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The Disordered Structure of WO_2Cl_2: A Powder Diffraction Study

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The crystal structure of the intercalation host WO_2Cl_2, F_w = 286.85, has been refined using powder neutron diffraction. Refinement was carried out in the orthorhombic space group, *Immm*, with a = 3.8414(1), b = 3.8851(1), c = 13.8720(4) Å, V = 207.03 Å^3, Z = 2. The final R factors are R_{wp} = 5.22%, R_{ex} = 4.74%, χ^2 = 1.21 for 26 basic variables with 7000 observations corresponding to 292 reflections. The structure consists of layers of tungsten oxide sandwiched between chloride ions to form trilayer blocks of general formula $[Cl–WO_2–Cl]_n$. These blocks stack in the c-direction to generate the three-dimensional structure. Only weak van der Waals forces hold the blocks together and as a result the compound is an excellent host for intercalation. The structure shows a distorted W environment accompanied by significant disorder in the layer planes.

Introduction

Intercalation hosts are an important class of compounds into which atoms, molecules, or ions may be reversibly inserted without major structural change. Where the intercalation of ions is involved, a compensating electronic charge is introduced onto the host lattice. Not only does intercalation represent a route to novel compounds but in addition these materials can have important technological applications, for example, as reversible electrodes in rechargeable batteries or electrochromic displays.

WO_2CL_2 is a layered material, with only weak van der Waals interactions between adjacent chloride layers, resulting in excellent intercalation properties between these layers. Li (*1*) and more recently Na (*2*, *3*)

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and Zn (*4*) have been successfully intercalated into WO_2Cl_2. Intercalation in these materials is accompanied by a color change from white to deep blue, making them of particular interest for electrochromic displays or smart windows. Structural studies of the sodium intercalate $NaWO_2Cl_2$ (*5*) have confirmed that the Na^+ ions reside between the chloride layers, preserving the overall layered structure, but with some layer slippage, causing an alteration in the orientation of the layers with respect to one another in order to create six-coordinate trigonal prismatic sites for the Na^+ ions.

The structure of WO_2Cl_2 was originally determined by Jarcow *et al.* (*6*), using single crystal X-ray diffraction methods. Both sharp and diffuse reflections were observed in the Weissenberg photographs. The presence of diffuse reflections was attributed to polytypic microtwinning. Considering all reflections, it was concluded that the basic symmetry of an untwinned individual was monoclinic. More recently X-ray powder diffraction has suggested that the true symmetry may in fact be orthorhombic (*7*). The proportion of the scattering due to oxygen is considerably greater for neutrons than for X-rays. Structure refinement of WO_2Cl_2 from neutron data should therefore be a more appropriate means of determining the detailed structure than X-ray diffraction techniques. We have undertaken a reexamination of the structure of WO_2Cl_2, using high-resolution powder neutron diffraction, in order to establish a clearer picture of its detailed structure and symmetry.

Experimental

Preparation

WO_2Cl_2 was prepared by solid-state reaction between WO_3 and WCl_6. Crystalline WCl_6 (99.9%, Aldrich) was ground and mixed with an equimolar amount of WO_3 (grade A1, Johnson Mathey) in an argon-filled Miller–Howe high-integrity glove box, in which the H_2O and O_2 contents were each maintained below 5 ppm. The reaction mixture was then sealed in a Pyrex tube and heated for 3 days at 290°C. Phase purity was confirmed by X-ray powder diffraction using a Stoe Guinier camera with Cu$K\alpha$ radiation (λ = 1.5418 Å).

Data Collection

Time-of-flight powder neutron diffraction data were collected on the HRPD diffractometer at ISIS, Rutherford Appleton Laboratory. Approximately 10 g of finely powdered material were sealed into a 12-mm diameter vanadium can in an argon-filled glove box and the sample placed 1 m in front of the backscattering detectors. Data were collected in the time-of-flight range 20–120 msec at 298 K, with only the data beween 30 and 100 msec used in refinement. Data were fitted by a modified Rietveld method using the program REFINE (*8*), with the neutron peak shape modeled by a convolution of a Gaussian and two exponential functions (*9*). A wavelength-dependent absorption correction was also applied (*9*). The scattering factors used were W = 0.477, O = 0.5805, and Cl = 0.9579 $\times$ 10^{-12} cm (*10*). Structural projections were generated using PLUTO (*11*) and profile plots using GENIE (*12*).

Structure Refinement

Automatic indexing of the powder pattern using the program TREOR (*13*) revealed a body-centered orthorhombic cell with approximate dimensions of a = 3.82, b = 3.84, and c = 13.87 Å. Systematic absences indicated that the cell was body centered; with no evidence of translational symmetry, the space group *Immm* was assigned. The refinement initially proceeded using an idealized model for WO_2Cl_2 based on the SnF_4 structure (*14, 15*), with tungsten at 0,0,0; oxygens at 0,0.5,0 and 0.5,0,0, and Cl at 0,0,0.16. Scale and five polynomial back-

TABLE I

REFINED ATOMIC PARAMETERS FOR WO_2Cl_2 WITH ESD'S IN PARENTHESES

R_{wp} = 5.22%, R_{ex} = 4.74% χ^2 = 1.21

a = 3.8414(1) Å, b = 3.8851(1) Å, c = 13.8720(4) Å

Atom	Site	x/a	y/b	z/c	B_{iso}	Occ
W	8*n*	0.066(1)	0.053(1)	0.0(—)	2.5(1)	0.25(—)
O(1)	4*f*	0.040(1)	0.5(—)	0.0(—)	2.44(8)	0.5(—)
O(2)	4*h*	0.5(—)	0.028(2)	0.0(—)	2.58(8)	0.5(—)
Cl	16*o*	0.014(2)	0.0304(9)	0.8382(1)	2.93(6)	0.25(—)

ground parameters were refined first, followed in subsequent refinements by peak shape, lattice, and absorption correction parameters. Refinement of the Cl z-parameter and isotropic thermal parameters for all atoms was then carried out. The isotropic thermal parameter for W refined to a particularly high value, in excess of 5 Å^2. It was noted that on attempting to refine anisotropic thermal parameters for tungsten, the B_{11} and B_{22} parameters refined to significantly higher values than the B_{33} parameter, which suggested positional disorder in the a/b plane. The tungsten was therefore allowed to refine away from the 2*a* site in the idealized model to an 8*n* site with a fixed site occupancy of 0.25. Similar action was taken with O(1) and O(2) atoms which showed high B_{11} and B_{22} parameters, respectively; these ions were successfully refined in fourfold sites with fixed site occupancies of 0.5. Cl was refined in a general 16*o* position with site occupancy fixed at 0.25. Attempts to refine anisotropic parameters at this stage resulted in poor convergence, reflecting the high correlation with positional parameters in the disordered structure. Isotropic thermal parameters were therefore refined for all atoms and resulted in significantly lower values than in the refinement of the idealized model. The final refinement terminated with R_{wp} = 5.22%, R_{ex} = 4.74%, and χ^2 = 1.21 for 26 basic variables with 7000 observations corresponding to 292 reflections. The final refined parameters are shown in Table I, with significant contact distances in Table II.

Discussion

The structure of WO_2Cl_2 is built from rectangular WO_4 units which corner share to form sheets (see Fig. 1). Each tungsten oxide layer is sandwiched between two layers of chloride ions, completing a distorted octahedral geometry for tungsten. These trilayer blocks of $[Cl–WO_2–Cl]_n$ are stacked

TABLE II

SELECTED CONTACT DISTANCES (Å) IN WO_2Cl_2, WITH ESD'S IN PARENTHESES

		Av.	Symm.
W–O(1)	2.151(6)	2.17	*x*, *y*, *z*
W–O(1′)	2.187(6)		−*x*, −*y*, −*z*
W–O(1″)	1.740(6)	1.76	*x*, *y*, *z*
W–O(1‴)	1.784(6)		−*x*, −*y*, −*z*
W–O(2)	2.177(4)	2.19	*x*, *y*, *z*
W–O(2′)	2.198(5)		−*x*, −*y*, −*z*
W–O(2″)	1.669(4)	1.68	*x*, *y*, *z*
W–O(2‴)	1.696(5)		−*x*, −*y*, −*z*
W–Cl	2.254(1)	2.27	*x*, *y*, *z*
W–Cl′	2.288(2)		−*x*, −*y*, −*z*
W–Cl″	2.276(2)	2.27	*x*, −*y*, −*z*
W–Cl‴	2.267(2)		−*x*, *y*, *z*

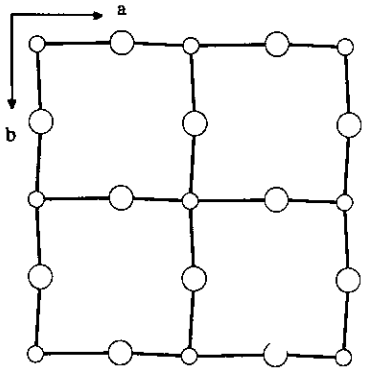

FIG. 1. Projection down c-axis of a single tungsten oxide layer. Open circles represent tungsten and oxygen atoms in order of increasing size. For clarity the projection shows only one set of partially occupied sites.

one on another in the c-direction to give the three-dimensional structure (Fig. 2). Interblock stabilisation is achieved by weak van der Waals bonding between chloride layers, with an inter-block separation of 2.45Å.

The stacking of the tungsten oxychloride layers is such that a translation vector of $x + \frac{1}{2}, y + \frac{1}{2}$ between layers is maintained and eclipsing of adjacent Cl^- ions is avoided. This results in two types of interstitial sites for occupation of ions on intercalation, viz., tetrahedral and square pyramidal (*2*). Additionally the relatively weak interactions between adjacent blocks means that layer slippage is possible in order to achieve favorable coordination environments for intercalated ions, such as in $NaWO_2Cl_2$ (*5*), where a trigonal prismatic coordination for Na^+ ions is observed.

As a result of disorder, the W, O, and Cl atoms only partially occupy their respective crystallographic positions. This leads to several possible but closely related coordination environments for W; all exhibit a distorted octahedral geometry, which in turn yields four possible distances from W to each of the vertices of the octahedron. One or more of these will be adopted in order to satisfy the local coordination requirements. Within a given trilayer block it is possible that one of the local coordination environments is adopted throughout the block and that disorder arises through random stacking of the blocks. Such stacking disorder is not uncommon in van der Waals bonded layered compounds. A description of the W coordination is therefore facilitated by considering an average W environment (Fig. 3), based on the average intersite contacts given in Table II. Each W is surrounded by two short (1.68 and 1.76 Å) and two longer (2.17 and 2.19Å) bonds to O. Six-coordinate geometry is completed by bonds to two apical chlorines (2.23 Å). The nature of the distortion seen in the present study is in broad agreement with that previously described for the structure of WO_2Cl_2 (*6*).

In the original structure determination of WO_2Cl_2 by Jarchow *et al.* (*6*) Weissenberg photographs showed both sharp and diffuse reflections and a monoclinic space group was obtained. However, the sharp reflections alone can be indexed on a body-cen-

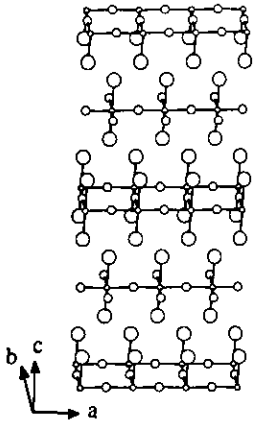

FIG. 2. View of the WO_2Cl_2 structure showing stacking of layers. Open circles represent tungsten, oxygen, and chlorine atoms in order of increasing size. For clarity the projection shows only one set of partially occupied sites.

tered orthorhombic cell (a = 3.84, b = 3.89, c = 13.90 Å). Our powder diffraction data exhibit only sharp reflections; these have been indexed on a similar body-centered orthorhombic cell. We see no evidence for the additional reflections corresponding to a monoclinic cell. The orthorhombic cell found in the present work is also in good agreement with one previously reported for the X-ray powder data (*7*). The differences between the present and previous structural studies may be indicative of different disorder between single crystal and powder samples. Alternatively, the single crystals examined by Jarchow *et al.* may not have been representative of the bulk material; indeed, these workers state that other crystals with alternative symmetries were found.

Some evidence was seen in other high-resolution neutron diffraction patterns of a tetragonal phase, which manifested itself in additional reflections between those of the orthorhombic phase (Fig. 4). This phase may be a less distorted form of WO_2Cl_2 closer to the ideal SnF_4 model, however, we cannot rule out a compound of different stoichiometry. This tetragonal material has as yet not been isolated.

The present study should enable a more detailed understanding of the intercalation of guest species into powdered WO_2Cl_2. The weak van der Waals bonding between adjacent layers may result in rapid diffusion of intercalated ions. Combined with the intense color change, these materials could show promise as the active compounds in electrochromic devices with faster switching than the systems presently under investigation.

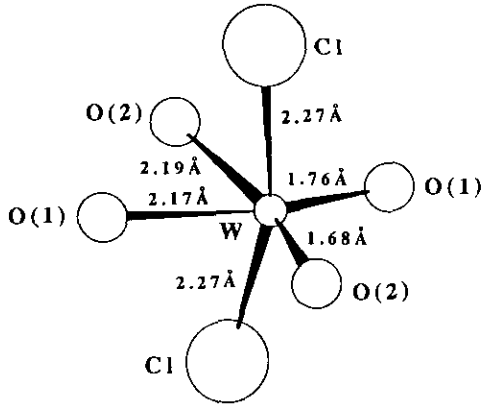

FIG. 3. Average coordination environment for W in WO_2Cl_2.

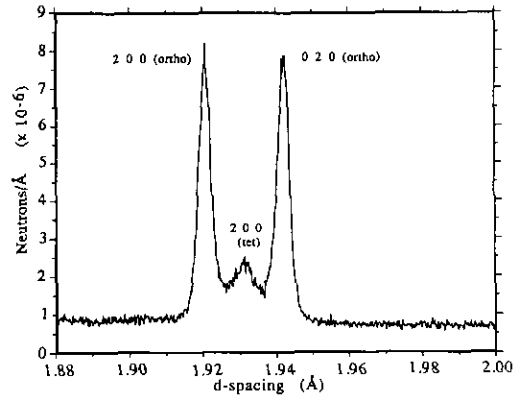

FIG. 4. Part of HRPD profile for a diphasic sample of WO_2Cl_2 showing orthorhombic reflections (ortho) and corresponding tetragonal reflection (tet).

Acknowledgments

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