

TOPICAL REVIEW

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Superstructure Ordering of Intermetallics: B8 Structures in the Pseudo-Cubic Regime

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Abstract

The structural chemistry of the intermetallic B8-type compounds is reviewed.

1. Introduction

Since the first structure determination of NiAs by Aminoff (1923), the number of known B8-type phases has grown steadily to a total today of more than 400 compounds. A parallel development has been the increasing diversification within the B8 group. Defect structures may be inferred from the non-stoichiometry of many B8 phases and as early as the turn of the century the higher chalcogenides of iron and chromium were known to show substantial phase width. Superstructures were observed early: Cu₆Sn₅ (Bernal, 1928) and Fe₇S₈ (Hägg & Sucksdorff, 1933), but the first examples of elucidations of superstructures did not appear until the fifties: Fe₇S₈ (Bertaut, 1953), Fe–Se (Okazaki & Hirakawa, 1956) and Cr₇S₈ (Jellinek, 1957). When the incommensurate structure analysis was first applied to long-period polytypes, pyrrhotite (Fe_{1-x}S) was again a natural choice (Yamamoto & Nakazawa, 1982).

In contrast to the more ionic chalcogenides, the intermetallic compounds between transition metals (*T*) and elements (*B*) from the triels, the carbon group, the pnictides and the chalcogenides that are at the focus of this survey tend to be transition-metal rich. At the extreme end there is the fully stuffed NiAs structure of Ni₂In solved in 1942 (Laves & Wallbaum, 1942), but the entire composition range between *TB* and *T₂B* is

possible. Superstructures are often formed in these materials, the first were solved during the sixties: Ni₃Sn₂ (Brand, 1967) and Pd₁₃Tl₉ (Bhan *et al.*, 1968), and the number of examples is now growing rapidly. The ubiquity of the B8 structure family together with its superstructural diversity makes it one of the most important structure types for intermetallics.

The basic structure of B8 (*P6₃/mmc*) is a hexagonal close packing [Wyckoff position 2(*c*)] of the main-group element (compressed along *c*) with the octahedral interstices [2(*a*)] occupied by the transition metal. In the stuffed variant the trigonal bipyramidal interstices [2(*d*)] are filled as well. In the more ionic chalcogenides, the non-stoichiometry is caused by vacancies on position 2(*a*), while in the intermetallics there is a partial filling of 2(*d*).

Synthesis of the intermetallic compounds is straightforward. The elements are combined in the desired proportions, pelletized, arc-melted or induction-heated and subsequently subjected to prolonged annealing. The superstructure ordering normally takes several weeks to fully develop for low-temperature phases. On the other hand, chemical analysis is difficult. Wide solid solution fields tend to phase-separate into phase bundles (an ensemble of line phases with fixed compositions that occur closely together) on annealing and several distinct compositions may coexist in what, to all intents and purposes, appears to be a macroscopically homogeneous sample. Normally the most expedient procedure is to combine electron diffraction with EDX (Energy Dispersive X-ray Spectroscopy, also abbreviated as EDS or EDXS) analysis to assess composition and structure simultaneously.

Structural analysis has traditionally been carried out with X-ray powder diffraction methods because of the difficulty in obtaining single crystal specimens, but data obtained exclusively with powder methods should be treated with care. Owing to the fairly weak superstructure ordering, the basic cell is normally metrically undistorted and this opens the scene for merohedral twinning, often with fairly small domains. This weakens the relative intensity of the satellite reflections and makes assignment of indices to them exceedingly tricky.

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To further complicate matters, the c/a ratio for the hexagonal base cell is normally close to 1.225 [pseudo-cubic, $a^*/c^* = (3/2)^{1/2}$] and the powder pattern may even be mistaken for gamma brass.

The structural elucidation technique of choice is electron diffraction, followed by quasi-single crystal measurements on multiply twinned specimens. Selected-area electron diffraction allows the unravelling of twinning and thus the unambiguous determination of the unit cell. Weak reflections from modulations (commensurate or otherwise) are also much more straightforward to detect.

There is a host of B8 intermetallics that are known to exhibit superstructure ordering that has not been elucidated at all or that are poorly characterized. More examples are needed in order to understand the basic rules underpinning superstructure ordering in these compounds. The interplay of order and disorder is clearly seen on the sliding scale from simple short-period superstructures, long-period commensurate superstructures, incommensurate structures and weakly ordered systems characterized by structured diffuse scattering. The B8 structure type is unique in that it offers such a rich flora of examples of diverse structural behaviour and the recombination of this information into a comprehensive theory of ordering in intermetallics must be a prime future goal in this particular field of structural chemistry.

2. Basic structures

There are two subclasses of the basic B8-type structure: B8₁ (NiAs) and B8₂ (Ni₂In), as shown in Fig. 1. They are both hexagonal, space group $P6_3/mmc$ (194) and the main-group element occupies Wyckoff position $2(c)$. The transition-metal position in NiAs and one of the positions in Ni₂In is $2(a)$, while the second transition-metal position in Ni₂In is $2(d)$. The atoms in position $2(c)$ may be considered to form a hexagonal close packing, while the positions $2(a)$ and $2(d)$ represent octahedral and trigonal bipyramidal interstices of that packing. In the large class of transition-metal rich ordered superstructures of the B8 type, the superstructure originates from the ordering of transition-metal atoms and vacancies on positions equivalent to $2(d)$ (trigonal bipyramidal interstices). In transition-metal poor compounds another ordering is common; nothing in $2(d)$, full occupancy of $2(c)$ and ordered vacancies in $2(a)$ (octahedral interstices). Many of the simple type structures may be derived from this family; in CdI₂ half the positions corresponding to $2(a)$ are occupied, forming alternating empty and filled sheets.

Apart from the more complex ordered superstructures of B8, two lower symmetry variants need to be considered: the orthorhombically distorted MnP (Rundqvist, 1962) and Co₂Si (Borén, 1933) variants. MnP- and Co₂Si-type structures are often rather

different from their B8 counterparts, but the c/a ratio is a good indicator; if this is in the pseudo-cubic regime, the structure types are often found together, with more or less continuous transformations in-between.

3. B8-type compounds

The NiAs–Ni₂In-type compounds are primarily of the type T_xB , where T is a transition metal and B is a main-group element. Their composition is highly variable and the range may conveniently be set as $0.75 \leq x \leq 2.33$. There are several reports of compounds that fall outside these specifications; the carbide CMn₄ and the nitride Fe₃N are well outside any reasonable composition range, while Ag₁₁Hg₉ (King & Massalski, 1961), AgAsBa (Mewis, 1979) and BiIn₂ (Giessen *et al.*, 1967) are not TB compounds at all. Variations on the theme are the alkali metal intercalates of CdI₂-type structures such as LiS₂Sn (le Blanc & Rouxel, 1972) and LiTe₂Ti (Patin & Balchin, 1985).

The problem of delimiting the class of compounds related to the B8 structure type is difficult to resolve; the MnP- and Co₂Si-type structures differ only by rather small orthorhombic distortions of NiAs and Ni₂In and the CdI₂-type may be viewed as a particular defect structure of NiAs. There are, however, two clearly distinguishable classes of B8-related TB compounds that differ in their c/a values as well as in their compositions. By limiting the scope of the investigation to the pseudo-cubic regime of the B8 structure family, *i.e.* to c/a values (or corresponding quantities for lower symmetry variants) above 1.2 (the perfectly pseudo-cubic value is 1.225) and significantly smaller than the ideal hexagonally close-packed value of 1.63,

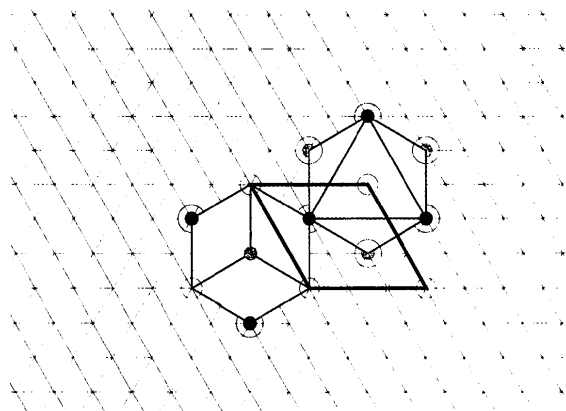


Fig. 1. The structures of NiAs and Ni₂In. Solid discs denote In positions, grey at $c = \frac{1}{4}$ and black at $c = \frac{3}{4}$. Open circles denote Ni positions, small at $c = 0$ and $\frac{1}{2}$, large grey at $c = \frac{1}{4}$ and large black at $c = \frac{3}{4}$. The Ni positions at $c = \frac{1}{4}$ and $c = \frac{3}{4}$ are unique to the Ni₂In structures; the remaining positions are the same for NiAs and Ni₂In. The unit cell is heavily outlined. The two different coordination polyhedra for Ni in Ni₂In are shown; an octahedron around 000 and an Edshammur polyhedron around $\frac{1}{3} \frac{2}{3} \frac{3}{4}$.

say 1.4, the field is narrowed down to the transition-metal rich class. This excludes the highly interesting B8-type transition-metal chalcogenides that have c/a ratios close to 1.63, but these constitute a rather different group of compounds that are transition-metal deficient and form in a different part of the periodic table. Likewise, most MnP-type compounds are excluded because of the c/a window allowed. For these compounds no value of the parameter corresponding to hexagonal c/a (a/b) has been found below 1.5 and for compounds with this structure type the composition is more fixed and superstructure ordering is rarer. Some systems that contain the structure type pair MnP–Co₂Si are, however, of interest, *i.e.* Rh–Ge, Ir–Si *etc.* The CdI₂-type structure is largely excluded; c/a is normally around 1.63, but some anomalously low values have been found for ditellurides: PdTe₂ (1.27), PtTe₂ (1.30), RhTe₂, IrTe₂, NiTe₂ (1.37–1.38) and the diselenide PtSe₂ (1.36) (Villars & Calvert, 1991). In several of these cases (PdTe₂, PtTe₂ and NiTe₂) there are reports of complete miscibility of the TB_2 phase with a TB phase with the NiAs-type structure (Furuseth *et al.*, 1965). This certainly indicates that for the compounds in question, the CdI₂-type structure is indeed to be treated as a defect B8-type structure, but on the transition-metal poor side. Apart from these larger structure classes, there are several structures with only a small number of representatives that are simple B8-type superstructures: Cu₇In₃, Cu₆Sn₅, Mn₈Sn₅, Co₃Sn₂, Pd₁₃Tl₉ *etc.* To highlight the frequency with which the B8-type phases occur for different element combinations, Table 1 shows binary TB phases with B8-related structures in the required c/a range, while the off-limits B8 structures are shown in Table 2. Pseudo-cubic NiAs structures are most prevalent among the later transition metals and the earlier main-group metals, while structures with larger c/a values are favoured by early transition metals and late main-group elements.

4. Synthesis and chemical analysis

In principle, the synthesis of the intermetallic compounds is straightforward. The elements are combined in the desired proportions, pelletized, arc-melted, induction-heated or melted in a conventional furnace to produce a homogeneous reaction mixture. What is typically formed during this treatment is a basic, high-temperature B8-type structure lacking superstructure ordering. The important step is the subsequent annealing which can be very time-consuming indeed. Superstructure ordering normally takes several weeks to fully develop, in some cases months for low-temperature phases. Most samples require rather low annealing temperatures and evacuated silica ampoules may be used.

Superstructure-ordered samples with a symmetry lower than the parent hexagonal cell tend to be pseudo-

merohedrally domain twinned, the parent lattice forming a contiguous sublattice. The procedure starting from the disordered high-temperature modification may be partially responsible for this, but we have attempted to grow Cu₅Sn₄ at 523 K (well below the transition temperature from the disordered, high-temperature hexagonal phase to the ordered intermediate temperature orthorhombic phase) by the reduction of Cu(CH₃CO₂)₂ with hydrazine in a tin melt. The result was a hexagonally pseudo-merohedrally twinned material indistinguishable from that resulting from a high-temperature synthesis and the conclusion must be that, at least in this case, the reasons for twinning are thermodynamic rather than kinetic.

Chemical analysis is difficult. Wide solid solution fields tend to phase separate into phase bundles on annealing and several distinct compositions may coexist in what, to all intents and purposes, appears to be a macroscopically homogeneous sample. There are even reported cases (Elding-Pontén, Stenberg, Larsson *et al.*, 1997) where two distinct phases of different composition coexist in a single crystallite, sharing a contiguous sublattice. Normally the most expedient procedure is to combine electron diffraction with EDX analysis to assess composition and structure simultaneously. For samples with narrow solid solution fields, line phases or well defined single phase materials grown from normal chemical analysis of dilute melts is a tractable route.

5. Structural analysis

Intermetallic phases are often difficult to crystallize properly. Stoichiometric mixtures tend to result in fine grained products unsuitable for single crystal work and few systems are accessible to flux methods. One important exception is tin-based systems, where tin may be used both as a flux and a reactant, and may be removed by leaching in dilute hydrochloric acid if the product is reasonably stable towards acid attack. Aluminium melts may be used in a similar way. The difficulty in producing good single crystals has made X-ray powder diffraction the method of choice for many investigations of intermetallic systems.

The simple X-ray powder fingerprint of a B8-type structure has made structure classification a fairly straightforward procedure. Unfortunately, this simplicity applies only to the basic structure. While the powder method is a powerful tool for distinguishing between different structural families, it fails when the problem concerns low-symmetry superstructures in high-symmetry settings. There are several reasons why this problem is particularly pronounced in the pseudo-cubic B8 intermetallics. First, the superstructure reflections are difficult to observe in a powder measurement. The satellite reflections are substantially weaker than the main reflections and since absorption is generally high in intermetallics, it may be difficult to

Table 1. A summary of the B8-type structures in the pseudo-cubic regime

For each transition metal the B8 phase forming main-group elements are given.

Sc:	Ti:	V:	Cr:	Mn:	Fe:	Co:	Ni:	Cu:
Al	Ga Ge Sn	P Ga	Si Sb Te	Ge Sn Sb Bi	Ge Sn Sb	Ge Sn Sb Te	Si Ga In Sn Sb As Te Bi	Al In Sn
Y:	Zr:	Nb:	Mo:	Tc:	Ru:	Rh:	Pd:	Ag:
In	Al Ga Sn Sb	Ga Ge Sn Sb			Si Ge Sn Pb Bi	Te	Al In Sn Sb Te Bi	Ga In
La:	Hf:	Ta:	W:	Re:	Os:	Ir:	Pt:	Au:
In	Sn	Ga				Si Sn Sb Te Pb	Al In Sn Sb Te Bi	Se Sn

Table 2. A summary of the B8-type structures outside the pseudo-cubic regime, $c/a > 14$

For each transition metal the B8 phase forming main-group elements are given. Note the trend towards more electronegative main-group elements compared with Table 1.

Sc:	Ti:	V:	Cr:	Mn:	Fe:	Co:	Ni:	Cu:
Al	Se	As S	P As	P As Te	P As	P As	Si Ge	
Y:	Zr:	Nb:	Mo:	Tc:	Ru:	Rh:	Pd:	Ag:
La:	Hf:	Ta:	W:	Re:	Os:	Ir:	Pt:	Au:
		As S	As P	As P	P As Sb	Si Ge As Sb	Si Ge	Se Sn

observe any extra reflections at all. This is compounded by the additional difficulty that the superstructures are often less well ordered. Incommensurate modulations are common and these yield even weaker satellites, and the indexing of a powder pattern from an incommensurately modulated structure is anything but simple. A few weak extra lines that do not fit with any reasonable superstructure of the main reflection lattice are easily disregarded as an impurity. Since the basic lattice is often undisturbed by the superstructure or modulation, the intensities and positions of the reflections will retain metric hexagonality, *i.e.* the relative magnitudes of distances corresponding to axes in the base cell will be retained in the supercell. Even well behaved extra reflections will therefore be next to impossible to index correctly, since the true symmetry of the superstructure is not recoverable from the powder pattern. Structures refined from powder patterns should be treated with caution and be closely inspected for characteristic signs of mistakes in the determination of cell and symmetry, *i.e.* split positions, partial occupancies and large thermal parameters.

A much safer approach is single crystal X-ray diffraction. Weak satellites are much easier to detect with this technique and some ambiguities of indexing are easily cleared up using three-dimensional data. Structural analysis of single crystal data tends to be dependable, but in some cases rather difficult. The two main difficulties lie in the pseudo-merohedral twinning and the incommensurability of the modulations, particularly at higher temperatures. If the twin domains of the crystal are small, they tend to be balanced, *i.e.* all possible domain orientations are equally represented. Neither the metric nor the intensity distribution then give any hints as to the twinned nature of the crystal. The warning signs are non-crystallographic absences and unrefinable datasets. The use of area detectors is a great advantage in data collection. Merohedral twins and incommensurate modulations tend to produce a great many possible reflections, and their correct measurement by conventional point-detector techniques becomes very tedious indeed. The structure of the modulated compound Mn_8Sn_3 was first solved from conventional point-detector data collected during a period of more than 2 weeks for one of the three twin parts. We later used the same crystal on various area-detector systems and the measuring time drops to 50 h, even for the most precise measurement. The number of observed independent reflections increases by a factor of 2.5 and the full material (all three twin individuals) may be used. A word of caution is again in order when dealing with poor data. Poor data quality is expected. Crystal quality is often bad, and macro- or mesoscopic twinning in highly absorbing substances leads to shadowing effects that are very difficult to correct for. This leads to refinements with rather high *R* values, and quite often to highly anisotropic displacement para-

meters. It can therefore be difficult to assess the reliability of the refinement. Mistakes in symmetry and cell determination may go unnoticed and even single crystal data must therefore be treated with some caution if the data quality is below par. This is not to say that bad crystals should not be used. Lack of good crystals means that we must make use of what we have. However, awareness of the weakness of the method for these materials is crucial.

Even with new and powerful detection methods for X-ray diffraction, the most efficient tool for proper cell and symmetry determination of crystals such as these is electron diffraction, and in particular selected-area electron diffraction (SAED). The possibility of studying very small domains makes the differentiation between low-symmetry merohedral twins and an untwinned higher symmetry cell relatively straightforward. In most twinned cases it is possible to find single domain regions in thin parts of the crystallites. Even when this is not possible, small regions are unbalanced with respect to the ratios of the different orientations and it is then possible to deduce the symmetry and the twinning laws from the intensity distribution of the diffraction patterns. This procedure has been used extensively on the systems Mn-Ge (Kifune & Komura, 1986), Cu-Sn (Larsson *et al.*, 1994, 1995a), Co-Sn (Larsson *et al.*, 1995b), Mn-Sn (Elding-Pontén, Stenberg & Larsson *et al.*, 1997), Cu-In (Elding-Pontén, 1997) and on the Ni-Ge system (Larsson & Withers, 1998). As with X-ray diffraction, it is often possible to deduce the presence of twinning from non-crystallographic absences, but in SAED this procedure is less reliable because of multiple diffraction, even between different domains. The continuous nature of the basic lattice, and the small amplitude of the distortions makes the whole multi-domain crystal scatter more or less coherently. In some cases this effect is so strong that reflections originating from multiple scattering effects are observable even in X-ray powder diffraction (Panteleimonov *et al.*, 1971).

In order to practise safe crystallography, the combination of electron and X-ray diffraction is recommended in these systems. Single crystal (or multiply twinned crystal) studies are naturally preferable to powder work, but again it is not always possible to choose and powder work can yield good results if the satellites are strong and the cell and symmetry are well determined from SAED.

6. Structural chemistry

The structures in question are intermetallics, and rather non-polar ones at that, hence formal atomic valences are difficult to estimate. The coordination, on the other hand, is worthy of some special attention. The standard description of the B8-type structure is that of hexagonally close-packed main-group atoms and transition-metal atoms in octahedral interstices. For the pseudo-

cubic structures this picture is rather misleading; the chains of centred face-sharing octahedra are uniaxially compressed, indicating transition metal-transition metal bonding along *c*. For the perfect pseudo-cubic *cla* value, the octahedra are actually truncated cubes and the transition metal sits in a perfect cubic coordination: six main-group atoms and two transition-metal atoms. The excess transition-metal atoms [position 2(*d*)] have a rather different coordination. They are surrounded by a trigonal bipyramid of main-group atoms [position 2(*c*)] and a trigonal prism of transition metals [position 2(*a*)]. Together the 11 atoms form an Edshammar polyhedron (Edshammar, 1969; Lidin *et al.*, 1992), as shown in Fig. 2. A common structural feature is that in sparse structures the extra transition-metal atoms tend to distribute evenly, rather than forming larger clusters. In the more transition-metal rich compounds, it is hard to discern any rules at all.

7. Superstructure types

The superstructures that have been featured above may conveniently be classified into successively more complex structural categories:

(*a*) Structures based purely on the ordered occupation of positions equivalent to 2(*d*) by extra transition-metal atoms and slight distortions of the basic lattice.

(*b*) Structures that also contain mixing of transition-metal and main-group metal atomic positions, *i.e.* transition-metal atoms in positions equivalent to 2(*c*) or main-group elements in positions equivalent to 2(*a*).

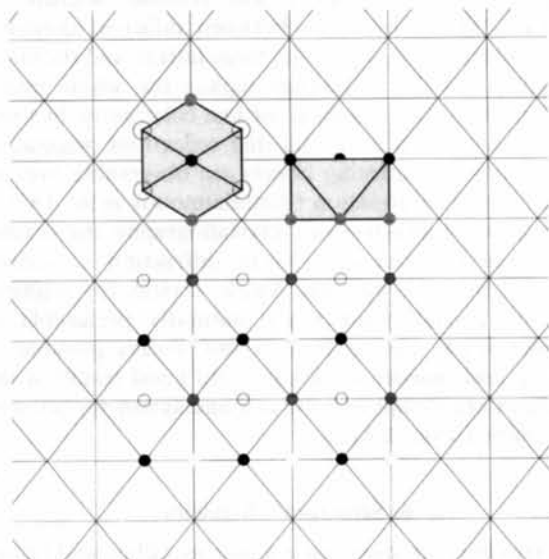


Fig. 2. Another view of the coordination polyhedra of transition-metal atoms. The projection axis is 110, a direction that normally shows no superstructure ordering. The symbols of the atoms at the polyhedral vertices are retained from Fig. 1. Below the coordination polyhedra the Wyckoff position 2(*d*) (centre of the Edshammar polyhedra) is shown. The colour code is: open circles at 0, light grey at $\frac{2}{6}$, dark grey at $\frac{3}{6}$, black at $\frac{5}{6}$ of the projection axis.

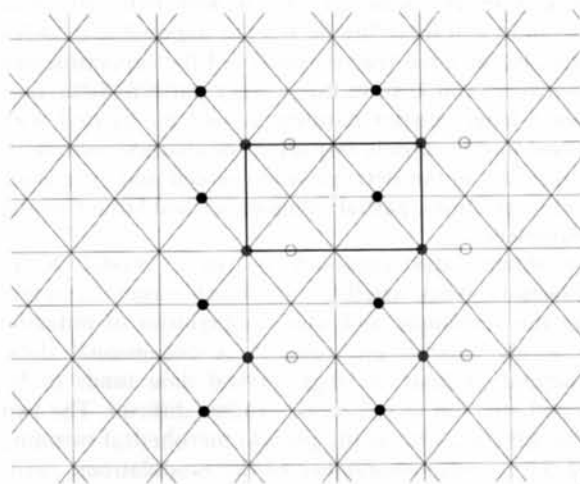
(*c*) Structures that also contain vacancies on positions equivalent to 2(*a*) or 2(*c*).

(*d*) Unknown structures.

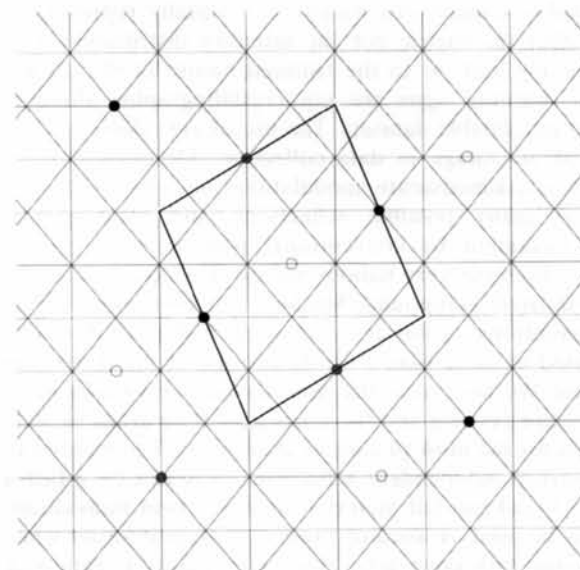
Table 3 summarizes the different structure types encountered so far. Examples of superstructure ordering are shown in Fig. 3.

8. Superstructure ordering in different systems

At moderate temperatures many transition-metal rich B8 systems exhibit simple commensurate superstructures, while at higher temperatures the ordering of



(*a*)



(*b*)

Fig. 3. Ordered arrangements of transition-metal atoms in position 2(*d*). Atoms at 2(*a*) and 2(*c*) positions have been omitted for clarity. Colour coding as in Fig. 2. (*a*) The structure of Co_3Sn_2 ; (*b*) the structure of Cu_6Sn_5 .

Table 3. The 32 known structure types of the pseudo-cubic B8 group

Structure type	Category	Reference
Co ₂ Si	A	Borén (1933)
CuAl	B	El-Boragy <i>et al.</i> (1972)
A-CuIn	A	Elding-Pontén (1997)
A'-CuIn	D	Elding-Pontén (1997)
C-CuIn	D	Elding-Pontén (1997)
Cu ₇ In ₃	C	Lidin <i>et al.</i> (1997)
Cu ₆ Sn ₅	A	Larsson <i>et al.</i> (1994)
η^6 -Cu ₅ Sn ₄	A	Larsson <i>et al.</i> (1995a)
η^8 -Cu ₅ Sn ₄	A	Larsson <i>et al.</i> (1995a)
Fe ₃ Ge ₂	C	Malaman <i>et al.</i> (1980)
Fe ₁₃ Ge ₈	A	Malaman <i>et al.</i> (1980)
GaGe ₂ Ni ₄	B	Bhargava & Schubert (1976)
MnBi	A	Göbel <i>et al.</i> (1976)
ζ^1 -Mn _{5,11} Ge ₂	B	Komura <i>et al.</i> (1987)
ζ^2 -Mn ₅ Ge ₂	B	Ohba <i>et al.</i> (1987)
MnP	A	Rundqvist (1962)
Mn ₈ Sn ₅	A	Elding-Pontén <i>et al.</i> (1997)
Mn ₁₂ Sn ₇	A	Elding-Pontén <i>et al.</i> (1997)
NiAs	A	Aminoff (1923)
Ni ₅ Ge ₃	A	Ellner <i>et al.</i> (1971)
Ni ₇ Ge ₄	A	Ellner <i>et al.</i> (1971)
Ni ₁₉ Ge ₁₂	A	Ellner <i>et al.</i> (1971)
Ni ₂ In	A	Laves & Wallbaum (1942)
Ni ₃ In ₂	A	Brand (1967)
Ni ₃ Sn ₂	A	Brand (1967)
Pd ₁₃ Pb ₉	B	Mayer <i>et al.</i> (1980)
Pd ₁₃ Tl ₉	B	Bhan <i>et al.</i> (1968)
Pt ₁₃ In ₉	B	Ellner <i>et al.</i> (1969)
Ti ₅ Ga ₄	B	Schubert <i>et al.</i> (1962)
α -Ti ₆ Sn ₅	B	van Fucht <i>et al.</i> (1964)
β -Ti ₆ Sn ₅	B	van Fucht <i>et al.</i> (1964)
ThTl	B	Palenzona <i>et al.</i> (1985)

the structures becomes progressively worse, passing through a temperature range with incommensurately modulated structures to a region where weak ordering rules as to the occupation of 2(*d*) positions give rise to structured diffuse scattering. The compilation below is fairly uncritical. The data should be treated with care and the comments about the reliability of structural methods above should be kept in mind. For easy reference, the phase information is summarized in Tables 4–8.

Out of the 77 B8-type systems in Table 1, a large number are reported to be non-stoichiometric or have substantial solid solution regions. The B8 phases with transition metals in group IIIB are reported as line phases and the lanthanide–indium systems display a very narrow solid solubility interval (Yatsenko *et al.*, 1983). In this group only Y₂Al is reported as deviating from the ideal B8-type structure. It has the Co₂Si-type structure (Dagerhamn, 1967)

The situation is much more complex with the transition metals in groups IV and VB. A few stoichiometric phases are reported, but also some ordered superstructures. These type structures are α -Sn₅Ti₆, β -Sn₅Ti₆

Table 4. Pseudo-cubic B8-related phases with group IVB and VB transition metals

Compound	Type	Reference
Ti ₅ P ₃	Ti ₅ Ga ₄	Bärnighausen <i>et al.</i> (1965)
Ti ₅ Sn ₆	α -Ti ₅ Sn ₆	van Fucht <i>et al.</i> (1964)
Ti ₆ Ge ₅	β -Ti ₅ Sn ₆	Hallais <i>et al.</i> (1968)
Ti ₅ Ga ₄	Ti ₅ Ga ₄	Schubert <i>et al.</i> (1962)
Ti ₅ Sn ₆	β -Ti ₅ Sn ₆	van Fucht <i>et al.</i> (1964)
Zr ₂ Al	Ni ₂ In	Wilson (1959)
Zr ₅ Al ₃	Ti ₅ Ga ₄	Schubert <i>et al.</i> (1962)
Zr ₅ Ga ₄	Ti ₅ Ga ₄	Schubert <i>et al.</i> (1962)
Zr ₅ Sn ₄	Ti ₅ Ga ₄	Schubert <i>et al.</i> (1962)
Zr ₅ Sb ₄	Ti ₅ Ga ₄	Garcia & Corbett (1988)
HfGa	ThTl	Markiv & Beljavina (1986)
Hf ₅ Sn ₄	Ti ₅ Ga ₄	Schubert <i>et al.</i> (1962)
V ₆ Si ₅	β -Ti ₆ Sn ₅	Hallais <i>et al.</i> (1967)
V ₆ Ga ₅	α -Ti ₆ Sn ₅	Schubert <i>et al.</i> (1963)
V ₃ Sb ₂	NiAs	Meissner & Schubert (1965)
V ₅ Sb ₇	NiAs	Bouwma <i>et al.</i> (1973)
Nb ₅ Ga ₄	Ti ₅ Ga ₄	Meissner & Schubert (1965)
Nb ₁₀ Ge ₇	Ti ₅ Ga ₄	Horyn & Kubiak (1971)
Nb ₄ Sn ₅	α -Ti ₆ Sn ₅	Ogren <i>et al.</i> (1965)
NbSb	NiAs	Myzenkova <i>et al.</i> (1966)
Ta ₆ Ga ₅	α -Ti ₆ Sn ₅	Popova & Putro (1979)

(van Fucht *et al.*, 1964), ThTl (Palenzona *et al.*, 1985) and Ga₄Ti₅ (Schubert *et al.*, 1962). These compounds exhibit typical B8 ordering, with some substitution; in α -Sn₅Ti₆ the 2(*d*) positions are filled to $\frac{3}{4}$, yielding an ideal composition of Sn₄Ti₇, but the composition is changed by the substitution of one 2(*a*) Ti site by Sn. The arrangement in the β -phase is similar, while in Ga₄Ti₅ and ThTl the substitution pattern is the same, but the ideal compositions, Ti₆Ga₃ and Th₂Tl, correspond to full occupancy of the 2(*d*) sites. The structure types of the various B8 compounds with groups IV and VB transition metals are given in Table 4. Reinvestigation of some of these phases by electron diffraction would be valuable. Hexagonal structures such as α -Sn₅Ti₆ and Ga₄Ti₅ are highly suspect and when they contain partial occupancies, as does Nb₁₀Ge₇, all alarm bells are ringing. The structure types Ge₅Ti₆, Ge₉Ho₁₀ and Mn₅Si₃ that all occur in these systems appear to be B8-unrelated.

With transition metals in groups VI and VIIIB and the Fe group, B8-type phases in the required *c/a* regime are reported only for first-row transition metals and Ru₂Si (Aronson & Åhselius, 1961). The antimonides are all slightly transition-metal rich, but no ordered arrangement of the extra atoms has been reported. Superstructures are reported for the systems Mn–Ge, Mn–Sn, Mn–Bi, Fe–Ge and Fe–Sn.

The complex B8 region of the Mn–Ge system has been elucidated by Ellner (1980), Komura *et al.* (1987) and Ohba *et al.* (1987). Three phases have been identified: χ -Mn₂Ge, ζ^1 -Mn_{5,11}Ge₂ and ζ^2 -Mn₅Ge₂. The two H phases occur as intergrowths, as proven by high-

Table 5. Pseudo-cubic B8-related phases with Cr, Mn and Fe

Compound	Type	Reference
CrSb	NiAs	Kjekshus & Walseth (1969)
χ -Mn ₂ Ge	Ni ₂ In	Ellner (1980)
ζ^1 -Mn _{5,11} Ge ₂	ζ^1 -Mn _{5,11} Ge ₂	Komura <i>et al.</i> (1987)
ζ^2 -Mn ₅ Ge ₂	ζ^2 -Mn ₅ Ge ₂	Ohba <i>et al.</i> (1987)
Mn ₃ Sn ₂	Ni ₃ Sn ₂	Elding-Pontén, Stenberg, Larsson <i>et al.</i> (1997)
Mn ₈ Sn ₅	Mn ₈ Sn ₅	Elding-Pontén, Stenberg, Lidin <i>et al.</i> (1997)
Mn ₁₂ Sn ₇	Mn ₁₂ Sn ₇	Elding-Pontén, Stenberg, Larsson <i>et al.</i> (1997)
MnSb	NiAs	Bouwma <i>et al.</i> (1973)
MnBi	MnBi	Göbel <i>et al.</i> (1976)
Fe ₂ Ge	Ni ₂ In	Kim & Kang (1989)
Fe ₃ Ge ₂	Fe ₃ Ge ₂	Malaman <i>et al.</i> (1980)
Fe ₃ Ge ₂	Pd ₁₃ Tl ₉	Panday & Schubert (1969)
Fe ₅ Ge ₃	Ni ₂ In	Kanematsu <i>et al.</i> (1963)
Fe ₁₃ Ge ₈	Fe ₁₃ Ge ₈	Malaman <i>et al.</i> (1980)
Fe ₂ Sn	Ni ₂ In	Djega-Mariadassou <i>et al.</i> (1970)
Fe ₅ Sn ₃	Ni ₂ In	Djega-Mariadassou <i>et al.</i> (1970)
Ru ₂ Si	Co ₂ Si	Aronson & Åhselius (1961)

Table 6. Pseudo-cubic B8-related phases with the Co group

Compound	Type	Reference
Co ₂ Si	Co ₂ Si	Borén (1933)
Co ₃ Ge ₂	Ni ₂ In	Ellner (1976)
Co ₅ Ge ₃	Ni ₂ In	Agalakova <i>et al.</i> (1973)
Co ₂ Ge	Ni ₂ In	Laves & Wallbaum (1942)
Co ₅ Ge ₂	Ni ₂ In	Daycr & Feschotte (1980)
Co ₃ Sn ₂	Ni ₃ Sn ₂	Jain <i>et al.</i> (1972)
Rh ₃ Si ₂	Ni ₂ In	Bhan & Schubert (1960)
Rh ₂ Si	Co ₂ Si	Engström (1963)
Rh ₂ Ge	Co ₂ Si	Geller (1955)
Ir ₂ Si	Co ₂ Si	Bhan & Schubert (1960)
Ir ₃ Si ₂	Ni ₂ In	Bhan & Schubert (1960)
IrSn	NiAs	Nowotny <i>et al.</i> (1946)
IrSb	NiAs	Kuz'min (1958)
IrPb	NiAs	Pfisterer & Schubert (1950)

resolution electron microscopy (Kifune & Komura, 1986), further complicating the structural elucidation. The ζ_1 phase corresponds to a very long period superstructure of B8 and it may be advantageous to describe it as a modulated structure.

The Mn–Sn system has been elucidated by Elding-Pontén, Stenberg, Larsson *et al.* (1997) and Elding-Pontén, Stenberg, Lidin *et al.* (1997). Three distinct phases have been identified by electron diffraction: Mn₃Sn₂, Mn₈Sn₅ and Mn₁₂Sn₇. The first is a regular superstructure, while the latter two are better described as incommensurate modulations of the basic lattice. All three superstructures are caused by the ordered occupation of the 2(*d*) sites in the basic B8 lattice.

MnBi has been reported to crystallize in an orthorhombic arrangement. Only X-ray powder data are available and in the two studies found (Göbel *et al.*, 1976; Andresen *et al.*, 1972) all atomic positions are partially occupied, some to more than 100%!

The Fe–Ge system contains a complex B8 region; Fe₂Ge is reported as simple Ni₂In by Kim & Kang (1989), Fe₃Ge₂ has been reported as a badly disordered type structure of its own (Malaman *et al.*, 1980) and as the Pd₁₃Tl₉ structure (Panday & Schubert, 1969), Fe₅Ge₃ has been ascribed a simple Ni₂In-type structure, either by disordered partial occupancy of the 2(*d*) position (Kanematsu *et al.*, 1963) or by total disordering of all constituent atoms (Castelliz, 1953; Bara *et al.*, 1981); Fe₁₃Ge₈ is a structure type of its own (Malaman *et al.*, 1980). Interestingly, Fe₆Ge₅ is not a B8-type arrangement (Malaman *et al.*, 1974). There is clearly a

highly interesting region in the Fe–Ge phase diagram from ~55 to 67% Fe that would be very much worthwhile studying by electron diffraction.

Fe–Sn is in many ways similar to Fe–Ge: Fe₂Sn is a pure Ni₂In structure, Fe₅Sn₃ is a defect Ni₂In structure without superstructure ordering (Djega-Mariadassou *et al.*, 1970), while the phase Fe₃Sn₂ has a structure type of its own, related to CoSn rather than B8 (Malaman *et al.*, 1976). The B8 region in the Fe–Sn phase diagram is a rather small region between 1053 and 1183 K and between 33 and 38% Sn. The phases reported are summarized in Table 5.

The largest number of pseudo-cubic B8-type intermetallics are found in the cobalt and nickel groups. The structural diversity is truly impressive and to a large extent still very imprecisely mapped.

Cobalt forms B8-type structures with Si, Ge, Sn, Sb and Te. Co₂Si is the type structure for an orthorhombically distorted Ni₂In (Borén, 1933). In the Co–Ge system the following compositions are reported to have a simple NiAs–Ni₂In-type structure: Co₅Ge₂ (Ellner, 1976), Co₅Ge₃ (Agalakova *et al.*, 1973), Co₂Ge (Laves & Wallbaum, 1942) and Co₅Ge₂ (Dayer & Feschotte, 1980). It is clear that the stability region is fairly large and substantial superstructure ordering should be expected, particularly at the more Co-rich end. Schubert & Pfisterer (1950) report superstructure lines in powder patterns from samples annealed at low temperature.

In the Co–Sn system the stability region is rather narrow. Samples annealed at high temperatures show extensive structured diffuse scattering (Larsson *et al.*, 1996). At lower temperatures Co₅Sn₂ has the orthorhombic Ni₃Sn₂-type structure (Jain *et al.*, 1972; Larsson *et al.*, 1995a). In this phase the pseudo-merohedral sandwich twinning yields such highly coherent systems that scattering between individual domains give contributions that are measurable even in X-ray powder investigations (Panteleimonov *et al.*, 1971).

Table 7. Pseudo-cubic B8-related phases with the Ni group

Compound	Type	Reference
Ni ₁₃ Ga ₉	Pt ₁₃ In ₉	Ellner <i>et al.</i> (1969)
Ni ₂ In	Ni ₂ In	Laves & Wallbaum (1942)
Ni ₃ In ₂	Ni ₃ In ₂	Brand (1967)
Ni ₁₃ In ₇	Ni ₂ In	Ellner (1976)
Ni ₁₃ In ₉	Pt ₁₃ In ₉	Ellner <i>et al.</i> (1969)
Ni ₂ Si	Ni ₂ In	Toman (1952)
Ni ₂ Si	Co ₂ Si	Ellner <i>et al.</i> (1979)
Ni ₂ Ge	Co ₂ Si	Laves & Wallbaum (1942)
Ni ₂ Ge	Ni ₂ In	Lecocq (1963)
Ni ₅ Ge ₃	Ni ₅ Ge ₃	Ellner <i>et al.</i> (1971)
Ni ₇ Ge ₄	Ni ₇ Ge ₄	Ellner <i>et al.</i> (1971)
Ni ₁₉ Ge ₁₂	Ni ₁₉ Ge ₁₂	Ellner <i>et al.</i> (1971)
Ni ₃ Sn ₂	Ni ₃ Sn ₂	Brand (1967)
Ni ₃ Sn ₂	Ni ₂ In	Lihl & Kirnbauer (1955)
NiPb	NiAs	Ricci Bitti <i>et al.</i> (1968)
NiAs	NiAs	Aminoff (1923)
NiSb	NiAs	Kjekshus & Walseth (1969)
NiBi	NiAs	Hägg & Funcke (1929)
Pd ₂ Al	Co ₂ Ni	Schubert <i>et al.</i> (1957)
Pd ₂ In	Co ₂ Ni	Schubert <i>et al.</i> (1957)
Pd ₂ Sn	Co ₂ Ni	Schubert <i>et al.</i> (1957)
Pd ₁₃ Tl ₉	Pd ₁₃ Tl ₉	Bhan <i>et al.</i> (1968)
Pd ₃ Sn ₂	Ni ₂ In	Nowotny <i>et al.</i> (1946)
Pd ₃ Pb ₂	Ni ₂ In	Nowotny <i>et al.</i> (1946)
Pd ₂₀ Sn ₁₃	GaGe ₂ Ni ₄	Sarah <i>et al.</i> (1981)
Pd ₅ Pb ₃	Ni ₅ Ge ₃	Ellner <i>et al.</i> (1973)
Pd ₁₃ Pb ₉	Pd ₁₃ Pb ₉	Mayer <i>et al.</i> (1980)
PdSb	NiAs	Kjekshus & Walseth (1969)
Pd ₅ Bi ₃	Ni ₂ In	Zhuravlev (1958)
Pt ₂ Al	Co ₂ Si	Chattopadhyay & Schubert (1975)
PtIn	CuAl	Heinrich & Schubert (1978)
Pt ₃ In ₂	Ni ₂ In	Jain & Bhan (1972)
Pt ₁₃ In ₉	Pt ₁₃ In ₉	Ellner <i>et al.</i> (1969)
PtSn	NiAs	Harris <i>et al.</i> (1968)
PtPb	NiAs	Nowotny <i>et al.</i> (1946)
PtSb ₉	NiAs	Thomassen (1929)

The large stability region of CoSb (43–49% Sb at room temperature) has not been shown to support any superstructure ordering, but for the Co–Te system there is a continuous change from the NiAs- to the CdI₂-type structure (de Meester *et al.*, 1971). This is a transition-metal poor system and outside the scope of this survey. The *c/a* ratio is also just inside the limits stated above.

For rhodium and iridium the data are not as complete as that for Co, but there are still six B8 systems known for Rh and four for Ir. With rhodium there is Rh–Si, Rh–Ge, Rh–Sn, Rh–Pb, Rh–Bi and Rh–Te, and for Ir, Ir–Sn, Ir–Pb, Ir–Sb and Ir–Te. RhSi can be crystallized in the MnP-type structure, while the composition Rh₃Si₂ yields the Ni₂In type (Bhan & Schubert, 1960) and Rh₂Si takes the Co₂Si type (Engström, 1963). This behaviour is mimicked by Rh–Ge; RhGe is MnP, while Rh₂Ge is Co₂Si (Geller, 1955). For the Co₂Si types the value corresponding to hexagonal *c/a* is around 1.35, while the value for the MnP types is around 1.5.

Table 8. Pseudo-cubic B8-type structures with noble metals

Compound	Type	Reference
CuAl	CuAl	El-Boragy <i>et al.</i> (1972)
Cu ₃ Al ₂	Ni ₂ In	El-Boragy <i>et al.</i> (1972)
Cu ₇ In ₃	Cu ₇ In ₃	Koster <i>et al.</i> (1980)
A-CuIn	A-CuIn	Elding-Pontén (1997)
B-CuIn	B-CuIn	Elding-Pontén (1997)
C-CuIn	C-CuIn	Elding-Pontén (1997)
Cu ₁₁ In ₉	CuAl	Rajasekharan & Schubert (1981)
Cu ₆ Sn ₅	Cu ₆ Sn ₅	Larsson <i>et al.</i> (1994)
η ⁶ -Cu ₅ Sn ₄	η ⁶ -Cu ₅ Sn ₄	Larsson <i>et al.</i> (1995a)
η ⁸ -Cu ₅ Sn ₄	η ⁸ -Cu ₅ Sn ₄	Larsson <i>et al.</i> (1995a)
Ag ₇ In ₃	Cu ₇ In ₃	Campbell <i>et al.</i> (1970)
Ag ₇ Ga ₃	Cu ₇ In ₃	Hoff <i>et al.</i> (1964)
AuSn	NiAs	Jan <i>et al.</i> (1963)
AuSe	NiAs	Srivastava & Srivastava (1972)

Iridium forms Ir₂Si with the Co₂Si structure and Ir₃Si₂ with the Ni₂In structure (Bhan & Schubert, 1960). IrSn (Nowotny *et al.*, 1946), IrSb (Kuz'min, 1958) and IrPb (Pfisterer & Schubert, 1950) are simple NiAs, while IrTe (NiAs type) and IrTe₂ (CdI₂ type) form with approximately the same cell parameters. These tellurides are outside the scope of the present paper. Table 6 gives an overview of the phases in the Co group.

Ni is the element that forms the largest number of B8 structures of all transition metals. With Ga, nickel forms Ni₁₃Ga₉ crystallizing in the Pt₁₃In₉ structure type (Ellner *et al.*, 1969). Ni–In is a phase rich system, where the type structure Ni₂In has some phase width; Ni₂In (Laves & Wallbaum, 1942) and Ni₁₃In₇ (Ellner, 1976) are both ascribed this structure. Ni₃In₂ (Brand, 1967) has an unknown structure and Ni₁₃In₉ is isostructural with Pt₁₃In₉ (Ellner *et al.*, 1969). Ni₂Si has a low-temperature modification in the Co₂Si form (Ellner *et al.*, 1979), while at elevated temperatures the structure is Ni₂In (Toman, 1952). In the original paper this is given in an unusual space group, but the atomic positions are identical to Ni₂In. Ni–Ge is again a complex system. A very large number of phases are reported: Ni₂Ge with the Co₂Si-type structure (Laves & Wallbaum, 1942), Ni₂Ge with the Ni₂In-type structure (Lecocq, 1963) and Ni₅Ge₃, Ni₇Ge₄ and Ni₁₉Ge₁₂ all with their own type structures (Ellner *et al.*, 1971). A recent electron diffraction study (Larsson & Withers, 1998) confirms the existence of Ni₅Ge₃ and Ni₁₉Ge₁₂. The latter phase has a rather wide existence range. Ni₇Ge₄ seems to consist of two separate phases. The stable Ni–Sn phase is Ni₃Sn₂ with a disordered Ni₂In high-temperature modification (Lihl & Kirnbauer, 1955) and the low-temperature type structure Ni₃Sn₂ (Brand, 1967). NiPb has only been made by simultaneous evaporation of the constituent elements. It has the NiAs structure (Ricci Bitti *et al.*, 1968). The pnictides, NiAs (Aminoff, 1923), NiSb (Kjekshus & Walseth,

1969) and NiBi (Hägg & Funcke, 1929) are all reported as transition-metal rich, with the NiAs-type structure. NiTe–NiTe₂ are a NiAs–CdI₂ pair outside the scope of the study.

The structure of Ni₂Al₃ is interesting. The atomic positions are close to those of a B8 phase, the difference being slight shifts along the *c* axis, but a more important difference, which is also reflected in the composition, is the ordering of the different atoms. Ni₂Al₃ is really a hexagonal defect CsCl structure (Ellner *et al.*, 1982) and should not be treated as B8 related. It occurs mainly for aluminides, gallides and indides (Villars & Calvert, 1991).

Pd forms the Co₂Ni-type structure with Al, In and Sn (Schubert *et al.*, 1957). With Tl the type structure Pd₁₃Tl₉ is formed (Bhan *et al.*, 1968). The Sn and Pb systems with Pd are fairly complex; Pd₅Sn₂ and Pd₃Pb₂ have the Ni₂In-type structure (Nowotny *et al.*, 1946), Pd₂₀Sn₁₃ has the GaGe₂Ni₄-type structure (Sarah *et al.*, 1981), Pd₅Pb₃ has the Ni₅Ge₃-type structure (Ellner *et al.*, 1973) and Pd₁₃Pb₉ is a type structure (Mayer *et al.*, 1980). The antimonide is a transition-metal rich NiAs (Kjekshus & Walseth, 1969), while the bismuthide is Pd₅Bi₃ in the Ni₂In-type structure (Zhuravlev, 1958). The tellurides are NiAs–CdI₂ systems not covered in this work.

Platinum greatly resembles palladium in its B8 phases. Pt₂Al is Co₂Si (Chattopadhyay & Schubert, 1975). InPt has the CuAl-type structure, Ni₂In with ordered vacancies and a mixed position (Heinrich & Schubert, 1978). Pt₃In₂ is Ni₂In at elevated temperatures (Jain & Bhan, 1972) and Pt₁₃In₉ is a type structure (Ellner *et al.*, 1969). The stannide (Harris *et al.*, 1968), plumbide (Nowotny *et al.*, 1946) and antimonide (Thomassen, 1929) are all simple transition-metal rich NiAs structures, while the bismuthide (Zhuravlev & Stepanovic, 1962; Schubert *et al.*, 1968) and telluride (Bhan *et al.*, 1969) are transition-metal poor NiAs–CdI₂ systems. The structure types Pt₅Ga₃ and Pt₃Tl₂ occurring in the system are not closely related to the B8 family. Table 7 summarizes the B8-type nickel group compounds.

The noble metals are less rich in their B8-type structural chemistry than are the transition metals in the preceding groups. Cu forms such compounds with the metals in the Al group, and Sn. CuAl is a B8-related type structure and Cu₃Al₂ is a Ni₂In-type structure with vacancies (El-Boragy *et al.*, 1972). The Cu–In system is exceedingly complex. The richest transition-metal compound is the triclinic Cu₇In₃ (Koster *et al.*, 1980; Lidin *et al.*, 1997), in the intermediate range there are several incommensurately modulated phases, *A*-, *B*- and *C*-CuIn (Elding-Pontén, 1997), and the poorest transition-metal compound is Cu₁₁In₉ with the CuAl structure (Rajasekharan & Schubert, 1981). The Cu–Sn system is also rich, with at least three B8-type phases identified, Cu₆Sn₅ (Larsson *et al.*, 1994), η^6 -Cu₅Sn₄ and

η^8 -Cu₅Sn₄ (Larsson *et al.*, 1995a). For silver, no B8 phases are reported, but the compounds Ag₇In₃ (Campbell *et al.*, 1970) and Ag₇Ga₃ (Hoff *et al.*, 1964) are suspected to be isostructural with Cu₇In₃. Gold forms AuSn (Jan *et al.*, 1963) and AuSe (Srivastava & Srivastava, 1972), both simple NiAs-type structures. The noble metal systems are collected in Table 8.

9. Less well ordered systems

Most of the pseudo-cubic B8 systems reported in the earlier literature are described either as well ordered or completely disordered with respect to the 2(*d*) site. In some recent studies it has been found that ordering often occurs at an intermediate level, either as incommensurate modulations or as weak ordering rules leading to more or less structured diffuse scattering. The modulations of the high-temperature phases η^8 -Cu₅Sn₄ and η^6 -Cu₅Sn₄ are clearly of an incommensurate nature (Larsson *et al.*, 1995a) and at higher temperatures structured diffuse scattering has been observed. The Mn–Sn system contains two distinct incommensurately modulated phases (Elding-Pontén, Stenberg, Larsson *et al.*, 1997; Elding-Pontén, Larsson, Lidin *et al.*, 1997) and the Cu–In system at least three (Elding-Pontén, 1997), in addition to structured diffuse scattering. NiAs itself displays modulations as well as diffuse scattering and has been studied extensively (Vincent & Withers, 1987; Withers *et al.*, 1988; Hua *et al.*, 1988; Thompson *et al.*, 1988; Withers *et al.*, 1989). The spectacular diffuse scattering of high-temperature annealed Co–Sn has been studied by Larsson *et al.* (1996) and the modulations (commensurate and incommensurate) of Ni–Ge have been studied together with diffuse scattering by Larsson & Withers (1998). The late date of the discoveries is irrelevant to the scarcity of occurrence of such phenomena. Rather, it is related to a heightened interest in, and new and improved methods for the detection of, diffuse scattering and incommensurate modulations. It is expected that hosts of new systems will be shown to exhibit similar behaviour, particularly after annealing at elevated temperatures.

10. Future directions

Some general trends are discernable in the development of our understanding of the intermetallic B8 phases. First of all, we need new and improved structural data for these systems in order to have a solid experimental background for the development of a theory that helps us understand the complexity of these systems. As this survey shows, much of the data on these systems stem from old investigations without the aid of modern techniques. One question is if the ideal NiAs structure exists at all for intermetallics; so far any system scrutinized by electron diffraction seems to show

ordering on a larger scale after proper annealing. The development of more efficient methods for the measurement of X-ray intensities of large datasets will be a great help in this work. Another important development will be that of electron crystallographic methods. Electron crystallography, while inherently less precise than X-ray methods, will be increasingly important for systems that show a high propensity for twinning and nano-scale intergrowth.

Structural solution and refinement methods for incommensurately modulated structures are already well established, but their use will increase further in this particular field and it must be followed by a development of more straightforward methods for the modelling and interpretation of structured diffuse scattering. Only full knowledge of the local ordering and the localized interatomic interactions will give us a satisfactory picture of what stabilizes the many different phases in pseudo-cubic B8 intermetallics.

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