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Superconducting and calorimetric properties of $ThPt_2B_2C$ and the anomalous T_c variation for nonmagnetic RPt_2B_2C systems (R = Y, Th, La)

F. S. Jeng, Y. B. You, and H. C. Ku
Department of Physics, National Tsing Hua University, Hsinchu, Taiwan 300, Republic of China

J. C. Ho
Department of Physics and National Institute for Aviation Research, Wichita State University, Wichita, Kansas 67260

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Superconducting quantum interference device dc magnetic susceptibility, ac magnetic susceptibility, ac electrical resistivity, and specific-heat measurements on bulk and powder samples of $ThPt_2B_2C$ shows a bulk superconducting transition T_c of 7 K with a transition width of 6.6–7.4 K. The low-temperature normal-state specific-heat data yield an electronic-term coefficient γ of 8.5 mJ/mol K^2, a Debye temperature θ_D of 330 K, and a bulk superconducting specific-heat jump ΔC at a T_c of 1.53 γT_c. Contrary to the smooth variation of T_c with the T-T in-plane distance for the nonmagnetic RT_2B_2C systems (R = Y, Th, La; T = Ni, Pd), an anomalous T_c variation with the Pt-Pt in-plane distance d(Pt-Pt) was observed for the nonmagnetic RPt_2B_2C system (R = Y, Th, La). This anomalous T_c-d(Pt-Pt) relationship, along with the specific-heat γ value and normal-state Pauli paramagnetic susceptibility of lower-T_c $ThPt_2B_2C$, suggests the importance of the Pt($5d$)-dominated conduction band.

I. INTRODUCTION

Relatively high superconducting transition temperatures T_c up to 23 K have been reported for the quaternary borocarbides RT_2B_2C (R = Sc, Y, Th, U, or a rare earth; T = Ni, Pd or Pt).[1–13] The superconducting phase has been identified to be of the body-centered-tetragonal $LuNi_2B_2C$ type. The structure with space group $I4/mmm$ is a three-dimensionally connected framework with LuC layers alternated withNi_2B_2 layers, where nickel is in tetrahedral coordination with four boron atoms.[4]

For the Ni system, T_c has a simple relationship with the Ni-Ni in-plane distance d(Ni-Ni) for the nonmagnetic compounds,[9] ranging from a maximum of 16.6 K for $LuNi_2B_2C$ to 15–16 K for YNi_2B_2C and metastable $ScNi_2B_2C$,[2,3,5] followed by 8 K for $ThNi_2B_2C$ and below 0.3 K for $LaNi_2B_2C$.[9,14] For magnetic rare-earth compounds, lower superconducting transitions were reported for R=Dy, Ho, Er, and Tm due to the magnetic pair-breaking effect[3,6,13] and a nearly reentrant behavior prevails in $HoNi_2B_2C$.[6,15,16]

For the Pd system, all superconducting compounds are basically metastable and nonmagnetic. A similar systematic variation of T_c with Pd-Pd in-plane distance d(Pd-Pd) was observed,[12] with a maximum T_c of 23 K for YPd_2B_2C,[2] followed by 14–21 K for $ThPd_2B_2C$ and 1.4–4.6 K for $LaPd_2B_2C$.[7,12]

For the Pt system, preliminary on three multiphase superconductors yielded a T_c of 10–11 K for YPt_2B_2C,[11] 6.5–6.7 K for $ThPt_2B_2C$ and 10 K for $LaPt_2B_2C$.[7,8,11] As part of an ongoing effort to study the systematic variation of T_c for all quaternary borocarbides, we report here the detailed studies on the relatively stable $ThPt_2B_2C$. In addition, two pseudoquaternary systems $(Th_{1-x}R_x)Pt_2B_2C$ (R = Y, La) were synthesized and characterized, providing another set of data base for analyzing the T_c variation in the platinum borocarbides.

II. EXPERIMENTS

The $ThPt_2B_2C$ and $(Th_{1-x}R_x)Pt_2B_2C$ (x=0.5, 0.75, and 1 for R=Y; x=0.5 and 1 for R=La) samples were prepared from high-purity elements (Th, Y, La: 99.9%, Pt foil: 99.99%, B: 99.9995%, and C: 99.995%) with stoichiometric starting composition (1:2:2:1) under an argon atmosphere in a Zr-gettered arc furnace. The starting ingredients were wrapped in the Pt foil and slowly arc-melted several times in order to ensure negligible weight loss and sample homogeneity. Crystallographic data were obtained with a Rigaku Rotate 18 kW rotating anode powder x-ray diffractometer using Cu $K\alpha$ radiation with a scanning rate of 1° in 2θ per min. A lazy pulverix-PC program was employed for phase identification and lattice parameter calculation.

The dc magnetic-susceptibility measurements were made with a μ-metal shielded Quantum Design $MPMS_2$ superconducting quantum interference device magnetometer down to 2 K in 10 G low dc magnetic field. A Lake Shore Model 7221 susceptometer/magnetometer provided ac measurements down to 4.2 K in an ac magnetic field 0.1 G (rms) at 1 kHz. The electrical resistivity (16 Hz) was carried out by the standard four-probe method with an ac excitation current of 3 mA (rms), in a RMC closed-cycle refrigerator down to 9 K, then single-shot cooling to 6.5 K. A relaxation calorimeter was employed for specific-heat measurements down to 1.2 K. Inside the calorimeter, the sample was thermally anchored to a sapphire holder on which thin films of germanium and nickel-chromium alloys were deposited to serve as temperature sensor and Joule heating element, respectively. The holder was thermally linked to a copper block. Following each heat pulse, the sample temperature relaxation rate τ was monitored. The specific-heat value was then calculated from

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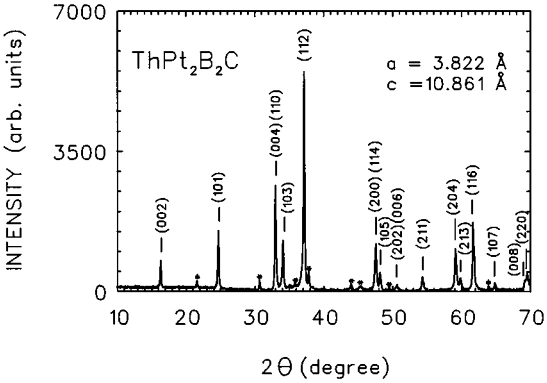

FIG. 1. Powder x-ray-diffraction pattern of as-melted $ThPt_2B_2C$ sample. Impurity lines are indicated by asterisks.

$C = k\tau$, where k is the thermal conductance of the wires. The heat capacity of the sample holder was separately measured for addenda correction.

III. RESULTS AND DISCUSSION

The powder x-ray diffraction pattern of the as-melted $ThPt_2B_2C$ sample is shown in Fig. 1. Except for very small amounts of ThB_6 ($T_c = 0.74$ K) and nonsuperconducting $ThPt_3$ impurities,[17,18] the diffraction pattern can be well indexed with the $LuNi_2B_2C$-type structure having tetragonal lattice parameters $a = 3.822(3)$ Å and $c = 10.861(6)$ Å and a unit-cell volume $V = 158.7(1)$ Å^3. Due to the incongruent melting and complex phase diagram, the minor impurities cannot be eliminated even after heat treatment at 1200 °C. The difficulty of single phase formation may also originate from the large size of platinum in the Pt_2B_2 layers.

Figure 2 presents the temperature dependence of 10 G field-cooled (FC) and zero-field-cooled (ZFC) mass magnetic susceptibility χ_g for the $ThPt_2B_2C$ samples. For the bulk sample, a diamagnetic superconducting transition T_c onset occurs at 7.4 K. It decreases slightly to 7 K for the powder sample. Due to a large supercurrent shielding effect for the bulk sample, there is a large ZFC diamagnetic signal of 1.31×10^{-2} emu/g G at 2 K. On the other hand, strong grain-boundary/impurity flux pinning in the bulk sample results in an extremely small FC signal of 6.7×10^{-5} emu/g G at 2 K. For powder samples, with little flux pinning, yields an almost identical FC/ZFC signal of 5.6×10^{-3} emu/g G at 2 K. Without consideration of the surface field penetration effect on powder samples, this value is already equivalent to 48% of the ideal Meissner value, thus assuring the bulk effect of the observed superconducting $LuNi_2B_2C$-type $ThPt_2B_2C$ phase. Above T_c, both samples exhibit a small temperature-independent Pauli-like paramagnetic susceptibility χ_n of 1.5×10^{-7} emu/g G or 1.0×10^{-4} cm^3/mol at normal state. This value is close to 1.9×10^{-4} cm^3/mol for $T_c = 8$ K $ThNi_2B_2C$.[9]

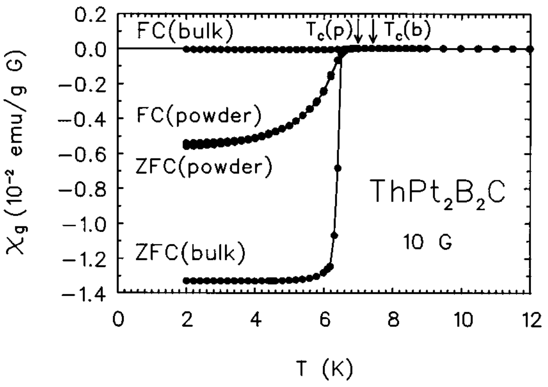

FIG. 2. Temperature dependence of 10-G field-cooled (FC) and zero-field-cooled (ZFC) mass magnetic susceptibility $\chi_g(T)$ of $ThPt_2B_2C$ bulk and powder samples.

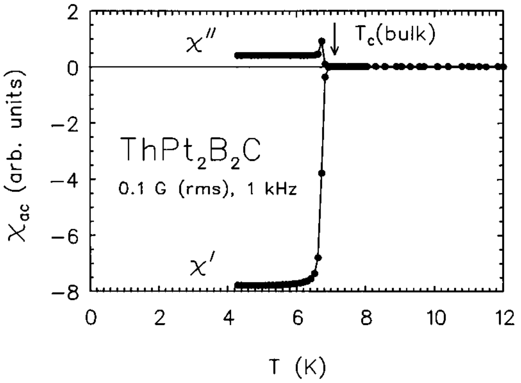

FIG. 3. Temperature dependence of ac magnetic susceptibility $\chi_{ac}(T)$ of $ThPt_2B_2C$ bulk sample in 0.1 G (rms) field at 1 kHz.

The temperature dependence of ac magnetic susceptibility χ_{ac} at 1 kHz and 0.1 G (rms) for the $ThPt_2B_2C$ bulk sample is shown in Fig. 3, revealing a very sharp real-part χ' superconducting transition at 7.1 K, with an imaginary-part χ'' dissipation peak at 6.8 K. The ac electrical resistivity $\rho(T)$ data (Fig. 4) shows a superconducting transition onset of 7.5 K, 50% transition midpoint of 7.2 K, and zero resistivity at 7 K. Large residual resistivity ρ(0 K) of 22 $\mu\Omega$ cm and low resistivity ratio ρ(300 K)/ρ(0 K) of 1.5 reflect the presence of impurities.

The bulk superconductivity nature of the $LuNi_2B_2C$-type $ThPt_2B_2C$ phase has been checked carefully by the calorimetric measurement. Figure 5 shows the molar specific heat for $ThPt_2B_2C$ in the form of C/T versus T. Data above 7.4 K can be well fitted with the formula $C = \gamma T + \beta T^3 + \alpha T^5$

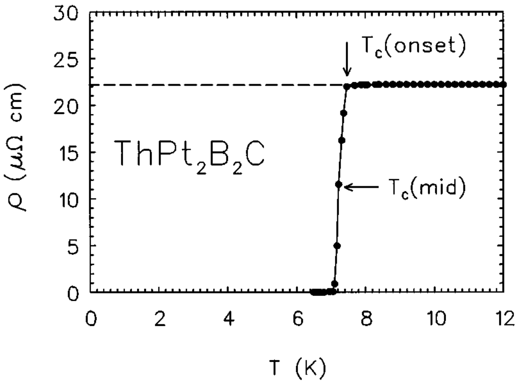

FIG. 4. Temperature dependence of ac (16 Hz) electrical resistivity $\rho(T)$ of $ThPt_2B_2C$.

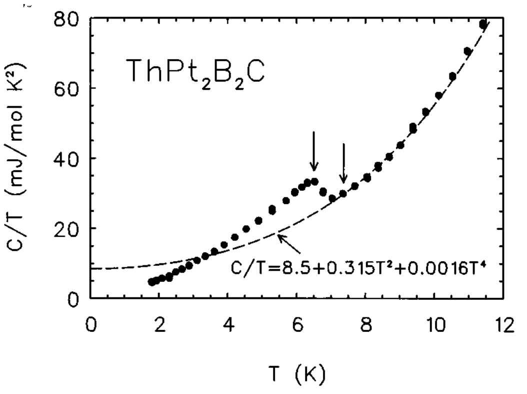

FIG. 5. C/T versus T for ThPt$_2$B$_2$C.

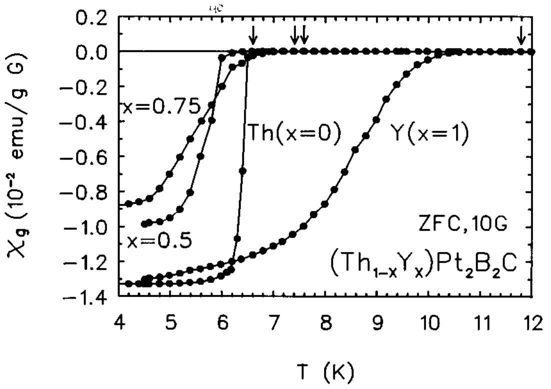

FIG. 6. Temperature dependence of 10-G zero-field-cooled (ZFC) mass magnetic susceptibility for the (Th$_{1-x}$Y$_x$)Pt$_2$B$_2$C system.

$=8.5T+0.315T^3+0.0016T^5$. The superconducting transition-induced deviation from the above relation indicates a T_c onset of 7.4 K, and reaches a peak at 6.6 K. The electronic-term coefficient $\gamma=8.5$ mJ/mol K^2 is smaller than 18.7–19 mJ/mol K^2 reported for nonmagnetic LuNi$_2$B$_2$C ($T_c=16.6$ K) and YNi$_2$B$_2$C ($T_c=15.6$ K).[19,20] The Debye temperature $\theta_D=330$ K derived from the lattice harmonic term coefficients β is smaller than 345 K for LuNi$_2$B$_2$C and 489 K for YNi$_2$B$_2$C,[19,20] but is larger than 310 K for LaPd$_2$B$_2$C.[12] Note that an anharmonic term αT^5 is necessary for high-temperature fitting up to 12 K, while no anharmonic term is required for temperature fitting up to 5 K for the 1.8 K superconductor LaPd$_2$B$_2$C.[12] Extrapolation of the specific-heat data above and below the transition to its middle point of 7 K yields a specific-heat jump $\Delta C=91$ mJ/mol K. The ratio of this jump to $\gamma T_c=8.5\times 7=59.5$ mJ/mol K is 1.53. In comparison, LuNi$_2$B$_2$C and YNi$_2$B$_2$C with higher T_c and larger γ has a larger $\Delta C/\gamma T_c=1.77$–1.8,[19,20] while LaPd$_2$B$_2$C with lower T_c and smaller γ of 7.1 mJ/mol K^2 has a smaller $\Delta C/\gamma T_c=1.4$.[12] All the above data affirm that superconductivity in ThPt$_2$B$_2$C is indeed a bulk effect with a transition temperature T_c of 7 K and transition width of 6.6–7.4 K. The observed T_c of 7 K is slightly higher than the reported T_c of 6.6 K.[7,8] If the phonon-mediated strong-coupling mechanism is valid as described by the McMillan T_c formula $T_c=(\theta_D/1.45)\exp\{-1.04(1+\lambda)/[\lambda-\mu^*(1+0.62\lambda)]\}$ with λ the electron-phonon coupling parameter and μ^* the effective Coulomb interaction parameter,[21] then the electron-phonon coupling parameter $\lambda=N(E_F)\langle I^2\rangle/M\langle\Omega^2\rangle$ is related to the Fermi-level density of states $N(E_F)$ with $\langle I^2\rangle$ the average of the square of the electron-phonon matrix element, M is the mass, and $\langle\Omega^2\rangle$ is the average of the square of phonon frequency. The $N(E_F)$ in turn is closely related to the experimental specific-heat coefficient γ or the Pauli normal-state paramagnetic susceptibility.

Magnetic susceptibility $\chi_g(T)$ for the (Th$_{1-x}$Y$_x$)Pt$_2$B$_2$C system in Fig. 6 shows that the diamagnetic T_c onset decreases slightly from 7.4 K for ThPt$_2$B$_2$C to 6.6 K for (Th$_{0.5}$Y$_{0.5}$)Pt$_2$B$_2$C, then increases slightly back to 7.6 K for (Th$_{0.25}$Y$_{0.75}$)Pt$_2$B$_2$C and then increases sharply to 11.8 K for YPt$_2$B$_2$C. For the (Th$_{1-x}$La$_x$)Pt$_2$B$_2$C system shown in Fig. 7, the diamagnetic T_c onset increases monotonically from 7.4 K for ThPt$_2$B$_2$C, 9.8 K for (Th$_{0.5}$La$_{0.5}$)Pt$_2$B$_2$C, and to 11 K for LaPt$_2$B$_2$C. The sample homogeneity problem during substitution is checked carefully through the observation of sharp x-ray-diffraction pattern with distinct gradual variation of tetragonal lattice parameters as well as T_c variation.

To unravel the origin of these nontrivial T_c variations, the T_c onset and the tetragonal unit-cell volume V for all parent RPt$_2$B$_2$C compounds ($R=$Y, La, Pr, Nd, Th) are plotted in Fig. 8 against the R^{3+} ionic radius except for ThPt$_2$B$_2$C, for which Th^{4+} ionic radius is used. As shown clearly, the unit-cell volume V increases linearly with increasing ionic sizes, from 153.5 Å^3 for Y^{3+}(0.893 Å), to 158.7 Å^3 for Th^{4+}(1.02 Å) and 160.5 Å^3 for La^{3+}(1.061 Å). This smooth T_c-R variation confirms the existence of the nonmagnetic Y^{3+}, Th^{4+} and La^{3+} ions as well as the magnetic Pr^{3+} and Nd^{3+} ions in RPt$_2$B$_2$C compounds. The T_c reduction from 11 K for nonmagnetic LaPt$_2$B$_2$C to 6 K for magnetic PrPt$_2$B$_2$C is due to the Pr^{3+} magnetic pair-breaking effect.[11] No superconducting transition occurs down to 1.8 K for magnetic NdPt$_2$B$_2$C due to a stronger pair-breaking effect.[11]

Contrary to the smoothly decreasing T_c with the increasing ionic radii for the nonmagnetic RT_2B$_2$C ($R=$Y, Th, La; $T=$Ni, Pd) compounds,[9,12] RPt$_2$B$_2$C ($R=$Y, Th, La) nonmagnetic compounds show an anomalous variation of T_c versus ionic radius with a local minimum of 7 K for ThPt$_2$B$_2$C. Since the insertion of different R ion can influence the in-plane as well as the c-axis Pt-Pt interatomic dis-

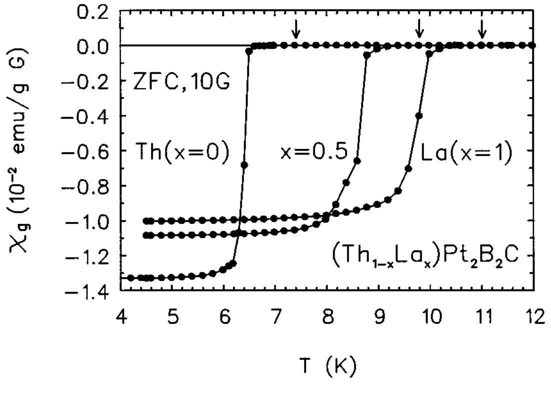

FIG. 7. Temperature dependence of 10-G zero-field-cooled (ZFC) mass magnetic susceptibility for the (Th$_{1-x}$La$_x$)Pt$_2$B$_2$C system.

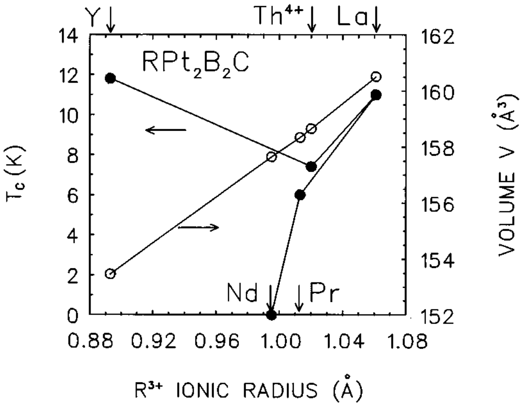

FIG. 8. Variation of T_c onset and tetragonal unit-cell volume V with the R^{3+} ionic radius for RPt$_2$B$_2$C (R=Y, La, Pr, Nd). Th^{4+} ionic radius is used for R=Th.

tances, the electronic structure and the Pt($5d$)-dominated conduction bandwidth are expected to change as a result. As shown in Fig. 9, the anomalous variation of T_c for the RPt$_2$B$_2$C system (R=Y, Th, La) seems to have a strong dependence on the Pt-Pt nearest-neighbor in-plane distance d(Pt-Pt)$=a/\sqrt{2}$ (a being the tetragonal in-plane lattice parameter). T_c decreases sharply with the increasing d(Pt-Pt) value from 11.8 K for YPt$_2$B$_2$C (d=2.688 Å) to a minimum value of 6.6 K for (Th$_{0.5}$Y$_{0.5}$)Pt$_2$B$_2$C (d=2.691 Å), and then increases monotonically to 7.4 K for ThPt$_2$B$_2$C (d=2.703 Å) and 11 K LaPt$_2$B$_2$C (d=2.735 Å). The smooth variation of the Pt-Pt distance as well as T_c during the (Th, R) substitution ruled out the possibility of sample inhomogeneity. The Pt-Pt bond lengths of 2.688–2.735 Å are smaller than the fcc Pt value of 2.77 Å, suggesting the presence of metal-metal bonds in this phase. Such an anomalous T_c-d(Pt-Pt) relationship, along with the relatively small specific-heat γ value and normal-state Pauli paramagnetic susceptibility χ_n for lower-T_c ThPt$_2$B$_2$C, suggests the importance of the Pt($5d$)-dominated conduction band. The conduction-band variation and the accompanied change in the Fermi-level density of states $N(E_F)$ are believed to be the determining factors for the anomalous T_c variation in the RPt$_2$B$_2$C system. On the contrary, the smooth variation of the Ni($3d$) and Pd($4d$) bands of the isostructural RT_2B$_2$C systems (T=Ni, Pd) are reflected through a smoothly decreasing T_c with the T-T in-plane distance $d(T$-$T)$ where no superconducting down to 0.3 K was observed for LaNi$_2$B$_2$C with the longest d(Ni-Ni) or a low T_c of 2 K was observed for LaPd$_2$B$_2$C with the longest d(Pd-Pd).[9,12,16]

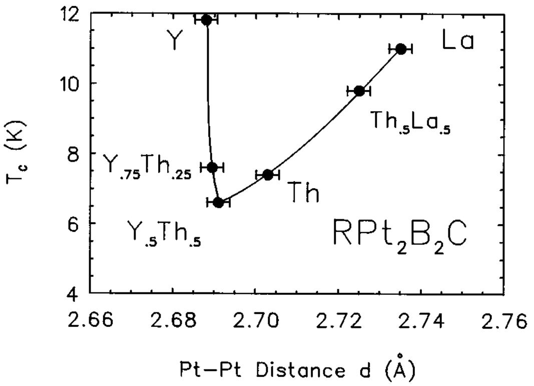

FIG. 9. Variation of T_c onset with the Pt-Pt in-plane distance for nonmagnetic compounds RPt$_2$B$_2$C (R=Y, Th, La).

IV. CONCLUSION

Measurements on bulk and powder samples of ThPt$_2$B$_2$C indicate a bulk superconducting transition temperature T_c of 7 K and a transition width of 6.6–7.4 K. The low-temperature normal-state specific-heat data yields an electronic-term coefficient γ of 8.5 mJ/mol K^2, a Debye temperature θ_D of 330 K, and a bulk superconducting specific-heat jump ratio $\Delta C/\gamma T_c$ of 1.53. Contrary to the isostructural RT_2B$_2$C system (R=Y, Th, La; T=Ni, Pd), an anomalous T_c variation with the Pt-Pt in-plane distance was observed for the nonmagnetic RPt$_2$B$_2$C system (R=Y, Th, La). Such an anomalous T_c-d(Pt-Pt) relationship, along with the specific-heat γ value and normal-state Pauli paramagnetic susceptibility χ_n of ThPt$_2$B$_2$C, suggests the importance of Pt($5d$)-dominated conduction band.

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