# Competing Anisotropies in the Ferromagnetic Kondo-Lattice Compound YbNiSn: Observation of a Complex Magnetic Ground State under High Pressure

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The $^{170}$Yb high pressure Mössbauer-effect technique has been used to investigate on a microscopic level the ground state properties of the ferromagnetic (FM) Kondo-lattice compound YbNiSn. Unlike general expectations, we find for $0 \leq p \leq 3$ GPa a stable moment behavior while $T_C$ is enhanced to its maximum value. For $p > 3$ GPa we observe a gradual change of the FM state to a complex magnetic ground state. This is suggested to be due to a volume dependent competition between the anisotropy of the magnetic exchange interaction and the crystal electric field anisotropy. [S0031-9007(96)01381-6]

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The discovery that some Yb intermetallic compounds reveal many of the interesting Kondo-related properties which are found in Ce compounds has generated considerable excitement [1,2]. This is due to the fact that $Yb^{3+}$ in its $4f^{13}$ configuration with one $4f$ hole can be considered as the counterpart to the $4f^1$ configuration of $Ce^{3+}$ with one $4f$ electron. The common point of interest in these systems is that their ground state critically depends on the competition between the indirect magnetic intersite interaction (RKKY) between $4f$ local moments via the conduction electrons and the on-site Kondo interaction which favors a nonmagnetic ground state via moment compensation [3]. The delicate balance between these two interactions (with characteristic energies $T_{\mathrm{RKKY}}$ and $T_K$, respectively) is theoretically described by Doniach [4] for a one-dimensional Kondo lattice in a magnetic phase diagram depending on the exchange interaction $J$ between $4f$ and conduction electrons.

Among Yb-based intermetallic compounds orthorhombic YbNiSn ($\epsilon$-TiNiSi structure) has recently attracted considerable interest as being a ferromagnetic (FM) ($T_C = 5.65$ K) Kondo-lattice (KL) system: At high temperatures the magnetic susceptibility reveals Curie-Weiss behavior with an effective moment $\mu_{\mathrm{eff}} \approx 4.3\mu_B$ [5] close to the value of the free $Yb^{3+}$ ion ($\mu_{\mathrm{eff}} \approx 4.54\mu_B$). At low temperatures the interionic magnetic exchange coupling is found to be strongly anisotropic and competes with the crystal electric field (CEF) anisotropy. This competition results in an unusual situation where the Yb magnetic moments lie along the $c$ axis although the $a$ axis is the easy magnetization axis [6]. For temperatures $T < T_C$ the Yb magnetic moments have a saturated value of $\mu_S = 0.85\mu_B$ which is lower than the value $\mu_{\mathrm{CEF}} = 1.1\mu_B$, as estimated from the analysis of the paramagnetic state by considering the influence of the CEF [6]. The reduction of $\mu_S$ is attributed to the hybridization of the localized $4f$-electrons with conduction electrons. At low temperatures YbNiSn reveals a relatively high electronic specific heat coefficient $\gamma \approx 300$ mJ mol$^{-1}$K$^{-2}$ [7] suggesting that a heavy electron state coexists with magnetic order of reduced magnetic moments.

These findings very recently have motivated several high pressure groups to investigate the effect of pressure $(p)$ on the transport, magnetic, and structural properties of YbNiSn. Measurements of the resistivity at pressures $p \leq 1.7$ GPa [8] have shown that $T_C$ strongly increases with $p$ reaching $T_C = 7.6$ K at $p = 1.7$ GPa. Very recent high pressure ac-susceptibility $[\chi_{\mathrm{ac}}(p)]$ measurements [9] on YbNiSn over an extended pressure range $0 \leq p \leq 38$ GPa reveal that the enhanced $T_C$ passes through a maximum at $p \approx 2$ GPa and then falls to $T_C = 5.3$ K for $6 \leq p \leq 9.4$ GPa. These results [8,9] have been qualitatively discussed within the Doniach model. At higher pressures, however, the authors [9] reported evidence for an unstable FM state of YbNiSn which cannot be simply understood within the Doniach model: the ferromagnetic $\chi_{\mathrm{ac}}$ signal *disappeared* for pressures $p \geq 9.4$ GPa, a fact which is taken as an indication of a transition from the FM state to an antiferromagnetic or nonmagnetic state. In contrast to this, recent high pressure resistivity measurements for $0 \leq p \leq 13$ GPa on YbNiSn reveal that $T_C$ is nearly pressure independent for $6 \leq p \leq 13$ GPa [10]; i.e., no indication of a discontinuous change of the type of magnetic order is observed at $p = 9.4$ GPa. Also a possible pressure-induced structural phase transition at $p = 9.4$ GPa could be excluded from high pressure x-ray diffraction measurements on YbNiSn which indicate a stable structure for $p \leq 26.4$ GPa [10].

Despite these extensive experimental efforts on YbNiSn such macroscopic high pressure experiments do not provide any information about the pressure effect on the Yb magnetic moment and the type of magnetic order which are known to be intimately connected to the crystal electric field anisotropy in many KL compounds [3,11].

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Obviously, this information is of fundamental interest for a better understanding of the ground state properties of magnetically ordered KL systems.

It is for this reason that we have investigated for the first time on a *microscopic* level the effect of pressure on the magnetic and electronic properties of a magnetically ordered Kondo-lattice system up to pressures of 7 GPa and temperatures $1.8 \leq T \leq 9$ K using the $^{170}$Yb high pressure Mössbauer effect (ME) technique [12]. This microscopic method is a powerful tool for the determination of pressure-induced changes of the Yb magnetic moment $[\mu_{\mathrm{Yb}}(p)]$, the Curie temperature $[T_C(p)]$ and the electric field gradient (EFG) at the Yb site which reflects the Yb local site symmetry. $\mu_{\mathrm{YB}}(p)$ is obtained by measuring the pressure dependence of the effective magnetic hyperfine (hf) field $B_{\mathrm{eff}}$ ($T \rightarrow 0$ K) at the $^{170}$Yb nucleus, since $B_{\mathrm{eff}}$ is directly proportional to $\mu_{\mathrm{Yb}}$ ($B_{\mathrm{eff}} = C\mu_{\mathrm{Yb}}, C = 102\ \mathrm{T}\ \mu_B^{-1}$ [6]). $T_C(p)$ is obtained by measuring the temperature dependence of $B_{\mathrm{eff}}$ at different pressures. The change of the EFG with $p$ is obtained from the pressure dependence of the quadrupole splitting $E_Q = eQV_{zz}$, where $V_{zz}$ is the EFG at the Yb nucleus and $Q$ is the nuclear quadrupole moment of the $I = 2$ excited state. Since the EFG in YbNiSn is dominated by the contribution from the aspherical charge distribution of $4f$ and $6p$ electrons [6,13], the pressure dependence of $E_Q$ should give information about the change of the CEF anisotropy with $p$.

Our results show that unlike general expectations the enhancement of $T_C$ for pressures $0 \leq p \leq 3$ GPa is *not* accompanied by a pressure-induced change of the Yb magnetic moment, which indicates a stable moment behavior. Most interesting is our finding of a gradual pressure-induced magnetic phase transition for $p > 3$ GPa from the FM ground state to a complex magnetic state. It is shown that the magnetic ground state properties of the FM KL compound YbNiSn are governed by a volume dependent competition between the magnetic exchange and CEF anisotropy.

For our high pressure study we have prepared a special $^{170}$TmB$_{12}$ high activity ($\sim$200 mCi) Mössbauer source on small active diameter of less than 3 mm. Polycrystalline YbNiSn was prepared by melting stoichiometric amounts of the constituents in a sealed molybdenum crucible and by postannealing the sample at 800 °C for several days. High pressure $^{170}$Yb-ME measurements up to 7 GPa and at temperatures $1.8 \leq T \leq 9$ K were performed using a Chester-Jones type high pressure setup as described elsewhere [14].

Figure 1 shows $^{170}$Yb ME spectra of YbNiSn in the paramagnetic phase ($T = 9$ K) at different pressures. All spectra were fitted assuming a pure quadrupole splitting. The asymmetry parameter $\eta$ of the EFG [$\eta = |(V_{xx} - V_{yy})/V_{zz}|$, where $V_{xx} \leq V_{yy} \leq V_{zz}$ and $\eta \leq 1$] is found to be $0.2 \leq \eta \leq 0.6$ and the values of $E_Q$ and $\eta$ at ambient pressure are in very good agreement with those previously reported [6]. As evident from Fig. 1 (and Fig. 3(a)) $E_Q$ is gradually enhanced with increasing $p$, particularly above $p = 3$ GPa.

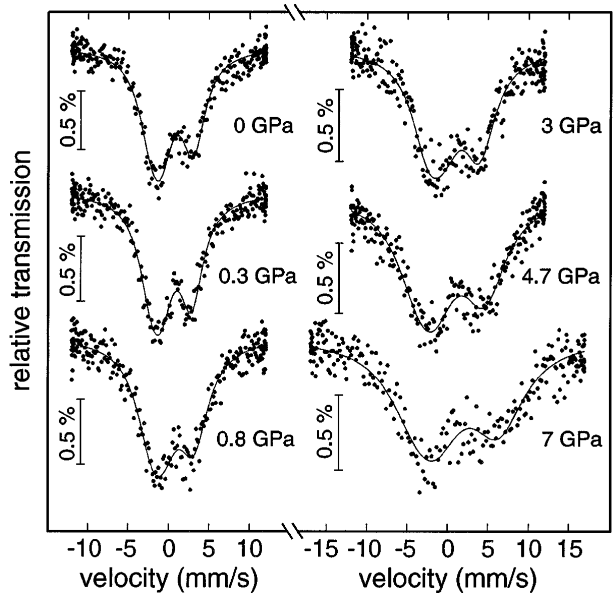


FIG. 1. Typical $^{170}$Yb ME spectra of YbNiSn in the paramagnetic state collected at $T = 9$ K and different pressures.

In Fig. 2 we show ME spectra in the magnetically ordered state ($T = 1.8$ K) for different pressures. The spectra were fitted with a full Hamiltonian assuming magnetic hyperfine fields as free parameters and by fixing

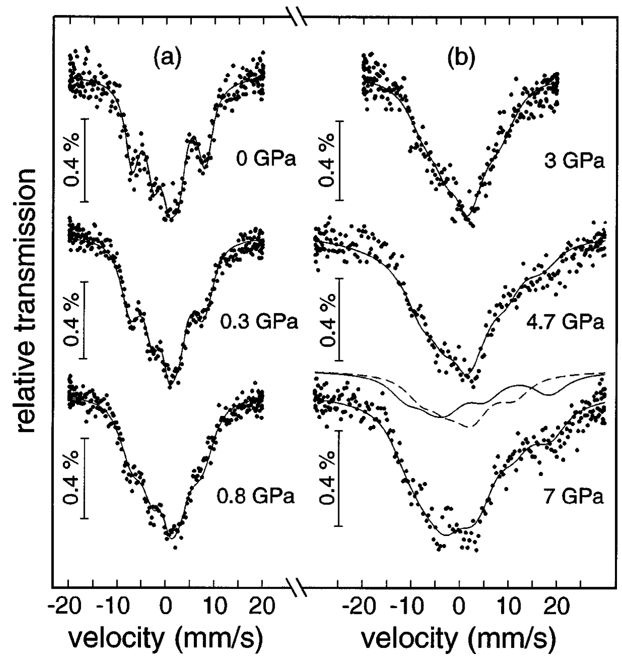


FIG. 2. Typical $^{170}$Yb ME spectra of YbNiSn in the magnetically ordered state collected at $T = 1.8$ K and different pressures. Dashed and solid lines in the ME spectrum at 7 GPa display subspectra of the low and high field components, respectively.

the values of $E_Q$ and the linewidth to values obtained in the paramagnetic phase. At low pressures $p < 3$ GPa $B_{\text{eff}}$ shows nearly constant values of $B_{\text{eff}} \approx 85$ T in good agreement with previous ambient $p$ results [6], revealing an almost pressure independent Yb magnetic moment. Above a critical pressure $(p_c)$ of about 3 GPa, a high field (moment) component appears with $B_{\text{eff}} \approx 175$ T [see also Fig. 3(b)], whose fraction grows at the cost of that of the low field component. This indicates a pressure-induced magnetic phase transition for $p \geq 3$ GPa from the FM state to a new, complex magnetic ground state. A *reversible* behavior upon releasing the pressure is observed. The pressure dependence of the two $B_{\text{eff}}$ components and their weight averaged value $\overline{B}_{\text{eff}}$ are shown in Fig. 3(b).

In addition, we have deduced the values of $T_C(p)$ from the temperature dependence of $B_{\text{eff}}$ at different pressures. The results of $T_C(p)$ are shown in Fig. 3(c) together with those observed in recent high pressure resistivity measurements on YbNiSn [10]. The agreement between the Mössbauer and resistivity data and previous results of others [8,9] is obvious.

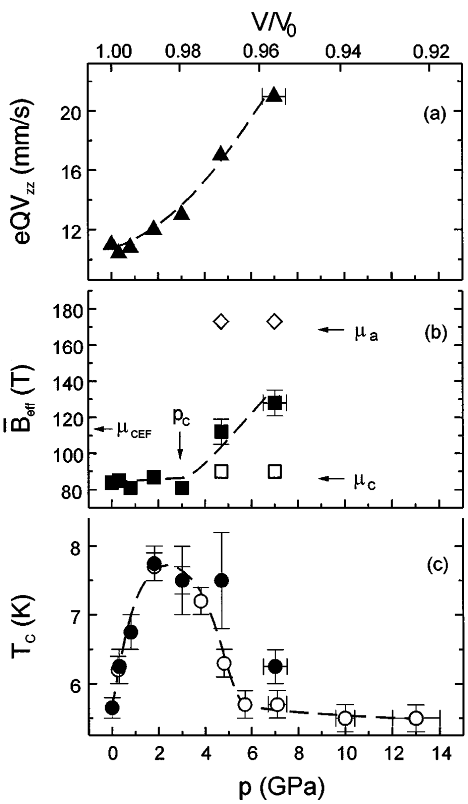


FIG. 3. (a) Pressure dependence of the quadrupole splitting $eQV_{zz}$ at $T = 9$ K; (b) pressure dependence of the average magnetic hf field $\overline{B}_{\text{eff}}$ (■) at $T = 1.8$ K. Symbols (□) and (◇) denote the pressure dependence of the low and high field components, respectively. Arrows mark the corresponding values of the Yb magnetic moment along the $c$ $(\mu_c)$ and $a$ axis $(\mu_a)$ and the estimated value of $\mu_{\text{CEF}}$ by considering CEF effects according to Ref. [6]. $p_c = 3$ GPa is the critical pressure; and (c) pressure dependence of $T_C$ as obtained from our high pressure $^{170}$Yb ME measurements on YbNiSn (•) and from high pressure resistivity measurements (∘) [10]. Dashed lines through data points are guides to the eye.

First, we discuss the pressure-induced changes of $\mu$ and $T_C$. As is evident from Fig. 3(b) the value of $\overline{B}_{\text{eff}} \approx 85$ T (or $\mu_{\text{Yb}} \approx 0.83\mu_B$) is almost pressure independent in the low pressure range $0 \leq p \leq 3$ GPa which is typical for stable moment systems [15–17]. On the other hand, $T_C$ is strongly enhanced with $p$ in the same pressure range to its maximum value ($T_C \approx 7.7$ K). This finding of a pressure independent $\mu_{\text{Yb}}$ is in contradiction to the suggestion that the magnetic ground state of YbNiSn exhibits a *reduced* Yb moment [6] due to Kondo screening. If one follows this suggestion in the framework of the Doniach model, one would expect a related increase of both the Yb magnetic moment and $T_C$ with increasing $p$ due to the dramatic decrease of the Kondo temperature $T_{\text{K}}$ with respect to $T_{\text{RKKY}}$. Here we want to mention that this theoretical picture works fairly well for the magnetically ordered Ce KL system $\text{CeSi}_x$ [15]. In this system it has been shown that the pressure dependence of the saturation magnetization is directly related to that of $T_C$. This indicates that the pressure dependence of $T_C$ and $\mu_{\text{Yb}}$ in YbNiSn cannot be simply understood on the basis of the Doniach model assuming a reduced Yb magnetic moment at ambient pressure. Our observation of a pressure-induced magnetic phase transition at higher pressures gives additional indication that the magnetic ground state properties of YbNiSn are more complex (see below).

Next, we discuss the pressure-induced changes of $\mu$ and $T_C$ in the pressure range $3 < p \leq 7$ GPa. As mentioned before, we find for $p > p_c$ that the FM state of YbNiSn becomes unstable: while $T_C$ decreases sharply with $p$, we observe the appearance of a high field component ($B_{\text{eff}} = 175$ T or $\mu = 1.72\mu_B$) whose fraction increases with increasing $p$. Thus the decrease of $T_C$ upon increasing $p$ is directly related to the transition from a low field to high field state which we attribute to a magnetic phase transition from the FM state at ambient pressure to a new, complex magnetic state. In order to explain the formation of such a state, we recall that the FM state at ambient pressure is governed by a competition between the anisotropy of the magnetic exchange interaction and that of the CEF. As shown in Ref. [6], the alignment of the Yb magnetic moments along the $c$ axis although the $a$ axis is the easy magnetization axis is related to the fact that the anisotropy of the magnetic exchange interaction *overcomes* the CEF anisotropy. Model calculations and magnetization measurements on single crystal YbNiSn [6] show that the saturation value of the Yb magnetic moment along the $a$ axis ($\mu_{\text{Yb}}^a \approx 1.65\mu_B$) is *twice* that along the $c$ axis. Here we emphasize that we find for $p > 3$ GPa a value of the high field component of $B_{\text{eff}} = 175$ T which is equivalent to the value of the Yb moment along the $a$

axis. This leads us to suggest that the pressure-induced magnetic ground state is accompanied by a corresponding change of the Yb moment orientation from the $c$ axis to the easy $a$ axis. The change of the moment direction is also evidenced by a change in the angle $\Theta$ between $B_{\mathrm{eff}}$ and $V_{zz}$. Such a phase transition is only possible if one assumes that pressure enhances the CEF anisotropy with respect to the anisotropy of the magnetic exchange interaction and thereby favors the orientation of the Yb moments along the easy magnetization $a$ axis. This interpretation is strongly supported by our finding of a gradual increase of $V_{zz}$ [see Fig. 3(a)] with pressure (particularly for $p > 3$ GPa) which displays a corresponding increase of the CEF anisotropy. As mentioned before, this increase of $V_{zz}$ with $p$ should arise from a corresponding change of the aspherical charge distribution of the $4f$ and/or $6p$ electrons with increasing pressure. However, our finding of a stable moment behavior for $p < p_c$ and a gradual change of the orientation of the local Yb moments for $p > p_c$ indicates that the ground state wave functions of the $4f$ electrons remain almost unchanged as pressure increases. Therefore, the observed increase of $V_{zz}$ with pressure should be mainly due to a pressure-induced change of the Yb $6p$ contribution to $V_{zz}$. Indeed, the $6p$ contribution to $V_{zz}$ in rare earth compounds is considerably large (e.g., $Gd^{3+}$ intermetallic compounds [13]) and is known to be very sensitive to volume changes (e.g., $Gd_2Co_{17}N_x$ [18]).

Here, we want to refer to our $^{170}$Yb ME measurements at ambient $p$ on the related isostructural antiferromagnetic KL compound YbPtAl ($T_N = 5.8$ K) [19]: in YbPtAl, with a lattice volume at ambient $p$ corresponding to that of YbNiSn at $p \approx 5$ GPa, we find [20] in the paramagnetic state a single, large value of $eQV_{zz} \approx 30$ mm/s. In addition, we observe at $T = 4.2$ K a coexistence of a high and a low field component with $B_{\mathrm{eff}}$ of 130 and 60 T, respectively, similar to YbNiSn at $p > p_c$. These results strongly support our high pressure results on YbNiSn.

Finally, our finding of a gradual change of the FM ground state of YbNiSn for $p > p_c = 3$ GPa to a complex magnetic state with $p$ can explain the loss of the FM signal in very recent $\chi_{ac}(p)$ measurements of YbNiSn for $p \geq 9.4$ GPa [9] if the pressure-induced magnetic state has a vanishing FM component.

In conclusion, we have shown that the magnetic ground state properties of the FM KL compound YbNiSn are governed by a volume dependent competition between the magnetic exchange and CEF anisotropy rather than by a direct competition between Kondo and RKKY interactions. We believe that our microscopic high pressure study should stimulate theoretical and experimental efforts for a better understanding of the ground state properties of KL systems.

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