

## Compounds with the Marcasite Type Crystal Structure. XII.

### Structural Data for $\text{RuP}_2$ , $\text{RuAs}_2$ , $\text{RuSb}_2$ , $\text{OsP}_2$ , $\text{OsAs}_2$ , and $\text{OsSb}_2$

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The  $\text{FeS}_2$ -*m* type structures of  $\text{RuP}_2$ ,  $\text{RuAs}_2$ ,  $\text{RuSb}_2$ ,  $\text{OsP}_2$ ,  $\text{OsAs}_2$ , and  $\text{OsSb}_2$  have been refined by powder neutron diffraction/profile refinement methods, and a brief discussion of structural data for  $\text{FeS}_2$ -*m* type compounds is presented.

In the second paper<sup>1</sup> of this series, structural data on a number of binary compounds with the  $\text{FeS}_2$ -*m* (*m*=marcasite) type crystal structure were reported. During a continuation<sup>2</sup> of this study, it became evident that some of the positional parameters given in that paper may be in error (originating from possible shortcomings in the treatment of the X-ray powder diffraction data). Apart from the more "obvious" cases (see Ref. 2) of  $\text{RuAs}_2$  and  $\text{OsP}_2$ , it is difficult to pick out those of the compounds which may be burdened with significant inaccuracies and it was accordingly decided to reexamine them all, *viz.*  $\text{RuP}_2$ ,  $\text{RuAs}_2$ ,  $\text{RuSb}_2$ ,  $\text{OsP}_2$ ,  $\text{OsAs}_2$ , and  $\text{OsSb}_2$  (data for  $\text{FeAs}_2$ ,  $\text{NiAs}_2$ , and  $\text{NiSb}_2$  were included in Ref. 2).

#### EXPERIMENTAL

The compounds  $\text{RuP}_2$ ,  $\text{RuAs}_2$ ,  $\text{RuSb}_2$ ,  $\text{OsP}_2$ ,  $\text{OsAs}_2$ , and  $\text{OsSb}_2$  were prepared by heating stoichiometric quantities of the elements [Ru, Os, As, Sb (Johnson, Matthey & Co.), and P (Koch-Light Laboratories); all of purity 99.999%] in evacuated, sealed silica tubes. All neutron diffraction samples were heated at a maximum temperature of 1200 °C for one day, followed by gradual cooling to 600 °C over a period of one week. As demonstrated on small scale samples, this procedure ascertained homogeneity for all, and apart from the antimonides, no improve-

ment in crystallinity could be detected on repeating the heating cycle. For the phosphides and arsenides the present procedure differs from that outlined in Ref. 1 by a substantial increase in maximum temperature. This simple change has thus eliminated the rather time-consuming grinding and reannealing cycles earlier used.<sup>1</sup> The crystallinity of the small scale antimonide samples were found to improve slightly on reannealing at 1200 °C, but weighed against the risk of contaminating the comparatively large scale neutron diffraction samples, the only slight gain in sample perfection was considered insignificant.

Attempts have also been made to prepare (by the sealed silica capsule technique)  $\text{FeS}_2$ -*m* type modifications of  $\text{FeS}_2$ ,  $\text{CoS}_2$ ,  $\text{CoSe}_2$ ,  $\text{NiS}_2$ ,  $\text{NiSe}_2$ ,  $\text{NiTe}_2$ ,  $\text{CuS}_2$  (from lower chalcogenides and added chalcogen), and  $\text{RuS}_2$ ,  $\text{RuSe}_2$ ,  $\text{RuTe}_2$ ,  $\text{OsS}_2$ ,  $\text{OsSe}_2$ , and  $\text{OsTe}_2$  (from the elements). The total heating periods used (so far) amounts to 2–3 years at fixed temperatures in the range 120–240 °C for the sulfides, 220–280 °C for the selenides, and 260–360 °C for the tellurides. Except for  $\text{RuTe}_2$  and  $\text{OsTe}_2$  all endeavours have, however, been totally in vain;  $\text{NiTe} + \text{Te}$  reacted to form the known  $\text{Cd}(\text{OH})_2$  type phase,  $\text{CuS} + \text{S}$  remained unreacted, and the others reacted (partly or completely) to their  $\text{FeS}_2$ -*p* (*p*=pyrite) type modifications without showing any traces of  $\text{FeS}_2$ -*m* type phases.

Some properties of the  $\text{FeS}_2$ -*m* type modification of  $\text{OsTe}_2$  have been reported earlier,<sup>2–4</sup> and promising indications for its possible preparation in pure form were at hand.<sup>4</sup> The supplementary information gained up to now can be summarized as follows. The  $\text{FeS}_2$ -*m* type modification of  $\text{OsTe}_2$  has been obtained only in admixture with the elements or its  $\text{FeS}_2$ -*p* type modification depending on both temperature and annealing period. With the reaction periods and temperatures used here (see above), it appears that the  $\text{FeS}_2$ -*m* type modification is the first one to be formed from

Table 1. Structural data for RuP<sub>2</sub>, OsP<sub>2</sub>, RuAs<sub>2</sub>, OsAs<sub>2</sub>, RuSb<sub>2</sub>, and OsSb<sub>2</sub>.

Notation	RuP <sub>2</sub>	OsP <sub>2</sub>	RuAs <sub>2</sub>	OsAs <sub>2</sub>	RuSb <sub>2</sub>	OsSb <sub>2</sub>
$a(\text{\AA})$	5.1169(12)	5.1012(14)	5.4279(7)	5.4115(15)	5.9514(10)	5.9411(10)
$b(\text{\AA})$	5.8915(11)	5.9022(13)	6.1834(8)	6.1900(16)	6.6743(12)	6.6873(12)
$c(\text{\AA})$	2.8709(7)	2.9183(8)	2.9685(6)	3.0127(7)	3.1790(7)	3.2109(7)
$x$	0.1617(7)	0.1634(10)	0.1700(7)	0.1701(9)	0.1812(6)	0.1848(7)
$y$	0.3727(5)	0.3723(6)	0.3666(5)	0.3671(5)	0.3590(5)	0.3596(6)
$d_1 =$	$T-X(\text{\AA}) \times 4$	2.371(3)	2.468(3)	2.477(4)	2.648(3)	2.639(3)
$d_2 =$	$T-X(\text{\AA}) \times 2$	2.347(3)	2.448(3)	2.452(3)	2.628(3)	2.644(4)
$l =$	$X-X(\text{\AA}) \times 1$	2.234(9)	2.475(10)	2.469(12)	2.863(10)	2.889(11)
$\theta_1 =$	$X-T-X(^{\circ}) \times 4$	87.79(10)	87.94(10)	87.87(12)	88.28(10)	88.34(11)
$\theta_2 = (\varphi_2 =)$	$X-T-X(^{\circ}) \times 4$	92.21(10)	92.06(10)	92.13(12)	91.72(10)	91.66(11)
	$X-T-X(^{\circ}) \times 2$	74.53(7)	73.94(7)	74.93(9)	73.78(7)	74.93(8)
$\varphi_1 =$	$X-T-X(^{\circ}) \times 2$	105.47(7)	106.06(7)	105.07(9)	106.22(7)	105.07(8)
	$T-X-T(^{\circ}) \times 2$	123.61(10)	125.67(10)	125.35(11)	128.18(10)	128.19(11)
$\varphi_2 = (\theta_2 =)$	$T-X-T(^{\circ}) \times 1$	74.53(7)	73.94(10)	74.93(9)	73.78(7)	74.93(8)
	$T-X-X(^{\circ}) \times 2$	109.18(12)	108.9(2)	108.56(12)	108.43(12)	107.94(13)
$\varphi_3 =$	$T-X-X(^{\circ}) \times 1$	111.54(17)	111.4(2)	109.65(16)	109.74(20)	106.00(16)

the elements, and as long as these are present, the  $FeS_2$ - $m$  type modification appears to be stabilized [present values for the unit cell dimensions:  $a=5.2804(4)$  Å,  $b=6.4018(4)$  Å, and  $c=4.0481(3)$  Å]. As the reaction proceeds, the  $FeS_2$ - $p$  type modification of  $OsTe_2$  appears in increasing amounts.

The reaction properties of  $RuTe_2$  seem to be quite similar to those of  $OsTe_2$ , except that its rate of formation is much lower under the same temperature conditions. No earlier report on

the  $FeS_2$ - $m$  type modification of  $RuTe_2$  is found in the literature; its unit cell dimensions are:  $a=5.271(1)$  Å,  $b=6.387(2)$  Å, and  $c=4.038(1)$  Å.

X-Ray powder diffraction data were obtained in a Guinier camera ( $CuK\alpha_1$  radiation,  $\lambda=1.54050$  Å; KCl as internal standard,  $a=6.2919$  Å) and unit cell dimensions derived by applying the method of least squares. In addition to X-ray (and neutron) diffraction, evidence for sample homogeneity was also obtained by metallographic methods.

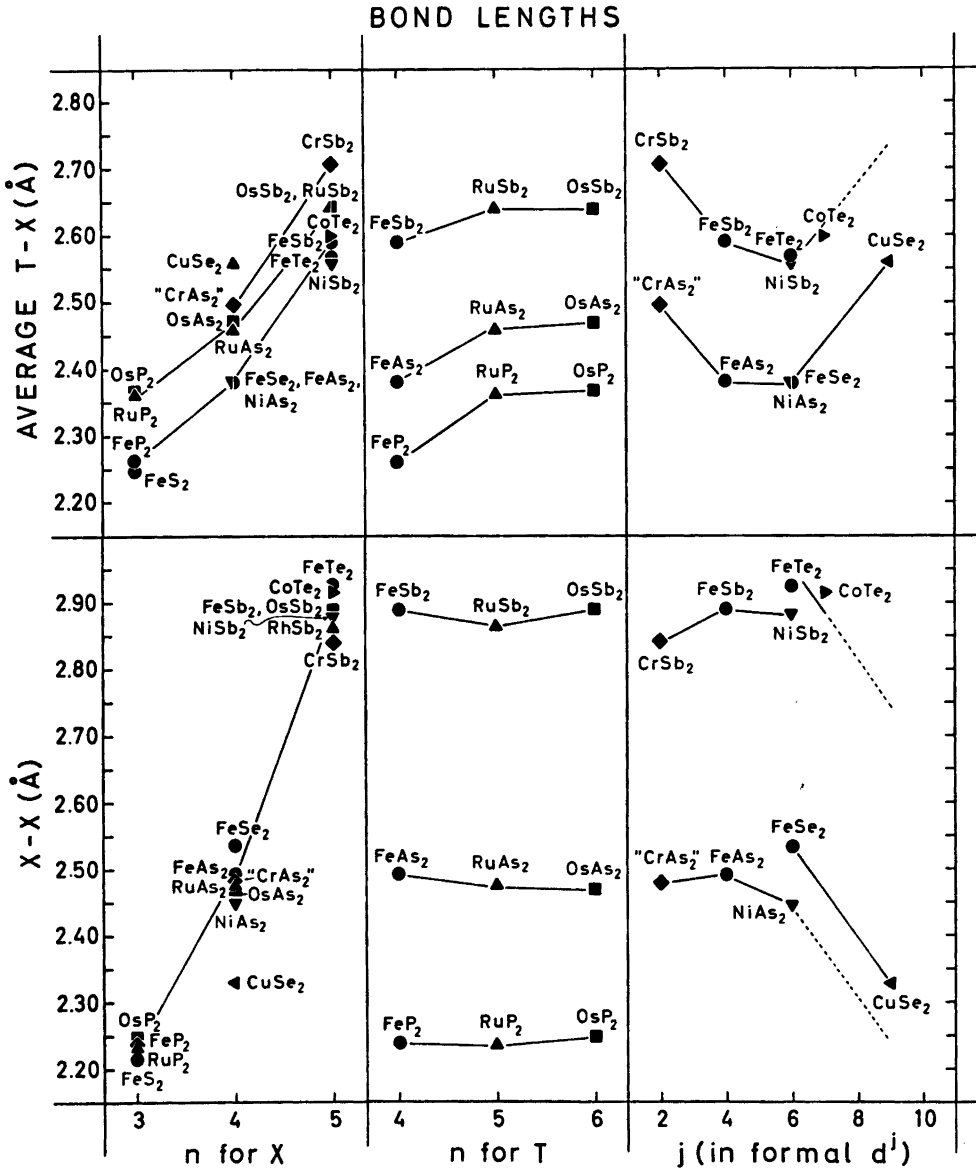


Fig. 1a. Dependence of bond lengths for compounds with  $FeS_2$ - $m$  type structure.

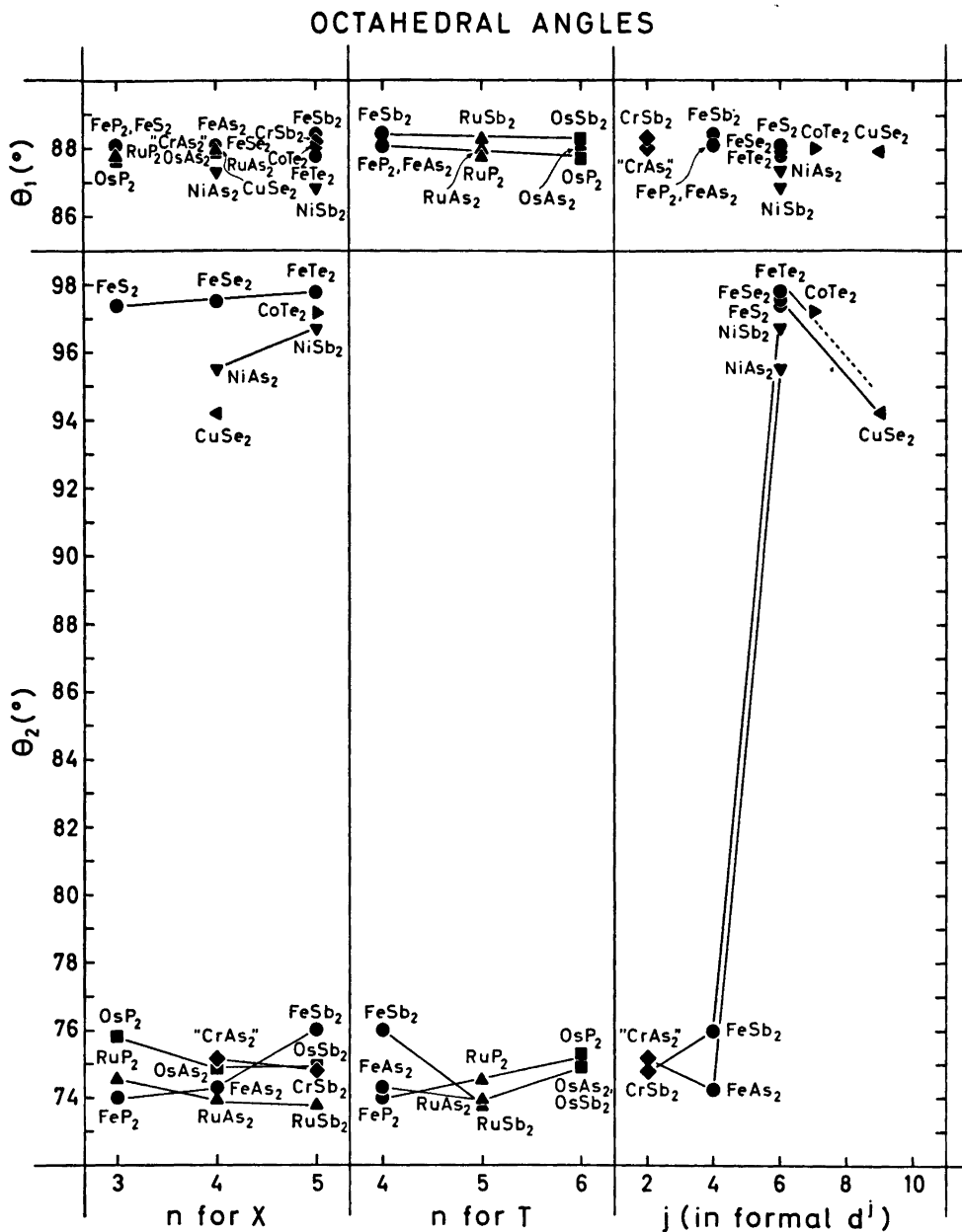


Fig. 1b. Dependence of octahedral angles for compounds with  $\text{FeS}_2\text{-}m$  type structure.

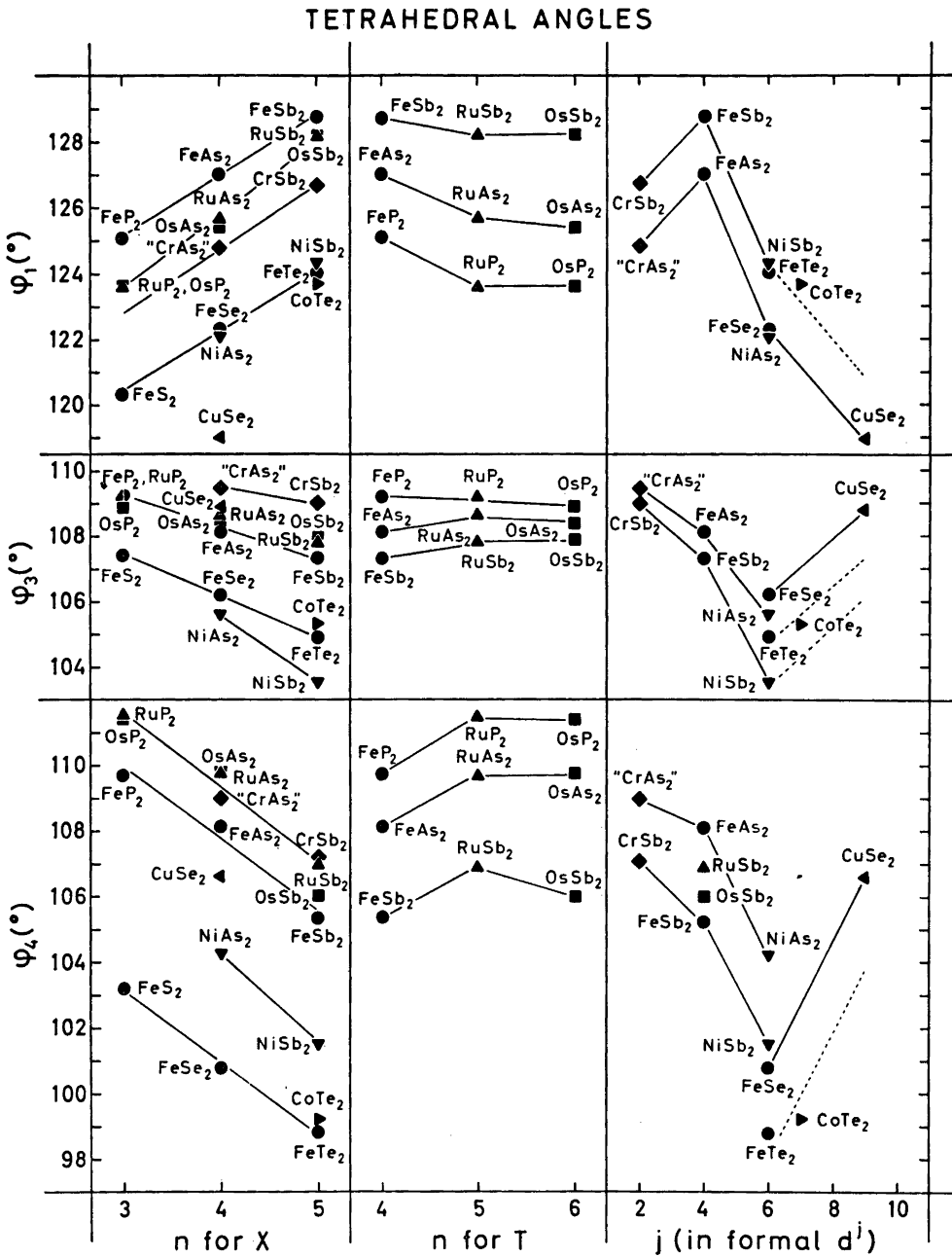


Fig. 1c. Dependence of tetrahedral angles for compounds with FeS<sub>2</sub>-m type structure.

Powder neutron diffraction data were collected at room temperature using cylindrical sample holders of vanadium. Neutrons of wavelength 1.877 Å were obtained from the Kjeller-reactor JEEP II. The nuclear scattering lengths ( $b_{\text{Ru}} = 0.73$ ,  $b_{\text{Os}} = 1.07$ ,  $b_{\text{P}} = 0.51$ ,  $b_{\text{As}} = 0.64$ , and  $b_{\text{Sb}} = 0.564$ , all  $\times 10^{-12}$  cm) were taken from Ref. 5. In all cases, the least squares profile refinement programme of Rietveld<sup>6</sup> was applied in the final fitting of the variable parameters.

## RESULTS AND DISCUSSION

The (orthorhombic) unit cell dimensions, positional parameters ( $x$  and  $y$ ), and derived bonding interatomic distances and angles are listed in Table 1. The rather low values for the final neutron diffraction profile reliability factors (ranging between 2.1 and 4.3 %) and circumstantial evidence from a thorough study<sup>7</sup> of the prototype compound, show that the assumption of space group  $Pnmm$  is justified. (For further comments, see Refs. 2 and 7.)

Comparison of the positional parameters in Table 1 with those in Ref. 1 show that highly significant discrepancies occur for  $\text{RuAs}_2$  ( $y$ ) and  $\text{OsP}_2$  ( $x$ ), as singled out in advance.<sup>3</sup> The earlier data<sup>1</sup> for  $\text{RuP}_2$  ( $x$ ) and  $\text{OsSb}_2$  ( $x$ ) are also somewhat erroneous. With these corrections, several interesting patterns are seen (Figs. 1 and 2) to emerge from the structural data for binary ( $TX_2$ ;  $T$  = transition element,  $X$  = pnigogen or chalcogen)  $\text{FeS}_2$ - $m$  type compounds (Refs. 2, 7–11 and including unpublished data for “ $\text{CrAs}_2$ ” extrapolated

from  $\text{Cr}_{1-x}\text{Fe}_x\text{As}_2$ <sup>12</sup>). The illustrations do not include data for axes or axial ratios since this is comprehensively covered in Ref. 13.

The thin lines in Fig. 1 connect points of homological (with respect to  $T$  or  $X$ ) series and serve the purpose of focusing attention on certain dependencies on the principal quantum numbers ( $n$ ) for  $T$  or  $X$ , or  $j$  in formal  $d^j$  manifolds of  $T$ . Among the trends emerging from Fig. 1, we like to draw attention to the essentially class-wise correlation of the octahedral angle  $\theta_2$ , and the remarkable constancy of the octahedral angle  $\theta_1$  as opposed to the systematic variations of the tetrahedral angles  $\varphi_1$ ,  $\varphi_3$ , and  $\varphi_4$ . (The bond angle notations are defined in Table 1.) In Fig. 1b the behaviour of  $\text{FeSb}_2$  with respect to  $\theta_2$  breaks the pattern, thus emphasizing once more (*cf.* Ref. 13 and references therein) the somewhat unique character of this compound.

A special variety among the correlations (Fig. 2) is that between the variable positional parameters  $x$  and  $y$ . This type of structural relationship was briefly taken up in Ref. 2 on what at first sight appears as an essentially proper semi-empirical geometrical basis. A closer examination unveils, however, that this approach<sup>3</sup> is marred by some circular logic in the chain of arguments. The approximate, but no means perfect fit between the experimental points and the “empirically averaged” lines for the classes A and B (Fig. 1 in Ref. 2), merely demonstrates that there is a correlation between the structural variables  $x$ ,  $y$ ,  $a/b$ , and  $c/b$ . The correlations emphasized in Fig. 2 are somewhat different in character with approximately parallel lines connecting  $TX_2$  combinations according to their positions in the Periodic System.

The unmistakable message contained in Fig. 2 has encouraged us to start a new search for geometrical conditions on the  $\text{FeS}_2$ - $m$  type atomic arrangement. In a reevaluation of geometrical aspects, a more thorough analysis of the  $\text{FeS}_2$ - $m$  type atomic architecture must be performed. Suitable starting points are the coordination polyhedra of  $T$  and  $X$ , but packing features are probably also of importance. An extension of the “ $\lambda$ -approach” from Ref. 13 may prove useful in this respect.

The term geometrical considerations occurs frequently in the above presentation as well

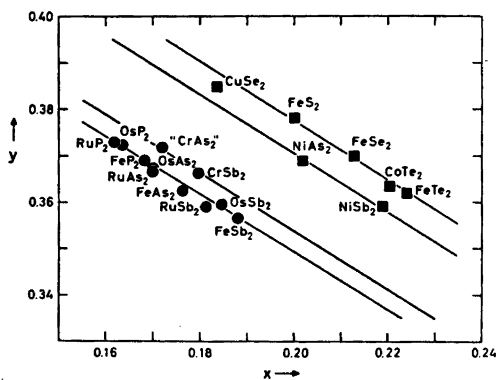


Fig. 2. Empirical correlations of positional parameters for compounds with  $\text{FeS}_2$ - $m$  type structure.

as in Ref. 13, and the importance of such considerations lies in that each postulate of geometrical models is expected to have parallel bonding interpretations. Further discussions on geometry and bonding in  $\text{FeS}_2$ - $m$  type compounds are postponed to forthcoming papers. Here, we would only like to comment briefly on two important aspects of this matter.

In a recent paper on  $\text{MnP}_4$ , Jeitschko and Donohue<sup>14</sup> propose that universal  $T-T$  bonding is the stabilizing element in the class A,  $\text{FeS}_2$ - $m$  type structure (where, according to them, each  $T$  forms two  $\sigma$  and two  $\pi$   $T-T$  half-bonds) and the  $\text{CoSb}_2$  type structure (one  $\sigma$   $T-T$  single bond per  $T$ ). Unfortunately, these authors do not present any arguments in favour of their hypothesis, neither do they discuss arguments for its rejection. (Rejection of the earlier, commonly assumed  $T-T$  bonding hypothesis for compounds with the  $\text{CoSb}_2$  type structure has already been announced by both Goodenough<sup>15</sup> and two of the present authors<sup>16</sup> and will not be recapitulated here.) Apart from the comparatively short  $c$  axes for class A compounds, [ranging from 2.72 Å ( $\text{FeP}_2$ ) to 3.27 Å ( $\text{CrSb}_2$ )], there is indeed no experimental evidence in favour of a regular type of  $T-T$  bonding in these compounds, whereas several indications for the opposite conclusion can be advanced.\*

(1) There are two unpaired electrons per Cr atom in  $\text{CrSb}_2$ .<sup>11</sup>

(2) The shortest  $T-T$  distances ( $=c$ ) in homological series  $TP_2-TAs_2-TSb_2$  and  $TS_2-TSe_2-TTe_2$  show consistent and virtually parallel dependencies (cf., e.g., Fig. 3 in Ref. 13) regardless of whether members of the classes A, A/B, or B are considered.

(3) The shortest  $T-T$  distances in the class A series  $TP_2-TAs_2-TSb_2$  ( $T=\text{Fe, Ru, Os}$ ) vary by about 0.5 Å from P to Sb.

(4) The shortest  $T-T$  distances in class A compounds equal the next shortest  $X-X$  distances. This observation is particularly relevant for  $X=\text{Sb}$  ( $c=3.18$  to 3.27 Å) where Sb itself must be regarded as comparatively large

(shortest Sb-Sb for  $\text{FeS}_2$ - $m$  type compounds range from 2.84 to 2.89 Å, cf. Fig. 1a).

These and possibly other questions must be accounted for if  $T-T$  bonding is to be accepted as the cause of the existence of class A,  $\text{FeS}_2$ - $m$ . Goodenough<sup>15</sup> has made a valuable contribution in this connection by pointing out that the secret may be hidden in the  $T-X$  bonds. As discussed in Ref. 16, Goodenough's *specialized* interpretation in terms of the enhanced  $T-X$  bonding in class A relative to class B is to some extent contradicted by experimental evidence. Pursuing, however, his *general idea* of utilizing (for  $T-X$  bonding) a  $d$ -orbital, awry-oriented with respect to a regular  $TX_6$  octahedron, a mechanism is at hand for varying the octahedral angle  $\theta_2$  (Fig. 1b). According to the  $\text{FeS}_2$ - $m$  type geometry, this angle is intimately coupled to the length of the  $c$  axis which plays a major role in the assignment of classes.

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\* Jeitschko and Donohue are aware of an apparent exception (from their  $T-T$  bonding assumption), " $\text{Mo}_{2/3}\text{As}_2$ ", which they try to explain away. However, " $\text{Mo}_{2/3}\text{As}_2$ " is in reality non-existent (confused with  $\text{FeAs}_2$  as demonstrated in Ref. 2) and represents no problem in this connection.