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The Relationship of the Chemical Bonding Topology of High Critical Temperature Copper Oxide Superconductors to that of the Chevrel Phases and the Ternary Lanthanide Rhodium Borides

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Our graph-theory derived treatment of metal cluster chemical bonding topology [1–5] has recently been extended to superconducting infinite metal clusters such as the ternary molybdenum chalcogenides (Chevrel phases) [6] and ternary lanthanide rhodium borides [7]. Relatively high superconducting transition temperatures for a given compound type were found to be associated with confinement of the delocalized bonding electrons to the edges of an infinite three-dimensional network of metal polyhedra which may be regarded as a 'conducting skeleton'. Such a rather special type of chemical bonding topology may be conveniently described as porously delocalized and contrasts with the more common global delocalization of the bonding electrons throughout the entire metal cluster volume such as occurs in the free metals themselves [8]. This letter shows that a completely analogous model can be used for the chemical bonding topology in the recently discovered high temperature superconductors derived from the copper oxide systems including the initially identified La–Ba–Cu–O perovskites [9, 10] and the subsequently discovered layered perovskites [11–15] exhibiting superconductivity above liquid nitrogen temperature. The much higher transition temperatures of the copper oxide superconductors relative to the metal cluster superconductors can then be attributed to major differences in the polarizabilities of the chemical bonds forming the conducting skeleton rather than differences in the overall chemical bonding topology. This point is of potential significance in the application of conventional physical theories of superconductivity [16–19] to the copper oxide systems.

Consider first the Chevrel phases [20, 21] such as $PbMo_6S_8$. Their structures consist of an infinite three-dimensional conducting skeleton of Mo_6 octahedra in close enough proximity for the interoctahedral as well as intraoctahedral Mo–Mo interactions [6]. The intraoctahedral Mo–Mo bonding is confined to the 1-skeletons [22] of the Mo_6 octahedra, namely the 12 Mo–Mo edges in each octahedron. Oxidation of the closed shell $Mo_6S_8{}^{4-}$ electronic configuration to $Mo_6S_8{}^{2-}$ (e.g., the Pb^{2+} counterion in $PbMo_6S_8$) coupled with the interoctahedral Mo–Mo interactions provides the holes in the valence band required for conductivity. In an analogous way the structures of the ternary lanthanide rhodium borides $LnRh_4B_4$ (Ln = Nd, Sm, Er, Tm, Lu) [23, 24] consist of an infinite three-dimensional conducting skeleton of Rh_4 tetrahedra with intratetrahedral Rh–Rh bonding confined to the 6 Rh–Rh edges, intertetrahedral Rh–Rh distances short enough for some chemical bonding, and oxidation of the closed shell $Rh_4B_4{}^{4-}$ electronic configuration to $Rh_4B_4{}^{3-}$ to create the holes in the valence band required for conductivity [7].

A similar model can be generated for the chemical bonding topology of the copper oxide superconductors by considering the following points:

(1) The infinite three-dimensional conducting skeleton is constructed from Cu–O–Cu bonds rather than direct Cu–Cu bonds.

(2) The relevant metal–metal interactions are antiferromagnetic interactions between the single unpaired electrons on two d^9 Cu(II) atoms separated by an oxygen bridge similar to antiferromagnetic Cu(II)–Cu(II) interactions in discrete binuclear complexes [25, 26]. This idea is closely related to the resonating valence bond models first proposed by Anderson in 1973 [27] and recently applied by him [28] to the copper oxide superconductors. Furthermore, pairwise antiferromagnetic interactions can generate the Cooper pairs of electrons required for superconductivity.

(3) The alkaline-earth and lanthanide positive counterions in the copper oxide superconductors play a role analogous to that of the positive counterions in the Chevrel phases (e.g., Pb^{2+} in $PbMo_6S_8$) and the ternary lanthanide rhodium borides (e.g., Ln^{3+} in $LnRh_4B_4$). In the copper oxide structures these counterions control the negative charge on the Cu–O skeleton and thus the oxidation states of the copper atoms.

(4) Partial oxidation of some of the Cu(II) to Cu(III) generates holes in the valence band required for conductivity. Thus La_2CuO_4, in which all of the copper is in the +2 oxidation state, is an insulator [29]. Replacement of some of the lanthanide ions with alkaline earth ions in the superconductors corresponds to partial oxidation of Cu(II) to Cu(III) with the average oxidation state of copper, for example, corresponding to +2.15 in the 36 K superconductor $La_{1.85}Sr_{0.15}CuO_4$ reported by Bednorz and Müller [9, 10].

These considerations lead to a porously delocalized chemical bonding topology for the copper oxide superconductors similar to the chemical bonding topologies of the Chevrel phases [6] and lanthan-

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ide rhodium borides [7]. However, in the copper oxide superconductors the conducting skeleton is constructed from metal–oxygen bonds rather than direct metal–metal bonds while using non-bonding antiferromagnetic metal–metal interactions for the electron transport required for conductivity. The much higher ionic character and thus much lower polarizability of metal–oxygen bonds relative to metal–metal bonds can then be related to the persistence of superconductivity in the copper oxides to much higher temperatures than in metal clusters such as the Chevrel phases and lanthanide rhodium borides. This model also suggests a search for other high temperature superconductors among oxides of other transition metals in mixed oxidation states including oxidation states which are paramagnetic in mononuclear metal complexes but demonstrated by the magnetic properties of their binuclear and/or polynuclear coordination complexes to exhibit antiferromagnetic interactions not involving direct metal–metal bonding [26].

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