

Coherent Resonant Pinning, Oxygen Ordering, and High-Temperature Superconductivity in the Multilayer Cuprates

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The emerging microscopic theory featuring the titled mechanisms quantitatively explains chemical trends in three multilayer cuprate superconductive families, $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+\delta}$, $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n+\delta}$, and $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2+2n+\delta}$ and relates superconductive properties directly to structure, not only for T_c but also for dT_c/dp as well. The theory is based on conventional electron-lattice interactions and utilizes no exotic concepts.

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While the high T_c 's of the layered cuprates have attracted unprecedented attention since their discovery [1] (~ 35000 publications so far), no consensus has emerged regarding the microscopic mechanism which could explain how T_c can be so large ($\gtrsim 150$ K compared to $\lesssim 25$ K for intermetallic compounds). A few scientists with extensive experience in materials science have argued [2-4] that the most likely explanation is a large peak in the density of electronic states $N(E)$ at $E=E_0$ associated with oxygen dopant vacancies or interstitials. By suitable processing E_0 can be tuned to E_F (resonant pinning). The processing must also produce short-range superlattice dopant ordering so that the states resonant with the dopants interact coherently [5]. Finally, the electron-boson interaction, as measured by a configurational excitation energy E_a of the oxygen dopants, should be considerably larger than that of optical phonons, so that a generalized Bardeen-Fröhlich interaction will be attractive over a larger energy range. Given these factors it is easy to obtain high T_c 's from strong-coupling formulas of the Allen-Dynes type [6].

The foregoing program is attractive because it requires minimal modifications of the BCS theory which has so far been highly successful in explaining superconductivity and has quantitatively predicted T_c in many elemental metals and intermetallic compounds [7]. Implementation of this program has progressed slowly, however, because of the difficulty of measuring any of its three essential features [$N(E_F)$, the oxygen ordering, or E_a] directly. In this Letter we summarize several exciting recent developments which show great progress in each of these three areas.

I. Resonant pinning.—The usual argument against resonant pinning is that any local configuration which produces a resonant peak in $N(E)$ at $E=E_0=E_F$ will lower its energy through a Jahn-Teller distortion which divides the peak into an occupied "bonding" peak with $E_1 < E_0=E_F$ and an unoccupied "antibonding" peak with $E_2 > E_0=E_F$. There are two counterexamples, both in layered compounds, which show that this argument, although usually correct, has exceptions. These are $\text{Bi}_2\text{Te}_3\text{:Bi}$ [8] and $\text{BaCo}_{1-x}\text{Ni}_x\text{S}_{2-y}$ [9]. Both of these

exceptions involve layered structures which, contrary to the usual systematics of metal-insulator transitions, are *more metallic at low temperatures*. Moreover, they both involve anions from the oxygen column, and the transition temperature increases from Te to S indicating that a resonant pinning state in a layered oxide can be stable to high temperatures $T \gtrsim 700$ K. The explanation for this *anti-Jahn-Teller* effect is that energy can be gained, especially in layered structures, by improved screening of long-range ionic potentials [10].

II. Oxygen ordering.—Here great progress is provided by the discovery of the highest- T_c materials, the Hg cuprates [11]. Like the bismates and thallates, these form multilayer families with n layers of CuO_2 planes grouped together in blocks ($n=1,2,3$). The systematics of $T_c(n)$ in these three families is very instructive, and it is illustrated in Fig. 1. The most obvious trend, and the one that initially attracted the most interest, is the increase of $T_c(n)$ with increasing n in each family. [The origin of this trend is easy to understand. The metallic CuO_2 layers and the semiconductive layers (such as BaO) have different intrinsic or prototypical lattice constants, even after adjustment of the interlayer spacing [12]. The internal stress generated by this interlayer misfit can be stabilized more easily without introducing stacking faults (such as partial edge dislocations) as n increases.] Now that we have data on three families, however, we can notice a second trend which is equally interesting. The formal (mixed) valences ($\bar{Z} = \bar{Z}_1, \bar{Z}_2$) of the cations which are placed symmetrically between the CuO_2 planar blocks are Hg(1,2), Tl(1,3), and Bi(3,5). As the figure shows, T_c increases with decreasing valence \bar{Z} of these cations, or T_c decreases as these valences \bar{Z} increase and these cations become more covalent and more susceptible to undesirable Jahn-Teller distortions. The worst cases in this regard are the Bi cuprates, because these are micaeous, with easy cleavage of Bi_2O_2 double layers. The most dramatic effect is the obvious suppression of T_c in the Bi(1) cuprate, marked by *A* in Fig. 1. In this case the Jahn-Teller distortion has been observed directly by diffraction as a periodic buckling of the layer structure [13]. In the other cases the buckling is too small to be

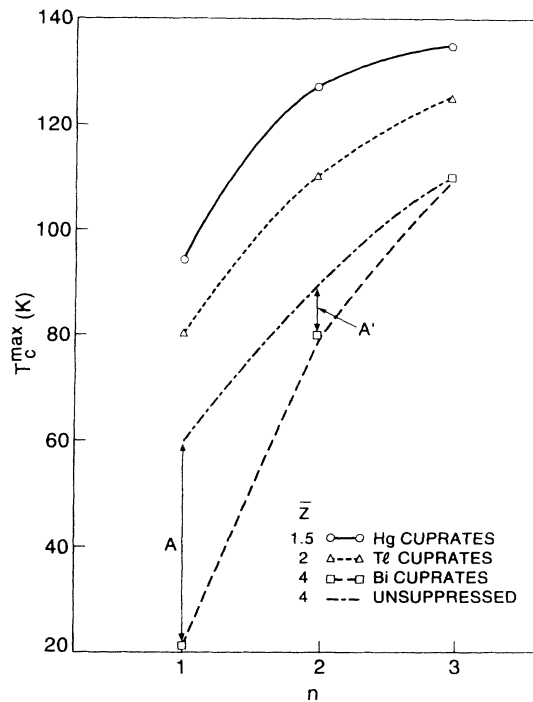


FIG. 1. Values of T_c^{\max} for the Hg-Cu(n), Tl-Cu(n), and Bi-Cu(n) families, from Refs. [13] and [14]. The curve marked "unsuppressed" refers to Bi-Cu(n) values in the absence of layer buckling, and it is only an estimate for a lower bound. [It is possible that $T_c(n)$ would be constant, or nearly so, for each family, in the complete absence of layer buckling.]

observed, but the chemical trends in Fig. 1 are unambiguously consistent with Jahn-Teller distortions as the explanation for the trends in $T_c(n)$ both with n and with cation valence \bar{Z} .

Given these remarks, we now know where to look for evidence for oxygen dopant ordering. The most favorable family is the Hg(n) family, where the tendency towards Jahn-Teller distortions is least, and where T_c is highest. Within this family oxygen dopant superlattice coherence should increase with increasing n . It has already been recognized that interstitial oxygen atoms at centers of Hg squares are the most natural dopants for these materials [11,14,15]. The measured fractional site occupancy $\delta(n)$ is plotted against n , together with $T_c(n)$, in Fig. 2. It is quite clear that $\delta \rightarrow 0.25$ as $n \rightarrow 3$, and that the suppression of δ for $n=1$ is a domain effect related to Jahn-Teller distortions of the type that so greatly suppressed $T_c(1)$ in the Bi family. The simplest interstitial superlattice consistent with tetragonal symmetry is the 2×2 with $\delta=0.25$. It is difficult to believe, in the context of the chemical trends shown in Fig. 1, that this is accidental.

While the effects of Jahn-Teller distortions, planar buckling, and extensive planar defects are most prominent in the Bi-Cu(n) series for $n=1$, the general similarities in chemical trends shown in Fig. 1 suggest that these same effects are present in the Hg-Cu(n) series, and be-

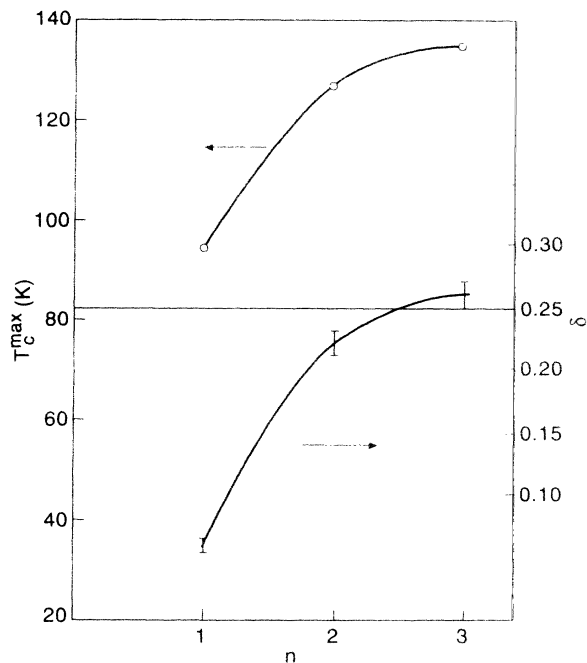


FIG. 2. For the Hg-Cu(n) family the occupancy factor $\delta(n)$ for the Hg plane oxygen interstitial site closely parallels $T_c(n)$ and appears to saturate near $\delta = \frac{1}{4}$ (Ref. [14]).

come small only for Hg-Cu(3). There is considerable evidence to support this conclusion from chemical trends in T_c and structural parameters under pressure. The Hg-Cu(n) family exhibits reversible values of $T_c(p)$ up to $p=0.9$ GPa [16], which suggests a low density of extensive planar defects and a larger energy for their formation. In Hg-Cu(3) application of pressure increases $T_c(p)$ up to $p=30$ GPa [17], whereas in Y-Ba-Cu-O (YBCO) T_c increases only up to 9 GPa and decreases thereafter (presumably because of oxygen disordering or the formation of more defects), even though YBCO has a comparatively low density of extended planar defects at $p=0$ [14]. From binary cohesive energies and compressibilities one would expect the relative compressibilities for c -axis Hg-O and Cu-O bonds to be larger for Hg-O and smaller for Cu-O. However, this is actually the case [14] only for Hg-Cu(3), but not for Hg-Cu(1) and Hg-Cu(2). The difference could be attributed to the presence of impurity phases [14], but the presence of these phases may also be related to the formation energies of associated cascades of extensive planar defects in the host Hg-Cu(n) superconductors.

The partial substitution of Hg by Pb in Hg-Cu(3) provides further support for the idea that oxygen ordering is maximal and layer buckling is minimized in HgCu(3). In general, high temperature superconductors with $T_c \gtrsim 100$ K always exhibit one-sided dopability; that is, they can be underdoped with decreasing T_c , but overdoping produces phase instabilities. There is no widely accepted microscopic explanation for this one-sided behavior, but it

was suggested [15] that the phase instability could be viewed as a kind of generalized Jahn-Teller instability driven by precipitation of resonant pinning centers in the overdoped composition range. We can view buckling as a precursor to such phase instabilities. Then when layer buckling is minimized, overdoping becomes possible, and it is indeed observed that (Hg,Pb) Cu(3) is the first example of an X -Cu(3) compound which can be both underdoped and overdoped [15].

III. The boson energy E_a .—So much attention has been focused on the CuO₂ a - b planes that relatively little discussion has been given to the problem of current flow along the c axis normal to these planes. Originally it was thought that c -axis current flow was thermally activated (semiconductive), but recent data have shown that $d\rho_c/dT < 0$ is the result of the presence of stacking faults and other a - b planar defects, and that $d\rho_c/dT > 0$ (and, in fact, nearly constant) just as $d\rho_{a,b}/dT$ is, in suitably processed samples [18,19]. This has been interpreted [19] to mean that there are resonant pinning centers located midway between the CuO₂ planar blocks which provide metallic conductivity paths [2] normal to the planes similar to those of the planes themselves (giving the same temperature dependence), but with a much lower density (making the overall c -axis resistivity ρ_c 10–100 times or more larger than the planar resistivity ρ_{ab}).

The resonant pinning centers donate carriers to the CuO₂ planar blocks above or below them. This suggests that these centers are bistable (double well configurational potential model), with the two positions separated by an activation energy E_a . This activation energy can be measured from Debye loss peaks in acoustic attenuation (internal friction peaks) which determine a bistable relaxation time $\tau(T)$. When $\tau(T)$ is described by Arrhenius activation, $\tau = \tau_0 \exp(-E_a/kT)$, measurements at several temperatures yield E_a [20]. Although these experiments are still in their early stages, the measured values are highly suggestive. First, in La_{2-x}Sr_xCuO₄ the strength $I(x)$ of the electronic Debye loss peak correlates well with the Meissner volume fraction $f_M(x)$, and second, the values of E_a in La-Sr-Cu-O, YBCO, and Bi-Sr-Ca-Cu-O are all approximately proportional to T_c [19]. From the viewpoint of strong-coupling theory [7], this is exactly what one would expect, especially when the quenching effects of stray internal magnetic fields on $\Delta(\omega)$ for $\hbar\omega > E_a$ are taken into account [19].

We have previously proposed [19] a heuristic formula which emphasizes the proportionality of T_c and E_a . Here we refine the formula somewhat to include the n dependence in the Hg, Tl, and Bi compounds with n CuO₂ planes per planar block:

$$T_c^{\max} = 2f(n)\theta_D E_A / W, \quad (1)$$

where $f(3) = 1$, and θ_D and W are the Debye temperature of CuO₂ planar vibrations ($\theta_D \approx 500 \text{ cm}^{-1}$) and the

CuO₂ d - p valence bandwidth ($W \sim 2 \text{ eV}$). This heuristic formula is helpful in thinking about the pressure dependence of T_c as well as the broader chemical trends. In the Hg-Cu(n) compounds we see that $f(n)$ is independent of p up to 0.9 GPa [16], because $d \ln T_c / d \ln V$ is independent of n in this range. The actual magnitude

$$\alpha = -d \ln T_c / d \ln V \quad (2)$$

in the Hg(n) compounds, as well as in the Bi(2) and Tl(2) compounds, is about +1.1(2). This is close to the Gruneisen constants for these materials [16],

$$\beta = -d \ln \bar{\omega} / d \ln V, \quad (3)$$

where $\bar{\omega}$ is the average phonon energy, $\beta = 1.7(4)$.

We can make more progress by examining the various factors in Eq. (1) more closely. Both θ_D and W refer to electronic properties over a wide energy range of order several eV, but $E_A \sim 0.16 \text{ eV}$ refers to a much smaller energy range. It is natural to group θ_D and W together, and to assume that the $d \ln \theta_D / d \ln V$ and $d \ln W / d \ln V$ contributions to α approximately cancel. This leaves us with $d \ln E_A / d \ln V$ as the primary factor which determines α . In this connection it is very interesting [16,21] that in YBCO, while $\beta(\text{Cu-Cu}) = 1.55$, $\beta(\text{O-O}) = 1.05$. These two values refer to specific Raman-active modes in YBCO, and it is clear that $\beta(\text{O-O})$ is much closer to α than $\beta(\text{Cu-Cu})$ or the average Gruneisen constant. The activation energy E_A of oxygen dopants probably involves primarily oxygen rearrangements, and the similarity between $\beta(\text{O-O})$ and α therefore is consistent with the general features of Eq. (1).

The (relatively) simple description of T_c^{\max} in Eq. (1) applies only at or very near optimal compositions where $T_c = T_{\max}$. Away from such compositions samples appear to consist of mixtures of two or more submicroscopic phases with length scales $\lesssim 100 \text{ \AA}$. In particular, at nonoptimal compositions in YBCO, T_c is greatly depressed by the presence of paramagnetic microphases which decrease T_c linearly with increases in their volume fraction f_P [22]. At nonoptimal compositions x , α is much larger ($\gtrsim 10\times$) than at optimal compositions x_0 , but $T_c(p, x)$ never exceeds $T_c(p, x_0)$. This is consistent with a large value of $-\partial f_P / \partial p$.

Although the oxygen isotope shift [23] is qualitatively similar to an internal pressure shift (in the sense that the composition dependences of $d \ln T_c / d \ln m_0$ and $d \ln T_c / d \ln V$ are similar), it is not clear at present whether or not both are driven by $\partial f_P / \partial p$. The pressure shifts are all measured at low temperatures, whereas the isotope shift is measured with "different" samples which have been either formed or transformed at high temperatures, where other micromorphological mechanisms can be important [24]. In any event one should not misinterpret Eq. (1) to imply that a large isotope shift should be found near the optimal composition $x = x_0$. Instead near x_0 , $d \ln T_c / d \ln m_0$ is usually small, presumably because E_A is the

rapidly varying factor and it is nearly independent of m_0 .

In conclusion, we have sketched a very simple picture which explains the origin of many similarities in properties and chemical trends in multilayer cuprate superconductors with $T_c \geq 100$ K. We found it reassuring that the systematics shown in Figs. 1 and 2 are here explained about as well as we were able to explain [25] the systematics of T_c in the TX ($T = \text{Zr, Ti, Nb, V}$; $X = \text{C, N, O}$) family with the NaCl structure, which is certainly very simple compared to the layered cuprates. In fact, the latter family was so simple that it never became the beneficiary of exotic theories (resonating valence bonds, anyons, d waves, marginal Fermi liquids, etc.) such as have appeared to describe the cuprates. The similar success here suggests that these theories, after all, may never have been needed. What is appropriate now are further realistic studies of electron-lattice interactions [26], especially at coherent resonant pinning centers.

Note added.—Recent angle-resolved photoemission data on $n=2$ bismates exhibit a $\sqrt{2} \times \sqrt{2}$ superlattice structure at $E = E_F$ [27]. The authors explain this as the result of an antiferromagnetic Cu superlattice and argue against an atomic superlattice, of the kind proposed here, because it is not observed by LEED, which would be the case for a microdomain size larger than 100 Å. However, even in YBCO_x, where it is generally believed that 2×1 superlattices exist near $x = 6.5$, unambiguous O chain ordering has never been established by LEED, presumably because the microdomain sizes are too small. The bismates show much stronger buckling effects which are certain to reduce microdomain sizes further, so the absence of LEED structure carries no weight.

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