Journal of Alloys and Compounds 480 (2009) 9–12

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: www.elsevier.com/locate/jallcom

Spin glass-like behaviour in Ce-based Kondo systems arising from d-type nonmagnetic atoms disorder

A. Ślebarski

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

ARTICLE INFO

Article history:
Received 23 June 2008
Received in revised form
16 September 2008
Accepted 19 September 2008
Available online 20 November 2008

PACS:
71.27.+a
72.15.Qm

Keywords:
Strongly correlated electron systems
Spin glass

ABSTRACT

The effect of Rh or Sb doping in Kondo insulator CeNiSn, and Rh doping in the Kondo lattice system CePdAl is investigated. The studies indicated the spin glass-like states in these materials caused by a statistical distribution of the nonmagnetic transition elements.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Ce-based Kondo lattice intermetallics exhibit a variety of unusual ground states, including complex magnetic structures [1], heavy fermion (HF) states both normal and superconducting [2], and paramagnetic insulating Kondo lattices (KI) [3]. The reason for such a diversity of physical phenomena is a delicate interplay between two competing mechanisms: the local on-site Kondo effect and the long-range Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction [4]. These two scales in the Kondo lattice, the Kondo temperature T_K and the temperature of the magnetic ordering (T_{RKKY}) depend, however, on the on-site hybridization between the localized f-electron and the d- and s-electron conduction states. There are known examples of Ce-Kondo lattices with *nonmagnetic* transition elements, which (if they are disordered in the crystal) introduce a varying electronic environment around the Ce ions occupying a periodic lattice. As the Ce–Ce exchange interactions depend on the random occupation in the vicinity of the Ce ions, a spin glass-like state would be possible at low temperatures which accounts for the large observed electronic specific heat $\gamma \equiv C/T$ value [5]. The CePd$_{1-x}$Rh$_x$Al series of alloys might be representative of so-called nonmagnetic atom disorder (NMAD) spin glasses. In the series, CePdAl is an antiferromagnetically ordered Kondo lattice compound [6], with 1/3 frustrated moments [7], while CeRhAl is antiferromagnetic Kondo lattice. The *ab initio* band structure calculations showed that randomness associated with the distribution of nonmagnetic atoms in the CePd$_{1-x}$Rh$_x$Al alloys may be responsible for the formation of inhomogeneous magnetic states. We also found that the random Ce–Ce exchange interactions give rise to the spin glass-like behaviour in the doped CeNiSn. CeNiSn is paramagnetic *Kondo insulator* (KI) with respect to that of magnetically ordered CePdAl or CeRhAl, it is of interest to examine the series of CeNi$_{1-x}$Rh$_x$Sn samples, to see the effect of decreasing number of the valence band states on the ground state properties. Very recently we have shown that the magnetic properties of the system gradually evolve from magnetic spin glass-like state ($x < 0.08$) to non-Fermi liquid behaviour, when Rh doping increases [8]. The spin glass-like state was discussed as an effect of NMDA disorder in Ce-based system.

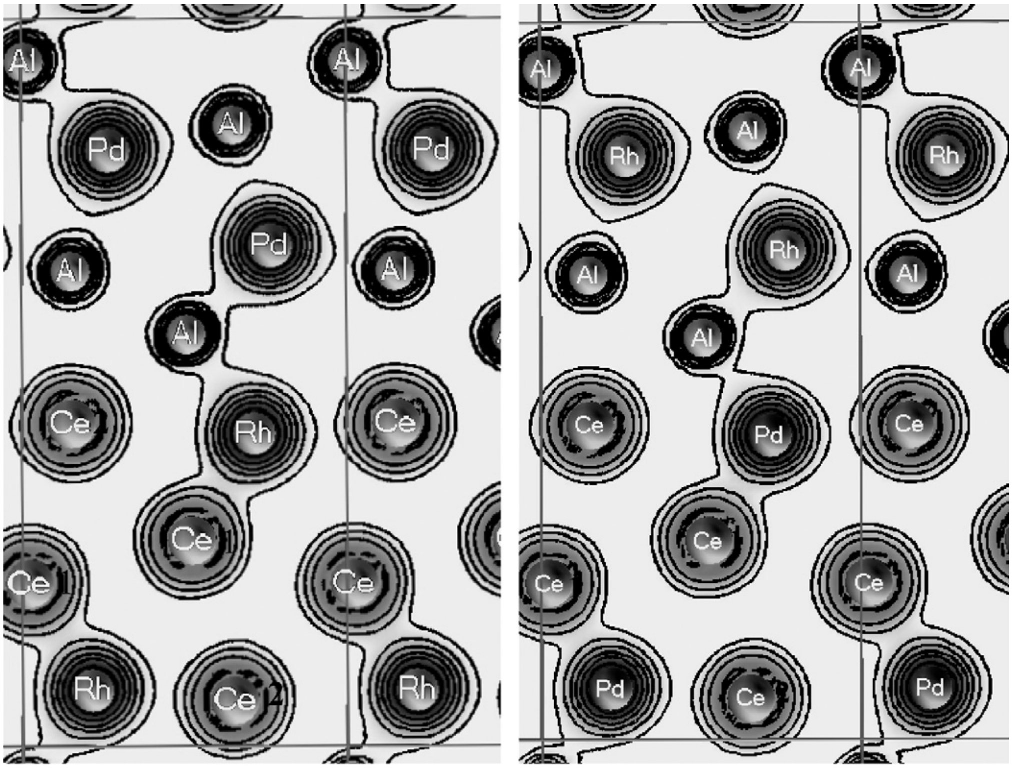
A third NMAD spin glass-like material is the off-stoichiometric CeNi$_{1-\delta}$ Sn$_{1+\delta-x}$Sb$_x$ system with $\delta \approx 0.06$ and $0 \le x < 0.22$, where Sb atoms randomly occupy the Sn and Ni sites [9].

In this paper I review the spin glass-like behaviours observed in different doped Ce-intermetallics, resulting from the localized Ce

---

E-mail address: andrzej.slebarski@us.edu.pl.

0925-8388/$ – see front matter © 2008 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2008.09.190



(1) (2)

Fig. 1. Total valence charge densities in CePd$_{0.5}$Rh$_{0.5}$Al (in electron/a.u.^{3}) for the plane (0 2 0), calculated (LAPW) for two different structures (1) and (2) with different occupation of the 4*c* sites by Pd and Rh atoms.

magnetic moments, and random distribution of the d- or p-electron *nonmagnetic* atoms.

2. Spin glass-like behaviour in CePd$_{1-x}$Rh$_x$Al

The samples CePd$_{1-x}$Rh$_x$Al with $0.2 \leq x \leq 1$ crystallize in orthorhombic structure of €-TiNiSi-type with space group Pnma. Pd and Rh atoms randomly occupy 4*c* atomic sites. The charge bonding between Ce1 and Pd or Rh atoms in the unit cell is much stronger than the bonding between Ce2 and Pd, Rh or Al. Consequently, in full potential linear augmented plane waves (LAPW) approach the calculated magnetic moments of Ce1 and Ce2 in CePd$_{0.5}$Rh$_{0.5}$Al are quite different and strongly dependent on the structural ordering of Pd and Rh atoms in 4*c* sublattice. The value of the Ce magnetic moment depends on the interatomic hybridization between Ce and Pd or Rh valence states. It is very likely that Pd/Rh atomic disorder at 4*c* sites changes the J_{fc} coupling between different Ce atoms, and just this effect can result in the spin glass behaviour in the CePd$_{1-x}$Rh$_x$Al series. In classical spin glasses, random freezing of the magnetic moments arises due to the dominant RKKY exchange interaction between the randomly placed magnetic moments. Ce atoms occupy a periodic lattice in CePd$_{1-x}$Rh$_x$Al, but the nonmagnetic elements (Pd, Rh, Al) are disordered and in this way they introduce varying electronic environment around the Ce ions. In consequence, spin glass state can be formed in the Kondo lattice CePd$_{1-x}$Rh$_x$Al, as was evidenced in Ref. [10].

Fig. 1 shows the total valence charge densities in (0 2 0) plane for CePd$_{1-x}$Rh$_x$Al with different atomic ordering: in (1) the atomic positions 4*c* (Pnma space group) are occupied by Ce1, Ce2; Rh, Pd; and Al1, Al2, while in structure (2) the atomic positions of Pd and Rh are switched. Within this simple approach, it was possible to find out that the overall shapes of the x-ray photoelectron spectroscopy (XPS) spectra are strongly sensitive to atom ordering [10]. Further discussion of this issue requires, however, more advanced theoretical modelling of the system.

3. Interplay between spin glass-like and non-Fermi liquid behaviour in CeNi$_{1-x}$Rh$_x$Sn

Kondo insulators are characterized as a class of nonmagnetic narrow gap Δ semiconductors and semimetals, which display a metallic HF state at $T > \Delta$. CeNiSn is an example of a small gap/pseudogap insulator, with the gap in the doped CeNiSn very sensitive to the degree of hybridization V between the f-electron and conduction electron states [8]. The gap is strongly reduced with Rh substitution. The magnetic properties of the system gradually evolve from magnetic spin glass-like (glassy) state observed for $0 < x < 0.08$, to NFL behaviour, when the Rh doping increases. The detailed investigations of magnetic properties for small *x*-value ($0 < x \leq 0.06$) suggest also an interplay between the spin glass-like and NFL ground states [8]. In Fig. 2 we present the ac and dc susceptibility and specific heat data, both characteristic for inhomogeneous magnetic state. Susceptibility is frequency dependent (panel (b)) and displays hysteretic features (c) typically related to the development of a SG-like state below freezing temperature T_{f}. In panel (a) specific heat shows a feature at 6 K characteristic for pseudogap formation in KI, while a peak at ∼3 K corresponds to SG ordering. However, the SG phenomena presented in Fig. 2 are not typical for an intrinsic spin glass transition, namely the magnetic susceptibility is sensitive to the magnitude of the applied field, and

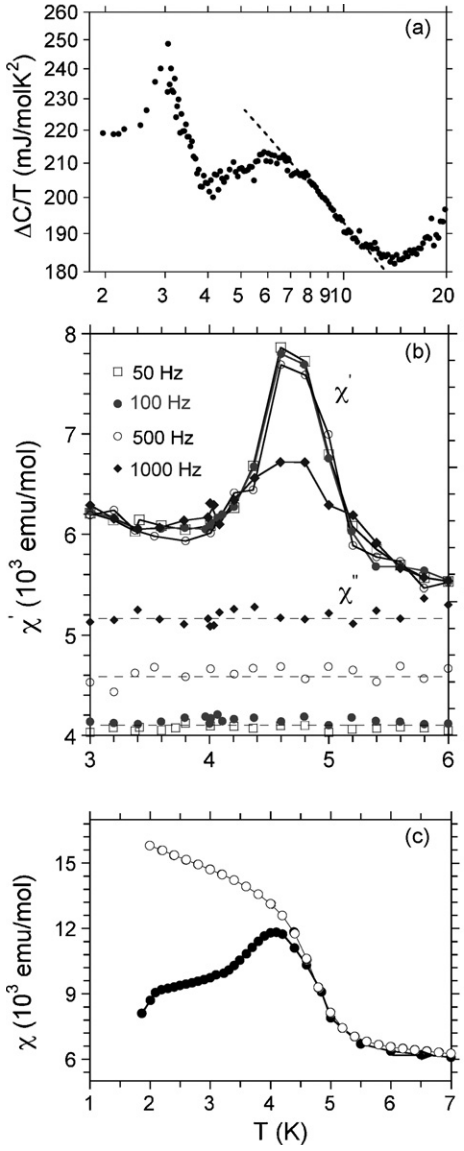


Fig. 2. CeNi$_{0.98}$Rh$_{0.02}$Sn; (a) specific heat $\Delta C = C$ (sample) − C (LaNiSn). For $6 < T < 13$ K, $\Delta C/T \sim T^{-n}$ with $n = 0.25$ (note, the susceptibility $\chi \sim T^{-n}$, with $n = 0.21$ at $T_f < T < 36$ K). At the lower temperatures than ~6 K $\Delta C/T$ displays the features characteristic for the gap formation (at 6 K) and at ~3 K, resulting from the spin glass-like state. (b) Real χ' and imaginary χ'' components of ac magnetic susceptibility with an applied field 10 Oe at different frequencies. (c) ZFC and FC dc susceptibility measured in the field 100 Oe.

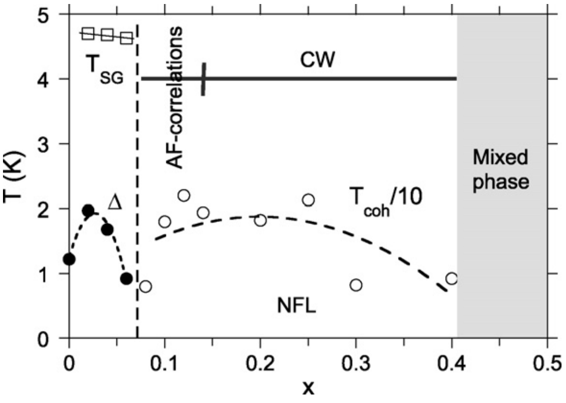


Fig. 3. Schematic phase diagram for CeNi$_{1-x}$Rh$_x$Sn system. Temperature Δ is obtained from the fit of expression $\rho(T) = \rho_0 \exp(\Delta/T)$ to the resistivity data in the Kondo insulating regime [4]. T_{SG} is a temperature of the maximum in the χ_{ac} data, T_{coh} is taken as T_{max} in the $\rho(T)$. With increasing x, the antiferromagnetic correlations are observed.

the strong frequency dependence is visible at $\nu > 500$ Hz. The amplitude of χ' decreases, and the shift of χ' maximum is downwards in temperature with decreasing frequency for $\nu \leq 100$ Hz, while the amplitude and position of χ' maximum is only slightly ν-dependent in the frequencies $\nu > 500$ Hz. Likewise, the observed freezing temperature does not change very much with Rh concentration, and in the imaginary part of the susceptibility no loss has been recorded. Moreover, in canonical spin glasses the peak in the specific heat is usually observed at temperatures exceeding the freezing temperature by about 20% and it usually shows a broad maximum, which is not observed for the investigated sample. These facts would mean that the spin glass transition is not intrinsic for the present system with the NFL character and is possibly due to the local atomic disorder. The low-frequency susceptibility curves of $x = 0.02$ sample look more like those of a short-range antiferromagnet with a small frequency dependence of χ' and almost no χ''. Such a short-range antiferromagnet may display a glassy behaviour associated with atomic disorder (discussed in Ref. [8]). The phase diagram of this system is shown in Fig. 3.

A similar SG-like formation is observed for CeNiSn, when Sn atoms are replaced by Sb. In this case the number of conduction electrons quasi-continuously increases. In Fig. 4 the phase diagram for the system CeNiSn$_{1-x}$Sb$_x$ is shown. The SG-like state results from the atomic disorder in the Sn-sites.

In conclusion, impurities (Rh or Sb) first stabilize the semiconducting gap in CeNiSn, if the x concentration is of about 2%. Such a stabilization of KI state upon substitution leads to the localization of 4f-electrons, as evidenced by the formation of the localized SG-like state in CeNi$_{1-x}$Rh$_x$Sn. Further increase of doping decreases the gap, which is reduced for x about 8%.

In the compounds studied, the Ce atoms occupy a periodic lattice, however, the nonmagnetic elements if they are disordered, introduce a varying electronic environment around the Ce ions. As the Ce–Ce exchange interactions depend on the random occupation in the vicinity of Ce, a spin glass-like state is possible. The effect is, however, dependent on the concentration of doping element, we observed the spin glass-like features for a small x concentrations in CeNiSn, which means that the atomic disorder leads to the formation of the SG state in the Ce-Kondo lattice. In the case of CeNiSn doped by Sb, the spin glass-like behaviour was observed for

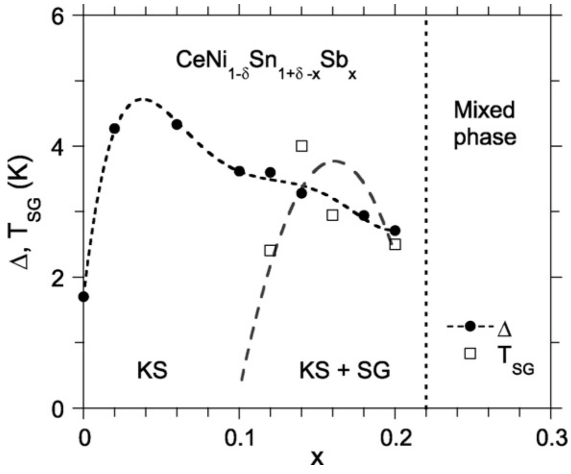


Fig. 4. Schematic phase diagram for off-stoichiometry CeNiSn$_{1-x}$Sb$_x$ system of alloys. KS means the Kondo semimetallic (Kondo insulating) phase.

$0.1 < x < 0.2$. The spin glass behaviour in $CePd_{1-x}Rh_xAl$ series may be caused by random distribution of the Pd, Rh, and Al. atoms. The SG arising from nonmagnetic atom disorder in these compounds could lead to apparent large γ values, characteristic for heavy fermions, which are known as false heavy fermions [5].

Acknowledgements

The author is very grateful to Jozef Spałek, M. Brian Maple, Dariusz Kaczorowski and Jerzy Goraus for discussion.

References

[1] R. Doradziński, J. Spałek, Phys. Rev. B 58 (1998) 3293–3301.
[2] N. Greve, F. Steglich, in: K.A. Gschneidner Jr., L. Eyring (Eds.), Heavy Fermions in Handbook on the Physics and Chemistry of Rare Earths, vol. 14, Elsevier Science Publishing B.V., 1991, pp. 343–473.
[3] Z. Fisk, Comments Condens. Matter Phys. 16 (1992) 155–165.
[4] S. Doniach, Physica B 91 (1977) 231–234.
[5] K.A. Gschneidner Jr., J. Tang, S.K. Dhar, A. Goldman, Physica B 163 (1990) 507–510.
[6] F. Hulliger, J. Alloys Compd. 196 (1993) 225–228.
[7] A. Dönni, G. Ehlers, H. Maletta, P. Fischer, H. Kitazawa, M. Zolliker, J. Phys.: Condens. Matter 8 (1996) 11213–11229.
[8] A. Ślebarski, M.B. Maple, R.E. Baumbach, T.A. Sayles, Phys. Rev. B 77 (2008) 245133–245141.
[9] J. Spałek, A. Ślebarski, Acta Phys. Pol., A 114 (2008) 7–14.
[10] A. Ślebarski, W. Głogowski, J. Goraus, D. Kaczorowski, Phys. Rev. B 77 (2008) 125135–125143.