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Compounds with the Marcasite Type Crystal Structure. IX. Structural Data for $FeAs_2$, $FeSe_2$, $NiAs_2$, $NiSb_2$, and $CuSe_2$

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The FeS_2-*m* type structures of $FeAs_2$, $FeSe_2$, $NiAs_2$, $NiSb_2$, and $CuSe_2$ have been redetermined by powder neutron diffraction/profile refinement methods, and a brief status report for structural data in this class is presented. An important result of the study is the identification of the assumed compound $Mo_{2/3}As_2$ as $FeAs_2$.

Except for the parameter-free structure types, few if any classes of compounds have a better covering with structural data than those with the FeS_2-*m* (*m* = marcasite) type (*cf.* Ref. 1). However, the quality of the data varies, mainly due to the experimental technique used. Among the binary compounds (TX_2; T = transition metal, X = main group V or VI element) with the FeS_2-*m* type structure, $FeSe_2$[2,3] and $CuSe_2$[4] appear to take extreme values (*viz.* relative to the commonly assumed[5] size of X) for the $X-X$ bond length. In order to ascertain that these distinctions are rooted in realities and not in experimental errors, redeterminations were called for, the results of which are being reported here.

In the course of the study, $FeAs_2$[6,7] was included motivated by its apparent deviation from trends outlined by isostructural compounds. The results for $FeAs_2$ provoked, in turn, renewed interest in other compounds, such as $NiAs_2$[6] and $NiSb_2$[6,7], results for which are also included in this report.

EXPERIMENTAL

The compounds were prepared by heating stoichiometric quantities of the elements (in the form of turnings from Fe, Ni, and Cu rods and crushed As, Sb, and Se from Johnson Matthey & Co., except for Cu (American Smelting and Refining Co.) and Se (Bolidens Gruvaktiebolag); spectroscopically standardized and of purity better than 99.995 %) in evacuated, sealed silica tubes. Samples of $FeSe_2$ were maintained for one week at 800 °C, slowly cooled, crushed, reannealed twice at 500 °C for, in all, six weeks, then cooled to 250 °C over a period of nine weeks, and finally quenched to room temperature. The $CuSe_2$ samples were prepared at 300 °C for two weeks, cooled to 200 °C over a further three week period, and quenched to room temperature. The same heating procedure was repeated from 280 °C after intervening crushing of the sample. (A preparation temperature of 200 °C, as suggested by Gattow,[4] appears to be too low since all samples synthesized at this temperature were invariably found *inter alia* to contain substantial amounts of the CuSe phase.)

The $NiSb_2$ sample was prepared as described previously,[8] and although $FeAs_2$ and $NiAs_2$ (*viz.* β-$NiAs_2$) can be synthesized according to the earlier procedure,[8] it was found more convenient (particularly in view of the relatively large sample quantities required) to make alterations in the procedure by which it became possible to reduce the number of intervening crushings as well as the overall annealing periods. Thus, $FeAs_2$ was made by two successive annealings (with intervening crushing) at 800 °C, followed by slow cooling to 600 °C and quenching to room temperature. The alteration introduced for $NiAs_2$ consisted of the initial preparation of NiAs by annealing at 850 °C. Subsequently, $NiAs_2$ was readily made by adding the appropriate amount of As, annealing at 800 °C, slow cooling to 600 °C, and quenching to room temperature.

Attempts have also been made to prepare FeS_2-*m* type phases with the following compositions: $OsTe_2$, $CoSe_2$, CuS_2, CuSSe, CuSeTe, and $CuTe_2$ by the sealed silica capsule technique under a variety of different thermal conditions. Although samples with compositions $OsTe_2$ and

$CoSe_2$ are readily made, all $CoSe_2$ samples were found to contain only the FeS_2-*p* (*p* = pyrite) type modification, while some $OsTe_2$ samples contained mixtures of FeS_2-*p* and FeS_2-*m* type modifications. The latter finding is in agreement with Ref. 9. The FeS_2-*m* type modification of $OsTe_2$ can be made to disappear by the use of an annealing temperature ≥ 550 °C. Attempts to remove the FeS_2-*p* type modification through lowering of the annealing temperature failed. This finding probably reflects an extremely sluggish transition, an inference open for verification. The reaction products obtained for the mentioned Cu samples were CuS + S, CuS + Se, CuSe + Te, or CuTe + Te, displacement reactions being observed for CuSe + S → CuS + Se and CuTe + Se → CuSe + Te. (Compounds with the compositions CuS_2, CuSSe, CuSeTe, and $CuTe_2$ can be synthesized [10] under high pressure conditions, but with the FeS_2-*p* rather than the FeS_2-*m* type structure.)

The experimental details concerning X-ray and neutron diffraction, density measurements, and computations are described in Ref. 7 and references therein.

RESULTS AND DISCUSSION

(i) *Space group.* One question which has received attention [11–13] at this Institute in recent years, concerns whether there is a mirror plane perpendicular to [001] in the FeS_2-*m* type structure. If the object of the present study had been to pursue this problem further, single crystal samples would have been called for. However, recent results [13] for the prototype compound suggest very strongly that the mirror plane is present or that the deviation is negligible for conventional structural considerations. The reasons for the first erroneous inferences [11,12] could be attributed [13] to the unforeseen influence on the final results of inappropriate absorption corrections. (Now we know that a spherically shaped crystal specimen is required in order to perform this task accurately.) On this background it seems highly probable that not only the prototype, but all compounds with the FeS_2-*m* type structure belong to space group *Pnnm*, at least to a very good approximation.

In this fortunate situation, single crystal specimens are no longer needed, since present experience shows that powder samples examined by neutron diffraction with subsequent least squares profile refinement provide overall structural data to an accuracy almost rivalling those obtained by single crystal techniques.

(ii) *Redetermined data.* The redetermined structural data for $FeAs_2$, $FeSe_2$ ($d_{pycn.}$ = 7.09 g cm^{-3}), $NiAs_2$, $NiSb_2$, and $CuSe_2$ ($d_{pycn.}$ = 6.24 g cm^{-3}) obtained at room temperature, are compiled in Table 1, the final profile reliability factors ranging between 2.7 and 4.3 %. Comparison shows excellent agreement with the positional parameters obtained by Buerger [14] for $FeAs_2$ ($x = 0.175$, $y = 0.361$), whereas deviating values in preceding papers [6,7] are due to

Table 1. Structural data for $FeAs_2$, $FeSe_2$, $NiAs_2$, $NiSb_2$, and $CuSe_2$.

	$FeAs_2$	$FeSe_2$	$NiAs_2$	$NiSb_2$	$CuSe_2$
a (Å)	5.3012(6)	4.8002(4)	4.7582(7)	5.1823(5)	5.0226(7)
b (Å)	5.9858(5)	5.7823(5)	5.7949(8)	6.3168(7)	6.1957(7)
c (Å)	2.8822(4)	3.5834(4)	3.5440(4)	3.8403(5)	3.7468(6)
x	0.1763(10)	0.2127(6)	0.2017(8)	0.2189(10)	0.1835(5)
y	0.3624(7)	0.3701(5)	0.3691(7)	0.3593(8)	0.3849(4)
4 *T*–*X* (Å)	2.388(4)	2.383(2)	2.394(3)	2.569(3)	2.558(2)
2 *T*–*X* (Å)	2.362(4)	2.371(3)	2.344(4)	2.537(5)	2.557(3)
1 *X*–*X* (Å)	2.492(7)	2.535(4)	2.447(6)	2.882(7)	2.331(4)
4 *X*–*T*–*X* (°)	88.1(2)	87.98(8)	87.3(1)	86.8(1)	87.94(7)
4 *X*–*T*–*X* (°)	91.9(2)	92.02(8)	92.7(1)	93.2(1)	92.06(7)
2 *X*–*T*–*X* (°)	74.3(1)	97.53(7)	95.5(1)	96.7(1)	94.15(6)
2 *X*–*T*–*X* (°)	105.7(1)	82.47(7)	84.5(1)	83.3(1)	85.85(6)
2 *T*–*X*–*T* (°)	127.0(1)	122.26(8)	122.1(1)	124.3(1)	118.95(7)
1 *T*–*X*–*T* (°)	74.3(1)	97.53(7)	95.5(1)	96.7(1)	94.15(6)
2 *T*–*X*–*X* (°)	108.1(2)	106.23(9)	105.6(1)	103.5(2)	108.71(8)
1 *T*–*X*–*X* (°)	108.1(2)	100.83(12)	104.2(2)	101.5(2)	106.60(11)

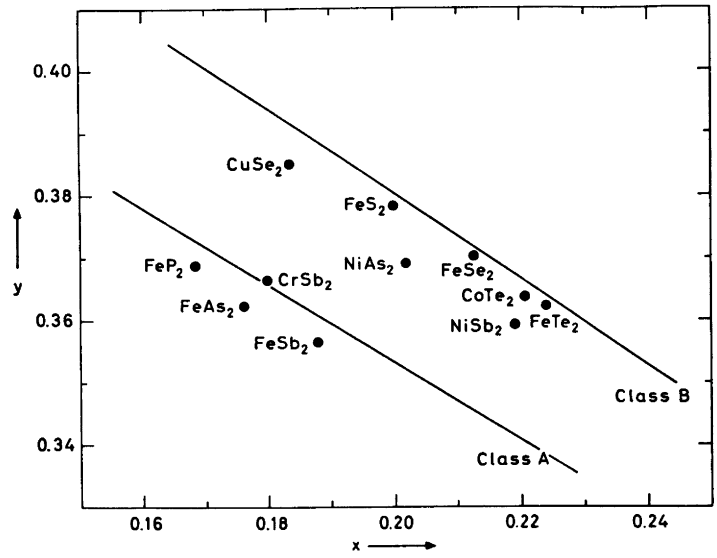

Fig. 1. Positional parameters for compounds with FeS_2-*m* type structure, eqns. 4 and 5 being included for comparison.

unfortunate copying mistakes. The earlier data for $FeSe_2$ ($x = 0.21$, $y = 0.37$)[2] and $CuSe_2$ ($x = 0.17$, $y = 0.38$)[4] concur reasonably well with the present ones when the limited accuracies of the studies are taken into account.

On the basis of the revised structural data for $FeSe_2$ and $CuSe_2$, a comment is called for on the previously inferred [15] relationships between $T-X$ and $X-X$ bond distances *versus* localized configurations (d^j) of essentially non-bonding electrons on T. However, although the new data to some extent follow the same trends as indicated on Figs. 1 and 2 in Ref. 15, this aspect deserves further attention and is conveniently included in a forthcoming, more general discussion of compounds with the FeS_2-*p*, FeS_2-*m*, and $CoSb_2$ structure types.

(iii) *Structural status report.* The data in Table 1 together with those for $CrSb_2$,[7] FeP_2,[16] $FeSb_2$,[11] FeS_2,[13] $FeTe_2$,[12] and $CoTe_2$[12] give rise to an interesting finding. (The earlier assignment of space group *Pnn*2 to $FeSb_2$, $FeTe_2$, and $CoTe_2$ is probably incorrect; this is open for experimental verification.) Using as the only assumption that the two non-equivalent $T-X$ bond distances

$$d_1 = [(1/2+x)^2a^2 + (1/2-y)^2b^2 + (c/2)^2]^{\frac{1}{2}} \quad (1)$$

$$d_2 = [x^2a^2 + y^2b^2]^{\frac{1}{2}} \quad (2)$$

of the FeS_2-*m* type structure (according to space group *Pnnm*) are equal, the relation

$$y = \frac{1}{4}\left[1 + \left(\frac{a}{b}\right)^2 + \left(\frac{c}{b}\right)^2\right] - \left(\frac{a}{b}\right)^2 x \quad (3)$$

results. When the empirical average values for the axial ratios [1] of classes A and B are substituted into Eqn. 3, the expressions

$$\text{class A: } y = 0.502 - 0.774x \quad (4)$$

$$\text{class B: } y = 0.519 - 0.691x \quad (5)$$

are obtained. As illustrated in Fig. 1, all well-determined structures (*viz.* those examined by single crystal X-ray or powder neutron/profile refinement techniques) closely follow these semi-empirical relations. An interesting detail to which attention may be drawn, is the fact that the two series of FeX_2 compounds trace out virtually parallel lines to those described by eqns. 4 and 5. (Concerning more details in $T-X$ bond distances, $CrSb_2$ is unique in exhibiting four short and two longer $T-X$ bonds.)

Of the binary compounds reported with the FeS_2-*m* type structure, those lacking in Fig. 1 are: NaO_2, $Mo_{2/3}As_2$, RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, $OsSb_2$, $OsTe_2$, and $CoSe_2$. Reasons for leaving out $Mo_{2/3}As_2$ are discussed separately in section iv. The present attempts to prepare

pure $OsTe_2$ with FeS_2-*m* type structure were unsuccessful (thus concurring with the earlier findings [9]) and information on the FeS_2-*m* type modification of $CoSe_2$ originates exclusively from a rather inaccurately characterized mineral sample.[17] Although data for RuP_2, $RuAs_2$, $RuSb_2$, OsP_2, $OsAs_2$, and $OsSb_2$ are given in an earlier paper [6] of this series, their accuracies may well be questioned due to possible shortcomings in the treatment of the X-ray powder diffraction data. Judging from trends (*cf.* Fig. 1, Fig. 1 in Ref. 17, *etc.*) outlined by the isostructural compounds, the data for at least some of these (notably $RuAs_2$ and OsP_2) appear to suffer from inaccurate determinations. Redeterminations on the basis of single crystal X-ray or powder neutron/profile refinement methods are therefore advisable. The same applies in some extent to NaO_2.[18]

(iv) *$Mo_{2/3}As_2$?* The perhaps most interesting deduction which can be made from the data in Table 1 concerns the defect FeS_2-*m* type compound $Mo_{2/3}As_2$. The knowledge on this compound may be summarized as:

(a) The only successful preparation is claimed by Brown.[19] Attempted duplication of the synthesis by others [8,20,21] has been unsuccessful.

(b) The only data originally communicated by Brown were structural information about the assigned space group *Pnnm*, the cell dimensions (in Å units) $a=5.299(2)$, $b=5.983(2)$, and $c=2.885(1)$, and the positional parameters $x=0.1762(3)$ and $y=0.3625(3)$ for a *de facto* unidentified compound. (No qualitative or quantitative chemical analyses were performed.)

(c) Brown originally gave the composition $Mo_{0.4}As_2$, but corrected this in a private communication to $Mo_{0.6}As_2$ with a specification of the yield to less than ten small crystals.

(d) The composition $Mo_{0.6}As_2$ was conveniently altered to $Mo_{2/3}As_2$, thus ascribing [1] the configuration d^0 to Mo. For this reason, the latter formula has, unfortunately without firm experimental facts, found its way into the literature.[1,12,15,22,23]

On comparing the structural data for the assumed compound $Mo_{2/3}As_2$ with those for $FeAs_2$ in Table 1, an almost perfect coincidence will be noted. Since coincidence in structural data commonly is believed to provide unambiguous identification of compounds, this inference alone strongly suggests that the assumed $Mo_{2/3}As_2$ is actually $FeAs_2$. Further evidence supporting this conclusion, stems from the way Brown utilized structural data to deduce the composition $Mo_{0.6}As_2$ through the use of the occupation number for Mo as a variable. The value 0.6 is remarkably close to the atomic ratio 0.62 for Fe/Mo as it would be if Mo had been confused with Fe.

The assumption of $Mo_{2/3}As_2$ being (in reality) $FeAs_2$ appears to provide a credible explanation also for the few, small crystals only once obtained by Brown, possibly due to a Fe impurity in his sample. Moreover, this also explains why other investigators have failed in attempted preparations. Finally, the non-existence of the assumed $Mo_{2/3}As_2$ would exclude the only example of a class A transition metal compound having a possible d^0 configuration, thus removing a marked inconsistency between transition and non-transition metal d^0 representatives, which otherwise would belong to different classes A and B, respectively, of the FeS_2-*m* structure type (*cf.* Ref. 24). This line will be pursued further in another context.

From the above evidence, the identification of $Mo_{2/3}As_2$ as $FeAs_2$ appears to be beyond reasonable doubt. The incorrect assignment made by Brown is understandable in view of the minute amount of sample available which did not permit ordinary chemical analyses.

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