Rare earth ion size effect on the physical properties of the doped $RBa_2Cu_3O_{7-y}$ superconductor systems

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ABSTRACT

A review of the detailed systematic studies of the rare-earth ion size effect on the crystal structure, resistivity ρ, susceptibility χ , specific heat c_p, antiferromagnetic (AFM) transition temperature T_N, and superconducting T_c of doped $RBa_2Cu_3O_{7-y}$ systems, where R stands for the rare-earth ions, is presented.

Key words: perovskite superconductors; insulator-superconductor transition; rare-earth ion size effect

1. INTRODUCTION

High-T_c superconductor (HTSC) $YBa_2Cu_3O_{7-y}$ has a triplicate perovskite structure with oxygen-deficiency and lattice-distortion. The substitution with rare earth elements (R) on the Y site and with transition or sp elements on the Cu site of HTSC $RBa_2Cu_3O_{7-y}$ is an important method for understanding the mechanism of the occurrence of superconductivity at high temperatures. In this paper we review the rare-earth ion size effect on the various physical properties of Pr-doped (on the R-site) $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems [1-3], Ga-doped (on Cu(1)-site of the Cu-O chain) $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems [4], and Zn-doped (on the Cu(2)-site of the Cu-O_2 plane) $RBa_2Cu_{3-x}Zn_xO_{7-y}$ systems [5].

1) A detailed study of Pr-doping at the R-site in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems (R=Lu, Yb, Tm, Er, Y, Ho, Dy, Gd, Eu, Sm and Nd) for x=0.5, 0.6, 0.7, 0.8, 0.9, and 1.0 shows that the temperature dependence of susceptibility χ follows the Curie-Weiss law in the range of 20-300 K and the paramagnetisms of Pr- and R-sublattice exist largely independently of one another. The AFM ordering temperature T_N of Pr ions in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems decreases monotonically with increasing R concentration (1-x). At a given x, T_N is R ion-size dependent. The slope in the T_N vs x curve is steeper for ion with smaller ionic radius. The observed results were interpreted in terms of the hybridization between the local states of Pr ion and the valence band states of the CuO_2 planes [1-3].

2) The investigation of Ga-doping at the Cu(1)-site in $RBa_2Cu_{3-x}Ga_xO_{7-y}$ (R=Yb, Er, Y, Dy, Gd, Eu and Nd, and x=0, 0.05, 0.1, 0.15, 0.2 and 0.3) systems shows that the melting point, the critical Ga concentration x_{O-T} (at which the samples undergo a phase transition from orthorhombic to tetragonal), the superconducting T_c, and the normal state resistivity ρ_n, are rare earth ion size dependent. It is suggested that the decrease of density of states $N(E_F)$ or localization of carriers due to Ga substitution are the possible mechanisms for suppression superconductivity. The Mott transition could be helpful for interpreting the superconducting-nonsuperconducting transition accompanied by a transition into semiconducting phase in these systems [4].

3) A systematic study of Zn-doping on the resistivity ρ, susceptibility χ and superconducting T_c of $RBa_2Cu_{3-x}Zn_xO_{7-y}$ systems (R=Yb, Er, Y, Dy, Gd, Eu, Sm, and Nd, and $0 \le x \le 0.3$) is reported. Doping with Zn on the Cu(2)-site in these systems causes a rapid nearly linear decrease of T_c as Zn content increases. The reduction of T_c for $RBa_2Cu_{3-x}Zn_xO_{7-y}$ is found to depend strongly on the ionic radius of the rare earth element R. The suppression of superconductivity by zinc and the rare earth ion size effect on T_c in these systems is interpreted in terms of a Mott spin bipolaron model[5].

2. Pr DOPING ON THE R-SITE IN $R_{1-x}Pr_xBa_2Cu_3O_{7-y}$

$PrBa_2Cu_3O_{7-y}$ is an exception among rare-earth substituted isomorphic $YBa_2Cu_3O_{7-y}$ compounds, which are all 90K-class superconductors. $PrBa_2Cu_3O_{7-y}$ is non-superconductor and insulator. Furthermore, specific heat and magnetization measurements of $PrBa_2Cu_3O_{7-y}$ showed an anomalous magnetic ordering at T_N=17K. Neutron diffraction and Mossbauer spectroscopy experiments suggest that this ordering is a simple three-dimensional commensure antiferromagnetic order in the Pr sublattice with a small value of the Pr magnetic moment (0.74 μ_B) in the ordering state. This T_N value (Neel temperature) is rather high with respect to that expected from dipole-dipole interactions or based on RKKY scaling of T_N in the other members of the $RBa_2Cu_3O_{7-y}$ (for example, R=Gd). Besides, the value of the Sommerfeld constant, g, determined from specific heat measurements is too high (94 or 265 mJ/mole-K^2), which is comparable to those of the heavy-fermion systems.

The quenching of superconductivity and the anomalous magnetic ordering in $PrBa_2Cu_3O_{7-y}$ have been puzzling aspects of the physics of this compound. This has simulated research efforts in understanding these anomalies. One approach in understanding these striking properties of $PrBa_2Cu_3O_{7-y}$ is to study the effect of Pr doping in $RBa_2Cu_3O_{7-y}$ compounds.

It is found that as Pr concentration, x, in a $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ system increases, its superconducting transition temperature, T_c, is depressed. At a critical Pr concentration, x_{cr}, the superconductivity is quenched[1], beyond which the system becomes insulating and displays magnetic ordering of both the Pr and Cu sublattices[1,2]. Thus, the $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ system can exhibit either superconductivity ($x<x_{cr}$) or AFM ordering of the Pr ions ($x>x_{cr}$); a coexistence of both remains controversial in these systems. It has been noted that T_c at a given Pr concentration in the $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems decreases approximately linearly with increasing radius of the R ions[1]; this also holds true for x_{cr}[1].

The suppression of T_c has been attributed to two possible mechanisms: the Abrikosov-Gor'kov (AG) pair-breaking or hole localization/filling, both due to hybridization of the Pr ion with the sandwiching CuO_2 planes. A proposed theoretical model for the electronic structure of $PrBa_2Cu_3O_7$ suggested that the difference between $PrBa_2Cu_3O_7$ and other $RBa_2Cu_3O_7$ superconductors comes from an enhanced stability of the Pr^{IV} state due to the hybridization with oxygen neighbors, and involves a transfer of holes from primarily planar $O2p_\sigma$ to $O2p_\pi$ states.

In parallel with work on the behavior of the $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems in the superconducting regime ($x<x_{cr}$), magnetic ordering temperature, T_N, of the Pr ion in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems has been determined from heat capacity[3] and magnetization measurements[2]. All the results suggest that T_N decreases monotonically with increasing content of R ions (1-x), from x=1.0 to x_{cr}.

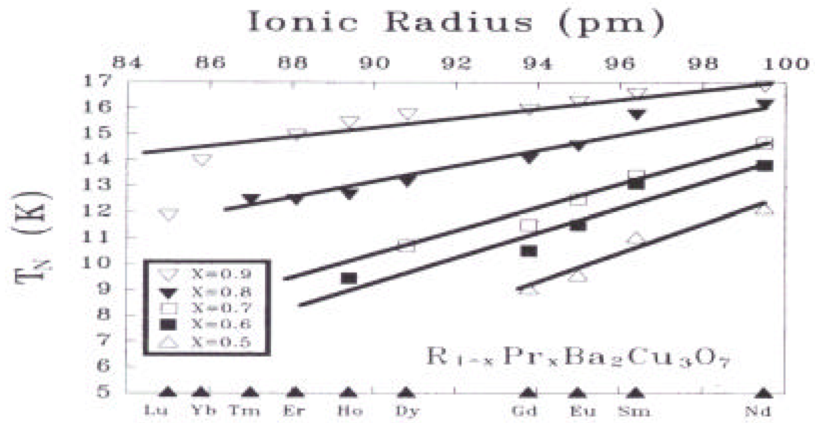

Fig.1. T_N vs ionic radius of R in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems.

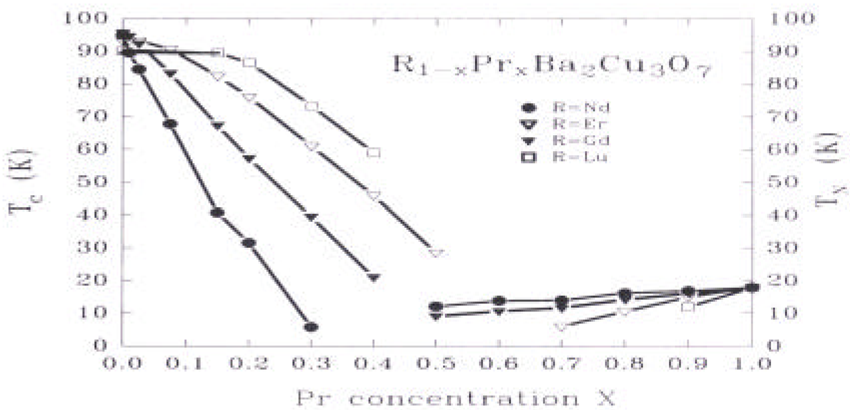

Fig.2. T_c and T_N vs x for $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems (R=Nd, Gd, Er, and Lu).

We carried out a systematic measurements of T_N in $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems (R=Lu, Yb, Tm, Er, Y, Ho, Dy, Gd, Eu, Sm, and Nd) and revealed the existence of a rare earth ion-size effect on T_N ($x>x_{cr}$), similar to that on T_c ($x<x_{cr}$)[1,2]. For a fixed R concentration (x=const.), the rate of depression of T_N with respect to x is smaller for R ions with a larger ionic radius[1,2]. This is in contrast to the rate of suppression of T_c with x[1,2], in that case the rate of depression of T_c with respect to x is larger for R ions with a larger ionic radius[1,2]. Our data show a clear ion-size effect on the evolution of T_N with x. A set of linear fit of T_N vs x yields a steeper slope for R with a smaller ionic radius[2]. Fig. 1 shows that for a given R concentration, T_N decreases

monotonically with decreasing ionic radius. In order to compare and to summarize the correlation between the unique magnetic properties and the superconducting properties of the $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems, the superconducting T_c vs x for $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ (R=Nd, Gd, Er, and Lu) together are plotted in Fig. 2 along with their $T_N(x)$.

These results were qualitatively interpreted in terms of the hybridization between the electron states of Pr ions and that of CuO_2 planes[2]. The most likely cause for the above observations is that the ion size of R influences this hybridization. The hybridization of the 4*f* states of Pr ions and the valence band states of CuO_2 is larger in the $(R_{1-x}Pr_x)Ba_2Cu_3O_7$ systems with larger R ionic radius. This effect gives rise to the suppression of superconductivity in the lower Pr concentration and the enhancement in superexchange interaction which is favorable for magnetic ordering in high-Pr-content compounds[2].

3. Ga-DOPING ON THE Cu(1)-SITE IN $RBa_2Cu_{3-x}Ga_xO_{7-y}$ SYSTEM

The effect of the substitution for copper in $YBa_2Cu_3O_{7-y}$ with various metallic elements M (M=V, Fe, Co, Ga, Al, Ni and Zn) have been widely investigated[4,5]. It was found by most of research groups that the nominally trivalent magnetic (Fe and Co) and nonmagnetic (Ga and Al) dopants substitute on the Cu(1) sites in Cu-O chains, whereas nominally divalent (Ni and Zn) dopants go onto the Cu(2) sites in Cu-O_2 planes[4,5], although TGA data indicate that at higher concentrations Fe goes to both Cu(1) and Cu(2) sites, and NMR results suggest that Zn does not substitute appreciably on the Cu(2) site[5]. All substitutions reduce T_C, but with very different rates, the largest being 13K/%atom for Zn substitution on the plane site and 5K/%atom for Co substitution on the chain site[4].

The substitution of Cu ions in Y $Ba_2Cu_3O_{7-y}$ by Ga with a closed-shell ($3d^{10}$) has been studied in detail. For Ga substitution the site occupancies have been investigated by using neutron diffraction and NMR. The preferential occupation of the Cu(1) sites by Ga is most effective in promoting the orthorhombic-tetragonal (O-T) structure transition. Doping with Ga leads to a decrease of T_c, and in the higher Ga concentration yields significant deviation from the linear "metal-like" temperature dependence of the normal state resistivity. The mechanisms that lead to this behavior are still not completely understood.

We present detailed investigation on the phase segregation, change of oxygen content, and magnetization of the Ga-substituted $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems (R=Yb, Er, Y, Dy, Gd, Eu and Nd) with x=0, 0.05, 0.1, 0.15, 0.2 and 0.3. It was observed that for $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems the melting point, the critical Ga concentration x_{O-T} (at which the samples undergo a phase transition from orthorhomb ic to tetragonal), the normal state resistivity ρ_n, and the superconducting T_c, are dependent upon the rare earth ion size[4]. Table I shows that as Ga content x increased to certain value, x_{O-T}, the structural transition from orthorhombic to tetragonal symmetry (O-T) took place. It is noticeable that the x_{O-T} shifted to lower values with increasing the radius of the rare earth ions. Different R ions have different influence on orthorhombic distortion (oxygen ordering) in the Cu-O chain plane, although the R ions are located on Y sites and far from Cu-O chain. The dependencies of $T_{c,mag}$ on Ga content, x, are displayed in Fig.3. $T_{c,mag}$ decrease approximately linearly with the progress of Ga substitution for all studied $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems (R=Yb, Er, Y, Dy, Gd, Eu and Nd). However, the T_c suppression rate, dT_c/dx, are quite different for various $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems. For example, at the same Ga concentration, x=0.15, $T_{c,mag}$=20K for $NdBa_2Cu_{2.85}Ga_{0.15}O_{7-y}$ and 89K for $YbBa_2Cu_{2.85}Ga_{0.15}O_{7-y}$ (Fig.3). This indicates that Ga is extremely more effective in suppressing superconductivity in $NdBa_2Cu_{3-x}Ga_xO_{7-y}$ than in $YbBa_2Cu_{3-x}Ga_xO_{7-y}$.

TABLE I. The structures of $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems at various x ("*O*" orthorhombic, "*T*" tetragonal).

	r_{ion} (pm)	$x=0$		$x=0.05$		$x=0.1$		$x=0.15$		$x=0.2$	$x=0.3$
$YbBa_2Cu_{3-x}Ga_xO_{7-y}$	85.8	*O*		*O*		*O*		*O*		*O*	*O*
$ErBa_2Cu_{3-x}Ga_xO_{7-y}$	88.1	*O*		*O*		*O*		*O*	→	*T*	*T*
$YBa_2Cu_{3-x}Ga_xO_{7-y}$	89.3	*O*		*O*		*O*	→	*T*		*T*	*T*
$DyBa_2Cu_{3-x}Ga_xO_{7-y}$	90.8	*O*		*O*	→	*T*		*T*		*T*	*T*
$EuBa_2Cu_{3-x}Ga_xO_{7-y}$	95.0	*O*	→	*T*		*T*		*T*		*T*	*T*
$NdBa_2Cu_{3-x}Ga_xO_{7-y}$	99.5	*O*	→	*T*		*T*		*T*		*T*	*T*

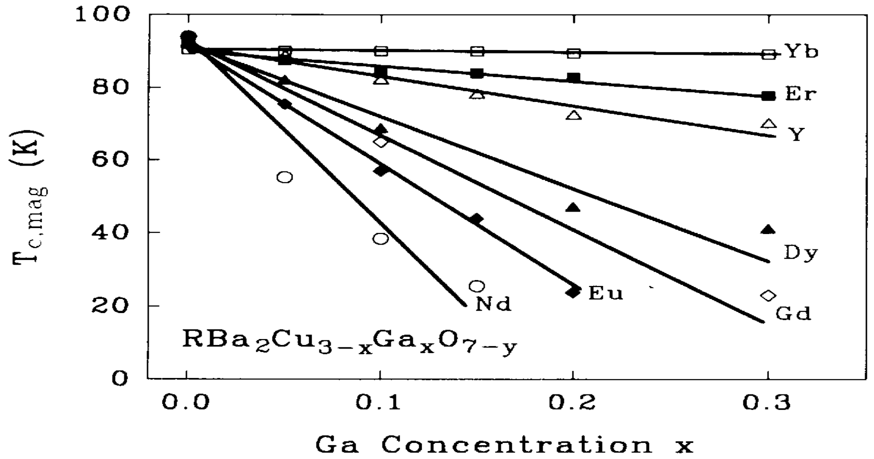

Fig.3. $T_{c,mag}$ as a function of Ga concentration for $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems (R=Yb, Er, Y, Dy, Gd, Eu and Nd).

The decrease in T_c due to Ga substitution can be attributed to the disordering effect and decrease in the carrier density. Ga ($3d^{10}4s^24p^1$) atoms have the completely filled 3*d* levels and no magnetic moment. The filled *d* orbital of Ga at Cu(1) site diminishes the overlap of Ga *d* orbitals with oxygen *p* orbitals (the radius of Ga^{3+} is only 0.62 angstrom), that would severely harm the charge transfer process, thus reduce the effective carrier concentration in Cu-O_2 planes leading to decrease in the density of states $N(E_F)$. The trivalent Ga will not change the charge balance within the Cu-O chain but may significantly disorder and disturb the alignment of Cu ($3d_{x2-y2}$) and O($2p_\sigma$) orbitals, result in the localization of mobile holes. The localization effect due to doping Ga atoms could account for the metal-insulator transition and simultaneously destruction of superconductivity. The rare earth ion size effect on T_c due to Ga substitution in $RBa_2Cu_{3-x}Ga_xO_{7-y}$ systems is not easy to understand, since the R ions at Y-site is located far from Cu(1) site occupied by Ga ions. If we consider the transition into a semiconducting phase in Ga-doped systems accompanied by a completely suppression of superconductivity as a Mott transition, the rare earth ion size effect on T_c observed here could be ascribed to the ion size effect on the position of b_{cr} in Mott transition. This means that the value of U_0 or explicit form of I(b), or both of them are rare earth ion size dependent[4].

4. Zn-DOPING ON THE Cu(2)-SITE IN $RBa_2Cu_{3-x}Zn_xO_{7-y}$ SYSTEM

With considerable interest in the drastic suppression of T_c, numerous studies on the substitution for Cu in $YBa_2Cu_3O_{7-y}$ with nonmagnetic Zn having a definite valence state 2+ and filled 3*d* levels have been carried out. Some consistent results were obtained: (1) the solution limit is 9~10%, (2) the orthorhombic structure is retained, (3) the oxygen content is little affected by 10% Zn doping (7-y≥6.9), (4) the rate of T_c reduction is 8-15K/%atom, the largest known to date[5]. The site occupancies of Zn atoms have been investigated by using neutron diffraction, Raman spectra, EXAFS, XANES, NMR, NQR, TGA and some other methods; however, the results of site occupation-probabilities of Zn are controversial. Most research groups find that zinc preferentially occupies the Cu(2) sites in Cu-O_2 planes in accord with our observations[5], although some groups claimed the substitution of Zn for both the Cu(1) and Cu(2) sites (described in Ref.5)[5].

A detailed investigation of Zn-doping-effect on the structural properties, resistivity ρ, dc susceptibility χ and superconductivity of $RBa_2Cu_{3-x}Zn_xO_{7-y}$ systems (R=Yb, Er, Y, Dy, Gd, Eu, Sm and Nd) with $0\le x\le 0.3$ was reported[5]. Fig.4 shows the temperature dependence of resistivity of $RBa_2Cu_{3-x}Zn_xO_{7-y}$ systems with Zn content x=0.01 and 0.1. The decrease of T_c with increasing Zn substitution levels is clearly demonstrated. In Fig.4 all the resistivity curves are shifted upwards with increasing x, implying that the primary effect of Zn scattering is to add a nominally temperature-independent contribution to the transport scattering rate. The samples of R=Yb, Er, Y and Dy are metallic in the substitution range $x\le 0.1$, with a positive temperature coefficient of resistivity (TCR). The average TCR for these systems increases as x increases in the range of $x\le 0.1$ and T>100K. This may be due to the localization of carriers, or an unsuspected temperature-dependent contribution by the Zn centers. A plot of $T_{c,mid}$ and $T_{c,mag}$ vs ionic radius of the rare earth elements R in $RBa_2Cu_{3-x}Zn_xO_{7-y}$ (R= Yb, Er, Y, Dy, Gd, Eu, Sm and Nd) is shown in Fig.5. A closely linear relationship between T_c and the radius of R ions at low concentrations of Zn can be observed. As the substitution of Zn progresses (x>0.06), the suppression of T_c is apparently increased by increasing the ionic radius of the rare earth elements R.

For Zn-doped YBCO Mott supposes that the effect of zinc, which produces disorder in the planes, is to prevent pairing and to render the polarons immobile (Anderson localization). The zinc will result in an increase