A Neutron Diffraction Study of Niobium Dioxide

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Abstract. The structure of NbO_2 at 295K has been examined by profile analysis of powder neutron diffraction data. Space group $I4_1/a$, $a = 13\cdot696$ (1), $c = 5\cdot981$ (1) Å. The structure can be described as a superstructure with a subcell of the rutile type. The Nb atoms occur in pairs, and an antiferroelectric displacement of Nb results in a tilting of the Nb–Nb pairs along **c**.

Introduction. NbO_2 undergoes a semiconductor–metal transition at approximately 1070K accompanied by a change in crystal structure (Rao, Ramma Rao & Rao, 1973). Nb–Nb pairing and vibrational mode softening are considered to be important factors in determining the mechanism of the transition (Shapiro, Axe, Shirane & Raccah, 1974). The structure of the low-temperature semiconducting phase was determined by X-ray diffraction (Marinder, 1962). The structure can be described as a superstructure with a subcell of the rutile type in which chains of edge-sharing NbO_6 octahedra are cross-linked by corner-sharing. The lattice parameters of the tetragonal supercell are related to the parameters of the rutile cell, a_r and c_r, by $a = 2\sqrt{2}a_r$ and $c = 2c_r$. The Nb–Nb distances along the edge-sharing chains are alternately 2·80 and 3·20 Å, corresponding to pairing of the metal atoms. Marinder found the NbO_6 octahedra to be almost regular with average Nb–O distances of $2\cdot05 \pm 0\cdot03$ Å, a surprising result since edge-sharing and Nb–Nb bonding might produce grossly distorted octahedra. In VO_2 for example, which also exhibits metal–metal bonding and a semiconductor–metal transition, the V–O distances show significant variations (Andersson, 1956). This is manifest as an antiferroelectric displacement of the metal atoms (Goodenough, 1971; Heckingbottom & Linnett, 1962) which leads to a tilting of the Nb–Nb pairs along **c**. The question arises whether NbO_2 behaves in a similar manner and we have therefore re-examined the structure by profile analysis of powder neutron diffraction data.

A polycrystalline sample of NbO_2 was prepared by hydrogen reduction of specpure Nb_2O_5 (Johnson Matthey Chemicals Ltd) at 1600K for 24 h. The stoichiometry was confirmed as $NbO_{2\cdot00}$ by gravimetric oxidation to Nb_2O_5.

Powder neutron diffraction data were collected at

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room temperature on the PANDA diffractometer at the PLUTO reactor, AERE Harwell. The sample was contained in a cylindrical vanadium can of diameter 10 mm. A mean neutron wavelength of 1·538 Å was obtained by reflexion from the (511) planes of a Ge monochromator at a take-off angle of 90°.

The data were analysed by profile analysis of the powder neutron diffraction pattern (Rietveld, 1969). The space group, $I4_1/a$, and the starting values for the least-squares refinement were taken from Marinder (1962). The neutron scattering length of O was assumed to be $0\cdot577 \times 10^{-14}$ m (Bacon, 1972) and the scattering length of Nb was refined relative to this value. No correction for absorption was necessary. Isotropic Debye–Waller factors were refined for Nb and O.

Results and discussion. The refinement converged rapidly to the structural parameters given in Table 1. Observed and calculated diffraction profiles are shown in Fig. 1. The final R based on profile intensities was 11·46%. Lattice parameters for the tetragonal cell were found to be $a = 13\cdot696$ (1), $c = 5\cdot981$ (1) Å; the values reported by Marinder are 13·70 and 5·987 Å. The final value for the scattering length of Nb was $0\cdot708 \pm 0\cdot008 \times 10^{-14}$ m which compares well with the value of 0·71 reported by Bacon (1972).

Table 1. *Atomic coordinates and thermal parameters for* NbO_2

The value in parentheses is the estimated standard deviation in the last place.

	x	y	z	B (Å²)
Nb(1)	0·116 (1)	0·123 (2)	0·488 (3)	0·55 (10)
Nb(2)	0·133 (1)	0·124 (2)	0·031 (2)	0·55 (10)
O(1)	0·987 (1)	0·133 (2)	−0·005 (3)	0·35 (8)
O(2)	0·976 (1)	0·126 (2)	0·485 (3)	0·35 (8)
O(3)	0·274 (1)	0·119 (2)	0·987 (3)	0·35 (8)
O(4)	0·265 (1)	0·126 (2)	0·509 (3)	0·35 (8)

Table 2. *Interatomic distances* (Å) *in* NbO_2

The value in parentheses is the estimated standard deviation in the last place.

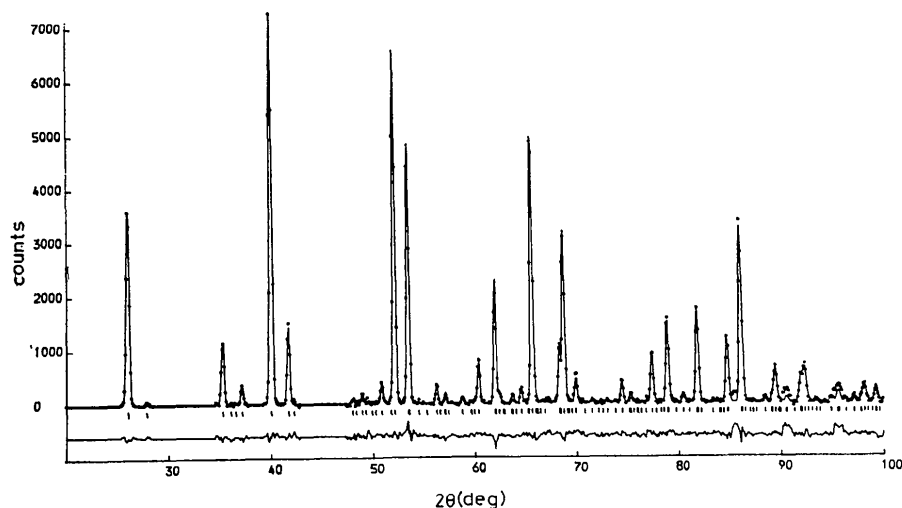|			
Nb(1)–Nb(2)	2·74 (2)	Nb(1)–O(4′)	2·01 (2)
Nb(1)–Nb(2′)	3·26 (2)	Nb(2)–O(1)	2·02 (2)
Nb(1)–O(1′)	2·10 (2)	Nb(2)–O(1′)	2·06 (2)
Nb(1)–O(2)	1·93 (2)	Nb(2)–O(2′)	2·11 (2)
Nb(1)–O(2′)	2·18 (2)	Nb(2)–O(3)	1·93 (2)
Nb(1)–O(3′)	2·02 (2)	Nb(2)–O(3′)	2·23 (2)
Nb(1)–O(4)	2·04 (2)	Nb(2)–O(4′)	2·03 (2)

Fig. 1. The observed and calculated diffraction profiles for NbO_2 (observed profile – dots; calculated profile – smooth curve). The difference profile and reflexion positions are also shown.

The principal structural element in NbO_2 is shown in Fig. 2 and the main interatomic distances are given in Table 2. The Nb–Nb distances are in agreement with those determined by Marinder but the Nb–O distances are significantly different. The Nb–O distances around Nb(1) fall in the range 1·93–2·18 Å and those about Nb(2) are between 1·93 and 2·23 Å. As in VO_2, we find an antiferroelectric displacement of the Nb atoms resulting in a tilting of the Nb–Nb pairs along c; the separation of Nb(1) and Nb(2) when projected along c is 0·22 Å. The corresponding separation in VO_2 is 0·32 Å. We conclude that the semiconducting phase of NbO_2 is very similar to that of VO_2 and that the Goodenough model for the electronic transition applies equally well to both compounds. Further studies are being undertaken to establish the behaviour of the third dioxide of Group Va, TaO_2.

Fig. 2. The NbO_2 structure; a section of the chain of edge-sharing NbO_6 octahedra.

References

ANDERSSON, G. (1956). Acta Chem. Scand. 10, 623–628.
BACON, G. E. (1972). Acta Cryst. A28, 357–358.
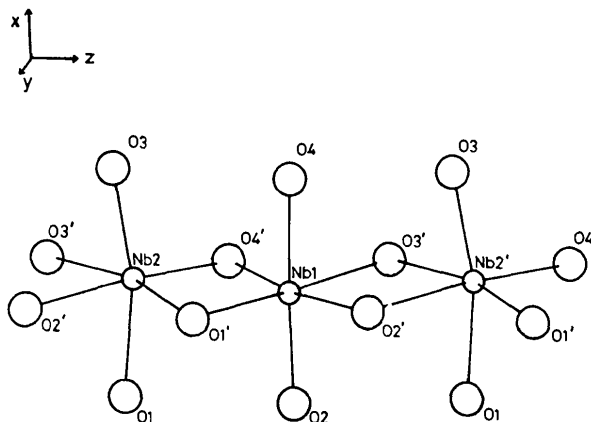GOODENOUGH, J. B. (1971). J. Solid State Chem. 3, 490–500.
HECKINGBOTTOM, R. & LINNETT, J. W. (1962). Nature, Lond. 194, 678.
MARINDER, B. (1962). Ark. Kem. 19, 435–446.
RAO, C. N. R., RAMMA RAO, G. & RAO, G. V. S. (1973). J. Solid State Chem. 6, 340–343.
RIETVELD, H. M. (1969). J. Appl. Cryst. 2, 65–71.
SHAPIRO, S. M., AXE, J. D., SHIRANE, G. & RACCAH, P. (1974). Solid State Commun. 15, 377–381.