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PHASE EQUILIBRIA IN THE SYSTEM Zn–Fe–Ga–S AT 900° AND 800°C

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ABSTRACT

Phase equilibria in the system Zn–Fe–Ga–S were investigated by dry synthesis at 900° and 800°C using four elements (Zn, Fe, Ga, S) and four synthetic sulfides (ZnS, FeS, GaS, Ga_2S_3) as starting materials. A wide range of $(Zn,Fe,Ga)_{1-x}S$ solid-solutions exist in the central portion of the system at both temperatures. Other solid solutions are phase V, phase U, phase Z, phase W, and phase X. Phase V, previously described as a solid solution in the Zn–Ga–S ternary, extends into the Zn–Fe–Ga–S tetrahedron; its maximum iron content is 12.5 at.% at 900°C and 11.9 at.% at 800°C. Phase U does not contain iron; this is a solid solution in the system Zn–Ga–S only. Phases Z and W do not contain zinc; these are solid solutions in the system Ga–Fe–S. Phase X, GaS, and Ga_2S_3 have very small areas of solid solution in the Zn–Fe–Ga–S tetrahedron. Stable phases along the Zn–S join are zinc liquid, sulfur liquid, and ZnS (sphalerite structure); along the Ga–S join, they are gallium liquid, sulfur liquid, GaS, and Ga_2S_3; along the Fe–S join, they are α-iron, sulfur liquid, and pyrrhotite solid-solution; along the Zn–Ga join, they are zinc liquid and gallium liquid; along the Ga–Fe join, they are gallium liquid, α-iron, and alloy Y, and along the Fe–Zn join, they are α-iron, zinc liquid, and the γ phase. Zinc liquid contains more iron than gallium, and gallium liquid contains more zinc than iron.

Keywords: system Zn–Fe–Ga–S, phase equilibria, dry synthesis, sphalerite, wurtzite, phase U, phase V, phase W, phase X, alloy Y, phase Z.

SOMMAIRE

Nous avons étudié les équilibres de phase dans le système Zn–Fe–Ga–S par synthèses à sec à 900° et 800°C; les matériaux de départ étaient Zn, Fe, Ga et S, et quatre sulfures synthétiques, ZnS, FeS, GaS et Ga_2S_3. Un vaste champ de stabilité de la solution solide $(Zn,Fe,Ga)_{1-x}S$ existe dans la partie centrale du système aux deux températures. Les autres solutions solides sont les phases V, U, Z, W, et X. La phase V, décrite antérieurement comme solution solide dans le système ternaire Zn–Ga–S, se prolonge dans le tétraèdre Zn–Fe–Ga–S; sa teneur maximale en fer est de 12.5 at.% à 900°C et 11.9 at.% à 800°C. La phase U ne contient pas de fer; il s'agit d'une solution solide dans le système Zn–Ga–S seulement. Les phases Z et W ne contiennent pas de zinc; elles sont donc des solutions solides dans le système Ga–Fe–S. Les phases X, GaS, et Ga_2S_3 varient de façon très restreinte en solution solide dans le tétraèdre Zn–Fe–Ga–S. Les phases stables dans le système binaire Zn–S sont zinc liquide, soufre liquide et ZnS (structure de la sphalérite); dans le système binaire Ga–S, elles sont gallium liquide, soufre liquide, GaS et Ga_2S_3; dans le système binaire Fe–S, elles sont fer-α, soufre liquide, et pyrrhotite (solution solide); dans le système binaire Zn–Ga, elles sont zinc liquide et gallium liquide; dans le système binaire Ga–Fe, elles sont gallium liquide, fer-α et l'alliage Y, et dans le système binaire Fe–Zn, elles sont fer-α, zinc liquide et la phase γ. Le zinc liquide contient plus de fer que de gallium, et le gallium liquide contient plus de zinc que de fer.

(Traduit par la Rédaction)

Mots-clés: système Zn–Fe–Ga–S, équilibres de phases, synthèses à sec, sphalérite, wurtzite, phase U, phase V, phase W, phase X, alliage Y, phase Z.

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Introduction

Phase relations of the bounding ternary portions of the quaternary Zn–Fe–Ga–S system have been reported over the past 45 years, including in our series of four papers in this journal (Ueno & Scott 1991, 1994, 1995, Ueno *et al.* 1996). In this paper, we present new experimental data that have elucidated for the first time the complete quaternary system at 900° and 800°C. Gallium-bearing sphalerite is one of the major sources of the world's gallium; the concentration of gallium varies between tens and hundreds of ppm (Sheka *et al.* 1966, Fontboté & Gorzawski 1990). Some high values of gallium have been reported in a zinc sulfide phase in meteorites (Rambaldi *et al.* 1986). The significance of this system in disciplines as diverse as meteoritics and electronics has been described by Gates & Edwards (1978), Rambaldi *et al.* (1986), and in our previous papers (Ueno & Scott 1991, 1994, 1995).

Review of Previous Work

Hahn *et al.* (1955) were the first to investigate the phase relations in the system Zn–Ga–S. Their experiments along the join Ga_2S_3–ZnS at 900°C established the presence of $ZnGa_2S_4$ as a phase. Subsequently, Gates & Edwards (1978) examined the phase relations along the join Ga_2S_3– $ZnGa_2S_4$ from 960° to 1150°C, and found a $Zn_xGa_2S_{3+x}$ solid solution ($0 < x < 0.07$) and a $ZnGa_8S_{13}$ phase. Ueno & Scott (1991) found the solubility of gallium in sphalerite and wurtzite to be 24.9 at.% Ga at 900°C and 16.3% at 800°C, regardless of the zinc sulfide polymorph (all compositions will be expressed in atom %). Ueno & Scott (1995) described the ternary system Zn–Ga–S at 900° and 800°C, and demonstrated the presence of phase V and phase U solid solutions. The $ZnGa_2S_4$ phase of Hahn *et al.* (1955) is included in the phase V solid solution, and the $ZnGa_8S_{13}$ phase of Gates & Edwards (1978) is similar to the phase U solid solution.

The ternary system Ga–Fe–S first was investigated by Pardo *et al.* (1981) along the join Ga_2S_3–FeS from 400° to 1200°C; they found a hexagonal Ga_2FeS_4 phase. Ueno & Scott (1994) determined the ternary phase relations at 900° and 800°C, and described the phase Z, phase W, and phase X solid solutions. The X-ray-diffraction data for the phase Ga_2FeS_4 determined by Pardo *et al.* (1981) are similar to those of phase W, but the composition is significantly different.

The third system that bounds the quaternary system Zn–Fe–Ga–S, Zn–Fe–S, has been investigated over a wide range of temperatures by several investigators (*e.g.*, Barton & Toulmin 1966, Scott & Barnes 1972, Lusk *et al.* 1993).

Within the quaternary system Zn–Fe–Ga–S, Ueno & Scott (1991) studied the solubility of gallium in Fe-bearing sphalerite and wurtzite at 800° and 900°C. Ueno *et al.* (1996) investigated the inversion between sphalerite- and wurtzite-type structures in this quaternary system and showed isothermal sections through the pseudoternary system ZnS–FeS–GaS at 900° and 800°C. To fully understand the controls on Ga content in zinc sulfide, the phase diagram for the quaternary system Zn–Fe–Ga–S must be constructed. We have achieved this objective by conducting some new synthetic phase-equilibria experiments at 900° and 800°C and by combining these results with others and our earlier findings.

Experimental

New dry-synthesis equilibrium experiments in the system Zn–Fe–Ga–S were performed in evacuated silica tubes following the procedures of Ueno & Scott (1991). The experiments in this study focused mainly on the central portion of the quaternary system (Table 1). A complete listing of all experimental results of this and our previous studies is available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 02S, Canada. Reactants were heated in an electric furnace at 900° and 800°C and quenched in cold water.

Products were examined by reflected light microscopy and by X-ray powder diffractometry (Mac Science high-energy X-ray diffractometer, Ni-filtered Cu$K\alpha$ radiation, 40 kV, 100 mA), with Si as an internal standard. Electron-microprobe analyses (Tables 2, 3) were performed on a JEOL 50A operated at 25 kV and 20 nA (measured on a MgO crystal). Synthetic ZnS, FeS, GaS, and Ga_2S_3 were used as standards. Analytical errors are within ±0.1 wt.%.

Solid Solutions

$(Zn,Fe,Ga)_{1-x}S$ solid-solution

As shown by Ueno *et al.* (1996), in projections of the pseudoternary system ZnS–FeS–GaS at 900° and 800°C, the $(Zn,Fe,Ga)_{1-x}S$ solid-solution extends over a broad region from the ZnS composition toward both FeS and GaS compositions. In some parts of the $(Zn,Fe,Ga)_{1-x}S$ field, the product has a sphalerite-type structure, and in others, it has a wurtzite-type structure or a mixture of sphalerite- and wurtzite-type structures. In this study, we have distinguished the sphalerite-type structure from the wurtzite-type structure in Table 1 (see also our previous papers), but not in the figures, where both are included in the field of $(Zn,Fe,Ga)_{1-x}S$ solid solution. The area of this solid solution is large, reaching a maximum of 28.6% Fe and 28.2% Ga at 900°C, and 26.4% Fe and 28.2% Ga at 800°C.

Phase V solid-solution

Although reported as a solid solution in the system Zn–Ga–S (Ueno & Scott 1995), phase V also can con-

TABLE 1. ADDITIONAL EXPERIMENTAL RESULTS FOR THE SYSTEM Zn-Fe-Ga-S AT 900° AND 800°C

Run no.	Temp. (°C)	Reactants	Bulk compositions (At. %) Zn	Fe	Ga	S	Heating days	Products
T044	900	ZnS+6FeS+6GaS+2Fe	3.6	28.6	21.4	46.4	17	Wz+Po+Alloy Y
T052	900	ZnS+2FeS+3GaS+2Fe	7.1	28.6	21.4	42.9	19	Wz+Alloy Y
T054	900	ZnS+2FeS+5GaS+2Fe	5.6	22.2	27.8	44.4	19	V+Wz+Alloy Y
T056	900	ZnS+2FeS+6GaS+2Fe	5.0	20.0	30.0	45.0	19	V+Sp+Alloy Y
T106	900	2FeS+5GaS+6S	0.0	10.0	25.0	65.0	21	Z+S^L
T107	900	FeS+8GaS+2S	0.0	5.0	40.0	55.0	21	GaS+Z
T229	900	7ZnS+3GaS	35.0	0.0	15.0	50.0	25	Wz+Ga^L+GaS
T240	900	ZnS+10FeS+9FeS	2.5	25.0	22.5	50.0	21	X+V+Alloy Y
T241	900	ZnS+8FeS+11GaS	2.5	20.0	27.5	50.0	21	V+Alloy Y
T242	900	ZnS+6FeS+13GaS	2.5	15.0	32.5	50.0	21	GaS+V+Alloy Y
T243	900	ZnS+4FeS+15GaS	2.5	10.0	37.5	50.0	21	GaS+V+Alloy Y
T244	900	Zn+2Fe+2Ga	20.0	40.0	40.0	0.0	20	Alloy Y +Zn^L
T045	800	ZnS+6FeS+6GaS+2Fe	3.6	28.6	21.4	46.4	28	Wz+X+Po
T053	800	ZnS+2FeS+3GaS+2Fe	7.1	28.6	21.4	42.9	26	Wz+Alloy Y
T055	800	ZnS+2FeS+5GaS+2Fe	5.6	22.2	27.8	44.4	30	V+Wz+Alloy Y
T057	800	ZnS+2FeS+6GaS+2Fe	5.0	20.0	30.0	45.0	30	V+Sp+Alloy Y
T109	800	2FeS+5GaS+6S	0.0	10.0	25.0	65.0	40	Z+S^L
T110	800	FeS+8GaS+2S	0.0	5.0	40.0	55.0	40	GaS+Z+Alloy Y
T111	800	3FeS+2GaS+10Fe	0.0	65.0	10.0	25.0	40	Po+α+Alloy Y
T223	800	7ZnS+3GaS	35.0	0.0	15.0	50.0	44	Sp+Ga^L+GaS
T234	800	ZnS+6FeS+GaS	6.25	37.5	6.25	50.0	30	Po+Wz
T235	800	6ZnS+FeS+GaS	37.5	6.25	6.25	50.0	30	Sp+Alloy Y
T236	800	ZnS+10FeS+9GaS	2.5	25.0	22.5	50.0	30	X+V+Alloy Y
T237	800	ZnS+8FeS+11GaS	2.5	20.0	27.5	50.0	30	V+Alloy Y
T238	800	ZnS+6FeS+13GaS	2.5	15.0	32.5	50.0	30	V+GaS+Alloy Y
T239	800	ZnS+4FeS+15GaS	2.5	10.0	37.5	50.0	30	GaS+V+Alloy Y
T245	800	Zn+2Fe+2Ga	20.0	40.0	40.0	0.0	30	Alloy Y+Zn^L

Sp,Sphalerite; Wz,Wurtzite; X,Phase X; Z,Phase Z; V,Phase V; Po,Pyrrhotite; α,α-iron; S^L,sulfur liquid; Ga^L,gallium liquid; Zn^L,zinc liquid

TABLE 2. ADDITIONAL COMPOSITION DATA OF PHASES IN THE Zn-Fe-Ga-S SYSTEM AT 900°C

Run no.	Weight % Zn	Fe	Ga	S	Total	Atomic % Zn	Fe	Ga	S
Wurtzite									
T044	6.0	30.6	24.3	38.8	99.7	4.2	24.9	15.9	55.0
T052	11.7	25.8	25.1	37.1	99.7	8.3	21.4	16.7	53.6
T054	7.3	13.3	41.8	37.7	100.1	5.3	11.2	28.2	55.3
Phase X									
T240	1.7	25.1	32.3	40.2	99.3	1.2	20.5	21.1	57.2
Phase V									
T054	9.2	10.9	40.4	39.2	99.7	6.6	9.1	27.1	57.2
T056	7.7	11.6	42.2	38.7	100.2	5.5	9.7	28.3	56.5
T242	6.0	13.7	41.1	39.5	100.3	4.2	11.4	27.3	57.1
Phase Z									
T106		10.0	48.0	40.1	98.1		8.5	32.5	59.0
T107		12.7	45.8	41.3	99.8		10.5	30.2	59.3
(Ga,Zn,Fe)S solid solution									
T242	0.4	0.9	65.8	31.5	98.6	0.3	0.8	48.5	50.4
Alloy Y									
T044	0.2	72.0	27.6	0.1	99.9	0.2	76.2	23.4	0.2
T052	0.0	70.4	29.6	0.1	100.1	0.0	74.7	25.1	0.2
T054	0.1	68.2	31.6	0.1	100.0	0.1	72.7	27.0	0.2
T056	0.1	58.7	40.8	0.1	99.7	0.1	64.0	35.7	0.2
T240	0.1	70.9	28.2	0.3	99.5	0.1	75.3	24.0	0.6
T241	0.3	64.8	34.5	0.2	99.8	0.3	69.6	29.7	0.4
T242	0.3	68.6	31.0	0.0	99.9	0.3	73.2	26.5	0.0
T243	0.1	66.9	33.0	0.2	100.2	0.1	71.3	28.2	0.4
T244	12.5	46.7	40.6	0.0	99.8	11.9	51.9	36.2	0.0
Zinc									
T244	96.5	1.5	1.6	0.0	99.6	96.7	1.8	1.5	0.0

TABLE 3. ADDITIONAL COMPOSITION DATA OF PHASES IN THE Zn-Fe-Ga-S SYSTEM AT 800°C

Run no.	Weight %					Atomic %			
	Zn	Fe	Ga	S	Total	Zn	Fe	Ga	S
Sphalerite									
T057	10.1	9.8	41.4	37.8	99.1	7.4	8.3	28.2	56.1
T235	40.8	11.0	8.4	40.0	100.2	28.5	9.0	5.5	57.0
Wurtzite									
T045	8.8	30.1	23.1	38.2	100.2	6.1	24.5	15.1	54.3
T053	11.2	25.7	24.0	38.9	99.8	7.8	21.0	15.7	55.5
T234	19.6	29.7	13.8	37.2	100.3	13.7	24.3	9.0	53.0
Phase X									
T045	1.6	27.0	31.6	39.2	99.4	1.1	22.1	20.8	56.0
T236	1.5	26.3	32.5	39.4	99.7	1.1	21.5	21.3	56.1
Phase V									
T237	3.9	16.4	40.5	38.9	99.7	2.8	13.7	27.0	56.5
T238	5.7	13.5	42.5	39.2	100.9	4.0	11.2	28.2	56.6
(Ga,Zn,Fe)S solid solution									
T238	0.2	0.1	67.3	31.7	99.3	0.1	0.1	49.3	50.5
Pyrrhotite solid solution									
T045	0.1	63.1	0.5	36.1	99.8	0.1	49.9	0.3	49.7
T234	0.2	62.0	1.4	36.2	99.8	0.1	49.1	0.9	49.9
Alloy Y									
T053	0.0	74.2	26.1	0.1	100.4	0.0	77.9	21.9	0.2
T057	0.1	70.0	29.9	0.1	100.1	0.1	74.3	25.4	0.2
T235	0.5	53.8	44.6	0.2	99.1	0.5	59.6	39.5	0.4
T236	0.6	55.9	43.2	0.0	99.7	0.6	61.4	38.0	0.0
T245	13.1	43.2	43.9	0.0	100.2	12.5	48.2	39.3	0.0
Zinc									
T245	97.5	1.2	1.0	0.0	99.7	97.7	1.4	0.9	0.0

TABLE 4. COMPOSITIONAL RANGES OF PHASE V SOLID SOLUTION

	Atomic %			
	Zn	Fe	Ga	S
900°C	3.3-17.4	0.0-12.5	24.3-31.0	56.5-59.2
800°C	2.5-17.0	0.0-13.7	25.0-32.1	55.8-58.8

tain a large amount of Fe, so the range of solid solution is large (Table 4). This phase exhibits tetragonal symmetry like the $ZnGa_2S_4$ phase of Hahn *et al.* (1955).

Phase U solid-solution

The phase U solid-solution in the system Zn–Ga–S (Ueno & Scott 1995) does not contain iron, so the composition is confined to this bounding ternary system. The composition of phase U ranges from $Zn_{7.3}Ga_{32.9}S_{59.8}$ to $Zn_{3.1}Ga_{37.1}S_{59.8}$ at 900°C and from $Zn_{5.3}Ga_{34.4}S_{60.3}$ to $Zn_{3.0}Ga_{37.2}S_{59.8}$ at 800°C. This phase possesses a cubic symmetry like the $ZnGa_8S_{13}$ phase of Gates & Edwards (1978).

Phase Z solid-solution

The phase Z solid-solution in the Ga–Fe–S system (Ueno & Scott 1994) does not contain zinc, so the composition is confined to this ternary system. The composition of phase Z ranges from $Ga_{37.7}Fe_{3.4}S_{58.9}$ to $Ga_{28.0}Fe_{13.7}S_{58.3}$ at 900°C and from $Ga_{35.9}Fe_{4.2}S_{59.9}$ to $Ga_{28.4}Fe_{13.9}S_{57.7}$ at 800°C. The X-ray-diffraction pattern indicates a sphalerite-type structure (Ueno & Scott 1994).

Phase W solid-solution

Like phase Z, phase W does not contain zinc (Ueno & Scott 1994). The composition of phase Z is confined to the system Ga–Fe–S, from $Ga_{24.2}Fe_{18.0}S_{57.8}$ to $Ga_{25.1}Fe_{17.0}S_{57.9}$ at 900°C and from $Ga_{23.7}Fe_{18.3}S_{58.0}$ to $Ga_{23.8}Fe_{18.3}S_{57.9}$ at 800°C. This phase shows hexagonal symmetry similar to that of the Ga_2FeS_4 phase of Pardo *et al.* (1981).

Phase X solid-solution

Although phase X has been reported to be a solid solution in the system Ga–Fe–S (Ueno & Scott 1994), the phase has a limited solid-solution extending into the Zn–Fe–Ga–S tetrahedron (Table 5). This phase shows tetragonal symmetry (Ueno & Scott 1994).

Pyrrhotite solid-solution

According to Kullerud & Yoder (1959) and Kullerud (1967), the pyrrhotite solid-solution extends from stoichiometric FeS to $Fe_{43.7}S_{56.3}$ at 900°C and to $Fe_{44.2}S_{55.8}$ at 800°C. In the quaternary system Zn–Fe–Ga–S, pyr-

TABLE 5. COMPOSITIONAL RANGES OF PHASE X SOLID SOLUTION

	Atomic %			
	Zn	Fe	Ga	S
900°C	0.0-1.2	20.5-22.2	20.9-21.8	55.6-57.2
800°C	0.0-1.1	21.5-22.1	20.1-21.3	56.0-57.4

rhotite contains up to 0.3% Zn and 0.5% Ga at 900°C, and 0.1% Zn and 0.9% Ga at 800°C. Optically, Ga-bearing pyrrhotite is similar to pure pyrrhotite in the system Fe–S.

Metal alloy phases

Five metal alloy phases exist in the system Zn–Fe–Ga at 900° and 800°C: gallium liquid, zinc liquid, γ phase, α-iron, and alloy Y. Both gallium (melting point 29.8°C, boiling point approximately 2300°C) and zinc (melting point 419.5°C, boiling point approximately 930°C) were in the liquid state during the experiments. The quenched liquids did not contain visible signs of exsolution when examined by reflected light microscopy at 400× or by electron microprobe (Table 6). Along the Zn–Fe join, zinc liquid contains approximately 12% Fe at 900°C and 8% Fe at 800°C, α-iron contains approximately 1% Zn at 900°C and 11% Zn at 800°C, and the γ phase exists between Zn_3Fe_{97} and $Zn_{34}Fe_{66}$ at 900°C and between $Zn_{15}Fe_{85}$ and $Zn_{41}Fe_{59}$ at 800°C (Hansen & Anderko 1958).

Alpha-iron developed well-formed cubic crystals, in isolated, solid-state aggregates of polyhedra up to 30 μm in diameter, according to powder X-ray diffraction and secondary electron images. Compositions range from Fe_{100} to $Fe_{82}Ga_{18}$ at 900°C and from Fe_{100} to $Fe_{89.9}Ga_{10.1}$ at 800°C in experiments in the system Ga–Fe–S (Ueno & Scott 1994).

According to Kroll (1932), gallium alloys easily with iron. Dasarathy (1964) reported an alloy of composition $Fe_{70}Ga_{30}$ with a primitive cubic cell. On the other hand, our alloy Y is tetragonal, according to powder X-ray diffraction (Ueno & Scott 1991), and has an extensive field of solid solution, from $Ga_{73.5}Fe_{26.3}S_{0.2}$ to $Ga_{22.7}Fe_{77.1}S_{0.2}$ at 900°C and from $Ga_{57.7}Fe_{42.1}S_{0.2}$ to $Ga_{21.9}Fe_{77.9}S_{0.2}$ at 800°C in the Ga–Fe–S system. Alloy Y contains 11.9% Zn at 900°C and 12.5% Zn at 800°C (Tables 2, 3).

Discussion

Phase diagrams of the quaternary system Zn–Fe–Ga–S at 900°C (Fig. 1) and at 800°C (Fig. 2) have been constructed from the experimental results in Tables 1 to 6 and from previous data. The data for the systems Zn–Fe–S, Ga–Fe–S, Zn–Ga–S, ZnS–FeS–GaS, and Zn–Fe–Ga are from Barton & Toulmin (1966), Ueno & Scott (1994, 1995), Ueno *et al.* (1996), and Hansen & Anderko (1958), respectively.

TABLE 6. COMPOSITIONAL RANGES OF GALLIUM AND ZINC LIQUIDS

	Atomic %			
	Zn	Fe	Ga	S
Gallium liquid				
900°C	0.0-8.7	0.0-1.7	89.2-100.0	0.0-0.4
800°C	0.0-5.3	0.0-1.1	93.2-100.0	0.0-0.4
Zinc liquid				
900°C	96.7-100.0	0.0-1.8	0.0-1.5	
800°C	97.7-100.0	0.0-1.4	0.0-0.9	

The largest field of solid solution in the central portion of this quaternary system, is occupied by $(Zn,Fe,Ga)_{1-x}S$. As described by Ueno *et al.* (1996), this field consists of three parts: a sphalerite-type phase region, a wurtzite-type phase region, and both types in a mixed region. In the system Fe–Zn–S (Kullerud 1953, Barton & Toulmin 1966), the inversion temperature was found to decrease with increasing FeS content in the (Zn,Fe)S solid-solution, to values as low as 850°–875°C at 56 mol.% FeS. The inversion temperature between sphalerite- and wurtzite-type structures depends on the chemical composition, and the rate of reaction in the inversion is very slow in both directions. Thus in this study, we treated these three regions as one solid solution. The solid solution stretches from stoichiometric ZnS composition toward stoichiometric FeS and toward the Ga_2S_3 composition instead of GaS, resulting in a nonstoichiometric phase (Ga omission). Tie lines extend from this solid solution to Zn liquid, Ga liquid, S liquid, pyrrhotite solid-solution, the γ phase [(Zn,Fe) alloy], alloy Y [(Ga,Fe) alloy], phase V solid-solution, and GaS. Compared to 900°C, the $(Zn,Fe,Ga)_{1-x}S$ solid-solution area becomes smaller on the Zn–Ga–S surface at 800°C, but it stretches equally far into the Zn–Fe–Ga–S tetrahedron.

The next largest field of solid solution in the central portion is phase V. Like the $(Zn,Fe,Ga)_{1-x}S$ solid-solution, phase V is a ternary solid-solution in the bounding Zn–Ga–S system and also extends well into the Zn–Fe–Ga–S tetrahedron at both temperatures. Tie lines extend to S liquid, the solid solutions $(Zn,Fe,Ga)_{1-x}S$, phases U and X, alloy Y, and GaS.

Phase U has a solid-solution area only in the Zn–Ga–S system and covers only one half the compositional range at 800°C compared to 900°C. Tie lines extend to S liquid, phase V solid solution, Ga_2S_3, and GaS.

Phases Z, W, and X, all solid solutions, exist essentially only in the Ga–Fe–S plane at both temperatures, although phase X can contain as much as 1% Zn at 900°C. Tie lines extend from phase Z to S liquid, Ga_2S_3, GaS, phase W and phase X solid-solutions, and alloy Y; from phase W to S liquid, pyrrhotite solid-solution, phase Z, and phase X; and from phase X to solid-solution phases Z, W, V, pyrrhotite, and alloy Y.

Some minor ternary and quaternary solid-solutions extend from the binary joins. Pyrrhotite solid-solution contains small amounts of gallium and zinc. Both GaS

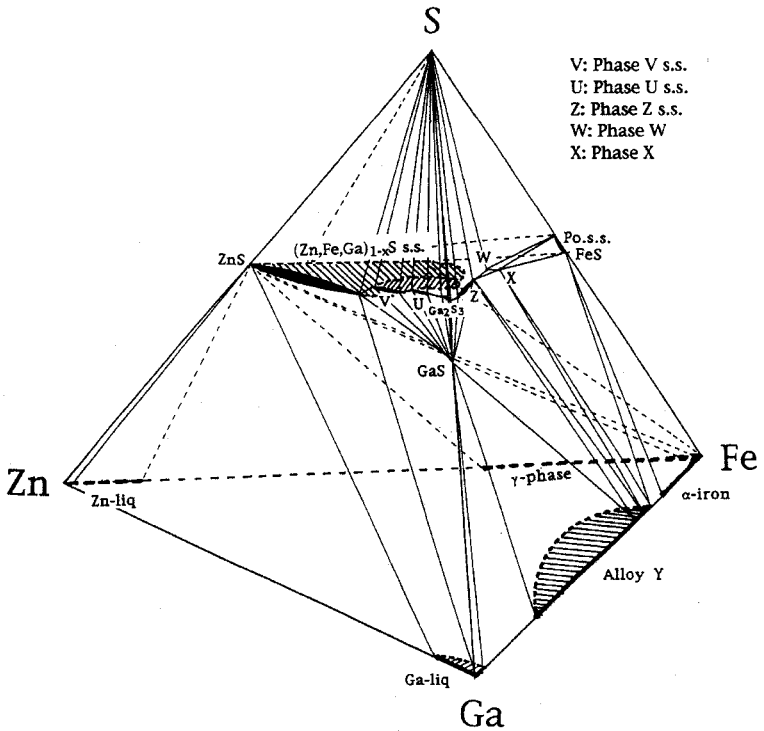

FIG. 1. Phase diagram for the system Zn–Fe–Ga–S at 900°C (shown in atomic %).

and Ga_2S_3 have small areas of solid solution into the Zn–Fe–Ga–S tetrahedron. Zinc liquid contains more iron than gallium, and gallium liquid contains more zinc than iron, although solubilities are less at 800° than at 900°C. On the Fe–Ga join, α-iron and alloy Y have solid-solution areas, and on the Fe–Zn join, the γ phase has a solid-solution area. The extent of the solid solution of alloy Y decreases at 800°C, especially in gallium content, and the gallium content of α-iron becomes one-third of that at 900°C.

CONCLUDING REMARKS

Our study of the system Zn–Fe–Ga–S at 900° and 800°C explains the gallium content of zinc-rich sulfide ores which, together with sulfates, silicates, and oxides, are a major commercial source of Ga (Sheka *et al.* 1966, Johan *et al.* 1983, Bernstein 1986, Dutrizac *et al.* 1986, Jambor *et al.* 1996). The reports that the sphalerite from MVT deposits contains up to 50 ppm Ga (Fontboté & Gorzawski 1990) and that the sphalerite in a metal sulfide nodule of the Qingzhen (EH3) chondrite contains between 2.05 and 3.70 wt.% Ga (Rambaldi *et al.* 1986) come as no surprise, now that the phase is known to have extensive solid-solution in the quaternary system. Gallium dissolves in both sphalerite and wurtzite to form a wide range of solid solution in the quaternary system Zn–Fe–Ga–S. The solid solution is nonstoichiometric $(Zn,Fe,Ga)_{1-x}S$, which gives this phase semiconducting properties of interest to the electronic industry (Gates & Edwards 1978).

Phase relations at significantly lower temperatures cannot be determined by the dry synthesis methods used in this study because of the refractory nature of sphalerite. However, the extensive $(Zn,Fe,Ga)_{1-x}S$ solid-solution at 800°C probably persists to lower temperatures, although perhaps with a more restricted composition. This would explain why no binary Ga–S minerals occur in nature.

Several synthetic phases encountered in this study (phases U, V, W, X, Z) have ternary or quaternary solid-solutions that also should be investigated for their physical properties (*e.g.*, semiconduction, magnetism, optics) for possible industrial applications. None of these phases yet are known as minerals, and if they exist, they would occur in very Ga-rich iron or zinc sulfide deposits (*e.g.*, at the Apex mine, Trappes deposit in the central Pyrénées, and Tsumeb in Namibia).

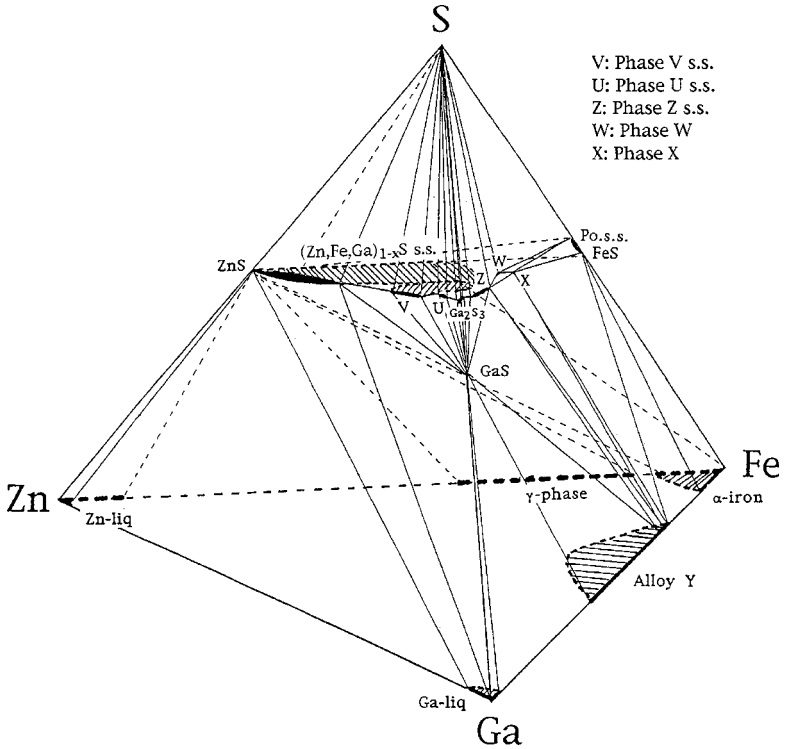

FIG. 2. Phase diagram for the system Zn–Fe–Ga–S at 800°C (shown in atomic %).

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