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Theory of magnetization and exchange-enhanced susceptibility of Pd-Ni alloys

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A recently developed new formalism is used to calculate the temperature-dependent, exchange-enhanced Pauli susceptibility, $\chi_P(c, T)$, of paramagnetic and weakly ferromagnetic Pd-Ni alloys. For the first time both the strong nonlinear effects of local chemical environment and of moment formation are included in the calculation of $\chi_P(c, T)$. Also, the effects of quantum and thermal spin fluctuations are included for the first time in alloy calculations away from the dilute limit. This is done through the use of a semiphenomenological theory consistent with scaling laws and with the results of renormalization-group theory for the single-impurity problem. In order to compare theory with experiment, we analyzed the theoretical results for $\chi_P(c, T)$ in exactly the same way as the experimental results. Two different calculational methods were used, one corresponding to an expansion in powers of the Ni concentration and the other involving the exact embedding of 55-site clusters in a self-consistently determined effective medium. Both methods yielded results superior to those of all previous theories and in good agreement with experiment.

I. INTRODUCTION

We have recently developed^{1,2} a new comprehensive theory of the saturation magnetization and the zero-temperature, field-dependent magnetic susceptibility of paramagnetic and weakly ferromagnetic substitutionally disordered alloys within the random-phase approximation (RPA). However, the use of the RPA in this theory precludes the treatment of spin-fluctuation effects, yielding a divergence in the local susceptibility for *all* sites at the point at which the local exchange enhancement reaches a critical value on *any* site. This neglect of spin fluctuations leads to an overestimate of the susceptibility at all concentrations for any alloy system. For alloy systems which possess a critical concentration for ferromagnetism, that overestimate is serious near that concentration. Moreover, the temperature dependence of the susceptibility is not treated within this theory. We have now succeeded³ in introducing semiphenomenologically the effects of quantum and thermal spin fluctuations in a way consistent with scaling laws and with the results⁴ of renormalization-group theory for a single impurity, obtaining the first alloy theory to include such fluctuations away from the dilute limit. The resultant theory is applicable to all metallic alloys, but is of greatest value for alloy systems in which the local susceptibility or local moment on an atom depends strongly on the local chemical and magnetic environment of that atom, especially alloys such as Cu-Ni, Pd-Ni, Pt-Ni, and Rh-Ni. However, for such alloy systems the calculated $\chi_P(c, T)$ cannot be compared directly to the experimentally measured $\chi_{\text{expt}}(c, T)$, because $\chi_{\text{expt}}(c, T)$ contains a substantial Curie-Weiss (CW) component arising from clusters of magnetic atoms. It is difficult to calculate the CW component because of cluster-cluster interactions and the effects of chemical ordering or clustering. Magnetization and susceptibility measurements⁵⁻⁷ on

paramagnetic and weakly ferromagnetic alloys have shown that $\chi_{\text{expt}}(c, T)$ can be resolved into the sum of two terms at low temperatures— $\chi_{\text{CW}}(c, T) = A_{\text{CW}}(c)/(T + \theta_{\text{CW}})$, which arises from magnetic clusters, and the relatively temperature-independent Pauli component $\chi'(c, T)$.

In alloys such as those considered here $\chi'(c, T) \neq \chi_P(c, T)$, because $\chi_P(c, T)$ also contains a substantial CW-like component arising from the large spin fluctuations associated with clusters which within the RPA either almost form or just barely form magnetic moments. For any given cluster these spin fluctuations give rise³ to a susceptibility which differs from the CW form by less than 1% for $T \gg 2T_K$, with the CW temperature of the cluster equal to $4T_K/3$, where T_K is the Kondo temperature⁴ for that cluster. Therefore, in order to compare our results for $\chi_P(c, T)$ with experiment, we assume the experimentally determined values of θ_{CW} to be the true CW temperatures, so that the calculated $\chi'(c, T)$ can be found^{3,8} by fitting $\chi_P(c, T)$ at low temperatures to the form, $\chi_P(c, T) = \chi'(c, T) + A'(c)/(T + \theta_{\text{CW}})$. Here, $\chi'(c, T)$ is assumed to be temperature independent in the limit of low T , and $A'(c)$ is the CW-like component arising from barely magnetic or highly exchange-enhanced Ni clusters. The experimental $A(c)$ is to be identified as the sum of $A'(c)$ and the CW constant $A_{\text{CW}}(c)$ associated with stable moments. The calculated values⁸ for $A(c)$ are in excellent agreement with experiment.^{6,7}

Among these Ni-based alloy systems, the $\text{Pd}_{1-c}\text{Ni}_c$ system has the lowest critical concentration ($c_{\text{cr}} \approx 2.35$ at. % Ni) for the onset of ferromagnetism,⁵⁻⁷ due to the highly polarizable, exchange-enhanced Pd host. Thus, one would expect the calculation to be least difficult for this system, because of the small value of c_{cr} . In this paper we use two different calculational methods to calculate $\chi'(c, 0)$ for paramagnetic and weakly ferromagnetic Pd-Ni alloys, and compare our results with experiment and previous theoretic-

cal calculations. In particular, those calculations based⁹⁻¹² on the single-site coherent-potential approximation (CPA), by virtue of the very nature of single-site averaging, fail to incorporate local-environment effects, which are very important in this class of Ni-based alloys. The previous cluster CPA theories,¹³ which represent approximations to the present formalism,¹ failed to include exchange enhancement in the effective medium or to treat atoms or clusters with a large susceptibility correctly. The theory of Kato and Mathon¹⁴ is the only previous theory of the exchange-enhanced susceptibility of concentrated alloys which gives a nondivergent susceptibility at all concentrations. However, this theory gives unphysical results which can be corrected only by abandoning self-consistency and introducing extra parameters.

II. THE METHOD

The formalism used has been described previously.^{1,2} A Hubbard Hamiltonian is used with hopping matrix elements included up through fourth-nearest neighbors. For pure Pd, the local band susceptibilities, $\Gamma_{ij} = \partial\mu_i / \partial H_j$ (where μ_i is the local moment on site i and H_j is the magnetic field applied on site j), and the intra-atomic Coulomb interaction u_{Pd} were chosen so as to yield the correct single-particle density of states at the Fermi energy, the uniform exchange-enhanced susceptibility $\tilde{\chi}(0)$, and the q -dependence of $\tilde{\chi}(q)$ found by neutron-scattering measurements¹⁵ on dilute ferromagnetic Pd-Ni alloys.

The enhancement of the local susceptibility in the vicinity of Ni atoms in Pd-Ni alloys arises^{1,2} from an enhancement of the Γ_{ij} if either or both of the sites i and j are Ni sites, and from the presumably larger value of u on Ni sites ($u_{\text{Ni}} = u_{\text{Pd}} + \delta u$). In the calculations reported here, we assumed the ratio $\eta^2 \equiv \Gamma_{ij}^{\text{Ni}} / \Gamma_{ij}^{\text{Pd}}$ to be independent of the i - j distance and treated off-diagonal disorder only within the geometric approximation.¹ Calculations were performed for three cases, with a single adjustable parameter in each case: (a) diagonal disorder ($\delta u \neq 0$; $\eta = 0$); (b) off-diagonal disorder only ($\delta u = 0$; $\eta \neq 0$); and (c) off-diagonal disorder with the value of η fixed at the value (1.36) found in the model band-structure calculations of Ref. 2 for clusters of one or two Ni impurities.

Two different methods were used to implement the formalism described above. In the first method, $\chi_P(c, T) - \chi_P(0, T)$ is expressed as a sum of incremental contributions $\Delta\chi_P^{(n)}(c, T)$ from sets of n Ni atoms embedded in pure Pd, with $\Delta\chi_P^{(n)}(c, T)$ defined⁸ so that it vanishes if any subset of the Ni atoms is moved far away from all of the remaining Ni atoms. Thus, this method corresponds to a power-series expansion in the Ni concentration. Because of the need to consider very spread-out clusters, we were able to calculate $\chi_P(c, T)$ only through order $n = 4$ using this method. From an expansion of the experimental⁵⁻⁷ $\chi'(c, 0)$ in powers of c , it is clear that this expansion up through $n = 4$ is valid approximately up to, but not beyond, $c = 1.85$ at. % Ni.

In the second method, compact 55-site clusters consisting of real Ni and Pd atoms are embedded in a self-consis-

tently determined effective medium having a uniform susceptibility $\bar{\chi}(c, T)$. The susceptibility of the effective medium is determined as a function of Ni concentration from the self-consistency condition,^{1,2} $\bar{\chi}(c, 0) = \chi_P(c, 0)$, where $\chi_P(c, 0)$ is the self-consistently determined value of the Pauli susceptibility at $T = 0$. In this method we considered up through six Ni atoms in a cluster, an expansion valid at least up to $c = 3.0$ at. % Ni. Thus, this second method permits a comparison with experiment and with earlier theories through the critical composition and into the weakly ferromagnetic range for Pd-Ni alloys. On the other hand, this second method does introduce sources of systematic error, to be discussed in Sec. III.

III. RESULTS AND DISCUSSION

Because the results found⁸ were essentially unchanged when off-diagonal disorder was included, results are presented here only for the case of diagonal disorder. The value of δu was chosen to be 1.276 eV, which gives the best agreement with experiment using our first method. The spin-fluctuation temperature, $\theta_{\text{SF}} = 2.45 T_K$,^{3,4} was found to be 450 K for an isolated Ni impurity, 130 K for a nearest-neighbor Ni pair, and 300 K for a second-nearest-neighbor Ni pair. Thus, isolated Ni impurities and Ni pairs contribute almost solely to $\chi'(c, 0)$ and hardly at all to the CW-like term in $\chi_P(c, T)$. All Ni triplets in which one Ni atom was a nearest neighbor to both of the others were found to form local moments within the RPA. However, almost all other isolated triplet configurations were found to have values of θ_{SF} above 100 K and, hence, to contribute primarily to χ' . Most nonmagnetic isolated Ni quartets considered were found to have values of θ_{SF} between 64 and 100 K and, hence, to also contribute primarily to χ' . However, a substantial fraction of these quartets were found to have $\theta_{\text{SF}} \leq 16$ K. Thus, for low Ni concentrations we found Ni quartets to be the dominant source of the CW-like term in $\chi_P(c, T)$.

FIG. 1. Results for $\chi'(c, 0)$ obtained using the first method, normalized to the susceptibility of pure Pd, plotted vs Ni concentration (solid curve), and compared with those of previous theoretical calculations: Ref. 9 (---), Ref. 10 (---), Ref. 11 (---), and Ref. 14 (-); the solid circles and triangles are the experimental results from Refs. 5 and 6, respectively.

FIG. 2. Results for $\chi'(c,0)$ obtained using the second method, normalized to the susceptibility of pure Pd, plotted vs Ni concentration (solid curve), and compared with those from previous theoretical calculations, Ref. 10 (····) and Ref. 14 (---); the open and solid circles are the experimental results from Refs. 5 and 7, respectively.

The numerical results for $\chi'(c,0)$ found using the first method, normalized to the susceptibility of pure Pd, $\tilde{\chi}(0) \equiv \chi'(0,0)$, are plotted as a function of Ni concentration in Fig. 1 (solid curve), and compared with the results of previous calculations^{9-11,14} and experiment.^{5,6} Our numerical results are in far better agreement with experiment than those of previous theoretical calculations over that concentration range. The corresponding results for $\chi'(c,0)$ obtained using our second, embedded-cluster, method are shown in Fig. 2 (solid curve), and compared with the results of previous calculations^{10,14} and experiment.^{5,7} These results were obtained using the value of δu which gave the best results at lower Ni concentrations using our first method, and thus in a sense are zero-parameter results. As can be seen, this value of $\delta u = 1.276$ eV gives results which are sys-

tematically too high using our second method, but which are qualitatively better than any previous results. In particular, these results show a broad peak in $\chi'(c,0)$ with very nearly the same width as the experimental results, unlike the results of previous calculations.^{10,14} Furthermore, these results were obtained without abandoning self-consistency or introducing extra parameters, as was done in Ref. 14. The origin of the systematic overestimate of $\chi'(c,0)$ given by our second method is easily understood. It results from the extremely nonlinear dependence of the susceptibility of an atom on its local environment coupled with the extremely long range of the susceptibility in Pd-Ni alloys. By embedding clusters in an effective medium, we replace that nonlinear dependence by a linear dependence. In the vicinity of the peak in $\chi'(c,0)$ this produces a systematic overestimate in χ' . We have shown that this overestimate is greatly amplified by positive feedback in establishing self-consistency, and by the large number of cluster configurations in which one or more Ni atoms is (are) very close to the cluster edge.

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