PHYSICAL REVIEW B VOLUME 37, NUMBER 7 1 MARCH 1988

Softening of Cu-O vibrational modes as a precursor to onset of superconductivity in $EuBa_2Cu_3O_{7-\delta}$

P. Boolchand, R. N. Enzweiler,* Ivan Zitkovsky, Jack Wells,† and Wayne Bresser‡
Department of Electrical and Computer Engineering and Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221

Darl McDaniel
Department of Chemistry, University of Cincinnati, Cincinnati, Ohio 45221

R. L. Meng, P. H. Hor, C. W. Chu
Department of Physics and Space Vacuum Epitaxy Center, University of Houston, Houston, Texas 77004

C. Y. Huang
Lockheed Palo Alto Research Center Laboratory, Palo Alto, California 94304

(Received 19 October 1987)

T-dependent ^{119}Sn Mössbauer Debye-Waller factors $f(T)$ in $EuBa_2Cu_{2.98}Sn_{0.02}O_{7-\delta}$ display evidence of a substantial softening in lattice vibrations at $T \lesssim 110$ K. In a previous ^{151}Eu study, no detectable softening in $f(T)$ was found at the rare-earth site. These results taken together show that Sn atoms as a dilute impurity replace predominantly Cu(1) sites in the Cu—O chains of the orthorhombic structure. It appears that a softening in vibrational modes localized onto the Cu—O linear chains occurs as a precursor to the onset of superconductivity. These results show that phonons do appear to play an important role in electron pairing in these high-T_c oxide superconductors.

The mechanism of electron pairing in the high-T_c oxide superconductors has evoked lively debates between theorists and experimentalists alike. Several alternative mechanisms to the conventional Bardeen-Cooper-Schrieffer (BCS) one have been discussed recently.[1] The observation of the elusive oxygen isotopes effect[2] in $YBa_2Cu_3O_{7-\delta}$ unequivocally shows that a conventional BCS phonon-mediated electron pairing mechanism cannot be overlooked in spite of the unexpectedly high transition temperatures. In this context, Phillips has suggested[3] that the surprisingly high T_c of these ternary oxides may be the consequence of the microscopically soft nature of these lattices which promotes giant electron-phonon interaction.

An issue of central importance is whether experimental evidence for anomalies in the density of vibrational states occur as a function of temperature in these materials. Inelastic neutron scattering measurements on $YBa_2Cu_3O_{7-\delta}$, when complete,[4] will undoubtedly provide important clues on the behavior of phonons. Neutron-powder-diffraction measurements indicate[5] that the mean-square displacement (MSD) of the oxygen site O(4) residing in the Ba plane is rather anisotropic as well as unusually large in relation to all other oxygen sites in the orthorhombic structure. It is also possible that site-specific measurements of mean-square displacement and local chemistry, as revealed by a local probelike NMR (Ref. 6) or Mössbauer spectroscopy,[7] for example, can also provide important clues in understanding the behavior of phonons and defects in these materials.

In a unit cell of the ABO_3 perovskite structure, as found with $BaSnO_3$, the cation A is centered in a cubic cell with 12 edge-centered O atoms as nearest neighbors. The B atoms occupy the vertices of the cube, and thus have six nearest O atoms as neighbors in an octahedral arrangement. The ratio of the AO distance to the BO distance is equal to $\sqrt{2}$ in the ideal perovskite structure. In $EuBa_2Cu_3O_{7-\delta}$, Eu replaces $\frac{1}{3}$ of the Ba atoms, but the smaller Eu atoms cannot support a coordination number (CN) of 12 (Fig. 1). The CN about Eu (with $\delta = 0$) is 8. The still smaller Cu atoms replace all of the Sn, and although the average Cu—O distance is about the same as the Sn—O distance in $BaSnO_3$, there is a high degree of anisotropy[5] in the Cu—O internuclear distances. The CN of Ba drops to 10 in the $\delta = 0$ structure. For charge balance, the high-T_c superconductor should be formulated as $YBa_2Cu^{2+}_{2+2\delta}Cu^{3+}_{1-2\delta}O_{7-\delta}$. From consideration of charge radius, and electronegativity, Sn^{4+} at very low concentration levels would be expected to replace Cu^{3+}. Since Sn also offers a particularly suitable Mössbauer spectroscopy probe,[7] we have performed T-dependent experiments on Sn-doped samples of $EuBa_2Cu_3O_{7-\delta}$ and report the results of these experiments in this paper.

The present ^{119}Sn Mössbauer experiments provide striking evidence of a substantial softening in lattice vibrations at $T \lesssim 110$ K. These results are in sharp contrast to previous ^{151}Eu Mössbauer spectroscopy results[7] on the present material where no evidence of softening in $f(T)$ could be detected at the rare-earth site. These Mössbauer results taken together lead us to conclude that phonons lo-

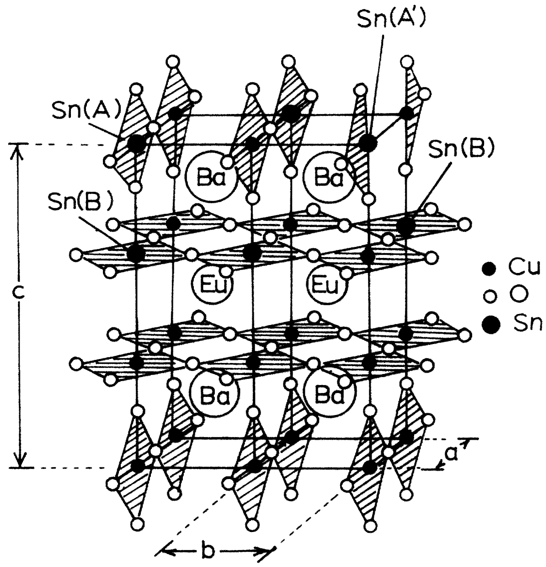

FIG. 1. Crystal structure of $EuBa_2Cu_3O_{7-\delta}$ showing various possible Sn sites. A Sn atom replacing a Cu(1) site and Cu(2) site in the structure is labeled respectively as Sn(A) and Sn(B) while a Sn(A) site processing an O(1) site vacancy is labeled as Sn(A') site.

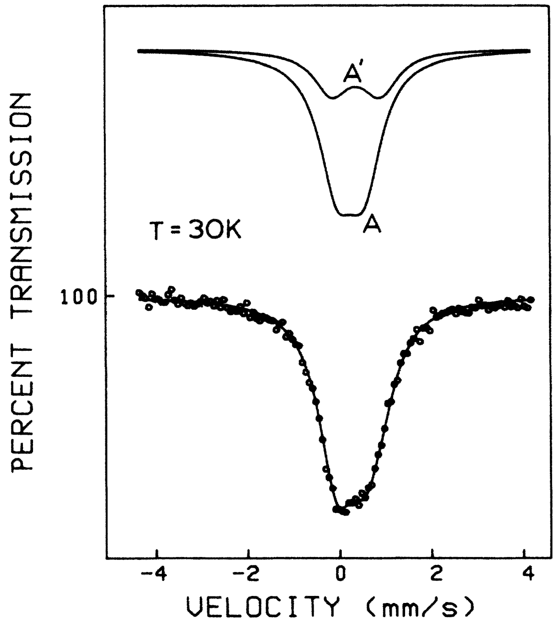

FIG. 2. ^{119}Sn Mössbauer spectrum of a slow cooled $EuBa_2Cu_{2.98}Sn_{0.02}O_{7-\delta}$ sample taken at indicated temperature is deconvoluted in terms of two quadrupole split sites A and A'. The microscopic site structure is shown in Fig. 4.

calized onto the Cu—O linear chains soften as a precursor to the onset of superconductivity. This result, along with several others,[2,3,8,9] shows that the BCS mechanism of electron pairing via phonons cannot be overlooked for these novel oxide superconductors.

Samples of $EuBa_2Cu_{2.98}Sn_{0.02}O_{7-\delta}$ composition were prepared[10] by thoroughly mixing and sintering Eu_2O_3, $BaCO_3$, CuO and isotopically enriched $^{119}SnO_2$ in the usual way at 950 °C. In the final step, samples were either slow cooled (925 °C to 100 °C in 5 h) or fast cooled (925 to 100 °C in 5 min) in an oxygen environment. T-dependent ^{119}Sn Mössbauer spectra of the samples in the range 300 K $\lesssim T \lesssim 12$ K were recorded using a closed-cycle refrigerator facility described elsewhere.[7]

The effect of sample preparation on the superconducting transition temperature onset (T_{c0}) follows a trend documented previously[11] for $YBa_2Cu_3O_{7-\delta}$. Fast-cooled $EuBa_2Bu_{2.98}Sn_{0.02}O_{7-\delta}$ samples display in general a lower T_{c0} ($\simeq 30$ K) then slow-cooled ones ($T_{c0} \simeq 85$ K) probably because of a structural change from orthorhombic to tetragonal and a reduced oxygen content. In the present work we will discuss results on slow cooled samples only. Spectra of such samples display in general a partially resolved asymmetric doublet (Fig. 2). At the outset we can state unambiguously that the isomer shift on the resonance resides in a region[12] characteristic of Sn in its 4+ state of oxidation. For reasons discussed later we have chosen to deconvolute the asymmetric line shape into two quadrupole doublets (A,A') as shown in Fig. 2, yielding a site intensity ratio $I_A/I_{A'} \sim 2.8$. The nuclear hyperfine structure parameters of these sites (A,A') are summarized in Table I.

In these experiments where the emitter ($^{119}Sn^m$ in $CaSnO_3$) is held at room temperature, the T dependence of the integrated area under the gamma resonance derives from the Debye-Waller factor $f(T)$ of the ternary oxide superconductor used as an absorber. Figure 3(b) summarizes results for a slow cooled sample. We note that at $T > 200$ K, $f(T)$ decreases linearly with T. On such a plot the slope $df(T)/dT$ at high T (> 200 K) uniquely fixes a characteristic Mössbauer-Debye temperature Θ_D. For the present case we note that a value of $\Theta_D \simeq 320(10)$ K is appropriate, and this value may be contrasted to a value of $\Theta_D = 400(10)$ K for monoclinic SnO_2,[13] the starting material used to prepare the high-T_c superconductor.

The central result to emerge from the present work is the anomalous low-T ($T \lesssim 110$ K) behavior in $f(T)$ [Fig. 3(b)] which displays evidence of a substantial softening in lattice vibrations. Specifically, the continuous line drawn in Fig. 3 is a plot of $f(T)$ calculated assuming a Debye-like density of vibrational states with the indicated Θ_D, while the broken line drawn through the data at low T is merely a guide to the eye. These results clearly demonstrate that as T is lowered to about $T_s = 120$ K there occurs a precursor effect: Vibrational modes of the ter-

TABLE I. Summarized nuclear hyperfine structure parameters of sites (A,A').

Slow-cooled $EuBa_2Cu_{2.98}Sn_{0.02}O_{7-\delta}$	Isomer shift[a] (mm/s)	Quadrupole splitting (mm/s)
Site A	0.15(5)	0.60(10)
Site A'	0.28(5)	1.05(10)

[a]Relative to $CaSnO_3$ at 300 K.

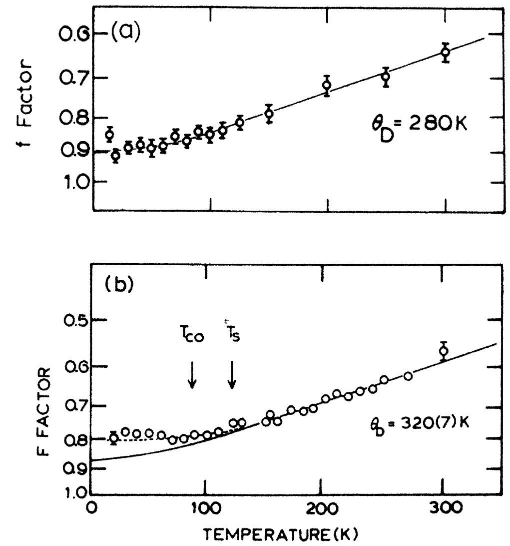

FIG. 3. (a) T dependence of ^{151}Eu recoil-free-fraction in $EuBa_2Cu_3O_{7-\delta}$ taken from Ref. 7. (b) T dependence of ^{119}Sn recoil-free fraction in $EuBa_2Cu_{2.98}Sn_{0.02}O_{7-\delta}$ sample obtained in the present work. Note that at $T=T\simeq120$ K; the f factor displays evidence of softening. The continuous line is a plot of the f factor assuming a Debye-like density of states with the indicated Debye temperature.

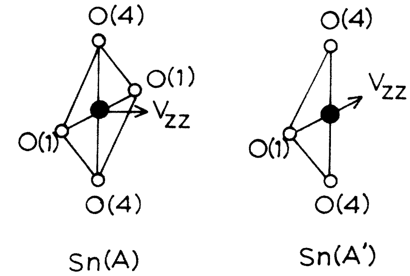

FIG. 4. Microscopic configurations of site A and site A' consist respectively of a square planar and a triangular coordination of oxygen near neighbors. The z component of the electric-field-gradient tensor is expected to be perpendicular to the square plane while it will lie along the twofold axis for the triangular configuration.

nary oxide soften before the onset of superconductivity at $T_{c0}\simeq80$ K. It is important to emphasize that the result of phonon softening is *independent* of the manner in which Mössbauer spectra are deconvoluted since what we have plotted in Fig. 3 is the *total* integrated area under the gamma resonance. In principle one can also obtain $f(T)$ for each of the sites (A and A') by deconvoluting the spectra. Result of such an analysis will be discussed elsewhere.

There are several compelling reasons to believe that Sn^{4+} ions as a *dilute impurity* in the orthorhombic structure would replace primarily Cu(1) sites in the chains. Apart from noting that the size of Sn^{4+} dictates that it will replace Cu rather than Ba or Eu, the anisotropy[5] of the Cu—O distances allows little choice between site Cu(1) and site Cu(2) based on ionic radii. However, Pauling's electrostatic valence rules[14] favor Sn^{4+} in Cu(1) sites. Furthermore, the high electronegativity of Sn^{4+} would cause it to seek a site of high electron density in a solid.[15] Second, on stoichiometric grounds[16] an oxygen count of 6.8, typical of high-T_c $YBa_2Cu_3O_{7-\delta}$, requires that there be on an average about one O(1) site vacant per unit cell and this leads to a pair of threefold coordinated Cu(1) sites for every six Cu(1) sites present in a square-planar geometry as illustrated in Fig. 1. Indeed the observed Mössbauer site intensity ratio $I_A/I_{A'}\sim3$ leads us to identify site $A(A')$ with Sn^{4+} present in a square-planar (triangular) configuration of oxygen near neighbors as shown in Figs. 1 and 4. The larger quadrupole splitting of the A' site in relation to the A site (Table I) is certainly in harmony with reduced local symmetry at A' site.

We additionally know that oxygen desorption from the samples at elevated temperatures in the range $300\,^\circ C < T < 500\,^\circ C$ systematically broadens the Mössbauer line shape. This result is due to a decrease in the site intensity ratio $I_A/I_{A'}$ as the concentration of O(1) vacancy sites increases, supporting the contention that the A' site is a vacancy associated site. Generally speaking the presence of such vacancies interrupts the quasi-one-dimensional chains and this disorder[17] is thought to destroy superconductivity.

The softening in $f(T)$ observed at ^{119}Sn sites in the present experiments [Fig. 3(a)] and the lack of such a softening at the rare-earth (^{151}Eu) site in the same material [Fig. 3(a)] provides an important clue. It suggests that the underlying local density of vibrational states at the ^{151}Eu site and the ^{119}Sn site have radically different character. One way to reconcile these results is to recognize that Sn atoms replace Cu(1) sites in the chains and it is the O(1) and O(4) near-neighbor oxygen sites that display an anomalous[5] vibrational behavior as a function of temperature as demonstrated by Caponi *et al.*[5] Since these particular oxygen sites are insulated from the rare-earth site, one expects a normal T dependence of $f(T)$ at the ^{151}Eu site.

Two recent experiments that bear on the issue of phonon softening in $YBa_2Cu_3O_{7-\delta}$ include light scattering[8,9] and lattice thermal expansion measurements.[18] Specifically, the Raman-active 335 cm^{-1} phonon, and the ir-active 279 cm^{-1} and 310 cm^{-1} phonons, each associated with a Cu—O breathing mode, display an unusual T dependence: These phonons generally blue shift as T is lowered below 300 K, only to have this trend qualitatively interrupted near $T\simeq100$ K, below which these phonons red shift, i.e., soften by about 4 cm^{-1} in the temperature range $10\text{ K} < T < 100\text{ K}$. The T dependence of the lattice thermal expansion [$\alpha(T)$] of sintered $YBa_2Cu_3O_{7-\delta}$ samples normalized to those of pure Cu [$\alpha_{Cu}(T)$], i.e., the ratio $\alpha(T)/\alpha_{Cu}(T)$, also displays[18] a threshold behavior near $T\simeq100$ K. At $T<100$ K, this ratio is found to increase rapidly as T is lowered, leading to the suggestion[18] that the Debye temperature Θ_D of the ternary oxide steadily decreases as T is lowered—and this macroscopic result correlates rather well in temperature with the present microscopic result on $f(T)$ displayed in Fig. 3.

In conclusion, we have presented new microscopic results using Mössbauer spectroscopy on Sn-doped $EuBa_2Cu_3O_{7-\delta}$ samples that are consistent with the notion that Sn atoms as a dilute impurity largely replace Cu atoms in Cu(1) sites in the orthorhombic structure. Furthermore, the T-dependence of the Debye-Waller factor $f(T)$ displays clear evidence of a softening in vibration modes at $T \lesssim 110$ K which represents a precursor effect to the onset of superconductivity. Such an anomaly in $f(T)$ was not found at the rare-earth site (Eu site) as documented previously. The present result on ^{119}Sn, along with our previous result on the ^{151} Eu site, demonstrate that the softening of lattice vibrations must be localized onto the Cu–O chains in the orthorhombic structure. The present results along with the observation of the isotope effect lend clear support to the notion that electron pairing in these novel oxide superconductors is probably of the BCS type involving optical phonons of the CuO chains.

This work was supported by National Science Foundation Grant No. DMR-8521005 at the University of Cincinnati, National Science Foundation Grant DMR-8616537, NASA Grants No. NAGW-977 and No. NAG8-51 at University of Houston, and Independent Research Funds at Lockheed.

*Permanent address: SUNY College at Cortland, Cortland, NY 13045.

†Permanent address: Thomas Moore College, Crestview Hills, KY 41017.

‡Permanent address: Xavier University, Cincinnati, OH 45221.

[1]Marvin L. Cohen, in *Novel Superconductivity,* Proceedings of the International workshop on Novel Mechanisms of Superconductivity, Berkeley, 1987, edited by S. A. Wolf and V. Z. Kresin (Plenum, New York, 1987), p. 1095.

[2]J. Leary, H. C. zur Loye, S. W. Keller, T. A. Faltens, W. K. Hain, J. N. Michaels, and A. M. Stacy, Phys. Rev. Lett. **59**, 1236 (1987).

[3]J. C. Phillips, Phys. Rev. B **36**, 861 (1987); J. C. Phillips, Phys. Rev. Lett. **59**, 1856 (1987).

[4]B. Renker, F. Gompf, E. Gering, N. Nucker, D. Ewert, W. Richardt, and H. Rietschel, Z. Phys. B **67**, 15 (1987).

[5]J. J. Caponi, C. Chaillout, A. W. Hewat, P. Lejay, M. Marezio, N. Nguyen, B. Raveau, J. L. Soubeyroux, J. L. Tholence, and R. Tournier, Europhys. Lett. **3**, 1301 (1987).

[6]W. W. Warren, Jr., R. E. Walstedt, G. F. Brennert, G. P. Espinosa, and J. P. Remeika, Phys. Rev. Lett. **59**, 1860 (1987).

[7]P. Boolchand, R. N. Enzweiler, Ivan Zitkovsky, R. L. Meng, P. H. Hor, C. W. Chu, and C. Y. Huang, Solid State Commun. **63**, 521 (1987).

[8]R. M. McFarlane, H. Rosen, and H. Seki (unpublished).

[9]D. A. Bonn, J. E. Greedan, C. V. Stager, T. Timusk, M. Doss, S. Herr, K. Kamaras, and D. A. Tanner, Phys. Rev. Lett. **58**, 2249 (1987).

[10]P. H. Hor, L. Gao, R. L. Meng, Z. J. Huang, Y. Q. Wang, K. Forster, J. Vassilious, C. W. Chu, M. K. Wu, J. R. Ashburn, and C. T. Torng, Phys. Rev. Lett. **58**, 911 (1987).

[11]Aravinda M. Kini, Urs Geiser, Huey-Chuen, I. Kao, K. Douglas Carlson, Han H. Wang, Marilyn R. Monaghan, and Jack M. Williams, Inorg. Chem. **26**, 1834 (1987).

[12]P. Boolchand, in *Physical Properties of Amorphous Materials,* edited by David Adler, Brian B. Schwartz, and Martin C. Steele (Plenum, New York, 1985), p. 221.

[13]Ray Enzweiler and P. Boolchand (unpublished).

[14]L. Pauling, *The Nature of the Chemical Bond,* 3rd ed. (Cornell Univ. Press, Ithaca, NY, 1960).

[15]J. K. Burdett, E. Canadell, and T. Hughbanks, J. Am. Chem. Soc. **108**, 3971 (1986).

[16]Presence of some oxygen vacancies in the linear chains, i.e., O(1) sites are widely believed to be critical to the existence of superconductivity in $YBa_2Cu_3O_{7-\delta}$ with $\delta \sim 0.2$. The presence of one O(1) vacant site in the triple layered perovskite structure leads to a stoichiometry of $YBa_2Cu_3O_{6.75}$ corresponding to $\delta \sim 0.25$. The presence of an O(1) oxygen vacancy leads to two types of Cu(1) sites in the chains, A and A' (as shown in Fig. 4) having a population ratio $N_A/N_{A'} = 3/1$.

[17]Ron Dagani, Chemical Engineering News **65**, 33 (1987), 21 September issue.

[18]R. W. McCallum, R. N. Shelton, M. A. Noack, J. D. Verhoeven, C. A. Swenson, M. A. Damento, K. A. Gschneider, E. D. Gibson, and A. R. Moodenbaugh, Ref. 1.