ANL/PPRNT--89-186

DE90 002998

SOLUBILITY AND SUPERCONDUCTIVITY IN $RE(Ba_{2-x}RE_x)Cu_3O_{7+\delta}$ (RE = Nd, Sm, Eu, Gd, Dy)*

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October 1987

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*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under Contract #W-31-109-ENG-38.

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Solubility and Superconductivity in RE($Ba_{2-x}RE_x$)$Cu_3O_{7+\delta}$ Systems (RE=Nd,Sm,Eu,Gd,Dy)

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International Classification for Physics # 7410
Superconductivity: occurrence, critical temperature

Abstract

Solid solutions of RE(Ba_{2-x} RE_x)$Cu_3O_{7-\delta}$ (RE=Nd,Sm,Eu,Gd,Dy) for x=0 to x=0.5 have been investigated. X-ray and resistivity measurements show that there exists a solid solution region, through which, the structure changes from orthorhombic to tetragonal and the superconducting properties are depressed. The solubility limits depend strongly on the size of the rare-earth ion, with the smallest (Dy) showing no appreciable solubility. The superconducting transition temperature versus x for all of the rare-earth ion substitutions falls on a universal curve, indicating that the Ba sites are extremely ionic and magnetically isolated.

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Shortly after the discovery and isolation of the 90K superconductor, $YBa_2Cu_3O_{7-\delta}$ [1-13] several papers appeared in which the Y was fully substituted by most of the rare-earth elements. Unlike previously studied superconducting materials, the presence of magnetic ions was not found to significantly alter the superconducting transition temperature, T_c [14-16]. Mossbauer studies on $GdBa_2Cu_3O_{7-\delta}$ showed that the rare-earth site could be considered strongly ionic and magnetically isolated from the rest of the crystal structure [17]. This is further proven by the results showing that the Neel temperature for the Gd sublattice in both orthorhombic and tetragonal structures is the same [18]. Among the trivalent rare-earths, La was found to be the most difficult to substitute for Y, generally resulting in multiphase samples and lower T_c's [12]. Subsequently, it was discovered that La was in fact partially substituting for Ba, giving a solid solution of the form $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ with a range $0.25 \leq x \leq 0.5$ [19,20].

The present work was motivated by the question of whether other large rare-earth ions could be substituted for Ba, effecting changes in T_c. Our results indicate that the ability of a rare-earth ion to substitute onto the Ba site depends only on its size and that such substitutions of a 3^+ (RE) ion for a 2^+ (Ba) ion result in changes in the electronic and structural properties of the compound, independent of the particular rare earth ion.

Between five and seven samples in the series $RE(Ba_{2-x}RE_x)Cu_3O_{7+\delta}$ were synthesized for each of the rare earths, Nd, Sm, Eu, Gd, Dy. The samples were prepared by mixing and grinding RE_2O_3, $BaCO_3$ and CuO powders in the correct metal stoichiometries and firing at 975°C under flowing oxygen. All the samples were then reground and refired several times in order to improve homogeneity. A final annealing at 500°C in flowing O_2 followed by furnace cooling to room temperature was important in obtaining the superconducting samples. X-ray diffraction data was obtained with a GE-XRD5 diffractometer using Cu K_α radiation with wavelength $\lambda = 1.5418$ Å, resistivities as a function of temperature were obtained in a closed-cycle refrigerator by the standard four-probe technique using Si diode thermometry traceable to NBS standards and accurate to about 0.5 K over the measured temperature range.

It should be noted that both solid solubility limits and superconducting transition temperatures presented here, are characteristic of the preparation conditions employed in this study. We have frequently observed noticeable variation of T_c as a function of x even for minor changes in firing temperature, cooling rate and annealing temperature. Since no systematic study was performed to optimize the firing procedure for each rare earth separately, we consistently used one firing scheme for all rare earths. Under these conditions, it was somewhat difficult to obtain good superconducting samples for Nd, Sm and, in particular La, which was the subject of our previous study [20].

Careful x-ray diffraction data have been taken for all five series in order to determine the solubility boundaries for the various rare earths. Figure 1 shows x-ray data for four representative Nd-substituted samples (x=0, 0.1, 0.2, 0.5). It can be seen that the stoichiometric $NdBa_2Cu_3O_{7-\delta}$ superconducting phase does not form under our preparation conditions, since the x=0 sample contains a small amount of $BaCuO_2$ besides the main 1:2:3 phase. Thus, the Nd is substituting on both Y and Ba sites, just as was found in the La system [20]. As x is increased, the characteristic orthorhombic splitting of the (020), (200) and (006) reflections at $2\theta \approx 47°$ becomes smaller and vanishes at x=0.2 within the resolution of the diffractometer. The lattice parameters for the Nd series are shown in Figure 2 as a function of x. These data were obtained by a least squares fit of the peak positions from the x-ray scans with an orthorhombic cell across the entire range ($0 \leq x \leq 0.5$). As x is increased, the b- and c- axes decrease monotonically, while the a-axis increases until it merges with the b-axis at $x \approx 0.2$. This collapse to an apparently tetragonal structure is a common feature in all of the series investigated here. It should be noted that our previous neutron diffraction study of the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ system, there was evidence for a slight orthorhombic distortion even when the lattice constants had collapsed [20].

Figure 3 presents the solid solution region for La [20] and the 5 systems reported here as a function of rare earth ionic radius. For the larger ions (La, Nd, Sm) the single phase region extends all the way to x=0.5. Values of x>0.5 have not been tried, but may indeed exist for these ions. For both La and Nd, the solid solution limits do not extend to the stoichiometric 1:2:3 composition. As the rare earth ion becomes smaller, the 1:2:3 compound is easily obtained and the maximum value of x for which there still exists a single phase becomes smaller until the solubility region collapses to a single point for Dy. Because Y is slightly smaller than Dy, we expect virtually no solubility region to exist and we have indeed confirmed this experimentally.

Figure 4 shows the superconducting transition temperatures as a function of x for all 5 systems investigated as well as La [20]. The error bars indicate the 90% and 10% points of the resistive transition. It is evident that for those rare earth ions which can substitute onto the Ba site, the T_c decreases as a function of x along a more-or-less universal curve. The Dy system, in which we observed no solid solubility by x-ray diffraction shows a distinctly different curve, with T_c remaining constant for all the samples, indicating the presence of only the stoichiometric 1:2:3 compound with Dy_2BaCuO_5 and CuO for those samples with $x>0$. For Gd and La, the T_c data deviates at $x\geq0.3$ and $x\leq0.2$ respectively, consistent with the solubility limits found by x-ray and neutron diffraction. When the individual resistivities as functions of temperature are examined across a particular series, it is seen that as x increases, the sample behaves more and more like a semiconductor, an effect already reported in the $La(Ba_{2-x}La_x)Cu_3O_{7+\delta}$ system [19,20].

The existence of a solid solubility regime for the $RE(Ba_{2-x}RE_x)Cu_3O_{7+\delta}$ systems can be easily explained by an ionic size argument. The lower bound of the solubility limit is controlled by whether the rare earth is small enough to comfortably substitute for the Y. The upper bound, on the other hand, extends to larger x only if the rare earth is large enough to fit in the Ba site. Thus,while it is difficult to obtain the stoichiometric 1:2:3 phase for the largest rare earths, La and Nd, it is entirely possible that the single phase solubility limit for these ions and Sm could extend to compositions $x>0.5$. This dependence on ionic size might also explain the difficulties in obtaining the stoichiometric 1:2:3 phase with Yb and Lu, the smallest of the rare earth ions. In neutron diffraction studies on the La system [20], the presence of La on the Ba site disorders the one-dimensional Cu-O chains which are present in the parent $YBa_2Cu_3O_{7-\delta}$

compound. This disordering was found to correlate well with the depression of the superconducting transition temperature [20]. In these systems we expect that the same effect is occurring and neutron diffraction experiments on the Nd and Eu series, which have broader solubility regions, are currently underway to further study this effect. The remarkable feature is that there exists a universal curve for T_c as a function of x, showing that magnetic moments on the Ba site have no noticeable effect on the superconductivity. This along with a similar result for the Y site [17], shows that both sites are extremely ionic and isolated from the conduction electrons which exist in the Cu-O layers.

The authors wish to thank R. Marasas for collecting some of the x-ray data. This work was supported by the U.S. Department of Energy BES-Materials Science under contract #W-31-109-ENG-38.

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Figure Captions

1. Powder x-ray diffraction data for four samples in the $Nd(Ba_{2-x}Nd_x)Cu_3O_{7+\delta}$ system. The presence of $BaCuO_2$ in the $x=0$ sample is indicated by characteristic peaks near $2\theta=29°$.

2. Orthorhombic lattice parameters a (■), b (-) and c (○) for the $Nd(Ba_{2-x}Nd_x)Cu_3O_{7+\delta}$ system as a function of x. The error bars for the $x=0$ data are representative of the error in measurement over the entire series. The lines are drawn as a guide to the eye.

3. Solid solubility regions for the $RE(Ba_{2-x}RE_x)Cu_3O_{7+\delta}$ systems with RE=La,Nd,Sm,Eu,Gd and Dy. The solid lines indicate the region in which a single phase is observed, while the dashed lines indicate the possible extension of the single phase into regions not studied.

4. Superconducting transition temperature (as measured resistively) as a function of x for the systems $RE(Ba_{2-x}RE_x)Cu_3O_{7+\delta}$ with RE=La,Nd,Sm,Eu,Gd and Dy. The error bars indicate the 90% and 10% points of the transition. Note deviations from universal behavior for La (○), Gd(-) and Dy (○), indicating the end of their solubility regions.

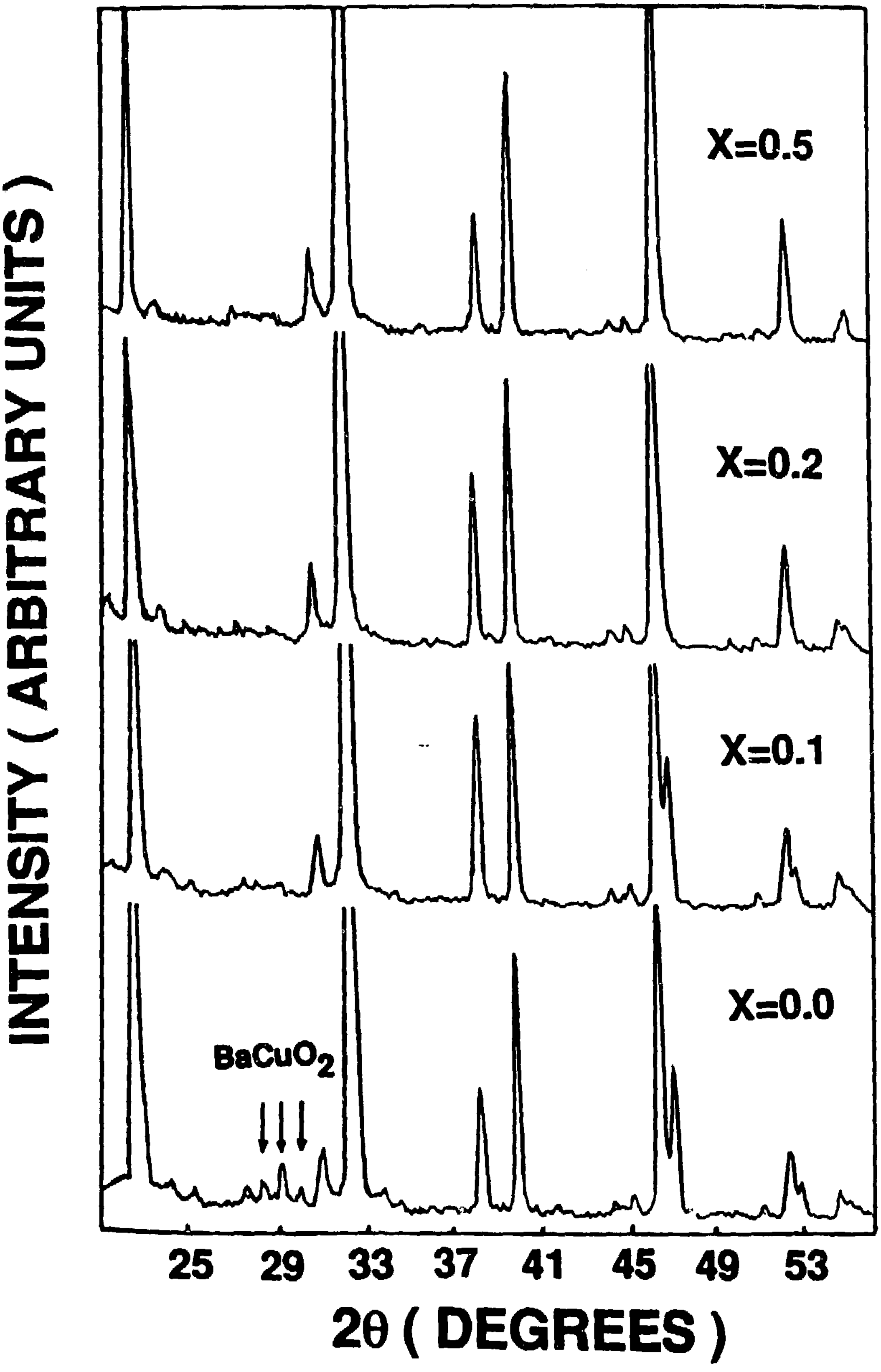
INTENSITY (ARBITRARY UNITS)
X=0.5
X=0.2
X=0.1
X=0.0
BaCuO$_2$
25
29
33
37
41
45
49
53
2θ (DEGREES)

Fig. 1

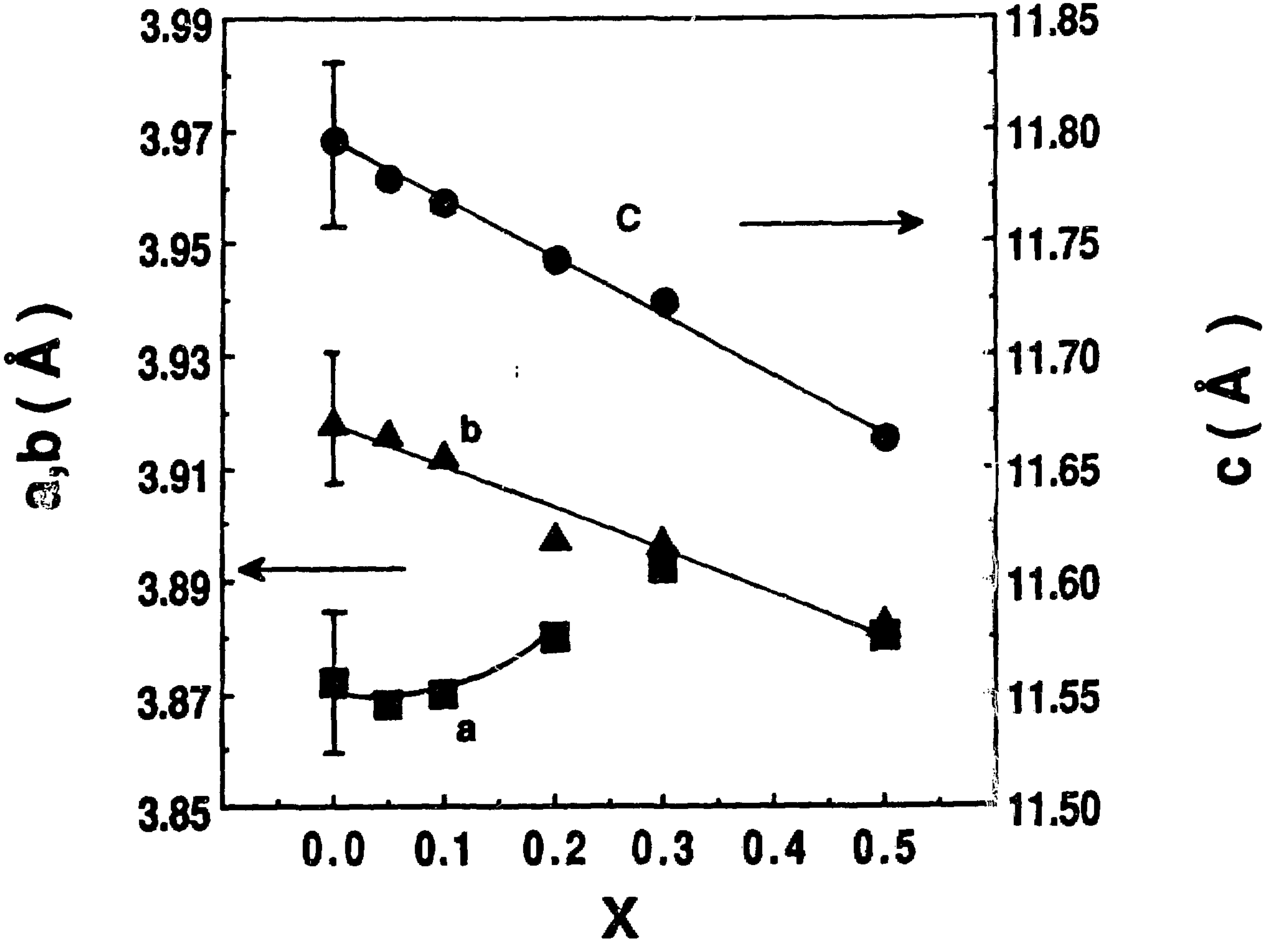
3.99
3.97
3.95
3.93
3.91
3.89
3.87
3.85
a,b (Å)
11.85
11.80
11.75
11.70
11.65
11.60
11.55
11.50
c (Å)
c
b
a
0.0
0.1
0.2
0.3
0.4
0.5
X

Fig. 2

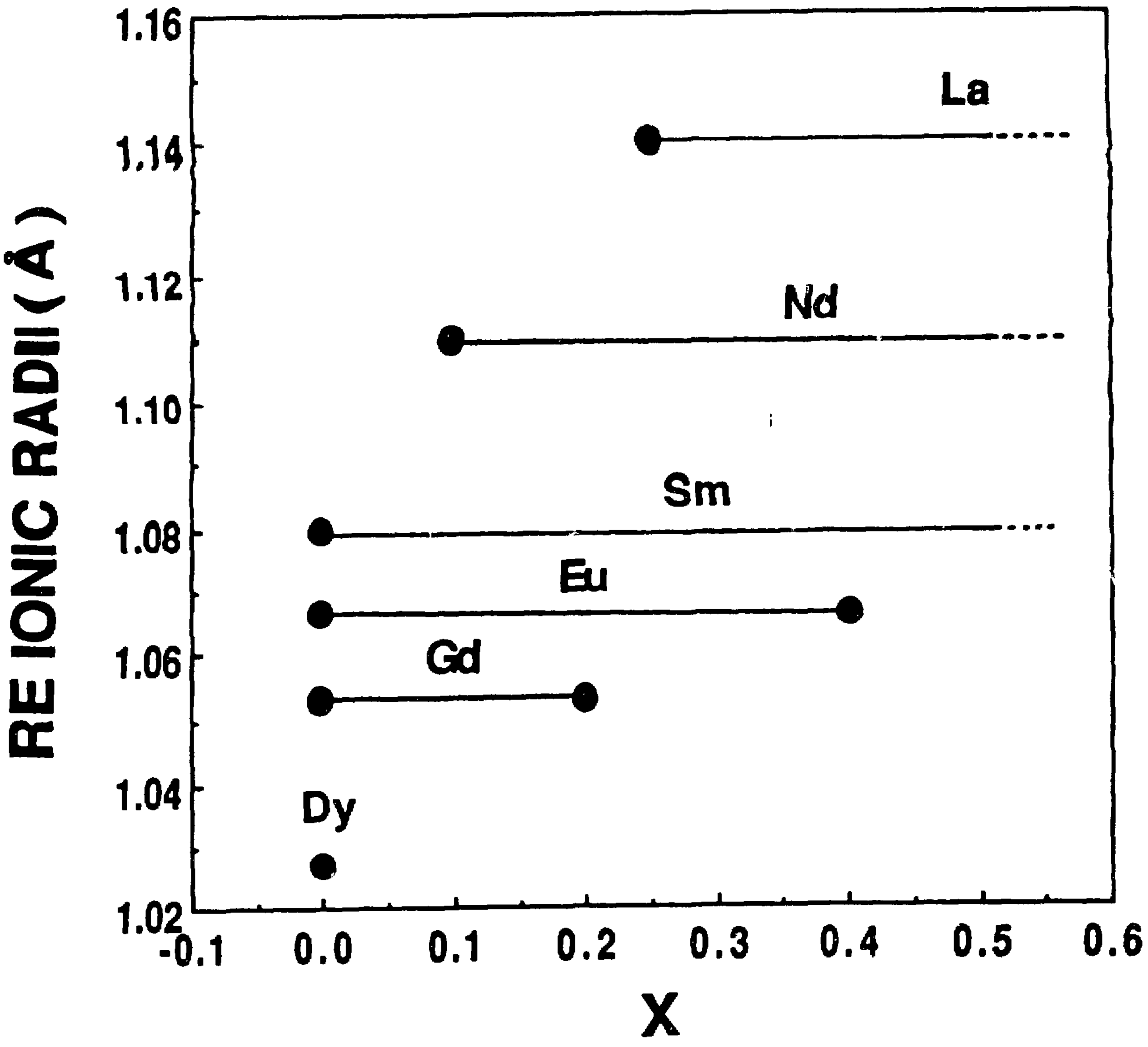
RE IONIC RADII (Å)
1.16
1.14
1.12
1.10
1.08
1.06
1.04
1.02
-0.1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
X
La
Nd
Sm
Eu
Gd
Dy

Fig. 3

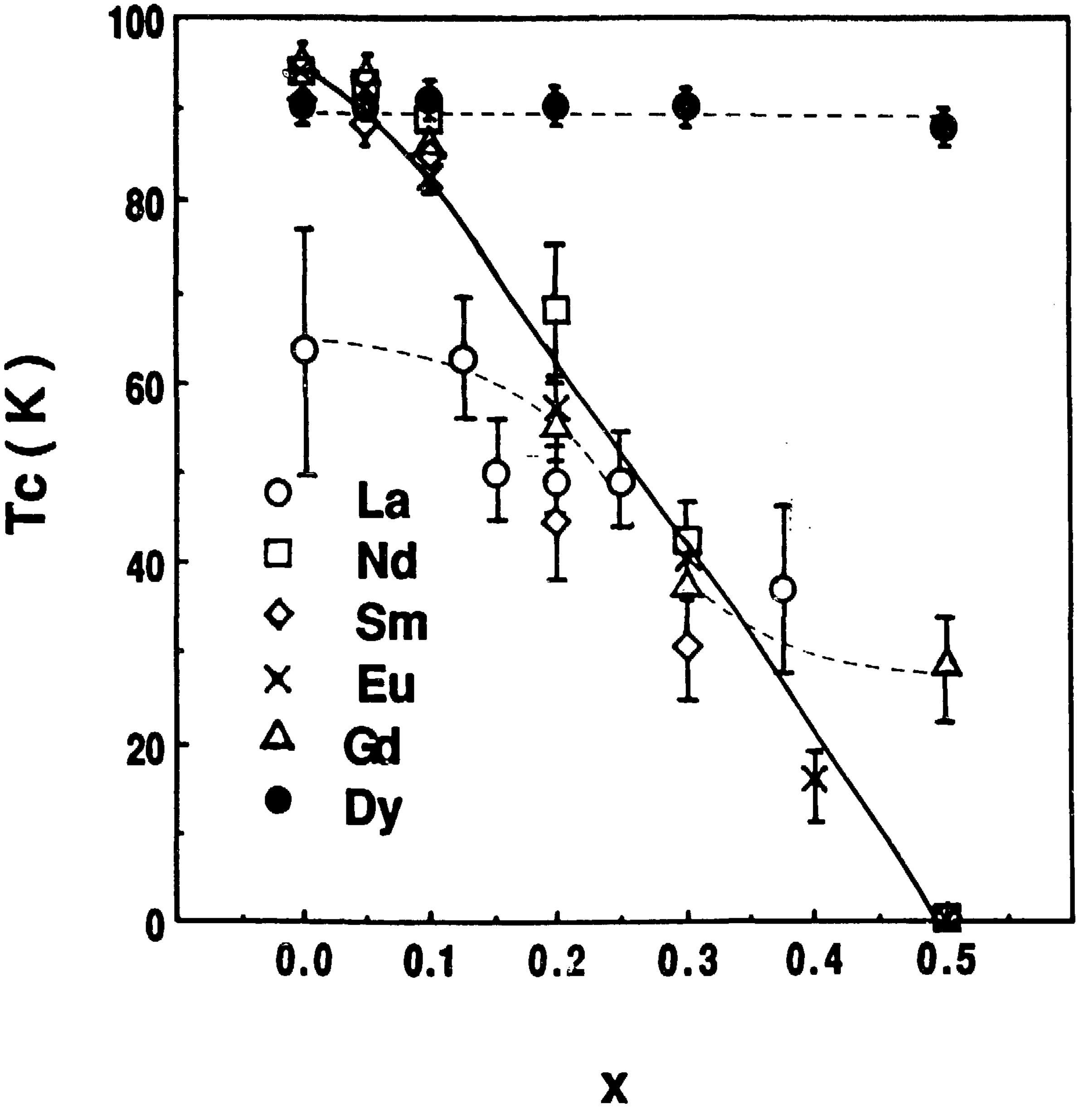

Fig. 4