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The Monoclinic, CrB-Related, Crystal Structure of Tb_3Ni_2, Dy_3Ni_2 and Ho_3Ni_2

BY J. M. MOREAU, D. PACCARD* AND E. PARTHÉ

Laboratoire de Cristallographie aux Rayons X, Université de Genève, 32 Bd d'Yvoy, CH-1211 Genève, Switzerland

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Dy_3Ni_2 is monoclinic, space group $C2/m$, with $a=13{\cdot}321$, $b=3{\cdot}662$, $c=9{\cdot}512$ Å, $\beta=105{\cdot}72°$, $Z=4$. Tb_3Ni_2 and the low-temperature modification of Ho_3Ni_2 are isotypic. The structure was solved by Patterson methods followed by a full-matrix least-squares refinement to an R of 0·08 for 538 counter reflexions. The structure is characterized by rare-earth trigonal prisms centred by Ni atoms. These prisms are similar to those found in the CrB-type structure and their arrangement is related to the CrB-type configuration.

Introduction

In a recent paper (Moreau, Paccard & Gignoux, 1974) the compound Ho_3Ni_2 was reported to crystallize in two modifications. Phase I is obtained when the alloy is rapidly cooled after melting and phase II appears after the sample is annealed below the melting point. Phase I (space group $R\bar{3}$, $a=8{\cdot}52$, $c=15{\cdot}75$ Å, $Z=9$) is isotypic with Er_3Ni_2. Phase II is isotypic with Dy_3Ni_2 and Tb_3Ni_2. The present investigation was undertaken to determine the crystal structure of phase II. To our knowledge no phase corresponding to this stoichiometry has previously been reported for the systems of Tb, Dy, or Ho with Ni.

Experimental

The alloys were made from commercially available elements of high purity: rare earth 99·9% and nickel 99·9%. After the constituents had been melted by a levitation technique, the alloy buttons were vacuum annealed in quartz tubes at temperatures ranging from 700 to 750 °C for three days. Crystals suitable for X-ray analysis were isolated by mechanical fragmentation. All crystals of Ho_3Ni_2 were twinned but it was possible to obtain some single crystals of Dy_3Ni_2. Preliminary Weissenberg and precession photographs showed the crystals to be monoclinic. The extinctions for hkl with $h+k=2n+1$ indicate as possible space group $C2/m$ (No. 12).

Lattice constants and intensities were measured with graphite-monochromated Mo $K\alpha$ radiation and a Philips PW-1100 computer-controlled four-circle goniometer. The crystallographic data are given in Table 1. θ–2θ scans were used to collect 1317 non-equivalent intensities out to a limit of $\sin\theta/\lambda=0{\cdot}8$ Å^{-1}. The largest dimension (60 μm) of the crystal was small enough to ignore an absorption correction ($\mu R=1{\cdot}8$).

Table 1. *Crystallographic data for* Dy_3Ni_2

Space group	$C2/m$ (No. 12)
a	13·321 (5) Å
b	3·662 (3)
c	9·512 (4)
β	105·72 (1)°
Z	4
D_x	9·14 g cm^{-3}
μ(Mo $K\alpha$)	594 cm^{-1}

Structure determination

The volume of the cell indicates that there are four formula units of Dy_3Ni_2 per cell. A Patterson map was constructed and showed peaks only on the $P(x,0,z)$ and $P(x,\frac{1}{2},z)$ sections. A trial structure was postulated with 12 Dy atoms in three different crystallographic sites. With this approximate model the x and z coordinates of these three atomic positions were refined with the program *STEPRF* (X-RAY system, 1972) and gave an R of 30% for 200 intensities with $(\sin\theta)/\lambda$ less than 0·5 Å^{-1}. A Fourier map was then computed and it was possible to place 8 Ni atoms in two different sites. All positional and isotropic thermal parameters refined satisfactorily with the least-squares program *CRYLSQ* (X-RAY system, 1972).

Hartree–Fock scattering factors were used for Dy and Ni (Cromer & Mann, 1968). Anomalous dispersion corrections were taken from *International Tables for X-ray Crystallography* (1968). $R(=\sum|\Delta F|/\sum|F_o|)$, calculated from 538 observed reflexions ($|F_o|>2\sigma$) with isotropic thermal parameters, was 0·081. A difference map did not show any significant electron density representing missing atoms in the structure. The final positional and thermal parameters are listed in Table 2. A comparison of calculated and observed structure factors is shown in Table 3. Coordination distances are given in Table 4.

As this structure is of a new type, a listing of the low-angle reflexions with corresponding intensities for X-ray powder diagram identification is given in Table 5 (Yvon, Jeitschko & Parthé, 1969).

* Institut Universitaire de Technologie, Annecy, et Laboratoire de Magnétisme, CNRS, Grenoble, France.

Table 2. *Atomic parameters for* Dy_3Ni_2

All atoms in position 4(*i*) of space group $C2/m$. Isotropic temperature factors are expressed as $T=\exp[-2\pi^2 10^{-2} U(2\sin\theta/\lambda)^2]$. E.s.d.'s are in parentheses.

	x	*y*	*z*	U(Å)^2
Dy(1)	0·1322 (2)	0	0·9972 (2)	1·06 (6)
Dy(2)	0·4038 (2)	0	0·3284 (2)	1·20 (6)
Dy(3)	0·1442 (2)	0	0·3696 (2)	1·05 (6)
Ni(1)	0·5352 (6)	0	0·1435 (7)	1·5 (1)
Ni(2)	0·7439 (4)	0	0·2266 (7)	1·4 (1)

Isotypic compounds and polymorphism of Ho_3Ni_2

In Table 6 are reported the lattice parameters of the Dy_3Ni_2 isotypic compounds Tb_3Ni_2 and Ho_3Ni_2 (annealed phase). The variation of these parameters follows the normal lanthanide contraction rule. For comparison we have also reported the lattice parameters of the rhombohedral Ho_3Ni_2 (quenched phase) and the isotypic Er_3Ni_2 (Moreau, Paccard & Gignoux, 1974). The calculated mean atomic volume is larger for the annealed phase. Thermal effects increase the apparent size of atoms and, as a consequence, annealed Ho_3Ni_2 adopts the structure in which bigger rare-earth atoms can be accommodated, *i.e.* Dy_3Ni_2 and Tb_3Ni_2.

Discussion

A projection of the crystal structure of Dy_3Ni_2 along **b** is shown in the third drawing of Fig. 1. The structure is characterized by columns of trigonal rare-earth prisms centred with Ni atoms along **b**, this being the direction of the prism axes. Four of these columns are joined to form a band such that each band has a four-atoms long Ni–Ni zigzag perpendicular to the band direction. The whole structure may be described as a simple packing of such prism bands.

Crystal chemical studies on other metallic structures with trigonal prisms have indicated that the relative dimensions of the trigonal prisms depend in a characteristic way on the elements involved (Parthé, 1970; Schob & Parthé, 1965; Hohnke & Parthé, 1966). To

Table 3. *Observed and calculated structure factors for* Dy_3Ni_2

Reading from left to right the columns contain the values *h*, *k*, *l*, $|F_o|$ and $|F_c|$.

Table 4. *Coordination distances* (Å) *in* Dy_3Ni_2

The standard deviations of the least significant figures are in parentheses.

Dy(1)	to		Dy(2)	to	
	2 Ni(1)	2·82 (1)		2 Ni(2)	2·78 (1)
	2 Ni(1)	2·92 (1)		Ni(1)	2·80 (1)
	2 Ni(2)	2·93 (1)		2 Dy(1)	3·518 (5)
	Ni(2)	3·03 (1)		Dy(2)	3·56 (2)
	Dy(3)	3·502 (4)		Dy(3)	3·585 (5)
	2 Dy(2)	3·518 (5)		2 Dy(3)	3·607 (6)
	Dy(1)	3·537 (3)		2 Dy(3)	3·616 (5)
	Dy(1)	3·621 (3)		2 Dy(2)	3·662 (3)
	2 Dy(1)	3·662 (3)			
Dy(3)	to				
	2 Ni(2)	2·82 (1)			
	2 Ni(1)	2·90 (1)			
	Dy(1)	3·502 (4)			
	Dy(1)	3·585 (5)			
	2 Dy(2)	3·607 (6)			
	2 Dy(2)	3·616 (5)			
	2 Dy(3)	3·662 (3)			
	2 Dy(3)	3·70 (2)			
Ni(1)	to		Ni(2)	to	
	Ni(1)	2·64 (1)		Ni(1)	2·68 (1)
	Ni(2)	2·68 (1)		2 Dy(2)	2·78 (1)
	Dy(2)	2·80 (1)		2 Dy(3)	2·82 (1)
	2 Dy(1)	2·82 (1)		2 Dy(1)	2·93 (1)
	2 Dy(3)	2·90 (1)		Dy(1)	3·03 (1)
	2 Dy(1)	2·92 (1)			

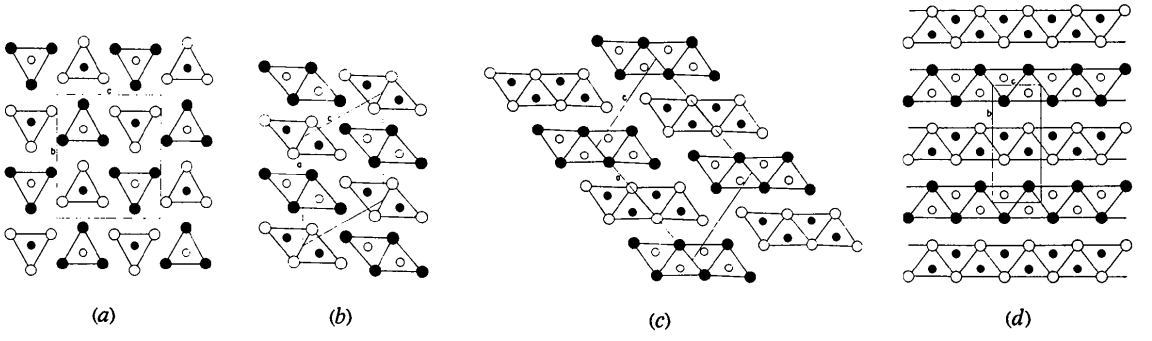
denote the prism dimensions, a parameter had been introduced which was the ratio of two prism side lengths, one perpendicular to the zigzag and the other parallel to the zigzag chain. This ratio varies from 1·1 (elongated prism side) for rare-earth silicides and germanides to 0·85 (shortened prism side) for rare-earth–copper or platinum compounds. It is known from RNi compounds with the CrB or FeB structure type that this ratio is close to 0·9. The prisms in Dy_3Ni_2 agree, having a measured value of 0·87.

Efforts have been made to find some unifying concepts for the large number of structures with trigonal prisms. For example, it has been found that the equiatomic structures of CrB, FeB, TbNi (high-temperature form) and TbNi (low-temperature form) may be con-

Table 5. *Calculated powder data for* Dy_3Ni_2 *for* Cr $K\alpha$ *radiation* ($\lambda = 2{\cdot}29092$ Å)

Intensities calculated from positions obtained from single-crystal data. $I = mF^2(1+\cos^2 2\theta)/(\sin^2\theta \cdot \cos\theta)$ is normalized to the strongest reflexion having intensity 1000.

h	k	l	$10^3 \cdot \sin^2\theta$	Intensity
0	0	1	15·65	34·8
2	0	0	31·91	0·7
2	0	−1	35·47	16·1
2	0	1	59·65	1·1
0	0	2	62·59	1·7
2	0	−2	70·32	2·2
1	1	0	105·82	2·5
1	1	−1	115·42	276·3
2	0	2	118·69	1·9
4	0	−1	119·11	21·1
1	1	1	127·51	13·6
4	0	0	127·65	504·6
2	0	−3	136·46	43·7
0	0	3	140·83	540·3
4	0	−2	141·87	3·3
1	1	−2	156·32	12·4
3	1	−1	167·15	128·2
4	0	1	167·49	72·1
3	1	0	169·65	410·7
1	1	2	180·50	1000·0
4	0	−3	195·92	540·1
3	1	−2	195·95	677·6
3	1	1	203·43	456·3
2	0	3	209·02	36·3
1	1	−3	228·51	230·9
2	0	−4	233·90	112·1
4	0	2	238·62	197·2
0	0	4	250·36	8·6
3	1	−3	256·05	101·8
1	1	3	264·79	0·4
6	0	−1	266·59	13·9
3	1	2	268·52	20·4
6	0	−2	277·25	102·1
4	0	−4	281·26	3·1
5	1	−1	282·71	399·8
6	0	0	287·22	2·9
5	1	0	297·30	4·1
5	1	−2	299·42	10·7
6	0	−3	319·20	17·7
2	0	4	330·65	0·5
1	1	−4	331·99	143·1
6	0	1	339·15	0·0
4	0	3	341·04	238·1
5	1	1	343·18	4·3
5	1	−3	347·42	0·0
3	1	−4	347·44	71·6



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

Fig. 1. Structural series of composition $M_{n+2}N_n$. Figures are in projection along the lattice direction parallel to the prism axes with full black circles at 0 and white circles at $\frac{1}{2}$. Large circles represent M atoms, small circles N atoms. (*a*) $Pu_3Co(Re_3B$ type), $n=1$. (*b*) Ge_2Os and As_2Nb, $n=2$. (*c*) Dy_3Ni_2, $n=4$. (*d*) CrB, $n=\infty$.

Table 6. *Cell parameters for* Ln_3Ni_2 *compounds*

V: Volume of the unit cell.
n: Number of atoms in the unit cell.

	Space group	a	b	c	β	$(V/n)^{1/3}$
Tb_3Ni_3	$C2/m$	9·64 Å	3·71 Å	13·38 Å	106·0°	2·84
Dy_3Ni_2	$C2/m$	9·512	3·662	13·321	105·72	2·82
Ho_3Ni_2(II)	$C2/m$	9·51	3·65	13·30	105·6	2·81
Ho_3Ni_2(I)	$R\bar{3}$	8·52	–	15·75	–	2·80
Er_3Ni_2	$R\bar{3}$	8·472	–	15·680	–	2·79

sidered as different stacking variations of a common structural slab formed by trigonal prisms (Lemaire & Paccard, 1970; Hohnke & Parthé, 1966). Engström (1965) has drawn attention to a structural series of composition $M_{(n2+n)}N_{(n2-n+1)}$ which contains the structures of Fe_2P ($n=2$), $V_{12}P_7$ with anti-Th_7S_{12} type ($n=3$) and $Rh_{20}Si_{13}$ ($n=4$). The characteristic features of this structural series are blocks of triangular prisms which themselves form a large triangle. Other structural series with other compositions are discussed by Pearson (1972).

The structure of Dy_3Ni_2 belongs to a new structural series of general composition $M_{(n+2)}N_{(n)}$. It exists with isolated prism columns ($n=1$), column pairs ($n=2$), wider column bands or finally column sheets ($n=\infty$): n indicates here the length of the zigzag chains perpendicular to the columns formed by the atoms which are in the centres of the trigonal prisms. In Fig. 1 examples for $n=1$, 2, 4 and ∞ are shown. Pu_3Co with the Re_3B structure contains only isolated trigonal prism columns (Larson, Cromer & Roof, 1963). An example for $n=2$ is the structure of $OsGe_2$ (Weitz, Born & Hellner, 1960) and $NbAs_2$ (Furuseth & Kjekshus, 1965).* In Dy_3Ni_2 the zigzag chain consists of four Ni atoms. Finally with $n=\infty$ one obtains the CrB type structure found for example with GdNi and homologous compounds.

A study of Fig. 1 reveals that the structure of Dy_3Ni_2 consists of undistorted segments of the CrB structure. It is thus possible to calculate the cell dimension of a hypothetical DyNi structure crystallizing with the CrB type from the relations:

$$a_{CrB}=b_{Dy_3Ni_2}$$

$$b_{CrB}=\sqrt{(\tfrac{1}{4}a^2_{Dy_3Ni_2}-c^2_{CrB})}$$

c_{CrB} = length of prism side parallel to zigzag chain.

As there are two prisms, one for Ni(1) and one for Ni(2) in Dy_3Ni_2, it is possible to take the mean of the two calculated values to obtain the parameter c_{CrB} (Table 7).

However DyNi does not crystallize with the CrB type but with the FeB type with $a=7{\cdot}043$, $b=4{\cdot}164$ and $c=5{\cdot}451$ Å (Dwight, Conner & Downey, 1965). Reversing a CrB → FeB transformation given earlier (Hohnke & Parthé, 1966) one obtains

$$a_{CrB}=\{c_{FeB}[2c_{FeB}-\sqrt{(4c^2_{FeB}-a^2_{FeB})}]\}^{1/2}$$

$$b_{CrB}=\{c_{FeB}[2c_{FeB}+\sqrt{(4c^2_{FeB}-a^2_{FeB})}]\}^{1/2}$$

$$c_{CrB}=b_{FeB}$$

which allow the calculation of the lattice constants of a hypothetical DyNi with CrB type. The agreement between the calculated values (Table 7) confirms the close relationship between the Dy_3Ni_2 and the CrB type structures.

Table 7. *Lattice constants for a hypothetical* DyNi *structure with* CrB *type*

	Calculated parameters from Dy_3Ni_2 (monoclinic)	Calculated parameters from DyNi (FeB type)
a	3·662 Å	3·236 Å
b	10·10	10·750
c	4·21	4·163

* Concerning the difference between the two structure types see the discussion by Jeitschko & Donohue (1973).

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