Vol. 34 (2003) ACTA PHYSICA POLONICA B No 2

DMFT SOLUTION OF THE FALICOV–KIMBALL MODEL WITH AN INTERNAL STRUCTURE*

Veljko Zlatić

Institute of Physics, Bijenička c. 46, 10 001 Zagreb, Croatia

and Jim Freericks

Department of Physics, Georgetown University, Washington, DC 20057, USA

(Received July 10, 2002)

Dynamical mean field theory is used to solve the Falicov–Kimball model in the case where the f-ions have an internal structure. The solution provides a qualitative description of the properties of Eu-based intermetallic compounds which show anomalies due to a valence-change transition.

PACS numbers: 71.10.–w, 71.30.+h, 72.10.–d

1. Introduction and definition of the model

Experimental studies [1–5] of a number of Eu intermetallic compounds, like $\mathrm{Eu(Pd_{1-x}Pt_x)_2Si_2}$ and $\mathrm{EuNi_2(Si_{1-x}Ge_x)_2}$, show that the valence state of Eu ions can change abruptly from Eu^{2+} (f^7) to Eu^{3+} (f^7) as the temperature or the magnetic field is varied. The transition takes place at ambient pressure above 50 K, and the state of the system appears to be completely different above and below T_v. In the low-temperature phase the physical properties are nearly temperature-independent. Here, the Eu ions are non-magnetic and the conduction band is a Fermi liquid (FL) with a large characteristic FL scale $T^\star \gg T_\mathrm{v}$. A magnetic field of about $H_\mathrm{c} \simeq k_\mathrm{B}T_\mathrm{v}/\mu_\mathrm{B}$ Tesla destabilizes the FL ground state and induces a transition into a paramagnetic (f^7) state. Similarly, at a temperature T_v there is a zero field transition into a semi-metallic state. For $T \geq T_\mathrm{v}$ or $H \geq H_\mathrm{c}$, the Eu ions behave as 'almost free spins' and the linear and non-linear magnetic response is well explained by the single-ion theory which assumes that Eu^{2+} is a pure spin-7/2 state, and that Eu^{3+} has a non-magnetic ground state and two excited magnetic

---

* Presented at the International Conference on Strongly Correlated Electron Systems, (SCES 02), Cracow, Poland, July 10–13, 2002.

states. The high electrical resistance of these compounds above T_{v} is difficult to associate with exchange scattering, because the logarithmic terms are absent and fields up to 40 Tesla have very little effect. Thus, above T_{v} or $H \geq H_{\mathrm{c}}$, it seems that we are dealing with magnetic Eu^{2+} ions embedded into a bad metal with the chemical potential in a pseudo-gap or a small gap. The thermopower of $\mathrm{EuNi_2(Si_{1-x}Ge_x)_2}$ [6] has a positive hump, indicating electron-like transport.

A qualitative description of these effects is provided by the Falicov–Kimball (FK) model [7] which takes into account the interaction between a 2-fold degenerate conduction band and a lattice of Eu ions with an internal structure. The Eu^{2+} ion is modeled by a spin $S = 7/2$ Hund's rule state, while the Eu^{3+} ion is described by a $S = 0$ Hund's rule ground state and two excited states (an excited triplet state at energy $E^{S=1}$ and an excited quintet at $E^{S=2}$). All other excited states of the Eu ions are neglected. The f-states are localized and neither the number of Eu^{3+} and Eu^{2+} ions nor the internal state of an ion can change, except by thermodynamic fluctuations, *i.e.* the quantum mechanical fluctuations of the f-states are neglected. The conduction electrons can hop between nearest-neighbor sites on the D-dimensional lattice, with a hopping matrix $-t_{ij} = -t^*/2\sqrt{D}$; we choose a scaling of the hopping matrix that yields a nontrivial limit in infinite-dimensions [8]. Finally, we assume that the additional electron of the f^7 configuration gives rise to a Coulomb interaction U between the d- and f-electrons that occupy the same lattice site. Thus, the Falicov–Kimball model for the lattice Eu ions is defined by the Hamiltonian [9, 10]

$$\mathcal{H}_{\mathrm{FK}} = \mathcal{H}_d^0 + \mathcal{H}_{d-f} + \mathcal{H}_{f^7} + \mathcal{H}_{f^6}\,, \tag{1}$$

where

$$\mathcal{H}_d^0 = \sum_{ij,\sigma}(-t_{ij} - \mu\delta_{ij})d_{i\sigma}^\dagger d_{j\sigma}\,, \tag{2}$$

$$\mathcal{H}_{f^7} = \sum_{i,\eta}(E^{7/2} - \mu)f_{i\eta}^\dagger f_{i\eta}\,, \tag{3}$$

$$\mathcal{H}_{d-f} = U\sum_{i,\sigma\eta} d_{i\sigma}^\dagger d_{i\sigma} f_{i\eta}^\dagger f_{i\eta}\,, \tag{4}$$

and

$$\mathcal{H}_{f^6} = \sum_{i}(1 - n_{f^7}^i)\mathcal{H}_i^S\,. \tag{5}$$

The conduction electrons are created or destroyed at site i by $d_{i\sigma}^\dagger$ or $d_{i\sigma}$, and localized electrons are created or destroyed at site i by $f_{i\eta}^\dagger$ or $f_{i\eta}$. We use σ to denote the spin of the d-electrons, and η for the f^7 states. The f^7 Hund's rule state is represented by a single fermion with an infinite mass and spin 7/2. The d- and f^7-number operators at each site are $n_d = \sum_\sigma n_{d\sigma}$ and $n_{f^7} = \sum_\eta n_{f\eta} \leq 1$, Since the Eu ions can only assume the Eu^{3+} or the Eu^{2+} configurations, a chemical potential μ is employed to conserve the total number of electrons $n_d + n_f{}^7 = n_{\text{tot}}$. The term $\mathcal{H}_{f^6}$ describes the multiplets of Eu^{3+} ions (the non-magnetic ground state, an excited triplet, and an excited quintet) and it vanishes at sites occupied by Eu^{2+}. These states do not couple directly to other states and do not contribute to the dynamics of the system but have to be taken into account when calculating the partition function or the magnetization. The numerical calculations are performed for a hypercubic lattice with a Gaussian noninteracting density of states $\rho(\varepsilon) = \exp[-\varepsilon^2/t^{*2}]/(\sqrt{\pi}t^*)$; and t^* is taken as the unit of energy ($t^* = 1$). We consider only the homogeneous phase, where all quantities are translationally invariant. In the presence of a magnetic field the magnetic degeneracy is lifted and for the field oriented along the z-direction, the Hamiltonian (1) is supplemented by a Zeeman term. Using the basis that diagonalizes simultaneously the single-ion Hamiltonian in zero field and the z-component of the spin operator, we have

$$\begin{aligned}\mathcal{H}_{\mathrm{Z}} \;=\; & g_d\mu_{\mathrm{B}}H\sum_{i\sigma}\sigma d^\dagger_{i\sigma}d_{j\sigma} + g^f_{7/2}\mu_{\mathrm{B}}H\sum_{i\eta}\eta f^\dagger_{i\eta}f_{i\eta} \\ & + g^f_1\mu_{\mathrm{B}}H\sum_{i\xi_1}(1-n^i_{f^7})\xi_1 + g^f_3\mu_{\mathrm{B}}H\sum_{i\xi_3}(1-n^i_{f^7})\xi_3\,, \end{aligned} \tag{6}$$

where g_d and g^f_S are the g-factors, σ is the spin label of the d-electron, and η, ξ_1 and ξ_3 are the spin labels of the f^7-octet, f^6-triplet and f^6-quintet, respectively.

2. Exact solution in infinite dimensions

The DMFT of an infinite-coordination lattice is based on the observation that the self energy of the conduction electrons is local [8] and is a functional of the local Green's function only. Hence, as noted by Brandt and Mielsch [9], the lattice self energy of the FK model coincides with the self energy of an atomic d-state coupled to an atomic f-state by the same Coulomb interaction as on the lattice, and perturbed by an external time-dependent field, $\lambda(\tau, \tau')$. The lattice problem reduces to finding the Green's functions of the FK atom in the presence of an arbitrary external field and, then, choosing the field in such a way that the local d-electron Green's function of the lattice coincides with the Green's function of the atomic d-state, $G^\sigma_{\text{loc}}(z) = G^\sigma_{\text{at}}(z)$, and the local f-electron propagator coincides with the atomic f-state propagator, $F^\sigma_{\text{loc}}(z) = F^\sigma_{\text{at}}(z)$.

The atomic problem is solved by using the functional derivative technique of Kadanoff and Baym [11]. That is, the atomic partition function $\mathcal{Z}_{\rm at}(\lambda)$ is written as a functional of an external field λ and the functional derivatives are used to generate $G^{\sigma}_{\rm at}(z)$ and $F^{\sigma}_{\rm at}(z)$. The equations of motion (EOM) are used to determine integral operators $G^{\sigma}_{\rm at}$ and $F^{\sigma}_{\rm at}$ for a given λ-field, and the partition function is obtained from the inverse of the Green's function as $\mathcal{Z}_{\rm at}(\lambda)=\det|[G^{\sigma}_{\rm at}]^{-1}|$.

The generating functional (the partition function of the FK atom) is defined in the interaction representation as,

$$\mathcal{Z}_{\rm at}(\mu,\lambda)={\rm Tr}_{df}\left[T_{\tau}{\rm e}^{-\beta\mathcal{H}_{\rm at}}S(\lambda)\right], \tag{7}$$

where the Hamiltonian of the FK atom,

$$\mathcal{H}_{\rm at}=-\mu\sum_{\sigma}d^{\dagger}_{\sigma}d_{\sigma}+(E_f-\mu)\sum_{\eta}f^{\dagger}_{\eta}f_{\eta}+U\sum_{\sigma\eta}d^{\dagger}_{\sigma}d_{\sigma}f^{\dagger}_{\eta}f_{\eta}+(1-n_{f^7})\mathcal{H}^S, \tag{8}$$

defines the time evolution of the operators, and the external field defines the time-evolution operator for the state vectors,

$$S(\lambda)=T_{\tau}\exp\left(-\int\limits_0^{\beta}d\tau\int\limits_0^{\beta}d\tau'\sum_{\sigma}\lambda^{\sigma}(\tau,\tau')d^{\dagger}_{\sigma}(\tau)d_{\sigma}(\tau')\right). \tag{9}$$

The term $\mathcal{H}^S$ describes the excited states within the non-magnetic f^6 configuration. In the presence of the magnetic field, we add to (8) the Zeeman term that is obtained from (6) in an obvious way. The statistical sum runs over all possible f- and d-configurations and depends on $\lambda^{\sigma}(\tau,\tau')$ for $\tau,\tau'\in(0,\beta)$. We assume that $\lambda^{\sigma}(\tau,\tau')$ is time-translation invariant and anti-periodic in imaginary time. The unperturbed atomic Hamiltonian (8) conserves the number of f- and d-electrons, and the evolution operator gives rise only to fluctuations in the d-occupancy. Thus, the f-occupancy (the number of f^7 ions) is a constant of motion and the Hilbert space can be decomposed into invariant subspaces with respect to n_{f^7}. The matrix elements in (7) can be evaluated within each invariant subspaces by replacing $\sum_{\eta}f^{\dagger}_{\eta}f_{\eta}$ by its eigenvalue (0 or 1), which gives,

$$\mathcal{Z}_{\rm at}(\mu,\lambda)=\mathcal{Z}_{f^6}\mathcal{Z}_0(\mu,\lambda)+\mathcal{Z}_{f^7}\mathcal{Z}_0(\mu-U,\lambda). \tag{10}$$

Here, $\mathcal{Z}_0(\mu,\lambda)$ is the partition function of a simplified d-state decoupled from the f-state and coupled only to the λ-field, and $\mathcal{Z}_{f^6}=1+\sum_{\xi}{\rm e}^{-\beta E^{(1)}_{\xi}}+\sum_{\xi}{\rm e}^{-\beta E^{(2)}_{\xi}}$ and $\mathcal{Z}_{f^7}=\sum_{\eta}{\rm e}^{-\beta E^{(7/2)}_{\eta}}$ are the partition functions of f^6 and f^7

ions decoupled from the lattice. In the presence of the magnetic field, ξ and η label the Zeeman levels of f^6 and f^7 ions, respectively. We have, in the interaction representation,

$$\mathcal{Z}_0(\mu,\lambda) \;=\; \prod_\sigma \mathcal{Z}_0^\sigma(\mu,\lambda), \tag{11}$$

where

$$\mathcal{Z}_0^\sigma(\mu,\lambda) \;=\; \mathrm{Tr}_d\left[T_\tau \mathrm{e}^{-\beta\mathcal{H}_0^\sigma} S(\mu,\lambda^\sigma)\right] \tag{12}$$

and

$$\mathcal{H}_0 \;=\; -\mu\sum_\sigma d_\sigma^\dagger d_\sigma. \tag{13}$$

The factorization (11) holds because the time evolution due to $\mathcal{H}_0$ is such that the operators with different σ-labels commute regardless of their time arguments, and the S-matrix (9) does not change the σ-label of a given state vector. Thus, the Hilbert space can be decomposed into invariant σ-subspaces and the trace in (12) is over each non-degenerate d_σ-state.

To find the functional derivatives of $\mathcal{Z}_0^\sigma(\mu,\lambda^\sigma)$ we shift the λ-field from an initial configuration $\lambda^\sigma(\tau,\tau')$ to a final configuration $\lambda^\sigma(\tau,\tau')+\delta\lambda^\sigma(\tau,\tau')$, find the variation $\delta\, S(\mu,\lambda^\sigma)$ due to $\delta\,\lambda^\sigma$, and obtain,

$$\delta\,\ln\mathcal{Z}_0^\sigma = \int_0^\beta d\tau \int_0^\beta d\tau'\,\delta\lambda^\sigma(\tau,\tau')G_0^\sigma(\tau',\tau)\,. \tag{14}$$

The functional derivative is, by definition, the coefficient of $\delta\lambda^\sigma(\tau,\tau')$,

$$G_0^\sigma(\tau,\tau') = -\frac{\delta\ln\mathcal{Z}_0^\sigma}{\delta\lambda^\sigma(\tau',\tau)}, \tag{15}$$

and is given by the expression,

$$G_0^\sigma(\tau,\tau') = -\frac{1}{\mathcal{Z}_0^\sigma}\mathrm{Tr}_d\left\{T_\tau \mathrm{e}^{-\beta\mathcal{H}_0} d_\sigma(\tau) d_\sigma^\dagger(\tau') S(\mu,\lambda^\sigma)\right\}, \tag{16}$$

which is the d-electron propagator for the $U=0$, $\lambda\neq 0$ problem. The derivative with respect to τ gives the EOM for $G_0^\sigma(\tau,\tau')$,

$$\left(-\frac{\partial}{\partial\tau}+\mu\right)G_0^\sigma(\tau,\tau') - \int_0^\beta d\tau''\lambda^\sigma(\tau,\tau'')G_0^\sigma(\tau'',\tau') = \delta(\tau-\tau'), \tag{17}$$

where the δ-function arises from the discontinuity in G_0 at $\tau=\tau'$. The first order differential equation (17), supplemented by the boundary condition

$G_0^\sigma(\tau,\tau') = G_0^\sigma(\tau+\beta,\tau')$ has a unique solution. The inverse of $[G_0^\sigma]$ is a differential operator, which can be written as,

$$[G_0^\sigma]^{-1}(\tau,\tau') = [g_0^\sigma]^{-1}(\tau,\tau') - \lambda^\sigma(\tau,\tau'), \tag{18}$$

where,

$$[g_0^\sigma]^{-1}(\tau,\tau') = \left(-\frac{\partial}{\partial\tau} + \mu\right)\delta(\tau-\tau'), \tag{19}$$

is the inverse of the Green's function for the $U = 0$ and $\lambda = 0$ problem. By definition,

$$g_{0\sigma}(\tau,\tau') = -\frac{1}{\mathcal{Z}_0^\sigma(\mu,\lambda=0)}\mathrm{Tr}_d\left\langle T_\tau \mathrm{e}^{-\beta\mathcal{H}_0^\sigma} d_\sigma(\tau) d_\sigma^\dagger(\tau')\right\rangle, \tag{20}$$

where

$$\mathcal{Z}_0^\sigma(\mu,\lambda=0) = 1 + \mathrm{e}^{\beta\mu}, \tag{21}$$

is the partition function of a d-electron described by $\mathcal{H}_0$. Using $d_\sigma(\tau) = d_\sigma(0)\exp(\mu\tau)$ we find,

$$\begin{aligned} g_{0\sigma}(\tau-\tau') &= -(1-f_0)\mathrm{e}^{\mu(\tau-\tau')}, &&\text{for} \quad \tau > \tau', \\ g_{0\sigma}(\tau-\tau') &= f_0\,\mathrm{e}^{\mu(\tau-\tau')}, &&\text{for} \quad \tau < \tau', \end{aligned} \tag{22}$$

where $f_0 = 1/(1+\mathrm{e}^{-\beta\mu})$ is the thermal occupation factor.

Next, we notice that the λ-field is completely arbitrary and the same functional derivative is obtained if the λ-field is shifted with respect to some constant field. In other words, the variation of $\ln\mathcal{Z}_0^\sigma(\mu,\lambda)$ is not changed if $\lambda^\sigma(\tau',\tau)$ is redefined as $\lambda^\sigma(\tau',\tau) - [g_0]^{-1}(\tau',\tau)$ and we take $\delta\lambda^\sigma = \delta(\lambda^\sigma - [g_0]^{-1}) = -\delta[G_0^\sigma]^{-1}$. This gives,

$$\delta\ln\mathcal{Z}_0^\sigma(\mu,\lambda) = \int_0^\beta d\tau (G_0^\sigma\,\delta[G_0^\sigma]^{-1})(\tau,\tau), \tag{23}$$

and, since G_0^σ is the inverse of $[G_0^\sigma]^{-1}$,

$$\delta\ln\mathcal{Z}_0^\sigma(\mu,\lambda) = \int_0^\beta d\tau\,\delta\ln\{[G_0^\sigma]^{-1}\}(\tau,\tau). \tag{24}$$

Thus, $\delta\ln\mathcal{Z}_0^\sigma$ follows from the variation of $\mathrm{Tr}\ \ln\{[G_0^\sigma]^{-1}\}$ and, up to an arbitrary constant, we have

$$\ln\mathcal{Z}_0^\sigma(\mu,\lambda) = \mathrm{Tr}\ \ln\{[G_0^\sigma]^{-1}\}. \tag{25}$$

The matrix identity Tr $\ln A = \ln \det A$ allow us to write the partition function as a continuous determinant,

$$\mathcal{Z}_0^\sigma(\mu,\lambda) = \det|[G_0^\sigma]^{-1}| \tag{26}$$

or, equivalently,

$$\mathcal{Z}_0^\sigma(\mu,\lambda) = \det|g_{0\sigma}^{-1}| \, \det|1 - g_{0\sigma}\,\lambda^\sigma|, \tag{27}$$

where $\det|g_{0\sigma}^{-1}| = \mathcal{Z}_0^\sigma(\mu, \lambda = 0)$. This provides the solution for the FK atom with no f particles. The partition function in the $n_{f^7} = 1$ subspace is obtained from the $n_{f^7} = 0$ solution simply by replacing μ by $\mu - U$ in $\mathcal{Z}_0^\sigma(\mu,\lambda)$.

The fully renormalized Green's function of the FK atom describes the renormalization effects due to the Coulomb interaction and is given by

$$G_{\rm at}^\sigma(\tau,\tau') = -\frac{1}{\mathcal{Z}_{\rm at}(\mu,\lambda)} \mathrm{Tr}_{df} \left\langle T_\tau \mathrm{e}^{-\beta\mathcal{H}_{\rm at}} d_\sigma(\tau) d_\sigma^\dagger(\tau') S(\lambda) \right\rangle . \tag{28}$$

$G_{\rm at}^\sigma$ is obtained from $\mathcal{Z}_{\rm at}$ by functional differentiation,

$$G^\sigma(\tau,\tau') = -\frac{1}{\mathcal{Z}_{\rm at}(\mu,\lambda)} \frac{\delta \mathcal{Z}_{\rm at}(\mu,\lambda)}{\delta\lambda^\sigma(\tau',\tau)}. \tag{29}$$

where $\mathcal{Z}_{\rm at}$ is given by Eq. (10). Using (15) we find

$$G_{\rm at}^\sigma(\tau,\tau') = N_{f^6}\; G_0^\sigma(\tau-\tau') + N_{f^7} G_0^\sigma(\tau-\tau')|_{\mu-U}, \tag{30}$$

where $N_{f^6} = \mathcal{Z}_{f^6}\mathcal{Z}_0(\mu,\lambda)/\mathcal{Z}_{\rm at}$, $N_{f^7} = \mathcal{Z}_{f^7}\mathcal{Z}_0(\mu-U,\lambda)/\mathcal{Z}_{\rm at}$, and where we indicated that the chemical potential in the second term is to be shifted by U. The weights N_{f^6} and N_{f^7} give the average number of Eu^{3+} and Eu^{2+} ions, respectively. Since G_0^σ is the Green's function of the $U = 0$ problem, we can define the self-energy as,

$$\Sigma^\sigma = [G_0^\sigma]^{-1} - [G_{\rm at}^\sigma]^{-1}. \tag{31}$$

The matrix elements of $[G_0^\sigma]^{-1}$, $[G_{\rm at}^\sigma]^{-1}$, Σ^σ and λ^σ depend on the time difference only and satisfy the imaginary-time boundary condition $f(0) = -f(-\beta)$. Thus, they can all be expressed in terms of Fourier components as, $f(\tau-\tau') = T\sum_n f_n \mathrm{e}^{-i\omega_n(\tau-\tau')}$, where $\omega_n = (2n+1)\pi/\beta$ is the Matsubara frequency. The Matsubara representation reduces the EOM to a set of decoupled algebraic equations for the diagonal components of $G_{\rm at}^\sigma$ in (discrete) frequency space,

$$G_{\rm at}^\sigma(i\omega_n) = \frac{N_{f^6}}{[G_0^\sigma(i\omega_n)]^{-1}} + \frac{N_{f^7}}{[G_0^\sigma]^{-1}(i\omega_n) - U}, \tag{32}$$

where $[G_0^\sigma]^{-1}(i\omega_n) = [g_0^\sigma]^{-1}(i\omega_n) - \lambda_n^\sigma$ and $[g_0^\sigma]^{-1}(i\omega_n) = i\omega_n + \mu\sigma\mu_{\rm B}g_dH$, and we included the magnetic field. Since λ_n^σ, $[g_0^\sigma](i\omega_n)$ and $[g_0^\sigma]^{-1}(i\omega_n)$ are diagonal matrices, the $U = 0$ partition function is an infinite product,

$$\mathcal{Z}_0^\sigma(\mu, \lambda) = (1 + \mathrm{e}^{\beta\mu}) \prod_n \left(1 - \frac{\lambda_n^\sigma}{i\omega_n + \mu + \sigma\mu_{\rm B}g_dH}\right) \tag{33}$$

and the full partition function follows from Eq. (10).

The numerical solution on the imaginary axis is obtained by solving (31), (32), and (33) together with the self-consistency condition, $G_{\rm at}^\sigma(z) = G_{\rm loc}^\sigma(z)$, which can be written as,

$$G_{\rm at}^\sigma(z) = \int \frac{\rho(\varepsilon)}{z + \mu + \sigma\mu_{\rm B}g_dH - \Sigma^\sigma(z) - \varepsilon} d\varepsilon, \tag{34}$$

where z is a complex variable. For an appropriate λ-field the functional dependence of Σ^σ on $G_{\rm at}^\sigma(z)$ is exactly the same as in the lattice case, *i.e.*, the DMFT replaces the lattice problem by a local time-dependent field and provides exact results for the lattice model [10, 12]. Furthermore, once the numbers N_{f^6} and N_{f^7} are obtained (for a given choice of parameters) by performing iterations on the imaginary axis, we can iterate (31), (32) and (34) on the real axis and find the retarded quantities. In infinite dimensions the vertex corrections to transport coefficients disappear and the electrical resistivity and the thermopower of the FK-model can be obtained from the d-electron's Green's function [13]. Note, because of the infinite-dimensional scaling of the hopping matrix elements, the electrical conductivity is of the order of $1/D$, where D is the dimensionality of the lattice. In what follows, use the DMFT to calculate the thermodynamic and transport properties of the model.

3. Results and discussion

The temperature dependence of the average occupation of magnetic Eu^{2+} ions is defined by N_{f^7} and is shown in Fig. 1 for $E_f = -0.6$, for $U = 2$, and for several band-fillings. We consider a conduction band that is more than half-filled at $T = 0$; the less than half-filled case is obtained by an electron–hole transformation. For $U = 2$ there is a small gap (pseudo-gap) in the conduction band of the hypercubic lattice. The main feature of the N_{f^7} curves is the cross-over from a low-temperature state in which there are no Eu^{2+} ions into a high-temperature state with a substantial occupation of magnetic Eu^{2+} ions. The effect of the excited states of Eu^{3+} on the average occupation of Eu^{2+} is small, at low temperatures, while the effect of the band-filling is pronounced. The transition sharpens as the total number of electrons is reduced and the conduction band approaches half-filling at $T = 0$. Similar behavior (a sharpening of the transition and a reduction of the transition temperature) is obtained if we shift the f^7-state closer to the chemical potential, so as to increase the average high-temperature occupation of the Eu^{2+} ions [12]. If we assume that pressure or chemical pressure reduce the average Eu^{2+} occupation, we find the same qualitative features as in the experimental data [2–5]. The temperature dependence of

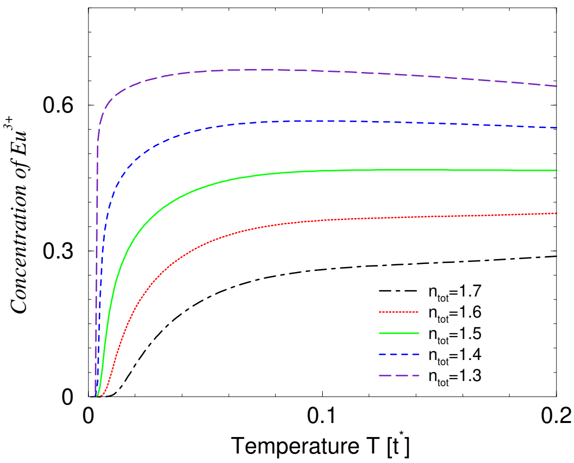

Fig. 1. Temperature dependence of the concentration of magnetic Eu^{3+} ions for the FK model with $U = 2$, $E^{(7/2)} = -0.6$, $E^{(1)} = 0.3$, $E^{(2)} = 0.6$, and for $n_{\mathrm{tot}} = 1.3$ (long-dashed line), 1.4 (dashed), 1.5 (solid), 1.6 (dotted), and 1.7 (chain-dotted).

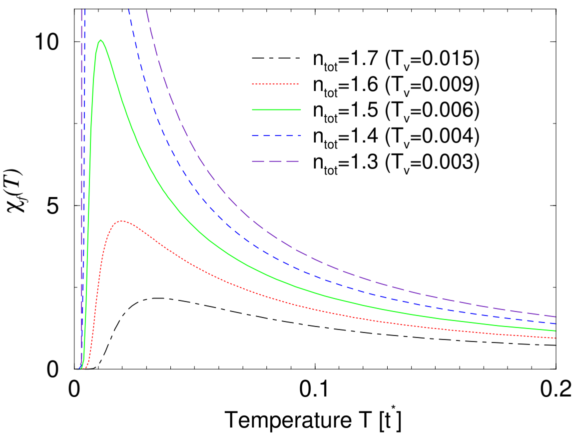

Fig. 2. Temperature dependence of the magnetic susceptibility of Eu ions for the FK model for the same parameters as in Fig. 1.

the linear magnetic susceptibility $\chi_f(T)$ of the Eu ions is shown in Fig. 2 for the same parameters as in Fig. 1. The contribution due to the conduction band has been subtracted and the Eu-contribution is well described by the Curie law, $\chi_f(T) \propto N_{f^7}/T$. The transition is seen more clearly in $\chi_f(T)$ than in N_{f^7}, and if we define $T_{\rm v}$ as the temperature at which $\chi_f(T_{\rm v})$ is half the maximum value we find, $T_{\rm v} = 0.015$, 0.009, 0.006, 0.004, and 0.003 for $n_{\rm tot} = 1.7$, 1.6, 1.5, 1.4, and 1.3, respectively. The data in Fig. 2 show that a small increase of the Curie constant can lead to a large reduction in $T_{\rm v}$.

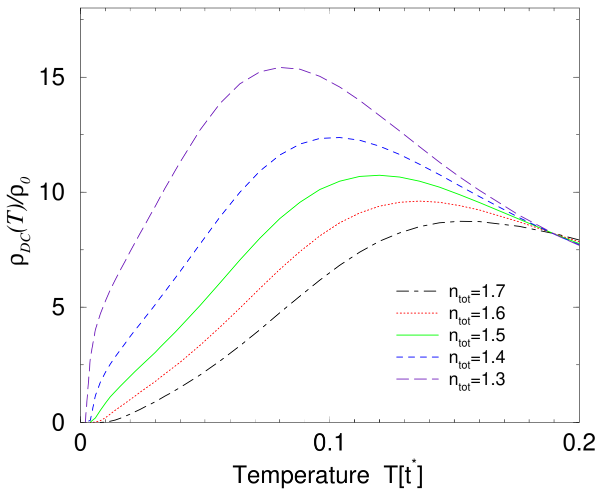

Fig. 3. DC resistivity for the FK model for the same parameters as in Fig. 1.

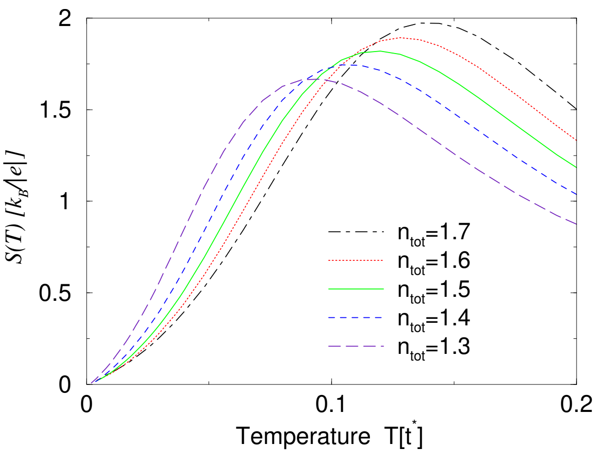

Fig. 4. Thermopower of the FK model for the same parameters as in Fig. 1.

The DC resistivity and the thermopower obtained for the same parameters as used in Fig. 1 are shown in Figs. 3 and 4, respectively. The resistivity is defined in units of $\rho_0 = hDa^{D-2}/e^2\pi^2$ (which is ill-defined in infinite dimensions but is approximately $2.3 \times 10^{-4}\Omega$-cm in $D = 3$ with $a \approx 3 \times 10^{-8}$ cm). The thermopower is plotted in units $k_{\mathrm{B}}/|e| \simeq 86\ \mu\mathrm{V}/k_{\mathrm{B}}$. The resistivity and the thermopower exhibit a broad maximum which is related to a pseudo-gap in the conduction electron density of states (DOS). That is, at low temperatures, the chemical potential is close to the center of the conduction band, where the DOS is large, and the system is a good metal. As the temperature increases μ shifts into the pseudo-gap region [12] and the resistivity and the thermopower increase. At very high temperatures μ is above the pseudo-gap, and the resistivity and the thermopower decrease again. Note, the pseudo-gaps or the gaps we are discussing here are not due to the details of the band-structure but are the many-body effects caused by large coupling for any non-interacting DOS. The changes in the band filling that lead to a huge variation of T_{v} have only a small effect on the position of the maximum in the transport coefficients. It is interesting to observe that the resistivity and the thermopower maxima shift in opposite directions. For small T_{v} the resistivity shows a steep rise, that follows the rapid increase of N_{f^7}. Above the maximum, the Falicov–Kimball interaction leads to a resistivity that has the same shape for all band-fillings. The thermopower does not show any significant variation around T_{v}.

Finally, we discuss the meta-magnetic transition induced by magnetic fields. We consider the z-component of the full magnetization of the FK lattice,

$$m^z(H) = \frac{1}{\mathcal{Z}_{\mathrm{FK}}}\mathrm{Tr}_{cf}[\mathrm{e}^{-\beta\mathcal{H}_{\mathrm{FK}}(H)}m_f^z], \tag{35}$$

where, the trace is over all the states of the lattice. In the DMFT this is equivalent to an effective atomic problem in which the λ-field mimics the lattice,

$$m^z(H) = \frac{1}{\mathcal{Z}_{\mathrm{at}}}\mathrm{Tr}_{cf}[\mathrm{e}^{-\beta\mathcal{H}_{\mathrm{at}}(H)}S(\lambda)m^z], \tag{36}$$

where $\mathcal{H}_{\mathrm{at}}$ contains the atomic Zeeman terms, $S(\lambda)$ is defined by Eq. (9) and the trace is performed in the basis which diagonalizes simultaneously $\mathcal{H}_{\mathrm{at}}$ at $H = 0$ and the z-components of the spin operators. We find,

$$\begin{aligned} m^z(H) \ =\ & g_d\mu_{\mathrm{B}}[n_{d\uparrow}(H) - n_{d\downarrow}(H)] + \frac{\mathcal{Z}_0(\mu - U)}{\mathcal{Z}_{\mathrm{at}}}\gamma_{7/2}\sum_{\eta=-7/2}^{7/2}\eta\mathrm{e}^{-\beta(E_\eta^{7/2}(H)-\mu)} \\ & + \frac{\mathcal{Z}_0(\mu)}{\mathcal{Z}_{\mathrm{at}}}\left\{\gamma_1\sum_{\xi=-1}^{1}\xi\mathrm{e}^{-\beta E_\xi^{(1)}(H)} + \gamma_3\sum_{\xi=-2}^{2}\xi\mathrm{e}^{-\beta E_\xi^{(2)}(H)}\right\}, \end{aligned} \tag{37}$$

where the first term describes the response of the conduction band, the second term describes the contribution due to Eu^{2+} ions, and the last two terms describe the contribution due to Eu^{3+} ions. The partition function $\mathcal{Z}_0(\mu)$ includes the Zeeman energy of the conduction electrons, $E_\eta^{(S)}(H)$ is the field-dependent eigenvalue of an isolated Eu-ion, $\eta \in (-S, S)$ is the spin label, and $\gamma_S = g_S^f \mu_{\mathrm{B}}$. Introducing the field-dependent magnetizations of isolated Eu-ions, $m_S^z(H) = \gamma_S \sum_\eta \eta \exp[-\beta E_\eta^{(S)}(H)]/\mathcal{Z}_f$ we find

$$\begin{aligned} m_{\mathrm{Eu}}^z(H) &= N_{f^6}\left\{\gamma_1 B_1(\gamma_1 H\beta) + 3\gamma_3 B_3(3\gamma_3 H\beta)\right\} \\ &\quad + N_{f^7}\frac{7\gamma_{7/2}}{2} B_{7/2}\left(\frac{7}{2}\gamma_{7/2} H\beta\right), \end{aligned} \tag{38}$$

where $B_S(x)$ is the Brillouin function.

The Falicov–Kimball interaction between an additional electron of the f^7 configuration and the conduction band gives rise to a temperature and field dependence of the occupation numbers N_{f^6} and N_{f^7} and modifies the single-ion response. For $U = 0$, the slope of $m_{\mathrm{Eu}}^z(H)$ decreases monotonically from the zero-field value and $m_{\mathrm{Eu}}^z(H)$ approaches the high-field limit in a typical paramagnetic fashion. For $U \neq 0$ and $T \geq T_{\mathrm{v}}$, we still find that $\partial m_{\mathrm{Eu}}^z(H)/\partial H$ has a maximum at $H = 0$ and $m_{\mathrm{Eu}}^z(H)$ saturates as in the $U = 0$ case. Below T_{v}, however, $\partial m_{\mathrm{Eu}}^z(H)/\partial H$ is a non-monotonic function which starts from zero at $H = 0$ and increases up to H_{c}. Above $H \geq H_{\mathrm{c}}$ the slope starts decreasing and the magnetization approaches the high-field limit in the usual way. At the critical field $\partial^2 m_{\mathrm{Eu}}^z(H)/\partial H^2$ changes sign and the 3rd order susceptibility $\partial^3 m_{\mathrm{Eu}}^z(H)/\partial H^3$ might diverge. The critical temperature above which the linear susceptibility $\lim_{H\to 0} \partial m_{\mathrm{Eu}}^z(H)/\partial H$ becomes non-zero and the critical field at which $\lim_{T\to 0} \partial^2 m_{\mathrm{Eu}}^z(H)/\partial H^2$ changes sign are about the same. The valence-change transition and the meta-magnetic transition are coupled together because the field brings the renormalized f-level closer to the chemical potential, enhances the thermal occupation of the f-states, and increases the magnetic entropy. At the transition, the energy loss due to the additional population of the f-states, and the entropy loss due to the reduction of the conduction electrons, are balanced by the magnetic entropy of the additional f-states.

In summary, the DMFT solution of the Falicov–Kimball model explains the qualitative features of the valence-change and the meta-magnetic transition in Eu-based intermetallic compounds. However, the model parameters and the absolute value of the temperature scale can not be uniquely determined from the static response functions and a quantitative analysis should also compare the dynamical properties of the model with the experimental data [12].

We acknowledge useful discussions with C. Geibel and J. Sarrao. We acknowledge the support by the National Science Foundation under grants DMR-0210717 and by the Office of Naval Research under grants N00014-99-1-0328. V.Z. acknowledges the support by the Swiss National Science Foundation, grant no. 7KRPJ65554.

REFERENCES

[1] E.V. Sampathkumaran, L.C. Gupta, R. Vijayaraghavan, K.V. Gopalkrishnan, R.G. Pillay, H.G. Devare, *J. Phys. C* **14**, L237 (1981).

[2] H. Wada, A. Nakamura, A. Mitsuda, M. Shiga, T. Tanaka, H. Mitamura, T. Goto, *J. Phys.: Condens. Matter* **9**, 7913 (1997).

[3] H. Wada, H. Gomi, A. Mitsuda, M. Shiga, *Solid State Commun.* **117**, 703 (2001).

[4] A. Mitsuda, H. Wada, M. Shiga, H. Aruga Katori, T. Goto, *Phys. Rev.* **B55**, 12474 (1997).

[5] H. Wada, M.F. Hundley, R. Movshovich, J.D. Thompson, *Phys. Rev.* **B59**, 1141 (1999).

[6] J. Sakurai, S. Fukuda, A. Mitsuda, H. Wada, M. Shiga, *Physica B* **281 & 282**, 134 (2000).

[7] L.M. Falicov, J.C. Kimball, *Phys. Rev. Lett.* **22**, 997 (1969).

[8] W. Metzner, D. Vollhardt, *Phys. Rev. Lett.* **62**, 324 (1989).

[9] U. Brandt, C. Mielsch, *Z. Phys.* **B75**, 365 (1989); U. Brandt, M.P. Urbanek, *Z. Phys.* **B89**, 297 (1992).

[10] J.K. Freericks, V. Zlatić, *Phys. Rev.* **B58**, 322 (1998).

[11] L.P. Kadanoff, G. Baym, *Quantum Statistical Physics*, W. A. Benjamin, Menlo Park, CA 1962.

[12] V. Zlatić, J.K. Freericks, R. Lemanski, G. Czycholl, *Philos. Mag.* **B81**, 1443 (2001).

[13] J.K. Freericks, V. Zlatić, *Phys. Rev.* **B64**, 245118 (2001).