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Mössbauer study of the lattice dynamics in ^{119}Sn-doped superconducting and nonsuperconducting $YBa_2Cu_3O_{7-\delta}$

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The temperature dependence of the relative recoil-free fraction of the the ^{119}Sn Mössbauer absorption has been measured in the orthorhombic superconducting and in the tetragonal nonsuperconducting phase of ^{119}Sn-doped $YBa_2Cu_3O_{7-\delta}$. For the superconducting $YBa_2Cu_3O_{7-\delta}$ phase, the recoil-free fraction shows softening which appears for $T < 150$ K, whereas for the nonsuperconducting $YBa_2Cu_3O_{7-\delta}$ phase, it agrees with that obtained using the measured phonon spectrum without any evidence of softening.

With the discovery of high-temperature superconductivity in $(La,Ba)_2CuO_4$ by Bednorz and Müller[1] and the more recent discovery of a much higher superconducting transition temperature, T_c, in $YBa_2Cu_3O_{7-\delta}$,[2] there has been an explosion of research activity. Much of this recent work has been focused at establishing the structure and electronic and magnetic properties of $YBa_2Cu_3O_{7-\delta}$ and the relationship of these properties and the structure to oxygen content.[3-8] $YBa_2Cu_3O_{7-\delta}$ with $\delta \lesssim 0$ crystallizes in an orthoromic structure for $T < 750\,^{\circ}C$ and can be prepared in nearly single-phase form with a narrow superconducting transition in the vicinity of 95 K.[3-6] Above 750 °C, there is a loss of oxygen and a transformation to a tetragonal structure.[6-8] If $YBa_2Cu_3O_{7-\delta}$ with $\delta \simeq 0$ is vacuum annealed at elevated temperatures, oxygen is lost from the system and the tetragonal structure is stable to low temperatures.[7,8] The oxygen-deficient, tetragonal structure, i.e., $YBa_2Cu_3O_{7-\delta}$ with $\delta \approx 1$, is a nonsuperconducting semiconductor.[7]

Structure studies of the orthorombic phase have established that the Y and Ba ions form an ordered arrangement which is centrally located along the *c* axis within the unit cell, the Cu—O bonds which are located midway between the Ba planes form closely coordinated linear chains along the *b* axis, and in addition there occurs an oxygen-deficient, distorted tetrahedron coordinating the Cu ions adjacent to the Y planes.[3-6] The oxygen-deficient, tetragonal phase is similar to the orthorombic phase except that the oxygen is removed from the closely coordinated Cu—O chains.[6-8] Studies of both $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}(Ba,Sr)_xCuO_4$ strongly suggest that the superconductivity observed within these systems is associated with the short Cu—O interionic coordination which is a common feature to these new superconductors.

One of the most significant open problems for these materials is the identification of the type of pairing and the origin of the effective electron-electron interactions which are responsible for the pairing. Models for the pairing interaction which have been most actively discussed include the electron-phonon interaction[9] as for conventional superconductivity, spin-fluctuation exchange[10] similar to the one believed responsible for heavy-fermion superconductivity, highly correlated resonating valence bonds,[11] an exciton-mediated interaction,[12] superconductivity due to bipolaron condensation,[13] and acoustic-plasmon-mediated interactions. To identify clearly which mechanism is the dominant interaction contributing to the pairing, more information is needed on the nature and dynamics of the electronic spins and phonon excitations present in these systems.

We have undertaken Mössbauer studies to examine the lattice properties of both the superconducting, orthorombic phase, and the nonsuperconducting, tetragonal phase of $YBa_2(Cu_{1-x}Sn_x)_3O_{7-\delta}$. The temperature dependence of the relative recoil-free fraction, $f(T)$ which is measured by the area under the Lorentzian absorption curves $A(T)$, is proportional to the mean-square displacement of the absorbing ion. Based on size considerations and other evidence, it appears that at dilute Sn concentration, i.e., $x \approx 0.04$, the Sn impurity substitutes on the two inequivalent Cu sites. Comparing the ionic radii for Sn^{4+} ($r_{Sn} = 0.71$ Å) with that of Cu^{2+} ($r_{Cu} = 0.72$ Å), Ba^{2+} ($r_{Ba} = 1.34$ Å), and Y^{3+}($r_Y = 0.89$ Å), and knowing from Mössbauer isomer shift data that Sn substituted in $YBa_2Cu_3O_{7-\delta}$ is in the 4+ valence state, it is unlikely that Sn will substitute on the Y and Ba sites within this compound. Thus, a measurement of the lattice properties using ^{119}Sn Mössbauer spectroscopy allows a site-specific determination of the temperature dependence of a moment of the vibrational spectra at the Cu site which is intimately involved in the superconductivity. Also, the results of these measurements on $YBa_2(Cu,Sn)_3O_{7-\delta}$ as a function of δ permit a comparison of the lattice properties between the superconducting and nonsuperconducting phases of this system. From our measurements, we find evidence of phonon softening in the orthorombic, superconducting phase which is absent in the tetragonal, nonsuperconducting phase.

The samples used in this study were prepared by solid-state reaction at 900 °C for 24 h of pressed pellets containing appropriate portions of high-purity Y_2O_3, $BaCO_3$, SnO_2 (84% enriched with ^{119}Sn), and CuO. After the initial solid-state reaction, the pellets were ground and again pressed into pellets. The latter were heat treated in flowing oxygen for 24 h at 900 °C followed by 6 h at 600 °C and then slow cooled to 200 °C over 6 h prior to removal from the flowing oxygen. An additional pellet was vacuum annealed at 900 °C for 24 h to produce the tetragonal phase. Each superconducting and nonsuperconducting pellet was divided into three pieces for resistivity, x-ray structure, and Mössbauer measurements.

The crystal structure and lattice constants for $YBa_2(Cu_{1-x}Sn_x)_3O_{7-\delta}$ were determined using a powder diffractometer with Cu $K\alpha 1$ radiation. The oxygen-annealed samples crystallized in the orthorombic phase whereas the vacuum-annealed samples were tetragonal. There was no evidence of a second phase in any of the samples and the lattice constants were consistent with those determined elsewhere.[3-5,7] The Sn-doped samples showed a very slight decrease in the lattice constant. Four-probe dc resistivity measurements were conducted. The normal-state resistivity was metalliclike for the oxygen-annealed samples and displayed a narrow transition to the superconducting state with $T_c = 95$ K and 93 K for $x = 0$ and $x = 0.04$, respectively. The vacuum-annealed samples were semiconducting and showed no evidence of superconductivity for $T > 1$ K. The samples used in the Mössbauer studies were carefully powdered and embedded in a thin lucite disc. The sample thickness was approximately 1.0 mg/cm^2 of ^{119}Sn. The Mössbauer measurements were performed using the 24-keV γ transition in ^{119}Sn and a 50-μm Pd filter to reduce the concomitant source x rays. The $CaSnO_3$ source was held at room temperature and driven in a triangular mode with a constant acceleration drive.

Shown in Fig. 1 is a ^{119}Sn Mössbauer spectrum at 4.2 K in the superconducting phase of $YBa_2(Cu_{.96}Sn_{.04})_3O_{7-\delta}$. A similar spectrum is observed for the oxygen-depleted, tetragonal phase. The Mössbauer spectra appear to consist of at least two unresolved Lorentzian patterns. Since the features are not sufficiently resolved, it is not possible to establish a definitive assignment for the Mössbauer parameters characterizing the individual patterns. A two quadrupole-split pattern would be expected if the Sn substitutes for the Cu in its two inequivalent sites. A fit to the absorption spectra using two weakly quadrupole-split patterns is shown in Fig. 1(a). The quadrupole-splitting parameters used are consistent with a scaling of similar data obtained from ^{57}Fe Mössbauer studies.[14] The linewidths in both patterns were temperature independent and very nearly equal to the nature linewidth of $CaSnO_3$. The isomer shifts clearly show that the Sn is in a 4+ state. As indicated earlier, based on a comparison of ionic diameters, the 4+ valent state of Sn would be expected if Sn substitutes for a Cu^{2+} ion, since the ionic radius of $Sn^{4+} = 0.71$ Å as compared to 0.72 Å for Cu^{2+}. The individual contributions to the Sn^{4+} spectra are not sufficiently resolved to justify a more extensive analysis of the patterns to determine the separate Mössbauer parameters characterizing the spectra. However, the temperature dependence of the recoil-free fractions of the ^{119}Sn Mössbauer absorption can be determined with high precision.

Shown in Fig. 2 is the temperature dependence of the recoil-free fraction as measured by the normalized area under the Mössbauer spectrum, $A(T)$, for the oxygen-annealed $YBa_2(Cu,Sn)_3O_{7-\delta}$ sample, i.e., $\delta \approx 0$. To

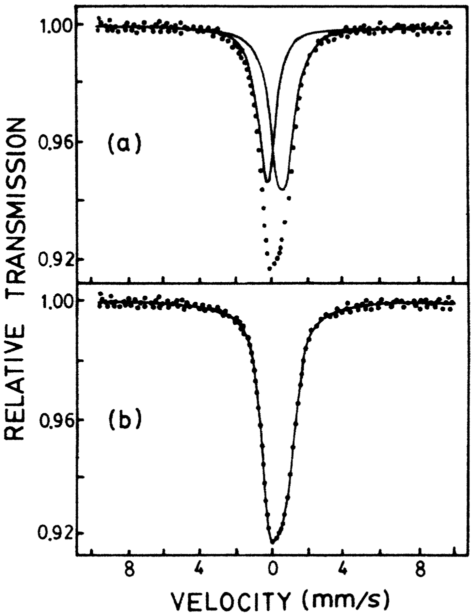

FIG. 1. Mössbauer spectrum of ^{119}Sn-doped $YBa_2Cu_3O_7$. (a) Individual fitted patterns indicating two distinct Sn sites. (b) Total fit.

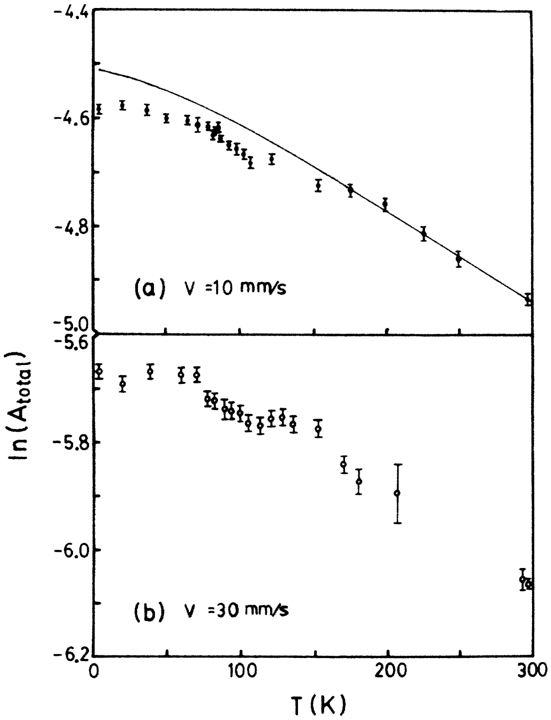

FIG. 2. Recoil-free fraction as measured by the normalized absorption area vs temperature at $v = 10$ mm/sec (a) and $v = 30$ mm/sec (b) of ^{119}Sn-doped superconducting $YBa_2Cu_3O_{7-\delta}$. Solid curve in (a) is the calculated recoil-free fraction using the measured phonon spectrum (Ref. 16).

avoid the systematic errors inherent in determining the area by fitting an underresolved spectrum, the absorption area was obtained directly from the data by means of a Simpson integration using a fitted-background subtraction. To check the consistency of our analysis, we measured the spectrum at two different velocity scales. The data with larger source velocity [Fig. 2(b)] were helpful in estimating the importance of the Lorentzian tails omitted in Fig. 2(a). A fit of the high-temperature linear behavior to $\ln(A) = k < x^2 >$ with $< x^2 >$ given by a single-peak Debye model yields a Debye temperature Θ_D of 313 K. This value is nearly equal to the value obtained from the analysis of the temperature-dependent low-temperature specific heat, i.e., $\Theta_D = 290$ K.[15] A more direct comparison to the anticipated temperature dependence of $A(T)$ is shown in Fig. 2(a). The solid curve is $A(T)$ calculated using the measured phonon density of states for the orthorombic, superconducting phase of $YBa_2Cu_3O_{7-\delta}$.[16] A clear departure from the anticipated behavior using the neutron-measured phonon density of states seen in Fig. 2 is indicative of a softening of the lattice for $T < 150$ K. Note that the softening occurs well above $T_c = 93$ K and thus cannot be associated with a change in the lattice properties driven by changes in the electronic structure in the superconducting state.

Shown in Fig. 3 is $\ln(A)$ vs T for the nonsuperconducting, tetragonal phase. A curve representing the anticipated behavior using the measured phonon spectrum is also shown in Fig. 3. There is no evidence of a corresponding lattice softening as seen in Fig. 2 for the orthorombic, superconducting phase. The recent neutron scattering measurements[16] revealed two main peaks in the phonon density of states of both, the superconducting compound $YBa_2Cu_3O_7$ and its nonsuperconducting analog $YBa_2Cu_3O_6$. The phonon density of states at 12 K and 120 K do not appear to differ significantly. This result is not necessarily inconsistent with our findings, since the Mössbauer technique probes directly the mean displacement at the Cu sites and is more sensitive to local changes than the overall density of states.

In recent isotope effect experiments[17,18] a considerable fraction of the ^{16}O in superconducting samples of $YBa_2Cu_3O_7$ was replaced by ^{18}O, but no significant change in T_c has been detected. More recent ^{18}O isotope studies in $YBa_2Cu_3O_{7-\delta}$ have shown a small isotope effect but the shift in T_c was much smaller than anticipated assuming $T_c \propto m^{-1/2}$.[19] Moreover, the Y ions can be substituted by most of the rare-earth ions (except the very light ones) without a substantial change in the critical temperature.[20,21] This represents a drastic variation of mass on the Y site with no effect on the superconductivity. The presence of at least a small isotope effect has been considered as evidence for some electron-phonon coupling contributing to the pairing. However, the weakness of the isotope effect obtained in $YBa_2Cu_3O_{7-\delta}$ does not exclude a phonon softening as presented here.

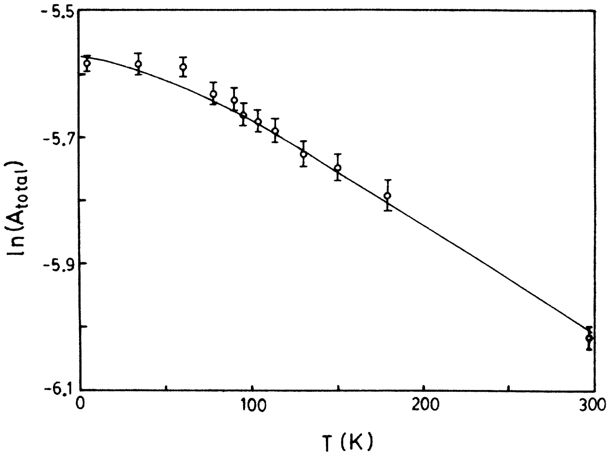

FIG. 3. Recoil-free fraction as measured by the normalized absorption area vs temperature of ^{119}Sn-doped, nonsuperconducting $YBa_2Cu_3O_{7-\delta}$. Solid curve is the calculated recoil-free fraction using the measured phonon spectrum (Ref. 16).

The softening of the mean displacement of the Sn ions substituting Cu ions below 150 K cannot be considered as evidence in favor of the electron-phonon mechanism giving rise to superconductivity for this compound. Most of the suggested mechanisms, e.g., the spin-fluctuation exchange,[10] resonating valence bonds,[11] exciton-mediated interaction[12] and acoustic-plasmon-mediated interactions, involve electronic excitation which are going to modify the dielectric function around and above the superconducting instability. On the other hand, $\epsilon(k,\omega)$ affects the screening and hence the force constants between the ions, changing in this way the mean displacements of the Cu ions.

Recent ^{115}Eu Mössbauer studies of $EuBa_2Cu_3O_{7.1}$ have established that Eu is trivalent and the parameters characterizing the Eu absorption spectra were essentially temperature independent for $4.2 < T < 300$ K.[22] These results further show that the trivalent Y sites apparently do not significantly participate in the pairing interaction. However, the ^{119}Sn Mössbauer measurements reported here provide a direct measurement of the mean-square displacement of ^{119}Sn at the Cu site of $YBa_2Cu_3O_{7-\delta}$ and a phonon softening is observed for the orthohombic, superconducting phase which is not seen for the tetragonal, nonsuperconducting phase. Our results provide further evidence for the important role played by the Cu—O bonds in the high-T_c superconductivity seen in these new materials.

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