Acta Chemica Scandinavica A 29 (1975) 443—452

Compounds with the Marcasite Type Crystal Structure. XI. High Temperature Studies of Chalcogenides

ARNE KJEKSHUS and TROND RAKKE

Kjemisk Institutt, Universitetet i Oslo, Blindern, Oslo 3, Norway

High temperature investigations by X-ray diffraction, DTA, and quenching experiments have been performed for FeS_2, $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$, and syntheses and characterizations of $OsTe_2$ are reported. The transition properties of these compounds are discussed in relation to the FeS_2-*m versus* FeS_2-*p* type structure.

Despite all endeavours already devoted to studies of the relationship between the FeS_2-*p* (*p* = pyrite) and FeS_2-*m* (*m* = marcasite) type structures (*cf.* Ref. 1 and references therein), mostly speculative thoughts rather than decisive facts have been accumulated. In all, eight binary dichalcogenides have so far been reported (see Ref. 1) to take both of these structure types, *viz.* NaO_2, FeS_2, $FeSe_2$, $FeTe_2$, $OsTe_2$, $CoSe_2$, $CoTe_2$, and $CuSe_2$. Of these, $CoSe_2$ is in a special position in that its FeS_2-*m* type modification refers [2] to a poorly characterized mineral sample whose existence may be stabilized by smaller or larger amounts of impurities (*e.g.* Fe).

The FeS_2-*p* type modifications of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ have hitherto only been generated by high pressure/high temperature syntheses,[3] whereas their FeS_2-*m* type modifications are easily obtained by the conventional sealed silica capsule technique.[4,5] For FeS_2 an opposite situation prevails in that its FeS_2-*m* modification appears to require hydrothermal conditions.[6]

The existence of two modifications of $OsTe_2$ has only rather recently been discovered [7] and the *pure* FeS_2-*m* variant of this compound has not yet been obtained. However, our prior knowledge [5] strongly suggests that the FeS_2-*m* type modification of $OsTe_2$ can be obtained in the pure form by syntheses at temperatures $< 500\,^{\circ}C$, whereas the pure FeS_2-*p* type phase is obtained at temperatures $\geqq 550\,^{\circ}C$. The implied question of the FeS_2-*m* and FeS_2-*p* type modifications as low and high temperature forms of $OsTe_2$ has its parallel for FeS_2; a discussion which has been carried on for many years (*cf.*, *e.g.*, Refs. 8, 9).

NaO_2 occupies a particular position among these compounds in undergoing reversible transformations between the FeS_2-*m*, FeS_2-*p*, and *random* FeS_2-*p* type structures as a function of temperature.[10]

The object of this paper is to report results of high temperature studies of FeS_2, $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$, including some preliminary data for $OsTe_2$.

EXPERIMENTAL

The natural *marcasite* sample used in this study originated from Joplin (U.S.A.) and was obtained from Mineralogisk-Geologisk Museum, Universitetet i Oslo; analytical data being included in Ref. 4. The syntheses of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ were performed as described in Refs. 4, 5. Samples with compositions on both sides of the stoichiometric ratio were made for $FeSe_2$ and $CuSe_2$ by heating the stoichiometric samples with lower selenides or excess selenium in evacuated, sealed silica capsules.

As a continuation of the synthetical work described in Ref. 4, numerous further attempts were made to prepare FeS_2 in its FeS_2-*m* modification. However, all endeavours were in vain, the FeS_2-*p* modification being obtained as the only reaction product above 350 °C. FeS_2-*p* is also obtained below this temperature, but, in

variable amounts (*viz.* incomplete reactions) depending on temperature, heating period, and number of intermediate crushings.

Samples of $OsTe_2$ were prepared by heating stoichiometric quantities of the elements [99.999 % Os (Johnson, Matthey & Co.) and 99.999 % Te (Koch-Light Laboratories)] in evacuated, sealed silica capsules. A variety of different reaction and annealing temperatures (400 – 950 °C) were tried. Below ~500 °C, the reaction rate is extremely slow, above ~650 °C the annealing of the samples leads to crystallization of the silica, but this does not become a serious problem until ~750 °C.

The temperature of the furnaces surrounding the specimens was kept constant to within ±0.5 °C during the annealing processes using Getrosist (Philips) temperature regulators and a Frigistor reference chamber for the cold points of the Pt/Pt-Rh thermocouples (0.00 ± 0.02 °C). The recorded annealing temperatures were measured separately with a calibrated Pt/Pt-Rh thermocouple. The silica capsules were made as short as possible in order to minimize effects of thermal gradients in the furnaces, and thin-walled ampoules were utilized for quenching experiments in order to ensure fast cooling rates. Following the conventional quenching technique, care was taken in initial experiments to drop the ampoules into ice-water without shattering. In the course of the study, the technique was modified to almost instantaneous mechanical shattering of the ampoules when brought in contact with ice-water. The overall gain in quenching rate on turning to the latter procedure is estimated to be a factor of about ten, but, apart from for the decomposition results, this improvement had no detectable influence.

The DTA data were collected with a Mettler Recording Vacuum Thermoanalyzer, using ~60 mg samples in sealed silica crucibles. The heating rate was generally 2 °C/min and Pd powder was used as reference. The X-ray powder diffraction techniques applied at ambient and higher temperatures are described in Ref. 11.

In an attempt to eliminate possible, arbitrary effects of inhomogeneity, impurity, non-stoichiometry, *etc.*, all results described in this paper for the (nominally) stoichiometric samples (except some of those for $OsTe_2$) refer to specimens taken from one and the same batch of each compound.

RESULTS

The scope of the present study is determined by the availability of FeS_2 in its FeS_2-*p* and FeS_2-*m* forms, $OsTe_2$ in one pure and one impure modification, and $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ only in their FeS_2-*m* type modifications. These distinctions in starting points are reflected in the subsequent presentation of our findings.

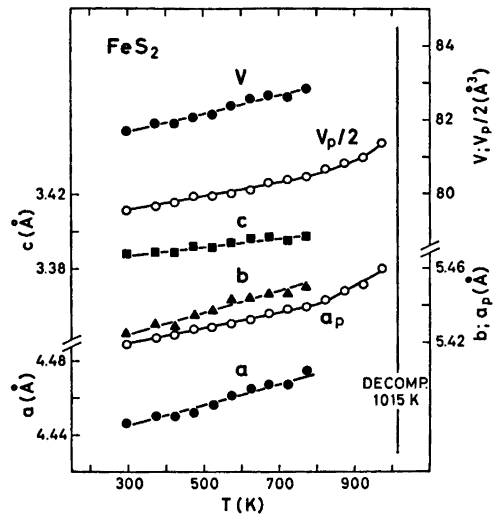

Fig. 1. Unit cell dimensions for *natural* FeS_2-*m* (*a*, *b*, *c*, *V*) and *synthetic* FeS_2-*p* (a_p, V_p) *versus* temperature. (Calculated standard deviations do not exceed size of symbols; correspondingly in Figs. 3 and 4.)

(i) *FeS_2-m versus FeS_2-p*. In line with earlier findings,[8,9] the FeS_2-*m*→FeS_2-*p* transition is induced by heat treatments, the transformation rate being extremely susceptible to the experimental conditions, notably the temperature. It was therefore, not surprising to find that this transition could not be detected by DTA. In fact, the DTA curves were featureless apart from endothermic peaks due to sample decomposition at 745 °C independent of whether FeS_2-*m* or FeS_2-*p* was used as the starting material. In order to establish the decomposition temperature more accurately, samples were heated at various temperatures between 730 and 760 °C until thermal equilibrium was achieved, and then quenched. Using this procedure on various samples of FeS_2-*m* and FeS_2-*p*, the decomposition temperature was established as 742 ± 6 °C, where the uncertainty refers to the reproducibility between different runs. This result was verified by high temperature X-ray diffraction.

An advantage of the sluggish FeS_2-*m*→FeS_2-*p* transition is that the former modification can

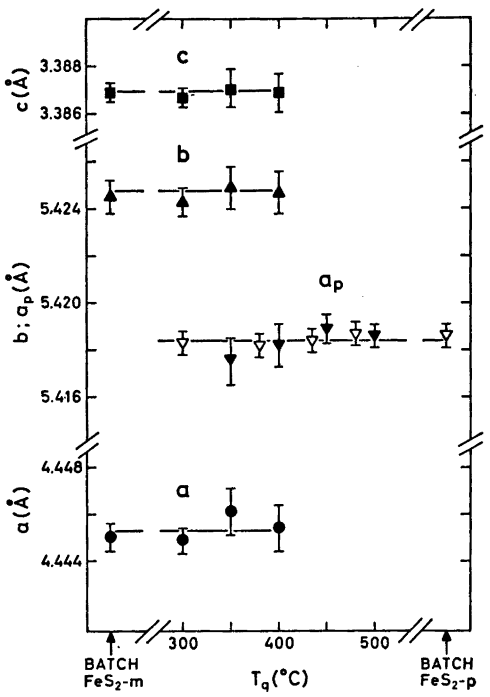

Fig. 2. Unit cell dimensions and corresponding standard deviations (as determined at room temperature) for samples (originally) of *natural* FeS_2-*m* (filled symbols) and *synthetic* FeS_2-*p* (open symbols), quenched from various temperatures (T_q).

be followed up to ~500 °C on high temperature X-ray diagrams. Hence, Fig. 1 shows the temperature dependence of the unit cell dimensions of FeS_2-*m* between 22 and 500 °C. Up to 450 °C, only reflections characteristic of FeS_2-*m* could be seen on the diagrams, whereas at 500 °C a mixture of FeS_2-*m* and FeS_2-*p* had emerged. For the purpose of comparison, the temperature variation of the FeS_2-*p* cell (synthetic sample) is also included in Fig. 1. Since the unit cell dimension of the synthetic FeS_2-*p* sample matches (within experimental error) that obtained from the transformed FeS_2-*m* sample at ≧500 °C, there can apparently not be any significant distinction in composition between the two lots of FeS_2.

In fact, this result was further substantiated by quenching experiments. As is evident from Fig. 2, the unit cell dimensions (as derived from room temperature Guinier photographs) of FeS_2-*m* and FeS_2-*p* are independent of the temperature (T_q) from which the samples were quenched.

The quenching experiments also showed that the onset of the reaction FeS_2-*m*→FeS_2-*p* under steady state conditions, takes place at a much lower temperature than the 500 °C found by high temperature X-ray diffraction. At ≦300 °C, heat treatments up to 14 months did not induce any changes in FeS_2-*m* samples, whereas an increase to 350 °C resulted in mixtures of FeS_2-*m* and FeS_2-*p* after the same annealing period. A further increase to 400 °C produced mixtures of the two modifications after annealing for only 1 month, and at this temperature, the FeS_2-*m*→FeS_2-*p* conversion was found to be completed within 4 months. At still higher temperatures, the conversion goes even more quickly to completion, *e.g.*, ≦1 month, ≦2 weeks, and ≦1 h at 450, 500, and 700 °C, respectively. The quenching experiments further emphasize the gradual nature of the FeS_2-*m*→FeS_2-*p* conversion, thus explaining why this reaction escapes DTA detection.

(ii) *Preliminary report on* $OsTe_2$. As briefly reported in an earlier communication,[5] the FeS_2-*p* type modification of $OsTe_2$ is easily synthesized above 550 °C. The upper preparation temperature is limited by the decomposition of $OsTe_2$ at 890 ± 10 °C, as presently determined by DTA and quenching experiments. The unit cell dimension is 6.3985(4) Å at room temperature and its temperature dependence is shown in Fig. 3.

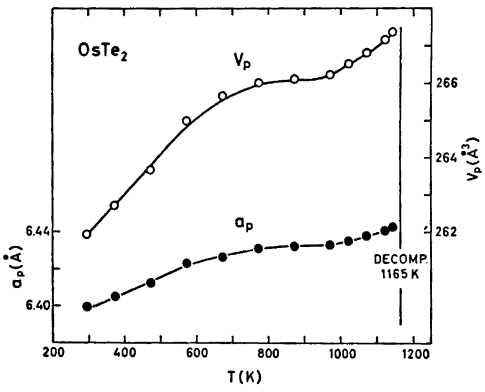

Fig. 3. Thermal expansion of the FeS_2-*p* type unit cell of $OsTe_2$.

Once the FeS_2-*p* type modification has been generated by a reaction above 550 °C it remains invariant to subsequent annealings at lower temperatures. However, on lowering both the preparation and annealing temperatures, a different situation arises. Thus, heat treatments at 480 – 500 °C (still complete reactions $Os + 2Te \rightarrow OsTe_2$) gave mixtures of the FeS_2-*p* and FeS_2-*m* type [$a = 5.280(2)$, $b = 6.402(3)$, $c = 4.048(2)$ Å] modifications in roughly equal amounts. Prolongation of the annealing period for such samples at these or lower temperatures did not result in detectable changes in the relative amounts of the two modifications. If, on the other hand, the same samples are subjected to subsequent annealings at $\geqq 550$ °C, the FeS_2-*p* type modification is obtained as the ultimate reaction product.

It should be emphasized that the above results refer to samples which were subjected to comparatively long term annealings (for $t \leqq 600$ °C, not less than 4 and up to 10 months). At higher temperatures (> 600 °C) equilibrium is attained much faster (*e.g.*, within 2 h at 850 °C; in complete accordance with the findings of Meijer [12]). At first sight, these results appear to contradict those of Sutarno *et al.*[7], who report preparation of mixtures of the FeS_2-*m* and FeS_2-*p* type modifications of $OsTe_2$ at 700 °C. However, these authors used only a one day reaction period which, according to the present results, is too short. The small amounts of the FeS_2-*m* type modification formed during the gradual heating in the furnace need about 3 days annealing at 700 °C for complete conversion into the FeS_2-*p* type modification.

Since reactions at 480 – 500 °C produced mixtures of the two $OsTe_2$ modifications and determination of relative yields as a function of temperature was not intended, the intervals $440 < t < 480$ °C and $500 < t < 550$ °C were not tried.

At temperatures $\leqq 440$ °C the reaction rate for $Os + 2Te \rightarrow OsTe_2$ is incredibly low and reaction periods up to 10 months have resulted mainly in unreacted reactants. However, the sample treated at 440 °C contained a measurable amount of $OsTe_2$, notably in its FeS_2-*m* type modification and without any detectable trace of its FeS_2-*p* type variant. This promising result suggests that the FeS_2-*m* type modification of $OsTe_2$ can be obtained in pure form by prolonged heat treatments at (say) 440 °C. Our continued engagement on the properties of $OsTe_2$ will undoubtedly be rather time consuming, which appears to justify presentation of some preliminary results here.

(iii) *On thermal properties of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$.* The findings for FeS_2 and $OsTe_2$ could lead one to believe that it would be worthwhile to search systematically for the FeS_2-*p* type modifications of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ at high temperatures (*viz.* preparational procedures which would make their expensive, high pressure/high temperature syntheses unnecessary), and this was in fact the original intention for the whole investigation. If this working hypothesis is rooted in realities, the conversions between the FeS_2-*m* and FeS_2-*p* type modifications of these compounds would most likely occur in relatively narrow regions below their decomposition temperatures, where, moreover, optimum conversion rates are to be expected.

The decomposition temperatures for $FeSe_2$, $FeTe_2$, and $CoTe_2$ as determined by DTA, quenching experiments, and high temperature X-ray diffraction show excellent mutual agreement, numerical values being 582 ± 3, 648 ± 3, and 767 ± 4 °C, respectively. The decomposition temperature of ~ 330 °C obtained by DTA for $CuSe_2$, differs appreciably from the value 285 ± 4 °C found by quenching experiments and high temperature X-ray diffraction. The former value matches that similarly derived from DTA by Gattow,[13] although it should be noted that the present DTA results for $CuSe_2$ showed variation with heating rates. The fairly slow sample decomposition encountered in this case, accounts for the distinction of the DTA results from those obtained under steady state conditions.

High temperature X-ray diffraction data (Fig. 4) show that the FeS_2-*m* type modifications of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ persist right up to sample decompositions. None of the many X-ray photographs taken just below their decomposition temperatures contained any reflections characteristic of the FeS_2-*p* type modifications. In order to exclude the possibility that the hypothetical conversions between FeS_2-*m* and FeS_2-*p* type modifications may be extremely sluggish, samples were an-

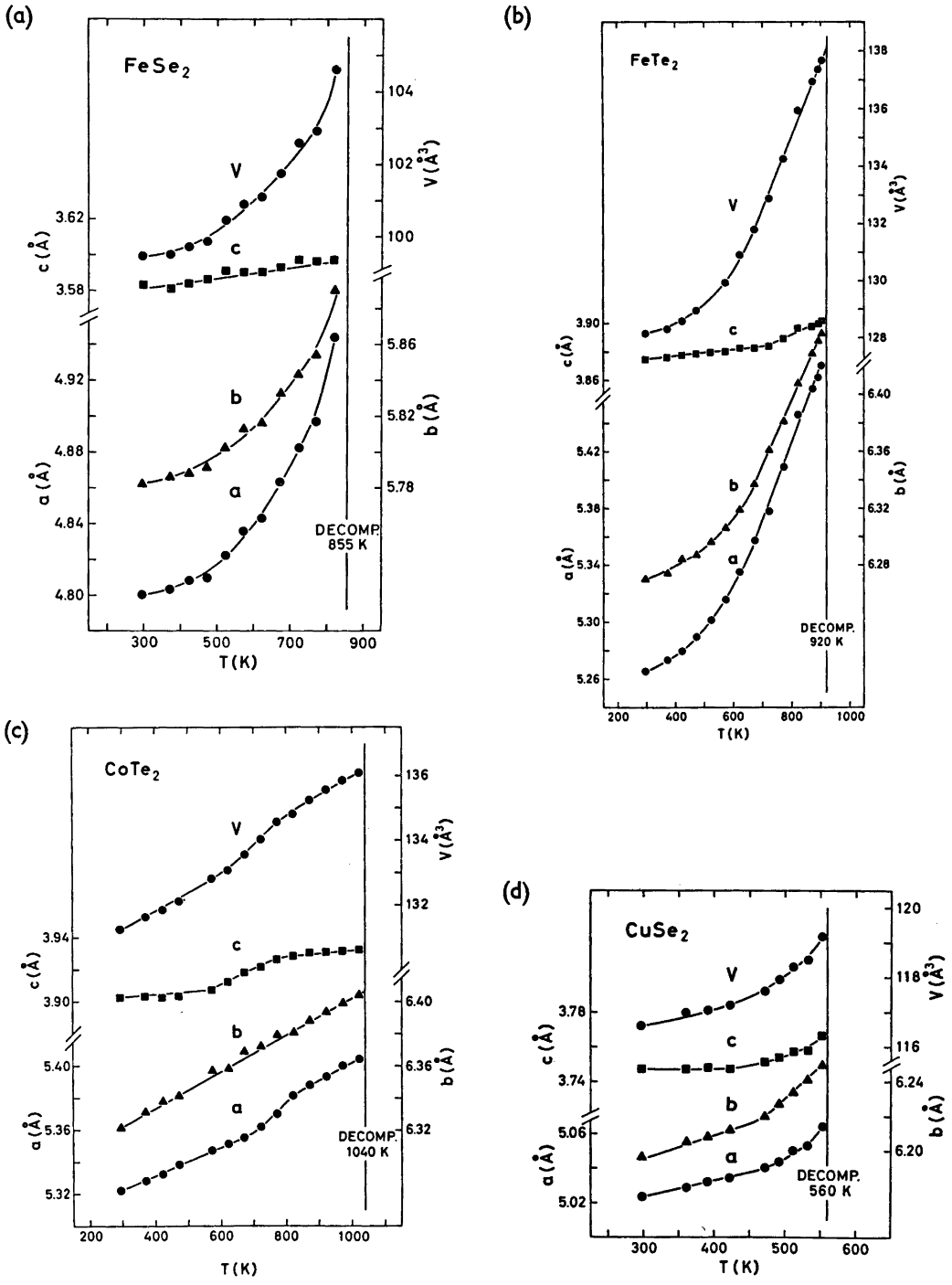

Fig. 4. Unit cell dimensions of: (a) $FeSe_2$, (b) $FeTe_2$, (c) $CoTe_2$, and (d) $CuSe_2$ as functions of temperature.

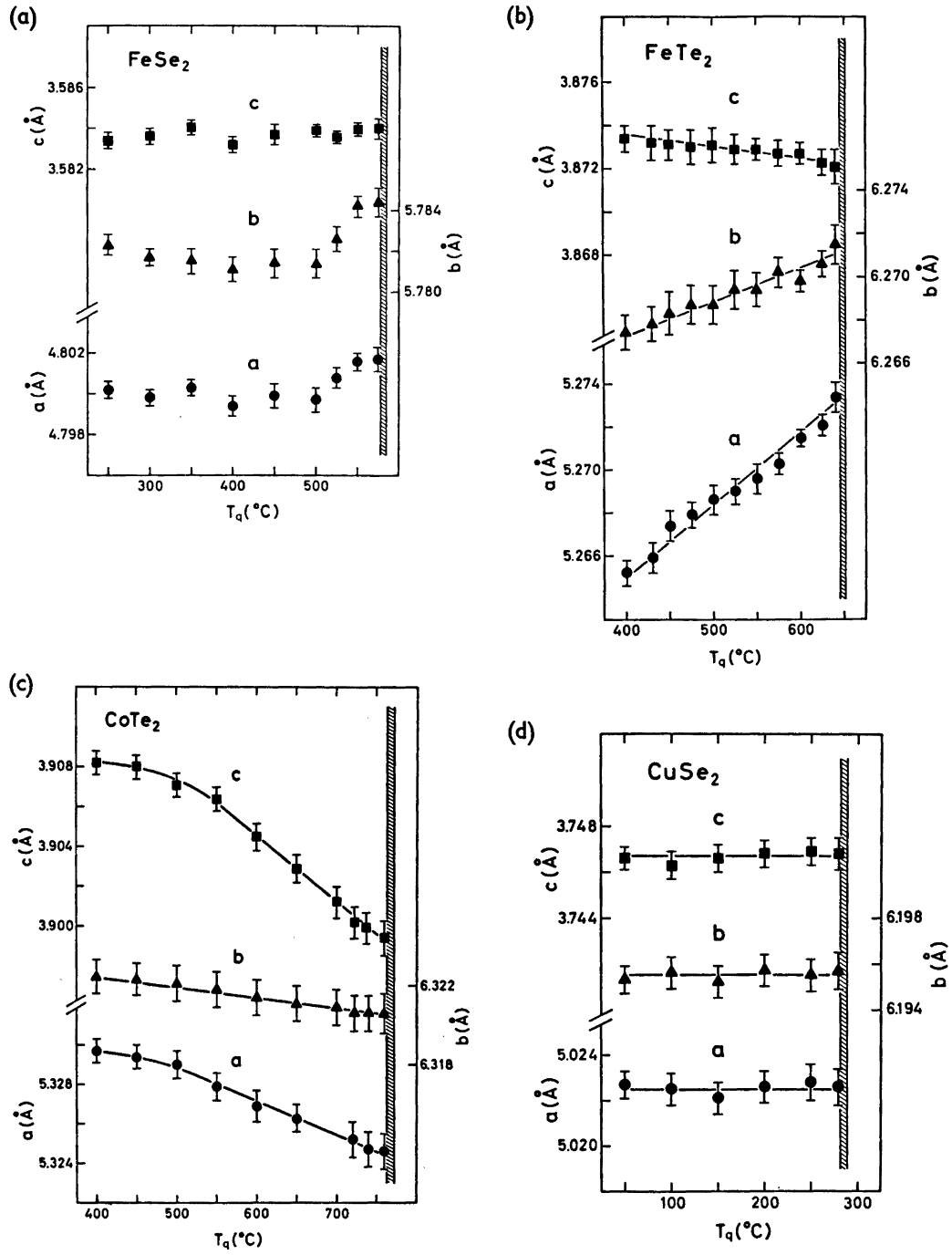

Fig. 5. Room temperature unit cell dimensions (with standard deviations) for samples of: (a) $FeSe_2$, (b) $FeTe_2$, (c) $CoTe_2$, and (d) $CuSe_2$ quenched from various temperatures (T_q).

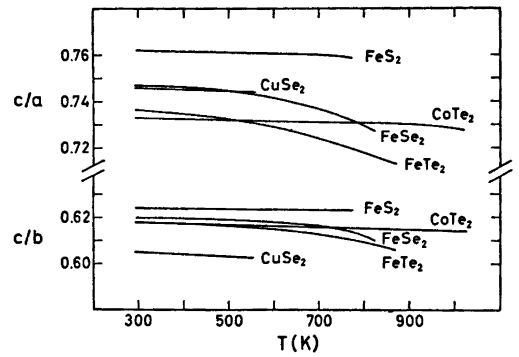

Fig. 6. Axial ratios *versus* temperature for FeS_2, $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$.

nealed below their decomposition temperatures for up to 14 months and then quenched. The results of the quenching experiments (Fig. 5) unequivocally confirm that the FeS_2-*p* type modifications of these compounds are unobtainable through the conventional sealed capsule technique.

The variation in unit cell dimensions of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ with quenching temperature (Fig. 5) also shed some light on the question of stoichiometry/non-stoichiometry of these compounds. The invariance in unit cell dimensions with T_q for $CuSe_2$ (Fig. 5d) together with similar results for samples with different initial compositions, show that $CuSe_2$ exhibits no appreciable range of homogeneity. Earlier findings [14] suggest that $FeSe_2$ takes a slight homogeneity range on the Fe-rich side of the stoichiometric ratio. Although the present results for stoichiometric (Fig. 5a) and non-stoichiometric $FeSe_2$ samples are not entirely conclusive, the homogeneity range for this compound appears to be more narrow than proposed in Ref. 14. The non-stoichiometric nature of $Fe_{1-u}Te_2$ ($0 \leqq u \leqq 0.03$; 450 °C) and $Co_{1-u}Te_2$ ($0 \leqq u \leqq 0.13$; 450 °C) is already well established.[4] The data presented in Fig. 5 b, c merely show that the metal-rich phase limit shifts from $u = 0.00$ at $\leqq 450$ °C to 0.01 and 0.06 for $Fe_{1-u}Te_2$ and $Co_{1-u}Te_2$, respectively, in the vicinity of their decomposition temperatures.

The present thermal expansion data are also relevant in relation to the use of unit cell proportions for classification of compounds with the FeS_2-*m* type structure. It is seen from Fig. 6 that the axial ratios for FeS_2, $CoTe_2$, and $CuSe_2$ are practically independent of temperature, as opposed to those for $FeSe_2$ and $FeTe_2$. Although, as pointed out in Ref. 1, the unit cell proportions are not even approximately constant from compound to compound within each class, but vary systematically, the marked temperature variations for $FeSe_2$ and $FeTe_2$ show that *c/a* and *c/b* may even not be entirely characteristic parameters for a given compound.

Similar *c/a* and *c/b* variations to those in Fig. 6 are observed [4] for $Fe_{1-u}Te_2$ as functions of the compositional parameter *u*, whereas the axial ratios for $Co_{1-u}Te_2$ are approximately independent of *u*. Due to the only slight temperature dependence of the Fe-rich phase limit in $Fe_{1-u}Te_2$ inferred above, the *c/a* and *c/b* *versus* *T* relationships (Fig. 6) cannot be attributed to compositional changes alone. For $FeSe_2$ no such explanation is appropriate.

DISCUSSION

The formation of and transformation modes between the FeS_2-*m* and FeS_2-*p* type structures for the eight MX_2 (M = metal, X = chalcogen) compounds which take both of these types, appear to suggest that they divide into four categories.

NaO_2:

$m \rightleftharpoons p$ reversible at −77 °C (Ref. 10).

$OsTe_2$:

$m \rightarrow p$ at $> \sim 480$ °C.

$p \rightarrow m$ unknown; requires complete decomposition (Os + 2Te) and anewed synthesis at $< \sim 440$ °C.

FeS_2:

$m \rightarrow p$ at $> \sim 300$ °C.

$p \rightarrow m$ unknown; a feasible path appears to involve dissolution and subsequent hydrothermal synthesis under slightly acidic conditions.[6]

$FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$:

$m \rightarrow p$ actually unknown, but since the *p* type modifications have been made by direct syntheses from the elements,[3] $m \rightarrow p$ can probably be generated under high temperature/high pressure conditions.

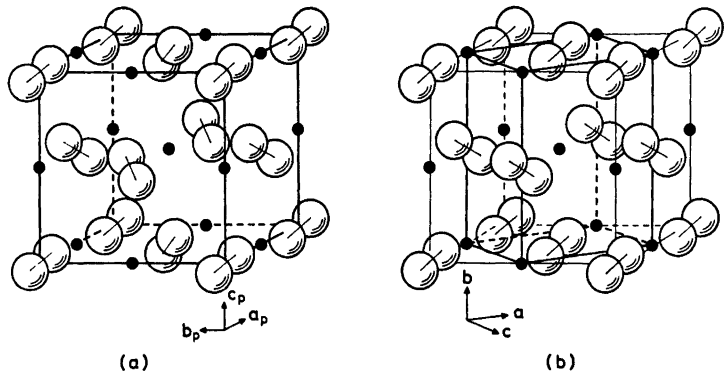

Fig. 7. Models for the (a) FeS_2-*p* and (b) FeS_2-*m* type structures.

p→*m* unknown; experience from other high temperature/high pressure induced syntheses (*cf.*, *e.g.*, Ref. 15) indicates conversion by conventional heat treatments in evacuated, sealed capsules.

The similarities and differences between the FeS_2-*p* and FeS_2-*m* type structures may be seen from Fig. 7. For a detailed discussion of these structure types and their mutual relationships, the reader is referred to Ref. 1.

The reversible nature of the FeS_2-*m*⇌FeS_2-*p* type transition in NaO_2 may be attributed to features of its $X-X$ pairs and bonding characteristics. The $X-X$ pairs in NaO_2 differ in at least two respects from those of the other compounds under consideration, *viz.* in size relative to M as well as in its more nearly spherical shape. Within this class of compounds, NaO_2 almost certainly distinguishes itself in having a more extreme charge distribution between M and $X-X$, *viz.* less directional character of the $M-X$ bonds. (It should be emphasized that the questions of size and shape of the $X-X$ pair are interrelated with bonding characteristics, thus making a distinction between cause and effect somewhat arbitrary.) These features of the $X-X$ and $M-X$ bonds facilitate the FeS_2-*m*⇌ FeS_2-*p* type *solid state* transition. This is compatible with the fact that NaO_2 also undergoes a further FeS_2-*p*⇌*random* FeS_2-*p* type transition at -50 °C. Neither of these transitions in NaO_2 are accompanied by any detectable changes in cell volume (per formula unit).

At the FeS_2-*m*→FeS_2-*p* type transition in $OsTe_2$, an appreciable volume contraction [$\Delta V/V=(V_p/2-V)/V=-0.041$] takes place. The volume change and irreversible nature of the transition distinguish $OsTe_2$ from NaO_2 and suggest that the transition in the former is not of the solid state type. On the contrary, the reaction is more likely to involve the vapour phase, through

$$\underset{(FeS_2\text{-}m\ \text{type})}{OsTe_{2(s)}} \rightleftharpoons Os_{(s)} + Te_{2(g)} \rightleftharpoons \underset{(FeS_2\text{-}p\ \text{type})}{OsTe_{2(s)}}$$

without taking an attitude to the actual molecular species of Te present in the vapour. The observed coexistence of the FeS_2-*m* and FeS_2-*p* type modifications over a range of temperatures, together with the irreversible nature of the transition, would thus demand approximately equal equilibrium partial pressures of Te for the two modifications as well as rather small Te total pressures.

It is natural to suspect that the *m*→*p* transition in FeS_2 should be governed by a mechanism similar to that proposed for $OsTe_2$. The sluggish nature of the transition as well as the accelerating effect [8] of added sulfur, support this assumption. In this case, however, one is faced with the puzzling question of why not even trace amounts of FeS_2-*m* have been obtained by the sealed silica capsule technique. The answer appears to be that the reaction rate for the synthesis of FeS_2 is too low at $t < \sim 300$ °C. The thus suggested similarity between FeS_2 and $OsTe_2$ is subject to future verification through long-term (say, several years) annealings. The volume contraction at the FeS_2-*m*→FeS_2-*p* transition amounts to $\Delta V/V=-0.026$.

Disconnected from the above discussion is the definite distinction in formation and transformation modes of FeS_2 and $OsTe_2$ on the one hand, and $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ on the other. Provided that this distinction is thermodynamical in origin, it is expected to be reflected also in structural parameters, *viz.* bond distances and angles. Since structure determinations have been carried out [4,5,16] for all FeS_2-*m* type modifications except $OsTe_2$, the implications are that the hitherto undetermined FeS_2-*p* type structures of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ carry a secret. (It is of little help in this connection that the structures of both modifications of FeS_2 have been explored in detail. [16,17])

Awaiting the results of the structure determinations advertised for, unit cell dimensions or proportions might be suspected to reflect some structural details. However, apart from the c/a ratio where NaO_2 ($c/a = 0.801$), FeS_2 ($c/a = 0.762$), and $OsTe_2$ ($c/a = 0.767$) take higher values than the others ($c/a \leqq 0.747$), no significant distinction could be traced. In view of the averaging effects operative in unit cell dimensions and proportions, this disappointing result is hardly unexpected.

The unit cell volume is an even more averaged parameter and as such, more featureless in the structural sense. Nevertheless, volume frequently enters into pressure considerations. The volume contractions $\Delta V/V$ are -0.026 for both FeS_2 and $FeTe_2$, -0.042 and -0.019 for $CoTe_2$ and $CuSe_2$, respectively. Thus, the lack of correlation is seen from the fact that the contractions for $FeSe_2$ and $FeTe_2$ are identical with that for FeS_2, and the contraction for $CoTe_2$ almost matches that for $OsTe_2$.

The whole discussion contains an inherent weakness in taking for granted that the high pressure induced modifications of $FeSe_2$, $FeTe_2$, $CoTe_2$, and $CuSe_2$ are replicas of the products searched in more conventional syntheses, *e.g.* evacuated, sealed capsule conditions. The effect of hydrostatic pressure on solids is visualized as a compression of the atomic electron clouds. For a given pressure the extent of the compression depends on the individual atoms as well as on their bonding situations. Thus, the various constituents of a compound may respond differently to applied pressure, which in turn may lead to smaller or larger structural rearrangements. When this pressure is released the atomic size and/or some structural details may not be fully relaxed. In other words, it is suggested that for a given structure type, the structural parameters, pressure, and free energy relationship may have more than one minimum. [The high pressure induced PdS_2(II) modification [18] may be a relevant example, and moreover, the situation has its probable parallel in structural rearrangements caused by the additional internal stress associated with paramagnetic→cooperative magnetic transitions.] The only way of proving or disproving such a hypothesis requires the synthesis of the FeS_2-*p* type modifications for at least one of $FeSe_2$, $FeTe_2$, $CoTe_2$, or $CuSe_2$, by means other than high temperature/high pressure methods, and the subsequent comparison of structural details between this and the corresponding high pressure product. It would, however, be interesting and almost equally decisive to subject the more conventionally synthesized FeS_2-*p* type modifications of:

NaO_2, MgO_2, $MgTe_2$, MnS_2, $MnSe_2$, $MnTe_2$, FeS_2, RuS_2, $RuSe_2$, $RuTe_2$, OsS_2, $OsSe_2$, $OsTe_2$, CoS_2, $CoSe_2$, $RhSe_2$, $RhTe_2$, NiS_2, $NiSe_2$, ZnO_2, CdO_2, $PdAs_2$, $PdSb_2$, PtP_2, $PtAs_2$, $PtSb_2$, $PtBi_2$, and SiP_2

(*cf.* Ref. 1 and references therein) to high temperature/high pressure treatment, followed by detailed structural analyses. Knowledge about what happens to the high pressure induced FeS_2-*p* type modifications of:

$FeSe_2$, $FeTe_2$, $CoTe_2$, $NiTe_2$, CuS_2, $CuSe_2$, $CuTe_2$, ZnS_2, $ZnSe_2$, CdS_2, $CdSe_2$, IrS_2, NiP_2, $NiAs_2$, and $SiAs_2$

(*cf.* Refs. 3, 19 – 21) when exposed to annealings in evacuated, sealed capsules at successively higher temperatures, would also contribute greatly to a better understanding of these problems.

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Received December 2, 1974.