

Structural chemistry and high-temperature superconductivity

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Phenomenological trends in the superconducting transition temperature T_c and the energy gap E_g as measured in many tunneling and isotope experiments are discussed for ternary metallic Cu oxides. Available data are consistent with the Bardeen-Fröhlich electron-phonon mechanism and the Bardeen-Cooper-Schrieffer microscopic theory. The role of Cu oxidation is discussed in the context of the mechanical stability of the perovskitelike lattice structure.

The discovery of high-temperature superconductivity in ternary Cu oxides has surprised almost everyone, because it seems unlikely that the highest transition temperatures should be found in materials which are barely metallic.^{1,2} Two paths of rationalization are immediately apparent. We can discard the conventional microscopic Bardeen-Cooper-Schrieffer (BCS) theory,³ with its attractive electron-phonon interaction,^{4,5} or we can examine the structural chemistry and explain through conventional electronic self-consistent field band-theory studies^{6,7} why the oxide alloys behave so differently from normal-metal alloys and compounds. I believe that the latter path will ultimately succeed, but that some useful comments of immediate value can be made without elaborate calculation. These include assessments of gap measurements and isotope shifts to show that they are fully consistent with BCS.

First consider the transition temperatures themselves. The plot shown in Fig. 1 of T_c versus experimental values of γ [proportional to the density of states $n(E)$ at $E = E_F$] has often been made.⁸ Conventional self-consistent field calculations^{6,7} have explained the points for $\text{Ba}(\text{Pb,Bi})\text{O}_3$ and $(\text{La,Sr})_2\text{CuO}_4$, so the major problem is to fit the data⁹ ($\gamma = 3-5$ per Cu atom in the units of Fig. 1, $T_c = 93$ K) of $\text{Ba}_2\text{YCu}_3\text{O}_7$ to the oxide dashed line. This can be done by assuming that T_c is determined by the Cu atoms in the central layer (sandwiched between Ba layers) of the unit cell, and that the measured value of γ is dominated by this layer, with the other two layers behaving much as in La_2CuO_4 . In fact, examination of the Cu coordination numbers and bond lengths¹⁰ in $\text{Ba}_2\text{YCu}_3\text{O}_7$ shows that the Cu atoms in the central layer have distinctively smaller coordination numbers and shorter Cu—O bond lengths than in the other two Cu layers. Moreover, the calculated⁶ density of states $n_i(E_F)$ for each atom site i is large for Cu and O atoms in the central layer. The contributions to γ from other sites may actually be zero if electrons bound to these sites are localized in the Mott sense.¹¹ Thus the effective value of γ for the central layer could lie in the range of 9–15 in the units of Fig. 1, and $T_c = 93$ K could lie on the dashed line within experimental uncertainties.

For materials which may well be inhomogeneous on scales as small as 20 Å or less a more sensitive test of the BCS theory is $E_g/k_B T_c$, which is 3.5 in the weak-coupling limit and even for very strong coupling is unlikely¹² to

exceed 7. Much larger ratios have been found in some recent tunneling experiments with point contacts,^{13,14} but values appropriate to strong coupling ($E_g/k_B T_c = 4$ to 5) have also been reported, especially by the break-junction method which utilizes *internal* contacts.¹⁵ One possible explanation for the La-Sr large gaps may be charging thresholds for 100-Å semiconductive particles with dielectric constants ϵ near 6 [giving a series of thresholds¹³ E_1, E_2, E_3 proportional to $q^2 - (q-1)^2 = 2q - 1$, for $q = 1, \dots, 3$]. Another explanation for Ba-Y would be 40-Å particles which are conductive only when charged ($q = 1$) and arranged in series to give ratios E_1, E_2, E_3 of 1, 2, 3. The viability of these explanations depends mainly on nearly constant particle sizes at the (free) sample surface. As we see later, this is expected on structural chemical grounds.

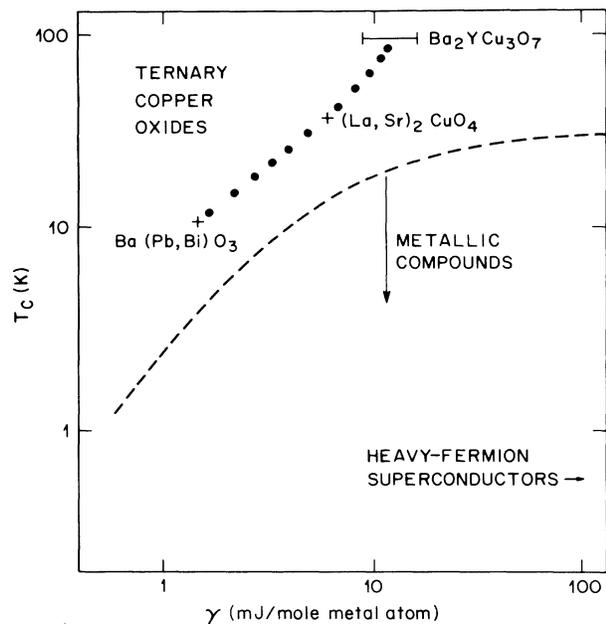


FIG. 1. Bulk superconductive transition temperatures vs Sommerfeld parameter γ (electronic specific-heat coefficient) measured per electronically active metal atom (Cu in the case of ternary Cu oxides). Upper bound of metallic compounds from Ref. 8, ternary Cu oxides from Refs. 8 and 9.

There remains one remarkable observation,¹³ $E_g = 60$ meV, measured by tunneling through a $(1-\mu\text{m})^2$ Pb electrode on a $(\text{La,Sr})_2\text{CuO}_4$ thin film prepared in a very special way,¹³ which corresponds to $E_g/k_B T_c = 20$. The surface of the film consists of 100-Å microcrystallites with their tetragonal axes in the plane of the film.¹³ These form 1- μm regions (domains) of constant ferroelastic texture, i.e., definite c -axis orientation in the plane of the film. Generally the electrode will overlap several ferroelastic domains, but occasionally it will cover only the center of one domain and no domain walls. This may be the case for sample A-9 in Fig. 2 of Ref. 13.

Next we must ask why the tetragonal axes of the microcrystallites lie in the plane of the film. After deposition, the film is an amorphous semiconductor which becomes metallic and crystalline only after heat treatment in oxygen.¹³ The oxidized surface layer is clamped by the as-deposited substrate and is laterally stressed because of its increased density after oxidation. If the tetragonal axis is the easy elastic axis, then the observed texture would be the natural one for ferroelastic stress relief. Increases in T_c of order 1 K/kbar under hydrostatic compression have been observed² in $(\text{La,Ba})_2\text{CuO}_4$, but these increases could be as much as 3 K/kbar for uniaxial stress which decouples layers. In fact, under such stress (which may correspond¹⁶ to a uniaxially applied stress of about 30 kbar) one could easily have $T_c^* = 4T_c$, so that $E_g = 5k_B T_c^*$. This value is similar to that of T_c in $\text{Ba}_2\text{YCu}_3\text{O}_7$ (i.e., 140 vs 93 K) and is achieved only in textured domain interiors, while T_c in domain walls determines the bulk transition temperature of 35 K. Thus the value $E_g = 20k_B T_c$ observed in sample A-9 could be the result of a (accidentally) very favorable contact geometry on a scale of 1 μm . I believe that this explanation of isolated regions with transition temperatures of $T_c^* = 4T_c$ embedded in a network with $T_c = 35$ K (which is mentioned much less specifically as a possibility in Ref. 13) is greatly to be preferred over a non-BCS mechanism. A similar two-phase model, with $E_g = 5k_B T_c^*$ and $T_c^* = 100$ K, while $T_c = 50$ K, can explain the temperature-dependent energy gaps reported in Pb electrode tunneling experiments¹⁷ on sintered $\text{Y}_{0.4}\text{B}_{0.6}\text{CuO}_{3-y}$, provided the junctions are in series.

The most general problem which arises for high- T_c superconductors is the nature of the Fröhlich instability⁴ (mechanical or chemical) which limits the value of T_c obtainable by alloying. The ferroelastic domain formation just discussed may be one of the more sophisticated mechanisms which limits the bulk T_c at the same time that a large fraction of the sample has become superconducting at a much higher temperature T_c^* . Other evidence¹⁸ bearing on this point is the composition dependence $T_c(x, \delta)$ in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-(x/2)+\delta}$. Here T_c is maximized¹⁹ near $x = 0.15$, below which the structure is strongly orthorhombically distorted and above which δ rapidly decreases.¹⁸

While no one foresaw high- T_c superconductivity in ternary Cu oxides, the discussion which most closely foreshadows these phenomena may be the one given by me in several papers on Martensitic and Fröhlich instabilities as manifested by ferroelastic behavior in metallic alloys.²⁰ I

emphasized the importance of equiaxed intrinsic precursor nuclei or clusters with characteristic or intrinsic stress-limited dimensions, and much microscopic evidence has accumulated subsequently to support this model.²¹ Such stress-limited clusters with dimensions of order 40–100 Å have been observed in evaporated films¹³ and, as mentioned above, can produce charging thresholds in point-contact I - V tunneling characteristics. The crucial element missing from my discussion at that time was a general procedure for predicting structural instabilities, especially phase separation (noncompound formation) in metallic alloys. This recipe has since been supplied by Villars in a series of classic papers.²² However, because of the large coordination numbers N_C in metals, Villars' discussion takes place in an abstract quantum coordinate space which specifically excludes oxides and halides, and their much smaller N_C and much poorer conductivities.

It turns out for the present purposes that the anomalous structures of oxides and halides are actually a blessing in disguise. The reason for this is that with small N_C one may regard structural instabilities and cluster formation as structurally vicinal to glass formation,²³ and a general microscopic theory for glass formation which regards the glass as an alloy vicinal to a stiffness threshold is now available.^{24,25} In the case of network glasses, this theory recognized bond-stretching and bond-bending forces, but for the present oxides because of the absence of s - p hybridization it may be that only nearest-neighbor central forces are large. Then the microscopic stiffness threshold occurs²⁴ for average $N_C = \bar{N}_C = 6$. In the La_2CuO_4 (or K_2NiF_4) structure $N_C(\text{Cu}) = 6$, $N_C(\text{O}) = 6$, and $N_C(\text{La}) = 9$. Thus the structure is near the central-force stiffness threshold, but it is slightly overcoordinated, $\bar{N}_C = 6.86$. In $\text{Ba}_2\text{YCu}_3\text{O}_9$ (ideal structure,¹⁰ no O vacancies), we would have $N_C(\text{Ba}) = 12$, $N_C(\text{Y}) = 12$, $N_C(\text{Cu}) = 6$, $N_C(\text{O}(1)) = 6$, $N_C(\text{O}(2), \text{O}(3)) = 2$, $N_C(\text{O}(4), \text{O}(5)) = 2$, $N_C(\text{O}(6)) = N_C(\text{O}(1))$. The weighted average coordination number is $\bar{N}_C = 5.6$, which is already undercoordinated. [The O(6) oxygens refer to the Y plane.]

In the structure of the actual compound,¹⁰ Ba_2YCuO_7 , the O(6) sites are vacant, as are half the O(4), O(5) sites. Then $\bar{N}_C = 5.0$, and we see that removal of two oxygen atoms has made \bar{N}_C substantially less than the ideal value of 6. Qualitatively we can say that $(\text{La,Sr})_2\text{CuO}_4$ is marginally stabilized by nearest-neighbor forces only, but that much weaker bond-bending forces are required to stabilize $\text{Ba}_2\text{YCu}_3\text{O}_7$, which produce a much stronger electron-phonon interaction. This qualitatively helps to explain $T_c = 93$ K in the latter material. It also suggests a general softening of the overall vibrational spectrum (measured by $\langle \omega^2 \rangle$) by a factor of about $5.0/6.8 = 0.73 = (0.85)^2$ on going from La_2CuO_4 to $\text{Ba}_2\text{YCu}_3\text{O}_7$.

Application of the constraint theory of glasses to ternary Cu oxides can be justified microscopically by their large unit cells and their proclivity for forming defect crystals with O vacancies. One of the qualitative predictions of the present theory is that the largest single crystals which can be grown of Ba_2YCuO_7 with $T_c \geq 90$ K will be several times smaller than those of $(\text{La,Sr})_2\text{CuO}_4$. Also, the surface of the former is expected to be quite

porous, so that satisfactory point-contact external surface tunneling is obtainable²⁶ only with the tip "driven deeply into the sample," giving $E_g = 4.3k_B T_c$. Note that these qualitative conclusions can be reached without aid of microscopic models of interatomic force fields.

The most difficult structural problem with the ternary Cu oxides is their ability to remain at least metastable with such large T_c . The present analysis suggests that for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ this metastability may be somewhat illusory, since values of T_c of order 140 K might have been obtained for $x > 0.15$ had additional O vacancies not emerged for these alloys.¹⁸ This view of O vacancy formation as the T_c -limiting instability is consistent with more than 20% formal O vacancies in $\text{Ba}_2\text{YCu}_3\text{O}_7\text{O}_2^\square$. It appears that in the ternary $A_x^{3+}B_y^{2+}\text{Cu}_z^v\text{O}_m^{2-}$ the formal valence v of the Cu ions is pinned, $2 < v < 3$; to produce Cu^{3+} is energetically unfavorable, which in turn tends to generate O vacancies and to maximize the electronic screening, i.e., $n(E_F)$. I expect that the defect concentration will therefore adjust to maximize T_c in equilibrium. This means that some of the usual tests for electron-phonon interactions (such as the isotope effect) may yield surprising results. Generally, the relaxation modes of a large number of internal coordinates which anharmonically and nonadiabatically stabilize a soft lattice (which would have been dynamically unstable without relaxation) will depend on atomic mass ratios in an alloy. (In an

extreme case, such as H interstitially dissolved in PdH_x , this dependence can even produce an inverse isotope effect.²⁷) Thus I do not interpret the nearly null isotope effect ($dT_c/dm_0 = 0$) observed²⁸ in $\text{Ba}_2\text{LnCu}_3\text{O}_7$ as evidence for failure of the Bardeen-Fröhlich mechanism. Rather this is the expected result when vibrational frequency changes are compensated through relaxation by internal coordinate changes in O^\square defect concentrations and site configurations. These maximize both $n(E_F)$ and T_c , and such behavior is consistent with the small value of dT_c/dP in these compounds.² Note also that in Ref. 28 the first isotope exchange cycle produced 50% exchange, so that three exchange cycles should have produced 87% exchange if all O sites were equivalent, instead of the 75% exchange actually observed, which indicates site selectivity of the isotope substitution. I would expect that in $\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$ (where $dT_c/dP > 0$ and the crystal structure is less complex) a normal isotope effect with $0 \ll \alpha \ll \frac{1}{2}$ (perhaps $\alpha \sim 0.2$) would be observed, with $\alpha = \frac{1}{2}$ corresponding to the case where no anharmonic internal coordinate relaxation occurs.

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