High pressure transport and micro-calorimetry studies on quantum phase transitions in Yb heavy fermion systems.

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Abstract. We present ac microcalorimetry and resistivity measurements under high pressure on new very pure single crystals of YbCu$_2$Si$_2$ having residual resistivity ratios of up to 130 and residual resistivities of less than 1 µΩcm. The onset of magnetic order at high pressure has been detected by ac micro-calorimetry in a diamond anvil cell, and the phase diagram has been established showing magnetic order appearing at 7.6 GPa and 0.95K, and suggesting a possible quantum critical point at a pressure of about 6.5 GPa. The resistivity has been measured under pressure in hydrostatic conditions, but no sign of superconductivity is found close to the expected critical pressure down to T=0.05 K. We discuss these results in comparison with results on cerium based heavy fermion systems.

1. Introduction

Recent studies on several cerium based systems have shown that when pressure is used to approach a magnetic Quantum Critical Point (QCP), that is a region of the phase diagram where a phase transition to a magnetically ordered state occurs at zero temperature, several novel phenomena are found, including deviations from Fermi liquid theory in the electronic terms of resistivity and specific heat, and most spectacularly, unconventional superconductivity. In heavy fermion compounds, the large renormalisation to lower values of the relevant energy scales make these systems ideally suited for the use of high pressure as an external parameter to tune their microscopic interactions and in many cerium based systems, pressures of a few GPa are sufficient to attain the QCP[1]. Today considerable attention has turned to ytterbium systems. In a simple picture Yb is often considered to be the “hole” equivalent of cerium. Pressure tends to drive Yb from its nonmagnetic Yb$^{2+}$ (4f$^{14}$) state to a magnetic Yb$^{3+}$ (4f$^{13}$) state, so in paramagnetic Yb systems, a transition towards magnetic order is expected to occur under pressure. However there are to date far fewer studies on Yb based compounds, and the picture is much more clear than for the cerium systems. From a practical point of view, aspects in working on the Yb based heavy fermion systems include in general the necessity of reaching higher pressures (often closer to 10 GPa) and the difficulty of obtaining single crystals with low residual resistivities. Understanding the differences between the QCPs of the two families is an important step, with an essential question: why has no superconductivity been found so far in the Yb systems? Several phenomena can play a role in preventing the occurrence of superconductivity. First, as the expected superconducting state is of an unconventional nature, any impurities will have a strong pair-breaking effect so very pure samples are necessary. Furthermore, the present models of spin fluctuation mediated superconductivity at a QCP rely on the existence of a 2$^{nd}$ order phase transition to magnetic order[2]. One of the clearest examples of pressure induced magnetic order in an Yb system is YbCu$_2$Si$_2$[3, 4], however in the previous studies where the phase diagram was established by resistivity or Mössbauer spectroscopy measurements, the conclusion was that the transition was probably of 1$^{st}$
order. We present here a new generation of experiments on high quality single crystals of the compound YbCu$_2$Si$_2$, with very low residual resistivities. We show that the diamond anvil cell ac-calorimetry technique provides quantitative information on the phase diagram of long range magnetic order, and qualitative information on the divergence of the specific heat near the critical point in YbCu$_2$Si$_2$. We also show a new development of the standard Bridgman high pressure technique to use a liquid medium, and its application to the study of and YbCu$_2$Si$_2$.

2. Experiment

For this study a new batch of Single crystals of YbCu$_2$Si$_2$ have been grown by an indium flux method. MgO crucibles were used in favor of their higher chemical stability. Following a dissolution period of four hours at 1200°C, a slow cooling (150°/h) was performed down to 850°C where the ampoule was spun. Crystals were then annealed in a vacuum, wrapped in a tantalum foil at 850°C for 15 days. The crystals were characterised by x-ray diffraction, resistivity and specific heat measurements. The main test of the crystal quality was the residual resistivity ratio (RRR) taken between 300K and 2K. Quite a large dispersion of RRR values was found among crystals of the same batch, however we found that it was possible to select crystals having an RRR as high as 130, corresponding to a residual resistivity of less than 1 µΩcm. For the high pressure micro-calorimetry measurements a Au/AuFe thermocouple was spot welded onto the sample and the sample was pressurized in a Diamond Anvil Cell (DAC) using argon as a pressure transmitting medium. The thermocouple measures the temperature oscillations of the sample induced by an alternating optical power source (laser or laser diode) transmitted to the sample via an optical fibre$^5$. The resistivity was also measured in the DAC by bonding four 10µm leads onto the sample. In both cases the cell was measured either in a standard ⁴He cryostat (T>1.5K) with the possibility of in-situ modulation of the pressure$^6$, or in a ³He cryostat (T>0.5K). In the latter case the pressure was changed at room temperature, but measured in situ at low temperature. The resistivity was also measured in the newly developed modified Bridgman cell$^7$ with Fluorinert as pressure transmitting medium. In this cell two nylon rings are inserted inside the usual pyrophyllite gasket in order to load the cell with liquid (fluorinert) and thus allowing measurement in hydrostatic conditions on relatively large samples (1mm). In this case the cell was also measured in a 3He/4He dilution refrigerator down to 50mK.

3. Results and discussion

In figure 1 we show the results of the microcalorimetry measurement. This technique does not give a quantitative measurement of the specific heat, so the curves have been normalized to the value of C/T at high temperature (7K) of the P=0 measurement. Under pressure, C/T increases at low temperature, becoming quite divergent with a sharp anomaly which is taken to be the antiferromagnetic ordering temperature, T$_N$. Using the in-situ pressure modulation facility this anomaly was detected down to the lowest attainable temperature, 1.5K, for a pressure of about 8.5 GPa. In order to follow the transition at lower temperatures a few fixed pressure points were measured in a ³He cryostat (see 7.6 GPa curve in the figure). The phase diagram obtained from all these points corresponding to 2 samples is shown in figure 2 in comparison with the previous resistivity measurement$^3$. The high pressure data are in quite good agreement. However the previous resistivity measurement could detect no sign of a transition below about 8.5GPa, where the ordering temperature was found to be about 1.3K, hence the near vertical dashed line on the phase diagram, and the original conclusion that the transition was 1$^{st}$ order. In contrast in the specific heat curves we have found a clear transition at 7.6 GPa, with T$_N$ = 0.95K. So far we cannot claim to prove that a second order QCP exists, but the results are compatible with a dependence of T$_N$ as (p-$p_c$)$^{2/3}$ expected for a 3D antiferromagnetic system$^{8}$ which would give a critical pressure of about 6.5 GPa, much lower than previously expected. At least we show that the magnetic transition can occur at temperatures below 1K, so quantum effects should start to be predominant. The absence of points at lower temperatures and pressures may be due to the experimental difficulties in measuring the ac calorimetry at very low temperatures. Further studies are
planned to search for the magnetic transition in this area. In figure 3 we show the resistivity under pressure on 2 samples, sample 1 was measured in the DAC (argon) and sample 2 in the modified Bridgman cell (fluorinert). The RRR of sample 2 was slightly less than sample 1, however even at the highest pressure the residual resistivity was less than 1 $\mu\Omega$cm. sample 2 was measured at 7.0 GPa, i.e. close to the expected critical pressure, down to $T=50$ mK, however no sign of superconductivity was seen. At very low temperature a dependence of the form $\rho=\rho_0+AT^2$ is found and the coefficient $A$ is found to increase with pressure by about 2 orders of magnitude from $0.04 \mu\Omega$cm/$T^2$ at $P=0$ to 3.5 $\mu\Omega$cm/$T^2$ at 7 GPa in agreement with the previous study $^{[3]}$. The divergence of $A$, and the increase of $C/T$ on approaching a QCP are qualitatively expected from spin fluctuation models. A fuller discussion of the effect of pressure on the temperature dependence of the resistivity, and a comparison with the specific heat data will be published elsewhere $^{[11]}$. These results show that 2 of the possible obstacles to spin fluctuation mediated superconductivity in YbCu$_2$Si$_2$ seem not to apply : the new single crystals we have prepared have residual resistivities of less than 1 $\mu\Omega$cm even at the critical pressure, comparable to that of the cerium based systems where superconductivity is found, and the magnetic transition is found to still occur at temperatures below 1K. The fact that still no superconductivity is found suggests that other reasons must be sought, which may well be found in the intrinsic differences between the behaviour of cerium and ytterbium at the QCP. Indeed the simple presentation of Yb as the “hole” analogue of cerium is certainly an oversimplification. In cerium systems the valence is actually quite stable, close to 3+, and the transition between paramagnetic and magnetic states occurs mainly via the Doniach model of competition between RKKY and Kondo interactions, whereas Yb is often in an intermediate valent state, and quite large changes of the valence are expected with pressure. Probably in this case when the valence of the magnetic ion is changing strongly with pressure, the simple spin fluctuation description of the critical point must be modified. We expect that these results should stimulate further theoretical and experimental studies.

4. Summary
We have prepared new very pure single crystals of YbCu$_2$Si$_2$ with residual resistivity ratios of up to 130 and residual resistivities of less than 1 $\mu\Omega$cm. The onset of magnetic order at high pressure has been detected by ac micro-calorimetry in a diamond anvil cell, and the phase diagram has been established showing magnetic order appearing at 7.6 GPa and 0.95K, and suggesting a possible Quantum Critical point with $P_c = 6.5$ GPa. The resistivity has been measured under pressure in hydrostatic conditions, but no sign of superconductivity is found close to the expected critical pressure down to $T=0.05$ K.

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Figure 1
Specific heat of YbCu$_2$Si$_2$ at selected pressures measured by the ac microcalorimetry technique in the diamond anvil cell. The curves under pressure have been normalized to the ambient pressure curve at T=7K. The curve at 7.6 GPa was measured in a $^3$He cryostat down to 0.5K. In the other measurements the lowest temperature was about 1.5K
Figure 2
Phase diagram of YbCu$_2$Si$_2$ obtained from the microcalorimetry measurements showing the paramagnetic (PM) and probably antiferromagnetic (AF) phases, compared to that obtained by a previous resistivity study\textsuperscript{[3]}. In the resistivity study no sign of magnetic order was found below 8 GPa at temperatures down to 50mK hence the almost vertical dashed line. The red dashed line is a fit of our data to the form $(p-p_C)^{2/3}$ expected for a 3D antiferromagnetic system.
Figure 3
Low temperature resistivity under pressure of 2 samples of YbCu$_2$Si$_2$. Sample 1 was measured in a diamond anvil cell (DAC). Sample 2 was measured at 7 GPa in the modified Bridgman cell (see text). The curve at 7GPa is close to the expected critical pressure but shows no sign of superconductivity down to T=50mK.