Magnetic order in Zr-doped CeNiSn

1998 J. Phys.: Condens. Matter 10 2021

(http://iopscience.iop.org/0953-8984/10/9/008)

J. Phys.: Condens. Matter **10** (1998) 2021–2027. Printed in the UK PII: S0953-8984(98)87199-3

Magnetic order in Zr-doped CeNiSn

B Buschinger†§, M Weiden†‡, O Trovarelli†‡, P Hellmann†, C Geibel†‡ and F Steglich†‡

† TU Darmstadt, Technische Physik, Hochschulstrasse 8, D-64289 Darmstadt, Germany
‡ Max-Planck-Institut für chemische Physik fester Stoffe, Bayreuther Strasse 40, D-01187 Dresden, Germany

Received 27 August 1997

Abstract. The effects of Zr doping on the low-temperature properties of CeNiSn were studied by means of measurements of the thermoelectric power, the electrical resistivity, the magnetic susceptibility and the specific heat. Even Zr concentrations as small as 3% were found to dramatically increase the low-temperature metallic character in this otherwise gapped material and to stabilize antiferromagnetic ordering below 5 K.

1. Introduction

Amongst the small number of compounds known as Kondo insulators [1], the orthorhombic (ε-TiNiSi-type) compound CeNiSn [2] has attracted considerable interest due to its puzzling low-temperature properties. Whilst investigations, e.g., by means of NMR [3], specific heat [4] or tunnelling spectroscopy [5], and also early observations of activated conductivity in polycrystalline samples [6], give clear evidence of an anisotropic gap in the density of states (DOS) of the order of 5 K, good single crystals show metallic conductivity [7] at low temperatures. Most of these contradictory experimental results can be explained in terms of an anisotropic V-shaped pseudogap in the electronic DOS [8]. In this model, a small residual DOS leads to a residual Sommerfeld-coefficient $C/T \approx 40$ mJ mol^{-1} K^{-2} below 1 K [9], and thus allows for metallic-like electronic transport properties [10]. However, an alternative description [11] claims that the observed gaplike features are due to peculiarities in the spinon spectrum of CeNiSn. In this model, the electronic DOS is not gapped at all.

A large number of doping studies has already been carried out on CeNiSn. Upon doping with Cu on the Ni site, the evolution of long-range magnetic ordering at temperatures below 4 K is observed at Cu concentrations of 10% and higher [12], whilst large concentrations of Co ($\geqslant$35%) are found to induce a valence transition occurring below 75 K [13]. There is also evidence for a magnetic phase transition below 6 K [14] in strongly off-stoichiometric samples such as $CeNi_{0.95}Sn_{1.05}$.

Doping studies on the Ce site with trivalent and tetravalent ions should allow the investigation of the cerium valency in further detail. Upon doping with trivalent La on the Ce site, the low-T properties are found to be rather strongly affected insofar as a total suppression of the gap is observed at around 10% doping level [15]. In contrast, the high-temperature properties stay almost unchanged as obvious from NMR studies [16] and L_{III} absorption studies [17], which show a Ce valency of 3.12 at 300 K even at 50% La doping.

§ Corresponding author. E-mail address: thermopower@cryogen.com

0953-8984/98/092021+07$19.50

On the other hand, doping with U on the Ce site [18, 19] induces a remarkable change of the low-temperature properties especially concerning the thermoelectric power (TEP). In this case, the typical upturn observed in the TEP of undoped material [10] below 7 K is fully suppressed at U concentrations as low as 1.6%. At higher U concentrations, the TEP changes sign and adopts large negative values at low temperatures. Finally, a magnetic transition is observed for $Ce_{0.8}U_{0.2}NiSn$ at approximately 5 K [20]. However, since the valence state of U can vary from 3^+ to 5^+, it is not clear which valence the U adopts in this case. To the best of our knowledge, no doping studies with a stable tetravalent dopant have been reported so far. Therefore, to study the Ce ground state in more detail, we have investigated the effects of doping with stable tetravalent Zr on the Ce site, and compared the results with those obtained upon doping with trivalent La.

2. Experiment

Several samples with nominal stoichiometry $Ce_{1-x}Zr_xNiSn_{1.01}$ ($x = 0 \ldots 0.12$) were synthesized by repeated argon arc-melting of the pure metallic elements, which were of 99.9% purity at least. In addition, one La-doped sample ($Ce_{0.95}La_{0.05}NiSn_{1.01}$) was produced for comparison. All samples were subsequently annealed in high vacuum at 800 °C for five days and afterwards characterized by means of x-ray diffraction. Samples with $x < 0.08$ were found to be single phase within the resolution of our diffractometer, whilst reflections due to impurity phases became obvious at higher Zr concentrations. The unit-cell volume was found to be only slightly decreased upon Zr doping ($\Delta V/V = -3.4\%$ at $x = 0.06$), and no further change was observed at doping levels $x > 0.08$. Thus, the solubility limit seems to be close to $x = 0.08$. A standard four-probe method was used to measure the electrical resistivities of all samples in the temperature range 1.5 or 4 K up to 300 K. Magnetic susceptibilities were measured using a SQUID magnetometer at temperatures between 2 and 350 K. Thermoelectric power measurements in the same temperature range were carried out on selected samples using a steady-state method. Finally, the specific heat of the sample with $x = 0.06$ was measured at temperatures below 30 K.

3. Results

The temperature dependence of the TEP for selected samples is depicted in figure 1 in comparison with low-temperature data [10] obtained on a high-quality single crystal (sc). Obviously, the effect of doping with Zr on the low-T TEP is much larger than that of doping with La. In the latter case, the strong increase seen in both the sc and the undoped polycrystal (pc) below approximately 7 K seems broadened and shifted to slightly higher temperatures, but the essential feature remains unchanged. In contrast, a very strong suppression of the low-T TEP is visible already for samples with small Zr concentration ($x = 0.03$). Instead of an increase below 7 K, the temperature dependence of the TEP shows a well pronounced downward kink. In samples with higher Zr concentrations the TEP is further suppressed, and the kink becomes visible already at slightly higher temperatures.

This strong effect on the low-T properties is also reflected in the temperature dependence of the electrical resistivity, cf. figure 2. At small doping levels, a low-T increase as common to pc samples is obvious. Starting at a critical concentration of $x = 0.04$, the resistivity curves show downward kinks which stop the low-T increase. However, the sizes and the exact temperatures of this anomaly do not scale with x. Moreover, a strong sample dependence is found as the temperature of the anomaly was found to vary between different

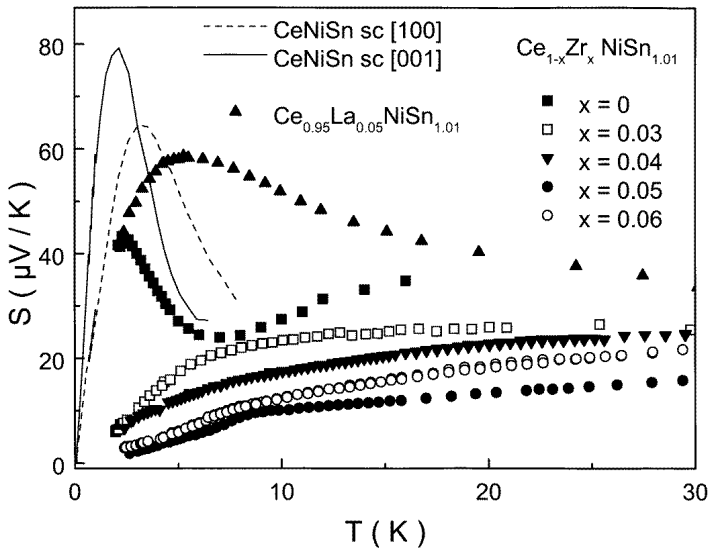

Figure 1. Temperature dependence of the TEP of $Ce_{1-x}Zr_xNiSn_{1.01}$ at 2 K $< T <$ 30 K, compared with TEP of single-crystalline material (lines, data from [10]) and $Ce_{0.95}La_{0.05}NiSn_{1.01}$.

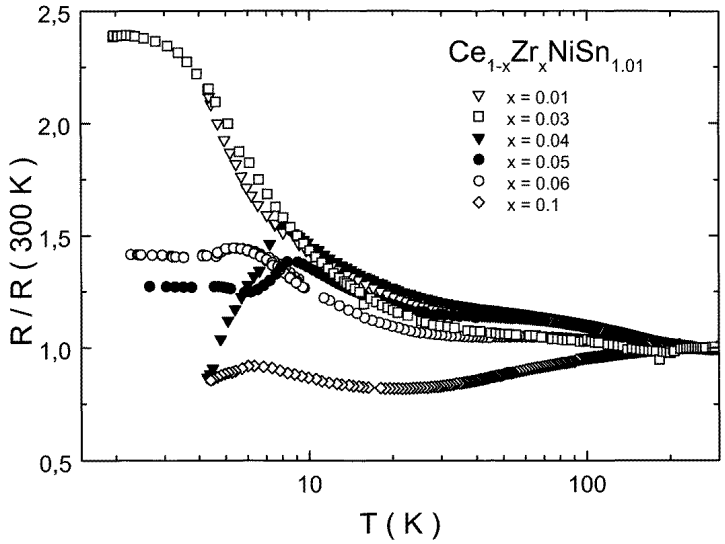

Figure 2. Temperature dependences of the electrical resistivities of $Ce_{1-x}Zr_xNiSn_{1.01}$, normalized to their room-temperature values, at 2 K $< T <$ 300 K.

samples with the same x by approximately 1 K. In addition, strong differences between as-cast and annealed samples are observed.

Measurements of the magnetic susceptibility (figure 3) clearly reveal anomalies pointing to antiferromagnetic ordering at approximately 5 K for all samples with $x \geqslant 0.03$, whilst both for samples with lower Zr concentration and for the La-doped sample no indications for magnetic ordering are visible.

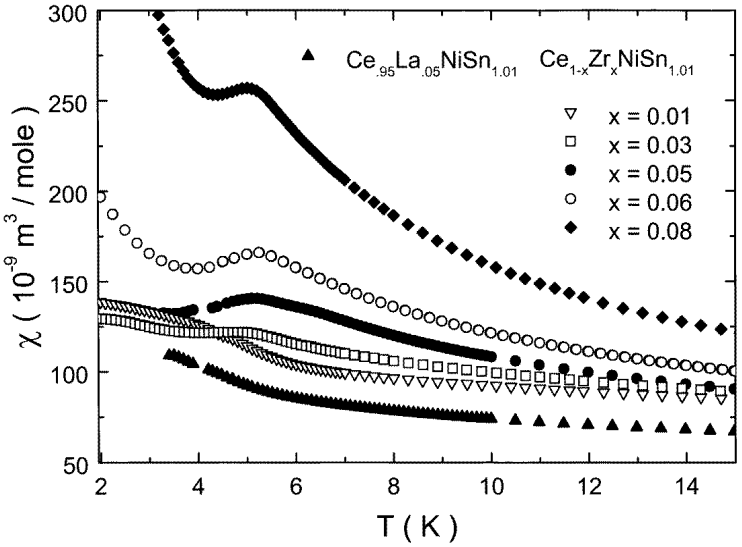

Figure 3. Temperature dependences of the magnetic susceptibilities of $Ce_{1-x}Zr_xNiSn_{1.01}$ and of $Ce_{0.95}La_{0.05}NiSn_{1.01}$ at low temperatures.

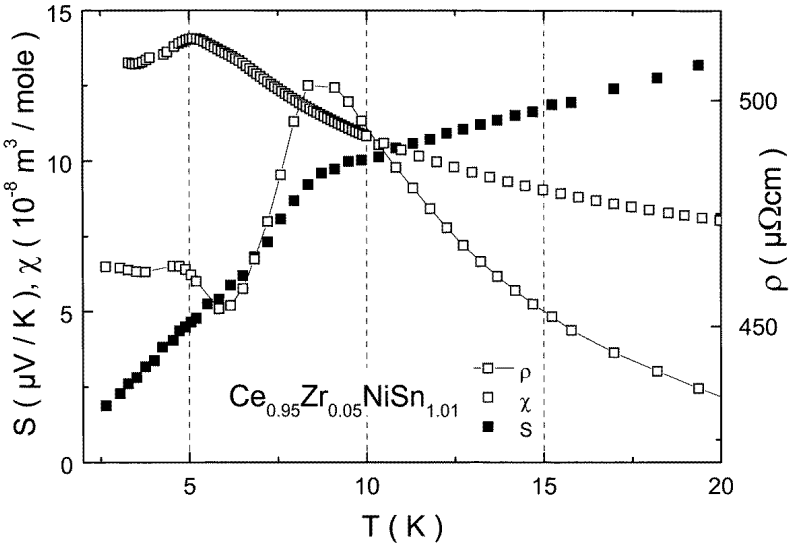

Figure 4. Low-temperature TEP (filled squares), susceptibility χ (open squares, both left scale), and resistivity (joined open squares, right scale) of $Ce_{0.95}Zr_{0.05}NiSn_{1.01}$ at 2.5 K $< T <$ 20 K.

Obviously, indications for magnetic ordering are only found for those samples which also exhibit a suppression of the TEP and, except for $x = 0.03$, of the resistivity at low temperatures. A crossover from semiconducting to metallic conductivity thus appears as a precursor to magnetic ordering.

A more detailed view of the low-T results for a sample with $x = 0.05$ is given in figure 4. Clearly, both the temperature dependences of the TEP and of the resistivity show

strong anomalies at approximately 8 K insofar as the resistance drops by approximately 11%, and the TEP shows a pronounced downward kink. These anomalies are not reflected in the magnetic susceptibility and thus have to be ascribed to an increase in carrier concentration. At approximately 5 K, the magnetic susceptibility shows a clear downward kink as expected for antiferromagnetic ordering. This anomaly is also clearly reflected as an abrupt change in the temperature dependence of the electrical resistivity. In addition, the slope of the TEP seems to change slightly. Finally, a further small anomaly is evident in the temperature dependences of both the resistivity and the magnetic susceptibility at approximately 6.5 K.

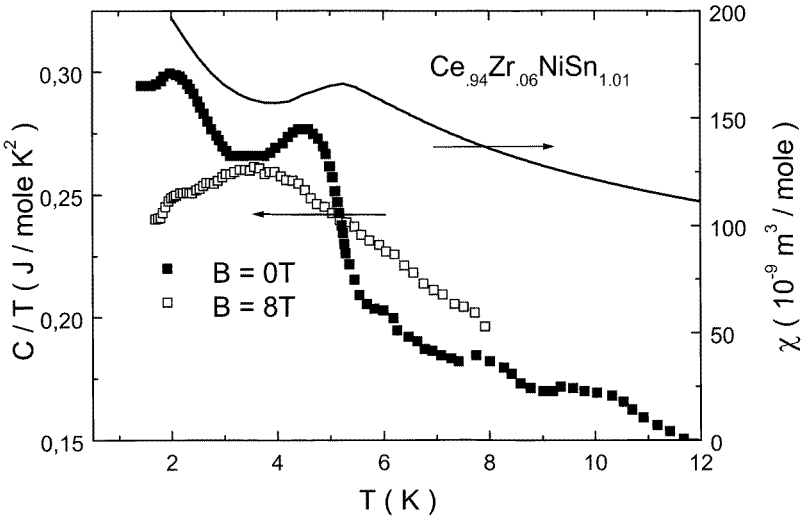

Figure 5. Specific heat of $Ce_{0.94}Zr_{0.06}NiSn_{1.01}$, plotted as C/T, at 1.2 K $< T <$ 12 K in applied magnetic field of 0 T and 8 T (squares, left scale), and magnetic susceptibility (line, right scale).

Measurements of the specific heat (figure 5) on $Ce_{0.94}Zr_{0.06}NiSn_{1.01}$ clearly reveal a phase transition at 5 K which presumably corresponds to the antiferromagnetic ordering seen in the magnetic susceptibility. The absolute sizes of the anomalies both in the specific heat and in the susceptibility are far too large to be explained with impurity contributions and thus show that magnetic ordering is a bulk phenomenon in Zr-doped CeNiSn. At lower temperatures, a second anomaly is obvious. This anomaly is not resolved in the other measurements due to the limited temperature range, but magnetically ordered compounds crystallizing in the TiNiSi structure, e.g. CePtAl [21], are well known to exhibit complex magnetic phase diagrams with several phase transitions at low temperatures. Thus, this low-T phase transition is most likely also of magnetic origin. With an applied field of 8 T, the first anomaly is shifted to lower temperatures as expected for antiferromagnetic order.

4. Discussion

From resistivity and TEP measurements, it is obvious that even Zr concentrations as low as 3% strongly increase the metallic character of the otherwise gapped ground state of pure CeNiSn. Both the resistivity and the TEP show a strong suppression compared to undoped material which sets in rather abruptly below 8 K. These sudden drops suggest that a semiconductor-to-metal transition occurs below 8 K. However, there is no systematic

dependence on the doping level, both concerning the exact temperature of the anomaly and the size of the drop.

Strong indications for antiferromagnetic ordering are found at temperatures of approximately 5 K for Zr concentrations between 3 and 8%. Again, the ordering temperatures are found to only slightly increase with increasing doping level. Moreover, some sample and annealing dependence of the exact ordering temperatures has been observed.

These investigations suggest that, starting from a critical Zr concentration of approximately 3%, the metallic low-temperature character of CeNiSn is strengthened in a manner similar to a semiconductor-to-metal transition which then allows for magnetic ordering below 5 K.

The overall effect of Zr doping shows some similarity to the effects of Cu doping on the Ni site. Doping with Cu increases the number of electrons and, thus, strengthens the metallic character. In this case, indications for antiferromagnetism are found starting from 6% Cu doping [16], and bulk antiferromagnetic ordering with a critical temperature of approximately 3.5 K [12] is found at 20% doping level.

However, there are some puzzling differences involved in doping with Zr: first, magnetic ordering is observed at even very small doping concentrations, and second, there is no clear dependence of the ordering temperature on the doping concentration.

A theoretical treatment of the hybridization in anisotropic semiconductors [22] shows the extreme sensitivity of the resulting DOS to impurity scattering. It is likely that doping with Zr strongly affects the hybridization process and thus alters the DOS much more effectively than doping with Cu does. Thus, a very small critical concentration of only 3% might be reasonable. Further increasing the Zr concentration then reduces the number of magnetic moments which might compensate the effects of a further increase of the carrier concentration.

The fact that doping with tetravalent Zr is much more efficient in changing the low-T properties than doping with trivalent La points to a cerium valency close to 3^+ in CeNiSn even at low temperatures. A cerium valency close to 3^+ is also likely to explain the nearness to magnetism of CeNiSn observed not only in many doped samples but also in undoped CeNiSn [23].

5. Summary

By means of resistivity, TEP, susceptibility and specific heat measurements, a low-temperature antiferromagnetic ordering at approximately 5 K has been found for Zr-doped CeNiSn even at Zr concentrations as low as 3%. As a precursor to magnetic ordering, a sudden change from semiconducting to metallic transport is found at temperatures of approximately 8 K. Doping with tetravalent Zr is found to much more efficiently change the low-temperature properties than doping with trivalent La. Both this result and the nearness to magnetic ordering might indicate that the Ce valence stays close to 3^+ in CeNiSn.

Acknowledgments

This work has been supported by the SFB 252 Darmstadt/Mainz/Frankfurt and the BMBF, grant No 13N6608/1. One of us (OT) acknowledges support from the Alexander von Humboldt foundation.

References

[1] For a review, see Aeppli G and Fisk Z 1992 *Comment. Condens. Matter. Phys.* **16** 155
[2] Takabatake T, Nakazawa Y and Ishikawa M 1987 *Japan. J. Appl. Phys.* **26** 547
[3] Kyogaku M, Kitaoka Y, Asayama K, Takabatake T, Teshima F and Fujii H 1990 *J. Phys. Soc. Japan* **59** 1728
[4] Takabatake T, Nakamoto G, Tamaka H, Fujii H, Nishigori S, Suzuki T, Fujita T, Ishikawa M, Oguro I, Kurisu M and Menovsky A A 1993 *Transport and Thermal Properties of f-electron Systems* ed G Oomi, H Fujii and T Fujita (New York: Plenum) p 111
[5] Ekino T, Takabatake T, Tanaka H and Fujii H 1995 *Phys. Rev. Lett.* **75** 4262
[6] Aliev F G 1991 *Physica* B **171** 199
[7] Nakamoto G, Takabatake T, Fujii H, Minami A, Maezawa K, Oguro I and Menovsky A A 1995 *J. Phys. Soc. Japan* **64** 4834
[8] Izawa K, Suzuki T, Kitamura M, Fujita T, Takabatake T, Nakamoto G, Fujii H and Maezawa K 1996 *J. Phys. Soc. Japan* **65** 3119
[9] Takabatake T *et al* 1996 *Physica* B **223/224** 413
[10] Hiess A, Geibel C, Sparn G, Bredl C D, Steglich F, Takabatake T and Fujii H 1994 *Physica* B **199/200** 437
[11] Yu Kagan, Kikoin K A and Mischenko A S 1997 *Phys. Rev.* B **55** 12 348
[12] Kalvius G M *et al* 1997 *Physica* B **230–232** 655
[13] Adroja D T and Rainford B D 1994 *Physica* B **199/200** 498
[14] Aliev F G, Villar R, Vieira S, Scolozdra R V and Takabatake T 1994 *Physica* B **199/200** 433
[15] Aliev F G, Brandt N B, Moshchalkov V V, Zalayalutdinov M K, Pak G I and Scolozdra R V 1988 *JETP Lett.* **48** 580
[16] Nakamura K, Kitaoka Y, Asayama K, Takabatake T, Nakamoto G, Tanaka H and Fujii H 1996 *Phys. Rev.* B **53** 6385
[17] Alekseev P A, Klement'ev E S, Lazukov V N, Nefedova E V, Sadikov I P, Khlopkin M N, Muzychka A Yu, Sashin I L, Efremova N N and Bührer W 1994 *JETP Lett.* **79** 665
[18] Park J-G, Ocko M and Coles B R 1994 *J. Phys.: Condens. Matter* **6** L781
[19] Park J-G, Ocko M and McEwen K A *Phys. Rev.* B at press
[20] Park J-G, Scott C, McEwen K A and Cywinski R 1977 *Physica* B **230–232** 673
[21] Dönni A, Kitazawa H, Fischer P, Tang J, Kohgi M, Endoh Y and Mori Y 1995 *J. Phys.: Condens. Matter* **7** 1663
[22] Ikeda H and Miyake K 1996 *J. Phys. Soc. Japan* **65** 1769
[23] Sato T J, Kadowaki H, Takabatake T, Fujii H and Isikawa Y 1996 *J. Phys.: Condens. Matter* **8** 8183