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Resistive and magnetic properties of $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ and $Y_{1-2x}Zr_xEu_xBa_2Cu_3O_{7-\delta}$ superconductive compounds

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The results of X-rays, electrical resistivities and magnetic studies performed on $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ and $Y_{1-2x}Zr_xEu_xBa_2Cu_3O_{7-\delta}$ superconducting compounds, in the temperature range 4.2–500 K and external fields up to 50 kOe are reported. The presence of zirconium decreases the superconducting transition temperatures, T_c. Below T_c, the hysteresis loops narrow when the zirconium content increases. From the magnetization curves, the critical current densities were determined. A time dependence of the magnetizations of logarithmic form was found. The flux-pinning energy was estimated to be $U \simeq 0.03$ eV. Above the transition temperatures, $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ samples show a Pauli-type paramagnetism, while $Y_{1-2x}Zr_xEu_xBa_2Cu_3O_{7-\delta}$ compounds have, in addition, temperature-dependent contributions to the magnetic susceptibilities. The effective europium moments are $\sim 3.40\,\mu_B$ suggesting that the ion is in (+ 3) valence state.

1. Introduction

The effect of ZrO_2 addition on the resistive behaviour of $YBa_2Cu_3O_{7-\delta}$-based compounds has been reported previously. The partial replacement of yttrium and both yttrium and barium by zirconium results in the formation of a multiphase superconducting system. The substitution of copper by zirconium leads to a single superconducting phase [1].

In this paper we report the physical properties of $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ and $Y_{1-2x}Zr_xEu_xBa_2Cu_3O_{7-\delta}$ superconducting compounds where yttrium has been gradually replaced by zirconium or both zirconium and europium. The evolution of the superconducting transition temperatures, hysteresis loops, critical fields, critical current densities, as well as the magnetic behaviour above the transition temperatures, were investigated. Yttrium is in the (+ 3) valence state, while zirconium has a (+ 4) valence. Europium ions may be in both (+ 2) and (+ 3) valence states. Thus, it is also of interest to analyse to what extent the presence of zirconium ions will induce a valence state other than (+ 3), characteristic for europium in $EuBa_2Cu_3O_{7-\delta}$ compound [2].

2. Experimental procedure

The samples were prepared by solid state reaction. A mixture of Y_2O_3, EuO, CuO, ZrO_2 and barium carbonate in the required proportions, was homogenized, finely ground, and calcined in the temperature range 920–950 °C in an oxygen atmosphere. After calcination, the structure of the sample was checked by X-rays. The formation of perovskite-type structure is evinced in all cases. The calcined samples were finely ground and then compacted at a pressure of 3 t cm^{-2}. The calcination and sintering temperatures required to obtain the highest superconducting transition points decrease when yttrium is gradually replaced by (Eu + Zr). Sintering was performed in the temperature range 930–960 °C, in an oxygen atmosphere. The samples were then slowly cooled.

The densities of the sintered materials were 88–95% theoretical density. After keeping for 8 months in air, no degradation of sample properties was found.

The final X-ray analysis show the presence of the orthorhombic-type structure. In addition, small quantities of ZrO_2 were found for samples having an initial content greater than $x = 0.2$ (Fig. 1). The free ZrO_2 content was no more than 20% of the initial content, after both calcination and sintering processes.

Electrical resistivity measurements were made by using a standard four-probe technique, in the temperature range 77–300 K.

The magnetic studies were performed with Oxford Instruments equipment in the temperature range 4.2–300 K and external fields up to 50 kOe. For temperatures higher than 300 K, the magnetic susceptibilities were determined using a Faraday-type balance.

3. Results

The temperature dependence of the electrical resistivities for some representative compounds is plotted in Fig. 2. The zirconium addition somewhat decreases the superconducting transition temperatures, T_c, although these still remain higher than 84 K for $x = 0.2$.

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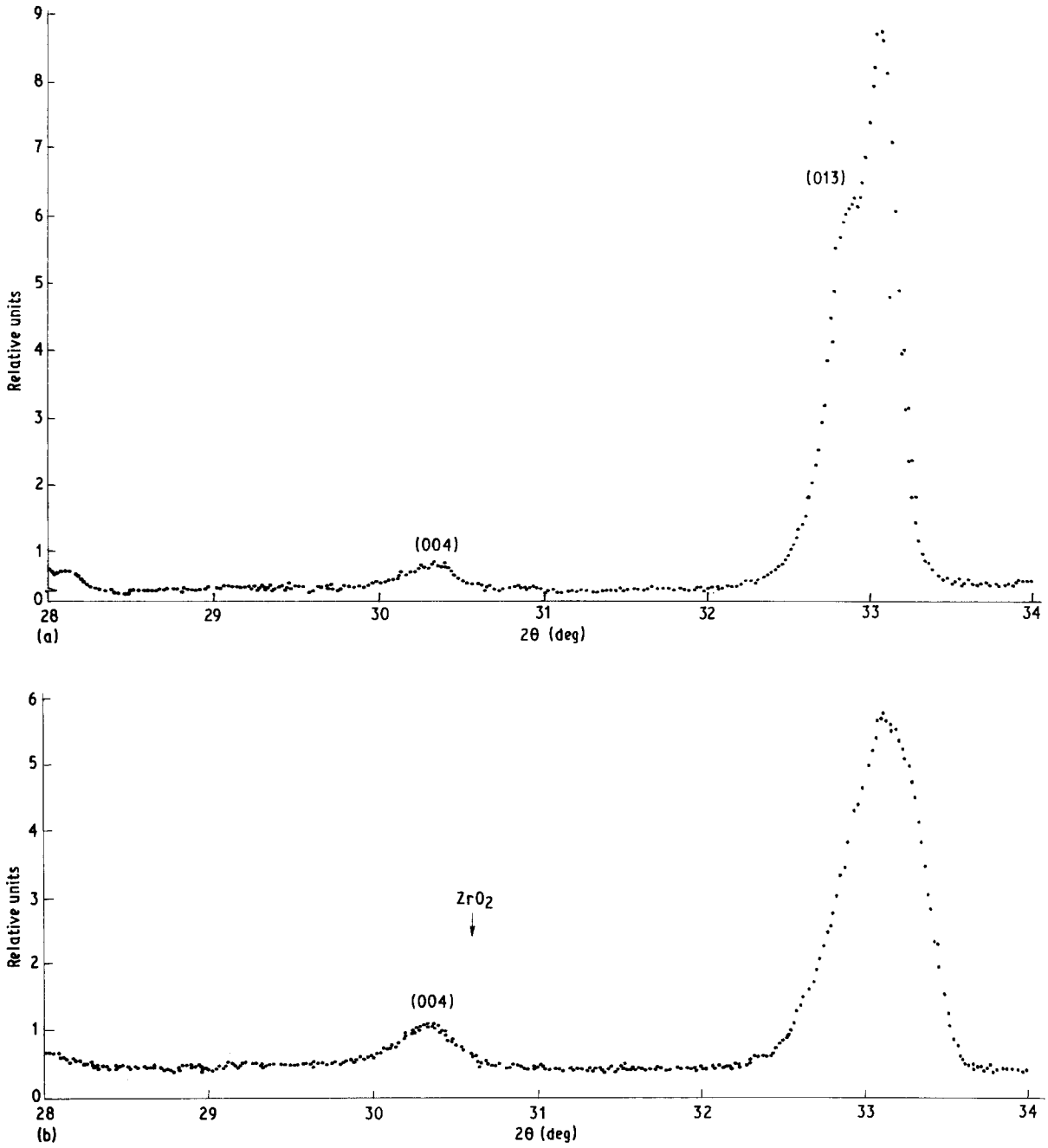

Figure 1 The X-ray patterns for $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ compounds with x = (a) 0.1 and (b) 0.2.

For the same initial zirconium content, the presence of europium increases the transition temperatures. As an example, in $Y_{0.6}Zr_{0.2}$ $Eu_{0.2}Ba_2Cu_3O_{7-\delta}$ compound, a value of $T_c \simeq 90$ K was determined.

The evolution with temperature of the hysteresis curves for $Y_{0.8}Zr_{0.1}Eu_{0.1}Ba_2Cu_3O_{7-\delta}$ compound is shown in Figs 3 and 4. As the temperature increases, the hysteresis loops narrow. Similar behaviour was found for other compounds. For the same zirconium content, the hysteresis loops are more constricted in samples without europium.

The field dependence of the magnetization at 4.2 K in a low external field is plotted in Fig. 5 for $Y_{0.7}$ $Zr_{0.3}Ba_2Cu_3O_{7-\delta}$ compound. Some "anomalies" in the magnetization curve can be observed. These suggest that two kinds of "material" coexist in the sample: superconducting grains and the boundary material between the grains. When $H < H_{c_1}^{w}$, where $H_{c_1}^{w} \simeq 10$ Oe for $Y_{0.7}Zr_{0.3}Ba_2Cu_3O_{7-\delta}$ compound, there is a shielding current around the surface of the whole sample, which is in the Meissner state. The magnetic penetration depth is the London penetration depth and the shielding currents result in a slope of magnetization which is greater than that obtained at higher fields. When $H = H_{c_1}^{w}$, where $H_{c_1}^{w}$ is the critical field for weak link granular superconductor [3], the magnetic flux begins to penetrate into the boundary material between the grains. Because of pinning, magnetic hysteresis appears (inset fig. 5) and the weak supercurrent around the whole sample exists inside all the magnetic penetration regions. For a field, $H_{c_2}^{w}$, the field of full penetration for a weak-link superconductor, the flux penetrates into the whole material situated between the grains. The $H_{c_2}^{w}$ field is identified in Fig. 5 by the upper field, characterizing the end of a small hysteresis loop.

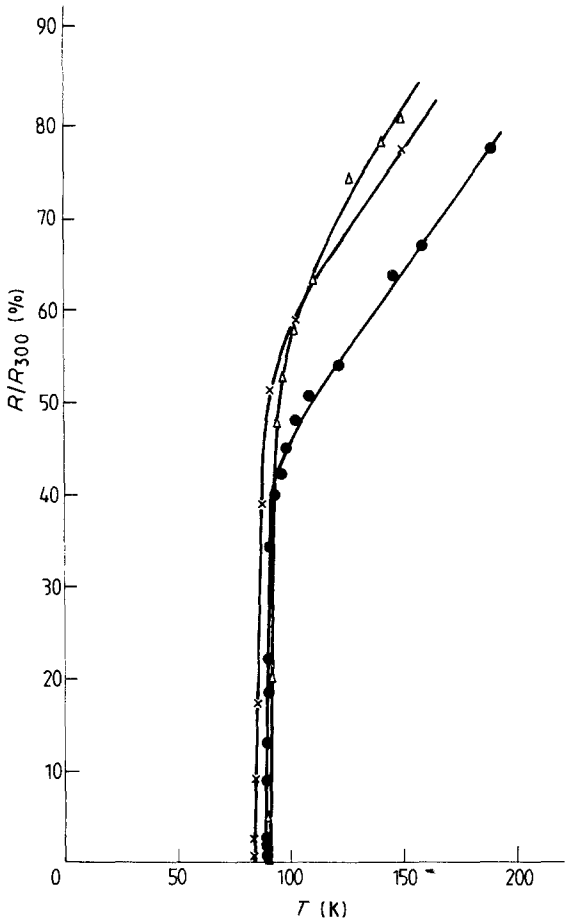

Figure 2 Temperature dependence of the electrical resistivities for some $YBa_2Cu_3O_{7-\delta}$-based compounds. (Δ) $YBa_2Cu_3O_{7-\delta}$, (x) $Y_{0.8}Zr_{0.2}Ba_2Cu_3O_{7-\delta}$, (●) $Yo_{0.6}Zr_{0.2}Eu_{0.2}Ba_2Cu_3O_{7-\delta}$.

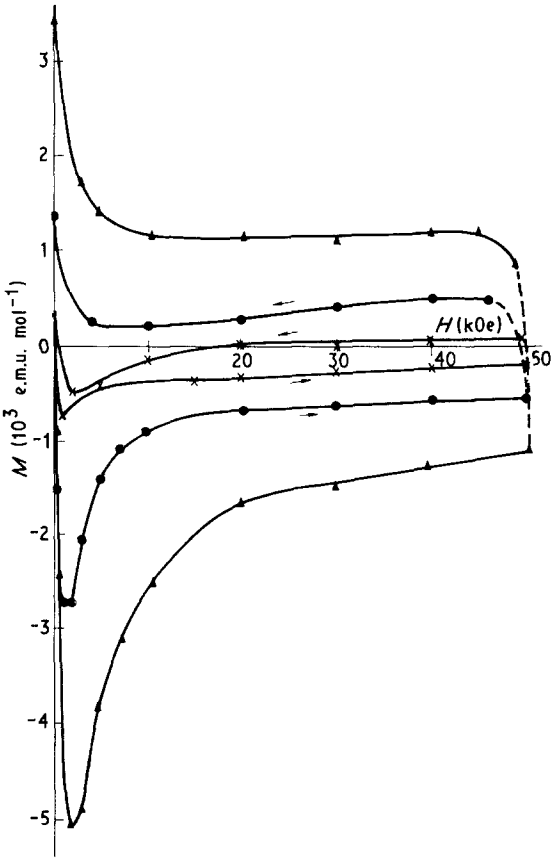

Figure 3 Magnetic hysteresis loops for $Y_{0.8}Zr_{0.1}Eu_{0.1}Ba_2Cu_3O_{7-\delta}$ at T = (▲) 9.64, (●) 19.4 and (×) 40.5 K.

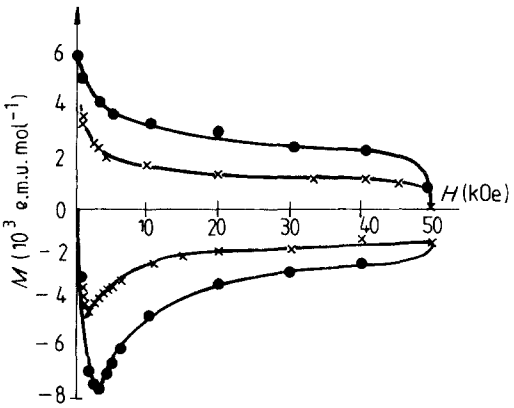

Figure 4 Magnetic hysteresis loops for (○) $Y_{0.8}Zr_{0.1}Eu_{0.1}Ba_2Cu_3O_{7-\delta}$ and (×) $Y_{0.8}Zr_{0.2}Ba_2Cu_3O_{7-\delta}$ compounds at T = 4.2 K.

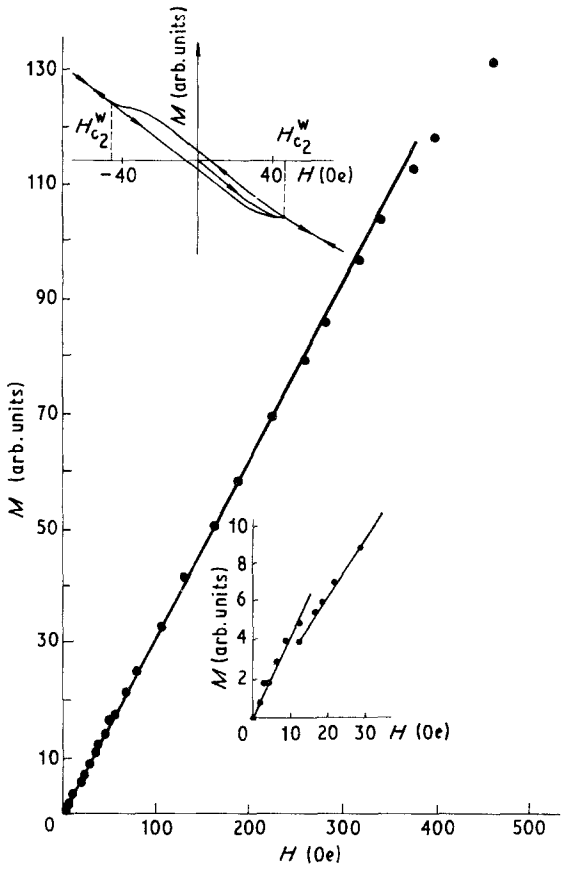

Figure 5 Field dependence of the magnetization, in low fields, at 4.2 K, for $Y_{0.7}Zr_{0.3}Ba_2Cu_3O_{7+\delta}$ compound.

The first critical field, H_{c_1}, of the superconducting grains is identified as the field where the $M(H)$ curve deviates from a linear behaviour (Fig. 5). For $Y_{0.7}Zr_{0.3}Ba_2Cu_3O_{7-\delta}$ compound a value H_{c_1} = 260 Oe was obtained at 4.2 K. The dependence of the H_{c_1} values, at 4.2 K, on the initial zirconium content is plotted in Fig. 6. The first critical field, H_{c_1}, decreases with increasing zirconium content.

From the magnetic hysteresis loops, the critical current density, $j_c(T, H)$, may be determined. According to the critical state model [4, 5], the $j_c(T, H)$ values within a grain of radius r are given by

$$j_c(T, H) = \frac{15}{r}[M_{\uparrow}(T, H) - M_{\downarrow}(T, H)] \quad (1)$$

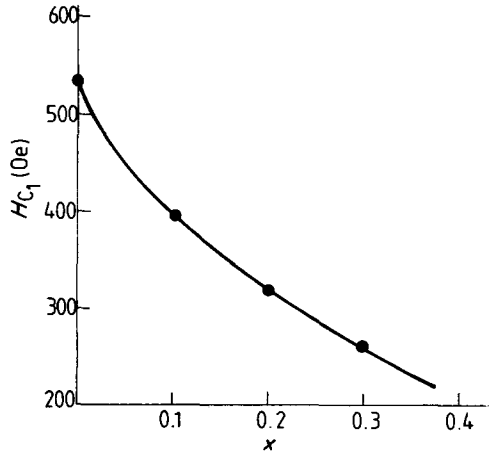

Figure 6 Composition dependence of the first critical field, H_{c_1}, at $T = 4.2$ K, for $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$.

where r is given in cm, the magnetizations, M, in e.m.u. cm^{-3} and $j_c(T, H)$ in A cm^{-2}. $M_\uparrow(T, H) - M_\downarrow(T, H)$ is the distance between the direct and returning branches of the magnetic cycle.

The mean values of the grain sizes were determined by electron microscope studies. Because of their distribution function, the grain size is typically known only within a factor of 10 [6]. Thus, the model should give accurate values within an order of magnitude, but should also exhibit the correct qualitative behaviour.

From Equation 1 we determined the critical current densities. As an example, Fig. 7 shows a plot of the temperature dependence of j_c determined from remanent magnetization for $Y_{0.8}Zr_{0.2}Ba_2Cu_3O_{7-\delta}$ compound. The critical current densities show an abrupt drop with temperature. In the temperature range 4.2–10 K, these decrease by nearly an order of magnitude. The composition dependences of j_c at 4.2 K, in $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ compounds decrease with increasing zirconium content (inset, Fig. 7).

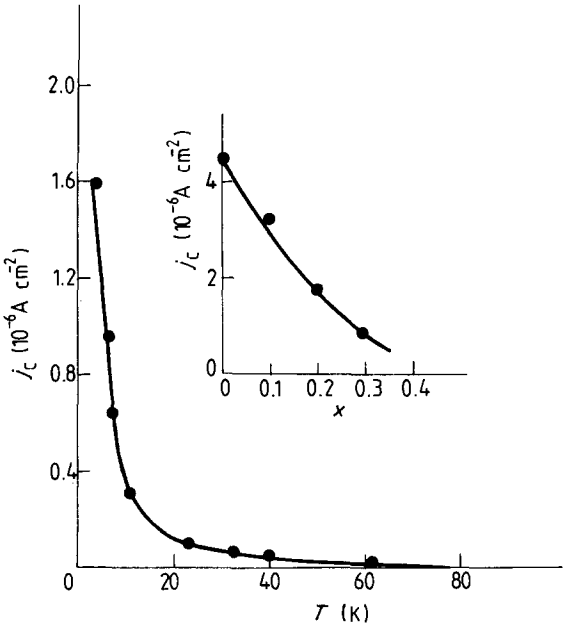

Figure 7 Temperature dependence of the critical current density for the $Y_{0.8}Zr_{0.2}Ba_2Cu_3O_{7-\delta}$ sample. Inset: the composition dependence of the critical current density, at $T = 4.2$ K, for $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ compounds.

The time dependences of the magnetizations in various external fields and temperatures were also analysed. Some data are plotted in Figs 8 and 9. After an initial period, the magnetizations show time dependences of a logarithmic form

$$M(T) = M_0(1 + S \ln t/t_0) \quad (2)$$

The classical flux creep model [7–10] was used to analyse the experimental data. The model considers a type II superconductor with a conventional Abrikosov vortex or flux line lattice. Inhomogeneities in the material cause pinning of these vortices in a potential valley of height U_0. Such pinning prevents motion of vortices in the presence of a current, thus controlling the critical current density, j_c. However, thermal activation of flux lines over the potential barrier induces magnetic relaxation and the reduction of critical current density [11]

$$j_c = j_{c_0}\left(1 - \frac{k_B T}{U_0} \ln t/t_0\right) \quad (3)$$

where j_{c_0} is the critical current in the absence of thermal fluctuations.

Taking into account the time dependence of magnetization, according to the Equation 3, we estimated the energy, U_0, for pinning of vortices. Typical values of $U_0 \simeq 0.03$ eV were obtained, which are close to that determined in $YBa_2Cu_3O_{7-\delta}$ single crystal, namely $U_0 = 0.02$ eV [11].

The field dependence of S values at 4.2 K, for $Y_{0.8}Zr_{0.2}Ba_2Cu_3O_{7-\delta}$ compound is plotted in Fig. 9a. In Fig. 9b, the temperature dependence of S values determined in $Y_{0.8}Zr_{0.1}Eu_{0.1}Ba_2Cu_3O_{7-\delta}$ compound, in a field of 6 kOe is shown. The S values increase up to $H \simeq 15$ kOe and then decrease [12]. A similar behaviour was observed for their temperature dependence where a maximum is suggested for $T \simeq 12$–15 K. In the region of $H < 15$ kOe, the data do not seem to follow a dependence of the form H^3, as found in a $YBa_2Cu_3O_{7-\delta}$ single crystal [13].

Above the transition temperature, T_c, the $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ compounds show a Pauli-type paramagnetism. For example, the susceptibility, χ, for the sample with $x = 0.1$ is 0.48×10^{-6} e.m.u. g^{-1}, and for the compound with $x = 0.2$, a value $\chi_0 = 0.87 \times 10^{-6}$ e.m.u g^{-1} was determined.

For $Y_{1-2x}Zr_xEu_xBa_2Cu_3O_{7-\delta}$ compounds, in addition to a Pauli paramagnetic contribution, χ_0, a temperature-dependent term is also present (Fig. 10). The thermal variations of susceptibilities may be described by the relation

$$\chi = \chi_0 + C(T - \theta)^{-1} \quad (4)$$

By fitting the experimental data according to the Equation 4, χ_0, C and θ were determined. The paramagnetic Curie temperatures, θ, are negative and smaller (in absolute magnitude) than 5 K. The temperature-independent contributions, χ_0, are close to the susceptibilities obtained in the corresponding $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ samples. From the Curie constants, C, the effective europium moments were determined. These values are around 3.40 μ_B, suggesting

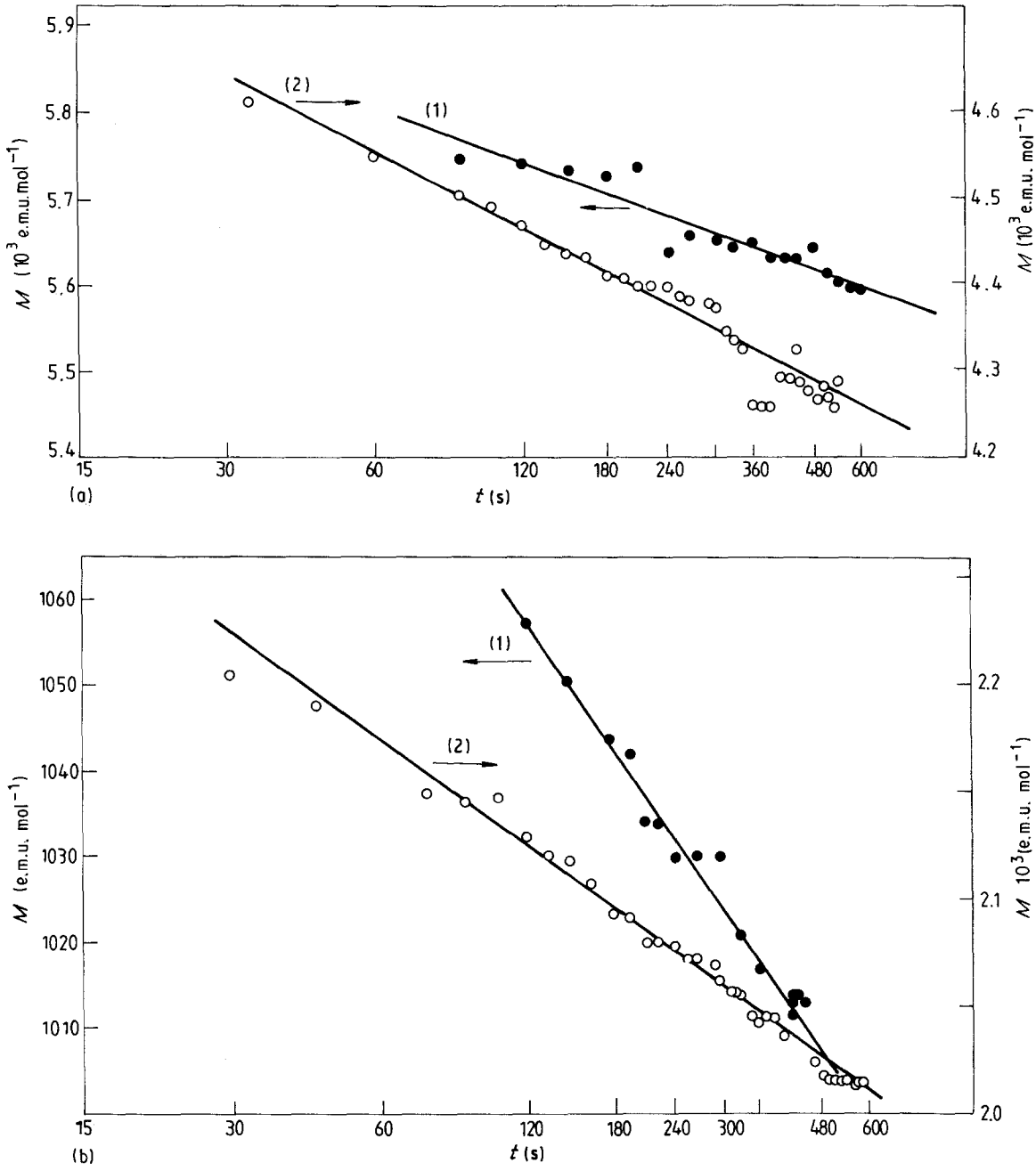

Figure 8 Time dependences of the magnetization for $Y_{0.8}Zr_{0.1}Eu_{0.1}Ba_2Cu_3O_{7-\delta}$ (a) at 4.2 K in various external fields: (1) $H = 6$kOe, (2) $H = 10$ kOe; and (b) fields: at different temperatures: (1) $H = 6$kOe, $T = 19.4$ K; (2) $H = 30$ kOe, $T = 4.2$ K.

that the europium ions are in the (+ 3) valence state. Thus the presence of Zr^{4+} ions, in addition to the europium ones, in perovskite-type structure do not seem to change the (+ 3) valence state of europium, as expected in the case of a change compensation mechanism involving europium ions.

4. Discussion

The presence of zirconium somewhat decreases the superconducting transition temperatures of $Y_{1-x}Zr_x Ba_2Cu_3O_{7-\delta}$-based materials. This decrease is partially recovered when yttrium is substituted by both zirconium and europium. A complex behaviour is found by magnetic measurements. This is a direct consequence of a hightly inhomogeneous distribution of the critical current densities within the sample. The critical currents depend on the local metallurgical defects, the most common being the barriers between the grains (weak superconducting links) and the surface of the grains. Thus, in addition to the familiar first critical field, H_{c_1}, two further characteristic fields were identified, at low external fields.

From the magnetization loops, the temperature and field dependences of the critical current densities were determined. The magnetizations show a time dependence of the logarithmic form. The experimental data were analysed in the classical flux creep model. The energy for flux pinning is of the order $U_0 \simeq 0.03$ eV. The magnetic creep constants, S, are dependent on temperature and field.

At temperatures greater than the transition points, the $Y_{1-x}Zr_xBa_2Cu_3O_{7-\delta}$ compounds are Pauli paramagnets. The europium addition leads to a temperature-dependent contribution to the susceptibilities. From the determined effective moments it is concluded that the europium is in the (+ 3) valence state.

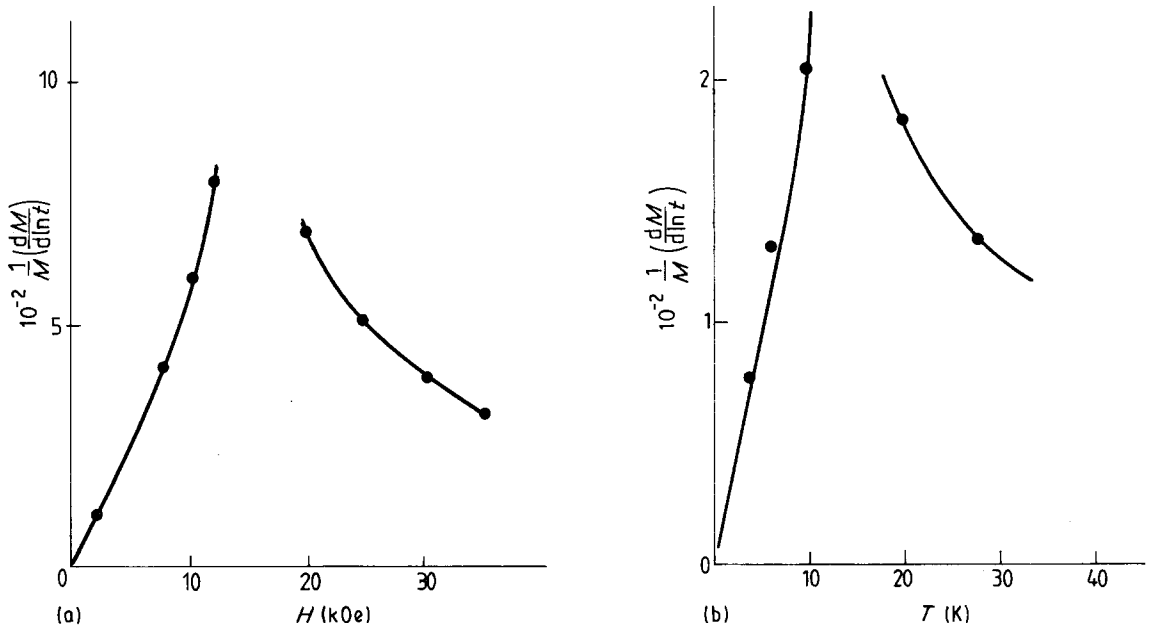

Figure 9 (a) The field dependence of the S values, at 4.2 K, for $Y_{0.8}Zr_{0.2}Ba_2Cu_3O_{7-\delta}$ compound, and (b) the temperature dependence of the S values for $Y_{0.8}Zr_{0.1}Eu_{0.1}Ba_2Cu_3O_{7-\delta}$, in an external field $H = 6$ kOe.

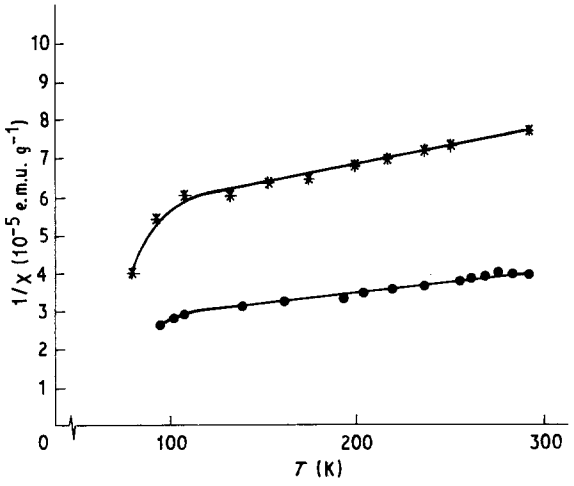

Figure 10 Thermal variations of reciprocal susceptibilities at $T > T_c$, in $Y_{1-2x}Zr_xEu_xBa_2Cu_3O_{7-\delta}$ compounds with $x = (*)$ 0.1 and (●) 0.2.

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