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Abstract. The ordered structure of β-PdD$_{0.78}$ at 70–75 K has been studied by time-resolved neutron powder diffraction. The ordered superlattice has a MoNi$_4$ structure with approximately four full D sites and one vacant D site in successive (420) planes, which is consistent with previous observations. Several superlattice lines not reported in previous single-crystal studies were observed. Quantitative information about the ordered structure was obtained by careful Rietveld analysis of the data, including anisotropic line broadening and diffuse peak background corrections. The structure refinement confirms a relaxation of D atoms towards the vacant planes and reveals a related second-order displacement of the D atoms in the octahedral sites towards a preferred vacant nearest-neighbour site. The thermal vibration along the c-axis is anisotropic as a result of the preferential relaxation.

1. Introduction

The low-temperature D ordering in β-phase Pd–D has recently been investigated by time-resolved neutron powder diffraction [1, 2] for several values of the deuterium-to-metal atomic ratio, D/M. At the lower D concentrations investigated (D/M = 0.58, 0.65), annealing at 54 K induced the formation of a superlattice with peaks at $(1\ 2n + \frac{1}{2}\ 0)$ positions. This was the first such observation by powder diffraction and is consistent with the previous neutron diffraction studies on single-crystal samples [3, 4, 5]. However, some faint peaks were also detected which were attributed to a cubic superstructure in space group $Pm\bar{3}n$ with a doubled cell constant relative to the disordered structure [1]. The neutron diffraction data were better modelled by the cubic superlattice than the previously supposed ordered structure of tetragonal $I4/amd$. Refinement of the structure [1] indicated diffusion of deuterium from the nearest-neighbour (nn) deuterium positions to the second-neighbour (nnn) positions, suggesting that repulsive nn interactions drive the order–disorder transition.

At a higher concentration, D/M = 0.77, the growth of superlattice lines at $(h \pm \frac{2}{5}\ h \pm \frac{4}{5}\ 0)$ and equivalent positions was observed during annealing at 70 K [2]. The ordered superstructure was confirmed to be of the tetragonal MoNi$_4$ ($I4/m$) type, in agreement with previous investigations using single-crystal samples [6, 7, 8, 9]. Owing to the sluggishness of the transition at 70 K, the superlattice did not develop completely and we were unable to uncover much structural detail from the analysis of the collected data [2]. A survey of the literature showed that detailed structural information such as accurate D locations and occupancies for this type of ordering was not obtained from the single-crystal studies [6, 7, 8, 9] either.

We report here a new study, by neutron powder diffraction, of D ordering in PdD$_{0.78}$ at low temperatures. Powder diffraction is experimentally difficult because of the low

intensity of the superlattice peaks but, in recompense, much of reciprocal space is sampled simultaneously. In the light of our previous experience, we were careful to cool slowly through the transition temperature, where the relaxation time of the ordering process is expected to diverge. In this way we obtained a high transformed fraction relatively quickly. All Miller indices refer to the Pd sublattice, except where a subscript 't' is used to denote the tetragonal cell.

2. Experimental details

Powdered Pd (14 g, particle size 45–400 μm, from Goodfellow Metals), packed in a thin-walled stainless-steel pressure cell, was charged with high-purity deuterium from a hydrogenator, and scanned ($\lambda = 1.664$ Å) using the MRPD (Medium Resolution Neutron Powder Diffractometer) at ANSTO. Further details of the measurements can be found in our previous papers [1, 2]. D/M = 0.78 (± 0.02) was initially estimated by measuring the pressure drop in the hydrogenator during D absorption at room temperature, and finally determined from the Rietveld refinement of the diffraction patterns.

The sample was initially cooled from room temperature to 100 K at about 0.3 K min^{-1}. Because of a reported observation that the ordering transition depends on the thermal history of the sample (slowly cooled crystals show well-defined peaks whereas rapidly cooled crystals show diffuse peaks [10], for the reason we have proposed above), the first three scans were collected when the temperature of the sample was held for six hours at 100 K, 90 K and 80 K. The temperature of the sample was then controlled at 70 K for three days, at 75 K for two days, and at 70 K again for another day while neutron powder patterns were continuously collected at six-hour intervals.

3. Results and discussion

The changes in the diffraction pattern between $2\theta = 10°$ and $90°$ with annealing time are shown in figure 1. A broad diffuse peak at around the ($1\ \frac{1}{2}\ 0$) position was present in the first scan at 100 K, indicating short-range order. When the temperature decreased from 100 K to 70 K, the peak became slightly narrower, and the centre of the diffuse peak shifted slightly towards higher angles. ($\frac{1}{5}\ \frac{2}{5}\ 1$) and ($\frac{6}{5}\ \frac{2}{5}\ 0$) superlattice peaks were just visible on the ($1\ \frac{1}{2}\ 0$) peak in the second scan at 70 K, but developed little during the following three days of annealing at 70 K. Increasing the temperature from 70 K to 75 K significantly increased the growth rate of the superlattice peaks, and all the superlattice peaks corresponding to the MoNi$_4$-type ordering were well developed after two six-hour scans at 75 K. It appears that the relaxation time of the transition increases rapidly between 75 and 70 K, explaining our previous observation of very slow ordering in PdD$_{0.77}$ annealed at 70 K [2]. Therefore we place the transition temperature at this concentration at about 70 K. All of the above observations are in good agreement with the development of the diffuse peak and superlattice peaks in PdD$_{0.78}$ observed in a single crystal by Blaschko *et al* [8].

In the single-crystal studies referred to, the strongest superlattice reflection was ($\frac{6}{5}\ \frac{2}{5}\ 0$), with an intensity of only 2% relative to the (200) sublattice reflection [8]. For this reason no structural refinements were reported for the single-crystal data. In our powder diffraction study, however, a ($\frac{1}{5}\ \frac{2}{5}\ 1$) superlattice peak (outside the range of the single-crystal data) was observed with an intensity of about 4% relative to (200) at best. The observation of this and a few other superlattice peaks with intensities above 1% of (200) has allowed us to carry out a meaningful structural refinement of the superlattice for the first time.
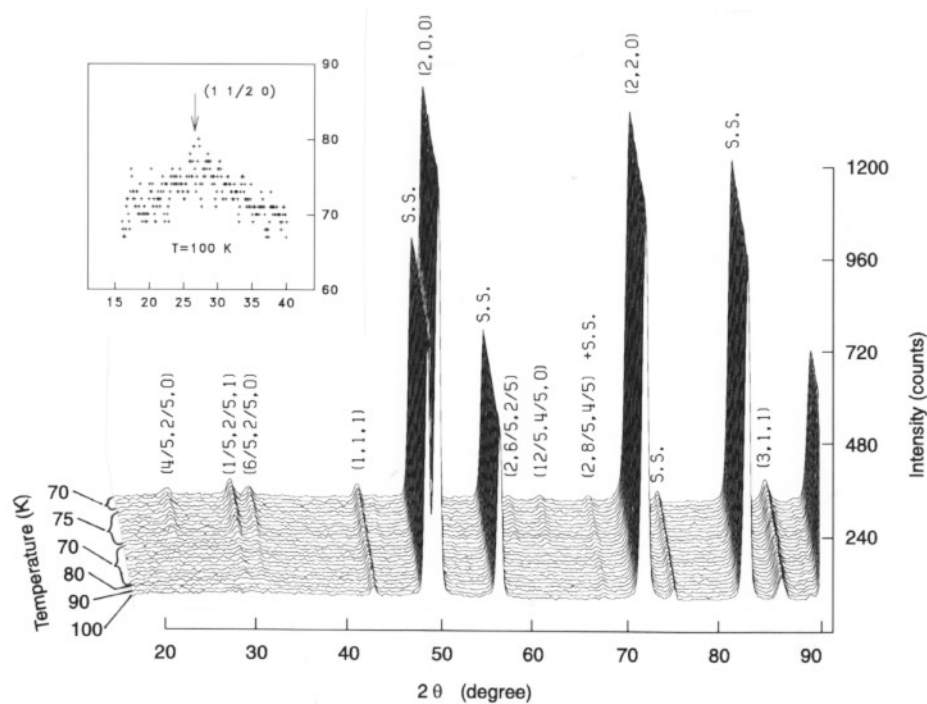
Figure 1. Evolution of the diffraction pattern during annealing at the indicated temperatures (in K). The time sequence is from front to back. The first three scans were at 100 K, 90 K and 80 K, the following 11 scans were at 70 K, the next 9 scans were at 75 K and the final 4 scans were at 70 K. Peaks from the stainless-steel sample can are denoted by 'S.S.'.

We used a Rietveld refinement program [11, 12] based on DWB 3.2. Although all of the patterns were analysed and showed good internal consistency, the final structural information was derived from refinement of a summation of four diffraction patterns collected in the last day of measurement at 70 K. An initial refinement was carried out according to the MoNi$_4$ ($I4/m$) model for the ordered structure [6, 7]. This gave a higher D concentration than is allowed in the 8h site and a negative temperature factor for D in the 2a sites, indicating that some factors were unaccounted for in this refinement.

Initially the background was modelled by a polynomial

$$y_i = \sum_{m=-1}^{2} B_m (2\theta_i)^m$$

where y_i is the background contribution at the ith step and the coefficients B_m are refinable parameters. Because the diffuse peak near (1 $\frac{1}{2}$ 0) was poorly described by the polynomial, it was fitted with a Lorentzian profile with intensity ∼0.1% relative to (200) and centred at $2\theta \simeq 29°$. The Lorentzian function gave a slightly better fit than a Gaussian and was then added to the polynomial background. The description of this diffuse peak in our background correction agrees reasonably with previous observations and fitting of the diffuse peak on single crystals [5, 8].

A second problem arises in index-related broadening of the sublattice peaks, which became apparent after refining the lattice parameters in the tetragonal unit cell. The relationship between broadening and scattering angle follows the trend observed in the cubic

superlattice ordering [1, 2]. Our previous work suggested that this broadening originates in anisotropic deformation of the f.c.c. Pd lattice by edge or screw dislocations which are induced by D absorption [2]. Since the symmetry of the Pd sublattice is unchanged by ordering of the interstitial D, we have adapted the anisotropic strain broadening correction from the cubic lattice to the tetragonal unit cell. We note in passing that it is uncertain whether anisotropic peak broadening was not observed in the single-crystal studies referred to because it was not resolvable, or because it was absent. The procedure by which the β-phase was formed in our sample—that is, by transiting the two-phase region below the critical point—induces misfit dislocations which would not occur in the procedure necessarily followed to prevent the partitioning of a single-crystal sample—that is, forming the β-phase above the critical point and cooling.

Assuming that the maximum strain occurs on the (001) planes of the Pd sublattice, the *hkl* functionality of the broadening expressed as r.m.s. strain $\varepsilon_{r.m.s.}(hkl)$ is derived for the tetragonal cell as

$$\varepsilon_{r.m.s.}(hkl) = \frac{l^*}{\sqrt{\frac{2}{5}(h^2 + k^2) + l^2}} \frac{\delta c}{c}$$

where l^* is the largest *l*-index in a group of *hkl* with the same denominator in the equation. This algorithm was applied to the FWHM of the Gaussian part of the Voigt function used to describe the peak profile [2, 13]. This is equivalent to allowing a distribution of the cell parameter $\delta c/c$ about its mean position. The index-related anisotropy in the sublattice peak broadening was well modelled in this way and a maximum r.m.s. strain of 3.1×10^{-3} in the [001] direction was determined.

Table 1. Final structural parameters for ordered $PdD_{0.78}$ at 70 K. Estimated standard deviations are in parentheses. *B* denotes temperature factors.

Space group $I4/m$ (No 87), $a = 6.391(1)$ Å, $c = 4.052(1)$ Å
$R_B = 0.15\%$, $R_p = 1.89\%$, $R_w = 2.68\%$, $R_e = 2.45\%$ and GOF = 1.20.

Atom	Position	x	y	z	B	Occupancy
Pd 1	2b	0	0	1/2	0.19(4)[a]	100%[b]
Pd 2	8h	0.1[b]	0.3[b]	0	0.19(4)[a]	100%[b]
D 1	2a	0	0	0	2(1)	13(1)%
D 2	8h	0.399(1)	0.208(1)	0	$\beta_{11} = 0.011(1)$	94(1)%
					$\beta_{22} = 0.011(2)$	
					$\beta_{33} = 0.039(3)$	
					$\beta_{12} = 0.002(1)$	

[a] Constrained to be equal.
[b] Fixed at this value.

Following this improvement to the initial refinement, anisotropic temperature factors were refined for the D atoms. For D atoms in the 8h site, the anisotropic temperature factors refined from different patterns agreed very well. The factors obtained for D atoms in 2a sites were inconsistent between patterns and sometimes even negative, so an isotropic temperature factor was retained for the 2a site. The results obtained by applying the above methods to the sum of the last four diffraction patterns recorded is shown in figure 2 and table 1. The refined D occupancies of 94% and 13% give a total D occupancy in excellent agreement with the D/M ratio measured manometrically.
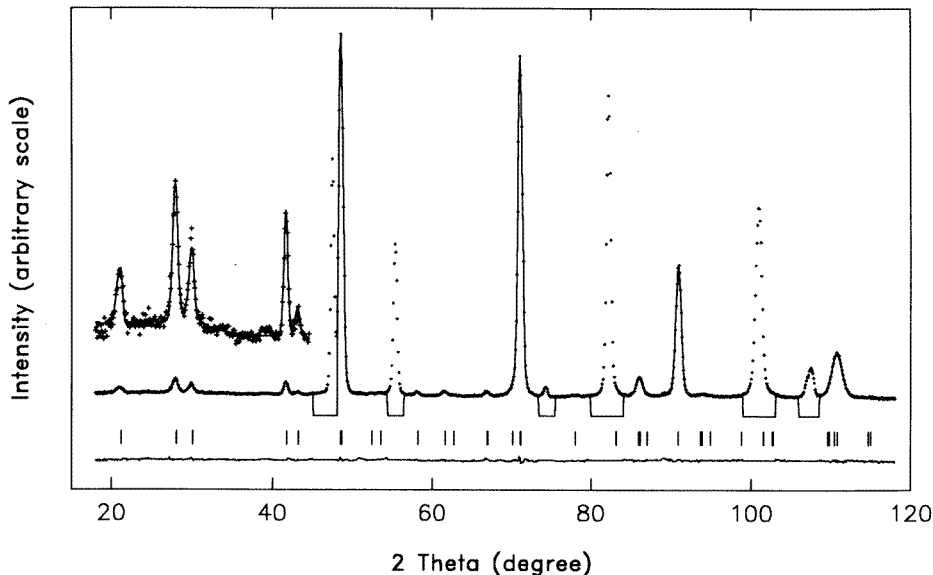
Figure 2. A Rietveld fit to neutron diffraction data from the sum of the last four diffraction patterns for PdD$_{0.78}$ annealed at 70 K. Crosses indicate observations; the solid line is the fit. Reflections from the stainless-steel container were excluded from the refinement. The profile at low angles is enlarged 10 times for clarity. The difference profile for the refinement and the reflection markers for the tetragonal $I4/m$ structure are shown below.

According to structure factor calculations for ideal MoNi$_4$-type D ordering, the superlattice reflections at $(\frac{4}{5}\ \frac{2}{5}\ 0)$ and $(\frac{6}{5}\ \frac{2}{5}\ 0)$ should have the same intensity, regardless of any corrections, whereas the diffraction patterns show significant differences between them. These differences were observed in single crystals and ascribed to a displacement of the deuterium atoms from their ideal interstitial sites [6, 7, 8, 9]. Blaschko *et al* [9] proposed a model for this displacement in which the D atoms relax towards vacant (interstitial) planes. This model is illustrated in figure 3. The nearest-neighbour vacancies of a D atom at $z = 0$ are three equivalent sites, one (denoted A) on the same level, and two (denoted B) above and below at $z = \pm0.5$. Equivalently, a D atom on the $z = \pm0.5$ level has as nearest vacant neighbours two A vacancies and one B vacancy. From the relationship between $I_{(4/5\,2/5\,0)}$ and $I_{(6/5\,2/5\,0)}$, Blaschko *et al* concluded that relaxation of the D atoms occurs via a displacement along $\langle 210\rangle_t$ directions in the tetragonal cell. It is readily found from figure 3 that, assuming equal attractive forces towards the three equidistant vacancies, the resultant force is in a $\langle 210\rangle_t$ direction.

Our measurements revealed the additional $(\frac{1}{5}\ \frac{2}{5}\ 1)$ peak and a careful refinement of all of the superlattice peaks led to a somewhat different conclusion. The refinement results agree in general with this displacement model. The displacement of D atoms from the ideal position derived from our refinement is 0.051 Å, which is slightly smaller than the 0.063 Å derived from triple-axis measurements on a single crystal [9]. The actual D displacement derived from our refinement for all of the collected patterns is always different to $\langle 210\rangle_t$, and is on average along $\langle 100\rangle_t$ directions (see table 1 and figure 3). This difference may be understood from the following argument, which shows that the displacement of a D
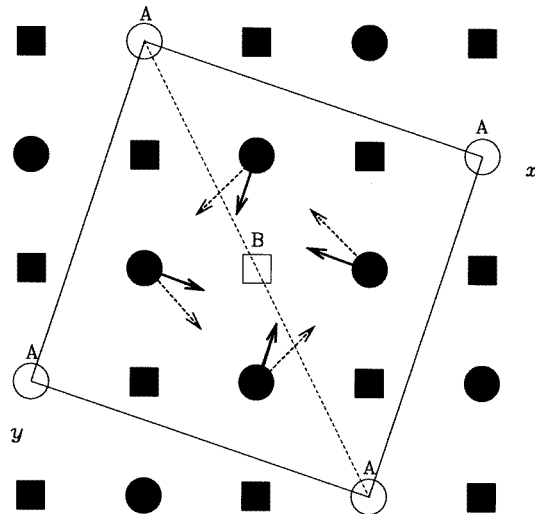
Figure 3. A model for the displacement of D atoms in the ordered structure. Only D sites are shown. Sites on $z = 0$ are represented by circles; sites on the $z = \pm 0.5$ levels are represented by squares. 8h sites are shaded; 2a sites are unshaded. The (420) reference plane for the f.c.c. sublattice is drawn as a dashed line across the diagonal of the unit cell. The displacement vector of a D atom projected onto the *a–b* plane at the $z = 0$ level is shown by a dashed arrow for the supposed $\langle 210 \rangle_t$ displacements and a solid arrow for the $\langle 100 \rangle_t$ displacements inferred from our analysis.

atom in $\langle 210 \rangle_t$ directions is inherently unstable. The fundamental origin of the effect is seen to be the absence of symmetry about the $\langle 210 \rangle_t$ directions, so any displacement from the ideal position of the D atom alters the balance of forces towards the neighbouring vacancies. Consider a D atom on the $z = 0$ level, with three nn vacancies at equal distances of say X. A displacement δ in a $\langle 210 \rangle_t$ direction will draw the D atom closer to the two B-type vacancies at $z = \pm 0.5$, with a resultant separation of $(X^2 - X\delta + \delta^2)^{1/2}$. This atom therefore moves away from the other nn vacancy (A-type) at $z = 0$ to a resultant separation of $(X^2 + \delta^2)^{1/2}$. This will alter the balance of attraction which formerly existed towards the three equivalent nn vacancies, attracting the D atom further towards the B sites until a new equilibrium is established. The resultant displacement is nearer to $\langle 100 \rangle_t$ than $\langle 210 \rangle_t$. The consequence of this displacement is that the three formerly equivalent vacancies neighbouring a D atom will become inequivalent. Only the two sites on the adjacent layers will constitute its real nn vacancies, and the D atoms will therefore diffuse more readily between these sites. This picture of the relaxation mechanism is further supported by the calculated anisotropic temperature factors of D atoms in the occupied sites: a significant anisotropic thermal vibration along the (tetragonal) *c*-axis of D atoms in 8h sites was inferred from our refinement (see table 1), indicating a preferential relaxation of D atoms in the occupied sites towards the nn vacancies on adjacent layers.

The D occupancies of the 'full' and 'vacant' sites were refined as 94% and 13%. Assuming that the vacancies are uncorrelated, the probability that zero, one or two of the 'vacant' sites neighbouring an occupied site are occupied is thus 66%, 30% or 4%. The probability that all vacancies are actually occupied is negligible. Re-examining the argument above for the 34% of D atoms which have one or two of the nn vacancies occupied, it is

readily found that the resultant force averaged over the possible configurations still points along $\langle 210\rangle_t$ directions while the D atom remains at its ideal location. For one occupied nn vacancy, displacement along $\langle 210\rangle_t$ is still unstable, but less so than for all nn vacancies unoccupied. For two nn vacancies occupied, the instability vanishes. Hence, in summary, the resultant force on a D atom at its ideal location is always along $\langle 210\rangle_t$, but changes direction towards $\langle 100\rangle_t$ as the atom is displaced under the action of this force. As the number of nn vacancies actually occupied rises, this instability decreases. From the total nn vacancy occupancy of 13% we can say that 96% of D atoms will be affected by this instability and will preferentially relax in directions closer to $\langle 100\rangle_t$, in accordance with the observations.

4. Conclusions

(1) Ordering of interstitial D atoms in PdD$_{0.78}$ at 70–75 K is described in a MoNi$_4$ structure with four 'full' D sites (94% occupancy) and one 'vacant' D site (13% occupancy) on the (420) planes, which is consistent with previous observations.

(2) Anisotropic peak broadening was observed and corrected by assuming a maximum strain in the [00l] direction of the sublattice, owing to dislocations.

(3) Rietveld refinement of the superlattice, including a previously unobserved peak, revealed the displacement of D atoms in the octahedral sites towards the nn vacancies in the neighbouring a–b planes, and anisotropic thermal vibration along the c-axis.

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