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# Phase Equilibria in the Systems $ZnS–Al_2S_3$ and $ZnAl_2S_4–ZnIn_2S_4$*

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Phase relationships between 720 and 1110°C were determined in the system $ZnS–Al_2S_3$ including: (a) the location of a eutectoid at 740°C and 15 mole% $Al_2S_3$, (b) the solubility limits of $Al_2S_3$ in the zinc blende and wurtzite forms of ZnS and the spinel and wurtzite forms of $ZnAl_2S_4$, and (c) the probable relationships at the liquidus. The system $ZnAl_2S_4–ZnIn_2S_4$ at 800 to 1050°C was found to be a simple eutectic type with the following features: (a) a eutectic point at 930–950°C and approximately 20 mole% $ZnIn_2S_4$, (b) a large region of $ZnIn_2S_4$ solid solutions, and (c) little solubility of $ZnIn_2S_4$ in $ZnAl_2S_4$.

## I. Introduction and Literature

The most important yellow and red inorganic pigments are based on cadmium sulfide (CdS) and solid solutions of cadmium sulfide and cadmium selenide, respectively. Alternative pigments based on elements less toxic than cadmium are being sought. The present work was undertaken to provide background data on certain sulfide systems in which such alternative pigments could be developed.

The limited data on the system $ZnS–Al_2S_3$ have been summarized by Flahaut *et al.* (*1*). The principal features of the system include one intermediate compound, $ZnAl_2S_4$, and three regions of solid solution. No firm estimate of the extent of the zinc blende solid solution region was made, but the wurtzite solid solution was said to extend to 33 mole% $Al_2S_3$ at 1200°C, and the $ZnAl_2S_4$ (spinel) solid solution to 83 mole%.

The structure and polymorphism of $ZnAl_2S_4$ were investigated by Hahn and Frank (*2*) and Steigmann (*3*). The low temperature form, $\alpha$-$ZnAl_2S_4$, is isostructural with spinel and the high temperature form, $\beta$-$ZnAl_2S_4$, has a wurtzite derivative structure. Aluminum sulfide, $Al_2S_3$, was reported by Flahaut (*4*) to exist in two stable modifications, a low temperature form isostructural with wurtzite and a high temperature form isostructural with corundum. The literature on the structure and polymorphism of ZnS is extensive and well known and need not be discussed here.

No previous data are available on the system $ZnAl_2S_4–ZnIn_2S_4$, but the structure of the end members is fairly well established. Lappe *et al.* (*5*) found $ZnIn_2S_4$ to have rhombohedral symmetry and described its structure as slightly distorted close-packing of sulfur with zinc occupying slightly enlarged tetrahedral interstices and indium occupying both tetrahedral and somewhat compressed octahedral sites. Range *et al.* (*6*) synthesized $ZnIn_2S_4$ with the spinel structure by heating under pressure and quenching to low temperature and pressure.

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## II. Experimental Procedure

### (1) Raw Materials and Sample Preparation

Chemically pure zinc sulfide,[1] aluminum powder,[2] sulfur,[3] and indium trisulfide ($In_2S_3$)[4] were used to prepare the samples for this study. Materials were weighed to an accuracy of 0.1 mg to make 0.5- to 2.0-g batches which were manually mixed in agate mortars under acetone and dried completely in air.

### (2) Encapsulation

Lengths of fused silica tubing (inside diameter 5 mm, wall thickness 1–2 mm) were sealed at one end in an oxygen–gas flame. Between 100 and 250 mg of material was placed in each tube, and a small, tight-fitting piece of fused silica rod was inserted above it. The rod served three purposes: (1) It prevented overheating the sample during subsequent sealing; (2) it prevented loss of sample powder during evacuation; and (3) it minimized free vapor space within the capsules. After the rods were inserted, narrow capillaries were drawn in the tubes, the open ends connected to a vacuum hose, and the system evacuated 1–2 min by a mechanical pump capable of attaining a vacuum of $10^{-4}$ Torr. The capsules were sealed by collapsing the capillaries in the oxygen–gas flame while the pump was maintaining vacuum. A more detailed discussion of this technique has been given by Kullerud (*7*).

### (3) Heat Treatment

The capsules were placed in electric furnaces at about 200°C and heated slowly (10–20°C/hr) to the desired equilibration temperature. Temperatures were monitored using Pt/Pt–10Rh thermocouples. Heating rates faster than the above resulted in decomposition of the starting sulfides and consequent explosion of the capsules. After soaking 24–240 hr at the equilibration temperature, capsules were quenched by removing from the furnace with tongs and plunging in cold water.

### (4) Phase Identification

Nickel filtered CuK$\alpha$ radiation from a diffractometer operated at 40 kV and 15 mA was used to identify phases present in quenched samples. Scanning was done in the range 60–20° $2\theta$ at 1° per minute. For precise determination of lattice parameters scanning was done at 1/4° $2\theta$ per minute with a silicon powder internal standard.

## III. Results and Discussion

### (1) The System $ZnS$–$Al_2S_3$

(*A*) *Subsolidus phase relations.* Since all the fired and quenched samples were finely powdered, phase indentification was dependent on the use of X-ray diffraction analysis without supplemental use of optical microscopy. This presented no problems in the high-ZnS portion of the system since zinc blende, wurtzite, and $ZnAl_2S_4$ yielded strong, well-defined diffraction peaks. On the other hand, the presence of $Al_2S_3$ was very difficult to detect. Even a 100% $Al_2S_3$ composition yielded a poorly defined diffraction pattern. Consequently, the subsolidus phase relationships in the high-$Al_2S_3$ region must be regarded as tentative.

(*B*) *Lattice parameters as a function of composition.* The lattice parameter of zinc blende was determined on samples quenched from 750 and 720°C. Both heat treatments showed a linear decrease from 0 to 13 mole% $ZnAl_2S_4$ as seen in Fig. 1.

The lattice parameters of wurtzite were determined on samples quenched from 1000 and 1050°C. In both cases a linear decrease extended to $ZnAl_2S_4$ as shown in Fig. 2. The apparent complete solid solution would be easily explainable if $\beta$-$ZnAl_2S_4$ is a wurtzite derivative with random distribution of zinc and aluminum, as originally proposed by

[1] Luminescent grade, General Electric Co., Cleveland, Ohio.

[2] Aluminum Company of America.

[3] Allied Chemical Company.

[4] 99.9% pure, ROC/RIC.

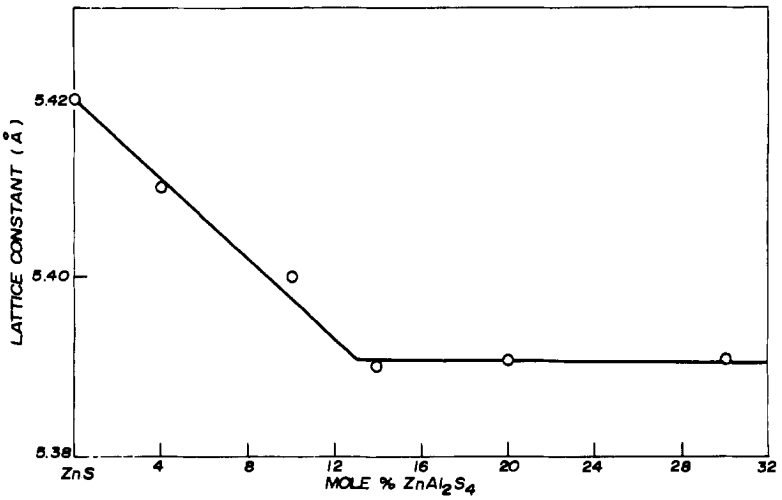


FIG. 1. Lattice constant of zinc blende solid solutions heat treated at 720°C.

Hahn and Frank (*2*). However, if it has an ordered structure as observed by Steigmann (*3*), it is more likely that a series of closely spaced, distinct phases exist rather than a continuous solid solution series. Craig and Scott (*8*) discuss both types of behavior in the system Fe–S. Pyrrhotite ($Fe_{1-x}S$) exists as a continuous series of solid solutions with random distribution of cation vacancies at temperatures between 308°C and its maximum melting temperature of 1190°C. There is increased ordering of vacancies with decreasing temperature giving rise to various superstructures. Below 308°C there are three distinct phases with compositions $Fe_{n-1}S_n$ ($n$ = 10, 11, and 12, respectively). In this study, superlattice peaks indicating ordering were just barely detectable in a few compositions near $ZnAl_2S_4$. Techniques more refined than those used in this study would be necessary to resolve the structural details of the phases in this portion of the system.

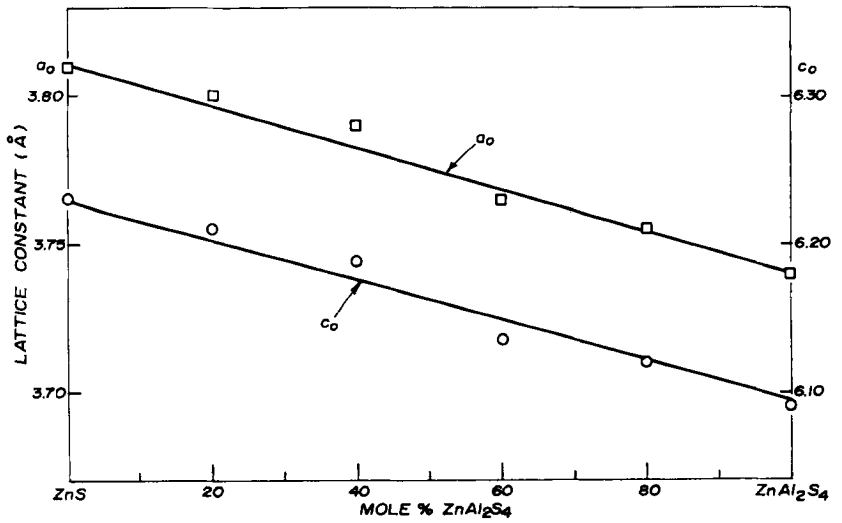


FIG. 2. Lattice constants of wurtzite solid solutions heat treated at 1000°C.

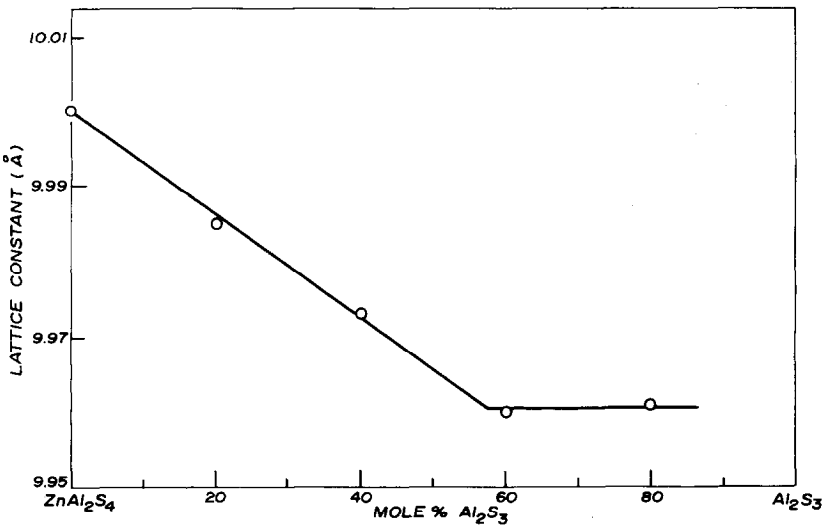


FIG. 3. Lattice constants of $ZnAl_2S_4$ (spinel) solid solutions heat treated at 900°C.

The lattice parameter of $\alpha$-$ZnAl_2S_4$ was determined on samples quenched from 800, 900, and 950°C. A linear decrease was observed between 0 and 56 mole% $Al_2S_3$ in $ZnAl_2S_4$ (or to the composition $22ZnS \cdot 78Al_2S_3$) as shown in Fig. 3. This is reasonable agreement with the limit determined by Flahaut *et al.* of $14.5Zns \cdot 85.5Al_2S_3$.

(*C*) *Liquidus phase relations.* The end member compounds, ZnS and $Al_2S_3$, are known to melt at 1850°C (at 150-atm pressure) (*9*) and 1100°C (*10*), respectively. The approximate melting point of $ZnAl_2S_4$ was determined in the following manner: (1) Prereacted $ZnAl_2S_4$ powder was encapsulated in clear fused silica tubing, (2) the capsule was placed in a furnace at a certain temperature for 10 min, (3) it was quenched in water, and (4) the sample was visually examined for evidence of melting. The procedure was repeated at a series of temperatures. In this fashion the melting point was found to be 1160 ± 10°C.

All samples in the subsolidus regions were loose, fine-grained powders. Fused samples indicated melt formation prior to quenching. Visual examination of samples to see if the fusion was partial or complete was used as a basis for proposing qualitative liquidus relationships.

(*D*) *Construction of the phase diagram.* From the data given in Table I, a phase diagram for the system ZnS–$Al_2S_3$ was constructed (Fig. 4). The diagram incorporates the following results: (a) solubility of $Al_2S_3$ in ZnS (zinc blende) of 6.5 mole% from 720 to 750°C, (b) complete intersolubility of ZnS (wurtzite) and $\beta$-$ZnAl_2S_4$, (c) solubility of $Al_2S_3$ in $\alpha$-$ZnAl_2S_4$ of 56 mole% between 800 and 950°C, (d) a eutectoid at 740°C and 15 mole% $Al_2S_3$, (e) a peritectic point involving equilibrium between solid solutions of the spinel and wurtzite forms of $ZnAl_2S_4$ and liquid at ≃1050°C, and (f) a eutectic point between $ZnAl_2S_4$ and $Al_2S_3$ at 950–1000°C. Features (a), (b), (c), and (d) can be regarded as well established and (e) and (f) as tentative.

### (2) *The System $ZnAl_2S_4$–$ZnIn_2S_4$*

(*A*) *Subsolidus phase relations.* To ensure attainment of equilibrium, it was found necessary to preform the end member compounds, $ZnAl_2S_4$ and $ZnIn_2S_4$, from the starting materials and subsequently to mix these to yield intermediate compositions. The $ZnAl_2S_4$–$ZnIn_2S_4$ mixtures were then encap-

TABLE I

COMPOSITIONS, HEAT TREATMENTS, AND PHASES PRESENT IN THE SYSTEM $ZnS–Al_2S_3$

| Mole% ZnS | Mole% $Al_2S_3$ | Final heat treatment (°C/hr) | Phases present[a] |
|---|---|---|---|
| 98 | 2 | 720/160 | Bss |
| | | 750/48 | Bss |
| | | 800/72 | Bss |
| | | 900/36 | Bss |
| 95 | 5 | 720/160 | Bss |
| | | 900/72 | W + B |
| 93 | 7 | 720/160 | B + Sp (trace) |
| | | 900/72 | Wss |
| 90 | 10 | 720/160 | B + Sp (trace) |
| | | 750/240 | W + B |
| | | 800/48 | W + B |
| | | 850/48 | W + B |
| | | 900/36 | Wss |
| | | 950/48 | Wss |
| | | 1000/48 | Wss |
| | | 1050/48 | Wss |
| | | 1110/24 | Wss |
| 85 | 15 | 720/96 | B + Sp |
| | | 900/72 | Wss |
| 80 | 20 | 750/240 | W + Sp |
| | | 800/48 | W + Sp |
| | | 850/48 | Wss |
| | | 900/36 | Wss |
| | | 950/48 | Wss |
| | | 1000/48 | Wss |
| | | 1050/48 | Wss |
| | | 1110/24 | Wss |
| 70 | 30 | 750/240 | W + Sp |
| | | 800/48 | W + Sp |
| | | 850/48 | W + Sp |
| | | 900/46 | W + Sp |
| | | 950/48 | Wss |
| | | 1000/48 | Wss |
| | | 1050/48 | Wss |
| | | 1110/24 | Wss |
| 60 | 40 | 750/240 | W + Sp |
| | | 800/48 | W + Sp |
| | | 850/48 | W + Sp |
| | | 900/36 | W + Sp |
| | | 950/48 | W + Sp |
| | | 1000/48 | Wss |
| | | 1050/48 | Wss |
| | | 1110/24 | Wss |
| 55 | 45 | 900/72 | W + Sp |
| | | 950/48 | W + Sp |
| | | 1000/48 | Wss |
| 52 | 48 | 900/72 | W + Sp |
| | | 950/48 | W + Sp |
| | | 1000/48 | Wss |
| 48 | 52 | 950/48 | Spss |
| | | 1000/48 | Spss |
| | | 1050/24 | Wss |
| | | 1100/24 | W + L |
| 45 | 55 | 950/48 | Spss |
| | | 1000/48 | Spss |
| | | 1050/24 | W + L |
| | | 1100/24 | W + L |
| 40 | 60 | 800/72 | Spss |
| | | 900/36 | Spss |
| | | 950/48 | Spss |
| | | 1000/48 | Sp + L |
| 30 | 70 | 800/72 | Spss |
| | | 900/36 | Spss |
| | | 950/48 | Spss |
| | | 1000/48 | Sp + L |
| 20 | 80 | 800/72 | Sp + α |
| | | 900/120 | Sp + α |
| | | 950/48 | Sp + α |
| | | 1000/48 | L |
| 10 | 90 | 800/72 | Sp + α |
| | | 900/120 | Sp + α |
| | | 950/48 | Sp + α |
| | | 1000/48 | L |
| 5 | 95 | 1000/48 | L |

[a] B, zinc blende; W, wurtzite; Sp, spinel; ss, solid solution; α, $\alpha$-$Al_2S_3$; L, liquid.

sulated, equilibrated, and quenched as previously described. Even with this procedure a small amount of a nonequilibrium phase (probably one of the many compounds in the system $ZnS–In_2S_3$) (*11*) was detected in compositions ranging from 10 to 40 mole% $ZnIn_2S_4$. The addition of 2 wt% of a 50NaCl–50KCl mineralizer aided in the attainment of equilibrium in these samples.

(*B*) *Lattice parameters as a function of composition.* The lattice parameters of $ZnIn_2S_4$

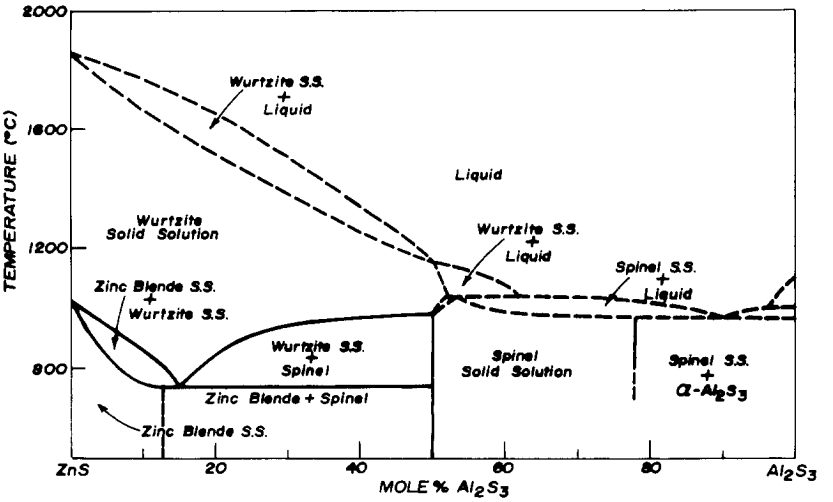


FIG. 4. The system $ZnS$–$Al_2S_3$.

were determined on samples quenched from 800 to 1050°C. The parameter ($a_0$) decreased linearly in the range 0 to 56 mole% $ZnAl_2S_4$ as shown in Fig. 5.

(*C*) *Liquidus phase relations.* The approximate melting point of $ZnIn_2S_4$ was determined by the same method as that used for $ZnAl_2S_4$. It was found to melt at 1125 ± 25°C.

Liquid was evident in some compositions heat treated at 950°C or higher. A eutectic point at about 20 mole% $ZnIn_2S_4$ was deduced from the following data on compositions equilibrated at 950°C: (1) A melt and $ZnAl_2S_4$ were found to coexist in compositions containing 5 and 10 mole% $ZnIn_2S_4$; (2) a composition containing 20 mole% $ZnIn_2S_4$ was completely fused; (3) a melt and crystals of $ZnIn_2S_4$ were observed in compositions con-

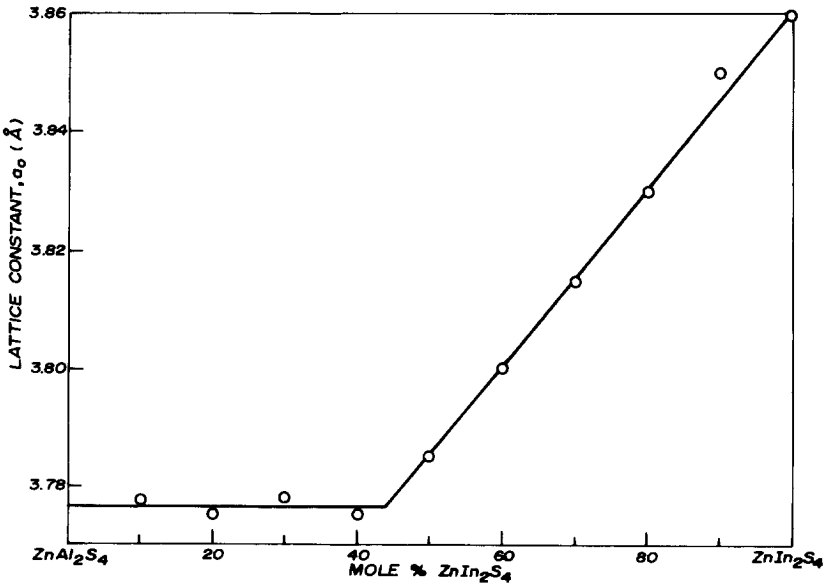


FIG. 5. Lattice constant ($a_0$) of $ZnIn_2S_4$ solid solutions heat treated at 900°C.

TABLE II

COMPOSITIONS, HEAT TREATMENTS, AND PHASES PRESENT IN THE SYSTEM $ZnAl_2S_4$–$ZnIn_2S_4$

| Mole% $ZnAl_2S_4$ | Mole% $ZnIn_2S_4$ | Final heat treatment (°C/hr) | Phases present[a] |
|---|---|---|---|
| 98 | 2 | 800/72 | Sp + ZI |
| | | 900/48 | Sp + ZI |
| 95 | 5 | 800/72 | Sp + ZI |
| | | 900/72 | Sp + ZI |
| | | 950/96 | Sp + L |
| | | 1000/24 | W + L |
| | | 1050/24 | W + L |
| 90 | 10 | 800/120 | Sp + ZI, UP |
| | | 850/120 | Sp + ZI, UP |
| | | 900/120 | Sp + ZI, UP |
| | | 950/96 | Sp + L |
| | | 1000/24 | W + L |
| | | 1050/24 | W + L |
| 80 | 20 | 800/120 | Sp + ZI, UP |
| | | 850/120 | Sp + ZI, UP |
| | | 900/120 | Sp + ZI, UP |
| | | 950/96 | L |
| | | 1000/24 | L |
| | | 1050/24 | L |
| 70 | 30 | 800/120 | Sp + ZI, UP |
| | | 850/120 | Sp + ZI, UP |
| | | 900/120 | Sp + ZI, UP |
| | | 950/96 | ZI + L |
| 60 | 40 | 800/120 | Sp + ZI, UP |
| | | 850/120 | Sp + ZI, UP |
| | | 900/120 | Sp + ZI, UP |
| | | 950/96 | ZI + L |
| 50 | 50 | 800/120 | ZIss |
| | | 850/120 | ZIss |
| | | 900/120 | ZIss |
| | | 950/96 | ZIss |
| 40 | 60 | 800/120 | ZIss |
| | | 850/120 | ZIss |
| | | 900/120 | ZIss |
| | | 950/96 | ZIss |
| 30 | 70 | 800/120 | ZIss |
| | | 850/120 | ZIss |
| | | 900/120 | ZIss |
| | | 950/96 | ZIss |
| | | 1000/24 | ZIss |
| | | 1050/24 | ZIss |
| 20 | 80 | 800/120 | ZIss |
| | | 850/120 | ZIss |
| | | 900/120 | ZIss |
| | | 950/96 | ZIss |
| | | 1000/24 | ZIss |
| | | 1050/24 | ZIss |
| 10 | 90 | 800/120 | ZIss |
| | | 850/120 | ZIss |
| | | 900/120 | ZIss |
| | | 950/96 | ZIss |
| | | 1000/24 | ZIss |
| | | 1050/24 | ZIss |
| (Refired with 2 wt% 50NaCl–50KCL flux) | | | |
| 90 | 10 | 800/120 | Sp + ZI |
| 80 | 20 | 800/120 | Sp + ZI |
| 70 | 30 | 800/120 | Sp + ZI |
| 60 | 40 | 800/120 | Sp + ZI |

[a] Sp, $ZnAl_2S_4$ (spinel); W, $ZnAl_2S_4$ (wurtzite); ZI, $ZnIn_2S_4$; L, Liquid; UP, Unidentified phase; ss, Solid solution.

taining 30 and 40 mole% $ZnIn_2S_4$; and (4) compositions containing 50% $ZnIn_2S_4$ or more were very finely divided loose powders which showed no evidence whatever of any solid state sintering or liquid development.

(*D*) *Construction of the phase diagram.* The phase diagram for the system $ZnAl_2S_4$–$ZnIn_2S_4$ (Fig. 6) was constructed using data given in Table II. The diagram includes these outstanding features: (a) solubility of $ZnAl_2S_4$ in $ZnIn_2S_4$ of 56 mole% from 800 to 900°C, (b) little solubility of $ZnIn_2S_4$ in $ZnAl_2S_4$, and (c) a eutectic point at 20 mole% $ZnIn_2S_4$ and 940°C.

## IV. Summary

(1) Phase relationships in the system $ZnS$–$Al_2S_3$ were completely determined including the solubility limits of $Al_2S_3$ in zinc blende, wurtzite, and $ZnAl_2S_4$, and qualitative liquidus relationships. (2) The system $ZnAl_2S_4$–$ZnIn_2S_4$ was found to be a simple eutectic type with extensive solid solubility of $ZnAl_2S_4$ in $ZnIn_2S_4$.

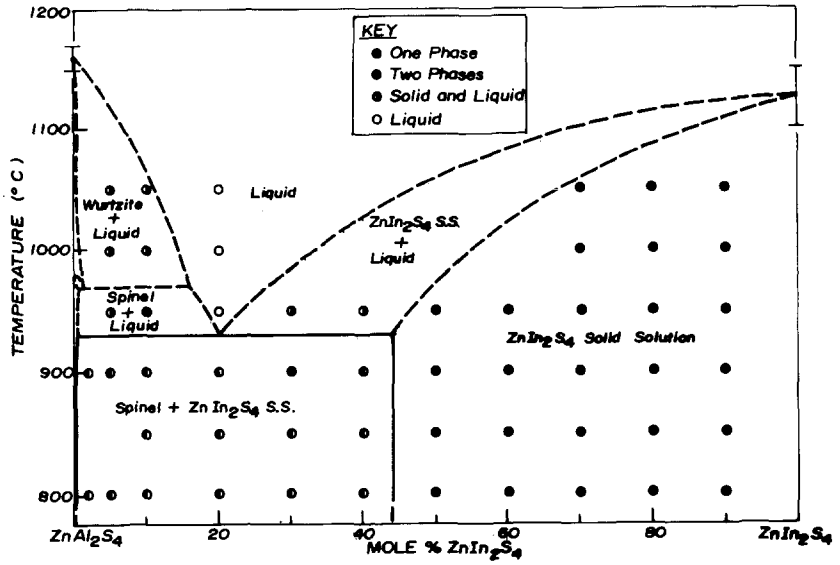


FIG. 6. The system $ZnAl_2S_4$–$ZnIn_2S_4$.

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