

On the Properties of α -MnS and MnS₂

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The phases α -MnS, β -MnS, γ -MnS, and MnS₂ have been prepared. Only α -MnS was obtained by direct reaction between the elements.

The rate of formation of α -MnS from manganese plates and gaseous sulfur has been studied at different temperatures.

The thermal expansion of α -MnS and MnS₂ has been studied, and the linear thermal expansion coefficients, β , determined. For α -MnS: $\beta = 16.3 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (225–591°C) and $\beta = 17.4 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (591–928°C) and for MnS₂: $\beta = 13.0 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (70–252°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 α -MnS, β -MnS, γ -MnS, and MnS₂.

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 α -MnS and MnS₂ were undertaken as a continuation of earlier studies¹⁻³ 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 α -MnS and MnS₂. Both phases crystallize with a NaCl-like structure. In α -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 MnS₂ (Fig. 1a) pairs of S atoms take the positions of the S atoms in α -MnS. It will be noticed that the centre of gravity of the S₂ pairs in Fig. 1a lies at the position of the S atoms in Fig. 1b. The axes of the S₂ 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

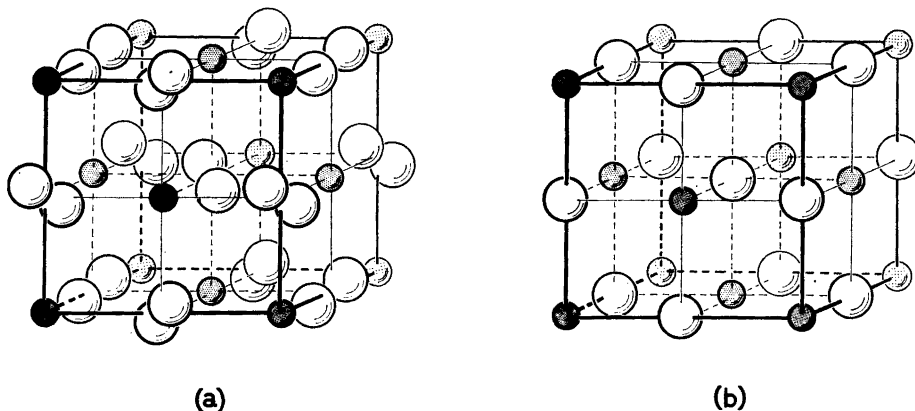


Fig. 1. The crystal structures of (a) MnS_2 and (b) $\alpha\text{-MnS}$.

the structural processes involved in the dissociation of MnS_2 . 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 hauerite (MnS_2) 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.

$\text{Mn}(\text{CH}_3\text{COO})_2$, MnCl_2 , MnSO_4 , and K_2S 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 $5 \times 7 \times 2$ 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.

$\beta\text{-MnS}$ and $\gamma\text{-MnS}$ were prepared by precipitation with H_2S from hot aqueous solutions of $\text{Mn}(\text{CH}_3\text{COO})_2$ and MnCl_2 , respectively (as described by Schnaase⁴). Synthetic MnS_2 was prepared hydrothermally (as described by Biltz and Wiechmann⁵).

X-Ray diffraction. Guinier photographs were taken in a camera of 80 mm diameter using strictly monochromatized $\text{CuK}\alpha_1$ -radiation ($\lambda(\text{CuK}\alpha_1) = 1.54050 \text{ \AA}$). Potassium chloride (Analar, The British Drug Houses Ltd., $a = 6.2919 \text{ \AA}$) was added to the specimen as an internal standard.

X-Ray powder photographs of $\alpha\text{-MnS}$ and MnS_2 were taken in a 190 mm Unicam high-temperature camera, with the samples sealed in thin-walled quartz capillaries.

By means of a voltage regulator, the registered temperature of the furnace surrounding the specimen was kept constant within $\pm 3^\circ\text{C}$ (20–400°C) or $\pm 5^\circ\text{C}$ (400–1000°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,⁶ 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 α -MnS, β -MnS, γ -MnS, and MnS₂ have been prepared in this study.

β -MnS and γ -MnS could not be prepared directly from the elements, so these phases were made by precipitation with H₂S-gas from aqueous manganous solutions. The lattice constants determined from Guinier powder photographs, $a = 5.60 \text{ \AA}$ for β -MnS and $a = 3.98_5 \text{ \AA}$, $c = 6.44_6 \text{ \AA}$, $c/a = 1.61_3$ for γ -MnS, are in reasonable agreement with the literature values.^{4,7} β -MnS and γ -MnS are irreversibly transformed to α -MnS at $\sim 200^\circ\text{C}$ and $\sim 300^\circ\text{C}$, 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 MnS₂, (for which $a = 6.1021 \text{ \AA}$) contained minor impurities of other phases and gave no information in addition to that obtained from the natural hauerite 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 α -MnS.

Even if kinetic phenomena prevent the formation of MnS₂ from powder mixtures, one might expect a thin layer of MnS₂ on the surface of the metal grains. This may be ascertained by metallographic methods (see for example Kjekshus⁸).

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 α -MnS, and any other manganese sulfide phase present (*e.g.* MnS₂) 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°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

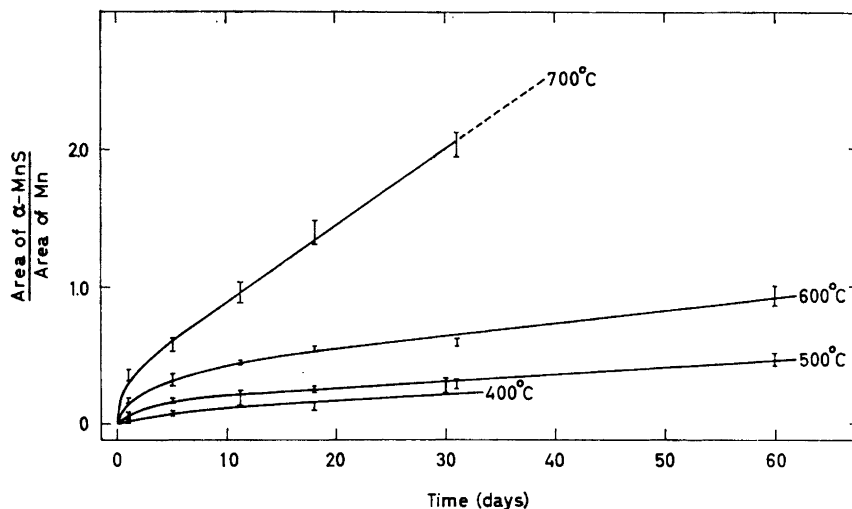


Fig. 2. Sulfidization of manganese as a function of time.

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 α -MnS. The lattice dimensions of MnS_2 and α -MnS at temperatures above room temperature are listed in Tables 1 and 2, and the relative changes in the lattice constants

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

with temperature will be seen from Fig. 3.

Table 1. Lattice constants and unit cell volumes of MnS_2 (hauerite) at different temperatures.

t (°C)	a (Å)	V (Å ³)
20	6.1016	227.160
45	6.1049	227.528
70	6.1077	227.842
110	6.1109	228.200
152	6.1141	228.559
185	6.1168	228.861
200	6.1180	228.996
228	6.1202	229.243
250	6.1222	229.468
252	6.1224	229.491
258	6.123	229.56

At 260°C decomposition to α -MnS; $a = 5.2490$ Å.

Table 2. Lattice constants and unit cell volumes of α -MnS at different temperatures.

t (°C)	a (Å)	V (Å ³)
20	5.2226	142.449
139	5.2360	143.549
200	5.2419	144.034
225	5.2448	144.273
331	5.2544	145.067
403	5.2607	145.590
449	5.2630	145.781
494	5.2670	146.113
591	5.2763	146.889
667	5.2820	147.365
774	5.2918	148.187
928	5.3052	149.316

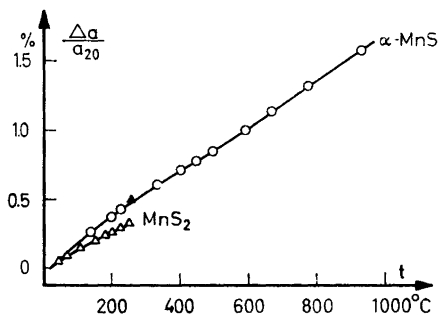


Fig. 3. Relative changes in lattice constants as a function of temperature.

The a -axis of MnS₂ increases approximately linearly between 70 and 252°C with expansion coefficient $\beta = 13.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$. (Between 20 and 70°C a increases more rapidly; β corresponding to the slope of the expansion curve at 20°C is $21.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$.) 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 Wiechmann⁵ 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 Nyrkov¹⁴ gave a considerably higher decomposition temperature (incipient at 345°C) in disagreement with the value reported above.

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

As the α -MnS and MnS₂ phases have cubic symmetry, and the β -values are small, the volume expansion coefficient, α , will be equal to 3β .

The expansion of the two phases MnS₂ and α -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 MnS₂ phase expands linearly up to the temperature of decomposition.

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