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Author: Andrzej Ślebarski, Adam Jezierski, M.B. Maple, A. Zygmunt

Citation style: Ślebarski Andrzej, Jezierski Adam, Maple M.B., Zygmunt A. (2001). Hybridization gap in some ternary f-electron and d-electron intermetallics."Acta Physica Polonica B" (Vol. 32, no. 10 (2001), s. 3331-3344).

Vol. 32 (2001) *ACTA PHYSICA POLONICA B* No 10 Special Issue

HYBRIDIZATION GAP IN SOME TERNARY *f*-ELECTRON AND *d*-ELECTRON INTERMETALLICS*

A. Ślebarski

Institute of Physics, University of Silesia
Uniwersytecka 4, 40-007 Katowice, Poland

A. Jezierski

Institute of Molecular Physics
Polish Academy of Sciences
Smoluchowskiego 17/19, 60-179 Poznań, Poland

M.B. Maple

Institute for Pure and Applied Physical Sciences, University of California
San Diego, La Jolla, CA 92093-0360, USA

and A. Zygmunt

W. Trzebiatowski Institute of Low Temperature and Structure Research
Polish Academy of Sciences
Okólna 2, 50-950 Wrocław, Poland

(Received June 21, 2001)

In this work we have discussed electronic structure, structural and magnetic properties of the CeMX-type compounds, where M is a transition metal and X is an *sp* element. The main goal of this presentation is to find the influence of metal M on the coherent gap formation at the Fermi level in the Ce-Kondo insulators. We also discuss a similar semiconductor-like resistance anomaly of Fe_2TiSn and CeNiSn-type Kondo insulators.

PACS numbers: 75.30.Hx

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[*] Presented at the XII School of Modern Physics on Phase Transitions and Critical Phenomena, Lądek Zdrój, Poland, June 21–24, 2001.

1. Introduction

CeNiSn and CeRhSb exhibit an puzzled ground state in the Kondo lattice [1–3]. The class of these materials, *e.g.*, "Kondo insulators", is characterized by their electronic properties, which at high temperatures is associated with a set of independent localized $4f$ moments interacting with the Conduction Electrons (CE), while at low temperatures the electronic properties resemble those of narrow gap of the order ~ 10 K (Ref. [4]). The energy gap opening in these compounds is believed to be due to the hybridization between the strongly correlated $4f$ electrons and a conduction band, which is almost half filled [5].

Among the "Kondo insulators" CeNiSn and its isostructural compounds (ε-TiNiSn type structure belonging to a space group $Pnma$) have attracted much attention, because they exhibit behaviors of anisotropic "semiconductors" with a highly renormalized energy gap. These compounds are also found to be very sensitive to a small amount of impurities such that the residual density of states (DOS) at the Fermi level increases drastically proportional to the square root of impurity concentration [6]. A V-shaped DOS near E_{F} was inferred from the nuclear magnetic relaxation rate [7] and thermodynamic properties [8]. CeNiSn thus seems to exhibit an apparent concentration of CE between the metallic conductivity and the gaprise behavior.

Band structure calculations predict CeNiSn and CeRhSb to be a semimetal with a pseudo gap that closes along some directions, [9–12] or small-gap insulator with an anisotropic hybridization gap and a V-shaped DOS at E_{F} [13]. The numerical calculations [11] and the XPS valence band spectra [12] also show that a V-shaped pseudo gap formation is strongly dependent both on the hybridization between the Ce $4f$ states and the transition metal-d states, and on the Ce $4f$–Sn sp hybridization. Thus it is of interest to investigate the properties of other members of the family of equiatomic ternary compounds. In this paper we report our results on the electronic structure and magnetic properties of CeMSn and CeMSb, where M is d-type metal.

Recently, we have been engaged in a systematic study of the cubic $L2_1$-type intermetallic compound $\mathrm{Fe_2TiSn}$, the physical properties of which are quite unusual [15, 16]. $\mathrm{Fe_2TiSn}$ is an excellent example of a Heusler-type alloy, in which the local environment profoundly influences the magnetic and electrical transport properties. $\mathrm{Fe_2TiSn}$ is a weakly ferromagnetic Kondo system with a semiconducting gap which, however, is strongly reduced by a local environment. A similar feature in the electronic structure and a semiconductor-like resistance anomaly have been observed in FeSi, which has been classified as a unique d-electron system that belongs to the family of the Kondo insulators [17]. Some Heusler -type alloys, *e.g.*, Fe_2VAl [14], Fe_2TiSn [15,16] are narrow gap semiconductors with unusual features which are shared with Ce-hybridization gap semiconductors or Ce-Kondo insulators. Another common behavior that is emerging for heavy fermion f-electron and d-electron intermetallics is that the chemical substitution on the local disordering tends to suppress the gap [16]. The main goal of this presentation is to find the influence of the electronic structure on the coherent gap formation at E_F in the Kondo-insulators.

2. Experimental details

Polycrystalline samples were arc-melted on a water cooled copper hearth in a high purity argon atmosphere with a Zr getter and annealed at 800 °C. The compound was carefully examined by X-ray diffraction analysis and was found to consist of a single-phase. The dc magnetization was measured using a commercial SQUID magnetometer from 1.8 K to 300 K in magnetic fields up to of 5 T. Electrical resistivity measurements were made with an ac resistance bridge operating at 16 Hz, using a standard four-wire technique. The specific heat C was measured in the temperature range 0.5 K–70 K with a ^{3}He relaxation calorimeter using the heat pulse technique. The XPS spectra were obtained with monochromatized Al K_α radiation at room temperature using a PHI 5700 ESCA spectrometer.

The electronic structure of the ordered compound was studied by the self-consistent tight binding Linearized Muffin-Tin Orbital (LMTO) method [18] within the Atomic Sphere Approximation (ASA) and the Local Spin Density (LSD) approximation. The exchange correlation potential was assumed in the form proposed by von Barth–Hedin [19] and Langreth–Mehl–Hu (LMH) corrections were included [20]. In the band calculations, we assumed an initial atomic configuration. The electronic structure was computed for the experimental lattice parameters for the supercell model. The values of the atomic sphere radii were taken in such a way that the sum of all atomic sphere volumes was equal to the volume of the unit cell.

3. Band gap stability in ternary intermetallic compounds

3.1. Gap suppression in CeNiSn and CeRhSb

In recent years, cerium-based ternary intermetallic compounds of the form CeMX, where M is a transition metal and X is an *sp* element, have been a subject of intensive studies [21]. These compounds have a number of different types of ground state including magnetic, metallic, and insulating, and they exhibit anomalous physical properties, such as the Kondo effect, Heavy Fermion (HF) behavior, Valence Fluctuations (VF) and also non-

Fermi liquid behavior. Tables I and II display these interesting properties of the compositionally similar compounds CeMSn to CeNiSn, and CeMSb to CeRhSb. We will discuss the properties when Rh or Ni is replaced by neighbour transition metals M in the periodic table. Only CeNiSn and CeRhSb have a hybridization gap (in Tables I and II), while the remaining compounds are magnetic and nonsemiconducting materials. Let us focus on CeNiSn, since it has been isoelectronic with Pd, naively, we would expect CePdSn to be Kondo insulator, however, CePdSn is found to be antiferromagnet. However, CePdSb has a ferromagnetic ground state which one can briefly comment on the base of Doniach diagram, [22] who has proposed mechanism for the heavy Fermi liquid to RKKY metal transition. The key ingredient of this mechanism is the competition between the Kondo energy (T_{K}) and the RKKY coupling (J_{sf}) between the local moments. While the RKKY interaction temperature $T_{\mathrm{RKKY}} \propto J_{sf}^2 N(\varepsilon_{\mathrm{F}})$, where $N(\varepsilon_{\mathrm{F}})$ is DOS at the Fermi level, the Kondo temperature is given by $T_{\mathrm{K}} \propto \exp(-1/|J_{sf}N(\varepsilon_{\mathrm{F}})|)$. Since in general the hybridization matrix element (and hence the Kondo coupling) between the conduction and Ce f-electrons decreases with increasing volume of the unit cell (Table 1 and 2), the RKKY interaction dominates over the Kondo effect and magnetic ordering can occur as in the case of CePdSn [44], CeCuSn [45], or CeAgSn [46]. An analogous situation is in the CeMSb series of alloys.

TABLE I

Crystallographic and magnetic properties of the ternary intermetallic alloys of the CeNiSn-type, when Ni is replaced by neighbour transition metals M in the periodic table. Symbols: P, AF, or F — paramagnetic, antiferromagnetic, or ferromagnetic ground state, VF — valence fluctuation of Ce ions, K- Kondo-like behavior, HG — hybridization gap at the Fermi level, DNE — the ternary Ce-intermetallic compound does not exist.

M=Co $3d^7 4s^2$ DNE	CeNiSn $3d^8 4s^2$ ε-TiNiSi, Pnma V/f.u. = 66 Å^3 P, K, VF, HG	M=Cu $3d^{10} 4s^1$ $\mathrm{CaIn_2}$ [21], $\mathrm{P6_3mmc}$ (GaGeLi [35], $\mathrm{P6_3mc}$) V/f.u. = 72 Å^3 AF, K (?)
M=Rh $3d^8 4s^1$ $\mathrm{Fe_2P}$, $\mathrm{P\bar{6}2m}$ V/f.u. = 98 Å^3 AF, K, VF	M=Pd $4d^{10}$ ε-TiNiSi, Pnma V/f.u. = 71 Å^3 AF, K	M=Ag $4d^{10} 5s^1$ $\mathrm{CaIn_2}$ [21], $\mathrm{P6_3mmc}$ (GaGeLi [35], $\mathrm{P6_3mc}$) V/f.u. = 77 Å^3 AF, K (?)

TABLE II

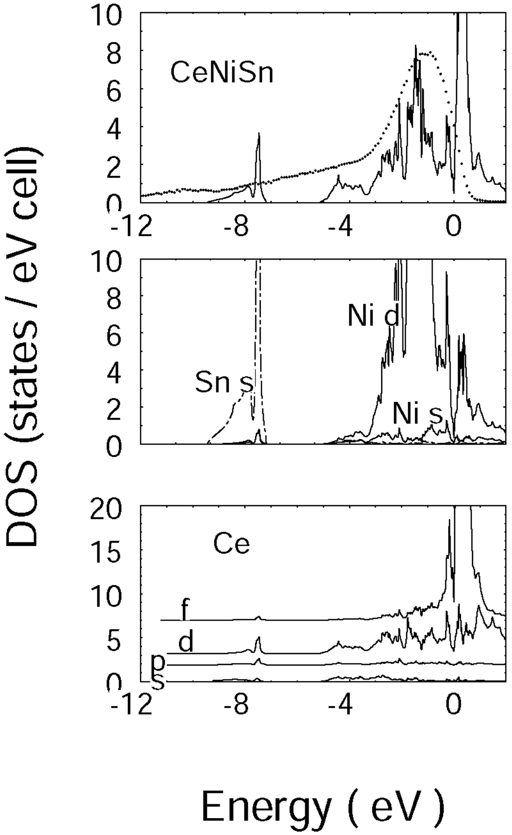
Crystallographic and magnetic properties of the ternary intermetallic alloys of the CeRhSb-type, when Rh is replaced by neighbour transition metals M in the periodic table. Symbols are the same as used in Table I.

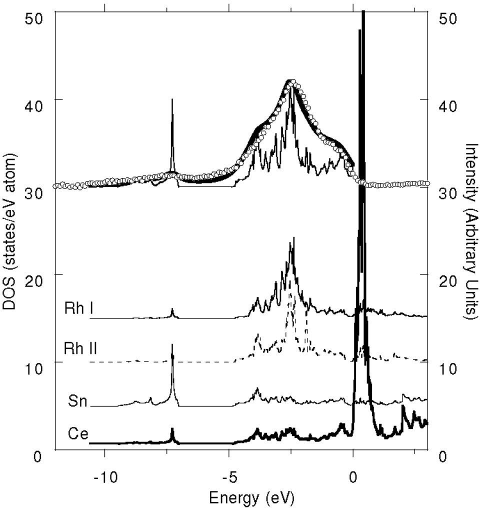
M=Fe $3d^6 4s^2$ DNE	M=Co $3d^7 4s^2$ DNE	M=Ni $3d^8 4s^2$ $\mathrm{CaIn_2}$, P6$_3$mmc (GaGeLi [35], P6$_3$mc) V/f.u. = 67 Å^3 F, K
M=Ru $4d^7 5s^1$ DNE	CeRhSb $4d^8 5s^1$ ε-TiNiSi, Pnma V/f.u. = 67 Å^3 P, K, VF, HG	M=Pd $4d^{10}$ $\mathrm{CaIn_2}$, P6$_3$mmc V/f.u. = 72 Å^3 F, K
M=Os $5d^6 6s^2$ DNE	M=Ir $5d^7 6s^2$ DNE	M=Pt $5d^9 4s^1$ $\mathrm{CaIn_2}$, P6$_3$mmc V/f.u. = 72 Å^3 F

In conclusion, a "volume effect" modifies the conduction electron bandwidth (see Fig. 1) either in CeNiSn or CeRhSb if Ni or Rh is substituted, *e.g.*, by Pd [23,24]. The doping at the Ni (Ref. [23]) or Rh (Ref. [24]) site leads to an increase in the unit cell volume, which reduces the Kondo coupling J_{sf}, so that, according to the phase diagram of Wang *et al.* (Ref. [25]) below a critical coupling the system has a magnetic ground state, moreover, the gap is suppressed by ~ 10 % substitution. Tables I and II display that CeCoSn and CeMSb, where M=Fe, Co, Ru, Os, and Ir have not been obtained as one-phase compounds. The question of the stability of the crystallographic structure of CeMSn or CeMSb is so complex that it is not easy answerable. However, the location of the *d*-electrons in the conduction band and the intra-atomic hybridization between f and d states seems to be important and deciding on the stability of the crystals.

3.2. Electronic structure

In Fig. 1 we compare DOS obtained from the LMTO calculations and the XPS valence band spectra of CeNiSn, CeRhSn, CeRhSb, and CeNiSb. DOS were convoluted with Lorentzians with a full width at half maximum 0.4 eV to account for the instrumental resolution. The partial DOS were multiplied


DOS (states / eV cell)
CeNiSn
Ni d
Sn s
Ni s
Ce
f
d
p
s
10
8
6
4
2
0
20
15
10
5
-12
-8
-4
0
Energy (eV)


DOS (states/eV atom)
Intensity (Arbitrary Units)
Rh I
Rh II
Sn
Ce
0
10
20
30
40
50
-10
-5
0
Energy (eV)

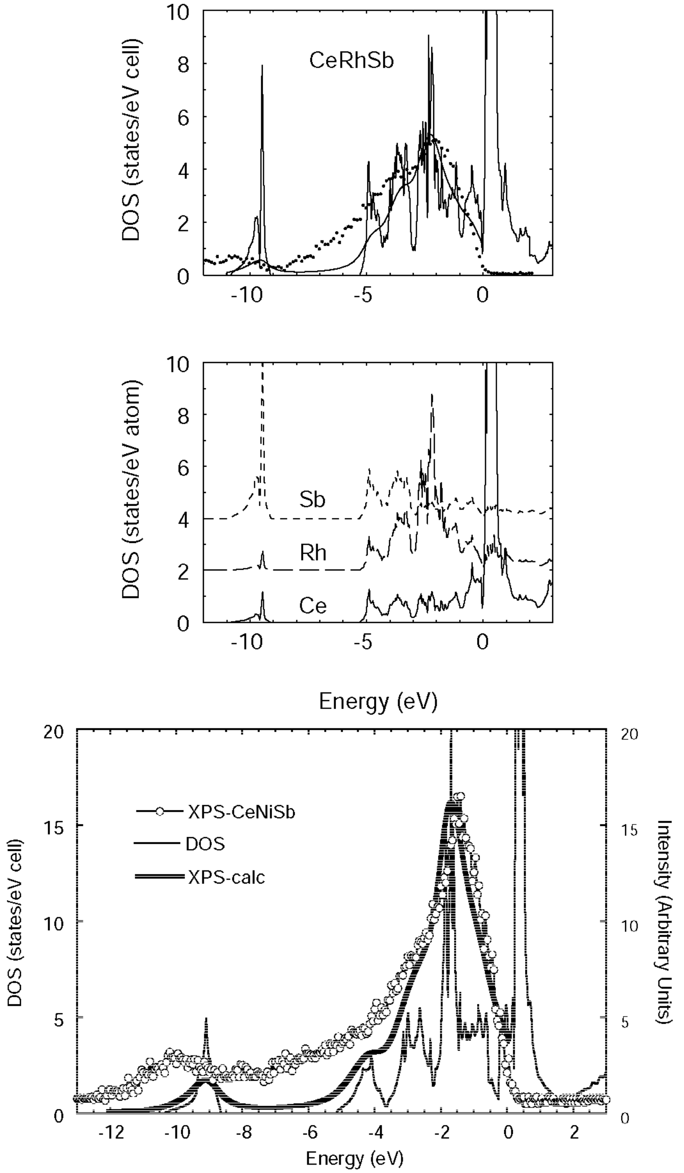


Fig. 1. Comparison of the total DOS calculated for CeNiSn (a), CeRhSn (b), CeRhSb (c), and CeNiSb (d); convolved by Lorentzians of half-width 0.4 eV, taking into account proper cross sections for bands with different l symmetry (thick curve), and measured XPS valence bands corrected by the background (points). The partial DOS curves are plotted below.

by corresponding cross sections [26]. A background, calculated by Tougaard and Sigmund algorithm [27] was subtracted from the XPS data. The spectra reveal a Valence Band (VB) that has a major peak mainly due to the Ni or Rh d states located near the Fermi energy. A half width of the VB XPS peak is about twice as wide in CeRhSb than in CeNiSb (Fig. 1), and is reduced from $\sim$ 5 eV in CeRhSb to $\sim$ 3.5 eV in CeRhSn, while for CeNiSn a half width of the d-band is only $\sim$ 2 eV. This indicates different partial distributions of the d-states in the bands and suggests different intersite hybridization between Ce $4f$- and d-band states. In our recent works we argued that the f–d hybridization determines the formation of the gap at E_{F}.

From the LMTO calculations we obtained a pseudo V-shape gap (Fig. 1) located at the Fermi level on CeNiSn and CeRhSb. This gap is not observed in the band of CeNiSb, however, an indirect gap having a very small number of DOS results from LMTO calculations in the partial DOS of Rh and Sn in CeRhSn, while Ce gives a main contribution to the total DOS at the Fermi level. Concerning also the fractional valence of Ce in CeRhSn and the hybridization energy V between f and the conduction states, which is similar to that of CeRhSb, we try to explain the contributions which remove a gap in CeRhSn. Probably the large volume of the unit cell of CeRhSn seems to be a reason which could induce a stronger localization of the f electrons in CeRhSn than in CeRhSb Kondo insulator, then a possible magnetic ground state (more itinerant than localized) may reduce the gap at E_{F}.

3.3. Ce 3d XPS spectra

The XPS spectra of the $3d$ core levels give more information about the $4f$ shell configurations and f-conduction electron state hybridization. The intermetallic compounds often show different final states depending on the occupation of the f shell: f^0, f^1 and f^2 (Refs. [28, 29]). Fig. 2 shows the Ce $3d$ XPS spectra obtained for CeNiSn, CeRhSn, CeRhSb, and CeNiSb. Three final-state contributions f^1, and f^2 are clearly observed, which exhibit a spin–orbit splitting $\Delta_{\mathrm{SO}} \cong 18.6$ eV. The appearance of the $3d^9f^0$ component in the 3d XPS spectrum of CeRhSb, CeRhSn, and CeNiSn is clear evidence of the intermediate valence behavior of Ce. Based on the Gunnarsson–Schönhammer theoretical model, [28, 29] the intensity ratio $I(f^0)/(I(f^0) + I(f^1) + I(f^2))$, which should be directly related to the f-occupation probability in the final states, indicates an f-occupation number n_f^{XPS}. The separation of the overlapping peaks in the Ce $3d$ XPS spectra was made on the basis of the Doniach–Šunjić theory [30]. The occupation number of the f shell n_f^{XPS} experimentally obtained from the Ce 3d XPS spectra is respectively 0.93 (CeRhSn), 0.86 (CeRhSb), 0.95 (CeNiSn), and $\sim$ 1 (CeNiSb).

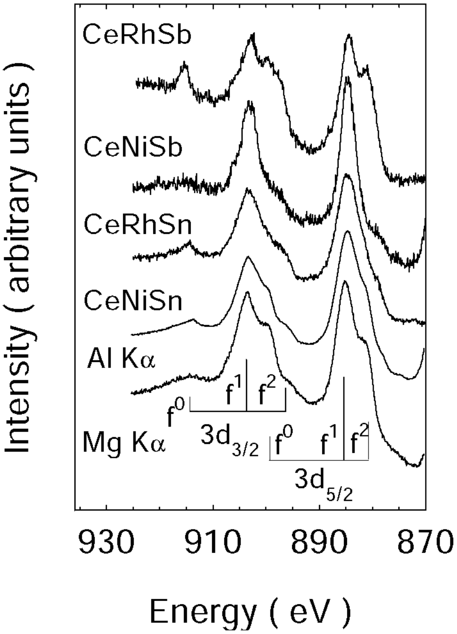


Fig. 2. Ce $3d$ XPS spectra obtained for CeNiSn, CeRhSn, CeRhSb, and CeNiSb. The $3d^94f^0$, $3d^94f^1$ and $3d^94f^2$ components are separated on the basis of the Doniach–Šunjić theory.

The $3d^9f^2$ components in the Ce $3d$ XPS spectra in Fig. 2 are attributed within the Gunnarsson–Schönhammer model to f-conduction electron hybridization. The hybridization energy Δ, which describes the hybridization part of the Anderson impurity Hamiltonian, [31] is defined as $\pi V^2\rho_{\max}$, where $\rho_{\max}$ is the maximum in the DOS and V is the hybridization matrix element. It is possible to estimate Δ from the ratio $r = I(f^2)/(I(f^1)+I(f^2))$, calculated as a function of Δ in Ref. [29], when the peaks of the Ce $3d$ XPS spectra that overlap in Fig. 2 are separated [30]. The intensity ratio gives for CeRhSb, CeRhSn, and CeNiSn a crude estimate of a hybridization width $\sim$ 150 meV, while for CeNiSb Δ is only $\sim$ 50 meV.

3.4. Magnetic properties

The magnetic susceptibility of CeNiSn [10] and CeRhSb [11] is typical for the cerium valence fluctuation compounds having a nonmagnetic ground state. However, if Ni is replaced by Rh, or Rh is replaced by Ni the magnetic ground state appears both in CeRhSn and CeNiSb, in agreement to the phase diagram of Wang [25]. However, the magnetic behaviors are in these alloys completely different.

CeNiSb:
Magnetic measurements suggest that CeNiSb is a ferromagnetic Kondo-lattice system [32]. We have shown that the magnetic behavior of the Kondo lattice compound CeNiSb can be explained in terms of the Doniach phase diagram where applied pressure increases the quantity $|J_{sf}N(\varepsilon_{\rm F})|$. The Ce $3d$ XPS spectra indicate that Ce is trivalent in CeNiSb and the f-conduction electron hybridization is small in comparison with that observed for CeNiSn. The hybridization energy Δ obtained from the $3d$ XPS spectra allowed us to estimate $|J_{sf}N(\varepsilon_{\rm F})|$, which is small [32]. This means that CeNiSb with its linear pressure-dependence of the Curie temperature is located at the low value of $|J_{sf}N(\varepsilon_{\rm F})|$ in the Doniach diagram. Electrical resistivity ρ *vs* T data at various applied hydrostatic pressures $P \propto |J_{sf}N(\varepsilon_{\rm F})|$ up to 18.6 kbar are shown in Fig. 3.

CeRhSn:
The ground state of CeRhSn is very unusual; heavy fermion behavior is observed in the presence of antiferromagnetic order. Provided that the interpretation that the low temperature upturn in $\Delta C/T$ is a result of a Kondo renormalized effective mass, the observation of the magnetic-type transition at 6.2 K complicates the understanding of the specific heat data, which display a logarithmic divergence over the temperature range $0.6 < T < 1.8$ K [33]. Such a behavior indicates heavy fermion behavior and is in striking contrast to a conventional Kondo effect where $\Delta C/T$ approaches a constant value which varies as $1/T_{\rm K}$ at low temperatures $T \ll T_{\rm K}$. Evidence for magnetic character of the phase transition would be the Curie–Weiss temperature $\theta = -6.2$ K determined from the susceptibility data $\chi(T)$ below 40 K, and a very small hump at ~ 6 K in the $\chi(T)$ curve of the CeRhSn sample. A possible interpretation of the small magnetic entropy obtained from a specific heat data is that the ground state of CeRhSn is an itinerant antiferromagnet. The specific heat $C(T)/T$ data estimate at ~ 600 mK $T_{\rm K}$ that exceed $T_{\rm N}$; in sense of Doniach's model, a non-magnetic ground state should exist. Such a non-magnetic ground state exists for a number of compounds including for example $CeAl_3$ [36] or $CeCu_2Si_2$, [37] however, nuclear magnetic resonance or muon spin rotation techniques [38] did not exclude a magnetic ground state in these compounds [39]. It is possible to explain such ordering with extremely small magnetic moments as in UPt_3 [40] or a metamagnetic transition occurring in the paramagnetic temperature range of certain Kondo compounds as $CeRu_2Si_2$ [41].

Electrical resistivity ρ, magnetic susceptibility χ, and specific heat C reveal non-Fermi liquid temperature dependences: $\rho(T) \sim T^{0.8}$, $\chi(T) \sim T^{-1/2}$, and $C(T)/T \sim -\log T$ with $C(T)/T \sim 370$ mJ/mol-K^2 at 1 K (Fig. 4). However, the $C(T)$ data reveal evidence of a phase transition

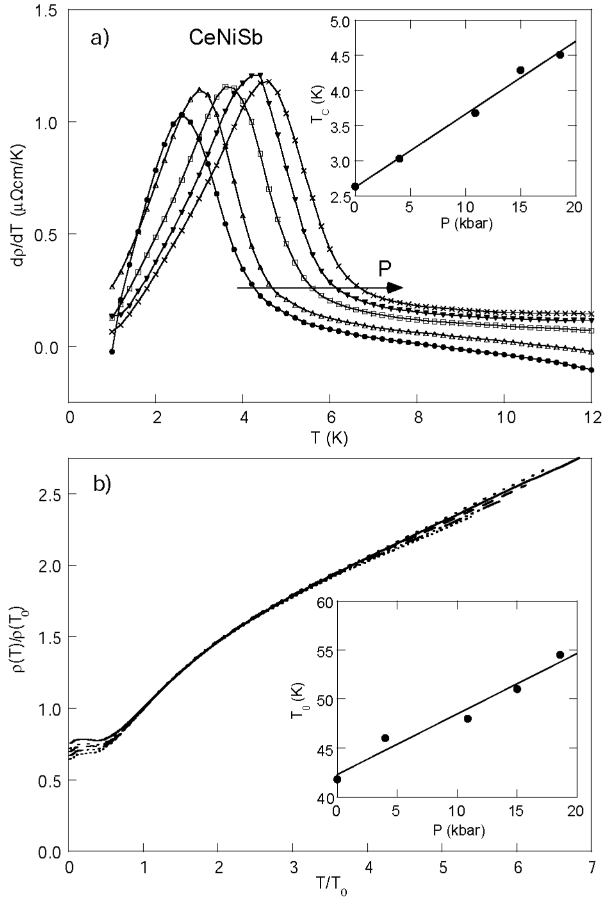


Fig. 3. (*a*) $d\rho/dT$ at different applied hydrostatic pressures for CeNiSb [32]. The inset shows a plot of the Curie temperature T_C, defined as the temperature of the maximum of $d\rho/dT$, *vs* P. (*b*) Normalized resistivity $\rho(T)/\rho(T_0)$ at different pressures *vs* normalized temperature T/T_0; T_0 is the temperature of the inflection point in $\rho(T)$. Inset; T_0 *vs* P. T_0 is often associated with the Kondo temperature.

at 6.2 K, possibly of itinerant magnetic origin. At high temperatures, the physical properties indicate Kondo/intermediate valence behavior. The XPS measurements are consistent with a Ce valence of 3.07 [33].

3.5. Is Fe_2TiSn a Kondo insulator?

In Refs. [15,32] Fe_2TiSn was identified as a weakly ferromagnetic Kondo system with a semiconducting gap which, however, is strongly reduced by the local environment. A similar feature in the electronic structure and a semiconductor-like resistance anomaly have been observed in FeSi, which has been classified [17] as a unique d-electron system that belongs to the family of Kondo insulators. An example of a Kondo insulator that has been thoroughly studied is the compound CeNiSn, [1,34] which has a pseudo gap and a small number of carriers at the Fermi level (~ 0.07 states/eV cell).

In Ref. [16] we discussed $\mathrm{Fe_2TiSn}$ and its Ni-alloys as a system of isolated spins, each of which has two distinct states: a ground state with $S = 0$ and an excited state with $S \neq 0$ a distance $k_B T_0$ above the nonmagnetic state (In the limit $T \gg T_0$, the susceptibility would have the form $\chi = \frac{C}{T} e^{-\frac{T_0}{T}}$ [42]). An interaction between the localized spin $S \neq 0$ and the conduction electrons spins through a Kondo interaction seems to be possible. In this picture, the weak ferromagnetism observed for $\mathrm{Fe_2TiSn}$ could arise from localized magnetic moments of Fe which are not Kondo compensated. The DOS at E_F strongly depends on the local environment and increases up to ~ 1 state/(eV cell) at E_F for a real $\mathrm{Fe_2TiSn}$ crystal with a known amount of disorder [15].

Anderson [43] has shown that if spin compensation is the dominant effect with regard to low temperature magnetic behavior, χ^{-1} varies as $T^{1/2}$ in the low temperature limit. The magnetic susceptibility χ is linear with T^{-n} for $\mathrm{Fe_2TiSn}$, where n is about 0.3 [16]. Also, the $\mu_\mathrm{eff} = (3k_\mathrm{B}/N)^{1/2}(\chi T)^{1/2}$ plot for $\mathrm{Fe_2TiSn}$ has a maximal value of 4.8 μ_B at ~ 180 K, while below this temperature it decreases smoothly to an estimated value of ~ 0.5 μ_B at $T = 0$. Similar behavior is observed for the Ni substituted alloys. This lends support to the idea that spin compensation is responsible for the partial reduction in χ by Kondo-like interaction.

One of us (AŚ) thank the Polish State Committee for Scientific Research (KBN) for financial support from Project no 5 P03B07920.

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