Systematic variation of superconductivity for the quaternary borocarbide system $R\mathrm{Ni_2B_2C}$ (R = Sc, Y, La, Th, U, or a lanthanide)

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(Received 1 July 1994; revised manuscript received 12 September 1994)

A superconducting transition temperature T_c of 8.0 K is reported for the nonmagnetic (Th^{4+}) $ThNi_2B_2C$ compound with the $LuNi_2B_2C$-type structure and a derived coherence length $\xi(0)$ of 230 Å and a penetration depth $\lambda(0)$ of 860 Å. No transition down to 2 K was observed for the magnetic, mixed-valence (U^{4+}/U^{6+} or average valence of +5.2) UNi_2B_2C compound with the same structure. Systematic variation of T_c for the quaternary and pseudoquaternary compounds in the $R\mathrm{Ni_2B_2C}$ system (R = Sc, Y, La, Lu, Th, U, or magnetic lanthanides) is studied through the variation of T_c with the R ionic radius, Ni-Ni nearest-neighbor in-plane distance, and the normal-state Pauli-like temperature-independent paramagnetic susceptibility. Maximum T_c at 16.6 K for $LuNi_2B_2C$ with an optimum Ni-Ni distance of 2.45 Å was observed, along with a large normal-state Pauli paramagnetic susceptibility. As a comparison, the 8.0-K $ThNi_2B_2C$ superconductor has a longer Ni-Ni distance of 2.60 Å and a smaller normal-state susceptibility. Variations of the Ni($3d$)-dominated conduction band and the density of states at the Fermi level $N(E_F)$ are believed to be the driving force for the T_c variation of nonmagnetic compounds in the present system.

I. INTRODUCTION

Superconducting intermetallic compounds with relatively high transition temperatures T_c up to 23 K have been reported in the RT_2B_2C compounds (R = Sc, Y, La or a lanthanide, and T = Ni, Pd, or Pt).[1–6] The superconducting phase has been identified as a quaternary $LuNi_2B_2C$-type body-centered-tetragonal structure with space group $I4/mmm$. The structure is a three dimensionally connected framework with LuC layers alternated with Ni_2B_2 layers, where nickel is tetrahedrally coordinated by four boron atoms.[4] In the Ni system, the phase formations were reported in $R\mathrm{Ni_2B_2C}$ compounds (R = Sc, Y, La, Ce, Sm, Tb, Dy, Ho, Er, Tm or Lu) with a maximum T_c of 16.6 K for the nonmagnetic $LuNi_2B_2C$, followed by 15–16 K for the nonmagnetic YNi_2B_2C and $ScNi_2B_2C$.[1,3–5] For magnetic rare-earth compounds, lower superconducting transition temperatures were observed for R = Ho, Er, and Tm, due to the magnetic pair-breaking effect.[3] No superconducting transition down to 5 K was observed for the nonmagnetic $LaNi_2B_2C$.[3] The electronic band properties have been calculated on $LuNi_2B_2C$ which features a density of states at the Fermi level $N(E_F)$ peak near the top of the nearly filled Ni($3d$) bands, with only modest admixture from B and C. All characteristics are indicative of a good, three-dimensional metal.[7,8] A strong-coupled phonon mechanism is deduced with a very large electron-phonon coupling parameter λ, which is related to an unusual combination of states at the Fermi level and a substantial contribution from the vibration of the light atoms.[8]

In addition to the important question concerning the mechanism and symmetry of superconductivity, two fundamental questions remain to be answered: (1) Are there any more isostructural superconductors? (2) What is the systematic of superconductivity for these superconductors?

From the simple R ionic size consideration and previous experiences on ternary boride superconductors,[9,10] we expect the phase formation of actinide compounds $R\mathrm{Ni_2B_2C}$ (Th or U). In addition, we expect the occurrence of superconductivity if these compounds are nonmagnetic (Th^{4+} or U^{6+}).

II. EXPERIMENTS

All quaternary and pseudoquaternary $R\mathrm{Ni_2B_2C}$ (R = Sc, Y, La, Th, U or a lanthanide) samples were prepared by arc melting the high-purity elements (R:99.9%, Ni:99.999%, B:99.9995%, and C:99.999%) under an argon atmosphere in a Zr-gettered arc furnace. Crystallographic data were obtained with a Rigaku Rotaflex rotating anode powder x-ray diffractometer using Cu K_α radiation with a scanning rate of 1° in 2θ per minute. A LAZY PULVERIX-PC program was employed for phase identification and lattice parameter calculations. Electrical resistivity measurements (16 Hz) were carried out by the standard four-probe method in a RMC Cryosystems closed-cycle refrigerator down to 9 K and using single shot cooling to 7 K. Magnetic susceptibility and magnetization measurements were made with a Quantum Design MPMS superconducting quantum interference device magnetometer down to 2 K in an applied field from 20 G to 5 T.

III. RESULTS AND DISCUSSION

The powder x-ray-diffraction patterns of $ThNi_2B_2C$ sample can be well indexed as the $LuNi_2B_2C$-type structure with tetragonal lattice parameters $a = 3.683(3)$ Å, $c = 10.22(1)$ Å, and unit-cell volume $V = 138.6(1)$ Å^3.

The powder x-ray-diffraction data for the UNi_2B_2C sample show multiphase patterns. However, a pattern search indicates that the majority phase is the $LuNi_2B_2C$-type phase with tetragonal lattice parameters $a=3.486(3)$ Å, $c=10.70(1)$ Å, and unit-cell volume $V=130.0(1)$ Å^3. By comparing the lattice parameters and R ionic radii of the present results with reported data for other nonmagnetic RNi_2B_2C (R^{3+}=Sc, Y, La, and Lu) compounds,[4,5] a nonmagnetic Th^{4+} character can be deduced for the $ThNi_2B_2C$ compound and a magnetic, mixed-valence U^{4+}/U^{6+} character with an average valence of +5.2 can be deduced for the UNi_2B_2C compound.

The temperature dependence of electrical resistivity $\rho(T)$ for $ThNi_2B_2C$ is shown collectively in Fig. 1. Both samples exhibit good metallic behavior. Zero resistivity T_c (zero) was observed at 8.0 K for $ThNi_2B_2C$, with a superconducting midpoint transition T_c (mid) at 8.4 K and onset (1% resistivity drop) T_c (onset) at 8.9 K.[11] The room-temperature resistivity is 139.6 $\mu\Omega$ cm, with a resistivity ratio $\rho(RT)/\rho(10\text{K})$ of 4.6. No superconducting transition down to 7 K was observed for the mixed-valence UNi_2B_2C compound as expected from the magnetic pair-breaking effect. The room-temperature resistivity is 111.3 $\mu\Omega$ cm and the resistivity ratio $\rho(RT)/\rho(10\text{ K})=7.5$.

The low-temperature mass magnetic susceptibilities $\chi_g(T)$ of the zero-field-cooled (ZFC) $ThNi_2B_2C$ and Th-based pseudoquaternary $(La_{0.5}Th_{0.5})Ni_2B_2C$ compounds are shown in Fig. 2 in a low applied field of 50 G. A diamagnetic superconducting signal was observed at 8.0 K for $ThNi_2B_2C$, which is consistent with the resistivity measurement.[11] A large ZFC shielding signal of -8.92×10^{-3} emu/(g G) at 2 K for the bulk polycrystalline sample indicates the bulk superconductivity effect (using the calculated x-ray density of 5.53 g/cm^3). Since the ionic radius of 1.02 Å for the nonmagnetic Th^{4+} ion is among 1.061 Å for the La^{3+} ion of the nonsuperconducting $LaNi_2B_2C$ compound and 0.893 Å for the Y^{3+} ion of the 15.6-K superconductor YNi_2B_2C,[9] the $ThNi_2B_2C$ compound is indeed expected to be superconducting around 8 K. Above T_c, normal-state susceptibility is Pauli-like temperature independent with a paramagnetic molar susceptibility value of 1.9×10^{-4} emu/(mol G). For the pseudoquaternary bulk sample $(La_{0.5}Th_{0.5})Ni_2B_2C$ [$a=3.746(3)$ Å, $c=9.929(1)$ Å] with a larger average ionic radius of 1.041 Å for ($La^{3+}Th^{4+}$), T_c decreases to 3.9 K with a ZFC shielding signal of -9.90×10^{-5} emu/(g G) at 2 K. No superconducting transition down to 2 K was observed for the light rare-earth compounds $LaNi_2B_2C$, $CeNi_2B_2C$, and compounds $PrNi_2B_2C$ and $NdNi_2B_2C$.[12]

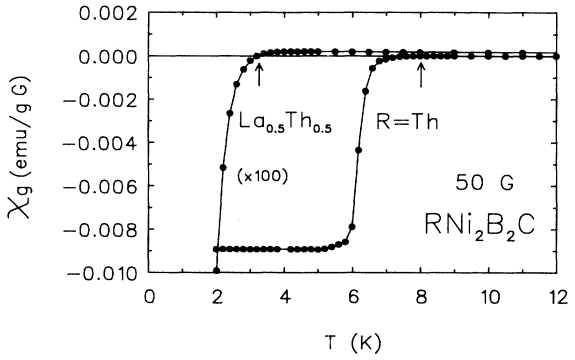

FIG. 2. Low-temperature mass magnetic susceptibility (zero-field-cooled) for superconducting $ThNi_2B_2C$ compound and Th-based $(La_{0.5}Th_{0.5})Ni_2B_2C$ compound.

The initial magnetization curves $M(H)$ at 2, 5 and 7 K for $ThNi_2B_2C$ are shown in Fig. 3. Lower critical field $H_{c1}(T)$ is determined from the deviation of linearity in the low-field region with H_{c1}(7 K) of 50 G, H_{c1} (5 K) of 210 G, and H_{21}(2 K) of 750 G. The extrapolated $H_{c1}(0)$ is 900 G. Upper critical field $H_{c2}(T)$ is determined from the deviations of linearity from the high-field paramagnetic region with H_{c2}(7 K) of 1.5 kG, H_{c2}(5 K) of 4 kG, and H_{c2}(2 K) of 8 kG. The extrapolated $H_{c2}(0)$ is 1 T. The derived coherence length $\xi(0)$ of 230 Å and the penetration depth $\lambda(0)$ of 860 Å indicate that this lower T_c compound is a type-II superconductor with the Ginzburg-Landau parameter κ value of 3.7.

The temperature dependence of mass magnetic susceptibility $\chi_g(T)$ for UNi_2B_2C shows no diamagnetic superconducting signals down to 2 K. Instead, an antiferromagnetic/weak ferromagnetic transition was ob-

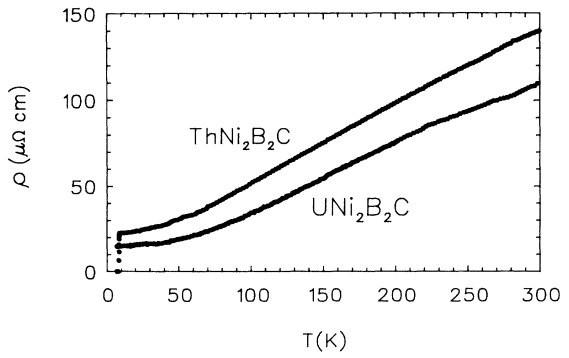

FIG. 1. Temperature dependence of the electrical resistivity for $ThNi_2B_2C$ and UNi_2B_2C compounds.

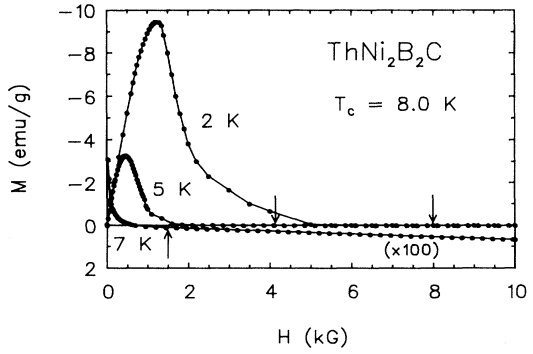

FIG. 3. Initial magnetization curves $M(H)$ at 2, 5, and 7 K for $ThNi_2B_2C$. Deviations of linearity from the high-field paramagnetic region is indicated by arrows.

served around 17 K. The magnetic data is consistent with the magnetic, mixed-valence U^{6+}/U^{6+} picture (with an average valence of +5.2). However, the 17-K transition may not arise from the tetragonal (1221) phase due to the multiphase nature of the sample. Careful sample improvement and magnetic studies are in progress.

To investigate the systematic of superconductivity in the borocarbide system, superconductivity of Lu-based compounds is also studied. The low-temperature mass magnetic susceptibility $\chi_g(T)$ of the nonmagnetic $LuNi_2B_2C$ and Lu-based pseudoquaternary $(R_{0.5}Lu_{0.5})Ni_2B_2C$ (R =Sc or La) compounds are shown in Fig. 4 for comparison. The superconducting transition at 16.6 K was obtained for the parent compound. Above T_c, normal-state susceptibility is also Pauli-like with a paramagnetic molar susceptibility value of 3.9×10^{-4} emu/(mol G). For the pseudoquaternary compound $(Sc_{0.5}Lu_{0.5})Ni_2B_2C$ [a=3.441(3) Å, c=10.66(1) Å], T_c of 15.6 K was observed with a ZFC shielding signal of $\sim8.41\times10^{-3}$ emu/(g G) at 5 K for the bulk sample. For the $(La_{0.5}Lu_{0.5})N_2B_2C$ compound [a=3.577(3) Å, c=10.44(1) Å], a T_c of 14.8 K was observed with a ZFC shielding signal of -1.01×10^{-2} emu/(g G) at 5 K.

The variation of superconducting transition temperature T_c with the ionic radius of both nonmagnetic and magnetic R^{3+} ions for the quarternary and pseudoquaternary compounds in the RNi_2B_2C system (R =Sc, Y, La, Gd, Dy, Ho, Er, Tm or Lu) is shown in Fig. 5. For the Th-based compounds, Th^{4+} ionic radius was used. For UNi_2B_2C, both U^{4+} and U^{6+} ionic radii are used for comparison. In the nonmagnetic compounds, T_c increases from 15.6 K from the smaller Sc^{3+} ion to a maximum T_c of 16.6 K for Lu^{3+}, and then decreases monotonically to 15.6 K for Y^{3+}, 8.0 K for the larger Th^{4+}, and not superconducting for the largest La^{3+} ion. For magnetic compounds (R =Tm, Er, Ho, Dy, Gd), T_c decreases sharply due to strong magnetic pair-breaking effect. Long-range antiferromagnetic/ferromagnetic transitions are expected for these magnetic superconductors. For $GdNi_2B_2C$, an antiferromagnetic transition at 19 K was observed.[12] The absence of superconductivity in UNi_2B_2C may be originated from the same reason,

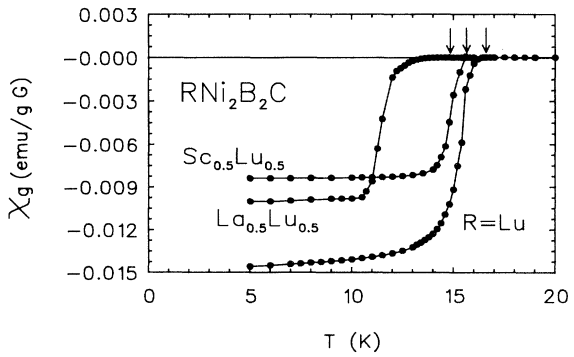

FIG. 4. Low-temperature mass magnetic susceptibility (zero-field-cooled) for superconducting $LuNi_2B_2C$ compound and Lu-based $(Sc_{0.5}Lu_{0.5})Ni_2B_2C$ and $(La_{0.5}Lu_{0.5})Ni_2B_2C$ compounds.

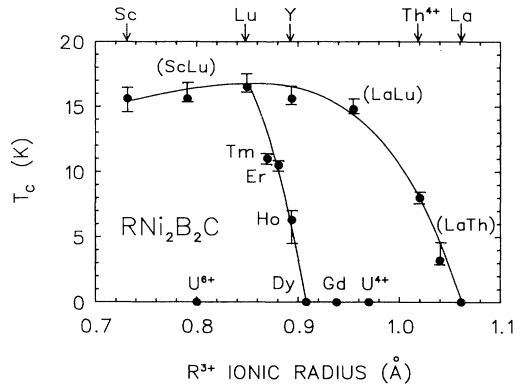

FIG. 5. Variation of superconducting transition temperature T_c with the ionic radius of R^{3+} ions for the RNi_2B_2C system (R =Sc, Y, La, Gd, Dy, Ho, Er, Tm or Lu). For Th-based compounds, Th^{4+} ionic radius was used. Both U^{4+} and U^{6+} are used for UNi_2B_2C. The solid lines are guides to the eyes only.

where the magnetic, mixed-valence U^{4+}/U^{6+} provides strong magnetic pair-breaking effect.

There is no obvious correlation between T_c and R ionic mass. This can be understood since the conduction band mainly arises from the Ni($3d$) electrons. The R atoms then influence T_c indirectly by their effect on the phonon structure, and by charge transfer to the conduction bands. The insertion of different R ions will change the in-plane and c-axis Ni-Ni distances and thus changes the electronic structure and bandwidths of the Ni($3d$)-dominated conduction bands.

Bear this in mind, we plot the variation of superconducting transition temperature T_c versus the nearest-neighbor in-plane Ni-Ni distance $d=\sqrt{2}a/2$ (a is the tetragonal lattice parameter) for the nonmagnetic RNi_2B_2C compounds (R =Sc, Y, La, Lu, Th) as shown in Fig. 6. The maximum T_c around 16.6 K for $LuNi_2B_2C$ with an optimum Ni-Ni distance of 2.449 Å was observed, along with a normal-state Pauli-like temperature-independent paramagnetic molar susceptibility value of 3.9×10^{-4} emu/(mol G). As a comparison, 15.6-K metastable $ScNi_2B_2C$ superconductor has a shorter Ni-Ni dis-

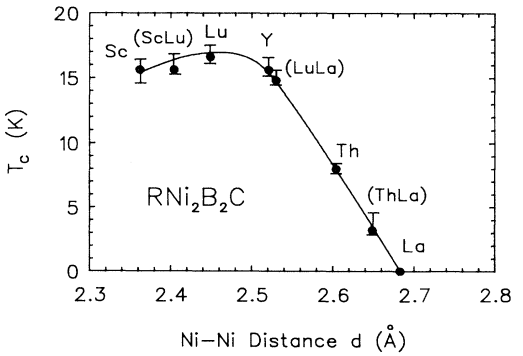

FIG. 6. Variation of superconducting transition temperature T_c with the nearest-neighbor Ni-Ni in-plane distance d for nonmagnetic RNi_2B_2C compounds (R =Sc, Y, La, Lu or Th). The nearest-neighbor Ni-Ni distance d is $\sqrt{2}a/2$. The solid line is a guide to the eyes only.

tance of 2.362 Å and a normal-state paramagnetic molar susceptibility value of 2.4×10^{-4} emu/(mol G).[5] The $ThNi_2B_2C$ superconductor with a T_c of 8 K has a longer Ni-Ni distance of 2.604 Å and a smaller normal-state paramagnetic molar susceptibility value of 1.9×10^{-4} emu/(mol G). A very long Ni-Ni distance of 2.683 Å was observed for nonsuperconducting $LaNi_2B_2C$. The variation of the Ni-Ni distance results in a variation of the electronic band structure and the Pauli paramagnetic susceptibility is a measure of the density of states at the Fermi level $N(E_F)$. This trend indicates the importance of the variation of the Ni($3d$)-dominated conduction-band structure and $N(E_F)$ for the systematic T_c variation of these nonmagnetic compounds. The derived $N(E_F)$ for the $LuNi_2B_2C$ sample from normal-state magnetic susceptibility is 5.9 states/eV cell, a value very close to the calculated 4.8 states/eV cell from band-structure calculations.[7,8]

Since this relatively high-T_c system is a three-dimensional good metal, the correlation with superconductivity is evident if the phonon-mediated McMillan T_c formula for strong coupling is valid, then the electron-phonon coupling parameter λ of the exponential factor of the T_c equation will be related to the density of states at the Fermi level $N(E_F)$ as λ can be written as $\lambda=N(E_F)\langle I^2\rangle/M\langle\Omega^2\rangle$, where $\langle I^2\rangle$ is the average of the square of the electron-phonon matrix elements, M is the mass, and $\langle\Omega^2\rangle$ is the average of the square of the phonon frequencies.[13] A very large coupling parameter λ of 2.6 was reported for $LuNi_2B_2C$ from band-structure calculations and resistivity data, which is related to an unusual combination of states at the Fermi level and a substantial contribution from the vibration of the light atoms.[8]

IV. CONCLUSION

Systematic variations of T_c for the quaternary and pseudoquaternary compounds in the RNi_2B_2C system (R =Sc, Y, La, Gd, Dy, Ho, Er, Tm, Lu, Th or U) are studied through the variation of R ionic radius, the Ni-Ni nearest-neighbor in-plane distance and the normal-state Pauli paramagnetic susceptibility. Variation of density of states at the Fermi level $N(E_F)$ seems to be the dominating factor for the T_c variation of nonmagnetic compounds in the present system.

ACKNOWLEDGMENTS

We thank Professor T. J. Yang, Professor T. W. Chen, Professor J. C. Ho, and Professor W. Y. Guan for helpful discussions. This work was supported by the National Science Council of Republic of China under Contract No. NSC83-0212-M007-069.

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[11]After completion of this work, we became aware of another report of superconductivity at 6 K for $ThNi_2B_2C$, which is a full 2 K lower than our result.

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