U doping effects in (Ce$_{1-x}$U$_x$)NiSn

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We have studied (Ce$_{1-x}$U$_x$)NiSn for 0≤x≤0.2 to investigate the effects of U doping on the low-temperature anomalies seen in CeNiSn. From resistivity and thermopower results, we conclude that with as small as 1.6% U doping the anomalies disappear. With further increasing U concentrations, the system becomes unstable towards a weakly antiferromagnetic transition. We discuss the effects due to small U doping at low temperatures in the light of chemical pressure effects and Fermi-level tuning.

I. INTRODUCTION

Since the discovery of some strongly correlated electron systems of Ce or U intermetallics with apparently small-gap behavior, so-called “low-carrier-density Kondo systems,” there has been renewed interest in small-gap, or pseudogap, materials with strong hybridization between f and conduction electrons. CeNiSn, initially studied by Takabatake et al., is exceptional among the low-carrier-density Kondo systems in having the ε-TiNiS orthorhombic structure. There have since been many intensive studies of CeNiSn, in particular of the low-temperature anomaly (an increase in resistivity), that have been interpreted as a signature of a gap opening at the Fermi surface at low temperatures. The gap parameters estimated from the resistivity data are 2.4, 5.5, and 5.0 K for the a, b, and c axes. The low-temperature increase in the resistivity disappears completely when a magnetic field of 14 T is applied along a magnetic easy axis, the a axis, suggesting some correlation between the resistivity increase and the low-temperature magnetic properties. The resistivity increase also disappears with a pressure of 20 kbar, and then the low-temperature resistivity becomes metallic, though like a very dirty metal, as the residual resistivity value is around ρ~70 μΩ cm under high pressure. Interestingly enough, it was shown recently that the low-temperature increase in the resistivity is very sensitive to the amount of impurities present in the samples: the more pure the sample the less distinct the resistivity increase is at low temperatures and it eventually becomes metallic. Nevertheless, it seems that a small amount of impurities does not affect the gap opening behavior in general.

Regarding the nature of the gap, it should be noted that the extrapolated electronic contribution to the heat capacity to T=0 is about 60 mJ/mol K$^2$. This excessive residual heat capacity can be best understood in such a way that CeNiSn has some residual density of states at the Fermi level, suggesting that the gap in CeNiSn is a partial gap, or a pseudogap in agreement with NMR data.

With CeNiSn having no magnetic transition itself down to 11 mK (there are only small changes in the dynamical behavior of mainly Ce moments according to muon spin-relaxation results), it was of primary interest what kind of effects short-range magnetic fluctuations, if any, have on the opening of a partial gap below 6 K. Neutron studies on CeNiSn have found two different spin gaps, which are well defined only in particular regions of momentum space. The two spin gaps disappear upon heating the sample. The smaller gap of 2 meV is well defined around (0,0,1.2), while the larger one with Δ=4 meV is seen only around (h,$\frac{1}{2}$,$\frac{1}{2}$).

In contrast to CeNiSn, UNiSn (Ref. 8) crystallizes in the MgAgAs cubic half-Heusler structure and has semiconducting properties at high temperatures with a gap value of about 1000 K. Most interesting of all, UNiSn has an antiferromagnetic transition at 47 K, and a semiconductor-metal transition at the same temperature. There have been some unsuccessful attempts to separate the magnetic transition from the semiconductor-metal transition. This failure suggests that the two transitions, one of electronic origin and the other of magnetic origin, are coupled strongly. We may conjecture that when UNiSn becomes antiferromagnetic below 47 K the Fermi surface becomes modified so much that it favors a metallic state or vice versa. It has a fairly modest electronic specific heat of γ~28 mJ/mol K$^2$, but this is still large compared with typical values for simple metals.

The present work was motivated by this conjecture of the effects of magnetic order on the transport properties of UNiSn and the unanswered question of the role of magnetic fluctuations in CeNiSn. By studying (Ce,U)NiSn, we aimed to understand the role of magnetic fluctuations in CeNiSn and the unanswered relationship between the antiferromagnetic transition and the semiconductor-metal transition in UNiSn. As it turned out, however, the solid solution of Ce in UNiSn is very limited. We thus concentrate on the effects of U doping in CeNiSn in this paper except for some general comments on the metallurgical side of the (Ce,U)NiSn studies.
II. EXPERIMENTAL DETAILS

We have prepared, using an arc furnace, (Ce$_{1-x}$U$_x$)NiSn with $x=0$, 0.016, 0.031, 0.05, 0.1, 0.15, 0.2, 0.3, 0.5, 0.75, 0.9, and 1. All samples with $x=0.3$ were annealed in vacuum-sealed quartz at 750 °C for at least 26 days. The remaining samples were annealed at 800 °C for 3 months. Subsequently, most samples were subject to metallurgical examinations and x-ray characterization using Cu Kα radiation in a Phillips PW1700 diffractometer.

A standard four-probe technique has been used for resistivity measurements from 300 to 2 K. Magnetization measurements have been made down to 2 K and up to 7 T using a superconducting quantum interference device magnetometer (Quantum Design MPMS7). The thermopower has been measured in situ against a high-$T_c$ YBaCuO compound ($T_c=82$ K) up to 70 K, and against pure lead at higher temperatures. We used the thermopower data of lead measured by Roberts$^{10}$ to determine the absolute thermopower values above 70 K. For the experimental details of thermopower measurements, see Ref. 11.

III. DATA AND ANALYSIS

Since our previous publications$^{12}$ on $x=0$, 0.1, 0.15, 0.2, and 0.3, we have concentrated on samples with smaller U concentrations. We also measured the compositions of new samples for consistency again.

After describing the characterization of all the samples, we will restrict ourselves to studies of U doping on CeNiSn as Ce-doped UNiSn samples show significant foreign phases even at 10% substitution of Ce for U.

A. Sample characterization

Our x-ray-diffraction results showed that U-doped CeNiSn forms in a single phase over a wider range of concentration than Ce-doped UNiSn. At up to 20% of U substitution in CeNiSn, all samples were found to be single phase. For (Ce$_{0.7}$U$_{0.3}$)NiSn, there appear some foreign phases in the x-ray-diffraction patterns, but we have included the thermopower data of the 30% U-doped CeNiSn in the appropriate section to illustrate a structural transformation occurring between 20% and 30% U-doped CeNiSn. In contrast, the solid solution region of Ce doping in UNiSn is limited to at best 10% substitution of Ce, and even (Ce$_{0.1}$U$_{0.9}$)NiSn shows signatures of foreign phases.

To summarize our findings, U-doped CeNiSn contracts with U concentrations whereas Ce-doped UNiSn appears to expand with Ce concentrations. With 20% U doping, there is about a 0.9% decrease in unit-cell volume. Relative reductions in lattice constants are 0.46% for the $a$ axis, 0.27% for the $b$ axis, and 0.18% for the $c$ axis, respectively. Compared with around 0.18% volume change induced by 1 kbar of pressure,$^{13}$ U substitution in CeNiSn thus seems to provide significant effects on the lattice constants. We recall that the low-temperature upturn in the resistivity disappears with 20 kbar.$^{3}$ We will therefore consider this chemical pressure effect carefully when we discuss general effects of U doping later in the discussion.

B. Resistivity

Since we have noticed some variations in the room-temperature resistivity values among the samples, we present resistivity ratio data instead. The resistivity values at room temperature are 191, 293, 253, 309, 220, 305, 155, and 196 $\mu\Omega$ cm for 0%, 1.6%, 3.1%, 5%, 10%, 15%, 20%, and 30% of U, respectively. The variations in the room-temperature resistivity values probably arise from small cracks present in the samples. Our resistivity data are shown in Fig. 1, and the data for CeNiSn are in good agreement with previously published results.$^1$ It is noticeable that for CeNiSn there appear two maxima around 100 and 15 K before a distinct upturn below 5 K. Compared with the single-crystal results,$^1$ it is suggested that the two maxima correspond to features appearing in the resistivity of the $a$- and $b$-axis CeNiSn. A fit of our pure CeNiSn data below 5 K using an activation formula produces a gap value of 3 K, close to the $a$-axis value of 2.4 K.

For small U concentrations of 1.6%, the resistivity ratio increases, but now we do not have the small-gap behavior. The continuous increase in the resistivity ratio is seen up to 7.1% U doping. It is also noticeable that over the whole temperature range the resistivity ratio increases with U concentrations. This overall increase in resistivity of slightly doped samples may be due to nonresonant scattering from impurities, which are dominant at low temperatures. As the U concentration increases above 5%, the resistivity ratio at low temperatures begins to fall.
With further increasing U concentrations, the low-temperature resistivity flattens off. What is more interesting with the relatively large U doping is that at 15% of U doping the resistivity shows a slight maximum around 2.5 K. In (Ce_{0.8}U_{0.2})NiSn, this maximum moves up in temperature and is seen around 5 K. We will discuss the origin of the maximum later.

Finally, there is a broad hump around 100 K seen in the resistivity for all samples. That it appears in all samples points probably to a single-ion effect as its origin. This might be a reflection of crystal-field effects. However, no crystal-field excitations have been observed so far in inelastic neutron data at the expected energy range of 10–30 meV, except for a very recent study of Ce(Ni,Pt)Sn by Adroja and co-workers. Their results show that two well-defined peaks seen in CePtSn become broad with increasing Ni concentrations. Eventually, the two excitations merge into a very broad hump centered at 28 meV for CeNiSn. This observation of crystal-field excitations in CeNiSn at appropriate energies is certainly encouraging to our interpretation of the broad hump as arising from scattering from excited crystal-field levels. Our recent experiment on a single-crystal CeNiSn also supports the observation. Several other measurements have indicated single-ion effects over a similar temperature range supporting our view about crystal fields being significant in CeNiSn.

A drastic change in the resistivity from 20% to 30% substitution of U, not shown in the figure, is in good agreement with x-ray results that beyond 20% the samples are no longer single phase.

C. Magnetization

The magnetization of CeNiSn has a modest Curie-Weiss behavior at high temperatures with some curvature around between 100 and 150 K (not shown here). The curvature may be due to crystal-field effects as in the resistivity discussed above. Below 50 K, the magnetization begins to deviate from a Curie-Weiss behavior and increases rather sharply. In our data for CeNiSn, we did not observe a peak previously seen around 12 K in the $a$-axis susceptibility of single-crystal CeNiSn despite the fact that a gap value obtained in our sample is close to that for the $a$-axis one. Instead, it continues to increase down to lowest temperatures measured. A slight hint of the 12-K peak was seen in our previous ac susceptibility study.

Figure 2 shows that the magnetization increases with increasing U concentration. We note that the Curie-Weiss temperature decreases with U doping. We will interpret these observations in the light of hybridization changes due to U doping later in the discussion.

It is noticeable that the magnetization for (Ce_{0.8}U_{0.2})NiSn shows a modest change in slope around 5 K, where previous ac susceptibility measurements show a peak that led us to suggest that this compound undergoes an antiferromagnetic transition at low temperatures. In fact, even (Ce_{0.85}U_{0.15})NiSn also seems to show a similar behavior at lower temperatures. Regarding the origin of the small feature in the magnetization, we can rule out the possibility of the effects of Ce$_2$O$_3$ impurities present in the sample, which has a magnetic transition temperature at 6 K. The reason is that we have seen a maximum in the resistivity at almost the same temperature (see Fig. 1) that naturally appears to be related to the feature in the magnetization.

Finally, magnetization measurements taken at 1 T with samples kept at 2 K show a smooth increase with perhaps a maximum around 15% of U, which we interpret as an indication that the transition toward an antiferromagnetic order is very gradual [see the inset in Fig. 2(b)].

D. Thermopower

Our results on polycrystalline (Ce,U)NiSn are presented in Fig. 3. When compared with results for single-crystal CeNiSn, our data on polycrystalline CeNiSn show three interesting features that we can correlate with those seen in single-crystal CeNiSn. The sharp peak at low temperatures represents features seen in the $a$- and $c$-axis data. The rounded maximum $C$ at 150 K corresponds to a maximum in the $b$-axis data of single-crystal CeNiSn while the maximum $B$ at around 20 K corresponds to shoulders in the $a$- and $b$-axis data.

Surprisingly, the thermopower results show that with U doping as small as 1.6% U the lowest-temperature peak (A)
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FIG. 3. Thermopower data are presented for all samples. Three features marked A, B, and C are described in the text. Data for pure CeNiSn are shown in both figures for comparison. The arrow indicates a kink-type structure seen in dilute U-doped CeNiSn.

disappears almost completely. This is a very drastic effect, considering that the rest of the features seen in CeNiSn remain intact. In fact, it is the first time, to our knowledge, that such a small concentration of doping brings about such visible effects on the thermopower results of CeNiSn.

Further U doping makes the low-temperature tail become negative until it reaches $S \approx -35 \mu V/K$ at 2 K for 3.1% U-doped CeNiSn. Compared with results for 3.1% U doping, the thermopower data for 5% U-doped CeNiSn are somewhat attenuated. It is also noticeable that with U doping a small kink-type of structure appears at low temperatures instead of the peak seen in CeNiSn. This feature moves towards higher temperatures in the dilute U-doped samples before disappearing above 10% U doping.

In the previous single-crystal studies, the increase in thermopower at lower temperatures was interpreted as arising from the opening of a pseudogap in the density of states, and the peak at lower temperatures was ascribed to the effects of small density of states within the gap with a temperature-dependent structure. Unlike the resistivity data whose low-temperature anomaly is much affected by sample quality, it was previously shown that the low-temperature features in thermopower are not so sensitive to the quality of single crystals. With these previous interpretations and results in mind, we therefore can rule out the possibility that what we observe in thermopower with small U doping is due to impurity effects. In searching for explanations for the disappearance of the peak by small U doping, we conclude that there is a sudden change by doping in the density of states very near the Fermi surface, probably in the region of $\varepsilon_F \pm 10$ K. Whether the substitution of 1.6% U leads to a complete collapse of the low-temperature partial gap structure in CeNiSn is difficult to tell. However, it is clear that the low-temperature feature is severely modified by as small as 1.6% U doping.

With further U doping, the maximum B now begins to move up in temperature and grows with U doping up to 3.1% before diminishing significantly for more U concentrations. In fact, it is hardly noticeable in 15% U-doped CeNiSn. At the same time, the thermopower results show a negative maximum at lower temperatures. Between 10% and 15% U doping, the most dramatic changes occur to the low-temperature negative maximum and the maximum B. Apart from the maximum B becoming very attenuated with U substitution, the magnitude of the negative maximum for 15% U-doped CeNiSn is reduced to about half the value for (Ce$_{0.9}$U$_{0.1}$)NiSn. Increasing U concentrations to 20% makes the overall magnitude of the thermopower even smaller. For comparison, results for (Ce$_{0.7}$U$_{0.3}$)NiSn illustrate a drastic change between 20% and 30% U-doped CeNiSn [see Fig. 3(b)]. Despite the changes seen in the thermopower from pure CeNiSn to (Ce$_{0.7}$-U$_{0.3}$)NiSn, peak C does not change much in temperature, in accord with the feature seen in the resistivity at high temperatures. This again supports our view that crystal-field effects are significant at high temperatures.

IV. DISCUSSION

To discuss the effects of U substitutions on the low-temperature partial gap in CeNiSn, we examine the changes to the system induced by U doping. First, we recall that in 20% U-doped CeNiSn there is about 0.9% reduction in unit-cell volume compared with CeNiSn. From chemical pressure effects alone U doping is thus expected to enhance significantly the hybridization between the f and the conduction electrons; the value of compressibility $\kappa$ is around $1.8 \times 10^{-11}$ m$^3$/N in CeNiSn. As 20 kbar of pressure was seen to destroy the low-temperature upturn in the resistivity, we can expect that 20% U doping may have sizable effects on the low-temperature anomaly on the ground of volume reduction alone. (The cell volume changes about 3.6% by a pressure of 20 kbar.) Regarding this chemical pressure effect, we recall that Pt-doped CeNiSn stabilizes antiferromagnetic order below 7.5 K in CePtSn, as Pt doping increases the cell volume, thus reducing the hybridization between f electrons and conduction electrons.

A second point of consideration is that U is not isoelectronc with Ce. The substitution of U is thus expected to add more f electrons, and probably an additional conduction electron also as U in UNiSn has 4+ valence. This kind of change in the number of conduction electrons, namely, Fermi-level tuning, was seen to be of primary importance in decreasing the hybridization in (Y,Up)Pd$_3$ with U doping. Here we recall the case of Ce(Ni,Co)Sn (Refs. 3 and 20); Co has one less d electron than Ni. Because of the one fewer d electron, Co doping on CeNiSn brings the Fermi surface closer to the localized f-electron states and thus increases the
hybridization between conduction and $f$ electrons, which is the exact opposite of the effects of U doping. With increasing hybridization, Co-doped CeNiSn is subsequently driven towards a valence fluctuation regime. In contrast, Cu doping in Ce(Ni,Cu)Sn (Ref. 21) increases the number of conduction electrons as well as expanding the lattice, thus reducing the hybridization between conduction and $f$ electrons. Hence Cu doping stabilizes an antiferromagnetic ordering at 13% Cu.

There are therefore two competing effects of the U doping on the hybridization strength. On balance, an increase in the number of conduction electrons by U doping, i.e., Fermi-level tuning, seems to be more instrumental in deciding the low-temperature properties of (Ce,U)NiSn, thus driving the system towards a magnetic ordering, not a charge fluctuation regime as in the case of Ce(Ni,Co)Sn.\(^3\) Such an interpretation of the effect of U doping helps us also to understand a decrease in the Curie-Weiss temperature. It was shown previously\(^2\) that Kondo temperatures can be estimated from susceptibility data as $T_K = \Theta_{CW}/4$. So, a decrease in Curie-Weiss temperature with U doping agrees well with the idea of hybridization being reduced due to U doping.

With this change of Fermi level due to U doping, we are also able to understand the marked change in the thermoelectric power with small U concentrations. After all, Cu doping with one more electron than Ni is seen to have more substantial effects on the low-temperature pseudogap behavior in recent NMR experiments\(^23\) than an equivalent concentration of Co or La.

It is to be noted that significant doping effects are visible below about 20 K, which is the coherence temperature of pure CeNiSn. Although the low-temperature peak in the thermopower data collapses easily with 1.6% U doping, thermopower data below 20 K continue to change markedly even until 10% of U substitution. (Similarly strong alloying effect in thermopower was found for another Ce low-carrier system, CeRhSb.\(^24\)) Simultaneously, the magnetization increases with doping at low temperature before showing the sign of the magnetic ordering for 20% U. The resistivity behaves also similarly with the most dominant changes due to doping occurring below 20 K. This kind of behavior together with previous measurements indicates that there are two energy scales in CeNiSn: one is the coherence energy of size 20 K and the other is probably the crystal-field splitting energy, and U doping with one more $f$ electron than Ce, i.e., increasing spin fluctuation affects the lower-energy scale most. It may be rather surprising that the coherence energy seems to exist even after the pseudogap behavior disappears in most measurements. In this context, we would like to recall recent inelastic neutron data on Ce(Ni,Co)Sn.\(^25\) According to this, the spin gap found in CeNiSn is still visible for 10% Co-doped CeNiSn although the Co-doped sample does not show the gap feature in thermodynamic data as noted. What is interesting with our data is that the magnetic ordering develops after the coherence energy, not the pseudogap feature, is more or less removed.

Finally, we discuss the antiferromagnetic ordering seen in (Ce$_{0.8}$U$_{0.2}$)NiSn. As we have indicated, the weak magnetic transition is likely to arise from less hybridized Ce moments due to U doping. From recent muon spin-relaxation experiments on similar compositions of (Ce,U)NiSn,\(^26\) we have found that the initial asymmetry indeed decreases markedly for 20% U substitution, which is in good agreement with the conclusion expressed here. From the analysis of the data using a stretched exponential function, it is suggested that the nucleation of magnetic order is inhomogeneous.

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