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PHASE DIAGRAMS OF THE ZnP_2-$ZnAs_2$ AND ZnP_2-CdP_2 SYSTEMS

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ABSTRACT

The fusibility diagrams of the ZnP_2-$ZnAs_2$ and ZnP_2-CdP_2 systems are studied. It is established that in the ZnP_2-$ZnAs_2$ system there exists a continuous series of solid solutions, while the ZnP_2-CdP_2 phase diagram belongs to the peritectic type with intermediate ordered phase.

INTRODUCTION

This work is aimed at investigating the fusibility diagram of the ZnP_2-CdP_2 and $ZnAs_2$-CdAs systems. The ZnP_2 compound exists steadily in two modifications: monoclinic with the space group C_{2h}^5, and tetragonal - with the space group D_4^8. The $ZnAs_2$ compound belongs to the space group C_{2h}^5 and the CdP_2 compound - to the space group D_4^8. The difference in the interatomic distances of the compounds in the investigated systems meets the requirements of the formation of solid solution continuous series.

RESULTS AND DISCUSSION

a) THE ZnP_2-$ZnAs_2$ SYSTEM

The alloys of the ZnP_2-$ZnAs_2$ systems have been synthesized from the starting substances in quartz ampoules evacuated to 10^{-3} Pa. The ampoule has been heated up to the temperature exceeding that of the supposed liquidus line, subjected to low frequency vibration for 2 hours, then the temperature has been lowered and the homogeneous annealing for 10 d has been carried out. The X-ray and microstructure analyses have shown that all the obtained samples have single phase and crystallize in monoclinic syngony, with the lattice parameters varying in accordance with Vegard's law. Thus, the quasi-binary section under investigation represents a continuous series of solid solutions. The differential thermal analyses (DTA) has been performed on an apparatus with the accuracy of temperature measurement up to 2 K. Calcinated alumina

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has been used as a reference material. The heating rate has been 3 to 5 K/min. The solidus and liquidus temperatures have been determined using only the heating curves, since the effects, appearing on the cooling curves, are due to nonequilibrium state of solid solutions.

The differential curves have been interpreted in accordance with /1/. Fig. 1 gives the obtained DTA data. From the experimental solidus and liquidus temperatures of the ZnP_2-$ZnAs_2$ system we have calculated the interaction parameters for the solid (k^s) and liquid (k^l) phases to be k^s= - 10000 J/mol and k^l= - 18800 J/mol. The interaction parameters do not depend on the solid solution composition.

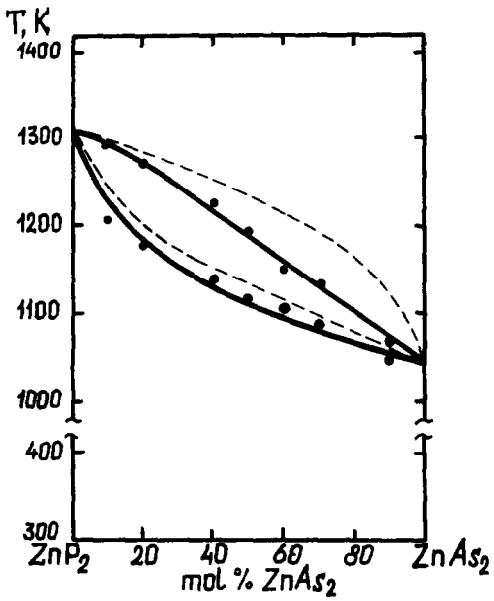

Fig. 1

The interaction parameter values have been used for calculating the solidus and liquidus lines in approximation of the theory of regular solutions:

$$\ln\frac{1-x^s}{1-x^l}=\frac{(x^l)^2\cdot K^l}{RT}-\frac{(x^s)^2\cdot K^s}{RT}-\frac{\Delta S_1}{R}\left(1-\frac{T_1}{T}\right),$$

$$\ln\frac{x^s}{x^l}=\frac{(1-x^l)^2\cdot K^l}{RT}-\frac{(1-x^s)^2\cdot K^s}{RT}-\frac{\Delta S_2}{R}\left(1-\frac{T_2}{T}\right),$$

where x^l and x^s - the concentration of ZnP_2 in the liquid and solid phases; S_1 - the entropy of fusion of ZnP_2; S_2 - the entropy of fusion of $ZnAs_2$; T_1 and T_2 - the temperatures of melting of ZnP_2 and $ZnAs_2$, respectively.

For calculations the empirically obtained entropies of fusion /2/ have been obtained.

Fig. 1 shows the liquidus and solidus lines in the ZnP_2-$ZnAs_2$ system calculated in approximation of the theory of ideal and

regular solutions. The approximation of regular solutions agree well with the experimental points. The heats of mixture in solid and liquid phases have been determined from the interaction parameters:

$$H^{s}_{mix} = K^{s} X (1-X); \quad H^{l}_{mix} = K^{l} X (1-X)$$

The concentration dependence of the heats of mixture is given in Fig. 2. Fig. 3 shows the concentration dependence of the activity of the components in the liquid and solid phases calculated by the relations:

$$\ln \gamma^{l}_{ZnP_2} = \frac{K^{l}}{RT}(1-X_{ZnP_2})^2; \quad \ln \gamma^{l}_{ZnAs_2} = \frac{K^{l}}{RT} X^{2}_{ZnP_2}$$

$$\ln \gamma^{s}_{ZnP_2} = \frac{K^{s}}{RT}(1-X_{ZnP_2})^2; \quad \ln \gamma^{s}_{ZnAs_2} = \frac{K^{s}}{RT} X^{2}_{ZnP_2}$$

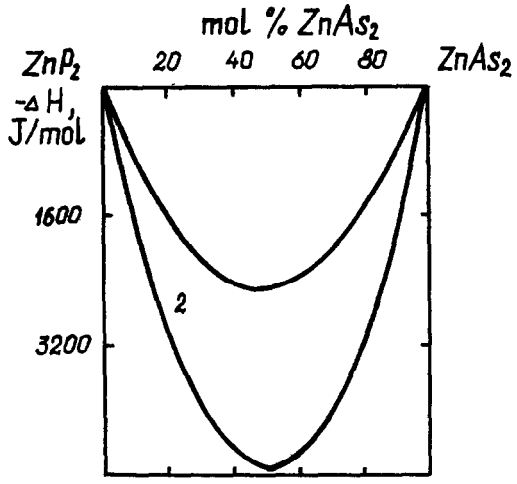

Fig. 2

where γ - the activity coefficient. Since the interaction parameters, liquid and solid phases and, consequently, the heats of mixture and deviations from Raoult's law are negative, it is obvious that in the ZnP_2-$ZnAs_2$ alloys there exists a strong interaction between different atoms, i.e. between P and As.

b) THE ZnP_2-CdP_2 SYSTEM

The synthesis of the alloys and DTA have been out using the procedure described above. To determine the solubility boundaries in solid state a part of alloys has been subjected to quenching at different temperatures.

Fig. 4 illustrates the ZnP_2-CdP_2 phase diagram plotted from the DTA and X-ray analyses data. The ZnP_2 - rich alloys have a monoclinic structure, with a monoclinic ordered phase occupying a considerable area. The solubility of ZnP_2 in the tetragonal CdP_2 is small. Large difference in the melting temperature of the components of the investigated system results in the

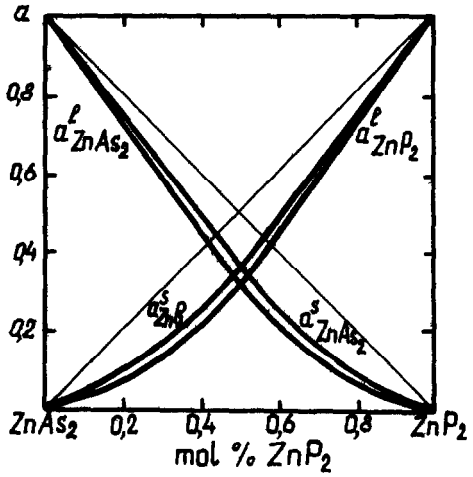

Fig. 3

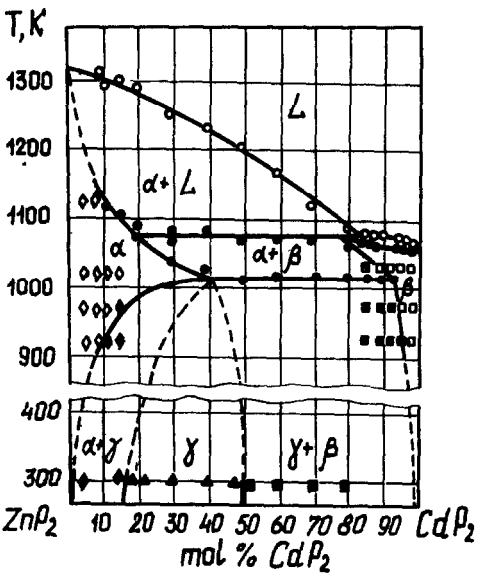

Fig. 4

existence of nonvariant peritectic equilibrium.

CONCLUSION

As could be expected the identity of the crystal lattice of the monoclinic $ZnAs_2$ and ZnP_2, small difference (6.7%) in interatomic distances leads to the formation of solid solutions over the whole concentration range. In the ZnP_2-CdP_2 system the distances between different atoms vary by 9.2%. Apparently, this fact combined with unfavourable entropy factor and substantial difference in melting temperatures hinder the formation of substitutional solid solutions and leads to a complex phase diagram.

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