

**Electronic mechanism of critical temperature variation in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$** 

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We have performed systematic studies of the trend of the critical temperature  $T_c$  due to both Madelung site potential difference between in-plane oxygen and copper sites  $\Delta V_M$  and interlayer effect in the optimally doped 123 superconductors  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ .  $\Delta V_M$  is found to decrease with the increase of the trivalent rare-earth ionic radius  $r_{R^{3+}}$ . This change enhances the next-nearest-neighbor hopping integral  $t'$ , which results in the experimentally observed increase of  $T_c$  with  $r_{R^{3+}}$ . The coherent interlayer single-particle hopping  $t_\perp$  has a more profound effect than  $t'$  on the nearly linear trend of  $T_c$  as a function of  $r_{R^{3+}}$ . These results reveal the importance of the electronic origin of the rare-earth ionic size effect on  $T_c$  in this family.

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**I. INTRODUCTION**

Ever since the discovery of the high-critical-temperature (high- $T_c$ ) superconductivity on cuprate ceramics, a satisfactory theory of this singular phenomenon has not been completed. Nevertheless, several features have been shown to play a key role in the appearance of superconductivity in these materials. These are a layered crystal structure, a strong antiferromagnetic coupling between neighbor  $\text{Cu}^{2+}$  ions to form two-dimensional magnetic layers, a peculiar electronic structure, and appropriate doping of the so-called “parent compounds,” typically  $\text{La}_2\text{CuO}_4$  or  $\text{YBa}_2\text{Cu}_3\text{O}_6$ . It is widely accepted that the stoichiometric proximity between the superconducting and insulating phases and the interaction of carriers with magnetic degrees of freedom are essential for the existence of high- $T_c$  superconductivity. Inspired by the pioneering ideas of Torrance and Metzger<sup>1</sup> about the relevance of the Madelung potential in determining the insulating, semiconductor, or metallic character of a large family of oxides, researchers<sup>2,3</sup> have been intensively studying whether charge transfer within the plane is via the long-range Madelung site potentials  $V_M$ . However, if the essential physics of the cuprates within the  $\text{CuO}_2$  layers is common to all superconducting compounds, then the origin of their widely differing values of the maximum  $T_c$  must originate outside of the  $\text{CuO}_2$  layers. The long-range nature of the Madelung site potential difference between in-plane oxygen and copper sites,  $\Delta V_M$ , has the advantage of incorporating the influence of interplanar interactions, which should play a considerable role in the determination of  $T_c$ . Therefore,  $\Delta V_M$  might have the capacity to incorporate interlayer effect. However, this is still an open question.

The typical 123 family of optimally doped bilayer compounds,  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  ( $\delta \sim 0$ ), is a good candidate for investigating this topic. Since the compositions in this study are at optimal doping, the dependence of charge transfer between the chain and plane is removed.  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  is the first high- $T_c$  superconductor whose  $T_c$  is above the boiling tem-

perature of liquid nitrogen (77 K). Substitution of Y with rare-earth elements leads to a systematic variation of  $T_c$  among the optimally doped  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  series. That is, the maximum  $T_c$  modestly increases with increasing the trivalent rare-earth ionic radius ( $r_{R^{3+}}$ ).<sup>4,5</sup> Optimally doped  $\text{NdBa}_2\text{Cu}_3\text{O}_{7-\delta}$  has a  $T_c$  as high as 96 K.<sup>5</sup> Understanding this ionic size effect in these materials is very important not only because it can shed light on a possible method to increase  $T_c$  at the ambient condition through the application of chemical pressure by element substitution, but also because it may provide an important clue in determining the possible mechanism responsible for the superconductivity in high- $T_c$  cuprates. Moreover, there is growing interest in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  for industrial applications. For example, in many bulk forms and multilayer applications, Y is replaced by Nd, Sm, or other rare-earth elements.<sup>6,7</sup> Although a nice trend of the maximum  $T_c$  in  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  superconductors has been revealed previously,<sup>4,5</sup> detailed studies at the microscopic scale are missing due to the complexity of both the geometry and electronic structures.

In this paper, we investigate the variation of  $\Delta V_M$  among the nearly optimally doped  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds. We find that  $\Delta V_M$  systematically increases with an increase of the trivalent rare-earth ionic radius. This systematic increase results in an enhancement of the next-nearest-neighbor hopping integral  $t'$ , accordingly. We therefore obtain a modest increase of  $T_c$  with the rare-earth ionic radius in this series on the basis of a  $d$ -wave BCS formalism by using a three-dimensional dispersion relation. The experimentally observed several Kelvin increase of  $T_c$  can be well reproduced when we considered the interlayer single-particle hopping. Our results suggest that the rare-earth ionic size effect is an electronic origin.

**II. MADELUNG SITE POTENTIALS**

Since the parent materials of high- $T_c$  cuprate superconductors can be considered as charge-transfer insulators, ionic

bonding makes a large contribution to the lattice energy. It suggests that the methods of conventional oxides can be applied to study atomistic phenomena in cuprates. The cuprates turn into superconductors at a proper doping level and temperature. However, the charge carrier density is very low compared with that of conventional metals. In addition, the charge carriers are confined within copper-oxygen planes. Consequently, the screening effect is not so strong as that of conventional metals. In fact, many previous theoretical investigations are based on such an ionic picture, generating lots of valuable information.<sup>8</sup>

Considering that  $T_c$  varies with doping level, we should choose structures at optimal-doped composition to explore the intrinsic trend among  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . Fortunately, a systematic low-temperature neutron diffraction study of the nearly optimally doped  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds has been done by Guillaume *et al.*<sup>9</sup> Our calculations are based on these structural data. In ionic crystals, the Madelung site potential at a given site is defined as the electrostatic potential due to charge monopoles, after the charge monopole located at that site has been removed—i.e., the potential due to all other monopoles in the system. The other points remain fixed for the sake of the calculation. The present calculations were done using the Ewald method.<sup>10</sup> In the formulation of Tosi the formulas are<sup>11</sup>

$$\begin{aligned} \phi(\vec{r}'_p) &= \frac{1}{\pi v} \sum_h ' S(\vec{h}) \vec{k}_h^{-2} \exp(-\pi^2 \eta^2 \vec{k}_h^2 + 2\pi i \vec{k}_h \vec{r}'_p) \\ &+ \sum_l ' \sum_p \zeta_p \frac{1 - F\left(\frac{|\vec{r}'_p - \vec{r}_l - \vec{r}_p|}{\eta}\right)}{|\vec{r}'_p - \vec{r}_l - \vec{r}_p|} - \frac{2\zeta'_p}{\eta\pi^{1/2}}, \\ S(\vec{h}) &= \sum_p \zeta_p \exp(-2\pi i \vec{k}_h \vec{r}_p), \\ F(m) &= 2\pi^{-1/2} \int_0^m \exp(-m^2) dm, \\ m &= \frac{|\vec{r}'_p - \vec{r}_l - \vec{r}_p|}{\eta}. \end{aligned} \quad (1)$$

The symbols have the following meaning:  $\vec{r}'_p$  and  $\zeta'_p$ , position vector and charge of the point at which the potential will be calculated;  $\vec{r}_p$  and  $\zeta_p$ , position vector and charge of other ions in the unit cell;  $\vec{k}_h = h_1 \vec{a}^* + h_2 \vec{b}^* + h_3 \vec{c}^*$  is in the reciprocal space;  $\vec{r}_l = l_1 \vec{a} + l_2 \vec{b} + l_3 \vec{c}$  is in the coordination space;  $\sum'_h$  runs over integers values of  $h_1, h_2, h_3$  except the zero point;  $\sum_p$  runs over all positions;  $\sum'_l$  runs over integers values of  $l_1, l_2, l_3$  except the zero point;  $\eta$  is the half-width of the Gaussian function;  $v$  is the volume of the unit cell.

A number of investigators have made use of the ionic crystal model as a starting point for the description of the electronic structure of cuprate superconductors, since their insulating parent materials can be regarded as ionic crystal to good accuracy. The Madelung potential at each lattice site can provide important information on the structural and electronic properties of this ionic system. In particular, the dif-

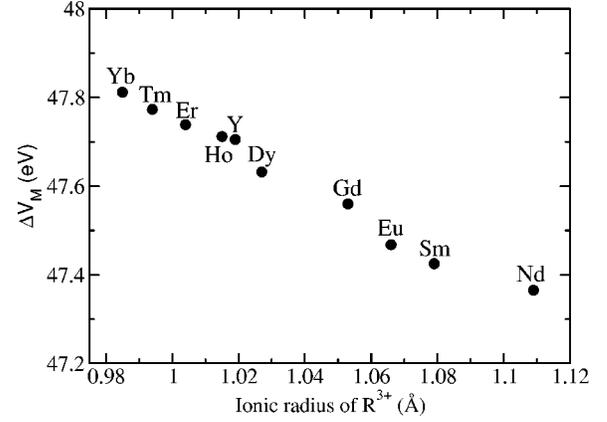


FIG. 1. Rare-earth ionic radius ( $r_{R^{3+}}$ ) dependence of the Madelung site potentials between in-plane oxygen and copper,  $\Delta V_M$ , for the nearly optimally doped  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds.

ference in the Madelung site potentials between in-plane oxygen and copper,<sup>1</sup>

$$\Delta V_M = V_M(\text{O}_{\text{plane}}) - V_M(\text{Cu}_{\text{plane}}), \quad (2)$$

has been proven to play an essential role in the characterization of the electronic structure.

Based on the neutron diffraction data of the nearly optimally doped  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ ,<sup>9</sup> we have calculated the difference of Madelung site potentials  $\Delta V_M$ . Figure 1 shows the calculated  $\Delta V_M$  as a function of the rare-earth ionic radius  $r_{R^{3+}}$ . The rare-earth ionic radii were taken from the work of Shannon.<sup>12</sup>  $\Delta V_M$  was observed to decrease with increasing  $r_{R^{3+}}$ . Considering the experimental fact that  $T_c$  modestly increases with increasing  $r_{R^{3+}}$ ,<sup>4,5</sup> our present results suggest that there is a nearly inverse linear relation between  $\Delta V_M$  and  $T_c$ . This inverse linear relation has also been observed previously in many hole-doped copper oxides.<sup>3</sup> Actually,  $\Delta V_M$  is more like a specific parameter which includes the contribution from both the apical oxygen and  $\text{CuO}_2$  plane.

Studies of charge distribution<sup>13,14</sup> have revealed that the optimal density of hole carriers  $n_H^{\text{opt}}$  decreases with increasing  $r_{R^{3+}}$  in the nearly optimally doped  $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ . This implies that both the difference of the Madelung site potentials and the hole carrier density reflect an essentially equivalent physical content. Therefore, at optimal doping, these two interesting quantities provide an effective measure of the intrinsic variation of the maximum value of  $T_c$ . That is, superconducting cuprates with larger  $T_c$  tend to have a smaller  $n_H^{\text{opt}}$  or  $\Delta V_M$ . This tendency has been found to be well held in typical monolayer cuprates.<sup>15</sup>

### III. NEXT-NEAREST-NEIGHBORING HOPPING INTEGRAL

In the following we consider the modification of the next-nearest-neighbor hopping integral  $t'$  to gain better understanding of the striking correlation between  $\Delta V_M$  and  $T_c$ . It is well established that the hole dispersion for the  $t$ - $t'$ - $J$  model is approximately given by<sup>16,17</sup>

$$\varepsilon_k = (J + 2t') \cos k_x \cos k_y + \frac{J}{4} (\cos 2k_x + \cos 2k_y). \quad (3)$$

The importance of  $t'$  has been emphasized by Lee<sup>18</sup> based on an idea that at low doping the  $t'$  term causes a different physics as compared with that of the original  $t$ - $J$  model, since a hole can propagate on the same sublattice without disturbing spins. The sign of  $t'$  in the resulting  $t$ - $t'$ - $J$  model changes between the hole and electron doping systems:  $t > 0$  and  $t' < 0$  for the hole-doped system and  $t < 0$  and  $t' > 0$  for the electron-doped system. The sign difference originates from the fact that the  $d^9$  state has a positive charge, while the  $d^{10}$  has a negative one as compared with the  $d^9$  state. Thus the location of the saddle points is largely determined by the intrasublattice hopping parameter  $t'$  rather than by  $t$  and/or  $J$ . The same holds for the flatness of the dispersion near the saddle points and thus for the width of the van Hove singularity.

The hopping parameter  $t'$  can be determined from the three- or more-band Hubbard model.<sup>17</sup> When the Cu-O hopping integral  $t_{pd}$  (between  $3d_{x^2-y^2}$  and  $p_\sigma$  orbitals) is much less than both the Cu-Cu Coulomb repulsion  $U_d$  at O site and Cu-O energy-level splitting  $\Delta$ , the dependence of  $t'$  on the initial parameters in the lowest order of  $t_{pd}/\Delta$  can be written as<sup>19</sup>

$$t' = 0.09 \frac{t_{pd}^2}{\Delta - 1.45t_{pp}} - 0.124t_{pp}, \quad (4)$$

for a hole-doped system. Here  $t_{pp}$  is the transfer integral between the nearest-neighbor oxygen  $p_\sigma$  orbitals.

The Cu-O energy-level (on O  $p_\sigma$  and Cu  $3d_{x^2-y^2}$  orbitals) splitting  $\Delta$  is given by<sup>3</sup>

$$\Delta = \frac{\Delta V_M}{\epsilon(\infty)} + \Delta_0. \quad (5)$$

Here we have taken into account the electrostatic potential changes due to the polarization of surrounding ions. Since the polarization is characterized by the dielectric factor at optical frequencies  $\epsilon(\infty)$ , representing the nonlocal charge relaxation at infinite frequencies caused by core polarization of to background ions. The Madelung site potential is approximated as  $\Delta V_M/\epsilon(\infty)$ . In addition, at the atomic limit three more quantities are needed to consider hole transfer from  $\text{Cu}^{2+}$  to  $\text{O}^{2-}$ : the second electron affinity of the  $\text{O}^{2-}$  ion, the third ionization energy of the  $\text{Cu}^{3+}$  ion, and the Coulombic interaction between the introduced electron and hole. For simplicity, they are combined into one parameter  $\Delta_0$ .  $\Delta V_M$  turns the large negative  $\Delta_0$  into the small level separation  $\Delta$  of positive sign.  $\Delta$  coincides with charge-transfer gap if there are no hopping interactions. Following Tohyama and Maekawa,<sup>20</sup> we chose the compound-independent parameters  $\epsilon(\infty) = 3.3$  and  $\Delta_0 = -10.88$  eV, which can give overall agreement with the observed values of the charge-transfer gap.

The hopping parameter  $t'$  can be directly estimated by using Eqs. (4) and (5). Recent studies<sup>15,21</sup> suggest that the appearance of apical oxygen outside the  $\text{CuO}_2$  planes affects superconductivity mainly via  $t'$ . We therefore need to include the effects of the Cu  $d_{3z^2-r^2}$  orbital and O  $p_z$  orbital at the

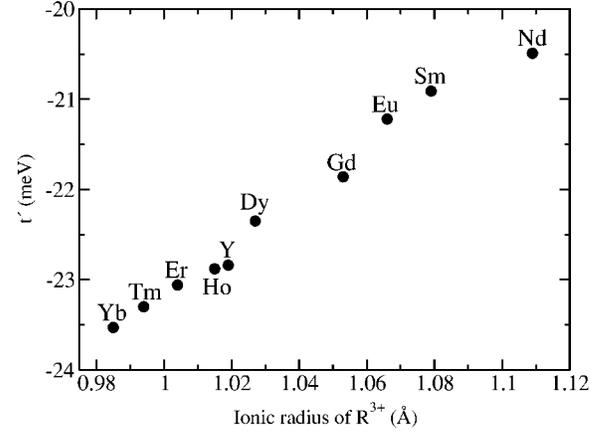


FIG. 2. Rare-earth ionic radius ( $r_{R^{3+}}$ ) dependence of the next-nearest-neighbor hopping integral  $t'$  for the nearly optimally doped  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds.

apex of the pyramid with respect to the hopping integral among those orbitals and O  $p_\sigma$  orbitals in the Cu-O plane. The apical oxygen affects the hopping integral due to new hopping processes via the hybridized states. This effect is assumed to be mainly reflected by the energy levels splitting  $\Delta$  rather than other parameters such as  $t_{pd}$  and  $t_{pp}$ , though they may contribute to the slight change of the hopping parameters in general.

We took  $t_{pd} = 1.3$  eV and  $t_{pp} = 0.65$  eV, which were estimated by the analysis of the photoelectron spectroscopy.<sup>22</sup> We then obtained the  $t'$  values using the above-determined parameters. The results are summarized in Fig. 2. As can be seen, the hopping integral  $t'$  is enhanced with increasing the rare-earth ionic radius in the nearly optimally doped  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  compounds. This systematic enhancement is mainly due to the state hybridizing between O:  $p_z$  and Cu:  $d_{3z^2-r^2}$  orbitals.<sup>23</sup> It has been found<sup>3</sup> that the superexchange interaction  $J$  does not depend significantly on the compounds. Experiments and calculations give a  $J = 0.128$  eV for cuprates.<sup>24</sup> Thus, the coefficient  $(J + 2t')$  of the  $\cos k_x \cos k_y$  term in Eq. (3) also increases with the radius of the trivalent rare-earth ion. The results confirm the previous observations<sup>15,21</sup> that a larger  $t'$  or  $J + 2t'$  is in favor of a higher  $T_c$ . Note that the optimal density of hole carriers  $n_H^{opt}$  systematically decreases with increasing  $t'$  when  $J + 2t' > 0$ ,<sup>15</sup> the present results shown in Fig. 2 indicate a modest reduction of  $n_H^{opt}$  with the increase in  $r_{R^{3+}}$  for the optimally doped  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$ . This is again self-consistent with the reported  $r_{R^{3+}}$  dependence of  $n_H^{opt}$  in this system.<sup>13,14</sup>

#### IV. CRITICAL TEMPERATURE VARIATION

Since we have established the systematic evolution of the hole dispersion in the  $\text{RBa}_2\text{Cu}_3\text{O}_{7-\delta}$  series, we are able to understand the experimentally observed variation of  $T_c$  in this series based on the developed theoretical model for the anisotropic bilayer superconductors.<sup>25</sup> Neglecting the anisotropy of interactions in both the  $ab$  direction and  $c$  direction, we obtain the  $T_c$  equation for a given chemical potential  $\mu$  (Ref. 25):

$$1 = \frac{1}{2N} \sum_k V g^2(k) (W_k^+ + W_k^-), \quad (6)$$

with  $W_k^\pm = |\xi_k^\pm - \mu|^{-1} \tanh[|\xi_k^\pm - \mu|/(2T_c)]$ , where  $g(k) = (\cos k_x - \cos k_y)/2$  and  $\xi_k^\pm = \varepsilon_k \pm t_\perp g^2(k)$ ,  $N$  is the number of  $k$  vectors,  $V$  is the in-plane pairing interaction, and  $t_\perp$  is the coherent interlayer single-particle hopping integral. The constraint condition for the hole carrier density  $n_H$  in conjunction with  $\mu$  is given by

$$n_H = \frac{1}{2} - \frac{1}{4N} \sum_k [(\xi_k^+ - \mu)W_k^+ + (\xi_k^- - \mu)W_k^-]. \quad (7)$$

Recent angle-resolved photoemission spectroscopy<sup>26</sup> and transport<sup>27,28</sup> measurements indicate the validity of this kind of  $d$ -wave BCS formalism in describing the superconducting state of high- $T_c$  superconductors.

In order to elucidate the effect of  $\Delta V_M$  and  $t'$  on  $T_c$ , we first neglect the interlayer effect by putting  $t_\perp = 0$  into Eqs. (6) and (7). Once having the knowledge of the hole dispersion  $\varepsilon_k$ , one can calculate the hole density dependence of  $T_c$  for different values of  $V$ . Thus,  $t'$  and  $V$  are only two parameters entered into Eqs. (6) and (7) to determine  $T_c$ . The basic experimental fact is that the maximum  $T_c$  increases but the optimal hole density  $n_H^{opt}$  decreases with increasing the trivalent rare-earth ionic radius in the nearly optimally doped  $RBa_2Cu_3O_{7-\delta}$  compounds. Therefore, the change of  $t'$  and/or  $V$  must reflect this experimental fact. We have examined which parameter is most probably responsible for the systematic change of both  $T_c$  and  $n_H^{opt}$ . We found that although  $T_c$  can monotonically increase with increasing  $V$ ,  $n_H^{opt}$  scarcely changes with  $V$ . However, assuming  $V$  to be compound independent but  $t'$  a dominant parameter, we obtained not only a systematic increase of  $T_c$  but also a monotonic decrease of  $n_H^{opt}$ , which is in agreement with the experiments.<sup>4,5,13,14</sup> This strongly indicates that  $t'$  is a dominant parameter for the ionic size effect, although  $V$  may vary slightly among the  $RBa_2Cu_3O_{7-\delta}$  series. It is therefore reasonable to assume  $V$  as a compound-independent parameter in this system. Furthermore, antiferromagnetic van Hove scenario has been proposed to account for many unusual normal state and superconducting properties of high- $T_c$  cuprates.<sup>29</sup> According to this scenario, the interaction  $V$  is proportional to the superexchange interaction  $J$ . A constant  $J$  chosen based on the theoretical analysis and experiments<sup>3,24</sup> is a good indicator of a compound-independent  $V$  for the cuprates. On the other hand, all cuprates, although being different, have an important common feature—namely, containing the same basis structural unit, the  $CuO_2$  plane. The driving force of superconductivity is believed to come mainly from the almost same  $CuO_2$  plane; the interlayer interaction  $V$  is expected not to be different among the cuprates. The choice of such a constant  $V$  has been recently found to be suitable in describing the variation of  $T_c$  among the hole-doped cuprates.<sup>15</sup> Thus, the assumption of a compound-independent  $V$  is physically reasonable in the present analysis.

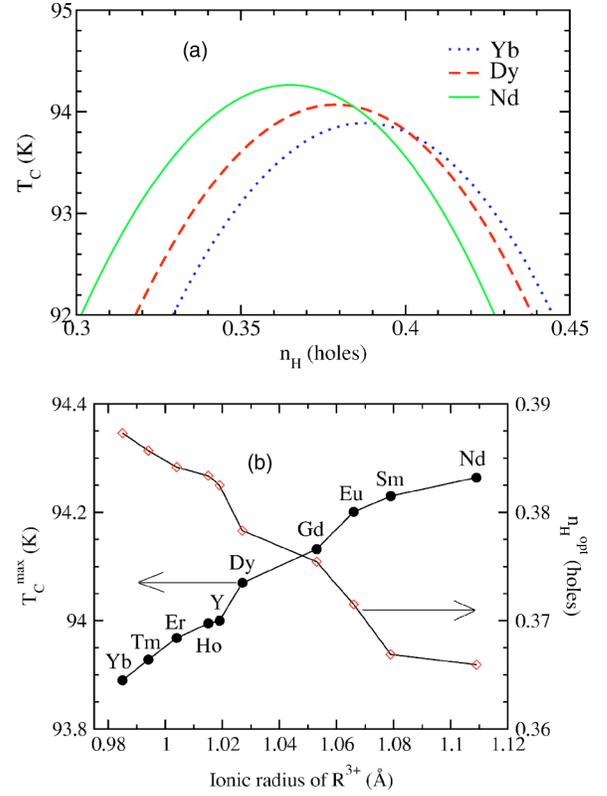


FIG. 3. (Color online) (a) Calculated critical temperature  $T_c$  versus hole carrier density  $n_H$  for selected  $RBa_2Cu_3O_{7-\delta}$  ( $R = Yb, Dy, Nd$ ) around optimal doping. (b) Rare-earth ionic radius ( $r_{R^{3+}}$ ) dependence of the maximum  $T_c$  and optimal density  $n_H^{opt}$  for the nearly optimally doped  $RBa_2Cu_3O_{7-\delta}$  compounds.

A value of  $V$  can be deduced from the experimental value of  $T_c = 94$  K for optimally doped  $YBa_2Cu_3O_{7-\delta}$ . Substituting the different hole dispersion relation into Eqs. (6) and (7), we obtain the relevant parabolic relation between  $T_c$  and  $n_H$  for various compounds. In Fig. 3(a), we plot the calculated  $T_c$  versus  $n_H$  curves for some selected  $RBa_2Cu_3O_{7-\delta}$  around optimal doping level by changing the rare-earth ion from smaller Yb through Dy to larger Nd. As clearly seen, with the increase in  $r_{R^{3+}}$ , the maximum  $T_c$  shifts to the high value at the expense of the reduction of the optimal density of hole carriers  $n_H^{opt}$ . Figure 3(b) shows the  $r_{R^{3+}}$  dependence of both the maximum  $T_c$  and  $n_H^{opt}$  for various optimally doped materials. Note that  $T_c$  modestly increases with increasing  $r_{R^{3+}}$ . The theoretical results are consistent with the experiments,<sup>4,5</sup> though the change of  $T_c$  is not significant. The obtained systematic reduction of  $n_H^{opt}$  with the rare-earth ionic radius also agrees well with the previous reports.<sup>13,14</sup> It is therefore indicated that the observed rare-earth ionic size effect on  $T_c$  in the optimally doped  $RBa_2Cu_3O_{7-\delta}$  is in reality due to the modification of the hole dispersion through changing  $t'$ .

A direct modification of the substitution of the trivalent rare-earth ion is the distance between the adjacent nearest  $CuO_2$  planes within a unit cell ( $d_{CuO_2}$ ). Neutron data<sup>9</sup> show a 7.2% increase of  $d_{CuO_2}$  from  $YbBa_2Cu_3O_7$  to  $NdBa_2Cu_3O_7$ . The interlayer coupling is then expected to play an important role in the variation of  $T_c$  in these materials. The increased

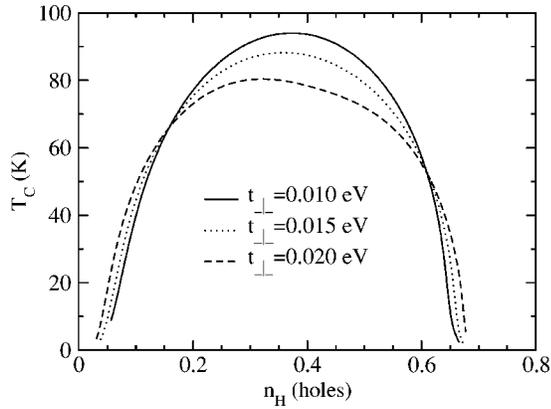


FIG. 4. Calculated critical temperature  $T_c$  versus hole carrier density  $n_H$  for  $t_{\perp}=0.010, 0.015,$  and  $0.020$  eV, respectively.  $V$  was chosen to give a maximum  $T_c$  of 94 K for a compound with  $t_{\perp}=0.010$  eV.

$d_{CuO_2}$  with trivalent rare-earth ionic radius would lead to the decrease of the interlayer single-particle hopping integral  $t_{\perp}$ . Optical measurements indicate a value of  $t_{\perp}$  in the range of 0.003 and 0.040 eV for  $YBa_2Cu_3O_{7-\delta}$ .<sup>30</sup> We have examined how  $T_c$  varies with the interlayer parameter  $t_{\perp}$ . Figure 4 shows that  $T_c$  is suppressed by increasing  $t_{\perp}$  around the optimal doping. It is clear that, at optimal doping, the increasing interlayer distance  $d_{CuO_2}$  with  $r_{R^{3+}}$  would result in the enhancement of  $T_c^{max}$  due to the reduction of  $t_{\perp}$ .

Assuming that  $t_{\perp} \propto d_{CuO_2}^{-2}$ , we would estimate the evolution of  $T_c$  with the interlayer effect. Taking the optimally doped  $YBa_2Cu_3O_{7-\delta}$  as a reference material, we have  $t_{\perp} = t_{\perp}^Y (d_{CuO_2}^Y / d_{CuO_2})^2$ . Using the experimentally observed  $d_{CuO_2}$  from neutron diffraction,<sup>9</sup> we can calculate the systematic change of  $T_c$  for various compounds once giving a value of  $t_{\perp}^Y$ . Figure 5 shows the rare-earth ionic radius dependence of  $T_c^{max}$  in the optimally doped  $RBa_2Cu_3O_{7-\delta}$  compounds for  $t_{\perp}^Y=0.010$  and  $0.020$  eV, respectively. In both cases,  $V$  was taken to yield a maximum  $T_c$  of 94 K for  $YBa_2Cu_3O_{7-\delta}$ . We also plot the relevant  $d_{CuO_2}$  evolution with the rare-earth ionic radius in the inset of Fig. 5. We noticed that the enhanced interlayer single-particle hopping greatly enlarges the difference of  $T_c^{max}$  from  $YbBa_2Cu_3O_7$  to  $NdBa_2Cu_3O_7$ . When  $t_{\perp}=0.020$  eV, the calculated  $T_c^{max}$  of 92.7 and 96.5 K for  $YbBa_2Cu_3O_7$  to  $NdBa_2Cu_3O_7$ , respectively, are in good agreement with the experimental values of 92.5 and 96.0 K.<sup>5</sup> The experimental observed several Kelvin increase of  $T_c^{max}$  with the rare-earth ionic radius<sup>4,5</sup> is therefore well reproduced by considering the interlayer effect. This further follows that the rare-earth ionic size effect in  $RBa_2Cu_3O_{7-\delta}$  compounds is an electronic origin.

## V. CONCLUSIONS

We have carried out systematic studies of the critical temperature  $T_c$  variation originating from the Madelung site po-

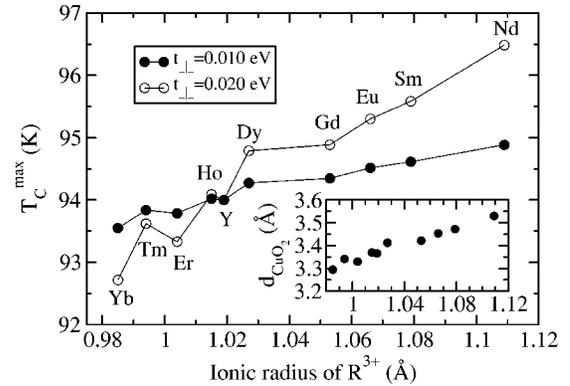


FIG. 5. Rare-earth ionic radius ( $r_{R^{3+}}$ ) dependence of the maximum critical temperature  $T_c$  calculated by using  $t_{\perp}^Y=0.010$  and  $0.020$  eV, respectively. The inset shows the  $r_{R^{3+}}$  dependence of the distance between the adjacent nearest  $CuO_2$  planes,  $d_{CuO_2}$ , for the nearly optimally doped  $RBa_2Cu_3O_{7-\delta}$  compounds.

tential difference between in-plane oxygen and copper sites,  $\Delta V_M$ , and from the interlayer effect for the family of the optimally doped  $RBa_2Cu_3O_{7-\delta}$  cuprates. It turns out that the apical oxygens notably modify the O:  $p$ -hole-band structure, which leads to the systematic reduction of  $\Delta V_M$  with an increase of the trivalent rare-earth ionic radius. This change enhances the next-nearest-neighbor hopping integral.  $T_c$  is in turn enhanced due to the shortened apical O in-plane Cu distance with increasing the rare-earth ionic radius. This trend is consistent with the experiments, although the magnitude of the variation of the maximum  $T_c$  due to the change of  $t_{\perp}$  is not significant. Note that there exist significant effects of the adjacent nearest  $CuO_2$  separation on interlayer coupling. We found that the interlayer single-particle hopping integral is the dominant factor responsible for the trend of the maximum  $T_c$  in the optimally doped  $RBa_2Cu_3O_{7-\delta}$  cuprates. This suggests that the Madelung potential studies give the correct physics in a qualitative picture. To reach quantitative agreement, the interlayer effect has to be included. Our approach has another more important impact in that it permits a fast prediction of the effect of a given structural modification in the  $T_c$  for searching new superconducting oxides. For example, it is a promising direction to increase  $T_c$  through enlarging the adjacent nearest  $CuO_2$  separation which could be realized by carefully doping larger trivalent ion at the Y site.

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