

07.6-1 A NEUTRON POWDER DIFFRACTION INVESTIGATION OF DEUTERATED Pd<sub>15</sub>P<sub>2</sub>. By Y. Andersson, S. Rundqvist and R. Tellgren, Department of Inorganic Chemistry, University of Uppsala, Sweden

Previous investigations have shown that hydrogen and deuterium can be dissolved to a considerable extent in palladium phosphides (Flanagan, Biehl, Clewley, Rundqvist, Andersson, J. Chem. Soc. Faraday Trans. 1. (1980) 76, 196 and Flanagan, Bowerman, Rundqvist, Andersson, Ibid. (1983) 79, 1605). By neutron powder diffraction techniques the dissolved H/D atoms in Pd<sub>3</sub>P<sub>0.80</sub> and Pd<sub>6</sub>P were found to occupy both square-pyramidal and octahedral interstices (Andersson, Rundqvist, Tellgren, Thomas, Flanagan, J. Solid State Chem. (1980) 32, 321 and Acta Cryst. (1981) B37, 1965 and Andersson, Rundqvist, Tellgren, J. Solid State Chem. in print).

In the crystal structure of Pd<sub>15</sub>P<sub>2</sub>, space group R<sub>3</sub> (No. 148), Z=3, (Andersson, Acta Chem. Scand. (1977) A31, 354) there are only tetrahedral interstices between the palladium atoms, corresponding to eleven 18-fold and two 6-fold positions. A neutron powder diffraction study of deuterated Pd<sub>15</sub>P<sub>2</sub> (500 kPa D<sub>2</sub> pressure, 296K) using Rietveld-type profile refinement techniques showed that deuterium partially occupied one of the 18-fold tetrahedral-type positions, corresponding to the formula Pd<sub>15</sub>P<sub>2</sub>D<sub>0.46</sub>.

The H/D atoms dissolved in the palladium phosphide structures preferentially occupy positions as far as possible from the phosphorus atoms, and the D-D (H-H) distances always exceed 2Å.

07.6-2 NEUTRON DIFFRACTION STUDY OF ZIRCONIUM PALLADIUM DEUTERIDE, Zr<sub>2</sub>PdD<sub>2</sub>. By A. Santoro, Institute for Materials Research, National Bureau of Standards, Washington, D.C. and A. J. Maeland, Corporate Research and Development, Allied Corporation, Morristown, N.J., U.S.A.

Zr<sub>2</sub>Pd which has the tetragonal MoSi<sub>2</sub> structure, reacts readily with hydrogen at room temperature to form hydrides (Maeland, J. Less-Common Met. (1983), 89, 173-182). There are several potential interstitial sites for hydrogen in the MoSi<sub>2</sub> structure. We have used neutron diffraction to establish which sites are occupied. Three compositions were studied Zr<sub>2</sub>PdD, Zr<sub>2</sub>PdD<sub>1.71</sub>, and Zr<sub>2</sub>PdD<sub>1.98</sub>. The structures were refined by the method of total profile analysis of the neutron diffraction powder patterns. The D atoms are located at the center of distorted tetrahedra of Zr atoms in all these samples. The results for Zr<sub>2</sub>PdD<sub>1.71</sub> are representative. Space group I4/mmm, Z=2, a=3.3208(2)Å, c=11.606(1)Å. The atomic coordinates are: Pd at 000 (2(a) positions), Zr at 00z (4(e) positions) with z=0.3565(2) and D at 0 1/2 1/4 (4(d) positions). Temperature factors were 0.4 for Pd and Zr and 1.0 for D. Final R factors: R<sub>N</sub>=9.53, R<sub>P</sub>=7.11, R<sub>w</sub>=9.06 and R<sub>E</sub>=5.80.

07.6-3 NEUTRON-DIFFRACTION STUDY OF β-CaNi<sub>5</sub>D. By L.D. Calvert\*, B.M. Powell\*\* and J.J. Murray\*, \*National Research Council of Canada and \*\*Atomic Energy of Canada Ltd.

A neutron diffraction powder pattern of β-CaNi<sub>5</sub>D<sub>77</sub> showed it to be orthorhombic, Pm2m, a=8.6033(13) b=5.0810(9) c=7.8557(15) Å contrary to earlier reports giving Im2m. (Gainsford et. al Adv. X-Ray Analysis (1983) 26 163) and Imam (Y.K. Cho et. al J. Less-Common Metals (1982) 88 125). Rietveld profile analysis based on the metal atom positions proposed by Gainsford et. al gave integrated intensities which were used to obtain possible deuterium positions from Fourier and difference syntheses calculated using the NRCC PDP-8 structure package. This model was refined successfully by a Rietveld profile refinement. Deuterium atoms occupy two octahedral sites equivalent to 3(f) positions in the parent P6/mmm CaCu<sub>5</sub> type structure. These "octahedra" are formed by 4 Ni atoms in the equatorial plane with 2 Ca atoms at the apices. The D atoms are displaced from the central position towards one Ca apex. Distances are D-Ni = 1.50 - 1.92 Å and D-Ca = 2.30 - 2.53 Å.

07.7-1 LITHIUM INTERCALATED GRAPHITE : MEASUREMENT OF THE ELECTRONIC CHANGE IN INTERCALATION. By G. Loupías, J. Chomilier, Laboratoire de Cristallographie, U.P.M.C., 4 Place Jussieu, 75230 Paris Cedex 05 and L.U.R.E., Bat 209C, 91405 Orsay Cedex, France and D. Guérard, Lab. Chimie Minérale Appliquée, Univ. Nancy I, 54506 Vandoeuvre Cedex, France.

Electron momentum distribution of the first stage lithium intercalated graphite (LiC<sub>6</sub>) is measured by X-Ray inelastic scattering and compared to the graphite one. The Compton profiles difference is consistent with a transfer of the lithium conduction electron to a *π*-like band as expected in a rigid band model. But this model is clearly insufficient to explain all the measured profile difference features which actually reflect the total variation of outer (both valence and conduction) electrons density. Two facts are to be taken into account :

- introduction of an excess outer electron.
- modification of the graphite charge distribution due to the presence of the partially or totally ionized lithium that can be illustrated in particular by the stacking change in intercalation.

The excellent agreement between this measured difference and the computed one (by Cohen group) from the Holzwarth wave functions points out, in particular, the importance of the valence distortion due to the lithium ion. (G. Loupías, J. Chomilier and D. Guérard, J. Physique Letters, April 1st 1984).