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Physics Procedia 71 (2015) 303 – 307

Physics Procedia

18th Conference on Plasma-Surface Interactions, PSI 2015, 5-6 February 2015, Moscow, Russian Federation and the 1st Conference on Plasma and Laser Research and Technologies, PLRT 2015, 18-20 February 2015

Long range order and spin-fluctuations in strongly correlated electron system with valence instability

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Abstract

Rare-earth based strongly correlated electron systems (SCES) exhibit a large variety of different ground states, ranging from the simple paramagnetism of crystal-field-split *f*-electron multiplets to highly unconventional Kondo-insulator states with a combination of charge gap, spin gap and valence instability, in which long-range magnetic order can eventually arise from an initially singlet state. The physical background for these properties of the electron subsystem may be clarified by performing detailed neutron scattering experiments, namely magnetic neutron scattering spectroscopy and diffraction. This report reviews the results of the previous and new experimental studies on a number of rare-earth intermetallic compounds, which shed light on peculiar features of those unusual ground states.

Keywords: X-ray and neutron spectroscopy; isomer shift; neutron diffraction; long-range magnetic order; spin-fluctuations; intermediate valence

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doi:10.1016/j.phpro.2015.08.331

1. Introduction

Magnetic order in rare-earth based metallic system is essentially different from that occurring in the case of *d*-elements, as it develops on an array of localized magnetic moments from the unfilled 4*f*-electron shells. Accordingly, *localized*, rather than *itinerant*, magnetism sets in at temperatures typically above a few kelvins, as a result of inter-site exchange interactions. The dominant (so-called Ruderman-Kittel-Kasuya-Yosida or "RKKY") term in these interactions arises from the spin polarization of the conduction-electron medium, which arises from an exchange coupling J_{sf} **Ss** between the spins of 4*f* (localized) **S** and conduction (itinerant) electrons **s**. In the case of antiparallel coupling, the same term gives rise to Kondo effect, which is thought to be responsible for heavy-fermion (HF) behavior occurring in a number of concentrated *f*-electron systems. In the limit of weak hybridisation it can actually be derived from Anderson Hamiltonian formalism through Schrieffer-Wolff transformation Brand and Moshchalkov (1984). In that limit, low-energy spin-fluctuations (by the order of 10 K) can occur through spin-flip scattering of conduction electrons interacting with localized magnetic moments.

Increasing the hybridization results in *f*-electron delocalization, with an increase in the spin fluctuation energy by one order of magnitude or more, leading to the formation of a so-called "intermediate valence" (IV) or "valence fluctuation" (VF) regime. The latter is characterized by a fractional average occupation of the *f*-electron shell, as revealed by X-ray absorption spectroscopy (XAS) experiments. It can be noted that, in this approach, the long-range magnetic order (LRMO) and the spin fluctuations, or the trend toward valence instability, have a common physical origin, and their competition is controlled by a single tuning parameter. This idea is the basis for the well-known "Doniach diagram" (Fig. 1) describing the dependence of the inter-site exchange interaction (k_BT_{RKKY}) and the Kondo energy (k_BT_K) as function of the *s*-*f* exchange constant J_{sf} Brand and Moshchalkov (1984).

Experimentally, LRMO, as well as spin fluctuations, can be addressed by means of neutron scattering (diffraction and spectroscopy) techniques. In the present report, recent experimental results from neutron scattering and L_3-edge XAS measurements are discussed in connection with previously published data to shed light on the variety of physical phenomena underlying the coexistence and/or competition of LRMO and spin-fluctuation in representative rare-earth-based compounds

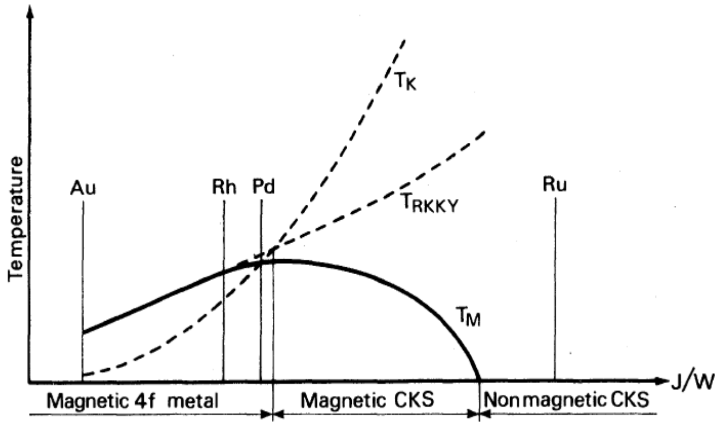

Fig. 1. Tentative classification of the condensed Kondo systems (CKS) according to the relative magnitudes of the two characteristic temperatures T_K and T_{RKKY} (dashed lines). T_M (solid line) is the magnetic ordering temperature ($T_M \equiv T_N$ for antiferromagnets, as considered in this paper), J the 4*f*–conduction electron exchange integral (J_{sf} in the text), and W is a scaling factor. Vertical marks correspond to the estimated J/W parameter values for selected $\mathrm{Ce}T_2\mathrm{Si}_2$ systems (T = Au, Rh, Pd, Ru) (taken from Ref. 3).

2. Long range magnetic order and spin fluctuations

2.1. Heavy fermion Ce-based systems

HF behavior is mainly observed in Ce- and Yb-based systems, some of which exhibit AF order in their ground state (with typical Néel temperatures of a few kelvins or less). In Refs. Knopp et al. (1989), Severing et al. (1989), Severing et al. (1989), several compounds from CeT_2Si_2 family (T: transition element) with $ThCr_2Si_2$ structure (hereafter "1-2-2") have been investigated by inelastic neutron scattering to characterize the crossover from the nonmagnetic HF regime to AF-LRMO regime. The magnetic spectral response shows that spin-fluctuation is gradually slowing down over a narrow temperature range below T_N, so that the quasielastic line width $\Gamma_{QE}(T)/2$ does not cross the k_BT line representing a Korringa-typethermal fluctuation rate. This is in contrast with the behavior observed in nonmagnetic HF or VF systems, where $\Gamma_{QE}/2$ retains a finite value (ultimately > k_BT) down to the lowest temperatures.

The interpretation proposed by Severing et al. (1989) was based on Doniach's picture, assuming that J_{sf} lies in the region close to the crossing point between the curves representing the variations of T_{RKKY} ($\propto J_{sf}^2$) and T_K ($\propto$exp [-$1/\rho J_{sf}$]) (see Fig. 1). The reduction of the ordered Ce magnetic moments with respect to the free-ion value observed by neutron diffraction was ascribed to a combination of crystal-field and Kondo-screening effects. This simple description deliberately overlooks a more complex (non-Fermi liquid) dynamics developing close to the magnetic **Q** vector in the quantum critical regime. Its observation require detailed single-crystal studies, which are beyond the scope of this report.

It must be emphasized that, both in Ce and Yb-based systems, the HF state is observed only for very weak deviations of the valence state (as defined, e.g., by L_3-edge spectroscopy) from the integer values corresponding, respectively, to one electron or one hole on the 4*f* shell. This actually corresponds to the situation where Schrieffer-Wolff transformation is valid.

2.2. Intermediate valence Eu-based systems

Eu-based compounds belonging to the same 1-2-2 structure as Ce-based systems described above are prone to pronounced valence instabilities Fukuda et al. (2003). $EuCu_2(Si_xGe_{1-x})_2$ solid solutions, in particular, possess a rich phase diagram as a function of the Si concentration x, as was shown from extensive thermodynamic and transport measurements Hossain et al. (2004). At low temperature, increasing x causes the suppression of the antiferromagnetic order found in pure $EuCu_2Ge_2$. The resulting paramagnetic ground state exhibits HF character in the composition range close to the transition to LRMO phase. The homogeneous IV state of Eu over the full concentration range, $0 \le x \le 1$, has been confirmed from XAS (L_3-edge) and Mössbauer (isomer shift) experiments Alekseev et al. (2014). For $0 \le x \le 0.6$, AF-LRMO has been characterized using magnetic neutron diffraction Alekseev et al. (2014). The obtained composition dependence of the average Eu valence is summarized in Fig. 2 for two temperatures.

Inelastic neutron scattering measurements by Alekseev et al. (2012) on samples from the same series have revealed that unconventional Eu spin fluctuations develop for $x > 0.6$, with a spin gap opening at temperatures below 100 K for $x > 0.75$ (most clearly observed for $x = 0.9$ and 1.0). This implies the existence of a *singlet* ground state in the IV state of Eu. At temperatures above the spin-gap region (100–150 K) fast spin-fluctuations are recovered with a characteristic linewidth $\Gamma_{QE}/2 \sim 10$ meV.

For lower Si concentrations, the inelastic part of the magnetic excitation spectra exhibits a strong shift to lower energies, as well as a substantial broadening. Furthermore, a quasielastic signal is now detected at the lowest temperature of 3 K. This reflects the formation of a paramagnetic ground state with a spin-fluctuation energy of the order of only 2 meV for $x = 0.75$. This concentration range corresponds to the HF regime in the phase diagram. At lower Si concentration ($x = 0.6$), only the quasielastic signal is observed in the magnetic excitation spectra for all temperatures, including in the magnetically ordered state where the condition $\Gamma_{QE}/2 < k_BT$ is fulfilled. The phase diagram summarizing the results from our recent magnetic neutron diffraction and neutron spectroscopy is shown in Fig. 3. The hatched area represents the concentration/temperature range in which spin-fluctuations occur, as is confirmed by a sizable quasielastic response. Two important observations should be made. First, the homogeneous ground state of IV Eu changes from nonmagnetic (spin-gapped) above $x \sim 0.75$ to spin-fluctuating below. The character of the magnetic excitation spectra in this region, along with the range of parameter values, is similar to the type of response found in Ce-based HF system. Secondly, within our present experimental resolution, spin-fluctuations coexist with AF-LRMO (at $T < T_N$) below $x = 0.6$, at least down to $x = 0.4$, which reinforces the similarity between the present Eu-based IV compounds and Ce-based HF systems in which spin fluctuations are also detected in a finite temperature range below T_N.

Comparing Figs. 1 and 3, one might assume that the Si concentration x acts as an external control parameter to tune the hybridization strength J/W as is depicted in Fig. 1. This is consistent with the increase observed in the quasielastic line width with increasing x. On the other hand, the physical mechanism responsible for the stabilization of the spin-gap state as x approaches 1 still has to be identified. It should be kept in mind that, unlike for Ce (or Yb), the nonmagnetic valence state of Eu does not arise from an empty or empty (or full) 4f shell, but from a more complex $J = 0$ multiplet state.

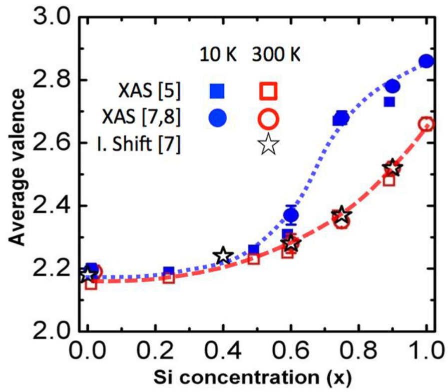

Fig. 2. Concentration dependence of the average valence derived from L_3-edge X-ray spectroscopy [from Refs. Fukuda et al. (2003) (squares) and Alekseev et al. (2014), Alekseev et al. (2012) (circles)]) and Mössbauer isomer shift [from Ref Alekseev et al. (2014) (stars)]. Open (closed) symbols denote values for $T = 300$ K (10 K). Lines are guides to the eye.

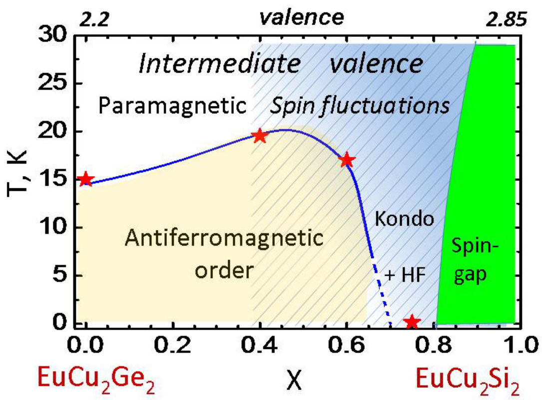

Fig. 3. Magnetic phase diagram of $EuCu_2(Si_xGe_{1-x})_2$. The solid blue line separating the paramagnetic and LRMO regions represents the results of Ref. Hossain et al. (2004). Stars indicate T_N values obtained our neutron diffraction study Alekseev et al. (2014). The green-colored area corresponds to the spin-gap regime, and the hatched area to the spin-fluctuation regime, in which a QE response is experimentally observed. A Kondo + HF region exists, according to Ref. Hossain et al. (2004), in between the spin-gap and LRMO states.

The spin dynamics of $EuCu_2(Si_xGe_{1-x})_2$ also contrasts with that of TmSe, one of the very few IV compounds showing AF-LRMO Ref. Holland-Moritz (1983). Important differences are the absence of overlap between the spin-fluctuation and LRMO phases, and the lack of any evidence of HF-type behavior for the TmSe-based cjmpounds. One possible reason could be that, in TmSe, the only electrons occupying the conduction band are those resulting from the valence fluctuation. It leads to a Kondo-insulator behavior, strongly at variance with the metallic character of the 1-2-2 compounds.

3. Conclusion

By comparing the IV system $EuCu_2(Si_xGe_{1-x})_2$ with Ce-based 1-2-2 HF compounds one infers that the competition between AF-LRO and (Kondo-type) spin-fluctuations can take place in the case of weak (HF) as well as strong (IV) valence instability. A detailed analysis of the spectroscopic data obtained by different techniques (L_3-edge XAS, Mössbauer isomer shift, neutron magnetic scattering) provides evidence that, as the average Eu valence varies as a function of the Si to Ge ratio in $EuCu_2(Si_xGe_{1-x})_2$, the ground state changes qualitatively from nonmagnetic singlet to spin fluctuations, but its homogeneous character is retained. The sequence of different ground states in the phase diagram includes a HF region between AF-LRMO and the spin-gap states, characterized by gapless paramagnetic QE spin fluctuations.

It will be interesting to analyze the pressure dependence of the spectroscopic characteristics of the x=0 composition $EuCu_2Ge_2$ based on the idea of proximity between concentration x and hybridization *J/W* parameters.

Acknowledgements

Authors are grateful to A.V. Gribanov, A. A. Nikonov, J.R. Stewart, R. I. Bewley, C. Pantalei, B. Klobes, R.P. Hermann for their significant contribution to experimental part of the work, to E.S. Clementyev and V. N. Lazukov for useful discussions. The partial support of the present work by RFBR (grant # 14-22-01002) is highly appreciated.

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