NQR and T_1 studies of the high-pressure phase in $YbInCu_4$

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The pressure and temperature phase diagram of $YbInCu_4$ has been investigated by nuclear quadrupolar resonance (NQR) and spin-lattice relaxation rate (T_1^{-1}) experiments. The pressure dependence of the ^{63}Cu NQR frequency indicates that the first-order valence transition temperature, T_v, does not vanish continuously at the critical pressure ($P_c \approx 23.7$ kbar) and thus there is no quantum critical point ($T_v = 0$) in $YbInCu_4$. This result is consistent with the T_1^{-1} data, which show no evidence for non-Fermi-liquid behavior near P_c. For pressures $P \gtrsim P_c$, T_1^{-1} increases sharply near 2.4 K, which suggests the presence of critical fluctuations associated with ferromagnetic (FM) ordering. We analyze the T_1^{-1}, resistivity, and the pressure-enhanced susceptibility data in the mixed-valent state of $YbInCu_4$ and find no evidence to indicate that the pressure-induced FM phase can be described by the Stoner theory for itinerant ferromagnetism. Rather, the pressure-induced FM order may be due to pressure-stabilized Yb^{3+} local moments. We also examine the possibility of FM order induced by an external magnetic field near P_c, but find no evidence down to 1.5 K.

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I. INTRODUCTION

The intermediate valence material $YbInCu_4$ is one of the most intriguing rare-earth intermetallic compounds, as it exhibits a first-order valence transition at ambient pressure[1–4] from a high-temperature (HT) Yb^{3+} local-moment state to a low-temperature (LT) $Yb^{2.9+}$ mixed-valence state.[2,5] In order to understand this transition, which is uncommon among rare-earth compounds, many experiments have been performed on this material and its related compounds: $Yb_{1-x}In_xCu_2$,[1–4] $Yb_{1-x}Y_xInCu_4$,[6] and $YbIn_{1-x}M_xCu_4$ (M=Au, Ag, In, Cd, Tl, and Mg).[7–10] This valence transition is isostructural but with a ($\sim$0.5%) unit-cell volume increase below the valence transition temperature T_v,[11,12] analogous to the γ-α transition in Ce metal.[13] Since both the valence transition and Kondo temperature (T_K) are strongly influenced by the volume change,[2,3,10] the Kondo volume collapse model[13,14] has been proposed to explain this valence transition.[9] However, the Gruneisen analysis of T_K at the valence transition of $YbInCu_4$ cannot be interpreted by this Kondo volume effect,[15] and the change of T_v by the substitution of Yb by Y and Lu is also inconsistent with the volume change.[16] Therefore, in addition to the volume effect, the modifications of the band structure and conduction electron density at the valence transition are suspected to play an important role as well.[15,17,18] Other mechanisms such as the Falicov-Kimball model,[19–21] the Mott transition,[22,23] and the Anderson impurity model[9,24] have also been applied to explain this first-order valence transition, but all have had only partial success.[16]

Interest in the high-pressure phase in $YbInCu_4$ has been rekindled by a detailed pressure study of the magnetic susceptibility of RInCu$_4$ (R=Yb, Er, Ho, Dy, Tb, and Gd) by Svechkarev *et al.*[25] They found evidence for a possible pressure-induced ferromagnetic (FM) phase. Their data indicated that a background indirect exchange interaction between f moments in $YbInCu_4$ is FM, and a FM phase can be induced by the application of pressure for $P > 20$ kbar. Subsequent experiments of the resistivity and ac susceptibility have revealed signatures of this putative phase in $YbInCu_4$.[26] Pressure experiments in $Yb_{0.8}Y_{0.2}InCu_4$, which has a similar phase diagram to the parent compound but with a smaller critical pressure, also show evidence of the pressure-induced FM phase.[27] The HT local-moment state of $YbInCu_4$ is known to be stabilized by hydrostatic pressure.[15,28,29] Since the valence transition in $YbInCu_4$ is suppressed by pressure and nearly vanishes at the critical pressure where the ferromagnetism is just induced,[25,26] one might expect *a priori* that the FM phase arises from the uncompensated Yb^{3+} local moments in the HT phase. However, the pressure-induced ferromagnetism in $Yb_{0.8}Y_{0.2}InCu_4$ is itinerant, with a small moment ($\sim 0.05\mu_B/Yb^{3+}$).[27] In order to investigate the nature of the ferromagnetism in $YbInCu_4$, as well as to investigate the details of the phase diagram in the vicinity of the critical point, we performed nuclear quadrupolar resonance (NQR) and nuclear magnetic resonance (NMR) on $YbInCu_4$ to measure spectra and the nuclear spin-lattice relaxation rate, T_1^{-1}, under high pressure up to 26.3 kbar.

We find that T_v is suppressed to $\sim$2.4 K near the critical pressure ($P_c \sim 23.7$ kbar). For $P > P_c$, the valence transition disappears, i.e., no NQR signal is found from the mixed-valent state. There is no evidence of a quantum critical point (QCP), $T_v \to 0$, for this valence transition. For $P < P_c$, T_1^{-1} from the mixed-valent state exhibits Korringa behavior ($T_1 T$=const), a typical feature for Fermi liquids.[30] This result implies that the mixed-valent phase remains a Fermi liquid up to the critical pressure. The absence of non-Fermi-liquid (NFL) behavior sometimes characterized by $T_1 T \neq$ const in the vicinity of a QCP[31–34] also suggests the absence of a QCP.[35]

For $P \gtrsim P_c$ in the high-temperature (HT) phase, we observed a rapid increase of T_1^{-1} with decreasing temperature as the temperature approached the FM phase-transition temperature, $T_c \approx 2.4$ K. This divergence suggests the emergence

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of the FM phase as suggested from other experiments,[26] because the critical slowing-down of the spin fluctuations near a magnetic transition can contribute to nuclear spin-lattice relaxation.[36,37] We observe a coexistence of the mixed-valence state and the pressured-induced FM phase at 23.7 kbar, in which 6% of the ^{63}Cu NQR signal persists below T_c, while the remaining 94% of the signal is wiped out in the FM phase. We find no coexistence above 23.7 kbar.

Since the pressure-induced FM in $Yb_{0.8}Y_{0.2}InCu_4$ has itinerant features,[27] we consider the Stoner theory[38] of itinerant ferromagnetism in $Yb_{0.8}Y_{0.2}InCu_4$ and also in the analysis of the T_1^{-1} data along with the resistivity and pressure-enhanced susceptibility in the mixed-valence state of $YbInCu_4$. Our analysis suggests that the pressure-induced FM order in $YbInCu_4$ is due to the pressure-stabilized Yb^{3+} local moments rather than from strong correlations among itinerant electrons in the mixed-valence state. We also investigated the possibility of a magnetic-field-induced FM phase in $YbInCu_4$ at 23 kbar (near P_c), but found no evidence of magnetic order down to 1.5 K for fields up to 4 T.

The article is organized as follows. Experimental aspects and data of NQR and T_1^{-1} are described in Sec. II. Experimental results are discussed in Sec. III. Section IV summarizes our conclusions.

II. EXPERIMENTS

A. Details

Heat treatment is crucial to synthesize a high-quality $YbInCu_4$ sample.[12,39] In order to study the intrinsic properties and avoid sample ambiguity, we studied a high-quality flux-grown single crystal.[15] A standard phase-coherent pulsed NMR technique was used to obtain the ^{63}Cu and ^{115}In NQR/NMR spectra. The ^{63}Cu T_1^{-1} was measured by a standard nuclear spin saturation-recovery technique. We estimated the skin depth at the rf frequency used in our experiments to be $\gtrsim 60\ \mu$m covering several atomic layers. Therefore, our NQR/NMR and T_1 experiments measure bulk properties.

The experiments under pressure were performed in a hydrostatic clamp pressure cell.[40,41] A small lead pellet was buried into the NQR coil along with the $YbInCu_4$ single crystal in order to measure the pressure at low temperature.[42] The pressure uncertainty is estimated to be 0.5 kbar. The low viscous silicone oil (PolyEthylSyloxane, Grade no. 1) was used as the pressure medium, which does not solidify at room temperature when applying high pressure. In addition, this liquid forms a glasslike state at low temperature, so the possibility of inhomogeneous pressure and shear force inside this medium is minimized.

B. NQR/NMR spectra

The ^{63}Cu nucleus ($I=3/2$) has a quadrupole moment and is ideal for NQR and NMR measurements. For ^{63}Cu in a crystal site symmetry lower than cubic as in $YbInCu_4$, the electrical field gradients (EFGs) split the degenerate states into $|\pm 1/2\rangle$ and $|\pm 3/2\rangle$. The energy difference between the two states is proportional to the EFG and can be measured by

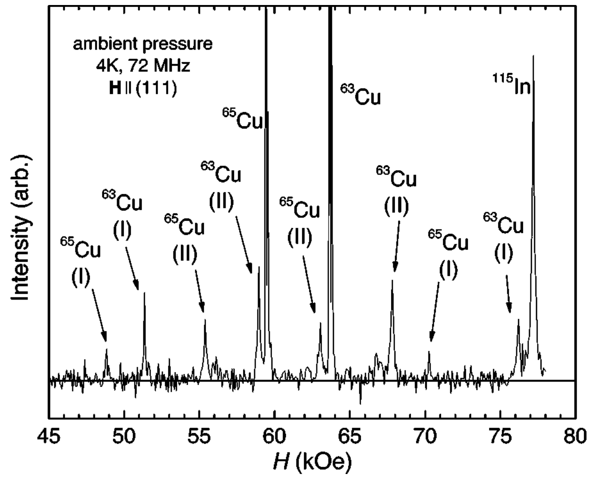

FIG. 1. Field-swept NMR spectrum of $YbInCu_4$ at a fixed frequency of 72 MHz for field $\mathbf{H}\|[111]$ direction at 4 K and ambient pressure. Two pairs of the quadrupolar peaks are symmetrically located on each side of the ^{63,65}Cu central peak and are denoted by (I) and (II).

NQR (i.e., NMR at zero field). The degeneracy can be further lifted by application of an external magnetic field and the transition between the states can be observed by NMR spectroscopy.

Figure 1 shows the field-swept NMR spectrum of our single crystal of $YbInCu_4$ measured at 72 MHz with the field $\mathbf{H}\|[111]$ direction at 4 K and ambient pressure. In the $F\bar{4}3m$ crystal structure of $YbInCu_4$,[43] there are four Cu sites per unit cell. By symmetry considerations, we expect the principal axes, $\vec{q}$, of the EFG to lie along the Yb-In-Cu bond in the [111] direction and to be axially symmetric.[44] For a field applied parallel to the [111] direction, there should be three transitions, with a splitting equal to the NQR frequency, ν_Q. However, only one of the four Cu sites will experience $\mathbf{H}\|\vec{q}$. For the other three sites, the angle between $\mathbf{H}$ and $\vec{q}$ should be $\theta=109°$. Indeed, we find two sets of lines for both the ^{63}Cu and ^{65}Cu, with intensity ratios $\sim 1:2.8$, labeled by (I) and (II) in Fig. 1. The (I) set corresponds to the Cu site for which $\mathbf{H}\|\vec{q}$, whereas the (II) set corresponds to the remaining three Cu sites. Therefore, we can conclude that the EFG is axially symmetric and $\vec{q}\|[111]$.

The ^{63}Cu NQR spectra have been measured in $YbInCu_4$ from ambient pressure to 26.3 kbar. We found that the ^{63}Cu NQR line shape has a Lorentzian form, as seen in other work.[44] Figure 2 gives the temperature dependence of the ^{63}Cu NQR frequency, ν_Q, and full width at half-maximum (FWHM) linewidth in $YbInCu_4$ at various pressures. The ambient pressure data were taken from Ref. 44. The steep change of ν_Q and the hysteresis seen at ambient pressure and 22.3 kbar (omitted at other pressures) at $T=T_v$ [Fig. 2(a)] is an indication of the first-order valence transition. The hysteresis is inferred from the coexistence of the HT and LT phases observed in the NQR spectra near T_v.[44] The discontinuous change of ν_Q at T_v is mainly due to the charge redistribution from the hybridization of the f and conduction electrons and only a small percent is due to a lattice-volume effect, which has been discussed in Ref. 44.

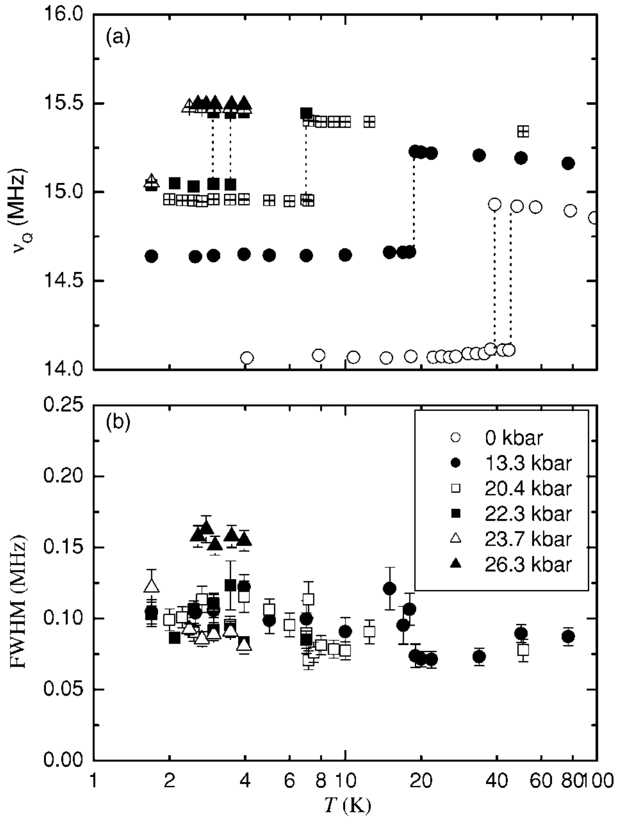

FIG. 2. Temperature dependence of the (a) NQR frequency ν_Q and (b) FWHM linewidth of the NQR spectra at various pressures. Dashed lines connect the discontinuous change of ν_Q. The two dashed lines at $P=0$ and 22.3 kbar indicate the hysteresis (omitted at other pressures).

Under pressure, T_v is suppressed, ν_Q increases for both HT and LT states, and the discontinuous jump of ν_Q at T_v decreases [Fig. 2(a)]. We find that for $P > 23.7$ kbar, the valence transition disappears and the ^{63}Cu signal from the HT phase vanishes for $T \lesssim 2.4$ K with no NQR signature of the LT mixed-valent state [see Fig. 3(c)]. At $P=23.7$ kbar, we observe a coexistence of the mixed-valent and FM phase at $T=1.5$ K, where the NQR spectrum in the LT state shows only $\sim$6% of the ^{63}Cu signal intensity compared to that of the HT state. Since this pressure $\sim$23.7 kbar is close to the published critical pressure 23.9 kbar,[26] the remaining signal may be wiped out in the putative FM phase, as suggested in Ref. 26. Above 23.7 kbar, all the ^{63}Cu signals from the LT state are wiped out for $T \lesssim 2.4$ K. The NQR signal in the putative FM phase has not been seen. However, NMR/NQR in a FM ordered phase is notoriously difficult as T_1 can be very short near the Curie temperature T_c, the linewidth becomes broad, and the internal magnetic fields from the FM order may also shift the resonance frequency beyond the tuning range of the NMR circuit.[36,37]

For $P \leqslant 23.7$ kbar, the linewidth is scattered around 0.1 MHz [Fig. 2(b)]. The broadening mechanism can be attributed to the distribution of the electric field gradients (EFGs), rather than magnetic inhomogeneity, because the ratio ($\sim$1.1) of the ^{63}Cu to ^{65}Cu NQR linewidths is approximately equal to the ratio ($\sim$1.082) of their quadrupole moments. This nearly temperature-independent NQR linewidth also provides another clue. If magnetic broadening were involved, the NQR linewidth would be expected to change with the temperature especially at $T=T_v$ as seen in the ^{115}In NMR linewidth,[39,45] because of the strong temperature dependence of the magnetic susceptibility.[39] X-ray experiments[2,4] on $YbInCu_4$ show no distortion of the crystal

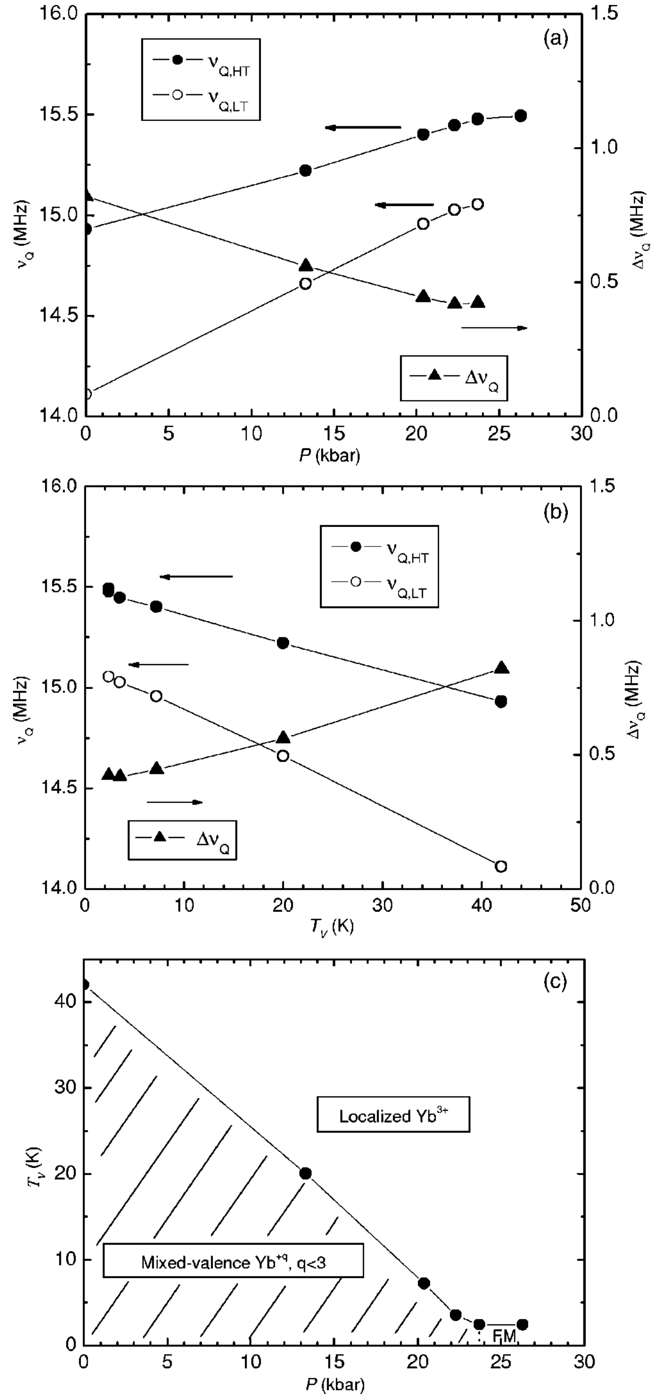

FIG. 3. (a) Pressure dependence of the NQR frequency ν_Q for ν_Q near $T=T_v$. Filled circles: ν_Q from the HT phase ($\nu_{Q,\mathrm{HT}}$). Open circles: ν_Q from the LT phase ($\nu_{Q,\mathrm{LT}}$). Triangles: the difference of ν_Q at T_v ($\Delta\nu_Q=\nu_{Q,\mathrm{HT}}-\nu_{Q,\mathrm{LT}}$). (b) The plots of ν_Q versus T_v and $\Delta\nu_Q$ versus T_v. (c) T_v-P phase diagram.

structure at the valence transition, except for the change of lattice constants. This result may explain why the NQR linewidth is nearly independent of temperature since the lattice disorder is not modified by the valence transition. The fact that the NQR linewidth [Fig. 2(b)] and the line shape[44] do not change across the valence transition suggests that the valence transition for $P<23.7$ kbar is nonmagnetic (not ferro- or antiferromagnetic).

The NQR linewidth given in Fig. 2(b) shows no obvious modification by pressure except for $P=26.3$ kbar, which suggests that the pressure is hydrostatic and there are no distortions to the crystal structure up to $P=23.7$ kbar. For $P=26.3$ kbar, the line broadening is still due to the distribution of EFGs rather than the magnetic broadening, as verified by the ratio of the ^{63}Cu to ^{65}Cu NQR linewidths. Therefore, the pressure gradient or distortion of the crystal structure may appear in the sample at this pressure.

The relations among ν_Q, T_v, and P obtained from Fig. 2(a) are plotted in Fig. 3. The values of T_v at various pressures were determined independently by the ac-susceptibility experiments. Figure 3(a) shows the pressure dependence of the NQR frequency for ν_Q near $T=T_v$. Both ν_Q from the LT phase ($\nu_{Q,\mathrm{LT}}$, open circles) and the HT phase ($\nu_{Q,\mathrm{HT}}$, filled circles) increase linearly with pressure. The former, however, increases faster by a factor of 2, in agreement with the result in Ref. 46. The difference, $\Delta\nu_Q$ $(=\nu_{Q,\mathrm{HT}}-\nu_{Q,\mathrm{LT}})$, is related to the valence difference of the HT and LT states[44] and is found to decrease with pressure [triangles in Fig. 3(a)]. Therefore, the valence of Yb in the mixed-valence state is expected to increase with P from +2.9 to close to +3 at the critical pressure.

The NQR frequency is linearly proportional to the EFG which arises from the ionic charges and itinerant electrons. We can write $\nu_Q=\nu_Q^{\mathrm{ion}}+\nu_Q^{e-}$, where ν_Q^{ion} and ν_Q^{e-} are the NQR frequencies from the ionic and electronic contributions, respectively.[44] The ions are considered as point charges at the lattice sites so that the EFG due to these ions is proportional to $1/V$, the inverse of the unit-cell volume. Therefore, ν_Q can be written as

$$\nu_Q=\nu_Q^{\mathrm{ion}}+\nu_Q^{e-}=\frac{\alpha}{V}+\nu_Q^{e-}, \tag{1}$$

where $\nu_Q^{\mathrm{ion}}=\alpha/V$ and α is a constant independent of temperature and pressure. With the assumption that ν_Q^{e-} is constant for $T<T_v$ and $T>T_v$, Nakamura *et al.* have compared the NQR with the thermal expansion data and obtained $\alpha=1.19\times10^4$ Å^3 MHz, $\nu_{Q,(T<T_v)}^{e-}=-18.61$ MHz, and $\nu_{Q,(T>T_v)}^{e-}=-17.94$ MHz.[44]

In order to understand the pressure dependence of ν_Q, we differentiate Eq. (1) with pressure as follows:

$$\frac{\partial\nu_Q}{\partial P}=\frac{\alpha}{V(0)}\left(\frac{-1}{V(0)}\frac{\partial V(P)}{\partial P}\right)_T+\frac{\partial\nu_Q^{e-}}{\partial P}=\frac{\alpha}{V(0)}\kappa_T+\frac{\partial\nu_Q^{e-}}{\partial P}$$

$$=(\nu_Q-\nu_Q^{e-})_{P=0}\kappa_T+\frac{\partial\nu_Q^{e-}}{\partial P}, \tag{2}$$

where κ_T is the isothermal compressibility. The slopes of ν_Q in Fig. 3(a) give $\partial\nu_Q/\partial P_{(T<T_v)}=0.0406$ MHz/kbar and $\partial\nu_Q/\partial P_{(T>T_v)}=0.0232$ MHz/kbar. According to Ref. 29, $\kappa_{T,(T<T_v)}=1.20$ Mbar^{-1} and $\kappa_{T,(T>T_v)}=0.99$ Mbar^{-1}, both of which are not expected to change much with temperature for $T>T_v$ and $T<T_v$ except at T_v.[11] With the compressibility and our NQR data, Eq. (2) gives $\partial\nu_Q^{e-}/\partial P_{(T<T_v)}=0.0013$ MHz/kbar and $\partial\nu_Q^{e-}/\partial P_{(T>T_v)}=-0.0093$ MHz/kbar. We found $\partial\nu_Q^{e-}/\partial P\ll\partial\nu_Q^{\mathrm{ion}}/\partial P$ in both the LT and HT states. This suggests that the pressure-dependent ν_Q in Fig. 3(a) is primarily dominated by the pressure-dependent unit-cell volume, not by the ν_Q^{e-}. Although $\partial\nu_Q^{e-}/\partial P\ll\partial\nu_Q^{\mathrm{ion}}/\partial P$, we found that the opposite sign of $\partial\nu_Q^{e-}/\partial P$ for the LT and HT states gives $\partial\nu_Q^{e-}/\partial P_{(T>T_v)}-\partial\nu_Q^{e-}/\partial P_{(T<T_v)}=-0.0106$ MHz/kbar, which is about 61% of the $\partial\Delta\nu_Q/\partial P$ [$=-0.0174$ MHz/kbar from Fig. 3(a)] at T_v. This result shows that pressure affects the charge distribution as well as the volume, and both are responsible for the pressure-dependent $\Delta\nu_Q$ in Fig. 3(a). In other words, the valence transition under pressure involves not only the change of volume but also of the electron distribution in $YbInCu_4$. That is reflected as well in a large increase in the Hall number below T_v.[17]

The linear pressure dependence of ν_Q in Fig. 3(a) can also be understood by Eq. (1). Since $\partial\nu_Q^{e-}/\partial P\ll\partial\nu_Q^{\mathrm{ion}}/\partial P$, we can write $\partial\nu_Q(P)/\partial P\approx\partial[\alpha/V(P)]/\partial P$. According to Ref. 29, the pressure-dependent unit-cell volume can be described by $V(P)=(1-P\kappa_T)V(0)$. Because $P\kappa_T\ll1$, we further obtain $\nu_Q(P)\approx[\alpha/V(0)](1+P\kappa_T)$, which therefore gives the linear dependence of $\nu_Q(P)$ on P. The slope $\alpha\kappa_T/V(0)$ with $V(0)$ from Ref. 11 is also quantitatively consistent with the slopes in Fig. 3(a).

Figure 3(b) shows ν_Q versus T_v. Note that $\Delta\nu_Q$ decreases with T_v, however $\Delta\nu_Q$ does not vanish as T_v is extrapolated to zero. This result suggests that the T_v cannot be suppressed to zero by any pressure, which is in agreement with our finding that T_v is only suppressed to $\sim$2.4 K at P_c and no valence transition is observed above the critical pressure. Therefore, we find there is no quantum critical point $(T_v=0)$ in the T_v-P phase diagram of $YbInCu_4$.

The T_v-P phase diagram is given in Fig. 3(c) and is similar to the one proposed by Mito *et al.*, except for the point near the critical pressure,[26] where we find that the T_v line terminates at 23.7 kbar rather than at 24.5 kbar. The discrepancy may be due the the uncertainties in determining T_v (because of hysteresis) and the pressure, or the phase diagram may be sample-dependent in the vicinity of the critical point. The boundary between the mixed-valent and FM phases is denoted by a dotted line since the coexistence of the two phases is observed from the NQR spectrum at 23.7 kbar as mentioned previously. However, whether the critical point at $P=P_c$ is a tricritical point or not is unclear from our NQR data.

C. Nuclear spin-lattice relaxation

The temperature dependence of T_1^{-1} measured at various pressures is given in Fig. 4. Once again, the first-order nature of the valence transition is evident from the discontinuity of T_1^{-1}. We find that T_1^{-1} is dominated by magnetic fluctuations rather than the EFG fluctuations, as the T_1^{-1} ratio of ^{63}Cu to

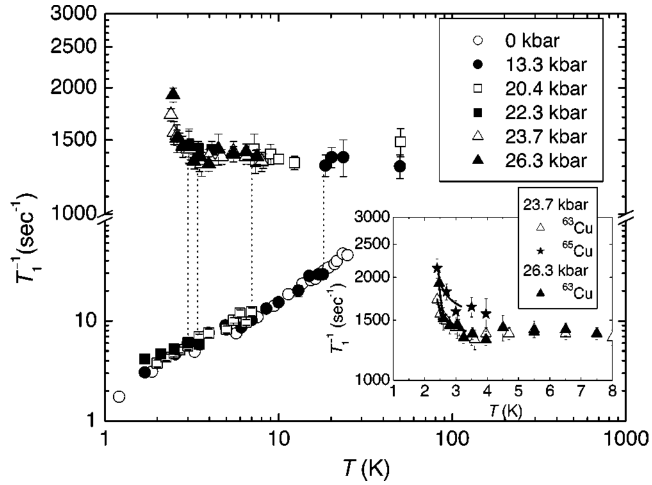

FIG. 4. Temperature dependence of the ^{63}Cu spin-lattice relaxation rate T_1^{-1} at several different pressures. Inset: T_1^{-1} of ^{63}Cu and ^{65}Cu at 23.7 and 26.3 kbar.

^{65}Cu is found to agree with $(^{65}\gamma/^{63}\gamma)^2$ (=1.148, γ: gyromagnetic ratio) (see Fig. 5). If EFG fluctuations were important, then the T_1^{-1} ratio would be equal to $(^{65}Q/^{63}Q)^2$ (=0.879, Q: nuclear quadrupole moment).[47]

In the HT state near the valence transition, T_1^{-1} is approximately independent of pressure for $P<23.7$ kbar. In the LT state, T_1^{-1} shows metallic behavior (T_1T=const),[47] where the constant is unchanged by P. For $P \geqslant 23.7$ kbar, however, T_1^{-1} in the HT state starts to increase near the putative FM phase-transition temperature, $T_c \approx 2.4$ K.[26] This increase is also verified by the ^{65}Cu T_1^{-1} (see the inset in Fig. 4). Since the spin-lattice relaxation is dominated by magnetic fluctuations, this increase is probably due to the critical slowing down of collective fluctuations near T_c,[36] suggesting that the underlying phase is magnetic in origin and is probably FM as revealed in other experiments.[26,27]

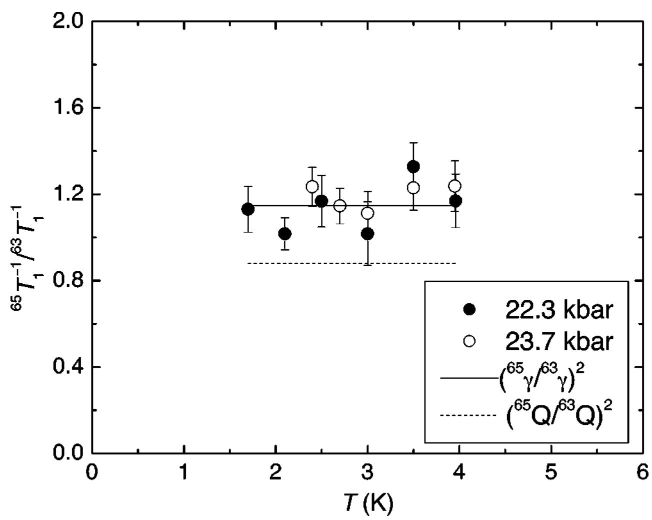

FIG. 5. The $(T_1^{-1})^2$ ratio of ^{63}Cu to ^{65}Cu at 22.3 kbar (filled circles) and 23.7 kbar (open circles). Solid line: $(^{65}\gamma/^{63}\gamma)^2=1.148$, the ratio of square of the gyromagnetic ratio γ of ^{65}Cu to ^{63}Cu. Dashed line: $(^{65}Q/^{63}Q)^2=0.879$, the ratio of square of the quadrupole moment Q of ^{65}Cu to ^{63}Cu.

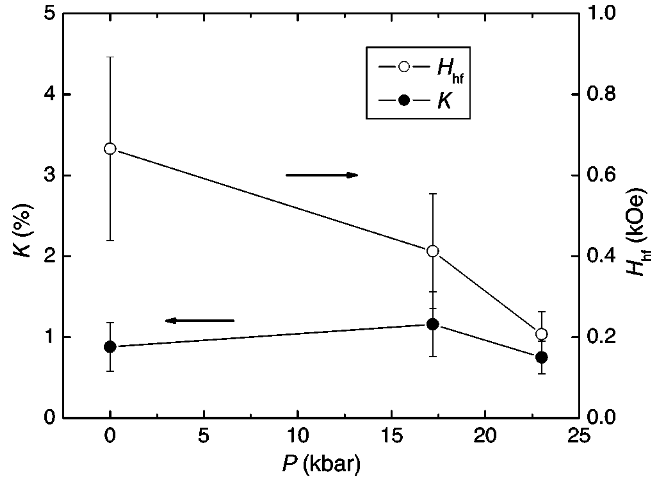

FIG. 6. ^{115}In NMR frequency shifts (K, filled circles) and hyperfine fields ($H_{\rm hf}$, open circles) at 1.5 K for different pressures.

In many Ce- and Yb-based intermetallic compounds, the spin-lattice relaxation is dominated by the magnetic fluctuations of the f local moments,[48] and is given by[49]

$$\frac{1}{T_1} \simeq (\gamma H_{\rm hf}/\mu_B)^2 k_B T \chi \frac{1}{\hbar\Gamma}, \tag{3}$$

where γ, μ_B, k_B, χ, and $\hbar$ are the gyromagnetic ratio, Bohr magneton, Boltzmann constant, magnetic susceptibility, and Planck's constant, respectively. $H_{\rm hf}$ is the transferred hyperfine field at the resonance nucleus and Γ is the fluctuation rate of the f-electron spins. For many Ce- and Yb-based compounds, $\Gamma \propto T_K$ and $\chi \propto 1/T_K$ for $T<T_K$, which gives[30]

$$\frac{1}{T_1 T} \propto \left(\frac{H_{\rm hf}}{T_K}\right)^2 \quad \text{for } T<T_K. \tag{4}$$

Unlike most Kondo systems, $YbInCu_4$ has two Kondo temperatures: $T_{K,\rm HT} \approx 20$ K and $T_{K,\rm LT} \approx 450$ K for the HT and LT states, due to the first-order valence transition.[9,50] Note that since $T \ll T_K$ in the LT state, we recover Korringa behavior in this phase, which explains the linear temperature dependence of T_1^{-1} in the mixed-valent state, as seen in Fig. 4. Since pressure is known to reduce $T_{K,\rm HT}$ as well as T_v,[25] one might expect $T_{K,\rm LT}$ to decrease with the pressure. Therefore, $\chi_{\rm LT}$ ($\propto 1/T_{K,\rm LT}$) would be expected to *increase* with pressure, exactly as observed in Refs. 15, 18, and 51. On the other hand, the value of $(T_1T)^{-1}$ in the LT state (Fig. 4) remains P-independent. This result is surprising since T_K in Eq. (4) decreases with pressure. In order for $(T_1T)^{-1}$ to remain constant, the value of $H_{\rm hf}$ must decrease with the pressure as T_K.

Information about the hyperfine field can be deduced from the Knight shift, which is related to $H_{\rm hf}$ by $K=[H_{\rm hf}/(N_A\mu_B)]\chi+K_0$, where N_A is Avogadro's constant.[47] K_0 is a temperature-independent term. Figure 6 shows the ^{115}In shifts at 1.5 K ($<T_v$) and at three different pressures. Although we do not know how K_0 changes with pressure, we find that K is roughly constant with pressure within experimental error (Fig. 6), which suggests that the term $[H_{\rm hf}/(N_A\mu_B)]\chi$ is likely independent of pressure. Since $\chi_{\rm LT}$

increases with pressure,[15,18] we infer, then, that H_{hf} does change with pressure (open circles in Fig. 6). This may not be surprising because H_{hf} is dominated by the RKKY-like transferred hyperfine interaction, which depends on the spatial distance, and it varies with pressure.[48] Evidence for such P-dependent hyperfine fields has been observed in other systems.[52] Since the product $H_{hf}\chi \propto H_{hf}/T_K$ is independent of pressure, $(T_1T)^{-1}$ in the mixed-valent state should not change with pressure [see Eq. (4)], consistent with our T_1 results (Fig. 4).

III. DISCUSSION

A. T_v-P phase diagram

The NQR and T_1 data indicate that the valence transition in $YbInCu_4$ is suppressed by the pressure and suggest the presence of a magnetic phase for $P \gtrsim 23.7$ kbar and $T \lesssim 2.4$ K. We also find that there is no QCP for $T_v=0$ in the T-P phase diagram. If T_v could be suppressed to zero, the discontinuity of ν_Q should vanish continuously at $T_v=0$, in contrast to our observation. Similarly, a discontinuity of the resistivity at T_v that does not vanish as T_v is extrapolated to zero, seen in Refs. 26 and 53, is further evidence against $T_v=0$. Furthermore, if there were a QCP point, one might expect non-Fermi-liquid (NFL) behavior to appear near the critical pressure, a feature we do not observe.

As mentioned in Sec. II coexistence of the mixed-valent and FM phase is observed at 1.5 K near P_c. Coexistence of the two phases has also been reported in Ref. 26, in which the system undergoes a valence transition first for $P < P_c$, and then a FM transition for $T < T_v$. This scenario is different from our observation of the two-phase coexistence. In both cases, inhomogeneity of the sample or pressure could explain the coexistence and we cannot conclude whether the coexistence is intrinsic or extrinsic.

B. Pressure-induced FM phase

In Sec. II C, a pressure-induced FM phase is inferred from the rapid increase of T_1^{-1} near the transition temperature for $P \gtrsim 23.7$ kbar. The critical slowing-down of spin fluctuations near T_c should enhance nuclear spin relaxation so that T_1^{-1} diverges at T_c and shows critical behavior of $T_1^{-1} \propto [T_c/(T-T_c)]^{\eta}$, where η is the critical exponent.[36] In general, η can depend on the crystal structure and hyperfine interaction and also may be model-dependent.[54] For example, Moriya proposed $\eta=3/2$ for a cubic ferromagnet.[55] We obtained $\eta \approx 0.20 \pm 0.03$ and $T_c=2.37 \pm 0.06$ K from the fits to the T_1^{-1} critical behavior for temperatures up to $1.25T_c \approx 3$ K (see the inset in Fig. 4), however the significance of $\eta \approx 0.2$ is unclear.

The pressure study of $Yb_{0.8}Y_{0.2}InCu_4$ given in Ref. 27 reveals a T_v-P phase diagram similar to that for $YbInCu_4$, except that $Yb_{0.8}Y_{0.2}InCu_4$ has a lower P_c. A pressure-induced FM phase is also found in $Yb_{0.8}Y_{0.2}InCu_4$ around 8 kbar with $T_c=1.7$ K and this FM order is claimed to be itinerant because of the small moment,[27] which suggests that the FM phase arises from itinerant electrons in the mixed-valent state rather than from local moments in the HT state.

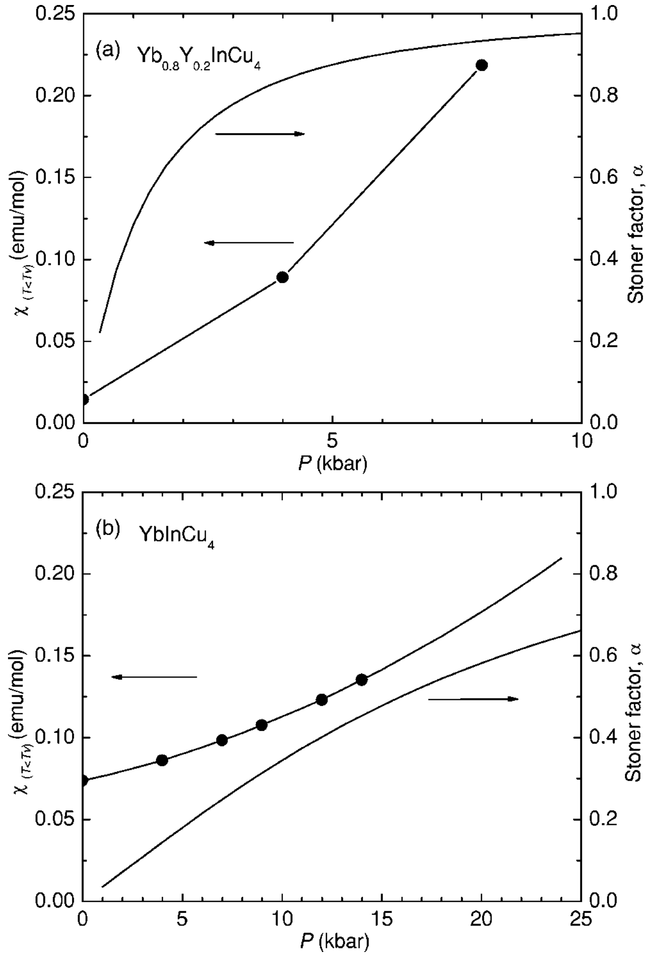

FIG. 7. Pressure dependence of the susceptibility (filled circles) for $T < T_v$ and the Stoner factor (solid line) (see text) in (a) $Yb_{0.8}Y_{0.2}InCu_4$ and (b) $YbInCu_4$. [Susceptibility data in (a) and (b) are taken from Refs. 27 and 18, respectively.]

We speculate, therefore, that Stoner theory can explain the ferromagnetism in $Yb_{0.8}Y_{0.2}InCu_4$. Stoner theory states that the strong e^--e^- interaction can enhance the itinerant-electron susceptibility by a factor of $1/(1-\alpha)$, i.e.,[36]

$$\chi = \frac{\chi_0}{1-\alpha}, \tag{5}$$

where χ_0 is the susceptibility without electron interactions and α is a parameter related to the conduction electron density of states and electron-electron interaction. For $\alpha \gtrsim 1$ (Stoner criteria), itinerant ferromagnetism can appear.[36]

Enhancement of χ_{LT} (a temperature-independent Pauli susceptibility for $T < T_v$) with pressure has been observed in $Yb_{0.8}Y_{0.2}InCu_4$, but has been attributed to the increasing contribution of magnetic Yb^{3+} with pressure.[27] In order to examine whether the pressure-enhanced χ_{LT} is due to the Stoner effect, we assume that $\alpha=\alpha(P)$ is a function of P and $\chi_0=\chi(P=0)$. By fitting the pressure-dependent $\chi_{LT}(P)$ with $\chi(P)=\chi(0)/[1-\alpha(P)]$, we obtain $\alpha(P)$ which is plotted in Fig. 7(a) for $Yb_{0.8}Y_{0.2}InCu_4$. We found that α is close to unity at 10 kbar where the FM phase arises. We speculate

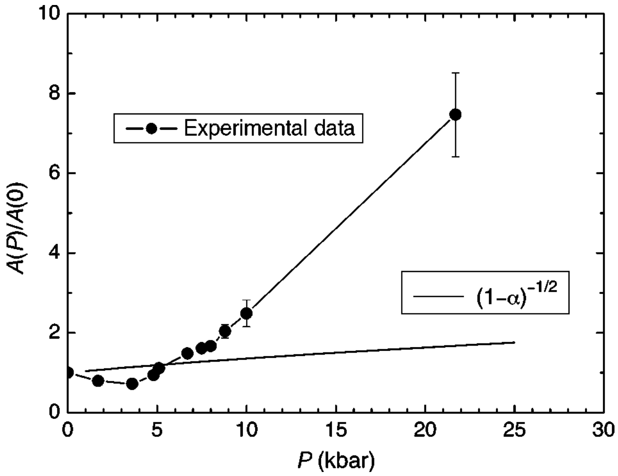

FIG. 8. The pressure-dependent $A(P)$ obtained from the resistivity experiments (Ref. 56) (circles) and calculated $(1-\alpha)^{-1/2}$ (line) (see text).

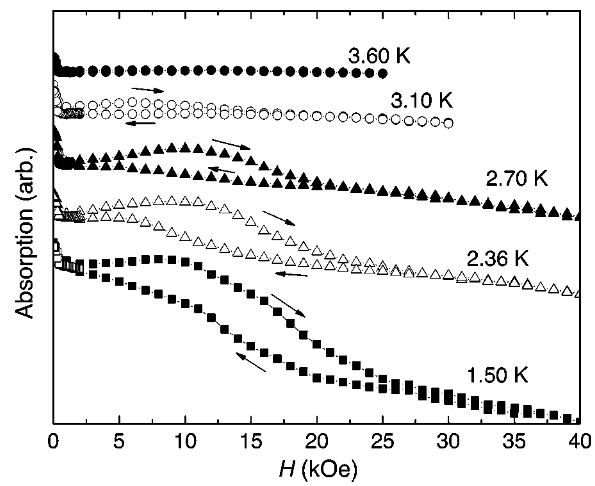

FIG. 9. Absorption power measured in the NMR coil containing $YbInCu_4$ at $P=23$ kbar as a function of applied magnetic field for various fixed temperatures. The initial drop of the absorption curves at fields below ~1 kOe is due to the Pb (served as manometer) superconducting transition ($H_c \approx 800$ Oe).

that if the true χ_0 instead of $\chi(P=0)$ were used in the analysis, α would be expected to be even closer to 1.

As mentioned in Sec. II C, the pressure-enhanced χ_{LT} of $YbInCu_4$ is attributed to the pressure-suppressed T_K.[18] Since the Stoner theory seems to explain the enhanced susceptibility for the itinerant ferromagnetism in $Yb_{0.8}Y_{0.2}InCu_4$, we consider the possible Stoner effect in $YbInCu_4$. According to Moriya's theory, the strong e^--e^- interaction can affect T_1^{-1} in metals as follows:

$$T_1^{-1} = (\pi\gamma^2\hbar k_B T/\mu_B^2)K^2F(\alpha), \quad (6)$$

where $F(\alpha)$ is a complicated function of α and can only be calculated numerically.[36] Therefore, if the pressure-induced FM phase of $YbInCu_4$ were due to a Stoner effect, a pressure-dependent T_1^{-1} in the mixed-valent state should be expected. However, as seen in Fig. 4, this is not the case, and argues against such a mechanism. If we do the same susceptibility analysis for $YbInCu_4$ [Fig. 7(b)] as for $Yb_{0.8}Y_{0.2}InCu_4$, we obtain $\alpha \approx 0.65$, which is far from unity as required for the Stoner itinerant ferromagnetism. Note that the extrapolated susceptibility has been used to obtain α, since the susceptibility for P higher than 15 kbar is not available.

Further evidence against a Stoner itinerant FM scenario is found in the LT resistivity, which exhibits Fermi-liquid behavior: $\rho(T)=\rho_0+AT^2$, where ρ_0 is the residual resistivity and A is a temperature-independent constant.[26] If the e^--e^- interaction were important, the prefactor A would depend on the strength of the interaction as $A \propto (1-\alpha)^{-1/2}$.[36] We therefore compare the calculated $A(\alpha)$ with the measured $A(P)$ under pressure as shown in Fig. 8. The discrepancy between the calculated and measured A is evident. We speculate, therefore, that the pressure-enhanced LT susceptibility in $YbInCu_4$ is due to the pressure-suppressed T_K. In this case, since the mixed-valent state has $1/\chi \propto T_{K,LT}$ and $T_K \propto T_v$, the linear relation of $1/\chi \propto T_v$ would be expected. This is indeed observed.[18] In addition, the Gruneisen parameter calculated from the pressure-enhanced susceptibility agrees with other thermodynamic estimates, which again supports that $1/\chi \propto T_K$ is correct for the mixed-valent state.[15,18] Therefore, our analyses argue against the Stoner mechanism for magnetism in $YbInCu_4$, leaving local moment magnetism as the reasonable alternative.

C. Field-induced FM phase?

Besides pressure, application of a magnetic field also suppressed T_v in $YbInCu_4$, and, further, the functional dependence of T_v on field appears to be independent of pressure.[8] These relationships suggest that, if $YbInCu_4$ were close to a FM instability under pressure ($P<P_c$), it might be possible to induce ferromagnetism by an applied magnetic field. From the results of Ref. 8, the critical field H_c is related to applied pressure approximately as H_c (kOe) $\approx 8.3T_v(P)$, so that, at $P=23$ kbar where $T_v(H=0) \approx 3.6$ K, $H_c(T=0) \approx 30$ kOe. We have searched for a signature of field-induced ferromagnetism at $P=23$ kbar by measuring the absorption power and resonance frequency of our NMR coil with a network analyzer. We found in fact that absorption power has better resolution than the resonance frequency.

Figure 9 shows field-swept results of the absorption power at different temperatures. A field-induced transition at $P=23$ kbar is apparent from the hysteresis loops for $T<T_v=3.6$ K. Although the hysteresis is too wide to determine H_c accurately, similar magnetic hysteresis also has been observed in magnetization experiments in $Yb_{0.8}Y_{0.2}InCu_4$.[27]

To help interpret the origin of this hysteresis, we show in Fig. 10 ^{115}In NMR spectra measured at 15.45 MHz for temperatures at 3.96 K and 1.5 K and at 13.9 MHz for $T=1.5$ K. The spectrum [Fig. 10(a)] at 3.96 K (above the transition temperature) is the signal from the HT phase, which shows a broad line centered at 17.49 kOe with positive field shift. The 13.9 MHz spectrum at 1.5 K [Fig. 10(c)] is the signal from the mixed-valent state, which shows a narrow peak around 14.75 kOe ($<H_c$) with negative field

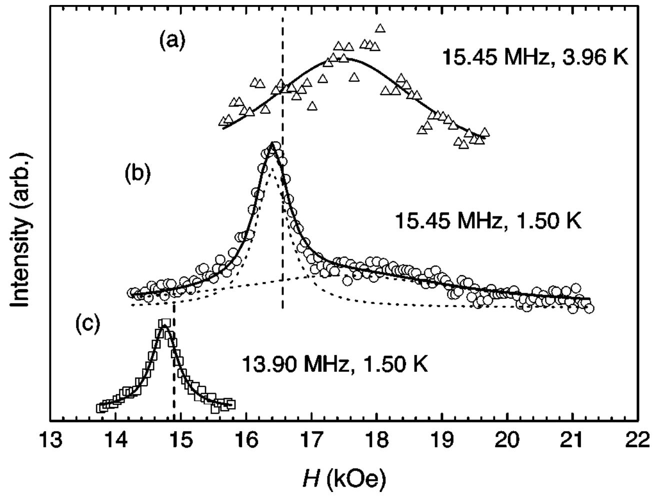

FIG. 10. ^{115}In NMR spectrum for $P=23$ kbar at (a) 15.45 MHz and 3.96 K (above the transition temperature, triangles), (b) 15.45 MHz and 1.5 K (near the critical field and below the transition temperature, circles), and (c) 13.90 MHz and 1.5 K (below the critical field and the transition temperature, rectangles). Dashed lines: ^{115}In reference field position. Solid curves: least-square fits to the Lorentzian function. Dotted curves: Lorentzian fit to two peaks.

shift. At 1.5 K, when the NMR frequency is set to 15.45 MHz so that the resonance field is closer to H_c, we observe two peaks in the field-swept spectrum [Fig. 10(b)]. Since these two peaks on the low-field and high-field sides have linewidths and field shifts similar to the ones from the mixed-valent and local moment states, respectively, and the areas under the two peaks (dotted curves) are nearly equal, these suggest that this magnetic-induced transition is simply a valence transition and there is no FM transition at 23 kbar for temperature down to 1.5 K. We note that magnetization experiments in $Yb_{0.8}Y_{0.2}InCu_4$ also show no obvious evidence of a field-induced FM phase at 0.6 K.[27] The pressure-induced FM phase has $T_c=1.7$ K and $P_c \approx 8$ kbar for $Yb_{0.8}Y_{0.2}InCu_4$ with $T_v(P=0)=13$ K (Ref. 27) and $T_c=2.4$ K and $P_c \approx 24$ kbar for $YbInCu_4$ with $T_v(P=0)=42$ K. The value of T_c approximately scales with P_c and T_v, i.e., T_c is smaller if P_c and T_v are smaller. This may also be the case that T_c could be small when H_c and T_v are small if there is a field-induced FM phase. Therefore, we cannot rule out the possibility of field-induced ferromagnetism below 1.5 K.

IV. CONCLUSIONS

We have investigated the phase diagram of $YbInCu_4$ at high pressures by ^{63}Cu and ^{115}In NQR/NMR experiments. Results of the NQR experiments under pressure suggest that the valence transition temperature does not vanish at the critical pressure 23.7 kbar, but rather gives way to a pressure-induced magnetic phase. We therefore find no signature for a QCP of $T_v=0$ in $YbInCu_4$. This is consistent with the fact that no NFL behavior is observed in T_1^{-1} near the critical pressure.

Evidence for a pressure-induced FM phase is revealed in the rapid increase of T_1^{-1} near the critical pressure. The Stoner theory of itinerant ferromagnetism has been discussed for the pressure-induced FM order in $YbInCu_4$ and $Yb_{0.8}Y_{0.2}InCu_4$ by examining the pressure-enhanced susceptibility in the mixed-valent state, T_1^{-1}, and resistivity data. We found that the Stoner model is consistent with the observed itinerant FM phase in $Yb_{0.8}Y_{0.2}InCu_4$ but not in $YbInCu_4$, although they have similar phase diagrams. The pressure-enhanced LT susceptibility is consistent with a pressure-suppressed T_K rather than a Stoner mechanism. This suggests that the pressure-induced FM phase in $YbInCu_4$ is due to the pressure-stablized Yb^{3+} local moment rather than from the itinerant electrons in the mixed-valent state.

We also considered the possibility of a magnetic-field-induced FM phase in $YbInCu_4$. At 23 kbar, the critical magnetic field for the valence transition is reduced, and there is no evidence for a field-induced ferromagnetism from our ^{115}In NMR spectra. This, however, cannot rule out the possibility of a magnetic-field-induced FM phase since T_c may be lower than 1.5 K.

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[1] I. Felner and I. Nowik, Phys. Rev. B **33**, 617 (1986).
[2] I. Felner *et al.*, Phys. Rev. B **35**, 6956 (1987).
[3] I. Nowik, I. Felner, J. Voiron, J. Beille, A. Najib, E. du Tremolet de Lacheisserie, and G. Gratz, Phys. Rev. B **37**, 5633 (1988).
[4] H. Müller, E. Bauer, E. Gratz, K. Yoshimura, T. Nitta, and M. Mekata, J. Magn. Magn. Mater. **76&77**, 159 (1988).
[5] S. Ogawa, S. Suga, M. Taniguchi, M. Fujisawa, A. Fujimori, T. Shimizu, H. Yasuoka, and K. Yoshimura, Solid State Commun. **67**, 1093 (1988).
[6] H. Nakamura and M. Shiga, Physica B **206&207**, 364 (1995).
[7] K. Yoshimura, T. Nitta, T. Shimizu, M. Mekata, H. Yasuoka, and K. Kosuge, J. Magn. Magn. Mater. **90–91**, 466 (1990).
[8] C. D. Immer, J. L. Sarrao, Z. Fisk, A. Lacerda, C. Mielke, and J. D. Thompson, Phys. Rev. B **56**, 71 (1997).
[9] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 12 207 (1996).
[10] T. Koyama, M. Matsumoto, T. Tanaka, H. Ishida, T. Mito, S. Wada, and J. L. Sarrao, Phys. Rev. B **66**, 014 420 (2002).
[11] B. Kindler, D. Finsterbusch, R. Graf, F. Ritter, W. Assmus, and B. Lüthi, Phys. Rev. B **50**, 704 (1994).

[12] J. M. Lawrence, G. H. Kwei, J. L. Sarrao, Z. Fisk, D. Mandrus, and J. D. Thompson, Phys. Rev. B **54**, 6011 (1996).
[13] J. W. Allen and L. Z. Liu, Phys. Rev. B **46**, 5047 (1992).
[14] J. W. Allen and R. M. Martin, Phys. Rev. Lett. **49**, 1106 (1982).
[15] J. L. Sarrao, A. P. Ramirez, T. W. Darling, F. Freibert, A. Migliori, C. D. Immer, Z. Fisk, and Y. Uwatoko, Phys. Rev. B **58**, 409 (1998).
[16] N. V. Mushnikov, T. Goto, F. Ishikawa, W. Zhang, K. Yoshimura, and V. S. Gaviko, J. Alloys Compd. **345**, 20 (2002).
[17] A. L. Cornelius, J. M. Lawrence, J. L. Sarrao, Z. Fisk, M. F. Hundley, G. H. Kwei, J. D. Thompson, C. H. Booth, and F. Bridges, Phys. Rev. B **56**, 7993 (1997).
[18] N. V. Mushnikov, T. Goto, A. V. Kolomiets, K. Yshimura, W. Zhang, and H. Kageyama, J. Phys.: Condens. Matter **16**, 2395 (2004).
[19] L. M. Falicov and J. C. Kimpball, Phys. Rev. Lett. **22**, 997 (1969).
[20] J. K. Freericks and V. Zlatic, Phys. Rev. B **58**, 322 (1998).
[21] J. K. Freericks and V. Zlatic, Phys. Status Solidi B **236**, 265 (2003).
[22] B. Johansson, Philos. Mag. **30**, 469 (1974).
[23] M. O. Dzero, L. P. Gor'kov, and A. K. Zvezdin, J. Phys.: Condens. Matter **12**, L711 (2000).
[24] A. V. Goltsev and G. Bruls, Phys. Rev. B **63**, 155109 (2001).
[25] I. V. Svechkarev, A. S. Panfilov, S. N. Dolja, H. Nakamura, and M. Shiga, J. Phys.: Condens. Matter **11**, 4381 (1999).
[26] T. Mito, T. Koyama, M. Shimoide, S. Wada, T. Muramatsu, T. C. Kobayashi, and J. L. Sarrao, Phys. Rev. B **67**, 224409 (2003).
[27] A. Mitsuda, T. Goto, K. Yoshimura, W. Zhang, N. Sato, K. Kosuge, and H. Wada, Phys. Rev. Lett. **88**, 137204 (2002).
[28] T. Matsumoto, T. Shimizu, Y. Yamada, and K. Yoshimura, J. Magn. Magn. Mater. **104–107**, 647 (1992).
[29] J. M. de Teresa, Z. Arnold, A. del Moral, M. R. Ibarra, J. Kamarád, D. T. Adroja, and B. Raindord, Solid State Commun. **99**, 911 (1996).
[30] A. C. Hewson, *The Kondo Problem to Heavy Fermions* (Cambridge University Press, Cambridge, 1993).
[31] A. M. Tsvelik and M. Reizer, Phys. Rev. B **48**, R9887 (1993).
[32] A. M. Sengupta and A. Georges, Phys. Rev. B **52**, 10 295 (1995).
[33] Q. Si, S. Rabello, K. Ingersent, and J. Lleweilun Smith, Nature (London) **413**, 804 (2001).
[34] K. Ishida *et al.*, Phys. Rev. B **68**, 184401 (2003).
[35] G. R. Stewart, Rev. Mod. Phys. **73**, 797 (2001).
[36] T. Moriya, *Spin Fluctuations in Itinerant Electron Magnetism* (Springer-Verlag, Berlin, 1985).
[37] E. Dormann, *Handbook on the Physics and Chemistry of Rare Earths* (Elsevier Science Publishers, Amsterdam, 1991), Vol. 14, Chap. 94, p. 63.
[38] E. C. Stoner, Proc. R. Soc. London, Ser. A **165**, 372 (1938).
[39] K. Kojima, H. Hayashi, A. Minami, Y. Kasamatsu, and T. Hihara, J. Magn. Magn. Mater. **81**, 267 (1989).
[40] See http://www.hppi. troitsk.ru/products/dizhur.htm.
[41] I. R. Walker, Rev. Sci. Instrum. **70**, 3402 (1999).
[42] J. D. Thompson, Rev. Sci. Instrum. **55**, 231 (1984).
[43] K. Kojima, Y. Nakai, T. Suzuki, H. Asano, F. Izumi, T. Fujita, and T. Hihara, J. Phys. Soc. Jpn. **59**, 792 (1990).
[44] H. Nakamkura, K. Nakajima, Y. Kitaoka, K. Asayama, K. Yoshimura, and T. Nitta, J. Phys. Soc. Jpn. **59**, 28 (1990).
[45] E. V. Sampathkumaran, N. Nambudripad, S. K. Dhar, R. Vijayaraghavan, and R. Kuentzler, Phys. Rev. B **35**, 2035 (1987).
[46] R. G. Graham, J. S. Lord, P. C. Riedi, Y. Yamada, H. Nakamura, and K. Yoshimura, J. Magn. Magn. Mater. **104–107**, 641 (1992).
[47] C. P. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1990).
[48] D. L. Cox, Phys. Rev. B **35**, 6504 (1987).
[49] D. E. MacLaughlin, O. Peña, and M. Lysak, Phys. Rev. B **23**, 1039 (1981).
[50] J. M. Lawrence, S. M. Shapiro, J. L. Sarrao, and Z. Fisk, Phys. Rev. B **55**, 14 467 (1997).
[51] Y. Uwatoko, T. Hotta, E. Matsuoka, H. Mori, T. Ohki, J. L. Sarrao, J. D. Thompson, N. Mōri, and G. Oomi, Rev. High Pressure Sci. Technol. **7**, 1508 (1998).
[52] A. Llobet *et al.*, Phys. Rev. B **69**, 024403 (2004).
[53] A. Uchida, M. Kosaka, N. Mori, T. Matsumoto, Y. Uwatoko, J. L. Sarrao, and J. D. Thompson, Physica B **312–313**, 339 (2002).
[54] A. Paja, H. Figiel, and P. Mietniowski, J. Phys.: Condens. Matter **14**, 9029 (2002).
[55] T. Moriya, Prog. Theor. Phys. **28**, 371 (1962).
[56] T. Park, V. A. Sidorov, J. L. Sarrao, and J. D. Thompson (unpublished).