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^{151}Eu Mössbauer studies on Zn-doped $EuBa_2Cu_3O_{7-y}$

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Abstract. ^{151}Eu Mössbauer studies have been performed on the compounds $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ with $x = 0{\cdot}0, 0{\cdot}025, 0{\cdot}05, 0{\cdot}075$ and $0{\cdot}1$. The parent compound, $EuBa_2Cu_3O_{7-y}$ is superconducting with a transition temperature (T_c) of 88 K. T_c is depressed as Zn is substituted for Cu in this system and the compounds with $x > 0{\cdot}05$ do not show superconductivity down to 12 K. ^{151}Eu Mössbauer studies at 295 K show a single Mössbauer line in all the compounds (whether superconducting or not) with isomer shift value typical of Eu^{3+} ion. Further, the isomer shift values are nearly independent of x and the temperatures down to 10 K. These observations imply that the Cu–O network responsible for superconductivity is very weakly coupled to the Eu sublattice.

Keywords. Oxide superconductors; T_c suppression, ^{151}Eu Mössbauer.

1. Introduction

One of the most interesting aspects of $YBa_2Cu_3O_{7-y}$ high temperature superconductor is that the high transition temperature, T_c, is not affected even when Y is replaced by most of the moment-carrying rare earths (see for instance, Fisk *et al* 1987; Murphy *et al* 1987). This is generally attributed to the weak coupling between the rare earth moments and the superconducting electrons. However, the substitution at the Cu site by a transition metal ion, generally, reduces the T_c. One of the sharpest decrease in T_c is obtained by substitution of Zn at the Cu sites (Xiao *et al* 1987; Yong *et al* 1988). This implies that the electronic states of the Cu–O subsystem are strongly influenced by this substitution. It is of interest to study the effect of Zn substitution on the ^{151}Eu Mössbauer isomer shift values at different temperatures in $EuBa_2Cu_3O_{7-y}$ system. Further, europium ion can exist in two valence states, namely, divalent and trivalent; the former carries a large magnetic moment while the latter exhibits only Van Vleck paramagnetism and the isomer shift values are very different for the two valence states. We report here the results of electrical resistivity, magnetic susceptibility and ^{151}Eu Mössbauer measurements on several $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ compounds in which superconductivity is suppressed for values of $x \geqslant 0{\cdot}05$.

2. Experimental

The compounds, $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$, ($x = 0{\cdot}0, 0{\cdot}025, 0{\cdot}05, 0{\cdot}075$ and $0{\cdot}1$) were prepared by the standard ceramic technique of heating the stoichiometric amounts of the constituent oxides. Powder X-ray diffraction patterns were obtained at room

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temperature using CuK_α radiation. Superconducting transition temperatures were measured by the standard four-probe dc method by a computer-controlled system and a closed cycle refrigerator (12–300 K). ^{151}Eu Mössbauer measurements were carried out at temperatures of 10, 80 and 295 K inside a closed cycle refrigerator. Magnetic susceptibility was measured in the temperature range of 4·2–300 K using a set-up based on Faraday method.

3. Results and discussion

X-ray diffraction measurements on $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ compounds show that the orthorhombic structure of the parent $EuBa_2Cu_3O_{7-y}$ compound is preserved upto $x = 0{\cdot}075$. The lattice parameters change only marginally (table 1). However, in the compound with 10 at.% Zn at the Cu site, no orthorhombic distortion is observed and the X-ray patterns can be fitted to a tetragonal unit cell.

Figure 1 shows the temperature dependence of electrical resistance for $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ compounds. For $x = 0$, the sample shows metallic behaviour

Table 1. Lattice parameters and superconducting transition temperature, T_c, (corresponding to zero resistance) for the compounds $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$.

x	a(Å)	b(Å)	c(Å)	T_c(K)
0·0	3·844	3·899	11·70	88
0·025	3·848	3·901	11·71	27
0·05	3·853	3·904	11·70	–
0·075	3·858	3·902	11·71	–
0·1	3·888	3·888	11·67	–

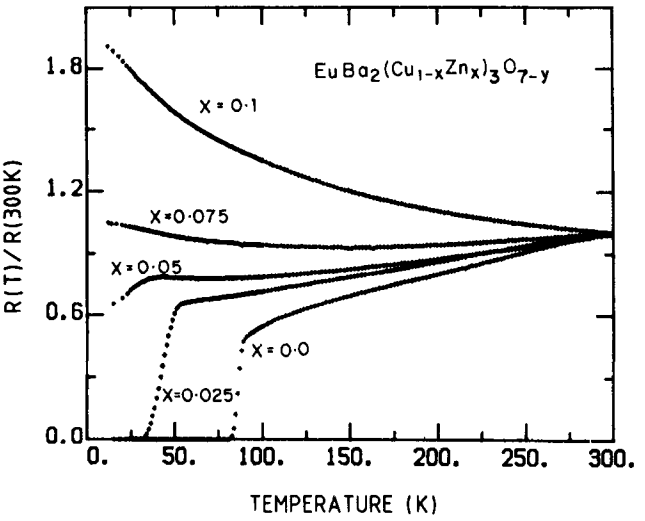

Figure 1. Resistance vs temperature for $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ compounds for various values of x.

with zero resistance at ~ 88 K. As x increases, superconducting transition temperature decreases. For the compound with $x = 0{\cdot}05$, the resistivity shows only a downward bent at 20 K, but does not go to zero down to 12 K. Thus, superconductivity is suppressed in $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ system for $x \geqslant 0{\cdot}05$. The present T_c values are in reasonable agreement with those reported earlier for the same system (Borges *et al* 1987).

The results of ^{151}Eu Mössbauer studies are shown in figures 2, 3 and 4. If the Zn substitution affects the valence state of europium or the *s*-electron density at the Eu site, it will be reflected in the isomer shift values since the isomer shift values for Eu resonance are quite sensitive to the charge state of europium. At room temperature, all the compounds show only a single line (figure 2) with isomer shift value of $(0{\cdot}8 \pm 0{\cdot}01$ mm/s), relative to $^{15}SmF_3$. This value of isomer shift is typical of trivalent Eu ions (Bauminger *et al* 1978). Figure 3 shows the spectra for the above samples at 10 K. The isomer shift values are nearly the same as the room temperature values, indicating no effect at low temperatures on the valence state of europium ions by Zn

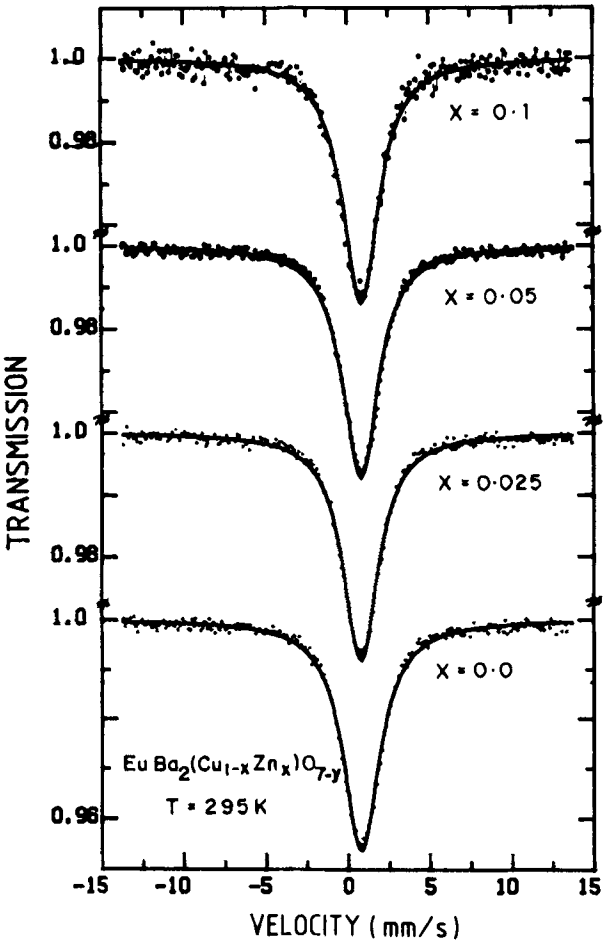

Figure 2. ^{151}Eu Mössbauer spectra at 295 K for $EuBa_2(Cu_{1-x}Zn_x)O_{7-y}$ compounds with $x = 0{\cdot}0, 0{\cdot}025, 0{\cdot}05$ and $0{\cdot}1$.

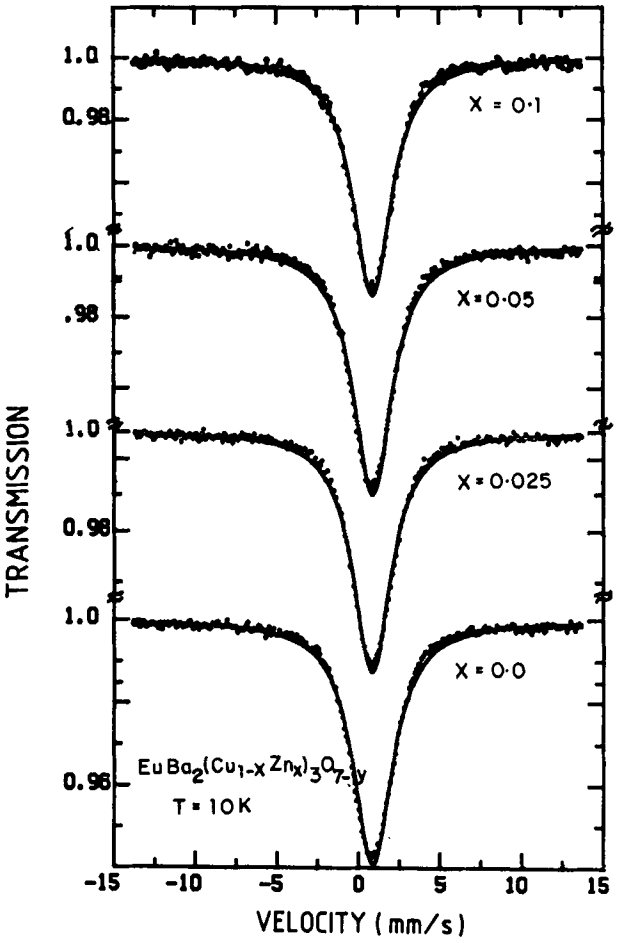

Figure 3. ^{151}Eu Mössbauer spectra in $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ compounds for $x = 0{\cdot}0$, 0·025, 0·05 and 0·1 at 10 K.

substitution. For $x = 0{\cdot}0$ and 0·025 samples, which exhibit superconductivity, the isomer shift does not show any distinct change across the superconducting transition, consistent with our earlier studies on undoped orthorhombic $EuBa_2Cu_3O_{7-y}$ compound. In fact, the isomer shift is found to be nearly temperature-independent down to 10 K in all the compounds (figure 4). However, a small line broadening is observed at low temperature in all the samples. Thus, the europium ions remain in the non-magnetic trivalent state in Zn-doped superconducting and non superconducting $EuBa_2Cu_3O_{7-y}$ samples. This is also confirmed by our susceptibility measurements which show that the susceptibility is typical of Eu^{3+} ions except for an upturn at very low temperatures.

In conclusion, we have investigated the effect of Zn substitution on the isomer shift values from ^{151}Eu Mössbauer studies in the system $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$ system. X-ray diffraction shows that orthorhombicity is destroyed only for the compound with 10 at.% of Zn. Mössbauer studies reveal no discernible change in the isomer shift values both with temperature and with Zn substitution. As mentioned earlier,

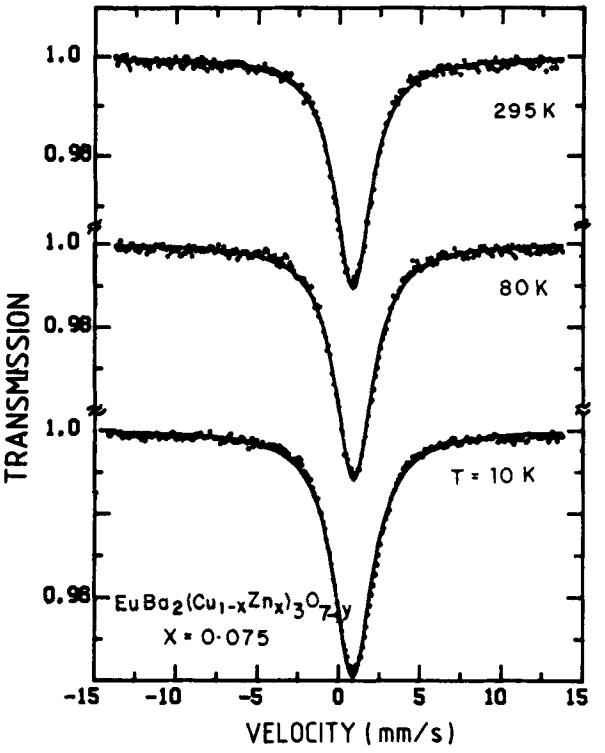

Figure 4. Temperature dependence of the ^{151}Eu Mössbauer spectra for $x = 0{\cdot}075$ in $EuBa_2(Cu_{1-x}Zn_x)_3O_{7-y}$.

the rare earth ions are decoupled from the Cu–O network. The present work again shows that even drastic changes at the Cu–O network (as inferred from large T_c suppression) have very little influence at the rare earth site consistent with the weak coupling between the two sublattices.

References

Bauminger E R, Kalvius G M and Nowik I 1978 in *Mössbauer isomer shift* (eds) G K Shenoy and F E Wagner (Amsterdam: North Holland) Ch. 10

Borges H A, Wells G L, Cheong S-W, Kwok R S, Thompson J D, Fisk Z and Oseroff S B 1987 in *LT 18 Conf. on superconductivity, Sendai, Japan*

Fisk Z, Thompson J D, Cheong S W, Aikin R M, Smith J L and Zirngaiebl 1987 *J. Magn. Magn. Mater.* **67** L139

Murphy D W, Sunshine S, Van Dover R B, Cava R J, Batlogg B, Zahurak S M and Schneemeyer L F 1987 *Phys. Rev. Lett.* **58** 1888

Tomy C V, Nagrajan R, Malik S K, Adroja D T, Soni N C and Ram Prasad 1987 *Solid State Commun.* **68** 531

Xiao G, Streitz F H, Gavrin A, Du Y W and Chien C L 1987 *Phys. Rev.* **B35** 8782

Yong Z, Han Z, Shifang S, Zhenpeng S, Zuyao C and Qirui Z 1988 *Solid State Commun.* **67** 33