

The Symmetry and Packing Fraction of The Body Centered Tetragonal Structure

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Abstract

It is shown that for different ratios of lattice parameters, c/a , the body centered tetragonal structure may be view as body centered tetragonal, body centered cubic, face centered cubic or hexagonal. This illustrates that the apparent symmetry of a lattice depends on the choice of the conventional unit cell.

Keywords: Solid-state physics, crystal structure, body centered tetragonal structure, crystallographic symmetry, packing fraction

Introduction

The packing of atoms in various crystal structures is a topic that appears in virtually all introductory solid state physics and crystallography text books (e.g. Ashcroft and Mermin (1996)). By viewing atoms as hard spheres it is straightforward to calculate the packing fraction for common crystal structures such as the simple cubic (0.524), the body centered cubic (0.680) and the face centered cubic (0.740) structures. It is sometimes through an analysis of the packing fraction that the interrelationship of different crystal structures becomes obvious. The utility of this approach has been discussed by Aziroff (1960). For example, the relationship between the hexagonal close packed (hcp) and face centered cubic (fcc) structures is well known (Kittel, 1996) as both maximize the packing fraction. The packing fraction of the body centered tetragonal (bct) structure provides interesting insight into the relationship of different crystal structures and emphasizes the point that the choice of non-primitive unit cells is not unique and does not always emphasize all of symmetry characteristics of the structure. The analysis of this structure provides a useful classroom example to introduce students to the concept of crystal symmetry and structure.

Analysis of the body centered tetragonal structure

The conventional unit cell of the body centered tetragonal structure is characterized by a lattice parameter a in the basal plane and a lattice parameter c in the z -direction. The packing fraction, f , of a crystal structure is defined as the maximum fraction of the volume of the structure that can be occupied by non-overlapping hard spheres. The packing fraction is thus given by the ratio of the volume of spheres, V_s , that can be accommodated within a unit cell to the total volume of the unit cell, V_c ;

$$f = V_s/V_c \tag{1}$$

For the body centered tetragonal structure there are two spheres contained within the conventional unit cell and the packing fraction may be determined as a function of the ratio of the basal plane lattice parameter, a , and the z -axis lattice parameter, c , that is, c/a , from a geometrical consideration of the packing of hard spheres. Three distinct regimes need to be considered on the basis of constraints placed on the diameter of the spheres by the geometry of the crystal structure. For $c/a < \sqrt{2/3}$ the distance between the spheres is limited along the z -direction. The spheres along a unit cell edge touch along the z -direction leading to the constraint that the radius of the spheres, r , is given by

$$r = c/2 \tag{1}$$

Thus the total volume of two spheres within the unit cell will be

$$V_s = 2 \times \frac{4\pi}{3} r^3 = \frac{\pi c^3}{3} \tag{2}$$

and for a unit cell volume of $V_c = a^2c$, the packing fraction, is found to be

$$f = \frac{\pi}{3} (c/a)^2 \tag{3}$$

For the region $\sqrt{2/3} < c/a < \sqrt{2}$ the distance between the spheres is limited along the body diagonal of the tetragonal cell. In this case the sphere radius is 1/4 of the body diagonal or

$$r = \frac{1}{4} (2a^2 + c^2)^{1/2} \tag{4}$$

and the total sphere volume will be

$$V_s = 2 \times \frac{4\pi}{3} \frac{(2a^2 + c^2)^{3/2}}{4^3} \tag{5}$$

Dividing by the cell volume and rearranging gives the packing fraction as

$$f = \frac{\pi}{24} \frac{1}{(c/a)} [(c/a)^2 + 2]^{3/2} \tag{6}$$

In the third regime $c/a > \sqrt{2}$ and the distance between the spheres is limited in the basal plane. Here

the radius will be one half of the basal plane lattice parameter or

$$r = a/2 \tag{7}$$

The total sphere volume will be

$$V_s = 2 \times \frac{4\pi}{3} r^3 = \frac{\pi a^3}{3} \tag{8}$$

and the packing fraction is found to be

$$f = \frac{\pi}{3} \frac{1}{(c/a)} \tag{9}$$

As expected, the above functions match at the appropriate values of c/a giving $f = 2\pi/9$ at $c/a = \sqrt{2/3}$ and $f = \sqrt{2}\pi/6$ at $c/a = \sqrt{2}$. The functions in equations (3), (6) and (9) are plotted as a function of (c/a) in Figure 1 over their appropriate ranges. Clearly, as anticipated, $f \rightarrow 0$ as either $c/a \rightarrow 0$ or $c/a \rightarrow \infty$. For intermediate values of c/a there are three situations as described below.

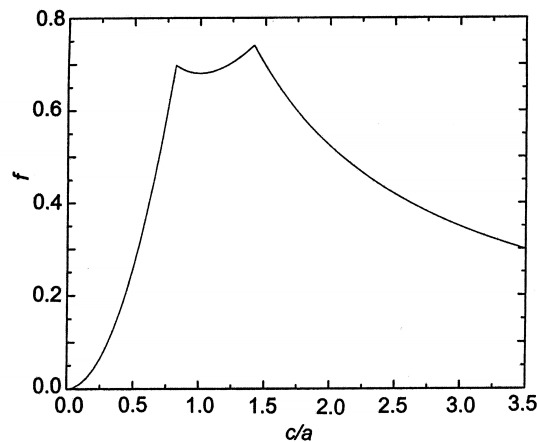


Figure 1. Packing fraction, f , as a function of c/a for the body centered tetragonal structure.

For a value of $c/a = \sqrt{2/3}$ there is a local maximum in the packing fraction. A section through the structure in the (110) plane is shown in Figure 2. The spheres in this plane are arranged in a simple hexagonal lattice. This simple two-dimensional hexagonal lattice forms the basis of both three dimensional close packed structures, the hexagonal close packed (hcp) structure and the face centered cubic (fcc) structure. The relationship of these structures is nicely illustrated by Figure 21 of Kittel (1996). The hcp structure is represented by two dimensional hexagonal planes of atoms in the sequence ABABABAB..., indicating that the second plane of atoms resides over spaces between the atoms in the first plane and atoms in the third plane reside above atoms in the first plane (that is above spaces

between the second plane atoms). The fcc structure is represented by two dimensional hexagonal planes of atoms in the sequence ABCABCABC..., indicating that the second plane of atoms resides over one set of spaces between the atoms in the first plane and atoms in the third plane reside over a second set of spaces between the atoms in the first plane. In both cases, the placement of each plane of hexagonally arranged atoms over spaces which are the centers of equilateral triangles formed by atoms in the plane below will maximize the packing fraction.

In the case of the bct structure with $c/a = \sqrt{2/3}$ the hexagonal planes as shown in Figure 2 follow a sequence ABABAB... but are not shifted relative to each other as they are for the hcp structure. Rather than residing above spaces that are the centers of triangles of three atoms, the second plane atoms lie above the center point of lines between two atoms in the plane below. The subsequent layer falls above the first layer giving a structure that (as for the hcp structure but without the close packing). The structure may, therefore, be thought of as a simple hexagonal structure with a basis of two atoms. In the figure it is seen that the basal plane lattice parameter for the hexagonal structure, a_{hex} , is just the z-axis lattice parameter for the bct structure (c). A simple calculation shows that this simple hexagonal structure has the ratio $(c/a)_{hex} = \sqrt{3}$ and a calculated packing fraction of $2\pi/9$, consistent with the value given by equations (3) and (6) and as shown in Figure 1.

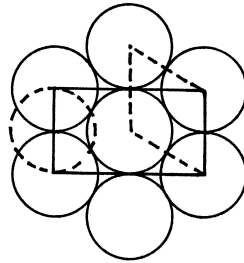


Figure 2. Hexagonal packing in the (110) plane of the bct structure for $c/a = \sqrt{2/3}$. The unit cell of the bct structure in the (110) plane is shown by the solid rectangle. The location of a typical sphere in the next layer along the [110] direction is shown by the dashed circle. The dashed rhombus shows the basal plane of the simple hexagonal cell.

For a value of $c/a = 1$, Figure 1 shows a local minimum in the packing fraction corresponding to the well-known body centered cubic (bcc) structure. From equation (6), the calculated packing fraction is found to be $f = \sqrt{3}\pi/8 = 0.680$.

For a value of $c/a = \sqrt{2}$ there is a maximum in the packing fraction and the bct structure can be shown to be the same as the fcc structure. The (110) plane of the bct structure forms the (100) plane of an fcc structure with a lattice parameter given in terms of the bct lattice parameter $a_{fcc} = c = \sqrt{2}a$. As illustrated in Figure 3, this is readily seen from an inspection of the spheres in the bct (001) plane (which remains the (001) plane for the fcc structure). The packing fraction from equation (6) is found to be $c/a = 2\pi/6 = 0.740$ as appropriate for the fcc structure. The bct structure has a basis of two atoms and the fcc structure has a basis of four atoms and this is clearly

illustrated by the differences in the volumes of the cells in terms of their lattice parameters as given above.

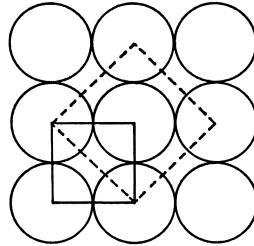


Figure 3. The (001) plane of the bct structure with $c/a = \sqrt{2}$. The solid square shows the bct unit cell and the dashed square shows the conventional unit cell of the fcc structure with a lattice parameter of $\sqrt{2} a$.

Discussion and Conclusions

From a practical standpoint the current discussion allows the crystal structure for certain materials to be viewed with some additional insight. Elements are certainly the most obvious candidates for a real analysis of packing fractions as they are comprised of a single type of atom. The majority of the elements have close packed structures (at room temperature), i.e. hcp or fcc or bcc. The alkali metals have the bcc structure. Some elements have more complex structures (Feng and Jin, 2005) for an overview of the structure of the elements). For the purpose of applying the concepts presented in the present manuscript, indium is an interesting example as it has the bct structure. The measured lattice parameters of indium are $a = 0.32530$ nm and $c = 0.49555$ nm giving a ratio $c/a=1.5234$ (Generalic, 2012)). These values, combined with the atomic mass of indium and the appropriate number of two atoms per bct unit cell, are consistent with the measured density of indium, 7.31×10^3 kg/m³ (Wolfram Alpha (2012)). The value of the c/a ratio as determined from lattice parameter measurements for indium places the structure in the bct regime described by equation (9), i.e. $1.5234 > \sqrt{2}$. From this equation, the calculated packing fraction of indium will be $f= 0.687$, slightly greater than the value of 0.680 for the bcc structure. Thus the tetragonal distortion of the bcc structure, which increases c/a , has yielded an increased density for indium.

The above analysis of the packing fraction of the bct structure shows the relationship of this structure to some other well-known structures for particular ratios of c/a . While packing fractions cannot exceed the value for the hcp and fcc structures, the current analysis illustrates that the packing fraction for the bct structure can exceed that of the bcc structure. Figure 1 clearly shows that introducing a tetragonal distortion to the bcc structure, either by increasing or decreasing the c/a ratio, will increase the packing fraction. The current analysis also nicely demonstrates that our view of conventional unit cells is not unique and does not always properly emphasize all of the symmetry characteristics of the structure. For the correct ratio of c/a the bct structure is merely the fcc viewed using a different unit cell, i.e. a unit cell which is smaller than the conventional fcc unit cell but one which is still not a primitive cell (as it has two atoms per unit cell).

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