

## CaZn<sub>3</sub>: a Structure with Mixed BaLi<sub>4</sub>- and CeCu<sub>2</sub>-Like Ordering

BY MARIA L. FORNASINI AND FRANCO MERLO

*Istituto di Chimica Fisica, Università di Genova, Corso Europa, Palazzo delle Scienze, 16132 Genova, Italy*

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### Abstract

The phase CaZn<sub>3</sub>, hexagonal, space group  $P6_3/mmc$ , exhibits a small homogeneity field from 74 to 75 at.% Zn, as detected by the observed range of lattice constants ( $a = 9.157\text{--}9.168$ ;  $c = 7.297\text{--}7.327$  Å) and experimental density values ( $D_m = 4.89\text{--}4.93$  Mg m<sup>-3</sup>). A single crystal selected from a 75 at.% Zn matrix, with lattice constants  $a = 9.168$  (2) and  $c = 7.327$  (2) Å, was used for the structure analysis. Three-dimensional intensity data were measured on a single-crystal automatic diffractometer. Absorption corrections were made by the semi-empirical method of North, Phillips & Mathews [*Acta Cryst.* (1968), A24, 351–359];  $\mu = 24.4$  mm<sup>-1</sup> for Mo  $K\alpha$ . The structure was solved by direct methods and refined with anisotropic thermal parameters to a final conventional  $R$  value of 0.034 for 275 observed reflexions. The occupation factors of three atomic positions, which were found to be partially filled, were also refined, giving mean numbers of 6.65 Ca and 20.23 Zn atoms in the elementary cell with a final formula CaZn<sub>3.04</sub> ( $D_x = 4.95$  Mg m<sup>-3</sup>). The structure can be regarded as a mixture of two types of elementary cells, with the same symmetry and dimensions, but different in stoichiometric content and atomic arrangement, which alternate randomly to generate the whole structure. One type of cell ( $\frac{2}{3}$  of the total number) is nearly identical to that of BaLi<sub>4</sub>, with a slight difference in composition caused by the incomplete occupancy of a Zn position. The other type of cell ( $\frac{1}{3}$ ) has the formula Ca<sub>8</sub>Zn<sub>16</sub> and presents an atomic arrangement very similar to that of CeCu<sub>2</sub>. Different occupancies of the partially filled sites can account for the composition range observed for this phase.

### Introduction

In the Ca–Zn equilibrium diagram studied by Messing, Adams & Steunenberg (1963), eight intermediate phases are reported, four of which have known structures, namely CaZn<sub>2</sub> (CeCu<sub>2</sub>-type), CaZn<sub>5</sub> (CaCu<sub>5</sub>-type), CaZn<sub>11</sub> (BaCd<sub>11</sub>-type) and CaZn<sub>13</sub> (NaZn<sub>13</sub>-type). Another phase with approximate composition Ca<sub>7</sub>Zn<sub>4</sub> was recently recognized to have the

stoichiometry Ca<sub>3</sub>Zn<sub>3</sub> with the Cr<sub>5</sub>B<sub>3</sub> structure type (Bruzzone, Franceschi & Merlo, 1978).

In this paper we describe the crystal structure of the compound reported in the diagram as Ca<sub>7</sub>Zn<sub>20</sub>.

### Experimental

The metals used were calcium, from Fluka Co., Switzerland, and zinc from Koch–Light, England, of 99.9 and 99.999 wt% purity, respectively. Some samples of slightly different composition in the range from 74 to 75 at.% Zn were prepared by melting stoichiometric amounts of the two metals in sealed tantalum crucibles. In some cases the alloys were annealed at 823 K. The micrographic examination and X-ray powder-pattern data showed the existence of a homogeneity field, which includes the whole composition range examined. Powder photographs, taken with Cu  $K\alpha$  radiation and a Debye–Scherrer camera of 114.6 mm diameter, were indexed on the basis of a hexagonal cell, with lattice constants ranging in the following way:  $a = 9.157\text{--}9.168$  Å;  $c = 7.297\text{--}7.327$  Å. The experimental density, measured by pycnometry, varied from 4.89 to 4.93 Mg m<sup>-3</sup>. The higher values, whether of lattice parameters or densities, are those of the Zn-rich alloys.

Several prismatic crystals were isolated in a sample with composition CaZn<sub>3</sub>; they were tested by the Laue method and found to be single. The crystal chosen for the structure determination, with dimensions 0.12 × 0.12 × 0.25 mm and elongated in the  $z$  direction, was examined by rotation and Weissenberg photographs. The Laue symmetry and the systematic absences ( $hhl$  present only with  $l = 2n$ ) enabled  $P6_3mc$ ,  $P\bar{6}2c$  and  $P6_3/mmc$  to be established as possible space groups. The lattice constants were determined by rotation patterns and found to be  $a = 9.168$  (2) and  $c = 7.327$  (2) Å.

Intensities were measured on a Philips PW 1100 automatic diffractometer with graphite-monochromated Mo  $K\alpha$  radiation. The crystal was mounted with the  $z$  axis approximately aligned with the  $\phi$  axis of the diffractometer. The  $\theta$ – $2\theta$  scanning technique was employed with a scan width of 1.2°, a scan speed of 0.05° s<sup>-1</sup>, and a background time of 10 s. Standard reflexions showed no systematic fluctuations. Al-

together 1021 reflexions were recorded up to  $\theta = 30^\circ$ , both  $hkl$  and  $khl$  equivalent reflexions being collected. Lorentz and polarization corrections were made; for the absorption correction the semi-empirical method of North, Phillips & Mathews (1968) was applied using 54  $\psi$ -scan data from three strong  $00l$  reflexions. The discrepancy index among equivalent reflexions, which amounted to 8.7%, reduced to 3.3% after absorption correction; averaging gave 288 independent reflexions.

### Structure resolution

The structure was solved by direct methods in the space group  $P6_3/mmc$ , indicated by intensity statistics as the most probable one. *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) was applied to 69 reflexions with  $E > 1.2$ , using 50 other very weak reflexions for the PSI ZERO test. The phase set with the best combined figure of merit gave an acceptable solution, enabling 6 Ca atoms in  $6(h)$  and 22 Zn atoms in  $12(k)$ ,  $6(h)$  and  $4(f)$  to be located. The atomic arrangement so obtained showed vacancies in the structure corresponding to the site set  $2(a)$ , which could be filled, on the basis of interatomic distances, by two Zn atoms. This position was thus added to the others and least-squares full-matrix refinement of the positional and isotropic thermal parameters led to a conventional  $R$  value of 0.142. At this stage the temperature factors of the Zn atoms in  $2(a)$  and  $6(h)$  were ten and three times, respectively, greater than those of the other Zn atoms, suggesting a partial filling of these sites. On the other hand, a difference electron-density map, calculated with the only atomic positions given by the *MULTAN* solution, revealed two peaks, one corresponding to the new position  $2(b)$  and the other, with half weight, corresponding again to position  $2(a)$ . So, taking into account the composition of the phase under examination, the interatomic distances and the impossibility of simultaneous occupation of the sites  $2(b)$  and  $2(a)$  on the one hand and  $2(b)$  and Zn  $6(h)$  on the other, assignment of Ca to  $2(b)$  and Zn to  $2(a)$  was proposed, with a partial filling of these two and the Zn  $6(h)$  positions.

Such a model was refined, introducing weights  $w = 1/\sigma^2(F_o)$ , over 275 observed reflexions with  $|F_o| > 6\sigma(F_o)$ . Owing to the strong correlation between site occupation and thermal parameters for the three partially filled positions, they were alternately fixed during several least-squares cycles, allowing all the other parameters to be varied. Convergence was finally obtained with  $R = 0.093$ . Three more cycles including anisotropic temperature factors for all atoms except Zn in  $2(a)$  reduced the  $R$  value to 0.034. For the structure refinement the *SHELX* 76 system of programs

Table 1. *Positional and occupational parameters of CaZn<sub>3</sub>*

Numbers in parentheses are e.s.d.'s in the least significant digits.

|       |       | x             | y             | z             | Occupancy (%) |
|-------|-------|---------------|---------------|---------------|---------------|
| Ca(1) | 6(h)  | 0.4740 (2)    | 0.9480 (4)    | $\frac{1}{2}$ | 100           |
| Ca(2) | 2(b)  | 0             | 0             | $\frac{1}{2}$ | 33 (3)        |
| Zn(1) | 12(k) | 0.1692 (1)    | 0.3384 (2)    | 0.5556 (2)    | 100           |
| Zn(2) | 6(h)  | 0.0978 (2)    | 0.1956 (4)    | $\frac{1}{2}$ | 66 (1)        |
| Zn(3) | 4(f)  | $\frac{1}{2}$ | $\frac{1}{2}$ | 0.5715 (3)    | 100           |
| Zn(4) | 2(a)  | 0             | 0             | 0             | 13 (2)        |

(Sheldrick, 1976) was used; scattering factors and dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974). Both the *MULTAN* 78 and *SHELX* 76 programs have already been satisfactorily employed in the structure resolution of the phase Sm<sub>10</sub>Pd<sub>21</sub> (Fornasini, Mugnoli & Palenzona, 1979).

The final positional parameters, together with the occupancy of each position, are reported in Table 1.\* In accordance with these results the elementary cell contains mean numbers of 6.65 (6) Ca and 20.23 (10) Zn atoms, providing the formula CaZn<sub>3.04(4)</sub> (75.2 at.% Zn), and a calculated density of 4.95 Mg m<sup>-3</sup>.

The homogeneity range, with the observed variations in the lattice parameters and density, can correspond to the possibility of different occupations of the partially filled sites. So, whilst the occupancy values found for the crystal examined refer to a Zn-rich sample, the Ca-rich side of this phase can be represented by slightly changing the occupation factors. For example, if occupancies of 43% and 57% are assigned to the Ca(2) and Zn(2) sites, respectively, maintaining an occupancy of 13% for the Zn(4) site, the formula Ca<sub>6.86</sub>Zn<sub>19.68</sub> (74 at.% Zn) and the density 4.89 Mg m<sup>-3</sup>, calculated with the shortest lattice constants, are obtained, in good agreement with the experimental data.

Intensities for powder-pattern indexing were calculated by the program *LAZY PULVERIX* (Yvon, Jeitschko & Parthé, 1977), and corrected for cylindrical-specimen absorption. A list of the observed and calculated low-angle reflexions is given in Table 2.

### Discussion

As noted above, if only the partially occupied atomic positions of CaZn<sub>3</sub> are considered, namely Ca(2), Zn(2) and Zn(4), the Ca sites are not compatible with the Zn sites, owing to the unreasonably small distances

\* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35229 (5 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Observed and calculated powder intensities ( $I_o, I_c$ ) and interplanar spacings ( $d_o, d_c$ ) for  $\text{CaZn}_3$ 

$I_c$  is normalized to the strongest reflexion which is given an intensity of 1000. Lorentz, polarization and absorption corrections were applied for a Debye-Scherrer camera with  $\text{Cu K}\alpha$  radiation.

| $d_o$ | $d_c$ | $hkl$ | $I_c$ | $I_o$     | $d_o$ | $d_c$ | $hkl$ | $I_c$ | $I_o$      | $d_o$ | $d_c$ | $hkl$ | $I_c$ | $I_o$     |
|-------|-------|-------|-------|-----------|-------|-------|-------|-------|------------|-------|-------|-------|-------|-----------|
| 7.76  | 7.94  | 1 0 0 | 60    | <i>mw</i> | 2.283 | 2.292 | 2 2 0 | 1000  | <i>vvs</i> | 1.740 | 1.745 | 4 0 2 | 152   | <i>m</i>  |
| 5.32  | 5.38  | 1 0 1 | 56    | <i>mw</i> | 2.140 | 2.145 | 3 0 2 | 38    | <i>w</i>   | 1.660 | 1.663 | 2 0 4 | 38    | <i>w</i>  |
| 3.93  | 3.970 | 2 0 0 | 99    | <i>m</i>  | 2.102 | 2.109 | 3 1 1 | 211   | <i>m</i>   | 1.633 | 1.635 | 3 1 3 | 124   | <i>m</i>  |
| 3.64  | 3.663 | 0 0 2 | 25    | <i>w</i>  | 2.072 | 2.080 | 2 0 3 | 250   | <i>m</i>   | 1.550 | 1.552 | 5 0 1 | 97    | <i>mw</i> |
| 3.324 | 3.326 | 1 0 2 | 17    | <i>vw</i> | 1.980 | 1.985 | 4 0 0 | 98    | <i>mw</i>  | 1.541 | 1.540 | 4 0 3 | 21    | <i>vw</i> |
| 2.991 | 3.001 | 2 1 0 | 15    | <i>vw</i> | 1.938 | 1.943 | 2 2 2 | 398   | <i>ms</i>  | 1.528 | 1.528 | 3 3 0 | 32    | <i>w</i>  |
| 2.761 | 2.777 | 2 1 1 | 112   | <i>m</i>  | 1.913 | 1.916 | 4 0 1 | 89    | <i>mw</i>  | 1.505 | 1.506 | 3 0 4 | 45    | <i>w</i>  |
| 2.677 | 2.692 | 2 0 2 | 667   | <i>vs</i> | 1.889 | 1.894 | 2 1 3 | 306   | <i>ms</i>  | 1.499 | 1.500 | 4 2 0 | 33    | <i>w</i>  |
| 2.646 | 2.647 | 3 0 0 | 27    | <i>w</i>  | 1.889 | 1.887 | 3 1 2 | 19    | <i>ms</i>  | 1.468 | 1.470 | 4 2 1 | 22    | <i>vw</i> |
| 2.476 | 2.489 | 3 0 1 | 224   | <i>ms</i> | 1.828 | 1.832 | 0 0 4 | 60    | <i>w</i>   | 1.458 | 1.460 | 3 2 3 | 475   | <i>s</i>  |
| 2.325 | 2.334 | 1 0 3 | 351   | <i>ms</i> | 1.791 | 1.795 | 3 0 3 | 87    | <i>mw</i>  | 1.458 | 1.457 | 5 0 2 | 38    | <i>s</i>  |
| 2.311 | 2.321 | 2 1 2 | 98    | <i>mw</i> | 1.781 | 1.785 | 1 0 4 | 26    | <i>vw</i>  |       |       |       |       |           |

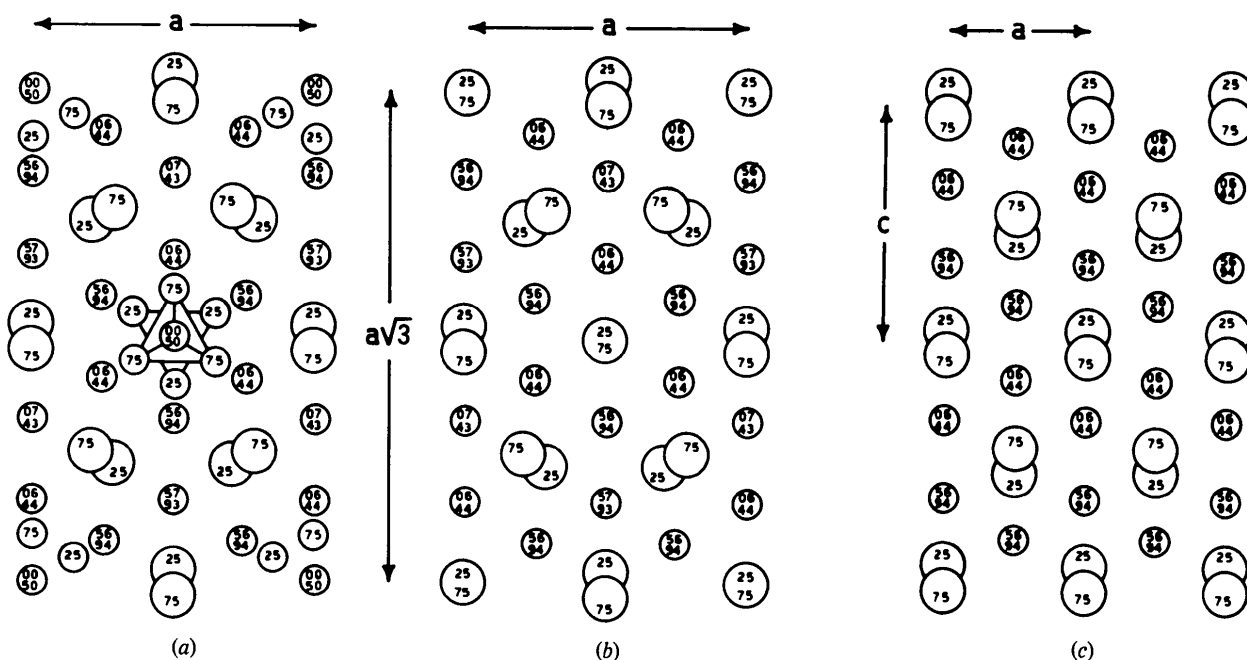


Fig. 1. (a) Projection on to (001) of the  $\text{BaLi}_4$ -like arrangement of  $\text{CaZn}_3$ ; the full lines connect the Zn(2) and Zn(4) atoms. (b) Projection on to (001) of the  $\text{CeCu}_2$ -like arrangement of  $\text{CaZn}_3$ . (c) Projection on to (010) of  $\text{CaZn}_2$ . The inscribed numbers are two-digit values ( $\times 100$ ) of the  $z$  parameters for  $\text{CaZn}_3$ , and the  $y$  parameters for  $\text{CaZn}_2$ . Large circles: Ca; small circles: Zn.

involved [Ca(2)–Zn(2) 1.55 and Ca(2)–Zn(4) 1.83 Å]. On the other hand, the sum of the occupational frequencies of Ca(2) and Zn(2) reaches the exact value of 100% within the limits of the error, whilst the Zn(4) site, although compatible with Zn(2), shows a lower occupational frequency than Zn(2).

Consequently, the structure can be described in terms of two types of elementary cells with the same symmetry and dimensions, but different in stoichiometry content and atomic arrangement. Two thirds of the cells contain only the Ca(1), Zn(1), Zn(2), Zn(3) and Zn(4) positions, and the remaining one third contains only the Ca(1), Ca(2), Zn(1) and Zn(3) positions,

all completely filled save Zn(4). Taking into account the absence of supercell reflexions, we can further say that these two types of cells are distributed randomly in the crystal. In accordance with this interpretation, the fractional values of the occupational parameters found for Ca(2), Zn(2) and, to a certain extent, Zn(4) are due to the contemporaneous occurrence of two atomic arrangements in the same structure.

The first type of atomic arrangement is nearly identical to the  $\text{BaLi}_4$  structure (Wang, Kanda, Miskell & King, 1965). The only difference is the presence of icosahedral holes, caused by the partial occupation of the Zn(4) position, which is empty in about 80% of the

Table 3. Comparison of the atomic parameters in the three structures BaLi<sub>4</sub>, CaZn<sub>3</sub> and CaZn<sub>2</sub>, all described in the space group *Cmcm*

BaLi<sub>4</sub> and CaZn<sub>3</sub> are referred to the orthohexagonal cell; CaZn<sub>2</sub> is referred to a new orthorhombic cell with lattice constants  $a = 2a_{\text{CaZn}_2}$ ,  $b = 2c_{\text{CaZn}_2}$ ,  $c = b_{\text{CaZn}_2}$ .

| BaLi <sub>4</sub>             |    |          |          | CaZn <sub>3</sub>            |    |          |          | CaZn <sub>2</sub>            |               |    |          |          |               |
|-------------------------------|----|----------|----------|------------------------------|----|----------|----------|------------------------------|---------------|----|----------|----------|---------------|
| $a = 11.026 \quad b = 19.098$ |    |          |          | $a = 9.168 \quad b = 15.879$ |    |          |          | $a = 9.182 \quad b = 15.334$ |               |    |          |          |               |
| $c = 8.891 \text{ \AA}$       |    |          |          | $c = 7.327 \text{ \AA}$      |    |          |          | $c = 7.337 \text{ \AA}$      |               |    |          |          |               |
| Position in <i>Cmcm</i>       |    | <i>x</i> | <i>y</i> | <i>z</i>                     |    | <i>x</i> | <i>y</i> | <i>z</i>                     | Occupancy (%) |    | <i>x</i> | <i>y</i> | <i>z</i>      |
| 8(g)                          | Ba | 0.208    | 0.264    | $\frac{1}{4}$                | Ca | 0.211    | 0.263    | $\frac{1}{4}$                | 100           | Ca | 0.250    | 0.276    | $\frac{1}{4}$ |
| 4(c)                          | Ba | 0.0      | 0.472    | $\frac{1}{4}$                | Ca | 0.0      | 0.474    | $\frac{1}{4}$                | 100           | Ca | 0.0      | 0.474    | $\frac{1}{4}$ |
| 4(c)                          | —  | —        | —        | —                            | Ca | 0.0      | 0.0      | $\frac{1}{4}$                | 33            | Ca | 0.0      | 0.974    | $\frac{1}{4}$ |
| 16(h)                         | Li | 0.743    | 0.419    | 0.562                        | Zn | 0.754    | 0.415    | 0.556                        | 100           | Zn | 0.750    | 0.418    | 0.557         |
| 8(f)                          | Li | 0.0      | 0.162    | 0.562                        | Zn | 0.0      | 0.169    | 0.556                        | 100           | Zn | 0.0      | 0.168    | 0.443         |
| 8(g)                          | Li | 0.654    | 0.449    | $\frac{1}{4}$                | Zn | 0.647    | 0.451    | $\frac{1}{4}$                | 66            | —  | —        | —        | —             |
| 4(c)                          | Li | 0.0      | 0.103    | $\frac{1}{4}$                | Zn | 0.0      | 0.098    | $\frac{1}{4}$                | 66            | —  | —        | —        | —             |
| 8(f)                          | Li | 0.0      | 0.333    | 0.581                        | Zn | 0.0      | 0.333    | 0.572                        | 100           | Zn | 0.0      | 0.333    | 0.557         |
| 4(a)                          | Li | 0.0      | 0.0      | 0.0                          | Zn | 0.0      | 0.0      | 0.0                          | 13            | —  | —        | —        | —             |

elementary cells with the BaLi<sub>4</sub>-like ordering. The second type of atomic arrangement is similar to that presented by CaZn<sub>2</sub> (Wieting, 1961), which crystallizes with the CeCu<sub>2</sub> structure type (Larson & Cromer, 1961). These similarities are outlined in Table 3 and Fig. 1.

Table 3 gives the atomic parameters of the three structures BaLi<sub>4</sub>, CaZn<sub>3</sub> and CaZn<sub>2</sub>, described in the same space group *Cmcm*.

Fig. 1 shows the two types of atomic arrangement of CaZn<sub>3</sub> compared with the structure of CaZn<sub>2</sub>. In the BaLi<sub>4</sub>-like ordering, Zn(2) and Zn(4) form columns of tetrahedra parallel to the *z* axis, alternately joined by a vertex and by a face (Fig. 1*a*). The CeCu<sub>2</sub>-like ordering is obtained by replacing all these tetrahedra with Ca(2) atoms (Fig. 1*b*). On the other hand, Fig. 1(*a*) and (*c*) makes evident the close geometrical likeness between the BaLi<sub>4</sub> and CeCu<sub>2</sub> structures.

Table 4 gives the interatomic distances in both types of ordering of CaZn<sub>3</sub> and in CaZn<sub>2</sub>.

In the BaLi<sub>4</sub>-like cells, the Ca(1) atoms are surrounded by twelve Zn atoms in a distorted hexagonal prism, with the bases capped by two Ca atoms. Two more Ca and two more Zn atoms are in contact with the central atom by enlarging four contiguous lateral faces of the hexagonal prism, which is higher on one side than on the other. The neighbors of Zn(1), Zn(2) and Zn(4) are 4 Ca + 8 Zn, 2 Ca + 10 Zn and 12 Zn, respectively, giving in every case a more or less distorted icosahedral coordination. Zn(3) is surrounded by six Ca atoms at the vertices of a trigonal prism; the rectangular faces are capped by three Zn atoms, and another Zn emerges from a trigonal basis, which is larger than the opposite one. Obviously, all these polyhedra are strictly similar to those found in BaLi<sub>4</sub>.

In the CeCu<sub>2</sub>-like cells the Zn(2) and Zn(4) atoms are absent. Zn(3) shows the same coordination polyhedron as above, namely a trigonal prism with four faces capped. Zn(1) changes its coordination completely, now surrounded by 6 Ca + 4 Zn, which form a polyhedron nearly identical to that of Zn(3). Therefore, disregarding some slight distortion, the coordination of Zn(1) and Zn(3) becomes very similar to that of the only Zn crystallographic site in CaZn<sub>2</sub>. Ca(1) retains the distorted hexagonal-prismatic coordination as in the other arrangement, but the two Zn atoms not belonging to the prism are replaced by two Ca atoms at 4.60 Å. In this way, a polyhedron identical to that of Ca in CaZn<sub>2</sub> is obtained. Ca(2) is coordinated to 12 Zn atoms at the vertices of a hexagonal prism with the bases waved and capped by two Ca atoms, and with six other Ca atoms equatorially placed at 4.60 Å. This environment gives a polyhedron identical to that of Ca in the CaIn<sub>2</sub> structure type (Iandelli, 1964). It should be remembered that both the CeCu<sub>2</sub> and CaIn<sub>2</sub> structures represent distortions of the AlB<sub>2</sub> type. The similarity between the interatomic distances found in this arrangement of CaZn<sub>3</sub> and in CaZn<sub>2</sub> is also observable in Table 4.

Most of the interatomic distances exhibit a contraction which does not exceed 10% of the sum of the corresponding metallic radii for coordination 12 (1.97 and 1.38 Å for Ca and Zn, respectively), as has been observed in many intermetallic compounds of the alkaline-earth elements. The only exception is the Zn(2)—Zn(4) distance, 2.40 Å, in the BaLi<sub>4</sub>-like cells, which is 13% shorter than the atomic diameter of Zn.

Also, in the BaLi<sub>4</sub> phase the corresponding Li—Li distance is the shortest, but with only a 6% contraction,

Table 4. *Interatomic distances (Å) in CaZn<sub>3</sub> (BaLi<sub>4</sub>-like and CeCu<sub>2</sub>-like ordering) and in CaZn<sub>2</sub> (CeCu<sub>2</sub>-type)*

E.s.d.'s are less than 0.01 Å. The multiplicity of bonds marked with an asterisk is dependent on the degree of occupancy of the Zn(4) position.

| CaZn <sub>3</sub>                |       | CeCu <sub>2</sub> -like ordering |      |
|----------------------------------|-------|----------------------------------|------|
| BaLi <sub>4</sub> -like ordering |       |                                  |      |
| Ca(1)–2Ca(1)                     | 3.76  | Ca(1)–2Ca(1)                     | 3.76 |
| –2Ca(1)                          | 3.87  | –2Ca(1)                          | 3.87 |
| –4Zn(1)                          | 3.20  | –2Ca(2)                          | 4.60 |
| –2Zn(3)                          | 3.25  | –4Zn(1)                          | 3.20 |
| –2Zn(2)                          | 3.26  | –2Zn(3)                          | 3.25 |
| –4Zn(1)                          | 3.31  | –4Zn(1)                          | 3.31 |
| –2Zn(3)                          | 3.33  | –2Zn(3)                          | 3.33 |
|                                  |       | Ca(2)–2Ca(2)                     | 3.66 |
|                                  |       | –6Ca(1)                          | 4.60 |
|                                  |       | –6Zn(1)                          | 3.04 |
|                                  |       | –6Zn(1)                          | 3.50 |
| Zn(1)–2Ca(1)                     | 3.20  | Zn(1)–1Ca(2)                     | 3.04 |
| –2Ca(1)                          | 3.31  | –2Ca(1)                          | 3.20 |
| –1Zn(2)                          | 2.51  | –2Ca(1)                          | 3.31 |
| –1Zn(3)                          | 2.61  | –1Ca(2)                          | 3.50 |
| –1Zn(4)                          | 2.72* | –1Zn(3)                          | 2.61 |
| –2Zn(2)                          | 2.74  | –2Zn(1)                          | 2.81 |
| –2Zn(1)                          | 2.81  | –1Zn(1)                          | 2.85 |
| –1Zn(1)                          | 2.85  |                                  |      |
| Zn(2)–2Ca(1)                     | 3.26  |                                  |      |
| –2Zn(4)                          | 2.40* |                                  |      |
| –2Zn(1)                          | 2.51  |                                  |      |
| –2Zn(2)                          | 2.69  |                                  |      |
| –4Zn(1)                          | 2.74  |                                  |      |
| Zn(3)–3Ca(1)                     | 3.25  | Zn(3)–3Ca(1)                     | 3.25 |
| –3Ca(1)                          | 3.33  | –3Ca(1)                          | 3.33 |
| –3Zn(1)                          | 2.61  | –3Zn(1)                          | 2.61 |
| –1Zn(3)                          | 2.62  | –1Zn(3)                          | 2.62 |
| Zn(4)–6Zn(2)                     | 2.40  |                                  |      |
| –6Zn(1)                          | 2.72  |                                  |      |
|                                  |       |                                  |      |
| CaZn <sub>2</sub>                |       | Zn–1Ca                           |      |
| Ca–2Ca                           | 3.76  | –2Ca                             | 3.17 |
| –2Ca                             | 3.79  | –1Ca                             | 3.29 |
| –2Ca                             | 4.59  | –2Ca                             | 3.33 |
| –2Zn                             | 3.12  | –2Zn                             | 2.64 |
| –4Zn                             | 3.17  | –1Zn                             | 2.67 |
| –2Zn                             | 3.29  | –1Zn                             | 2.83 |
| –4Zn                             | 3.33  |                                  |      |

almost all the other distances being larger than the sum of the metallic radii. So, although geometrical features, such as the *c/a* ratio, the atomic parameters and the size ratio between the partner atoms, are very similar, CaZn<sub>3</sub> shows much more contracted distances than BaLi<sub>4</sub>. This fact, connected with the larger electronegativity difference displayed by Ca and Zn ( $\Delta x = 0.6$ ; Pauling electronegativity values) compared to Ba and Li ( $\Delta x = 0.1$ ), is probably indicative of greater bond strengths.

The most important effect of the general shortening of distances on going from BaLi<sub>4</sub> to CaZn<sub>3</sub> is the strong

compression exerted by six Zn(2) atoms, at the vertices of a trigonal antiprism, on the Zn(4) atoms. This feature should account for the very low filling of the Zn(4) position and the consequent occurrence of vacancies in the BaLi<sub>4</sub>-like cells of CaZn<sub>3</sub>.

The contraction of the distances and the good space filling, shown by the values of the average coordination numbers (18.2 and 10.6 for Ca and Zn, respectively), causes a volume contraction of 10.8%, calculated on the basis of the elemental atomic volumes. This value lies within the range observed for other phases of the Ca–Zn system (Ca<sub>3</sub>Zn<sub>3</sub> 7.3, CaZn<sub>2</sub> 12.7, CaZn<sub>3</sub> 10.9, CaZn<sub>11</sub> 7.3 and CaZn<sub>13</sub> 7.0%).

It is noteworthy that all the compounds formed by Li with Ca, Sr and Ba whose structures have been determined so far show a corresponding isostructural phase formed by the alkaline-earth metals with Mg or another bivalent element of Group IIb. In fact, the CaLi<sub>2</sub>, CaMg<sub>2</sub>, SrMg<sub>2</sub>, BaMg<sub>2</sub> and  $\alpha$ -CaCd<sub>2</sub> phases occur with the same MgZn<sub>2</sub> structure type; Sr<sub>6</sub>Li<sub>23</sub>, Sr<sub>6</sub>Mg<sub>23</sub> and Ba<sub>6</sub>Mg<sub>23</sub> belong to the Th<sub>6</sub>Mn<sub>23</sub> type; Sr<sub>3</sub>Li<sub>2</sub> and Ca<sub>3</sub>Cd<sub>2</sub> crystallize with the Gd<sub>3</sub>Al<sub>2</sub> structure. BaLi<sub>4</sub>, which is the only phase with this structural type, can correspond to one of the two atomic arrangements of CaZn<sub>3</sub>. This occurrence of isostructural compounds formed by Li on the one hand, and Mg, Zn or Cd on the other, may be considered as an example of the 'diagonal relationships', which describe the chemical resemblances between Li and Mg, Be and Al or B and Si (Cotton & Wilkinson, 1962).

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## Structure de Cd<sub>3</sub>AsCl<sub>3</sub> et Données Cristallographiques de Cd<sub>3</sub>PCl<sub>3</sub>

PAR A. REBBAH, J. YAZBECK ET A. DESCHANVRES

Laboratoire de Cristallographie et Chimie du Solide, LA 251, ISMRA, Université de Caen, 14032 Caen CEDEX, France

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### Abstract

Cd<sub>3</sub>AsCl<sub>3</sub>,  $M_r = 518.48$ , and Cd<sub>3</sub>PCl<sub>3</sub>,  $M_r = 474.53$ , crystallize in space group *Pnma* with four formula units per cell of dimensions: Cd<sub>3</sub>AsCl<sub>3</sub>  $a = 13.144$  (5),  $b = 8.102$  (2),  $c = 7.082$  (3) Å,  $V = 764.18$  Å<sup>3</sup>,  $Z = 4$ ,  $d_m = 4.58$  (3),  $d_c = 4.56$  Mg m<sup>-3</sup>; Cd<sub>3</sub>PCl<sub>3</sub>  $a = 12.97$  (1),  $b = 7.92$  (1),  $c = 6.95$  (2) Å,  $V = 713.92$  Å<sup>3</sup>,  $Z = 4$ ,  $d_m = 4.44$  (3),  $d_c = 4.41$  Mg m<sup>-3</sup>. The Cd<sub>3</sub>AsCl<sub>3</sub> structure was refined by anisotropic least-squares calculations based on 1505 independent reflections recorded with an automatic four-circle diffractometer. The final  $R$  is 0.056 ( $R_w = 0.066$ ). The chlorine atoms form two layers about the levels  $z = \frac{1}{4}$  and  $z = \frac{3}{4}$ . The projection of the chlorine atoms on these planes builds a Kagomé lattice but with rhombic symmetry. In this rectangular lattice, the centers of the hexagons which are vacant correspond to the AsCd<sub>4</sub> tetrahedra and the stacking of the chlorine layers is distorted hexagonal.

### I. Introduction

L'étude systématique des systèmes II–V–VII permet de mettre en évidence plusieurs types de phases dont la structure a pu être déterminée.

Dans les différents composés étudiés jusqu'ici le rapport  $N_e/N_a$  est inférieur à 8 et les composés étudiés montrent des liaisons polyanioniques, c'est le cas de Cd<sub>4</sub>As<sub>2</sub>I<sub>3</sub> (Gallay, Allais & Deschanvres, 1975) et Cd<sub>2</sub>As<sub>3</sub>I (Rebbah, Leclaire, Yazbeck & Deschanvres, 1979).

Lors de la synthèse de cristaux de Cd<sub>2</sub>XCl<sub>2</sub> ( $X = \text{As, P}$ ) par transport en phase vapeur, il peut apparaître d'autres combinaisons: c'est ainsi que nous avons

obtenu les deux composés isotypes Cd<sub>3</sub>PCl<sub>3</sub> de couleur vert foncé et Cd<sub>3</sub>AsCl<sub>3</sub> de couleur vert clair dont l'existence avait été mentionnée par Puff & Berg (1966). Pour ces phases le rapport  $N_e/N_a$  est égal à 8 ce qui, d'après le critère de Pearson (1964), nous permet de penser que leurs structures correspondent à des composés de valences normaux.

### II. Partie expérimentale

Nous avons préparé Cd<sub>3</sub>XCl<sub>3</sub> ( $X = \text{As, P}$ ) par transport en phase vapeur suivant le schéma réactionnel:



Pratiquement, on introduit le mélange homogène dans une ampoule de verre scellée sous vide. Ce mélange est placé en zone chaude (693 K), les cristaux se forment au bout de 48 h en zone froide dans une gamme de température s'étendant de 613 à 653 K.

La densité des cristaux, mesurée à 298 K dans le tétrachlorure de carbone par la méthode pycnométrique, et leur analyse chimique conduisent aux résultats donnés dans le Tableau 1.

#### 1. Caractéristiques cristallines

L'étude préliminaire de monocristaux de Cd<sub>3</sub>PCl<sub>3</sub> et Cd<sub>3</sub>AsCl<sub>3</sub> à la chambre de précession montre que les mailles sont orthorhombiques. Les extinctions observées dans les deux cas sont celles des groupes *Pn2<sub>1</sub>a* et *Pnma*. Ces caractéristiques cristallines, résumées dans le Tableau 1, sont en accord avec celles publiées par Puff & Berg (1966) pour le composé Cd<sub>3</sub>AsCl<sub>3</sub>. Les paramètres de la maille de Cd<sub>3</sub>AsCl<sub>3</sub> ainsi que leurs