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2000 J. Phys.: Condens. Matter 12 8249

(http://iopscience.iop.org/0953-8984/12/38/302)

J. Phys.: Condens. Matter **12** (2000) 8249–8255. Printed in the UK PII: S0953-8984(00)14149-9

On the magnetization of the $Ho(Co_{1-x}Rh_x)_2$ pseudobinary

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Received 23 May 2000

Abstract. In this paper we study the effects of temperature and Rh concentration on the magnetization of the $Ho(Co_{1-x}Rh_x)_2$ pseudobinary. To this end we use a model in which the localized spins are immersed in an effective subsystem of itinerant electrons. Using functional integral techniques combined with the molecular-field approximation, we calculate the temperature dependence of the magnetization for several values of the Rh concentration. The curve obtained for the clean limit $x = 0$ shows a first-order phase transition. Above a critical Rh concentration of 10%, the phase transition changes to second order, in good agreement with experimental data from thermal and magnetostriction measurements.

1. Introduction

The rare-earth Laves phase intermetallic compounds RB_2, where R stands for a rare-earth element and B for a non-rare-earth element, have been extensively studied in the literature [1–13]. These intermetallics with a cubic (C15) or hexagonal structure (C14) present a great variety of magnetic properties and many technological applications. In particular, in the cases of rare-earth–transition metal intermetallics RT_2, where T stands for a transition atom, the total magnetization is associated with the localized 4f spins of the rare-earth and the *n*d itinerant electrons of the transition element. This interesting mixed nature of the magnetization produces unusual behaviour in the total-magnetization curve of these intermetallics. For instance, it is well known that the magnetization curves of RCo_2 intermetallics (R = Er, Dy, Ho) present a first-order magnetic phase transition [2–13], which is attributed to the spin fluctuations at the Co sites. Recently, experimental data have shown that the nature of the magnetic phase transition in these intermetallics changes from first to second order above a critical impurity concentration at Co sites [8–10]. In particular, Zochowski *et al* [8] showed by thermal and magnetostriction measurements that the magnetic phase transition in the pseudobinary $Ho(Co_{1-x}Rh_x)_2$ changes from first to second order above 8% Rh concentration.

In spite of the great development in the understanding of the magnetic properties of these rare-earth Laves phase intermetallics, the complete description of the magnetization, the nature of the magnetic phase transition, and other questions concerning the pressure effect and change of the magnetization direction still remain open. Also, the search for new materials with a giant magnetocaloric effect [14, 15], associated with a first-order magnetic phase transition, has recently renewed interest in the study of the rare-earth intermetallic compounds. As many experimental data become available, it is necessary to find a reasonable theoretical description of them and sometimes to develop new alternative models.

Motivated by these considerations, we study quantitatively and qualitatively the effects of temperature and Rh concentration on the magnetization of the pseudobinary $Ho(Co_{1-x}Rh_x)_2$.

0953-8984/00/388249+07$30.00

We use a model in which the 4f localized spins of the rare-earth ions interact via an effective subsystem of itinerant electrons containing disorder. Here we use functional integral techniques to treat the Coulomb interaction between itinerant electrons of the transition elements, and the molecular-field approximation to deal with the indirect exchange interaction between the localized 4f spin of the Ho ions. The disorder introduced by the substitution of Rh for the Co atom is treated through the off-diagonal coherent potential approximation (CPA) which takes into account the changes in the energy hopping involving sites occupied by different atoms. The magnetization curves obtained with this model show that for the clean limit of $HoCo_2$ (i.e. $x = 0$), the magnetic phase transition is of first order, and as soon as the Rh concentration reaches a critical value of 10%, the magnetic phase transition changes to second order as observed experimentally [8].

2. Formulation

In order to describe the pseudobinary $Ho(Co_{1-x}Rh_x)_2$ we begin with a model Hamiltonian in which the localized spins of the rare-earth ions are coupled to an effective subsystem of itinerant electrons. In the approximation of five identical d subbands, we have

$$H = \sum_{l\sigma} \varepsilon^{\mathrm{I}}_{0\sigma} |l\sigma\rangle\langle l\sigma| + \sum_{ljs} T^{\mathrm{II}'}_{ljs} |l\sigma\rangle\langle js| + U^{\mathrm{I}} \sum_{l} n_{l\uparrow} n_{l\downarrow} - \tilde{J}_{\mathrm{df}} \sum_{l} J^{\mathrm{f}}_{l} s^{\mathrm{d}}_{l}. \tag{1}$$

In this Hamiltonian the energy $\varepsilon^{\mathrm{I}}_{0\sigma}$ of itinerant electrons can assume the values $\varepsilon^{\mathrm{Co}}_{0\sigma}$ or $\varepsilon^{\mathrm{Rh}}_{0\sigma}$ depending on the occupancy of the site by a Co or Rh atom. The term $T^{\mathrm{II}'}_{ljs}$ (I, I′ stand for Co or Rh) represents the energy of the electron hopping between two different sites and also depends on its occupancy. The term U^{I} (I stands for Co or Rh) is the parameter describing the Coulomb interaction between itinerant electrons, and $n_{l\uparrow}$ ($n_{l\downarrow}$) is the electron occupation number with up (down) spin at Co and Rh sites. Here $\tilde{J}_{\mathrm{df}} = (g_i - 1)J_{\mathrm{df}}$, where J_{df} is the parameter describing the exchange interaction between localized 4f spins and itinerant electrons, and g_i is the Landé factor of the rare-earth ions. Finally J^{f} is the total angular momentum of the rare-earth ions and s^{d}_{l} is the spin of the itinerant electrons. In this model we neglect the crystal-field effect on the localized 4f levels of rare-earth ions, since it produces only a small renormalization of the total magnetization of the compound.

Using a simple mean-field approximation to deal with the last term in Hamiltonian (1), we can decouple it into two effective Hamiltonians H_{d} and H_{f} describing subsystems of itinerant electrons and localized spins:

$$H_{\mathrm{d}} = \sum_{l\sigma} \varepsilon^{\mathrm{I}}_{0\sigma} |l\sigma\rangle\langle l\sigma| + \sum_{ljs} T^{\mathrm{II}'}_{ljs} |l\sigma\rangle\langle js| + U^{\mathrm{I}} \sum_{l} n_{l\uparrow} n_{l\downarrow} - \tilde{J}_{\mathrm{df}} \sum_{l} \left\langle J^{\mathrm{f}}_{l} \right\rangle s^{\mathrm{d}}_{l} \tag{2}$$

$$H_{\mathrm{f}} = -\sum_{l \neq j} J^{\mathrm{f}}_{l} \left[\frac{1}{2} \left(\frac{\tilde{J}_{\mathrm{df}}}{g_e \mu_B} \right)^2 \chi^{\mathrm{d}} \right] J^{\mathrm{f}}_{j} \tag{3}$$

where μ_B is the Bohr magneton and g_e is the Landé factor of itinerant electrons. The effective Hamiltonian H_{f} describes a subsystem of localized 4f spins coupled to itinerant electrons via the electronic magnetic susceptibility χ^{d}. The term in the brackets in the Hamiltonian H_{f} defines an effective exchange interaction between localized 4f spins. This interaction establishes a connection between the magnetization associated with localized spins and the electronic structure of the itinerant electrons. It is easy to see that any change in the magnetic susceptibility χ^{d} modifies the effective interaction and consequently the magnitude of the magnetization associated with localized spins. From the Hamiltonian H_{f}, we obtain that the temperature dependence of the magnetization associated with localized spins is given by

$$M^R = g_i \mu_B \left\langle J^{\mathrm{f}} \right\rangle \tag{4}$$

where $\langle J^{\mathrm{f}} \rangle$ is the average of the total angular momentum of rare-earth ions. Here, for the sake of numerical simplicity, we use the molecular-field approach to treat the interaction between localized spins. In this case, given the magnetic susceptibility χ^{d}, the average $\langle J^{\mathrm{f}} \rangle$ is easily calculated in terms of the Brillouin function.

For the subsystem of itinerant electrons, we use functional integral techniques [16–19] to deal with the Coulomb interaction between electrons. In this approach, the Hamiltonian H_{d} for the subsystem of itinerant electrons turns out to be

$$\tilde{H}_{\mathrm{d}} = \sum_{l\sigma} \varepsilon^{\mathrm{I}}_{l\sigma} |l\sigma\rangle\langle l\sigma| + \sum_{lj\sigma} T^{\mathrm{II}'}_{lj\sigma} |l\sigma\rangle\langle j\sigma| \tag{5}$$

with the effective energies $\varepsilon^{\mathrm{I}}_{l\sigma}$ given by

$$\varepsilon^{\mathrm{I}}_{l\sigma} = \varepsilon^{\mathrm{I}}_{0\sigma} - \frac{U^{\mathrm{I}}}{2}(\mathrm{i}\nu_l + \sigma\xi_l) - \frac{1}{2}\sigma\tilde{J}_{\mathrm{df}}\left\langle J^{\mathrm{f}}_l \right\rangle \tag{6}$$

where ν_l and ξ_l are fluctuating charge and spin fields introduced by the functional integral method. The Hamiltonian $\tilde{H}_{\mathrm{d}}$ describes an effective subsystem of itinerant electrons moving in the presence of fluctuating fields and under the action of the effective magnetic field generated by the localized 4f spins. In this Hamiltonian there are two kinds of disorder, namely, the implicit disorder associated with the fluctuating fields and the chemical disorder associated with the substitution of Rh for Co atoms. We deal with the disorder in this Hamiltonian by extending the off-diagonal coherent potential approximation (CPA) [20] to this problem. In this approximation, the energy hopping involving sites occupied by different atoms is parametrized by

$$T^{\mathrm{II}'}_{lj} = \lambda^{\mathrm{I}}_l T_0 \lambda^{\mathrm{I}'}_j \tag{7}$$

where T_0 is a reference energy hopping when the sites l and j are occupied by Co atoms and the parameters λ^{I}_l and $\lambda^{\mathrm{I}'}_j$ (I, I′ = Co or Rh) should be taken consistent with the extent of the d wave functions of Co and Rh atoms. With this approximation we can write the Green's function for the effective Hamiltonian $\tilde{H}_{\mathrm{d}}$ as [20]

$$g^{-1}(z) = (z - \tilde{H}_{\mathrm{d}})^{-1} = \lambda^{\mathrm{I}}_l \left[\sum_{l\sigma} \tilde{\varepsilon}^{\mathrm{I}}_{l\sigma} |l\sigma\rangle\langle l\sigma| - \sum_{lj\sigma} T_{0\sigma} |l\sigma\rangle\langle j\sigma| \right] \lambda^{\mathrm{I}'}_j \tag{8}$$

where $z = \varepsilon + \mathrm{i}0$ and the new effective energy $\tilde{\varepsilon}^{\mathrm{I}}_{l\sigma}$ is given by

$$\tilde{\varepsilon}^{\mathrm{I}}_{l\sigma}(z) = \frac{z - \varepsilon^{\mathrm{I}}_{l\sigma}}{(\lambda^{\mathrm{I}}_l)^2}. \tag{9}$$

In order to deal with the diagonal disorder in equation (8), we follow the standard procedure of the single-site CPA, by introducing an effective medium with self-energy Σ_σ to restore the translational invariance of the subsystem of itinerant electrons. In order to determine the self-energy, we generate a Slater–Koster problem by replacing at a given site '0' one atom of the effective medium by an atom with energy $\tilde{\varepsilon}^{\mathrm{I}}_{l\sigma}$ (I = Co or Rh). Using Dyson's equation, the average of the perturbed Green's function $G_{lj\sigma}$ for the Slater–Koster problem, in the site representation, is given by [20]

$$\left\langle\left\langle G_{lj\sigma}(z) \right\rangle\right\rangle = \left\langle\left\langle g_{lj\sigma}(z) \right\rangle\right\rangle + \left\langle\left\langle g_{l0\sigma}(z) \right\rangle\right\rangle (\Sigma_\sigma(z) - \tilde{\varepsilon}^{\mathrm{I}}_{l\sigma}(z)) \left\langle\left\langle G_{0j\sigma}(z) \right\rangle\right\rangle \tag{10}$$

where $g_{lj\sigma}$ is the unperturbed Green's function obtained by replacing in equation (8) the effective energy $\tilde{\varepsilon}^{\mathrm{I}}_{l\sigma}$ by the self-energy Σ_σ. In equation (10), the double average should be taken over the Rh concentration and over the charge- and spin-fluctuating fields. We are more interested in the magnetic effects and thus, for the sake of numerical simplicity, we neglect the fluctuation in the charge field and take only the average over the spin field and the Rh

concentration. After some work, we obtain the following CPA equation for determining the self-energy Σ_σ:

$$(1-x)\int \mathrm{d}\xi \; \frac{V_\sigma^{\mathrm{Co}}(\xi,z)}{1-V_\sigma^{\mathrm{Co}}(\xi,z)F_\sigma(z)}P^{\mathrm{Co}}(\xi)+x\int \mathrm{d}\xi \; \frac{V_\sigma^{\mathrm{Rh}}(\xi,z)}{1-V_\sigma^{\mathrm{Rh}}(\xi,z)F_\sigma(z)}P^{\mathrm{Rh}}(\xi)=0. \quad (11)$$

Here the probability function $P^{\mathrm{I}}(\xi)$, I = Co or Rh, is given by

$$P^{\mathrm{I}}(\xi)=\mathrm{e}^{-\beta\Psi^{\mathrm{I}}(\xi)}\Big/\left(\int \mathrm{d}\xi \; \mathrm{e}^{-\beta\Psi^{\mathrm{I}}(\xi)}\right) \quad (12)$$

where $\beta = 1/kT$. The free energy Ψ^{I} is given by

$$\Psi^{\mathrm{I}}(\xi)=\left\{\frac{U^{\mathrm{I}}\xi^2}{4}+\frac{1}{\pi}\int \mathrm{d}z \; f(z)\,\mathrm{Im}\sum_\sigma \ln[1-V_\sigma^{\mathrm{I}}(\xi,z)F_\sigma(z)]\right\} \quad (13)$$

with $f(z)$ being the Fermi function. The potentials $V_\sigma^{\mathrm{I}}(\xi,z)$ are given by

$$V_\sigma^{\mathrm{I}}(\xi,z)=\Sigma_\sigma(z)-\tilde{\varepsilon}_{l\sigma}^{\mathrm{I}}(\xi,z). \quad (14)$$

The diagonal Green's function, $F_\sigma(z)$, is

$$F_\sigma(z)=\int \mathrm{d}\varepsilon \; \frac{\rho_0(\varepsilon)}{\Sigma_\sigma(z)-\varepsilon} \quad (15)$$

where $\rho_0(\varepsilon)$ is a standard model for the d density of states. Once the self-energy $\Sigma_\sigma(z)$ is self-consistently determined, the effects of temperature and Rh concentration on the magnetization of the subsystem of itinerant electrons is given by

$$M^{\mathrm{d}}=(1-x)\int \xi\, P^{\mathrm{Co}}(\xi)\,\mathrm{d}\xi + x\int \xi\, P^{\mathrm{Rh}}(\xi)\,\mathrm{d}\xi. \quad (16)$$

The total magnetization is given by the summation of the contribution of itinerant electrons (M^{d}) and localized spins (M^R).

3. Numerical results

In order to calculate the temperature dependence of the magnetization of the pseudobinary $\mathrm{Ho(Co_{1-x}Rh_x)_2}$ we have to specify the set of model parameters. For the subsystem of localized spins, we use the total angular momentum $J^{\mathrm{f}} = 8$; the exchange interaction parameter $J_{\mathrm{df}} = 0.015$ eV, and the g_i-factor was extracted from Hund's rule ($g_i = 5/4$). For the subsystem of itinerant electrons, we choose the Coulomb interaction parameters to ensure that the Stoner criterion for magnetism is not fulfilled, so the magnetism associated with the itinerant electrons is induced by the localized spins. The factors λ^{I} (I = Co, Rh) parametrizing deviations in the energy hopping were properly chosen to be consistent with the ratio between the extension of the 3d and 4d wave functions of Co and Rh atoms. Here we take $\lambda^{\mathrm{Co}} = 1.0$ and $\lambda^{\mathrm{Rh}} = 1.03$. All these parameters are kept fixed during the whole process of achieving self-consistency. As far as the electronic structure is concerned, we adopt a model d density of states extracted from an *ab initio* calculation [21]. The initial d-electron occupation numbers at the Co and Rh sites were taken from the atomic configurations in the periodic table. In the particular case of the $\mathrm{Ho(Co_{1-x}Rh_x)_2}$ pseudobinary, the substitution of Rh for Co does not change the total charge of the system. However, the charge transfer between sites should be determined self-consistently by the solution of the coupled equations discussed above.

In order to achieve self-consistency, we put an initial value of $\langle J^{\mathrm{f}}\rangle$ into the equations for the subsystem of itinerant electrons to calculate the electronic magnetic susceptibility χ^{d} and the magnetization M^{d}. The electronic magnetic susceptibility χ^{d} is calculated numerically

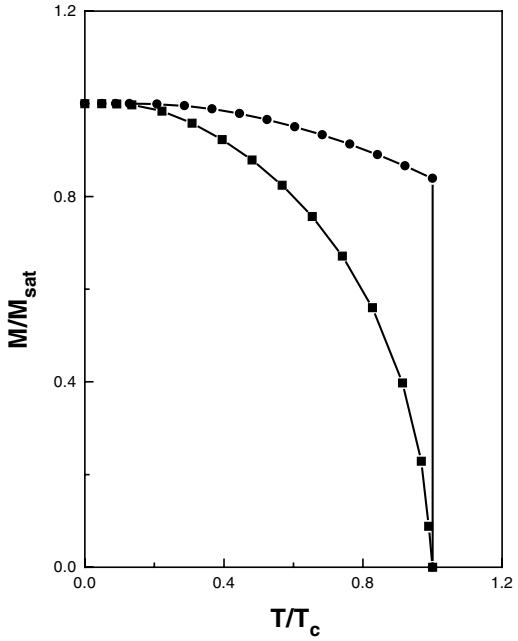

Figure 1. The temperature dependence of the total magnetization of the pseudobinary $Ho(Co_{1-x}Rh_x)_2$. The circles represent the clean limit for $x = 0$ where a first-order magnetic phase transition takes place. The squares represent the critical concentration where the magnetic phase transition changes from first to second order. The lines are guides for the eyes.

from the expression M^{d}/h, where h is the effective magnetic field produced by the rare-earth ions acting on the itinerant-electron subsystem. Using the value of χ^{d}, we calculate the new effective exchange interaction between the localized spins and turn to the equations for the subsystem of localized spins to obtain another value of $\langle J^{\mathrm{f}} \rangle$. Then we return to the equations for the subsystem of itinerant electrons to calculate new values of the magnetic susceptibility χ^{d} and the magnetization M^{d}. We repeat this process until a self-consistent value of the physical quantity $\langle J^{\mathrm{f}} \rangle$ is obtained with the desired numerical precision. The total-magnetization curve calculated in the limit of a vanishing Rh concentration, represented by the circles of figure 1, shows a first-order phase transition. That occurs since the localized magnetic moments at rare-earth sites induce a metamagnetic transition in the subsystem of itinerant electrons. This metamagnetic transition, which is associated with the position of the Fermi level close to a sharp peak in the d density of states, produces an abrupt enhancement in the electronic magnetic susceptibility, giving rise to a significant increase in the effective interaction between localized spins. As a result, the total magnetization shows a first-order phase transition, as has already been predicted by Bloch *et al* [6] and observed experimentally [8].

When we increase the Rh concentration, the total electronic density of states of the itinerant electrons becomes wider. In our model, this fact is taken into account by the parameters adopted, λ^{Co} and λ^{Rh}. The broadening of the density of states is such that the Fermi level moves away from the peak in the d density of states, causing the magnetic susceptibility and thus the effective interaction between localized spins to decrease. Hence the critical temperature is reduced with increasing Rh concentration in good agreement with experimental data [8]. In figure 2 we plot the calculated critical temperature as a function of Rh concentration. In addition, above a critical Rh concentration, the broadening of the density of states is such that

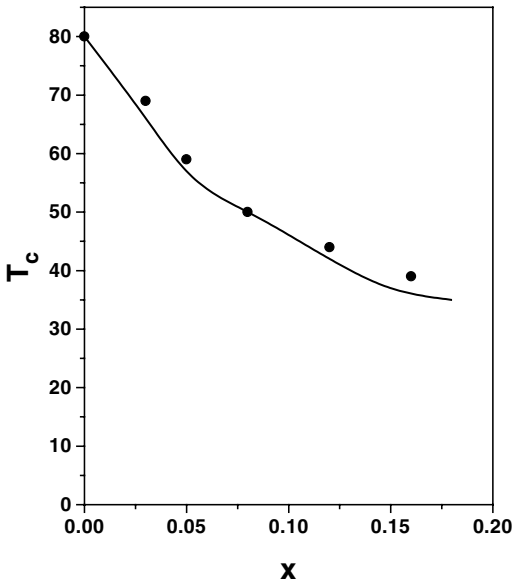

Figure 2. Critical temperature as a function of Rh concentration for the pseudobinary $Ho(Co_{1-x}Rh_x)_2$. The circles are experimental data collected from reference [8].

the effective exchange interaction between localized spins varies smoothly around the critical temperature, leading to a usual second-order magnetic phase transition. In our work, we obtain that the critical Rh concentration for the appearance of the second-order phase transition in this pseudobinary is around 10%, which is in good agreement with experimental data [8]. The total-magnetization curve for the critical concentration $x = 0.1$ where the magnetic phase transition changes from first to second order is represented by the squares of figure 1.

In conclusion, in this paper we have calculated the effects of temperature and Rh concentration on the total magnetization of the pseudobinary $Ho(Co_{1-x}Rh_x)_2$. Despite the approximations used in the model, the magnetization curves obtained in this work show that above a critical Rh concentration the magnetic phase transition changes from first to second order, which is consistent with experimental data from thermal and magnetostriction measurements [8]. We can straightforwardly extend the present model to study the effect of external pressure and anisotropy on the magnetic properties of this class of rare-earth pseudobinaries. However, in order to consider the effects of orbital degeneracy and disorder at the rare-earth sites on its magnetic properties, a more general and detailed treatment of the electronic structure should be carried out. In addition, the cases of pseudobinaries such as $Ho(Co_{1-x}Si_x)_2$ and $Er(Co_{1-x}Si_x)_2$ can easily be cast in the language of this paper. Calculations in these directions are now in progress and will be published elsewhere.

Acknowledgments

We are very grateful to Professor Affonso Gomes for enlightening discussions related to this subject over many years. N A de Oliveira is grateful to the Department of Physics and Astronomy at Rutgers University for kind hospitality during a Post-Doctoral stay when part of this work was done. This work was partially supported by CNPq and FAPERJ (Brazilian funding agencies).

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