Anomalous behavior of the temperature dependence of the parameters of the Mössbauer spectra of the superconducting ceramics $YBa_2Cu_{2.95}Fe_{0.05}O_{7-y}$

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The isomeric shift, quadrupole splitting, linewidth, and asymmetry parameter in the Gol'danskiĭ-Karyagin effect were found to behave anomalously in the ceramic of the 1–2–3 composition near the transition to the superconducting state. The Mössbauer spectroscopy of the ^{57}Fe impurity nuclei was used in the experiments.

Extensive experimental study of various physical characteristics of the recently discovered superconducting ceramics, aimed at identifying the link between the electron and phonon subsystems, has made it possible to determine many systematic features in the temperature dependence of the lattice constants,[1] sound velocity and elastic moduli,[2] positron annihilation,[3] etc. Anomalous behavior of the Mössbauer spectra of the 1–2–3 ceramic at temperatures above T_c has also been reported.[4]

In the present letter we are reporting the results of an analysis of Mössbauer spectra of ^{57}Fe in the positions where it replaces copper in the ceramic of the composition $YBa_2Cu_{2.95}Fe_{0.05}O_{7-y}$ ($y = 0.2 \pm 0.1$), which were measured above and below $T_c \approx 75$ K ($\Delta T_c \approx 15$ K). Our interpretation of the results is different from that in Ref. 4. The samples were synthesized by a method described in Ref. 5. This method involved annealing the samples in the three stages at temperatures of 850, 900, and 930 °C, which resulted in approximately equal population of the nonequivalent copper positions (1) and (2) by iron atoms (we use the notation of Ref. 6). An x-ray structural analysis showed that the sample has a single-phase orthorhombic structure with lattice constants $a = 3.878$ Å, $b = 3.840$ Å, and $c = 11.69$ Å.

The Mössbauer spectra are a superposition of three doublets of different intensities (the third doublet was ignored in Ref. 4 in the analysis of the spectra), whose parameters change slightly at temperatures $T \sim 200$ K and $T \sim T_c$ (Figs. 2 and 3). Outside these regions the doublet parameters are essentially constant within the measurement error. The average values of these parameters are given in Table I.

The most important factor in the interpretation of the observed spectra is the correct correlation of the partial spectra of doublets 1 and 2 with the distribution of iron atoms in positions (1) and (2), which depends considerably on the conditions under which the samples were synthesized.[7] In particular, Tsurin *et al.*,[4] assigned the spectrum of doublet 1 with a large quadrupole splitting, $\epsilon_1 \approx 2$ mm/s, to the Cu position (2), assuming that the electron state of the iron ion is close to Fe^{2+}. It follows from the values of the isomeric shift $\delta_{1,2}$ of the two doublets, however, that the electron state of the iron ion is close to Fe^{3+}. This circumstance makes it possible to

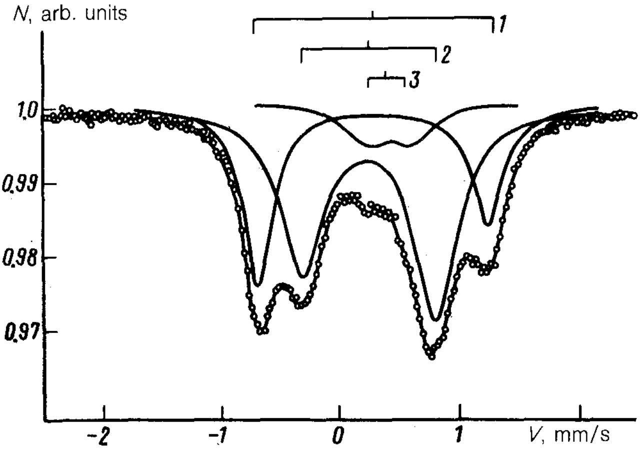

FIG. 1. The Mössbauer spectrum of the $YBa_2Cu_{2.95}Fe_{0.05}O_{7-y}$ sample with a $^{57}Co(Cr)$ source, measured at $T = 96$ K. The solid curves were obtained by the method of least squares in the Lorentz-line approximation.

reduce in the first approximation the estimate of the electric field gradient in positions (1) and (2) to the calculation of the lattice contribution which is attributable to the nearest-neighborhood ions. Our calculation shows (in accordance with the results of Ref. 7) that the value of the electric field gradient for position (1) is nearly twice as large as that for position (2), and the sign of the electric field gradient is positive for

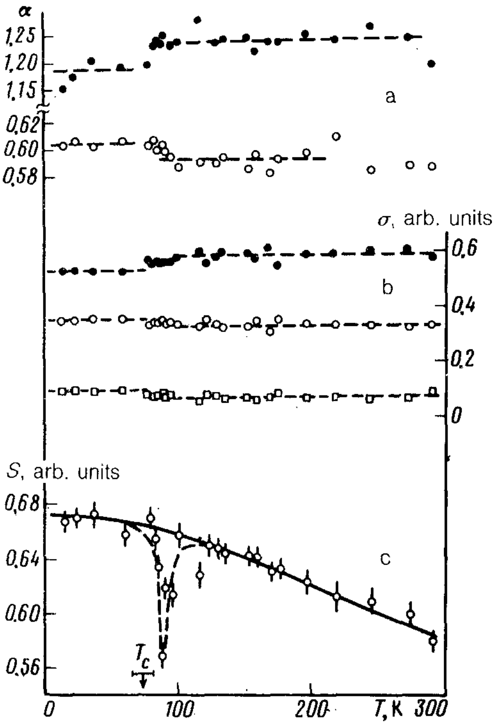

FIG. 2. Temperature dependence of the parameters of the Mössbauer spectra. a—The ratio of the line intensities $\alpha = I_\pi / I_\sigma$ in doublet 1 (open circles) and doublet 2 (filled circles); b—relative areas of the doublets, σ: 1 (open circles), 2 (filled circles), and 3 (squares); c—the total area of the spectrum, S. Solid line—Calculation based on the Debye model with $\Theta_D = 450$ K.

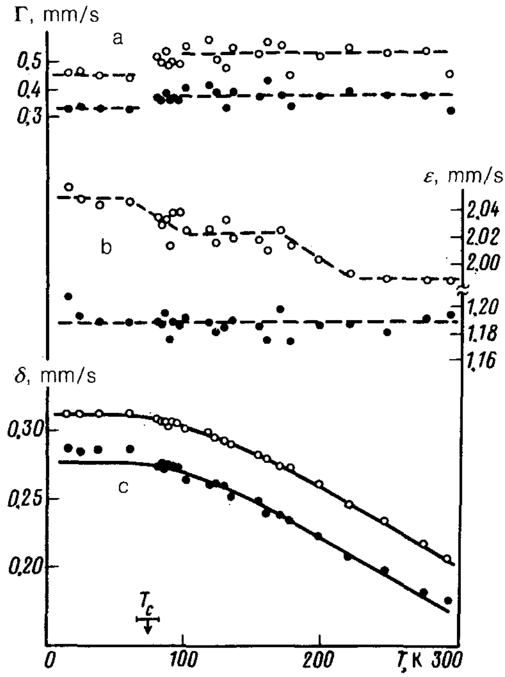

FIG. 3. Temperature dependence of the parameters of the partial spectra of doublet 1 (open circles) and doublet 2 (filled circles). a—Linewidth Γ; b—quadrupole splitting ϵ; c—isomeric shift δ. Solid lines—Calculation based on the Debye model with $\Theta_D = 450$ K.

both positions; i.e., in the doublets the components with π polarization are situated to the right of the components with σ polarization.[8] This conclusion is important for the interpretation of the difference in the intensities of the components in each of the two doublets 1 and 2, which is attributable to the Gol'danskiĭ-Karyagin[8] effect and which shows the presence of anisotropy in the Lamb-Mössbauer factor f. The quantity

Table I. Average parameter values of the Mössbauer spectra for the temperature intervals.

Parameter	$T < T_c$	$T_c < T < 200$ K	200 K $< T <$ 300 K
ϵ (1), mm/s	2.05 (1)	2.02 (1)	1.99 (1)
ϵ (2), mm/s	1.19 (1)	1.19 (1)	1.19 (1)
Γ (1), mm/s	0.33 (1)	0.37 (1)	0.38 (1)
Γ (2), mm/s	0.45 (1)	0.52 (1)	0.52 (1)
α (1)	0.604 (2)	0.592 (5)	0.585 (2)
α (2)	1.18 (2)	1.24 (2)	1.23 (2)
$\delta(1) - \delta(2)$ mm/s	0.027 (1)	0.036 (2)	0.036 (1)
σ (1)	0.36 (1)	0.34 (1)	0.33 (1)
σ (2)	0.54 (1)	0.58 (2)	0.60 (1)
Θ_D, K	430 (20)	450 (10)	470 (30)

$\beta\alpha(\langle x_{\parallel}\rangle^2 - \langle x_{\perp}\rangle^2)$, which characterizes the difference in the mean-square displacements of atoms in the directions parallel and perpendicular to the major axis of the electric-field-gradient tensor, can be estimated from the ratio of the intensities of the components of the doublet $\alpha = I_\pi / I_\sigma$. A comparison of the quantities $\alpha_1 \approx 0.6$ and $\alpha_2 \approx 1.25$ shows that the anisotropy β for positions (1), which are surrounded by four oxygen ions in the *b*, c plane, is considerably stronger than that for positions (2), which are surrounded by a pyramid consisting of five oxygen ions, where the oscillation amplitude of the Fe atom along the *c* axis is much smaller than that in the *a*, *b* plane.

The temperature dependence of the Mössbauer effect *f* (the area *S* of the spectrum) shows that slightly above T_c its behavior is highly anomalous (Fig. 2c), which Tsurin *et al.*[4], also observed in its initial stage. A decrease in *f* apparently is related to the softening of the phonon spectrum of the system and to a change in the nature of the oscillation of the Fe atom, as indicated by the change in the values of α_1 and α_2 (Fig. 2a) in this temperature range and by the anomalous change in the lattice constants[1] due to the decrease in the volume of the unit cell. We see that at $T < T_c$ the quantities $f(T)$ recover almost completely to the values calculated in the Debye approximation for the region $T_c < T < 200$ K (solid line in Fig. 2c) at $\Theta_D = 450$ K. At $T < T_c$ a slight deviation from the value calculated at $\Theta_D = 450$ K also goes through $\delta_2(T)$ (solid lines in Fig. 3c).

It is difficult to give a consistent explanation of the observed anomalies on the basis of the available data. This difficulty is compounded by the circumstance that nearly all temperature dependences of the parameters of the spectra change slightly after repeated measurements in the region of the superconducting transition temperatures (a single measurement cycle requires about a month). This circumstance and the analogous effects reported in Refs. 1, 2, and 9 might be related to the low-temperature ordering of oxygen vacancies. In the next paper we will analyze the data in more detail, along with the results of the measurements based on the ^{119}Sn impurity nuclei in the ceramic of the same composition.

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