

# Mathematical Inorganic Chemistry: From Gas-Phase Metal Clusters to Superconducting Solids

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## 1. Introduction

The development of essentially all areas of theoretical chemistry has been highly dependent on diverse areas of mathematics. Examples cited by Prelog<sup>1</sup> include the uses of calculus in chemical thermodynamics and kinetics, linear algebra in quantum chemical calculations, and group theory in molecular spectroscopy. The recognition of the importance of ideas from mathematics in the understanding of chemical phenomena has led to the recent emergence of the discipline of mathematical chemistry, which searches for new applications of mathematics to chemical problems. In many cases relevant areas of mathematics had been developed for several decades before recognition of their applications in chemistry. An interesting case is the ubiquitous wave equation<sup>2</sup> proposed by Schrödinger in 1926 based on spherical harmonics which already had been described in detail in an 1893 textbook.<sup>3</sup>

One of my major research interests during the past two decades has been mathematical inorganic chemistry, namely, the application of mathematics to problems in inorganic chemistry. A major driving force behind my interest in this area has been a desire to understand the interesting geometries and electron counts of metal clusters. The general area of mathematics relevant to this problem is topology, namely, the study of neighborhood relationships between members of a set, which in this case consists of pertinent atoms or orbitals. Our initial work on metal cluster topology came through a collaboration with Dennis Rouvray in spring 1976 to apply ideas originating from the subdiscipline of topology called algebraic graph theory<sup>4-6</sup> to describe the skeletal chemical bonding in polyhedral boranes, carboranes, and metal clusters.<sup>7</sup> This graph-theory-derived approach complements the numerous other methods for treating metal cluster skeletal bonding including the polyhedral skeletal electron pair theory of Wade and Mingos,<sup>8-10</sup> the extended Hückel calculations of Lauher,<sup>11</sup> the tensor surface harmonic theory developed by Stone<sup>12-15</sup> and elaborated by Mingos and collaborators,<sup>16,17</sup> and the topological electron counting method of Teo.<sup>18-21</sup> Strengths of our graph-theory-derived methods include the following: (1) the ability to derive important information about the electron counts and shapes of diverse metal clusters using a minimum of computation; (2) the ability to generate

electron-precise bonding models for metal clusters that appear intractable by other methods not requiring heavy computation; (3) the ease of obtaining information on the distribution of total cluster electron counts between skeletal bonding within the cluster polyhedral network and bonding to external ligands; (4) the ability to differentiate between different degrees of localization in the skeletal bonding in the cluster polyhedral network.

Molecular transition metal clusters treated explicitly by our graph-theory-derived methods include osmium carbonyl clusters,<sup>22</sup> platinum carbonyl clusters<sup>23,24</sup> rhodium carbonyl clusters built from fused polyhedra,<sup>25,26</sup> cobalt carbonyl clusters containing interstitial carbon atoms,<sup>27</sup> metal carbonyl clusters containing alkylphosphinidene vertices,<sup>28</sup> and nickel carbonyl clusters.<sup>29</sup>

In a recent article I summarized applications of these graph-theory-derived models to the skeletal bonding in molecular metal carbonyl clusters.<sup>30</sup> This Account surveys applications of these methods to other types of inorganic substances ranging from gas-phase bare metal

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clusters to infinite solid-state materials including bulk metals and superconducting solids. Further details on each of these applications are available in the references cited throughout this Account.

## 2. Graph Theory and Metal Cluster Skeletal Bonding

Graph theory may be regarded as a branch of topology concerned with the use of graphs to depict neighborhood relationships. In this context a graph  $G$  is defined<sup>5</sup> as a finite nonempty set  $V$  (the "vertices") together with a (possibly empty) set  $E$  (the "edges"; disjoint from  $V$ ) of two-element subsets of (distinct) elements of  $V$ . In a graph  $G$  used to model chemical bonding, the set  $V$  (vertices) represents atoms or orbitals and the set  $E$  (edges) represents bonding relationships. The adjacency matrix<sup>6</sup>  $A$  of a graph  $G$  with  $n$  vertices is an  $n \times n$  matrix defined as follows:

$$A_{ij} = \begin{cases} 0 & \text{if } i = j \\ 1 & \text{if vertices } v_i \text{ and } v_j \text{ are connected by an edge} \\ 0 & \text{if vertices } v_i \text{ and } v_j \text{ are not connected by an edge} \end{cases} \quad (1)$$

The eigenvalues  $x_k$  of  $A$  are obtained by solution of the determinantal equation

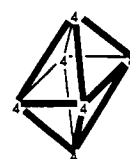
$$|A - xI| = 0 \quad (2)$$

in which  $I$  is the  $n \times n$  square unit matrix ( $I_{ij} = 1$  and  $I_{ij} = 0$  for  $i \neq j$ ). It has been shown elsewhere<sup>7,31-33</sup> that the eigenvalues  $x_k$  of  $A$  are related to the Hückel theory molecular orbital energy parameters by the following equation:

$$E_k = \frac{\alpha + x_k \beta}{1 + x_k S} \quad (3)$$

In eq 3,  $\alpha$  is the standard Coulomb integral,  $\beta$  is the resonance integral, and  $S$  is the overlap integral. Positive and negative eigenvalues  $x_k$  in eq 3 arising from solutions of eq 2 thus correspond to bonding and antibonding orbitals, respectively.

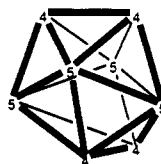
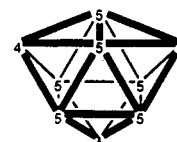
The two extreme types of skeletal bonding in metal clusters may be called edge-localized and globally delocalized.<sup>7,34</sup> An edge-localized cluster has two-electron two-center bonds along each edge of the cluster polyhedron. A globally delocalized cluster has a multicenter core bond in the center of the cluster polyhedron. Intermediate degrees of delocalization are also found, either in face-localized polyhedra<sup>35,36</sup> or in clusters formed by fusion of an edge-localized polyhedron to a globally delocalized polyhedron. Delocalized skeletal bonding occurs in metal clusters in which the number of internal orbitals provided by a vertex atom for the skeletal bonding does not match the number of edges meeting at that vertex, namely, the vertex degree. Thus in the case of normal vertex atoms providing three internal orbitals, fully edge-localized bonding occurs in cluster polyhedra in which all vertices have degree 3 such as the tetrahedron, cube, and trigonal prism. Planar polygonal molecules having normal vertex atoms



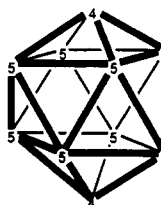
Octahedron



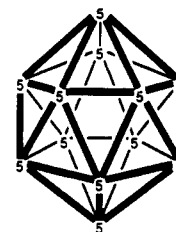
Pentagonal Bipyramid

Bisdisphenoid  
("D<sub>2d</sub> Dodecahedron")

3,3,3-Tricapped Trigonal Prism



4,4-Bicapped Square Antiprism



Regular Icosahedron

**Figure 1.** The six deltahedra which have only degree 4 and/or degree 5 vertices. Each vertex is labeled by its degree.

(e.g., benzene) are globally delocalized since all vertices of any polygon have degree 2. Furthermore, polyhedral clusters having all normal vertex atoms are globally delocalized if all vertices of the polyhedron have degree 4 or higher. The simplest such polyhedron is the regular octahedron in which all vertices have degree 4. There are six topologically possible deltahedra (i.e., polyhedra in which all faces are triangles) with only degree 4 and/or degree 5 vertices (Figure 1.)<sup>37</sup> All of these deltahedra are found in borane dianions  $B_nH_n^{2-}$  ( $6 \leq n \leq 12$ )<sup>38</sup> and the isoelectronic neutral carboranes  $C_2B_{n-2}H_n$ .<sup>39</sup>

A major achievement of the graph-theory-derived approach to the chemical bonding topology of globally delocalized structures is the demonstration of the close analogy between the bonding in two-dimensional planar aromatic structures such as benzene and that in three-dimensional deltahedral boranes and carboranes.<sup>7,34</sup> In such systems with  $n$  normal vertices, whether two- or three-dimensional, the three internal orbitals on each vertex atom are partitioned into two twin internal orbitals (called tangential in some other methods<sup>8-10</sup>) and a single unique internal orbital (called radial in some other methods<sup>9-10</sup>). Pairwise overlap of the  $2n$  twin internal orbitals is responsible for the peripheral bonding (i.e.,  $\sigma$ -bonding) of the polygonal framework or the surface bonding of the deltahedral framework and leads to the splitting of these  $2n$  orbitals into  $n$  bonding and  $n$  antibonding orbitals corresponding to equal numbers of positive and negative eigenvalues, respectively, in eq 3. These bonding and anti-

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bonding orbitals formed by pairwise overlap of the  $2n$  twin internal orbitals in a globally delocalized cluster are supplemented by additional bonding and antibonding orbitals formed by core bonding involving overlap of the  $n$  unique internal orbitals. This core bonding topology can be described by a graph  $G_c$  in which the vertices correspond to the vertex atoms of the polygon or deltahedron, or equivalently their unique internal orbitals, and the edges represent pairs of overlapping unique internal orbitals. The relative energies of the additional molecular orbitals from the core bonding are determined from the eigenvalues of the adjacency matrix  $A_c$  (eq 1 and 2) of the graph  $G_c$ . In the case of planar polygonal two-dimensional aromatic systems such as benzene, the graph  $G_c$  is a  $C_n$  cyclic graph, which for all  $n$  has an odd number of positive eigenvalues<sup>4</sup> leading to the familiar  $4k + 2$   $\pi$ -electrons<sup>40</sup> for planar aromatic hydrocarbons. In the case of deltahedral three-dimensional aromatic systems with  $n$  vertices such as  $B_nH_n^{2-}$  ( $6 \leq n \leq 12$ ), the two limiting possibilities for  $G_c$  are the deltahedral graph  $D_n$  and the complete graph  $K_n$ . In the deltahedral graph  $D_n$  two vertices are connected by an edge if and only if the corresponding vertices of the cluster deltahedron are connected by an edge. In the complete graph  $K_n$  every pair of vertices is connected by an edge, leading to a total of  $n(n-1)/2$  edges.<sup>4</sup> The graph-theory-derived model for metal cluster bonding<sup>7,34</sup> uses the corresponding complete graph  $K_n$  to describe the core bonding of the unique internal orbitals in globally delocalized deltahedra. The single core bonding orbital arising from the single positive eigenvalue, namely,  $n-1$ , of the  $K_n$  graph combined with the  $n$  surface bonding orbitals leads to  $n+1$  skeletal bonding orbitals. Filling each of these  $n+1$  skeletal bonding orbitals with an electron pair leads to  $2n+2$  skeletal electrons in accord with experimental observations on the deltahedral borane anions  $B_nH_n^{2-}$  ( $6 \leq n \leq 12$ ), the neutral carboranes  $C_2B_{n-2}H_n$ , and metal carbonyl analogues such as  $M_6(CO)_{16}$  ( $M = Co, Rh, Ir$ ).

The consequences of deviation from the  $2n+2$  skeletal electrons for an  $n$ -vertex globally delocalized deltahedron are of interest. Electron-rich polyhedra with more than  $2n+2$  apparent skeletal electrons have one or more nontriangular faces, which may be regarded topologically as "holes" in the otherwise closed surface.<sup>34</sup> The electron richness of such systems arises by splitting the single  $n$ -center core bond of a  $2n+2$  skeletal electron globally delocalized system into a set of two or more bonds consisting of a multicenter core bond using fewer than  $n$  unique internal orbitals and one or more additional multicenter bonds localized above each of the "holes" (i.e., nontriangular faces).<sup>7,34</sup> Electron-poor polyhedra with fewer than  $2n+2$  skeletal electrons have structures based on a central deltahedron having one or more capped faces to generate a tetrahedral chamber for each cap. The electron poverty of such systems is an indirect result of the use of more than three internal orbitals by the vertex atoms at the capped face of the central deltahedron.<sup>25,26</sup> Conversion of a globally delocalized deltahedron to an electron-rich deltahedron by removal of a vertex and its associated edges may be regarded as an inverse or dual process to the conversion of a deltahedron to a larger, electron-

poor capped deltahedron by addition of a capping vertex and its associated edges.

### 3. Bare Post-Transition-Element Clusters

The graph-theory-derived methods can be used to study the chemical-bonding topology of clusters of post-transition elements without any external ligands, i.e., "bare" post-transition-element clusters.<sup>41-43</sup> Such clusters have been found both in the condensed phase as ionic species<sup>44,45</sup> and in the gas phase as neutral or charged species.<sup>46-55</sup> The use of three internal orbitals from a normal bare post-transition-element vertex atom for the skeletal bonding in a cluster leaves six external orbitals from the nine-orbital  $sp^3d^5$  manifold for a total of six lone electron pairs, which require 12 (external) electrons. Thus Ga, In, and Tl vertices are donors of  $13 - 12 = 1$  skeletal electron; Ge, Sn, and Pb vertices are donors of  $14 - 12 = 2$  skeletal electrons, isoelectronic and isolobal with BH vertices; and As, Sb, and Bi vertices are donors of  $15 - 12 = 3$  skeletal electrons, isoelectronic and isolobal with CH vertices. The condensed-phase bare transition metal cluster ions<sup>44,45</sup> have been found by X-ray crystallography to have the following structures corresponding to the indicated chemical bonding topologies.

**Square:**  $Bi_4^{2-}$ ,  $Se_4^{2+}$ , and  $Te_4^{2+}$  isoelectronic and isolobal with the cyclobutadiene dianion with 14 skeletal electrons, eight for the four  $\sigma$ -bonds and six for the  $\pi$ -bonding.

**Tetrahedron:**  $Pb_2Sb_2^{2-}$  with 12 skeletal electrons for localized bonds along the six edges of the tetrahedron.

**Trigonal bipyramid:**  $Sn_5^{2-}$ ,  $Pb_5^{2-}$ , and  $Bi_5^{3+}$  with 12 skeletal electrons analogous to the  $C_2B_3H_5$  carborane.

**Capped square antiprism:**  $Ge_9^{4-}$ ,  $Sn_9^{4-}$ , and  $Pb_9^{4-}$  with the  $2n+4 = 22$  skeletal electrons required for an electron-rich  $n = 9$  vertex  $C_{4v}$  polyhedron having 12 triangular faces and one square face.

**Tricapped trigonal prism (Figure 1):**  $Ge_9^{2-}$  and  $TlSn_9^{3-}$  with the  $2n+2 = 20$  skeletal electrons required for an  $n = 9$  vertex globally delocalized  $D_{3h}$  deltahedron analogous to  $B_9H_9^{2-}$ ,  $Bi_9^{5+}$  anomalously having 22 rather than the expected 20 skeletal electrons suggesting<sup>41</sup> incomplete overlap of the unique internal orbitals directed toward the core of the deltahedron.

**Bicapped square antiprism (Figure 1):**  $TlSn_9^{3-}$  with the  $2n+2 = 22$  skeletal electrons required for an

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$n = 10$  vertex globally delocalized  $D_{4d}$  deltahedron analogous to that found in the  $B_{10}H_{10}^{2-}$  anion.

The gas-phase post-transition-element clusters listed below were generated in the greatest abundances in the molecular beam experiments using either resistive heating<sup>46-49</sup> or laser vaporization.<sup>50-55</sup> Stoichiometries and relative abundances were measured by mass spectrometry. Definitive experimental proofs of the structures of these clusters are not yet available. Thus the structures postulated below may be regarded as predictions of the results to be obtained when unequivocal experimental methods become available for structure determination.

**Neutral bismuth clusters:**  $Bi_4$  with 12 skeletal electrons postulated to have a tetrahedral structure like  $P_4$ .

**Cationic bismuth clusters:**  $Bi_3^+$  isoelectronic with the cyclopropenyl cation  $C_3H_3^+$  and thus postulated to have an equilateral triangular structure;  $Bi_5^+$  with 14 skeletal electrons isoelectronic with  $B_5H_9$  and thus postulated to have a square pyramidal structure.

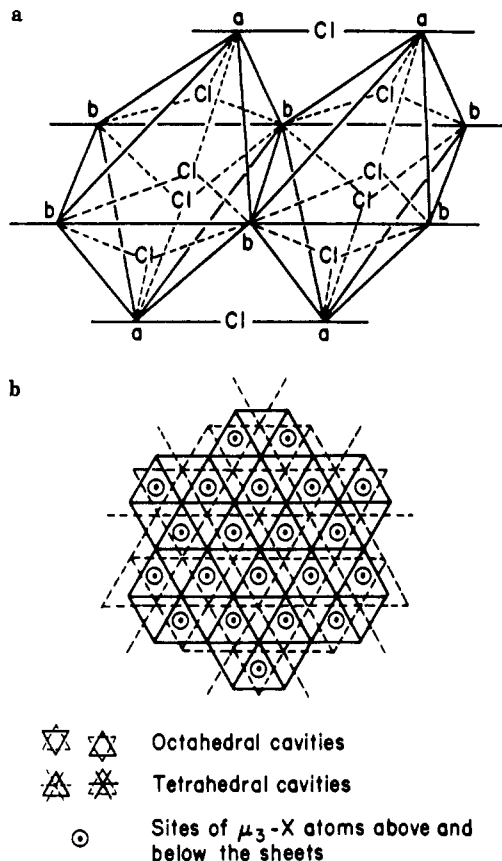
**Anionic bismuth clusters:**  $Bi_2^-$  and  $Bi_5^-$  isoelectronic with NO and  $C_5H_5^-$ , respectively.

**Tin and lead clusters:** The neutral electron-poor  $2n$  apparent skeletal electron systems  $E_7$  and  $E_{10}$  ( $E = Sn, Pb$ ) postulated to have capped octahedron and 3,4,4,4-tetracapped trigonal prism structures, respectively, each having  $C_{3v}$  symmetry and one tetrahedral chamber.

**Mixed post-transition-metal clusters:**  $Pb_5Sb_4$  and  $Sn_5Bi_4$  isoelectronic with  $Sn_9^{4-}$  and  $Bi_9^{5+}$  observed in condensed phases<sup>44,45</sup> and postulated to have an electron-rich  $C_{4v}$  capped square antiprism structure analogous to  $Sn_9^{4-}$ ;  $Pb_3Sb_2$ ,  $Pb_4Sb_2$ , and  $Pb_5Sb_2$  having  $2n + 2$  skeletal electrons and isoelectronic with the deltahedral carboranes  $C_2B_3H_5$ ,  $C_2B_4H_6$ , and  $C_2B_5H_7$  known<sup>39</sup> to have trigonal bipyramid, octahedron, and pentagonal bipyramid structures, respectively.

#### 4. Bulk Metals

Many structures of bulk metals<sup>56</sup> can be regarded as infinite arrays of fused octahedra in all three dimensions. The chemical bonding within a single isolated metal octahedron is most commonly globally delocalized with a single six-center core bond (e.g.,  $Rh_6(CO)_{16}$ ) although examples of face-localized metal octahedra with three-center bonds in each of the eight faces (e.g.,  $Nb_6X_{12}L_6^{2+}$ ) and edge-localized metal octahedra with two-center bonds along each of the 12 edges (e.g.,  $Mo_6X_{38}L_4^{4+}$ ) are also known.<sup>35,36</sup> Extrapolation of graph-theory-derived models of metal cluster bonding from finite molecules and ions to infinite structures provides insight into the relationship of the chemical bonding in metals to that in finite molecules. Such extrapolation to bulk metals can occur sequentially via one-dimensional infinite chains of fused metal octahedra in the lanthanide halides  $M_2Cl_3$  ( $M = Gd$  etc.) and two-dimensional infinite sheets of fused metal octahedra in early-transition-metal monohalides such as  $ZrCl$ .<sup>35</sup> All of these infinite structures (Figure 2) contain two tetrahedral cavities for each octahedral cavity and exhibit skeletal electron and orbital counts consistent with a multicenter bond in each cavity whether octa-



**Figure 2.** (a) Lanthanide halide structures (e.g.,  $Gd_2Cl_3$ ) based on edge-fused octahedra showing a unit of two octahedra. For clarity, electron-pair donation from halogens in other chains to each vertex metal atom is not shown. The vertices labeled a are the axial vertices and the vertices labeled b are the equatorial vertices relative to the  $Gd_6$  octahedra. (b) A top view of a segment of the two stacked hexagonal sheets of metal atoms in the zirconium monohalide structure. The sheet indicated in dotted lines is below the sheet indicated in solid lines. Circled dots indicate the sites of face-bridging halogen atoms above and below the sheets.

hedral or tetrahedral.<sup>35</sup> In  $Gd_2Cl_3$  the  $Gd_6$  octahedral cavities contain two axial and four equatorial gadolinium atoms ( $a^2b^4$  in Figure 2a), and the  $Gd_4$  tetrahedral cavities contain two axial and two equatorial gadolinium atoms ( $a^2b^2$  in Figure 2a). The octahedral and tetrahedral cavities in  $ZrCl$  are indicated in Figure 2b. This approach is essentially a topological electron- and orbital-oriented description of the interstitial electron model for the structure of metals and alloys presented by Johnson approximately two decades ago.<sup>57-62</sup>

In a bulk metal all of the metal valence orbitals are internal orbitals. In frequently encountered metal structures such as the cubic close packed structures with two tetrahedral cavities for each octahedral cavity like the infinite chains and sheets of metal octahedra, each metal atom is shared by six octahedral cavities. Since an octahedral cavity is necessarily formed by six metal atoms, the number of valence electrons for each octahedral cavity is equal to the number of valence electrons of the metal. Formation of one multicenter two-electron bond each in each octahedral cavity and in the two

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tetrahedral cavities for each octahedral cavity requires six electrons per octahedral cavity, corresponding to a group 6 metal atom with six valence electrons such as Cr, Mo, or W. This correlates with the experimental observation of maximum heat of atomization in the 5d transition series (i.e., maximum stability of the metal lattice) with the group 6 metal tungsten<sup>63</sup> as well as the role of the transition-metal divide<sup>64</sup> at the group 6 metals in determining the composition, structure, and properties of certain transition-metal alloys such as the  $\beta$ -tungsten phases. In the 3d and 4d transition series the correlations are not quite as good since the maximum heats of atomization are found in the group 5 metals V and Nb rather than the corresponding group 6 metals Cr and Mo, respectively,<sup>63</sup> this may be related to the s-d shear hypothesis of Stone.<sup>64</sup>

This model for the chemical-bonding topology of bulk metals provides insight into the superconducting critical temperatures ( $T_c$ 's) of the early transition metals and their alloys. The pure group 6 metals, Cr, Mo, and W, have very low  $T_c$ 's (<0.1 K),<sup>65,66</sup> in accord with the fully dense bonding topology implied by electron pairs in all of the cavities whether tetrahedral or octahedral,<sup>35</sup> such dense bonding is very unfavorable for the mobile electron pairs required for superconductivity. However, the group 5 metals V, Nb, and Ta in the above bonding model have only a single electron rather than an electron pair for one of the three multicenter bonds associated with a given octahedral cavity (including two tetrahedral cavities for a given octahedral cavity). These single electrons can interact to form the Cooper pairs required for superconductivity, accounting for the much higher  $T_c$ 's of group 5 metals relative to the group 6 metals and the local maximum in the  $T_c$  versus  $Z_{av}$  curve at  $Z_{av} = 4.8$  for transition-metal alloys<sup>65,66</sup> ( $Z_{av}$  = average number of valence electrons). Similarly, for the group 7 metals Tc and Re, the above bonding model leaves an extra electron after providing electron pairs for each of the three multicenter bonds associated with a given octahedral cavity. Pairing of these extra electrons can lead to the Cooper pairs required for superconductivity, thereby accounting for the much higher  $T_c$ 's of group 7 metals relative to the group 6 metals and the local maximum in the  $T_c$  versus  $Z_{av}$  curve at  $Z_{av} = 7$  for transition-metal alloys.<sup>65,66</sup>

## 5. Superconducting Solids

Metal-metal interactions are a key feature of the structures of solids exhibiting superconductivity. In many cases such metal-metal interactions arise from direct metal-metal bonding. However, in the case of the high- $T_c$  copper oxides, the required copper-copper interactions occur through oxygen bridges similar to the copper-copper interactions in antiferromagnetic binuclear copper(II) complexes.<sup>67</sup> The key role played by metal-metal interactions in superconducting solids makes the topological approach to metal cluster bonding relevant to understanding the types of solid-state structures exhibiting superconductivity. In particular,

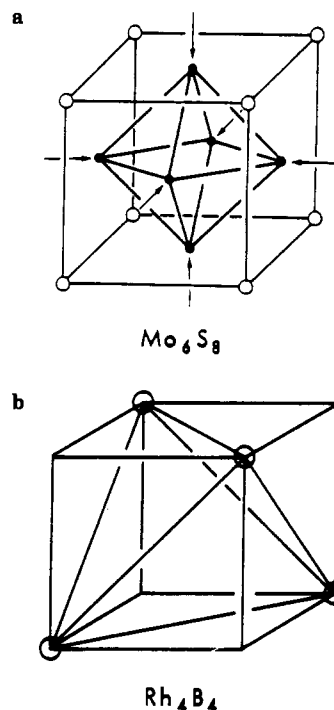
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**Figure 3.** (a) The  $\text{Mo}_6\text{S}_8$  octahedron inside an  $\text{S}_8$  cube which forms the fundamental  $\text{Mo}_6\text{S}_8$  building block of the Chevrel phases  $\text{MMo}_6\text{S}_8$ . (b) The  $\text{Rh}_4\text{B}_4$  building block of the ternary lanthanide rhodium borides  $\text{LnRh}_4\text{B}_4$ .

infinite metal-metal-bonded structures with edge-localized bonding and with slightly fewer electrons than the closed-shell electronic configuration appear to be the best candidates for superconductors. The connection between edge-localized bonding and superconductivity appears to be related to the physical idea<sup>68</sup> that increased localization of the conduction electron wave function leads to an extremely short mean free path and/or a low Fermi velocity corresponding to a small coherence length.

These ideas are more clearly illustrated by the ternary molybdenum chalcogenides, commonly known as the Chevrel phases.<sup>69</sup> These phases were the first type of superconducting ternary system found to have relatively high  $T_c$ 's and exhibit the highest known critical magnetic fields ( $H_{c2}$ ) before discovery of the copper oxide superconductors.

The most important type of Chevrel phases have the general formula  $\text{M}_n\text{Mo}_6\text{E}_8$  (E = S or Se; M = Ba, Sn, Pb, Ag, lanthanides, Fe, Co, Ni, etc.).<sup>69</sup> The fundamental building blocks of their structures are  $\text{Mo}_6\text{E}_8$  units containing a bonded  $\text{Mo}_6$  octahedron (Mo-Mo distances in the range 2.67-2.78 Å) with a chalcogen atom capping each of the eight faces leading to an  $\text{Mo}_6$  octahedron within an  $\text{E}_8$  cube (Figure 3a). Each (neutral) chalcogen atom of the  $\text{E}_8$  cube functions as a donor of four skeletal electrons to the  $\text{Mo}_6$  octahedron within that  $\text{E}_8$  cube, leaving an electron pair from that chalcogen atom to function as a ligand to the Mo atom in an adjacent  $\text{Mo}_6$  octahedron. Maximizing this sulfur electron pair donation to the appropriate Mo atom in an adjacent  $\text{Mo}_6$  octahedron results in a tilting of the  $\text{Mo}_6$  octahedron by about 20° within the cubic array of

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the other metal atoms  $M$ .<sup>70</sup> These other metal atoms  $M$  furnish electrons to the  $Mo_6E_8$  units, allowing them to approach but not attain the  $Mo_6E_8^{4-}$  closed shell electronic configuration. The resulting deficiency in the number of skeletal electrons corresponds to the presence of holes in an otherwise filled valence band, thereby providing a mechanism for p-type conductivity. In addition, electronic bridging between  $Mo_6$  octahedra is provided by interoctahedral metal-metal interactions, with the nearest interoctahedral Mo-Mo distances falling in the 3.08–3.49 Å range. The  $Mo_6E_8^{4-}$  closed shell electronic configuration for the fundamental Chevrel phase building block is isoelectronic with the Mo(II) halide derivatives<sup>71</sup> consisting of discrete  $Mo_6X_8L_6^{4+}$  octahedra ( $X = \text{halogen}$ ,  $L = \text{two-electron donor ligand}$ ); remember that each Mo vertex receives an electron pair from a chalcogen atom of an adjacent  $Mo_6X_8$  unit. The species  $Mo_6E_8^{4-}$  and  $Mo_6X_8L_6^{4+}$  have 24 skeletal electrons exactly as required for an edge-localized  $Mo_6$  octahedron having two-electron two-center bonds along each of the 12 edges.

Another interesting class of metal cluster superconductors consists of the ternary lanthanide rhodium borides  $LnRh_4B_4$  ( $Ln = \text{certain lanthanides such as Nd, Sm, Er, Tm, and Lu}$ ),<sup>72</sup> which exhibit significantly higher  $T_c$ 's than other types of metal borides. The structures of these rhodium borides consist of electronically linked  $Rh_4$  tetrahedra in which each of the four triangular faces of each  $Rh_4$  tetrahedron is capped by a boron atom of a  $B_2$  unit ( $B-B$  distance 1.86 Å in  $YRh_4B_4$ ), leading to  $Rh_4B_4$  cubes (Figure 3b) in which the edges (average length 2.17 Å in  $YRh_4B_4$ ) correspond to 12  $Rh-B$  bonds and single diagonals of each face (average length 2.71 Å in  $YRh_4B_4$ ) correspond to six  $Rh-Rh$  bonds. The ratio between these two lengths, namely,  $2.71/2.17 = 1.25$ , is only about 13% less than the ideal  $2^{1/2} = 1.414$  ratio for a cube. The  $Rh-Rh$  distances of 2.71 Å in these  $Rh_4B_4$  cubes are essentially identical to the mean  $Rh-Rh$  distance in the discrete molecular tetrahedral  $Rh$  cluster  $Rh_4(CO)_{12}$ ,<sup>73</sup> regarded as a prototypical example of an edge-localized tetrahedron.<sup>25,26</sup> Electron counting in an  $Rh_4B_4$  unit assuming all edge-localized bonds leads to  $Rh_4B_4^{4-}$  as a closed shell electronic configuration.<sup>74</sup> Since the lanthanides also present in the lattice form tripositive rather than tetrapositive ions, the  $LnRh_4B_4$  borides must be  $Ln^{3+}Rh_4B_4^{3-}$  with the  $Rh_4B_4^{3-}$  anion having one electron less than the closed shell electronic configuration  $Rh_4B_4^{4-}$ . As in the Chevrel phases discussed above, this electron deficiency of one electron per  $Rh_4$  tetrahedron corresponds to the presence of holes in an otherwise filled valence band, thereby providing a mechanism for p-type conductivity.

The field of superconductivity was revolutionized by the discovery of the high- $T_c$  copper oxide superconductors.<sup>75</sup> The first copper oxide superconductors to be discovered were the superconductors  $La_{2-x}M_xCuO_{4-y}$  in which the conducting skeleton consists of a single Cu-O plane<sup>75-77</sup> and whose  $T_c$  of 40 K was higher than

any known  $T_c$  at that time. Subsequent work led to the superconductors  $YBa_2Cu_3O_{7-y}$  in which the conducting skeleton consists of two Cu-O planes braced by a Cu-O chain<sup>77-79</sup> and whose  $T_c$  of 90 K made the observation of superconductivity at liquid nitrogen temperature possible for the first time. Further improvements in  $T_c$  were obtained in the homologous series of bismuth copper oxide superconductors<sup>80,81</sup>  $Bi_2Sr_2Ca_{n-1}Cu_nO_{5+2n-1+x}$  ( $n = 1, 2, 3$ ) consisting of a layer sequence  $BiSr(CaCu)_{n-1}SrBi$  and thallium copper oxide superconductors<sup>82</sup>  $Tl_2Ba_2Ca_{n-1}Cu_nO_{5+2n-1+x}$  ( $n = 1, 2, 3$ ) consisting of a layer sequence  $TlBaCu(CaCu)_{n-1}BaTl$  and exhibiting  $T_c$ 's as high as 122 K for materials isolated in the pure state.

The two-dimensional conducting skeletons in these copper oxide superconductors are related to the three-dimensional conducting skeletons in the Chevrel phases and  $LnRh_4B_4$  discussed above. However, the conducting skeletons in these copper oxide superconductors are constructed from M-O-M bonds rather than direct M-M bonds ( $M = Cu$ ). The much higher ionic character and thus much lower polarizability and higher "rigidity" of M-O bonds relative to M-M bonds can be related to the persistence of superconductivity in copper oxides to much higher temperatures than in metal clusters. The required M...M interactions for a conducting skeleton in the copper oxide superconductors are antiferromagnetic interactions between the single unpaired electrons of two  $d^9$  Cu(II) atoms separated by an oxygen bridge similar to antiferromagnetic Cu(II)-...Cu(II) interactions in discrete binuclear complexes.<sup>87</sup> This idea is closely related to the resonating valence bond model of Anderson.<sup>83,84</sup> The positive counterions in the copper oxide superconductors control the negative charge on the Cu-O skeleton and therefore the oxidation states of the copper atoms. Partial oxidation of some of the Cu(II) to Cu(III) generates holes in the valence band required for conductivity with holes as the charge carriers. Copper oxide superconductors of the type  $Nd_{2-x}Ce_xCuO_4$  are also known in which partial reduction of Cu(II) to Cu(I) leads to electrons in the conduction band as the charge carriers.<sup>85</sup>

## 6. Concluding Remarks

In this Account I have shown how topological ideas derived from mathematical chemistry provide insight into the structure and bonding of diverse inorganic

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substances including solid-state materials. Such ideas can relate two-dimensional aromaticity in planar aromatic hydrocarbons such as benzene to three-dimensional aromaticity in deltahedral boranes such as  $B_nH_n^{2-}$  ( $6 \leq n \leq 12$ ). In addition, topological ideas have been essential for the development of the chemistry of bare gas-phase post-transition-element clusters by suggesting key experiments. In the case of infinite solid-state structures, ideas derived from topology not only relate chemical structure and bonding to superconductivity as discussed in this Account but also provide the first viable approach to chemical bonding in icosahedral

quasicrystals.<sup>86</sup> These diverse examples clearly demonstrate the wide applicability of mathematical methods to structure and bonding in inorganic chemistry.

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## Dynamic Monte Carlo Simulations of Surface-Rate Processes

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Monte Carlo methods have been widely used in many areas of chemical physics.<sup>1,2</sup> In recent years they have been employed to study various equilibrium and dynamic problems in surface science.<sup>3-12</sup> When Monte Carlo methods are used in studying equilibrium phenomena, many replicas of the system of interest are generated according to some sampling algorithm. Although consideration must be given to finite-size effects, rather accurate results may be obtained if a sufficient number of replicas of the system are generated. In the case of dynamic phenomena, however, an additional basic issue must be addressed to ensure that the Monte Carlo simulations yield correct results. The correspondence between each step in a Monte Carlo simulation and real time must be established. In the section Dynamic Monte Carlo Simulations, we review some work<sup>13,14</sup> in which this correspondence has been studied and discuss the dynamical interpretation of Monte Carlo simulations. In the section Applications, we review two applications of dynamic Monte Carlo simu-

lations, one concerning surface diffusion and the other concerning the compensation effect in surface reactions. In the first application the importance of the appropriate choice of transition probabilities is demonstrated. In the second application we show how Monte Carlo simulations can provide useful results for a reacting lattice-gas system.

### Dynamic Monte Carlo Simulations

We begin this section by describing a simple algorithm for a dynamic Monte Carlo simulation of the surface diffusion of atoms or molecules adsorbed on a crystal surface. In this algorithm for surface diffusion, particles (atoms or molecules) hop from one site to another on a lattice which has a coordination number dictated by the symmetry of the crystal surface. The lattice is initially populated randomly at some specified

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