All of our structure-factor coding utilizes the general form of the structure-factor expression so that no special coding is needed for particular space groups. Consequently, the above expressions may be used directly, in the form of 'code words' (Sparks *et al.*, 1956) appropriate for each particular equivalent position. This, of course, is not possible when the Lonsdale expressions are used.

Atoms in special positions are treated in the same manner as atoms in general positions, except that the form factor used in the former case is $(m/N)f_i$, where N is the order of the space group and m is the order of the special position in question. This procedure avoids the need for using different sets of equivalent positions, and thus different code words, for atoms in positions of different symmetry.

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The Crystal Structures of $SrZn_5$ and $BaZn_5$

By N. C. Baenziger and J. W. Conant

Department of Chemistry, State University of Iowa, Iowa City, Iowa, U.S.A.

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The crystal structures of $SrZn_5$ and $BaZn_5$ have been determined from Weissenberg and precession camera data. The orthorhombic unit-cell dimensions are for $SrZn_5$, $a = 5{\cdot}32$, $b = 6{\cdot}72$, $c = 13{\cdot}15$ Å, $Z = 4$, $Pmcn$; for $BaZn_5$, $a = 5{\cdot}32$, $b = 8{\cdot}44$, $c = 10{\cdot}78$ Å, $Amam$. The structures are related to the $CaZn_5$ structure.

Introduction

The crystal structures of $SrZn_5$ and $BaZn_5$ were determined as part of a program of study of the compounds formed by major groups I and II and the rare earths (A) and minor group II (B) elements. In the barium–zinc and strontium–zinc systems, the structures of the corresponding AZn_{13} compounds have been determined (Zintl & Häucke, 1937, 1938; Ketelaar, 1937). In the calcium–zinc system, in addition to the $CaZn_{13}$ compound, the structure of $CaZn_5$ has been reported (Häucke, 1940). Investigation of the barium and strontium systems in this region led to the determination of two new structures which are related to the $CaZn_5$ structure.

Experimental procedure

A bomb made of $1\frac{1}{2}$ in. $\times$ 6 in. steel pipe with a cap at each end containing an alundum crucible was used as the reaction vessel for the preparation of the AZn_5 compounds by direct combination of their elements. An extra piece of group IIa metal was used outside the alundum crucible to act as a 'getter'. The bomb was heated in a resistance furnace to 1000° C. and allowed to cool slowly.

The crystals formed were brittle, shiny, and dulled very slowly in a moist atmosphere. If prepared with an excess of group IIa metal in order to prevent welding by AZn_{13} or zinc, an abundance of crystals could be separated by placing the reaction product on a wire screen and flushing off the group IIa rich portion with water. A duplicate chemical analysis made on $BaZn_5$ by precipitating the barium as the sulfate and the zinc as the pyrophosphate showed 28·5% (26·6%) barium and 69·6% (69·5%) zinc, indicating $BaZn_{5.12}$. X-ray analysis alone was used to determine the composition of $SrZn_5$.

Single crystals were chosen and mounted in 0·3 mm. diameter capillaries. Multiple-film Weissenberg (Cu $K\alpha$) diagrams were taken of the zero to third levels of the [100] zone for both compounds. Precession (Mo $K\alpha$) diagrams were taken for the ($hk0$) and ($h0l$) data. The intensities of the diffraction spots were estimated by visual comparison to a graded scale. Absorption corrections were made for the Cu $K\alpha$ radiation by assuming a cylindrical shape of the crystals.

Determination of the structures

The cell constants of the orthorhombic crystals are given in Table 1.

Patterson projections were made from ($hk0$), ($h0l$) and ($0kl$) data. Both structures appeared to have all atoms spaced by 0, $\frac{1}{4}a$ or $\frac{1}{2}a$ in the a direction.

Table 1. *Cell constants*

	$BaZn_5$	$SrZn_5$
a (Å)	5·32±0·01	5·32±0·01
b (Å)	8·44±0·02	6·72±0·02
c (Å)	10·78±0·03	13·15±0·04
U (Å^3)	484·03	470·12
Z	4	4
D_X (g.cm.$^{-3}$)	6·37	5·86
Possible space groups	$A2_1am$–C_{2v}^{12}	$P2_1cn$–C_{2v}^{9}
	$Amam$–D_{2h}^{17}	$Pmcn$–D_{2h}^{16}

$BaZn_5$

A rough structure of $BaZn_5$ was obtained from the Patterson projections and by trial and error. Electron-density projections (Fig. 1), evaluated at $\frac{1}{60}$ths of a cell, were used to refine the parameters. The F_o values were fitted to F_c by a least-squares calculation of scale and temperature factors.* The backshift method was used to correct the final parameters shown in Table 2. The standard deviations were calculated by Cruickshank's method (Cruickshank, 1949; Cruickshank & Rollett, 1953). The discrepancy factor, $R = \Sigma||F_o|-|F_c||\div\Sigma|F_o|$, is 0·16 (0·12 for observed reflections only). Since satisfactory agreement was obtained, space group $A2_1am$ was not considered. The interatomic distances are given in Table 3.

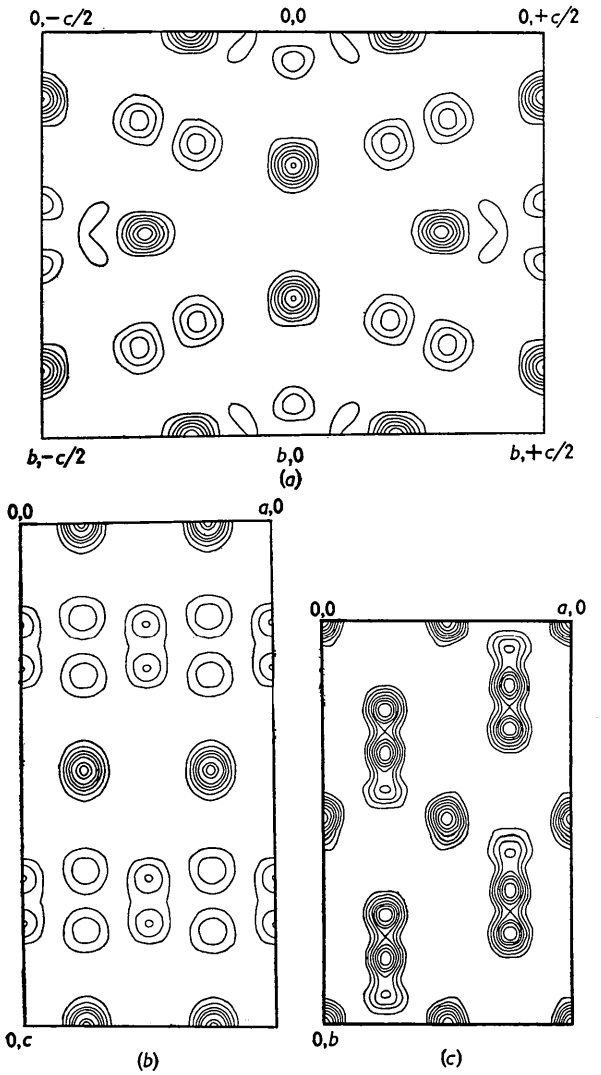

Fig. 1. Electron-density projection of $BaZn_5$ (*a*) on to (100), (*b*) on to (010), (*c*) on to (001).

Table 2. *Final parameters for* $BaZn_5$

Space group $Amam$; (0, 0, 0; 0, ½, ½)+

8 Zn (*g*): $\frac{1}{4}, y, z$; $\frac{1}{4}, y, \bar{z}$; $\frac{3}{4}, \bar{y}, z$; $\frac{3}{4}, \bar{y}, \bar{z}$; with $y = 0{\cdot}226$, $z = 0{\cdot}309$. Standard error in peak position = ±0·009 Å.

8 Zn (*e*): 0, 0, z; 0, 0, $\bar{z}$; ½, 0, z; ½, 0, $\bar{z}$; with $z = 0{\cdot}204$. Standard error in peak position = ±0·004 Å.

4 Zn (*c*): $\frac{1}{4}, y$, 0; $\frac{3}{4}, \bar{y}$, 0; with $y = 0{\cdot}926$. Standard error in peak position = ±0·008 Å.

4 Ba (*c*): with $y = 0{\cdot}335$. Standard error in peak position = ±0·004 Å.

Table 3. *Interatomic distances in* $BaZn_5$

Zn(*e*):	2 Zn	2·59 Å	Zn(*c*):	4 Zn	2·64 Å
	2 Zn	2·64		2 Zn	2·66
	2 Zn	2·66		2 Zn	2·93
	2 Zn	2·69		1 Ba	3·45
	2 Ba	3·73		2 Ba	3·46
	2 Ba	3·82			
			Ba(*c*):	4 Zn	3·40
Zn(*g*):	2 Zn	2·59		3 Zn	3·45
	1 Zn	2·66		2 Zn	3·46
	2 Zn	2·67		4 Zn	3·73
	2 Zn	2·97		4 Zn	3·82
	2 Ba	3·40		2 Zn	3·89
	1 Ba	3·45		2 Ba	3·85
	1 Ba	3·89			

$SrZn_5$

Three-dimensional Patterson sections (Harker, 1936) evaluated at $U = 0, \frac{1}{4}, \frac{1}{2}$, were used to obtain a rough structure for $SrZn_5$. The same method described for $BaZn_5$ was used to refine the parameters. The (*h*0*l*) and (0*kl*) electron-density projections are shown in Fig. 2 and atomic parameters in Table 4.*

The discrepancy factor for $SrZn_5$ is 0·20 (0·13 for observed reflections only). Since the structure-factor agreement was satisfactory, space group $P2_1cn$ was not considered further. The interatomic distances are shown in Table 5.

* Tables of F_o and F_c for $BaZn_5$ and $SrZn_5$ have been deposited as Document No. 4717 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D.C., U.S.A. A copy may be secured by citing the Document number and by remitting $1·25 for photoprints, or $1·25 for 35 mm. microfilm. Advance payment is required. Make checks or money orders payable to: Chief, Photoduplication Service, Library of Congress.

Table 4. *Final parameters for* $SrZn_5$

Space group *Pmcn*

8 Zn (*d*): x, y, z; $\frac{1}{2}-x, \frac{1}{2}-y, \frac{1}{2}+z$; $\frac{1}{2}+x, \bar{y}, \bar{z}$; $\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z$; $\bar{x}, \bar{y}, \bar{z}$; $\frac{1}{2}+x, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{2}-x, y, z$; $x, \frac{1}{2}-y, \frac{1}{2}+z$; with $x = 0$, $y = 0{\cdot}150$, $z = 0{\cdot}144$. Standard error in peak position $= \pm 0{\cdot}003$ Å.

4 Zn_1 (*c*): $\frac{1}{4}, y, z$; $\frac{3}{4}, \bar{y}, \bar{z}$; $\frac{3}{4}, \frac{1}{2}+y, \frac{1}{2}-z$; $\frac{1}{4}, \frac{1}{2}-y, \frac{1}{2}+z$; with $y = 0{\cdot}601$, $z = 0{\cdot}521$. Standard error in peak position $= \pm 0{\cdot}006$ Å.

4 Zn_2 (*c*): with $y = 0{\cdot}660$, $z = 0{\cdot}715$. Standard error in peak position $= \pm 0{\cdot}004$ Å.

4 Zn_3 (*c*): with $y = 0{\cdot}455$, $z = 0{\cdot}202$. Standard error in peak position $= \pm 0{\cdot}006$ Å.

4 Sr (*c*): with $y = 0{\cdot}144$, $z = 0{\cdot}412$. Standard error in peak position $= \pm 0{\cdot}003$ Å.

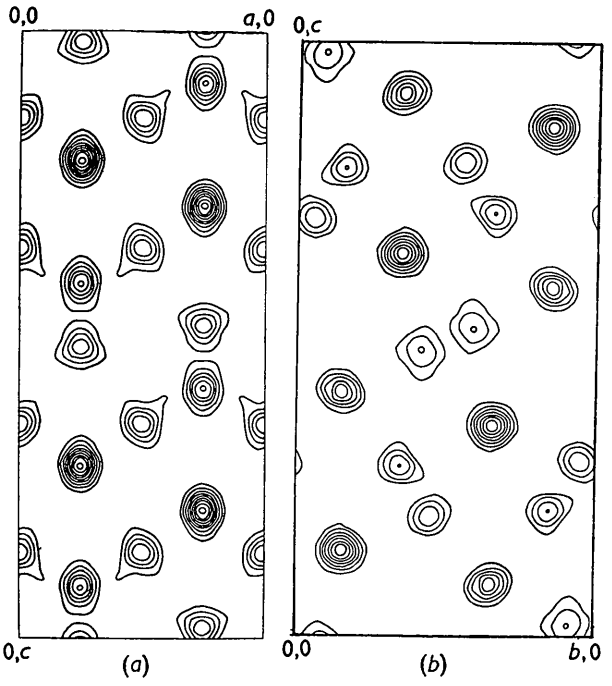

Fig. 2. Electron-density projection of $SrZn_5$ (*a*) on to (010), (*b*) on to (100).

Discussion

It is perhaps not surprising that the compounds $BaZn_5$ and $SrZn_5$ should have different structures from $CaZn_5$, but it is surprising that these structures differ from one another. Nevertheless, an interesting structural parallel can be traced through all these structures.

The $CaZn_5$ structure is the $CaCu_5$ type (*Structure Reports*, **11**, 60), and many examples of its occurrence are known. A characteristic feature of this structure type, as well as of the $NaZn_{13}$ and $BaCd_{11}$ types, is that the structure is determined by the Zn–Zn-type contacts. These metal atoms form cages in which the more electropositive element resides. The cell dimensions remain nearly the same as atoms of different size are placed in this cage, as long as the atoms are smaller than the size of the cage. The conditions for the

Table 5. *Near-neighbor distances in* $SrZn_5$

Zn(*d*):	1 Zn	2·56 Å	Zn_3(*c*):	2 Zn	2·56 Å
	1 Zn	2·57		1 Zn	2·60
	1 Zn	2·61		2 Zn	2·76
	1 Zn	2·64		2 Zn	2·98
	2 Zn	2·66		1 Zn	3·81
	1 Zn	2·69		2 Sr	3·31
	1 Zn	2·76		1 Sr	3·46
	1 Sr	3·60		1 Sr	3·87
	1 Sr	3·65			
	1 Sr	3·73	Sr(*c*):	1 Zn	3·25
	1 Sr	3·76		2 Zn	3·28
				2 Zn	3·31
Zn_1(*c*):	2 Zn	2·57		1 Zn	3·39
	1 Zn	2·58		2 Zn	3·41
	2 Zn	2·69		1 Zn	3·46
	2 Zn	3·04		2 Zn	3·60
	1 Zn	3·81		2 Zn	3·65
	2 Sr	3·28		2 Zn	3·73
	1 Sr	3·39		2 Zn	3·76
	1 Sr	3·92		1 Zn	3·87
				1 Zn	3·92
Zn_2(*c*):	3 Zn	2·58		2 Sr	4·02
	1 Zn	2·59			
	2 Zn	2·61			
	2 Zn	2·98			
	1 Sr	3·25			
	2 Sr	3·41			

$CaZn_5$ structure is that $R_A = \sqrt{(8/3)} \times R_B$; observed structures lie between 1·37 and 1·58 R_B. With Zn as the type *B* metal atom, only $CaZn_5$ ($R_{Ca} = 1{\cdot}97$ Å), $LaZn_5$ ($R_{La} = 1{\cdot}86$ Å), and $(Th_{0.6}Zn_{0.4})Zn_5$ ($R_{Th} = 1{\cdot}79$ Å) have been reported. Choosing a zinc radius of 1·33 Å, the maximum radius for a type *A* atom would be $R_A = \sqrt{(8/3)} \times R_B = 1{\cdot}633 \times 1{\cdot}33 = 2{\cdot}17$ Å. The atomic radius is 2·14 Å for strontium and 2·17 Å for barium. These atoms are at the upper limit in size, and they form related structures instead.

If one chooses an end-centered orthorhombic cell instead of the normal hexagonal cell of $CaZn_5$, with

$$a_{orth.} = a_{hex.},\ b_{orth.} = \sqrt{3} \times b_{hex.},\ c_{orth.} = c_{hex.}$$

and then compares the (100) projection of $CaZn_5$ (Fig. 3(*a*)) with the (100) projections of $BaZn_5$ (Fig. 3(*b*)) and $SrZn_5$ (Fig. 3(*c*)), an interesting parallel can be observed. First, the *a* cell dimensions are comparable:

$CaZn_5$, $a = 5{\cdot}40$ Å; $SrZn_5$, $a = 5{\cdot}32$ Å; $BaZn_5$, $a = 5{\cdot}32$ Å.

Secondly, the appearance of the projections is similar. The basic structural unit appears to be a six-sided unit with the vertices being linear chains of Zn atoms which go through the whole structure perpendicular to the plane of the projection. In the $CaZn_5$ structure, these chains are lined up so that the unit is rectangular. In the $SrZn_5$ and $BaZn_5$ structures, this rectangle has been changed into a six-sided figure. The structural units in the $SrZn_5$ and $BaZn_5$ structures are almost superimposable, the chief difference between structures being in the manner in which the six-sided figures pack together.

A third comparison between the structures is the

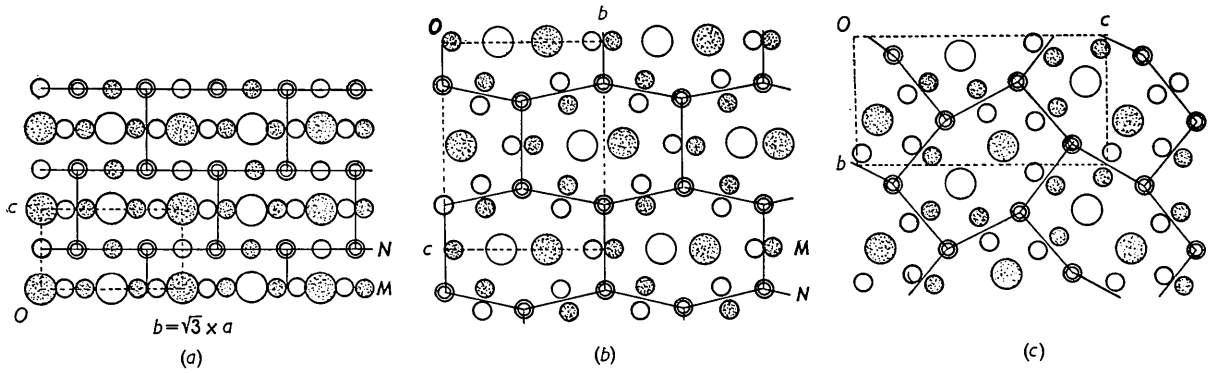

Fig. 3. The (100) orthorhombic projection of (*a*) the $CaZn_5$ structure, (*b*) the $BaZn_5$ structure, (*c*) the $SrZn_5$ structure. Open circles are atoms at $x = \frac{1}{4}$, shaded circles are atoms at $x = \frac{3}{4}$. The double concentric circles are zinc atoms at $x = 0$ and $\frac{1}{2}$.

comparison of the *M* and *N* layers perpendicular to the (100) projection. The *M* and *N* layers of the $CaZn_5$ structure are shown in Fig. 4(*a*); the corresponding layers for the $BaZn_5$ structure are shown in Fig. 4(*b*). If a Zn atom moves from the *M* layer of the $CaZn_5$ structure into the *N* layer to form a puckered hexagonal close-packed net of Zn atoms, the Ba atoms and Zn atoms remaining in the *M* layer are permitted to shift into a zigzag chain and the *M* and *N* layers of $BaZn_5$ result. The zigzag chain also exists in the $SrZn_5$ structure and may be considered another common feature of the alkali, alkaline earth–Zn- or Hg-type

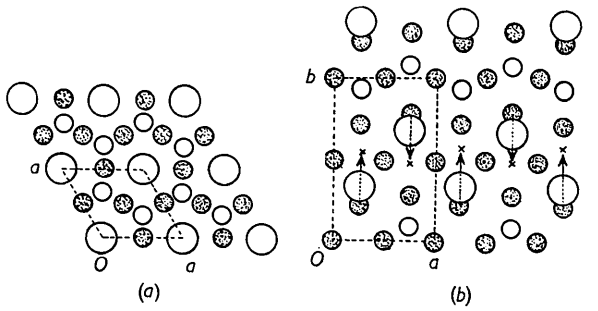

Fig. 4. (*a*) The projection of the $CaZn_5$ structure on (001). (*b*) The half-cell projection of the $BaZn_5$ structure on (001). The open circles are the atoms in the *M* layer. The shaded atoms are in the *N* layer.

intermetallic compound. Similar chains of the more electropositive atoms occur in the NaHg (zigzag), the KHg_2 (zigzag) and the related $NaHg_2$ (linear) structures. Accompanying this puckering is a pronounced decrease in metal–metal distance along the chain. In the $CaZn_5$ structure, the chain runs in the [001] direction, with the Ca–Ca distance greater than in the metal (6·5%). In $SrZn_5$, the distance is 6·1% shorter, and in $BaZn_5$ 11·3% shorter. The shortening is 13% in $NaHg_2$, 12% in NaHg, and 9% in KHg_2.

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