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^{63}Cu NMR and Susceptibility Studies of YbCu_2Si_2 Single Crystal

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The temperature dependences of susceptibility and ^{63}Cu Knight shift in YbCu_2Si_2 single crystal have been measured for the fields parallel and perpendicular to the c -axis in the temperature range between 4.2 K and 300 K. The anisotropy of the susceptibility was found to be quite increased with decreasing temperature between 20 K and 200 K, suggesting that the crystalline electric field (CEF) effect is important in YbCu_2Si_2 . It was also observed that the linear relation between the Knight shift and the susceptibility is broken around 100 K for both the directions, and that the hyperfine coupling is highly anisotropic even at higher temperatures. The origins of the non-linearity and the anisotropy of the hyperfine coupling has been attributed to a nature of the orbitally dependent exchange interaction between 4f and conduction electrons.

[concentrated Kondo system, YbCu_2Si_2 single crystal, ^{63}Cu NMR, magnetic susceptibility, crystalline electric field effect, exchange interaction, conduction electron spin polarization]

§1. Introduction

Some rare-earth (RE) intermetallic compounds show anomalous properties associated with the unstable 4f ionic moments.^{1,2)} Since the RE ions which exhibit Kondo like behaviors construct a lattice, these materials has been called as the “concentrated Kondo systems (CKS)”. It has been suggested that the CKS undergoes a crossover from an isolated Kondo like behaviour at higher temperatures to a correlated state called as the “coherent Kondo state” at lower temperatures. One would like to know the electron state both above and below the characteristic temperatures, such as the crossover temperature of the Kondo temperature.

NMR is sensitive to detect the static and dynamical behaviour of the local electronic and magnetic environment of the nuclei,^{3,4)} and so is a useful tool for the study of CKS. In fact the NMR studies at the magnetic sites such as ^{171}Yb NMR in YbAl_3 , YbAl_2 and YbCu_2 have revealed a Fermi liquid nature in the ground state of the CKS.⁵⁾ It has been found

experimentally that the atomic 4f character survives the mixing interaction with the conduction electrons, and that the Fermi contact hyperfine field due to the conduction electron spin polarization is almost equivalent to that of the non-magnetic isostructural substance. It is of important to note that any anomalous behaviour arising from the concentrated effect is not observed in the hyperfine interaction at the Yb nuclei. These experiments have also indicated that the exchange interaction of the 4f electrons with the conduction electrons have less effect on the s-wave conduction electrons at the Yb sites. Therefore it is expected that the exchange interaction which is realized in the CKS is different from the traditional sf exchange, because the traditional expression is usually given as an isotropic interaction.^{6,7)}

To understand anomalous properties in the coherent Kondo state, the knowledge of the nature of the actual exchange interaction between the 4f and the conduction electrons is required. In contrast with the ^{171}Yb NMR which probes the hyperfine field predominantly due to the 4f shell of itself, the NMR at the non-

magnetic sites is appropriate for measuring the conduction electron spin polarization, and therefore observing the properties of the exchange interaction. Since the hyperfine mechanism at the non-magnetic sites is the Fermi contact interaction, the effective field acting on the nuclei is proportional to the conduction electron spin polarization density $\sigma_z(\mathbf{r})$. In the present work, we have investigated the nature of conduction electron spin polarization at the Cu sites in a typical CKS, YbCu_2Si_2 , through the anisotropic nature of ^{63}Cu Knight shift and susceptibility. Since YbCu_2Si_2 undergoes neither the structural nor the electronic phase transition,⁸⁻¹⁰ it is suitable for studying the properties arising from the exchange interaction of our interest over the whole temperature range. For YbCu_2Si_2 the Kondo temperature T_K has been estimated to be about 40 K by the neutron quasielastic scattering.⁹

The crystal structure of YbCu_2Si_2 is the tetragonal ThCr_2Si_2 .¹¹ The ground J multiplet of the Hund's rule ($J=7/2$) splits into four doublets due to the tetragonal CEF, and the energy splittings are inferred as 18, 23, 32 meV away from the ground CEF level.⁹

§2. Experimental Procedure

The crystal was grown from a tin flux. All samples used for various measurements described here were cut from the same ingot. The X-ray diffraction pattern of the pulverized specimen exhibits only the single phase of the tetragonal unit cell, and the lattice parameters are in good agreement with the literature data.¹⁰

The magnetic susceptibility of the single crystals has been measured in the external field up to 11 kOe at temperatures between 4.2 K and 300 K by a pendulum magnetometer. We have performed two measurements on different pieces cut from the same crystal. The results for the two are in good agreement within experimental errors.

NMR measurements were carried out in external fields up to 18 kOe at temperatures between 4.2 K and 200 K using a phase-sensitive pulsed NMR spectrometer. At several fixed frequencies, the field-swept spectra were obtained by integrating the spin echo amplitude.

The external fields are measured by a Hall probe which is calibrated over the field range of measurements using the ^{51}V -NMR in NaVO_3 . A single crystal was also used for the NMR measurements. The crystal has formed into sphere of 3.0 mm in diameter, so as to make the demagnetization factor to be isotropic and to balance the demagnetization field with the Lorentz local field. We have obtained the ^{63}Cu Knight shift accurately within $\pm 0.01\%$, assuming the ratio of the gyromagnetic ratios $\gamma(^{63}\text{Cu})/\gamma(^{51}\text{V})=1.1285/1.11925$.¹²

The nuclear quadrupole resonance (NQR) experiment in zero applied field was also carried out using a phase-sensitive pulsed spectrometer. The frequency-swept NQR spectra were obtained by averaging the spin echo amplitudes at each frequency. NQR spectra permit direct determination of the frequency of nuclear quadrupole interaction ν_Q ,¹³ without interference of the nuclear Zeeman interaction in contrast to the NMR spectra. For the ^{63}Cu NQR measurements in YbCu_2Si_2 we crushed the crystals into powders. Unfortunately the temperature range where the ^{63}Cu NQR signal could be discerned was limited to the lower temperatures than 10 K, so that we have used the NQR spectra only to ensure the quadrupolar frequency ν_Q extracted from the NMR spectra at 4.2 K.

§3. Experimental Results and Discussion

3.1 Magnetic susceptibility

In Fig. 1 the inverse of the susceptibility χ measured at 11 kOe is plotted against the temperature. We denote the susceptibilities for the two directions $H\parallel c$ and $H\perp c$, as χ'' and $\chi^\perp$, respectively, where c is the tetragonal axis. At the temperatures of 4.2 K as well as 290 K, the magnetization curve for the two directions was found to be dependent linearly on the applied field between 2 kOe and 11 kOe. No spurious upturns at low temperatures have been observed for both χ'' and $\chi^\perp$, in contrast to the most of Yb-based CKS in which some magnetic impurities (about 1 wt.%) are likely responsible for the low temperature upturns.¹⁴

In YbCu_2Si_2 the Pauli paramagnetism is considered to be negligible in the observed temperature range, because a nonmagnetic isostruc-

Fig. 1. Inverse magnetic susceptibility versus temperature. The thin curve is a calculated result of polycrystalline susceptibility by using the relation $\chi_{\text{poly}} = 1/3 (\chi'' + 2\chi^{\perp})$.

tural compound LaCu_2Si_2 shows a small susceptibility $\chi = 2.4 \times 10^{-4}$ emu/mole. This assumption is consistent with the neutron experiment which has indicated that the q -dependence of the magnetic form factor remains that expected for the $4f^{13}$ atomic configuration at the temperatures of $T = 5$ K and 250 K.

χ'' is found to be temperature independent below 10 K, but decreases monotonically with increasing temperature and goes gradually into a Curie-Weiss region. Like $\chi''(T)$, $\chi^{\perp}$ also shows no temperature dependence below 10 K. Thus the temperature of $T = 10$ K may be considered to be a temperature characteristic of the ground state of YbCu_2Si_2 . At higher temperatures, however, $\chi^{\perp}(T)$ exhibits a peak around $T_{\text{max}} = 45$ K and followed by a Curie-Weiss like behaviour at higher temperatures.

The temperature independent susceptibility has commonly been observed in the ground state of the paramagnetic CKS, and has been argued to a result due to the Kondo type singlet ground state. Susceptibility maximum is consistent with the prediction in the orbitally degenerate Kondo impurity model ($J > 1/2$).¹⁵⁾ The temperature exhibiting the susceptibility maximum is usually used to be a measure of the Kondo temperature T_K . In Yb-

Cu_2Si_2 , however, the relationship between T_K and T_{max} is not so clear since T_{max} in YbCu_2Si_2 is quite anisotropic that is not expected from the energy eigenvalue of the Hamiltonian of the electron system.

If we fit the data above 200 K to the Curie-Weiss law without any temperature independent term, we get the following parameters: $p_{\text{eff}} = 4.9 \pm 0.3 \mu_B$, $\theta = -75 \pm 1$ K for $1/\chi''$ and $p_{\text{eff}} = 5.1 \pm 0.5 \mu_B$, $\theta = -229 \pm 2$ K for $1/\chi^{\perp}$. The values of p_{eff} obtained here are too large compared with the p_{eff} for free Yb^{3+} ($p_{\text{eff}} = 4.54 \mu_B$). It follows that a Curie-Weiss region, if any, is not yet reached below 300 K. This is not surprising, considering the magnitudes of the CEF splittings. In this connection, it is significant to note that the energy separations of the CEF levels are very close to a characteristic temperature $T = 200$ K at which the anisotropy of the susceptibility begin to increase abruptly, as shown in Fig. 2. The anisotropy in the susceptibility shows a definite $\log T$ temperature dependence between 30 K and 200 K, and is constant with the ratio $\chi''/\chi^{\perp} = 3.2$ below 10 K. It is then reasonable to conclude that (1) below 10 K only a CEF ground state is populated and the magnetization is highly anisotropic, (2) above 300 K the most of the CEF excited states are

Fig. 2. Anisotropy ($\chi'' - \chi^+$) versus temperature in logarithmic scale.

equally populated by virtue of thermal excitations and the magnetization becomes isotropic, and at the same time the free ion value of p_{eff} is reached. Although the CEF effect has been conjectural in the neutron experiment, the CEF effect manifests clearly itself in the anisotropy of the susceptibility. It should be pointed out, however, that YbCu_2Si_2 occupies a unique position among the CKS, *e.g.* the temperature induced spin fluctuations arising from the CEF excitations, which have been observed commonly by the neutron quasielastic scattering for the CKS with definite CEF levels,^{9,16} have not been observed for YbCu_2Si_2 .

3.2 ^{63}Cu NMR

Figure 3 shows angular dependence of the peak position of the ^{63}Cu NMR lines at fixed frequency $\nu_0 = 15.00005$ MHz. Here, θ is the angle between the direction of the external field and the tetragonal c -axis. For simplicity, the results of the spectra for the ^{65}Cu NMR are not shown.

Because of the nuclear electric quadrupole effect, the spectra split into three resonance lines corresponding to the $m = +1/2 \leftrightarrow -1/2$ central, the $m = -1/2 \leftrightarrow -3/2$ and the $m = +3/2 \leftrightarrow +1/2$ satellite transitions.^{3,13} The quadrupole effect have been explained completely by perturbation up to the third order on the Zeeman interaction.

The three transition lines are shifted further by a Knight shift. Even though the Knight shift and the quadrupolar shift present

simultaneously, we can extract accurate informations on both the Knight shift and the electric field gradient (EFG) in the case of single crystal.

From the local symmetry of the Cu sites, both the Knight shift tensor and the EFG tensor are uniaxial having the same principal axis along the tetragonal c -axis. Then the principal components of the Knight shift tensor for the $m = 1/2$ central transition can be written as

Fig. 3. Angular dependence of the peak positions of the quadrupolar split ^{63}Cu NMR lines at a fixed frequency $\nu_0 = 15.00005$ MHz. The angle θ represents the direction of the external field with respect to the tetragonal c -axis. The dotted line is the position of $K=0$.

$$K'' = \frac{2\pi\nu_0}{\gamma_N H_{\text{ext}}} - 1, \quad (1)$$

and

$$K^\perp = \frac{\pi\nu_0 + \pi\sqrt{\nu_0^2 - (3/4)\nu_Q^2}}{\gamma_N H_{\text{ext}}} - 1, \quad (2)$$

where H_{ext} is the external field, and ν_Q is the magnitude of the nuclear quadrupole interaction on the frequency scale as usual definition,

$$\nu_Q(T) = \frac{3e^2Qq(T)}{2I(2I-1)\hbar}. \quad (3)$$

We note here the accuracy of expressions (1) and (2). The matrix elements of the quadrupole Hamiltonian H_Q in the representation which diagonalizes the Zeeman Hamiltonian depend on the angle θ . In the case of zero asymmetry parameter in the quadrupole effect ($\eta=0$) we can see easily that all the off-diagonal matrix elements of H_Q are zero at $\theta=0$, and thus all the higher than first order quadrupole effects for both central and satellite transition vanish at $\theta=0$. Then the equation describing the transition frequency ν_m between the m -th and the $(m-1)$ -th levels is reduced to be as follows:

$$\nu_m(\theta=0) = \nu_L(0) \left[1 \pm \frac{\nu_Q}{2\nu_L} (2m-1) \right], \quad (4)$$

where $\nu_L(\theta)$ is the nuclear Larmor frequency associated with the Knight shift as,

$$\nu_L(\theta) = \frac{\gamma_N}{2\pi} [1 + K(\theta)] H_{\text{ext}}. \quad (5)$$

Consequently eq. (1) is proved to be exact relation, irrespective of the quadrupole effect. On the other hand, at $\theta=\pi/2$ the higher than first order quadrupole effects appear in principle. We can get eq. (2) by taking account of the 2nd order quadrupole effect. Nevertheless we find that the eq. (2) is accurate for the third order accuracy, because it is known that at arbitrary θ the central transition is never shifted by any odd-order quadrupole effects.³⁾ We could have neglected the higher than fourth order quadrupole effect, by estimating the order of the magnitude.

According to eq. (2) the knowledge of temperature dependence of ν_Q is necessary to obtain the temperature dependence of $K^\perp$. The

most direct way to obtain ν_Q is to measure the zero applied field NQR spectra. We have actually performed it for ⁶³Cu in YbCu₂Si₂, and obtained $\nu_Q = 2.572 \pm 0.005$ MHz at 4.2 K (see Fig. 5). The ν_Q was found to be temperature independent below 4.2 K. The NQR signal, however, has become less distinguishable at higher temperatures because of the poor signal to noise ratio. Hence, in order to obtain the higher temperature data of $\nu_Q(T)$, we have made use of the NMR satellite spectra. Measuring the separation between two satellite transition lines in external field at the fixed angle $\theta=0$, we can extract ν_Q from the following relation,

$$\nu_Q = \frac{\gamma_N}{4\pi} (1 + K'') [H_{\text{ext}}(-1/2 \rightarrow -3/2) - H_{\text{ext}}(3/2 \rightarrow 1/2)]. \quad (6)$$

This expression is derived directly from eq. (4), and therefore accurate irrespective of the higher orders of the quadrupole effect. Determination of K'' in eq. (6) can be made independently by the measurement for the central transition (eq. (1)).

We show the experimental results of the $K''(T)$ and the $\nu_Q(T)$ in Figs. 4 and 5, respectively. The value of the ν_Q at 4.2 K is in good agreement with the NQR result. Using the data of the $\nu_Q(T)$, we have extracted the $K^\perp(T)$, and the result is also shown in Fig. 4.

Together with the susceptibility $\chi^\alpha(T)$ ($\alpha = \parallel$ and $\perp$), the Knight shift $K^\alpha(T)$ yields various informations on the local electronic structure. The dependence of K^α on χ^α is shown in Figs. 6 and 7. For both the directions $K-\chi$ relation is not found to obey a simple linear relation. Similar anomalous $K-\chi$ relation has been observed in other CKS (see Table I), but the origin has remained unknown. An interesting mechanism proposed tentatively by some authors have involved a modification of the electronic structure associated with the onset of the coherent Kondo state.¹⁷⁾ However, it seems to be difficult for the interpretation to prevail over the other possible mechanisms, because the onset temperature of the anomaly in the $K-\chi$ relation has not been necessarily correlated with the Kondo temperature. Since it has been demonstrated by both experimentally and

Fig. 4. ^{63}Cu Knight shift versus temperature. Fig. 5. Quadrupolar frequency ν_Q versus temperature. The thin curve is a guide to the eye. Arrow is the NQR result in zero applied field at $T=4.2$ K.

theoretically that the coherence length in the single site Kondo effect which represents the spatial extent of the spin correlation between the localized moment and the conduction electron spin is inversely proportional to the Kondo temperature T_K , it is natural to expect that effect of the inter-site correlation becomes more important for the system having the lower T_K .¹⁸⁻²⁰⁾ In Table I, we have summarized the characteristic temperatures for various CKS: onset of the $K-\chi$ anomaly, the Kondo temperature T_K , and the lower lying CEF split-

ting Δ_1 . In this paper we propose another possible mechanism of the $K-\chi$ anomaly, which results essentially from a single site phenomenon.

It is obvious that the magnetism is crucially associated with the 4f electrons at the Yb ions. Since the near neighbour distance between the Yb site and the Cu site is much larger than the radial extent of the 4f wave function, the magnetic shift in the Cu NMR is attributed to be an indirect hyperfine coupling to the Yb moment. The indirect hyperfine field is due not

Fig. 6. ^{63}Cu Knight shift versus magnetic susceptibility. The closed symbols are the data for the observed Knight shifts; K'' (cross), $K^\perp$ (closed circle). The open symbols are the data for the Knight shifts subtracted by the dipolar contributions; K''_{ce} (open triangle), $K^\perp_{\text{ce}}$ (open circle).

only to the dipole field of the Yb moment but also to the transferred hyperfine field via the conduction electrons on the Fermi surface. First we show that the dipolar contribution to the hyperfine field is not responsible for the $K-\chi$ anomaly. Second we introduce the effective Hamiltonian for the transferred hyperfine coupling between the Cu nuclear spin and the Yb 4f electrons, and show that the orbitally dependent exchange interaction between the 4f and the conduction electrons is responsible

for the anomaly in the hyperfine coupling.

Since the $J=7/2$ spin-orbit ground state lies about 1.3 eV below the $J=5/2$ excited multiplet, the electronic state of a Yb ion can be expressed in terms of the total angular momentum $J=L+S$ below the room temperature.³⁷⁾ This situation is unchanged in Yb intermetallic compounds, because the interactions with CEF and the mixing of the conduction electrons are much smaller than the interaction among the atomic 4f electrons.

Fig. 7. ^{63}Cu Knight shift versus magnetic susceptibility for $H \perp C$ data. This figure is the expanded for the same data as the closed circles in Fig. 6.

Then, in the paramagnetic state, the dipolar contribution to the hyperfine interaction can be written as a bilinear relation,

$$H = \gamma_N \hbar I_N \cdot \mathbf{A}_{\text{dip}} \langle \mu_f \rangle, \quad (7)$$

with a definite tensor coupling,

$$A_{\text{dip}}^\alpha = \sum_i \frac{3 \cos^2 \Theta_i - 1}{r_i^3}, \quad (8)$$

Table I. Summary of the characteristic temperatures for various CKS.

Substance	Onset of $K-\chi$ anomaly (K)	T_K (K)	CEF splitting Δ_1 (K)
CeSn ₃	130 ^a	130 ^b	
CeCu ₂ Si ₂	10(Si-NMR) ^b	10 ⁱ	140 ^j
CeAl ₃	40 ^c	6 ^j	60 ⁿ
CeAl ₂	60 ^d	6 ^k	100 ^o
CeAs	60 ^e		140 ^p
CeP	60 ^e		200 ^q
YbCuAl	30(Al-NMR) ^a	60-130 ^l	60 ^r
YbP	100 ^f	10 ^f	228 ^s
YbCu ₂ Si ₂	100(Cu-NMR) ^g	40 ^m	200 ^m

References: a=17, b=21, c=22, d=23, e=24, f=25, g=present work, h=26, i=27, j=28, k=29, l=30, m=9, n=31, o=32, p=33, q=34, r=35, s=36.

where μ_f is the magnetic moments of the Yb ion, $\langle \rangle$ means the thermal average over the electronic states in the appropriate CEF levels, r_i the length of the radial vector between the Cu nuclei and the i -th Yb ion, and Θ_i the angle between the radial vector and the direction ($\alpha = //c$ and $\perp c$) of the 4f magnetization due to the applied field. Then the dipolar contribution to the Knight shift is given by

$$K_{\text{dip}}^\alpha = A_{\text{dip}}^\alpha \chi^\alpha, \quad (9)$$

$$\chi^\alpha = N_A \frac{\langle \mu_f \rangle^\alpha}{H_{\text{ext}}}. \quad (10)$$

We have calculated the temperature dependent coupling A_{dip}^α by the use of the literature data of the temperature dependent lattice parameters.¹⁰⁾ The calculation has been made by taking account of the contributions up to the seventh nearest neighbour Yb ions (containing about a thousand Yb ions). The convergence of the calculation has been fairly good (within $\pm 1\%$). As a result, we have found that the whole variation in the coupling A_{dip}^α with temperature is less than 1%, and clearly negligible. Therefore the temperature

dependence of the dipolar contribution to the Knight shift must be proportional to the observed susceptibility. It is also important to point out that this is consistent with the result for valence fluctuation system like YbB₁₂ where the Knight shift in the ¹¹B NMR is dominated by the dipolar contribution and the $K-\chi$ relation is linear.³⁸⁾ Therefore, it is no doubt that the anomaly in the $K-\chi$ relation originates only in the transferred hyperfine coupling.

To see the anomalous dependences of the Knight shift on both the susceptibility and the temperature more clearly, we have plotted the Knight shifts subtracted by the dipolar contributions in Figs. 6 and 8, respectively. We define the corrected Knight shift as K_{ce}^{α} , where the subscript means the hyperfine mechanism due to the conduction electrons. The hyperfine field due to the conduction electrons consists of two parts; the one is due to the Pauli paramagnetism of the conduction electrons free from the 4f electrons, the other is the transferred hyperfine field which is produced by the conduction electron spin polarization induced via the exchange interaction. Even though the Pauli contribution to the susceptibility χ_0 is negligible as mentioned earlier, the contribution to the Knight shift is not necessarily so because of the large coupling of the Fermi contact interaction. Consequently

K_{ce}^{α} can be written as a sum

$$K_{\text{ce}}^{\alpha} = K_0^{\alpha} + K_{\text{tr}}^{\alpha}. \quad (11)$$

Corresponding to the assumption of the temperature independent Pauli susceptibility, it is reasonable to assume that the K_0^{α} is also temperature independent. Then it follows that the anomalous behaviour of the $K-\chi$ relation can be expressed in terms of the temperature dependence of the hyperfine coupling for the K_{tr}^{α} . As is seen in Fig. 6, the intersections of the $K''-\chi''$ plot and the $K_{\text{ce}}''-\chi''$ plot at the temperatures above $T=100$ K to the zero susceptibility coincide with each other. This fact indicates that (1) the transferred hyperfine coupling A_{tr}'' is temperature independent above 100 K, (2) the temperature independent part of the susceptibility χ_0'' is negligible compared with the temperature dependent part, and (3) the Pauli contribution to the Knight shift K_0'' is determined to be +0.11%. Similar behaviour can also be seen for the $H \perp C$ data where we have obtained $K_0^{\perp} = +0.15\%$.

Now we deduce the temperature dependence of the transferred hyperfine coupling A_{tr}^{α} using the following relation,

$$A_{\text{tr}}^{\alpha}(T) = \frac{K_{\text{ce}}^{\alpha}(T) - K_0^{\alpha}}{\chi^{\alpha}(T)}. \quad (12)$$

The results are shown in Fig. 9. We see that the temperature variation of the A_{tr}^{α} is pro-

Fig. 8. Temperature dependence of the ⁶³Cu Knight shift subtracted by the dipolar contribution.

Fig. 9. Temperature dependence of the transferred hyperfine coupling defined by eq. (12) in the text.

nounced around $T=50$ K for both the directions. It is evident that the $K-\chi$ anomaly is not correlated with the susceptibility maximum. It should be noted here that the anisotropy of the transferred hyperfine coupling becomes larger at higher temperatures in contrast to the fact that the anisotropy of the susceptibility gets smaller.

We consider the mechanism of the transferred hyperfine interaction. That is an indirect magnetic interaction between the Cu nuclear spin and the 4f electrons via the conduction electrons on the Fermi surface. Let us denote the conduction electron on the Fermi surface with wave vector $\mathbf{k}$ and spin σ as $|\mathbf{k}\sigma\rangle$. The effective Hamiltonian of the transferred hyperfine interaction can be expressed as follows,

$$H_{12} = \sum_{\substack{\mathbf{k}\sigma \\ \mathbf{k}'\sigma'}} \frac{\langle \mathbf{k}\sigma | H_2 | \mathbf{k}'\sigma' \rangle \langle \mathbf{k}'\sigma' | H_1 | \mathbf{k}\sigma \rangle}{E_{\mathbf{k}'} - E_{\mathbf{k}}}, \quad (13)$$

where H_1 denotes the exchange interaction between the conduction electrons and the 4f elec-

trons, and H_2 denotes the Fermi contact hyperfine interaction between the Cu nuclear spin and the conduction electron spin,

$$H_2 = \frac{8\pi}{3} \gamma_c \gamma_N \hbar^2 I_N \sum_j s_j \delta(\mathbf{r}). \quad (14)$$

To assume that only the Fermi contact hyperfine interaction is important for the Cu hyperfine mechanism is a good approximation for YbCu_2Si_2 , because the Cu 3d band is located deeply below the Fermi surface.³⁹⁾ Hence the Knight shift measures essentially the conduction electron spin polarization $\langle \sigma_z \rangle$ at the Cu sites. Since the coupling of the Fermi contact interaction H_2 is isotropic, the observed anisotropy in the transferred hyperfine field or the $\langle \sigma_z \rangle$ originates in the exchange interaction H_1 .

The form of H_1 has to be examined by both theoretical and experimental studies. Up to now, three different types of the mechanisms have been considered.^{6,7)} The two among them are the Heisenberg type exchange interaction between the 4f spin and the conduction electron spin, and therefore deal with mostly

isotropic part. They are conventionally written as follows,

$$H_1 = -2J_s \cdot S \quad (15)$$

and

$$H_1 = -2J(g_J - 1)s \cdot J. \quad (16)$$

If one wants to explain the observed anisotropy of the conduction electron spin polarization in the frame work of these exchange mechanisms, more practical calculation such as containing the CEF effect and the conduction band structure are needed. If only the distorted 4f wave function due to the CEF effect⁴⁰⁾ would be taken into consideration, the observed anisotropy can not be explained. This is because the observed anisotropy of the conduction electron spin polarization becomes larger at higher temperatures where the CEF effect is reduced. The third exchange mechanism is the Coqblin-Schrieffer type exchange originating from the mixing interaction between the 4f and conduction electrons,⁶⁾

$$H_1^{cs} = -J \sum_{kk'} c_{kM'}^+ f_{M'}^+ c_{kM}. \quad (17)$$

This leads to an essentially anisotropic exchange interaction, if the mixing potential is predominantly spherically symmetric. It is generally accepted that in the CKS the mixing interaction is important because of the proximity of the 4f level to the Fermi surface. Therefore, it is reasonable to conclude that the Coqblin-Schrieffer type exchange prevails in YbCu₂Si₂. This is consistent with the suggestion mentioned in Introduction, where it is suggested from the point of view of the ¹⁷¹Yb-NMR experiments⁵⁾ that the exchange interaction should be highly anisotropic.

It is noteworthy that the traditional K/χ plot does not necessarily present hyperfine coupling constants in contrast to the most cases of the d-electron magnetism. Unless the exchange energy H_1 is dependent linearly on the 4f magnetization, the ratio K/χ does not yield the hyperfine coupling.²⁴⁾ Whether the exchange H_1 is of the form proportional to the magnetization or not depends on the strength of the spin-orbit coupling in the localized electrons. In the case of the dilute Kondo alloys (d-electron impurities), the exchange does not

so strongly depend on the orbital because of the weak spin-orbit coupling and therefore the ratio K/χ corresponds to a hyperfine coupling constant.^{18,19)} But in the case of the Coqblin-Schrieffer type exchange, this is not so. Nevertheless, it is expected that the ratio K/χ is a measure of the hyperfine coupling. Especially the study on the relative variation of K/χ with the angle or the temperature is useful to investigate the microscopic properties of the exchange H_1 .

We consider the origin of the anomalous temperature dependence of the $K-\chi$, on the basis of the transferred hyperfine Hamiltonian H_{12} (eqs. (13), (14), (17)). It is found from Table I that the onset temperature of the $K-\chi$ anomaly has a tendency to correlate with the CEF splitting. Since the Coqblin-Schrieffer type exchange strongly depends on the orbital of the 4f state, the matrix elements may be differ for the CEF states. When the population in the CEF states varies with temperature, thermally averaged exchange coupling will be changed. Although quantitative argument requires the details of the CEF states and the conduction band structure, it is physically essentially to consider that the CEF effect manifests itself in the K/χ anomaly through the orbitally dependent exchange such as the Coqblin-Schrieffer exchange.

So far we have mentioned the magnetic properties in YbCu₂Si₂. The quadrupolar frequency ν_Q , on the other hand, yields informations on electrostatic properties in the material. As can be seen in Fig. 5, ν_Q shows a broad peak around $T=100$ K. Using the literature data of the temperature dependence of lattice parameters,¹⁰⁾ the temperature dependence of ν_Q is found to be correlated with the anomalous temperature dependence of the ratio c/a (see Fig. 10). If the shielding effect on the quadrupole interaction due to the conduction electrons was known at the whole temperature range, the dependence of ν_Q on c/a could solve the problem whether the anomalous temperature dependence of the lattice parameters is due to the distortion of the 4f shell originating from the CEF effect⁴⁰⁾ or to the temperature variation of the Yb valence. Further experiments for the investigation are needed.

Fig. 10. The ratio c/a versus temperature for the isostructural compounds LaCu_2Si_2 , YbCu_2Si_2 and LuCu_2Si_2 . LaCu_2Si_2 and LuCu_2Si_2 are the reference materials for YbCu_2Si_2 . The data of the lattice parameters were taken from ref. 10.

§4. Conclusion

The magnetic susceptibility shows a highly anisotropic behavior at lower temperatures in YbCu_2Si_2 . The anisotropy in χ is reasonably attributed to the CEF effect on the 4f electrons. By measuring the transferred hyperfine field for the ^{63}Cu NMR in the two directions of $H \parallel c$ and $H \perp c$, we have found the anisotropy of the conduction electron spin polarization density. The amplitude of the conduction electron spin polarization is no longer isotropic type of the traditional RKKY spin oscillation. The CEF effect is not essential mechanism for the anisotropy of the conduction electron spin polarization in contrast with that of χ . The anisotropy of the conduction electron spin polarization is an evidence for that exchange interaction between the 4f and the conduction electrons strongly depends on the orbital angular momentum. Anomalous temperature dependence of the $K-\chi$ relation has also been observed. Only if the exchange interaction is taken to be an orbitally dependent one, the

anomaly can be interpreted as a CEF effect in the framework of the single site model. Consequently, it is also suggested that the Coqblin-Schrieffer type exchange is a more reasonable model than the traditional sf exchange.

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