Structure refinements on NbS_2 films

NbS_2 is known to form with two structure types which have been classified as 3R (forms below 850°C) and 2H (forms above 800°C). The 3R structure was a poor match to the PXD data. The 2H NbS_2 structure[1] gives a similar diffraction pattern to the observed data, however the 1T structure as adopted by some other transition metal dichalcogenides (e.g. TaS_2)[2] was also a close match.

The 2H structure consists of close packed sulfur atoms with an AABB repeat unit, Nb is located in half of the trigonal prismatic sites. The double layer repeat unit is shown in Fig. 1, the structure in the xy plane is of edge-linked NbS_6 trigonal prisms. The 1T structure contains hexagonal close packed sulfur atoms (AB repeat unit) with Nb filling half of the octahedral holes in every other layer. Hence the structure is of edge linked NbS_6 octahedra. Two layers of the repeat unit are shown.

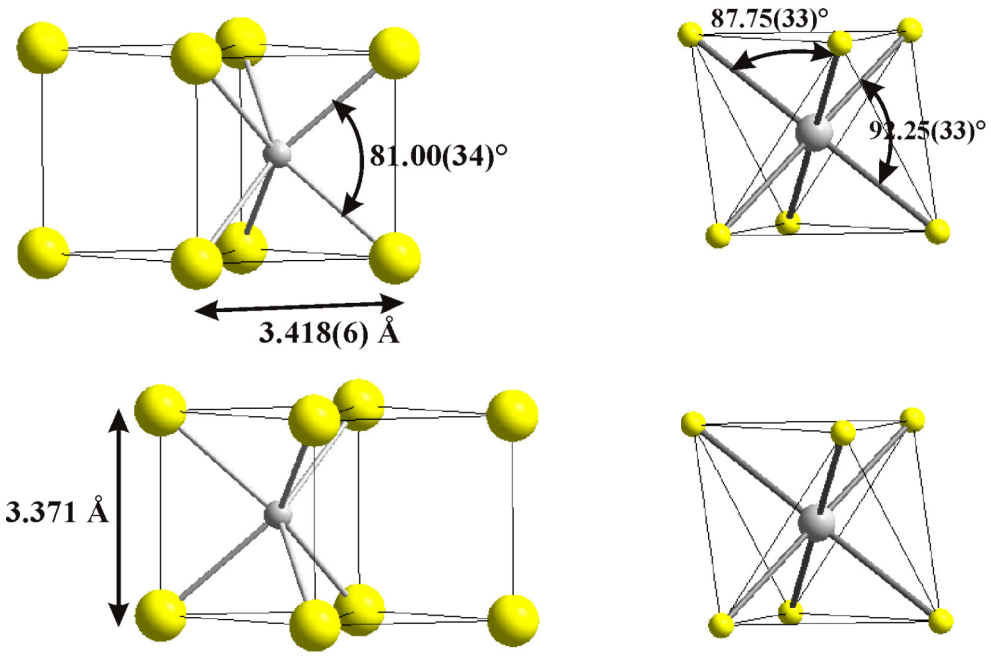

Figure 1 2H (left) and 1T (right) NbS_2 structures distances and angles shown are as refined from the NbS_2 thin films by PXD. Thermal ellipsoids are shown at the 50% probability level.

Grazing incidence data were collected at ambient temperature on station 2.3 at the UK Synchrotron Radiation Source with 1.2982 Å X-rays and an incidence angle of 1.5°. The data contained a large glass background and this was removed by subtracting a heavily smoothed and normalised dataset collected on a glass substrate. Data collected with a copper standard was used to obtain an instrumental Gaussian peak shape, this was then kept fixed when fitting the NbS_2 data.

Rietveld refinements using the 2H and 1T structure models were performed with the GSAS package [3]. Both were stable and converged. A cosine Fourier series (GSAS #2) with 6 terms was used to model the background and lattice parameters, zero point and scale factor were allowed to refine. Using profile function #2 the Gaussian terms were fixed at the values obtained with the Cu standard. The particle size broadening term was refined but no strain broadening was found. Transparency was also refined to a fairly high value (unsurprising

since the glass substrate was observed in the data, hence the offset in the tick marks on the fit diagrams. Particle size in Å is defined as $p = 18000K\lambda / \pi X$ [4] where K is the Scherrer constant and X is the particle size associated Lorentzian term from the Rietveld refinement. Our values were 38 and 36 for the 2H and 1T structures respectively, corresponding to an average crystallite size of around 180Å. Preferred orientation ratio along 0,0,1 refined to values of 1.18 (2H) and 1.27 (1T). Growth of the layers perpendicular to the substrate is common in dichalcogenide films and this is apparent in preferential c-axis growth.

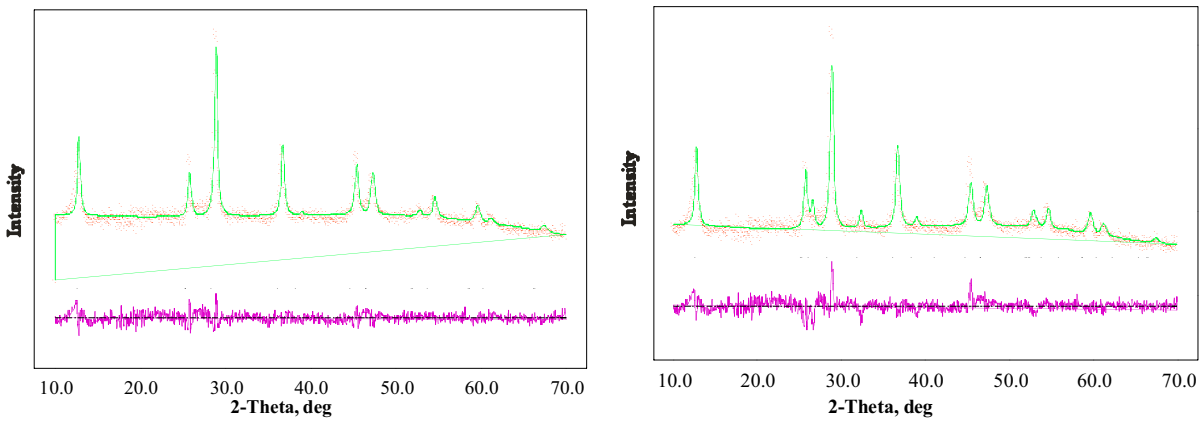

Figure 2 Rietveld fits to the structure of NbS_2 thin film using the 1T (left) and 2H (right) structure models. The pink line is the difference between the calculated (green line) and observed (red crosses) intensity. Tick marks show the allowed reflection positions.

The fit statistics are better for the 1T structure to a significant degree, Table 1. In addition, the 2H structure should have extra reflections, compared with the 1T, at 26.5° (*101*) and 32.5° (*103*) since it has a doubled c axis. These are not observed.

Table 1 Refined crystallographic parameters for NbS_2 with the 1T and 2H structure models.

	1T structure	2H structure
Space group	$P\bar{3}m1$ (No. 164)	$P6_3/mmc$ (No. 194)
a, c (Å)	3.420(6), 5.938(11)	3.418(6), 11.860(23)
Cell volume (Å^3)	60.16(19)	120.0(4)
Nb site	*1a*	*2b*
x, *y*, *z*	0, 0, 0	0, 0, ¼
U_{iso} (Å^2 × 100)	3.5(4)	2.4(3)
S site	*2d*	*4f*
x, *y*, *z*	⅓, ⅔, 0.2491(29)	⅓, ⅔, 0.1079(16)
U_{iso} (Å^2 × 100)	1.6(6)	7.8(7)
χ^2	1.893	2.363
R_{wp}	6.52%	7.29%
R_p	5.20%	5.67%
Nb-S (Å)	2.467(11)	2.595(13)
Nb-S-Nb (°)	87.8(5)	82.4(5)

The Nb thermal parameter in the 1T structure is slightly high but the S thermal parameter in the 2H structure is very high. This is of questionable significance since the data used are, inevitably with a thin film, not of the highest quality. For the same reason, no atom fractional occupancies were refined.

References

1) F. Jellinek, G. Brauer and H. Müller, *Nature*, 1960, **185**, 376.

2) A. Spijkerman, J. L. de Boer, A. Meetsma, G. A. Wiegers and S. van Smaalen, *Phys. Rev. B*, 1997, **56**, 13757.

3) R. B. von Dreele and A. C. Larson, "GSAS: general structure analysis system," Neutron Scattering Centre, MS-H805, Los Alamos National Laboratory, Los Alamos, NM (2001).

4) GSAS technical manual.