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Compounds with the Marcasite Type Crystal Structure

II. On the Crystal Structures of the Binary Pnictides

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The FeS_2-*m* type crystal structures of $CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, β-$NiAs_2$, $NiSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$ have been refined by least squares from X-ray powder diffractometer data using individual temperature factors. Stepwise refinements of the positional parameters x and y for all these structures have been performed on the basis of $R(x,y)$ maps. Secondary minima in the $R(x,y)$ maps, which affect the refinement processes according to the method of least squares, are detected for $CrSb_2$, β-$NiAs_2$, $NiSb_2$, $RuSb_2$, and OsP_2.

A brief discussion of the interatomic distances and angles is presented.

In continuing our examination of the properties of compounds with the FeS_2-*m* type crystal structure,[1] we present here some structural data (collected by X-ray powder diffraction methods) for the binary di-pnictides with this structure type. All hitherto known pnictides with this structure type are included in this study with the exception of $Mo_{0.6}As_2$ which we have been unable to synthesize.[1] (A detailed structure determination of $Mo_{0.6}As_2$ on the basis of three-dimensional single crystal data has recently been published by Brown.[2])

The crystal structure of the prototype FeS_2-*m* was first solved by Buerger,[3] who also was the first to notice [4] that there appear to be two distinct groups of compounds with this structure type according to the shapes of their unit cells. Using the setting in space group *Pnnm* for the FeS_2-*m* type unit cell (as suggested by Buerger [3]), the axial ratios c/a and c/b of one class are about 0.74 and 0.62, respectively, and of the other about 0.55 and 0.48, respectively.* Binary compounds with this structure type belong to one or the other of these groups, no binary compound with intermediate values for the axial ratios

* Buerger named the former group of compounds marcasites and the latter loellingites. Hulliger and Mooser [5,6] have suggested the names anomalous and Jahn-Teller marcasites, respectively, whereas Pearson [7] prefers the designations normal and compressed marcasites.

being known. The binary di-pnictides contain representatives from both categories.

Although the FeS_2-*m* type structure is common and simple, the positional parameters of the pnigogen atoms for these compounds have not been determined with an accuracy that would seem warranted by the simplicity of the structure. In fact of the 12 compounds included in this study, only the unit cell dimensions are known for five of them (*i.e.* RuP_2, $RuAs_2$, OsP_2, $OsAs_2$, and $OsSb_2$), the atomic parameters for three others (*i.e.* $CrSb_2$,[8] FeP_2,[9] and $RuSb_2$[10]) are only known to the second decimal place, and even the atomic coordinates of the four remaining compounds (*i.e.* $FeAs_2$,[11] $FeSb_2$,[12,13] β-$NiAs_2$,[14] and $NiSb_2$[13]) may not be known very accurately. Meaningful comparisons of the interatomic distances and angles are thus difficult to make. In order to provide a partial remedy to this unsatisfactory situation the structure refinements reported here were undertaken.

EXPERIMENTAL

The samples were prepared as described in the preceding paper.[1] Only samples with the stoichiometric 1:2 composition were utilized in the present study.

Integrated X-ray intensities were obtained by 2θ counting scans of the peaks at $1/8°(2\theta)$/min and subtracting appropriate background counts. Generous allowance was made for the background on both sides of each peak. Three complete scans were taken of each compound and additional data were compiled whenever it was considered desirable. Both strip-chart recording and timer/counter combination were used to register the experimental data. A Philips wide angle powder X-ray diffractometer with proportional counter and pulse-height analyzer was used throughout this study. (The diffractometer was calibrated before and after the experiments, using Si as a standard.) Nickel-filtered Cu$K\alpha$-radiation ($\lambda = 1.54178$ Å) and 1° slits were employed in all experiments.

Special attention was paid to the preparation of the specimens. Fine powders of each compound were obtained by careful crushing followed by light grinding in a motor-driven agate mortar. After this treatment the powders easily passed through a 325-mesh screen. The powders could then be pressed into the flat sample-holder, thus making the use of an agglutinant superfluous. The results showed no indication of preferential orientation and good reproducibility was obtained whenever two or more mounts of the same sample were measured.

The intensity data were corrected for the combined Lorentz and polarization factor and partially overlapping reflections were resolved graphically. For the calculation of F_c-values the atomic scattering factors were taken from Hanson *et al.*[15] The refinements were carried out according to the programme of Gantzel *et al.*[16] The agreement between F_o and F_c is expressed by the reliability index $R = \sum||F_o| - |F_c||/\sum|F_o|$, including the undetected reflections.

RESULTS AND DISCUSSION

(i) *Unit cell and space group.* The unit cell dimensions of the compounds subjected to this study [1] are listed in Table 1. None of the compounds has an appreciable range of homogeneity and they all assume the stoichiometric 1:2 composition.[1] The unit cells of all these compounds contain $2TX_2$-groups according to comparisons of observed and calculated densities.

The only systematic extinctions in the X-ray powder diffraction data are of the type $0kl$ absent when $k+l=2n+1$ and $h0l$ absent when $h+l=2n+1$. These conditions also characterize the possible space groups (*Pnnm* and *Pnn*2)

Table 1. Unit cell dimensions for $CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, β-$NiAs_2$, $NiSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$, together with their corresponding standard deviations. (Quoted from Holseth and Kjekshus.[1])

Compound	a (Å)	b (Å)	c (Å)
$CrSb_2$	6.0275 ± 0.0006	6.8738 ± 0.0009	3.2715 ± 0.0007
FeP_2	4.9732 ± 0.0005	5.6570 ± 0.0005	2.7235 ± 0.0003
$FeAs_2$	5.3013 ± 0.0007	5.9859 ± 0.0006	2.8822 ± 0.0003
$FeSb_2$	5.8328 ± 0.0005	6.5376 ± 0.0005	3.1973 ± 0.0003
β-$NiAs_2$	4.7583 ± 0.0008	5.7954 ± 0.0007	3.5449 ± 0.0004
$NiSb_2$	5.1837 ± 0.0006	6.3184 ± 0.0010	3.8408 ± 0.0006
RuP_2	5.1173 ± 0.0006	5.8932 ± 0.0007	2.8711 ± 0.0005
$RuAs_2$	5.4302 ± 0.0007	6.1834 ± 0.0007	2.9714 ± 0.0004
$RuSb_2$	5.9524 ± 0.0006	6.6737 ± 0.0009	3.1803 ± 0.0005
OsP_2	5.1001 ± 0.0010	5.9012 ± 0.0014	2.9182 ± 0.0008
$OsAs_2$	5.4129 ± 0.0010	6.1910 ± 0.0010	3.0126 ± 0.0004
$OsSb_2$	5.9409 ± 0.0009	6.6880 ± 0.0008	3.2112 ± 0.0003

for FeS_2-m. According to Buerger[3] the atomic arrangement of the FeS_2-m type structure (Fig. 1) is as follows in terms of the highest symmetric space group $Pnnm$:

$2T$ in (a) $0,0,0$; $\frac{1}{2},\frac{1}{2},\frac{1}{2}$
$4X$ in (g) $\pm(x,y,0;\ \frac{1}{2}+x,\frac{1}{2}-y,\frac{1}{2})$

Thus, while the positions of the metal atoms are fixed, two parameters (x and y) are necessary to establish the positions of the non-metal atoms for each compound.

(ii) *Refinement of the structures.* Since there was no decisive reason to question the overall correctness of the FeS_2-m type structure for any of the compounds, least squares refinements were started at once. These calculations were considered straightforward and for the purpose of simplification the same set x,y of input parameters was used for all compounds. One of the first set of data to be processed belonged to β-$NiAs_2$ where the calculations con-

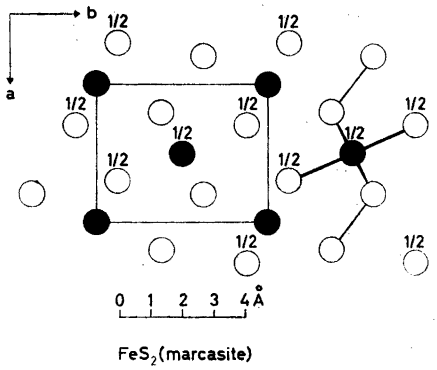


Fig. 1. The FeS_2-m type crystal structure projected along [001]. The filled and open circles represent the metal (T) and the non-metal (X) atoms, respectively.

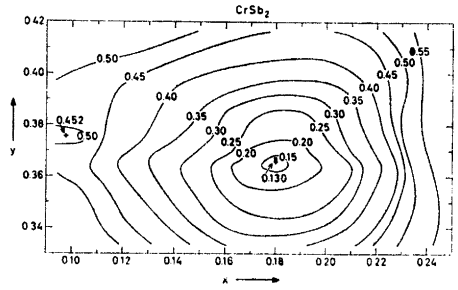
verged to $x=0.148$, $y=0.378$, $B_T=3.9$ Å^2, and $B_X=2.7$ Å^2 with $R=0.201$. This R-value was surprisingly high since the intensity data for β-$NiAs_2$ were considered to be very good. The suspicion consequently arose that there might be a second minimum in the function $R(x,y,B_T,B_X)$, somewhere near to the first. The suspicion was in fact confirmed by calculations based on other input parameters which gave another termination point with a considerably lower R (Table 2).

In order to check and avoid this problem more systematically for all compounds a computer programme was written to survey the function $R(x,y)$. Constant values for the thermal parameters $B_T=B_X=0.5$ Å^2 were chosen in order to simplify the calculations and this simplification furthermore permits the results to be visualized graphically. The assumption of constant B-values is not a serious limitation since R generally is known to be a slowly varying function of the thermal parameters.

Making the reasonable assumption that the bonding interatomic $T-X$ and/or $X-X$ distances (*vide infra*) have to be within certain limits, the ranges of x and y to be surveyed are restricted to $0.09<x<0.25$ and $0.33<y<0.42$. R-values were calculated for each of the compounds by varying x and y in steps of 0.0002 throughout these ranges. The resulting $R(x,y)$ maps (Fig. 2) show substantial variations within the ranges of x and y and from one compound to the other. Secondary (false) minima are found for $CrSb_2$, β-$NiAs_2$, $NiSb_2$, $RuSb_2$, and OsP_2, their positions being indicated in Fig. 2. However, excepting the case of OsP_2, the R-values of the secondary minima are so high that they scarcely could be mistaken for the primary (absolute) minima. In accordance with convention the primary minima indicate the most probable values for the positional parameters (see Fig. 2) and their error limits are related to the curvatures of the R-surfaces in the vicinity of these minima. The "watersheds" in Fig. 2 indicate how the refinement process according to the method of least squares will be influenced by the choice of input parameters for x and y.

The positional and thermal parameters with the corresponding standard deviations found according to the least squares calculations are listed in Table 2. The refinements have been started on the appropriate sides of the "watersheds", whenever secondary minima have been detected in the $R(x,y)$ maps. The final x,y parameters obtained by the least squares refinements have also been indicated on Fig. 2 showing remarkably good agreements with those found from the $R(x,y)$ maps. The thermal parameters (B_T and B_X) given in Table 2, however, differ considerably from the constant value 0.5 Å^2 used in the calculations of the $R(x,y)$ maps (*vide supra*).

Good agreements for the positional parameters of $CrSb_2$, $FeAs_2$, $FeSb_2$, and $NiSb_2$ have also been obtained by least squares refinements of the powder neutron diffraction data for these compounds.[17] Except for the compound $FeAs_2$, the previously published [8-14] x,y parameters agree reasonably well with those listed in Table 2. The value $x=0.175\pm0.005$ for $FeAs_2$ found by Buerger [11] is, however, significantly different from that given in Table 2. Buerger examined the mineral loellingite, which might have contained some sulphur (*cf. e.g.* Neumann *et al.*[18]).


CrSb2
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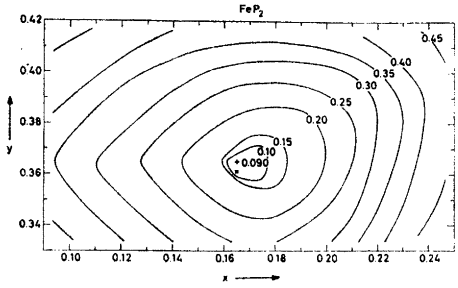
x
y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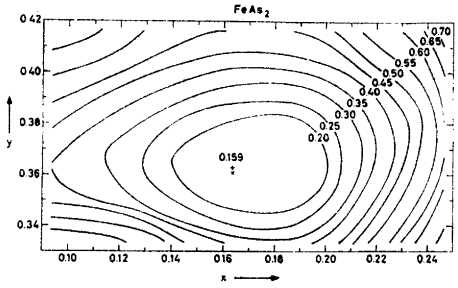
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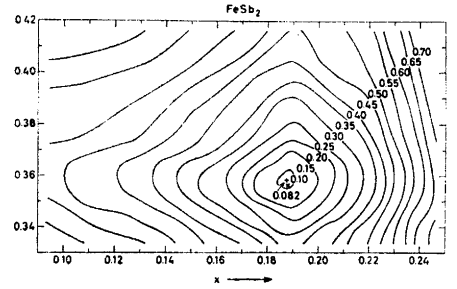
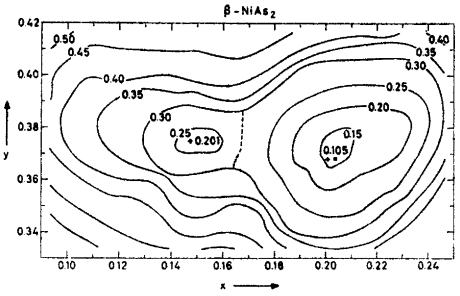
x
y


FeSb2
0.082
x
y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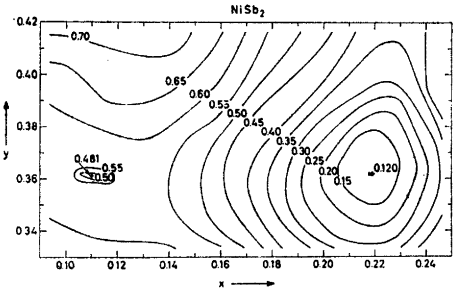
0.105
x
y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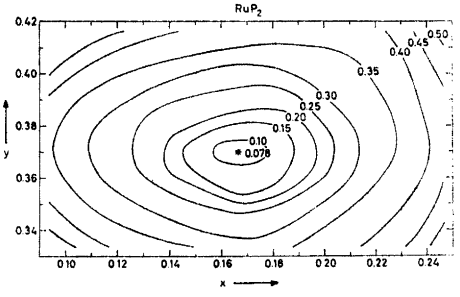
0.120
x
y


RuP2
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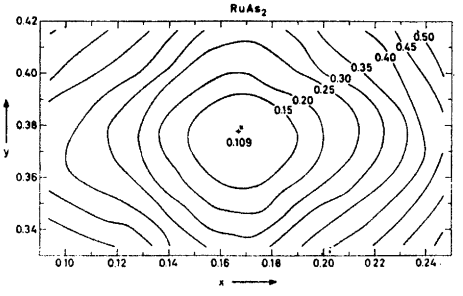
x
y


RuAs2
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x
y

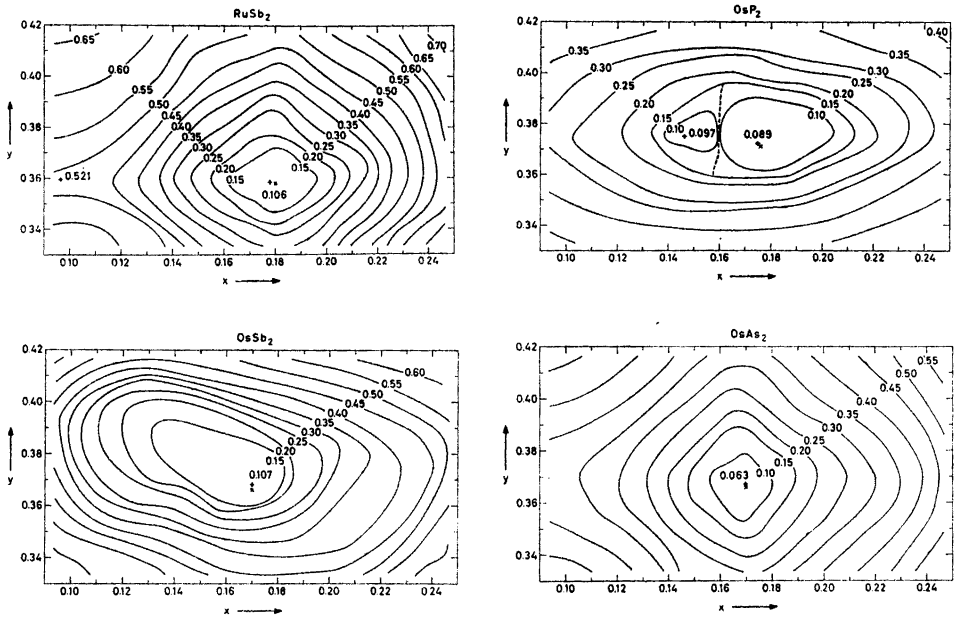

Fig. 2. Projection on the x,y plane of $R(x,y)$ for $CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, β-$NiAs_2$, $NiSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$. Contours (solid curves) are drawn at constant values of R. The broken curves indicate the location of the "watersheds". The positions of the minima in $R(x,y)$ are given by +, and × indicates the final x,y parameters according to the least squares calculations.

Table 2. Final parameters for $CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, β-$NiAs_2$, $NiSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$, together with their corresponding standard deviations. (According to the least squares refinements.)

Compound	x	y	B_T (Å²)	B_X (Å²)	R
$CrSb_2$	0.180±0.001	0.367±0.001	5.4±0.7	2.6±0.4	0.129
FeP_2	0.165±0.003	0.361±0.001	1.6±0.3	1.5±0.4	0.115
$FeAs_2$	0.164±0.002	0.361±0.002	1.6±0.7	4.1±0.7	0.158
$FeSb_2$	0.188±0.001	0.357±0.001	3.2±0.4	2.7±0.3	0.082
β-$NiAs_2$	0.203±0.001	0.368±0.001	4.0±0.3	2.4±0.2	0.105
$NiSb_2$	0.219±0.001	0.362±0.001	3.8±0.3	2.1±0.2	0.113
RuP_2	0.167±0.003	0.370±0.002	5.1±0.2	1.8±0.3	0.080
$RuAs_2$	0.168±0.001	0.379±0.001	1.5±0.2	1.8±0.2	0.108
$RuSb_2$	0.180±0.001	0.358±0.001	6.0±0.3	2.6±0.3	0.106
OsP_2	0.176±0.002	0.371±0.002	2.4±0.1	1.5±0.1	0.089
$OsAs_2$	0.170±0.001	0.366±0.001	2.4±0.1	2.2±0.1	0.062
$OsSb_2$	0.180±0.001	0.359±0.001	2.5±0.2	1.7±0.3	0.105

Table 3. Some important interatomic distances and angles in the crystal structures of $CrSb_2$, FeP_2, $FeAs_2$, $FeSb_2$, β-$NiAs_2$, $NiSb_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$. (The indicated error limits correspond to the standard deviations in Table 1 or 2.)

Interatomic distances (Å)

Compound	Bonding interatomic distances			Possible bonding interatomic distances		Shortest interatomic distances neglected as bonding		
	$T-X$ (2) $X-T$ (1)	$T-X$ (4) $X-T$ (2)	$X-X$ (1)	$X-X$ (2)	$T-T$ (2)	$T-X$	$X-X$	$T-T$
$CrSb_2$	2.746±0.008	2.689±0.009	2.84±0.02	—	—	4.271±0.005	3.2715±0.0007	3.2715±0.0007
FeP_2	2.20 ±0.01	2.29 ±0.02	2.27±0.04	—	2.7235±0.0003	3.502±0.009	2.7235±0.0003	4.0047±0.0005
$FeAs_2$	2.33 ±0.02	2.44 ±0.01	2.41±0.03	—	2.8822±0.0003	3.71 ±0.01	2.8822±0.0003	4.2498±0.0005
$FeSb_2$	2.575±0.006	2.598±0.005	2.89±0.01	3.1973±0.0003	—	4.105±0.004	3.61 ±0.01	3.1973±0.0003
β-$NiAs_2$	2.337±0.007	2.398±0.006	2.45±0.02	—	—	3.785±0.006	3.23 ±0.01	3.5449±0.0004
$NiSb_2$	2.553±0.006	2.563±0.004	2.86±0.01	—	—	4.188±0.006	3.40 ±0.01	3.8408±0.0006
RuP_2	2.34 ±0.02	2.35 ±0.02	2.30±0.04	—	2.8711±0.0005	3.71 ±0.01	2.8711±0.0005	4.1581±0.0006
$RuAs_2$	2.52 ±0.01	2.453±0.009	2.36±0.02	—	2.9714±0.0004	3.893±0.008	2.9714±0.0004	4.3746±0.0006
$RuSb_2$	2.618±0.007	2.656±0.005	2.86±0.01	3.1803±0.0003	—	4.119±0.004	3.67 ±0.01	3.1803±0.0003
OsP_2	2.37 ±0.02	2.33 ±0.01	2.35±0.02	—	2.9182±0.0008	3.76 ±0.01	2.9182±0.0008	4.164 ±0.001
$OsAs_2$	2.445±0.006	2.479±0.004	2.48±0.01	—	3.0126±0.0004	3.880±0.004	3.0126±0.0004	4.3790±0.0008
$OsSb_2$	2.628±0.007	2.661±0.005	2.85±0.02	3.2112±0.0003	—	4.150±0.004	3.68 ±0.01	3.2112±0.0003

Interatomic angles (°)

Compound	Type							
	$X-T-X$ (2)	$X-T-X$ (4)	$X-T-X$ (4)	$X-T-X$ (2)	$T-X-T$ (1)	$T-X-T$ (2)	$X-X-T$ (1)	$X-X-T$ (2)
$CrSb_2$	74.9±0.4	88.3±0.5	91.7±0.5	105.1±0.4	74.9±0.4	126.6±0.5	106.8±0.4	109.2±0.4
FeP_2	72.9±0.7	87.3±0.8	92.7±0.8	107.1±0.9	72.9±0.7	126.1±0.6	111.9±0.9	106.7±0.8
$FeAs_2$	72.5±0.4	87.5±0.6	92.5±0.6	107.5±0.4	72.5±0.4	126.1±0.8	111.8±0.9	107.0±0.7
$FeSb_2$	75.9±0.3	88.3±0.3	91.7±0.4	104.1±0.5	75.9±0.3	128.7±0.5	105.4±0.5	107.3±0.4
β-$NiAs_2$	95.3±0.3	87.2±0.3	92.8±0.3	84.7±0.3	95.3±0.3	122.3±0.4	104.5±0.5	105.3±0.5
$NiSb_2$	97.0±0.3	87.0±0.3	93.0±0.3	83.0±0.3	97.0±0.3	123.9±0.3	101.1±0.4	104.1±0.3
RuP_2	75.1±0.8	87.8±0.7	92.2±0.6	104.9±0.6	75.1±0.8	124.5±0.7	110.5±0.8	108.8±0.8
$RuAs_2$	74.5±0.4	89.0±0.5	91.0±0.5	105.4±0.3	74.5±0.4	123.4±0.5	108.1±0.6	112.0±0.6
$RuSb_2$	73.6±0.2	88.2±0.2	91.8±0.2	106.4±0.3	73.6±0.2	128.2±0.3	107.3±0.2	107.5±0.2
OsP_2	77.5±0.6	88.1±0.6	91.9±0.5	102.5±0.5	77.5±0.6	124.8±0.8	108.0±0.8	109.2±0.9
$OsAs_2$	74.8±0.2	87.8±0.3	92.2±0.3	105.2±0.2	74.8±0.2	125.5±0.3	109.9±0.3	108.1±0.3
$OsSb_2$	74.2±0.2	88.1±0.2	91.9±0.3	105.8±0.4	74.2±0.2	127.9±0.4	107.4±0.4	107.5±0.4

Attempts have been made to refine the structure factor data for all compounds in terms of space group *Pnn*2. However, the X-ray powder data were quite unsuitable for removal of the space group ambiguity, since only a few reflections with $l \neq 0$ were experimentally accessible. The least squares calculations invariably gave large standard deviations for the z parameters and for β-$NiAs_2$, $RuAs_2$, $RuSb_2$, and OsP_2 the refinements did not even converge.

(iii) *Interatomic distances and angles.* Some important interatomic distances and angles calculated from the data in Tables 1 and 2 are listed in Table 3. In the FeS_2-*m* type structure (Fig. 1) each T atom is octahedrally coordinated to six near X atoms and each X atom is surrounded by three near T and one near X atoms located at the corners of a tetrahedron. Neither of these coordination polyhedra are of regular shapes, *cf.* Table 3.

The lengths of the shortest interatomic $T-X$, $X-T$, and $X-X$ distances (Table 3) definitely confirm that these represent bonding distances. As indicated in Table 3, there occur also some other, relatively short interatomic $X-X$ or $T-T$ distances which cannot safely be neglected as possible bonding distances. This possibility was first pointed out by Buerger [4] and a modified version has been advanced by Pearson.[7] The shortest interatomic $T-T$ distances in FeP_2, RuP_2, and OsP_2 have sizes which might give confidence in Pearsons model, whereas the corresponding distances in the antimonides $FeSb_2$, $RuSb_2$, and $OsSb_2$ appear to be too long for bonding. The interpretation towards a general $T-T$ bonding in all these compounds is opposed by the monotonic (almost linear) increase of the length of the shortest $T-T$ distance with increasing diameter of the X atom in the sequences $FeP_2-FeAs_2-FeSb_2$, $RuP_2-RuAs_2-RuSb_2$, and $OsP_2-OsAs_2-OsSb_2$. The comparatively short interatomic distances within the linear $T-T$ chains parallel to [001] may accordingly only be caused by the geometry of the FeS_2-*m* type crystal structure. Further experiments are necessary in order to prove or disprove the physical reality of the possible bonding interatomic $X-X$ and $T-T$ distances (Table 3).

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