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NEUTRON DIFFRACTION STUDY OF ANTIFERROMAGNETIC $Pd_3MnD_{0.5}$

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Neutron diffraction measurments were made on polycrystalline metal hybrid $Pd_3MnD_{0.5}$ at liquid helium temperature. Four pseudocubic cells form tetragonal crystal structure, space group I 4/mmm . Antiferromagnetism of the antiphase domain structure has been found. The angle between antiferromagnetic vector and c-axis corresponds to the body cubic diagonal angle. Magnetic moment of Mn atom is close to the low temperature theoretical value.

The crystal structure of Pd_3Mn, below a temperature of approximately 800 K, is described in the space group I 4/mmm, where the c, d and e positions are predominantly occupied by Pd atoms and e positions by Mn atoms (1,2). This structure of Al_3Zr type (3), with a long range order parameter S=0.88, is described in details (2), and the antiferromagnetic colinear structure below T_N=200 K is found, where the magnetic moments lie about 11° from the tetragonal axis (1). $Pd_3MnD_{0.5}$ is described in the same space group I 4/mmm where hydrogen atoms occupy two positions: b, with coordinates (1/2, 1/2, 0) and e, with coordinates (1/2, 1/2, 1/4).

Measuring thermodynamic properties, Phutela and Kleppa (4) concluded that hydrogen atoms are nonradomly distributed and occupy exclusively or predominantly available interstitial sites surrounded by palladium atoms. Measuring hydrogen solubilities and extrapolating from ordered to disordered region, the authors found that Pd_3Mn dissolves more hydrogen in the ordered tetragonal superstructure than in the disordered face centered cubic structure above 750–800 K (4). From a direct comparison of the two solubilities at 523 K, Flanagan and co-authors confirmed that the ordered form dissolves considerably more hydrogen than the disordered one (5,6).

The magnetic structure is characterized by appearing of magnetic reflexions of the h+k+l = 2n+1. This type of reflexions is forbidden in the crystal space group I 4/mmm and confirms that the antiferromagnetic ordering is related with the antitranslation element along the body diagonal characteristic for the $P_I(I_p)$ lattice. Comparing the neutron powder data for Pd_3Mn and $Pd_3MnD_{0.5}$ one can see that the difference exists only in the relative intensities of the magnetic reflexions, e.g. reflexion (100) is much more pronounced in a deuterized sample. The intensity in this reflexion depends on $\sin^2\phi$, where ϕ describes the angle between the magnetic moment orientation and the tetragonal axis. Therefore, it can be concluded that: the angle in $Pd_3MnD_{0.5}$ overcomes the ϕ angle in Pd_3Mn, the wave vector k=(0,0,1) and the ordering of the type A=(+,-,-,+) are characteristic for a deuterized as well as for a nondeuterized compound. The nonexistence of essential differences between the neutron powder data on Pd_3Mn and $Pd_3MnD_{0.5}$, the same type of reflexions with differences only in intensities, gave a strong indication that the basic model used in magnetic structure refinement of Pd_3Mn (1) can be useful in this case too. In the refinement we have assumed that Pd and Mn atoms occupy the same 4c, 4d and 4e positions (starting compound was partially disordered) (1), but keeping full occupation of these Wyckoff's positions on (Pd+Mn). We have varied the occupancy of 2b and 4e hydrogen positions (2). Among all the mentioned positions only the 4e has freedom in the z-direction. Carrying out the refinement we have noticed that a satisfactory agreement can be achieved by using the same codewords for occupancy in all the Pd positions; the same codewords are used for the displacements of Pd and Mn atoms in the same site, but different ones for the displacement withih the site mainly occupied by Mn atoms (with the small amount of Pd atoms). Magnetic structure has been refined varying independently the Mx(My) and Mz components of magnetization. We have also assumed Debye-Waller factors, isotropic and independent of the site, only on deuterium and manganese atoms, keeping the B value at zero for heavy palladium atoms at low temperature. 18 independent parameters have been used in the refinement, where one for scala factor, one for zeropoint, three for halfwidths and two for cell constants have also been included. The magnetic structure is shown in figure 1, the main results in Table I. The profile and weighted profile R values are big in comparison with Bragg's R values as the consequence of Pd-Mn disorder and lattice deformation.

Table I

Results of the crystall and magnetic structure of $Pd_3MnD_{0.5}$. The palladium and manganese sites are fully occupied; occupancy is given in terms of full occupation.

Rexpected	3.59
Regeneral	3.62
Rnuclear	3.47
Rmagnetic	3.92
Rprofile	14.07
Rw. profile	15.74
a(Å)	3.9270(4)
c(Å)	15.677(3)
$N(Pd)_{c,d,e}$	0.958(5)
$N(Mn)_e$	0.87(2)
$N(H)_e$	0.80(2)
$N(H)_e$	0.13(1)
M(B/Mn)	4.8(1)
ø (°)	55(3)

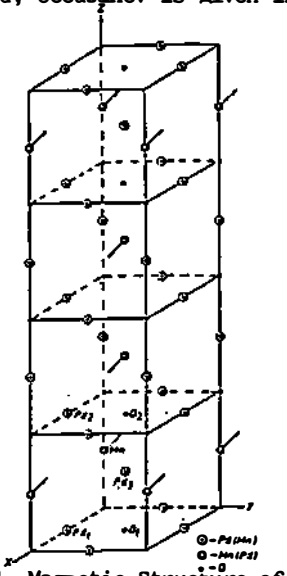

Figure 1. Magnetic Structure of $Pd_3MnD_{0.5}$ at 4.2 K.

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