Compounds with the Marcasite Type Crystal Structure. XII.
Structural Data for RuP₂, RuAs₂, RuSb₂, OsP₂, OsAs₂, and OsSb₂

ARNE KJEKSHUS, a TROND RAKKE a and ARNE F. ANDRESEN b

a Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway and b Institutt for Atomenergi, Kjeller, Norway

The Fe₅S₄·m type structures of RuP₂, RuAs₂, RuSb₂, OsP₂, OsAs₂, and OsSb₂ have been refined by powder neutron diffraction/profile refinement methods, and a brief discussion of structural data for Fe₅S₄·m type compounds is presented.

In the second paper 1 of this series, structural data on a number of binary compounds with the Fe₅S₄·m (m = marcasite) type crystal structure were reported. During a continuation 2 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 RuAs₂ and OsP₂, 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. RuP₂, RuAs₂, RuSb₂, OsP₂, OsAs₂, and OsSb₂ (data for Fe₅As₂, NiAs₂, and NiSb₂ were included in Ref. 2).

EXPERIMENTAL

The compounds RuP₂, RuAs₂, RuSb₂, OsP₂, OsAs₂, and OsSb₂ were prepared by heating stochiometric 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-

Acta Chem. Scand. A 31 (1977) No. 4
Table 1. Structural data for RuP₂, OsP₂, RuAs₂, OsAs₂, RuSb₂, and OsSb₂.

<table>
<thead>
<tr>
<th>Notation</th>
<th>RuP₂</th>
<th>OsP₂</th>
<th>RuAs₂</th>
<th>OsAs₂</th>
<th>RuSb₂</th>
<th>OsSb₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>a(Å)</td>
<td>5.1169(12)</td>
<td>5.1012(14)</td>
<td>5.4279(7)</td>
<td>5.4115(15)</td>
<td>5.8514(10)</td>
<td>5.9411(10)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>5.8015(11)</td>
<td>5.9022(13)</td>
<td>6.1834(8)</td>
<td>6.1900(16)</td>
<td>6.8743(12)</td>
<td>6.6873(12)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>2.8709(7)</td>
<td>2.9183(8)</td>
<td>2.9685(6)</td>
<td>3.0127(7)</td>
<td>3.1790(7)</td>
<td>3.2109(7)</td>
</tr>
<tr>
<td>z</td>
<td>0.1617(7)</td>
<td>0.1634(10)</td>
<td>0.1700(7)</td>
<td>0.1701(9)</td>
<td>0.1812(6)</td>
<td>0.1848(7)</td>
</tr>
<tr>
<td>y</td>
<td>0.3727(5)</td>
<td>0.3723(6)</td>
<td>0.3666(5)</td>
<td>0.3671(5)</td>
<td>0.3590(5)</td>
<td>0.3506(6)</td>
</tr>
<tr>
<td>(d_{1})</td>
<td>(T - X(Å) \times 4)</td>
<td>2.371(3)</td>
<td>2.376(4)</td>
<td>2.468(3)</td>
<td>2.477(4)</td>
<td>2.648(3)</td>
</tr>
<tr>
<td>(d_{2})</td>
<td>(T - X(Å) \times 2)</td>
<td>2.347(3)</td>
<td>2.350(4)</td>
<td>2.448(3)</td>
<td>2.452(3)</td>
<td>2.628(3)</td>
</tr>
<tr>
<td>(l)</td>
<td>(X - X(Å) \times 1)</td>
<td>2.234(9)</td>
<td>2.248(12)</td>
<td>2.475(10)</td>
<td>2.469(12)</td>
<td>2.863(10)</td>
</tr>
<tr>
<td>(\theta_{1})</td>
<td>(X - T - X(°) \times 4)</td>
<td>87.79(10)</td>
<td>87.7(1)</td>
<td>87.94(10)</td>
<td>87.87(12)</td>
<td>88.28(10)</td>
</tr>
<tr>
<td>(\theta_{2})</td>
<td>(X - T - X(°) \times 2)</td>
<td>92.21(10)</td>
<td>92.3(1)</td>
<td>92.06(10)</td>
<td>92.13(12)</td>
<td>91.72(10)</td>
</tr>
<tr>
<td>(\theta_{3})</td>
<td>(X - T - X(°) \times 2)</td>
<td>74.53(7)</td>
<td>75.8(1)</td>
<td>73.94(7)</td>
<td>74.93(9)</td>
<td>73.78(7)</td>
</tr>
<tr>
<td>(\psi_{1})</td>
<td>(T - X - T(°) \times 2)</td>
<td>105.47(7)</td>
<td>104.2(1)</td>
<td>106.06(7)</td>
<td>105.07(9)</td>
<td>106.22(7)</td>
</tr>
<tr>
<td>(\psi_{2})</td>
<td>(T - X - X(°) \times 1)</td>
<td>123.61(10)</td>
<td>123.6(1)</td>
<td>125.67(10)</td>
<td>125.35(11)</td>
<td>128.18(10)</td>
</tr>
<tr>
<td>(\psi_{3})</td>
<td>(T - X - X(°) \times 2)</td>
<td>74.53(7)</td>
<td>75.8(1)</td>
<td>73.94(10)</td>
<td>74.93(9)</td>
<td>73.78(7)</td>
</tr>
<tr>
<td>(\psi_{4})</td>
<td>(T - X - X(°) \times 1)</td>
<td>109.18(12)</td>
<td>108.9(2)</td>
<td>108.56(12)</td>
<td>108.43(12)</td>
<td>107.83(11)</td>
</tr>
<tr>
<td>(\psi_{5})</td>
<td>(T - X - X(°) \times 1)</td>
<td>111.64(17)</td>
<td>111.4(2)</td>
<td>109.56(16)</td>
<td>109.74(20)</td>
<td>106.88(14)</td>
</tr>
</tbody>
</table>
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$_\alpha$ 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.

*Acta Chem. Scand. A 31 (1977) No. 4*
Fig. 1b. Dependence of octahedral angles for compounds with FeS$_2$m type structure.
Fig. 1c. Dependence of tetrahedral angles for compounds with FeS$_x$-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 \( b_{Ru} = 0.73 \), \( b_{Os} = 1.07 \), \( b_{P} = 0.51 \), \( b_{As} = 0.64 \), and \( b_{Se} = 0.564 \), all \( \times 10^{-12} \text{ cm} \) were taken from Ref. 5. In all cases, the least squares profile refinement programme of Rietveld was applied in the final fitting of the variable parameters.

RESULTS AND DISCUSSION

The (orthorhombic) unit cell dimensions, positional parameters \((x, y)\), 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\(^7\) 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 RuAs\(_4\) \((y)\) and OsP\(_4\) \((x)\), as singled out in advance.\(^8\) The earlier data\(^1\) for RuP\(_4\) \((x)\) and OsSb\(_4\) \((x)\) 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_x; \text{T = transition element, } X = \text{pnigogen or chalcogen}) \text{ FeS}_2\text{-m type compounds (Refs. 2, 7–11 and including unpublished data for “CrAs\(_2\)” extrap}}

from \(\text{CrAs\(_2\)}\)), 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 homologous (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 \(\varphi_1\), \(\varphi_2\), and \(\varphi_3\). (The bond angle notations are defined in Table 1.) In Fig. 1b the behaviour of FeSb\(_4\) 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 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\text{-m type atomic arrangement. In a revaluation of geometrical aspects, a more thorough analysis of the \(\text{FeS}_2\text{-m type atomic architecture must be performed. Suitable starting points are the coordination polyhedra of } T \text{ and } X, \text{ but packing features are probably also of importance. An extension of the “λ-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\text{-m type structure.}

Acta Chem. Scand. A 31 (1977) No. 4
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 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 MnP$_4$, Jeitschko and Donohue$^{14}$ propose that universal $T-T$ bonding is the stabilizing element in the class A, FeS$_2$-m type structure (where, according to them, each $T$ forms two $\sigma$ and two $\pi$ $T-T$ half-bonds) and the CoSb$_4$ 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 CoSb$_4$ type structure has already been announced by both Goodenough$^{15}$ and two of the present authors$^{16}$ and will not be recapitulated here.) Apart from the comparatively short $c$ axes for class A compounds, [ranging from 2.72 Å (FeP$_4$) to 3.27 Å (CrSb$_4$)], 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 CrSb$_4$.$^{11}$

(2) The shortest $T-T$ distances (c) in homologous series TP$_4$-TA$_8$-TSb$_4$ and TS$_4$-TE$_8$-TE$_2$ show consistent and virtually parallel dependencies (q.e., 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$_4$-TA$_8$-TSb$_4$ ($T$=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 $X$=Sb ($c$=3.18 to 3.27 Å) where Sb itself must be regarded as comparatively large

$^{*}$ Jeitschko and Donohue are aware of an apparent exception (from their $T-T$ bonding assumption), "Mo$_2$As$_4"$, which they try to explain away. However, "Mo$_2$As$_4"$ is in reality non-existent (confused with Fe$_3$As$_2$ as demonstrated in Ref. 2) and represents no problem in this connection.

**Acknowledgement.** The assistance of cand. mag. Per G. Peterzén in the neutron diffraction measurements is greatly appreciated.

REFERENCES

5. The 1975-compilation of the Neutron Diffraction Commission.

Received November 19, 1976.