Stabilization of the collective Kondo semiconducting state by Sb doping in CeNiSn$_{1-x}$Sb$_x$ and the criterion of its appearance

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Semimetallic CeNiSn is shown to transform into a Kondo semiconductor upon the substitution of few percent of Sb for Sn. The full-gap formation is not decisively influenced by the atomic disorder introduced by the substitution. Instead, the extra valence electrons introduced with the Sb doping (one per Sb atom) contribute to the formation of the collective Kondo spin-singlet state at low temperatures, as seen by a reduction of magnetic susceptibility. The definition of the Kondo semiconductor is provided and the difference with either the band-Kondo or the Mott-Hubbard insulators is stressed.

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Kondo insulators (KI) have been discovered some time ago [1] and belong to the class of either nonmagnetic semiconductors with the narrow gap known or to semimetals, both with a heavy-fermion metallic state setting in gradually at elevated temperatures $T > \Delta$. Their nature is known to a lesser extent than that of heavy fermion metals. CeRhSb is an example of the full-gap semiconductor with the conductivity gap $\Delta \approx 7.6$ K [2] whereas CeNiSn is a semimetallic system [3] with the gap vanishing at least in some directions in reciprocal space. Recently, we have discovered a quantum critical point for the system CeRhSb$_{1-x}$Sn$_x$ with $x \approx 0.12$, when the system undergoes a transition from the KI state to the metallic (non-Fermi liquid, NFL) state. In that system the carrier concentration diminishes upon the Sn substitution for Sb. Therefore, one can ask the basic questions: what happens when by doping we act in the opposite direction, i.e. increase the carrier concentration, (e.g. synthetize the system CeNiSn$_{1-x}$Sb$_x$)? Will the increased concentration of carriers produce a Kondo semiconducting state with a Kondo-singlet collective state reducing essentially the magnetic susceptibility and thus producing at the same time a gap, which can be seen in the temperature dependence of the electrical resistivity $\rho(T)$? We show here that this is indeed the case, i.e. the substitution of 2% of Sb for Sn in CeNiSn produces a gap of magnitude $\Delta \approx 4$ K (the polycrystalline-sample data for $x = 0$ exhibit an overall gap $\Delta \approx 1.7$ K). The gap, associated in the following with the collective-Kondo-state formation, is most directly singled out by an intrinsic magnetic susceptibility $\chi(T)$ reduction when lowering the temperature. Furthermore, the universal scaling law $\rho(T)\chi(T) = \text{const}$ is obeyed when lowering $T$ and is claimed to represent a universal characteristic of those strongly correlated systems. The above three features (activated behavior of $\rho(T)$, reduction of $\chi(T)$, $\rho(T)\chi(T) = \text{const}$) constitute unique, in our view for the first time, complete definition of the Kondo semiconductor (insulator at $T > \Delta$) from an experimental side. In this respect, the present data confirm the earlier results for CeRhSb$_{1-x}$Sn$_x$ [2]. Additionally, with the increasing temperature the system evolves from Kondo semiconducting state into a (moderately) heavy fermion state. We also provide the analysis of the systematic evolution of the CeNiSn$_{1-x}$Sb$_x$ systems as a function of $x \ll 1$.

It follows from our analysis, that the formation of the Kondo-insulator state is mainly due to the formation of a collective spin-singlet state and may not be necessarily connected with the particular (integer) number of electrons involved. Hence in this case, the KI state is not either a full-band insulator composed of heavy quasiparticles or the Mott-Hubbard-type magnetic semiconductor, as the band filling is noninteger. The difference between the Kondo-band and the Kondo collective state has been shown in Fig. 5 of Ref. 3b. In this paper the latter picture is confirmed directly. The effect of the atomic disorder introduced by the substitution is not regarded as crucial (see below).

We start with presentation of our experimental results and only then draw the conclusions specified already above. Polycrystalline samples of CeNiSn$_{1-x}$Sb$_x$ have been prepared by arc melting of $(1-x)$ (CeNiSn) and $x$ (CeNiSb) on a water cooled copper hearth in a high purity argon atmosphere with Al getter. Each sample was remelted several times and annealed at 800°C for 2 weeks. Analysis of the x-ray diffraction pattern with the Powdered-Cell program revealed that the samples with $x \leq 0.22$ crystallize in an orthorhombic $\epsilon$-TiNiSn structure. The lattice parameters of the components are practically $x$ independent because of similar atomic radii of Sn and Sb. However, measurements of the specific heat displayed weak anomalies at $\sim 6$ K, which are attributed to the magnetic ordering of the impurity phases of CeO$_3$. The impurity inclusion is present in most of the CeNiSn samples (see e.g. Ref. 4). Electrical resistivity measurements were carried out using a standard four-wire technique. The ac susceptibility was measured in the magnetic field of 10 Oe using Lake Shore susceptometer.

In Fig. 1 we plot the temperature dependence of the resistivity $\rho(T)$ for the CeNiSn$_{1-x}$Sb$_x$ samples. Note that the
are quite heavy as well. 

$T$ for CeNiSn is almost linear with $\chi$, the curves follow then the $x$ states. Namely, the number of excited carriers in the zero-gap sample is of the magnitude $10^{-4}$, of $\chi$ of the collective Kondo singlet type of state. Although the decrease in $T$ strongest for $\chi$ dependence of $\chi$. The circumstance that the resistivity is of the order $10^{-2} \mu \Omega \text{cm}$ speaks in favor of good quality of our polycrystalline samples. The most important fact here is that the intentional impurities (Sb) stabilize the semiconducting-gap state and thus produce a true Kondo semiconducting state even though the doping nominally composes a fractional filling of the valence band. The reference level $\rho_0$ of $\rho(T)$ increases with the increasing substitution $x$ and thus must be due to the atomic disorder.

An important conclusion can be drawn already at this stage. Namely, the presence of this semiconducting state cannot be related to any particular band filling, as would be the case for either the nonmagnetic Kondo-band state or the Mott-Hubbard magnetic semiconductors. So, by Kondo semiconducting state we mean a binding of all electrons involved into a collective spin-singlet state, as discussed next.

In Fig. 2 we present the temperature dependence of $ac$ magnetic susceptibility $\chi$. While $\chi(T)$ for the pure system ($x = 0$) is increasing with the decreasing temperature for $T \leq 25$ K, the corresponding data for $x > 0$ exhibit the $\chi(T)$ downturn when $T$ is lowered. The systems exhibit also a sharp upturn at low temperatures $T \leq 5$ K. Important is to note that in that low-$T$ range $\chi(T) = \chi_0 + nC/(T - \Theta)$ for pure system, with $\chi_0 = 5.6 \times 10^{-4} \text{emu/mol}$, $C = 1.86 \times 10^{-3} \text{emu/K mol}$, and $\Theta = -0.7$ K. In view of the circumstance, that the molar Curie constant for Ce$^{3+}$ ion is $C = 0.807$ emu/K mol, this upturn is ascribed to the Ce interstitial impurities of the concentration $n = 0.4\%$. Conversely, the samples with $x > 0$ exhibit a pronounced downturn, which is attributed to the formation of the collective Kondo singlet type of state. Although the decrease in $\chi(T)$ here is not as spectacular as in the CeRhSb$_{1-x}$Sn$_x$ case, it must be associated with the formation of a nonmagnetic collective state and the effect is the strongest for $T \leq 20$ K. The sharp increase of $\chi$ as $T \to 0$ is regarded again as due to the impurity phase Ce$_2$O$_3$, as all the curves follow then the $x = 0$ dependence, with only moderately changed parameters. Note also that the $\chi$ decrease for CeNiSn is almost linear with $T$ reflecting the intrasices of the pseudogap shape of the quasiparticle density of states. Namely, the number of excited carriers in the zero-gap sample is $\sim k_B T \rho(\epsilon_F)$, where $\rho(\epsilon_F)$ is the density of states at the Fermi level. Also, the magnetic susceptibility is proportional to that carrier concentration, if their appearance comes from breaking of the collective Kondo-spin-singlet state (with $\chi \approx 0$). In effect, the temperature dependence of $\chi$ will be roughly linear in $T$, as observed. This is not the case in the full-gap state for $x > 0$. The value of $\chi_0$ depends in a nonsystematic manner on $x$; hence, it must be ascribed to the impurity narrow-band contribution of the magnitude $10^{-4} - 10^{-3} \text{emu/mol}$, which is a quite large number. This means that the impurity-band electrons are quite heavy as well.

In Fig. 3 we plot the scaling $\rho^{-1}$ vs. $\chi$ and regard it as one of the basic properties of the Kondo semiconducting...
FIG. 2: The susceptibility vs. temperature for the pure \((x = 0)\) and Sn doped samples of CeNiSb\(_{1-x}\)Sn\(_x\). Note a pronounced linear \(T\) behavior for \((x = 0)\) and a value \(\chi_0\) which is of a nonsystematic nature (and attributed to extrinsic impurity-band contribution).

FIG. 3: Scaling of the inverse resistivity with the magnetic susceptibility. The data for \((x = 0.02)\) and \((x = 0.06)\) fall into a single curve when shifted vertically.

systems. This type of scaling is absent for the pure CeNiSn system. Therefore, only the system with \(x > 0\) can be regarded as such. One sees that the \(\chi(T)\) diminution is a clearer sign of the onset of the collective Kondo-singlet state rather than the activated character resistivity \(\rho = \rho(T)\). This is partly because the impurity band is present even for pure samples (cf. Fig. 1). The overall decrease of \(\chi\) with the increasing \(x\) may be influenced to some degree to the disorder, but this cannot be singled out at present.

In principle, it is possible that the disorder creates localized states in the pseudogap region. This is in agreement with the trend observed in Fig. 1, where the most heavily doped samples \((x = 0.1\) and \(0.14)\) have the highest resistivity caused by the \(\rho_0\) increase. Nevertheless, the activated behavior is reduced then \((\Delta \simeq 3.7\) K), so the effect of the disorder should not be crucial. Therefore, we assign the full-gap KI state for low \(x\) as primarily due to the increased binding energy caused by the carrier-concentration increase achieved by the substitution.
FIG. 4: Temperature dependence of the (molar) specific heat $C/T$ - for CeNiSn$_{0.82}$Sb$_{0.18}$. The extrapolated value of the linear-specific-heat coefficient is $\gamma = 174$ mJ/molK$^2$. 

The question remains whether the growing value of $\chi$ in the low-$T$ range (cf. Fig. 2) may indicate an onset of a magnetic ordering or of enhanced magnetic correlations below about 5 K. For that purpose the specific heat has been measured, as displayed in Fig. 4 for the sample with $x = 0.18$. The value of $\gamma = 174$ mJ/molK$^2$ has been extracted from the $C/T$ data vs. $T^2$ in the higher-$T$ regime, as shown. Those data indeed show for lower $x$ a cusp-like behavior near the lowest temperature measured. It is tempting to say that it provides an evidence for a disordered antiferromagnetic arrangement ($\Theta < 0$) of impurity phase containing Ce$^{3+}$ 4$f$ spins. This means that the Kondo screening of the $(17 + x)$ valence electrons of the 4$f^1$ spin moment of Ce$^{3+}$ impurities ions is not complete but, the Kondo binding energy ($2\Delta$) is a well defined bulk effect. In other words, impurity Ce$^{3+}$ spins do not hybridize with valence states. These impurities are unfortunately always present in this class of compounds, in both poly- or monocrystalline. Also, the present study is complementary to that for CeRhSb$_{1-x}$Sn$_x$, where a well defined Kondo-lattice insulating has been destroyed at critical value of $x \simeq 0.12$, where a quantum critical point and a phase transition KI$\rightarrow$NFL have been detected. Here we did not observe such a quantum phase transition to the KI state, as the pure system CeNiSn exhibits already the KI semi-insulating behavior (cf. Fig. 1). Nevertheless, the stabilization of the full-gap state is an interesting phenomenon by itself, as the combined role of the disorder and the increased carrier concentration (and atomic disorder, to a lesser extent) can be seen in a clear fashion.

One should note that a gradual evolution from the heavy fermion state ($T \gtrsim 10$ K) into a Kondo semiconductor ($T \lesssim \Delta$) is related to the onset of localization of 4$f$ electrons with a concomitant formation of the compensation cloud bound to those localized moments. The effect is collective because almost all Ce$^{3+}$ moments in the lattice are being compensated. In the opposite regime of high temperatures, the quantum coherence (itineracy) of $f$ electrons is destroyed by the thermal disorder. So, in principle, we should distinguish between the coherence temperature $T_{coh}$ and the effective Kondo temperature $\Delta$; at least for the system evolving with the decreased temperature from metal with localized $f$ electrons, through the (moderately) heavy-fermion phase, to a Kondo semiconductor (insulator at $T = 0$) or a semimetal. The heavy-fermion state requiring itineracy of electrons, takes place in the temperature range $\Delta \lesssim T \lesssim T_{coh}$. The scaling $\chi \sim \rho^{-1}$ implies that there is a single energy scale for both the thermal activation ($\rho$) and the singlet binding ($\chi$).

The semimetallic nature of CeNiSn means that the sizeable part of the hybridization between 4$f$ and the remaining valence electrons is of intersite nature in that case and vanishes in some directions in reciprocal space. With the Sn doping, the intraatomic part of this hybridization dominates and leads to the reduction of the density of states at the Fermi level, as seen in our photoemission data to be analyzed elsewhere. In effect, the intraatomic Kondo coupling is also strengthened upon Sn substitution.
In summary, we have shown that a Kondo semiconducting state can be created by the Sb doping of semimetallic CeNiSn. Let us stress again, atomic disorder introduced by the doping is not of primary relevance, but the extra electrons introduced with the Sb. The fractional (noninteger) number of introduced electrons must create a collective bound state of the Kondo type, and eliminates other possibilities, namely, the formation of either a Kondo band insulator or a Mott-Hubbard or Anderson insulating types of states. The formation of the collective Kondo-singlet state is determined by a (essential) reduction of the magnetic susceptibility in low-\(T\) range, as well by the presence of the scaling \(\chi(T)\rho(T) = const\), not only by the activated behavior of \(\rho(T)\). This work should be supported further by experiments on high-quality monocrystalline samples.

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