

# Principles determining the structure of high-pressure forms of metals: The structures of cesium(IV) and cesium(V)

(atomic volumes/triangular coordination polyhedra/icosahedral packing)

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Contributed by Linus Pauling, December 9, 1988

**ABSTRACT** Consideration of the relation between bond length and bond number and the average atomic volume for different ways of packing atoms leads to the conclusion that the average ligancy of atoms in a metal should increase when a phase change occurs on increasing the pressure. Minimum volume for each value of the ligancy results from triangular coordination polyhedra (with triangular faces), such as the icosahedron and the Friauf polyhedron. Electron transfer may permit atoms of an element to assume different ligancies. Application of these principles to Cs(IV) and Cs(V), which were previously assigned structures with ligancy 8 and 6, respectively, has led to the assignment to Cs(IV) of a primitive cubic unit cell with  $a = 16.11 \text{ \AA}$  and with about 122 atoms in the cube and to Cs(V) of a primitive cubic unit cell resembling that of  $\text{Mg}_{32}(\text{Al,Zn})_{49}$ , with  $a = 16.97 \text{ \AA}$  and with 162 atoms in the cube.

I was led to think about the structure of high-pressure forms of metals by reading a paper on the x-ray diffraction pattern and structure of Cs(V), which is formed from Cs(IV) at a pressure of about 10 GPa (1). The authors, Takemura and Syassen, found three possible structures from the x-ray pattern, one with a tetragonal unit containing eight atoms and two with an orthorhombic unit containing four atoms. In all three structures the ligancy is 6, with bond lengths of 3.0 to 3.1  $\text{\AA}$  at 18 GPa. Takemura *et al.* (2) had interpreted the x-ray diffraction pattern at 8 GPa as giving a four-atom tetragonal unit for Cs(IV), with the atoms having ligancy  $L = 8$  and bond lengths 3.35  $\text{\AA}$  and 3.54  $\text{\AA}$ .

Both Cs(II) (stable between 2.37 and 4.22 GPa) and Cs(III) (stable between 4.22 and 4.27 GPa) have the cubic close-packed structure (3), with ligancy 12. The unusual phase change (decrease in volume by 8.9%) without change in atomic arrangement is usually attributed to a change in hybridization of the bond orbital, a large increase in the amount of 5*d* character.

It is unlikely that the ligancy would decrease from 12 to 8 and then to 6 with increase in pressure. It is accordingly hard to accept the proposed structures for Cs(IV) and Cs(V).

A decrease in volume without a change in ligancy might also occur through the reorientation of the bonds. For example, such a rearrangement of the bonds can occur for ligancy 12, with the coordination polyhedron changing from the cuboctahedron, with 6 square faces and 8 triangular faces, to the icosahedron, with 20 triangular faces. In general, the closest packing results from coordination polyhedra with all faces triangular. Structures of this sort are called triangular or tetrahedral (each triangular face together with the central atom forms a tetrahedron, which usually is not regular). The distance from the center to the corner of a regular icosahedron is 0.9511 times the edge, so that icosahedral coordina-

tion is expected when the central atom is 10% smaller than the average of the 12 surrounding atoms.

Icosahedra cannot fill space, but many structures are known in which there are many icosahedra and also atoms with larger ligancy, 13, 14, 15, 16, or more, with coordination polyhedra with mainly triangular faces. An example is the Friauf polyhedron, discovered by Friauf (4) in 1927 when he determined the structure of the intermetallic compound  $\text{Cu}_2\text{Mg}$ . The Friauf polyhedron,  $L = 16$ , is a truncated tetrahedron with four additional corners, one out from the center of each hexagonal face. Each Mg atom, at the center of this polyhedron, is surrounded by 12 Cu and 4 Mg atoms. The 8 Mg atoms in the cubic crystal lie at the positions of the carbon atoms in diamond, forming a diamond framework, and the 16 Cu atoms are at the positions of the C—C bonds in another diamond framework filling the interstices of the first. Each Cu atom is surrounded icosahedrally by 6 Cu and 6 Mg atoms, so that the crystal can be described as two-thirds icosahedral.

An interesting hemi-icosahedral structure, discovered by Jacob and Warren (5), is that of  $\alpha$ -uranium, the stable form of the element under normal conditions.  $\alpha$ -U is orthorhombic, with  $a = 2.854 \text{ \AA}$ ,  $b = 5.870 \text{ \AA}$ , and  $c = 4.955 \text{ \AA}$ . The four atoms in the unit are equivalent. It was pointed out by Donohue (6) that the coordination polyhedron, with ligancy 12, is related to hexagonal close packing; it can be described as two-thirds of an icosahedron plus one-third of the tetrakaidecahedron of hexagonal close packing. It has 16 triangular faces and 2 square faces with a common edge and can also be described as an icosahedron in which two edges have been elongated to become the diagonals of two squares. Some distortion is involved, the bond lengths being 2 at 2.753  $\text{\AA}$ , 2 at 2.854  $\text{\AA}$ , 4 at 3.263  $\text{\AA}$ , and 4 at 3.343  $\text{\AA}$ . It is to be expected from its partially icosahedral character that this structure would be formed from the close-packed structures with a decrease in volume and accordingly would occur as the high-pressure form for some metals, especially those with a tendency to form four stronger bonds and eight weaker bonds. It has, in fact, been assigned to high-pressure forms of several metals: Ce, above 51 GPa (7); Pr, above 21 GPa (8); Am, above 10 GPa (9); Bk, above 25 GPa (10); and Cf, above 41 GPa (10). Reasonably reliable values for the change in volume for the transition from a close-packed structure to the  $\alpha$ -U structure are Pr, -9.8%; Bk, -12%, and Cf, -16%.

I have compared the x-ray powder patterns of metals with the  $\alpha$ -U structure with those of Cs(IV) and Cs(V), with correction for the difference in atomic volume, and have found that neither Cs(IV) nor Cs(V) has this structure.

General discussions of icosahedral structures have been given by several authors (11-14).

The atoms of an element with an icosahedral structure must be of two or more kinds, with a larger effective radius for those with larger ligancy than for those with ligancy 12. For an element this difference might be achieved by partial electron transfer, increasing the valence for some atoms and decreasing it for others (15). This effect has been discussed

Table 1. Atomic volumes of some metals in stable form at room temperature

Metal	Atomic vol, Å <sup>3</sup>	Metal	Atomic vol, Å <sup>3</sup>	Metal	Atomic vol, Å <sup>3</sup>
Fe	11.78	Ru	13.57	Os	13.99
Co	11.13	Rh	13.75	Ir	14.15
Ni	10.94	Pd	14.72	Pt	15.10
Cu	11.81	Ag	17.05	Au	16.96
Zn	15.20	Cd	21.58	Hg	23.2

by Shoemaker *et al.* (16) for the cubic crystal NaZn<sub>13</sub>. All of the Zn atoms have icosahedral liganacy. The central Zn of the Zn<sub>13</sub> icosahedron forms 12 bonds 2.659 Å long, and the 10 Zn—Zn bonds formed by the outer Zn atoms (which also form 2 Zn—Na bonds) average 2% longer. The Na atoms have liganacy 24. The value of the cube edge changes only slightly, by 0.6%, with change from NaZn<sub>13</sub> to KZn<sub>13</sub>, far less than the 5% increase expected if the alkali atoms exhibited the same atomic volumes as in the elementary state. A still more striking example is the pair RbCd<sub>13</sub> and CsCd<sub>13</sub>, with nearly identical values of the cube edge, 13.91 and 13.92 Å, respectively. [Experimental values are from Donohue (6) and Pearson (17, 18).] An increase by 0.29 Å would be expected if the alkali atoms retained their atomic volumes.

In fact, the alkali metals, alkaline-earth metals, and others with large radii are easily compressed. Crystals containing them cannot be used to obtain a value for the decrease in volume on going from the cuboctahedron to the icosahedron. Moreover, compounds of a hypoelectronic metal and a hyper-electronic metal cannot be used because electron transfer increases the valence and decreases the atomic volume of each of the elements (15). I have chosen the elements Fe, Co, Ni, Cu, and Zn and their congeners for this purpose. Their atomic volumes in their normal states, mostly with close-packed or cubic-body-centered structures, are given in Table 1. These values are summed for various intermetallic compounds with largely icosahedral structures and compared in Table 2 with the experimental values of the volume of the unit cube. It is seen that the change to icosahedral packing and increase in liganacy of the larger atoms result in a decrease in volume of about 5.0%.

My conclusion is that high-pressure phases of metals may be expected to have these largely icosahedral structures. For an element such a structure requires that some of the atoms differ from others in having liganacy greater than 12. This might be achieved by electron transfer, decreasing their valence and increasing that of those with liganacy 12, as was reported for the Zn atoms in NaZn<sub>13</sub>. A stabilizing factor is the increased resonance energy accompanying increase in liganacy (19–21). It is obvious that assumption of an icosahedral structure would be more apt to occur for a soft elemental metal than for a hard one.

Table 2. Percentage amount of change in volume on forming a cubic crystal with some icosahedral coordination from the elements

	A	a, Å	Change in volume, %		A	a, Å	Change in volume, %
CdCuZn	24	7.16	-5.6	γ-Co <sub>5</sub> Zn <sub>21</sub>	52	8.908	-5.7
γ-Cu <sub>5</sub> Zn <sub>8</sub>	52	8.84	-4.4	γ-Rh <sub>5</sub> Zn <sub>21</sub>	52	9.089	-3.2
γ-Cu <sub>5</sub> Cd <sub>8</sub>	52	9.596	-4.7	γ-Ni <sub>5</sub> Zn <sub>21</sub>	52	8.904	-5.6
γ-Ag <sub>5</sub> Zn <sub>8</sub>	52	9.325	-2.0	γ-Ni <sub>5</sub> Cd <sub>21</sub>	416	19.546	-8.1
γ-Ag <sub>5</sub> Cd <sub>8</sub>	52	9.963	-4.1	γ-Pd <sub>5</sub> Zn <sub>21</sub>	52	9.111	-3.8
γ-Ag <sub>2</sub> Hg <sub>3</sub>	52	10.046	-6.0	γ-Pd <sub>5</sub> Cd <sub>21</sub>	52	9.960	-6.8
γ-AuZn <sub>3</sub>	52	9.223	-3.5	γ-Pt <sub>5</sub> Zn <sub>21</sub>	416	18.115	-5.9
γ-Fe <sub>3</sub> Zn <sub>10</sub>	52	8.956	-4.1	γ-Pt <sub>5</sub> Cd <sub>21</sub>	52	9.897	-8.8
Cu <sub>4</sub> Cd <sub>3</sub>	1124	25.871	-3.7	Average			-5.0

A, number of atoms in the unit cube.

Table 3. Analysis of x-ray powder diffraction maxima for the high-pressure form Cs(IV) at 8.0 GPa

I*	d, Å	a, Å	h k l
1	3.93	16.2	4 1 0
1	3.82	16.2	4 1 1
1	3.70	16.1	3 3 1
1	3.59	16.1	4 2 0
1	3.49	16.0	4 2 1
1	3.42	16.0	3 3 2
100	3.246	16.23	5 0 0
40	2.612	16.10	6 1 1
140	2.215	16.13	7 2 0
5	1.672	16.12	8 5 2
16	1.565	16.11	9 5 0
20	1.482	16.10	10 3 3
16	1.411	16.09	11 3 0
10	1.284	16.09	12 3 2
5	1.186	16.08	12 6 2
5	1.143	16.09	14 1 1
10	1.110	16.09	13 5 4
5	1.082	16.09	14 5 0
Average			16.11

Values of the interplanar distance *d* for weak peaks (intensity *I* = 1) were obtained by measurement of figure 1c of ref. 2; the other values are from table 1 of ref. 2.

\*All weak peaks are given the value *I* = 1; the others are the averages for figure 1 *a* and *c* of ref. 2.

A characteristic feature of the powder diffraction pattern of a cubic crystal is that the differences  $\Delta Q^2$  of the values of  $Q^2$  for successive diffraction maxima are all integral multiples of a constant,  $Q_1^2$ , that is, each is equal to  $nQ_1^2$ , with *n* an integer and  $a = 2\pi/Q_1$  (*a* is the edge of the unit cube and  $Q = 2\pi/d$ , with *d* the interplanar distance of the diffraction maxima). Adherence to this relationship is a test for a cubic unit of structure.

#### Cs(IV) at 8 GPa

The x-ray powder diffraction pattern of Cs(IV) at 8.0 GPa was reported by Takemura *et al.* (2), who gave values of the spacings of 12 planes and reproduced two diffraction curves. I checked the values of  $Q^2$  and found that  $\Delta Q^2/n$  (where  $\Delta Q^2$  is the difference in  $Q^2$  of successive peaks and *n* is an integer) were all nearly the same, equal to 0.1530(13) Å<sup>-2</sup>. This fact supports the assumption that the crystal is cubic. The value 0.1530(13) Å<sup>-2</sup> corresponds to the value 16.06(6) Å for the edge of the unit cube. I then measured the *Q* values of 50 weak or very weak peaks on the curve reproduced in figure 1c of ref. 2, out to  $Q = 4 \text{ \AA}^{-1}$ , and found that the values were compatible with the 16.06-Å cubic unit. The first 6 weak peaks and all of the stronger ones are listed in Table 3. They give the average value 16.11 Å for the edge of the primitive unit cube. This value

and the value  $34.9 \text{ \AA}^3$  for the atomic volume at 8 GPa (from figure 4 of ref. 2) lead to 119.8 for the number of atoms in the unit cube.

### Cs(V) at 18 GPa

The x-ray powder diffraction pattern of Cs(V) at 18 GPa was reported by Takemura and Syassen (1), who gave values of the intensities and spacings of 15 planes. The values of  $\Delta Q^2$  lead to about  $16.8 \text{ \AA}$  for the edge of a cubic unit of structure, and the first five values of  $d$ , 3.256, 2.899, 2.816, 2.584, and  $2.301 \text{ \AA}$ , lead to  $16.92 \text{ \AA}$  with  $h^2 + k^2 + \ell^2$  equal to 27, 34, 36, 43, and 54, respectively. I measured the values of the Bragg angle for the weak peaks on the two diffraction curves of figure 1 of ref. 1 and obtained the values of  $d$  for many weak peaks, with the first 10 and all of the peaks listed in ref. 1 given in Table 4. The average value of  $a$  is  $16.97 \text{ \AA}$ .

The atomic volume at 18 GPa is about  $30.0 \text{ \AA}^3$  (from figure 3 of ref. 1), which leads to 162.9 atoms in the unit cube.

### Discussion

There are many intermetallic compounds that form cubic crystals containing clusters with approximate icosahedral symmetry, with many atoms at the centers of an icosahedron ( $L = 12$ ) and others with larger ligancy. An example is  $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$  (22, 23), in which there are two 117-atom icosahedral clusters centered at  $0\ 0\ 0$  and  $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ , with the

Table 4. Analysis of x-ray powder diffraction maxima for the high-pressure form Cs(V) at 18 GPa

$I^*$	$d, \text{ \AA}$	$a, \text{ \AA}$	$h\ k\ \ell$
1	4.01	17.0	3 3 0
1	3.92	17.1	3 3 1
1	3.83	17.1	4 2 0
1	3.72	17.0	4 2 1
1	3.64	17.1	3 3 2
1	3.47	17.0	4 2 2
1	3.39	16.9	5 0 0
1	3.33	17.0	5 1 0
15	3.256	16.92	3 3 3
1	3.11	17.0	5 2 1
1	3.01	17.0	4 4 0
32	2.899†	16.90	5 3 0
100	2.816	16.90	6 0 0
24	2.584	16.94	5 3 3
31	2.301	16.91	7 2 1
6	2.126	17.01	8 0 0
29	2.027	16.96	6 5 3
11	1.766	17.03	8 5 2
7	1.628	16.92	10 2 2
23	1.569	16.97	10 4 1
25	1.516	16.95	11 4 0
16	1.457	16.99	10 6 0
18	1.415	16.98	12 0 0
8	1.288	16.99	13 2 1
7	1.211	16.95	14 0 0
Average		16.97	

Values of the interplanar distance  $d$  for weak peaks (intensity  $I = 1$ ) were obtained by measurement of the curves of figure 1 a and c of ref. 1; the other values are from table 1 of ref. 1.

\*Intensity values other than 1 are from ref. 1.

†Value from ref. 1 for a line overlapping a strong peak.

atoms of the outer shells shared to reduce the number of atoms in the unit cube to 162. An alternative structure, with the cluster at  $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$  not in parallel orientation to that at  $0\ 0\ 0$ , would have a primitive cubic unit containing 162 atoms. I suggest that this may be the structure of Cs(V).

There is no intermetallic compound that has been reported to have  $120 \pm 10$  atoms in a primitive cubic unit. A surmise about a possible structure for Cs(IV) may be made in the following way. Several "icosahedral quasicrystals" have been assigned a primitive cubic structure based on the  $\beta$ -W arrangement, with two icosahedral clusters at  $0\ 0\ 0$  and  $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$  and six larger clusters at  $0\ \frac{1}{2}\ \frac{1}{4}$ , etc. (24). I suggest that in Cs(IV) there are icosahedral clusters of 13 atoms at  $0\ 0\ 0$  and  $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$  and six clusters of 15 atoms (a central atom surrounded by a hexagonal antiprism with two caps) in the six other positions, giving a total of 116 atoms. The space group (no. 223) does not allow 4 additional atoms but does allow 6 atoms, at  $\frac{1}{2}\ 0\ \frac{1}{4}$ , etc., giving a total of 122 atoms, which is acceptable, corresponding to atomic volume  $34.27 \text{ \AA}^3$ .

The assignment of these structures is based on the assumption that the crystals are cubic. This assumption is a reasonable one, inasmuch as Cs(I), Cs(II), and Cs(III) are cubic, as are many other metallic elements and compounds.

1. Takemura, K. & Syassen, K. (1985) *Phys. Rev. B* **32**, 2213–2217.
2. Takemura, K., Minomura, S. & Shimomura, O. (1982) *Phys. Rev. Lett.* **49**, 1772–1775.
3. Hall, H. T., Merrill, L. & Barnett, J. D. (1964) *Science* **146**, 1297–1299.
4. Friauf, J. B. (1927) *J. Am. Chem. Soc.* **49**, 3107–3114.
5. Jacob, C. W. & Warren, B. E. (1937) *J. Am. Chem. Soc.* **59**, 2988–2991.
6. Donohue, J. (1974) *The Structures of the Elements* (Wiley, New York).
7. Zachariasen, W. H. & Ellinger, F. H. (1977) *Acta Crystallogr. A* **33**, 155–160.
8. Smith, G. S. & Akella, J. (1982) *J. Appl. Phys.* **53**, 9212–9213.
9. Roof, R. B., Haire, R. G., Schiferl, D., Schwalbe, L. A., Kmetko, E. A. & Smith, J. L. (1980) *Science* **207**, 1353–1354.
10. Benedict, U., Peterson, J. R., Haire, R. G. & Dufour, C. (1984) *J. Phys. F* **14**, L43–L47.
11. Pauling, L. (1960) *The Nature of the Chemical Bond* (Cornell Univ. Press, Ithaca, NY), 3rd. Ed.
12. Samson, S. (1968) in *Structural Chemistry and Molecular Biology*, eds. Rich, A. & Davidson, N. (Freeman, San Francisco), pp. 688–717.
13. Shoemaker, D. P. & Shoemaker, C. B. (1968) in *Structural Chemistry and Molecular Biology*, eds. Rich, A. & Davidson, N. (Freeman, San Francisco), pp. 718–730.
14. Shoemaker, D. P. & Shoemaker, C. B. (1986) *Acta Crystallogr. B* **42**, 3–11.
15. Pauling, L. (1950) *Proc. Natl. Acad. Sci. USA* **36**, 533–538.
16. Shoemaker, D. P., Marsh, R. E., Ewing, F. J. & Pauling, L. (1952) *Acta Crystallogr.* **5**, 637–644.
17. Pearson, W. B. (1958) *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, London), Vol. 1.
18. Pearson, W. B. (1967) *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon, London), Vol. 2.
19. Pauling, L. (1984) *J. Solid State Chem.* **54**, 297–307.
20. Kamb, B. & Pauling, L. (1985) *Proc. Natl. Acad. Sci. USA* **82**, 8284–8285.
21. Pauling, L. & Kamb, B. (1986) *Proc. Natl. Acad. Sci. USA* **83**, 3569–3571.
22. Bergman, G., Waugh, J. L. T. & Pauling, L. (1952) *Nature (London)* **169**, 1057.
23. Bergman, G., Waugh, J. L. T. & Pauling, L. (1957) *Acta Crystallogr.* **10**, 254–259.
24. Pauling, L. (1988) *Proc. Natl. Acad. Sci. USA* **85**, 4587–4590.