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Supplementary Material Available: Listings of initial rates and observed rate constants for the autoxidation of $[(NH_3)_5Ru(Asc)]^+$ and $[(NH_3)_5Ru(TMRA)]^+$, oxygen dependence of the autoxidation of $[(NH_3)_5Ru(Asc)]^+$ and $[(NH_3)_5Ru(TMRA)]^+$, observed rate constant and second-order specific rate constants for the autoxidation of reductate complexes as a function of temperature at pH 7, effect of superoxide dismutase and catalase on the autoxidation of ruthenium reductate complexes, the oxidation of $[(NH_3)_5Ru(TMRA)]^+$ and $[(NH_3)_5Ru(TMRA)]^+$ by hydrogen peroxide and oxygen, and reduction potential versus pH for $[(NH_3)_5Ru(TMRA)]^+$ and a figure of EPR of $[(Asc)(NH_3)_5Ru]^+$ (6 pages). Ordering information given on any current masthead page.

Crystal Chemistry of $Ba_2YCu_3O_7$ and Related Compounds

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Abstract: The role of electropositive elements in stabilizing high oxidation states in crystals of transition elements such as copper is emphasized. An analysis of bond valences in the superconductor $Ba_2YCu_3O_7$ indicates that the valences of the two crystallographically distinct Cu atoms in the structure are intermediate between Cu(II) and Cu(III). Observed bond lengths, including the irregular coordination of Ba, can be understood when allowance is made for the differences in Cu–O bonds. A similar analysis of the insulating phase $Ba_2YCu_3O_6$ reveals well-defined Cu(I) and Cu(II) sites and rationalizes the presence of large displacements for two atoms in the structure. Defect structures in $Ba_2YCu_3O_7$ are discussed: bond lengths in a planar defect layer with composition $Ba_2Y_2Cu_4O_9$ are predicted and a model for {110} twinning is presented.

In view of the current intense interest in oxide superconductors it is worth examining their chemistry and structure from the point of view of a crystal chemist. This is done in this paper with particular emphasis on $Ba_2YCu_3O_7$, which is the highest temperature superconductor of which we are currently aware. First, attention is drawn to the role played by the larger, electropositive elements in stabilizing the structure and then attention is directed to the individual bond lengths and what they tell us about the atomic valences. We deliberately use the language of the solid-state chemist, with its strong bias to an intuitive "tight binding" description of the solid, rather than the band structure–oriented approach normally preferred by physicists.

Stabilization of High Valence States and/or Low Coordination Numbers

It has been documented elsewhere[1-3] that binary compounds, such as oxides, of particularly the heavier (more electropositive) alkali and alkaline earth metals (hereafter generically represented by A) are less stable to dissociation to atoms than might be expected from an examination of the thermodynamics of ternary etc. compounds involving also more-electronegative, higher valent elements (B). A plausible explanation has been offered[3] for this observation, but for our present purposes it is sufficient to note that compounds with a relatively high ratio of A atoms to anions X are less stable with respect to dissociation to atoms (or the normal elemental states) than those in which the corresponding ratio is less. Also relevant to the present discussion is the observation that a relatively large A/X ratio favors low coordination numbers for the cations B.[3]

We take a specific example to illustrate: K_2O has a much lower bond energy than expected from ternary etc. potassium oxides[1] and the coordination number of potassium by oxygen (four) in the binary oxide is significantly lower than is usually observed for potassium in oxides (eight to twelve). Now let us consider the following thermodynamic processes (it is irrelevant whether or not they can be realized directly in the laboratory).

For a process in which K_2O reacts with a high oxidation state transition metal oxide, e.g.

$$K_2O(s) + Cu_2O_3(s) \rightarrow 2KCuO_2(s) \qquad \Delta G^\circ < 0, \text{ say } -\gamma$$

Now consider

$$2CuO(s) + {}^1/_2O_2(g) \rightarrow Cu_2O_3(s) \qquad \Delta G^\circ{}_1 \qquad (1)$$

$$K_2O(s) + 2CuO(s) + {}^1/_2O_2(g) \rightarrow 2KCuO_2(s) \qquad \Delta G^\circ{}_2 = \Delta G^\circ{}_1 - \gamma \qquad (2)$$

In these equations s and g stand for solid and gaseous states. Elementary thermodynamic relationships then yield for the ratio of the oxygen equilibrium oxygen pressures for (1) and (2)

$$P_1/P_2 = \exp(2\gamma/RT) > 0 \qquad (3)$$

Thus it is expected to be easier (i.e., feasible at lower oxygen pressures) to obtain Cu(III) in the ternary compound with K than in a binary compound.[4] Indeed it is observed[5] that $KCuO_2$ can be prepared in 1 atm of oxygen at 450 °C, whereas it has not proved possible so far to prepare anhydrous Cu_2O_3 by direct combination of CuO and oxygen or indeed by any other means.[6] Many other examples of the stabilization of high oxidation states of transition metals when combined with alkaline or alkaline-earth oxides may be adduced.[3] Note that when an oxide like K_2O is heated in oxygen, because the K(II) level is so low lying, the oxygen is oxidized instead to peroxide.

The significance for the preparation of superconducting materials is that the combination of transition metals and large A

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[1] O'Keeffe, M.; Stuart, J. A. *Inorg. Chem.* **1983**, *22*, 177.

[2] McGuire, N. K.; O'Keeffe, M. *J. Solid State Chem.* **1984**, *54*, 49.

[3] O'Keeffe, M.; Hyde, B. G. *Nature (London)* **1984**, *309*, 411.

[4] A reasonable estimate (1) for γ is $\sim$200 kJ mol^{-1} so that at 1000 °C, $P_1/P_2 \sim 10^{16}$! Of course, eq 3 only holds in the limit of low pressures.

[5] Hestermann, K.; Hoppe, R. *Z. Anorg. Allg. Chem.* **1969**, *367*, 249.

[6] *Gmelins Handbook of Anorganische Chemie*; Verlag Chemie: Weinheim, 1958; Vol. 60, p 137.

Table I. The Connectivity Matrix for $Ba_2YCu_3O_7$[a]

	2O(1)	2O(2)	2O(3)	O(4)
2Ba	8	4	4	4
Y	·	4	4	·
Cu(1)	2	·	·	2
2Cu(2)	2	4	4	·

[a] Numbers before the atom symbols are the number of that type of atom per formula unit. Numbers in the matrix are the number of bonds (per formula unit) between atom pairs.

atoms allows oxidation at accessible oxygen activities to a point where the d manifold of the transition metal begins to overlap (in energy) the O 2p band. The conduction band has then a large oxygen component with consequent strong coupling between metal d electrons and oxygen displacements.[7] In simple transition metal oxides such as NiO the d levels are typically some eV above the oxygen 2p levels, so that the conduction band is strongly localized on the metal atoms.[8]

Oxygen is rarely more than four-coordinated by metal atoms in oxides (the relatively unstable alkali and alkaline-earth oxides with oxygen coordination numbers ≥6 are notable exceptions), so that low coordination numbers for metal atoms in metal-rich oxides are commonplace [e.g., two-coordinated Ni(II) in K_2NiO_2[9]]. This observation is possibly relevant to the preparation of highly oxidized mixed-valence conductors as square-planar coordination is preferred for both Cu(II) and (low spin) Cu(III). Cu and its congeners are unique among transition metals in this respect. The other electronic configuration [d^4 as in Mn(III) and Fe(IV)] favoring planar four coordination is flanked by oxidation states with configurations (d^3 and d^5) generally preferring octahedral coordination.

Bond Lengths and Valences in Copper Oxides

In recent years it has become clear[10,11] that the preferred way of discussing bond lengths in solids, especially those with irregular coordination figures, is in terms of the valence v_{ij} of the bond between atoms i and j. The bond valences are defined to have the property that the sum of the bond valences at a given atom is equal to the valence (the magnitude of the oxidation state), V, of the atom:

$$\sum_j v_{ij} = V_i$$

Bond valences, so defined, are the major factor in determining bond length, d, and an excellent approximation in most instances[12] is

$$d_{ij} = R_{ij} - b \ln v_{ij}$$

where R_{ij} is an empirically determined constant for a given atom pair, and to a good approximation b = 0.37 Å may be taken as a universal constant. Brown and Altermatt[12] give the values of R (appropriate to the above choice of b) for bonds between oxygen and Cu(II), Ba, and Y as 1.679, 2.285, and 2.019 Å, respectively; and these are used in what follows. We estimate from the observed bond lengths in oxides such as Cu_2O, Cu_4O_3,[13] and delafossites, $A^{III}CuO_2$,[14] that R for bonds between oxygen and Cu(I) is 1.593 Å. For bonds between *low spin* Cu(III) and oxygen, we use the structures of $NaCuO_2$[15] and $KCuO_2$[5] in each of which Cu(III) forms four equal and coplanar bonds to O (with $v = {}^3/_4$) and obtain R = 1.74 Å. Note the fairly uniform progression of R with oxidation state of Cu.

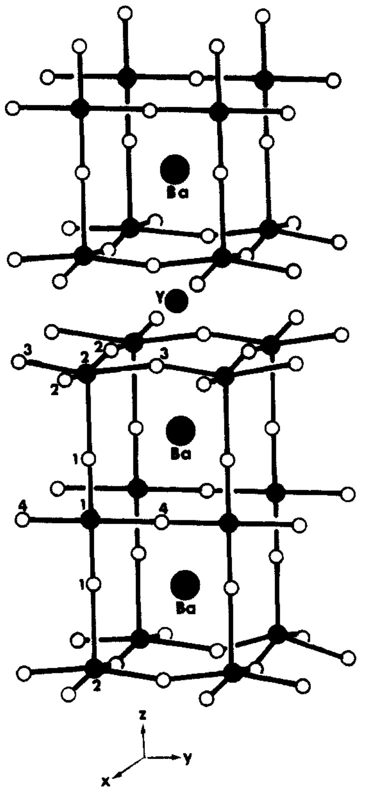

Figure 1. The structure of $Ba_2YCu_3O_7$.[17] Small filled circles represent Cu and open circles O.

Table II. Bond Lengths (in Å from ref 17) and Calculated Bond Valences (v) and Atomic Valences (V) in $Ba_2YCu_3O_7$

		d	v	V
Ba	O(1)	2.741	0.29 (4×)	2.20
	O(2)	2.984	0.15 (2×)	
	O(3)	2.960	0.16 (2×)	
	O(4)	2.874	0.20 (2×)	
Y	O(2)	2.409	0.35 (4×)	2.88
	O(3)	2.386	0.37 (4×)	
Cu(1)	O(1)	1.846	0.68 (2×)	2.42
	O(4)	1.943	0.53 (2×)	
Cu(2)	O(1)	2.295	0.20 (1×)	2.29
	O(2)	1.930	0.54 (2×)	
	O(3)	1.961	0.50 (2×)	
O(1)	Ba	2.741	0.29 (4×)	2.05
	Cu(1)	1.846	0.68 (1×)	
	Cu(2)	2.295	0.20 (1×)	
O(2)	Ba	2.984	0.16 (2×)	2.09
	Y	2.409	0.35 (2×)	
	Cu(2)	1.930	0.54 (2×)	
O(3)	Ba	2.960	0.16 (2×)	2.07
	Y	2.386	0.37 (2×)	
	Cu(2)	1.961	0.50 (2×)	
O(4)	Ba	2.874	0.20 (4×)	1.87
	Cu(1)	1.943	0.53 (2×)	

The $Ba_2YCu_3O_7$ Structure

The structure[16,17] of $Ba_2YCu_3O_7$ (*Pmmm*; a = 3.82 Å, b = 3.89 Å, c = 11.67 Å) is illustrated in Figure 1. The connectivity matrix

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Table III. Connectivity Matrix for $Ba_2YCu_3O_7$ as in Table I, but Now Entries for O(2) and O(3) are Merged and Greek Symbols Represent Bond Valences

	2O(1)	4O(2,3)	O(4)
2Ba	8α	8β	4γ
Y	·	8 × $^3/_8$	·
Cu(1)	2δ	·	2ϵ
2Cu(2)	2ζ	8η	·

for the structure is displayed in Table I, in which the number of each kind of atom and bond is entered.

If there were well-defined valencies, one would expect 2Cu(II) + 1Cu(III), and the most obvious interpretation of the structure would be that Cu(1) were Cu(III) and that Cu(2) were Cu(II). However, by using the appropriate values of R the bond valence sums are calculated to be 2.66 at Cu(1) and 2.14 at Cu(2). An alternative hypothesis is that the valence distribution is uniform. We then take for the Cu atoms a common value of $R = 1.705$ Å, chosen so that the total Cu valence is 7.0. The individual valences of Cu(1) and Cu(2) are now calculated to be 2.42 and 2.29, respectively, approaching the value of 2.33 for a completely uniform valence distribution. In Table II, we list the bond and atom valences calculated on this basis. It is satisfying that the valences at oxygen are close to 2.0, except perhaps for O(4). In this connection we note that the temperature factor found[17] for this atom is significantly larger than that for the other oxygen atoms by a factor of about 3 even at 10 K, suggesting static displacements of O(4) from an average position. A similar, but more obvious, situation is found in $Ba_2YCu_3O_6$ and is treated below in the discussion of the structure of that compound.

It is at first sight somewhat surprising that the conductivity is metallic, as there might be expected to be an energy barrier for the electron transfer:

$$Cu^{III}_1 + Cu^{II}_2 \rightarrow Cu^{II}_1 + Cu^{III}_2$$

(Here the subscripts refer to the two crystallographically distinct Cu sites.) And it is expected that the highest occupied MO is essentially a $pd_{x^2-y^2}$ σ^* level located at a Cu(II) site. Band structure calculations[6] indicate, however, that the Cu(1) and Cu(2) pd σ^* bands overlap resulting in a degree of self doping in accord with the intermediate valences found in our calculations.

The conductivity at room temperature is about 2×10^5 S m^{-1}[18] and the density of Cu sites is 1.7×10^{28} m^{-3}. Supposing that the carrier concentration is about $^1/_3$ of the Cu site concentration (i.e., one hole per formula unit), an estimate of the mobility is 2×10^{-4} m^2 V^{-1} s^{-1}, well above the threshold for itinerant electron conduction.[19]

The rather unusual situation in the copper oxide (with intermediate valences on two sites of different coordination geometries) might be contrasted with that in the mixed valence silver oxides Ag_7O_8X (X = F, NO_3, etc.) which are also superconductors.[20] In these compounds "Ag(II)" and "Ag(III)" occupy indistinguishable sites.[21]

It is also informative to attempt to predict bond valences in structures of this type. We do this using the common value of R quoted above for the Cu–O bonds. The connectivity matrix of Table I shows that there are eleven different types of bonded atom pair. On the other hand there are only eight kinds of atom, so only seven independent bond valence sums (the requirement of equality of total anion and cation valences removes one degree of freedom). Of possible *ansätze* that have been proposed, it has been found[11] that the following procedure yields reliable results for this type of structure. We note first that the entries for the O(2) and O(3) columns in Table I are the same so we suppose that the bond valences in corresponding rows of these columns are equal and they are therefore combined. [A simple justification for this procedure can be given[11].] The reduced matrix is shown in Table III with Greek symbols for the individual bond valences. (Note that we have entered the value $v = {}^3/_8$ for the Y–O bonds.) We now have seven undetermined bond valences and five independent bond valence sums. At this stage the best way to determine expected valences for the stronger bonds is to make all the lower valent bonds from Ba to oxygen equal (i.e., $\alpha = \beta = \gamma = {}^1/_5$). This procedure is a good approximation, as relatively large fractional errors in the lower valences do not contribute much in absolute terms to the valence sums. The other predicted valences are then readily determined from bond valence sums, with the results shown in Table IV. Predicted and observed bond valences (and hence bond lengths) are in generally fair agreement.

Table IV. Observed and Calculated Bond Valences and Bond Lengths (in Å) in $Ba_2YCu_3O_7$

bond	symbol	v (obsd)	v (calcd)	d (obsd)	d (calcd)
Ba–O(1)	α	0.29	0.200	2.74	2.88
Ba–O(2)	β	0.15	0.200	2.98	2.88
Ba–O(3)	β	0.16	0.200	2.96	2.88
Ba–O(4)	γ	0.20	0.200	2.87	2.88
Y–O(2)		0.35	0.375	2.41	2.38
Y–O(3)		0.37	0.375	2.39	2.38
Cu(1)–O(1)	δ	0.68	0.567	1.85	1.92
Cu(1)–O(4)	ϵ	0.53	0.600	1.94	1.89
Cu(2)–O(1)	ζ	0.20	0.633	2.30	1.87
Cu(2)–O(2)	η	0.54	0.425	1.93	2.02
Cu(2)–O(3)	η	0.50	0.425	1.96	2.02

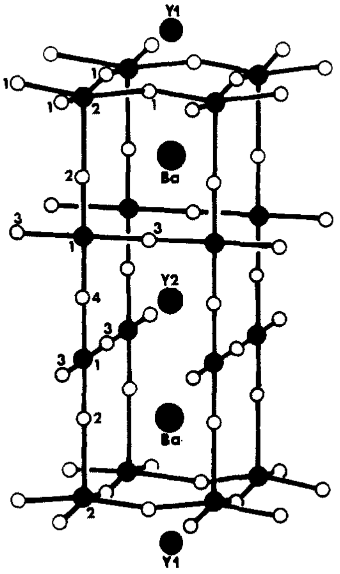

Figure 2. A proposed structure for "$Ba_2YCu_4O_9$"; symbols as for Figure 1.

The bond lengths about Cu(1) and Cu(2) are incorrectly ordered; the reason for this becomes clear when it is realized that the (approximately) in-plane $pd_{x^2-y^2}$ antibonding orbital centered on Cu(2) is only partly occupied, whereas the pd_{z^2} antibonding orbital is fully occupied. The basal bonds from Cu(2) to O(2) and O(3) are therefore stronger (shorter), and the apical bond longer, than the simple analysis (that treated these bonds a priori on an equal footing) suggested.[22] As a consequence of the distortion of the CuO_5 polyhedron, in order to keep the correct bond strength sums at oxygen, the bonds from O(2) and O(3) to Ba are a little longer, and the bonds from O(1) to Ba and Cu(1) shorter than calculated. Thus all the major discrepancies in Table

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(22) We note that simple treatments of interatomic distances using bond length–bond strength correlations (or, for that matter, ionic radii) do not allow for "Jahn-Teller" or other distortions in coordination polyhedra.

Table V. Connectivity Matrix for "$Ba_2Y_2Cu_4O_9$"

	4O(1)	2O(2)	2O(3)	O(4)
2Ba	$8 \times {}^1/_5$	$8 \times {}^1/_5$	$4 \times {}^1/_5$	·
Y(1)	$8 \times {}^3/_8$	·	·	·
Y(2)	·	·	4α	4β
2Cu(2)	8γ	2δ	·	·
2Cu(1)·	2ϵ	4ζ	2η	

Table VI. Calculated Bond Valences (v) and Bond Lengths (d, in Å) for "$Ba_2Y_2Cu_4O_9$"

bond	symbol	v	d
Ba–O	·	0.200 (10×)	2.88
Y(1)–O(1)	·	0.375 (8×)	2.38
Y(2)–O(3)	α	0.410 (4×)	2.35
Y(2)–O(4)	β	0.340 (4×)	2.42
Cu(1)–O(2)	ϵ	0.900 (1×)	1.72
Cu(1)–O(3)	ζ	0.390 (2×)	2.03
Cu(1)–O(4)	η	0.320 (1×)	2.10
Cu(2)–O(1)	γ	0.425 (4×)	2.00
Cu(2)–O(2)	δ	0.300 (1×)	2.12

IV can be accounted for as a "chain reaction" arising from the differences in bonding character between the basal and apical bonds from Cu(2).

Defect Structures and "$Ba_2Y_2Cu_4O_9$"

High-resolution electron microscopy[23] has provided clear evidence for the existence of intergrowth defects in $Ba_2YCu_3O_7$. These consist of slabs of material with four Cu layers normal to c, and the proposed structure is shown in Figure 2. The composition of a crystal obtained by repeating the slab is $Ba_2Y_2Cu_4O_9$ and contains only Cu(II). Note that we have drawn the slab so that the Cu(1)–O–Cu(1)–O... strings perpendicular to the long (z) axis run in two directions (along x and y) so that the symmetry is tetragonal ($P\bar{4}m2$ as drawn). The strings could also run only along x or y (orthorhombic symmetry).

Table V shows the connectivity matrix using the notation of Figure 2. In this table we have again assumed that the bond valences for Ba–O bonds are all equal to ${}^1/_5$. There are now seven bond valences to determine and six independent bond sums. For the seventh equation we use a constraint equivalent to one proposed by Brown.[24] This[11] requires that the difference in valences for the Y(2)–O(3) and Y(2)–O(4) bonds is equal to the difference in valences for the Cu(2)–O(3) and the Cu(2)–O(4) bonds, i.e., $\alpha - \beta = \zeta - \eta$. Table VI lists the bond valences and lengths calculated for this structure. If this compound were to be prepared we would expect a relaxation of the bond lengths in the $Cu(1)O_5$ polyhedron in an analogous manner as found for $Ba_2YCu_3O_7$.

The bonds in the linear chain (along b in the drawing) are now weaker (and subsequently longer) in $Ba_2Y_2Cu_4O_9$ so that b will be increased in that compound. This observation suggests that an intergrown slab of $Ba_2Y_2Cu_4O_9$ will not be commensurate in the directions normal to c with the host $Ba_2YCu_3O_7$ crystal. There is some evidence for this in electron micrographs, and it is noteworthy that the observed[23] planar defects have only finite extent.

$Ba_2YCu_3O_6$

The structure[25] of this compound ($P4/mmm$; a = 3.86 Å, c = 11.83 Å) is simply derived from that of $Ba_2YCu_3O_7$ by removal of O(4) from the latter so that the coordination of Cu(1) is changed from square planar to linear twofold. The structure is illustrated in Figure 3 and its connectivity matrix shown in Table VII. Table VIII shows the bond and atom valences calculated from the observed[25] bond lengths. The calculated atomic valences are in accord with the values expected, except those for Ba and O(1), which are too low. Clearly Cu(1) in linear coordination is now Cu(I) and Cu(2) is Cu(II). If instead we use a common R (1.641 Å) chosen such that the sum of the Cu valences is 5.0, the valence at Cu(1) is found to be 1.27 and that at Cu(2) is 1.87 contradicting the idea that these atoms have the same valence.

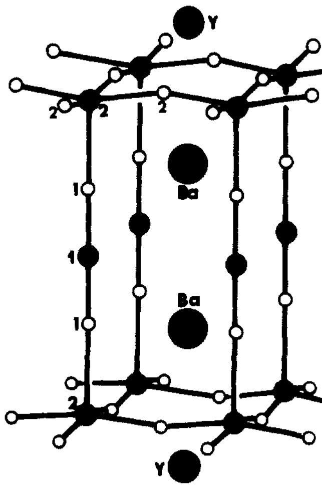

Figure 3. The structure of $Ba_2YCu_3O_6$.[25]

Table VII. Connectivity Matrix for $Ba_2YCu_3O_6$

	2O(1)	4O(2)
2Ba	8α	8β
Y	·	$8 \times {}^3/_8$
Cu(1)	$2 \times {}^1/_2$	·
2Cu(2)	2γ	8δ

Table VIII. Bond Lengths (d, in Å) and Calculated Bond Valences (v) and Atomic Valences (V) in $Ba_2YCu_3O_6$

bond	d	v	V
Ba–O(1)	2.773	0.27 (4×)	1.77
Ba–O(2)	2.927	0.18 (4×)	
Y–O(2)	2.402	0.36 (8×)	2.84
Cu(1)–O(1)	1.81	0.56 (2×)	1.11
Cu(2)–O(1)	2.45	0.12 (1×)	2.08
Cu(2)–O(2)	1.944	0.49 (4×)	
O(1)–Ba	2.773	0.27 (4×)	1.75
O(1)–Cu(1)	1.81	0.56 (1×)	
O(1)–Cu(2)	2.45	0.12 (1×)	
O(2)–Y	2.402	0.36 (2×)	2.04
O(2)–Ba	2.927	0.18 (2×)	
O(2)–Cu(2)	1.944	0.49 (2×)	

Before discussing the discrepancy at O(1) and Ba, we first enquire into the bond valences and lengths that we would calculate for this structure. If, as before for $Ba_2YCu_3O_7$, we take the bonds from Ba to O to have equal strength ($\alpha = \beta = {}^1/_4$ in Table VII), one finds for the bond from Cu(2) to O(1) $v = \gamma = {}^1/_2$ and for the bonds from Cu(2) to O(2) $v = \delta = {}^3/_8$. This again results in the unlikely coordination figure in which the apical bond in the square prism is considerably shorter than the other four. Lengthening the apical bond to O(1) (and shortening the basal bonds as observed) requires, again as before, a compensating decrease in the length of the bond from Ba to O(1). However, if we accept the reported symmetry and lattice parameters it is easily demonstrated that the Ba–O(1) bond cannot be made short enough.

We suggest that the solution to this problem may be that O(1) is displaced from $0,0,z$ to (e.g.) δ,δ,z resulting in one shorter and one longer Ba–O(1) bond. A value of δ = 0.065 Å would make the valence sums at Ba and O(1) equal to 2.01 and 1.99, respectively, and result in insignificant changes in the other bond lengths (<0.001 Å) and valences. In the reported structure,[25] the

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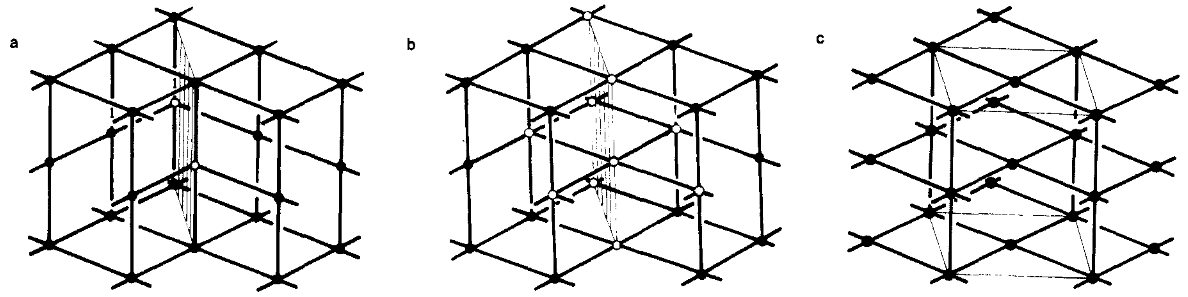

Figure 4. (a) A schematic drawing of twinned $Ba_2YCu_3O_7$. Only the Cu atoms are shown; open circles represent Cu atoms in the wrong coordination. O atoms lie approximately at the center of the heavy lines joining Cu atoms. (b) As in part a with O atoms moved in the twin region to more likely positions. (c) The tetragonal structure proposed by Er-Rahko et al.[28] drawn for comparison with part b.

temperature factors for O(1) ($U_{11} = U_{22} = 0.023$ Å^2), and to a lesser extent for Ba ($U_{11} = U_{22} = 0.01$ Å^2), indicate large excursions of these atoms along $\langle 110 \rangle$. Whether these are dynamic or random static displacements remains to be determined.

Twinning in, and Other Proposed Structures for, $Ba_2YCu_3O_7$

At high temperatures (~1000 °C) preparations of "$Ba_2YCu_3O_7$" are oxygen deficient and apparently tetragonal and possibly exist as intergrowths of $Ba_2YCu_3O_7$ and $Ba_2YCu_3O_6$. Superconducting samples annealed at lower temperatures in oxygen are heavily twinned[26] on $\{110\}$.

Figure 4a shows a portion of a twin of the $Ba_2YCu_3O_7$ structure in which a (110) plane is a mirror plane. To be noted is the fact that the simple reflection operation leaves some Cu(1) atoms (open circles in the figure) with an unlikely "see-saw" coordination (such as found in molecules like SF_4). A more plausible structure (and the only simple one that we can find) for the twin region is shown in Figure 4b. Now all the Cu atoms have square-planar or -pyramidal coordination. To transform from the structure in Figure 4a to that in Figure 4b, all that is required is the transfer of one O atom per unit cell from a bond Cu(1)–O(1)–Cu(2) to a bond Cu(1)–O–Cu(1). Open circles in Figure 4b represent atoms with local topology different from that in the parent structure.

It is interesting that the structure in the twin (contact) plane in Figure 4b is an element of the tetragonal structure originally proposed[27] for $(Ba,La)_2LaCu_3O_7$. A fragment of this structure is shown in Figure 4c. It should be clear that this tetragonal structure is generated from the orthorhombic structure (Figure 1) by repeated application, on every second (110) plane, of the twinning operation we have discussed.

We note also that a second tetragonal structure proposed for $Ba_2YCu_3O_7$[28] involves O atom disorder and is intermediate between the two structures described above. Clearly careful electron microscopy directed at determining the microstructure of different preparations would be rewarding.

Conclusion

In this paper we have delineated the essential role played by the large (A) atoms in stabilizing high oxidation states of transition elements. Such high oxidation states will be necessary if high temperature superconductivity is associated with (among other things!) the metal d orbitals being close in energy to the oxygen levels so that there is a large oxygen component in the highest occupied crystal orbitals (conduction band). Thus it may not be coincidence that electropositive elements such as Ba, Sr, La, and Y are found in superconducting compositions or that superconductivity appears to be a sensitive function of average oxidation state.

We have also shown that in the mixed valence oxide $Ba_2YCu_3O_7$ valences intermediate between Cu(II) and Cu(III) are found on the crystallographically distinct sites and that on the other hand Cu(I) and Cu(II) exist in $Ba_2YCu_3O_6$. It should be emphasized that the bond length method determines atomic *valences*; we have inferred *oxidation states* from these valences on the assumption of O(II). The results do not exclude the possibility[29] that the one hole per formula unit in $Ba_2YCu_3O_7$ may be largely localized on one or more oxygen atoms.

In the structures of $Ba_2YCu_3O_7$ and $Ba_2YCu_3O_6$, bond length calculations that treat all the Cu–O bonds in the CuO_5 polyhedron on an equal footing result in a short apical Cu–O bond in contrast to the observed situation. The observed structures (including the irregular Ba coordination) show that the different nature of the apical and basal Cu–O bonds must be explicitly taken into account in order to reproduce the correct bond lengths. It would be of considerable interest in this connection to prepare analogous compounds in which Cu were replaced with an atom such as Mg—in such a situation one might expect one short and four long Mg–O bonds in the square-pyramid sites.

The possibility of twinning and intergrowth structures has been indicated; these may be of significance for the electronic properties of the superconducting copper oxides.

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Registry No. $Ba_2YCu_3O_7$, 109064-29-1; $Ba_2YCu_3O_6$, 109489-85-2.

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