JOURNAL OF SOLID STATE CHEMISTRY **70**, 88–92 (1987)

The Homogeneity Ranges, Order–Disorder Transition, and Structures of the Nonstoichiometric Monosulfides of Zirconium*

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Received February 19, 1987; in revised form March 4, 1987

Two structures are known for defect zirconium monosulfides, the hypostoichiometric sulfide with the WC-type structure and the hyperstoichiometric sulfide with a NaCl-type superstructure. The approximate (±0.02 for S/Zr) homogeneity limits for the phases were determined for carefully equilibrated samples cooled to room temperature. The order–disorder transition in hyperstoichiometric monosulfide was observed to occur at about 1250°C (± about 20°C), and the refined superstructure was determined to be the $CdCl_2$ vacancy ordering by Rietveld full-profile analysis.

Introduction

The nonstoichiometric monosulfides of zirconium have been studied by a number of groups since the earliest investigation in 1939 (*1*). The first report suggested a defect NaCl-type structure for phases in the homogeneity range $1.20 \leq S/Zr \leq 1.49$. Later it was reported that compounds in the range $0.9 \leq S/Zr \leq 1.5$ exhibit a superstructure of the NaCl type, and that those in the range $0.5 \leq S/Zr \leq 0.8$ have the defect WC-type structure (*2*). These and other early results were discussed by F. Jellinek (*3*) in 1963 as part of a review that formed the basis for our understanding of the phase behavior and structures of the early transition-metal sulfides for more than a decade. In this review it was suggested that hyperstoichiometric zirconium monosulfide has a primitive cubic or rhombohedral structure of the $CdCl_2$ type. McTaggert and Wadsley (*4*) suggested that phases in the range $0.9 \leq S/Zr \leq 1.6$ have a primitive cubic lattice with $a = 10.25$ Å. Early work from this group yielded a WC-type structure for the range $0.6 \leq S/Zr \leq 0.8$ and a monoclinic superstructure for $Zr_{0.77}S$ (*5, 6*). Furthermore, defect ZrS has been found to be a superconductor (*7*), and electron diffraction results (*8*) showed a 2×2 superstructure together with ordering in every third plane perpendicular to the $\bar{1}10$ rhombohedral direction. This result is very similar to that found for $Sc_{1-x}S$ (*9*).

Experimental

The samples were prepared directly from Zr metal (99.9% purity from Ames Laboratory) and elemental S (Alfa Ventron 99.999% pure). The desired amounts of Zr and S (for samples with starting compositions in the range $0.5 < S/Zr < 1.5$) were placed in outgassed fused silica tubes which

* Dedicated to Franz Jellinek.

0022-4596/87 $3.00

were evacuated, sealed, and placed in a tube furnace at 440 to 500°C. It required between 2 and 7 days for the sulfur to react completely with the zirconium. When sulfur vapor was no longer visible in the tubes at 500°C the samples were removed and then annealed at 1400 to 1750°C (lower temperatures for $S/Zr > 1$) for 8–10 hr. These high-temperature anneals were performed in an inductively heated tungsten container under high vacuum (10^{-6} Torr).

The phases present in the sample were determined by powder diffraction techniques. The room-temperature powder diffraction patterns were taken using a Model XDC-700 Guinier camera (IRDAB, Stockholm). The final samples were analyzed for S/Zr values gravimetrically by oxidizing to ZrO_2 in a Pt crucible in air at 900°C.

The structure and order–disorder of $Zr_{0.75}S$ were studied using a Rigaku θ–θ diffractometer utilizing an E. Bühler sample chamber and controlled high-temperature powder supply. Cu$K\alpha$ radiation diffraction data were obtained from the sample at temperatures between room temperature and 1500°C. The chamber was pumped to a residual pressure of 10^{-6} Torr. For the structural study a full-profile pattern fitting (Rietveld-type) least-squares program (*10*) was used.

Results

From the phases present vs composition data it was determined that Zr_2S and WC type coexist when $S/Zr = 0.88$, WC type alone occurs for $S/Zr = 0.90$ and 0.99, WC type coexists with the NaCl-type superstructure when $S/Zr = 1.05$ and 1.21, and the NaCl-type superstructure occurs alone for $S/Zr = 1.28$ and 1.30. A diffuse impurity line at low θ was observed to occur with the NaCl-type superstructure pattern for $S/Zr = 1.40$.

A sample with $S/Zr = 1.34$ on a Mo holder was examined by high-temperature X-ray diffractometry at temperatures up to 1500°C. At temperatures below 1250 ± 20°C the NaCl-type superstructure was observed, while for higher temperatures the pattern was that of the NaCl type alone, except that after a few hours at the highest temperatures the WC-type pattern grew with time.

A sample with $S/Zr = 1.34$ was examined at room temperature and the data were analyzed by Rietveld analysis. A fit to a superstructure of the $CdCl_2$ type with $R\bar{3}m$ symmetry was obtained (profile R factor = 12.9%, derived Bragg R factor = 4.6%), with the region below $2\theta = 25°$ excluded. This is the region for which the intensity of scattered X rays is observed to drop because of spreading of the X-ray beam which follows the decrease in the angle of incidence. Two weak impurity lines at $2\theta = 28.7$ and 31.6° were identified as the two strongest diffraction lines of monoclinic ZrO_2, indicating that the zirconium sulfide sample was slightly surface oxidized at high temperature even though the residual pressure at the sample was less than 10^{-6} Torr. The refined structure was obtained from the powder data assuming mixed $K\alpha_1$–$K\alpha_2$ radiation, standard Lorentz and polarization corrections, constant exit monochromator correction, Pearson VII line shape, and individual isotropic thermal parameters. The following parameters were refined: overall scale factor, zero point, hexagonal a and c in $R\bar{3}m$, peak half-width, the profile parameter, background (four parameters), sample area, sulfur position parameters, thermal parameters and occupation parameters. The zirconium positions are fixed, and the refined sulfur positions did not vary from their locations in the cubic structure. The final refined structural parameters in the hexagonal cell are given in Table I. Statistical uncertainties are indicated by parenthetical values. The rhombohedral lattice parameters are $\alpha = 33.377(3)$ and $a = 6.3194(6)$ (see Fig. 1). The occupation

TABLE I

REFINED PARAMETERS FOR $Zr_{1-x}S$ IN THE HEXAGONAL CELL[a]

Atom	Position	Occupancy	Thermal
Zr(a)	$x = 0, y = 0, z = 0$	1.05(5)	0.7(3)
Zr(b)	$x = 0, y = 0, z = \frac{1}{2}$	0.50(2)	0.8(3)
S(s)	$x = 0, y = 0, z = 0.249(1)$	2.00	0.3(3)

[a] Unit cell: $a = 3.6295(7)$, $c = 17.885(2)$ Å.

parameters are in excellent agreement with the combustion analysis results which yielded S/Zr = 1.34(1). The model fit the data well not only in the sense of a low Bragg R value (see Table II for I_{obs} and I_{calc}), but also in the sense of fitting the split (relative to the cubic structure) diffraction peaks. The calculated and observed diffraction patterns are shown in Fig. 2.

The room-temperature Guinier powder diffraction pattern of a sample with S/Zr = 1.37 was found to exhibit three very weak (barely discernible) diffraction lines at 2θ = 16.73, 18.82, and 22.61°. These lines could be indexed using the cell that results from tripling the periodicity along the $\bar{1}10$ direc-

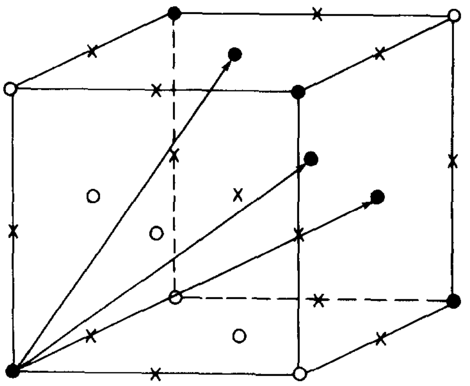

FIG. 1. The cubic unit cell of substructure NaCl-type zirconium monosulfide and the inscribed rhombohedral cell that results from ordering of metal vacancies in alternate planes along the 111 direction (differentiated by open and dark circles). The rhombohedral angle would be 33.56° if there were no relaxation of the cubic lattice.

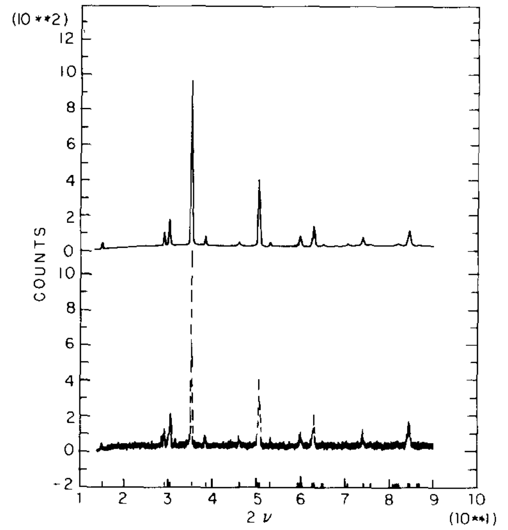

FIG. 2. Calculated (top) and observed (bottom) powder diffraction profile of $Zr_{0.75}S$. Vertical strokes indicate calculated Bragg-peak position.

TABLE II

CALCULATED 2θ VALUES AND CALCULATED AND OBSERVED INTENSITIES FOR $Zr_{1-x}S$ LINES IDENTIFIED BY HEXAGONAL INDEXING

hkl (hex)	2θ (α_1 and α_2)	I_{calc} ($\times 10^{-5}$)	I_{obs} ($\times 10^{-5}$)	Superstructure reflections
1 0 1	28.82	8.48	9.31	x
1 0 1	28.99	4.23	4.61	x
0 0 6	29.95	5.16	5.27	
0 0 6	30.03	2.57	2.65	
0 1 2	30.11	1.54	1.58	
0 1 2	30.19	0.76	0.79	
1 0 4	34.86	102	108	
1 0 4	34.95	50.6	53.8	
0 1 5	38.08	4.88	4.94	x
0 1 5	38.18	2.43	2.45	x
0 0 9	45.61	0.99	1.11	x
1 0 7	45.72	2.44	2.72	x
0 0 9	45.73	0.49	0.55	x
1 0 7	45.84	1.21	1.35	x
0 1 8	50.02	33.5	32.8	
0 1 8	50.15	16.7	16.4	
1 1 0	50.23	33.1	32.4	
1 1 0	50.36	16.4	16.1	
1 1 3	52.68	3.28	3.15	x
1 1 3	52.82	1.63	1.57	x
0 2 1	58.95	1.19	1.16	x

TABLE II—*Continued*

hkl (hex)	2θ (α_1 and α_2)	I_{calc} ($\times 10^{-5}$)	I_{obs} ($\times 10^{-5}$)	Superstructure reflections
0 2 1	59.14	0.59	0.58	x
1 0 10	59.41	2.48	2.45	
1 0 10	59.57	1.23	1.22	
1 1 6	59.60	4.90	4.87	
2 0 2	59.69	2.43	2.44	
1 1 6	59.75	2.43	2.45	
2 0 2	59.85	1.21	1.21	
0 0 12	62.24	5.47	6.05	
0 0 12	62.40	2.72	3.00	
0 2 4	62.60	16.11	17.88	
0 2 4	62.77	8.01	8.93	
0 1 11	64.47	0.77	0.81	x
0 1 11	64.64	0.38	0.40	x
2 0 5	64.74	0.92	0.96	x
2 0 5	64.91	0.46	0.48	x
1 1 9	70.17	1.49	1.56	x
0 2 7	70.26	0.61	0.64	x
1 1 9	70.37	0.74	0.78	x
0 2 7	70.45	0.30	0.32	x
2 0 8	73.61	9.66	10.02	
2 0 8	73.82	4.80	4.98	
1 0 13	75.35	0.63	0.65	x
1 0 13	75.56	0.31	0.33	x
0 0 15	80.48	0.12	0.13	x
0 0 15	80.72	0.06	0.06	x
2 1 1	81.06	0.89	0.91	x
0 1 14	81.21	0.85	0.88	
2 1 1	81.29	0.44	0.45	x
0 1 14	81.45	0.43	0.44	
0 2 10	81.46	0.84	0.87	
0 2 10	81.69	0.42	0.43	
1 2 2	81.70	1.67	1.72	
1 2 2	81.94	0.83	0.86	
1 1 12	83.95	13.4	13.9	
1 1 12	84.19	6.70	6.89	
2 1 4	84.27	13.33	13.73	
2 1 4	84.52	6.64	6.82	
2 0 11	85.95	0.33	0.33	x
1 2 5	86.19	0.80	0.81	x
2 0 11	86.20	0.16	0.17	x
1 2 5	86.45	0.40	0.40	x

tion, yielding a monoclinic (pseudoorthorhombic) cell with $a = 10.86$ Å, $b = 6.28$ Å, and $c = 17.88$ Å and α, β, and γ all essentially 90°.

Discussion

The phases present vs chemical composition data show, in general agreement with earlier results, that the WC-type structure exists for hypostoichiometric (and perhaps stoichiometric) monosulfide with the approximate stoichiometry range given by $0.90 \leq \mathrm{S/Zr} \leq 1.00$, and that the hyperstoichiometric monosulfide exists for a narrow range of stoichiometry about the composition given by S/Zr = 1.32. This compound occurs in a structure that can be described rather accurately as $CdCl_2$ type ($R\bar{3}m$ symmetry), a superstructure that arises from a vacancy ordering in alternate planes perpendicular to the body diagonal of the cubic NaCl-type cell. There is a slight relaxation (from $\alpha = 33.56°$ in the cubic structure to $\alpha = 33.38°$ in the rhombohedral structure) of the lattice.

The vacancies in this structure order weakly within the planes, and this ordering triples the periodicity along the rhombohedral $\bar{1}10$ direction. These results are in good agreement with those from electron diffraction experiments (*8*) and show a remarkable similarity to those found for $Sc_{1-x}S$ (*9*).

A question that remains is the identity of the previously reported monoclinic $Zr_{0.77}S$ structure (*6*). It appears likely that this structure is closely related to that which results from the secondary ordering along the $\bar{1}10$ direction of the rhombohedral lattice. Since the superstructure reflections reported in (*6*) were very weak, the reported monoclinic structure could be in error, a suggestion that was made previously (*11*). Furthermore, the reported structure was based on data from a single crystal, and it is possible when studying ordering processes to obtain regions in which the ordering is not that characteristic of the bulk. Accordingly, it is concluded here that the best description of the ordering in bulk $Zr_{1-x}S$ is that it occurs initially in alternate planes along the cube body diagonal at about 1250°C. Since this ordering can, by symmetry arguments (*11*), occur via a second-order transition and since the results gave no evidence of a two-phase mixture, it is suggested that this ordering transition is second order. There is then a further weak ordering along the $\bar{1}10$ direction so as to triple the periodicity in this direction.

Acknowledgments

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.

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