

A DOUBLE d -BAND MODEL OF TRANSITION METAL: APPLICATION TO MAGNETIC SUSCEPTIBILITY OF EXCHANGE ENHANCED DILUTE PARAMAGNETIC ALLOYS

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The temperature dependence of magnetic susceptibility of exchange enhanced dilute paramagnetic alloys has been analysed in simple approximation. A double d -band model for the host and the modified Zener model for the solute metal have been applied. General discussion and comparison with experimental data is given. Even within rough approximation agreement with experimental results is reasonable.

1. Introduction

A double d -band model of exchange enhanced transition paramagnet has been proposed by the present author and applied successfully in investigation of the temperature dependence of magnetic susceptibility of Pd and Pt [1-3]. Itinerant (d_1) and localized (d_2) d electrons have been assumed to exist and be coupled via exchange interaction when at the same lattice site. As shown in [1] this leads within RPA decoupling scheme to the modification of Coulomb intraatomic interaction between itinerant electrons. The result for dynamical magnetic susceptibility takes on the same form as in the case of single band Hubbard-like model [4] but with the Coulomb parameter in which the role of localized d electrons and their coupling to the itinerant d electrons is contained. To be more reasonable one should include mixing interaction between localized and itinerant electrons. Such a calculus has been performed in [2]. The result is that mixing does not affect static properties significantly. However, its role may be important when dynamical reaction considered (in paramagnetic region). Since we are interested in static susceptibility, mixing interaction will be neglected here.

We want to examine the temperature dependence of magnetic susceptibility of transition metals dilute paramagnetic alloys. Strictly speaking, we are interested in alloys which

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exhibit magnetic susceptibility over the whole range of temperature larger than that of the host. So, PtCr and PdNi fall under discussion when below critical concentration. To be consequent, in conviction that d electrons are neither completely local nor completely itinerant, we assume the applicability of the modified Zener model (MZM) [5] for solute metals. Although it has been found theoretically [6] that Ni atoms almost satisfy the local moment formation criterion (the PdNi system becomes ferromagnetic at small Ni concentration) the situation is not quite clear and the less or more commonly accepted point of view is that Ni does not exhibit the existence of a well-defined localized moment when its concentration in PdNi is lower than critical one (see [7-9] for discussion and references). The applicability of the modified Zener model (MZM) for Ni has not been established [10], however the existence of localized spin on Ni atoms cannot be completely disregarded especially in the vicinity of critical concentration and the parameters which will be used in final result correspond to the case of PdNi alloy.

We believe that our considerations, although being rough, may give some contribution to answer the question: Can we attribute the localized moment to Ni when dissolved in Pd, or not?

2. Magnetic susceptibility in simple approximation

Let us write down the model Hamiltonian

$$H = H_{01} + H_{02} + H_{c1} + H_{c2} + H_{12} + H'_{c1} + H_{1m},$$

where

$$\begin{aligned} H_{01} &= \sum_k \varepsilon_k a_{1k\alpha}^+ a_{1k\alpha} \equiv \sum_{k,\alpha} \varepsilon_k n_{1k\alpha}, \\ H_{02} &= E \sum_{i_A, \alpha} n_{2i_A \alpha}, \\ H_{c1} &= I_1 \sum_{i_A} n_{1i_A \uparrow} n_{1i_A \downarrow} \\ &= \frac{I_1}{N^2} \sum_{\substack{k_1 \sim k_4 \\ i_A}} \exp [i(k_1 - k_2 + k_3 - k_4)r_{i_A}] a_{1k_1 \uparrow}^+ a_{1k_2 \downarrow} a_{1k_3 \uparrow}^+ a_{1k_4 \downarrow}, \\ H_{c2} &= I_2 \sum_{i_A} n_{2i_A \uparrow} n_{2i_A \downarrow}, \\ H_{12} &= -2J \sum_{i_A} S_1(i_A) \cdot S_2(i_A) \\ &= -\frac{J}{2N^2} \sum_{\substack{k_1 \sim k_4 \\ i_A}} \exp [i(k_1 - k_2 + k_3 - k_4)r_{i_A}] \sigma_{\alpha\alpha} \sigma_{\beta\beta'} a_{1k_1 \alpha}^+ a_{1k_2 \alpha'} a_{2k_3 \beta}^+ a_{2k_4 \beta'}, \end{aligned}$$

$$\begin{aligned}
 H'_{c1} &= I'_1 \sum_{i_B} n_{1i_B} n_{1i_B}, \\
 H_{1m} &= -2J' \sum_{i_B} \mathbf{S}_1(i_B) \cdot \mathbf{S}(i_B) \\
 &= -\frac{J'}{N} \sum_{\substack{k_1, k_2 \\ i_B}} \exp [i(\mathbf{k}_1 - \mathbf{k}_2) \mathbf{r}_{i_B}] \sigma_{\alpha\alpha'} \mathbf{S} a_{1k_1\alpha}^+ a_{1k_2\alpha'}.
 \end{aligned}$$

Indices "1" and "2" refer to itinerant and localized d electrons respectively. Localized d_2 electrons which do not couple to give the well-defined localized moment are assumed to exist only in host sites i_A . In solute sites, i_B , the localized spin \mathbf{S} is present. I_1 and I'_1 stand for the intraatomic Coulomb interaction between itinerant electrons in host and solute sites respectively. J and J' denote the exchange coupling constants of itinerant d electrons with localized d electrons of the host (J) and with the impurities spin (J'). a^+ 's and a 's stand for creation and annihilation operators. $\sigma_{\mu\nu}$ are the Pauli matrices.

It is obvious that elegant treatment of such a model Hamiltonian is practically impossible. The simplest approach to an alloy problem lies in restoring of the translational invariance which is absent in starting Hamiltonian. Let us consider for a moment a system which contains only itinerant d_1 electrons coupled by the intraatomic Coulomb interaction. Let us suppose further that the strength of this interaction is not the same in all sites but it takes on the value I_A in some of them and I_B in others. The most simple approximation (so called Virtual Crystal Approximation, VCA, [11]), which brings us back to the translationally invariant system, lies in assumption that in all sites Coulomb parameter is the same one

$$I = (1-c)I_A + cI_B,$$

where

$$c = \frac{N_B}{N}.$$

N_B is the number of B -type sites and N is the total number of sites. More sophisticated methods e. g. ATA or CPA [11] are difficult to be applied for the above model practically.

It must be noted that the introduction of an average intraatomic Coulomb interaction I does not provide an adequate description of a dilute alloy system when transport properties (connected with dynamical reaction) considered. This is due to the fact that the spatial inhomogeneity of the system produces local spin-density fluctuations in the vicinity of the impurity cell with amplitude large compared to the amplitude in the host matrix [12]. However, for our qualitative discussion of static properties this approximation is not quite bad and seems to work reasonably.

In our case the presence of localized d electrons for the host and localized moment for solute metal may be taken into account by the modification of the Coulomb interaction between itinerant electrons, as shown in [1] and [5]. Applying the Green functions

equation of motion method we come to the purely itinerant model of the type mentioned above with

$$I_A = I_1 - J^2 \frac{\Delta N_2}{\omega - J\Delta N_1},$$

$$I_B = I_1' - J'^2 \frac{2\langle S_z \rangle}{\omega - J'\Delta N_1}.$$

$\langle S_z \rangle$ stands for the thermal average of the local spin per site and $\Delta N_{1,2}$ are magnetizations of itinerant and localized electrons. Within our simple approximation we come to the translationally invariant system with the effective Coulomb interaction which is both temperature and energy dependent. It is easy to see [1, 3, 5] that the magnetic susceptibility takes on the form

$$\chi(T) = 2\mu_B^2 \frac{\varrho(T)}{1 - I^{\text{eff}}(T)\varrho(T)},$$

where

$$\varrho(T) = \varrho(\varepsilon_F) \left(1 + \frac{\pi^2}{6} \eta k^2 T^2 \right)$$

$$\eta = \{(\varrho''/\varrho) - (\varrho'/\varrho)^2\}$$

$$I^{\text{eff}}(T) = (1-c) [I_1 + J^2 \beta e^{\beta \tilde{E}} (e^{\beta \tilde{E}} + 1)^{-2}] + c \left[I_1' + J'^2 \frac{2S(S+1)}{3kT + \lambda S(S+1)} \right]$$

$$\tilde{E} = E + I_2 \frac{N_2}{2}, \quad \beta = \frac{1}{kT}.$$

ϱ , ϱ' and ϱ'' are the zeroth, first and second order derivatives with respect to energy of the density of states ϱ evaluated at the Fermi level ε_F . N_2 is the number of localized d_2 electrons per atom.

Some comment on λ must be added. In original work of Bartel [5] λ appears through the self energy term which is taken into account in order to avoid the divergence of the effective Coulomb interaction at $T \rightarrow 0$ (see [5] for details). Since Bartel was not interested in low temperatures the value of λ did not play any essential role in his calculus. We have found nothing better than to treat λ as a parameter. However, its value is restricted in some manner. If an alloy becomes ferromagnetic above some concentration the denominator in the expression for magnetic susceptibility must vanish at $T = 0$ for $c = c_{\text{crit}}$. So, having established I_1 , J , \tilde{E} , I_1' and $\varrho(\varepsilon_F)$, the value of $J'^2 \lambda^{-1}$ can be found. If we put up with the applicability of MZM to Ni then it can be assumed that for PdNi $c_{\text{crit}} = 2.4$ at % Ni. (Even very small amount of magnetic contamination has influence on experimentally determined c_{crit} and the low temperature susceptibility as well [8, 13]). It has been found that $J'^2 \lambda^{-1} \approx 1.69$ eV for $I_1' = 0.9$ eV and remaining parameters the same as before [3].

for pure Pd i.e. $I_1 = 0.68$ eV, $\tilde{E} = -0.0125$ eV, $J = 0.023$ eV, $\rho(\epsilon_F) = 1.3$ eV $^{-1}$ (states per atom spin direction) and the same shape of the model density of states function.

In Fig. 1(a-c) the magnetic susceptibility versus temperature is plotted for concentrations 0.5, 1.0 and 2.0 at % respectively ($S = 1/2$). For each concentration three different values of J' are considered ($J'^2\lambda^{-1}$ is kept to be constant). Pure palladium susceptibility is also presented for comparison. Maximum observed for pure palladium is suppressed

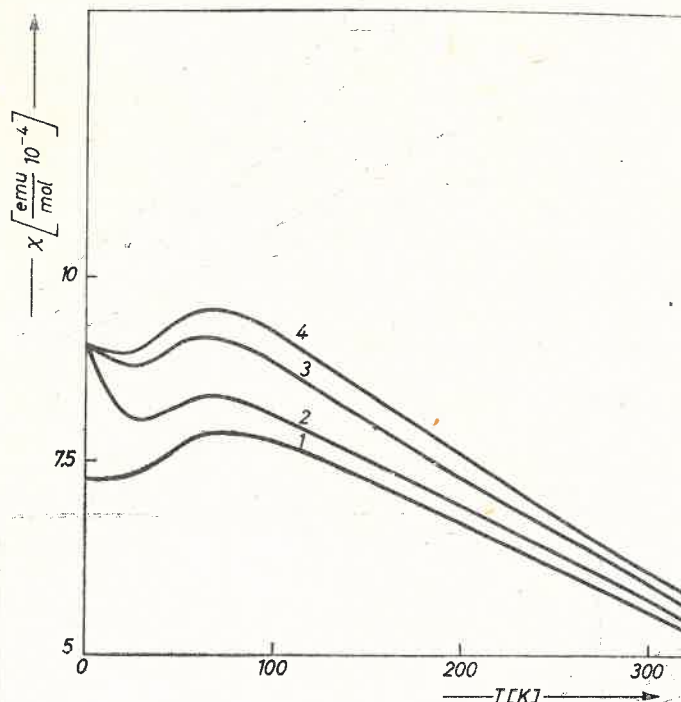


Fig. 1a. PdNi magnetic susceptibility versus temperature. Curve 1 corresponds to the case of pure Pd, curves 2-4 refer to $c = 0.5$ at % Ni and to $J' = 0.104, 0.26$ and 0.39 eV respectively

with increasing concentration of impurities and small shift to lower temperatures can be noted. When J' becomes large the behaviour of magnetic susceptibility is similar to that of pure Pd but its value is greater, depending on concentration. This will be discussed later. Curves corresponding to $J' = 0.26$ eV seem to be representative ones for the behaviour of dilute PdNi alloys.

When one looks at the experimental results of Shaltiel et al. [14] qualitative agreement seems to be good. In our results very small maximum is observed at $T \approx 50$ K for $c = 1$ at % and in this point a discrepancy between experimental data and our theory is present. We suggest that this is due partially to the deficiencies of the theory and partially to the presence of small amount of magnetic contaminations in measured samples (which is evident in [14] when compared with the pure Pd results of Van Dam [8]).

Quantitative agreement with experimental data [14] is reasonable although experimental values are permanently higher and the largest difference is for $c = 2$ at % Ni.

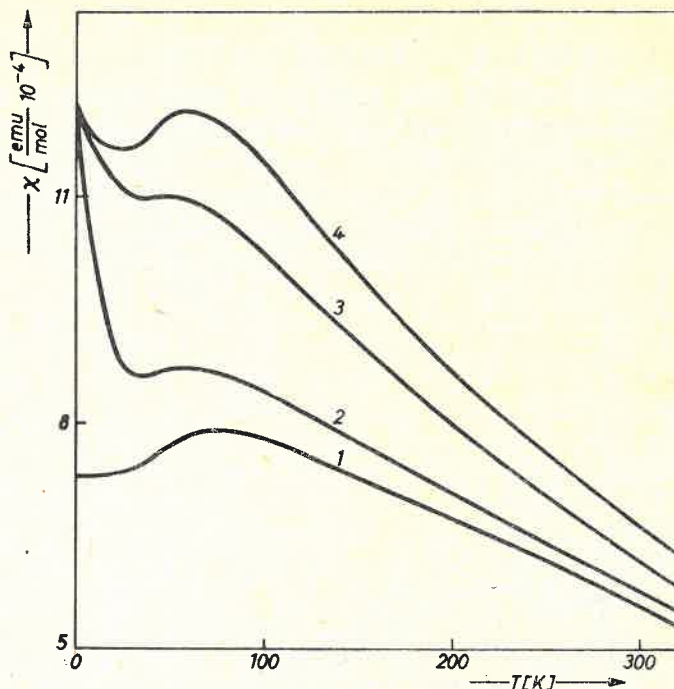


Fig. 1b. PdNi magnetic susceptibility versus temperature. Curve 1 corresponds to the case of pure Pd, curves 2-4 refer to $c = 1.0$ at % Ni and to $J' = 0.091, 0.26$ and 0.39 eV respectively

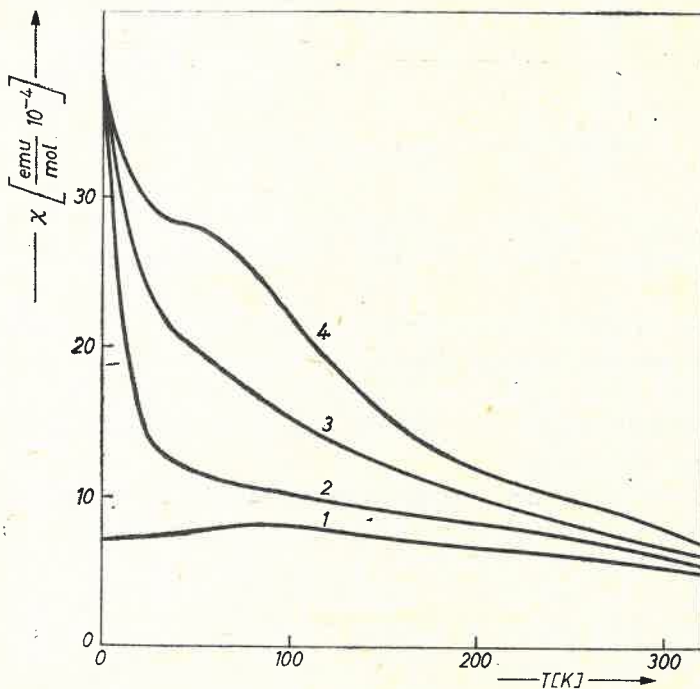


Fig. 1c. PdNi magnetic susceptibility versus temperature. Curve 1 corresponds to the case of pure Pd, curves 2-4 refer to $c = 2.0$ at % Ni and to $J' = 0.13, 0.26$ and 0.39 eV respectively

Since this value is close to the critical one, influence of magnetic contamination is more pronounced (lower than 2.4 at % Ni concentration is expected) and the susceptibility is larger than for "pure" alloy system.

We have applied the model described above to dilute PtCr alloys mainly in order to have direct comparison with experimental data. The results for $I_1' = 0.85$ eV, $J'^2\lambda^{-1} \approx 2.56$ eV and remaining parameters the same as for pure Pt [3] i.e. $I_1 = 0.78$ eV, J

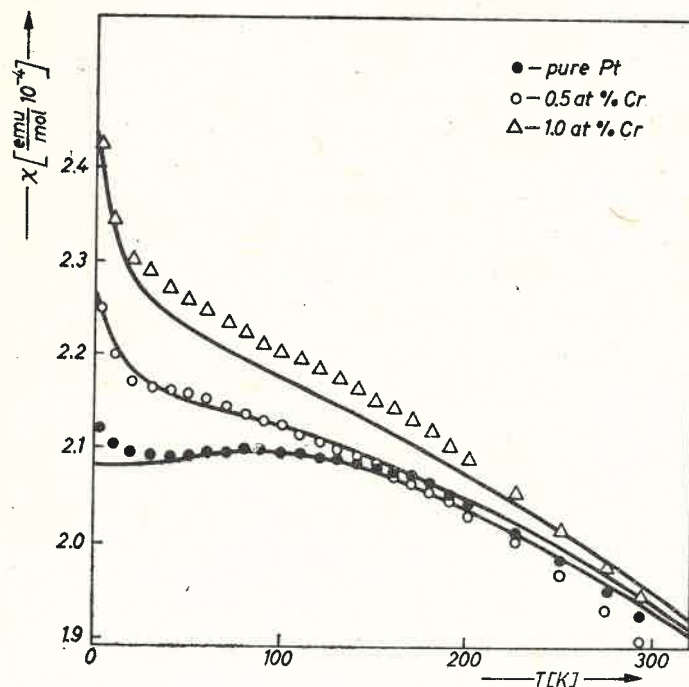


Fig. 2. Magnetic susceptibility of PtCr versus temperature ($J' = 0.145$ eV). Experimental points are those of Van Dam [8]

$= 0.0175$ eV, $\tilde{E} = -0.017$ eV, $\rho(\epsilon_F) = 0.92$ eV $^{-1}$ (states per atom per spin direction) and the same shape of the model density of states function are presented in Fig. 2. Agreement with experimental data of Van Dam [8] seems to be good, although some deviation over wide range of temperature for $c = 1.0$ at % Cr is observed. The reasons for that are supposedly the same as those for PdNi mentioned above. It must be mentioned that the small increase of magnetic susceptibility of pure Pt at low temperatures is due to the presence of magnetic contaminations (Fe). This affects the behaviour of an alloys susceptibility as well.

3. Discussion

Magnetic susceptibility of exchange enhanced dilute paramagnetic alloys of transition metals has been investigated within simple approximation (VCA). Although it is hard to discuss the physical picture in details when such a rough approximation is utilized we

shall try to make some suggestions concerning the mechanism which may give contribution to observed behaviour.

In our opinion, for alloys considered above, the magnetic properties of the host must be well understood if any discussion is wanted to be possible. Many approaches have been used to explain the anomalous temperature dependence of magnetic susceptibility of Pd and Pt (see [15] and [8] for discussion and references). Some of them were less and some more successful but the situation can not be said to be clear. As mentioned above there are reasons for which the d electrons in transition metals can not be treated as being completely local or completely itinerant. Since there is not experimental evidence for existence of localized moments in exchange enhanced paramagnets as Pd and Pt, their properties are usually interpreted in terms of localized spin fluctuations (see [8] and references cited therein). In our model [1-3], when treated within RPA decoupling scheme, the modification of intraatomic Coulomb interaction (which is one of characteristic quantities for localized spin fluctuations) can be interpreted as the effect of indirect coupling between fluctuating moments in lattice sites. We believe that one is not far from the truth if one says that the interaction of such a type gives some contribution to anomalous magnetic and transport properties [3, 16].

Now let us return to the behaviour of magnetic susceptibility when the value of J' increases. When J' increases the same must be expected for λ because $J'^2\lambda^{-1}$ has to remain constant. If $\lambda S(S+1) \gg 3kT$ then impurity contribution to $I^{\text{eff}}(T)$ is very weakly temperature dependent and its role is reduced to the host susceptibility enhancement. So, the dynamical behaviour of localized moment can be disregarded when low concentrations considered. Impurities moments are strongly coupled to the fluctuating moments of the host atoms and the mechanism of fluctuations is an overwhelming one for the behaviour of an alloy. It must be stressed that such an interpretation may be valid only for low concentrations, not in the vicinity of critical one. In our opinion this may give some contribution to answer the question: Can we attribute the localized moment to Ni when dissolved in Pd, or not? Certainly, more accurate treatment of the present model is needed.

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