estimate of 1.58×10^{-8} still appears to be somewhat high.

Very recently, Rice[3] has calculated L_e as a function of the Stoner enhancement factor. His results predict an L_e which increases as enhancement decreases, and approaches a value of 1.02×10^{-8} in the limit where the enhancement factor reaches unity. In the light of this theory, our present results would seem to indicate that enhancement does not contribute to the L_e of pure palladium. For the present, however, this conclusion must be regarded as tentative, for current estimates of the enhancement factor of pure Pd range from 3 to 50.[9]

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INTRA-ATOMIC COULOMB INTERACTIONS AND LOCAL EXCHANGE-ENHANCEMENT EFFECTS IN DILUTE TRANSITION-METAL ALLOYS

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(Received 7 December 1967)

A number of properties of pure transition metals may be interpreted by presuming the value of the intra-atomic Coulomb interaction U between two d electrons in the same unit cell varies from one metal to another in a systematic fashion. In this Letter, we shall discuss a number of striking properties of dilute alloys of $3d$ impurities in isoelectronic $4d$ or $5d$ hosts which can be interpreted by assuming the major effect of the impurity ion is to change the value of U locally.[1]

The purpose of this Letter is to point out that very strong variations with concentration of the electronic specific heat of dilute alloys are predicted by the local exchange-enhancement model we have previously employed[2] to analyze susceptibility and electrical resistivity data on dilute alloys of Ni in Pd. Recent measurements of the specific heat of the Pd-Ni system[3] show a striking, strong dependence of the electronic specific heat on Ni concentration. As Schindler and Mackliet[3] have pointed out, an extension of the uniform-enhancement model[4] to the disordered system obtained by introducing a concentration dependent, spatially averaged exchange-enhancement factor deduced from susceptibility data fails to account for the magnitude and concentration dependence of the effect of alloying on the electronic specific heat of this system.

In this paper we present a discussion of the concentration dependence of the coefficient γ of the term linear in temperature in the specific heat for the case when the host exchange enhancement is unimportant. For this case, the structure of the theory is sufficiently clean that the essential physics is clearly exhibited, and the expression for $\gamma^{-1}d\gamma/dc$ is simple in structure. We apply our model to analyze recent NMR studies of Rh:Co alloys. This enables us to predict the value of $\gamma^{-1}d\gamma/dc$ near $c=0$. The extension of the theory to systems in which exchange enhancement is important in the host is discussed by Englesberg and co-workers.[5]

Consider first the Pd:Ni system. It is now well known that in pure Pd, the intra-atomic Coulomb interactions between the d electrons enhance the static magnetic susceptibility χ by roughly a factor of 10. This implies that in pure Pd, U is nearly large enough to produce a transition to the ferromagnetic state. Associated with the proximity of the system to the instability, one finds that large-amplitude, low-frequency fluctuations in the d-electron spin density fluctuations produce an enhanced value of the specific-heat density of states $n^*(0)$.[4] Band calculations[6] indicate that $n^*(0)/n(0) \simeq 2$.

Introduction of a Ni impurity into the system increases U in the Ni cell above the pure-Pd value. The spin polarizability of the matrix and the amplitude of the spin-density fluctuations are then strongly enhanced near the impurity. If only a single impurity is present, then a time-dependent molecular field theory applied to the terms in the Hamiltonian involving U yields an expression for the susceptibility function $\chi(\vec{r}\vec{r}',\Omega)$ of the alloy in the coordinate space form[2]:

$$\chi(\vec{r}\vec{r}',\Omega)=\chi_{\mathrm{Pd}}(\vec{r}-\vec{r}',\Omega)+\Delta U\frac{\chi_{\mathrm{Pd}}(\vec{r},\Omega)\chi_{\mathrm{Pd}}(\vec{r}'\Omega)}{I-\Delta U\chi_{\mathrm{Pd}}(0,\Omega)}, \qquad (1)$$

where $\chi_{\mathrm{Pd}}(\vec{r}-\vec{r}',\Omega)$ is the exchange-enhanced susceptibility of the pure Pd matrix. The second term is the impurity contribution to χ and explicitly exhibits the enhancement of χ near the impurity site $\vec{r}=0$, for $\Delta U>0$. In a previous paper,[2] we have applied the form in Eq. (1) to a discussion of the concentration dependence of the susceptibility of the Pd:Ni system for concentrations $c<1\%$ and the striking concentration dependence of the T^2 term in the low-temperature electrical resistivity observed by Schindler and Rice.[7] We found a semiquantitative account of the data could be given if the parameter $\Delta U\alpha/U_0 \approx 10\text{-}13$, where $\alpha=[1-\Delta U\chi_0(0,0)]^{-1}$. Also, from (1), we obtain $\chi^{-1}d\chi/dc=\Delta Un(0)\alpha_0\alpha$, where $\alpha_0=[1-U_0n(0)]^{-1}$ is the exchange-enhancement parameter associated with the host.

The low-frequency fluctuations in spin density induced by the impurity will contribute to the density of low-lying excited states of the alloy and thus affect the specific heat. We find that when the parameter $\alpha \gg 1$ and $U_0=0$, a simple model gives the slope of a plot of the dependence on concentration c of the coefficient γ of the term in the electronic specific heat linear in the temperature of the form

$$\frac{1}{\gamma}\frac{d\gamma}{dc}=3\frac{n(0)}{n^*(0)}\Delta Un(0)\alpha. \qquad (2)$$

Then combining (1) and (2) we obtain

$$R=\frac{1}{\gamma}\frac{d\gamma}{dc}\Big/\frac{1}{\chi}\frac{d\chi}{dc}=3\frac{n(0)}{n^*(0)}. \qquad (2')$$

In this expression, $n^*(0)$ is the observed specific-heat density of states of the host, including all mass-renormalization effects, and $n(0)$ is the bare-band-structure density of states at the Fermi level. Equation (2′) should be an upper limit for R. When $U_0 \neq 0$, the static susceptibility increases with c like α_0^2. However, $d\gamma/dc$ involves an average of the dynamic susceptibility of the host over $\vec{q}$ and increases more slowly than χ. This point is illustrated by the calculation of Ref. 5. The observed value of $\gamma^{-1}d\gamma/dc$ in Pd:Ni is smaller than Eq. (2′) predicts but is too large to be explained on the basis on one electron theory. For isoelectronic alloys, the impurity scatters weakly and the change in density of states is small. The residual resistivity of Ni in Pd has been found small.[7] Since the contribution to γ exhibited in Eq. (2) is a one-impurity effect, the model produces a linear variation of γ with c.

We should also mention the model does not contain terms with the $T^3\ln T$ temperature correction found in the application of the uniform-enhancement model to nearly ferromagnetic alloys.[3] The first correction to the linear term in the specific heat is proportional to T^3, for our model with $U_0=0$. When $U_0\neq 0$, it has been shown that at small c, the impurity contribution to γ contains a $T^3\ln(T/T_S)$ term, where T_S is the characteristic temperature for spin fluctuations in the host. This term may be comparable with the impurity T^3 term in the range $0.3°\mathrm{K}<T<3.0°\mathrm{K}$.[8] No $T^3\ln T$ term has been found in the specific heat of Pd:Ni alloys, although they have been searched for.[2]

We conclude the discussion of the Pd:Ni system by noting that the local exchange-enhancement picture accounts for a number of properties of this system in a consistent, quantitative fashion. The use of a spatially averaged exchange-enhancement factor fails to provide an adequate account of the effects of alloying on the low-temperature electrical resistivity[2] and the specific heat.

Other evidence of the importance of local exchange-enhancement effects is provided by recent NMR data[9] on the Rh:Co system. Walstedt et al. have measured the Knight shift at the Co site and found that the d-spin contribution to the polarizability of the Co cell is strongly enhanced. They estimated $\alpha=7$. The data[9] on the magnetic susceptibility indicate that $\chi^{-1}(d\chi/dc)=20=\alpha\Delta U\times\chi_0(q=0)$, whence $\Delta U\chi_0(q=0)\simeq 3$. This would indicate that $\frac{2}{3}$ of the increase in magnetic susceptibility resides outside the impurity cell, which seems somewhat large for Rh. It seems possible that a more complete analysis of the data may lead to an increased value for α, from 10 to 15.[10]

Associated with the locally enhanced Knight shift, one expects[11] the core-polarization (cp) part of nuclear relaxation rate T_1 at the Co site to be very short, compared with the T_1 deduced from a model of noninteracting d electrons. Walstedt et al.[9] indeed find that T_1 is shorter by one order of magnitude than the rate which they estimate by adding the rates from relaxation to the s electrons, the spin fluctuations in the d band, and orbital relaxation. While these authors conclude the dominant contribution to $1/T_1$ is of orbital origin, they have neglected the fact that the enhanced d-spin contribution to the Knight shift necessarily implies that the cp part of the relaxation rate is strongly enhanced, as we have previously pointed out.[11] If we assume the local exchange-enhancement factor of Co-Rh is $\alpha \approx 10$-15, then one must multiply the estimate of the cp contribution to $1/T_1$ by α^2. Taking $\alpha \approx 10$-15, we obtain $(T_1T)_{\text{cp}}^{-1} \simeq 10$-20 sec^{-1}, in good accord with experiment. This success of the theory leads us to the conclusion that if our interpretation of the existing data on Rh:Co is correct, the model may be employed to predict $\gamma^{-1}d\gamma/dc$ for this system. Equation (2′) then predicts that

$$\gamma^{-1}d\gamma/dc_{\text{Rh:Co}} = \frac{n(0)}{n^*(0)} \times 3 \times 20 \simeq 60\frac{n(0)}{n^*(0)}.$$

Measurements of the concentration dependence of γ for small c would provide an important check on the picture of the Rh:Co system presented here.

Because $\alpha_{0\text{Rh}} \simeq \frac{1}{10}\alpha_{0\text{Pd}}$, the coefficient A of the T^2 term in the electrical resistivity of pure Rh from s-d scattering should be smaller than that of pure Pd by a factor of roughly 100.[5] At the same time, $A^{-1}dA/dc$ should be much smaller for Rh:Co. We estimate that $A^{-1}dA/dc \approx 6$ for Rh:Co, to be compared with the value 750 observed in Pd:Ni. Indeed, no T^2 term in the electrical resistivity has yet been observed.[12]

Let us now turn to the calculation of $\gamma^{-1}d\gamma/dc$ in the case $U_0 = 0$. We assume a one-band model, with a Hamiltonian of the form $H = H_0 + H_1$, where $H_0 = T$ describes the host material, and $H_1 = \Delta U_0 n_{0\uparrow} \times n_{0\downarrow}$ the perturbation produced by the impurity.[2] $n_{i\sigma}$ is the number of electrons in cell i with spin σ, and T the kinetic energy of the electrons in the host. When the impurity produces a local perturbation in the matrix, the Fourier transform of the imaginary-time, single-particle Green's function assumes the form

$$G(\vec{k}\vec{k}', i\omega_n) = \delta_{\vec{k}\vec{k}'}G_0(\vec{k}, i\omega_n) + \frac{t(i\omega_n)}{N}G_0(\vec{k}, i\omega_n)G_0(\vec{k}', i\omega_n)[1 - t(i\omega_n)F(i\omega_n)]^{-1},$$

where $G_0(\vec{k}, i\omega_n)$ is the propagator in the host

$$F(i\omega_n) = N^{-1}\sum_{\vec{k}} G_0(\vec{k}, i\omega_n),$$

$t(i\omega_n)$ describes scattering of the electron from the impurity. The mean value of the energy is

$$\langle H\rangle = \int \frac{d\epsilon}{i\pi} f(\epsilon - \mu)\sum_{\vec{k}}\{\epsilon + \epsilon(\vec{k})\}\,\text{Im}\,G(\vec{k}\vec{k}, \epsilon + i\eta), \tag{4}$$

$f(x)$ is the Fermi factor, $G(\vec{k}\vec{k}, \epsilon + i\eta)$ is the analytic continuation of Eq. (4) off the imaginary axis to just above the real axis in the energy plane, and μ is found from

$$N = \int \frac{d\epsilon}{i\pi} f(\epsilon - \mu)\sum_{\vec{k}}\text{Im}\{G(\vec{k}\vec{k}, \epsilon + i\eta)\}. \tag{5}$$

We shall see that when the impurity center is almost magnetic, in the sense that $\alpha \gg 1$, then the real part of $t(\epsilon + i\eta)$, $t_{\text{Re}}(\epsilon)$, varies rapidly near the Fermi energy over a range $\Delta\epsilon_s$ that satisfies $k_BT \ll \Delta\epsilon_s \ll \epsilon_F$ in the temperature region of interest. Since $\Delta\epsilon_s \gg k_BT$, the integrals over the Fermi factors may be expanded in powers of k_BT in the standard manner. Because of the rapid variation of $t_{\text{Re}}(\epsilon)$ near μ, the dominant terms in $\langle H\rangle$ of order T^2 will be those proportional to $t_{\text{Re}}' = (\partial t_{\text{Re}}/\partial\epsilon)$. Before proceeding, we need an explicit form for the function $t(\epsilon)$. First, consider the inelastic scattering of an electron from the fluctuations in the transverse component of spin density. The t matrix may be found by summing the diagrams indicated in the second line of Fig. 1. By standard methods, one finds

$$t(z)=\Delta U\int\frac{d\epsilon' d\epsilon''}{(i\pi)^2}\,\frac{\mathrm{Im}\{F(\epsilon')\}\,\mathrm{Im}\{\Gamma(\epsilon'')\}}{\epsilon'-\mu+\epsilon''-z}\,[f(\epsilon'-\mu)+n(\epsilon'')],$$

where $n(\epsilon'')=[\exp(\beta\epsilon'')-1]^{-1}$, and $\Gamma(z)=1/[1-\Delta U\chi_0(0,z)]$, with

$$\chi_0(0,z)=(1/N)\textstyle\sum_{\vec{q}}\chi_0(\vec{q},z), \qquad (6)$$

where $\chi_0(\vec{q},z)$ is the dynamic susceptibility of the host.

We first examine the term containing the Fermi factor. The ϵ'' integration may be done by using a Kramers-Kronig relation to give

$$t^{(F)}(z)=\Delta U\int d\epsilon' f(\epsilon'-\mu)\,\mathrm{Im}\{F(\epsilon')\}[1-\Delta U\chi_0(0,z-\epsilon')]^{-1}. \qquad (7)$$

When the center is nearly magnetic, $1-\Delta U\chi_0(0,0)\equiv\alpha^{-1}\ll 1$, so that for $z=\epsilon+i\eta$, a large contribution to the integral in Eq. (7) comes from values of $\epsilon'\approx\epsilon$. We assume that this region dominates in the integral, and replace the denominator by a form valid for small $(\epsilon-\epsilon')$: $1-\Delta U\chi_0(0,\epsilon-\epsilon'+i\eta)=\alpha^{-1}+i\pi\Delta U n_0^{\,2}(\epsilon-\epsilon')$. With this approximation, one may easily integrate Eq. (7) at $T=0$ to find at ϵ_F $(\partial t_\mathrm{Re}^{(F)}/\partial\epsilon)=-\Delta U n_0\alpha$ and $t_\mathrm{Re}^{(F)}=(2n_0)^{-1}$, while $(\partial t_\mathrm{Im}^{(F)}/\partial\epsilon)=0$. Thus $t_\mathrm{Re}^{(F)}(\epsilon)$ varies rapidly near ϵ_F over an energy range $\Delta\epsilon_s\approx(n_0^{\,2}\Delta U\alpha)^{-1}$. We have also examined the term in $t(\epsilon)$ involving the Bose factor; however, this quantity does not vary rapidly near ϵ_F for parameters in the range of interest. Thus, we consider only the factor $t^{(F)}$ of $t(\epsilon)$ discussed above in the computation of $\gamma^{-1}d\gamma/dc$. Furthermore, we only consider the term first order in t, since the total scattering amplitude is small in isoelectronic alloys.

It is a straightforward matter to solve for the impurity contribution to $\langle H\rangle$ employing Eqs. (4) and (5) in the framework of the approximation scheme just described. It is important to realize that there is a term proportional to N^{-1} and the local exchange-enhancement parameter α in the temperature-dependent part of μ, and a term proportional to $T^2\alpha$ from the temperature-dependent part of $t_\mathrm{Re}^{(F)}(\epsilon)$. In addition, one must include the diagrams illustrated in the lower line of Fig. 1, which describe scattering of an electron from longitudinal fluctuations in spin density. The result of Eq. (2) then follows.

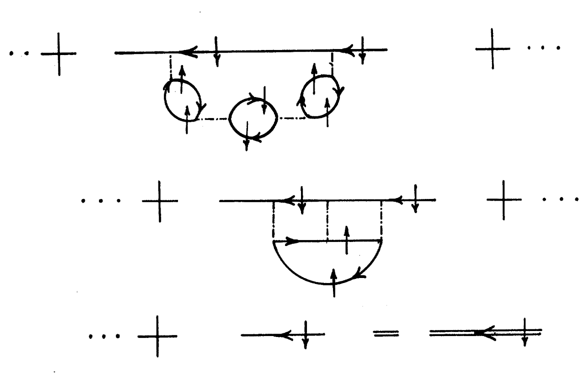

FIG. 1. Diagrams included in the single-particle Green's function. Dotted lines represent the interaction ΔU.

The theory presented here contains no hint of the Kondo effect. It is equivalent to a Fermi-liquid theory in which the strength of the two-body interaction varies in space. For example, notice that all of the experimental quantities are given by simple analytic functions of ΔU. The model gives a good account of a number of observed properties of $4d$ and $5d$ transition-metal hosts containing nonmagnetic $3d$ impurities. One may inquire whether the same data could be explained in a complete way by assuming that the impurity is in a condensed Kondo state with the Kondo temperature $T_\mathrm{K}\gg T$. We feel the T^2 variation of the impurity contribution to the resistivity of the Pd:Ni system, and the linear variation with T of the impurity contribution to the specific heat at low T offer strong evidence that these alloys may be described as "normal" Fermi systems.

We conclude that a measurement of $\gamma(c)$ in dilute Rh:Co alloys would be of great interest, since our analysis of the NMR data has led us to predict $\gamma^{-1}d\gamma/dc\sim 60n/n^*$ for low c. Also, specific heat, susceptibility, and NMR data on other dilute isoelectronic alloys such as Pt:Ni, Ir:Co, Ru:Fe, Os:Fe, Re:Mn, etc., would help to check the validity of our hypothesis on the ground state in these alloys, and serve to determine the value of the parameters α, ΔU, and $n^*(0)/n(0)$. Orbital degeneracy and Hund's rule coupling may bring about qualitative changes which would shed light on these effects.

We would like to thank Dr. A. I. Schindler and R. Tournier for communication of their data prior to publication, and R. Tournier for helpful comments.

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†Work supported by the Air Force Office of Scientific Research, Office of Aerospace Research, U. S. Air Force, under Grant No. 1080-66.

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THEORY OF THE LOW-TEMPERATURE PROPERTIES OF NEARLY FERROMAGNETIC DILUTE ALLOYS

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(Received 16 February 1968)

The temperature dependence of the low-temperature specific heat of alloys of the class Pd:Ni is calculated using a localized exchange model in the dilute limit. An approximate extension of the theory leads to a singular mass enhancement at the ferromagnetic critical concentration and a strong $T^3 \ln T$ dependence in this region.

Recent measurements by Schindler and Mackliet[1] and by Chouteau et al.[2] have shown a striking increase in low-temperature electronic specific heat as small amounts of Ni are alloyed with Pd. While this effect seems closely related to the mass-enhancement effects in uniform systems[3-5] with large exchange enhancement, it has been pointed out by Lederer and Mills[6,7] that relative localization of exchange interactions on the Ni atoms in the alloy will lead to important changes in the details of the mass-enhancement mechanism.

In the first part of the present communication we report an investigation of the detailed temperature dependence of the specific heat predicted by the localized-exchange-enhancement model. We show that the dominant deviations, in the single-impurity limit, from linear temperature dependence vary as $T^3 \ln T$ and are similar in magnitude to those predicted for pure Pd. There is also a T^3 term as suggested by Lederer and Mills which, however, is small compared with the T^3 term due to phonons.

Because the Pd:Ni system becomes ferromagnetic for a rather low critical concentration, c_{crit}, in the region of 2.2%, deviations from the single-impurity limit may be expected to occur at relatively low concentrations of Ni. In the second part of the present work we give an approximate treatment of the exchange-enhanced