CRYSTAL SYMMETRY, X-RAY DIFFRACTION, AND PHYSICAL PROPERTIES

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Lecture 54: Decoding the International Tables - III

This lecture constitutes the final lecture of the X-ray diffraction part of this course. In this lecture, the International Tables for Crystallography are revisited once more, specifically from the point of view of diffraction.

Let us consider the space group $P2_1$. In this space group, as discussed earlier, a twofold screw axis is added to a primitive monoclinic lattice. The twofold screw axes are located at the corners, at the centers of the edges, and at the center of the unit cell. As a consequence, the motifs, or more generally the general positions, are rotated by the action of the screw axis at all four corners of the unit cell.

We now directly examine the general positions for this space group. If an atom is placed at a general position with coordinates (x, y, z), a second atom is generated at $(-x, y + \frac{1}{2}, -z)$. This corresponds to a rotation by 180° followed by a translation of one-half along the screw axis, which in this case lies along the y-direction. Therefore, there are two atoms per unit cell for this general position.

We now focus on the reflection conditions associated with this space group. The reflection condition states that reflections of the type $(0k0)$ occur only when k is an even integer, that is, $k = 2n$. To understand the origin of this condition, consider placing an atom at a general position. The screw axis generates a second atom. If atoms are placed at $n/2$ different general positions, the action of the 2_1 screw axis generates another $n/2$ atoms, leading to a total of n atoms in the unit cell. These atoms need not all be identical; $n/2$ of them may be distinct, depending on the structure.

The structure factor F can therefore be written by summing over $n/2$ atoms. For the jth atom with scattering factor f_j placed at (x_j, y_j, z_j), the structure factor contains a term

$$f_j e^{i2\pi(hx_j+ky_j+lz_j)}.$$

The second atom generated by the screw axis contributes an additional term

$$f_j e^{i2\pi(-hx_j+k(y_j+\frac{1}{2})-lz_j)}.$$

Now, consider reflections of the type $(0k0)$. Substituting $h = 0$ and $l = 0$, the structure factor becomes

$$F = \sum_{j=1}^{n/2} f_j \left[e^{i2\pi k y_j} + e^{i2\pi k(y_j+\frac{1}{2})} \right].$$

Factoring out $e^{i2\pi k y_j}$ gives

$$F = \sum_{j=1}^{n/2} f_j e^{i2\pi k y_j} \left(1 + e^{i\pi k}\right).$$

The term $e^{i\pi k}$ is equal to $+\ 1$ when $k = 2m$ and $-\ 1$ when $k = 2m + 1$, where m is an integer. Therefore, the structure factor vanishes when k is odd and is nonzero when k is even. This explains the reflection condition that $(0k0)$ reflections occur only for even values of k.

Thus, even though the lattice is primitive, the presence of a screw axis leads to systematic extinctions. In general, any symmetry element that involves a translational component, such as a screw axis or a glide plane, gives rise to systematic absences. Similarly, centering translations in body-centered or face-centered lattices also lead to extinctions.

This example is relatively simple, and it is important to note that no special positions are involved here. When special positions are present, atoms placed on those positions must also be examined to determine whether they introduce additional reflection conditions.

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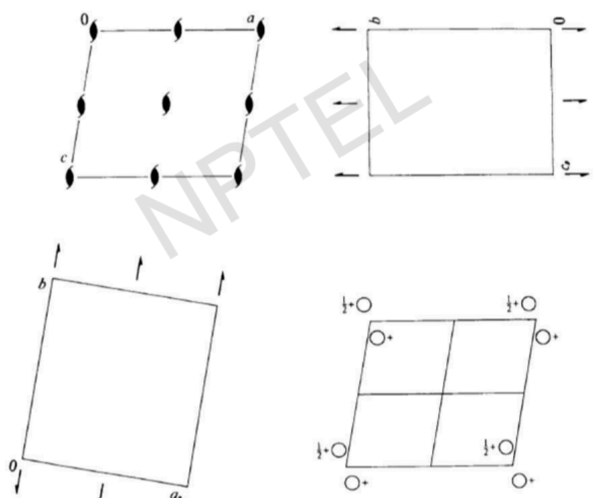
$P2_1$	C_2^2	2	Monoclinic
No. 4	$P12_11$		Patterson symmetry $P12/m1$

UNIQUE AXIS b



Excerpt from International Tables for Crystallography, Volume A

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Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		Reflection conditions
					General:
2	a	1	(1) x, y, z	(2) $\bar{x}, y+\frac{1}{2}, \bar{z}$	$0k0: \; k = 2n$

$n/2$ atoms at general positions $\Rightarrow$ total "n" atoms

$$F = \sum_{j=1}^{n/2} f_j \left[e^{i2\pi(hx_j + ky_j + lz_j)} + e^{i2\pi(-hx_j + k(y_j + \frac{1}{2}) - lz_j)} \right]$$

plane $(0k0) \Rightarrow F = \sum_{j=1}^{n/2} f_j \left[e^{i2\pi k y_j} + e^{i2\pi k (y_j + \frac{1}{2})} \right] = \sum_{j=1}^{n/2} f_j e^{i2\pi k y_j} \left(1 + e^{i\pi k} \right)$

$e^{i\pi k} = +1$ $k = 2m$

$= -1$ $k = 2m+1$

$F = 0$ when $k = 2m+1$

$\neq 0$ (reflection) when $k = 2m$

Excerpt from International Tables for Crystallography, Volume A

We now consider space group number 5, $C2$, which corresponds to an end-centered monoclinic crystal with the unique axis along b, a twofold rotation axis, and a centering translation corresponding to the C-centering. The a- and c-axes lie in the basal plane, with the b-axis vertical. The centering translation is given by $(\frac{1}{2}, \frac{1}{2}, 0)$.

Let us examine the Wyckoff positions for this space group. When an atom is placed at a general position (x, y, z), the twofold rotation generates a second atom at $(-x, y, -z)$. Applying the centering translation to both positions generates two additional atoms. Thus, placing one atom at a general position generates four atoms in total, and the multiplicity of the general position is four.

The four atomic positions are (x, y, z), $(-x, y, -z)$, $(x + \frac{1}{2}, y + \frac{1}{2}, z)$, and $(-x + \frac{1}{2}, y + \frac{1}{2}, -z)$.

To analyze the reflection conditions, it is sufficient to write the structure factor for a single atom and its symmetry-generated equivalents. The structure factor can be written as

$$F = e^{i2\pi(hx+ky+lz)} + e^{i2\pi(-hx+ky-lz)} + e^{i2\pi(h(x+\frac{1}{2})+k(y+\frac{1}{2})+lz)} + e^{i2\pi(-h(x-\frac{1}{2})+k(y+\frac{1}{2})-lz)}.$$

This expression can be rearranged to show that it contains a factor of

$$1 + e^{i\pi(h+k)}.$$

This factor is equal to $+1$ when $h + k$ is even and -1 when $h + k$ is odd. Consequently, the structure factor vanishes when $h + k$ is odd, leading to systematic absences. This result is consistent with the reflection conditions listed in the International Tables, such as (hkl) reflections occurring only when $h + k = 2n$, and similar conditions for special cases like $(h0l)$ and $(hk0)$.

If an atom is placed at a special position, the analysis must be repeated. Consider a special position with multiplicity two. Placing an atom at this position and applying the

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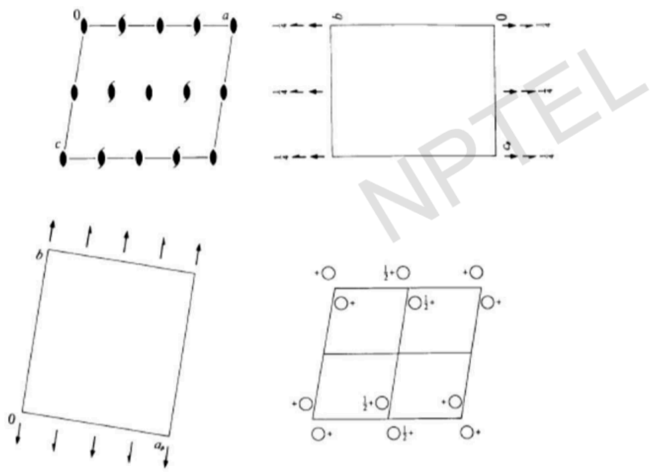
$C2$	C_2^3	2	Monoclinic
No. 5	$C121$		Patterson symmetry $C12/m1$

UNIQUE AXIS b, CELL CHOICE 1



Excerpt from International Tables for Crystallography, Volume A

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Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates $(0,0,0)+ \quad (\frac{1}{2},\frac{1}{2},0)+$		Reflection conditions
					General:
4	c	1	(1) x,y,z	(2) $\bar{x},y,\bar{z}$	$hkl: h+k=2n$
			$x+\frac{1}{2}, y+\frac{1}{2}, z$ and $\bar{x}+\frac{1}{2}, y+\frac{1}{2}, \bar{z}$		$h0l: h=2n$
					$0kl: k=2n$
					$hk0: h+k=2n$
					$0k0: k=2n$
					$h00: h=2n$
					Special: no extra conditions
2	b	2	$0,y,\frac{1}{2}$		
2	a	2	$0,y,0$ → $0,y,0 \quad \frac{1}{2},y+\frac{1}{2},0$		

NPTEL

Excerpt from International Tables for Crystallography, Volume A

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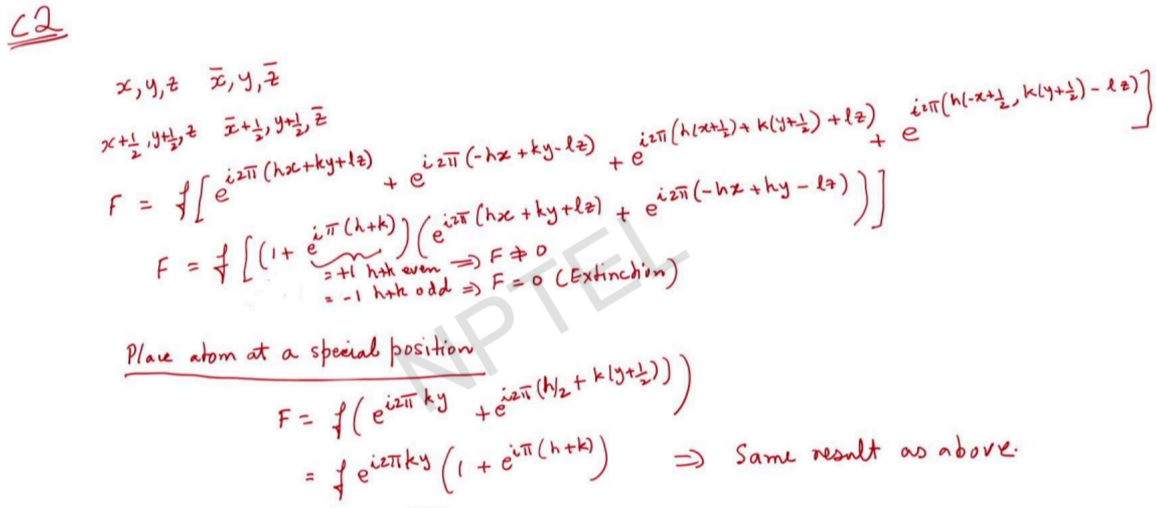

centering translation generates only two atoms. Writing the structure factor for these two atoms and simplifying again leads to a factor of $e^{i\pi(h+k)}$, which yields the same reflection condition as obtained from the general position. In this case, no additional reflection conditions arise from the special position, although in many other space groups special positions do introduce extra conditions.

As a final example, consider the space group $P2_1/c$, which contains a 2_1 screw axis along the b-axis and a glide plane in the ac-plane. The screw axis is perpendicular to the glide plane. The Wyckoff positions for this space group generate four symmetry-related atomic positions. Writing the structure factor for these positions and examining reflections of the type $(00l)$ leads to a structure factor proportional to

$$1 + e^{i\pi l},$$

which implies that the structure factor is zero when l is odd and nonzero when l is even. Thus, the reflection condition for these planes is that l must be even.

Now consider a special position, denoted as position $2d$, with multiplicity two. Atoms placed at this special position generate two symmetry-related atoms. The structure factor for this case can be written as

$$F = e^{i\pi(h+l)} + e^{i\pi(h+k)}.$$

Factoring out $e^{i\pi h}$ yields

$$F = e^{i\pi h}\left(e^{i\pi l} + e^{i\pi k}\right).$$

The bracketed term vanishes when one of k or l is even and the other is odd, leading to extinction. When both k and l are either even or odd, the structure factor is nonzero. This gives the reflection condition that $k + l$ must be even, which matches the condition listed in the International Tables for this special position and is in addition to the general reflection conditions.

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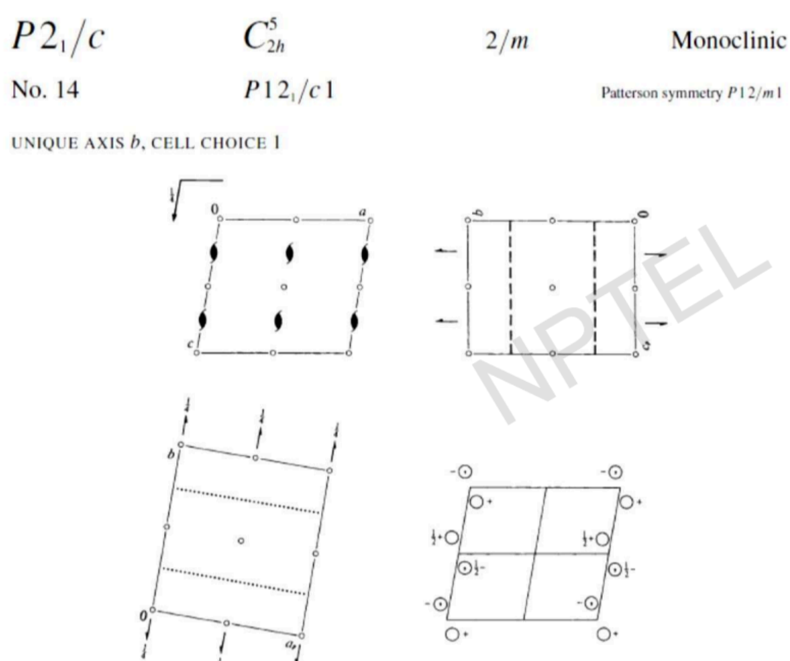

Excerpt from International Tables for Crystallography, Volume A

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Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates				Reflection conditions
							General:
4	*e*	1	(1) x, y, z	(2) $\bar{x}, y+\frac{1}{2}, \bar{z}+\frac{1}{2}$	(3) $\bar{x}, \bar{y}, \bar{z}$	(4) $x, \bar{y}+\frac{1}{2}, z+\frac{1}{2}$	$h0l: l=2n$ $0k0: k=2n$ $00l: l=2n$
							Special: as above, plus
2	*d*	$\bar{1}$	$\frac{1}{2}, 0, \frac{1}{2}$	$\frac{1}{2}, \frac{1}{2}, 0$			$hkl: k+l=2n$
2	*c*	$\bar{1}$	$0, 0, \frac{1}{2}$	$0, \frac{1}{2}, 0$			$hkl: k+l=2n$
2	*b*	$\bar{1}$	$\frac{1}{2}, 0, 0$	$\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$			$hkl: k+l=2n$
2	*a*	$\bar{1}$	$0, 0, 0$	$0, \frac{1}{2}, \frac{1}{2}$			$hkl: k+l=2n$

Excerpt from International Tables for Crystallography, Volume A

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for Plane (00l)

$$F = f\left(1+e^{i\pi l}\right)\left(e^{i2\pi lz} + e^{i2\pi(-lz)}\right)$$

$F = 0$ if l = odd

$\neq 0$ if l is even

Special position 2d

$\left(\frac{1}{2}, 0, \frac{1}{2}\right) \quad \left(\frac{1}{2}, \frac{1}{2}, 0\right)$

$$F = f\left[e^{\pi i(h+l)} + e^{\pi i(h+k)}\right] = f e^{\pi i h}\left(\underbrace{\overset{\pm 1}{e^{\pi i l}} + \overset{\pm 1}{e^{\pi i k}}}\right)$$

if l even k odd $\Rightarrow F = 0$ (Extinction)

if l odd k even $\Rightarrow$

both k, l odd or even $\Rightarrow k+l$ = even $\Rightarrow$ Reflection condition

With this, the discussion of the relevant parts of the International Tables for Crystallography is complete. Some space groups exhibit a large number of reflection conditions, while others have relatively few. This concludes the lecture, and in the next lecture the final part of the course will begin, focusing on the physical properties of crystals.