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# Calculation of the Spin Susceptibility of Disordered Binary Alloys: Application to Pt-Pd, Rh-Pd, Ni-Rh, and Ni-Pd[†]

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Recently the spin susceptibility $\chi$ of a one-band model for a disordered binary alloy with intra-atomic Coulomb interactions and short-range scattering potentials was calculated using the coherent-potential approximation (CPA). The formal expression for $\chi$, which is applicable to alloys of arbitrary concentration and potential-scattering strengths, was found to reduce to previously obtained expressions for the susceptibility in the dilute-alloy limit and to contain as a special case the uniform-enhancement model for $\chi$. In the present paper this theory for the spin susceptibility is applied to several binary Ni, Rh, and Pd alloys. Good agreement with experiment is obtained for $\chi$ as a function of $x$ in $\mathrm{Pt}_x\mathrm{Pd}_{1-x}$, $\mathrm{Rh}_x\mathrm{Pd}_{1-x}$, $\mathrm{Ni}_x\mathrm{Rh}_{1-x}$, and $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$ when a simple "steeple model" for the density of $d$-electron states is used. The sign of the potential-scattering parameter is obtained from renormalized-atom calculations; its magnitude is allowed to vary arbitrarily. Good agreement between theory and experiment makes it possible to determine the physical mechanisms which govern the behavior of $\chi$ in the four alloy systems considered. It is shown that potential-scattering effects which change the density of states at the Fermi energy in the alloy from the value in the pure crystals must be included in calculations of $\chi$ in $\mathrm{Pt}_x\mathrm{Pd}_{1-x}$. A uniform-enhancement model, in which the alloy is replaced by a periodic crystal at each site of which the Coulomb interaction energy is given by the average of the intra-atomic Coulomb energies, is found to approximate the calculated spin susceptibility in $\mathrm{Pt}_x\mathrm{Pd}_{1-x}$ to within an accuracy of 10%. For $\mathrm{Rh}_x\mathrm{Pd}_{1-x}$ alloys it is concluded that it is more likely that the nonmonotonic $x$ dependence of $\chi$ is due to a relatively large contribution to the susceptibility associated with Rh sites than to a rigid-band density-of-states effect. This conclusion is in agreement with recent NMR data. The theoretically determined spin susceptibility in $\mathrm{Ni}_x\mathrm{Rh}_{1-x}$ alloys for $x \leq 0.50$ may be approximated to within an accuracy of 10% by a uniform-enhancement model, providing the density of states at the Fermi energy is calculated self-consistently at each concentration $x$ using the CPA. Thus both the Ni and Rh atoms may be viewed as participating equally in the ferromagnetic phase transition in $\mathrm{Ni}_x\mathrm{Rh}_{1-x}$ which takes place for $x \geq 0.63$. By contrast, for $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$ alloys in which it is found that the Ni sites make a relatively large contribution to the susceptibility, the Ni atoms appear to be mainly responsible for the ferromagnetic phase transition which occurs at very low Ni concentrations $x \geq 0.022$.

## I. INTRODUCTION

There exist a number of disordered magnetic or nearly magnetic alloys $A_xB_{1-x}$ which form solid solutions over a wide range of concentrations. Among these are Pt-Pd, Rh-Pd, Ni-Rh, and Ni-Pd. All of these systems show interesting and different magnetic behavior in the nondilute alloy limits. For example, the susceptibility in the $\mathrm{Pt}_x\mathrm{Pd}_{1-x}$ system[1,2] monotonically decreases with increasing $x$. In $\mathrm{Rh}_x\mathrm{Pd}_{1-x}$, the spin susceptibility $\chi$ exhibits a maximum at $x = 5$ at.% and then decreases monotonically.[3] $\mathrm{Ni}_x\mathrm{Rh}_{1-x}$ is ferromagnetic at low temperatures $T$ for $x \geqq 63$ at.%,[4] whereas $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$ is ferromagnetic at $T \simeq 0$ for $x \geqq 2.2$ at.%.[5]

Until recently the theoretical understanding of the susceptibility of exchange-enhanced alloys has been limited. Previous theories were only valid for dilute alloys[6-12] or uniformly exchange-enhanced alloys[13] and were thus of limited applicability. Within the last year several authors[14-17] have used slightly different approaches to apply the coherent-potential approximation (CPA)[18] to calculations of the susceptibility of nondilute alloys. However, none of these authors has attempted to explain the experimentally observed concentration dependence of the susceptibility in Rh-Pd and Ni-Rh. While Harris and Zuckermann[16] examined the concentration dependence of $\chi$ in Ni-Pd alloys and Levin *et al.*[14] studied that of $\chi$ in Pt-Pd, both of these sets of authors used approximate forms of the more general CPA expressions in the numerical analysis. In addition, the effects of potential scattering, which are important in these alloy systems, were ignored by both groups of investigators.

It is the purpose of the present paper to discuss in detail a theory for the spin susceptibility of nondilute alloys which was briefly presented in an earlier paper.[14] The general theory which includes potential-scattering effects is then applied to four transition-metal alloy systems: Rh-Pd, Pt-Pd, Ni-Rh, and Ni-Pd. Good quantitative agreement with experiment is obtained for the concentration dependence of $\chi$ in all these alloys.

The binary alloy $A_xB_{1-x}$ is approximated by a simple one-band model with self-consistently determined short-range scattering potentials. The intra-atomic Coulomb interactions are treated in the Hartree-Fock approximation. Because only the diagonal matrix elements in Wannier space of the alloy Hamiltonian $\mathcal{H}$ are random, the coherent-potential approximation[18] may be easily applied to $\mathcal{H}$ to obtain an approximate configuration-averaged one-electron Green's function for the alloy. The uniform static spin susceptibility is then easily calculated from the average Green's function computed in the presence of an external magnetic field.

In calculations of the susceptibility of transition-metal alloys it is assumed for simplicity that Ni, Pd, Pt, and Rh have the same $d$-band shape (i.e., a rigid-band model for the pure metals[19] is adopted) which can be approximated by the simple steeple model considered in previous[15,20] calculations of transition-metal alloy properties. While the theory presented here can easily be generalized to treat hybridizing $s$ and $d$ bands,[21] the numerical calculations become excessively complicated when $s$ electrons are included; consequently $s$ electrons will be neglected here. The Fermi energy in the alloys is calculated by assuming conservation of $d$ electrons. For simplicity it is also assumed that Ni, Pd, and Pt, which are in the same column of the Periodic Table, have the same number of $d$ electrons. Rh which lies directly to the left of Ni in the Periodic Table is assumed to have approximately one less $d$ electron than Ni. Despite these approximations it is believed that the results obtained here for the concentration dependence of $\chi$ are qualitatively correct.

The relative positions of the center of gravity of the $d$ bands, $\epsilon^{\text{pure}}$, in the pure crystals can be calculated from a renormalized-atom theory.[22] The sign of the potential-scattering parameter of the pure metals which is measured relative to the average half-bandwidth $W$ and given by $\delta^{\text{pure}} = (\epsilon^{A\text{ pure}} - \epsilon^{B\text{ pure}})/W$ is taken from these calculations. In order to fit the susceptibility data in the alloys the magnitude of $\delta^{\text{pure}}$, which is allowed to vary arbitrarily, is in general found to be smaller than that predicted theoretically[22] (by at most a factor of 4). This suggests that charge-transfer effects may be important in the alloys.[21]

A detailed outline of the paper will now be given. In Sec. II a model for the alloy in a uniform external magnetic field $H$ is discussed and the configuration-averaged single-electron resolvent $G(z,H)$ for the model is calculated using the CPA.

In Sec. III A a general expression for the paramagnetic susceptibility $\chi$ for the model alloy is obtained from $G(z, H)$. The weak-scattering limit of $\chi$ is discussed in Sec. III B. It is shown that, in this limit, $\chi$ can be written in the usual RPA form with an effective Coulomb interaction energy $U^{\text{eff}}$ which satisfies an equation analogous to the Soven equation[18] for the self-energy in the CPA. The expression obtained for $\chi$ can be viewed as an extension to nondilute alloys of the Lederer and Mills[6] theory which is appropriate to isoelectronic alloys in which there is no potential scattering. In Sec. III C, the dilute-alloy limit ($x \ll 1$) of $\chi$ is discussed. It is shown that there are three contributions to $\chi$ which are linear in $x$: a potential-scattering term which reflects the first-order change with $x$ in the alloy density of states, a Coulombic-scattering term, and a mixed term which contains combined potential- and Coulombic-scattering effects. Comparisons with other dilute-alloy theories are also discussed in Sec. III, and it is shown that the present theory contains those terms previously considered.

Finally in Sec. IV the theoretical expression for $\chi$ is applied to the four alloy systems: Pt-Pd, Rh-Pd, Ni-Rh, and Ni-Pd. In Sec. IV A a brief discussion of the pure-metal parameters used in the model is given. In Sec. IV B the susceptibility of $\text{Pt}_x\text{Pd}_{1-x}$ alloys is discussed. The theoretical curves of $\chi$ vs $x$ are plotted for several values of the potential-scattering parameter $\delta^{\text{pure}}$. It is shown that potential-scattering effects which change the density of states at the Fermi energy in the alloy from the value in the pure crystals must be included in calculations of $\chi$ in $\text{Pt}_x\text{Pd}_{1-x}$. A uniform-enhancement model[13] in which the alloy is replaced by a periodic crystal at each site of which the Coulomb interaction energy $U^{\text{av}}$ is given by the average of the intra-atomic Coulomb energies $U^{\text{av}} = xU^{\text{Pt}} + (1-x)U^{\text{Pd}}$ is found to approximate the calculated spin susceptibility in $\text{Pt}_x\text{Pd}_{1-x}$ to within an accuracy of 10%. Good agreement with experiment for all $x$ is found for $\delta^{\text{pure}} = 0.07$. No theoretical estimates of $\delta^{\text{pure}}$ for this alloy system are yet available, but arguments are given which show that a positive sign of $\delta^{\text{pure}}$ is reasonable.

In Sec. IV C the concentration dependence of $\chi$ for $\text{Rh}_x\text{Pd}_{1-x}$ alloys is discussed with particular attention given to the low-concentration ($x < 0.10$) limits where it is found experimentally[3] that $\chi$ exhibits a maximum as a function of $x$. The two mechanisms which have been postulated to explain this maximum are as follows: (i) The maximum in $\chi$ is due to a maximum in the density of states at the Fermi energy which arises in the rigid-band approximation.[23] (ii) The initial increase in $\chi$ at small $x$ is due to a large contribution to the susceptibility associated with Rh sites[24]; for larger $x$, $\chi$ must decrease (since $\chi$ in pure Rh is less than that in Pd), thus giving rise to a maximum in the susceptibility. Renormalized-atom-theory calculations[22] indicate that $\delta^{\text{pure}} \simeq 0.7$ for $\text{Rh}_x\text{Pd}_{1-x}$. If the first mechanism is responsible for the maximum, it is shown here using two different band models that agreement with the susceptibility data is only possible when $\delta^{\text{pure}}$ is chosen to be $\simeq 0.01$. In view of the fact that this value of $\delta^{\text{pure}}$ seems improbably small, it is argued that the first mechanism is unlikely to occur in Pd-Rh. On the other hand, good agreement with experimental values of $\chi$ for all $x$ is obtained for larger $\delta^{\text{pure}} = 0.2$. For this value of the scattering parameter it is shown that in the dilute limit the contribution to the susceptibility of a Rh site is several times larger than that of a Pd site. Because this larger value of $\delta^{\text{pure}}$ is in reasonable agreement with renormalized-atom calculations, it is concluded that the second mechanism is more likely to be responsible for the maximum in $\chi$ than the first. This conclusion is consistent with recent NMR data.[25] Arguments are given to explain why the present value found for $\delta^{\text{pure}}$ could be smaller than that calculated using renormalized-atom theory for the pure metals.

In Sec. IV D the concentration dependence of $\chi$ for $\text{Ni}_x\text{Rh}_{1-x}$ and for $\text{Ni}_x\text{Pd}_{1-x}$ is calculated and compared with experiment.[4,5] Emphasis in this section is on explaining why $\text{Ni}_x\text{Pd}_{1-x}$ becomes ferromagnetic for much smaller $x$ than $\text{Ni}_x\text{Rh}_{1-x}$. The much larger contribution to the susceptibility of a Ni site compared to that of a Pd site is seen to be mainly responsible for the tendency to ferromagnetism as Ni is added to Pd. The Ni atoms thus appear to trigger the ferromagnetic phase transition which occurs at very low Ni concentrations $x \geqslant 0.022$. On the other hand in $\text{Ni}_x\text{Rh}_{1-x}$ the present calculations demonstrate that the theoretically determined spin susceptibility for $x \leqslant 0.50$ may be approximated to within an accuracy of 10% by a uniform-enhancement model[13] in which the effective Coulomb energy at each site, $U^{\text{av}}$, is given by the average of the intra-atomic Coulomb energies in Ni and Rh $U^{\text{av}} = xU^{\text{Ni}} + (1-x)U^{\text{Rh}}$. However, the density of states at the Fermi energy which is found to increase monotonically with $x$ must be calculated self-consistently at each concentration $x$, using the CPA. Thus both the Ni and Rh atoms may be viewed as participating equally in the ferromagnetic phase transition which takes place for $x \geqslant 0.63$. Good agreement with the experimentally observed concentration dependence of $\chi$ is obtained for $\text{Ni}_x\text{Rh}_{1-x}$ when $\delta^{\text{pure}} = -0.125$ and for $\text{Ni}_x\text{Pd}_{1-x}$ when $\delta^{\text{pure}} = 0.16$. These values are in reasonable agreement with renormalized-atom calculations[22] which predict values of $\delta^{\text{pure}}$ equal to $-0.075$ and 0.78, respectively.

## II. DESCRIPTION OF THE ALLOY MODEL AND ITS ONE-ELECTRON PROPERTIES

In this section the one-electron properties of single-band disordered binary alloys $A_xB_{1-x}$ are reviewed within the context of the coherent-potential approximation.[18] The tight-binding Hamiltonian assumed to describe the essential features of either ferromagnetic or paramagnetic alloys in an external magnetic field $H$ is given by

$$\mathcal{H} = \sum_{\substack{i \neq j \\ \sigma}} T_{ij} a^\dagger_{i\sigma} a_{j\sigma} + \sum_{i,\sigma} \epsilon^i_\sigma(H) a^\dagger_{i\sigma} a_{i\sigma} \quad , \tag{2.1}$$

$$\mathcal{H} = \hat{T} + \hat{V}(H) \ , \tag{2.2}$$

where $\epsilon^i_\sigma(H)$ can take on one of two $x$-dependent values $\epsilon^A_0 + U^A n^A_{-\sigma}(H)$ or $\epsilon^B_0 + U^B n^B_{-\sigma}(H)$ depending on whether an $A$ or a $B$ atom is at site $i$, and $U^A$ and $U^B$ are the intra-atomic Coulomb repulsion energies on $A$ and $B$ sites, respectively, which are treated in the Hartree-Fock[26] approximation. The Hamiltonian is thus a Hartree-Fock Hubbard[27] Hamiltonian for the binary alloy. In Eq. (2.1) the $T_{ij}$ are the hopping integrals assumed to be the same for both pure-$A$ and -$B$ crystals. Thus, the operator $\hat{T}$ is translationally invariant. The alloy disorder is described by the short-range scattering term $\hat{V}(H)$. Since the present paper will not be concerned with diamagnetic effects, the field dependence of the kinetic energy term $\hat{T}$ is neglected. In addition spin-orbit coupling effects are neglected in the present calculations. The fact that the energy levels at a given site are constrained to take on one of two values, which corresponds to the *average* $d$-level position on $A$ and $B$ sites independent of the atomic configuration on nearby sites, is an oversimplification without which the problem is not in general soluble. It is expected that this assumption will not lead to significant errors in calculations of bulk or average properties which are insensitive to the spatial variation of the $d$-level positions, such as the density of states or the uniform static spin susceptibility.

The parameters characterizing the alloy Hamiltonian are $\delta^{\text{pure}}_\sigma \equiv [\epsilon^A_0 + U^A(n^A_{-\sigma})^{\text{pure}} - \epsilon^B_0 - U^B(n^B_{-\sigma})^{\text{pure}}]$, $U^A$, $U^B$, $(n^A_\sigma)^{\text{pure}}$, $(n^B_\sigma)^{\text{pure}}$, and the hopping term $\hat{T}$. Here $(n^A_\sigma)^{\text{pure}}$ and $(n^B_\sigma)^{\text{pure}}$ are the number of electrons per atom in the pure-$A$ and -$B$ crystals. In order to satisfy the Friedel sum rule

$$d\mu/dx\,|_{x=0} = d\mu/dx\,|_{x=1} = 0 \quad ,$$

these parameters must *not* be chosen independently.[28] However, because the present Hamiltonian neglects $s$ electrons and thereby only approximates that appropriate to real transition metals, the Fermi energy $\mu$ is not computed here exactly. It therefore seems unreasonable to force the alloy parameters to satisfy the Friedel sum rule in the present paper. Consequently, all the alloy parameters except $\delta^{\text{pure}}_\sigma$ will be chosen to be consistent with spin-susceptibility data and band calculations for the pure-$A$ and -$B$ crystals. The parameter $\delta^{\text{pure}}_\sigma$ will be an adjustable parameter in the theory.

The $x$-dependent quantities $n^A_\sigma(H)$ and $n^B_\sigma(H)$

represent the contribution of $A$ and $B$ sites to the total number of electrons per site in the alloy. $n_\sigma^i(H)$ can be obtained from the configuration-averaged resolvent:

$$G_\sigma(z,\ H) \equiv [z - \Sigma_\sigma(z,\ H) - \hat{T}\,]^{-1} \tag{2.3}$$

using

$$n_\sigma^i(H) = -(\pi N)^{-1}\,\mathrm{Im}\,\mathrm{Tr} \int_{-\infty}^{\infty} dE\, G_\sigma^i(E,\ H) f(E - \mu \mp \mu_B H)\ , \tag{2.4}$$

where

$$G_\sigma^i(z,\ H) = G_\sigma(z,\ H) + G_\sigma(z,\ H)[\epsilon_\sigma^i(H) - \Sigma_\sigma(z,\ H)]\, G_\sigma^i(z,\ H)\ , \tag{2.5}$$

and the minus and plus signs in Eq. (2.4) correspond to electrons whose spins are, respectively, parallel and antiparallel to the external magnetic field. $\Sigma_\sigma(z,\ H)$ is the self-energy operator, $f(E)$ is the Fermi function, and $\mu$ and $\mu_B$ are the Fermi energy and the Bohr magneton, respectively. It may be seen from Eq. (2.5) that $G^A(z,\ H)$ and $G^B(z,\ H)$ are just the propagators for an electron in the configuration-averaged alloy in which single-$A$ or -$B$ atoms are substitutionally embedded.

The Hamiltonian of Eq. (2.1) differs from the nonmagnetic Hamiltonian which has been commonly adopted by other investigators[18, 20, 21] in two respects: (i) An intra-atomic Hartree-Fock Coulomb interaction term acting between opposite-spin electrons is added to the short-range scattering term of Refs. 18, 20, and 21; and (ii) the energy levels $\epsilon_\sigma^i(H)$ are assumed to depend upon an externally applied magnetic field as well as on the concentration $x$. Because of the dependence of $\epsilon_\sigma^i(H)$ on $n_\sigma^i(H)$, the quantities $G_\sigma(z,\ H)$ and $G_{-\sigma}(z,\ H)$ must be calculated self-consistently using Eqs. (2.4) and (2.5). In the zero-magnetic-field limit, the Hamiltonian has been previously considered.[29, 30]

An approximate form for $G_\sigma(z,\ H)$ may be obtained from the coherent-potential approximation[18] which is a self-consistent procedure based on a single-site decoupling of the multiple-scattering equations. It follows from Ref. 18 that the self-energy of the model Hamiltonian is given by

$$\Sigma_\sigma(z,\ H) = x\epsilon_\sigma^A(H) + y\epsilon_\sigma^B(H) - [\epsilon_\sigma^A(H) - \Sigma_\sigma(z,\ H)] \times F(z - \Sigma_\sigma(z,\ H))[\epsilon_\sigma^B(H) - \Sigma_\sigma(z,\ H)]\ , \tag{2.6}$$

where $y = 1 - x$ and

$$F(z - \Sigma_\sigma(z,\ H)) = N^{-1}\,\mathrm{Tr}G_\sigma(z,\ H)\ . \tag{2.7}$$

The spin- and $x$-dependent potential-scattering-strength parameter $\delta_\sigma(H)$ is defined as

$$\delta_\sigma(H) = \epsilon_\sigma^A(H) - \epsilon_\sigma^B(H)\ . \tag{2.8}$$

It is convenient at this point to establish some notational conventions. All energies are measured relative to the half-bandwidth $W$. Consequently, $U^i$ and $\delta_\sigma(H)$ will be treated as the dimensionless variables $U^i/W$, $\delta_\sigma(H)/W$, etc. Additionally if the argument $H$ is omitted in $n_\sigma$, $\Sigma_\sigma(z)$, etc., it is understood that these quantities refer to their zero-field counterparts. The Fermi energy $\mu$ is always understood to be independent of the external magnetic field.

The electronic density of states per atom of spin $\sigma$ is given by

$$\rho_\sigma(E,\ H) = -\pi^{-1}\,\mathrm{Im}\,F(E + i0 - \Sigma_\sigma(E + i0,\ H))\ . \tag{2.9}$$

Similarly the contribution to the density of states associated with $A$ or $B$ sites and spin $\sigma$ is given by

$$\rho_\sigma^i(E, H) = -(N\pi)^{-1}\,\mathrm{Im}\,\mathrm{Tr}G_\sigma^i(E + i0, H), \tag{2.10}$$

where $i = A$ or $B$. Thus, using Eqs. (2.4), (2.9), and (2.10) it follows that

$$n_\sigma^i(H) = -\frac{1}{\pi}\,\mathrm{Im}\int_{-\infty}^{\infty} dE\, f(E - \mu \mp \mu_B H) F(E - \Sigma_\sigma(E, H)) \times \{1 - [\epsilon_\sigma^i(H) - \Sigma_\sigma(E, H)] F(E - \Sigma_\sigma(E, H))\}^{-1}\ . \tag{2.11}$$

From now on the small positive imaginary part of $E$ will not be written explicitly even when $\Sigma_\sigma(E, H)$ is real.

Using Eqs. (2.6) and (2.11) in the ferromagnetic case a set of seven coupled integral equations for $\mu$, $\Sigma_\sigma(z, H)$, $\Sigma_{-\sigma}(z, H)$, $n_\sigma^{A,B}(H)$, and $n_{-\sigma}^{A,B}(H)$ is obtained. In the paramagnetic case these seven equations reduce to four.

It may be verified from Eq. (2.6) that $\rho_\sigma(E, H) = x\rho_\sigma^A(E, H) + y\rho_\sigma^B(E, H)$. Thus the average number of electrons of spin $\sigma$ per atom, given by

$$n_\sigma(H) = -\pi^{-1}\,\mathrm{Im} \int_{-\infty}^{\infty} dE\, f(E - \mu \mp \mu_B H) \times F(E - \Sigma_\sigma(E, H)), \tag{2.12}$$

satisfies the particle-conservation equation

$$n_\sigma(H) = x n_\sigma^A(H) + y n_\sigma^B(H). \tag{2.13}$$

In the zero-magnetic-field limit, Eq. (2.12) is used to determine the Fermi energy $\mu$ in terms of the number of particles per site $(n_\sigma + n_{-\sigma})$.

## III. PARAMAGNETIC SPIN SUSCEPTIBILITY IN THE COHERENT-POTENTIAL APPROXIMATION AT $T = 0$

### A. General Expression for $\chi$

The uniform static spin susceptibility is given by

$$\chi = \lim_{H \to 0} \mu_B \left(\frac{n_\sigma(H) - n_{-\sigma}(H)}{H}\right)\ . \tag{3.1}$$

For simplicity only the paramagnetic case at $T = 0$ is considered here; the theory can be easily extended to ferromagnetic alloys and to arbitrary temperatures. For this reason the spin index $\sigma$ on $\delta_\sigma$, $\Sigma_\sigma$, etc., will often be omitted. From the conservation-of-particles equation [Eq. (2.13)] it follows that $\chi$ can be written

$$\chi = x\chi^A + y\chi^B, \tag{3.2}$$

where ($i = A, B$)

$$\chi^i = \lim_{H\to 0} \mu_B \left(\frac{n_\sigma^i(H) - n_{-\sigma}^i(H)}{H}\right). \tag{3.3}$$

The quantities $\chi^A$ and $\chi^B$ can be viewed as the contributions to the total susceptibility of $A$ and $B$ sites, respectively. By writing

$$n_\sigma^i(H) = n_\sigma^i \pm \tfrac{1}{2}\mu_B H \chi^i + O(H^2), \tag{3.4}$$

where the plus and minus signs refer to electrons with spins parallel and antiparallel to $H$, respectively, Eq. (2.11) may be expanded to first order in the magnetic field $H$. A set of simultaneous equations for $\chi^A$ and $\chi^B$ then results. These equations may be easily solved to yield

$$\chi^A = 2\mu_B{}^2 \left(\frac{\rho^A(\mu)(1 + U^B f^{BB}) - \rho^B(\mu)U^B f^{AB}}{(1 + U^A f^{AA})(1 + U^B f^{BB}) - U^A U^B f^{AB} f^{BA}}\right) \tag{3.5}$$

and

$$\chi^B = 2\mu_B{}^2 \left(\frac{\rho^B(\mu)(1 + U^A f^{AA}) - \rho^A(\mu)U^A f^{BA}}{(1 + u^A f^{AA})(1 + u^B f^{BB}) - U^A U^B f^{AB} f^{BA}}\right), \tag{3.6}$$

where

$$f^{ij} = \frac{\partial n_\sigma^i}{\partial \epsilon_\sigma^j} \tag{3.7a}$$

and

$$\rho^i(\mu) = \frac{\partial n^i}{\partial \mu}. \tag{3.7b}$$

Recently, Hasegawa and Kanamori[15] obtained an expression for $\chi$ equivalent to Eqs. (3.2), (3.5), and (3.6). These three equations express the paramagnetic susceptibility per atom as a complicated function of the (zero-field) self-energy and the quantities $n^A$ and $n^B$. All of these variables may be eliminated by solving Eqs. (2.6) and (2.11) self-consistently in the limit $H = 0$. The present theory may be directly applied to transition-metal alloys. In the model for these alloys adopted here, it is assumed that the five $d$ bands for a single-spin state are degenerate. The expression for $\chi$ [Eqs. (3.2), (3.5), and (3.6)] is then the susceptibility per atom for a single one of these bands. While numerical techniques must be used in the general case, it is possible to obtain in a simple way some information about $\chi$ by considering two special cases which have been considered previously. These are (i) the weak-scattering limit ($\delta \ll 1$) and (ii) the dilute-alloy limit ($x \ll 1$).

### B. Expression for $\chi$ in the Weak-Scattering Limit

In the weak-scattering limit ($\delta \ll 1$) it follows from Eq. (2.6) that the self-energy $\Sigma(z)$ is given by $\Sigma(z) = x\epsilon^A + y\epsilon^B$. In this limit the quantities $f^{AA}$ and $f^{AB}$ appearing in the general expression for $\chi^A$ and $\chi^B$ [Eqs. (3.5) and (3.6)] become

$$f^{AA} = -y\tilde{\chi}_0 - x\rho(\mu) \tag{3.8}$$

and

$$f^{AB} = y[\tilde{\chi}_0 - \rho(\mu)], \tag{3.9}$$

where

$$\tilde{\chi}_0 = \pi^{-1}\,\mathrm{Im} \int_{-\infty}^{\mu} dE\,[F(E - \Sigma(E))]^2. \tag{3.10}$$

The equations for $f^{BB}$ and $f^{BA}$ may be obtained from Eqs. (3.8) and (3.9) by replacing $A \leftrightarrow B$ and $x \leftrightarrow y$. Equations (3.2), (3.5), and (3.6) may then be written

$$\chi = 2\mu_B{}^2 \rho(\mu)[1 - U^{\mathrm{eff}}\rho(\mu)]^{-1}, \tag{3.11}$$

where

$$U^{\mathrm{eff}} = xU^A + yU^B - (U^A - U^{\mathrm{eff}})\frac{\tilde{\chi}_0}{1 - U^{\mathrm{eff}}\tilde{\chi}_0}(U^B - U^{\mathrm{eff}}). \tag{3.12}$$

In Eqs. (3.8)–(3.11), $\rho(\mu) = -\pi^{-1}\,\mathrm{Im}F(\mu - \Sigma(\mu))$ is the density of states at the Fermi energy in the alloy which like $\tilde{\chi}_0$ is independent of $x$ for isoelectronic alloys.

Equations (3.11) and (3.12) may be compared with the expression for the paramagnetic spin susceptibility found by Harris and Zuckermann.[16] In the theory of Ref. 16, which is applicable to isoelectronic alloys in which there is no potential scattering, the susceptibility is given by Eqs. (3.11) and (3.12) with $\tilde{\chi}_0(1 - U^{\mathrm{eff}}\tilde{\chi}_0)^{-1}$ replaced by $\sum_q \chi(q)[1 - U^{\mathrm{eff}}\chi(q)]^{-1}$, where $\chi(q)$ is the wave-number-dependent static susceptibility of the pure-unenhanced crystals. For isoelectronic alloys $\tilde{\chi}_0$ reduces to $\sum_q \chi(q)$. Consequently, in the weak-scattering limit the present theory and that of Ref. 16 are similar. The difference between the two theoretical results arises from the different decoupling assumptions made in treating the intra-atomic Coulomb interactions and the multiple-scattering equations.

### C. Expression for $\chi$ in the Dilute-Alloy Limit

In the dilute-alloy limit ($x \ll 1$) the self-energy is given by $\Sigma(z) = \epsilon^B + x\,\delta^0/[1 - \delta^0 F(z - \epsilon^B)]$, where $\delta^0$ is the value of $\delta$ at $x = 0$, and it is understood that $\epsilon^A$ and $\epsilon^B$ are evaluated at $x = 0$. Using Eqs. (3.2), (3.5), and (3.6), the susceptibility to first order in $x$ is

$$\chi = \chi_B^{\mathrm{pure}} + \chi^{\mathrm{pot}}(x) + \chi^{\mathrm{Coul}}(x) + \chi^{\mathrm{mixed}}(x), \tag{3.13}$$

where

$$\chi^{\text{pot}}(x)=\frac{x\,2\,\mu_B{}^2[(n^A)^{\text{pure}}-(n^B)^{\text{pure}}]\,\partial\rho^B(\mu^0)/\partial\mu^0[\rho^B(\mu^0)]^{-1}}{[1-U^B\rho^B(\mu^0)]^2}+x\,2\,\mu_B{}^2\pi^{-1}\frac{[\partial\rho^B(\mu^0)/\partial\mu^0][\rho^B(\mu^0)]^{-1}\operatorname{Im}\ln[1-\delta^0F(\mu^0-\epsilon^B)]}{[1-U^B\rho^B(\mu^0)]^2}$$

$$\times\frac{-x\,2\mu_B{}^2\,\pi^{-1}\,\partial\{\operatorname{Im}\ln[1-\delta^0F(\mu^0-\epsilon^B)]\}/\partial\mu^0}{[1-U^B\rho^B(\mu^0)]^2}\,, \qquad (3.14)$$

$$\chi^{\text{Coul}}(x)=\frac{x(\chi_B^{\text{pure}})^2\,(U^A-U^B)}{2\mu_B^2[1-(U^A-U^B)\,\tilde{\chi}]}\,, \qquad (3.15)$$

and

$$\chi^{\text{mixed}}(x)=2\,\mu_B{}^2\,x\left(\frac{\{[\rho^A(\mu^0)]^2-[\rho^B(\mu^0)]^2\}(U^A-U^B)+[\rho^A(\mu^0)-\rho^B(\mu^0)]^2\,U^B}{[1-U^B\rho^B(\mu^0)]^2(1+U^Af_0^{AA})}\right). \qquad (3.16)$$

The susceptibility in the pure host crystal is

$$\chi_B^{\text{pure}}=2\mu_B{}^2\rho^B(\mu^0)/[1-U^B\rho^B(\mu^0)] \qquad (3.17)$$

and

$$\tilde{\chi}=-f_0^{AA}/(1+U^Bf_0^{AA}). \qquad (3.18)$$

In Eqs. (3.14)–(3.17), $\rho^B(\mu^0)=-\pi^{-1}\operatorname{Im}F(\mu^0-\epsilon^B)$ is the density of states at the Fermi energy $\mu^0$ of the pure host crystal and $\rho^A(\mu^0)=-\pi^{-1}\operatorname{Im}\{F(\mu^0-\epsilon^B)/[1-\delta^0F(\mu^0-\epsilon^B)]\}$ is the partial density of $A$ states, for a single $A$ atom in a $B$ host, at the host Fermi energy. The quantity $f_0^{AA}$ appearing in Eq. (3.18) which is equal to $f^{AA}$ evaluated at $x=0$ is

$$f_0^{AA}=-\pi^{-1}\operatorname{Im}\int_{-\infty}^{\mu^0}dE\left(\frac{F(E-\epsilon^B)}{1-\delta^0F(E-\epsilon^B)}\right)^2, \qquad (3.19)$$

and $(n^A)^{\text{pure}}$ and $(n^B)^{\text{pure}}$ represent the number of electrons per atom in the pure-$A$ and -$B$ crystals, respectively. It can be seen that in the dilute-alloy limit $\chi$ contains a pole when $1+U^Af_0^{AA}=0$. This coincides with the condition for local magnetic moment formation derived by Moriya.[31] It follows from Eqs. (3.5) and (3.6) in the limit $x\to 0$ that the impurity contribution to the susceptibility $\chi^A$ will be very much larger than the host contribution $\chi^B$ when $1+U^Af_0^{AA}\simeq 0$. It should be emphasized that the quantity $f_0^{AA}$ which plays an important role in determining the behavior of the susceptibility at low concentrations depends only on (a) the pure-host band shape, (b) the host Fermi energy $\mu^0$, and (c) the scattering parameter $\delta^0$.

The first $x$-dependent contribution to $\chi$ appearing in Eq. (3.13), called $\chi^{\text{pot}}(x)$, arises from potential-scattering effects. For isoelectronic alloys in which $(n^A)^{\text{pure}}=(n^B)^{\text{pure}}$, $\chi^{\text{pot}}(x)$ is proportional to $(\epsilon^A-\epsilon^B)^2=(\delta^0)^2$ and thus vanishes when there is no potential scattering. The second $x$-dependent contribution to $\chi$ called $\chi^{\text{Coul}}(x)$ arises from Coulombic-scattering effects and is proportional to $(U^A-U^B)$. The last contribution to $\chi$ called $\chi^{\text{mixed}}(x)$ is proportional to $(U^A-U^B)\delta^0$. It thus arises from a combination of potential and Coulombic scattering.

The numerator in the expression for $\chi^{\text{pot}}(x)$ divided by $2\mu_B^2$ represents the first-order change in $x$ in the density of states at the Fermi energy. The three contributions in the numerator may be understood as follows. The first term reflects the fact that the density of states at the Fermi energy must change if the number of electrons per atom in the host metal is different from that of the impurity metal. The second term arises from the effect on the density of states of the shift of the Fermi energy with $x$. The last contribution to the change in the density of states arises from the change in band shape with alloying. The last two terms have opposite signs, and for small $\delta^0$ they completely cancel one another. Numerical calculations[32] for several different band shapes show that for isoelectronic alloys with nearly filled bands as in Ni, Pt, and Pd the contribution of $\chi^{\text{pot}}(x)$ is almost always negative for all reasonable $\delta^0$. On the other hand, for the band model that will be used here to approximate transition-metal band shapes, it is found that, for isoelectronic alloys, $\chi^{\text{pot}}(x)$ is positive for all reasonable $\delta^0$ when the host Fermi energy $\mu^0$ is chosen to be appropriate to that of pure Rh. For nonisoelectronic alloys, however, the first term in Eq. (3.14) may be important in determining the sign of $\chi^{\text{pot}}(x)$.

In the limit $U^A=U^B$ the expression for $\chi^{\text{pot}}(x)$ contains all terms formerly considered by de Gennes[33] ($U^A=U^B=0$) and by Fulde and Luther[34] ($U^A=U^B\neq 0$). While these authors included terms up to second order in $\delta^0$, the present theory treats $\delta^0$ to all orders. The expression for $\chi^{\text{pot}}(x)$ also contains that found by Yamada and Shimizu[35] who included only first-order terms in $\delta^0$.

The Coulombic-scattering contribution $\chi^{\text{Coul}}(x)$ is very similar to the expression for the susceptibility found by Lederer and Mills.[6] In the limit $U^B=0$ and $\delta^0=0$ the Lederer and Mills theory, which is applicable to isoelectronic alloys in which the potential scattering is negligible, is identical to the present one. For isoelectronic alloys, when $U^B\neq 0$ but $\delta^0=0$ the present theory coincides with that of Ref. 6 if

$$\tilde{\chi}=\sum_q \chi(q)/[1-U^B\sum_q\chi(q)]$$

in Eq. (3.18) is replaced by

$$\sum_q\{\chi(q)/[1-U^B\chi(q)]\},$$

where as in Sec. III B $\chi(q)$ is the wave-number-dependent susceptibility of the pure crystals. The difference between the present theory in the dilute limit and that of Lederer and Mills (which gives an exact RPA expression for $\chi$ in the limit $\delta^0=0$ for the Hubbard Hamiltonian[27]) arises from the assumption in the model Hamiltonian that the energy levels at a given site can take on only one of two values corresponding to the average $d$-level positions in the alloy of $A$ or $B$ sites. In the single-impurity limit this means that all host levels, even those near the impurity site, are the same as in the pure-host metal. However, because the quantity $\tilde{\chi}$ is generally determined empirically[2,7,16] it is felt that the difference between the present theory in the dilute limit and that of Lederer and Mills is not significant.

While the separate potential- and Coulombic-scattering contributions to $\chi$ in the dilute limit have been considered by previous authors, $\chi^{\text{mixed}}$ has only been considered in the limit $U^B=0$, in which limit the present theory contains the expression for the impurity contribution to the susceptibility derived by Anderson.[36]

Which of the three terms, if any, dominates the behavior of $\chi$ at small concentrations depends sensitively on the specific alloy parameters $\delta^0$, $U^A$, $U^B$, $(n^A)^{\text{pure}}$, $(n^B)^{\text{pure}}$ and the band shape. It should be noted that if the impurity atoms are on the verge of having local moments (i.e., $1+U^Af_0^{AA}\simeq 0$) then $[\chi^{\text{Coul}}(x)+\chi^{\text{mixed}}(x)]$ will be dominant. On the other hand, if the impurity atoms are far from satisfying the local-moment-formation criterion (i.e., $1+U^A f_0^{AA}\simeq 1$) then any one of the three contributions to $\chi$ may be dominant. The transition-metal alloy systems to be discussed in Sec. IV demonstrate clearly the competition between the three mechanisms—potential scattering, Coulombic scattering, and combined potential and Coulombic scattering—which contribute to the susceptibility in the dilute-alloy limit.

## IV. NUMERICAL RESULTS AND DISCUSSION

### A. Parameters for the Pure Metals and Dilute Alloys

With the exception of Ni[37] and Pd,[38] band theory for the transition metals is relatively incomplete. In this paper, because of the difficulty of numerical calculations in alloys involving both $s$ and $d$ bands, the $s$ electrons have been neglected altogether. It seems reasonable, in view of this approximation and of the dearth of reliable band calculations for Rh and Pt, to adopt here a steeple model similar to that previously used by Kirkpatrick *et al.*[20] and by Hasegawa and Kanamori[15] for the $d$ bands. This band shape contains a peak in the density of states at the top of the $d$ band, approximating that found from band calculations for Ni and Pd, which peak is thought to play an essential role in the magnetic properties of Ni[39] as well as in the other transition metals. The steeple model is illustrated in the insert of Fig. 1(a). Because Ni, Pt, and Pd are all in the same column of the Periodic Table, it is assumed that they have the same number of $d$ electrons. This assumption, which is consistent with the neglect of $s$ electrons and the overly simplified band shape, is not entirely justifiable. However it is made for simplicity and in order to keep the number of parameters which vary at a minimum. Because paramagnetic band calculations show that the Fermi energy of Ni[37] and that of Pd[38] lie slightly to the right of the peak in the density of states near the top of the $d$ band, it is assumed that in the steeple band shape the number of $d$ electrons in pure Ni and Pd is 9.5. This number, which is somewhat higher than the number 8.8 found from band calculations for Ni,[37] is chosen in order to make the Ni and Pd band shapes near the Fermi energy coincide with those found from band theory.

While the band theory for Rh is not as complete as that of Ni and Pd, recent calculations[40] show that the density of states at the Fermi energy in Rh is about 60% that of Pd. Because Rh has one less electron per atom than Ni, the Fermi energy of Rh is placed to the left of the peak in the density of states at a position such that the number of $d$ electrons in Rh is 8.2 per atom, or approximately one less than the number of $d$ electrons in Ni or Pd. This corresponds to a density of states at the Fermi energy in Rh of about 60% of that of Pd. This choice of the Fermi energies of metallic Rh and Pd relative to the peak in the density of states coincides with the usual rigid-band picture[23] which has been previously adopted to analyze the susceptibility data in Pd-Rh alloys.

The approximations used for Ni, Pd, and Rh are considerably less appropriate for Pt, in which the $d$-band width is expected to be comparable to that of the $s$ band. A tight-binding approximation may not be reliable for Pt, and the present theory may be regarded with some skepticism. Nevertheless in the absence of any better or more complete calculation it is not entirely unreasonable to apply the present theory to Pt alloys.

The additional parameters needed for the alloy calculations are the relative positions of the paramagnetic $d$ bands, the $d$-band widths, and the exchange-enhancement factors in the pure metals. In Table I are shown the positions of the center of gravity of the $d$ bands and the $d$-band widths $2W$ as calculated from renormalized-atom theory by Hodges *et al.*[22] The Pt calculations have not been

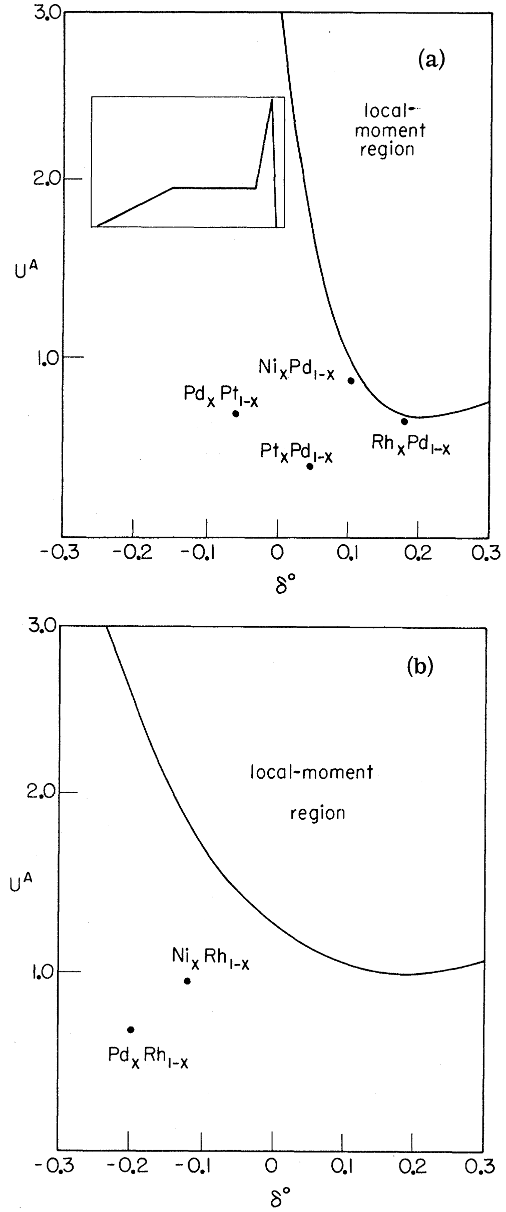

FIG. 1. Phase diagrams for the formation of local moments in steeple band for alloys $A_xB_{1-x}$, $x \ll 1$. (a) corresponds to Ni, Pt, or Pd hosts, and (b) to a Rh host. The insert in (a) plots schematically the steeple band shape.

performed as yet. The values for the quantities $[U\rho_0(\mu)]$ of Ni[41] and of Pd[6,7] were taken from previous theoretical calculations. For Rh and for Pt they were determined by fitting the end points of the calculated susceptibility versus $x$ curves of Pd-Rh and of Pd-Pt alloys to the experimental values. The chosen values for Pt and Rh agree with other theoretical estimates which give $U\rho_0(\mu) \simeq 0.4$ for Pt[40] and $U\rho_0(\mu) \simeq 0$ to $0.4$ for Rh.[6] It should be noted that the $d$-band widths vary considerably in going from Ni to Rh. Thus the assumption that the hopping matrix elements in the alloy Hamiltonian $T_{ij}$ are independent of $i$ and $j$ represents an approximation (without which the problem is not easily solvable).

As can be seen from the table, for alloys $A_xB_{1-x}$, the separations of the paramagnetic bands in the pure crystals relative to the average half-bandwidth is

$$\delta^{\text{pure}} \equiv \epsilon_0^A - \epsilon_0^B + U^A (n^A)^{\text{pure}} - U^B (n^B)^{\text{pure}}$$

$$= \epsilon^{A\,\text{pure}} - \epsilon^{B\,\text{pure}} , \qquad (4.1)$$

which equals 0.78 for $Ni_x Pd_{1-x}$, $\delta^{\text{pure}} = -0.075$ for $Ni_xRh_{1-x}$, and $\delta^{\text{pure}} = 0.705$ for $Rh_xPd_{1-x}$. If the relative positions of the center of gravity of the $d$ bands of Ni, Pd, and Pt are the same as those of the noble metals Cu, Ag, and Au,[22] then it follows that the Pt $d$-band center of gravity lies above that of Pd but below that of Ni. It will be shown in Sec. IV B that reasonable agreement with the experimentally observed values of $\chi$ vs $x$ for $Pt_x Pd_{1-x}$ alloys is obtained when $\delta^{\text{pure}}$ is greater than zero.

It is probable that in the transition-metal alloys as in some noble-metal alloys there is a transfer of $s$ charge from one type of atom to the other. As has been discussed in connection with Au-Ag alloys[21] this $s$ charge transfer will change the relative positions of the spin-independent part of the $d$-energy levels in the alloy, $\epsilon_0^A$ and $\epsilon_0^B$, and thus affect $\delta^{\text{pure}}$. The value of $\delta^{\text{pure}}$ computed from alloy calculations may then not be the same as that computed from properties of the pure crystals. If, for example, the Fermi energy of Ni lies higher than that of Pd, then a Thomas-Fermi calculation indicates that in the alloy $s$ electrons are transferred from Ni to Pd sites. As a result of $s$-$d$ Coulomb repulsion this charge transfer decreases $\epsilon_0^{\text{Ni}}$ and increases $\epsilon_0^{\text{Pd}}$. The net result is that $\delta^{\text{pure}}$ may be effectively decreased. As will be discussed in the following sections, susceptibility data show that the values of $\delta^{\text{pure}}$ in Ni-Pd and Rh-Pd are smaller than renormalized-atom-theory calculations indicate, which suggests that $s$ charge may be transferred from Ni sites to Pd sites in Ni-Pd and from Rh sites to Pd sites in Rh-Pd. Because the

TABLE I. Parameters for paramagnetic transition metals.

| | $\epsilon^{\text{pure}\,a}$ (Ry) | $2W^a$ (Ry) | $U\rho_0(\mu)$ |
|---|---|---|---|
| Ni | −0.31 | 0.35 | 1.2[b] |
| Pd | −0.47 | 0.48 | 0.86[c] |
| Rh | −0.28 | 0.60 | 0.45 |
| Pt | ? | ? | 0.51 |

[a] Reference 22.
[b] Reference 41.
[c] Reference 6.

$d$ bands of Ni and Rh lie considerably higher than those of Pd, this direction of $s$ charge transfer seems consistent with Thomas-Fermi theory.

The susceptibility calculations for alloys $A_xB_{1-x}$ which are discussed in Secs. IV B–IV D were done numerically using Eqs. (3.2), (3.5), and (3.6) by solving simultaneous equations for the Fermi energy $\mu$ and $\delta$ as functions of concentration. The quantity

$$\delta\,|_{x=0} \equiv \delta^0 = \epsilon_0^A - \epsilon_0^B + U^A n^A|_{x=0} - U^B (n^B)^{\text{pure}} \quad (4.2)$$

was used as the arbitrarily chosen input parameter instead of $\delta^{\text{pure}}$. In this way it was possible to use a two-dimensional iterative Newton-Raphson technique[42] to obtain $\mu$ and $\delta$ at each concentration $x$, with the starting values for the iteration scheme at concentration $x$ chosen to be the solutions for $\mu$ and $\delta$ at a slightly smaller concentration $x$-$\Delta x$. Once $\delta^0$ and the pure-metal parameters are selected the susceptibility over the entire concentration range $0 \leqslant x \leqslant 1$ is determined. For each alloy system $A_xB_{1-x}$, $\delta^0$ is chosen to give the best (visually obtained) fit of the theoretical curve of $\chi$ vs $x$ to the experimental data. When $\delta^0$ is determined, the quantity $\delta^{\text{pure}}$ may be obtained from the equation $\delta^{\text{pure}} = \delta^0 + U^A[(n^A)^{\text{pure}} - n^A|_{x=0}]$ and compared with the value predicted by renormalized-atom theory. In all four alloy systems considered here, the sign of $\delta^0$ which coincides with the sign of $\{\delta^0 + U^A \times [(n^A)^{\text{pure}} - n^A|_{x=0}]\}$ was chosen to agree with the sign of $\delta^{\text{pure}}$ as calculated from renormalized-atom theory.

The importance of choosing the correct sign of $\delta^0$ in calculations of $\chi$ can be demonstrated by examining in detail the condition for the formation of local magnetic moments: $1 + U^A f_0^{AA} \leqslant 0$, where $f_0^{AA}$ is defined in Eq. (3.19). The phase diagrams for local moment formation in the steeple band shape used here are illustrated in Fig. 1 for the value of the host Fermi energy corresponding to that of Ni, Pd, or Pt. [Fig. 1(a)] and that of Rh [Fig. 1(b)]. Also indicated are the values of $\delta^0$ and $U^A$ chosen for the dilute alloys ($x \ll 1$), $\text{Pt}_x\text{Pd}_{1-x}$, $\text{Pd}_x\text{Pt}_{1-x}$, $\text{Rh}_x\text{Pd}_{1-x}$, $\text{Pd}_x\text{Rh}_{1-x}$, $\text{Ni}_x\text{Rh}_{1-x}$, and $\text{Ni}_x\text{Pd}_{1-x}$. The quantity $\delta^0$ for the alloy $B_xA_{1-x}$ is related to $\delta^0$ for the alloy $A_xB_{1-x}$. The parameter $\delta^0$ for each of these alloys will be discussed in more detail in Secs. IV B–IV D. Local moments are stable for all pairs of values of $U^A$ and $\delta^0$ which lie above the curve corresponding to the appropriate host Fermi energy. It can easily be noted that it is difficult to satisfy the local-moment-formation criterion in transition-metal hosts when the impurity level lies lower than that of the host (i.e., $\delta^0 < 0$). On the other hand for positive $\delta^0$ ($\cong 0.1$ in the present band model) it is easier to satisfy the local-moment-formation criterion. These arguments are expected to be independent of the band shape and to depend only on the fact that the host band is nearly full. For nearly empty host bands, local moments are most easily formed for negative $\delta^0$.

It follows directly from the renormalized-atom calculations summarized in Table I (from which the sign of $\delta^0$ is obtained) that Ni or Pd impurities in Rh are far from satisfying the local-moment-formation criterion, whereas Rh and Ni impurities in Pd nearly form local moments. These results are also summarized in Fig. 1.

### B. Concentration Dependence of $\chi$ in $\text{Pt}_x\text{Pd}_{1-x}$

In Fig. 2(a) are plotted the experimentally determined[2] values of $\chi$ at each concentration $x$ for $\text{Pt}_x\text{Pd}_{1-x}$ alloys. Also shown is the theoretical curve of $\chi$ vs $x$ for $\delta^0 = 0.06$. This value of $\delta^0$ corresponds to $\delta^{\text{pure}} = 0.07$. Very good agreement with experiment is obtained throughout most of the concentration range for this value of $\delta^0$. There is some deviation from the experimental data around 60 at.% Pt; the measured susceptibility appears to be independent of $x$ between 40 and 60 at.% Pt, unlike the calculated susceptibility. This feature of the experimental curves[1,2] cannot be reproduced within the present theory. Within an accuracy of 10% the theoretical curve for $\chi$ vs $x$ with $\delta^0 = 0.06$ can be analytically described by the equation $\chi \propto \rho(\mu)/[1 - U^{\text{av}}\rho(\mu)]$, where $U^{\text{av}} = x\,U^{\text{Pt}} + y\,U^{\text{Pd}}$, and $\rho(\mu)$ is the density of states in the alloy. This corresponds to a uniform-enhancement model.[13] The calculated values of $\rho(\mu)$ show that $\rho(\mu)$ exhibits a shallow minimum at $x \simeq 0.4$.

Also plotted in Fig. 2(a) is the theoretical curve of $\chi$ vs $x$ for Pd-Pt when $\delta^0 = 0.01$. This curve represents the weak-scattering limit of the present theory which was discussed in Sec. III B. In a previous paper[14] this special case of the more general theory was applied to Pt-Pd alloys. The quantity $\tilde{\chi}_0$ defined in Eq. (3.10) was chosen arbitrarily to fit the experimental data. The measured susceptibility per gram rather than that per atom was incorrectly used in this previous paper so that the good agreement found between experiment and theory was partially accidental. In the present paper using the experimental values for the susceptibility per atom, it is clear that the weak-scattering theory is probably not appropriate to Pt-Pd. Thus distortion of the band shape with alloying must be taken into consideration in this alloy system.

In order to investigate the effects resulting from changing the sign and magnitude of $\delta^0$ in Pt-Pd alloys, the theoretical curves of $\chi$ vs $x$ are plotted in Fig. 2(b) for $\delta^0 = +0.15$ and $\delta^0 = -0.15$. The experimental points are also shown. The differences between the behavior of $\chi$ in the low-con-

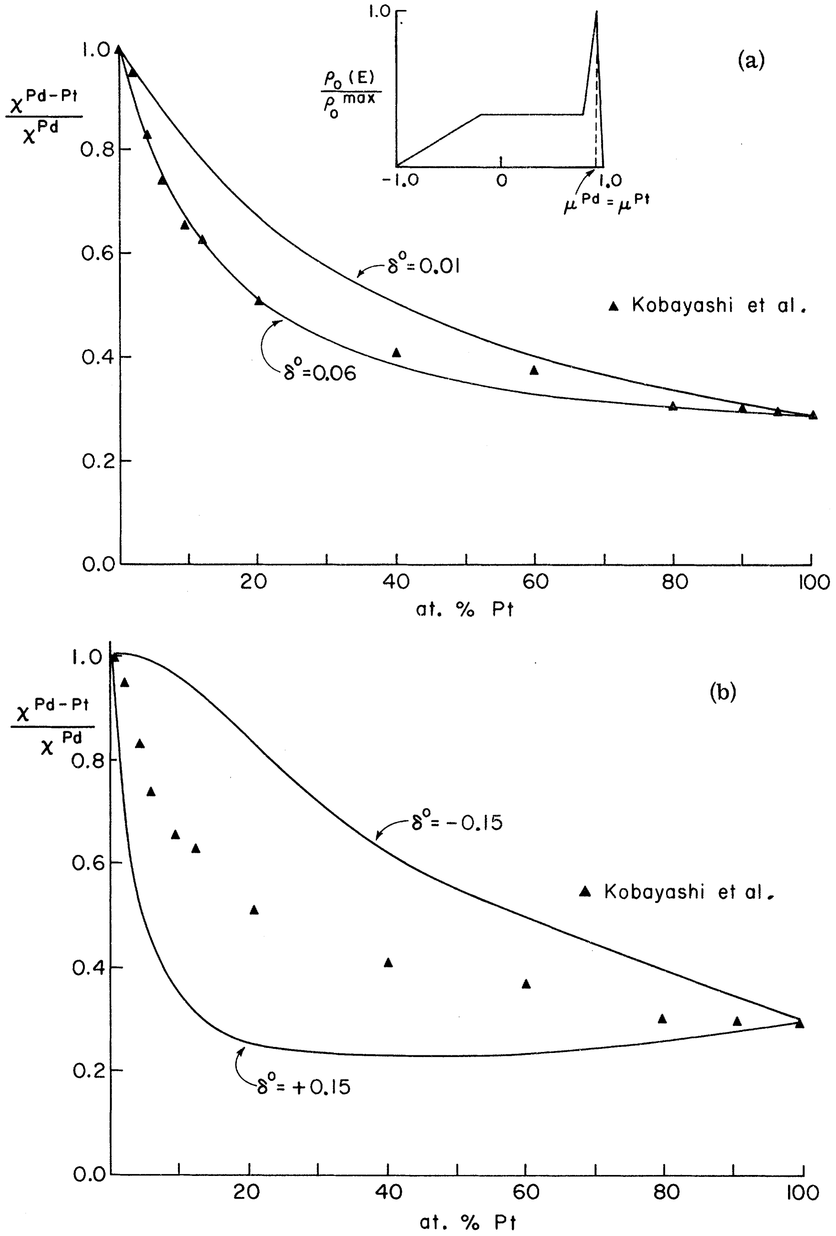

FIG. 2. Susceptibility vs $x$ in $\text{Pt}_x\text{Pd}_{1-x}$. The solid lines correspond to theoretical curves of $\chi$ vs $x$ for values of (a) $\delta^0=0.06$ and $0.01$ and (b) $\delta^0=+0.15$ and $-0.15$. In the insert of (a) is plotted the density of states for the pure crystals; the positions of the pure-crystal Fermi energies are indicated.

centration limits $x\simeq 0$ and $x\simeq 1$ for the two values of $\delta^0$ are striking and can be analyzed as in Sec. III C by examining the signs of $\chi^{\text{pot}}(x)$, $\chi^{\text{Coul}}(x)$, and $\chi^{\text{mixed}}(x)$ in these two dilute limits. For simplicity, only the case $x\simeq 0$ will be examined here. When $\delta^0=-0.15$, $\chi$ increases slightly with $x$ near $x=0$; when $\delta^0=+0.15$, $\chi$ decreases rapidly as a function of $x$, near $x=0$. Because $(1+U^{\text{Pt}}f_0^{\text{PtPt}})\simeq 1$ for both values of $\delta^0$, all three terms $\chi^{\text{pot}}(x)$, $\chi^{\text{Coul}}(x)$, and $\chi^{\text{mixed}}(x)$ are approximately of the same order of magnitude in both cases. For $\delta^0=+0.15$, $\chi^{\text{Coul}}(x)$ is negative and approximately equal to the value of $\chi^{\text{Coul}}(x)$ for the case $\delta^0=-0.15$. The differences in $\chi$ at small $x$ can then be understood in terms of the differences in the quantities $[\chi^{\text{mixed}}(x)+\chi^{\text{pot}}(x)]$. $\chi^{\text{mixed}}(x)$ is negative for $\delta^0=+0.15$ and positive for $\delta^0=-0.15$. On the other hand, $\chi^{\text{pot}}(x)$ is large and negative for $\delta^0=+0.15$ and small and negative for $\delta^0=0.15$. Thus, for $\delta^0=+0.15$, all three contributions to $\chi$ near $x=0$ are negative and $\chi$ decreases rapidly with small $x$, as shown in Fig. 2(b). For $\delta^0=-0.15$, $\chi^{\text{pot}}(x)$ and $\chi^{\text{Coul}}(x)$ are negative while $\chi^{\text{mixed}}(x)$ is positive. The net result is that $\chi$ increases slightly with small $x$. The same analysis may be applied to explain the difference in the calculated values of $\chi$ for $\delta^0=+0.15$ and $\delta^0=-0.15$ in the limit $x\simeq 1$.

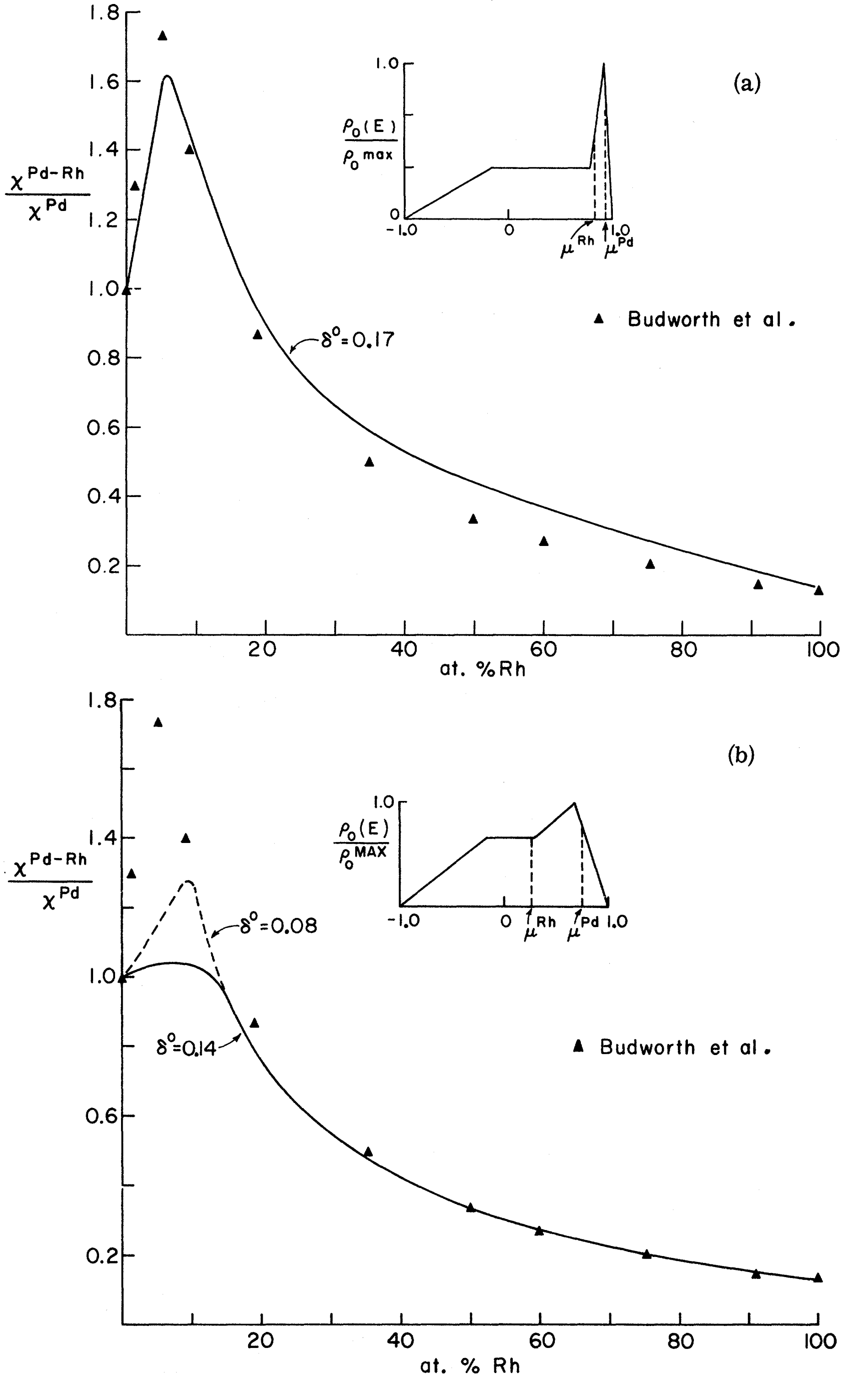

FIG. 3. Susceptibility vs $x$ in $Rh_xPd_{1-x}$ for two different band shapes. In the inserts are plotted the densities of states for the pure crystals; also indicated is the position of the pure-crystal Fermi energies: (dotted lines). The solid lines are the theoretical curves of $\chi$ vs $x$ for (a) $\delta^0 = 0.17$ and (b) $\delta^0 = 0.14$. The dotted line in (b) plots the calculated susceptibility for $\delta^0 = 0.08$ and for small $x$.

### C. Concentration Dependence of $\chi$ in $Rh_xPd_{1-x}$

The experimental data[3] for the susceptibility in Rh-Pd alloys are plotted in Fig. 3(a). The maximun in $\chi$ at $x \simeq 5$ at.% has been the subject of considerable interest and controversy. As stated in the Introduction there have been two theories advanced to explain the maximum. One,[23] it arises from a maximum in the rigid-band density of states as Rh is added to Pd. Using the insert of Fig. 3(a), this can be simply understood. Because pure Rh has fewer electrons per atom than pure Pd, according to rigid-band theory[43] the density of states at the Fermi energy will first increase and then decrease with $x$ as Rh is added to Pd. Two,[24] the maximum arises from a relatively large contribution to the susceptibility of Rh sites in Pd, which indicates the existence of real or incipient local moments on Rh sites. The susceptibility will then initially increase. It must decrease eventually, however, because pure Rh has a smaller susceptibility than pure Pd. This then leads to a maximum in $\chi$. In support of the second mechanism, NMR data[25] have shown that the local susceptibility of Rh in Pd is, indeed, strongly enhanced, and the low-temperature ($T \simeq (1-4)\,^\circ\mathrm{K}$) data suggest that Rh in Pd does not have a local moment. (The temperature dependence[44] of the Knight shift at higher temperature has been interpreted as indicating that Rh may have local moments in Pd.) In addition, x-ray experiments,[45] which indicate that the density of states at the Fermi energy in the alloy does not exhibit a maximum as a function of $x$, also provide evidence against the first mechanism.

The theoretical curve of $\chi$ vs $x$ for $\delta^0 = 0.17$ shown in Fig. 3(a) has a maximum at small $x$ qualitatively similar to the experimentally observed susceptibility. For this value of $\delta^0$ the contribution to the susceptibility of Rh $\chi^{\mathrm{Rh}}$ is several times larger than $\chi^{\mathrm{Pd}}$, and there is almost, but not quite, a local moment on Rh sites $[(1 + U^{\mathrm{Rh}} f_0^{\mathrm{RhRh}}) \simeq 0.3$ at $x \simeq 0\,]$. The density of states at the Fermi energy decreases for all $x$, and the absence of a maximum in $\rho(\mu)$ is consistent with x-ray data.[45] It follows that the maximum in $\chi$ arises solely from the large susceptibility associated with Rh atoms in Pd. This shows that for $\delta^0 = 0.17$, which corresponds to $\delta^{\mathrm{pure}} = 0.18$, the second mechanism is entirely possible within the present theory. This value of $\delta^{\mathrm{pure}}$ should be compared with the value 0.71 predicted from renormalized-atom calculations.[22] As discussed in Sec. IV A the discrepancy in magnitude may be due to $s$-charge-transfer effects.

In connection with NMR experiments, it should be mentioned that the usual expression[2,6] for the local susceptibility on the $A$-impurity site measured in an NMR experiment coincides with $\chi^A|_{x\approx 0,\delta=0}$ providing Eq. (3.18) is used to define $\tilde{\chi}$. In interpreting NMR data, however, it is necessary to know the magnitude of the indirect contribution of the $d$-electron spin polarization to the effective magnetic field experienced by the nuclei. NMR experiments are not a direct measure of $\chi^A|_{x\approx 0,\delta=0}$. The present calculations show that in $\mathrm{Rh}_x\mathrm{Pd}_{1-x}$ the ratios of the component spin susceptibilities to the susceptibility in pure Pd $\chi^{\mathrm{Rh}}/(\chi_{\mathrm{Pd}}{}^{\mathrm{pure}})$ and $\chi^{\mathrm{Pd}}/(\chi_{\mathrm{Pd}}{}^{\mathrm{pure}})$ reach a maximum of 7.35 and 1.25, respectively, at $x = 0.05$. Consequently, the component susceptibility of the Pd atoms is a also enhanced over that of pure Pd as is suggested by NMR experiments.[25] It must be emphasized, however, that in the present theory it is not possible to determine the spatial dependence of $\chi$; only the uniform spin susceptibility has been calculated. The quantities $\chi^A$ and $\chi^B$ which are calculated by averaging over all atomic configurations around the $A$ or $B$ sites, in general, provide only a crude estimate of the magnitude of the local susceptibilities associated with the different sites in the alloy. They do not necessarily give information about the local susceptibility on a given site for a specific configuration of surrounding atoms.

If $\delta^0$ is chosen to be less than $\simeq 0.06$, rigid-band theory[43] is appropriate for describing the concentration dependence of the density of states at the Fermi energy. However, for the present band model for $\delta^0 \simeq 0.06$ the system undergoes a ferromagnetic transition at $x \simeq 0.2$ and then becomes paramagnetic again at $x \simeq 0.35$. Consequently, for this band model good agreement with the experimentally observed susceptibility is not obtainable in the rigid-band approximation.

In the insert of Fig. 3(b) is shown a slightly different band model from which a maximum can be obtained in the calculated susceptibility curves for sufficiently small $\delta^0$. The value of the enhancement factor in Rh is different from that used in the previous Rh-Pd calculation in order to fit the end points of the $\chi$ vs $x$ curves. The solid line plots $\chi$ vs $x$ for $\delta^0 = 0.14$. In this band model, for $\delta^0 = 0.14$, $\chi^{\mathrm{Rh}}/\chi^{\mathrm{Pd}} < 1$. Thus, the Rh sites do not make as large a contribution to $\chi$ as in the previous model for $\delta^0 = 0.17$, and the slight maximum in $\chi$ shown in the curve is due entirely to a density-of-states effect. Agreement with experiment in the low-concentration range is not particularly good. Also shown in Fig. 3(b) (dotted line) is the calculated value of $\chi$ for small $x$ with $\delta^0 = 0.08$. For this value of $\delta^0$ the rigid-band theory is roughly applicable and the maximum in $\chi$, which reflects the maximum of the density of states at the Fermi energy, is in fair agreement with experiment. This value of $\delta^0$ corresponds to a value of $\delta^{\mathrm{pure}} = 0.01$ which is about $\frac{1}{70}$ of the value of $\delta^{\mathrm{pure}}$ predicted from renormalized-atom calculations.[22]

In summary, it appears that good qualitative agreement with the experimentally observed values of $\chi$ vs $x$ can be obtained in the present theory assuming either of the two mechanisms is responsible for the maximum. The evidence, however, suggests that the maximum in $\chi$ is not entirely due to a maximum in the density of states at the Fermi energy which results from rigid-band theory because (i) this would require an unreasonably small value of the potential-scattering parameter $\delta^{\mathrm{pure}}$ and (ii) recent NMR data[25] suggest that the Rh sites make a relatively large contribution to the susceptibility of the dilute ($x \ll 1$) alloy. It is nevertheless possible that a combination of a maximum in the density of states at the Fermi energy and a large ratio of $\chi^{\mathrm{Rh}}$ to $\chi^{\mathrm{Pd}}$ at $x \ll 1$ is responsible

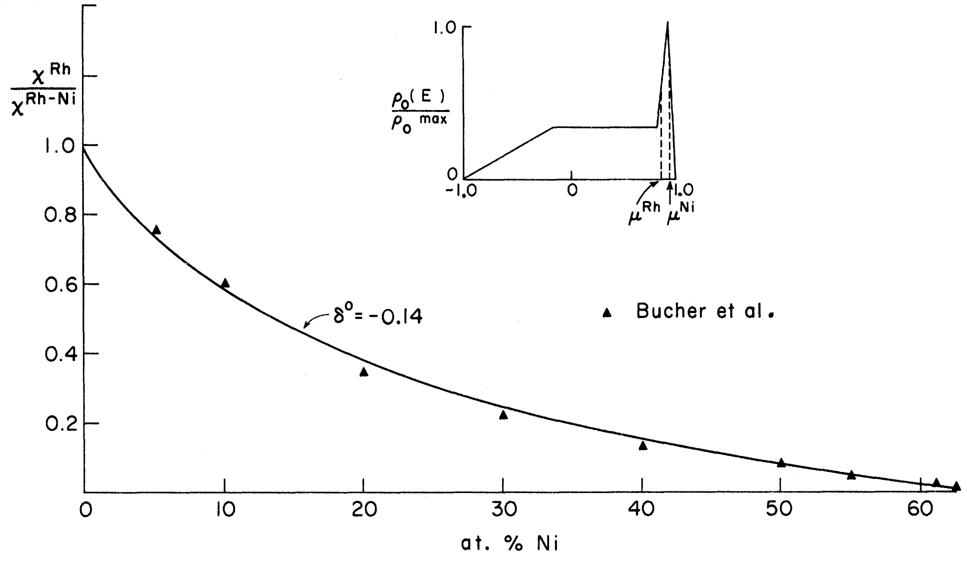

FIG. 4. Susceptibility vs $x$ in $Ni_xRh_{1-x}$. The solid line plots $\chi^{-1}$ for the "best" value of $\delta^0 = -0.12$. In the insert is plotted the density of states for the pure crystals; the pure-crystal Fermi energies are indicated by dotted lines.

for the observed concentration dependence of $\chi$ in Rh-Pd alloys.

### D. Concentration Dependence of $\chi$ in $Ni_xRh_{1-x}$ and $Ni_xPd_{1-x}$

The experimentally observed spin susceptibilities for Ni-Rh[4] and for Ni-Pd[5] are plotted as a function of $x$ in Figs. 4 and 5, respectively. It is seen that Ni-Pd becomes ferromagnetic at much lower Ni concentrations than Ni-Rh. The solid line in Fig. 4 plots the calculated susceptibility in $Ni_xRh_{1-x}$ alloys for $\delta^0 = -0.14$. This value of $\delta^0$, chosen to make $\chi$ diverge at the critical concentration, corresponds to $\delta^{pure} = -0.125$ which compares favorably with the value of $\delta^{pure} = -0.075$ obtained from renormalized-atom calculations. Unexpectedly good agreement with experiment is obtained over the entire paramagnetic concentration range. As a result of the position of the Fermi level of pure Rh and the value of $\delta^0$, at $x \simeq 0$, $\chi^{Ni}$ is not larger than $\chi^{Rh}$, and the Ni atoms are far from having local moments in Rh $[(1 + U^{Ni} f_0^{NiNi}) \simeq 0.7]$. Instead, the increase of $\chi$ with increasing Ni concentration arises from an increase in the density of states at the Fermi energy. The theoretical curve for $\chi$ vs $x$ in Fig. 4 for $x \leq 0.50$ can be approximated to within an accuracy of 10% by the equation $\chi \propto \rho(\mu)/[1 - U^{av}\rho(\mu)]$, where $U^{av} = xU^{Ni} + yU^{Rh}$ and $\rho(\mu)$ is the density of states at the Fermi energy in the alloy. This corresponds to a uniform-enhancement model for the susceptibility. Thus both the Ni and Rh atoms may be viewed as participating equally in the ferromagnetic phase transition which occurs

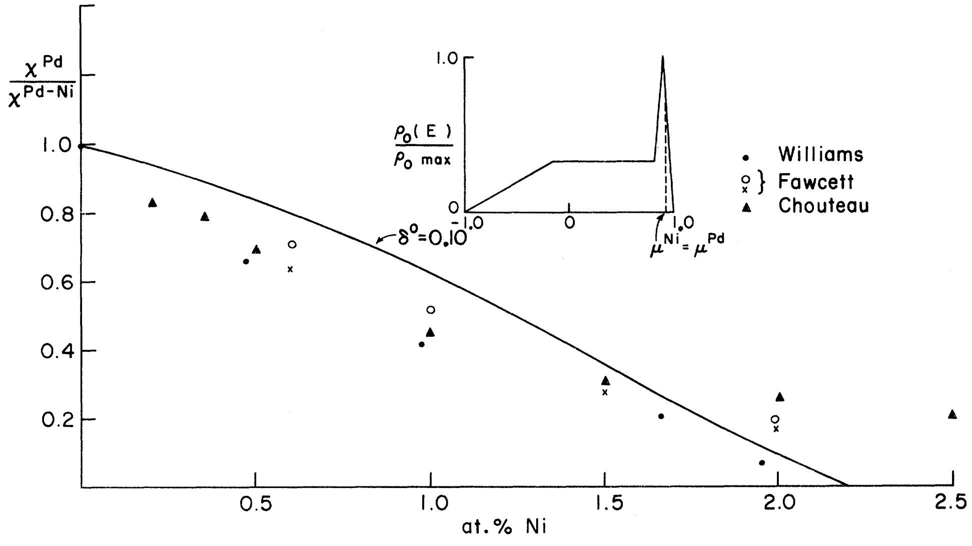

FIG. 5. Susceptibility vs $x$ in $Ni_xPd_{1-x}$. The solid line plots $\chi^{-1}$ for the "best" value of $\delta^0 = 0.10$. In the insert is plotted the density of states for the pure crystals; the pure-crystal Fermi energies are indicated by dotted lines.

for $x \geqslant 0.63$. The critical concentration in the uniform-enhancement model is $x \simeq 0.60$. This picture is in qualitative agreement with previous analyses[46] of the magnetic behavior of Ni-Rh alloys which show that the ferromagnetism in Ni-Rh is itinerant in nature and is not associated with localized moments on the Ni sites. It further supports a conjecture of Schindler[47] that the uniform-enhancement model might be applicable to paramagnetic Ni-Rh alloys.

The behavior of $\chi$ vs $x$ in $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$ is strikingly different as can be seen from Fig. 5. This system becomes ferromagnetic at $x = 0.022$. The solid line plots the calculated susceptibility for $\delta^0 = 0.10$ (which corresponds to $\delta^{\mathrm{pure}} = 0.16$). This value of $\delta^0$ was chosen to make $\chi$ diverge at the experimentally observed critical concentration $x = 0.022$. The quantity $f^{\mathrm{Ni\,Ni}}$, and hence the critical concentration, are extremely sensitive to $\delta^0$ for $\delta^0 \simeq 0.10$. Agreement between experiment and the present theory is fair for this alloy system. Better agreement with experiment can be obtained by using the weak-scattering limit of the present theory [Eq. (3.11)] and choosing $\tilde{\chi}_0$ arbitrarily.[32] Harris and Zuckermann,[16] using their weak-scattering theory, also obtained more satisfactory agreement with the experimental data. However, renormalized-atom calculations, which indicate that $\delta^{\mathrm{pure}}$ for $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$ is 0.78 (and is thus *not* small), suggest that such weak-scattering approximations are not valid.

The ratio of the contribution to the susceptibility of Ni to that of Pd in $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$, $\chi^{\mathrm{Ni}}/\chi^{\mathrm{Pd}}$, is several times larger than one, and the Ni atoms almost satisfy the local-moment-formation criterion $[1 + U^{\mathrm{Ni}} f_0^{\mathrm{Ni\,Ni}} \simeq 0.25]$. In addition, the system becomes ferromagnetic at small Ni concentrations $x$. This suggests that the Ni atoms appear to be mainly responsible for the transition to ferromagnetism. The present calculations show that the density of states at the Fermi energy decreases with $x$. This behavior should be contrasted with that of Ni in Rh which was discussed above. As discussed in connection with Fig. 1 the difference in $f_0^{\mathrm{Ni\,Ni}}$ and thus in the $x$ dependence of $\chi$ for these two alloy systems in the dilute limit arises mainly from the difference in the sign of $\delta^0$. It is, therefore, clear that potential scattering plays an important role in these alloys. Within the present model, very poor agreement with the experimentally observed susceptibility in both $\mathrm{Ni}_x\mathrm{Pd}_{1-x}$ and $\mathrm{Ni}_x\mathrm{Rh}_{1-x}$ is obtained when it is assumed that $\delta = 0$.

In summary, the present theory provides an internally consistent explanation of the observed concentration dependence of $\chi$ in Pt-Pd, Rh-Pd, Ni-Rh, and Ni-Pd despite the fact that $s$ electrons are neglected and an overly simplified $d$-band shape is used. The greatest uncertainty in the present calculations probably arises from the uncertainty in the magnitude of the concentration-dependent scattering-strength parameter $\delta$. It is of considerable interest to perform photoemission and x-ray studies of these alloys to determine $\delta$ more accurately.

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[34] Fulde and Luther's expression for $\chi \propto \chi^{\mathrm{imp}}(x)/[1-U\chi^{\mathrm{imp}}(x)]$ (see Ref. 8) is formally identical to $\chi_B^{\mathrm{pure}}+\chi^{\mathrm{pot}}(x)$ to order $\delta^2$ if changes in the Fermi energy with concentration are neglected in the present theory. In addition in the limit $U^A=U^B \neq 0$, the present theory contains an additional contribution from $\chi(x)^{\mathrm{mixed}}$ which was not included by Fulde and Luther.

[35] Yamada and Shimzu's expressions for $\chi$ (see Ref. 10) is formally identical to that found in the present theory in the dilute limit to first order in $\delta$ and $U^A-U^B$, when changes in the Fermi energy with concentration are neglected.

[36] Anderson (see Ref. 11) evaluated the contribution to the susceptibility for a single $A$ impurity in a $B$ host metal and found this contribution to be $\chi^A \propto \rho^A(\mu)/(1+U^A f_0^{AA})$ which coincides with Eq. (3.5) in the single-impurity limit.

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