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LETTER TO THE EDITOR

A structural instability at $T \lesssim T_c$ in the Fe-doped $La_{1.85}Ba_{0.15}CuO_{4-y}$ superconductor

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Abstract. Mössbauer effect measurements at room temperature and at temperatures from 80 K down to 10 K were performed for the polycrystalline $La_{1.85}Ba_{0.15}Cu_{0.995}Fe_{0.005}O_{3.97}$ superconductor with T_c(onset) = 25 K. A lattice softening was found to occur below T_c(onset) and was ascribed to a structural instability, which may be associated with the appearance of the superconductivity. In addition, asymmetry and line broadening of the Mössbauer quadrupole splitting spectrum at room temperature were observed and can be attributed to a distortion of the octahedral O coordination around the Cu atom in the sample.

High-T_c superconductivity has generated an enormous amount of interest and research, but has so far eluded theoretical understanding. In order to study the possible mechanism responsible for the high transition temperature, it is useful to seek out the particular features that may be common to several of these high-T_c superconductors. In recent years, much effort has been devoted to studies of the vibrational behaviour of the Cu atoms [1–4] and rare-earth atoms [5, 6] in the $REBa_2Cu_3O_{7-\delta}$ (RE=rare-earth elements) system. The lattice softening in the vibrational behaviour observed at Cu sites of the superconducting phase and the lack of such a softening at rare-earth sites provide evidence for the important role played by the Cu–O bonds. However, it is still doubtful whether the softening results from the Cu(1) site or/and from the Cu(2) site in the $REBa_2Cu_3O_{7-\delta}$ system. Since only one Cu site in the CuO_2 layer exists in Bi-2212 and La-214 superconductors, the study of the relation between superconductivity and vibrational behaviour of the Cu atom in these systems would give clearer information. From our previous Mössbauer studies on two Bi-based superconductors, $Bi_2Sr_2CaCu_2O_{8+y}$ [7] and $Bi_4Sr_3Ca_3Cu_4O_{16+y}$ [8], the Cu atom in the former can be viewed as vibrating in an asymmetric double-well potential, which induces a structural instability in a wide temperature range, and below T_c has a drastic decrease in the atomic mean square displacement. This phenomenon was thought to be related to the multiple phases present in $Bi_2Sr_2CaCu_2O_{8+y}$. In the purer $Bi_4Sr_3Ca_3Cu_4O_{16+y}$ superconductor, the vibrational behaviour of the Cu atom is quite different from that in $Bi_2Sr_2CaCu_2O_{8+y}$ and shows a lattice softening occurring near T_c [8].

It is well known that the superconducting behaviour of $La_{2-x}Ba_xCuO_{4-\delta}$ is surprisingly complex. The T_c of this system as a function of Ba content has two maxima near compositions $x = 0.09$ and $x = 0.15$, both with $T_c \simeq 25$ K. Between these two maxima is a local minimum at $x = 0.12$ with T_c about 5 K [9]. Apparently, subtle changes in crystal structure and electronic state may drastically affect superconductivity. In the present work, we examine the temperature-dependent vibrational behaviour of the Fe atom by Mössbauer spectroscopy in $La_{2-x}Ba_xCu_{0.995}Fe_{0.005}O_{4-\delta}$ with $x = 0.15$. In addition, studies concerning

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the influence of the Ba dopant on the lattice vibration of $La_{2-x}Ba_xCu_{0.995}Fe_{0.005}O_{4-\delta}$ with similar O content are in progress. From our present measurements the dependence of T_c on the Ba concentration in $La_{2-x}Ba_xCu_{0.995}Fe_{0.005}O_{4-\delta}$ is similar to that in $La_{2-x}Ba_xCuO_{4-\delta}$.

The polycrystalline $La_{1.85}Ba_{0.15}Cu_{0.995}Fe_{0.005}O_{4-y}$ sample was prepared by the solid state reaction method. 99% pure powders of La_2O_3, $BaCo_3$, CuO and Fe_2O_3 (95% enriched in ^{57}Fe) were thoroughly mixed and calcined at 900 °C for 20 h. The reacted material was twice ground, pressed into a pellet, heated at 920 °C and 950 °C, respectively, for 20 h and then sintered at 1000 °C for 30 h. Finally, the sintered pellet was annealed in flowing O_2 gas at 900 °C for 12 h. Following this preparation procedure, we can also obtain the $La_{2-x}Ba_xCuO_{4-\delta}$ compounds with similar O content for different x values.

The x-ray powder diffractogram of the sample, using Cu Kα radiation, is shown in figure 1. We index the diffraction peaks following the method of Takagi and co-workers [10] and find that the structure has a tetragonal unit cell with $a = b \simeq 3.79$ Å and $c \simeq 13.30$ Å. From the temperature-dependent resistivity of the sample, the values of T_c(onset), $T_c(R = 50\%)$ and T_c(offset) are determined to be about 25 K, 15 K and 6 K, respectively. The average O content of the sample was determined to be 3.97 by a chemical iodommetry titration method. The influence of a small amount of Fe dopant upon the measured O content was ignored.

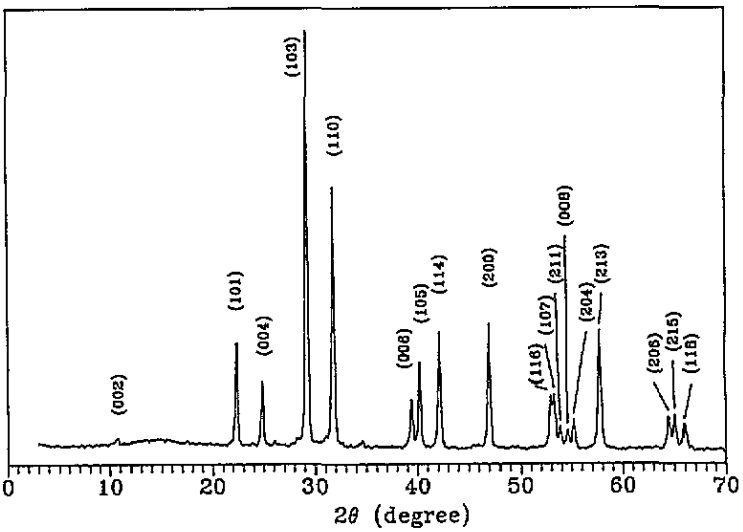

Figure 1. The x-ray diffraction pattern for $La_{1.85}Ba_{0.15}Cu_{0.995}Fe_{0.005}O_{4-y}$.

Mössbauer spectra at several temperatures for $La_{1.85}Ba_{0.15}Cu_{0.995}Fe_{0.005}O_{3.97}$ are shown in figure 2; all of them present a slightly asymmetric quadrupole splitting pattern. These spectra were first fitted using two symmetric quadrupole doublets. For the room-temperature spectrum, the line shifts δ (relative to α-Fe), quadrupole splittings ΔQ, fractional absorption areas A and full line widths at half maximum $\Delta\Gamma$ of these two doublets are determined as follows: $\delta = (0.29, 0.27)$ mm s^{-1}; $\Delta Q = (1.66, 1.25)$ mm s^{-1}; $A = (24\%, 76\%)$; $\Delta\Gamma = (0.28, 0.42)$ mm s^{-1}, respectively, and the reduced chi-square χ^2 is 0.61. Despite the fact that there is only one Cu site in the La_2CuO_4 system, most of the Mössbauer spectra reported by other groups always show the presence of several quadrupole doublets

[11]. This unusual result may be due to the distorted octahedral O environment around the Cu (or Fe) atom or the defects in the sample. In general, except for the main doublet, with much larger absorption area, and which can be attributed to the Fe site with octahedral O coordination, it is difficult to make exact assignments for the other doublets, with smaller absorption area, since these spectra are fairly unresolvable and can be fitted by many models with similar values of $\chi^2 < 1$. In our measurements the widths of the two absorption lines of the Mössbauer spectra in figure 2 are very near 0.5 mm s^{-1}, and we also fit them by using a quadrupole distribution model. It is assumed in this model that there is a correlation between quadrupole splitting and line shift, $\delta = \delta_0 + m\Delta Q$, responsible for the asymmetry of the spectrum, where δ_0 is the line shift corresponding to the zero quadrupole splitting and m is a proportionality constant. The theoretical curve is shown in figure 2 by a solid line. For the room-temperature spectrum the values of the parameters δ_0 and m are fitted to be 0.227 mm s^{-1} and 0.035, respectively, and the χ^2 value is 0.54. The corresponding quadrupole distribution curve is depicted in figure 3. Notably only one main peak, centring at $\Delta Q = 1.42$ mm s^{-1} (corresponding to $\delta = 0.28$ mm s^{-1}) is present in the distribution curve. This fact implies that the O octahedrons around the Cu atoms possess many kinds of slight distortion. Therefore it may be unnecessary to hypothesize that there are distinct Cu sites or impurity phases in the sample to explain the asymmetric Mössbauer spectrum of La_2CuO_4. Nevertheless more experiments are still required to identify the local structure around the Cu atom.

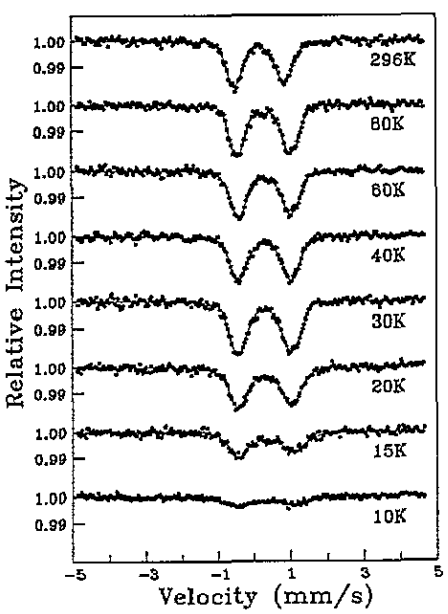

Figure 2. Typical Mössbauer spectra for $La_{1.85}Ba_{0.15}Cu_{0.995}Fe_{0.005}O_{4-y}$ at various temperatures. The solid line is the fitting curve using a quadrupole distribution model.

Figure 4 shows the logarithm of the total Mössbauer absorption area $\log A$ at low temperatures near T_c for the superconducting $La_{1.85}Ba_{0.15}Cu_{0.995}Fe_{0.005}O_{3.98}$. It should be noted that the absorption area is independent of the fitting model. For a thin absorber, $\log A = C - K_\gamma^2\langle u_i^2\rangle$, where C is a positive constant, K_γ is the amplitude of the wave

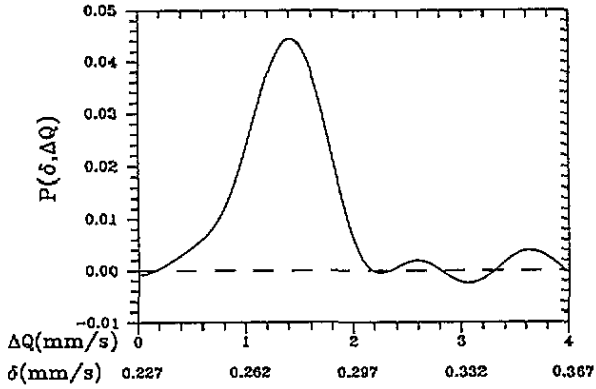

Figure 3. The distribution curve of the quadrupole splitting and line shift obtained from the Mössbauer spectrum at 296 K.

vector of the γ-ray, and $\langle u_i^2 \rangle$ is the average mean square displacement of Fe atoms. In figure 4 a successive drop in $\log A$, corresponding to the increase in $\langle u_i^2 \rangle$, is observed at $T \lesssim T_c(\text{onset})$. This anomalous behaviour is due to the softening of the lattice vibration and it indicates that there are structural changes or lattice instabilities. According to the report of Paul *et al* [12], $La_{1.85}Ba_{0.15}CuO_4$ ($T_c(\text{onset}) = 35$ K) has two temperature-induced structure changes: one happens at $T = 180$ K for the tetragonal-to-orthorhombic phase transition, another at $T \cong 60$ K for an abrupt change in the orthorhombic distortion. So the lattice softening below $T_c(\text{onset})$ observed in our measurements should be related to the superconductivity phenomenon. In addition, it is well known that a structural change always induces a dip in the $\log A$ value, as observed in ferroelectric materials [13], but not a successive drop. Hence the lattice softening at temperatures from $T_c(\text{onset})$ down to 10 K in our sample might be due to a structural instability. However, it is not understood clearly whether the electron pairing results in the structural instability or the structural instability enhances the electron pairing.

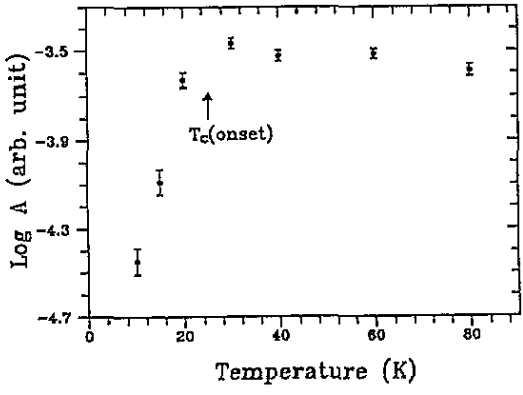

Figure 4. The logarithm of the absorption area $\log A$ as a function of temperature.

In figure 5 the temperature dependence of the Mössbauer average line shift $\langle \delta \rangle$, which is calculated by the relation

$$\langle\delta\rangle = \int \delta P(\Delta Q)\,\mathrm{d}\Delta Q \Big/ \int P(\Delta Q)\,\mathrm{d}\Delta Q$$

also shows a drastic decrease at $T \lesssim T_c$(onset), but no anomaly near or below T_c was observed in the temperature dependence of the average quadrupole splitting. This may be due to the large experimental errors of the data resulting from the weak Mössbauer effect of the spectra at low temperatures.

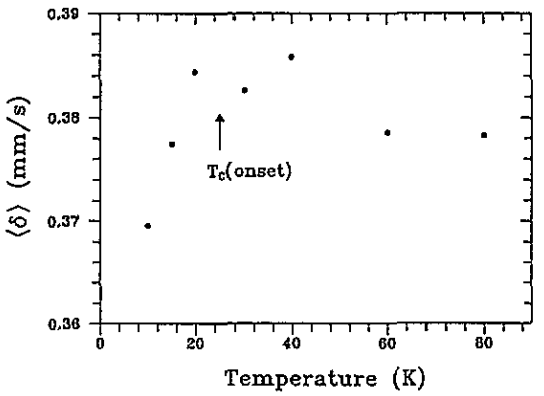

Figure 5. The average line shift $\langle\delta\rangle$ relative to α-Fe as a function of temperature.

In conclusion, we first found an apparent lattice softening due to a structural instability in the Fe-doped $La_{1.85}Ba_{0.15}CuO_4$ superconductor, which was observed from T_c(onset) = 25 K down to 10 K. The anomalous behaviours of its Mössbauer absorption area and average line shift are quite similar to those observed in the $Bi_4Sr_3Ca_3(Cu,Fe)_4O_{16+y}$ [8] and $YBa_2(Cu,Fe)_4O_8$ [14] superconductors. In addition, the asymmetry in its room-temperature Mössbauer spectrum can be fitted by using a one-peak quadrupole distribution model, which indicates a distortion of the octahedral O environment around the Cu atom.

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