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1990 J. Phys.: Condens. Matter 2 7309

(http://iopscience.iop.org/0953-8984/2/35/006)

J. Phys.: Condens. Matter 2 (1990) 7309–7315. Printed in the UK

Ferromagnetism and atomic short range order in dilute PdMn alloys

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Received 11 April 1989, in final form 8 March 1990

Abstract. Polarised neutron scattering and magnetisation measurements on dilute **Pd**Mn alloys have been analysed with a local environment model of ferromagnetic interactions and atomic short range order. The analysis allows us to calculate several magnetic properties of **Pd**Mn such as exchange constants of ferromagnetism, range of magnetisation clouds and chemical short range order parameters. Critical temperatures of ferromagnetism, which are low in dilute **Pd**Mn alloys compared to those in other typical giant moment systems such as **Pd**Fe, were calculated using the Monte Carlo simulation method and the results, which included atomic short range order, were compared with experimental data. The comparison shows a good agreement between experimental and calculated values for the concentrations considered.

1. Introduction

Giant moments are usually present in metallic alloys with Fe or Co as the impurities. The solvent is generally a strongly exchange enhanced material such as Pd or Pt. It is known, however, that **Pd**Mn is also a ferromagnet at dilute concentrations of the impurity, with an expected enhancement of the Pd moment. The magnetisation work of Star *et al* (1975), showed that Mn has giant moments of about 7.5 μ_B in Pd with approximately 4.0 μ_B located in Mn and the rest of the giant moment distributed among the atoms. The polarised neutron scattering data of Cable and David (1977), however, do not show these giant moments. It has also been shown that critical temperatures are much lower in **Pd**Mn than in other dilute giant moment systems (Star *et al* 1975).

We have developed a model (Medina and Parra, 1982), that has been applied successfully to other giant moment systems such as **Pd**Fe, **Pt**Fe and **Pt**Co. This model has allowed us to predict critical temperatures, magnetisation and several other magnetic properties of these materials. In this paper we apply this model to study the interesting magnetic behaviour of **Pd**Mn described above, taking into account atomic short range order and assuming a ferromagnetic polarisation of Pd atoms due to the moment of the impurity.

2. Model and analysis

We assume a model where atomic short range order (ASRO) and ferromagnetic Pd–Mn interactions are present at all concentrations, becoming increasingly important as the

0953-8984/90/357309 + 07 $03.50

Mn concentration is augmented. We therefore analysed the neutron scattering results $m(\boldsymbol{K})$ of Cable and David (1977) for **Pd**Mn in the concentration region $0.23 \leqslant c \leqslant 1.91$ at.% Mn with a function:

$$m(\boldsymbol{K}) = M(\boldsymbol{K})S(\boldsymbol{K}) \tag{1}$$

where $S(\boldsymbol{K})$ is the usual ASRO function:

$$S(\boldsymbol{K}) = \sum_{j=0}^{n} Z_j a(R_j)\, \mathrm{e}^{\mathrm{i}\boldsymbol{K}\cdot\boldsymbol{R}_j} \tag{2}$$

where we sum over the n near neighbour shells, with Z_j as the coordination numbers and $a(R_j)$ as Cowley's ASRO parameters. The relation between the ASRO parameters and the probabilities P of finding an impurity atom as a j neighbour of a matrix atom is $a_j = (1 - P_j/c)$, and the number N of Mn atoms as a j neighbour of Pd atoms is given by $N_j = P_j Z_j$.

To analyse the ferromagnetic correlations $M(\boldsymbol{K})$, we apply a magnetic environment model to the polarised neutron scattering data. In this model (Medina and Parra 1982) the moment of a Pd atom at site $\boldsymbol{n}$ is given by

$$\mu_n = \chi_0 h_n \tag{3}$$

where χ_0 is the non-enhanced susceptibility and h_n is a local field given by

$$h_n = b_n - J_{\mathrm{Pd}} \sum_{\delta} \mu_{n+\delta}[1 + (\alpha - 1)P_{n+\delta}]. \tag{4}$$

Here b_n is the external field, J_{Pd} is the exchange constant between Pd atoms, αJ_{Pd} is the exchange constant between Mn atoms and P_n is a site occupation operator.

With no impurities present we obtain from (3) and (4)

$$\chi = \chi_0/(1 - \Gamma) \tag{5}$$

where $\Gamma = J_{\mathrm{Pd}} Z_1 \chi_0$. The parameter Γ is the susceptibility enhancement parameter of Pd and was determined by Parra and Medina (1980) as $\Gamma = 0.947 \pm 0.009$, from experimental neutron data. Using the reported value of $\chi = 6.85\ 10^{-6}$ emu g^{-1} (Verbeek *et al* 1980) and (5), Medina and Parra (1982) obtained $\chi_0 = 3.63\ 10^{-7}$ emu g^{-1} and $J_{\mathrm{Pd}} = (766 \pm 100)$ K.

The Fourier transform of (3) gives us an expression for the magnetisation cloud that can be related to the neutron scattering data:

$$M(\boldsymbol{K}) = \mu_{\mathrm{Mn}} f_{\mathrm{Mn}}(\boldsymbol{K})[\![\alpha/\{\varphi_0[1 - \Gamma F_1(\boldsymbol{K})]\} + (1 - \alpha)]\!] \tag{6}$$

where $F_1(\boldsymbol{K})$ is the first neighbour shell structure factor and φ_0 is given by

$$\varphi_0 = \frac{1}{V_c^*} \int \frac{\mathrm{d}^3 K}{1 - \Gamma F_1(K)} \tag{7}$$

which were determined by Medina and Parra (1982). To be able to use this equation we needed the values of μ_{Mn} for each concentration. These were obtained by fitting the neutron data of Cable and David (1977) with the following equations, valid for polarised neutrons:

$$\underset{K \geqslant 1}{m(\boldsymbol{K})} = \mu_{\mathrm{Mn}} f_{\mathrm{Mn}}(\boldsymbol{K}) - \mu_{\mathrm{Pd}} f_{\mathrm{Pd}}(\boldsymbol{K}) \tag{8}$$

$$\mu = \mu_{\mathrm{Mn}} c + (1 - c)\mu_{\mathrm{Pd}}. \tag{9}$$

Table 1. Values of individual average magnetic moments of Mn and Pd, first neighbour moment perturbations (calculated using (12)) and range parameter of magnetisation clouds in dilute **Pd**Mn alloys.

c (at.% Mn)	μ_{Mn}	μ_{Pd}	φ_1	K_0
0.23	3.58	$7.78\,10^{-3}$	$3.63\,10^{-2}$	0.2010
0.46	4.14	$1.10\,10^{-2}$	$3.10\,10^{-2}$	0.2031
0.99	3.52	$2.34\,10^{-2}$	$3.71\,10^{-2}$	0.2008
1.91	3.62	$3.04\,10^{-2}$	$3.71\,10^{-2}$	0.2056
	±0.07	$\pm 0.02\,10^{-2}$	$\pm 0.04\,10^{-2}$	±0.0001

In these expressions we used $f_{Mn}(K) = \exp(-0.069\,K^2)$ and $f_{Pd}(K) = \exp(-0.1\,K^2)$, which closely approximate the experimental form factors, and μ values obtained from magnetisation data. The results for μ_{Mn} and μ_{Pd} are given in table 1 for each concentration. With these values we can obtain J_{PdMn} knowing the total moment of the cloud $M(0)$. Star *et al* (1975) report several values for $M(0)$ in this concentration range. We used an average value of $M(0) = 7.12\,\mu_B$/Mn in this range. Using (6) we then calculate J_{PdMn} obtaining an average value of $J_{PdMn} = (48 \pm 7)$ °K.

According to this model, calculation of $M(\boldsymbol{K})$ using (6), should give us the experimental neutron $m(\boldsymbol{K})$ values for a ferromagnet. We would now like to obtain more information on the ferromagnetic interactions of this alloy and the magnetisation cloud associated with it. We therefore fit these calculated values using Marshall's (1968) model equation:

$$M(\boldsymbol{K}) = \mu_{Mn} f_{Mn}(\boldsymbol{K}) - \mu_{Pd} f_{Pd}(\boldsymbol{K}) + \sum_i Z_i \varphi_i \frac{\sin KR_i}{KR_i} \tag{10}$$

where the φ_i have the form of a Yukawa potential

$$\varphi_i = (R_1/R_i)\varphi_1 \exp[-K_0(R_i - R_1)]. \tag{11}$$

In this equation K_0 represents the range of the magnetisation clouds and the φ values are the moment perturbations. Substituting (11) into (10) we obtain the following fitting function:

$$M(\boldsymbol{K}) = \mu_{Mn} f_{Mn}(\boldsymbol{K}) - \mu_{Pd} f_{Pd}(\boldsymbol{K}) + \sum_i Z_i \frac{R_1}{R_i} \varphi_1 \frac{\sin KR_i}{KR_i} \exp[-K_0(R_i - R_1)]. \tag{12}$$

The fitting of the data was made by a non-linear least squares method with parameters φ_1 and K_0. The results are shown in table 1, and a comparison of the fitting with calculated $M(K)$ values and the experimental $m(K)$ is presented in figure 1. Since $M(K)$ comes from a ferromagnetic model, it is noticeable that for $c = 0.23$ at.% Mn, ferromagnetic interactions are predominant, while at $c = 1.91$ at.% Mn ASRO plays an important part in the neutron scattering data. K_0 is the width of the peak at small K, and its average value for these concentrations is $K_0 = 0.203$, which indicates the presence of magnetisation clouds with a range of 15.5 Å due to ferromagnetic interactions.

A fitting of $m(\boldsymbol{K})$ for a polycrystal to equation (1) is shown in figure 2, where $M(\boldsymbol{K})$ are the values calculated using equations (6) and (12), and $S(\boldsymbol{K})$ is given by (2). Values

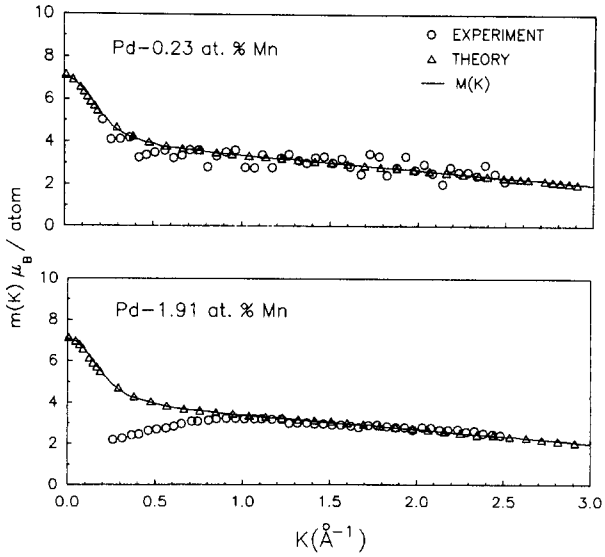

Figure 1. Experimental neutron scattering data from Cable and David (1977) are compared with the values obtained from the model (theory) and from the fitting ($M(K)$) of those values obtained using (12).

of the $a(R_j)$ parameters are presented in table 2. These values tend to alternate in sign as expected, the first parameter being negative, indicating the preference of the impurity to have matrix atoms as first neighbours. They also show an increasing importance of this order as the concentration of Mn is raised. The fitting with these equations describe quite well the neutron scattering data.

ASRO has been found in Pd-9.95 at.% Mn by Morgownik *et al* (1987) and its importance for the spin glass behaviour of **Pd**Mn at this concentration has been shown by those authors. Their parameters are compared with ours in table 3 and show good agreement.

The model that we are using also allows the calculation of the critical temperature of ferromagnetism. This is important because **Pd**Mn shows critical temperatures for the onset of ferromagnetism that are roughly ten times smaller than the critical temperatures of **Pd**Fe, a typical giant moment system, for the same concentration. We then made Monte Carlo calculations for $c = 0.23$, 0.46, 0.99 and 1.91 at.% Mn, and considered a system of classical spins obeying the following Hamiltonian:

$$H = (-1/2) \sum_{\substack{i,j \\ i \neq j}} J_{ij}(R_{ij}) \boldsymbol{S}_i \cdot \boldsymbol{S}_j \tag{13}$$

where the values of J_{ij} were calculated by Medina and Parra (1982). For each concentration we used samples of 100 spins with 2000 Monte Carlo steps per spin. We calculated, for several temperatures, the energy E, the z component and the magnitude of the magnetic moment M, the susceptibility χ (from the average fluctuation of a component of M) and a quantity $\tilde{\chi}$ which is given by the fluctuation of the magnitude of the total moment and which is equal to χ for an infinite system. $\tilde{\chi}$ is given by

$$\tilde{\chi} = \frac{\langle (M - \langle M \rangle)^2 \rangle}{NkT} \tag{14}$$

where N is the number of spins. Critical temperatures were obtained from the maximum

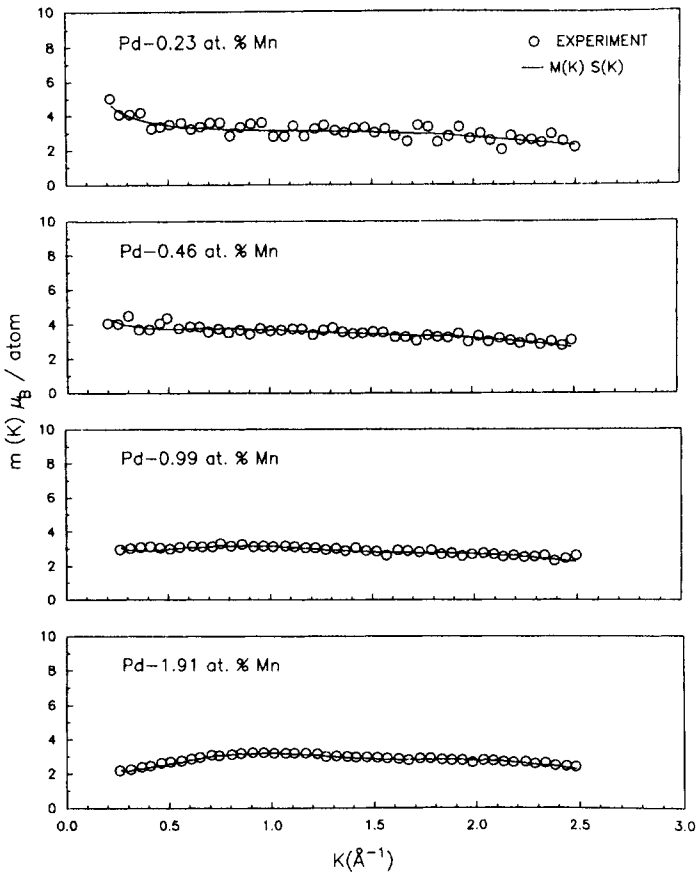

Figure 2. Neutron scattering $m(K)$ from Cable and David (1977) compared with results obtained from the model. $M(K)$ is the ferromagnetic part of the model and $S(K)$ is the atomic short range order.

Table 2. Atomic short range order parameters of dilute **Pd**Mn alloys, as calculated with the model. The ASRO parameters for a 9.95 at.% Mn, obtained by Morgownick *et al* (1987), are also shown.

c (at.% Mn)	$a(0)$	$a(R_1)$	$a(R_2)$	$a(R_3)$
0.23	1.007(17)	−0.016(6)	0.017(28)	−0.0008(60)
0.46	0.988(9)	−0.017(3)	0.032(15)	−0.0087(30)
0.99	0.985(6)	−0.023(2)	0.043(9)	−0.0168(20)
1.91	0.966(3)	−0.031(1)	0.044(5)	−0.0214(10)
9.95	1.000	−0.068(3)	0.027(6)	−0.0030(10)

of $\tilde{\chi}$ against temperature. To compare the calculated critical temperatures with the experimental ones (in kelvin) one must in general multiply the calculated T_c values by a factor $J_0 = J_{Pd}(\alpha\mu_{Mn})^2$ which comes from (6). Notice, however, that we are analysing

Table 3. Comparison of the number N_j of Mn atoms as j neighbours of Pd atoms, using our calculated ASRO parameters on a 0.99 at.% Mn and the ones obtained by Morgownick *et al* (1987) on a 9.95 at.% Mn sample, with approximately the same heat treatment. N for the 9.95 at.% Mn sample is nearly 10 times larger than N for the 0.99 at.% Mn sample, as expected.

c (at.% Mn)	N_1	N_2	N_3
0.99	0.1215	0.0569	0.2416
9.95	1.2752	0.5809	2.3808

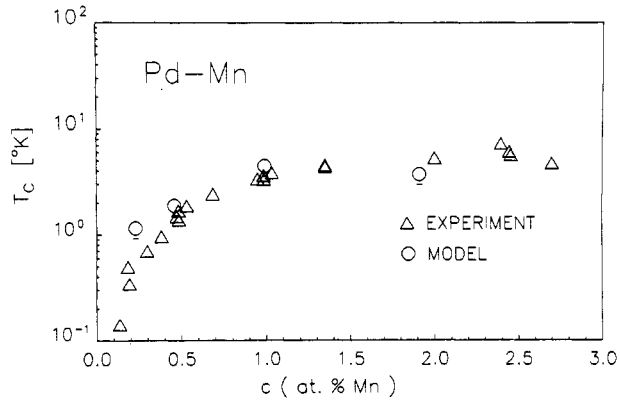

Figure 3. Experimental critical temperatures of ferromagnetism from Star *et al* (1975) compared with the ones obtained by Monte Carlo calculations using the model.

the neutron scattering $m(\boldsymbol{K})$ with a function $M(\boldsymbol{K})S(\boldsymbol{K})$ and therefore our factor J_0 must be:

$$J_0 = J_{\mathrm{Pd}}[\alpha\mu_{\mathrm{Mn}}S(0)]^2 \tag{15}$$

where $S(0)$ is the calculated value of $S(\boldsymbol{K})$ at $K = 0$. In this way we are taking into account the ASRO. The T_c values obtained this way are compared in figure 3 with experimental values. We observe that the calculated values agree, in general, with experimental T_c values.

3. Conclusions

Two problems are remarkable concerning the ferromagnetism of dilute **Pd**Mn alloys. First, magnetisation measurements by Star *et al* (1975) showed that giant moments could be measured in **Pd**Mn alloys, just as in **Pd**Fe or in **Pd**Co, which are typical giant moment systems. However, polarised neutron scattering data (Cable and David 1977) on **Pd**Mn do not show the giant moments found by magnetisation measurements. The other problem is that **Pd**Mn was very different to other giant moment systems regarding the onset of ferromagnetism which occurs in **Pd**Mn at much lower critical temperatures. In this paper we have presented an analysis of **Pd**Mn data with a magnetic environment model which, with simple assumptions, establishes a compatibility between neutron and magnetisation measurements. The model also allows the calculation, by Monte Carlo

simulation, of the critical temperatures of ferromagnetism which agree well with experimental ones. In this model, for very low concentrations ferromagnetic interactions dominate making possible the formation of giant moments. As the Mn concentration is increased ASRO becomes important. This introduces a preference of Pd atoms as first neighbours of Mn atoms and this opposes the long range ferromagnetic order, which up to now was attributed to antiferromagnetic interactions among Mn atoms. The coexistence of these two characteristics makes possible their measurement by different experimental techniques. The presence of ASRO forces critical temperatures to be lower than in other giant moment systems where only ferromagnetic interactions are present.

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