Anomalies in the temperature dependence of the Mössbauer-effect probability for impurity tin nuclei in a 1–2–3 superconducting ceramic

V. M. Cherepanov, M. A. Chuev, S. S. Yakimov, V. Ya. Goncharov, S. A. Smirnov, and A. A. Bush
I. V. Kurchatov Institute of Atomic Energy, Moscow

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Mössbauer spectroscopy has revealed anomalies in the probability for the Mössbauer effect of impurity tin atoms in a 1–2–3 ceramic as the temperature was scanned. These anomalies are evidence of a softening of the phonon spectrum near $T_c \approx 83$ and $T_n \approx 190$ K.

Several recent studies of high-temperature superconductors with the composition $YBa_2Cu_3O_{7-y}$ (1–2–3 compounds) by spectroscopic,[1] acoustic,[2] and x-ray structural[3] methods indicate a definite relationship between the electron and phonon subsystems. In Mössbauer spectroscopy the parameter which is most sensitive to changes in the phonon spectrum of the lattice is the probability for the effect, f, which in the Debye approximation is given by the same expression as that for the Debye-Waller temperature factor.[4] In particular, two anomalies in $f(T)$ for impurity iron nuclei in copper substitutional positions were found in Refs. 5 and 6 in a 1–2–3 high-temperature superconductor near the superconducting transition temperature T_c and also at $T_n \approx 200$ K. It was suggested there that structural changes occur in a system of oxygen vacancies.[7] In the present study we have undertaken a search for corresponding anomalies in f for impurity tin atoms in a 1–2–3 ceramic. The characteristics of the coupling of tin atoms with their nearest oxygen neighborhood are different from those of ^{57}Fe (Ref. 8).

Samples of a substituted superconducting ceramic with the composition $YBa_2(Cu_{1-x}Sn_x)_3O_{7-y}$ [$x = 0.033, T_c \approx 83$ K, $\Delta T_c \approx 10$ K, $y \approx 0.2(1)$] and also of an unsubstituted 1–2–3 ceramic ($x = 0, T_c \approx 92$ K, $\Delta T_c \approx 1$ K) were synthesized under the same conditions as for the samples containing an iron impurity.[6] An x-ray analysis revealed a single-phase orthorhombic structure with the parameter values $a = 3.821$ Å, $b = 3.889$ Å, $c = 11.670$ Å, which are similar to the corresponding values for the unsubstituted samples ($a = 3.819$ Å, $b = 3.887$ Å, $c = 11.685$ Å). Furthermore, through quenching from 900 °C in liquid nitrogen we synthesized some nonsuperconducting samples with tetragonal-structure parameters $a = 3.859$ Å, $c = 11.808$ Å in the case of the substituted samples, and $a = 3.859$ Å, $c = 11.836$ Å in the case of the unsubstituted samples.

Over the entire temperature range studied, 30–300 K, the Mössbauer spectra of the samples of the two types remain essentially constant in shape, consisting of a broadened asymmetric line (Fig. 1) similar to that which was observed in Refs. 9–11. Poorly resolved spectra of this type are difficult to interpret unambiguously, and this

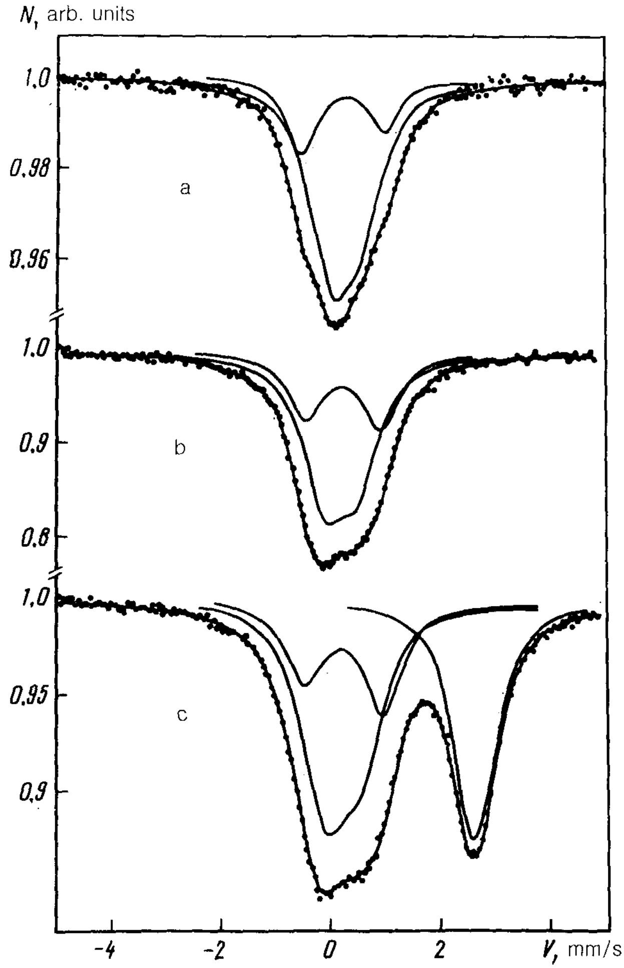

FIG. 1. Mössbauer spectra of ^{119}Sn nuclei in a $YBa_2Cu_{2.9}Sn_{0.1}O_{7-y}$ ceramic at room temperature. The solid lines are the result of a least-squares analysis of the spectra in the approximation of a Lorentzian lineshape. a—Nonsuperconducting sample [$y \approx 0.9(1)$]; b—superconducting sample [$y \approx 0.2(1), T_c \approx 83$ K]; c—spectrum of sample b in an experiment in which a standard β-Sn absorber, outside the cryostat, was placed in the beam.

difficulty influenced the conclusions reached in Refs. 9–11. For example, in Refs. 9 and 10 the spectra were represented as a superposition of either two singlets or of a singlet and a doublet. In Ref. 11, where a europium-based 1–2–3 ceramic high-temperature superconductor was studied ($x = 0.06, T_c \approx 85$ K), the spectra were decomposed into two symmetric doublets. In contrast with Refs. 9–11, we represent the spectra as a superposition of two asymmetric doublets, by analogy with the spectra of ^{57}Fe impurity atoms.[6] This model makes it possible to incorporate a possible effect of texture and/or a Gol'danskiĭ-Karyagin effect on the shape of the spectra.[4]

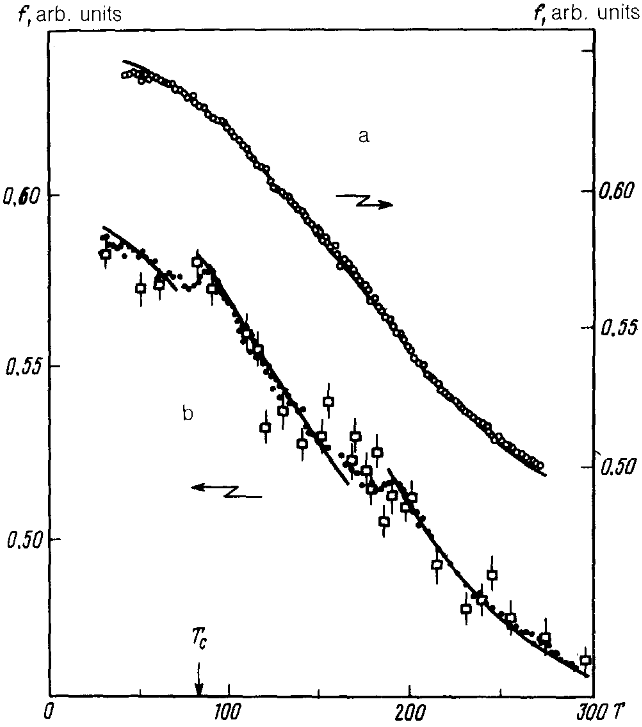

FIG. 2. Temperature dependence of the relative probability (f) for the Mössbauer effect at ^{119}Sn nuclei in a 1–2–3 ceramic. Squares—Found from the ratio of the areas under the partial spectra of the sample and of the standard, f_s; circles—measured through a temperature scan of the γ-ray count rate with the $BaSnO_3$ source at rest; solid lines—results calculated in the single-parameter Debye model. a) Nonsuperconducting sample, $\theta_D = 365(10)$ K; b) superconducting sample.

The temperature dependence of the quadrupole splitting, the linewidth, and the parameters of the isomer shift, found by the method of least squares, reveals no anomalies within the experimental error. It is also difficult to reach a definite conclusion regarding the nature of the temperature dependence of the probability for the effect, $f_s(T)$ (the squares in Fig. 2b) found directly from the ratio of the area under the partial spectrum of the ceramic (the left-side of the spectrum in Fig. 1c) to the area under the spectrum of a standard β-Sn absorber (the right-side of the spectrum in Fig. 1c), which was placed in the γ–ray beam outside the cryostat. However, since the shape of the spectra does not change as the temperature is varied, since there is a fairly wide minimum in the spectra near a zero velocity of the $BaSnO_3$ source, and since the change in the temperature-induced spectral shift ($\Delta\delta_T \approx 0.1$ mm/s) is small in comparison with the linewidth $\Gamma \approx 1$ mm/s, it was found possible to improve the relative accuracy of the measurement of $f(T)$ through a temperature scan of the count rate, $N_0(T)$, of the γ rays which passed through the sample while the source was at rest (Figs. 2, a and b).

It can be seen from Fig. 2 that for the superconducting sample the dependence established in this manner, $f_0(T) \propto N_0\ (T)$, is close to $f_s(T)$, but at the same time we can see two anomalies, in the form of dips, near $T_c \approx 83$ K and $T_n \approx 190$ K, where there are no anomalies on the corresponding $f(T)$ curve for the nonsuperconducting sample. The characteristic temperature Θ_D found from the data on $f_0(T)$ in the Debye approximation decreases from 340 K at $T > 200$ K to 315 K at 90 K $< T <$ 170 K and finally to 275 K at $T < 70$ K. It is natural to link the observed anomalies, which are evidence of a softening of the phonon spectrum of the ceramic at these temperatures, with corresponding anomalies which have been seen previously for an iron impurity in a 1–2–3 ceramic.[5,6] Furthermore, as in Ref. 6, we observed some small reproducible shifts of the anomalies and a hysteresis on the $f_0(T)$ curve (particularly at the transition through T_n of a sample in a vacuum $\approx 10^{-4}$ torr). This effect of a "low-temperature annealing" on the various parameters of the high-temperature superconductor, which has been attributed to a redistribution and a change in the degree of order of oxygen vacancies, has also been seen in several other studies.[12] We would simply like to point out the striking similarity between the dips found in $f_0(T)$ and dips which have been observed on the temperature dependence of the Raman shift of the mode at ≈ 644 cm^{-1} in an unsubstituted 1–2–3 high-temperature superconducting ceramic at the same temperatures.[13]

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