

field at Fe^{57} nuclei at 0°K than Mn neighbors, while, as first discussed, Mn causes a much larger change in the temperature dependence. This shows that there is no simple relation between the spin-density disturbance caused by an impurity and the exchange interaction. This is in agreement with the conclusion of Stearns⁷ who has interpreted the dependence of the hyperfine field on the number of impurity atoms in neighboring shells with the Ruderman-Kittel-Kasuya-Yosida spin-density oscillations, which, however, leads to an antiferromagnetic exchange interaction between nearest-neighbor iron atoms.

In conclusion, (1) the exchange coupling felt by a magnetic moment of a particular iron atom is not locally disturbed by the presence of Si atoms in neighboring shells. Ferromagnetism in metallic iron cannot be explained by a localized-moment model with only short-range exchange interactions. The decrease in T_c of FeSi with increasing Si concentrations shows a decrease in the average exchange coupling as a simple dilution effect. (2) The distribution of hyperfine fields in FeSi alloys is a result of local spin-density disturbances caused by the lack of a magnetic moment on the Si atoms. These local spin-density disturbances, however, have little if any effect on the exchange coupling of the neighboring iron magnetic moments. (3) The different temperature dependences of H_{hf} of Fe^{57} nuclei in different Fe-Mn surroundings show that there is a local variation in the exchange coupling of an iron magnetic moment, which is most likely due to a direct nearest-neighbor Mn-Fe exchange interaction. Such a direct exchange interaction, howev-

er, is not characteristic for the pure host.

The experimental results obtained from the FeMn and FeSi alloys lead to the conclusion that iron should be treated as a material with localized magnetic moments which are, however, coupled via long-range exchange interactions. Preliminary calculations based on this model indicate that the experimental results given here can in fact be explained satisfactorily. It is interesting to note that the recent band-structure calculations of Duff and Das⁸ yield qualitatively the same physical model for the origin of ferromagnetism in iron. In a subsequent paper we will discuss the results in terms of this model.

Similar studies of the iron based alloys containing Al, V, Cr, Co, and Ni are in progress.

*Work supported by the Foundation for Fundamental Research of Matter of The Netherlands.

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Spin Susceptibility of Disordered Binary Alloys*

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(Received 13 July 1971)

A new theory based on the coherent-potential approximation is presented for the spin susceptibility χ in disordered binary alloys having arbitrary concentration and scattering-potential strengths. In the dilute-alloy limit the susceptibility contains all formerly derived expressions for χ as well as new physically significant terms. In the weak-scattering limit, an extension of the local-exchange-enhancement model is obtained which can be satisfactorily applied to nondilute Pd-Pt.

There exist a number of magnetic or nearly magnetic disordered alloys $A_x B_{1-x}$ which form solid solutions over a wide range of concentrations. Among these are Ni-Rh, Ni-Pd, Rh-Pd, and Pt-Pd. All of these systems show interest-

ing magnetic behavior in the nondilute alloy limits. For example, Ni-Rh becomes ferromagnetic¹ at 63 at.% Ni; the spin susceptibility of Ni-Pd increases nonlinearly with Ni concentration² below 2 at.%; in Rh-Pd alloys, χ exhibits a max-

imum³ at 5 at.% Pd; finally, the susceptibility in the Pt-Pd system increases monotonically and nonlinearly with concentration in going from pure Pt to pure Pd.⁴

Previous theories of the susceptibility of these exchange-enhanced alloys have been of two types: *dilute-alloy*⁵⁻⁸ and *uniform-exchange-enhancement theories*.⁹ Both of these have limited applicability. The former applies only to the extreme concentration limits ($x \ll 1, y \equiv 1 - x \ll 1$) and the latter to alloys whose component atoms are very similar. Furthermore, these previous theories have not included the effect of changes in the band shape, resulting from potential scattering, on the susceptibility. Theoretical studies of the electronic properties of non-exchange-enhanced alloys suggest that these effects are important.¹⁰ Photoemission data indicate, in general, a considerable distortion of the band shape upon alloying even in isoelectronic alloys.¹¹

It is the purpose of this Letter to derive a more general expression for the susceptibility which is applicable to nondilute alloys and to alloys whose component atoms are very dissimilar, and which properly takes into account the change-

es in electronic structure which occur upon alloying. The resulting expression for χ can then be used to analyze the large amount of experimental data which cannot be explained using either the dilute-alloy theory⁵⁻⁸ or the uniform-exchange-enhancement model.¹²

The tight-binding model Hamiltonian for the alloy in a magnetic field H is given by

$$\mathcal{H} = \sum_{i \neq j, \sigma} T_{ij} c_{i\sigma}^\dagger c_{j\sigma} + \sum_{i, \sigma} \epsilon_\sigma^i(H) c_{i\sigma}^\dagger c_{i\sigma}, \quad (1)$$

where $\epsilon_\sigma^i(H) \equiv \epsilon^i + U^i n_{-\sigma}^i(H) - \mu_B \sigma H$ can take on one of two values depending on whether an A or a B atom is at site i , $c_{i\sigma}^\dagger$ and $c_{i\sigma}$ are the usual creation and annihilation operators for electrons of spin σ and magnetic moment μ_B , and U^i is the intra-atomic Coulomb repulsion on the i th site treated in the Hartree-Fock approximation. In Eq. (1), the T_{ij} are hopping integrals assumed to be the same for pure A and pure B crystals, and n_σ^i represents the contribution of the i th site to the total number of electrons per site in the configuration-averaged alloy, which is given, within the coherent-potential approximation (CPA),¹⁰ by

$$n_\sigma^i = -\frac{1}{\pi} \text{Im} \int \frac{dE G_{ii\sigma}^i(E)}{1 + \exp[\beta(E - \mu)]}, \quad G_{ii\sigma}^i(E) = \frac{G_{ii\sigma}(E)}{1 - [\epsilon_\sigma^i(H) - \Sigma_\sigma] G_{ii\sigma}(E)} + \dots, \quad (2)$$

where $G_{ii\sigma}(E) \equiv \langle i | G_\sigma(E) | i \rangle = \langle i | (E - \Sigma_\sigma - W)^{-1} | i \rangle$, W is the kinetic-energy part of the Hamiltonian, and $\Sigma_\sigma(E, H)$ is the field-dependent electron self-energy. In Eq. (2), μ is the Fermi energy computed self-consistently at each alloy concentration. The correction terms " \dots " in Eq. (2) which will be neglected here arise from deviations in the local environment of A and B atoms from their average environment in the alloy.¹⁰

The configuration-averaged susceptibility in the alloy is given by

$$\chi = x \chi^A + y \chi^B. \quad (3)$$

If we assume for simplicity that the alloy is paramagnetic, then

$$\chi^i = \lim_{H \rightarrow 0} \mu_B [n_\uparrow^i(H) - n_\downarrow^i(H)] / H.$$

The theory can easily be extended to the more general case. Equation (3) follows from the particle-conservation equation¹⁰ $n_\sigma(H) = n_{\sigma^A}(H)x + n_{\sigma^B}(H)y$. By using Eq. (2) and the expression for χ^i , χ^A may be written

$$\chi^A = 2\mu_B^2 \left[\frac{(1 + U^B f^{BB}) \partial n^A / \partial \mu - U^B f^{AB} \partial n^B / \partial \mu}{(1 + U^A f^{AA})(1 + U^B f^{BB}) - U^A U^B f^{AB} f^{BA}} \right], \quad (4)$$

where $f^{ij} = (\partial n_\sigma^i / \partial \epsilon_\sigma^j)$. An expression for χ^B can be obtained from Eq. (4) by interchanging the subscripts A and B .

Equations (3) and (4) represent a general expression for the temperature-dependent paramagnetic susceptibility in a binary alloy having arbitrary concentration and scattering-potential strengths. This expression for χ can be applied to explain the behavior of the four transition-metal alloy systems mentioned above. In the following discussion two important special cases will be considered: (1) the *weak-scattering limit* in which $\delta_\sigma = \epsilon_{\sigma^A} - \epsilon_{\sigma^B}$ is small compared to the half-bandwidth w and (2) the *dilute-*

alloy limit $x \ll 1$. For these two cases, it will be shown that Eqs. (3) and (4) contain new and interesting results and, in addition, reduce to all previously considered expressions for χ in the appropriate limits.⁵⁻⁸

In the weak-scattering limit, for which $\Sigma_\sigma = x\epsilon_\sigma^A + y\epsilon_\sigma^B$, it follows that $f^{AA} = -y\tilde{\chi}_0 - x\partial n/\partial\mu$, $f^{AB} = -y(\partial n/\partial\mu - \tilde{\chi}_0)$, where $\tilde{\chi}_0 = \pi^{-1} \text{Im} \int dE \{1 + \exp[\beta(E - \mu)]\}^{-1} [G_{ii\sigma}(E)]^2$. Then Eq. (3) can be rewritten as

$$\chi = 2\mu_B^2(\partial n/\partial\mu)(1 - U^{\text{eff}}\partial n/\partial\mu)^{-1}, \quad (5)$$

where

$$U^{\text{eff}} = xU^A + yU^B - \frac{(U^A - U^{\text{eff}})(U^B - U^{\text{eff}})\tilde{\chi}_0}{1 - U^{\text{eff}}\tilde{\chi}_0}. \quad (6)$$

In Eq. (5), $\partial n/\partial\mu$ is the density of states at the Fermi energy in the alloy. For simplicity it will be assumed in the remainder of the paper that the alloy is isoelectronic. It may be noted from Eq. (6) that U^{eff} satisfies an equation analogous to the usual CPA equation for the self-energy.¹⁰ Equation (6) represents a natural generalization of the theory of Lederer and Mills^{5,12} to concentrated alloys.¹³ To first order in $U^A - U^B$, Eqs. (5) and (6) are equivalent to the susceptibility obtained in a uniform-exchange-enhancement model⁹ with $U^{\text{eff}} = xU^A + yU^B$.

These results may be applied to the $\text{Pt}_x\text{Pd}_{1-x}$ system which is both isoelectronic and paramagnetic at all concentrations. A comparison of the theoretical curve [Eq. (5)] with the experimental points⁴ is shown in Fig. 1. The theory is seen to be in good agreement with experiment when the enhancement factor for pure Pd is assumed, as in Ref. 5, to be ≈ 8.3 , that for Pt ≈ 1.2 , and the ratio $\tilde{\chi}_0/(\partial n/\partial\mu)$ is taken to be ≈ 0.15 . Once the endpoint at $x = 1$ of the curve of χ vs x is fitted the only free parameter in the theory is $\tilde{\chi}_0/(\partial n/\partial\mu)$. A first-principles calculation of this quantity requires a detailed knowledge of the band structure of Pd and Pt. At present the ratio can

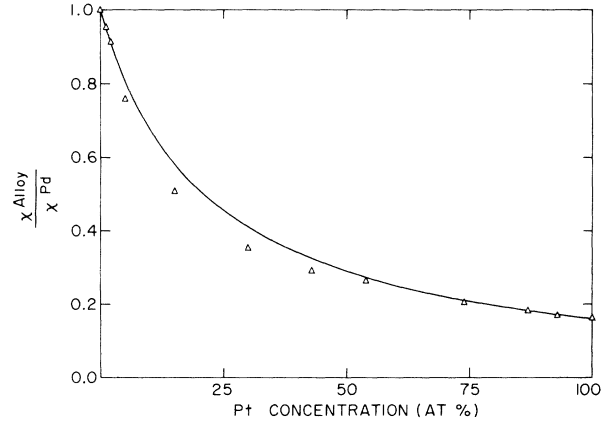


FIG. 1. $\chi^{\text{alloy}}/\chi^{\text{Pd}}$ vs x . The solid line is the theoretical curve; the triangles plot the experimental points of Ref. 4.

only be determined empirically. Even better agreement with experiment may be obtained when potential-scattering effects are included. These more detailed calculations, which are quite difficult to perform, will be presented in a later publication. It should be noted, however, that the present approximate theory is in good agreement with experiment over the entire concentration range.

In the dilute-alloy limit, for which¹⁰ $\Sigma_\sigma(E) = \epsilon_\sigma^B + x\delta_\sigma/[1 - \delta_\sigma G_{ii\sigma}(E)]$, it follows from Eqs. (3) and (4) that, to lowest order in x ,

$$\chi = \chi_{\text{pure}}^B + \chi^{\text{pot}}(x) + \chi^{\text{mag}}(x) + \chi^{\text{mixed}}(x), \quad (7)$$

where

$$\chi_{\text{pure}}^B = 2\mu_B^2(\partial n^B/\partial\mu)(1 - U^B\partial n^B/\partial\mu)^{-1} \quad (8)$$

is the susceptibility in the pure host crystal. In Eq. (7), the potential scattering contribution to χ is

$$\chi^{\text{pot}}(x) = x2\mu_B^2(\partial n/\partial\mu)_1[1 - U^B(\partial n^B/\partial\mu)]^{-2}, \quad (9)$$

where

$$\left(\frac{\partial n}{\partial\mu}\right)_1 = -\frac{1}{\pi} \left(\frac{\partial^2 n^B/\partial\mu^2}{\partial n^B/\partial\mu} - \frac{\partial}{\partial\mu} \right) \arg[1 - \delta_\sigma G_{ii\sigma}^0(\mu)] \quad (10)$$

represents the first-order change in the alloy density of states at the Fermi energy obtained by expanding $G_\sigma(E)$ and μ to lowest order in x . $G_{ii\sigma}^0(E)$ is the pure-crystal Green's function. The two terms in Eq. (10) correspond, respectively, to the contribution to $(\partial n/\partial\mu)_1$ arising from the change in band shape and from the shift in μ with alloying. In the limit $U^A = U^B$, the expression for $\chi^{\text{pot}}(x)$ contains all terms formerly considered by de Gennes¹⁴ ($U^A = U^B = 0$) and by Fulde and Luther⁶ ($U^A = U^B \neq 0$). In addition, the present theory also contains terms which arise from the change in the density of states at the Fermi energy, which has been previously neglected. While de Gennes and Fulde and Luther included terms up to second order in δ_σ , the present theory treats δ_σ in all orders. The expression

for $\chi^{\text{pot}}(x)$ also contains that found by Yamada and Shimizu,⁷ who included only first-order terms in δ_σ and neglected the change in μ with concentration. It should be noted, however, that when the shift in the Fermi energy is included, the linear terms in δ_σ can be seen to cancel. This cancelation is an expected result in this rigid-band approximation. Consequently, *for isoelectronic alloys, there is no contribution to the potential-scattering term in χ to lowest order to δ_σ .*

In Eq. (7) the magnetic scattering contribution to χ is given by

$$\chi^{\text{mag}}(x) = \frac{x}{2\mu_B^2} \frac{(\chi_{\text{pure}^B})^2(U^A - U^B)}{1 - (U^A - U^B)\tilde{\chi}(U^B)}, \quad (11)$$

where $\tilde{\chi}(U^B) = -f^{AA}/(1 + U^B f^{AA})$. This magnetic scattering term was first calculated by Lederer and Mills.^{5,12} Except for a slight redefinition of $\tilde{\chi}(U^B)$, the present theory reduces to that of Lederer and Mills in the limit $\delta_\sigma = 0$.

The last expression in Eq. (7) arises from a combination of potential and magnetic scattering. This contribution to χ , which has only been previously considered⁸ in the limit $U^B = 0$, is given by

$$\chi^{\text{mixed}}(x) = x 2\mu_B^2 \left\{ \frac{[(\partial n^A/\partial \mu)^2 - (\partial n^B/\partial \mu)^2](U^A - U^B) + U^B(\partial n^A/\partial \mu - \partial n^B/\partial \mu)^2}{(1 - U^B \partial n^B/\partial \mu)^2 (1 + U^A f^{AA})} \right\}. \quad (12)$$

In the limit $U^B = 0$, the present theory contains the expression for the susceptibility derived by Anderson⁸ as well as additional contributions which arise from the effect of the impurity Zeeman splitting on the host atoms, the change in the number of host atoms, and the change in the host band shape. In the limit $U^A = U^B \neq 0$, the mixed terms also contribute to χ although their contribution was neglected by Fulde and Luther.⁶ For nonvanishing $U^A = U^B$ this mixed term is to be expected on general physical grounds for it reflects the possibility of having local moments ($1 + U^A f^{AA} \leq 0$) in such a system.¹⁵ The omission of this term precludes the existence of local moments for any $U^A = U^B$. While it has often been assumed that, for isoelectronic alloys, $\chi^{\text{mag}}(x)$ is the dominant contribution to χ ,^{5,12,13} it can be seen by comparing Eqs. (11) and (12) that $\chi^{\text{mixed}}(x)$ may be of the same order of magnitude as $\chi^{\text{mag}}(x)$ even for isoelectronic alloys.

The physical justification of these new terms arising from combined potential and magnetic scattering is straightforward. The first mixed term in brackets in Eq. (12) reflects the fact that magnetism is favored (i.e., χ increases with x) if those atoms with the higher component density of states at the Fermi energy also have larger Coulomb repulsion U . The second mixed term (proportional to δ_σ^2), which is always positive, is, in general, small since for most alloy systems of interest $\delta_\sigma < W$. However, it is important near the critical condition for local moment formation⁸ ($1 + U^A f^{AA} = 0$) and when $U^A = U^B$. This term reflects the fact that when the impurity is nearly magnetic, magnetism in the alloy is favored whenever the host atoms also have a nonvanishing Coulomb repulsion. It thus represents

a positive "feedback" to the host atoms of large impurity-associated susceptibilities.

By including in Eq. (2) the correction terms,¹⁰ it is possible to treat local-environmental effects in χ which have been observed in Ni-Rh and Ni-Cu, for example.¹⁶

The authors wish to acknowledge helpful conversations with M. J. Zuckermann. One of us (K.L.) would like to thank B. Velický for useful discussions.

*Work supported by U. S. Office of Naval Research.

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Seebeck Coefficient at the Curie Temperature: Specific Heat of Charge Carriers in Ferromagnets*

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(Received 27 May 1971)

The Seebeck coefficient can be related to the specific heat of the charge carriers. Experiments on the itinerant ferromagnet nickel show that the specific heat determined from the Seebeck effect agrees closely with that determined from conventional specific-heat measurements.

Magnetic systems undergoing second-order phase transitions are found to exhibit thermodynamic singularities. While in insulating magnets it is generally found that localized spin Hamiltonians such as in the Ising or the Heisenberg model are adequate for describing most observations of the phase transition, in conducting magnets this is not the case.¹ There is no obvious way to distinguish between localized magnetism and itinerant-electron magnetism.² It thus becomes of interest to develop an experimental technique that allows the study of the magnetic ordering of charge carriers.

In several recent investigations of the thermopower of nickel and iron near their Curie temperatures,^{3,4} the focus has been on the oscillatory behavior in some samples. In this Letter we report a measurement of the Seebeck coefficient, or equivalently the thermopower, which we interpret directly in terms of the magnetic contribution to the specific heat associated with the charge carriers in nickel. We find that in the case of this extreme itinerant ferromagnet this specific heat is identical to that found in conventional specific-heat experiments. The oscillation in thermopower reported by Nagy and Pal³ was not observed. This question is examined later. The relation between the Seebeck coefficient and the specific heat was noted many years ago.⁵⁻⁷

The experimental technique and interpretation

can be understood with reference to Fig. 1. The sample S is connected in a differential thermocouple configuration with platinum reference electrodes R and is mounted isothermally in a vacuum furnace capable of slow temperature scanning. There are four platinum electrodes to permit measurement of sample resistance. A constant temperature difference ΔT , maintained by a separate heater coupled to a temperature controller, is superimposed on an ambient temperature T . The value of ΔT is typically 1°K over a sample length of 3 cm. The thermal potential difference ϵ is measured with nanovolt amplifiers.

In the limit of ΔT small compared to T , the voltmeter reads

$$\epsilon \approx \frac{\Delta T}{e} \left(\frac{\partial \bar{\mu}_S}{\partial T} - \frac{\partial \bar{\mu}_R}{\partial T} \right). \quad (1)$$

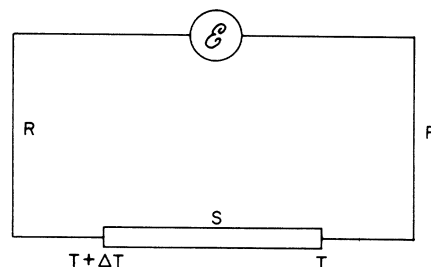


FIG. 1. The thermoelectric circuit is formed from the sample S and reference electrodes R , with a constant temperature difference ΔT .