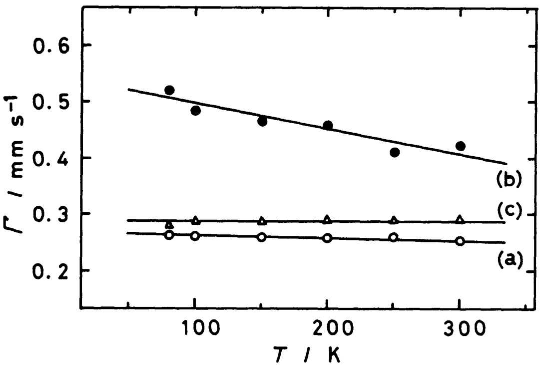

Fig. 7. Temperature dependency of linewidth (Γ). (a): doublet (a), (b): doublet (b), (c): doublet (c).

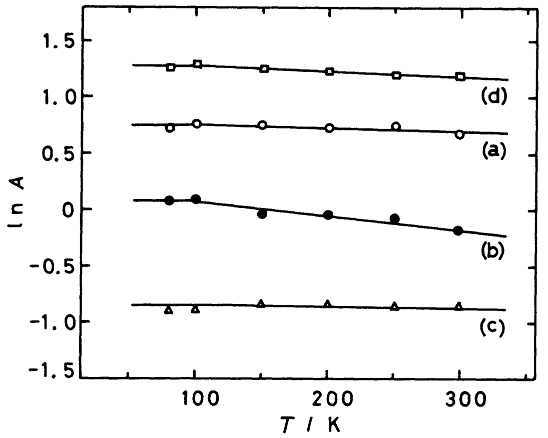

Fig. 8. Temperature dependency of absorption area (A). (a): doublet (a), (b): doublet (b), (c): doublet (c), (d): total absorption.

Relative absorption area of three doublets is shown in Fig. 8. Characteristic feature of Fig. 8 is similar to that of Figs. 5 and 7, i.e., absorption area of doublet (b) shows a pronounced decrease with increasing temperature. In contrast to this, absorption areas for doublets (a) and (c) are almost constant irrespective of the temperature, suggesting a high Debye temperature (Θ). A parameter of intermolecular force constant, Θ^2M, is calculated according to the formula,[41–43]

$$\Theta^2M = 3E^2/kc^2(-\mathrm{d}\ln f/\mathrm{d}T)^{-1}, \qquad (1)$$

where M is the mass of Mössbauer nucleus and E is a Mössbauer transition energy. In Eq. 1, k and c are Boltzmann constant and velocity of light, respectively. When a very thin sample is measured, $\mathrm{d}\ln f/\mathrm{d}T$ can be approximated by $\mathrm{d}\ln A/\mathrm{d}T$,[41–43] where A and f are absorption area and recoil-free fraction, respectively. Several Θ^2M values have already been obtained for K_2O–GeO_2–SnO_2,[41] BaF_2–ZrF_4–FeF_2,[42] and K_2SO_4–$ZnSO_4$–$Fe_2(SO_4)_3$[43] glasses by Nishida et al. As a result, Θ^2M proved to be in a range of 1.9—8.7×10^6 in these glasses, depending on the composition and structure of the glass matrix. In case of BaF_2–ZrF_4–FeF_2 glasses,[42] a phase transition was observed around 225 K, where isomer shift and absorption area showed a different composition dependency. It is expected that Θ^2M of ionic compound will be much larger than those obtained for the glasses.[41–43] A Θ^2M value obtained from the total absorption area (Fig. 8d) amounts to 15.5×10^6, which corresponds to a Debye temperature (Θ) of 521 K if we substitute 57 for M. A little lower Debye temperatures have been obtained in Mössbauer studies of superconducting $YBa_2Cu_3O_{7-\delta}$[27] (455 K) and $EuBa_2Cu_3O_{7-\delta}$ [28] (468 K) ceramics. Zhou et al.[27] reported that these Θ values are not exceptionally large. If we introduce a concept of "partial Debye temperature," which depends on each Mössbauer site, we can get some information corresponding to the amplitude of atomic vibrations at the individual sites. In this way, a Debye temperature of 330 K (Θ^2M= 6.2×10^6) is obtained from a slope of Fig. 8b. The relatively small Θ value is consistent with one-dimensional chains composed of $Cu(1)O_4$ square planars. On the other hand, "partial Debye temperature" amounts to 740 K (Θ^2M=31×10^6) in case of two-dimensional layers composed of "dimpled" $Cu(2)O_4$ planes (Fig. 8a). This higher Debye temperature will suggest a superconduction in the two-dimensional layers. "Partial Debye temperature" obtained from Fig. 8c (FeO_4 tetrahedra present along the b-axis) amounts to 1010 K (Θ^2M=58×10^6), for most of the absorption areas are almost constant irrespective of the temperature. Figure 8 indicates that an absorption area of each doublet measured at 78 K has the same magnitude as that measured at 100 K. Similar and more detailed results have recently been reported in case of ^{119}Sn-Mössbauer studies of $EuBa_2Cu_3O_{7-\delta}$[44] and $YBa_2Cu_3O_{7-\delta}$[45] superconductors doped with ^{119}Sn. In these studies,[44,45] it was suggested that phonons play an important role in electron pairing process. Temperature dependency of absorption area (Fig. 8) is similar to that of isomer shift shown in Fig. 5. It is understood from Figs. 5 and 8 that isomer shift is more sensitive to the change of temperature, because it is correlated with a square velocity ($\langle v^2\rangle$) of atomic vibrations, as described above. Anyhow, when a superconduction occurs in $YBa_2Cu_3O_{7-\delta}$ ceramics, amplitude of atomic vibrations concerned with "dimpled" $Cu(2)O_4$ planes (and also $Cu(1)O_4$ square planars) will be retained in spite of the decrease in temperature. This will cause a strong phonon-electron coupling in the superconducting state.

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