

where

$$A = \frac{zs(n-2v_0)+d^{*2}}{2\left[1-s^2\left(\frac{n}{2}-v_0\right)^2\right]^{\frac{1}{2}}}$$

The direction cosines of a diffracted beam are given by:

$$\epsilon_1 = \frac{x_1}{B}, \quad \epsilon_2 = \frac{y_1+1}{B}, \quad \epsilon_3 = \frac{z_1}{B}$$

where x_1, y_1, z_1 are given by:

$$\{x_1 y_1 z_1\} = (d_{ij}) \{xyz\}$$

and are the coordinates of the point when it is in reflecting position,

$$(d_{ij}) = \begin{pmatrix} \cos \omega & \sin \omega & 0 \\ -\sin \omega \cos \mu & \cos \omega \cos \mu & \sin \mu \\ \sin \omega \sin \mu & -\cos \omega \sin \mu & \cos \mu \end{pmatrix}$$

where ω is obtained from equation (2), and $B = x_1^2 + (y_1 + 1)^2 + z_1^2 = 1$, since the radius of the reflection sphere is equal to one.

Let us define now a reference system X', Y', Z' , attached to the crystal, so that, for $\mu = \omega = 0^\circ$, and after the crystal has been oriented, it is coincident with X, Y, Z .

It follows immediately that the direction cosines of the incident beam in the system X', Y', Z' are:

$$\gamma_i = \Sigma_j d_{ij}$$

and those of the diffracted beam in the same system are:

$$\delta_i = \Sigma_j d_{ij} \epsilon_j$$

In some cases it is convenient to choose X', Y', Z' non-coincident with X, Y, Z under the above conditions; in such cases, the two systems are related by rotations on the two arcs of the goniometer head and on the dial, *i.e.* they are related by the transformation

$$\{xyz\} = (S_{ij}) \{x_0 y_0 z_0\}$$

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Alkaline earth silicides, germanides and stannides with CrB structure type. By W. RIEGER and E. PARTHÉ, *School of Metallurgical Engineering and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.*

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Five new alkaline earth compounds: SrGe, SrSn, BaSi, BaGe and BaSn are found to crystallize with the CrB (*B33*) structure type. It is shown that a relationship exists between the *c/b* axial ratio, the *y* parameter of the Si, Ge or Sn positions and the chain angle α of the Si-Si, Ge-Ge or Sn-Sn chains. The new compounds are discussed under the aspect of the general valence equation.

In continuation of investigations on monosilicides and monogermanides with CrB- and FeB-type structure (Schob & Parthé, 1965; Hohnke & Parthé, 1966) we found it of interest to ascertain whether these structure types occur also with silicides, germanides and stannides of the alkaline earth elements. Since these compounds contain no transition elements and have one component to the right of the Zintl line it is possible to apply the general valence equation (Mooser & Pearson, 1956; Pearson, 1964; Kjekshus, 1964; Hulliger & Mooser, 1965; Parthé, 1966). With an electron to anion ratio of 6 and under the assumption that the cation-anion bonds are negligible the general valence equation suggests the presence of anion-anion chains. Such anion-anion chains are the particular structural feature not only of the CrB and FeB structure types but also of the MoB and the monoclinic LiAs structure types.

Five alkaline earth compounds with group 4B elements are already known. All of them crystallize in the orthorhombic CrB structure type: CaSi (Hellner, 1950), CaGe (Eckerlin, Meyer & Wölfel, 1955), CaSn (Eckerlin, Meyer & Wölfel, 1955), SrSi (Rocktäschel & Weiss, 1962) and also BaPb (Sands, Wood & Ramsey, 1959). After our investiga-

tions were completed, we received information on two additional compounds: BaSi and BaGe (Burnashowa & Gladyshevskii, 1966) which crystallize also in the CrB structure type.

Samples of CaSi, CaPb, SrSi, SrGe, SrSn, SrPb, BaSi, BaGe and BaSn were prepared by arc melting the elements under argon atmosphere. The arc melting procedure was done with great care to avoid losses of the materials by vaporization. Weight losses were checked and proved not to exceed an average of 5%; thus the reacted samples were assumed not to be far off stoichiometry. Since the reactions were violent and complete, it was not necessary to homogenize the alloys. The materials were crystallized in the shape of platelets; all of them proved to react violently with moisture, and powder patterns (CrK α radiation) were therefore taken in glass capillaries under dried ligroin.

The powder diffraction patterns of CaSi, SrSi, SrGe, SrSn, BaSi, BaGe and BaSn could be indexed orthorhombic with the lattice constants given in Table 1. The extinctions of *hkl* with $h+k=2n+1$ and *h0l* with $l=2n+1$ led to the possible space groups: *Cmc*2₁(*C*_{2v}¹²), *C2cm*(*C*_{2v}¹⁶) and *Cmcm*(*D*_{2h}⁷). The similarity of the diffraction patterns of

the new compounds to those of the already known alkaline earth silicides, germanides, *etc.* immediately indicated that the new compounds also crystallize with the CrB structure type. Thus we assumed space group $Cmcm (D_{2h}^{17})$ and placed tentatively 4 alkaline earth elements in equipoint 4(c) with $y \sim 0.14$ and four of the 4B metals also in 4(c) with $y \sim 0.44$. The relatively good agreement between observed and calculated intensities showed that these compounds are isotypic with CrB. The powder diffraction patterns of CaPb and SrPb, however, displayed the pattern of unreacted lead metal and other weak lines, some of which are probably due to oxidation products.

The refinement of the adjustable parameters was difficult because the samples were contained in capillaries and the absorption effects were considerable. In addition, even carefully powdered specimens showed increased intensities for reflections for planes which are parallel or nearly parallel to the plane of the platelets (0k0). The adjustable parameters given in Table 1 were refined by systematically varying the y parameters for both the 4(c) positions in steps of 0.002 and comparison with the visually recorded intensities.

An example of an intensity calculation is given in Table 2 for BaSi with the lattice constants and adjustable parameters as given in Table 1. For compounds with large differences between the scattering factors of the two elements, for example BaSi and BaGe, the error limits of the adjustable parameters of Si or Ge are naturally bigger since the intensities are not very sensible to small changes of the $y(\text{Si})$ or $y(\text{Ge})$ parameter.

Two systematic relationships seem to exist between the values of the c/b axial ratios, the $y(\text{anion})$ parameters and the chain angle α of the anion (4B-element)-chains for the reported compounds:

(a) The c/b ratios are inversely proportional to the size of the alkaline earth metal and directly proportional to the size of the 4B element.

(b) The chain angle α depends on $y(\text{anion})$ and c/b according to

$$\tan\left(\frac{\alpha}{2}\right) = \frac{c}{b(2-4y)}.$$

Table 2. Intensity calculation for BaSi with CrB structure type

		CrK α -radiation			
<i>h</i>	<i>k l</i>	$\sin^2 \theta \times 1000$ obs.	$\sin^2 \theta \times 1000$ calc.	Intensity	Intensity calc.
0	2 0	—	36.88	—	0.2
1	1 0	63.1	61.12	<i>wm</i>	361.3
0	2 1	115.9	113.77	<i>ms</i>	634.2
1	3 0	137.9	134.88	<i>ms</i>	684.8
1	1 1	140.3	138.01	<i>vs</i>	1000.0
0	4 0	150.2	147.53	<i>m</i>	258.8
2	0 0	210.4	207.60	<i>wm</i>	279.6
1	3 1	214.6	211.77	<i>ms</i>	331.5
0	4 1	226.2	224.41	<i>w</i>	113.0
2	2 0	—	244.48	—	0.3
1	5 0	—	282.41	—	15.6
0	0 2	310.2	307.55	<i>wm</i>	151.6
2	2 1	323.2	321.37	<i>m</i>	275.5
0	6 0	—	331.94	—	15.9
0	2 2	—	344.43	—	0.2
2	4 0	357.2	355.13	<i>m</i>	137.2
1	5 1	360.5	359.30	<i>m</i>	184.1
1	1 2	369.7	368.67	<i>vw</i>	61.9
0	6 1	411.5	408.82	<i>m</i>	141.2
2	4 1	433.9	432.01	<i>vw</i>	84.7
1	3 2	444.3	442.43	<i>ms</i>	234.8
0	4 2	456.4	455.07	<i>w</i>	98.7
3	1 0	—	476.32	—	22.4
1	7 0	505.2	503.70	<i>ms</i>	147.2
2	0 2	515.7	515.15	<i>wm</i>	155.4
2	6 0	—	539.54	—	17.7
3	3 0	550.5	550.09	<i>w</i>	96.0
2	2 2	—	552.03	—	0.2
3	1 1	554.0	553.21	<i>m⁺</i>	144.5
1	7 1	—	580.59	—	0.0

Table 1. Lattice constants of CrB-type phases with alkaline earth metals

	Setting $Cmcm$					Reference*
	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	y_A	y_B	
Silicides						
CaSi	4.545 ± 0.003	10.728 ± 0.01	3.890 ± 0.003	—	—	(1)
	4.59 ± 5	10.795 ± 8	3.91 ± 4	0.14	0.43	(2)†
SrSi	4.826 ± 0.008	11.287 ± 0.010	4.042 ± 0.003	—	—	(1)
	4.83 ± 0.01	11.33 ± 0.01	4.04 ± 0.01	0.140 ± 0.001	0.434 ± 0.002	(3)‡
BaSi	5.028 ± 0.005	11.929 ± 0.006	4.131 ± 0.003	0.140 ± 0.005	0.438 ± 0.006	(1)
	5.00 ± 0.01	11.96 ± 0.02	4.16 ± 0.01	0.14	0.43	(6)
Germanides						
CaGe	4.575 ± 0.002	10.845 ± 0.001	4.001 ± 0.001	0.136	0.424	(4)†
SrGe	4.808 ± 0.004	11.360 ± 0.010	4.169 ± 0.003	0.138 ± 0.002	0.430 ± 0.003	(1)
BaGe	5.057 ± 0.020	11.942 ± 0.015	4.299 ± 0.006	0.140 ± 0.003	0.436 ± 0.004	(1)
	5.07 ± 0.01	11.98 ± 0.02	4.30 ± 0.01	0.14	0.43	(6)
Stannides						
CaSn	4.821 ± 0.004	11.52 ± 0.02	4.349 ± 0.004	0.133	0.416	(4)†
SrSn	5.033 ± 0.006	12.00 ± 0.02	4.493 ± 0.003	0.132 ± 0.002	0.422 ± 0.003	(1)
BaSn	5.310 ± 0.010	12.485 ± 0.015	4.650 ± 0.005	0.132 ± 0.002	0.425 ± 0.004	(1)
Plumbides						
BaPb	5.29 ± 0.01	12.60 ± 0.02	4.78 ± 0.01	0.1266 ± 0.0008	0.4198 ± 0.0003	(5)

* (1) This work. (2) Hellner (1950). (3) Rocktäschel & Weiss (1962). (4) Eckerlin, Meyer & Wölfel (1955). (5) Sands, Wood & Ramsey (1964). (6) Burnashova & Gladyshevskii (1966).

† No error limits given for the adjustable parameters. The published data are either given for a different space group setting or with a change of origin.

‡ The error limits for the adjustable parameters were evaluated from the R values for different layer lines as given in the original paper.

Table 2 (cont.)

<i>h</i>	<i>k</i>	<i>l</i>	$\sin^2 \theta \times 1000$		Intensity	Intensity calc.
			obs.	calc.		
1	5	2	—	589.96	—	13.0
0	8	0	—	590.11	—	13.6
2	6	1	617.6	616.42	<i>m</i> +	200.8
3	3	1	627.7	626.97	<i>vw</i>	86.7
0	6	2	—	639.48	—	16.8
2	4	2	662.8	662.67	<i>ms</i>	161.2
0	8	1	666.9	666.99	<i>vw</i>	40.0
3	5	0	—	697.61	—	6.6
0	2	3	730.1	728.86	<i>w</i>	74.0
1	1	3	753.0	753.10	<i>m</i>	154.0
3	5	1	775.2	774.50	<i>w</i>	125.8
3	1	2	—	783.87	—	44.8
2	8	0	—	797.71	—	32.6
1	9	0	—	798.76	—	2.4
1	7	2	812.6	811.25	<i>s</i>	331.0
1	3	3	826.7	826.86	<i>m</i> +	113.1
4	0	0	—	830.40	—	93.8
0	4	3	—	839.50	—	43.7
2	6	2	847.3	847.08	<i>vw</i>	46.8
3	3	2	857.2	857.63	<i>m</i>	265.5
4	2	0	—	867.29	—	0.1
2	8	1	875.1	874.60	<i>vs</i>	{ 122.1 283.2
1	9	1	—	875.64		
0	8	2	—	897.65		
3	7	0	919.3	918.90	<i>ms</i> ,	{ 255.8 94.6
0	10	0	922.0	922.04	diffuse	
2	2	3	936.5	936.46	<i>m</i>	304.9

With compounds having equal differences between the principal quantum number of the alkaline earth metal and the 4B element, for example CaSi, SrGe and BaSn, a tendency to obtain approximately equal chain angles is observed.

These results are shown graphically in Fig. 1, where the *c/b* ratios of all the compounds are plotted *versus* the cor-

responding $y(\text{anion})$ parameters. The data plots are actually rectangles if the error limits are taken into consideration independently. (It was found necessary to redetermine the lattice constants of CaSi and SrSi, since the reported error limits were too large to permit comparative studies with the other compounds.) Dotted lines in Fig. 1 connect loci for equal chain angles α .

There seems to exist only one outstanding relation for the interatomic distances. As shown in Table 3 the shortest Si-Si, Ge-Ge and Sn-Sn distances in these structures do not change very much with the alkaline earth component.

Table 3. Shortest distances within the 'anion' chains

	Ca	Sr	Ba
Si-Si	2.46* Å	2.51 ± 0.03 Å	2.51 ± 0.07 Å
Ge-Ge	2.60*	2.62 ± 0.04	2.63 ± 0.05
Sn-Sn	2.91*	2.92 ± 0.09	2.97 ± 0.05

* No error limits given for the adjustable parameters

The nearly constant B-atom distances explain the change of the chain angle if the alkaline earth metal component is changed. An increase in the size of the alkaline earth metal leads to an increase in $y(\text{anion})$ and related to it an increase of the chain angle. The constancy of the 'anion' distances is in agreement with the assumption that the anion chains are the important structural features of these compounds.

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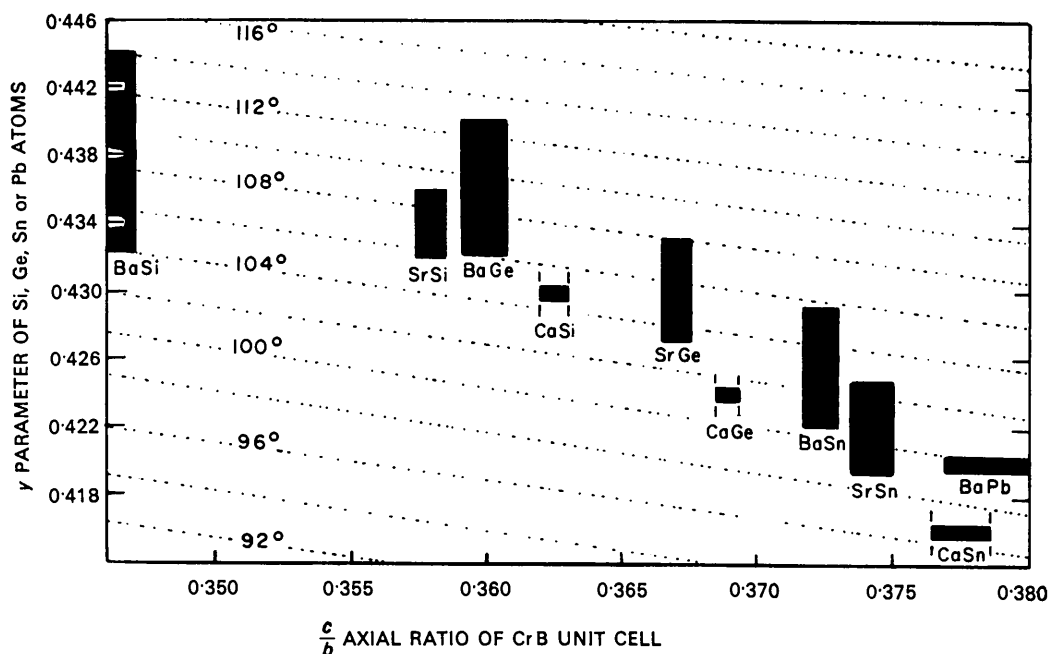


Fig. 1. *c/b* axial ratio, chain angle α and $y(\text{anion})$ values for the alkaline earth compounds with CrB structure type. (Since for CaSi, CaGe and CaSn no error limits are given for the $y(\text{anion})$ parameters, the rectangles might be extended in the direction indicated by the dashed lines. However, extension of the rectangles does not affect the general features of the plot.)

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Bond lengths in bis-salicylaldoximato-nickel. By R. C. SRIVASTAVA, E. C. LINGAFELTER and PREM C. JAIN, *Department of Chemistry, University of Washington, Seattle, Washington, U.S.A.*

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A full-matrix least-squares refinement of the crystal structure of bis-salicylaldoximato-nickel has been carried out, using the original three-dimensional Cu $K\alpha$ intensity data of Merritt, Guare & Lessor. The bond lengths in the refined structure are in satisfactory agreement with those found in other substituted salicylaldimine chelates.

One of the first crystal structures to be reported of a metal chelate of a Schiff base was that of bis-salicylaldoximato-nickel (Merritt, Guare & Lessor, 1956). Partial three-dimensional X-ray diffraction intensity data were collected, but the structure was only partially refined. Recently, in comparing the bond distances in a number of salicylaldimine chelates (Lingafelter & Braun, 1966) we have noticed several bond-length discrepancies in bis-salicylaldoximato-nickel, one as large as 0.1 Å, and have therefore completed the refinement, using the Cu $K\alpha$ data of Merritt, Guare & Lessor (1956). Professor Merritt has kindly given us corrected values for the observed structure factors of several reflections. Correct values of F_o are: 113, 20.0; 16, 1.4, <0.9; 14, 3, 2, <0.9; 14, 3, 4, <0.9; 443, 19.7; 462, 7.6. In addition, 561 and 562 should be deleted from the list of reflections.

Our refinement has been carried out by full-matrix least squares, using our modification of the program of Busing & Levy (1959). The function minimized was $\sum w(F_o - F_c)^2$, with a Hughes (1941) weighting scheme: $\sqrt{w} = 1.0$ for $F_o \leq 4.0$, $\sqrt{w} = 4.0/F_o$ for $F_o > 4.0$. The scattering factors used were from Viervoll & Øgrim (1949) for Ni; from Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for oxygen, nitrogen and carbon; and from McWeeny (1951) for hydrogen.

The hydrogen atoms were placed at the positions of Merritt, Guare & Lessor for all cycles except the final set and for the final set of cycles were placed in recalculated positions, assuming trigonal bonding and a C-H distance of 1.05 Å. The temperature factor for each hydrogen atom was initially assigned equal to that of the atom to which it was attached.

After six cycles of refinement (of the non-hydrogen atoms only) with individual atom isotropic temperature factors, and three with individual anisotropic temperature factors, the value of $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ (observed reflections only) had decreased from 0.19 to 0.15 and the shifts in parameters in the final cycle were all less than one-half of the estimated standard deviations. Mean values of the

standard deviations in positional parameters were: C 0.009 Å; N 0.007 Å; O 0.007 Å.

At this time we received the corrected F_o values from Professor Merritt and carried out a final set of refinement cycles using the revised data. A series of four cycles, refining positions of all atoms, anisotropic temperature factors for the non-hydrogen atoms, and isotropic temperature factors for the hydrogen atoms, reduced R to a final value of 0.14. Although the parameters of the hydrogen atoms were refined, their values are not considered to be significant and are not reported. The final values of the parameters of the non-hydrogen atoms, and their estimated standard deviations, are listed in Table 1. In the final cycle the maximum parameter shifts were 0.9 σ in position and 1.0 σ in thermal parameters.

Since there are a number of reflections with rather large differences between observed and calculated structure factors, we have carried out an additional series of refinement cycles in which those reflections having $\sqrt{w}\Delta F > 3$ (18 reflections) were omitted. The maximum change in any bond length caused by these omissions was 2 σ and the mean was about 1 σ .

The bond distances, with their estimated standard deviations, are given in Table 2. Examination of the table shows that the refined bond distances agree more closely with those reported for other substituted salicylaldimine chelates, although the C(9)-N(10) distance still appears to differ considerably. It is doubtful that this difference is significant in view of the fact that the estimated standard deviations are probably underestimated, as is apparent from the magnitudes of the shifts in parameters in the final cycle and in the refinement with 18 reflections omitted.

Although the results of Merritt, Guare & Lessor showed no significant deviation of the molecule from planarity, the present refinement shows a clear deviation from complete planarity. The atoms of the benzene ring and the carbon and oxygen atoms attached to the ring are strictly coplanar (no atom deviates from the least-squares plane by more