

# Metastability in $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ studied by $^{119}\text{Sn}$ and $^{151}\text{Eu}$ Mössbauer spectroscopy

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The metallic oxide compound system  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$  ( $x=0.05, 0.10, 0.20$ ) was prepared for investigation with  $^{151}\text{Eu}$  and  $^{119}\text{Sn}$  Mössbauer spectroscopy. The best fits of the  $^{119}\text{Sn}$  Mössbauer lines reveal at least two different  $\text{Sn}^{\text{IV}}$  sites. The  $^{151}\text{Eu}$  spectra are characteristic for  $\text{Eu}^{\text{III}}$  state in these compounds. We have found a considerable difference between the shapes of  $^{119}\text{Sn}$  Mössbauer spectra recorded at room temperature and those recorded at the temperature of liquid nitrogen in the case of the sample having the highest tin content. Nevertheless, there is no evidence that this difference has a direct connection with the superconducting behavior. A time-dependent splitting was found in the  $^{119}\text{Sn}$  spectra of  $\text{EuBa}_2(\text{Cu}_{0.8}\text{Sn}_{0.2})_3\text{O}_{7-y}$  at 78 K. It had a maximum at about 350 h after the synthesis of the sample. Some anomalous temperature dependences were also found in the  $^{151}\text{Eu}$  and  $^{119}\text{Sn}$  Mössbauer parameters. Our findings can be associated with different Sn sites as well as low-temperature phase transformation in these oxide compounds.

## INTRODUCTION

Since the discovery of Bednorz and Müller,<sup>1</sup> high- $T_c$  superconductivity was found for several metallic oxide materials.<sup>2-8</sup> The as-prepared superconductors often lose their superconductivity after a certain time,<sup>5,9</sup> so that any detectable change in the structure<sup>10</sup> of these materials can lead to a better understanding of the properties of superconductors. Mössbauer spectroscopy can provide useful information about the structure of superconducting cuprates if such nuclides as  $^{151}\text{Eu}$ ,  $^{57}\text{Fe}$ ,  $^{57}\text{Co}$ ,  $^{119}\text{Sn}$ , etc., are present in the sample investigated.<sup>11-18</sup>

Recently, our Mössbauer measurements of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-y}$  led to surprising results.<sup>11</sup> A singlet line—characterizing the  $\text{Eu}^{\text{III}}$  state—could be seen in the  $^{151}\text{Eu}$  Mössbauer spectra recorded at room temperature, while two separate lines appeared in the spectra below the  $T_c$ . The transition took place gradually with the temperature around the  $T_c$ . The isomer shift of these two lines were<sup>12</sup> unusual compared with those of the  $\text{Eu}^{\text{II}}$  and  $\text{Eu}^{\text{III}}$  compounds. This may be associated with the electron hopping process between two Eu states, as found similarly in the case of  $\text{Eu}_3\text{S}_4$ .<sup>13,14</sup>

This phenomenon showed a special time dependence. Some weeks after the preparation of the sample only a singlet line could be found in the spectra recorded below the  $T_c$ , the isomer shift of which is in agreement with that measured by others.<sup>15,16</sup>

In this work, we replaced the Cu atoms partially by Sn atoms, the ionic radii of which is close to that of  $\text{Cu}^{\text{II}}$ .

With this substitution, the investigation of the state of another lattice site (different from that of Eu) also became possible by Mössbauer spectroscopy.

## EXPERIMENT

The starting reagents were weighted out so that the composition of the final products become  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$  with  $x=0.05, 0.10$ , and  $0.20$  after the reaction.

$\text{Eu}_2\text{O}_3$ ,  $\text{BaCO}_3$ ,  $\text{CuO}$ , and  $\text{SnO}_2$  were well ground, mixed, and homogenized with a small amount of ethanol. They were dried at  $110^\circ\text{C}$  for 4 h and calcined in quartz tubes at  $920 \pm 20^\circ\text{C}$  for 14 h. The obtained powders were reground and sintered at  $920 \pm 20^\circ\text{C}$  for 14 h in air and cooled slowly to room temperature. Finally, the reacted powders were annealed at  $420 \pm 10^\circ\text{C}$  for 4 h in air. These powders served as samples (S1, S2, and S3) for Mössbauer measurements.

A part of the powders were then pressed into pellets of 16 mm diameter under 10 kbar pressure and sintered once more.

Photographs taken by scanning electron microscopy (JEOL JXA-50A) on the pellets show that the samples can be considered as homogeneous, well-sintered single-phase systems. It was supported by x-ray results reflecting an orthorhombic phase (Fig. 1).

Electrical resistivity measurements were also carried out on these pellets by conventional four-point technique

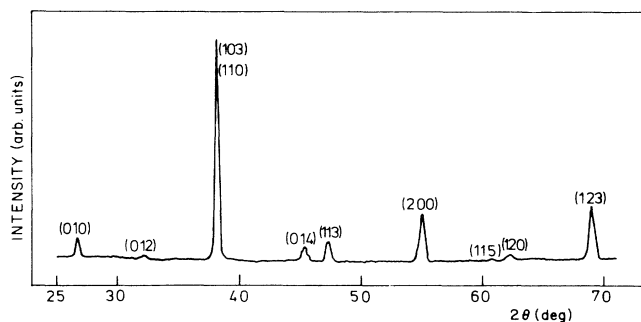


FIG. 1. X-ray diffractogram of sample of  $\text{EuBa}_2(\text{Cu}_{0.8}\text{Sn}_{0.2})_3\text{O}_{7-y}$ .  $\text{Co K}\alpha$  x-ray radiation was used.

some weeks later. In contrast with expectations, the samples did not show superconductivity down to the temperature of liquid helium. The resistivity curves at and below the temperature of liquid nitrogen have a semiconductor-like behavior with a rising tendency. The first set of the conductivity measurements were performed three weeks after the recording of the Mössbauer spectra. There was another set of the measurements on similar samples 3, 7, and 14 days after the preparation with the same results.

The oxygen content of the samples was not checked experimentally. However, samples prepared earlier in the above-described way showed superconductivity.

In order to change the oxygen content, the highest Sn-containing pellets (sample S4) were heat treated at  $950 \pm 20^\circ\text{C}$  for 24 h (sample S5) as well as at  $420 \pm 10^\circ\text{C}$  for 24 h (sample S6) in air. The oxygen concentration decreases by the former, and increases by the latter heat treatment. Except while measuring, the samples were kept in an exsiccator with KOH at  $10^5$  Pa pressure at room temperature.

For the Mössbauer measurements, the powdered samples were dispersed into paraffin; the surface density was kept constant.

The Mössbauer measurements of the samples were performed with conventional Mössbauer spectrometers in constant acceleration mode. Transmission spectra of  $^{151}\text{Eu}$  and  $^{119}\text{Sn}$  were taken at room temperature and at the temperature of liquid nitrogen. A temperature-controlled cryostat (Leybold) was used for the low-temperature measurements. A  $10^9$ -Bq  $\text{Ca}^{119}\text{SnO}_3$  source, as well as a  $10^{10}$ -Bq  $^{151}\text{SmF}_3$  source, provided the  $\gamma$  rays. Isomer shifts are given relative to the sources. The evaluation of the Mössbauer spectra was carried out by least-squares fitting the lines.

## RESULTS

Figure 2 shows the  $^{119}\text{Sn}$  Mössbauer spectra of samples S1, S2, and S3 recorded both at room temperature and at temperature of liquid nitrogen. In case of the low-Sn concentrations, single-line envelopes appear while in the case of the highest Sn concentration, a doubletlike spectra can be observed at temperature of liquid nitrogen.

The spectrum in Fig. 2(a) (S3) was fitted by three lines. This was the simplest way of the decomposition

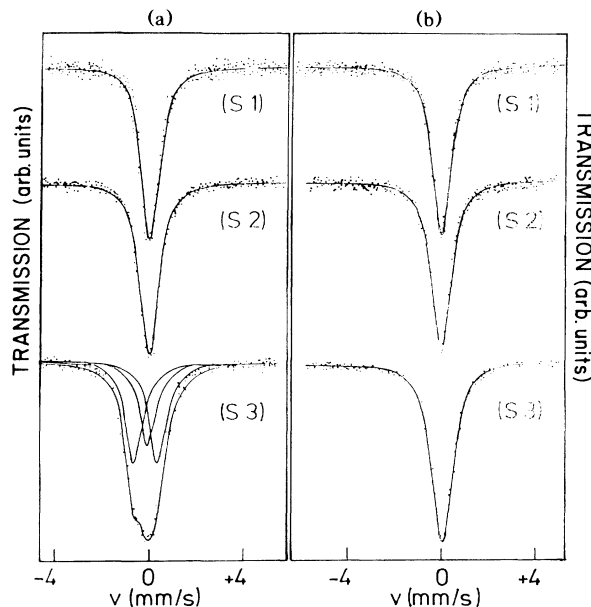


FIG. 2.  $^{119}\text{Sn}$  Mössbauer spectra of samples of  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ . S1:  $x=0.05$ , S2:  $x=0.10$ , and S3:  $x=0.20$ , recorded (a) at temperature of liquid nitrogen and (b) at room temperature.

(i.e., supposing the minimum number of lines) which resulted in a satisfactory fit. When this spectrum was decomposed into one or two lines the relative  $\chi^2$ 's were unacceptable. This is valid for the spectra showing a single line envelope, too. In case of well-resolved spectra the evaluations without any restrictions gave the same linewidths for all the three lines. Consequently, we restricted the linewidth to be equal (but not fixed) for the three lines in all spectra.

In the room-temperature Mössbauer spectra [Fig. 2(b)] the relative area of the lines belonging to the different tin states varied with the Sn content (Fig. 3).

Figure 4 shows the  $^{151}\text{Eu}$  Mössbauer spectra of samples S1, S2, and S3 recorded at temperature of liquid nitrogen. The spectra were fitted as a single line, the parameters of which are shown in Fig. 5 as a function of tin concentration (see also Table I).

The measurements of the Mössbauer spectra of the

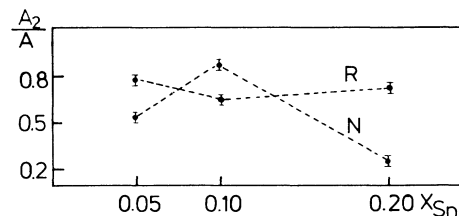


FIG. 3. Dependence of area fraction of second  $^{119}\text{Sn}$  Mössbauer line on tin concentration in  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ . R: room temperature, N: temperature of liquid nitrogen.

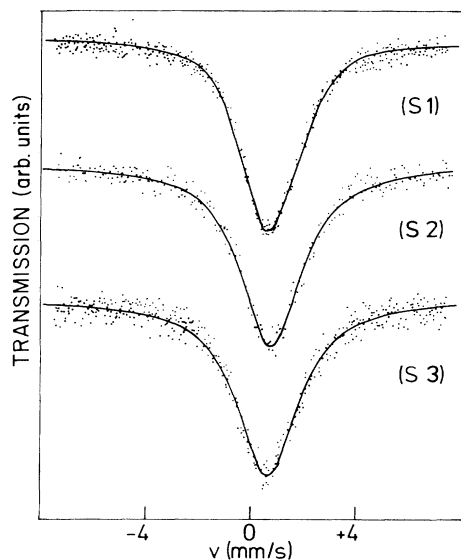


FIG. 4.  $^{151}\text{Eu}$  Mössbauer spectra of samples of  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ . S1:  $x=0.05$ , S2:  $x=0.10$ , and S3:  $x=0.20$ , recorded at temperature of liquid nitrogen.

sample of the highest tin content were repeated several times in defined periods after the preparation of the sample. The shape of the spectra (Fig. 6) changed drastically as a function of time. Mössbauer data presented in Table II and Fig. 7 clearly indicate that the relative area of line 2 has a minimum at about 350 h after the synthesis of the sample. No similar changes were observed in the spectra recorded at room temperature. Considering the outermost lines as a doublet, time dependence of the quadrupole splitting and isomer shift of the doublet is also presented in Fig. 7.

Similar time dependence was observed again in the case of sample S4 (resintered four weeks after the original preparation). In the decomposed Mössbauer spectra the distance between the outer lines decreased, while the area fraction of the central line increased monotonically with

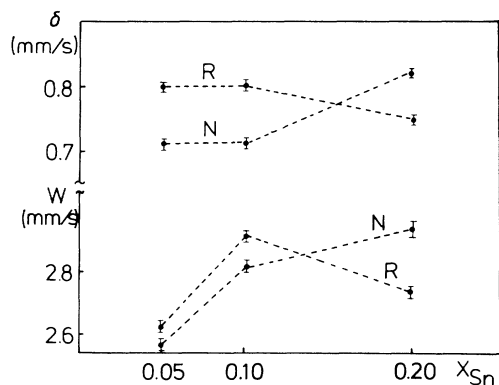


FIG. 5. Dependence of isomer shift and linewidth of  $^{151}\text{Eu}$  Mössbauer spectra on tin concentration in  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ . R: room temperature, N: temperature of liquid nitrogen.

TABLE I.  $^{151}\text{Eu}$  Mössbauer data of  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ . R: room temperature; N: temperature of liquid nitrogen.

Sample	Measured temperature	Isomer shift (mm/s)	Linewidth (mm/s)
S1 ( $x=0.05$ )	R	0.805	2.73
S2 ( $x=0.10$ )	R	0.804	3.04
S3 ( $x=0.20$ )	R	0.747	2.84
S1 ( $x=0.05$ )	N	0.728	2.57
S2 ( $x=0.10$ )	N	0.713	2.84
S3 ( $x=0.20$ )	N	0.858	2.96
S5 (950 °C)	R	0.819	3.17
S6 (420 °C)	R	0.791	2.87
S5 (950 °C)	N	0.843	3.54
S6 (420 °C)	N	0.754	3.00

increasing time, as shown in Fig. 8.

No considerable changes were observed in the  $^{119}\text{Sn}$  Mössbauer spectra of samples (S5, S6) containing different amount of oxygen (Fig. 9).

In the  $^{151}\text{Eu}$  spectra of these samples, however, the linewidth showed a slight difference.

## DISCUSSION

Isomer shifts of the  $^{151}\text{Eu}$  Mössbauer spectra show  $\text{Eu}^{\text{III}}$  state in all cases, while those of  $^{119}\text{Sn}$  Mössbauer

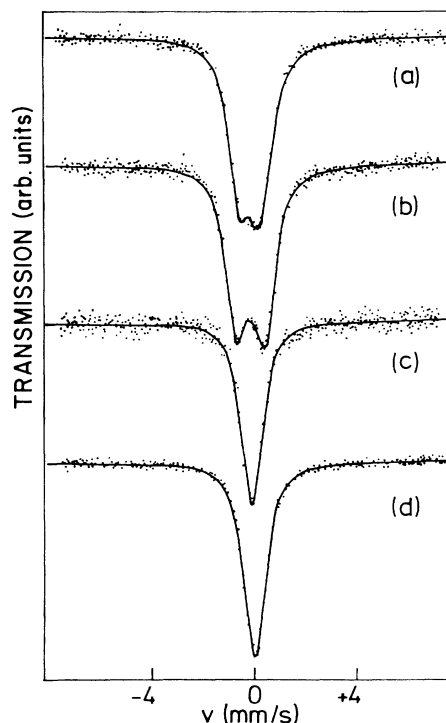


FIG. 6.  $^{119}\text{Sn}$  Mössbauer spectra of  $\text{EuBa}_2\text{Cu}_{2.4}\text{Sn}_{0.6}\text{O}_{7-y}$  recorded at temperature of liquid nitrogen (a) 215 h, (b) 340 h, (c) 500 h, and (d) 680 h after the preparation of sample.

TABLE II.  $^{119}\text{Sn}$  Mössbauer data of  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$ . *R*: room temperature; *N*: temperature of liquid nitrogen.

Sample	Measured temperature	Isomer shift (mm/s)			Linewidth (mm/s)
		$\delta_1$	$\delta_2$	$\delta_3$	
S1 ( $x=0.05$ )	<i>R</i>	-0.273	0.0285	0.5812	0.82
S2 ( $x=0.10$ )	<i>R</i>	-0.2145	0.0285	0.523	0.86
S3 ( $x=0.20$ )	<i>R</i>	-0.305	0.0285	0.510	0.89
S1 ( $x=0.05$ )	<i>N</i>	-0.222	0.0285	0.5917	0.74
S2 ( $x=0.10$ )	<i>N</i>	-0.3815	0.0355	0.4085	0.88
S3 ( $x=0.20$ )	<i>N</i>	-0.4636	0.0285	0.5442	0.92
S3 (repeat 1)	<i>N</i>	-0.5699	0.0285	0.6322	0.93
S3 (repeat 2)	<i>N</i>	-0.3815	0.0285	0.625	0.77
S3 (repeat 3)	<i>N</i>	-0.2405	0.0285	0.4635	0.85
S4 ( $x=0.20$ )	<i>N</i>	-0.5635	0.0415	0.6855	1.07
S4 (repeat 1)	<i>N</i>	-0.4935	0.0335	0.6235	1.05
S4 (repeat 2)	<i>N</i>	-0.3985	0.0285	0.526	1.02
S4 (repeat 3)	<i>N</i>	-0.3625	0.0285	0.510	1.02
S5 (950 °C)	<i>R</i>	-0.451	0.0286	0.5465	0.98
S6 (420 °C)	<i>R</i>	-0.3815	0.0605	0.5635	0.92
S5 (950 °C)	<i>N</i>	-0.2954	0.0285	0.5043	0.99
S6 (420 °C)	<i>N</i>	-0.2583	0.0285	0.4772	0.93

lines are characteristic of  $\text{Sn}^{\text{IV}}$  compounds. The isomer shifts of the decomposed tin spectra are equal to those measured by Giapintzakis *et al.* in a  $(\text{La},\text{Sr})(\text{Cu},\text{Sn})\text{O}_4$  superconductor.<sup>18</sup>

According to the three-line decomposition of  $^{119}\text{Sn}$  spectra, which proved to be optimum, two or three Sn states can be associated with the lines. Simultaneous

changes of the area fractions of lines 1 and 3 (see, e.g., Fig. 8) suggest that these lines can be considered as a quadrupole doublet. It means that the central and the two outer lines represent two different states of Sn atoms. We should mention here that the three-line decomposition is the simplest one and it cannot be excluded that the central singlet, actually, is an unresolved quadrupole doublet. Of course, in such a case the other fitted parameters may be slightly affected, but it surely does not influence our qualitative conclusions regarding the time- and temperature-dependent changes discussed below.

Since there are two nonequivalent Cu sites in the lattice of this perovskite (see Fig. 9), it seems to be evident that these Cu sites are replaced by tin atoms. The Cu(1) site occupied by Sn atoms in the  $\text{CuO}_2$  layer can be associated with the quadrupole split component in the  $^{119}\text{Sn}$  Mössbauer spectra. Sn atoms being in Cu(2) sites can be connected with the central singlet in the Sn spectra. These correspondences are based principally on considerations that a higher electric field gradient (EFG)<sup>19</sup> is expected for Cu(1) site than for Cu(2).<sup>20</sup>

With the assumption that there is no significant difference between the Mössbauer-Lamb factor of two sites at room temperature, the relative areas of the Mössbauer lines (Fig. 3) show that the Sn atoms prefer the Cu(2) sites.

The anomalously changes in Mössbauer parameters can be explained similarly as was done by Giapintzakis *et al.*<sup>18</sup> in the case of a superconducting oxide having  $\text{K}_2\text{NiF}_4$  structure. (i) The observed changes in the  $^{151}\text{Eu}$  line positions measured at room temperature and at temperature of liquid nitrogen in case of samples S1 and S2 (Fig. 5) contradict the expectation based on the usual temperature dependence. Hence, it can be associated with low-temperature phase transformation. A detailed discussion of  $^{151}\text{Eu}$  data will be presented elsewhere.

(ii) The temperature-dependent changes of the area fractions in the  $^{119}\text{Sn}$  Mössbauer spectra of samples S1

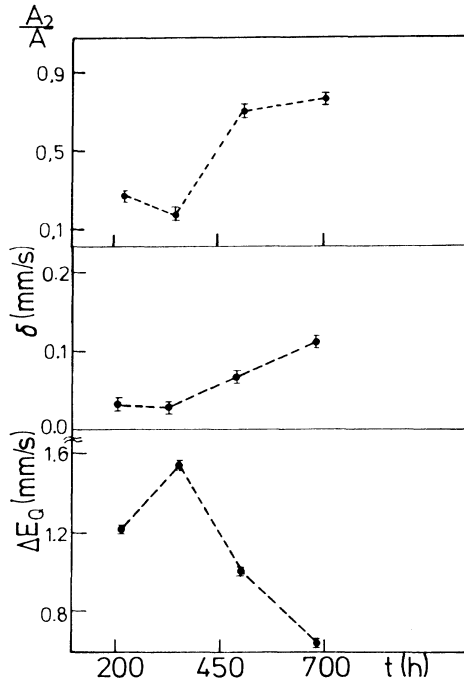


FIG. 7. Time dependence of the area fraction of central singlet  $^{119}\text{Sn}$  Mössbauer line and of the quadrupole splitting and isomer shift of the doublet (created from the two outermost lines) at temperature of liquid nitrogen in sample S3.

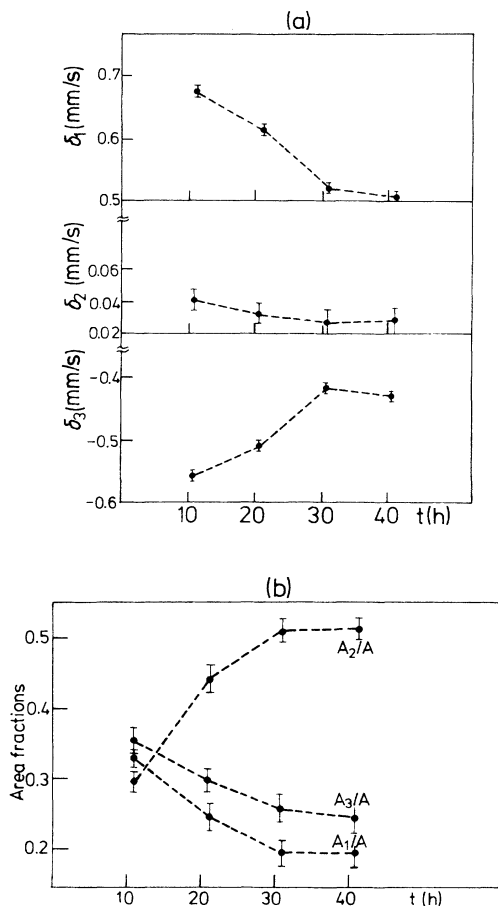


FIG. 8. Time dependence of (a) line positions and (b) area fractions of  $^{119}\text{Sn}$  Mössbauer lines after the resintering of sample  $\text{EuBa}_2(\text{Cu}_{0.8}\text{Sn}_{0.2})_3\text{O}_{7-y}$ .

and  $S2$  cannot be explained by considering only two Debye temperatures (one for each site). These anomalous changes can be interpreted assuming phonon softening. [After the present article was submitted for publication, a copy of a paper<sup>17</sup> containing results on Mössbauer measurements of  $\text{EuBa}_2(\text{Cu}_{2.98}\text{Sn}_{0.02})\text{O}_{7-y}$  superconducting material with a similar interpretation to that of ours arrived at our laboratory.]

Our most striking results about the time-dependent changes in the sample having the highest tin content can be interpreted in the following way. The large quadrupole splitting (see Fig. 7) compared to the value belonging to tin atoms in  $\text{Cu}(1)$  site show the appearance of another position of tin with higher EFG at the tin nucleus. For this new tin position, we suppose an extraordinary Sn atom between the  $\text{CuO}_{2+y}$  layers near the Eu atoms (see Fig. 9). This latter statement is based on the changes of  $^{151}\text{Eu}$  Mössbauer parameters in comparison to those of samples  $S1$  and  $S2$  (Fig. 5). It is not surprising that the metastable extraordinary Sn atoms can be found only in sample  $S3$  where the lattice strain, due to the high tin concentration, can hamper the occupation of the regular  $\text{Cu}(2)$  sites.

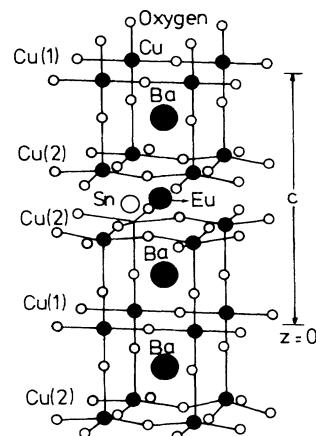


FIG. 9. Structure model of  $\text{EuBa}_2(\text{Cu}_{1-x}\text{Sn}_x)_3\text{O}_{7-y}$  perovskite. Metastable Sn position assumed at temperature of liquid nitrogen in  $\text{EuBa}_2(\text{Cu}_{0.8}\text{Sn}_{0.2})_3\text{O}_{7-y}$  is included. Regular  $\text{Cu}(1)$  and  $\text{Cu}(2)$  positions can be replaced by Sn atoms.

At room temperature, however, the Sn atoms occupy the regular Cu sites as shown by the Mössbauer parameters in this case [see Fig. 2(b) ( $S3$ )]. It also shows the existence of low-temperature phase transformation, and, additionally, indicates that the tin atoms at  $\text{Cu}(2)$  sites came into extraordinary position only at low temperature.

The time dependence of the Mössbauer parameters can be associated with the change of the position of the extraordinary Sn atoms. The observed changes can be connected with the relaxation of the extraordinary Sn atoms to the regular  $\text{Cu}(2)$  site. This idea is supported by the observation that the intensity of the central singlet, which corresponds to the regular  $\text{Cu}(2)$  site, increases very intensively with time (Fig. 7). In the spectra where the intensity of the singlet is low, the remaining doublet is an unresolved sum of the doublet belonging to Sn in  $\text{Cu}(1)$  position and that belonging to the extraordinary Sn. On the basis of this assumption it is understandable that the Mössbauer parameters of the doublet component tend to those of Sn in  $\text{Cu}(1)$  site during the time-dependent process (see Fig. 7).

The large difference between the area fractions of Sn Mössbauer spectra of sample  $S3$  recorded at liquid-nitrogen temperature [Fig. 2(a) ( $S3$ )] and that measured subsequently at room temperature [Fig. 2(b) ( $S3$ )] is consistent with the idea that the extraordinary tin atoms, at liquid-nitrogen temperature, are in the transitional stage of a low-temperature phase transformation.

On the electrical resistivity curves, there were some irregularities which may indicate a low-temperature phase transformation, too. However, it is not evident from these measurements alone. Time-dependent behavior was not observed.

From the very slight changes of Sn spectra of samples having different oxygen content (Table II) it can be concluded that the change in oxygen surrounding the tin atoms is not the predominant factor of the time-dependent changes.

## ACKNOWLEDGMENTS

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