Physica B 186–188 (1993) 547–549
North-Holland

PHYSICA B

Specific heat of ytterbium monopnictides under magnetic fields

D.X. Li[a], A. Oyamada[a], H. Shida[a], T. Suzuki[a], T. Kasuya[a], A. Dönni[a] and F. Hulliger[b]

[a]*Department of Physics, Faculty of Science, Tohoku University, Sendai, Japan*
[b]*Laboratory for Solid State Physics, ETH Zürich, Switzerland*

The specific heat of the ytterbium monopnictides YbX (X = N, P, As, Sb) measured in magnetic fields up to 10 T shows a different field dependence of the broad peak around 5 K in the four compounds. The zero-field data are analyzed with a new model including both Kondo effect and magnetic excitations.

1. Introduction

With respect to the competition of Kondo hybridization and magnetic interactions the ytterbium monopnictides are of particular interest. Recently, the magnetic ordering of stoichiometric compounds of YbX (X = N, P, As, Sb) was investigated by neutron diffraction experiments. YbN [1] and YbAs [2] exhibit long-range FCC antiferromagnetic type-III ordering below $T_N = 0.79$ K and $T_N = 0.7$ K, respectively. YbP [3] shows long-range FCC antiferromagnetic type-II ordering below $T_N = 0.66$ K and in YbSb [4] no long-range magnetic ordering was found down to 7 mK. Probably due to Kondo hybridization the magnetic saturation moments in YbN, YbP and YbAs are significantly reduced below the value 1.33 μ_B expected from the crystalline-electric field ground-state doublet Γ_6. For all three compounds the specific heat anomaly at the magnetic phase transition [5] contains only about 20% of the entropy $R \ln 2$ expected from the Γ_6 doublet. The total entropy $R \ln 2$ is only released if the temperature is raised to about 20 K [5].

We measured the specific heat of polycrystalline samples YbN and YbSb and single crystals of YbP and YbAs in the temperature range $2\,\mathrm{K} < T < 60\,\mathrm{K}$ under magnetic fields up to 10 T. In the crystals the magnetic field was applied along the [1 0 0] direction. The zero-field data are analyzed with a new model including both Kondo effect and magnetic excitations.

Correspondence to: D.X. Li, Department of Physics, Faculty of Science, Tohoku University, Sendai 980, Japan.

2. Sample preparation

A polycrystalline sample of YbN was prepared by reacting flakes of Yb metal in an open tungsten crucible under a nitrogen pressure of 1000 atm at 1600°C for 3 hours. Single crystals of YbP and YbAs were prepared by the Bridgeman method by synthesizing initial material of the required composition in a closed quartz tube at 800°C (YbP) and 450°C (YbAs) for 4 weeks. Polycrystalline YbSb was synthesized by a prereaction of the constituent elements in an evacuated quartz ampule at 700–770°C below the melting temperature of antimony.

3. Results and discussion

The specific heat measured in magnetic fields up to 10 T is shown in figs. 1–4 for all compounds YbX (X = N, P, As, Sb). At zero field we observe the excess specific heat peak at 3.2 K (YbN), 4.2 K (YbP), 5.7 K (YbAs) and 4.6 K (YbSb). The four samples show a different magnetic field dependence of the specific heat. Applying a magnetic field to YbN and YbAs the peak in the specific heat slightly shifts to higher and to lower temperature, respectively, and both intensities decrease. In YbP and YbSb the peak position remains unchanged and both intensities increase. In YbAs at 10 T a kink appears in the curve which is similar to the zero-field kink observed in YbSb.

The $s = 1/2$ single-impurity Kondo model [7] yields a broad peak in the specific heat at low temperatures

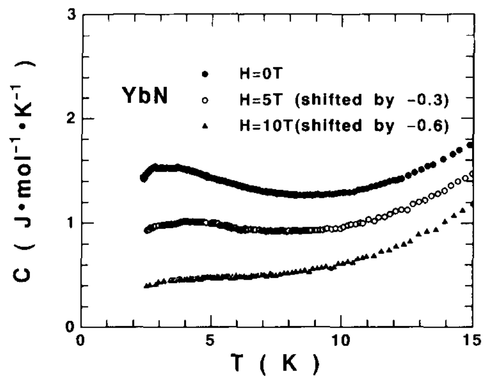

Fig. 1. Specific heat of YbN in magnetic fields of 0, 5 and 10 T.

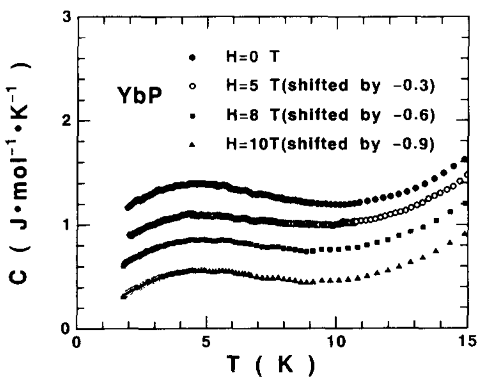

Fig. 2. Specific heat of YbP in magnetic fields of 0, 5, 8 and 10 T.

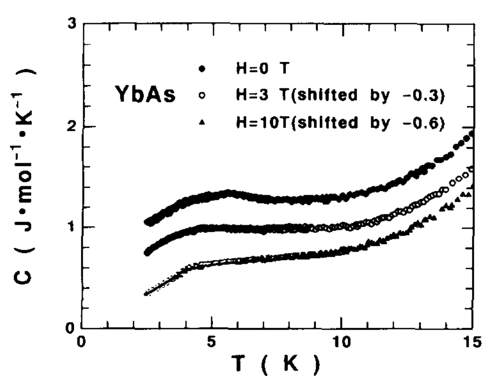

Fig. 3. Specific heat of YbAs in magnetic fields of 0, 3 and 10 T.

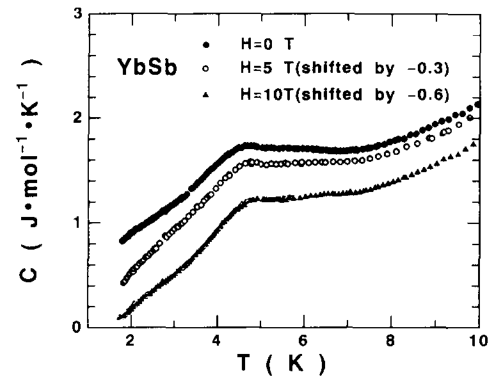

Fig. 4. Specific heat of YbSb in magnetic fields of 0, 5 and 10 T.

as observed in the ytterbium monopnictides. Applying a magnetic field the model predicts a shift of the peak to higher temperature and an increase of the strength of the peak. The observed magnetic field dependence in YbN, YbP, YbAs and YbSb disagree with model predictions.

A bandstructure calculation from Monnier et al. [6] interpreted the specific heat peaks in YbN, YbP and YbAs around 5 K as due to the Kondo effect for the crystalline-electric-field ground-state doublet Γ_6. This model neglects magnetic exchange interactions. However, Mössbauer results [8] indicate that in the ytterbium monopnictides magnetic exchange interactions have a strength of about 10 K stronger than the Néel temperatures below 1 K. Indeed, the observed magnetic field dependence of the specific heat (figs. 1–4) correlates with the difference in magnetic exchange interactions. For YbN and YbAs with the same antiferromagnetic structure [1,2] the magnetic field dependence of the specific heat is similar. In a successful analysis of the observed magnetic field dependence of the specific heat the contributions from magnetic exchange interactions can not be neglected.

For YbX (X = N, P, As) above 20 K where the magnetic entropy of the Γ_6 groundstate is fully released there is large deviation between the observed magnetic part of the zero-field specific heat (obtained by subtracting the data of LuX from YbX) and a Schottky-type specific heat (YbP is shown in fig. 5). We have to exclude YbSb because the data for LuSb are unknown. Where stems this excess entropy above 20 K from? Now we proceed to analyze the zero-field data for YbX (X = N, P, As) with a new simplified model including both Kondo effect and magnetic exchange interactions. We assume the excited CEF states have a rather broad and low state density which cannot be detected by usual neutron scattering experi-

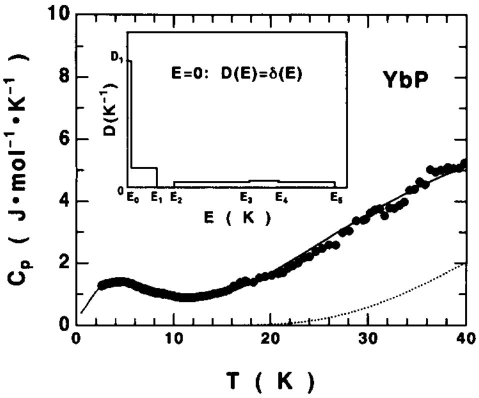

Fig. 5. Temperature dependence of the magnetic part of the specific heat of YbP. Black circle: experimental data; solid line: fit with the model explained in the text; dashed line: Schottky-type specific heat. The insert is the sketch figure of the density of states of the model explained in the text.

ments. In order to see it easily, the sketch figure of the density of states $D(E)$ of the model is shown in the insert in fig. 5. At $E=0$, let $D(E)=\delta(E)$ correspond to the Kondo singlets of the ground state Γ_6 and the range of $E<E_1$ corresponds to magnetic interaction of the ground state doublet Γ_6. The range of $E_3<E<E_4$ corresponds to the Kondo effect of the excited state Γ_8, and the range of $E_2<E<E_3$ and $E_4<E<E_5$ represent magnetic exchange interactions of the excited CEF states Γ_8 and Γ_7 which have not yet been observed by neutron scattering experiment. We fix the position $(E_4+E_3)/2$ at the experimentally observed $\Gamma_6 \rightarrow \Gamma_8$ splitting and the width of $E_4-E_3=60$ K obtained by neutron scattering experiment. The areas for $E<E_1$ and $E_3<E<E_4$ are both normalized to 1. The total area of the extended tails $E_2<E<E_3$ and $E_4<E<E_5$ is fixed to 5. The independent fitting parameters left are D_1, E_0, E_1, E_2 and E_5. The resulting specific heat is given by

$$C_P=\beta^2\left[Z\frac{\mathrm{d}^2Z}{\mathrm{d}T^2}-\left(\frac{\mathrm{d}Z}{\mathrm{d}T}\right)^2\right]/Z^2 \qquad (1)$$

with $\beta=1/T$ and with the partition function $Z(\beta)=\int_0^\infty \mathrm{e}^{-\beta E}D(E)\,\mathrm{d}E$. The best fitting parameters for YbX (X = N, P, As) are listed in table 1. Figure 5 shows the fitted curve for YbP.

Table 1
'Best fit' values for the specific heat model parameters of YbN, YbP and YbAs.

	YbN	YbP	YbAs
D_1 [K^{-1}]	1.0	1.2	1.3
E_0 [K]	0.25	0.25	0.25
E_1 [K]	12	15	18
E_2 [K]	30	70	80
E_3 [K]	350	190	170
E_4 [K]	410	250	230
E_5 [K]	410	330	380

The obtained parameters D_1 and E_1 increase from YbN to YbP and to YbAs giving rise to a reasonable decrease of the Kondo temperature T_K when going from YbN to YbAs. The Kondo effects come from the ground states Γ_6 mainly, and the excited states Γ_8 have only a little contribution. In addition, the 'best fit' values for the specific heat model parameters of YbX show that the densities of the excited CEF states have longer and flatter tails. These include not only the spin-flip transition which is sensitive to neutron scattering, but also non-spin-flip transition due to magnetic correlation or the Kondo effect.

References

[1] A. Dönni, P. Fischer, A. Furrer, W. Bacsa and P. Wachter, Z. Phys. B 80 (1990) 269.
[2] A. Dönni, P. Fischer, A. Furrer and F. Hulliger, Solid State Commun. 71 (1989) 365.
[3] L. Keller, P. Fischer, A. Furrer, A. Dönni, D.X. Li and T. Suzuki, Physica B 186–188 (1993) 553.
[4] A. Dönni, A. Furrer, P. Fischer, F. Hulliger, P. Wachter and H.R. Ott, J. Magn. Magn. Mater. 90&91 (1990) 143.
[5] H.R. Ott, H. Rudigier and F. Hulliger, Solid State Commun. 55 (1985) 113.
[6] R. Monnier and L. Degiorgi, Phys. Rev. B 41 (1990) 573.
[7] V.T. Rajan, J.H. Löwenstein and N. Andrei, Phys. Rev. Lett. 49 (1982) 491.
[8] P. Bonville, J.A. Hodges, F. Hulliger, P. Imbert, G. Jéhanno, J.B. Marimom da Cunha and H.R. Ott, J. Magn. Magn. Mater. 76&77 (1988) 473.