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Anomalous hydrostatic pressure dependence of the Curie temperature of the Kondo-lattice compound YbNiSn to 38 GPa

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The dependence of the Curie temperature T_o of ferromagnetic YbNiSn on hydrostatic pressure to 38 GPa has been determined in an ac susceptibility measurement in a diamond-anvil cell loaded with dense helium as a pressure medium. The Curie temperature $T_o(0) \simeq 5.5$ K initially increases with applied pressure at the rate +1.7 K/GPa, passing through a maximum value $T_o^{\max} \simeq 7.7$ K at ~2 GPa. No transition was detected above 2 K for 9.4 GPa$<P<$38 GPa. The present results are discussed within the framework of a phase diagram proposed by Doniach for Kondo-lattice systems. The observed asymmetry in $T_o(P)$ about $P_m = P(T_o^{\max})$, which is opposite to that found in Ce compounds, can be readily understood in Doniach's model if the Kondo temperature of YbNiSn *decreases* under pressure.

In elemental form, as well as for the majority of their metallic compounds and alloys, the rare-earth elements cerium and ytterbium exhibit magnetic ($4f^1$) trivalent and nonmagnetic ($4f^{14}$) divalent states, respectively. Under the application of high pressure, the valence of rare-earth ions generally increases as an electron is squeezed out of the $4f$ shell, leading to the demagnetization of cerium $\mathrm{Ce}^{3+}(4f^1) \rightarrow \mathrm{Ce}^{4+}(4f^0)$ and the magnetization of ytterbium $\mathrm{Yb}^{2+}(4f^{14}) \rightarrow \mathrm{Yb}^{3+}(4f^{13})$. Since Ce and Yb lie at opposite ends of the rare-earth series, the pressure-induced magnetization of Yb^{2+} should be the "mirror image" of the demagnetization of Ce^{3+}. However, the relatively strong localization of Yb's $4f$ orbital [$4f$-radius 0.25 Å (Ref. 1)] compared to that of Ce [$4f$-radius 0.37 Å (Ref. 1)] would be expected in the former case to lead to reduced hybridization with the itinerant electrons and thus to sizable differences in the magnetic properties. Klaase *et al.*[2] have pointed out that compared to trivalent Ce, trivalent Yb forms relatively few compounds which order magnetically above helium temperatures, even though Yb^{3+} has a larger de Gennes factor. It is thus of considerable interest to compare the high-pressure evolution of the magnetic state for systems containing Ce to that for systems containing Yb.[3–5]

Kondo-lattice systems are characterized by a competition between the magnetic ordering of local moments through Ruderman-Kittel-Kasuya-Yosida (RKKY) interactions and the eventual demagnetization of the local moments by Kondo spin compensation. The magnetic behavior of a Kondo-lattice system is largely dictated by the parameter $\alpha \equiv |J_f N(E_F)|$, where J_f is the magnetic exchange coupling strength between conduction electrons and the $4f$ local moment and $N(E_F)$ is the density of conduction electron states at the Fermi energy.[5] Some time ago, Doniach[6] examined the one-dimensional "Kondo-necklace" problem in the mean-field approximation and obtained an antiferromagnetic ground state with the simple phase diagram shown schematically in Fig. 1, where the magnetic ordering temperature T_o is shown as a function of α. The competition between the RKKY interaction and Kondo spin compensation gives rise to a maximum in $T_o(\alpha)$ which is *markedly asymmetrical* about α_m, where $\alpha = \alpha_m$ when $T_o = T_o^{\max}$. This asymmetry in T_o versus α is anticipated on general grounds, since for $\alpha \ll \alpha_m$, T_o increases only gradually as $T_o \propto \alpha^2$, whereas for $\alpha \gg \alpha_m$, T_o falls off precipitously due to the exponential rise of the Kondo temperature $T_K \propto \exp(-1/\alpha)$ and the accompanying spin compensation (demagnetization) of the local moment. Doniach[6] has suggested that this general behavior should also hold for three-dimensional Kondo-lattice systems. The phase diagram in Fig. 1 has been shown to give a good qualitative account of experimental results on many Ce compounds[5,7] where the application of pressure is known to *increase* the value of α (and T_K),[8] thus moving the system to the right. In contrast, for Yb compounds both α and T_K would be expected to *decrease* with pressure since Yb's $4f^{13}$ magnetic state is stabilized when pressure is applied.[3,5,9]

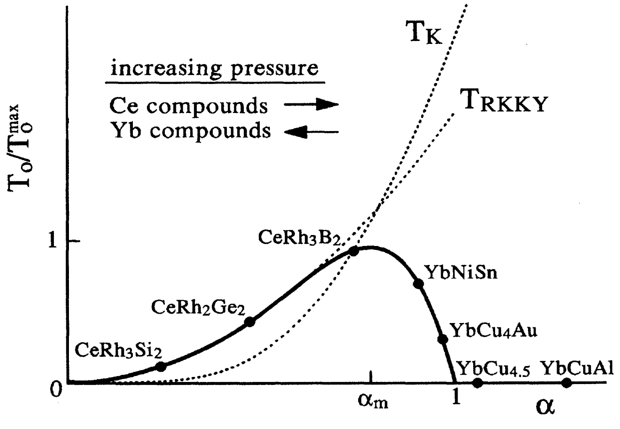

FIG. 1. Schematic representation of Doniach's phase diagram for a one-dimensional "Kondo necklace" adapted from Ref. 6. T_o is the magnetic ordering temperature, T_{RKKY} the RKKY interaction temperature, T_K the Kondo temperature, and $\alpha \equiv |J_f N(E_F)|$, where J_f is the exchange coupling and $N(E_F)$ the density of states. Estimated locations of various Ce and Yb compounds are indicated qualitatively (see text). The position of a given Ce (Yb) system in this diagram moves to the right (left) as pressure is applied.

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The asymmetry in the pressure dependence of T_o about $P_m \equiv P(T_o^{\max})$ should thus be in the opposite sense for Ce and Yb compounds.

Relatively few high-pressure studies of magnetic ordering have been carried out on Yb systems. The starting positions of three of these compounds at ambient pressure, as surmised from their high-pressure behavior, are displayed in Fig. 1. $YbCu_4Au$ orders antiferromagnetically at $T_o = 0.6$ K; the application of pressure causes the temperature of a resistivity anomaly T_ρ to pass through a maximum value near 2 K at 5 GPa,[10] but the relation of T_ρ to magnetic ordering is unclear. Both $YbCu_{4.5}$ and YbCuAl are nonmagnetic at ambient pressure; at pressures above 0.5 GPa for $YbCu_{4.5}$ (Ref. 11) and 10 GPa for YbCuAl,[9] anomalies in resistivity data are interpreted as indicating the onset of magnetic order. The Néel temperature $[T_o(0) \simeq 1.2$ K] of $YbBe_{13}$ is found to increase under pressure.[12] Further work is clearly necessary to fully characterize the change in the magnetic state of these systems under pressure.

The rare-earth compounds CeNiSn and YbNiSn crystallize in the orthorhombic ε-TiNiSi structure,[13] but display very different magnetic properties: CeNiSn is a Kondo insulator with an energy gap of ~6 K,[14] while YbNiSn is metallic and orders ferromagnetically below ~5.5 K,[15–18] with the magnetization along the c axis.[19] The magnetic susceptibility of YbNiSn reveals Curie-Weiss behavior at high temperatures with an effective moment of $\mu_{\text{eff}} \approx 4.3\mu_B$/Yb,[15,17] a value quite close to that ($4.54\mu_B$ /Yb) for free Yb^{3+}.

Previous hydrostatic high-pressure studies on YbNiSn to 1.7 GPa show that initially the Curie temperature T_o increases at the rapid rate $dT_o/dP \approx +2$ K/GPa, but appears to level off at higher pressures.[17] Since α decreases under pressure for Yb systems, these results would indicate that YbNiSn must lie to the right of the maximum in the phase diagram in Fig. 1, as indicated. It would be useful to extend these measurements to higher hydrostatic pressures to map out a larger portion of the phase diagram. In this work we have measured $T_o(P)$ for YbNiSn in a diamond-anvil cell (DAC) as a function of hydrostatic pressures as high as 38 GPa. $T_o(P)$ is found to pass through a maximum near $P_m \simeq 2$ GPa, exhibiting the asymmetric dependence of T_o on α seen in Fig. 1. For pressures above 9.4 GPa, no ferromagnetic transition could be detected.

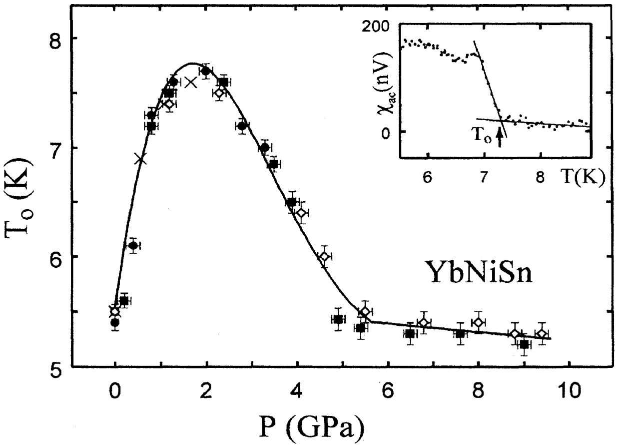

FIG. 2. The dependence of the Curie temperature T_o of YbNiSn on increasing hydrostatic pressure. (●,■,◇) data from present experiments. (×) data from Ref. 17. The solid line is a guide to eye. Inset: measured ac-susceptibility signal in nanovolts for a ~1-μg sample of YbNiSn at 0.8 GPa after subtraction of a temperature-dependent background. The applied ac field is 18 Oe at 2.2 kHz. The onset of the magnetic transition defines T_o.

The polycrystalline sample of YbNiSn was prepared by melting stoichiometric amounts of the constituent elements in a sealed molybdenum crucible and post annealing at 750 °C for five days.[17] The sample was found to have the anticipated ε-TiNiSi structure.[13] The high-pressure apparatus consists of a Cu-Be diamond-anvil clamp using 1/6 carat diamonds with 0.5-mm culets. Gaskets of Ta-W with diameter 3 mm and thickness 300 μm are preindented to 60 μm. The ~1-μg sample (~80-μm diam) with volume $\sim 10^{-4}$ mm^3 is placed together with small pieces (~20-μm diam) of ruby in a 330-μm diam hole drilled through the center of the gasket. The pressure clamp is placed in a continuous flow cryostat and superfluid ^{4}He is loaded into the gasket hole at 2 K to serve as the pressure medium. The pressure in the gasket hole is changed at room temperature by loading a membrane[20] with helium gas to force the diamonds together. The melting curve of ^{4}He lies above room temperature for $P \geq 12$ GPa. Care was taken that neither the anvil faces nor the gasket walls press directly onto the sample. The magnitude of the pressure in the cell is determined by the standard ruby fluorescence technique.[21] The good hydrostaticity of the pressure, even at pressures (38 GPa) well above the melting curve of He, is indicated by the fact that the ruby fluorescence lines remain sharp. The Curie temperature is detected inductively by a sensitive measurement of the ac susceptibility $\chi_{\text{ac}}(T)$ using a PAR 124 lock-in amplifier. After the subtraction of a temperature-dependent background from $\chi_{\text{ac}}(T)$,[7] the ferromagnetic transition becomes clearly visible, as seen in the inset in Fig. 2. Further details of the high-pressure techniques used are given elsewhere.[22]

The pressure dependence of T_o for YbNiSn was determined in three separate experiments on three distinct pieces taken from the same sample. For all three pieces the ambient pressure value, $T_o(0) = 5.45 \pm 0.07$ K, is in excellent agreement with previous studies.[15–18] In Fig. 2 we compare the $T_o(P)$ dependence in the present work to results from the previous study to 1.7 GPa.[17] $T_o(P)$ is seen to rapidly increase with pressure at the rate +1.7 K/GPa, pass through a maximum at $P_m \approx 2$ GPa, and then decrease at a slower rate, exhibiting the anticipated asymmetry about $P = P_m$ for decreasing α seen in Fig. 1. Between 5 and 9 GPa, T_o decreases only relatively slowly with pressure. For 9.4 GPa $\leq P \leq 38$ GPa no ferromagnetic transition whatsoever could be detected above 2 K. Upon release of pressure to 0 GPa from the highest pressure in the experiment, T_o always returned to its original ambient pressure value.

The phase diagram in Fig. 1 has been used to account for the behavior of many Ce compounds.[7,23–28] In Fig. 3 we show T_o data for the selected Ce compounds $CeRh_3(B_{1-x}Si_x)_2$ (Refs. 7 and 29), $CeRh_2(Si_{1-x}Ge_x)_2$,[24,26] and $CePd_2(Si_{1-x}Ge_x)_2$,[25,26] where a large portion of the Doniach phase diagram is mapped out either by the application of hydrostatic pressure for $x = 0$ (relative volume V/V_m decreases) or by the substitution of Si for B or Ge for

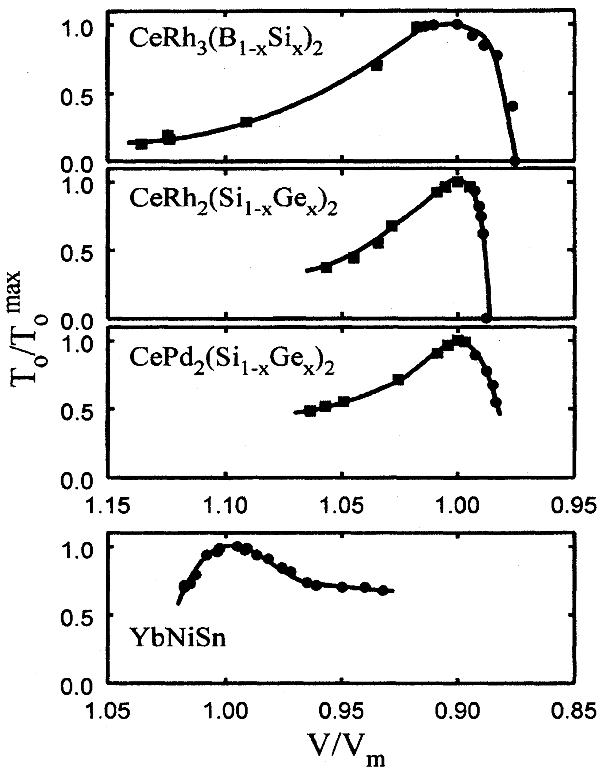

FIG. 3. The relative ordering temperature $T_o/T_o^{\max}$ for CeRh$_3$(B$_{1-x}$Si$_x$)$_2$ ($T_o^{\max}\simeq120$ K), CeRh$_2$(Si$_{1-x}$Ge$_x$)$_2$ ($T_o^{\max}\simeq38$ K), CePd$_2$(Si$_{1-x}$Ge$_x$)$_2$ ($T_o^{\max}\simeq11$ K), and YbNiSn ($T_o^{\max}\simeq7.7$ K) versus relative volume V/V_m, where V_m is the volume at which $T_o=T_o^{\max}$. Value of V at given pressure is estimated as discussed in Ref. 32. Circles (●) give results of high-pressure experiment for $x=0$, squares (■) for substitution experiments (see Ref. 7 for details). Solid lines are a guide to eye.

Si which expands the lattice (relative volume V/V_m increases). For all three Ce systems the dependence of T_o on the relative volume V/V_m bears a close resemblance to the phase diagram in Fig. 1, where α increases under pressure. The marked asymmetry in $T_o(V)$ about $V=V_m$ is apparent for the data in Fig. 3. That this asymmetry is real, and not due to an inequivalence of decreasing V/V_m through applied pressure or increasing V/V_m through chemical substitution, is indicated by the fact that for CeRh$_2$Ge$_2$, the dependence of T_o on sample volume is approximately the same, $d\ln T_o/d\ln V\simeq-12$ to -15, in both hydrostatic pressure[30] and substitution[24] (Si for Ge) experiments.

At the bottom of Fig. 3 we also include the data for YbNiSn from Fig. 2 to the same scale as for the Ce compounds. The asymmetry in T_o about $V=V_m$ is apparent, but is seen to run in the opposite sense compared to the Ce compounds. This is because for Yb compounds, in contrast to Ce compounds, both α and T_K are known to *decrease* with pressure, as emphasized above. The sign of dT_K/dP is opposite in Ce and Yb compounds, but how do the respective magnitudes compare? Changes in T_K are best estimated from bodily shifts of the magnetic contribution to solid-state properties, such as the electrical resistivity, magnetic susceptibility, thermoelectric power, and specific heat, along the logarithmic temperature axis.[8] If less data is available, dT_K/dP can be estimated by a careful determination of the pressure dependence of various coefficients and characteristic temperatures which scale with T_K. Examples are $A^{-1/2}$, θ_p, θ_m, and γ^{-1}, where A is the coefficient of the quadratic temperature dependence of the resistivity at low temperatures, θ_p is the paramagnetic Curie temperature, θ_m is the temperature of the susceptibility maximum, and γ is the low-temperature specific-heat coefficient.[5,31] To characterize the dependence of T_K on pressure or sample volume for a given system, it is convenient to define a "Kondo" Grüneisen parameter $\Omega_K\equiv-\partial\ln T_K/\partial\ln V=B(\partial\ln T_K/\partial P)$. For a complete discussion of Grüneisen parameters for Ce, Yb, and U compounds, see Ref. 5. Some values of (Ω_K) from Ref. 5 are CeRu$_2$Si$_2$ (80), CeCu$_6$ (115), CePt$_2$Si$_2$ (26), CeInCu$_2$ (83), CePtSi$_2$ (47), YbCu$_2$Si$_2$ (−48), YbCu$_{4.5}$ (−23), YbCuAl (−50), and YbCu$_4$Ag (−28). It can be seen that the values of Ω_K for most Ce and Yb compounds are comparable in magnitude, but opposite in sign. It is thus not surprising that the dependence of T_o on (V/V_m) for YbNiSn in Fig. 3 bears some resemblance to that for the Ce systems. A notable difference in the YbNiSn data is the flattening out in T$_o(V)$ for $V/V_m<0.96$. A possible explanation can be given by considering the relation $T_o\propto J^2$, where the total exchange interaction J between the conduction electrons and a local $4f$ moment can be divided up into its s, p, d, and f partial-wave components, $J=J_s-3J_p+5J_d-7J_f$.[8] For YbNiSn at ambient pressure, J_f dominates and Kondo-lattice-like behavior (Fig. 1) is obtained. However, at sufficiently high pressure $|J_f|$ will have decreased to the extent that the relatively slow pressure dependence of $J\approx J_s-3J_p+5J_d$ will determine that of T_o. The disappearance of the ferromagnetic transition for $P>9.4$ GPa signals either a ferromagnetic→paramagnetic transition or perhaps a ferromagnetic→antiferromagnetic transition; the present apparatus is unable to detect the weak transition to antiferromagnetic order. Such magnetic transitions may or may not be accompanied by structural transitions.

In conclusion, we have found that the Curie temperature of YbNiSn passes through a maximum as a function of hydrostatic pressure in a markedly asymmetric fashion. This asymmetry in $T_o(P)$ is opposite to that for Ce compounds. Within Doniach's Kondo-lattice model it is shown that this asymmetry can be readily understood as originating from the fact that the Kondo temperature increases with pressure for Ce compounds, but decreases for Yb compounds.

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[1] J. T. Waber and D. T. Cromer, J. Chem. Phys. **42**, 4116 (1965).

[2] J. C. P. Klaase, F. R. de Boer, and P. F. de Châtel, Physica B **106**, 178 (1981).

[3] J. S. Schilling, in *Physics of Solids Under High Pressure*, edited by J. S. Schilling and R. N. Shelton (North-Holland, Amsterdam, 1981), p. 345.

[4] J. S. Schilling, Physica B **139-140**, 369 (1986).

[5] J. D. Thompson and J. M. Lawrence, in *Handbook on the Physics and Chemistry of Rare Earths*, edited by K. A. Gschneidner, Jr., L. Eyring, G. H. Lander, and G. R. Choppin (North-Holland, Amsterdam, 1994), p. 383.

[6] S. Doniach, in *Valence Instability and Related Narrow Band Phenomena*, edited by R. D. Parks (Plenum, New York, 1977).

[7] A. L. Cornelius and J. S. Schilling, Phys. Rev. B **49**, 3955 (1994).

[8] J. S. Schilling, Adv. Phys. **28**, 657 (1979).

[9] J. M. Mignot and J. Wittig, in *Physics of Solids Under High Pressure* (Ref. 3), p. 311.

[10] E. Bauer, E. Gratz, R. Hauser, L. Tuan, A. Galatanu, A. Kottar, H. Michor, W. Perthold, G. Hilscher, T. Kagayama, G. Oomi, N. Ichimiya, and S. Endo, Phys. Rev. B **50**, 9300 (1994).

[11] L. Spendeler, D. Jaccard, J. Sierro, and M. François, J. Low Temp. Phys. **94**, 585 (1994).

[12] J. D. Thompson, Z. Fisk, and J. O. Willis, in *17th International Conference on Low Temperature Physics*, edited by U. Eckern, A. Schmid, W. Weber, and H. Wühl (North-Holland, Amsterdam, 1984), p. 323.

[13] A. E. Dwight, J. Less-Common Met. **93**, 411 (1983).

[14] F. G. Aliev, V. V. Moschalkow, V. V. Kozyrkov, M. K. Zalyalyutdinow, V. V. Pryadun, and R. V. Skolzdra, J. Magn. Magn. Mater. **76-77**, 295 (1988).

[15] M. Kasaya, T. Tani, F. Iga, and T. Kasuya, J. Magn. Magn. Mater. **76-77**, 278 (1988).

[16] P. Bonville, P. Bellot, J. A. Hodges, P. Imbert, G. Jéhanno, G. Le Bras, J. Hammann, G. Chevrier, P. Thuéry, L. D. D'Onofrio, A. Hamzić, and A. Barthélémy, Physica B **182**, 105 (1992).

[17] G. Sparn, J. D. Thompson, and A. Hamzić, J. Alloys Compd. **181**, 197 (1992).

[18] L. D'Onofrio, A. Hamzić, and A. Fert, Physica B **171**, 266 (1991).

[19] M. Kasaya, T. Tani, K. Kawate, T. Mizushima, Y. Isikawa, and K. Sato, J. Phys. Soc. Jpn. **60**, 3145 (1991).

[20] W. B. Daniels and W. Ryschkewitsch, Rev. Sci. Instrum. **54**, 115 (1983).

[21] G. J. Piermarini, S. Block J. D. Barnett, and R. A. Forman, J. Appl. Phys. **46**, 2774 (1975).

[22] S. Klotz, J. S. Schilling, and P. Müller, in *Frontiers of High-Pressure Research*, edited by H. D. Hochheimer and E. D. Etters (Plenum, New York, 1991).

[23] A. Eiling and J. S. Schilling, Phys. Rev. Lett. **46**, 364 (1981).

[24] C. Godart, L. C. Gupta, C. V. Tomy, J. D. Thompson, and R. Vijayaraghavan, Europhys. Lett. **8**, 375 (1989).

[25] I. Das and E. V. Sampathkumaran, Phys. Rev. B **44**, 9711 (1991).

[26] J. D. Thompson, R. D. Parks, and H. Borges, J. Magn. Magn. Mater. **54-57**, 377 (1986).

[27] D. Gignoux and J. Voiron, J. Magn. Magn. Mater. **54-57**, 363 (1986).

[28] S. A. Shaheen, J. S. Schilling, M. Abd-Elmeguid, H. Micklitz, P. Klavins, and R. N. Shelton, Physica B **139-140**, 410 (1986).

[29] S. K. Malik, G. K. Shenoy, S. K. Dhar, P. L. Paulose, and R. Vijayaraghavan, Phys. Rev. B **34**, 8196 (1986).

[30] J. D. Thompson, Y. Uwatoko, T. Graf, M. F. Hundley, D. Mandrus, C. Godart, L. C. Gupta, P. C. Canfield, A. Migliori, and H. A. Borges, Physica B **199-200**, 589 (1994).

[31] N. B. Brandt and V. V. Moshchalkov, Adv. Phys. **33**, 373 (1984).

[32] The volumes are estimated using the Birch equation of state $V/V_0=(1+B'P/B)^{-1/B'}$. For $CeRh_3B_2$, the value of $B=141$ GPa is taken from K. S. Athreya, Ph.D. thesis, Iowa State University, 1986, and an estimated $B'=4$ was used. Since the bulk modulus for $CeRh_2Si_2$, $CePd_2Si_2$, and YbNiSn have not as yet been measured, the relationship $BV_0=$constant as determined for the RAl_2 series from T. Penney *et al.*, Solid State Commun. **44**, 1199 (1982), was used to estimate B from a measured compound. The values used are 117 GPa for $CeRh_2Si_2$ and 112 GPa for $CePd_2Si_2$ and $B'=4.6$ for both are estimated using the values for isostructural $CeCu_2Si_2$ of $B=120$ GPa and $B'=4.6$ from I. L. Spain *et al.*, Physica B **130-140**, 449 (1986). For YbNiSn an estimated $B'=4$ and $B=83$ GPa, scaled from the values for RAl_2 of Penney *et al.*, are used.