

Time-of-Flight Single-Crystal Neutron and X-ray Diffraction Study of $K_{0.26}WO_3$

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Abstract. Time-of-flight neutron diffraction data from a single crystal of $K_{0.26}WO_3$ were refined with space group $P6_3$ using only $l = 2n$ reflections [$R(F) = 0.051$]. The odd- l data were not included in the refinement because of poor agreement with the structural model, indicating that the model is correct for a superposition of the two-layer structure into a single layer, but a characterization of the individual layers was not obtained. These results are consistent with previously reported single-crystal X-ray and powder neutron diffraction analyses, although a different space group was chosen. In addition, satellite reflections were observed which may be due to a superlattice structure involving K vacancies and modulation of the positions of the O atoms. The absence of satellite reflections in X-ray diffraction patterns indicates that the W atoms are not involved in the superstructure. The results of a single-crystal X-ray analysis are $M_r = 241.99$, hexagonal, $P6_3$, $a = 7.389$ (1), $c = 7.508$ (2) Å, $V = 355.0$ (1) Å³, $Z = 6$, $D_x = 6.79$ Mg m⁻³, $\lambda(\text{Mo K}\alpha) = 0.7107$ Å, $\mu = 50.30$ mm⁻¹, $F(000) = 761.64$, $T = 295$ K, final $R = 0.046$ for 804 observed data.

Introduction. Recent studies of the hexagonal tungsten bronzes (HTB's) of the type M_xWO_3 , where $M = K$, Rb or Cs for $0.20 < x < 0.33$, reveal correlations between electronic transport properties and composition (Caldwell, Morris & Moulton, 1981). For instance, the superconducting transition temperature, T_c , is a continuous function of x for Cs but exhibits a discontinuity at $x = 0.25$ for K and Rb. The structures of the HTB's as determined by Magnéli (1953) using X-ray diffraction film techniques have a hexagonal space group $P6_3/mcm$ and consist of layers of corner-sharing WO_6 distorted octahedra in the $z = \frac{1}{4}$ and $z = \frac{3}{4}$ planes of the unit cell. The M atoms reside in one-dimensional channels parallel to the c axis in crystallographic sites which are fully occupied when $x = \frac{1}{3}$ and three-fourths occupied when $x = \frac{2}{3}$. This same

structure type has been observed in an extensive series of HTB crystals, with $M = Rb$, In and Tl, based on X-ray diffractometer data (Labbe, Goreaud, Raveau & Monier, 1978, 1979).

A powder neutron diffraction investigation of $K_{0.26}WO_3$ revealed the presence of observable $h0\bar{h}l$ peaks with l odd, indicating that the c -glide plane is not present and that space group $P6_3/mcm$ is not correct (Pye & Dickens, 1979). A structural model with space group $P6_322$ was refined with single-crystal X-ray data. However, attempts at neutron diffraction profile refinements of data from $K_{0.26}WO_3$, $Rb_{0.26}WO_3$ and $Tl_{0.3}WO_3$ were not successful, which indicated that the model was not completely correct (Pye, 1978).

Electron diffraction investigations of single crystals of K_xWO_3 reveal the existence of a complex superstructure (Krause, Moulton & Morris, 1985). In the c -axis direction, the superposition of domains with superlattice periodicities of $c' = (4N + 2)$ layers produces apparently incommensurate superlattice Bragg peaks in the diffraction pattern. Values of N range from 3 to 16 or more and are dependent on the value of x . For $K_{0.26}WO_3$, the superlattice pattern can be understood as a superposition of domains with $N = 4$ and $N = 5$. In addition, commensurate superlattice peaks in the $hk0$ plane of the hexagonal reciprocal lattice were observed in some samples. It was proposed that long-range ordering of the K vacancies, possibly associated with an overall lattice distortion, are responsible for the superlattice. Neutron diffraction evidence of a structural phase transition in a powder sample of Rb_xWO_3 has also been reported (Sato, Grier & Shirane, 1982).

In this paper we present a room-temperature neutron and X-ray diffraction study of single crystals of $K_{0.26}WO_3$.

Experimental. *Neutron diffraction data collection and analysis.* Single-crystal neutron diffraction time-of-flight (TOF) data were obtained at the Intense Pulsed Neutron Source (IPNS) in a manner previously described in detail (Schultz, Srinivasan, Teller, Williams & Lukehart, 1984). The data were collected with the 30×30 cm position-sensitive neutron scintillation

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detector centered about the 2θ angle of 90° and with a sample-to-detector distance of 27.0 cm. A total of 15 histograms were measured for 15 different χ and φ diffractometer crystal settings covering more than an octant of reciprocal space ($-7 \leq h \leq 10$, $-11 \leq k \leq 3$, $0 \leq l \leq 11$). The neutron wavelength range for each histogram was 1.0 to 3.0 Å. The crystal used for data collection was an hexagonal prism with a diameter of 1.5 mm and a length of 4.5 mm.

The incoherent scattering from a vanadium sample was used to correct the data for the wavelength dependence of the incident neutron flux and the detector efficiency. The absorption correction was calculated (Schultz *et al.*, 1984) using a linear absorption coefficient obtained by a linear interpolation between $\lambda = 1.0 \text{ \AA}$ ($\mu = 0.45 \text{ cm}^{-1}$) and $\lambda = 3.0 \text{ \AA}$ ($\mu = 1.34 \text{ cm}^{-1}$).

Analysis of the two-layer structure. The results of previous structural studies are presented in Table 1. The structures of K_{0.27}WO₃ and K_{0.31}WO₃ reported by Magnéli (1953) are based on fitting the X-ray powder pattern of K_xWO₃ to a model based on the single-crystal X-ray (film) structure of Rb_{0.27}WO₃. In the study by Pye & Dickens (1979), the final parameters were obtained from a refinement of single-crystal X-ray data using the space group $P6_322$ based on an examination of neutron powder diffraction data. Our single-crystal data also clearly show $h0\bar{h}l$ peaks (Fig. 1) indicating that the c -glide plane is not present.

Table 1. Atomic coordinates (x, y, z) from previous studies

	$P6_3/mcm^*$		$P6_322^\dagger$	
W	6(g)	0.47, 0, $\frac{1}{2}$	6(g)	0.479, 0, 0
O(1)	12(f)	0.42, 0.21, $\frac{1}{2}$	12(i)	0.426, 0.217, -0.028
O(2)	6(f)	$\frac{1}{2}$, 0, 0	6(h)	0.484, -0.033, $\frac{1}{2}$
K	2(b)	0, 0, 0	4(e)	0, 0, 0.220

* Magnéli (1953).

† Pye & Dickens (1979).

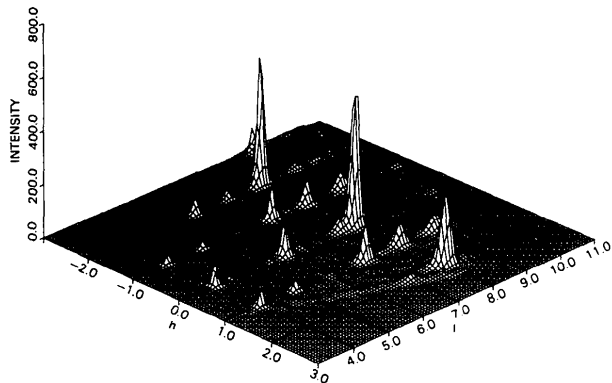


Fig. 1. A plot of a portion of the $h0\bar{h}l$ plane. Note the intense reflections for $l = 5, 7$ and 9 . Also note the appearance of superlattice satellite reflections.

Refinements of the single-crystal neutron data were carried out in each of the three space groups $P6_3/m$, $P6_3/22$ and $P6_3$. Although the refinements converged in all three space groups with relatively small differences in the R factors, the overall agreement between observed and calculated structure factors remained poor with the best refinements yielding $R(F) = 0.20$ and $R(F^2) = 0.35$. Agreement factors at this level were also obtained by Pye (1978) with neutron powder diffraction profile refinements of the Tl, Rb and In tungsten bronzes. For each of the single-crystal data refinements, the fit was better for even- l data in comparison to the odd- l data which are generally much weaker. However, the disagreement appears to be a fundamental one, rather than due to poor counting statistics.

Thus, in order to obtain a model which at least provides some information about the structure, it was refined using only the even- l data. The model is therefore a superposition of the two-layer structure into a single layer. The best refinement in space group $P6_322$ led to $R(F) = 0.077$ and $wR(F^2) = 0.146$ using isotropic thermal parameters, one extinction parameter and 15 scale factors (one for each histogram). By comparison, in space group $P6_3$, the refinement converged to $R(F) = 0.051$ and $wR(F^2) = 0.105$, such that this space group was used in the final calculations. Reflection data were analyzed using a locally modified least-squares program for variable-wavelength data (Schultz *et al.*, 1984). The function $\sum w(F_{\text{obs}}^2 - F_{\text{calc}}^2)^2$ was minimized, where $w = 1/\sigma(F_{\text{obs}}^2)$ and $\sigma(F_{\text{obs}}^2) = [\sigma_{\text{counting}}^2(F_{\text{obs}}^2) + (0.02F_{\text{obs}}^2)^2]^{1/2}$. It was also necessary to constrain the O(1B) thermal parameter to be equal to that of O(1A) and to fix $z = 0.0$ for O(2). Table 2 contains the final positional and thermal atomic parameters and Table 3 presents selected bond distances and angles.* Ratio of maximum least-squares shift to e.s.d. was 0.012. The neutron model using only the 231 even- l data with $F^2 \geq 3\sigma(F^2)$ is completely consistent with the X-ray model based on all the data (see below). The maximum height in the final difference Fourier synthesis was 3.5% of an O atom.

X-ray diffraction data collection and analysis. A crystal of K_{0.26}WO₃ shaped like a hexagonal prism with dimensions of $0.04 \times 0.04 \times 0.12$ mm was epoxied to the end of a glass fiber. Data were collected on a Picker diffractometer automated with the Krisel Control System and equipped with a graphite monochromator. Unit-cell parameters were obtained from a least-squares refinement of the angular settings of 24 automatically centered reflections ($21^\circ \leq 2\theta \leq 36^\circ$). Data were measured out to $2\theta_{\text{max}} = 60^\circ$ [$\lambda(\text{Mo } K\alpha) = 0.71073 \text{ \AA}$]

* Lists of neutron and X-ray structure factors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42728 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Atomic positional coordinates and isotropic temperature parameters, space group $P6_3$

The two lines for each atom are the neutron and X-ray structure parameters, respectively. In the case of the neutron structure, for each atom x, y, z a related atom at $x, y, \frac{1}{2} + z$ was generated, all atoms with occupancies of one-half.

	x	y	z	$B(\text{\AA}^2)$
W	0.477 (1)	-0.002 (1)	0.25	0.08 (8)
	0.47305 (6)	-0.00006 (6)	0.25	0.30 (2)
O(1A)	0.431 (2)	0.216 (2)	0.279 (2)	0.18 (7)
	0.429 (2)	0.221 (1)	0.280 (2)	0.63 (8)
O(1B)	0.204 (2)	0.411 (2)	0.224 (2)	0.18
	0.212 (2)	0.413 (2)	0.228 (2)	0.63
O(2)	0.526 (1)	0.001 (1)	0.0	1.4 (1)
	0.510 (7)	-0.008 (3)	0.0	3.1 (6)
K	0.0	0.0	0.053 (5)	4.9 (8)
	0.0	0.0	0.059 (5)	4.3 (4)

Table 3. Selected interatomic distances (\AA) and angles ($^\circ$)

	Neutron	X-ray	Neutron	X-ray
W-O(1A)	1.816 (14)	1.835 (10)	W-O(1B ^a)	2.067 (13)
W-O(1A')	2.029 (16)	2.009 (10)	W-O(2)	1.910 (2)
W-O(1B)	1.810 (16)	1.835 (11)	W-O(2 ^b)	1.877 (1)
K-O(1A)	3.24 (2)	3.21 (2)	K-O(1B ^b)	3.61 (3)
K-O(1A ^b)	3.45 (3)	3.45 (3)	K-O(2)	3.53 (7)
K-O(1B)	2.93 (2)	2.93 (2)	K-K ^c	3.754 (1)

	Neutron	X-ray
O(2)-W-O(2 ^b)	170.1 (3)	167.94 (5)
O(2)-W-O(1A)	103.0 (5)	104 (1)
O(2)-W-O(1A')	87.9 (4)	90 (1)
O(2)-W-O(1B)	91.7 (5)	90 (1)
O(2)-W-O(1B')	76.9 (4)	77 (1)
O(1A)-W-O(1A')	85.4 (7)	86.5 (6)
O(1A)-W-O(1B)	97.4 (4)	99.4 (4)
O(1A)-W-O(1B')	83.7 (4)	81.3 (4)
O(1B)-W-O(1B')	93.5 (7)	92.8 (6)
W-O(2)-W ^c	168.5 (3)	173 (3)

Symmetry operations: (i) $1-x, x-y, z$; (ii) $1-x, -y, \frac{1}{2} + z$; (iii) $-x, -y, -\frac{1}{2} + z$; (iv) $-x, -y, \frac{1}{2} + z$; (v) $1-x, -y, -\frac{1}{2} + z$.

using $\theta-2\theta$ step scans. Three check reflections measured periodically during the data collection did not show any significant variation in their intensities. The data were corrected for Lorentz and polarization factors and for absorption. The 4711 reflections ($-10 \leq h \leq 10, -10 \leq k \leq 10, 0 \leq l \leq 10$) were merged based on $6/m$ Laue symmetry to yield 897 unique reflections with merging R factors of $R(F^2) = 0.052$ and $wR(F^2) = 0.050$. In the least-squares calculations, the atomic form factors were corrected for anomalous scattering (*International Tables for X-ray Crystallography*, 1974) and an extinction parameter was refined (Schultz *et al.*, 1984). The final least-squares cycles only included the 804 data with an extinction-correction factor $\gamma \geq 0.7$ and with $F^2 \geq 3\sigma(F^2)$. The final atomic parameters are given in Table 2 and interatomic distances and angles are given in Table 3.* The ratio of maximum least-squares shift to e.s.d. was 0.0002. The maximum height in the final difference Fourier synthesis was 2.1% of a W atom.

* See deposition footnote.

Discussion. *The two-layer structure.* The results of the neutron and X-ray diffraction studies are in substantial agreement. Most significantly, both analyses lead to a structure in which O(1A) and O(1B) atoms are displaced from $z = \frac{1}{2}$ such that their z coordinates differ by $\pm c/20$. This is substantially the same result obtained by Pye & Dickens (1979), although in space group $P6_322$ O(1A) and O(1B) are related by a twofold symmetry axis, whereas in $P6_3$ this constraint is removed.

The X-ray data are dominated by scattering from the W atoms such that, without the knowledge of the neutron diffraction results, space group $P6_3/mcm$ could not be easily disputed. This is because those odd- l $h0\bar{h}l$ data that are greater than 3σ are nonetheless still very weak. However, it appears the lower symmetry indicated by the neutron data is corroborated by the essential similarity between the refined structures on the X-ray and neutron data. Fig. 2 is a stereoview of the unit cell. All W-O distances (Table 2) are in the range of 1.81 to 2.07 \AA , which is entirely consistent with values obtained from previous studies of this and related materials (Labbé, Goreaud, Raveau & Monier, 1979; Pye & Dickens, 1979).

We believe that the poor agreement between the observed and calculated structure factors when the odd- l data are included is very probably due to the effect of some type of long-range modulation of the two-layer structure. Since the odd- l data are weak, the effect on their intensities of a superstructure or of antiphase domains is proportionally greater, and, until the long-range model can be included in the calculations, the agreement for these data will remain poor. It is likely that these same factors account for the problems encountered by Pye (1978) with the neutron powder diffraction data.

The superlattice structure. The satellite peaks are most easily observed along the $00l$ reciprocal-lattice vector, as shown in Fig. 3, at positions where clusters of strong superlattice peaks also appear in the electron diffraction patterns. From the electron diffraction study it was proposed that the superstructure for $K_{0.26}WO_3$ consists of 3 or 4 layers with occupied K sites separated by a layer with vacant K sites and with a periodicity of

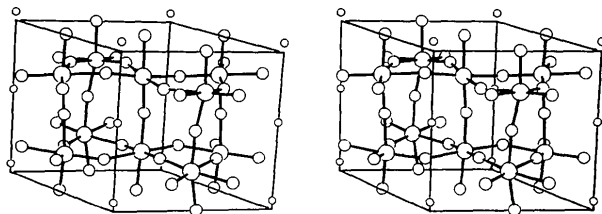


Fig. 2. A stereoscopic view of the $K_{0.26}WO_3$ unit cell based on the X-ray data. The circles, in increasing size, represent K, O and W atoms, respectively.

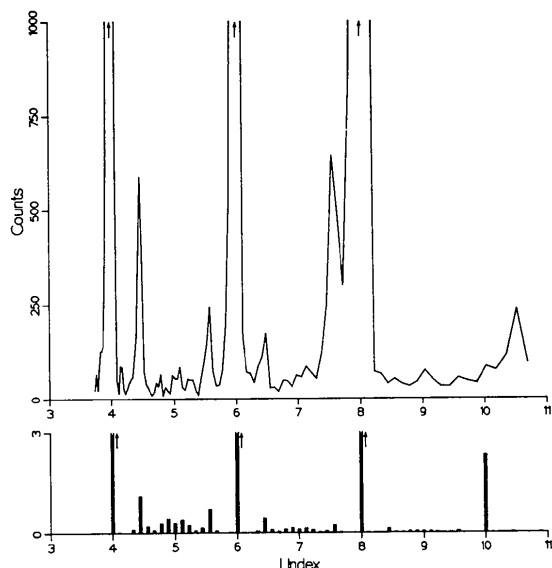


Fig. 3. Plot of intensity vs l value for the $00l$ reciprocal-lattice vector. Superlattice peaks are observable at $4 + \delta$, $6 \pm \delta$, $8 - \delta$ and $10 + \delta$, with $\delta = 0.44$. The lower plot is based on a calculated 18-layer superlattice with K vacancies in layers 1, 6, 10 and 14 (see text) and is normalized so that the fundamental Bragg reflections are properly scaled to the observed reflections in the upper plot. The satellite reflections calculated from long-range ordering of the K⁺ ions are about 200 times less intense than the observed satellites and do not qualitatively exhibit the intensity variation around the 008 and 0,0,10 reflections.

18 or 22 layers. We calculated the scattering along the $00l$ direction with several models for the K vacancies, such as $vKKKvKKKvKKKvKKK$ (v = vacancy) for 18 layers, and with an ordered two-layer structure for the W and O atoms (Fig. 3). In all cases, the

calculated intensities of the satellite peaks were at least two orders of magnitude less than the observed peaks, indicating that the satellite peaks must contain contributions from atoms other than K. In addition, with conventional X-ray diffraction techniques the satellite peaks are nearly unobservable, which indicates that the W atoms do not contribute to their intensities. It therefore appears that the positions of the O atoms are modulated to some extent by the K vacancies. We are presently attempting to obtain a model for the O modulation which will agree with the observed satellite reflections.

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Struktur von Natrium-pentafluoromanganat(III)

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Abstract. Na₂MnF₅, monoclinic, $P2_1/c$, $a = 7.719$ (1), $b = 5.236$ (1), $c = 10.862$ (2) Å, $\beta = 108.99$ (1)°, $V = 415.1$ (1) Å³, $Z = 4$, $D_x = 3.135$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7107$ Å, $\mu = 32.0$ cm⁻¹, $F(000) = 368$, $T = 295$ (1) K, final $R = 0.027$ for 1679 observed reflections. Crystals were grown from an aqueous hydro-

fluoric acid solution of MnF₃ and NaF. The structure shows strongly kinked chains [angle Mn–F–Mn 132.5 (1)°] of distorted MnF₆³⁻ octahedra sharing opposite vertices [mean $d(\text{Mn–F})$ axial 2.109, equatorial 1.849 Å]. The weakening of the axial bonds is half due to the structural bridging effect, half to the