

Study of the properties of oxygen-deficient compounds $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{6+\delta}$ on the basis of the Mössbauer spectroscopy data

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The results of the Mössbauer measurements of the system $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{6+\delta}$ ($x = 0.015, 0.005, \text{ and } 0.001$) are presented. The CuI positions are replaced primarily by Fe atoms. The spectrum was found to have a fine structure which is associated with different number of vacancies at the CuI positions. The data on the characteristics of local fields were obtained by measuring the parameters of the spectra of texturized samples.

The compound $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{6-\delta}$ is characterized by an unusual sensitivity of its structure and superconducting properties to the oxygen concentration. We have studied in detail the replacement of the CuI and CuII positions by resonant atoms and determined the particular way in which the O4 oxygen positions are filled when δ is varied from 0.05 to 0.95, the range in which a transition from the tetragonal to the

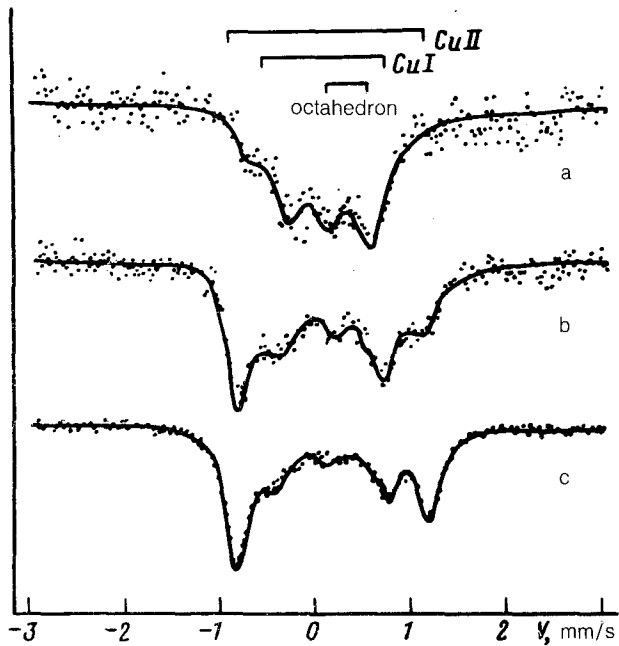


FIG. 1. Mössbauer spectra of $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{6.95}$ samples with various Fe concentrations; a— $x = 0.001$; b— $x = 0.005$; c— $x = 0.015$.

orthorhombic structure occurs (the notation for the positions of atoms is the same as that in Ref. 1).

The parameters of the Mössbauer spectrum depend essentially on the degree to which the samples are doped with Fe atoms and on the oxygen content δ (Refs. 2 and 3). To eliminate the possibility for the appearance of foreign, iron-containing phases and to minimize the nonuniformity of Fe distribution, we synthesized samples with a small concentration of iron, $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{6+\delta}$ ($x = 0.015, 0.005, \text{ and } 0.001$). The composition, the structure, and the uniformity of the distribution of the iron atoms were controlled by x-ray structural microanalysis. Samples with different levels of oxygen deficiency were synthesized from the $\text{YBa}_2\text{Cu}_{3-x}\text{Fe}_x\text{O}_{6.95}$ phase by reducing heat treatment with a controlled oxygen pressure, in accordance with the equilibrium P_0 - T - δ diagram. The oxygen concentration was determined from the data on the thermogravimetric analysis.⁴ Figure 1 shows the Mössbauer spectra of samples with various iron concentrations and the same oxygen parameter $\delta = 0.95 \pm 0.03$, which were recorded at a temperature of 300 K. A clearly defined structure of the spectra shows that three doublets are superimposed on each other (in the previous study³ the third doublet was ignored because of its low intensity). The ratio of the areas of the doublets corresponding to the resonant nuclei in the CuI and CuII positions changes with the iron concentration and does not correspond to the statistically uniform distribution. When $x = 0.001$, principally the lines from the CuI position are present; when $x = 0.005$, the intensities of the doublets become more nearly equal; and when $x = 0.015$, the ratio of the areas of the doublets approaches 2:1. This behavior is presumably attributable to the fact that the sites between the Ba layers are filled preferentially with Fe atoms. The difference in the parameters of the doublets indicates

that the positions of the copper atoms are structurally nonequivalent. In Ref. 5 the spectra were interpreted in accordance with the calculations of the lattice contribution to the electric-field gradient of the nucleus which is governed by the nearest-neighborhood ions. The electric-field gradient determined from such an approximate calculation differs appreciably, however, from the experimental value, suggesting that the electronic contribution must be taken into account. Since the antishielding factor depends strongly on the electronic structure of the ions, the Cu sites are difficult to identify strictly from the lattice contribution. The same view has also been expressed by the authors of Ref. 6, who concluded on the basis of the nuclear-quadrupole-resonance data that the CuII site has the larger electric-field gradient. We note that the ratio of the areas of the doublets in the spectrum depends on the measurement temperature, which is apparently the result of the degree of mobility of the Fe atoms in the CuI and CuII positions. The third doublet in the Mössbauer spectrum corresponds, in our view, to the metastable CuO_6 complexes which can form in the regions with filled vacancies, such as those at the grain walls. Evidence in favor of this assumption are the measurements of the sample which was synthesized by deposition of a finely divided fraction from a suspension. A calculation of the spectrum showed that the area of the third doublet increased by 10% compared with the spectrum of the sample synthesized by the standard method in paraffin. Since the surface of the finely divided sample is large, its contribution in the spectrum increases accordingly.

Figure 2 shows the distribution function of the quadrupole splitting $P(QS)$ obtained from the Mössbauer spectrum of the sample with $\delta = 0.8$. It consists of three lines whose peaks correspond to the three nonequivalent positions of iron. We call attention to the fine structure which is seen on the curve for the CuI position and which is linked with various numbers of vacancies in the neighborhood of the resonant atom. Using the parameters found from the curve, we calculated the spectrum under the assumption that there are four doublets, two of which correspond to Fe in the Cu'I and Cu''II positions. The results of the calculation are shown in Fig. 2b. The ratio of the areas of Cu'I and Cu''II (with different oxygen coordination numbers) agrees quite well with the vacancy filling probabilities calculated for the given oxygen concentration under the condition that the oxygen deficiency affects principally the decrease in the concentration of the CuI-O4 chains. Calculation of the Mössbauer spectra of the samples with $\delta = 0.95, 0.8, 0.2,$ and 0.05 showed that the parameters of the doublet corresponding to the CuII position remain nearly constant and that for the CuI position the ratio of the intensities and the parameters of the hyperfine structure are determined by the probability for the filling of the O4 positions by the oxygen atoms. These quantities represent the actual O4-CuI-O4 configurations. The results of the analysis of the spectra are shown in Table I. Analysis of the data shows that the isomer shift is proportional to the number of oxygen atoms in the nearest neighborhood of the resonant atom, suggesting that the density of the s electrons changes as a result of variation of the oxygen parameter. The observable difference in the intensities of the components of the doublets for the positions in question (Fig. 1) is generally explained by the anisotropy of the Debye-Waller factor (the Gol'danskiĭ-Karyagin effect).⁵ Such a definitive interpretation of the Mössbauer spectra is, however, not entirely justifiable since there are many reasons for the appearance of the asymmetry of the lines.⁷ The reason for the asymmetry can be determined by measuring the

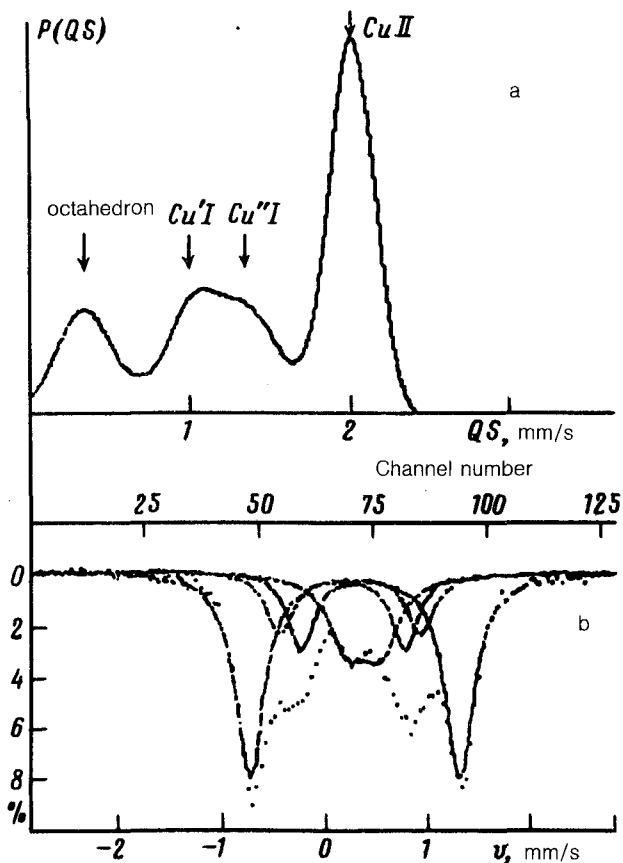


FIG. 2. (a) The distribution function $P(QS)$ reconstructed from the Mössbauer spectrum of the sample with $\delta = 0.8$; (b) decomposition of the Mössbauer spectrum into four doublets.

polycrystalline samples while varying the orientation angle of the sample relative to the γ -ray beam. The comparative measurements of the isotropic samples carried out by us for all compositions x and for various oxygen concentrations δ have shown that the asymmetry of the lines varies, which should not be the case if only the Gol'danskiï-

TABLE I. Parameters of the hyperfine structure obtained from the calculation of the Mössbauer spectra of the $YBa_2Cu_{3-x}Fe_xO_{6+\delta}$ samples with different values of δ .

Site	Coordination number	Isomer shift, mm/s	QS , mm/s	$\Gamma_{1/2}$, mm/s
octahedron	6	0.453 ± 0.013	0.33 ± 0.03	0.39 ± 0.04
CuII	5	0.404 ± 0.002	2.03 ± 0.01	0.32 ± 0.01
Cu' I	4	0.383 ± 0.002	1.00 ± 0.01	0.32 ± 0.03
Cu'' I	3	0.36 ± 0.02	1.36 ± 0.01	0.30 ± 0.03
Cu''' I	2	0.32 ± 0.02	0.77 ± 0.02	0.30 ± 0.03

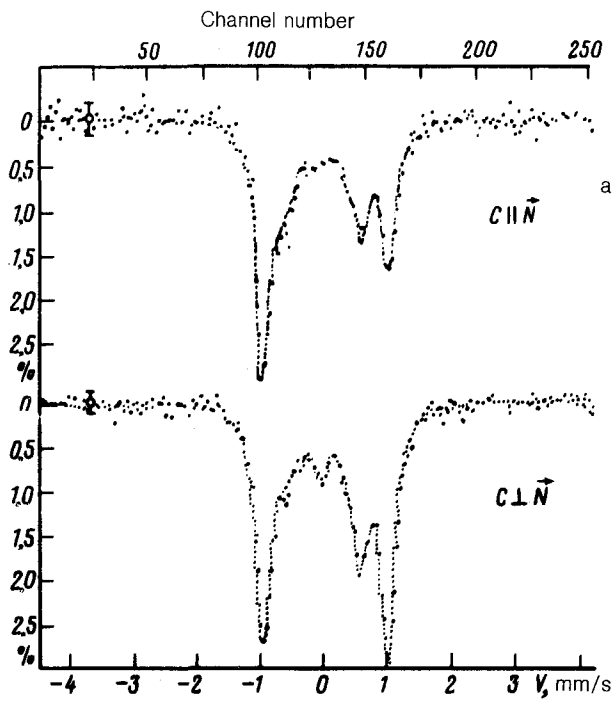
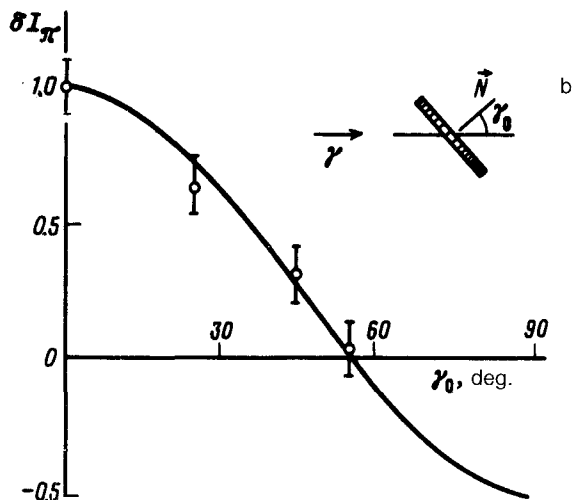


FIG. 3. (a) Mössbauer spectra of a texturized ceramic sample ($x = 0.015$, $\delta = 0.95$) with various orientations of the C axis with respect to the normal of the sample; (b) angular dependence of δI_{π} ; the solid line is constructed from (1).



Karyagin effect is manifested. These measurements also showed that the crystal orientation is only partial, i.e., that there is a textural effect. We found that synthesizing the sample by pressing it from a powder into a pellet in paraffin under external pressure in a paste-like state causes the ceramic particles to be oriented. The degree to which the

textural effect in the sample is achieved depends on the oxygen concentration and reaches a peak at $\delta = 0.95$. We thus obtain a texture in which a certain preferred direction of particles, \mathbf{n} , which coincides with the C axis, is oriented normal to the sample's surface. The normal, along with the axis of the spectrometer, forms an angle γ_0 and the angle between the principal axis of the tensor of the electric field gradient and the direction \mathbf{n} of the particle is θ_0 . Figure 3a is a plot of the intensities of the doublet lines as a function of the direction of the C axis relative to the normal to the surface of the sample with $x = 0.015$ and $\delta = 0.95$. The deviation of the relative intensity of the Π component of the doublet, δI_π , as a function of its intensity in the spectrum of the isotropic sample has been analyzed in Ref. 8:

$$\delta I_\pi = (1 - \cos^2 \gamma_0) F(a, \theta_0, \beta_0). \quad (1)$$

The first factor, which is known, depends on the experimental conditions and the second factor depends on the parameter of the local field a , which is related to the asymmetry parameter: $a = \eta [\sqrt{3}(1 + \sqrt{1 + \eta^2/3})]^{-1}$, and to the particular features of the texture used: the θ_0 and β_0 angles. The corollary of Eq. (1) is the criterion which makes it possible to determine the sign of the principal component q_{zz} of the electric-field-gradient tensor from the angular dependence of the same texture.

Figure 3b shows the angular dependence $\delta I_\pi = \delta I_\pi(\gamma_0)/\delta I_\pi(\gamma_0 = 0)$ for the CuII doublet. This dependence is in good agreement with the calculated dependence for the spectral lines at lower velocities of the source; i.e., this angular dependence is the π component which corresponds to the $1/2 \rightarrow 3/2$ transition. The sign of the principal component of the electric-field-gradient tensor is therefore negative. $Qq_{zz} < 0$ and the level of the excited nucleus, with $\pm 1/2$ spin projection, is higher than the $\pm 3/2$ level. The fact that the intensities of the components of the doublet are the same at $\gamma_0 = 55^\circ$ for CuII suggests that the Debye-Waller factor is isotropic. For the CuI position the Debye-Waller factor is strongly anisotropic. This anisotropy is seen in the increase of the asymmetry of the doublet as γ_0 is varied. Measurements at different angles show, moreover, that the ratio of the areas of the doublets corresponding to the two positions changes. This fact indicates that the anisotropy of the Debye-Waller factor must be taken into account in the analysis of the distribution of Fe atoms in the CuI and CuII positions. The presence of anisotropy provides a further means for studying the dynamics of the vibration of atoms at various temperatures and a means for detecting the displacement of atoms in a single structure during the phase transitions.

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