

Origin of the R -ion effect on T_c in $R\text{Ba}_2\text{Cu}_3\text{O}_7$

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T_c and dT_c/dP have been systematically measured for fully oxygenated $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (R -123) with $R = \text{Yb, Tm, Ho, Dy, Gd, Sm, and Nd}$. T_c has been observed to increase from 88 to 94 K with increasing radius of the R ion (r) from 0.98 to 1.12 Å. Based on the lattice strains and our dT_c/dP data, we have calculated T_c for the series of R -123 and compared them with the measured T_c . Good agreement between the experimental and the calculated results strongly suggests that the R effect on T_c in R -123 originates from the strain-induced charge redistribution between the charge reservoir and the CuO_2 plane.

While the microscopic mechanism of high-temperature superconductors (HTS) is still elusive, the electronic structure of relevant cuprates has been characterized by a phase diagram of temperature (T) and the carrier concentration (n).¹ This T - n diagram shows that the superconductivity occurs in a certain range of n , and the superconducting transition temperature (T_c) is approximately a parabolic function of n . From the structural point of view, it is widely believed that the CuO_2 plane is the principal site for the superconducting activity, and the metal oxide (i.e., MO , where M is Cu, La, Hg, Tl, or Bi) serves as a charge reservoir to supply carriers into the CuO_2 plane. Other structural components such as rare-earth and alkaline elements work as counter cations to stabilize the structure. However, some evidences²⁻⁴ have shown that the influence of rare-earth elements (R) on T_c should not be ignored. For $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-123), it was demonstrated that the substitution of some magnetic R ions have no significant effect on T_c ,⁵ thus leading to an assumption that the R site in the R -123 structure was electronically isolated from conduction electrons. Although a T_c variation in the series of oxygenated R -123 had been noticed by Neumeier,⁶ the relatively large scattering in the values of T_c made a quantitative analysis difficult. Later, the work by Fernandes *et al.*⁷ with a good control of sample quality showed that the T_c value for fully oxygenated $\text{Gd}_{1-x}\text{Y}_x\text{Ba}_2\text{Cu}_3\text{O}_7$ decreased linearly with increasing x . This result confirmed a significant R effect on T_c in R -123. Very recently, Ramesh and Hedge⁸ reported that, based on a calculation of the bond-valence sums for R -123, the valence of the in-plane copper $\text{Cu}(2)$ increases with decreasing radius of the R ion (r), implying an increase of carrier concentration in the CuO_2 plane with decreasing r . Then, the combination of the experimental results of Fernandes *et al.* and the calculation of Ramesh and Hedge gives rise to a conclusion that T_c can be lower when n is higher in the series of R -123. This conclusion contradicts with the general belief that T_c should increase with increasing carrier concentration and raises an interesting issue regarding the relationship between

T_c and n in these materials. We therefore have performed a systematic measurement of T_c and pressure effect of T_c for a series of fully-oxygenated R -123 samples with an attempt to delineate the implication of the R effect on T_c .

In this work, polycrystalline $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ with $R = \text{Yb, Tm, Ho, Dy, Gd, Sm, and Nd}$ were prepared by the standard solid-state reaction technique. The oxygen contents of fully oxygenated samples were determined by the idometric titration method to be 6.97 ± 0.03 for all samples. X-ray powder diffraction was employed to confirm the phase purity of the samples, and the Meissner effect at field cooling was measured to check their homogeneity. The sample was individually sealed in a Teflon cell with 3M Florinert fluid as pressure medium and the cell was contained in a Be-Cu high-pressure bomb to generate hydrostatic pressure, P , up to 1.8 GPa. The standard four-point method was employed for resistivity measurements. T_c was defined as the temperature at which the electrical resistivity drops to 50% of its extrapolated normal-state value; the transition width (ΔT_c) was defined as the temperature difference between 100% and 0% in the extrapolated normal-state resistivity values (T_0 and T_f , respectively). Since the pressure effect of T_c depends critically on the sample quality,⁹ and is reliable only when both the resistive and magnetic transition are sharp, we have also measured T_c with the diamagnetic transition for comparison. For a typical sample used in this work, the resistive T_c agrees with magnetic T_c within 2 K. The value of ΔT_c is < 1 K determined resistively and < 3 K determined magnetically for all measured R -123 samples except Yb-123. For Yb-123, we have found that $\Delta T_c \approx 2$ K resistively and ≈ 5 K magnetically.

Figure 1 displays T_c as a function of r , with the attached bars representing the resistive transition widths. It indicates a T_c increase from 87.9 to 94.4 K with increasing r from 0.98 to 1.12 Å. In Fig. 1, the open bar refers the T_c of Y-123 obtained by Neumeier and Zimmermann.¹⁰ Figure 2 shows the $\rho(T)$ curves for a typical R -123 sample (Gd-123) at vari-

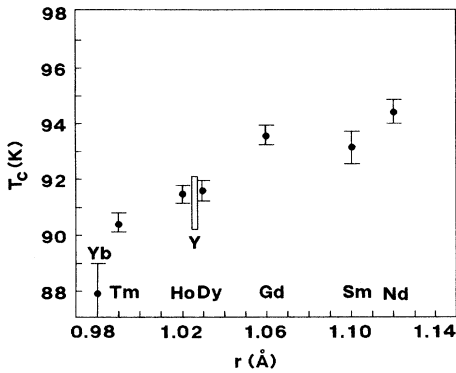


FIG. 1. T_c vs ionic radius of R for various R -123. Ionic radii are taken from Ref. 15. The solid circles represent the measured T_c values with the vertical bars showing the transition widths, and the open bar is the data for Y-123 for reference.

ous pressures. For all measured R -123, the normal state ρ is decreased by the application of pressure, and the $d \ln \rho / dP$ at normal state is found to be $10 \pm 2 \%$ /GPa which is consistent with the previous reports for most of HTS.¹¹ Figure 3 demonstrates T_c vs P for R from Nd to Yb. We have fitted the data to the straight lines by the law of least square. As shown in Fig. 3, there is a gradual decrease of the slope (dT_c/dP) from 1.21 K/GPa for Nd-123 to -0.51 K/GPa for Yb-123. In this figure, two sets of data for the sample of Yb-123 are presented. The data marked as Yb-123* is for the T_0 defined as the onset of the resistive transition, giving $dT_0/dP = -0.01$ K/GPa. The other is for the T_c defined as the midpoint of the resistive transition, yielding $dT_c/dP = -0.51$ K/GPa (note that dT_0/dP is in agreement with dT_c/dP within the experimental errors for other measured R -123). The discrepancy between dT_0/dP and dT_c/dP for Yb-123 indicates a broadening of ΔT_c under pressure. A possible explanation for this broadening of ΔT_c is the existence of a second phase which is less than 5% of

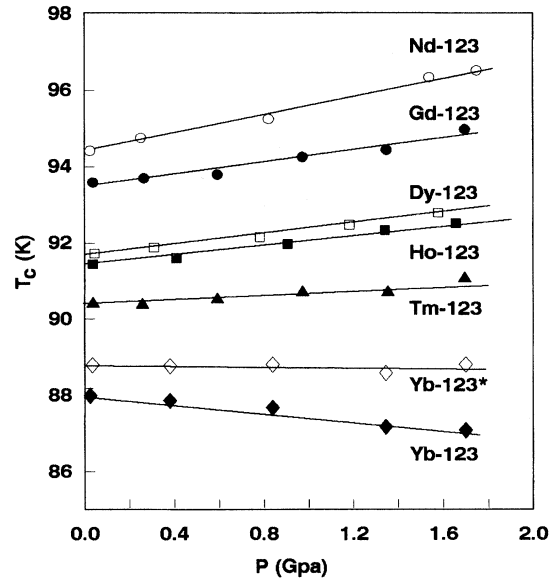


FIG. 3. T_c vs pressure (P) for various R -123. The symbols represent the experimental data, and the solid lines are the guidance for eyes. Data marked with Yb-123* is the pressure effect on T_0 .

total mass such that x-ray-diffraction patterns could not reflect it. In such case, dT_c/dP represents the pressure effect on T_c for the major phase of this sample, while dT_0/dP is attributable to the phase with the higher T_c . Both dT_c/dP and dT_0/dP are negative, which may be regarded as a general property of a well-overdoped material as those demonstrated previously in the high-pressure studies of $(\text{Y,La,Ca})\text{Ba}_2\text{Cu}_3\text{O}_7$.¹⁰ To display clearly the R dependence of dT_c/dP , we plot dT_c/dP vs r for various R -123 in Fig. 4, with the associated solid bars giving the experimental uncertainties and the open bar referring the data of Y-123 taken by Neumeier and Zimmermann.¹⁰ It indicates that dT_c/dP increases with increasing r , in a similar fashion of T_c vs r

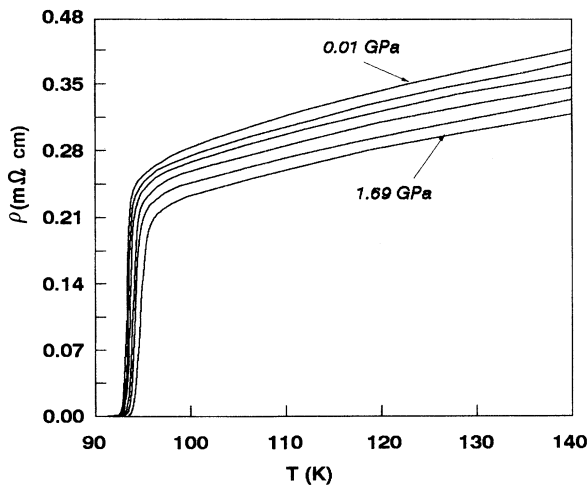


FIG. 2. ρ vs T for Gd-123 with pressure increasing from 0.01 GPa (the top curve) to 1.69 GPa (the bottom curve).

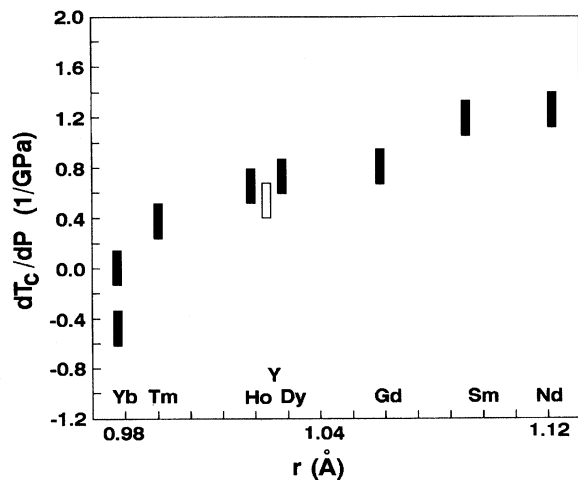


FIG. 4. dT_c/dP vs r for R -123. Vertical solid bars include the obtained data and the estimated uncertainties while the open bar is the data of Y-123 for reference.

TABLE I. T_c data for various R -123 in comparison with the calculated value based on the changes in their lattice parameters a , b , and c with respect to those of Y-123.

R	$(a-a_0)/a_0$ ($\times 10^{-3}$)	$(b-b_0)/b_0$ ($\times 10^{-3}$)	$(c-c_0)/c_0$ ($\times 10^{-3}$)	$T_{c,calc}$ (K)	$T_{c,meas}$ (K)
Nd	10.45	7.47	7.65	93.4	94.4
Sm	8.38	3.86	4.96	92.1	93.1
Dy	0.26	0.26	1.38	91.4	91.7
Ho	0.26	0.00	0.00	90.9	91.5
Tm	-4.19	-3.09	-1.46	90.9	90.4
Yb	-5.50	-4.38	-1.72	90.6	87.9

(as shown in Fig. 1). This similarity implies a close correlation between dT_c/dP and T_c .

Based on a change in lattice parameters due to the R substitution in R -123,¹² the effect of lattice expansion (for larger R) or lattice contraction (for smaller R) should play an important role in the T_c variation. In principle, the change of the lattice parameters may induce a strain in the unit cell, and a lattice strain can be simulated by the application of external pressure along three crystal axes. According to the result of the uniaxial pressure effect on T_c for Y-123,¹³ the effect of hydrostatic pressure on T_c is essentially a summation of the uniaxial stresses along the a , b , and c directions. By analogy with the uniaxial pressure effect, we postulate a formula to calculate the T_c variation based on the changes in the lattice parameters a , b , and c with respect to a reference material:

$$T_c - T_c^r = \frac{\partial T_c}{\partial \varepsilon_1} \frac{a - a_0}{a} + \frac{\partial T_c}{\partial \varepsilon_2} \frac{b - b_0}{b} + \frac{\partial T_c}{\partial \varepsilon_3} \frac{c - c_0}{c}, \quad (1)$$

where T_c^r , a_0 , b_0 , and c_0 are the T_c and lattice parameters for a reference material and ε_1 , ε_2 , and ε_3 denote the strains along the a , b , and c directions, respectively. Here $\partial T_c / \partial \varepsilon_i$ is related to the uniaxial pressure effect $\partial T_c / \partial P_j$ ($j=1,2,3$) by

$$\frac{\partial T_c}{\partial \varepsilon_i} = - \sum_j C_{ij} \frac{\partial T_c}{\partial P_j} \quad (2)$$

in which C_{ij} are the components of the elastic tensor and have been determined for the untwinned Y-123 single crystal.¹⁴ We have chosen an untwinned Y-123 single crystal as our reference material, and have calculated the relative changes of lattice parameters for other R -123 based on their lattice parameters determined from the neutron powder diffraction (NPD).⁸ The results are listed in the first three columns of Table I with a_0 , b_0 , and c_0 being the lattice parameters of Y-123 and equaling 3.817, 3.883, and 11.633 Å, respectively. In Ref. 13, the uniaxial pressure data of the Y-123 single crystal were obtained: $dT_c/dP_a = -2.0$ K/GPa, $dT_c/dP_b = 1.9$ K/GPa, and $dT_c/dP_c = -0.3$ K/GPa, and then the values of $\partial T_c / \partial \varepsilon_1$, $\partial T_c / \partial \varepsilon_2$, and $\partial T_c / \partial \varepsilon_3$ were derived as 230, -220, and 18 K, respectively. We inserted these values into Eq. (1), and obtained the T_c values for the series of R -123 as listed in the fifth column of Table I. As shown in Table I, these calculated T_c agree with the measured values within 1 K except for Yb-123. The discrepancy between the calculated T_c and the measured T_c for Yb-123 is

understandable since the Yb-123 sample used for the NPD measurement in Ref. 8 was later found to be multiphased.

Although we have shown that the lattice strains could account for the observed T_c variations in R -123, further knowledge of the relationship between the lattice strains and the carrier concentration (n) is useful for understanding the mechanism of the T_c variations in these materials. By comparing Fig. 1 with Fig. 4, it is evident that T_c and dT_c/dP are correlated as seen from the similarity in their r dependence. In order to obtain the information of n from the measured dT_c/dP values, we have adopted the model of pressure induced charge transfer, in which the value of dT_c/dP depends on n and the pressure-induced increase in n .¹⁰ Based on an empirical T_c - n curve found for (Y,La,Ca)-123,¹⁰ we first assume the following parabolic $T_c(n)$ relation to hold for the whole series of R -123:

$$T_c = T_{c0} - A(n_0 - n)^2. \quad (3)$$

Then, the rate of increase of T_c with pressure is given by

$$dT_c/dP = dT_{c0}/dP + 2A(n_0 - n)dn/dP, \quad (4)$$

where T_{c0} is the maximum T_c corresponding to an optimal carrier concentration (n_0), and dn/dP is the derivative of the number of carriers with pressure. The empirical values of dT_{c0}/dP , dn/dP , and A are positive constants. Assuming material is underdoped, i.e., $(n_0 - n) > 0$, a larger dT_c/dP gives a larger $(n_0 - n)$ in Eq. (4). According to Eq. (3), a larger $(n_0 - n)$ corresponds to a lower T_c . Then, a material with a larger dT_c/dP should have a lower T_c . This is opposite to the observations in Fig. 1 and Fig. 4 where Nd-123 has the highest T_c (=94.4 K) as well as the highest dT_c/dP (=1.2 K/GPa). On the other hand, if one assumes material is overdoped, i.e., $(n_0 - n) < 0$, a larger dT_c/dP yields a smaller $|n_0 - n|$ and the smaller $|n_0 - n|$ the higher T_c . This trend of dT_c/dP vs T_c is in agreement with our observations and thus implies that the series of R -123 from Nd-123 to Yb-123 is likely to lie in the overdoped region of the T_c - n curve. Since the empirical T_{c0} (≈ 94.2 K) obtained by Neumeier and Zimmermann¹⁰ is very close to the T_c of Nd-123 (=94.4 K, the highest T_c among R -123), we have chosen dT_c/dP of Nd-123 to be dT_{c0}/dP (i.e., $dT_{c0}/dP = 1.2$ K/GPa). Using the values of A , dn/dP from Ref. 11 (590 K/hole², and 0.01 holes/GPa, respectively) along with our measured dT_c/dP , we have deduced $(n - n_0)$ from Eq. (4) for various R -123. Then, by inserting these values of $(n - n_0)$ into Eq. (3), we have found T_c to be 94.1, 92.1, 91.8, 89.6, and 88.2 K for Sm-, Dy-, Ho-, Tm-, and Yb-123, respectively. These calculated T_c again agree with the measured ones (as shown in Table I) within 1 K. This remarkable agreement clearly demonstrates the applicability of the parabolic $T_c(n)$ function in explaining the T_c - r relation for the series of R -123. We therefore attribute the decrease in T_c with decreasing r to the increase in n . In addition, the variation of n must come from a charge redistribution between the CuO₂ plane and other structural components (serving as a charge reservoir) since the oxygen contents of these material are all 6.97 ± 0.03 . Very recently, Ramesh and Hedge⁸ have shown that the bond valence sum (BVS) of the in-plane copper increases with decreasing r , while the BVS of the R ion decreases with decreasing r for a

series of R -123. It is indicative of a strain-induced charge transfer from the R ion to the CuO_2 plane, resulting to an increase of n with decreasing r . Therefore it is possible that the R effect on T_c in R -123 originate from the strain-induced charge redistribution between the R ion and the CuO_2 plane.

In summary, T_c and dT_c/dP for fully oxygenated R -123 with $R=\text{Yb, Tm, Y, Ho, Dy, Gd, Sm, and Nd}$ have been systematically measured. We have observed a nearly linear r dependence of T_c and dT_c/dP , suggesting that the series of R -123 is likely to be in the overdoped region of the T_c - n diagram. We have calculated the T_c values for R -123 based

on the relative changes of their lattice parameters, and also from the measured dT_c/dP data. The agreement of the calculated T_c with the measured T_c strongly suggests that the origin of the observed R effect on T_c in R -123 is the strain-induced charge redistribution between the charge reservoir and the CuO_2 plane.

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