Note on the Crystal Structure of Niobium Dioxide *

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Niobium dioxide was prepared by heating an intimate mixture of niobium metal powder and niobium pentoxide in a sealed, evacuated silica tube at about 1 250° C for eight days and also by reducing niobium pentoxide with hydrogen at about 1 120° C. X-ray powder photographs were taken in a Guinier focusing camera of 80 mm diameter using Cu$K\alpha$ radiation. Potassium chloride (a = 6.293 Å) [1] was added to the specimens as an internal standard. The diagrams given by the two samples were found to be identical and in fair agreement with the data reported by Brauer [2].

The results confirmed the statement of Brauer that all reflexions of major intensity are consistent with a rutile type lattice and that, in addition, a considerable number of weak reflexions is present. In order to account for these superstructure lines it was first attempted to interpret the powder pattern on the basis of a monoclinic unit cell of MoO_2-type [3]. This turned out to be impossible and it was thus obvious that the kind of distortion of the rutile type structure present in niobium dioxide is different from that found in the dioxides of several transition elements of the fifth, sixth and seventh groups of the periodic system, *viz.* vanadium [4], molybdenum [5], wolfram [5], technetium [6] and rhenium [6].

Table 1 gives part of the powder photograph of niobium dioxide. It is compatible with a tetragonal unit cell with the dimensions $a = 2\sqrt{2}a_r = 13.71$ Å and $c = 2c_r = 5.985$ Å, $a_r = 4.846$ Å, and $c_r = 2.993$ Å being the dimensions of the subcell of rutile type. This suggests a unit cell content of 32 formula units of NbO_2 (calculated density 5.90, observed density 5.98). It must be very difficult to find the structural details of this compound from powder data. Attempts to prepare samples suitable for investigations by single crystal methods have so far been unsuccessful.

Table 1. Part of powder photograph of niobium dioxide. CuKα radiation. (The reflexions marked with (r) are compatible with the basic rutile type structure.)

I	$\sin^2\Theta_{obs}$	hkl	$\sin^2\Theta_{calc}$
vw	0.0197	101	0.0198
vw	0.0323	211	0.0324
w	0.0451	301	0.0451
st+	0.0507	400 (r)	0.0506
w	0.0577	321	0.0577
vw	0.0702	411	0.0703
st	0.0918	222 (r) 520	0.0917
w	0.0956	501 431	0.0956
m	0.1011	440 (r)	0.1012
vw	0.1083	521	0.1083
w	0.1169	402 (r)	0.1170
vw	0.1264	620 (r)	0.1265
vvw	0.1462	541	0.1462
vw	0.1522	103	0.1525
vw	0.1588	631	0.1589
vw	0.1649	640 213	0.1644 0.1651
vw	0.1712	701	0.1715
vw	0.1774	303	0.1778
w	0.1839	612 730 721	0.1833 0.1834 0.1842
vw	0.1903	323	0.1904
st	0.1929	622 (r) 650	0.1928 0.1929
m	0.2025	800 (r)	0.2024

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