# Origin of  $T_c$  suppression due to  $R = Eu$ , Nd, and Pr in superconducting  $(La_{1-x}R_x)_{1.82}Sr_{0.18}CuO_4$

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The origin of  $T_c$  suppression due to substitution of rare-earth elements  $(R)$  is investigated for the samples of  $(La_{1-x}R_x)_{1.82}Sr_{0.18}CuO_4$ ,  $(R=Eu, Nd, Pr)$  through the measurements of electrical resistivity and lattice parameters. With increasing  $x$ , three phases,  $T$ ,  $T^*$ , and  $T'$  appear successively and the critical concentration for disappearance of superconductivity exists in the *T*-phase region, each of which is  $x=0.12$ , 0.4, and 0.6 for *R*=Eu, Nd, and Pr, respectively, indicating that the smaller the ionic radius of the substituted *R* element, the stronger the  $T_c$  suppression. Temperature dependence of the conductivity is described by  $\sigma \propto \ln T$  above  $x=0.08$ and 0.1 for  $R$ =Eu and Nd, respectively, but not for  $R$ =Pr. The origin of  $T_c$  suppression is discussed in terms of two contributions; the reduction of the Madelung site potential at apical oxygen sites and the random potential scattering on the CuO<sub>2</sub> planes which is effective for pair breaking in *d*-wave superconductors, both of which are caused by displacement of apical oxygens due to substitution of *R* elements.  $[ S0163-1829(96)06741-0 ]$ 

### **I. INTRODUCTION**

Many copper oxide superconductors have been found so far, from which their common characteristics have been revealed. Their parent compounds are all antiferromagnetic insulators of  $CuO<sub>2</sub>$  planes but as the antiferromagnetic order is destroyed by doping holes or electrons, they become metallic, resulting in superconductivity at low temperature. The superconducting critical temperature  $T_c$  depends on carrier density and the optimum values per unit  $CuO<sub>2</sub>$  plane for a maximum  $T_c$  of each high- $T_c$  compound is commonly about 0.15–0.2. Whether the carriers in high- $T_c$  cuprates are holes or electrons is determined by oxygen coordination around copper ions in these compounds; hole carriers for octahedral and pyramidal coordination of oxygen ions around Cu ions, and electron carriers for their square coordination around Cu  $\mu$ ions.<sup>1–3</sup> These three types of oxygen coordination in the structure with single layer  $CuO<sub>2</sub>$  sheets are usually called the  $T, T^*$ , and  $T'$  phases, respectively. A typical example of a  $T$ phase is  $(La, Sr)_{2}CuO_{4}$ , which has apical oxygens above and below the CuO<sub>2</sub> plane, and a  $T^*$  phase with apical oxygen on one side of  $CuO<sub>2</sub>$  plane is observed in  $(Nd,Ce,Sr)<sub>2</sub>CuO<sub>4</sub>,<sup>4–6</sup>$ and a  $T'$  phase with no apical oxygen appears in  $L_2CuO<sub>4</sub>$  $(L=Pr, Nd, Sm, Eu, and Gd).$ <sup>3,7</sup> By optimal carrier doping, superconductivity is known to take place in any of these three phases but the maximum value of  $T_c$  depends on the species of the constituent rare-earth elements.<sup>8</sup> Furthermore, it is well known that  $T_c$  is always suppressed by the substitution of any *R* elements for La,  $^{9,10}$  even in the La214 superconductors with optimal holes. Therefore, to clarify the mechnism of  $T_c$  suppression, it is significant to investigate the roles of apical oxygens and *R* ions which construct the structural framework of the La214 superconductors with the simplest structure. Ohta, Tohyama, and Maekawa have examined the relation between  $T_c$  values and the Madelung site potentials of oxygens at apex sites and in-plane for a number of high- $T_c$  materials and have found the correlation between the Madelung site potential and the maximum  $T_c$  of each family of the hole-carrier superconductors. $11$  This suggests that the electronic-energy-level structure by which the dynamics of the carriers are constrained, is determined by the Madelung site potential at apex sites in the insulating parent compounds since the Madelung site potential is exactly defined in ionic crystals. The energy-level structure in the compounds can be expected to be changed by the substitution of *R* elements with different ionic radius.

On the other hand, in superconductivity with anisotropic gap opposite to isotropic *s*-wave superconductivity, even nonmagnetic impurity has been suggested to cause severe pair breaking.<sup>12</sup> Therefore, it is expected that the substitution of *R* elements with different ion radius for  $La^{3+}$  brings about random potential on  $CuO<sub>2</sub>$  plane, resulting in pair breaking.

In this paper, we investigate how the  $T_c$ 's, lattice parameters, and the conductivity on the  $CuO<sub>2</sub>$  plane are influenced by the substitution of *R* elements such as Eu, Nd, and Pr having different ion radius and magnetic characteristics for La in the La214 superconductor, and point out that substitution of *R* elements reduces the Madelung potential between apex and in-plane oxygens and furthermore, induces random potential on the  $CuO<sub>2</sub>$  plane, both of which are responsible for  $T_c$  suppression.

# **II. SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE**

The samples of  $(La_{1-x}R_x)_{1.82}Sr_{0.18}CuO_4$ ,  $(R=Eu,Nd,Pr)$ , where the Sr concentration was fixed at 0.18 to study the substitution effect of the La site, were prepared by solid-state reaction in oxygen atmosphere. A nominal amount of oxide powders such as  $La_2O_3$ , SrCO<sub>3</sub>, CuO, Eu<sub>2</sub>O<sub>3</sub>, Nd<sub>2</sub>O<sub>3</sub>, and  $Pr_2O_3$  with 99.99% purity was thoroughly mixed by the ballmill method using a  $ZrO<sub>2</sub>$  ball for 24 h and calcined at 1100 °C for 30 h in oxygen flow, during which intermediate pulverization was carried out two times at room temperature. The calcined powder was ground and pressed into a pellet and sintered at 1100 °C for 50 h in flowing oxygen. The pellet was ground into powders with a particle diameter less than 45  $\mu$ m and the powder was pressed into pellets again.

The pellets were again sintered at  $1100\degree C$  for 15 h and annealed at 450 °C for 12 h in flowing oxygen. Electrical resistivity was measured by the ordinary four-probe method, from which superconducting critical temperature  $T_c$  was determined, where  $T_c$  was defined as the temperature at the midpoint of the resistive transition. The crystal structure and lattice parameters were determined by the x-ray diffraction method at room temperature. Oxygen content was measured using the iodometric titration method.

#### **III. EXPERIMENTAL RESULTS**

## **A. Phase diagram**

The variation of the crystal structure was examined by x-ray diffraction for the samples of  $(La_{1-x}R_x)_{1.82}Sr_{0.18} CuO_{4-z}$  ( $R=Eu, Nd, Pr$ ), where Sr concentration is fixed at 0.18 and only the concentration of rare-earth element *x* is changed. The sample  $(La_{0.91}Sr_{0.09})_2CuO_{4-z}$  with  $x=0$  has a  $T_c \sim 40$  K and is tetragonal having apex oxygens above and below  $CuO<sub>2</sub>$  plane, that is, the  $T$  phase. With increasing  $x$ , the  $T$  phase transforms to the  $T^*$  phase and the  $T<sup>'</sup>$  phase. The critical concentration of each phase depends on the *R* element. The *R*-concentration dependence of the volume fraction of each phase is shown in Fig. 1 for  $R = Eu$ , Nd, and Pr, which were determined by x-ray-diffraction methods. For  $R=Eu$ , a single-phase *T* exists below  $x=0.12$  and with increasing *x* above 0.12, the *T* phase decreases as the *T*\* phase increases and above  $x=0.5$ , the  $T'$  phase appears, while the  $T$  phase disappears. For  $R=Nd$ , the critical concentration for the single-phase *T* extends to about  $x=0.4$ , where there exist a tetragonal *T* phase below  $x=0.2$  and an orthorhombic *T* phase between  $x=0.2$  and 0.6, but the  $T^*$  phase does not appear and the *T'* phase increases above  $x=0.5$ . For  $R=Pr$ , the single-phase *T* range extends further to about  $x=0.6$  and three phases coexist between  $x=0.6$  and 0.8 but above  $x=0.8$ , the *T* phase disappears while the *T*<sup>\*</sup> and *T*<sup>'</sup> phases remain. This indicates that the stability of the *T* phase depends on ionic radius of the substituted *R* elements; the smaller the ionic radius of the *R* element, the less stable the *T* phase.

## **B. Electrical resistivity, superconducting critical temperature** *Tc* **, and lattice parameters**

Figure 2 shows temperature dependence of the resistivity for the superconducting samples of  $(La_{1-x}R_x)_{1.82}$  Sr<sub>0.18</sub>CuO<sub>4-z</sub> (R=Eu,Nd,Pr). The resistivity is increased and  $T_c$  is suppressed by the substitution of  $R$  elements. We further notice the different effect of these elements on the superconductivity and the temperature dependence of the resistivity. For the substitution of Eu and Nd below about  $x=0.08$  and about 0.1, respectively, the resistivity decreases linearly until the on-set of superconductivity with decreasing temperature but the resistivity of the samples with more than these concentrations shows an upturn around 30 K before superconductivity starts, indicating weak localization on the  $CuO<sub>2</sub>$  plane. On the other hand, for Pr substitution, an upturn of the resistivity at low temperature cannot be observed but in the nonsuperconducting samples with more than  $x=0.8$ , the resistivity goes up sharply below room



FIG. 1. Concentration dependence of the volume fraction,  $(a)$  $R = Eu$ , (b)  $R = Nd$ , and (c)  $R = Pr$ .

temperature like a semiconductor, which is not shown here. *T<sub>c</sub>*'s are determined from these resistivity data and are shown in Fig. 3. For the case of Eu substitution,  $T_c$  decreases linearly with increasing *x* below  $x=0.12$ , that is, only the single-phase *T* region as can be seen in the phase diagram of Fig. 1. When the  $T^*$  phase starts to form and consequently both the phases coexist above this concentration,  $T_c$  rises again a little among  $x=0.15$  and 0.3, and disappears as the *T* phase fades above  $x=0.3$ . For the cases of Nd and Pr substitution,  $T_c$  decreases linearly with increasing x in the singlephase *T* region such as  $x \le 0.4$  for Nd and  $x \le 0.6$  for Pr as shown in Fig. 1, and still decreases rapidly with formation of the  $T^*$  or  $T'$  phases above these concentrations. To under-



FIG. 2. Temperature dependence of the resistivity, (a)  $R = Eu$ , (b)  $R = Nd$ , and (c)  $R = Pr$ .

stand the strange behavior of  $T_c$ , the lattice parameters  $a$  and *c* of *R*-substituted samples were measured, the typical example of which is shown for Eu-substituted samples in Fig. 4. With increasing *x*, lattice parameters *c* and *a* decrease linearly in the single-phase *T* region below about  $x=0.12$ , while the lattice parameters of the *T* phase increase a little and those of the *T*\* phase decrease sharply, not shown here, between  $x=0.12$  and 0.3 where the *T* and  $T^*$  phases coexist. The lattice parameters of Nd- or Pr-substituted samples also show analogous behavior to the case of Eu substitution. This behavior of the *T*-phase lattice parameters in the two-phase region shown in Fig. 4 is similar to the behavior of  $T_c$  which is shown in Fig.  $3(a)$ . These results indicate that Eu concentration in the clusters of the *T*\* phase is stronger than that of the *T* phase in this region since *R* ions with smaller size tend to gather together,<sup>13</sup> leading to rapid formation of the  $T^*$ 



FIG. 3. Concentration dependence of the superconducting critical temperature  $T_c$ , (a)  $R = Eu$ , (b)  $R = Nd$ , and (c)  $R = Pr$ .

phase. Therefore, a little rise of  $T_c$  and the lattice parameters in the two-phase region does not come from  $T^*$  phases but originates from the decrease of Eu concentration in the *T* phase, implying that superconductivity takes place in the *T* phase. Thus, to investigate the intrinsic cause of the  $T_c$  suppression due to *R* elements, we should concentrate our attention on the single-phase *T* region.

# **C.** Oxygen content in  $T$ ,  $T^*$ , and  $T'$  phases

Since superconducting properties are well known to be associated with carrier density which depends on oxygen content, variation of oxygen content due to substitution of *R*



FIG. 4. Eu-concentration dependence of *T*-phase lattice parameters,  $(a) c$  and  $(b) a$ .

ions should be examined. Figure 5 shows *R*-concentration dependence of oxygen content  $(4-\delta)$ , where critical concentration of each *R* ion for the *T* phase is indicated by arrows and calculated carrier concentration (*p*) is also displayed. Oxygen content is almost constant in the concentration region of the single-phase *T* but decreases rapidly when the *T*\* or  $T'$  phase begin to form, leading also to rapid decrease of carrier concentration *p*. This means that when *R* ions with smaller size are substituted for  $La^{3+}$  ions, the neighboring apical oxygens hardly stay at the original apex sites and consequently, displace slightly in the *T*-phase structure but further displacement of apical oxygens due to greater increase of *R*-ion concentration leads to formation of the  $T^*$  or  $T^*$ phase, which is also accompanied by oxygen reduction. Therefore, it may be reasonable to consider that since the appearance of the  $T^*$  or  $T'$  phase involves reduction of oxy-



FIG. 5. *R*-concentration dependence of oxygen contents  $(4-\delta)$ in each sample. The arrows indicate the critical concentration of the single-phase *T* for each *R*-substituted sample.



FIG. 6. *R*-concentration dependence of  $(a)$  lattice parameter  $c$ and (b)  $T_c$  in the single-phase  $T$  of  $R$ -substituted samples.

gen, superconductivity never occurs in these phases with oxygen deficiency although some papers have reported that superconductivity appears even in the  $T^*$  phase.<sup>14,15</sup> It is predicted that the linear decrease of  $T_c$  with increasing  $x$  in the region of the single-phase *T* is clearly not due to the decrease of oxygen content, or reduction of hole carriers but is related to the modification of environment around substituted  *ions such as displacement of the neighboring oxygen* ions.

#### **IV. DISCUSSION AND SUMMARY**

From the experimental results, we conclude that superconductivity does not take place in the  $T^*$  or  $T'$  phase but in the *T* phase, and  $T_c$  decreases linearly with increasing *x* in the single-phase *T*. Then, in Fig. 6, we display again the lattice parameter  $c$  and  $T_c$  in the concentration region where only the single-phase *T* exists. As for magnetic properties of *R* ions,  $Nd^{3+}$  and  $Pr^{3+}$  are magnetic ions, having local moments of  $P_{\text{eff}}$ =3.62  $\mu$ B and 3.58  $\mu$ B, respectively while the  $Eu<sup>3+</sup>$  ion is nonmagnetic at low temperature in the absence of a magnetic field, i.e., Van Vleck paramagnet. Therefore, lowering of  $T_c$  is not related to the magnetism of  $R$  ions but rather depends on their ionic size; the smaller the ionic radius, the larger the  $|dT_c/dx|$ , as can be seen in the figure. Furthermore, the gradient of lattice parameter  $|dc/dx|$  also depends on the *R* ionic size, which resembles the  $|dT_c/dx|$ behavior. However, there is no common critical lattice parameter *c* independent of the *R* element for the single-phase *T* or for the disappearance of superconductivity. Therefore, we come to the conclusion that not only phase stability but also  $T_c$  are not directly governed by the lattice parameter variation but rather by the local change of surroundings around the *R* ions which is caused by the difference of ionic radius between substituted  $R^{3+}$  and  $La^{3+}$  ions. Then, let us consider the reason why superconductivity is easily de-

stroyed by substitution of an *R* ion having smaller ion radius. Since substitution of the *R* elements such as Eu, Nd, and Pr are less effective at destroying superconductivity than the substitution of transition elements for Cu, it is natural to consider that these rare-earth elements do not work directly at breaking Cooper pairs on CuO<sub>2</sub> plane but influence  $T_c$ through the local deformation caused by substituted *R* ions or transformation of the crystal structure. This reminds us of the physical pressure effect on  $T_c$  in high- $T_c$  superconductors;  $T_c$  of hole-carrier superconductors having apical oxygens is enhanced by applied pressure, which is also accompanied by reduction of lattice parameters.<sup>16,17</sup> Furthermore, an interesting experimental result has been reported that when pressure is applied, apical oxygen ions move towards the  $CuO<sub>2</sub>$  planes more rapidly than lattice parameter decreases, which may be responsible for large effect of pressure on  $T_c$  enhancement.<sup>18,19</sup> Both the physical pressure and the  $R$  element substitution (we call it chemical pressure) make the lattice parameters shorten but their effect on  $T_c$  is quite opposite.<sup>20</sup> Ohta, Tohyama, and Maekawa<sup>11</sup> have examined the relation among the maximum  $T_c$  in each high- $T_c$ family, and the energy level of the apex oxygen atoms, charge-transfer gap, crystal-field splitting and copper-oxygen bond length, and consequently have found that there exists a correlation between  $T_c$  and  $\Delta V_A$  which is the difference in Madelung site potential between an apex oxygen O(*A*) and an in-plane oxygen  $O(P)$ . According to the Zhang-Rice model,<sup>21</sup> doped holes enter into  $O(P)2p_{\sigma}$  orbitals which are hybridized with Cu  $3d_{x^2-y^2}$  orbitals and consequently, spin singlets (Zhang-Rice singlet) are formed between two holes of these orbitals and therefore, the motion of the doped holes is considered to be the propagation of the spin singlets.<sup>22,23</sup> By cluster model calculations,<sup>11</sup> Ohta, Tohyama, and Maekawa have also pointed out that the spin singlets are stabilized by the increase of  $\Delta V_A$ , which is closely related to the  $T_c$  values of the hole-carrier superconductors. Since the electrostatic potential  $\Delta V_A$  is increased by shortening of  $O(P)$ -O(*A*) bond length, the enhancement of  $T_c$  due to applied pressure can be explained by the increase of  $\Delta V_A$ . Although the chemical pressure, that is, substitution of *R* ions with smaller ion radius decreases the lattice parameters, *T<sub>c</sub>*'s are not enhanced as already shown. From the point of view of  $\Delta V_A$ , it must be expected that chemical pressure expands the  $O(P)-O(A)$  distance contrary to the physical pressure and consequently, decreases  $\Delta V_A$ , leading to the  $T_c$ drop. This prediction is supported by the following experimental fact that when  $La^{3+}$  ions are replaced by  $Sr^{2+}$  or  $Ba^{2+}$ ions which have larger ionic radii than that of  $La^{3+}$ , the distance of  $Cu(P)-O(A)$  shrinks although the lattice parameters *a* and *c* increase.<sup>24-26</sup> The fact that Eu elements which have the smallest ion radius in the three rare-earth elements suppress  $T_c$  most severely can be understood by the strongest reduction of  $\Delta V_A$  as mentioned above. Therefore, it follows that Eu substitution makes the distance of  $Cu(P)-O(A)$  expand the most of the three  $R$  ions. Then, we try to infer what change of ion configuration takes place around  $Eu^{3+}$  ions when  $La^{3+}$  ions are replaced by  $Eu^{3+}$  ions. Assuming that La sites are fixed even for the substitution of Eu with the smallest ion radius, their adjacent apical oxygens displace to the direction of Eu ions, leading to the extension of the Cu(*P*)- O(*A*) distance. As a result, apex oxygens adjacent to Eu ions



FIG. 7. Plots of conductivity  $(\sigma)$  vs ln*T*, showing almost linear lines, which indicates weak localization on the  $CuO<sub>2</sub>$  plane.

sit hardly on the same level surface as the other apex oxygens. This random configuration of apical oxygens induces random potential on the  $CuO<sub>2</sub>$  plane, the evidence of which can be seen in the temperature dependence of the resistivity in Figs.  $2(a)$  and  $2(b)$ . The resistivity upturn at low temperature is attributable to the random potential on the  $CuO<sub>2</sub>$  plane induced by random displacement of apical oxygens since the temperature dependence of the conductivity  $\sigma(T)$  for the Euor Nd-substituted samples presenting superconductivity can be well fitted to the equation  $\sigma = \sigma_0 + A \ln T$ , indicating weak localization on the two-dimensional  $CuO<sub>2</sub>$  plane,<sup>27</sup> which is shown in Fig. 7. After all, that even the substitution of small quantities of Eu brings about the strong upturn of the resistivity implies that the smaller the ionic size of the substituted *R* elements, the larger the displacement of apical oxygens, resulting in the decrease of  $\Delta V_A$  contrary to the physical pressure effect. Some papers<sup>28,29</sup> have pointed out the importance of the tilt of  $CuO<sub>6</sub>$  octahedra which may destroy superconductivity. In our opinion, since the distortion of the oxygen ions from original sites due to the substituted *R* ions should involve the tilt of  $CuO<sub>6</sub>$  octahedra, our present analysis is not so inconsistent with the tilting model.

It is well known that in conventional *s*-wave superconductors with isotropic gap symmetry, a nonmagnetic impurity has no effect on superconductivity as indicated by Anderson theory<sup>30</sup> but a magnetic impurity causes pair breaking, leading to suppression of  $T_c$  as described by Abrikosov-Gor'kov  $(AG)$  theory.<sup>31</sup> It has been suggested that in *d*-wave superconductivity with anisotropic gap symmetry, even impurity potential scattering causes severe  $T_c$ suppression.<sup>32,33</sup> The normal- and superconducting-state properties of the high- $T_c$  copper oxides have been reported to be interpretable in terms of an antiferromagnetic spinfluctuation  $(AFSF)$  mechanism.<sup>34–37</sup> If AFSF should work well for the appearance of high- $T_c$  superconductivity,<sup>38</sup> this mechanism leads to *d*-wave superconductivity. In this case, it is possible to investigate the nonmagnetic impurityinduced  $T_c$  suppression on the basis of AG scaling theory. This is expressed as follows:

$$
\ln(T_{c0}/T_c) = g[\psi(\Gamma/2\pi k_B T_c) - \psi(1/2)],\tag{1}
$$

where  $\psi(z)$  is the di-gamma function,  $\Gamma$  is a pair-breaking parameter,  $g(\leq 1)$  is a constant related to gap anisotropy and  $T_{c0}$  is the critical temperature of the pure sample. In the Born approximation, that is, weak potential scattering limit,  $\Gamma$  is expressed as  $\Gamma = \pi N_0 x u^2$ , where *x* is the impurity (*R*element) concentration,  $N_0$  is the state density at the Fermi level, and *u* is the scattering potential.<sup>39,40</sup> When *x* is small, the following approximate equation can be obtained:

$$
T_c = T_{c0} - g \pi^2 N_0 u^2 x / 4k_B. \tag{2}
$$

Since  $T_c$  suppression in Eqs. (1) and (2) is due to impurity potential scattering, that due to the decrease of Madelung potential  $\Delta V_A$  discussed above also must be taken into account. Here, let us consider this part qualitatively. The electrostatic potential  $\Delta V_A$  should be inversely proportional to the bond length *d* between  $O(P)$ - $O(A)$  as  $\Delta V_A \propto 1/d$ . By substitution of *R* elements for La, the mean bond length  $\langle d \rangle$  is changed as  $\langle d \rangle = d_0 + \Delta dx$ , where  $d_0$  is the *d* value at  $x=0$ ,  $\Delta d$  is the displacement of an oxygen ion adjacent to a substituted *R* element ion and *x* is the *R*-element concentration. This displacement  $\Delta d$  is derived from the difference of the ionic radius  $(R_0 - R)$ , where  $R_0$  is the ionic radius of  $La^{3+}$  and *R* is that of the *R* element, and is expressed as  $\Delta d \propto (R_0 - R) = \Delta R$ , leading to  $\Delta V_A = c/(d_0 + \Delta Rx)$ , where *c* is a constant. Considering  $d_0 \ge \Delta R$ ,  $\Delta V_A \approx (c/d_0)(1 - \Delta Rx/d_0)$  is obtained for small *x*. Assuming that  $T_c - T_{c0} \propto \delta(\Delta V_A)$  holds for small *x*, we obtain the following equation:

$$
T_c = T_{c0} - c\,\Delta R x / d_0^2. \tag{3}
$$

When  $R$  elements are substituted for La,  $T_c$  suppression may be given by the addition of both the contribution expressed by Eqs.  $(2)$  and  $(3)$  for small *x*.

$$
T_c = T_{c0} - g \pi^2 N_0 u^2 x / 4k_B - c \Delta R x / d_0^2
$$
  
=  $T_{c0} - \alpha u^2 x - \beta \Delta R x$ , (4)

where  $\alpha$  and  $\beta$  are constants, and *u* and  $\Delta R$  depend on the *R* element. Then the gradient  $(dT_c/dx)$ <sup>R</sup> is expressed as

$$
(dT_c/dx)_R = -\alpha u^2 - \beta (\Delta R)_R. \tag{5}
$$

Here, let us recall the temperature dependence of the resistivity for each sample which is shown in Fig. 3; the resistivity upturn at low temperature is observed for Eu- and Ndsubstituted samples but not for the Pr-substituted sample. Since these resistivity upturns come from weak localization effects on the  $CuO<sub>2</sub>$  plane, Pr substitution does not produce

TABLE I.  $T_{c0}$  is the critical temperature of the samples with  $x=0$  in  $(La_{1-x}R_x)_{1.82}Sr_{0.18}CuO_4$ ,  $(R=Eu, Nd, Pr)$ ,  $dT_c/dx$  is the gradient of  $T_c$  to impurity concentration near  $x=0$ ,  $\Delta R = R_0 - R$ , where  $R_0$  and  $R$  are the ionic radii of  $La^{3+}$  and  $R$  ions, respectively,  $\alpha u^2$  is the  $T_c$  suppression due to potential scattering,  $\rho_0$  is the residual resistivity of the sample with  $x=0$  at 0 K,  $\rho_{0R}$  is the residual resistivity at 0 K for the samples with  $x=0.15$  for  $R=Eu$ , Nd, and Pr, respectively.

	$R = Eu$	$R = Nd$	$R = Pr$
$T_{c0}$ (K)	40	40	40
$\left  dT_c/dx \right $	150	60	18
$\Delta R$ (Å)	0.16	0.1	0.08
$\alpha u^2$	114	38	0
$\rho_0$ (m $\Omega$ cm)	0.22	0.22	0.22
$\rho_{0R}$ (m $\Omega$ cm)	1.85	0.68	1.0

such a large random potential on the  $CuO<sub>2</sub>$  plane as localization effects are brought about. Therefore,  $T_c$  suppression due to random potential scattering may scarcely occur in Prsubstituted samples and consequently, the first term on the right-hand side in Eq.  $(5)$  can be neglected, resulting in  $(dT_c/dx)_{\text{Pr}} = -\beta(\Delta R)_{\text{Pr}}$  in this sample. This allows us to determine the universal constant  $\beta$  independent of the  $R$  element, which  $\beta = -(dT_c/dx)_{\text{Pr}}/(\Delta R)_{\text{Pr}} = 18/0.08 = 225$  (K/Å). Using this value,  $\alpha(u^2)_R$  are calculated and listed in Table I together with other values experimentally obtained. Since the state density  $N_0$  dependence on x is not clear, the net u value is hard to obtain, however assuming constant  $N_0$  for small  $x$ , the ratio of  $u^2$  for Eu- and Nd-substituted samples can be determined, which is  $(u^2)_{Eu}/(u^2)_{Nd} \approx 3.0$ . Since the scattering rate is proportional to the square of scattering potential  $u^2$ , the electrical resistivity should be proportional to  $u^2$ . Therefore, the value of  $u^2$  may be evaluated by using the residual resistivity at 0 K. Then, for the samples with  $x=0.15$  we calculate the value of the next equation  $(\Delta \rho)_{\text{0Eu}}/(\Delta \rho)_{\text{0Nd}} = (\rho_{\text{0Eu}} - \rho_0)/(\rho_{\text{0Nd}} - \rho_0)$ , where  $\rho_0$ ,  $\rho_{\text{0Eu}}$ , and  $\rho_{0Nd}$  are the residual resistivity at 0 K for  $x=0$  and for  $x=0.15$  for Eu and Nd, respectively. We obtain  $(\Delta \rho)_{\text{0Eu}}/(\Delta \rho)_{\text{0Nd}} \approx 3.5$ , which is comparable to the value of  $(u^2)_{Eu}/(u^2)_{Nd}$ . Therefore, it is confirmed that  $(u^2)_{Eu}/(u^2)_{Nd} \simeq (\Delta \rho)_{0Eu}/(\Delta \rho)_{0Nd}$  holds. This indicates that the assumption of *d*-wave superconductivity and the analysis of  $(dT_c/dx)_R$  performed to get  $u^2$  seems to be reliable. As for the  $T_c$  drop due to  $R$ -element substitution, using the obtained value of  $\alpha u^2$  we can separately estimate both the contribution from the potential scattering and the change of Madelung potential; about 76 and 63 % of the  $T_c$  drop can be attributable to the potential scattering for Eu- and Ndsubstituted samples, respectively.

In summary, we measured the lattice parameters against concentration, temperature dependence of the resistivity, and oxygen contents in  $T$ ,  $T^*$ , and  $T'$  phases for the samples  $(La_{1-x}R_x)_{1.82}Sr_{0.18}CuO_4 (R=Eu, Nd, Pr)$ , from which  $T_c$ 's are also determined. It is revealed that superconductivity takes place only in the single-phase  $T$  and  $T_c$ 's are suppressed more strongly by the substitution of *R* elements in order of Eu, Nd, and Pr, that is, the nonmagnetic Eu ions having the smallest ionic radius of the three *R* elements is most harmful for superconductivity. The resistivity upturn at low temperature is most striking for Eu substitution, while weak for Nd substitution and not observed for Pr substitution, indicating that the substitution of Eu ions induces the strongest randomness on the CuO<sub>2</sub> planes of the three  $R$  ions. Considering the reported experimental fact that the Cu(*P*)-O(*A*) bond length is decreased with substitution of  $Sr^{2+}$  whose ion radius is larger than that of  $La^{3+}$ , we deduce that when *R* elements having smaller ion radius are substituted, the oxygen ions adjacent to the substituted  $R$  ions are displaced away from  $CuO<sub>2</sub>$  plane contrary to the physical pressure effect, although the lattice parameter  $c$  is decreased. Therefore, it is concluded that the suppression of  $T_c$  can be attributed to two contributions; the decrease of the Madelung site potential at

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 $O(A)$  and the random potential scattering on the  $CuO<sub>2</sub>$  plane, both of which are caused by the displacement of oxygen ions, and furthermore, the  $T_c$  drop due to the potential scattering amounts to about 76 and 63 % for Eu- and Ndsubstituted samples, respectively, leading to the experimental fact that the smaller the ion radius of the *R* element, the larger the  $T_c$  drop.

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