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Role of phonons and Coulomb interactions in fluctuating-valence europium compounds

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An extended Anderson model including Coulomb interactions and electron-phonon coupling is discussed within the Hartree-Fock approximation. This model is used to describe valence fluctuations in europium intermetallic compounds. The total $4f$ occupation number and the $4f$ level width are shown to be in qualitative agreement with experimental data. A connection to charge screening invoked in a previous work is also made, and the conclusions tend to support the phenomenological approach developed in that work.

I. INTRODUCTION

A phenomenological model to discuss qualitatively the valence of europium atoms in intermetallic compounds was recently developed.[1] Emphasis was given on the role of the charge screening in the valence-fluctuation phenomena. The systematic trend of the europium valence, including homogeneous mixed valence states in a large variety of intermetallic compounds could be then qualitatively understood.

Although successful in this qualitative understanding, drawbacks of this picture should be pointed out. The first one concerns the origin and value of the effective $4f$ level width Δ, together with the general approach of Ref. 1 in considering separately $4f$ ions and d-band electrons coupled only through a phenomenological interaction γ_d. Clearly the values of Δ play a fundamental role to understand experimental results, e.g., isomer shifts,[2] and x-ray photoemission[3] (XPS) measurements in fluctuating systems. Although it is possible, within the framework of this picture, suitably extended to include temperature effects,[4] to extract from experimental data, excitation energies between two europium configuration, and the effective level widths, the problem of the origin of these widths remains. In particular, one must understand how Δ changes when one crosses from a Eu^{3+} configuration to a Eu^{2+} by changing of the x concentration in compounds like $Eu(A_{1-x}B_x)_2$, where A and B are transition metals.

Another limitation of the model developed in Ref. 1 is to understand the existence of magnetic order associated with the $4f^7$ configuration and a nonmagnetic state for the $4f^6$ configuration. In that work[1] only limiting cases $x = 0$ and $x = 1$ could be described using Hund's rule, but in the $x = 1$ case the origin of the long-range magnetic order was not discussed. Both problems involve among other interactions, the hybridization between the d band and localized f states, which is completely absent in Ref. 1.

In this work one intends to improve the previous one[1] in several respects. Although conserving the one-center picture, one introduces one-electron hybridization between the local and conduction states. Then one chooses an Anderson-type approach for the f electrons in a metal. The usual Anderson model, incorporating intraorbital Coulomb interaction will be supplemented here by introducing (i) local Coulomb interaction between the local f electrons and the d band, (ii) the electron-phonon interaction between d-band states and lattice vibrations. So, one expects to discuss a mechanism which may account for the features observed in Eu intermetallic compounds.

The motivation of this extension goes as follows: hybridization introduces naturally a source of f-level width; intra-f-orbital Coulomb interaction is usually invoked to describe local moment formation and magnetic ordering. The coupling between f and d electrons introduces in a natural way correlations between f-level and d-band occupation at the impurity site. Finally and perhaps more importantly, electron-phonon interactions are expected to be present in the valence-fluctuating systems as suggested by lattice deformations observed in these systems.[2] However it should be stressed that one incorporates the coupling between d electrons and the lattice and not between the f occupation number and the lattice.[5,6] The reason for this choice follows from the role played by the d electrons in the cohesion of these systems. If an f electron hops to the d band, the change in the d electron density is expected to alter the cohesion forces and so lattice distortion follows.

In the literature several extensions of the Anderson model have been discussed in connection with valence-fluctuation systems. The Coulomb interaction between d and f electrons has been introduced in the Anderson model by Khomskii and Kocharjan,[7] within the Hartree-Fock approximation in order to discuss the $\gamma-\alpha-\gamma'$ transitions in Ce and metal-insulator transition in SmS.

These authors assumed a suitable ground state of excitonic nature and an extra f-level width appears due to this excitonic pairing in addition to the usual level width associated with hybridization.

The d-f Coulomb interaction was invoked also by Haldane,[5] together with a two-channel description of the coupled Anderson model: one channel (fast) associated with the d electrons is used to ensure overall charge neutrality during the relatively slow f-electron-number fluctuation. Within the framework of the Tomonaga approximation this problem is shown[5] to be equivalent to a fermionlike problem (the Anderson Hamiltonian) coupled to a boson field (the screening field). A formally identical picture is provided by Riseborough's work,[6] where the fermion operators n_f are coupled, via an electron-phonon coupling, to the phonons. In both points of view, due to the formal similarity one would say, following Haldane,[5] that valence fluctuations are purely electronic phenomena. The inclusion of the electron-phonon coupling to the d states enables one to bridge between cohesive energy arguments and valence fluctuations. Also, as will be discussed in the approximations of this model, electron-phonon interaction will play a fundamental role in the screening of the charge and so besides providing a microscopic view of the phenomenological screening potential,[1] it connects also the electronic nature of valence fluctuations to lattice distortions.

This work is divided in four sections. Section II is devoted to describe the model and approximations to deal with the many-body terms. In Sec. III the formalism is developed. Section IV contains the numerical results and some discussions to generalize the one-electron problem to europium atoms. Finally, Sec. V includes general discussions and final comments.

II. MODEL AND APPROXIMATIONS

The conduction states are assumed to be of d character, and will be discussed within the tight-binding approximation. In second-quantization form the Hamiltonian for conduction states reads

$$H^{(d)}=\sum_{i,j,\sigma}T_{ij}^{(d)}d_{i\sigma}^{\dagger}d_{j\sigma} \tag{1}$$

where $T_{ij}^{(d)}$ is the hopping integral leading to a dispersion relation $\epsilon_k^{(d)}$ and $d_{i\sigma}^{\dagger}$ ($d_{i\sigma}$) are creation (destruction) operators for a d electron with spin σ at the site i. For simplicity, one neglects the Coulomb interaction U_{dd} among d states and so one assumes that Eq. (1) contains all the relevant information for the unperturbed d band.

Concerning the f states, one adopts the one-center picture,[1,4-6] as a zeroth-order approximation for valence-fluctuating systems. The one-center Hamiltonian for f electrons reads then

$$H^{(f)}=\sum_{\sigma}\epsilon_f n_{0\sigma}^f+U_{ff}n_{0\uparrow}^f n_{0\downarrow}^f\,,\quad n_{0\sigma}^f=f_{0\sigma}^{\dagger}f_{0\sigma}\,. \tag{2}$$

In Eq. (2) $f_{0\sigma}^{\dagger}$ ($f_{0\sigma}$) creates (destroys) an electron with spin σ and energy ϵ_f at the origin. For the moment a nondegenerate level will be adopted; an approximate description of the many-electron nature of Eu atoms will be made later on.

The interactions between the d conduction states and the localized states are of two kinds.

(i) A one-electron hybridization term between the local f states and the conduction d states

$$H^{(\mathrm{mix})}=V_{df}\sum_{\sigma}d_{0\sigma}^{\dagger}f_{0\sigma}+V_{fd}\sum_{\sigma}f_{0\sigma}^{\dagger}d_{0\sigma}\,. \tag{3}$$

This mixing term contains the usual phenomenological aspects, namely, it acts only at the origin, and the matrix element $|V_{df}|^2$ is to be thought of as a parameter of the theory. Alternative formulations would involve[8] the different parity of d and f electrons and a next-neighbor overlap. This implies k-dependent matrix elements and for simplicity one adopts the phenomenological approach.

(ii) A Coulomb interaction (intrasite) between the $4f$ electrons and the d band; the complete term reads

$$H^{(df)}=\sum_{\sigma,\sigma'}U_{df}n_{0\sigma'}^{d}n_{0\sigma}^{f}\,. \tag{4}$$

The Hamiltonians Eq. (1)–(4) are the terms of the usual extended Anderson Hamiltonian with the Coulomb interaction among d and f electrons. If the one-center picture is applied to valence-fluctuating systems another term is to be included to account for peculiar effects associated to these systems. One refers to lattice deformations induced by valence changes. As mentioned in the Introduction such deformations are understandable since the transfer of a $4f$ electron to the conduction band is expected to change the elastic forces between neighboring atoms. If the cohesive energy in these metals is to be ascribed to the itinerant d states, it seems physically reasonable to expect that the electron-phonon interaction between d electrons and lattice vibrations should play an essential role in the formulation of the valence-fluctuation problem. In view of these remarks one considers the following term:

$$\begin{aligned}H^{(\mathrm{latt})}=&\sum_{\vec{q}}\omega_{\vec{q}}a_{\vec{q}}^{\dagger}a_{\vec{q}}\\&+\sum_{i,\vec{q},\sigma}C_{\vec{q}}\left(a_{\vec{q}}e^{i\vec{q}\cdot\vec{R}_i}-a_{\vec{q}}^{\dagger}e^{-i\vec{q}\cdot\vec{R}_i}\right)n_{i\sigma}^{d}\,,\end{aligned} \tag{5}$$

where $a^{\dagger}_{\vec{q}}$ ($a_{\vec{q}}$) stand for creation (annihilation) operators for a phonon of wave vector $\vec{q}$ and energy $\omega_{\vec{q}}$. $C_{\vec{q}}$ is the electron-phonon coupling. Instead of adding Eq. (5) to the model Hamiltonian, one follows Bari[9] and adds the effective electron-electron interaction among d electrons mediated via phonon excitation, namely,

$$H^{(dd)}_{\text{el-ph}} = -\sum_{i} C_{ii}\left(\sum_{\sigma} n^{d}_{i\sigma}\right)^{2} . \tag{6}$$

In Bari's work,[9] this term arises through the classical canonical transformation eliminating phonon variables from the Hamiltonian. One has made in Eq. (6), the approximation of keeping only intrasite terms, where C_{ii} characterizes the strength of the electron-phonon interaction between d states and lattice vibrations. It should be mentioned that the validity of (6) to describe phonon-mediated coupling between d electrons is an important assumption of this work.

The total Hamiltonian is given by

$$H = H^{(d)} + H^{(f)} + H^{(\text{mix})} + H^{(df)} + H^{(dd)}_{\text{el-ph}} . \tag{7}$$

Due to the many-body nature of the total Hamiltonian one needs some approximate method to deal with correlations. The extended version of the Anderson model has been treated using several methods. In particular for $C_{ii} = 0$, Haldane[5] using Tomonaga's method reduces the problem to a coupled fermion-boson one, which is treated within the mean-field approximation. On the other hand, a functional-integral technique, together with the saddle-point method was used by Riseborough[6] to treat the Anderson model coupled with phonons through the f electron occupation. Due to the complexity of the Hamiltonian, Eq. (7), we decided to work within the simplest approximation, namely, the Hartree-Fock approximation, as in other similar works[5,7,10] dealing with valence fluctuations.

One starts by linearizing the electron-electron interaction terms. The intra-f-orbital Coulomb term is linearized in the usual way, but the d-f interaction terms needs some discussion. As mentioned in Ref. 7 an important question arises when one considers the full Hartree-Fock linearization of Eq. (4).

$$\begin{aligned} H^{(df)} = {} & \sum_{\sigma\sigma'} U_{df}\big(\langle f^{\dagger}_{0\sigma} f_{0\sigma}\rangle d^{\dagger}_{0\sigma'} d_{0\sigma'} \\ & \qquad + \langle d^{\dagger}_{0\sigma} d_{0\sigma}\rangle f^{\dagger}_{0\sigma'} f_{0\sigma'}\big) \\ & + \sum_{\sigma,\sigma'} U_{df}\big(\langle f^{\dagger}_{0\sigma} d_{0\sigma}\rangle d^{\dagger}_{0\sigma'} f_{0\sigma'} \\ & \qquad + \langle d^{\dagger}_{0\sigma} f_{0\sigma}\rangle f^{\dagger}_{0\sigma'} d_{0\sigma'}\big) . \end{aligned} \tag{8}$$

The last two terms of Eq. (8) are those invoked by Khomskii and Kocharjan[7] to describe the extra f-level width due to excitonic pairing, which persist in the absence of one-electron hybridization. The existence of self-consistent solutions exhibiting nonzero values of the "order parameter" $\langle d^{\dagger}_{0\sigma} f_{0\sigma}\rangle$ assume a ground state of different nature from the usual one assumed for the Anderson model. We argue however that the behavior for the f-level width can be explained without this extra assumption, provided the first two terms of Eq. (8) are properly included. Moreover, one expects that the $4f$ width should go to zero in the absence of one-electron hybridization[10], except for extra broadening effects which are not included in this picture. Hence, we neglect the second term of Eq. (8). The other terms of the total Hamiltonian are linearized in the usual way and one gets the effective Hamiltonian

$$H = \tilde{H}^{(d)} + \tilde{H}^{(f)} + H^{(\text{mix})} , \tag{9}$$

where

$$\begin{aligned} \tilde{H}^{(d)} = \sum_{i,j,\sigma} \Bigg(& T^{(d)}_{ij} + U_{df} \sum_{\sigma'} \langle n^{f}_{0\sigma'}\rangle \delta_{ij}\delta_{i0} \\ & - C_{ii} \sum_{\sigma'} \langle n^{d}_{i\sigma'}\rangle \delta_{ij} \Bigg) d^{\dagger}_{i\sigma} d_{j\sigma} \end{aligned} \tag{10}$$

and

$$\tilde{H}^{(f)} = \sum_{\sigma} \left(\epsilon_{f} + U_{ff}\langle n^{f}_{0-\sigma}\rangle + U_{df} \sum_{0'} \langle n^{d}_{0\sigma'}\rangle \right) n^{f}_{0\sigma} . \tag{11}$$

The mixing term remains unaltered. Concerning the nonhybridized f states, Eq. (11), the Hartree-Fock linearization introduces apart from the usual Coulomb shift $U_{ff}\langle n^{f}_{0-\sigma}\rangle$, an extra shift due to the repulsion energy among d and f electrons. From Eq. (10) one observes that the U_{df} coupling introduces a localized perturbation, with strength proportional to the f-orbital occupation number, which may strongly deform the unperturbed d-band density of states. Within the Hartree-Fock approximation one sees that the electron-phonon term acts twofoldly. If one rewrites this term as

$$\begin{aligned} & -\sum_{i,\sigma} C_{ii} \left(\sum_{\sigma} \langle n^{d}_{i\sigma}\rangle \right) n^{d}_{i\sigma} \\ & \qquad = -\sum_{i,\sigma} C_{ii} \left(\sum_{\sigma'} \langle n^{d(0)}_{i\sigma'}\rangle \right) n^{d}_{i\sigma} - \sum_{i,\sigma} C_{ii} \left(\sum_{\sigma'} \delta n^{(d)}_{i\sigma'} \right) n^{d}_{i\sigma} \end{aligned}$$

two contributions appear. The first one, associated with the translationally invariant occupation members, just shifts the center of the band, and so is unimportant. The second one however, introduces a new scattering source for d electrons. This term is nonlocalized in nature, due to usual Friedel-like oscillations, and the solution of such a potential scattering problem is mathematically and numerically complex. Clearly, one could assume a perturbation localized at the central site and next neighbors, treating the perturbation associated with the latter within the Born approximation. If one assumes the potential to be restricted to the central site, this term together with the U_{df} one, will provide a Slater-Koster impurity problem[11] which is exactly treatable. Postponing a better discussion for Sec. IV, for the moment one restricts to the central cell and approximates the Eq. (10) by

$$\tilde{H}^{(d)} = \sum_{i,j,\sigma} T^{(d)}_{ij} d^\dagger_{i\sigma} d_{j\sigma} + V n^d_{i\sigma} , \tag{12}$$

where the local scattering potential is defined by

$$V = U_{df} \sum_\sigma \langle n^f_{0\sigma'} \rangle - C\delta n^d_0 . \tag{13}$$

Equations (12) and (13) in the absence of the mixing term $H^{(\mathrm{mix})}$ define the above-mentioned Slater-Koster problem. If the mixing is used, Eqs. (11), (3), (12), and (13) define an Anderson-Moriya[12] problem coupled to a Slater-Koster one. The same formalism has been used in other contexts, namely, the formation of actinide-impurity magnetic moment in disordered transition hosts[13] and rare-earth impurities in s-p hosts.[14] The mathematical solution of this problem together with the suitable sum rules for the electron occupations numbers is the subject of the Sec. III.

III. FORMALISM

The effective Hartree-Fock Hamiltonian, Eqs. (10), (3), and (11), can be treated in two steps. Using the Green's function formalism one defines an "intermediate" Green's function $\tilde{g}$ to describe the scattering of the extended d states. In such a way one solves the extended Slater-Koster problem defined in Eqs. (12) and (13) through the Dyson-like equation

$$\tilde{g}_\sigma = g + gV\tilde{g}_\sigma , \tag{14}$$

where g has the following matrix elements:

$$g^{dd}_{ij}(\omega) = \sum_k e^{i\vec{k}\cdot(\vec{R}_i - \vec{R}_j)}/(\omega - \epsilon^d_{\vec{k}}) ,$$

$\epsilon^d_{\vec{k}}$ being the band dispersion relation.

Equation (11) yields for the diagonal matrix element

$$\tilde{g}^{dd}_{ii}(\omega) = g^{dd}_{ii}(\omega) + g^{dd}_{i0}(\omega)\frac{V}{1 - Vg^{dd}_{00}(\omega)} g^{dd}_{0i}(\omega) . \tag{15}$$

One has at the origin

$$\tilde{g}^{dd}_{00}(\omega) = \frac{g^{dd}_{00}(\omega)}{1 - Vg^{dd}_{00}(\omega)} = \frac{F_d(\omega)}{1 - VF_d(\omega)} = \tilde{F}_{d,0}(\omega) , \tag{16}$$

where $F_d(\omega)$ has real and imaginary parts, i.e.,

$$F_d(\omega + i\epsilon) = F^R_d(\omega) - i\pi\rho_d(\omega), \quad \epsilon \to 0^+$$

$F^R_d(\omega)$ being the Hilbert transform defined by

$$F^R_d(\omega) = \mathcal{P}\int_{E_b}^{E_t} \frac{\rho_d(\omega')}{\omega - \omega'} d\omega' .$$

E_b and E_t are the bottom and the top of the d band, respectively. Similarly $\tilde{F}^R_{d,0}(\omega)$ is the Hilbert transform associated with the perturbed d band $\tilde{\rho}_{d,0}(\omega) = -(1/\pi)\mathrm{Im}\,\tilde{g}^{dd}_{00}(\omega)$.

The second step consists of solving a generalized Anderson-Moriya problem. The bare f-f Hartree-Fock propagator reads [cf. Eq. (11)]

$$g^{ff}_{ij\sigma}(\omega) = \delta_{ij}\delta_{i0}/(\omega - \epsilon^\sigma_f) ,$$

where

$$\epsilon^\sigma_f = \epsilon_f + U_{ff}\langle n^+_{0-\sigma}\rangle + U_{df}\sum_{\sigma'}\langle n^d_{0\sigma'}\rangle .$$

The Anderson-Moriya problem, formulated in terms of a Dyson-like equation, can be defined by

$$G = \bar{g} + \bar{g}V'G ,$$

where the matrix elements $\bar{g}$ between d and f states are noted as $\tilde{g}^{dd}$ and g^{ff}. The f-f propator is obtained from the two coupled equations

$$G^{ff}_{ii\sigma}(\omega) = g^{ff}_{ii\sigma}(\omega) + g^{ff}_{i0\sigma}(\omega)V_{fd}G^{df}_{0i\sigma}(\omega) ,$$

$$G^{df}_{0i\sigma}(\omega) = \tilde{g}^{dd}_{00\sigma}(\omega)V_{df}G^{ff}_{0i\sigma}(\omega) .$$

The solution of the coupled equations is

$$G^{ff}_{00\sigma}(\omega) = \frac{1}{[g^{ff}_{00\sigma}(\omega)]^{-1} - |V_{df}|^2\tilde{g}^{dd}_{00}(\omega)}, \tag{17}$$

The $G^{dd}_{ii\sigma}(\omega)$ propagator is given by

$$G^{dd}_{ii\sigma}(\omega) = \tilde{g}^{dd}_{ii\sigma}(\omega) + \tilde{g}^{dd}_{i0\sigma}(\omega)V_{df}G^{fd}_{0i\sigma}(\omega) , \tag{18a}$$

$$G^{fd}_{0i\sigma}(\omega) = g^{ff}_{00\sigma}(\omega)V_{fd}G^{dd}_{0i}(\omega) \tag{18b}$$

and from Eqs. (15), (16), (18a), and (18b) one gets

$$\begin{aligned} G^{dd}_{ii\sigma}(\omega) = {} & g^{dd}_{ii}(\omega) + g^{dd}_{i0}(\omega)\frac{V}{1 - Vg^{dd}_{00}(\omega)} g^{dd}_{i0}(\omega) \\ & + \frac{g^{dd}_{0i}(\omega)}{1 - Vg^{dd}_{00}(\omega)} \frac{|V_{df}|^2}{[g^{ff}_{00\sigma}(\omega)]^{-1} - |V_{df}|^2\tilde{g}^{dd}_{00}(\omega)} \\ & \times \frac{g^{dd}_{0i}(\omega)}{1 - Vg^{dd}_{00}(\omega)} \end{aligned} \tag{19}$$

The $4f$ occupation number is obtained from

$$\begin{aligned} \sum_\sigma \langle n^f_{0\sigma}\rangle &= -\frac{1}{\pi}\mathrm{Im}\sum_\sigma \int_{-\infty}^{E_f} G^{ff}_{00\sigma}(\omega)d\omega \\ &= -\frac{1}{\pi}\mathrm{Im}\sum_\sigma \int_{-\infty}^{E_f} \frac{d\omega}{\omega - \epsilon^\sigma_f - |V_{df}|^2\tilde{F}_{d,0}(\omega)} , \end{aligned} \tag{20}$$

where E_F is the Fermi level.

A convenient way to take into account the possibility of f-bound states below the d band is to divide the integral of Eq. (20) into two parts: (i)

$$\sum_\sigma \langle n^f_{0\sigma}\rangle_{\text{ext}} = -\frac{1}{\pi}\,\text{Im}\sum_\sigma \int_{E_b}^{E_F} \frac{d\omega}{\omega-\epsilon^\sigma_f-|V_{df}|^2\tilde{F}_{d,0}(\omega)} \tag{21}$$

including the contribution from the extended states in energy and (ii) if bound states are present, they contribute as

$$\sum_\sigma \langle n^f_0\rangle_{\text{bound}} = \sum_\sigma \frac{1}{1-|V_{df}|^2[\partial\tilde{F}^R_{d,0}(\omega)/\partial\omega]\,|_{E_{p,\sigma}}}\,, \tag{22}$$

where $E_{p,\sigma}$ is position of the pole corresponding to the $4f_\sigma$ propagator. As expected the total $4f$ occupation goes to 1 when $\epsilon^\sigma_f \to -\infty$.

The localized-state occupation number is given by Eq. (21) if bound states are absent or Eq. (21) plus (22) when a bound state exists below the d band.

On the other hand the total change of d occupation number is

$$\delta n^d = -\frac{1}{\pi}\text{Im}\sum_\sigma \int_{-\infty}^{E_F} \sum_i [G^{dd}_{ii\sigma}(\omega)-g^{dd}_{ii\sigma}(\omega)]\,d\omega\,.$$

Using Eq. (19) one gets

$$\delta n^d = \frac{10}{\pi}\arctan\frac{\pi V\rho_d(E_F)}{1-VF^R_d(E_F)} - \frac{1}{\pi}\,\text{Im}\sum_\sigma \int_{-\infty}^{E_F} \frac{-|V_{df}|^2[\partial\tilde{F}_{d,0}(\omega)/\partial\omega]}{\omega-\epsilon^\sigma_f-|V_{df}|^2\tilde{F}_{d,0}(\omega)}\,d\omega\,, \tag{23}$$

where the factor of 10 in the first term accounts for d-band degeneracy. The integral in Eq. (23) can be treated similarly as done for Eq. (20). The Eq. (23) becomes

$$\begin{aligned}\delta n^d = {}&\frac{10}{\pi}\arctan\frac{\pi V\rho_d(E_F)}{1-VF^R_d(E_F)}\\ &-\frac{1}{\pi}\,\text{Im}\sum_\sigma \int_{E_b}^{E_F} \frac{-|V_{df}|^2[\tilde{F}_{d,0}(\omega)/\partial\omega]}{\omega-\epsilon^f_\sigma-|V_{df}|^2\tilde{F}_{d,0}(\omega)}\,d\omega\\ &-\sum_\sigma \frac{|V_{df}|^2[\partial\tilde{F}^R_{d,0}(\omega)/\partial\omega]}{1-|V_{df}|^2[\partial\tilde{F}^R_{d,0}(\omega)/\partial\omega]}\bigg|_{E_{p,\sigma}}\,.\end{aligned} \tag{24}$$

Summing Eqs. (21), (22), and (24) one has

$$\begin{aligned}\sum_\sigma \langle n^f_{0\sigma}\rangle + \partial n^d = {}&\frac{10}{\pi}\arctan\frac{\pi V\rho_d(E_F)}{1-VF^R_d(E_F)}\\ &+\frac{1}{\pi}\sum_\sigma \arctan\frac{\pi|V_{df}|^2\tilde{\rho}_{d,0}(E_F)}{E_F-\epsilon^\sigma_f-|V_{df}|^2\tilde{F}^R_{d,0}(E_F)}\\ &+(1-\alpha)\,,\end{aligned} \tag{25}$$

where $\alpha = 0$ or 1, if one has a bound state or not, respectively.

By imposing

$$\sum_\sigma \langle n^f_{0\sigma}\rangle + \delta n^d = 1\,, \tag{26}$$

one gets the sum rule which governs the self-consistent procedure and contains the essential physical requirement of charge neutrality. Two limiting cases are to be pointed out. If $\sum_\sigma \langle n^f_{0\sigma}\rangle = 1$, which corresponds to the Eu^{2+} configuration, then $\delta n_d = 0$. The othe limit, $\sum_\sigma \langle n^f_{0\sigma}\rangle = 0$, corresponding to the Eu^{3+} should satisfy for $\delta n^d = 1$. This means that the f electron is transferred to the d band and the screening is performed entirely by the d states. A word of comparison with Ref. 1 is in order. In that case two ionic configurations were present and the electron transferred to the d band was screened by the localized potential. In the present approach, the two-level nature of the problem (two configurations of the $4f$ ions) is replaced by the average occupations $\sum_\sigma \langle n^f_{0\sigma}\rangle$, but the screening associated with the d band is still present.

IV. NUMERICAL RESULTS AND DISCUSSIONS

The ideas discussed in Sects. II and III could be applied to general pseudobinary compounds like $\text{Eu}(A_{1-x}B_x)_n$, A and B standing for transition metals and $n = 1, 2, 3, \ldots$. The concentration x ranges from $x = 0$ to $x = 1$. In these limits, the europium valence is assumed to be 3^+ and 2^+, respectively. One is interested in this work in exhibiting a smooth and continuous change with concentration of the europium valence state. To our knowledge such behavior has only been experimentally observed in the $\text{Eu}(\text{Ir}_{1-x}\text{Pt}_x)_2$ system.[2] However, Table I of Ref. 1 may suggest other experimental possibilities. Based on these comments, one keeps the notation $\text{Eu}(A_{1-x}B_x)_2$ throughout the work. Since no detailed information is available concerning the density of states of the intermetallics $\text{Eu}A_2$ and $\text{Eu}B_2$ to justify a coherent-potential approximation (CPA) calculation, we use the simplest approach, namely, the virtual-crystal approximation. One adopts a parabolic Moriya density of states[12] defined by

$$\rho_d(\omega) = (3/4\Delta_d)(1-\omega^2/\Delta_d^2)\,, \tag{27}$$

the half bandwidth Δ_d being chosen equal to 1 in the numerical calculations. One assumes also that for a $\text{Eu}B_2$ compound the Fermi level lies at the top of the d band, whereas in the $\text{Eu}A_2$ compound the A atom has one less electron than B. The Fermi level is fixed for $x = 0$ imposing the d-band occupation equal to 9. For intermediate concentrations the Fermi level lies between these limits. The self-consistent determination of the f level occupation is defined by the Slater-Koster problem coupled to the Anderson-Moriya one. As was shown in Eq. (25), the Slater-Koster potential depends on the $4f$ occupation number. For $x=0$ one has a Eu^{3+} configuration corresponding in the present picture to $\sum_\sigma \langle n^f_{0\sigma}\rangle = 0$. This means f levels far above the top of the d band. In fact, if one takes $|V_{df}|^2 =$ const, there exists a critical distance between the f level and the top of the d band above which the Anderson-Moriya occupation number can be neglected. In this case the sum rule, Eq. (26), with $\alpha = 1$ imposes the Slater-Koster potential to satisfy

$$\frac{10}{\pi} \arctan \frac{\pi V(x=0)\rho_d(E_F)}{1 - V(x=0)F_d(E_F)} = 1 ,$$

where $V(x=0)$ denotes the value of the Slater-Koster potential corresponding to $x=0$ and it is given from Eq. (13) by

$$V(x=0) = -C\delta n^d_0 .$$

Recall that δn^d_0 is the change in the d occupation number at the origin. If one approximates δn^d_0 by δn^d, defined in Eq. (24), which amounts to assume a perfect local screening, one may use the sum rule, Eq. (26), to rewrite the potential for an arbitrary concentration x:

$$V \simeq (U_{df} + C) \sum_{\sigma'} \langle n^f_{0\sigma}\rangle - C . \qquad (28)$$

For $x=0$ the potential $V(x=0)$ is equal to $-C$, and with the adopted band structure it is determined to be $C = 0.3351$. Then the difficulty of estimating electron-phonon interactions and phonon spectra is circumvented using this approximation.

In the $x=1$ limit, $\rho_d(E_F) = 0$ since ϵ_F lies at the top of the d band. This implies that the Slater-Koster phase shift vanishes. So, in the sum rule, Eq. (26), only the Anderson-Moriya contributions remain, which should be equal to 1. One may ask if a self-consistent solution can be achieved for an effective f level, ϵ_f, lying within the d band. Since $\rho_d(E_F)$ vanishes and so does $\tilde{\rho}_{d,0}(E_F)$, thus implying that the phase shift associated with $\uparrow$ or $\downarrow$ spins is equal to π. This situation violates the sum rule and is dropped out. Another possibility is to try a solution involving a filled and an empty f bound state. As mentioned above the constant V_{df} assumption ($|V_{df}|^2 = 0.05$) implies in taking these levels one far below and the other far above the d band respectively. Since one takes $\langle n^f_{0\uparrow}\rangle = 1$ and $\langle n^f_{0\downarrow}\rangle = 0$, one sees that a quite large value of U_{ff} ($\sim 20\Delta_d$) is necessary. Although the validity of the Hartree-Fock scheme could be questioned, one argues that this is an artifact of the constant $|V_{df}|^2$ parameter. So, much smaller values of U_{ff} (e.g., $\sim 2\Delta_d$) can be used if hybridization is properly taken into account. Then the boundary condition, $x=1$, is only satisfied by the magnetic solution $\langle n^f_{0\uparrow}\rangle = 1$ and $\langle n^f_{0\downarrow}\rangle = 0$.

In principle the complete self-consistent problem for intermediate concentrations could be solved numerically using Eq. (28) together with the equations of Sec. III. One has preferred however to restrict the parameter space of the problem introducing another simplification concerning the potential V. This is based on the following remark concerning the Slater-Koster phase shift. Suppose that the potential V is constant. For an attractive potential (it is true for Eu^{3+} configuration) the phase shift starts from zero at the bottom of the d band, increases to attain a maximum and decreases to zero at the top of the band. One fixes such potential to warrant a screening equal to 1 for $x=0$. This gives the same value of $C = 0.3351$ obtained before. At the top of the band one obtains also the same behavior as before. For intermediate concentrations the U_{df} repulsive term in Eq. (28) does not destroy the tendency of the phase shift observed for a potential which is attractive and constant. Then the sum rule Eq. (26) which contains the more important physical aspect of the problem is satisfied in the same way, that means the charge difference $1 - \sum_\sigma \langle n^f_{0\sigma}\rangle$ is always attracted in the d band.

Within the above discussed approximations one solves the self-consistent problem.

One uses the model density of states [Eq. (27)]; the Fermi level as a function of concentration being defined in terms of the band fillings at the limiting concentrations. It is assumed that the d-band occupation number changes by 1 in going from $x=0$ to $x=1$. Within the proposed simplification of constant $V = -C$, the parameters of the model are fixed by the boundary conditions at $x=0$ and $x=1$, namely, Eu^{3+} and Eu^{2+}, respectively. For intermediate concentrations, the self-consistent procedure is defined by Eqs. (2), (23), and the general sum rule, Eq. (26). The results are shown in Fig. 1, which can be compared qualitatively with the experimental observations of the valence state of the $\mathrm{Eu(Ir_{1-x}Pt_x)_2}$ system.[2] For comparison one has plotted also in Fig. 1 the results obtained within the phenomenological model in Ref. 1 (cf. Fig. 3 of Ref. 1). In both cases, the screening condition plays a central role. However, in the present work, hybridization effects give a natural origin for the width introduced phenomenologically in Ref. 1. One believes that present approach can be considered as a step further in avoiding the phenomenological aspects of Ref. 1. The $4f$-level width, due to distortions of the usual Lorentizian form were estimated com-

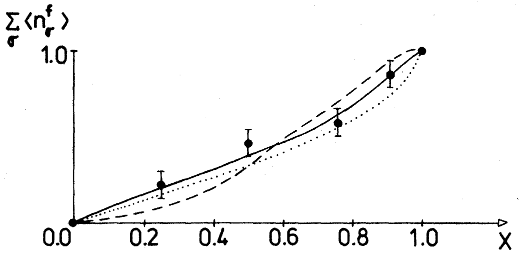

FIG. 1. Change of the total $4f$ occupation number with the x concentration in the pseudobinary intermetallic systems $\mathrm{Eu}(A_{1-x}B_x)_2$. The full line represents the paramagnetic solution and the dotted line the magnetic one. The dashed line shows for comparison the results obtained in Ref. 1 within the phenomenological model. The experimental data are obtained from interpolation of lattice-parameter measurements in the $\mathrm{Eu(Ir}_{1-x}\mathrm{Pt}_x)_2$ system (Ref. 2).

puting the second moment of the f density of states. The behavior of the level width as a function of the concentration shows a rapid increase from zero to attain a plateau value of the order of 600 K and decreases, in the same way, at the other limit of the concentration range. Such behavior suggests that the fast-valence-fluctuation regime persists along the concentration range except in the borders of the concentration limits.

Up to now, a nondegenerate f level was assumed. The question one raises naturally is under which assumptions the above results are meaningful for many-electron ions like europium. In particular one may ask how physical quantities relevant to europium intermetallics may be obtained from the crossover curve obtained under the hypothesis of a nondegenerate f level. One wants to propose the following picture: the binding energy of an Eu atom is such that during the fluctuation process, six electrons remain tightly bound to the ion core by the strong ionic potential. So, only one electron is active during the fluctuation process. The natural set of states to describe this situation could consist in a complete set of atomiclike states, properly symmetrized to preserve atomic symmetries, describing a $4f^7$ configuration and a $4f^6 5d^1$ configuration. In the literature, to our knowledge, only few works[15-17] discuss the many-electron nature of the f ions. One adopts here the formulation introduced in Ref. 17, which although more appropriate to a perturbation scheme may suggest a way to formalize the present picture. These authors[17] construct a many-electron ionic function starting from one-electron Bloch wave functions (or their Wannier transforms) for f and d states.

The states corresponding to an Eu ion in the Eu^{2+} and Eu^{3+} configurations read

$$|\psi_{J,M_J}^{(2+)}\rangle = \sum_{\substack{\sigma_i=\sigma_1\\ m_1=m_1}}^{\sigma_7,m_7} A(M_J,J,\sigma_i,m_i) \times f_{m_1\sigma_1}^{+} f_{m_2\sigma_2}^{+} \cdots f_{m_6\sigma_6}^{+} f_{m_7\sigma_7}^{+} |\tilde{0}\rangle\,, \tag{29a}$$

$$|\psi_{J',M_{J'}}^{(3+)}\rangle = \sum_{\substack{\sigma_1=\sigma_1\\ m_1=m_1}}^{\sigma_1,m_6} A(M_{J'}J',\sigma_i,m_i) \times f_{m_1\sigma_1}^{+} f_{m_2\sigma_2}^{+} \cdots f_{m_6\sigma_6}^{+} d_{\sigma_7}^{+} |\tilde{0}\rangle\,, \tag{29b}$$

where J and M_J stands, respectively, for the angular momentum and its z component, respectively. In Eq. (29a) and (29b) suitable combinations of atomiclike functions, with the appropriate symmetry of states Eu^{2+} (J,M_J) and Eu^{3+} $(J',M_{J'})$ are provided by the proper choice of the coefficients $A(M_J,J)$ and $A(M_{J'},J')$. $|\tilde{0}\rangle$ is defined as the extended vacuum consisting of all core electrons and filled bands. These states are assumed to be eigenstates of the uncoupled f- and d-band Hamiltonians and, in principle, intraionic interactions are contained from the beginning, giving rise to spectroscopic energies. Then d-f hybridization or whatever interaction among d and f electrons will mix these states. Moreover one expects that Eqs. (29a) and (29b) form a suitable complete set for perturbation theory, that is, a good zeroth-order approximation for the coupled system.

Our approximation goes in the reverse sense; one wants to suggest modifications to be made in Eqs. (29a) and (29b) in order to include qualitatively the effects of the coupling without making any further perturbation theory. One has developed an one-electron theory along this work. From this one-electron picture one extracts occupations numbers which include hybridization effects, the role of d-d interactions mediated by phonons and Coulomb interactions. We propose then to use this information to construct many electron states like Eqs. (29a) and (29b) but keeping the idea of a fixed "shell" of six electrons during the fluctuation. So, one conserves six purely atomic f-like functions denoted by $|f_{m_i\sigma_i}\rangle$ and adds two modified (weighted) ones:

$$|f_{7\sigma_7}\rangle = \Big(\sum_{\sigma'}\langle n_{0\sigma'}^{f}\rangle\Big)|f_{7\sigma_7}\rangle\,,$$

$$|d_{7\sigma_7}\rangle = \Big(1-\sum_{\sigma'}\langle n_{0\sigma'}^{f}\rangle\Big)|d_{7\sigma_7}\rangle$$

Starting from these new functions, one constructs many-electron functions using the above-mentioned scheme.

Symmetry requirements are incorporated again through the quantities $C(M_J, J)$. The final result is clearly equivalent to multiplying Eqs. (29a) and (29b) by the weights $\sum_{0'}\langle n^f_{0\sigma'}\rangle$ and $1-\sum_{\sigma'}\langle n^f_{0\sigma'}\rangle$, respectively. Such a simplified picture neglects all intraionic relaxation processes which occur when a f electron hops into the d band. In view of this picture, the isomer shift of the fluctuating Eu ion can be described from the crossover curves of Fig. 1. Moreover, one argues that behind the experimental determination of the valence states through the Mössbauer experiments these assumptions are implicitly included. From the known values, respect to a given source, of the isomer shift associated with Eu^{2+} and Eu^{3+} configurations, one fits the observed shifts using weight factors like those introduced above. Then, the present picture connects these data to some electronic parameters.

One has discussed in this section the one-electron results, in particular the crossover curves and the $4f$-level width. In Fig. 1 one has plotted the paramagnetic solution (full line) and the magnetic one (dotted line). The level-width behavior for the magnetic solution shows essentially the same behavior as in the paramagnetic case.

It is experimentally known that a $4f^7$ configuration shows a $7\mu_B$ net moment in agreement with Hund's rule. In some cases, e.g., $EuPt_2$, this magnetic moment couples with neighboring ones and produces long-range order. The magnetic order in $EuPt_2$ has been usually ascribed to Rudermann-Kittel-Kasuya-Yosida interactions mediated by the highly mobile s electrons of the compound.

An interesting question to be discussed concerns the persistence or not of magnetic order for increasing Ir concentration in $Eu(Ir_xPt_{1-x})_2$. The small concentration region $x < 0.1$ has not, to our knowledge, been experimentally studied: such an experimental study is in our view very illuminating. In fact, if fast charge fluctuation starts to occur, no more Curie-Weiss behavior is expected to occur. According to our predictions, the width increases steeply as a function of concentration to attain a plateau of the order of 600 °K. This width would correspond to a fluctuation time of the order of 10^{-13} sec. Clearly this prediction depends on the particular choice of the value of the $|V_{df}|^2$ matrix element. If experimental data become available, one can check the validity of our assumption for this parameter. On the other hand, if experimental results indicate that magnetic order persists over a broader concentration region, our $|V_{df}|^2$ assumption should be revised taking into account a better description of the hybridization matrix element (cf. Ref. 8).

V. FINAL REMARKS

In this section one summarizes the principal results and indicates possible extensions of this work. One has developed an extended Anderson Hamiltonian which includes among other interactions the coupling of the d band to lattice vibrations. A general formulation within the Hartree-Fock approximation was developed and the numerical results obtained using some simplifications. The general results support a previous view[1] of the role of d-band screening of the extra charge transferred during the fluctuation process. This screening is connected to a phonon-mediated interaction among d electrons. From the numerical results, crossover curves could be compared with experimental data. Also, the $4f$ level width which is computed from the self-consistent solution shows a plateau for a large concentration range and a rapid decrease to zero in the neighborhood of the concentrations limits ($x = 0$ and $x = 1$) of the pseudobinary intermetallic system $Eu(A_{1-x}B_x)_2$. These two facts show the consistency of our view of fluctuating systems, in particular respect to the role of the d-band screening via a general sum rule. One has developed also a qualitative view of the many-electron ions like Eu and connected some experimental information, extracted from isomer shifts measurements, to the microscopic parameters of the model via the total f occupation numbers derived from the one-electron problem. Finally one has pointed out the limitations of the suggested picture with respect to magnetic properties.

The above-mentioned ideas can be generalized to treat extended versions of the one-center Hamiltonian discussed here. More specifically the so called alloy analogy treatment of strong correlations[18] can be used to describe a collection of f levels and a d band. The same couplings invoked here can be treated within this approximation and in particular the phonon-mediated coupling among d states may be of central importance.[19]

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