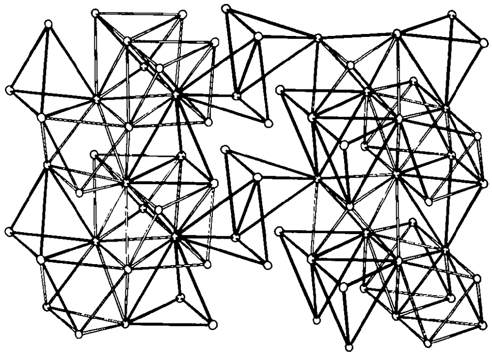

Fig. 2. The connection of occupied octahedra and tetrahedra in $MnIn_2Te_4$-II (*ORTEP*, Johnson, 1965).

one octahedra layer *via* two edges and two corners (see Fig. 2) and strengthen the layer. The bond distances and angles (see Table 2) agree well with the tendencies derived from the distortion of the square nets. The very small angle Te(4)–In(2)–Te(4) 98·70° is a consequence of the edge sharing. An enlargement of the angle would cause an approach of the central atoms.

The resulting structure is more densely packed than that of the normal-pressure modification (decrease of volume 7·1% at the transition $MnIn_2Te_4$-I → $MnIn_2Te_4$-II) and represents a new structure type for AB_2X_4 compounds.

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Structure of Vacancy-Ordered Titanium Heminitride δ'-Ti_2N by Powder Neutron Diffraction

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Abstract. $M_r = 109·8$, tetragonal, $I4_1/amd$, $a = 4·1493$ (2), $c = 8·7858$ (5) Å, $V = 151·26$ Å^3, $Z = 4$, $D_x = 4·82$ g cm^{-3}, $\lambda = 1·909$ Å, $T = 5$ K, final $R_p = 6·1$% for 34 reflections. The structure is obtained by ordering N atoms and vacancies in substoichiometric rocksalt structure $TiN_{0.5}$. A shift [by 0·123 (3) Å] of the Ti atoms along the tetragonal axis away from the first neighbour vacancy and towards the first neighbour N was found.

Introduction. Titanium mononitride has the NaCl structure over a wide range of composition ($TiN_{0.42}$ to $TiN_{1.00}$, Ehrlich, 1949), with a random vacancy distribution on the f.c.c. N sublattice. By annealing TiN_x samples (in which $0·5 < x < 0·6$) at about 773 K a long-range-ordered structure based on the composition Ti_2N is obtained (Lobier & Marcon, 1969; Nagakura & Kusunoki, 1977); this δ'-Ti_2N compound occurs in multidomain twins. From X-ray powder and electron diffraction studies a tetragonal structure with space group $I4_1/amd$ has been suggested (Lobier & Marcon, 1969; Nagakura & Kusunoki, 1977). This is

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shown in Fig. 1. N atoms occupy either the 4(*a*) or the 4(*b*) sites, with no displacement allowed, and Ti atoms occupy the 8(*e*) sites, with a degree of freedom along the fourfold axis.

However, some discrepancy is found in the literature concerning the direction of the shift of the Ti atoms, as deduced from X-ray spectra: either 0·16 Å towards the first neighbouring vacant site of the N sublattice (Nagakura & Kusunoki, 1977) or 0·13 Å towards the first neighbouring occupied site (Lobier & Marcon, 1969).

The aim of this work was to confirm the ordered structure of δ'-Ti_2N and to obtain precise information about these atomic displacements from neutron diffraction spectra. Indeed, lattice distortion around metalloid vacancies should modify the charge transfer and influence the dependence of the electronic properties of the compound on nonstoichiometry. The order–disorder transformation in Ti_2N, which occurs at about 1073 K, was also investigated by Alamo & de Novion (1982).

Experimental. A Ti_2N sample was prepared by the reaction at 1573 K of nitrogen on (dissociated) titanium hydride, and homogenization at 1773 K under vacuum for 12 h. By fast cooling in the furnace (from above 1273 K) the f.c.c. disordered phase was obtained (nevertheless the neutron scattering experiments showed weak diffuse maxima at room temperature, characteristic of short-range order).

For the structural investigation a long-range-ordered specimen was made by annealing the Ti_2N sample in vacuum (10^{-3}Pa) at 973 K for 1 d. The degree of long-range order was checked by X-ray powder diffraction studies. This is possible in δ'-Ti_2N because of a large tetragonal distortion, $(c-2a)/2a = 6\%$, resulting in the splitting of a number of reflections (Alamo & de Novion, 1982). No disordered phase seemed to remain, but the sample contained a small quantity (less than 2%) of the ε-Ti_2N phase with the antirutile structure (Holmberg, 1962).

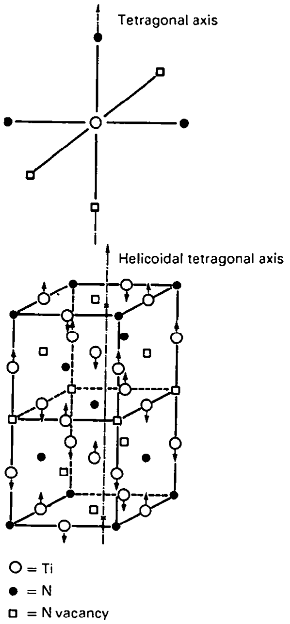

Fig. 1. The crystal structure of δ'-Ti_2N.

The composition of the sample ($TiN_{0.50\,\pm\,0.01}$) was deduced from chemical analysis and from X-ray lattice-parameter measurements on the disordered phase: $a_{\rm dis(f.c.c.)} = 4{\cdot}2156\,(3)$ Å.

The oxygen content was measured to be $\simeq 1$ at. %.

The diffraction pattern of the ordered phase was measured at 5 K on the high-resolution D1A spectrometer at HFR–ILL (Grenoble, France), using 1·909 (2) Å wavelength neutrons (see description in Institut Laue–Langevin, 1981); a He circulation cryostat with a vanadium tail was used. The powder sample, 7·9 g, was housed in a 12 mm diameter vanadium container and the diagram was recorded in the 2θ range 6 to 157° with steps of 0·05°. Fig. 2 shows the corresponding spectrum.

The indexing of the recorded lines gave good agreement with the unit-cell parameters of the compounds (the δ'-Ti_2N ordered phase and the ε-Ti_2N impurity).

The Hewat–Rietveld profile-refinement program (Rietveld, 1969; Hewat, 1973) was used in the structural refinement. The scattering lengths used were Ti −3·438, N 9·210 fm (Koester & Rauch, 1981). No correction for absorption was made (the max. and min. values for absorption differ by less than 2%). The starting parameters were derived from the model of Nagakura & Kusunoki (1977). In addition to the parameters related to the method of refinement (three halfwidth parameters, zero point of diffraction pattern, two unit-cell parameters), the refined parameters were one scale factor, two occupancy factors for the N sites (constrained to give the composition $TiN_{0.50}$), one positional parameter (z, coordinate along the tetragonal axis) for the Ti atom, and the isotropic Debye–Waller factors. $(\Delta/\sigma)_{\rm max} = 0{\cdot}00046$ (last cycle, shift relative to the σ on Ti Debye–Waller factor). Main correlation matrix element concerning two structural parameters is 49% [between Debye–Waller factor for Ti and occupation number for N(2)].

Discussion. The results are listed in Table 1. The difference between experimental and calculated profiles is given in Fig. 2.*

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* A list of numerical intensity data corresponding to Fig. 2 has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42132 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Results of refinement of the structure of* δ'-Ti_2N *at* 5 K

$R_p = 6\cdot1\%$ $[R_p = \sum|I(\text{obs.})-(1/c)I(\text{calc.})|/\sum I(\text{obs.})$; c = scale factor]; $R_{wp} = 15\cdot85\%$ $(R_{wp} = \{\sum w[I(\text{obs.})-(1/c)I(\text{calc.})]^2/\sum w[I(\text{obs.})]^2\}^{1/2})$; expected statistical $R = 2\cdot04\%$. Standard deviations are in parentheses. Occupancy of the Ti sites was not refined.

	Position	Occupancy	x	y	z	B(Å^2)
Ti(1)	8(*e*)	1·0	0	$\frac{3}{4}$	0·8890 (3)	0·94 (7)
N(1)	4(*a*)	0·932 (2)	0	$\frac{3}{4}$	$\frac{1}{8}$	0·20 (4)
N(2)	4(*b*)	0·068 (2)	0	$\frac{3}{4}$	$\frac{5}{8}$	0·20 (4)

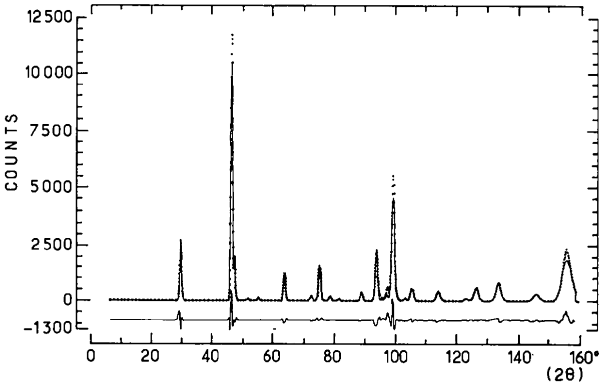

Fig. 2. Observed (dotted line), calculated (full line) and difference profiles for δ'-Ti_2N with $\lambda = 1\cdot909$ Å on the D1A at 5 K. A small quantity of ε-Ti_2N phase is also present on the observed profile.

The agreement between measured and calculated profiles confirms the δ'-Ti_2N structure proposed previously. The refined atom coordinates yield interatomic distances along the tetragonal axis Ti—N(1) = 2·073 (3) and Ti—N(2) = 2·320 (3) Å, and therefore a displacement of the Ti atom of 0·123 (3) Å *towards the occupied* N *site.*

This value of the shift is in good agreement with the results reported by Lobier & Marcon (1969), but its sign is opposite to that reported by Nagakura & Kusunoki (1977).

Amongst the transition-metal carbides and nitrides that have been investigated, one group shows the same kind of influence of a metalloid vacancy on the nearest-neighbour metal atom. In short-range-ordered $NbC_{0.73}$ and $TiC_{0.76}$, studied by single-crystal neutron diffuse scattering (Moisy-Maurice, de Novion, Christensen & Just, 1981), the metal atom shifts 0·03–0·04 Å towards the occupied site. A study of long-range-ordered Ti_2C also yielded the same qualitative result (Moisy-Maurice, Lorenzelli, de Novion & Convert, 1982). But the opposite tendency (displacement of the metal atom towards the largely vacant site) is found in γ-Nb_4N_3 (Heger & Baumgartner, 1980; Christensen, Hazell & Lehmann, 1981). This difference might be correlated to the larger charge transfer from metal to metalloid occurring in NbC and TiN compared to δ-NbN (Kress, Roedhammer, Bilz, Teuchert & Christensen, 1978; Christensen, Dietrich, Kress, Teuchert & Currat, 1979).

From Feldman's (1975) calculation for stoichiometric carbides (TaC, ZrC, HfC), thermal Debye–Waller factors at 5 K may be estimated for each type of atom by applying Hewat's (1972) result for the zero-point vibrations:

$$(B_{\rm Ti})_{\rm thermal} \simeq (B_{\rm Ta})_{\rm thermal} \times (m_{\rm Ta}/m_{\rm Ti})^{1/2}$$
$$(B_{\rm N})_{\rm thermal} \simeq (B_{\rm C})_{\rm thermal} \times (m_{\rm C}/m_{\rm N})^{1/2}$$

where m is the atomic mass; thus $(B_{\rm Ti})_{\rm thermal} \simeq 0\cdot1$ Å^2 and $(B_{\rm N})_{\rm thermal} \simeq 0\cdot2$ Å^2 at 5 K.

The Debye–Waller factor deduced from our neutron experiment for the Ti atom ($B_{\rm Ti} \simeq 0\cdot94$ Å^2) is much larger than the thermal value estimated above, whereas the measured $B_{\rm N}$ is of the order of the calculated thermal value for the N atom. The difference for the Ti atom could be interpreted as remaining static (incoherent) displacements ($\sqrt{\Delta x^2_{\rm Ti}} \simeq 0\cdot18$ Å) from the refined average positions determined above.

Nevertheless, the experimentally determined isotropic Debye–Waller factor values (Table 1) must be considered with caution, as temperature-factor parameters and occupancy-factor parameters are strongly correlated, and as the determination of the background function of the pattern is somewhat imprecise due to the many overlapping reflections.

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