

Structure of 2H-TaS₂

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Abstract. Tantalum disulfide, 2H-TaS₂, $M_r = 245.07$, hexagonal, $P6_3/mmc$, $a = 3.314(1)$, $c = 12.097(1)$ Å, $V = 115.06(5)$ Å³, $Z = 2$, $D_x = 7.073$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 485.3$ cm⁻¹, $F(000) = 210$, $T = 295$ K, $R_F = 0.032$ for 210 observed reflections with $I \geq 2.5\sigma(I)$. The structure determination confirms the structure known from powder data. Ta is in trigonal-prismatic coordination by S and the Ta—S distances are 2.468(2) Å.

Introduction. Several modifications [see Hulliger (1976) for a review] are known for tantalum disulfide, the forms extensively studied being 1T-TaS₂, space group $P3m1$ [Cd(OH)₂-type structure], with Ta in octahedral coordination by S, and 2H-TaS₂, space group $P6_3/mmc$ with Ta in trigonal-prismatic coordination by S. The 1T modification is stable at high temperatures but by quenching it can easily be retained to room temperature (Revelli & Philips, 1974). By annealing at 823 K (Revelli, 1979) the 1T form transforms into the 2H form during which stacking faults occur. These results conflict with those of Conroy & Pisharody (1972) who reported the growth of crystals of 2H-TaS₂ at 1073 K by vapor transport using I₂ as transport agent in a gradient of 1273–1073 K. 1T-TaS₂ has been studied extensively by single-crystal X-ray diffraction, the interesting feature being the incommensurate (already present at room temperature) and commensurate lattice distortions owing to charge-density waves. The structure of 2H-TaS₂ as determined by Jellinek (1962) from powder data, is described in space group $P6_3/mmc$ with the atoms on special positions: Ta at $2(b)$: $(0, 0, \frac{1}{4})$ and S at $4(f)$: $(\frac{1}{3}, \frac{2}{3}, z)$ with $z = \frac{1}{8}$. Because of the large difference in the scattering factors of Ta and S, it is not possible to obtain the z coordinate of S accurately from powder data. In an attempt to grow a misfit layer compound (HoS)_{*n*}TaS₂ (Wiegiers *et al.*, 1989) by vapor transport [temperature gradient 1273–1073 K, chlorine from (NH₄)₂PbCl₆ as transport agent], crystals of 2H-TaS₂ without stacking faults were formed. Refinement using data from a single crystal was considered to be

worthwhile, accurate Ta—S distances being of importance for band-structure calculations, for discussions on bonding in intercalates of 2H-TaS₂ (e.g. In_{0.67}TaS₂; Abriel & Lerf, 1988) and misfit layer compounds with TaS₂ sandwiches as building units [e.g. (PbS)_{1.13}TaS₂ (Wulff, Meetsma, van Smaalen, Haange, de Boer & Wiegiers, 1990), (SmS)_{1.19}TaS₂ (Wiegiers *et al.*, 1989)]. In this paper the refinement of 2H-TaS₂ is described. A study of the lattice distortions in the PLD-CDW state (below about 75 K; Tidman, Singh, Curzon & Frindt, 1974) will be performed when we have access to low-temperature facilities.

Experimental. A suitable plate-shaped crystal (0.08 × 0.06 × 0.0015 mm) was glued on the top of a glass fibre and mounted on an Enraf–Nonius CAD-4F diffractometer [295 K; graphite-monochromated Mo $K\alpha$ radiation; 2133 reflections scanned; $\omega/2\theta$ scan, $\Delta\omega = (1.0 + 0.35\tan\theta)^\circ$; $1.69 < \theta < 45.0^\circ$; $(\sin\theta)_{\text{max}}/\lambda = 0.9949$ Å⁻¹; h 0 → 6; k -6 → 5; l -24 → 24]. Unit-cell dimensions and their standard deviations were determined from the setting angles of 22 reflections in the range $28.61 < \theta < 29.85^\circ$ in four alternate settings (de Boer & Duisenberg, 1984). The three check reflections were measured every 2 h of exposure (014: r.m.s.d. 0.40%; 112: r.m.s.d. 0.34%; 014: r.m.s.d. 0.45%); these showed no decay during the 35.2 h of X-ray exposure time. Analysis of the reflections revealed that they could be indexed using a hexagonal unit cell; the space group was derived from the observed systematic absences. A 360° ψ scan for the close-to-axial reflection (310) showed an intensity variation up to 43% about the mean value. The intensity data were corrected for the scale variation, Lorentz and polarization effects and for absorption using a Gaussian integration method (Spek, 1983; grid: 6 × 6 × 12, corrections in the range 2.06 to 13.51). Standard deviations in the intensities based on counting statistics were increased according to an analysis of the excess variance (McCandlish, Stout & Andrews, 1975) of the three reference reflections: $\sigma^2(I) = \sigma_{\text{cs}}^2(I) + (0.0035I)^2$; equivalent reflections were averaged resulting in 211 reflections satisfying the $I \geq 2.5\sigma(I)$ criterion of observability.

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Table 1. Final fractional atomic coordinates and mean-square amplitudes (\AA^2) with e.s.d.'s in parentheses

$$F(\mathbf{h}) = F_o(\mathbf{h}) \exp(-2\pi^2 \sum_{i=1}^3 \sum_{j=1}^3 h_i h_j a_i^* a_j^* U_{ij}).$$

	x	y	z	U_{11}	U_{33}
Ta(1)	0	0	$\frac{1}{4}$	0.0034 (1)	0.0065 (2)
S(1)	$\frac{1}{3}$	$\frac{2}{3}$	0.1212 (2)	0.0048 (5)	0.0068 (8)

Notes: $U_{11} = U_{22} = 2U_{12}$; $U_{13} = U_{23} = 0$.

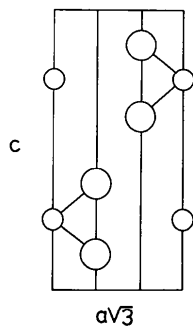


Fig. 1. $(11\bar{2}0)$ section of the structure of $2H\text{-TaS}_2$; large and small circles represent Ta and S atoms, respectively. The Ta—S bonds are indicated.

Refinements by full-matrix least squares on F performed in space group $P6_3/mmc$ (No. 194; *International Tables for Crystallography*, 1983) with Ta at $2(b)$ and S at $4(f)$ and anisotropic thermal parameters converged at $R_F = 0.032$, $wR = 0.037$, $S = 1.868$; $w = 1$; six parameters refined; $\langle \Delta/\sigma \rangle = 0.0013$, max. $\Delta/\sigma = 0.007$. The reflection (002) with $w(|F_o| - |F_c|) > 20$ was excluded from the refinement. The final difference Fourier map revealed a residual peak of 15.0 e \AA^{-3} at the origin; refinement of the s.o.f. of a Ta or Ho atom at this position led to a value of zero. Min. and max. (besides the origin peak) residual densities in final Fourier map -5.5 and 2.5 e \AA^{-3} . Final fractional atomic coordinates and anisotropic thermal parameters for the atoms are given in Table 1.* Scattering factors from Cromer & Mann (1968). Anomalous-dispersion factors from Cromer & Liberman (1970). All calculations carried out on the CDC-Cyber 170/760 computer of the University of Groningen with *XTAL* (Hall & Stewart, 1987) and *EUCLID* (Spek, 1982; calculation of geometric data).

* A list of structure factors has been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52890 (2 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Discussion. Atomic coordinates are shown in Table 1. The unit-cell dimensions from this study, $a = 3.314$ (1), $c = 12.097$ (1) \AA are in good agreement with those found from X-ray powder diffraction: $a = 3.315$, $c = 12.10$ \AA (Jellinek, 1962); $a = 3.316$ (2), $c = 12.070$ (2) \AA (Conroy & Pisharody, 1972). An accurate value for the c axis, 12.100 (3) \AA , was reported by Givens & Fredericks (1977). Our study confirms the structure proposed from powder data (Jellinek, 1962). The structure is described in space group $P6_3/mmc$ with the atoms on special positions: Ta in $2(b)$: $0, 0, \frac{1}{4}$; S in $4(f)$: $\frac{1}{3}, \frac{2}{3}, 0.1212$ (2). The z coordinate of S does not deviate much from the accepted value $z = \frac{1}{8}$ for which sulfur planes are at equal distances. The structure is built of TaS_2 sandwiches with Ta in trigonal-prismatic coordination by S (Fig. 1). The sandwich height is 3.116 \AA and the distances between neighboring sandwiches is 2.932 \AA . There are no indications for an occupancy of octahedral or tetrahedral sites in the van der Waals gap.

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