SPECIFIC HEAT, RESISTIVITY AND NEUTRON SCATTERING STUDIES IN THE KONDO LATTICE $CeNi_2Ge_2$

G. KNOPP, A. LOIDL

Institut für Physik, Universität Mainz, D-6500 Mainz, Fed. Rep. Germany

R. CASPARY, U. GOTTWICK, C.D. BREDL, H. SPILLE, F. STEGLICH

Institut für Festkörperphysik, T.H. Darmstadt, D-6100 Darmstadt, Fed. Rep. Germany

and

A.P. MURANI

Institut Laue Langevin, F-38042 Grenoble, France

Specific heat, resistivity and inelastic neutron scattering experiments are reported, which demonstrate that $CeNi_2Ge_2$ exhibits a heavy-fermion groundstate which is neither magnetic nor superconducting. The specific heat coefficient $\gamma(T)$ reaches 350 mJ/K^2mol and exhibits a peak at 0.4 K showing that coherence effects become important at low temperatures. The magnetic relaxation rates as measured via the line width in inelastic neutron scattering experiments are strongly enhanced and deviate from a Korringa law behaviour. The Kondo temperature $T_K \approx 30$ K was determined from the magnetic relaxation rates and from the specific heat data.

1. Introduction

Heavy-fermion systems are metallic systems characterized by unusual low temperature properties [1]: strongly enhanced values of the linear term of the specific heat and of the temperature independent Pauli spin susceptibility correspond to high effective masses of the conduction electrons. Ce-based ternary compounds with the $ThCr_2Si_2$ structure include heavy-fermion systems with very different ground states: $CeCu_2Si_2$ was the first compound reported [2] to exhibit heavy-fermion superconductivity. $CeCu_2Ge_2$ was classified as a heavy-fermion system with a magnetic ground state [3,4]. Finally, $CeRu_2Si_2$ is a system characterized by high effective electron masses and undergoing neither a magnetic nor a superconducting phase transition [5]. However, highly anisotropic short range magnetic correlations have been reported in this compound [6].

The high effective masses of the systems under consideration result from the hybridization of the Ce 4f-electron with the conduction electrons. In calorimetric experiments this many-body effect becomes apparent through a large metallic linear term in the specific heat. In addition, several of these materials exhibit a peak in the specific heat coefficient $\gamma(T) = C(T)/T$ below 1 K which has been ascribed to the opening of a pseudogap in the electronic density of states at the Fermi level [7]. This fine structure at the Fermi level is a characterisic feature of a Kondo lattice where coherence effects between the single ion Kondo sites become important [8].

For the Kondo lattice, the temperature dependence of the resistivity shows an unusual behaviour as compared to a normal metallic behaviour. A broad peak in $\rho(T)$ near the Kondo temperature is followed by a strong decrease of the resistivity for further decreasing temperatures.

For $T \ll T_K$ the resistivity follows a T^2 dependence which can be interpreted within a Fermi-liquid theory [9].

Neutrons can interact with the magnetic moment of a rare earth compound via the dipole force. The differential cross section is proportional to the dynamic structure factor which in turn is related to the dynamic susceptibility. For the ground state multiplet of a non-interacting local moment the dynamic structure factor will exhibit a sharp, resolution limited peak at zero energy transfer. Interactions of the 4f-moment with the conduction electrons introduce relaxation effects giving Lorentzian line shapes with an intrinsic width. In rare-earth compounds with a stable 4f-configuration one expects a Korringa type of behaviour for the quasielastic line width, namely $\Gamma = \alpha k_B T$ where α is typically 10^{-3} [10]. Due to the strong coupling between conduction electrons and the 4f-electrons heavy fermion compounds behave completely differently: Usually they are characterized by a finite line width for $T \to 0$ and deviate significantly from a linear T-dependence [11,12]. A finite value of the quasielastic line width was first predicted by Götze and Schlottman [13] for a Kondo impurity system. During the last few years a number of theoretical models have been developed which predict the temperature dependence of the quasielastic linewidth as observed in inelastic neutron scattering experiments in Ce compounds with a non-stable 4f-configuration [14–18]. The main results, depending on the model used and depending on the strength of the 4f-conduction electron hybridization, were: an enhancement and non-linear behaviour of $\Gamma(T)$; a minimum in the temperature dependence near the Kondo temperature; a finite line width for $T \to 0$ K and deviations from a simple Lorentzian line shape at low temperatures ($T \ll T_K$).

2. Experimental results and discussion

2.1. Sample preparation and characterization

Polycrystalline sample of $CeNi_2Ge_2$ were melted from stoichiometric amounts of high purity elements in an argon arc furnace. The X-ray powder diffraction analysis at room temperature showed that the samples were of single phase ($ThCr_2Si_2$ structure). The lattice parameters were found to be $a = 4.150$ Å and $c = 9.854$ Å. Ac susceptibility measurements (117 Hz) performed at earth magnetic fields plus an ac-amplitude of 5 μT do not show any indication of either a magnetic or a superconducting phase transition down to 30 mK.

2.2. Calorimetric investigations

Standard calorimetric techniques were applied to measure the specific heat in a temperature range 70 mK < T < 5 K and external fields up to 4 T. The results are shown in Fig. 1. Here we plotted the temperature dependence of the coefficient of the linear term $\gamma(T) = C(T)/T$ versus temperature for different magnetic fields. To begin the discussion with the zero-field results, we find a continuous decrease of $\Gamma(T)$ with increasing temperatures for $T \geq 0.3$ K. This decrease is very smooth and changes from 350 mJ/K^2 mol at 0.3 K to 250 mJ/K^2mol at 5 K. At $T = 0.3$ K $\gamma(T)$ exhibits a maximum and decreases on further cooling. This decrease is attributed to the onset of lattice coherence effects where a fine structure develops in the electron density of states near the Fermi level: within this picture the opening of a pseudogap reduces the density of states at the Fermi energy [8].

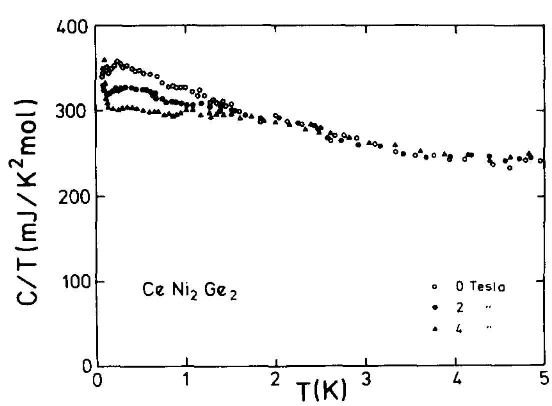

Fig. 1. Temperature dependence of the linear term $\gamma(T) = C(T)/T$ of the specific heat in $CeNi_2Ge_2$ for magnetic fields up to 4 T.

The results of $\gamma(T)$ as a function of magnetic field show that an external field gives rise to a moderate suppression of the peak maximum and a slight shift to higher temperatures, thus indicating that a magnetic field smears out the fine structure in the electron density of states [7,8]. The upturn of $C(T)/T$ for $T \leq 0.07$ K is due to a nuclear Zeeman splitting.

Only in an external field of $B = 4$ T $C(T)$ can quantitatively be explained with a spin-1/2 impurity Kondo model as derived by Desgranges and Schotte [19]. A Kondo temperature of 29 K yields a good description of the results of fig. 1. With this formalism the Kondo temperature is related to γ $(T = 0)$ via $T_K = \pi R/3\gamma$ $(T = 0)$. Of course, the coherence effects in zero field cannot be fitted within this single-ion model.

2.3. Electrical resistivity

Resistivity measurements utilizing a standard four-lead technique on rectangular shaped pellets were performed for temperatures 4.2 K $\leq T \leq$ 300 K. In fig. 2 we show the absolute resistivity $\rho(T)$ for $CeNi_2Ge_2$ and for the isostructural La-reference compound $LaNi_2Ge_2$. The resistivity of $CeNi_2Ge_2$ as measured does not exhibit the typical non-monotonic behaviour of some heavy-fermion compounds like $CeCu_2Si_2$ [20], with a low temperature peak near the Kondo temperature. However, if one subtracts $\rho(R)$ of the non-magnetic reference compound to get rid of the phonon contribution, a broad peak in the Ce-increment $\rho_l(T)$ near 100 K remains. This behaviour is found in intermediate valence systems [21], but also closely resembles the temperature dependence of $\rho(T)$ of the heavy-fermion compounds $CeRu_2Si_2$ [5] and UPt_3 [22].

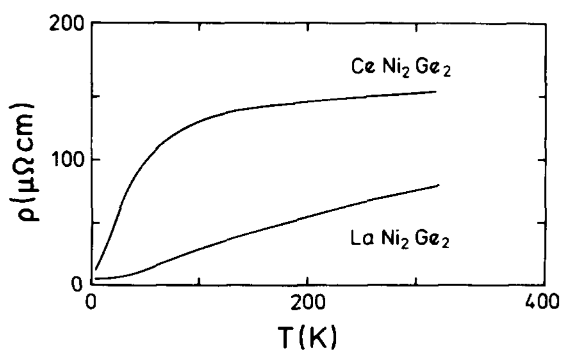

Fig. 2. Temperature dependence of the resistivity in $CeNi_2Ge_2$ and $LaNi_2Ge_2$.

2.4. Inelastic neutron scattering

The measurements of the quasielastic line width in $CeNi_2Ge_2$ have been performed on the time-of-flight spectrometers IN4 (located on a thermal neutron source) and IN6 (located on a cold source) at the high flux reactor at the Institut Laue-Langevin in Grenoble. Incoming neutron energies from 12.5 meV (IN4) and 3.15 meV (IN6) have been chosen. To correct the spectra for contributions due to pure phonon scattering, $LaNi_2Ge_2$ was used as a reference sample. The scattered intensities in both samples were scaled to a phonon peak at high temperatures and then subtracted. For a further check to distinguish between nuclear and magnetic contributions the spectra in $CeNi_2Ge_2$ were measured at different scattering angles. In fig. 3 we show the results of a weighted difference between the spectra of the La- and the Ce-com-

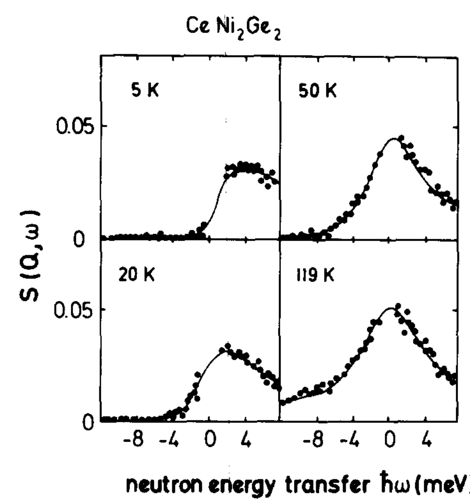

Fig. 3. Scattering law $S(Q, \omega)$ versus neutron energy transfer for an average scattering angle of $\Theta = 12°$ as obtained for $CeNi_2Ge_2$ at different temperatures (the scattering angle corresponds to a momentum transfer $Q = 0.48$ Å^{-1}). These spectra were measured at IN4 with an incident neutron energy of 12.5 meV.

pounds as measured at the TOF-spectrometer IN4 at different temperatures. Hence fig. 3 shows the magnetic contributions to the quasielastic scattered neutron intensities only (the intensities in the region of purely elastic scattering, which is determined by the width of the experimental energy resolution, are omitted; here the counting statistics are low due to the fact that the intensities of the elastic incoherent scattering are larger by a factor 10^4 than the quasielastic scattered magnetic intensities). Already from a first inspection it is clear that the magnetic relaxation rate as defined by the half width at half maximum (HWHM) of the quasielastic lines, is strongly enhanced when compared to rare earth systems with a stable moment, but that the temperature dependence is rather weak pointing towards a large residual line width at $T = 0$ K. All the spectra were analysed by fitting the experimental results with a Lorentzian lineshape weighted with a temperature factor. For the temperatures investigated (4 K $\leq T \leq$ 300 K) the quasielastic lines are well described by a Lorentzian lineshape including a detailed balance factor (solid lines in fig. 3). The temperature dependence of Γ as determined by these fits is shown in fig. 4. The results from the measurements at both spectrometers, IN4 and IN6 respectively, are included. For $T \geq 40$ K the magnetic relaxation rate increases smoothly with increasing temperatures reaching values of 6 meV at 200 K. Approximately at 30 K Γ (T) passes through

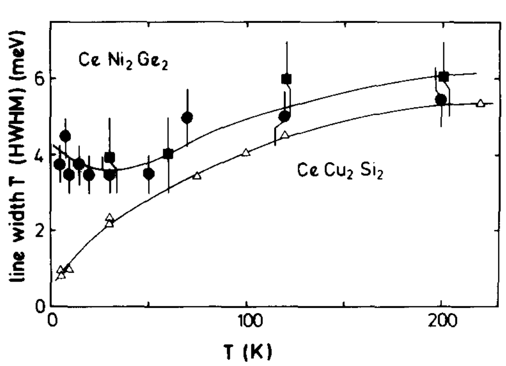

Fig. 4. Temperature dependence of the quasielastic line width Γ (half width at half maximum: HWHM) for $CeNi_2Ge_2$: (■) IN6, (●) IN4. For comparison the relaxation rates as measured in $CeCu_2Si_2$ are included (Horn et al. [12]): (△). The lines are drawn to guide the eye.

minimum and increases again when the temperature is lowered further. For comparison we included the temperature dependence of the line width as observed in the prototype heavy fermion system $CeCu_2Si_2$ [12]. At high temperatures the magnetic relaxation rates of the two isostructural compounds nearly coincide. However, with decreasing temperatures Γ(T) in $CeCu_2Si_2$ decreases continuously down to the lowest temperatures pointing towards a low residual line width which is a characteristic feature of compounds with a low Kondo temperature.

With both incident energies the spectra in $CeNi_2Ge_2$ were measured at different scattering angles. Thereby a range of momentum transfers 0.4 $Å^{-1} \leq Q \leq 3$ $Å^{-1}$ was covered. Within the accuracy of the present experiments no significant Q-dependence of the magnetic relaxation rates could be detected. It is worth noting, that within a Fermi-liquid description of the heavy-fermion state Γ increases linearly with Q. Our data show that Γ is roughly independent of Q over a wide range of momentum transfers and thus the present results in $CeNi_2Ge_2$ are in conflict with a Fermi-liquid model.

For a comparison of the present experimental results with recent theoretical models we outline some of the relevant theoretical predictions:

– Czycholl and Leder [14] calculated the dynamic magnetic susceptibility within an "alloy analog approximation" where the many-particles Hamiltonian is mapped on an effective single-particle model. This model yields a broad quasielastic line corresponding to a high magnetic relaxation rate which is nearly temperature independent. For large hybridization a flat minimum in $\Gamma(T)$ was found. In addition, deviations from a simple Lorentzian line shape are predicted; an inelastic transition becomes apparent due to the fact that the maximum of the 4f-peak near the Fermi level is slightly shifted apart from the Fermi energy.

– Kojima, Kuramoto and Tachiki [15] calculated the dynamic properties of Ce-systems in the intermediate valence and in the nearly integral valence regime (here the latter corresponds to heavy fermion or dense Kondo systems) using a self-consistent perturbation theory. For the nearly integral valence limit the magnetic relaxation rate follows

a linear temperature dependence but is considerably enhanced over the Korringa value; in addition they find a finite value at $T = 0$ K. Deviations from the Lorentzian line shape are insignificant in this regime at all temperatures. For intermediate valence systems the line width increases with decreasing temperatures corresponding to strong deviations from the Lorentzian line shapes.
– Cox, Bickers and Wilkins [16] performed a calculation of the magnetic relaxation rate for systems with non-stable 4f-electron configurations in a wide temperature range ($0.01T_K \leq T \leq 40T_K$). The found that i) Γ is nonmonotonic passing through a minimum near the Kondo temperature T_K with $\Gamma(T_K) = 0.75T_K$ and reaching a limiting low temperature value of $1.35T_K$; ii) the magnetic relaxation rate shows a non-linear high temperature behaviour which is well fitted by a square-root law and iii) significant deviations from a Lorentzian line shape appear for $T \ll T_K$.

These models neglect effects due the crystal electric field [15] or are restricted to ionic ground states with a degeneracy $N_f \geq 4$ [16]. Recently the magnetic relaxation rates in Kondo systems have been calculated taking crystal field effects into account [17,18].

The present neutron scattering results as presented in fig. 4 can directly be compared with the results derived by Cox et al. [16]. We find a square root dependence of the relaxation rate at high temperatures, a minimum at the Kondo temperature with $\Gamma(T_K) \approx 40$ K and a residual line width $\Gamma(T = 0\ \mathrm{K}) \approx 45$ K; the Kondo temperature as defined by the minimum of $\Gamma(T)$ roughly gives $T_K \approx 30$ K. The minimum observed experimentally is much flatter than theoretically predicted, and its value does not obey the scaling relation $\Gamma(T_K) = 0.75T_K$. This might be due to the fact that the calculations are correct for systems with a ground state degeneracy $N_f \geq 4$ only. In the tetragonal compound under investigation the crystal electric field splits the $J = 5/2$ multiplet of the Ce-ion into three dubletts yielding a ground state degeneracy of 2. This might also explain the absence of deviations from the Lorentzian line shape: as mentioned above all the quasielastic neutron scattering intensities could be reasonably well described using a single Lorentzian line shape. The inelastic hump in the differential neutron cross section as theoretically predicted results from the off-fermion level position of the Kondo resonance for systems with $N_f \geq 4$ and vanishes for a lower ground state degeneracy [16].

3. Conclusions

The main experimental results can be summarized as follows:
– A maximum in $\gamma(T) = C(T)/T$ demonstrates that coherence effects become important at temperatures $T \leq 0.3$ K. An external magnetic field yields a slight suppression of this peak corresponding to a smearing out of the fine structure in the electronic density of states near the Fermi level. The specific heat can be described by a spin-1/2 Kondo model with a Kondo temperature $T_K = 29$ K.
– The temperature dependence of the magnetic relaxation rate as measured via inelastic neutron scattering strongly deviates from a Korringa type of behaviour and exhibits a flat minimum at $T \approx 30$ K defining the Kondo temperature in good agreement with the results as obtained from the calorimetric experiments. In a wide temperature range ($4\ \mathrm{K} \leq T \leq 300$ K) the quasielastic neutron profiles can be properly described by assuming a single Lorentzian line shape.

Utilizing susceptibility, specific heat, resistivity and inelastic neutron scattering techniques, we have characterized $CeNi_2Ge_2$ as a new heavy-fermion compound exhibiting neither a magnetic nor a superconducting phase transition. The size of the coefficient of the linear term in the specific heat at low temperatures, which reaches 350 $\mathrm{mJ/K^2 mol}$ makes $CeNi_2Ge_2$ comparable to the isostructural compound $CeRu_2Si_2$ [5]. It is interesting to note, that both systems have a very similar unit cell volume: 169.7 Å^3 ($CeNi_2Ge_2$) and 172.4 Å^3 ($CeRu_2Si_2$) [23]. Compounds with $ThCr_2Si_2$ structure and smaller volumes are characterized by unstable 4f electron configurations: For example $CeNi_2Si_2$ ($V = 155.6$ Å^3) is an intermediate valence system [24]. Compounds with larger volumes exhibit stable 4f-electrons and undergo magnetic phase transitions: $CeRu_2Ge_2$ ($V = 182.9$ Å^3) exhibits a ferromagnetic groundstate [24]. In all of these compounds the separation of the Ce-ions is far beyond Hill's limit and the relevant empirical parameter seems to be the rare earth–transition metal distance [24].

Acknowledgements

We thank P. van Aken for performing the measurements of the ac susceptibility as well as U. Rauchschwalbe, N. Grewe and D.L. Cox for stimulating discussions.

This work was supported by the Bundesministerium für Forschung und Technologie under the contract number 03-LO1MAI-0 (C4-57) and by the Sonderforschungsbereich 252, Darmstadt/Frankfurt/Mainz/Stuttgart.

References

[1] P. Fulde, J. Keller and G. Zwicknagl, Solid State Phys. to be published.
[2] For a review see: F. Steglich, in: Theory of Heavy Fermion Systems and Valence Fluctuations, eds. T. Kasuya and T. Saso, Springer Series in Solid-State Sciences 62 (1985) 23.
[3] F.R. de Boer, J.C.P. Klaasse, P.A. Veenhuizen, A. Böhm, C.D. Bredl, U. Gottwick, H.M. Mayer, U. Rauchschwalbe, H. Spille and F. Steglich, J. Magn. Magn. Mat. 63 & 64 (1987) 91.
[4] G. Knopp, H. Spille, A. Loidl, K. Knorr, U. Rauchschwalbe, R. Felten, G. Weber, F. Steglich and A.P. Murani, J. Magn. Magn. Mat. 63 & 64 (1987) 88.
[5] L.C. Gupta, D.E. MacLaughlin, Cheng Tien, C. Godart, M.A. Edwards and R.D. Parks, Phys. Rev. B28 (1983) 3673.
M.J. Besnus, J.P. Kappler, P. Lehmann and A. Meyer, Solid State Commun. 55 (1985) 779.
[6] See, e.g. P. Haen, J. Flouquet, F. Lapierre, P. Lejay, J.-M. Mignot, A. Pouchet and J. Voiron, J. Magn. Magn. Mat. 63 & 64 (1987) 320.
[7] R.M. Martin, Phys. Rev. Lett. 48 (1982) 362.
C.D. Bredl, S. Horn, F. Steglich, B. Lüthi and R.M. Martin, Phys. Rev. Lett. 52 (1984) 1982.
[8] C. Lacroix, J. Magn. Magn. Mat. 60 (1986) 145.
[9] A.J. Mills and P.A. Lee, Phys. Rev. B35 (1987) 3394.
P. Coleman, Phys. Rev. Lett. 59 (1987) 240.
[10] P. Fulde and M. Loewenhaupt, Advan. Phys. 34 (1987) 589.
[11] A.P. Murani, K. Knorr, K.H.J. Buschow, A. Benoit and J. Flouquet, Solid State Commun. 36 (1980) 523.
[12] S. Horn, F. Steglich, M. Loewenhaupt and E. Holland-Moritz, Physica B 107 (1981) 103.
[13] W. Götze and P. Schlottmann, J. Low Temp. Phys. 16 (1974) 87.
[14] G. Czycholl and H.J. Leder, Z. Physik B 48 (1982) 67.
[15] H. Kojima, Y. Kuramoto and M. Tachiki, Z. Physik B54 (1984) 293.
[16] D.L. Cox, N.E. Bickers and J.W. Wilkins, J. Appl. Phys. 57 (1985) 3166; J. Magn. Magn. Mat. 54–57 (1986) 333.
N.E. Bickers, D.L. Cox and J.W. Wilkins, Phys. Rev. Lett. 54 (1985) 230; Phys. Rev. B 36 (1987) 2036.
[17] S. Maekawa, S. Kashiba. S. Takahashi and M. Tachiki, J. Magn. Magn. Mat. 52 (1985) 149.
[18] T. Höhn and J. Keller, J. Magn. Magn. Mat. 63 & 64 (1987) 219.
[19] H.-U. Desgranges and K.D. Schotte, Phys. Lett. A 91 (1982) 240.
[20] W. Franz, A. Griessel, F. Steglich and W. Wohlleben, Z. Physik 31 (1978) 7.
[21] E.g. P. Scoboria, J.E. Crow and T. Mihalisin, J. Appl. Phys. 50 (1979) 1895.
[22] G.R. Stewart, Z. Fisk, J.O. Willis and J.L. Smith, Phys. Rev. Lett. 52 (1984) 679.
[23] G. Knopp, A. Loidl, R. Caspary, U. Gottwich, F. Steglich and A.P. Murani, to be published.
[24] E.V. Sampathkumaran and R. Vijayaraghavan, Phys. Rev. Lett. 56 (1986) 2851.