YU ISSN 0015—3206
FZKAAA 21 (2) 139 (1989)

MOLECULAR FIELD IN Pd_3Mn

DUBRAVKO RODIĆ, VOJISLAV SPASOJEVIĆ and ROLAND TELLGREN*

Laboratory for Solid State Physics and Radiation Chemistry, »Boris Kidrič« Institute of Nuclear Sciences, P. O. Box 522, 11001 Belgrade, Yugoslavia

** Neutron Research Laboratory, Studsvik, Sweden*

Received 10 November 1988

Revised manuscript received 4 January 1989

UDC 538.955

Original scientific paper

The crystal structure of Pd_3Mn is of the Al_3Zr type and belongs to the space group I4/mmm. Below Neel's temperature a colinear antiferromagnetic structure is characterized by the $A = (+, -, -, +)$ type, the propagation vector $\vec{k} = (0, 0, 1)$ and four magnetic sublattices. The temperature dependence of magnetization was obtained by neutron scattering following magnetic (100) and nuclear (004) reflections on the sample with the long range order parameter $S = 0.88$. Below $T_N = 199$ K the molecular field coefficient $\lambda = 17000$ (is a sum of λ_{ij}) fits the experimental results. Neel's temperature, as well as the angle between the antiferromagnetic and tetragonal axes, is dependent on the long range order parameter. The $T_N(S)$ dependence can be realized by a change of Mn-Mn coordination versus long range order parameter.

1. Introduction

Nowadays, Pd_3Mn is an interesting compound because of its suitability for hydrogen absorption[1]. Metal hydrides are important as hydrogen containers, i. e. »energy storage«. In this paper we investigate Pd_3Mn as a basic substance for its metal hydride.

Magnetic properties of the stoichiometric Pd_3Mn have been investigated several times and a strong dependence on the long range order parameter has been found. Disordered Pd_3Mn crystallizes in a face-centered-cubic cell and is described as a cluster glass with the freezing temperature at 45 K[2]. With increasing of

order parameter, Pd_3Mn becomes tetragonal and its structure consists of four pseudocubic cells. In the sample with $S = 0.63$, T_N is 170 K and magnetic moments of Mn and Pd atoms lie in basal planes[3]. In the sample with $S = 0.90$ the antiferromagnetic vector lies 8 degrees from the tetragonal axis, this angle is independent of temperature and T_N is 190 K[4]. The change of magnetic properties with a concentration of Mn around the stoichiometric ratio 3 : 1 has also been considered, the well ordered sample $Pd_{74.7}Mn_{25.3}$ is characterized by $T_N = 220$ K[5]. In the already mentioned papers, the crystal and magnetic structures of ordered alloy are described in a noncentrosymmetric space group I 4mm. It is even better to describe this structure in the centrosymmetric I4/mmm space group[6]. This group was used for the refinement of crystal and magnetic structure of Pd_3Mn[7]. There are discussions about magnetic moments of Pd in Pd_3Mn. The Pd magnetic moment was found in some experimental papers[3,6], in others not[4,5]. In all[3-6] papers nothing is said about Mn moments on *c*, *d*, *e* positions, which are mainly occupied by Pd atoms. In our opinion, it is more appropriate that the moments on *c* and *e* sites be attributed to Mn atoms than to paramagnetic Pd, which also follows from Rietveld's refinement[8] of Pd_3Mn[7].

The theoretical study of electronic structure of Pd_3Mn in paramagnetic phase predicts magnetic ordering[9].

2. *Experiment*

In our neutron diffraction experiments we measured the temperature dependence of an intensity from 10 K to 300 K in the region around $2\Theta = 15.75°$, where a contribution from nuclear (004) and magnetic (100) reflections appears. The cell parameters at room temperature, $c = 1.5602$ nm and $a = 0.38984$ nm, show $c \approx 4a$ and the corresponding angle for the two mentioned reflections is practically the same. In the measured region there is also a much smaller contribution from nuclear (011) reflection. Substracting the measured intensity at high temperatures, region from the total intensity at low temperatures, region one can obtain an intensity of pure magnetic reflection. The intensity of antiferromagnetic peaks is proportional to the square of sublattice magnetization in any sublattice and hence the experiment allows to find the relative values of magnetization. In order to get the absolute values we have supposed that $\mu = 5\,\mu_B$/Mn at $T = 0$ K, which is in agreement with the value 5.1 (1) obtained by the refinement in the previous work[7]. The ground state of Mn^{2+} — $^6S_{5/2}$ speaks in favour of negligible crystal field effects and hence this system is appreciable for a molecular field analysis on the basis of the Brillouin type $M(T)$ behaviour. In this approach the change of the Debay-Waller factor with temperature[7] gives small correction, so it has been neglected.

3. *Calculation of molecular field coefficient*

We have divided magnetic lattice of Pd_3Mn in four magnetic sublattices. The aim of this division is to obtain the distances between ions in the same sublattice

— $d_{i,i}$ longer than the ones between ions in different sublattices — $d_{i,j}$. Another requirement is that magnetic moments in a sublattice are oriented in the same direction. The magnetic sublattices are denoted in Fig. 1. Distances between ions in different sublattices are given by:

$$d_{i,i+2} = a \tag{1a}$$

$$d_{i,i+1} = d_{i,i+3} = \sqrt{\frac{5}{4}}a \tag{1b}$$

and in the same:

$$d_{i,i} = \sqrt{2}\,a \tag{1c}$$

for $i = 1, 2, 3, 4$.

Considering Pd_3Mn with $S = 1$ and $S = 0$[2] it is easy to show that for $0 < S < 1$ there are no contributions of Mn atoms in Pd sites to molecular field.

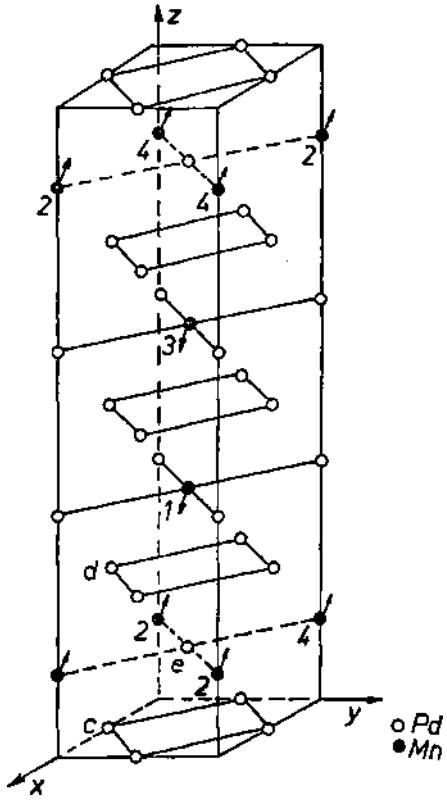

Fig. 1. Crystal and magnetic structures of Pd_3Mn with the long-range order parameter $S = 0.88$. The stacking sequences, magnetic sublattices 1, 2, 3, 4 and c, d, e Pd sites are denoted.

In the following calculation, only Mn atoms on Mn sites are taken into account. The equations for the effective fields of each sublattice are written in matrix form:

$$\begin{bmatrix} \vec{H}_1 \\ \vec{H}_2 \\ \vec{H}_3 \\ \vec{H}_4 \end{bmatrix} = \begin{bmatrix} \lambda_{11} & \lambda_{12} & \lambda_{13} & \lambda_{14} \\ \lambda_{21} & \lambda_{22} & \lambda_{23} & \lambda_{24} \\ \lambda_{31} & \lambda_{32} & \lambda_{33} & \lambda_{34} \\ \lambda_{41} & \lambda_{42} & \lambda_{43} & \lambda_{44} \end{bmatrix} \begin{bmatrix} \vec{\sigma}_1 \\ \vec{\sigma}_2 \\ \vec{\sigma}_3 \\ \vec{\sigma}_4 \end{bmatrix} \tag{2}$$

where $H_i's$ are molecular fields on the sublattice with magnetization $\vec{\sigma}_i$ and $\lambda_{ij}'s$ are the temperature independent molecular field coefficients. From the magneto-structural properties[7] follows:

$$\vec{\sigma}_1 = -\vec{\sigma}_2 = \vec{\sigma}_3 = -\vec{\sigma}_4. \tag{3}$$

The accepted division of magnetic lattice into sublattices is suitable because the molecular field coefficients λ_{ij} in which the sum of indexes $i + j$ is an even number correspond to the ferromagnetic interaction, and if $i + j$ is odd, they correspond to antiferromagnetic interaction (see Fig. 1).

Equations for the sublattice magnetization may be written as follows:

$$\vec{\sigma}_i = \vec{\sigma}_{i0} B_{5/2}\left(\frac{3.359 \cdot 10^{-4}}{T} \lambda \sigma_i\right), \qquad i = 1, 4 \tag{4}$$

where λ represents a linear combination of different ij coefficients:

$$\lambda = \lambda_{11} - \lambda_{12} + \lambda_{13} - \lambda_{14} \tag{5}$$

and so forth for each row of matrix in Eq. (2). From the Brillouin equation (4) the coefficient $\lambda = 17000 \pm 1000$ (in the e. m. s. units) was determined by trial and error method. The accuracy was estimated from the accuracy of experimental data, which was 2—5%. The dependence of exchange constants on distance in the Rudermann-Kittel-Kasuya-Yoshida model does not allow any conclusion about mutual values of coefficients λ_{ij}. The experimental data, experimental magnetization versus temperature and fitted curve are given in Fig. 2.

4. Discussion and conclusion

In the mean-field theory, Neel's temperature is linearly dependent on the molecular field coefficients, and the molecular field coefficients are proportional to coordination number. For our purpose it is necessary to find the z vs. S dependence. Ions from the lattice i are surrounded by the z_{ij} ions from the sublattice j;

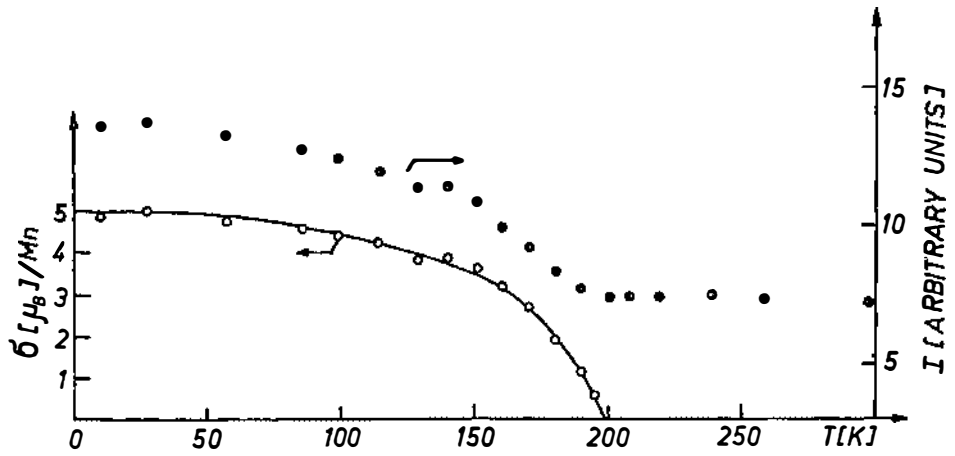

Fig. 2. Temperature dependences of: ● — measured intensities, ○ — experimental magnetization — — magnetization obtained from the mean field treatment.

the change of z_{ij} is caused by the change of the long-range order parameter and in the Pd_3Mn structure (Fig. 1) is given by:

$$z_{11} = z_{21} = z_{23} = z_{33} = z_{41} = z_{43} = 3S + 1 \tag{6a}$$

$$z_{22} = z_{44} = 9/2\,S + 3/2 \tag{6b}$$

$$z_{13} = z_{24} = z_{31} = z_{42} = 15/4\,S + 5/4 \tag{6c}$$

$$z_{12} = z_{14} = z_{32} = z_{34} = 3/2\,S + 1/2. \tag{6d}$$

From Eq. (6) the linear dependence $z_{ij}(S)$ follows. On the other hand, the molecular field theory predicts linear dependences of $T_N(\lambda_{ij})$ and $\lambda_{ij}(z_{ij})$. Hence, the dependences of $\lambda_{ij}(S)$ and $T_N(S)$ are also linear. For example, in all the cases (6a, b, c, d) follows: $z_{S-1}/z_{S-0} = 4$ and one could estimate $T_{N(S-1)}/T_{N(S-0)} = 4$ and except a corresponding change of λ_{ij} if the lattice is the same.

In conclusion, we have found that $\sigma(T)$ dependence is of the Brillouin type, that the molecular field coefficient ($\lambda = 17000 \pm 1000$) fith the experimental data within experimental accuracy.

In this approach we have considered the molecular field coefficient as a function of coordination numbers. Dependence of T_N on coordination numbers follows from it. It is also possible to consider the pressure dependence of T_N and λ, which can be useful for the studies of $T_N(r)$ and $\lambda(r)$[10].

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MOLEKULSKO POLJE U Pd_3Mn

DUBRAVKO RODIĆ, VOJISLAV SPASOJEVIĆ i ROLAND TELLGREN*

Institut za fiziku čvrstog stanja i radijacionu hemiju, Institut za nuklearne nauke »Boris Kidrič«, p. p. 522, 11001 Beograd

** Neutron Research Laboratory, Studsvik, Sweden*

UDK 938.955

Originalni naučni rad

Kristalna struktura Pd_3Mn pripada Al_3Zr tipu i prostornoj grupi I4/mmm. Ispod Néel-ove temperature kolinearna antiferomagnetna struktura opisuje se tipom $A = (+, -, -, +)$, talasnim vektorom $k = (0, 0, 1)$ i sa četiri magnetne podrešetke. Temperaturska zavisnost magnetizacije dobijena je praćenjem magnetne (100) i nuklearne (004) refleksije metodom neutronskog rasejanja, na uzorku sa parametrom dalekodometnog uređenja $S = 0{,}88$. Ispod $T_N = 199$ K koeficijent molekulskog polja $\lambda = 17000$ (gdje je λ zbir λ_{ij}) fituje eksperimentalne rezultate. Néel-ova temperatura i ugao između tetragonalne i antiferomagnetne ose zavise od parametra dalekog uređenja. $T_N(S)$ zavisnost može se shvatiti preko promene Mn-Mn koordinacije sa promenom parametra dalekodometnog uređenja.