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Valence and magnetic transitions in $YbInCu_4$ probed using ^{63}Cu nuclear quadrupole resonance under high pressure

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Abstract

Applying pressure to the valence fluctuating compound $YbInCu_4$ lowers the valence transition temperature and stabilizes the high temperature (HT) localized spin state. For pressure above 2.4 GPa, the valence transition is completely suppressed and the magnetically ordered state arises as a new ground state below 2.4 K. In order to elucidate microscopically the relation between the valence and magnetic transitions in f electron system, we performed ^{63}Cu NQR measurements of $YbInCu_4$ under pressure up to 2.5 GPa. The experimental results provide clear evidence for the onset of the magnetic ordering in the pressure-stabilized HT state above 2.3 GPa. The nuclear spin–lattice relaxation rate $1/T_1$ in the HT state shows $1/T_1 =$ constant behaviour down to 3.0 K and a divergence increase just below 2.4 K. We concluded that the pressure-stabilized localized electron state of $YbInCu_4$ transforms directly into a magnetically ordered state, without displaying any intermediate heavy Fermi liquid behaviour.

1. Introduction

$YbInCu_4$ is the sole stoichiometric compound which shows a temperature-induced first-order isostructural valence transition at $T_V \simeq 42$ K and ambient pressure [1, 2]. The valence change of the Yb ion at T_V is estimated as 0.1 from x-ray absorption spectra and thermal expansion measurements with a subsequent valence of 2.9 below T_V [2, 3]. Above T_V the magnetic susceptibility follows Curie–Weiss-type behaviour, indicating well localized 4f moments. At $T = T_V$, the magnetic susceptibility shows a sudden drop with a concomitant unit-cell volume expansion of 0.5% [2, 4]. Below $T < T_V$ $YbInCu_4$ takes on an itinerant electron state with a moderately enhanced linear coefficient of specific heat ($\gamma = 50$ mJ mol^{-1} K^{-2}) [2, 5].

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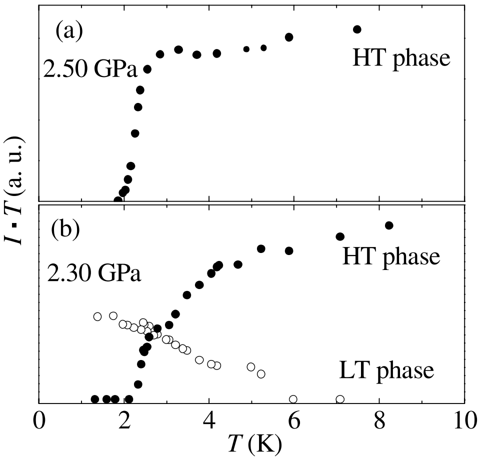

Figure 1. ^{63}Cu NQR intensity multiplied by temperature ($I \cdot T$) plotted against temperature at (a) 2.50 and (b) 2.30 GPa.

Applying pressure lowers the valence transition temperature and stabilizes the localized f electron high temperature (HT) state. This is presumably because pressure suppresses the volume expansion at the valence transition. It is interesting to study the ground state realized in the HT phase of YbInCu$_4$ after the valence transition is completely suppressed. Recent magnetization measurements for Yb$_{0.8}$Y$_{0.2}$InCu$_4$ [6] and electrical resistivity and ac susceptibility measurements for YbInCu$_4$ [7] revealed that the pressure-stabilized HT state has a ferromagnetic ordering ground state below 1.7 and 2.4 K, respectively. The mechanism of this magnetic ordering observed only under pressure is an important subject for clarification. In this paper we present the results of nuclear quadrupole resonance (NQR) measurements of ^{63}Cu in YbInCu$_4$ at high pressures up to 2.5 GPa. Our results provide clear evidence for a direct transition of the pressure-stabilized localized f electron state into a magnetically ordered state, without displaying any intermediate Fermi liquid behaviour.

2. Experimental results

YbInCu$_4$ crystallizes in the cubic AuBe$_5$-type structure with $F43m$ space symmetry and single crystals are grown using a flux method [8]. For the NQR measurements under pressure several single crystals were mounted inside a piston–cylinder pressure cell made of nonmagnetic NiCrAl/BeCu alloy and Daphne oil 7373 was used as a pressure-transmitting medium. The magnitude of the pressure was determined by monitoring the superconducting transition of a tin manometer. The ^{63}Cu NQR (nuclear spin $I = 3/2$) measurements at zero magnetic field were carried out using a phase-coherent spin-echo spectrometer. The resonance frequency ν_Q of the ^{63}Cu NQR in the localized f electron high temperature (HT) phase suddenly shifts to a lower frequency at the transition $T_V(P)$ to the valence fluctuating low temperature (LT) phase [9]. The value of $T_V(P)$ under pressure is determined as the mid-point temperature of the resonance frequency shift.

At 2.50 GPa, the NQR spectrum originating from the HT phase is observed at 15.5 MHz down to 2.4 K without the sudden frequency shift. This provides clear evidence for complete suppression of the valence transition. The NQR signal from the HT phase at 2.50 GPa shows an abrupt intensity decrease below $\simeq$2.4 K and completely disappears below 1.9 K as shown in figure 1(a), although the signal from the LT phase is not observed. It is expected that the NQR intensity $I(T)$ multiplied by temperature, $I(T) \cdot T$, would be nearly temperature independent if the system did not show any transition. The disappearance of the NQR signal is

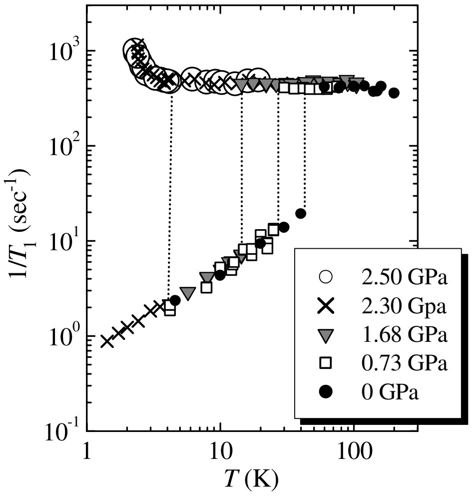

Figure 2. The temperature dependence of the ^{63}Cu spin–lattice relaxation rate $1/T_1$ in a pressure range between 0 and 2.50 GPa.

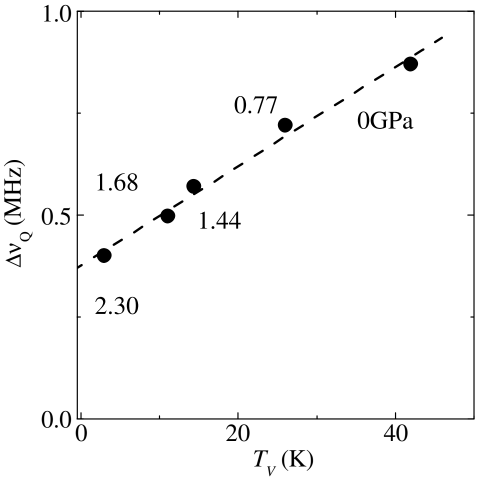

Figure 3. The dependence on T_V of the NQR frequency shift $\Delta\nu_Q = \nu_Q(\mathrm{HT}) - \nu_Q(\mathrm{LT})$ associated with the valence transition.

an indication that the pressure-stabilized HT phase transforms into a magnetically ordered state below $T_M = 2.4$ K for $P \geqslant 2.4$ GPa. This result is consistent with previous ac susceptibility measurements [7]. In the magnetically ordered state, in addition to a severe broadening and/or shift of the NQR spectrum, the spin–lattice relaxation rate might be substantially enhanced, making observation of the signal difficult.

In order to study the interplay between valence and magnetic transitions in more detail, we focus our interest on the critical pressure region near 2.30 GPa. Two distinct resonance lines are observed at around 15.1 and 15.5 MHz in the temperature range between 2.4 and 5.0 K. Each signal intensity gradually changes with varying temperature through the valence transition. Below $\simeq$2.4 K the signal from the HT phase decreases more rapidly than above 2.6 K and completely disappears below 1.9 K as observed at 2.50 GPa, although the signal from the LT phase persists. This suggests that the magnetically ordered phase coexists with the LT phase at 2.30 GPa and below 2.4 K. The volume fraction of the LT phase at 1.6 K is estimated to be about 50% from NQR intensity consideration (figure 1(b)).

Figure 2 indicates the temperature dependence of the ^{63}Cu spin–lattice relaxation rate $1/T_1$ in the pressure range between 0 and 2.50 GPa. The temperature independent relaxation behaviour in the HT phase below 2.30 GPa suddenly changes into T_1T = constant metallic behaviour in the LT phase. The former indicates that the Yb 4f moments are well localized and the latter is characteristic of a Fermi liquid state. Applying pressure lowers $T_V(P)$ and extends the range of temperature independent $1/T_1$ behaviour of the HT state to lower temperature. The most important result can be seen in the $1/T_1$ behaviour of the HT phase stabilized by pressures of 2.30 and 2.50 GPa. $1/T_1$ remains constant down to $\sim$3.0 K and exhibits a divergent increase near 2.4 K. This behaviour is due to the critical slowing down of f spin fluctuations and is a precursor of long range magnetic ordering. The lack of a gradual change from the T_1 = constant to T_1T = constant behaviour, which is generally observed in many heavy fermion systems, indicates that the localized f electrons in the HT phase stabilized by pressure directly transform to the magnetically ordered state without taking any intermediate heavy fermion state.

3. Discussion

We show in figure 3 the frequency shift $\Delta\nu_{\mathrm{Q}} = \nu_{\mathrm{Q}}(\mathrm{HT}) - \nu_{\mathrm{Q}}(\mathrm{LT})$ at $T_{\mathrm{V}}(P)$ plotted against $T_{\mathrm{V}}(P)$ with pressure being an implicit parameter. It has been shown that the decrease in the volume expansion at T_{V} strongly correlates with the decrease in $\Delta\nu_{\mathrm{Q}}$ at T_{V} [10]. We found that $\Delta\nu_{\mathrm{Q}}$ versus T_{V} has a linear dependence and the extrapolation to $T_{\mathrm{V}}(P) = 0$ gives a finite intercept. This suggests that volume expansion occurs at the transition from the valence fluctuating Fermi liquid state to the magnetically ordered state, i.e., at the first-order transition. The complete suppression of the valence transition with pressure above $\simeq$2.4 GPa indicates the energy loss required for the volume expansion to exceed the energy gain of the electron system transforming to the Fermi liquid state. For pressure above $\simeq$2.4 GPa, the present NQR experiments provide clear evidence for a second-order magnetic phase transition from the localized f electron HT phase to the magnetically ordered state. The spin entropy in the pressure-stabilized HT phase is released by magnetic ordering.

4. Conclusion

In order to study microscopically the pressure effect on the valence and magnetic transition of $\mathrm{YbInCu_4}$, we performed an ^{63}Cu NQR experiment under high pressure up to 2.5 GPa. The experimental result provides clear evidence for the onset of magnetic ordering for pressure above $\simeq$2.4 GPa: the nuclear spin–lattice relaxation rate $1/T_1$ shows nearly temperature independent behaviour down to $\sim$3.0 K and exhibits a divergent increase just above 2.4 K. We conclude that the paramagnetic Yb spins of $\mathrm{YbInCu_4}$ at high pressure order magnetically by exchange interactions, and no signature of any Kondo spin compensation was observed.

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