1987

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AIP Journal of Applied Physics

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Citation: Journal of Applied Physics **61**, 3693 (1987); doi: 10.1063/1.338664
View online: http://dx.doi.org/10.1063/1.338664
View Table of Contents: http://scitation.aip.org/content/aip/journal/jap/61/8?ver=pdfcov
Published by the AIP Publishing

Interaction between magnetic and compositional order in Ni-rich Ni_cFe_{1-c} alloys (invited)

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We have developed a first-principles electronic theory of concentration fluctuations in spin polarized binary alloys. It is a mean field theory of the state of compositional order and it is based on the local spin density (LSD) approximation for describing the electrons. The usual averages over the statistical mechanical ensemble are carried out with the aid of the self-consistent Korringe–Kohn–Rostoker coherent-potential approximation (SCF-KKR-CPA). To illustrate the main consequences of the theory we study the compositional short-range order in the Ni_cFe_{1-c} alloy system. We find that the ordering energy is almost entirely of magnetic origin.

I. INTRODUCTION

Most metallic magnets are multicomponent alloys.[1] When the state of magnetic and compositional order are strongly coupled a number of physically interesting and technologically important new phenomena arise. For instance, to mention but one example, some alloys, such as Ni_cFe_{1-c}, develop "directional chemical order" when annealed in a magnetic field.[2] Naturally the study of how compositional and magnetic fluctuations influence each other has been vigorously pursued for a long time.[3] However, progress has been slow, not the least because a theory which deals with both kinds of fluctuations on equal footing and in quantitative detail is very difficult to construct. In this paper, as a step towards such a theory, we investigate the effects of magnetic order on the tendency towards compositional order in Ni-rich Ni_cFe_{1-c} alloys within a fully first-principles, electronic, conceptual framework.

That the above might be a fruitful enterprise in its own right follows from fairly simple considerations. As is well known when Fe is added to Ni, at high temperatures where they form a fcc solid solution, both the Curie temperature T_C and the average moment $\bar{\mu}$ per site rises with increasing Fe concentration. Surprisingly, near $c \sim 0.75$ T_C begins to decline while $\bar{\mu}$ continues to increase all the way to the INVAR region ($c \sim 0.36$) where it collapses. A plausible explanation for this unexpected behavior is that the exchange interaction between local moments on the Fe sites is antiferromagnetic and this destabilizes the ferromagnetic state once the number of nearest-neighbor Fe pairs is large enough. Simple, spin-only models based on this idea do reproduce the above experimental observations.[4,5] Moreover, there is theoretical evidence that Fe on an fcc lattice, with lattice parameter close to that of the Ni_3Fe alloy, would be antiferromagnetic.[6] Such antiferromagnetic frustration is also predicted by Kakahashi[7] and Hasegawa[8] on the basis of fully itinerant models. What interests us here is that, taken at its face value, the above physical picture implies a strong tendency towards chemical order. Namely, it prompts the conjecture that the system orders chemically in order to reduce the number of nearest-neighbor Fe pairs. Indeed, Ni_cFe_{1-c} orders into $L1_2$ at $c \sim 0.75$ and into $L1_0$ structure at $c \sim 0.5$. Our principal aim is to investigate the plausibility of the intriguing suggestion that this chemical order is of magnetic origin on the basis of reliable and parameter-free calculations.

The theory we shall be using is based on the spin polarized SCF-KKR-CPA calculations of Johnson *et al.*[9] and is a generalization of the electronic theory of short range order by Gyorffy and Stocks.[10] It also incorporates, as a significant feature, the effects of nonrigid moments following the arguments of Staunton *et al.*[11] The structure of our paper should be clear from the section headings.

II. A THEORY OF CHEMICAL SHORT-RANGED ORDER IN SPIN-POLARIZED RANDOM ALLOYS

The approach of Gyorffy and Stocks[11] readily generalizes to the case of alloys, such as Ni_cFe_{1-c}, in the ferromagnetic state. The theory has two parts: the first deals with the statistical mechanics of the alloy configurations in the mean field approximation, the second implements the instructions of the first on the basis of a spin-density functional description of the electronic energies for each configurations.

In this paper we restrict our attention to the study of pair correlations. These are described by the pair correlation function q_{ij}. In terms of the occupation variables ξ_i, which take on the value 1 if the ith site is occupied by an A atom and 0 if there is a B atom at i, it is defined by

$$q_{ij} = \beta(\langle \xi_i \xi_j \rangle - \langle \xi_i \rangle \langle \xi_j \rangle), \quad (1)$$

where

$$c_i = \langle \xi_i \rangle.$$

Working out the thermal averages denoted by $\langle\ \rangle$ in the mean field approximation and in the disordered state we find

0021-8979/87/083693-04$02.40

$$q(\mathbf{k}) = \frac{2\beta c(1-c)}{1-\beta c(1-c)S^{(2)}(\mathbf{k})}, \tag{2}$$

where $q(q)$ is the lattice Fourier transform of q_{ij} and $S^{(2)}(\mathbf{k})$ is that of the direct correlation function defined by

$$S_{ij}^{(2)} = \left(\frac{\partial^2\Omega(\{c_i\})}{\partial c_i \partial c_j}\right)_{c_i=\bar{c}\forall i}. \tag{3}$$

It is one of the central results of the theory that the quantity $\Omega(\{c_i\})$ is the average of the electronic grand potential for each configuration $\Omega(\{\xi_i\})$ over the inhomogeneous product distribution

$$P_i(\{\xi_i\}) = \prod_i P_i(\xi_i), \tag{4}$$

parametrized by

$$P_i(\xi_i) = c_i\xi_i + (1-c_i)(1-\xi_i). \tag{5}$$

We now turn to the second, electronic part of the theory, namely, the evaluation of $\Omega(\{c_i\})$. To be consistent with mean field approximation we have already made, this is to be carried out within the coherent potential approximation. To simplify matters, we aim for a theory at temperatures T above the ordering temperature $T_0(\sim 780$ K for $\text{Ni}_{0.75}\text{Fe}_{0.25}$) but below the Curie temperature T_C (~ 870 K for $\text{Ni}_{0.75}\text{Fe}_{0.25}$). Then, for this exploratory part of our investigation, we to consider the case of a fully spin-polarized alloy only. That is to say, as far as the magnetic fluctuations are concerned the system is assumed to be in its ground state and is described by the spin-polarized SCF-KKR-CPA calculations of Johnson *et al.*,[9] but the local occupation numbers $\{\xi_i\}$ are allowed to undergo the normal thermal fluctuations.

It is fairly straightforward to write down, formally, an inhomogeneous version of the spin polarized SCF-KKR-CPA. An inhomogeneous CPA in that on every site the CPA equations must be solved to determine the local nonequilibrium concentrations c_i. This implies a definite expression for $\Omega(\{c_i\})$ and, therefore, for the derivatives in Eq. (3). When, in this expression, c_i is set equal to $\bar{c}$ for all i the result is a response function of the homogeneous spin-polarized SCF-KKR-CPA which can be evaluated numerically.

The details of the theory will be described elsewhere. Here we shall make only two general comments before moving on to the presentation of the results. Firstly, we observe that $\bar{\Omega}$ depends on the local concentrations $\{c_i\}$ directly, as in the non-spin-polarized theory of Gyorffy and Stocks,[10] and indirectly through the local moments $\{\mu_i\}$ which arise in the spin-polarized theory for each configuration. As a consequency $S_{ij}^{(2)}$ turns out to consist of three contrbutions

$$S_{ij}^{(2)} = S_{ij}^{c,c} + \sum_l S_{il}^{c_i\mu^A}\gamma_{lj}^A + \sum_l S_{il}^{c_i\mu^B}\gamma_{lj}^B, \tag{6}$$

where, in terms of the local chemical potential $S_i^{(1)} = \partial\Omega/\partial c_i$,

$$S_{ij}^{c,c} = \left(\frac{\partial S_i^{(1)}}{\partial c_j}\right)_{\{\mu_i\}}; \quad S_{ij}^{c_i\mu^\alpha} = \left(\frac{\partial S_i^{(1)}}{\partial \mu_j^\alpha}\right)_{\{c_i\}} \tag{7}$$

for $\alpha = A$ or B and

$$\gamma_{ij}^\alpha = \left(\frac{\partial \mu_i^\alpha}{\partial c_j}\right). \tag{8}$$

If there were no spins and the system were described by a pair-wise interacting lattice gas model in the random-phase approximation, Eq. (2) would be the Krivoglaz–Moss–Clapp formula. Then $S_{ij}^{(2)}$ would be the interchange energy $V_{ij} = v_{ij}^{AA} + v_{ij}^{BB} - 2v_{ij}^{AB}$ where $v_{ij}^{\alpha\beta}$ is a self-explanatory notation for the various interaction energies involved. For a lattice gas model with magnetic moments interacting through phenomenological exchange interactions J_{ij}^{AA}, J_{ij}^{BB}, and J_{ij}^{AB}, in an all moments lined up state $S_{ij}^{(2)} = V_{ij} + J_{ij}^{AA} + J_{ij}^{BB} - 2J_{ij}^{AB}$. Thus, $S_{ij}^{c,c}$ can be interpreted as an effective pairwise ordering energy enhanced by the presence of rigid moments. Evidently, γ_{ij}^α measures the effect of the chemical environment on an α moment at i, and, hence, quintessentially a nonrigid moment, itinerant effect. It is an interesting quantity because it can be measured in spin-polarized neutron diffraction experiment.[12,13]

Our second comment concerns the fact that Ω is conventionally split into two parts: the single particle contribution Ω_{sp} and the so-called double-counting correction.[10] When taking the derivatives of the latter, as required by Eq. (3), we have taken into account the local changes in the magnetic moments only and neglected the charge fluctuations with environements.

III. ORDERING IN $\text{Ni}_c\text{Fe}_{1-c}$ ALLOYS

In Fig. 1 we show $S^{(2)}(\mathbf{k})$ for Ni_3Fe in the (100) and (110) directions. Evidently, it rises as $\mathbf{k}$ varies from $\mathbf{k} = 0$ to the zone boundary. Thus the theory predicts ordering. Unfortunately, our calculations do not predict absolute maxima at the (100) and (110) point which correspond to the ex-

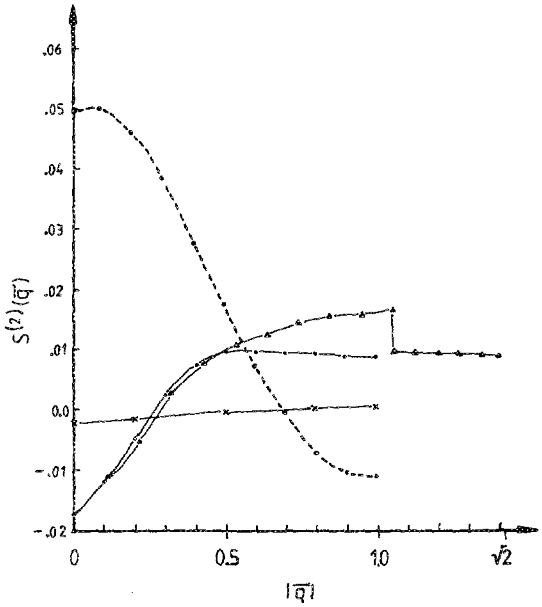

FIG. 1. $S^{(2)}(\mathbf{k})$ (in dimensionless units) vs $\mathbf{k}$ is shown from the Γ to X points. The solid line with circles [triangles] is the ferromagnetic results for (100) [(110)] direction. The dashed line is the Stoner paramagnetic results. 0.05 dimensionless units is approximately 2000 K.

perimentally observed L_{12} structure.[14] In fact, our accuracy is insufficient to distinguish between the highlights of the various peaks near the zone boundary. As expected in a relatively good moment alloy like Ni_3Fe the nonrigid-moment effect is fairly innocuous.

To examine the effect of magnetism we have repeated the whole calculation treating the alloy as a Stoner paramagnet, that is to say, we implemented the non-spin-polarized theory in Ref. 10. The results are presented in Fig. 1 with the dashed line. Evidently, this peaks at $\mathbf{k} = 0$ and therefore corresponds to a clustering tendency. That is to say, the paramagnetic calculation predicts a phase separation. This implies that the ordering tendency is entirely of magnetic origin.

It should be stressed that the above result does not necessarily mean that above T_C the diffuse scattering intensity[14] should correspond to clustering. Within the present framework, above T_C the system should be in a disordered local moment (DLM) state[11] which is not the same as the Stoner paramagnetic state studied above. To study the DLM state we must relax the "all moments lined up" restriction of the present theory. We shall return to the study of this interesting version elsewhere. Indeed, this appears to be a necessary consideration even below the Curie temperature for FeNi.

IV. WHAT DRIVES THE ORDERING PROCESS?

To understand the above phenomenon of clustering in the paramagnetic state but ordering in the ferromagnetic state, we recall some general features of the electronic forces responsible for order and disorder in metallic alloys. In transition metal alloys where the *d* band is roughly half-filled, ordering is expected. This is because under such circumstances only bonding states are filled and the bonding states of the ordered state are lower than those of the disordered state due to level repulsion. On the other hand, almost completely empty or almost completely filled bands can be expected to lead to clustering. A most modern discussion of these rules have been given recently by Heine and Samson.[15]

As can be seen by the inspecting Fig. 2(a) the averaged *d* band is almost completely filled in the Stoner paramagnetic state. Accordingly, clustering is expected in agreement with the prediction of our calculation of the direct correlation function $S^{(2)}(\mathbf{k})$.

When the bands are exchange split the majority band is completely filled. Such filled bands are fairly neutral with respect to compositional order. They are particularly ineffective in the present case because as was discovered by Johnson *et al.*[9] the majority spin states have very long lifetimes, indicating that the corresponding electorns "see" roughly the same potentials on the Ni sites as on the Fe sites. Indeed we find that the majority spin electrons contribute only a few percent to $S^{(2)}(\mathbf{k})$.

Thus the state of compositional order is determined by the minority spin electrons. Since the majority band became completely filled on exchange splitting the filling of the minority bands has been reduced making them more nearly half filled. This can be seen in Fig. 2(b). Apparently, this shift brought ϵ_F sufficiently close to the half-filled mark to make the alloy ordering. Sampson and Heine[15] find that the upper limit of ordering is $n_d = 3.4$ electrons per spin. We find that in the paramagnetic state $n_d = 3.7$ and in the ferromagnetic state $n_d = 3.25$. Evidently this supports the above interpretation of our $S^{(2)}(\mathbf{k})$ calculation.

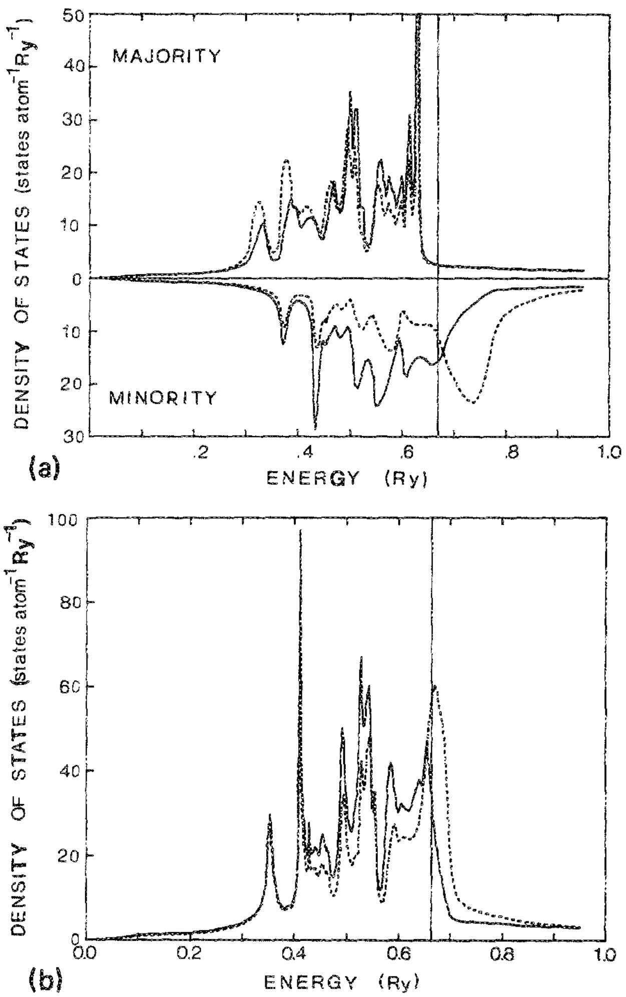

FIG. 2. Partially averaged *d*-electron density of state (without concentration factors) are shown for (a) ferromagnetic and (b) Stoner paramagnetic $Ni_{0.75}Fe_{0.25}$. The solid (dashed) line is the nickel (iron) contribution. The solid vertical line is the Fermi energy and the energy zeros are with respect to the majority muffin-tin zeros.

Interestingly, the high-temperature thermochemical data[19] also implies phase separation at low temperatures. So far this is the only experimental support for the above mechanism driving the compositional order. Evidently, further experimental confirmation will be needed before the suggestion that the compositional order is of magnetic origin can be said to be established.

Finally, we note that having calculated γ_{ij}^{α} we can study both the moments μ^{α} and average moment $\bar{\mu}$ as a function of environment using the relation $\delta\mu^{\alpha} = \bar{\mu}^{\alpha} + \Sigma_j \gamma_{ij}^{\alpha} \delta c_j$. For instance, with an environment consistent with ordered Ni_3Fe alloy, we find that the average moment increases by $\delta\bar{\mu} = 0.5\mu_B$ compared with the average moment in the disordered state $\bar{\mu} = 1.00\mu_B$. This result is in good agreement with the 5% increase in the magnetization found experimentally.

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