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.

We would like to thank Professor R. A. Tahir-Kheli for his interest in this work and for discussions. We would also like to thank Professor T. K. Lim for reading this manuscript.

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*Work is part of a dissertation submitted to Temple University in partial fulfillment of the requirements of the Ph.D. degree.

†Work supported by the U. S. Office of Naval Research.

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PHYSICAL REVIEW B VOLUME 5, NUMBER 1 1 JANUARY 1972

Magnetic Properties of Disordered Transition-Metal Alloys*

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(Received 23 June 1971)

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 in nondilute transition-metal alloys. The formalism of the method is presented in Sec. II, and a detailed comparison with the susceptibility of paramagnetic Pd-Ni and the Curie temperature of ferromagnetic Pd-Ni is given in Sec. III. The final section discusses the limitations of the theory and ways in which it might be improved.

II. SPIN FLUCTUATIONS IN DISORDERED TRANSITION-METALS ALLOYS

A. Dynamic Susceptibility

The alloys under consideration are binary alloys AB in which both components are transition metals. The electronic structure is described by a single conduction band, and their magnetic character is described by a Hamiltonian due to Hubbard[10]:

$$H=\sum_{ij\sigma} T_{ij}\, c^\dagger_{i\sigma} c_{j\sigma} + \sum_{i\subset A} I_A n_{i\uparrow} n_{i\downarrow} + \sum_{i\subset B} n_{i\uparrow} n_{i\downarrow}\ , \quad n_{i\sigma}=c^\dagger_{i\sigma} c_{i\sigma}\ . \tag{2.1}$$

$c^\dagger_{i\sigma}$ and $c_{i\sigma}$ are creation and anihilation operators for the conduction electrons in Wannier representation; σ is a spin index, and i labels a lattice site. I_A and I_B are the intra-atomic exchange constants for atoms A and B, respectively. All interatomic exchange effects are neglected and the restricted sums on the right-hand side of (2.1) run over lattice sites A and B, respectively.[10]

The spin excitations of the alloy are described by the dynamic spin susceptibility $\chi_{AB}(q, q', \omega)$, which is temperature dependent. For the particular case of an alloy composed of only one A atom in an otherwise pure B matrix, and for which $I_B=0$, Lederer and Mills[5] have shown that $\chi_{AB}(q, q', \omega)$ in the random-phase approximation (RPA) is

$$\chi_{AB}(q, q', \omega)=\chi^0_B(q, \omega)\delta_{qq'} + \frac{\chi^0_B(q, \omega) I_A \chi^0(q', \omega)}{1 - I_A \chi^{\text{loc}}_B(\omega)}\ , \tag{2.2a}$$

where

$$\chi^{\text{loc}}_B(\omega)=\sum\nolimits_q \chi^0_B(q, \omega)\ . \tag{2.2b}$$

The alloy is in a paramagnetic state. $\chi^0_B(q, \omega)$ is the noninteracting dynamic susceptibility of the pure B matrix, and q, q', and ω are the momentum and frequency coordinates of the spin excitations which no longer possess translational invariance. Equation (2.2) shows that a single A atom scatters the spin excitations of the B matrix from state $|q, \omega\rangle$ to state $|q', \omega\rangle$; this multiple scattering is described by a t matrix

$$T_A(\omega)=\frac{I_A}{1 - I_A \chi^{\text{loc}}_B(\omega)}\ , \tag{2.3}$$

whose poles correspond, in the absence of a local magnetic moment, to localized spin fluctuations on the A atom.[5]

For a concentrated AB alloy described by the Hamiltonian of (2.1) the assumption of an average band structure reintroduces translational invariance and leads to a noninteracting susceptibility $\chi_{\text{alloy}}(q, \omega)$. In the average crystal the interaction between the electrons is approximated by an average exchange constant $I_{\text{eff}}(\omega)$ which has to be evaluated as a function of alloy composition. $I_{\text{eff}}(\omega)$ is a function of frequency and has an imaginary part for $\omega \neq 0$. The dynamic susceptibility $\chi_{\text{eff}}(q, \omega)$ of the concentrated alloy in the RPA is then given by

$$\chi_{\text{eff}}(q, \omega)=\frac{\chi_{\text{alloy}}(q, \omega)}{1 - I_{\text{eff}}(\omega)\chi_{\text{alloy}}(q, \omega)}\ . \tag{2.4}$$

The excess exchange scattering on each lattice site is thus $I_\alpha - I_{\text{eff}}(\omega)$, where $\alpha = A$ or B, and from (2.3) the t matrix for such excess scattering is

$$T_\alpha(\omega)=\frac{I_\alpha - I_{\text{eff}}(\omega)}{1 - \chi^{\text{loc}}_{\text{eff}}(\omega)[I_\alpha - I_{\text{eff}}(\omega)]}\ . \tag{2.5}$$

$\chi^{\text{loc}}_{\text{eff}}(\omega)$ is the average over all lattice sites of the local spin susceptibility, and is given by

$$\chi^{\text{loc}}_{\text{eff}}(\omega)=\sum\nolimits_q \chi_{\text{eff}}(q, \omega)\ . \tag{2.6}$$

A direct analogy with the coherent potential approximation of Soven[7] suggests that $I_{\text{eff}}(\omega)$ should be determined by equating to zero the average over all lattice sites of the *excess* exchange scattering. In terms of the t matrices of (2.5) this becomes

$$n_A T_A(\omega) + n_B T_B(\omega)=0\ , \tag{2.7}$$

where n_A and n_B are the concentrations of A and B atoms, respectively. From (2.5) and (2.7) the self-consistent equation for $I_{\text{eff}}(\omega)$ becomes

$$I_{\text{eff}}(\omega)=n_A I_A + n_B I_B - [I_A - I_{\text{eff}}(\omega)] \times \chi^{\text{loc}}_{\text{eff}}(\omega)[I_B - I_{\text{eff}}(\omega)]\ , \tag{2.8}$$

and this equation, together with (2.6) and (2.4), provides a description of the spin dynamics of a transition-metal alloy in the paramagnetic state.

In the limit of a dilute alloy of A in B ($n_A \ll 1$), Eq. (2.8) for $I_{\text{eff}}(\omega)$ can be written in the explicit form

$$I_{\text{eff}}(\omega)=I_B + \frac{n_A(I_A - I_B)}{1 - (I_A - I_B)\chi^{\text{loc}}_B(\omega)}\ , \tag{2.9}$$

where $\chi^{\text{loc}}_B(\omega)$, defined in (2.2), depends only on I_B. Equations (2.4) and (2.9) are then identical with the result of Englesberg, Brinkman, and Doniach[6] (EBD) for the susceptibility of a dilute binary alloy.

The actual local susceptibilities on A or B sites will, of course, differ from the average value $\chi^{\text{loc}}_{\text{eff}}(\omega)$. By analogy with the CPA expressions for the local density of electron states,[7] the actual values may be written as

$$\chi_\alpha'^{\mathrm{loc}}(\omega)=\frac{\chi_{\mathrm{eff}}^{\mathrm{loc}}(\omega)}{1-[I_\alpha-I_{\mathrm{eff}}(\omega)]\chi_{\mathrm{eff}}^{\mathrm{loc}}(\omega)}\,, \tag{2.10}$$

and this expression describes the localized spin fluctuations on A and B sites in the disordered alloy.

The bulk spin susceptibility of the alloy is given by the limit of $\chi_{\mathrm{eff}}(q,\omega)$ as q and ω tend to zero, so that, from (2.4),

$$\chi^{\mathrm{bulk}}=\frac{\chi_{\mathrm{alloy}}(0,0)}{1-I_{\mathrm{eff}}(0)\chi_{\mathrm{alloy}}(0,0)}\,. \tag{2.11a}$$

$\chi_{\mathrm{alloy}}(0,0)$ is the static bulk spin susceptibility of the alloy in the absence of interactions.

At zero temperature $\chi_{\mathrm{alloy}}(0,0)$ is equal to Γ_{av}, the average density of free-electron states at the Fermi level. Thus, at $T=0$, the expression for the bulk susceptibility becomes

$$(\chi^{\mathrm{bulk}})_{T=0}=\frac{\Gamma_{\mathrm{av}}}{1-[I_{\mathrm{eff}}(0)]_{T=0}\Gamma_{\mathrm{av}}}\,. \tag{2.11b}$$

For isoelectronic alloys such as Pd-Ni Γ_{av} may be assumed to be independent of concentration, but for other alloys it is necessary to include band-structure effects explicitly.[11] For some discussion of this point, see both Secs. III and IV.

B. Critical Concentration: Curie Temperature

A particular class of alloys to which the present model is appropriate corresponds to $\Gamma_{\mathrm{av}}I_B<1$ and $\Gamma_{\mathrm{av}}I_A>1$, so that within the RPA, metal B is an enhanced paramagnet and metal A a Stoner ferromagnet.[12] Such alloys exhibit a paramagnetic-ferromagnetic phase transition at a concentration $n_A=n_{\mathrm{crit}}$. Since the static limit of the bulk spin susceptibility becomes infinite at the ferromagnetic phase boundary, the implicit equation for n_{crit} is, from (2.11b),

$$1=\Gamma_{\mathrm{av}}[I_{\mathrm{eff}}(0)]_{T=0}\,. \tag{2.12}$$

At concentrations $n_A>n_{\mathrm{crit}}$ the alloy will exist in a ferromagnetic state at temperatures less than a Curie temperature T_c which depends on concentration. T_c is the temperature at which χ^{bulk} of (2.11a) becomes infinite, so that

$$1=[\chi_{\mathrm{alloy}}(0,0)I_{\mathrm{eff}}(0)]_{T=T_c}\,. \tag{2.13}$$

$\chi_{\mathrm{alloy}}(0,0)$ may be expanded to second order in kT_c/ϵ_F, where ϵ_F is the Fermi energy, and since $kT_c\ll\epsilon_F$, this expression may be rewritten as

$$\frac{T_c}{T_c^A}=\left(\frac{\Gamma_{\mathrm{av}}[I_{\mathrm{eff}}(0)]_{T=T_c}-1}{\Gamma_{\mathrm{av}}I_A-1}\right)^{1/2}\,. \tag{2.14}$$

T_c^A is the Curie temperature of the pure A metal.

$[I_{\mathrm{eff}}(0)]_{T=T_c}$ may be determined from (2.8) if the temperature-dependent local susceptibility is expanded as

$$\chi_{\mathrm{eff}}^{\mathrm{loc}}(0)_{T=T_c}\approx\Gamma_{\mathrm{av}}[C-D(kT_c/\epsilon_F)^2]\,. \tag{2.15}$$

$\Gamma_{\mathrm{av}}C$ is the value of $\chi_{\mathrm{eff}}^{\mathrm{loc}}(0)$ at zero temperature and at the critical concentration n_{crit}: It may therefore be determined from the bulk susceptibility in the manner described in Sec. III. D is a parameter which depends only on the band structure of the alloy: Its value may be explicitly derived in an approximation which treats the conduction band as free-electron-like, but, in general, it may be used as a fitting parameter. The Fermi energy ϵ_F is assumed not to change with alloy composition: It is determined from the value of T_c^A.

From Eqs. (2.14) and (2.15) the expression for T_c becomes

$$\begin{aligned}(T_c/T_c^A)^2=(\{[1-\Gamma_{\mathrm{av}}C(I_A-I_B)]^2+4n_A\Gamma_{\mathrm{av}}C(I_A-I_B)\}^{1/2}\\ -1+\Gamma_{\mathrm{av}}C(I_A-I_B)+2C)/[(1+\phi)2C]\,,\end{aligned} \tag{2.16a}$$

where ϕ is given by

$$\phi=\frac{D}{8\pi^2C^2}\times\left(1-\frac{|1-\Gamma_{\mathrm{av}}C(I_A-I_B)(1-2n_A)|}{\{[1-\Gamma_{\mathrm{av}}C(I_A-I_B)]^2+4n_A\Gamma_{\mathrm{av}}C(I_A-I_B)\}^{1/2}}\right)\,. \tag{2.16b}$$

III. COMPARISON WITH EXPERIMENT

The theory developed in Sec. II is now used to analyze the experimental data for Pd-Ni.

Pd-Ni is paramagnetic for Ni concentrations less than about 2.2 at.% and is ferromagnetic for Ni concentrations greater than this. The two metals are isoelectronic and happen to have densities of states at the Fermi level of almost the same value (2.3 states/eV/atom).[13,14] Consequently, in the paramagnetic region, it is a reasonable approximation to assume Γ_{av} [Eq. (2.11b)] to be constant at this same value, provided that the Ni and Pd conduction bands have the same shape and are not displaced relative to one another.

Under these circumstances, the theory of Sec. II A can be applied directly.

The dynamic susceptibility for Pd-Ni to lowest order in Ni concentration is given from (2.4) and (2.9) as

$$\chi_{\mathrm{eff}}(q,\omega)\approx\chi_{\mathrm{Pd}}(q,\omega)\left(\delta_{qq'}+n_{\mathrm{Ni}}\frac{(I_{\mathrm{Ni}}-I_{\mathrm{Pd}})\chi_{\mathrm{Pd}}(q,\omega)}{1-(I_{\mathrm{Ni}}-I_{\mathrm{Pd}})\chi_{\mathrm{Pd}}^{\mathrm{loc}}(\omega)}\right)\,. \tag{3.1}$$

In this approximation, the average local susceptibility is given from (2.2b), (2.6), and (3.1) as

$$\chi_{\mathrm{eff}}^{\mathrm{loc}}(\omega)\approx\chi_{\mathrm{Pd}}^{\mathrm{loc}}(\omega)+n_{\mathrm{Ni}}\frac{(I_{\mathrm{Ni}}-I_{\mathrm{Pd}})\chi_{\mathrm{Pd}}^{(2)}(\omega)}{1-(I_{\mathrm{Ni}}-I_{\mathrm{Pd}})\chi_{\mathrm{Pd}}^{\mathrm{loc}}(\omega)}\,, \tag{3.2}$$

where

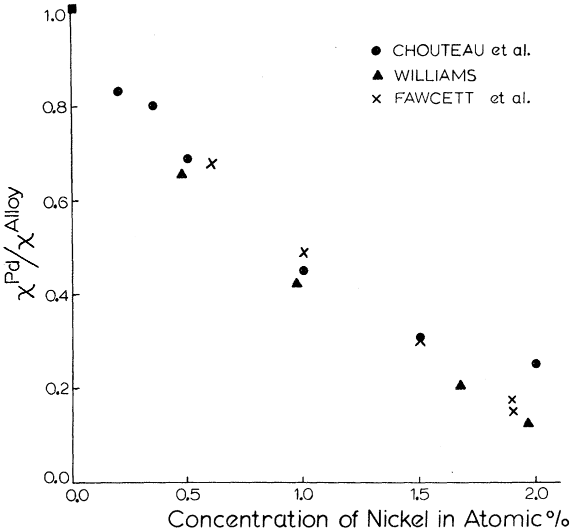

FIG. 1. Susceptibility data for paramagnetic Pd-Ni alloys (Refs. 2–4).

$$\chi_{\mathrm{Pd}}^{(2)} = \sum\nolimits_q \left[\chi_{\mathrm{Pd}}(q, \omega)\right]^2 \ . \tag{3.3}$$

The dynamic susceptibility to a higher order in Ni concentration is obtained by substituting $\chi_{\mathrm{eff}}^{\mathrm{loc}}(\omega)$, given by (3.2), into (2.8) to obtain $I_{\mathrm{eff}}(\omega)$, and then substituting for $I_{\mathrm{eff}}(\omega)$ in (2.4). This approximation is valid for Pd-Ni since the Ni concentration is very small in the paramagnetic regime. The static limit, as expressed by (2.11b), then gives an explicit (but cumbersome) expression for the zero-temperature spin susceptibility.

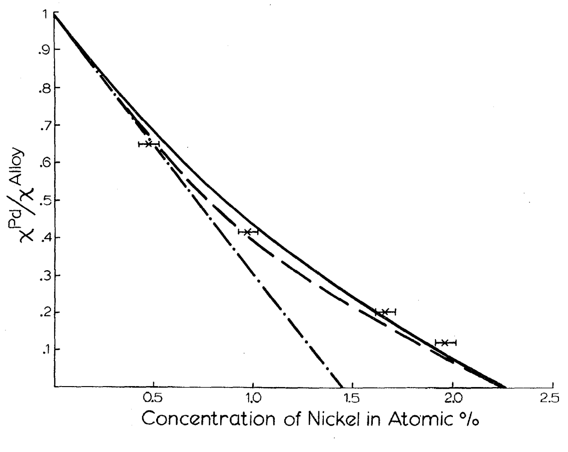

FIG. 2. Theoretical fit to the data of Williams (Ref. 2). Error bars for the concentrations (A. I. Schindler, private communication) are shown. The full curve uses $\Gamma_{\mathrm{av}} I_{\mathrm{Pd}} = 0.88$, $\Gamma_{\mathrm{av}} I_{\mathrm{Ni}} = 1.16$, $C_1 = 3.45$, and $C_2 = 108$; the dashed curve uses $\Gamma_{\mathrm{av}} I_{\mathrm{Pd}} = 0.80$, $\Gamma_{\mathrm{av}} I_{\mathrm{Ni}} = 1.20$, $C_1 = 2.43$, and $C_2 = 102$. Both curves correspond to an initial slope of $\eta = 70$, which is drawn as a dash-dotted line and corresponds to the EBD theory.

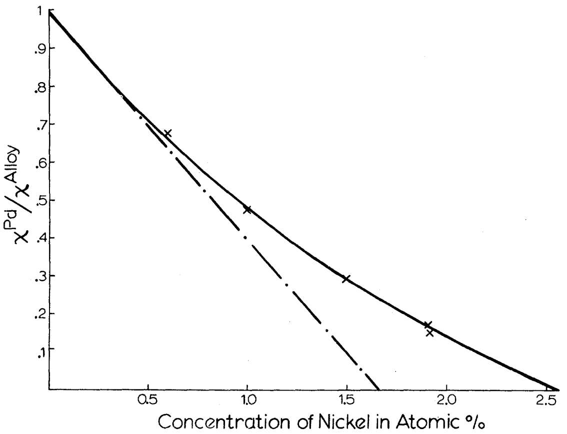

FIG. 3. Theoretical fit to the data of Fawcett *et al.* (Ref. 4), using $\Gamma_{\mathrm{av}} I_{\mathrm{Pd}} = 0.88$, $\Gamma_{\mathrm{av}} I_{\mathrm{Ni}} = 1.16$, $C_1 = 3.43$, and $C_2 = 96$. The initial slope has a value $\eta = 60$.

The following expressions for the critical concentration n_{crit} and the initial slope, η, of the susceptibility as a function of concentration are obtained:

$$n_{\mathrm{crit}} = \frac{(1 - I_{\mathrm{Pd}}\Gamma_{\mathrm{av}})[1 - (I_{\mathrm{Ni}} - I_{\mathrm{Pd}})C_1]}{(I_{\mathrm{Ni}} - I_{\mathrm{Pd}})\Gamma_{\mathrm{av}} + \alpha' C_2 (I_{\mathrm{Ni}}\Gamma_{\mathrm{av}} - 1)(I_{\mathrm{Pd}}\Gamma_{\mathrm{av}} - 1)} \ , \tag{3.4a}$$

$$\eta \equiv \left[\frac{1}{\chi_{\mathrm{Pd}}^{\mathrm{bulk}}} \frac{\partial \chi_{\mathrm{alloy}}^{\mathrm{bulk}}}{\partial n_{\mathrm{Ni}}}\right]_{n_{\mathrm{Ni}} \to 0} = \frac{1 - I_{\mathrm{Pd}}\Gamma_{\mathrm{av}}}{\alpha'} \ , \tag{3.4b}$$

where

$$\alpha' = \Gamma_{\mathrm{av}}(I_{\mathrm{Ni}} - I_{\mathrm{Pd}})/[1 - (I_{\mathrm{Ni}} - I_{\mathrm{Pd}})\Gamma_{\mathrm{av}} C] \ , \tag{3.5a}$$

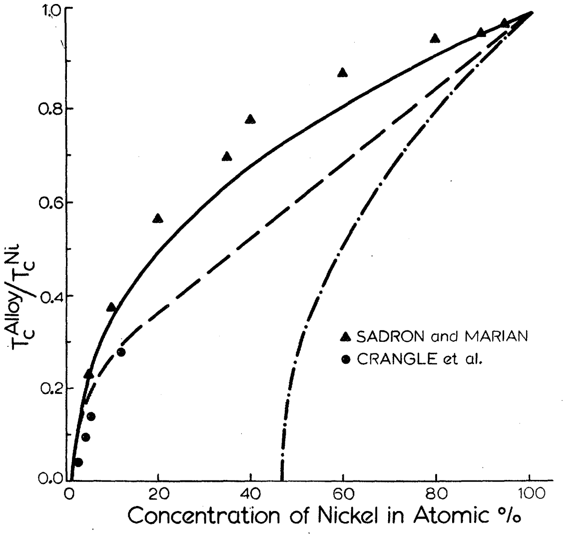

FIG. 4. Curie temperatures of Pd-Ni alloys, showing theoretical fits to the experimental data (Refs. 19 and 20). The full curve has $D = 0.25$, and the dashed curve has $D = 1.50$. The dash-dotted curve is the prediction of the uniform enhancement model (see text).

TABLE I. Exchange constants for Pd and Ni.

Material	$\Gamma_{av}I$	Ref.
Pd	0.8	13, 17
Pd	0.84	16
Pd	0.88	15
Ni	1.16	15
Ni	1.20	18

$$\Gamma_{av}C_1=\sum_q \chi_{Pd}(q, 0)\equiv\chi_{Pd}^{loc}(0)\ , \qquad (3.5b)$$

$$(\Gamma_{av})^2C_2=\sum_q [\chi_{Pd}(q, 0)]^2\equiv\chi_{Pd}^{(2)}\ . \qquad (3.5c)$$

The available data for the bulk spin susceptibility of paramagnetic Pd-Ni are shown in Fig. 1. In order to fit the theory to these data it is necessary to choose values for $\Gamma_{av}I_{Ni}$ and $\Gamma_{av}I_{Pd}$, and then to determine from the data best values for the parameters C_1 and C_2 of (3.5). The values of $\Gamma_{av}I_{Ni}$ and $\Gamma_{av}I_{Pd}$ which have been suggested by other workers[13,15–18] are shown in Table I, and the solid lines in Figs. 2 and 3 use the values of Shimizu.[15] These two figures represent best fits of the theory to the data of Williams and of Fawcett *et al.*, respectively.

In order to indicate the extent to which the theoretical curves depend on the values of the exchange constants, Fig. 2 also shows a dotted curve which is a best fit to Williams's data[2] using $\Gamma_{av}I_{Ni}=1.2$ and $\Gamma_{av}I_{Pd}=0.8$. It is noticeable that the three theoretical curves do not correspond to the same values of the parameters C_1 and C_2 [Eq. (3.5)], and so it is not possible to state unambiguous values for these parameters; however, this is a result of the considerable scatter of the data points.

In both Figs. 2 and 3 the dash-dotted line is the prediction of the EBD theory [(2.4) and (2.9)] fitted to the appropriate values of η from (3.4b) which are 70 and 60, respectively. It is noticeable that neither value is as high as the value of 87 usually quoted in the literature.[1] The critical concentrations corresponding to the two sets of data are also different: 2.3 and 2.5 at.%, respectively. Values of the critical concentration obtained from resistivity and specific-heat measurements are typically 2.2 at.%, favoring the theoretical extrapolation from Williams's data.[2] However, the theory does not include either the effects of clustering or the effects of critical fluctuations, and so it is probable that the critical concentrations are overestimated.

In order to fit the Curie-temperature data,[19,20] it is again convenient to assume that Γ_{av} does not change with alloy concentration. The justification for this assumption is much weaker than that for the paramagnetic alloys—but its use does not strongly affect the theoretical predictions.

The data are displayed in Fig. 4, and the solid line corresponds to a best fit which uses the values of C_1 and C_2 from Williams's data[2] to give a value of the local susceptibility at the critical concentration as 13.2 states/eV/atom. The corresponding value of the parameter D is 0.25, and the sensitivity to the variation of D is indicated by the dashed curve, which corresponds to $D=1.50$. The general agreement of the theory with experiment should be contrasted with the prediction of the simplest "virtual-crystal-like" theory, which sets $I_{eff}(0) = n_{Ni}I_{Ni}+n_{Pd}I_{Pd}$, and yields the dash-dotted curve. Better agreement with experiment might be expected if the theory took better account of changes in the band structure, and if the effect of Ni-Ni interatomic exchange were included.

IV. CONCLUSION

A method for examining the properties of concentrated transition-metal alloys in RPA has been presented above. The method is applicable to isoelectronic alloys and, in particular, explains experimental data for paramagnetic Pd-Ni. Its extension to describe the magnetization and the spin-wave spectrum of the ferromagnetic alloy is under way.

The advantage of the theory is that it can describe the properties of an alloy such as Pd-Ni at all concentrations, but its disadvantage is that it is based on the intra-atomic scattering of spin excitations. Thus it does not include interatomic exchange interactions or clustering effects, although the latter might be included by the use of "pair correction" terms.[7]

It is also difficult to extend the theory directly to alloys for which potential scattering is important. In this case the scattering of spin excitations can no longer be described in terms of a t matrix, since the electron-hole pairs which make up the spin excitations are destroyed by potential scattering. Band-structure effects add further difficulties to the calculation of the dynamic susceptibility, but this problem is also under investigation.

ACKNOWLEDGMENTS

The authors wish to thank the following people for stimulating and useful conversations: R. Bass, W. F. Brinkman, A. Caillé, L. M. Falicov, K. Levin, A. Luther, M. Shimizu, and P. Soven. They are grateful to E. Fawcett, A. Schindler, and G. Williams for helpful discussion of their susceptibility data, and to F. T. Hedgcock, W. B. Muir, and J. O. Ström-Olsen for critical readings of the manuscript.

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[*] Work supported by the N. R. C. of Canada.

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High-Temperature Entropy and Specific Heat of Interacting Electrons in a Solid*

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(Received 23 July 1971)

The virial expansion for a fermion system is employed to derive an expression for the high-temperature entropy of electrons which interact according to the Hubbard Hamiltonian. The results are applied to an itinerant electron ferromagnet at temperatures well above the Curie temperature. In contrast with the results of the Stoner theory, a nonvanishing interaction contribution to the entropy and specific heat is obtained above T_C.

INTRODUCTION

In two previous reports, the virial expansion has been considered for a system of electrons in a solid[1,2] which interact with an effective short-range repulsion (the Hubbard Hamiltonian[3]). The virial-expansion technique is applicable to low-density systems at high temperatures. While these are not the usual conditions which prevail in solid-state problems, it is possible to use this technique to study an itinerant electron ferromagnet, for example, at temperatures higher than the Curie temperature. In some such systems it is possible to satisfy this condition and still have the temperature quite small relative to other characteristic parameters (e.g., bandwidth).

In the usual treatments of itinerant electron ferromagnetism, it is found that the magnetic entropy and specific heat vanish above the Curie temperature.[4] Such results are characteristic of molecular field theories, and are at variance with nature. In contrast, the virial expansion is an exact procedure which will yield nonvanishing results for these quantities. The specific heat of the ferromagnet $\mathrm{Sc_3In}$ ($T_C = 6.7$ °K) has been measured by Isaacs and Knapp.[5] The present theory should be applicable to such a system.

Our previous calculations have yielded exact expressions for the second virial coefficient for a system of electrons interacting according to the Hubbard model. An exact expression has also been obtained for the third virial coefficient, but we are unable to evaluate it completely. The results presented here should be essentially exact in regard to the first-order correction to the results for a noninteracting system, but are only approximate in the next order.

THEORY

Let Z be the grand partition function for the system, which has temperature T. The free energy F and entropy S are given by

$$F = -k_B T \ln Z , \tag{1}$$

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,\mu} \tag{2}$$

(in which V is the volume and μ is the chemical potential of the system). The virial expansion for Z is