On the Properties of $\alpha$-MnS and MnS$_2$

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The phases $\alpha$-MnS, $\beta$-MnS, $\gamma$-MnS, and MnS$_2$ have been prepared. Only $\alpha$-MnS was obtained by direct reaction between the elements. The rate of formation of $\alpha$-MnS from manganese plates and gaseous sulfur has been studied at different temperatures.

The thermal expansion of $\alpha$-MnS and MnS$_2$ has been studied, and the linear thermal expansion coefficients, $\beta$, determined. For $\alpha$-MnS: $\beta = 16.3 \times 10^{-6} \degree C^{-1}$ (225–591$\degree$C) and $\beta = 17.4 \times 10^{-6} \degree C^{-1}$ (591–925$\degree$C) and for MnS$_2$: $\beta = 13.0 \times 10^{-6} \degree C^{-1}$ (70–252$\degree$C).

The sharp distinction between many properties of the manganese chalcogenide phases and chalcogenide phases of other 3d transition metals (Ti–Ni), makes the manganese chalcogenides an interesting class of substances. This paper is an integral part of continued investigations concerning the physical and chemical properties of manganese sulfides. It deals with various aspects of sulfidization of manganese, syntheses and thermal properties of $\alpha$-MnS, $\beta$-MnS, $\gamma$-MnS, and MnS$_2$.

The special interest related to sulfidization of manganese, concerns the mechanism of diffusion of the reactants through sulfide scales with an apparently rather small deviation from stoichiometric composition, and furthermore the relation of this reactivity to similar observations on other transition metal sulfide systems with higher defect concentrations.

High temperature X-ray studies of $\alpha$-MnS and MnS$_2$ were undertaken as a continuation of earlier studies on thermal expansion of solids, and as a means to studying the relative thermal properties of these sulfides. As shown in Fig. 1, there is a close relationship between the structures of $\alpha$-MnS and MnS$_2$. Both phases crystallize with a NaCl-like structure. In $\alpha$-MnS (Fig. 1b) the arrangement of manganese and sulfur atoms is the same as for sodium and chlorine atoms in the rocksalt structure, whereas in the pyrite type structure of MnS$_2$ (Fig. 1a) pairs of S atoms take the positions of the S atoms in $\alpha$-MnS. It will be noticed that the centre of gravity of the S$_2$ pairs in Fig. 1a lies at the position of the S atoms in Fig. 1b. The axes of the S$_2$ pairs are parallel to the various body diagonals. A detailed knowledge of the thermal movements of the atoms in these two crystals would thus explain some of

Acta Chem. Scand. 19 (1965) No. 6
Fig. 1. The crystal structures of (a) MnS₂ and (b) α-MnS.

the structural processes involved in the dissociation of MnS₂. Although such a detailed investigation was not carried out, some information was obtained from the study of the thermal expansion of these phases.

EXPERIMENTAL

Materials. Electrolytic manganese of 99.9+ % purity was obtained from Electro Manganese Corp. The sulfur was “Spectrographically pure sulfur” from American Smelting and Refining Co., in which no impurities had been detected by spectrographic analysis (99.999+ % S).

The high purity hauselite (MnS₄) crystals from Raddusa, Sicily, were obtained through Ward’s Natural Science Establishment, Inc., Rochester, New York. A spectrographic analysis showed the presence of the following impurities: 0.1 % Fe, 0.1 % Si, 0.03 % V, 0.03 % Mg, 0.01 % Sn, 0.003 % Cr, and less than 0.001 % of Ni, Cu, and Ag.

Mn(CH₃COO)₂, MnCl₂, MnSO₄, and K₂S of p.a. purity were obtained from Riedel-de Haën A. G. or E. Merck A. G.

Preparation. Some samples were prepared from the elements by heating accurately weighed quantities, with compositions between 50.00 and 66.67 atomic %, S, of the powdered components in evacuated and sealed silica tubes at temperatures between 250 and 700°C for 30 days, and finally quenching the silica capsules in ice water.

Samples for metallographic investigation were prepared by enclosing manganese plates of approximate size 5 × 7 × 2 mm in evacuated and sealed silica tubes together with excess of sulfur. The tubes had been shaped to prevent contact between the metal and the sulfur except via the gaseous phase. The reaction was started by dropping the silica tubes into a furnace at the desired temperature (250, 400, 500, 600, or 700°C). After a heating period ranging from 1 to 60 days the reaction was stopped by quenching the silica tubes in ice water.

β-MnS and γ-MnS were prepared by precipitation with H₂S from hot aqueous solutions of Mn(CH₃COO)₂ and MnCl₂, respectively (as described by Schmaas ⁴). Synthetic MnS₂ was prepared hydrothermally (as described by Biltz and Wiechmann ⁵).

X-Ray diffraction. Guinier photographs were taken in a camera of 80 mm diameter using strictly monochromatized CuKα₁-radiation (λ(CuKα₁) = 1.54050 Å). Potassium chloride (Analar, The British Drug Houses Ltd., a = 6.2919 Å) was added to the specimen as an internal standard.

X-Ray powder photographs of α-MnS and MnS₂ were taken in a 190 mm Unicam high-temperature camera, with the samples sealed in thin-walled quartz capillaries.

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By means of a voltage regulator, the registered temperature of the furnace surrounding the specimen was kept constant within $\pm 3^\circ$C ($20 - 400^\circ$C) or $\pm 5^\circ$C ($400 - 1000^\circ$C). The Pt/Pt-Rh thermocouples of the furnace had been calibrated with a standard couple located at the position of the specimen. The lattice constants were calculated by the extrapolation method of Nelson and Riley, using the high angle reflections only. The probable error in the lattice constant determinations at temperatures above room temperatures is estimated to be less than 0.01%.

**Metallographic studies.** Samples made from manganese plates were mounted in araldite. After grinding and polishing with levigated alumina, transverse sections of the specimens were examined with a Reichert universal camera microscope.

The cross section areas of the sulfide scales were graphically integrated and the area of metal sulfide per unit area of metal was calculated. To increase and check the accuracy, repeated measurements were carried out at different grinding heights. The relative error is estimated to be about 5%.

**RESULTS**

*Formation of manganese sulfides.* All the previously known phases $\alpha$-$\text{MnS}$, $\beta$-$\text{MnS}$, $\gamma$-$\text{MnS}$, and $\text{MnS}_2$ have been prepared in this study.

$\beta$-$\text{MnS}$ and $\gamma$-$\text{MnS}$ could not be prepared directly from the elements, so these phases were made by precipitation with $\text{H}_2\text{S}$-gas from aqueous manganese solutions. The lattice constants determined from Guinier powder photographs, $a = 5.60$ Å for $\beta$-$\text{MnS}$ and $a = 3.98_5$ Å, $c = 6.44_6$ Å, $c/a = 1.61_8$, for $\gamma$-$\text{MnS}$, are in reasonable agreement with the literature values. $\beta$-$\text{MnS}$ and $\gamma$-$\text{MnS}$ are irreversibly transformed to $\alpha$-$\text{MnS}$ at $\sim 200^\circ$C and $\sim 300^\circ$C, respectively. However, the Guinier photographs of these phases showed that they were impure, and further investigations were not performed on these phases.

The samples obtained by hydrothermal syntheses of $\text{MnS}_2$, (for which $a = 6.1021$ Å) contained minor impurities of other phases and gave no information in addition to that obtained from the natural hauzerite sample. The continuation of this study was accordingly carried out on the mineral sample.

Attempts to prepare sulfides directly by heating powdered mixtures of the elements always resulted in $\alpha$-$\text{MnS}$.

Even if kinetic phenomena prevent the formation of $\text{MnS}_2$ from powder mixtures, one might expect a thin layer of $\text{MnS}_2$ on the surface of the metal grains. This may be ascertained by metallographic methods (see for example Kjekshus).

For this purpose metallographic specimens were prepared by reaction between manganese plates and gaseous sulfur. After the reaction the plates were covered by a continuous, firmly adherent scale, which did not spall from the nucleus during or after cooling of the specimens to room temperature. A microscopic investigation revealed only one phase which proved to be $\alpha$-$\text{MnS}$, and any other manganese sulfide phase present (e.g. $\text{MnS}_2$) must form an extremely thin layer.

The reaction between the metal plates and gaseous sulfur was carried out at different temperatures between 250 and 700$^\circ$C and the rate of reaction was determined. The results are shown in Fig. 2. It will be seen that the reaction follows an approximately parabolic rate law in this temperature range.

The sulfidization of Cr, Fe, Co, Ni, and Cu under similar conditions to those of the present study is reported in the literature (cf. e.g. Refs. 9—13). Sulfide

coatings comparable to those obtained after some 5 — 60 days in the case of manganese needed only 1/4 — 8 h for Cr, Fe, Co, Ni, and Cu. The sulfidization of Mn is therefore considerably slower than that of these metals.

*High temperature studies of MnS$_2$ and $\alpha$-MnS.* The lattice dimensions of MnS$_2$ and $\alpha$-MnS at temperatures above room temperature are listed in Tables 1 and 2, and the relative changes in the lattice constants

$$ \frac{a_t - a_{20}}{a_{20}} = \Delta a/a_{20} $$

with temperature will be seen from Fig. 3.

*Table 1. Lattice constants and unit cell volumes of MnS$_2$ (haugerite) at different temperatures.*

<table>
<thead>
<tr>
<th>$t$ (°C)</th>
<th>$a$ (Å)</th>
<th>$V$ (Å$^3$)</th>
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</thead>
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<tr>
<td>20</td>
<td>6.1016</td>
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<td>45</td>
<td>6.1049</td>
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<td>70</td>
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<td>152</td>
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<td>185</td>
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<td>200</td>
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<td>250</td>
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<td>229.491</td>
</tr>
<tr>
<td>258</td>
<td>6.123</td>
<td>229.56</td>
</tr>
</tbody>
</table>

At 260°C decomposition to $\alpha$-MnS; $a = 5.2490$ Å.
Table 2. Lattice constants and unit cell volumes of α-MnS at different temperatures.

<table>
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<tr>
<th>t (°C)</th>
<th>a (Å)</th>
<th>V (Å³)</th>
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<td>5.2360</td>
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<td>494</td>
<td>5.2670</td>
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<td>591</td>
<td>5.2763</td>
<td>146.889</td>
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<tr>
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<td>774</td>
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<tr>
<td>928</td>
<td>5.3052</td>
<td>149.316</td>
</tr>
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</table>

Fig. 3. Relative changes in lattice constants as a function of temperature.

The a-axis of MnS₂ increases approximately linearly between 70 and 252°C with expansion coefficient $β = 13.0 \times 10^{-6}$ °C⁻¹. (Between 20 and 70°C $a$ increases more rapidly; $β$ corresponding to the slope of the expansion curve at 20°C is $21.6 \times 10^{-6}$ °C⁻¹.) The intensities and the line profiles of the reflections on the X-ray photographs taken in the range 20 — 252°C are almost unchanged. The atomic parameter $x$ of the sulfur atoms, being the only variable parameter in the pyrite type structure, must thus be nearly constant in this temperature range. (Because of the cubic symmetry, the thermal expansion of the interatomic distances is thus approximately equal to the expansion of the $a$-axis (Fig. 3).) The X-ray photographs taken at 258°C were diffuse, showing a sudden change in the vibrational state of MnS₂. However, the obtained lattice constant fitted reasonably well with the linear expansion curve (Fig. 3). The photographs taken at 260°C, showed the reflections of $α$-MnS only, and the corresponding lattice constant joined nicely to the expansion curve of $α$-MnS shown in Fig. 3. According to the present data, the thermal decomposition of MnS₂ to $α$-MnS therefore takes place in a rather narrow temperature region. Indications of a gradual, or some degree of partial decomposition of MnS₂ have not been found in this study.

Biltz and Wiechmann ⁵ measured the vapor pressure of a hauerite specimen at temperatures down to 304°C, and found it equal to the vapor pressure over
sulfur. Hauerite must therefore according to Biltz and Wiechmann decompose below 304°C, i.e., a result being consistent with the present decomposition temperature of 260°C. A recent investigation by Nykro14 gave a considerably higher decomposition temperature (incipient at 345°C) in disagreement with the value reported above.

The $\alpha$-axis of $\alpha$-MnS increases almost linearly from 225 to 591°C, and the linear coefficient of expansion, $\beta$, evaluated from the curve shown in Fig. 2 is $16.3 \times 10^{-6} \, ^\circ\text{C}^{-1}$ ($\beta = 23 \times 10^{-6} \, ^\circ\text{C}^{-1}$ at 20°C). Above $\sim 591^\circ$C the expansion is still linear, but $\beta$ is increased to $17.4 \times 10^{-6} \, ^\circ\text{C}^{-1}$ (591 — 928°C).

As the $\alpha$-MnS and MnS$_2$ phases have cubic symmetry, and the $\beta$-values are small, the volume expansion coefficient, $\alpha$, will be equal to 3$\beta$.

The expansion of the two phases MnS$_2$ and $\alpha$-MnS is linear over great temperature ranges, and the curves show no sudden increase in the expansion at the highest temperatures. It is worth mentioning that the MnS$_2$ phase expands linearly up to the temperature of decomposition.

Acknowledgement. The authors wish to thank Professor Haakon Haraldsen for his interest in this study and for placing laboratory facilities at their disposal.

REFERENCES


Received May 5, 1965.