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Superconductivity in $R\mathrm{Pt_2B_2C}$

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Superconductivity for lanthanide platinum boron carbide quaternary intermetallic phases is reported. For $R\mathrm{Pt_2B_2C}$, superconducting T_c's are approximately 10 K for R=La and Y and 6 K for R=Pr, reflecting the influence of magnetic pair breaking. The crystal structure for one of the analogs, $\mathrm{LaPt_2B_2C}$, was determined by single-crystal x-ray diffraction. These materials are isostructural with the recently discovered $R\mathrm{Ni_2B_2C}$ superconductors, but apparently can accommodate some nonstoichiometry. The density of states at the Fermi level for $\mathrm{LaPt_2B_2C}$ is estimated to be approximately 5 mJ/mole $\mathrm{K^2}$ through measurements of the critical fields and the normal-state susceptibility.

INTRODUCTION

The chemistry and physics of copper oxides has dominated superconductivity research for the past several years due to their very high superconducting transition temperatures. Conversely, research on intermetallic superconductors has been relatively dormant, as no new high-T_c intermetallic phases have been discovered in some time.[1] Recently we reported superconductivity at 23 K in an intermetallic system based on yttrium, palladium, boron and carbon,[2] which is, to our knowledge, the highest T_c ever reported for a bulk intermetallic material. Superconductivity has also recently been reported for Y-Ni-B-C (Ref. 3) and $R\mathrm{Ni_2B_2C}$ [R=Lu (T_c = 16.6 K), Y, Tm, Er, and Ho],[4] and the crystal structure of the latter materials determined.[5] The layered crystal structure can be considered a derivative of the $\mathrm{ThCr_2Si_2}$ type: tetrahedrally coordinated $\mathrm{NiB_2}$ layers are separated by RC rocksalt layers.[5] The presence of the transition metals Ni and Pd, generally magnetic in intermetallic compounds, makes the occurrence of superconductivity in these materials particularly interesting. Here we report our discovery of superconductivity in a related material based on the 5d transition metal Pt. Superconductivity above 4.2 K is observed for $R\mathrm{Pt_2B_2C}$ for R=La and Y ($T_c \cong 10$ K), and Pr ($T_c \cong 6$ K). Unlike the case for the $R\mathrm{Ni_2B_2C}$ compounds, which appear to be perfectly stoichiometric materials, our initial characterization suggests that a range of stochiometries is allowed for the $R\mathrm{Pt_2B_2C}$ analogs.

SYNTHESIS AND CRYSTAL STRUCTURE

Samples were made by arc melting. Starting materials were lanthanide metal shavings or sublimed dendrites (99.9 or 99.99%), Pt sheet (99.99%) and coarse C (99.99%) and B (99.6%) powder. Samples of 0.75 gram total weight were first pressed into 0.25 inch diameter pellets. They were then arc melted under Ar on a standard water cooled copper hearth three times, with the button turned over between each melt. Weight loss was 1% or less. Small single crystals of $\mathrm{LaPt_2B_2C}$ were picked out of an as-melted pellet of that composition and employed for the x-ray crystal structure determination. In order to investigate the apparent stoichiometry range displayed by $\mathrm{LaPt_2B_2C}$, arc melted pellets made at a variety of compositions, especially in the range LaPtBC–$\mathrm{LaPt_4B_4C}$, were wrapped in Ta foil, sealed in evacuated quartz tubes and annealed at temperatures between 1100 and 1275 °C for three days. The phase was found to form for the rare earths La, Ce, Pr, Nd, and Y, but not for R; other rare earths were not investigated. Single phase materials were not obtained at the stoichiometry $R\mathrm{Pt_2B_2C}$, either in the as-melted state or on annealing, for any of the rare earths studied, though that phase was present in large proportion. Powder x-ray diffraction analysis and measurement of the superconducting properties clearly showed that superconductivity was associated with that phase, and material of composition $\mathrm{LaPt_{2.2}B_2C}$ (annealed at 1275 °C, for 3 days, quenched in water) was 90% pure and was a bulk superconductor. Annealing as-melted superconducting samples of $\mathrm{YPt_2B_2C}$ resulted in the disappearance of superconductivity, suggesting, along with the nonformation of the phase for Lu, that the stability of the phase decreases for the smaller rare earths. The fact that the $R\mathrm{Pt_2B_2C}$ phases display a range of stoichiometry is evidenced both by the observation that their lattice parameters are variable depending on sample preparation, and also that a considerable range of T_c's was observed. We do not know what the origin of the stoichiometry variation is at the present time. Annealing at temperatures up to 1275 °C was not effective in changing the phase assemblage of as-melted $R\mathrm{Pt_2B_2C}$ pellets, suggesting that the phase is refractory, and that annealing techniques which can access higher temperatures than are available in sealed

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TABLE I. Crystallographic data for $\mathrm{LaPt_2B_2C}$. Space group $I4/mmm$, $a = 3.8681(6)$Å, $c = 10.705(2)$Å, $Z = 2$, $R = 0.042$, $R_w = 0.035$ (495 independent reflections, 440 observed $[I > 2.5\sigma(I)]$, 9 parameters).

	x	y	z	B_{iso} (Å^2)
La	0	0	0	0.511(15)
Pt	$\frac{1}{2}$	0	$\frac{1}{4}$	0.434(8)
B	0	0	0.3617(20)	0.95(20)
C	$\frac{1}{2}$	$\frac{1}{2}$	0	0.84(22)

quartz tubes would be necessary for equilibrium phase studies. Why a non-site-conserving composition such as $\mathrm{LaPt_{2.2}B_2C}$ should be so close to single phase is not clear, but we note that a similar problem has been long standing for much studied $\mathrm{CeCu_{2.2}Si_2}$,[6] which has a related crystal structure. One possibility is that such a composition results in the formation of a small amount of melt phase during annealing, not visible on visual inspection of the cooled pellet, which enhances reaction rate at low temperatures.

Single crystal x-ray diffraction was performed on a small (0.12×0.08×0.02 mm) single crystal of $\mathrm{LaPt_2B_2C}$ on an Enraf-Nonius diffractometer using graphite monochromated Mo $K\alpha$ radiation. Lattice parameters were obtained by determining the absolute 2θ values at high angles of 35 reflections. A Gaussian integration absorption correction was applied to the intensity data, and the structure was refined using the NRCVAX programs.[7] The results are summarized in Table I, which presents all structural parameters. The light atom positions are determined with good precision, but highly precise characterization of B and C will require the use of neutron diffraction methods. Analysis of models for various types of nonstoichiometry revealed that the crystal was stoichiometric $\mathrm{LaPt_2B_2C}$.

PHYSICAL PROPERTIES

Superconducting properties of polycrystalline materials were measured on a commercial superconducting quantum interference device (SQUID) magnetometer in fields of 5–20 Oe. Figure 1 shows the magnetically measured superconducting transition for a polycrystalline multiple phase sample of stoichiometry $\mathrm{LaPt_2B_2C}$ in its as-melted state. The sample cooled in the earth's field and warmed in 10 Oe showed a magnetic shielding signal approximately equal (when corrected for demagnetization effects) to 100% of that expected for perfect diamagnetism. On cooling in the field (Meissner effect), the flux expulsion value corresponds to approximately 10% of that expected for perfect diamagnetism, showing that the superconductivity is a bulk effect. The magnitude of the flux expulsion is equivalent to what is observed for single phase $R\mathrm{Ni_2B_2C}$.[4] The existence of hysteresis between zero field cooling and field cooling indicates that these materials are type-II superconductors.

The superconducting transitions for a variety of samples cooled in a field of 10 Oe are shown in Fig. 2. $\mathrm{LaPt_2B_2C}$ and $\mathrm{YPt_2B_2C}$ in their as-melted state are

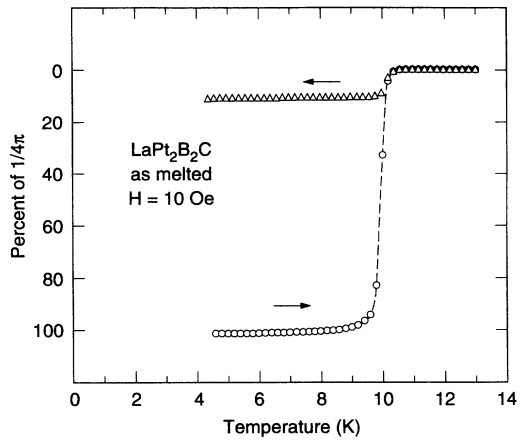

FIG. 1. Temperature-dependent magnetization as a percent of $1/4\pi$ for $\mathrm{LaPt_2B_2C}$ showing the superconducting transition. Arrows show data for warming after cooling in the earth's field and data for cooling in a field of 10 Oe.

seen to display superconducting T_c's near 10.5 K. For $\mathrm{YPt_2B_2C}$, however the transition is quite broad, reflecting sample inhomogeneity or other imperfection, perhaps poor crystallinity, which would be consistent with its apparent metastability. $\mathrm{PrPt_2B_2C}$ in its as-melted state displays a magnetically measured T_c of approximately 6 K. The suppression of T_c by magnetic rare earths has also been observed for $R\mathrm{Ni_2B_2C}$.[4,8] More detailed exploration of the interaction between magnetism and superconductivity for the $R\mathrm{Pt_2B_2C}$ superconductors must await improved phase purity. Finally, the superconducting transition for $\mathrm{LaPt_{2.2}B_2C}$, annealed for 3 days at 1275 °C, yielding a phase purity of 90% or better, is also shown. The transition is somewhat broader and at a lower temperature than for the as-melted less pure stoichiometric material, suggesting that the suppression of T_c has to do with sample inhomogeneity brought about by nonstoichiometry. Our data suggest that different stochiometries (with different T_c's) of $\mathrm{LaPt_2B_2C}$ solid solution exist at elevated temperatures much the same way as is observed for many of the A15 superconductors,[1] with the important treatment temperatures being greater than 1275 °C.

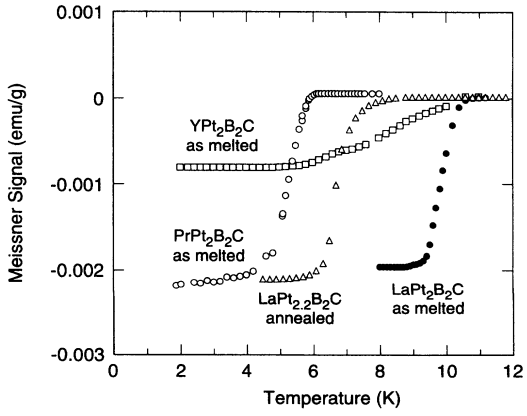

FIG. 2. Field cooled ($H = 10$ Oe) magnetizations for polycrystalline samples of $R\mathrm{Pt_2B_2C}$ as melted, and annealed $\mathrm{LaPt_{2.2}B_2C}$ showing the superconducting transitions.

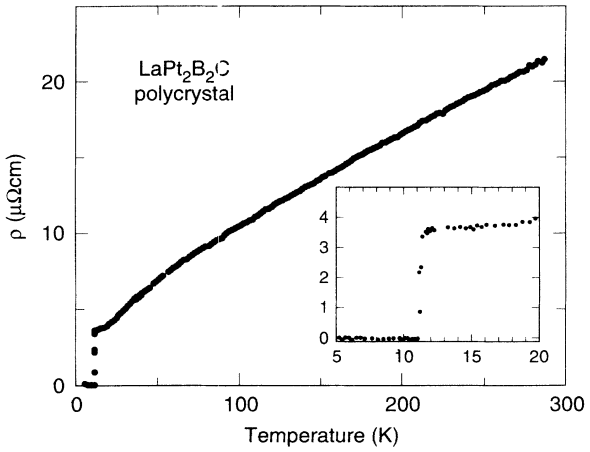

FIG. 3. Temperature-dependent resistivity for polycrystalline sample of $LaPt_2B_2C$. Inset: detail of the region in the vicinity of T_c.

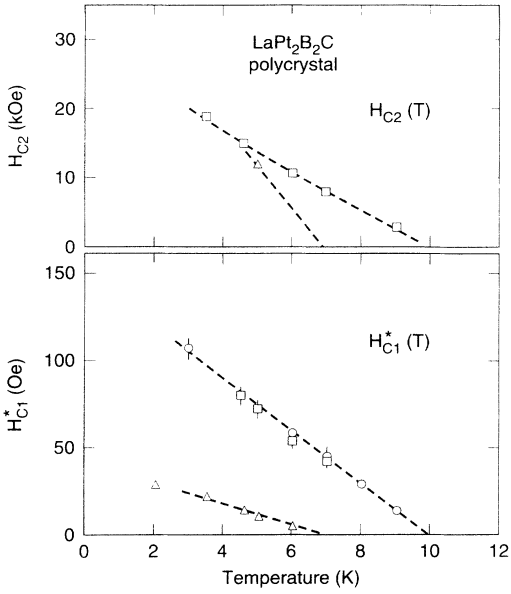

FIG. 4. Temperature-dependent upper (H_{c2}) and apparent lower (H^*_{c1}) critical fields for as-melted $LaPt_2B_2C$ (higher T_c) and annealed $LaPt_{2.2}B_2C$ (lower T_c) polycrystalline samples. (H^*_{c1} is lower than the true H_{c1} due to demagnetization effects.) Different symbols represent results on different samples.

The temperature-dependent resistivity for a multiple phase as-melted polycrystalline sample of $LaPt_2B_2C$ is shown in Fig. 3. The room temperature resistivity is approximately 20 $\mu\Omega$ cm, and just above T_c, 4 $\mu\Omega$ cm. These resistivities are comparable to what is seen for RNi_2B_2C (Ref. 4) but the detailed behavior of $\rho(T)$ may be affected by the presence of the impurity phases. The inset shows the region near T_c in detail. The resistive onset of superconductivity is seen to be near 11 K, with a 10–90 % transition width of approximately 0.5 K.

The apparent lower critical field (H^*_{c1}) values for $LaPt_2B_2C$ were determined by low field magnetization measurements in the SQUID magnetometer. H^*_{c1} at various temperatures was chosen as the point of deviation of $M(H)$ from the linear M-H relationship seen at low fields. The lower critical field $H_{c1}(T)$ was calculated from H^*_{c1} by applying the independently measured corrections for the demagnetization factor. The upper critical field (H_{c2}) was identified as the field beyond which no significant diamagnetic contribution due to superconductivity could be found. The results are summarized in Fig. 4. The temperature dependence of H^*_{c1} and H_{c2} is shown for both as-melted $LaPt_2B_2C$ ($T_c \sim$ 10.5–11 K) and annealed $LaPt_{2.2}B_2C$ ($T_c \sim$ 6.5–7 K). The measured and derived superconducting properties of these materials are summarized in Table II. The density of states at E_F is estimated from the slopes of H_{c1} and H_{c2} using standard thermodynamic relationships, and assuming that the specific heat anomaly at T_c is given by the weak-coupling value $\Delta C = 1.43\gamma T_c$. (An upper bound of the true γ, since strong coupling would increase ΔC with respect to T_c.) For both samples, the Sommerfeld parameter γ is approximately 5 mJ/mol K^2. These compounds are type-II superconductors with $\kappa(=\lambda/\xi)$ ranging from 15 to 40.

TABLE II. Measured and derived superconducting properties of as-melted $LaPt_2B_2C$ and $LaPt_{2.2}B_2C$ annealed at 1275 °C for 3 days.

	$LaPt_2B_2C$	$LaPt_{2.2}B_2C$
T_c	10.5–11	6.5–7
$-dH_{c1}/dT$ (Oe/K)	21	10
$-dH_{c2}/dT$ (Oe/K)	2700	7500
$-dH_c/dT$ (Oe/K)	134	133
γ (mJ/mole K^2)	4.9(2)	4.8(2)
ξ (Å)	110(10)	90(8)
λ (Å)	1650(150)	3550(150)

The normal state susceptibility provides another means for estimating the density of states at E_F. The measured susceptibility for as-melted $LaPt_2B_2C$, $-0.15(1)\times10^{-4}$ emu/mole, is the sum of the core diamagnetism, estimated to be ~ -0.9 to -1.2×10^{-4} emu/mole (depending on the value taken for the Pt core diamagnetism) and the Pauli paramagnetism of the conduction electrons, which therefore is in the range 0.75–1.05×10^{-4} emu/mole. Assuming a standard Wilson ratio, this yields $\gamma \approx 5$ to 8 mJ/mole K^2, which considering the possible contribution of impurity phases to the measured susceptibility is in good agreement with the estimate based on $H_{c1}(T)$ and $H_{c2}(T)$.

CONCLUSIONS

We have found the quaternary intermetallic compounds RPt_2B_2C to be superconducting above 4.2 K for R = La, Pr, and Y. The phase becomes metastable and finally unstable for decreasing rare earth size. Through variation in unit cell dimension and T_c it is apparent that some type of nonstoichiometry is present, which appears to require access to high-temperature annealing for more detailed study.

Although we have found the phases RM_2B_2C to exist

for M =Ni (Ref. 4), Pd (Ref. 9), and Pt, their superconducting behavior is quite different with regard to R size. RNi_2B_2C can be made across the whole R series but is superconducting above 1.5 K only for the small rare earths. RPd_2B_2C again is stable only for the larger rare earths, with the stable phases nonsuperconducting. Band structure calculations place the Fermi level within a transition metal dominated d band in all cases[10,11] and so phase stability and superconductivity may involve additional influences. The experimentally estimated density of states at the Fermi level for $LaPt_2B_2C$ is approximately one quarter that observed for RNi_2B_2C (Refs. 12 and 13) suggesting that its lower T_c is at least in part due to a lower density of states at the Fermi level. The γ and T_c of $LaPt_2B_2C$ are similar to those of TaC and NbC, considered to be conventional electron-phonon coupled superconductors. The influence of the transition metal magnetism in RNi_2B_2C is yet to be fully explored; comparison of the properties of the $3d$ based RNi_2B_2C and the $5d$ based RPt_2B_2C superconductors, the latter expected to show a reduced tendency for local moment magnetism, will help to clarify whether magnetism plays an important role in the occurrence of the superconductivity.

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