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Alexander Krimmel, Manfred Reehuis, Alois Loidl

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CF effects and disorder versus Kondo lattice behavior in $CeTSi_3$ (T = Rh, Ir)

A. Krimmel*, M. Reehuis, A. Loidl

Experimentalphysik V, Elektronische Korrelationen und Magnetismus, Institut für Physik, Universität Augsburg, Universitätsstr. 1, 86159 Augsburg, Germany

Abstract. On the basis of specific heat, magnetic susceptibility and electrical resistivity measurements, $CeTSi_3$ (T = Rh, Ir) have recently been characterized as magnetically ordered Kondo lattice compounds. However, no magnetic Bragg peaks could be observed by powder neutron diffraction, resulting in an upper limit of the ordered magnetic moment of $0.25\,\mu_B$. An additional quasi-elastic neutron scattering study on $CeRhSi_3$ did not reveal any appreciable magnetic signal at low temperatures ($T \leq 40$ K) and only very weak scattering contributions at elevated temperatures ($80\,\text{K} \leq T \leq 300\,\text{K}$). For a proper characterization of $CeMSi_3$ (M = Rh, Ir), we propose the inclusion of crystal-field (CF) effects and nonmagnetic atomic disorder. This may also hold true for other compounds of the $CeTX_3$ (T = transition metal, X = Si, Ge) intermetallics showing similar magnetic behavior.

Heavy fermion compounds have been in the focus of scientific research as an outstanding example of strongly correlated electron systems (for a review see, for example, [1]). One intensively studied class of heavy fermion systems are the CeT_2X_2 (T = transition metal, X = Ge, Si) intermetallics (for a review see, for example, [2]). Much less work has been devoted to the closely related class of $CeTX_3$ compounds. Many of the $CeTX_3$ compounds crystallize in the $BaNiSn_3$ structure characterized by space group $I4mm$, in which Ba, Ni and one Sn ion occupy the Wyckoff position $2a$ and a second, inequivalent Sn ion is found at the $4b$ position [3]. Several $CeTSi_3$ compounds have been investigated recently [4–8], and they revealed interesting magnetic properties with a stable trivalent Ce valence, except for T = Co, Ru and Os [4]. $CeFeGe_3$ seems to possess a stable valency in spite of its high Kondo temperature of more than 100 K [8]. A similar behavior has recently been found for T = Rh, Ir [9]. $CeRhSi_3$ and $CeIrSi_3$ (as well as their Ge homologue compounds) have been investigated by means of specific heat, magnetic susceptibility and resistivity measurements [9]. Antiferromagnetic order is found below $T_N = 1.8$ K (T = Rh) and $T_N = 5.0$ K (T = Ir). Both compounds show a significantly enhanced Sommerfeld coefficient of about $120\,\text{mJ/mol K}^2$, indicating an enhanced density of states at the Fermi level. The magnetic entropy at the phase transition amounts to only a small fraction of $R \ln 2$, thus pointing towards strong Kondo compensation effects [9]. Very high negative values of the Weiss temperature (-128 K for $CeRhSi_3$ and -142 K for $CeIrSi_3$, respectively) are often found in intermediate valence compounds. A pronounced maximum of the resistivity has also been interpreted in terms of a Kondo temperature of the order of 100 K. On the other hand, the perfectly obeyed Curie–Weiss behaviour above 150 K indicates a stable trivalent valence state despite the high Kondo temperature [9], similar to what has been observed in $CeFeGe_3$ [8]. In order to obtain greater insight into this contrasting magnetic behaviour, we performed neutron scattering experiments on $CeTSi_3$ (T = Rh, Ir).

1 Experimental details and results

Polycrystalline samples of $CeTSi_3$ (T = Rh, Ir) were synthesized by argon arc melting of commercially available high purity elements. The samples were subsequently tempered at 1200 K for 2 weeks and characterized by X-ray (Cu-$K_{\alpha 1}$ radiation) powder diffraction at room temperature. All diffraction data were analyzed by the standard Rietveld method [10] employing the FULLPROF program [11]. Both compounds showed the nominal $BaNiSn_3$ structure. The lattice constants were refined to $a = 4.235(2)$ Å, $c = 9.788(2)$ Å for Rh and $a = 4.247(2)$ Å, $c = 9.701(2)$ Å for Ir, with the corresponding Bragg reliability factors, $R_{\text{Bragg}} = 5.6\%$ (T = Rh) and 8.2% (T = Ir). The lattice constants are in agreement with the values reported in the literature [9]. Whereas the Rh compound was very nearly single phase, significant Bragg reflections of a spurious phase showed up in the diffraction pattern of the Ir compound. A pattern decomposition analysis re-

*Corresponding author. (Fax: +49-821/598-3649,
E-mail: alexander.krimmel@physik.uni-augsburg.de)

vealed $Ce_2Ir_3Si_5$ as being the most probable candidate for the parasitic phase.

Neutron powder diffraction experiments were performed on the diffractometer E6 at HMI, Berlin. An incident neutron wavelength of $\lambda = 2.42$ Å was selected by a pyrolytic graphite monochromator. The diffraction patterns of $CeTSi_3$ (T = Rh, Ir) are shown in Fig. 1. The crystallographic $BaNiSn_3$ structure could be confirmed. When subtracting the intensities at high temperatures within the paramagnetic regime from the low-temperature intensities within the magnetically ordered state, the nuclear scattering contributions vanish leaving intensities of magnetic origin only. As evident from Fig. 1, for both compounds, no magnetic Bragg peaks could be observed, resulting in an upper limit of the ordered magnetic moment of $\mu_{\rm ord} \leq 0.25\,\mu_{\rm B}$.

A fundamental property of any magnetic system is the dynamical susceptibility, $\chi''(Q, \omega, T)$, which can be measured via the dynamic structure factor, $S(Q, \omega, T)$, in inelastic neutron scattering experiments. We therefore performed additional quasi-elastic neutron scattering experiments for the single-phase compound $CeRhSi_3$. The experiments were performed on the time-of-flight spectrometer IN6 at the Institut Laue Langevin (ILL), Grenoble. An incident neutron energy of 3.1 meV was used. Measurements were made at $T = 1.8$, 4, 8, 15, 25, 40, 80 and 150 K. Additionally, a vanadium plate and an empty sample holder were measured to account for detector efficiency and background signal, respectively. The raw data were corrected in a standard way, employing routines of the ILL. Due to the extremely weak (in fact, even vanishing) intensities, all detectors in the range of $10.33° \leq 2\Theta \leq 52.69°$ have been summed up. The corrected average spectra are shown in Fig. 2. Only the elastic line could be fitted by a delta peak, convoluted with the instrumental resolution. Note that the resolution function displays small tails up to approximately ±0.5 meV energy transfer (see Fig. 2). The entire intensity scale of Fig. 2 corresponds to only 0.1% of the peak intensity of the elastic line. At low temperatures, no appreciable quasi-elastic intensity could be detected. At $T = 80$ K a rather broad (width of about 3 meV) and very weak quasi-elastic signal starts to develop and increases in intensity upon heating to $T = 150$ K (see Fig. 2).

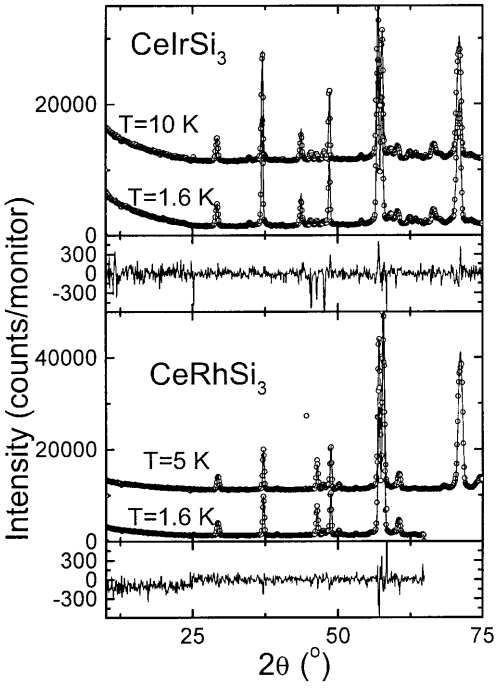

Fig. 1. Neutron powder diffraction patterns of $CeTSi_3$ (T = Ir, Rh) for different temperatures. *Open circles* and *full lines* correspond to observed and calculated intensities, respectively. At the bottom of each panel, the difference between low-temperature and high-temperature diffraction patterns (corresponding to magnetic intensities) is shown on an expanded scale

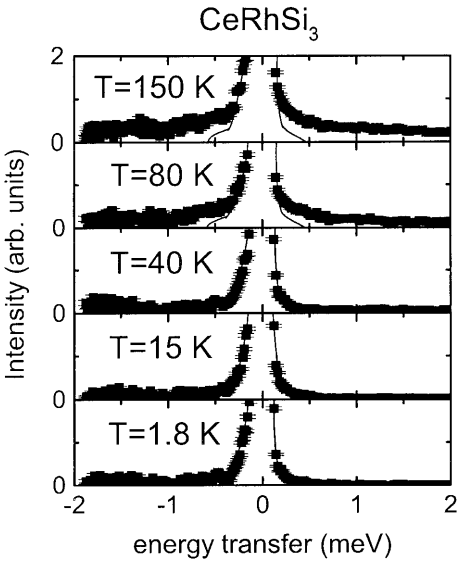

Fig. 2. Quasi-elastic neutron scattering spectra of $CeRhSi_3$ for different temperatures, $1.8\,{\rm K} \leq T \leq 150\,{\rm K}$, corrected for background and detector efficiency

2 Discussion and conclusion

A possible Kondo lattice behavior of $CeRhSi_3$ was observed using specific heat, magnetic susceptibility and electrical resistivity measurements [9]. However, a large decrease in the inverse susceptibility, related to a similar variation of the resistivity, may, at least to a major part, be accounted for by crystal-field (CF) effects. In this case only the low-temperature part of the susceptibility would be significant, displaying a paramagnetic Weiss constant of a few Kelvin, in agreement with the low ordering temperatures. The strongest experimental evidence for Kondo lattice behaviour of $CeTSi_3$ (T = Rh, Ir) is based on a strongly reduced magnetic entropy at the magnetic phase transition, reaching only 12% of $R \ln 2$, together with an enhanced electronic contribution of the specific heat at low temperatures [9]. The low value of the magnetic entropy is consistent with the fact that no magnetic Bragg peaks could be observed in our neutron powder diffraction experiments, corresponding to very small ordered magnetic moments. On the other hand, an enhanced Sommerfeld coefficient of $120\,{\rm mJ/mol\,K^2}$ would correspond to a Kondo temperature of the order of 100 K. This should lead to a significant magnetic response in the quasi-elastic neutron scattering spectra. On the basis of well-established magnetic-relaxation-rate studies of other heavy fermion systems (in particular, the CeT_2X_2 compounds), quasi-elastic scattering signals of magnetic origin are expected with about two orders

of magnitude stronger intensities. The present neutron scattering experiments therefore reveal that the static (ordered magnetic moment) part as well as the low-energy dynamic (quasielastic) part of the susceptibility represents only a minor contribution. Consequently, the high-energy ($\hbar\omega \geq 5$ meV) spectral response will play a crucial role in the magnetic properties of $CeTSi_3$ (T = Rh, Ir), corresponding to a dominant influence of CF effects, as already indicated by the temperature dependence of the susceptibility and resistivity.

Already some years ago, Gschneidner et al. [12] suggested the possible appearance of non-magnetic disorder spin glasses in Ce and U compounds. He argued that structural disorder around the f atoms causes a distribution of RKKY interactions, yielding a frustrated ground state due to random bonds. Concomitantly, strong spin fluctuations arising from the frustration and CF effects are responsible for the high values of the linear term of the specific heat and therefore are often falsely interpreted as heavy fermion compounds [12]. The effect of disorder and frustration on the physical behavior of traditional f-electron heavy fermion compounds has been discussed by Mydosh [13]. Recently, it has been found that nonmagnetic atomic disorder and magnetic frustration lead to a heavy fermion spin glass in URh_2Ge_2 [13, 14]. The disorder has been explained as an amalgamation of the two crystallographic structures possible for 1:2:2 compounds [14]. Another, similar example of a fully stoichiometric 1:2:2 compound displaying spin glass behavior is $PrAu_2Si_2$ [15]. It is interesting to note that also in $PrAu_2Si_2$ an enhanced value of the Sommerfeld coefficient of 120 mJ/mol K^2 is observed [15]. Despite a careful heat treatment it was only possible to synthesize approximately single phase materials of $CeTSi_3$ (T = Rh, Ir), thus pointing to considerable nonmagnetic atomic disorder, which (together with crystal field effects) may lead to an enhanced Sommerfeld coefficient of the specific heat. The low ordering temperatures of $CeTSi_3$ (T = Rh, Ir) reveal a small value of the magnetic exchange constant, J. This indicates that the magnetic exchange is close to a knot of the oscillatory RKKY interaction responsible for the onset of long-range magnetic order in these intermetallic compounds. Therefore the details of the local atomic environment around the Ce ions will considerably influence the magnetic exchange. Disorder can easily suppress magnetic ordering by either shifting J towards 0 or changing its sign, thus leading to random bonds. This will lead to a reduced value of the averaged ordered magnetic moment and a correspondingly reduced value of the magnetic entropy when entering the magnetically ordered state. We conclude that a Kondo lattice behavior of $CeRhSi_3$ may not be necessary to explain the results of the macroscopic measurements but is difficult to reconcile with the present neutron scattering results.

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