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# PROTON DENSITY MODULATION OF D ATOMS IN $PdD_{1-x}$



by

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# PROTON DENSITY MODULATION OF D ATOMS IN $PdD_{1-x}$

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## ABSTRACT

Recent resistivity and neutron diffraction measurements have provided evidence for ordering of D(H) atoms on the octahedral interstitial sites of $PdD_{1-x}$. This order-disorder transition is responsible for the "50 K anomaly" which has been reported in many of the physical properties. Neutron diffraction measurements on a $PdD_{0.76}$ single crystal revealed satellite reflection at (4/5,2/5,0) and equivalent positions. These satellites can be accounted for by a multi-domained tetragonal unit cell with $a_t = a_c\sqrt{5/2}$ and $c_t = c_a$. This ordered state can be described as a deuteron density wave along a <420> cubic direction. This density is modulated such that four fully occupied planes (Pd & D) are followed by a vacant plane (Pd only).

## INTRODUCTION

Many properties of $PdD_{1-x}$, such as resistivity, specific heat, internal friction and Hall effect, have shown an anomaly at ~50 K. The features of these anomalies have pointed towards an ordering of the D(H) atoms. In a recent article,[1] the present authors reported the results of a resistivity and neutron diffraction study on a single crystal of $PdD_{0.76}$. This study was carried out as a function of temperature and time which provided direct evidence for an order-disorder transformation. It is the purpose of the present article to expand on the crystallographic aspects of this ordered structure.

## EXPERIMENTAL

A single crystal of Pd (0.32 cm dia x 2.5 cm length) was charged with deuterium under pressure and temperature to a composition of $PdD_{0.76}$ with an accompanying volume increase of ~10%. The crystal was mounted in the cryoorienter and held for ~100 hrs at 70 K before scanning in reciprocal space for superlattice reflections with neutrons, $\lambda = 1.03$ Å. The positions at the normal lattice reflections and a series of satellites are shown in Fig. 1. In the specific scan (heavy arrow) from the (200) through the (1,½,0) [W point] it was observed that (1) the ratio of the (200) to the satellite was approximately 350:1, (2) a peak was not observed at (1,½,0) and (3) an observed satellite originates from one of 6 possible domain orientations. All domains were found to have nearly equal volume as judged by the diffracted intensities. Intensity data was then obtained for

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17 different satellite reflections belonging to one domain. A later separate cool down and anneal resulted in ∿50 reflections, however, considerable increase of intensity on a standard (200) reflection resulted in a normalization factor of 2x with time and an overall increase of intensity of 2x from the original set.

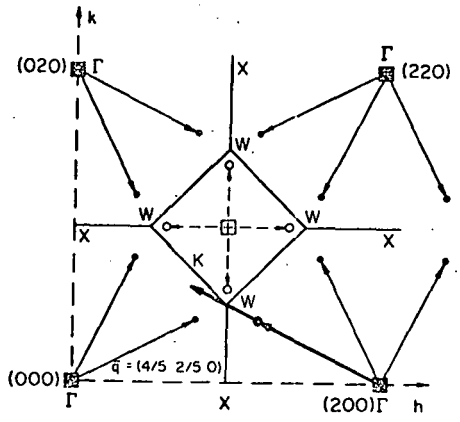


Fig. 1. Location of satellites in reciprocal space on the hk0 plane. The open square is a projection from (1,1,±1) and the open circles are projections of satellites in the (h,k,±0.2) planes. The heavy arrow marks a special scan as discussed in the text.

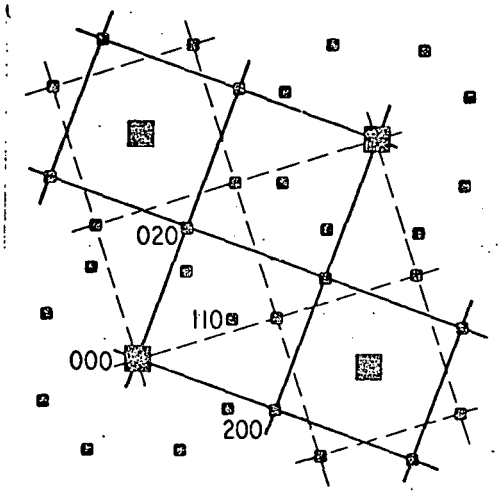


Fig. 2. Normal reciprocal lattice (▩) and reciprocal lattice (◍) of two orientations of the ordered cell. All satellite reflections can be accounted for by a domained structure.

## DISCUSSION

Fig. 2 is a reciprocal lattice plot showing the relation of the normal lattice reflections to the ordered domained cell. Note the normal lattice reflections periodically fall on the reciprocal lattice ordered cell and all the satellite reflections can be accounted for on a domained structure.

The real tetragonal unit cell of the ordered structure is shown in Fig. 3. Above the ordering temperature (∿70 K) for $PdD_{0.76}$ the D atoms occupy the octahedral sites at random thus leaving a random array of vacant sites. Upon annealing at the appropriate temperature the vacancies order as shown in Fig. 3 creating vacancies at the origin and at $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. The lattice constants are as follows: $a_t = a_c\sqrt{5/2}$ and $c_t = a_c$. This tetragonal cell, possible S.G. I4/m, has 18 atoms as follows: 2 Pd at (b) $00\frac{1}{2}$; 8 Pd at (h) xyo where $x \simeq 0.1$, $y \simeq 0.3$ and 8D (actually 7.6 atoms random) at (h) xyo where $x \simeq 0.2$, $y \simeq 0.6$. A careful look at Fig. 3 reveals a series of parallel (420) planes (shown by long dashed lines) which represents a modulated deuteron

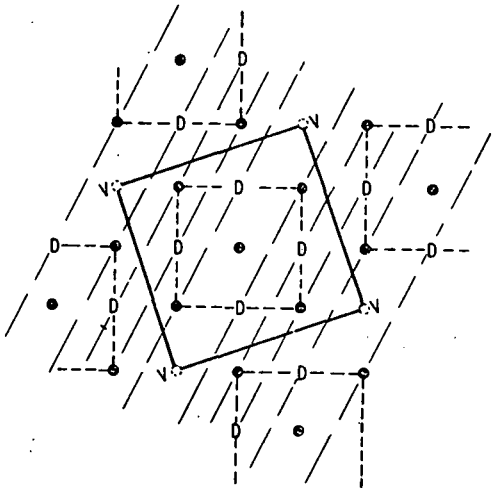

Fig. 3. Normal real cell showing relationship to ordered unit cell with vacancies (V) at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ positions.

density wave consisting of four fully occupied $(420)_c$ planes (i.e., all octahedral sites filled with Pd and D atoms) followed by one vacant plane (i.e., Pd atoms only). From a least squares solution on the 17 original observed satellites there is evidence that the D atoms are displaced slightly from their ideal sites (~0.6 Å) towards the vacant planes whereas the Pd atoms show less displacement (~0.015 Å). Although the set of ~50 reflections showed the same basic ordered structure there is an indication of lowered symmetry as judged by nonequivalence of pairs of reflections such as (301) ≠ (031) and (402) ≠ (042).

This dynamic ordering system requires considerable time to reach equilibrium hence could result in a slight change of structure with time (in addition to perfection) and therefore slight change in symmetry. Due to the domained structure we have confined our refinement to the satellite reflections only. It is also possible that the period of the modulation may change with composition, for example, a peak at $(1,\frac{1}{2},0)$ was recently reported.[2] Elastic free energy calculations[3] for $PdD_{1-x}$ shows free energy minimas for D concentration waves with wave vectors in the vicinity of (4/5,2/5,0) in good agreement with the experimental observation. The displacements of Pd and D atoms in I4/m involve a cooperative rotation towards the vacancy plane, however, nonequivalence of certain reflections (sited above) may require a motion of all D atoms directly towards the vacant (110) type planes.

## REFERENCES


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