JOURNAL OF SOLID STATE CHEMISTRY 73, 440–451 (1988)

A Synthetic and Structural Study of the Zirconium–Antimony System

EDUARDO GARCIA AND JOHN D. CORBETT

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011*

Received April 20, 1987; in revised form September 11, 1987

Ten phases have been obtained in the Zr–Sb system using arc-melting, annealing, powder sintering, vapor-phase transport, vaporization, and metal flux methods. In addition to the previous reported compositions (and structure types) Zr_3Sb (Ni_3P), Zr_5Sb_3 (Mn_5Si_3), and $ZrSb_2$ ($ZrSb_2$), there also exist Zr_2Sb (La_2Sb), high temperature Zr_5Sb_3 (Y_5Bi_3), $ZrSb_{1-x}$ (FeSi), ZrSb (ZrSb–*Cmcm*), and low temperature $ZrSb_{2-x}$ ($PbCl_2$). There are also phases of unknown structure near the Zr_2Sb composition at high temperatures and for Zr_2Sb_3 that are provisionally primitive orthorhombic and tetragonal, respectively. The Mn_5Si_3-type phase Zr_5Sb_{3+x} is a true binary and nonstoichiometric over the ranges $0.0 \leq x$ 0.4. Guinier lattice constant data are reported for all the phases.

Introduction

Our interest in the zirconium–antimony binary system stemmed from extensive investigations we have made into Zr–Sb–*Z* ternary systems, where *Z* is a wide variety of third elements (*1*). Some experiments during the course of these yielded evidently new binary phases, and it became apparent that what had been reported in the literature about the Zr–Sb system was very incomplete. Early work on Zr–Sb alloys over the range 0–40 at% antimony indicated that Zr_2Sb was the most zirconium-rich binary alloy and that its powder and single crystal diffraction data could be indexed on the basis of a hexagonal cell ($a = 8.4$, $c = 5.6$ Å) (*2*). The solubility of antimony in zirconium could not be determined because of both the high oxygen and nitrogen content of the starting zirconium and the additional contamination that occurred when the alloying reactions were run in a graphite crucible. Results of this investigation were therefore considered very suspect, and this led to a reexamination of the phase diagram in the 0–5 at% region (*3*). The purity of the zirconium metal used in this study was 99.95%, and the reactions were carried out by arc-melting the elements and annealing the product, a process which eliminates any container contribution to contamination. (These experiments revealed that the α–β transition of zirconium was raised by about 10°C at 0.5 at% Sb, the limit of solubility in α-Zr).

In addition to these limited studies on the phase relationships in the system, there are

---

* The Ames Laboratory is operated for the U.S. Department of Energy by Iowa State University under Contract W-7405-Eng-82. This research was supported by the Office of Basic Energy Sciences, Materials Sciences Division.

0022-4596/88 $3.00

several reports of the synthesis of binary compounds. The first well-identified compound was Zr_5Sb_3 (*4, 5*) with the hexagonal Mn_5Si_3 structure. Lattice parameters reported (a = 8.46, c = 5.80 Å (*4*) and a = 8.53, c = 5.84 Å (*5*)) make it seem likely that this was the actual composition of the "Zr_2Sb" phase previously postulated. Notwithstanding the previous assertion that Zr_2 Sb was the most zirconium-rich phase, a Zr_3Sb compound with the Fe_3P structure (a = 11.35, c = 5.67 Å) was subsequently synthesized (*6*). Unfortunately, the experimental details could not be ascertained since the results were presented simply as a list of compounds, structure types and lattice parameter data.

A later, more thorough report confirmed the existence of Zr_3Sb and also described a Zr_2Sb phase with apparently two structural modifications (*7*). An unidentified powder pattern was obtained when a Zr_2Sb composition was annealed at 1150°C while the resultant pattern could be indexed on the basis of a primitive tetragonal cell after the alloy was annealed at 1000°C. The slightly more antimony-rich composition $Zr_{1.70}Sb$ contained a second unidentified phase as well as Zr_5Sb_3. Since the atomic volume derived from the unit cell of Zr_5Sb_3 was about 4.5% larger than interpolated from then-assigned phases, the latter was postulated to not be a true binary compound but rather an oxygen-stabilized ternary phase. The zirconium used was a reactor grade but the purity of the antimony was not described. One further compound was discovered in this work and identified as Zr Sb_3, with a powder pattern that could be indexed on the basis of a primitive orthorhombic cell (a = 14.98, b = 9.94, c = 3.86 Å). The crystal structure of this phase was later twice determined by single crystal X-ray diffraction, and the actual composition was shown to be $ZrSb_2$ (*8, 9*).

In light of all the uncertainty and contradictions in the literature, a reinvestigation of the Zr–Sb system was deemed appropriate and necessary in order to identify products obtained from ternary zirconium–antimony reactions.

Experimental Procedures

Materials. The zirconium metal used in all experiments was reactor-grade crystal bar. This was cold rolled and cut into pieces ca. 0.5 × 10 × 10 mm. Powdered zirconium was obtained via ZrH_2. The latter was made by reaction of Zr strips with H_2 at 750°C, the product ground into a powder, passed through a sieve with a nominal opening of 150 μm, and then heated slowly to 700°C under vacuum (10^{-5} Torr) in a molybdenum boat until no further H_2 was evolved. The lattice parameters of the metal powder thus obtained were within experimental error of literature values (*10*). The material was handled only under vacuum or dry box conditions. The reagent-grade antimony (Allied Chemical and Dye Co.) produced no dross upon fusion, and its SEM-EDX analysis showed no detectable impurities. The material was powdered by grinding. All ground samples were handled only in the dry box as were all bulk samples with $Zr:Sb > 1:1$ as these are not stable in air overnight.

Some of the compounds were prepared by arc-melting in a Centorr 55A single arc furnace using pieces of the elements on a water-cooled copper hearth and argon pressures slightly greater than atmospheric. The atmosphere was gettered by melting zirconium before proceeding to the reaction mixture. Antimony was added in a slight (~10%) excess in order to compensate for losses through vaporization that occurred for the most part in the initial 2–3 sec. The final composition was determined by the weight loss with the assumption that this arose solely from antimony volatilization. The correctness of this procedure was basically confirmed by the ability to obtain single-phase samples of known compositions in this way which for the usual Guinier powder X-ray diffraction sensitivity meant that any impurity phase was present at less than 2–4 mole%. The equilibrium vapor pressure of antimony above the molten Zr–Sb alloys is low enough that the solidified button could be turned over and remelted repeatedly with only a slight weight change. The arc-melted buttons were annealed in open Ta crucibles which had been sealed in fused silica jackets under an atmosphere of Ar.

Other compounds were prepared by reaction of the powders at elevated temperatures (~1100°C). Stoichiometric amounts of the elements were ground together in an agate mortar and pestle in the dry box and then pressed into a pellet at 8 kbar. This mixture was allowed to react in a Ta crucible which was again sealed in a fused silica jacket under an atmosphere of Ar. The temperature of the reaction was maintained at 550°C overnight before going to higher temperatures so as to allow the elements to react without antimony fusion. Any melting in the pellet would have a deleterious effect since this would reduce the diffusion interface between the compacted grains.

An additional synthetic technique utilized was vapor-phase transport using powders of the elements in stoichiometric proportions. These were contained in weld-sealed Ta tubes that were themselves sealed inside a silica jacket to prevent oxidation. Iodine used as the transport agent was added to the reaction container in the form of ZrI_4.

X-Ray Diffraction

Powder patterns of samples mounted on cellophane tape were obtained utilizing an Enraf–Nonius Guinier camera, Cu$K\alpha$ radiation (λ = 1.54056 Å), and NBS silicon as an internal standard. The 2θ values of the standard lines were fit to a quadratic in line position, and lattice constants of the sample were calculated by a least-squares fit to indexed 2θ values. This procedure regularly produces lattice constants with standard deviations of a few parts in 10^4. The identification of structure type by powder pattern means was accomplished by comparing line position and intensity in the experimental pattern with the distribution calculated for a known structure by the program POWD 5 (*11*).

Results

The binary compounds found in the Zr–Sb system and their structure types are outlined in Table I; a representative list of reaction methods, conditions, and results is given in Table II; structure-type information and lattice parameters for the phases so identified are listed in Table III. In the following text the bracketed italicized number following alloy compositions identify the reaction numbers in Tables II and III. The reader should note that three nominal compositions each yield a pair of structure types depending on the composition or temperature used, namely Zr_5Sb_3, ZrSb, and $ZrSb_2$.

Zr_3Sb

In accord with reports in the literature (*7*), the most zirconium-rich binary compound observed in Zr_3Sb. The compound is found in equilibrium with elemental Zr or Zr_2Sb (discussed below) in neighboring compositional ranges. The Fe_3P structure for Zr_3Sb was confirmed by the powder pattern, and the essential invariance of the lattice parameters over a wide composition (Table II) implies a small range of nonstoichiometry.

An overall composition $Zr_{0.81}Sb_{0.19}$ [*1*] prepared by arc-melting the elements and annealing the product for 2 days at 1100°C and an additional 2 days at 850°C resulted in a mixture of α-Zr and Zr_3Sb. It is evident from the position of the lines in the Guinier pattern that there is a very limited solubility

TABLE I

Compounds in the Zirconium–Antimony System[a]

Phases		Structures		
Phase composition	Reference	Structure type	Space group	Reference
Zr_3Sb	(*6*)	Ni_3P	$I\bar{4}$	(*6*)
Zr_2Sb	(*7*)	La_2Sb	$I4/mmm$	This work
X (~Zr_2Sb)	(*7*)	Unknown	Primitive orthorhombic	This work
Zr_5Sb_3	This work	Y_5Bi_3	*Pnma*	This work
Zr_5Sb_3	(*4, 5*)	Mn_5Si_3	$P6_3/mcm$	(*4, 5*)
ZrSb	This work	FeSi	$P2_13$	This work
ZrSb	This work	ZrSb	*Cmcm*	This work
Zr_2Sb_3	This work	Unknown	Primitive tetragonal	This work
$ZrSb_2$	This work	$PbCl_2$	*Pnma*	This work
$ZrSb_2$	(*8, 9*)	$ZrSb_2$	*Pnnm*	(*8, 9*)

[a] See text regarding stoichiometric differences between pairs of Zr_5Sb_3, ZrSb, and $ZrSb_2$ types. The first listed in each is antimony poorer.

TABLE II

Summary of Zirconium–Antimony Reaction Types and Products

		Synthesis			
			Conditions		
Reaction[a]	Product composition (atomic)	Method[b]	Temp. (°C)	Time[d]	Products[c]
1	$Zr_{0.81}Sb_{0.19}$	AM	1000	2	
			850	2	Zr, Zr_3Sb
2-1	$Zr_{0.68}Sb_{0.32}$	AM	As-cast		Zr_3Sb, Zr_5Sb_3
2-2	$Zr_{0.68}Sb_{0.32}$	AM	950	2	Zr_2Sb (Zr_3Sb)
3	$Zr_{0.72}Sb_{0.28}$	AM	950	1	Zr_3Sb, Zr_2Sb
4	$Zr_{0.66}Sb_{0.34}$	AM	1200	0.6	X,[d] Zr_5Sb_3
5	$Zr_{0.65}Sb_{0.35}$	AM	950	2	Zr_2Sb, Zr_5Sb_{3+x}
6	$Zr_{0.626}Sb_{0.374}$	AM	As-cast		Zr_5Sb_3, Zr_5Sb_{3+x}
7	$Zr_{0.60}Sb_{0.40}$	AM	1100	4	
			750	1	Zr_5Sb_{3+x}
8	$Zr_{0.56}Sb_{0.44}$	AM	900	5	Zr_5Sb_{3+x}, $ZrSb_{1-x}$
9-1	Unknown	V	1000	1	ZrSb, Zr_2Sb_3
9-2	Unknown	V	1000	2	$ZrSb_{1-x}$, ZrSb
10	$Zr_{0.50}Sb_{0.50}$	VT	950	21	ZrSb
11	$Zr_{0.400}Sb_{0.600}$	PP	900	6	Zr_2Sb_3
12	Zr + excess Sb	MF	1100	0.5	$ZrSb_2$, Sb
13	$Zr_{0.250}Sb_{0.750}$	P	850	1	
			550	1	$ZrSb_2$, Sb
14	$Zr_{0.25}Sb_{0.75}$	VT	700	7	$ZrSb_{2-x}$

[a] Referenced in text with bracketed italicized numbers.

[b] Abbreviations: AM, arc-melted, conditions refer to annealing; V, vaporization of Sb from $ZrSb_2$ in vacuum; VT, vapor transport; PP, pressed pellet of ground powders; MF, Sb metal flux; P, ground mixture of powders.

[c] The groups Zr_5Sb_3, Zr_5Sb_{3+x}; $ZrSb_{1-x}$, ZrSb; $ZrSb_{2-x}$ (x ~ 0.04), $ZrSb_2$ each involved a pair of different structure types.

[d] See text.

of Sb in α-Zr at 850°C. An as-cast sample of composition $Zr_{0.68}Sb_{0.32}$ ($Zr_{2.13}Sb$) [*2-1*] prepared by arc-melting exhibits the pattern of Zr_3Sb plus an unknown component with many weak lines. This is presumably the unidentified phase that had been observed previously (*7*), and it will be shown (below) to be a new structure for Zr_5Sb_3. A powder pattern of a third sample, $Zr_{0.72}Sb_{0.28}$ [*3*], that was prepared by arc-melting and then annealed at 950°C for 1 day revealed a mixture of Zr_3Sb and Zr_2Sb appropriate to the composition. The formation of Zr_3Sb is not dependent on postcasting thermal treatment, but the thermal history is important in determining the adjacent, antimony-richer phase.

Zr_2Sb

Such a low temperature phase had been previously obtained following annealing of a Zr_2Sb composition at 1000°C, and its powder pattern had been indexed on the basis of a primitive tetragonal cell (a = 6.52, c = 7.90 Å) but for an unidentified structure (*7*). In an attempt to verify the reported cell, an alloy of composition $Zr_{0.68}Sb_{0.32}$ [*2-2*] was prepared by arc-melting and subsequently

TABLE III

STRUCTURE TYPES AND LATTICE PARAMETERS FOR ZIRCONIUM–ANTIMONY REACTIONS (TABLE II)

Reaction	Product	Structure type[a] (space group)	Lattice parameters (Å)[b]
1	Zr_3Sb	Fe_3P ($I\bar{4}$)	a = 11.351(1) c = 5.671(1)
2-1	Zr_3Sb	Fe_3P	a = 11.337(3) b = 5.669(2)
2-1	Zr_5Sb_3	Y_5Bi_3 (*Pnma*)	a = 7.468(1) b = 8.787(3) c = 10.865(3)
2-2	Zr_2Sb	La_2Sb (*I4/mmm*)	a = 4.1154(5) c = 15.786(3)
3	Zr_3Sb	Fe_3P	a = 11.3386(6) c = 5.6692(3)
3	Zr_2Sb	La_2Sb	a = 4.1172(6) c = 15.771(3)
4	Zr_5Sb_3	Y_5Bi_3	a = 7.465(1) b = 8.801(1) c = 10.865(2)
4	*X* (~Zr_2Sb)	Orthorhombic (*P*)	a = 14.652(5) b = 9.058(4) c = 7.756(3)
5	Zr_2Sb	La_2Sb	a = 4.1156(4) c = 15.774(3)
5	Zr_5Sb_{3+x}	Mn_5Si_3 ($P6_3/mcm$)	a = 8.4175(6) c = 5.7678(6)
6	Zr_5Sb_3	Y_5Bi_3	a = 7.467(1) b = 8.797(1) c = 10.872(2)
6	Zr_5Sb_{3+x}	Mn_5Si_3	a = 8.468(1) c = 5.800(1)
7	Zr_5Sb_{3+x}	Mn_5Si_3	a = 8.518(1) c = 5.844(1)

TABLE III—*Continued*

Reaction	Product	Structure type[a] (space group)	Lattice parameters (Å)[b]
8	Zr_5Sb_{3+x}	Mn_5Si_3	$a = 8.573(1)$ $c = 5.872(1)$
8	$ZrSb_{1-x}$	FeSi ($P2_13$)	$a = 5.6358(4)$
9-1	$ZrSb_{1-x}$	FeSi	$a = 5.6355(3)$
9-1	ZrSb	ZrSb (*Cmcm*)	$a = 3.809(1)$ $b = 10.421(1)$ $c = 14.045(2)$
9-2	ZrSb	ZrSb	$a = 3.808(4)$ $b = 10.410(8)$ $c = 14.059(6)$
9-2	Zr_2Sb_3	Tetragonal (*P*)	$a = 9.567(2)$ $c = 5.294(1)$
11	Zr_2Sb_3	Tetragonal	$a = 9.565(1)$ $c = 5.288(1)$
14	$ZrSb_{2-x}$	$PbCl_2$ (*Pnma*)	$a = 7.393(1)$ $b = 3.9870(7)$ $c = 9.581(1)$
13	$ZrSb_2$	$ZrSb_2$ (*Pnnm*)	$a = 14.963(3)$ $b = 9.963(2)$ $c = 3.8779(7)$

[a] Reference (*12*).

[b] Based on indexed lines in Guinier pattern.

annealed at 950°C for 2 days. A trace of Zr_3Sb could be seen in the powder pattern, but the remainder was presumably the low temperature modification of Zr_2Sb. Although the latter can be poorly described with the previously reported primitive tetragonal cell, the diffraction pattern is more properly indexed [*13*] on the basis of a body-centered tetragonal cell ($a = 4.1154(5)$, $c = 15.786(3)$ Å). More importantly, the observed intensity distribution demonstrates that the compound in question possesses the La_2Sb-type structure. A comparison of observed and calculated intensities is given in Table IV. In this structure the positional parameters of one zirconium atom are fixed by symmetry but those of a second zirconium and the antimony atoms have variable z values. The calculated powder pattern was based on the positional parameters of these atoms in La_2Sb and is therefore only an approximation.

The powder diffraction pattern of the above $Zr_{0.68}Sb_{0.32}$ [*2-1*] as cast did not exhibit any lines of either low temperature Zr_2Sb or phase X (below). It did, however, contain many more diffraction lines from Zr_3Sb (estimated yield 30%) than did the annealed product, indicating that the second phase was more antimony-rich than Zr_2Sb. It was subsequently determined that the latter is Zr_5Sb_3 in the Y_5Bi_3-type structure (below) and that this is also the unidentified phase noted above that is in equilibrium with Zr_3Sb in as-cast samples.

X (~Zr_2Sb)

A product of composition $Zr_{0.66}Sb_{0.34}$ ($Zr_{1.94}Sb$) [*4*] was prepared by arc-melting and subsequently annealed at 1200°C for 15 hr. The powder pattern of this alloy, in contrast to the as-cast result, did not exhibit any lines from Zr_3Sb but did contain lines from Zr_5Sb_3 (Y_5Bi_3-type) and a second phase X that is presumably the high temperature form of Zr_2Sb. All 23 of the extra lines listed in Table V can be indexed on the basis of the primitive orthorhombic cell listed in Table III. Experience has shown that unit cells determined solely on the basis of d-spacings and indexing without corroboration from single crystal data or by identification of the structure-type must be regarded as only tentative. That is the case in this instance. There is also no conclusive evidence for describing this compound as Zr_2Sb although the composition must be near this stoichiometry. It can, however, be stated with certainty that this phase has a thermal stability bounded by ~1000–1100°C and the effective quenching temperature of as-cast samples (~1400°C).

TABLE IV

OBSERVED AND CALCULATED POWDER PATTERNS FOR Zr_2Sb (La_2Sb TYPE)

d_{obs} (Å)	d_{calc} (Å)	h	k	l	I_{obs}[a]	I_{calc}[a]
7.94	7.89	0	0	2	2	2
3.985	3.982	1	0	1	5	12
3.952	3.947	0	0	4	3	3
2.912	2.910	1	1	0	25	26
2.729	2.730	1	1	2	80	90
2.630	2.631	0	0	6	50	37
2.504	2.505	1	0	5	20	34
2.340	2.342	1	1	4	100	100
1.9744	1.9777	0	0	8	15	20
1.6210	1.6209	2	0	6	20	37
1.5903	1.5900	2	1	5	10	19
1.4554	1.4550	2	2	0	15	25
1.4253	1.4259	2	1	7	10	16
1.3877	1.3876	1	1	10	7	11
1.3551	1.3551	1	0	11	9	20
1.2846	1.2841	3	1	2	10	23
1.2734	1.2733	2	2	6	12	20
1.2353	1.2359	3	1	4	20	37

[a] $CuK\alpha$ radiation.

Zr_5Sb_3

The question of whether this compound, which had been reported previously to have the Mn_5Si_3 structure, is an impurity-stabilized ternary compound [*8*] or a real binary was addressed by a series of reactions leading to products near the ideal 5 : 3 stoichiometric ratio. The results of these reactions show that the question cannot be cast so simply, for there are actually two Zr_5Sb_3 phases. One, which may be better formulated as Zr_5Sb_{3+x}, does indeed have a Mn_5Si_3-type structure (Zr_5Sb_3–M). The second compound is stoichiometric Zr_5Sb_3 with the Y_5Bi_3-type structure (Zr_5Sb_3–Y). A full presentation of the temperature relationships, crystal structure refinements, and superstructure formation of these two compounds is beyond the scope of the present work. The pertinent highlights will be presented here and the results fully described in a later paper (*1*).

The stoichiometric phase Zr_5Sb_3–Y was first seen in the powder pattern of an as-cast sample of overall composition Zr_2Sb [*2-1*]. The pattern indicated about a 50 : 50 mixture of Zr_3Sb and a second phase that had not been previously identified. The same phase was also observed in as-cast samples with a final composition near Zr_5Sb_3 [*6*]. A single crystal from this material was indexed on the diffractometer and the structure was determined and refined as Zr_5Sb_3 in the Y_5Bi_3-type structure (*1*). The refined atomic occupancies with one of the two zirconium atoms fixed indicated that the stoichiometry is substantially ideal, $Zr_{4.99(4)}Sb_{3.01(3)}$. The lattice parameters of this compound in equilibrium with either Zr_3Sb or Zr_5Sb_3–M are essentially identical ([*2-1*] and [*6*], Table II), indicating that it is a line compound. It was only observed as a product when the synthesis is carried out by arc-melting.

In contrast to this behavior, the Mn_5Si_3-type Zr_5Sb_3–M exhibits an extensive range of nonstoichiometry. The compound oc-

TABLE V

INDEXED POWDER DATA FOR STRUCTURALLY UNDETERMINED Zr–Sb PHASES[a]

X (~Zr_2Sb)			Zr_2Sb_3		
d (Å)	h k l	I_{obs}	d (Å)	h k l	I_{obs}
3.877	0 0 2	10	3.380	2 2 0	2
3.850	2 2 0	5	2.849	2 2 1	100
3.779	1 2 1	5	2.727	3 0 1	100
3.393	4 1 0	10	2.647	0 0 2	100
2.741	5 0 1	20	2.392	4 0 0	50
2.731	2 2 2	20	2.371	2 3 1	50
2.554	4 1 2	20	2.248	2 1 2	10
2.543	1 0 3	20	2.118	1 4 1	10
2.521	3 2 2	50	2.084	2 2 2	75
2.484	0 1 3	100	1.9089	3 4 0	5
2.436	2 0 3	10	1.8718	3 2 2	2
2.382	0 3 2	5	1.7054	1 1 3	50
2.363	6 1 0	5	1.6109	4 4 1	10
2.335	5 0 2	20	1.5685	3 5 1	10
2.280	3 0 3	2	1.5125	6 2 0	35
2.264	2 3 2	2	1.5049	1 6 1	10
2.245	0 2 3	75	1.4739	5 2 2	10
2.231	4 3 1	75	1.4373	4 5 1	5
2.174	0 4 1	50	1.4238	4 4 2	2
2.156	1 4 1	5	1.3768	3 6 1	50
2.013	6 1 2	10	1.3214	0 0 4	10
1.9342	5 0 3	75	1.3131	2 6 2	10
1.8366	2 1 4	10	1.2846	5 1 3	15
1.8159	3 4 2	2	1.2508	2 5 3	5
1.7709	1 2 4	5	1.2322	2 2 4	10
1.5934	9 0 1	10	1.2243	6 5 0	10
1.4402	6 2 4	5			
1.3312	8 0 4	2			
1.3056	0 6 3	10			
1.2437	0 2 6	2			

[a] Guinier data, CuKα radiation; cell constants in Table III.

curs at and on the antimony-rich side of the Zr_5Sb_3 composition in the phase diagram and may of course be formulated in two ways, i.e., $Zr_{5-y}Sb_3$ or Zr_5Sb_{3+x}. There are compelling reasons for selecting the latter rather than the former.

There is a site in the center of a zirconium trigonal antiprism, the origin of the unit cell, that is empty for $x = 0$. In many other cases, (*1*, *15*, *16*) a small nonmetal impurity is found or is thought to occur at this site and to stabilize the structure, and this was also suspected for Zr_5Sb_3–*M*. However, this possibility can be eliminated by the reproducible, 100% yields of Zr_5Sb_3–*M* obtained in many different reactions. Furthermore, the lattice parameters of the phase demonstrate a linear dependence on antimony content [*1*]. The conclusion that this is a truly binary phase can be fully appreciated only in the light of experimental results obtained with many possible impurity elements. For example, the stipulation that the phase is essentially oxygen-free is buttressed by results when oxygen is intentionally added to the system. Sintered powdered Zr, Sb, and ZrO_2 produce a Mn_5Si_3-type phase with much smaller lattice parameters, $a = 8.3146(6)$, $c = 5.6954(4)$ Å (compare Table III, reactions [*6*] and [*7*]) [*1*].

It is possible that the empty site rather than being occupied by a ternary element is in fact occupied by the excess antimony. This type of behavior is known for Ti_5Ga_4 [*17*] which has a "filled" Mn_5Si_3 structure in which the fourth gallium occurs in the so-called interstitial site, viz., Ti_5Ga_3Ga. This structure is also found with Zr_5Sn_4 [*18*, *19*], and a similar behavior with antimony is reasonable. This circumstance was confirmed by a single crystal structural investigation [*1*] which revealed excess electron density at the interstitial site corresponding to $(Zr_5Sb_3)Sb_{0.16}$. The range of nonstoichiometry for Zr_5Sb_3–*M* of approximately $0.0 \leq x \leq 0.4$ has been determined by the appearance of a second phase in the powder pattern following a 1000°C reaction of sintered powders. The lattice parameters for the two extremes are given in Table II for reactions [*5*] and [*8*], the volume at $x(\min) \simeq 0.0$ being 1% less than that of Zr_5Sb_3–Y. It should be noted that $x \sim 0.16$ when $Zr_5Sb_{3+x}(M)$ is in equilibrium with Zr_5Sb_3–Y at higher temperatures, as demonstrated by the data for reaction [*6*].

ZrSb

The phase in equilibrium with Zr_5Sb_3–*M* at the antimony-rich limit is not the $ZrSb_2$ expected on the bases of published reports. A sample of composition $Zr_{0.56}Sb_{0.44}$ [*8*] obtained by arc-melting and annealing for 5 days at 900°C gave powder pattern lines that could be ascribed to Zr_5Sb_3–*M* plus a second phase with a primitive cubic unit cell, $a = 5.6358(4)$ Å. The latter was identified from the intensity distribution as characteristic of the FeSi-type structure (Table VI). This indicates the phase is the previously unidentified ZrSb, although the isostructural HfSb has been observed (*7*). The phase is described as $ZrSb_{1-x}$ in the tables based on an expected substoichiometry in antimony (see below).

The antimony-rich phase adjacent to $ZrSb_{1-x}$ is, once again, not $ZrSb_2$ but a ZrSb phase that crystallizes in an orthorhombic C-centered unit cell. The same type of cell had also been observed in the Hf–Sb system and attributed to an impurity-stabilized HfSb phase (*7*).

This second phase can be prepared by vapor transport reactions as well as by arc-melting or via pressed pellet reactions of the elements. The stoichiometric mixture of the powders plus ZrI_4 as a transporting agent heated at 950°C for 3 weeks in a sealed Ta tube [*10*] yielded crystals in the form of rectangular plates that radiated from a central nucleus. Crystals could also be grown in about 2 days in a hot wire apparatus employing a Ta wire at 950°C and a Pyrex vessel at 300°C, again with I_2 as the transport agent.

The results of the single-crystal X-ray diffraction of the new structure type for ZrSb are described separately [*14*].

Paradoxically, whereas no ZrSb compound had been previously reported, the above results indicate that there are two phases with a ZrSb composition. The thermodynamic parameter determining which structure modification is obtained is not temperature but composition. This conclusion is based on the results of reaction [*9*] in which antimony was volatilized from $ZrSb_2$ at 1000°C under dynamic vacuum. The initial products were Zr_2Sb_3 (see below) and the new orthorhombic ZrSb. After further evaporation, ZrSb was found in both the cubic FeSi and the orthorhombic structures. Since the single crystal refinement indicated that the orthorhombic unit cell composition was ZrSb, we are inclined to formulate the cubic phase at $ZrSb_{1-x}$. This phase is also consistently found to be in equilibrium with Zr_5Sb_{3+x} [*8*]. Both ZrSb phases appear to be line compounds judging from their basically invariant lattice parameters. Unfortunately, attempts to elucidate the nature of the FeSi-type phase by single crystal X-ray methods were unsuccessful because the crystals obtained were always twinned.

TABLE VI

OBSERVED AND CALCULATED POWDER PATTERNS FOR $ZrSb_{1-x}$ (FeSi TYPE)

d_{obs} (Å)	d_{calc} (Å)	*h k l*	$I_{obs}{}^a$	$I_{calc}{}^a$
3.983	3.985	1 1 0	1	0.1
3.253	3.254	1 1 1	15	13
2.818	2.818	0 0 2	10	9
2.520	2.521	0 2 1	100	100
2.300	2.301	1 1 2	50	56
1.992	1.993	2 2 0	1	0.8
1.879	1.879	0 0 3	7	7
1.782	1.782	3 1 0	4	2
1.700	1.699	1 1 3	9	13
1.5630	1.5630	2 0 3	5	5
1.5064	1.5063	3 1 2	35	40
1.4088	1.4091	0 0 4	6	11
1.3670	1.3670	4 0 1	6	8
1.3284	1.3285	1 1 4	5	5
1.2931	1.2930	3 1 3	8	15
1.2606	1.2603	2 0 4	4	2
1.2302	1.2299	4 2 1	17	22
1.2013	1.2016	3 3 2	4	4

[a] CuKα radiation.

Zr_2Sb_3

A third phase between Zr_5Sb_{3+x} and $ZrSb_2$ that had not been previously noted was observed to be the lone product of the pressed pellet reaction [*11*] and in equilibrium with ZrSb at antimony-poorer compositions [*9-1*]. The powder pattern of this compound, which has a composition close to Zr_2Sb_3, can be well indexed on the basis of a primitive tetragonal cell a = 9.565(1), c = 5.288(1) Å. A single crystal of suitable size could not be obtained, and the structure-type has not been identified. Once again, the indexing of the powder pattern given in Table VI must be regarded as only tentative. The phase has also been obtained from vapor-phase transport and arc-melting reactions.

$ZrSb_{2-x}$

In an attempt to grown single crystals of Zr_2Sb_3, a stoichiometric mixture of Zr and Sb powders was sealed in a silica container under vacuum with CdI_2 as a transport agent. The reactants were heated at 700°C while the opposite end of the tube was maintained at 650°C for 9 days [*14*]. It was evident afterward that the fused silica had been attacked by zirconium and that an antimony-richer product should be expected. Some material had transported to the cool end of the reaction container but most (75%) remained in the hot end. The two products were visually identical and in the form of rod crystals about 1.0 × 0.1 × 0.1 mm. The powder patterns confirmed that the two products were identical but different from the expected $ZrSb_2$.

A single crystal allowed the unit cell to be determined by oscillation and Weissenberg techniques, and lattice parameters were then obtained by a least-squares fit to Guinier powder diffraction data. The cell was found to be primitive orthorhombic a = 7.393(1), b = 3.9870(1), c = 9.581(1) Å. The small unit cell and especially the short b-axis indicated that this was most likely a previously unreported Zr–Sb binary compound, and a structural determination was deemed appropriate.

The elucidation and refinement of the structure as a $PbCl_2$ (or Co_2Si) (*12*) type is described separately (*14*). The compound appears to be substoichiometric in antimony, $ZrSb_{1.956(4)}$, as revealed by the refined multiplicities, a result reminiscent of the pair of compounds at the equiatomic composition, $ZrSb_{1-x}$ (FeSi) and ZrSb (ZrSb). Unfortunately, the compositional dependence of the free energy of formation is not as well established since attempts to synthesize $ZrSb_{1.96}$ by sintering of powders has produced only the previously reported $ZrSb_2$ (below). It has been obtained only from transport reactions at 700–850°C in silica containers, but no significant amount of silicon or oxygen could be discerned in the refined crystal structure (*14*). There may also be kinetic barriers at low temperatures which prevent the interconversion of the more antimony-rich $ZrSb_2$ to the $PbCl_2$ polymorph.

$ZrSb_2$

The most antimony-rich compound found is the known $ZrSb_2$. Large rod crystals about 1 cm in length can be formed by dissolving zirconium powder in a large excess of antimony and allowing the latter to slowly evaporate [*12*]. This was accomplished at 1000°C in an Al_2O_3 crucible under 100 Torr of argon. Reaction of elemental powders in a 1:3 stoichiometric ratio at 850°C for 1 day followed by annealing at 550°C for 1 day resulted in a mixture of Zr Sb_2 and Sb [*13*].

The structure of $ZrSb_2$ has been previously reported (*8*, *9*). The experimental powder pattern agreed well with the calculated one, and the invariant lattice parameters confirmed the absence of a significant range of homogeneity.

Discussion

It is seen that, despite several investigations, previous knowledge of binary Zr–Sb compounds was far from complete. A total of 10 phases have now been identified (Table I). The phases $ZrSb_{1.96}$, Zr_2Sb_3, ZrSb, and $ZrSb_{1-x}$ had not been observed previously, and the known Zr_2Sb and one form of Zr_5Sb_3 had not been structurally characterized before. Two phases, Zr_2Sb_3 and X ($\sim Zr_2Sb$), remain structurally undetermined.

The Zr–Sb system is also intriguing because of the occurrence of three pairs of compounds that differ only slightly in their compositions, Zr_5Sb_3 and Zr_5Sb_{3+x}, $ZrSb_{1-x}$ and ZrSb, and $ZrSb_{1.96}$ and $ZrSb_2$, and a fourth possibility exists near Zr_2Sb. The thermodynamic relation between these pairs of compounds should provide a fertile area of study.

The fact that previous investigators failed to observe a considerable number of phases in the Zr–Sb system may be only an aberration, but if such an oversight can be ascribed to inadequate synthetic techniques or impure starting materials, this system may not be unique in its incompleteness. Such factors, singly or in combination, may have led investigators astray in other systems, and it may be that a wealth of compounds in other transition metal–main-group metal systems wait to be unearthed.

An examination of the known structural data and surmised interatomic interactions (*14*) indicates that the antimony-rich compounds contain significant Sb–Sb bonding, and this must play a critical role in determining structural stability, while there is minimal contribution from Zr–Zr interactions. The reverse is true in the most Zr-rich compounds, but Zr–Sb interactions probably constitute the greatest part of the lattice energy in all the phases. It would be interesting to quantify by theoretical means the transition from compounds with a main-group metallic character to compounds dominated by transition metal interactions, as postulated.

Compounds in the zirconium–antimony system can be categorized as intermetallic but this classification does not provide much insight into the electronic nature of the phases since many intermetallic compounds have a strong ionic or covalent contribution to the bonding. The Zintl phases are a good example of this (*20*). A good understanding of the zirconium–antimony compounds will require further study since, as demonstrated above, even such basic knowledge as the number and structure of the phases is incomplete. Obviously, very little is known of the physical characteristic of these compounds. Some preliminary conclusions can, however, be drawn from the synthetic and structural investigations reported here.

References

1. E. GARCIA AND J. D. CORBETT, to be submitted for publication.

2. R. F. RUSSI AND H. A. WILHELM, "U.S. Atomic Energy Commission Publication AECD-3610" (1951).

3. J. O. BETTERTON AND W. M. SPICER, *Trans. Amer. Inst. Min. Metall. Pet. Eng.* **212,** 456 (1958).

4. H. BOLLER AND E. PARTHÉ, *Monatsh. Chem.* **94,** 225 (1962).

5. K. SCHUBERT, H. G. MEISSNER, M. PÖTZSCHKE, W. ROSSTEUTSCHER AND E. STOLZ, *Naturwissenschaften* **49,** 57 (1962).

6. K. SCHUBERT, A. RAMAN, AND W. ROSSTEUTSCHER, *Naturwissenschaften* **51,** 506 (1964).

7. W. ROSSTEUTSCHER AND K. SCHUBERT, *Z. Metallkd.* **56,** 813 (1965).

8. D. EBERLE AND K. SCHUBERT, *Z. Metallkd.* **59,** 306 (1968).

9. A. KJEKSHUS, *Acta Chem. Scand.* **26,** 1633 (1972).

10. B. HOLMBERG AND T. DAGERHAM, *Acta Chem. Scand.* **15,** 919 (1961).

11. C. M. CLARK, D. K. SMITH, AND G. J. JOHNSON, "A FORTRAN IV Program for Calculating X-Ray Diffraction Patterns: Version V," Department of Geosciences, The Pennsylvania State University, University Park (1973).

12. P. VILLARS AND L. D. CALVERT, "Pearson's Handbook of Crystallographic Data for Intermetallic Phases," Vol. 1–3, Amer. Soc. Metals, Metals Park, OH (1985).

13. P. E. Werner, "TREOR-4 Trial and Error Program for Indexing of Unknown Powder Patterns," Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm (1984).
14. E. Garcia and J. D. Corbett, *J. Solid State Chem.* **73,** 452 (1988).
15. H. Nowotny and F. Benesovsky, *in* "Phase Stability in Metals and Alloys" (P. S. Rudman, J. Stringer, and R. I. Jaffee, Eds.), p. 319, McGraw–Hill, New York (1966).
16. W. B. Pearson, "The Crystal Chemistry and Physics of Metals and Alloys," p. 718, Wiley–Interscience, New York (1972).
17. M. Pötzschke and K. Schubert, *Z. Metallkd.* **53,** 474 (1962).
18. K. Schubert, H. G. Meissner, A. Raman, and W. Rossteucher, *Naturwissenschaften* **54,** 284 (1964).
19. Y.-U. Kwon and J. D. Corbett, unpublished research.
20. H. Schäfer and B. Eisenmann, *Rev. Inorg. Chem.* **3,** 29 (1981).