Influence of the Magnetic State on the Chemical Order-Disorder Transition Temperature in Fe-Ni Permalloy

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In magnetic alloys, the effect of finite temperature magnetic excitations on phase stability below the Curie temperature is poorly investigated, although many systems undergo phase transitions in this temperature range. We consider random Ni-rich Fe-Ni alloys, which undergo chemical order-disorder transition approximately 100 K below their Curie temperature, to demonstrate from *ab initio* calculations that deviations of the global magnetic state from ideal ferromagnetic order due to temperature induced magnetization reduction have a crucial effect on the chemical transition temperature. We propose a scheme where the magnetic state is described by partially disordered local magnetic moments, which in combination with Heisenberg Monte Carlo simulations of the magnetization allows us to reproduce the transition temperature in good agreement with experimental data.

The physics of phase stability and phase transformations belongs to the most fundamental problems of modern condensed matter theory, and the field of research is expanding to new systems [1–3] and phenomena [4–7]. State-of-the-art methods for parameter-free simulations of phase equilibria have been developed [8,9]. However, the majority of simulations are still carried out either for nonmagnetic or for fully magnetically ordered states, because only they are usually accessible by the most accurate full potential *ab initio* techniques [10]. At the same time, as was recognized a long time ago [11], the effective chemical interactions are sensitive to the magnetic state since the interaction between magnetic atoms depends on the relative orientation of their local magnetic moments through the corresponding exchange interactions. So, from a general point of view, it is clear that the corresponding configurational Hamiltonian must include the magnetic degrees of freedom.

The latter is actually a highly nontrivial issue in itself, and in addition, an *ab initio* description of the finite temperature magnetic state is usually possible only in simplified models, like for instance, the disordered local moment (DLM) approach to the Heisenberg-type paramagnet [12], where the orientation of the spins on different atoms is supposed to be random. Still, inclusion of the Heisenberg-like model would enormously complicate the full statistical thermodynamics consideration of the chemical configurational thermodynamics. What makes it feasible in the end is the huge leap in the time scale of the relevant magnetic and chemical excitations which are connected with the spin reorientation and the rate of atomic jumps. This means that it is possible to average out the magnetic degrees of freedom assuming that the magnetic state of the atoms

participating in the configurational equilibration may be represented by its time average [13].

As has already been demonstrated in a number of articles, the magnetically disordered state leads to significant modifications of the chemical interactions [13–15]. In particular, as shown in Ref. [14], the pronounced ordering tendency in Fe-rich Fe-Ni fcc alloys close to the Invar composition almost completely disappears in the paramagnetic state.

For alloys undergoing transitions in the ferromagnetic (FM) regime, it is common to assume a completely ordered ferromagnetic reference state, and the effect of finite temperature excitations on the chemical interactions in this state is little investigated. However, as demonstrated by Ruban *et al.* [16], reduced magnetization in FM Fe-Cr alloys leads to strong nonlinear renormalization of the effective chemical interactions.

In this Letter we show that temperature induced magnetization reduction does have a profound effect on phase stability in magnetic systems. We have chosen the fcc Fe-Ni alloy with 70–80 at. % Ni content as a model system to demonstrate the effect. In this composition range we find the technologically important Permalloy, which is used in such diverse applications as power transformer cores, magnetic recording devices, and spin valves due to its high permeability [17]. This system was investigated earlier by Staunton *et al.* [11] using the concentration fluctuation (or $S^{(2)}$) formalism within the self-consistent Korringa-Kohn-Rostocker coherent potential approximation method. However, only "Stoner paramagnetic," i.e., nonmagnetic, and completely FM states were considered. For nonmagnetic calculations, the authors found no ordering tendency at all, while in the FM calculations the

ordering-type behavior in Ni_3Fe turned out to be unclear due to very close values of $S^{(2)}(\mathbf{k})$ at the (110) and (100) points. The mutual influence of magnetic and chemical interaction in Fe-Ni alloys was recently studied in Ref. [18] by means of phenomenological calculations. It was found that magnetic interaction increases the temperature of order-disorder phase transition.

Ni_3Fe alloy undergoes ordering phase transition into $L1_2$ structure [(100)-type of ordering] at approximately 780 K in the FM state, but this is in fact in close proximity of the Curie temperature, which is about 80 K higher [19]. This means that the magnetization is not saturated, and taking into consideration the sensitivity of the interactions to the global magnetization close to the Curie temperature [16], one may expect to see a strong effect in this system.

Neglecting the dependence of the chemical effective interactions on the local environment, which in principle may affect the local magnetic state and thereby all the corresponding interatomic interactions, we adopt the following Ising-type Hamiltonian for the chemical part of the problem:

$$H_{\text{conf}} = \frac{1}{2}\sum_p V_p^{(2)} \sum_{i,j\in p} \delta c_i \delta c_j + \frac{1}{3}\sum_q V_q^{(3)} \sum_{i,j,k\in q} \delta c_i \delta c_j \delta c_k$$
$$+ \frac{1}{4}\sum_r V_r^{(4)} \sum_{i,j,k,l\in r} \delta c_i \delta c_j \delta c_k \delta c_l + \cdots. \qquad (1)$$

Here, V_t^n are the effective cluster interactions (ECI) of order n and type t, and $\delta c_i = c_i - c$ the concentration fluctuations at site i, where occupation number c_i takes on values 1 and 0 depending on which type of atom occupies site i, and c is the concentration. The ECI here depend on volume, temperature, alloy concentration, and global magnetization as described below.

The parameters of the above Hamiltonian (1) are determined from *ab initio* calculations within the framework of density functional theory. The starting point here is a model for the FM state with a reduced magnetization corresponding to the given temperature. In general it is an open question what it could be in the case of itinerant magnet, in which the magnetic moments of one of the alloy components, in our case Ni, are extremely sensitive to the global magnetization. It is clear that an accurate account of magnetism requires inclusion of longitudinal spin fluctuations.

However, this is too cumbersome in the case of alloys, and too uncertain. Thus, in this work we choose a simplified scheme, assuming that the reduced magnetization is mainly due to magnetic moment disorder on Fe atoms, while magnetic moments on Ni atoms simply follow the corresponding global magnetization. Formally, this is done within the so-called partial disordered local moment (PDLM) model, in which the initial binary alloy, $Fe_{1-c}Ni_c$, is substituted by the three-component alloy $((Fe_{1-y}^{\uparrow}Fe_y^{\downarrow})_{1-c}Ni_c)$. Here, the parameter y determines the

degree of global magnetization $m = 1 - 2y$, and $y = 0.5$ in the full DLM state. A similar model has been used in Ref. [16] for Fe-Cr alloys.

The determination of the magnetic state is actually a tricky point in this system for several reasons. First of all, this is an itinerant magnet, whose magnetic interactions are sensitive to, e.g., the magnetic state itself. However, taking into consideration that we are mostly interested in the FM state, we will neglect such a dependence and use the Heisenberg magnetic Hamiltonian [20,21],

$$H_{\text{mag}} = -\sum_{p,\alpha,\beta} J_p^{\alpha\beta} \sum_{i,j\in p} \mathbf{e}_i c_i^\alpha \mathbf{e}_j c_j^\beta, \qquad (2)$$

where $J_p^{\alpha\beta}$ are the magnetic exchange interactions in the FM state at the pth coordination shell between α and β types of atoms (α, β = Fe, Ni), $\mathbf{e}_i$ the direction of the spin, and c_i^α are the occupation numbers defined above.

To calculate the electronic structure of such a *random* alloy we have used the coherent potential approximation within the exact muffin-tin orbitals method [22] and the generalized gradient approximation [23] to the exchange-correlation potential and energy [19].

The theoretical value of the equilibrium lattice constant was found to be very close to the low temperature experimental value, and the change in transition temperature from using either one does not change our results qualitatively. To account for the effect of thermal expansion we used the experimental lattice constant corresponding to 773 K [24] in the entire composition range.

In Fig. 1 we show the magnetic moments obtained for the random fcc-$Fe_{0.25}Ni_{0.75}$ alloy in the PDLM model as a function of reduced magnetization m. The large magnetic moments of Fe are approximately constant in the whole
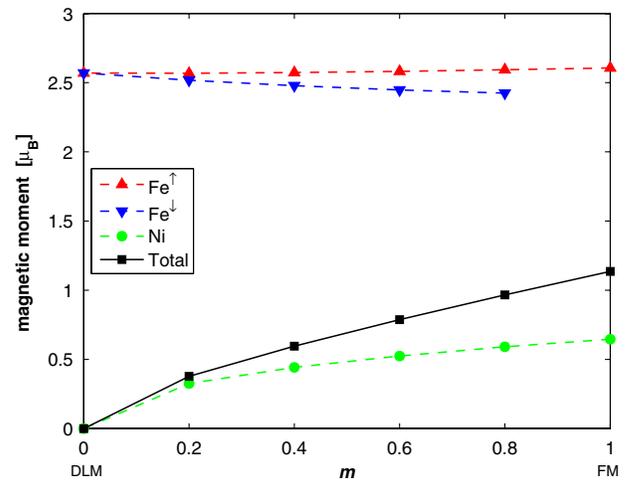

FIG. 1 (color online). Net (black squares) magnetic moment and local magnetic moments at $Fe^{\uparrow}$ (triangle pointing up), $Fe^{\downarrow}$ (triangles pointing down), and Ni (circles) as a function of magnetic order parameter m in the fcc-$(Fe_{(1+m)/2}^{\uparrow}Fe_{(1-m)/2}^{\downarrow})_{0.25}Ni_{0.75}$ alloy simulated by means of the PDLM model.

magnetization range, from fully FM to the DLM (para-magnetic) states. Ni moments are non-negligible but also show only weak dependence on the global magnetization for $m > 0.4$. This result supports the choice of the Heisenberg model (2) for the magnetic Hamiltonian.

The chemical ECI have been determined using the screened generalized perturbation method [13,25] adopted for the PDLM state [16]. It was demonstrated in Ref. [26] that the influence of local lattice relaxations on the energetics of Fe-Ni alloys is small, which may be expected as the size mismatch of Fe and Ni atoms is relatively small. We have therefore neglected the contribution from strain induced interactions in the ECI.

In order to investigate the dependence of the order-disorder phase transition on the magnetization, we have performed Ising Monte Carlo (MC) simulations with the first 20 2-site and 20 3-site ECI, as well as five 4-site interactions [19]. The ordering energy at 75% Ni content in the magnetically ordered state ($m = 1$) obtained by cluster expansion matches that of a direct calculation to within 0.03 mRy. In Fig. 2 we show results of the MC simulations of the ordering transition temperature as a function of composition for different values of m, along with the experimental phase boundary redrawn from Ref. [27]. Figure 2 clearly demonstrates that calculated chemical order-disorder phase transition temperature shows very strong dependence on the degree of magnetic order. Indeed, the calculated transition temperature is seen to span almost 500 K in the whole range of global magnetization. Also, the shape of the phase boundary strongly depends on the magnetic state, with the peak being shifted to lower Ni concentration with increased magnetization.
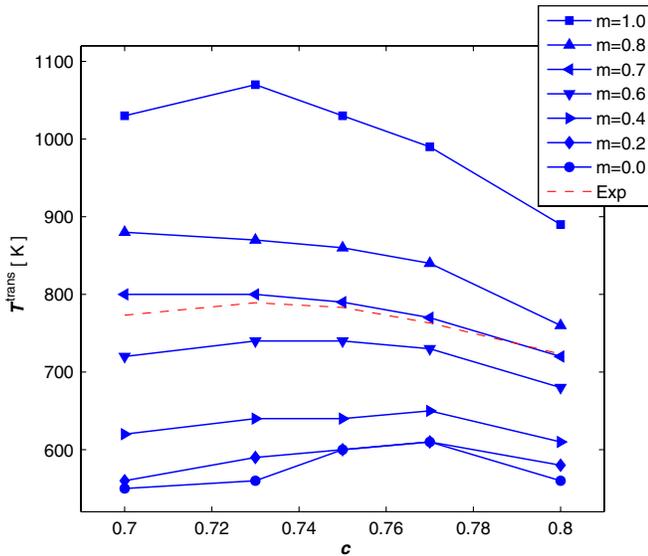
Clearly, neither the FM nor DLM states correctly describe the phase boundary even qualitatively.

We have determined the order-disorder phase transition temperature entirely from *ab initio* theory by means of calculating magnetization as a function of temperature in Heisenberg MC simulations for a random $Fe_{0.25}Ni_{0.75}$ alloy. Since chemical order should affect both the magnetic exchange interactions and the global magnetic state, this means that the corresponding statistical thermodynamic simulations should in principle be done considering both chemical and magnetic degrees of freedom together. However, this would enormously complicate the task and can be done only with a number of additional assumptions and approximations. Thus, in our magnetic simulations we fix random alloy configuration, which is a reasonable approach as far as we are interested only in finding the temperature of the order-disorder phase transition. Indeed, in our search for the chemical transition temperature we use the MC method, and approach the transition from high temperature, so the alloy is in the random state at temperatures just a little bit above the transition temperature, although with substantial amount of short-range order. The magnetic exchange interaction parameters were obtained for a FM random alloy by the magnetic force theorem [20,21] implemented in the exact muffin-tin orbitals framework. In the MC simulations, we included the first 20 exchange interaction parameters [19].

The results for the magnetization are shown in Fig. 3. In the same figure we also show the chemical ordering transition temperature in $Fe_{0.25}Ni_{0.75}$ for the corresponding magnetization, taken from Fig. 2. It is clear that the

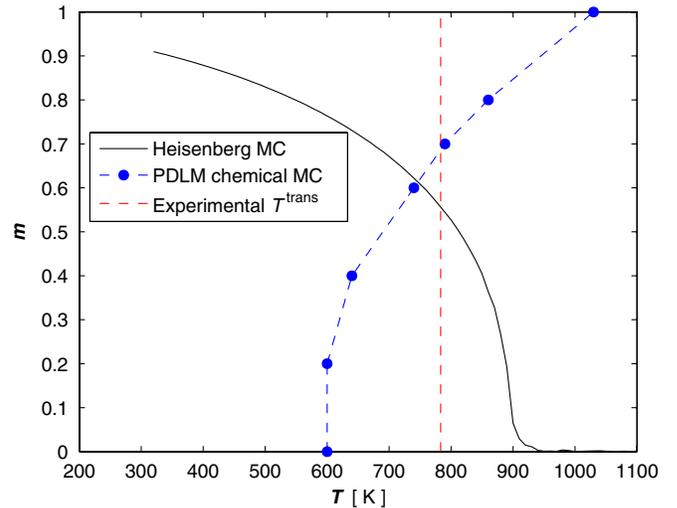FIG. 2 (color online).   Chemical order-disorder transition temperature in $Fe_{1-c}Ni_c$ as a function of Ni concentration c obtained from MC calculations with various magnetic reference states, characterized by magnetic order parameter m. The experimental phase boundary is indicated by the dashed line.

FIG. 3 (color online).   Magnetization m for $Ni_{0.75}Fe_{0.25}$ as a function of temperature obtained from Heisenberg MC calculations (solid line) shown together with the chemical transition temperature calculated using the PDLM reference state corresponding to each value of m (dashed line with circles). For comparison, we include the experimental transition temperature (vertical dashed line).

intersection of the two curves should determine both the transition temperature and the corresponding magnetization at the chemical phase transition. In this particular case, we find the theoretical magnetization $m = 0.61$ at the point of chemical order-disorder phase transition, which corresponds to the transition temperature 747 K. This value is in very good agreement with the experimental order-disorder transition temperature of $Fe_{0.25}Ni_{0.75}$, which is $\sim$783 K [19,27]. Let us note that the experimental data for the magnetization at elevated temperature [28] indicate that in the region of chemical phase transition, the magnetization is reduced by approximately 40%. The magnetization parameter, $m \sim 0.6$, may therefore be considered in reasonable agreement with experiment. Indeed, we see that the phase boundary obtained using $m = 0.6$ reproduces experiment. Moreover, with $m = 0.6$ we correctly reproduce the concentration dependence and the position of the order-disorder phase boundary, as seen in Fig. 2.

In summary, we have shown that the temperature induced magnetization reduction has a strong impact upon chemical effective interactions in transition metal alloys, even in the ferromagnetic state. Using the Ni-rich fcc FeNi alloy as a model system, we demonstrate that deviations of the magnetic state in metallic alloys from either ideal order or disorder result in a large spread of the obtained order-disorder transition temperatures. We also propose a scheme capable of incorporating this effect in *ab initio* simulations without explicitly treating the highly intricate mutual interplay between chemical and magnetic degrees of freedom. Although our theoretical approach is based on a number of assumptions concerning the finite temperature magnetic excitations, the type of magnetic and atomic configurational Hamiltonians, and the coupling of the chemical and magnetic degrees of freedom, we are able to reproduce quite accurately not only the experimental ordering transition temperature, but also its behavior as a function of the alloy composition. Our work points out the general importance of temperature induced magnetic effects for alloy stability even in the magnetically ordered state. It adds a new aspect to the development of accurate *ab initio* theory of alloy phase stability.

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