

결정 구조들의 해석을 위한 컴퓨터 프로그래밍

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요약

본 논문에서는 면심입방정 (FCC)과 체심입방정 (BCC) 틀에 있어서의 최인접 원자들에 대한 컴퓨터 프로그래밍이 각각의 결정 구조들을 이해하기 위한 하나의 접근방식으로 제안되어졌다. 이러한 컴퓨터 프로그래밍을 이용하여 기준 원자와 최인접 원자들간의 거리 값들과 최인접 원자들의 숫자들이 면심입방정과 체심입방정에 대하여 계산되어졌고 상호 비교되었다. 이 프로그램의 알고리즘에 있어서 결정 내에서의 원자들은 모서리원자와 체심 또는 면심 원자의 두 종류로 분류되어 각각 고려되어졌다. 이차 최인접 원자들을 제외하고는 동일 차수의 최인접 원자들에 있어서 기준 원자로부터의 거리 값들이 면심입방정들의 경우가 체심입방정들의 경우에 비하여 작았다. 또한 일차 및 삼차 최인접 원자들의 숫자가 체심입방정의 경우보다 면심입방정의 경우에 더 많았다. 이러한 차이점은 면심입방정과 체심입방정들에 있어서의 원자 충전율의 비교분석에 의하여 설명되어졌다. 본 프로그래밍에서 이용된 알고리즘은 다른 결정구조의 해석에도 확장 응용이 가능하다고 판단된다.

A Computer Programming for the Analysis of Crystal Structures

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ABSTRACT

In this paper a computer programming for the expression of nearest neighbor atoms in face-centered cubic (FCC) and body-centered cubic (BCC) crystals was suggested as one of the approaches to understand each of the crystal structures. By using this computer programming the distance values between a reference atom and the nearest neighbor atoms, and the numbers of the nearest neighbor atoms were calculated and compared for the FCC and BCC crystals. In this algorithm, the positions of the atoms in a crystal were defined as two categories, the corner atoms and face- or body-centered atoms, and considered respectively. For the same order of nearest neighbor atoms except the second order ones the distance values from the reference atom were smaller in the FCC crystals than those in the BCC. Also, the numbers of the first and third nearest neighbor atoms in the FCC crystals were larger than those in the BCC. This difference was explained by the comparison of each atomic packing ratio of the FCC and BCC crystals. The algorithm used in this programming can also be expanded to the analysis of other crystal structures.

1. Introduction

Although variety of computational methods are being employed in solving scientific or engineering problems

[1-3], it appears that they are relatively rarely used in figuring the structure of a crystal which has a specific arrangement of atoms or ions in a space. Instead, many people depend upon an elaborate geometric consideration to understand nature of the crystal structures [4, 5]. The structure of a crystal in general determines its overall

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characteristics such as electrical, optical, magnetic, mechanical, and chemical properties [4, 5]. Thus, a thorough understanding of the structure of a crystal is of special importance for the prediction and explanation of its various properties, being one of the major research topics in materials science, mineralogy, organic chemistry, solid state physics, solid mechanics, and so on [4-10].

The structures of crystals can be classified into the Bravais 14 lattices and understanding of detail nature of each crystal structure can be done by careful consideration of numbers and distances of nearest neighbor atoms included in each of the crystals [4, 5]. The two factors, numbers and distances of nearest neighbor atoms, can be geometrically determined using a trigonometric operation. However, as the order of the nearest neighbor atoms increases this calculation becomes dramatically difficult.

For the present study, numbers and distances of high order nearest neighbor atoms in the face-centered cubic (FCC) and body-centered cubic (BCC) crystals which are the most common structures in crystalline materials, were obtained by using a new computer programming and the results were compared for each other. Also, it was suggested that the algorithm in this programming be used in establishing programs for the expression of other crystal structures.

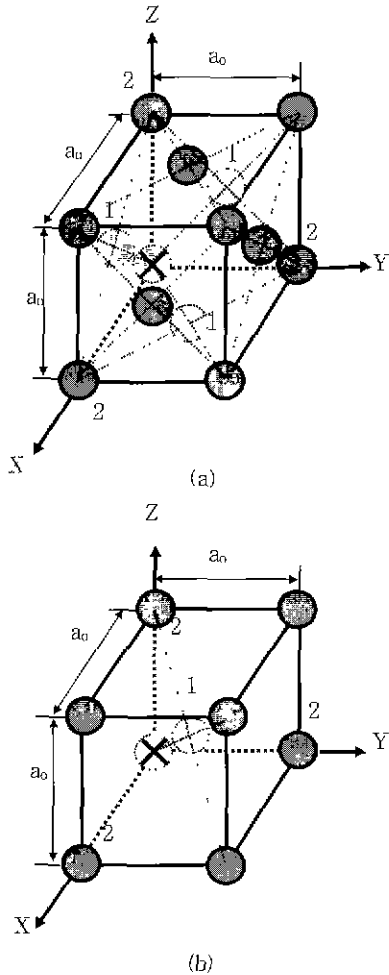
2. Background

A unit cell would be defined as the minimum three-dimensional building block which can construct a whole crystal by simple multiplication [11, 12]. According to the lengths of unit-cell axes and the angles between them, overall crystal structures can be classified as cubic, tetragonal, hexagonal, orthorhombic, monoclinic, and triclinic [11, 12]. Each category contains some of body-centered, face-centered, base-centered, or primitive structure. Thus, totally the crystal structures can be characterized as so called the Bravais 14 lattices [11, 12]. Among them face-centered cubic (FCC) and body-centered cubic (BCC) are the most commonly encountering

structures especially in metallic materials such as copper, aluminum, nickel, platinum, iron, chromium, molybdenum, tungsten, etc. [4, 5]. Moreover, some minerals with a rock salt structure including sodium chloride (NaCl) and periclase (MgO) show the FCC array of the negative ions (anions) [4, 5]. (Fig. 1 (a)) shows the schematic diagram of the unit cell of a face-centered cubic (FCC) crystal. The definition of a cubic unit cell is that its edges are equal in length and all the angles between them are 90° [11, 12]. This diagram was exaggerated for easy understanding. In reality, the corner and face-center atoms are touching each other to the direction of the dotted lines. Eight and six atoms go to the corners and face-centers of the FCC unit cell, respectively. However, a corner atom is shared by eight unit cells and a face-center atom is shared by two unit cells. Thus, totally four atoms are included in an FCC unit cell. (Fig. 1 (b)) shows the schematic diagram of the unit cell of a BCC crystal. Here, as the same case with the FCC crystal shown in (Fig. 1 (a)) in reality the corner and body-center atoms are touching each other to the direction of the dotted lines. There are eight corner atoms and one body-center atom in the diagram. Thus, there are totally two atoms in a BCC unit cell.

The lengths of the unit cell edges are called as the lattice parameters which are symbolized as a_0 , b_0 , and c_0 for the x, y and z axes, respectively [11, 12]. Since the three lattice parameters in a cubic crystal are identical, only a_0 is used to represent all the three lattice parameters for the x, y and z axes. This lattice parameter is the unique property of a material depending upon the atom size and crystal structure. In an FCC crystal shown in (Fig. 1 (a)) the three first nearest neighbor atoms for the reference atom which is marked as x, are indicated as the atoms numbered as 1. Since the position of an atom in a cubic crystal can be identified by using the Cartesian coordination, (i, j, k) [13, 14] the position of the reference atom at the origin marked as x becomes (0, 0, 0), and one of the first nearest neighbor atoms numbered as 1 is located at $(a_0/2, a_0/2, 0)$.

The equation for the length of a vector in the Cartesian



(Fig 1) Schematic diagrams of a face-centered cubic (FCC) unit cell (a) and a body-centered cubic (BCC) unit cell (b).

coordination can be written as following [13, 14]

$$\text{Length of a vector with } (i, j, k) = [(i)^2 + (j)^2 + (k)^2]^{1/2} \quad (1)$$

Therefore, the distances between the reference atom and the first nearest neighbor atoms can be calculated as following :

$$[(a_0/2)^2 + (a_0/2)^2 + (0)^2]^{1/2} = (\sqrt{2}/2)a_0 = 0.707a_0 \quad (2)$$

In reality, there are 11 more positions which are

equivalent to the \$(a_0/2, a_0/2, 0)\$ and \$0.707a_0\$ away from the origin. Totally, there are 12 first nearest neighbor atoms located at \$(\pm a_0/2, \pm a_0/2, 0); (-a_0/2, 0, \pm a_0/2); (0, \pm a_0/2, \pm a_0/2)\$

The second nearest neighbor atoms are located at the positions marked as 2 and the distance can be calculated as following:

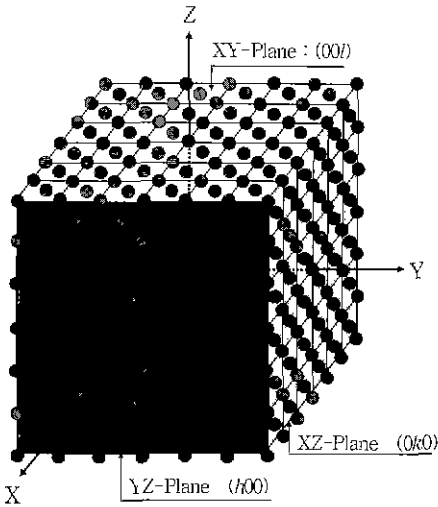
$$[(a_0)^2 + (0)^2 + (0)^2]^{1/2} = a_0 \quad (3)$$

Totally, there are 6 equivalent positions which are \$a_0\$ away from the origin : \$(\pm a_0, 0, 0); (0, \pm a_0, 0); (0, 0, \pm a_0)\$.

The same method can be applied to the BCC crystal. There are eight first nearest neighbor atoms which are marked as 1 and \$(\sqrt{3}/2)a_0\$ away from the origin. Also, there are six second nearest neighbor atoms which are marked as 2 and \$a_0\$ away from the origin. This kind of geometric operation for the nearest neighbor atoms with a higher order becomes extremely complicate. In order to count the high-order nearest neighbor atoms, huge number of unit cells and atoms must be considered as shown in (Fig 2). This figure shows 216 unit cells of an FCC crystal. Imagine how many unit cells and atoms must be considered to obtain information of 20th nearest neighbor atoms. It is almost impossible that one can successfully apply this trigonometric operation to the 20th nearest neighbor atoms. Therefore, a computational analysis based on the regularity in the atomic arrangement is absolutely required to resolve this problem.

3. Algorithm

The FCC structure was taken into account prior to the BCC structure. (Fig. 2) shows the multiplied FCC structure consisting of 216 unit cells. This structure was constructed based upon the three \$(x, y, z)\$ axes and each of the angles between them is \$90^\circ\$. The atoms in the structure were divided into two groups: corner atoms and face-center atoms. The indices of \$i, j, k\$ for the corner atoms could be simply \$0, \pm a_0, \pm 2a_0, \pm 3a_0, \dots\$, that is the integer times \$a_0\$. The indices of the face-center atoms could be \$\pm 0.5a_0, \pm 1.5a_0, \pm 2.5a_0, \dots\$, that is the



(Fig. 2) A multiplied face-centered cubic (FCC) structure including 216 unit cells.

fraction times a_0 . The corner and face-center atoms were considered up to $\pm 3a_0$. Thus, the positions of corner atoms can be defined as the combination of the indices: $i = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$; $j = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$; $k = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$.

Special care was taken for the determination of the positions of the face-center atoms in an FCC crystal. As shown in (Fig. 2) the planes were distinguished into three types: the yz -planes perpendicular to the x -axis; the xz -planes perpendicular to the y -axis; the xy -planes perpendicular to the z -axis. Each group of the planes was considered respectively. For example, the positions of the 36 face-center atoms in one of the yz -planes which is indicated as a heavily-grayed plane and can be expressed as $(h00)$ by using Miller indices [14, 15], have the combination of the indices. $i = 3a_0$; $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$. That is, every i value is $3a_0$, and j and k values are fractions ranging from $-2.5a_0$ to $2.5a_0$.

The positions of the face-center atoms at the next inner yz -plane which also can be expressed as another $(h00)$, can be defined as the combination of the indices $i = 2a_0$; $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$. There is only the

variation in the i values for the rest of the yz -planes.

The same consideration can be applied to the xz - and xy -planes. Therefore, the positions of face-center atoms in the seven yz -planes can be defined as the combination of the indices: $i = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$; $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$, those in the seven xz -planes as: $i = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $j = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$; $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$, and those in the seven xy -planes as: $i = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $k = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$. In (Fig. 2) one of the xz -planes, $(0k0)$ is indicated as lightly grayed one and one of the xy -planes, $(00l)$ as normal white one.

The distance between the reference atom located at the origin $(0, 0, 0)$ and each of the nearest neighbor atoms can be calculated using Equation 1. The number of each of the nearest neighbor atoms can be obtained by the summation of the number of each of the corner or face-center atoms with the same distance. Following is the summary of the algorithm for this calculation:

Positions of atoms: (i, j, k)

Corner atoms: $i = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$
 $j = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$
 $k = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$

Face-center atoms in yz-planes (h00)

$i = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$
 $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$
 $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$

Face-center atoms in xz-planes (0k0)

$i = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$
 $j = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$
 $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$

Face-center atoms in xy-planes (00l)

$i = 2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$
 $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$
 $k = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$

Distance between the atoms: $\sqrt{i^2 + j^2 + k^2}$

For a BCC crystal a similar algorithm can be applied. The positions of the corner atoms can be defined as 0,

$\pm a_0, \pm 2a_0, \pm 3a_0, \dots$. Accordingly, those of the body-center atoms $\pm 0.5a_0, \pm 1.5a_0, \pm 2.5a_0, \dots$. That is, if we consider the corner atoms up to $\pm 3a_0$ and body-center atoms up to $\pm 2.5a_0$ those for the corner atoms can be defined as the combination of the indices $i = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$; $j = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$; $k = -3a_0, -2a_0, -a_0, 0, a_0, 2a_0, 3a_0$. The determination of the positions of the body-center atoms is very simple compared to that of the face-centered atoms in an FCC crystal. The indices of the body-centered atoms can be described as the combination of $i = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $j = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$; $k = -2.5a_0, -1.5a_0, -0.5a_0, 0.5a_0, 1.5a_0, 2.5a_0$. All of the indices of i, j and k for the body-center atoms are the fraction times a_0 . Thus, only simple modification to the programming for the FCC crystal is needed for the calculation of the nearest neighbor atoms in the BCC.

4. Results and Discussion

<Table 1> lists the results of the distances and numbers of the nearest neighbor atoms of the FCC and BCC crystals up to 20th order. Although the data both for the FCC and BCC crystals were listed up to 20th order one may increase the order of the data as high as he or she wants. The number of the first nearest neighbor atoms in the FCC is 12 while that in the BCC is 8. The distance between the origin and the first nearest neighbor atoms in the FCC is $0.7071a_0$ while that in the BCC is $0.866a_0$. The number of the second nearest neighbor atoms were 6 both for the FCC and BCC crystals. The distance between the second nearest neighbor atoms and the origin was a_0 both for the FCC and BCC crystals. These results are identical to those obtained by the geometric calculation. Further, the FCC crystals showed 24 third nearest neighbor atoms $\sqrt{3/2}a_0$ ($= 1.2247a_0$) away from the origin while the BCC crystals 12 third nearest neighbor atoms $\sqrt{2}a_0$ ($= 1.414a_0$) away. For the rest orders of the nearest neighbor atoms the FCC crystals showed smaller distances from the origin than the BCC did.

In order to explain this difference, the atomic packing

<Table 1> Comparison in the numbers and distances of the nearest neighbor atoms of FCC and BCC crystals

| order | numbers | | distances(a_0) | |
|-------|---------|-----|--------------------|--------|
| | FCC | BCC | FCC | BCC |
| 1 | 12 | 8 | 0.7071 | 0.8660 |
| 2 | 6 | 6 | 1.0000 | 1.0000 |
| 3 | 24 | 12 | 1.2247 | 1.4142 |
| 4 | 12 | 24 | 1.4142 | 1.6583 |
| 5 | 24 | 8 | 1.5811 | 1.7321 |
| 6 | 8 | 6 | 1.7321 | 2.0000 |
| 7 | 48 | 24 | 1.8708 | 2.1794 |
| 8 | 6 | 24 | 2.0000 | 2.2361 |
| 9 | 36 | 24 | 2.1213 | 2.4495 |
| 10 | 24 | 32 | 2.2360 | 2.5981 |
| 11 | 24 | 12 | 2.3452 | 2.8284 |
| 12 | 24 | 48 | 2.4495 | 2.9580 |
| 13 | 72 | 30 | 2.5495 | 3.0000 |
| 14 | 48 | 24 | 2.7386 | 3.1623 |
| 15 | 12 | 24 | 2.8284 | 3.2787 |
| 16 | 48 | 24 | 2.9155 | 3.3166 |
| 17 | 30 | 8 | 3.0000 | 3.4641 |
| 18 | 72 | 48 | 3.0822 | 3.5707 |
| 19 | 24 | 24 | 3.1623 | 3.6056 |
| 20 | 48 | 48 | 3.2404 | 3.7417 |

ratio which tells how densely the atoms are stacked in a unit cell was considered both for the FCC and BCC crystals. The atomic packing ratio, symbolized as ρ , can be defined as the ratio of the total volume of the atoms in a unit cell to the unit cell volume, and can be expressed as following [5]

$$\rho = \frac{\left(\frac{4}{3}\pi r^3\right) \times n}{a_0^3} \quad (4)$$

where $\left(\frac{4}{3}\pi r^3\right)$ is the volume of a spherical shape atom; n is the number of atoms per unit cell; a_0 is the length of unit cell edges. The n is 4 for the FCC and 2 for the BCC as described in the previous section. Thus, the term of $\left(\frac{4}{3}\pi r^3\right) \times n$ becomes the total volume of atoms in a unit cell. The term of a_0^3 is the volume of a unit cell. The atomic radius

in terms of a_0 can be obtained by using trigonometric method for the closed packed direction of atoms. As described in the previous section for the FCC crystals in (Fig. 1(a)) the reference atom at the origin and the face-center atoms numbered as 1 are touching each other and the distance between the centers of them is $r+r=2r$ which is equivalent to $(\sqrt{2}/2)a_0 (=0.7071a_0)$ obtained from Equation 2. Thus, r becomes $(\sqrt{2}/4)a_0 (=0.3536a_0)$.

For the BCC crystals shown in (Fig. 1(b)) the reference atom at the origin and the body-center atom are touching each other and the distance between the centers of them is $r+r=2r$ which is equivalent to $(\sqrt{3}/2)a_0 (=0.8660a_0)$. Thus, r becomes $(\sqrt{3}/4)a_0 (=0.4330a_0)$. By substituting the n and r values into the Equation 4 for each of the FCC and BCC crystals following results were obtained :

$$\text{FCC : } \rho = \frac{\frac{4}{3} \pi \times \left(\frac{\sqrt{2} a_0}{4}\right)^3 \times 4}{a_0^3} = 0.7405 (= 74.05\%) \quad (5)$$

$$\text{BCC : } \rho = \frac{\frac{4}{3} \pi \times \left(\frac{\sqrt{3} a_0}{4}\right)^3 \times 2}{a_0^3} = 0.6802 (= 68.02\%) \quad (6)$$

The atomic packing ratio of the FCC crystals is higher than that of the BCC crystals, which explains that the distances between the origin and the nearest neighbor atoms in the FCC is smaller than those in the BCC, and the numbers of the first and third nearest neighbor atoms in the FCC crystals are larger than those of the BCC crystals

5. Summary

The numbers and distances of the nearest neighbor atoms of the FCC and BCC crystals were successfully obtained via a computer programming. For the FCC crystals the positions of corner atoms and face-center atoms were considered respectively in the programming. In order to define the positions of the face-center atoms the atomic planes were classified into three types : yz ($h00$), xz ($0k0$) and xy ($00l$) planes. The algorithm for the BCC crystals was very simple and obtained by the

simple modification of that for the FCC. The distance values between the reference atom and nearest neighbor atoms except the second order were smaller in the FCC crystals than those in the BCC. The numbers of the first and third nearest neighbor atoms were larger in the FCC crystals than those in the BCC. This difference was explained by the fact that the FCC crystals have higher atomic packing ratio than the BCC. This computational approach for the FCC and BCC crystals would be a useful guide to help people in various science and engineering fields understand the crystal structures. Moreover, with only simple modification this algorithm would be expanded to the analysis of the other crystals having the rest of 12 Bravais lattices.

Acknowledgement

This study was initiated by the request of Professor Yun-Mo Sung in Advanced Materials Sci. & Eng. Dept. at Daegu University, who wanted to develop a computer program to understand crystal structures in terms of numbers and distances of nearest neighbor atoms. Professor Sung supplied basic knowledge on crystal structures.

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