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LETTER TO THE EDITOR

The anomalous temperature dependence of the vibrational behaviour and quadrupole splitting of Fe nuclei in $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_y$

C M Lin and S T Lin

Department of Physics, National Cheng Kung University, Tainan, Taiwan, Republic of China

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Abstract. Lattice softening is found to occur at about 30 K in $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_{16.38}$. The average quadrupole splitting of Fe nuclei decreases with increasing temperature between 40 K and 297 K and its reduction follows a $T^{3/2}$ law. Below 30 K the rapid drop in the average quadrupole splitting is closely related to lattice softening. The lattice vibrational behaviours of Fe-doped Bi-4334 and Fe-doped Bi-2212 are quite different.

Many experiments have shown the close relationship between structural instabilities and T_c in cuprate superconductors [1–7]. This suggests the importance of the lattice vibration in high-T_c superconductors. Recently we have also found [8] that the vibrational behaviour of Fe atoms in $Bi_2Sr_2Ca_1Cu_{1.96}Fe_{0.04}O_y$ is very anharmonic and this anharmonic behaviour can be explained by local structural excitations between two or more states supposedly existing in the material rather than by usual phonon–phonon interactions. In addition, we found that the enhancement in T_c for the annealed $Bi_2Sr_2Ca_1Cu_{1.96}Fe_{0.04}O_y$ having been reported by several authors [9] can be related to the increase in local structural instabilities. Since single-phase Bi-2212 is hard to obtain, the prepared Bi-2212 samples usually contain traces of Bi-2201 and Bi-2223 phases. Thus it is interesting and important to see if the anomalous behaviour of the lattice vibration observed in Fe-doped Bi-2212 also appears in purer samples. According to Yoshida's report [10], a single-phase Bi-2, 1.5, 1.5, 2 (equivalent to Bi-4334) is more easily prepared than single-phase Bi-2212. Therefore in this work, we will report our studies on the temperature dependence of the vibrational motion and quadrupole splitting of Fe nuclei in $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_y$ by means of Mössbauer spectroscopy. We find that the lattice vibrational behaviour of Fe-doped Bi-4334 is quite different from that of Fe-doped Bi-2212 and the temperature dependence of the quadrupole splitting of Fe nuclei at low temperatures is quite anomalous.

$Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_y$ samples were prepared by a solid-state reaction method. Detailed description of the sample preparation procedure has been presented elsewhere [8]. The x-ray diffraction pattern of the sample is similar to that of $Bi_2Sr_2Ca_1Cu_{1.96}Fe_{0.04}O_y$. No trace of Bi-2201 and Bi-2223 phases was observed in the x-ray diffractogram. This indicates that the prepared sample is approximately single phase. The value of y determined by chemical iodometry titration is about 16.36. The transition temperature is determined from the plot of resistance R versus temperature T. The values of T_c ($R = 50\%$) and T_c' ($R = 0$) are measured to be 53 K and 33 K, respectively. Unlike what is found for Fe-doped Bi-2212, annealing the sample at 300 °C for 30 min does not change T_c significantly, and

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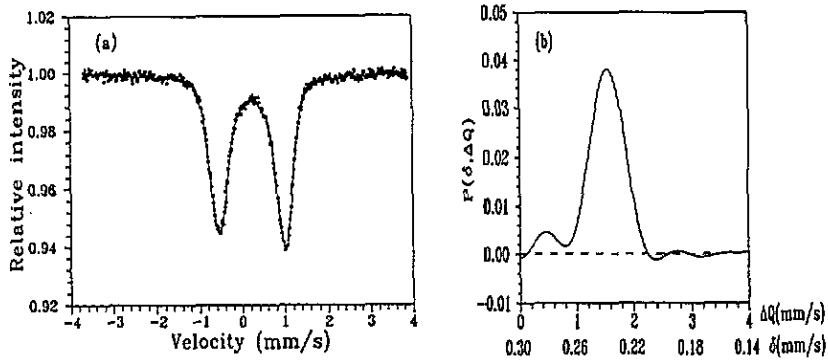

Figure 1. (*a*) Mössbauer spectrum at 297 K. The black dots represent the experimental data. The solid curve represents the theoretical calculation with consideration of the quadrupole splitting and line shift distribution. (*b*) The obtained distribution of the quadrupole splitting and line shift.

the sample becomes non-superconducting when it is annealed at 400 °C for 30 min. These effects may be due to the prepared sample having a lower oxygen content.

The room temperature Mössbauer spectrum of $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_{16.36}$ is shown in figure 1(*a*). This spectrum, like the spectrum of Fe-doped Bi-2212, can be well-fitted with three doublets having linewidths much larger than the natural linewidth ($\simeq 0.23$ mm s^{-1}). Large linewidths indicate a distribution of quadrupole splittings. This means that Cu atoms are surrounded by a variety of environments and is evidence of the modulation structure of Bi-based superconductors. Since the spectrum is poorly resolved, it is difficult to determine accurately the Mössbauer parameters of each doublet. Therefore, in this work we will assume that (i) the distribution $P(\Delta Q)$ of quadrupole splittings ΔQ, according to Window [11], is expressed as a Fourier series i.e. $P(\Delta Q) = \sum_{n=1}^{N} C_n[\cos(n\pi\Delta Q/\Delta Q_{max}) - (-1)^n]$ where C_n is the Fourier coefficient, and ΔQ_{max} is set large enough to ensure that $P(\Delta Q_{max}) = 0$; and (*ii*) the line shift δ is linearly related to the quadrupole splitting. The relation is given as: $\delta = \delta_0 + m\Delta Q$, where δ_0 is the line shift corresponding to zero quadrupole splitting and m is a proportionality constant. The Mössbauer spectra were then analysed with a modified Window method to obtain the best values of C_n and m. The obtained distribution $P(\Delta Q)$ of quadrupole splittings is displayed in figure 1(*b*). Theoretical calculation of the spectrum is indicated by the solid line in figure 1(*a*). It can be seen that the data are fitted very well. The absorption area A is then calculated and the logarithm of the absortion area plotted against temperature is shown in figure 2. For a thin absorber, $\log A \simeq C - K_\gamma^2\langle u_i^2\rangle$, where C is a positive constant, K_γ is the amplitude of the wave vector of the γ-ray, and $\langle u_i^2\rangle$ is the average mean square displacement (MSD) of Fe atoms. It is seen from figure 2 that the $\langle u_i^2\rangle$ for $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_{16.36}$ decreases and follows the Debye curve as the temperature is reduced down to around 50 K, then it deviates from the Debye curve and rises rapidly around 30 K. In the sense of the Mössbauer effect, a rapid reduction in $\langle u_i^2\rangle$ can be regarded as an indication of lattice softening. This implies that the lattice softening starts to occur around 30 K in this sample. Similar phenomena were also observed in $YBa_2(Cu_{0.98}Fe_{0.02})_4O_8$ by the Mössbauer effect measurements [13]. The exhibited behaviour in the lattice vibration of Fe-doped Bi-4334 is quite different from that observed in Fe-doped Bi-2212 [8], where the MSD of Fe (or Cu) atoms is unusually large in the temperature range 4.2 K–296 K. We think that a larger Ca content stabilizing the structure of Bi-4334 [10] may be the main reason for the normal temperature dependence

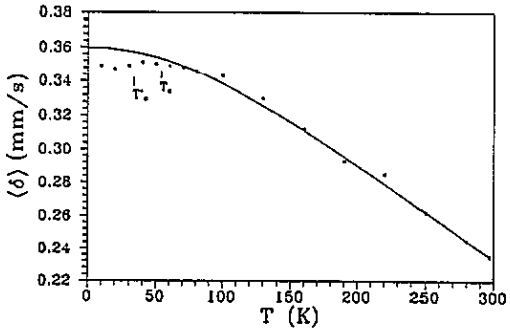

Figure 2. Logarithm of the absorption area log A as a function of temperature.

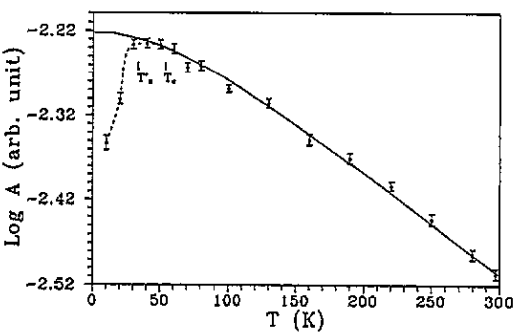

Figure 3. The average line shift $\langle\delta\rangle$ as a function of temperature. $\langle\delta\rangle$ is measured with respect to α-Fe at room temperature.

of MSD of Fe atoms in $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_{16.36}$ until lattice softening occurs.

From figure 1(b), we can see there are two peaks in $P(\Delta Q)$. The larger peak in $P(\Delta Q)$ with the value of ΔQ ranging from $\simeq 0.8$ mm s^{-1} to $\simeq 2.2$ mm s^{-1} can be attributed to Fe (or Cu) cations with regular pyramidal, distorted pyramidal, and trigonal bipyramidal coordination (especially for $\Delta Q \gtrsim 2$ mm s^{-1}) [8, 12]. The smaller peak with much smaller values of $\langle\Delta Q\rangle$ may result from Fe (or Cu) cations with six oxygen neighbours arranged in different ways.

The average line shift $\langle\delta\rangle$ can be written as $\langle\delta\rangle = \delta_0 + m\langle\Delta Q\rangle$, where $\langle\Delta Q\rangle$ is the average quadrupole splitting, which can be calculated by the relation

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

The values of $\langle\delta\rangle$ and $\langle\Delta Q\rangle$ as a function of temperature are shown in figures 3 and 4(a), respectively. The line shift δ consists of two contributions: one is the second-order Doppler shift δ_{sod} and the other is the isomer shift δ_{IS}. δ_{sod} is proportional to the mean square velocity $\langle v^2\rangle$ of Fe atoms, i.e. $\delta_{\mathrm{sod}} = -\langle v^2\rangle/2c$, where c is the velocity of light; δ_{IS} is proportional to the s electron density at the Fe nucleus. The solid line in figure 3 represents the theoretical calculation of δ_{sod}. It can only explain the data between 297 K and about 50 K. Below 50 K, the data deviate down from the solid curve. This implies that the variation of electron density due to the thermal expansion of the lattice and/or the effect of lattice softening must also be taken into account to explain the behaviour of the line shift at low temperatures.

The value of $\langle\Delta Q\rangle$ is seen to increase with decreasing temperature, but it precipitously drops around 30 K. Its temperature dependence between 40 K and 297 K is found to follow a $T^{3/2}$ law better than a T law (see figure 4(b)). The $T^{3/2}$ dependence of $\langle\Delta Q\rangle$ has been found already in impurities and host metals in many non-cubic metals. Theoretically, it was related to the temperature dependence of the electric field gradients created by both the surrounding lattice and conduction electrons; the temperature dependence of both the lattice and electronic fields is mainly due to the thermal expansion of the lattice and the influence of the lattice vibration, respectively [14]. The above proposed theory, we believe, may also be applied to interpret the $T^{3/2}$ dependence of $\langle\Delta Q\rangle$ at Fe^{3+} with a spin equal to 5/2 in the $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_{16.36}$ superconductor.

In summary, the lattice softening is found to occur at about 30 K in $Bi_4Sr_3Ca_3Cu_{3.92}Fe_{0.08}O_{16.36}$. The temperature dependence of the average quadrupole splitting between 40 K and 297 K is shown to follow a $T^{3/2}$ law. Below 30 K, the rapid

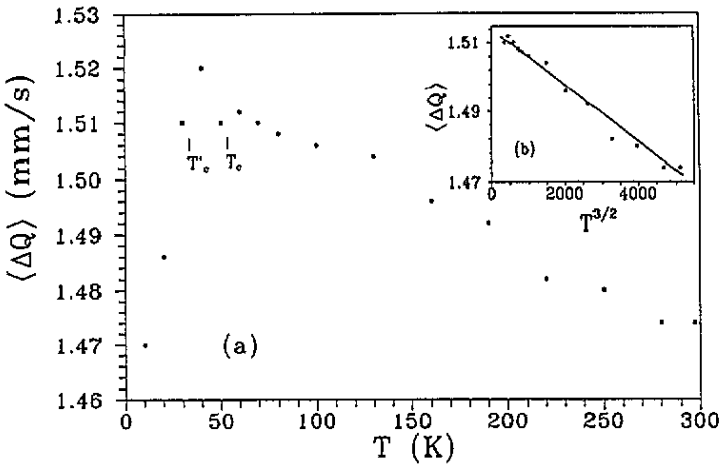

Figure 4. (*a*) T dependence of the average quadrupole splitting $\langle \Delta Q \rangle$; (*b*) $T^{3/2}$ dependence of the average quadrupole splitting $\langle \Delta Q \rangle$.

drop in quadrupole splitting may imply a local structural change, concomitant with lattice softening. The lattice vibrational behaviour of Fe-doped Bi-4334 and Fe-doped Bi-2212 is quite different. Since lattice softening starts to occur at a temperature close to T_c' ($R = 0$), the possible connection between the origin of superconductivity and structural instabilities deserves further studies.

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