

Origin of the Spatial Variation of the Pairing Gap in Bi-Based High Temperature Cuprate Superconductors

Michiyasu Mori,¹ Giniyat Khaliullin,² Takami Tohyama,³ and Sadamichi Maekawa^{1,4}

¹*Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan*

²*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*

³*Yukawa Institute for Theoretical Physics, Kyoto University, Kyoto 606-8502, Japan*

⁴*CREST, Japan Science and Technology Agency, Kawaguchi 433-0012, Japan*

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Recently, scanning tunneling microscopy on the Bi-2212 cuprate superconductor has revealed a spatial variation of the energy gap that is directly correlated with a modulation of the apical oxygen position. We identify two mechanisms by which out-of-plane oxygens can modulate the pairing interaction within the CuO₂ layer: a covalency between the x^2-y^2 band and apical p orbital, and a screening of correlation U by apical oxygen polarization. Both effects strongly depend on the apical oxygen position, and their cooperative action explains the experiment.

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Various types of high- T_c cuprates have been discovered for the last few decades. As a function of density of charge carriers doped into the CuO₂ planes, a superconducting critical temperature T_c shows in general a maximum which varies strongly from one family of cuprates to another. For hole-doped cuprates, a correlation between the maximum T_c and the energy-level separation of in-plane oxygens (O_P) and apical ones (O_A) has been noticed early on [1,2]. Hence, a role of apical oxygen on T_c is of considerable interest [1–7].

In Bi₂Sr₂CaCu₂O₈ (Bi-2212), a mismatch between the rock-salt BiO₂ layers and the CuO₂ planes causes an extra modulation of the crystal structure with a period about 26 Å. In such a “supermodulated” lattice, the distance d from the CuO₂ layer to the apical oxygen O_A is periodically varied within the range of $\sim \pm 6\%$ [8]. Given that bonds within the CuO₂ plane itself are much less affected by supermodulation, Bi-2212 material provides a unique opportunity to study the impact of apical oxygen on superconductivity, by monitoring local electronic properties as a function of d that varies spatially within a supermodulation period. This is precisely what is done in the recent scanning tunneling microscopy (STM) experiment by Slezak *et al.* [9,10] (see also Ref. [11]).

Slezak *et al.* measured the gap Δ in a local density of electronic states and found nearly 10% spatial variation of Δ with the same periodicity as supermodulation. They have emphasized that the gap variation is anticorrelated with the Cu- O_A distance variation, $\delta\Delta \propto -\delta d$; i.e., the gap increases when O_A gets closer to the CuO₂ plane and vice versa.

This remarkable observation has already been addressed in several papers by introducing variations of coupling constants on a phenomenological level [12,13]. However, the underlying microscopic mechanism that links the strength of pairing interactions *within* CuO₂ planes with

the position of *out-of-plane* O_A remains elusive. In this Letter, we discuss the physical origin of high sensitivity of the pairing gap to the Cu- O_A distance and explain the anticorrelation effect $\delta\Delta \propto -\delta d$ observed.

Quite in general, the structural shift of apical oxygen may influence the energy gap either via the hopping parameters (hence density of states on the Fermi level), or via the strength of the pairing interaction. In particular, there is a well-known relation between the next-nearest-neighbor hopping t' and T_c , based on the band structure calculations by Pavarini *et al.* [4]. One has to notice, however, that this observation concerns a comparison between different families of cuprates with different lattice structure. In fact, Pavarini *et al.* predicted that the variation of the Cu- O_A distance within a given compound hardly affects the hopping parameters [14]. Therefore, we focus here on possible electronic mechanisms by which apical oxygens may affect the strength of the pairing potential within the x^2-y^2 band [15].

We find two different ways how the apical oxygen may enter the game. First, a hybridization of “useful” x^2-y^2 band with the “pairing-inert” orbitals of apical oxygens reduces the pairing interaction. Such a destructive effect of covalency is controlled by a relative energy separation between the orbital levels that depends on Cu- O_A distance. We illustrate this by an explicit calculation of the Madelung potential as a function of d . Second, we show that the superexchange interaction J , which is believed to be essential for magnetic correlations and possibly for superconductivity, is very sensitive to the apical O_A position. This is due to the high polarizability of O^{2-} anion which has the effect of screening and reducing the energy U needed to move an electron from one ion to another [16,17]. In Bi-2212, the screening effect and hence the strength of magnetic correlations $J \propto 1/U$ are spatially modulated because the closer the apical O_A is, the stronger

the screening is. Remarkably, we find that the above two effects, covalency and screening, both favor an antiphase relation between Δ and d variations.

Covalency.—We address this effect in terms of the following Hamiltonian:

$$H = \sum_{k\sigma} \epsilon_k c_{k\sigma}^\dagger c_{k\sigma} - \sum_k \Delta (\gamma_k^d c_{k\uparrow}^\dagger c_{-k\downarrow}^\dagger + \text{H.c.}) + \sum_{k\sigma} \epsilon_A a_{k\sigma}^\dagger a_{k\sigma} + \sum_{k\sigma} \nu_k (a_{k\sigma}^\dagger c_{k\sigma} + \text{H.c.}) \quad (1)$$

Here, the first term corresponds to the in-plane $pd\sigma$ -band of x^2-y^2 symmetry made of Cu and O_P orbitals, and a conventional form of dispersion [4] $\epsilon_k = -2t(\cos k_x + \cos k_y) + 4t' \cos k_x \cos k_y - 2t''(\cos 2k_x + \cos 2k_y) - \mu$, where μ is the chemical potential, is adopted. The second term shows that this band is supposed to host a superconductivity of d -wave symmetry, with the gap function $\gamma_k^d = (\cos k_x - \cos k_y)/2$ and the gap magnitude $\Delta = g \sum_k \gamma_k^d \langle c_{-k\downarrow} c_{k\uparrow} \rangle$ determined by the strength g of a pairing potential (whose origin is not specified).

The third term in Eq. (1) represents holes on the $2p_z$ orbital of apical O_A with energy ϵ_A . While a complete model may consider the rich internal structure of the ‘‘axial’’ orbital by Pavarini *et al.* including $3d_{3z^2-r^2}$ and $4s$ states of Cu [4], we consider here a minimal model that captures the essential effects of the axial orbitals. Finally, the last term accounts for a covalent mixing of the x^2-y^2 and p_z orbitals. d -wave symmetry of the matrix element $\nu_k = 4\nu \gamma_k^d$ is imposed by the hopping geometry: a transfer integral ν from x^2-y^2 type Zhang-Rice orbital to the neighboring p_z states of axial symmetry must have different signs along x and y directions.

Physically, we associate ϵ_A with the energy-level separation of holes residing on in-plane O_P and apical O_A sites, as shown schematically in Fig. 1(b). A magnitude of ϵ_A can then be estimated from the Madelung potentials on O_P and O_A [18] using the structural data of Ref. [8]. To calculate variations of ϵ_A caused by supermodulation, we use the displacement pattern, Fig. 1(a), inferred from the structural data. This way, we quantify ϵ_A in terms of the distance d from the top CuO_2 layer (relevant for STM) to O_A above it, making thereby a link between the model and supermodulation.

Below, we use representative hopping parameters $t = 0.4$ eV, $t'/t = 0.3$, $t'' = t'/2$, and $\nu/t = 0.35$. The d -wave momentum dependence of ν_k renormalizes the t' , t'' values, but we compensate this numerically by adding a counterterm $\propto \nu^2/\epsilon_A$ and keep the actual values of t' , t'' invariant against the O_A shifts (as found in the band structure calculations [4]). The covalency effect is then entirely due to the spectral weight shifts between x^2-y^2 and axial orbitals.

Calculating the expectation value $\langle c_{-k\downarrow} c_{k\uparrow} \rangle$ in the model (1), we find the following gap equation:

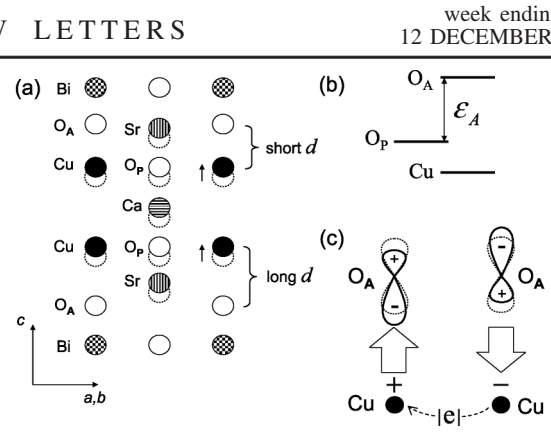


FIG. 1. (a) Local atomic displacements along the c axis due to the supermodulation (exaggerated). The Bi- O_A bond length does not change much, but other atoms (Cu, O_P , Sr, and Ca) are shifted such that the Cu- O_A bond is most affected [8]. The direction (up/down) and amplitude of the shift δd modulate along the a axis with a period ~ 26 Å, resulting in a $\delta d \sim \pm 6\%$ variation of the Cu- O_A bond length [8]. (b) Energy-level scheme of Cu, O_P , and O_A . (c) Schematic picture of the screening effect: Once a charge is moved from one Cu ion to another (at the energy cost U , initially), the apical oxygen orbitals experience an electric field (arrows) of excited charges and are polarized. An energy gain from the polarization process reduces a virtual charge excitation energy U .

$$1 = g \sum_k \sum_{\pm} \frac{Z_{\pm}}{2E_{\pm}} \tanh \frac{E_{\pm}}{2T} |\gamma_k^d|^2. \quad (2)$$

The quasiparticle energies are given by $E_{\pm} = \frac{1}{\sqrt{2}} \times [(\epsilon_k^2 + \Delta_k^2 + \epsilon_A^2 + 2\nu_k^2 \pm R^2)]^{1/2}$, where $R^2 = \{(\epsilon_k^2 - \epsilon_A^2 - \Delta_k^2)^2 + 4\nu_k^2[(\epsilon_k + \epsilon_A)^2 + \Delta_k^2]\}^{1/2}$. Equation (2) is composed of two parts where $Z_{\pm} = (E_{\pm}^2 - \epsilon_A^2)/(E_{\pm}^2 - E_{\mp}^2)$ represent the spectral weights of the pairing-active x^2-y^2 orbital on the two bands E_{\pm} . We note that Z_- (which is the most relevant one) is reduced from its bare value ($= 1$ at $\nu = 0$) due to the orbital mixing. This has the effect of reducing effective value of g in Eq. (2).

First, we regard ϵ_A as a free parameter and consider how its variation affects the gap. Solving Eq. (2) at $g/4t = 0.9$ and $T = 0$, we obtained a sizable variation of the gap as a function of ϵ_A as shown in Fig. 2(a). This is due to the covalency effect that reduces the spectral weight of the x^2-y^2 states near the Fermi-level, by transferring it to the higher energy apical states. An amount of hole transferred into the apical level is rather small, of the order of several percent, see Fig. 2(b). However, it may be observed in the nuclear quadrupole resonance (NQR) which is sensitive to the hole concentration [20].

Next, we consider how ϵ_A is shifted by the structural modulation. From the Madelung potential calculation, we obtained a linear relation $\epsilon_A(d)/t = (\bar{\epsilon}_A/t)[1 - a(d/d_0 - 1)]$, with $\bar{\epsilon}_A/t = 3.85$ [21] and $a = 1.6$. $d_0 \approx 2.4$ Å is an average Cu- O_A distance [8]. The inset of Fig. 2(a) shows that the energy-level separation ϵ_A increases as the apical site O_A comes closer to the Cu-ion. Consequently, the

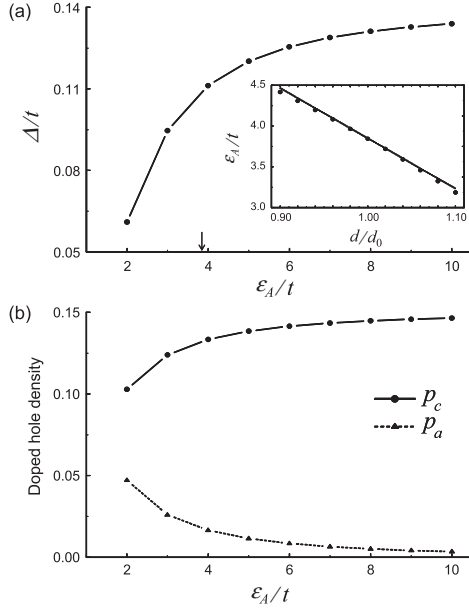


FIG. 2. (a) The pairing gap Δ as a function of the energy-level separation ϵ_A between the apical orbital a and the x^2 - y^2 band. Arrow indicates ϵ_A at $d = d_0$. Inset: ϵ_A vs Cu-O_A distance d . The data are fitted by a linear relation $\epsilon_A(d)/t = 3.85[1 - 1.6(d/d_0 - 1)]$. (b) Distribution of doped holes among the x^2 - y^2 and the a bands, denoted by p_c and p_a , respectively. Total density of holes is fixed to $p_c + p_a = 0.15$.

pairing gap is also increased [see Fig. 2(a)] since the strength of the hybridization is reduced.

Having obtained the relations Δ vs ϵ_A and ϵ_A vs d , we are now in position to show the gap Δ variations as a function of d directly. The result is presented in Fig. 3 by the broken line, which shows that the $\pm 6\%$ change of d leads to a sizable variation of Δ .

Screening.—This effect is based on an observation [16,17] that anion polarization renormalizes the energy of virtual charge excitations. This physics is relevant here since the O_A-contribution to the screening of in-plane interactions should strongly depend on d .

Let us consider how U and magnetic correlations within the CuO₂ planes are modified by apical O_A. In the U -excited intermediate state, both an unoccupied and doubly occupied Cu sites strongly polarize apical sites just above each Cu site, see Fig. 1(c). Apical oxygen obtains a dipole moment $p = \alpha F$ where α is the polarizability of O²⁻ ion, and $F \approx e/d^2$ is an electric field on oxygen induced by an extra charge (hole or electron) on Cu site which is created by U -excitation. (We ignored dipole-field corrections to F from further located ions for simplicity). Energy gain due to this polarization process in a virtual state reduces the U -excitation energy to $U_{\text{eff}}(d) = U - E_{\text{pol}}(d)$, where $E_{\text{pol}}(d) = 2(pF/2) = \alpha F^2 \approx \alpha(e/d^2)^2$ is an interaction energy between the induced dipole moments p on O_A and an excited hole (electron) at the unoccupied (doubly occupied) Cu sites. Since O²⁻ ion

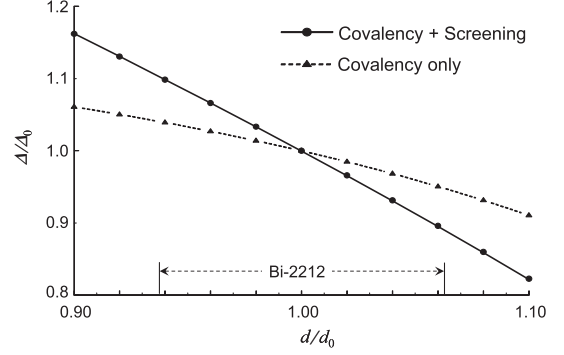


FIG. 3. The gap Δ as a function of d , where $\Delta_0 \equiv \Delta(d_0)$. The broken line shows the covalency effect only; i.e., the gap variation is solely due to modulation of $\epsilon_A(d)$ at fixed $g/4t = 0.9$. The solid line includes also the screening effect through the d -dependence of the coupling constant $g(d)$ (see text). In Bi-2212, Cu-O_A distance varies within the range indicated.

has large polarizability, $\alpha \approx 2 \text{ \AA}^3$ [23], energy $E_{\text{pol}}(d)$ is sizable: for the average Cu-O_A distance $d_0 \approx 2.4 \text{ \AA}$, we estimate $E_0 \equiv E_{\text{pol}}(d_0) \approx 0.9 \text{ eV}$. It is important to realize that, due to the strong d -dependence of $E_{\text{pol}}(d) \propto 1/d^4$, the effective repulsion U_{eff} becomes highly sensitive to the Cu-O_A distance: $\delta U_{\text{eff}}(d) = -\delta E_{\text{pol}}(d) = 4E_0 \delta d/d_0$. An immediate consequence of this observation is that the antiferromagnetic exchange interaction $J \approx 4t^2/U_{\text{eff}}$ between the Cu spins obtains the same strong modulation as a function of d : $\delta J(d)/J_0 = -(4E_0/U_0)(d/d_0 - 1)$, where $U_0 \equiv U_{\text{eff}}(d_0)$ and $J_0 \equiv J(d_0)$. With the above estimate for E_0 and using a representative value $U_0 \approx 7 \text{ eV}$, we find that $\delta J(d)/J_0 = -\beta(d/d_0 - 1)$ with $\beta \approx 1/2$. Thus, in a modulated structure of Bi-2212, the J value strongly increases as the Cu-O_A distance d decreases and vice versa; i.e., it shows the same anticorrelation effect with d as the pairing gap Δ does in the experiment.

Now, we assume that the superexchange driven magnetic correlations are essential for the pairing in cuprates as widely believed. Indeed, e.g., in the t - J model, J plays a role of pairing potential same as g in Eq. (2). It is then natural to consider that the pairing potential g in Eq. (2) is modulated in the same functional form as J . We therefore implement a relation $g(d) = g[1 - \beta(d/d_0 - 1)]$ with $\beta = 1/4$ [24] and calculate the gap values from Eq. (2) for different d . The obtained gap modulation is presented in Fig. 3 by the solid line. A combined action of the covalency and the screening effects can be summarized by a relation $\delta \Delta/\Delta_0 \approx -A \delta d/d_0$, with $A \approx 1.6$.

For a comparison of this result with experiment [10], we notice that the measured gap $\Delta(\mathbf{r})$ is in fact determined by a ‘‘coarse-grained’’ value $\tilde{d}(\mathbf{r}) \approx \langle d(\mathbf{r}) \rangle_\xi$ of the actual Cu-O_A distances. Such a coarse graining of $\delta d \propto \cos(2\pi r_a/\lambda)$ [10] gives $\delta \tilde{d}(\mathbf{r}) \approx f \delta d(\mathbf{r})$; i.e., the modulation ‘‘seen’’ by Cooper pairs is reduced by a factor f that depends on the ratio of the coherence length ξ and the

supermodulation period $\lambda \approx 26 \text{ \AA}$ [25]. At $\xi \approx 20 \text{ \AA}$, we find $f \approx 0.43$. The above relation $\delta\Delta$ vs δd reads then as $\delta\Delta/\Delta_0 \approx -\tilde{A}\delta d/d_0$, where $\tilde{A} \approx 0.7$. This gives $\approx 9\%$ total variation in Δ due to $\pm 6.25\%$ modulation of d , just as observed by Slezak *et al.*

In a broader context, it should be emphasized that while we are concerned here with the variations of apical oxygen position within a given structure of a given material, the effects discussed—spectral weight transfer and screening of effective U —are generic and relevant for the gap and T_c variations among different cuprate families. However, many other things must be kept in mind when we compare different cuprates. In particular, apical oxygens may have a negative impact on T_c by communicating a destructive effect of out-of-plane disorder to the CuO_2 planes [5,6]. Anticorrelation between the energy gap and the distance to the apical oxygen observed by Slezak *et al.* in Bi-2212 implies that the effects we discussed here overcome the disorder related physics (which would result in a trend opposite to what observed). A key question is then how this competition is resolved in different cuprate families. To address this issue and better understand the T_c trends in cuprates, our model has to be implemented by out-of-plane disorder effects.

Finally, we argued that effective U hence J values are renormalized by O_A , and thus they become sensitive to the O_A -position. This inevitably turns the exchange interaction in Bi-2212 into inhomogeneous one in space. In other words, we expect that the strength of local spin correlations follow the lattice supermodulation. The resulting broad distribution of relaxation times could possibly be tested by the NMR/NQR experiments. In fact, the recent neutron scattering work has revealed an intrinsic broadening of the spin excitations in Bi-2212 [26], an observation that seems natural in a light of our picture.

To conclude, we discussed the physical origin of the relationship between the pairing energy gap and the atomic displacements in the supermodulated structure of Bi-2212. A covalent mixing of the x^2-y^2 orbital with apical p -level, and a screening of effective U values via the polarization of apical oxygens are found to act cooperatively and modulate the pairing correlation as a function of the Cu- O_A distance. This leads to the spatial variations of the energy gap as observed in the experiment.

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