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The CrB and Related Structure Types Interpreted by Periodic Unit-Cell Twinning of Close-Packed Structures

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It is shown that the CrB, the two TbNi and the FeB structure types can be geometrically derived from close-packed element structures with stackings $(c)_3$, $(hcc)_2$, $(hhhhcc)_3$ and $(h)_2$ respectively. Twinning at the unit-cell level of these close-packed structures leads to the formation of trigonal prismatic holes at the twin planes which are assumed to be occupied by the alloying partner. If the twin planes are placed as close as possible, atom arrangements result which correspond to the CrB, the two TbNi and the FeB structure types respectively. The concept of unit-cell twinning not only allows one to predict other related structure types but also offers a suggestion for a possible formation mechanism of compounds having such structures.

Introduction

Twinning at the unit-cell level as a structure-building operation in the solid state has been discussed by Andersson & Hyde (1974) and Hyde, Bagshaw, Andersson & O'Keeffe (1974). It has been shown by these authors that the unit-cell twinning of the hexagonal and the cubic close-packed structures along particular planes leads to the formation of trigonal prismatic holes on the twin planes. These holes in a twinned close-packed structure formed by atoms M can be occupied by the alloying partner X. By varying the width of the untwinned segments, different crystal structures of composition $MX_{0\leq y\leq 1}$ can be obtained. In particular the above authors could interpret the FeB structure as a hexagonal close-packed Fe structure with closely spaced twin planes where the B atoms occupy the trigonal prismatic holes on the twin planes.

Several equiatomic compounds composed of transition elements and *b* elements (those to the right of the Ni, Pd and Pt group) crystallize with the CrB or the FeB structure type, both characterized by trigonal prisms. In rare earth (Ln) compounds a structure change from one to the other type is frequently observed within the series from La to Lu (Schob & Parthé, 1965; Hohnke & Parthé, 1966). Of special interest here are two transition structure types which were both found in TbNi and which have structural elements corresponding to the CrB and the FeB type (Lemaire & Paccard, 1970). A relationship between these structures based on structure block shifting has been proposed (Hohnke & Parthé, 1966; Lemaire & Paccard, 1970); however, the reasons for this relationship were not clear.

It was of interest to investigate if the CrB structure type and the two TbNi modifications could also be explained by unit-cell twinning. It is well known that all Ln elements have close-packed structures. Besides the hexagonal and cubic close-packed structures, more complicated stackings are known. The question arises whether it might not be possible to interpret the CrB structure as unit-cell twinning of a cubic close-packed structure and the two TbNi modifications as unit-cell twinning of close-packed structures with more complicated stackings.

Formation of trigonal prismatic holes

We consider general close-packed structures with N hexagonal layers in the hexagonal unit cell. To denote the stacking of the layers we use the conventional Jagodzinski–Wyckoff notation consisting of letters *h* (hexagonal), *c* (cubic). However, in order to obtain easily the number of layers in the unit cell the Jagodzinski–Wyckoff symbols are placed in parentheses followed by a subscript. The number of letters *h* and *c* inside the parentheses multiplied by the subscript gives *N*, the number of layers in the hexagonal unit cell.

The hexagonal unit cells have the parameters a_H, and $c_H=N\sqrt{\frac{2}{3}}a_H$. For our purposes it is convenient to use the corresponding orthohexagonal unit cells where $a_{OH}=a_H$, $b_{OH}=\sqrt{3}a_H$, $c_{OH}=N\sqrt{\frac{2}{3}}a_H$.

Projections along c_{OH} of the orthohexagonal unit cells for the hexagonal and cubic close-packed structures are presented in Fig. 1. Since the twin planes, as will be shown later, are parallel to b_{OH} it is advantageous to study projections along b_{OH}. Such projections are given in Fig. 2 for four close-packed structures with stacking $(h)_2$, $(hhhhcc)_3$, $(hcc)_2$ and $(c)_3$. In order to have trigonal prismatic holes at the twin plane the Miller indices of these planes must be of the $\{20N\}$ (or $\{20\bar{N}\}$) family. The trace of one of these planes is indicated in each drawing by dotted lines. Fig. 3 shows where the trigonal prismatic holes are formed at the twin plane for the hexagonal and the cubic close-packed structures. To distinguish between the two segments of the twin, one has been stippled and the other left clear. The black circles correspond to extra atoms which lie at the centres of the trigonal prismatic holes.

Equiatomic structures obtained by unit-cell twinning

In order to obtain a periodic atomic arrangement the twin planes, of course, have to be placed periodically. Since the alloying partner is found only on the twin planes, a change of the width of the untwinned segments corresponds to a change in the composition of the compound. To obtain equiatomic structures of composition MX the twin planes must be placed in close sequence so that the untwinned segments have the smallest possible width. In Fig. 4 are shown four equiatomic structures derived from close-packed structures $(h)_2$, $(hhhhcc)_3$, $(hcc)_2$ and $(c)_3$ by repeated unit-cell twinning and occupation of all trigonal prismatic holes. The untwinned segments have been alternately stippled and left clear. In this drawing the contour lines of the trigonal prisms are no longer indicated; however, a study of the inscribed fractional parameters of the X atoms at the prism centres and the surrounding M atoms should allow one to recognize the trigonal prisms and to construct these contour lines without difficulty. The structure on the left is the FeB structure, followed by the low- and the high-temperature modification of TbNi. The structure on the right corresponds to the CrB structure. The unit cells indicated for FeB and TbNi (h.t.) already correspond to the conventional unit cells for these structure types. However, in FeB $\frac{2}{3}$ has to be added to all the *z* values inscribed in the circles and in TbNi (h.t.) it should be $\frac{5}{6}$ in order to obtain point positions which agree with *International Tables for X-ray Crystallography*. To recognize the conventional monoclinic and orthorhombic unit cells of TbNi (l.t.) and CrB it is necessary to turn the drawings in Fig. 4 through 90° about the long axes. The results are presented in Fig. 5 where now the contour lines of the trigonal prisms are also drawn.

The derivation of these equiatomic structure types from the concept of unit-cell twinning permits the calculation of theoretical structure data. These are compiled in Table 1.

Unit-cell twinning and compound formation

The explanation of the atomic arrangement in metallic crystal structures is a difficult problem for which there has not really been any significant success. It seems that the concept of unit-cell twinning provides not only a novel way to explain the atomic arrangement in certain metallic crystal structures but also a clue as to how these compounds are formed from the melt.

One may explain the formation of the FeB, TbNi and CrB structure types with the Ln–Ni, Pd or Pt alloys by assuming that both Ln atoms and Ni, Pd or Pt atoms prefer to retain in the compounds their individual bonding characteristics as much as possible.

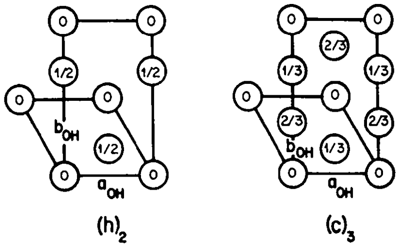


Fig. 1. Projections along c_{OH} of the orthohexagonal unit cells for the hexagonal and cubic close-packed structures.

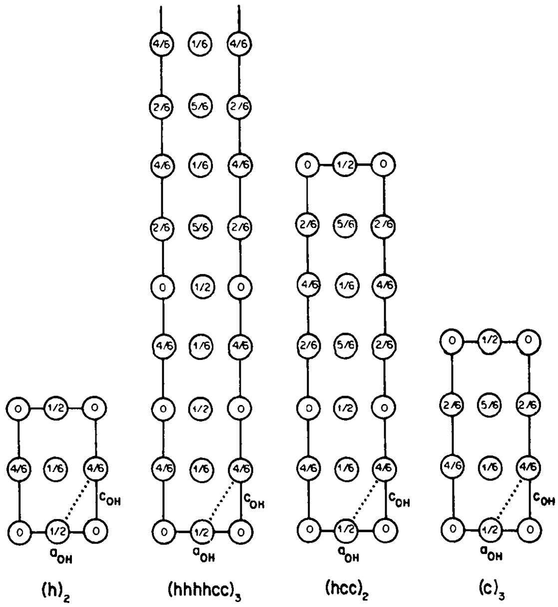


Fig. 2. Four different close-packed structures described with orthohexagonal unit cells and projected along b_{OH}. Traces of the $(20N)$ planes are indicated by dotted lines.

Hence (*a*) the Ln atoms themselves prefer to have close-packed arrangements. This is evident from the structures of the pure Ln elements. The type of stacking may vary, but the structures are always close packed. (*b*) Ni, Pd and Pt atoms, when surrounded by Ln atoms, prefer to have a trigonal prismatic coordination.

Imagine the formation of a thin layer of close-packed Ln atoms as the first step in the crystallization from the melt. The type of stacking of this layer depends on secondary factors which are not really understood. With the depletion of Ln atoms in the melt near the surface, Ni, Pd or Pt atoms will attach themselves to

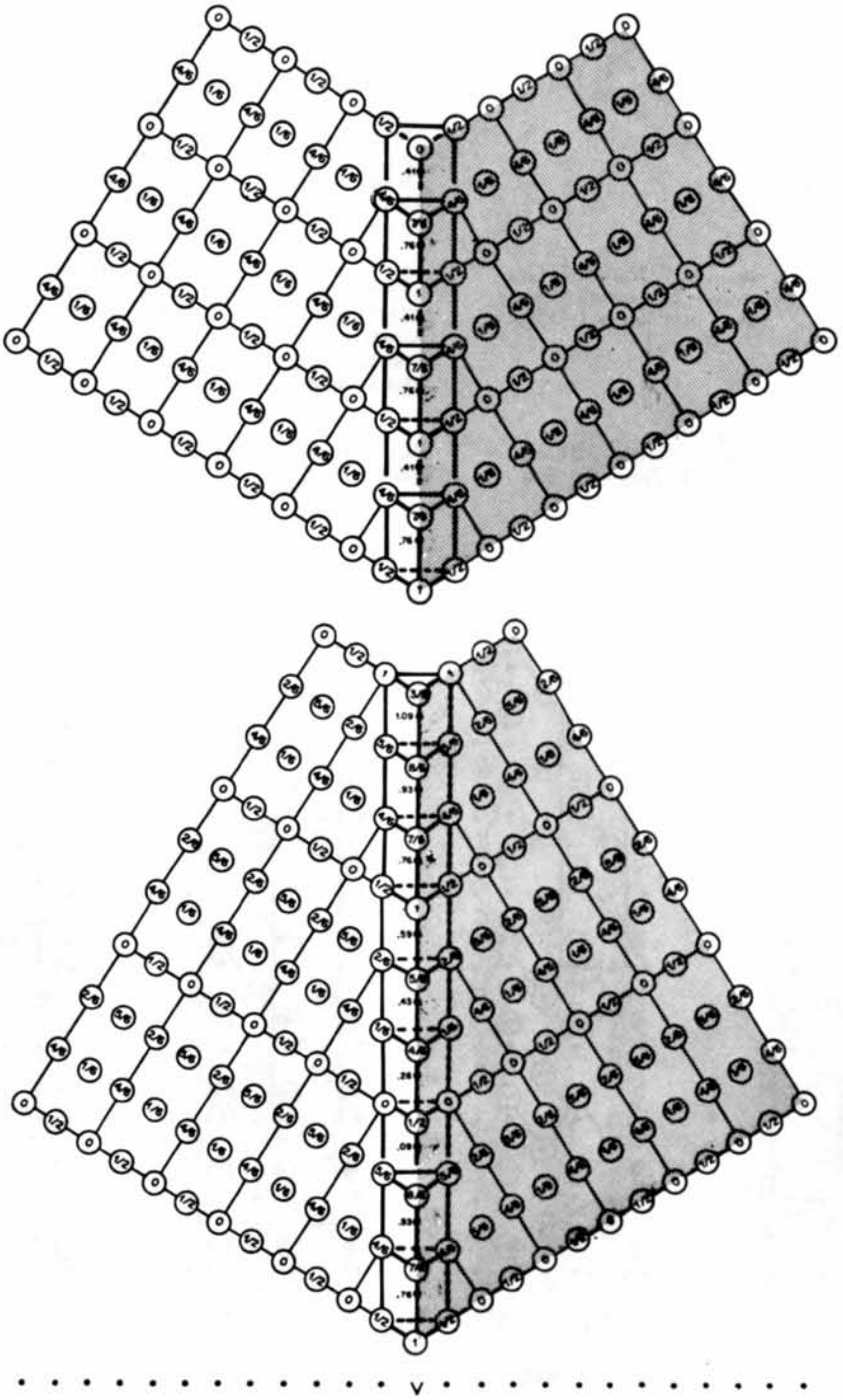
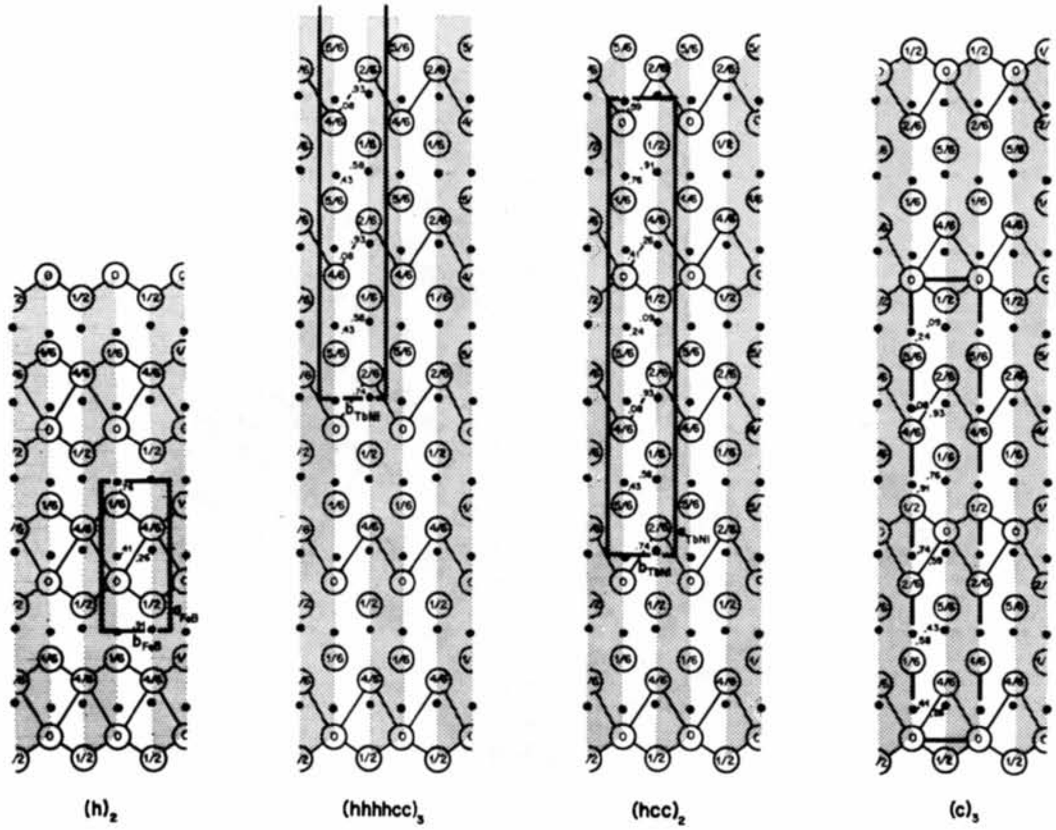


Fig. 3. The formation of trigonal prismatic holes on the twin planes of two twinned crystals, the upper consisting of a hexagonal and the lower of a cubic close-packed structure.

Table 1. *Theoretical structure data for the* FeB, TbNi *and* CrB *structure types*

	Space group	Unit-cell dimensions	Idealized point positions		x	z
FeB	*Pnma*	$a_{\mathrm{FeB}}=\sqrt{\frac{11}{3}}a_H=1{\cdot}915a_H$	4Fe	in 4(c)	$\frac{2}{11}$ ($\equiv$0·182)	$\frac{1}{6}$ ($\equiv$0·167)
		$b_{\mathrm{FeB}}=2\sqrt{\frac{2}{11}}a_H=0{\cdot}853a_H$	4B	in 4(c)	0·020	0·575
		$c_{\mathrm{FeB}}=\sqrt{3}a_H=1{\cdot}732a_H$				
TbNi (l.t.)	$P2_1/m$	$a_{\mathrm{TbNi}}=\sqrt{\frac{103}{3}}a_H=5{\cdot}859a_H$	2Tb(1)	in 2(e)	$\frac{7}{66}$ ($\equiv$0·106)	$\frac{179}{198}$ ($\equiv$0·904)
		$b_{\mathrm{TbNi}}=2\sqrt{\frac{2}{11}}a_H=0{\cdot}853a_H$	2Tb(2)	in 2(e)	$\frac{3}{11}$ ($\equiv$0·273)	$\frac{2}{11}$ ($\equiv$0·182)
		$c_{\mathrm{TbNi}}=\sqrt{3}a_H=1{\cdot}732a_H$	2Tb(3)	in 2(e)	$\frac{29}{66}$ ($\equiv$0·439)	$\frac{25}{198}$ ($\equiv$0·126)
		$\beta=101{\cdot}36°$	2Tb(4)	in 2(e)	$\frac{20}{33}$ ($\equiv$0·606)	$\frac{40}{99}$ ($\equiv$0·404)
		$\mathrm{tg}\,(\beta-90)=\frac{2}{\sqrt{99}}$	2Tb(5)	in 2(e)	$\frac{17}{22}$ ($\equiv$0·773)	$\frac{23}{66}$ ($\equiv$0·348)
			2Tb(6)	in 2(e)	$\frac{31}{33}$ ($\equiv$0·939)	$\frac{62}{99}$ ($\equiv$0·626)
			2Ni(1)	in 2(e)	0·159	0·35
			2Ni(2)	in 2(e)	0·327	0·80
			2Ni(3)	in 2(e)	0·492	0·57
			2Ni(4)	in 2(e)	0·660	0·02
			2Ni(5)	in 2(e)	0·828	0·79
			2Ni(6)	in 2(e)	0·993	0·07
TbNi (h.t.)	*Pnma*	$a_{\mathrm{TbNi}}=\sqrt{33}a_H=5{\cdot}744_5a_H$	4Tb(1)	in 4(c)	$\frac{2}{33}$ ($\equiv$0·0606)	$\frac{1}{6}$ ($\equiv$0·167)
		$b_{\mathrm{TbNi}}=2\sqrt{\frac{2}{11}}a_H=0{\cdot}853a_H$	4Tb(2)	in 4(c)	$\frac{13}{33}$ ($\equiv$0·394)	$\frac{1}{6}$ ($\equiv$0·167)
		$c_{\mathrm{TbNi}}=\sqrt{3}a_H=1{\cdot}732a_H$	4Tb(3)	in 4(c)	$\frac{5}{22}$ ($\equiv$0·227)	0
			4Ni(1)	in 4(c)	0·007	0·58
			4Ni(2)	in 4(c)	0·173	0·41
			4Ni(3)	in 4(c)	0·339	0·76
CrB	*Cmcm*	$a_{\mathrm{CrB}}=a_H$			y	
		$b_{\mathrm{CrB}}=\sqrt{11}a_H=3{\cdot}317a_H$	4Cr	in 4(c)	$\frac{3}{22}$ ($\equiv$0·136)	
		$c_{\mathrm{CrB}}=2\sqrt{\frac{2}{11}}a_H=0{\cdot}853a_H$	4B	in 4(c)	0·46	



(h)$_2$ (hhhhcc)$_3$ (hcc)$_2$ (c)$_3$

Fig. 4. Equiatomic structures derived from four different close-packed structures by unit-cell twinning and occupation of the trigonal prismatic holes by the alloying partner.

three Ln atoms of the initial layer thus forming one half of a trigonal prism. In order to satisfy the desire of the Ni, Pd or Pt atoms to form a trigonal prism, Ln atoms from the melt are positioned in the desired place. These Ln atoms now form a new close-packed layer in a twinned position to the initial close-packed layer. This process repeats itself continuously until the whole crystal has been formed.

If the proposed formation model is correct it should be possible to predict crystal structures for different Ln–Ni, Pd or Pt ratios. If there is less Ni, Pd or Pt in the melt, the initial close-packed Ln atom layer will be thicker before the first Ni, Pd or Pt atoms are attached to it. Thus one should find crystal structures based on unit-cell twinning with wider untwinned segments. A list of a few structure types with different compositions all derived by unit-cell twinning of close-packed structures with different stackings and having different widths of the untwinned segments is given in Table 2.

Table 2. *Structure types derived by unit-cell twinning from different close-packed structures*

The symbols at the head of the columns indicate the width and the period of the untwinned segments. V indicates a twin plane layer while • indicates an untwinned layer. The orientation of the layers corresponds to the layers perpendicular to the plane of projection, as shown in Fig. 3.

Stacking notation	Percentage of hexagonal stacking	M •	M_3X V••	M_5X_2 V••V•	MX V
$(h)_2$	100	Mg	Fe_3C	Mn_5C_2	FeB
$(hhc)_3$	67	Sm			
$(hhhhcc)_3$	67				TbNi (l.t.)
$(hc)_2$	50	Nd			
$(hcc)_2$	33				TbNi (h.t.)
$(c)_3$	0	Cu	Re_3B		CrB

In reference to Table 2, a phase with the Fe_3C structure type has been observed in nearly all Ln–Ni systems (Lemaire & Paccard, 1967). This structure type has also been reported for Yb_3Pd. The Mn_5C_2 structure type is found with Eu_5Pd_2, Yb_5Pd_2 and Yb_5Pt_2 (Iandelli & Palenzona, 1973, 1974, 1975). Many more hypothetical structure types can be derived with this concept but have not yet been found experimentally. There are, however, other phases with trigonal prisms, as for example those with the Th_7Fe_3 type found in Ln–Ni, Pd and Pt alloys (Moreau & Parthé, 1973; Olcese, 1973), which can be explained only by a more complicated twinning mechanism (Hyde, Bagshaw, Andersson & O'Keeffe, 1974). There are still more known phases characterized by trigonal prisms which as yet cannot be explained by any known mechanism (Parthé & Moreau, 1976).

Thus the model is not completely satisfactory because not all occurring structures can be interpreted in this way. Further there remains the difficulty of explaining why a particular type of stacking has been adopted. Efforts in this direction have been made for example by Blandin, Friedel & Saada (1966), Gschneid-

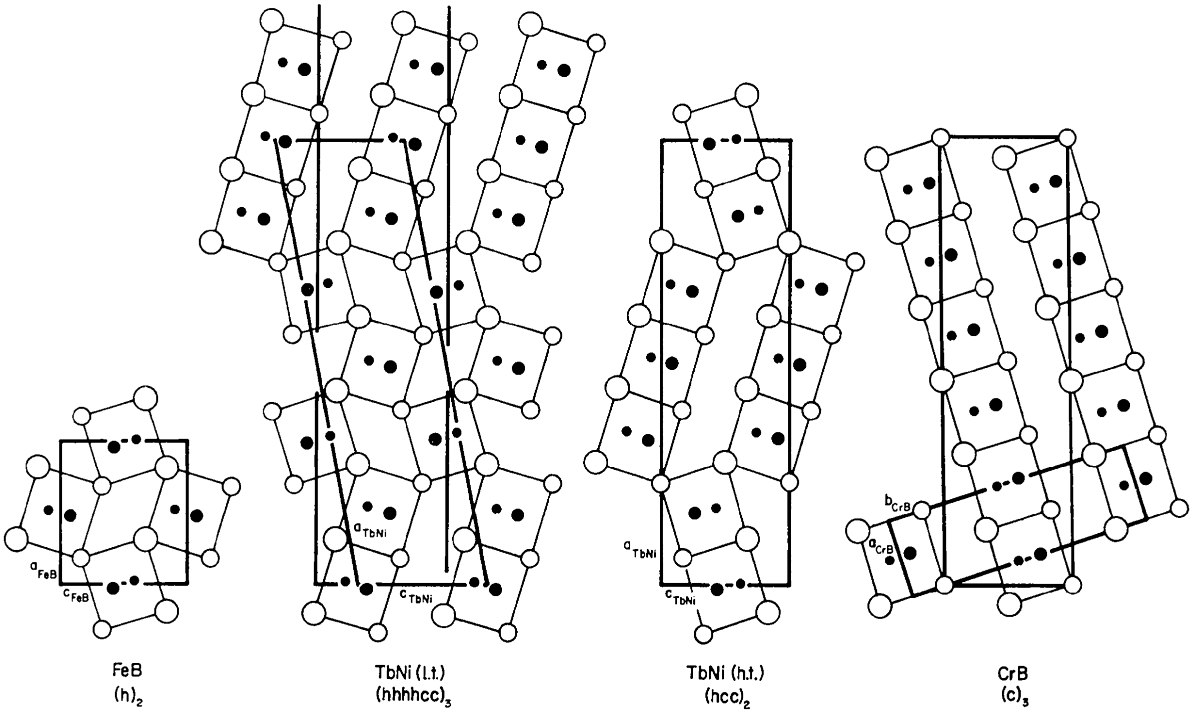


Fig. 5. Drawings of the FeB, the two TbNi and the CrB structure types obtained from Fig. 4 after rotation through 90° about the long axes. Open circles correspond to Fe, Tb or Cr atom sites and closed circles represent the sites of the alloying partners. Small circles are at height $\frac{1}{4}$, large circles at height $\frac{3}{4}$.

ner & Valletta (1968), Gschneidner & Pearson (1968), and Havinga, van Vucht & Buschow (1969). However, an application for these kinds of compounds seems difficult.

A certain caution is appropriate with respect to the expected relative unit-cell dimensions and point positions for these theoretical structures. The model used in this work is based on an ideally close-packed structure with $c_H/a_H = N\sqrt{2}/\sqrt{3}$. This leads to trigonal prisms with a base of $a_H \times \sqrt{\frac{8}{11}}a_H$ where the short edge is parallel to the B–B chains in FeB and CrB respectively. Such a prism has elongated prism sides which means that the ratio of the prism length perpendicular to the zigzag chain to the length parallel to the zigzag chain is 1·17. It has been shown by Parthé (1970) and Hohnke & Parthé (1966) how this ratio changes with different compounds having CrB or FeB structure types. Actually it was possible to classify the approximately 100 different compounds having CrB or FeB structures into two different groups. Group I compounds have in the prism centres B, Si, Ge, Ga atoms with ratios $>1 \le 1{\cdot}1$, while group II compounds have in their prism centres transition elements such as Ni, Pd, Pt and others. CrB and FeB structures of group II have ratios $\ge 0{\cdot}85 < 1$.

We note here an important influence of the alloying partner occupying the trigonal prismatic holes on the actual shape of the trigonal prisms and thus on the relative unit-cell dimensions and the actual point positions of the atoms. The alloying partner determines the angles between the bonds within the trigonal prisms. Hence the close-packed layers of the Ln elements have to expand or contract in accordance with the special character of their prism centring partners. As a consequence. the relative unit-cell dimensions and point positions of the crystal structures actually observed will be somewhat different from the values given in Table 1, particularly if the alloying partners are elements of group II. In Table 3 are listed the experimental structure data for LuNi (FeB type), the two TbNi modifications and GdNi (CrB type) which may be compared with the theoretical values given in Table 1. With the two TbNi structures there is good agreement for the x parameters which apply to the long a axes, but there are certain deviations for the z parameters. However, even if the theoretical point positions derived from the unit-cell twinning model do not agree exactly with the experimental values the concept of unit-cell twinning developed by Andersson, Hyde and others permits one to understand some crystal structures which were previously unexplainable. It seems not impossible that further study on other twinning mechanisms might eventually help to systematize other metallic crystal structures which up to now have always been a mystery in as far as answering the question 'why is a particular atomic arrangement adopted in the first place?'

Table 3. *Experimental structure data for* LuNi (FeB *type*), *the two* TbNi *modifications and* GdNi (CrB *type*)

The structure data for LuNi and GdNi are from Dwight, Conner & Downey (1965) while those for TbNi are from Lemaire & Paccard (1970).

	Space group	Unit-cell parameters	Point positions				
						x	z
LuNi	*Pnma*	$a = 6{\cdot}912$ Å	4Lu	in	4(*c*)	0·185	0·144
		$b = 4{\cdot}073$	4Ni	in	4(*c*)	0·040	0·653
		$c = 5{\cdot}366$					
TbNi (l.t.)	*P*2$_1$/*m*	$a = 21{\cdot}26$ Å	2Tb(1)	in	2(*e*)	0·1074	0·9214
		$b = 4{\cdot}21$	2Tb(2)	in	2(*e*)	0·2708	0·2382
		$c = 5{\cdot}45$	2Tb(3)	in	2(*e*)	0·4406	0·1050
		$\beta = 97°25'$	2Tb(4)	in	2(*e*)	0·6064	0·4175
			2Tb(5)	in	2(*e*)	0·7708	0·2853
			2Tb(6)	in	2(*e*)	0·9394	0·6090
			2Ni(1)	in	2(*e*)	0·1632	0·4675
			2Ni(2)	in	2(*e*)	0·3298	0·8000
			2Ni(3)	in	2(*e*)	0·4939	0·6325
			2Ni(4)	in	2(*e*)	0·6605	0·9450
			2Ni(5)	in	2(*e*)	0·8288	0·8000
			2Ni(6)	in	2(*e*)	0·9946	0·1325
TbNi (h.t.)	*Pnma*	$a = 21{\cdot}09$ Å	4Tb(1)	in	4(*c*)	0·0606	0·1393
		$b = 4{\cdot}22$	4Tb(2)	in	4(*c*)	0·3926	0·1323
		$c = 5{\cdot}45$	4Tb(3)	in	4(*c*)	0·2292	0·8792
			4Ni(1)	in	4(*c*)	0·0121	0·6403
			4Ni(2)	in	4(*c*)	0·1790	0·3911
			4Ni(3)	in	4(*c*)	0·3463	0·6209
GdNi	*Cmcm*	$a = 3{\cdot}766$ Å				y	
		$b = 10{\cdot}316$	4Gd	in	4(*c*)	0·135	
		$c = 4{\cdot}244$	4Ni	in	4(*c*)	0·435	

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