Chemical Bonding Topology of Superconductors

II. Ternary Lanthanide Rhodium Borides

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Graph theory-derived methods are used to derive the chemical bonding topology of the closed-shell $Rh_4B_4^{4-}$ building blocks of the superconducting lanthanide rhodium borides, $LnRh_4B_4$ (Ln = lanthanides such as Nd, Sm, Er, Tm, Lu). The resulting chemical bonding topology consists of edge-localized Rh_4 tetrahedra electronically linked in a three-dimensional lattice by exotetrahedral Rh–Rh bonds. This work thus provides an example of an additional class of relatively high-temperature superconductors exhibiting porously delocalized chemical bonding topology like the Chevrel phases discussed in the previous paper of this series.   © 1987 Academic Press, Inc.

1. Introduction

The previous paper of this series (*1*) uses previously reported graph theory-derived methods (*2, 3*) to develop a model for the chemical bonding topology of the ternary molybdenum chalcogenides (Chevrel phases) of interest as superconductors exhibiting relatively high critical temperatures and critical magnetic fields. The chemical bonding topology indicated by these methods consists of a lattice of edge-localized rather than globally delocalized Mo_6 octahedra electronically linked to each other in all three directions. The infinite delocalization in such a system is thus porous rather than dense. This leads naturally to the suggestion that porous infinite delocalization is a feature of the chemical bonding topology of superconductors exhibiting relatively high critical temperatures and critical magnetic fields.

This paper tests these ideas further by a similar analysis of the chemical bonding topology of the ternary lanthanide rhodium borides, $LnRh_4B_4$ (Ln = certain lanthanides such as Nd, Sm, Er, Tm, Lu), another class of high-temperature superconductors (*4, 5*) exhibiting significantly higher superconducting transition temperatures than other types of metal borides. These rhodium borides have a structure consisting of electronically linked discrete Rh_4 tetrahedra and thus provide further support of the general idea of Vandenberg and Matthias (*6*) that most high-temperature superconductors contain discrete metal clusters in their crystal lattices. This paper shows that a reasonable chemical bonding model can be derived for the Rh_4B_4 building blocks of these clusters in which the Rh_4 tetrahedra are edge-localized like the Mo_6 octahedra in the Chevrel phases. This observation provides further support for the idea that porous infinite delocalization is a feature of at least certain types of superconductors exhibiting relatively high critical temperatures and critical magnetic fields. In addition, this paper is apparently the first attempt to treat chemical bonding in the Rh_4B_4 building

blocks of these ternary borides by any theoretical chemical method.

2. Structure and Bonding in the Ternary Lanthanide Rhodium Borides

The topology of an individual Rh_4B_4 unit in these ternary borides is that of a tetracapped tetrahedron of T_d symmetry (Fig. 1) in which the four degree-6 vertices correspond to rhodium atoms and the four degree-3 vertices correspond to boron atoms. Such a tetracapped tetrahedron is topologically equivalent to a cube with six diagonals drawn to preserve T_d overall symmetry (Fig. 1). The diagonals of the cube correspond to 6 Rh–Rh bonds (average length 2.71 Å in YRh_4B_4) (7) and the edges of the cube correspond to 12 Rh–B bonds (average length 2.17 Å inYRh_4B_4) (7). The ratio between these two lengths, namely 2.71/2.17 = 1.25, is only about 13% less than the $\sqrt{2} = 1.414$ ratio of these lengths in an ideal cube, suggesting that the Rh_4B_4 building blocks can be approximated by a cube in the three-dimensional lattice. The Rh–Rh distances of 2.71 Å in these Rh_4B_4 units are essentially identical to the mean Rh–Rh distance in the discrete molecular tetrahedral rhodium cluster (8) $Rh_4(CO)_{12}$ regarded as a prototypical example of an edge-localized tetrahedron (2, 3).

The arrangement of the Rh_4B_4 units as

FIG. 2. Primitive tetragonal structure of $LnRh_4B_4$ (5). The solid circles represent the lanthanide atoms. The cubes, not drawn to scale, represent the Rh_4B_4 units; the rhodium vertices are circled and individual Rh–Rh and B–B bonds are omitted for clarity. The dotted lines connecting the Rh_4B_4 cubes correspond to one B–B bond (~1.86 Å), one Rh–Rh bond (~2.68 Å) and two Rh–Rh bonds (~3.14 Å).
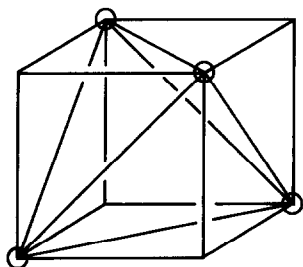

FIG. 1. The tetracapped tetrahedron which is topologically equivalent to a cube with six diagonals. The degree-6 vertices are circled for clarity.
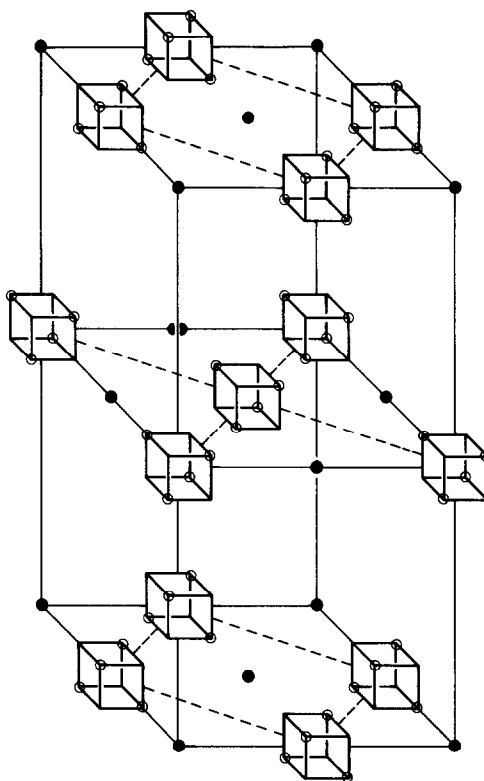
sheets in the primitive tetragonal lattice of $LnRh_4B_4$ is shown in Fig. 2. In addition, the projection of a given sheet of Rh_4 tetrahedra along the [001] plane including an Rh_4 tetrahedron on an adjacent sheet is shown in Fig. 3 in order to indicate the key intertetrahedral Rh–Rh distances. All of the valence orbitals of both the boron and rhodium atoms are involved in the formation of 4 and 9, respectively, two-center bonds. The four bonds formed by a boron atom using its sp^3 bonding orbital manifold are as follows:

(1) Three bonds to rhodium atoms in the same Rh_4B_4 cube (average Rh–B distance 2.17 Å in YRh_4B_4).

(2) One bond to the nearest boron atom in an adjacent Rh_4B_4 cube (B–B distance 1.86 Å in YRh_4B_4), thereby leading to discrete B_2 units in the structure.

The nine bonds formed by a rhodium atom using its sp^3d^5 bonding orbital manifold are as follows:

(1) Three bonds to rhodium atoms in the same Rh_4 tetrahedron (average Rh–Rh distance 2.71 Å in YRh_4B_4).

(2) Three bonds to boron atoms in the same Rh_4B_4 cube (average Rh–B distance 2.17 Å in YRh_4B_4).

(3) One bond to the nearest rhodium atom in another Rh_4B_4 cube in the same sheet (Rh–Rh distance 2.68 Å in YRh_4B_4).

(4) Two bonds to the next-nearest rhodium atoms in adjacent Rh_4B_4 cubes (Rh–Rh distances 3.14 Å in YRh_4B_4).

In deriving the chemical bonding topology each boron atom is considered to have three internal orbitals and one external orbital and is therefore a donor of two skeletal electrons since one of the three boron valence electrons is needed for the B–B bond using its external orbital. Similarly each rhodium atom has six internal orbitals and three external orbitals and is therefore a donor of six skeletal electrons since three of the nine rhodium valence electrons are needed for the three external Rh–Rh bonds formed by a given rhodium atom.

These considerations indicate that a neutral Rh_4B_4 unit in the $LnRh_4B_4$ borides has 32 skeletal electrons as follows:

4 Rh vertices (4)(6) = 24 electrons
4 B vertices (4)(2) = <u>8 electrons</u>

   Total skeletal
     electrons for
     each Rh_4B_4 unit   32 electrons

Since a tetracapped tetrahedron or the topologically equivalent cube with six diagonals (Fig. 1) has 18 edges corresponding to 6 Rh–Rh bonds and 12 Rh–B bonds as outlined above, a closed-shell edge-localized Rh_4B_4 unit requires (2)(18) = 36 skeletal electrons corresponding to the tetraanion $Rh_4B_4^{4-}$. 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 $Rh_4B_4^{4-}$. This situation is similar to that in the ternary molybdenum chalcogenides discussed previously (1) where, for example, the Chevrel phase $PbMo_6S_8$ has $Mo_6S_8^{2-}$ units with 2 electrons less than the closed-shell electronic configuration $Mo_6S_8^{4-}$ and the infinite chain conductors $M_2^{I}Mo_6S_6$ have octahedral $Mo_{6/2}S_{6/2}^{-}$ units with one electron less than the closed-shell electronic configuration $Mo_{6/2}S_{6/2}^{2-}$. These electron deficiencies appear to be an important feature of these highly conducting systems since they provide partially filled conduction bands for electron transport.
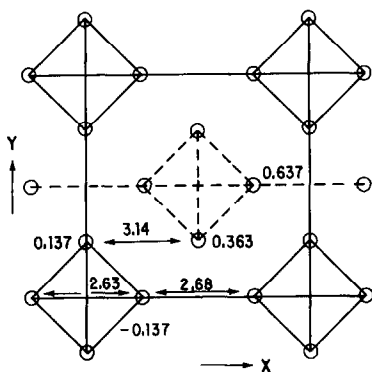

FIG. 3. Projection of the Rh_4 tetrahedra along [001] (4). The heights of the rhodium atoms and the Rh–Rh bond lengths (in Å) are indicated. The four solid Rh_4 tetrahedra are in the same sheet, whereas the dashed Rh_4 tetrahedron in the center is in the sheet above or below.

3. Conclusion

This paper presents a model for the chemical bonding topology of the $LnRh_4B_4$ borides containing edge-localized Rh_4 tetrahedra electronically linked in a three-dimensional lattice by exotetrahedral Rh–Rh bonds. This model thus provides a further example of a relatively high-temperature superconductor exhibiting infinite porous delocalization as defined in the first paper of this series (1). Hopefully the use of the graph theory-derived methods for metal cluster bonding to identify common features in the chemical bonding topology in two diverse types of relatively high-temperature superconductors, namely the Chevrel phases and the ternary lanthanide rhodium borides, will stimulate efforts by theoretical physicists to relate the essential features of infinite porous delocalization (i.e., the one-dimensional transport of electrons along polyhedral edges) to physical models of superconductivity.

References

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