bring about qualitative changes which would shed light on these effects.

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

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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

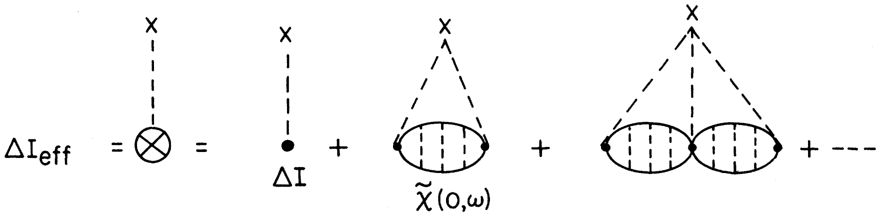

FIG. 1. Contributions to ΔI_{eff} for a single impurity.

dynamical susceptibility of the more concentrated alloy which can be used through the critical concentration region. We use this to estimate the concentration at which the single-impurity limit may be expected to break down, and to explore the mass enhancement in the critical region. We find that both m^*/m and the coefficient of the $T^3 \ln T$ term become singular for alloys with $C \rightarrow C_{\text{crit}}$. However, the range of temperatures over which the $T^3 \ln T$ dependence may be expected to hold may become very small in this region. We start from a localized enhancement model which should apply to a class of alloys of isoelectronic transition metals such as Pd:Ni, Rh:Co, which do not appear to form local moments.[1,2,8] For convenience we will refer to the Pd:Ni case for which we take

$$H_{\text{alloy}} = H_{\text{Pd}} + \Delta I \sum_{\text{Ni sites}} n_{i\uparrow} n_{i\downarrow}, \tag{1}$$

where the sum is over lattice sites occupied by the nickel atoms and

$$H_{\text{Pd}} = \sum \epsilon_p c_{p\sigma}^{\dagger} c_{p\sigma} + I \sum_{\text{all sites}} n_{i\uparrow} n_{i\downarrow} \tag{2}$$

is the Hamiltonian for pure Pd in a one-band model. In the single-impurity limit, corrections to the retarded nonlocal susceptibility $\tilde{\chi}_{\text{Pd}}(\vec{r}-\vec{r}', \omega)$ (where tilde denotes $\vec{r}$-space functions) will occur because of multiple scattering from a single Ni site (placed at the origin). This may be evaluated by summing the diagrams in Fig. 1 to be of the form given by Lederer and Mills,[6,7]

$$\tilde{\chi}_{\text{alloy}}(\vec{r}, \vec{r}', \omega) = \tilde{\chi}_{\text{Pd}}(\vec{r}-\vec{r}', \omega) + \tilde{\chi}_{\text{Pd}}(\vec{r}, \omega) \Delta I_{\text{eff}}(\omega) \tilde{\chi}_{\text{Pd}}(-\vec{r}', \omega), \tag{3}$$

where

$$\Delta I_{\text{eff}}(\omega) = \Delta I / [1 - \Delta I \tilde{\chi}_{\text{Pd}}(0, \omega)] \tag{4}$$

and $\tilde{\chi}_{\text{Pd}}(\vec{r}-\vec{r}', \omega)$ is the transform of $\chi_{\text{Pd}}(q, \omega) = \chi^0(q, \omega)/[1 - I\chi^0(q, \omega)]$. For a system in which we assume a local moment has not yet occurred, one has $\Delta I \tilde{\chi}_{\text{Pd}}(0, 0) < 1$. The shift in the thermodynamic potential per Ni atom is obtained in this dilute limit as[9]

$$\Delta \Omega = \int_0^{\Delta I} d(\Delta I') \langle n_{0\uparrow} n_{0\downarrow} \rangle, \tag{5}$$

$$= \frac{3}{2} \frac{2}{\pi} \int_0^{\infty} d\omega [n(\omega) + \tfrac{1}{2}] \operatorname{Im}\{\ln[1 - \Delta I \tilde{\chi}_{\text{Pd}}(0, \omega)]\}, \tag{6}$$

where $n(\omega) = 1/(e^{\beta\omega} - 1)$. Using the low-$q$ expansion of $\tilde{\chi}_{\text{Pd}}(q, \omega)$,[4] we have

$$\tilde{\chi}_{\text{Pd}}(0, \omega) = \frac{1}{2\pi^2} \int_0^{2p_{\text{F}}} q^2 dq \frac{N(0)}{(\kappa_0^2 + \bar{I}\sigma q^2/12) - i\frac{1}{4}\pi \bar{I}\bar{\omega}/q}, \tag{7}$$

where σ is a range parameter for the host interaction,[10,11] $\bar{I} = IN(0)$, $\kappa_0^2 = 1 - \bar{I}$, $\bar{\omega} = \omega/\epsilon_{\text{F}}$, and $\bar{q} = q/p_{\text{F}}$ leading to

$$\operatorname{Im}\tilde{\chi}_{\text{Pd}}(0, \omega) = \frac{N(0)n_e}{\kappa_0^2} \left\{ \frac{\frac{3}{4}\pi\bar{\omega}}{\kappa_0^2 + \frac{1}{3}\bar{I}\sigma} - \frac{3\pi^3}{256} \frac{\bar{I}^2}{\kappa_0^6} \bar{\omega}^3 \ln\left[1 + \frac{4\kappa_0^4}{(\frac{1}{4}\pi\bar{I}\bar{\omega})^2}\right] \right\}, \tag{8}$$

$$\operatorname{Re}\tilde{\chi}_{\text{Pd}}(0, \omega) = \tfrac{3}{2} N(0) n_e \left\{ \frac{24}{\bar{I}} - \left[\left(\frac{12}{\bar{I}\sigma} \right)^3 \kappa_0^2 \right]^{1/2} \tan^{-1}\left[2 \left(\frac{\bar{I}\sigma}{12\kappa_0^2} \right)^{1/2} \right] \right\} + O(\omega^2), \tag{9}$$

where $n_e = N_e =$ No. of electrons/atom. Defining a localized-enhancement parameter $1/\eta$ through

$$\Delta\bar{I}_{\text{eff}}(\omega=0)=\frac{N(0)\Delta I}{1-\Delta I\tilde{\chi}(0,0)}=\frac{\kappa_0^2}{\eta}, \tag{10}$$

one has from (3) in the single-impurity limit

$$\frac{1}{\chi_{\text{Pd}}}\frac{d\chi_{\text{alloy}}}{dc}(q=0,\omega=0)=\frac{\Delta\bar{I}_{\text{eff}}(0)}{\kappa_0^2}=\frac{1}{\eta}. \tag{11}$$

From the experimental data,[1,2] one finds $1/\eta \cong 87$. Inserting (8) and (9) into (6) and calculating to $O(T^2)$ with the coefficient of T^2 to leading order in $(1/\eta)^3$, we find

$$\frac{\Delta C_v}{C_v^{\;0}}=\frac{3c}{2\eta}\left\{\left(\kappa_0^{\;2}+\frac{\bar{I}\sigma}{3}\right)^{-1}+\frac{6\pi^2}{5}\frac{\bar{I}}{\kappa_0^{\;2}}\left[\frac{T}{T_s^{\;\text{Pd}}}\right]^2\ln\left[\frac{T}{T_s^{\;\text{Pd}}}\right]-\frac{9\pi^4}{20}n_e^{\;2}\left[\frac{T}{\eta T_{\text{F}}}\right]^2\left(\kappa_0^{\;2}+\frac{\bar{I}\sigma}{3}\right)^{-3}\right\}, \tag{12}$$

where

$$T_s^{\;\text{Pd}}=\frac{4\kappa_0^{\;2}}{\pi\bar{I}}T_{\text{F}},\quad C_v^{\;0}=\frac{2\pi^2}{3}N(0)k_{\text{B}}^{\;2}T,$$

and c is the concentration. It is to be noted that the $T^2\ln T$ dependence results from the logarithmic form of the local palladium susceptibility given in (8). Using the observed value,[1,2]

$$\left(\frac{m}{m^*}\right)_{\text{Pd}}\frac{\Delta C_v}{C_v^{\;0}}=\frac{1}{\gamma_{\text{Pd}}}\frac{\partial\gamma_{\text{alloy}}}{\partial c}\cong 15. \tag{13}$$

$\kappa_0^{\;2} \cong \frac{1}{10}$ and (12) thus gives a value of σ of order 13. The corresponding value for pure palladium is of order 6.[10] The discrepancy between these values may be associated with changes in the range of the exchange interaction in the region of the impurity atom.

The $T^2\ln T$ term in (12) is precisely that in pure palladium multiplied by $3c/\eta \cong 2.7$ for 1% alloy. This suggests that this term might be observable under conditions (at sufficiently low temperatures) where it would be observable for pure Pd. The magnitude of the T^3 term is predicted to be

$$\frac{1}{\gamma}\frac{\partial\gamma}{\partial c}=15[1-0.85\times10^{-3}(T\,^\circ\text{K})^2]. \tag{14}$$

(However, the T^2 term depends on σ^3, and so cannot be predicted very accurately.) This leads to a correction $C_v^{\text{alloy}}/T=\gamma+(\beta_{\text{Pd}}-\Delta\beta)T^2$ in the alloy specific heat, where $\Delta\beta/\beta_{\text{Pd}}=1.3\,\%$ at $c=1\,\%$. This change is too small to be seen in the published data.[1]

In order to estimate the properties of the localized exchange model beyond the single-impurity limit, we introduce an approximate treatment of the dynamic susceptibility for the many-impurity system in which the one-impurity scattering diagrams of Fig. 1 are repeated at successive Ni sites in the alloy as shown in Fig. 2. All interference between scattering at different sites is neglected. An

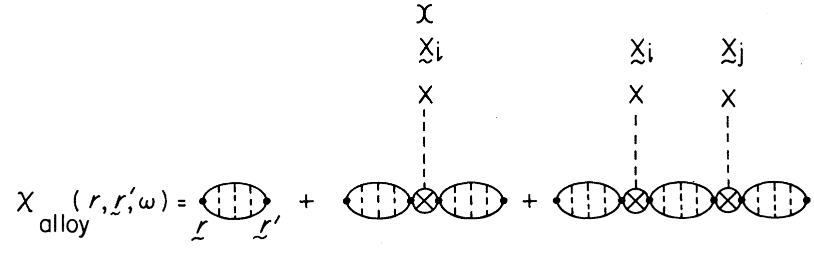

FIG. 2. Contributions to $\tilde{\chi}_{\text{alloy}}$. In the ensemble average over impurity positions $\vec{x}_i, \vec{x}_j, \cdots$, only terms in which $x_i \neq x_j$, etc., are included.

ensemble average over all possible Ni positions (without correlations) is taken leading to an integral equation for the ensemble-averaged susceptibility

$$\tilde{\chi}_{\text{alloy}}(\vec{r}-\vec{r}\,',\omega)=\tilde{\chi}_{\text{Pd}}(\vec{r}-\vec{r}\,',\omega)+\frac{c}{\text{Vol}}\int d^3\vec{r}\,''\,\tilde{\chi}_{\text{Pd}}(\vec{r}-\vec{r}\,'',\omega)\Delta I_{\text{eff}}(\omega)\tilde{\chi}_{\text{alloy}}(\vec{r}\,''-\vec{r}\,',\omega), \tag{15}$$

with solution

$$\chi_{\text{alloy}}(q,\omega)=\frac{\chi_{\text{Pd}}(q,\omega)}{1-c\Delta I_{\text{eff}}(\omega)\chi_{\text{Pd}}(q,\omega)}. \tag{16}$$

At q and $\omega=0$, this leads to a value for the critical concentration [at which $\chi_{\text{alloy}}(0,0)=\infty$] of

$$C_{\text{crit}}=[\Delta I_{\text{eff}}(0)\chi_{\text{Pd}}(0,0)]^{-1}=\eta. \tag{17}$$

Using the above value of η gives $C_{\text{crit}}=1.1\,\%$, which is low compared with the experimental value of $2.2\,\%$.[12] This is not too bad, considering that the approximation (16) neglects all concentration fluctuation effects and is also a random-phase-approximation estimate. In order to obtain a consistent expression for the thermodynamic potential in this approximation, we sum all diagrams of the form shown in Fig. 3. The resulting expression, on averaging over impurity positions and taking care to avoid overcounting, is

$$\Omega_{\text{alloy}}=\Omega_0-\frac{3}{2}\frac{2}{\pi}\int_0^\infty d\omega[n(\omega)+\tfrac{1}{2}]\,\text{Im}\Phi(\omega), \tag{18}$$

where

$$\Phi(\omega)=\frac{c\Delta I\tilde{\chi}_{\text{Pd}}(0,\omega)}{1-\Delta I\tilde{\chi}_{\text{Pd}}(0,\omega)}+c\ln[1-\Delta I\tilde{\chi}_{\text{Pd}}(0,\omega)]+\sum_q\ln\{1-[I+c\Delta I_{\text{eff}}(\omega)]\chi^0(q,\omega)\} \tag{19}$$

and Ω_0 is the thermodynamic potential for the noninteracting gas. We extract the dominant contributions to m^*/m and the $T^3\ln T$ term in the specific heat in the region $C\cong C_{\text{crit}}$. We find

$$\frac{m^*}{m}-1=\frac{9}{2\sigma}\ln\left[1+\frac{\sigma}{3}\left(\frac{1-\kappa_0^2(1-\tilde{c})}{\kappa_0^2(1-\tilde{c})}\right)\right], \tag{20}$$

where $\tilde{c}=C/C_{\text{crit}}$. In the limit $C\to C_{\text{crit}}$, one then has

$$\frac{m^*}{m}\simeq\frac{9}{2\sigma}\ln\left(\frac{1}{C_{\text{crit}}-C}\right).$$

Equation (20) also agrees with the single-impurity limit to order C. The $T^2\ln T$ contribution is given

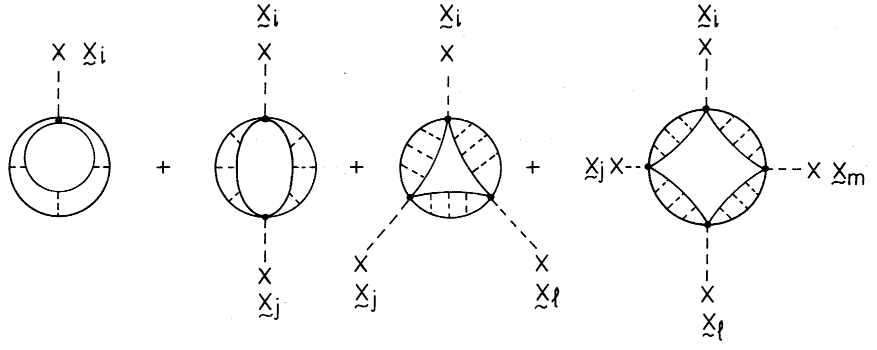

FIG. 3. Contributions to Ω_{alloy}. In the ensemble average the only terms included are those for which scattering from a given impurity takes place at adjacent vertices.

by

$$\frac{\Delta C_v}{C_v^0}=\frac{3\pi^2}{5}\left(\frac{1-\kappa_0^2(1-\bar{c})}{\kappa_0^2(1-\bar{c})}\right)\left(\frac{T}{T_s^{\text{alloy}}}\right)^2\ln\left(\frac{T}{T_s^{\text{alloy}}}\right), \tag{21}$$

which is equivalent to the $T^2\ln T$ term in a bulk material with an effective fluctuation temperature

$$T_s^{\text{alloy}}=\left(\frac{4\kappa_0^2(1-\bar{c})}{\pi[1-\kappa_0^2(1-\bar{c})]}\right)T_{\text{F}}.$$

Numerical calculations[13] of the temperature dependence of the specific heat suggest the $T^3\ln T$ approximation is only valid below about $T_s/100$, so that the above formula may only be expected to hold below about $3(1-\bar{c})$°K. Finally, the next contribution to C_v is of order T^3. The coefficient of this term has a contribution proportional to C which turns out to come entirely from the second term in (19), as the linear term in C from the first and third terms cancels. This contribution is identical to the last term in (12). The term in T^3 in the region of $C\cong C_{\text{crit}}$ of leading order in $1/\eta\equiv 1/C_{\text{crit}}$ comes out to be

$$\left[\frac{\Delta C_v}{C_v^0}\right]_{T^2}=\frac{-27}{10}\frac{\pi^7}{\eta}\left[\frac{\bar{c}\kappa_0^2 n_e}{(\kappa_0^2+\frac{1}{3}\bar{I}\sigma)[\frac{1}{3}\sigma+\kappa_0^2(1-\sigma\nu 3)(1-\bar{c})]}\right]^3\left[\frac{T}{\eta T_{\text{F}}}\right]^2. \tag{22}$$

The following conclusions are drawn from these results: (1) The concentration dependence of the mass enhancement (20) is not very strong, and use of the low-concentration formula leads to errors of ≲25% below $\bar{c}=50\%$. (2) In the low-concentration limit there occurs an additional $T^3\ln T$ contribution to the specific heat of the same order of magnitude as that predicted for pure Pd per 1% of added Ni. The T^3 term in the specific heat is predicted to be in the region of 1.3% of the phonon term for a 1% alloy in this limit. (3) The $T^3\ln T$ term (21) will become increasingly important as $C\to C_{\text{crit}}$. The temperature range over which this term is expected to show up is expected to decrease in this limit, but its possible presence should be kept in mind when examining the experimental data for alloys close to the critical concentration.

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