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Coherent-Potential Approximation for Disordered Ferromagnetic Binary Alloys

E-Ni Foo
Department of Physics, Drexel University, Philadelphia, Pennsylvania 19104

and

Der-Hsueh Wu*†
Department of Physics, Temple University, Philadelphia, Pennsylvania 19122

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The magnetic properties of spin-$\frac{1}{2}$ Heisenberg ferromagnetic alloys are calculated. We calculate the spin-wave Green's function in the random-phase approximation and treat the disordered composition-dependent exchange interaction in a coherent-potential approximation (CPA). In the weak-scattering limit, the CPA reproduces the result of the mean-field theory as expected, and in the strong-scattering limit, the CPA predicts such properties as critical concentration, which is beyond the scope of the mean-field theory.

The properties of alloys are presently the focus of attention in solid-state physics. The spin-wave spectrum in a ferromagnetic alloy is the most convenient for experimental study and is worth special attention. However, theoretical studies of ferromagnetic alloys are still limited to either the dilute case[1] or the weak-perturbation limit.[2] This paper considers the case of arbitrary concentration and of strong coupling.

The theory of alloys in one type of physical system has a close formal relationship with theories for other types of systems. In recent years, the theory of the electronic density of states has been advanced a great deal by the coherent-potential approximation (CPA).[3,4] The CPA serves as an interpolating scheme over a whole range of concentrations and coupling strengths. It has been modified and extended from the original single-site approximation by including the effects of clustering[5] and of random off-diagonal potentials.[6] In this paper we apply the modified CPA to calculate the magnetic properties of a ferromagnetic alloy in which the composition-dependent exchange interactions are randomly distributed.

We consider a spin-$\frac{1}{2}$ Heisenberg ferromagnet in zero magnetic field. In the random-phase approximation, the equation of motion for the Green's function $G(\omega/\sigma)$ becomes[2]

$$2\pi\sum_{j}\left[\left(\frac{\omega}{\sigma}-\frac{1}{2}\sum_{j'}J(i,j')\right)\delta_{ij}+\tfrac{1}{2}J(i,j)\right]G_{il}\left(\frac{\omega}{\sigma}\right)=\delta_{il}\,, \tag{1}$$

where the magnetization σ is determined self-consistently from[7]

$$\tfrac{1}{2}(1-\sigma)=\int_{-\infty}^{\infty}d\omega\,N^{-1}\mathrm{Tr}\,\mathrm{Im}\,G(\omega/\sigma)\,(e^{\beta\omega}-1)^{-1}. \tag{2}$$

For an $A_{1-x}B_x$ alloy, in which x represents the concentration of B atoms, the composition-dependent $J(i,j)$ is equal to J_{AA}, J_{BB}, or J_{AB} when the pair sites i and j are occupied by two A atoms, two B atoms, or one A atom and one B atom, respectively.

In the spirit of the CPA, we consider a single exchange interaction $J(i,j)$ immersed in an effective medium of which the Hamiltonian, with a coherent exchange interaction J_c, is assumed to retain the same functional form as that of a pure crystal. Then J_c is determined by requiring the net scattering from a single scatterer $J(i,j)$ to vanish on the average. Then the criterion for determining J_c becomes[6]

$$\langle\underline{\mathrm{T}}(i,j)\rangle\equiv(1-x)^2\,\underline{\mathrm{T}}_{AA}+2x(1-x)\,\underline{\mathrm{T}}_{AB}+x^2\,\underline{\mathrm{T}}_{BB}, \tag{3}$$

where $\underline{\mathrm{T}}_{AA}$, $\underline{\mathrm{T}}_{BB}$, and $\underline{\mathrm{T}}_{AB}$ denote the t matrices when $J(i,j)$ is equal to J_{AA}, J_{BB}, and J_{AB}, respectively. The matrix elements of $\underline{\mathrm{T}}(i,j)$ are

$$T_{ii}(i,j)=-T_{ij}(i,j)=\tfrac{1}{2}[J(i,j)-J_c]\times\{1-[J(i,j)-J_c](G_0-G_1)\}^{-1}, \tag{4}$$

where G_0 and G_1 are the ii and ij components of the coherent Green's function G_c. For a simple cubic lattice, they are

$$G_0=\textstyle\sum_k[E-3J_c+J_c(\cos k_xa+\cos k_ya+\cos k_za)]^{-1} \tag{5}$$

and

$$G_1=(1/3J_c)\,[1+(3J_c-E)G_0], \tag{6}$$

where $E=(\omega/\sigma)$ and G_0 can be computed numerically by the method derived by Wolfram and Callaway.[8] The spin-wave density of states can then be obtained from

$$\rho(E)=(-1/\pi)\mathrm{Im}\,G_0. \tag{7}$$

The lowest-order correction to G_0 is of fourth order in the t matrix, provided that the correlation between $J(i,j)$ and $J(j,k)$ can be neglected. However, the validity of CPA can be examined by evaluating some correlated terms in the perturbation series.[4] The class of terms that appears to yield the largest correction to G_0 is that involving multiple scattering between a nearest-neighbor pair of J's. Because of the exponential damping of $G_{ll'}$, the overwhelming contribution usually comes from the smallest lattice vector. Hence it is reasonable to keep only those terms involving the first two lattice vectors in our calculation. The analytical expression corresponding to the correlated terms can be expressed as

$$\Delta G = -\eta\left(\frac{\partial G_0}{\partial E} - 2\,\frac{\partial G_1}{\partial E}\right)\left((G_0 - 2G_1)\left\langle\frac{T^2}{1 - T^2(G_0 - 2G_1)^2}\right\rangle + (G_0 - 2G_1)^2\left\langle\frac{T^3}{1 - T^2(G_0 - 2G_1)^2}\right\rangle\right), \qquad (8)$$

where η denotes the number of nearest-neighbor pairs of J's associated with site j.

The Curie temperature T_C, which is defined as the temperature at which the magnetization vanishes, can be determined from Eq. (2). It is well known that T_C is proportional to J. Here T_C is proportional to $J_c(0)$, which is the value of J_c evaluated at $E = 0$. One can obtain $J_c(0)$ very easily by solving Eq. (3) at $E = 0$, such as

$$\begin{aligned}\alpha^2 J_c^3 &+ [\alpha(J_{AA} + J_{BB} + J_{AB}) - \alpha(1+\alpha)\langle J\rangle]\, J_c^2 \\ &+ [(1+\alpha) J_{AA} J_{BB} J_{AB} \langle 1/J\rangle \\ &- \alpha(J_{AA}J_{BB} + J_{AB}J_{AA} + J_{AB}J_{BB})]\, J_c \\ &- J_{AA}J_{BB}J_{AB} = 0, \qquad (9)\end{aligned}$$

where $\alpha = \frac{1}{2}z - 1$, z is the number of nearest neighbors, and $\langle\rangle$ denotes a composition average similar to that in Eq. (3).

In Fig. 1, we plot the $\rho(E)$ for an alloy with $J_{AA} = 1$, $J_{BB} = 2$, and $J_{AB} = 1.5$, and x varying from 0 to 1. The general features of $\rho(E)$ can be summed up as follows: (i) The bandwidth is wider than that of mean-field theory ($J = \langle J\rangle$); (ii) there is an increase of $\rho(E)$ in the lower-energy side and a decrease in the higher-energy side. This result is in general agreement with the result of Montgomery *et al.* for amorphous ferromagnets.[2] The correction term ΔG is calculated for the case of $x = 0.5$. The density of states $\rho(E)$, including the correction, is described by the dashed curve in Fig. 1. Here $\rho(E)$ is further enhanced in the lower-energy side and depressed in the higher-energy side by ΔG. Near $E = 0$, however, $\rho(E)$ is slightly depressed. The maximum deviation (ΔG) is about 7%, which occurs near the Von Hove singularities. The shift in T_C is positive and less than 3%.

In Fig. 2, we plot T_C as a function of x. We choose $J_{AA} = 1$, $J_{BB} = 2$, and allow J_{AB} to vary from 0.05 to 2.5. T_C in CPA (solid curves) is compared with T_C in mean-field theory (dashed curves). We find that T_C in the CPA is always lower than that of mean-field theory.

Next we consider an alloy of which the B atom (with spin $\frac{1}{2}$) has zero or very small exchange interaction, such that $J_{AA} = 1$ and $J_{BB} = J_{AB} = 0$. From Eq. (9) we obtain

$$\begin{aligned} J_c(0) &= [z(1-x)^2 - 2]/(z-2) && \text{for } 1 - x > \sqrt{2}/z \\ &= 0 && \text{for } 1 - x < \sqrt{2}/z\,, \qquad (10)\end{aligned}$$

which is shown in Fig. 2. The critical concentration c is defined as the minimum concentration of magnetic atom A, $1 - x$, above which ferromagnetism will occur. In other words, c is the magnetic concentration at which $T_C = 0$, or is no longer well defined. From Eq. (10) we conclude $c = \sqrt{2}/z$. The physical meaning of our result can be interpreted as follows: The concentration of J_{AA} which produces ferromagnetism is equal to $(1-x)^2$. In order to allow each magnetic atom to contribute effectively to the formation of spin waves, we need at least

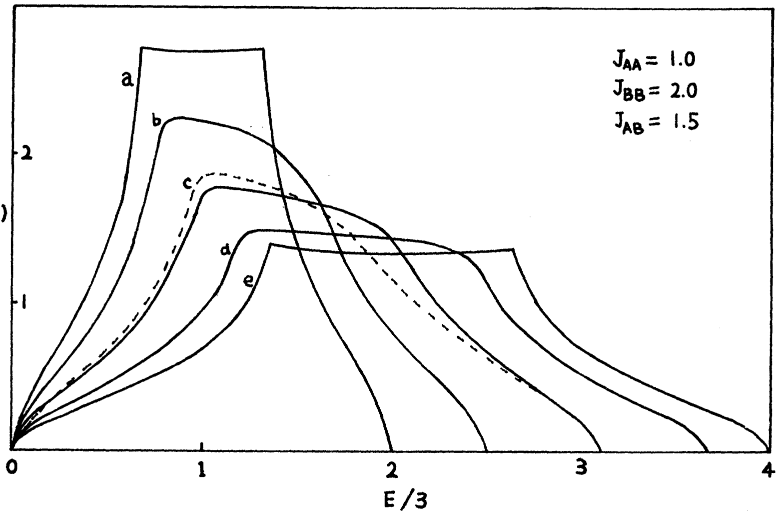

FIG. 1. Spin-wave density of states for a ferromagnetic alloy $A_{1-x}B_x$ with $J_{AA} = 1$, $J_{BB} = 2$, and $J_{AB} = 1.5$. Curves: (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.5$, (d) $x = 0.8$, and (e) $x = 1$. The dashed curve represents the density of states with contributions for correlated terms for the case of $x = 0.5$.

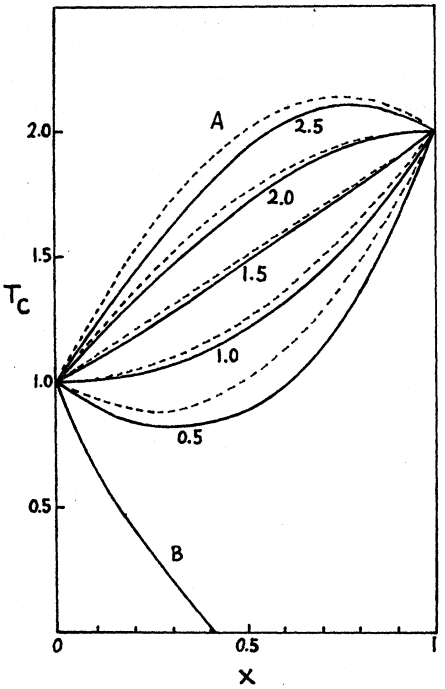

FIG. 2. Curie temperature T_C for alloy $A_{1-x}B_x$ as function of x. (a) Curves A for $J_{AA}=1$, $J_{BB}=2$, and J_{AB} vary from 0.5 to 2.5. Solid curves indicate T_C in CPA, and dashed curves represent T_C in mean-field theory. (b) Curve B for $J_{AA}=1$ and $J_{AB}=J_{BB}=0$. Here the units of T_C are normalized for pure-A lattice.

two J_{AA} (out of z nearest neighbors) to bridge this magnetic atom to its neighbors. From this simple argument, the critical concentration is determined by $c^2=2/z$, which agrees with the CPA result. For a simple cubic crystal, $c=0.58$. In Ref. 9 the authors considered a different type of ferromagnetic alloy in which the nonmagnetic atom has no spin and found that T_C is linear in x and $c=0.3$.

Our model calculation can be applied to the class of ferromagnets with face-center-cubic lattices, of which only one exchange integral (J_1 or J_2) is dominant. The exchange integral J depends not only on metallic elements through direct exchanges, but also on nonmetallic elements through superexchanges. Thus there are two types of alloys, of which the first type is to alloy the metallic element such as $Ni_{1-x}Co_xO$ (antiferromagnetic), and the second type is to alloy the nonmetallic element such as $GdN_{1-x}O_x$. For the case $J_1 \gg J_2$, the correlation between neighboring J's is stronger in the first type than in the second type. For example, the neighboring J's which are 180° opposite each other are correlated in the first type, but not in the second type. For the case of $J_2 \gg J_1$, such as NiO,[10] one can treat it as if it consists of two noninteracting simple cubic lattices. The nonmetallic element O is located between the two metallic elements Ni. In this kind of arrangement, each J_2 depends solely on a single nonmetallic element. There is no correlation between J's in the second type of alloy in which J_2 is dominant, such as $NiO_{1-x}S_x$. Unfortunately, there is no such experimental result available at present. Thus we compare our model calculation to a less ideal case of $GdN_{1-x}O_x$, in which J_1 is dominant.

Gambino *et al.*[11] measured the magnetic moment of $GdN_{1-x}O_x$. GdN is shown to be ferromagnetic, but small amounts of oxygen (with $x=0.05$) cause paramagnetism and short-range antiferromagnetic order to set in. They found that the J for GdN is 0.55 °K and for GdO is estimated to be − 0.80 °K. In order to compare our theory with their experimental results,[12] we set $J_{NN}=1$, $J_{OO}=-1.45$, and vary J_{NO}, such that the ferromagnetic state no longer exists beyond $x=0.05$. J_{NO} is determined to be 0.22. This effect can be attributed to unusually strong scattering caused by the impurity exchange interaction with opposite sign, which produces a singularity in the t matrix and prevents propagation of spin waves. The T_C, including contributions from correlated terms, is described by the dashed curves in Fig. 3. The correction is

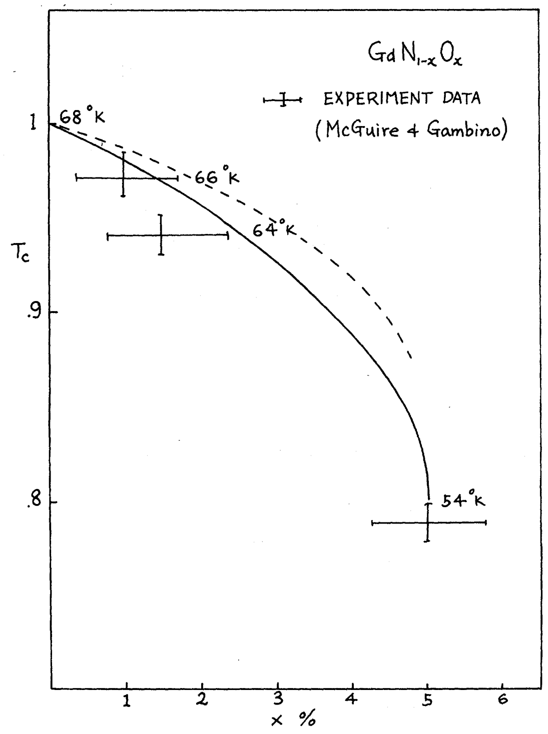

FIG. 3. Curie temperature T_C for $G_dN_{1-x}O_x$. Here $J_{NN}=1$, $J_{OO}=-1.45$, and $J_{NO}=0.22$ is described by the solid curve. The crosses represent experimental data of McGuire and Gambino. The dashed curve represents T_C including contributions from correlated terms.

about 3%. We therefore can conclude that the CPA is a reasonably good approximation even if scattering potentials are correlated.

In this paper, we have presented a simple formalism for a modified CPA which takes into account effects of off-diagonal randomness self-consistently. Our formalism is perhaps most suitable for treating disorder in Heisenberg ferromagnetic alloys. In the weak-scattering limit, the CPA reproduces the result of the mean-field theory as expected. In the strong-coupling limit, the CPA goes beyond the mean-field theory in that it predicts such properties as critical concentration, which has so far been beyond the scope of the mean-field theory. The contribution from correlated terms is estimated to be only a few percent corrections.

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[1] D. Hone, H. Callen, and L. R. Walker, Phys. Rev. 144, 283 (1966).

[2] C. G. Montgommery, J. I. Krugler, and R. M. Stubbs, Phys. Rev. Letters 25, 669 (1970).

[3] P. Soven, Phys. Rev. 156, 809 (1967).

[4] P. Soven, Phys. Rev. 178, 1136 (1969).

[5] K. F. Freed and M. H. Cohen, Phys. Rev. B 3, 3400 (1971).

[6] E. Foo, H. Amar, and M. Ausloos, Bull. Am. Phys. Soc. 15, 774 (1970); Phys. Rev. B 4, 3350 (1971).

[7] D. N. Zubarev, Usp. Fiz. Nauk 71, 71 (1960) [Sov. Phys. Usp. 3, 320 (1960)].

[8] T. Wolfram and J. Callaway, Phys. Rev. 130, 2207 (1963).

[9] T. Kaneyoshi, Progr. Theoret. Phys. (Kyoto) 42, 477 (1969).

[10] M. T. Hutchings and E. J. Samuelsen (unpublished).

[11] R. J. Gambino, T. R. McGuire, H. A. Alperin, and S. J. Pickart, J. Appl. Phys. 41, 933 (1970).

[12] T. R. McGuire and R. J. Gambino (private communication).

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Magnetic Properties of Disordered Transition-Metal Alloys*

R. Harris and M. J. Zuckermann

Eaton Electronics Research Laboratory, McGill University, P.O. Box 6070, Montreal 101, Canada

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A theory of spin fluctuations is presented for transition-metal alloys of arbitrary concentration using an analog of the coherent-potential approximation of Soven. The model is used to analyze experimental data for the spin susceptibility of paramagnetic Pd-Ni alloys, and it is also possible to calculate the Curie temperatures of ferromagnetic Pd-Ni alloys.

I. INTRODUCTION

There have recently been a number of experiments which have measured the bulk susceptibility, the electronic specific heat, the electrical resistivity, and other properties of nearly magnetic transition-metal alloys.[1] All these quantities show dramatic behavior as the concentration of the alloys is varied. For example, the bulk susceptibility of Pd-Ni[2-4] exhibits a sharp increase as the concentration of Ni is increased, and the alloy becomes ferromagnetic when this concentration reaches about 2.2 at.%.

The theory of localized spin fluctuations has been extremely successful in describing such alloys: It has been treated in detail by Lederer and Mills,[5] and by Englesberg, Brinkman, and Doniach.[6] However, the validity of this theory is restricted to dilute alloys—so that it concerns itself only with the initial behavior of experimental quantities, for example, in Pd-Ni, the initial slope of the susceptibility as a function of Ni concentration.

There is here a strong analogy with the now well-understood theory of dilute nonmagnetic alloys, which is also limited to the description of initial behavior. In this case, however, a successful technique has been developed to extend the theory to higher concentrations of impurities and, in principle, to substitutional alloys of arbitrary composition. This technique is the coherent-potential approximation (CPA) of Soven,[7] which has been discussed by a number of authors,[8] and which recently has been used to describe disordered Cu-Ni alloys.[9]

In the present paper, an analog of the CPA is used to develop a new approach to spin fluctuations