SOFTENING OF VIBRATIONAL MODES OF THE HIGH-T_c PHASE OF Bi-SYSTEM SUPERCONDUCTOR

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ABSTRACT

The temperature dependent ^{57}Fe Mössbauer and X-ray diffraction measurement on Bi-system 2:2:2:3 phase have been carried out from 77 K to 300 K. It was found that there are two anomalous behaviors of lattice vibrational modes near 125 K and 220 K. This phenomena of lattice softening above T_c is taken as a precursor effect of superconductivity.

Keywords: Mössbauer effect High-T_c superconductor Lattice softening X-ray diffraction

1 INTRODUCTION

Since novel high-T_c superconductors were discovered, theorists and experimentalists have been seeking out the relationship between traditional and novel superconductors in order to research further the possible mechanism responsible for the high transition temperature. As is well known. In A15 system, for instance V_3Si and Nb_3Sn structural phase transitions have been observed above, but relatively close to, the transition temperature (T_c+4 K and T_c+22 K respectively)[1,2]. On the other hand. In Y-system oxide superconductor, the striking lattice softenings have been observed above T_c and at higher temperature by means of Mössbauer and ultrasonic measurements[3,4]. In Bi-system superconductors, it is important and significant to study further the anomalous behavior of lattice above T_c for finding the relationship between superconductivity and softening of vibrational modes. So that we have performed temperature dependent Mössbauer and X-ray diffraction measurements to investigate the anomalous behavior of Bi-based high-T_c phase. In the Fe-doped sample, from consideration of ionic radius and electronegativity. Fe at very low concentration levels would be expected to replace Cu sites and ^{57}Fe also offers a particularly suitable probe of Mössbauer spectroscopy. We have performed

T-dependent Mössbauer experiments on Fe-doped high-T_c phase of Bi-system. In addition, T-dependent X-ray diffraction have been undertaken on same sample.

2 EXPERIMENTAL

The Fe-doped polycrystalline samples were prepared by mixing Bi_2O_3, $SrCO_3$, $CaCO_3$, CuO and Fe_2O_3 (74% enriched ^{57}Fe), and calcining for 24 h at 800 °C. The powder was twice ground and calcined in order to ensure homogeneity. The pellet was then pressed and sintered at 880 °C in air for 240 h. In order to increase the relative amount of the high-T_c phase, an unstoichiometric nominal composition of 2:2:3:4 was used. This composition has a more beneficial effect on the formation of the homogeneity phase of 2223 than 2:2:2:3. The crystal structure and lattice constant for $Bi_{1.6}Pb_{0.4}Sr_2Ca_3(Cu_{0.98}Fe_{0.02})_4O_y$ were determined by powder X-ray diffraction with a Phillips PW1700 diffractometer and Cu K_α radiation. The diffraction intensity of (002) plane and lattice constant were measured by means of stepscan. The step height and sampling time is 0.02 degree and 1000 s/deg, respectively. According to XRD measurement the main component in the sample was 2223 phase. Besides the diffraction data of the majority 2223 phase, the diffraction of the minority phase (Bi, Pb)-Sr-Ca-Cu-O (or 2212 phase), unreacted CuO and others were presented in X-ray diffraction pattern. Four-probe dc resistivity and ac susceptibility measurements were conducted. The normal-state resistivity was metalliclike and displayed a narrow transition to the superconducting state with $T_{c0} = 90$ K. The ^{57}Fe Mössbauer absorption spectra were obtained in a standard transition geometry with a conventional acceleration spectrometer. The $^{57}Co/Rh$ source was held at room temperature. The sample thickness was approximately 1.0 mg/cm^2 of ^{57}Fe.

3 RESULTS AND DISCUSSIONS

As shown in Fig.1, Mössbauer spectrum at 121 K appears to consist of at least two unresolved Lorentzian doublets. The site-intensity ratio of two doublets is close to 1/2. The isomer shifts clearly show that the Fe is in a high-spin 3+ state. As indicated early, based on a comparison of ionic diameters, the 3+ valence state of Fe would be expected to substitute for the Cu^{2+} ion. Two quadrupole-split doublets are assigned to two inequivalent pyramidal and square sites, respectively[5].

The curve shown in Fig.2 represents the temperature dependence of recoil-free fraction measured by the normalized area under the Mössbauer spectrum, $A(T)$, for the $Bi_{1.6}Pb_{0.4}Sr_2Ca_3(Cu_{0.98}Fe_{0.02})_4O_y$ sample. To avoid the systemic errors inherent in determining the area by fitting an unresolved spectrum, the absorption area was obtained directly from the data by means of a Simpson integration using a fitted-background subtraction. As shown in Fig.2, we can see two anomalies, in the

form of dips, near 125 K and 220 K. The characteristic temperature θ_D: found from the data for $f(T)$. Based on Debye model, a fit of the linear behavior to $\ln(A)=k<x^2>$ yields a Debye temperature $\theta_D = 310$ K and 330 K within temperature region $150\text{ K}<T<220\text{ K}$ and $T>220$ K respectively. A more direct comparison to anticipated

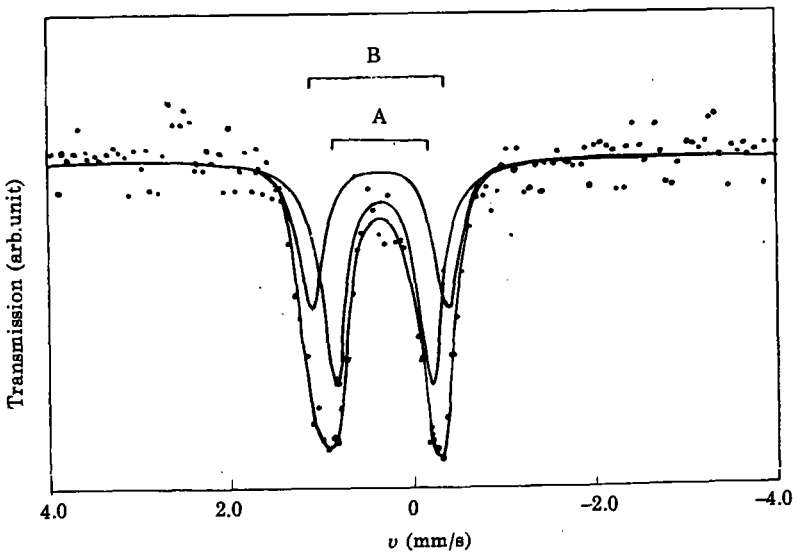

Fig.1 Mössbauer spectrum of Bi—2223 phase taken at 121 K

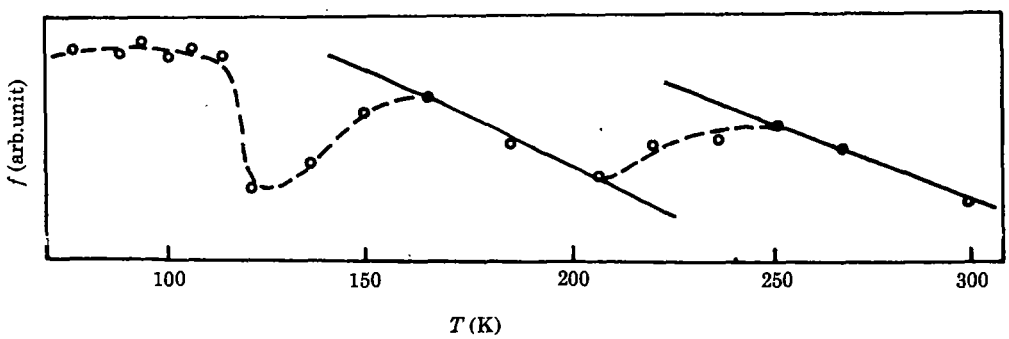

Fig.2 Temperature dependence of recoil—free fraction of Bi—2223 phase

temperature dependence of $A(T)$ is shown in Fig.2. The solid curve is $A(T)$ calculated using the Debye model, the clearly departure from the anticipated behavior in Fig.2 is a indication of softening in lattice vibration for $T<150$ K and $T<220$ K respectively. It is worth emphasizing that the anomalous behavior of $f(T)$ at low temperature ($T<150$ K) is more striking. Using ^{57}Fe Mössbauer spectroscopy we can determine the temperature dependence of a moment of the vibration spectra at Cu site which is tightly involved in the superconductivity. The Mössbauer analysis leads us to conclude that the softening of the phonons localized onto the Cu–O layers may be as a

precursor before the onset of superconductivity. On the other hand, the lattice instability occurring at high temperature ($T<220$ K) may be the pretransition of low temperature ($T<150$ K) anomaly. In Y-system 1-2-3 phase, the similar lattice properties have also been observed[3,4]. Such lattice instabilities related to softening of vibrational modes, like the case in A15 structural superconductors, might be a general feature for novel oxide superconductor and might have a close relation with their high-T_c superconductivity.

We focus our X-ray diffraction study on stronger peak reflecting from (002) plane. Such peak is considered as a diagnostic feature of the high-T_c phase. The variation of intensity and lattice constant directly provides the information of lattice vibration and interatomic distance of Cu-O and Bi-O layers X-ray diffraction experiments also show that in such two temperature regions there are anomalous low-T and high-T behaviors for intensity $I(T)$ and lattice constant $C(T)$.

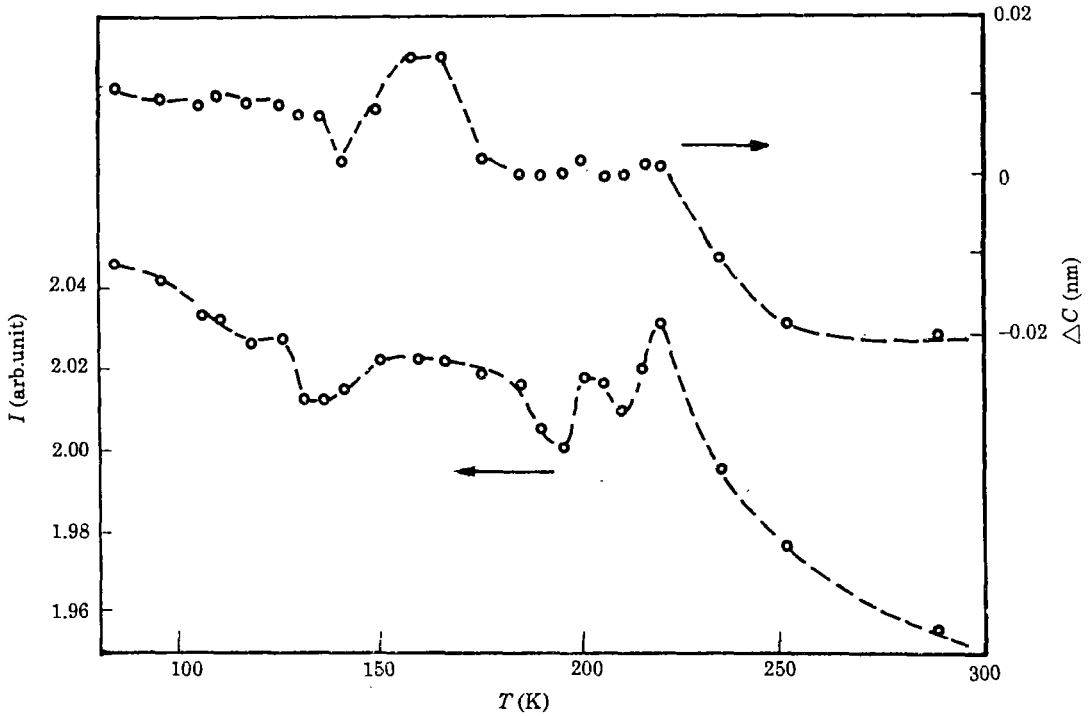

Fig.3 Temperature dependent lattice parameter $C(T)$ and intensity $I(T)$

Fig.3 shows the results of diffraction intensity and lattice constant of (002) plane versus temperature for sample $Bi_{1.6}Pb_{0.4}Sr_2Ca_3(Cu_{0.98}Fe_{0.02})_4O_y$. In diffraction pattern no distinct change was observed with temperature variety. However the change tendency of lattice constant shows anomalies: the lattice constant decreases with increasing temperature, especially at about 140 K and 220 K lattice constant shows sudden change. Above result shows that framework of lattice structure has no change in this temperature region; however, some subtle change in fine structure could occur, for

instance. regulation of atomic coordination and separation. In addition diffraction intensity of (002) peak shows a large dip at about 140 K corresponding to lattice expansion. Clearly, phase-transition-like anomaly centered at 125 K takes place. The substantial weakening of Bragg reflection on (002) plane implies that the amplitudes of lattice vibration increase and the atoms deviate from original equilibrium positions, and the strength of interaction between the atoms becomes weak. It is natural to link the observed anomalies, which are evidence of softening of the phonon spectrum of ceramic at these temperatures, with corresponding anomalies which have been seen previously for Mössbauer experimental result. Moreover a big M-shaped fluctuation in intensity at about 220 K is observed in Fig.3. Along with ultrasonic study[6]. The present Mössbauer effect and X-ray diffraction results demonstrate the evidence of Bi-softening of lattice vibration, which might be important for superconductivity in oxide superconductors. No matter which superconducting mechanism is the dominant interaction contributing to pairing, such softenings surely give affects on superconductivity. Therefore the anomalous phonon behavior related to the softening of lattice vibration cannot be overlooked for the high-T_c superconductors.

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