μSR studies on the development of magnetism in the Kondo semimetal CeNiSn caused by doping with La, Cu and Pt

1996 J. Phys.: Condens. Matter 8 6967

(http://iopscience.iop.org/0953-8984/8/37/018)

J. Phys.: Condens. Matter **8** (1996) 6967–6983. Printed in the UK

μSR studies on the development of magnetism in the Kondo semimetal CeNiSn caused by doping with La, Cu and Pt

S J Flaschin†, A Kratzer†, F J Burghart†, G M Kalvius†, R Wäppling‡, D R Noakes§, R Kadono‖, I Watanabe‖, T Takabatake¶, K Kobayashi¶, G Nakamoto+ and H Fujii+

† Department of Physics, Technical University Munich, D-85747 Garching, Germany
‡ Institute of Physics, University of Uppsala, S-75121 Uppsala, Sweden
§ Department of Physics, Virginia State University, Petersburg, VA 23806, USA
‖ Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan
¶ Faculty of Science, Hiroshima University, Higashi–Hiroshima 724, Japan
+ Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi–Hiroshima 739, Japan

Received 8 March 1996, in final form 12 July 1996

Abstract. Muon spin-rotation–relaxation (μSR) experiments were performed at low temperature in transverse, zero and longitudinal field on $Ce_{0.85}La_{0.15}NiSn$, $CePt_{0.12}Ni_{0.88}Sn$, $CePt_{0.2}Ni_{0.8}Sn$ and $CeCu_{0.1}Ni_{0.9}Sn$ as an extension of our previous studies of the CeTSn (T = Ni, Pt, Pd) series. In CeNiSn we have proven the formation of weakly dynamic paramagnetic spin correlations, below 1 K which, however, do not lead to long-range magnetic order even at $T = 10$ mK. For $Ce_{0.85}La_{0.15}NiSn$ the predicted heavy-hole gas antiferromagnetism is not seen, but rather a reduction of magnetic correlations. Both Pt-doped compounds exhibit no significant enhancement of spin correlations although CePtSn is an antiferromagnet with $T_N \approx 7$ K. The magnetic correlations increase strongly for $CeCu_{0.1}Ni_{0.9}Sn$ up to the point of forming a spin–glass-like state at $T < 0.9$ K. Doping with either 20% Pt or 10% Cu increases the unit cell volume by roughly 1%. Volume expansion in CeTSn is a known cause for a reduction of the hybridization between f electron states and conduction electrons, thereby strengthening magnetic interactions. Yet, the marked differences in magnetic behaviour between replacing Ni in part by either isoelectronic Pt or by Cu, which has two more d electrons, indicates that the dominating effect must be the increase of the d electron density instead.

1. Introduction

The system CeTSn, where T stands for a d transition element like Ni, Pd or Pt has attracted considerable interest worldwide within the field of highly correlated electron systems. Various methods like transport measurements, bulk magnetic studies and neutron diffraction have been applied (see, for example, [1]) and the research is still in progress. We study the series CeTSn and related materials by μSR in order to gain information on the development of magnetic correlations and on the spin-dynamic behaviour at very low temperatures [2–4].

Within the CeTSn compounds, CeNiSn exhibits the most unusual features. Unfortunately, as time progressed, these features changed partly and also new types of behaviour were detected. Since a general, detailed theoretical understanding is lacking, a proliferation of terms describing CeNiSn and related systems took place. One finds the terms ‘Kondo insulators’ [5] or ‘Kondo semiconductors’ [1] to name just the most common

0953-8984/96/376967+17$19.50

ones. As the prototype of this class, CeNiSn possesses Kondo lattice properties at elevated temperatures while at low temperatures showing a semiconductor-like increase of electrical resistivity originally interpreted to be caused by the opening of a very narrow gap (≈ 6 K) in the density of states at the Fermi surface. From NMR data it was concluded that the gap is V-shaped [6] and should be referred to as a 'pseudogap'. According to transport and neutron diffraction data the gap does not extend over the whole Fermi surface [7–9]. However, recent specific heat [10] and resistivity [11] data on new samples with a smaller impurity content established a basically metallic behaviour for CeNiSn at very low temperatures. Especially in view of recent results on magnetoresistance [12] the term 'Kondo semimetal' is more appropriate. While the strong semiconductor-like increase in resistivity is absent in the new samples, other established observations, like the T^2 dependence of the specific heat, remain unaffected and CeNiSn is thought to enter a heavy fermion state at low temperatures. It must be concluded that those properties which have been explained by the presence of a pseudogap are particularly sensitive to sample purity [9]. As outlined in more detail below, our previous μSR data [2, 3] showed the absence of long-range magnetic order down to 10 mK.

Table 1. Lattice parameters of CeNiSn and related compounds.

Compound	a (Å)	b (Å)	c (Å)	V (Å^3)	ΔV (%)	c/a
CeNiSn	7.542	4.601	7.617	264.3	± 0	1.010
$Ce_{0.85}La_{0.15}NiSn$	7.570	4.610	7.620	265.9	$+0.6$	1.006
$CeCu_{0.1}Ni_{0.9}Sn$	7.562	4.621	7.637	266.9	$+1$	1.010
$CePt_{0.12}Ni_{0.88}Sn$	7.535	4.605	7.662	265.9	$+0.6$	1.017
$CePt_{0.2}Ni_{0.8}Sn$	7.526	4.607	7.697	266.9	$+1$	1.022
CePtSn	7.463	4.628	8.016	276.9	$+5$	1.074
CePdSn	7.536	4.704	7.965	282.4	$+7$	1.056

CePtSn and CePdSn are antiferromagnetic Kondo metals with Néel temperatures around 7 K. The cause of the magnetic ordering is most probably the increase of unit cell volume by 5–7% when comparing CeNiSn with CePtSn or CePdSn (see table 1). This volume expansion reduces the hybridization of the 4f states with the conduction electrons and in turn allows the RKKY interaction to overcome the Kondo compensation. The weakening of hybridization is supported by photoemission studies [13].

The most important results of our previous μSR studies on pure CeNiSn, which were carried out down to 10 mK, are as follows [2, 3]:

(i) Static magnetic order is absent.

(ii) Below ~ 1 K the muon spin relaxation rate λ first rises with decreasing temperature in a fashion typical for the relaxation behaviour in a paramagnet near the magnetic transition temperature but then saturates and perhaps even decreases at temperatures below ~ 100 mK.

(iii) A concomitant saturation behaviour is seen in the muonic Knight shift. In addition, the dependence on applied field is not linear, as should be the case for a free-electron paramagnet.

(iv) From longitudinal field decoupling data it is apparent that the electronic spin correlations responsible for the muon depolarization are of a dynamic nature even at the lowest temperatures (~ 10 mK).

These results led to the conjecture [14] that the μSR behaviour of CeNiSn originates from the presence of a very small difference in the ground-state energy of the spin-liquid phase and a magnetically ordered phase. In essence, this causes quasi-critical behaviour equivalent to the appearance of an effective critical temperature, located formally in the negative temperature region (at -0.15 K). Application of mean-field theory gave satisfactory explanations of the relaxation and Knight shift data. In particular, it explained the observed $\sqrt{T}$ dependence of the muon spin relaxation rate. A $T^{1/2}$ law has been predicted for the conduction-electron-driven fluctuation rate of rare-earth moments in the regime $T \leqslant 5T_{\mathrm{Kondo}}$ [15]. This explanation does not apply here, since we are well below $T_{\mathrm{Kondo}} \approx 10$ K.

Preliminary data taken with two different samples of CeNiSn, showing significant differences in their specific heat below 1 K, gave rather similar μSR results in this temperature range [16], indicating that the magnetic properties seen by μSR are little, if at all, affected by a small impurity content of the samples.

Various properties of CeNiSn can be profoundly influenced by a partial replacement of either Ce by La or Ni by Pt or Cu. It is believed that completely random alloys are formed. Doping, especially with Pt or Cu, causes the unit cell volume to increase monotonically. This, together with a possible change of d electron density in the case of Cu, could initiate a change of the hybridization of 4f electrons with conduction electrons and, as a consequence, alter the magnetic properties.

The picture emerging from transport and bulk magnetic data implies that CeNiSn moves from the valence fluctuation regime via a heavy fermion state to antiferromagnetism with rising content of the dopant Pt or Cu. More details of results obtained with methods other than μSR will be listed at the beginning of the discussion sections of the different compounds. Unfortunately no bulk probe data are available for $T < 1$ K as far as we are aware. The μSR measurements reported here, probe the formation of magnetic correlations in a first selection of doped samples of CeNiSn at temperatures extending down to at least 50 mK. As will be seen, the temperature regime below 1 K is crucial in these cases.

2. μSR spectroscopy

In a μSR experiment positive muons are implanted with their spins fixed in a given spatial direction (100% muon polarization). Due to their positive charge, each muon comes to rest at an interstitial site in the solid. From previous studies [17], the stopping site of muons in the orthorhombic lattice [18] of CeTSn is known. In addition, it has been confirmed that muons do not diffuse in the CeTSn lattice at low temperatures. A μSR study is concerned with the temporal development of the muon spin orientation. This is measured via the angular distribution of positrons emitted in muon decay ($\tau_\mu = 2.2$ μs). Of primary interest in the present study is the loss of the initial 100% muon spin polarization with time. This so-called muon spin relaxation is caused by interaction with non-uniform magnetic fields at the muon site (static relaxation) and/or by fluctuations of these fields in time (dynamic relaxation).

We shall briefly explain the basic features of μSR data. The μSR spectrum is a plot of the count-rate asymmetry between two detectors, one placed upstream, the other downstream of the sample as a function of elapsed time from the moment of muon implantation. We refer for details of how this count-rate asymmetry is formed and how a μSR experiment is carried out to a previous publication [19] and monographs on the subject, for example, [20, 21]. The asymmetry shows oscillatory behaviour if muon spin precession occurs, but we do not show spectra of this type. The asymmetry also decays with time, because it is proportional to the polarization of the muon ensemble, or more precisely, it reflects the spin autocorrelation function

$$G_z(t) = 4\langle \boldsymbol{S}\mu(0)\boldsymbol{S}\mu(t)\rangle.$$

$\boldsymbol{S}\mu$ is the muon spin vector. For a sample containing magnetic moments with random orientations, $G_z(t)$ takes the form of a so-called Kubo–Toyabe function [22]. In the case of static moments it relaxes towards $a_0/3$ for long times where a_0 is the initial ($t = 0$) asymmetry. In longitudinal fields $B_L \geqslant 5\Delta_B$, where Δ_B is the static width of the distribution of magnetic field B_μ at the muon site, the muon spin relaxation can be suppressed completely. One finds $a(t) = a_0$ at all times. Dynamic moments, in contrast, cause relaxation towards $a_0 = 0$. Much larger longitudinal fields (compared to the static case) are now needed to reduce the muon spin relaxation rate. If the magnetic moments in the sample are spatially ordered (ferro- or antiferromagnetism) one observes without an applied field the oscillatory behaviour mentioned above in the asymmetry spectrum. μSR cannot strictly distinguish between long- and short-range order. The presence of a spin precession pattern in zero field means that at least over the range of several lattice parameters the host moments are lined up in a simple manner. With disorder in the moment system one approaches the Kubo–Toyabe relaxation. In the intermediary case one may observe an extremely damped oscillatory pattern.

3. Experimental

The measurements were carried out in transverse, zero and longitudinal fields using mainly the dilution refrigerator set-ups at the ‘M15’ beam line at TRIUMF ($Ce_{0.85}La_{0.15}NiSn$, $CePt_{0.12}Ni_{0.88}Sn$) and at the ISIS ‘MuSR’ spectrometer at the Rutherford–Appleton Laboratory ($CePt_{0.2}Ni_{0.8}Sn$, $CeCu_{0.1}Ni_{0.9}Sn$). Both facilities operate with low-energy muons (surface beams). At TRIUMF we deal with a continuous muon beam, while at ISIS the beam is pulsed. The former has better time resolution and allows the μSR signal to be well observed at very early times ($t < 0.2$ μs). The strength of the latter is the extension of the observation time of the μSR spectrum beyond the ‘normal’ ~ 8 μs up to ~ 15 μs. The samples were mosaics of thin (0.5 mm) slices cut either from polycrystalline ($Ce_{0.85}La_{0.15}NiSn$, $CePt_{0.2}Ni_{0.8}Sn$, $CeCu_{0.1}Ni_{0.9}Sn$) or single crystalline ($CePt_{0.12}Ni_{0.88}Sn$) ingots glued with GE varnish onto silver plates and covered by thin silver foils for better heat contact. A series of ‘dummy’ (Al, Ag, Cu) measurements were performed under comparable conditions to determine the magnitude of the background signal arising from muons stopped in the sample holder or cryostat windows. All data were corrected for this background in the analysis. Its influence on the muon spin relaxation rates is in general weak and has been discussed in [2]. The data were analysed using the TRIUMF MSRFIT program which performs a least-squares fit of the selected theory function to the measured count-rate asymmetry.

4. Results

We restrict ourselves in this communication to a discussion of the muon spin relaxation rates, especially at low temperatures.

4.1. $Ce_{0.85}La_{0.15}NiSn$

For this material only transverse field ($B_T = 1$ kG) data are available. The signal damping (i.e. muon spin depolarization) is very weak and could only be resolved for $T < 0.3$ K. Figure 1 presents the results in comparison with equivalent data for CeNiSn.

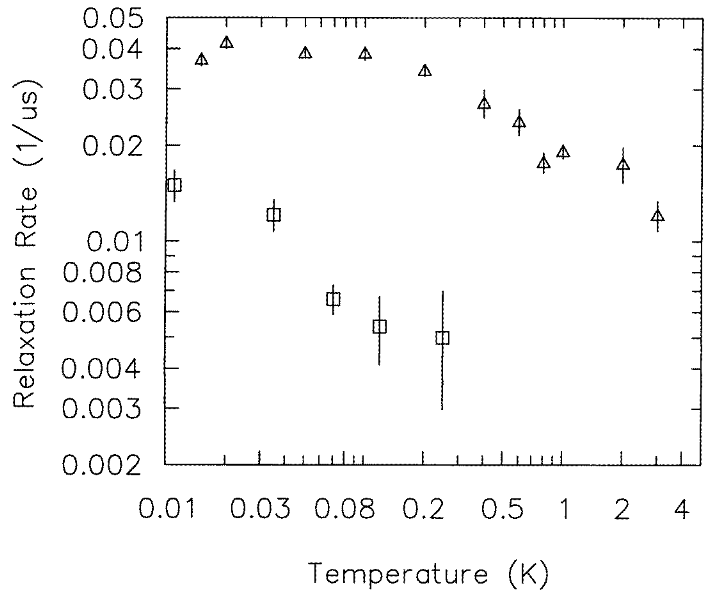

Figure 1. Comparison of the transverse field (1 kG) muon spin relaxation rate at low temperatures for polycrystalline samples of $Ce_{0.85}La_{0.15}NiSn$ (squares) and CeNiSn (triangles), showing that doping with La reduces the strength of magnetic correlations.

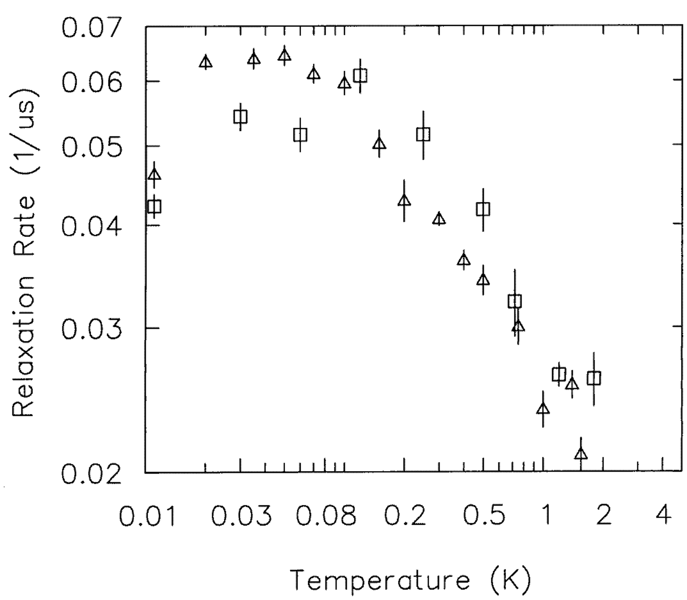

Figure 2. Comparison of the transverse field (1 kG) muon spin relaxation rate at low temperatures for single crystalline (*a* ∥ beam) samples of $CePt_{0.12}Ni_{0.98}Sn$ (squares) and CeNiSn (triangles), showing that the two materials behave essentially alike.

4.2. $CePt_{0.12}Ni_{0.88}Sn$

For single-crystal $CePt_{0.12}Ni_{0.88}Sn$ again only data taken in a 1 kG transverse field are available at present. In figure 2 these data are compared to corresponding results for single-crystal CeNiSn. Both samples of figure 2 were oriented with their a-axis parallel to the muon beam. The muon spin was turned perpendicular to the beam axis and the field applied along the a-axis.

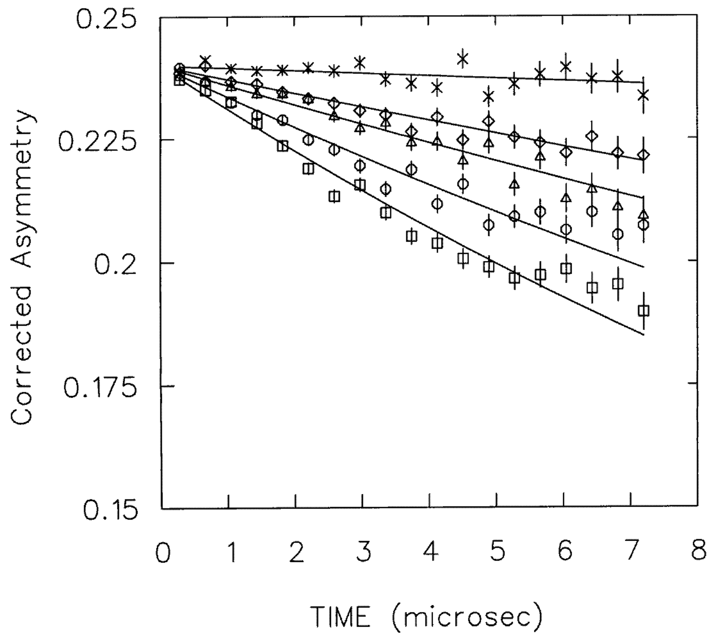

Figure 3. Longitudinal field μSR spectra of $CePt_{0.2}Ni_{0.8}Sn$ in 10 G (squares), 20 G (circles), 50 G (triangles), 100 G (diamonds) and 500 G (crosses) at 0.045 K. The fit to the data points (full curves) assumes a single exponential decay of muon polarization. An applied longitudinal field reduces the depolarization rate (decoupling effect), but weaker than expected in the static limit.

4.3. $CePt_{0.20}Ni_{0.80}Sn$

The study of polycrystalline $CePt_{0.2}Ni_{0.8}Sn$ involved primarily zero and longitudinal field measurements. A few 20 G transverse field runs were used to establish the signal amplitude. In the 'dummy' measurements we found a weakly damped background signal in zero field which is difficult to separate from the sample signal. It probably arises from the numerous beam windows in the dilution refrigerator. A longitudinal field of 10 G results in an undamped background signal which is easier to take account of in the data analysis. This 10 G longitudinal field also suppresses any depolarizing influence of the ^{195}Pt nuclear moments, but, as indicated by a series of low longitudinal field data, has no effect on the depolarization rate caused by electronic dipole moments surrounding the muon. For these reasons we shall discuss only data taken in longitudinal fields of 10 G and higher. Examples of such spectra are depicted in figure 3, while figure 4 presents the temperature dependence of the muon spin relaxation rates in a 10 G longitudinal field. The rates are rather slow

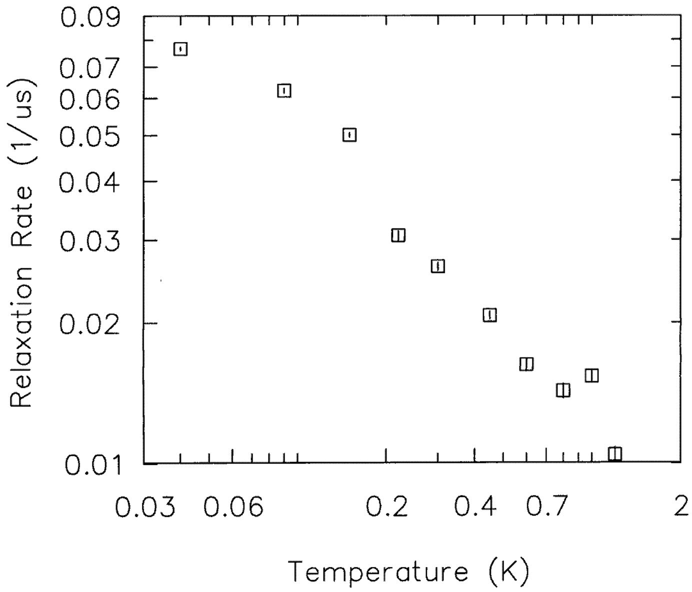

Figure 4. Temperature dependence of the muon spin relaxation rate in $CePt_{0.2}Ni_{0.8}Sn$ taken in a 10 G longitudinal field. As discussed in the text, a comparison with the data for pure CeNiSn reveals that magnetic correlations have increased only little, if at all.

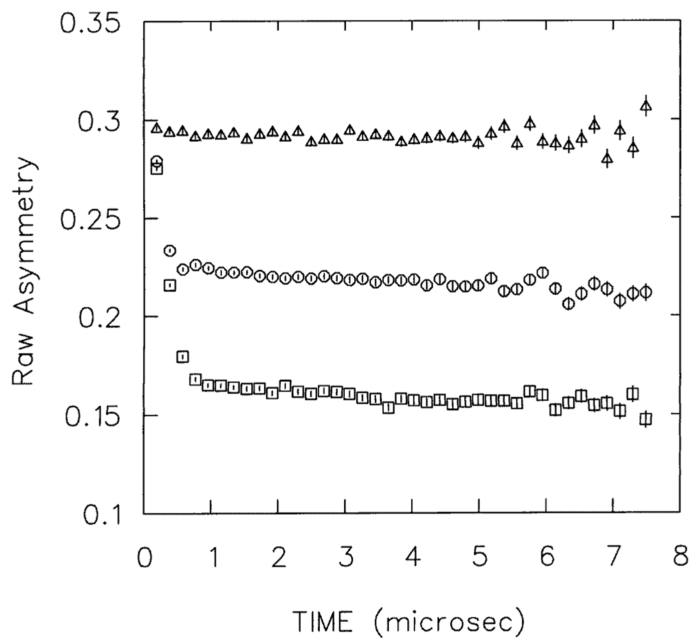

Figure 5. Raw spectra of $CeCu_{0.1}Ni_{0.9}Sn$ at 0.1 K in zero (squares), 100 G (circles) and 1000 G (triangles) longitudinal fields. No fits are shown due to the problems with data analysis discussed in the text. The term 'raw spectra' means that the asymmetry is plotted as measured without the usual correction for different sensitivities of the forward and backward detector (see [19]. Consequently, the 'base line' of asymmetry is at some arbitrary value.

and only weakly enhanced over those previously observed in pure CeNiSn. According to figure 3, stronger longitudinal fields reduce the relaxation rate in the low-temperature regime. All data were fitted to an exponential relaxation $P(t) = a_0 e^{-\lambda t}$ with a_0 (signal amplitude) taken to be independent of field magnitude.

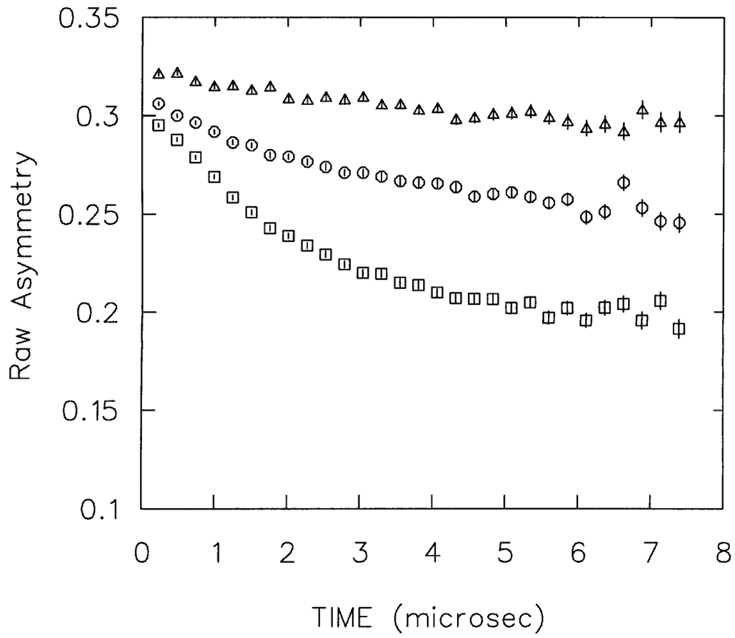

Figure 6. Same plots as figure 5 but for $T = 0.95$ K.

4.4. $CeCu_{0.1}Ni_{0.9}Sn$

The zero and longitudinal field spectra for $CeCu_{0.1}Ni_{0.9}Sn$ at 0.1 and 0.95 K are depicted in figures 5 and 6, respectively. Since the relaxation at low temperatures is fast, the weakly relaxing background signal can easily be included in the zero-field fits. Its amplitude is know from corresponding 'dummy' data and amounts to $a_0^b = 0.05$ (compared to a signal amplitude of $a_0^s = 0.17$). The sample signal also contains the depolarization caused by Cu nuclear dipoles. This effect is determined separately from data taken at higher temperatures ($T > 3$ K) in zero and weak longitudinal fields. As expected, this part of muon spin relaxation (Gaussian decay with $\sigma \approx 0.03\ \mu s^{-1}$) is temperature independent. Consequently, it was included as a fixed parameter in the analysis of the low-temperature data.

In figure 7 selected zero-field spectra for $T \leqslant 1.4$ K are presented. None of the spectra show any spontaneous muon spin precession. The damping rate rises rapidly between 0.9 and 0.5 K. At first sight, the spectra resemble the results of Uemura *et al* [23] for typical dilute spin glasses like 1% manganese in copper. If this notion were correct, the zero and longitudinal field spectra at very low temperatures (e.g. 0.04 K) should be representable by the Lorentzian Kubo–Toyabe relaxation function [22], but fits to this model for data taken at $T \leqslant 0.6$ K failed badly. The longitudinal field spectra, with obviously flat long-time asymptotes that increase in magnitude with field are only consistent with a static field

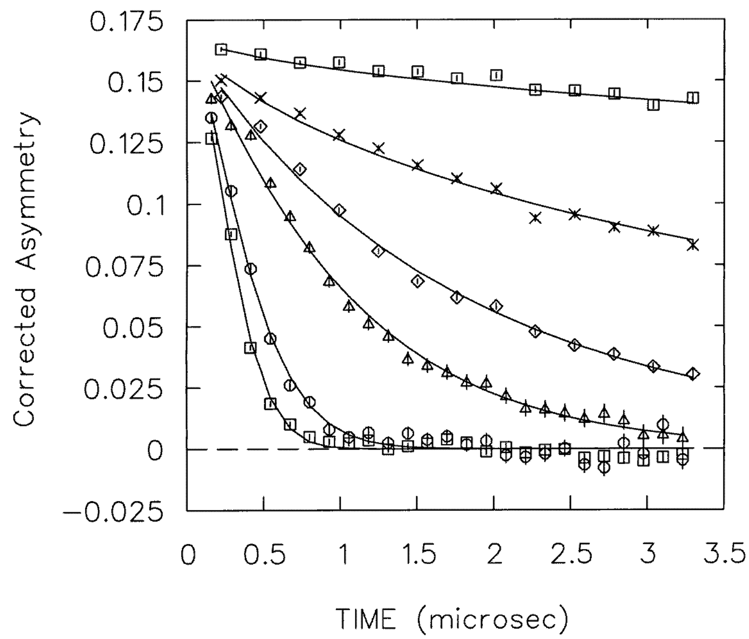

Figure 7. Selected zero-field spectra of $CeCu_{0.1}Ni_{0.9}Sn$ at various temperatures (from bottom to top: 0.04, 0.5, 0.8, 0.9, 1.0 and 1.4 K). A power exponential relaxation function (see the text) was used for fitting (full curves). The background signal from the sample holder etc is subtracted.

distribution at the muon site. However, in this case we should have an asymptote of $\frac{1}{3}$ of the initial asymmetry in the zero field. But the spectra shown in figure 5 decay to zero asymmetrically instead. This could simply be an experimental problem of uncertainty in the determination of the 'base line'.

A rather analogous situation as to the failure of a systematic fit of zero and longitudinal field spectra was encountered by Luke *et al* [24] in $CeCu_{2.2}Si_2$. Hence, we adopt the procedure used by these authors, that is, a power exponential decay of the muon spin polarization

$$P(t) = a_0 \exp[-(\lambda t)^{\beta}]$$

as a phenomenological fit to the zero-field data. We have not attempted to fit the longitudinal field data for $T \leqslant 0.8$ K because of the failure of the Kubo–Toyabe model. In fact, the exact description of muon spin depolarization is not crucial for the conclusions drawn from those spectra. In the range of 0.8 to ~ 2 K it is possible to treat the data in the dynamic spin–glass limit, that is, using a root square damping function [23]. The implications of these approaches will be discussed in the next section. Beyond 2 K the power moves towards $\beta = 1$, but above ~ 5 K the relaxation rate becomes too small to extract a meaningful value of β and pure exponential relaxation was used.

5. Discussion

5.1. $Ce_{0.85}La_{0.15}NiSn$

The doping of CeNiSn with 15% La was selected because at this concentration transport measurements indicate gap closure [26]. A theoretical treatment [25] suggested that doping a Kondo insulator with small amounts of La might produce a dilute heavy-hole gas. Hole–hole exchange coupling would then lead to an antiferromagnetic ground state. Our data for $Ce_{0.85}La_{0.15}NiSn$ as presented in figure 1 show that this is not the case, at least at the La concentration chosen. The decrease in strength of the magnetic correlations observed is the typical behaviour of a rare-earth paramagnet diluted with non-magnetic La.

5.2. $CePt_xNi_{1-x}Sn$ (x= 0.12, 0.20)

In $CePt_xNi_{1-x}Sn$, the specific heat divided by temperature (C/T) at low temperatures increases markedly with rising Pt content up to $CePt_{0.2}Ni_{0.8}Sn$ suggesting the recovery of density of states at the Fermi level (gap closure) [27]. From a comparison with data for LaNiSn, the magnetic part of C/T is estimated. Its increase with x has been explained by assuming the presence of isolated Kondo impurities having $T_K = 25$ K. For $CePt_{0.33}Ni_{0.67}Sn$, a peak appears in the specific heat around 2 K, indicating the onset of magnetic order. It is inferred that the material has become, at this level of Pt doping, an antiferromagnetic Kondo metal like pure CePtSn.

In contrast to these results we find no change in the muon spin relaxation rate when doping with 12% Pt (see figure 2). The relaxation rate λ found for a Pt doping of 20% (figure 4) cannot compared directly be to the results for CeNiSn presented in figure 1, since the former was taken in a 10 G longitudinal field and the latter in 1 kG transverse field. It has been established previously [2] that λ rises significantly with transverse field strength in CeNiSn according to [3], the corresponding relaxation rate in 100 G longitudinal field is $\lambda \approx 0.025\ \mu s^{-1}$ at lowest temperature. A detailed temperature dependence in zero or weak longitudinal fields has not been measured to date because of the smallness of λ. Hence, the relaxation rates in $CePt_{0.2}Ni_{0.8}Sn$ below ~ 0.7 K are probably slightly enhanced, at most by a factor of two. This effect is rather small when compared to $CeCu_{0.1}Ni_{0.9}Sn$.

On the whole we conclude for the cases of 12% and 20% Pt doping that the magnetic correlations present in the low-temperature (heavy fermion) regime are not greatly increased, if at all, meaning that gap closure effects have little influence on the low-temperature magnetic properties sensed by μSR. As can be seen from table 1, the volume increase for the 20% alloy is about 1%. This is apparently insufficient to change the f electron hybridization enough to allow the RKKY interaction to overpower the Kondo compensation.

As outlined in the section on μSR spectroscopy, longitudinal field experiments address the important question of whether the magnetic spin system responsible for the muon spin depolarization is static or dynamic in nature. In the static limit, muon spin relaxation will be completely suppressed for $B_L \geqslant 5\Delta_B$. If we assume that the depolarization rate of $\sim 0.07\ \mu s^{-1}$ found in $CePt_{0.2}Ni_{0.8}Sn$ at 0.045 K in zero field were solely due to static interactions with surrounding electronic dipoles, then a field distribution width of $\Delta_B \approx 1$ G is deduced. Consequently, a field of $B_L = 10$ G should suffice to suppress muon spin relaxation altogether, which clearly is not the case (see figure 3). This proves conclusively that spin fluctuations are still active at very low temperatures, a result similar to our previous findings in pure CeNiSn. Assuming that the applied field does not affect the spin dynamics themselves, the influence of B_L on the muon spin relaxation rate λ is given by [28]:

$$\lambda(B_L) = \frac{\lambda(0)}{1 + [\gamma_\mu B_L \tau_S]^2} \tag{1}$$

where $\gamma_\mu = 2\pi \times 13.55$ kHz G^{-1} is the muon gyromagnetic ratio and $1/\tau_S$ is the fluctuation rate of the magnetic spins. In figure 8, the field dependence of λ at 0.045 K is plotted. A convenient parameter to describe the dynamic decoupling behaviour is the field $B_{1/2}$ at which one has $\lambda(B_{1/2})/\lambda(0) = 0.5$. From equation (1) it follows that $1/\tau_S = \gamma_\mu B_{1/2}$. The data of figure 8 give $B_{1/2} = 35$ G and $1/\tau_S \approx 3\ \mu s^{-1}$, respectively. These are roughly one order of magnitude smaller than previously found in CeNiSn [3]. It appears that the doping with Pt slows down the fluctuations in the magnetic spin system. This might be interpreted as a move towards magnetic order. This important point, however, requires more detailed measurements on different samples of CeNiSn and $CePt_xNi_{1-x}Sn$. Although $\lambda(0)$ decreases with rising temperature (see figure 4), we find no significant change in $B_{1/2}$ up to 0.6 K and consequently, τ_S remains constant in the temperature range from 0.045 to 0.7 K. Beyond 0.7 K the damping is so small that it is difficult to derive a value for $B_{1/2}$. In the dynamic regime one has $\lambda(0) = \gamma_\mu \langle B_\mu^2 \rangle \tau_S$ [28] and definite conclusions as to the behaviour of either $\langle B_\mu^2 \rangle$ or τ_S separately cannot be drawn.

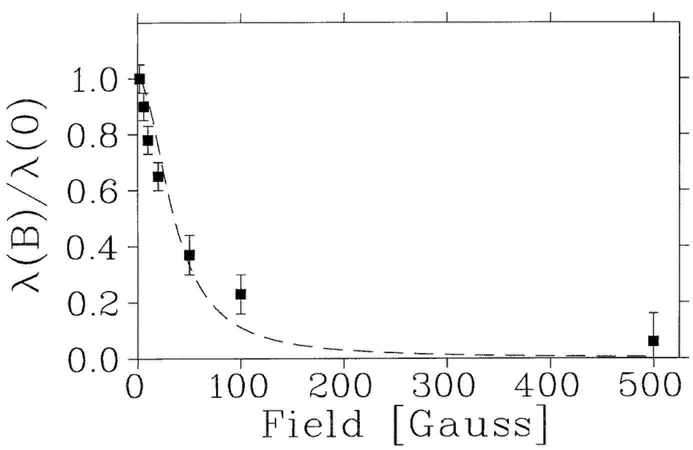

Figure 8. Dependence of the muon spin relaxation rate in $CePt_{0.2}Ni_{0.8}Sn$ at 0.045 K in a longitudinal field. A single exponential decay was used for the muon spin depolarization. The broken curve represents (1) with the parameters given in the text.

5.3. $CeCu_{0.1}Ni_{0.9}Sn$

In $CeCu_xNi_{1-x}Sn$ a linear increase of lattice parameters is observed up to $x = 0.5$ [29]. Resistivity measurements indicate the closure of the pseudogap at $x = 0.1$. For $x = 0.13$, the data suggest the onset of long-range magnetic order near 2.5 K. The ordering temperature rises first sharply, then rather slowly with increasing Cu content and reaches 6 K for $x = 0.5$. The extrapolation of magnetic ordering temperature versus x indicates that $x \approx 0.1$ is the critical concentration. The low-temperature value of C/T is strongly enhanced for $x = 0.1$. Takabatake *et al* [29] suggest that the heavy fermion regime is formed after gap closure and before the onset of long-range order. Susceptibility data [31] at $T > 200$ K show that the high paramagnetic Curie temperature of pure CeNiSn ($\Theta_p = -187$ K) is strongly reduced with increasing Cu content, e.g. $\Theta_p \approx -110$ K for $x = 0.1$ and $\Theta_p \approx -30$ K for $x = 0.5$). The negative value of Θ_p verifies that we deal with antiferromagnetic correlations throughout. The rapid decrease of Θ_p for $0 \leqslant x \leqslant 0.1$ is interpreted as being caused by a decrease in Kondo temperature. From high field magnetization ($T = 1.3$ K, $B = 10$ T), a slow rise of magnetic moment per cerium atom from $\mu = 0.115\mu_B$ for $x = 0$ to $\mu = 0.264\mu_B$ for $x = 0.2$ was estimated. Thermal expansion studies on $CeCu_{0.1}Ni_{0.9}Sn$ were interpreted as to the occurrence of an antiferromagnetic transition near 1.5 K [30].

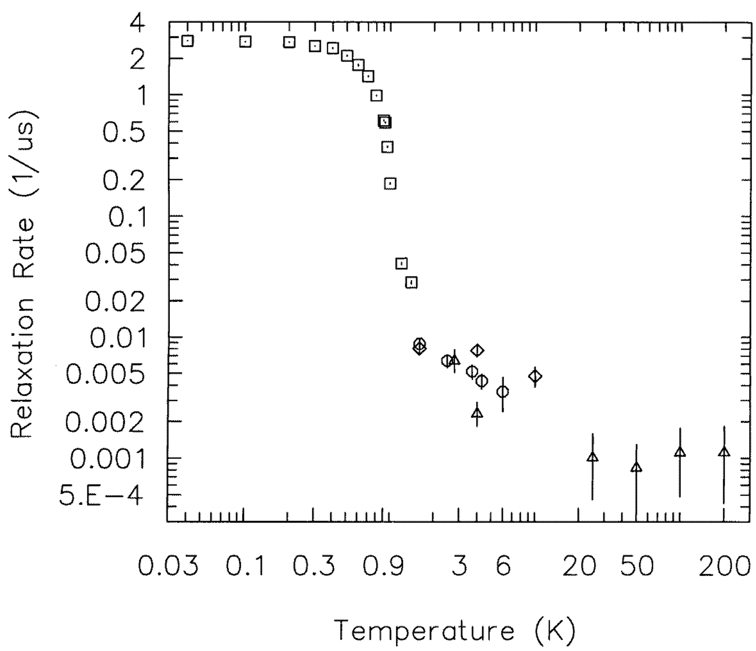

Figure 9. Temperature dependence of the damping rate λ in $CeCu_{0.1}Ni_{0.9}Sn$. The data stem from fits as shown in figure 7. The various symbols refer to different runs. Below 0.9 K the relaxation rate increases rapidly which is interpreted as the formation of a strongly disordered, quasi-static spin structure (spin freezing).

Although the transport and bulk magnetic measurements for Pt- and Cu-doped samples are basically not much different, the μSR spectra exhibit a fundamental change. In figure 9, the temperature dependence of the muon spin relaxation rate in $CeCu_{0.1}Ni_{0.9}Sn$ caused by electronic dipolar moments in the sample is presented. Above $\sim$1.5 K, the rate is very low, and is quite comparable to that of pure CeNiSn. As the temperature decreases to $T \leqslant 400$ mK the relaxation rate increases sharply around 0.9 K to a magnitude about 20 times the value seen in either CeNiSn or Pt-doped CeNiSn. No indication of a magnetic transition near 1.5 K, as claimed by [30] was found. The longitudinal field data given in figure 5 demonstrate that muon spin depolarization can be completely suppressed by applied longitudinal fields of order 1 kG in the low-temperature limit. At lower fields (e.g. 100 G), the initial depolarization is only partially suppressed, but the tail at times $t > 1$ μs shows practically no polarization decay. This is characteristic of depolarization by a *static* distribution of internal fields. As stated before, the spectra cannot be treated within the diluted spin–glass model, meaning that we do not simply have a freezing of random dilute spins. On the other hand, we do not observe spontaneous spin precession. If long-range order is present, the width of the static field distribution is at least comparable in magnitude to the mean field at the muon site (here 50–100 G). This situation indicates an extremely disordered magnetic structure. A non-commensurate spin-wave structure, which also results in a broad distribution of fields, has a characteristic peak in this distribution which would result in a zero-field μSR spectrum often showing a few oscillations before being completely relaxed [32]. According to neutron scattering data, the compounds CePdSn and CePtSn form an incommensurate spiral spin structure [33, 34] below $\sim$7 K. The μSR spectra in this regime, however, consist of one, or several, rather well defined muon spin precession signals indicating that locally well established spin order must be present [4]. As stated such a feature was not observed for $CeCu_{0.1}Ni_{0.9}Sn$.

The rapid increase in muon spin relaxation rate with decreasing temperature below $\sim$0.9 K (see figure 9) has the characteristic shape of the temperature variation of spontaneous magnetization. Since the rate is proportional to $B_{\rm rms} = \sqrt{\langle B_\mu{}^2\rangle}$ at the muon site this behaviour indicates the presence of strongly disordered magnetism (or spin freezing) with a characteristic temperature T_M around 0.9 K. From the partially decoupled longitudinal field runs, a correlation time greater than 5 μs can be estimated.

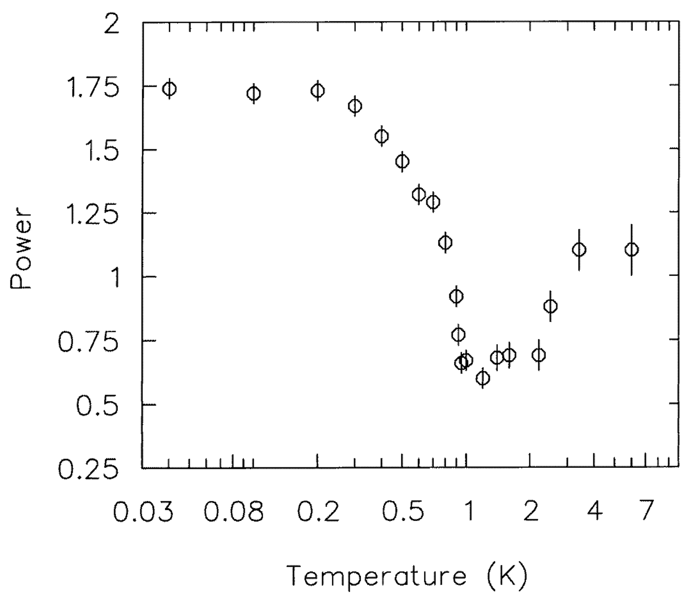

Figure 10. Temperature dependence of the power β of the power exponential function used in the fit to the muon spin depolarization (see the text and figure 7) in $CeCu_{0.1}Ni_{0.9}Sn$. The data do not extend in temperature as much as in figure 9, because the very small depolarization rate for $T > 5$ K does not allow a meaningful determination of β.

The shape of the relaxation function reflects the shape of the local field distribution. For a dense random system of quasi-static spins one finds a Gaussian shape for a dilute system, in contrast, a Lorentzian shape. According to Monte Carlo type simulations the crossover occurs beyond a concentration of 10% magnetic spins [35]. In figure 10, the temperature variation of the power β in the fit function $P(t) = a_0 \exp[-(\lambda t)^\beta]$ is plotted. For $T \to 0$, we find $\beta = 1.8$, i.e. a nearly Gaussian shape. Near T_M, we reach $\beta \approx 1$, indicating that the field distribution is now dynamic. This is also supported by longitudinal field spectra (figure 6). Above T_M, the value of β is close to 0.5, corresponding to a root exponential relaxation as expected for a dynamic spin glass. With further increasing temperature, the exponential limit ($\beta = 1$) is approached again. This latter behaviour has not only been observed in dilute spin glasses [36], but in concentrated random spin systems (amorphous magnets) as well [37].

In summary, the μSR spectra of $CeCu_{0.1}Ni_{0.9}Sn$ at low temperature indicate the transition into a magnetic state around $T_M = 0.9$ K. This state must possess a highly disordered spin structure and might represent a dense spin–glass system. It is probably quite similar to the magnetic state found in $CeCu_{2.2}Si_2$ below ~ 1 K [38, 24, 39]. In the latter case, the magnetic volume fraction decreases with decreasing temperature since the onset of superconductivity competes with the magnetism. In the present case we find that the magnetic signal always arises from the sample as a whole. In a recent NMR study of $CeCu_{0.1}Ni_{0.9}Sn$ the signal was lost below 1.3 K [40] due to excessive line broadening, suggesting magnetic order with a wide variety of local magnetic environments. This fits well with our observations. The lower resolving power of μSR allows us to follow the signal into the magnetic state even in the presence of strong disorder.

The magnetic moments seen must clearly be on the Ce^{3+} ions. Unfortunately, the μSR data do not allow us to distinguish between two scenarios: (i) all Ce^{3+} ions carry a small moment ($\sim 2 \times 10^{-3}\mu_B$) or (ii) only a few per cent of Ce^{3+} ions carry a larger moment ($\sim 0.1\mu_B$). The estimate of moment size is based on Monte Carlo calculations [37, 17]. The larger moments are present if their formation is a local effect which requires that at least one Cu atom is located in the near-neighbour shell of Ce^{3+} ions. The low moments would arise if they were due to a non-local electronic effect, like a change in band structure.

Finally, we point out that the μSR result is also consistent with a somewhat different picture: large moments are present on *all* Ce^{3+} ions even at low temperatures but fluctuate rapidly and hence are ineffective in causing muon spin depolarization. For the Ce^{3+} ions with a Cu in its neighbourhood the fluctuation rate is greatly reduced (to the near-static limit) and hence produces the static field distribution responsible for the observed strong depolarization at low temperatures. This picture may not be compatible with the specific heat results of [29] and with neutron diffraction data [44] whose time window would allow detection of such fluctuations. Furthermore, this picture makes spin fluctuations a purely local phenomenon.

5.4. Induced moment spin glass

In $CeCu_{0.1}Ni_{0.9}Sn$ the situation is fundamentally different from a dilute spin glass, in which magnetic impurities (e.g. Mn) are introduced into a non-magnetic host (e.g. Cu). Here we have a basically magnetic host lattice (Ce^{3+}) whose moments, however, are largely suppressed by the Kondo interaction. Introducing a non-magnetic impurity (Cu) changes the electronic structure in such a way that moments reappear at the Ce^{3+} ions. An analogous situation was found in non-stoichiometric PrP [41, 42] and was termed 'induced moment spin glass'. PrP crystallizes in the NaCl structure and crystalline electric field (CEF) interactions produce a fairly isolated (non-magnetic) singlet as the ground state of the Pr^{3+} ions. In the case of non-stoichiometry (i.e. $PrP_{0.9}$) some of the Pr^{3+} ions have a vacancy in the nearest-neighbour shell. This causes a reduction in local symmetry, and by the thus altered CEF interaction, a magnetic ground state moves near the singlet state leading to a moment on the Pr^{3+} ions via the Van Vleck mechanism. In the case of $CeCu_{0.1}Ni_{0.9}Sn$ it is doubtful that CEF interactions are important, although the local symmetry is surely influenced by the replacement of a nearest-neighbour Ni by Cu. Yet, the point symmetry of the CeTSn structure is very low to begin with and a further distortion will probably have little influence. It should be kept in mind, however, that Kagan *et al* [43] explain the unusual features of CeNiSn by the presence of a low-lying CEF level embedded in the heavy fermion band.

6. Conclusions

μSR experiments were carried out on CeNiSn samples where either Ce had been replaced in part by La or Ni in part by either Pt or Cu. The aim of this investigation was to study the changes in the magnetic spin correlations observed previously in pure CeNiSn. Only for $T < 1$ K could the essential features be observed.

In $Ce_{0.85}La_{0.15}NiSn$ the predicted change of electronic structure leading to antiferromagnetism was not observed. The system rather behaves like a rare-earth paramagnet diluted with non-magnetic La.

The effect of doping CeNiSn with either 12% or 20% Pt on the low-temperature magnetic properties sensed by μSR is minimal. The longitudinal field data, probing the dynamic nature of the magnetic spin system, indicated for the 20% Pt sample a possible slowing down of spin fluctuation rates at very low temperatures when compared to pure CeNiSn. However, these spin fluctuations are in any case rather low (3–50 MHz). A Pt concentration of 20% is obviously insufficient to strengthen the RKKY interaction enough, relative to the Kondo compensation, to induce antiferromagnetism.

In contrast, doping with 10% Cu has a pronounced effect on the magnetic correlations below 1 K. We find around 0.9 K the formation of a highly disordered magnetic state which is discussed in terms of a concentrated spin glass. Below about 500 mK the magnetic spins are static. At higher temperatures dynamic behaviour sets in.

The fact that the partial replacement of Ni by Pt has little effect on the low temperature magnetic correlations, while Cu as a dopant has a very strong effect, is the most salient feature of the present study. As can be seen from table 1, an increase of unit cell volume of $\sim 1\%$ is caused either by 20% Pt or 10% Cu doping. Hence, the global increase of volume cannot be the dominant mechanism altering the magnetic correlations. Admittedly, a distortion of the unit cell (as indicated by the c/a ratio) is noticeable in the Pt case and absent in the Cu case. It is, however, more probable that the decisive difference between Pt and Cu as a dopant rests in the fact that Pt is isoelectronic with Ni while Cu has two more d electrons. We conclude that the filling of d states appears to be the important factor. According to photoemission studies in pure CeNiSn [13], the Ni 3d band is located close to the Fermi level and is incompletely filled due to the hybridization with the unoccupied Sn 5p states. We also mention in this connection that a recent study with polarized neutrons on the induced magnetic moment density in CeNiSn in a 46.5 kG applied field shows, at low temperatures, a small but definite moment density around Ni [45]. The d electrons of Ni clearly are involved in the magnetic properties of CeNiSn.

Acknowledgments

This work was supported by the BMBF, Federal Republic of Germany under contract 03-KA4-TU1-9, by the Swedish National Science Research Council, by USDOE grant DE-FG05-88ER45353 and by a Grant-in-Aid for Scientific Research, Japanese Ministry of

Education, Science and Culture. We also thank Dr C A Scott of the ISIS μSR facility and Dr S R Kreitzman of TRIUMF for their support in carrying out the measurements.

References

[1] Takabatake T and Fujii H 1993 *Japan. J. Appl. Phys.* **8** 254
[2] Kratzer A, Kalvius G M, Takabatake T, Nakamoto G, Fujii H and Kreitzman S R 1992 *Europhys. Lett.* **19** 649
[3] Kalvius G M, Kratzer A, Wäppling R, Takabatake T, Nakamoto G, Fujii H, Kiefl R F and Kreitzman S R 1995 *Physica* **206–207B** 807
[4] Kalvius G M, Kratzer A, Noakes D R, Münch K H, Wäppling R, Tanaka H, Takabatake T and Kiefl R 1955 *Physica* **206–207B** 205
[5] Aeppli G and Fisk Z 1992 *Commun. Cond. Matt. Phys.* **16** 155
[6] Kyogaku M, Kitaoka Y, Nakamura H, Asayama K, Takabatake T, Teshima F and Fujii H 1990 *J. Phys. Soc. Japan.* **59** 1728
[7] Mason T E, Aeppli G, Ramirez A P, Clausen K N, Broholm C, Stücheli N, Bucher E and Palstra T T M 1992 *Phys. Rev. Lett.* **69** 490
[8] Kadowaki H, Sato T, Yoshizawa H, Ekino T, Takabatake T, Fujii H, Regnault L P and Isikawa H 1994 *J. Phys. Soc. Japan* **63** 2074
[9] Takabatake T *et al* 1996 *Physica* B **223–224B** 413
[10] Brückl A, Takabatake T, Kalvius G M, Andres K and Neumaier K 1995 *Verh. Deut. Phys. Gesellschaft* **7** 1726
[11] Nakamoto G *et al* 1995 *Physica* **206–207B** 840
[12] Inada Y, Azuma H, Settai R, Aoki D, Onuki Y, Kobayashi K, Takabatake T, Nakamoto G, Fujii H and Maezawa K 1996 *J. Phys. Soc. Japan* **65** 1158
[13] Nohara S, Namatame H, Fujimori A and Takabatake T 1993 *Phys. Rev.* B **47** 1754
[14] Kagan Yu and Kalvius G M 1995 *JETP Lett.* **61** 758
[15] Cox D L, Bickers N E and Williams J W 1985 *J. Appl. Phys.* **57** 3166
[16] Kalvius G M *et al* 1996 *Proc.* μSR *96 (Nikko) Hyperfine Interactions* to be published
[17] Burghart F J 1992 *Diplom-Thesis* Physics Department, Technical University Munich, unpublished
[18] Higashi I, Kobayashi K, Takabatake T and Kasaya M 1993 *J. Alloys Compounds* **193** 300
[19] Noakes D R, Brewer J H, Harshman D R, Ansaldo E J and Huang C Y 1987 *Phys. Rev.* B **35** 6597
[20] Chappert J 1984 *Muons and Pions in Materials Research* ed J Chappert and R I Grynspan (Amsterdam: North-Holland) p 35
[21] Schenck A 1985 *Muon Spin Rotation Spectroscopy* (Bristol: Hilger)
[22] Kubo R 1981 *Hyperfine Interactions* **8** 731
[23] Uemura Y J, Nishiyama K, Yamazaki T and Nakai R 1981 *Solid State Commun.* **39** 461
[24] Luke G M, Keren A, Kojima K, Le L P, Sternlieb B J, Wu W D and Uemura Y J 1994 *Phys. Rev. Lett.* **73** 1853
[25] Doniach S and Fazekas P 1992 *Phil. Mag.* **65** 1171
[26] Aliev F G, Moshchalkov V V, Zalyalyutdinov M K, Pak G I, Scolozdra R V, Alekseev P A, Lazukov V N and Sadikov I P 1990 *Physica* **163B** 358
[27] Nishigori S, Goshima H, Suzuki T, Fujita T, Nakamoto G, Takabatake T, Fujii H and Sakurai J 1993 *Physica* **186–188B** 406
[28] Slichter C P 1978 *Principles of Magnetic Resonance* (Berlin: Springer) ch 5
[29] Takabatake T, Nakazawa Y, Ishikawa M, Sakakibara T and Koga K 1988 *J. Magn. Magn. Mat.* **76–77** 87
[30] Aliev F G, Villar R, Viera S, Lopez de la Torre M A, Scolodzdra R V and Maple M B 1993 *Phys. Rev.* B **47** 769
[31] Takabatake T, Nakazawa Y and Ishikawa M 1987 *Japan. J. Appl. Phys.* **26** (Suppl. 26-3) 547
[32] Le L P *et al* 1993 *Phys. Rev.* B **48** 7284
[33] Kadowaki H, Ekino T, Iwasaki H, Takabatake T, Fujii H and Sakurai J 1993 *J. Phys. Soc. Japan* **62** 4426
[34] Kadowaki H, Kohgi M, Ohoyama K and Kasaya M 1994 *J. Phys. Soc. Japan* **63** 2337
[35] Kittel C and Abrahams A 1953 *Phys. Rev.* **90** 238
[36] Campbell I A, Amato A, Gygax F N, Herlach D, Schenck A, Cywinski R and Kilcoyne S H 1994 *Phys. Rev. Lett.* **72** 1291
[37] Kalvius G M *et al* 1986 *Hyperfine Interactions* **31** 303
[38] Uemura Y J *et al* 1989 *Phys. Rev.* B **39** 4726

[39] Feyerherm R *et al* 1995 *Physica* **206–207B** 596

[40] Nakamura K, Kitaoka Y, Asayama K, Takabatake T, Nakamoto G, Tanaka H and Fujii H 1996 *Phys. Rev.* B **53** 6385

[41] Hasanain S K, Guertin R P, Westerholt K, Guyot M and Foner S 1981 *Phys. Rev.* B **24** 5165

[42] Yoshizawa H, Shapiro S M, Hasanain S K and Guertin R P 1983 *Phys. Rev.* B **27** 448

[43] Kagan Yu, Kikoin K A and Prokof'ev N V 1993 *JETP Lett.* **57** 600

[44] Sato T J, Kadowaki H, Ishizawa H, Ekino T, Takabatake T, Fujii H, Regnault L P and Ishikawa Y 1996 *J. Phys. Condens. Matter* to be published

[45] Hiess A ILL Grenoble Nov. 95 Private communication by Lander G