

CCA-659

542.65-162

Original Scientific Paper

## Formation of Cadmium Sulphide — Manganese(2)Sulphide Solid Solutions by Coprecipitation from Aqueous Solutions of Corresponding Sulphate by Ammonium Sulphide

M. Paić

Institute of Physics of the University, Zagreb, Croatia, Yugoslavia

Received April 3, 1971

When a 0.27 M aqueous solution of  $(\text{NH}_4)_2\text{S}$ , in a quantity 10 mol% short of the stoichiometric value, is added to an aqueous solution of  $\text{CdSO}_4$  and  $\text{MnSO}_4$  of various compositions, with  $\text{SO}_4^{2-}$  being 0.3 M, a continuous  $\text{CdS}:\text{MnS}$  solid solution is not formed: saturation is reached for at most about 0.1 mol%  $\text{MnS}$ , the corresponding relative concentration of  $\text{MnSO}_4$  being 4 mol%. With increasing this concentration to 20 mol%,  $\text{MnS}$  begins to precipitate in substantial amounts, reaching 19.8 mol% for  $\text{MnSO}_4$  equal to 50 mol%. Debye-Scherrer diagrams show that the precipitates are quasi amorphous, composed essentially of cubic  $\text{CdS}$  with certain quantities of hexagonal  $\text{CdS}$  and  $\text{MnS}$ . This makes it impossible to distinguish, by these diagrams only, mechanical mixtures from solid solutions.

### INTRODUCTION

In order to investigate various physical properties of amorphous cadmium sulphide—manganese(2)sulphide solid solutions, we tried to prepare these compounds by coprecipitation from aqueous solutions of the corresponding sulphates by means of ammonium sulphide<sup>1,2</sup>

### EXPERIMENTAL

#### Preparation

In a beaker of 1000 cm<sup>3</sup> (Fig. 1), x cm<sup>3</sup> 0.3 M aqueous solution of  $\text{MnSO}_4$  and 300-x cm<sup>3</sup> 0.3 M  $\text{CdSO}_4$  were mixed. The relative molar composition of the solution is therefore  $p_{\text{MnSO}_4} = x/3$  mol% and  $p_{\text{CdSO}_4} = 100-x/3$  mol%. From vessel A (Fig. 1), 300 cm<sup>3</sup> 0.27 M aqueous solution of  $(\text{NH}_4)_2\text{S}$  ran into the beaker, at  $19 \pm 1^\circ\text{C}$ , for  $19 \pm 1$  min. (Chemicals were reagent grade and redistilled water was used for all operations). During the reaction the beaker rotated ( $\sim 1$  Hz) which caused a continuous relative motion of the solution of both sulphates to the incoming solution of  $(\text{NH}_4)_2\text{S}$ . The stirring of the liquid was enhanced through an immersed glass rod (B). For complete stoichiometric precipitation of the corresponding sulphides there was a lack of 10 mol% of  $(\text{NH}_4)_2\text{S}$ . The precipitate was separated from the liquid by a centrifuge ( $\sim 25$  Hz) after the reaction as well as during washing (ten times with  $\sim 250$  cm<sup>3</sup> water). The precipitates were dried in a desiccator over sulphuric acid. When dry, they were kept over Silicagel. The yield of pure  $\text{CdS}$  obtained by this procedure is 96% of the theoretical amount.

We gave  $p_{\text{MnSO}_4}$  seventeen different values, from 0 to 100 mol%. During the washing of the precipitates it was observed that a certain quantity of precipitate, especially for  $p_{\text{MnSO}_4} > 20$  mol%, passed into a colloidal solution which could not be separated by the centrifuge we used. Furthermore, the yield diminishes

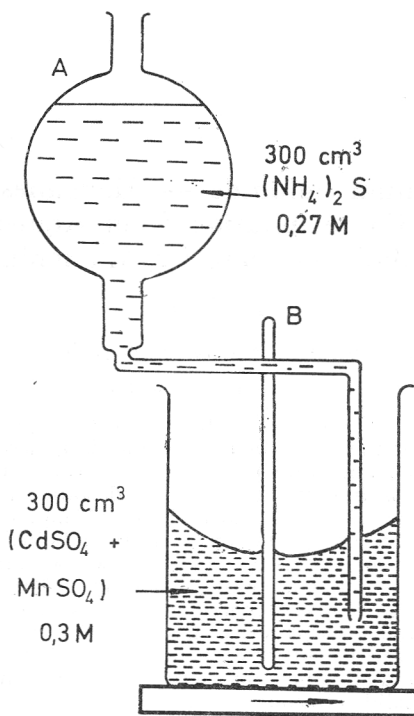


Fig. 1. Reaction apparatus.

when  $p_{\text{MnSO}_4}$  rises: for  $p_{\text{MnSO}_4} = 100$  mol % it is only 50% of the stoichiometric value. With  $p_{\text{MnSO}_4} \geq 40$  mol % the precipitates take a brownish colour on the surface when *not* under water. This phenomenon is enhanced during drying. The brownish layer is evidently the result of oxidation of MnS in the presence of moisture and atmospheric oxygen.

These facts indicate the probability that from a certain  $p_{\text{MnSO}_4}$  value separate precipitation of the two sulphides occur. This supposition was confirmed by an experiment in which  $(\text{NH}_4)_2\text{S}$  0.27 M was added to a  $p_{\text{MnSO}_4} = 90$  mol % solution in small, equal, successive portions, the precipitates being separated after each new addition. The appearance of the successive precipitates shows that the CdS phase precipitates first, followed by the precipitation of the pink modification of MnS, in according with the fact that MnS is about four times more soluble in water than CdS<sup>3</sup>.

In the light of these observations we considered all precipitates obtained with  $p_{\text{MnSO}_4} > 50$  mol % to be a mechanical mixture of the two sulfides. Therefore we did not investigate them further.

Qualitatively we observed, by gentle heating in a glass tube, that all precipitates contain a small quantity of water and elementary sulphur. A detailed thermogravimetric study of these systems is reported in the next paper. Manganese was determined spectrophotometrically<sup>4</sup>. Fig. 2 represents the function  $\log(p_{\text{MnS}}) = f(p_{\text{MnSO}_4})$ , where  $p_{\text{MnS}}$  is the mol % content of MnS in the precipitate.

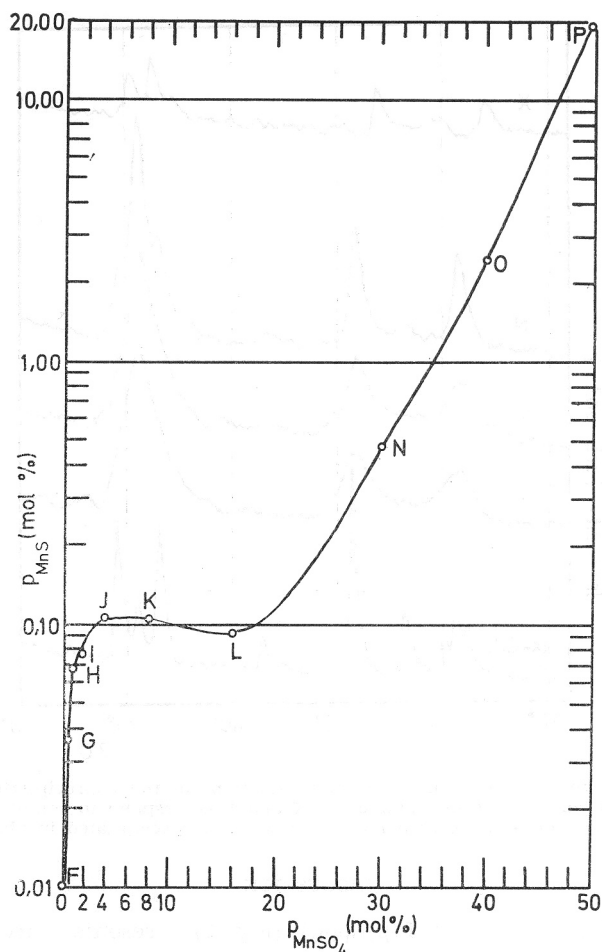


Fig. 2. Amount of MnS in the precipitate (logarithmic scale), dried over Silicagel, as function of the relative percentage amount of  $\text{MnSO}_4$  in aqueous solution containing a 0.3 M mixture of  $\text{CdSO}_4$  and  $\text{MnSO}_4$ .

### X-Ray Examination

The diffractographic method was used with X-rays monochromatised by reflection (CoK  $\alpha$  radiation,  $\lambda = 1.7902 \text{ \AA}$ ). Four typical diffractographic curves are shown in Fig. 3. Preparation G ( $p_{\text{MnS}} = 0.0366 \text{ mol \%}$ ) shows only the three strongest lines of cubic  $\beta$ -CdS. Preparation K ( $p_{\text{MnS}} = 0.105 \text{ mol \%}$ ), basically  $\beta$ -CdS, contains a small quantity of hexagonal  $\alpha$ -CdS. In preparation N ( $p_{\text{MnS}} = 0.464 \text{ mol \%}$ ) there is more  $\alpha$ -CdS than in K. Preparation X, obtained with  $p_{\text{MnSO}_4} = 100 \text{ mol \%}$ , corresponds to the pink  $\beta$ -hexagonal modification of MnS as it presents the same type of Debye-Scherrer pattern as  $\alpha$ -CdS. This fact and width of lines of all X-ray diagrams makes it impossible to decide by these means whether a preparation is a solid solution of the two sulphides or a mechanical mixture. At the same time it shows that all preparations are nearly amorphous.

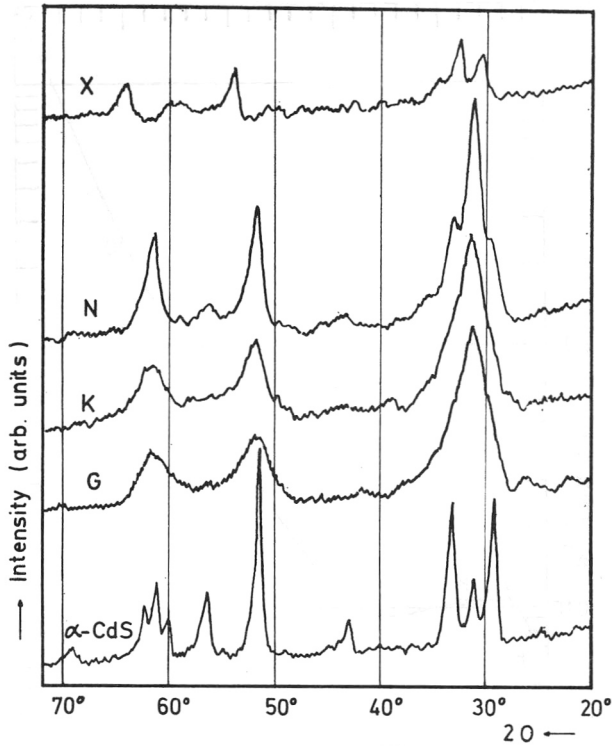


Fig. 3. Debye-Scherrer diffractograms (Co-K  $\alpha$  radiation) of the coprecipitated sulphides and of well crystallised hexagonal CdS. Samples G, K and N correspond to conditions of precipitation given in Figs. 2 and 4; X corresponds to the sulphide precipitated in absence of CdSO<sub>4</sub>.

#### DISCUSSION

The function  $\log p_{\text{MnS}} = f(p_{\text{MnSO}_4})$  (Fig. 2) presents three remarkable  $\log p_{\text{MnSO}_4}$  sections:

(i) In the interval  $0 < p_{\text{MnSO}_4} < 4$  mol %,  $p_{\text{MnS}}$  grows rapidly from 0 to about 0.1 mol % MnS. In our opinion, in this region the precipitates are solid solutions of the two sulphides. The amount of MnS is not a linear function of  $p_{\text{MnSO}_4}$ , which is also shown in Fig. 4: the function  $100 p_{\text{MnS}}/p_{\text{MnSO}_4} = f(p_{\text{MnSO}_4})$  is not constant in this interval of  $p_{\text{MnSO}_4}$  but decreases rapidly.

II From  $\sim 4 < p_{\text{MnSO}_4} < \sim 20$  mol %,  $p_{\text{MnS}}$  remains approximately constant. It means, we believe, that the CdS:MnS solid solution has reached its saturation for at most about 0.1 mol % MnS.

III For  $p_{\text{MnSO}_4} > \sim 20$  mol % the content of MnS of the precipitates rises more rapidly than exponentially. The function in Fig. 4 also rises from the very low minimum at  $p_{\text{MnSO}_4} = 20$  mol %. It means that in this region, with growing  $p_{\text{MnSO}_4}$  larger and larger amounts of MnS are precipitated. Thus a mechanical mixture of CdS and MnS is formed, CdS containing at most about 0.1 mol % MnS in the solid solution.

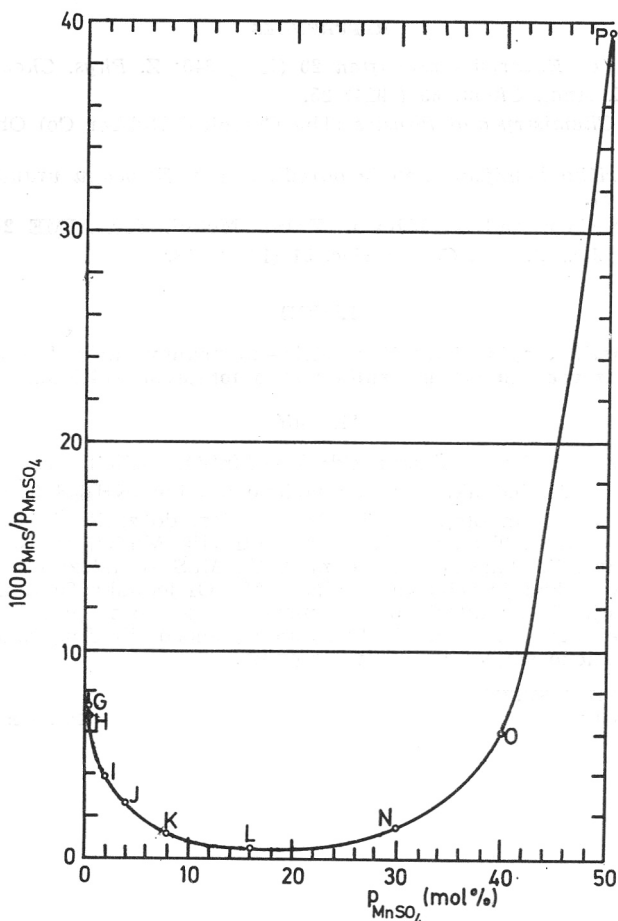


Fig. 4. Relative percentage amount of precipitated MnS as function of the concentration of  $MnSO_4$ .

#### CONCLUSIONS

In our conditions of operation a solid solution of MnS in CdS contains *at most* about 0.1 mol % MnS. This saturation concentration is reached when the aqueous solution of the mixture of corresponding sulphate contains about 4 mol %  $MnSO_4$ . Further increase in this content does not, at first, increase the amount of manganese in the precipitate. Notable precipitation of MnS follows the precipitation of CdS when the relative amount of  $MnSO_4$  in aqueous solution reaches 20 mol %. The order of precipitation, except for the formation of the dilute solid solution, corresponds to the solubilities of CdS and MnS in water at 18° C. At high temperatures, H. Wiedemeier and A. Khan<sup>5</sup> as well as W. R. Cook<sup>6</sup> showed that there exists a considerable solubility of MnS in CdS and to a smaller extent, of CdS in MnS. Since the crystalline structures of the two kinds of solid solutions are different, there exists a considerable miscibility gap.

*Acknowledgement.* The financial assistance of the Yugoslav Federal Council of Research is gratefully acknowledged.

## REFERENCES

1. H. Schnaase, *Naturwissenschaften* **20** (1932) 640; *Z. Phys. Chem.* **20** (1933) 89.
2. F. Feigl, *Z. Anal. Chem.* **65** (1924) 25.
3. *Handbook of Chemistry and Physics* (The Chemical Rubber Co) Ohio, 1968—1969, B-218, B-185.
4. *Hemijske i fizičko hemijske metode određivanja nečistoća u uranu*, SKNE, Beograd, 1967, 3. 67.
5. H. Wiedemeier and A. Khan, *Trans. Metall. Soc. AIME* **242** (1969) 1968.
6. W. R. Cook Jr., *J. Am. Ceram. Soc.* **51** (1968) 518.

## IZVOD

**Stvaranje čvrstih otopina kadmijev sulfid—manganov sulfid koprecipitacijom iz vodenih otopina sulfata sa amonijevim sulfidom***M. Paić*

Dodaje li se vodenim otopinama  $\text{CdSO}_4 + \text{MnSO}_4$  različitih sastava, no kojima je  $\text{SO}_4^{2-}$  stalno 0,4 M, jednaki volumen vodene otopine  $(\text{NH}_4)_2\text{S}$  0,27 M, ne stvara se neprekinuti niz čvrstih otopina  $\text{CdS}:\text{MnS}$ : dolazi do zasićenja kad talog sadrži najviše 0,1 mol% MnS. Tada relativna koncentracija  $\text{MnSO}_4$  iznosi 4 mol%. Ako relativna koncentracija  $\text{MnSO}_4$  naraste na 20%, MnS se taloži u znatnoj količini i dostiže 19,8 mol% kad je relativna količina  $\text{MnSO}_4$  jednaka 50%. Debye-Scherrer dijagrami pokazuju da su talozi gotovo amorfni i da sadrže pretežno kubični CdS s primjesama heksagonalnog CdS i MnS. Samo pomoću tih dijagrama nije moguće razlikovati mehaničke smjese od čvrstih otopina.

INSTITUT ZA FIZIKU SVEUČILIŠTA  
ZAGREB

Primljeno 3. travnja 1971.