

# Systematics and bonding of nickel arsenide phases

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The incidence of nickel arsenide phases in the Periodic Table is considered and illustrated by several graphical and tabular methods. Duplex synoptic diagrams have proved particularly useful, and from these it is deduced that the phases are normal valency compounds with a contribution to the structure from the transition metal component of two to three electrons. The question of the relative proportions of ionic and covalent bonding is briefly discussed.

## 1. Introduction

The incidence of binary nickel arsenide phases and its relation to the bond arrangements in the crystal was discussed by Raynor in 1958 [1]. Some years later [2] Kubaschewski and Nowotny noted that little further thermochemical work had been carried out on this class of compound. More recently, the present author has elaborated [3, 4] the method of plotting alloy trends in synoptic diagrams [5], and this allows us to formulate a semiquantitative statement of bonding in this compound. We first present a brief summary of the incidence of these phases.

## 2. The incidence of NiAs phases in the Periodic Table

We can derive a general impression of this by taking one of the published lists, such as that of Hume-Rothery *et al.* [6], and plotting the frequency of the metal (including IB and IIB elements where appropriate) and B elements, respectively (Fig. 1). From this it is clear that the metallic (or A) component is a member of the block of elements to the left of the composite divide [8]. In the well known group of brass-like or Hume-Rothery phases, such metals form beta or gamma structures with elements immediately to the right of that divide such as zinc or aluminium. However, in the NiAs type, the B component comes from further to the right in the long Periodic Table, and often the A component is of low A Group number. If we plot the same information [6] in the form of a Goldschmidt diagram (lines drawn between

components; not illustrated), these aspects become clarified. It is found that a lever rule operates insofar as the higher the Group number of the B element, the further to the left in the transition series is the element with which it forms compounds. Also, a tendency exists for a partner to come from within the same Period. These two findings suggest that a necessary condition for formation of a NiAs phase is a similar scaling ratio of sizes of A to B atoms.

The incidence of these phases may also be described in terms of a drum version of the Periodic Table. Suppose that a copy of the long Table be bent into the form of a cylinder so that the noble gases, normally to the left and right, coincide. In plan (Fig. 2) we then have arcs  $A_1$ ,  $A_2$ ,  $B_1$  and  $B_2$ , representing early and late A elements, early and late B elements, separated by four divides, of which the join *i* represents the ionic divide, *cv* the covalent, *cp* the composite, and *tm* the transition metal divide. The NiAs structure allows ready adaptability to a variety of (alloy) conditions by change of axial ratio and composition [1]. Nickel arsenide compounds in decreasing order of axial ratio are classed  $A_1B_2$ , followed by  $A_2B_2$ , and lastly  $A_2B_1$ ; category  $A_1B_1$  is not represented.

## 3. The use of synoptic diagrams

This type of diagram has already been described [3], and the duplex variant used here in Fig. 3 has a row of elements, such as titanium to the halogen, marked on a central ordinate, whilst the left- and right-hand sides or ordinates represent

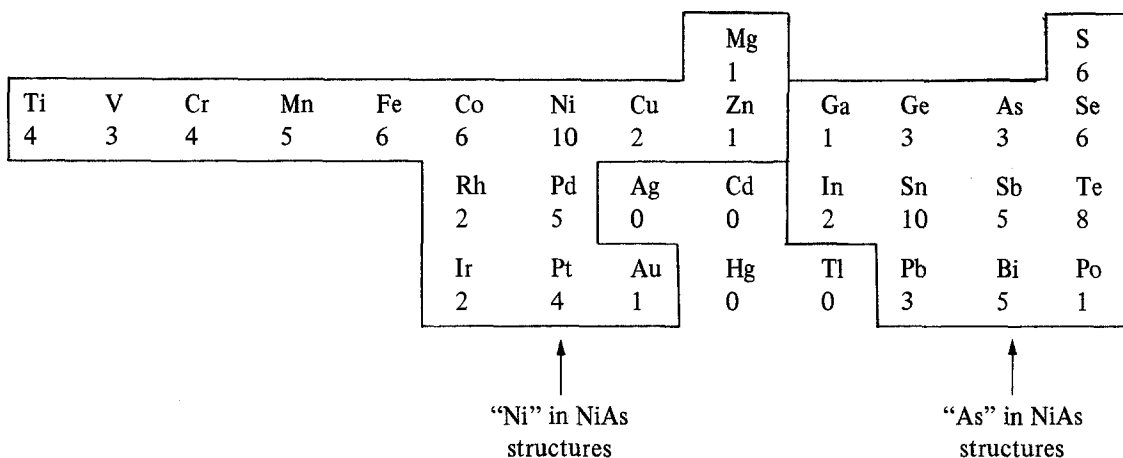


Figure 1 Frequency of occurrence of components of NiAs phases (see also Schubert [7]).

only one element each (e.g. copper). Points or lines of appropriate length on the tie lines in such diagrams represent the compositions of known compounds. Many such duplex diagrams have been plotted in this investigation, and details of the number of certain key types of phase occurring in each of a series of diagrams are given in Table I. The first column shows the characteristic pair of elements used on the outer ordinates of each duplex diagram, the second, third and fourth summarize the incidence of the beta-brass, gamma-brass and NiAs structures, respectively. The nature of a duplex diagram is such that each line in Table I represents a sampling from up to 13 binary systems. Each characteristic pair of elements has been chosen to be symmetrical across the composite divide. However, many of the pairs are "mixed"; for example, with Cd–Cu the B element is from the Second Long Period, the copper from the First. Three other diagrams were plotted, namely the Pb–Rh, Pb–Ir and Bi–Fe, which are

not abstracted in Table I. In these a total of five NiAs phases were noted, and no beta or gamma.

Of the data from Table I, the most valuable, selected for further discussion, are the first four, and the information relating to intermetallic phases in these systems is represented in more detail in the synoptic diagrams Figs. 3a to d inclusive. We begin by considering Fig. 3a, the Cd–Cu synoptic. Here there is a well-defined S or double-hyperbola curve for gamma-brass structures, as would be expected for elements adjacent to the composite divide [3, 8]. It is positioned such that it makes an intercept at the central ordinate of AGN 1.6 ( $\phi$ ; cf. normal valency phases, below). The presence of beta structures

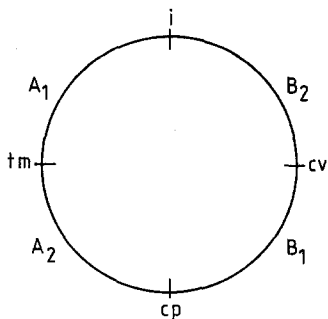
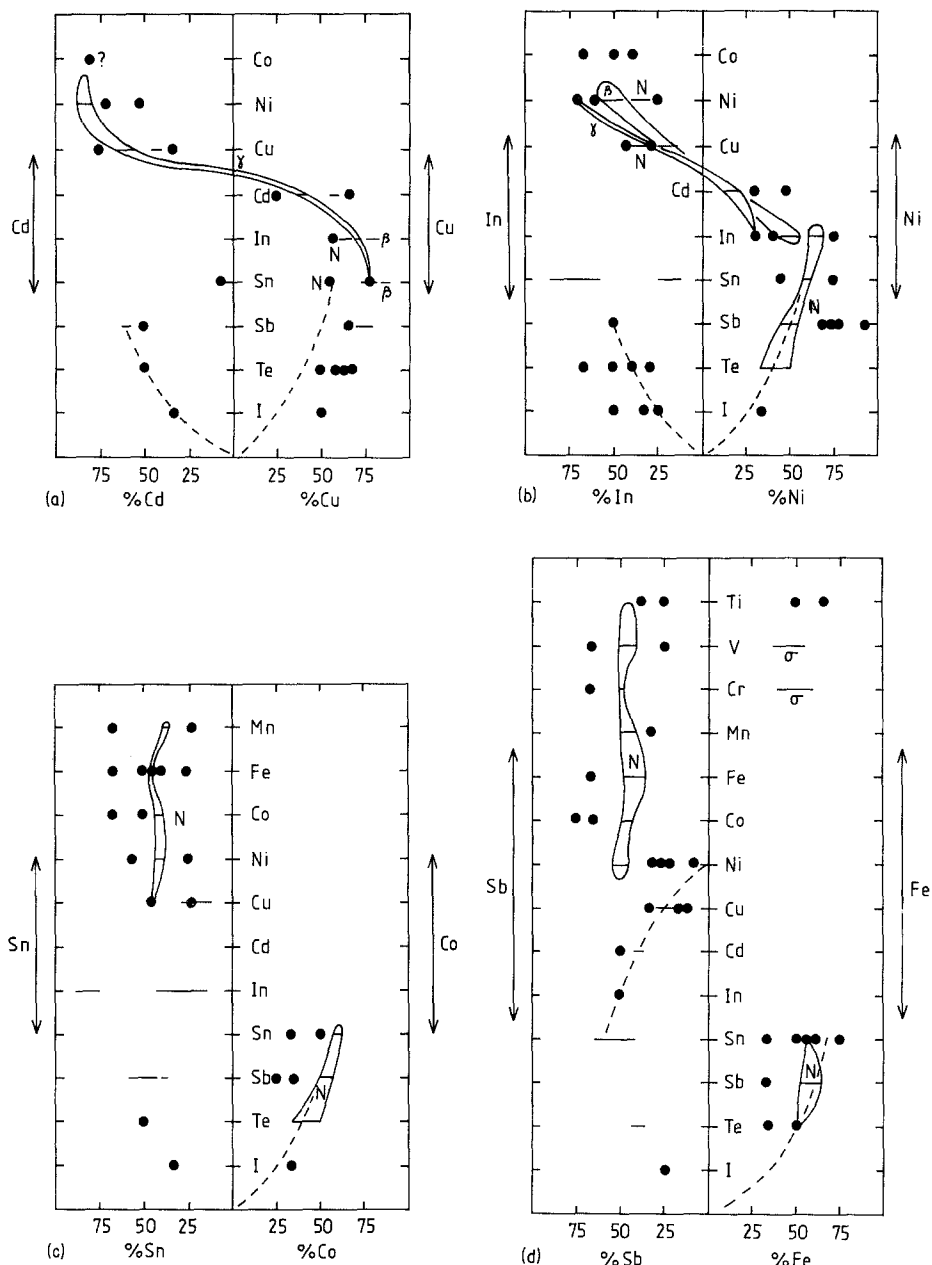


Figure 2 Drum version of the Periodic Table (Long Periods), in plan.

TABLE I Frequency of occurrence of structures in certain groups of binary systems

Characteristic pair of elements in synoptic diagram	No. of binary systems containing the following structures		
	beta	gamma	NiAs
Cd–Cu	2	4	2
In–Ni	2	3	5
Sn–Co	1	1	8
Sb–Fe	0	0	9
Te–Mn	0	1	9
Zn–Cu	5	7	0
Ga–Ni	4	3	2
Ge–Co	1	2	6
As–Fe	0	0	9
Se–Mn	1	1	8
S–Mn	0	1	7
Cd–Ag	3	3	0
In–Pd	4	3	3
Sn–Rh	1	1	3



**Figure 3** Duplex synoptic diagrams for four groups of binary systems. Each binary system is considered as a tie line in one of these diagrams, and the intermetallic compounds are indicated either by points (filled circles) or, if of some variability in stoichiometry, by lines (sections of tie lines). For example, in the Cd–Ni system (Fig. 3a top left) there are three compounds at approx 50, 30 and 19 at %, respectively. The latter is of variable stoichiometry and is a gamma brass structure. A closed area connecting the composition limits for gamma brass structures has been marked in (a) and (b); similarly treated are beta brass structures in (b) and NiAs structures in (b), (c) and (d) (marked “N”). The dashed lines are hyperbolae of normal valency type; the assumed valency for the transition element lower right in (a), (b), (c) and (d) are 3, 3, 3 and 2, respectively. All compositions are in at %. The sources of information are Hansen and Anderko, and Supplements [12]. In this paper, “beta” and “gamma” refer solely to the respective types of electron compound. In (b), the way in which the beta region somewhat overlies the gamma zone appears to be a characteristic of the Ga–Ni and In–Ni systems. Also in (b) we note a hyperbola of normal valency type lower left counting the normal valencies of In and the other B Group elements. In (d) a similar type of hyperbola can be drawn counting Ni zero to Sn 4, where Sb is forming compounds across the covalent divide with the early B Group elements. CdI<sub>2</sub> and filled NiAs structures are included as NiAs type. MnP structures occur in place of NiAs when the non-metal component is phosphorus or arsenic, and these are included with the NiAs in Table I.

is minimal, being confined to the In–Cu and Sn–Cu systems, and this is also true of the incidence of NiAs structures. In Fig. 3b (based on In–Ni) the gamma curve – the gamma importance – has diminished, though curiously there is a strong beta presence. More relevant to the present purpose is the fact that there are four Ni–B–Group systems where NiAs phases occur, and their compositions fall on a normal valency hyperbola which can be drawn counting Ni 3, Sn 4 to Xe zero. In Fig. 3c the presence of beta and gamma phases is confined to the Cu–Sn system, there are three NiAs phases noted in the lower right-hand portion of the diagram, and another feature has appeared in strength in the top left-hand region. There we note the NiAs structures formed between tin and several transition elements, and observe that they occur to a first approximation along a line of constant content of tin. In Fig. 3d there is no beta or gamma, there are three NiAs phases lower right, however, which better fall on a hyperbola of transition metal valency 2 (cf. Figs. 3b and c), and the NiAs phases marked in top left occur with Ti to Ni inclusive at a B Group content which is somewhat more than with tin as a component. The Te–Mn synoptic diagram (not illustrated) is similar to Fig. 3d and calls for no further comment except that the content of Te in Te–3d NiAs compounds is a little greater than Sb in the Sb–3d series.

The changes in B element content of NiAs phases with Group Number of B element are well known, but what is particularly valuable about the illustrative process in Fig. 3 is the way it brings out the contrast between the constant A/B ratio where the B element is held constant, with the normal valency hyperbolae where the transition element is constant. These relations clearly indicate NiAs phases to be normal valency compounds, in conformity with Hume-Rothery's classification [10] and furthermore they give us an estimate of the number of electrons involved in the bonding. Using an assumption of normal valency on the B element, the behaviour displayed in Fig. 3 may be accounted for by assuming the participation of 2 to 3 electrons from the transition element. This is gratifying since this number generally corresponds with a typical chemical valency of the transition element, as shown in Table II. It is true that trivalency is unusual in copper compounds, but this very fact is consistent with the poor representation of that metal in NiAs phases.

TABLE II Valencies of transition metals in NiAs phases as deduced from the positions of hyperbolae in Fig. 3

Mn	Fe	Co	Ni	Cu	Rh	Pd
2 or 3	2, 3	2, 3	3	3	2?, 3	2, 3

#### 4. Further observations on the bonding

Let us now pose the question as to whether, regarding A–B interactions, one can more accurately speak of an ionic or covalent configuration, since the presence of normal valency hyperbolae in themselves do not decide this for us unequivocally. Reading Raynor's paper, the author felt that the description metallic-ionic was to be inferred (see also [9]); in contrast, Kubaschewski and Nowotny clearly thought that metallic-covalent was more accurate. In order to consider this question we will have recourse to other arguments as follows. Firstly, let us consider, simply because it allows us an uncomplicated basis for comparison, the simplified duplex synoptic diagram for inter-Second Short Period compounds (Fig. 4). It is well known that the compounds near the noble gas ends of the diagram tend to be ionic whereas in mid-diagram we expect covalencies. Applied to Fig. 3, lower right portions, we conclude that compounds of Group VIB elements are

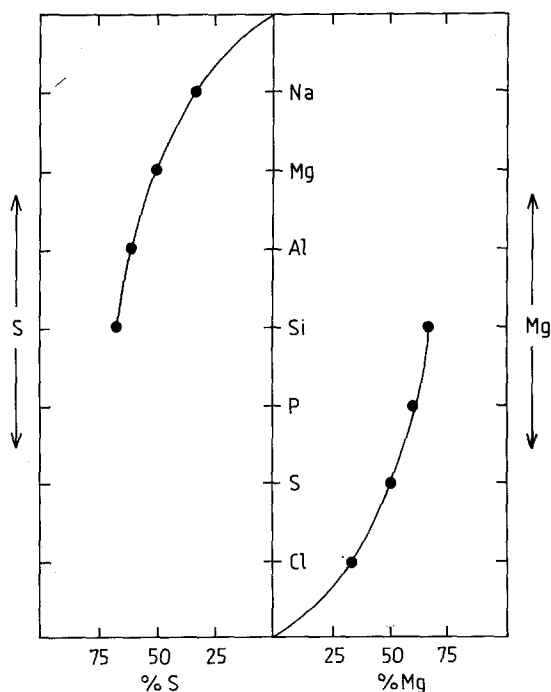


Figure 4 Duplex synoptic diagram for inter-Second Short Period compounds.

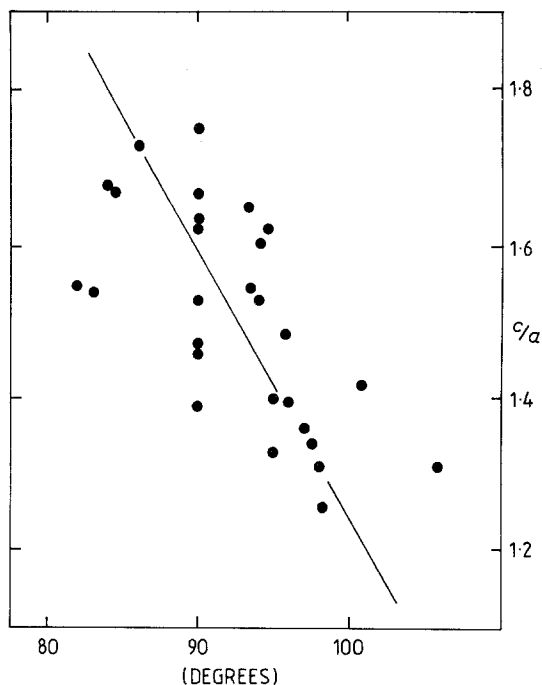


Figure 5 Axial ratio of NiAs compounds plotted against direction of Fajans' arrow. Arrow angles defined by reference to the usual presentation of the Long Periodic Table, for example  $\text{Cu} \leftarrow \text{Mg} = 45^\circ$ ,  $\text{Cu} \leftarrow \text{Zn} = 90^\circ$ .

most ionic, compounds of IIIB elements most covalent. Secondly, the author has proposed [8] that the strong ionic direction for bonding across the composite divide is represented by an arrow from "Al" to "Cu"; correspondingly, a weak direction is "Cd" to "Cu". On this basis we should expect FeS to be more ionic than NiSb. One may consider the force of this argument to be diminished insofar as the components in these latter examples are far from the composite divide, but in fact quite a good correlation is obtained (Fig. 5) if the angle of Fajans' arrow (the direction of a line joining the components on the Periodic Table) across the composite divide be plotted against the axial ratio.

A characteristic feature of NiAs compounds remains to be discussed, namely, their ranges of composition stability. Strongly ionic and strongly covalent compounds would be expected to be inflexible in their bonding arrangements, and therefore line compounds on phase diagrams are probably representative of such; conversely, structures bound at least in part by the mechanism of s-d resonance [11], would be expected to have some flexibility in this regard. However, it is not self-evident here that range of stoichiometry *per se* is a measure of inter-metal bonding,

since there is no clear variation of stoichiometry range with nature of the component elements (Fig. 3). It may be that the range of stoichiometry is particularly sensitive to the geometry of the normal and defect sites, in a manner which does not result in simple recognizable trends. On the other hand, if  $\text{CdI}_2$ -type structures in Figs. 3b and c be not included with the NiAs, we would then systematically have range decreases on going from a Group VB to a VIB component; this seems more in keeping with the presence of an element such as tellurium which unalloyed will have chains of atoms. Also there is no mistaking the increase in stoichiometry range in the series of compounds of manganese with B-Group elements from the Second Short, First Long and Second Long Periods, respectively, in that order, as would be expected from an application of Fajans' rule across the ionic divide, and with the premise that the decrease in ionic character will favour resonance between the metal atoms.

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