

# Study of the superconducting ceramic $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ by the Mössbauer effect in $^{119}\text{Sn}$

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The temperature dependence of the Mössbauer effect in  $^{119}\text{Sn}$  has been measured in the temperature range 5–300 K for the superconducting ceramic  $\text{EuBa}_2(\text{Cu}_{1-y}\text{Sn}_y)_3\text{O}_{7-x}$  ( $y = 0.006$ ). Near  $T_c$  the temperature dependence reveals a slightly anomalous behavior which is attributable to the softening of the phonon mode corresponding to the vibrations of Cu atoms.

Study of superconducting ceramics with a Mössbauer atomic probe introduced into the lattice as a small impurity can yield information on the vibrational states of the lattice (based on the magnitude of the Mössbauer effect) and on the impurity-related distortion of the electronic and crystal structures. This information can be used to establish a correlation between these distortions and the properties of the superconductor. In solving these problems one must first know the position the Mössbauer atom occupies in the crystal lattice. The following can be said about the tin atoms. The ion radius of  $\text{Sn}^{4+}$  ( $r = 0.71 \text{ \AA}$ ) is nearly the same as the ion radius of  $\text{Cu}^{2+}$  ( $r = 0.72 \text{ \AA}$ ) but differs appreciably from the ion radii of other cations ( $\text{Ba}^{2+}$ ,  $\text{Eu}^{3+}$ ). There are, moreover, several tin compounds with a perovskite structure (e.g.,  $\text{BaSnO}_3$ ), in which the tin atoms occupy a crystallographic position similar to the positions the copper atoms occupy in the ceramic 1–2–3. All these facts clearly suggest that tin impurity replaces copper as a result of the introduction of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  into the ceramic. Unfortunately, we do not have direct information on the localization of tin atoms in the lattice of the ceramic 1–2–3.

The samples of the  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  ceramic tested by us were synthesized by the method of solid-state reaction.<sup>1</sup> Tin in the concentrations 0.3, 0.6, 1.2% relative to the Cu atoms was introduced by adding an appropriate amount of  $\text{SnO}_2$  enriched with  $^{119}\text{Sn}$  isotope. The superconducting transition temperature determined from the temperature dependence of the resistance was about 92 K for all samples, with a transition width of approximately 1 K. Since the samples had identical Mössbauer spectra, we measured carefully only one of the samples with 0.6% Sn. X-ray structural analysis of this sample revealed that it has an orthorhombic structure with the parameters  $a = 3.873 \text{ \AA}$ ,  $b = 3.922 \text{ \AA}$ , and  $c = 11.711 \text{ \AA}$ .

Part of the ceramic sample was converted to a tetragonal phase by annealing a piece of it in air at 900 °C and then quenching it in liquid nitrogen. X-ray structural analysis confirmed the formation of the tetragonal phase with the parameters  $a = 3.891 \text{ \AA}$  and  $c = 11.787 \text{ \AA}$ .

The Mössbauer measurements were carried out at temperatures in the range 5–

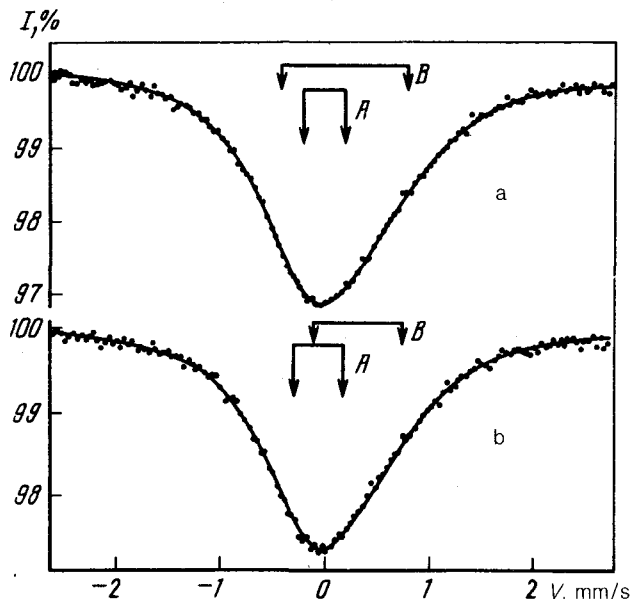


FIG. 1. Spectra of the ceramic  $\text{EuBa}_2(\text{Cu}_{0.994}\text{Sn}_{0.006})_3\text{O}_{7-x}$  at  $T = 300$  K. (a) Orthorhombic phase; (b) tetragonal phase. Solid line—Mathematical analysis of the spectrum. The arrows indicate the line positions of the doublets *A* and *B*.

300 K in a continuous-flow helium cryostat. As a radioactive source we used the compound  $\text{Ca}^{119m}\text{SnO}_3$ . The instrumental linewidth of the source (with the same absorber) was  $\Gamma_0 = 0.6$  mm/s.

Figure 1 shows the spectra of the orthorhombic and tetragonal phases of the ceramic  $\text{EuBa}_2(\text{Cu}_{0.994}\text{Sn}_{0.006})_3\text{O}_{7-x}$  at room temperature. The shape of the spectra remains essentially constant over the entire temperature interval studied. The position of the Mössbauer line unambiguously shows that the tin ion is in a state close to that of  $\text{Sn}^{4+}$ . The line position changes only slightly with the temperature, which is attributable to the temperature-induced red shift of the Mössbauer spectrum.

The spectrum of each phase can best be described by means of a superposition of two quadrupole doublets, whose parameters for the two temperatures are given in Table I. The description, we might note, is not always unambiguous in the mathematical sense (in particular, this problem affects the parameters of the doublet *B*), which stems from the unresolved nature of the spectra. Several conclusions can nonetheless be drawn from the results of mathematical analysis.

The doublet *A*, whose parameters remain nearly constant upon a transition from the orthorhombic phase to the tetragonal phase, can naturally be linked with the tin atoms which occupy the Cu2 positions ("planes") since the oxygen environment of Cu2 is known to be the same for each phase. Accordingly, the doublet *B* will then correspond to the tin atoms in the Cu1 positions ("chains"). The number of oxygen vacancies in the nearest neighborhood of Cu1 for the orthorhombic phase is different

TABLE I.

Phase	$T, K$	Doublet	$I_A / I_B$	Isomer shift, mm/s (for $\text{CaSnO}_3$ )	Quadrupole splitting, mm/s	mm/s
Orthorhombic	300	<i>A</i>	2.4 (1)	0.00 (1)	0.38 (2)	0.96 (4)
		<i>B</i>		0.18 (2)	1.19 (3)	
	8	<i>A</i>	2.4 (3)	0.06 (1)	0.36 (2)	0.98 (5)
		<i>B</i>		0.22 (2)	1.11 (5)	
Tetragonal	300	<i>A</i>	2.6 (2)	-0.05 (2)	0.46 (3)	1.00 (4)
		<i>B</i>		0.25 (4)	0.85 (6)	
	5	<i>A</i>	2.4 (1)	-0.06 (2)	0.49 (3)	1.04 (4)
		<i>B</i>		0.33 (2)	0.67 (3)	

from that of the tetragonal phase, which accounts for the different values of the electric-field gradient in the Cu1 sites. Such an interpretation is consistent with the fact that the ratio of the doublet intensities,  $I_A/I_B \approx 2.5$ , is approximately equal to the relative number of the crystallographic Cu2 and Cu1 positions (there are twice as many Cu2 positions). Unfortunately, it is difficult to calculate directly the electric-field gradient at the  $^{119}\text{Sn}$  nucleus for the particular configurations of the oxygen surroundings of tin in the Cu1 and Cu2 positions, since the contribution to the electric-field gradient from the electronic orbitals, which link tin with oxygen, cannot be determined exactly. This circumstance accounts for the difficulty in comparing the parameters of the quadrupole doublets *A* and *B* with the various configurations of the surroundings. Relating doublet *B* to the Cu1 position, one should bear in mind, however, that the impurity tin atom can form the nearest neighborhood which is different from the neighborhood of the copper ion. In particular, one vacancy in the tin neighborhood may be occupied by an "additional" oxygen atom in order to satisfy the "excess" valence (in comparison with copper ions) of  $\text{Sn}^{4+}$ .

We have measured the temperature dependence for the probability of the Mössbauer effect occurring in the sample of the orthorhombic phase. The probability was defined as the area of the experimental spectrum. The results of the measurements are shown in Fig. 2. The solid curve corresponds to the calculation based on the Debye model with a Debye temperature  $\Theta = 290$  K. We see that the overall experimental dependence is consistent with the Debye behavior, in contrast with the situation in Refs. 2 and 3, where a deviation from the Debye curve corresponding to  $\Theta = 310\text{--}320$  K was found to increase, beginning at 120–150 K and continuing to the liquid-helium temperature. Such a result, however, depends essentially on whether the calculated curve corresponds to the behavior of the experimental curve at high temperature or to its average behavior. The distinguishing features of the experimental curve obtained by us are its slightly irregular behavior below about 150 K and a slight anomaly in the form of a dip, which appears immediately after the superconducting transition. This

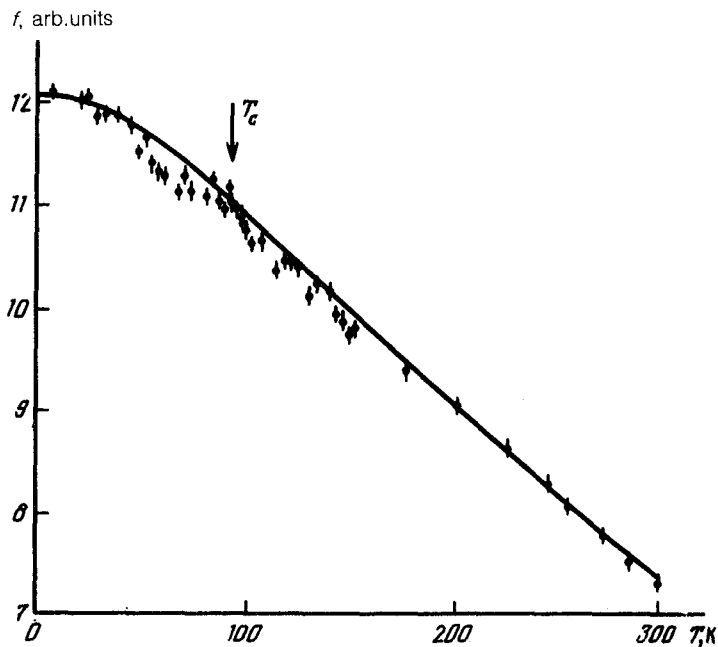


FIG. 2. Temperature dependence of the Mössbauer effect (area under the spectrum). Solid curve—Calculation based on the Debye model with  $\Theta = 290$  K.

anomaly suggests that the vibration amplitude of the tin impurity atoms increases slightly near  $T_c$ . Since tin occupies the copper positions, we can attribute such an increase in the vibrations to the softening of the phonon mode which corresponds to the mutual vibrations of the copper and oxygen atoms.<sup>4</sup> The temperature-dependent Mössbauer effect in  $^{151}\text{Eu}$  nuclei of the same ceramic does not reveal any anomalies or deviations from the Debye curve<sup>5,6</sup>; i.e., the vibrations of rare-earth atoms are not sensitive to the superconducting transitions.

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