Double Oxides of Gallium and Niobium

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A combination of lattice-imaging electron microscopy and powder X-ray diffraction methods has been used to identify the ternary oxide phases and their structures in the system gallium oxide–niobium oxide. In addition to $GaNbO_4$, $GaNb_{11}O_{29}$, isostructural with $Ti_2Nb_{10}O_{29}$ and $GaNb_{49}O_{124}$, isostructural with $TiNb_{24}O_{62}$, are equilibrium phases. $GaNb_5O_{14}$, isostructural with $TiNb_2O_7$, can exist as coherently intergrown lamellae in $GaNb_{11}O_{29}$. Extended defects observed in low-temperature preparations are discussed.

In a study of the ternary compounds formed between Nb_2O_5 (and Ta_2O_5) and the oxides of the trivalent metals, Iyer & Smith (1967) reported the existence of a compound $GaNb_5O_{14}$, to which they assigned the orthorhombic cell dimensions $a = 3·81$, $b = 20·67$, $c = 28·62$ Å, space group $Cmc2_1$. The composition of their preparation was based on analogy with the series of compounds $LaNb_5O_{14}$ formed by the lanthanides (Masuno, 1964; Dyer & White, 1964; Bodiot, 1968, 1969). The cell dimensions were determined on a single crystal picked from the preparation, and a potentially dangerous assumption was made: that this crystal had the same composition as the whole preparation, even though no evidence was advanced that the product was monophasic. The structure was not solved.

Since a [in Iyer & Smith's (1967) assignment] clearly corresponds to one coordination polyhedron (a typical octahedron diagonal length) it appeared that the essentials of the crystal structure should be deducible by the methods of real-space crystallography, from the lattice image observed in [100] projection. Lattice images at once showed that the formula assigned by Iyer & Smith (1967) was incorrect and that material of composition $Ga_2O_3.5Nb_2O_5$ must be diphasic. By combining lattice imaging with the usual diffraction techniques, the structural chemistry of the system Ga_2O_5–Nb_2O_5 has been elucidated and shown to involve $GaNbO_4$ and, at higher Nb_2O_5 contents, a succession of 'block structure' double oxides.

Experimental

Materials were prepared from Johnson–Matthey 'Specpure' Ga_2O_3 and Nb_2O_5. Mixtures with $Ga_2O_3 : Nb_2O_5$ $= 1:0·5$, $1:1$, $1:2$, $1:3$, $1:5$, $1:11$ and $1:49$ were well ground and fired at $1300°C$ in sealed Pt capsules for 50–100 h. In addition, one preparation ($1:5$) was carried out at $1000°C$ for 50 h. X-ray diffraction patterns were recorded in a Hagg–Guinier focusing camera with Cu $K\alpha$ radiation.

For lattice imaging, samples were finely ground, dispersed on carbon films, and examined with a Siemens Elmiskop 102, at 100 kV and, usually, × 500 000 to × 700 000 magnification. Crystal flakes with thin edges (< 100 Å) were oriented so that the short axis was exactly parallel to the electron beam, and micrographs were recorded at around 900 Å defocus with an objective aperture to include all diffracted beams out to approximately 0·35 Å^{-1}. Under these conditions, the image contrast approximates closely to the projected charge density in the crystal and can be interpreted directly in terms of the projected positions of the heavy atoms.

Results

$GaNb_{11}O_{29}$

As noted by Iyer & Smith (1967), and as follows from the large unit cell of at least one of the compounds in the system, all preparations $Ga_2O_3.xNb_2O_5$ ($x \geq 2$) gave X-ray diffraction patterns very rich in lines, in which it is difficult to detect with certainty the lines arising from some second phase. For all these samples, the electron diffraction patterns of many crystals were typical of the niobium oxide 'block' structures, and over the range $2 \leq x \leq 11$ those crystals from $1300°C$ preparations furnished identical lattice images, typified by Fig. 1. It is evident that this is indeed a block structure, with columns measuring (3×4) octahedra in cross section, linked in infinite zigzag ribbons. It is isostructural with the orthorhombic modifications of $Ti_2Nb_{10}O_{29}$ and $Nb_{12}O_{29}$, and the cell dimensions reported by Iyer & Smith (1967) relate to this material, since they agree well (apart from interchanged labelling of axes) with Wadsley's (1961) data. In the subsequent discussion we shall adopt Wadsley's axial labelling, taking the short cell dimension as b. Since, in the family of block structures there is a direct relation between structure and composition, this phase can be unambiguously formulated as $GaNb_{11}O_{29}$. In agreement with this, the X-ray diffraction pattern of $Ga_2O_3.11Nb_2O_5$ could be completely indexed in terms of the $M_{12}O_{29}$ structures, whereas close examination revealed the presence of additional lines in the diffraction pattern of $Ga_2O_3.5Nb_2O_5$.

Crystals from the $1000°C$ preparation also furnished lattice images identifiable as the $(3 \times 4)_\infty$ block structure

of $GaNb_{11}O_{29}$, but predominantly of the monoclinic modification (Fig. 2). Thus $GaNb_{11}O_{29}$, like other known $(3 \times 4)_\infty$ block-structure compounds, is dimorphic, with the orthorhombic mode of linking columns as the structure stable at high temperatures.

In the analogous system, $Al_2O_3-Nb_2O_5$, Layden (1963) reported the existence of phases with compositions close to $Al_2O_3.9Nb_2O_5$ and $Al_2O_3.25Nb_2O_5$, which Trunov, Kovba & Pol'shchikova (1968) identified as $AlNb_{11}O_{29}$ and $Al_{0.5}Nb_{24.5}O_{62}$ respectively. Tilloca (1973) confirmed the existence of monoclinic $AlNb_{11}O_{29}$ and also reported the existence of both monoclinic and orthorhombic $GaNb_{11}O_{29}$, but without giving any details. Our work shows that his phase II in the $Ga_2O_3-Nb_2O_5$ system was correctly identified and establishes its structure.

Since octahedrally coordinated Ga^{3+} enters into the $(3 \times 4)_\infty$ block structure, it is probable that other block structure phases $MO_x(M = Ga + Nb; 2.417 \leq x < 2.500)$ will exist. Tilloca (1973) found only two intermediate phases between Nb_2O_5 and $MNbO_4$ in both the Al and Ga systems, but, apparently misinterpreting the experimental evidence in the $TiO_2-Nb_2O_5$ system, he assigned to his phase I the composition $M_{0.5}Nb_{14.5}O_{37}$ ($M = Al, Ga$), with the $(5 \times 3)_\infty$ structure known for $MgNb_{14}O_{35}F_2$. Fig. 3 shows a lattice image from our 1:49 preparation. This is identical with the lattice image from $TiNb_{24}O_{62}$, a $(3 \times 4)_2$ structure, and proves the existence of $Ga_{0.5}Nb_{24.5}O_{62}$, as proposed by Trunov *et al.* (1968). In principle, it seems likely that ordered intergrowth phases between the $GaNb_{11}O_{29}$ and $Ga_{0.5}Nb_{24.5}O_{62}$ structures, and between $Ga_{0.5}Nb_{24.5}O_{62}$ and $H-Nb_2O_5$ could be prepared. These parts of the phase diagram have not been explored by electron microscopy and, from the work of Allpress (1970) on the $TiO_2-Nb_2O_5$ system, it is likely that the requisite ordering processes would be very sluggish.

Defects in $GaNb_{11}O_{29}$

After annealing at 1300°C, the crystals of orthorhombic $GaNb_{11}O_{29}$ were very perfect. However, both the formation reaction from the constituent oxides and the subsequent ordering are dependent upon cation diffusion processes and proceed much more slowly at 1000°. The material prepared at the lower temperature showed extensive domains of disorder in many crystals.

Lattice images from such crystals show features similar to those found by Iijima, Kimura & Goto (1973) in slightly oxygen-deficient $Nb_{12}O_{29}$, and identified by them as arising from point defects. Fig. 4 shows a lattice image in which contrast anomalies attributable to point defects are indicated by the arrows. Extended defects and domains of disorder are shown in Figs. 5 and 6; the structure of relevant portions of Fig. 5 is drawn out in Fig. 7. In both micrographs, the areas M are composed of the monoclinic modification of $GaNb_{11}O_{29}$ in one orientation; the areas T are also of the monoclinic form, but with the orientation rotated through 90°. In extensive work, we have frequently ob-

served that $Nb_{12}O_{29}$ and other $(3 \times 4)_\infty$ block structures have two permitted modes of fault-free twinning: across $(10\bar{1})$, a 45° composition plane, and across (001), a 90° composition plane. In the present case, the boundary between the twinned orientations does not lie on the permitted composition plane, but is irregular. It follows from the topology of the block structures that, in these circumstances, it is impossible to form a fault-free boundary between the twinned domains: misfit dislocations or substantial modifications of the column structure are unavoidable. A succession of such faults recurring at spacings of 60–100 Å along the boundary, can be seen in Fig. 5, in the circled areas labelled $D1$, $D2...D6$.

These faults can be analysed in terms of the principles governing dislocations in block structures, which we discuss in another place (Anderson & Hutchison, to be published). In brief, edge dislocations can be described in terms of the insertion, or deletion, of half sheets either containing anion sites only, or containing cation sites, as separate operations. Each involves a Burgers vector of $\frac{1}{2}a_R[uvw]$ (a_R = side of the ReO_3 subcell), and each involves also a change in the number of crystallographic shear interfaces between columns. From the way in which structure is locally modified, it is possible to identify the nature of the edge dislocations concerned.

In Fig. 5, faults $D1$, $D2$ and $D3$ (and probably $D4$ and $D5$, which are in a thicker part of the crystal wedge and not clearly resolved) are essentially similar; fault $D2$ is drawn out in detail in Fig. 8. In each case, one horizontal sheet of anion sites, on the left-hand side, terminates in the fault; an extra sheet of cation sites originates in the fault and runs off to the right. The nett displacement is $-\frac{1}{2}a_r + \frac{1}{2}a_r = 0$, so that there is no overall dimensional change. A vertical sheet of cation sites terminates in the fault and is replaced, in the domain M, by a sheet of anion sites. There is no resultant change of dimensions, and good crystal structure can join up around the fault. Within the fault, however, the number of interfaces, and hence the number, dimensions and linkage of the ReO_3-like columns, is changed. This set of faults does not present the external characteristics of a dislocation. The faults $D1$ and $D2$ in Fig. 6 are essentially similar in structure and origin.

In fault $D6$ (Fig. 5), a vertical sheet of cation sites in the upper portion T is again replaced by a sheet of anion sites, in the lower portion M, without dimensional change. A horizontal row of anion sites, on the left, terminates without compensating replacement by a cation sheet. Thus one half sheet of sites has been deleted from the crystal to the right of $D6$; mapping around the fault leaves a closure gap of $\frac{1}{2}a_R$ accommodated by distortions in the structure, a Burgers vector of $\frac{1}{2}a_R[100]$ with respect to the monoclinic domain M (Fig. 9). This type of dislocation has the further consequence that the regular alternations of cation levels at $y = 0$, $y = \frac{1}{2}$ cannot be preserved around the fault. Columns with cations at the same level appear
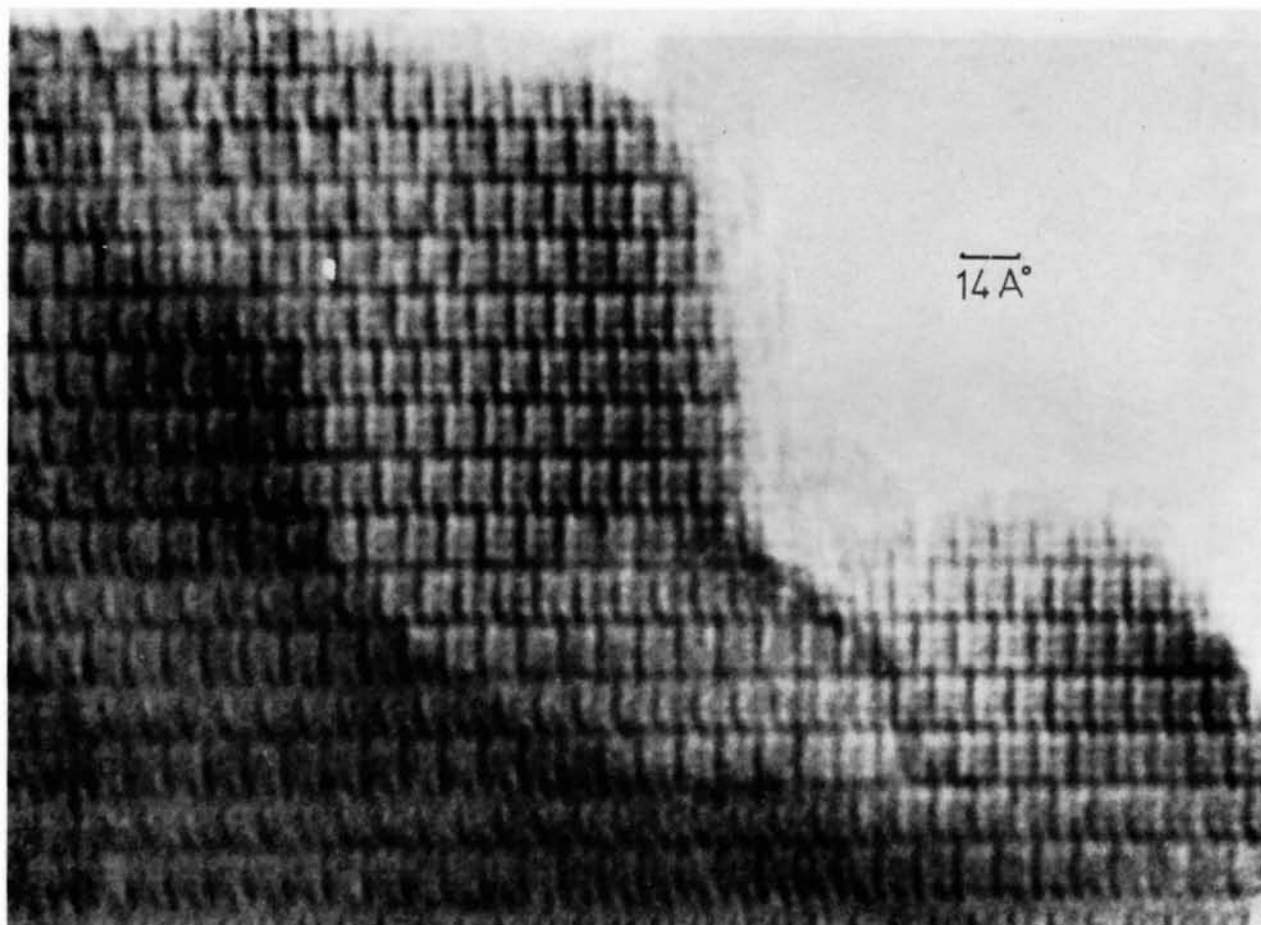
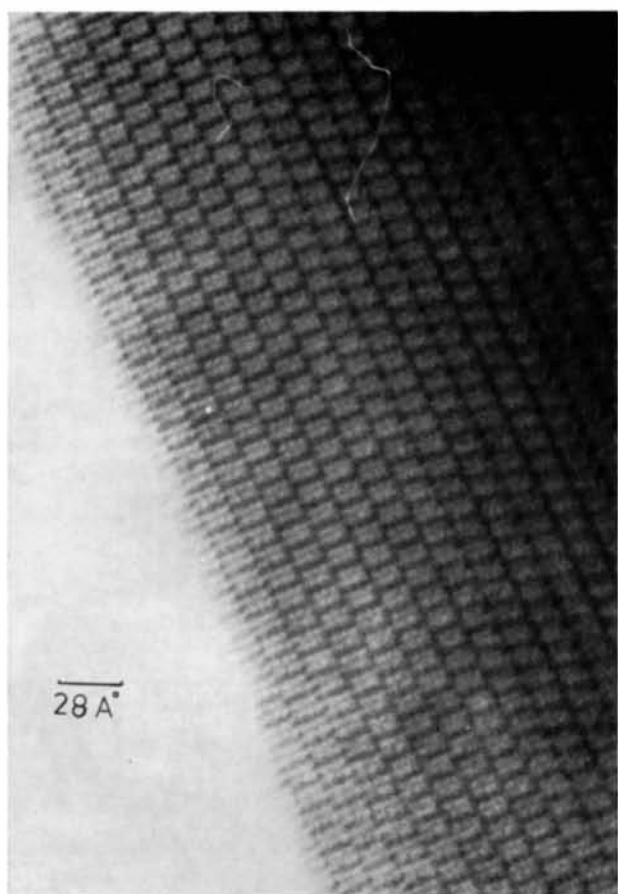Fig. 1. Lattice image of orthorhombic $GaNb_{11}O_{29}$ prepared at 1300 °C.

Fig. 2. Monoclinic $GaNb_{11}O_{29}$: lattice image of $1000\,^{\circ}C$ preparation.
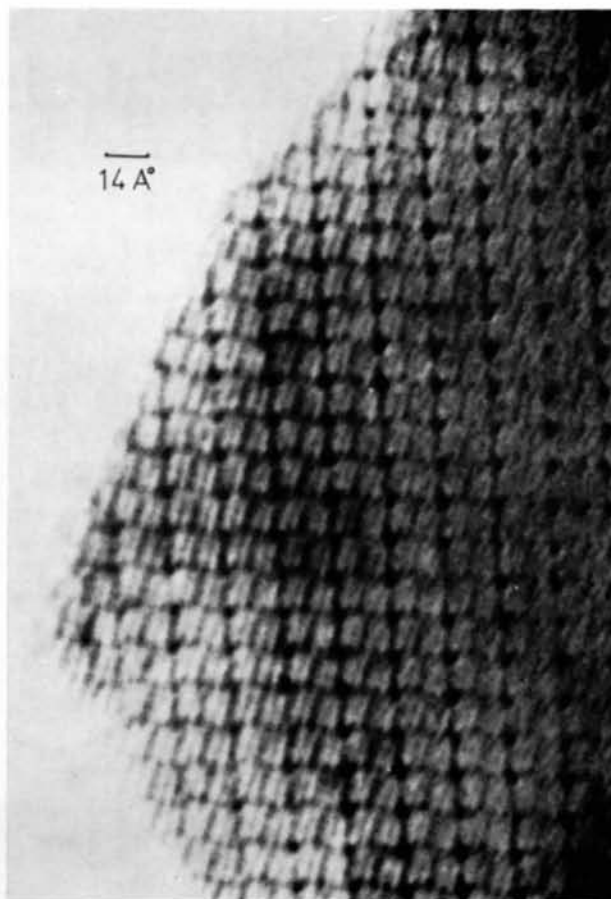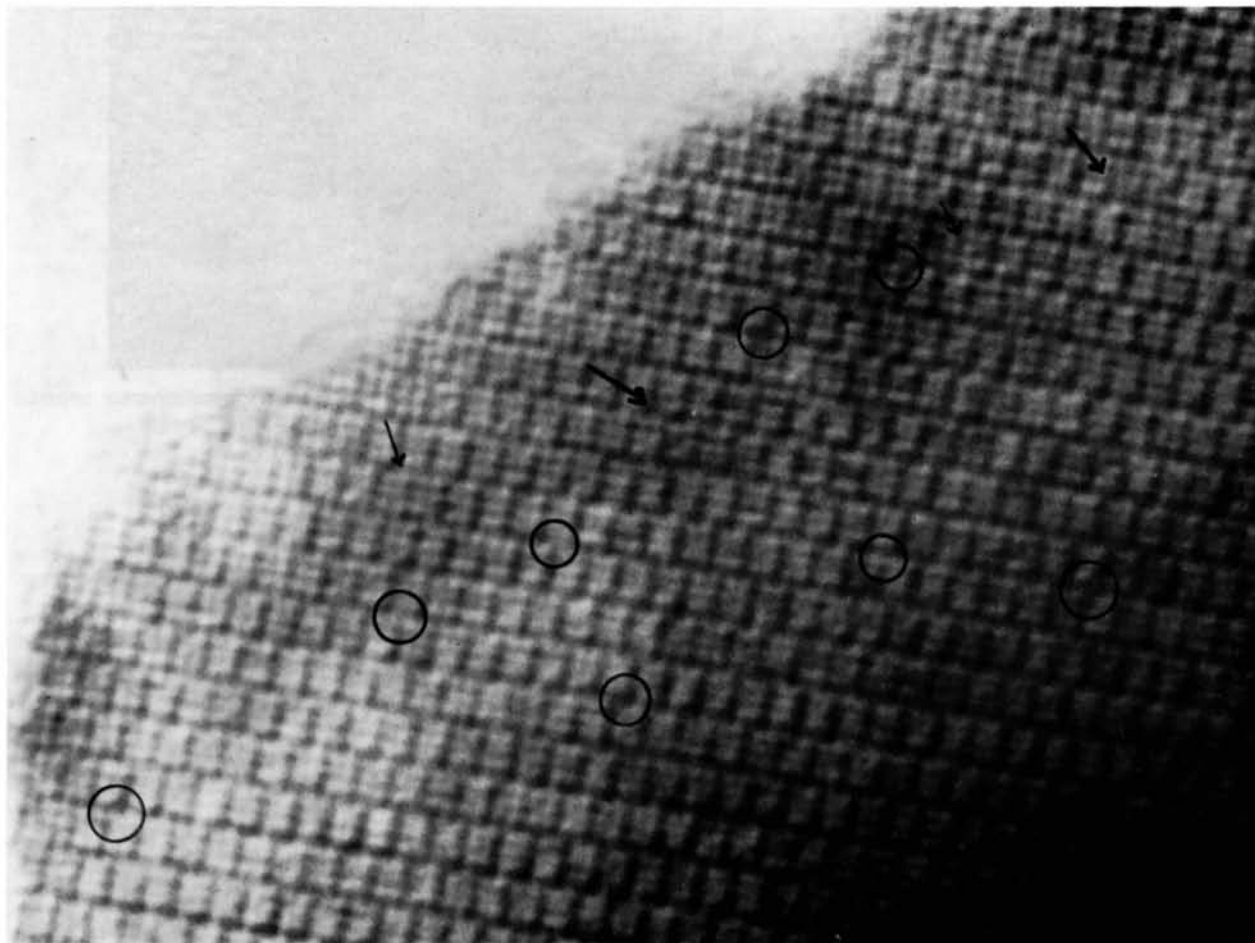
Fig. 3. Lattice image of $GaNb_{49}O_{124}$.

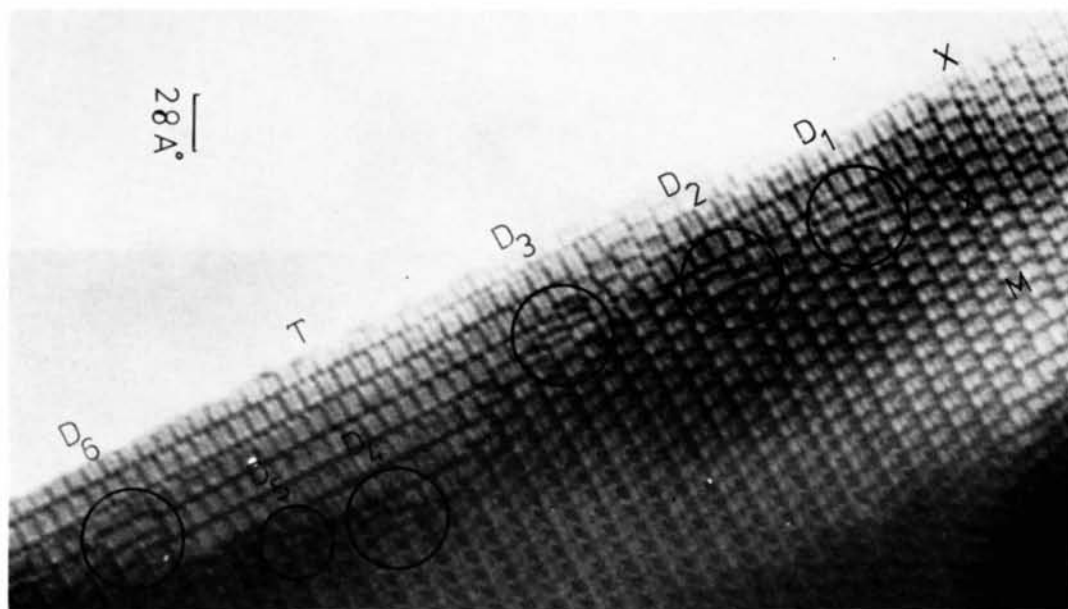Fig. 4. $GaNb_{11}O_{29}$: contrast anomalies indicative of point defects in the 1000 °C preparation.

Fig. 5. Indeterminate boundary between twin orientations (*M* and *T*) of monoclinic $GaNb_{11}O_{29}$. Faults in semicoherent boundary labelled *D*1 to *D*6. *X* – coherently intergrown lamellae of $GaNb_5O_{14}$ structure.
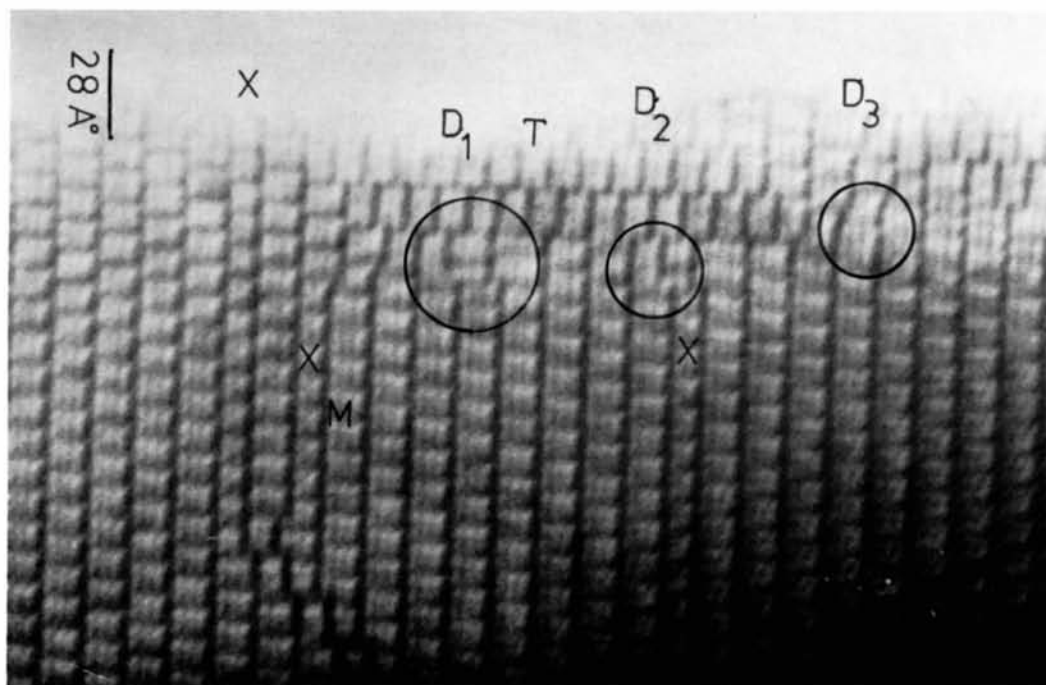

Fig. 6. Faulted twin boundary and intergrowth of $GaNb_5O_{14}$.
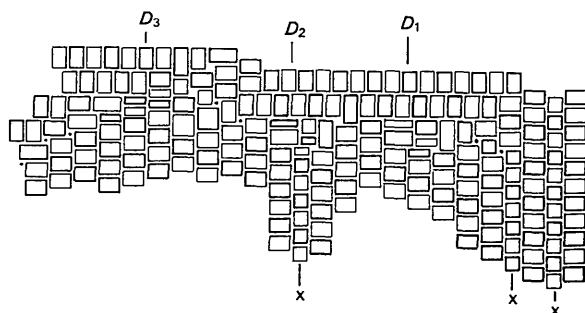
Fig. 7. Structure of the area shown in Fig. 5. Columns of the block structure schematically shown by rectangles defining outer cation positions.
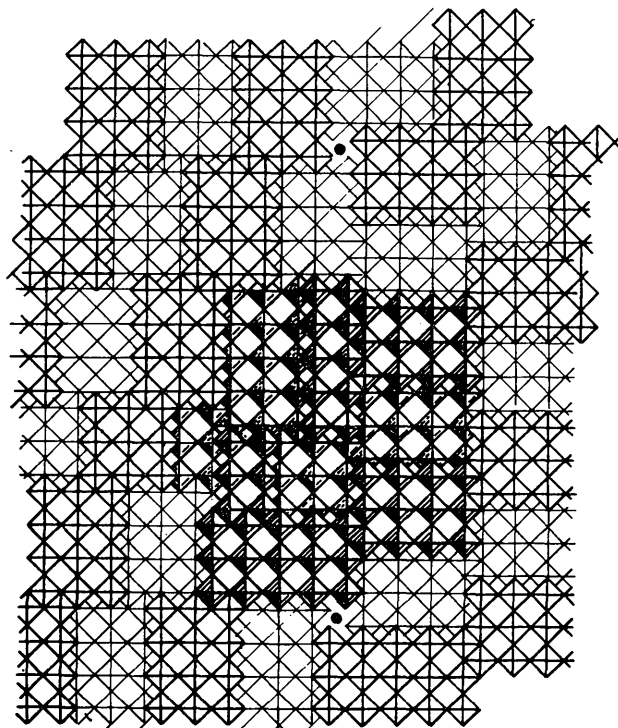

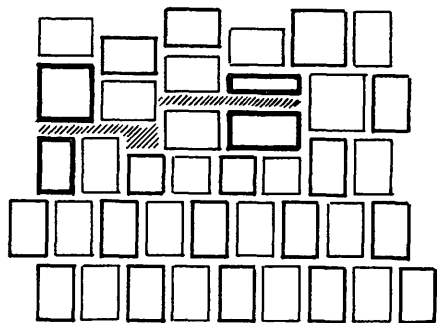Fig. 8. Detailed structure of the misfit fault D2 in Fig. 5.

Fig. 9. Dislocation D6 (Fig. 5) drawn to idealized dimensions and showing closure gap in the Burgers' circuit and mismatch of cation levels resulting from the dislocation.

to be juxtaposed across the closure gap. The layers of sites must necessarily be canted and buckled, as was first recognized by Iijima (1973).

In Figs. 5 and 6 the files of columns marked X are of particular interest. These are files of (3×3) columns, corner-sharing at the same cation level, as in $TiNb_2O_7$, and constituting lamellar intergrowths of a different composition. The composition of these lamellae necessarily corresponds to $GaNb_5O_{14}$, the compound supposedly prepared by Iyer & Smith (1967). We obtained no evidence that this is capable of existence either as a pure structure or in extended domains, but it can be formed, presumably as a metastable structure, in the form of Wadsley defects, in low-temperature reactions.

$GaNbO_4$

Since $GaNb_{11}O_{29}$ is still an abundant constituent in $Ga_2O_3 . 2Nb_2O_5$, it is evident that it coexists with some compound rich in Ga_2O_3. The diffraction pattern of the 1:1 preparation, which contained all the supernumary diffraction lines observed for $2 < x < 5$, could be completely indexed analytically, by de Wolff's methods, in terms of a monoclinic structure with $a = 11·77$, $b = 3·749$, $c = 6·25$ Å, $\beta = 107·6°$. Comparison with the recorded data for $AlNbO_4$ ($a = 12·13$, $b = 3·726$, $c = 6·46$ Å, $\beta = 107·2°$) makes it evident that the 1:1 preparation is monophasic and consists of $GaNbO_4$, isostructural with the Al compound.

$Ga_2O_3 . 0·5Nb_2O_5$ was biphasic, the second phase being identified as β-Ga_2O_3. It follows that $GaNbO_4$ is the only compound intermediate between Ga_2O_3 and the block structure phases.

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