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**$^{151}\text{Eu}$  MÖSSBAUER STUDIES ON  $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$  OXIDE SYSTEMS**

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Mössbauer parameters of  $^{151}\text{Eu}$  in  $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$  have been studied as a function of temperature, for  $x = 0.15$  and  $x = 0.25$ . The areas of the absorption spectra for the two samples are almost equal. This could mean that the  $f$ -Mössbauer factor for  $^{151}\text{Eu}$  at the barium sites is much smaller than that for  $^{151}\text{Eu}$  at the rare earth sites, i.e. we only observe the spectra of the latter sites. According to this, the fits of the spectra with a single quadrupolar pattern and with two quadrupolar patterns have given equivalent  $\chi^2$  values.

**1. Introduction**

From the early days of the high- $T_c$  superconductivity, the Mössbauer spectroscopy has been applied in order to study high- $T_c$  superconducting oxides [1]. In these experiments the material has to be doped with a given concentration of Mössbauer isotopes, which must occupy the lattice sites that we want to study.

In many papers, substitutions of  $^{151}\text{Eu}$  for Y in the 90 K superconductors have been presented [2–6]. These experiments show that the isomer shift of Eu looks like trivalent Eu [2]. Moreover, in more recent high resolution  $^{151}\text{Eu}$ -Mössbauer measurements on  $\text{EuBa}_2\text{Cu}_3\text{O}_{7+\delta}$ , no anomalies around  $T_c$  have been observed in the isomer shift and in the  $f$ -factor (recoil-free fraction) [3]. The reported values at room temperature of the quadrupole splitting  $eQ_g V_{zz} \approx -5$  mm/s and asymmetry parameter  $\eta \approx 0.8$  are in agreement between the various authors [2–6].

Our aim in this paper is to investigate the Ba site, by substituting  $^{151}\text{Eu}$  for Ba in  $\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$  oxide superconductors [7–11]. For this we note the following. First, in order to obtain a single-phase superconducting compound, the concentration of substituted Ba must be not greater than 20% [12]. Second, we have to substitute Eu for both Ba (partially) and Y (wholly), so that each Mössbauer spectrum is the superposition of two spectra. By assuming that the  $f$ -factor values are the same for the two sites, the two lines have a relative intensity about equal to  $x$ . Since the Eu valence at both sites is almost the same, it can be very cumbersome to detect and characterize the line corresponding to

thin and homogeneous samples, so as to reduce, as far as possible, the broadening of the spectrum lines.

Following ref. [11], where Mössbauer spectra of  $\text{Eu}_{1.25}\text{Ba}_{1.75}\text{Cu}_3\text{O}_{7+\delta}$  at 90 K and 300 K have been reported, we have taken into account the quadrupole structure of the source:  $eQ_g V_{zz} = -3.6$  mm/s and  $\eta = 0$  [13].

## 2. Experiments and results

$\text{Eu}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{7+\delta}$  samples were prepared by an oxalate coprecipitation method which allows one to obtain a more precise stoichiometry than the ordinary solid state reaction method [14]. The powders have been characterized by SEM, TEM and XRD analyses. The SEM and TEM analyses have shown that the grains have a well defined shape, are well linked between each other and homogeneous in size: the average dimension is about 7  $\mu\text{m}$ . The Ba and Eu stoichiometry has been checked by energy dispersion spectrometry, connected with TEM. The XRD analyses have shown that the materials consist of one orthorhombic single phase with a trend to a tetragonal transition as  $x$  increases.

Resistivity measurements have shown a transition temperature decreasing as  $x$  increases. It changes from 92 K for  $x = 0$  to 60 K for  $x = 0.15$  and 40 K for  $x = 0.25$ .

Absorbers were prepared, with a small thickness ( $\approx 3.5$  mg  $^{151}\text{Eu}/\text{cm}^2$ ), so as to avoid line distortions due to absorption saturation. Mössbauer spectra between 25 K and room temperature for each sample were collected, using a 50 mCi  $^{151}\text{SmF}_3$  source at 300 K. All of them exhibit only a single line (fig. 1), around 0.6 mm/s, since europium has nominal oxidation number +3 in both sites [10,11].

First we fitted the spectra with a single quadrupolar pattern. Then we made another fit with two quadrupolar patterns, whose relative intensity was assumed equal to  $x$ . In the latter case our values at 90 K and 300 K are in agreement with those reported in ref. [11] for  $\text{Eu}_{1.25}\text{Ba}_{1.75}\text{Cu}_3\text{O}_7$ . However, the two fits gave equivalent values of  $\chi^2$ .

Moreover, we found the area of the absorption spectrum almost equal for the two samples, at all temperatures (fig. 2). Thus, it seems that the contribution of Eu at the Ba site may be somehow negligible. On the other hand, in ref. [11] Bauminger et al. report Mössbauer parameters of  $^{151}\text{Eu}$  at the barium site, obtained from a double quadrupole fit on  $\text{Eu}_{1.25}\text{Ba}_{1.75}\text{Cu}_3\text{O}_7$ . These values are very close to the values obtained from a fit on  $\text{EuCaBaCu}_3\text{O}_7$ . In this latter compound it is assumed that Ca occupies the rare earth sites and Eu is located in the Ba sites, since it was proved [15], that the same substitution occurs with La in  $\text{LaCaBaCu}_3\text{O}_7$ . However, this assumption is not entirely convincing. In fact, by considering the ionic radii of  $\text{Eu}^{3+}$  (98 pm),  $\text{Ca}^{2+}$  (106 pm),  $\text{Y}^{3+}$  (106 pm),  $\text{La}^{3+}$  (122 pm) and  $\text{Ba}^{2+}$  (143 pm) [16], one can understand why  $\text{La}^{3+}$ , instead of  $\text{Ca}^{2+}$ , can wholly substitute for  $\text{Ba}^{2+}$ , but it does not seem that this should be the same

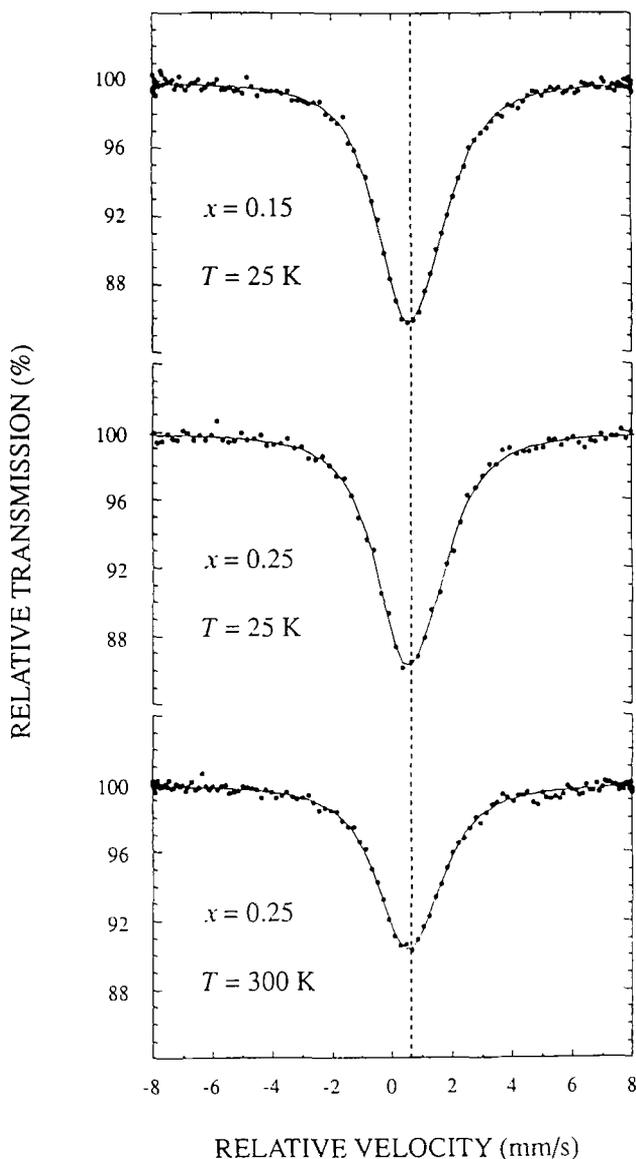


Fig. 1. Spectra for the  $x = 0.15$  and  $x = 0.25$  samples at the indicated temperatures. The dotted line is drawn at 0.65 mm/s. It can be seen, from the two spectra at  $T = 25$  K, that the maximum absorption depth is almost the same for the two samples.

for Eu. In fact, in ref. [12] it is shown that the ability of a rare earth ion to substitute onto the Ba site, to form a single-phase compound, decreases with the ionic radius. Moreover, in ref. [17] it is shown that the solubility of Eu with Ba is practically absent in  $\text{YBa}_{2-x}\text{Eu}_x\text{Cu}_3\text{O}_7$  and that these compounds are not single-phase. Thus, it is possible that we do not observe the spectrum of Eu at the

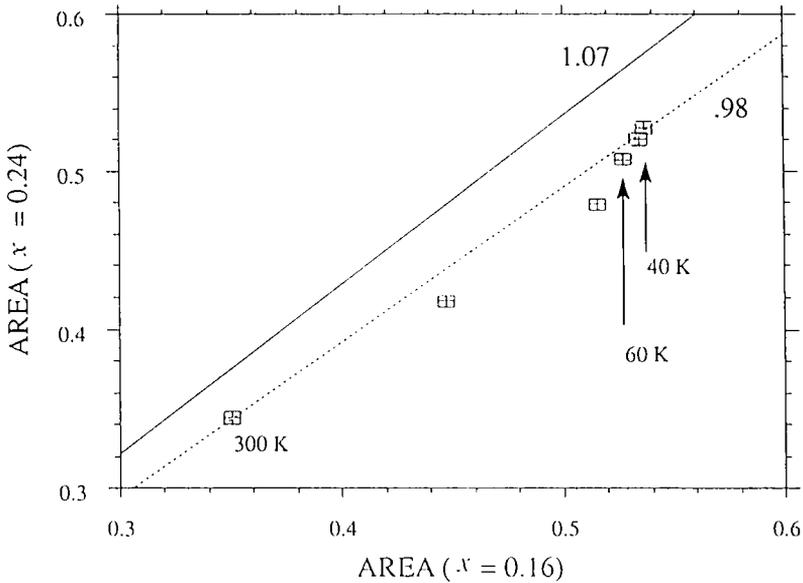


Fig. 2. Area of the absorption line of the more doped sample vs. the area of the absorption line of the less doped one. The full straight line corresponds to a ratio of the areas equal to the ratio of the actual concentrations of Eu in the two samples ( $1.24/1.16 = 1.07$ ). The experimental points are shown with their error bars.

Ba site. This could be due to the fact that the corresponding  $f$ -factor is much smaller than that for Eu at the rare earth site. In fact the  $\text{Eu}^{3+}$  ion, substituting for  $\text{Ba}^{2+}$ , occupies a region appreciably larger than its ionic size, so that it could be loosely held in a potential which is flattened in its central region. Such a

Table 1

Isomer shift ( $IS$ ) and quadrupole splitting ( $eQ_v V_{zz}$ ) for the samples studied. The value of the asymmetry parameter  $\eta$ , determined by the fits, is about equal to zero at all temperatures.

Compounds	$T$ (K)	Isomer shift $IS$ (mm/s)	Quadrupole interaction $eQ_v V_{zz}$ (mm/s)
$\text{Eu}_{1.15}\text{Ba}_{1.85}\text{Cu}_3\text{O}_{7+\delta}$	25	0.65(1)	-5.1(2)
	40	0.66(1)	-5.2(2)
	60	0.66(1)	-5.3(2)
	90	0.64(1)	-4.7(2)
	200	0.63(1)	-5.2(2)
	300	0.61(1)	-5.0(2)
$\text{Eu}_{1.25}\text{Ba}_{1.75}\text{Cu}_3\text{O}_{7+\delta}$	25	0.64(1)	-5.0(2)
	40	0.64(1)	-4.7(2)
	60	0.64(1)	-4.8(2)
	90	0.64(1)	-5.0(2)
	200	0.62(1)	-5.0(2)
	300	0.61(1)	-5.1(2)

phenomenon is not new, i.e.: the occurrence of very low  $f$ -factors in some compounds has been explained in this way [18]. From the above discussion, it is our opinion that the spectra are only due to the europium located at the rare earth sites.

The single quadrupole fit has given values of  $eQ_{\text{g}}V_{zz}$  and  $IS$  almost equal for the two samples:  $x = 0.15$  and  $x = 0.25$ . The differences are within the errors (see table 1). The values are in agreement with those reported in literature for  $\text{EuBa}_2\text{Cu}_3\text{O}_7$ . On the contrary, our value of  $\eta$  ( $\approx 0$ ) is closer to that reported by Bauminger et al. (0.3) than the ones reported by the other authors (0.8) [3–6]. Most likely this difference is due to the fact that the hyperfine structure of the source has been taken into account in the fitting procedure.

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