

The author is indebted to Prof. G. N. Ramachandran for the valuable guidance and keen interest he took in this study. The author is grateful to Prof. E. Katchalski of the Weismann Institute, Israel, for the sample of the polymer which enabled him to carry out this study. His thanks are due to the Government of India for the award of a fellowship during the tenure of which this work was carried out.

### References

- AHMED, F. R. & CRUICKSHANK, D. W. J. (1953). *Acta Cryst.* **6**, 385.  
 COREY, R. B. & PAULING, L. (1953). *Proc. Roy. Soc. B*, **141**, 10.  
 COWAN, P. M. & MCGAVIN, S. (1955). *Nature, Lond.* **176**, 501.  
 DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.  
 DONOHUE, J. & TRUEBLOOD, K. N. (1952). *Acta Cryst.* **5**, 419.  
 KATCHALSKI, E., KURTZ, J., FASMAN, G. & BERGER, A. (1956). *Bull. Research Council of Israel, A*, **5**, 264.  
 KURTZ, J., BERGER, A. & KATCHALSKI, E. (1958). *Recent Advances in Gelatine and Glue Research*, p. 131. Edited by Stainsby. London: Pergamonn Press.  
 KURTZ, J., FASMAN, G., BERGER, A. & KATCHALSKI, E. (1958). *Recent Advances in Gelatine and Glue Research*, p. 271. Edited by Stainsby. London: Pergamonn Press.  
 SASISEKHARAN, V. (1959). *Acta Cryst.* **12**, 897.  
 SRINIVASAN, R. (1958). Ph.D. Thesis (Madras).  
 VIERVOLL, H. & Øgrim, O. (1949). *Acta Cryst.* **2**, 277.  
 YAKEL, H. L. & HUGHES, E. W. (1954). *Acta Cryst.* **7**, 291.

*Acta Cryst.* (1959). **12**, 909

## The Crystal Structure of $Ti_2Ni$

BY G. A. YURKO, J. W. BARTON AND J. GORDON PARR

*Department of Mining and Metallurgy, University of Alberta, Edmonton, Alberta, Canada*

(Received 23 March 1959)

The crystal structure of  $Ti_2Ni$  has been determined from powder specimens. The unit cell is face-centered cubic with 96 atoms and dimension  $a = 11.278 \pm 0.001 \text{ \AA}$  at  $21^\circ \text{C}$ . The space group is  $O_h^k-Fd3m$ . 64 titanium atoms are in positions 48f and 16c, and 32 nickel atoms are in positions 32e. The atomic parameters,  $X_{Ni} = 0.215 \pm 0.001$  and  $X_{Ti} = 0.810 \pm 0.002$ , were determined by trial and error.

### Introduction

Laves & Wallbaum (1939) stated that the  $Ti_2Ni$  phase had a complex face-centered cubic structure with 96 atoms per unit cell. No value of cell constant was given. Duwez & Taylor (1950) investigated several  $Ti_2X$  phases and found  $Ti_2Ni$  to be face-centered cubic with a density of  $5.77 \text{ g.cm.}^{-3}$  and lattice constant of  $11.310 \text{ kX. units}$ —giving 96 atoms per unit cell. Rostoker (1952) reported the structure for  $Ti_2Ni$  to be face-centered cubic ( $Fe_3W_3C$  type) and the cell side to be  $11.29 \text{ \AA}$ . Yurko *et al.* (1958) found the cell side to be  $11.278 \text{ \AA}$  at  $21^\circ \text{C}$ . The purpose of the present investigation was to obtain the complete crystal structure of the phase.

### Experimental

The stoichiometric alloy (33.33 at. % Ni) was prepared from iodide titanium and spectrographic standard nickel by levitation melting (Yurko *et al.*, 1958). The ingots were crushed and  $-200$  mesh particles were annealed at  $700^\circ \text{C}$ . and examined by both powder camera and Geiger diffractometer techniques using  $Co K\alpha$  radiation. The density was determined by the

pycnometer method on a 25 g. sample of the crushed and annealed powder, making the usual corrections. The cell constant was determined by methods previously described (Yurko *et al.*, 1958).

Intensity data were obtained by measuring with a planimeter the areas under reflection peaks on two diffractometer charts. Values obtained for the two charts generally agreed within 5%. An average figure was taken. The intensities of reflections too weak to be measured in this way were estimated from a powder photograph, taken with a Philips 11.483 cm. diameter camera of the Straumanis type. The estimation was made visually, by comparing the weak lines with slightly stronger reflections whose intensities had been measured on the diffractometer chart.

### Unit cell and space group

From the cell constant of  $11.278 \pm 0.001 \text{ \AA}$  and the measured density of  $5.723 \pm 0.001 \text{ g.cm.}^{-3}$ , the number of atoms per unit cell is evaluated at 96.0.

The systematic absences were found to obey the following rules:

$hkl$ : absent for  $hkl$  mixed odd and even,  
 $hhl$ : absent for  $h+l=2n+1$ ,  
 $0kl$ : absent for  $k+l=4n$ .

Hence the most probable space group is  $O_h^7-Fd3m$ .

### Determination of structure

The *International Tables* (1952) show the  $O_h^7$  space group to have several possible arrangements of 96 atoms. The  $96g$  and  $96h$  positions were rejected since a preliminary examination showed that structures giving line intensities approaching those observed would contain unreasonably small interatomic distances. There remained several possible combinations of  $48f$ ,  $32e$ ,  $16d$ ,  $16c$ ,  $8b$  and  $8a$ . In order that the distances between pairs of atoms should be approximately the same as the sum of the atomic radii of the constituent atoms, the most probable coordinates may be shown to be those of  $48f$ ,  $32e$  and  $16c$ . The 32 nickel atoms are most likely to occupy the  $32e$  positions and the 64 titanium atoms the  $48f$  and  $16c$  positions.

The parameters for nickel and titanium atoms were determined by trial and error. The intensities of reflections that do not depend on the positions of the  $48f$

titanium atoms depend only on the value of the nickel parameter, since the  $16c$  titanium atoms are invariant. These reflections are 222; 442; 622; 662; 644; 842; 882 and 10, 4, 4; and 10, 6, 2. A comparison of observed and calculated intensities of these reflections gives a best value of  $0.215 \pm 0.001$  for the parameter of the nickel atoms. For these reflections, the discrepancy factor ( $R = \sum |I_o - I_c| / \sum I_o$ ) is 0.19. (It should be noted that this discrepancy factor is calculated from intensity values rather than from structure-factor values, in order that more reflections may be included. The discrepancy based upon structure-factor values would be smaller.) The change in discrepancy factor with parameter justifies the accuracy quoted. Using this value for the nickel atoms, the parameter of the  $48f$  titanium atoms was found by trial and error to be  $0.810 \pm 0.002$ .

The comparison of observed and calculated intensities is recorded in Table 1. No correction is made for absorption or temperature factors. The discrepancy factor for all 43 reflections is 0.10.

### Discussion of structure

In the structure, as in the parent metals, the coordination number of all atoms is 12. The nickel atoms ( $32e$ ) form regular tetrahedra and the titanium atoms ( $48f$ ) regular octahedra. This is indicated in Fig. 1, which shows a representative portion of the cell. Each nickel atom has 3 nickel atoms and 9 titanium atoms as nearest neighbours, while the titanium atoms have either 2 nickel and 10 titanium, 4 nickel and 8 titanium, or 6 nickel and 6 titanium atoms as nearest neighbours. These results, together with the interatomic distances, are summarized in Table 2.

The titanium atoms are approximately the same distance apart as in pure titanium (2.93 Å), while the distance between nickel atoms is greater than that in pure nickel (2.49 Å). On the basis of atomic radii, one would expect the Ti-Ni distance to be 2.71 Å,

Table 1. Observed and calculated intensities

$$I_c = P(1 + \cos^2 2\theta) / (\sin^2 \theta \cos \theta) \cdot \{F_{hkl}\}^2$$

$hkl$	$I_o$	$I_c$	$hkl$	$I_o$	$I_c$
111	16	18.4	842	13	13.8
200	nd	0	664	nd	0.03
220	2*	2.6	931	4	2.3
311	nd	0.08	844	nd	0.02
222	9	11.8	933		27.2
400	3*	4.2	771	45	1.2
331	6	7.7	755		13.7
422	49	44.8	10,0,0	nd	0
511	164	{ 120.2	862	10	{ 2.3
333			{ 45.3		
440	46	43.5	951	13	6.4
531	8	10.4	773		3.6
600	13	{ 0	666	10	{ 0.6
442			{ 15.4		
620	nd	0.06	775		6.7
533	2*	0.9	11,1,1	9	0.5
622	2*	0.9	955		0.3
444	6	5.6	971	6	5.0
711	7	{ 5.6	11,3,1	18	{ 0.2
551			{ 1.8		
642	3*	3.2	10,4,4		11.5
731	10	{ 5.9	866	2*	{ 0.02
553			{ 4.1		
800	2*	2.9	10,6,2	12	10.5
733	2*	1.2	12,0,0		12.8
644	nd	0.4	884	35	24.0
822	44	{ 14.4	11,5,1	47	{ 44.4
660			{ 30.4		
751	14	{ 0.7	12,2,2	57	{ 2.4
555			{ 11.9		
662	2*	1.6	11,5,3		2.8
840	nd	0.2	9,7,5	8	2.8
911	10	{ 3.4			
753			{ 4.2		

nd = not detected.

\* Intensity estimated from powder photograph.

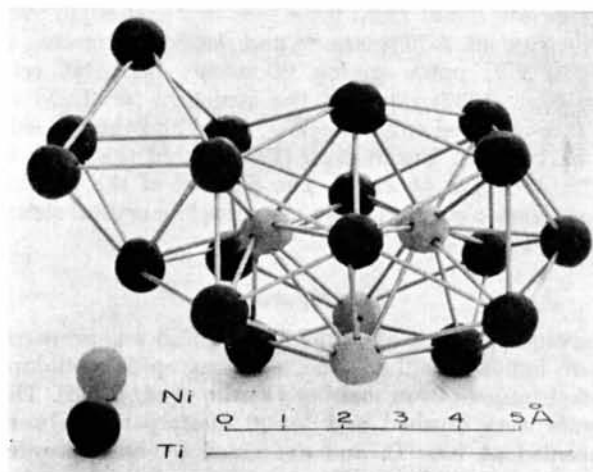


Fig. 1. Representative portion of cell.

Table 2. *Interatomic distances in Ti<sub>2</sub>Ni*

Atom	Bond	Number of bonds	Distance
Ni	Ni-Ni	3	2.87 ± 0.04 Å
	Ni-Ti	3	2.49 ± 0.02
	Ni-Ti	3	2.57 ± 0.05
	Ni-Ti	3	2.91 ± 0.05
		12	
Ti	Ti-Ni	2	2.57 ± 0.05
	Ti-Ti	2	2.93 ± 0.02
	Ti-Ti	8	2.95 ± 0.05
		12	
Ti	Ti-Ni	2	2.57 ± 0.05
	Ti-Ni	2	2.91 ± 0.05
	Ti-Ti	2	2.93 ± 0.02
	Ti-Ti	6	2.95 ± 0.05
		12	
Ti	Ti-Ni	6	2.49 ± 0.02
	Ti-Ti	6	2.93 ± 0.00
		12	

whereas the actual distances are  $2.49 \pm 0.02$ ,  $2.57 \pm 0.05$  and  $2.91 \pm 0.05$  Å, with an average of  $2.6(6)$  Å, since there are equal numbers of each type. The close approach indicates an increased tendency towards covalency between titanium and nickel atoms. Pauling

(1947) and Hume-Rothery & Coles (1954) have discussed this behaviour with particular reference to the transition metals. The strength of the Ti-Ni bond is consistent with the large Ni-Ni distance, since each group of 4 nickel atoms is completely surrounded by titanium atoms.

This work forms part of a project that is supported by the Defence Research Board of Canada (7510-27), and by the International Nickel Company of Canada, Limited.

### References

- DUWEZ, P. & TAYLOR, J. L. (1950). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **188**, 1173.  
 HUME-ROTHERY, W. & COLES, B. R. (1954). *Advances in Physics*, **3**, 149.  
*International Tables for X-ray Crystallography* (1952). Birmingham: Kynoch Press.  
 LAVES, F. & WALLBAUM, H. J. (1939). *Naturwiss.* **27**, 674.  
 PAULING, L. (1947). *J. Amer. Chem. Soc.* **69**, 542.  
 ROSTOKER, W. (1952). *Trans. Amer. Inst. Min. (Metall.) Engrs.* **194**, 209.  
 YURKO, G. A., BARTON, J. W. & PARR, J. GORDON (1958). *Transactions of the Metallurgical Society of Amer. Inst. Min. (Metall.) Engrs.* **212**, 698.

*Acta Cryst.* (1959). **12**, 911

## Structure Cristalline du Cyano-9-Anthracène

PAR M<sup>lle</sup> H. RABAUD ET J. CLASTRE

*Laboratoire de Minéralogie et de Rayons X, Faculté des Sciences, Université de Bordeaux, France*

(Reçu le 21 mars 1959)

The structure of 9-cyano-anthracene has been determined from rotation and retigraph diagrams. Space group  $P2_12_12_1$ , axial lengths  $a = 17.1$ ,  $b = 15.1$ ,  $c = 3.93$  Å; four molecules per cell, X-ray density  $1.30 \text{ g.cm.}^{-3}$ . All carbon and nitrogen positions have been determined. The anthracene portion of the molecule is found deformed from regularity in a very similar way as in anthracene. The CN group has normal internal CN distance (1.15 Å) and lies rather close to the central C of the anthracene group (CC = 1.43 Å). The isomorphous Br-9-methyl-10 anthracene is under study.

### Introduction

Le Cyano-9-anthracène  $C_8H_4.CHC(CN).C_8H_4$  fait partie d'une série de dérivés anthracéniques substitués en 9-10, préparés au Laboratoire de Chimie Organique du Professeur R. Calas de la Faculté des Sciences de Bordeaux.

Nous avons remarqué que le Cyano-9-anthracène présente la même maille et le même groupe spatial que le Bromo-9-méthyl-10-anthracène:

Cyano-9-anthracène

$a = 17,1$  Å  
 $b = 15,1$   
 $c = 3,93$   
 $P2_12_12_1$

Bromo-9-méthyl-10-anthracène

$a = 17,6$  Å  
 $b = 16,2$   
 $c = 3,98$   
 $P2_12_12_1$

Cette identité faisant prévoir une similitude de structure, et par là-même une similitude des champs de forces de Van der Waals qui unissent les molécules les unes aux autres dans le cristal, nous avons pensé