

Role of the Madelung Energy in Hole Conductivity in Copper Oxides: Difference between Semiconductors and High- T_c Superconductors

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The difference in the Madelung site potential, ΔV_M , between a hole on a copper site and one on an oxygen site can control the hole's site preference and ability to delocalize. Among a variety of copper oxide structures, $e\Delta V_M$ is shown to vary by ~ 3 eV and to clearly separate two classes of compounds: Those with $e\Delta V_M > 47$ eV are metallic with high T_c and delocalized holes, whereas those with lower ΔV_M are semiconducting because their holes are self-trapped on oxygen.

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The common structural feature¹ of all copper oxide high-temperature superconductors is sheets of CuO_2 . There is strong evidence that the carriers responsible for the superconductivity are pairs of holes in these sheets. The energy of these holes is one of the most important input parameters to theories of this phenomenon, and the electrostatic Madelung energy is expected to give a major contribution to this energy in these partially ionic oxides. Several authors²⁻⁴ have recently shown that this energy can account for how these holes are distributed⁵ among the sheets and chains in $\text{YBa}_2\text{Cu}_3\text{O}_y$, for example. In this Letter, we examine a wide variety of copper oxides and calculate the *difference* in the Madelung site potential for a hole on a copper site and one on an oxygen site within the CuO_2 sheets; this helps to understand which site the holes prefer, and what is the barrier to conduction for a hole to move from Cu to O, for example. We show here that the Madelung site potential makes a contribution to this energy that is large and that varies among copper oxide compounds by as much as 3 eV. We suggest that this variation explains why, among compounds which have virtually the same sheets of CuO_2 , some are metallic and others semiconducting.

The layered copper oxide compounds of interest may be viewed as containing partially covalently bonded CuO_2 sheets, embedded in an ionic lattice of counterions. We calculate the electrostatic effects of these counterions on the CuO_2 sheets for a wide variety of different structures. As a useful starting point, we assume an ionic model, in which we neglect the covalent interactions and bandwidths within the sheets. Such an ionic approximation has been shown⁶ to be complementary to normal band-structure calculations. More accurate calculations will improve and go beyond this model, but the essential physics will remain.

Thus, consider the undoped compounds, which have sheets containing Cu^{+2} and O^{-2} ions, shown schematically at the top of Fig. 1; let us ask what would be the

energy of a hole if the compound were doped. The hole could reside on a copper site, in the form of Cu^{+3} (with energy E_h^{Cu}), or on an oxygen site, in the form of O^{-} (with energy E_h^{O}). The energy of a hole on an oxygen site, E_h^{O} , is the energy required to add a positive charge to O^{-2} , i.e., A_2^{O} , the second electron affinity of oxygen,⁷ plus eV_M^{O} , where V_M^{O} is the electrostatic Madelung site potential on the oxygen site (and e is the electronic charge). Similarly, the energy, E_h^{Cu} , to add a positive charge onto a Cu^{+2} ion is I_3^{Cu} , the third ionization potential of copper (a substantial cost) plus eV_M^{Cu} . The energy difference, ΔE_h , between a hole on an oxygen and one on a copper site is then given by

$$\Delta E_h = E_h^{\text{O}} - E_h^{\text{Cu}} = (A_2^{\text{O}} - I_3^{\text{Cu}}) + e(V_M^{\text{O}} - V_M^{\text{Cu}}), \quad (1)$$

where there is an atomic and a Madelung contribution. Both contributions of the former favor the hole to be centered on oxygen, while both the Madelung contributions favor the hole on copper. Using the atomic values^{7,8} of A_2^{O} (-8.1 eV) and I_3^{Cu} ($+36.8$ eV), we estimate that $A_2^{\text{O}} - I_3^{\text{Cu}} \sim -45$ eV. A typical value for the difference in site potentials ($\sim +47$ eV) gives $\Delta E_h \sim 0$, indicating that the calculated energies of a hole on Cu^{+2} and of one on O^{-2} are comparable.

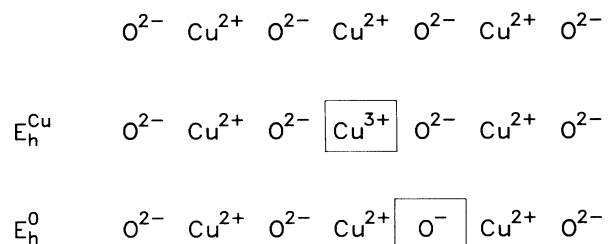


FIG. 1. Schematic figure of ionic CuO_2 sheets with no holes, with a hole on the copper site as Cu^{+3} , and with a hole on oxygen as O^{-} .

TABLE I. For the layered copper oxides in Fig. 2, the electrostatic site potentials, V_M^{Cu} and V_M^O , for the copper and oxygen sites, respectively, and the difference between them, $e\Delta V_M$, with the maximum T_c observed.

Label	Compound	V_M^{Cu}	V_M^O	$e\Delta V_M$	T_c^{Max}
		V	V		
A	$Sr_2CuO_2Cl_2$	-24.61	21.43	46.04	semi.
B	Sr_2CuO_3 (chain)	-24.18	22.11 (20.09)	46.29	semi.
C	Nd_2CuO_4	-24.42	21.95	46.37	semi.
D	Gd_2CuO_4	-24.97	21.98	46.95	semi.
E	$Ca_{0.86}Sr_{0.14}CuO_2$	-24.71	21.94	46.65	semi.
F	$Tl_2Ba_2CuO_6$	-36.54	10.54 (19.49)	47.08	95
G	$Tl_2Ba_2CaCu_2O_8$	-35.29	11.59 (22.80)	46.87	108
H	$Tl_2Ba_2Ca_2Cu_3O_{10}$	-37.92	8.67 11.92 (24.56)	46.59 47.08	125
I	$Y(LaBa)Cu_3O_6$	-27.33	20.43 (20.06)	47.76	50
J	$Y(LaBa)Cu_3O_7$ (sheet)	-26.71	21.40 21.32 (20.67)	48.11 48.03	90
	(chain)	-26.22	20.39 (20.67)	46.60	semi.
K	$Y_2(LaBa)_2Cu_7O_{15}$	-26.82	21.30 21.29 (18.38)	48.11 48.11	65
	(sheet)	-25.25	22.78 22.75 (22.54)	48.03 48.00	
L	$Dy(LaBa)Cu_4O_8$ (sheet)	-26.04	22.08 22.02 (21.13)	48.12 48.06	80
M	$Nd_{1.4}Ce_{0.2}Sr_{0.4}CuO_4(T^*)$	-26.55	21.44 (25.21)	47.99	30
N	$La_2CaCu_2O_6$	-27.21	20.97 (21.25)	48.18	metal
P	$La_2SrCu_2O_6$	-27.56	20.04 (22.28)	47.59	metal
Q	$Bi_2Sr_2CaCu_2O_8$	-42.61	5.63 (16.52)	48.23	85
R	$Bi_2Sr_2CuO_6$	-37.66	10.71 (17.91)	48.38	15
S	La_2CuO_4	-27.57	21.65 (19.83)	49.22	35
T	La_2NiO_4	-28.32	21.26 (20.05)	49.58 $\frac{+1.67}{51.25}$	semi.

Within this ionic picture, we consider insulating sheets of CuO_2 which have no holes and use standard Ewald techniques⁹ to calculate the electrostatic site potentials which contribute [Eq. (1)] to the energy to add a hole. In Table I we list the known compounds that contain such sheets of Cu^{+2} and O^{-2} . Such insulating sheets are contained in the structure of $YBa_2Cu_3O_6$, while the sheets in $YBa_2Cu_3O_y$ generally have holes. Therefore, we consider the related hypothetical, hole-free compound $Y(LaBa)Cu_3O_7$, which would have La on half the Ba sites. Similarly, we consider $Y_2(LaBa)_2Cu_7O_{15}$ and $Y_2(LaBa)_2Cu_8O_{16}$ for the 2:4:7 and 2:4:8 compounds. The compounds $Y(LaBa)Cu_3O_7$ and Sr_2CuO_3 both contain chains, which are included for comparison. The resulting Madelung site potentials for the copper (V_M^{Cu}) and for the oxygen (V_M^O) sites in the sheet are summarized in Table I. Directly beneath the latter value (and in parentheses) is the site potential for the apical oxygen (where the structure contains one). Included in the fifth column of Table I is the most important parameter, $e\Delta V_M = eV_M^O - eV_M^{Cu}$, which is the electrostatic contribution to the energy difference ΔE_h of Eq. (1). It is seen that this energy is large, of order 47 eV. Although the structures of the CuO_2 sheets are virtually the same, the variations in the position and composition of the counterions give rise to significant variations in $e\Delta V_M$, by as much as 3 eV, which is considerably larger than the estimated variations in the bandwidth, for example. This result indicates that the nature of the holes (as O^- or Cu^{+3}) will vary among the copper oxide compounds.

In order to examine possible correlations with the conduction properties, we plot in Fig. 2 the dependence on $e\Delta V_M$ of the maximum T_c observed for the compounds in Table I when they are doped with holes. The coordination of the copper sites is indicated by the symbols and is seen to correlate with $e\Delta V_M$: For four-coordinated copper sites, $e\Delta V_M$ lies near 46 eV, for five-coordinated copper near 47–48 eV, while for six oxygen neighbors $e\Delta V_M > 49$ eV. Thus, the copper coordination can be

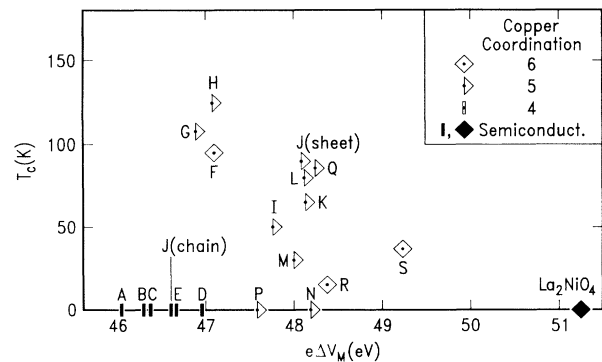


FIG. 2. Plot of the dependence of $e\Delta V_M$ of the maximum superconducting transition temperature for the compounds listed in Table I.

used as a rough guide for the value of ΔV_M , but there are notable exceptions, due to large apical oxygen distances and because the Madelung energy involves a sum over many distant neighbors.

The semiconducting compounds are shown in Fig. 2 by the solid symbols. The most striking feature of these data is the clear separation between the compounds which are semiconductors and those which are metallic, with a well-defined boundary near $e\Delta V_M = 47$ eV. The most dramatic examples of the semiconducting compounds are Sr- and Ca-doped Gd_2CuO_4 and Nd_2CuO_4 , which have¹⁰⁻¹² a hole concentration as high as 10% and yet their conductivity is more than 4 orders of magnitude worse than the corresponding La compounds at 300 K. The infinite-layer compound, $Ca_{0.86}Sr_{0.14}CuO_2$, is also semiconducting, although it is difficult to dope,^{12,13} as is the case for¹⁴ Na-doped $Sr_2CuO_2Cl_2$. A further example is the chains in $YBa_2Cu_3O_7$ which are semiconducting.⁵

One of the effects of covalency in the CuO_2 sheets is to reduce the effective charges on the ions from the ionic values of Cu^{+2} and O^{-2} that we have assumed above. In order to simulate this effect, we have calculated the Madelung site potentials for $Cu^{+1.5}(O^{-1.75})_2$ and $Cu^{+1}(O^{-1.5})_2$ for several of the compounds in Table I. In these less-ionic-model compounds, we find that the values of $e\Delta V_M$ do indeed decrease; however, the magnitude of the decrease (8.0–8.3 eV per 0.5 change in the Cu charge) is approximately the same for each compound. Thus, the effect of considering a CuO_2 sheet with reduced charges is to linearly shift the values of $e\Delta V_M$ in Fig. 2 to lower values, but retaining their relative order.

Let us now consider a simple picture which can account for the boundary between semiconducting and metallic conductivity. In an ionic model, a hole localized on a copper site can conduct if it can hop onto a neighboring oxygen site, which involves an energy barrier of $\Delta = |\Delta E_h| = |E_h^O - E_h^{Cu}|$. Similarly, if the hole were

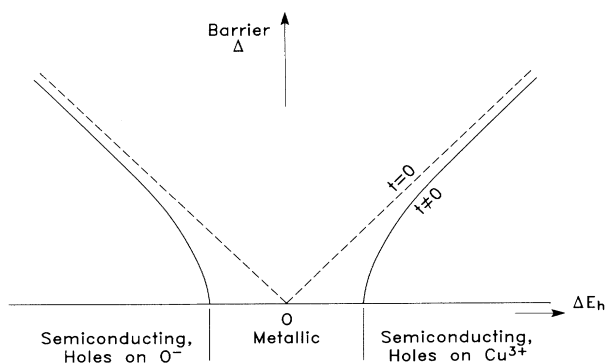


FIG. 3. Schematic figure of the barrier to conduction of charge between copper and oxygen sites for the ionic ($t=0$) model and for the case of finite bandwidth, showing holes self-trapped on oxygen (copper) sites for large and negative (positive) $\Delta E_h/4t$.

localized on an oxygen site ($\Delta E_h < 0$), the barrier to hopping through the copper site would be $\Delta = |\Delta E_h|$. This barrier is plotted in Fig. 3 vs ΔE_h in the ionic ($t=0$) model that we have been discussing. In this simple case, the conduction would be metallic (i.e., would have no barrier) at the unique condition $\Delta E_h = 0$. A finite bandwidth ($t \neq 0$) broadens the metallic region: If the barrier is finite, but still less than or comparable to the bandwidth, the hole would encounter no barrier to conduction. Because of the interaction with phonons, these holes may become large polarons but still exhibit metallic conductivity. However, if the barrier were sufficiently large compared to the bandwidth, the holes would become severely self-trapped (by phonons and the doping cations), forming small polarons, and be able to move only by thermally assisted hopping.¹⁵ As shown schematically in Fig. 3, the holes would be (1) largely localized on O^- sites if $\Delta E_h/4t$ were large and negative (to the left in Fig. 3), (2) largely localized on Cu^{+3} sites if $\Delta E_h/4t$ were large and positive (to the right of Fig. 3), and (3) metallic in between. In this metallic regime, holes would be delocalized over both O and Cu sites.

Let us now compare Figs. 2 and 3, in order to see how the compounds in Fig. 2 could fit into the simple conductivity of Fig. 3. The semiconductors on the left in Fig. 2 have relatively lower values of ΔV_M and hence ΔE_h than the metals on the other side of the boundary. These semiconductors must then correspond to those on the left in Fig. 3 which have holes localized on O^- . The conclusion is then that the semiconductors have such a large and negative ΔE_h that the holes are strongly centered on the O sites and become self-trapped, small polarons, which exhibit thermally assisted hopping (i.e., semiconducting) behavior. The compounds toward the right in Fig. 2 have apical oxygens, which tend to favor holes on the copper site, thus decreasing the extreme localization present in the semiconductors and making metallic conductivity possible. In these metals, the barrier which tended to localize the holes on O^- in the semiconductors is smaller than the bandwidth. Note that this trend continues for compounds with increasingly larger values of ΔV_M to La_2CuO_4 , in which the holes are least favored on O^- of all the copper oxides.

We believe that the above conclusions are quite sound. Three, more speculative extensions are given below:

(1) The semiconducting nature¹⁶ of $PrBa_2Cu_3O_7$ would be understood in this picture as caused by the strong hybridization¹⁷ of the Pr^{+3} ion and the O^- holes on the sheets with the (Pr^{+4}, O^{-2}) excited state. This hybridization would decrease the energy of the O^- holes with respect to those on copper by more than 1 eV, shifting $PrBa_2Cu_3O_7$ to the left (i.e., semiconducting) side of the boundary in Fig. 2.

(2) Extending this work to include La_2NiO_4 , we find a large effective value of $e\Delta V_M$, increased by the 1.67-eV difference in⁸ I_3 for the Cu^{+2} and Ni^{+2} ions [Eq. (1)]. The semiconducting behavior¹⁸ of Sr-doped La_2NiO_4

would be understood if this compound belonged in the semiconducting state to the right of Fig. 3, in which the holes are localized on Ni^{+3} . Then the metallic phase of Fig. 3 would be centered near $e\Delta V_M \sim 48\text{--}49$ eV in Fig. 2, compared to the estimate of 45 eV for the purely ionic model. This conclusion suggests that the metallic nature of these copper oxides is due to the near degeneracy of the energies of holes on copper and oxygen sites (in contrast to the view that the holes in the superconductors are largely in oxygen-based orbitals).

(3) An interesting question is whether the holes localized on O^- in the semiconductors condense to form peroxides, $(\text{O}_2)^{-2}$, in the CuO_2 sheets.

In conclusion, the variation in conductivity behavior among a wide variety of copper oxides is caused by the large variation (up to 3 eV) of the Madelung site potential induced in the CuO_2 sheets by the differences in the counterions.¹⁹ The semiconducting compounds are shown to have deep holes, self-trapped on the oxygen sites. The higher coordination of copper in the other compounds tends to equalize the energies for holes on copper and oxygen sites and hence allows for delocalization and metallic conductivity.

¹See articles by B. Raveau, T. Siegrist, S. S. P. Parkin, and C. C. Torardi, in *High Temperature Superconductivity: The First Two Years*, edited by R. M. Metzger (Gordon and Breach, New York, 1988).

²E. Iguchi and Y. Yonezawa, *Jpn. J. Appl. Phys.* **26**, L1492 (1987).

³J. Kondo, Y. Asai, and S. Nagai, *J. Phys. Soc. Jpn.* **57**,

4334 (1988).

⁴L. F. Feiner and D. M. de Leeuw (to be published).

⁵Y. Tokura, J. B. Torrance, T. C. Huang, and A. I. Nazzal, *Phys. Rev. B* **38**, 7156 (1988).

⁶R. E. Cohen, W. E. Pickett, H. Krakauer, and L. L. Boyer, *Physica (Amsterdam)* **150B**, 61 (1988).

⁷Since atomic O^{-2} does not exist, estimates of A_2^0 must be used with caution.

⁸J. E. Huheey, *Inorganic Chemistry* (Harper and Row, New York, 1983), 3rd ed.

⁹R. M. Metzger, *J. Chem. Phys.* **57**, 1870 (1972); **64**, 2069 (1976).

¹⁰I. S. Shaplygin, B. G. Kakhan, and V. B. Lazarev, *Russ. J. Inorg. Chem.* **24**, 820 (1979).

¹¹J. Gopalakrishnan *et al.*, *Mater. Res. Bull.* **24**, 321 (1989).

¹²J. B. Torrance, A. I. Nazzal, E. Moran, and T. C. Huang (to be published).

¹³B. A. Scott (private communication).

¹⁴J. H. Cho *et al.*, *Bull. Am. Phys. Soc.* **34**, 931 (1989).

¹⁵D. Emin, *Phys. Rev. Lett.* **62**, 1544 (1989); D. Emin and M. S. Hillery, *Phys. Rev. B* **39**, 6575 (1989); Y. H. Kim *et al.*, *Phys. Rev. B* **38**, 6478 (1988).

¹⁶E. M. Engler *et al.*, *J. Am. Chem. Soc.* **109**, 2848 (1987); L. Soderholm *et al.*, *Nature (London)* **328**, 604 (1987); B. Okai *et al.*, *Jpn. J. Appl. Phys.* **26**, L1648 (1987); E. Moran *et al.*, *Physica (Amsterdam)* **151-153C**, 423 (1988); A. P. Gonçalves *et al.*, *Phys. Rev. B* **37**, 7476 (1988); M. Lopez-Morales *et al.* (to be published).

¹⁷J.-S. Kang *et al.*, *J. Less-Common Met.* (to be published); J. J. Neumeier, M. B. Maple, and M. S. Torikachvili, *Physica (Amsterdam)* **156C**, 574 (1988).

¹⁸M. Khairy, P. Odier, and J. Choisnet, *J. Phys. (Paris) Colloq.* **47**, C1-831 (1986).

¹⁹For further details, see R. M. Metzger and J. B. Torrance, in *Proceedings of the Materials Research Society Spring Meeting*, San Diego, California, 1989 (to be published).