MAGNETIC BEHAVIOUR OF Yb_5Si_4 AND Yb_3Si_4*

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Yb_5Si_4 and Yb_3Si_4 are two new compounds with three and two inequivalent lattice sites for Yb ions, respectively. Using susceptibility, heat capacity and ^{170}Yb Mössbauer spectroscopy, we find that only about 1/3rd of Yb ions order magnetically below 1.65 K in Yb_5Si_4, with a substantial saturated moment of 1.9 μ_B/Yb at 80 mK. The remaining Yb ions are paramagnetic down to 80 mK, but with a valency close to 3, presumably due to appreciable hybridisation. In Yb_3Si_4 the hybridisation is stronger and half of Yb ions orders magnetically below 3 K, with a very small saturated moment of just 0.28 μ_B/Yb at 80 mK.

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In a very recent investigation of the phase diagram of the Yb-Si system [1], two new compounds Yb_5Si_4 and Yb_3Si_4 were identified. Both compounds crystallise with orthorhombic unit cells having Sm_5Ge_4-type and Ho_3Si_4-type structure [2], respectively. While three different types of near neighbour environments are present for Yb ions in Yb_5Si_4, there are two different crystallographic sites for Yb ions in Yb_3Si_4. From previous work in

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the literature, it is known that Yb ions at two sites in hexagonal Yb_5Si_3 exist with different hybridization strengths and remain paramagnetic at least down to 0.03 K [3]. It is therefore of interest to probe the magnetic behaviour of Yb ions in other silicides, and the results in Yb_5Si_4 and Yb_3Si_4 are presented here.

The alloys Yb_5Si_4 and Yb_3Si_4 were prepared in closed Ta containers and annealed at 1000 and 950°C for 7 and 14 days, respectively. X-ray diffraction and metallographic examination showed the presence of a few percent of extra phase Yb_5Si_3 in Yb_5Si_4 and YbSi (CrB-type) in Yb_3Si_4. The lattice parameters match well with the values reported in Ref. [1].

Fig. 1 left shows the thermal variation of the inverse susceptibility between 1.7 and 300 K. The field dependence of the magnetization up to 10 T is shown in the inset. The susceptibility shows Curie-Weiss behaviour above 150 K with $\mu_{\rm eff} = 3.63$ and $4.23\,\mu_{\rm B}$/Yb and $\theta_{\rm p} = -49.6$ and -97.8 K in Yb_5Si_4 and Yb_3Si_4, respectively. The effective moment is less than the free ion value of Yb^{3+} ($4.54\,\mu_{\rm B}$) and there is no apparent signature of magnetic ordering in the data down to 1.7 K. The reduced effective moment and large negative $\theta_{\rm p}$ indicate a significant hybridization (which is site dependent, see below) of the Yb $4f$ orbitals with the conduction electron states. The magnetisation at 1.8 K reaches $0.80\,\mu_{\rm B}$/Yb at 10 T in Yb_5Si_4, and shows a clear curvature. In Yb_3Si_4, the magnetisation reaches $0.63\,\mu_{\rm B}$ at 10 T and is almost linear with the field. The heat capacity C of Yb_5Si_4 increases

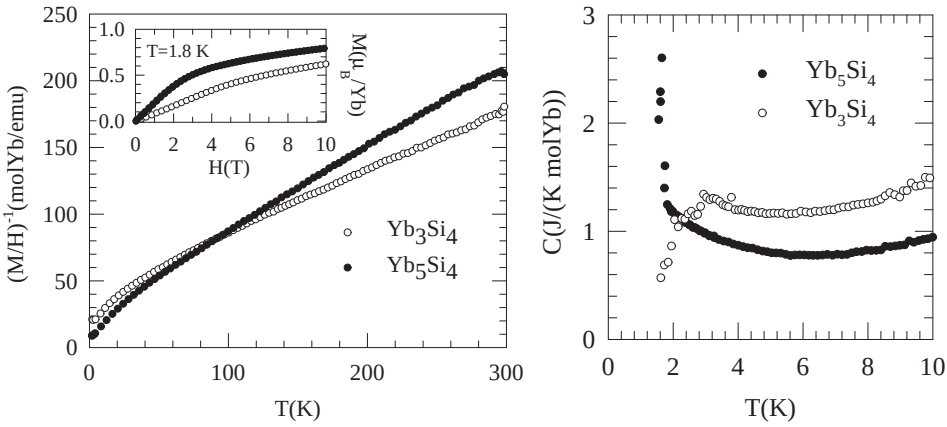

Fig. 1. Left: inverse magnetic susceptibility in Yb_5Si_4 and Yb_3Si_4; inset: magnetisation curves at 1.8 K. Right: Heat capacity in Yb_5Si_4 and Yb_3Si_4.

rapidly below 2.5 K (Fig. 1 right), and shows a well defined peak with $C_{\rm max}$= 3 J/(K molYb) at $T_{\rm N} \simeq 1.65$ K indicative of magnetic ordering. The measurements could not be performed to low enough temperatures below $T_{\rm N}$ so that a reliable value of the entropy change could be derived. On the other

hand the heat capacity data in Yb_3Si_4 show a small peak, with $C_{max} \simeq 1.4\,J/(K\ molYb)$, near 3 K. In case this feature arises from the magnetic ordering of Yb ions, the moments must be appreciably reduced due to hybridization.

The ^{170}Yb Mössbauer spectra between 80 mK and 4.2 K are shown in Fig. 2. In Yb_5Si_4 (Fig. 2 left), the spectrum at 80 mK can be resolved into two components: *(i)* 30-35% of a magnetic hyperfine spectrum with a Yb^{3+} spontaneous moment of 1.9 μ_B which decreases to 1.1 μ_B at 1.5 K, and *(ii)* a quadrupolar non-magnetic spectrum (65-70%) which remains unchanged up to 4.2 K and can correspond to Yb^{2+} or intermediate valent Yb. As a first

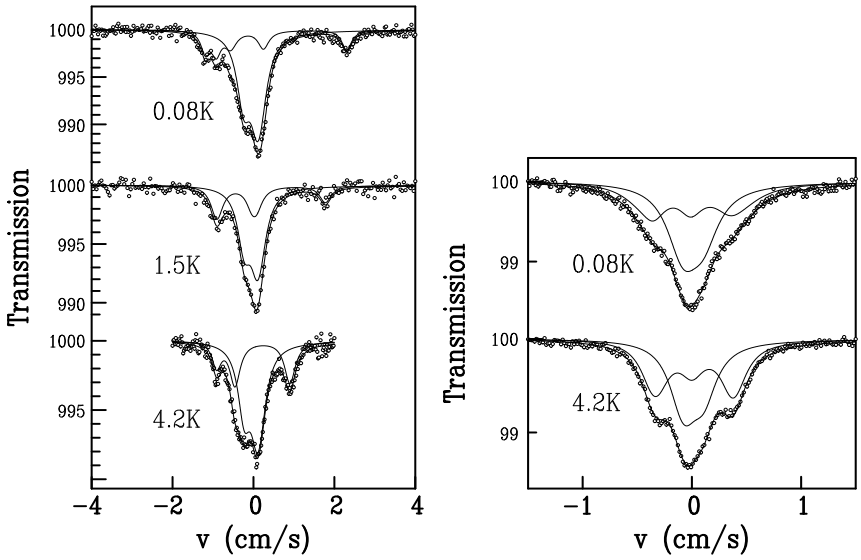

Fig. 2. Left: ^{170}Yb Mössbauer spectra in Yb_5Si_4 at 80 mK, 1.5 and 4.2 K. The subspectrum with the largest splitting corresponds to Yb^{3+} with magnetic ordering. Right: ^{170}Yb Mössbauer spectra in Yb_3Si_4 at 80 mK and 4.2 K. The two subspectra have equal intensities, and that with the largest splitting shows a line-broadening at 80 mK which could indicate magnetic ordering of Yb^{3+} ions.

check for this latter valence state, we performed simulations of the powder magnetisation at 1.8 K, assuming that 1/3 of the Yb ions have a saturated moment of 1.9 μ_B and that 2/3 are non-magnetic. Comparing with the measured magnetisation curve, we find that this latter assumption cannot hold, *i.e.* that all the Yb ions must have a paramagnetic response to the magnetic field. Therefore, our data suggest that, in Yb_5Si_4, 1/3 of the Yb ions are trivalent and undergo magnetic ordering while the remaining 2/3 have a valency close to 3, but experience a strong $4f$-conduction electron hybridisation which hinders magnetic ordering to set in. The assignment

of the Yb^{3+} fraction to a given site in the orthorhombic unit cell is not straightforward, as the ratio 1:2 does not correspond to any combinations of the known multiplicities of the 3 possible sites (1:4 or 2:3). It could happen that the different Yb sites have slightly different Mössbauer f-factors, which could restore the actual ratio of the site populations to a crystallographically correct value (1:4 or 2:3).

In Yb_3Si_4 (Fig. 2 right), the spectra can again be resolved into two components with nearly equal intensity, which are likely to correspond to the two crystal sites. One subspectrum is not resolved and does not seem to change down to 80 mK. The other one shows a split quadrupolar pattern at 4.2 K and undergoes some line broadening at 1.5 K and 80 mK. This latter feature can be attributed to magnetic ordering with very small moments, of about 0.1 μ_B/Yb at 1.5 K and 0.28 μ_B/Yb at 80 mK. Then the small peak at 3 K in the specific heat data would correspond to the magnetic transition. In another Yb silicide, YbSi, where the Yb^{3+} magnetic moment is also much reduced (0.23μ_B/Yb at saturation [4]), the peak of the specific heat at the magnetic transition (T_N =1.6 K) has a small amplitude of 1.8 J/(K molYb) [5].

In conclusion we have shown that the Yb ions at inequivalent lattice sites in Yb_5Si_4 and Yb_3Si_4 show site dependent magnetic behaviour due to varying degree of hybridization. In both compounds, only a fraction of the Yb ions are magnetically ordered (at 1.65 K in Yb_5Si_4 and presumably at 3 K in Yb_3Si_4), while the rest remain paramagnetic down to 80 mK. X-ray absorption experiments at the Yb L_{III} edge are planned in order to determine the Yb valencies in these materials.

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