

## On Phase Transitions between the MnP and NiAs Type Structures

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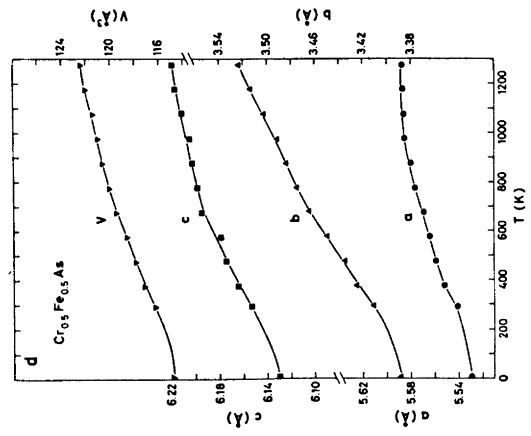
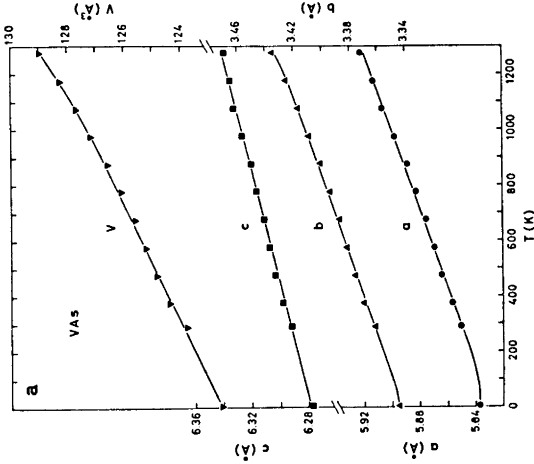
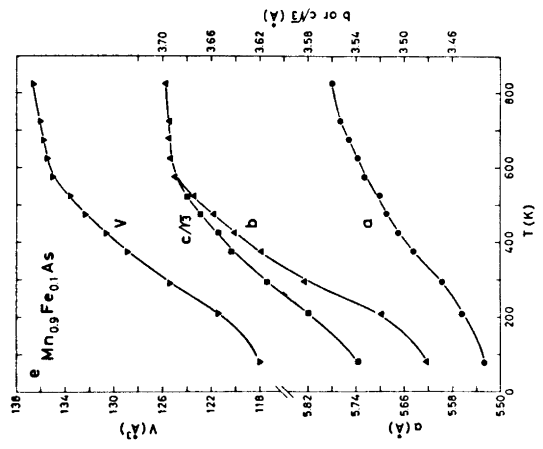
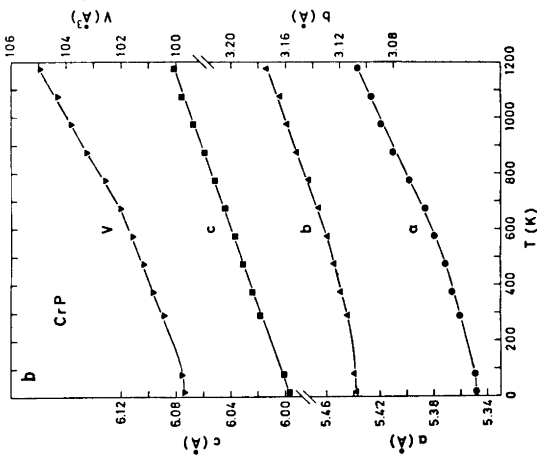
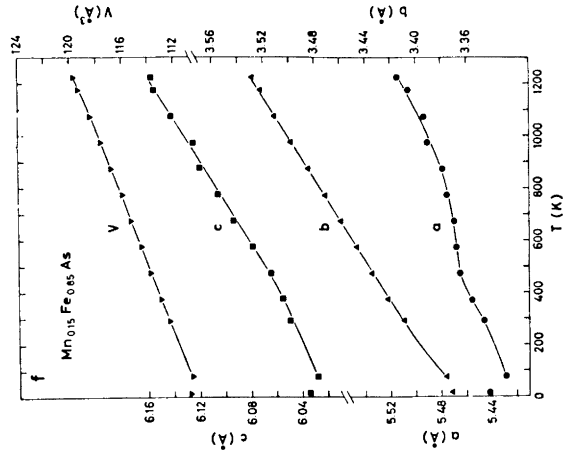
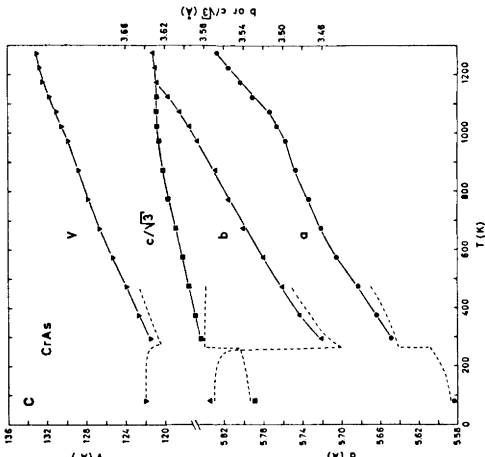
High and low temperature X-ray diffraction studies of TiAs, TiSb, VP, VAs, CrP, CrAs,  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$ ,  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ ,  $\text{Mn}_{0.15}\text{Fe}_{0.85}\text{As}$ , CoP, CoAs, NiAs, and RhSb show that continuous phase transitions between the MnP and NiAs type structures take place in CrAs ( $1173 \pm 20$  K),  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$  ( $553 \pm 50$  K), and CoAs ( $1248 \pm 20$  K). The results are discussed mainly in terms of a geometrical model for the relationship between the two structure types.

Considering the amount of effort which has been devoted to studies of the physical and chemical properties of the phases with the NiAs and MnP type structures (*cf.*, *e.g.*, surveys in Refs. 1–3) surprisingly little attention has been paid to the phase transitions between these structure types (see Refs. 4–16). However, for so closely related structure types as NiAs and MnP, fundamental information concerning the factors which lead to preference for one of them in the particular case must be hidden in the transformation characteristics with temperature, pressure, composition, *etc.* as the variables. For this reason, a low and high temperature X-ray study of carefully selected phases with NiAs or MnP type structure was carried out as a part of a protracted research programme on such phases.

### EXPERIMENTAL

Samples of VP, VAs, CrP, CrAs, and CoAs were prepared and characterized by Guinier photographic X-ray data as described previously.<sup>17–20</sup> Samples of TiAs, TiSb, CoP, NiAs, RhSb,  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$ ,  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ , and  $\text{Mn}_{0.15}\text{Fe}_{0.85}\text{As}$  were prepared similarly at 850°C, crushed, subjected to 2–3 further annealings at the same temperature (with intermediate crushings), and finally cooled slowly to room temperature. The ternary samples were made from appropriate mixtures of the binary compounds.

The experimental details concerning the low and high temperature X-ray diffraction measurements are described by Furuseth *et al.*<sup>21</sup>



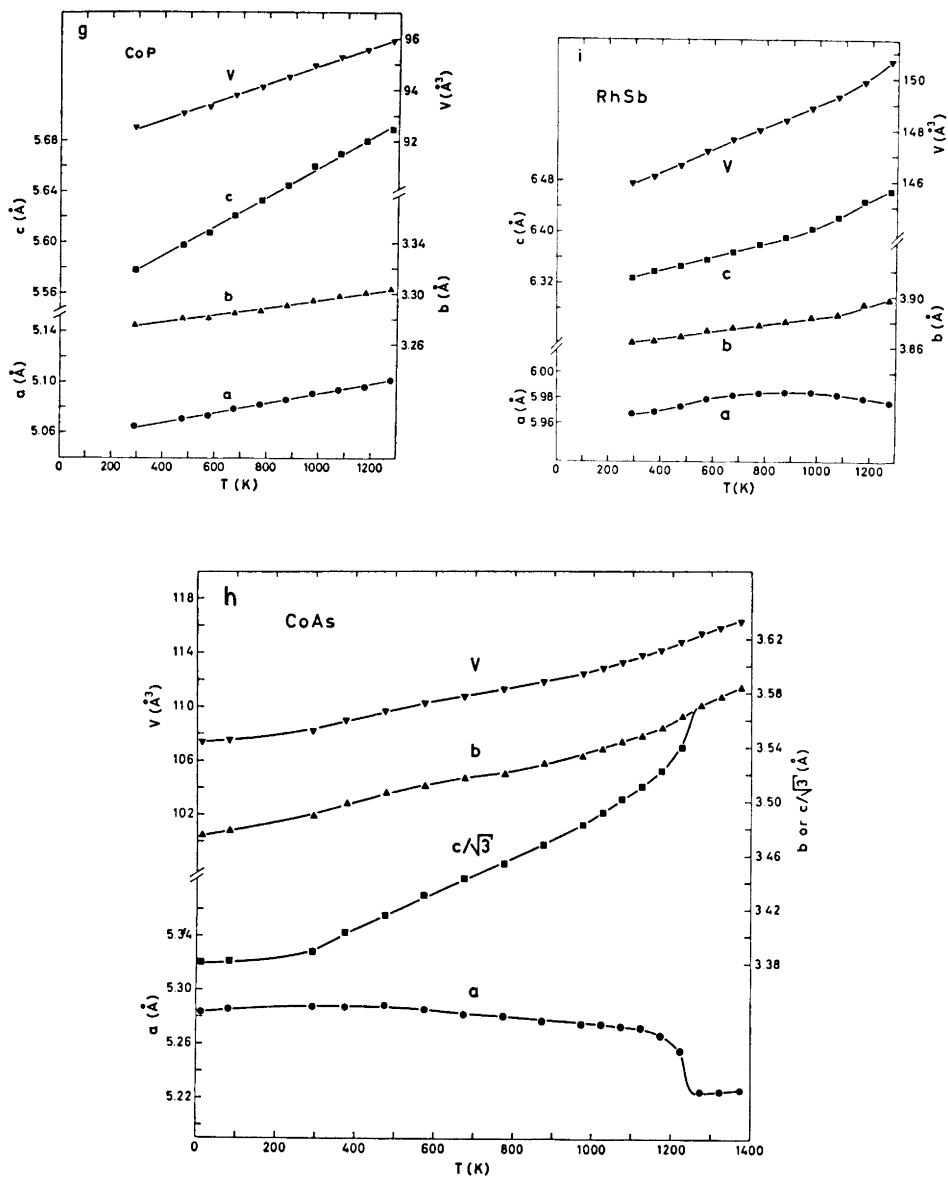


Fig. 1. Unit cell dimensions of (a) VAs, (b) CrP, (c) CrAs, (d)  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$ , (e)  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ , (f)  $\text{Mn}_{0.18}\text{Fe}_{0.82}\text{As}$ , (g) CoP, (h) CoAs, and (i) RhSb as functions of temperature. Broken curves in (c) indicate changes in unit cell dimensions induced at the first order magnetic transformation.<sup>15</sup>

## RESULTS

Prior to this work, transformations from the MnP to the NiAs type structure had been detected above room temperature in MnAs,<sup>4,6-8,13</sup> MnAs<sub>0.9</sub>P<sub>0.1</sub>,<sup>9,14</sup> Cr<sub>1-x</sub>Mn<sub>x</sub>As,<sup>15</sup> and CoAs.<sup>5</sup> These observations together with thermodynamic considerations based on the symmetries of the coordination polyhedra in the two structure types, suggest that other phases with MnP type structure may show the same behaviour. As clearly evinced by data for, e.g., FeAs,<sup>22</sup> phases with MnP type structure do not necessarily transform to NiAs type before the melting point is reached.

A representative selection of binary and a few ternary pnictides (VAs, CrP, CrAs, Cr<sub>0.5</sub>Fe<sub>0.5</sub>As, Mn<sub>0.9</sub>Fe<sub>0.1</sub>As, Mn<sub>0.15</sub>Fe<sub>0.85</sub>As, CoP, CoAs, and RhSb) with the MnP type structure at room temperature have been subjected to a high temperature X-ray study. The temperature dependences of the unit cell dimensions are shown in Fig. 1a-i.

In the same way that phases which possess the MnP type structure at room temperature may transform to the NiAs type at higher temperatures, those with the latter type at room temperature may transform to the MnP type at lower temperatures. Thus, a few potential candidates for such a transformation, viz. TiAs, TiSb, VP, and NiAs, were examined down to liquid helium temperature. However, none of the X-ray diagrams gave indication of transformation. It should be emphasized that the occurrence of additional

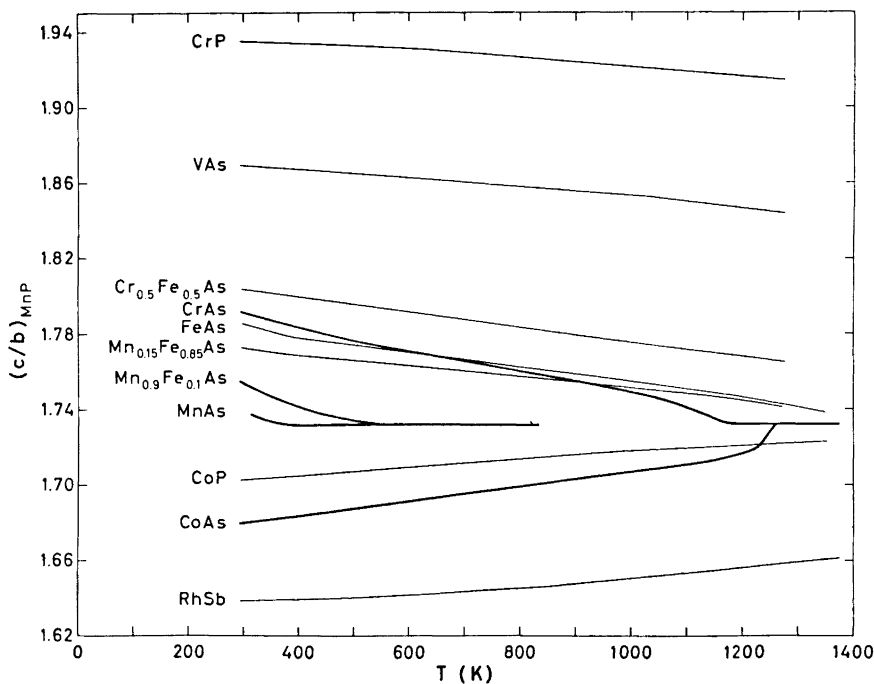


Fig. 2. Temperature dependence of axial ratios  $(c/b)_{\text{MnP}}$ . Heavy lines indicate phases which transform from MnP to NiAs type structure.

reflections and the splitting of those which would be characteristic of the MnP type cell are difficult to detect at the onset of the transformation.

The results of the high temperature study are conveniently divided into three categories:

(1) VAs, CrP, and RhSb show no sign of a beginning transformation up to  $\sim 1300$  K.

(2) Judging from the close approach of  $c/b$  to  $\sqrt{3}$ ,  $\text{Mn}_{0.15}\text{Fe}_{0.85}\text{As}$  and FeAs are probably in an intermediate state (see Discussion) near the melting points of  $1293 \pm 20$  and  $1343 \pm 20$  K, respectively.  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$  and CoP are in a similar situation at the highest temperature of investigation ( $\sim 1300$  K).

(3) CrAs,  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ , and CoAs transform, as seen from Fig. 1c, e, and h, at temperatures of  $1173 \pm 20$ ,  $553 \pm 50$ , and  $1248 \pm 20$  K, respectively.

The most important experimental inference of points (1)–(3) is illustrated in Fig. 2, which gives the temperature dependence of the axial ratios  $(c/b)_{\text{MnP}}$ .

In common with the results for MnAs,  $\text{MnAs}_{0.9}\text{P}_{0.1}$ , and  $\text{Cr}_{1-t}\text{Mn}_t\text{As}$  quoted above, the data in Figs. 1 and 2 show that the unit cell dimensions vary continuously in the region of transformation, which accordingly must be of second or higher order.

A comparison of the curves in Fig. 1a–i reveals a large degree of individuality in the thermal expansion of the various substances. Due to differences in presentation of the expansion curves the mutual variations are larger than apparent at first sight. In order to elucidate this fact, the relative expansion coefficients ( $\alpha_a = (a_T - a_{T'})/a_{300}(T - T')$ , and analogously for  $\alpha_b$  and  $\alpha_c$ ) of the various phases have been calculated and listed in Table 1. Apart

Table 1. Relative expansion coefficients ( $\alpha_a$ ,  $\alpha_b$ , and  $\alpha_c$ ) for phases with MnP type crystal structure.

Phase	$\alpha_a \times 10^6$ (K <sup>-1</sup> )	$\alpha_b \times 10^6$ (K <sup>-1</sup> )	$\alpha_c \times 10^6$ (K <sup>-1</sup> )	Temp. range (K)
VAs	12.2	20.8	7.7	300–1200
CrP	15(av.)	21(av.)	12.1	300–1200
CrAs	29(av.)	51(av.)	18(av.)	300–1000
$\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$	8(av.)	37(av.)	13(av.)	300–1000
$\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$	80(av.)	110(av.)	75(av.)	300–550
$\text{Mn}_{0.15}\text{Fe}_{0.85}\text{As}$	11(av.)	37.4	20.8	300–1200
FeAs <sup>a</sup>	11(av.)	44(av.)	22(av.)	500–1200
CoP	7.7	8.8	20.7	300–1200
CoAs	-3.5	19(av.)	41.3	300–1000
RhSb	5(av.)	7.0	16.9	300–1000

<sup>a</sup> Extracted from Ref. 22.

from the small negative value of  $\alpha_a$  for CoAs, the most extreme values in Table 1 are associated with the expansion coefficients for  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ . The generally much larger values for  $\alpha_a$ ,  $\alpha_b$ , and  $\alpha_c$  for Mn-rich samples of the  $\text{Mn}_{1-t}\text{Fe}_t\text{As}$  and other  $\text{Mn}_{1-t}\text{TAs}$  phases can almost certainly be associated with variations

in electronic band structure (*viz.* number of "localized" unpaired electrons) as a function of temperature.<sup>23</sup> Among the remainder of the phases in Table 1, the values for  $\alpha_a$  of CrAs,  $\alpha_b$  of CrAs,  $\text{Cr}_{0.5}\text{Fe}_{0.5}\text{As}$ ,  $\text{Mn}_{0.15}\text{Fe}_{0.85}\text{As}$ , and FeAs, and  $\alpha_c$  for CoAs are notably larger than the other expansion coefficients. Comparison of the data in Fig. 1 and Table 1 shows that a larger expansion coefficient for one or two of the axes is always balanced by a smaller coefficient for the others, giving rise to an approximately constant volume expansion. There is no distinction between the categories (1)–(3) in this respect.

The transformation process between the NiAs and the completely deformed MnP type structure takes place over a temperature interval which varies from  $\sim 50$  K in CoAs to  $\sim 300$  K in  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ . Since  $\text{Mn}_{0.9}\text{Fe}_{0.1}\text{As}$ , moreover, has a relatively low transformation temperature, this phase has been selected for a careful examination of both unit cell dimensions and positional parameters as a function of temperature.

#### DISCUSSION

A schematic presentation of the relationship between the NiAs and MnP type structures is shown in Fig. 3. The illustration is clearly rather simplified and does not, for example, convey the information that the hexagonal NiAs type structure belongs to space group  $P6_3/mmc$  and the orthorhombic MnP type to  $Pnma$ . The setting of the orthohexagonal NiAs unit cell is in accordance with the latter space group. The projection shows the positions of metal and non-metal atoms in the NiAs arrangement, whereas the lengths and directions of the arrows give their main displacements in the MnP type cell.

Important supplementary information for binary  $TX$  phases ( $T$ :  $3d$  metal;  $X$ : P, As, or Sb) with MnP and/or NiAs type structure is given in Table 2. As immediately evident from the table the NiAs type structure has only one structural degree of freedom,  $(c/a)_{\text{NiAs}} \approx (a/b)_{\text{MnP}}$ , in addition to the compositional variable  $t$  according to the formula  $T_{1+t}X$ . All carefully examined binary compounds with the MnP type structure exhibit a stoichiometric 1:1 composition, whereas the nominal number of structural variables are increased considerably. The real number of structural variables are smaller. Firstly, only two of the axial ratios are free variables. Secondly, Table 2 shows that the following empirical constraints are obeyed for most compounds with MnP type structure:  $(c/a)_{\text{MnP}} \approx 1.10$ ,  $x_T \approx 0$ ,  $z_T \approx x_X \approx 0.20$  and  $z_X \approx 7/12$ . It is perhaps noteworthy that  $(a/b)_{\text{MnP}}$  varies less than  $(c/a)_{\text{NiAs}}$  in accordance with the fact that relative sizes of the components are more restricted for the MnP type structure (*vide infra*).

Table 2 comprises representatives with  $(c/b)_{\text{MnP}}$  both larger and smaller than  $\sqrt{3}$ , which is the criterion distinguishing between the two sub-classes within the MnP type structure according to Pfisterer and Schubert.<sup>31</sup> As seen from the table, no such distinction is manifested in the positional parameters which satisfy the above approximate constraints equally well regardless of the value of  $(c/b)_{\text{MnP}}$ . Even on a more detailed level such a classification is obscure as may be evidenced by comparisons of the corresponding interatomic distances and angles in FeAs and CoAs,<sup>18,22,29,30</sup> or perhaps even more clearly

Table 2. Axial ratios and positional parameters of binary TX phases (T: 3d metal; X: P, As, or Sb) with MnP and/or NiAs type structure. Unless explicitly stated, data refer to room temperature, those for phases with NiAs type structure being converted to an orthohexagonal cell with setting according to space group *Pnma*.

Phase	<i>c/a</i>	<i>c/b</i>	<i>a/b</i>	<i>x<sub>T</sub></i>	<i>z<sub>T</sub></i>	<i>x<sub>X</sub></i>	<i>z<sub>X</sub></i>	Ref.
$\beta$ -TiAs	1.02	$\sqrt{3}$	1.69	0	1/4	1/4	7/12	1
TiSb <sup>a</sup>	1.118	$\sqrt{3}$	1.549	0	1/4	1/4	7/12	1
VP	0.885	$\sqrt{3}$	1.957	0	1/4	1/4	7/12	20
VAs	1.076	1.872	1.740	0.0054(10)	0.1890(4)	0.1969(6)	0.5734(3)	20
VSb <sup>a</sup>	1.358	$\sqrt{3}$	1.276	0	1/4	1/4	7/12	1
CrP	1.122	1.933	1.722	0.0073(3)	0.1929(3)	0.1853(5)	0.5653(3)	24, 25
CrAs	1.099	1.794	1.632	0.0065(10)	0.2001(8)	0.2012(4)	0.5770(6)	17
CrAs, 1173 K	1.085	$\sqrt{3}$	1.597	0	1/4	1/4	7/12	26
CrSb <sup>b</sup>	1.311	$\sqrt{3}$	1.321	0	1/4	1/4	7/12	24, 25
MnP	1.126	1.866	1.658	0.0049(3)	0.1965(2)	0.1879(5)	0.5684(4)	8
MnAs, 328 K	1.112	1.736	1.561	0.0047(10)	0.2229(22)	0.2255(16)	0.5816(12)	27
MnAs, 403 K	1.112	$\sqrt{3}$	1.557	0	1/4	1/4	7/12	1
MnSb <sup>b</sup>	1.235	$\sqrt{3}$	1.402	0	1/4	1/4	7/12	27
FeP	1.115	1.869	1.676	0.0020(4)	0.2004(3)	0.1912(7)	0.5684(6)	28
FeAs	1.108	1.787	1.614	0.0033(1)	0.1992(1)	0.1992(1)	0.5773(1)	29, 30
FeSb <sup>a</sup>	1.369	$\sqrt{3}$	1.265	0	1/4	1/4	7/12	26
CoP	1.100	1.703	1.547	0.0007(3)	0.1976(3)	0.1913(6)	0.5816(6)	24, 25
CoAs	1.110	1.682	1.515	0.0023(10)	0.2000(5)	0.1996(7)	0.5869(3)	18
CoAs, 1248 K	1.183	$\sqrt{3}$	1.464	0	1/4	1/4	7/12	26
CoSb <sup>b</sup>	1.296	$\sqrt{3}$	1.336	0	1/4	1/4	7/12	1
NiAs	1.245	$\sqrt{3}$	1.391	0	1/4	1/4	7/12	1
NiSb <sup>b</sup>	1.322	$\sqrt{3}$	1.310	0	1/4	1/4	7/12	26

<sup>a</sup> The phase is reported to deviate from 1:1 composition. <sup>b</sup> The phase is reported to exhibit a range of homogeneity, quoted values refer to 1:1 composition.

seen in CrAs above and below the Néel temperature of 261–272 K.<sup>17</sup> As pointed out by, *e.g.*, Rundqvist,<sup>24</sup> there is a degree of correlation between  $(c/b)_{\text{MnP}}$  and the total number of “valence” electrons per formula unit, although this may be a reflection of a consistent trend in the size of the  $T$  component rather than the cause of the distinction.

As a reflection of the empirical constraints on the positional parameters, the center of gravity of the six  $X$  atoms surrounding each  $T$  is shifted in the direction opposite to that of the “central”  $T$  atom, and as seen from Fig. 3

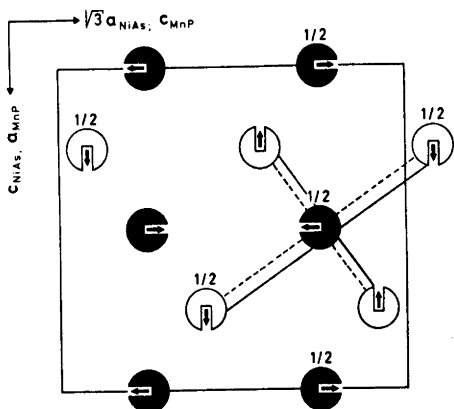


Fig. 3. Relationship between the NiAs and MnP type structures. Filled and open circles represent metal and non-metal atoms, respectively, in the NiAs arrangement. Lengths and directions of arrows give their main displacements in the MnP type cell.

these shifts are of approximately equal magnitude. The most important consequence of this rearrangement is the production of four roughly equal  $T-T$  contacts in the MnP type structure as opposed to generally \* two in the NiAs type (*vide infra*). This happens on the expense of the symmetry of the  $TX_6$  coordination octahedron, the six equal  $T-X$  bonds in the NiAs type structure being splitted into four non-equivalent (2+2+1+1) bond lengths in the MnP type according to  $Pnma$ . The immediate implication of this non-equivalence is that no single “radius” can be attributed to  $T$  or  $X$  in the MnP type structure (*vide infra*).

On account of the experimental facts for compounds with the MnP and NiAs type structures it is possible to formulate a set of postulates or hypotheses which geometrically governs the occurrence of one or the other of the structure types concerned. Among the most natural and obvious set of such geometrical conditions, some prove to be dependent on others, and the object of the following analysis is to sort them in the two categories. Three unambiguously independent postulates are:

(1) Using the NiAs type structure as the starting point no essential change in the coordination number and symmetry of the  $6X$  around  $T$ , and *vice versa*, is permitted.

(2) An approximately equal size of  $T$  and  $X$  is required in the MnP type structure.

\* In the NiAs type structure of (say) VP there are 2+6 approximately equal  $T-T$  contacts.<sup>20</sup>



(3) The number of  $T-T$  contacts are two and four in the NiAs and MnP type structures, respectively.

An additional requirement which is closely associated with (1) can be formulated as:

(4) The average  $T-X$  bond length is maintained in the transformation from the NiAs to the MnP type structure, with a minimum scatter in these distances for the latter type.

Symmetry considerations on the basis of (1) and (3) show that the displacements of the  $T$  atoms must be perpendicular to  $c_{\text{NiAs}}$ , and are most efficient, alternately, along  $\pm b_{\text{NiAs}}$  ( $= \pm \sqrt{3}a_{\text{NiAs}} \approx \pm c_{\text{MnP}}$ ). The resulting unit cell must consequently be of orthorhombic symmetry. Postulate (2) enters into the considerations as a selection criterion for possible candidates for the MnP type structure. In terms of the unit cell in Fig. 3, the above deduction is summarized as:

(5) The positional parameters of the  $T$  atoms in the MnP type structure are restrained by  $x_T \approx 0$  (and  $y_T \approx 0$ , according to  $Pn2_1a$ , or  $y_T = 0$ , according to  $Pnma$ ) whereas  $z_T \neq 1/4$ .

As a consequence of these metal displacements, symmetry considerations based on the hypotheses (1)–(4) show that the non-metal atoms must be shifted mainly along  $\pm c_{\text{NiAs}}$  ( $\approx \pm a_{\text{MnP}}$ ), viz.:

(6) The positional parameters of the  $X$  atoms in the MnP type structures are  $x_X \neq 1/4$ , with the constraint(s)  $z_X \approx 7/12$  (and  $y_T \approx 0$  or  $y_T = 0$ , according to  $Pn2_1a$  or  $Pnma$ ).

In order to establish semi-theoretical values for  $z_T$  and  $x_X$  it is convenient first to present some partly incorrect results based only on hypotheses (2) and (3) and simple geometrical considerations. Assuming that  $T$  and  $X$  are rigid spheres of equal radii which make 6  $T-X$  and 2  $T-T$  contacts in the NiAs type structure, a value of  $4/3$  is obtained for  $(c/a)_{\text{NiAs}}$ . Presuming, moreover, that the axial ratios are maintained in the transformation from the NiAs to a MnP type arrangement together with hypothesis (3) it is found that  $z_T = 0.157$ . Provided the unit cell dimensions are kept constant this gives rise to a 15 % increase in  $T-T$ . This paradoxical conclusion implies that either the first or the latter assumption of this sequence is erroneous. On more careful examination it is seen that already the starting point is incorrect in that the  $T$  and  $X$  atoms cannot be of spherical shape (and, moreover,  $T-T$  in phosphides and arsenides with the MnP type structure appears to be some 10–20 % larger than  $T-X$ ). As one may expect, an extension of the above speculations to the non-metal atoms turns out to be even less realistic.

In order to obtain further progress it is necessary to take experimental facts into account as additional hypotheses:

(7) Compounds with the MnP type structure satisfy the empirical constraint(s)  $(c/a)_{\text{MnP}} = 1.10$  (and  $1.63 < (c/b)_{\text{MnP}} < 1.93$ ). As a direct consequence potential candidates for a continuous transformation from the NiAs to the MnP type structure must fulfil the requirement,  $(c/a)_{\text{NiAs}} \approx 1.6$ .

(8) The shortest interatomic  $X-X$  distances in the MnP type structure are caused by the geometry of the atomic arrangement, and are consequently non-bonding. This condition acts as the limiting factor for the magnitude of the deformation of the NiAs arrangement.

Equating the two sets of bonding  $T-T$  distances in an idealized MnP type arrangement based on hypotheses (1), (3), and (5):

$$\left\{ \left( \frac{a}{2} \right)^2 + [2(\frac{1}{4} - z_T)c]^2 \right\}^{\frac{1}{2}} = \left\{ \left( \frac{b}{2} \right)^2 + \left[ \frac{c}{2} - 2(\frac{1}{4} - z_T)c \right]^2 \right\}^{\frac{1}{2}}$$

it follows that

$$z_T = \frac{1}{4} - \frac{1}{8} \left( 1 + \frac{b^2}{c^2} - \frac{a^2}{c^2} \right)$$

Taking advantage of hypothesis (7) one finds that

$$0.181 < z_T < 0.195$$

(Compared with an NiAs type arrangement of the same unit cell dimensions [ $(c/a)_{\text{NiAs}} = 1.6$ ] this means < 4 % increase in  $T-T$  distance, which is consistent with postulate (3) as well as with the observed data.)

Since the deduced range for  $z_T$  is in remarkable accordance with the values listed in Table 2, it is worthwhile to present the results of a similar derivation for  $x_X$ . This deduction is based on hypotheses (2), (6), and (8), using a 20 % increased average (r.m.s.)  $T-X$  bond distance as the limiting value for the shortest permissible  $X-X$  distance. (Although the figure of 20 % appears to be somewhat arbitrary at first sight, this criterion is based on experience from a large number of transition metal compounds.) The calculations show that

$$x_X \approx \frac{1}{4} - \left( \frac{5}{64} - \frac{c^2}{36a^2} \right) \approx 0.20$$

Thus, the above deductions fully match the experimental facts in Table 2 and this gives rise to a further more precise specification of (5) and (6):

(9) The geometrical constraints on the positional parameters of the MnP type structure are  $x_T \approx 0$ ,  $z_T \approx x_X \approx 0.20$ , and  $z_X \approx 7/12$  (according to  $Pnma$ ).

The fact that the displacements of  $T$  and  $X$  relative to the idealized NiAs type arrangement must be of the same magnitude, follows in an intuitive manner directly from Fig. 3, bearing in mind that the two kinds of atoms are of approximately equal size.

Towards the end of the geometrical considerations it is tempting to formulate, as a separate point, the conditions governing the volume, although the content of which follows immediately from (1) and (4):

(10) The volume per formula unit is maintained during the continuous  $\text{MnP} \rightleftharpoons \text{NiAs}$  type phase transition, provided the size of  $T$  remains virtually constant.

The limitation on (10) applies to the situation in MnAs and ternary Mn-rich phases of the type  $\text{Mn}_{1-x}\text{T}_x\text{As}$ , where the size of Mn is sensitive to the number of unpaired electrons. The latter fact provides a natural explanation as to why phase transitions ( $\text{NiAs} \rightarrow \text{MnP}$ ) can be induced in these phases on the application of high pressures.

In summarizing the above discussion the most important geometrical condition which governs the preference of the MnP type structure in relation to the NiAs type is the approximately equal size of  $T$  and  $X$  which in turn permits an increase from two to four  $T-T$  contacts in the former structure type.

NiP breaks the pattern formed by pnictides of the  $3d$  series in that it adopts a unique crystal structure, which according to Larsson<sup>32</sup> is closely related to both the NiAs and MnP types. The NiP type atomic arrangement can in a somewhat superficial way be said to be intermediate between the NiAs and MnP types in that each  $T$  obtains three close  $T-T$  contacts. For this reason it is tempting to apply a geometrical reasoning for the hypothetical transition from NiAs to NiP type structure. Without going into details, the  $T$  atoms are shifted (from their positions in the NiAs type cell) perpendicular to  $c_{\text{NiAs}}$  and mainly, in an alternating manner, along the plus and minus directions of the two hexagonal axes. This corresponds to one of the most efficient ways to produce 3  $T-T$  contacts from an NiAs type arrangement. The resulting unit cell is of orthorhombic symmetry, and in the case of NiP it has a four times larger volume than the NiAs type cell. As a consequence of the displacements of the  $T$  atoms, the  $X$  atoms in NiP are shifted mainly along  $\pm c_{\text{NiAs}}$  ( $\approx \pm b_{\text{NiP}}$ ), and in a manner which gives rise to five  $T-X$  bond distances of approximately equal length, whereas, as a compromise, the sixth necessarily has to be considerably elongated. A characteristic feature of the deformation in the NiP type structure is the rather short  $X-X$  distance [2.430(1) Å, *i.e.* only 10 % larger than the expectation value for the P-P single bond length<sup>33</sup>]. In line with the above geometrical considerations for the relationship between the NiAs and MnP type structures it is suggested that the condition that rules the occurrence of the NiP type structure is the 3  $T-T$  contacts per  $T$  atom. The limiting factor is once more the shortest  $X-X$  distances, which can be regarded as non-bonding. Contrary to the suggestions of Larsson,<sup>32</sup> we propose therefore that each  $T$  is coordinated to 6  $X$  and 3  $T$ . The choice between the MnP and NiP type structures cannot be governed by a size factor, since the average Ni-P distance is comparable with the average Co-P distance in CoP with MnP type structure.

The geometrical considerations on the relationship between the NiAs and MnP type structures have necessarily been limited to the initial and final stages of the transition. Since the transitions in all known cases are continuous of second or higher order, more information is at hand. However, the problem is how to utilize this information. Although no experimental evidence concerning the lattice modes of vibration is available, it is probably possible to describe the dynamical mechanism of the NiAs  $\rightleftharpoons$  MnP type transition in terms of the "soft modes" formalism.<sup>34</sup> The most fundamental question in this connection appears to be how the transition is initiated in the high temperature phase. In order to approach this problem further it is necessary to get some insight into the nature and implications of the  $T-T$  contacts. The two  $T-T$  contacts in the NiAs type structure and the four in the MnP type unquestionably reflect bonding interaction between the atoms concerned, but the degree of localization and kinds of orbitals involved in these bonds represent a hitherto unsolved problem. Carter<sup>35,36</sup> has, for example, recently advanced a "quasi free electron" model for the  $T-T$  interactions in compounds with the NiAs type structure. Provided such a model conveys a reasonable degree of correctness about the nature of these bonds, it is tempting to suggest that the relation between the Fermi surface and the Brillouin zone faces may release the transformation. The increase from two to four  $T-T$  contacts is in any case definitely associated with a decrease in the number of "localized" unpaired electrons, and may possibly result from splitting of electronic bands. Without distinguishing between bonding, non-bonding, and possibly anti-bonding bands the experimental evidences show that the MnP type structure occurs at a valence electron concentration of 10–14 per  $TX$  unit. This provides an "explanation" as to why TiSb does not obtain a MnP type arrangement despite the fact that its unit cell proportions should

be favourable. The monochalcogenides of the 3d metals appear to prefer the NiAs type structure which permits a larger number of unpaired electrons and variable compositions.

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