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The Crystal Structure of a Samarium–Zinc Compound with Approximate Composition SmZn₁₁*

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The crystal structure of the high temperature form of the most zinc-rich compound in the Sm–Zn system has been found to be hexagonal with lattice constants $a = 8.974$, $c = 8.918$ Å and space group $P6/mmm$. The structure is disordered and was found to have a stoichiometry of approximately SmZn₁₁. This is a new structure type in the family of structures related to the CaZn₅ ($D2d$) type. The relations of this new structure to the AB_5 structure and the low temperature tetragonal form of SmZn₁₂ are discussed. A simple mechanism for the transformation from the hexagonal to the tetragonal form is proposed.

Introduction

A number of investigations of the binary phase diagrams of the rare earths with Group IIB elements have revealed the presence of a large number of intermetallic compounds (Gschneidner, 1961). Common features of these systems are: (a) the occurrence of no less than three to four compounds with more than 50 atomic per cent of the Group B element, (b) the existence of most of the compounds as line compounds or with a very limited composition range, (c) the uncertainties of the stoichiometric description of some of the compounds and the lack of agreement between various workers (Kuz'ma, Kripyakevich & Ugrin, 1966; Chiotti & Mason, 1967; Veleckis, Schablaske, Johnson & Feder, 1967) as to the number of compounds present. The last remarks apply particularly to the area of the phase diagrams with high Group IIB element content. These are also the areas which are of most practical importance in the field of reprocessing of fuel elements (Chiotti & Klepfer, 1965).

The most zinc-rich compound in the samarium–zinc system has been reported by both Kuz'ma, Kripyakevich & Ugrin (1966) and Iandelli & Palenzona (1967). Both investigators used powder diffraction methods only and concluded that the compound in question was SmZn₁₂ of the crystal type ThMn₁₂ (space group $14/mmm$). The lattice constants reported by Iandelli & Palenzona were: $a = 8.927 \pm 0.003$, $c = 5.215 \pm 0.002$ Å. Veleckis, Schablaske & Tani (1966) also did powder work and found two modifications of SmZn₁₂. The low temperature form prepared at 475°C was of the ThMn₁₂ type. The high temperature form of the compound prepared at 600°C was hexagonal with lattice parameters of $a = 8.972$ and $c = 8.912$ Å.

Chiotti & Mason (1967) investigated the samarium–zinc system but did not positively identify the stoichiometry of the most zinc-rich compound. The present work was undertaken to determine the crystal structure and thus the stoichiometry of the high-temperature form of this compound.

Experimental procedure

The materials and general techniques used for preparing samarium–zinc alloys have been outlined by Chiotti & Mason (1967). Owing to the difficulty in obtaining homogeneous bulk samples, meaningful

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density measurements and chemical analysis were not possible. In order to obtain crystals of the most zinc-rich compound two different alloys of 95 and 98 wt.% zinc were equilibrated for three hours at 925°C in tantalum crucibles enclosed in stainless steel, and then slowly cooled to precipitate the compound. The crystallites thus formed were isolated by selectively dissolving away the zinc matrix with concentrated NaOH.

X-ray diffraction patterns of powdered specimens of these crystallites were taken with nickel filtered copper radiation (Cu $K\alpha = 1.54178$) and a Debye-Scherrer camera of 114.6 mm diameter. Seven different crystallites were picked from the two alloys and examined by oscillation, Weissenberg and precession methods. All crystals had the same Laue symmetry and appeared to be of the same phase. The approximate lattice constants obtained from Weissenberg and oscillation photographs were utilized to index the powder pattern. The final lattice parameters were obtained by a least-squares procedure utilizing the Nelson-Riley extrapolation function. The compound was found to be hexagonal with $a = 8.974 \pm 0.002$ and $c = 8.918 \pm 0.003$ Å.

The observed Laue symmetry is $6/mmm$. The absence of any extinction conditions puts the compound in either the centric space group $P6/mmm$ or one of the acentric groups $P\bar{6}m2$, $P6mm$, $P622$ or $P\bar{6}2m$. Relative intensity data were obtained by the 2θ scan technique using a General Electric single-crystal orienter equipped with a scintillation counter. Zirconium filtered $MoK\alpha$ radiation was used ($\lambda = 0.7107$ Å). All reflections of the type hkl with $h \geq k$ were examined in the range $0-70^\circ 2\theta$. The intensity of all symmetrically related reflections for several of the stronger hkl reflections was also observed in order to determine the ρ dependence and check the absorption correction. The crystal used had a length of 0.14 mm and a hexagonal cross-section with a maximum dimension of 0.068 mm. The intensities were corrected for absorption using a modified version of the method given by

Busing & Levy (1957) for a crystal of this shape. With this correction the observed ρ dependence of the intensities was less than 5%.

Structure determination

The initial trials were all based on the centric space group $P6/mmm$. By analogy with similar rare earth-zinc systems the stoichiometry of the compound should be in the region of ten to thirteen zinc atoms per samarium atom. This consideration combined with a unit-cell volume of 622.1 \AA^3 indicated the presence of three samarium atoms. Spatial considerations restrict the equivalent positions $24(r)$, $12(g)$ and $12(p)$ from being occupied by the zinc atoms. A three-dimensional Patterson map showed that the samarium atoms were related by a $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ translation. This eliminated the $3(g)$ and $3(f)$ positions. The first trial structure was based on samarium atoms in the $1(a)$ and $2(d)$ positions. A typical heavy-atom type of determination by successive Fourier syntheses and least-squares refinement cycles led to a basic structure with three samarium and thirty-six zinc atoms or SmZn_{12} stoichiometry.

The parameters were refined by a modified version of the least-squares program by Busing, Martin & Levy (1962). The estimated standard deviations given in Table 1 were obtained from this program. The atomic scattering factors and anomalous dispersion terms used were taken from *International Tables for X-ray Crystallography* (1962). The criterion used for considering a reflection to be observed was that $(I - \text{background}) \geq 2.5(I + \text{background})^{1/2}$. This resulted in 343 observed reflections. The refinement was based on ωF with $\omega = 1/(\text{standard deviation})^2$. The R values reported were derived from the expression

$$R = \frac{\sum |F_o| - |\sum F_c|}{\sum |F_o|}$$

Initially isotropic temperature factors were assumed for all atoms and the structure refined giving an R value of 0.115. The samarium atoms were then allowed

Table 1. *Least-squares parameters for SmZn₁₂ - space group P6/mmm*

Values in parentheses are standard deviations in rightmost digits.

Wyckoff notation	x	y	z	β_{11}^* ($\times 10^4$)	β_{22} ($\times 10^4$)	β_{33} ($\times 10^4$)	β_{12} ($\times 10^4$)	β_{13} ($\times 10^4$)	β_{23} ($\times 10^4$)	Occupancy (%)	
Zn(1)	12(0)	0.1671 (2)	2x	0.2415 (3)	48 (2)	56 (3)	50 (2)	$\frac{1}{2}\beta_{22}$	1 (1)	$2\beta_{13}$	100
Zn(2)	6(j)	0.3552 (6)	0	0	92 (5)	200 (12)	43 (5)	$\frac{1}{2}\beta_{22}$	-	-	100
Zn(3)	6(k)	0.2944 (5)	0	$\frac{1}{2}$	73 (4)	29 (4)	31 (4)	$\frac{1}{2}\beta_{22}$	-	-	100
Zn(4)	6(i)	$\frac{1}{2}$	0	0.2742 (5)	40 (3)	65 (6)	58 (4)	$\frac{1}{2}\beta_{22}$	-	-	100
Zn(5)	2(e)	0	0	0.3544 (8)	58 (6)	β_{11}	39 (9)	$\frac{1}{2}\beta_{22}$	-	-	96
Zn(6)	4(h)	$\frac{1}{2}$	$\frac{2}{3}$	0.1457 (7)	68 (5)	β_{11}	37 (7)	$\frac{1}{2}\beta_{22}$	-	-	85
Sm(1)	1(a)	0	0	0	34 (3)	β_{11}	27 (4)	$\frac{1}{2}\beta_{22}$	-	-	100
Sm(2)	2(d)	$\frac{1}{2}$	$\frac{2}{3}$	$\frac{1}{2}$	37 (2)	β_{11}	24 (3)	$\frac{1}{2}\beta_{22}$	-	-	100
Sm(3)†	2(c)	$\frac{1}{2}$	$\frac{2}{3}$	0	36	β_{11}	26	$\frac{1}{2}\beta_{22}$	-	-	15
Sm(4)†	1(b)	0	0	$\frac{1}{2}$	36	β_{11}	26	$\frac{1}{2}\beta_{22}$	-	-	4

* The anisotropic temperature factor used is defined as

$$\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$$

† Temperature terms for Sm(3) and Sm(4) were held constant during the final refinement cycles.

Zn(6) atoms. The ring of six Zn atoms above and below the Sm(2) atom, however, is not derived from an equivalent set of twelve as is the case with Sm(1),

but rather each ring is made up of three Zn(1) atoms and three Zn(4) atoms. This gives a slightly corrugated effect to the Zn atoms in the $z = \frac{1}{4}$ and $\frac{3}{4}$ planes.

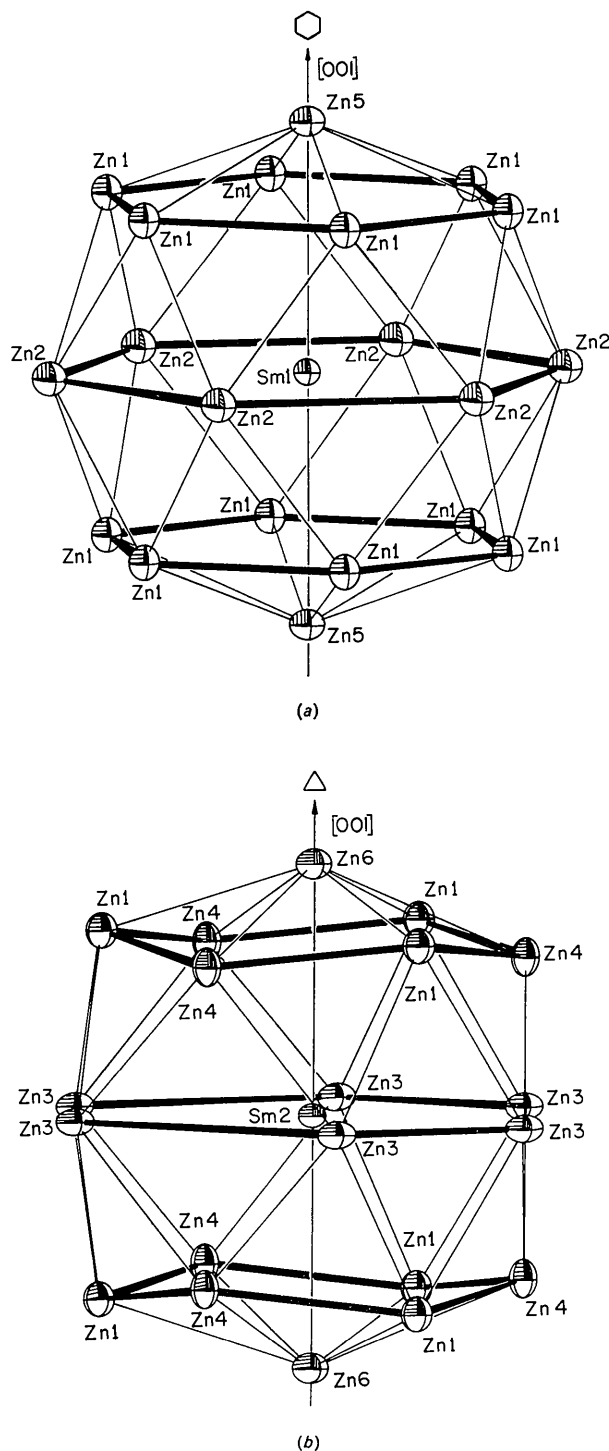


Fig. 1. Coordination polyhedra about Sm (1) and Sm (2). (a) Coordination polyhedron about Sm (1). (b) Coordination polyhedron about Sm (2). (The thermal ellipsoids in (a) and (b) are scaled to a 50% probability.)

Table 3. *Interatomic distances*

	Type	No. of	Distance	
	neighbor	neighbors		
Sm(1)	Zn(5)	2	3.161 Å	
	Zn(2)	6	3.188	
	Zn(1)	12	3.374	
Sm(2)	Zn(6)	2	3.160	
	Zn(3)	6	3.180	
	Zn(4)	6	3.281	
Sm(3)	Zn(1)	6	3.463	
	Zn(2)	6	2.898*	
	Zn(4)	6	3.562	
Sm(4)	Zn(3)	6	2.642*	
	Zn(1)	12	3.473	
Zn(1)	Zn(1)	2	2.597	
	Zn(4)	2	2.604	
	Zn(3)	2	2.675	
	Zn(2)	2	2.685	
	Zn(6)	1	2.721	
	Zn(5)	1	2.786	
	Sm(3)	1	3.364	
	Sm(1)	1	3.374	
	Sm(2)	1	3.463	
	Sm(4)	1	3.473	
Zn(2)	Zn(2)	1	2.599	
	Zn(1)	4	2.685	
	Zn(4)	2	2.770	
	Sm(3)	2	2.898	
	Zn(6)	4	3.177	
	Zn(2)	2	3.188	
	Sm(1)	1	3.188	
	Zn(3)	Sm(4)	1	2.642*
		Zn(3)	2	2.642
		Zn(1)	4	2.675
Zn(4)		2	2.732	
Zn(5)		2	2.944	
Sm(2)		2	3.180	
Zn(3)		1	3.690	
Zn(4)	Zn(1)	4	2.604	
	Zn(3)	2	2.732	
	Zn(2)	2	2.770	
	Zn(6)	6	2.832	
	Sm(2)	2	3.282	
	Sm(3)	1	3.563	
Zn(5)	Zn(5)	1	2.598	
	Zn(1)	6	2.786	
	Zn(3)	6	2.944	
Zn(6)	Sm(1)	1	3.161	
	Zn(6)	1	2.601	
	Zn(1)	3	2.721	
	Zn(4)	3	2.832	
	Sm(2)	1	3.160	
Zn(2)	6	3.177		

* The Sm (4)–Zn (3) distance shows an unrealistically exaggerated contraction since the Zn (3) distance from the position $00\frac{1}{2}$ is an average distance. As expected this effect is also apparent to a much lesser degree in the Sm (3)–Zn (2) distance.

Sm (3)–Zn (6) and Sm (4)–Zn (5) pairs do not occur simultaneously.

The disordered atoms Sm(3) and Sm(4) are both surrounded by similar polyhedra which are composed of 18 zinc atoms instead of 20. The Sm(3) atom is surrounded by six Zn(2) atoms in the basal plane

with a corrugated six-membered ring of Zn(1) and Zn(4) atoms in planes directly above and below the basal plane. There are no zinc atoms along the z axis directly above or below the samarium atom in this case. Similarly the Sm(4) is surrounded by six Zn(3) atoms, with a six-membered ring of Zn(1) atoms in planes directly above and below it.

The family of binary compounds of the type AB_x with x from 7–12 that are related to the $CaZn_5$, $D2_d$ type structure (Haucke, 1940) has been described by many authors. A recent summary by Johnson & Smith (1968) shows how the structure types Pu_3Zn_{22} , Ce_5Mg_{42} , Th_2Zn_{17} , Th_2Ni_{17} and $ThMn_{12}$ are related to the $D2_d$ structure.

The $SmZn_{12}$ structure determined in this investigation is another member of this group. Its relationship to the $D2_d$ type structure and the $SmZn_{12}$ tetragonal structure can be readily seen in Fig. 2. The basal plane of hexagonal $SmZn_{12}$ is outlined by the heavy atoms at coordinate positions $A2$, $D1$, $G2$ and $D3$. The unit cell is two AB_5 unit cells high and encompasses a total of six AB_5 cells. The ac projection of the tetragonal unit cell for the low-temperature form of $SmZn_{12}$, ($ThMn_{12}$ type structure, Florio, Rundle & Snow, 1952) is delineated by positions $D3$, $E2$, $H3$ and $G4$. This unit cell contains four AB_5 cells. In the AB_5 structure planes of A and B atoms are separated by planes containing only B atoms. The A atoms extend in rows normal to the plane of the Figure. Both $SmZn_{12}$ structures may be derived from this structure by alternately substituting pairs of zinc atoms for samarium atoms along these rows. The sequence is such that in the basal plane of the hexagonal unit cell outlined in Fig. 2 the samarium atoms at $C2$ and $E2$ are replaced by a pair of zinc atoms while in the other four rows originating at $A2$, $D3$, $G2$ and $D1$, the samarium atoms at the $0,0,\frac{1}{2}$ position are replaced. This results in close packed rows of samarium and zinc pairs. In the tetragonal unit cell outlined in Fig. 2 the sequence is such that the samarium atom at $F3$ is replaced by a pair of zinc atoms while along the rows originating at $E2$, $D3$, $G4$ and $H3$ the samarium atoms at $\frac{1}{2},0,0$ are replaced. Here the a axis extends normal to the plane of the Figure or normal to the ac projection. It is readily apparent that the major difference between the high and low-temperature $SmZn_{12}$ structures is the sequence in which the light atom pairs are substituted for the heavy atoms.

The transformation from the hexagonal to the tetragonal form of $SmZn_{12}$ can be visualized as a slip of one half a unit cell in the z direction of all rows containing the samarium atom at the $\frac{2}{3}, \frac{1}{3}, \frac{1}{2}$ position, or $E2$ of Fig. 2, the samarium atom in the $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ position, or $C2$ of Fig. 2, remaining fixed. This could occur by movement of a vacancy along these rows. Such a systematic shift of half of the Sm(2) atoms aligns all atoms so that only a small adjustment of positions is needed to satisfy the symmetry of the low-temperature tetragonal form.

The major disorder in the hexagonal $SmZn_{12}$ results from the occasional substitution of a samarium atom for a pair of zinc atoms. The smaller peaks in the difference Fourier synthesis mentioned above were not affected by the addition of the Sm(3) and Sm(4) atoms. These peaks amount to approximately -2.2 , 0.9 , -3.1 and 0.4 electrons about the positions 000 ; $0,0,\frac{1}{4}$; $\frac{1}{3}, \frac{2}{3}, \frac{1}{2}$ and $\frac{1}{3}, \frac{2}{3}, \frac{1}{4}$ respectively. This suggests that to a small extent Sm(1) and Sm(2) atoms may be replaced either by a vacant site, a single zinc, or by a pair of zinc atoms. Size considerations permit the replacement of a samarium atom by a pair of zinc atoms only when zinc atoms in adjacent positions are absent; *i.e.* it must be coupled with a Sm(3) or Sm(4) substitution. This type of substitution would not change the stoichiometry and could occur by a slip mechanism similar to the transformation slip discussed above. The replacement of a samarium atom by one zinc atom or by a vacancy would increase the zinc to samarium atom ratio. Attempts to determine the extent of these various substitutions were inconclusive and the stoichiometry could not be precisely determined from the X-ray data alone. If the only disorder considered is the substitution of the Sm(3) and Sm(4) atoms for pairs of zinc atoms then a minimum of 10.6 for the zinc to samarium atom ratio is obtained. However the Fourier difference synthesis indicates that some substitution of Sm(1) and Sm(2) is also taking place. If this substitution is by single zinc atoms, then the atom ratio could increase up to 11.4. If different substitution mechanisms are assumed, then intermediate values of the atom ratio can be achieved.

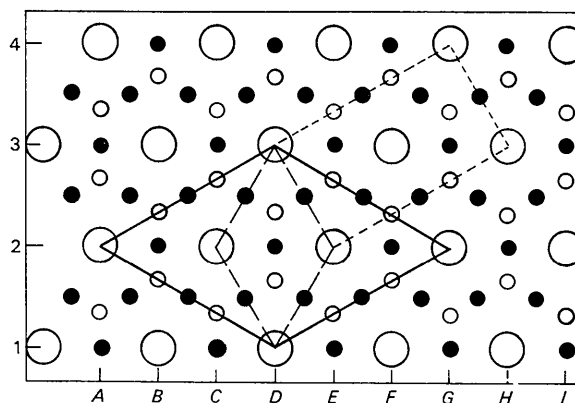


Fig. 2. Relationship of hexagonal $SmZn_{12}$ and tetragonal $SmZn_{12}$ type structures to the $D2_d$ structure. The grid represents the projection of an AB_5 structure of the $D2_d$ type onto the (001) plane. Large circles are A type atoms; small circles are B type atoms. Open circles are in the (001) plane; filled circles represent atoms in planes which are $\frac{1}{2}$ above and below the (001) plane. The AB_5 unit cell is outlined by the long-dash lines, the $SmZn_{12}$ tetragonal unit cell by the short-dash lines, and the $SmZn_{12}$ hexagonal unit cell by the solid lines.

Electron microprobe analysis of the SmZn_{12} crystallites in the zinc matrix of the alloys described above indicates variation in the composition of these crystals and gives an average stoichiometry of $\text{SmZn}_{10.9}$. Some variation in lattice constants was also indicated by X-ray powder diffraction data. Consideration of the single-crystal data obtained indicates a probable Zn/Sm ratio of 11.0 ± 0.5 . The electron microprobe data indicate a similar range in composition; however, whether this is the result of an actual variation in composition or of the uncertainty in the analysis is not known.

A similar type of disordered structure was observed by Johnson & Smith (1967) for $\text{CeMg}_{10.3}$. They started with a basic $\text{Th}_2\text{Ni}_{17}$ type structure in which the disorder occurred by the occasional substitution of a pair of light atoms for a heavy atom. It is interesting to note that if in the hexagonal SmZn_{12} structure all the pairs of zinc atoms in the Sm(1) rows along the z axis are replaced by samarium atoms, the resulting stoichiometry is $\text{Sm}_2\text{Zn}_{17}$. Disorder of a similar type very probably also occurs in $\text{CeZn}_{5.25}$ ($D2_d$ type) which exists with a composition range of 70.4 to 71.1 wt.% zinc (Lott & Chiotti, 1966).

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The Crystal Structure of 1,2-Bis-(*N*-methyl-4-pyridinium)ethylene Tetracyanonickelate(II)

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The crystal structure of the title compound ($\text{C}_{18}\text{H}_{16}\text{N}_6\text{Ni}$) was determined by means of three-dimensional X-ray analysis. The space group is $P2_1/n$ (C_{2h}^2), and the cell dimensions are $a = 6.864$, $b = 12.96$, $c = 10.05$ Å, $\beta = 107.0^\circ$. The corresponding Pd and Pt compounds are isomorphous with the Ni compound. The Ni atoms lie on a centre of symmetry so that the $\text{Ni}(\text{CN})_4^{2-}$ ion is centrosymmetric. The $\text{Ni}(\text{CN})_4^{2-}$ ion is square planar and the bond lengths are: Ni-C 1.85 and C-N 1.16 Å (average). The centre of the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion also lies on a centre of symmetry, so that the two rings are approximately coplanar, while the bond lengths in the ion agree very well with those in pyridine. The distance between the N atoms in the 1,2-bis-(*N*-methyl-4-pyridinium)ethylene ion is 9.27 Å, which is thus approximately the distance between the two positive charges on the divalent cation.

Introduction

The complex cyanides previously studied were mainly those with simple monovalent and divalent cations, e.g. K^+ and Ca^{2+} . The structure of 1,2-bis-(*N*-methyl-4-pyridinium)ethylene tetracyanonickelate(II) has been

determined as part of a programme for the study of complex cyanides with varying types of cation to find the effect of the cation structure on that of the complex formed. When the two positive charges on the cation are separated, as in this case, the complex is expected to assume a different structure to that of the complexes