



Onsite hybridization between Ce 4*f* and 5*d* states as the indicator of the transition from Kondo insulator to metallic state in CeRhSb

Jerzy Goraus*, Andrzej Ślebarski

Institute of Physics, University of Silesia, 40-007 Katowice, Poland

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ABSTRACT

We discuss and determine the conditions under which a Kondo-insulator phase is stable. We show for CeRhSb that the dependence of the onsite hybridization energy V_{df} between the Ce 5*d* and Ce 4*f* states on the number of valence electrons or the unit cell volume is decisive for the hybridization Kondo gap formation. We also propose the method for determining the energy V_{df} from the *ab initio* calculations. This approach supplies an accurate Kondo-insulator–metal transition in agreement with the recent experimental data.

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1. Introduction

Ce-based Kondo-lattice intermetallics exhibit a variety of unusual ground states, including complex magnetic structures, heavy fermion (HF) states both normal and superconducting, and paramagnetic insulating Kondo lattices (KI). The magnetic/nonmagnetic behavior of a dense Kondo system is largely controlled by the strength of the on-site hybridization V_{cf} among conduction and *f*-electron states. The strength of the *c*–*f* exchange interaction can be tuned by either the composition or pressure and results in a competition between the intrasite Kondo and the intersite Ruderman–Kittel–Kasuya–Yosida (RKKY) interactions. The first such model of the HF metals was proposed by Doniach [1], who obtained a simple phase diagram which displays the magnetic ordering temperature T_{RKKY} as a function of $J_{cf}N(\epsilon_F)$, where the exchange-coupling $J_{cf} \sim V_{cf}^2$ and $N(\epsilon_F)$ is the density of states (DOS) at the Fermi level. The J_{cf} can be varied by chemical substitution. A good deal of theoretical work (e.g., Ref. [2]) on Kondo three-dimensional lattices has been carried out since Doniach's work. The essence of physics in the low-temperature region is grasped by periodic Anderson model. It has been shown [2], that the stability of the magnetic ground state in the Kondo-lattice limit is first of all strongly dependent on V_{cf} and the number of valence electrons n_e . The theoretical phase diagram on the V_{cf} – n_e plane

has been shown to provide a qualitative account for experimental results on the series of Ce-ternary intermetallics [3]. Within the periodic Anderson model the paramagnetic Kondo-insulator state was obtained [2] for CeRhSb and CeNiSn in the $n_e = 2$ limit and for large hybridization energy V_{cf} .¹ Our systematic study has also shown that the gap in the doped CeRhSb or CeNiSn Kondo insulators is very sensitive to the degree of hybridization. The transition from KI to a metallic region observed as a function of variable valence electron number induced by substitution of Rh for Ni (Ref. [4]) in CeNiSn, Pd for Rh in CeRhSb [5], or La for Ce in the both KIs [6] and of accompanying effect of the significant change of hybridization parameter² $\Delta = \pi V_{cf}^2 N(\epsilon_F)$ at the critical concentration ~ 6 –10% of the doping element give evidence for the universal behavior in Kondo insulators. Recently [8, 9] we have discovered a quantum critical point with $x = x_c \approx 0.12$, when the system CeRhSb_{1–x}Sn_x undergoes from the KI state to

¹ In Ref. [2], the Kondo insulating state is obtained for $n_e = 2$ and the hybridization energy $V_{cf} > 0.35 W$, where V_{cf} is in the band width units. For the Kondo-insulator limit we roughly estimated the value of $V_{cf} > 0.35$ eV, considering the band width $W \sim 1$ –2 eV and very low density of the residual states located in the gap (pseudogap). Note, $V_{cf} = \sqrt{\frac{\Delta}{\pi N(\epsilon_F)}}$ is mostly determined by the value of DOSs at the Fermi level. In case of KI state, $N(\epsilon_F)$ is very small either from *ab initio* calculations or from XPS valence band spectra.

² The quantitative analysis of the Ce-3*d* XPS spectra can be done on the Gunnarsson and Schönhammer (GS) model calculations [7]. The hybridization parameter $\Delta = \pi V_{cf}^2 N(\epsilon_F)$. According to the GS model, the Δ value can be estimated from the ratio $I(f^2)/[I(f^1) + I(f^2)]$, where $I(f^n)$ is the intensity of the f^n peak in the Ce-3*d* XPS spectra.

* Corresponding author.

E-mail addresses: jerzy.goraus@us.edu.pl (J. Goraus), andrzej.slebarski@us.edu.pl (A. Ślebarski).

the metallic (*non-Fermi liquid*, NFL) state.³ In that system the carrier concentration diminishes upon the Sn substitution for Sb, also the rapid decrease of energy Δ has been experimentally obtained at this critical concentration, which separates the KI region with $\Delta \approx 150$ meV from the metallic one with $\Delta \approx 80$ meV.

Here, we present theoretical argumentation for the Kondo-insulator–metal transition in the series of $\text{CeRhSb}_{1-x}\text{Sn}_x$ compounds, basing on full potential local orbital (FPLO) calculations within virtual crystal approximation (VCA). With the substitution of Sn for Sb we diminish by one the number of valence electrons, so we can study the Kondo insulating state as a function of carrier number and its subsequent metalization within VCA. We analyzed theoretically the onsite hybridization energy V_{df} between the Ce-5d and Ce-4f states as obtained from the band structure calculations, and found a drastic change of V_{df} at the concentration $x = 0.12$, which well agrees with x_c obtained experimentally for $\text{CeRhSb}_{1-x}\text{Sn}_x$. For comparison we also present the V_{df} calculations for the series of hypothetical metallic $\text{CeRhSn}_{1-x}\text{In}_x$ compounds, where the anomalous $V_{df}(x)$ behavior is absent in our calculations. We also calculated the pressure dependence of the matrix element V_{df} in CeRhSb and we found its anomalous change at critical pressure that separates the KI region from the metallic one.

Our recent studies of different Ce-based intermetallic compounds on the base of theoretical phase diagram [2] V_{cf} – n_e allowed us to interpret magnetic ground state of the Kondo lattice system, assuming that V_{cf} and n_e are independent variables. Inside the general two band model considerations these two variables can be independent, however, in the real intermetallic compound the change of the number of carriers induces the change of the hybridization. Within one-electron approach used in the DFT theory this can be understood on the following basis: the change of the number of carriers induces the change in the local atomic potential which influences the shape of the local orbitals obtained in the self-consistent procedure. Therefore the analysis of the Kondo-insulator–metal transition in $\text{CeRhSb}_{1-x}\text{Sn}_x$ (to see the effect of the decreasing number of conduction electrons on the gap formation in CeRhSb) on the base of the model in Ref. [2] is rather qualitative. In this Letter we study the onsite hybridization between Ce-5d and Ce-4f states V_{df} , which in contrast to V_{cf} doesn't depict the interaction of f state with all Bloch waves; we are limiting our investigations only to the 5d states on the same atom. Note, that in this approach V_{cf} and V_{df} should not be directly compared. It seems to be clear, that the hybridization V_{df} points to critical behavior in $\text{CeRhSb}_{1-x}\text{Sn}_x$ series and can be crucial in explaining quantum critical phenomena at $x \approx 0.12$.

2. Calculation details

The electronic structure of the $\text{CeRhSb}_{1-x}\text{Sn}_x$ series was studied using the FPLO method (FPLO5-00-20 computer code [10]) accomplished within VCA approach. The calculations were performed for $x < 0.3$ with the step $\Delta x = 0.03$ for the lattice parameters obtained experimentally. The lattice parameters of the compounds $\text{CeRhSb}_{1-x}\text{Sn}_x$ are practically independent of x because of the similar atomic radii of Sb and Sn atoms. The exchange cor-

³ Our previous alloying studies [9] showed that the $\text{CeRhSb}_{1-x}\text{Sn}_x$ series contains the single-phase with ϵ -TiNiSi-type structure only for $0 \leq x \leq 0.2$ (for $0.78 \leq x \leq 1$ the Fe_2P -structure exists, whereas for $0.2 \leq x \leq 0.78$, the samples are not single phase). On the Sb-rich side [8] ($0 \leq x \leq 0.2$) the Kondo semiconducting state evolves (as a function of the number of carriers) into non-Fermi liquid metallic state via a quantum critical point located at $x = 0.12$. We noted, however, that the residual density of states at the Fermi level continuously increase with doping due to an atomic disorder. On the Sn-rich side (metallic state for $0.78 \leq x \leq 1$) we observed [9] both the singular quantum fluctuations associated with the 4f electrons and the 4d-spin fluctuations.

relation potential V_{xc} was used in the form proposed by Perdew and Wang [11]. Calculations were carried out in scalar relativistic, spin resolved way; in all cases, however, we obtained nonmagnetic ground state (what is in agreement with experimental data). We considered (6s, 6p, 5d) as valence states for Ce and (5s, 5p, 4d) for Rh, Sb, Sn. Following states were considered as semicore states: (4f, 5s, 5p) states for Ce and (4s, 4p) states for Rh, Sb, Sn. Polarization states 5d were included in case of Sb, Sn, Rh. The calculations were carried out for 343 k-points in irreducible Brillouin zone. Coulomb correlations were included within LSDA + U [12,13] approach, with $U = 6$ eV (which is a typical value for strongly correlated Ce systems).

FPLO5 code allows to output radial part of the local orbitals, as well as the onsite atomic potential including also the non-spherical part in a basis of spherical harmonics. Moreover, it allows the evaluation of the total potential at the arbitrary point in a unit cell (which includes also the influence of neighboring atoms). In this Letter we have used two approaches: one which used the local potential (LP) which is the sum of Ewald, Hartree and V_{xc} at an atomic site (it neglects the influence of the neighboring atoms), and the second which used total potential (TP) at an atomic site (the sum of all contributions to potential at a given point in real space). The total potential was evaluated on the uniform spherical grid with the center at one of the equivalent 4c Wyckoff positions occupied by the Ce atom. The radial grid included 2000 points (up to 10 atomic units). The both, azimuthal grid and zenith angle grid contained 60 points. This total potential was evaluated in real space and then projected onto the Y_{lm} basis for $l < 6$ so that $V_{lm}(r)$ was obtained.

All the presented results were carefully checked for convergence, with total energy convergence better than 10^{-6} Hartree. The onsite hybridization between Ce 5d and 4f states is defined in Eq. (1).

$$V_{hyb}(n_1, l_1, n_2, l_2) = \sum_{l,m} \int \bar{\psi}_{n_1 l_1 m_1}(r, \theta, \phi) V_{lm}(r) Y_{lm}(\theta, \phi) \times \psi_{n_2 l_2 m_2}(r, \theta, \phi) r^2 \sin \theta d\theta d\phi dr \quad (1)$$

In a spherical atomic potential approximation the onsite hybridization between the states with different l or m quantum numbers is impossible due to the orthogonality condition for the spherical harmonics $\int Y_l^m Y_l^{m'} \sin \theta d\theta d\phi = \delta_{ll'} \delta_{mm'}$. This is, however, not the case of a non-spherical potential, which can be expressed in a basis of spherical harmonics. Namely, for a given crystal symmetry only some l and m numbers are allowed. Then, the integral equation (1) can be separated on spherical part (Eq. (2)) and angular one, which is effectively present in Φ_{m,l,l_1,l_2} shown in the expression for $V_{l_1,l_2}(r)$ (Eq. (3)).

$$V_{hyb}(n_1, l_1, n_2, l_2) = \int R_{n_1 l_1}(r) V_{l_1,l_2}(r) R_{n_2 l_2} r^2 dr \quad (2)$$

$$V_{l_1,l_2}(r) = \sum_{l,m} \Phi_{m,l,l_1,l_2} V_{lm}(r) \quad (3)$$

The hybridization between states of different l and m is possible according to Eq. (4).

$$\Phi_{m,l,l_1,l_2} = \sum_{\substack{-l_1 \leq m_1 \leq l_1 \\ -l_2 \leq m_2 \leq l_2}} (-1)^{m_1} \int Y_{l_1}^{-m_1} Y_l^m Y_{l_2}^{m_2} \sin \theta d\theta d\phi \quad (4)$$

The integral in Eq. (4) can be calculated from Wigner 3j symbols as is shown in Eq. (5).

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