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Y_3Ni_2: A New Tetragonal Phase with Ni-Centred Trigonal Prisms

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Y_3Ni_2 crystallizes with a new tetragonal structure type. Space group $P4_12_12$; $a = 7{\cdot}104$ (1), $c = 36{\cdot}597$ (5) Å, $Z = 16$, $D_x = 5{\cdot}52$ g cm^{-3}, FW 384·1, $F(000) = 2768$, μ(Mo $K\alpha$) = 463 cm^{-1}, $R = 0{\cdot}11$. The structure is characterized by Ni-centred trigonal prisms of Y atoms. Always four prisms are joined to form a characteristic prism grouping which has been found before in the structure of Y_8Co_5. Y_3Ni_2 and Y_8Co_5 are members of a new structural series with formula $R_{2(n+1)}T_{n+2}$, where a block R_2T_2 (corresponding to a slice of the FeB type) is stacked with n blocks R_2T (corresponding to a slice of the As_2Nb or Ge_2Os type).

Introduction

Phase diagrams for the system Y–Ni have been published independently by Beaudry & Daane (1960) and by Domagala, Rausch & Levinson (1961). On the Y-rich side, two phases were reported on both diagrams: Y_3Ni with the Fe_3C type and Y_3Ni_2 with an unknown structure. Recently, compounds have been investigated in the rare-earth (R) rich part of the systems R–Ni and two new structure types have been discovered, corresponding to the same stoichiometry: rhombohedral Er_3Ni_2 (Moreau, Paccard & Gignoux, 1974) and monoclinic Dy_3Ni_2 (Moreau, Paccard & Parthé, 1974). In both types all Ni atoms are at the centres of trigonal prisms formed by R atoms. This crystallo-chemical feature appears in many other R–T (T = transition metal) structures (Parthé & Moreau, 1977) and it was of interest to determine whether or not the Y_3Ni_2 structure belongs to this family.

Experimental

The alloy was made from commercially available elements of high purity: Y 99·9%, Ni 99·99%. Samples were prepared by conventional arc melting techniques. Initial stoichiometries were such that the Ni content ranged from 35 to 45 at.%. X-ray photographs from powdered samples were obtained on a Guinier camera with Cu $K\alpha$ radiation. Small crystals suitable for X-ray analysis were isolated by mechanical fragmentation from the sample containing 40 at.% Ni. Weissenberg

Table 1. *Crystallographic data for* Y_3Ni_2

Space group $P4_12_12$	
$a = 7{\cdot}104$ (1) Å	$F(000) = 2768$
$c = 36{\cdot}597$ (5)	$D_x = 5{\cdot}52$ g cm^{-3}
$Z = 16$	μ(Mo $K\alpha$) = 463 cm^{-1}

photographs showed the crystal to have space group $P4_12_12$ (systematic absences, $00l$: $l \neq 4n$, $h00$: $h \neq 2n$).

Lattice constants and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation on a computer-controlled four-circle goniometer in the θ–2θ scan mode. Lattice parameters (Table 1) were refined by least squares (*PARAM*: XRAY system, 1976) to fit values for 20 independent reflexions. The 580 measured intensities were corrected for background, Lorentz and polarization factors with *DATCO5* and *DATRDN* (XRAY system, 1976).

Structure determination and refinement

The phases of the 108 largest ($E > 1.3$) normalized structure factors were determined with *SINGEN* and *TANGEN* (XRAY system, 1976). *PEKPIK* (XRAY system, 1976) revealed 48 Y atoms and 32 Ni atoms on the corresponding E map. This was in agreement with calculations based on the atomic volume of the elements which indicated that the unit cell could accommodate 16 Y_3Ni_2 units. Moreover, this stoichiometry agrees with the original composition of the sample from which the crystal was chosen and with the composition given on the phase diagrams previously published. Positional and isotropic thermal parameters refined satisfactorily with *CRYLSQ* (XRAY system, 1976). Scattering factors were from Cromer & Mann (1968) and anomalous dispersion corrections from *International Tables for X-ray Crystallography* (1974). $R(\equiv \Sigma|\Delta F|/\Sigma|F_o|)$ was 0.11 for 456 observed reflexions.*

The final atomic parameters are listed in Table 2. As this structure is of a new type, a listing of the low-angle reflexions with corresponding calculated intensities for X-ray powder diagram identification is available (Yvon, Jeitschko & Parthé, 1977).*

* Lists of structure factors and the calculated powder data have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32699 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. *Atomic parameters for* Y_3Ni_2 *with e.s.d.'s in parentheses*

The Debye–Waller factor is defined as $\exp[-2\pi^2 \times 10^{-2} U(2 \sin\theta/\lambda)^2]$. Space group $P4_12_12$.

	Equipoint	x ($\times 10^3$)	y ($\times 10^3$)	z ($\times 10^4$)	U (Å^2)
Y(1)	4(*a*)	966 (2)	966 (2)	0	2·1 (7)
Y(2)	4(*a*)	317 (2)	317 (2)	0	1·6 (6)
Y(3)	8(*b*)	808 (2)	443 (2)	156 (4)	1·3 (5)
Y(4)	8(*b*)	163 (2)	659 (2)	680 (4)	1·1 (4)
Y(5)	8(*b*)	645 (2)	809 (2)	747 (4)	1·2 (4)
Y(6)	8(*b*)	12 (2)	163 (2)	891 (4)	1·2 (4)
Y(7)	8(*b*)	514 (2)	293 (2)	933 (4)	1·4 (4)
Ni(1)	8(*b*)	310 (3)	8 (3)	484 (4)	1·0 (5)
Ni(2)	8(*b*)	630 (3)	101 (3)	257 (5)	1·6 (6)
Ni(3)	8(*b*)	840 (3)	510 (3)	1063 (5)	1·2 (5)
Ni(4)	8(*b*)	322 (3)	943 (3)	1167 (5)	1·0 (5)

Discussion

Fig. 1 shows the [100] projection. Table 3 gives the interatomic distances involving Ni atoms. Every Ni atom is at the centre of a trigonal prism and every Y atom participates in the formation of such prisms. Thus the structure can be built up exclusively with Ni-centred trigonal prisms of Y atoms. *T*-centred trigonal prisms formed by *R* (or Y) atoms are frequently found as construction elements in the structures of R_xT compounds where $x \geq 1$. Structures composed exclusively

* See previous footnote.

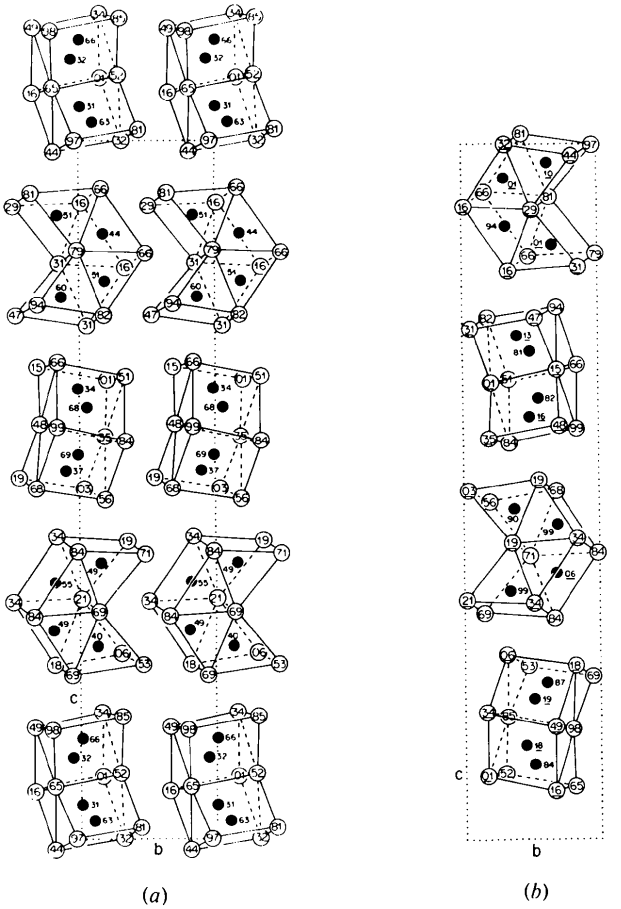


Fig. 1. The linkage of trigonal prisms in Y_3Ni_2 in projection down **a**. Large circles represent Y atoms, small circles, in the centres of the prisms, the Ni atoms. The inscribed numbers correspond to the x parameters multiplied by 100. (*a*) Arrangement of prisms centred by Ni atoms with $\frac{1}{4} < x < \frac{3}{4}$. (*b*) Arrangement of prisms centred by Ni atoms with $\frac{3}{4} < x < \frac{5}{4}$. The drawing of the trigonal prisms becomes significant if 100 is added to the underlined inscribed values of $100x$.

of centred trigonal prisms can be described by the formula R_6T_{LC} where LC stands for the trigonal prism linkage coefficient (Parthé & Moreau, 1977). The calculation of LC for Y_3Ni_2 is conveniently done, as demonstrated in Table 4 where one finds that $LC(Y_3Ni_2) = 4$.

Table 3. *Interatomic distances* (Å) *of* Ni *atoms in* Y_3Ni_2 *up to* 3·8 Å

All e.s.d.'s are <0·03. The Y atoms forming the surrounding trigonal prism are marked with asterisks.

Ni(1)–Ni(2)	2·52	Ni(3)–Ni(4)	2·63
Ni(4)	2·54	Y(5)*	2·79
Y(4)*	2·78	Y(7)*	2·82
Y(6)*	2·81	Y(6)*	2·82
Y(2)*	2·82	Y(4)*	2·89
Y(3)*	2·90	Y(5)*	2·90
Y(5)*	2·93	Y(7)*	2·92
Y(7)*	2·98	Y(3)	3·36
Y(1)	3·03	Y(6)	3·38
Ni(2)–Ni(1)	2·52	Ni(4)–Ni(1)	2·54
Y(1)*	2·73	Ni(3)	2·63
Y(5)*	2·74	Y(6)*	2·82
Y(3)*	2·76	Y(4)*	2·83
Y(2)*	2·87	Y(6)*	2·88
Y(3)*	2·90	Y(4)*	2·92
Y(7)*	2·94	Y(5)*	2·93
Y(4)	3·47	Y(7)*	2·96
Y(6)	3·60	Y(7)	3·00
		Ni(4)	3·75

The tetragonal Y_3Ni_2 type represents the sixth structure type found in the R_3T_2 series of compounds. The others are: (i) the tetragonal Y_3Rh_2 type (Moreau, Paccard & Parthé, 1976*b*), (ii) the orthorhombic Y_3Co_2 type (Moreau, Parthé & Paccard, 1975), (iii) the rhombohedral Er_3Ni_2 type (Moreau, Paccard & Gignoux, 1974) (found also in Y_3Pd_2; Le Roy, Moreau, Paccard & Parthé, 1977), (iv) the monoclinic Dy_3Ni_2 type (Moreau, Paccard & Parthé, 1974), (v) the tetragonal U_3Si_2 type (Zachariasen, 1949; Beattie,

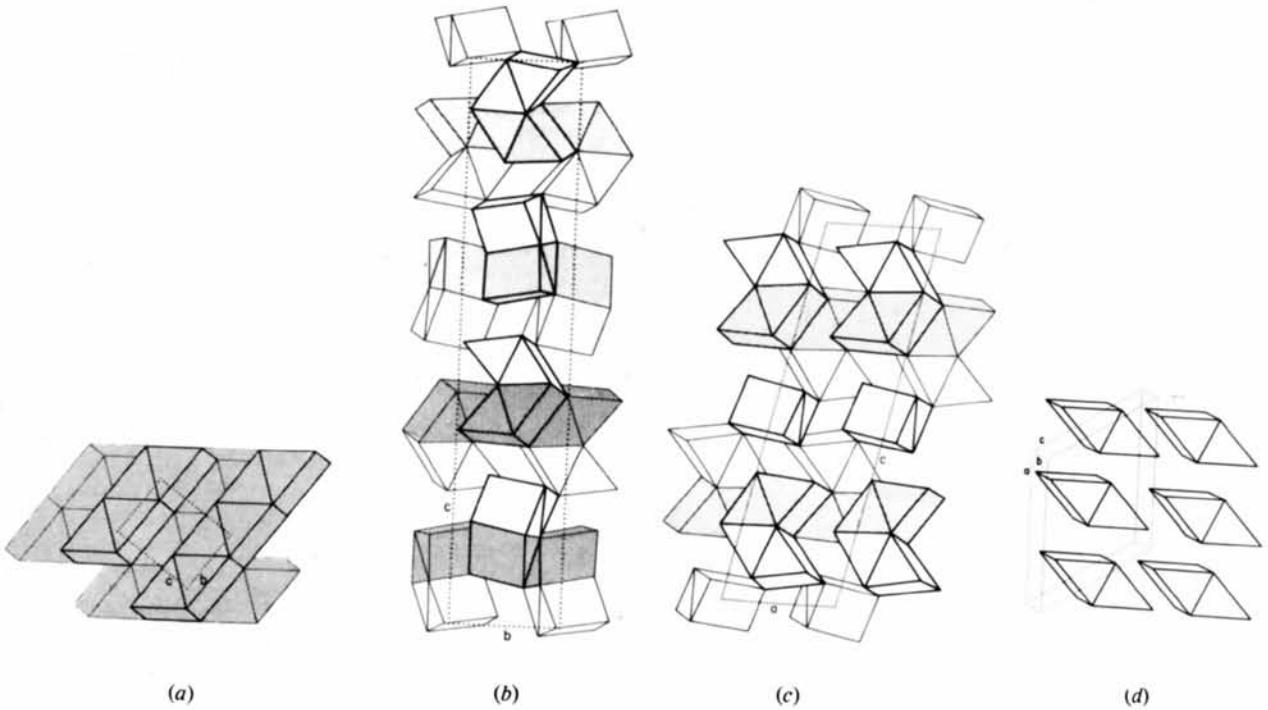
Table 4. *Participation of the* Y *atoms in the formation of the four different trigonal prisms in* Y_3Ni_2

All Ni atoms are in equipoint 8(*b*) of space group $P4_12_12$.

	Y(1) in 4(*a*)	Y(2) in 4(*a*)	Y(3) in 8(*b*)	Y(4) in 8(*b*)	Y(5) in 8(*b*)	Y(6) in 8(*b*)	Y(7) in 8(*b*)	
Ni(1)	0	1	1	1	1	1	1	6
Ni(2)	1	1	2	0	1	0	1	6
Ni(3)	0	0	0	1	2	1	2	6
Ni(4)	0	0	0	2	1	2	1	6
Number of prisms in which each Y atom participates	$\frac{8}{4} \times 1 = 2$	$\frac{8}{4} \times 2 = 4$	3	4	5	4	5	

$LC(Y_3Ni_2) = [4 \times 2 + 4 \times 4 + 8(3 + 4 + 5 + 4 + 5)]/48 = 4$

$R_6T_{LC} = R_6T_4 \equiv R_3T_2$



(*a*) (*b*) (*c*) (*d*)

Fig. 2. Members of the structure series $R_{2(n+1)}T_{n+2}$ for $n = 0$, 2, 3 and ∞. (*a*) FeB ($n = 0$), (*b*) Y_3Ni_2 ($n = 2$), (*c*) Y_8Co_5 ($n = 3$), (*d*) As_2Nb ($n = \infty$). Only the outlines of the trigonal prisms are shown. Layers with composition $[R_2T_2]$ corresponding to the FeB type are stippled, while the layers corresponding to the As_2Nb type are left unshaded.

1958) (found also in R_3Pd_2 compounds; Loebich & Raub, 1973).

All the Y_2T_2 compounds (T = Co, Rh, Ni, Pd) have different crystal structures. In all structure types listed above T atoms are at the centres of trigonal prisms formed by R elements. The only exception is the Y_3Rh_2 structure type where one finds four different types of coordination polyhedra. Er_3Ni_2 and U_3Si_2 form a group by themselves because not all R atoms participate in the formation of trigonal prisms. There is also an R atom at the centre of the R cubes in these structures (Le Roy, Moreau, Paccard & Parthé, 1977). In Dy_3Ni_2, Y_3Co_2 and Y_3Ni_2, on the other hand, all R (or Y) atoms participate in the formation of trigonal prisms. In these three structure types, one finds groups of four joined trigonal prisms. Let us consider the arrangement of the T atoms inside these four joined trigonal prisms. In Dy_3Ni_2 and Y_3Co_2, the Ni or Co atoms form a four-element-segment of a zigzag chain, while in Y_3Ni_2 the Ni atoms are at the four corners of a halved hexagon. This characteristic four-prism group has already been found in Y_8Co_5 (Moreau, Paccard & Parthé, 1976*a*).

Y_3Ni_2 and Y_8Co_5 are members of a new structure series with general formula $R_{2(n+1)}T_{n+2}$ which may be described as a stacking of layers with compositions $[R_2T_2]$ and $[R_2T]$. This series can be classified with the other structure series found in the T-rich R–T alloys where stacking of the $[R_2T_4]$ and $[RT_5]$ blocks leads to the $R_{n+1}T_{5n-1}$ structure series and stacking of the $[R_2T_7]$ and $[RT_5]$ blocks to the $R_{n+1}T_{5n+2}$ series (Parthé & Lemaire, 1975). The $[R_2T_2]$ block corresponds to a segment of the FeB type parallel to (011). The $[R_2T]$ blocks are segments of the As_2Nb or Ge_2Os structure type. The stacking of these layers is presented in Fig. 2 where the $[R_2T_2]$ layers are shown stippled and the $[R_2T]$ layers are left unshaded. The Y_3Ni_2 structure is made up of four triple layers, each triple layer consisting of one $[Y_2Ni_2]$ and two $[Y_2Ni]$ layers. The four triple layers are related by a 4_1 axis. The resulting composition corresponds to

$$[Y_2Ni_2] + 2[Y_2Ni] = Y_6Ni_4 \equiv Y_3Ni_2.$$

The Y_8Co_5 structure consists of two quadruple layers, each quadruple layer containing one $[Y_2Co_2]$ and three $[Y_2Co]$ layers. The two quadruple layers are related by a centre of symmetry. The resulting composition corresponds to

$$[Y_2Co_2] + 3[Y_2Co] = Y_8Co_5.$$

The general formula of the series is $R_{2(n+1)}T_{n+2}$ where n gives the ratio of the number of $[R_2T]$ to the number of $[R_2T_2]$ layers. The structure for $n = 1$ with composition R_4T_3 has not yet been found. The only members known so far are FeB ($n = 0$), Y_3Ni_2 ($n = 2$), Y_8Co_5 ($n = 3$) and As_2Nb ($n = \infty$).

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