Magnetic relaxation in $UCu_{4+x}Al_{8-x}$

A. Krimmel[1,2], **A. Severing**[3], **R. Spitzfaden**[1], **A. Grauel**[1], **B. Buschinger**[1], **C. Geibel**[1], **A. Loidl**[1]

[1] Institut für Festkörperphysik, Technische Hochschule Darmstadt, Hochschulstrasse 6, D-64289 Darmstadt, Germany
(Tel.: + 49-6151/16-5568, Fax: + 49-6151/162833)
[2] BENSC, Hahn Meitner Institut, D-14109 Berlin, Germany
[3] Institut Laue Langevin, BP 156X, F-38042 Grenoble, France

Abstract. A quasielastic neutron scattering study has been performed on $UCu_{4+x}Al_{8-x}$, a system which reveals an alloying-induced transition from magnetic order to heavy-fermion behavior. The magnetic response can be described by a broad quasielastic Lorentzian for all concentrations. No crystal field excitations could be detected. Remarkably, the linewidth decreases with increasing hybridization strength and seems to be no measure of the Kondo lattice temperature T*. In addition, electron spin resonance (ESR) experiments were performed which revealed that, even in the heavy-fermion regime, spin fluctuations play an important role. Both experimental findings are in distinct contrast to cerium-based heavy fermion systems.

I. Introduction

In the last decade, heavy-fermion (HF) compounds have attracted much interest due to their unusual physical properties. Concerning Ce-based HF compounds, the valence state of the Ce ion is known to be Ce^{3+} with an electronic $4f^1$ ($J = 5/2$) Hund's rule configuration. Depending on the symmetry of the crystal, this sixfold degenerate level is split into either three doublets or a doublet and a quartet. At temperatures below the Kondo lattice temperature T*, the degeneracy is lifted by the Kondo effect giving rise to the typical HF effects. The low temperature properties can often be described by Fermi-liquid theory. For U-based HF systems the situation is much more unclear. For many systems it is not well established, whether the 5f electrons are of itinerant character and therefore can best be described by conventional band structure calculations, or whether they are strongly localized allowing for a single-particle description. Furthermore, the valence state of the U ion usually is not known and even if so, it is by no means clear whether the 5f-electrons can be described by the total angular momentum J or if the 5f-electrons should be handeled within a band-theory approach. For the light actinide compounds the importance of including spin-orbit coupling in any theories addressing systems that order with small magnetic moments has been demonstrated and in principle the neutrons are capable of determining spin and orbital moments separately [1].

$UCu_{4+x}Al_{8-x}$ are intermetallic compounds which reveal an alloying induced transition from an antiferromagnetically ordered state ($x \leq 1.25$) to a nonmagnetic HF-liquid state ($x > 1.25$) [2, 3]. The size of the ordered moment close to the phase boundary between antiferromagnetic order and the Kondo regime was estimated to be smaller than 0.25 μ_B [4]. Traditionally, such a behavior has been understood within the framework of Doniach's phase diagram [5]. The electronic specific heat reaches 100 mJ/mol K^2 in the magnetically ordered state and almost 800 mJ/mol K^2 for the nonmagnetic homologues. Magnetic susceptibility and electrical resistivity measurements [2, 3], as well as a neutron diffraction study [4] pointed towards a local moment description. It is important to note that $UCu_{4+x}Al_{8-x}$ reveals a very low concentration of uranium ions per unit cell [5]. Hence, the nearest neighbour distance between two mutual U ions is well beyond Hill's limit, i.e. direct overlap of the 5f shells can be definitively excluded. Therefore, $UCu_{4+x}Al_{8-x}$ is ideally suited to test the importance of the spin-orbit coupling in systems that order with small magnetic moments.

II. Experimental results and discussion

II.1. Neutron scattering experiments

The samples were melted in an arc furnance and subsequently annealed for five days at 750°C. Since $UCu_{4+x}Al_{8-x}$ forms peritectically, the annealing procedure is essential to get single-phase material. Polycrystalline samples with concentrations $x = 0.25$, 0.5, 0.75 and 1.5, approximately 40 g each, have been prepared and investigated. The inelastic neutron scattering experiments were performed using the time-of-flight (TOF) spectrometer IN4 at the high-flux reactor of the ILL, Grenoble. The incident neutron energy was selected to either 17 meV or 69 meV with corresponding energy resolutions of 0.8 meV and 3.4 meV, respectively. In addition, the spectra of an empty sample holder, a cadmium plate and a vanadium standard have been recorded to correct for background and detector efficiency. The measurement for the vanadium standard allowed for a calculation of the intensities in absolute units. Since we are interested in the magnetic scattering contributions only, it is important to take proper account of the phonon part of the scattered intensities. To do so, the isostructural but nonmagnetic reference compound $ThCu_{4.5}Al_{7.5}$ has been measured. In the latter compound the phonon spectrum has been approximated by five Gaussians at energies of approximately 13, 22, 30, 36 and 43 meV. To describe the phonon part of $UCu_{4+x}Al_{8-x}$ the positions and widths of the phonon modes were kept fixed, whereas the intensities were allowed to vary. However, the integral over all phonon intensities was constrained to its corresponding value according to the mean scattering-length approximation. For details of the correction procedures see [6]. After treating the phonon part in this way, the magnetic quasielastic scattering contributions were fitted assuming a single Lorentzian line wheighted by the detailed balance factor. The experiments with an incident neutron energy of 17 meV confirmed the results of the investigation using neutron energies of 69 meV, but gave no new physical insight. Hence, the presentation of the data will be limited to the latter.

Figure 1 shows the corrected TOF-spectra of $UCu_{5.5}Al_{6.5}$, converted to an energy-transfer scale, at different temperatures. This compound stays paramagnetic down to the lowest temperatures. Three different scattering processes contribute to the dynamic structure factor $S(Q, \omega)$, namely the nuclear incoherent scattering (narrow elastic peak at zero energy transfer), scattering due to phonons and finally, the magnetic scattering (shaded areas). The phonon contributions have been determined from the reference compound as described above. The magnetic scattering can be described by a single broad quasielastic Lorentzian, weighted by the detailed balance factor (solid line). Even at 5K the magnetic scattering is only a small fraction of the total scattered intensity (dashed line). Hence, the magnetic intensities, as well as the widths are tainted with relatively large errors. From the temperature dependence of $S(Q, \omega)$ and from the comparison with the non-magnetic reference compound we concluded, that the data reveal no indications of crystal field excitations. This holds true even in the weak hybridization limit ($x < 1$). Despite the large uncertainties, the data provide some evidence that the width of the quasielastic line narrows with decreasing temperature.

Figure 2 shows the spectra for $UCu_{4+x}Al_{8-x}$ as a function of concentration x in the paramagnetic regime at T = 50K. Already a first inspection of Fig. 2 shows that the width of the quasielastic Lorentzian line is similar for all compounds, despite the fact that the hybridization strength, according to bulk measurements, strongly increases with increasing x. The increase of the hybridization between the 5f electrons and the band states which is indicated by the strong increase of the electronic specific heat [2,3], is reflected by the reduction of the magnetic ordering temperature and concomitally by a reduction of the ordered moment, which is completely suppressed for $x > 1.25$ [4]. From transport data it was suggested that the Kondo-lattice temperature increases from $T^* \approx 0$ K ($x = 0.25$) to $T^* \approx 50$ K ($x = 1.75$) [2,3]. Obviously, the linewidths of the quasielastic scattered magnetic intensities, which in Ce compounds roughly can be taken as a measure of T*, in $UCu_{4+x}Al_{8-x}$ are not correlated with the hybridization strength. This is true, even if large error bars in the half width Γ are taken into account. To elucidate this behavior in more detail, we fitted the data for all x and at all temperatures as outlined above and as shown in Figs. 1 and 2.

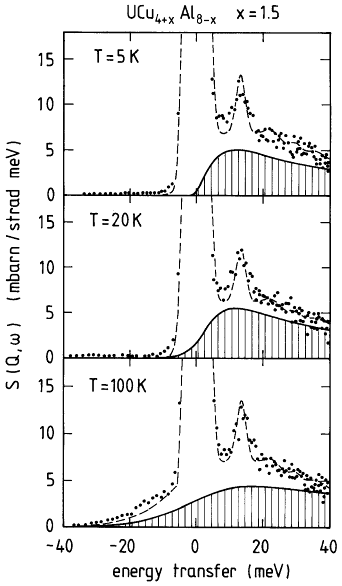

Fig. 1. Dynamic structure factor $S(Q, \omega)$ vs energy transfer for $UCu_{6.5}Al_{6.5}$ at three different temperatures. The dashed lines characterize the total scattered intensities. The solid lines (dashed area) are due to the magnetic scattering only. The phonon contributions have been calculated using measurements of a non-magnetic reference compound. The incident neutron energy was 69 meV

The results of the temperature dependences of the linewidths Γ (HWHM) are plotted in Fig. 3 and are listed in Table 1. The values are subject to large error bars for two reasons: i.) Because of the large absolute values of the linewidths and the limited range of the energy transfer, any variation of the linewidth has only a weak influence on the fit quality. ii.) The transformation of the time-of-flight (TOF) scale into an energy-transfer scale involves a factor t^3. Consequently, the uncertainties become larger for high values of TOF, giving rise to considerable scattering of the data points for high energy transfers. The consequence is again a weak dependence of the fit quality on the linewidth. For $T > T_N$, Γ exhibits a slight decrease for all concentrations (empty symbols), however pointing towards a large residual width for $T \Rightarrow 0$. Γ increases slightly below T_N ($T < T_N$: full symbols), probably due to the presence of overdamped magnetic excitations.

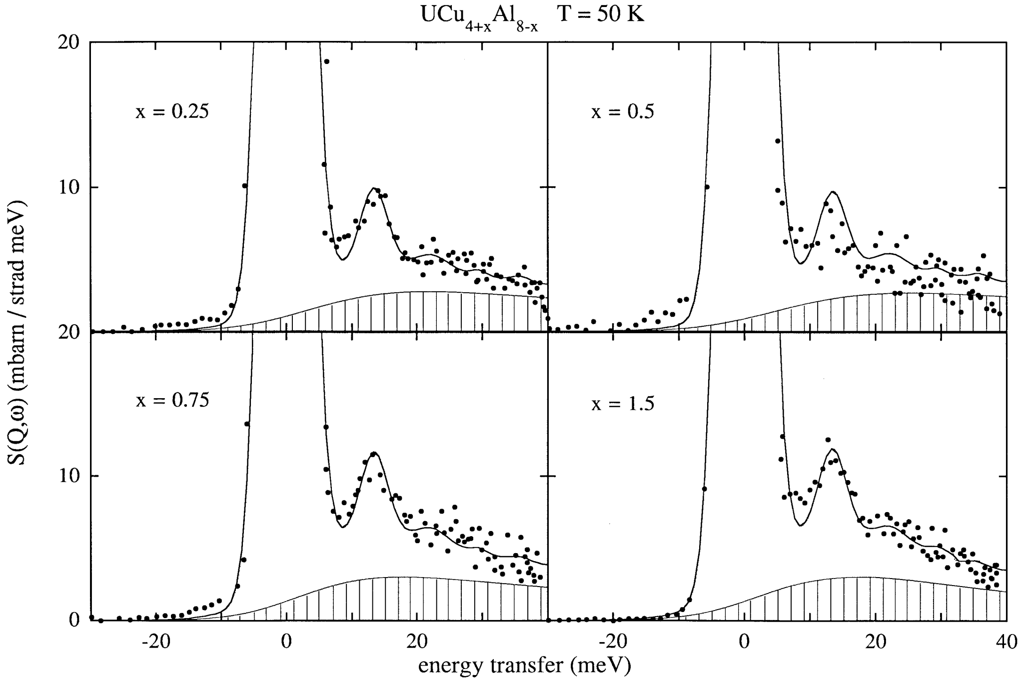

Fig. 2. Dynamic structure factor vs energy transfer in $UCu_{4+x}Al_{8-x}$ for concentrations x = 0.25, 0.5, 0.75 and 1.5, in the paramagnetic regime at T = 50 K

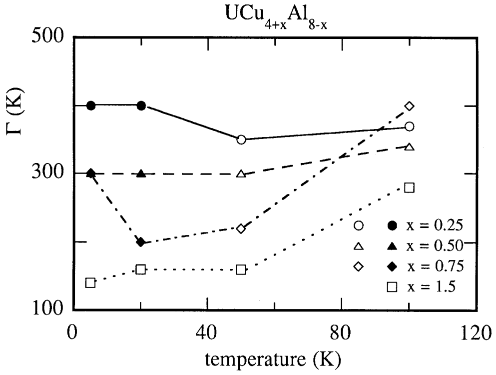

Fig. 3. Temperature dependence of the quasielastic linewidth Γ (HWHM) in $UCu_{4+x}Al_{8-x}$. The lines are drawn to guide the eye. Empty symbols are used for $T > T_N$, while full symbols indicate temperatures $T < T_N$

Table 1. Line width Γ (HWHM) of $UCu_{4+x}Al_{8-x}$ as function of concentration and temperature. For each x the magnetic ordering temperature is indicated

T(K)	5	20	50	100
x = 0.25	$T_N = 37$ K			
Γ(K)	400 (150)	400 (150)	350 (50)	370 (70)
x = 0.5	$T_N = 35$ K			
Γ(K)	300 (50)	300 (50)	300 (50)	340 (60)
x = 0.75	$T_N = 27$ K			
Γ(K)	300 (50)	200 (50)	220 (70)	400 (50)
x = 1.5	no order			
Γ(K)	140 (50)	160 (40)	160 (50)	280 (50)

A similar behavior has been found in U_2Zn_{17} [7]. Only for x = 1.5, the compound in which no long range magnetic order develops down to the lowest temperatures, Γ decreases linearly with a residual width of approximately 12 meV. In general, the quasielastic linewidth in uranium compounds is of the order of 10 meV. Quite often, this value is much larger than the magnetic correlation energy k_BT_N and changes only slightly when passing through the magnetic transition temperature. The temperature dependence of Γ in the strong hybridization regime is in clear disagreement with the behavior as observed in cerium-based HF-compounds. In those, Γ scales with $\sqrt{T}$ for $T > T^*$ with a residual linewidth of order of the Kondo-lattice temperature for $T < T^*$ [8]. The magnetic relaxation rate Γ in $UCu_{5.5}Al_{6.5}$ reveals a "normal" Korringa-type of behavior, however, with a large residual linewidth. It is well known that the 5f electrons in the actinide systems behave different compared to rare earth compounds. The uranium 5f-electrons are rather extended and the strength of the spin-orbit coupling is comparable to the crystalline electric field energies. Indeed, form-factor anomalies have been found experimentally [9, 10] and were explained theoretically [11] to arise due to the fact that the spin and orbital moments evolve separately, oppose each other and compensate at low **Q** values. It has been pointed out that it may be important to include this spin-orbit coupling in any theories and interpretations addressing to systems that order with small magnetic moments [9].

To compare our results in $UCu_{4+x}Al_{8-x}$ with bulk measurements, we calculated the static susceptibilities. In addition, we analyzed the magnetic intensities as a function of wave vector **Q**. In a first step we analyzed the magnetic intensities as function of momentum transfer. In principle, the integrated intensities should be proportional to the square of the neutron magnetic form factor. Of course, due to the average over the Brillouin zone by measuring polycrystalline samples, as well as due to the large error bars and possibly some variations of the scattering law in dependence on momentum transfer, this analysis cannot be considered as a quantative form-factor measurement. Nevertheless, the **Q** dependence of the magnetic intensities directly reflects the magnetic density of states in reciprocal space and therefore may give support to either a local-moment description or to a rather band-like (itinerant) form of magnetism. Figure 4 shows the result of such an analysis. Obviously, the magnetic intensities do not follow a smooth fall-off with increasing momentum transfer (solid line in Fig. 4). In contrast for $x = 0.25$ and $x = 0.5$, clear indications of a maximum occur at around 5Å^{-1}. However, we believe that this anomalous dependence of the magnetic intensities can be interpreted by the assumption of magnetic correlations. And indeed, a momentum transfer of 4Å^{-1}–6Å^{-1} corresponds to the Q values of the first magnetic Bragg reflections [4]. The fact that the anomaly is smeared out with increasing x yields additional support for this interpretation. However, it should be noted that a maximum in the magnetic intensities as a function of momentum transfer close to 4Å^{-1} has been reported for uranium compounds and was interpreted as a cancellation of contributions due to the orbital and the spin moments [9, 10]. On the basis of our present data, it is impossible to obtain more and clearer informations about the details of the electronic configuration of the uranium ions of $UCu_{4+x}Al_{8-x}$. Further investigations using polarized neutrons and single crystalline material are highly warranted.

In a second step we wanted to determine the static susceptibilities and to compare the results with those obtained from bulk measurements. The magnetic neutron scattering cross section is proportional to $X''(\mathbf{Q}, \omega)$, the imaginary part of the generalized susceptibility. Integration along $\hbar\omega$ and performing a Kramers-Kronig transformation yields and zero-frequency bulk susceptibility [12]. Bulk measurements of the magnetic susceptibilities have been performed employing a SQUID magnetometer. The results of the different experiments are compared in Table 2. With the exception of the low-temperature values ($T = 5$ K and $T = 20$ K) for the sample with $x = 0.25$, the agreement is at, or even below, the 10% level for all measurements. In view of the fact, that part of the experiments have been performed in the antiferromagnetically ordered state and bearing in mind the large uncertainties of the linewidths, this agreement is very satisfying. Small macroscopic moments, but finite microscopic magnetization densities would be further indications of an intermediate coupling scheme [9]. However, due to the strong antiferromagnetic correlations between different U ions, one also would expect that the local moment sensed by neutron scattering experiments is found to be larger than the bulk susceptibility. This is a further explanation for the cases of disaccord, namely $x = 0.25$ at $T = 5$ K and $T = 20$ K, respectively. This compound displays the weakest hybridization and the highest Néel temperature and consequently should reveal the strongest magnetic correlations. It should be noted that the Curie-Weiss temperatures, deduced from bulk measurements, vary between -129 K and -172 K. Such large values are typical for Ce- based intermediate valence compounds. Nevertheless, the quasielastic linewidth always exceeds the Curie-Weiss temperature, especially for concentrations with strong hybridization.

Table 2. Comparison of the real part, zero frequency magnetic susceptibility of $UCu_{4+x}Al_{8-x}$, measured by either neutron scattering experiments (N) or by a SQUID-magnetometer (SQUID). The values of the susceptibility are given in units of 10^{-8} m^3/mol

T(K)	5	20	50	100
$x = 0.25$	$T_N = 37$ K			
X_N	5.19	4.54	5.09	4.21
X_{SQUID}	2.74	3.33	4.47	3.76
$x = 0.5$	$T_N = 35$ K			
X_N	3.64	3.89	4.57	3.86
X_{SQUID}	3.69	3.82	5.41	4.28
$x = 0.75$	$T_N = 27$ K			
X_N	5.23	6.79	7.17	5.71
X_{SQUID}	4.75	5.97	6.40	4.89
$x = 1.5$				
X_N	7.89	6.95	5.97	5.19
X_{SQUID}	8.92	7.99	6.57	5.08

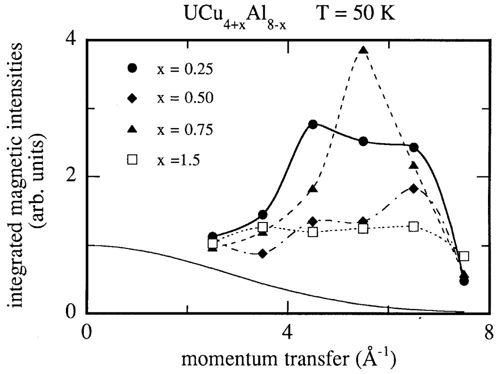

Fig. 4. Integrated magnetic intensities as a function of momentum transfer in $UCu_{4+x}Al_{8-x}$ in comparison with the neutron magnetic form factor of U^{4+} (corresponding to the lowest solid line in the plot) within the dipole approximation (taken from the tables of magnetic form factors, ILL note 1988, by P.J. Brown). The experimental values have been normalized to 1 at the lowest Q values

II.2. Results of the electron spin resonance (ESR) experiments

To gain further insight into the complex magnetic behavior of $UCu_{4+x}Al_{8-x}$ we performed Gd-ESR experiments in compounds with concentrations $x = 0.75$ and $x = 1.75$ doped with 2%, 5% and 10% Gd, respectively. ESR experiments provide detailed informations on the local dynamical susceptibilities. Gd substitutes for U and in Gd-ESR measurements the linewidth at resonance absorption is determined by the electronic density of states at the site of the ESR probe and by the dynamical susceptibility of the 5f system. In the case of localized 5f moments, the spin dynamics of the U subsystem is probed via RKKY-type of interactions and is summed over contributions from all neighbouring U sites [13].

The experiments were performed using a standard cw technique with a VARIAN-spectrometer operated at 9.3 GHz and magnetic field sweeps from $0 \leq H \leq 10$ kOe. The modulation frequency was 100 kHz. Figure 5 shows the temperature dependence of the linewidth of the absorption lines ΔH, which in metals can be taken as a measure of $1/T_1$, the spin-lattice relaxation time. Both compounds behave like normal metals for temperatures $T > 70$ K, with a Korringa-like (linear) increase of the relaxation rate of order $\Delta HH/T = 10$ Oe/K with increasing temperatures. But both compounds exhibit an unusual large residual linewidth ΔH_0 (it is determined by an extrapolation of the high-temperature Korringa behavior of ΔH towards $T = 0$). The residual linewidth decreases with increasing Cu concentration x and hence, seems to be determined mainly by internal magnetic fields. The smooth increase of ΔH in $UCu_{4.75}Al_{7.25}$ for $T < 70$ K indicates the onset of spin-fluctuation effects. Finally, at $T = 30$ K, which is close to the magnetic ordering temperature, the absorption line is too broad to be observed, exceeding a width of 10 kG. In this regime, static magnetic order, which is short ranged above and long ranged below T_N, leads to an inhomogeneous broadening of the absorption line. Astonishingly, also the linewidth in $UCu_{5.75}Al_{6.25}$ steadily increases below $T = 60$ K, revealing the importance of spin fluctuations even far below T^*. This observation is rather unusual for heavy-fermion compounds, where one expects a pure Korringa behavior with a significantly enhanced slope for $T < T^*$. This experimentally observed increase of the linewidth towards low temperatures has to be attributed to an inhomogeneous broadening due to frozen spin configurations and could point towards a spin-glass type of behavior. But it may also be attributed to the rather delocalized 5f-electron wave functions and may indicate a characteristic feature of Uranium-based heavy femion systems. To test the possible influence of the Gd substitution, we also have performed magnetic susceptibility measurements on the Gd doped compounds [14]. No significant doping effects were detected for $x = 0.75$. For $x = 1.75$, 2% and 5% Gd doping induced magnetic order at $T = 3.5$ K and 5.5 K, respectively. Hence, we cannot exclude that a spin-glass type of behavior is induced by the ESR probe itself at low temperatures. But we do not believe that the increase of the linewidth below 70 K can be explained by the Gd substitution. We believe that the unusual behavior of $\Delta H(t)$ is due to the more extended character of the 5f electrons and due to the fact that ESR experiments are especially sensitive to intersite fluctuation effects. The broad quasielastic linewidth observed in the neutron scattering experiments also points towards sizable exchange interactions giving rise to dispersion effects.

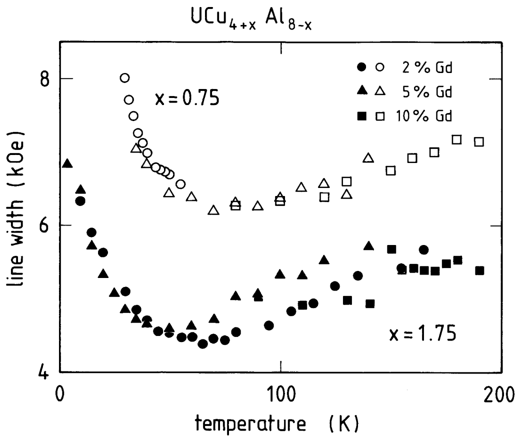

Fig. 5. Temperature dependence of the Gd-ESR linewidth at resonance absorption in $UCu_{4+x}Al_{8-x}$ for $x = 0.75$ and 1.75. The linewidth corresponds to the spin-lattice relaxation rate. At high temperature $\Delta H(T)$ follows a normal metallic Korringa-type of behavior

III. Conclusions

In this paper detailed quasielastic neutron scattering studies on the ternary compounds $UCu_{4+x}Al_{8-x}$ are reported. Mixed crystals with Cu concentrations $4 + x = 4.25$, 4.50, 4.75 and 5.5 were investigated. The quasielastic line can be approximated by a Lorentzian line shape, indicating exponential decays of the spin correlations. Any more detailed analysis (see e.g. Ref. 12) is hampered by the large phonon contributions (Fig. 1). One important result is that the HWHM for $T \to 0$, which in Ce compounds can be taken as a measure of the Kondo-lattice temperature is almost anticorrelated with $T^*(x)$ [3] (see Fig. 2 and Table 1). Furthermore, we observed characteristic anomalies in the Q-dependence of the magnetic intensities which probably indicate magnetic correlations. Finally, we performed Gd-ESR experiments in which we measured the temperature dependence of the linewidth ΔH of the resonance absorption for two samples with concentrations $x = 0.75$ and $x = 1.75$. From these experiments we find a strong increase of the linewidths with decreasing temperatures. For the sample with $x = 0.75$ this increase indicates local magnetic order. For $x = 1.75$ the increase of the linewidth can not be explained by a typical heavy-fermion behavior. It may be due frozen-in magnetic correlations (spin-glass type of behavior) or due to the extended wave functions of the 5f electrons responsible for a itinerant type of magnetism. Furthermore, also the temperature dependences of the width of the quasielastic scattered intensities. e.g., the increase in linewidth with decreasing temperatures that has been detected for the compounds with concentrations $x = 0.25$ and 0.75 and the large residual linewidth characteristic for all compounds investigated, may signal dispersion effects due to magnetic interactions. Dispersion effects could also explain the anomalous concentration dependence of the magnetic relaxation rate Γ. In conclusion, these quasielastic neutron scattering and ESR experiments provide further experimental evidence that on the microscopic level Ce- and U-based HF systems behave rather different, as has been recently pointed out by Steglich et al. [15].

This work has been supported by the BMFT under the contract number 03-LO3 DAR (A5-K02) and by the SFB 252 (Darmstadt/Frankfurt/Mainz/Stuttgart).

References

1. Lander, G.H., Brooks, M.S.S., Johansson, B.: Phys. Rev. B **43**, 13672 (1991)
2. Steglich, F., Ahlheim, U., Schank, C., Geibel, C., Horn, S., Lang, M., Sparn, G., Loidl, A., Krimmel, A.: J. Magn. Magn. Mater. **84**, 271 (1990); Steglich, F., Geibel, C., Horn, S., Ahlheim, U., Lang, M., Sparn, G., Loidl, A., Krimmel, A., Assmus, W.: J. Magn. Magn. Mater. **90&91**, 383 (1990)
3. Geibel, C., Ahlheim, U., Giogi, A.L., Sparn, G., Spille, H., Steglich, F., Suski, W.: Physica B **163**, 194 (1990)
4. Krimmel, A., Loidl, A., Geibel, C., Steglich, F., McIntyre, G.J.: J. Magn. Magn. Mater. **103**, 73 (1992)
5. Doniach, S.: Physica B **91**, 231 (1997)
6. Murani, A.P.: Phys. Rev. B **28**, 2308 (1983); Murani, A.P.: J. Phys. C **33**, 6359 (1983)
7. Broholm, C., Kjems, J.K., Aeppli, G., Fisk, Z., Smith, J.L., Shapiro, S.M., Shirane, G., Ott, H.R.: Phys. Rev. Lett. **58**, 917 (1987)
8. Severing, A., Holland-Moritz, E., Frick, B.: Phys. Rev. B **39**, 2557 (1989) Severing, A., Holland-Moritz, E., Rainford, B., Culverhouse, S., Frick, B.: Phys. Rev. B **39**, 4164 (1989); Loidl, A., Knorr, K., Knopp, G., Krimmel, A., Caspary, R., . Böhm, A., Sparn, G., Geibel, C., Steglich, F.: Phys. Rev. B **46**, 9341 (1992)
9. Wulff, M., Lander, G.H., Lebech, B., Delapalme. A.: Phys. Rev. B **39**, 4719, (1989)
10. Fourier, et al.: Less. Comm. Met. **121**, 249 (1986)
11. Brooks, M.S.S., Kelly, P.J.: Phys. Rev. Lett. **51**, 1708 (1983); Brooks, M.S.S., Eriksson, O., Johansson, B., Franse, J.J.M., Frings, P.H.: J. Phys. F. **18**, L33 (1988)
12. For a detailed discussion see e.g.: Holland-Moritz, E., Lander, G.H.: in Handbook on the Physics and Chemistry of Rare Earths, Vol. 19 Gschneider, K., Lander, G.H. (eds), Amsterdam: North Holland 1994
13. Coldea, M., Schaeffer, H., Weissenberger, V., Elschner, B.: Z. Phys. **B68**, 427 (1986)
14. Buschinger, B.: Diplomarbeit, TH Darmstadt 1994
15. Steglich, F., Geibel, C., Modler, R., Lang, M., Hellmann, P., Gegenwart, P.: J. Low Temp. Phys. **99**, 267 (1995)