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High-Pressure Neutron Diffraction Studies of the Magnetic Structures of Cubic Pd_3Mn and $Pd_3MnD_{0.7}$

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High-pressure anvil technique and neutron powder diffraction have been used to study the magnetic structures of cubic Pd_3Mn and $Pd_3MnD_{0.7}$ at pressure of 4.6 GPa and 4.2 GPa, respectively. The incommensurate helix structure of Pd_3Mn is retained under pressure. The ferrimagnetic structure of $Pd_3MnD_{0.7}$ obtained at ambient pressure changes to a pure ferromagnetic one with the moments in the [100] direction. © 2001 Academic Press

Key Words: **high pressure; neutron diffraction; magnetic structures; low temperature.**

INTRODUCTION

Above a temperature of 800 K Pd_3Mn crystallizes in a disordered fcc structure. Lowering the temperature below 800 K, the compound slowly orders to a tetragonal structure of the Al_3Zr-type with the *c*-axes approximately 4 times the *a*- and *b*-axes (1–3). If the tetragonal phase is kept under a hydrogen pressure of 5 MPa at an elevated temperature of about 523 K a slow transition to an ordered cubic phase of the Cu_3Au-type occurs (4).

The crystal and magnetic structures of the cubic phase, $a = 3.9014(5)$ Å at 295 K, space group *Pm*3*m*, have been studied with neutron powder diffraction and Rietveld technique (5). The magnetic moments of the manganese atoms order below 190 K in an incommensurate helical cone structure running in the [111] direction with a propagation vector $k = [0.0972, 0.0972, 0.0972]$.

The lattice can accommodate a hydrogen or deuterium atom in the center of the cube. This will not alter the crystal structure but increases the cell axis with about 1%. The magnetic structure changes to a commensurate ferrimagnetic structure, *k*-vector $\frac{1}{4}c^*$ (6).

It is well known that the magnetic ordering is sensitive to high pressure which causes changes in the lattice parameters and interatomic distances. Cubic Pd_3Mn and $Pd_3MnD_{0.7}$, which have been shown to be sensitive to small changes in the interatomic distances at ambient pressure were considered to be good candidates for detailed studies at the high-pressure facility of Laboratoire Léon Brillouin.

EXPERIMENTAL

High-Pressure Technique

In a joint project between Laboratoire Léon Brillouin (LLB), Saclay, France, and the Kurchatov Institute, Moscow, Russia, a high-pressure cell, working at low temperature, has been installed on the G6.1 diffractometer at the Orphee reactor (7). The nonmagnetic high-pressure cell is made of a Cu–Be alloy with sapphire anvils. The dimension of the cell ($\varnothing$ = 45 mm) is chosen to fit a standard helium flow cryostat (for a detailed description see Ref. (8)). The sample of about 1 mm^3 was mixed with a small amount of NaCl to make it more transparent and placed between the anvils inside an Al gasket. A thin layer of ruby powder

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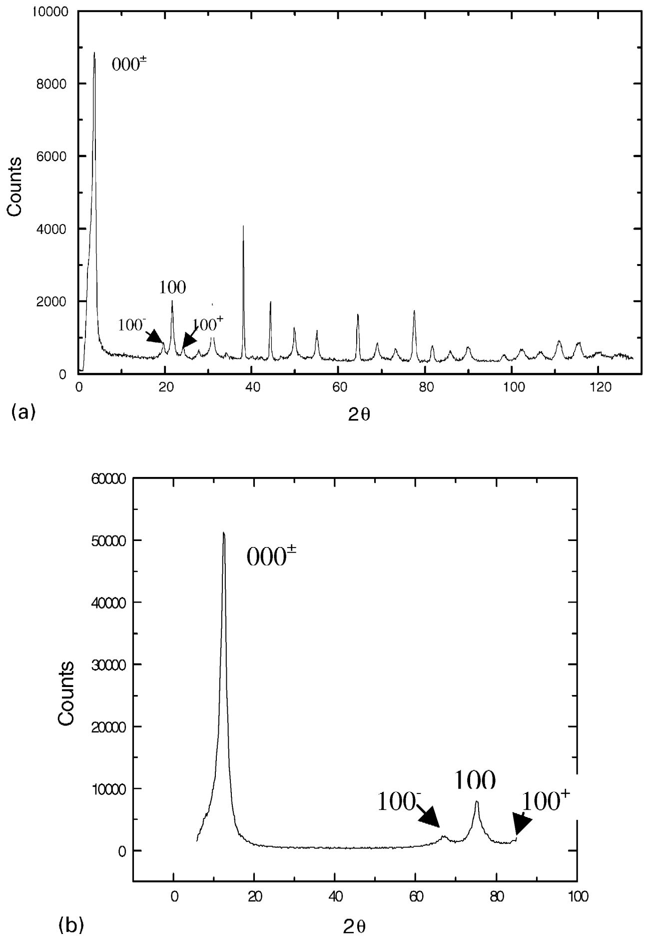

FIG. 1. Diffractogram of Pd_3Mn at ambient pressure: (a) obtained by Önnerud *et al.* ($\lambda = 1.470$ Å); (b) from this investigation ($\lambda = 4.734$ Å).

was added to measure the applied pressure by the ruby fluorescence technique.

Neutron Powder Diffraction

The neutron powder diffraction data was collected at the multidetector diffractometer G6.1 in the guide hall of the ORPHEE reactor. The main problem with a sample volume of ≤ 1 mm^3 is the signal-to-noise ratio. Extensive work was done to reduce the background neutrons coming from the primary beam and the surrounding. The wavelength from the graphite monochromator was 4.734(4) Å. The multidetector consists of 400 cells with a separation of 0.2° thus covering a 2θ range of 80°. Data were collected at several temperatures between 1.4 K and 295 K with a typical measuring time of 6–8 h/diffractogram. For comparison and control of the samples data collection was also performed at ambient pressure with a sample volume of about 1 cm^3.

RESULTS

Pd_3Mn

In a previous investigation by Önnerud *et al.* (5) it was found that the magnetic moments of the manganese atoms in Pd_3Mn order below 190 K to an incommensurate conical helix structure running in the [111] direction with a propagation vector $\mathbf{k} = (0.0972, 0.0972, 0.0972)$ at 10 K. The ferromagnetic moment in the direction of the helix was 2.9(1) μ_B and the antiferromagnetic moment perpendicular to this direction 4.11(4) μ_B.

Our first goal was to show that the crystal and magnetic structure of our sample was identical with that of the previous one at ambient pressure. Figure 1a shows the diffractogram obtained by Önnerud *et al.* at 10 K and Fig. 1b our measurement at 1.4 K. The $(000)^{\pm}$ reflection and the satellites at the nuclear (100) reflection are clearly seen.

Changing to the sample of ~ 0.8 mm^3 at a pressure of 4.6 GPa we collected data at five different temperatures: 1.4, 72.9, 103.1, 131.2, and 185.5 K. To get the magnetic signal as pure as possible we subtracted the data obtained at 185.5 K from the data at the four lower temperatures.

The differences are plotted in Fig. 2. If the result is compared with Figs 3a and 3b, where subtracted data at ambient pressure in the immediate surrounding of the $(000)^{\pm}$ and the $(100)^{-}$ reflections are shown, it is obvious that the incommensurate helix structure still exists (the $(000)^{\pm}$ reflection), with a calculated spiral length of 23.1 Å at 1.4 K.

Whether the ferromagnetic contribution to the nuclear (100) reflection has disappeared is impossible to see in our high-pressure data. That means we cannot say if the helix is still conical or has changed to a flat

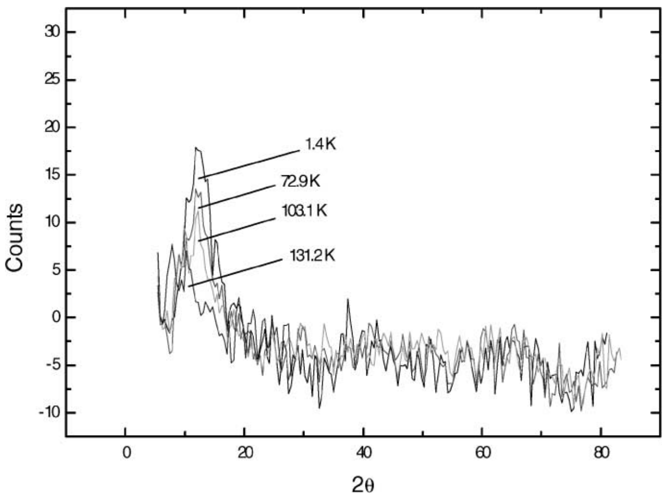

FIG. 2. Subtracted data of Pd_3Mn showing the magnetic contribution at 4.6 GPa.

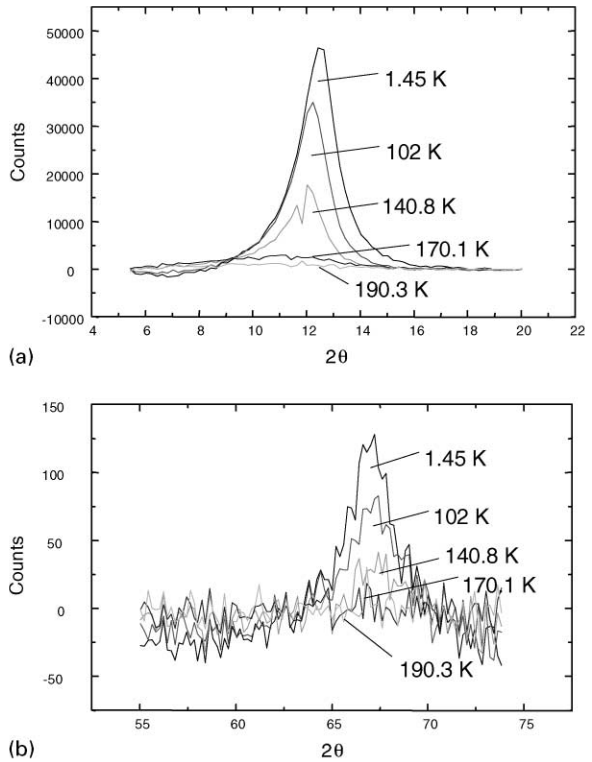

FIG. 3. Subtracted data of Pd_3Mn at ambient pressure showing the magnetic contribution around (a) the $(000)^{\pm}$ and (b) the $(100)^{-}$ reflection.

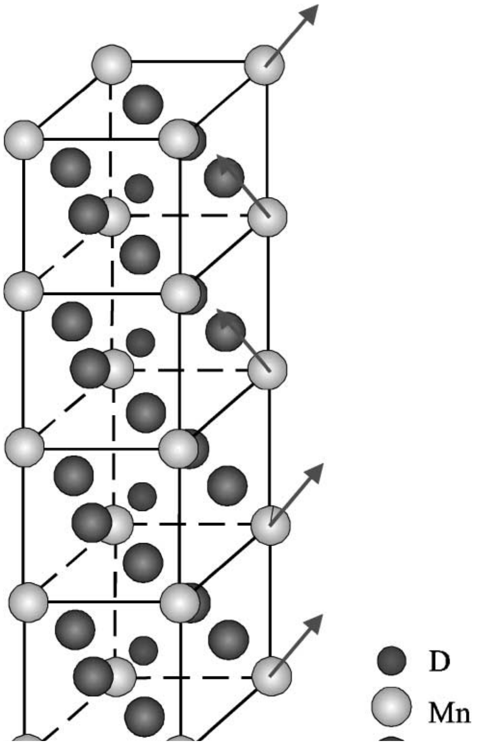

FIG. 4. Ferrimagnetic structure of $Pd_3MnD_{0.7}$. The cubic crystal structure is only $\frac{1}{4}$ in the c-direction.

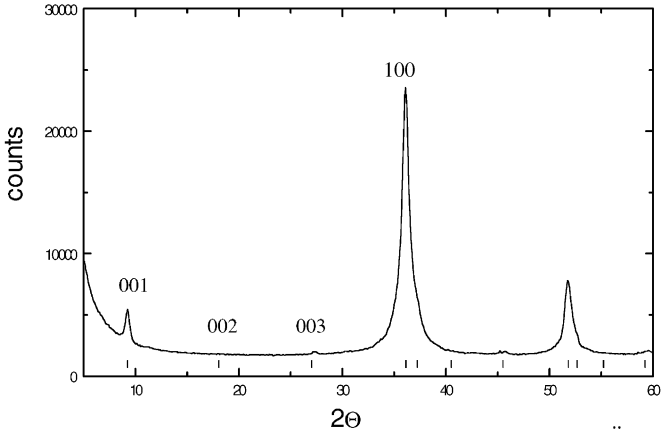

FIG. 5. Diffractogram of $Pd_3MnD_{0.7}$ at ambient pressure from Önnerud *et al.*

circular with the moments perpendicular to the helix axes. T_c is still close to 190 K, the value found at ambient pressure (5).

$Pd_3MnD_{0.7}$

The ferrimagnetic structure of $Pd_3MnD_{0.7}$ at ambient pressure as determined by Önnerud *et al.* (6) is shown in Fig. 4. The magnetic ordering gives an antiferromagnetic reflection (001) (indexed in the magnetic unit cell) at $2\theta = 9.3°$ (cf. Fig. 5).

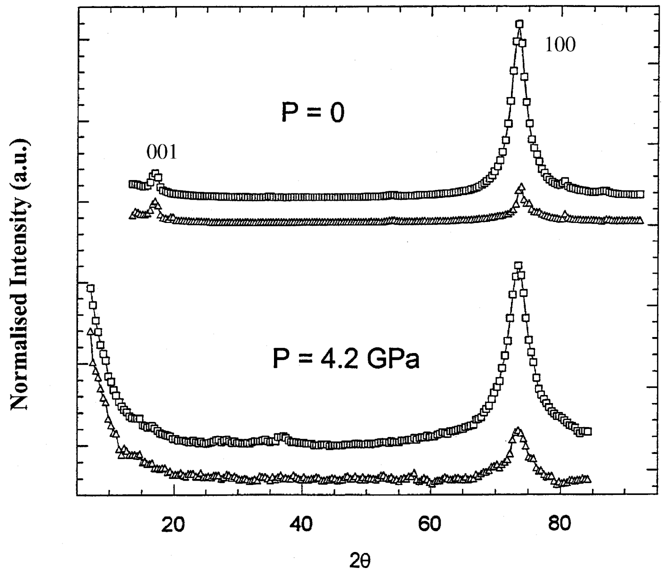

FIG. 6. Neutron diffraction spectra of $Pd_3MnD_{0.7}$ at 1.4 K at ambient pressure and at a pressure of 4.2 GPa. The upper lines (□) are the raw data. The lower lines (△) show the pure magnetic contribution, i.e., the difference between the 1.4 K data and data measured in the paramagnetic range.

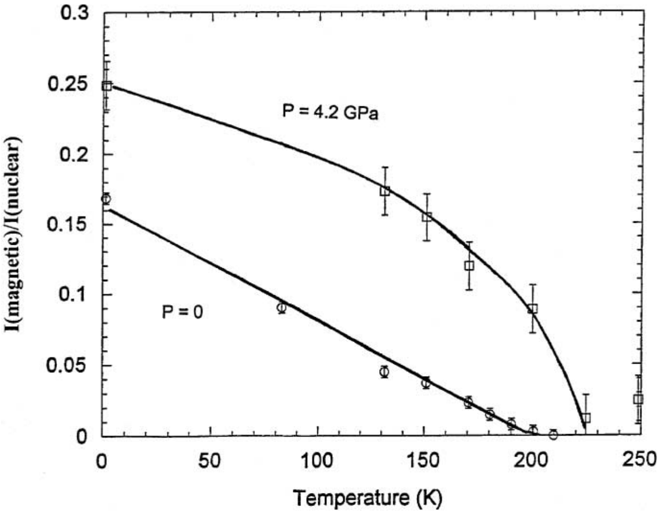

FIG. 7. Temperature dependence of the ferromagnetic contribution to the intensity of the (100) reflection in $Pd_3MnD_{0.7}$ at ambient pressure and at a pressure of 4.2 GPa.

When the pressure is raised to 4.2 GPa this reflection disappears. This can be seen in Fig. 6, where the low-temperature data have been subtracted from data measured in the paramagnetic range. The antiferromagnetic peak (001) at $2\theta = 17.2^\circ$ at ambient pressure cannot be seen at 4.2 GPa. This means that the ferrimagnetic structure of $Pd_3MnD_{0.7}$ at ambient pressure has changed to a pure ferromagnetic one with a magnetic unit cell no longer $a, a, 4a$ but coinciding with the cubic cell of the nuclear structure. The applied pressure pushes the manganese atoms closer to each other and the exchange energy favors a ferromagnetic arrangement with all moments pointing in the same direction.

To see if this has any effect on the ferromagnetic contribution to the nuclear (100) reflection we have plotted in Fig. 7 the ratio of the ferromagnetic to nuclear contribution at different temperatures.

The temperature dependence which is close to linear at ambient pressure deviates strongly from linearity at 4.2 GPa and seems closer to a Brillouin curve.

An estimate of T_c at 4.2 GPa gives a value of 225 K, and at ambient pressure 200 K. The latter is a little higher than the value of 190 K found by Önnerud *et al.* but the plot indicates that T_c increases with pressure.

An analysis of the integrated intensities shows that the ferromagnetic contribution has increased from 12.2% to 19.4% of the total intensity at 1.4 K. If the ferromagnetic moment on the manganese atoms at 1.4 K and ambient pressure is assumed to have a value of 4.06 μ_B as found by Önnerud *et al.* it could be calculated from a comparison of the integrated intensities to have increased to 5.2 μ_B at 4.2 GPa. This is very close to the moments found on the manganese atoms in the collinear antiferromagnetic structure of the tetragonal phase of Pd_3Mn and $Pd_3MnD_{0.7}$ (3, 9).

ACKNOWLEDGMENTS

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