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ALLOYING-INDUCED TRANSITION FROM LOCAL-MOMENT TO ITINERANT HEAVY FERMION MAGNETISM IN $Ce(Cu_{1-x}Ni_x)_2Ge_2$

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A monotonous increase of the Kondo temperature in $Ce(Cu_{1-x}Ni_x)_2Ge_2$ from 7 ($x = 0$) to 30 K ($x = 1$) is accompanied by drastic changes of ground state properties: for $x \leqslant 0.2$, a modulated magnetic structure ($\boldsymbol{q}_{01} = (0.28, 0.28, 0.54)$) involving Kondo-reduced local Ce moments ($\mu_s = 0.74\mu_B$/Ce for $x = 0$) forms below $T_{N1}(x)$. $T_{N1} = 4.1$ K for $CeCu_2Ge_2$ is strongly depressed upon increasing x. At $x \geqslant 0.2$, a different modulation develops below $T_{N2}(x)$ which becomes maximum ($\simeq 4$ K) for $x = 0.5$. Since this is characterized by a very small value of $\boldsymbol{q}_{02}$ ($=(0, 0, 0.13)$ at $x = 0.5$) and a gradually decreasing ordered moment (reaching $\mu_s \leqslant 0.2\mu_B$/Ce for $x \geqslant 0.65$), we ascribe it to "heavy fermion band magnetism". For $0.02 \leqslant x \leqslant 0.3$, the two modulations seem to be superposed at sufficiently low temperatures. A non-magnetic heavy fermion ground state exists for $x > 0.75$.

1. Introduction

The formation of itinerant electronic quasiparticles with very large effective mass well below a characteristic temperature T^* in certain 4f- and 5f-compounds is usually ascribed to a mechanism related to the Kondo effect [1]. According to Doniach [2], the ground state of such a compound is determined by the relative strengths of the single-site Kondo interaction, which tends to demagnetize the f ions, and the interionic magnetic RKKY interaction by which the local moments become restored. Both interactions are determined by the coupling constant $g = N_F J$. N_F is the conduction-band density of states at the Fermi energy E_F, while $J < 0$ is the f electron–conduction electron exchange constant. If $T_{RKKY} \sim g^2$ exceeds $T^* \sim \exp(1/g)$, magnetic ordering between local moments develops at low temperatures while the local moments become quenched if T^* is sufficiently larger than T_{RKKY} [2]. The first category mainly covers Ce compounds with T^* of the order of several K, e.g. the antiferromagnets $CeAl_2$ and CeB_6 with Néel temperatures $T_N = 3.9$ and 2.3 K, respectively. They are characterized by (Kondo-) reduced ordered moments and enhanced electronic specific heats γT ($\gamma > 100$ mJ/K^{2}mol Ce) in the magnetically ordered state [3]. In the second category one finds "heavy Fermi liquids" like $CeAl_3$ and $CeCu_6$ and "heavy fermion superconductors" like $CeCu_2Si_2$ and UBe_{13} [3]. However, it has recently become evident [3] that such Fermi liquids can also show a cooperative antiferromagnetic state [3]. Exemplary systems are UPt_3 ($T_N \simeq 5$ K) and URu_2Si_2 ($T_N = 17$ K), for which antiferromagnetism and superconductivity coexist below $T_c \simeq 0.5$ and 1.5 K, respectively. Since the ordered moments μ_s can be very small ($\lesssim 10^{-2}\mu_B$/U-ion), these systems are considered as "heavy fermion band magnets" which are to be distinguished conceptually [4] from the local-moment antiferromagnets ($\mu_s \simeq$ several $10^{-1}\mu_B$/f-ion) like $CeAl_2$.

In this paper we report an investigation of the quasibinary system $Ce(Cu_{1-x}Ni_x)_2Ge_2$ which was initiated to induce a transition from local-moment ordering to heavy fermion band magnetism. Such an alloy system is well suited for this purpose since changes in the physical properties can be achieved without disturbing the lattice of Ce ions.

2. $CeCu_2Ge_2$ and $CeNi_2Ge_2$

The compound $CeCu_2Ge_2$, which crystallizes in the tetragonal $ThCr_2Si_2$ structure (with lattice parameters $a = 4.17$ Å and $c = 10.20$ Å), appeared as an ideal system to start with: the Kondo-binding energy $k_B T^*$($T^* \simeq 6$–8 K [5]) is of the same magnitude as the magnetic interaction energy, since short-range ordering was inferred to set in at $T_{RKKY} \simeq 7$ K [5]. Long-range antiferromagnetic order has been discovered by several techniques [6, 5] below $T_N = 4.1$ K. The magnetic structure of $CeCu_2Ge_2$ is incommensurate with the chemical cell (see below). The ordered moment μ_s at $T = 1.5$ K amounts to $0.74\mu_B$/Ce. This is smaller by a factor of two compared to μ_s as calculated within the crystal-field (CF) ground state doublet. The latter has been determined by inelastic neutron scattering experiments [5]. Because $T^* \simeq T_{RKKY}$, the reduction of the Ce moment is ascribed to the Kondo effect. It is related to the observation of quasi-elastic magnetic neutron scattering intensity which occurs in the antiferromagnetic state, in addition to inelastic spin-wave derived scattering intensity [5]. Moreover, we find it intriguing that these phenomena are accompanied by a Fermi-liquid behavior in the low-T specific heat [6]: a strongly enhanced electronic specific heat $C_e(T) = \gamma(T) \cdot T$ was discovered well below T_N, i.e., in the presence of magnon-derived and nuclear contributions. The temperature dependence of $\gamma(T)$ exhibits a maximum at 0.45 K and, thus, strongly resembles $\gamma(T)$ established for prototypical heavy fermion compounds like $CeAl_3$ and normal-state $CeCu_2Si_2$ [7].

$CeNi_2Ge_2$ is isostructural to $CeCu_2Ge_2$ with somewhat reduced lattice parameters ($a = 4.15$ Å, $c = 9.84$ Å). No magnetism could be detected for this material, which rather exhibits the signatures of a Kondo lattice, such as a maximum in the Sommerfeld coefficient $\gamma(T)$ at 0.3 K. Both $\gamma_{max} \simeq 0.4$ J/K^2 mol and $T^* \simeq 30$ K characterize $CeNi_2Ge_2$ as a heavy fermion compound [8]. No indications of CF excitations were found for this system [8].

3. $Ce(Cu_{1-x}Ni_x)_2Ge_2$ alloys

$Ce(Cu_{1-x}Ni_x)_2Ge_2$ alloys have been investigated utilizing thermal expansion, $\alpha(T)$, specific heat, $C(T)$, and electrical resistivity, $\rho(T)$, experiments. These data supplement preliminary results which have been reported earlier [9].

Figure 1(a) shows the concentration dependence of the characteristic temperature T^*, as determined by the residual value of the quasi-elastic neutron line width (HWHM) $\Gamma(T)$, linearly extrapolated from $T > 50$ K to $T = 0$. $T^*(x)$ is tracked by the positions of broad $\alpha(T)$ maxima (fig. 2) and by low-T $\rho(T)$ peaks, which in accord with theoretical expectations [10] occur at somewhat lower temperatures. T^* increases steadily as a function of Ni concentration so that finally, the binding energy for the Kondo-singlet state exceeds the gain in energy due to the formation of magnetic order. Interestingly enough, cooperative magnetism disappears near $x = 0.75$, where $T^*(x)$ shows a distinct increase in slope. Further unique observations for the composition range $x = 0.65$–0.75 are a disappearance of CF-splitting derived anomalies and the formation of a minimum near $T = T^*$ in $\Gamma(T)$. A forthcoming paper [11] will emphasize especially the observed anomalies in the neutron-scattering spectra.

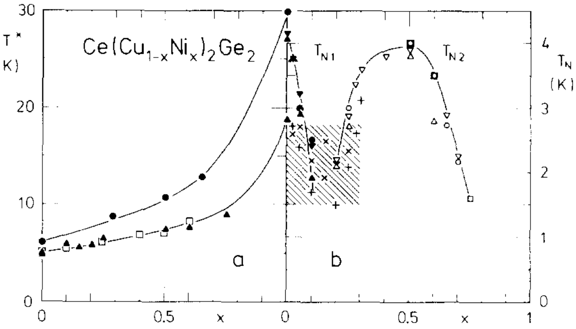

Fig. 1. (a) Characteristic temperature T^* read off positions of broad thermal-expansion, $\alpha(T)$, peaks (□, see fig. 2), resistivity, $\rho(T)$, peaks (▲) as well as residual quasi-elastic line widths (HWHM), $\Gamma(0)$, extrapolated from $T > 50$ K to $T = 0$ K (●). In order to match $\alpha(T)$ and $\rho(T)$ results, $\rho(T)$ peak positions are scaled by factor 1.25. (b) Positions of extrema, indicating antiferromagnetic phase transitions, in $\alpha(T)$ (▲, △, ×), specific heat, $C(T)$ (▼, ▽, +), $\rho(T)$ (□) and dc-susceptibility (●, ○). Closed symbols refer to onset of "local-moment ordering" below $T_{N1}(x)$, open symbols indicate formation of "itinerant magnetism" below $T_{N2}(x)$, crosses are ascribed to superposition of two modulated structures at intermediate composition (hatched), see text.

Figure 1(b) shows the concentration dependence of the Néel temperature, $T_N(x)$, as determined from $\alpha(T)$ (fig. 2), $C(T)$ (fig. 3) and $\chi(T)$ measurements: small substitution of Ni for Cu in $CeCu_2Ge_2$ causes a rapid drop of the Néel temperature $T_{N1}(x)$, which extrapolates to zero near 20 at% Ni. However, a second branch, $T_{N2}(x)$, develops for $x \geqslant 0.2$. It assumes a maximum of $\simeq 4$ K near $x = 0.5$ and can be monitored up to $x = 0.75$. Different kinds of magnetic ordering below T_{N1} and T_{N2} have already been inferred in ref. [9] from the different signs in the jump-like $\alpha(T)$ anomalies associated with these phase transitions, cf. fig. 2.

In addition to our preliminary results [9], we have observed double-peak structures in $\alpha(T)$ and $C(T)$ for concentrations $0.02 \leqslant x \leqslant 0.3$. Already 2 at% Ni substitution results in pronounced anomalies below the Néel temperature $T_{N1} \simeq 3.8$ K, i.e., a sharp peak in $C(T)$ (fig. 3) and a large negative jump in $\alpha(T)$ which

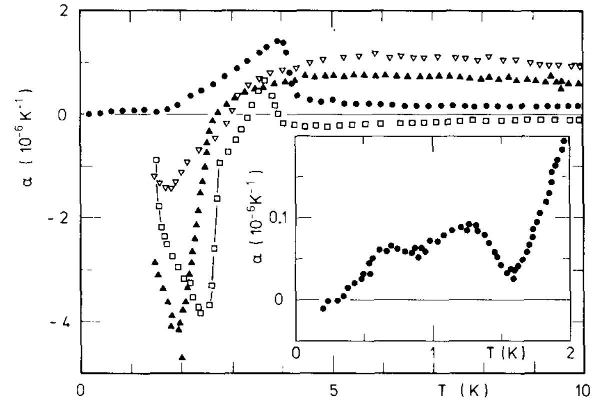

Fig. 2. α vs. T for $Ce(Cu_{1-x}Ni_x)_2Ge_2$ with $x = 0$(●), 0.02(□), 0.1(▲) and 0.25(▽). Solid lines are guides to the eye. Inset shows low-T data for $x = 0$.

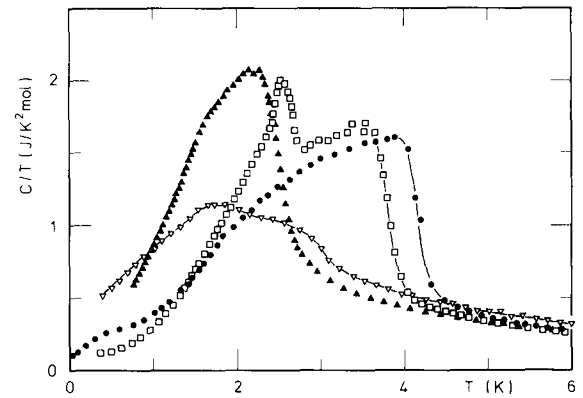

Fig. 3. C/T vs. T for same $Ce(Cu_{1-x}Ni_x)_2Ge_2$ alloys (indicated by same symbols) as in fig. 2. Solid lines are guides to the eye.

contrasts to the positive one at T_{N1} (fig. 2). Whereas the two anomalies nearly merge and can therefore not easily be separated in the intermediate concentration range $0.1 \leq x \leq 0.2$, the data points for the 25 at% Ni system again reveal two distinguishable maxima which, for $\alpha(T)$, both appear to be of negative sign (fig. 2). The additional low-T anomalies seem to track the concentration dependencies of the respective $T_{N1}(x)$ and $T_{N2}(x)$ values. An exception is found for the pure $CeCu_2Ge_2$ compound where additional structure occurs in $\alpha(T)$ below 1.6 K (inset of fig. 2).

In order to determine the magnetic structures and the size of the ordered moments in these materials, neutron powder-diffraction experiments have been performed, utilizing the multidetector diffractometer D1b located on a thermal neutron guide at the HFR of the ILL, Grenoble. The wavelength of the incident neutrons was 2.55 Å. The powder diffraction spectra previously obtained for $CeCu_2Ge_2$ [5] are reproduced in fig. 4(a) and compared with the corresponding spectra for $Ce(Cu_{1-x}Ni_x)_2Ge_2$ alloys with $x = 0.1$, 0.28 and 0.5 (figs. 4b–d). In all cases, the intensities as measured in the paramagnetic phase (at $T = 6$ K) were subtracted from the spectra as measured in the magnetically ordered phase at 1.5 K. All the systems studied exhibit a magnetic structure incommensurate with the chemical lattice. The positions of the magnetic reflections can be indexed in terms of $\boldsymbol{Q} = \boldsymbol{\tau}_{hkl} \pm \boldsymbol{q}_0$, where $\boldsymbol{\tau}_{hkl}$ is a vector of the nuclear reciprocal lattice and $\boldsymbol{q}_0$ is the propagation vector of a modulated spin arrangement. In $CeCu_2Ge_2$ the best fits to the observed magnetic intensities were obtained by choosing a single-plane spiral, with the plane of rotation perpendicular to the propagation vector (whose components are given in units of $2\pi/a$, $2\pi/a$ and $2\pi/c$), $\boldsymbol{q}_0 = (0.28, 0.28, 0.54)$. The results for the 10 at% Ni sample shown in fig. 4b look very similar, although the modulation vector is slightly changed to $\boldsymbol{q}_0 = (0.28, 0.28, 0.41)$. Dramatic changes of the diffraction patterns occur, however, for $x = 0.28$ (fig. 4(c)) and $x = 0.5$ (fig. 4(d)). The Bragg angles of the magnetic reflections for $x = 0.5$ can be indexed assuming that the two dominating lines are satellites of the nuclear (0 0 2) reflection. This yields a propagation vector $\boldsymbol{q}_0 = (0, 0, 0.13)$. Future work on single crystals will be necessary to check this assignment. Such experiments are also required to reveal the x depen-

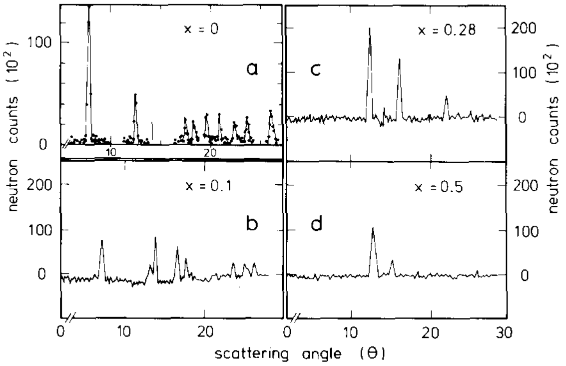

Fig. 4. Neutron powder-diffraction patterns, scattering intensity vs. scattering angle, for $CeCu_2Ge_2$ (a) and $Ce(Cu_{1-x}Ni_x)_2Ge_2$ with different x (b–d). Difference spectra ($I(1.5\,K)-I(6\,K)$) are shown to display magnetic satellites to nuclear Bragg reflexes only. For indexing of statellites in (a), cf. [5], and in (b–d), cf. [11].

dence of the ordered moment μ_s. The present powder-diffraction data suggest a gradual decrease of $\mu_s(x)$, reaching a value of the order of $\simeq 0.5\mu_B$/Ce for $x = 0.5$. For $x = 0.65$, no long-range magnetic order can be resolved by neutron diffraction, in contrast to the $\alpha(T)$ and $C(T)$ measurements which reveal clear-cut phase transition anomalies (fig. 1(b)). Therefore, μ_s is estimated to be smaller than $0.2\mu_B$/Ce for $x \geqslant 0.65$.

Our neutron-diffraction results support the conclusion derived from bulk measurements that two different kinds of antiferromagnetic order exist below $T_{N1}(x)$ and $T_{N2}(x)$. Since both magnetic structures are incommensurate with the lattice, with modulation vectors $\boldsymbol{q}_{01}$ and $\boldsymbol{q}_{02}$, a superposition of them may cause a further increase of the magnetic condensation energy. Taking into account the existence of double-phase transitions in the concentration range $0.02 \leqslant x \leqslant 0.3$, we propose as a working hypothesis for future studies: (1) the upper of these two transitions indicates the formation of a modulated magnetic structure characterized either by $\boldsymbol{q}_{01}$ if $x < 0.15$, or by $\boldsymbol{q}_{02}$ for $x > 0.15$ (cf. fig. 1b), and (2) at the lower transition, this structure becomes superposed by that one with the alternate $\boldsymbol{q}_0$ vector, so that actually a state characterized by $\boldsymbol{q}_{01} \pm \boldsymbol{q}_{02}$ is formed at sufficiently low T. In fact, superposition of the $\boldsymbol{q}_0$ vectors determined in the limiting cases $x = 0$ and $x = 0.5$ explains $\boldsymbol{q}_0 = (0.28, 0.28, 0.41)$ as measured for the system with intermediate concentration, $x = 0.1$.

The occurrence of extremely short propagation vectors which characterize a modulated spin arrangement extending over almost ten lattice constants appears very puzzling at first glance. However, in a perturbational approach to the Anderson lattice using an idealized hybridized band structure, Grewe and Welslau [4] predicted that "band magnetism", developing out of the heavy Fermi-liquid phase of a Kondo-lattice system, should involve $\boldsymbol{q}_0$ vectors as short as the one derived from our powder spectra.

4. Summary and outlook

A combination of bulk thermodynamic, magnetic [9], transport [9] and neutron-diffraction measurements on $CeCu_2Ge_2$ and its Ni-based quasibinary alloys strongly suggests that increasing N_F and $|J|$ values lead to a considerable rise of the characteristic temperature T^*. Since $T^* \simeq 6$–8 K is almost coinciding with $T_{RKKY} > T_{N1} = 4.1$ K, the ordered moment of the modulated magnetic structure with large $\boldsymbol{q}_0$ in $CeCu_2Ge_2$ is reduced by a factor of two. Further rise in T^* leads to a rapid depression of $T_{N1}(x)$ since, in the spirit of Doniach's [2] phase diagram, the critical coupling constant g_{cr} is reached at which a Kondo-singlet (heavy Fermi-liquid) ground state develops. Rather than being non-magnetic, however, the systems with moderate Ni concentration also show a modulated spin structure, i.e., with a very small $\boldsymbol{q}_0$ value. We hope to prove convincingly via subsequent experiments on high-quality single crystals that this short-$\boldsymbol{q}_0$ phase is an itinerant type of heavy-fermion magnetism as predicted by Grewe and Welslau [4].

The alloy system $Ce(Cu_{1-x}Ni_x)_2Ge_2$ is the first heavy fermion system for which a transition from local-moment to band magnetism has been observed so far. Based on the available data we preliminarily suggest the following two-band picture: in the $CeCu_2Ge_2$ compound (as well as in the CeM_2Ge_2, M = Ag, Au homologs [12]) coherent Fermi-liquid effects in the specific heat as well as quasi-elastic neutron-scattering intensity coexist with local-moment ordering including inelastic spin-wave excitations, presumably on different parts of the Fermi surface. Already a small Ni substitution (2 at%) leads to a disappearance of the "coherence peak" in $\gamma(T)$ and to the development of the small-$\boldsymbol{q}_0$ ordering, which seems to be superposed with the large-$\boldsymbol{q}_0$ modulation forming below $T_{N1} = 3.8$ K (fig. 3). The strong "initial" increase in $T_{N2}(x)$, when x is increased from 0.2 to 0.5, may reflect the increasing portion of the Fermi surface involved in the itinerant magnetic phase. Finally, for $x > x_m = 0.75$ no magnetic order can exist owing to the Kondo interaction, now dominating over any kind of magnetic interactions. So far, thorough measurements of the lattice parameters through $x = x_m$ do not support any essential role played by charge ("valence") fluctuations in this demagnetization.

Acknowledgements

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References

[1] See, e.g., P. Fulde, J. Keller and G. Zwicknagl, Solid State Phys. 41 (1988) 1.

[2] S. Doniach, Physica B 91 (1977) 231.

[3] For more details, see:
G.R. Stewart, Rev. Mod. Phys. 56 (1984) 755.
F. Steglich, Springer-Series in Solid-State Sciences 62 (1985) 23.
H.R. Ott, Progr. Low Temp. Phys. XI (1987) 217.
N. Grewe and F. Steglich, in: Handbook on the Physics and Chemistry of Rare Earths, Vol. 14, K.A. Gschneidner, Jr. and L. Eyring eds. (North-Holland, Amsterdam, 1990) forthcoming.

[4] N. Grewe and B. Welslau, Solid State Commun. 65 (1988) 437.

[5] G. Knopp, A. Loidl, K. Knorr, L. Pawlak, M. Duczmal, R. Caspary, U. Gottwick, H. Spille, F. Steglich and A.P. Murani, Z. Phys. B 77 (1989) 95.

[6] F.R. de Boer, J.C.P. Klaasse, P.A. Veenhuizen, A. Böhm, C.D. Bredl, U. Gottwick, H.M. Mayer, L. Pawlak, U. Rauchschwalbe, H. Spille and F. Steglich, J. Magn. Magn. Mat. 63 & 64 (1987) 91.

[7] C.D. Bredl, S. Horn, F. Steglich, B. Lüthi and R.M. Martin, Phys. Rev. Lett. 52 (1984) 1982.

[8] G. Knopp, A. Loidl, R. Caspary, U. Gottwick, C.D. Bredl, H. Spille, F. Steglich and A.P. Murani, J. Magn. Magn. Mat. 74 (1988) 341.

[9] G. Sparn, R. Caspary, U. Gottwick, A. Grauel, U. Habel, M. Lang, M. Nowak, R. Schefzyk, W. Schiebeling, H. Spille, M. Winkelmann, A. Zuber, F. Steglich and A. Loidl, J. Magn. Magn. Mat. 76 & 77 (1988) 153.

[10] D.L. Cox and N. Grewe, Z. Phys. B 71 (1988) 321.

[11] A. Loidl, A. Krimmel, K. Knorr, G. Sparn, M. Lang, S. Horn, F. Steglich and A.P. Murani, to be published.

[12] A. Böhm, R. Caspary, U. Habel, L. Pawlak, A. Zuber, F. Steglich and A. Loidl, J. Magn. Magn. Mat. 76 & 77 (1988) 150.