Nuclear magnetic resonance study of magnetic correlation in the heavy-fermion superconductor $CeCu_2Si_2$

1992 J. Phys.: Condens. Matter 4 473

(http://iopscience.iop.org/0953-8984/4/2/015)

J. Phys.: Condens. Matter 4 (1992) 473–486. Printed in the UK

Nuclear magnetic resonance study of magnetic correlation in the heavy-fermion superconductor $CeCu_2Si_2$

H Nakamura†, Y Kitaoka, T Iwai‡, H Yamada‡ and K Asayama
Department of Material Physics, Faculty of Engineering Science, Osaka University,
Toyonaka, Osaka 560, Japan

Received 22 March 1991, in final form 25 July 1991

Abstract. Magnetic correlation in the heavy-fermion superconductor $CeCu_2Si_2$ has been investigated by Cu nuclear magnetic resonance (NMR) and nuclear quadrupole resonance (NQR). For $CeCu_{2.02}Si_2$ with $T_c = 0.72$ K, a magnetic transition has been found at around 0.8 K in applied fields up to 3.5 T, which presumably also exists in zero magnetic field. Below the transition temperature, Cu NMR loses intensity suddenly without any broadening and shift of the spectrum, and the spin-echo decay rate, $1/T_2$, at $H = 13.3$ kOe, increases with decreasing temperature, which is different from the behaviour expected in a static magnetically ordered state. The magnetic transition just above T_c is quite unusual in the sense that the ordered state is not in a completely static regime, but possesses some dynamic aspect. The unusual magnetic state is considered to coexist with superconductivity below T_c. We present a magnetic phase diagram in the field–temperature plane for $CeCu_{2.02}Si_2$.

1. Introduction

$CeCu_2Si_2$ shows dense Kondo behaviour characterized by periodic local moments of Ce atoms at high temperature; while it forms a coherent Kondo state at low temperature, suggesting the presence of itinerant quasi-particles with heavy effective mass. The discovery of superconductivity in $CeCu_2Si_2$ had a great influence on solid-state physics (Steglich *et al* 1979). This is because superconductivity caused by the condensation of highly correlated 4f electrons (heavy quasi-particles) is not in accord with the conventional understanding of superconductivity. Following $CeCu_2Si_2$, heavy-fermion (HF) superconductivity was successively found in UBe_{13} (Ott *et al* 1983), UPt_3 (Stewart *et al* 1984, de Visser *et al* 1984) and URu_2Si_2 (Palstra *et al* 1985, Maple *et al* 1986, Schlabitz *et al* 1986). After extensive investigations, it was revealed that the pairing mechanism of electrons in HF superconductors cannot be explained in terms of the conventional Bardeen–Cooper–Schrieffer (BCS) theory.

In contrast to a BCS superconductor, the physical properties of $CeCu_2Si_2$ show power-law temperature dependence below T_c, implying the presence of a low-lying excitation associated with an anisotropic energy gap (see Steglich 1985). In particular, that the

---

† Present address: Department of Metal Science and Technology, Kyoto University, Kyoto 606-01, Japan.
‡ Present address: Fujitsu Laboratories Ltd, Atsugi 243-01, Japan.

0953-8984/92/020473 + 14 $03.50

nuclear spin–lattice relaxation rate, $1/T_1$, obeys a T^3 law was understood in terms of an anisotropic energy gap model in which the gap vanishes along lines on the Fermi surface (Kitaoka *et al* 1986). The appreciable reduction of the Knight shift below T_c proves that the Cooper pairing is of singlet type (Ueda *et al* 1987). Thus, nuclear magnetic resonance (NMR) experiments suggested that $CeCu_2Si_2$ bearing a strong on-site Coulomb repulsive interaction forms a d-wave superconductivity. It should be stressed that the relaxation behaviour of UBe_{13} (MacLaughlin *et al* 1984) and UPt_3 (Kohori *et al* 1988) is similar to that of $CeCu_2Si_2$.

An intimate correlation between superconductivity and magnetism in HF superconductors has been suggested by both theory and experiment. Experimentally, by neutron diffraction and muon spin relaxation (μSR) experiments at low temperature, a complex antiferromagnetic state with extremely small ordered moments was found to coexist with superconductivity in all HF superconductors. URu_2Si_2 was the first compound in which an antiferromagnetic transition was observed at 17 K followed by a superconducting transition at 1.5 K (Palstra *et al* 1985, Maple *et al* 1986, Schlabitz *et al* 1986). For UPt_3, Aeppli *et al* (1988, 1989) found a magnetic ordering below 5 K by neutron diffraction measurements. For UBe_{13}, some antiferromagnetic ordering was first suggested by specific-heat measurements in applied fields below 150 mK (Brison *et al* 1988). Recently Kleiman *et al* (1990) claimed an antiferromagnetic transition at a much higher temperature of 8.8 K from a measurement of magnetostriction.

As for $CeCu_2Si_2$, early macroscopic measurements did not detect any magnetic ordering at low temperature (for example, Horn *et al* 1981). But the development of some magnetic correlation was suggested by several experiments. For example, the temperature linear coefficient of specific heat, C/T, in external fields above the superconducting upper critical field, H_{c2}, has a broad maximum below 1 K (Bredl *et al* 1984, Steglich *et al* 1984). Recently, Uemura *et al* (1989) reported the results of a μSR study, which showed the presence of a static magnetic ordering below $T_M = 0.8$ K in $CeCu_{2.1}Si_2$. They observed a wide distribution of static random local fields at muon sites and claimed that the ordering was either a spin-glass or incommensurate spin-density-wave (SDW) state. The averaged ordered moment at 0.05 K was estimated to be of the order of 0.1 μ_B/Ce. Independently, we reported a marked decrease of ^{63}Cu NMR intensity around 0.6 K and suggested the onset of some static magnetic ordering above T_c (Nakamura *et al* 1988). It was implied that the magnetic transition was not of spin-glass type, but presumably of SDW type, which induced a large distribution of hyperfine field at the Cu site.

In the current study of HF physics, it is of great importance to clarify the nature of the ground state. NMR is a useful method to elucidate this problem because it is very sensitive to microscopic properties, and it has been successfully applied to the study of HF systems (see e.g. MacLaughlin 1985, Kitaoka *et al* 1987, Asayama *et al* 1988). The purpose of the present paper is to investigate microscopically the low-temperature magnetic properties of $CeCu_2Si_2$ by Cu NMR and nuclear quadrupole resonance (NQR). We have measured the temperature dependence of Cu NMR intensity, the lineshape, the nuclear spin–lattice relaxation time (T_1) and the spin-echo decay time (T_2), and then show the development of magnetic correlation below about 1 K. As is well known, the superconductivity of $CeCu_2Si_2$ is easily suppressed by the off-stoichiometry of Cu, which induces magnetic inhomogeneity caused by unquenched Ce^{3+} moments. Therefore, we will present the results of systematic Cu NMR and NQR measurements of several compounds with different Cu concentrations and annealing conditions. We will deduce an intrinsic magnetic property and establish the magnetic phase diagram of $CeCu_{2.02}Si_2$.

Table 1. Samples used in the present study.

Label	Nominal composition	Heat treatment	T_c (K)
A	$CeCu_{2.02}Si_2$	1000 °C, 4 days	0.72
B	$CeCu_{1.99}Si_2$	1000 °C, 4 days	0.65
C	$CeCu_{1.99}Si_2$	Unannealed	0.45
D	$CeCu_{1.9}Si_2$	1000 °C, 4 days	0 ($T_g = 2.5$)[a]

[a] T_g is the spin-glass freezing temperature.

In contrast to the proposal in the previous paper (Nakamura *et al* 1988), we emphasize that the magnetic transition in $CeCu_2Si_2$ possesses an unusual nature, pointing to a dynamic aspect.

Recently, Tien (1991) reported the Cu NQR study of $CeCu_2Si_2$ at low temperature. He claimed that some static magnetic ordering occurred in $CeCu_2Si_2$ with $T_c = 0.65$ K. His results are somewhat different from those of $CeCu_{2.02}Si_2$ with rather higher quality and higher T_c. The origin of the disagreement will also be commented upon.

2. Experimental procedures

The samples used in the present study were supplied by Professor F Steglich. We used four samples denoted as samples A, B, C and D with different qualities, of which the nominal concentration, heat treatment and T_c are presented in table 1. Here the content of Cu corresponds to the starting composition before melting. The content of unquenched Ce^{3+} is considered to increase in going from sample A to sample D. Sample D with no T_c is known to exhibit a spin-glass ordering at $T_g = 2.5$ K. For NQR and NMR experiments, the samples were crushed into a powder with a size smaller than the skin depth. In NMR experiments, the powder is oriented with the tetragonal *c* axis parallel to the external magnetic field by taking advantage of the large anisotropy of the susceptibility.

For NMR experiments, a conventional phase-coherent-type pulsed spectrometer was used. The NMR intensity was obtained by integrating the whole spin-echo signal averaged by a digital memory and a signal averager. The NMR field-swept spectra and NQR spectra were obtained by plotting the integrated intensity as a function of magnetic field H and frequency ν, respectively. In measuring the intensity as a function of temperature T, we paid attention to the diamagnetic shielding of the RF field associated with the onset of superconductivity. The nuclear spin–lattice relaxation time was measured by observing the recovery of the spin-echo amplitude after a saturation pulse. Low temperatures below 1.3 K were obtained by a conventional ^3He refrigerator. For measurements at low temperature, heating of the sample caused by eddy currents was carefully avoided.

3. Experimental results

3.1. Spectrum and T dependence of signal intensity

3.1.1. NQR study in zero magnetic field. $CeCu_2Si_2$ with the tetragonal $ThCr_2Si_2$-type structure has a unique Cu site crystallographically. Then one NQR signal is observed for

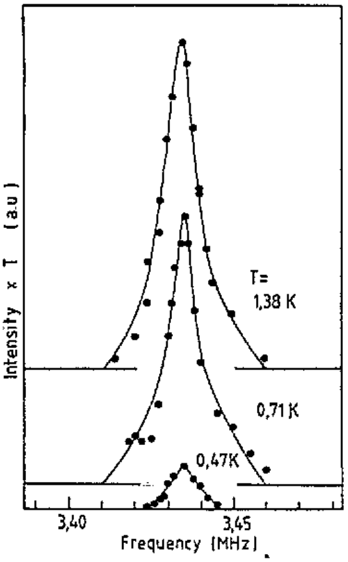

Figure 1. ^{63}Cu NQR spectra of $CeCu_{2.02}Si_2$ (sample A) at $T = 1.38$, 0.71 and 0.47 K. The increase of intensity with decreasing temperature is normalized by multiplying by the temperature.

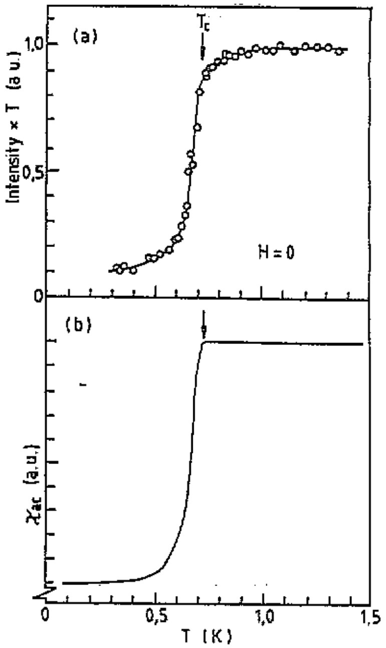

Figure 2. (*a*) Product of ^{63}Cu NQR intensity and temperature for $CeCu_{2.02}Si_2$ (sample A) plotted against temperature. (*b*) Temperature dependence of AC susceptibility of the same sample. Arrows indicate T_c.

^{63}Cu with nuclear spin $I = 3/2$, corresponding to the transition between $m = \pm 1/2$ and $\pm 3/2$ levels split by the nuclear quadrupolar interaction. The resonance frequency, ν_Q, of $CeCu_{2.02}Si_2$ (sample A) with $T_c = 0.72$ K is 3.435 MHz for ^{63}Cu. In order to obtain information on magnetic correlation under zero external field, we measured the T dependence of the ^{63}Cu NQR spectrum. Figure 1 shows the ^{63}Cu NQR spectrum at 1.38 K (well above T_c), 0.71 K (near T_c) and 0.47 K (below T_c). The half-linewidth of the spectrum is very narrow (50 kHz), indicating the high quality of the sample. We did not find any change of the lineshape, such as broadening and frequency shift, within experimental accuracy. Figure 2 presents the T dependence of the integrated intensity of the ^{63}Cu spin-echo signal together with the result of AC susceptibility of the same sample. In figure 2(*a*), the signal intensity is multiplied by temperature to normalize the variation of temperature, because the spectral intensity increases with decreasing temperature following the Curie law of nuclear spin susceptibility. As clearly seen from the figure, the NQR intensity decreases rapidly around 0.65 K in a similar way to the T variation of the diamagnetic susceptibility. Accordingly, the appreciable reduction of NQR intensity is mainly ascribed to the diamagnetic shielding of the RF field associated with the superconductivity. It should be noted, however, that the ^{63}Cu NQR intensity starts to decrease at about 0.8 K, which is slightly higher than T_c. But the effect of diamagnetic shielding due to superconductivity on the intensity reduction would be too dominant to identify unambiguously the magnetic transition at $T_M = 0.8$ K suggested by Uemura *et al.* (1989).

Recently Tien (1991) published the Cu NQR study of $CeCu_2Si_2$ at low temperature. His experimental results and conclusion are different from ours. In his experiment, the linewidth of the ^{63}Cu NQR spectrum of superconducting $CeCu_2Si_2$ with $T_c = 0.65$ K increases with decreasing temperature below 1.1 K, in contrast to no broadening of our $CeCu_{2.02}Si_2$ with $T_c = 0.72$ K. Their result was explained as due to the onset of a static random local field. It should be noted that the linewidth of about 140 kHz above 1.1 K is already wider than that of our $CeCu_{2.02}Si_2$, about 50 kHz. The point is that the magnetic transition is very sensitive to sample quality, which is crucial to a discussion of magnetic properties at low temperature. Hence, precise characterization of the sample is extremely important. We suppose that a small amount of magnetic impurities decreases T_c and, at the same time, may stabilize some static magnetic ordering well above T_c, as will be shown below in detail.

Uemura *et al* (1989) reported the result of a μSR study of $CeCu_{2.1}Si_2$ with $T_c = 0.65$ K under zero external field and showed the onset of some static magnetic ordering below $T_M = 0.8$ K, which was either the spin-glass or the incommensurate SDW. We suspect that it is not certain in μSR experiments whether the magnetic ordered state is completely static.

In contrast to the indications from μSR and recent NQR experiments on compounds with $T_c = 0.65$ K, the magnetic correlation in $CeCu_{2.02}Si_2$ with $T_c = 0.72$ K, which will be identified clearly in an applied field, is unusual as compared with the static magnetic ordering and must be an intrinsic feature of a compound with high quality and high T_c. We suggest that the magnetic state, which continues to have some dynamic aspect even below T_M, is stabilized first and is followed by the onset of superconductivity just below T_M. Especially, it is interesting to make comparisons with Th-doped compounds, $Ce_{1-x}Th_xCu_{2.2}Si_2$ with $x \geqslant 0.08$, which manifest a static magnetic ordering. An apparent broadening of the NQR spectrum was observed, associated with the onset of the static hyperfine field (Kitaoka *et al* 1991).

3.1.2. NMR study in an applied magnetic field. The Cu site of $CeCu_2Si_2$ has uniaxial symmetry. In NMR experiments of ^{63}Cu with $I = 3/2$, the NMR spectrum is split into three resonances due to the nuclear electric quadrupolar interaction corresponding to the central ($m = 1/2 \leftrightarrow -1/2$) and two satellite ($m = -1/2 \leftrightarrow -3/2$; $m = 3/2 \leftrightarrow 1/2$) transitions.

First, we studied $CeCu_{2.02}Si_2$ (sample A) with high quality as expected from the high T_c of 0.72 K and the narrow linewidth of the NQR spectrum. Figure 3 shows a series of ^{63}Cu NMR spectra of $CeCu_{2.02}Si_2$ below 1.27 K at 32.3 MHz, in which only the central transition ($m = 1/2 \leftrightarrow -1/2$) is shown. The corresponding applied field is about 28.6 kOe, being larger than $H_{c2} = 26$ kOe. The peak of the spectrum arises mainly from the grains whose tetragonal c axis is aligned with the applied field. The intensity of the spectrum reduces markedly on decreasing the temperature without any appreciable change of both lineshape and position.

Figure 4 shows the T dependence of the product of temperature and spin-echo intensity at the peak position of the spectrum in several fields. As indicated by open arrows, T_c decreases with increasing field. It is apparent that the NMR intensity starts to decrease above T_c, demonstrating that the rapid reduction of NMR intensity cannot be ascribed to the diamagnetic shielding of the RF field associated with the superconductivity. In the field range of 8.9–12.5 kOe, the intensity drops sharply between 0.8 K and T_c. The intensity ceases to decrease at around T_c and exhibits a plateau followed by a further gradual decrease. This feature may indicate that the magnetic

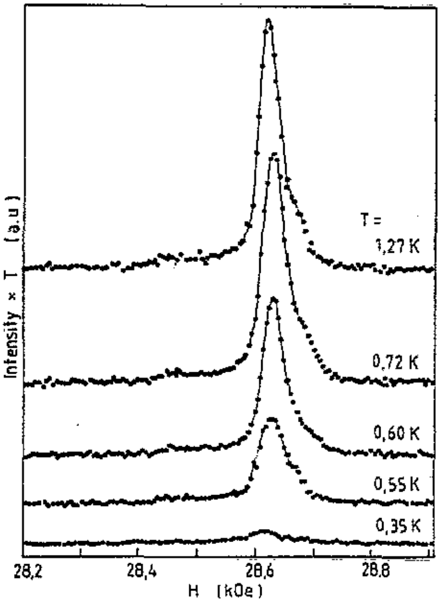

Figure 3. Temperature variation of ^{63}Cu NMR spectrum at 32.3 MHz for $CeCu_{2.02}Si_2$ (sample A). Only the central transition ($m = 1/2 \leftrightarrow -1/2$) is shown. The increase of intensity with decreasing temperature is normalized by multiplying by the temperature.

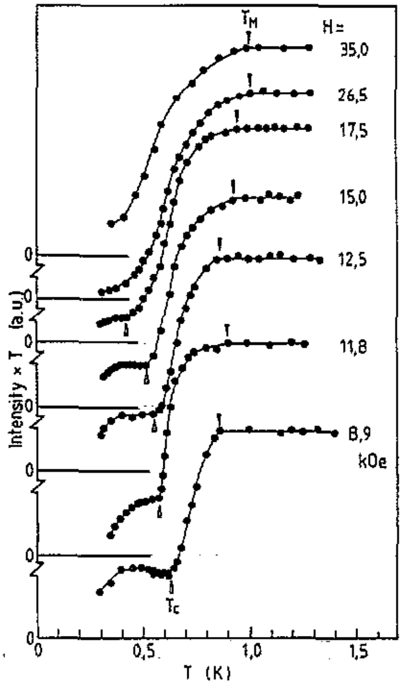

Figure 4. Temperature dependence of product of ^{63}Cu NMR intensity and temperature in several fields for $CeCu_{2.02}Si_2$ (sample A). Full and open arrows indicate T_M and T_c, respectively. T_M was defined as the temperature where the intensity starts to decrease.

correlation stops developing at T_c. In the higher-field region, T_M, the temperature where the NMR intensity starts to decrease, gradually goes up to about 1 K at around H_{c2}, and the intensity at 0.3 K becomes less than 10% of the initial intensity. It is incredible that the system remains in the paramagnetic state at low temperature, because the intensity multiplied by temperature should be constant in such a case. Therefore, it is reasonable to think that the system experiences some kind of magnetic transition below T_M. If some long-range ordering was realized, the lineshape of ^{63}Cu should be modified by the hyperfine field induced by the magnetic moments. However, we could not detect any broadening within experimental accuracy. One of the possible origins of the result is an enormous distribution of the static hyperfine field. In an earlier paper (Nakamura *et al* 1988), we claimed the onset of static magnetic ordering such as SDW, which yields a large distribution of the hyperfine field. However, the transition is not so simple, as is inferred from the anomalous temperature dependence of the spin-echo decay time, T_2, which will be described below. Especially, it should be stressed that the behaviour is completely different from that of the Th-doped compounds, $Ce_{1-x}Th_xCu_{2.2}Si_2$ with $x \geqslant 0.08$, which manifest a static magnetic ordering (Kitaoka *et al* 1991). We have observed a marked broadening of the NMR spectrum as well as the NQR spectrum associated with the generation of the static hyperfine field. The other anomalous properties of the magnetic ordered state in $CeCu_2Si_2$ will be evidenced by measurements of the relaxation time, as presented below.

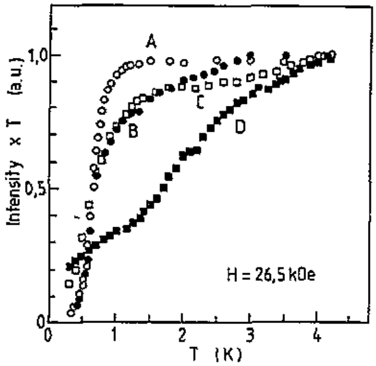

Figure 5. Temperature dependence of product of ^{63}Cu NMR intensity and temperature in $H =$ 26.5 kOe for samples A (○), B (●), C (□) and D (■).

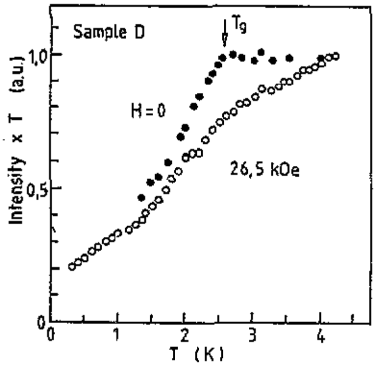

Figure 6. Temperature dependence of product of temperature and ^{63}Cu NMR intensity in $H =$ 26.5 kOe (○) and that of temperature and ^{63}Cu NQR intensity (●) for sample D. The arrow indicates the spin-glass freezing temperature, T_g.

3.1.3. Sample dependence. It should be noted that, in Ce-based HF compounds, a small amount of Ce^{3+} impurities may order magnetically at very low temperature since one cannot expect a perfect sample. In order to check whether the magnetic state is an intrinsic ordering of the Ce lattice or an extrinsic one of Ce^{3+} impurities, we inspected the sample dependence of the magnetic transition by changing the Cu concentration from stoichiometry, which affects sensitively the superconducting and magnetic properties. We have made measurements on four samples (A, B, C and D), of which the parameters are tabulated in table 1. These samples are considered to contain more Ce^{3+} impurities in going from A to D.

Figure 5 shows the T dependence of ^{63}Cu NMR intensity of samples A, B, C and D at 26.5 kOe, above H_{c2}. In contrast to the behaviour of sample A, showing a sharp reduction below 0.85 K, the intensity of samples B and C starts to decrease from considerably higher temperatures of about 3–4 K, though it reduces most rapidly at about 0.6 K in similar manner to sample A. It is important that the rapid reduction around 0.6 K is never due to the superconductivity because the field exceeds H_{c2}.

On the other hand, the behaviour of sample D with no T_c is quite different from the others, reflecting that the compound exhibits a spin-glass ordering at $T_g = 2.5$ K caused by Ce^{3+} impurities. Figure 6 presents the temperature variation of the intensity for sample D at 26.5 kOe and zero field. The latter was measured by ^{63}Cu NQR in zero field. The unquenched Ce^{3+} moments polarized by the magnetic field give rise to an inhomogeneously distributed hyperfine field at Cu sites through the conduction-electron spin polarization. The hyperfine field at Cu sites increases on increasing the number of magnetic moments (n) and the magnetic field (H) and on decreasing the temperature (T), as expected from the relation $M \sim nH/(T + \theta)$, where θ is the Weiss constant. Therefore, if the Ce^{3+} moments dominate the magnetic property, the NMR intensity decreases gradually with decreasing temperature and in proportion to the concentration of Ce^{3+}. As seen in figure 6, the intensity of sample D at zero field decreases distinctly below $T_g = 2.5$ K, characterizing the spin-glass transition. The transition is smeared out by applying a large external field. The behaviour is attributable to the growth of Ce^{3+} impurity moments with increasing field and with decreasing temperature.

Furthermore, we should pay attention to the fact that the residual intensity of sample A approaches nearly zero at the lowest temperature of 0.3 K, whereas that of sample D remains considerable, being 20% of the value at high temperatures. If the intensity loss is dominated by Ce^{3+} impurities, the residual intensity should be larger for sample A including less Ce^{3+} moments. Accordingly, it is evident that the sharp intensity loss below 0.85 K for $CeCu_{2.02}Si_2$ cannot be ascribed to the spin-glass ordering of Ce^{3+} impurities but to an intrinsic magnetic transition. It is noteworthy that such a magnetic transition appears near T_c only for the superconducting samples A, B and C. In this context, it is likely that the gradual loss of intensity above 1 K in samples B and C is due to the presence of unquenched Ce^{3+} impurities, as in the case of sample D. The spin-glass-like transition is considered to occur in samples B and C at lower temperatures than $T_g = 2.5$ K for sample D since samples B and C contain less Ce^{3+} impurities. Similarly, the static magnetic ordering at 1.1 K in zero field, which Tien has reported from a Cu NQR experiment on a sample with $T_c = 0.65$ K, may be induced by some impurities, pointing to this sample being in the same category as sample B.

It is notable that the magnetic transition, identified clearly by applying a field, has nothing to do with static magnetic correlation enhanced by the presence of Ce^{3+} impurities, but is generated by the formation of the HF state. The characteristic feature is that the transition occurs just above T_c and is almost independent of magnetic field up to 35 kOe. We will present below further anomalous properties of the magnetic transition, the results of the relaxation time.

3.2. *Nuclear spin–lattice relaxation of $CeCu_{2.02}Si_2$ (sample A)*

The results of the nuclear spin–lattice relaxation time, T_1, of ^{63}Cu have already been published (Kitaoka *et al* 1984, 1986). Above 10 K, T_1 is nearly independent of temperature, indicating the local moment behaviour of Ce moments, while T_1 obeys the law $T_1T =$ constant, manifesting a Fermi liquid nature in the T range between the coherence temperature $T^* \simeq 2.5$ K and T_c. Here we show the H dependence of T_1 of ^{63}Cu in $CeCu_{2.02}Si_2$. Figure 7 shows the T-dependence of $1/(T_1T)$ at magnetic fields of 5.72, 12.5 and 26.5 kOe. At 5.72 kOe, $1/(T_1T)$ remains nearly constant down to 1 K, reflecting the Fermi liquid nature. With decreasing temperature, $1/(T_1T)$ is enhanced slightly below 1 K and followed by a rapid decrease due to the development of the superconducting energy gap. In a field above H_{c2}, 26.5 kOe, $1/(T_1T)$ has a broad maximum at around 0.6 K. Hence, the slight deviation from the $T_1T =$ constant law below 1 K should be ascribed to the development of magnetic correlation and is correlated with the sharp reduction of NMR intensity. Here it should be emphasized that T_1 presented was selectively measured for the Cu NMR signal coming from the nucleus, which feels no hyperfine field. Then, the Cu nucleus affected predominantly by the magnetic transition may have highly enhanced $1/T_1$ around T_M, which made observation difficult. This may be one reason why the intensity decreases rapidly without a broadening of the spectrum. In order to get further information, the spin-echo decay rate, $1/T_2$, was measured.

3.3. *Spin-echo decay time T_2 of $CeCu_{2.02}Si_2$ (sample A)*

In general, the spin-echo decay rate, $1/T_2$, is determined by the combined mechanisms of direct coupling among nuclear spins through the dipole–dipole interaction, indirect

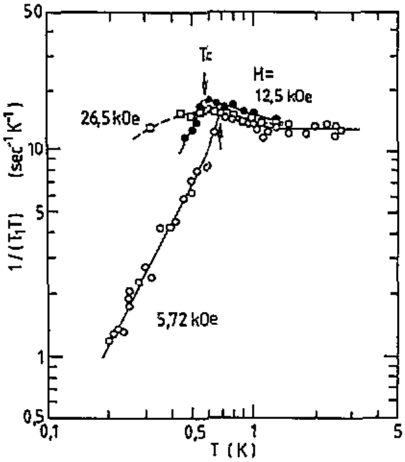

Figure 7. Temperature dependence of $1/(T_1T)$ of $CeCu_{2.02}Si_2$ (sample A) measured in $H =$ 5.72 kOe (○), 12.5 kOe (●) and 26.5 kOe (□). Arrows indicate T_c in the fields.

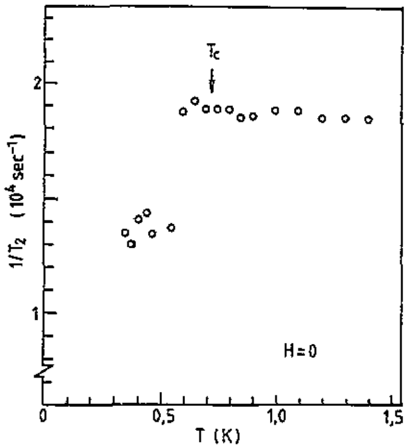

Figure 8. Temperature dependence of spin-echo decay rate, $1/T_2$, of ^{63}Cu NQR signal for $CeCu_{2.02}Si_2$ (sample A). The arrow indicates T_c.

coupling through the conduction spin polarization or spin fluctuations with low energy and the T_1 process through the nuclear spin–lattice coupling. Figure 8 shows the T-dependence of $1/T_2$ measured by the Cu NQR experiment in zero field. Above 0.6 K, $1/T_2$ is independent of temperature with the value of $1.9 \times 10^4\ s^{-1}$, which cannot be interpreted by a tentative estimation of the dipole–dipole interaction and is larger by three orders of magnitude than the nuclear spin–lattice relaxation rate, $1/T_1$. Therefore the spin-echo decay in the system is dominated by indirect coupling. In the HF state, the effective bandwidth becomes very small as compared with that of a normal metal, e.g. ~10 K for $CeCu_2Si_2$ (see Steglich 1985). Namely, the nuclear spins couple strongly with each other through the spin polarization of heavy electrons, i.e. such indirect coupling proportional to the inverse of the bandwidth is much stronger in $CeCu_2Si_2$ than in a normal metal and can be a predominant mechanism for decay of the spin-echo amplitude. Below T_c, the energy gap is developed on the Fermi surface associated with the superconductivity. In this case, it is expected that indirect coupling is appreciably diminished because the energy gap with $\Delta \sim 1$ K (see Steglich 1985) is not so small as compared with the bandwidth of about 10 K. As a matter of fact, as seen in figure 8, $1/T_2$ drops suddenly at 0.6 K just below T_c around which the energy gap grows significantly.

Next, we discuss the behaviour of the spin-echo decay in applied magnetic fields in order to obtain information on he Cu sites influenced by the magnetic transition. In the temperature range where NMR loses intensity, the spin-echo decay manifests anomalous behaviour. Figure 9 shows typical spin-echo decay curves at several temperatures at 15.0 MHz, i.e. $H = 13.3$ kOe. At 0.90 K, it is convex upwards, indicating the existence of Gaussian-type relaxation. With decreasing temperature, the Gaussian-type behaviour disappears and only the Lorentzian-type relaxation becomes dominant. At 0.47 K, the decay curve behaves almost single-exponentially. Because T_c is about 0.55 K in the corresponding applied field, the variation of spin-echo decay is not attributable to superconductivity but to the magnetic transition. At the lower temperature the decay curve becomes convex downwards, which is interpreted to be due to the distribution of

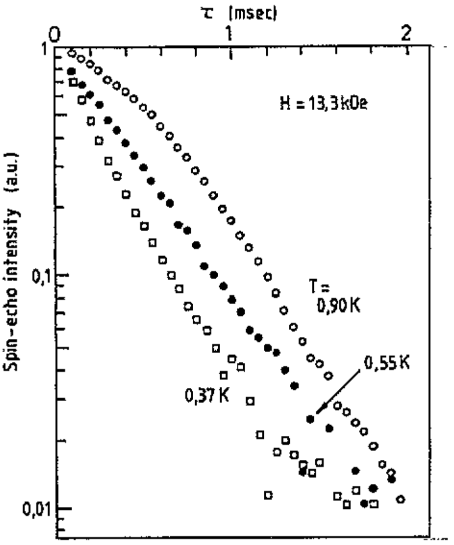

Figure 9. Spin-echo decay curves of ^{63}Cu NMR signal for CeCu$_{2.02}$Si$_2$ (sample A) in $H = 13.3$ kOe at $T = 0.90$ K (○), 0.55 K (●) and 0.37 K (□).

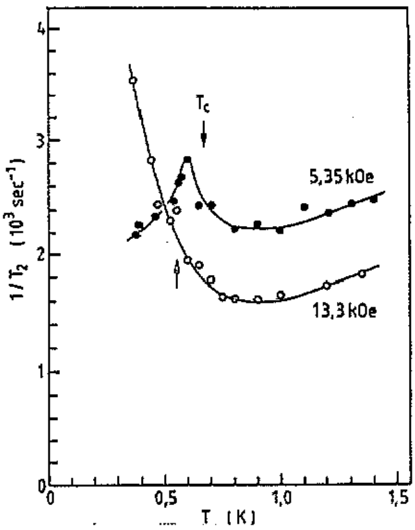

Figure 10. Temperature dependence of spin-echo decay rate, $1/T_2$, for CeCu$_{2.02}$Si$_2$ (sample A) in $H = 5.35$ kOe (●) and 13.30 kOe (○). Here, T_2 was defined as the time when the spin-echo amplitude reduces to 1/e of the initial intensity at $\tau = 0$ (τ is the pulse interval of two-pulse spin-echo measurement). Arrows indicate T_c in the fields. Full curves are to guide the eye.

T_2. Here it should be noted that T_2 was mainly measured for Cu sites not appreciably influenced by the magnetic transition, i.e. for the Cu NMR signal still being observable even below T_M. The complex behaviour of the decay curves reflects indirectly the unusual feature of the unobserved Cu sites, which are strongly affected by the magnetic transition and hence escape observation with development of the magnetic correlation.

Next we discuss the T dependence of $1/T_2$. We define T_2 as the time when the spin-echo intensity reduces to 1/e of the initial value at $\tau = 0$, where τ is the pulse interval of the two-pulse spin-echo measurement. Figure 10 shows the T dependence of $1/T_2$ thus obtained in fields of 5.35 and 13.3 kOe. The arrow in the figure indicates T_c at each field. At 5.35 kOe, $1/T_2$ increases somewhat from 0.8 K down to T_c and has a peak at around T_c followed by a reduction at lower temperatures. At 13.30 kOe, $1/T_2$ increases rapidly and monotonically with decreasing temperature from 0.8 K to even below T_c. Here, it is essential that $1/T_2$ increases with the progress of the magnetic transition. Usually, if a static magnetic ordering occurs, $1/T_2$ is rather expected to decrease due to the detuning effect associated with the distribution of the hyperfine field. Actually, for the Th-doped compounds Ce$_{1-x}$Th$_x$Cu$_{2.2}$Si$_2$ ($x \geqslant 0.08$) with a static magnetic ordering, $1/T_2$ decreases below the transition temperature, T_N (Kitaoka *et al* 1991). The opposite tendency in CeCu$_{2.02}$Si$_2$ suggests that the magnetic correlation in CeCu$_2$Si$_2$ should be distinguished from the static magnetic ordering. To explain the T dependence, indirect coupling other than the T_1 process should be taken into account because $1/T_1$ is sufficiently smaller than $1/T_2$ as mentioned above. Indirect coupling through the virtual excitation of spin fluctuations with low frequency may be the best candidate because the coupling is

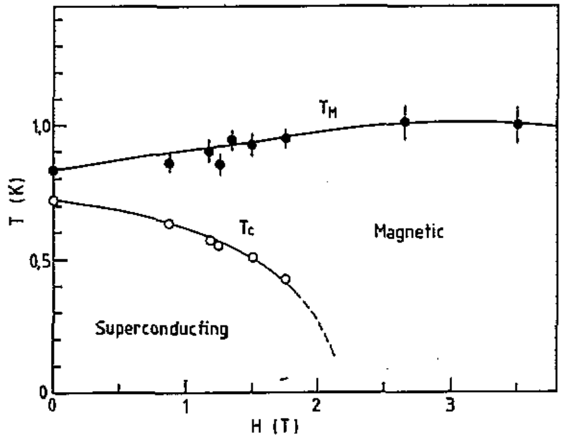

Figure 11. Magnetic phase diagram of $CeCu_{2.02}Si_2$ (sample A). Full circles indicate T_M, which is defined as the temperature where the spin-echo intensity starts to decrease as shown by full arrows in figure 4. Open circles indicate T_c, which is shown by open arrows in figure 4.

enhanced on decreasing the characteristic frequency and increasing the magnetic coherence length. This mechanism explains reasonably the enhancement of $1/T_2$ of the Cu sites unaffected by the magnetic transition and the marked intensity reduction caused by the enormous $1/T_2$ of those affected by the transition. Thus it is crucial that the magnetic transition is unusual in the sense that the magnetic state is not completely static, but may possess a dynamic nature. The different T dependence of $1/T_2$ below T_c for 5.35 and 13.3 kOe may be explained as follows: indirect coupling among nuclear spins reduces markedly associated with the formation of superconducting energy gap, as discussed above to explain the $1/T_2$ of NQR, and affects more strongly the spin-echo decay in the lower field.

4. Discussion

4.1. Magnetic phase diagram of $CeCu_{2.02}Si_2$

The systematic NMR study demonstrated that the exotic magnetic transition observed in $CeCu_{2.02}Si_2$ is an intrinsic property to be distinguished from the static magnetic ordering induced by some Ce^{3+} impurities. The characteristic experimental results of $CeCu_{2.02}Si_2$ observed at the transition are summarized as follows.

(i) The Cu NMR intensity decreases rapidly below T_M, but neither a broadening nor a shift of the spectrum was observed below T_M.

(ii) The spin-echo decay rate, $1/T_2$, is distributed and enhanced below T_M.

Here it is of great interest to obtain the magnetic phase boundary to know the relationship between the HF superconductivity and the exotic magnetic ordering. In the previous paper (Nakamura *et al* 1988), we reported the magnetic phase diagram of $CeCu_{2.02}Si_2$, in which T_M was defined as the temperature where the NMR intensity decreases most markedly. The magnetic transition width was defined as the temperature range where the NMR intensity decreases from 90% to 10%. However, it is better to define T_M as the temperature where the intensity starts to decrease if the transition has a magnetic origin. The magnetic phase diagram thus obtained is shown in figure 11. In this figure, T_c in finite fields is defined as the inflection point of the temperature dependence of the relative intensity as shown in figure 4 by open arrows. The data are in good accord with those obtained by a macroscopic measurement (Assmus *et al* 1984). Below H_{c2}, the magnetic transition occurs first around $T_M = 0.8$ K and is followed by the superconducting transition. Above H_{c2}, only the magnetic state is stable and T_M is almost independent of the magnetic field. Though we have no valid evidence from NQR experiments whether magnetic ordering is present at zero field for $CeCu_{2.02}Si_2$, we plot T_M at $T = 0.8$ K and $H = 0$ in the figure referring to the μSR result of $CeCu_{2.1}Si_2$ (Uemura *et al* 1989).

Recently, Steglich (1989; see also Steglich *et al* 1990) and Hunt *et al* (1990) showed the high-field boundary of the phase diagram by utilizing the data of the field dependence of magnetoresistance and de Haas–van Alphen (dHvA) effects, respectively. The magnetic state is depressed by the field of about 7 T. The field dependence of the Cu NMR up to high fields will be measured in the near future.

4.2. *Magnetic ordering of heavy-fermion superconductors*

Such an exotic magnetic ordering as above has also been found in other HF superconductors. For UPt_3 with $T_c = 0.55$ K, Aeppli *et al* (1988, 1989) reported results of neutron diffraction experiments, proving the onset of antiferromagnetism below 5 K with an ordered moment of $0.02 \pm 0.01\ \mu_B/U$. But the features of the antiferromagnetism are quite different from the long-range ordering observed in $U_{1-x}Th_xPt_3$ (Goldman *et al* 1986) and $U(Pd_{1-x}Pt_x)_3$ (Frings *et al* 1987). An early μSR study also suggested the presence of magnetic ordering below about 6 K with a moment of the order of $10^{-3}\ \mu_B/U$ (Cooke *et al* 1986). In UBe_{13} with $T_c = 0.9$ K, an antiferromagnetic transition was suggested by macroscopic measurements such as a specific-heat experiment in finite external fields (Brison *et al* 1988) and a magnetostriction measurement (Kleiman *et al* 1990). For URu_2Si_2, an antiferromagnetic ordering directed along the tetragonal *c* axis with the ordered moment of $0.03 \pm 0.01\ \mu_B/U$ was found by neutron diffraction measurements below 17.5 K, which coexists with superconductivity below 1 K (Broholm *et al* 1987).

These orderings were detected by certain experiments but frequently not by others. This may be ascribed to the different experimental conditions and techniques. Though these magnetic orderings have not been sufficiently established yet, the common features can be generalized as follows:

(i) an itinerant magnetism in the Fermi liquid state and unclear phase transition;
(ii) very small averaged ordered moments compared with the expected value from the crystal-field ground state;
(iii) a complex magnetic structure or state;
(iv) delicate field dependence; and
(v) very short coherence length or a dynamic aspect.

The itinerant character of the magnetic ordering should be emphasized. The magnetic ordering may be one of the necessary conditions to induce superconductivity. As suggested by dHvA effects of $CeCu_2Si_2$ (Hunt *et al* 1990), the superconducting state is formed in a fully developed coherent Fermi liquid state. Then the transition detected by the dHvA experiment should be recognized as an anomaly of the Fermi surface. As for the pairing mechanism of superconductivity, it is supposed that the antiferromagnetic spin fluctuations mediate the virtual attraction for the Cooper pairing in HF compounds.

5. Concluding remarks

The exotic magnetic transition $CeCu_2Si_2$ was revealed by Cu NMR and NQR studies. The nature of the magnetic state is completely different from the conventional static magnetic ordering such as the state observed in $Cu_{1-x}Th_xCu_{2.2}Si_2$ ($x \geqslant 0.08$) (Kitaoka *et al* 1991). The magnetic state below T_M should have a more or less dynamic nature. In particular, to inspect the dynamic aspect of the unusual magnetic state found in $CeCu_2Si_2$, a neutron scattering experiment is desired. We believe that such an exotic magnetic state exists commonly in HF superconductors as one of the necessary conditions for the appearance of HF superconductivity. Finally, we emphasize that careful sample characterization and systematic measurements of the same sample by various experimental methods ranging from high- to low-energy excitation are necessary to discuss the dynamics of the magnetism.

Acknowledgments

The authors are much indebted to Professor F Steglich and Dr U Rauchschwalbe for supplying the samples. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture, Japan.

References

Aeppli G, Bishop D, Broholm G, Bucher E, Siemendmeyer K, Steiner M and Stusser N 1989 *Phys. Rev. Lett.* **63** 676

Aeppli G, Bucher E, Broholm G, Kjems J K, Baumann J and Hufnagl J 1988 *Phys. Rev. Lett.* **60** 615

Asayama K, Kitaoka Y and Kohori Y 1988 *J. Magn. Magn. Mater.* **76/77** 449

Assmus W, Herrmann M, Rauchschwalbe U, Riegel S, Lieke W, Spille H, Horn S, Weber G, Steglich F and Cordier G 1984 *Phys. Rev. Lett.* **52** 469

Bredl C D, Horn S, Steglich F, Lüthi B and Martin R M 1984 *Phys. Rev. Lett.* **52** 1982

Brison J P, Ravex A, Flouquet J, Fisk Z and Smith J L 1988 *J. Magn. Magn. Mater.* **76/77** 525

Broholm C, Kjems J K, Buyers W J L, Matthews P, Palstra T T M, Menovsky A A and Mydosh J A 1987 *Phys. Rev. Lett.* **58** 1467

Cooke D W, Heffner R H, Hutson R L, Schillaci M S, Smith J L, Willis J O, MacLaughlin D E, Boekema C, Lichti R L, Denison A B and Oostens J 1986 *Hyperfine Interact.* **31** 425

de Visser A, Franse J J M, Menovsky A A and Palstra T T M 1984 *Physica* B **127** 442

Frings P H, Renker B and Vettier C 1987 *J. Magn. Magn. Mater.* **63/64** 202

Goldman A I, Shirane G, Aeppli G, Batlogg B and Bucher E 1986 *Phys. Rev.* B **34** 6564

Horn A, Holland-Morits E, Loewenhaupt M, Steglich F, Scheuer H, Benoit A and Flouquet J 1981 *Phys. Rev.* B **23** 3171

Hunt M, Meeson P, Probst P A, Reinders P, Springford M, Assmus W and Sun W 1990 *J. Phys.: Condens. Matter* **2** 6859

Kitaoka Y, Nakamura H, Iwai T, Asayama K, Ahlheim U, Geibel C, Schank C and Steglich F 1991 *J. Phys. Soc. Japan* **60** 2122

Kitaoka Y, Ueda K, Fujiwara K, Arimoto H, Iida H and Asayama K 1986 *J. Phys. Soc. Japan* **55** 723

Kitaoka Y, Ueda K, Kohara T and Asayama K 1984 *Solid State Commun.* **51** 461

Kitaoka Y, Ueda K, Kohara T, Kohori Y and Asayama K 1987 *Theoretical and Experimental Aspects of Valence Fluctuations and Heavy Fermions* ed L C Gupta and S K Malik (New York: Plenum) p 297

Kleiman R N, Bishop D J, Ott H R, Fisk Z and Smith J L 1990 *Phys. Rev. Lett.* **64** 1975

Kohori Y, Kohara T, Shibai H, Oda Y, Kitaoka Y and Asayama K 1988 *J. Phys. Soc. Japan* **57** 395

MacLaughlin D E 1985 *J. Magn. Magn. Mater.* **47/48** 121

MacLaughlin D E, Tien C, Clark W G, Lan M D, Fisk Z, Smith J L and Ott H R 1984 *Phys. Rev. Lett.* **53** 1833

Maple M B, Chen J W, Dalichaouch Y, Kohara Y, Rossel C, Torikachivili M S, McElfresh H W and Tompson J D 1986 *Phys. Rev. Lett.* **56** 185

Nakamura H, Kitaoka Y, Yamada H and Asayama K 1988 *J. Magn. Magn. Mater.* **76/77** 676

Ott H R, Rudigier H, Fisk Z and Smith J L 1983 *Phys. Rev. Lett.* **50** 1595

Palstra T T M, Menovsky A A, van den Berg J, Dirkmaat A J, Niewenhuys J G and Mydosh J A 1985 *Phys. Rev. Lett.* **55** 2727

Schlabitz W, Baumann J, Pollit B, Rauchschwalbe U, Mayer H M, Ahlheim U and Bredl C D 1986 *Z. Phys.* B **62** 171

Steglich F 1985 *Theory of Heavy Fermion and Valence Fluctuations* ed T Kasuya and T Saso (Berlin: Springer) p 23

—— 1989 *J. Phys. Chem. Solids* **50** 225

Steglich F, Aarts J, Bredl C D, Lieke W, Meschede D, Franz W and Schafer H 1979 *Phys. Rev. Lett.* **43** 1892

Steglich F, Bredl C D, Lieke W, Rauchschwalbe U and Sparn G 1984 *Physica* B **126** 82

Steglich F, Geibel C, Horn S, Ahlheim U, Lang M, Sparn G, Loidl A, Krimmel A and Assmus W 1990 *J. Magn. Magn. Mater.* **90/91** 383

Stewart G R, Fisk Z, Willis J O and Smith J L 1984 *Phys. Rev. Lett.* **52** 679

Tien C 1991 *Phys. Rev.* B **43** 83

Ueda K, Kitaoka Y, Yamada H, Kohori Y, Kohara T and Asayama K 1987 *J. Phys. Soc. Japan* **56** 867

Uemura Y J, Kossler W J, Yu X H, Schone H E, Kempton J R, Stronach C E, Barth S, Gygax F N, Hitti B, Schenck A, Baines C, Lankford W F, Ōnuki Y and Komatsubara T 1989 *Phys. Rev.* B **39** 4726