Thermal expansion of the heavy fermion borocarbide \text{YbNi}_2\text{B}_2\text{C}

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Abstract. We have measured the thermal expansion of the heavy fermion borocarbide \text{YbNi}_2\text{B}_2\text{C} from room temperature to about 0.5 K using a capacitive dilatometer. The thermal expansion is anisotropic, is consistent with a crystal-field splitting on the order of 120 K, and with intermediate-valence behavior at low temperatures. The effective Grüneisen parameter is temperature dependent and we estimate its value at \(T = 0\) to be about -7, consistent with a moderately enhanced heavy fermion state.

1. Introduction
The rare-earth nickel borocarbides crystallize in a tetragonal, layered structure (\textit{R}Ni\textsubscript{2}B\textsubscript{2}C where \textit{R} represents a rare earth element) resulting in a series of compounds in which only the nature of the local moment varies \cite{1, 2, 3}. Superconductivity and antiferromagnetism coexist in several \textit{R}Ni\textsubscript{2}B\textsubscript{2}C compounds, some with a higher Neél temperature \(T_N\) and some with a higher superconducting critical temperature \(T_c\). A variety of interesting magnetic states exist including commensurate antiferromagnetism, spin density wave states, a spiral state in HoNi\textsubscript{2}B\textsubscript{2}C \cite{4}, and a weak ferromagnetic state that coexists with the superconducting state in ErNi\textsubscript{2}B\textsubscript{2}C \cite{5}. As one moves across the lanthanides from \textit{R} = Dy to Lu in the \textit{R}Ni\textsubscript{2}B\textsubscript{2}C compounds, \(T_N\) and \(T_c\) generally decrease and increase respectively, scaling with the de Gennes factor of the rare earth constituent \cite{6}. This scaling predicts a \(T_c\) near 13 K and a \(T_N\) near 0.4 K for \text{YbNi}_2\text{B}_2\text{C}, yet no phase transition of any kind is observed down to at least 50 mK \cite{7}. Instead, an anisotropic heavy fermion state appears with a Sommerfeld coefficient of 530 mJ/mol K\textsuperscript{2} and a Kondo temperature of about 10 K \cite{8}. It has been suggested that \text{YbNi}_2\text{B}_2\text{C} “may be close to a quantum critical point on the nonmagnetic side” \cite{9}.

Neutron scattering studies reveal strong crystal electric field (CEF) effects, splitting the ground state of the trivalent Yb ion by about 100 K and inducing a temperature dependence to the Kondo interaction \cite{9}. X-ray absorption measurements confirm that Yb ions are “nearly” trivalent at 300 K \cite{10}. Though one generally expects to find the rare-earth ions in intermetallic compounds in a 3+ state, an integral valence would be surprising at low temperatures because

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of the tendency of Yb ions to “fluctuate” to a non-magnetic divalent state that fills the 4f band and screens the nuclear charge more effectively [11]. One generally expects to find the 4f ions in heavy fermion compounds in an intermediate valence (IV) state [12], and we believe that such effects manifest in the thermal expansion measurements we present below, measurements undertaken to better characterize the heavy fermion state itself and to address the question of why YbNi$_2$B$_2$C behaves so differently from its neighboring compounds in this series of materials.

2. Experimental Details, Results, and Discussion

Our single crystal of YbNi$_2$B$_2$C was grown in Ni$_2$B flux [8] and annealed at 950 °C for 100 hours (annealing can significantly affect the transport properties of YbNi$_2$B$_2$C but not its thermodynamic quantities [13]). These plate-like crystals grow along a well-defined c-axis but the basal plane orientation is less easily identified, so we denote the direction perpendicular to the c-axis as the ab-axis. The sample had a thickness of 0.83 mm along the c-axis and 1.93 mm along the ab-axis. The linear thermal expansion, $\alpha = \frac{d(ln L)}{dT}$ where $L$ is the length of the sample, was measured with a capacitive dilatometer described elsewhere [14]. The volume thermal expansion is determined from the linear thermal expansion: $\beta = \frac{d(ln V)}{dT} = 2\alpha_{ab} + \alpha_c$, where $V$ is the volume, $\alpha_{ab}$ is the thermal expansion perpendicular to the c-axis and $\alpha_c$ is the thermal expansion along the c-axis. Our results are shown in Fig. 1.

![Figure 1](image_url)

Figure 1. The linear $\alpha$ and volume $\beta$ thermal expansions of YbNi$_2$B$_2$C from 0.5 to 300 K. The linear thermal expansion of copper is shown for comparison. The right-hand panel expands the low temperature data.

The thermal expansion is anisotropic with $\alpha_{ab} \approx 3.4\alpha_c$ near room temperature where the volume thermal expansion is about half that of copper. The linear thermal expansion in the basal plane is negative below about 33 K, the thermal expansion along the c-axis remains positive above about 2 K, but turns negative as $T \to 0$. Negative thermal expansion is not uncommon in magnetic (and other) materials and can be due to several mechanisms [15]. We suspect the Yb ions are in an IV state as described above.

The magnetic contribution to the volume thermal expansion is isolated by subtracting the volume thermal expansion of the non-magnetic superconductor YNi$_2$B$_2$C [16]. Though the uncertainty in this procedure (due to sample-to-sample variations in the YNi$_2$B$_2$C data and a small feature at $T_c$) is non-trivial, two broad features (not shown) are clearly observed: a broad maximum centered near 120 K in qualitative agreement with the CEF splitting, and a minimum centered near 5 K which may be associated with heavy fermion/IV behavior. If this minimum is
a manifestation of IV behavior we note that it is smaller than similar features observed in other Yb compounds [11], the smaller size may be due to CEF effects [17]. The presence of IV behavior can suppress both magnetic order and superconductivity (e.g. Ce doped into superconducting La [18]), perhaps this is part of the reason why YbNi$_2$B$_2$C does not behave as its neighbors do.

We now consider the heavy fermion behavior of YbNi$_2$B$_2$C. At low temperatures the specific heat (thermal expansion) takes the form $C_p = c_1 T + c_2 T^3 (\beta = a_1 T + a_2 T^3)$ where the first term embodies the electronic contribution. The low temperature limits of $c_1$ and $a_1$ are found by extrapolating a plot of $C_p/T (\beta/T)$ vs. $T^2$ to $T = 0$. Such plots are shown in Fig. 2 where the specific heat, measured with a thermal relaxation technique and in good agreement with earlier measurements [8], is shown with the thermal expansion. We find $c_1 = 480 \text{ mJ/mol K}^2$ in reasonable agreement with earlier results and $a_1 = -3.75 \times 10^{-7} \text{ K}^{-2}$.

![Figure 2](image1.png)  
**Figure 2.** The volume thermal expansion and specific heat of YbNi$_2$B$_2$C plotted as $\beta/T$ and $C_p/T$ vs. $T^2$ (see text).

![Figure 3](image2.png)  
**Figure 3.** The effective Grüneisen parameter of YbNi$_2$B$_2$C below 35 K.

To characterize the energy scales in this system an effective Grüneisen parameter $\Gamma_{eff}$ is defined [15]. $\Gamma_{eff}$ is directly related to the volume dependence of the characteristic energy (or energies) in the system of interest:

$$\Gamma_{eff} = -\frac{\partial \ln T^*}{\partial \ln V} = \frac{V_m \beta}{\kappa C_V},$$

(1)

where $V_m$ is the molar volume (38.62 cm$^3$ [4]), $\kappa$ is the isothermal compressibility (which has not been measured for YbNi$_2$B$_2$C to the best of our knowledge, we used $\kappa = 5 \times 10^{-12} \text{ Pa}^{-1}$ a typical value for YNi$_2$B$_2$C from the literature), $C_V$ is the molar specific heat and $T^*$ is the characteristic energy of the system. For ordinary metals at low temperatures $\Gamma_{eff}$ is (nearly) a constant of order unity (indicating that $\beta(T) \propto C_V(T)$ since the temperature dependence of $\kappa$ is usually small). In the ‘classic’ heavy fermion systems $\Gamma_{eff}$ is strongly temperature dependent (indicating multiple energy scales) and varies from about 50 to over 150 at low temperatures [19]. The temperature dependence of the effective Grüneisen parameter of YbNi$_2$B$_2$C below 35 K is shown in Fig. 3, where the uncertainties do not include our estimation of $\kappa$, and where apparent features are artifacts of the cubic spline fits used to determine the derivatives underlying $\beta$ [14]. As defined, the effective Grüneisen parameter includes phonon contributions, CEF contributions, etc., each component contributes to $\Gamma_{eff}$ in a weighted average where the component’s contribution to the specific heat acts as the weight parameter [15]. In such a scheme one expects the electronic contribution of a heavy fermion compound to dominate at
low temperatures. To focus on the electronic contribution as \( T \to 0 \) we use the extrapolated values of \( c_1 \) and \( a_1 \) above to define
\[
\Gamma_{HF} = \frac{V_m a_1}{\kappa c_1},
\]
and find \( \Gamma_{HF} = -6 \), comparable to \( \Gamma_{eff}(0) \) within experimental uncertainty. These low temperature Grüneisen parameters are consistent with moderate heavy fermion behavior in \( \text{YbNi}_2\text{B}_2\text{C} \), but are an order of magnitude smaller than those observed for the ‘classic’ heavy fermion compounds [19]. Perhaps this is due to \( \text{YbNi}_2\text{B}_2\text{C}'s ‘distance’ from the quantum critical point responsible for heavy fermion behavior.

3. Conclusions
We have measured the anisotropic thermal expansion of \( \text{YbNi}_2\text{B}_2\text{C} \) from room temperature to about 0.5 K. Our results are consistent with crystal field splitting on the order of 120 K. We suggest that IV behavior is responsible for the negative thermal expansion observed at low temperatures. The effective Grüneisen parameter extrapolates to a value of about -7 as \( T \to 0 \), consistent with a moderately enhanced heavy fermion compound.

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5. References
[1] Bud’ko S L and Canfield P C 2006 C.R. Physique 7 56
[2] Gupta L C 2006 Adv. Phys. 55 691
[3] Mazumdar C and Nagarajan R 2005 Curr. Sci. 88 83
[4] Lynn J, Skanthakumar S, Huang Q, Sinha S, Hossain Z, Gupta L, Nagarajan R and Godart C 1997 Phys. Rev. B 55 6584
[5] Choi S M, Lynn J W, Lopez D, Gammel P L, Canfield P C and Bud’ko S L 2001 Phys. Rev. Lett. 87 107001
[6] Cho B K, Canfield P C and Johnston D C 1996 Phys. Rev. Lett. 77 163
[7] Lacerda A, Yatskar A, Schmiedeshoff G M, Beyermann W P and Canfield P C 1996 Philos. Mag. B 641
[8] Yatskar A, Budraa N K, Beyermann W P, Canfield P C and Bud’ko S L 1996 Phys. Rev. B 54 R3772
[9] Boothroyd A T, Barratt J P, Bonville P, Canfield P C, Murani A, Wildes A R and Bewley R I 2003 Phys. Rev. B 67 104407
[10] Dhar S K, Nagarajan R, Jossain Z, Tominez E, Godart C, Gupta L C and Vijayaraghavan R 1996 Sol. St. Comm. 98 985
[11] Wohlleben D K 1981 Valence Fluctuations in Solids ed Falicov L M, Hanke W and Maple M B (North-Holland) p 1
[12] Wachter P 1993 Handbook on the Physics and Chemistry of Rare Earths ed Gschmeidner K A, Eyring L, Lander G H and Choppin G R (North Holland, Amsterdam) chap 132
[13] Avila M A, Budko S L and Canfield P C 2002 Phys. Rev. B 66 132504
[14] Schmiedeshoff G M, Lounsbury A W, Luna D J, Tracy S J, Schramm A, Tozer S W, Correa V F, Hannahs S T, Murphy T P, Palm E C, Lacerda A H, Bud’ko S L, Canfield P C, Smith J L, Lashley J C and Cooley J C 2006 Rev. Sci. Instrum. 77 123907 cond-mat/0610396
[15] Barron T H K and White G K 1999 Heat Capacity and Thermal Expansion at Low Temperatures (New York: Kluwer Academic/Plenum Publishers) and references therein
[16] Bud’ko S L, Schmiedeshoff G M, Lapertot G and Canfield P C 2006 J. Phys. C: Condens. Matt. 18 8353
[17] Kumar S, Aihulwala P K and Sharma K C 1990 Sol. St. Comm. 73 65
[18] Matthias B, Suhl H and Corenzwit E 1958 Phys. Rev. Lett. 1 92
[19] de Visser A, Flouquet J, Franse J J M, Haen P, Hasselbach K, Lacerda A and Taillefer L 1991 Physica B 171 190