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Anomalous behaviour of the lattice vibration of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$ and its possible correlation with T_c

C M Lin and S T Lin

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

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Abstract. The vibrational motion of Fe atoms in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$ studied by means of Mössbauer spectroscopy was found to be very anharmonic. This anharmonic behaviour can be explained by local structural excitations between two or more states supposedly existing in the material rather than by the usual phonon–phonon interactions. The increase in T_c for the annealed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$ is attributed to the increase in local structural instabilities which enhances the effective electron–electron pairing.

1. Introduction

Recent studies on the effect of annealing on the T_c of Bi 2212 superconductors have indicated that annealing these either in air or in a vacuum can increase T_c by as much as 25 K [1–4]. The increase in T_c was attributed to the desorption of oxygen during annealing and the sample containing less oxygen was found to have a lower carrier concentration [2]. This is apparently contrary to what was observed in $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ superconductors where T_c decreases with decreasing oxygen content.

The structure of Bi 2212 has incommensurate modulation [5, 6]. According to the explanation of Y LePage *et al* [7], the modulation is mainly caused by the lattice mismatch (attributed to the ordering of short Bi–O bonds) and the byproduct (or the origin) of this modulation is the insertion of extra oxygen into Bi–O layers. As the sample is annealed in a vacuum, the release of oxygen will cause the change in modulation structure, and the local structure around Cu, as revealed by our previous Mössbauer studies [4]. This leads us to believe that the increase in T_c for the annealed Bi 2212 is chiefly related to the distortion of Cu–O layers arising from the change in the modulation structure of Bi–O layers caused by the desorption of oxygen due to vacuum annealing.

In view of the importance of understanding the local properties around Cu, we here substitute Fe for Cu in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$ and investigate the vibrational behaviour of Fe atoms in both annealed and non-annealed Bi 2212 samples.

2. Experiment

Samples were prepared by solid state reaction methods to form compounds of nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$: 99% pure powders of Bi_2O_3 , SrCO_3 , CaCO_3 ,

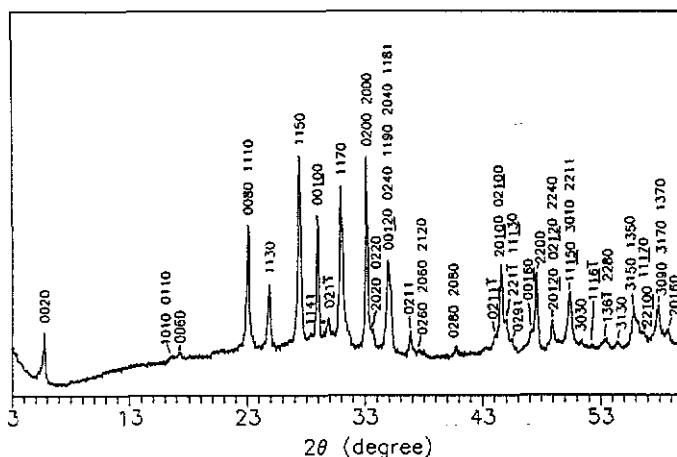


Figure 1. The x-ray powder diffraction pattern with Cu $K\alpha$ radiation. Reflections are assigned by four integers: h , k , l and m . The peak marked by * possibly arises from the Bi 2201 phase.

CuO and Fe_2O_3 (93% enriched in ^{57}Fe) were thoroughly mixed and heated in air at 800°C for 16 h. The reacted powder was then pulverized, pressed and sintered at 855°C for 5 days in air and subsequently cooled in the furnace to room temperature. The x-ray powder diffractogram of the sample is shown in figure 1. Following the method of Onoda *et al* [8] all the diffraction peaks including satellites, except the peak marked by an asterisk, can be indexed with $ha^* + kb^* + lc^* + mk$, where the a^* , b^* , c^* are the unit vectors reciprocal to a , b , c and k ($= b^*/4.8$) is the wave vector of the modulation wave. The sample was also checked by EDS. The data revealed that the Sr–Ca ratio was slightly larger than 2. The peak marked by an asterisk was found to result from the $\text{Bi}_2(\text{Sr}, \text{Ca})_2\text{CuO}_y$ phase. T_c was determined from the plot of resistivity versus temperature. For non-annealed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$ the value of T_c is 63 K. As the sample is annealed at 400°C for 30 min, its T_c is increased up to 80 K. Mössbauer experiments were run with a velocity scanning from -8 to 8 mm s^{-1} for absorption area measurements and a radioactive source of ^{57}Co in a Rh matrix.

3. Results and discussion

The room temperature Mössbauer spectrum of the non-annealed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$ is shown in figure 2. The spectrum can be fitted well by using three pairs of quadrupole doublets denoted by 1, 2, and 3. The line shifts δ , quadrupole splittings ΔQ , intensity ratios I and full widths at half maximum $\Delta\Gamma$ for the non-annealed sample at room temperature are determined as follows: $\delta = 0.19, 0.25$ and 0.26 mm s^{-1} ; $\Delta Q = 1.82, 1.40$ and 0.66 mm s^{-1} ; $I = 21.7\%, 51.5\%$ and 26.8% ; $\Delta\Gamma = 0.34, 0.42$ and 0.45 mm s^{-1} . The fact that the spectrum consists of more than one doublet and the measured line widths are much larger than the natural line width (0.23 mm s^{-1}) indicates that there is a distribution of quadrupole splittings in Fe-based Bi 2212. This means that Cu atoms are surrounded by a variety of environments and is evidence of the modulation structure existing in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_y$, as revealed by high-resolution electron diffraction studies [9]. Therefore, to analyse the spectrum with finite pairs of doublets is only an

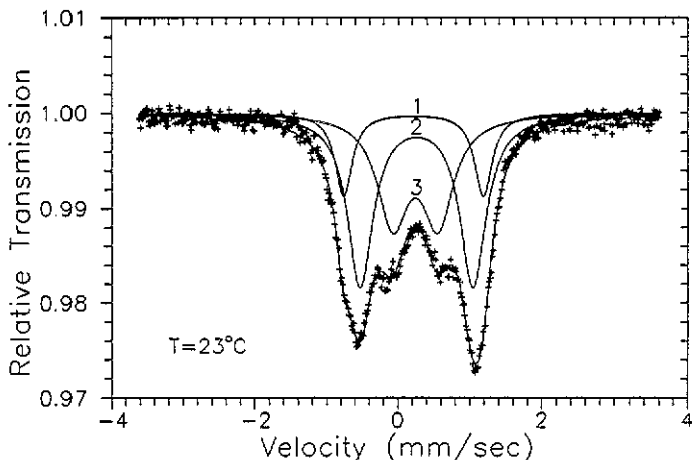


Figure 2. Room-temperature Mössbauer spectrum of non-annealed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$.

approximation. Some authors also did similar measurements [10–14]. Our results are in better agreement with those obtained by Tittonen *et al* [12], Tang *et al* [14], and Saragovi *et al* [11]. The difference in the measured values of quadrupole splittings and intensity ratios among these groups is possibly due to the difference in the actual compositions and preparation conditions of the sample.

Since the crystal structure has been shown to have one Cu site with five oxygen neighbours, doublet 2 with $\Delta Q_2 = 1.40 \text{ mm s}^{-1}$ can be attributed to Fe (or Cu) cations with possibly distorted pyramidal coordination, while doublet 1 with a much larger value of quadrupole splitting ($\Delta Q_1 = 1.82 \text{ mm s}^{-1}$) must be associated with Fe sites having lower local symmetry. After examining in detail the modulated structure of Bi 2212 revealed by recent x-ray and neutron diffraction data [15], we found that doublet 1 can be attributed to Fe cations residing in five-coordination trigonal bipyramidal sites. Since Fe in these sites can generate values of quadrupole splittings around 2 mm s^{-1} [16], it is thus unnecessary to relate ΔQ_1 to Fe cations with planar four-fold coordination in the faulted CuO_2 planes as suggested by Tang *et al* [14]. Doublet 3 with a much smaller quadrupole splitting $\Delta Q_3 \approx 0.66 \text{ mm s}^{-1}$ may only be attributed to an Fe cation with six oxygen neighbours. This doublet can arise either from a Bi 2201 phase or from Fe cations (still in the Bi 2212 phase) attracting one excess oxygen to form six coordination, as occurs in Fe-doped $(\text{Y, Gd})_1\text{Ba}_2\text{Cu}_3\text{O}_y$. However, we think the latter is more likely for the following reason. Tarascon *et al* [17] have shown that the Mössbauer spectrum of an Fe-doped Bi 2201 phase consists of two doublets (one with $\Delta Q_1 \approx 0.64 \text{ mm s}^{-1}$, the other with $\Delta Q_2 \approx 1.60 \text{ mm s}^{-1}$) rather than a single doublet. Thus, if we take these two doublets into account in analysing the observed Mössbauer spectrum, they will occupy more than 27% of the total absorption area. This seems quite impossible since only a small amount of Bi 2201 phase was observed in our x-ray diffractogram (see figure 1).

Figures 3(a) and (b) show the logarithm of the total Mössbauer absorption area $\log A$ as a function of temperature for non-annealed and annealed samples. For a thin absorber, $\log A \approx C_1 - K_\gamma^2 \langle u_i^2 \rangle$, where C_1 is a positive constant, K_γ is the amplitude of the wave vector of the incident γ -ray and $\langle u_i^2 \rangle$ is the average mean-squared displacement of Fe atoms. The values obtained for $\langle u_i^2 \rangle$ s for both samples are seen to decrease quite

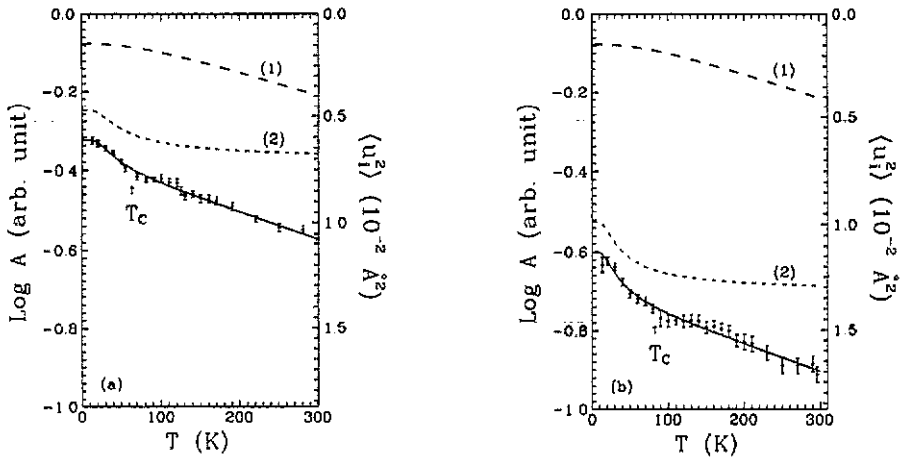


Figure 3. Logarithm of the total absorption area, $\log A$, and average mean squared displacement, $\langle u_i^2 \rangle$, as a function of temperature for (a) non-annealed and (b) annealed $\text{Bi}_7\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_v$. Curves (1) and (2) represent contributions from harmonic potential and phonon-LSE interaction.

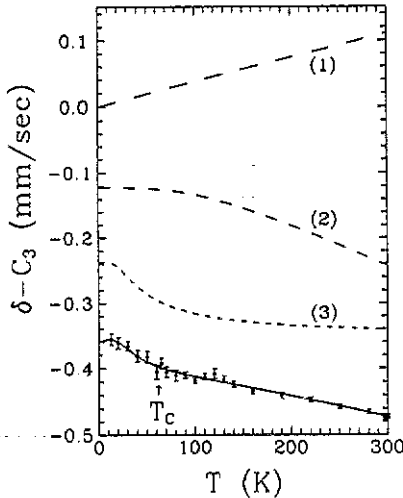


Figure 4. Line shift δ minus C_3 for non-annealed $\text{Bi}_7\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_v$ as a function of temperature. Curves (1), (2) and (3) represent contributions from thermal expansion, from harmonic potential and from phonon-LSE interaction, respectively ($C_3 = 0.73 \text{ mm s}^{-1}$).

rapidly below about T_c . The temperature dependence of $\langle u_i^2 \rangle$ is unusual in the sense that its behaviour cannot be explained by the harmonic potential or the usual phonon-phonon interactions.

To determine the line shift, the Mössbauer experiment was re-run with a smaller velocity range (-4 to 4 mm s^{-1}) to obtain a better resolved spectrum. The line shift δ determined from the quadrupole splitting of doublet 2 for the non-annealed sample is shown in figure 4. It can evidently be seen that the anomalous behaviour also appears

below T_c in the line shift. In fact, other shifts determined from doublet 1 and 3 also exhibit similar behaviour. As these two doublets are less populated and poorly resolved, the data obtained have large experimental errors and therefore will not be used for theoretical analysis.

The measured value of $\langle u_i^2 \rangle$ is much larger than the harmonic value (see figure 3), indicating that the structure of Bi 2212 is locally very unstable. The model which we used for the structural instabilities, characterized by local structural excitations (LSEs) between two or more ground-state configurations existing in superconductors, was first proposed by Ngai and Reinecke in 1977 [18]. They considered a number of isolated LSEs interacting with the harmonic phonons and the total Hamiltonian was written in the following form

$$H = H_s + H_p + H_{sp} \tag{1}$$

where

$$H_s = \sum_j \Delta_j \sigma_j^z$$

$$H_p = \sum_{k\alpha} \omega_{k\alpha} a_{k\alpha}^\dagger a_{k\alpha}$$

$$H_{sp} = 2N^{-1/2} \sum_{k\alpha j} g_{k\alpha j} \sigma_j^x (a_{k\alpha}^\dagger + a_{k\alpha}) \exp(i\theta_{k_j})$$

$a_{k\alpha}$ is the annihilation operator for a phonon of wave vector k and polarization α whose energy is $\hbar\omega_{k\alpha}$. Here the LSEs are taken to have only two levels which are separated by the energy Δ_j and which are spanned by the Pauli spin operators σ_j . The third term represents the interaction between LSEs and phonons where the $g_{k\alpha j}$ is the coupling parameter. The free energy $F^{(2)}$ (to order g^2) has been calculated in detail by Sheard and Toombs [19]. The total internal energy is given by $E^{(2)} = \partial(\beta F^{(2)})/\partial\beta$, where $\beta = 1/(k_B T)$. It includes contributions from the phonon system, from the LSE system, and from the LSE-phonon interaction energy. Then the $\langle u_i^2 \rangle$ can be written as

$$\langle u_i^2 \rangle = \langle u_i^2 \rangle_0 + (\hbar/MN) \sum_{k\alpha j} \omega_{k\alpha}^{-2} E_{k\alpha j}^{(2)} \tag{2}$$

where $\langle u_i^2 \rangle_0$ is the value in harmonic approximation and $E_{k\alpha j}^{(2)}$ is a contribution to the internal energy of the phonon system (to order g^2) which is given by $E_{ph}^{(2)} = \sum_{k\alpha j} E_{k\alpha j}^{(2)}(T)$. The second term in equation (2) can be thought of as resulting from an increase in the occupation number of $k\alpha$ phonon modes. Owing to the density of states, the main contribution of the second term in equation (2) comes from large k . For relatively small Δ_j , the second term can be expanded in terms of $O(\Delta_j/\omega_{k\alpha})$. This gives

$$\begin{aligned} \langle u_i^2 \rangle = \langle u_i^2 \rangle_0 + (9\hbar/MN) \left\{ \sum_j (G^2/\omega_D^3)(\omega_D - \omega_L) - [2 \ln(\omega_D/\omega_L)] \right. \\ \left. \times \sum_j (G/\omega_D)^2 (\Delta_j/\omega_D) \tanh(\frac{1}{2}\beta\Delta_j) \right\}. \end{aligned} \tag{3}$$

Evaluating equation (2), we have replaced $\sum_{k\alpha}$ by $\int_{\omega_L}^{\omega_D} \mathcal{D}(\omega) d\omega$ where $\mathcal{D}(\omega)$ is the density of phonon states and ω_D is the Debye frequency. To be consistent with the expansion used in equation (2), ω_L must be greater than Δ_j . Since it cannot be defined unambiguously, we introduce it as an adjustable parameter. Using the Debye approximation, we have let $g_{k\alpha j}^2 = G^2 k [20]$, $\omega_{k j} = \nu k$, where ν is the velocity of sound. Equation

(3) was derived by Ngai and Reinecke, but the lower limit ω_L of the integral was treated differently [18]. The first term in the braces of equation (3) is the leading contribution and it arises from modifications of zero point energy. Then the logarithm of the total absorption area, $\log A$, can be expressed as

$$\log A = C_1 - \frac{6E_r}{\omega_D} \left\{ \frac{1}{4} + \left(\frac{k_B T}{\omega_D} \right)^2 \int_0^{\omega_D/(k_B T)} \frac{x dx}{e^x - 1} \right\} - \frac{18E_r N_L}{\hbar v N} \{ (G^2/\omega_D^3) \\ \times (\omega_D - \omega_L) - [2 \ln(\omega_D/\omega_L)] (G/\omega_D)^2 (\Delta/\omega_D) \tanh(\Delta/2k_B T) \} \quad (4)$$

where E_r is the recoil energy of the free Fe^{57} atom and, for simplicity, we have replaced Δ_j by a single value Δ . Therefore Σ_j is equal to N_L , the number of sites with LSE.

The measured line shift δ of the absorber relative to metallic iron at room temperature is given by

$$\delta(T) = \delta_{\text{th}}(T) + C_2 T + C_3. \quad (5)$$

The thermal shift δ_{th} is equal to $-\langle v_i^2 \rangle / (2c)$, where $\langle v_i^2 \rangle$ is the average mean-squared velocity of Fe atoms and c is the velocity of light. $C_2 T$ is the term used for correcting the effects of thermal expansion, $C_2 = -(\beta/\kappa) [\partial \delta_{\text{IS}} / \partial P]_T$, where β is the thermal expansion coefficient, κ is the compressibility, and $[\partial \delta_{\text{IS}} / \partial P]_T$ is the derivative of the isomer shift δ_{IS} with respect to pressure at constant temperature. C_3 is a temperature-independent constant. Using the above formulations, we can obtain

$$\langle v_i^2 \rangle = \langle v_i^2 \rangle_0 + \frac{\hbar}{MN} \sum_{k\alpha j} E_{k\alpha j}^{(2)}. \quad (6)$$

The first term in equation (6) is the contribution of the harmonic potential and the second term arises from the phonon-LSE interaction. Treating the summation over $k\alpha$ and j as before, the result is

$$\delta = -\frac{9}{2cM} \left\{ \frac{\omega_D}{8} + \frac{(k_B T)^4}{\omega_D^3} \int_0^{\omega_D/(k_B T)} \frac{x^3 dx}{e^x - 1} \right\} - (9N_L/2cvMN\hbar) \{ (G^2/\omega_D^3) (\omega_D^3 - \omega_L^3) \\ - (\omega_D^2 - \omega_L^2) (G/\omega_D)^2 (\Delta/\omega_D) \tanh(\Delta/2k_B T) \} + C_2 T + C_3. \quad (7)$$

The measured $\log A$ and line shift δ are then fitted to equations (4) and (7). The measured values of the parameters $\theta_D (= \hbar\omega_D/k_B)$ and Δ are respectively 450 K and 6.0 meV for non-annealed and 448 K and 4.6 meV for annealed $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$. The ratio of the coupling constant for the annealed sample to that for the non-annealed one, $G'^{(2)}/G^2$, is 1.87 by assuming $N'_L/N = N_L/N$. The C_2 is predicted to be $3.7 \times 10^{-4} \text{ mm (s K)}^{-1}$. Taking $\beta = 45 \times 10^{-6} \text{ K}^{-1}$ [21] and $\kappa = 1.50 \times 10^{-6} \text{ bar}^{-1}$ [21, 22], $[\partial \delta_{\text{IS}} / \partial P]_T$ is estimated to be $-1.2 \times 10^{-5} \text{ mm (s bar)}^{-1}$, which is larger than the value for metallic iron ($-0.82 \times 10^{-6} \text{ mm (s bar)}^{-1}$) by about one order. The unusually large value of $[\partial \delta_{\text{IS}} / \partial P]_T$ may either indicate that the line shift δ extracted from the poorly resolved spectrum may not be very reliable or implies that there is large electron transfer (for example, from d to p) between the overlapping bands [23, 24] as the sample is compressed (note that the compressibility of Bi 2212 ($1.5 \times 10^{-6} \text{ bar}^{-1}$) is much larger than that of metallic iron ($5.8 \times 10^{-7} \text{ bar}^{-1}$) [25]).

Fortunately, even if the line shift data is unreliable, the measured values of θ_D , Δ , and $G'^{(2)}/G^2$ still remain valid. Direct measurements of the pressure coefficient of the isomer shift would be helpful in elucidating this problem. The measured value of ω_L is

34 meV. This indicates that the principal contribution to LSEs comes from the range of phonon energy between 34 meV and 39 meV (Debye phonon energy). A large value of ω_L and a small value of Δ justify the assumption that $E_{k\alpha}^{(2)}$ in equation (2) can be expanded in terms of $O(\Delta_j/\omega_{k\alpha})$. In figures 3(a) and (b), curves (1) and (2) represent the contributions of the harmonic potential and the phonon-LSE interaction to $\langle u_i^2 \rangle$, respectively. It is clearly seen that the latter effect is much larger than the former effect and the rapid decrease in $\langle u_i^2 \rangle$ for temperatures below T_c is mainly due to phonon-LSE interactions. The sum of curves (1) and (2) is indicated by the full curve, which is in good agreement with the experimental values of $\langle u_i^2 \rangle$.

Figure 4 shows that the relative line shift δ includes contributions from the harmonic potential, from the phonon-LSE interaction and from thermal expansion. It is seen that the phonon-LSE interaction is also mainly responsible for the rapid drop in δ below T_c . The full curve representing the sum of curves (1), (2) and (3) also fits the experimental data for δ fairly well.

Thus our theoretical calculations based on the idea of LSEs are able to explain the anomalous behaviour observed in $\log A$ and δ for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_{1.96}\text{Fe}_{0.04}\text{O}_y$ quite satisfactorily. The materials which possibly have structural instabilities, as pointed out by Ngai and Reinicke, are those exhibiting more than one phase as a function of composition (or temperature and pressure) and characterized by defects such as vacancies, impurities, and/or non-stoichiometry [18]. It is now well known that the composition of Bi-based superconductors can be expressed by a general formula $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$ with $n = 1, 2, 3$. This means that by varying the value of n (not necessarily integral), a superconductor can be transformed from one phase to another phase. Additionally, Bi-based superconductors are non-stoichiometric cuprates containing oxygen vacancies, impurities and exhibiting an incommensurate modulation structure (which can be viewed as a kind of defect). Thus, this series of superconductors indeed possesses most of the conditions required for having structural instabilities. Although the origin of LSE is still unclear, we think the LSE associated with Fe (or Cu atoms) in the Bi 2212 phase might be due to the structural instabilities between the Bi 2212 phase and the Bi 2201 (or Bi 2223) phase caused by the local variation of the Sr-Ca ratio [26].

We discuss the possible correlation of T_c with local structural instabilities below. It has been shown in the earlier section that the value of Δ ($= 4.6$ meV) for the annealed sample is less than the value of Δ ($= 6.0$ meV) for the non-annealed one and $G^{(2)} > G^2$. This shows that vacuum annealing can decrease the energy separation Δ between two local states but increase the phonon-LSE coupling constant.

Annealed samples in which LSE states with lower values of Δ and higher values of $G^{(2)}$ (smaller potential barrier) will be more unstable in local structure and will have larger values of $\langle u_i^2 \rangle$ (see figure 3). A larger value of $\langle u_i^2 \rangle$ can thus lead to larger electron-phonon interaction and therefore to an enhancement of T_c . In addition, electrons interacting directly with LSEs having smaller energy splitting Δ and a smaller potential barrier can also increase electron pairing and further enhance T_c [18, 27, 28].

Therefore, we believe that the increase in T_c for Bi 2212 superconductors subjected to annealing is possibly due to the increase in local structural instabilities which enhances both electron-phonon coupling and electron-electron pairing directly by LSEs [18]. This explains why the annealed Bi 2212 with lower carrier concentration can have higher T_c than the non-annealed Bi 2212 with higher carrier concentration.

It must be mentioned that we have also studied the vibrational motion of Fe atoms in $\text{Y}_1\text{Ba}_2\text{Cu}_{2.95}\text{Fe}_{0.05}\text{O}_{7-\delta}$. No anomalous behaviour was observed. This does not contradict

the recent findings by Conradson *et al* [29] that the structural instabilities in $Y_1Ba_2Cu_3O_{7-\delta}$ superconductors are possibly associated with axial oxygen rather than with Cu atoms.

4. Conclusion

A large value of the mean-squared displacement of Fe atoms observed in $Bi_2Sr_2Ca_1Cu_{1.96}Fe_{0.04}O_y$ suggests that the local structure of this superconductor is quite unstable. The unusual behaviour of the vibrational motion of Fe atoms can be explained by local structural excitations between two states supposedly existing in the material. The energy separation and the potential barrier between two local states for the annealed sample were found to be smaller than those for the non-annealed one. This implies that the increase in T_c for the annealed $Bi_2Sr_2Ca_1Cu_{1.96}Fe_{0.04}O_y$ is possibly due to the increase in local structural instabilities which enhances the effective electron-electron (or hole-hole) pairing. To understand the origin of LSE in $Bi_2Sr_2Ca_1Cu_2O_y$, detailed studies of the structural stabilities of Bi-based superconductors by other experimental techniques are necessary.

Acknowledgments

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Note added in proof. After completing the paper, we became aware of a paper by Mook *et al* [30] which reports that there is a sudden drop in the average kinetic energy $\langle E \rangle$ at T_c for the motion of Cu atoms in the Cu-O planes of the Bi 2212 phase. The average kinetic energy $\langle E \rangle$ is proportional to the thermal shift $\langle v^2 \rangle / 2c$ which is included in our line shift measurements. However, our results show that the thermal shift (the sum of curves (2) and (3) in figure 4) decreases rapidly below T_c rather than drops suddenly at T_c . Therefore, we also observed the rapid decrease in $\langle u^2 \rangle$ but they did not.

References

- [1] Dinia M A, Pefia O, Perrin C and Sergent M 1990 *Solid State Commun.* **63** 715
- [2] Groen W A, deLeeuw D M and Feiner L F 1990 *Physica C* **165** 35
- [3] Zhao J, Wu M, Abdul-Razzaq W and Seehra M S 1990 *Physica C* **165** 135
- [4] Lin S T, Chung W S, Chou C Y and Lin C M 1990 *J. Phys.: Condens. Matter* **2** 8763
- [5] Shindo D, Hiraga K, Hirabayashi M, Kikuchi M and Syono Y 1988 *Japan. J. Appl. Phys.* **27** L1018
- [6] Subramanian M A, Tovaradi C C, Calabrese J C, Gopalakrishnan J, Morrissey K J, Askew T R, Flippen R B, Chowdhury U and Sleight A W 1988 *Science* **239** 1015
- [7] LePage Y, McKinnon W R, Tarascon J M and Barbour P 1989 *Phys. Rev. B* **40** 6810
- [8] Onoda M, Yamamoto A, Takayama-Muromachi E and Takaekawa S 1988 *Japan. J. Appl. Phys.* **27** L833
- [9] Shindo D, Hiraga K, Hirabayashi M, Kikuchi M and Syono Y 1988 *Japan. J. Appl. Phys.* **27** L1018
- [10] Bremert O, Michaelsen C and Krebs H U 1989 *J. Appl. Phys.* **65** 1018
- [11] Saragovi C, Fainstein C, Etchegoin P and Duhalde S 1990 *Physica C* **168** 493
- [12] Tittonen I, Hietaniemi J, Huttunen J, Linden J, Katila T, Karlemo T, Karppinen M, Niinisto L and Ullakku K 1990 *Phys. Rev. B* **42** 4212
- [13] Micklite H, Zimmermann W, Moshchalkov V and Leonjuk L 1990 *Solid State Commun.* **75** 995
- [14] Tang H, Qiu Z Q, Du Y W and Walker J C 1990 *Hyperfine Interact.* **62** 65

- [15] Yamamoto A, Onoda M, Takayama-Muromachi E and Izumi F 1990 *Phys. Rev. B* **42** 4228
- [16] Burns R G and Burns V M 1984 *J. Geophys. Res.* **89** Suppl. C 313
- [17] Tarascon J M, LePage Y, McKinnon W R, Ramesh R, Eibschute M, Tselepis E, Wang E and Hull G W 1990 *Physica C* **167** 20
- [18] Ngai K L and Reinecke T L 1977 *Phys. Rev. B* **16** 1077
- [19] Sheard F W and Toombs G A 1971 *J. Phys. C: Solid State Phys.* **4** 313
- [20] Elliott R J and Parkinson J B 1967 *Proc. Phys. Soc.* **92** 1024
- [21] Gavarrı J R, Monnerer O, Vacquier G, Carel C and Vettier C 1990 *Physica C* **172** 213
- [22] Tajima Y, Hikita M, Suzuki M and Hidaka Y 1989 *Physica C* **158** 237
- [23] Hybertsen M S and Matteis L F 1988 *Phys. Rev. Lett.* **60** 1661
Herman F, Kasowski R V and Hsu W Y 1988 *Phys. Rev. B* **38** 204
- [24] Wells B O, Shen Z X, Dessau D S, Spicer W E, Olson C G, Mitsi D B, Kapitulnik A, List R S and Arki A 1988 *Phys. Rev. Lett.* **65** 3056
- [25] Williamson D L 1978 *Mössbauer Isomer Shifts* ed G K Shenoy and F E Wagner (Amsterdam: North-Holland) p 319-358
- [26] Yoshida M 1988 *Japan. J. Appl. Phys.* **27** L2044
- [27] Plakida N M, Aksenov V L and Drechsler S L 1987 *Europhys. Lett.* **4** 1309
- [28] Hardy J R and Flocken J W 1990 *Phys. Rev. Lett.* **60** 2191
- [29] Conradson S D, Raistrick I D and Bishop A R 1990 *Science* **248** 1394
- [30] Mook H A, Mostoller M, Harvey J A, Hill N W, Chakoumakos B C and Sales B C 1990 *Phys. Rev. Lett.* **65** 2712