Pressure Dependence of Magnetic Order in Single Crystalline CePtGa_{1-x}

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We present measurements of the susceptibility, the specific heat and the resistivity under hydrostatic pressure on single crystals of an antiferromagnetically ordered Kondo lattice compound CePtGa_{1-x} ($T_N=4.2$ K). We observe a positive temperature response of T_N on application of hydrostatic pressure up to 1.7 GPa.
[CePtGa, pressure, TiNiSi, structure, specific heat, susceptibility]

1. Introduction

The current interest in Cerium ternary intermetallics is brought about because of (i) the competition between intersite (RKKY type) and intrasite (Kondo type) interactions between conduction electrons and local 4f magnetism which can lead to exotic magnetic as well as non-magnetic ground states, (ii) the potential occurrence of quantum fluctuations in the vicinity of a quantum ($T=0$) magnetic phase transition and (iii) the formation of heavy quasiparticle bands, including the possibility of an instability against a superconducting ground state. The variety of these phenomena seems to be a crucial characteristic of Ce intermetallics and to a similar extent of U, Yb, Np and supposedly Pu intermetallics.

CePtGa is known to be a Kondo metal with an antiferromagnetic ground state [1-4]. By stoichiometric variation and/or application of external pressure, it should be possible to tune the magnetic (RKKY dominated) ground state towards a nonmagnetic ground state because Doniach's picture [5] is believed to be applicable to a wide range of Ce compounds: It now depends on the actual value of the coupling parameter $g=J/W$ ($J<0$, which is the local exchange integral and W , the conduction-band width) whether the antiferromagnetic ordering temperature will first rise at moderate pressures [6] or decrease towards $T=0$ as soon as the exponential increase of the Kondo interaction ($k_B T_K \sim e^{-1/g}$) surpasses the RKKY coupling strength ($k_B T_{RKKY} \sim g^2$) [5]. It has been reported that by application of moderate hydrostatic pressures ($p \leq 1$ GPa) the antiferromagnetic ground state of CePtGa could be suppressed [7].

In this paper we present the first experimental results on flux-grown single crystals of CePtGa_{1-x}. The structural characterization, the specific heat, susceptibility and pressure dependent resistivity were investigated. The latter will show that the suppression of the antiferromagnetic order in these single crystals seems to occur at much higher pressures compared to the previous results on a polycrystalline CePtGa sample [7].

2. Sample Preparation and Characterization

We utilized the flux-growth technique [8] to prepare single crystals of CePtGa. Attempts to use excess Gallium as a flux medium turned out not to be successful for the preferred Ce:Pt:Ga stoichiometry of 1:1:1. A starting atomic ratio of 5:1:2, i.e. using excess cerium as flux, subsequently led to single crystalline whiskers of about 4mm length. Some of these single crystals were crushed and used for powder x-ray analysis. The powder x-ray diffraction spectra of these single crystals are consistent with the expected pattern of the orthorhombic TiNiSi-type structure (space group Pnma) which was reported previously for polycrystalline

CePtGa samples [1-4,9]. The parameters of the unit cell were refined from the reciprocal space positions of 16 strong and well separated high-angle reflections using the least-squares method; the obtained values were: $a = (7.2189 \pm 0.0014)$ Å, $b = (4.4744 \pm 0.0004)$ Å, $c = (7.7951 \pm 0.0024)$ Å, which yield a unit cell volume of $V=251.7879$ Å³. These values are in good agreement with the previously reported cell parameters of polycrystalline samples [1-4]. Our subsequent, more detailed structural investigation which was done by means of electron diffraction as well as 4-circle single crystal x-ray diffraction, however, revealed extra, weak reflections that *cannot* be detected by powder (classic) x-ray diffraction. Although the orthorhombic crystallographic symmetry is not affected, an indexation of these extra reflections within the space group Pnma is *not possible*. Energy dispersive x-ray spectroscopy (EDXS) shows that there are equal atomic portions of Ce and Pt present, but less than half of the expected amount of Ga is actually going into the structure, even though we can exclude evaporation of Ga during crystal growth because our growth proceeded under hermetically sealed conditions. The Gallium deficiency is a rather surprising result in the sense that flux techniques utilize much lower synthesis temperatures than does arc-melting. One might expect that arc-melted samples would generally be more susceptible to Gallium deficiency. The fact that our single crystals are Ga deficient compared to an ideal 1:1:1 stoichiometry is taken into account when writing our sum formula

Fig. 1. Resistivity ρ vs T of single crystalline CePtGa_{1-x} at hydrostatic pressures $p=0$ and 1.7 GPa. The resistivity was measured along the crystallographic b-axis. The inset shows an expanded view of the pressure response in ρ vs T at $p=0, 0.6, 1.1$ and 1.7 GPa for $T < 25$ K.

as CePtGa_{1-x} , where x will be estimated more accurately later from results of specific heat and susceptibility. More details about the structural investigation are forthcoming [10].

The crystal that we used for resistivity studies under pressure had the shape of a long parallelepiped of size $2.3 \times 0.43 \times 0.14 \text{ mm}^3$, the long axis of which is along the [010] crystallographic direction, as determined by precession photographs. The electrical contacts were attached with silver epoxy and resistivity was measured along the crystallographic b axis. Hydrostatic pressure was applied in a standard self-clamping Be-Cu pressure cell with a pressure range up to $\sim 1.9 \text{ GPa}$ [11]. We used flourinert as the pressure transmission medium and a superconducting tin manometer to measure the actual hydrostatic pressure in the cell. The pressure cell was attached to a commercial Heliox ^3He cryostat with an effective temperature range between $0.35 \text{ K} < T < 300 \text{ K}$. Thermalization of sample and cell has been insured by computerized temperature control during the data acquisition. The specific heat was measured using a standard relaxation method and susceptibility data were obtained with a commercial SQUID susceptometer.

3. Results and Discussion

Fig. 1 shows the resistivity of the single crystalline sample measured along the b -axis. It very much resembles the resistivity which has been found in other 1:1:1 compounds like e.g. CeGeGa [2], CePdSn [12], CeRhGe and CeIrGe [13]. The slight curvature in $\rho(T)$ has to be attributed to crystal-field effects. At low temperature $\rho(T)$ reaches a maximum before it drops below the antiferromagnetic transition by about 15%, due to the freezing of spin-disorder resistivity in the magnetically ordered state. The Néel temperature which we determine from the kink in $\rho(T)$ yields $T_N = (4.2 \pm 0.1) \text{ K}$ at $p=0$. This value compares to a Néel temperature of 3.5 K for polycrystalline CePtGa of presumably stoichiometric composition [7].

When turning to results of the susceptibility (Fig. 2), we observe a strong magnetic anisotropy of CePtGa_{1-x} for fields applied parallel and perpendicular to the crystallographic b axis.

Fig. 2. The anisotropic susceptibility $\chi_{\parallel b, \perp b}$ vs T , parallel (○) and perpendicular (●) to the needle, respectively.

Fig. 3. Inverse susceptibility as a function of temperature of CePtGa_{1-x} , parallel (○) and perpendicular (●) to the crystallographic b axis.

Since the maximum in the susceptibility occurs in a measurement perpendicular to b , we assume that the antiferromagnetically staggered Ce moments lie within the a - c plane.

At high temperature, above 250 K , the inverse susceptibility (Fig. 3) shows a typical Curie-Weiss-like behavior ($\theta_{p\perp b} = -65.1 \text{ K}$, $\theta_{p\parallel b} = -27.7 \text{ K}$). Presuming an equiatomic $\text{Ce}_1\text{Pt}_1\text{Ga}_1$ stoichiometry, we would evaluate an (unrealistic) effective magnetic moment of $\mu_{\text{eff}} = 2.69 \mu_B/\text{Ce}$; however, if we attribute this misfit in μ_{eff} to Ga depletion, as suggested by our EDXS results, we estimate a Ga content of about 0.37 ($x=0.63$) for a full Ce moment of $\mu_{\text{eff}} = 2.54 \mu_B$. Deviations from the Curie-Weiss behavior start already below about 250 K and have to be attributed to crystal-field effects.

Fig. 4 shows the specific heat C/T vs T^2 of the single crystal. A linear extrapolation of the specific heat from above the antiferromagnetic phase transition results in a moderately enhanced Sommerfeld coefficient of about 76 mJ/mol K^2 which

Fig. 4. Specific heat as C/T vs T^2 of CePtGa_{1-x} . We obtain the values for the Sommerfeld coefficient ($\gamma = 76 \text{ mJ/mol K}^2$) and the phonon contribution ($\beta = 0.60 \text{ J/mol K}^4$, $\Theta_D = 213 \text{ K}$). The inset shows the full-scale plot of the specific heat of CePtGa_{1-x} as C/T vs T^2 .

should be interpreted as due to the presence of Kondo type interactions that lead to an enhancement of the effective mass of charge carriers.

A subtraction of the phononic contribution to the specific heat yields the remaining magnetic contribution which is plotted as C/T vs T in Fig. 5. The ordering temperature observed in the specific heat agrees well with the results from susceptibility and resistivity data. The entropy involved in the magnetic phase transition amounts to $R \ln 2$ if we assume a $\text{CePtGa}_{0.40}$ stoichiometry, supporting the results of EDXS and susceptibility. However, we still observe a ground state doublet which is in agreement with inelastic neutron scattering data on polycrystalline CePtGa [3]. Thus, the crystal-field level scheme seems to be rather robust against the substantial Gallium depletion in our sample. This would also explain why the resistivity does not appear to be influenced much by the stoichiometric deviation since also the resistivity seems to be considerably crystal-field dominated.

Fig. 5. The magnetic specific heat of CeGaPt as C/T vs T (the phonon contribution is subtracted), as well as the magnetic entropy S vs T .

We now want to focus on the pressure response of the antiferromagnetic phase transition as shown in the inset of Fig. 1. With the application of hydrostatic pressure, we observe an overall increase of the resistivity which is in good agreement with previous results on polycrystalline CePtGa [7]. A clear explanation for this enhancement of the resistivity, however, is not yet at hand. When going to higher pressures, we furthermore notice a pronounced upturn of the resistivity above the antiferromagnetic phase transition. We speculate that this upturn might be due to incipient ferromagnetic fluctuations that contribute to an increased scattering of the charge carriers. Such an upturn in $\rho(T)$ seems generally to occur in the polycrystalline sample of Ref.[7]. If we now track the Néel temperature of our single crystal as a function of external pressure, however, we get a positive pressure dependence of $\partial T_N/\partial p = +0.65$ K/GPa (Fig. 6) which is diametrically opposed to the pressure dependence of $\partial T_N/\partial p = -0.7$ K/GPa that was obtained from the aforementioned polycrystal studies.

Fig. 6. Pressure dependence of the antiferromagnetic ordering temperature of single crystalline CePtGa_{1-x} ($\circ$). T_N varies linearly with a positive pressure coefficient of $\partial T_N/\partial p = +0.665$ K/GPa. For comparison, the results on polycrystalline CePtGa ($\circ$) by Y. Uwatoko *et al.* [7] are added.

The most obvious reason for this discrepancy might originate from the different stoichiometry of our single crystalline samples compared to the presumably stoichiometric polycrystals. However, simple arguments in terms of chemical pressure seem not to work since, first of all, the lattice parameters are nearly unaffected, and secondly, the reduction of the Ga content should decrease the effective volume of the unit cell and thus apply a positive pressure which should lead to a lower ordering temperature if we compare it to the pressure dependence derived in Ref.[7]. Rather the reverse effect (an enhanced T_N) is observed. The only remaining obvious way would be a major change in the electronic structure by the reduction of the Ga content. This has to be understood in the sense that the effective coupling constant g is reduced compared to the stoichiometric compound, thus leading to a higher order temperature and a positive pressure coefficient, which is due to the enhanced distance from the quantum critical point. To support this hypothesis, however, further-reaching low-temperature studies on high-quality stoichiometric CePtGa crystals have to be undertaken.

4. Summary and Conclusion

We have presented experimental results on the first single crystals of CePtGa_{1-x} . From our crystallographic investigations, as well as from our measurements of the susceptibility and the specific heat, we estimate a Gallium content of 0.4. We have to emphasize that even such a large change does not necessarily affect the x-ray powder diffraction patterns, which qualifies to some extent also previous polycrystal studies where powder x-ray diffraction has been the main means of characterizing the samples. However, there are surprising experimental indications, that the depletion of Ga does not affect the physical properties of the system too severe. This can be observed, e.g., in the preserved

ground-state Kramers doublet, the unchanged lattice parameters as well as in the high (and well defined) magnetic ordering temperature. We thus believe that the TiNiSi structure is still preserved in the single crystals, however, with a strong disorder on the Gallium sites, especially in form of vacancies. It turns out to be an interesting fact that the physics of this structure is so robust against such major distortions. The pressure dependence of the Néel temperature seems to be the only severe disagreement, so far.

We further observed indications of Kondo interactions that are reflected in an enhanced Sommerfeld coefficient of the specific heat. Since we measured a positive pressure response of the magnetic ordering temperature, we believe that the critical point can only be approached by application of much higher pressures, but due to the presence of already clearly observable Kondo interactions, the critical point is expected to lie in a pressure range that should in principal be experimentally accessible.

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