PHYSICAL REVIEW B VOLUME 49, NUMBER 18 1 MAY 1994-II

Electronic properties of superconducting $LuNi_2B_2C$ and related boride carbide phases

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(Received 24 January 1994)

Band properties of the quaternary superconductor $LuNi_2B_2C$ ($T_c \approx 17$ K) and related intermetallic phases (including, for example, LuNiBC and YNi_2B_2C) have been calculated in the local-density approximation via the linear augmented-plane-wave method. The results feature a density-of-states peak near the top of nearly filled Ni($3d$) bands, with only modest B and C orbital admixture. The calculated $LuNi_2B_2C$ bands suggest that these interesting boride carbide phases represent a family of conventional (rather than high-T_c) superconductors.

Recently, Cava *et al.*[1] have discovered superconductivity at 23 K in the quaternary Y-Pd-B-C system, thereby equaling the previous T_c record[2] that existed prior to the advent in 1986 of the high-T_c era. Unfortunately, the composition of the superconducting phase has not yet been identified. (Multiphase superconducting samples were obtained from melt compositions with an average stoichiometry of $\sim YPd_5B_3C_{0.3}$.) However, superconductivity has also been observed[3] in the closely related R-Ni-B-C system (R=Y, Tm, Er, Ho, and Lu), though with slightly lower critical temperatures (up to $\sim$ 16.6 K). In this case, the composition[3] (i.e., RNi_2B_2C) and structure[4] ($ThCr_2Si_2$-like with filled $2b$ sites) of the superconducting phase have been determined. These findings provide a possible explanation for the earlier report[5] of superconductivity at 12 K in the Y-Ni-B system.

The purpose of the present investigation is to calculate the electronic properties of these superconductors in order to help clarify the issue as to whether these materials should be regarded as conventional intermetallic superconductors or the first members of a possible family of high-T_c boride carbide phases. We consider here only the nonmagnetic compounds for which the rare-earth f levels are either completely filled (i.e., R=Lu) or completely empty (R=Y). Based on the results that are presented below, it appears that $LuNi_2B_2C$ (and related compounds) are conventional intermetallic superconductors whose promising transition temperatures ($\sim$ 16.6 K at present) are derived from a standard electron-phonon mechanism in which the light mass of the B and C constituents leads to high-frequency phonons and enhanced T_c's.

The structure of the $LuNi_2B_2C$ phase[4] is illustrated in Fig. 1(a). It consists basically of the body-centered-tetragonal (bct) $ThCr_2Si_2$ structure (space group $I4/mmm$), but with an extra constituent (namely, carbon) at the $2b$ site in the basal plane. Thus, $LuNi_2B_2C$ is related structurally to the well-known heavy-Fermion superconductor $CeCu_2Si_2$ (Ref. 6). The observed $LuNi_2B_2C$ lattice parameters ($a \approx 3.46$ Å, $c \approx 10.63$ Å) and atom-position parameters[4] produce nearly ideal NiB_4 tetrahedra with B-Ni-B bond angles of 108.8° and 110.9° and a Ni-B bond distance of 2.1 Å. The $\sim$ 2.45 Å Ni-Ni bondlength is slightly smaller than the fcc Ni value ($\sim$ 2.50 Å), thus suggesting the presence of metal-metal bonds in this phase. The B-C bondlength ($\sim$ 1.47 Å) is slightly smaller than the value for hexagonal B_4C ($\sim$ 1.64 Å). Although this bct structure is analogous to those adopted by many of the cuprate high-T_c superconductors, the calculated electronic properties for $LuNi_2B_2C$ are shown below to exhibit three-dimensional (3D) rather than 2D characteristics.

The structure of a closely related simple-tetragonal (st) LuNiBC phase[4] (which has not yet been found to superconduct) is illustrated in Fig. 1(b). This compound contains a rocksalt-type Lu_2C_2 double layer in place of the $LuNi_2B_2C$ monolayer, and this changes the Bravais lattice from bct to st ($a \approx 3.50$ Å, $c \approx 7.75$ Å). The resulting nonsymmorphic space group exhibits $P4/nmm$ symmetry. As Siegrist *et al.*[4] have noted, both structures possess remarkably similar bond distances and bond angles. This strongly suggests that the electronic and bonding characteristics of both materials are comparable.

In the present study, the self-consistent band structure for bct $LuNi_2B_2C$ and st LuNiBC have been calculated in the local-density approximation (LDA) with the use

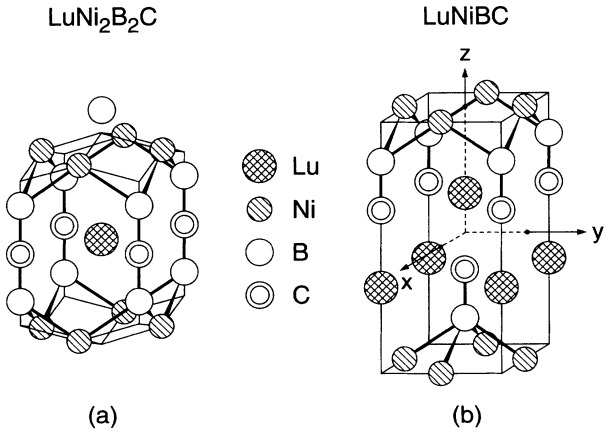

FIG. 1. Comparison of the primitive unit cells for (a) body-centered-tetragonal (bct) $LuNi_2B_2C$, and (b) simple-tetragonal (st) LuNiBC.

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of a scalar-relativistic version[7] of the linear augmented-plane-wave (LAPW) method.[8] The present LAPW implementation imposes no shape approximations on either the charge density or potential. The LAPW basis has included plane waves with a 1.36 Ry cutoff (~60–70 LAPW's per atom) and spherical-harmonic terms through $l = 8$ (Lu,Ni) or $l = 6$ (B,C) within the corresponding muffin-tin spheres. The crystalline charge density and potential have been expanded using ~ 4500–5500 plane waves (64 Ry) in the interstitial region and lattice-harmonic expansions ($l_{max} = 6$) within the muffin tins. A twelve-point **k** sample in the $\frac{1}{8}$ irreducible wedge has been used to carry out Brillouin-zone (BZ) integrations.

Exchange and correlation effects have been included within the LDA framework with the use of the Wigner interpolation formula.[9] The atomic Lu($5d^16s^2$), Ni($3d^94s^1$), B($2s^22p^1$), and C($2s^22p^2$) states are treated as valence electrons in these calculations, while a frozen-core approximation has been applied to the more tightly bound core-type levels, including the Lu($4f$) electrons. This rigid-core Lu($4f$) treatment, which has been validated by a separate calculation where these electrons are treated as valence states, helps to simplify an already complicated valence-band manifold. The assumed LAPW muffin-tin radii are 1.32 (Lu), 1.20 (Ni), 0.75 (B), and 0.72 (C) Å.

The results of the present LAPW calculations for $LuNi_2B_2C$ are shown in the left-hand panel of Fig. 2.

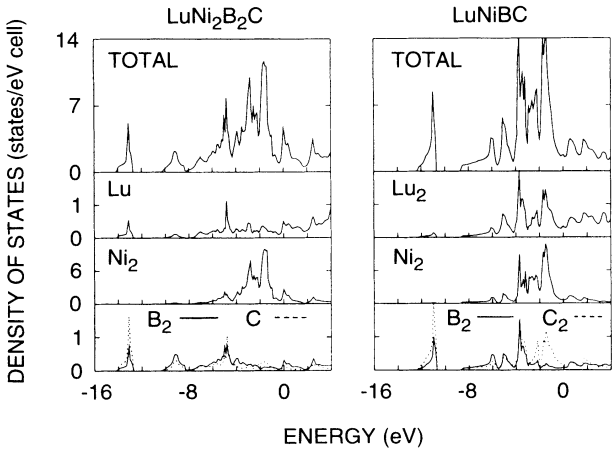

FIG. 3. Total and muffin-tin-projected density-of-states results for $LuNi_2B_2C$ and LuNiBC.

The lowest band originates from the C($2s$) levels while the upper valence-band complex that begins at ~ −10 eV evolves gradually from B($2s$) to B($2p$)-C($2p$), and finally to Ni($3d$) character near E_F. The $LuNi_2B_2C$ Fermi level occurs near the top of the Ni($3d$) bands. However, the lowest subband of the Lu($5d$) manifold (which exhibits mainly $d_{x^2-y^2}$ character) dips slightly below E_F at Γ, thereby producing a small pocket of Lu($5d$) carriers in this material.

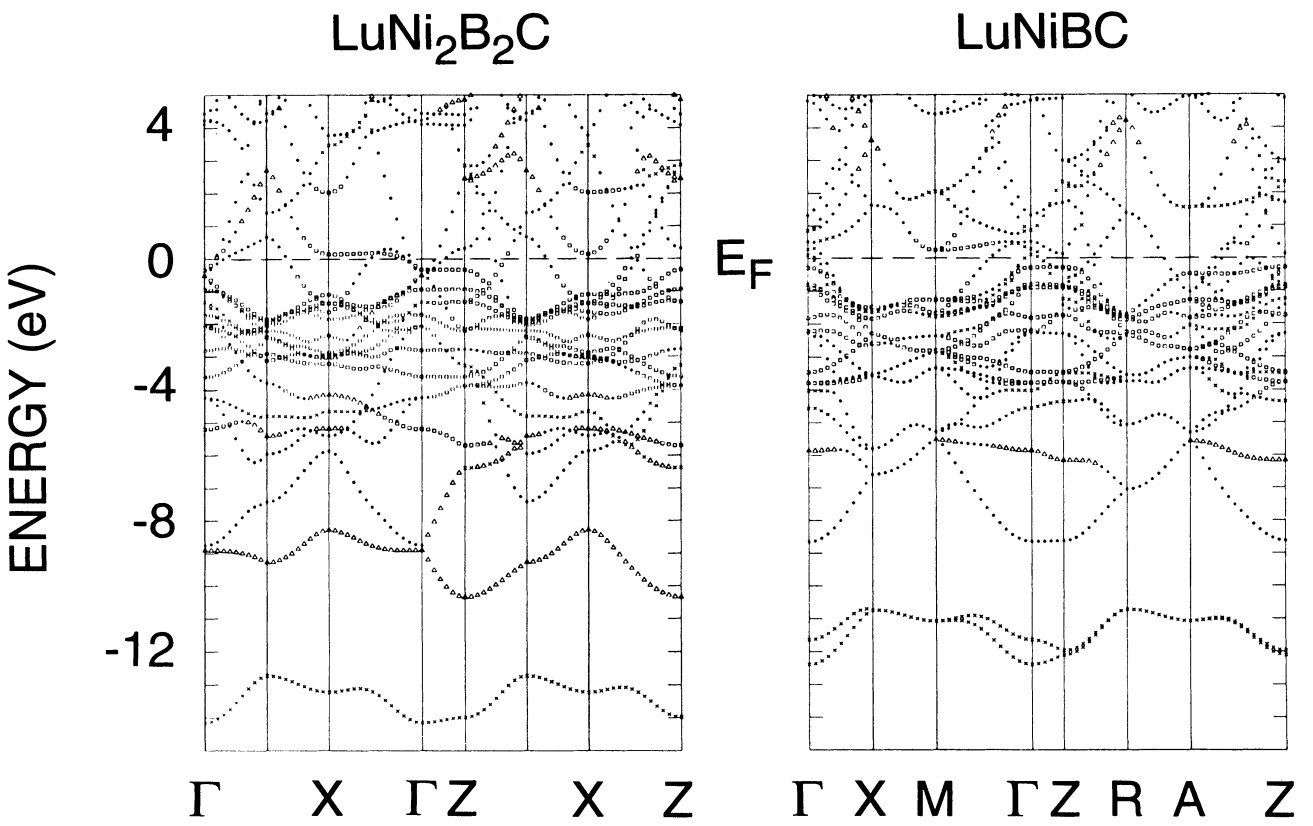

FIG. 2. LAPW energy-band results along comparable Brillouin-zone directions for bct $LuNi_2B_2C$ and st LuNiBC. Bands with significant Ni, B, and C orbital character are labeled with squares ($\omega_{Ni} > 0.5$), triangles ($\omega_B > 0.12$), and crosses ($\omega_C > 0.12$), respectively. The rigid-core approximation places the filled Lu($4f$) levels (not shown) at binding energies of ~ 3.8 and 2.9 eV, respectively.

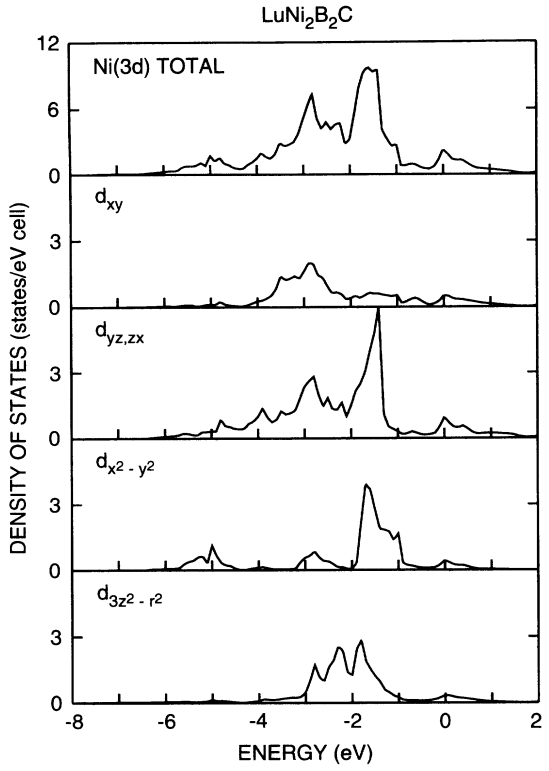

FIG. 4. Projected Ni(3d) density-of-states results for $LuNi_2B_2C$, including total and individual-orbital components.

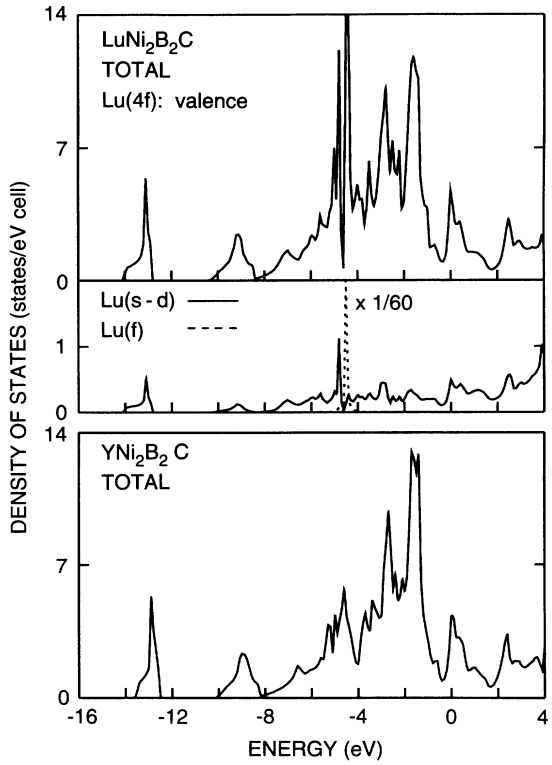

FIG. 5. Total and Lu-projected density-of-states results for $LuNi_2B_2C$ in which the Lu(4f) states are treated as valence electrons. Total YNi_2B_2C density-of-states results are shown below.

The LAPW band results for st LuNiBC that are shown to the right in Fig. 2 exhibit qualitative similarities with the bct $LuNi_2B_2C$ results, although structural differences preclude a direct band-by-band comparison. To minimize these structural differences, the bct $LuNi_2B_2C$ results in Fig. 2 are plotted along symmetry lines of the st BZ, thus ignoring the actual shape of the bct BZ. In both compounds, the Lu(4f) levels (not shown) lie near the bottom of the Ni(3d) bands, well below E_F. This is confirmed below by a separate $LuNi_2B_2C$ calculation with Lu(4f)-type valence states, where relaxation increases the Lu(4f) rigid-core binding energy by ~ 0.7 to ~ 4.5 eV.

A comprehensive overview of the $LuNi_2B_2C$ and LuNiBC electronic properties is provided by the density-of-states results $N(E)$ that are shown in Fig. 3. The $LuNi_2B_2C$ Fermi level coincides with a $N(E)$ peak where $N(E_F) \approx 2.4$ states/eV Ni. This is about 1.8 times larger than that calculated[10] for a typical cuprate superconductor such as La_2CuO_4, where $N(E_F) \approx 1.3$ states/eV Cu. In fact, the $LuNi_2B_2C$ value for $N(E_F)$ is comparable (on a per-atom basis) to that calculated[11] for V_3Si, where $N(E_F) \approx 2.5$ states/eV V. Thus, even ignoring enhancement effects, this calculated band-structure value for $N(E_F)$ places $LuNi_2B_2C$ among the "conventional" superconductors when this material is added to the plot[12] of T_c vs γ.

Comparing the $LuNi_2B_2C$ and LuNiBC $N(E)$ results, one concludes that an important difference between the two phases is the fact that the LuNiBC Fermi level occurs at an $N(E)$ minimum, just below the corresponding $LuNi_2B_2C$ peak. This suggests that the superconducting prospects for LuNiBC will be improved if the Fermi level can be raised (by about 1 electron/cell) by substitutional doping until it coincides with the unoccupied LuNiBC peak. In this regard, it is noteworthy that the Lu contribution to $N(E_F)$ is not totally negligible in these materials. Thus, substitutional doping at this site is less favorable than in typical cuprate superconductors such as La_2CuO_4 where the La component is small.[10]

The present boride carbide phases differ from the cuprates in that they suggest no obvious "few-band" model that summarizes the essential features of their electronic structure. This is evident from the projected Ni(3d) density-of states results in Fig. 4. All five Ni(3d) subbands contribute in roughly equal proportions to the $N(E)$ peak near E_F. In fact, the d_{xy} and $d_{yz,zx}$ $N(E_F)$ components exhibit a slight enhancement (by $\sim 16\%$ and 6%, respectively) relative to the corresponding $d_{x^2-y^2}$ and $d_{3z^2-r^2}$ terms.

The $LuNi_2B_2C$ results in Figs. 2–4 are essentially unchanged when the Lu(4f) levels are treated as valence bands rather than rigid-core states. As shown in Fig. 5, the $LuNi_2B_2C$ total and Lu-projected $N(E)$ results are visually indistinguishable from the previous frozen-core results in Fig. 3. Shown below are the corresponding $N(E)$ results that have been derived from an analogous LAPW calculation[13] for isostructural YNi_2B_2C. In view of the obvious YNi_2B_2C-$LuNi_2B_2C$ band similarities, it is

not surprising that the T_c's for these two phases ($\sim$ 15.6 K for YNi_2B_2C and $\sim$ 16.6 K for $LuNi_2B_2C$) are comparable.

Finally, we consider the question of whether these Ln-Ni-B-C phases should be regarded as conventional rather than high-T_c superconductors. The present boride carbide phases do not satisfy the *ad hoc* band criteria that have been proposed[14] for identifying possible high-T_c candidates. The key element of these criteria is the presence of half-filled σ^* bands that are due to strong nearest-neighbor bonds between nearly degenerate cation-anion levels. Compared to the cuprates, the reduced B and C binding energies (relative to oxygen) yield nearly degenerate Ni($3d$)-B($2s$) or Ni($3d$)-C($2p$) orbital combinations. However, there are no readily identifiable σ^* bands near E_F in these Ln-Ni-B-C phases that satisfy the "half-filled" requirement.

The tetrahedrally coordinated Ni produces Ni-B bonds that are relatively weak, and this leads to Ni-B hybridization effects that are moderate in strength. As a result, the bands near the $LuNi_2B_2C$ Fermi level exhibit predominant Ni($3d$) orbital character. A simple model calculation illustrates the basic differences between the planar p_σ-$d_{x^2-y^2}$ geometry of typical cuprate high-T_c superconductors[10] and the tetrahedral NiB_4 coordination of $LuNi_2B_2C$ in their ability to produce strong σ bonds and a large σ-σ^* bandwidth. For example, a tight-binding calculation[14] for a hypothetical $CaNiN_2$ phase that contains NiN_2 planes and degenerate Ni($3d$)-N($2p$) orbitals yields a total valence bandwidth of 11.6 eV. However, an analogous calculation for $LuNi_2B_2C$ that includes the same tight-binding parameters produces an overall bandwidth of only 6.1 eV for this geometry.

In summary, the results of LAPW band calculations for the recently discovered intermetallic superconductors $LuNi_2B_2C$ and YNi_2B_2C predict a density-of-states peak at E_F that exhibits predominant Ni($3d$) orbital character. Analysis of these LDA results suggests that the observed superconducting properties seem to place these materials in the category of conventional rather than high-T_c superconductors.

I am pleased to acknowledge valuable discussions with R. J. Cava and T. Siegrist on the subject of this investigation.

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