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Superconductivity to 21 K in intermetallic thorium-based boride carbides

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Abstract

We report the observation of superconductivity in intermetallic thorium-based boride carbides. For ThM_2B_2C, superconducting T_c's of 6 K (M=Ni), 6.5 K (M=Pt), and 14.5 K (M=Pd) have been measured. These compounds are isostructural with the recently reported $LnNi_2B_2C$ superconductors. We have also observed bulk superconductivity in an as-yet-undetermined thorium–palladium–boron–carbon quaternary phase at 21.5 K. Critical-field measurements on the two palladium-based superconductors, as well as the pressure dependence of T_c for the 21.5 K superconductor, are reported.

Very recently there has been a surge of activity in the study of superconductivity in intermetallic compounds containing boron and carbon [1,2]. Superconductivity has been observed not only at a new bulk intermetallic record of 23 K in a quaternary alloy of yttrium, palladium, boron and carbon [2] but also in numerous single-phase compounds of the nominal composition LnM_2B_2C where Ln is a lanthanide and M is one of the late transition metals Ni or Pt [3,4]. Transition temperatures range from 5 K to 17 K. The crystal structure of these latter compounds (hereafter called the 1221 structure) has also been determined [5]. They have a layered body-centered tetragonal structure which is somewhat reminiscent of the high-T_c cuprates.

Here we extend this work to the actinides. While no superconductivity was found in uranium compounds, we have observed bulk superconductivity in

ThNi$_2$B$_2$C, ThPt$_2$B$_2$C, and ThPd$_2$B$_2$C with transition temperatures of 6 K, 6.5 K, and 14.5 K, respectively. We also report superconductivity near 21.5 K in an as-yet-undetermined thorium–palladium–boron–carbon compound. This represents the highest T_c ever reported for a thorium-based intermetallic compound [6].

Samples were prepared by arc-melting. Starting materials of typical purity 99.9% were melted in an argon atmosphere on a standard water-cooled copper hearth. The boules were flipped and re-melted several times to ensure homogeneity and then wrapped in tantalum foil, sealed in evacuated quartz tubes and annealed at 1050°C for several days.

Similar to their lanthanide analogs, both ThNi$_2$B$_2$C and ThPt$_2$B$_2$C form readily. The arc-melted buttons display crystalline facets, suggesting that single crystals could probably be grown [7]. Powder X-ray diffraction measurements reveal the compounds to be essentially single phase. While this is not sur-

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prising for $ThNi_2B_2C$ because many of the lanthanide analogs are single phase [3], the fact that the nominal composition $ThPt_2B_2C$ contains less than 10% of impurity phases is notable [4]. The diffraction patterns were indexed on a body-centered tetragonal structure, and lattice constants of $a_0 = 3.70$ Å (3.83 Å) and $c_0 = 10.19$ Å (10.86 Å) were extracted for the Ni (Pt) compound. The electrical resistance, measured in the standard four-wire configuration, and magnetic susceptibility, determined with a commercial SQUID magnetometer, for these two compounds are shown in Fig. 1. The onset of superconductivity occurs near 6 K for $ThNi_2B_2C$ and at 6.5 K for $ThPt_2B_2C$ with transition widths of about 1 K and 0.5 K, respectively. While the absolute values of the electrical resistivity and the corrections due to demagnetization effects are hard to calculate because of the irregular shapes of our samples, we estimate

$\rho(10$ K$) \simeq 100$ $\mu\Omega$ cm for both $ThNi_2B_2C$ and $ThPt_2B_2C$ and conclude that they each display approximately full-shielding diamagnetism ($M_0 = 0.028$ emu/gm (0.013 emu/gm) for $ThNi_2B_2C$ ($ThPt_2B_2C$)). Field-cooled measurements indicate a Meissner fraction of about 10% for each sample, comparable to what is observed for single-phase $LnNi_2B_2C$ [3].

The Pd variant of the 1221 structure does not form as cleanly as do the Pt and Ni ones. In the thorium-palladium–boron–carbon quaternary system we have observed two distinct superconducting transitions. The electrical resistance and magnetic susceptibility for each of the Th–Pd–B–C superconductors are shown in Fig. 2. $\rho(25$ K$)$ is approximately 100 $\mu\Omega$ cm for each sample, and $M_0 = 0.012$ emu/gm (0.016 emu/gm) for the 14.5 K (21 K) superconductor, un-
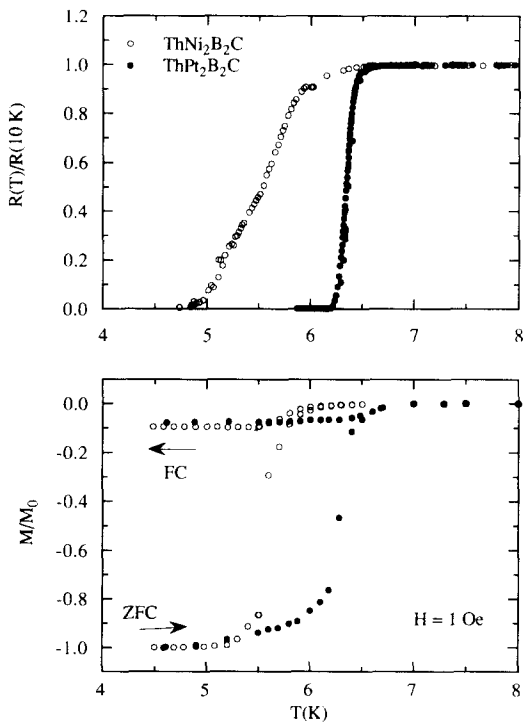

Fig. 1. Electrical resistance and magnetization of $ThPt_2B_2C$ and $ThNi_2B_2C$ as a function of temperature. The resistance data are normalized with respect to the resistance of each sample at 10 K, and the magnetization data are normalized with respect to the maximum zero-field-cooled diamagnetic signal. For each sample this value corresponds to approximately complete diamagnetic shielding. See the text for details.
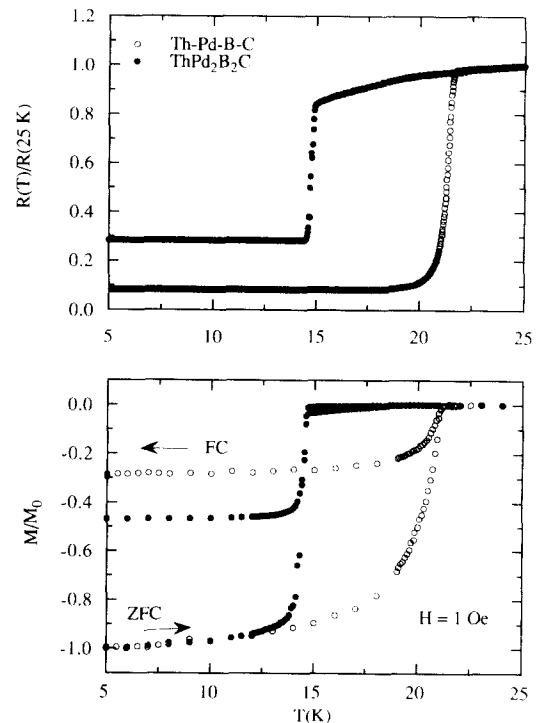

Fig. 2. Electrical resistance and magnetization of two multi-phase Th–Pd–B–C superconductors. The majority phase of the 14.5 K superconductor (the nominal composition for this sample was $ThPd_2B_2C$) is $ThPd_3B_2C$, while the 21 K superconducting phase (the nominal composition for this sample was $ThPd_3B_2C$) has yet to be determined. The data are normalized in a manner similar to Fig. 1 (see text). The maximum diamagnetic signals correspond to full diamagnetic shielding.

corrected for demagnetization effects. Field-cooled measurements indicate Meissner fractions of 45% for the 14 K superconductor and 30% for the 21 K superconductor. The origin of the large non-zero resistance in the superconducting state, especially given the significant Meissner fractions, is unclear.

The majority phase of samples prepared from the nominal composition $ThPd_2B_2C$ and from samples with a 10% Pd deficiency can be indexed on the 1221 structure with lattice constants of $a_0 = 3.84$ Å and $c_0 = 10.67$ Å. Such samples display an onset of superconductivity near 14.5 K with a transition width of 0.5 K.

For samples which are prepared with excess boron and palladium ($ThPd_3B_3C$, for example), superconductivity is observed at temperatures as high as 21.5 K. Although we have been unable to unambiguously identify the phase(s) present in this material, it is clear that little of the 1221 phase is present. For example, some as-melted samples have broad superconducting transitions with onset temperatures near 21 K, but bulk superconductivity is not achieved until 14 K (not shown in the figures). Powder diffraction patterns for these samples indicate that the 1221 structure is present at least as a minority phase. Annealing the samples produces a single sharp (0.5 K) transition at 21.5 K, such as is seen in Fig. 2. Diffraction patterns for the annealed samples have no intensity at d-spacings corresponding to the 1221 structure. Thus, annealing seems to destroy the 1221 phase responsible for superconductivity at 14.5 K, leaving the unidentified 21 K superconductor.

It is not unreasonable to suppose that the structure of the 21 K superconductor in Th–Pd–B–C is the same as that of the 23 K superconductor in Y–Pd–B–C. This hypothesis seems inconsistent, however, with the recent report of Fujii et al. that the structure of the yttrium compound is very similar to the 1221 structure [8] and the fact that annealing destroys superconductivity in the yttrium-based compound [2] rather than enhancing it. The compound $ThPd_3$ exists as a minority phase in both Th based superconductors, and we assume that this is the origin of the large non-zero resistance in the superconducting state of the samples. A large fraction of the 21 K superconducting samples appears to have a crystal structure related to $ThPd_4$ (cubic with $a_0 = 4.11$ Å). T_c's near 21 K have been observed in samples with such differ-

ent nominal compositions as $ThPd_2B_2C$, $ThPd_3B_3C$, and $ThPd_3B_2C$, with the most consistent results being produced in samples with nominal composition $ThPd_3B_3C$. Excluding B and/or C from the arc-melted samples produces no superconductivity. Although it cannot be ruled out that the 21 K superconductor is a boron and carbon stabilized version of $ThPd_4$'s Cu_3Au structure, we have no clear evidence for this. Sample-to-sample variations in T_c of about 1 K may indicate variations in stoichiometry.

Although neither of the Pd compounds has been produced in single phase form, the respective multiphase samples can be systematically reproduced, and the measured X-ray diffraction patterns correlated with the observed superconducting transitions. Furthermore, crushing the samples does not reduce the size or temperature dependence of their diamagnetic signals, indicating that the superconductivity is not primarily filamentary. While a careful study of the superconducting state of each of the palladium-based superconductors must wait for single-phase and preferably single-crystal samples, we have performed more detailed measurements on our majority phase samples to provide at least preliminary insight into their superconducting properties and to verify the distinctness of the two phases.

The pressure dependence of the transition temperature for the 21 K superconducting phase has been measured. Hydrostatic pressures of up to 15 kilobar have been produced using a Be–Cu pressure clamp with Flourinert FC75 as the pressure transmitting medium. AC susceptibility measurements were used to determine T_c and the pressure was measured using a lead manometer. We find the pressure dependence of the 21 K superconducting phase to be small and negative with $dT_c/dP = -0.012$ K/kbar (see Fig. 3).

Resistance measurements as a function of applied magnetic field to 8 T have also been made to determine $H_{c2}(T)$. These results are shown in Figs. 4 and 5. Onset transition temperatures were used to extract the H–T phase boundaries shown in the inset of these figures. For the $ThPd_2B_2C$ phase, we find $dH_{c2}/dT \simeq -0.15$ T/K and estimate $H_{c2}(0) \simeq 1.6$ T, assuming $H_{c2}(0) = -0.7T_c(dH_{c2}/dT)_{T=T_c}$ [9]. These values are reasonably close to those reported by Xu et al. [7], who measured single crystals of YNi_2B_2C. On the other hand the 21 K superconducting phase is much more robust with respect to applied fields. We
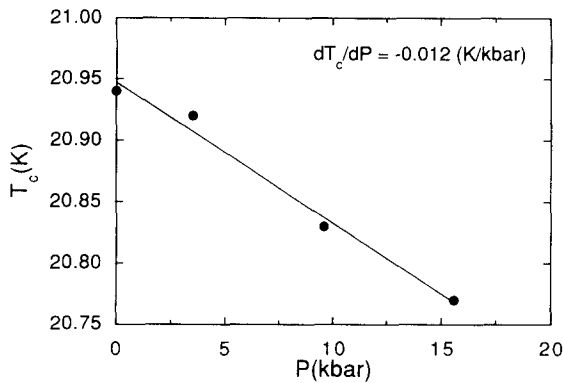
Fig. 3. Hydrostatic-pressure dependence of T_c for the 21 K superconducting phase of Th–Pd–B–C. The lower T_c for this sample (nominal composition $ThPd_3B_2C$) as compared with the one used for critical-field measurements may indicate non-stoichiometry.
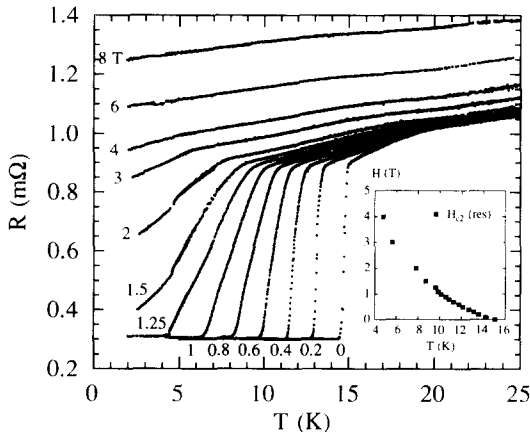

Fig. 5. The resistive superconducting transition for the 21 K superconducting phase of Th–Pd–B–C in various magnetic fields. The inset shows $H_{c2}(T)$ extracted from these data, as well as from a magnetic determination of $H_{c2}(T)$.

Fig. 4. The resistive superconducting transition for $ThPd_2B_2C$ in various magnetic fields. Data are shown at 1 T intervals. The inset shows $H_{c2}(T)$ extracted from these data.

find $dH_{c2}/dT \simeq -1.0$ T/K and $H_{c2}(0) \simeq 17$ T. While the Werthamer–Helfand–Hohenberg estimates of $H_{c2}(0)$ may significantly understate the true $H_{c2}(0)$ values due to the large positive deviations from linearity observed at high fields, they at least illustrate the significant differences between the two superconducting Th–Pd–B–C phases. Magnetic measurements of $H_{c2}(T)$ for the 21 K superconductor show less deviation from linearity. Further study on higher-quality samples is required, however, before much significance can be ascribed to these high-field deviations. We also observe a large positive normal-state magnetoresistance in both samples which is approx-
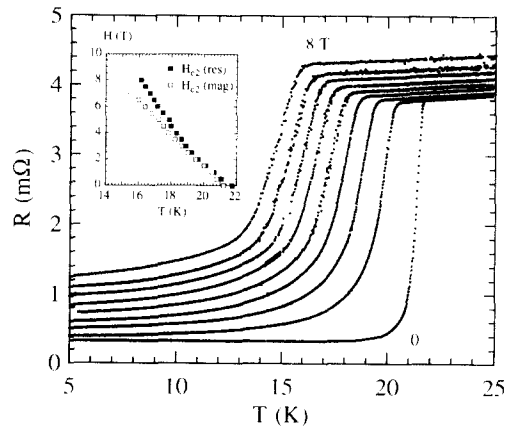
imately quadratic as a function of the applied field (fitting the data of Fig. 5 at 25 K gives $R(H) \propto H^{1.86 \pm 0.06}$), similar to the behavior reported by Takagi et al. for $LuNi_2B_2C$ [10].

In summary, we have extended the observations of superconductivity in LnM_2B_2C based compounds to the actinides. Arc-melted samples of ThM_2B_2C display superconductivity for M=Ni, Pt, and Pd with transition temperatures of 6 K, 6.5 K, and 14.5 K, respectively. We have also observed superconductivity at temperatures as high as 21.5 K in a separate as-yet-undetermined phase of Th–Pd–B–C. Although much work is needed to improve sample purity, the absence, as determined by powder X-ray diffraction, of the 1221 phase, as well as our critical-field measurements on both Pd based compounds, provides evidence that the 21.5 K superconducting phase may represent another new structure in which to study superconductivity in intermetallic compounds.

Acknowledgements

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