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^{171}Yb and ^{63}Cu magnetic resonance studies on the fluctuating valent compound YbInCu$_4$

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We report a nuclear magnetic resonance (NMR) investigation on the fluctuating valent compound YbInCu$_4$, which exhibits the first-order isostructural valence transition at $T_V = 45-50$ K. ^{171}Yb NMR was observed in the range between 1.9–4.2 K in the low-temperature (LT) phase with the Knight shift of 101.3%. The hyperfine coupling constant of 0.88×10^6 Oe/μ_B is about 24% smaller than the value expected for the $J=\frac{7}{2}$ state of free Yb^{3+} ions. The strongly enhanced paramagnetic behavior with large Korringa-like relaxation rate, $(T_1T)^{-1} \simeq 1.1\times 10^4$ (s K)$^{-1}$, is consistent with the formation of s-f resonance bands. ^{63}Cu Knight shift $K(^{63}\mathrm{Cu})$ shows a Curie-Weiss-type behavior in high-temperature (HT) phase, and a temperature-independent behavior in the LT phase. It is found that $K(^{63}\mathrm{Cu})$ vs $\nu(^{63}\mathrm{Cu})$ (electric-quadrupole frequency) plots in the HT phase are on a straight line for the most part, and deviate slightly from the line as the temperature approaches T_V. In the LT phase, on the other hand, the plots exhibit a small deviation from the line in the opposite direction. As the increase in $\nu(^{63}\mathrm{Cu})$ for YbInCu$_4$ is caused by the decrease in the cell volume, it is concluded that the Kondo volume collapse (expansion) model may describe the physics of YbInCu$_4$ associated with the valence fluctuations. The deviation from the line is thought to be due to the variation of the coupling J_{af} between the conduction electron density and Yb's $4f$ electrons.

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The physical properties associated with valence fluctuations of Yb ions in the face-centered-cubic Yb*X*Cu$_4$ series with $X=$ Ag, Au, Cd, In, Mg, Tl, and Zn have drawn much attention.[1] Among Yb*X*Cu$_4$ compounds, YbInCu$_4$ has been rather well studied and represents the most extreme limit of mixed-valence behavior of Yb$^{3+}(f^{13})$ and Yb$^{2+}(f^{14})$.[2–10] At high temperatures, the magnetic susceptibility[7] follows the Curie-Weiss law with nearly the fully free Yb ion moment and antiferromagnetic Weiss temperature of −15 K. At low temperatures below the first-order isostructural valence transition at $T_V = 40-50$ K where a volume expansion of 0.5% occurs, the magnetic susceptibility χ was found to exhibit the paramagnetic behavior. The Kondo temperature is estimated from χ as $T_K^H = 25$ K for the high-temperature (HT) phase and $T_K^L = 400$ K for the low-temperature (LT) phase,[6,10] within the single-impurity theory in the Kondo limit (Coqblin-Schrieffer model).[11] The enhanced coefficient γ of the electronic specific heat in the LT phase is 50 mJ/mol K^2.[10]

The Yb*X*Cu$_4$ compounds ($C15b$-type structure) are appropriate for a nuclear magnetic-resonance (NMR) study, since it is in principle possible to observe almost all the constituent nuclear species.[12–18] Several authors have reported the results of rather easily observable pure-quadrupole-resonance (PQR) of Cu nuclei[12–15] (^{63}Cu, nuclear spin $I=\frac{3}{2}$; ^{65}Cu, $I=\frac{3}{2}$), and NMR of ^{115}In (Refs. 16–18) and ^{205}Tl (Ref. 12) on the *nonmagnetic* $4c$ and $16e$ sites. On the other hand, there has been no report on the NMR of Yb nuclei (^{171}Yb, $I=\frac{1}{2}$; ^{172}Yb, $I=\frac{5}{2}$) on the *magnetic* $4a$ site. In an unstable *f*-electron system, the nuclear spin-lattice relaxation is expected to be strongly enhanced, which gives rise to difficulties in observing the spin-echo NMR signal of Yb.

In this paper, we briefly report the result of the first NMR measurement of ^{171}Yb in YbInCu$_4$ at low temperatures. These data provide direct information on the ground state of the $4f$ electrons. We also measured the Knight shift and the quadrupole frequency of ^{63}Cu in high field. The former is a measure of the local susceptibilities and provides information on the magnetic state of Yb ions through the transferred hyperfine interactions, and the latter the local electron distribution around Cu nuclei.

We used a single-crystal specimen of YbInCu$_4$ and crushed it into powder with grain size smaller than the skin depth. The NMR experiment was carried out utilizing a wide-band phase-coherent spin-echo spectrometer. The NMR spectrum was obtained in a field-sweeping procedure at constant frequencies utilizing a boxcar integrator.

At 75 MHz, as is shown in Fig. 1(a), we first found a small ^{171}Yb spin-echo signal at the field just below the satellite line for $\theta = 0$ of the quadrupole-split ^{63}CuNMR described below. The time interval between the $\pi/2$ and π rf pulses was 10 μs. The spectrum at a higher frequency of 115 MHz is shown in Fig. 1(b), which is well separated from the satellite line of the ^{63}Cu NMR. The resonance field was directly proportional to the frequency, and the Knight shift of 101.3% defined at the peak intensity is independent of the temperature in the range between 1.9 and 4.2 K. The full width at half maximum is about 2.9 kOe. Taking the values of the Knight shift and the susceptibility $\chi(0) = 6.37\times 10^{-3}$ emu/mol (Ref. 6), the hyperfine field of ^{171}Yb in the LT phase is estimated as 0.88×10^6 Oe/μ_B. The ^{171}Yb spin-lattice relaxation time T_1 was too short to measure directly with the usual saturation rf-comb-pulse method. Therefore

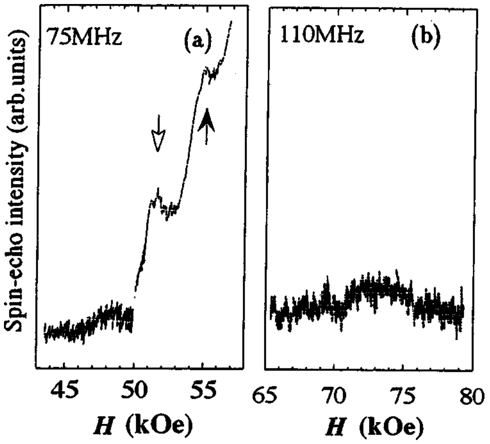

FIG. 1. NMR spectra of ^{171}Yb in YbInCu$_4$ at 4.2 K, observed at constant frequencies of 75 MHz (a) and 110 MHz; (b). In (a), the satellite lines of the electric-quadrupole split ^{63}Cu NMR at $\theta=0$ and $\pi/2$ are indicated by open and closed arrows, respectively.

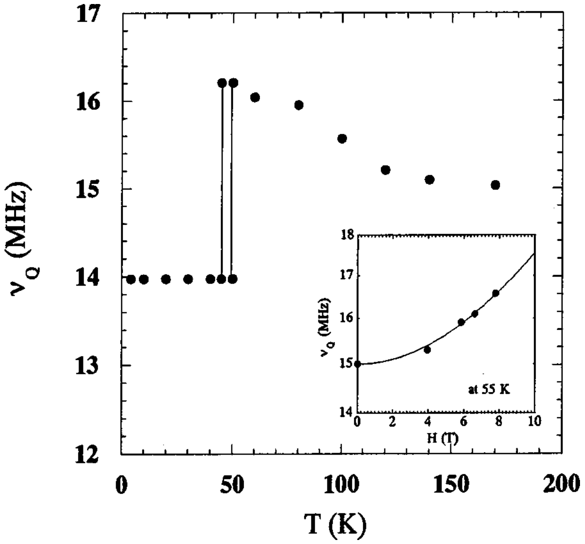

FIG. 2. Temperature dependence of the electric-quadrupole frequency of ^{63}Cu in YbInCu$_4$. The inset of the figure shows the dependence of ν_Q at 55 K on the external magnetic field.

we measured the transverse relaxation time T_2, which is composed of a temperature-independent spin-spin relaxation term T_2^* and a temperature-dependent longitudinal relaxation term T_1 as[19,20]

$$\frac{1}{T_2}=\frac{1}{T_2^*}+\frac{\alpha}{T_1}, \tag{1}$$

where α for ^{171}Yb is $(I+\frac{1}{2})^2=1$. When T_1^{-1} is sufficiently larger than $(T_2^*)^{-1}$, T_2^{-1} gives a measure of T_1^{-1}. We determined T_1 from the decay curve of the spin-echo intensity focused at 2τ after $\pi/2$-π rf pulses separated by the time τ. Here we used a digital signal averager to improve satisfactorily the signal-to-noise ratio. In the temperature range between 1.9 and 4.2 K, T_2^{-1} for ^{171}Yb is directly proportional to the temperature, and we obtained a Korringa-like relaxation rate, $(T_2T)^{-1}=(T_1T)^{-1}\simeq 1.1\times 10^4\,(\mathrm{s\,K})^{-1}$, which is four orders of magnitude larger than the value of $(T_1T)^{-1}$ for ^{63}Cu (Ref. 14). The strongly enhanced $T_1T=$const behavior of ^{171}Yb in the LT phase is consistent with the formation of a quasiparticle Fermi liquid with enhanced mass.

The ^{63}Cu spin-echo signal in YbInCu$_4$ was observed in a temperature range between 4.2 and 170 K. The ^{63}Cu NMR spectrum has the general quadrupole powder pattern with zero anisotropy factor η of the electric-field gradient:[21] a second-order split central line with maxima at ν_{I} ($\theta=\pi/2$) and ν_{II} ($\theta=\cos^{-1}\sqrt{\frac{5}{9}}$); and equally split satellite lines with maximum at $\theta=\pi/2$ and shoulder at $\theta=0$. Here θ is the angle of the applied field H with respect to the principal Z axis of the electric field gradient q.

The values of the electric-quadrupole frequency, $\nu_Q(^{63}\mathrm{Cu})=e^2qQ/2\hbar$, and the isotropic Knight shift, $K(^{63}\mathrm{Cu})$, deduced from the spectrum analysis of the central line, are plotted in Figs. 2 and 3, respectively, as a function of the temperature. The temperature dependence of $\nu_Q(^{63}\mathrm{Cu})$ is similar in shape to that reported previously in the PQR measurement for the polycrystalline specimen.[14] We found, however, that the value of $\nu_Q(^{63}\mathrm{Cu})$ just above T_V depends on the external magnetic field H as is shown in the inset of Fig. 2. The data can be reproduced by the following formula:

$$\nu_Q(^{63}\mathrm{Cu})=15.0+0.0255H^2\ \ \mathrm{MHz}, \tag{2}$$

as is drawn in the inset by the solid curve.

The temperature-independent $K(^{63}\mathrm{Cu})$ of 0.22% at the LT phase is consistent with the high Kondo temperature, $T_K^L\simeq 400\,\mathrm{K}$. On the other hand, the temperature-dependent $K(^{63}\mathrm{Cu})$ in the HT phase can be fitted by the following formula:

$$K(^{63}\mathrm{Cu})=0.14-\frac{14.5}{T+21.2}\,\%, \tag{3}$$

as is drawn in the figure by the solid curve.

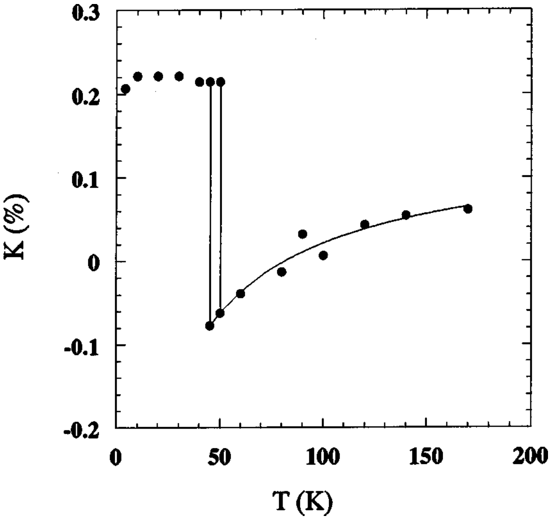

FIG. 3. Temperature dependence of the ^{63}Cu Knight shift in YbInCu$_4$.

In rare-earth ions with nonvanishing orbital momentum, the principal contribution to the hyperfine field H_{hf} is the large magnetic field $H_{\mathrm{hf}}(\mathrm{orb})$ set up by the orbital motion of $4f$ electrons.[19] The Hartree-Fock value of $\langle 1/r^3\rangle = 13.83$ a.u. for a free Yb^{3+} ion[22] gives $H_{\mathrm{hf}}(\mathrm{orb}) = 5.194\times 10^6$ Oe. There is also a spin-dipolar field $H_{\mathrm{hf}}(\mathrm{sd})$ from the intrinsic spin moments of $4f$ electrons. The $4f$ electron also contributes indirectly to the total hyperfine field by the mechanism known as core polarization field $H_{\mathrm{hf}}(\mathrm{cp})$. Both $H_{\mathrm{hf}}(\mathrm{sd})$ and $H_{\mathrm{hf}}(\mathrm{cp})$ are an order of magnitude smaller than $H_{\mathrm{hf}}(\mathrm{orb})$. For the fluctuating valent compound YbAl_3 (Ref. 23) and the Kondo semiconductor YbB_{12} (Ref. 24), the values of the hyperfine field derived from the ^{171}Yb Knight shift and the susceptibility were nearly equal to the calculated value (1.154×10^6 Oe) for the free Yb^{3+} ion with the saturation moment of $gJ = 4\,\mu_B$.[24]

The present empirical value of 0.88×10^6 Oe/μ_B at the LT phase of YbInCu_4 does not differ much from the value expected for the free Yb^{3+} ion. In YbInCu_4, a small change in the Yb valence by ~0.1 was observed in the x-ray absorption spectra[10] below T_V: Yb^{3+} at the HT phase changes to $\mathrm{Yb}^{2.9+}$ in the LT phase. The valence change reduces the value of $\langle 1/r^3\rangle$, which gives rise to a decrease in the value of $H_{\mathrm{hf}}(\mathrm{orb})$. The paramagnetic behavior of YbInCu_4 in the LT phase also suggests an additional reduction of $\langle 1/r^3\rangle$, as is generally expected for metals.

The impurity nuclear relaxation at low temperatures is expected to follow a Korringa relation,[23]

$$T_1TK^2 = \frac{C(2J+1)}{2\pi\hbar\gamma_n^2}, \tag{4}$$

where $C = g^2\mu^2 J(J+1)/3k_B$ is the Curie constant. For the $J = \frac{7}{2}$ ground state of the Yb^{3+} ion, Eq. (4) gives $T_1TK^2 = 2.29\times 10^{-4}$ s K. The Korringa constant derived from the experimental values of T_1T and K of ^{171}Yb in YbInCu_4 is

$$T_1TK^2 \simeq 0.92\times 10^{-4}\ \mathrm{s\,K}, \tag{5}$$

which is about two times smaller than the calculated value, suggesting that the $4f$ spin fluctuations in the LT phase of the Kondo lattice are not well localized.

In the HT phase, the temperature-dependent second term of $K(^{63}\mathrm{Cu})$ in Eq. (3) originates from the negative transferred hyperfine coupling with the neighboring Yb ions. The Weiss temperature of -21.2 K does not differ much from the value deduced from the χ measurement.[7] The positive value of the temperature-independent first term, 0.14%, in the HT phase is indicative of dominant Van Vleck orbital and conduction s electron contributions. The temperature-independent $K(^{63}\mathrm{Cu})$ increases by 0.08% in the LT phase. This is an indication that the negative contribution from the Yb spins almost vanishes, and the density of states $N(E_F)$ of the quasiparticle bands at the Fermi level significantly increases in the LT phase.

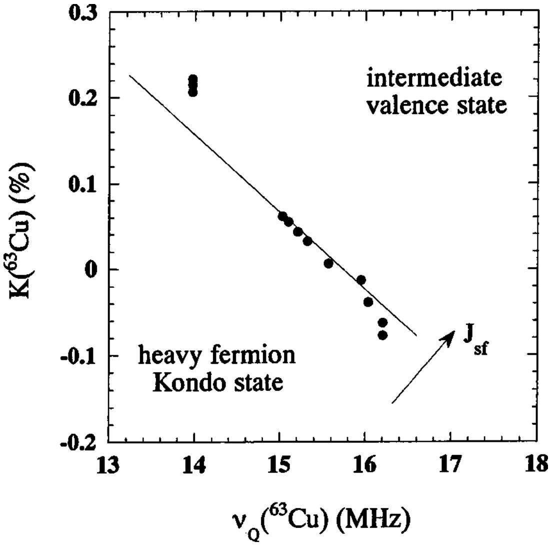

FIG. 4. Knight shift vs electric-quadrupole frequency plots for ^{63}Cu in YbInCu_4 with temperature being the implicit parameter.

Shown in Fig. 4 is $K(^{63}\mathrm{Cu})$ vs $\nu_Q(^{63}\mathrm{Cu})$ plots with temperature being the implicit parameter. The plots in the HT phase are on a straight line for the most part, and show a small deviation as the temperature approaches T_V. The plots in the LT phase are also close to the line, and the small deviation is in the opposite direction to that observed near T_V in the HT phase. The electric-field gradient q consists of the contributions from the ionic charge on the lattice sites around the Cu nucleus, q_{lat}, and the intra-atomic electron distribution, q_{el}. Comparing the contrasting behavior of $\nu(^{63}\mathrm{Cu})$ (Fig. 2) with that of lattice constant,[7] the increase in $\nu(^{63}\mathrm{Cu})$ in YbInCu_4 originates from the increase in q_{lat} and, therefore, the decrease in the cell volume, as was noted in Ref. 14. Thus, the present $K(^{63}\mathrm{Cu})$ vs $\nu_Q(^{63}\mathrm{Cu})$ plots indicate that the physics of YbInCu_4 with the valence fluctuations is mainly controlled by the cell volume and, therefore, may be described by the Kondo volume collapse (expansion) model. The deviation of the $K(^{63}\mathrm{Cu})$ vs $\nu_Q(^{63}\mathrm{Cu})$ plots from the line is thought to be an indication of the changes in the coupling J_{ef} between the conduction electron density and Yb's $4f$ electrons, as is illustrated in Fig. 4 by an arrow.

The thermodynamical analysis of the valence transition[25] indicates that the volume change at T_V is not enough for the Kondo volume collapse to work, emphasizing the importance of the carrier-density changes with the transition. Together the increases in $N(E_F)$ and J_{af} in the LT phase, deduced from the present ^{65}Cu NMR data, would allow to adequately describe the isostructural valence transition.

In summary, we have carried out ^{171}Yb and ^{63}Cu NMR investigation on the fluctuating valent compound YbInCu_4. ^{171}Yb NMR was observed in the range 1.9–4.2 K in the LT phase with the Knight shift of 101.3%. The strongly enchanced paramagnetic behavior with large Korringa-like relaxation rate, $(T_1T)^{-1} \simeq 1.1\times 10^4\ (\mathrm{s\,K})^{-1}$ is consistent with the formation of s-f resonance bands. ^{63}Cu Knight shift shows a Curie-Weiss-type behavior in the HT phase, and a temperature-independent behavior in the LT phase. The $K(^{63}\mathrm{Cu})$ vs $\nu(^{63}\mathrm{Cu})$ plots are on a straight line for the most part, indicating that the physics of YbInCu_4 may be described by the Kondo volume collapse (expansion) model. The small deviation from the line is thought to be an indication of the changes in J_{sf}.

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