

# Mössbauer-spectrum temperature-dependence anomalies of $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$

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Mössbauer spectroscopy has been used to study the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$  ( $y \approx 2$ ) with impurity  $^{57}\text{Fe}$  nuclei. This compound exhibits a superconductivity ( $T_c = 93$  K). Measurements of the temperature dependence over the range 77–300 K reveal an anomalous behavior of the probability for the effect,  $f_a(T)$ , near  $T_c$ .

Important topics in the research on compounds exhibiting a high-temperature superconductivity, in addition to the symmetry of the crystal lattice, the temperatures of phase transitions, and the electrical properties, are the spatial distribution of the electron density and the role played by various copper sites in the electrical conductivity.<sup>1</sup>

In this letter we report a study of samples of the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$  ( $y \approx 2$ ) by Mössbauer spectroscopy with the impurity nucleus  $^{57}\text{Fe}$ . A particularly favorable combination of properties (lifetime, energy of the excited state, etc.) makes this nuclide the most convenient choice for Mössbauer studies. In the experiments we used samples with different  $^{57}\text{Fe}$  concentrations (0.5% and 1.0% by weight). The source was  $^{57}\text{Co}$  in Cr. Data on the line shifts are given with respect to sodium nitroprusside. The temperature of the superconducting transition is  $T_c = 93$  K. The width of the transition is 5–7 K. An x-ray structural study revealed that the samples are of a single phase. No changes in the lattice constants were observed upon the introduction of the iron.

According to the structure of this compound, the unit cell contains two types of Cu atoms, which have one and two vacancies, respectively, in the octahedral surroundings of the oxygen.<sup>2</sup> The ratio of the numbers of ions in the positions CuII (between Y and Ba layers) and CuI (between Ba layers) is  $N_{\text{II}}:N_{\text{I}} = 2:1$ . The Mössbauer spectrum (Fig. 1) consists of two subspectra, which correspond to two structurally nonequivalent positions of the iron. This result is evidence that the Fe atoms replace Cu atoms. The  $\text{Fe}^{2+}$  ion occupies an asymmetric position in the oxygen octahedron surrounding it, so a large quadrupole splitting is caused by the eccentric displacement. As a result, the Fe–O bonds along different directions are nonequivalent. For the CuII position, the asymmetry, which is determined by the distance from the central atom to the oxygen atom, is considerably greater than for CuI. The quadrupole splitting is affected as a result. The difference between the magnitudes of the isomer shifts for the two positions,  $\delta^{\text{I}}$  and  $\delta^{\text{II}}$ , results from a predominant effect of the overlap

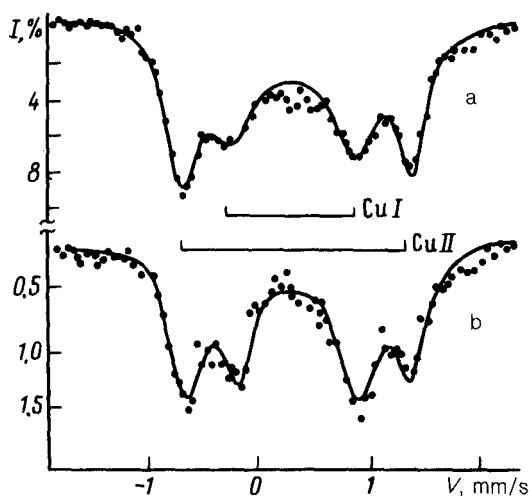


FIG. 1. Mössbauer spectra of the compound  $\text{YBa}_2\text{Cu}_3\text{O}_{9-y}$  at 77 K for the case of  $^{57}\text{Fe}$  impurity nuclei. a—1.0% Fe by weight; b—0.5%.

of the  $3s$  orbitals of Fe with the  $2p$  orbitals of oxygen. The increase in the metal-ligand distance for the CuII site leads to a decrease in the electron density at the  $^{57}\text{Fe}$  nucleus; correspondingly, the experimental shift  $\delta^{\text{II}}$  is greater than that for the CuI site.

If the Fe atoms replaced the Cu in a statistically uniform way, the intensity ratio of the two doublets would be 2:1. The experiments show that this relation does not hold; the actual relation depends on the concentration of the Fe impurity. Analysis of the Mössbauer spectra of samples with 0.5% and 1.0% iron by weight (Fig. 1) shows that the CuI positions are replaced preferentially. The reason for this result should apparently be sought in either the circumstance that the positions do not correspond to the actual positions of the ions (possibly because of a rotation of oxygen octahedra) or an effect of a preferential filling of sites between barium layers by the iron atoms. The large linewidth of the CuI doublet may be due to a distribution of the isomer shift due to mobile vacancies.

To study the temperature dependence of the properties of the compound, we measured the Mössbauer spectra over the range 77–300 K. Our study of the dynamic effects was based on the strong dependence of the probability on the vibrations of the impurity atom, which is an integral quantity over the phonon spectrum. Figure 2a shows the temperature dependence of the probability for the effect,  $f_a$ ; it is not monotonic. An approximation of the two parts of the curve by a single-parameter Debye model yields effective Debye temperatures:  $\Theta_{\text{eff}} = 300 \pm 20$  K for the high-temperature phase and  $\Theta_{\text{eff}} = 270 \pm 20$  K for the low-temperature phase. The temperature of the phase transition is  $220 \pm 15$  K. The behavior of the probability for the effect near  $T_c$  indicates a softening of the phonon spectrum.

Figure 2b shows the temperature dependence of the isomer shift for the two iron positions. The reason for the difference between the shifts in the low- and high-temperature Mössbauer spectra is a second-order Doppler shift. The deviations from a linear dependence indicate anomalies at 22 K and 150 K, apparently due to phase

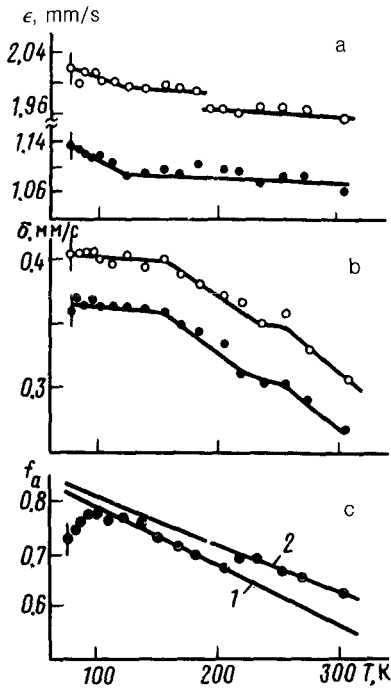


FIG. 2. Temperature dependence of parameters of the Mössbauer spectra. a: Probability for the effect,  $f_a(T)$ . Solid lines—approximation by the Debye model. 1)  $\Theta_{\text{eff}} = 270$  K; 2)  $\Theta_{\text{eff}} = 300$  K. b: Behavior of the isomer shift  $\delta$  for the two lattice sites. Filled circles) CuI; open circles) CuII. c: Quadrupole splitting  $\epsilon(T)$ .

transitions. The effect can be seen more clearly on the temperature dependence of the difference between the isomer shifts,  $(\sigma^{\text{II}} - \delta^{\text{I}})$ , in Fig. 3). Since the effective temperatures at the  $^{57}\text{Fe}$  impurities at the CuII and CuI sites differ only slightly, we assume  $(\delta_T^{\text{II}} - \delta_T^{\text{I}}) \cong 0$ . We are thus left with only the electronic component. The high-temperature maximum observed at 220 K and the rise of the curve near  $T_c$  imply a change in the electron density due to an overlap. The softening of the corresponding phonon modes apparently causes a distortion or rotation of the octahedra in the unit cell, leading to structural phase transitions with a change in Fe-O distances. These changes are reflected in the charge and spin densities of the electrons.

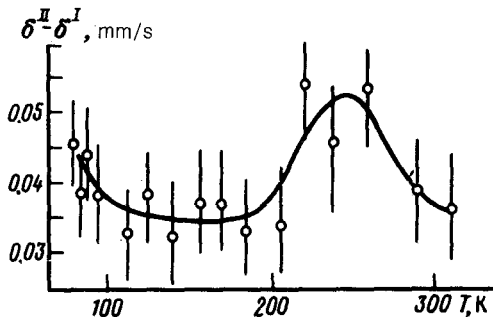


FIG. 3. Difference between the isomer shifts,  $\delta^{\text{II}} - \delta^{\text{I}}$ , at the  $^{57}\text{Fe}$  nuclei at the two positions CuI and CuII.

The quadrupole splitting  $\epsilon$  behaves in the same way for the different sites (Fig. 2c), but in the case of the CuII site, there is small jump near 170 K. The change in the quadrupole splitting between 120 K and  $T_c$  can be linked with an increase in the tetragonality of the lattice which accompanies the transition to the superconducting state.

<sup>1</sup>Y. Maeno, T. Nojima, Y. Aoki *et al.*, Jpn. J. Appl. Phys. **26**, L774 (1987).

<sup>2</sup>J. J. Capponi, C. Challoy, and A. W. Hawat, Preprint, Submitted to Europhysics Letters, March, 1987.

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