

# The Pythagorean Theorem and the Solid State

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Crystals form from atoms, ions, or molecules packed together in a variety of geometric arrangements. The unit cell is the smallest repeating three-dimensional representation of the crystal structure. If the unit-cell structure is known, then packing efficiency and crystal density may be calculated from basic geometric principles employing the Pythagorean theorem (1, 2). In this article, such calculations are illustrated for closest-packed A type and also for compound AB structures (simpler cases are often discussed in standard inorganic textbooks, refs 3–15). The primary requirement is to find the unit-cell volume in terms of particle radii, from which crystal density follows. The procedures illustrated here have applicability in courses such as general chemistry, intermediate and advanced inorganic, materials science, and solid-state physics.

## The Face-Centered Cubic Lattice

In the cubic closest-packed (ccp) unit-cell structure (Figure 1), there are four particles per unit cell. Three of the face particles are shown as dark spheres. In an A-type ccp structure, the particles touch along the face diagonal  $d$ , so that  $d = 4r$ , where  $r$  is the particle radius. Application of the Pythagorean theorem gives

$$V = s^3 = (2\sqrt{2}r)^3 = 16\sqrt{2}r^3 \quad (1)$$

where  $V$  is the unit-cell volume and  $s$  is the side length of the unit cell.

In nickel, for example, which crystallizes in this form (16), the metallic radius is  $1.25 \times 10^{-8}$  cm (17), and the calculated density is

$$\rho = \frac{m}{V} = \frac{\left[ \frac{(4)(58.69)(\text{g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right]}{(16\sqrt{2})(1.25 \times 10^{-8} \text{ cm})^3} = 8.821 \frac{\text{g}}{\text{cm}^3} \quad (2)$$

where the numerator is the mass of the four Ni atoms in the unit cell and the denominator is the unit-cell volume. The observed density is  $8.90 \text{ g/cm}^3$  (18). The packing efficiency is given by the volume of the spherical particles divided by the unit-cell volume

$$\frac{4 \left( \frac{4}{3} \right) \pi r^3}{16\sqrt{2} r^3} \left( \frac{\pi}{3\sqrt{2}} \right) = 0.7408 \quad (3)$$

The value of 0.7408 is the maximum possible, that is, a closest-packed structure.

This unit-cell geometry is straightforward. Density calculations for more complex unit cells require knowledge of the geometry of a tetrahedron.

## The Hexagonal Closest-Packed Lattice

The hexagonal closest-packed (hcp) unit cell is shown in Figure 2. There are six particles per unit cell. In the top and bottom hexagonal faces of an A-type hcp structure, the particles touch along the three face diagonals and also along the sides of the faces, as indicated in Figure 3. There are three pairs of touching tetrahedra per cell, one pair of which is shown in bold in Figure 2.

The unit-cell volume  $V$  is the product of the area  $A$  of the hexagonal face and unit-cell height  $H$ . The hexagonal face, as shown in Figure 3, may be subdivided into four  $30^\circ$ – $60^\circ$ – $90^\circ$  right triangles and one rectangle; the sum of these areas is  $A = 6\sqrt{3}r^2$ . In terms of  $s_h$ , the side length of the hexagonal face, the area is

$$A = 6\sqrt{3}r^2 = \frac{3\sqrt{3}}{2}s_h^2 \quad (4)$$

A unit-cell tetrahedron is shown in Figure 4. The height is given by length  $\overline{AG}$ , a line drawn from vertex A to point G, which is the intersection of the three bisectors of the equilateral triangular base of the tetrahedron. Length  $\overline{AD}$  is the side length  $s_t$  of the tetrahedron, so that  $s_t = 2r$  if the corner spheres touch. Length  $\overline{GD}$  is one leg of triangle GDF, a  $30^\circ$ – $60^\circ$ – $90^\circ$  right triangle with side-length ratios  $2:\sqrt{3}:1$ . Because length  $\overline{DF} = r$ , length  $\overline{GD}$  must be  $2r/\sqrt{3}$ . Applying the Pythagorean theorem to triangle ADG, length  $\overline{AG}$  becomes

$$\overline{AG} = h = 2\sqrt{\frac{2}{3}}r = \sqrt{\frac{2}{3}}s_t \quad (5)$$

This relationship between the side length and height of a tetrahedron is actually valid for any unit-cell tetrahedron, whether or not the corner spheres are touching. Consequently, the height  $H$  and volume  $V$  of the hcp unit cell become

$$H = 2h = 4\sqrt{\frac{2}{3}}r \quad (6)$$

$$V = AH = (6\sqrt{3}r^2) \left( 4\sqrt{\frac{2}{3}}r \right) = 24\sqrt{2}r^3 \quad (7)$$

In magnesium, which crystallizes in the hcp lattice (16), the metallic radius is given as  $1.60 \times 10^{-8}$  cm (17). The calculated density of Mg is therefore

$$\rho = \frac{\left[ \frac{(6)(24.31)(\text{g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right]}{24\sqrt{2}(1.60 \times 10^{-8} \text{ cm})^3} = 1.74 \frac{\text{g}}{\text{cm}^3} \quad (8)$$

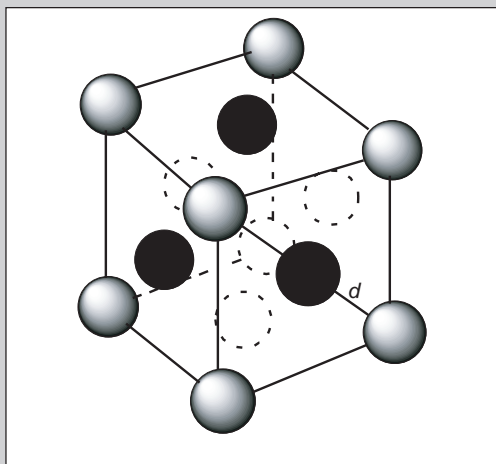


Figure 1. The face-centered cubic unit cell. The three face-centered particles are shown with dark spheres.

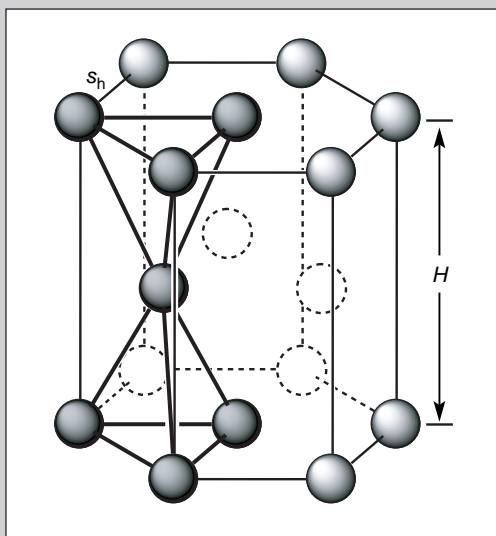


Figure 2. The hexagonal closest-packing unit cell. Two touching tetrahedra are shown with dark spheres.

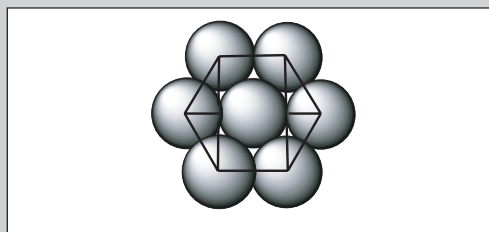


Figure 3. The face of the hexagonal closest-packed unit cell.

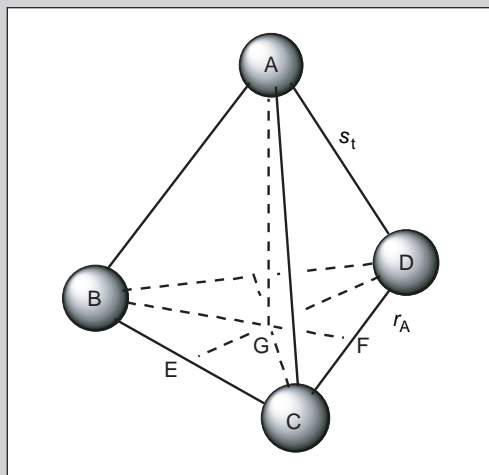


Figure 4. The geometry of the tetrahedron.

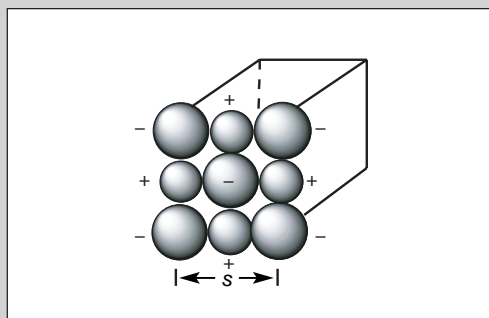


Figure 5. One face of the sodium chloride unit cell. Chloride ions form fcc unit cell; sodium ions occupy all octahedral holes in lattice.

compared to the observed density of  $1.74 \text{ g/cm}^3$  (18). The packing efficiency is

$$\frac{6\left(\frac{4}{3}\right)\pi r^3}{24\sqrt{2}r^3} = \frac{\pi}{3\sqrt{2}} = 0.7408 \quad (9)$$

which is identical to the ccp lattice.

### Compound AB Lattices

The unit-cell structures of binary ionic compounds (AB lattices) may generally be viewed as having the larger anions at the corners and faces of the unit cell with the smaller cations occupying octahedral or tetrahedral holes.

### The Sodium Chloride Lattice

One face of the unit cell is shown in Figure 5. It consists of a fcc array of  $\text{Cl}^-$  ions with  $\text{Na}^+$  occupying octahedral holes along the cell edges. Hence, there are four  $\text{Na}^+$  and four  $\text{Cl}^-$  per unit cell. The  $\text{Na}^+$  and  $\text{Cl}^-$  ions touch along the unit-cell edge; therefore,  $s$  is  $2(r_A + r_B)$  and  $V$  is  $8(r_A + r_B)^3$ , where  $r_A$  is the radius of atom A and  $r_B$  is the radius of atom B. Ionic radii are  $1.16 \times 10^{-8} \text{ cm}$  for  $\text{Na}^+$  and  $1.67 \times 10^{-8} \text{ cm}$  for  $\text{Cl}^-$  (19), and the calculated density is

$$\rho = \frac{\left[ \frac{(4)(22.99 + 35.453)(\text{g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right]}{8(2.83 \times 10^{-8} \text{ cm})^3} = 2.14 \frac{\text{g}}{\text{cm}^3} \quad (10)$$

compared to the observed density of  $2.165 \text{ g/cm}^3$  (18). The packing efficiency is

$$\frac{4\left(\frac{4}{3}\right)\pi\left[\left(1.16 \times 10^{-8} \text{ cm}\right)^3 + \left(1.67 \times 10^{-8} \text{ cm}\right)^3\right]}{8\left(2.83 \times 10^{-8} \text{ cm}\right)^3} \quad (11)$$

$$= 0.578$$

compared to 0.7408 for the closest-packing efficiency.

### The Cesium Chloride Lattice

The cesium chloride lattice consists of interlocked simple cubic arrays of  $\text{Cl}^-$  and  $\text{Cs}^+$  ions. The unit-cell structure may be envisioned as having eight  $\text{Cs}^+$  ions at the corners of the

cubic unit cell and one  $\text{Cl}^-$  ion at the center (Figure 6). Oppositely charged ions touch along the body diagonal  $D$  so that  $D = 2(r_A + r_B)$ . The face diagonal  $d = (\sqrt{2})s$  so that application of the Pythagorean theorem to right triangle ABC of Figure 6 gives

$$\left[2(r_A + r_B)\right]^2 = 3s^2 \quad (12)$$

from which  $s$  is

$$s = \frac{2}{\sqrt{3}}(r_A + r_B) \quad (13)$$

and  $V$  becomes

$$V = s^3 = \frac{8}{3\sqrt{3}}(r_A + r_B)^3 \quad (14)$$

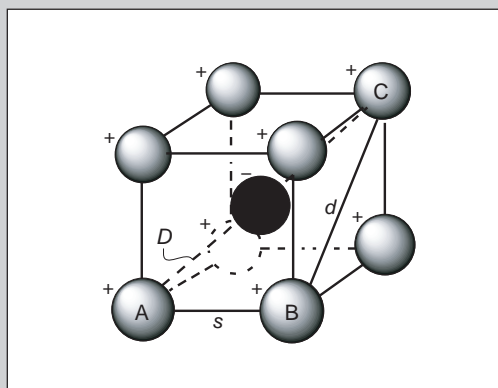


Figure 6. The cesium chloride unit cell. Cesium ions form simple cubic unit cell; chloride ion occupies cubic hole in cell.

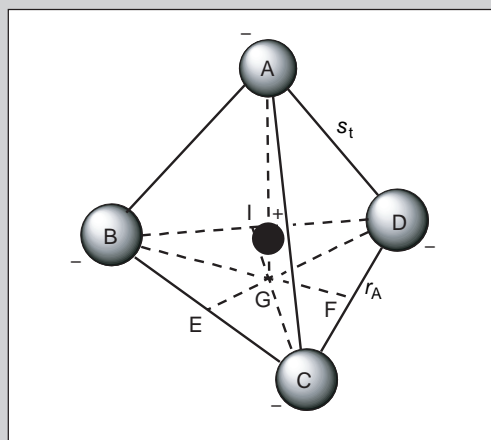


Figure 8. A cation occupying a tetrahedral hole within four anions.

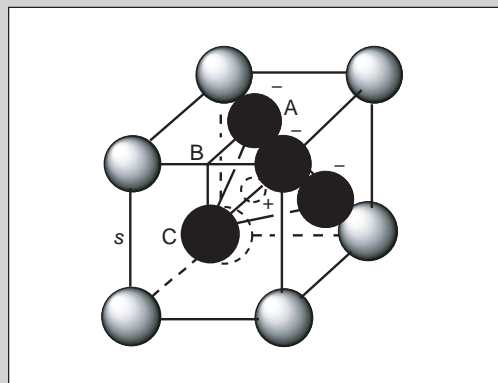


Figure 7. The zinc blende or sphalerite lattice unit cell. One corner tetrahedron is shown with dark spheres. Zinc ions occupy half the tetrahedral holes.

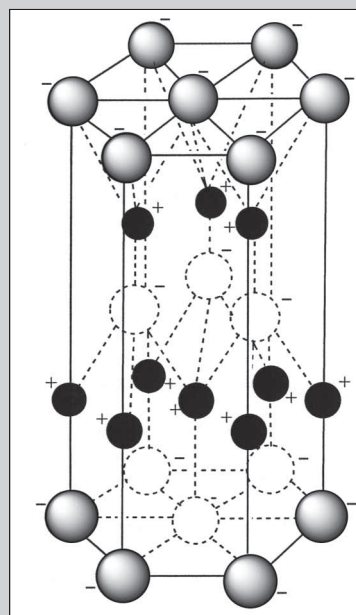


Figure 9. The wurtzite lattice unit cell. Small dark spheres are zinc ions and the larger spheres are sulfide ions.

For CsCl, the appropriate radii are  $r_A = 1.88 \times 10^{-8}$  cm and  $r_B = 1.67 \times 10^{-8}$  cm (19). The calculated density is

$$\rho = \frac{\left\{ \frac{[(1)(132.9) + (1)(35.453)](\text{g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right\}}{\frac{8}{3\sqrt{3}} (3.55 \times 10^{-8} \text{ cm})^3} = 4.06 \frac{\text{g}}{\text{cm}^3} \quad (15)$$

compared to the observed density of  $3.97 \text{ g/cm}^3$  (18). The packing efficiency is

$$\frac{\frac{4}{3} \pi [(1.88 \times 10^{-8} \text{ cm})^3 + (1.67 \times 10^{-8} \text{ cm})^3]}{\frac{8}{3\sqrt{3}} (3.55 \times 10^{-8} \text{ cm})^3} \quad (16)$$

$$= 0.687$$

which is similar to that of a body-centered cubic unit cell of the A type (0.68).

### The Zinc Blende (Sphalerite) Lattice

The zinc blende (ZnS) unit cell is a face-centered cubic array of  $\text{S}^{2-}$  ions with  $\text{Zn}^{2+}$  ions occupying half the tetrahedral holes in the cell (Figure 7). The tetrahedral holes are associated with the corners of the unit cell (see shaded spheres). In this structure, the corner anions cannot touch because the cations are relatively large.

Consider the right triangle ABC of Figure 7, where  $\overline{AB} = \overline{BC} = s/2$ . Length  $\overline{AC} = s_t$ , the side length of a corner tetrahedron, so that  $s_t = s/\sqrt{2}$ . At this point, we refer to Figure 8, which shows a tetrahedron of height  $\overline{AG}$  as discussed previously. It is useful to divide  $\overline{AG}$  into segment  $\overline{AI}$  and  $\overline{IG}$ , where point I is at the center of a cation of radius  $r_A$  occupying the tetrahedral hole generated by touching anionic corner spheres of radius  $r_B$  (spheres labeled A, B, C, and D of Figure 8). Length  $\overline{AI}$  is given by  $r_A + r_B$ . If the anions touch, the radius-ratio rule for tetrahedral holes (4, 12, 14) gives  $r_A = [(3/2)^{1/2} - 1]r_B$ , so  $\overline{AI}$  is found to be  $(3/2)^{1/2}r_B$ . From eq 5,  $\overline{AG} = 2(2/3)^{1/2}r_B$ , so length  $\overline{IG}$  is found to be  $\{[2(2/3)^{1/2}r_B] - [(3/2)^{1/2}r_B]\} = (1/\sqrt{6})r_B$ .

Lengths  $\overline{AI}$  and  $\overline{IG}$  are in the ratio 3:1, which is valid whether or not the anions touch. Therefore, when the tetrahedron is expanded by a large cation, length  $\overline{AI} = r_A + r_B$ , length  $\overline{IG} = (1/3)(r_A + r_B)$ , and the height of the expanded tetrahedron becomes

$$h = \frac{4}{3}(r_A + r_B) \quad (17)$$

From eq 5,  $s_t = (3/2)^{1/2}h$ . Since  $s = (\sqrt{2})s_t$ , we find  $s = (4/\sqrt{3})(r_A + r_B)$ , and the unit-cell volume is

$$V = s^3 = \frac{64}{3\sqrt{3}}(r_A + r_B)^3 \quad (18)$$

The ionic radii of  $\text{Zn}^{2+}$  and  $\text{S}^{2-}$  are  $0.74 \times 10^{-8}$  and  $1.70 \times 10^{-8}$  cm, respectively (19), and the calculated density of zinc blende becomes

$$\rho = \frac{\left\{ \frac{[(4)(65.39) + (4)(32.07)](\text{g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right\}}{\frac{64}{3\sqrt{3}} (2.44 \times 10^{-8} \text{ cm})^3} = 3.62 \frac{\text{g}}{\text{cm}^3} \quad (19)$$

The density value is not close to the observed density of  $4.087 \text{ g/cm}^3$  (18). However, since the bonds in sphalerite have considerable covalent character (20, 21), the propriety of using ionic radii is questionable. Using covalent radii ( $1.31 \times 10^{-8}$  cm for Zn and  $1.04 \times 10^{-8}$  cm for S; ref 21), the calculated density becomes  $4.050 \text{ g/cm}^3$ , which is more consistent with the observed value. Using a different set of covalent radii (Zn =  $1.31 \times 10^{-8}$  cm and S =  $1.02 \times 10^{-8}$  cm; ref 13), the calculated density is  $4.155 \text{ g/cm}^3$ . For sphalerite and wurtzite, the sum of the covalent radii correlates well with the observed interatomic spacings (20).

The packing efficiency of this unit cell, using covalent radii, is

$$\frac{4 \left( \frac{4}{3} \right) \pi [(1.3 \times 10^{-8} \text{ cm})^3 + (1.04 \times 10^{-8} \text{ cm})^3]}{\frac{64}{3\sqrt{3}} (2.35 \times 10^{-8} \text{ cm})^3} \quad (20)$$

$$= 0.354$$

which undoubtedly reflects the large number of unoccupied holes in the structure.

### The Wurtzite Lattice

Wurtzite crystallizes in a hcp unit cell of sulfide ions with zinc ions occupying six half the tetrahedral holes (Figure 9). The sulfide ions do not touch, but the zinc and sulfide ions touch within the unit-cell tetrahedra. The unit-cell volume is the product of the area of the hexagonal face and the height of the cell. From eq 17, the height of a unit-cell tetrahedron is  $(4/3)(r_A + r_B)$ , and the height  $H$  of the unit cell is therefore  $(8/3)(r_A + r_B)$ .

In terms of  $s_h$ , the side length of the hexagonal face of the unit cell,  $s_h = s_t = (3/2)^{1/2}h$  (eq 6), where  $h$  is the height of the tetrahedron, so  $s_h = 2(2/3)^{1/2}(r_A + r_B)$ . From eq 4, the area of the hexagonal face is given as  $A = [(3\sqrt{3})/2]s_h^2$ . In terms of particle radii, the area becomes

$$A = \frac{3\sqrt{3}}{2} \left[ 2\sqrt{\frac{2}{3}}(r_A + r_B) \right]^2 = 4\sqrt{3}(r_A + r_B)^2 \quad (21)$$

and the unit-cell volume is

$$V = AH = \frac{32}{\sqrt{3}}(r_A + r_B)^3 \quad (22)$$

Table 1. Packing Efficiency and Density Formulas for Various Types of Crystal Lattices

Lattice Designation	Lattice Type	CN	Fractional Occupancy	Density Expression
sc	A	6	$\frac{\pi}{6}$	$\frac{\left(\frac{1 m_a}{N_{Av}}\right)}{8r^3}$
bcc	A	8	$\frac{\sqrt{3}\pi}{8}$	$\frac{\left(\frac{2 m_a}{N_{Av}}\right)}{\left(\frac{64}{3\sqrt{3}} r^3\right)}$
fcc	A	12	$\frac{\pi}{3\sqrt{2}}$	$\frac{\left(\frac{4 m_a}{N_{Av}}\right)}{16\sqrt{2}r^3}$
hcp	A	12	$\frac{\pi}{3\sqrt{2}}$	$\frac{\left(\frac{6 m_a}{N_{Av}}\right)}{24\sqrt{2}r^3}$
NaCl, fcc	AB	6	$\frac{2\pi}{3} \frac{[(r_A)^3 + (r_B)^3]}{(r_A + r_B)^3}$	$\frac{\left[\frac{4 m_a(A) + 4 m_a(B)}{N_{Av}}\right]}{8(r_A + r_B)^3}$
CsCl, bcc	AB	8	$\frac{\sqrt{3}\pi[(r_A)^3 + (r_B)^3]}{2(r_A + r_B)^3}$	$\frac{\left[\frac{1 m_a(A) + 1 m_a(B)}{N_{Av}}\right]}{\frac{8}{3\sqrt{3}}(r_A + r_B)^3}$
Zinc Blende	AB	4	$\frac{\sqrt{3}\pi[(r_A)^3 + (r_B)^3]}{4(r_A + r_B)^3}$	$\frac{\left[\frac{4 m_a(A) + 4 m_a(B)}{N_{Av}}\right]}{\frac{64}{3\sqrt{3}}(r_A + r_B)^3}$
Wurtzite	AB	4	$\frac{\sqrt{3}\pi[(r_A)^3 + (r_B)^3]}{4(r_A + r_B)^3}$	$\frac{\left[\frac{6 m_a(A) + 6 m_a(B)}{N_{Av}}\right]}{\frac{32}{\sqrt{3}}(r_A + r_B)^3}$

NOTE: Avogadro's number is represented by  $N_{Av}$ .

Using  $r_A = 0.74 \times 10^{-8}$  cm and  $r_B = 1.70 \times 10^{-8}$  cm for  $Zn^{2+}$  and  $S^{2-}$  (19), the calculated density is

$$\rho = \frac{\left\{ \frac{[(6)(65.39) + (6)(32.07)](\text{g/mol})}{6.022 \times 10^{23} \text{ mol}^{-1}} \right\}}{\frac{32}{\sqrt{3}} (2.44 \times 10^{-8} \text{ cm})^3} = 3.62 \frac{\text{g}}{\text{cm}^3} \quad (23)$$

but if covalent radii are used, the density becomes 4.05 or 4.15 g/cm<sup>3</sup> depending on which set of radii are used. The observed density is 4.102 g/cm<sup>3</sup> (18).

Clearly, density calculations are extremely sensitive to the values of  $r_A$  and  $r_B$ . The sum ( $r_A + r_B$ ) may be found from X-ray measurements, but individual ionic radii may not be so measured. Therefore, other methods must be used (22), and the Shannon–Prewitt radii (23) determined from data on oxides and fluorides are recommended (24). However, as indicated for sphalerite and wurtzite, ionic radii do not always give the best results when used in density calculations.

If the density formulas derived for AB lattices (eqs 10, 15, 19, and 23) are valid, then substitution of the observed interatomic or interionic distances into these formulas should result in density values close to the observed values. This was found to be true for sphalerite and wurtzite. As another example, using a slightly modified version of eq 19 for fluorite, CaF<sub>2</sub>, which forms a fcc array of Ca<sup>2+</sup> ions with F<sup>-</sup> ions occupying all the tetrahedral holes, density calculations give values of 2.86 g/cm<sup>3</sup> using Shannon–Prewitt ionic radii (23), and 3.20 g/cm<sup>3</sup> using the observed interionic spacing (25) compared to the observed density of 3.18 g/cm<sup>3</sup> (18).

## Conclusion

The preceding calculations demonstrate a consistently high positive correlation between unit-cell geometry and crystal density; formulas are summarized in Table 1. In the standard texts, neither the calculations nor the resulting formulas are given much attention. However, the methods of this article are potentially useful in making more tangible the classroom discussion of crystal lattices. Some of the derivations of density formulas might reasonably be included in those courses in which the solid state is discussed.

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