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Electrical Resistivity of Dilute *Pd*Ni Alloys; Local Exchange Enhancement Effects

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The contribution to the electrical resistivity of transition-metal alloys from scattering of s electrons from spin-density fluctuations in the d band is discussed. The resistivity is expressed in terms of the dynamic magnetic susceptibility of the alloy. A time-dependent molecular-field approximation is employed to obtain an approximate expression for the dynamic susceptibility, valid in the dilute limit, for host materials in which exchange-enhancement effects are important. If the isolated impurity center is almost magnetic, a large concentration-dependent contribution to the resistivity proportional to T^2 is found. The theory is shown to account for the recent measurements by Schindler and Rice of the temperature dependence of the electrical resistivity of dilute *Pd*Ni alloys.

I. INTRODUCTION

THE magnetic properties of palladium metal are most interesting. If measured values of the static spin susceptibility are compared with the Pauli paramagnetic susceptibility computed from the band-structure density of states, it is found that the measured values of the susceptibility are roughly one order of magnitude larger than the simple Pauli susceptibility deduced from the free-electron model of metals.[1] It is believed that short-range, intra-atomic Coulomb interactions between the d electrons strongly enhance the susceptibility of Pd over the value expected from the one-electron theory. Specifically, if we denote the density of states at the Fermi level in the d band by $N(0)$, and the intra-atomic Coulomb interaction between two electrons in the same unit cell by U_0, then a simple Hartree-Fock (HF) theory[2] indicates that the susceptibility of the metal is larger than the Pauli free-electron susceptibility by the factor $[1-U_0N(0)]^{-1}$. If $U_0N(0)>1$, the HF theory predicts the system is unstable with respect to the ferromagnetic state. For Pd, evidently $U_0N(0)\cong 0.9$, if $N(0)$ is deduced from specific-heat data when taking mass-renormalization effects into account.[3]

Because the parameter $U_0N(0)$ for Pd is very close to unity, the repulsive intra-atomic Coulomb interactions are so strong that the d band is near the threshold of instability with respect to the ferromagnetic state. In this situation, one expects to find the long-wavelength, low-frequency fluctuations in the spin density of the d electrons have a large amplitude. Indeed, recent work[3] has indicated that such fluctuations make a large contribution to the effective mass of the d electrons, and to the specific heat. Berk and Schrieffer[4] have shown that when the static magnetic susceptibility is strongly exchange-enhanced, a large repulsive contribution to the kernel of the BCS equation results. These authors suggest this interaction may be sufficiently strong to completely suppress the superconducting transition in Pd.

The principal contribution to the electrical conductivity of pure Pd comes from the s electrons, since their effective mass is much smaller than the d electrons. The contribution to the transport relaxation rate from scattering of the s electrons from the spin-density fluctuations in the d band of the pure metal has been discussed by us.[5] One finds a contribution to the resistivity proportional to T^2 from this process. Thus at sufficiently low temperatures, where the phonon scattering is frozen out, one may expect to observe the contribution to the resistivity from the s-d spin-flip scattering. In a material like Pd, where exchange-enhancement effects are strong, it seems probable that spin-flip scattering from large amplitude fluctuations in d-electron spin density will dominate the non-spin-flip scattering discussed many years ago by Baber.[6] As we shall see in more detail below, Schindler and Rice[7] find that the resistivity of Pd does indeed exhibit a T^2 term that exceeds the T^5 scattering from the phonons below 9°K.

The magnetic properties of a number of alloys of Pd with small amounts of $3d$ impurity ions have been studied. For example, the local moment associated with Fe and Co dissolved in Pd is anomalously large, the

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[2] E. C. Stoner, Proc. Roy. Soc. (London) **A165**, 372 (1938).

[3] S. Doniach and S. Engelsberg, Phys. Rev. Letters **17**, 750 (1966).

[4] N. Berk and J. Schrieffer, Phys. Rev. Letters **17**, 433 (1966).

[5] D. L. Mills and P. Lederer, J. Phy. Chem. Solids **27**, 1805 (1966).

[6] W. G. Baber, Proc. Roy. Soc. (London) **A153**, 699 (1936).

[7] A. I. Schindler and M. J. Rice, Phys. Rev. (to be published).

order of 10 or 12 Bohr magnetons.[8] Neutron-diffraction studies[9] have shown that the spin density surrounding a given impurity cell is spread over a region of large spatial extent, with a radius of the order of 10 Å.

The purpose of this paper is to discuss some properties of dilute *Pd*Ni alloys. If the Ni concentration is less than roughly 2%, this alloy is nonmagnetic.[7,10] However, if the Ni concentration exceeds 2%, the Ni sites acquire a moment and the spins order. Thus, while it is evidently energetically unfavorable for an isolated Ni ion in a Pd matrix to acquire a local moment, the energy decrease associated with the ordering process is apparently sufficiently large that the ordered magnetic state has lower energy than the nonmagnetic state, when the impurity concentration exceeds 2% or so.[11] Since the gain in energy/impurity realized from the ordering process is clearly not large in such a dilute alloy, this implies that the intra-atomic Coulomb interaction U_I associated with a Ni cell is very close to the critical value required for moment formation. If $U_I > U_0$, then one expects the region of space in the vicinity of the Ni cell to be much closer to the magnetic instability than the host Pd matrix.

If the remarks in the preceding paragraph are correct, then one should expect to find the amplitude of the low-frequency fluctuations in spin density in the d band enhanced in the vicinity of the impurity cell, compared to their amplitude in the host material far from the impurity. If one examines the electrical resistivity of the alloy, the s electrons may scatter from the local fluctuations. Since the amplitude of the fluctuations varies with the temperature, this leads to a single-impurity contribution to the resistivity that is temperature-dependent. In this paper, a simple model is employed to calculate the contribution to the electrical resistivity from an almost magnetic center. It is found that the impurity contribution is proportional to T^2. This law is obtained because the scattering mechanism is an electron-electron collision process; the s electrons scatter inelastically against the local d-electron spin fluctuations, the amplitude of which is temperature-dependent. Thus, when this scattering is important, one expects the coefficient of the T^2 term in the resistivity of the alloy to contain a contribution proportional to the impurity concentration.

Striking evidence of the importance of local exchange enhancement effects in the spin-density fluctuations associated with the d electrons comes from the recent experiments of Schindler and Rice on the *Pd*Ni system.[7] As mentioned above, Schindler and Rice find a contribution to the resistivity of pure Pd proportional to T^2 dominates the phonon contribution for $T < 10°\text{K}$. They find the coefficient of the T^2 term in a *Pd*Ni alloy containing 1% Ni larger by a factor of 10 than the same quantity for the pure metal. The change in the coefficient varies linearly with impurity concentration c for $c < 1\%$. In this work, we analyze Schindler and Rice's data using the result of a simple model calculation. The model is able to account for a number of features of the data in a consistent, semiquantitative manner.

If the impurity is close to the magnetic stability, then the contribution of the impurity to the static spin susceptibility, the Knight shift, and longitudinal nuclear spin relaxation rate at the impurity site will be increased by the local exchange enhancement. We have discussed these effects in a separate paper.[12] While the forms exhibited in Ref. 12 do not apply to alloys in which exchange-enhancement effects in the host are important, it is straightforward to employ the dynamical susceptibility described below to derive expressions for the above-mentioned quantities applicable to alloys where exchange enhancement in the host is important.

In their paper, Schindler and Rice have presented a theoretical interpretation of the data. In essence, they have considered the contribution to the electrical resistivity and thermal conductivity from the scattering of s electrons from spin fluctuations in the d band using a formalism quite similar to that described in our earlier work.[5] To apply the theory to the alloy, they introduce an *average* intra-atomic Coulomb interaction $\bar{U}$ that increases with increasing impurity concentration. In this manner, they account for the concentration dependence of the coefficient of the T^2 term in the electrical resistivity. However, a plot of the observed values of coefficient A of the T^2 term in the electrical resistivity versus the static magnetic susceptibility χ of the alloy shows that A varies linearly with χ. The theory of Schindler and Rice predicts that A is proportional to χ^2, in disagreement with the experimental observations.

It is not clear to us that the introduction of an average intra-atomic Coulomb interaction $\bar{U}$ provides an adequate description of a dilute alloy, especially when an important contribution to the electrical resistivity comes from scattering of conduction electrons off spin-density fluctuations with wavelength short compared to the mean impurity-impurity separation. As mentioned above, we believe that the spatial inhomogeneity of the effective exchange field produces *local* spin-density fluctuations in the vicinity of the impurity cell with amplitude large compared to the amplitude in the host matrix. Such effects are not described by introducing an average Coulomb interaction $\bar{U}$.

From the present theory, we find the coefficient A introduced above varies linearly with the susceptibility

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[8] A. M. Clogston *et al.*, Phys. Rev. **125**, 541 (1962); D. Shaltiel *et al.*, *ibid.* **135**, A1346 (1964).

[9] G. Low and T. Holden, Proc. Phys. Soc. (London) **89**, 119 (1966).

[10] T. Moriya, in *Proceedings of the International School of Physics "Enrico Fermi," Varenna Lectures, 1966* (Academic Press Inc., New York, 1966).

[11] For a theoretical discussion of the conditions when this kind of ordering may occur, see A. Blandin and P. Lederer, Phil. Mag. **14**, 363 (1966).

[12] P. Lederer and D. L. Mills, Solid State Commun. **5**, 131 (1967).

χ for low impurity concentrations, in accord with the measurements.

II. GENERAL DISCUSSION

First, consider the spin-dependent coupling between the *s* electrons and the *d* electrons in the pure metal. If one describes the motion of the *s* electron by employing the HF equations in a form suitable for a magnetically ordered material, then the exchange terms give an *s*-*d* interaction of the form

$$H_{s\text{-}d}=V_cJ\int \mathbf{s}(\mathbf{r})\cdot\mathbf{S}(\mathbf{r})d^3\mathbf{r}, \tag{1}$$

provided that the nonlocal exchange potential is approximated by a local operator.[13] The notation in Eq. (1) is the same as employed in Ref. 5. The volume of the unit cell is V_c, $\mathbf{s}(\mathbf{r})$ is the spin-density operator for the *s* electrons, and J is the *s*-*d* interaction parameter. The integral in Eq. (1) is taken over the whole volume of the crystal.

In this work, we shall only be interested in studying the properties of very dilute alloys, where impurity-impurity correlations may be neglected. In this limit, it will be sufficient to consider the contribution to the resistivity from a single, isolated impurity ion, and multiply the final result by the number of impurities present. Thus we consider a metal containing a single impurity, placed for convenience at the origin of the coordinate system. Equation (1) then becomes

$$H_{s\text{-}d}=V_c\sum_i J_i\int_{\text{cell } i}\mathbf{s}(r)\cdot\mathbf{S}(r)d^3\mathbf{r}, \tag{2}$$

where $J_i=J$ for $i\neq0$, and $J_0=J_I$. In this paper, we shall want to apply the theory to the Pd-Ni system. Since Ni and Pd are isoelectronic, one does not expect J and J_I to differ greatly. To simplify the remaining discussion, we shall assume $J_I\approx J$. We consider the most important effect of the Ni impurity is to locally increase the exchange field seen by the *d* electrons, so the *d* band is driven closer to the magnetic-instability limit. The qualitative features of the present theory would not be affected greatly if J_I and J were different. Thus the *s*-*d* coupling will be assumed to have the form given in Eq. (1).

The method employed previously by us may be used to compute the contribution to the relaxation rate from *s*-*d* spin-flip scattering. One finds the relaxation time τ is given by

$$\frac{1}{\tau}=\frac{3\xi}{32}\frac{J^2}{m_sk_BT}\int dkdk'f_s(k)[1-f_s(k')]\{1+n[\Omega(k,k')]\}\times\int_0^{\eta_M}\eta^3|F(k_s\eta)|^2A[k_s\eta,\Omega(k,k')]d\eta. \tag{3}$$

This result is the same as the expression employed in Ref. 5. If n is the number of unit cells/unit volume, and n_s is the number of *s* electrons per unit volume, then $\xi=n_s/n$. The function $f_s(k)$ is the Fermi-Dirac distribution function for the *s* electrons, $\Omega(k,k')=(k^2-k'^2)/2m_s$, and $n(x)=\{\exp\beta x+1\}^{-1}$. It has been assumed that the *s*-electron energy band is parabolic, with effective mass m_s. The Bloch functions of the *d* band have been approximated by functions of the tight-binding form, and $F(\mathbf{q})$ is the form factor of the *d* orbital,[14] normalized so that $F(0)=1$. The function $A[k_s\eta,\Omega(k,k')]$ is (within a multiplicative constant) the square of the amplitude of a spin-density fluctuation of frequency $\Omega(k,k')$ and wave vector $k_s\eta$. We shall relate this function to the appropriate wave vector and frequency-dependent susceptibility of the alloy. For simplicity, we have assumed $A(\mathbf{q},\Omega)$ and $F(\mathbf{q})$ are functions only of $|\mathbf{q}|$. While this certainly will be a bad approximation if the theory is to be applied to real metals in a quantitative way, nonetheless, for the simple model employed in this work, we believe that the qualitative conclusions of this paper will not be seriously affected by this simplification.

Suppose the system is placed in a time varying, circularly polarized magnetic field of magnitude

$$\mu_B\mathbf{H}(\mathbf{x},t)=h(\mathbf{x}+i\mathbf{y})\exp(i\mathbf{q}\cdot\mathbf{x})\exp(-i\Omega t).$$

Let $\langle S_{(-)}(\mathbf{q}',t)\rangle$ be the amplitude of the transverse component of spin density induced in the *d* band by the time-varying field. The time dependence of $\langle S_{(+)}(\mathbf{q}',t)\rangle$ will be the same as that of $\mathbf{H}$;

$$\langle S_{(-)}(\mathbf{q}',t)\rangle=\langle S_{(-)}(\mathbf{q}')\rangle\exp(-i\Omega t).$$

If the external field h is weak, the amplitude of the $\mathbf{q}$th Fourier component of spin density induced in the *d* electrons of the alloy may be related to the amplitude of the external field by means of a generalized susceptibility function

$$\langle S_{(-)}(\mathbf{q}')\rangle=F(\mathbf{q})F(\mathbf{q}')\chi_r(\mathbf{q}\mathbf{q}',\Omega)h. \tag{4}$$

The form of the function $\chi_r(\mathbf{q}',\mathbf{q},\Omega)$ has been studied previously[5,15] for the case where exchange enhancement in the host is unimportant.

In the alloy, the presence of the impurity destroys the translational invariance of the system. Hence $\chi_r(\mathbf{q}'\mathbf{q},\Omega)$ has nonzero components for general values of $\mathbf{q}'\neq\mathbf{q}$.

The spectral function $A(\mathbf{q},\Omega)$ that appears in the result for the relaxation time can be shown by standard methods[14] to be related to the generalized susceptibility $\chi(\mathbf{q}\mathbf{q},\Omega)$;

$$A(\mathbf{q},\Omega)=i[\chi_r(\mathbf{q}\mathbf{q},\Omega+i\epsilon)-\chi_r(\mathbf{q}\mathbf{q},\Omega-i\epsilon)]. \tag{5}$$

In Eq. (5), ϵ is a small, positive infinitesimal number.

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[13] E. D. Thompson, Ann. Phys. (N. Y.) **22**, 309 (1963).

[14] See T. Izuyama, D. J. Kim and R. Kubo, J. Phys. Soc. Japan **18**, 1025 (1963).

[15] D. L. Mills and P. Lederer, Phys. Rev. **160**, 590 (1967).

To proceed with the discussion of the electrical resistivity of the alloy, we require an expression for the susceptibility function $\chi(\mathbf{qq}',\Omega)$.

III. APPROXIMATE EXPRESSION FOR THE GENERALIZED SUSCEPTIBILITY

Up to this point, the discussion has been quite general. To compute the generalized susceptibility function introduced above, we need to employ a specific model of the d electrons. We shall use a simple form of the model introduced by Wolff in his discussion of the formation of local moments in transition metal alloys.[16] We consider the properties of a single, narrow band of electrons. The Bloch functions are assumed to be well approximated by functions of the tight-binding form. Two electrons are assumed to interact via the intra-atomic Coulomb interaction only when they occupy Wannier functions in the same cell. Consequently, the single-band assumption allows only interactions between electrons with antiparallel spins.

The Hamiltonian of the pure metal thus has the form

$$H_0=T+U_0\sum_i n_{i\uparrow}n_{i\downarrow}\,,$$

where $n_{i\sigma}$ is the number operator $c_{i\sigma}{}^\dagger c_{i\sigma}$, where $c_{i\sigma}{}^\dagger(c_{i\sigma})$ creates (annihilates) an electron in the Wannier orbital associated with the ith unit cell. The kinetic energy of the electrons is

$$T=\sum_{\mathbf{k}\sigma}\epsilon(k)c_{\mathbf{k}\sigma}{}^\dagger c_{\mathbf{k}\sigma}\,.$$

Now suppose a single impurity is placed in the cell $i=0$. The impurity perturbs the motion of the electrons, since the crystal potential will be changed in the vicinity of the impurity host. Since the impurity potential will be efficiently screened by the electrons in the unfilled narrow band, for most purposes it will suffice to assume the change in crystal potential is localized to within the impurity cell. This approximation is particularly valid for the Ni-Pd system, since the one-electron scattering potential is very small for alloys constructed from constituents in the same row of the periodic table. Also, the intra-atomic Coulomb integral associated with the impurity cell will differ from the value U_0 appropriate to the host. Thus in the presence of a single impurity, the model Hamiltonian becomes

$$H=T+U_0\sum_i n_{i\uparrow}n_{i\downarrow}+V\sum_\sigma n_{0\sigma}+\delta U n_{0\uparrow}n_{0\downarrow}\,,\qquad(6)$$

where $\delta U=U_I-U_0$. If the model is applied to obtain a description of Ni in Pd, the discussion in Sec. I leads one to suppose that $\delta U>0$.

To compute the dynamic susceptibility of the alloy, one may relate this function to the particle-hole propagator. By making a suitable approximation in the equation of motion of the particle-hole propagator it is often possible to obtain explicit expressions for $\chi(\mathbf{q},\mathbf{q}',\Omega)$. This has been done for the pure metal by Izuyama *et al.*,[14] and extended to apply to simple alloys.[12,15] In our earlier work on alloys, we have ignored exchange-enhancement effects in the host matrix.

In this paper, we shall employ a simple dynamic molecular-field approximation to obtain an expression for $\chi(\mathbf{qq}',\Omega)$. This method gives some insight into the physical nature of the approximations, and yields results equivalent to the generalized random-phase approximation (RPA) employed in Refs. 14 and 15.

We wish to find the response of the system to a time and spatially varying magnetic field

$$\mathbf{H}=H(\mathbf{x}+i\mathbf{y})\exp(i\mathbf{q}\cdot\mathbf{x})\exp i\Omega t\,.$$

Since we have already implicitly chosen a preferred axis in space by introducing the up and down spin operators in the Hamiltonian, it will be easier to apply the molecular-field approximation to the calculation of the response of the system to a field applied parallel to the z axis. Define the longitudinal response function $\chi_l(\mathbf{qq}',\Omega)$ by the equation

$$\langle S_z(\mathbf{q}')\rangle=\tfrac{1}{2}F(\mathbf{q}')F(\mathbf{q})\chi_l(\mathbf{qq}',\Omega)h_z\,,$$

where $h_z=\mu_B H_z$. In the absence of an external field and in the absence of magnetic order, one has $\chi_l(\mathbf{qq}',\Omega)=\chi_r(\mathbf{qq}',\Omega)$ for an isotropic system. We shall compute the longitudinal response functions $\chi_l(\mathbf{qq}',\Omega)$ and use this function to obtain the spectral density $A(\mathbf{q},\Omega)$.

In the presence of a field parallel to the z axis, one adds to the Hamiltonian the term

$$H_{\text{ext}}=\tfrac{1}{2}hF(\mathbf{q})(\exp i\Omega t)\sum_i\{n_{i\uparrow}-n_{i\downarrow}\}\exp i\mathbf{q}\cdot\mathbf{x}_i$$

to describe the interaction of the electrons with the externally applied magnetic field.

The difficulty in computing the susceptibility in a rigorous way stems from the terms from the intra-atomic Coulomb interaction, since in the presence of these terms, one is faced with a many-body problem. We shall replace these terms by time-dependent one-particle potentials by replacing the combination of operators $n_{i\uparrow}n_{i\downarrow}$ by $\langle n_{i\uparrow}\rangle n_{i\downarrow}+\langle n_{i\downarrow}\rangle n_{i\uparrow}$, where $\langle n_{i\sigma}\rangle$ is the number of particles in the cell i with spin σ in the presence of the external time-varying field. It is then necessary to compute $\langle n_{i\sigma}\rangle$ in a self-consistent manner. In the presence of the external magnetic field, we write

$$\langle n_{i\uparrow}\rangle=\bar{n}_i-\tfrac{1}{2}\Delta_i\exp i\Omega t\,,$$

$$\langle n_{i\downarrow}\rangle=\bar{n}_i+\tfrac{1}{2}\Delta_i\exp i\Omega t\,,$$

where the numbers Δ_i are to be determined self-consistently.

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[16] P. A. Wolff, Phys. Rev. **124**, 1030 (1961).

Inserting the above expressions into the Hamiltonian of Eq. (6) yields the effective Hamiltonian

$$H_{\text{eff}}=T+V_{\text{HF}}\sum_{\sigma} n_{0\sigma}+\tfrac{1}{2}\sum_{i} h_i^{(e)}[n_{i\uparrow}-n_{i\downarrow}]\exp i\Omega t\,, \quad (7)$$

where

$$h_i^{(e)}=hF(\mathbf{q})\exp i\mathbf{q}\cdot\mathbf{x}_i+U_0\Delta_i+\delta U\Delta_0\delta_{i,0}\,, \quad (8)$$

and

$$V_{\text{HF}}=V+\delta U\bar{n}_0\,.$$

Some constant terms have been dropped from the Hamiltonian of Eq. (7). Equation (7) is a one-electron Hamiltonian that describes a band of particles moving in the presence of the HF potential V_{HF} and driven by spatially nonuniform magnetic field $h_i^{(e)}$. An electron moving through the crystal sees an internal magnetic with spatial variation described in the last two terms of Eq. (8). Far from the impurity the Δ_i will vary as $\exp i\mathbf{q}\cdot\mathbf{x}_i$. As the impurity is approached by an incoming particle, a localized disturbance is encountered.

Since Pd and Ni are isoelectronic, the HF impurity potential V_{HF} should be quite small. We shall assume that this is so, and ignore the effect of this term in the subsequent discussion. This approximation seems reasonable, since Schindler and Rice[7] find the residual resistivity associated with Ni in Pd is very small. The addition of 1% Ni to Pd increases the resistivity only 0.2 μΩ cm above the pure Pd resistivity at 4°K.

When the second term of Eq. (7) is dropped, the effective Hamiltonian describes a band of noninteracting electrons moving in the time-varying, spatially nonuniform magnetic field $h_i^{(e)}\exp i\Omega t$. We next Fourier transform the quantities Δ_i and $h_i^{(e)}$.

$$\Delta_i=\sum_{\mathbf{k}}\Delta(\mathbf{k})\exp i\mathbf{k}\cdot\mathbf{x}_i\,,$$

$$h_i^{(e)}=\sum_{\mathbf{k}}h^{(e)}(\mathbf{k})\exp i\mathbf{k}\cdot\mathbf{x}_i\,.$$

One finds

$$h^{(e)}(\mathbf{k})=hF(\mathbf{q})\delta_{q,k}+U_0\Delta(\mathbf{k})+(\delta U/N)\Delta_0\,. \quad (9)$$

The response of the band of noninteracting electrons to the space- and time-varying field is described by a generalized susceptibility function we denote by $\Gamma(\mathbf{k},\Omega)$, following a notation similar to Ref. 14.

$$\langle S_z(\mathbf{k})\rangle=\tfrac{1}{2}F(\mathbf{k})\Gamma(\mathbf{k},\Omega)h^{(e)}(\mathbf{k})\,, \quad (10)$$

where

$$\Gamma(\mathbf{k},\Omega)=\frac{1}{N}\sum_{\mathbf{k}'}\frac{n(\mathbf{k}'+\mathbf{k})-n(\mathbf{k}')}{\epsilon(\mathbf{k}')-\epsilon(\mathbf{k}'+\mathbf{k})+\Omega+i\epsilon}\,.$$

Since $\langle S_z(\mathbf{k})\rangle=\tfrac{1}{2}F(\mathbf{k})\Delta(\mathbf{k})$, use of Eqs. (9) and (10) yield an equation for $\Delta(\mathbf{k})$.

$$\Delta(\mathbf{k})=hF(\mathbf{q})\Gamma(\mathbf{q},\Omega)\delta_{q,k}+U_0\Gamma(\mathbf{k},\Omega)\Delta(\mathbf{k})+(\delta U/N)\Gamma(\mathbf{k},\Omega)\Delta_0\,. \quad (11)$$

Equation (11) may be solved at once for $\Delta(\mathbf{k})$:

$$\Delta(\mathbf{k})=hF(\mathbf{q})\chi_0(\mathbf{q},\Omega)\delta_{q,k}+(\delta U/N)\chi_0(\mathbf{k},\Omega)\Delta_0\,. \quad (12)$$

We have introduced the function

$$\chi_0(\mathbf{q},\Omega)=\Gamma(\mathbf{q},\Omega)/[1-U_0\Gamma(\mathbf{q},\Omega)]\,.$$

This function may be recognized as the exchange-enhanced, reduced susceptibility for the pure metal, obtained previously by Izuyama *et al.*[14] Indeed, if the term proportional to δU is dropped from Eq. (12), we recover the results of Ref 14 identically. By noting that $\Delta_0=(1/N)\sum_{\mathbf{k}}\Delta(\mathbf{k})$, one may eliminate Δ_0 from Eq. (12) and obtain an explicit expression for $\Delta(\mathbf{k})$. The result is

$$\Delta(\mathbf{k})=hF(\mathbf{q})\left[\chi_0(\mathbf{q},\Omega)\delta_{\mathbf{q},\mathbf{k}}+\frac{\delta U}{N}\frac{\chi_0(\mathbf{k},\Omega)\chi_0(\mathbf{q},\Omega)}{1-\delta U\bar{\chi}(\Omega)}\right], \quad (13)$$

where $\bar{\chi}(\Omega)=(1/N)\sum_{\mathbf{k}}\chi_0(\mathbf{k},\Omega)$. By relating this result to $\langle S_z(\mathbf{k})\rangle$, and recalling the definition of the reduced-susceptibility function $\chi_l(\mathbf{k}'\mathbf{k},\Omega)$, one has

$$\chi_l(\mathbf{k}'\mathbf{k},\Omega)=\chi_0(\mathbf{k},\Omega)\delta_{\mathbf{k}\mathbf{k}'}+\frac{\delta U}{N}\frac{\chi_0(\mathbf{k},\Omega)\chi_0(\mathbf{k}'\Omega)}{1-\delta U\bar{\chi}(\Omega)}\,. \quad (14)$$

Equation (14) is the result that we shall use to compute the spectral function $A(\mathbf{k},\Omega)$ required for the resistivity calculation. However, before proceeding with a study of the impurity contribution to the resistivity, it will be useful to relate the result in Eq. (14) to the work of other authors.

First of all, we remarked above that Eq. (14) reduces to the result of Izuyama, Kim, and Kubo[14] for the pure metal when $\delta U=0$. If δU is increased by increasing U_I, then the static ($\Omega=0$) susceptibility acquires a pole when $\delta U\bar{\chi}(0)=1$. Thus when $\delta U>\delta U_c=\bar{\chi}(0)^{-1}$, the theory predicts a local moment will form in the impurity cell. This same criterion for local moment formation in exchange-enhanced host materials has been obtained previously in Ref. 11 by examining the stability of the nonmagnetic HF ground state in the presence of a local increase in the intra-atomic Coulomb integral. In Ref. 11, the scattering effects represented by V_{HF} were also ignored. In our previous work,[12,15] an expression for the reduced susceptibility of the alloy was obtained including the scattering effects described by V_{HF}. The expression obtained from Eq. (14) with $U_0=0$ is the same as our earlier susceptibility when $V_{\text{HF}}=0$. When both $U_0=V_{\text{HF}}=0$, but $U_I\neq 0$, the criterion for local moment formation is precisely the same as the one obtained by applying the HF criterion to this very special case of the Wolff model.

Thus the result in Eq. (14) is consistent with previous work, provided that one takes care to note the physical content of the approximations in the present and earlier work. Equation (14) provides a description of the magnetic properties of alloys in which exchange-enhancement effects in the host matrix are important. However, all single-particle scattering effects contained in the one-electron potential V_{HF} have been ignored. Including a finite V_{HF} complicates the problem in a nontrivial way when U_0 is finite, since it does not appear to be possible to solve in a general way the self-consistent equations that result.

IV. CALCULATION TO THE IMPURITY CONTRIBUTION TO THE ELECTRICAL RESISTIVITY

We need the function $A(\mathbf{q},\Omega)$ defined in Eq. (5). Since $\chi_r(\mathbf{qq};\Omega-i\epsilon)=\chi_r^*(\mathbf{qq},\Omega+i\epsilon)$,

$$A(\mathbf{q},\Omega)=2i\,\mathrm{Im}\{\chi_r(\mathbf{qq},\Omega+i\epsilon)\}.$$

Now write

$$\chi_0(\mathbf{q},\Omega-i\epsilon)=\chi_R(\mathbf{q},\Omega)-i\chi_I(\mathbf{q},\Omega),$$
$$\bar{\chi}(\Omega-i\epsilon)=\bar{\chi}_R(\Omega)-i\bar{\chi}_I(\Omega).$$

Then

$$A(\mathbf{q},\Omega)=A_0(\mathbf{q},\Omega)+(1/N)A_I(\mathbf{q},\Omega),$$

where $A_0(\mathbf{q},\Omega)=2\chi_I(\mathbf{q},\Omega)$ describes the spin-density fluctuations in the host metal, and the contribution from the impurity center is

$$A_I(\mathbf{q},\Omega)=\delta U\frac{\delta\bar{\chi}_I(\Omega)[\chi_R{}^2(\mathbf{q},\Omega)-\chi_I{}^2(\mathbf{q},\Omega)]+2\chi_R(\mathbf{q},\Omega)\chi_I(\mathbf{q},\Omega)[1-\delta U\bar{\chi}_R(\Omega)]}{[1-\delta U\bar{\chi}_R(\Omega)]^2+\delta U^2\bar{\chi}_I{}^2(\Omega)}. \tag{15}$$

If Ref. 14, it is shown that at low temperatures the contribution to the relaxation rate from the part $A_0(\mathbf{q},\Omega)$ that describes the spin-density fluctuations in the pure metal is given by

$$\left(\frac{1}{\tau_0}\right)=\left(\frac{3}{32}\right)^2\left(\frac{J^2\xi}{\epsilon_s}\right)\left(\frac{v_s\epsilon_d}{v_d\epsilon_s}\right)\left(\frac{kT}{\epsilon_d}\right)^2\beta\mathcal{J}\equiv A_0T^2, \tag{16}$$

where v_s, v_d, ϵ_s, and ϵ_d are the Fermi velocities of the d and s electrons, and Fermi energies measured from the bottom of the band. Both the s and d bands have been assumed parabolic to obtain the result in this form.

The quantity $\mathcal{J}$ is a temperature-independent, dimensionless number given by

$$\mathcal{J}=\int_{-\infty}^{+\infty}\frac{dydy'\exp(y-y')}{\exp(y-y')-1}\times\frac{(y-y')}{[\exp y+1][1+\exp(-y')]} \tag{17a}$$

and

$$\beta\cong\int_0^{\eta_M}\frac{\eta^2|F(k_s\eta)|^2}{[1-U_0\Gamma_R(k_s\eta,0)]^2}d\eta, \tag{17b}$$

where $\Gamma_R(k_s\eta,0)$ is the real part of the free-electron susceptibility introduced in Eq. (10). The quantity β is larger the closer the metal is to the instability criterion $\Gamma_R(0,0)=1/U_0$.

The expression for $A_I(\mathbf{q},\Omega)$ may be simplified considerably. First, at low temperatures, only very small values of the frequency Ω will enter, since the Bose-Einstein factor will cut off the integral over energy transfer at $\Omega(k,k')\approx k_BT$. Also, $\bar{\chi}_I(\Omega)$ and $\chi_I(\mathbf{q},\Omega)$ vanish when $\Omega=0$. The denominator in the expression for $A_I(\mathbf{q},\Omega)$ may then be replaced by $[1-\delta U\bar{\chi}_R(0)]^{-2}\equiv\alpha^2$. Also, in the numerator of Eq. (15), one may neglect $\chi_I{}^2(\mathbf{q},\Omega)$ compared to $\chi_R{}^2(\mathbf{q},\Omega)$, since $\chi_I{}^2(\mathbf{q},\Omega)$ is proportional to Ω^2 for very small Ω^2, and $\chi_R{}^2$, and $\chi_R{}^2(\mathbf{q},0)$ is finite. Then

$$A_I(\mathbf{q},\Omega)\cong\delta U\alpha^2[\delta U\bar{\chi}_I(\Omega)\chi_R{}^2(\mathbf{q},0)+(2/\alpha)\chi_R(\mathbf{q},0)\chi_I(\mathbf{q},\Omega)]. \tag{18}$$

In the second term of Eq. (18), α will be large compared to unity when the impurity is almost magnetic. Because of the large exchange enhancement in the host Pd matrix, $\chi_R(\mathbf{q},0)$ will be strongly peaked for small values of $\mathbf{q}$. This will result in an integral [similar to Eq. (17a)] over wave-vector transfer in the impurity contribution to the relaxation rate strongly peaked at small $\mathbf{q}$. The first term, in which the exchange-enhancement factor for the host appears squared for small $\mathbf{q}$, will then give the dominant contribution to the integral.

Thus we assume $A_I(\mathbf{q},\Omega)$ well approximated by

$$A_I(\mathbf{q},\Omega)=(\delta U\alpha)^2\bar{\chi}_I(\Omega)\chi_R{}^2(\mathbf{q},0).$$

In the Appendix it is suggested that $\bar{\chi}_I(\Omega)$ may be approximated by (for $\Omega\ll\epsilon_F$);

$$\bar{\chi}_I(\Omega)=(n_d\alpha_0{}^2/4\epsilon_dv_dq_B)\Omega,$$

where $\alpha_0=[1-U_0N(0)]^{-1}$ is the HF exchange-enhancement factor for the host, n_d is the number of d holes per atom, and $q_B=2\pi/a$, where a is the lattice constant.

The expression for $A_I(\mathbf{q},\Omega)$ may now be inserted into Eq. (3) to obtain the impurity contribution to the electrical resistivity. We shall assume that the one impurity contribution may be multiplied by the number of impurities N_I to obtain the contribution to the resistivity from a finite concentration $c=(N_I/N)$ of impurities. After a bit of manipulation one finds the total relaxation time may be written in the form

$$1/\tau=1/\tau_0+1/\tau_I=A(c)T^2,$$

where

$$A(c)=A_0\{1+[(\delta U/U_0)\alpha]^2\gamma c\},$$

with

$$\gamma=\frac{2}{3\pi}\frac{a\epsilon_s}{\hbar v_s}n_d\alpha_0{}^2\frac{\beta_I}{\beta}$$

and

$$\beta_I=\int^{\eta_M}\frac{\eta^3|F(k_s\eta)|^2}{[1-U_0\Gamma_R(k_s\eta,0)]^2}d\eta.$$

We may compare β_I with β if the function Γ_R in the integrand is approximated by the form employed in the Appendix, and the form factor in the integrand is ignored. Employing $\eta_M = 2k_d/k_s$, one expects with these approximations that $\beta_I \cong \frac{3}{2}(k_d/k_s)\beta$. For the cylindrical hole surfaces in the d band of Pd, $4k_d \cong q_B$.[17] Finally, the parameter γ is estimated to be

$$\gamma \cong (\tfrac{1}{4}n_d)\alpha_0^2 .$$

For the Pd matrix, one has $n_d \cong 0.3$ holes/atom, and $\alpha_0 \cong 10$. Then $\gamma \cong 7.5$.

It is now possible to compare the results obtained above to the experimental measurements of Schindler and Rice. For $c < 1\%$, the coefficient of the T^2 term varies in roughly a linear fashion with concentration. From the data,

$$(1/A)dA/dc \approx 750 \quad \text{for} \quad c < 1\% .$$

Evidently, one may then fit the data with the choice

$$(\delta U/U_0)\alpha \approx 10 .$$

This seems to be a reasonable value of this parameter, since one must have $\alpha \gg 1$ if our conjecture about the almost magnetic character of the impurity center is correct.

An independent estimate of the parameter $\delta U\alpha/U_0$ may be obtained from susceptibility data on the dilute *Pd*Ni system. The present theory may be used to obtain an expression for the slope of the concentration-dependent susceptibility at $c = 0$:

$$\frac{1}{\chi}\frac{d\chi}{dc}\bigg|_{c=0} = \left(\frac{\delta U}{U_0}\alpha\right) U_0\chi(0) . \qquad (19)$$

From the data of Shaltiel *et al.*, one finds

$$(1/\chi)d\chi/dc \cong 115 .$$

In the above analysis, we have assumed $[1 - U_0 N(0)]^{-1} \cong 10$, so that $U_0\chi(0) \cong 9$. The susceptibility data then lead us to estimate that

$$(\delta U/U_0)\alpha \cong 13 .$$

Considering the many crude approximations made in the computation of the electrical resistivity, we believe that the agreement between the value of the parameter $\delta U\alpha/U_0$ deduced from the resistivity data and the value deduced from the susceptibility data to be quite good.

The change in the coefficient A is predicted to depend linearly on the change in the susceptibility:

$$\frac{A(c)}{A(0)} = 1 - \frac{\gamma}{U_0\chi(0)}\left(\frac{\delta U}{U_0}\alpha\right) + \frac{\gamma}{U_0\chi(0)}\left(\frac{\delta U}{U_0}\alpha\right)\frac{\chi(c)}{\chi(0)} .$$

If one assumes $\gamma = 7.5$, $U_0\chi(0) = 0.9$, and $(\delta U/U_0)\alpha = 10$, then we find

$$A_{th}(c) = -190 + 32\chi(c) ,$$

where χ is measured in emu/gram and A in units of 10^{-6} $\mu\Omega$ cm/°K^2. Schindler and Rice find the experimental result $A_{\text{expt}}(c) = -130 + 22\chi(c)$, in fair agreement with the value deduced from the theory. [In obtaining the numerical expression for $A_{\text{expt}}(c)$, we have used the data only for the points $c = 0$, 0.5, and 1.0%. Consequently, we obtain a line with a slope steeper than the line in the plot of Ref. 7, where the best line was drawn through the four points $c = 0$, 0.5, 1, and 1.66%. The resistivity data indicate clearly that impurity-impurity interactions are important at $c = 1.66\%$, so we compare our low-c theory only with the data for $c \leq 1\%$.]

We conclude by estimating the fractional change $\delta U/U_0$ in the intra-atomic Coulomb integral required to fit the data. In Ref. 11, the value of the ratio $\bar{\chi}_R(0)/\chi(0)$ was determined to be roughly $\frac{1}{5}$ for the Pd matrix. Then if $(\delta U/U_0)\alpha = 10$, we may determine $\delta U/U_0$;

$$10 = \frac{\delta U}{U_0}\frac{1}{1 - \delta U\bar{\chi}_R(0)} = \frac{\delta U}{U_0}\left[1 - \frac{\delta U}{U_0}\left(\frac{\bar{\chi}_R(0)}{\chi(0)}\right)(U_0\chi(0))\right]^{-1} .$$

With $\bar{\chi}_R/\chi(0) = \frac{1}{5}$, and $U_0\chi(0) = 9$, one finds

$$\delta U/U_0 \approx \tfrac{1}{2} .$$

This estimate indicates that a reasonable value of δU allows the susceptibility and resistivity data to be fitted in a plausible manner.

In conclusion, we consider that the present theory is able to give a good semiquantitative account of Schindler and Rice's resistivity measurements and the susceptibility of *Pd*Ni alloys for low concentrations.

V. CONCLUSION

We have used a simple model to describe isoelectronic alloys such as *Pd*Ni alloys. We have taken into account only a change in the strength of the intra-atomic Coulomb repulsion of the impurity cell. This is quite reasonable since pure Ni is ferromagnetic while pure Pd is nonmagnetic, and the 3d Ni orbitals have a smaller spatial extension than the 4d orbitals of Pd.

This local increase of intra-atomic Coulomb potential enhances the susceptibility of the alloy around the impurity cell. The fluctuations of the magnetization have locally a larger amplitude, at lower frequencies, than in pure Pd. This effect is capable of explaining the large increase in the T^2 form of the resistivity of *Pd*Ni upon alloying. The T^2 law is just an electron-electron scattering law and reflects the fact that the magnetic fluctuations have a temperature-dependent amplitude, and that the scattering processes are inelastic. The change in intra-atomic Coulomb integral is of course also capable of explaining the large increase of the uniform static susceptibility of Pd upon alloying with Ni.

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[17] F. Gautier, thesis, Universite de Paris (Orsay), 1964 (unpublished).

It should be pointed out that in view of the discussions[18] on the nature of the interactions responsible for magnetism in transition metals, the success of our simple model seems to lend support to the idea of the importance of intra-atomic Coulomb interactions at least for Pd and Ni metals. No interatomic interaction other than the transfer terms that give rise to the single-particle bandwidth have been assumed.

Finally, it appears[19] that *Pd*Ni alloys exhibit a large variation of specific heat with concentration. The variation is linear in concentration, as we expect it to be below $c=1\%$. This is an important indication that the theory of specific heat has to take magnetic fluctuations into account in a way similar to the Berk-Schrieffer[3,4] treatment of pure metals. Calculations on this subject will be reported in a short time.

Also, we would like to point out that similar effects are expected to occur in alloys such as *Pt*Ni, *Rh*Co, *Ru*Fe, etc., which are isoelectronic alloys where Ni, Co, and Fe impurities are nonmagnetic at low concentrations. In Co and Fe alloys, the importance of Hund's rule coupling might bring about different behavior from that in Ni alloys.

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APPENDIX

The purpose of the Appendix is to provide an approximate expression for the quantity $\bar{\chi}_I(\Omega)$ required for the resistivity computation. One has

$$\bar{\chi}_I(\Omega)=\frac{1}{N}\sum_{\mathbf{q}}\frac{\Gamma_I(\mathbf{q},\Omega)}{[1-U_0\Gamma_R(\mathbf{q},\Omega)]^2+U_0^2\Gamma_I^2(\mathbf{q},\Omega)}, \qquad (\mathrm{A1})$$

where the sum is over the first Brillouin zone. Recall that $\Gamma_R(0,0)=N(0)$, the density of states at the Fermi level. We shall have to be satisfied with a very crude approximation to the integrand, since the Fermi surface of Pd is very complicated. It is believed[17,20,21] there are 12 roughly cylindrical pockets of holes located on the square faces of the fcc Brillouin zone. We denote the radius of one of the cylinders by k_d. For a degenerate gas of free electrons with a Fermi surface of radius k_F, the function $\Gamma_R(\mathbf{q},\Omega)$ for small Ω varies slowly with q for $q<2k_F$ and falls off rapidly to zero when $q>2k_F$. Similarly, the response of the d electrons in Pd presumably will fall off rapidly when $q>2k_d$, although $\Gamma_R(\mathbf{q},\Omega)$ will presumably depend on the direction of $\mathbf{q}$. We shall ignore the anisotropy, and further suppose that for $\Omega\ll\epsilon_d$, the Fermi energy of the d electrons,

$$\begin{aligned}\Gamma_R(\mathbf{q},\Omega)&=N(0)\,, & q&<2k_d\\ &=0\,, & q&>2k_d\,.\end{aligned}$$

For $\Gamma_I(\mathbf{q},\Omega)$, we use the free-electron approximation

$$\begin{aligned}\Gamma_I(\mathbf{q},\Omega)&=\frac{3}{8\epsilon_d}\frac{\Omega}{v_dq}\,, & 2k_d&>q>\Omega/v_d\\ &=0\,, & &\text{otherwise.}\end{aligned}$$

For small Ω, the factor of $U_0^2\Gamma_I^2(\mathbf{q},\Omega)$ may be neglected in the denominator of Eq. (A1). One then finds

$$\bar{\chi}_I(\Omega)=\frac{3\pi}{W}\frac{k_d^2\alpha_0^2}{\epsilon_dv_d}\Omega\,,\quad \alpha_0=[1-U_0N(0)]^{-1}\,,$$

and W is the volume of the Brillouin zone. In the cylindrical model, the number of d holes/atom is

$$n_d=\frac{12\pi k_d^2q_B}{W}\,,\quad q_B=\frac{2\pi}{a}\,.$$

The approximate expression for $\bar{\chi}_I(\Omega)$ then may be written in the form given by Eq. (18).

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