

LuNi₂B₂C: A Novel Ni-Based Strong-Coupling Superconductor

Warren E. Pickett and David J. Singh

Complex Systems Theory Branch, Naval Research Laboratory, Washington, D.C. 20375-5345

(Received 22 February 1994)

The surprising recent discovery of superconductivity up to $T_c = 23$ K in Ni- and Pd-based rare-earth borocarbides raises the question of whether or not these materials constitute a new class of high temperature superconductors (HTS). For LuNi₂B₂C, with $T_c = 16.6$ K and a (known) layered crystal structure $I4/mmm$, electronic structure calculations indicate that it is a strongly 3D metal with all atoms contributing to the metallic character, completely unlike the cuprate HTS. Incorporating resistivity data we deduce a very strong electron-phonon coupling $\lambda_{tr} = 2.6$, which we relate to an unusual combination of states at the Fermi level and substantial contributions from the vibrations of the light atoms.

PACS numbers: 74.70.Ad, 63.20.Kr, 71.25.Pi, 74.25.Jb

Observation of superconductivity with critical temperatures T_c up to 23 K in Ni- and Pd-based rare-earth borocarbides [1-3] has raised new questions about our understanding of the origins of superconductivity. It is rare to find superconductors with appreciable amounts of nickel, and PdH_x ($T_c \sim 10$ K) is one of the few Pd-based superconductors. The crystal structure of one of the members, LuNi₂B₂C with $T_c = 16.6$ K, was determined by Siegrist *et al.* [4] to be a strongly anisotropic, tetragonal layered structure. The alternating layers of composition LuC and Ni₂B₂ and the $I4/mmm$ space group that it shares with several cuprate high- T_c superconductors raises the possibility that these materials might form the basis of a class of quasi two-dimensional (2D) HTS compounds analogous to the cuprates. Replacement of copper by related transition metals and oxygen by related small, electronegative ions such as N, C, or B has been anticipated [5] to produce conditions favorable for superconductivity.

By carrying out extensive studies of its bonding properties and spectral distribution, and initiating calculations of its transport, magnetic, and vibrational behavior, we have learned that LuNi₂B₂C is distinctly *unlike* the cuprates. This compound is thoroughly metallic, since none of the atoms is closed shell, and there is a large density of states $N(E_F)$ at the Fermi level that is roughly half from Ni states but with important contributions from all atoms. Coupled with resistivity (ρ) measurements we identify a very large electron-phonon coupling $\lambda_{tr} = 2.6$ that accounts for the robust superconductivity.

The crystal structure [4] of LuNi₂B₂C is pictured in Fig. 1 and involves three parameters, the two lattice constants $a = 3.464$ Å and $c = 10.631$ Å and one internal parameter, the height z of the B atom above the Lu-C plane ($z/c = 0.1379$). The short B-C separation (1.46 Å, compared to, e.g., the B-C distance of 1.62 Å in the tetragonal B₂C₂La structure class) is representative of covalently bonded solids, and may reflect some charge transfer off of these atoms. The Ni atoms are nearly ideally tetrahedrally coordinated with four neighboring B atoms, but in addition the Ni-Ni separations of 2.45 Å in the a - b plane are even smaller than in Ni metal (2.50 Å), so Ni-Ni interactions will be strong. The electronic structure in the

local density approximation as parametrized by Vosko, Wilk, and Nusair [6] was calculated with an extension of the general potential linearized plane wave method [7,8]. Sphere radii of 2.70, 2.25, 1.35, and 1.28 a.u. were chosen for Lu, Ni, B, and C, respectively, and approximately 950 basis functions were used. Self-consistency was carried out on an 84 point mesh in the irreducible zone.

The band structure and the total and local densities of states (DOS) are shown in Figs. 2 and 3, respectively. The Lu f bands were treated self-consistently with the band states, and were found to lie 5 eV below the Fermi level E_F and to hybridize only weakly with the valence band states. The DOS in Fig. 3 indicates that, although Ni dominates near E_F , all four atoms are involved in the bands at and just above E_F ; note especially that Lu is not fully ionized to the 3+ state. The characters at E_F con-

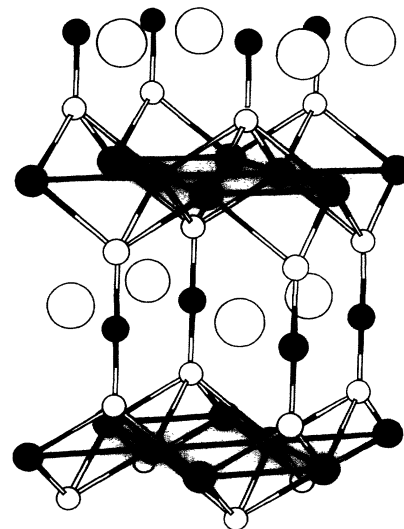


FIG. 1. Crystal structure of LuNi₂B₂C reported in Ref. [4]. Ni atoms (larger dark spheres) form a square lattice, and each Ni is tetrahedrally coordinated to four B atoms (small white spheres). C atoms (small dark spheres) are bonded linearly to two B atoms, and lie in the same plane as the Lu atoms (large white spheres).

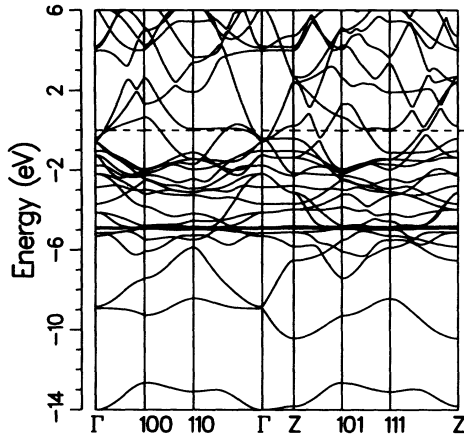


FIG. 2. Band structure of $\text{LuNi}_2\text{B}_2\text{C}$ along the representative directions in the Brillouin zone; Z denotes $(0,0,2\pi/c)$. Bands below -8 eV are primarily C and B $2s$ states. The flat $5f$ bands of Lu are evident at -5 eV. The dashed line at zero energy denotes the Fermi level.

sist primarily of Ni d , B p , C p , and Lu d .

The calculated Fermi surface is complicated. There are two spheroids centered at the center of the Brillouin zone, with Lu d character and with Ni d + B p character. Figure 2 illustrates that the dispersion of these bands along the c direction is comparable to that in the plane, giving a strongly three dimensional (3D) character. The third band that crosses E_F gives rise to a very large sheet, of dominantly Ni d character, that is multiply connected. All characteristics are indicative of a good metal, with $N(E_F) = 4.80 \text{ (eV cell)}^{-1}$. This value, on a per-Ni-atom basis, is about 60% of the very large value [9] for paramagnetic Ni that drives its ferromagnetic instability.

Of particular interest is the flat band at E_F along the (110) direction and around the (11ξ) line [in units of $(\pi/a, \pi/a, 2\pi/c)$] and the related DOS peak. At (110) where it is very flat, this band is characterized by strong antibonding $dd\sigma^*$ interactions as well as d_{z^2} character within the square Ni sublattice, and bonding interactions between the Ni d states and a symmetric bonding combination of B p states. An appreciable amount of Lu d_{xz} and d_{yz} character is also present. In spite of the short tetrahedral coordination of the Ni atom with four B atoms, for a range of the uppermost bonding states (within 2–3 below E_F) there is very little B p character. This DOS peak, which has strong Ni d character but nevertheless is separated from the main Ni d bands, is the distinguishing feature of this compound's electronic structure. The main Ni d bands in Fig. 3 are narrower than in Ni metal, and their separation from E_F by almost 1 eV suggests charge transfer to Ni in this compound.

We have found no comparable split-off peak above the main d bands for either the Ni monolayer or for an isolated Ni_2B_2 layer of this structure. When the bridging C atoms are included (giving the fictitious compound

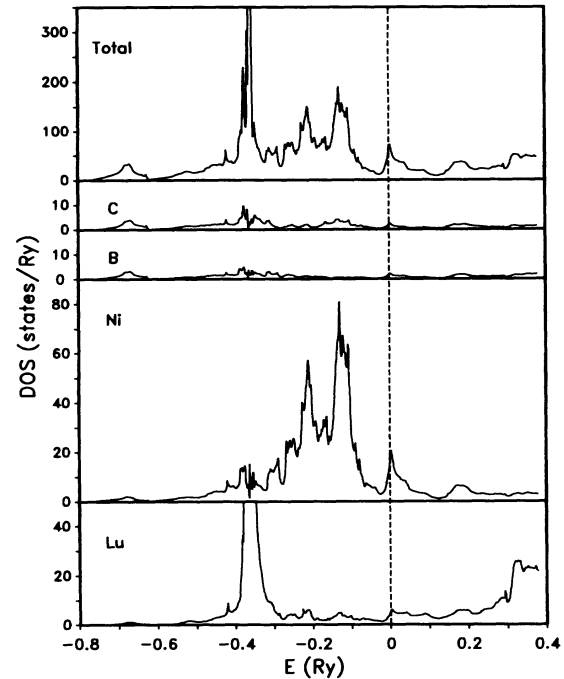


FIG. 3. Total and site-projected density of states of $\text{LuNi}_2\text{B}_2\text{C}$. The prominent peak at the Fermi energy (zero of energy) has Lu, B, and C character complementing the strong Ni d character. The peak at ~ -0.35 Ry is from the Lu $5f$ bands.

$\text{Ni}_2\text{B}_2\text{C}$) a strong peak, split off from the main Ni d bands, appears at E_F , comprised of Ni and C states. Only upon including the Lu atom, which interacts substantially with the C, is the final DOS structure achieved, indicating that the electronic structure at E_F is a feature of extended bonding throughout the material.

This flat band gives rise to the large density of states peak almost at E_F ; 0.2 additional electron would put E_F precisely at the peak and might raise T_c marginally. Coupled with the known ferromagnetic character of Ni metal and the Ni monolayer, this DOS peak suggests the possibility of a Stoner (ferromagnetic) instability analogous to the case of Ni. By performing self-consistent calculations with an imposed spin moment [10] we established that there is *no* ferromagnetic instability in this material that would preclude conventional superconductivity. The Stoner enhancement of the magnetic susceptibility is $\chi/\chi_0 \approx 1.3 \pm 0.2$, suggesting correlation effects may not be large.

Cava *et al.* [3] have reported good metallic behavior of the resistivity $\rho(T)$ even in polycrystalline samples, which have a nearly linear behavior above 50 K with temperature coefficient of resistivity $d\rho/dT \approx 0.4 \mu\Omega \text{ cm/K}$ and very small residual value $\rho(0)$. To begin to understand transport, we have calculated the Fermi velocities, obtaining $v_{F,x} = v_{F,y} = 2.12$, $v_{F,z} = 2.09$, in 10^7 cm/sec . The corresponding Drude plasma energies $\hbar^2 \Omega_{p,ii}^2 = 4\pi e^2 N(E_F)$

$\times v_{F,i}^2$, $i = x, y, z$, are also nearly equal, at 5.1 eV. (Individual sheets of Fermi surface are more anisotropic than their sum.) The Hall tensor R^H calculated in the constant relaxation time approximation [11] (often valid except at low temperature) is also nearly isotropic, with a value $R^H = -3 \times 10^{-9} \text{ m}^3/\text{C}$ that is representative of metallic behavior but also reflects canceling contributions from various parts of the Fermi surface.

Bloch-Grüneisen transport theory leads to the relation

$$dp/dT = (8\pi^2/\hbar \Omega_p^2) k_B \lambda_{tr} \quad (1)$$

at moderate to high temperature, where λ_{tr} is similar to the electron-phonon interaction (EPI) strength λ but weighted by angular (scattering) factors. The experimental temperature coefficient $0.4 \mu\Omega \text{ cm/K}$ and the calculated plasma energy leads to the remarkably large value $\lambda_{tr} = 2.6$. We return to this quantity below.

The EPI coupling strength is given by

$$\lambda = \left[\sum_a \frac{\eta_a}{M_a} \right] / \langle \omega^2 \rangle \equiv \omega_{el}^2 / \omega_{ph}^2, \quad (2)$$

where M_a is the mass of atom a . $\omega_{ph} = \langle \omega^2 \rangle^{1/2}$ is a coupling-strength-weighted mean square phonon frequency that is difficult to estimate the multicomponent compounds, and $M_{ave} \omega_{el}^2$ is a total "electronic stiffness" defined by Eq. (2) (M_{ave} is the average atomic mass). The strongly metallic, 3D character suggests that electron-phonon coupling may be estimated using the Gaspari-Gyorffy ("rigid muffin tin") theory [12]. The McMillan-Hopfield factors $\eta_a = N(E_F) \langle I_a^2 \rangle$ and dominant scattering channels ($l \rightarrow l+1$) are found to be, in $\text{eV}/\text{\AA}^2$, 0.33 for Lu ($p \rightarrow d$), 1.16 for Ni (comparable $p \rightarrow d$ and $d \rightarrow f$), 0.67 for B ($p \rightarrow d$), and 0.84 for C ($p \rightarrow d$). Although these values will be somewhat dependent on the sphere sizes used in the evaluation, they indicate contributions from all atoms and a substantial contribution from the Ni atoms. For comparison, the corresponding value [13] for elemental Ni is $\eta_{Ni} = 1.76 \text{ eV}/\text{\AA}^2$, while values for C in the metal carbides [14] extend up to $3 \text{ eV}/\text{\AA}^2$ for the high DOS compounds. The resulting value is $\omega_{el} = 31.3 \text{ meV}$; due to the inverse mass weighting the contributions to ω_{el}^2 are roughly 50% B, 30% C, and 20% Ni, i.e., the light atoms contribute strongly.

We have calculated the energy versus displacement of the Raman active A_{1g} mode that involves only symmetric B motion along the c axis, finding that the predicted position of the B atom is within $0.025 \text{ \AA}$ of the measured value. The calculated frequency is 850 cm^{-1} ($=106 \text{ meV}$); since this is the B-C bond stretching mode it may be the highest frequency in the material. If, as in conventional 3D metals $\lambda \sim \lambda_{tr} = 2.6$, the required mean frequency is $\omega_{ph} = 20 \text{ meV}$ which suggests either soft modes or strong contributions from the heavier atoms.

It is instructive to learn what is necessary to account for the observed value of T_c within conventional superconductivity theory. We use the Allen-Dynes [15] equa-

tion $T_c = f(\lambda, \mu^*, \omega_{ph}, \omega_{log})$, assuming as is common a Coulomb pseudopotential $\mu^* = 0.15$ and taking $\omega_{log} = 0.7\omega_{ph}$. Our general conclusions are not sensitive to these choices. Using the calculated ω_{el} and varying ω_{ph} , we find $T_c \approx 30 \text{ K}$ for $\lambda = 2.6$ (i.e., $\omega_{ph} = 20 \text{ meV}$). To obtain $T_c = 17 \text{ K}$ requires (i) $\lambda = 1.2$ (i.e., $\omega_{ph} = 30 \text{ meV}$) with ω_{el} as calculated, or (ii) with λ fixed at 2.6, reduce ω_{el} to 18 meV . This latter scenario seems to require much too small a mean lattice frequency, however. Since λ_{tr} is proportional to $(dp/dT) \Omega_p^2$, either improved samples (which would likely have a reduced temperature coefficient) or renormalization effects (which would lower Ω_p^2) could result in somewhat smaller derived values of λ_{tr} . The results we obtain provide a convincing indication of 3D metallic character of $\text{LuNi}_2\text{B}_2\text{C}$, nothing like the high- T_c cuprate superconductors but similar in this sense to conventional superconductors. The multicomponent nature of this compound is central in producing an unusually complex band at E_F , strongly coupled to phonons, that appears to be responsible for its robust superconductivity. It is pertinent to review these new materials in terms of the conditions, compiled by Geballe [5], that might be expected of new high- T_c materials. The conditions are the following: (1) multicomponent structures — *satisfied*; (2),(3) near a Mott insulating phase — *apparently not satisfied*; (4) strongly antibonding states without extended metal-metal bonds — *not well satisfied*; (5) two dimensional or cluster structures — *satisfied*, although the electronic properties are not 2D. The search for higher T_c in this new class of materials should further clarify our understanding of conditions conducive to superconductivity.

We gratefully acknowledge R. J. Cava for sending preprints of Refs. [3] and [4] prior to publication, and a critical reading of the manuscript by D. A. Papaconstantopoulos. This work was supported by Office of Naval Research Contract No. N00014-94-WX-23005.

-
- [1] R. Nagarajan *et al.*, Phys. Rev. Lett. **72**, 274 (1994).
 - [2] R. J. Cava *et al.*, Nature (London) **367**, 146 (1994).
 - [3] R. J. Cava *et al.*, Nature (London) **367**, 252 (1994).
 - [4] T. Siegrist *et al.*, Nature (London) **367**, 254 (1994).
 - [5] T. H. Geballe, Science **259**, 1550 (1993); F. J. DiSalvo, Science **247**, 649 (1992).
 - [6] S. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. **58**, 1200 (1980).
 - [7] O. K. Andersen, Phys. Rev. B **12**, 3060 (1975); S. H. Wei and H. Krakauer, Phys. Rev. Lett. **55**, 1200 (1985).
 - [8] D. Singh, *Planewaves, Pseudopotentials, and the LAPW Method* (Kluwer, Boston, 1994); D. Singh, Phys. Rev. B **43**, 6388 (1991).
 - [9] D. A. Papaconstantopoulos, *Band Structure of Elemental Solids* (Plenum, New York, 1986), p. 302.
 - [10] K. Schwartz and P. Mohn, J. Phys. F **14**, L129 (1984); A. R. Williams, V. Moruzzi, J. Kubler, and K. Schwarz, Bull. Am. Phys. Soc. **29**, 278 (1984).

-
- [11] P. B. Allen, W. E. Pickett, and H. Krakauer, Phys. Rev. B **37**, 7482 (1988).
- [12] G. D. Gaspari and B. L. Gyorffy, Phys. Rev. Lett. **29**, 801 (1972).
- [13] D. A. Papaconstantopoulos *et al.*, Phys. Rev. B **15**, 4221 (1977).
- [14] B. M. Klein and W. E. Pickett, in *Superconductivity in d- and f-Band Metals 1982*, edited by W. Buckel and W. Weber (Kernforschungszentrum Karlsruhe GmbH, Karlsruhe, 1982), p. 477.
- [15] P. B. Allen and R. C. Dynes, Phys. Rev. B **12**, 905 (1975).

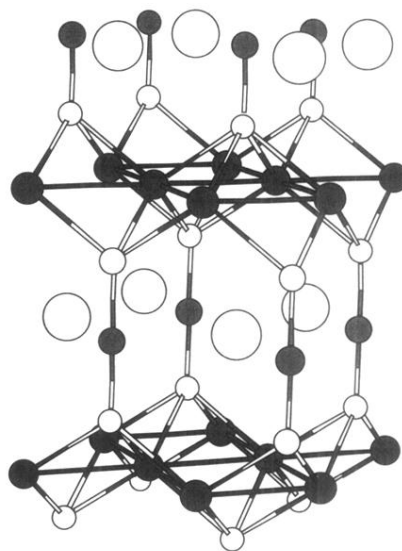


FIG. 1. Crystal structure of $\text{LuNi}_2\text{B}_2\text{C}$ reported in Ref. [4]. Ni atoms (larger dark spheres) form a square lattice, and each Ni is tetrahedrally coordinated to four B atoms (small white spheres). C atoms (small dark spheres) are bonded linearly to two B atoms, and lie in the same plane as the Lu atoms (large white spheres).