Spin fluctuations in $(U_{1-x}M_x)(Al_{1-y}Co_y)_2$ compounds

N. A. de Oliveira, A. A. Gomes, and A. Troper

Centro Brasileiro de Pesquisas Fisicas, Rua Dr. Xavier Sigaud 150, Urca, Rio de Janeiro, RJ, 22290 Brazil
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Experimental results involving the substitution of U atoms by $M=$Gd, Dy, Y, and La or Al by Co in the spin-fluctuation system UAl_2 are studied in terms of a model calculation of the $5f$-electron susceptibility. In the case of rare-earth impurities, besides the intraband f-f Coulomb interaction, the model includes the Zener coupling between localized $4f$ spins and itinerant $5f$ states. The effective f-f interaction in the case of rare-earth impurities or the one-electron impurity-induced effects in the case of Y and La increases the proximity to a magnetic instability. Substitutional Co impurities introduce only small effects and have almost no influence on the magnetic properties of the compound.

Recently experimental results have been obtained for the magnetic properties of UAl_2-based pseudobindary compounds,[1,2] replacing U atoms by magnetic rare earths (RE) Gd, Dy, or by nonmagnetic transition metals Y or La. The case of Co atoms replacing Al has also been considered.[3] These two sublattice Laves phase materials can be adequately described by a simple model.[4] Although originally conceived to describe the transition-metal pseudobinaries, the model[4] can be easily extended to deal with $5f$ band compounds. The general Hamiltonian describing all the cases considered in this work is

$$H = H^{(f)} + H^{(d)} + H^{\text{mix}} + H^{\text{RE}} , \tag{1a}$$

$$H^{(f)} = \sum_{i \notin \{0\}} \varepsilon_i^{A(U)} f_{i\sigma}^\dagger f_{i\sigma} + \sum_{i \in \{0\}} \varepsilon_i^{A(M)} f_{i\sigma}^\dagger f_{i\sigma}$$
$$+ \sum_{ii'\sigma} T_{ii'}^{(f)AA} f_{i\sigma}^\dagger f_{i'} + \sum_{i \notin \{0\}} U_f^{(U)} n_{i\uparrow}^f n_{i\downarrow}^f , \tag{1b}$$

$$H^{(d)} = \sum_j \varepsilon_j^{(B)} d_{j\sigma}^\dagger d_{j\sigma} + \sum_{jj'\sigma} T_{jj'}^{(d)BB} d_{j\sigma}^\dagger d_{j'\sigma}$$
$$+ U_d^{(B)} \sum_j n_{j\uparrow}^{(d)} n_{j\downarrow}^{(d)} + \sum_i \varepsilon_i^{(A)} d_{i\sigma}^\dagger d_{i\sigma}$$
$$+ \sum_{ii'\sigma} T_{ii'}^{(d)AA} d_{i\sigma}^\dagger d_{i'\sigma} + U_d^{(A)} \sum_i n_{i\uparrow}^{(d)} n_{i\downarrow}^{(d)} , \tag{1c}$$

$$H^{\text{mix}} = \sum_{ij\sigma} T_{ij}^{AB}(d_{i\sigma}^\dagger d_{j\sigma} + \text{H.c.}) + V^{df} \sum_{i\sigma}(d_{i\sigma}^\dagger f_{i\sigma} + \text{H.c.}) , \tag{1d}$$

$$H^{\text{RE}} = \sum_{i \in \{0\}} J_{ff} \mathbf{J}_i^{(f)} \cdot \mathbf{S}_i^{(f)} + \sum_{i \in \{0\}} J_{df} \mathbf{J}_i^{(f)} \cdot \mathbf{S}_i^{(d)} , \tag{1e}$$

where M are the rare earths Gd, Dy or the transition elements Y and La. In (1) the operators $f_{1\sigma}$ ($d_{1\sigma}$) destroy electrons in the f or sd states at sites l, the notation $i(j)$ denotes sites at the A and B sublattices, respectively; also $\{0\}$ correspond to the RE or transition-metal impurity sites in the A sublattice. In (1b) we have introduced the parameters characterizing the energy levels $\varepsilon_i^{A(U)}$, $\varepsilon_i^{A(M)}$ at the A sublattice. Equation (1c) includes the corresponding description of the d states.

In H^{mix} we include the following mechanisms: the coupling between A and B sublattices and d-f hybridization. The first term of (1d) is the hopping of sd electrons between sites A and B,[4] and such a term exists in all two-sublattice intermetallics. The second term, however, is typical of U compounds, that is, the hybridization between the $5f$ and the corresponding sd states at the A sites. Finally, and only in the case of magnetic rare earths, (1e) describes the Zener coupling between the local moments of the $4f$ states of the RE ($J_i^{(f)}$) and the itinerant states.

We now proceed systematically introducing approximations. In the first part of this work no disorder is assumed to exist in the B sublattice, thus making ε_j^B independent of site j. We ignore the site occupancy dependence of the f-f Coulomb interaction; thus, we only consider $U_f^{(U)}$, responsible for the spin-fluctuation character of UAl_2. We consider separately the cases of rare-earth impurities $M=$Gd, Dy from the transition metals $M=$Y or La. The effect of localized spins on the magnetic susceptibility of strongly exchange enhanced transition-metal hosts has been studied by Doniach and Wohlfarth (DW),[5] using the simple one-band Hubbard Hamiltonian together with the Zener term. The stable RE's Gd and Dy provide concrete examples of that formulation.[5]

In both cases ($M=$rare earth or $M=$La,Y) disorder exists only in the A sublattice and is described here through the coherent potential approximation (CPA) self-energy $M_f^A(z;x)$, x being the RE or transition-metal concentration and $z=\varepsilon+i\delta$; this procedure restores translation invariance. In the Appendix we briefly describe the procedure to obtain the self-energy $M_f^A(z;x)$. In order to get a still simpler approximation, we include the d-d Coulomb interaction within the Hartree-Fock approximation in all cases $M=$rare earth, Y, La, or with Al being replaced by Co with concentration y. The self-energy $M_d^A(z;x,y)$ can be calculated following the same lines of the Appendix in terms of the A site impurity concentration x and/or the Co concentration y. This self-energy is considered here as an external parameter. We neglect the RE coupling with d states in (1e), since our main purpose is to discuss its role on the $5f$ states.

Using the restored translation invariance, the Hamil-

tonian using the k representation thus becomes

$$H = \sum_k [M_f^{(A)}(z;x) + A_{(A)}^{(f)}\varepsilon_k]f_{k\sigma}^\dagger f_{k\sigma} + \sum_i U_f^{(U)}n_{i\uparrow}^f n_{i\downarrow}^f$$
$$+ \sum_k [M_{d\sigma}^{(A)}(z;x) + A_{(A)}^{(d)}\varepsilon_k]d_{k\sigma}^{A+}d_{k\sigma}^A$$
$$+ V^{df}\sum_k (d_k^{A+}f_{k\sigma} + \text{H.c.}) + \sum_{i\in\{0\}} J_{ff}\mathbf{J}_i^{(f)}\cdot\mathbf{S}_i^{(f)} ,$$

$$(2)$$

where $A_{(A)}^{(f)}$ and $A_{(A)}^{(d)}$ are the scale factors for the f and d bands[4] and we stress that only the corresponding A sublattice creation-destruction operators are included in (2). Clearly the last term is pertinent only for the rare-earth impurity case. The simplified version (2) reduces exactly to DW (Ref. 5) for itinerant f electrons, in the absence of d states, d-f hybridization V_{df} and $M_{d\sigma}^A(z;x,y)$. The solution of (2) can be obtained using the equation-of-motion method of DW; let us introduce, however, a still simpler version. Since hybridization shifts the center of the f band and changes its width, let us parametrize these effects by δ_f and $\overline{A}_{(A)}^{(f)}$; thus, except for the renormalized parameters, the next equation (3) is very similar to DW:

$$H_{\text{ren}} = \sum_k [M_f^{(A)}(z;x) + \delta_f + \overline{A}_{(A)}^{(f)}\varepsilon_k]f_{k\sigma}^\dagger f_{k\sigma}$$
$$+ \sum_i U_f^{(U)}n_{i\uparrow}^f n_{i\downarrow}^f + \sum_{i\in\{0\}} J_{ff}\mathbf{J}_i^{(f)}\cdot\mathbf{S}_i^{(f)} .$$

$$(3)$$

The solution follows the same steps of DW:[5] the fundamental difference occurs in the unenhanced susceptibility $\chi^{(0)}(\mathbf{q},w;x)$, which now depends explicitly on the impurity concentration x. This susceptibility should now be calculated using CPA methods. Once solved for $\mathbf{q}=w=0$, Eq. (3) gives for the susceptibility a result which is *formally* identical to DW:

$$\chi(0,0;x) = \chi^{(0)}(0,0;x)[1 - U_{\text{eff}}(x)\chi^{(0)}(0,0;x)]^{-1} , \qquad (4)$$

where the effective Coulomb interaction is given by

$$U_{\text{eff}}(x) = U_f^{(U)} + 2J_{ff}[R'(x)/R(x)] ,$$

R'/R being the ratio of the induced localized and itinerant moments.

This result indicates a way to interpret the experimental data.[1] The combined effects of the CPA-induced modification of $\chi^{(0)}(0,0;x)$ and $U_{\text{eff}}(x)$ can make the product $U_{\text{eff}}(x)\chi^{(0)}(0,0;x)$ close to 1, thus approaching $\chi(0,0;x)$ to the magnetic instability. This is what we mean by quenching of the spin fluctuations in UAl_2, which corresponds to a change in sign of the paramagnetic Curie temperature.[1] In the numerical results we separately discuss the effects only associated to pure one-electron impurity scattering and those due also to the Zener interaction.

In the case of transition-metal impurities diluted in A, clearly $U_{\text{eff}}(x)$ reduces to the bare value of $U_f^{(U)}$. In this situation, as will be shown later, the concentration-dependent unenhanced susceptibility $\chi^{(0)}(0,0;x)$ plays the major role in introducing a quasiquenching of the spin fluctuations.[2]

To illustrate our points, we use for the density of states of the $5f$ band a simplification of the result obtained in a recent[6] first-principles calculation of the electronic structure of UNi_2. We hope to model adequately the $5f$ density of states of UAl_2 since the Ni d local density of states is almost completely filled,[6] with mainly sp states around the Fermi level of the compound remaining. The adopted density of states is shown in Fig. 1. The obtained occupation number of $5f$ electrons[6] fixes the Fermi level in our model. An approximation for $\chi^{(0)}(0,0;x)$ is obtained, for estimated values of δ_f and $\overline{A}_{(A)}^{(f)}$, adjusting the value of $\varepsilon^{A(M)} - \varepsilon^{A(U)}$.

The adequate choice of these one-electron parameters, in particular $\overline{A}_{(A)}^{(f)}$, is critical in understanding the difference between Y and La impurities replacing U^2. Since Y is a $4d$ element in contrast with La which is $5d$, one expects a larger d-f hybridization for Y than for La. This is due to the corresponding extension of the wave functions, shorter for Y than for La; thus, $\overline{A}_{(A)}^{(f)}(Y) > \overline{A}_{(A)}^{(f)}(La)$. As a consequence, the density of states (or the uniform static susceptibility) is larger for La than for Y impurities. Taking identical values for the energy levels in the two cases (Y and La), period effects being accounted for in the d-f hybridization, the product $\beta = U_{\text{eff}}\chi^{(0)}(0,0;x)$ as a function of x is larger for La than for Y as shown in Fig. 2.

In the case of rare earths, the field-induced value of $R'(x)$, which in DW is proportional to the concentration x, can be obtained from a Brillouin function. In Fig. 3, the product $\beta = U_{\text{eff}}\chi^{(0)}(0,0;x)$ (solid line) is shown as a function of x, together with (dashed line) $U_{\text{eff}}^{(U)}\chi^{(0)}(0,0;x)$. We have included the last result in order to clearly exhibit the separate contribution of one-electron impurity scattering, which is mixed to the rare-earth spin effects in the β curve. One sees that β approaches 1 for a critical concentration, thus quenching the spin fluctuations. From the experimental results,[1] one associates the
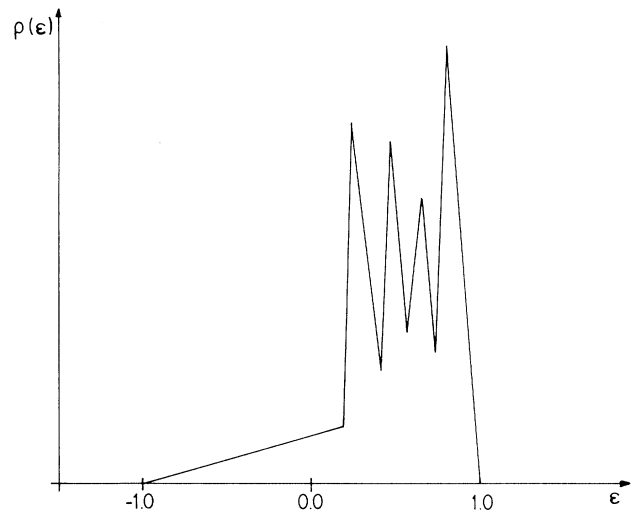
FIG. 1. Model density of states for the $5f$ band, including only the main features obtained in the first-principles calculation (Ref. 6).
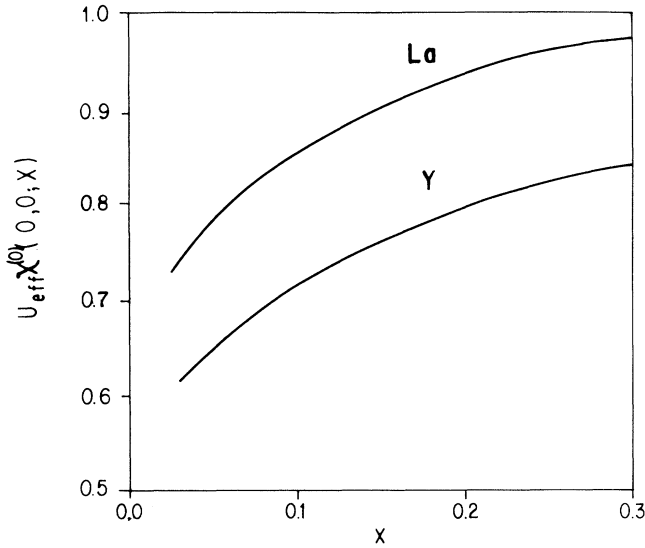
FIG. 2. Numerical results for transition-metal impurities: $U_{eff}\chi^{(0)}(0,0;x)$ as a function of concentration x for $\delta_f = 0.2$, $\varepsilon^{A(M)} - \varepsilon^{A(U)} = 0.45$, $\overline{A}\,^{(f)}_{A} = 1.05$ (La), and $\overline{A}\,^{(f)}_{A} = 1.2$ (Y).

quenching of spin fluctuations to the change in sign of the paramagnetic Curie temperature $\theta_p(x)$; on the contrary, in the case of nonmagnetic impurities this change in sign does not occur.[2]

The experimental result,[1] that the quenching of spin fluctuations occurs for higher Dy concentrations as compared to Gd impurities, can be understood in terms of the effective spin $s_{eff} = (g_J - 1)J$. Since s_{eff} has a higher value for Gd as compared to Dy, one needs a higher Dy con-
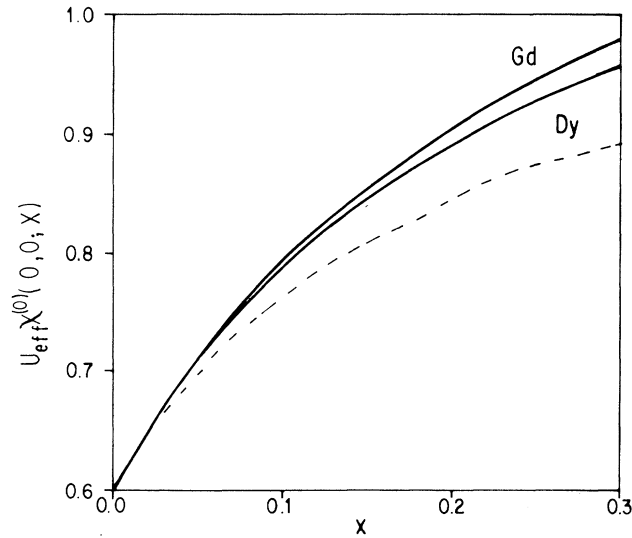

FIG. 3. Numerical results for rare-earth impurities: $\beta = U_{eff}\chi^{(0)}(0,0;x)$ (solid line) as a function of concentration x for $\delta_f = 0.2$, $\varepsilon^{A(M)} - \varepsilon^{A(U)} = 0.45$, $\overline{A}\,^{(f)}_{A} = 1.2$. The dashed line shows $U_{eff}\chi^{(0)}(0,0;x)$ as a function of x in the absence of f spins (case of Y).

centration to get positive values for the paramagnetic Curie temperature $\theta_p(x)$. In both cases the disorder introduced by the rare-earth levels is taken to be the same for both Gd and Dy. More detailed numerical results based on the approach described in the Appendix, which uses a more self-consistent procedure, are in progress[7] to obtain better estimates of $\chi^{(0)}$ and U_{eff}.

The case of Co impurities replacing Al is quite different from those considered above. In fact, the changes in local $5f$ density of states at the U sites are associated, through d-f hybridization, to Co impurity-induced changes in the local A sublattice $6d$ density of states. The Co impurities introduce changes in local B sublattice density of states and these propagate to the A sublattice through the hopping interaction between A and B sublattices. The effect of the hopping is shown[4] to introduce only small effects in the total d density of states of the A sublattice. Thus, the changes in $5f$ susceptibility, as mediated by d-f hybridization, are expected to be small; as a consequence the spin-fluctuation regime is not significantly altered with respect to UAl_2, as experimentally observed.[3]

APPENDIX

Following the formulation,[4] let us indicate the procedure to extend the calculation of the self-energies in transition-metal two-sublattice pseudobinary intermetallics, to the case of U compounds. Consider the situation where impurities are dissolved in the A sublattice. This disordered sublattice is described by an effective medium self-energy M_f^A which is determined replacing one effective atom by a U or M atom with probabilities $1-x$ and x; a similar method can be used for impurities in the B sublattice.

This procedure defines a one-center scattering problem,

$$G = g + gVG \ , \tag{A1}$$

where G and g are 2×2 matrices and the V potentials are

$$V^f = \begin{bmatrix} \varepsilon^\lambda - M_f^A & 0 \\ 0 & 0 \end{bmatrix} \ , \tag{A2a}$$

$$V^d = \begin{bmatrix} 0 & 0 \\ 0 & \varepsilon^{\lambda'} - M_d^B \end{bmatrix} \tag{A2b}$$

with $\lambda = U, M$ and $\lambda' = Al, Co$. In (A1) the corresponding unperturbed Green's functions are defined by

$$\begin{bmatrix} g_{ff}^{AA} & g_{fd}^{AA} \\ g_{df}^{AA} & g_{dd}^{AA} \end{bmatrix} = \begin{bmatrix} Z - M_f^A - A_f \varepsilon_k^{eff(d)} & -V_{fd} \\ -V_{df} & z - \varepsilon_k^{eff(d)} \end{bmatrix}^{-1} \ , \tag{A3a}$$

$$\begin{bmatrix} g_d^{AA} & g_d^{AB} \\ g_d^{BA} & g_d^{BB} \end{bmatrix} = \begin{bmatrix} z - \varepsilon_0^A - \varepsilon_{dk}^A & -\Gamma_k \\ -\Gamma_k & z - M_d^B - \varepsilon_{dk}^B \end{bmatrix}^{-1} \ . \tag{A3b}$$

The 2×2 matrix reflects in (A3b) the two-sublattice nature of the compound,[4] and in (A3a), the two-band character (d,f) of U compounds. We use the homothetic band approximation[4] to rewrite $\varepsilon_{d\mathbf{k}}^{A}$, $\varepsilon_{d\mathbf{k}}^{B}$, $\Gamma_{\mathbf{k}}$ in terms of a common dispersion relation ε_{k}. The effective dispersion relation $\varepsilon_{\mathbf{k}}^{\mathrm{eff}(d)}$ is defined from (A3b) using the local density of states at the A sublattice

$$\rho_{d}^{A}(\varepsilon)=-1/\pi\,\mathrm{Im}g_{d}^{AA}=\sum_{\mathbf{k}}\delta[\varepsilon-\varepsilon_{\mathbf{k}}^{\mathrm{eff}(d)}]\ .$$

The scale factor A_{f} accounts for the f-band width, associated to the U atoms at the A sublattice and the hybridization V_{df} is taken as a constant parameter.

Due to the peculiar form of (A2a), the scattering problem is easily solved. The self-consistent condition determining M_{f}^{A} is

$$(1-x)\frac{\varepsilon^{U}-M_{f}^{A}}{1-[\varepsilon^{U}-M_{f}^{A}]F_{f}^{A}}+x\frac{\varepsilon^{M}-M_{f}^{A}}{1-[\varepsilon^{M}-M_{f}^{A}]F_{f}^{A}}=0\ ,$$

where F_{f}^{A} is the real-space diagonal matrix element[4] of the ff element of (A3a). Again one recovers the usual CPA form, but the F_{f}^{A} propagator includes, through $\varepsilon_{\mathbf{k}}^{\mathrm{eff}(d)}$, the effect of off-diagonal terms of (A3b) describing the existence of intersublattice hopping. The homothetic band approximation enables[4] one to obtain a simple expression for F_{f}^{A} in terms of the density of states $\rho^{A}(\varepsilon)$. Using analogous procedures one determines M_{d}^{B} in terms of the values for the d levels and the concentration y and the model density of states $\rho(\varepsilon)$ for the B sublattice.

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