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Magnetic moment formation at dilute Cd impurities in $R\mathrm{Ni}_2$ and $R\mathrm{Co}_2$ intermetallic compounds

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In this work, we study the local magnetic-moment formation and the systematics of the magnetic hyperfine fields at a Cd impurity diluted on the R site of the Laves phase intermetallic compounds $R\mathrm{Ni}_2$ and $R\mathrm{Co}_2$ (R = rare earth). In the case of $R\mathrm{Ni}_2$ intermetallic hosts, we use a Daniel-Friedel-like model in which the $R\mathrm{Ni}_2$ intermetallics are considered as effective ferromagnetic rare-earth hosts. In the case of $R\mathrm{Co}_2$ intermetallic hosts, we also consider the contribution arising from the neighboring Co magnetic moments. The calculated total magnetic hyperfine fields are in good agreement with the available experimental data.

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I. INTRODUCTION

The Laves phase intermetallic compounds of formula RT_2 (R stands for rare-earth elements and T for transition elements) crystallize either in the cubic $C15$ or hexagonal $C14$ structure. They exhibit an interesting variety of behaviors related to the changes in their magnetic, electronic, and lattice structures. For instance, in the intermetallic compounds $R\mathrm{Ni}_2$ the magnetic order is sustained only by the indirect interaction between the localized spins of the rare-earth ions and Ni is always nonmagnetic.[1,2] Moreover, experimental data[3] show that the magnetization of the $R\mathrm{Ni}_2$ intermetallic compounds is somewhat larger than the contribution from the local magnetic moments of the rare-earth ions as estimated by Hund's rule. Electronic structure calculations[3] show that this excess of magnetization comes from the polarization of the d and s-p bands at the rare-earth sites. On the other hand, in the heavy $R\mathrm{Co}_2$ (R = Gd, Tb, Dy, Ho, Er) intermetallic compounds, a magnetic moment of the order of $1\mu_B$ at the Co site is induced antiparallel to the spin magnetic moments of the rare-earth ions,[4] whereas for light $R\mathrm{Co}_2$ (R = Pr, Nd, Pm, Sm) compounds one finds almost always small magnetic moments at the Co site.[2]

The calculation of the magnetic moments and hyperfine fields at the impurity site have been developed using either *ab initio* calculations[5,6] or model approaches.[7–14] In the early 1990's, a formulation including the change in the hopping energy applied to the case of Pd based alloys, suggested a connection between first-principles calculations and the model approaches for the impurity problem.[15–17] We have extended that formulation for a ferromagnetic $3d$ host in order to discuss the problem of transition element impurities diluted in Fe host.[18] In the present work, we study the local-moment formation and the systematics of the magnetic hyperfine fields at the nonmagnetic s-p Cd impurity diluted on the R site of the Laves phase intermetallic compounds $R\mathrm{Co}_2$ and $R\mathrm{Ni}_2$. In order to calculate the local magnetic moment at a Cd impurity diluted in $R\mathrm{Ni}_2$, we use a Daniel-Friedel-like model,[19] in which $R\mathrm{Ni}_2$, compounds are considered as effective ferromagnetic rare-earth hosts.[20] In the case of the $R\mathrm{Co}_2$ hosts, we include in the model an extra magnetic term, located at a distance $\vec{R}_0$ from the impurity site, to account for the contribution arising from the Co magnetic moments. We have in this case a two-center Blandin-Campbell-like model,[21–23] where a magnetic $3d$-element located at a distance $\vec{R}_0$ from the Cd impurity gives an extra magnetization to a polarized electron gas which is strongly charge perturbed at the impurity site. We also include in the model, the nearest-neighbor perturbation due to the translational invariance breaking introduced by the impurity.[15–17]

In Sec. II, we formulate the general problem, in order to describe a Cd impurity diluted in both $R\mathrm{Ni}_2$ and $R\mathrm{Co}_2$ hosts. In Sec. III, we exhibit the self-consistent numerical calculations, comparing our results to available experimental data. We also make some predictions arising from our model.

II. FORMULATION OF THE PROBLEM

We start the description of a Cd impurity diluted in RT_2 (T = Ni, Co) intermetallic hosts, by considering that the local magnetic moments and the total magnetic hyperfine fields have two important contributions, namely: (i) the contribution from R ions; (ii) the contribution from the coupling with the induced magnetic moments at the Co sites.[2] In order to account for both contributions to the formation of the local magnetic moments, we consider the RT_2 intermetallic compounds as being effective ferromagnetic rare-earth hosts,[20] with an extra term to account for the polarization arising from the magnetic moments of the transition elements surrounding the impurity site.[23] In the framework of our model, the Hamiltonian to describe the formation of the local s-p magnetic moment and hyperfine field at Cd impurity embedded in RT_2 intermetallic hosts is

$$H=\sum_{i\sigma} \varepsilon_{0\sigma}c_{i\sigma}^{\dagger}c_{i\sigma}+\sum_{ij\sigma} t_{ij}c_{i\sigma}^{\dagger}c_{j\sigma}+V_{0\sigma}c_{0\sigma}^{\dagger}c_{0\sigma} +\tau\sum_{i\neq 0\sigma} t_{0l}(c_{0\sigma}^{\dagger}c_{i\sigma}+c_{i\sigma}^{\dagger}c_{0\sigma})+\sum_{n\neq 0} V_{n\sigma}c_{n\sigma}^{\dagger}c_{n\sigma}. \tag{1}$$

In this Hamiltonian, $\varepsilon_{0\sigma}$ is the center of the energy band, which depends on the $4f$ polarization from the effective rare-earth host and on the $5d$ polarized conduction electrons. The term t_{ij} is the electron hopping energy and $c_{i\sigma}^{\dagger}(c_{i\sigma})$ is the creation (annihilation) operator of conduction electrons at site i with spin σ. τ is a parameter which takes into account the nondiagonal term in the energy hopping due to the translational invariance breaking associated with the presence of the impurity.[15–18] $V_{0\sigma}$ is the local potential and $V_{n\sigma}$, is the potential due to a magnetic moment of the transition element surrounding the impurity site, i.e.,

$$V_{n\sigma}=-\sigma J^{sd}\langle S^{T}\rangle, \tag{2}$$

where $\langle S^T\rangle$ is the magnetic moment at the transition $3d$ element. J^{sd} is an exchange parameter of the model. Notice that in case of Cd impurity diluted in $R\mathrm{Ni}_2$ intermetallic hosts, $V_{n\sigma}=-\sigma J^{sd}\langle S^{\mathrm{Ni}}\rangle=0$, since in these intermetallics, Ni is nonmagnetic. Therefore, for $R\mathrm{Ni}_2$ hosts one has an extended Daniel-Friedel problem.[19]

Let us first solve the problem defined by Eq. (1) considering only the charge perturbation, i.e., $V_{n\sigma}=0$. Using the Dyson equation, one has

$$\tilde{g}_{ij\sigma}(z)=g_{ij\sigma}(z)+g_{i0\sigma}(z)V_{0\sigma}\tilde{g}_{0j\sigma}(z) +\tau\left[\sum_{p\neq 0} g_{ip\sigma}(z)t_{p0}^{\mathrm{hh}}\right]\tilde{g}_{0j\sigma}(z) +\tau g_{i0\sigma}(z)\left[\sum_{p\neq 0} t_{0p}^{\mathrm{hh}}\tilde{g}_{pj\sigma}(z)\right]. \tag{3}$$

t_{0p}^{hh} is the host hopping term, $g_{ij\sigma}(z)$ is the Green function for the pure host system with $z=\varepsilon+i0$, and $\tilde{g}_{ij\sigma}(z)$ is the modified Green function due to the charge perturbation at the origin. After some algebra, the Green function $\tilde{g}_{ij\sigma}(z)$ can be written in the form

$$\tilde{g}_{ij\sigma}(z)=g_{ij\sigma}(z)+g_{i0\sigma}(z)\frac{V_{\sigma}^{\mathrm{eff}}(z)}{\alpha^2-g_{00\sigma}(z)V_{\sigma}^{\mathrm{eff}}(z)}g_{0j\sigma}(z)+(\alpha-1)\frac{(\alpha-1)g_{00\sigma}(z)\delta_{i0}\delta_{0j}-\alpha[g_{i0\sigma}(z)\delta_{0j}+\delta_{i0}g_{0j\sigma}(z)]}{\alpha^2-g_{00\sigma}(z)V_{\sigma}^{\mathrm{eff}}(z)}. \tag{4}$$

Here, the effective potential $V_{\sigma}^{\mathrm{eff}}(z)$ is given by

$$V_{\sigma}^{\mathrm{eff}}(z)=V_{0\sigma}+(\alpha^2-1)(z-\varepsilon_c), \tag{5}$$

with $\alpha=\tau+1$ and ε_c being the center of the energy band. Once $\tilde{g}_{00\sigma}(z)$ is obtained, one gets the occupation number with spin σ, and then the local magnetic moment $\tilde{m}_R(0)$ due to the R ions [see below, Eq. (12)]. Now we solve the general problem, defined by Eq. (1) considering the potential $V_{n\sigma}$. Using the Dyson equation $G_{ij\sigma}(z)=\tilde{g}_{ij}(z)+\Sigma_{n\neq 0}\tilde{g}_{in}(z)V_{n\sigma}G_{nj}(z)$, the perturbed Green function $G_{ij\sigma}(z)$ for the total Hamiltonian (1) is given by

$$G_{ij\sigma}(z)=\tilde{g}_{ij}(z)+\sum_{n\neq 0} \tilde{g}_{in}(z)T_{n\sigma}\tilde{g}_{nj}(z), \tag{6}$$

with

$$T_{n\sigma}=\frac{V_{n\sigma}}{1-\tilde{g}_{nn\sigma}(z)V_{n\sigma}}. \tag{7}$$

After some algebra, the local Green function $G_{00\sigma}(z)$ can be written in the form

$$G_{00\sigma}(z)=\frac{g_{00\sigma}(z)}{\alpha^2-g_{00\sigma}(z)V_{\sigma}^{\mathrm{eff}}(z)}+\frac{\alpha^2\sum_{n\neq 0} g_{0n\sigma}(z)T_{n\sigma}g_{n0\sigma}(z)}{[\alpha^2-g_{00\sigma}(z)V_{\sigma}^{\mathrm{eff}}(z)]^2}. \tag{8}$$

Since the spin potential $V_{n\sigma}$ is small as compared to the strong charge perturbation V_0, we take the Born approximation ($T_{n\sigma}\approx V_{n\sigma}$). So one has

$$G_{00\sigma}(z)=\frac{g_{00\sigma}(z)}{\alpha^2-g_{00\sigma}(z)V_{\sigma}^{\mathrm{eff}}(z)}-\frac{\sigma\alpha^2J^{sd}\langle S^T\rangle}{[\alpha^2-g_{00\sigma}(z)V_{\sigma}^{\mathrm{eff}}(z)]^2} \times\left[Z_n\frac{\partial g_{00\sigma}(z)}{\partial z}+g_{00\sigma}^2(z)\right], \tag{9}$$

where Z_n is the number of the first next neighbors of T ions surrounding the Cd impurity. The local potential $V_{0\sigma}$ is self-consistently determined using the Friedel screening condition[18,20] for the total charge difference between impurity and host atoms ΔZ, i.e., $\Delta Z=\Delta Z_{\uparrow}+\Delta Z_{\downarrow}$, where

$$\Delta Z_{\sigma}=-\frac{1}{\pi}\mathrm{Im}\,\ln[\alpha^2-g_{00\sigma}(\epsilon_{\mathrm{F}})V_{\sigma}^{\mathrm{eff}}(\epsilon_{\mathrm{F}})], \tag{10}$$

where ϵ_{F} is the Fermi energy. The local density of states per spin direction at the impurity site is given by $\rho_{0\sigma}(\varepsilon)$

$=(-1/\pi)\mathrm{Im}\,G_{00\sigma}(z)$. The local electron occupation number $(n_{0\sigma})$ is obtained by integrating the local density of states up to the Fermi level, $n_{0\sigma}=\int_{-\infty}^{\epsilon_F}\rho_{0\sigma}(\varepsilon)d\varepsilon$. The local magnetic moment $\tilde{m}(0)=\Sigma_\sigma \sigma n_{0\sigma}$, at a Cd impurity is then

$$\tilde{m}(0)=\tilde{m}_R(0)+\tilde{m}_{\mathrm{ind}}(0), \qquad (11)$$

where

$$\tilde{m}_R(0)=-\frac{1}{\pi}\sum_\sigma \int_{-\infty}^{\epsilon_F}\mathrm{Im}\frac{g_{00\sigma}(z)}{\alpha^2-g_{00\sigma}(z)V_\sigma^{\mathrm{eff}}(z)}dz \qquad (12)$$

and

$$\tilde{m}_{\mathrm{ind}}(0)=-\frac{1}{\pi}\sum_\sigma \int_{-\infty}^{\epsilon_F}\mathrm{Im}\frac{\sigma\alpha^2 J^{sd}\langle S^T\rangle}{[\alpha^2-g_{00\sigma}(z)V_\sigma^{\mathrm{eff}}(z)]^2}\times\left[Z_n\frac{\partial g_{00\sigma}(z)}{\partial z}+g_{00\sigma}^2(z)\right]dz. \qquad (13)$$

The term $\tilde{m}_R(0)$ gives the contribution from the R ions and $\tilde{m}_{\mathrm{ind}}(0)$ gives the contribution from the Co $3d$ ions. Note again that in the case of $R\mathrm{Ni}_2$ intermetallic hosts, $\langle S^{\mathrm{Ni}}\rangle=0$, so that one has only the contribution to the local magnetic moment at a Cd impurity arising from the rare-earth ions. The total magnetic hyperfine field at a Cd impurity site is given by

$$B_{hf}=A(Z_{\mathrm{imp}})[\tilde{m}_R(0)+\tilde{m}_{\mathrm{ind}}(0)], \qquad (14)$$

where $A(Z_{\mathrm{imp}})$ is the Fermi-Segrè contact coupling parameter.[12]

III. RESULTS AND DISCUSSION

In order to calculate the local moments and the magnetic hyperfine fields at a Cd impurity diluted in the $R\mathrm{Ni}_2$ and $R\mathrm{Co}_2$ intermetallic hosts, we have to fix some model parameters. Here, we adopt a standard paramagnetic s-p density of states extracted from first-principles calculations.[4] The exchange splitting in the s-p energy bands induced by the local moments of the rare-earth ions, was properly chosen to yield the s-p magnetic moment at the R sites of the host, which is assumed to be of the order of 0.1 of the d magnetization at the R sites. The parameter α which renormalizes the hopping energy involving the impurity site, was chosen by taking the ratio between the extension of the host and impurity s-p wave functions. In the case of $R\mathrm{Ni}_2$, we assumed $J^{sd}\langle S^{\mathrm{Ni}}\rangle=0$. In the case of $R\mathrm{Co}_2$ intermetallics, we adopted $J^{sd}=0.4\times10^{-3}$ for heavy rare-earth ions and $J^{sd}=0.5\times10^{-3}$ for light rare-earth ions in units of the s-p bandwidth of $R\mathrm{Co}_2$ hosts. The magnetic moments at the Co site in $R\mathrm{Co}_2$ intermetallic compounds $\langle S^{\mathrm{Co}}\rangle$ were estimated from Ref. 2. Keeping fixed these parameters, we self-consistently determined the local magnetic moment and the corresponding magnetic hyperfine field at the Cd impurity.

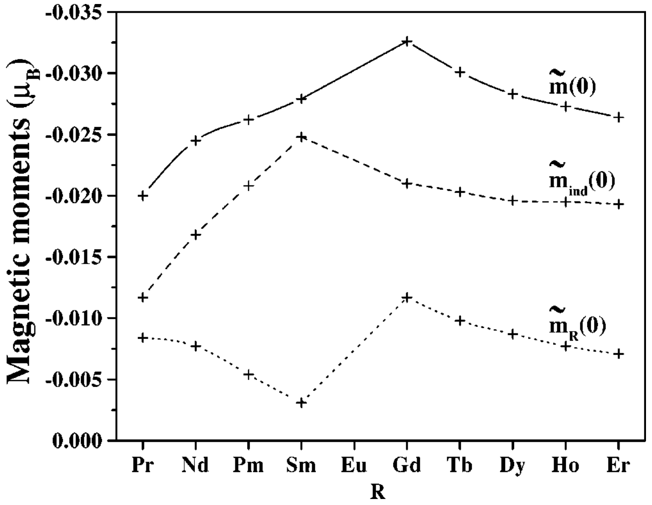

FIG. 1. Calculated magnetic moments at Cd impurity diluted in $R\mathrm{Co}_2$ intermetallic hosts. The dotted line corresponds to the contribution from the rare earth $\tilde{m}_R(0)$, whereas the dashed line corresponds to the contribution from the Co ions $\tilde{m}_{\mathrm{ind}}(0)$. The solid line represents the total magnetic moments $\tilde{m}(0)$. The term $\tilde{m}_R(0)$ stands for the total magnetic moment in the case of $R\mathrm{Ni}_2$ hosts (see text).

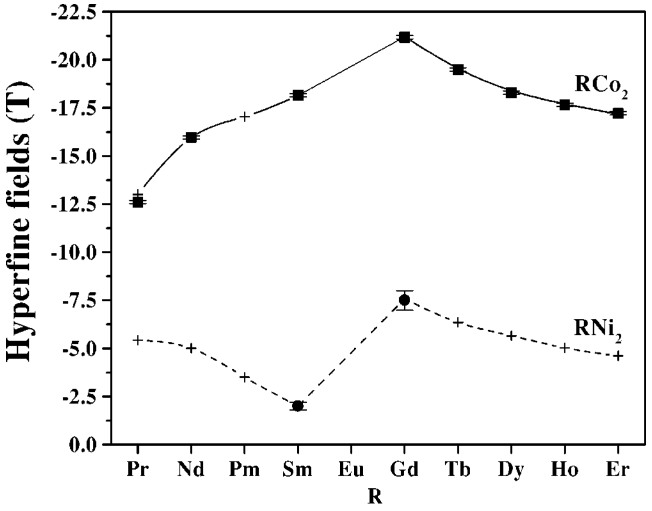

FIG. 2. Calculated total magnetic hyperfine fields at Cd impurity diluted in $R\mathrm{Ni}_2$ (dotted line) and $R\mathrm{Co}_2$ (solid line) intermetallic hosts. Circles and squares represent experimental data collected from Ref. 2.

In Fig. 1, we plot the rare-earth contribution to the local magnetic moment $[\tilde{m}_R(0)]$ as well as the contribution to the local magnetic moment, originated from the Co neighboring ions $[\tilde{m}_{\mathrm{ind}}(0)]$. First of all, notice that in the case of $R\mathrm{Ni}_2$, one has only a $\tilde{m}_R(0)$ contribution, which is a Daniel-Friedel-like one. In the case of $R\mathrm{Co}_2$, one has $\tilde{m}(0)=\tilde{m}_R(0)+\tilde{m}_{\mathrm{ind}}(0)$. We assumed that the contribution arising from the rare-earth ions, is the same in $R\mathrm{Co}_2$ and in $R\mathrm{Ni}_2$, i.e., $\tilde{m}_R(0{:}RNi_2)=\tilde{m}_R(0{:}R\mathrm{Co}_2)$. The self-consistent calculations show that the Blandin-Campbell-like term[21,22] $\tilde{m}_{\mathrm{ind}}(0)$ dominates over $\tilde{m}_R(0)$, both for heavy and light rare earths. From Fig. 1 one can see that the contribution to the magnetic hyperfine field arising from the Co neighboring ions $[B_{hf}^{\mathrm{ind}}=A(Z_{\mathrm{imp}})\widetilde{m}_{\mathrm{ind}}(0)]$ is larger than the contribution originated from the rare-earth ions $[B_{hf}^{R}=A(Z_{\mathrm{imp}})\widetilde{m}_{R}(0)]$. Moreover, for heavy rare-earths $|B_{hf}^{\mathrm{ind}}=A(Z_{\mathrm{imp}})\widetilde{m}_{\mathrm{ind}}(0)|$ decreases monotonically, being, however, always greater than $|B_{hf}^{R}=A(Z_{\mathrm{imp}})\widetilde{m}_{R}(0)|$, i.e., one has again a dominance arising from the contribution from the Co ions.

Figure 2 exhibits the self-consistently calculated magnetic hyperfine fields at a Cd impurity site, diluted in RNi$_2$ (dotted line) and RCo$_2$ (solid line). This figure shows that our theoretical model *predicts* that as we go from Gd to Er, (heavy rare earths) $|B_{hf}|$ *decreases*, whereas when we go from Gd to Pr, (light rare earths) $|B_{hf}|$ *increases*. The total self-consistently calculated magnetic hyperfine fields for RCo$_2$ hosts, plotted in full line exhibit an excellent agreement with available experimental data.[2] It should be useful to calculate the local magnetic moments and the magnetic hyperfine fields of systems like $T{:}R$Co$_2$ and $T{:}R$Ni$_2$ ($T=nd$ transition element, $n=3,\ 4,\ 5$), in order to check our model in the more complex cases, where one has contact as well as core polarization contributions to the magnetic hyperfine field.

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[1] A. Troper and A.A. Gomes, Phys. Rev. **34**, 6487 (1986).
[2] P. de la Presa, S. Müller, A.F. Pasquevich, and M. Forker, J. Phys.: Condens. Matter **12**, 3423 (2000).
[3] K.H.J. Buschow, Rep. Prog. Phys. **40**, 1179 (1977).
[4] H. Yamada, J. Inoue, K. Terao, S. Kanda, and M. Shimizu, J. Phys. F: Met. Phys. **14**, 1943 (1984).
[5] H. Akai, M. Akai, S. Blugel, and B. Dederich, Prog. Theor. Phys. Suppl. **101**, 261 (1990).
[6] P.H. Dederichs, R. Zeller, H. Akai, and H. Herbert, J. Magn. Magn. Mater. **100**, 261 (1991).
[7] J. Friedel, Nuovo Cimento, Suppl. **7**, 287 (1958).
[8] P.A. Wolff, Phys. Rev. **124**, 1030 (1961).
[9] A.M. Clogston, B.T. Matthias, N. Peter, H.J. Williams, E. Orenzwit, and R.J. Sherwood, Phys. Rev. **125**, 541 (1962).
[10] J. Kanamori, J. Appl. Phys. **16**, 929 (1965).
[11] I.A. Campbell and A.A. Gomes, Proc. R. Soc. (London) **91**, 319 (1967).
[12] I.A. Campbell, J. Phys. C **12**, 1338 (1969).
[13] I.A. Campbell, J. Phys. F: Met. Phys. **2**, L47 (1972).
[14] I.A. Campbell, W.D. Brewer, J. Flouquet, A. Benoit, B.W. Mardsen, and N.J. Stone, Solid State Commun. **15**, 711 (1974).
[15] W. Speier, J.F. van Acker, and R. Zeller, Phys. Rev. B **41**, 2753 (1990).
[16] J.F. van Acker, W. Speier, and R. Zeller, Phys. Rev. B **43**, 9558 (1991).
[17] J.F. van Acker, W. Speier, J.C. Fuggle, and R. Zeller, Phys. Rev. B **43**, 13 916 (1991).
[18] N.A. de Oliveira, A.A. Gomes, and A. Troper, Phys. Rev. B **52**, 9137 (1995).
[19] A.L. de Oliveira, M.V. Tovar Costa, N.A. de Oliveira, and A. Troper, J. Appl. Phys. **81**, 4215 (1997).
[20] A.L. de Oliveira, M.V. Tovar Costa, N.A. de Oliveira, and A. Troper, J. Magn. Magn. Mater. **177-181**, 1091 (1998).
[21] A. Blandin and I.A. Campbell, Phys. Rev. Lett. **31**, 51 (1973).
[22] I.A. Campbell and A. Blandin, J. Magn. Magn. Mater. **1**, 1 (1975).
[23] A.L. de Oliveira, V.P. Ramunni, M.V. Tovar Costa, N.A. de Oliveira, and A. Troper, J. Appl. Phys. **83**, 6971 (1998).