What makes a Kondo insulator/semiconductor?

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Abstract. We provide a brief critical assessment of the concept of Kondo insulator (semiconductor) in view of the experimental results and a simple mean-field-like picture of correlated states within the Anderson-lattice model. A brief distinction between the Kondo semiconductors and either ordinary- or magnetic- (including Mott-Hubbard) -semiconductors is discussed.

1. Introduction
The Kondo insulators (KI) belong to the class of strongly correlated materials forming a group of either nonmagnetic semiconductors [1] with the narrowest gap known (i.e. in the conductivity gap $\Delta$ in the Kelvin range) or to semimetals [2], both with a heavy-fermion metallic state setting in at elevated temperature $T \geq \Delta$. Their nature is known to a lesser extent than that of the stable heavy-Fermi-liquid metals [3]. CeRhSb is an example of the full-gap semiconductor with $\Delta \approx 7.6$ K [1], whereas CeNiSn is an anisotropic semimetallic system [2]. The understanding of these materials is partly obscured by the circumstance that the relatively small values of magnetic susceptibility and the gap when $T \to 0$ lead to their properties alternation by a minute content of magnetic or other impurities [4]. In effect, it is often difficult to differentiate between intrinsic and extrinsic features of these systems. The situation is, in some sense, analogous to that in the early-stage research of semiconductors until the role of nonintentional impurities in, e.g., Ge or Si has been established. Also, a clear distinction from either ordinary, magnetic, and Mott-Hubbard semiconductors should be singled out. The purpose of this critical brief paper is to propose criteria defining the Kondo insulator/semiconductor and then address in an elementary manner the question about the nature of FeSi [5], probably the first system of this type containing 3d electrons.

2. A canonical theoretical interpretation: Kondo semiconductors
The present critical assessment of these Kondo-lattice materials arises from our earlier research on CeRhSb$_{1-x}$Sn$_x$ [6] and CeNi$_{1-\delta}$Sn$_{1+\delta}$/Sb$_x$ [7] systems, as well as that on Ce$_3$Bi$_4$Pt$_3$ [8] and FeSi [5]. The interpretation is based on the earlier saddle-point solution of the Anderson-lattice model [9]. From this accumulated material it follows that the Kondo insulating state can be characterized by the following features:

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The number of valence electrons is an even number. For example, in case of CeRhSb it is 18 electrons (including one 4f electron due to Ce). So has CeNiSn, whereas Ce,Bi,Pt has 54 such electrons and FeSi has 12. From that one can see that a single magnetic moment of either Ce\(^{3+}\) or Fe\(^{3+}\) can be screened to a substantial extent within a single chemical formula if the coupling of the surrounding screening carrier cloud is of antiferromagnetic character. The remaining washing out of the magnetic moment can be achieved by autoscreening, i.e., the intersite antiferromagnetic correlations between the relevant 4f or 3d electrons; as is explicitly seen for the Anderson-lattice model [9].

The resistivity \(\rho(T)\) is often thermally activated in the limited temperature range with a small (or even extremely small [6]) activation gap. A small value of the gap is sometimes not easy to detect as the "very shallow" impurity in-gap states can form impurity bands overlapping with the upper and/or the lower hybridization bands, thus leading to a semimetallic behaviour. The semimetallic state can also be caused by the absence of an intraatomic part of the hybridization and vanishing intersite hybridization in some directions in \(k\) space. For example, the intraatomic part of hybridization between 4f and either 5d or 6s states of Ce vanishes as they have different parity. So does that between 3d states Fe and 3p states of Si, but in this case it is possible between 3d and 4s states, so FeSi from this perspective should be a full-gap system. Also, a residual intraatomic part of hybridization between 4f states due to Ce and 5p states due to Sb can produce a full-gap state. However, this simple rationalization does not work for CeNiSn, which in this view should also be regarded as being in the same category, as CeRhSb.

The magnetic susceptibility \(\chi(T)\) is strongly temperature dependent and diminishes remarkably as \(T\) is reduced below a characteristic temperature and the system does not order magnetically (provided the impurity contribution is identified and properly subtracted).

The resistivity and magnetic susceptibility obey [6] a simple scaling law \(\chi(T)\rho(T)=\text{const}\), particularly in the regime \(k_BT<\Delta\), i.e., when the number of excited carriers is small.

The semiconducting (or semimetallic) state transforms gradually into a moderately heavy-electron metallic state in the region \(k_BT>\Delta\) and/or into a system of localized f or d electrons if either \(k_BT>>\Delta\) or \(\Delta\) is large (\(10^7\) K or larger).

One should note that the features (i), (ii) and (iv) may also be obeyed by intrinsic semiconductors if the susceptibility of excited carriers (after substituting the diamagnetism of filled bands) is detectable. Obviously, neither Mott-Hubbard insulators nor magnetic semiconductors do not fall in this category, as they order magnetically (no screening effect of the carriers; they are also closer to ionic systems). Thus the specific features for the Kondo insulators/semiconductors are those listed under the headings (iii)-(v). Additionally, those systems exhibit a quantum critical behaviour upon electron doping [6], but these topics will not be discussed here.

Universal scaling law: \(\chi(T)\rho(T)=\text{const}\)

We summarize first evidence for the Kondo insulating/semiconducting character of the CeRhSb system and then discuss a situation in Ce,Bi,Pt and FeSi. If the scaling \(\chi(T)\rho(T)=\text{const}\) is characteristic and universal for the Kondo insulators, it should be obeyed for the all known Kondo insulators. In figure 1a-c we have collected the main properties of the full-gap semiconductor CeRhSb\(_{1-x}\)Sn\(_x\), with the conductivity gap \(\Delta = 7.6\) K (a). The scaling law \(\chi(T)\rho(T)=\text{const}\) is clearly obeyed for \(x \leq 0.08\) (b) [6], and the magnetic susceptibility (after subtracting by the impurity effect) \(\chi\rightarrow 0\) when \(T\rightarrow 0\). In figure 2 the scaling law \(\chi\sim\rho^{-1}\) is illustrated for Ce,Bi,Pt. The susceptibility \(\chi(T)\) and resistivity \(\rho(T)\) data obtained for the single crystalline sample are taken from Ref. [10]. In the original \(\chi(T)\) plot, Ce,Bi,Pt exhibits a sharp upturn in the susceptibility at the low temperatures \(T<13\) K. This impurity upturn is described by the presence of Ce interstitial impurities with the concentration of about 1%. In effect, with correction for impurities, the scaling \(\chi\) versus \(\rho^{-1}\) is clearly observed in the temperature region \(4.5\) K < \(T\) < 100 K for Ce,Bi,Pt, (for Ce,Bi,Pt\(_{1-x}\)Sn\(_x\), the gap \(\Delta \approx 60\) K, therefore the
Figure 2. Linear scaling law between the inverse resistivity $\rho$ and the susceptibility $\chi$ for Ce$_3$Bi$_4$Pt$_3$ for 4.5 K $<$ T $<$ 100K. The data are taken from [10].

Figure 2. FeSi; $\rho^{-1}$ vs. $\chi$ for 130 K $<$ T $<$ 300 K. The $\chi$ and $\rho$ data are from [11]. The impurity effect is small for T $>$ 130 K.
impurity effect does not dominate in the temperature region $T > 10$K).

We discuss next evidence for the Kondo insulating character of FeSi which is a nonmagnetic narrow gap semiconductor [5] with unusual features it shares with a class of Ce-Kondo insulators. Very interesting feature, which one encounters in this system, is the fact that the gap ($\Delta \approx 300$ K) disappears gradually at $T_0$ with increasing temperature $T$ [12,13] which has been ascribed theoretically as a typical behaviour for a Kondo semiconductor. The temperature $T_0$ [13] is not identified with the Kondo temperature $T_K$, but represents an instability point of the paramagnetic Kondo semiconductor. Particularly important is the linear $[\Delta(T) \sim (T - T_0)]$ dependence of the gap when approaching $T_0$ (for FeSi, $T_0 \approx 200$ K). A very similar $\Delta(T)$ behaviour was also experimentally observed for the Kondo insulator CeRhSb and CeNiSn semimetal [14]. In contradiction to these data, it has been also reported [15] that FeSi is an itinerant semiconductor whose properties can be explained without a local Kondo-like interaction. We therefore elaborate now more detail about our criteria for FeSi. We should note that the features (i), (ii), and (iii) are obeyed [11]. Figure 3 also illustrates the scaling behaviour $\chi(T) \rho(T) = $ const in the temperature region $130$ K $< T < 300$ K (i.e., in the temperature range where the impurity contribution to $\rho$ and $\chi$ is negligible). Within our criteria a Kondo insulator description seems to be appropriate also for FeSi.

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