Reduction of the zero-phonon ^{57}Fe Mössbauer fraction just above T_c in the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ superconductor

Th. Sinnemann, R. Job, and M. Rosenberg
Experimentalphysik VI, Ruhr-Universität, PB 102148, 4630 Bochum, Germany
(Received 16 October 1991)

A decrease of the zero-phonon fraction of the ^{57}Fe Mössbauer absorption was observed in the temperature range 93–120 K in an Fe-doped $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$-type high-temperature superconductor indicating an anomalous behavior of the lattice vibrations. The isomer shift changes slightly in the same temperature range. The absence of a Goldanskii-Karyagin effect shows that the Fe mean-square displacement is isotropic. Between 150 and 550 K, the temperature dependence of the zero-phonon fraction follows a Debye model with a Mössbauer Debye temperature of 350 ±20 K.

In the high-temperature superconducting oxides, copper can be partially substituted by a Mössbauer isotope without destroying the superconductivity. In this way one has access to a component of the vibrational spectrum via the measurement of the zero-phonon fraction of the Mössbauer absorption. In the $YBa_2Cu_3O_{7-\delta}$ system, an anomalous decrease of the zero-phonon fraction of Fe and Sn dopants above T_c has been reported,[1–3] which was absent in the nonsuperconducting $YBa_2Cu_3O_6$ phase.[1] In our study a similar behavior is found for a $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$-type (Bi 2:2:2:3) high-temperature superconductor (HTSC), which makes a relation between the observed effect and superconducting transition even more probable. Additional information is gained by measuring the temperature dependence of the isomer shift, linewidth, and electric-field gradient. This can be done very precisely since the ^{57}Fe Mössbauer spectrum of the Pb-substituted Bi 2:2:2:3 consists only of one doublet, in contrast to the $YBa_2Cu_3O_{7-\delta}$ system with a superposition of several subspectra.

The samples were prepared[4] by solid-state reaction, using a nominal composition of $Bi_{1.84}Pb_{0.34}Sr_{2.03}Ca_{1.9}(Cu_{0.97}Fe_{0.03})_3O_y$. From susceptibility measurements a T_c of 95.5 K is found, and secondary contributions from the 2:2:1:2 phase are detected. For the Mössbauer absorbers, powdered sample material was mixed with epoxy resin or high-temperature cement and coated from both sides with aluminum foil, in order to minimize temperature gradients. Two samples produced under the same conditions were measured, each in a warming cycle after cooling down to 2.0 K. In the vicinity of the superconducting transition, we increased the temperature in steps of 2 K for the high-resolution spectra, but short-time measurements were performed every 0.5 K.

The absorbers had approximate thicknesses of 0.034 and 0.043 mg $(^{57}Fe)/cm^2$, respectively. The spectra were recorded in two conventional setups in the temperature ranges 2.0–300 and 300–600 K, with the source kept at room temperature. For a correct determination of the background intensity, the base line should be perfectly flat at maximum velocity. We used the velocity range ±6 mm/s above 77 K and ±18 mm/s below 77 K, where magnetic hyperfine-splitting effects are observed. The background was determined from the outermost 136 channels, each with about 2×10^6 counts, at ±6 mm/s, and from the outermost 100 channels, each with about 6×10^6 counts, at ±18 mm/s. Area data from measurements made on different setups or at different velocity scales were matched in the overlapping regions. The resonant area was then obtained by subtraction of the measured intensity from the background.

These values have to be corrected for the finite thickness of the absorber. The effective absorber thickness t is given by

$$t = n\sigma_0 f_a' , \tag{1}$$

where n is the number of ^{57}Fe atoms per unit area in the correct hyperfine state, σ_0 is the nuclear resonant cross section, and f_a' is the absorber recoilless fraction. We took f_a' from the temperature dependence of the measured area before the correction, setting $f_a'=0.7$ at 77 K. The tabulated data of Lang[5] for Lorentzian line shapes were then used to calculate the damping of the spectral area, giving values between 91% and 95%. As shown in Fig. 1, the Mössbauer spectrum taken at $T=4.2$ K is magnetically split, leading to a reduction of the effective thickness. For the determination of the resonant area, this spectrum was treated in the thin-absorber approximation, i.e., without an area correction. The isomer shift, quadrupole splitting, and linewidth were determined by a least-squares fitting procedure, each with an accuracy of 0.01 mm/s.

A typical Mössbauer spectrum of a 3% Fe-doped 2:2:2:3 sample is shown in Fig. 2. In a previous study,[6] based on a comparison of the ^{57}Fe Mössbauer spectra of Bi 2:2:1:2 and Bi 2:2:2:3 type HTSC's, we concluded that in both compounds such a spectrum originates from Fe atoms substituting for Cu on the lattice site with square pyramidal oxygen configuration, but that probably oxygen octahedra are formed around the iron atoms. The resulting room-temperature spectrum consists of a slightly asymmetric doublet, with a quadrupole splitting of 1.12 mm/s. The asymmetry is a result of texture effects and vanishes when the sample is measured in "magic-angle" geometry,[7] which means 54.7° between γ rays and the sample normal. Typical linewidths are around 0.40 mm/s, which is larger than the natural linewidth and in-

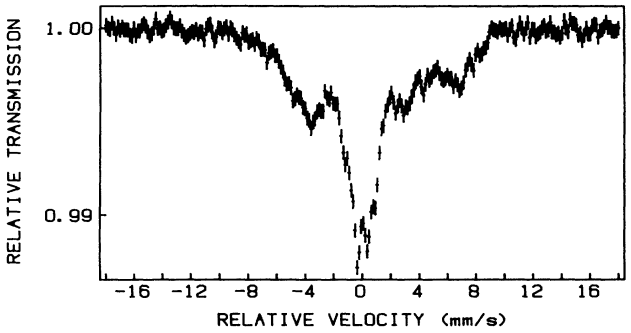

FIG. 1. Mössbauer spectrum of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ doped with 3% ^{57}Fe taken at a temperature of 4.2 K.

dicates a distribution of slightly different local environments around the Fe atoms. The room-temperature isomer shift of 0.25 mm/s relative to α-Fe shows that the Fe atoms are in the 3+ state. At temperatures around 25 K, a slowing down of Fe spin fluctuations is observed,[6] leading to magnetically split Mössbauer spectra. Therefore, we restrict the temperature range where a spectrum is described as a doublet to 30–550 K.

In Fig. 3 the temperature dependence of the spectral area is shown in a semilogarithmic plot in the temperature range 4.2–550 K. Sample 2 was thinner than sample 1, leading to a reduced spectral area and to a constant vertical shift when compared to sample 1 in such a diagram. In sample 1 a drop in the area curve extending from $T=93$ K to $T=120$ K is well observed, which is much less pronounced and shifted to higher temperatures in sample 2. The intensity of both peaks of the doublet is reduced by the same amount. The onset of the drop is visible well above the superconducting transition temperature of 95.5 K. In the same temperature range, a decrease in the linewidth occurs, as shown in Fig. 4(a). For the isomer shift (IS), a deviation from normal behavior is found between 100 and 115 K in sample 2, which is not clearly detectable in sample 1. The quadrupole splitting decreases between 100 and 550 K linearly with a slope of -0.025 mm/s per 100 K.

In a Mössbauer experiment, one has access to the vibrational spectrum of the absorber via the zero-phonon fraction and second-order Doppler shift. In the following

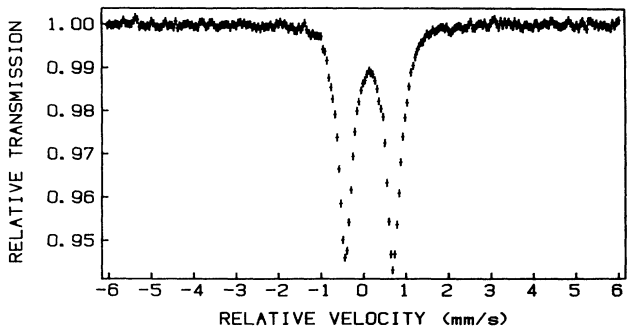

FIG. 2. Mössbauer spectrum of $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ doped with 3% ^{57}Fe taken at room temperature.

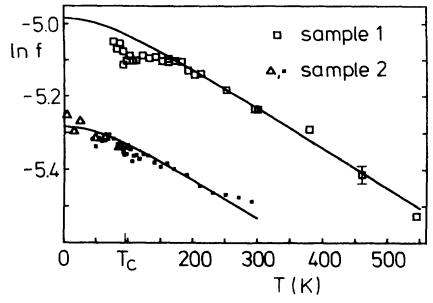

FIG. 3. Temperature dependence of the relative zero-phonon fraction f for two different $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ absorbers doped with 3% ^{57}Fe. Data obtained with a maximum velocity of 18 mm/s (triangles) were matched to those obtained with 6 mm/s (solid squares). The indicated error represents the statistical uncertainty.

the high-temperature data are shown to be consistent with a Debye model. For an interpretation of the observed anomalies around T_c, additional information of short-range character from the electric-field gradient and linewidth is included.

The zero-phonon fraction f, which is proportional to the measured resonant area, is determined by the γ rays

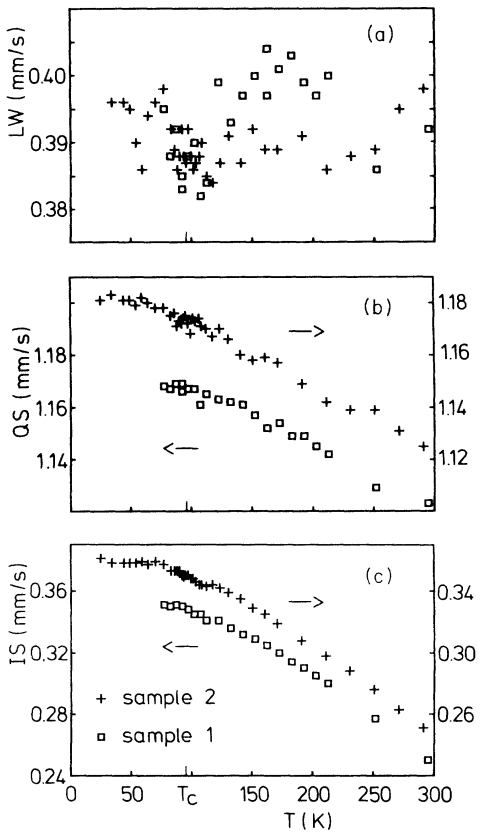

FIG. 4. Temperature dependence of the parameters derived from fitting the $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ Mössbauer spectra with one doublet. (a) Linewidth, (b) quadrupole splitting, and (c) isomer shift. The accuracy is 0.01 mm/s in all cases.

emitted or absorbed by a nucleus bound in a crystal without a change in the quantum state of the lattice. It is given by[8]

$$f=[|\langle i|e^{i\mathbf{k}\cdot\mathbf{r}}|i\rangle|]_{\text{th}} , \tag{2}$$

where "th" denotes a thermal average over initial lattice states $\langle i|$, and $\mathbf{k}$ is the wave vector of the γ ray. In a lattice with harmonic forces, f is related to the mean-square displacement $\langle x^2\rangle$ of the atom along the γ-ray direction by[9]

$$f=\exp(-\mathbf{k}^2\langle x^2\rangle) . \tag{3}$$

Because of zero-point motions, f is always smaller than 1. The exponent $-\ln f$ in this equation is the Debye-Waller factor (DWF). In a Debye solid, the temperature dependence of the DWF is[9]

$$\ln f(T)=-\frac{3E_R}{2k_B\Theta_D}\left[1+4\left[\frac{T}{\Theta_D}\right]^2\int_0^{\Theta_D/T}\frac{x\,dx}{e^x-1}\right] . \tag{4}$$

Here k_B is the Boltzmann constant and $E_R=0.002$ eV is the recoil energy of the free ^{57}Fe nucleus. Such a curve is plotted in Fig. 3. At low temperatures the zero-phonon fraction is nearly constant, and near the Debye temperature Θ_D it shows approximately a linear decrease. Such a behavior is found for iron,[10] for iron impurities in metals,[11] or in iron oxides.[12,13] In our measurement of the relative DWF, the slope of the curve at high temperatures gives a Mössbauer Debye temperature of 350±20 K.

The Mössbauer Debye temperature is dependent on the mass of the dopant, which is Fe in our case. According to Elliot,[14] the results for the mean-square displacement of different dopants are almost the same as one obtains by modifying the Debye temperature with the mass to

$$\Theta_{D,\text{dop}}=\Theta_D\left[\frac{m}{m_{\text{dop}}}\right]^{1/2} . \tag{5}$$

Although the Debye model is a rather crude approximation for the HTSC's, the Mössbauer Debye temperatures increase, as expected, with the Mössbauer isotopes ^{151}Eu, ^{119}Sn, and ^{57}Fe in $YBa_2Cu_3O_{7-\delta}$ and give roughly the same values when weighted with the square root of their atomic mass (see Table I). In comparison to the $YBa_2Cu_3O_{7-\delta}$ superconductors, the Mössbauer Debye temperature of our Bi 2:2:2:3 is significantly lower. It should be mentioned that these values are not to be compared with Debye temperatures from specific-heat data, because they are determined by different weighted averages over the frequency spectrum.

An interesting point is the absence of any Goldanskii-Karyagin effect,[15] which might have been expected from the crystal structure. An anisotropic mean-square displacement would result in a temperature-dependent ratio of the areas belonging to the two different lines of the doublet, as was found for ^{57}Fe in polycrystalline Zn.[16] In the Bi 2:2:2:3 superconductor, the area ratio is constant to within ±2% at all measured temperatures. This demonstrates that the iron mean-square displacement is fully isotropic.

A quantity which is related to the phonon spectrum in a similar way as the mean-square displacement is the mean-square velocity. The experimentally derived isomer shift δ is the sum of a term depending on the electron density at the ^{57}Fe nucleus, δ_{ed}, and of the temperature-dependent second-order Doppler shift δ_{soD}, given by

$$\delta_{\text{soD}}=-\frac{\langle v^2\rangle}{2c} , \tag{6}$$

where c is the velocity of light. In the Debye model, the mean-square velocity is

$$\langle v^2\rangle=\frac{9k}{8m}\Theta_D+\frac{9kT}{m}\left[\frac{T}{\Theta_D}\right]^3\int_0^{\Theta_D/T}\frac{x^3\,dx}{e^x-1} . \tag{7}$$

The measured isomer shifts give no indications for a temperature-dependent electron-density shift. The behavior shown in Fig. 4(c) is well described by a pure second-order Doppler shift, with the exception of the temperature range 100–115 K.

In conclusion, one sees that the mean-square displacement and mean-square velocity in the temperature range 150–550 K can be satisfactorily described in the Debye approximation.

Below 150 K the resonant area and isomer shift show anomalies which are not consistent either with a Debye or an Einstein solid. Experimental examples for a sudden drop in the resonant area are the ferroelectric transitions in $BaTiO_3$ (Ref. 17) and $PbTiO_3$ (Ref. 18) and the cubic-

TABLE I. Mössbauer Debye temperature $\Theta_{D,\text{dop}}$ and corresponding temperature for a Debye host lattice with $m_{\text{host}}=57$, calculated according to Eq. (5).

Host	Mössbauer dopant	$\Theta_{D,\text{dop}}$ (K)	$\Theta_{D,\text{dop}}\left[\frac{m_{\text{dop}}}{57}\right]^{1/2}$ (K)	Ref.
(Bi, Pb)$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$	^{57}Fe	350	350	This work
$YBa_2Cu_3O_{7-\delta}$	^{151}Eu	255 (average)	415	27
	^{119}Sn	313	452	1
	^{119}Sn	294–320	425–462	3
	^{119}Sn	340 ($T>200$ K)	491	2
	^{119}Sn	315 ($90>T>170$ K)	455	2
	^{57}Fe	450	450	28

to-rhombohedral phase transition in $Ge_xSn_{1-x}Te$.[19] The origin of this effect is the critical behavior of some specific phonon branches.[20] If the observed DWF anomaly is connected with the superconducting transition, then the Mössbauer-parameter quadrupole splitting, linewidth, and isomer shift can give information about the change in the equilibrium conditions when going form the normal to the superconducting state. But none of these parameters give evidence about significant differences above and below T_c.

The quadrupole splitting (QS), given by the main axis and asymmetry parameter of the electric-field-gradient tensor, is for an Fe^{3+} ion, with its spherically symmetric electron configuration only determined by the distribution of charges in the surrounding lattice. One might argue that there is a change in the slope of the QS-versus-temperature curve at T_c in Fig. 4(b). But it is also possible to describe the QS with a $T^{3/2}$ dependence up to $T=250$ K, as is usually found in noncubic metals.[21] The typical linewidth of 0.40 mm/s can be attributed to a distribution of slightly different electric-field gradients. Although a minimum around $T=100$ K is observed, there a charge redistribution between the CuO_2 planes and BiO "reservoir" planes, as was suggested by Kusmartsev and Khomskii.[22] But since we observe a phonon instability via the Debye-Waller factor, we think it more likely that this effect also influences the second-order Doppler shift and is responsible for the isomer-shift anomaly.

Summing up, we find no significant difference between the normal and superconducting states, in the parameters accessible with ^{57}Fe Mössbauer spectroscopy, but the observed anomaly in the Debye-Waller factor gives evidence for a phonon softening just above T_c.

A possible mechanism leading to a lattice instability was recently suggested on the basis of electron coupling to selected high-frequency modes. According to Jarlborg,[23] the energetics of the phonon modes should be changed at T_c because of the opening of a dynamical gap, leading to a screening of the Madelung potential and to a structural instability. Experimental evidence for structural softening or instabilities has been found also for other high-T_c materials with various techniques.[24–26] This supports the view of a close relation between high-T_c superconductivity and structural instability.