X-ray Crystallography

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A large number of solid materials are of crystalline structure and have been studied in depth from early times. Studies of non-crystalline materials can also benefit from the understanding of crystalline materials. X-ray diffraction has been the primary tool to find out the precise construction of crystalline materials. In fact, many advancements in modern science are direct results of X-ray crystallography such as advanced metals, medicine ingredients, and the DNA double helix construct.

Laue Condition and Bragg's Law

X-ray crystallography is the study of the patterns of diffracted (scattered) X-ray beam from a (polycrystalline) solid upon incident of a monochromatic X-ray beam. Assuming the wave vector, k, of the incident beam and the wave vector, $k^{'}$, of the diffracted beam, the necessary condition for the diffraction is known as the Laue condition:

$$k^{'} - k = G$$

where G is a lattice vector in the reciprocal space of the crystal. This is equivalent to the Bragg's law:

$$n\lambda = 2dsin\theta$$

where n is an integer, λ the X-ray wavelength, d the spacing between two planes of atoms in the crystal, and θ the diffraction angle. The equivalency between Laue condition and the Bragg's law can be explained as below, starting with the Laue condition using the relation of $k = 2\pi/\lambda\hat{k}$:

$$\frac{2\pi}{\lambda}(\hat{k} - \hat{k^{'}}) = G$$

$$\hat{G}\frac{2\pi}{\lambda}(\hat{k} - \hat{k^{'}}) = \hat{G}G$$

$$2\pi(\sin\theta - \sin\theta^{'}) = \lambda\left|G\right|$$

$$2d\sin\theta = \lambda$$

This is exactly the Bragg's law and the relations $\theta = -\theta^{'}$ and $d = 2\pi/|G|$ are employed in the derivation. In addition, Laue condition is also a result of the scattering equation:

$$\Gamma(k^{'}, k) = \frac{2\pi}{\hbar}\left|\left\langle k^{'}|V|k\right\rangle\right|^{2}\delta(E_{k^{'}} - E_{k})$$

where V is the potential of the lattice points.

$$\left\langle k^{'}|V|k\right\rangle = \left[\frac{1}{L^{3}}\sum_{R} e^{-i(k^{'}-k)R}\right]\left[\int_{unit\,cell} dxe^{-i(k^{'}-k)x}V(x)\right]$$

The first term in the bracket is zero unless the Laue condition is satisfied. The integral in the second bracket is called the structure factor for a specific Miller index plane in the lattice.

$$S(h,k,l) = \int_{unit\ cell} dx e^{iG(h,k,l)x} V(x) = \sum_{atom\ j\ in\ unit\ cell} f_j e^{i(hx_j+ky_j+lz_j)}$$

Selection Rules

Selection rules for X-ray diffraction provide the conditions of constructive interference in a given lattice. Specific examples of cubit lattices are given below.

Simple Cubic (SC): $S_{hkl} = f_0$; all h, k, l are constructive

Body Centered Cubic (BCC): $S_{hkl} = f_0 + f_1 e^{2\pi i(h,k,l)[1/2,1/2,1/2]} = f_0 + f_1(-1)^{h+k+l}$; the sum of h, k, l must be even to be constructive

Face Centered Cubic (FCC):
$S_{hkl} = f_0 + f_1 e^{2\pi i(h,k,l)[1/2,1/2,0]} + f_2 e^{2\pi i(h,k,l)[1/2,0,1/2]} + f_3 e^{2\pi i(h,k,l)[0,1/2,1/2]}$
$S_{hkl} = f_0 + f_1 e^{i\pi(h+k)} f_2 e^{i\pi(h+l)} f_2 e^{i\pi(k+l)}$; h, k, l must be either all even or all odd to be constructive

Table below is the summary of the selection rules of cubic lattices.

{h, k, l}	$N = h^2 + k^2 + l^2$	**Multiplicity**	**Simple Cubic**	**BCC**	**FCC**
100	1	6	√		
110	2	12	√	√	
111	3	8	√		√
200	4	6	√	√	√
210	5	24	√		
211	6	24	√	√	
220	8	12	√	√	√
221	9	24	√		
300	9	6	√		
310	10	24	√	√	
311	11	24	√		√
222	12	8	√	√	√

Multiplicity Factor

The multiplicity factor accounts for the number of equivalent planes in a family of Miller index. For example, there are 6 planes for {1 0 0}: (100), (010), (001), $(\bar{1}00)$, $(0\bar{1}0)$, and $(00\bar{1})$. The combinatorial relation is as follows:

$$\frac{M!}{n!}2^{M-Z}$$

where M is the total digits in the Miller index (3 for 3D lattices), n the number of repeated digits including zeros. The factor 2 is to count for plus and minus digits that is not zero, and Z is the number of zeros in the index since plus zero and minus zero are the same.

h,k,l	**h00**	**hh0**	**hhh**	**hk0**	**hkk**	**hkl**
multiplicity	6	12	8	24	24	48

Examples

Aluminum:

The table below shows the measured diffraction angles of polycrystalline aluminum on the first column. The second column is the computed lattice spacing using the CuKα X-ray wavelength of 1.54056 A. The third column lists the ratio between the spacing squared and the spacing of first line squared. This will established the sum of $h^2 + k^2 + l^2$:

$$N = h^2 + k^2 + l^2 = \frac{a^2}{d^2}$$

The fourth column lists N by multiplying the numbers in the third column by 3 and the fifth column is the round N. Based on the selection rules in the table above (the constructive Ns), aluminum is of a FCC lattice. As such, the corresponding Miller indexes are listed in the sixth column followed by the computed lattice constants in the last column.

(2θ)	d=λ/2sin(θ)	d1^2/d^2	d1^2/d^2*3	N	h k l	a=d√N
38.43	2.3405	1.0000	3.000	3	111	4.0538
44.67	2.0269	1.3333	4.000	4	200	4.0539
65.02	1.4332	2.6667	8.000	8	220	4.0538
78.13	1.2223	3.6666	11.000	11	311	4.0538
82.33	1.1702	4.0000	12.000	12	222	4.0538
98.93	1.0135	5.3327	15.998	16	400	4.0541
111.83	0.9301	6.3327	18.998	19	331	4.0540
116.36	0.9065	6.6657	19.997	20	420	4.0541

The theoretical density that agrees with the actual measurement is:

$$\frac{n \times MW}{a^3 \times N_A} = \frac{4 \times 26.982}{4.0538^3 \times 10^{-24} \times 6.022 \times 10^{23}} = 2.69013 \frac{g}{cm^3}$$

Silicon:

The next table shows the 2θ measurements of an X-ray powder diffraction pattern of silicon using the CuKα X-ray radiation. The computed N number sequence matches the FCC lattice selection rules, but several important lattice planes are missing: (200), (222), and (420) among others. Also, the computed theoretical density deviates from the laboratory data (2.33 g/cm^3).

$$\frac{n \times MW}{a^3 \times N_A} = \frac{4 \times 28.0855}{5.4331^3 \times 10^{-24} \times 6.022 \times 10^{23}} = 1.1632\frac{g}{cm^3}$$

(2θ)	d=λ/2sin(θ)	d1^2/d^2	d1^2/d^2*3	N	h k l	a=d*√N
28.41	3.1390	1.0000	3.000	3	111	5.4369
47.33	1.9190	2.6755	8.027	8	220	5.4279
56.11	1.6378	3.6734	11.020	11	311	5.4319
69.08	1.3586	5.3385	16.015	16	400	5.4343
76.34	1.2464	6.3424	19.027	19	331	5.4330
88.03	1.1086	8.0178	24.054	24	422	5.4308
94.95	1.0452	9.0197	27.059	27	511	5.4309
116.36	0.9065	11.9900	35.970	36	600	5.4391

However, if there are 8 instead of 4 silicon atoms inside the unit cell, the theoretical density becomes consistent with the laboratory measurements.

$$\frac{n \times MW}{a^3 \times N_A} = \frac{8 \times 28.0855}{5.4331^3 \times 10^{-24} \times 6.022 \times 10^{23}} = 2.3264\frac{g}{cm^3}$$

This suggests that the 4 extra silicon atoms may occupy either the octahedral voids [1/2, 1/2, 1/2] or the tetrahedral voids [1/4, 1/4, 1/4] in the FCC lattice. The structure factors become:

$$S_{hkl,oct} = f_{Si} + f_{Si}e^{2\pi i(h,k,l)[1/2,1/2,1/2]} = f_{Si}\left(1 + 1^{h+k+l}\right) = 2f_{Si}$$

$$S_{hkl,tetra} = f_{Si} + f_{Si}e^{2\pi i(h,k,l)[1/4,1/4,1/4]} = f_{Si}\left(1 + \sqrt{-1}^{h+k+l}\right)$$

The octahedral occupancy does not change the FCC selection rule, not consistent with the data. On the other hand, the tetrahedral occupancy suggests a destructive interference when the sum of h, k, l is a factor or 2, but not factor of 4 ($h + k + l = 4n + 2$). This explains the missing of (200), (222), and (420) planes in the silicon diffraction data. Therefore, silicon has a diamond-like FCC lattice.

Concluding Remarks

The crystal structures of most “simple” metallic materials, other inorganic materials, even some organic materials have been solved using the X-ray crystallography techniques as summarized in this article. The current challenges in X-ray crystallography are to solve the complex structures of protein molecules. Due to their complexity, growth and preservation of protein single crystals has become an active area of research. The experimental techniques have also made great progresses in sub 100 K freezing, ultra bright X-ray sources (synchrotron), fast data acquisition and comprehensive data processing. The Fourier transformation of the Laue patterns can construct the electron density distribution in the 3D space, thus providing important clues in the molecular structure.

Before the advent of the alpha-fold artificial intelligence model, X-ray crystallography is the only tool in solving the protein fold problems. Even today, X-ray crystallography is still an important tool to validate the protein fold AI model predictions.