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2010 J. Phys.: Condens. Matter 22 126004

(http://iopscience.iop.org/0953-8984/22/12/126004)

J. Phys.: Condens. Matter **22** (2010) 126004 (4pp) doi:10.1088/0953-8984/22/12/126004

Suppression of quadrupolar order on Si doping in $YbRu_2(Ge_{1-x}Si_x)_2$

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Received 2 December 2009, in final form 1 February 2010
Published 12 March 2010
Online at stacks.iop.org/JPhysCM/22/126004

Abstract

We have investigated the magnetic properties of polycrystalline $YbRu_2(Ge_{1-x}Si_x)_2$ samples using magnetic susceptibility, electrical resistivity, and specific heat measurements. All the results indicate that the Yb ions in $YbRu_2(Ge_{1-x}Si_x)_2$ are in a stable trivalent state. The antiferromagnetic ordering shifts to lower temperature with increasing Si concentration (x). The weak Kondo-like resistivity minimum observed in the resistivity data for $x = 0$ shifts toward lower temperature with an increase in the Si content and finally disappears. The most dramatic observation is the complete suppression of the quadrupolar ordering in $YbRu_2Ge_2$ ($T_Q = 10$ K) even for 2% Si doping.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Quadrupolar ordering in rare-earth intermetallic compounds has drawn considerable attention for the last few decades. In several cases it has been observed that the presence of quadrupolar order affects the magnetic properties to a great extent and leads to many interesting properties. Quadrupolar order is commonly seen in Ce-, Pr-, Tm-, and Yb-based intermetallic compounds. A couple of well known antiferroquadrupolar compounds are $PrPb_3$ [1] and $PrCu_2$ [2] whereas ferroquadrupolar ordering is realized in TmCd, TmZn, $TmAu_2$ etc [3–6]. It is also seen that application of pressure has a strong influence on the properties of the compound with quadrupolar ordering. For example, for CeB_6, T_N shifts to higher temperature with the application of pressure but T_Q remains unaffected [7–9]. TmTe is another interesting compound that exhibits antiferromagnetic quadrupolar order at 1.8 K together with an antiferromagnetic ordering below 0.4 K. With the application of external pressure, T_Q increases up to 0.4 GPa and then decreases until it disappears at 1.6 GPa [10, 11]. Recently, quadrupolar ordering has been observed in $YbRu_2Ge_2$ which shows complex magnetic behavior [12]. This anomalous behavior is understood through mean-field theory using the quasi-quartet model [13]. As observed in the above examples, one can anticipate that application of pressure (externally applied or chemical) will have a strong influence on the magnetic and quadrupolar order of $YbRu_2Ge_2$. Therefore, we have prepared $YbRu_2(Ge_{1-x}Si_x)_2$ and investigated the effect of chemical pressure on its magnetic properties using powder x-ray diffraction, magnetic susceptibility, specific heat and resistivity measurements.

2. Experimental details

We prepared polycrystalline samples of $YbRu_2(Ge_{1-x}Si_x)_2$ ($x = 0$, 0.02, 0.05, 0.10, 0.25, 0.50, 0.75 and 1.0) by the method of solid state reaction. The high purity elements taken in the stoichiometric ratio were sealed in a tantalum crucible. The Ta crucible was heated to 1150 °C at a rate of 300 °C h^{-1} and held at this temperature for four days under a dynamic vacuum. Afterwards it was cooled to room temperature at 300 °C h^{-1}. In a next step, the sample was powdered and repelletized. After sealing it inside a tantalum container, the heat treatment was repeated for seven more days at 1150 °C. The phase purity and crystal structures of the samples were determined using powder x-ray diffraction and scanning electron microscopy. The compositions of the samples were checked by means of energy dispersive x-ray analysis (EDAX). Magnetization measurements on the samples were performed using a commercial superconducting quantum interference device (SQUID) magnetometer. Electrical resistivity and specific heat measurements were carried out using the AC transport and heat capacity options of a physical properties measurement system (PPMS, Quantum Design).

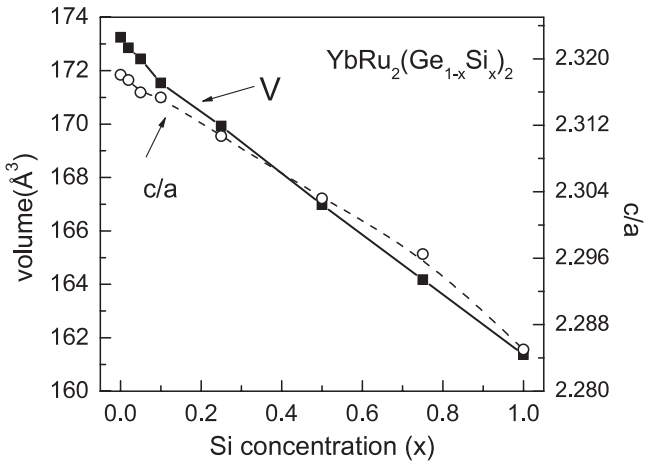

Figure 1. The volume and lattice parameter ratio c/a of $YbRu_2(Ge_{1-x}Si_x)$ as a function of the Si concentration.

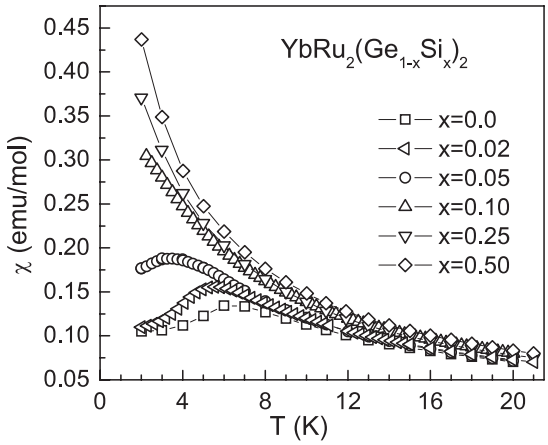

Figure 2. Magnetic susceptibility data for an $YbRu_2(Ge_{1-x}Si_x)_2$ polycrystalline sample as a function of temperature for a $B = 1$ T applied magnetic field.

3. Results and discussion

Powder x-ray diffraction patterns of $YbRu_2(Ge_{1-x}Si_x)_2$ samples confirm $ThCr_2Si_2$ type tetragonal structure in these compounds. Since the atomic radius of Si is smaller than that of Ge, replacing Ge by Si in $YbRu_2Ge_2$ should result in a decrease in unit cell volume as well as the lattice parameters. Such a behavior is clearly seen from figure 1, where an almost linear decrease in volume as well as the lattice parameter c/a is observed with increase in the Si content. This suggests that the valence state of Yb is not affected by Si doping. The EDAX analysis confirms the desired composition of our samples.

The magnetic susceptibility (not shown) of pure $YbRu_2Ge_2$ ($x = 0$) single crystal has anisotropic magnetic properties. For $B \parallel c$, χ_c exhibits quadrupolar ordering at $T_Q = 10.2$ K and an antiferromagnetic transition at $T_1 = 6.5$ K. However, for $B \parallel ab$ there is no anomaly corresponding to quadrupolar ordering in χ_{ab} data; only a magnetic transition is observed at $T_1 = 6.5$ K [12]. In figure 2, we have plotted the magnetic susceptibility of $YbRu_2(Ge_{1-x}Si_x)_2$ for $x = 0$, 0.02, 0.05, 0.1, 0.25 and 0.50 for a $B = 1$ T applied field. Our polycrystalline sample $YbRu_2Ge_2$ also exhibits a magnetic transition at 6.5 K as in the case of single crystals. But we do not see any clear anomaly due to the quadrupolar order at T_Q in the $\chi(T)$ data. This suggests that the contribution coming from $B \parallel ab$ in the randomly oriented microcrystals of the polycrystalline sample dominates the magnetic susceptibility behavior. Further, our results show that an increase in Si doping in polycrystalline $YbRu_2(Ge_{1-x}Si_x)_2$ causes a suppression of the antiferromagnetic transition temperature from $T_N = 6.5$ K for $x = 0$ to $T_N = 4$ K for $x = 0.05$. On further increase of the Si doping in $YbRu_2Ge_2$, the transition temperature shifts to even lower temperature. The high temperature susceptibility follows a Curie–Weiss behavior for all Si concentrations (x) ranging from $x = 0$ to 1 with $\mu_{eff} = 4.5\mu_B$ as expected for trivalent Yb ions. The Weiss temperature is less than 12 K for all the doped samples.

Figure 3 shows the specific heat data (a C/T versus T plot) for polycrystalline $YbRu_2(Ge_{1-x}Si_x)_2$ samples for $x = 0$, 0.02, 0.05, 0.1, 0.25 and 0.50. Since $LuRu_2Ge_2$ does not form, it is not possible to subtract the phonon contribution from $C(T)$ for calculating the magnetic specific heat. The prominent shoulder in the specific heat data for the $x = 0$ sample at $T_Q \sim 10.5$ K and peaks at $T_1 = 6.5$ K and $T_2 = 5.7$ K correspond to quadrupole ordering and two successive antiferromagnetic transitions. It is quite interesting to note that even for the slight Si doping of $x = 0.02$ the quadrupolar ordering disappeared abruptly whereas the magnetic ordering temperature is reduced by 0.6 K. Also, the two magnetic transitions merge together into a single transition which is seen in all doped samples. The peak at T_N shifts from 6.5 K for $x = 0$ to 0.8 K for $x = 0.50$. The large value of C/T at low temperature for $x > 0.5$ indicates that either the transition shifted below 0.4 K or it disappeared completely (see figure 4). In the inset of figure 4 we show the effect of a magnetic field on the transition temperature for $x = 0.02$. The transition temperature gets suppressed with increase in the field, as expected for antiferromagnetic ordering.

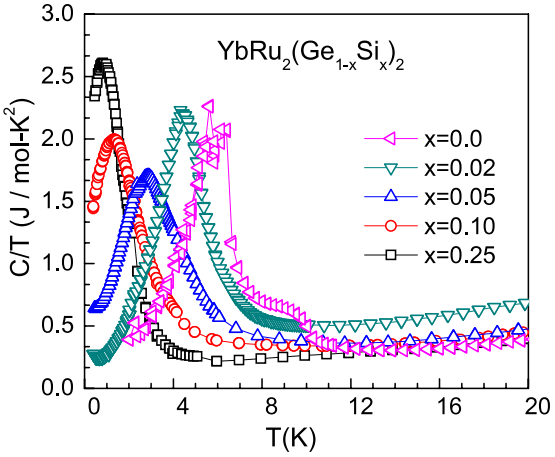

Figure 3. The temperature dependence of the specific heat C/T of $YbRu_2(Ge_{1-x}Si_x)_2$ for $x = 0.0$–0.25.

The entropy obtained by integrating C/T is shown in figure 5. The continuous increase in the $S(T)$ value with

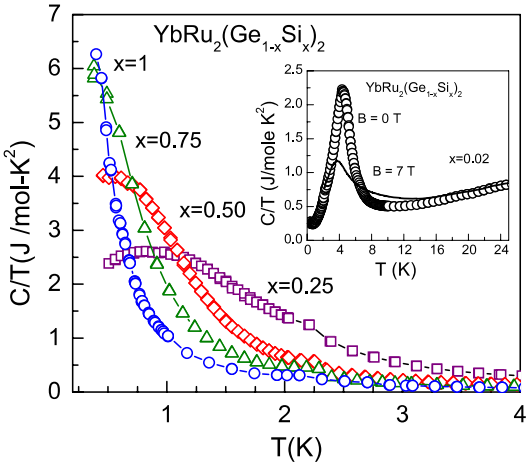

Figure 4. The temperature dependence of the specific heat C/T of $YbRu_2(Ge_{1-x}Si_x)_2$ for $x = 0.25$–1.00. The inset shows a C/T plot for $x = 0.02$ under the application of a magnetic field.

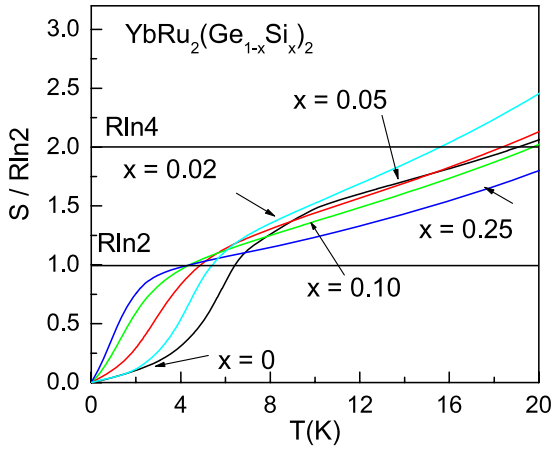

Figure 5. The temperature dependence of the entropy of $YbRu_2(Ge_{1-x}Si_x)_2$ for $x = 0.0$–0.50.

temperature indicates that the first excited state in not very far. At 20 K the entropy is approximately $R \ln 4$. For $x = 0.25$ the magnetic entropy is considerably lowered. The entropy at the magnetic transition is nearly $R \ln 2$.

Figure 6 displays the normalized electrical resistivity $\rho(T)/\rho$ (300 K) for $YbRu_2(Ge_{1-x}Si_x)_2$ polycrystalline samples. For samples with $x < 0.25$, the high temperature resistivity follows linear metallic behavior, while at lower temperature it shows a logarithmic increase followed by a broad maximum which is far above T_N evidencing a weak Kondo interaction. The position of this maximum shifts from $T(\rho_{max}) \sim 11$ K for pure $YbRu_2Ge_2$ ($x = 0$) to less than 4 K for $x = 0.1$. On further increase in the Si concentration, the Kondo type behavior disappears completely. In the magnetically ordered state $\rho(T)$ exhibits a rapid decrease due to the loss of spin disorder scattering.

On the basis of the above magnetic susceptibility and specific heat measurements we have plotted a magnetic phase diagram, between the transition temperature and the Si concentration (see figure 7). The magnetic transition temperature follows an exponential decrease with increase in

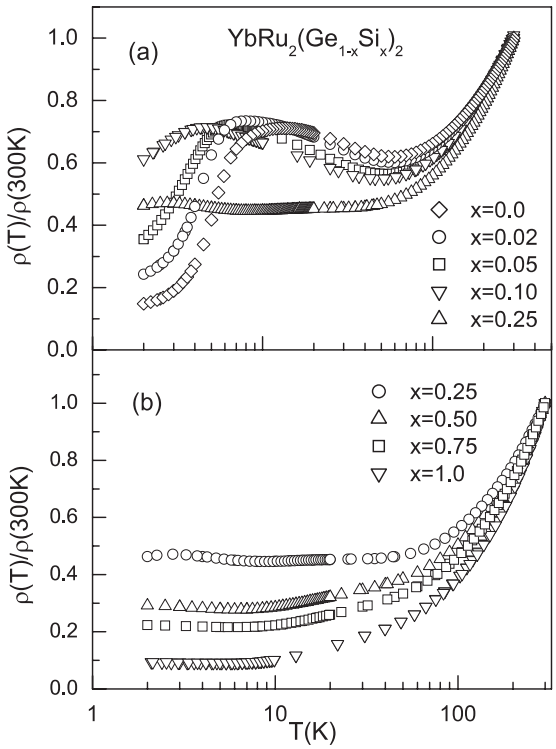

Figure 6. Zero-field in-plane resistivity of an $YbRu_2(Ge_{1-x}Si_x)_2$ polycrystalline sample as a function of temperature in the temperature range 2–300 K.

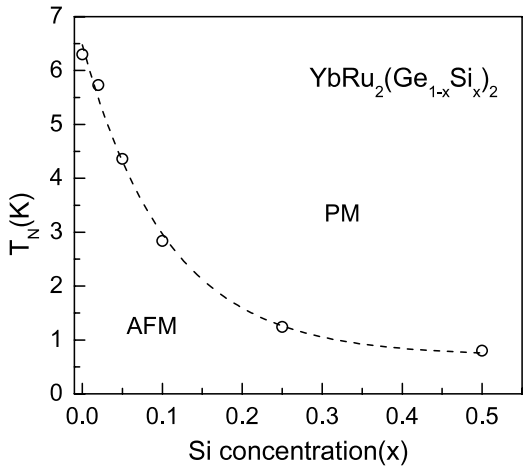

Figure 7. The T_N–x phase diagram of a $YbRu_2(Ge_{1-x}Si_x)_2$ polycrystalline sample for $x = 0$–0.5.

the Si concentration in $YbRu_2(Ge_{1-x}Si_x)_2$ which is shown by the dashed curve in figure 7. The quadrupolar order is suppressed altogether even for 2% Si doping. These results are in sharp contrast to the results obtained under externally applied hydrostatic pressure. While the externally applied pressure has little influence on the quadrupolar order, the magnetic transitions shift to lower temperature with increasing pressure [14]. The suppression of the quadrupolar order by 2% Si doping confirms the extreme sensitivity of the quadrupolar order to crystalline imperfections and disorder. In the case of $PrPb_3$, also the quadrupolar ordering is destroyed if more than 2% of the Pr is replaced by La [15].

4. Conclusions

We have investigated the effect of Si doping on the quadrupolar and magnetic ordering of $YbRu_2(Ge_{1-x}Si_x)_2$ polycrystalline samples by means of magnetization, specific heat and resistivity measurements. In these compounds Yb ions are in a stable trivalent state. The magnetic susceptibility and specific heat data for the samples with $x \leqslant 0.5$ show that T_N shifts toward lower temperatures with increase in the Si doping, which is very unusual among Yb-based systems. The T_N–x phase diagram shows exponential dependence of T_N on x. For a sample with $x < 0.10$, weak Kondo type behavior is seen in the resistivity data which disappears completely on increasing the Si content. Our results also establish that the quadrupolar ordering present in $YbRu_2Ge_2$ samples is very sensitive to doping. Even 2% Si doping suppresses the quadrupolar ordering. This study further reveals that T_N decreases with increasing chemical pressure in this series. Further investigations are highly desired, to understand this unusual behavior.

Acknowledgments

Financial assistance from BRNS, Mumbai, and the Indian Institute of Technology, Kanpur, are acknowledged.

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