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## LETTER TO THE EDITOR

# Ordering of deuterium in PdD<sub>0.65</sub> at 54 K

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**Abstract.** Neutron powder diffraction studies on PdD<sub>0.65</sub> demonstrate that the 50 K anomaly is due to an order–disorder transition of deuterium within octahedral interstitial sites. The slow transition to the ordered phase involves diffusion of deuterium from the nearest-neighbour deuterium positions to the second-nearest-neighbour positions. The ordered crystal structure remains cubic, and is accurately described in space group  $Pm\bar{3}n$  by doubling the cell constant relative to the disordered structure (space group  $Fm\bar{3}m$ ).

An anomaly in the heat capacity of palladium hydride in the vicinity of 50 K was first reported by Nace and Aston in 1957 [1]. Since then, anomalies have also been found in other physical parameters e.g. electrical resistance and internal friction. The temperature of the anomaly is concentration dependent and peaks at  $\sim 62$  K for PdD<sub>0.74</sub> [2]. These anomalies have been interpreted as due to a movement of hydrogen (deuterium) within the palladium lattice [2–4]. A number of experimental techniques including x-ray and neutron diffraction have been applied in attempts to determine the origin of these anomalies. The crystallographic studies have been hampered by the sluggishness of this transition, which takes several days to complete. Early powder diffraction results suggested a phase transition involving migration of H (or D) atoms from sites of octahedral symmetry to sites of tetrahedral symmetry e.g. [5]. Later evidence from two independent single-crystal neutron diffraction studies both indicated an order–disorder transition within the octahedral sites [6–8], but disagreed on the details of the ordering. That these experiments were performed at two different deuterium concentrations appears to be highly significant. Neither the octahedral nor the tetrahedral description of the symmetry of the transition has found global support because conclusive evidence has not been produced [9]. The present time-resolved powder diffraction study of PdD<sub>0.65</sub> at 54 K using the medium resolution neutron powder diffractometer (MRPD) [10] at the HIFAR research reactor (ANSTO, Sydney) has provided conclusive evidence for the order–disorder transition and accurate new information on the structure of the ordered state. Our description of the structure of the ordered phase is similar to that reported by Anderson *et al* [8], but involves no loss of cubic symmetry and also accounts for several diffuse peaks seen at other superlattice positions.

The MRPD is a conventional two-axis neutron powder diffractometer with a variable wavelength and vertically focussed Ge monochromator. It has a monochromator takeoff angle of  $100^\circ$  and is currently fitted with 15 He<sup>3</sup> detectors spaced  $4^\circ$  apart. These measurements were performed with a neutron wavelength  $\lambda = 1.664$  Å.

Powdered Pd (14 g with particle size 45–400  $\mu\text{m}$  from Goodfellow Metals) was packed in a thin-walled stainless steel container and charged with deuterium at room temperature from an *in situ* hydrogenator. The diffraction pattern was monitored during charging until the sample was wholly within the single-phase  $\beta$  region of the Pd–D phase diagram. The deuterium concentration was initially determined by measuring the pressure drop in the hydrogenator during D absorption. Rietveld refinement of the neutron powder diffraction pattern, using space group  $Fm\bar{3}m$  gave a lattice parameter of 4.017(1) Å, and a value for the deuterium-to-palladium ratio  $D/Pd = 0.65 \pm 0.01$ , in agreement with the concentration determined from the pressure drop. Patterns were collected covering a  $2\theta$  range from  $2^\circ$  to  $138^\circ$  in steps of  $0.1^\circ$  as the sample was cooled to 54 K in a closed-cycle helium refrigerator. Thereafter patterns were collected continuously for  $\sim 280$  hours at  $\sim 5\frac{1}{2}$  hour intervals while the sample was annealing at  $54 \pm 0.5$  K.

The changes in the diffraction pattern between  $2\theta = 10^\circ$  and  $90^\circ$  with annealing time at 54 K are shown in figure 1. The strong reflections can be indexed as  $\beta$  PdD<sub>0.65</sub> and the stainless steel sample can. A diffuse peak can be seen around  $(1\frac{1}{2}0)$  in the early patterns indicating the presence of short-range order at the onset of the annealing time. During the next few hours a superlattice reflection appears at the same position, saturating after about 30 hours. The observation of the  $(1\frac{1}{2}0)$  superlattice reflection is consistent with the neutron diffraction study on single-crystal PdD<sub>0.64</sub> at 46 K by Anderson *et al* [6]. In addition to this reflection, our powder diffraction data display superlattice reflections of similar intensity at  $(1\frac{3}{2}0)$  and  $(1\frac{5}{2}0)$ , and other smaller reflections at  $(100)$  and  $(1\frac{1}{2}\frac{1}{2})$ .

Based on these reflections, a superlattice with cell constant  $a$  twice that of the room temperature structure ( $Fm\bar{3}m$ ) in space group of  $Pm\bar{3}n$  was derived. Structure factor calculations with this space group attribute the appearance of the superlattice reflection series to an occupancy difference in crystallographic c and d sites, and thus a structure model for the order–disorder transition of deuterium within the octahedral sites can be established. This ordered structure is shown in figure 2. The small closed and open circles indicate the positions of the favoured and unfavoured sites, respectively. This ordering is consistent with a minimization of deuterium nearest-neighbour repulsive interactions.

Neutron diffraction data were analysed using a Rietveld refinement program [11, 12] according to this structural model. After the initial refinement, it was apparent that in addition to isotropic strain broadening, there is anisotropic line broadening which is most pronounced along  $[00l]$ . A correction to the reflection widths was included in the program assuming that strain is along  $[00l]$  to take into account the anisotropic strain broadening [13]. An excellent fit between observed and calculated intensities was obtained (see for example figure 3), with  $R_p < 4.0\%$  and  $R_B < 1.0\%$  for all 53 diffraction patterns at 54 K. The refinement returned a value of less than 1% for the preferred orientation.

The reflection line widths incorporate sample contributions of two distinct origins. These are Lorentzian line broadening equivalent to a mean isotropic particle size of  $\sim 750$  Å, and Gaussian line broadening equivalent to an anisotropic RMS strain of  $3.2 \times 10^{-3}$  (maximum in  $[00l]$  directions). This anisotropic line broadening also exists in the disordered phase and may be due to dislocations generated in the  $\alpha \rightarrow \beta$  phase transition. The atomic positions used and the site occupancies determined in the refinements of the ordered PdD<sub>0.65</sub> are included in table 1. The variation of the refined site occupancies for the c and d sites with time (logarithmic scale) are plotted in figure 4. The initial slow migration of deuterium appears to accelerate after  $\sim 8$  h annealing and slows again from  $\sim 32$  h. Although the transition is nearly complete after 32 h, there is still some slight migration of deuterium up to 280 h. The occupancies of the c and d sites eventually reached 97% and 33% respectively.

The superlattice reflections  $(1\frac{1}{2}0)$   $(1\frac{3}{2}0)$  and  $(1\frac{5}{2}0)$  are consistent with the second report

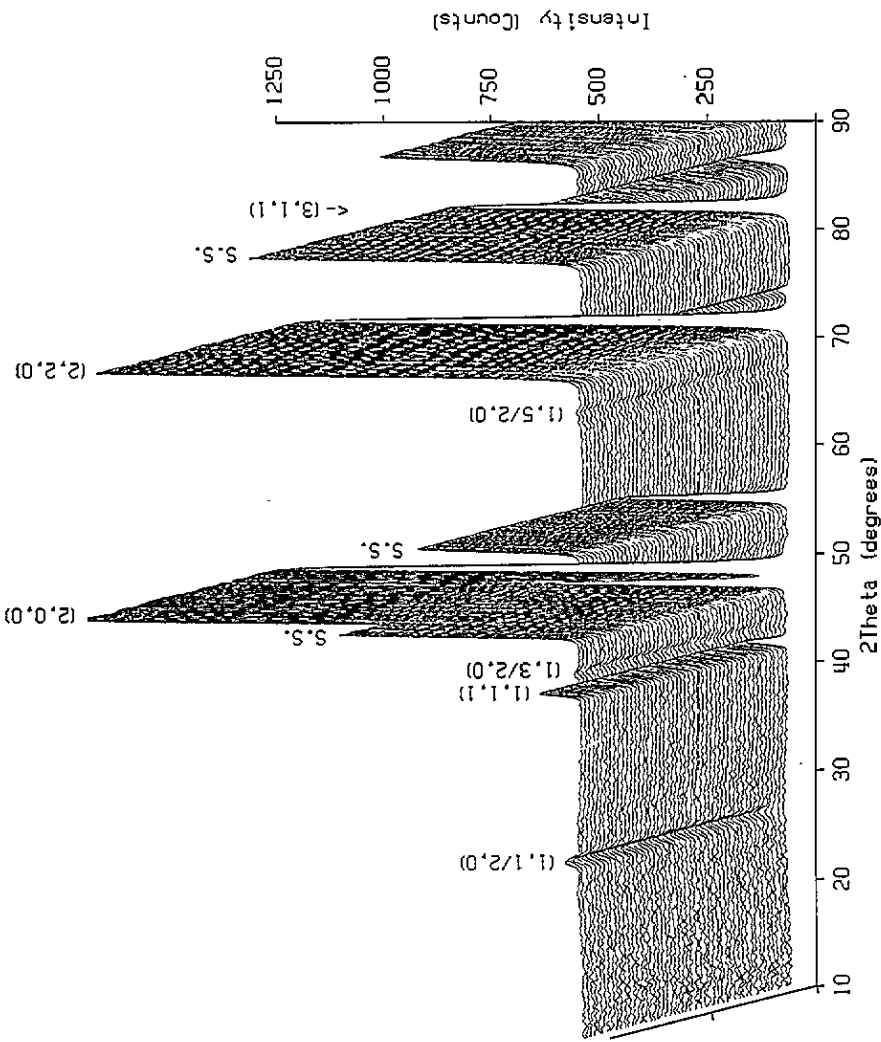
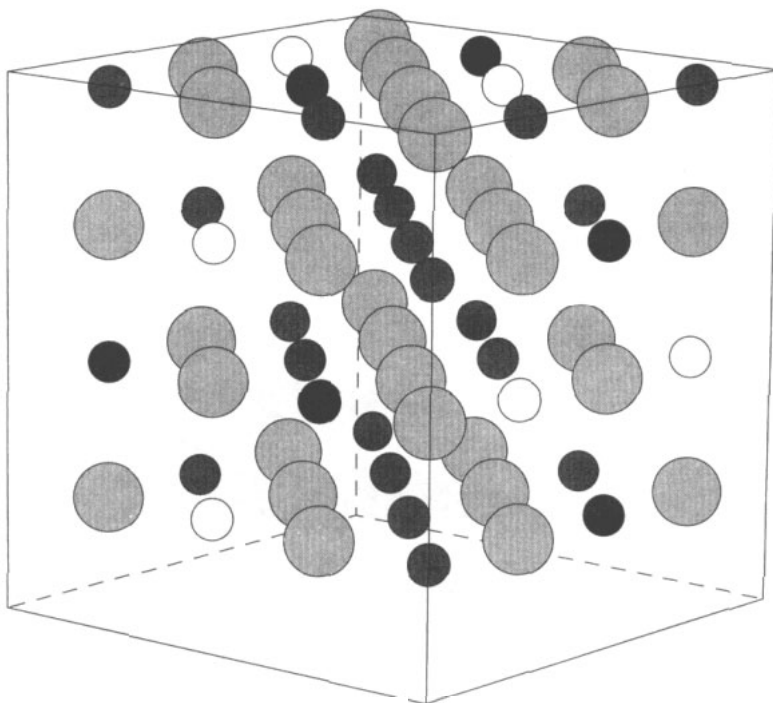


Figure 1. Changes in the diffraction pattern between  $2\theta = 10^\circ$  and  $90^\circ$  with annealing time at 54 K. The (hkl) indices of  $\beta$ -PdD are indicated along with the lines from the stainless steel sample can (SS).



**Figure 2.** The unit cell of the ordered structure in space group  $Pm\bar{3}n$ . Palladium sites: large open circles; deuterium sites: c small closed circles, d small open circles, and e and f small shaded circles. The cubic cell has sides of length  $a = 8.036(1)$  Å at 54 K. The deuterium atoms diffuse from interstitial sites d to neighbouring sites c. All D sites are equivalent in the disordered structure ( $Fm\bar{3}m$ ) and the cell constant reduces to  $\frac{1}{2}a$ .

by Anderson *et al* [8], who derived a tetragonal model in space group  $I4_1amd$  to explain their results. In fact this space group only accounts for the *ordered* component of the deuterium lattice, that is the component of the deuterium sublattice which produces the superlattice reflections. It can be used in conjunction with the space group of the average structure ( $Fm\bar{3}m$ ) in a two-phase model to fit the powder diffraction data. Alternatively a single-phase tetragonal description of the whole ordered PdD lattice can be generated in  $I4_1md$ , with the advantage that we may easily quantify the degree of deuterium migration. The most significant difference between the  $I4_1md$  model and the  $Pm\bar{3}n$  model lies in the extra reflections allowed by the  $Pm\bar{3}n$  model. More detail on the reflections of the superlattice was obtained by summation of the 40 diffraction patterns collected in the ordered state. The results of this summation are shown in figure 5, where the diffraction pattern from  $4^\circ$  to  $100^\circ$  in  $2\theta$  is plotted, magnified by a factor of 10 relative to figure 3. Also shown in the figure are the reflection markers for the ordered cubic ( $Pm\bar{3}n$ ) and ordered tetragonal ( $I4_1md$ ) space groups, as well as the contribution from the sample can. Both the ordered tetragonal space group and ordered cubic space group are able to index the lines  $(1\frac{1}{2}0)$   $(1\frac{3}{2}0)$  and  $(1\frac{5}{2}0)$ , however the small reflections at  $(100)$  and  $(1\frac{1}{2}\frac{1}{2})$  can only be indexed with the cubic space group ( $Pm\bar{3}n$ ). These may be the same reflections as the unexplained *weak spots* of *complex non-integer indices* referred to in [8]. As discussed earlier, the larger superlattice lines correspond to a migration of deuterium from the d sites to the c sites of table 1; this amounts to movement of  $\sim 9\%$  of the available deuterium atoms, and is readily

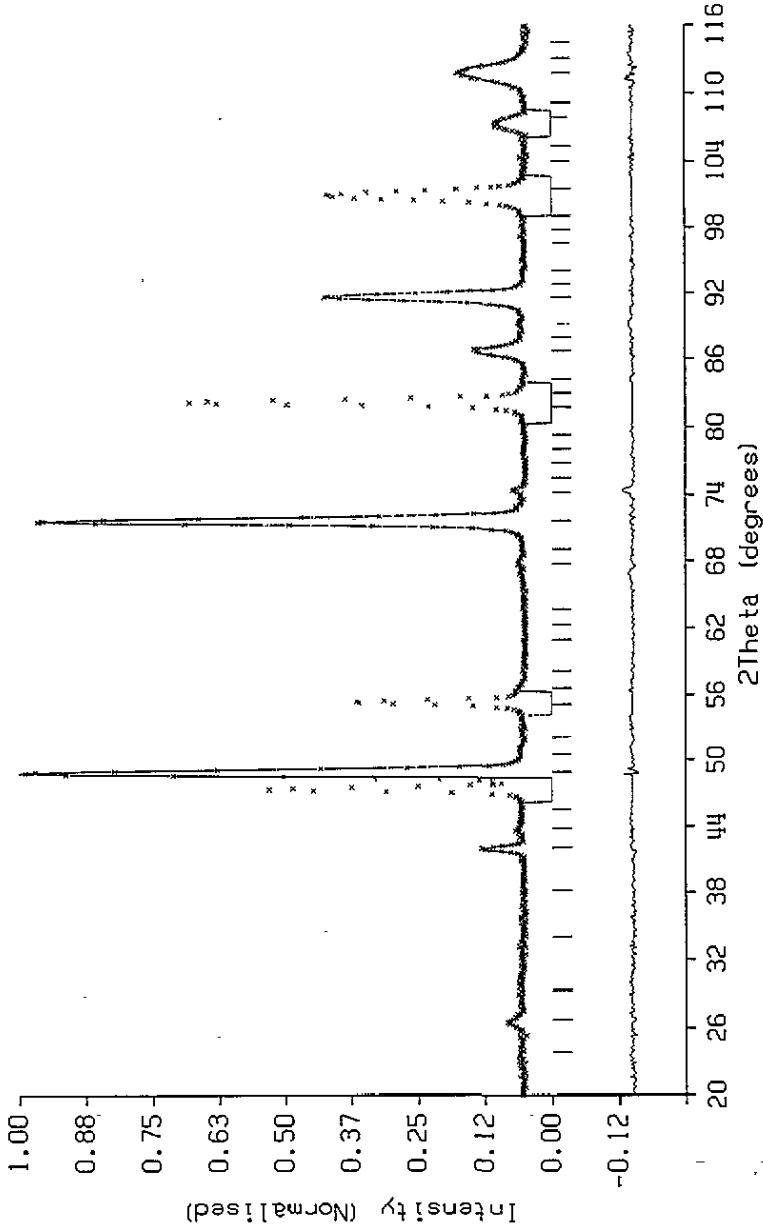
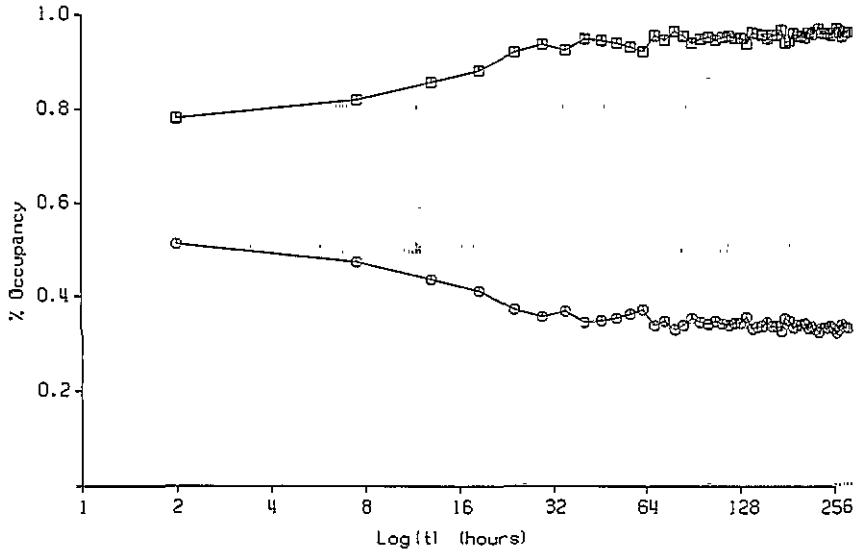


Figure 3. Rietveld fit of the neutron diffraction data from PdD<sub>0.65</sub> after annealing at 54 K for 270 h. The reflections from the stainless steel container have been excluded from the refinement. The derived refinement factors are  $R_p = 3.25\%$ ,  $R_{wp} = 4.48\%$ ,  $R_B = 0.17\%$  and goodness of fit = 2.14.

**Table 1.** Atomic coordinates of ordered PdD<sub>0.65</sub> using space group  $Pm\bar{3}n$ .  $a = 8.036(1)$  Å. Deuterium occupancies after 250 h at 54 K. (Errors in parentheses are at 1 esd.)

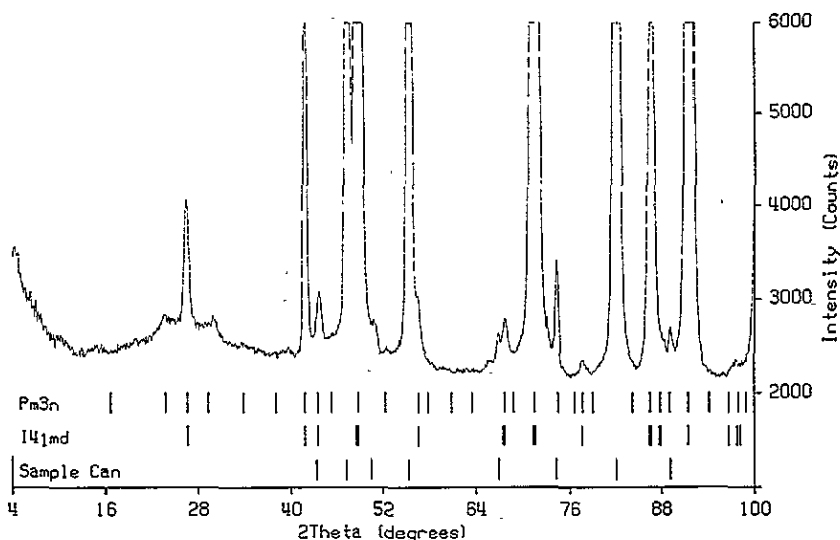
Atom	Site	(x, y, z)	Occupancy
Pd(1)	2a	0,0,0	1.0
Pd(2)	6b	$0, \frac{1}{2}, \frac{1}{2}$	1.0
Pd(3)	24k	$0, \frac{1}{4}, \frac{1}{4}$	1.0
D(1)	6c	$\frac{1}{4}, 0, \frac{1}{2}$	0.971(6)
D(2)	6d	$\frac{1}{4}, \frac{1}{2}, 0$	0.327(6)
D(3)	8e	$\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$	0.649(7)
D(4)	12f	$\frac{1}{4}, 0, 0$	0.649(6)



**Figure 4.** The refined site occupancies for c site (squares) and d site (circles) as a function of annealing time (log scale) at 54 K.

fitted to the models. The smaller superlattice lines are produced by considerably smaller concentration imbalances between the four deuterium sites, and this imbalance is therefore more difficult to quantify. The problem is further compounded by the relatively large diffuse background which peaks at  $(1\frac{1}{2}0)$ . However, consideration of the structure factors of these reflections indicates that they are likely to be evidence of movements of deuterium either to or from the f sites of table 1. Broadening of the widths of these lines suggests that this more subtle ordering is not fully established.

For comparison we have applied the model in  $I4_1md$  to the sum of 40 diffraction patterns from the ordered phase and found a deuterium occupancy of 0.820(6) at the (0,0,0) position and a deuterium occupancy of 0.468(5) at the  $(0,0,\frac{1}{2})$  position. These two models ( $I4_1md$  and  $Pm\bar{3}n$ ) provide a fit of similar quality, but offer differing interpretations. Refinement using  $Pm\bar{3}n$  returns slightly better quality factors ( $R_p = 2.05\%$ ,  $R_B = 0.58\%$ ) than the refinement using  $I4_1md$  ( $R_p = 2.44\%$ ,  $R_B = 0.82\%$ ). In the  $Pm\bar{3}n$  model, anisotropic line broadening is ascribed to anisotropic strain broadening as described above, and in the  $I4_1md$  model it can be ascribed to tetragonal distortion of the lattice  $c/2a = 1.004$ . A



**Figure 5.** Magnification of the lower 10% of the diffraction pattern (summed over 12 days). Reflection markers for the cubic ( $Pm\bar{3}n$ ) and tetragonal ( $I4_1md$ ) ordered phases, as well as those of the sample can have been included.

tetragonal distortion of this magnitude should be well-resolved on MRPD. For example, the separation of (008) from the (400) and (040) reflections should be  $\sim 0.75^\circ$  (see figure 3 at  $2\theta \sim 112^\circ$ ). This represents an increase in peak width of  $> 2$  times the instrument linewidth at that angle, and a commensurate decrease in peak height. Even if a tetragonal distortion was accompanied by significant line broadening, multiplicity factors would tend to skew the peak towards lower angle. That this splitting is not visible indicates that anisotropic strain broadening is the dominant factor, and that the specimen contains a continuous distribution of distortions. The anisotropic line broadening is not restricted to the ordered phase, being  $\sim 2.8 \times 10^{-3}$  at 84 K, where there are no superlattice reflections but some diffuse scattering is evident around  $(1\frac{1}{2}0)$ . This last point is significant because it indicates that strain fields exist even before the deuterium orders. Consequently, as the deuterium ordering proceeds there is no fundamental change in the nature of the strain fields, only their distribution.

The present results differ markedly from those on  $PdD_{0.76}$  at 70 K by Ellis *et al* [7] who observed a set of superlattice reflections which could be indexed on a tetragonal cell ( $a \approx 6.38 \text{ \AA}$ ,  $c \approx 4.02 \text{ \AA}$ ) with the  $ac$  cell faces composed of (420) planes of the disordered structure ( $Fm\bar{3}m$ ). Our preliminary measurements of  $PdD_{0.76}$  agree with the results of Ellis *et al* indicating that the nature of the ordering of deuterium is concentration-dependent. We are continuing our study of the ordering at higher deuterium concentration.

Finally, we note that these results and our analysis are to some extent at variance with the calculations of Sanchez and de Fontaine [14] and Bond and Ross [15], which have been used to produce phase diagrams for ordered Pd-H and Pd-D. However, the broad predictions of these calculations (i.e. the existence of two ordered phases and the transition temperatures) are not in question, only the precise structure and stoichiometry of the ordered compounds. Our model for the ordered phase of  $PdD_{0.65}$  appears to have no simple stoichiometric limits, but we are unable to state at this stage whether or not this represents a significant deficiency in the model.

In summary, our neutron powder diffraction results demonstrate that the '50 K anomaly'



is due to a slow disorder  $\rightarrow$  order transition of deuterium within octahedral interstitial sites. The transition to the ordered phase appears to be associated with the existence of a deuterium nearest-neighbour repulsive interaction. Cubic symmetry is preserved in the ordered phase, which is accurately described in space group  $Pm\bar{3}n$  by doubling the lattice constant from the high-temperature structure ( $Fm\bar{3}m$ ). The transition primarily involves diffusion of deuterium from specific interstitial d sites to the neighbouring c sites (equivalent in the disordered state), with some smaller movements involving the f sites. Therefore relative to the randomly distributed deuterium atoms in the 'disordered' state, the deuterium occupancy of the nearest-neighbour d site is decreased and the occupancy of the second-nearest-neighbour c site is enhanced.

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