

Twinning and defects in $N\text{-Nb}_2\text{O}_5$ Franziska E. Rohrer^a and
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$N\text{-Nb}_2\text{O}_5$ [$C2/m$ (No. 12), $a = 28.51$, $b = 3.830$ and $c = 17.48$ Å, and $\beta = 124.8^\circ$] has been investigated by means of selected-area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM). $N\text{-Nb}_2\text{O}_5$ is domain twinned, with the twin plane perpendicular to the c^* axis. The domains are rather small and the domain twinning can sometimes be best explained as stacking faults. A second type of coherent twinning at an angle of 90° to the other two domain directions was also found. These domains are linked together by areas containing blocks of different sizes, similar to the disordered block arrangement observed in $M\text{-Nb}_2\text{O}_5$.

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1. Introduction

Two modifications of Nb_2O_5 with the same building block of 4×4 metal–oxygen octahedra have been reported to date, $N\text{-Nb}_2\text{O}_5$ (Andersson, 1967) and $M\text{-Nb}_2\text{O}_5$ (Mertin *et al.*, 1970), differing only in the arrangement of the building blocks.

$N\text{-Nb}_2\text{O}_5$ was first synthesized by Schäfer *et al.* (1964) and the crystal structure was reported by Andersson (1967). $N\text{-Nb}_2\text{O}_5$ crystallizes in $C2/m$ (No. 12) with $a = 28.51$, $b = 3.830$ and $c = 17.48$ Å, and $\beta = 124.8^\circ$. The conventional idealized projection along the b axis is illustrated in Fig. 1*a*. The structure contains 4×4 blocks of corner-sharing metal–oxygen octahedra, infinite in extension along \mathbf{b} . These blocks are joined *via* edge sharing to identical blocks at the same level along \mathbf{b} , as well as being shifted by $\frac{1}{2}$ along the b axis.

Although several ways of preparing this compound are known, single crystals suitable for X-ray investigations could only be obtained in the presence of F or OH (Andersson, 1967; Schäfer *et al.*, 1966). The crystals were invariably twinned. HRTEM images of $N\text{-Nb}_2\text{O}_5$ have been published earlier by Uyeda *et al.* (1984), where the compound was used as a standard test specimen in order to examine the effectiveness of HRTEM observations in deducing information about atomic arrangement in thin crystals. However, no detailed description for the different types of twinning in $N\text{-Nb}_2\text{O}_5$ was given. Using electron diffraction to study different crystallites and different regions within crystallites, it has been possible to propose a model for the twinning which can be verified by high-resolution images.

The second modification of Nb_2O_5 with the same building block, $M\text{-Nb}_2\text{O}_5$, was reported by Mertin *et al.* (1970). They suggested a structural model containing corner-linked 4×4 blocks (*cf.* Fig. 1*b*), leading to a tetragonal space group. The structure was determined at that time by X-ray investigation using strongly disordered crystals. Subsequent HRTEM investigations of WO_3 -containing Nb_2O_5 revealed a disordered arrangement of different sized blocks, 3×4 and $3 \times n$, with $n = 3\text{--}9$ (Heurung & Gruehn, 1982).

2. Experimental

$N\text{-Nb}_2\text{O}_5$ was obtained as a by-product during investigations of the oxygen-rich part of the Nb/O/F system. Nb_2O_5 and NbO_2F (prepared according to Frevel & Rinn, 1956) were ground together in different mole ratios and heated in sealed platinum tubes for 1 week at temperatures between 1250 and 1370 K. The samples resulting from these procedures were multiphase and contained $N\text{-Nb}_2\text{O}_5$.

The specimens for the TEM investigations were prepared by grinding under ethanol and dispersing onto perforated carbon film supported by a copper grid. The characterization was performed by SAED (selected-area electron diffraction) using a JEOL 2000FX and by HRTEM (high-resolution transmission electron microscopy) using a JEOL 3010UHR transmission electron microscope operated at 300 kV, with a structural resolution of 0.17 nm and a spherical aberration coefficient C_s of 0.6 mm. Image calculation was performed using the program *MacTempas* (Kilaas, 1994).

3. Electron diffraction

A SAED pattern from $N\text{-Nb}_2\text{O}_5$ (zone axis [010]) is shown in Fig. 2(a). All the observed reflections can be indexed using the unit cell and space group from the simple structural model shown in Fig. 1. However, such a pattern from a single domain could only very seldom be recorded. Most frequently, the SAED patterns were composed of the reciprocal lattice of two different domains twinned perpendicular to the c^* axis. In Figs. 2(b) and (c) two SAED patterns of such twinned domains are shown. Comparing Fig. 2(b) with Fig. 2(a), it becomes clear that one domain is strongly dominant in Fig. 2(b). Considering Fig. 2(c), an equal distribution between the two twin directions is now observed. Most frequently, both domains were present in roughly equal proportions, leading to a diffraction pattern similar to that shown in Fig. 2(c). Only by moving the beam to the edge of a crystal could patterns with different proportions of the two twin directions (Fig. 2b) or of a totally untwinned domain (Fig. 2a) be recorded. All the reflections in Figs. 2(b) and (c) can be described by the scattering from two different domain directions of $N\text{-Nb}_2\text{O}_5$, which are related by a mirror plane perpendicular to the c^* axis. Very weak diffuse scat-

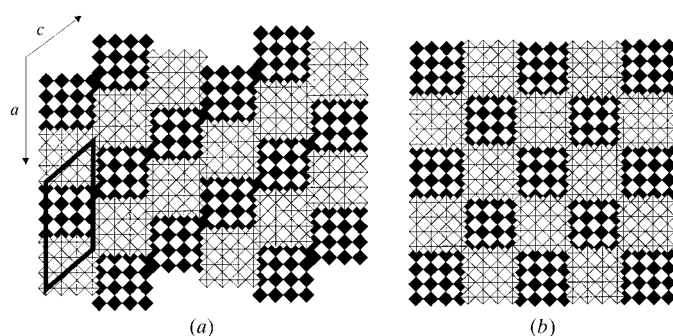


Figure 1

(a). The structure of $N\text{-Nb}_2\text{O}_5$ along \mathbf{b} drawn as a set of idealized octahedra; (b) the earlier proposed structure of $M\text{-Nb}_2\text{O}_5$ (Mertin *et al.*, 1970).

tering indicating stacking disorder can be seen connecting the reciprocal lattice points, but this diffuse streaking was never observed to be very prominent.

On rare occasions, even more complex SAED patterns (Fig. 2d) could be recorded. A diffraction pattern, as shown in Fig. 2(d), is achieved by taking two sets of twinned domains (Fig. 2c) and rotating one of them by 90° around the b axis. Therefore, all the observed reflections in Fig. 2(d) can be indexed by two twinned domains, as in Fig. 2(c), plus, in addition, two twinned domains rotated by 90° around the b axis. Such patterns with these two types of twinning, as shown in Fig. 2(d), were only recorded on rare occasions. They exhibit a striking similarity with the reported electron-diffraction pattern of an $M\text{-Nb}_2\text{O}_5$ sample containing a small amount of WO_3 (Heuring & Gruehn, 1982).

4. High-resolution electron microscopy

The HRTEM observations were performed at the thin edges of crystallites which were oriented with the b axis parallel to the beam direction. All the images were recorded close to the Scherzer focus. Bright spots correspond to channels in the arrangement of the octahedra and dark spots to the positions of the octahedra. The arrangement of the blocks of octahedra (blocks of ReO_3 -type structure) are divided by crystallographic shear planes.

Although SAED patterns of single domains were observed and larger single domains exist in the bulk, we could not record HRTEM images from a totally ideal crystal with no twinning. In Fig. 3, the image of a twinned crystal is shown together with an inset of a simulated image produced using the

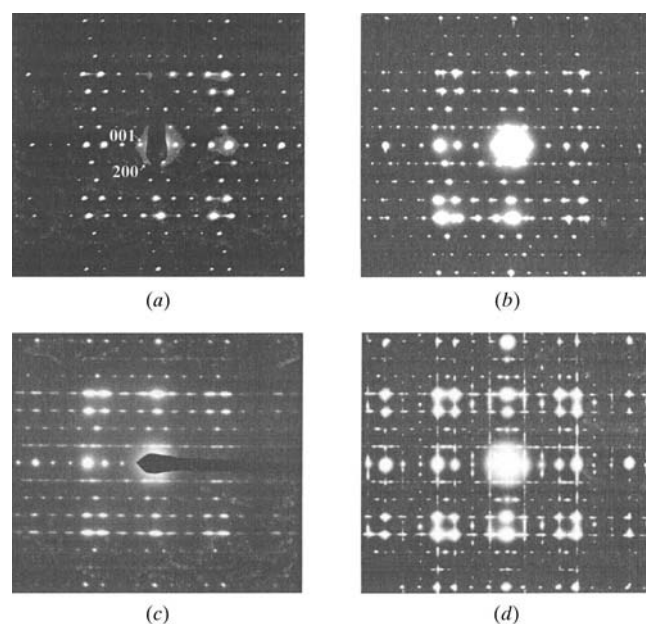


Figure 2

SAED patterns from the [010] zone axis of $N\text{-Nb}_2\text{O}_5$. (a) The SAED pattern from a single domain; (b) the SAED pattern of a twinned crystal with a mirror plane perpendicular to c^* and an uneven distribution of the two twins; (c) the SAED pattern from a multiply twinned crystallite; (d) the SAED pattern from two twinned domains rotated 90° around the b axis.

structure model given by Andersson (1967). The crystallographic shear planes can be observed as dark vertical lines. It is evident here that the twin planes are not well ordered and that they occur with uneven frequency, leading to zigzag lines. This explains the streaking in the SAED patterns. Taking a 4×4 block as a building unit and counting these units from one mirror plane to the next, a sequence of the form 3 4 4 3 3 2 7 in Fig. 3 explains the appearance of SAED patterns with equal proportions of both twins.

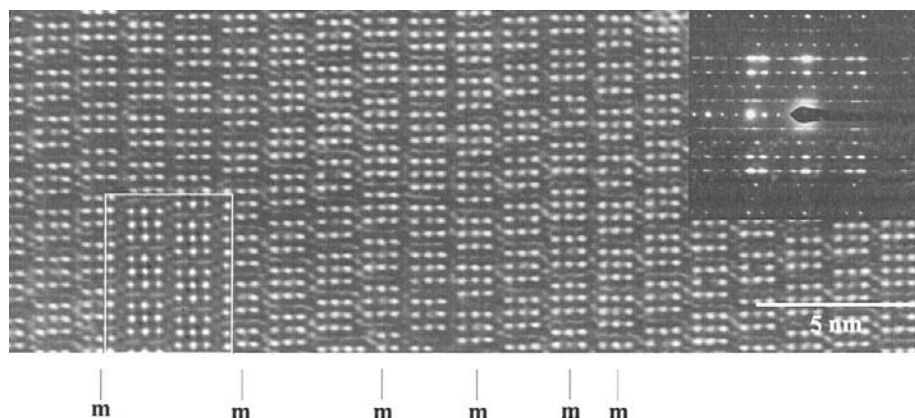


Figure 3
The HRTEM image and inserted simulated image of an $N\text{-Nb}_2\text{O}_5$ crystal along b , with several mirror planes perpendicular to the c^* axis. The insert was calculated for a thickness of 20 unit cells and a defocus value of -500 nm.

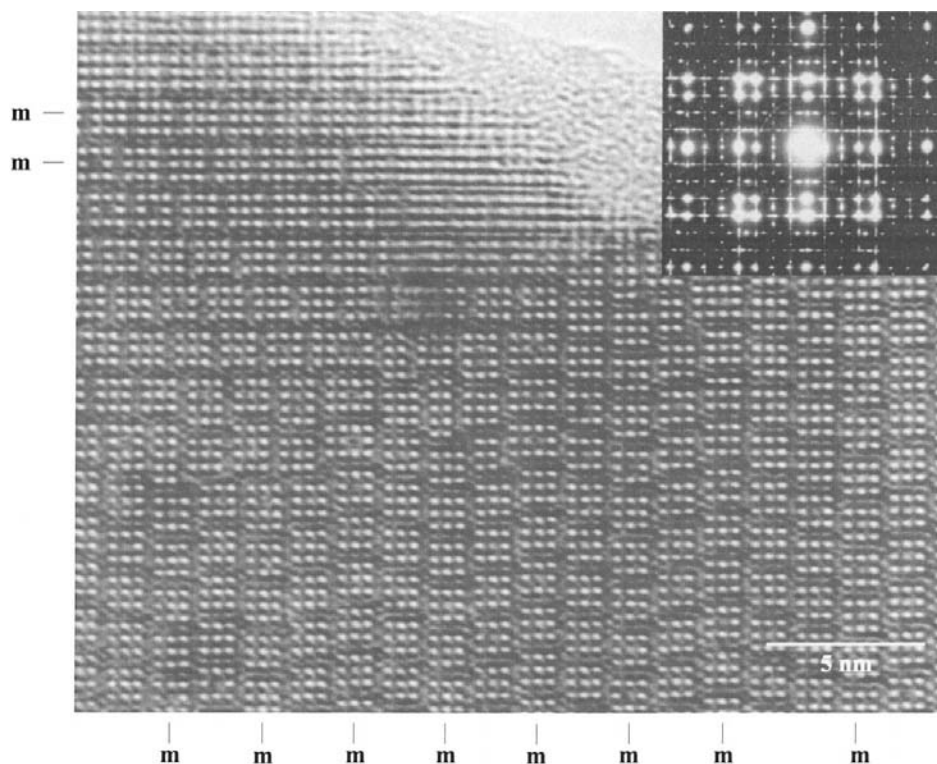


Figure 4
The HRTEM image of a 'double-twinned' $N\text{-Nb}_2\text{O}_5$ crystal along b . The image reveals that there are no simple solutions for the connection between the two rotated twin domains. In this special example the connection is performed by joining different-sized blocks of corner-shared octahedra (ReO_3 -type structure).

In Figs. 4 and 5, HRTEM images of 'double-twinned' regions reveal that there is no simple way of connecting two domains rotated 90° relative to each other around the b axis.

The incompatibility between the two domains is accommodated by ReO_3 -type blocks of different sizes (Fig. 4). Following the border between the two domains, it becomes obvious that there is no order in the size and arrangement of these connecting blocks. Sometimes, small regions of different block types can be observed extending rather far into one of

the two domains. In the border regions on the left-hand side of Fig. 5 a rather large domain is found, containing an ordered arrangement of 3×5 and 3×6 blocks. This corresponds to the block arrangement found by Andersson (1965) and Åström (1966) in $\text{Nb}_{17}\text{O}_{42}\text{F}$, as well as in $HT\text{-Nb}_2\text{O}_5$ (Gatehouse & Wadsley, 1964). It is noteworthy that the region with the $\text{Nb}_{17}\text{O}_{42}\text{F}$ -type structure is connected to the $N\text{-Nb}_2\text{O}_5$ domain to the right without any additional defects. However, the connection to the rotated $N\text{-Nb}_2\text{O}_5$ domain to the left is more complicated. Again, arrangements of different sized blocks leading to local defects are necessary for the connection. Therefore, the formation of a region with an $\text{Nb}_{17}\text{O}_{42}\text{F}$ -type structure leads only to a straightforward connection to one of the two twinned domains, which again stresses the non-existence of a simple solution. Only crystallites in which the two twinned domains were rotated exactly 90° around the b axis were found; no other arrangement seems to be possible.

In some cases another kind of defect could be observed. The HRTEM images in Fig. 6 show two regions where two domains are shifted against each other perpendicular to the a axis. In Fig. 6(a) the shift is the length of one metal-oxygen octahedron. The two domains on the right-hand side of Fig. 6(a) are directly connected (*cf.* the model below), but complications arise in the presence of a mirror plane in the twinned domains. Thus, the preferred solution in this type of defect is the insertion of 3×4 blocks combined with 3×5 blocks, as can be seen on the left-hand side in Fig. 6(a). This block arrangement is also

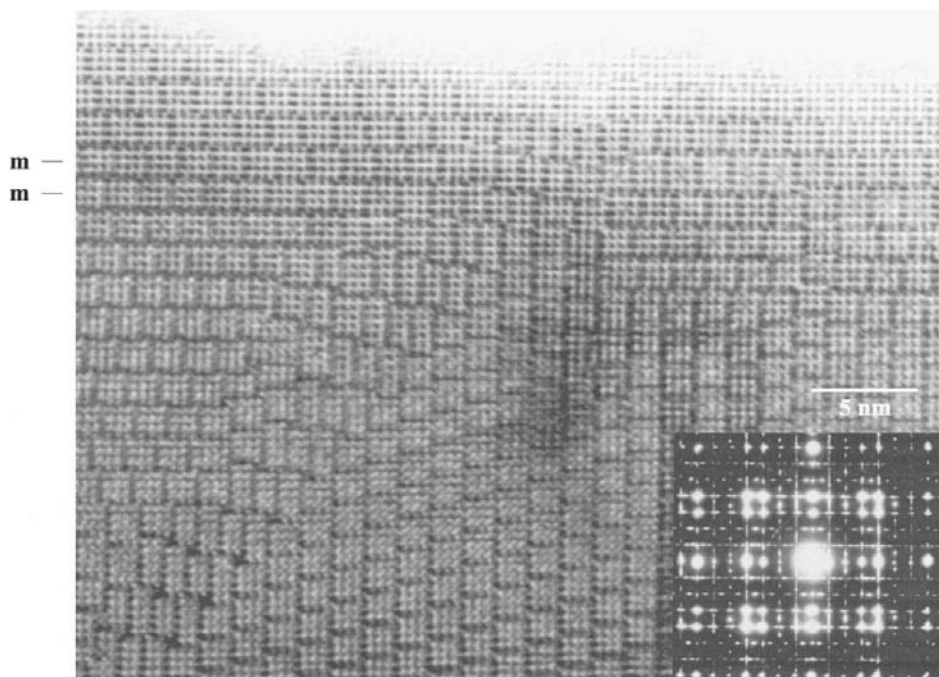


Figure 5
The HRTEM image of a 'double-twinned' $N\text{-Nb}_2\text{O}_5$ crystal along **b**. In this special case a region with $\text{Nb}_{17}\text{O}_{42}\text{F}$ -type structure (block structure containing 3×5 and 3×6 blocks; Andersson, 1965; Åström, 1966) is observed as the connection between the two rotated twinned domains.

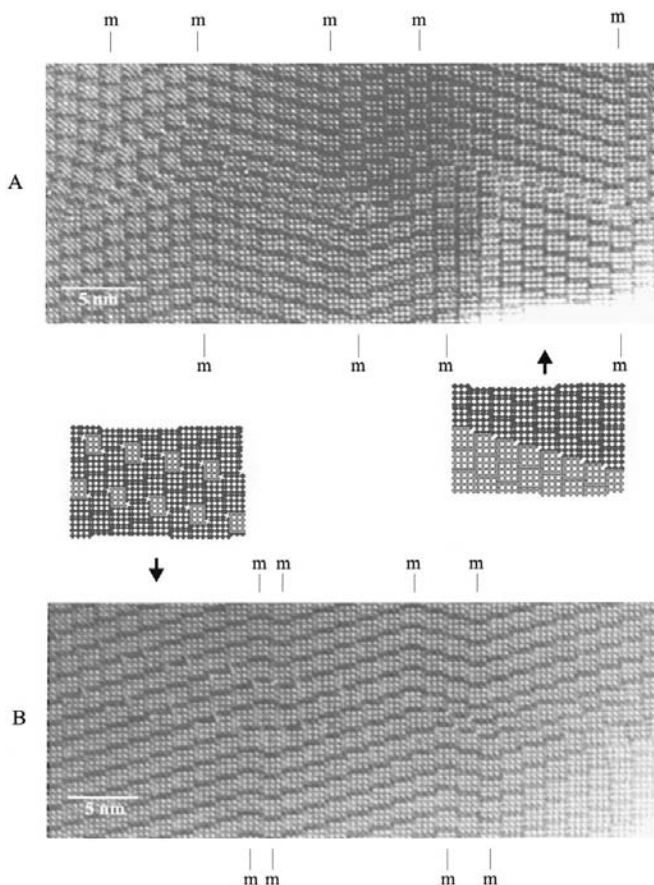


Figure 6
HRTEM images of the $N\text{-Nb}_2\text{O}_5$ crystal along **b**. The images show regions where two domains are shifted relative to each other in a direction perpendicular to the a axis. The shift is the length of one metal–oxygen octahedron in (a) and of two in (b).

found by Anderson *et al.* (1972) in $H\text{-Nb}_2\text{O}_5$. By allowing the two domains to be shifted by the length of two metal–oxygen octahedra a very distinct solution is achieved, as observed on the left-hand side of Fig. 6(*b*). By replacing just one 4×4 block in every row along **a** by a 3×4 block, as shown in the model to the left in Fig. 6, the shift is performed stepwise along the a axis. The presence of mirror planes again causes local defects and once more leads to an arrangement of 3×4 and 3×5 blocks (Fig. 6*a*).

In the case of twinning or the occurrence of shifts, the structures of local domains consist mainly of 3×4 , 3×5 and/or 3×6 blocks. It is noteworthy that during all these investigations no areas were found where the 4×4 metal–oxygen octahedral blocks were linked by their corners, an arrangement first reported for the compound $M\text{-Nb}_2\text{O}_5$ (Mertin *et al.*, 1970). Electron microscopy investigations

of WO_3 -containing Nb_2O_5 have revealed a disordered arrangement of blocks connected perpendicular to each other and differing very much in size (Heurung & Gruehn, 1982). A characteristic linkage of block edges as assumed in the first model would lead to a rather low stability.

5. Conclusions

The electron-diffraction patterns of the multiply twinned compound $N\text{-Nb}_2\text{O}_5$ reveal a fourfold symmetry and are very similar to the published diffraction patterns of $M\text{-Nb}_2\text{O}_5$. Considering the perfectly ordered monoclinic $N\text{-Nb}_2\text{O}_5$, seldom observed without twin planes perpendicular to c^* , and allowing for some domains to rotate by 90° , blocks of different sizes need to be introduced into the domain border areas. If the $N\text{-Nb}_2\text{O}_5$ domain size were to decrease, the block arrangement in the border areas would become more dominant and approach a disordered arrangement, as observed in the published images of $M\text{-Nb}_2\text{O}_5$ (see Figs. 5 and 6 in Heurung & Gruehn, 1982). This would involve a gradual change from the perfectly ordered monoclinic $N\text{-Nb}_2\text{O}_5$, via the multiply twinned variant of $N\text{-Nb}_2\text{O}_5$, to the disordered $M\text{-Nb}_2\text{O}_5$ consisting of several different-sized blocks.

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