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# 学位論文

# Physical Properties of the Dense Kondo Compounds YbXCu<sub>4</sub> (X=Au, Ag, In, Cd, Tl, Mg and Zn) Probed by NMR

高密度近藤系 YbXCu4 (X=Au, Ag, In, Cd, Tl, Mg and Zn)

のNMRによる物性研究

January 2003

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# Symbol lists

- A : coefficient of the T<sup>2</sup> term in the resistivity
- a : lattice constant
- $D(E_{\rm F})$ : the conduction-band density-of-state at the Fermi level
- $E_{\rm F}$  : Fermi energy
- $E_f$ : energy of the 4f level
- g : g-factor
- $g_J$ : Landé *g*-factor
- h: planck's constant ( $\hbar = h/2\pi$ )
- $H_0$ : applied magnetic filed
- $H_1$ : radiofrequency magnetic field
- *I* : nuclear spin angular momentum
- J: total angular momentum
- $J_{cf}$ : c-f exchange integral between conduction electrons and the local moment
- $J_{ff}$  : exchange interaction between f electrons
- $k_{\rm B}$  : Boltzman constant
- $k_{\rm F}$  : Fermi wave vector

- L : total orbital angular momentum
- l: orbital angular momentum
- $m^*$ : effective electron mass
- N : Avogadro's number
- P : magnitude of pressure
- Q : nuclear electric quadrupole moment
- q : electric filed gradient
- **q** : wave vector
- **r** : position vector
- S: total spin momentum
- *s* : spin polarization of conduction electrons
- T : absolute temperature
- $T_{\rm K}$  : Kondo tempareture
- $T_1$ : spin-lattice relaxation time
- $T_2$ : transversal relaxation time
- $T_2^*$ : spin-spin relaxation time
- t: time
- V : electric field
- $V_{cf}$ : the matrix element for hybridization of an f state with the conduction electrons

- z : the number of nearest magnetic atoms
- $\gamma$  : liner coefficient of specific heat per mol
- $\gamma_{\rm e}$  : electronic gyromagnetic ratio
- $\gamma_n$ : nuclear gyromagnetic ratio
- $\Delta$ ; width of f level due to hybridization,  $\Delta = \pi D(E_{\rm F})V_{cf}^2$
- $\Delta H$ : internal magnetic field
- $\eta$ : asymmetry parameter of electric field gradient
- $\mu_{\rm B}$  : Bohr magneton
- $\nu_{\rm Q}$  : nuclear quadrupole frequency
- $\Phi$  : wave functin
- $\rho$  : electrical resictivity
- $\Delta \rho_0$  : residual resistivity
- $\chi$  : magnetic susceptibility
- $\chi_{\rm ac}$  : ac-susceptibility
- $\omega_{\text{ex}}$  : exchange frequency
- $\omega_0$  : NMR radiofrequency

# 1 Introduction

Over the past one decade a new branch of metal physics has come out and rapidly developed. It addresses the systems containing Lanthanide or Actinide ions, which have exotic properties at low temperatures mainly associating with the extent of hybridization  $J_{cf}$  between the localized f electrons and conduction electrons. When  $J_{cf}$  is large enough, originating from the charge instability of the rare earth ions, the system takes an intermediate valence or valence fluctuating state. With the decrease in  $J_{cf}$ , the freedom of charge in the 4f electron is suppressed while the freedom of the spin is retained and the system shows unusual low temperature properties with both the localized and itinerant electrons. At high temperatures, the system are usually can be described by a well localized f electrons and by conduction electrons with conventional masses. The former possesses magnetic moments associated with them, and the magnetic susceptibility following the Cure-Weiss law at high temperatures. Both type of electrons interact by means of a standard exchange type of interaction or a generalization of it. These magnetic behaviors can completely change at low temperatures. Below a temperature, which is of the order of Kelvin, they behave like Fermi liquid. They have a temperature linear specific heat and an approximately temperature-independent Pauli spin susceptibility with values corresponding to formation of the heavy quasi-particles and huge electron density of state. What apparently happens is that the system gains energy by losing the magnetic moments associated with f electrons. At the same time, the f electrons become a part of the Fermi surface, implying that they are no longer perfectly localized. Due to the presence of low-energy excitation or quasi particle with effective mass, these system has been referred to as "heavy-Fermion" system.

A situation where, due to an energy gain, a magnetic moment is lost was first encountered in the Kondo effect. Because of strong many-body effects, the magnetic moment of f electron disappears and the spin singlet state is formed with binding energy  $k_{\rm B}T_{\rm K}$ . Here the Kondo temperature  $T_{\rm K}$  is the single energy scale and can vary a broad range, i.e., between a fraction of a degree a several hundred Kelvin. The disappearance of the localized moment is due to the formation of a spin-compensating cloud of the conduction electron around local moment. When the spin-compensation of the localized moment is incomplete, the Ruderman-Kittel-Kasuya-Yosida interaction between the remnant moments sometimes brings about a magnetic ordering at low temperatures.

As the degree of freedom of both charge and spin is very sensitive to the crystallographic environment and around given ions, the variation in temperature and application of magnetic field or pressure can easily control the physical properties of the system. In fact the pressure-induced magnetic ordering and/or superconditing transition were recently discovered in Ce- and U-based heavy-Fermion systems and those properties have been attracted considerable interests.

A set of isostructual ytterbium-based compounds  $YbXCu_4$  with X=Au, Cu, Ag, In, Cd, Tl, Mg and Zn have been known to have wide range of  $T_{\rm K}$ from about 1 to nearly  $10^3$  K and to display a rich variety of physical properties such as the valence fluctuation, heavy-Fermion and magnetic ordering, depending on the species of X atoms. I carried out the nuclear magnetic resonance (NMR) experiment on  $YbXCu_4$  series to deduce the varied impact of variation in effective valence, unite-cell volume, crystal-electric-field splitting and c-f hybridization. Those can define more clearly what we do not understand. In this paper, I report the result of the systematic experiment for  $YbXCu_4$  series. Based on the NMR data, I succeed to establish a magnetic phase diagram for  $YbXCu_4$  series, which corresponds to Doniach's phase diagram. Moreover, in order to elucidate the ground state of the pressurestabilized high-temperature (HT) phase of the valence fluctuating compound YbInCu<sub>4</sub>, I have carried out an electrical resistivity  $\rho$  and ac-susceptibility  $\chi_{\rm ac}$  measurements under high pressure. For the pressure above 2.49 GPa, the first order valence transition is almost completely suppressed. While, above 2.3 GPa, we firstly found a clear peak in  $\chi_{ac}$  at around  $T_{M}=2.3$  K, which provides clear evidence for a long-range ferromagnetic ordering of the HT phase ground state. These experimental results give noble information to understand the inner meaning of the magnetism and possible superconductivity in strongly correlated electron on Yb-based compounds.

1A	2A	3B	4B	5B	6B	7B	8			1B	2B	3B	4A	5A	6A	7A	0
<sup>1</sup> H													<sup>2</sup> He				
<sup>3</sup> Li	<sup>4</sup> Be <sup>5</sup> B <sup>6</sup> C <sup>7</sup> N <sup>8</sup> O													9F	<sup>10</sup> Ne		
<sup>11</sup> Na	<sup>12</sup> Mg											<sup>13</sup> Al	<sup>14</sup> Si	<sup>15</sup> P	<sup>16</sup> S	<sup>17</sup> Cl	<sup>18</sup> Ar
<sup>19</sup> K	<sup>20</sup> Ca	<sup>21</sup> Sc	<sup>22</sup> Ti	$^{23}V$	<sup>24</sup> Cr	<sup>25</sup> Mn	<sup>26</sup> Fe	<sup>27</sup> Co	<sup>28</sup> Ni	<sup>29</sup> Cu	<sup>30</sup> Zn	<sup>31</sup> Ga	<sup>32</sup> Ge	<sup>33</sup> As	<sup>34</sup> Se	<sup>35</sup> Br	<sup>36</sup> Kr
<sup>37</sup> Rb	<sup>38</sup> Sr	<sup>39</sup> Y	<sup>40</sup> Zr	<sup>41</sup> Nb	<sup>42</sup> Mo	<sup>43</sup> Tc	<sup>44</sup> Ru	<sup>45</sup> Rh	<sup>46</sup> Pd	<sup>47</sup> Ag	<sup>48</sup> Cd	<sup>49</sup> In	<sup>50</sup> Sn	<sup>51</sup> Sb	<sup>52</sup> Te	<sup>53</sup> I	<sup>54</sup> Xe
<sup>55</sup> Cs	<sup>56</sup> Ba	57-71	<sup>72</sup> Hf	<sup>73</sup> Ta	<sup>74</sup> W	<sup>75</sup> Re	<sup>76</sup> Os	<sup>77</sup> Ir	<sup>78</sup> Pt	<sup>79</sup> Au	<sup>80</sup> Hg	<sup>81</sup> Tl	<sup>82</sup> Pb	<sup>83</sup> Bi	<sup>84</sup> Po	<sup>85</sup> At	<sup>86</sup> Rn
<sup>87</sup> Fr	<sup>88</sup> Ra	89-102	<sup>104</sup> Rf	<sup>105</sup> Ha	<sup>106</sup> Sg	<sup>107</sup> Bh	<sup>108</sup> Hs	<sup>109</sup> Mt	<sup>110</sup> Uun	111Uuu	<sup>112</sup> Uub						
Lantl	hanid	es	<sup>57</sup> La	<sup>58</sup> Ce	<sup>59</sup> Pr	<sup>60</sup> Nd	<sup>61</sup> Pm	<sup>62</sup> Sm	<sup>63</sup> Eu	<sup>64</sup> Gd	<sup>65</sup> Tb	<sup>66</sup> Dy	<sup>67</sup> Ho	<sup>68</sup> Er	<sup>69</sup> Tm	<sup>70</sup> Yb	<sup>71</sup> Lu
Actinides			<sup>89</sup> Ac	<sup>90</sup> Th	<sup>91</sup> Pa	<sup>92</sup> U	<sup>93</sup> Np	<sup>94</sup> Pu	<sup>95</sup> Am	<sup>96</sup> Cm	<sup>97</sup> Bk	98Cf	99Es	<sup>100</sup> Fm	<sup>101</sup> Md	<sup>102</sup> No	<sup>103</sup> Lr

Figure 1: Periodic table.

### **1.1** Rare earth elements

The most striking feature of the chemistry of the rare earth elements is in their extraordinary similarity in the valency in most of the pure metals. All belong to a group of 3B elements in periodic table (**Fig. 1**). This arises from the fact that with increasing the atomic number, the number of electron in 4f shell increase without changing that of outer valence. The 4f electrons are well shielded from their neighboring atoms by the outer closed s or p shells and therefore hardly play a role in chemical bonding. On the other hand the f electrons in partially filled shell have a large angular momentum, which is responsible for the magnetic properties of the system.

### **1.2** Magnetism of rare earth compounds

The ground state is given by Hund's Rule, i.e. with maximum total spin S for the configuration and maximum L for that S. Spin-orbit coupling is relatively strong so that only the lowest J multiplet is normally populated at room temperature. This has the value  $L \pm S$  according as the shell is more or less than half full. The rare earth atoms in a crystal interact with their environment through electrostatic forces. These take the form of a

crystal field from the classical Coulomb terms, and exchange terms. Both turn out to give energies of interaction which are small compared to the spin-orbit coupling energy, and smaller than or comparable to  $k_{\rm B}T$  at room temperature. Thus, to a rough approximation, we expect many rare earth crystal to have magnetic properties similar to those of an assembly of free ions, particularly above room temperature.

Atoms of a transition or rare earth element dissolved in an ordinary metal often retain localized magnetic moments. The interaction between impurity ions with partially filled d or f electron shells and the conduction electrons of the metallic host can lead to variations in certain physical properties with temperature and magnetic field, which have come to be associated with the "Kondo effect" and/or "RKKY interaction". The former is the effect to screen local spin, on the other hand, latter is the effect to stabilize local moment. Both originally stem from the interaction between local moment and conduction electrons but the characteristic competition between the on-site Kondo effect and the long range RKKY interaction between moments leads to the possibility of both non-magnetic and magnetic ground states. Therefore, that competition gives rise to a lot of interesting physical properties.

### 1.2.1 Kondo state and valence fluctuation

#### Kondo state

The electric resistivity of ordinary metals usually decreases with decreasing temperature and approaches a certain finite value termed "residual resistivity" at absolute zero Kelvin. On the other hand, compounds containing a small amount of magnetic ions show the logarithmic increase of the resistivity and at low temperature the resistivity saturates to the so-called "unitary limit" at  $T \rightarrow 0$ . This logarithmic increase of the resistivity originates from the spin-flip scattering of the localized spin with the conduction electrons of the metal host. Kondo explicated this phenomena successfully by calculating the scattering process in the second Born approximation [1]. After reaching unitary limit, the resistivity takes a constant value in the single impurity Kondo model.

In the Kondo picture, for the system with rare earth elements, the local

4f moment is gradually screened by conduction electron spin polarization for the temperature approach a characteristic temperature, so-called "Kondo temperature"  $T_{\rm K}$ , and a many-body non-magnetic singlet ground state is formed around the Fermi level [2]. For a single spin (S=1/2) Kondo impurity embedded in a metallic host, Kondo temperature is given by

$$k_{\rm B}T_{\rm K} = \frac{1}{D(E_{\rm F})} \exp\left(-\frac{1}{|J_{cf}|D(E_{\rm F})}\right) \tag{1}$$

where  $D(E_{\rm F})$  is the conduction-band density-of-states at the Fermi level and  $J_{cf}$  is the antiferromagnetic exchange interaction between conduction electrons and local moments.

The dense Kondo systems, which contain the rare earth ions such as  $Ce^{3+}$ and  $Yb^{3+}$  in high concentration, also show the logarithmic increase of the resistivity with decreasing temperature but below  $T_K$  the resistivity decreases through maximum and then approaches to zero at  $T \rightarrow 0$ . (Note; This is the case for magnetic resistivity alone. Actually residual resistivity still exists.) This is caused by the fact that the deep 4f levels are arranged on the periodic lattice and consequently they act as the periodic potential to the conduction electrons. The periodicity makes the scattering coherent [3].

In these low temperature regions, the conduction electrons will behave as heavy Fermi-liquids because they must retain the localized 4f electron character in the Kondo state. The heavy-Fermion system can become superconducing when enough attractive force exists between the heavy-Fermions to overcome repulsive force arising from the c-f exchange. In this case, the attractive interactions between electrons well apart to avoid the c-f exchange interaction, bring about the p- or d- symmetry of cooper pair.

### Valence fluctuations

Generally, in ordinary metal or compounds, electron configuration is usually well defined. But in some of the rare earth compounds, the lanthanide ions tend to have non-integer valence originating from the charge instability of the ions. This state is called "valence fluctuation" or mixed valence.

In the periodic Anderson model, because of hybridization between the localized spin and conduction electrons, the f level broadens to a band width

 $\Delta = \pi D(E_{\rm F})V_{cf}^2$ , where  $V_{cf}$  is the matrix element that mixes the conduction and f electron wavefunctions. If the energy level of f electron  $E_f$  is above Fermi energy  $E_{\rm F}$  and  $E_f - E_{\rm F} \gg \Delta$  is realized, the number of f electron is much smaller than unity and Coulomb repulsion counts little. When  $E_f$  is small and  $E_f - E_{\rm F} \simeq \Delta$ , it is energetically favorable for the f electron to spend a fraction of its time in the conduction electron band so that f-count is no longer integer. In this mixed-valence limit, the ground state is a quantum mechanical admixture of  $f^n$  and  $f^{n-1}$  wavefunctions and spin fluctuation are induced primarily by charge fluctuation. Mixed-valence behavior is well documented in a number Ce-, Sm-, Yb- and Eu-based compounds.

The characteristics of the valence fluctuation compounds are as,

- 1.  $\gamma$  value of specific heat is about ten times the value of a normal metal.
- 2. BIS peak (Bremsstrahlung Isochromat Spectroscopy) can be observable just above Fermi energy.
- 3. An itinerant electron band model assures the structure of Fermi surface.

#### **Heavy-Fermion**

The two phenomena, intermediate valence and heavy-Fermion, are inherently connected inasmuch as every heavy-Fermion is simultaneously intermediate valent, however, not every intermediate-valent material is a heavy-Fermion. The most important quantity with which to recognize heavy-Fermion is the Sommerfeld coefficient  $\gamma$  of the electronic specific heat. In Fermi-liquid theory,  $\gamma$  is proportional to quasi-particle density of states at  $E_{\rm F}$  or to the effective mass. The origin of heavy mass has to be traced to the physics of strong local correlation as studies in connection with magnetic impurities in metals.

The formation of a singlet ground state requires the local magnetic moment to be screened by a spin polarization of the surrounding conduction electrons. This magnetic screening mechanism involves low-lying particlehole excitations, thereby introducing a narrow scattering resonance in the one-particle spectrum near  $E_{\rm E}$ . Therefore, relatively large density of states of conduction electron is realized near the Fermi level.

#### **RKKY** interaction

There exists an indirect exchange interaction between localized moments via conduction electrons, so-called the "Ruderman-Kittel-Kasuya-Yosida (RKKY) interaction". That is caused by an oscillatory behavior of the conduction electron spin polarization for long-range interaction, which stabilizes the local moment and gives rise to a magnetic ordering [4] [5] [6].

The conduction electrons are representable by  $\Phi_k(\mathbf{r}) = U_k(\mathbf{r})e^{i\mathbf{k}\cdot\mathbf{r}}$ , where  $U_k(\mathbf{r})$  has the periodicity of the lattice. The conduction electrons with wavevector  $\mathbf{k}$  are scattered by a magnetic 4f ion at position  $\mathbf{R}_i$ . The wavevector after scattering is  $\mathbf{k}'$ . Due to c-f exchange interaction, this scattering is independent of spin, resulting in a conduction electron spin polarization around the scattering center. By projecting  $\mathbf{S}$  on the  $\mathbf{J}$  direction, the c-f exchange interaction can be shown to be

$$\mathcal{H}_{\text{exch}} = -\frac{2J_{cf}}{N}(g-1)\sum_{i}\sum_{q}e^{iq\cdot(r_i-R_n)}(\boldsymbol{s}_i\cdot\boldsymbol{J}_n)$$
(2)

where  $s_i$  is the conduction electron spin density and  $J_n$  the angular momentum of 4f scattering center,  $J_{cf}$  the exchange integral of c-f interaction. In usual RKKY model, the q-independent  $J_{cf}$  and spherical Fermi surface (free electrons) are simply assumed. Then the RKKY interaction between 4f spin is given by

$$\mathcal{H} = -\frac{9\pi}{2} \left(\frac{N_{\rm e}}{N}\right) \frac{J_{cf}^2}{E_{\rm F}} (g_j - 1)^2 \sum_{n \neq m} F(2k_{\rm F} |\boldsymbol{R}_n - \boldsymbol{R}_m|) (\boldsymbol{S}_n \cdot \boldsymbol{S}_m), \qquad (3)$$

where

$$E_{\rm F} = \frac{\hbar^2 k^2}{2m^*}, \quad F(x) = \frac{\sin x - x \cos x}{x^4}.$$
 (4)

Here S should be written J originally but, for convenience' sake, we use the notation S which means local f spin.

### 1.2.2 Doniach's phase diagram

The magnetism of Kondo lattice is characterized by a competition between the RKKY interactions and the Kondo effect. The magnetic behavior of Kondo lattice system is largely dictated by a parameter  $\alpha \equiv |J_{cf}D(E_{\rm F})|$ :  $T_{\rm K} \propto e^{1/\alpha}$  and  $T_{\rm RKKY} \propto \alpha^2$ . Doniach considered the competition between RKKY and Kondo interactions in a one-dimensional Kondo lattice, and suggested that the general behavior should also hold for three-dimensional Kondo lattice systems [7]. A schematic representation of these effects is shown in **Fig. 2**, which is referred to as a "Doniach's phase diagram". The diagram gives a good qualitative account of experimental results on many Ce compounds [8]. The point where  $T_{\rm M}$  is nearly zero is called the quantum critical point (QCP) and some heavy-Fermion superconductors ; CeCu<sub>2</sub>Si<sub>2</sub> [9] and CeCoIn<sub>5</sub> [10], and substance with non-Fermi liquid behavior ; CeCu<sub>6-x</sub>Au<sub>x</sub> [11] and YbRh<sub>2</sub>Si<sub>2</sub> [12] are considered to be located around QCP. However, there are no known Yb-based heavy-Fermion superconductors up to now.



Figure 2: Doniach's phase diagram

# **2** NMR

Nuclear magnetic resonance (NMR), first demonstrate by Purcell *et al.* [13] and Bloch *et al.* [14] in 1946, is now established as being one of standard experimental methods to investigate microscopically substances in physical, biological and even in medical science. In the simplest form of NMR experiment, transitions between the quantized energy levels of the nuclear spin separated by a applied magnetic field are induced by weak pertubating electromagnetic field with radio frequency.

In general, the energy separation between the nuclear spin levels is determined not only by the applied magnetic field, but also by the internal field induced by the external field on the d or f electron on neighboring ions and conduction electrons. In addition, when the observed nucleus possesses an electric quadrupole moment, it interacts with the gradient of total electrostatic field at the nucleus and the nuclear spin level in energy is shifted. The NMR for solids gives information on static and dynamical properties of local magnetic field on a nuclei though hyperfine interaction between nuclear spin and electron spin.

### 2.1 Fundamental of nuclear magnetic resonance theory

A nucleus with spin angular momentum  $\hbar I$  possesses a magnetic moment,  $\mu_n = g_N \mu_N I$ , and the energies of which in a magnetic field  $H_0$  are given by the eigenvalues of the Hamiltonian,

$$\mathcal{H}_{z} = -\boldsymbol{\mu}_{n} \cdot \boldsymbol{H}_{0} = -\gamma_{n} \hbar H_{0} I_{z}, \qquad (5)$$

which gives 2I+1 equally-spaced levels, the so-called Zeeman levels, corresponding to 2I+1 values of the z component quantum number m(m = -I, -I+1, ..., I-1, I).

The perturbation most commonly used to produce magnetic transition between the nuclear spin levels is an alternating magnetic field applied perpendicular to the static field. If we write the alternating field in term of an amplitude  $H_1$ , we get a perturbing term in the Hamiltonian of

$$\mathcal{H}_{\rm p} = -\gamma_{\rm n} \hbar I_x H_1 \cos \omega_0 t. \tag{6}$$

Consequently the allowed transitions are between levels adjacent in energy, giving

$$\hbar\omega_0 = \gamma_{\rm n}\hbar H_0 \quad \text{or} \quad \omega_0 = \gamma_{\rm n}H_0. \tag{7}$$

From eqn.(7) we can compute the frequency needed to observe a resonance in principle.

# 2.2 Hyperfine interactions

The interaction of a nucleus with its electronic environment is usually called "hyperfine interaction". We can obtain information about electron states in solid through the hyperfine interaction.

The hyperfine interaction, which acts upon a nuclear spin  $I_i$  on crystallographic *i*-th site is given by the Hamiltonian

$$\mathcal{H} = \boldsymbol{I}_i \hat{A}_{ij} \boldsymbol{S}_j, \tag{8}$$

where,  $S_j$  is electron spin on j-th site,  $\tilde{A}_{ij}$  is hyperfine interaction between i and j-th sites. The term for i = j gives the on-site interaction between the observed nuclear spins and electrons of the same atom.  $\tilde{A}_{ii}$  consists of following four terms,

Magnetic dipole interaction Magnetic dipole interaction between nuclear spin I and electron spin S is written as,

$$\mathcal{H}_{\rm dip} = -\gamma_{\rm e} \gamma_{\rm n} \hbar^2 \boldsymbol{I} \cdot \left[ \frac{\boldsymbol{s}}{r^3} - 3 \frac{\boldsymbol{r}(\boldsymbol{s} \cdot \boldsymbol{r})}{r^5} \right]. \tag{9}$$

where  $\boldsymbol{r}$  is the distance between these spins.

Fermi contact interaction s electrons have finite density at the nucleus, therefore, interaction of nuclear spin with s electron spin is given by

$$\mathcal{H}_{\rm F} = \frac{8\pi}{3} \gamma_{\rm e} \gamma_{\rm n} \hbar^2 \boldsymbol{I} \cdot \boldsymbol{s} \delta(\boldsymbol{r}). \tag{10}$$

**Orbitgal interaction** The interaction between nuclear spin and orbital angular momentum of electron with  $l \ge 1$  (p, d, f, ... electron) is given by

$$\mathcal{H}_{\rm orb} = \frac{e\hbar}{mc} \gamma_{\rm n} \frac{\boldsymbol{I} \cdot \boldsymbol{l}}{r^3} \tag{11}$$

where r is the separation of nuclear spin and an orbital angular momentum of electrons.

**Core polarization interaction** Core polarization contribution to the hyperfine field arises from the alternation in the radial wavefunction of s electrons inner closed shells brought about by the their exchange couplings with the d or f spin polarization and given as,

$$\mathcal{H}_{\text{core}} = \frac{8\pi}{3} \gamma_{\text{e}} \gamma_{\text{n}} \hbar^2 \boldsymbol{I} \cdot \boldsymbol{S} \sum_{i} (|\psi_{i}^{\uparrow}|^2 - |\psi_{i}^{\downarrow}|^2), \qquad (12)$$

where  $|\psi_i^{\uparrow}|^2 - |\psi_i^{\downarrow}|^2$  is a magnitude of the unbalanced spin density at the nucleus due to closed *s* shells.

The term for  $j \neq i$  in eqn.(5.1) gives interactions between the observed nuclei and electron spins in the neighboring atoms

**Transferred hyperfine interaction** The nuclei of non-magnetic elements also feel the internal field caused by the neighboring magnetic ions via coupling between the *s*-electron wavefunctions and the d or f electron wave functions of magnetic ions.

# 2.3 Knight shift

In the paramagnetic metals and compounds, the resonance field is shifted from that in free atom given by eqn.(7). This effect referred to as "Knight shift" [15], defined as

$$K = \frac{\Delta H}{H_o},\tag{13}$$

where  $\Delta H$  is an internal magnetic field and  $H_o$  is an applied field. Knight shift is a measure of local magnetic susceptibility and provides information on the static magnetic state of 4f electrons.

# 2.4 Nuclear quadrupole interaction

The electric quadrupole interaction arises from the orientation dependent energy of the non-spherical nucleus  $(I \ge 1)$  in the gradient of the electrostatic field at the nuclear site. The quadrupole Hamiltonian is given by

$$\mathcal{H}_{Q} = \frac{e^{2}qQ}{4I(2I-1)} \Big[ (3I_{z}^{2} - I^{2}) + \frac{1}{2}\eta(I_{+}^{2} + I_{-}^{2}) \Big]$$
(14)  
$$q \equiv \frac{\partial^{2}V}{\partial z^{2}},$$
  
$$\eta \equiv \frac{\partial^{2}V/\partial x^{2} - \partial^{2}V/\partial y^{2}}{\partial^{2}V/\partial z^{2}}.$$

In case of axial symmetry of the field gradient  $\eta=0$ , the eigenvalues of eqn.(14) is obtained as

$$E_m = A[3m^2 - I(I+1)], \quad A \equiv \frac{e^2 qQ}{4I(2I-1)}$$
(15)

and for  $I = \frac{3}{2}$ , the nuclear quadrupole resonance (NQR) or pure quadrupole resonance (PQR) spectrum consists of the single transition between the  $\pm \frac{1}{2}$  and  $\pm \frac{3}{2}$  levels, and given by

$$\nu_{\rm Q} = \frac{3e^2 q Q}{2\hbar I (2I-1)}.$$
 (16)

The electric field gradient q generally consists of contributions from the ionic charge on the neighboring lattice sites around the observed nucleus,  $eq_{\text{lat}}$ , and intra-atomic electron distribution,  $eq_{\text{val}}$ , as

$$eq = eq_{\text{lat}}(1 - \gamma_{\infty}) + eq_{\text{val}}, \tag{17}$$

where  $\gamma_{\infty}$  is the Sternheimer antishielding factor [16] which arises from the charge redistribution of core electrons induced by the charge of the surrounding ions.  $eq_{\text{lat}}$  relates to the unite cell volume V as roughly  $eq_{\text{lat}} \propto 1/V$ .

# 2.5 Nuclear spin-lattice relaxation time

The dynamical properties of the electron spins can be reflected by measuring the relaxation time of the nuclear spin system. There are two types of relaxation times, the spin-lattice relaxation time  $T_1$  and the spin-spin relaxation time  $T_2$ .  $T_1$  is the relaxation time of the nuclear spin magnetization to its thermal equilibrium value and is indicative of the rate at which the nuclear spin system exchanges energy with its external surroundings. Whereas  $T_2$  is the time which characterizes the return of the transverse component of the nuclear spin magnetization to its equilibrium value of zero and is indicative of the rate at which energy is exchanged within the spin system itself.

The nuclear spin magnetic relaxation is express by the Fourier transform of the correlation function for the fluctuating component of local field, which can be replaced by the electron spin density. In the fluctuation-dissipation theorem [17], the correlation function of spin density is replaced by the dynamical susceptibility  $\chi(q, \omega)$ . Then we have generally

$$\frac{1}{T_1} = \frac{2\gamma_{\rm n}^2 k_{\rm B} T}{(\gamma_{\rm e}\hbar)^2} \sum_q A_q A_{-q} \frac{\chi_\perp''(\boldsymbol{q},\omega_0)}{\omega_0}$$
(18)

where  $\chi''(\boldsymbol{q}, \omega_0)$  is the imaginary part of dynamical susceptibility of electron spins, A(q) is the q-dependent hyperfine coupling and  $\hbar\omega_0 \ll k_{\rm B}T$  [18].

 $T_1$  provides information on the dynamical property of f electrons or conduction electrons. For a well localize f electron system in which f electrons weakly interact with conduction electrons, the experimental value of the nuclear spin-lattice relaxation rate  $1/T_1$  is composed of two contributions as

$$\left(\frac{1}{T_1}\right) \approx \left(\frac{1}{T_1}\right)_f + \left(\frac{1}{T_1}\right)_c,$$
 (19)

where the first and second terms are the contributions from localized f electrons and conduction, respectively. In this case, the first term is much larger than the second one which follows the Korringa law [19]. We usually use the value  $1/T_1$  in a non-magnetic reference substance as  $(1/T_1)_c$ .

On the other hand, when the hybridization between f and conduction electrons is large, the f and conduction electron contributions are no more independent, and the assumption would be controversial. In this case it should be assumed as

$$\left(\frac{1}{T_1}\right) \approx \left(\frac{1}{T_1}\right)_{f+c},$$
 (20)

where f + c means the renormalized heavy quasi-particles. Thus, the evaluation of the f electron contribution depends largely on the analysis and is sometimes ambiguous.

# 3 Physical properties of the dense Kondo compounds YbXCu<sub>4</sub> (X=Au, Ag, In, Cd, Tl, Mg and Zn) probed by NMR

# 3.1 Introduction

Many of ytterbium based compounds display intermediated valence or heavy-Fermion behavior at low temperatures because of the two energetically close  $4f^{13}$  and  $4f^{14}$  electron configuration for Yb ions. This feature may be thought of as the "f-hole" analog of Ce's  $4f^1$  and  $4f^0$  configuration. The near degeneracy in energy of the two electron/hole configurations is easily affected by crystallographic environment around Yb ion, which results in the various physical properties.

The variation in physical properties in Ce- and Yb-based compounds is mainly derived from the change in the extent of hybridization between localized f electron and conduction electrons. Coqblin-Schrieffer model [20], which takes the change in the degree of freedom (2J+1) of f electrons after scattering with conduction electron into account and modifies the singleimpurity Anderson model [21], quantitatively accounts for the physical properties of Yb compounds.

Among the Yb-based compounds, a set of isostructural YbXCu<sub>4</sub> with X = Au, Cu, Ag, In, Cd, Tl, Mg and Zn have broad range of Kondo temperatures  $T_{\rm K}$  from about 1 to nearly 10<sup>3</sup> K [22], and show a wide range of physical properties associating with the extent of hybridization between f electrons and conduction electron density. Although the single-impurity model quantitatively accounts for much of the physical properties, universal behavior cannot be inferred by only account for the variations in the  $T_{\rm K}$ .

In order to shed light on the compound-to-compound variation of these physical properties from microscopic point of view, we have performed nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR) studies systematically. This paper reports results of systematic investigation for YbXCu<sub>4</sub> series and deduced the varied impact of crystal field-splitting, variations in effective valence, *c*-*f* hybridization and unit-cell volume, on their physics.

The basic properties of the  $YbXCu_4$  series reported by previous experience are as follows:

**YbAuCu**<sub>4</sub> YbAuCu<sub>4</sub> has a rather large linear specific heat coefficient  $\gamma = 150$  mJ/mol·K<sup>2</sup> and shows an antifferomagnetic ordering below 1 K [23]. The Curie-Weiss (CW) type behavior of the magnetic susceptibility  $\chi$  except at low temperature is associated with the nearly localized Yb<sup>3+</sup> moment (**Fig. 3(a)**). Significant effects of crystal electric field were observed in the specific heat and the electrical resistivity [24]. Inelastic neutron scattering study revealed a  $\Gamma_7$  doublet as the ground state, followed by a  $\Gamma_8$  quartet, 3.89 meV above it, while  $\Gamma_6$  is 6.88 meV above the ground state doublet [25]. The <sup>170</sup>Yb Mössbauer experiment showed the ordered moment as 1.46 ±0.07 $\mu_B$  at 50 mK [26], which is reduced by the Kondo compensation from the expected value of 1.71  $\mu_B$  for the  $\Gamma_7$  ground state in the cubic symmetry.

 $YbAgCu_4$  YbAgCu<sub>4</sub> has been considered to be between the localized and mixed-valence regimes with non-magnetic ground state [23] [25] [27] [28]. It has a large  $\gamma \sim 210 \text{ mJ/mol} \cdot \text{K}^2$ . Above 100 K,  $\chi$  obeys CW-law with  $\mu_{\rm eff} = 4.64 \mu_{\rm B}$ , indicating nearly localized 4f electrons. With decreasing temperature,  $\chi$  takes a local maximum at around 40 K (Fig. 3(b)), which can be reproduced by the theoretical curve [29] of the Coqblin-Schrieffer model [20] with a fixed angular momentum J=7/2 [23] [22]. The field-dependence measurement of the magnetization at low temperatures reveals a positive curvature above about 10 T [30] [22], which is expected for the J=7/2 magnetic impurity in case of N > 3 [31], where N being the degeneracy of the ground state. However, this dose not coincide with crystal electric field level scheme. The inelastic neutron scattering measurement indicated that  $\Gamma_7$  doublet is the ground state.  $\Gamma_6$  doublet and  $\Gamma_8$  quartet are located 9.3 meV, 7.2 meV above the ground state, respectively. Temperature variation of the electrical resistivity  $\rho(T)$  exhibits Kondo like behavior at high temperatures and follows the Fermi-liquid law, i.e.,  $\rho(T) = \Delta \rho_0 + AT^2$  at low temperatures



Figure 3: Susceptibility as a function of temperature for YbXCu<sub>4</sub> (X=Au, Ag, In, Cd, Mg and Tl).

(**Fig.4**).

**YbInCu**<sub>4</sub> YbInCu<sub>4</sub> has been most extensively studied among the YbXCu<sub>4</sub> series for its first-order valence transition. The valence transition was first reported on the study of cubic Leaves phase compounds Yb<sub>1-x</sub>In<sub>x</sub>Cu<sub>2</sub> with x=0.3-0.6 [32], Afterward, it was revealed that YbInCu<sub>4</sub> with C15b type crystal structure is responsible for the valence transition.

YbInCu<sub>4</sub> undergoes the first-order isostructural valence transition at  $T_{\rm V}$ =42 K accompanying a volume expansion of 0.5 %. The valence change at  $T_{\rm V}$  is estimated as 0.1 from the X-ray absorption spectra and thermal expansion experiments [26] [33], resulting in the valence of 2.9 below  $T_{\rm V}$ .  $\chi$  at high temperatures follows the CW-law with full free-ion moment of Yb (4.53) $\mu_{\rm B}$ ) with antiferromagnetic Weiss temperature ( $\theta \sim 11$  K). At  $T_{\rm V} \chi$  drops precipitously and takes a small constant value below  $T_{\rm V}$ , suggesting Pauli paramagnetic ground state (Fig. 3(c)). The Kondo temperature estimated from the  $\chi$  data is  $T_{\rm K}^{\rm H}=25$  K for high-temperature (HT) phase and  $T_{\rm K}^{\rm L}=$ 400 K for low-temperature (LT) phase [34] [35]. The electrical resistivity  $\rho$ decreases gradually with decreasing temperature at the HT phase and shows a sudden decrease at  $T_{\rm V}$ . Below  $T_{\rm V}$ ,  $\rho$  is less than 10  $\mu\Omega$ cm and shows metallic behavior [26]. The specific heat measurement showed that  $\gamma$  for the LT phase is measured to be 50 mJ/mol  $K^2$  [26] [43]. In the LT phase the ratio of the temperature independent susceptibility to the  $\gamma$  (LT phase) is consistent with the Wilson ratio for J=7/2, indicating the Fermi liquid state [36]. In the LT phase magnetic field induced valence transition phase was observed at  $\sim 300$  kOe. This is considered to be the same mechanism of transition with induced by temperature [30]. Following a band calculation for the HT phase, 13 4f bands are occupied and one 4f hole is above  $E_{\rm F}$ . Then the band structure is semi metallic similar to  $LuInCu_4$ . On the other hand, heavy-Fermion state is realized in the LT phase [37]. The crystal level scheme is deduced with the level sequence  $\Gamma_7$ - $\Gamma_8$  (3.2 meV)- $\Gamma_6$  (3.8 meV) above  $T_{\rm V}$  from inelastic neutron scattering experiments. Below  $T_{\rm V}$ , however, the crystal field transitions and the quasi-elastic scattering are absent [38].

**YbCdCu**<sub>4</sub>, **YbMgCu**<sub>4</sub>, **YbTlCu**<sub>4</sub> These compounds have a non-magnetic ground state.  $\chi$  shows a local maximum around 130 and 260 K for YbMgCu<sub>4</sub> and YbTlCu<sub>4</sub>, respectively. On the other hand,  $\chi$  for YbCdCu<sub>4</sub> displays the CW like behavior at high temperatures, and below 80 K, deviates from CW-law and shows a small kink around 30 K [22] (Fig. 3). Those suggests the compounds to being in a valence fluctuating regime.

**YbZnCu**<sub>4</sub> No magnetic ordering has been observed at low temperature in spite of the large CW behavior with nearly full Yb<sup>3+</sup> moment (**Fig. 5**).  $\rho(T)$ exhibits an upturn at low temperatures, which can be completely suppressed by applying a 300 kOe magnetic field (**Fig. 4**). The Hall coefficients at low temperatures is rather large compared with the other compounds in this series. Therefore, YbZnCu<sub>4</sub> has been considered to be a "failed Kondo semi metal" [22].

Data of  $T_{\rm K}$ ,  $\gamma$ ,  $\mu_{\rm eff}$  and  $\theta$  are summarized in the **Table 1**, **Fig. 3**, **Fig. 4** and **Fig. 5** show the magnetic susceptibility  $\chi$  and the electrical resistivity as a function of temperature for YbXCu<sub>4</sub> with X=Au, Ag, In, Cd, Mg, Tl and Zn [22].

# 3.2 Experimental details

#### **3.2.1** Experimental procedures

Single crystal of YbXCu<sub>4</sub> were grown by combining stoichiometric ratios of the constituent elements in 1:1:4 ratios with variety of X-Cu flux. Additionally, single crystals of YbMgCu<sub>4</sub> were grown from a lead flux. The high-purity metals (minimum 99.99 % purity) were placed in an alumina crucible and sealed in an evacuated quartz tube. The sample was then heated to 1100 °C and cooled slowly (20 °C/h) to 800 °C, at which the excess flux was spun off with a centrifuge, leaving tetrahedrally shaped crystals with a typical dimension of several millimeters [22] [34].

All samples we used for NMR and NQR experiment were provided by Dr. Sarrao, Los Alamos National Laboratory. We used single-crystal specimen



Figure 4: Electrical resistivity as a function of temperature for each of the  $YbXCu_4$  compounds.



Figure 5: Susceptibility as a function of temperature for YbZnCu<sub>4</sub>.

	$T_{\rm K}({\rm K})$	$\gamma \; (mJ/mol \; K^2)$	$\mu_{\rm eff}(\mu_{\rm B})$	θ
YbAuCu <sub>4</sub>	2	150	4.35	6
$YbAgCu_4$	100	210	4.64	51
$YbCdCu_4$	221	180	5.41	167
$YbMgCu_4$	855	60		$\sim 72$
$YbTlCu_4$	740	30		
$YbZnCu_4$	97	230	4.63	79
$YbInCu_4$ (HT)	25		4.22	11
$YbInCu_4$ (LT)	400	50		

Table 1: Kondo temperatures, electronic specific heat coefficients, effectivemagnetic moments and Weiss temperatures.

of each  $YbXCu_4$  and crushed them in a marble mortar into power smaller than skin depth.

#### 3.2.2 Crystallography

YbXCu<sub>4</sub> crystallized in the cubic AuBe<sub>5</sub> (C15b) type structure in which Yb atoms (4a site) and X atoms (4c site) are ordered in the zince regular lattice; the 4a and 4c sites are crystallography equivalent. The Cu site is characterized by small tetrahedrons (16e site). This structure belongs to the space group F43m ( $T_d^2$ ). As illustrated in **Fig. 6**, Yb, X and Cu are described by the following coordinates with the face-centering translation (0, 0, 0)+,(0, 1/2, 1/2)+, (1/2, 0, 1/2)+ and (1/2, 1/2, 0)+;

4a site (0, 0, 0) 4c site (1/4, 1/4, 1/4) 16e site (5/8,5/8,5/8), (5/8,-5/8,-5/8), (-5/8,5/8,-5/8), (-5/8,-5/8,5/8).

It should be noted that the 4a and 4c sites are local cubic symmetry (43m) whereas the 16e site is less symmetric, i.e. trigonal (3m) around on of  $\langle 111 \rangle$  axes. As will be discussed later, some X-Cu site disorder cannot be rule out [22] [39].

# 3.3 <sup>171</sup>Yb NMR study on the fluctuating valent state of YbInCu<sub>4</sub>

#### 3.3.1 Experimantal results

The YbInCu<sub>4</sub> is a appropriate compound for NMR, study since it is in principle possible to observe all the constituent atoms. The NMR studies on YbInCu<sub>4</sub> have been, however, restricted to nonlanthanide nucleus, such as NQR and NMR of Cu nuclei [40] [41] [42] [44] [46] and NMR of <sup>115</sup>In [43] [45] because it is generally difficult to find the NMR signal of a magnetic ions with an unstable *f*-electrons due to the large orbital moment and very short relaxation time. We first succeeded to observe <sup>171</sup>Yb NMR signal and measured



Figure 6: Schematic crystal structure of  $YbXCu_4$ : C15b type.

the Knight shift and relaxation time in the HT phase. The observation of Yb-NMR is essentially important to provide direct information on the ground state of 4f electrons.

The NMR experiment was performed utilizing a wide-band phase-coherent spectrometer. The NMR spectrum was obtained in a field-sweeping procedure at constant frequencies with boxcar integrator.

The observed spin-echo spectra of <sup>171</sup>Yb at 4.2 K are shown in **Fig. 7**. A small <sup>171</sup>Yb signal at 75 MHz is located at a field just below the satellite line for  $\theta=0$  of the quadrupole-split for <sup>65</sup>Cu NMR  $|\frac{3}{2}\rangle \leftrightarrow |\frac{1}{2}\rangle$  transition. (**Fig. 7(a)**). Here,  $\theta$  is the angle between the applied field and the principal Z axis of the electric field gradient q. The time interval between the  $\pi/2$  and  $\pi$  rf pulses was  $10\mu$ s. At a higher frequency 110 MHz, <sup>171</sup>Yb spectrum is detached from the <sup>65</sup>Cu satellite line as shown in **Fig. 7(b)**. The resonance field was directly proportional to the frequency and we obtained the Knight shift K as 101.3 %, determined at the peak intensity point, and K is independent of temperature in the range of 1.9-4.2 K. The full-width at half-maximum is about 2.9 kOe. Above 4.2 K, it was difficult to observe the signal because of



Figure 7: NMR spectra of <sup>171</sup>Yb in YbInCu<sub>4</sub> 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 <sup>65</sup>Cu at  $\theta=0$  and  $\pi/2$  are indicated by open and closed arrows, respectively.

the very weak intensity.

Transverse relaxation time  $T_2$  was determined from the decay of the spinecho intensity at  $2\tau$  by changing the interval time  $\tau$  between  $\pi/2$  and  $\pi$  rf pulse. Here, we used a digital signal averager to improve satisfactorily the signal-to-noise ratio. Assuming that both the fluctuating internal field and hyperfine field are isotropic,  $1/T_2$  is decomposed into two contributions as [47]

$$\frac{1}{T_2} = \frac{1}{T_2^*} + \frac{\alpha}{T_1},\tag{21}$$

where  $\alpha$  for <sup>171</sup>Yb is  $(I + \frac{1}{2})^2 = 1$ ,  $1/T_2^*$  is the temperature-independent spinspin relaxation term and  $1/T_1$  is a temperature dependent longitudinal relaxation term. When  $1/T_1$  is enough larger than  $1/T_2^*$ , the temperature dependent component of  $1/T_2$  gives a measure of  $1/T_1$ . The experimentally observed value  $1/T_2$  for <sup>171</sup>Yb is directly proportional to the temperature in the range 1.9-4.2 K. We obtained a temperature-independent relaxation rate  $(T_2T)^{-1} = (T_1T)^{-1} \simeq 1.1 \times 10^4 (\text{sK})^{-1}$ , which is much larger than the value of  ${}^{63}$ Cu ; 0.47 (sK)<sup>-1</sup> [40], and of  ${}^{115}$ In ; 1.1 (sK)<sup>-1</sup> [45], in the LT phase. The large  $(T_1T)^{-1}$  value of  ${}^{171}$ Yb confirms the formation of a quasi-particle Fermi-liquid with largely enhanced mass, that is, the LT phase of YbInCu<sub>4</sub> is an enhanced Pauli paramagnetic state.

#### 3.3.2 Discussion

The use of NMR as a local probe for electron properties has a long and fruitful tradition. The Knight shift and magnetic susceptibility give an important information. Usually the Knight shift due to the on-site 4f electrons is given by

$$K_{4f} = H_{\rm hf} \frac{\chi_{4f}}{N\mu_{\rm B}} \tag{22}$$

and hyperfine field  $H_{\rm hf}$  is composed of the orbital  $H_{\rm hf}^{\rm orb}$ , spin dipolar  $H_{\rm hf}^{\rm sd}$ fields. Using a Hartree-Fock value of 13.83 a.u. for  $\langle r^{-3} \rangle$  [48]  $H_{\rm hf}$  can be calculated as  $H_{\rm hf}$ =1.15×10<sup>6</sup> Oe/ $\mu_{\rm B}$  for a free Yb<sup>3+</sup> ion with J=7/2 ground state. The 4f electrons also contribute to hyperfine field by the mechanism known as corepolarization field. This value is also calculated to be  $H_{\rm hf}^{\rm cp} =$  $-0.014 \times 10^6$  Oe/ $\mu_{\rm B}$  [50], which is much smaller than  $H_{\rm hf}$ .

Taking the experimental value of the Knight shift and susceptibility  $\chi(0) = 6.37 \times 10^{-3}$  emu/mol [34], we obtained the hyperfine field  $H_{\rm hf}$  of <sup>171</sup>Yb in the LT phase as  $0.88 \times 10^6$  Oe/ $\mu_{\rm B}$ . This value dose not much differ from the expected value for free Yb<sup>3+</sup> ions. The change in the Yb ions' valence from 3+ to 2.9+ at  $T_{\rm V}$  induces the reduction of  $\langle r^{-3} \rangle$  which results in the  $H_{\rm hf}$  decrease. The paramagnetic behavior in the LT phase of YnInCu<sub>4</sub> also suggests an additional reduction of  $\langle r^{-3} \rangle$ , as is generally expected for metals.

Generally the relaxation rate  $(T_1T)^{-1}$  consists of the *s* contact, corepolarization, orbital, magnetic dipolar and quadrupole contributions. If we tentatively assumed that the orbital relaxation process is dominant in this system, the density of states  $D(E_{\rm F})$  of Yb's 4*f* electrons at Fermi level in the LT phase can be evaluated as  $D(E_{\rm F}) \simeq 19.5$  state/eV/Yb using a relation

$$\frac{1}{T_1 T} = \frac{4\pi}{\hbar} (\gamma_{\rm n} \hbar H_{\rm hf}^{\rm orb})^2 D(E_{\rm F})^2 k_{\rm B}.$$
(23)

Here we took the experimental  $(T_1T)^{-1} \simeq 1.1 \times 10^6 \text{ (sK)}^{-1}$  and  $H_{\text{hf}}^{\text{orb}} = 0.88 \times 10^6 \text{ Oe}/\mu_{\text{b}}$ . According to the band structure calculation for YbInCu<sub>4</sub> [37],

 $D(E_{\rm F})$  of Yb's 4f in the HT phase is 2.29 state/eV/Yb. From the Sommerfeld coefficient of the electronic specific heat  $\gamma$ =50 mJ/mol·K<sup>2</sup>, the total density of state of YbInCu<sub>4</sub> is also calculated to be 10.6 state/eV/Yb. The large  $D(E_{\rm F})$  evaluated from  $(T_1T)^{-1}$  in the LT phase is an indication that the valence transition largely modifies the density of state of Yb 4f. Despite the rough assumption in the analysis, the density of the state of YbInCu<sub>4</sub> estimated from  $(T_1T)^{-1}$  is comparable with that from specific heat coefficient. Therefore we conclude that the density of state at the Fermi level of YbInCu<sub>4</sub> dominated by the 4f electrons of the Yb atoms.

Shiba calculated the nuclear spin-lattice relaxation of transition metal impurities and showed that Korringa relation is valid at low temperatures  $T \ll T_{\rm K}$  for any order of the Coulomb interaction between *d* electron [51]. This relation has been extended to the case of rare earth single impurity by Kuramoto *et al.* [52]. The Korringa relation for the impurity nuclear spin-latticed relaxation at low temperatures  $T \ll T_{\rm K}$  is given by

$$T_1 T K^2 = \frac{C(2J+1)}{2\pi\hbar\gamma^2_{\rm n}},$$
(24)

where  $C = g_J^2 \mu^2_B J(J+1)/3k_B$  is the Curie constant. The calculated value for the J=7/2 ground state Yb<sup>3+</sup> is  $2.29 \times 10^{-4}$  sK. The measured Knight shift and  $T_1$  gives  $T_1 T K^2 \simeq 0.92 \times 10^{-4}$  sK for <sup>171</sup>Yb in YbInCu<sub>4</sub>, which is about two times smaller than the calculated value. This discrepancy might originate from the inherent difference in the dynamical behavior between dilute and periodic impurity system or anisotropic wavefunction due to CEF(Crystal electric field) ground state.

# 3.4 <sup>63</sup>Cu NMR in YbXCu<sub>4</sub> compounds (X=Au, Ag, In, Cd, Mg, Tl, and Zn)

#### 3.4.1 Quadrupole resonance frequency

Because of the local trigonal symmetry of the 16e site (Cu site), the finite electric field gradient(EFG) gives a single NQR (Nuclear Quadrupole Resonance) line, corresponding to the transition between the levels  $|\pm \frac{1}{2}\rangle$  and  $|\pm \frac{3}{2}\rangle$ . Then one can observe the zero field NMR for each of <sup>63</sup>Cu (<sup>63</sup>Q=-0.211)

barns) and  ${}^{65}$ Cu ( ${}^{65}Q$ = -0.195 barns) nucleus. The resonance frequency  $\nu_Q$  is given eqn.(16).



Figure 8: <sup>63</sup>Cu and <sup>65</sup>Cu NQR spectrum for YbMgCu<sub>4</sub> at 4.2 K.

Figure 8 shows nuclear resonance spectra of YbMgCu<sub>4</sub> observed at zero magnetic field. As is shown in Fig. 8, we can roughly reproduce the spectra with two Lorentzian line shapes. The relative intensities are nearly equal to that of natural abundance of  $^{63}$ Cu to  $^{65}$ Cu (7:3), and the resonance frequencies  $\nu_{\rm Q}$  are 10.91 and 10.05 MHz, of which ratio is almost equal to that of the nuclear quadrupole moment of  $^{63}$ Cu to  $^{65}$ Cu,  $^{63}Q/^{65}Q=1.07$ .  $\nu_{\rm Q}$  of  $^{63}$ Cu for other compounds at 4.2 K are determined in the same way ;  $^{63}\nu_{\rm Q}=8.92$  MHz for YbAuCu<sub>4</sub>, 10.7 MHz for YbAgCu<sub>4</sub>, 14.05 MHz for YbInCu<sub>4</sub>, 110.91 MHz for YbMgCu<sub>4</sub>, 13.2 MHz for YbTlCu<sub>4</sub> and 12.59 MHz for YbZnCu<sub>4</sub>. Some of  $^{63}\nu_{\rm Q}$  for YbXCu<sub>4</sub> (X = Au, Ag, In, Cd, Tl) have previously reported and present results are in agreement with them [40] [46] [53]. It should be noted that the value of  $\nu_{\rm Q}$  of YbInCu<sub>4</sub> depends on temperature, above  $T_{\rm V}$ ,  $\nu_{\rm Q}$  increases gradually with decreasing temperature, and is proportional to the reciprocal unit cell volume [42].  $\nu_{\rm Q}$  changes discontinuously at  $T_{\rm V}$  and takes almost a constant value in the LT phase.

#### 3.4.2 NMR spectra and analysis

We have carried out the <sup>63,65</sup>Cu NMR measurements utilizing a wide-band phase-coherent spectrometer in a temperature range between 4.2 and 250 K. Figure 9 shows <sup>63,65</sup>Cu NMR spectra for YbMgCu<sub>4</sub> at 4.2 K obtained at a constant frequency of 75 MHz. The spectra for all of the compounds have general electric-quadrupole pattern [54]: a second-order split central line and first-order equally-split satellite lines with maximum at  $\theta = \pi/2$ . The quadrupole-split spectra are assigned to  $^{63,65}$ Cu on the 16e site with noncubic local symmetry. A nonzero asymmetry parameter  $\eta$  of the EFG q at Cu nuclei is to result in shoulders on the both side of central line and also on the satellite lines  $\phi=0$  ( $\theta=0$ ) [55]. Here  $\theta$  is the angle of the applied field  $H_{appl}$  with respect to the principle Z axis of q, and  $\phi$  the azimuthal angle. Lack of clear shoulders either on the central line or satellite lines in those spectra indicates that the value of  $\eta$  in YbXCu<sub>4</sub> is rather small. In this case the interval between the first satellite lines gives us a measure of  $\nu_{\rm Q}$ , which is in good agreement with the value obtained from NQR spectra in all compounds.

The second-order effect of the electric quadrupole interaction is to result in the splitting of the central resonance line. **Figure 10** shows the line shape of central resonance line for a powdered sample. Because of the particular orientation dependence, the central line shape possesses two maxima at  $\cos \theta = 0$  and  $\cos^2 \theta = 5/9$  [56]. In addition to these maxima, a small discontinuity or step appears at  $\cos \theta = 1$ . When dipolar broadening effects are taken into account, this step is very much smoothed over so that it is rarely discernible experimentally. The splitting of the second-order quadrupole splitting is proportional to  $1/H_{appl}$ .

In case that nuclei are located at the lower symmetry site, the anisotropic hyperfine interaction leads to the anisotropic Knight shift depending on the angle  $\theta'$  between the axial symmetry axis and external magnetic field  $H_{\text{appl}}$ . The angle dependence Knight shift  $K(\theta')$  is given by

$$K(\theta') = K_{\rm iso} + K_{\rm ax}(3\cos^2\theta' - 1).$$
<sup>(25)</sup>

Here  $K_{iso}$  and  $K_{ax}$  are the isotropic and axial components of the Knight shift tensor. A calculated resonance line shape for the powdered sample without



Figure 9:  $^{63}$ Cu and  $^{65}$ Cu NMR spectrum for YbMgCu<sub>4</sub> at 4.2 K measured at a constant frequency of 75 MHz.



Figure 10: Spectrum of a central resonance for the case where second order quadrupole effects present.
quadrupole interaction is shown **Fig.11** [57]. One can see a maximum at  $\cos \theta' = 0$  which is written as  $K_{\parallel}$  and a shoulder at  $\cos \theta' = 1$  as  $K_{\perp}$ .

$$K_{\rm iso} = \frac{K_{\parallel} + 2K_{\perp}}{3} \tag{26}$$

$$K_{\rm ax} = \frac{K_{\parallel} - K_{\perp}}{3} \tag{27}$$

 $K_{\parallel} - K_{\perp}$  increases in proportion to  $H_{\text{appl}}$ .

$$K(\theta') \models K_{iso} + K_{ax} (3\cos^2 \theta' - 1)$$

$$K_{iso} > 0, K_{ax} > 0$$

$$\cos \theta' = \pm 1$$

$$\cos \theta' = 0$$

$$H_{appl}$$

Figure 11: Resonance spectrum with axial Knight shift.  $\theta'$  is a angle between the axial symmetry axis and the external magnetic field  $H_{\text{appl}}$ .

The determination of the Knight shift from the  $^{63}$ Cu NMR spectra at 16e site in YbXCu<sub>4</sub> compounds requires a more complicated procedures due to the presence of both the electric quadrupole interaction and anisotoropic Knight shift with nearly the same order of magnitudes. Insofar we know, the value of Cu Knight shift have not been reported except for YbInCu<sub>4</sub> [44]. We have succeeded to deduce the value of the  $K_{iso}$  and  $K_{ax}$  from the measurement of the dependence of the NMR spectra on the applied field 5-15 T.

We shall suppose that the magnetic shift tensor is axially symmetric, and that the major axes of the electric field gradient and magnetic shift tensors are coincident ( $\theta = \theta'$ ). If this were not present case, each of the quadrupole split lines would be split into four lines or severely broadened. It seems to be a reasonable assumption that both EFG and internal magnetic field at 16e site largely determined by Yb atoms with partially filled 4f electrons. For the case that the axial Knight shift and second-order quadrupole effect are present simultaneously in the absence of quadrupole asymmetry factor  $\eta \sim 0$ , Jones *et al.* [58] and McCart*et al.* [59] calculated that NMR line shape possess two singularities, which occur at  $\cos \theta_{\rm I}=0$  and at

$$\cos \theta_{\rm II} = \pm \left\{ \frac{5}{9} - \frac{8a\nu_0^2}{3\nu_{\rm Q}^2 [I(I+1) - \frac{3}{4}]} \right\}^{1/2}.$$
 (28)

Here we employed the notation  $a=K_{\rm ax}/(1+K_{\rm iso})$ . The 5/9 term is that for the electric quadrupole interaction alone. For the NMR spectra obtained in the field sweeping procedure at a constant frequency  $\nu_0$ , the resonance fields  $H_{\rm I}$  and  $H_{\rm II}$  corresponding to the two maxima of central line ( $H_{\rm I}$  is low field side and  $H_{\rm II}$  is high side) are given by

$$h\nu_{0}(\theta_{\rm I}) = \gamma_{\rm n}\hbar H_{\rm I}(1+K_{\rm iso}-K_{\rm ax}) + \frac{hb}{\nu_{0}}, \text{ and}$$
(29)  
$$h\nu_{0}(\theta_{\rm II}) = \gamma_{\rm n}\hbar H_{\rm II} \left\{ 1+K_{\rm iso} + K_{\rm ax} \left(\frac{2}{3} - \frac{a\nu_{0}^{2}}{2b}\right) \right\} - h \left\{ \frac{16b}{9\nu_{0}} - \frac{a^{2}\nu_{0}^{3}}{4b} \right\}.$$
(30)

Where

$$b = \frac{\nu_{\rm Q}^2}{16} [I(I+1) - \frac{3}{4}].$$

The value of  $K_{\rm iso}$  and  $K_{\rm ax}$  can be obtained by solving from equations (29) and (30), and  $\nu_{\rm Q}$  obtained from NQR measurement.

The results for <sup>63</sup>Cu on the 16e site in each YbXCu<sub>4</sub> are plotted in **Fig. 12** and **Fig. 13** against temperature. The spectra for X=Au and Zn below 55 K did not provide any reliable values of  $H_{\rm I}$  and  $H_{\rm II}$  because of the large CW-type broadening of line shape at low temperatures. Then we calculated  $K_{\rm iso}$  and  $K_{\rm ax}$  only for the temperature above ~ 55 K.

Shown in **Fig. 14** is the dependence of the splitting of the central line on the applied magnetic field for X=In, Ag. The splitting of central line is given by [58]

$$\Delta_{\rm I,II} = \frac{25b}{9\nu_0} - \frac{5a\nu_0}{3} + \frac{a^2\nu_0^3}{4b}.$$
(31)

As drawn by dotted curves in **Fig. 14**,  $\Delta_{I,II}$  from experimental data were reproduced satisfactory with calculated  $K_{iso}$  and  $K_{ax}$  in spite of our rude approximation.



Figure 12: Temperature dependence of isotropic and axial Knight shifts of  $^{63}$ Cu on 16e site in each YbXCu<sub>4</sub> compounds with X=Au, Ag, In, Cd, Mg and Tl, calculated from resonance fields at two maxima of the central NMR line.



Figure 13: Temperature dependence of isotropic and axial Knight shifts of  $^{63}$ Cu on 16e site in YbZnCu<sub>4</sub>.



Figure 14: Dependence on applied magnetic field  $H_{\rm appl}$  of central NMR line splitting of  $^{63}$ Cu at 16e site in YbInCu<sub>4</sub> and YbAgCu<sub>4</sub>. Dotted curves are splitting of the central NMR line calculated through the procedure described in the text.

At high temperatures, the isotropic Knight shift  $K_{iso}$  for X=Au, Ag, Cd. In and Zn exhibit a CW-type negative increase.  $K_{iso}$  for X=Mg increases monotonously with decreasing temperature.  $K_{iso}$  for X=Tl is almost independent of temperature. At low temperatures,  $K_{iso}$  for each of the compounds shows distinct behavior: further CW-type increase for X=Au and Zn; a step increase at 45 K associated with the valence transition for X=In; an negative maximum at ~40 K for X=Ag and at ~140 K for X=Cd; monotonous positive increase down to 30 K and followed by saturation behavior for X=Mg. The axial Knight shift  $K_{ax}$  is rather small for X=Ag(at LT), Cd, Mg, Tl, indicating that the Knight shift is rather isotropic in these compounds.



Figure 15:  $^{63}$ Cu central resonance line which consists of the two maxima at  $H_{\rm I}$  and  $H_{\rm II}$ , and an additional single line (open arrow) for YbCdCu<sub>4</sub> at 75 MHz and 260 K.

We found an additional resonance line between  $H_{\rm I}$  and  $H_{\rm II}$  for  $X={\rm Cd}$ , Tl and Zn at high temperatures, which is shown for in **Fig. 15** with an open arrow for  $X={\rm Cd}$ . With lowering temperature, the single resonance line approaches the maximum  $H_{\rm II}$  and which makes it difficult to deduce the reliable value of K. As shown in **Fig. 16**, the negative K for  $X={\rm Cd}$ , Tl and Zn exhibit CW-type increase. K for Tl takes a minimum at around

50 K. This additional resonance line is reasonably assigned to Cu on the 4c site with local cubic symmetry ( $\nu_{\rm Q}=0$ ). The possible site-disorder has been pointed out by some authors [22] [39]. This is an evidence for the Cu-X site of about 10% or less being estimated from the signal intensity.



Figure 16: Temperature dependence of Knight shifts of  ${}^{63}$ Cu on 4c site in YbXCu<sub>4</sub> with X=Cd, Tl and Zn.

#### 3.4.3 Lattice constant for YbAgCu<sub>4</sub>

We have carried out an X-ray diffraction measurement for YbAgCu<sub>4</sub> at low temperatures. The lattice constant a of YbAgCu<sub>4</sub> shows characteristic temperature dependent as seen in **Fig. 17**. With lowering temperature, the value of a decreases at high temperatures as in the ordinary metals, but takes a minimum at around 40 K, where the  $\chi$  data exhibit a local maximum.



Figure 17: Plots of the lattice constant against temperature for  $YbAgCu_4$ , measured by low-temperature x-ray diffraction.

#### 3.4.4 Discussion

In rare-earth compounds, the Knight shift K(T) measured at the nuclei of no-magnetic ligand ions is consist of two interaction terms: the interaction term between the nuclei and on-site electrons, and the interaction between the nucleus and neighboring f electrons. Therefore, we may write [54]

$$K(T) = K_s + \frac{H_{\rm hf}}{\mu_{\rm B}N}\chi(T)$$
(32)

where  $H_{\rm hf}$  is the transferred hyperfine field and  $K_s$  is the on-site contribution which consists of a conduction electron term  $K_c$  and a field-induced Van Vleck orbital term  $K_{\rm VV}$  as

$$K_s = K_c + K_{\rm VV}.\tag{33}$$

Here we neglected contributions from the Landau and ion-core diamagnetic terms which are generally much smaller than those from the paramagnetic terms for transition-metal elements.

 $K_{\rm iso}$  versus  $\chi$  plot for <sup>63</sup>Cu at 16e site for each YbXCu<sub>4</sub> compounds are shown in **Fig. 18** with temperature as an implicate parameter. Data are on

the straight line for X=Au, Ag, In (HT phase) and Zn as drawn in the figure, and the slope yields  $H_{\rm hf}$ =-0.63, -0.72, -0.45 and -1.3 kOe/ $\mu_{\rm B}$ , respectively. The intersection of the straight line and vertical  $K_{\rm iso}$  axis gives an estimate of the temperature-independent term  $K_{\rm s}$  at high temperature as 0.33, 0.46, 0.17 and 0.36 % for X=Au, Ag, In and Zn, respectively.



Figure 18: Isotoropic Knight shift versus magnetic susceptibility for  $^{63}$ Cu on the 16e site of YbXCu<sub>4</sub> (X=Au, Ag, In, Cd, Mg, Tl and Zn).

In contrast,  $K_{\rm iso}$  for  $X={\rm Cd}$ , Tl, Mg exhibits variety of behavior. For  $X={\rm Cd}$ , data above 140 K are roughly on the straight line with  $H_{\rm hf}=-0.52$  kOe/ $\mu_{\rm B}$  and  $K_{\rm s}=0.15$  %.  $K_{\rm iso}$  below 140 K increases irrespective of the saturating behavior of  $\chi$ . If we reasonably assume that the on-site Knight shift  $K_c$  is near independent of temperature, the  $K-\chi$  plots indicate that the negative  $H_{\rm hf}$  begins to decrease, changes sign at around 50 K, and increases to 0.47 kOe/ $\mu_{\rm B}$  at 4.2 K. For  $X={\rm Mg}$ , ant linear relation in  $K_{\rm iso}-\chi$  plots are not observed in our experimental temperature range. We tentatively estimate the value of  $K_s$  using the CW-type relation for K,  $K = K_s + \alpha/(T+\theta)$ , with  $\theta=72$  K deduced form  $\chi$  data. Then the  $K_{\rm iso}-\chi$  plot indicates that  $H_{\rm hf} \sim 2.7$  kOe/ $\mu_{\rm B}$  at 250 K and increases to  $\sim 5.4$  kOe/ $\mu_{\rm B}$  at 30 K. The increase in  $H_{\rm hf}$  is similar to  $X={\rm Cd}$ . For  $X={\rm Tl}$ , the nearly temperature-independent behavior of  $K_{\rm iso}$  gives  $K_s \sim 0.20$  %.

**Figure 19** shows the Knight shift K of <sup>63</sup>Cu for the 4c site versus  $\chi$  plots for X=Cd, Tl and Zn. The data for X=Cd and Zn at high temperatures

above 140 and 70 K, respectively, lie on the straight line, which is consistent with the  $K_{\rm iso}$ - $\chi$  plots for 16e site. Each slope gives  $H_{\rm hf}$ =-0.32 kOe/ $\mu_{\rm B}$ ,  $K_s$ =0.17 % for X=Cd and  $H_{\rm hf}$ =-0.31 kOe/ $\mu_{\rm B}$ ,  $K_s$ =0.30 %, respectively. The plots for X=Tl are somewhat scattered because of the small  $\chi$  value.



Figure 19: Knight shift versus magnetic susceptibility plots for  ${}^{63}$ Cu on the 4c site of YbXCu<sub>4</sub> (X=Cd, Tl and Zn).

Temperature dependent transferred hyperfine field The linear dependence of  $K_{iso}$  with  $\chi$  observed for the compounds with X=Au, Ag, In(HT phase) and Zn is a clear evidence for the fact that both  $K_{iso}$  and  $\chi$  is dominated by the localized f spins of Yb ions. The observation of a nonlinear relation K- $\chi$  for X=Cd and Mg implies that either value of  $H_{hf}$  varies with temperature or the experimental  $\chi$  includes possible extrinsic susceptibility. As for the extrinsic  $\chi$  due to some magnetic impurity ions, it is hard to expect a dominant contribution at high temperatures.

As mentioned in the previous paragraph,  $K_{\rm iso}$  for <sup>63</sup>Cu versus  $\chi$  plots for both X=Cd (T < 50 K) and Mg shows a nonlinear relation. For X=Cd, a linear relationship between  $K_{\rm iso}$  and  $\chi$  was observed only above ~140 K which the bulk susceptibility follows the CW-law. Below  $\sim 140$  K which  $\chi$  begins to saturate, the  $K_{\rm sio}$ - $\chi$  plots begins to deviate from the linear relation. This is a indication that the value of the transferred hyperfine field  $H_{\rm hf}$  varies at low temperatures. Similar temperature dependent behavior of  $H_{\rm hf}$  was reported for <sup>27</sup>Al Knight shift in intermediate valence compound YbCuAl [61]. But in case of YbCuAl, the collapse of the linear relation occurs at the temperature which  $\chi$  takes local maximum. MacLaughlin *et al.* speculated that the onset of non-linearity in  $K-\chi$  plots was attributed to a temperature-dependent effect of intermediate valence on the transferred hyperfine coupling between the Yb moments and the <sup>27</sup>Al nuclei [61]. For X=Mg, we did not observe the any linear relation within present experimental temperature range (4.2-250)K). The  $\chi$  data for this compound starts to deviate from CW-law at around 300 K. Then, it is worth noting that a temperature below which the CW-law for  $\chi$  collapse almost coincides with the temperature below which  $H_{\rm hf}$  begins to increase for both X=Cd and Mg, The variation in the value of  $H_{\rm hf}$ observed for X = Cd nd Mg is considered to be ascribed to the valence fluctuations as well as YbAlCu. The variation in the CEF energy level scheme of Yb ions, associated with the transformation of the system from the localized spin state into the mixed-valence state, is expected to largely change the anisotropic mixing between the Yb 4f hole states and conduction electrons and, thereby, the transferred hyperfine coupling tensor. As can be seen in Fig. 12, the Knight shift of  $^{63}$ Cu for in the compounds with X=Cd, Mg, Ag (T < 20 K), In (LT phase) which are expected to be in the mixed-valence regime, are rather isotropic  $(K_{iso})$  when compared with that in localized spin regime. We did not make any reliable analysis for X=Tl due to the small values of both  $H_{\rm hf}$  and  $\chi$ .

Variation of physical quantities with the species of X atoms As shown in Fig. 20, we found a good correlation between the on-site Knight shift  $K_s$  (closed circle) and low temperature specific heat coefficient  $\gamma$  (open circle) for X=Au, Ag and In (LT phase). Since  $\gamma$  is proportional to the density of state  $D(E_{\rm F})$  of the *c*-*f* resonance band, we may conclude that  $K_s$  of Cu is dominated by  $D(E_{\rm F})$  in YbXCu<sub>4</sub> series and the orbital term  $K_{\rm VV}$  in eqn.(33) is considered to be enough small. This is consistent with non-magnetic  $d^{10}$  configuration of Cu ions.

If we take only relatively large  $\gamma$  value into account, both X=Cd and Zn seem to be heavy-Fermion compounds. But the electrical resistivity  $\rho(T)$  for them do not show heavy-Fermion behavior at all [22]. For X=Cd,  $\rho(T)$  data decreases gradually with decreasing temperature as well as the mixed-valence compounds of X=Mg and Tl (Fig. 4). The small  $K_s$  for X=Cd indicates that  $D(E_{\rm F})$  of c-f conduction bands is comparable in magnitude with that for X=In (LT phase), Mg and Tl. Moreover, the temperature dependent  $H_{\rm hf}$  at low temperatures suggests that YbCdCu<sub>4</sub> also belongs to a group of mixed-valence compounds. Then the enhanced  $\gamma$  value for X=Cd would attribute to possible extrinsic magnetic contribution. On the other hand,  $\rho(T)$  of X=Zn is about five times larger than that of the other YbXCu<sub>4</sub> compounds and shows upturn at low temperatures (Fig. 4). The  $\chi$  data do not level off at low temperatures but keep increasing with decreasing temperature (Fig. 5). Those experimental results indicate that the strength of c-f mixing in YbZnCu<sub>4</sub> is very small and 4f hole of Yb ions retains a local moments even at low temperatures. The large  $\gamma$  value estimated for X=Zn probably originates from some extrinsic magnetic contributions.

As shown in **Fig. 17**, the temperature dependence lattice constant a for YbAgCu<sub>4</sub> shows a minimum at around 40 K where  $\chi$  takes the local maximum. As the unite-cell expansion is favorable for non-magnetic Yb<sup>2+</sup> rather than magnetic Yb<sup>3+</sup>, we may conclude YbAgCu<sub>4</sub> undergoes crossover from local moment regime to mixed-valence regime around 40 K, which is consistent with resonant inelastic x-ray scattering (RIXS) measurement [62]. The CW behaviors of  $\chi$  and the Knight shift for YbAuCu<sub>4</sub> can reasonably ascribe to an almost stable Yb<sup>3+</sup> state with well defined localized moments. Moreover, large  $\gamma$  and  $K_s$  allude the formation of resonance band at Fermi level.

In the end of this section, we propose a phase diagram for YbXCu<sub>4</sub> series in **Fig. 20**, which corresponds to Doniach's phase diagram [7]. In the figure,  $K_s$  are derived from the  $K_{\rm iso}$  data of <sup>63</sup>Cu at 16e site, and  $\gamma$  and  $T_{\rm K}$  are cited from various reports [22] [23] [25] [24] [27] [39] [63]. The variation of  $K_s$ with the species of X elements roughly correlates with that of  $\gamma$  excepting

Х	Metallic radious	$a_0(YbXCu_4)$	$a_0(\mathrm{Lu}X\mathrm{Cu}_4)$
Zn	1.394 Å	7.046 Å	7.034 Å
Au	1.442	7.046	7.037
Ag	1.445	7.083	7.094
In	1.663	7.158 (HT)	7.148
		7.146 (LT)	
$\operatorname{Cd}$	1.568	7.135	7.123
Mg	1.602	7.194	7.129
Tl	1.716	7.155	7.125

Table 2: Lattice constant of  $YbXCu_4$  and  $LuXCu_4$  at room temperature. Only that of  $YbInCu_4$  at low temperature phase is at 4.2 K.

X=Cd and Zn. The anomalously large  $\gamma$  for X=Cd and Zn is considered to originate not only from the conduction electron bands contribution but a magnetic contribution. We tentatively place YbZnCu<sub>4</sub> on the left side of diagram because of nonmetallic behavior of the resistivity. The position of YbInCu<sub>4</sub> in the diagram is determined from the LT phase data. The property of HT phase is discuss in section 4.5.

The lattice constant for  $RXCu_4$  at room temperature cited from Sarrao *et al.* are shown in **Table 2** [22]. For the Lu compounds, the lattice constants appear to be governed by the metallic radii of the X elements. The lattice constants of YbXCu<sub>4</sub> increase in an order of X=Zn, Au, Ag, Cd, In(LT), Tl, Mg. This is almost corresponding to the order of Lu compounds, and furthermore that of the order in the phase diagram (**Fig. 20**) except for X=In. We conclude that the increase of mixing between Yb's 4f electrons and conduction electrons leads to the larger unit cell volume, because of the increase of the rate Yb<sup>2+</sup>/Yb<sup>3+</sup>. In that sense, application of pressure is thought to tune the mixing strength.



Figure 20: Schematic phase diagram for YbXCu<sub>4</sub> series. Variation with the species of X atoms of on site Knight shift  $K_s$  and electronic specific heat coefficient and Kondo temperature.

#### 3.5 Nuclear spin-lattice relaxation rate

The spin-lattice relaxation time  $T_1$ 's of  ${}^{63}$ Cu in YbXCu<sub>4</sub> were measured using NQR. The magnetization recovery M(t) was measured as a function of time t after an initial saturation pulse.  $T_1$  for NQR of I=3/2 was determined by fitting the data with

$$M(t) = M(\infty) \left\{ 1 - \exp\left(-\frac{3t}{T_1}\right) \right\}.$$
(34)

#### 3.5.1 Relaxation bahaivor in the HT and LT phase of YbInCu<sub>4</sub>



Figure 21: Tempereture dependence of the  ${}^{63}$ Cu relaxation rate  $T_1^{-1}$  in YbInCu<sub>4</sub>.

We show in Fig. 21 the temperature dependence of relaxation rate  $1/T_1$  for YbInCu<sub>4</sub> on a log-log scale. The data are in good agreement with the

value reported by Nakamura *et al.* [40]. Above  $T_V$ ,  $1/T_1$  is weakly temperature independent. The near  $1/T_1 = const.(=4.2times10^2 s^{-1})$  behavior is indicative of a dominant relaxation process to neighboring Yb<sup>3+</sup> spins which are fluctuating by the exchange interaction [65]. At  $T_V$ ,  $1/T_1$  shows a step decrease and follows the  $T_1T=const.(=0.47 \text{ (sK)}^{-1})$  relation ,i.e., Korringa type relaxation. In the case of dilute Kondo system, it was proved that Korringa law hold folds at  $T \ll T_K$  [51]. In the dense Kondo system,  $T_1T=const$ . behavior has also been observed at low temperatures [64]. Therefore relaxation rate in the LT phase is dominated by the relaxation process to the conduction electrons.

These behavior of  $T_1^{-1}$  also assures that character of f electrons in YbInCu<sub>4</sub> suddenly changes from local to itinerant below  $T_V$ .

## 3.5.2 Relaxation in valence fluctuating compounds $YbXCu_4$ with X=Ag, Cd, Mg, Tl

Figure 22 shows the temperature dependence of  $1/T_1$  for each of YbXCu<sub>4</sub> compounds with X=Ag, Cd, Mg and Tl. For X=Ag, Cd and Mg,  $T_1$  data display similar temperature dependence each other;  $1/T_1$  is proportional to the temperature at low temperatures and tends to saturate at high temperatures. This indicates that the system transforms gradually from local spin to Fermi-liquid regimes. The  $(T_1T)^{-1}$  value for each of the compounds at low temperatures is about 3.0, 2.0, 2.5 and 0.5 (sK)<sup>-1</sup> for X=Ag, Cd, Mg and Tl, respectively.

In the Fermi liquid state,  $(T_1T)^{-1}$  is proportional to the square of the density states  $D(E_{\rm F})$  of quasi-particle band. In the heavy-Fermion state,  $(T_1T)^{-1}$  is considered to be proportional to the square  $D(E_{\rm F})$  of the quasiparticle band. In contrast to the case of Knight shift,  $(T_1T)^{-1}$  is usually determined mainly by the on-site orbital  $H_{\rm hf}^{\rm orb}$  and corepolaization hyperfine interactions  $H_{\rm hf}^{\rm core}$  on Cu site, because those values are much larger than transferred hyperfine interaction  $H_{\rm hf}^{\rm trans}$ . Then the values of the slopes for  $1/T_1$  data for temperature shown in **Fig. 22** give a variation in  $D(E_{\rm F})$ , which is reasonable agreement with the result deduced from  $K_s$  in section 3.4.4 except for  $X={\rm Mg}$ .



Figure 22: Tempereture dependence of the  ${}^{63}$ Cu relaxation rate  $T_1^{-1}$  in YbXCu<sub>4</sub> (X=Ag, Cd, Mg. Tl).

# 3.5.3 Spin fluctuations in the localized spin system of YbAuCu<sub>4</sub> and YbZnCu<sub>4</sub> with localized moment

We measured the spin-lattice relaxation time  $T_1$  for YbAuCu<sub>4</sub> and YbZnCu<sub>4</sub> at the peak intensity point of the NQR spectra. For YbZnCu<sub>4</sub>, the recovery data at low temperatures could not be reproduced with eqn.(34). Then we assumed the date is composed of two recovery terms. In Fig. ??(a) we plotted  $1/T_1$  of the shorter term for YbZnCu<sub>4</sub>. In order to study field dependence of  $T_1$ , we have measured  $T_1$  using NMR spectrum at ~4 T in the temperature range 4.3-50 K. The experimental recovery curves under magnetic field could be reproduced successfully with a following equation [66],

$$M(t) = M(\infty) \left\{ 1 - \alpha \exp\left(-\frac{1}{T_1}\right) - \beta \exp\left(-\frac{6t}{T_1}\right) \right\},\tag{35}$$

where  $\alpha + \beta = 1$ .  $1/T_1$  values obtained under the magnetic field of 4T accord with those of short  $T_1$  obtained zero field. This indicates that  $1/T_1$  is independent of magnetic field and the component with smaller  $1/T_1$  observed in NQR measurement attributes to any magnetic impurities. Then we took the component with shorter  $T_1$  as intrinsic relaxation value.

Figure 23 shows temperate dependence  $1/T_1$  of <sup>63</sup>Cu in each of YbAuCu<sub>4</sub> and YbZnCu<sub>4</sub>. The data for YbAuCu<sub>4</sub> are in good agreement with those reported previously by Nakamura *et al.* [42]. The  $T_1$  data for each compounds do not follow the Korringa law  $(T_1T=const.)$  [19] in present experimental temperature range. For YbAuCu<sub>4</sub>,  $1/T_1$  is nearly constant above ~50 K but at low temperatures increases prominently as the temperature lowered.  $1/T_1$ of YbZnCu<sub>4</sub>, in contrast, decrease monotonously as decreasing temperature. We plotted in Fig. 24 the  $(T_1T)^{-1}$  data against the corresponding susceptibility  $\chi$ .  $(T_1T)^{-1}$  is proportional to  $\chi$  above 50 K for YbAuCu<sub>4</sub> and above 1.4 K for YbZnCu<sub>4</sub>, respectively.



Figure 23: Temperature dependence of the  ${}^{63}$ Cu relaxation rate  $T_1^{-1}$ .

In general, this spin-lattice relaxation is related to the imaginary part of the dynamical susceptibility  $\chi(q, \omega_0)$  as eqn.(18). For the relaxation process to the fluctuating local moments with the correlation time  $\tau_f$  is given by

$$\frac{1}{T_1 T} = 2z\gamma_{\rm n}k_{\rm B}\left\{\frac{H_{\rm hf}}{z}\right\}^2 \frac{\chi}{\mu_{\rm B}^2 N}\tau_f,\tag{36}$$

neglecting the dependence of susceptibility on the wave number and assuming a Lorentzian energy spectrum for the f spin fluctuations [60]. Here, z is the number of neighboring spins (z=3). The experimental  $1/T_1$  values have contributions from both f and conduction electrons as eqn.(19). Since the contribution from the former is expected to dominate, we have assumed that  $(1/T_1)_f \gg (1/T_1)_c$ .

The linear dependence of  $(T_1T)^{-1}$  on  $\chi$  for YbZnCu<sub>4</sub> and YbAuCu<sub>4</sub> above ~50 K indicates that  $\tau_f$  is nearly independent of temperature. Using the experimental values of  $(T_1T)^{-1}$  and isotropic transferred hyperfine field  $H_{\rm hf}$  on 16e site at high temperature in section 3.4.4, we can evaluate an order of f spin fluctuation energy  $T_f(=h/K_{\rm B}\tau_f)$  as ~100 K for YbZnCu<sub>4</sub> and ~10 K for YbAuCu<sub>4</sub>, respectively.



Figure 24:  $(T_1T)^{-1}$  vs.  $\chi$  plots for each of YbAuCu<sub>4</sub> (•) and YbZnCu<sub>4</sub> (•).

For YbAuCu<sub>4</sub> below 50 K,  $(T_1T)^{-1}$  is no longer linear to  $\chi$  and exhibits prominent increase. If we tentatively use eqn.(36) for  $(T_1T)^{-1}$  data below 50 K, spin fluctuation rate  $1/\tau_f$  decreases monotonously and approaches the order of 1 K. This value is consistent with the quasielastic linewidth obtained by Lorentzian fitting in neutron scattering experiment at low temperatures [25]. It is worth noting that  $T_f \sim \! 1~{\rm K}$  can be reasonably compared with  $T_{\rm K}.$ 

### 4 Pressure effect on YbInCu<sub>4</sub>

#### 4.1 Introduction

The magnetic properties of Kondo lattice system is largely controlled by the strength of the *c*-*f* hybridization  $J_{cf}$  between magnetic *f* electrons and the conduction electrons. As mentioned in section 1.2.2, Doniach considered the one-dimensional Kondo lattice in the mean-field approximation and suggested the simple phase diagram shown in **Fig. 2** [7]. Application of pressure is known to increase the value of  $J_{cf}D(E_{\rm F})$  for Ce compounds. With increasing pressure, therefore, magnetic ordering temperature  $T_{\rm M}$  would be expected to initially increase, then pass through a maximum and decrease rapidly. Pressure dependence of  $T_{\rm M}$  was investigated in some ferromagnetic compounds such as CeAg [67] and CeRh<sub>4</sub>B<sub>2</sub> [68] and the results agree well with Donich' s diagram. Pressure induced superconductivities have also reported; for example, CeCu<sub>2</sub>Ge<sub>2</sub> [69], CePd<sub>2</sub>Si<sub>2</sub> [70], and CeIn<sub>3</sub> [71]. The superconductivity appears at pressures close to the critical pressure where magnetic ordering vanishes.

In contrast, since Ce and Yb lie at the opposite side of the rare earth series, the missing 4f electron in the magnetic  $4f^{13}$  configuration can be interpreted as the presence of a 4f hole, in analogy to the  $4f^1$  electron in Ce<sup>3+</sup>. For Yb compounds, therefore,  $J_{cf}$  would be expected to decrease with applying pressure and  $4f^{13}$  magnetic state is stabilized [8]. Pressure induced magnetic ordering was observed in some Yb-based compounds, such as YbCuAl (P > 20 Gpa) [72], YbCu<sub>2</sub>Si<sub>2</sub> (P > 8 GPa) [73], YbNi<sub>2</sub>Al (P > 8 GPa) [74], and YbNi<sub>2</sub>Ge<sub>2</sub> (P > 5 GPa) [75]. However, Yb-based superconductor have not so far found. Moreover, it was also reported the pressure-induced change of the type of magnetic order for CePd<sub>2</sub>Ga<sub>3</sub> [76] and YbNiSn [77].

As mentioned in the section 3.1, YbInCu<sub>4</sub> exhibits a first-order valence transition at  $T_V=42$  K with the volume expansion of about of 0.5 %. Applied pressure pushes the valence transition to lower temperatures [78] [79] [80] [81]. This is presumably because under pressure the smaller Yb<sup>3+</sup> electron configuration is favored over larger Yb<sup>2+</sup> configuration. Recently electrical resistivity measurement by Uchida *et al.* implied that  $T_V$  is depressed to below 1.5 K at 2.5 GPa [81]. Svechkarev *et al.* predicted the occurrence of a ferromagnetic ordering in YbInCu<sub>4</sub> at a pressure where  $T_{\rm V}$  vanishes [82]. Magnetization measurement by Mitsuda *et al.* revealed that the ground state of the 20 % Y-substituted compound Yb<sub>0.8</sub>Y<sub>0.2</sub>InCu<sub>4</sub> is weakly ferromagnetic under pressure [83]. It is of interest to study the pressure effect on YbInCu<sub>4</sub> microscopically, therefore, we have performed NQR experiment under pressure. In addition, we have carried out the electrical resistivity and ac-susceptibility  $\chi_{\rm ac}$  measurement in order to explored the ground state of pressure-stabilized the HT phase.

#### 4.2 Pressure techniques

We used two types of "piston cylinder" made of CuBe for NQR (0.8 GPa) and NiCrAl for resistivity and  $\chi_{ac}$  measurement (2.1-2.7GPa). In this section, I mention the pressure techniques for the NiCrAl cell.

Clamped cell material Figure 25 shows a cross-section drawing of the pressure cell which we used for the resistivity and  $\chi_{ac}$  measurement. The body, obturator and piston, are made of NiCrAl alloy (39-40%Cr, 3-4%Al the rest is Ni by weight). NiCrAl alloy of hardness up to 64-67 HRC is expected to durable up to ~3 GPa and is one of the best materials for high-pressure cell even at low temperature. In spite of high Ni content in the alloy, it remains paramagnetic even at liquid helium temperature, as in Fig. 26 [84]. It has a larger magnetic susceptibility at room temperature, but only three times higher than that of CuBe alloy (98% Cu, 2% Be) at 4.2 K. It has the feature that its magnetic properties do not depend on temperature over a larger temperature range.

**Preparation** We passed a bundle of about 20 copper wires through a hole in obturator and sealed them with stycast epoxy resin. Special care was undertaken in preparation of the seal: the metal surface was carefully cleaned, and dried. In addition the epoxy was degassed before used.

**Pressure-transmitting media** The pressure-transmitting medium must translate the uniform pressure into the sample. We used Daphne 7373 as a



Figure 25: Crosss-section view of piston cylinder pressure cell used for resistivity and  $\chi_{\rm ac}$  measurement.



Figure 26: Dependence of magnetic susceptibility on temperature for CuBe alloy and NiCrAl alloy.

transmitting medium for hydrostatic pressure. The pressure deference of this media between 4.2 and 300 K is always approximately 1.5 kbar, irrespective of the initial pressures at room temperature [85].

**Pressurization Figure 27** shows the drawing of the sample setting. The sample for resistivity measurement was connected with the gold wire ( $\phi = 20\mu$ m) and set on the obturator. In order to measure  $\chi_{ac}$ , the another piece of crystals was placed in primary coil and pick-up coils. Manganin and tin wires were attached below the coils to measure the magnitude of pressure at room and low temperatures, respectively. After mounting the sample and wires, the gauge and the obturator is pushed into the Teflon capsule filled with pressure medium. Then oboturator was introduced into the bore of the pressure cell.



Figure 27: Arrangement of sample and electrodes on obturator.

Pressure was smoothly increased with continuous control of the force in the press, the pressure inside the cell and displacement of the piston being monitored. After a desired pressure was achieved, the upper screw was fixed with a small force. Then we released the load and the cell was slowly cooled down over a period of some hours. **Superconducting gauge** We determined the magnitude of pressure by monitoring the superconducting transition of tin mounted inside the Teflon capsule. The superconducting transition was observed as a sharp drop of resistivity. Following equation was used to determine the magnitude of pressure,

$$T_{\rm C}(P) = 3.72 - 4.63 \times 10^{-5}P + 2.16 \times 10^{-10}P^2,$$
 (37)

where  $T_{\rm C}(P)$  is the superconducting transition temperature at pressure P.

**Measurement of temperature** It is usually assumed that the temperature inside the cell is the same as the temperature of the surface of the cell because thermal energy is probably conducted through about 20 copper wires. Moreover temperature sweeping was carried out slowly enough to reach thermal equilibrium.

#### 4.3 NQR study for YbInCu<sub>4</sub> under pressure

We used the same powder samples, which had been used for NMR and NQR experiment under ambient pressure. The high-pressure apparatus consists of CuBe piston-cylinder. Daphne oil 7373 was loaded into the cylinder to serve as the pressure medium. The magnitude of pressure was determined by the superconducting transition of tin manometer with the magnetic susceptibility measurement.

Figure 28 shows <sup>63</sup>Cu and <sup>65</sup>Cu NQR spectra in the LT (4.2 K) and HT (30 K) phases at P=0.8 GPa. A fitting with a Lorentzian line shape to the experimental data gives  ${}^{63}\nu_{\rm Q}=14.41$  MHz and  ${}^{65}\nu_{\rm Q}=13.34$  MHz at 4.2 K, and  ${}^{63}\nu_{\rm Q}=15.12$  MHz and  ${}^{65}\nu_{\rm Q}=14.01$  MHz at 30 K. The values are almost in agreement with the value reported previously [87]. The lineshapes and width are scarcely modified at the transition as well as under ambient pressure. Figure 29 shows the temperature dependence of  ${}^{63}\nu_{\rm Q}$  at 0.8 GPa and at ambient pressure in the temperature range 4.2 -75 K. In both of the LT and HT phases, the magnitude of  ${}^{63}\nu_{\rm Q}$  at 0.8 GPa are larger than at ambient pressure. The magnitude of the change  $,\Delta\nu_{\rm Q} = \Delta\nu_{\rm Q}({\rm HT})-\Delta\nu_{\rm Q}({\rm LT}),$ at the transition is ~0.71 MHz at 0.8 GPa, which is smaller than at ambient pressure ( $\Delta\nu_{\rm Q} \sim 0.82$  MHz). This is mainly due to the suppression of the



Figure 28:  ${}^{63}$ Cu and  ${}^{65}$ Cu NQR spectra of YbInCu<sub>4</sub> at 4.2 and 30 K under P=0.8 GPa. Arrows indicate the peak position at 4.2 K ambient pressure.



Figure 29: Temperature dependence of the resonance frequency of  $^{63}$ Cu NQR at 0.8 GPa (•) and ambient pressure ( $\circ$ ).

volume expansion at  $T_{\rm V}$  by application of pressure [80]. But lack of the pressure dependence unit-cell volume data does not allow us an accurate interpretation of these results.



Figure 30: Temperature dependence of  $1/T_1$  for <sup>63</sup>Cu in YbInCu<sub>4</sub> at 0.8 GPa (•) and ambient pressure ( $\circ$ ).

The spin-lattice relaxation time  $T_1$  was measured in the same way as described in section 3.5. In **Fig. 30**, we show the result of  $1/T_1$  measurement as a function of temperature with the data at ambient pressure. Above  $T_V$ ,  $1/T_1$  is almost constant, which is 3 typical feature for well-localized electron systems. In contrast, below  $T_V$ ,  $T_1$  follows the  $T_1T=const$ . behavior as  $(T_1T)^{-1}=0.47$  (sK)<sup>-1</sup>, indicating the dominant relaxation process to conduction electrons. It should be noted that the values of  $1/T_1$  in the HT phase and  $1/T_1T$  in the LT phase are almost same with the data under ambient pressure. The temperature independent  $T_1$  in the HT phase is ascribed only to the weak temperature dependence of the correlation time  $\tau_f$ . Within the molecular field approximation  $J_{ff}$  is related to the exchange interaction  $J_{cf}$ between f electron and conductions. If the fluctuation is characterized by the exchange interaction between local moments, the correlation time  $\tau$  of spins at far above magnetic transition temperature is described by the exchange frequency  $\omega_{ex}$  as [86]

$$\frac{1}{\tau_f} \sim \frac{\hbar\omega_{\rm ex}}{k_{\rm B}} \propto z J_{ff} \sqrt{(g-1)^2 J(J+1)}$$
(38)

where  $J_{ff}$  denotes the exchange interaction between f electrons. In this case  $1/\tau_f$  is expected to be roughly proportional to  $\omega_{ex}$  and  $J_{ff}$ . Thereby temperature independent  $T_1$  suggests that  $J_{ff}$  is not sensitive to the applying pressure at least up to 0.8 GPa. This observation lead to conclusion that the application of the pressure shifts  $T_V$  toward lower temperature and stabilized the localized state of 4f electrons.

## 4.4 Magnetic ordering in the pressre-stabilized hightemperature phase

In order to elucidate the ground state of the pressure-stabilized high temperature (HT) phase of YnInCu<sub>4</sub>, we carried out the electrical resistivity  $\rho$ and ac magnetic susceptibility  $\chi_{ac}$  measurement at high pressure. For the  $\rho$ measurement, four gold wires were attached on a single crystal of YnInCu<sub>4</sub> with spotwell method. A primary and compensated pick-up coil were filled with many small crystals and an excitation coil was attached outside of them for the  $\chi_{ac}$  measurement. Both coil were made of copper. Arrangement of sample and electrode is drawn in **Fig. 27**. To measure  $\rho$  and  $\chi_{ac}$  at exactly the same pressure, both samples were mounted inside the piston cylinder cell. For the experiment below 1 K, the pressure cell was assembled in a <sup>3</sup>He/<sup>4</sup>He dilution refrigerator.  $\rho$  was measured by a conventional four-probe ac resistance bridge (Linear Research, LR-700). The  $\chi_{ac}$  measurement was performed by the conventional method with lock-in amplifier at a frequency of 132 Hz.





Figure 31: Temperature dependence of electrical resisitivity.

Figure 31 shows the temperature dependence of the electrical resistivity at several pressures. Above ~40 K, resistivity have linear dependence of temperature and hardly depends on the applied pressure. With decreasing temperature, below ~30 K,  $\rho$  starts to deviated from *T*-linear behavior. For pressure smaller than 2.44 GPa,  $\rho$  shows the sharp drop at low temperature, which originates from the valence transition of Yb ions from magnetic HT phase to non-magnetic low temperature (LT) phase. As seen in Fig. 31(b), increasing pressure shifts the valence transition temperature  $T_V$  to low temperature. The dependence of  $T_V$  on pressure is shown in Fig. 35 and the value of  $dT_V/dP \simeq -18.5$  K/GPa is comparable with the value reported previously [79] [80] [81]. At high pressure above 2.49 GPa, no sign of valence transition was observed down to ~80 mK and a small kink appeared at around T=2.4 K instead. The appearance of this new  $\rho$  anomaly can seen more clearly in the *T*-derivative of the resistivity  $d\rho/dT$  plotted in Fig. 32.



Figure 32: (a) Dependence of the temperature-derivative of the electrical resistivity  $d\rho/dT$  on the temperature for YbInCu<sub>4</sub> at 2.49 GPa. (b) The electrical resistivity versus  $T^2$  plot at 2.49 GPa.

Figure 33 shows the temperature dependence of  $\rho$  and  $\chi_{ac}$  measured at P=2.21, 2.39 and 2.49 GPa. At the pressure of 2.21 GPa (Fig. 33(a)),  $\chi_{ac}$  drops at  $\sim 7$  K which  $\rho$  shows sharp drop. The small drop in  $\chi_{ac}$  is considered

to be associated with the valence transition from the HT phase to the LT phase. Whereas at 2.49 GPa we observed a clear peak in  $\chi_{ac}$  at around 2.4 K with  $\rho$  a small kink in  $\rho$  as mentioned above. We found that the peak of  $\chi_{ac}$  can be easily suppressed by applying a small magnetic field H and almost disappeared for H >500 kOe (**Fig. 34**). These characteristic behavior of  $\chi_{ac}$  was usually considered to be associated with the onset of long-range ferromagnetic ordering. Then we may conclude that the pressure stabilized HT phase of YbInCu<sub>4</sub> has most probably a ferromagnetic ordering with small ordered moment on Yb<sub>0.8</sub>Y<sub>0.2</sub>InCu<sub>4</sub> under P > 0.8 GPa [83]. However, with  $\chi_{ac}$  data alone, we could not rule out the possibility of canted anti-ferromagnetic state as ground state. To determine the magnetic structure and the magnitude of the ordered moment, NMR and/or neutron scattering experiment under pressure are required.

Figure 33(b) shows the  $\rho$  and  $\chi_{ac}$  data at P=2.39 GPa.  $\rho$  shows a drop at around 3.5 K and  $\chi_{ac}$  has a clear peak as well as P=2.49 GPa. The former is reasonably associated with the valence transition from the HT phase to the LT phase with decreasing temperature. The latter is attributed to the long-range magnetic ordering. Here we note that the decrease of  $\chi_{ac}$  at the valence transition is much smaller than the peak appeared at  $T_{\rm M}$  where longrange magnetic ordering at the same pressure is probably due to the pressure inhomogenity in the cell. Then we conclude that the critical pressure between the collapse of valence transition and magnetic ordering is located at 2.4 GPa. The present experiment results are summarized in the pressure-temperature diagram in Fig. 35.

As shown in Fig. 32(b),  $\rho$  below  $T_{\rm M}$  is roughly correspond to the form

$$\rho(T) = \Delta \rho_0 + AT^2, \tag{39}$$

where  $\Delta \rho_0$  is the residual resistivity and A is the quadratic coefficient. The value of  $\Delta \rho_0$  at 2.49 GPa is about five times larger in magnitude than that for P < 2.4 GPa. A is estimated as 10  $\mu\Omega$ cm/K<sup>2</sup>. The incrimination of  $\Delta \rho_0$ with the application of pressure was also observed in the ferromagnetic phase of UGe<sub>2</sub> [88] and this lead us to expect an occurrence of superconductivity



Figure 33: Temperature dependence of the electrical resistivity and acsusceptibility of YbInCu<sub>4</sub> at (a) 2.21GPa, (b) 2.39 GPa and (c) 2.49 GPa.



Figure 34: Magnetic field dependence of ac susceptibility versus temperature for 2.49 GPa.

at low temperatures. Then we measured  $\rho$  down to ~80 mK but  $\rho$  showed any symptom of superconducting transition.

In conclusion we carried out electrical resistivity and ac-susceptibility measurement for YbInCu<sub>4</sub> under high pressure up to 2.58 GPa and temperature down to ~80 mK. The  $T_{\rm V}$  was shifted to lower temperature by applying pressure and the valence transition was completely suppressed above 2.49 GPa. The  $\chi_{\rm ac}$  data showed a clear peak at  $T_{\rm M}=2.4$  K with the small kink in the electrical resistivity, which can be ascribed to the onset of a long-range ferromagnetic ordering. This finding of pressure induced magnetic ordering for Yb-based compound under conventionally obtainable pressures will shed light on the mechanism of magnetic ordering in the Yb-based compounds.

#### 4.5 Discussion

The high temperature (HT) phase of YbInCu<sub>4</sub> at ambient pressure is characterized by well localized 4f electron from the experimental data such as CW-type magnetic susceptibility  $\chi$  and temperature independent relaxation



Figure 35: The temperature-pressure phase diagram for YbInCu<sub>4</sub>. The valence transition  $T_{\rm V}$  and magnetic transition temperature  $T_{\rm M}$  are expressed by cross (×) and open circle ( $\circ$ ), respectively.

behavior. It is well known that application of pressure lowers the valence transition temperature  $T_{\rm V}$  but coincidentally what kind of effect is brought about by pressure in the HT phase? In this section, we discuss the physical properties of YbInCu<sub>4</sub> in pressure stabilized the HT phase and mention the position of it on the Doniach phase diagram.

The result of present NQR measurement shows that temperature independent  $T_1$  behavior holds up to 0.8 GPa and the value of  $1/T_1$  is scarcely modified by pressure. The electrical resistivity  $\rho$  both at ambient and under pressures exhibits near *T*-linear behavior and no clear maximum. The present ac-susceptibility measurement under high pressure shows that the magnetic ordering temperature  $T_{\rm M}$  is insensitive to applied of pressure within the present experimental range of 2.3-2.58 GPa. Thompson *et al.* observed a weakly pressure independent  $T_{\rm M}$  in antiferromagnetic compound YbBe<sub>13</sub> up to 1.6 GPa and speculated that this compound is already in the weak *c*-*f* hybridization regime at ambient pressure [89].

Taking those results into account, we speculate that the HT phase of YbInCu<sub>4</sub> is located in localized regime on the Doniach phase diagram where Kondo temperature  $T_{\rm K}$  is very small compared to YbAuCu<sub>4</sub> which orders magnetically below 1 K. We do not have the value of specific heat coefficient  $\gamma$  for the HT phase of YbInCu<sub>4</sub>. But when we tentatively estimate the density of state of Fermi level  $D(E_{\rm F})$  from  $K_s$  data (section 3.4.4) and assume that the  $D(E_{\rm F})$  is insensitive to pressure,  $D(E_{\rm F})$  of YbInCu<sub>4</sub> in the HT phase is smaller than that of YbAuCu<sub>4</sub>. This may support that the HT phase of YbInCu<sub>4</sub> located in the localized spin regime on Doniach's phase diagram.

## 5 Appendix

#### 5.1 Calulation to the hyperfine field

Here we present a caluculation procedure of  $H_{\rm hf}$ . For the lanthanides the main contribution of the hyperfine interaction comes from the orbital motion of the electrons, which generates a field  $H_1$  at the nucleus

$$\boldsymbol{H}_{l} = -2\mu_{\rm B} \sum_{i} \langle r_{l}^{-3} \rangle_{i} \boldsymbol{l}_{i}$$

$$\tag{40}$$

where the subscript *i* refers to the *i*-th electron with orbital momentum  $l_i$ and a mean inverse cube  $\langle r_l^{-3} \rangle_i$  of its distance from the nucleus, averaged over the orbital wave function. In *LS*-coupling, if we assume that all electrons in the same shell have the same value of  $\langle r_l^{-3} \rangle$ , summation over the various electrons gives

$$\boldsymbol{H}_{L} = -2\mu_{\rm B} \langle r^{-3} \rangle \boldsymbol{L}. \tag{41}$$

When L and S are coupled to form a resultant J (=L+S), we may project L onto J giving

$$L \rightarrow \frac{L \cdot J}{J^2} J = \frac{(L \cdot J)J}{J(J+1)}$$
 (42)

then

$$\boldsymbol{H}_{L} = -2\mu_{\rm B} \langle r^{-3} \rangle \frac{(\boldsymbol{L} \cdot \boldsymbol{J})}{J(J+1)} \boldsymbol{J}$$
(43)

where

$$(\mathbf{L} \cdot \mathbf{J}) = \frac{1}{2} \Big\{ J(J+1) + L(L+1) - S(S+1) \Big\}.$$
 (44)

A useful relation is

(

$$\frac{(\boldsymbol{L}\cdot\boldsymbol{J})}{J(J+1)} = 2 - g_J \tag{45}$$

where  $g_J$  is Landé g-factor. Then eqn.(43) can be written as

$$\boldsymbol{H}_{L} = -2\mu_{\rm B} \langle r^{-3} \rangle (2 - g_J) \boldsymbol{J}.$$
(46)

Next we consider the contribution from the spin magnetization of the electrons. For f electrons, whose wave function vanish at the nucleus, the magnetic field generated at nucleus is given by the simple dipolar interaction

$$\boldsymbol{H}_{\rm dip} = g\mu_{\rm B} \sum_{i} \langle r_{sC}^{-3} \rangle_i \left\{ \boldsymbol{s}_i + \frac{3(\boldsymbol{L}_i \cdot \boldsymbol{r}_0)}{r_i^2} \right\}$$
(47)

where g is the g-factor of the electron spin  $s_i$ ,  $\langle r_{sC}^{-3} \rangle_i$  is the mean inverse cube of the distance of the *i*-th electron from the nucleus, and  $r_0$  is a unit vector drawn from the nucleus towards the position of the *i*-th electron. Using the Wigner-Eckart theorem, this equation can be expressed with total spin S and maximum L as

$$\boldsymbol{H}_{\rm dip} = g\mu_{\rm B} \langle r_{sC}^{-3} \rangle \xi \left\{ L(L+1)\boldsymbol{S} - \frac{3}{2}\boldsymbol{L}(\boldsymbol{L}\cdot\boldsymbol{S}) - \frac{3}{2}(\boldsymbol{L}\cdot\boldsymbol{S})\boldsymbol{L} \right\}$$
(48)

where

$$\xi = \frac{2l+1-4S}{S(2l-1)(2l+3)(2L-1)}$$
(49)

and assuming the value of  $\langle r_{sC}^{-3} \rangle$  to be the same for all electrons in the shell. Finally, projection onto J gives

$$\boldsymbol{H}_{\rm dip} = g\mu_{\rm B} \langle r_{sC}^{-3} \rangle \frac{\xi}{J(J+1)} \Big\{ L(L+1)\boldsymbol{S} \cdot \boldsymbol{J} - 3(\boldsymbol{L} \cdot \boldsymbol{J})(\boldsymbol{L} \cdot \boldsymbol{S}) \Big\} \boldsymbol{J}$$
(50)

where

$$(\mathbf{S} \cdot \mathbf{J}) = \frac{1}{2} \Big\{ J(J+1) + S(S+1) - L(L+1) \Big\}$$
(51)

$$(\boldsymbol{L} \cdot \boldsymbol{S}) = \frac{1}{2} \Big\{ J(J+1) - L(L+1) - S(S+1) \Big\}.$$
 (52)

Here again useful relation is

$$\frac{(\boldsymbol{S}\cdot\boldsymbol{J})}{J(J+1)} = g_J - 1 \tag{53}$$

and then eqn.(48) can be witten as

$$\boldsymbol{H}_{\rm dip} = g\mu_{\rm B} \langle r_{sC}^{-3} \rangle \xi \Big\{ L(L+1)(g-1) - 3(2-g)(\boldsymbol{L} \cdot \boldsymbol{S}) \Big\} \boldsymbol{J}.$$
(54)

Here we employ the following expression as

$$\langle J \| N_{\rm L} \| J \rangle = 2 - g \tag{55}$$

$$\langle J \| N_{\rm dip} \| J \rangle = -\xi \Big\{ L(L+1)(g-1) - 3(2-g)(\boldsymbol{L} \cdot \boldsymbol{S}) \Big\}.$$
 (56)

The value of these quantities are listed in **Table 3**, for the ground states of each configuration  $f^n$ . It is assumed that

$$\langle r_L^{-3} \rangle = \langle r_{sC}^{-3} \rangle = \langle r^{-3} \rangle \tag{57}$$
	L	S	J	ξ	$\langle J \  N_{\rm L} \  J \rangle$	$\langle J \  N_{\rm dip} \  J \rangle$
$f^1$	3	1/2	5/2	2/45	8/7	8/35
$f^2$	5	1	4	1/135	6/5	26/225
$f^3$	6	3/2	9/2	2/1485	14/11	14/363
$f^4$	6	2	4	-1/990	7/5	-7/165
$f^5$	5	5/2	5/2	-2/675	12/7	-52/315
$f^6$	3	3	0	-1/135	-	-
$f^7$	0	7/2	7/2	2/45	0	0
$f^8$	3	3	6	-1/135	1/2	1/18
$f^9$	5	5/2	15/2	-2/675	2/3	2/45
$f^{10}$	6	2	8	-1/990	3/4	1/60
$f^{11}$	6	3/2	15/2	2/1485	4/5	-4/225
$f^{12}$	5	1	6	1/135	5/6	-1/18
$f^{13}$	3	1/2	7/2	2/45	6/7	-2/21
$f^{14}$	0	0	0	-	-	-

Table 3: Values of L, S, J various hyperfine parameters for the ground state of the lanthanide ion.

and g is taken equal to 2, the sum of orbital and dipolar interaction is given by

$$H_{\rm hf} = 2\langle r^{-3}\rangle \langle J \| N \| J \rangle \mu_{\rm B} / g_J$$
  
$$\langle J \| N \| J \rangle \equiv \langle J \| N_{\rm L} \| J \rangle + \langle J \| N_{\rm dip} \| J \rangle.$$
(58)

Therefore, for a free Yb<sup>3+</sup> ion with J=7/2 we substitute 13.83 a.u. for  $\langle r^{-3} \rangle$  [48] and 16/21 for  $\langle r^{-3} \rangle \langle J \| N \| J \rangle$  then we find  $H_{\rm hf} = 1.15 \times 10^6 \text{ Oe}/\mu_{\rm B}$ .

$$H_{\rm hf} = 2 \times 13.83 \times (5.29 \times 10^{-9})^{-3} \times \frac{16}{21} \times 9.27 \times 10^{-21} \times \frac{7}{8}$$
  
= 1.15 \times 10<sup>6</sup>[Oe/\mu\_B] (59)

Ref. [49] [90]

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