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Stabilization of Kondo Semiconductor State by Sb Doping of $CeNi_{1-\delta}Sn_{1+\delta}$ and the General Criterion of Its Appearance

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Semimetallic off-stoichiometric $CeNi_{1-\delta}Sn_{1+\delta-x}Sb_x$ system with $\delta \approx 0.06$ is shown to transform into a *Kondo semiconductor* upon the substitution of few percent of Sb for Sn. The full-gap formation is associated with f-electron localization induced by the combined effect of the collective Kondo-singlet formation and the atomic disorder. Namely, the extra valence electrons introduced with the Sb doping (one per Sb atom) contribute additionally to the formation of the collective *Kondo spin-singlet* state at low temperatures, as seen by a substantial reduction of the magnetic susceptibility. The precise general definition of the *Kondo semiconductor* is provided and the difference with either the simple band or the Mott–Hubbard insulators is stressed.

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1. Introduction

The Kondo insulators (KI) have been discovered some time ago [1] and belong to the class of either nonmagnetic semiconductors with the narrowest gap known, i.e. with the conductivity gap Δ in the kelvin range or to semimetals, both with a heavy-fermion metallic state setting in gradually at elevated temperatures $T \geq \Delta$. Their nature is known to a lesser extent than that of the heavy-Fermi-liquid metals. CeRhSb is an example of the full-gap semiconductor with the conductivity activation energy $\Delta \approx 7.6$ K [1], whereas CeNiSn is an anisotropic semimetallic system [2], with the gap vanishing at least in some directions. Recently, we have discovered [3] a quantum critical point for the system $CeRhSn_{1-x}Sb_x$ 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 Sb substitution for Sn and in effect, the collective Kondo-singlet state is destroyed. 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 $CeNiSn_{1-x}Sb_x$ system? 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 $\rho(T)$?

Here we show that this is indeed the case, i.e. addition of 2% of Sb (nominal amount) for Sn in $CeNi_{1-\delta}Sn_{1+\delta-x}Sb_x$ leads to the activation energy of magnitude $\Delta \approx 4$ K (the polycrystalline-sample data for $x = 0$ exhibit an overall value of $\Delta \approx 1.7$ K). The gap, at least partly associated in the following with the *collective-Kondo spin-singlet-state formation*, is most directly singled out by an intrinsic magnetic susceptibility $\chi(T)$ reduction when lowering the temperature. Furthermore, the universal scaling law $\rho(T)\chi(T) = \text{const}(x)$ is obeyed when lowering T and is claimed to represent a universal characteristic of those strongly correlated systems. The above three features: (i) an activated behavior of $\rho(T)$, (ii) reduction of $\chi(T)$, and (iii) the scaling law $\rho(T)\chi(T) = \text{const}$ constitute *unique*, in our view for the first time, complete definition of the Kondo semiconductor (insulator at $T = 0$) from an experimental side. In this respect, the present data confirm the earlier results for $CeRhSn_{1-x}Sb_x$ [3]. Additionally, (iv) with the increasing temperature the system evolves from the *Kondo semiconducting state* into a (moderately) heavy fermion state. This last feature rules out the possibility that the Kondo semiconductors are band semiconductors or disorder induced Anderson insulators. We also provide the analysis of the systematic evolution of the $CeNi_{1-\delta}Sn_{1+\delta-x}Sb_x$ systems as a function of x in the $x \ll 1$ regime. In the whole paper for the sake of clarity we keep the off-stoichiometry parameter fixed at $\delta = 0.06$.

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. In this case, the KI state is neither a full-band insulator composed of heavy quasiparticles [4] nor a Mott–Anderson-type magnetic semiconductor, as the band filling is noninteger. Hence we are forced to conclude that the full-gap state can be then induced only by the formation of a collective Kondo singlet state. The difference between the Kondo-band and the Kondo collective spin-singlet state has been shown in Fig. 5 of Ref. [3]. In this paper the latter picture is confirmed directly. It is important to note that in KI state f electrons are *localized*, i.e. the Ce^{3+} state is realized in the KI ground state.

2. Experimental

We start with presentation of our experimental results and only then draw the conclusions specified already above. Polycrystalline samples of

$CeNi_{1-\delta}Sn_{1+\delta}Sb_x$ with $\delta \approx 0.06$ 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 ϵ-TiNiSn structure (as CeNiSn). Stoichiometry and homogeneity was checked by the microprobe technique (scanning microscope JSM-5410) and the deviations from the nominal composition were small but substantial. Namely, the CeNiSn sample has the composition $CeNi_{0.94}Sn_{1.06}$, when normalized to Ce content. The same happens for *all* Sb-doped samples. Nonetheless, all off-stoichiometric samples are homogeneous, except rather small islands of highly non-stoichiometric Ce–Ni–Sb–Sn systems. 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 ≈ 6 K, which are attributed to the influence of the impurity phases. The impurity inclusion is present in most of the CeNiSn samples (see e.g. Refs. [5] and particularly [6]). 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.

3. Results and discussion

In Fig. 1 we plot the temperature dependence of the resistivity $\rho(T)$ for the $CeNi_{1-\delta}Sn_{1+\delta-x}Sb_x$ samples. Let us note that the substitution of Sb for Sn increases nominally the number of carriers by one per formula. Nevertheless, this produces an enhanced activated behavior $\rho(T) = \rho_0 + A\exp(\Delta/k_{\rm B}T)$, with the conductivity gap $\Delta \approx 4.3 \pm 0.1$ K for x in the range $0.02 \div 0.06$, as com-

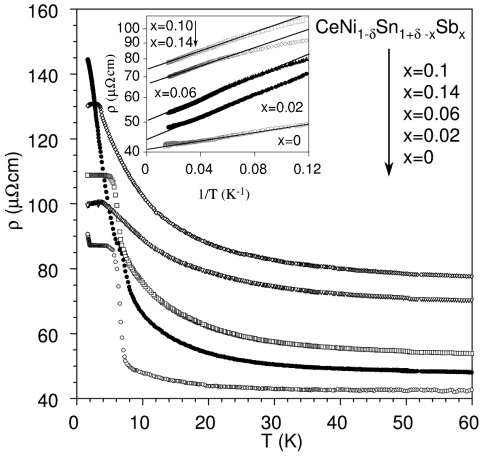

Fig. 1. Temperature dependence of the resistivity in linear and logarithmic (see inset) scales. The presence of plateau indicates an extrinsic (impurity-band) contribution. The activation energy is weakly dependent on x.

pared to the value of the overall gap $\Delta \approx 1.7 \pm 0.1$ K for this off-stoichiometric system $CeNi_{1-\delta}Sn_{1+\delta}$ (see the inset; such activated behavior has also been observed by Aliev et al. [5] for $T < 30$ K). Hence, part of the gap is created by the off-stoichiometry [5]. A leveling of the resistivity is most probably due to the impurity band (as exemplified also by the presence of ρ_0). The circumstance that the resistivity is of the order 10^2 $\mu\Omega$ 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. Such a stabilization of the Kondo insulating state upon substitution necessitates the localization of $4f$ electrons upon minute substitution, as evidenced below [5]. The reference level ρ_0 of $\rho(T)$ increases with the increasing substitution x and thus must be due to the substitutional 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 [4] or the Mott–Hubbard magnetic semiconductors. Therefore, by the 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 χ. While $\chi(T)$ for the nominally 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

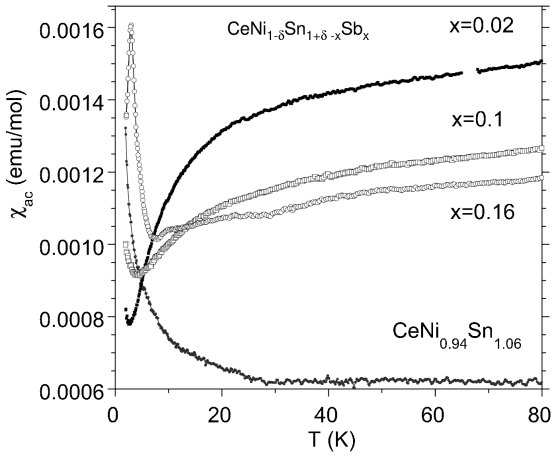

Fig. 2. The susceptibility vs. temperature for the nominally pure ($x = 0$) and Sn doped samples of $CeNi_{1-\delta}Sn_{1+\delta-x}Sb_x$. Let us note a pronounced linear T behavior for $x = 0$ and a value χ_0 which is of a nonsystematic nature (and attributed to extrinsic impurity-band contribution).

range $\chi(T) = \chi_0 + nC/(T - \Theta)$ for pure system, with $\chi_0 = 5.6 \times 10^{-4}$ emu/mol, $C = 1.86 \times 10^{-3}$ 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 $n = 0.4\%$ [3, 5, 7].

However, the samples with $x > 0$ exhibit a pronounced downturn, which is attributed to the formation of the collective Kondo singlet type of state, the formation of which is evident even if the impurity contribution is not subtracted. Although the decrease in $\chi(T)$ here is not as spectacular as in the $CeRhSn_{1-x}Sb_x$ case [3], 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 in χ as $T \to 0$ is regarded again as due to the impurity phase, as all the curves follow then the $x = 0$ dependence, with only moderately changed parameters. The value of χ_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} emu/mol, a quite sizable value. This means that the impurity-band electrons are quite heavy as well. More importantly, the susceptibility for $x = 0.02$ is much higher than that for $x = 0$ sample; this comes from the f-electron localization, and the full--gap formation. It should be mentioned that the nominally pure samples CeNiSn are in reality $CeNi_{0.94}Sn_{1.06}$, as mentioned above. This is the reason why those χ results differ from those for monocrystals [2].

In Fig. 3 we plot the scaling ρ^{-1} vs. χ for selected concentrations and regard it as one of the basic properties of the Kondo semiconducting systems. The scaling $\rho(T)\chi(T) \approx$ const is clearly observed for $x > 0$ and is absent for the pure CeNiSn system. Therefore, only the impure system can be regarded as such [3]. One sees that the $\chi(T)$ diminution is a clearer sign of the onset of the collective Kondo-

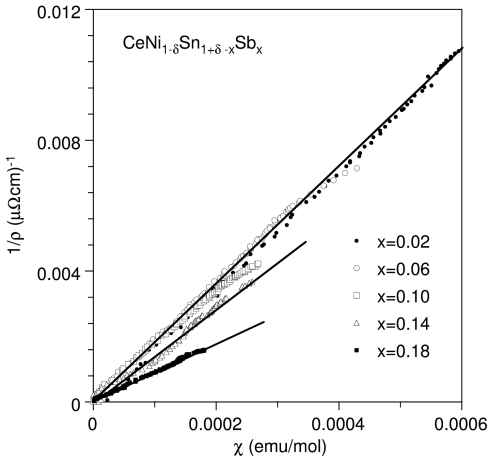

Fig. 3. Scaling of the inverse resistivity with the magnetic susceptibility. The data for $x = 0.02$ and $x = 0.06$ fall into a single curve when shifted. The χ and $1/\rho$ for different x are shifted to the zero values at the minimal positions [3]. The solid lines are only guide to eye.

-singlet state than the activated character resistivity $\rho = \rho(T)$. This is partly because the impurity band is present even for undoped samples (cf. Fig. 1). The overall decrease in χ with the increasing x may be influenced by disorder, but this cannot be singled out clearly 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 ρ_0 increase. Nevertheless, the activated behavior is reduced then only slightly ($\Delta \approx 3.7$ K), so the direct 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, with the concomitant *f-electron localization*.

The question remains whether the growing value of χ 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 samples with $x = 0.04$ and $x = 0.16$. The value of $\gamma = 178$ mJ/(mol K^2) for $x = 0.04$ has been extracted from the C/T data vs. T^2 in the higher-T regime, as shown. A similar value of γ is obtained even for $x = 0.16$. 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+} $4f$ spins. This means that the Kondo screening of the $(17 + x)$ valence electrons of the $4f^1$ spin moment of Ce^{3+} impurities ions is not complete but the Kondo binding energy (2Δ) is a well defined bulk effect. On the

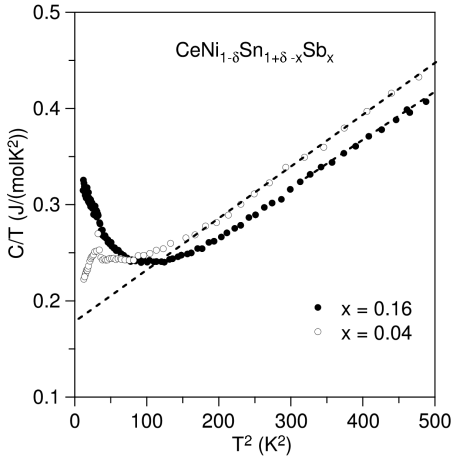

Fig. 4. Temperature dependence of the (molar) specific heat C/T for $CeNi_{1-\delta}Sn_{1+\delta}Sb_x$ with $x = 0.04$ and 0.16. The extrapolated value of the linear-specific-heat coefficient is $\gamma = 178$ mJ/(mol K^2) for $x = 0.04$ and $\gamma = 170$ mJ/(mol K^2) for $x = 0.16$. The low-temperature peak signals a magnetic transition induced by impurities [8].

contrary, 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 samples [4]. Also, the present study is complementary to that for $CeRhSn_{1-x}Sb_x$, where a well defined Kondo-lattice insulating has been destroyed at critical value of $x \approx 0.12$, and 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 $CeNi_{1-\delta}Sn_{1+\delta}$ 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 can be seen in a clear fashion.

One should note that a gradual evolution from the heavy fermion state ($T \geq 10$ K) into a Kondo semiconductor ($T \leq \Delta$) is related to the *onset of localization* of $4f$ electrons with a concomitant formation of the compensation cloud bound to those localized moments. In the opposite regime of high temperatures, the quantum coherence (*itineracy*) of f electrons is destroyed by the thermal disorder. Therefore, in principle, we should distinguish between the coherence temperature $T_{\rm coh}$ below which the f electrons become itinerant heavy quasiparticles and the effective Kondo temperature Δ. In effect, the system evolves with the decreasing temperature from metal with localized f electrons, through the (moderately) heavy-fermion metallic 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 $\Delta \leq T \leq T_{\rm coh}$. The scaling $\chi \sim \rho^{-1}$ implies that there is a single energy scale for both the thermal activation (ρ) and the singlet binding (χ).

The semimetallic nature of CeNiSn means that the sizeable part of the hybridization between $4f$ and the remaining valence electrons is of intersite nature. In that situation the hybridization matrix element is anisotropic and can vanish in some directions in reciprocal space. With the Sb doping, the intraatomic (i.e. $\boldsymbol{k}$-independent) part of the hybridization dominates and leads to the reduction of the density of states at the Fermi level, as seen also in our photoemission data to be analyzed elsewhere. In effect, the Kondo coupling is also strengthened upon Sb substitution.

4. Conclusion

In summary, we have shown that a Kondo semiconducting state can be created by the Sb doping of semimetallic slightly off-stoichiometric CeNiSn. Let us stress again, atomic disorder introduced by the doping is not the only factor, but also the extra electrons introduced with the Sb, in the f-electron localization. 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 [4] or a Mott–Hubbard insulating type of state. Actually, the disorder-free Kondo insulating state contains both the aspect features of both band insulator of heavy quasiparticles and the Kondo

compensating correlations [3]. 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 $\chi(T)\rho(T) = \text{const}$, in addition to the well-known activated behavior of $\rho(T)$. This work should be refined further by experiments on high-quality monocrystalline samples.

Acknowledgments

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