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Ordering of the point defects in nonstoichiometric crystals of $Nb_{12}O_{29}$.

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Iijima's [*Acta Cryst.* (1975). A**31**, 784–790] electron microscopic study of oxidized orthorhombic $Nb_{12}O_{29}$ agrees in all respects with results previously published [Browne & Anderson (1974). *Proc. Roy. Soc.* A**339**, 463–482; *Diffraction Studies of Real Atoms and Real Crystals*, p. 157, Australian Academy of Science], which showed the observed superlattice to be that of a metastable modification of Nb_2O_5. Subsequent partial transformation of this to the stable H-Nb_2O_5 structure accounts for the degradation of the superlattice on continued heating.

In a recent publication, Iijima (1975) discusses the formation of domains of some superlattice structure, in crystals of $Nb_{12}O_{29}$ containing a small stoichiometric excess of oxygen, as a result of exposure to the electron beam in the electron microscope. This is ascribed, without doubt correctly, to the aggregation and ordering of the defects whereby the stoichiometric excess of oxygen was randomly accommodated in the original sample. In his paper, he makes reference only to our preliminary account of work on a closely related theme, the oxidation of $Nb_{12}O_{29}$ to Nb_2O_5 (Browne, Hutchison & Anderson, 1972), but not to our fuller record of both the microscopic and the chemical evidence, which bears directly upon the interpretation of his results (Browne, 1973; Browne & Anderson, 1974*a* – hereinafter referred to as BA; 1974*b*).

The electron diffraction patterns and micrographs published by Iijima (Figs. 2, 3 and 6) agree in all respects with those recorded by us (BA, Figs. 4, 11 and 12), so that the superstructure is involved in both pieces of work. Our microscopy was fully supported by chemical evidence; microbalance experiments showed that formation of the superlattice corresponded to complete oxidation to (colourless) Nb_2O_5 and all the definitive microscopy was carried out on chemically authenticated material prepared outside the microscope. Contrary to Iijima's (1975, p. 786) statement, the composition of the superlattice is not in doubt. We confirmed that the doubling of the *b* axis is real and, moreover, showed that it appeared in the earliest stages of the process, so that the defects which become ordered into the superlattice are inherently two-layered in structure. The superlattice structure must be such as to accommodate two extra O atoms per unit cell of the original orthorhombic $Nb_{12}O_{29}$. Subject to this constraint which, through reasoning set out in BA, led us to the view that the displaced Nb atoms are in octahedral rather than tetrahedral coordination, our interpretation of the superstructure and the image contrast was closely related to that advanced by Iijima. Whether image-contrast calculations will enable the structure to be established with any certainty remains to be seen; we found that completely regular ordering of the superstructure, with its large unit cell, was never achieved, so that a full crystal structure determination by X-ray or neutron diffraction may be impracticable.

From our combination of thermogravimetric chemical work and electron microscopy, it was evident that the mobility of atoms in the $Nb_{12}O_{29}$ structure is very high. The fully oxidized superstructure was rapidly formed at 380°C and localized reaction was observable after reaction at only 110°C (BA, Figs. 7 and 9). Mobility relates here to individual atomic jumps from original to superstructure site (hence the difficulty in correlating the superstructure over extensive regions) and in Iijima's experiments the operative factor was probably the heating of the specimen in the electron beam. With prolonged heating at <400°C, or at higher temperatures, the superstructure becomes degraded [*cf.* BA, Fig. 4(*c*)] but, in the case of the superstructure of oxidized orthorhombic $Nb_{12}O_{29}$, OXII, it does not transform into another ordered structure. The corresponding superstructure from oxidized monoclinic $Nb_{12}O_{29}$, OXI, transforms into the $(3\times3)_1$ block structure of $Nb_{10}O_{25}$ as the next stage of reaction. OXI, OXII and $Nb_{10}O_{25}$ are all metastable with respect to the H-Nb_2O_5 structure. This fact is relevant to the interpretation of Iijima's Fig. 7(*b*). Transformation of the superstructure into the H-Nb_2O_5 structure requires cooperative movements of the cations in order to effect a reorganization and displacement of the crystallographic shear-plane interfaces between the blocks – the Andersson–Wadsley (1966) mechanism for diffusion and reaction in CS structures. This becomes facile only at temperatures higher than those needed for the oxidation and formation of the superstructure ($T \geq 450$°C). At the higher temperatures it provides a second rapid mechanism for the oxidation reaction (*cf.* BA, Fig. 18). The changes of block sizes – formation of (5×3) blocks – observed by Iijima need such a migration of CS interfaces, and represent the initial stages in the reorganization of the metastable superlattice into the stable structure that is compatible with the local composition of the crystal.

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