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SOLUBILITY OF GALLIUM IN SPHALERITE AND WURTZITE AT 800°C AND 900°C

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ABSTRACT

Solubilities of gallium in sphalerite and wurtzite were investigated at 800°C and 900°C by means of phase-equilibrium experiments. In the system Zn–Ga–S, the maximum solubility of Ga in sphalerite is 24.9 atomic % at 900°C and 16.3 atomic % at 800°C. In the system Zn–Fe–Ga–S, gallium solubility is more than 21.4 atomic % in wurtzite at 900°C, more than 15.6 atomic % in wurtzite at 800°C, and more than 27.4 atomic % in sphalerite at 800°C. The cell parameters of Ga-bearing sphalerite and Ga-bearing wurtzite decrease dramatically with increasing gallium content.

Keywords: gallium, solid solution, sphalerite, wurtzite, cell parameters.

SOMMAIRE

Nous avons étudié la solubilité du gallium dans la sphalérite et la wurtzite à 800° et 900°C en utilisant des expériences de synthèse. Dans le système Zn–Ga–S, la sphalérite peut contenir jusqu'à 24.9% de Ga (base atomique) à 900°C, et 16.3% à 800°C. Dans le système Zn–Fe–Ga–S, la solubilité du gallium dans la wurtzite est supérieure à 21.4% à 900°C et 15.6% à 800°C, tandis qu'elle est supérieure à 27.4% dans la sphalérite à 800°C. Les paramètres du réseau de la sphalérite et de la wurtzite gallifères diminuent de façon dramatique à mesure qu'augmente la teneur en gallium.

(Traduit par la Rédaction)

Mots-clés: gallium, solution solide, sphalérite, wurtzite, paramètres réticulaires.

INTRODUCTION

Gallium is found in nature in oxide, silicate and sulfide minerals (Johan *et al.* 1983, Bernstein 1986). The main Ga-containing sulfide minerals are renierite, germanite and gallite. According to Sheka *et al.* (1966), the dominant host of Ga in sulfide ores is sphalerite; the concentration of Ga varies between tens and hundreds of ppm. Some high values of gallium have been reported in a zinc sulfide phase in meteorites. A zinc sulfide found in the Yamato-74370 (EH4) chondrite contains up to 5.8 wt.% Ga (Nagahara & El Goresy 1984), and that from the Qingzhen (EH3) chondrite, up to 1700 ppm Ga (Woolum *et al.* 1984). Sphalerite in a metal sulfide nodule of the Qingzhen (EH3) chondrite contains between 2.05 and 3.70 wt.% Ga (Rambaldi *et al.* 1986).

We have measured the solubilities of gallium in sphalerite and wurtzite by synthetic phase-equilibrium experiments, and here present results on the first study of the system Zn–Fe–Ga–S. Natural Ga-bearing zinc sulfide, particularly that in meteorites, commonly contains considerable Fe, so that this system is of greater relevance than the Fe-free system Zn–Ga–S, which had previously been studied at 900°C by Hahn *et al.* (1955).

STARTING MATERIALS AND THEIR SYNTHESIS

Three elements (Fe, Ga and S), all of 99.9% or better purity, and three synthetic monosulfides (ZnS, FeS and GaS) were used as starting materials. ZnS was used as a commercially available white, powdered reagent, in wurtzite form. FeS was synthesized by reacting iron and sulfur in an evacuated silica glass tube at 400°C for two days in order to obtain initial reaction without bursting the tube, and then at 500°C for five days to obtain homogenization. The product was determined by X-ray powder diffraction (Fe$K\alpha$ radiation) to be troilite (FeS).

The synthesis of GaS was difficult. Gallium melts at 29.8°C, and its liquid does not mix with liquid sulfur, which melts at 119°C, because a thin layer of gallium sulfide forms at the interface and inhibits further reaction. Despite this, Klemm & Vogel (1934) managed to synthesize GaS from elements using a V-shaped silica tube. Rustamov & Mardakhaev (1964) used an oscillation method to react gallium and sulfur completely. Lieth *et al.* (1966, 1967) synthesized GaS by sublimation using a silica boat in a long silica tube.

Our method for synthesizing GaS was as follows. Gallium and sulfur in an atomic ratio of 1 to 1 were sealed in a 20-cm-long evacuated silica glass tube. The sample tube was heated from 200°C to 850°C in a furnace that was inclined at about 10°; the temperature was increased by 50°C per day for 14 days. The sample tube was removed from the furnace a few times a day and shaken in order to mix unreacted molten gallium and sulfur. Yellow homogeneous GaS was obtained. The X-ray powder data for our synthetic GaS are compared in Table 1 with those for synthetic GaS obtained by Hahn & Frank (1955b). Goodman *et al.* (1985) proposed that there are in fact three polymorphs of GaS: β-GaS, HP-GaS and ε-GaS. Beta-GaS is a well-established polymorph that is stable at room temperature and pressure; it crystallizes in the hexagonal space-group $P6_3/mmc$, and its unit-cell dimensions are: *a* 3.585, *c* 15.50 Å (Hahn & Frank 1955b, Wyckoff 1963). This is the polymorph that we synthesized. HP-GaS has a high-pressure structure that can be derived from the β structure. ε-GaS has a lower symmetry, *P6m2* (Goodman *et al.* 1985). Both HP-GaS and ε-GaS are metastable forms of GaS, and their fields of stability are not known precisely. If the heating rate is too high during synthesis or the mixing between liquid gallium and liquid sulfur is inefficient, a sugar-like, transparent white crystalline material that has excess gallium metal is produced. This material is Ga_2S_3, as determined by X-ray powder diffraction and electron-microprobe analysis. According to Hahn & Frank (1955a), Ga_2S_3 also has three polymorphs, named α, β and γ. Beta-Ga_2S_3 is the disordered, high-temperature phase that has a wurtzite structure, γ-Ga_2S_3 is the disordered, low-temperature phase that has a sphalerite structure, and α-Ga_2S_3 is a superstructure phase with a wurtzite structure. The fields of thermal stability of these three phases are not well known. As shown in Table 2, X-ray data for our Ga_2S_3 agree with those for α-Ga_2S_3 obtained by Goodyear *et al.* (1961).

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR GaS

Hahn & Frank (1955b)			This study. T001-1		
d(Å)	I	hkl	d_{obs}(Å)	d_{calc}(Å)	I
7.75	st(-)	002	7.75	7.73	59
3.875	st(-)	004	3.870	3.866	100
3.105	st	100	3.100	3.101	3
3.044	st	101	3.036	3.047	2
2.882	ss	102	2.876	2.878	1
2.661	m	103	2.653	2.657	2
2.583	s	006	2.576	2.577	17
2.423	s-m	104	2.419	2.419	1
2.194	m(+)	105	2.187	2.190	5
1.986	ss	106	1.9831	1.9820	1
1.938	sss	008	1.9333	1.9328	2
1.803	st(+)	107	1.7989	1.7992	11
1.793	st	110	1.7897	1.7905	7
1.746	ss(-)	112	1.7445	1.7443	1
1.644	-	108	1.6399	1.6403	1
1.627	s-m	114	1.6247	1.6247	1
1.552	ss(-)	200	1.5516	1.5506	1
1.550	-	00<u>10</u>	1.5465	1.5462	1
hex.			hex.		
a 3.585 Å			a 3.5810(7) Å		
c 15.50 Å			c 15.462(3) Å		

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR α-Ga_2S_3

Goodyear et al. (1961)			This study, T026		
d(Å)	I	khl	d_{obs}(Å)	d_{calc}(Å)	I
5.33	ms	110	5.34	5.33	20
4.77	m	200	4.775	4.769	16
4.73	w	111	4.732	4.728	7
3.515	w	311	3.519	3.518	5
3.488	wm	202	3.496	3.494	9
3.209	vs	020	3.215	3.211	64
3.010	s	402	3.014	3.013	100
2.844	wm	310	2.848	2.849	15
2.824	ms	112	2.830	2.828	25
2.742	wm	021	2.748	2.749	5
2.654	w(b)	220	2.663	2.663	4
		002	2.658	2.657	3
2.378	vw	400	2.384	2.384	1
2.359	vw	222	2.363	2.364	1
2.206	m	511	2.209	2.209	13
2.193	w	203	2.197	2.197	7
2.185	w	313	2.190	2.190	7
2.098	vw	602	2.103	2.102	3
2.085	wm	513	2.089	2.090	6
2.040	w		2.046		3
1.903	vw(b)				
1.884	vw		1.8868		2
1.851	vs		1.8533		29
1.824	w				
1.810	vw				
a 12.637 Å			a 12.852(4) Å		
b 6.41_1 Å			b 6.421(3) Å		
c 7.03_8 Å			c 7.048(2) Å		
β=131.07°			β=131.07(3)°		

b=rather broad

SYNTHETIC PHASE-EQUILIBRIUM EXPERIMENTS IN THE SYSTEM Zn–Fe–Ga–S

Meteorites that contain a Ga-bearing zinc sulfide contain metallic iron and troilite and, therefore, have formed at a low sulfur fugacity. Thus, many of our experiments incorporated an FeS + Fe buffer. Five assemblages of starting materials were used: A: (ZnS + GaS) + 2(FeS + Fe), B: (ZnS + 2GaS) + 2(FeS + Fe), C: (ZnS + 4GaS) + 2(FeS + Fe), D: ZnS + GaS + FeS, and E: ZnS + 2GaS. Starting materials were mixed by grinding in an agate mortar and were sealed in evacuated silica tubes. These were heated in an electric furnace at 900°C or 800°C and were quenched in cold water after heating for 13 to 41 days (900°C runs) or for 26 to 56 days (800°C runs).

Products were examined by reflected light microscopy and by X-ray powder diffractometry (Mn-filtered Fe*K*α radiation), with Si as an internal standard. Cell parameters were calculated for some phases by the least-squares method from precisely measured *d*-values. The phase assemblages produced are shown in Table 3. The chemical compositions of the phases were determined with an ETEC electron microprobe using metallic iron, GaP, synthetic sphalerite and synthetic troilite as standards. The analytical results, each an average of several grains, are shown in Table 4. All analytical errors are within 0.1 wt.%.

(Fe,Ga) alloy

An alloy of Fe and Ga was obtained in runs T009,

TABLE 3. EXPERIMENTAL RESULTS FOR THE SYSTEM Zn-Fe-Ga-S AT 900°C AND 800°C

Run no.	Temp.(°C)	Reactants	Bulk compositions (At.%) Zn	Fe	Ga	S	Heating days	Products
T009	900	ZnS+GaS +2(FeS+Fe)	10.0	40.0	10.0	40.0	41	wz+po+Y
T022	900	ZnS+2GaS +2(FeS+Fe)	8.3	33.3	16.7	41.7	20	wz+Y
T039	900	ZnS+GaS +FeS	16.7	16.7	16.7	50.0	13	wz+Y
T033	900	ZnS+4GaS +2(FeS+Fe)	6.2	25.0	25.0	43.8	19	wz+Y
T027	900	ZnS+2GaS	16.7	0.0	33.3	50.0	22	sp+GaS+Ga
T010	800	ZnS+GaS +2(FeS+Fe)	10.0	40.0	10.0	40.0	56	wz+po+Y
T023	800	ZnS+2GaS +2(FeS+Fe)	8.3	33.3	16.7	41.7	34	wz+Y
T040	800	ZnS+GaS +FeS	16.7	16.7	16.7	50.0	29	wz+Y
T034	800	ZnS+4GaS +2(FeS+Fe)	6.2	25.0	25.0	43.8	26	sp+Y
T028	800	ZnS+2GaS	16.7	0.0	33.3	50.0	28	sp+GaS+Ga

wz:wurtzite, po:pyrrhotite, Y:alloy (Fe,Ga), sp:sphalerite

TABLE 4. CHEMICAL COMPOSITION OF ALLOY Y, PYRRHOTITE AND SPHALERITE-WURTZITE

Run no.		Temp.(°C)	Weight % Zn	Fe	Ga	S	total	Atomic % Zn	Fe	Ga	S
alloy Y											
T009		900	0.0	73.7	27.1	0.0	100.8	0.0	77.3	22.7	0.0
T022		900	0.0	69.3	29.2	0.0	98.5	0.0	74.8	25.2	0.0
T039		900	0.0	69.2	31.6	0.0	100.8	0.0	73.2	26.8	0.0
T033		900	0.0	67.1	32.7	0.0	99.8	0.0	72.0	28.0	0.0
T010		800	0.0	73.8	26.1	0.0	99.9	0.0	77.9	22.1	0.0
T023		800	0.0	72.6	26.3	0.0	98.9	0.0	77.5	22.5	0.0
T040		800	0.0	69.4	28.1	0.0	97.5	0.0	75.5	24.5	0.0
T034		800	0.0	70.3	31.0	0.0	101.3	0.0	73.9	26.1	0.0
pyrrhotite											
T009		900	0.0	63.7	0.0	36.6	100.3	0.0	50.0	0.0	50.0
T010		800	0.0	63.2	0.0	36.6	99.8	0.0	49.8	0.0	50.2
sphalerite-wurtzite											
T009	wz	900	18.6	34.2	10.9	37.8	101.5	12.7	27.4	7.1	52.8
T022	wz	900	16.1	23.2	23.1	37.0	99.4	11.5	19.3	15.4	53.8
T039	wz	900	25.0	16.1	22.0	37.0	100.1	17.9	13.5	14.7	53.9
T033	wz	900	11.4	17.5	32.0	38.3	99.1	8.2	14.6	21.4	55.8
T027	sp	900	27.6	0.0	36.6	36.9	101.1	20.1	0.0	24.9	55.0
T010	wz	800	21.0	34.2	6.9	36.5	98.5	14.8	28.2	4.5	52.5
T023	wz	800	15.6	22.6	23.5	37.8	99.5	11.1	18.7	15.6	54.6
T040	wz	800	25.4	15.3	21.9	36.9	99.5	18.2	12.9	14.8	54.1
T034	sp	800	10.9	8.8	40.2	38.6	98.5	7.9	7.5	27.4	57.2
T028	sp	800	40.3	0.0	23.8	36.3	100.4	29.5	0.0	16.3	54.2

T022, T039 and T033 at 900°C and T010, T023, T040 and T034 at 800°C. The alloy is yellowish white in reflected light and shows no anisotropism. It is optically similar to iron, but has a distinctly different X-ray-diffraction pattern. Table 5 shows the X-ray data of α-iron, an alloy of composition $Fe_{70}Ga_{30}$ (Dasarathy 1964), and our alloy $Fe_{77.9}Ga_{22.1}$ (run T010). Alpha-iron has a body-centered cubic cell, whereas alloy $Fe_{70}Ga_{30}$ has a primitive cubic cell (Dasarathy 1964). The five diffraction lines observed for our alloy ($Fe_{77.9}Ga_{22.1}$)

TABLE 5. X-RAY POWDER-DIFFRACTION DATA FOR α-IRON AND ALLOY Y

1. α-iron d(Å)	I	hkl	2. alloy, $Fe_{70}Ga_{30}$ d(Å)	I	hkl	3. alloy, $Fe_{77.9}Ga_{22.1}$ d_{obs}(Å)	d_{calc}(Å)	I	hkl
			3.7000	w	100				
			2.5903	w	110				
			2.1210	vvs	111	2.148	2.144	100	112
2.0268	100	110				2.054	2.056	88	103
			1.8384	vs	200	1.8594	1.8602	86	200
			1.6457	vw	210				
			1.5080	vvw	211				
1.4332	20	200							
			1.3010	s	220	1.3153	1.3154	85	220
			1.2280	vvw	221	1.2394	1.2394	74	222
1.1702	30	211	1.1664	vvw	310				
cubic a 2.8664 Å			cubic a 3.6834 Å			tetragonal a 3.720(1) Å, c 7.40(1) Å			

1: PDF 6-0696 2: Dasarathy (1964) 3: this study, T010-800°C

TABLE 6. X-RAY POWDER-DIFFRACTION DATA FOR SPHALERITE

PDF 5-566			T028		T027		T034	
Ga content			16.3 at.%		24.9 at.%		27.4 at.%	
d(Å)	I	hkl	d(Å)	I	d(Å)	I	d(Å)	I
3.123	100	111	3.070	100	3.044	100	3.037	100
2.705	10	200	2.656	2	2.641	4	2.627	1
1.912	51	220	1.8785	43	1.8648	40	1.8570	44
a	5.4060 Å		5.313(1) Å		5.276(2) Å		5.253(2) Å	

TABLE 7. X-RAY POWDER-DIFFRACTION DATA FOR WURTZITE

PDF 5-492			T009		T022		T039		T033	
Ga content			7.1 at.%		15.4 at.%		14.7 at.%		21.4 at.%	
d(Å)	I	hkl	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I
3.309	100	100	3.300	100	3.273	100	3.271	100	3.255	96
3.128	86	002	3.115	77	3.087	83	3.087	75	3.066	100
2.925	84	101	2.918	68	2.891	80	2.888	82	2.873	68
2.273	29	102	2.267	33	2.245	40	2.245	40	2.232	32
1.911	74	110	1.9085	62	1.8901	66	1.8895	79	1.8777	92
1.764	52	103	1.7592	58	1.7433	63	1.7433	71	1.7327	67
a	3.820 Å		3.818(1) Å		3.780(1) Å		3.778(1) Å		3.756(1) Å	
c	6.260 Å		6.233(2) Å		6.177(2) Å		6.178(2) Å		6.140(2) Å	

can be indexed using a tetragonal cell having *a* 3.720(1), *c* 7.40(1) Å (Table 5). We have named this alloy "phase Y". Compositions are listed in Table 4. At 900°C, gallium contents of alloy Y vary from 22.7 to 28.0 atomic %, and at 800°C from 22.1 to 26.1 atomic %. These compositional variations are consistent with the gallium contents of the bulk compositions of the reactants. We did not obtain the $Fe_{70}Ga_{30}$ phase reported by Dasarathy (1964).

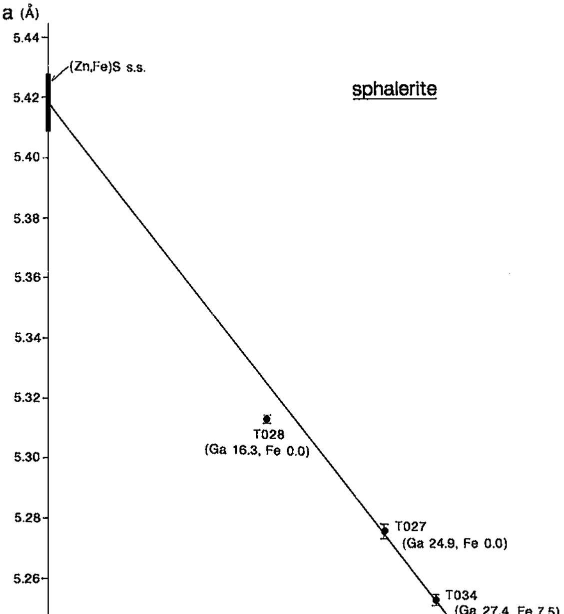

Fig. 1. Relationship between unit-cell parameter *a* of Ga-bearing sphalerite and composition, expressed as Ga/(Zn+Fe+Ga) ratio. The range in *a* of Ga-free sphalerite is from Barton & Toulmin (1966). Numbers in brackets express the atomic % of Ga and Fe.

Sulfides

Pyrrhotite was obtained in runs T009 at 900°C and T010 at 800°C (Table 3). It contains neither Zn nor Ga and is nearly stoichiometric FeS (troilite) (Table 4). Ga-bearing sphalerite, Ga-bearing wurtzite, or their mixture were obtained from all runs (Table 3). Microscopically, both Ga-bearing sphalerite and Ga-bearing wurtzite are grey with bluish tint, have no anisotropism, and are very similar in appearance to Ga-free sphalerite or Ga-free wurtzite. These two minerals could be distinguished only by X-ray powder diffraction (Tables 6, 7). Results of microprobe analyses are listed in Table 4.

DISCUSSION

Variations of cell parameters of sphalerite and wurtzite

Barton & Toulmin (1966) determined the dependence of the unit-cell parameter *a* of sphalerite on its Fe content: $a = 5.4093 + 0.0005637X - 0.000004107X^2$, where X is mole % FeS in solid solution. The maximum value of *a* they obtained is 5.4280 Å for sphalerite containing 56 mole % FeS. The maximum increase in *a* thus is only 0.0187 Å. In contrast, the effects of Ga on the unit-cell parameters of sphalerite and wurtzite are very large (Tables 6 and 7, respectively). Figure 1 is a plot of the unit-cell parameter *a* of Ga-bearing sphalerite *versus* chemical composition, given as the atomic ratio Ga/(Zn+Fe+Ga). Figure 2 is a similar plot for Ga-bearing wurtzite. The unit-cell parameters of sphalerite and wurtzite decrease dramatically with increasing gallium content. On the other hand, an increase in the iron content increases the cell parameters of both phases. Therefore, for Ga-bearing zinc sulfide containing much iron (*e.g.*, T009 with 27.4 atomic % Fe), the values of *a* and *c* deviate from the straight lines in Figures 1 and 2. The difference in *a* between Ga-free sphalerite and Ga-rich (27.4 atomic % Ga) sphalerite T034 at the same Fe content of 7.5 atomic % is 0.164 Å, almost an order of magnitude larger (and in the opposite direction) than the entire range that results from Fe substitution (Barton & Toulmin 1966). The differences in *a* and *c* between pure wurtzite and Fe-bearing, Ga-rich wurtzite T033 are 0.064 Å and 0.12 Å, respectively.

Hahn *et al.* (1955) measured the variations of cell parameters of phases along the Ga_2S_3–ZnS binary join at 900°C. About 20 mole % ZnS can be accommodated in solid solution in Ga_2S_3. The solid solution has the sphalerite structure, and *a* increases with increasing ZnS content. More than 30 mole % Ga_2S_3 can be incorporated in ZnS. This solid solution has the wurtzite structure, and *a* and *c* decrease with increasing Ga_2S_3 content. Hahn *et al.* suggested that a tetragonal $ZnGa_2S_4$ phase occupies the middle range along this binary join. Dissolution of 30 mole % Ga_2S_3 in ZnS produces the composition $Zn_{24.1}Ga_{20.7}S_{55.2}$. In our investigation of the GaS–ZnS binary join, Ga-bearing sphalerite was obtained over the compositional range from $Zn_{20.1}Ga_{24.9}S_{55.0}$ at 900°C to $Zn_{29.5}Ga_{16.3}S_{54.2}$ at 800°C, with no indication of a tetragonal $ZnGa_2S_4$ phase.

The dramatic decrease in cell volume of Ga-bearing zinc sulfide with increasing Ga content is explained by considerations of ionic size and valence. The ionic radii of Zn^{2+} and Ga^{3+} are 0.74 Å and 0.62 Å, respectively. Furthermore, in order for Ga to enter into the sphalerite or wurtzite solid solution, vacancies must be created to maintain charge balance. The probable solid-solution model is written $(Zn,Fe,Ga,\square)S$, where $\square$ represents a vacancy, or $(Zn,Fe,Ga)_{1-x}S$.

Stability relations between wurtzite and sphalerite in the system Zn–Fe–Ga–S

Scott & Barnes (1972) determined a univariant sphalerite–wurtzite boundary as a function of sulfur fugacity and temperature at 1 bar. They proposed that in the pure Zn–S system, sphalerite is stable at relatively high sulfur fugacity, and wurtzite is stable at low sulfur fugacity. The effect of solid solutions on this relationship is not well known, although substitution of Fe for Zn increases the sulfur fugacity over which sphalerite is stable (Barton & Toulmin 1966, Hutchison & Scott 1981). As shown in Table 3, most runs in the present experiments were performed by using FeS + Fe as reactants and thus should have been buffered at or near the low sulfur fugacity defined by the pair iron + troilite. However, iron was totally consumed in many of these experiments. Runs T009 at 900°C and T010 at 800°C were buffered by pyrrhotite + alloy Y and produced wurtzite, in agreement with the stability relations of Scott & Barnes (1972). The products of runs T022, T039, and T033 at 900°C and of runs T023 and T040 at 800°C are wurtzite + alloy Y, which indicates that they, too, were carried out at low sulfur fugacity. Run T027 at 900°C and runs T034 and T028 at 800°C produced sphalerite, indicative of high sulfur fugacity. Our data are not yet sufficiently numerous to provide unequivocal phase diagrams for the system Ga–Fe–Zn–S.

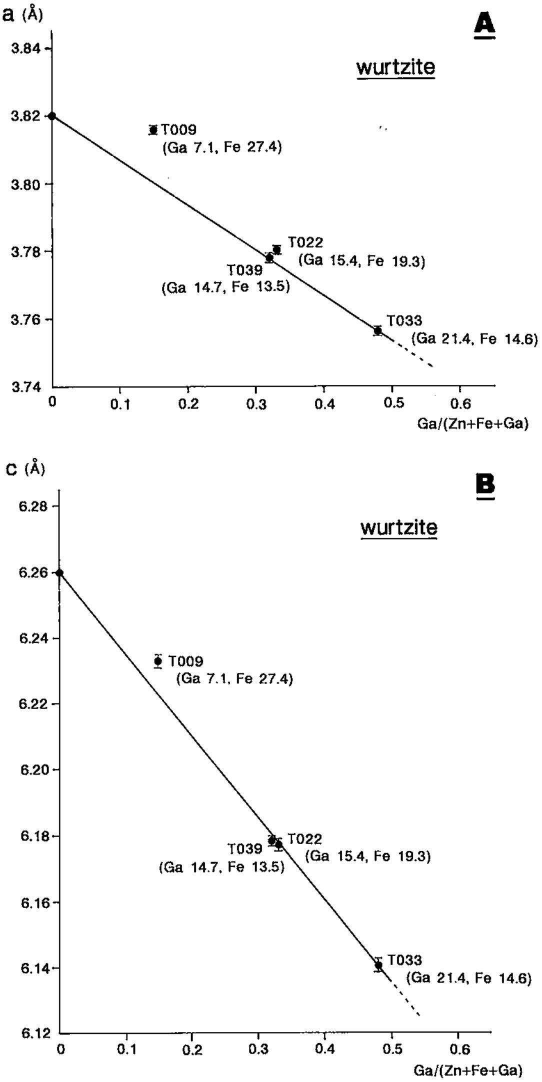

Fig. 2. Relationship between unit-cell parameters of Ga-bearing wurtzite and composition, expressed as Ga/(Zn + Fe + Ga) ratio. A) Data for *a*; B) data for *c*. Values of *a* and *c* of Ga-free wurtzite are from PDF 5–0492. Numbers in brackets express the atomic % of Ga and Fe.

Solubility of gallium in sphalerite and wurtzite

Runs T027 at 900°C and T028 at 800°C, with reactants ZnS + 2GaS, produced the univariant assemblage sphalerite + GaS + Ga. Therefore, 24.9 atomic % Ga for T027 and 16.3 atomic % Ga for T028 are the maximum solubilities of Ga in sphalerite in the ternary system Zn–Ga–S at 900°C and 800°C, respectively. Univariant assemblages were not obtained in the system Zn–Fe–Ga–S, so that the maximum solubility of Ga in zinc sulfide is not known for the quaternary system. The maximum Ga contents measured were 21.4 atomic % Ga for wurtzite at 900°C (run T033), 15.6 atomic % Ga for wurtzite at 800°C (run T023), and 27.4 atomic % Ga for sphalerite at 800°C (run T034). These values are considerably larger than those reported for Ga-bearing zinc sulfides in meteorites (Nagahara & El Goresy 1984, Woolum *et al.* 1984, Rambaldi *et al.* 1986), which indicates, not unexpectedly, that the zinc sulfide in these meteorites is not saturated with Ga and therefore can provide no P–T information.

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