Acta Cryst. (1965). **18**, 60

The Structure of YNi*

By J. F. Smith and D. A. Hansen

Institute for Atomic Research and Department of Metallurgy, Iowa State University, Ames, Iowa, U.S.A.

(*Received* 3 *February* 1964)

The structure of the intermediate phase YNi was determined by X-ray diffraction with single-crystal techniques. YNi crystallizes with monoclinic symmetry in space group $P2_1/b$ (C_{2h}^5). The lattice parameters are $a=4{\cdot}114$, $b=7{\cdot}14$, and $c=5{\cdot}501$ Å with $\gamma=90{\cdot}0\pm0{\cdot}5°$. The atomic arrangement is pseudo-orthorhombic and differs from the $B27$ type structure only in a displacement of atomic coordinates along the short crystallographic axis.

Introduction

The phase relationships in the yttrium–nickel system have been investigated independently by Beaudry & Daane (1960) and by Domagala, Rausch & Levinson (1961). While these two investigations show some disparity in the nickel-rich portion of the system, they are otherwise in good agreement and both indicate that one of the intermediate phases is a congruently melting compound with stoichiometry YNi. On the basis of Weissenberg patterns taken of single crystals with Cu $K\alpha$ radiation, Beaudry & Daane have reported that YNi appears to be orthorhombic with mmm (D_{2h}) diffraction symmetry. Their values for the lattice parameters are

$$a=4{\cdot}10\pm0{\cdot}02,\ b=5{\cdot}51\pm0{\cdot}02,\ c=7{\cdot}12\pm0{\cdot}02\ \text{Å}$$

which with their measured density of 6·1 g.cm^{-3} indicate that there should be four atoms of each species per unit cell. Beaudry & Daane made no attempt to determine the atomic coordinates within the unit cell. However, these investigators were kind enough to furnish crystals for the present investigation. The chemical analyses of the constituent elements which were used to prepare the crystals are quoted in the original paper. A subsequent electron probe microanalysis of one of the crystals indicates a nickel content of 50 ± 3 at.% in agreement with the stoichiometry YNi.

Symmetry and unit cell dimensions

The available crystals of the compound were all irregularly shaped. Examination of Weissenberg patterns taken with Cu $K\alpha$ radiation showed that the positions of the diffraction maxima were in accord with the symmetry mmm (D_{2h}) reported by Beaudry & Daane; however, the intensities of symmetry-related reflections showed marked inconsistencies with this diffraction symmetry. The irregular shapes of the crystals combined with the high absorption of Cu $K\alpha$ radiation by YNi made the significance of these intensity violations highly questionable. Additional patterns were then taken with Ag $K\alpha$ radiation since the absorption problem with this radiation is not severe. The definitive patterns were the $0kl$ and $hk0$ precession patterns. The $0kl$ precession pattern exhibited C_{2l} symmetry in both the position and intensity of symmetry-related reflections while the $hk0$ precession pattern showed intensity violations of the mirror relations of C_{2l} symmetry even though the positions of the diffraction maxima were consistent with this symmetry. Thus the true symmetry around the c axis was indicated to be C_2 rather than C_{2l}, and on this basis it was concluded that the actual symmetry of the atomic arrangement was monoclinic $2/m$ (C_{2h}), the symmetry mmm (D_{2h}) being a pseudosymmetry.

The following lattice parameters were obtained:

$$a_0=4{\cdot}114\pm0{\cdot}004,\ b_0=7{\cdot}14\pm0{\cdot}01,$$
$$c_0=5{\cdot}501\pm0{\cdot}008\ \text{Å};\ \gamma=90{\cdot}0\pm0{\cdot}5°.$$

The monoclinic angle was determined from measurements of the interaxial angle on an $hk0$ precession pattern. The parameter b_0 was determined from the layer line spacings on a rotation film. The parameters c_0 and $a_0 \sin\gamma$ were determined with somewhat better precision from a back-reflection Weissenberg pattern with 21 observed reflections in the range $42°<\theta<72°$. These latter data were fit by the method of least squares to the Nelson & Riley (1945) function to evaluate c_0 and $a_0 \sin\gamma$. Since $\gamma=90{\cdot}0\pm0{\cdot}5°$, then $\sin\gamma=1\pm0{\cdot}00004$ and $a_0 \sin\gamma$ is within the uncertainty equal to a_0. It may be noted that these lattice parameters with appropriate interchange of notation are in accord with those reported by Beaudry & Daane.

Examination of the diffraction data for char-

* Contribution No. 1456. Work was performed in the Ames Laboratory of the Atomic Energy Commission.

acteristic extinctions showed that reflections occurred as follows:

hkl	no conditions
$hk0$	$k=2n$
$00l$	$l=2n$.

These conditions combined with the diffraction symmetry imply that the space group symmetry is $P2_1/b$ (C_{2h}^5).

Structure determination

Intensity data were accumulated for 31 independent reflections of the type $hk0$ and 27 independent reflections of the type $0kl$. The intensity data were obtained by visual estimation of timed exposures taken with a precession camera and Ag $K\alpha$ radiation. Standard corrections were made for Lorentz and polarization factors, but no additional corrections were applied. These data were used to synthesize $P(x, y)$ and $P(y, z)$ Patterson functions. Since there was no indication that reflections with $k+l=2n$ were especially strong as required by occupancy of the special positions in space group $P2_1/b$ (C_{2h}^5), it was postulated that both atomic species should be placed in fourfold general sets of the type 4(e): $\pm(xyz)$, $\pm(x, \frac{1}{2}+y, \frac{1}{2}-z)$. Interpretation of the Patterson functions in terms of these positional considerations led to the postulation of the following trial structure: $x_{Ni} \sim x_Y \sim \frac{1}{4}$; $y_{Ni} \sim \frac{1}{20}$; $y_Y \sim \frac{1}{5}$; $z_{Ni} \sim \frac{5}{8}$; and $z_Y \sim \frac{3}{20}$. This trial structure was refined by the method of least squares on an IBM 7074 computer with the program of Busing, Martin & Levy (1960). In order to check the consistency of the data, values for the y parameters were obtained by refining each of the two sets of data independently; the resulting values were $y_{Ni}=0{\cdot}037\pm0{\cdot}001$ and $y_Y=0{\cdot}181\pm0{\cdot}001$ from $hk0$ data and $y_{Ni}=0{\cdot}035\pm0{\cdot}002$ and $y_Y=0{\cdot}179\pm0{\cdot}001$ from $0kl$ data. Subsequent refinement of the composite data led to the positional coordinates and isotropic temperature factors shown in Table 1 with a residual, $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, of 8·1%.

Table 1. *Refined structural parameters for* YNi

Ni in 4(e)	Y in 4(e)
$x=0{\cdot}245\pm0{\cdot}006$	$x=0{\cdot}249\pm0{\cdot}004$
$y=0{\cdot}037\pm0{\cdot}001$	$y=0{\cdot}181\pm0{\cdot}001$
$z=0{\cdot}622\pm0{\cdot}002$	$z=0{\cdot}132\pm0{\cdot}001$
$B/\lambda^2=0{\cdot}653\pm0{\cdot}215$	$B/\lambda^2=0{\cdot}075\pm0{\cdot}106$

Table 2. *Observed and calculated structure factors for* YNi

0kℓ	$\|F_{obs}\|$	F_{calc}	hk0	$\|F_{obs}\|$	F_{calc}
040	11.5	12.0	040	11.7	12.0
060	41.3	42.1	060	39.1	42.1
080	36.8	-38.2	080	38.1	-38.2
004	76.9	-75.4	400	59.0	62.2
013	5.8	4.9	320	42.0	45.0
014	6.6	7.0	520	37.3	-30.9
015	8.5	9.0	140	22.4	24.5
016	40.6	35.9	240	12.8	-10.5
023	9.7	-12.7	340	23.5	-22.1
025	21.0	19.0	440	8.2	6.8
031	58.7	-59.0	540	21.0	19.2
032	8.9	- 8.5	160	46.6	-45.3
033	55.9	52.7	260	52.3	-39.8
035	32.3	32.9	360	45.1	36.1
037	33.6	-33.8	460	40.5	33.2
041	52.2	56.4	180	32.0	-30.6
043	47.0	43.2	280	38.7	34.4
045	43.3	-41.1	380	37.3	26.6
047	21.9	-22.4	$\bar{3}20$	46.5	-48.6
051	15.7	17.1	$\bar{5}20$	32.3	34.4
053	20.7	-20.1	$\bar{1}40$	17.1	-23.2
064	38.3	-34.0	$\bar{2}40$	10.3	- 8.8
072	51.9	-58.0	$\bar{3}40$	20.6	19.5
084	32.6	32.4	$\bar{5}40$	17.8	-16.5
091	6.1	- 9.5	$\bar{1}60$	33.0	46.0
093	10.2	12.0	$\bar{2}60$	30.2	-36.4
0,10,1	25.3	27.8	$\bar{3}60$	34.1	-38.2
			$\bar{4}60$	34.1	28.0
			$\bar{1}80$	26.2	29.8
			$\bar{2}80$	28.8	36.8
			$\bar{3}80$	28.0	-24.6

Table 3. *Interatomic distances and coordination in* YNi

Atom	Neighbor	Number of neighbors	Distance
Ni	Ni	1	2·48 Å
	Ni	1	2·55
	Y	1	2·87
	Y	2	2·89
	Y	2	2·90
	Y	1	2·93
	Y	1	2·99
Y	Ni	1	2·87
	Ni	2	2·89
	Ni	2	2·90
	Ni	1	2·93
	Ni	1	2·99
	Y	1	3·57
	Y	1	3·58
	Y	1	3·60
	Y	1	3·61
	Y	2	3·80

A comparison of observed and calculated structure factors is shown in Table 2. Interatomic distances and coordination are shown in Table 3.

Since the x parameters are both quite near $\frac{1}{4}$, convergence of the refinement program was checked by arbitrarily displacing the yttrium and nickel coordinates in the various possible combinations of $\frac{1}{4}^+$ and $\frac{1}{4}^-$. In all cases the x parameters refined back to the tabulated values. Further, it may be noted that even though the uncertainties indicate that both x coordinates could be at $\frac{1}{4}$ such positioning would place the structure in mmm (D_{2h}) symmetry and would require that $h+l=2n$ in $h0l$ data. Examination of $h0l$ reflections showed that 403 and 304 were weak but definitely observable. Thus at least one of the x coordinates is other than $\frac{1}{4}$.

Because of the limited number of observed reflec-

tions, particularly of the type $00l$, there existed the possibility that the observed characteristic extinctions were fortuitous. Therefore refinements were also performed in space groups $P2_1$ and Pb. In both cases the refinement converged to the same positional parameters and temperature factors as for $P2_1/b$. In addition the general set in both these non-centric space groups is twofold, two such sets being occupied by nickel and two by yttrium. The Busing, Martin & Levy program generates a correlation matrix during the refinement procedure. In both space groups this correlation matrix indicated correlation probabilities of 90–99% between twofold sets containing the same atomic species, and thus the correlation indicates a relationship which generates the fourfold sets of $P2_1/b$.

Discussion

The YNi structure is closely related to the orthorhombic ThNi structure (Florio, Baenziger & Rundle, 1956). The structural relationship can be shown by choosing a double unit cell for YNi with $a = 14{\cdot}28$, $b = 4{\cdot}11$, and $c = 5{\cdot}50$ Å. Then in comparison the ThNi lattice parameters are $a = 14{\cdot}15$, $b = 4{\cdot}31$, and $c = 5{\cdot}73$ Å. The atoms are arranged in this large YNi unit cell in two sets of the type $\pm(xyz;\ \frac{1}{4}+x, y, \frac{1}{2}-z;\ \frac{1}{2}+x, y, z;\ \frac{3}{4}+x, y, \frac{1}{2}-z)$ with $x_{Ni} = 0{\cdot}019$, $y_{Ni} = 0{\cdot}245$, $z_{Ni} = 0{\cdot}622$ and $x_Y = 0{\cdot}090$, $y_Y = 0{\cdot}249$, $z_Y = 0{\cdot}132$. Again in comparison the atoms in the ThNi structure are in two sets of the type $\pm(xyz;\ \frac{1}{4}+x, y, z;\ \frac{1}{2}+x, y, \frac{1}{2}-z;\ \frac{3}{4}+x, y, \frac{1}{2}-z)$ with $x_{Ni} = 0{\cdot}018$, $y_{Ni} = 0{\cdot}250$, $z_{Ni} = 0{\cdot}630$ and $x_{Th} = 0{\cdot}094$, $y_{Th} = 0{\cdot}250$, $z_{Th} = 0{\cdot}140$. Thus a definite structural relationship is evident, the primary difference being in the sequence of the z parameters. A second significant difference is in symmetry with the lower symmetry of YNi resulting from the failure of the atoms to occupy the $y = \frac{1}{4}$ positions.

This failure of the yttrium and nickel atoms to occupy the $\frac{1}{4}$ and $\frac{3}{4}$ positions along the short axis is the only structural feature which differentiates the YNi structure from the $B27$ type structure (Pearson, 1958) typified by FeB (Bjurström & Arnfelt, 1929; Bjurström, 1933). Otherwise, the positional parameters and axial ratios of YNi are quite comparable to known $B27$ structures, and for classification purposes YNi should be included with this latter group.

The authors are indebted to Mr B. J. Beaudry for pertinent discussions relative to the original investigation and for allowing examination of the diffraction patterns used in the original symmetry determination. Acknowledgment is also due to Mr R. N. Kniseley for performing the electron probe microanalysis. One of the authors (D. A. H.) takes this opportunity to thank the United States Steel Fellowship Foundation for its support during the course of this investigation.

References

Beaudry, B. J. & Daane, A. H. (1960). *Trans. Amer. Inst. Min. (metall.) Engrs*,**218**, 854.

Busing, W. R., Martin, K. O. & Levy, H. A. (1960). U.S. Atomic Energy Commission Report No. ORNL–YM—305.

Bjurström, T. (1933). Ark. Kem. *11*A, No. 5.

Bjurström, T. & Arnfelt, H. (1929). *Z. phys. Chem.* B**4**, 469.

Domagala, R. F., Rausch, J. J. & Levinson, D. W. (1961). *Trans. Amer. Soc. Met.* **53**, 137.

Florio, J. V., Baenziger, N. C. & Rundle, R. E. (1956). *Acta Cryst.* **9**, 367.

Nelson, J. B. & Riley, D. P. (1945). *Proc. Phys. Soc. Lond.* **57**, 160.

Pearson, W. B. (1958). *Handbook of Lattice Spacings and Structures of Metals and Alloys*, p. 93. New York: Pergamon Press.

Acta Cryst. (1965). **18**, 62

The Crystal Structure of the α-Modification of *p*-Nitrophenol near 90 °K

By Philip Coppens and G. M. J. Schmidt

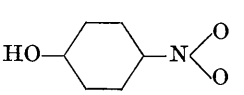
Department of X-ray Crystallography, Weizmann Institute of Science, Rehovoth, Israel

(*Received* 20 *November* 1963)

The crystal structure of the α modification of *p*-nitrophenol near 90 °K has been determined by the use of partial three-dimensional data. The cell dimensions are $a = 11{\cdot}66$, $b = 8{\cdot}78$, $c = 6{\cdot}098$ Å, $\beta = 107°\ 32'$. The space group is $P2_1/n$ and $Z = 4$. The crystals contain chains of hydrogen-bonded molecules. The benzene ring is planar but the nitrogen and oxygen atoms are displaced from the benzene-ring plane by amounts varying from 0·03–0·07 Å.

Introduction

The structure analysis of the α modification of *p*-nitrophenol (I), started in 1957 and reported in this



(I)