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Electron density of states in the borocarbide intermetallic superconductors

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We present heat-capacity measurements in a magnetic field up to 7.7 T on the recently discovered borocarbide intermetallic superconductors $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$. For $LuNi_2B_2C$ with $T_c = 16.5$ K, we find a large density of states at the Fermi level, $\gamma \sim 19(2)$ mJ/mole K^2, and an effective Debye temperature Θ_D of 345 K. In comparison, $LaPt_{1.7}Au_{0.3}B_2C$, with $T_c = 10.2$ K, has a γ of 7.5(1.5) mJ/mole K^2 and a smaller Debye temperature Θ_D of 220 K. Through comparison with the specific-heat anomaly at T_c, $\Delta C/\gamma T_c$, the magnetic susceptibility, and the calculated band structure, these compounds are found to be in the weak-to-intermediate coupling limit with $\lambda \approx 0.5-1.0$. Their position on the γ-T_c plot indicates dominant phonon-mediated electron pairing.

Superconductivity has been discovered recently in a family of borocarbide intermetallics, Y-Pd-B-C ($T_c = 23.2$ K),[1] Y-Ni-B-C ($T_c = 12.0$ K),[2] RNi_2B_2C (R = Lu, Y, Tm, Er, and Ho),[3] and $RPt_{1.7}Au_{0.3}B_2C$ (R = Lu, Y, Pr).[4,5] These compounds crystallize in a layered crystal structure,[6] and contain the light elements B and C which are expected to result in high phonon frequencies and late transition metals such as Ni, which generally give rise to magnetism in intermetallic phases. These similarities with cuprate superconductors suggest that perhaps a nonphonon pairing mechanism may be involved in their relatively high T_c's. Measurements of the density of states at the Fermi surface and comparison with T_c can provide a good indication whether or not such unconventional superconductivity is present; however, such measurements on the borocarbide superconductors have been in disagreement. Heat-capacity measurements on multiphase Y-Ni-B-C reveal small values for the density of states,[2] while transport and magnetic characterizations of single-phase $LuNi_2B_2C$ materials suggest a relatively high density of states exists at the Fermi level.[7]

In this study, we resolve this issue by addressing the nature of the normal and superconducting state of single-phase $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$ through heat-capacity measurements in a magnetic field. We find in both systems a moderately high Sommerfeld constant γ which together with the measured specific-heat anomaly at T_c, magnetic-susceptibility measurements, and band-structure calculations are entirely consistent with electron-phonon-mediated superconductivity in the weak-to-intermediate coupling range.

Polycrystalline samples of single phase $LuNi_2B_2C$ (Refs. 1 and 3) and $LaPt_{1.7}Au_{0.3}B_2C$ (Ref. 5) were prepared by arc melting and annealing as described elsewhere. The heat capacity was measured using a standard dc pulse-relaxation technique on samples of typically 200 mg. The data in magnetic field were taken between 0 and 7.7 T where the magnetoresistance of the Cermac thermometer[8] and the sample heater were both less than 0.5%. A carbon-chip resistor monitored the sample temperature and was calibrated against the Cermac thermometer during every run. Errors in the absolute values of the heat capacity are less than 1% at zero field and 2% in a magnetic field, and the typical scatter of the data is

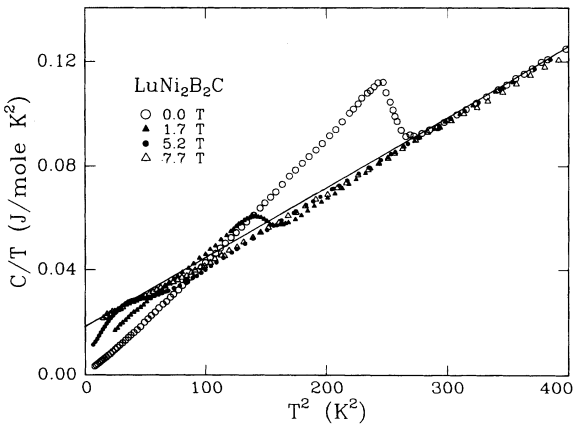

FIG. 1. C/T vs T^2 heat-capacity data for $LuNi_2B_2C$ at 0, 1.7, 5.2, and 7.7 T. Fits to the from $\gamma T + \beta T^3$ yield $\gamma \sim 19(2)$ mJ/mole K^2 and $\beta \sim 2.67 \times 10^{-4}(0.1 \times 10^{-4})$ J/mole K^4.

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less than a few tenths of a percent.

In Fig. 1, we graph C/T versus T^2 for $LuNi_2B_2C$ at 0, 1.7, 5.2, and 7.7 T. By 7.7 T, the superconducting transition temperature is below our measurement range. The solid line shows the fit to the form $\gamma T+\beta T^3$, where $\gamma \sim 19(2)$ mJ/mole K^2 and $\beta \sim 2.67(0.1)10^{-4}$. A slight suppression of γ occurs with increasing magnetic field, but the moderate Debye temperature Θ_D of 345 K is field independent. The present determination of γ is significantly higher than values of 1 to 7 mJ/mole K^2 reported on mixed phase Y-Ni-B-C compounds,[2] but lower than the value estimated from previous preliminary magnetic measurements on $LuNi_2B_2C$ which assumed a superconducting state in the weak-coupling limit.[7] Nonetheless, our measurements imply that a large density of states, comparable to the A-15 superconductors, is a probable explanation for the high T_c.

The electronic part C_{el} of the specific heat is shown in Fig. 2. To obtain C_{el}, we have assumed for the lattice specific heat a simple functional from $C_l=\beta T^3$, which is a good approximation below 25 K, but would not capture possible deviations from the Debye phonon density of states proportional to ω^2. The superconducting onset of the specific-heat anomaly at T_c agrees very well with the onset of diamagnetism (16.5–16.6 K) and the sharpness of the transition testifies to the homogeneity of the single phase sample. Extrapolation of the heat capacity to the $T\rightarrow 0$ limit yields a maximum γ_0 of 0.5 mJ/mole K^2, indicating that over 97% of the sample is superconducting. The entropy of the superconducting state is 13% smaller than in the normal state but is consistent with entropy being conserved within the error bars of the simple parametrization. Assuming a discontinuous entropy-conserved superconducting transition, we find a value for the heat-capacity anomaly at T_c, $\Delta C/T_c$, of 34(1) mJ/mole K^2. Using the Sommerfeld value $\gamma \sim 19$ mJ/mole K^2, the normalized anomaly $\Delta C/\gamma T_c=1.8(0.2)$.

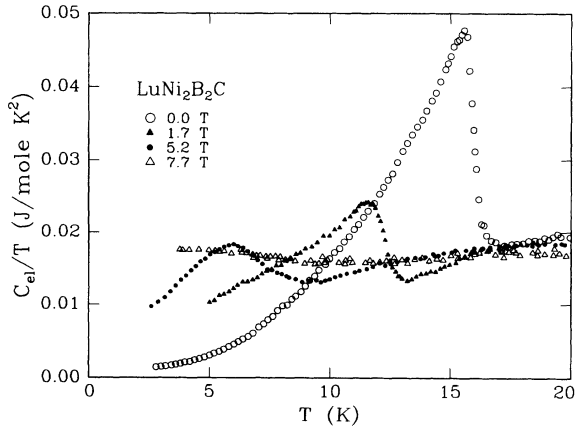

FIG. 2. C/T vs T for $LuNi_2B_2C$ at 0, 1.7, and 5.2 T with the lattice contribution, C_l ($2.67\times10^{-4}T^3$), subtracted. At $H=0$, $\Delta C/\gamma T_c=1.80(0.20)$, consistent with this material being near the weak-to-intermediate coupling limit. The transition temperature T_c and the $\Delta C/T_c$ rapidly decrease and the transition broadens with increasing magnetic field.

TABLE I. The superconducting transition temperature T_c (midpoint), the change in heat capacity at the superconducting transition $\Delta C/T_c$, and γ for $LuNi_2B_2C$ as a function of magnetic field.

H (T)	T_c(10/90% wd)	$\Delta C/T_c$ (mJ/mole K^2)	γ(mJ/mole K^2)
0.0	16.0 (0.5)	34 (1)	20.0 (2.0)
1.7	12.3 (0.8)	13 (2)	18.0 (1.0)
5.2	7.3 (2.0)	10 (4)	18.0 (0.5)
7.7	< 4.0		17.0 (0.5)

The results for the changes in T_c, $\Delta C/T_c$, and γ for $LuNi_2B_2C$ as a function of magnetic field are summarized in Table I. The observed field dependence of T_c is consistent with magnetic H_{c2} measurements on these materials.[6] The broadening of the transition and the reduction in $\Delta C/T_c$ with magnetic field is expected because our measurements are on polycrystalline materials and H_{c2} is known to be anisotropic in these layered compounds.[9] Finally, we observe a decrease in heat capacity away from linear behavior several degrees before the superconducting transition. This precursor behavior is not observed in magnetic-susceptibility measurements or in $LaPt_{1.7}Au_{0.3}B_2C$ and is presently under further investigation.

To test for universal behavior in this class of superconductors, we show in Fig. 3 C/T versus T^2 at 0 and 3 T for $LaPt_{1.7}Au_{0.3}B_2C$. The transition temperature of 10.2 K is much lower in this material, and the superconducting transition is suppressed below our measurement range in a magnetic field of 3 T. As in Fig. 1, the solid line shows the fit to the from $\gamma T+\beta T^3$, where $\gamma \sim 7.5(1)$ mJ/mole K^2 and $\beta \sim 1.10(0.1)10^{-3}$. The smaller value of γ is consistent with the lower T_c. The Debye temperature Θ_D of 220 K is smaller than in $LuNi_2B_2C$, reflecting a higher phonon density of states at low energies which are likely due to the presence of the ~3 times heavier (Pt,Au) compared to Ni.

Following the previous analysis, we present in Fig. 4 C_{el}/T versus T. As before, the transition temperature is

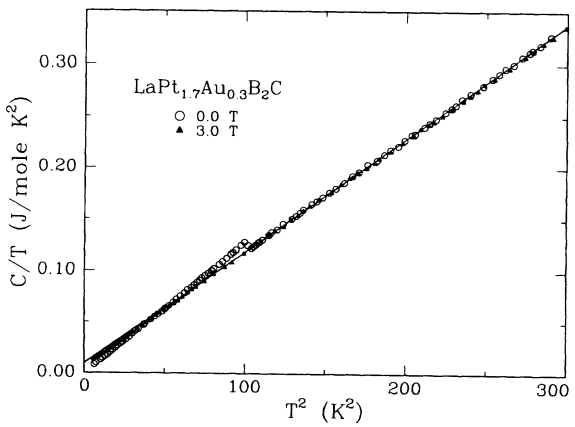

FIG. 3. C/T vs T^2 for $LaPt_{1.7}Au_{0.3}B_2C$ at 0 and 3.0 T. Fits to the form $\gamma T+\beta T^3$ yield $\gamma \sim 7.5(1)$ mJ/mole K^2 and $\beta \sim 1.10\times10^{-3}(0.1\times10^{-3})$ J/mole K^4.

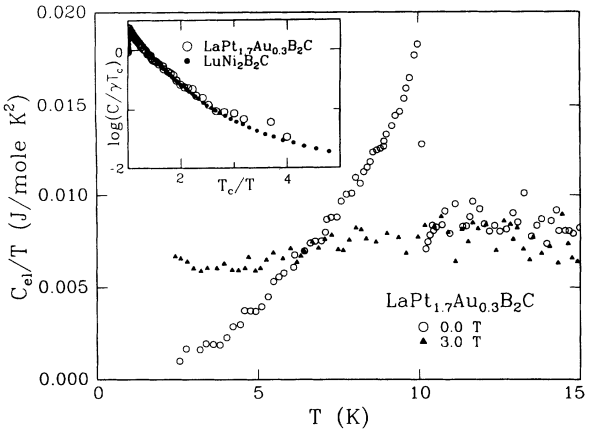

FIG. 4. C/T vs T for $LaPt_{1.7}Au_{0.3}B_2C$ at 0 and 3.0 T with the lattice contribution, C_l $(1.10\times10^{-3}T^3)$, subtracted. At $H=0$, $\Delta C/\gamma T_c=1.70(0.20)$, consistent with this material being near the weak-to-intermediate coupling limit. The inset shows $\log_{10}C/\gamma T_c$ versus T_c/T for both $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$.

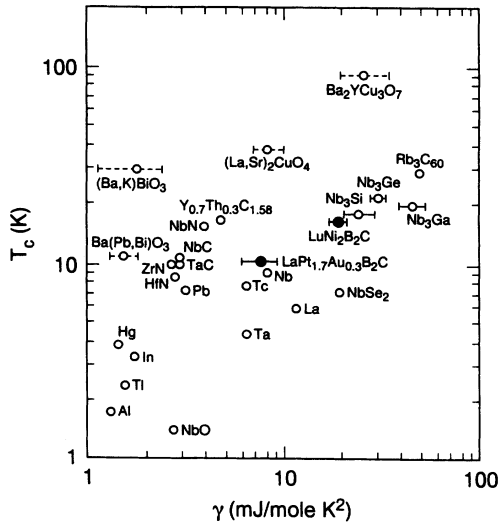

FIG. 5. A log-log plot of T_c vs γ for several superconductors showing that $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$ fall in the region associated with electron-phonon-mediated superconductivity (Ref. 14).

sharp reflecting sample homogeneity, and the electronic entropy in the normal and superconducting states are the same within the ~12% uncertainty. The requirement for strict entropy balance could be used to further refine the values of γ and β, but the modifications will be small and will not affect the conclusions. We estimate that over 90% of the sample is superconducting from the $T\rightarrow0$ extrapolation. The change in the specific heat at T_c, $\Delta C/T_c=13(2)$ mJ/mole K^2. Using the Sommerfeld value $\gamma\sim7.5$ mJ/mole K^2, $\Delta C/\gamma T_c=1.7(0.2)$ which places these intermetallic superconductors near the weak-to-intermediate coupling limit. In the inset of Fig. 4, $\log C/\gamma T_c$ versus T_c/T for both the $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$ samples is shown. Exponential behavior does not appear to be observed over an appreciable range for either sample.

The temperature independent dc magnetic susceptibility χ is $1.3(0.1)10^{-4}$ emu/mole f.u. and $-0.15(0.01)10^{-4}$ emu/mole f.u. for $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$, respectively. From this, we can estimate the several contributions to the measured value, including the diamagnetism of the core electrons, χ_{core}, the Van Vleck-type paramagnetism, χ_{vv}, and the conduction-electron contribution, χ_{ce}. To compare χ_{ce} with the electronic density of states, we estimate χ_{core} based on standard tables to be $-1.3(0.1)10^{-4}$ emu/mole f.u. for $LuNi_2B_2C$ and $-1.05(0.15)10^{-4}$ emu/mole f.u. for $LaPt_{1.7}Au_{0.3}B_2C$. (The uncertainties stem from ascribing an "effective valence" to the various constituents.) If we then neglect χ_{vv}, due to virtual excitations between occupied and empty band states, an upper limit for the conduction-electron contribution χ_{ce} is then $2.6(0.2)10^{-4}$ emu/mole f.u. and $0.90(0.15)10^{-4}$ emu/mole f.u. for the Ni and (Pt,Au) compounds, respectively. Comparing these values with free-electron values calculated from the measured Sommerfeld parameters γ [$2.6(0.3)10^{-4}$ emu/mole f.u. and $1.0(0.2)10^{-4}$ emu/mole f.u., respectively], one is led to conclude that the static susceptibility is not significantly enhanced.

The strength of the electron-phonon coupling λ can be estimated using the values of γ and $\Delta C/\gamma T_c$ obtained above and from band-structure calculations of γ,γ_{bstr}. For the $LuNi_2B_2C$ system, $\gamma\sim19$ mJ/mole K^2, $\Delta C/\gamma T_c\sim1.8$, and γ_{bstr} of 11.1 and 11.3 mJ/mole K^2 (Refs. 10 and 11) which yields λ values within the ranges of 0.7–1.0, 0.8–1.0, and 0.5–0.9 using empirical relations for $\Delta C/\gamma T_c$, $\Delta C/\gamma_{bstr}T_c$ and the relation $\gamma=(1+\lambda)\gamma_{bstr}$, respectively.[12] Similar analysis for $LaPt_{1.7}Au_{0.3}B_2C$ using $\gamma\sim7.5$ mJ/mole K^2, $\Delta C/\gamma T_c\sim1.7$, and γ_{bstr} of 5.9 mJ/mole K^2 (Ref. 13) gives λ ranges of 0.5–0.9, 0.5–0.7, and 0.2–0.5. With λ on the order of 0.8 for $LuNi_2B_2C$ and 0.5 for $LaPt_{1.7}Au_{0.3}B_2C$, these results, summarized in Table II, indicate that the borocorbide superconductors are weak-to-intermediate coupled electron-phonon-mediated superconductors with the high-T_c's resulting from a relatively large density of states at the Fermi level.

In Fig. 5, the $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$ superconductors are compared to other materials on the log-log plot of the superconducting transition temperature,

TABLE II. The superconducting transition temperature T_c (onset), the Sommerfeld constant γ, the Debye temperature Θ_D, the specific-heat anomaly at T_c, $\Delta C/T_c$, the band-structure calculation of γ,γ_{bstr}, and the average value for λ for both $LuNi_2Bi_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$.

	$LuNi_2B_2C$	$LaPt_{1.7}Au_{0.3}B_2C$
T_c (K)	16.5 (0.1)	10.2 (0.1)
γ (mJ/mole K^2)	19 (2)	7.5 (1.5)
Θ_D (K)	345 (10)	220 (10)
$\Delta C/T_c$ (mJ/mole K^2)	34 (1)	13 (2)
γ_{bstr} (mJ/mole K^2)	11.2 (0.1)	5.9 (0.1)
λ	0.8 (0.2)	0.5 (0.3)

T_c, versus the electronic specific heat γ. The T_c's and γ's of both borocarbides fall in the region associated with electron-phonon-mediated superconductivity. In particular, the moderately high T_c's are due to a density of states that approaches that of the A-15 class of compounds. By implication, we expect that the Pd-borocarbide with the 23 K T_c to have an even higher density of states at E_F. While the electronic states near the Fermi level are mainly derived from the transition-metal d states (the d states are almost completely filled), there are non-negligible contributions present also from the other constituents[10,11] thus allowing for contributions of high-frequency B and C phonons to the coupling function $\alpha^2F(\omega)$. Since the band-structure estimates of γ_{bstr} and the experimental determination of γ yield similar values for λ, our data does not allow for large additional enhancements to the density of states either from electron-electron or magnetic correlations. Moreover, it does not appear the substitution of Pt and Au for Ni significantly affects the superconducting state.

We have presented here a set of field-dependent heat-capacity measurements for the borocarbide superconductors $LuNi_2B_2C$ and $LaPt_{1.7}Au_{0.3}B_2C$. We find a large density of states at the Fermi level which is a plausible explanation for the observed high T_c. In addition, analysis of the magnetic-susceptibility measurements, band-structure calculations, and the specific-heat anomaly at T_c consistently place these materials into the class of weak-to-intermediate coupled superconductors, with electron pairing dominantly mediated by electron-phonon interaction.

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