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Apex oxygen and critical temperature in copper oxide superconductors: Universal correlation with the stability of local singlets

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Electronic-energy-level structures of the layered Cu oxide compounds are drawn within the ionic model. Correlations between the level separations obtained and the superconducting critical temperature T_c are examined for all families of the Cu oxide superconductors. It is proposed that the position of the energy level of the apex oxygen atoms is of primary importance for the electronic states of the CuO_2 plane and governs the optimum T_c's of all families of hole-carrier suprconductors. The pressure effect of T_c is discussed within this framework. Based on cluster-model calculations, where the covalency neglected in the ionic model is fully taken into account, we argue that the role of the apex oxygen atoms is to prescribe the stability of local singlet states made of two holes in the Cu $3d_{x^2-y^2}$ and O $2p_\sigma$ orbitals of the CuO_2 plane, and thereby to control the maximum T_c of each family.

I. INTRODUCTION

Many Cu oxide superconductors have been discovered so far. Among the variety of their layered structures,[1] the hole-carrier superconductors contain the CuO_2 plane with apex oxygen atoms as a common structural unit. It is either pyramidal or octahedral copper coordination whose apical sites are occupied by oxygen atoms. It has been observed[2-5] that the superconducting critical temperature T_c changes universally as a function of the doping rate p of the CuO_2 plane: the antiferromagnetic long-range order disappears at $p \simeq 0.04$ (per unit CuO_2) and T_c shows a maximum uniquely at $p \simeq 0.15-0.2$. However, the maximum T_c's are dispersed from 40 K in the La family, 90 K in the Y family, to 125 K in the Tl family. An obvious question is what is the decisive factor that governs the maximum T_c of each family.

One of the important directions for studying the mechanism of high-T_c superconductivity is to extract systematics from a large database complied for the Cu oxides. We construct a database for this purpose and present it in the Appendix. In this paper we examine the maximum T_c's among a number of measured quantities because T_c is always measured and most directly related to the mechanism of superconductivity. A number of empirical variables to scale with T_c have been proposed so far. They include electronegativity,[6,7] bond lengths,[8,9] interlayer spacings,[10,11] bond-valence sums,[12,13] and carrier numbers.[2-5,14,15] Some[2-5,9,12] are used within each family of superconductors and others[6-8,10,11,13-15] are applied over the different families. A meaningful correlation must, however, be compatible with the microscopic description of the electronic states of the CuO_2 plane which are characteristic of the strong electron correlation.[16,17] Useful suggestions for the elucidation of the mechanism will be made only through such a successful correlation.

In this paper we extract a variable which governs the maximum T_c on a quantum-mechanical microscopic basis. Any mechanism for high-T_c superconductivity may be constructed basically upon the electronic-energy-level structure by which the dynamics of the carriers are constrained. It is thus important to see how the change in the energy-level structure affects the superconducting properties including the T_c. The ionic model has successfully been used for describing the carrier distributions[18-22] and for their characterization.[23] We will show in this paper that the Madelung site potential calculated in the ionic model may be a direct measure of the one-body energy level of each orbital. The positions of the energy levels for the $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals of copper and the $2p$ orbitals of apex and in-plane oxygen atoms are estimated quantitatively for each parent compound. The correlation between the obtained level structures and the T_c's are thus examined. Our brief reports may be seen in Refs. 24 and 25.

Importance of the role of apex oxygens in high-T_c superconductivity has been suggested in several experiments and theories.[26-30] For example, it is empirically known that the presence of apex oxygen atoms makes the CuO_2 plane easier to dope with holes; compounds with the square coordination have not yet been doped successfully but those with the octahedral coordination have been made overdoped.[2] Another example is the pressure effect of T_c; the superconductors with the apex oxygen atoms, e.g., the T^*-phase superconductor with the pyramidal copper coordination, show a very large pressure enhancement of T_c, whereas, in the T'-phase superconductor which has no apex oxygen atoms, the pressure coefficient of T_c is negligibly small.[27] In this paper we will propose a new scaling variable of T_c, i.e., ΔV_A. ΔV_A is the difference in the Madelung site potentials for a hole between the apex and in-plane oxygen atoms and a measure of the position of the energy level of the p_z orbital on apex oxygens. We will show that ΔV_A is a primary parameter for the electronic states of the CuO_2 plane and governs the optimum T_c's throughout all the families of Cu oxide superconductors. It will be shown that the pressure effect of T_c may be understood within this framework. Some suggestions for the material designing will also be made.

Another important aspect of the electronic states of the CuO_2 plane, which is not taken into account in the ionic model, is covalency. We examine its importance in terms of the cluster-model calculation. This approach has been used successfully[17,30–33] for explaining the local electronic states of the highly correlated electron systems. The antiferromagnetic superexchange interaction J and transfer energy of the Zhang-Rice local singlet[34] t has been evaluated by this approach.[30–33] They are the parameters of the so-called t-J model.[16] The t-J model has been used[31,35] for explaining dynamical properties of the hole introduced into the CuO_2 plane, and is one of the candidates for explaining the pairing mechanism in high-T_c superconductors. We will employ the cluster-model approach to calculate the electronic states of the CuO_2 plane, and show that the transfer parameter of the local singlet t is controlled primarily by the energy level of apex oxygens (or ΔV_A). The local singlet is well defined and stable when the energy level of the apex oxygen atoms is sufficiently high, but with its decrease other components are mixed up with the singlet and destabilize the local-singlet picture. The decrease in t is associated with this destabilization. We argue that the T_c versus ΔV_A correlation is a direct consequence of this effect.

The rest of the paper is organized as follows. In Sec. II we describe the ionic model and deduce quantitatively the energy-level structure of the CuO_2 plane plus the apex oxygen atoms for the large variety of Cu oxide compounds. In Sec. III we examine correlations between the maximum T_c's and energy-level separations. We show that the parameter ΔV_A is of primary importance and governs the maximum T_c's. In Sec. IV we take the model for high-T_c superconductivity and examine the T_c versus ΔV_A correlation further in terms of the cluster-model calculation. We argue that the stability of Zhang-Rice local singlet is the essence of the correlation with T_c. Conclusions are given in Sec. V. In the Appendix we give the database of Cu oxides on which our calculations are based.

II. ENERGY-LEVEL SCHEME IN IONIC MODEL

We employ the ionic model; i.e., the crystal is supposed to be an assembly of polarizable point charges. Justifications of the model may be given from the following considerations: (i) The system is a charge-transfer-type insulator[36] when there are no carriers in the CuO_2 plane, for which the ionic model description is an acceptable starting point. Even if a small number of carriers are introduced, the ionicity may persist strongly. (ii) The ionicity between the layers is retained predominantly even though the covalency within the CuO_2 plane is rather strong. The latter (ii) may be why their carrier distribution has been explained successfully by the ionic model.[18,19] (iii) Band calculations provide the same tendency for the electronic-level structures as the ionic model provides. We will see this point in Sec. III. In this section we show that the parameters characterizing the electronic states, especially the energy-level structures, may be extracted for the Cu oxide compounds within the framework of the ionic model.[37] The energy levels are given in the hole representation throughout this paper.

A central role is played by the Madelung site potentials. The Madelung potential for a hole at the i site is defined for a given assembly of point charges $\{Z_j\}$ as

$$V_i=\sum_{j\neq i}\frac{Z_je^2}{|\mathbf{r}_j-\mathbf{r}_i|}\ , \tag{1}$$

where $\mathbf{r}_j$ is the position of jth ion and Z_je is its associated charge. We assume the lattice periodicity and total charge neutrality $\sum_j Z_j=0$. The standard Ewald method[38] is used for the lattice summation. V_i is the electrostatic energy to bring a hole from infinity to the i site. Note that the potential from the ith ion itself is excluded in V_i; we count it in the atomic ionization or electron affinity energy. In the actual systems we should take into account the reduction of the Madelung site potential due to the polarization of surrounding ions. Because the polarization is characterized by the dielectric constant at optical frequencies $\epsilon(\infty)$, the effective Madelung site potential is expressed as $V_i/\epsilon(\infty)$.

We focus our attention on the CuO_2 plane plus the apex oxygen atoms. It is the charge-transfer-type insulator when there are no extra holes (or when the formal valence states are Cu^{2+} and O^{2-}). We are to draw its energy-level structure. The so-called d-p model description[39] of the CuO_2 plane is referred to for this purpose. Hereafter we denote the in-plane copper and oxygen as Cu(P) and O(P), respectively, and the apex oxygen as O(A).

First we consider the energy to introduce a hole into a Cu(P) site of the undoped CuO_2 plane. Demanding consistency between the d-p and ionic models, we write it as

$$\varepsilon_d+U_d=V_{\mathrm{Cu}(P)}/\epsilon(\infty)+I_{\mathrm{Cu}}(3)\ , \tag{2}$$

where U_d is the Coulombic repulsion when two holes are on a Cu(P) site and $I_{\mathrm{Cu}}(3)$ is the third ionization energy of copper. The potential for a hole introduced into an O(P) site is similarly written as

$$\varepsilon_p=V_{\mathrm{O}(P)}/\epsilon(\infty)+A_{\mathrm{O}}(2)\ , \tag{3}$$

where $A_{\mathrm{O}}(2)$ is the second electron affinity of oxygen.

The energy-level difference Δ may be defined in the ionic model as the energy required to move a hole of the undoped Cu(P) site to one of the neighboring O(P) sites. Since this is the energy to introduce an electron into Cu(P) and a hole into O(P), we obtain

$$\Delta=\Delta V_M/\epsilon(\infty)-I_{\mathrm{Cu}}(2)+A_{\mathrm{O}}(2)-e^2/d_P \tag{4}$$

with

$$\Delta V_M = V_{O(P)} - V_{Cu(P)} \ , \tag{5}$$

where $I_{Cu}(2)$ is the second ionization energy of copper. We note that the Coulombic attraction between the introduced electron and hole, $-e^2/d_P$ [where d_P is the Cu(P)-O(P) bond length], must be taken into account since this energy is not included in Madelung site potentials. We will see in Sec. III C that ΔV_M (or Δ) is a measure of the charge-transfer gap E_g. The energy ε_d may be defined as

$$\varepsilon_d = \varepsilon_p - \Delta \ . \tag{6}$$

This energy corresponds to the energy of the d level of the d-p model.

From Eqs. (1)–(6) we find the on-site Coulomb repulsion on the Cu(P) site to be written as

$$U_d = I_{Cu}(3) - I_{Cu}(2) - e^2/d_P \ , \tag{7}$$

where we note that the atomic Coulomb repulsion

$$U_{atom} = I_{Cu}(3) - I_{Cu}(2)$$

is reduced by e^2/d_P. The value of U_d determined from the experimental ionization energies of copper, $U_d = 9.0$ eV, is consistent with the values determined from the analysis of the photoemission spectroscopy.[33,39]

The energy level of O(A) relative to ε_p may be written as

$$\Delta\varepsilon_A = \Delta V_A / \epsilon(\infty) \tag{8}$$

with

$$\Delta V_A = V_{O(A)} - V_{O(P)} \ . \tag{9}$$

We will emphasize the importance of ΔV_A in connection with the superconducting critical temperature T_c.

The crystal-field splitting of the d orbitals of Cu(P) may also be calculated from the spatial variation of the Coulombic potentials around the Cu(P) ion. Here we take six points along the Cu(P)-O(P) and Cu(P)-O(A) bond directions at which the atomic wave function of the copper 3d orbital is maximum [or at points 0.32 Å apart[40] from the Cu(P) site], and evaluate the Madelung potentials there. We define ΔV_d to be an average of the potential differences, those along the Cu(P)-O(A) bond direction minus those along the Cu(P)-O(P) bond directions. The crystal-field splitting of the copper 3d orbital may thus be approximated as

$$\Delta\varepsilon_d = \Delta V_d / \epsilon(\infty) \ . \tag{10}$$

Thus, in terms of $\varepsilon_d + U_d$, Δ, $\Delta\varepsilon_A$, and $\Delta\varepsilon_d$, we can draw the energy-level scheme for the CuO$_2$ plane plus O(A) quantitatively. We see that the whole crystal structure affects the energy-level positions; the position of the energy level of O(A) is especially very sensitive to the structure. The energy-level scheme obtained is illustrated schematically in Fig. 1.

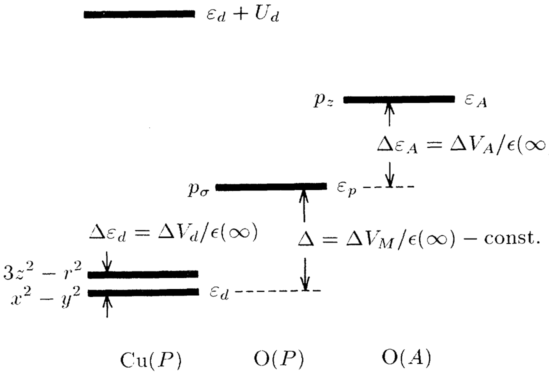

FIG. 1. Schematic energy-level structure of a hole on the CuO$_2$ plane plus the apex oxygen atoms deduced from the ionic model. The constant in Δ is given in Eq. (4), and U_d is expressed by Eq. (7).

Contributions which we have not taken into account so far are twofold: (i) the covalency due to hopping of holes and (ii) the local Coulombic and exchange interactions appearing due to the hopping. Such quantum-mechanical effects are examined by the cluster-model calculation in Sec. IV. Note that the hole-hole repulsion in the doped compounds should be taken into account as an additional Coulombic interaction, not as a change in the Madelung site potentials. Such an interaction among moving holes is subject to the strong dynamical screening.

The Madelung site potentials are calculated for the parent compounds so that we can draw their energy-level structure. We consider that the information concerning the maximum T_c's of superconductors, which are attained when they are optimally doped, is already contained in their parent compounds. The well-defined parent compounds exist in most cases; e.g., La$_2$CuO$_4$ for the La$_{2-x}$Sr$_x$CuO$_4$ superconductor. They are the undoped compounds whose CuO$_2$ plane is directly doped when a hole is introduced. However, care must be taken in some cases. In Tl monolayer families, a compound TlBa$_2$YCu$_2$O$_7$ which has Y in place of Ca, for example, could be called a parent since no holes are doped in the CuO$_2$ plane. But holes introduced by the Ca substitution for Y first sit on the Tl layer rather than the CuO$_2$ plane.[19] Here we do not adopt such a compound for the parent because the carrier distributions are rather different from those in the optimally doped superconducting compound. In Tl double-layer families, it has been suggested[19,41–43] that the change in the valence of the TlO layer produces a small number of holes (self-doping). In such cases we adopt the hypothetically undoped compounds, i.e., the compounds with Tl^{3+}. Collected compounds and their parents are summarized in the Appendix. They cover all the representative families of the layered Cu oxides including electron-carrier as well as hole-carrier superconductors. Assigned ionic charges and crystal structures used for the calculation are also listed. Note that most of the compounds have been well examined by experiment and their maximum T_c's are well settled, but some are still under examination. We list here the present best available data.

Calculated results for the differences in Madelung site potentials ΔV_A, ΔV_M, and ΔV_d, are summarized in the

Appendix. To evaluate the energy levels from Eqs. (2)–(10), we further need the values of $\epsilon(\infty)$, $I_{\mathrm{Cu}}(2)$, and $A_{\mathrm{O}}(2)$. We assume that $\epsilon(\infty)=3.5$ and

$$I_{\mathrm{Cu}}(2)-A_{\mathrm{O}}(2)+e^2/d_P=10.9 \text{ eV}$$

independently of compounds. These values are determined[30] through the cluster-model calculation (see Sec. IV) so as to fit the energies of the charge-transfer gap E_g (see Sec. III C) of the T-, T', and T^*-phase compounds measured from the optical conductivity experiment.[44] This value of $\epsilon(\infty)$ agrees with values for the usual transition-metal oxides. The on-site Coulomb repulsion U_d is determined in Sec. IV. The obtained energy ranges for the energy-level separations are $2.3 \lesssim \Delta \lesssim 3.3$, $-0.8 \lesssim \Delta\varepsilon_A \lesssim 3.6$, and $0.2 \lesssim \Delta\varepsilon_d \lesssim 0.3$ eV. They are consistent with the values usually supposed. A large variation in $\Delta\varepsilon_A$ among families reflects the variety of their constituent layer types, especially those above O(A) and/or below Cu(P). The layers containing O(A), such as the BaO and SrO layers, are characteristic of the strong ionicity and thus the energy level of O(A) directly reflects the electrostatic potentials from the layers above O(A).

III. FACTORS GOVERNING T_c

In this section we examine correlations between the energy-level structure derived in Sec. II and the observed maximum T_c's. We first take the variables ΔV_A in Sec. III A and demonstrate a clear correlation with the T_c's. In terms of this correlation we discuss the pressure effect of T_c in Sec. III B. Correlations with other level separations are examined in Sec. III C by taking the variables ΔV_M and ΔV_d. Correlations with the Cu(P)-O(P) and Cu(P)-O(A) bond lengths are also examined. We hope that the factors governing the T_c's will thus be revealed.

A. T_c versus ΔV_A correlation

The maximum T_c's of hole-carrier superconductors, which have been achieved by optimum doping, are plotted in Fig. 2 as a function of ΔV_A. We find that T_c scales very well with ΔV_A; all the compounds (except Z, see below) are located in the shaded area which exhibits a characteristic curve. The curve indicates that (i) compounds with a larger ΔV_A have a higher T_c, (ii) T_c appears at $\Delta V_A \simeq -2$ eV and increases rapidly with increasing ΔV_A, (iii) below this threshold the system is metallic but not superconducting, and (iv) the curve tends to have a smaller gradient $dT_c/d\Delta V_A$ for larger ΔV_A. We call this correlation the T_c versus ΔV_A correlation and the characteristic curve the T_c versus ΔV_A curve. We consider that this is not just an empirical correlation but the energy level of the apex oxygen atom plays an essential role in the electronic states of the doped holes and thereby determines the maximum T_c's. In Sec. IV we will examine the origin of this correlation on the basis of the cluster-model calculation and propose that the correlation comes from the stability of Zhang-Rice local singlet.

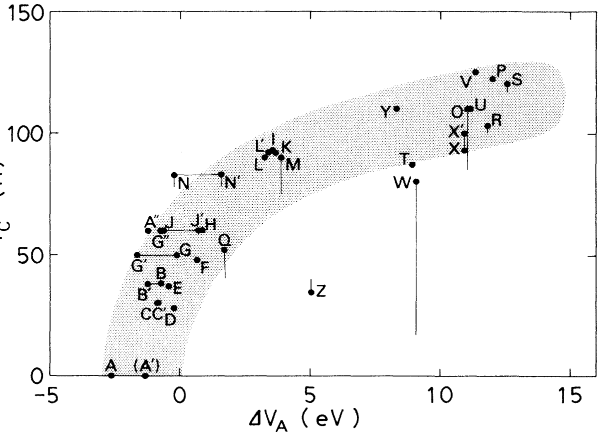

FIG. 2. The T_c vs ΔV_A correlation. Compounds labeled A–Z are summarized in the Appendix.

Let us give some descriptions of the plotted compounds. For detailed descriptions see the Appendix. Compound A, $La_2SrCu_2O_{6.2}$, is known to be metallic but not superconducting.[45] We attribute the reason to a large negative value of ΔV_A. This does not mean that the holes are introduced into O(A)'s instead of the CuO_2 plane. We see that most of the holes are in the CuO_2 plane because of the lowering of the energy level of O(P) due to the strong covalency between O(P) and Cu(P). We will show in Sec. IV that the Zhang-Rice local singlet, which is argued to be essential for the superconductivity, becomes unstable for such a small value of ΔV_A. Compound A', $La_2CaCu_2O_6$, is isostructural to A. This compound is not superconducting simply because there are no holes in the CuO_2 plane.[46] The position of A' in Fig. 2 suggests that it will become superconducting if the hole doping an be operated successfully. In Fig. 2, point A' is enclosed in parentheses in this sense.

Compounds B and C are the well-known La families of superconductors, where the CuO_2 plane has the octahedral coordination. Compounds D and E are of the so-called T^* phase. The ionic charge is assigned for each site by taking into account the observed site occupancy.

Compounds G, H, and I are the Y family of superconductors, $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.11}$,[47] $YBa_2Cu_3O_{6.5}$, and $YBa_2Cu_3O_7$, respectively. These three points are clearly on the T_c versus ΔV_A curve. This family provides a possibility to separate the structural effect on the magnitude of T_c from the hole concentration effect. Compound G is tetragonal with $T_c=50$ K. Very few oxygens are in the chain block. Cu ions in this block are in the Cu^{1+} valence state. On the contrary, compound I is orthorhombic with $T_c=93$ K. The lattice constants and bond lengths are significantly different from those of G. The parent compound adopted is orthorhombic $YBa_2Cu_3O_{6.5}$ where the CuO chains with Cu^{2+} and O^{2-} are formed. The difference in ΔV_A between these two compounds amounts to ~4 eV, which we argue is the origin of the difference in T_c. Compound H is the so-called 60-K-class Y-family superconductor. Here we assume that oxygen atoms are randomly distributed without forming the chains and the structure is tetragonal. The parent compound adopted is $YBa_2Cu_3O_{6.5}$. A formal ionic charge is assigned in each ion. We thus argue that not only p but the structure that determines ΔV_A is also an important factor governing the magnitude of T_c in this family.

The compounds $R-V$ are the Tl families and X and Y are the Bi families of superconductors, respectively. The large values of ΔV_A are common in these high-T_c compounds. The CuO_2 layer inserted between the two pyramidal CuO_2 layers, in e.g., $Tl_2Sr_2Ca_2Cu_3O_{10}$, which has no apex oxygen atoms, are quite depleted of holes as shown by a number of studies.[19,48] Here we take the CuO_2 plane next to the apex oxygen atoms to be active in superconductivity.

Compounds R, $TlBa_2CaCu_2O_{7-\delta}$, and I, $YBa_2Cu_3O_7$, are isostructural to each other if the TlO layer in R is identified with the CuO chain layer in I. Note, however, that the maximum T_c of R (~ 100 K) is considerably larger than that of I (~ 90 K). An important structural difference is that the Tl^{3+} and Ca^{2+} sites in R are occupied, respectively, by Cu^{2+} and Y^{3+} ions in I. This site selection of cations produces a significant difference in the electrostatic potentials and leads to different values of ΔV_A. We argue that these two classes of T_c's are due to this difference in ΔV_A. The comparison between these two families thus supports our electrostatic viewpoint on T_c and may provide a suggestion to material designing for obtaining higher T_c's.

Compound Z, $Bi_2Sr_2(Gd_{1-x}Ce_x)Cu_2O_{10+y}$, shows a very low T_c.[49] The number of holes so far doped in experiment[50] is rather small ($p \lesssim 0.1$); we expect a higher T_c at optimum doping, which can be consistent with our correlation. The experiment also suggests a valley in T_c versus p curve, which may be another reason of the low T_c. Further experimental works are desired.

Compounds B, C, Q, T, and W are of the octahedral copper coordination. All of these points are on the T_c versus ΔV_A curve, indicating that the T_c's are not simply related to the copper coordination. $La_{1.8}Sr_{0.2}CuO_4$ and $Tl_2Ba_2CuO_6$ are typical examples with lower and higher T_c's, respectively.

The trend that the compounds with a higher T_c have larger ΔV_A is also seen in the results of band calculation. Although the band calculation in the local-density approximation does not describe the highly correlated electron systems well, the ground-state charge density can be determined self-consistently and the covalency, as well as ionicity, is taken into account. A complementary knowledge to the ionic model may thus be extracted from the results of the band calculation.[51] Comparing the results[52-54] for a number of compounds, we note that the local density of states of electrons on O(A) apparently shifts to lower energies (by up to ~ 2 eV) in accordance with the increase in T_c (or with La→Y→Bi→Tl families). This is consistent with the T_c versus ΔV_A correlation. This means that the effect of the Madelung term contained in the band calculation persists under the effect of covalency. These results also imply that the ionicity between the layers remains strong in the layered Cu-oxide compounds.

Through the perspective obtained in the above discussions, we note that the rather local geometry of the ions surrounding the CuO_2 plane has comparatively large contributions to the Madelung site potentials. It may thus be possible to make some suggestions useful for material designing, especially how to synthesize compounds with higher T_c. They are (i) to arrange cations with a higher valence in the O(A) side, (ii) to arrange cations with a smaller valence below the CuO_2 plane of the pyramidal coordination, (iii) to put O(A) close to the CuO_2 plane by applying pressures (see Sec. III B for details). This may be the case for $YBa_2Cu_4O_3$, but we note that smaller Cu(P)-O(A) bond lengths do not necessarily mean large ΔV_A (see Sec. III C). The whole structure is important. (iv) The last is to dope the square-coordinated CuO_2 planes [without O(A)'s] with holes. Although such suggestions may be possible, we should note that the T_c versus ΔV_A correlation has a rather broad width and thus the origin of the width must be clarified first of all. We hope that the experimental works will be made in the directions suggested above and will provide stringent tests on the T_c versus ΔV_A correlation.

B. Pressure effect of T_c

Applied pressure generally enhances T_c in hole-carrier superconductors.[27] An issue is whether this effect can be explained in terms of the change in p, the hole concentration in the CuO_2 plane due to charge redistribution. If the T_c enhancement is just due to the effect of the change in p, then nothing new may be seen through the pressure experiments since the same effect has been seen in the substitution and oxidation experiments. However, Hall-effect measurements[55,56] suggest that p does not change due to pressure. T_c enhancements are observed in optimally doped (and even overdoped) samples.[56] The chemical pressure with fixed p also changes T_c.[57] These experimental facts indicate that changes in the electronic states other than the change in p play an essential role in the pressure effect of T_c. In this subsection we consider the pressure effect of T_c in terms of the T_c versus ΔV_A correlation.

Take the ionic model and let the lattice compression be uniform, then ΔV_A simply scales with the change in volumes without inducing the charge redistribution. This effect is rather small, $d\Delta V_A/dP \simeq 9.4\times 10^{-3}$ eV/GPa, for a compound with $\Delta V_A \simeq 3.2$ eV if we assume a bulk modulus of 1.14 Mbar,[58] so that we can expect a rather small change in T_c. However, let the shortening of the Cu(P)-O(A) bond be a major effect of pressure, as in $YBa_2Cu_4O_8$ (see below),[26] then ΔV_A increases largely due to the decrease in the hole potential of Cu(P). We thus expect a larger enhancement of T_c. We consider that the important part of the pressure enhancement of T_c is explained in terms of this increase in ΔV_A. If the crystal has the reservoir block with holes, then p may increase due to charge flow.[59] The increase in p, however, does not always mean the enhancement of T_c as mentioned above.

In a quantitative argument, e.g., in $YBa_2Cu_4O_8$, a measured[26] distortion

$$d\ \ln d_A/dP \simeq -2.5\%/\mathrm{GPa}$$

[where d_A is the Cu(P)-O(A) bond length], a calculated change

$$d\Delta V_A/d\ \ln d_A = -14.7\ \mathrm{eV}$$

(where only the shift of d_A is taken into account), and a gradient roughly estimated from Fig. 2,

$$dT_c/d\Delta V_A \simeq 10\ \mathrm{K/GPa}\ ,$$

lead to a theoretical value of

$$dT_c/dP \simeq 3.7\ \mathrm{K/GPa}\ .$$

If we use the structural data[26] of the whole crystal at 1 GPa then we obtain $d\Delta V_A/dP \simeq 0.12$ eV/GPa, which leads to an estimation of

$$dT_c/dP \simeq 1.2\ \mathrm{K/GPa}\ .$$

Experimentally, the pressure coefficient of

$$dT_c/dP \simeq 2.6\text{–}5.5\ \mathrm{K/GPa}$$

has been reported[26,60] in $Y_{1-x}Ca_xBa_2Cu_4O_8$ depending on x or the hole concentration, and even in optimally doped samples dT_c/dP seems not to vanish.[60] Our results are thus consistent with experiment. The separation between the intrinsic structural effect and the hole-concentration effect should be clarified through further experimental studies.

A trend has been found[27] that the pressure derivatives of T_c (or $d\ \ln T_c/dP$) observed for various hole-carrier superconductors scale with the T_c's of the compounds onto a decreasing line (see Fig. 4 of Ref. 27); i.e., the compounds with lower T_c's show larger pressure dependence and those with higher T_c's show smaller dependence. Supposing that the pressure derivatives of ΔV_A are not quite dependent on compounds, we may argue that this trend is consistent with the T_c versus ΔV_A curve because the gradient of the curve decreases with increasing ΔV_A.

The negligible pressure coefficient of T_c in the T'-phase compound,[27] which suggests the importance of the role of O(A) played in the pressure enhancement of T_c, is also understood within the present framework. This system does not contain O(A)'s whose effect, we argue, works to enhance the T_c.

We therefore consider that the intrinsic part of the pressure effect of T_c may be understood in terms of the change in ΔV_A, or the position of the energy level of O(A), induced by the structural change. Detailed structural data for various compounds under pressures are required for further investigations. The experimental studies which enable one to separate the intrinsic structural effect on T_c from the hole-concentration effect are especially highly desired.

C. Other correlations

We examine possible correlations between the T_c and other level separations, namely, Δ and $\Delta\varepsilon_d$, which relate to ΔV_M and ΔV_d, respectively. The T_c's are plotted in Figs. 3(a) and 3(b) as a function of ΔV_M and ΔV_d. Fair correlations may be seen: the compounds with a higher T_c have a smaller value of ΔV_M and/or a larger value of ΔV_d. The former correlation with ΔV_M has been noticed in the band calculation.[52] As for the latter T_c versus ΔV_d correlation, we notice, by comparing Fig. 3(b) with Fig. 2, that the change in ΔV_d is in rough connection with the change in ΔV_A. This is because the Coulombic potential around Cu(P) reflects the potential difference between O(A) and O(P). In Sec. IV we will show that the effect of ΔV_d is rather small and unimportant.

Torrance and Metzger have argued in their pioneering work[23] that the Madelung site potential ΔV_M plays an important role in the hole conductivity in Cu oxides. Their conclusion is that ΔV_M separates two classes of compounds; those with $\Delta V_M \gtrsim 47$ eV are metallic with high T_c and delocalized holes, whereas those with lower ΔV_M are semiconducting because their holes are self-

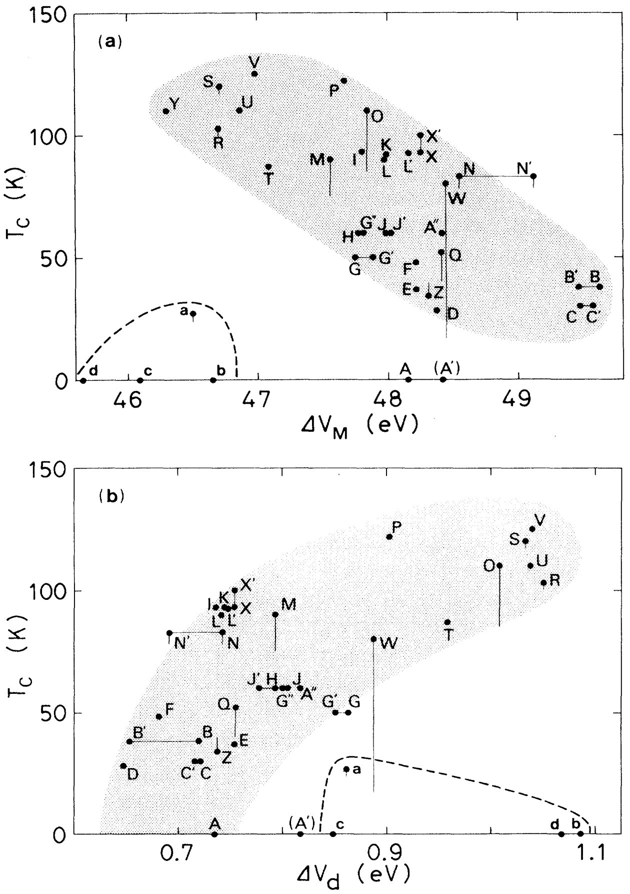

FIG. 3. The (a) T_c vs ΔV_M and (b) T_c vs ΔV_d correlations. Compounds labeled A–Z (pyramidal or octahedral coordination) and a–d (square coordination) are summarized in the Appendix.

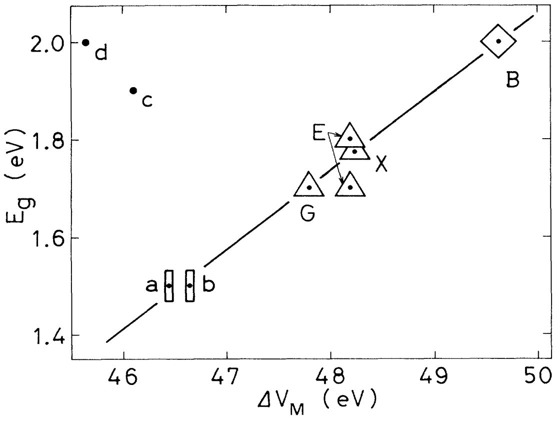

FIG. 4. The E_g vs ΔV_M correlation. Symbols (□), (△), and (◇) denote the square, pyramidal, and octahedral coordinations of copper, respectively. Small circles are the compounds difficult to dope. Descriptions of the compounds are given in the Appendix.

trapped on oxygen atoms. The problem we consider is thus whether the T_c versus ΔV_M correlation involves important aspects of the origin of the difference in T_c's or it is just a result reflecting the T_c versus ΔV_A correlation, and if both contributions play roles then which is dominant quantitatively. It is possible to point out the following: (i) By comparing Fig. 2 with Fig. 3(a), it is seen that ΔV_A scales with T_c better than ΔV_M does. (ii) The pressure dependence of T_c suggests that ΔV_A rather than ΔV_M is essential because both ΔV_A and ΔV_M increase by pressure but only the former is consistent with the observed[27] positive pressure coefficient of T_c. Further arguments must be waited until any model for high-T_c superconductivity is assumed. In Sec. IV, we take the model that the Zhang-Rice local singlet is an important ingredient for the superconductivity, and discuss this point further.

The charge-transfer gap E_g observed in the optical conductivity experiments[44,61,62] is a direct measure of Δ because Δ coincides with E_g in the ionic model [see Eq. (4)]. We show the correlation between E_g and ΔV_M in Fig. 4. The compounds that can be doped to make them superconducting are clearly on a straight line. This correlation provides a partial justification of the ionic model description for the energy-level structure. Two compounds falling off the line in Fig. 4. may be due to the following peculiarity of these compounds: $Sr_2CuO_2Cl_2$ has an exceptionally large Cu(P)-O(P) bond length. This reduces the hopping integral between the p_σ orbitals of the O(P)'s and thus gives a larger value of E_g. Sr_2CuO_3 has no CuO_2 planes but has CuO_4 chains running along the a direction so that the oxygen bandwidth can be reduced considerably.

The bond length is the most direct measure of the magnitude of covalency since the hopping integrals are directly related to the bond lengths. In Figs. 5(a) and 5(b) we plot the T_c's as a function of d_P [one-half of the nearest Cu(P)-Cu(P) distance, which is roughly equal to Cu(P)-O(P) bond length] and d_A [the Cu(P)-O(A) bond length]. No correlation may be seen in both figures. For example, both d_A and d_P are large in the Tl family which shows very high T_c, whereas the Bi family, which has rather small bond lengths, also shows very high T_c. This result suggests that the magnitude of covalency itself is not a major factor governing the T_c. We have argued that the shifts in the one-body energy levels are of primary importance in layered Cu oxides. Such systems are characterized by the strong ionicity and the intuition valid for covalent bonded systems does not necessarily hold. We examine this point further in Sec. IV. Within each family some correlations between the bond lengths and T_c have been noticed.[8] We consider that the changes in d_P are just a result of the changes in the hole concentration which correlates with T_c; the hole concentration may contribute to the cohesion of the Cu(P)-O(P) bonds as well as to T_c.

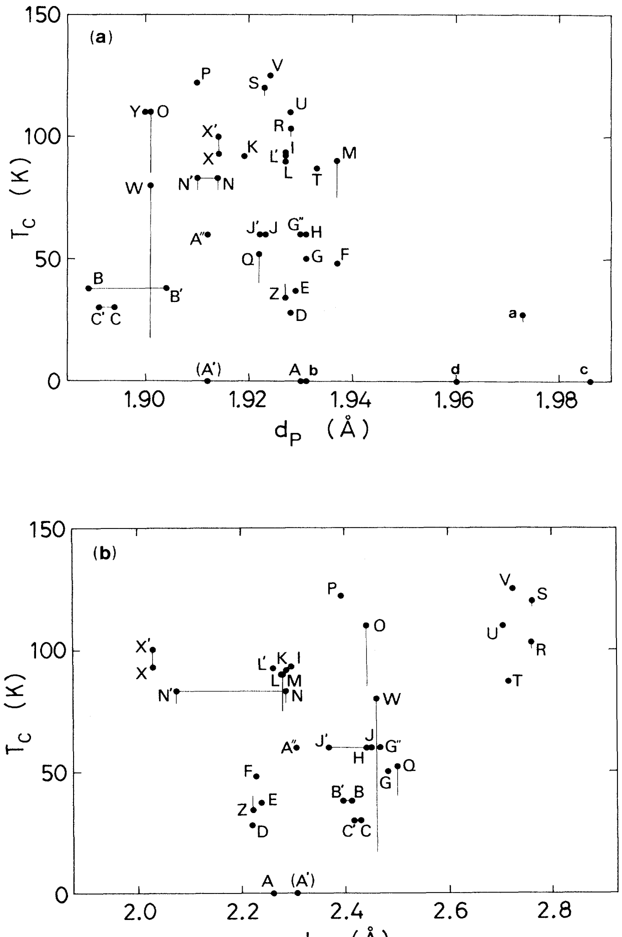

FIG. 5. (a) The T_c vs d_P and (b) the T_c vs d_A correlations. d_P is one-half of the nearest Cu(P)-Cu(P) bond length and d_A is the Cu(P)-O(A) bond length. The average distance is shown for orthorhombic compounds. See the Appendix for the detailed descriptions.

IV. STABILITY OF LOCAL SINGLET

The correlations extracted through the ionic model strongly suggest that the maximum T_c's of hole-carrier superconductors are essentially governed by the one-body energy levels of the relevant orbitals, especially by that of the apex oxygen atoms. However, since the mechanism of high-T_c superconductivity is unknown yet, a direct connection of the energy levels with T_c is impossible at present. Instead we seek hints on the mechanism from such correlations. The best way for this may be to take one of the possible models for high-T_c superconductivity and examine how the relevant electronic states are affected by the energy levels. Attention should be focused here on the electronic states of the doped holes. In this paper we take the picture that the Zhang-Rice singlet,[34] the spin-singlet made of two holes in the $3d_{x^2-y^2}$ orbital of Cu(P) and p_σ orbital of O(P), is an important ingredient for the superconductivity. Then our procedure is to examine what happens to the singlet when the energy-level structure changes.

We take the cluster-model approach. Basic roles of O(A) revealed for a CuO_5 cluster with the C_{4v} symmetry are (i) the singlet state is well-defined and actually stable in a possible parameter range even in the presence of O(A) and (ii) there is a crossover to the triplet state when the energy level of O(A) becomes low (or $\Delta\varepsilon_A \lesssim -1.5$ eV in our calculation). These have been pointed out first by Fujimori.[17] However, since we assume that the local singlet is mobile, its dispersive behavior (or propagation) has to be examined as a next step. The propagation of the local singlet may be examined by the linked cluster containing two Cu ions, e.g., Cu_2O_7 and Cu_2O_{11} cluster. It has been found[31,32] that the ground state in such clusters is represented very well by the "bonding" state of local singlets, each of the two being formed between the doped spin and each of the two Cu(P) spins. It has also been found[31,33] that the first-excited state is mainly represented by the "antibonding" state of the two local singlets. The difference between these lowest two energy eigenvalues may thus be a measure of the transfer energy of the local singlet. We define a parameter t to be one-half of this energy difference. The parameter t of the t-J model has thus been extracted.[31,33] Note that these arguments are appropriate, in particular, when there are no effects of O(A)'s. Let us now consider the role of O(A) explicitly. We note[30] that the stability of the singlet propagation is influence strongly by the other (mainly triplet) components involved in the first-excited states; a ratio of the singlet component to all the other components involved in the first-excited state decreases associating with the decrease in the energy level of O(A). The decrease in this ratio is nearly proportional to the decrease in the energy difference $2t$. There occurs, therefore, a crossover to a state where the first-excited states are not well written by the antibonding states of the two local singlets. This crossover actually happens around $-1 \lesssim \Delta\varepsilon_A \lesssim 0$ eV. With a further decrease in the energy level of O(A) (or $\Delta\varepsilon_A \lesssim -2$ eV), the local-singlet picture totally breaks down. The first-excited-state energy crosses the ground-state energy at $\Delta\varepsilon_A \lesssim -2.0$ eV and t vanishes. Note that the singlet state unstable for $-2 \lesssim \Delta\varepsilon_A \lesssim -1.5$ eV in the CuO_5 cluster becomes stable in the Cu_2O_9 cluster. This is because the local singlet is stabilized by its propagation. Hereafter we refer to t as a measure of the stability of the local singlet. Note that this t tends to a parameter t of the t-J model at $\Delta\varepsilon_A \to \infty$, because in this limit the ground- and first-excited states are very accurately written by the bonding and antibonding states of the local singlet, respectively.

We demonstrate in this section that the maximum T_c's are determined basically by the stability of the local singlet. For this purpose we evaluate t through the cluster-model calculations by using the parameters obtained in Sec. II for each compound. We set up the calculation as follows (see Ref. 30 for further details of the calculation). The Cu_2O_9 and Cu_2O_{11} clusters are taken for simulating the pyramidal and octahedral CuO_2 planes, respectively. We put relevant orbitals on each site [see Figs. 6(a) and 6(b)]; they are the $3d_{x^2-y^2}$ and $3d_{3z^2-r^2}$ orbitals on Cu(P), the p_σ orbital on O(P), and the p_z orbital on O(A). Other orbitals, whose contributions are less important, are neglected for simplicity. Small rhombic distortions and shifts of O(P)'s are also neglected. The hopping integrals are assumed to have the dependence r^{-3} and r^{-4} for the p-p and p-d interactions, respectively, where r is the interatomic distance. Their proportionality coefficients are determined from the band calculation.[63] Values of the hopping integrals determined for La_2CuO_4, are $T_{pp}=0.49$ and 0.29 eV between the neighboring p_σ orbitals, and between the p_σ and p_z orbitals, respectively, and $T_{pd}=1.13$, 0.65, and 0.49 eV between the $3d_{x^2-y^2}$ and

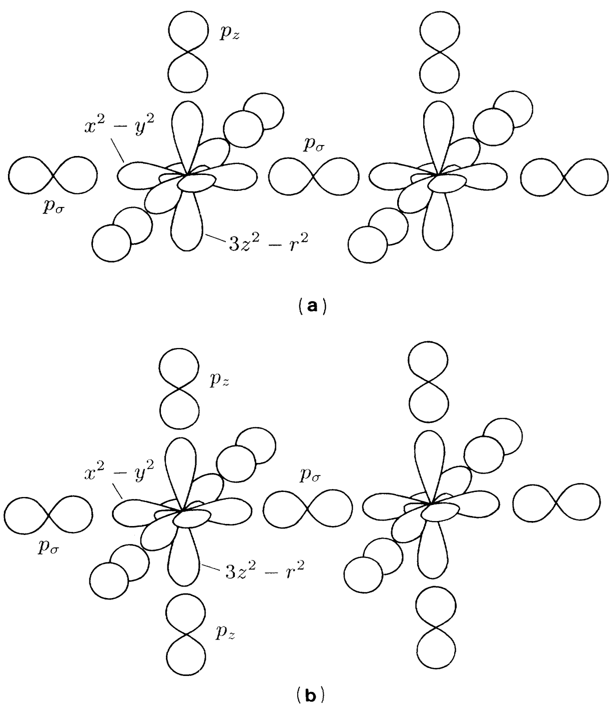

FIG. 6. (a) The Cu_2O_9 and (b) the Cu_2O_{11} clusters with their assigned orbitals.

p_σ orbitals, the $3d_{3z^2-r^2}$ and p_σ orbitals, and the $3d_{3z^2-r^2}$ and p_z orbitals, respectively. The bond lengths used for calculations are taken from the experimental data for each compound and listed in the Appendix. We use the intraorbital Coulombic interactions U_d and U_p calculated by the constrained-occupation local-density method;[63] the values are consistent with those of the photoemission spectroscopy experiments. The interorbital Coulombic and exchange interactions J_d and K_d, respectively, are also taken into account by using the Racah parameters. We assume that these interactions U_d, U_p, J_d, and K_d are independent of compounds and have values 8.5, 4.1, 7.62, and 2.36 eV, respectively. There are three parameters for the one-body energy levels i.e., $\Delta\varepsilon_A$, $\Delta\varepsilon_d$, and Δ. $\Delta\varepsilon_A$ is the energy level of the p_z orbital of O(A) relative to the energy level of the p_σ orbital of O(P), $\Delta\varepsilon_d$ is for the $3d_{3z^2-r^2}$ orbital of Cu(P) relative to the $3d_{x^2-y^2}$ orbital of Cu(P), and Δ is for the p_σ orbital of O(P) relative to the $3d_{x^2-y^2}$ orbital of Cu(P). Their values depend critically on compounds; we use the values determined in Sec. II. Now we put three holes in the cluster and diagonalize the Hamiltonian exactly to examine the electronic states of the doped hole.

First, we evaluate t of all the compounds using their individual data and show how the level separations scale with t when all the contributions are put on. The results are plotted in Figs. 7(a)–7(c) as a function of $\Delta\varepsilon_A$, Δ, and $\Delta\varepsilon_d$, respectively. It is found that there exist fair correlations between t and the level separations, and each correlation resembles the corresponding one given in Sec. III (see Figs. 2 and 3). This implies that our electrostatic description of the energy levels works well and the covalency has no primary significance in determining the magnitude of t. This result also suggests that t may be a good measure of the T_c (see below). To show more explicitly how t is affected by the energy-level splittings, we calculate the dependence of t on $\Delta\varepsilon_A$, Δ, and $\Delta\varepsilon_d$ by using the pyramidal Cu_2O_9 cluster with the fixed hopping parameters. The results are given in Fig. 8. We see that t behaves just like the survey given in the first part of this section: the local singlet is well defined when the energy level of O(A) is sufficiently high, but with decreasing $\Delta\varepsilon_A$, t decreases predominantly accompanied by the destabilization of the local singlet, i.e., the local-singlet picture is most strongly affected by $\Delta\varepsilon_A$. Although, when Δ is small and/or $\Delta\varepsilon_d$ is large, comparatively large values of t result, these effects are only about one-sixth of the change in t due to $\Delta\varepsilon_A$ and quantitatively small (see Fig. 8). We thus consider that the correlations with Δ and $\Delta\varepsilon_d$ shown in Fig. 7(b) and 7(c) (and the correlations with ΔV_M and ΔV_d shown in Fig. 3) are shadows of the correlation with $\Delta\varepsilon_A$; i.e., these level separations are described by the electrostatic potentials and come from the common ionic charge distribution, so that ΔV_M and ΔV_d correlate eventually with ΔV_A, through which the above correlations are seen. Results calculated for the octahedral Cu_2O_{11} cluster indicate a slightly faster decrease in t with respect to the decrease in $\Delta\varepsilon_A$, but general features of the curves are the same as the above results. We may therefore conclude that the energy level of O(A) primarily determines the value of the parameter t, i.e., the stability of the Zhang-Rice local singlet. We argue that this is the most important effect persisting against all the other effects and a basic origin of the T_c versus ΔV_A correlation.

Let us now examine the correlation between t and the maximum T_c. The result is shown in Fig. 9. It is found that the maximum T_c correlates linearly with t; the T_c appears for $t \gtrsim 0.22$ eV and increases linearly with increasing t. We may thus conclude that the maximum T_c

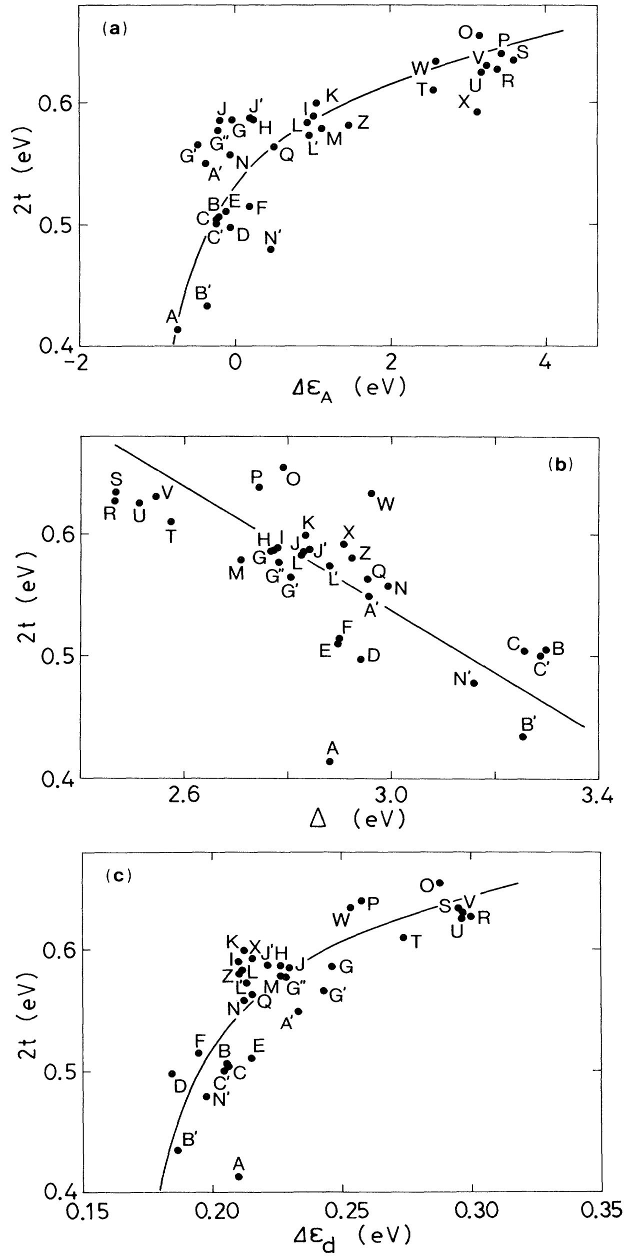

FIG. 7. The correlations between $2t$ and (a) $\Delta\varepsilon_A$, (b) Δ, and (c) $\Delta\varepsilon_d$. Compounds labeled A–Z are summarized in the Appendix.

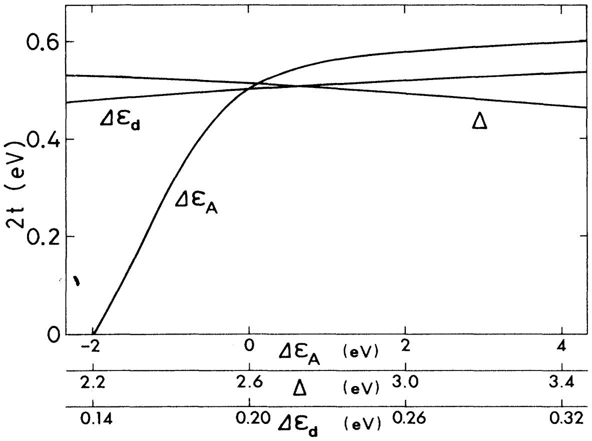

FIG. 8. Dependence of $2t$ on the level separations $\Delta\varepsilon_A$, Δ, and $\Delta\varepsilon_d$. The Cu_2O_9 cluster with the parameters of the T^*-phase compound (D in the Appendix) is used.

of hole-carrier superconductors scales universally with t, the stability of the Zhang-Rice local singlet. Because t directly reflects the energy level of O(A) as shown above, the T_c versus ΔV_A correlation given in Sec. III A is a direct consequence of this effect. We may point out from Fig. 9 that the compound A' ($La_2CaCu_2O_6$) will be a superconductor, in contrast with the compound A ($La_2SrCu_2O_6$), if successful hole doping can be operated. The square-coordinated compounds Nd_2CuO_4, $Ca_{0.86}Sr_{0.14}CuO_2$, and $Sr_2CuO_2Cl_2$ have the calculated values of $2t$ of 0.57, 0.63, and 0.55 eV, respectively, reflecting their large bond-length d_P characteristic of the square-coordinated compounds, so that if they were successful in hole doping then we would expect fairly high T_c's of ~70, ~100, and ~60 K, respectively, from Fig. 9. It will be interesting to see whether the T_c of electron-carrier superconductors[64] may be understood in terms of this universal correlation with the stability of a local singlet. A possibility is that the Cu 4s orbital strongly destabilizes the local singlet,[65] which leads to a rather low T_c observed. The negative pressure coefficient of T_c observed[64] could be due to an enhancement of the overlap of the Cu 4s orbitals. The T_c versus t correlation further suggests an interesting hypothesis that the T_c of any layered Cu oxides at arbitrary doping rates is written in terms of a single variable. This variable would express the amount of the mobile local-singlet component.

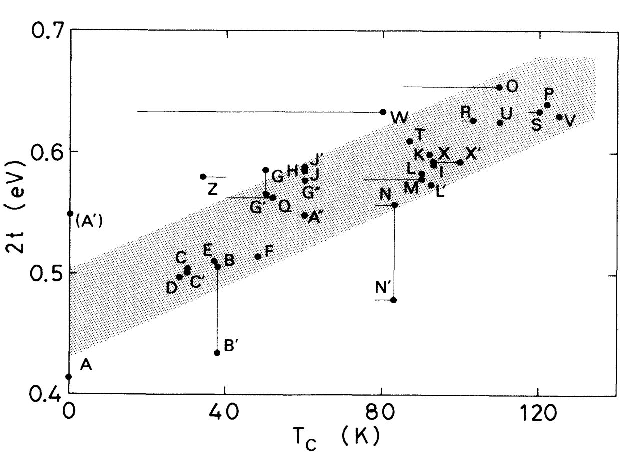

FIG. 9. The correlation between $2t$ and T_c. Compounds labeled A–Z are summarized in the Appendix.

We have calculated the antiferromagnetic superexchange interaction J and found that the calculated values $J \simeq 0.15$ eV do not depend significantly on the compounds. We therefore conclude that J does not correlate with T_c.

The bond lengths are not the major factor as seen in Fig. 5; the smaller d_A does not necessarily mean the larger ΔV_A (or a higher T_c). The pressure experiments will provide a possible test on this argument. If we assume that the pressure brings O(A) close to the CuO_2 plane,[26] then the hybridization between the p_z orbital of O(A) and the $3d_{3z^2-r^2}$ orbital of Cu(P) is enhanced. The local singlet is thus destabilized. This effect is opposite to the effect of ΔV_A examined in Sec. III B, so that we need a quantitative study to clarify which effect survives. However, data on the pressure dependence of atomic positional parameters are quite limited at present, and thus we cannot make reliable cluster-model calculations for this point. The experimental works are highly desired.

It has been reported from the polarized Cu L_3 XAS (x-ray absorption spectroscopy) experiments[66] that a part of the hole carriers is of the $3z^2-r^2$ character and the relative intensity of the spectrum with this symmetry increases with increasing the doping rate. It may be possible to argue, however, that the holes with the x^2-y^2 symmetry which contribute to form the local singlet must also increase with the doping rate and this contribution is essential to increase T_c. The increase in the holes with the x^2-y^2 symmetry with the doping rate is actually seen in the results[30,67] of the cluster-model calculation.

Implication of the three-dimensionality is as follows. We note from our arguments that T_c would increase if there were no effects of the O(A)'s. However, without the O(A)'s, it is difficult to dope the CuO_2 plane with holes, as it is known empirically. In the actual system with the O(A)'s, the whole structural block determines the energy level of the O(A)'s, and this energy level controls the stability of the Zhang-Rice local singlet in the two-dimensional CuO_2 plane.

V. CONCLUSIONS

The ionic model has been used to draw the electronic-energy-level structures of the layered Cu oxide compounds including all the known families of both hole-carrier and electron-carrier superconductors. The correlations have been examined between the maximum T_c observed for each family and the energy level of the apex oxygen atoms, charge-transfer gap, crystal-field splitting, and copper-oxygen bond lengths; among these, the energy level of the apex oxygen atoms has been shown to play a fundamental role in the electronic states of the CuO_2 plane and govern the maximum T_c of each family of the hole-carrier superconductors. The pressure effect of T_c has been explained in this context. Some suggestions for the material designing have also been made.

The cluster-model calculations have been employed to examine the electronic states of the doped hole. The covalency neglected in the ionic model has been fully taken into account in this model. We have shown, by taking the picture that the Zhang-Rice local singlet plays an essential role for high-T_c superconductivity, that the maximum T_c of each family is determined basically by the parameter t, a measure of the stability of the local singlet. The T_c appears for $t \gtrsim 0.22$ eV and increases linearly with t. We have seen that the value of t is primarily determined by the energy level of the apex oxygen atoms and argued that the T_c versus ΔV_A correlation is a direct consequence of this effect. We have thus obtained the universal correlation with T_c of all the known Cu oxide hole-carrier superconductors.

After we finished writing this paper we were informed of the recent experiment by Cava *et al.*,[68] who succeeded in introducing holes into the compound A' ($La_2CaCu_2O_6$) by replacing La partially with Sr and observed the superconductivity with $T_c \simeq 60$ K. This observation agrees with our prediction[24,25] as seen in Figs. 2 and 9. We have added this compound in Figs. 2, 3, 5, and 9 as A'', assuming that the crystal structure is the same as A'.

ACKNOWLEDGMENTS

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APPENDIX

Database for the layered Cu oxide compounds. Listed are (i) the observed maximum T_c, (ii) formal hole concentration p (per unit CuO_2) at which the maximum T_c is observed, (iii) reference for the structural data used, (iv) coordination number of Cu(P), (v) adopted parent compound, (vi) assigned ionic charges, (vii) one-half of the nearest Cu(P)-Cu(P) distance d_P (an average distance is shown for the orthorhombic compounds), the Cu(P)-O(A) bond length d_A, and calculated results for the differences in the Madelung site potentials ΔV_A, ΔV_M, and ΔV_d, and (viii) some notes. The bond lengths and Madelung potential differences are given in units of Å and eV, respectively. The labels A–Z and a–d below are used in Figs. 2–5, 7, and 9 to distinguish the compounds.

A: $La_2SrCu_2O_{6.2}$. (i) $T_c=0$ K (Ref. 45). (ii) $p=0.2$. (iii) Structure: Ref. 69. (iv) Cu-coordination: 5. (v) Parent compound: $La_2SrCu_2O_6$. (vi) Assigned ionic charges: formal. (vii) $d_P=1.930$, $d_A=2.260$, $\Delta V_A=-2.639$, $\Delta V_M=48.154$, and $\Delta V_d=0.735$. (viii) Note: Reported to be metallic but not superconducting.[45,46] An isostructural compound $La_{1.9}Ca_{1.1}Cu_2O_6$ is semiconducting because no successful hole doping has been operated.[46] Parameters obtained for $La_{1.9}Ca_{1.1}Cu_2O_6$ are $d_P=1.912$, $d_A=2.305$, $\Delta V_A=-1.316$, $\Delta V_M=48.416$, and $\Delta V_d=0.817$, where we use the stuctural data in Ref. 70 and assign the charges 2.92+ at the 4e site and 2.16+ at the 2a site. This compound, $La_{1.9}Ca_{1.1}Cu_2O_6$, is plotted as A' in parentheses. If we use the structural data in Ref. 69 instead and assign the charges 3+ at the 4e site and 2+ at the 2a site then we have $d_P=1.910$, $d_A=2.361$, $\Delta V_A=0.277$, $\Delta V_M=48.236$, and $\Delta V_d=0.854$. In $La_2SrCu_2O_{6.2}$, it is reported[71] that excess oxygens are inserted between the two CuO_2 planes.

B: $La_{1.85}Sr_{0.15}CuO_4$. (i) $T_c=38$ K (Ref. 2). (ii) $p=0.15$. (iii) Structure: Ref. 72. (iv) Cu coordination: 6. (v) Parent compound: La_2CuO_4. (vi) Assigned ionic charges: formal. (vii) $d_P=1.889$, $d_A=2.412$, $\Delta V_A=-0.750$, $\Delta V_M=49.620$, and $\Delta V_d=0.719$. (viii) Note: Data for room-temperature tetragonal phase are used. If we use the structural data for La_2CuO_4 reported in Ref. 73, we have $d_P=1.904$, $d_A=2.397$, $\Delta V_A=-1.267$, $\Delta V_M=49.461$, and $\Delta V_d=0.653$. This is plotted as B'.

C: $La_{1.85}Ba_{0.15}CuO_4$. (i) $T_c=30$ K (Ref. 74). (ii) $p=0.15$. (iii) Structure: Ref. 75. (iv) Cu coordination: 6. (v) Parent compound: La_2CuO_4. (vi) Assigned ionic charges: formal. (vii) $d_P=1.894$, $d_A=2.429$, $\Delta V_A=-0.861$, $\Delta V_M=49.467$, and $\Delta V_d=0.721$. (viii) Note: T_c versus p curve has a valley at $p=0.12$.[74] Structural data at $T=295$ K are used. If we use the data[75] at 10 K, we have $d_P=1.891$, $d_A=2.417$, $\Delta V_A=-0.861$, $\Delta V_M=49.577$, and $\Delta V_d=0.716$. C' shows this case.

D: $Nd_{2-x-y}Sr_xCe_yCuO_4$ with $x=0.205$ and $y=0.135$. (i) $T_c=28$ K (Refs. 76 and 77). (ii) $p=0.13$. (iii) Structure: Ref. 76. (iv) Cu coordination: 5. (v) parent compound: $MM'CuO_{4-\delta}$ (T^* phase). (vi) Assigned ionic charges: $M=2.8+$ and $M'=3.2+$. (vii) $d_P=1.928$, $d_A=2.220$, $\Delta V_A=-0.224$, $\Delta V_M=48.366$, and $\Delta V_d=0.646$, (viii) Note: Isostructural to E.

E: $Sm_1La_{0.75}Sr_{0.25}CuO_{3.95}$. (i) $T_c=37$ K (Ref. 78). (ii) $p=0.15$. (iii) Structure: Ref. 78. (iv) Cu coordination: 5. (v) Parent compound: T^* phase. (vi) Assigned ionic charges: Sm^{3+}, $(La-Sr)^{2.7+}$, and $O(A)^{1.7-}$. (vii) $d_P=1.929$, $d_A=2.238$, $\Delta V_A=-0.463$, $\Delta V_M=48.209$, and $\Delta V_d=0.753$. (viii) Note: Deficient nature of O(A) (Ref. 78) results in its average valence state of 1.7−.

F: $(Ba_{1-x}Eu_x)_2(Eu_{1-y}Ce_y)_2Cu_3O_{8+z}$ with $x=y=0.33$. (i) $T_c=48$ K (Refs. 79 and 80). (ii) $p=z-x-y$: unknown. (iii) Structure: Ref. 81. (iv) Cu coordination: 5. (v) Parent compound: $M_2M'_2Cu_3O_{8+z}$. (vi) Assigned ionic charges: $M=2.4+$, $M'=3.38+$, and $z=0.78$. (vii) $d_P=1.937$, $d_A=2.228$, $\Delta V_A=0.630$, $\Delta V_M=48.216$, and $\Delta V_d=0.681$. (viii) Note: Experiment for T_c versus p relation is absent at present.

G: $Y_{0.8}Ca_{0.2}Ba_2Cu_3O_{6.11}$. (i) $T_c=50$ K (Ref. 47). (ii) $p=0.1$. (iii) Structure: Ref. 47. (iv) Cu coordination: 5. (v) Parent compound: $Y_{0.9}Ca_{0.1}Ba_2Cu_3O_{6.1}$. (vi) Assigned ionic charges: Cu in the oxygen-deficient block is in the 1+ valence state. (vii) $d_P=1.931$, $d_A=2.482$, $\Delta V_A=-0.141$, $\Delta V_M=47.756$, and $\Delta V_d=0.863$. (viii) Note: If we adopt $YBa_2Cu_3O_6$ as a parent we have $\Delta V_A=-1.691$, $\Delta V_M=47.892$, and $\Delta V_d=0.851$. G'

shows this case. If we use the structural data for $YBa_2Cu_3O_{6.09}$ (Ref. 82) and assign the charge 1+ to Cu in the oxygen-deficient block, we have $d_P=1.930$, $d_A=2.466$, $\Delta V_A=-0.770$, $\Delta V_M=47.808$, and $\Delta V_d=0.800$. G'' shows this case. This compound may be a parent of the 60-K-class superconductor of the Y family.

H: $YBa_2Cu_3O_{6.5}$. (i) $T_c=60$ K. (ii) $p=0.12$.[4] (iii) Structure: Ref. 82. (iv) Cu coordination: 5. (v) Parent compound: $YBa_2Cu_3O_{6.5}$. (vi) Assigned ionic charges: formal. (vii) $d_P=1.931$, $d_A=2.440$, $\Delta V_A=0.815$, $\Delta V_M=47.776$, and $\Delta V_d=0.793$. (viii) Note: A tetragonal compound with random oxygen atoms in the oxygen-deficient block, which could be achieved by rapid quenching.

I: $YBa_2Cu_3O_7$. (i) $T_c=93$ K (Refs. 82 and 83). (ii) $p=0.2$.[4] (iii) Structure: Ref. 82. (iv) Cu coordination: 5. (v) Parent compound: $YBa_2Cu_3O_{6.5}$. (vi) Assigned ionic charges: formal. (vii) $d_P=1.927$, $d_A=2.296$, $\Delta V_A=3.533$, $\Delta V_M=47.802$, and $\Delta V_d=0.736$. (viii) Note: Orthorhombic phase. Listed are the averaged parameter values. The valence states of Cu and O in the CuO chain block are assumed ot be 2+ and 1− (in average), respectively, for the parent compound.

J: $ErBa_2Cu_3O_{6.53}$. (i) $T_c=60$ K (Ref. 84). (ii) $p=0.12$.[4] (iii) Structure: Ref. 84. (iv) Cu coordination: 5. (v) Parent compound: $ErBa_2Cu_3O_6$ (tetragonal). (vi) Assigned ionic charges: Cu in the oxygen-deficient block is in the 1+ valence state. (vii) $d_P=1.923$, $d_A=2.450$, $\Delta V_A=-0.698$, $\Delta V_M=47.979$, and $\Delta V_d=0.805$. (viii) Note: If we adopt an orthorhombic structure ($ErBa_2Cu_3O_{6.53}$) as a parent and assign the same ionic charges as above, we have $d_P=1.922$, $d_A=2.368$, $\Delta V_A=0.716$, $\Delta V_M=48.018$, and $\Delta V_d=0.777$. J' shows this case.

K: $ErBa_2Cu_3O_7$. (i) $T_c=92$ K (Ref. 84). (ii) $p=0.12$.[4] (iii) Structure: Ref. 84. (iv) Cu coordination: 5. (v) Parent compound: $ErBa_2Cu_3O_{6.5}$. (vi) Assigned ionic charges: formal. (vii) $d_P=1.919$, $d_A=2.284$, $\Delta V_A=3.679$, $\Delta V_M=47.992$, and $\Delta V_d=0.743$. (viii) Note: Listed are the average parameter values. Valences in the CuO chain block are O^{1-} (in average) and Cu^{2+}.

L: $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$. (i) $T_c=90$ K (Ref. 85). (ii) *p*: unknown. (iii) Structure: Ref. 26. (iv) Cu coordination: 5. (v) Parent compound: $YBa_2Cu_4O_8$. (vi) Assigned ionic charges: oxygen atoms in the CuO chain are in the average valence state of 1.5−. (vii) $d_P=1.927$, $d_A=2.275$, $\Delta V_A=3.244$, $\Delta V_M=47.967$, and $\Delta V_d=0.741$. (viii) Note: In $YBa_2Cu_4O_8$, 0.5 holes per unit formula distribute between the plane and reservoir blocks, resulting in a small number of mobile holes in the CuO_2 plane. We thus assume that oxygens in the chain block are in the average valence state of 1.5− in the parent compound. If we use the structure under 1 GPa pressure [at which $T_c=92.4$ K (Ref. 26)], we have $d_P=1.927$, $d_A=2.226$, $\Delta V_A=3.362$, $\Delta V_M=48.156$, and $\Delta V_d=0.747$. L' shows this case. If we use the structural data in Ref. 86, we have $d_P=1.930$, $d_A=2.299$, $\Delta V_A=2.837$, $\Delta V_M=47.803$, and $\Delta V_d=0.728$.

M: $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})Cu_3O_{6+\delta}$. (i) $T_c=75-90$ K (Ref. 87). (ii) *p*: unknown. (iii) Structure: Ref. 25. (iv) Cu coordination: 5. (v) Parent compound: $(Ca_{0.5}La_{0.5})(Ba_{1.25}La_{0.75})$ $Cu_3O_{6.625}$. (vi) Assigned ionic charges: $(Ca\text{-}La)^{2.5+}$, $(Ba\text{-}La)^{2.375+}$. Oxygen atoms in the deficient CuO block are in the average valence state of 0.625−. (vii) $d_P=1.937$, $d_A=2.278$, $\Delta V_A=3.896$, $\Delta V_M=47.556$, and $\Delta V_d=0.793$. (viii) Note: A pseudo-"$CaBaLaCu_3O_7$" compound. Tetragonal phase. Oxygens are randomly distributed in the "chain" block.

N: $Pb_2Sr_2Y_{0.5}Ca_{0.5}Cu_3O_8$. (i) $T_c=78-83$ K (Refs. 88 and 89). (ii) $p=0.25$. (iii) Structure: Ref. 90. (iv) Cu coordination: 5. (v) Parent compound: $Pb_2Sr_2YCu_3O_8$. (vi) Assigned ionic charges: Cu in the oxygen-deficient block is in the 1+ valence state and Pb is in the 2+ valence state. (vii) $d_P=1.914$, $d_A=2.284$, $\Delta V_A=-0.242$, $\Delta V_M=48.550$, and $\Delta V_d=0.743$. (viii) Note: if we use the stductural data cited in Ref. 91, we have $d_P=1.910$, $d_A=2.074$, $\Delta V_A=1.560$, $\Delta V_M=49.123$, and $\Delta V_d=0.691$. N' shows this case.

O: $Pb_{0.5}Tl_{0.5}Sr_2CaCu_2O_7$. (i) $T_c=85-110$ K (Refs. 92 and 93). (ii) $p=0.25$. (iii) Structure: Ref. 93 (iv) Cu coordination: 5. (v) Parent compound: $Pb_{1-x}Tl_xSr_2CaCu_2O_7$ with $x=0$. (vi) Assigned ionic charges: Tl^{3+} and Pb^{4+}.[93] (vii) $d_P=1.901$, $d_A=2.443$, $\Delta V_A=11.033$, $\Delta V_M=47.840$, and $\Delta V_d=1.008$. (viii) Note: Isostructural to *R*.

P: $Pb_{0.5}Tl_{0.5}Sr_2Ca_2Cu_3O_9$. (i) $T_c=122-125$ K (Refs. 93 and 94). (ii) $p=0.25$. (iii) Structure: Ref. 93. (iv) Cu coordination: 5. (v) Parent compound: $Pb_{1-x}Tl_xSr_2Ca_2Cu_3O_9$ with $x=0$. (vi) Assigned ionic charges: Tl^{3+} and Pb^{4+}.[93] (vii) $d_P=1.910$, $d_A=2.392$, $\Delta V_A=12.008$, $\Delta V_M=47.671$, and $\Delta V_d=0.903$. (viii) Note: Isostructural to *S*. Square-coordinated CuO_2 planes are inactive for the superconductivity.[19,48]

Q: $Tl(Ba_{0.6}La_{0.4})_2CuO_{5-\delta}$. (i) $T_c=40-52$ K (Refs. 95 and 97). (ii) *p*: unknown. (iii) Structure: Ref. 95. (iv) Cu coordination: 6. (v) Parent compound: $Tl_{0.7}(Ba_{0.35}La_{0.65})_2CuO_{4.7}$. (vi) Assigned ionic charges: formal. (vii) $d_P=1.992$, $d_A=2.499$, $\Delta V_A=1.739$, $\Delta V_M=48.409$, and $\Delta V_d=0.755$. (viii) Note: Tl and O atoms are rather deficient,[95] so that the above parent is taken. The T_c versus *p* experiment is unclear at present.

R: $TlBa_2CaCu_2O_{7-\delta}$. (i) $T_c=100-103$ K (Refs. 98 and 99). (ii): *p*: unknown. (iii) Structure: Ref.99. (iv) Cu coordination: 5. (v) Parent compound: $TlBa_2CaCu_2O_7$. (vi) Assigned ionic charges: O in the Tl layer has the 1− valence, and Tl^{3+}. (vii) $d_P=1.928$, $d_A=2.761$, $\Delta V_A=11.812$, $\Delta V_M=46.698$, and $\Delta V_d=1.051$. (viii) Note: Oxygen atoms in the Tl layer are somewhat deficient. Holes distribute between oxygens in Tl layer and CuO_2 plane,[19] so that we adopt the above parent compound.

S: $TlBa_2Ca_2Cu_3O_{9-\delta}$. (i) $T_c=117-120$ K (Refs. 100 and 101). (ii) *p*: unknown. (iii) Structure: Ref. 101. (iv) Cu coordination: 5. (v) Parent compound: $TlBa_2Ca_2Cu_3O_9$. (vi) Assigned ionic charges: Oxygen atoms in the Tl layer are in the 1− valence state, and Tl^{3+}. (vii) $d_P=1.923$, $d_A=2.763$, $\Delta V_A=12.584$, $\Delta V_M=46.706$, and $\Delta V_d=1.033$. (viii) Note: Oxygen atoms in the Tl layer are somewhat deficient. Holes distribute between oxygens in the Tl layer and CuO$_2$ plane,[19] so that we adopt the above parent compound. The results are for the pyramidal CuO$_2$ layers. The square-coordinated CuO$_2$ layers are inactive for the superconductivity.[19,48]

T: Tl$_2$Ba$_2$CuO$_6$. (i) $T_c = 87$ K (Refs. 42 and 102). (ii) p: unknown. (iii) Structure: Ref. 103. (iv) Cu coordination: 6. (v) Parent compound: Tl$_2$Ba$_2$CuO$_6$. (vi) Assigned ionic charges: formal. (vii). $d_P = 1.933$. $d_A = 2.714$, $\Delta V_A = 8.942$, $\Delta V_M = 47.081$, and $\Delta V_d = 0.959$. (viii) Note: Mechanism of hole doping (self-doping,[41,42] Cu in the Tl site, oxygen defect, etc.) is controversial.

U: Tl$_2$Ba$_2$CaCu$_2$O$_8$. (i) $T_c = 110$ K (Ref. 102). (ii) p: unknown. (iii) Structure: Ref. 104. (iv) Cu coordination: 5. (v) Parent compound: Tl$_2$Ba$_2$CaCu$_2$O$_8$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.928$, $d_A = 2.704$, $\Delta V_A = 11.112$, $\Delta V_M = 46.864$, and $\Delta V_d = 1.038$. (viii) Note: As in T.

V: Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$. (i) $T_c = 125$ K (Ref. 105). (ii) p: unknown. (iii) Structure: Ref. 104. (iv) Cu coordination: 5. (v) Parent compound: Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.924$, $d_A = 2.725$, $\Delta V_A = 11.346$, $\Delta V_M = 46.981$, and $\Delta V_d = 1.039$. (viii) Note: As in T. The CuO$_2$ layer inserted between the two pyramidal CuO$_2$ layers is quite depleted of holes,[19,48] so that we take the CuO$_2$ plane next to O(A).

W: Bi$_2$Sr$_2$CuO$_{6+\delta}$. (i) $T_c = 17-80$ K (Refs. 106–110). (ii) p: unknown. (iii) Structure: Ref. 111. (iv) Cu coordination: 6. (v) Parent compound: Bi$_2$Sr$_2$CuO$_6$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.901$. $d_A = 2.461$, $\Delta V_A = 9.088$, $\Delta V_M = 48.437$, and $\Delta V_d = 0.888$. (viii) Note: Maximum T_c is ambiguous; in the main text we show the reported highest T_c with an error bar. Observed small orthorhombic distortion is neglected in the calculation.

X: Bi$_2$Sr$_2$Ca$_{0.9}$Y$_{0.1}$Cu$_2$O$_{8.24}$. (i) $T_c = 93$ K (Refs. 112 and 113). (ii) $p = 0.19$. (iii) Structure: Ref. 114. (iv) Cu coordination: 5. (v) Parent compound: Bi$_2$Sr$_2$CaCu$_2$O$_8$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.914$, $d_A = 2.029$, $\Delta V_A = 10.901$, $\Delta V_M = 48.247$, and $\Delta V_d = 0.754$. (viii) Note: Small orthorhombic distortion is neglected in the calculation. A monoclinic phase with a higher T_c of 99 K, Bi$_{1.6}$Pb$_{0.4}$Sr$_2$CaCu$_2$O$_y$, has recently been discovered[115] in this family. A nonstoichiometric compound Bi$_{2+x}$Sr$_{2+y}$Ca$_{1+z}$Cu$_2$O$_{8-\delta}$ ($x+y+z \simeq 0.1$) with $T_c = 99-100$ K has also been synthesized[116] in this family. We assume the same parameter values as above and label those compounds X'.

Y: Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$. (i) $T_c = 110$ K (Refs. 106, 107, and 117). (ii) p: unknown. (iii) Structure: Refs. 107 and 118. (iv) Cu coordination: 5. (v) Parent compound: Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.90$, $\Delta V_A = 8.3$, and $\Delta V_M = 46.3$. (viii) Note: A single phase sample is difficult to synthesize. The calculated Madelung potentials are taken from Ref. 19.

Z: Bi$_2$Sr$_2$(Gd$_{1-x}$Ce$_x$)$_2$Cu$_2$O$_{10+y}$ with $x = 0.18$ and $y = 0.24$. (i) $T_c = 34-40$ K (Refs. 49 and 50). (ii) $p \simeq 0.1$. (iii) Structure: Ref. 49. (iv) Cu coordination: 5. (v) Parent compound: Bi$_2$Sr$_2$(Gd$_{0.75}$Ce$_{0.25}$) Cu$_2$O$_{10.25}$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.927$, $d_A = 2.221$, $\Delta V_A = 5.056$, $\Delta V_M = 48.310$, and $\Delta V_d = 0.737$. (viii) Note: Relatively low T_c may be due to a small hole concentration or a valley in T_c versus p curve.

a: Nd$_{1.85}$Ce$_{0.15}$CuO$_4$. (i) $T_c = 24-27$ K (Refs. 119 and 120). (ii) $p = -0.15$. (iii) Structure: Ref. 121. (iv) Cu coordination: 4. (v) Parent: Nd$_2$CuO$_4$. (vi) Assigned ionic charges: formal. (vii) $d_p = 1.973$, $\Delta V_M = 46.435$, and $\Delta V_d = 0.858$. (viii) Note: Electron-carrier superconductor with CuO$_2$ plane without O(A). If we use the structural data in Ref. 122 for a superconducting sample at 11 K, we have $d_P = 1.971$, $\Delta V_M = 46.500$, and $\Delta V_d = 0.861$.

b: Ca$_{0.86}$Sr$_{0.14}$CuO$_2$. (iii) Structure: Ref. 123. (iv) Cu coordination: 4. (v) Parent: (Ca-Sr) CuO$_2$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.931$, $\Delta V_M = 46.646$, and $\Delta V_d = 1.086$. (viii) Note: Semiconductor. The CuO$_2$ plane without O(A).

c: Sr$_2$CuO$_2$Cl$_2$. (iii) Structure: Ref. 124. (iv) Cu coordination: 4. (v) Parent: Sr$_2$CuO$_2$Cl$_2$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.986$, $\Delta V_M = 46.089$, and $\Delta V_d = 0.849$. (viii) Note: Semiconductor. The CuO$_2$ plane without O(A).

d: Sr$_2$CuO$_3$. (iii) Structure: Ref. 125. (iv) Cu coordination: 4. (v) Parent: Sr$_2$CuO$_3$. (vi) Assigned ionic charges: formal. (vii) $d_P = 1.96$, $\Delta V_M = 45.653$, and $\Delta V_d = 1.068$. (viii) Note: Semiconductor. The CuO$_4$ chain.

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