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Fe-Ga-S-Zn (Iron-Gallium-Sulfur-Zinc)

V. Raghavan

Extraction of Ga from Fe-bearing sphalerite (or wurtzite) requires an understanding of the phase relationships in this quaternary system. In a series of papers [1991Uen, 1994Uen, 1995Uen, 1996Uen, 2002Uen], Ueno and Scott studied the phase equilibria of this quaternary system and the related ternary systems.

Binary Systems

The Fe-Ga system [1993Oka] is characterized by the presence of a closed γ loop and several ordered forms of the Fe-based body-centered-cubic (bcc) solid solution (αFe). α' has the CsCl type cubic structure. The structure of α'' is not known. α''' has the BiF_3 type cubic structure. The intermediate phases of the system are: Fe_3Ga, Fe_6Ga_5, Fe_3Ga_4, and $FeGa_3$. The first two have high- and low-temperature modifications. For brief descriptions of the Fe-S, Fe-Zn, and Zn-S phase diagrams, see the Fe-S-Zn update in this issue. A partial phase diagram of the Ga-S system [Massalski2] depicts four intermediate phases: Ga_2S, GaS, Ga_4S_5, and Ga_2S_3. The Ga-Zn phase diagram [Massalski2] is a simple eutectic system, with the mutual solid solubility between Ga and Zn of about 1 at.%. For crystal structure data, see [Pearson3].

Ternary Systems

[1994Uen] determined two isothermal sections for the Fe-Ga-S system at 900 and 800 °C. Three ternary phases were found at these temperatures approximately along the FeS-Ga_2S_3 line. The phase denoted Z by [1994Uen] has the ZnS (sphalerite *sp*) type structure and a homogeneity range of $Fe_{3.4}Ga_{37.7}S_{58.9}$-$Fe_{13.7}Ga_{28.0}S_{58.3}$ at 900 °C and $Fe_{4.2}Ga_{35.9}S_{59.9}$-$Fe_{13.9}Ga_{28.4}S_{57.7}$ at 800 °C. The phase denoted W by [1994Uen] is hexagonal [1981Par] and has an x-ray pattern similar to that of $FeGa_2S_4$ (low temperature modification, see [Pearson3]), but a different composition of $Fe_9Ga_{12}S_{29}$. The third phase denoted X by [1994Uen] is tetragonal with the composition of $Fe_{22}Ga_{21}S_{57}$. Ga_4S_5 was not found by [1994Uen]. GaS dissolves 0.1 at.% Fe and Ga_2S_3 dissolves 1.0-1.8 at.% Fe. $Fe_{1-x}S$ dissolves 0.4-0.5 at.% Ga. The phases along the Fe-Ga side found by [1994Uen] do not agree with the binary data accepted here. The isothermal section of [1994Uen] at 800 °C is redrawn in Fig. 1, omitting the tie lines to the Fe-Ga side. The section at 900 °C (not shown here) is very similar to the one at 800 °C.

An update on the Fe-S-Zn phase diagram appears in this issue. There are no ternary phases in this system. ZnS dis-

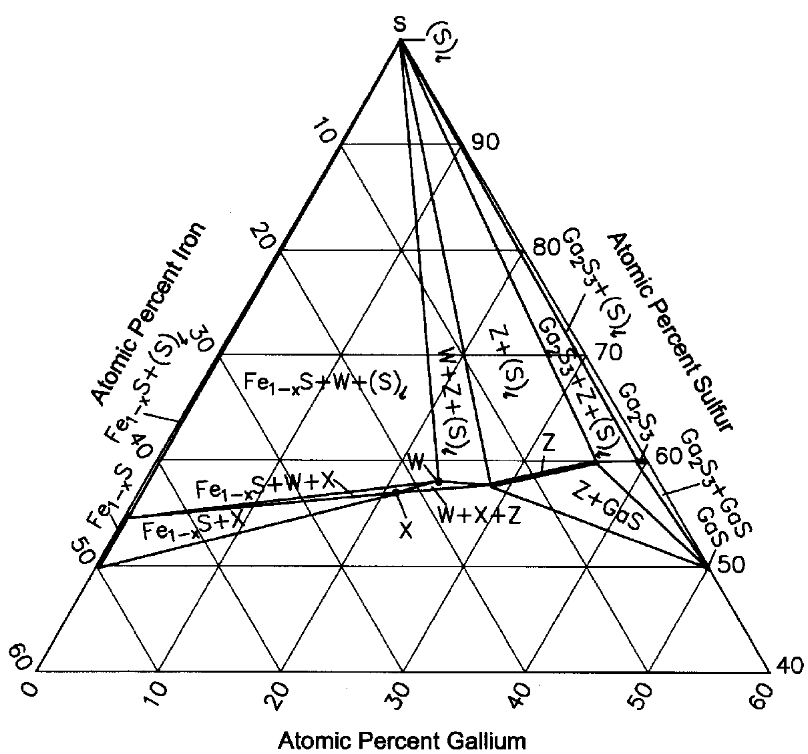

Fig. 1 Fe-Ga-S isothermal section at 800 °C [1994Uen]. Narrow two-phase regions and tie lines to the Fe-Ga side are omitted.

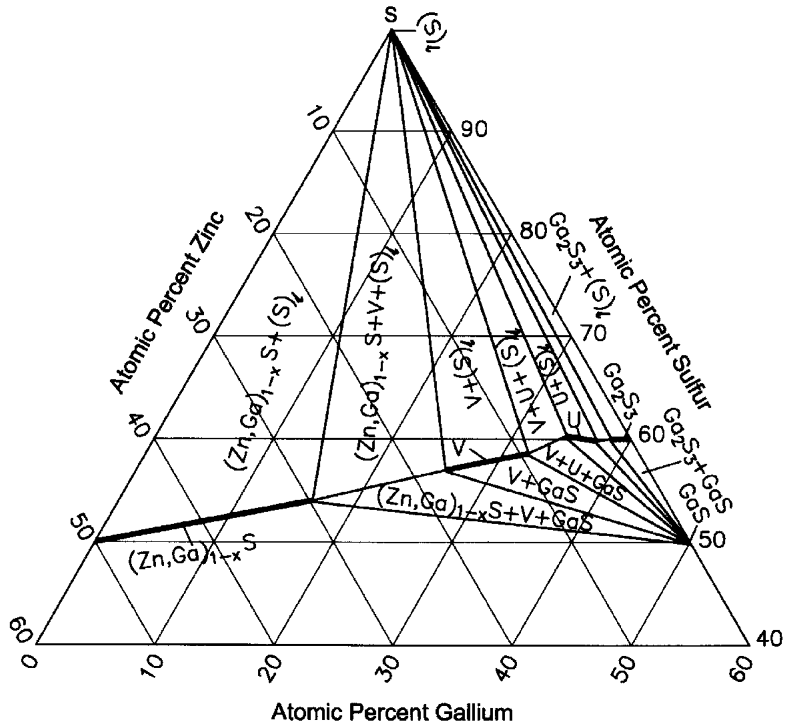

Fig. 2 Ga-S-Zn isothermal section at 800 °C [1995Uen]. Tie lines to the Fe-Ga side are omitted.

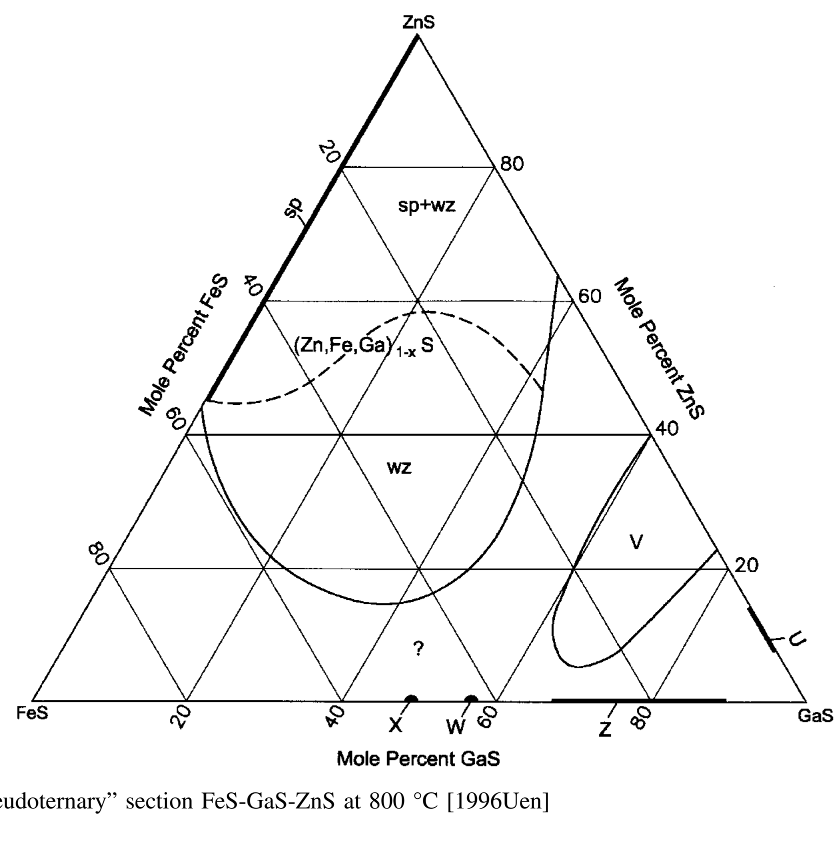

Fig. 3 Fe-Ga-S-Zn "pseudoternary" section FeS-GaS-ZnS at 800 °C [1996Uen]

solves a large amount of FeS. FeS, on the other hand, does not dissolve any ZnS. The Ga-S-Zn phase relations at 900 and 800 °C were determined by [1995Uen]. Two ternary phases were found to lie approximately along the ZnS-Ga_2S_3 join. Phase V [1995Uen] is tetragonal ($CdAl_2S_4$ type) and occurs around the composition $ZnGa_2S_4$, with a range

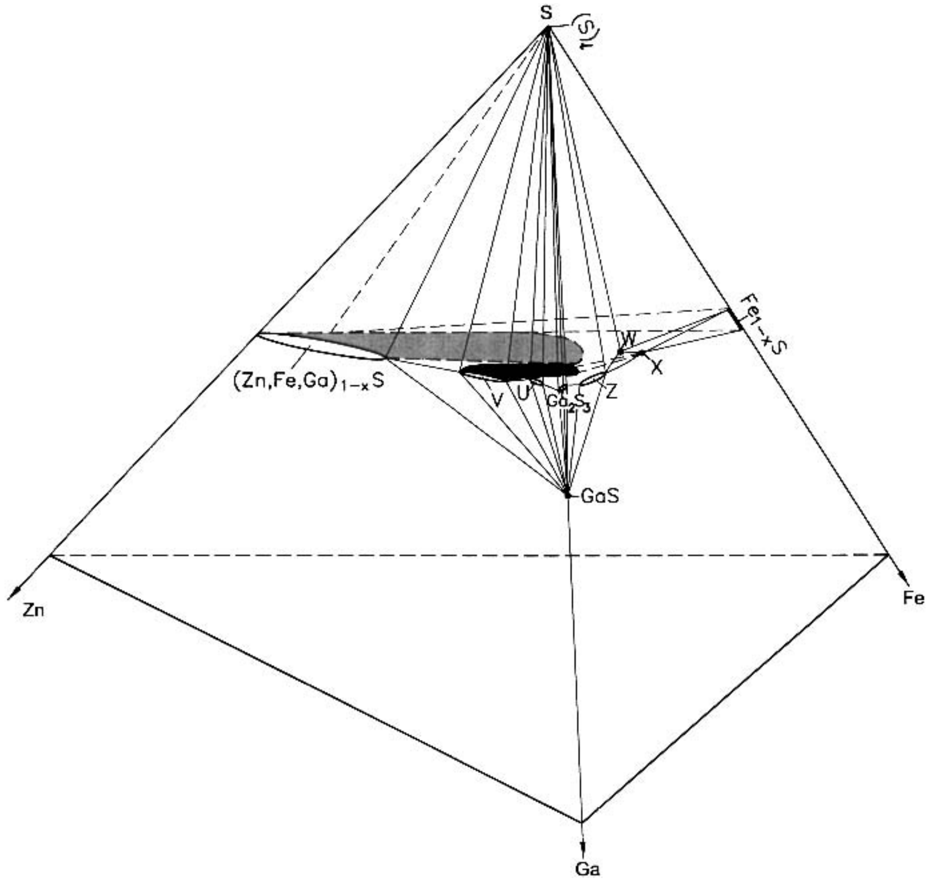

Fig. 4 Fe-Ga-S-Zn perspective view of phase relationships at 800 °C [2002Uen]. Tie lines to the lower part of the tetrahedron are omitted.

Table 1 Fe-Ga-S-Zn Composition Limits of the Quaternary Solid Solutions (V and X) (at.%)

Temperature, °C	Fe	Ga	Zn	S
Phase V				
900	0.0-12.5	24.3-31.0	3.3-17.4	56.5-59.2
800	0.0-13.7	25.0-32.1	2.5-17.0	55.5-58.8
Phase X				
900	20.5-22.2	20.9-21.8	0.0-1.2	55.6-57.2
800	21.5-22.1	20.1-21.3	0.0-1.1	56.0-57.4

of $Zn_{17.4}Ga_{25.7}S_{56.9}$-$Zn_{10.7}Ga_{31.0}S_{58.3}$ at 900 °C and $Zn_{17.0}Ga_{26.0}S_{57.0}$-$Zn_{9.3}Ga_{32.1}S_{58.6}$ at 800 °C. Phase U is cubic (a = 1.0444-1.0493 nm), with a homogeneity range of $Zn_{7.3}Ga_{32.9}S_{59.8}$-$Zn_{3.1}Ga_{37.1}S_{59.8}$ at 900 °C and $Zn_{5.3}Ga_{34.4}S_{60.3}$-$Zn_{3.0}Ga_{37.2}S_{59.8}$ at 800 °C. Ga_4S_5 was not found by [1994Uen]. The solubility of Ga in ZnS is 24.9 at.% at 900 °C and 16.3 at.% at 800 °C [1991Uen]. The solubility of Zn in Ga_2S_3 is 2.2 at.% at 900 °C and 1.7 at.% at 800 °C. Along the Ga-Zn side, in place of a single liquid expected at 900 and 800 °C [Massalski2], [1995Uen] found a Zn-rich liquid and a Ga-rich liquid, with a miscibility gap between them. The isothermal section of [1995Uen] at 800 °C is redrawn in Fig. 2, omitting the tie lines to the Ga-Zn side. The section at 900 °C (not shown here) is very similar to the one at 800 °C.

Quaternary Phase Equilibria

Using synthetic mixtures of monosulfides: FeS, ZnS, and GaS, [1996Uen] studied the effect of composition on the wurtzite → sphalerite transition in ZnS. The transition temperature is strongly dependent on composition and also on kinetic factors. For the composition $(ZnS)_{70}(GaS)_{30}$, the transition temperature is ~875 °C, as compared with 1020 °C for pure ZnS. The results on FeS-GaS-ZnS mixtures were plotted as two "pseudoternary" sections at 900 and 800 °C. The section at 800 °C is redrawn in Fig. 3. Along the FeS-ZnS join, sphalerite is the only stable form and extends as a solid solution from the ZnS end up to ~55 mol% FeS. Addition of GaS results in the appearance of the (*sp* + *wz*) two-phase mixture. Further addition of FeS stabilizes the wurtzite form. Phases Z, W, and X along the FeS-GaS side do not dissolve any ZnS. The phase U along the ZnS-GaS side does not dissolve any FeS. The phase V along ZnS-GaS, however, dissolves up to about 29 mol% FeS. The phase distribution at 900 °C (not shown here) is somewhat similar to that at 800 °C, except that the wurtzite phase field is somewhat larger and the (*sp* + *wz*) field reappears along the ZnS-GaS side between 30 and 55 mol% GaS. There are limitations about the pseudoternary sections constructed by [1996Uen]. The phases shown in Fig. 3 lie approximately on the FeS-Ga_2S_3 join or the ZnS-Ga_2S_3 join (Fig. 1 and 2). On the FeS-GaS-ZnS plane, they are expected to be in equilibrium with other phases (Fig. 1 and 2). In view of this, the sections given by [1996Uen] are not strictly pseudoternary.

[2002Uen] extended their earlier investigations to the quaternary system and found that the solid solution between the three monosulfides (with the structure of sphalerite, wurtzite, or both) extends over a large region, reaching a maximum of 28.6 at.% Fe and 28.2 at.% Ga at 900 °C and 26.4 at.% Fe and 28.2 at.% Ga at 800 °C. The compositional limits of phase V of the Ga-S-Zn system, which dissolves appreciable amounts of Fe, and phase X of the Fe-Ga-S system, which dissolves a limited amount of Zn, are listed in Table 1. [2002Uen] constructed two composition tetrahedra at 900 and 800 °C. A perspective view of the central part of the tetrahedron at 800 °C is shown in Fig. 4. The tie lines extending to $Fe_{1-x}S$, GaS, and $(S)_l$ are shown. The tie lines to the binary sides of Fe-Ga, Fe-Zn, and Ga-Zn are not shown, due to the uncertainty in the binary data adopted or found by the authors.

References

1981Par: M.P. Pardo, L. Dogguy-Smiri, J. Flahaut, and N.H. Dung: "System Ga_2S_3-FeS: Phase Diagram and Crystallographic Study," *Mater. Res. Bull.,* 1981, *16*(11), pp. 1375-84 (in French).

1991Uen: T. Ueno and S.D. Scott: "Solubility of Gallium in Sphalerite and Wurtzite at 800 °C and 900 °C," *Canad. Mineralogist,* 1991, *29,* pp. 143-48.

1993Oka: H. Okamoto: "Fe-Ga (Iron-Gallium)," in *Phase Diagrams of Binary Iron Alloys,* H. Okamoto, ed., ASM International, Materials Park, OH, 1993, pp. 147-51.

1994Uen: T. Ueno and S.D. Scott: "Phase Relations in the System Ga-Fe-S at 900 °C and 800 °C," *Canad. Mineralogist,* 1994, *32,* pp. 203-10.

1995Uen: T. Ueno and S.D. Scott: "Phase Relations in the System Zn-Ga-S at 900 °C and 800 °C," *Canad. Mineralogist,* 1995, *33,* pp. 129-36.

1996Uen: T. Ueno and S.D. Scott: "Inversion Between Sphalerite and Wurtzite-Type Structures in the System Zn-Fe-Ga-S," *Canad. Mineralogist,* 1996, *34,* pp. 949-58.

2002Uen: T. Ueno and S.D. Scott: "Phase Equilibria in the System Zn-Fe-Ga-S at 900 °C and 800 °C," *Canad. Mineralogist,* 2002, *40,* pp. 563-70.