JOURNAL OF SOLID STATE CHEMISTRY **124,** 329–332 (1996)
ARTICLE NO. 0245

Chemical Bonding Topology of Superconductors

III. Layered Quaternary Lanthanide Nickel Borocarbides and Boronitrides

R. B. King

Department of Chemistry, University of Georgia, Athens, Georgia 30602

Received March 13, 1996; accepted April 18, 1996

DEDICATED TO PROF. DR. ERWIN WEISS ON THE OCCASION OF HIS 70TH BIRTHDAY

The concept of porous delocalization has been extended to the conducting skeletons of quaternary lanthanide nickel borocarbide and boronitride superconductors and related nonsuperconducting materials. Such materials exhibit layered structures of the general type $(LnX)_n(Ni_2B_2)$ (Ln = lanthanide, particularly the nonmagnetic La^{III} or Lu^{III}; X = C or N; n = 1, 2, or 3) containing planar square Ni nets bonded to BCB^{2-} ligands in the superconducting $LnNi_2B_2C$, BC^{3-} ligands in the nonsuperconducting LnNiBC and Ln_2NiBC_2, and BN^{2-} ligands in the superconducting $La_3Ni_2B_2N_3$. The linear BCB^{2-} bridges linking adjacent Ni layers in $LnNi_2B_2C$ lead to a porous conducting skeleton in $LnNi_2B_2C$. The BC^{3-} ligands in the nonsuperconducting LuNiBC and the closely related Ln_2NiBC_2 = $Ln_2C_2 \cdot 2Ln$NiBC do *not* link adjacent Ni layers in LuNiBC so that LuNiBC has only a two-dimensional conducting skeleton, which is not necessarily porous in these two dimensions. The superconducting $La_3Ni_2B_2N_3$ = LaN · 2LaNiBN has a similar local Ni environment as LuNiBC but with BN^{2-} rather than the isoelectronic BC^{3-} ligands above and below each Ni layer. However, in $La_3Ni_2B_2N_3$ unlike LuNiBC the LaNiBN units are linked electronically by the La atoms in the intermediate LaN layer leading to a three-dimensional conducting skeleton in $La_3Ni_2B_2N_3$ rather than the two-dimensional conducting skeleton of LuNiBC. The linear BNLaNB units linking the Ni layers in $La_3Ni_2B_2N_3$ lead to a porous conducting skeleton similar to that in the $LnNi_2B_2C$ superconductors. © 1996 Academic Press, Inc.

INTRODUCTION

Previous work by the author in the 1980s on the application of graph-theory derived methods (2–5) to the study of the chemical bonding topology in the superconducting ternary molybdenum chalcogenides MMo_6S_8 (Chevrel phases (6) and ternary lanthanide rhodium borides (1) has suggested a connection between relatively high superconducting critical temperatures (e.g., T_c's > 4 K) and a conducting skeleton having an edge-localized chemical bonding topology with holes in the valence band conveniently designated as porous delocalization. Such ideas were subsequently extended to other types of compounds (7) including other ternary metal borides and silicides, the A-15 alloy superconductors M_3E (M = V, Nb, Ta; E = Si, Ge, Sn), and transition metal alloys. In addition, these ideas were shown to apply to the high T_c copper oxide superconductors to provide a simple rationalization why the T_c's of the copper oxide superconductors are much higher than any of the known metal cluster superconductors (8, 9).

Since completion of this theoretical work in 1990, a new class of layered quaternary metal boride superconductors has been discovered, which exhibits significantly higher T_c's than the ternary metal borides studied earlier (Table 1) (1, 7). The first members of this new class of superconducting metal borides to be discovered were metal borocarbide superconductors with the general formula LnM_2B_2C (Ln = lanthanide, particularly the nonmagnetic La^{III} or Lu^{III}, M = Ni, Pd, Pt) and were found to exhibit T_c's as high as 16.6 K in the case of $LuNi_2B_2C$ (10). Subsequent very recent work (11) led to the discovery of related boronitride superconductors with the general formula $Ln_3Ni_2B_2N_3$, among which the lanthanum derivative $La_3Ni_2B_2N_3$ was found to exhibit a T_c around 12 K. This paper discusses the extension of the previously used graph-theory derived methods to the chemical bonding topology in the conducting skeleton of this new class of layered quaternary metal boride superconductors. Of interest in connection with these new superconductors are not only their relatively high T_c's for nonoxide superconductors but also the presence of novel B_2C^{2-} and BN^{2-} building blocks in their structures. The BN^{2-} unit in the $Ln_3Ni_2B_2N_3$ structure, which is directly bonded to several Ni atoms in a single layer through its boron atom, is also significant in being isoelectronic with numerous important ligands in transition metal organometallic and coordination chemistry including the carbonyl (CO), cyanide (CN^-), nitrosyl (NO^+), and dinitrogen (N_2) ligands.

0022-4596/96 $18.00

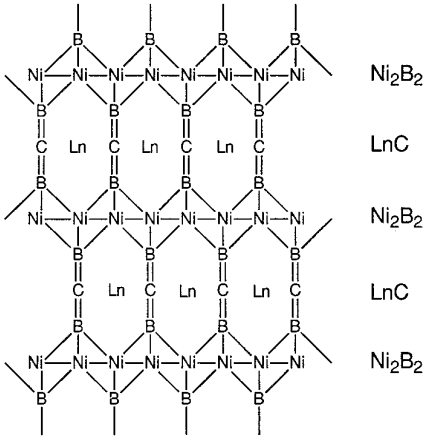

FIG. 1. Schematic representation of the layer structure of the LnNi$_2$B$_2$C superconductors.

LAYERED NICKEL BORIDE STRUCTURES

The structures of the LnM_2B_2C superconductors (Fig. 1), the nonsuperconductors of the general type LnNiBX (X = C, N: Fig. 2), and the $Ln_3Ni_2B_2N_3$ superconductors (Fig. 3) can be constructed by alternating Ni_2B_2 layers with one to three LnX (X = C or N) layers, respectively (Table 1) (12). These structures are related to that of $ThCr_2Si_2$ and consist of a square net of Ni atoms (Fig. 4a) with B atoms above and below the Ni nets. A related layer structure is found in nonsuperconducting Lu_2NiBC_2 = $Lu_2C_2 \cdot 2LuNiBC$ in which a sequence of Lu/C_2/Lu layers containing bonded carbon pairs as discrete C_2^{6-} ligands separates two LnC layers in the LuNiBC structure (Fig. 2: X = C) (13). The conducting skeletons in these materials consist of the Ni–B–(C, N) subskeletons although the lanthanide atoms bridging two BN groups through their N atoms in $Ln_3Ni_2B_2N_3$ appear to be an essential part of the conducting skeleton (see below).

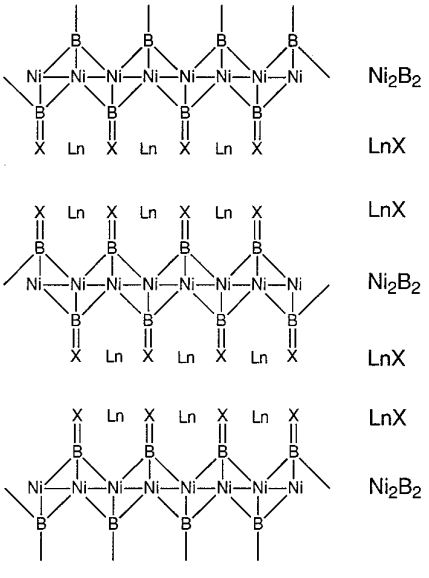

FIG. 2. Schematic representation of the layer structure of LnNiBX (X = C or N).

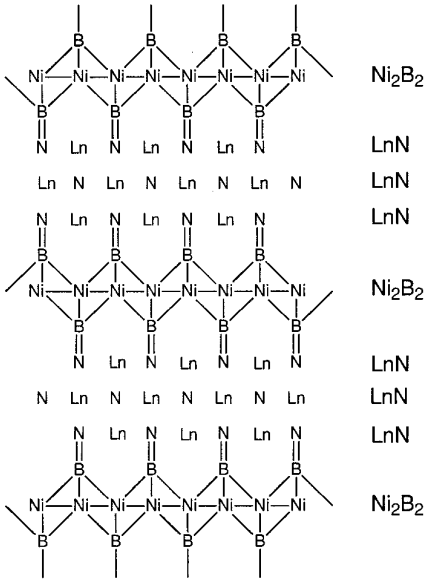

FIG. 3. Schematic representation of the layer structure of $La_3Ni_2B_2N_3$ = $LaN \cdot 2LaNiBN$.

In the LnNi$_2$B$_2$C$_2$ superconductors the Ni layers in the conducting skeleton are linked by bridging linear $[:B{=}C{=}B:]^{2-}$ ligands (Fig. 5) which, because of their short B=C distances (1.47 Å) and linear two-coordinate C atom, can be considered to have B–C multiple bonds with an *sp* hybridized C atom. The B atoms of such BCB ligands (Fig. 5a) can also be regarded as *sp* hybridized with an electron pair in an *sp* hybrid on each B atom pointing away from the central C atom as well as an empty *p* orbital similar to the empty *p* orbital in simple boron trihalides BX_3 (X = F, Cl, Br, I). In the Ni$_2$B$_2$C conducting skeletons of LnNi$_2$B$_2$C derivatives the electron deficiency of this empty *p* orbital on each B atom of the BCB ligands is relieved by forming a multicenter bond with filled *d* orbitals on the Ni atoms of the Ni square net (Fig. 4b). In addition, another multicenter bond is formed between the B *sp* hybrid orbital with the lone pair and a pair of Ni atoms. Each BCB ligand is linked to a total of eight Ni atoms through such multicenter bonding and any given Ni atom is linked to four B atoms in an approximately tetrahedral arrangement leading to Ni(BCB)$_{4/8}$ as a descriptor of the ligands around a single Ni atom. Halet (14) uses the oxidation state formalism $(Ln^{2+})(Ni^0)_2(B_2C^{2-})$ to describe LnNi$_2$B$_2$C and notes the resemblance of the tetrahedral Ni^0B_4 unit in LnNi$_2$B$_2$C to the tetrahedral Ni^0C_4 unit in Ni(CO)$_4$.

TABLE 1
Some Properties of Layered Quaternary Lanthanide Nickel Borocarbides and Boronitrides

Compound	T_c, K	Layer structure	B/C/N unit	B = X distance, Å	Closed shell unit	Electron deficiency/Ni
LnNi$_2$B$_2$C	16.6 (Lu)	(LnC)(Ni$_2$B$_2$)	BCB^{2-}	1.47	Ni(B$_2$C)$^{3-}_{4/8}$	1.5
LnNiBC	*a*	(LnC)$_2$(Ni$_2$B$_2$)	BC^{3-}	1.52	Ni(BC)$^{5-}_{4/4}$	2
Lu$_2$NiBC$_2$	*a*	(Lu$_2$C$_2$)(LuC)Ni$_2$B$_2$(LuC)	BC^{3-}, C$_2^{6-}$		Ni(BC)$^{5-}_{4/4}$	2
LnNiBN	*a*	(LnN)$_2$(Ni$_2$B$_2$)	BN^{2-}		Ni(BN)$^{4-}_{4/4}$	1
Ln_3Ni$_2$B$_2$N$_3$	12 (La)	(LnN)$_3$(Ni$_2$B$_2$)	BN^{2-}	1.44	Ni(BN)$^{4-}_{4/4}$	1

[a] No superconductivity has been observed in this phase.

However, the direct bonding of a given nickel atom to four other Ni atoms in the Ni layer of LnNi$_2$B$_2$C as contrasted with the absence of Ni–Ni bonds in Ni(CO)$_4$ suggests that this resemblance is fortuitous.

The B atoms in the structures of the other quaternary nickel borocarbides and nickel boronitrides occur as multiply bonded BN^{2-} or BC^{3-} units isoelectronic with the metal carbonyl group (Fig. 5). Unlike the BCB^{2-} unit containing two B atoms, the BN^{2-} or BC^{3-} units containing a single B atom are not sufficient to provide an electronic bridge between two adjacent Ni layers in the conducting skeletons of these materials. In the case of LnNiBC there is no electronic connection between the BC units from adjacent Ni$_2$B$_2$ layers in the Ni(BC)$_{4/4}$ conducting skeleton. In the case of La$_3$Ni$_2$B$_2$N$_3$ = LaN · 2LaNiBN, the La atoms in the middle LaN layer of a stack of three LaN layers link the N atoms of BN units pointing downward from the next upper Ni layer with the N atoms of BN units pointing upward from the next lower Ni layer (Fig. 3). The La atoms in the middle LaN layer thus can provide an electronic connection between adjacent Ni$_2$B$_2$ layers in the Ni(BN)$_{4/4}$ subskeleton similar to the electronic connection between adjacent Ni layers in the conducting skeleton of LnM$_2$B$_2$C provided by the BCB bridges (Fig. 1). These La atoms as well as all of the Ni, B, and N atoms may thus be regarded as part of the conducting skeleton in La$_3$Ni$_2$B$_2$N$_3$ with BNLaNB serving as the electronic connection between adjacent Ni layers. The ability of LaN linkages to be part of the conducting skeleton in La$_3$Ni$_2$B$_2$N$_3$ is consistent with the experimentally observed (15) high conductivity of pure LaN.

ELECTRON COUNTING IN LAYERED NICKEL BORIDES

Elementary electron counting suggests that Ni(B$_2$C)$^{3-}_{4/8}$ is a closed shell configuration for the conducting skeleton

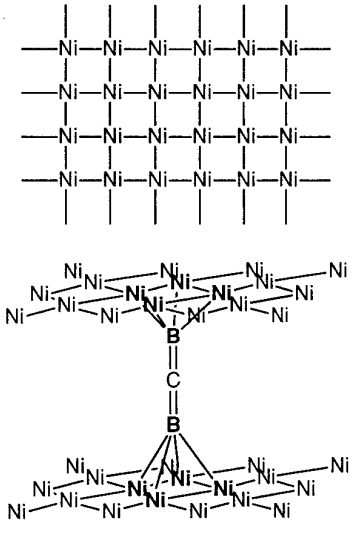

FIG. 4. (a) A square nickel layer in the LnNi$_2$B$_2$C superconductors; (b) Illustration of a single BCB^{2-} bridge between two nickel layers with the symbols of the atoms involved in the bonding (BNi$_4$ to each layer) given in boldface type.

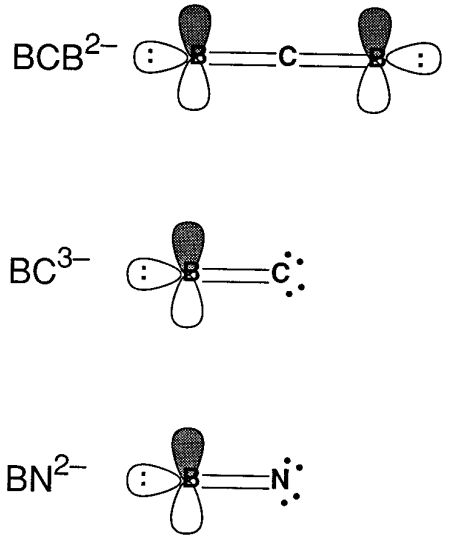

FIG. 5. The BCB^{2-}, BC^{3-}, and BN^{2-} units found in the layered quaternary lanthanide nickel borocarbide and boronitride structures showing the empty *p* orbital of the B atom and the boron *sp* hybrids each containing an electron pair for donation to the Ni layers.

in the $LnNi_2B_2C$ structure (Fig. 1). Thus the actual formula $LnNi_2B_2C$ corresponding to $Ni(B_2C)_{4/8}^{1.5-}$ is deficient by 1.5 electrons per Ni atom although the partial multiple bonding in the square Ni layer implied by the Ni–Ni distances of 2.45 Å, slightly shorter than those of 2.50 Å in metallic Ni, suggests that the actual electron deficiency might not be that large. The BCB^{2-} dianionic ligand considered above can donate an electron pair to the Ni layers both "above" and "below" the BCB ligand indicating that a *neutral* BCB ligand serves as a net two-electron donor with one electron being donated to each Ni layer. The closed shell 18-electron Ni configuration for an $Ni(B_2C)_{4/8}^{3-}$ unit can then be obtained as follows:

Neutral nickel atom	10 electrons
The 4 Ni–Ni bonds to the central Ni atom (4)(1) =	4 electrons
The $(BCB)_{4/8}$ ligand environment $(\frac{1}{2})(2)$ =	1 electron
The −3 charge	3 electrons
Total electronic configuration for each nickel atom in an $Ni(B_2C)_{4/8}^{3-}$ unit	18 electrons.

The apparent electron deficiency of up to 1.5 electrons per Ni atoms for a closed shell electronic configuration in the conducting skeleton of $LnNi_2B_2C$ corresponds to holes in the valence band leading to *p*-type conductivity.

Similar electron counting procedures can be used for the conducting skeletons of the other lanthanide nickel borocarbides and boronitrides. The BC^{3-} and BN^{2-} units each are donors of a single electron pair to the nickel layer so that *neutral* BC and BN units are net donors of −1 and 0 electrons, respectively. Electron counting similar to that outlined above for the $Ni(B_2C)_{4/8}^{3-}$ unit indicate that $Ni(BC)_{4/4}^{5-}$ and $Ni(BN)_{4/4}^{4-}$ are closed-shell electronic configurations for $LnNiBC$ and $La_3Ni_2B_2N_3 = LaN \cdot 2LaNiBN$, respectively, corresponding to apparent electron deficiencies of 2 and 1 electrons per Ni atom, respectively, for closed shell electronic configurations.

CONCLUSIONS

The $LnNi_2B_2C$ structure (Fig. 1) can be regarded as a highly anisotropic three-dimensional structure with the two-dimensional Ni layers linked electronically by the unsaturated BCB bridges in the third dimension leading to the layer sequence $(LnC)(Ni_2B_2)$. The linear nature of the BCB bridges makes the conducting skeleton of $LnNi_2B_2C$ porous. The nonsuperconducting LuNiBC (Fig. 2) has a similar local environment around each Ni atom but with BC ligands above and below each Ni layer leading to the layer sequence $(LuC)_2Ni_2B_2$. The BC ligands do *not* link adjacent Ni layers in LuNiBC so that LuNiBC has a two-dimensional conducting skeleton, which is not necessarily porous in these two dimensions. The superconducting $La_3Ni_2B_2N_3 = LaN \cdot 2LaNiBN$ with the layer sequence $(LaN)_3(Ni_2B_2)$ (Fig. 3) has a similar local environment as LuNiBC around each Ni atom but with BN rather than BC ligands above and below each Ni layer. However, in $La_3Ni_2B_2N_3$ unlike LuNiBC the LaNiBN units are linked electronically by the La atoms in the intermediate LaN layer leading to a three-dimensional conducting skeleton in $La_3Ni_2B_2N_3$ rather than the two-dimensional conducting skeleton in LuNiBC. The linear BNLaNB units linking the Ni layers in $La_3Ni_2B_2N_3$ lead to a porous conducting skeleton similar to that in the $LnNi_2B_2C$ superconductors.

REFERENCES

1. For part II of this series see R. B. King, *J. Solid State Chem.* **71,** 233 (1987).
2. R. B. King and D. H. Rouvray, *J. Am. Chem. Soc.* **99,** 7834 (1977).
3. R. B. King, *in* "Chemical Applications of Topology and Graph Theory," (R. B. King, Ed.), pp. 99–123. Elsevier, Amsterdam, 1983.
4. R. B. King, *in* "Molecular Structure and Energetics," (J. F. Liebman and A. Greenberg, Eds.), pp. 123–148. VCH Publishers, Deerfield Beach, Florida, 1986.
5. R. B. King, "Applications of Graph Theory and Topology in Inorganic Cluster and Coordination Chemistry." CRC Press, Boca Raton, Florida, 1993.
6. R. B. King, *J. Solid State Chem.* **71,** 224 (1987).
7. R. B. King, *Inorg. Chem.* **29,** 2164 (1990).
8. R. B. King, *Inorg. Chim. Acta* **15,** 143 (1988).
9. R. B. King, *J. Mater. Sci. Lett.* **9,** 5 (1990).
10. R. J. Cava, H. Takagi, H. W. Zandbergen, J. J. Krajewski, W. F. Peck, Jr., T. Siegrist, B. Batlogg, R. B. van Dover, R. J. Felder, K. Mizuhashi, J. O. Lee, H. Eisaki, and S. Uchida, *Nature* **367,** 252 (1994).
11. R. J. Cava, H. W. Zandbergen, B. Batlogg, H. Eisaki, H. Takagi, J. J. Krajewski, W. F. Peck, Jr., E. M. Gyorgy, and S. Uchida, *Nature* **372,** 245 (1994).
12. T. Siegrist, H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., *Nature* **367,** 254 (1994).
13. H. W. Zandbergen, R. J. Cava, J. J. Krajewski, and W. F. Peck, Jr., *J. Solid State Chem.,* **110,** 196 (1994).
14. J.-F. Halet, *Inorg. Chem.* **33,** 4173 (1994).
15. R. P. Lesunova, L. S. Karenina, S. P. Palguev, and E. I. Burmakin, *Solid State Ionics,* **36,** 275 (1989).