Exercise 4 SAMS

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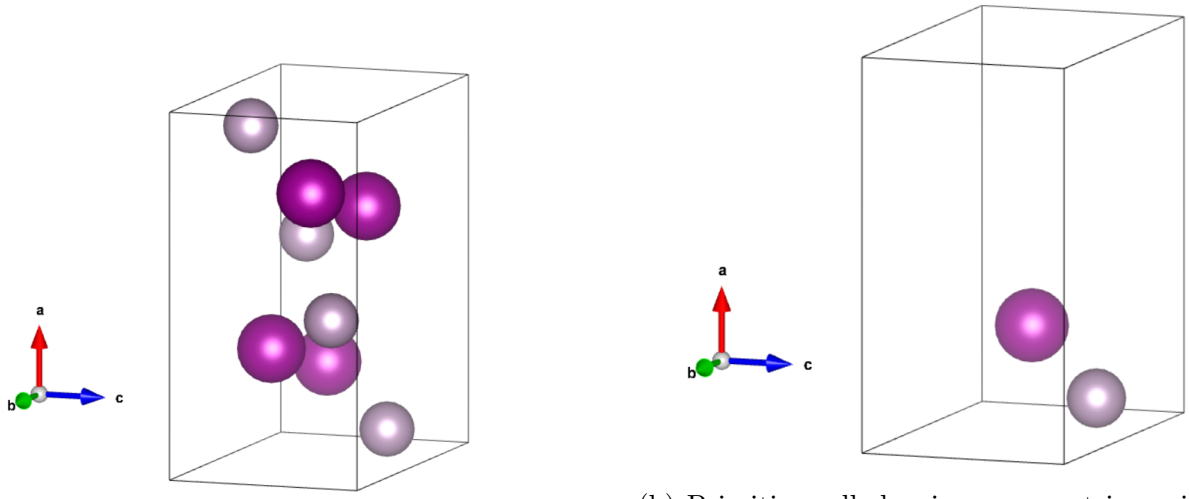
1 An orthorrhombic material containing Mn and P has the following lattice parameters a = 5.916 Å, b = 5.260 Å y c = 3.173 Å and belongs to a spacial group with the symbols bnm. Inside the conventional cell there are 8 atoms, 4 Mn and 4 P, situated at (with respect to the origin of the cell) ±(u, v, $\frac{1}{4}$) y ±(1/2–u, v+1/2, $\frac{1}{4}$) where u(Mn) = 0.20, v(Mn) = 0.005, u(P) = 0.57 y v(P) = 0.19.

a) Draw the conventional cell with all its atoms



(a) Conventional cell

(b) Primitive cell showing asymmetric positions

Figure 1: MnP cells drawn with VESTA

The first image ("Conventional cell") shows the conventional crystalline cell of MnP, containing four manganese (Mn) atoms represented in fuchsia and four phosphorus (P) atoms shown in light purple. This conventional representation highlights the periodic distribution of all atoms within the structure. The second image ("Primitive cell showing asymmetric positions") illustrates the primitive cell, displaying only the asymmetric (unique) atomic positions necessary to describe the full crystal structure. Specifically, the asymmetric positions shown are (0.2, 0.005, 0.25) for Mn and (0.57, 0.19, 0.25) for P. Both images were created using VESTA software[1].

b) Find the kind of lattice, basis and formula of the material as well as its density (atomic weights for Mn y P are, respectively, 55.94 y 30.97).

The kind of lattice is orthorhombic composed of Mn and P has lattice parameters:

$$a = 5.916\,\text{Å}, \quad b = 5.260\,\text{Å}, \quad c = 3.173\,\text{Å}$$

and belongs to the orthorhombic primitive lattice with space group Pbnm.

The basis is the set of atoms along with their relative positions within the unit cell that, when repeated at every lattice point, generate the entire crystal structure.

For the MnP material, the conventional unit cell (which is orthorhombic and primitive) contains a total of 8 atoms: 4 Mn atoms and 4 P atoms. However, the fundamental basis consists of 1 Mn atom and 1 P atom located at specific fractional positions within the cell:

- For Mn, one of the positions is given by

  $$(u,\, v,\, 1/4)$$

  with $u = 0.20$ and $v = 0.005$.

- For P, one of the positions is given by

  $$(u,\, v,\, 1/4)$$

  with $u = 0.57$ and $v = 0.19$.

When the symmetry operations of the space group (Pbnm, in this case) are applied, these positions are transoformed onto the other equivalent positions, resulting in 4 positions for Mn and 4 for P within the conventional cell.

Thus, the basis is the collection of these atoms (one Mn and one P in asymmetric positions) that, when combined with the lattice (which provides the periodic repetition), defines the complete crystal structure of MnP. Therefore the empiric formula of the material is MnP in proportion 1:1.

The density (ρ) is calculated using the formula:

$$\rho = \frac{m}{V}$$

where:

- m is the **mass of the unit cell** (in g),
- V is the **volume of the unit cell** (in cm^3),
- N_A is **Avogadro's number** ($6.022 \times 10^{23}\,\text{mol}^{-1}$).

The unit cell contains **4 Mn and 4 P atoms**, so the total mass is:

$$m = 4 \times 55.94 + 4 \times 30.97$$

$$m = 223.76 + 123.88 = 347.64\,\text{g/mol}$$

$$V = a \times b \times c$$

Substituting the given lattice parameters:

$$V = (5.916 \times 5.260 \times 3.173)\,\text{Å}^3$$

$$V = 98.69\,\text{Å}^3$$

Since $1\,\text{Å}^3 = 10^{-24}\,\text{cm}^3$, we convert:

$$V = 98.69 \times 10^{-24}\,\text{cm}^3$$

$$\rho = \frac{m}{V \times N_A}$$

$$\rho = \frac{347.64}{(98.69 \times 10^{-24}) \times (6.022 \times 10^{23})}$$

$$\rho = \frac{347.64}{5.94 \times 10^{-22}}$$

$$\boxed{\rho \approx 5.85\,\text{g/cm}^3}$$

c) Find the point group from which the space group comes.

The space group *Pbnm* belongs to the dipyramidal orthorhombic crystal class, denoted by the Herman–Mauguin notation *mmm*. The point group notation *mmm* indicates mirror symmetry perpendicular to the crystallographic axes *a*, *b*, and *c*. Specifically, the *Pbnm* structure is centrosymmetric and includes symmetry operations such as inversion centers, mirror planes, and glide reflections in all directions [2]. In short, the structure *Pbnm* has 8 symmetry operations and is invariant under inversion and 180° rotations around the *a*, *b*, and *c* axes.

d) Plot the symmetry elements contained in the indexes of the space group in 2D projections of the cell.

Identity (E) The first symmetry element is the identity, *E*, which every crystal structure possesses.

In the spacial group *Pbnm* each letter indicates the presence of two glide planes and one mirror plane perpendicular to each of the axis *a*, *b* and *c*.

Mirror Plane (m) Perpendicular to c Next, there is a mirror plane, m, perpendicular to the c axis, as shown in Figure 2.

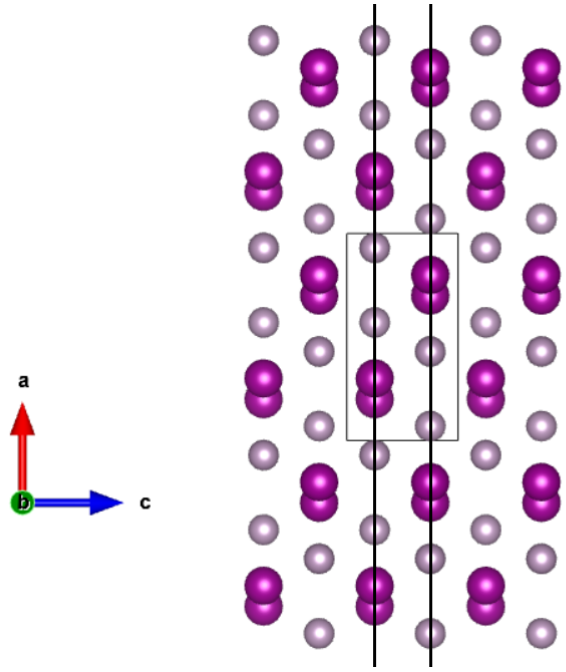


Figure 2: Plane of symmetry perpendicular to c (labeled m).

Glide Planes Finally, there are two glide planes: One perpendicular to the a axis (b) as shown in Figure 3.

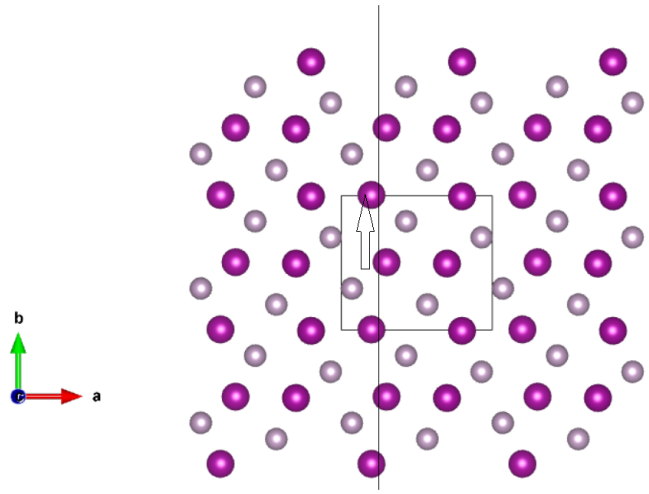


Figure 3: Glide plane perpendicular to a (labeled b).

One perpendicular to the b axis (c) as shown in Figure 4.

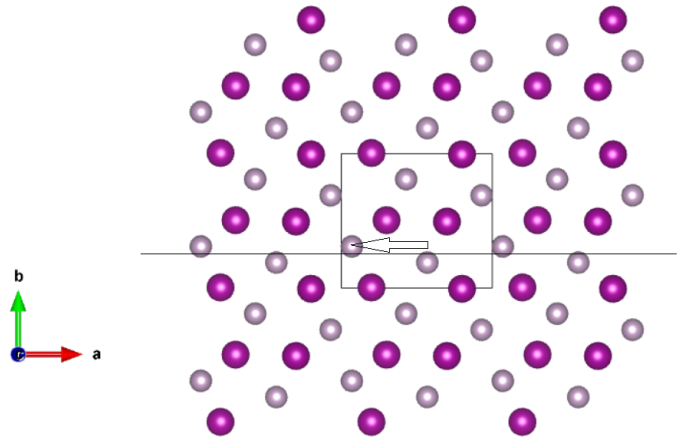


Figure 4: Glide plane perpendicular to b (labeled n).

C_2 screw rotation axes There are three screw C_2 axes, one parallel to each axis a,b and c

There is one C_2 screw axis parallel to a as shown in Figure 5

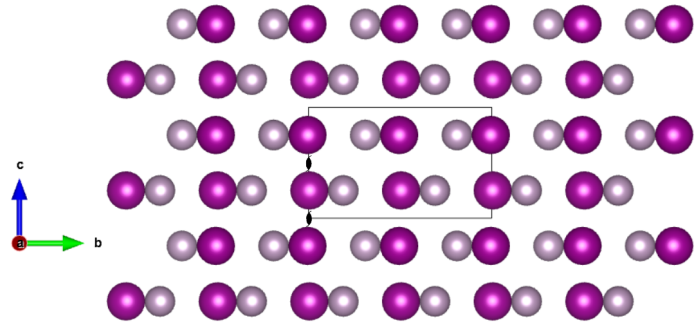


Figure 5: C_2 screw axis parallel to a.

There is another C_2 screw axis parallel to b as shown in Figure 6.

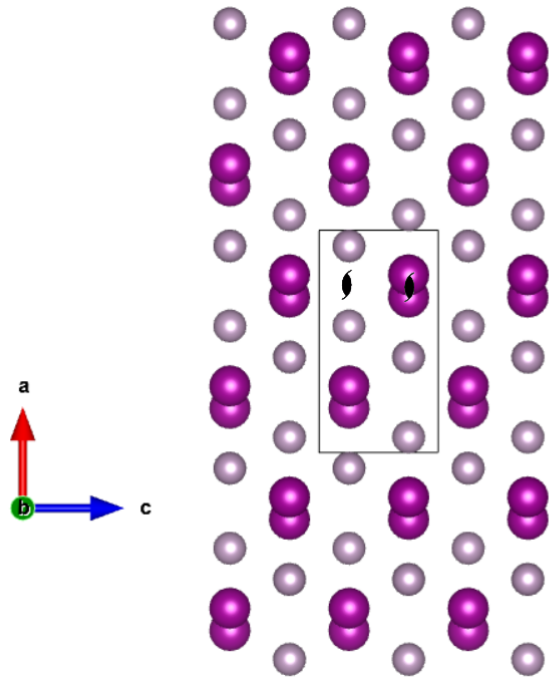


Figure 6: C_2 rotation axis parallel to b.

There is another C_2 screw axis parallel to c as shown in Figure 7

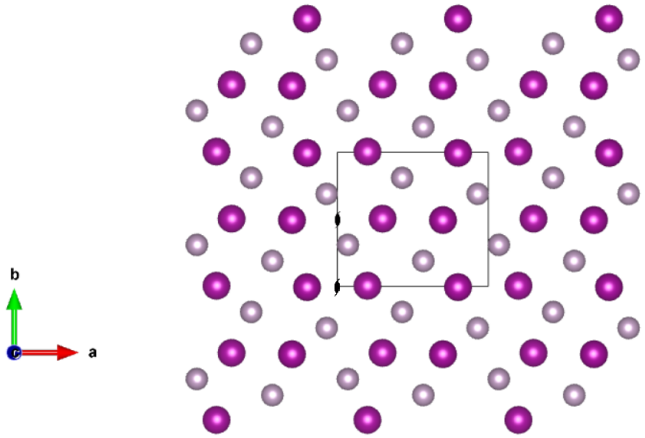


Figure 7: C_2 screw axis parallel to c.

Inversion center Finally there is another symmetry element which is an inversion center shown in Figure 8.

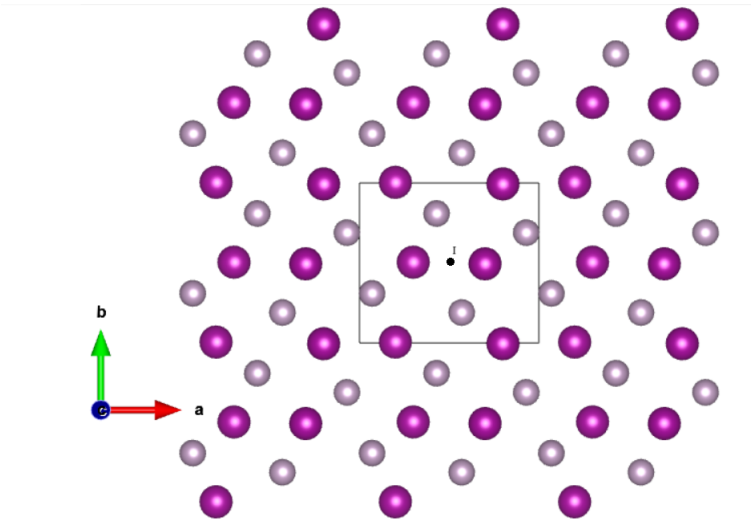


Figure 8: Inversion center (I).

References

[1] Momma, K., Izumi, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography, 44*(6), 1272–1276. https://doi.org/10.1107/S0021889811038970

[2] Globalsino. (n.d.). *Symmetry of Crystals and Point Groups*. Retrieved March 7, 2025, from `https://www.globalsino.com/EM/page3013.html`