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## Original article

## Interplay of magnetism and valence instabilities in lanthanide systems

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## ABSTRACT

The valence instability in lanthanide systems is described within an extended periodic Anderson Hamiltonian (EPAM) which includes Coulomb repulsion between *f*- and conduction- electrons, allowing to describe both discontinuous and continuous valence variations. We investigate the connection between valence and magnetism in this model and show that it can be applied to several lanthanide compounds showing both magnetic and valence instabilities.

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## 1. Introduction

Intermetallic lanthanide compounds are usually classified into normal and anomalous rare earth systems. In normal systems, the valence of the rare earth is well defined (usually 3+), the magnetic moment is determined by Hund's rules and crystal field interactions, and RKKY exchange interactions are responsible for magnetic order. However there are compounds in which this scheme fails; such anomalous systems are often observed with Ce, Yb, Eu, Sm or Tm. In this paper we are interested in compounds in which the valence may change with pressure, magnetic field, or doping. Such valence change is accompanied by a change of the 4*f*-magnetic moment, and in many cases (Ce, Sm, Eu or Yb) one of the valence state is non-magnetic. For example Yb may change from Yb<sup>2+</sup>, which is non-magnetic, to Yb<sup>3+</sup> which is magnetic. This paper presents a model based on an extension of the Periodic Anderson Model that includes inter-orbital Coulomb repulsion appropriate to discuss the interplay of magnetic and valence transitions in such compounds.

## 2. Model and approximations

We study an Extended Periodic Anderson Model (EPAM) which can be written in the following form:

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$$H = \sum_{\mathbf{k}\sigma} (\epsilon_{\mathbf{k}} - \mu) c_{\mathbf{k}\sigma}^{\dagger} c_{\mathbf{k}\sigma} + (E_f - \mu) \sum_{i\sigma} f_{i\sigma}^{\dagger} f_{i\sigma} + V \sum_{i\sigma} (c_{i\sigma}^{\dagger} f_{i\sigma} + f_{i\sigma}^{\dagger} c_{i\sigma}) + U \sum_i \hat{n}_{i\uparrow}^f \hat{n}_{i\downarrow}^f + U_{fc} \sum_{i\sigma\sigma'} \hat{n}_{i\sigma}^f \hat{n}_{i\sigma'}^c, \quad (1)$$

where  $c_{i\sigma}^{(\dagger)}$  and  $f_{i\sigma}^{(\dagger)}$  respectively denote annihilation (creation) operators of conduction- and *f*-electrons on a lattice site *i* with spin component  $\sigma = \uparrow, \downarrow$ . The spin-dependent *f*-occupation operator is defined as  $\hat{n}_{i\sigma}^f \equiv f_{i\sigma}^{\dagger} f_{i\sigma}$  and a similar definition is held for  $\hat{n}_{i\sigma}^c$ . The conduction electrons are characterized by their non-interacting density of states  $\rho_0(\omega) \equiv \sum_{\mathbf{k}} \delta(\omega - \epsilon_{\mathbf{k}})$ , where  $\mathbf{k}$  denotes the momentum. This model differs from the Periodic Anderson Model by the Coulomb repulsion term between *f* and conduction electrons,  $U_{fc}$ . This repulsion was introduced by Falicov and Kimball to describe discontinuous valence transitions in a spinless model [1]. Without this interaction, valence variation may occur by varying the *f*-level position  $E_f$  and the hybridization *V* but it is always second order. This Coulomb repulsion  $U_{fc}$  is much smaller than the *f*-*f* Coulomb repulsion *U*, and it will be treated in mean field approximation, while the *f*-*f* repulsion, which is one order of magnitude larger, is treated using Hubbard I approximation [2]. This approximation is appropriate to describe charge instability since the weights of lower and upper Hubbard bands are calculated correctly in this approximation, which is crucial to describe valence variations.

The chemical potential  $\mu$  is determined such that the thermal average of the total local occupation is homogeneous and fixed to  $n_{\text{tot}} \equiv \langle \hat{n}_{i\uparrow}^c \rangle + \langle \hat{n}_{i\downarrow}^c \rangle + \langle \hat{n}_{i\uparrow}^f \rangle + \langle \hat{n}_{i\downarrow}^f \rangle \equiv n_c + n_f$ .

Invoking these approximations for the model Hamiltonian (1) in the limit  $U=+\infty$ , the local density of states for conduction and  $f$ -electrons are given by  $\rho_c(\omega) = \rho_0(\omega + \mu - \Sigma(\omega))$  and  $\rho_f(\omega) = \frac{|\Sigma(\omega)|^2}{V^2} \rho_0(\omega + \mu - \Sigma(\omega))$ , where the local self-energy is given by

$$\Sigma(\omega) \equiv \frac{\left(1 - \frac{n_f}{2}\right) V^2}{\omega - E_f + \mu - U_{fc} n_c}. \quad (2)$$

The parameters  $n_f = n_{\text{tot}} - n_c$  and  $\mu$  have to be determined self-consistently by solving the two equations  $n_{f/c} = 2 \int_{-\infty}^{+\infty} \rho_{f/c}(\omega) n_F(\omega) d\omega$  where  $n_F$  is the Fermi function. Numerical results presented hereafter were computed with a constant non-interacting density of states:  $\rho_0(\omega) = \frac{1}{2D}$  for  $|\omega| < D$  and  $\rho_0(\omega) = 0$  otherwise.

In the absence of external magnetic field, study of the paramagnetic solution indicates a valence change as a function of either  $U_{fc}$  or  $E_f$  (see Fig. 1). For small values of  $U_{fc}$  the valence changes continuously as a function of  $E_f$ , while for large values of  $U_{fc}$  there is a first order transition from  $n_f=1$  to  $n_f=0$  when  $E_f$  increases.

### 3. Magnetism and valence

*Intrinsic magnetism of the EPAM.* In the absence of external magnetic field, Fig. 1 shows the variation of valence as a function of  $E_f$  and  $U_{fc}$ . However a magnetic instability may occur in this paramagnetic phase. Fig. 2 shows that for low  $U_{fc}$ , ferromagnetism appears spontaneously in the intermediate valence region. There are two distinct regions where ferromagnetism appears spontaneously: (i) for large negative  $E_f$  and large  $U_{fc}$ ,  $n_f=1$ , this corresponds to ordering of localized  $f$ -moments through RKKY interactions. (ii) in the intermediate valence regime, ferromagnetic instability occurs within the  $f$ -band which is then located near the Fermi level. In this second case, the ferromagnetic instability is then a Stoner-like instability occurring when density of states at the Fermi level of the  $f$ -band is large. Increasing  $E_f$ , the system is then going from a region with nearly integer valence, where magnetism can be induced by additional RKKY interactions, to an intermediate ferromagnetic region, and finally to a region where rare earth ions are non-magnetic due to the valence change.

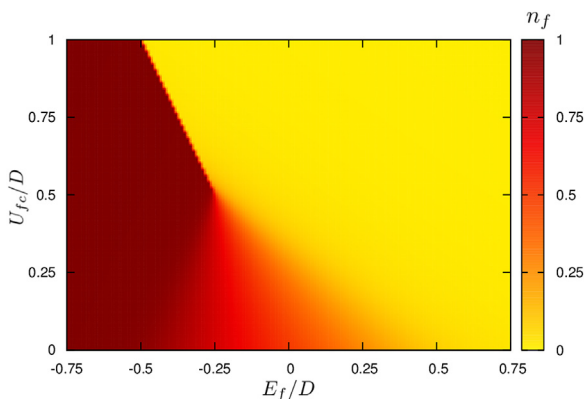


Fig. 1. Phase diagram for the paramagnetic phase at  $T=0$  K,  $n_{\text{tot}} = 1.5$ ,  $V = 0.1D$ . The critical end point is located at  $U_{fc} = 0.53D$ ,  $E_f = -0.23D$ .

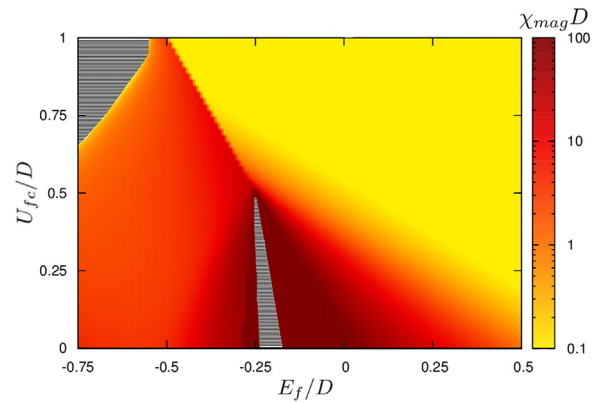


Fig. 2. Intrinsic ferromagnetic regions as a function of  $U_{fc}$  and  $E_f$ . This figure shows the magnetic susceptibility as a function of  $E_f$  and  $U_{fc}$ . In the regions coloured in grey, the magnetic susceptibility is divergent, indicating a ferromagnetic instability (same parameters as in Fig. 1).

### Magnetism in the presence of $f$ - $f$ exchange interaction application to $\text{YbCu}_2 \text{Si}_2$

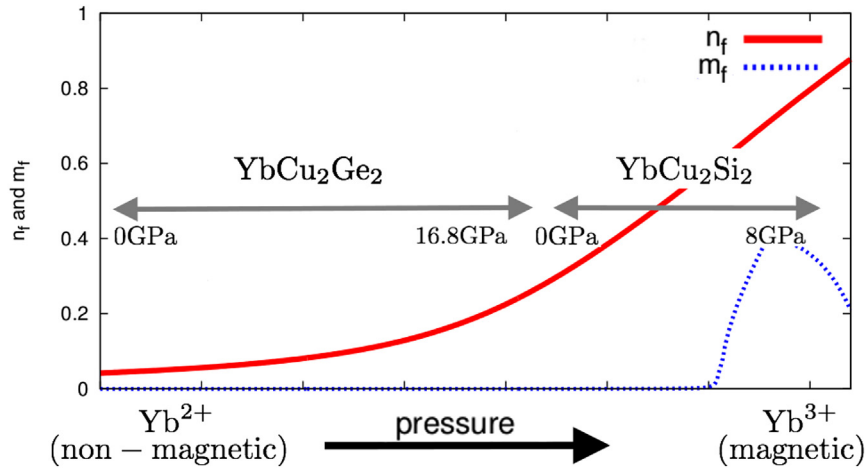
The intrinsic ferromagnetic instability is enhanced by RKKY exchange, if it is ferromagnetic, allowing to enlarge the ferromagnetic region of the phase diagram. In particular, close to the instability regions of Fig. 2, a very small exchange is sufficient to induce ferromagnetism. This model can be applied to  $\text{YbCu}_2 \text{Si}_2$  which exhibits a ferromagnetic instability under pressure in the intermediate valence phase [3]. Fig. 3 shows the results obtained using our model with additional intersite exchange  $J$ . Increasing pressure the valence of Yb changes from almost  $2+$  ( $4f^{14}$ ) to  $3+$  ( $4f^{13}$ ) and ferromagnetism appears for a valence around 2.85.

### Effect of applied field

Ferromagnetic instability may also occur under applied magnetic field, or under internal effective magnetic field as in  $\text{YbMn}_6 \text{Ge}_{6-x} \text{Sn}_x$  where Mn moments are ordered up to room temperature, acting as an effective ferromagnetic field on the Yb ions [6,7]. In this system, Yb sublattice remains magnetically ordered up to 90 K (for  $x=4.4$ ) which is very large for Yb system, while for the same composition, Yb ions are in the intermediate valence state ( $2.9+$ ). For the composition  $x=3.8$ , the valence is nearly  $3+$ , and the Yb moments remain ferromagnetic only up to 50 K: this can be understood in our model, where external field has a much stronger effect in the intermediate valence regime, where the Fermi level lies in a region of large  $f$ -density of states. On the other hand, in the integer valence regime,  $f$ -level is well below the Fermi level, and less influenced by external parameters.

### 4. Conclusions

The model proposed in this paper shows that magnetic and valence instabilities are strongly connected since in most cases, valence fluctuations occur between a magnetic and a non-magnetic valence state. This is the case of Yb compounds where valence fluctuates between  $4f^{13}$  and  $4f^{14}$  states, but also of Eu (or Sm) compounds which fluctuate between  $4f^6$  and  $4f^7$  (or  $4f^5$ ) since in the  $4f^6$  configuration, orbital and spin moments compensate and the ground state is non-magnetic. Of course Ce compounds are in the same class of compounds (fluctuations between  $4f^0$  and  $4f^1$ ), but usually volume effects are important in Ce systems, and the valence transitions are accompanied by large volume effects, which were



**Fig. 3.** Schematic comparison between the results obtained with EPAM and experiments on  $\text{YbCu}_2(\text{Si/Ge})_2$ . Red solid and blue dashed lines: numerical results obtained with  $V = 0.1D$ ,  $n_{\text{tot}} = 1.2$ ,  $U_{fc} = 0.4D$ , and intersite exchange  $J = 0.01D$ .  $E_f$  varies from  $-0.1D$  to  $-0.5D$ . These variations are in good agreement with experimental results either under pressure, or on replacing Si by Ge (for experimental results: see Refs. [4] and [5]).

not included in this model. Several Tm compounds also exhibit valence fluctuations, but in this case both valence states ( $4f^{12}$  and  $4f^{13}$ ) are magnetic: the description of such system requires to include  $4f$  degeneracy in the model.

In the intermediate valence region, the  $4f$ -density of states is large near the Fermi level, and this is the reason why a magnetic instability can be induced very easily. The model presented in this paper, with additional magnetic interactions if necessary, is able to describe various situations observed in lanthanide compounds, where valence and magnetism variations under pressure, temperature, or alloying, appear to be connected.

This paper is dedicated to the memory of Pr. Peter Brommer in appreciation of his constant efforts in the cooperation with Vietnamese Universities and Institutes in the field of rare earth intermetallics magnetism.

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