Crystallography

- The unit cell
- Space groups
- Bragg's law
- The structure factor

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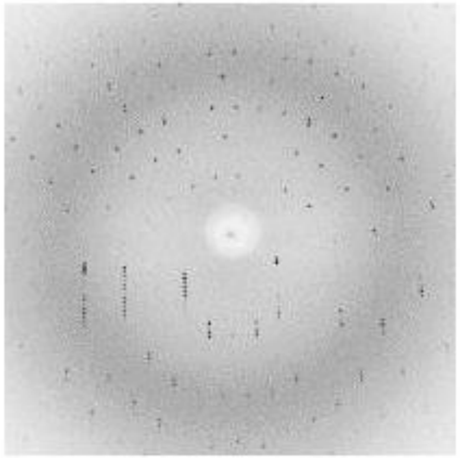
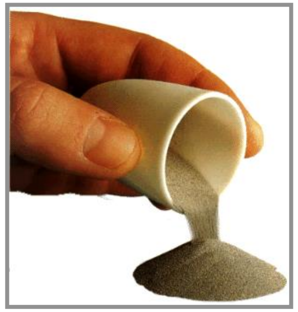
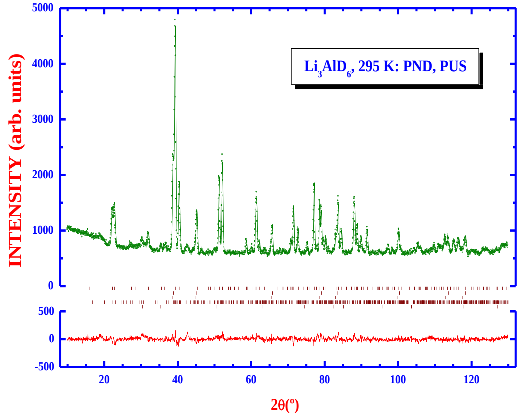
Motivation

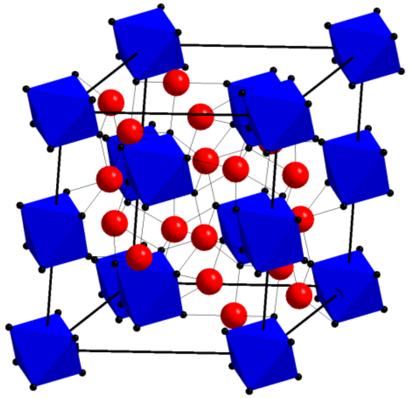
Single crystals



Powder





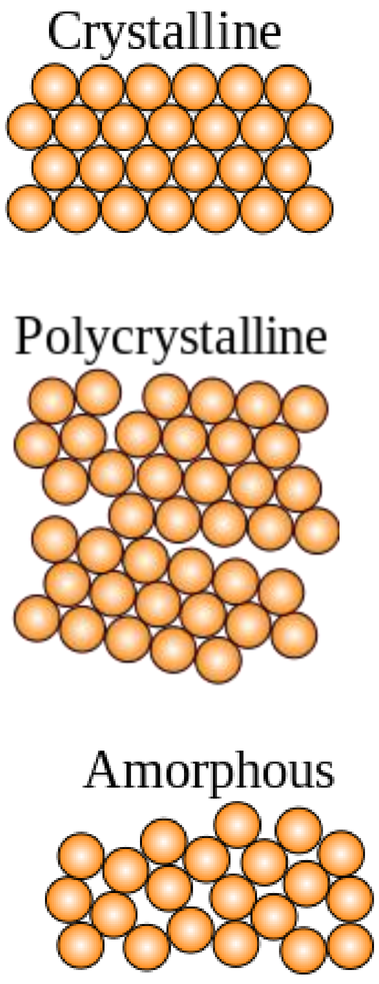


Some definitions

Crystal or crystalline solid: a solid material whose constituents, such as atoms, molecules or ions, are arranged in a highly ordered microscopic structure.

Polycrystalline materials (*powder*) are solids that are composed of many crystallites of varying size and orientation. Crystallites are also referred to as grains.

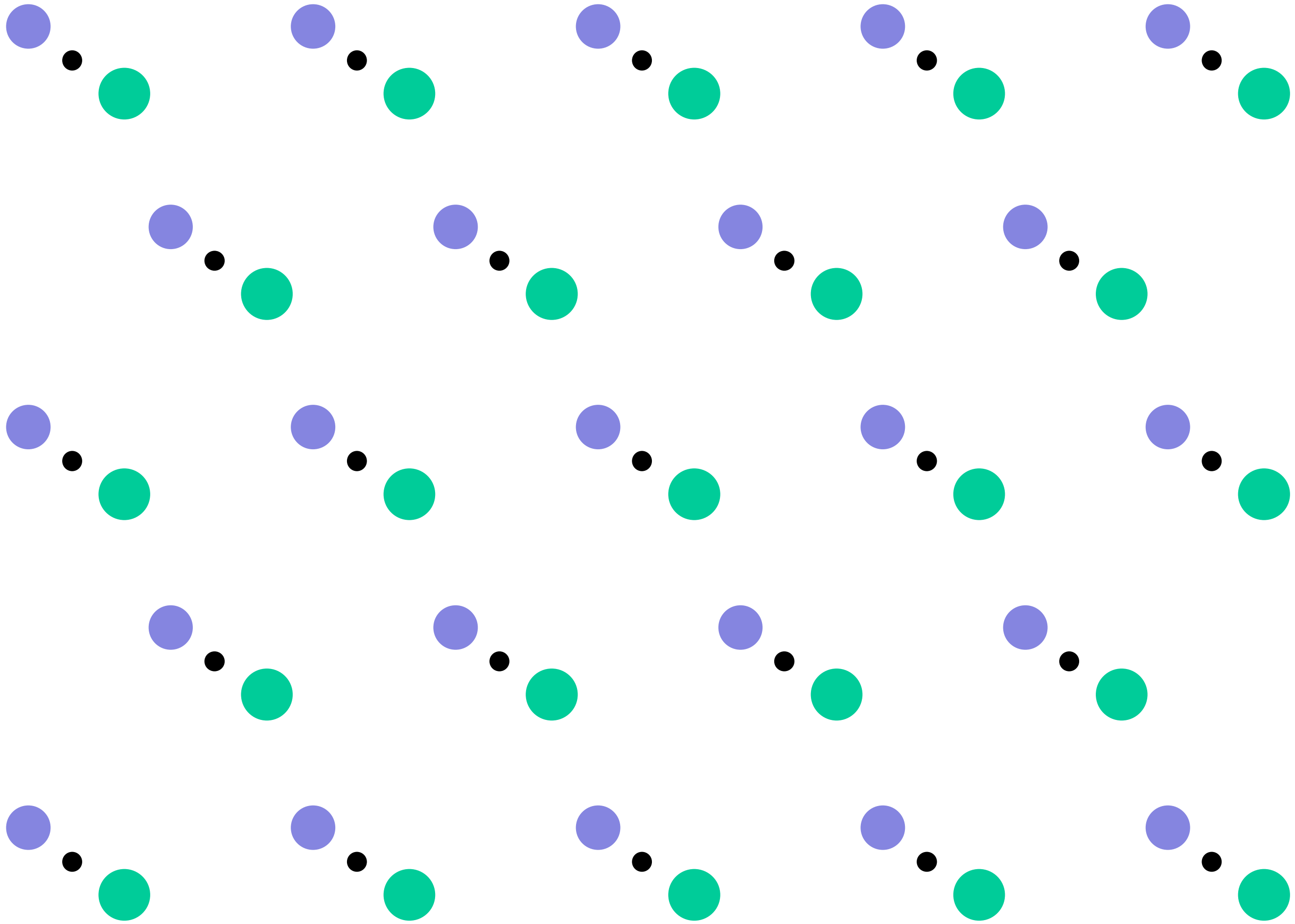
Amorphous solids: the atoms have no periodic structure whatsoever.

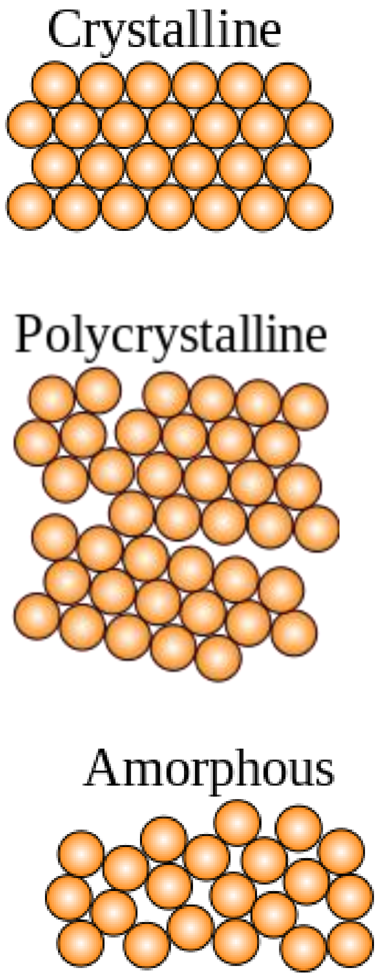


Wikipedia

Some definitions

Lattice points are points that have identical surroundings in the crystal structure.





Wikipedia

Some definitions

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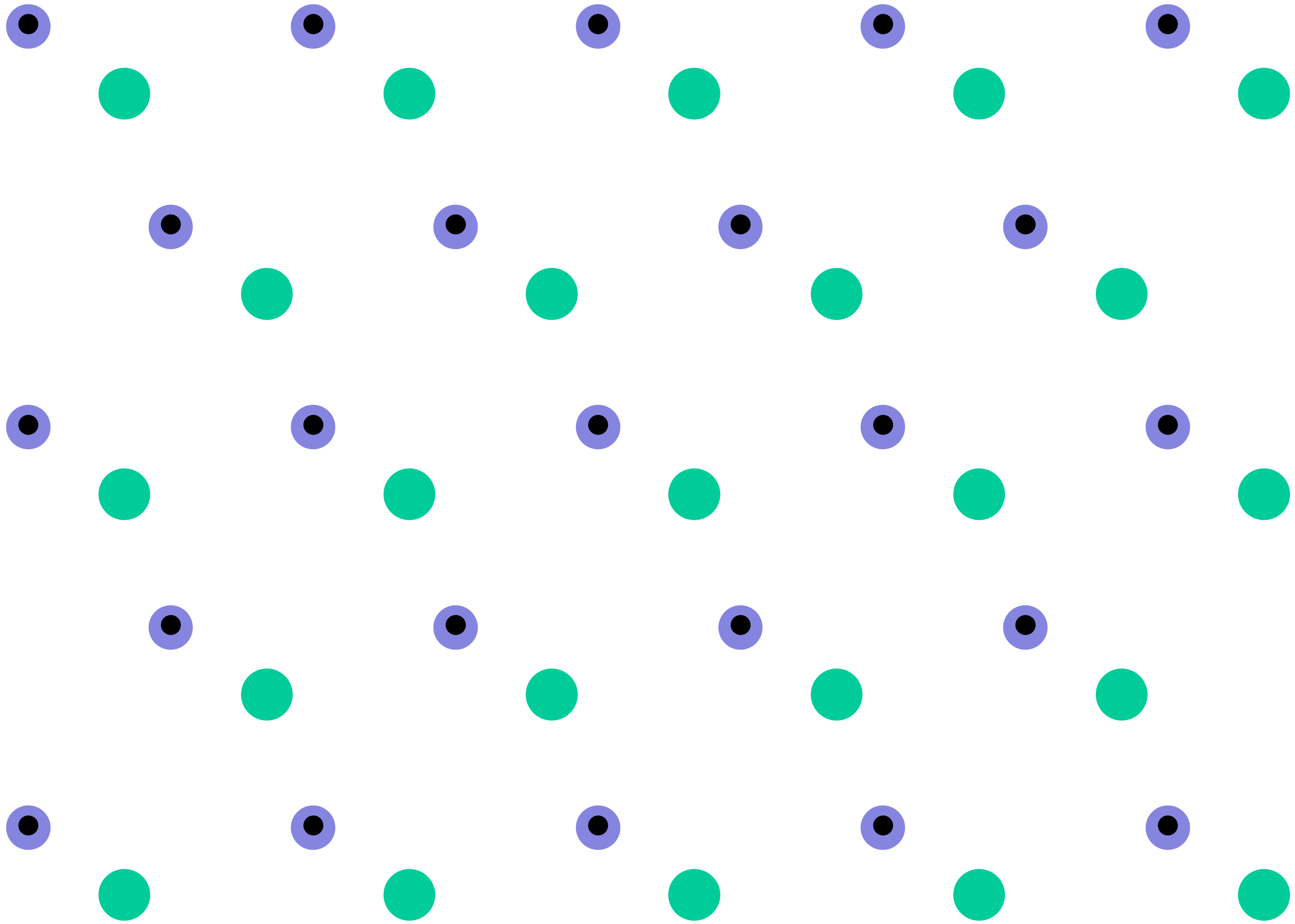
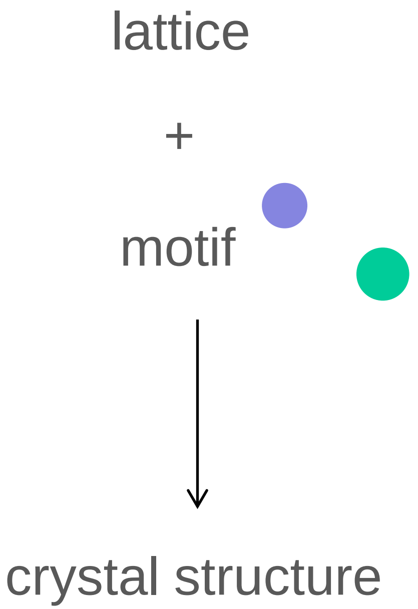
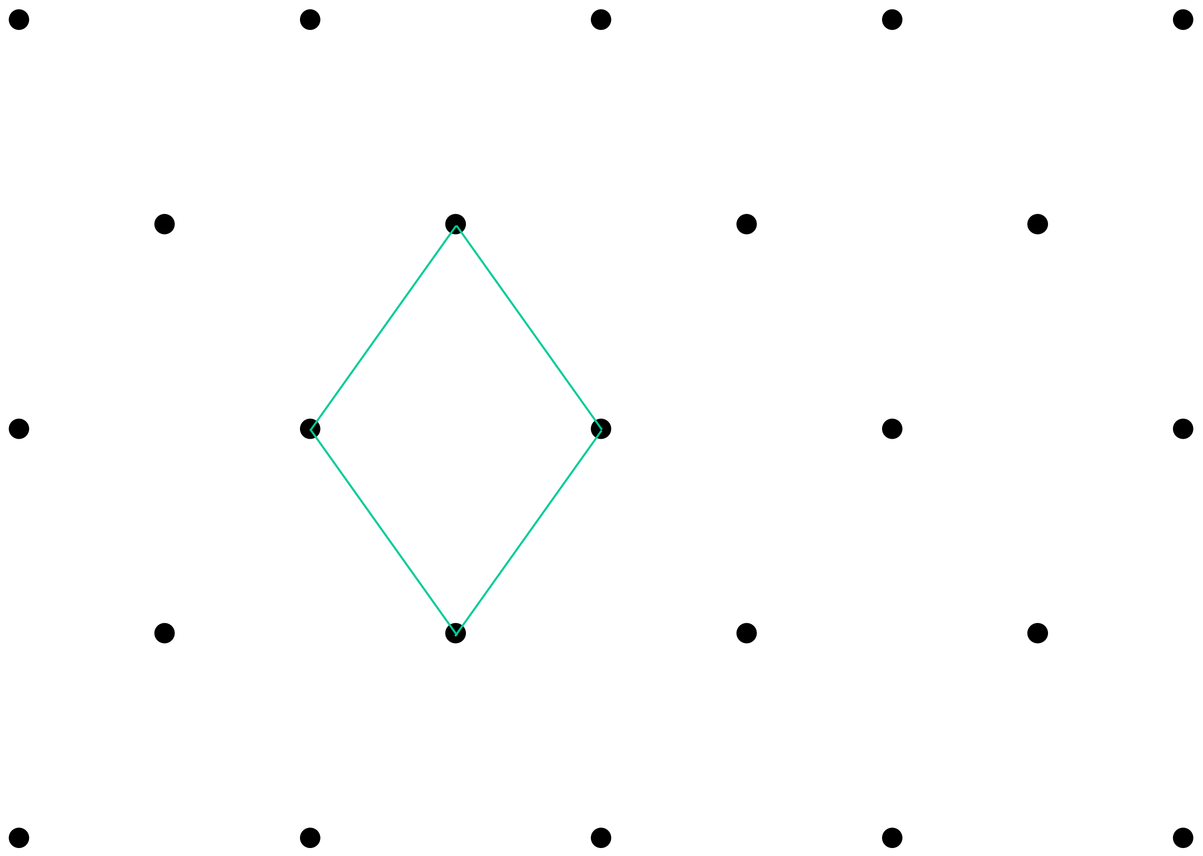




The unit cell

The *smallest* unit (“box”) that can be repeated in all directions to build up the crystal structure *and* shows the full symmetry of the crystal structure.



Is this the unit cell?

The unit cell

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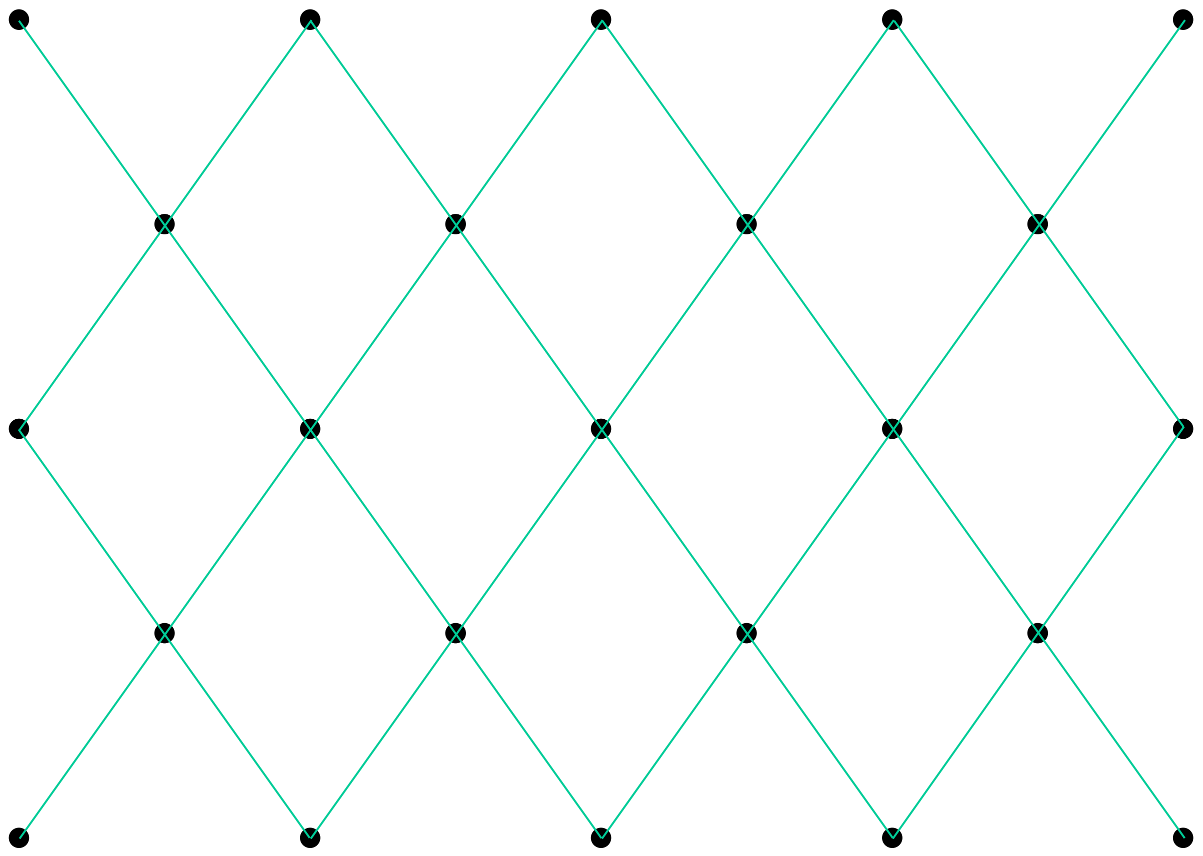

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The unit cell

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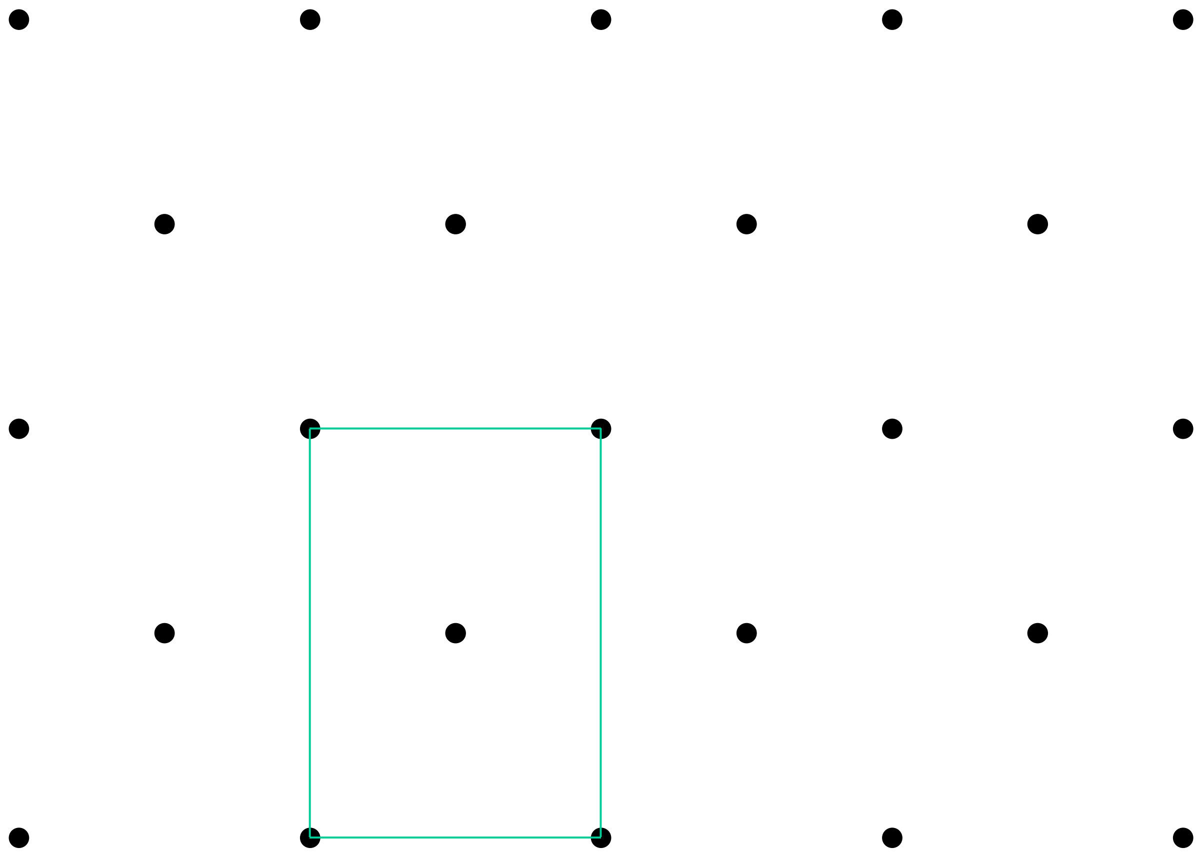
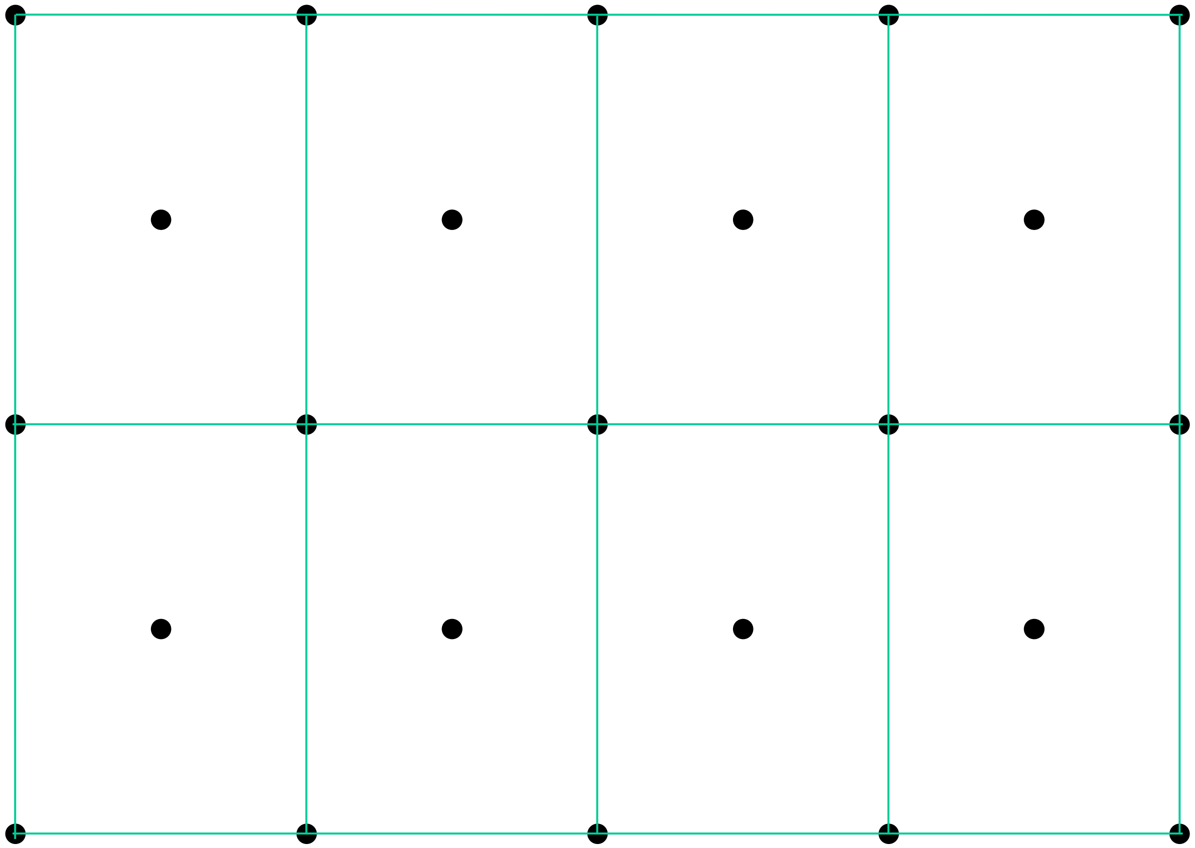


Is the unit cell?

The unit cell

The *smallest* unit (“box”) that can be repeated in all directions to build up the crystal structure *and* shows the full symmetry of the crystal structure.

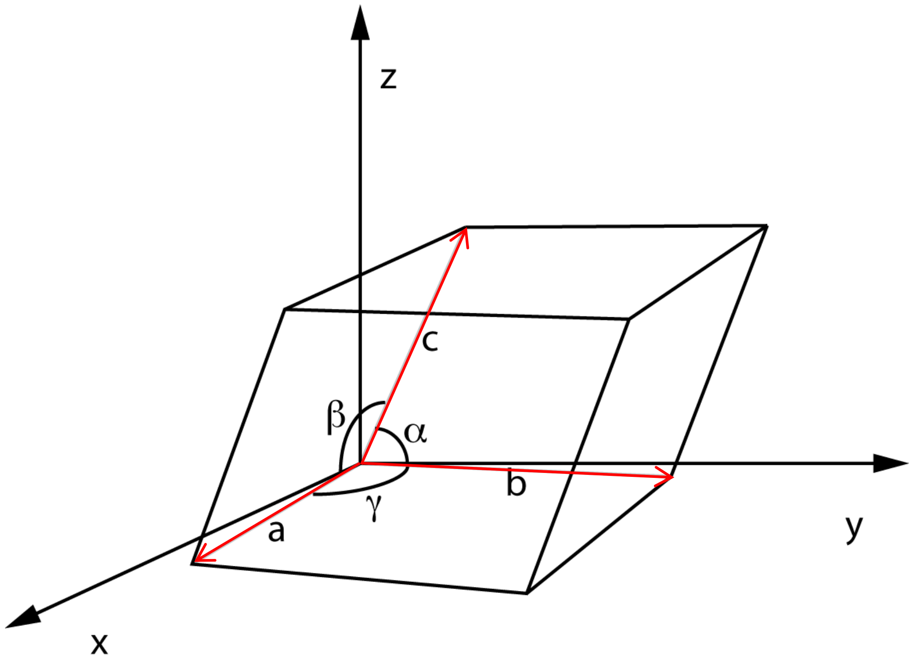


Is the unit cell?

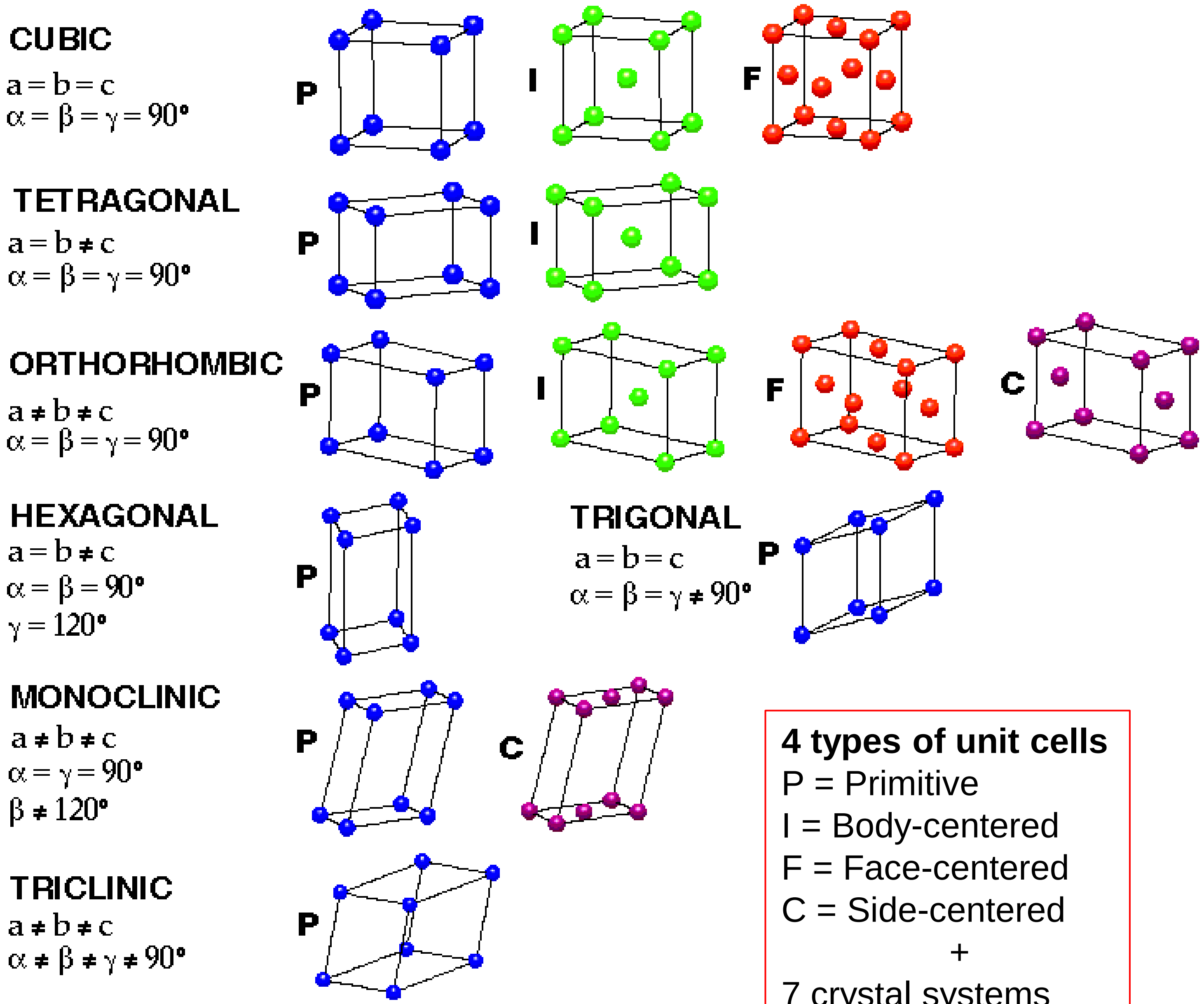
Yes! With «centered rectangular» symmetry

The unit cell

The *smallest* unit that can be repeated in all all directions to build up the crystal structure *and* shows the full symmetry of the crystal structure.



Unit cell dimensions: a, b, c, angles: **α, β, γ**
or defined by three vectors **a**, **b**, **c**



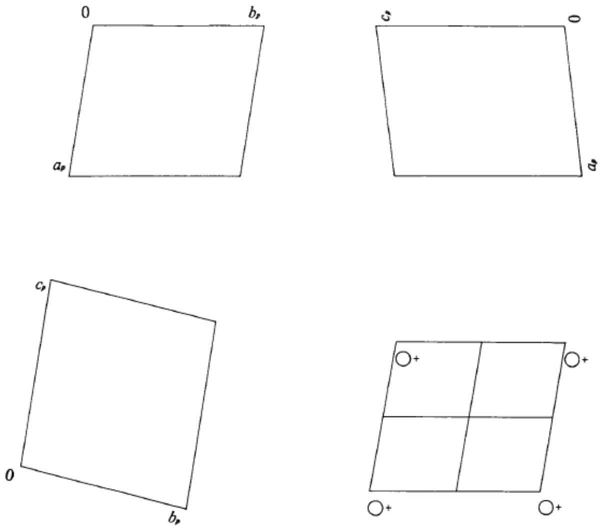
4 types of unit cells
P = Primitive
I = Body-centered
F = Face-centered
C = Side-centered
+
7 crystal systems
→ 14 Bravais lattices

Space group

14 Bravais lattices + symmetry elements (centre of symmetry, rotation axes, mirror plane, glide planes, screw axes, inversion axes).

$P1$ | C_1^1 | 1 | Triclinic

No. 1 | $P1$ | | Patterson symmetry $P\bar{1}$



Drawings for type II cell. Proper cell reduction (Chapter 9.2) gives either a type I (α, β, γ acute) or a type II (α, β, γ non-acute) cell.

Origin arbitrary

Asymmetric unit $0 \le x \le 1$; $0 \le y \le 1$; $0 \le z \le 1$

Symmetry operations

(1) 1

CONTINUED | No. 1 | $P1$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$

Positions

Multiplicity, Wyckoff letter, Site symmetry	Coordinates	Reflection conditions
		General:
1 *a* 1	(1) x,y,z	no conditions

Symmetry of special projections

Along [001] $p1$
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}_p$
Origin at $0,0,z$

Along [100] $p1$
$\mathbf{a}' = \mathbf{b}_p$ $\mathbf{b}' = \mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p1$
$\mathbf{a}' = \mathbf{c}_p$ $\mathbf{b}' = \mathbf{a}_p$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I none
IIa none
IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P1$ ($\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{b}' = 2\mathbf{b}$ or $\mathbf{c}' = 2\mathbf{c}$ or $\mathbf{b}' = \mathbf{b}+\mathbf{c}, \mathbf{c}' = -\mathbf{b}+\mathbf{c}$ or $\mathbf{a}' = \mathbf{a}-\mathbf{c}, \mathbf{c}' = \mathbf{a}+\mathbf{c}$ or $\mathbf{a}' = \mathbf{a}+\mathbf{b}, \mathbf{b}' = -\mathbf{a}+\mathbf{b}$ or $\mathbf{a}' = \mathbf{b}+\mathbf{c}, \mathbf{b}' = \mathbf{a}+\mathbf{c}, \mathbf{c}' = \mathbf{a}+\mathbf{b}$) (1)

Minimal non-isomorphic supergroups

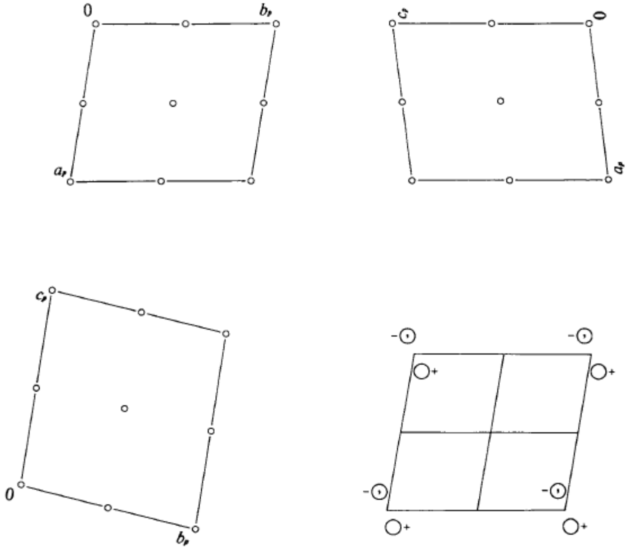
I [2] $P\bar{1}$ (2); [2] $P2$ (3); [2] $P2_1$ (4); [2] $C2$ (5); [2] Pm (6); [2] Pc (7); [2] Cm (8); [2] Cc (9); [3] $P3$ (143); [3] $P3_1$ (144); [3] $P3_2$ (145); [3] $R3$ (146)
II none

Space group

14 Bravais lattices + symmetry elements (centre of symmetry, rotation axes, mirror plane, glide planes, screw axes, inversion axes).

$P\bar{1}$ | C_i^1 | $\bar{1}$ | Triclinic

No. 2 | $P\bar{1}$ | Patterson symmetry $P\bar{1}$



Drawings for type II cell. Proper cell reduction (Chapter 9.2) gives either a type I (α, β, γ acute) or a type II (α, β, γ non-acute) cell.

Origin at $\bar{1}$

Asymmetric unit $0 \le x \le \frac{1}{2}$; $0 \le y \le 1$; $0 \le z \le 1$

Symmetry operations

(1) 1 (2) $\bar{1}$ 0,0,0

CONTINUED No. 2 $P\bar{1}$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		Reflection conditions
					General:
2	*i*	1	(1) x,y,z	(2) $\bar{x},\bar{y},\bar{z}$	no conditions
					Special: no extra conditions
1	*h*	$\bar{1}$	$\frac{1}{2},\frac{1}{2},\frac{1}{2}$		
1	*g*	$\bar{1}$	$0,\frac{1}{2},\frac{1}{2}$		
1	*f*	$\bar{1}$	$\frac{1}{2},0,\frac{1}{2}$		
1	*e*	$\bar{1}$	$\frac{1}{2},\frac{1}{2},0$		
1	*d*	$\bar{1}$	$\frac{1}{2},0,0$		
1	*c*	$\bar{1}$	$0,\frac{1}{2},0$		
1	*b*	$\bar{1}$	$0,0,\frac{1}{2}$		
1	*a*	$\bar{1}$	$0,0,0$		

Symmetry of special projections

Along [001] $p2$
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}_p$
Origin at $0,0,z$

Along [100] $p2$
$\mathbf{a}' = \mathbf{b}_p$ $\mathbf{b}' = \mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}' = \mathbf{c}_p$ $\mathbf{b}' = \mathbf{a}_p$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P1$ (1) 1
IIa none
IIb none

Maximal isomorphic subgroups of lowest index

IIc [2] $P\bar{1}$ ($\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{b}' = 2\mathbf{b}$ or $\mathbf{c}' = 2\mathbf{c}$ or $\mathbf{b}' = \mathbf{b}+\mathbf{c}, \mathbf{c}' = -\mathbf{b}+\mathbf{c}$ or $\mathbf{a}' = \mathbf{a}-\mathbf{c}, \mathbf{c}' = \mathbf{a}+\mathbf{c}$ or $\mathbf{a}' = \mathbf{a}+\mathbf{b}, \mathbf{b}' = -\mathbf{a}+\mathbf{b}$ or $\mathbf{a}' = \mathbf{b}+\mathbf{c}, \mathbf{b}' = \mathbf{a}+\mathbf{c}, \mathbf{c}' = \mathbf{a}+\mathbf{b}$) (2)

Minimal non-isomorphic supergroups

I [2] $P2/m$ (10); [2] $P2_1/m$ (11); [2] $C2/m$ (12); [2] $P2/c$ (13); [2] $P2_1/c$ (14); [2] $C2/c$ (15); [3] $P\bar{3}$ (147); [3] $R\bar{3}$ (148)
II none

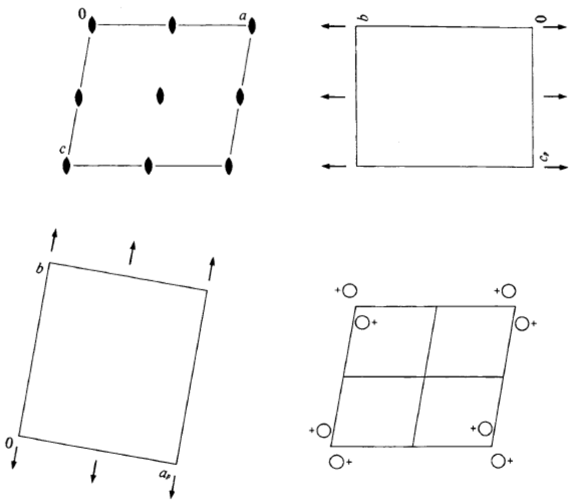
Space group

14 Bravais lattices + symmetry elements (centre of symmetry, rotation axes, mirror plane, glide planes, screw axes, inversion axes).

$P2$ | C_2^1 | 2 | Monoclinic

No. 3 | $P121$ | Patterson symmetry $P12/m1$

UNIQUE AXIS b



Origin on 2

Asymmetric unit $0 \le x \le 1;\quad 0 \le y \le 1;\quad 0 \le z \le \frac{1}{2}$

Symmetry operations

(1) 1 (2) 2 $0,y,0$

CONTINUED No. 3 $P2$

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; (2)

Positions

Multiplicity, Wyckoff letter, Site symmetry			Coordinates		Reflection conditions
					General:
2	e	1	(1) x,y,z	(2) $\bar{x},y,\bar{z}$	no conditions
					Special: no extra conditions
1	d	2	$\frac{1}{2},y,\frac{1}{2}$		
1	c	2	$\frac{1}{2},y,0$		
1	b	2	$0,y,\frac{1}{2}$		
1	a	2	$0,y,0$		

Symmetry of special projections

Along [001] $p1m1$
$\mathbf{a}' = \mathbf{a}_p$ $\mathbf{b}' = \mathbf{b}$
Origin at $0,0,z$

Along [100] $p11m$
$\mathbf{a}' = \mathbf{b}$ $\mathbf{b}' = \mathbf{c}_p$
Origin at $x,0,0$

Along [010] $p2$
$\mathbf{a}' = \mathbf{c}$ $\mathbf{b}' = \mathbf{a}$
Origin at $0,y,0$

Maximal non-isomorphic subgroups

I [2] $P1$ (1) 1

IIa none

IIb [2] $P12_11$ ($\mathbf{b}' = 2\mathbf{b}$) ($P2_1$, 4); [2] $C121$ ($\mathbf{a}' = 2\mathbf{a}, \mathbf{b}' = 2\mathbf{b}$) ($C2$, 5); [2] $A121$ ($\mathbf{b}' = 2\mathbf{b}, \mathbf{c}' = 2\mathbf{c}$) ($C2$, 5); [2] $F121$ ($\mathbf{a}' = 2\mathbf{a}, \mathbf{b}' = 2\mathbf{b}, \mathbf{c}' = 2\mathbf{c}$) ($C2$, 5)

Maximal isomorphic subgroups of lowest index

IIc [2] $P121$ ($\mathbf{b}' = 2\mathbf{b}$) ($P2$, 3); [2] $P121$ ($\mathbf{c}' = 2\mathbf{c}$ or $\mathbf{a}' = 2\mathbf{a}$ or $\mathbf{a}' = \mathbf{a}+\mathbf{c}, \mathbf{c}' = -\mathbf{a}+\mathbf{c}$) ($P2$, 3)

Minimal non-isomorphic supergroups

I [2] $P2/m$ (10); [2] $P2/c$ (13); [2] $P222$ (16); [2] $P222_1$ (17); [2] $P2_12_12$ (18); [2] $C222$ (21); [2] $Pmm2$ (25); [2] $Pcc2$ (27); [2] $Pma2$ (28); [2] $Pnc2$ (30); [2] $Pba2$ (32); [2] $Pnn2$ (34); [2] $Cmm2$ (35); [2] $Ccc2$ (37); [2] $P4$ (75); [2] $P4_2$ (77); [2] $P\bar{4}$ (81); [3] $P6$ (168); [3] $P6_2$ (171); [3] $P6_4$ (172)

II [2] $C121$ ($C2$, 5); [2] $A121$ ($C2$, 5); [2] $I121$ ($C2$, 5)

Space group

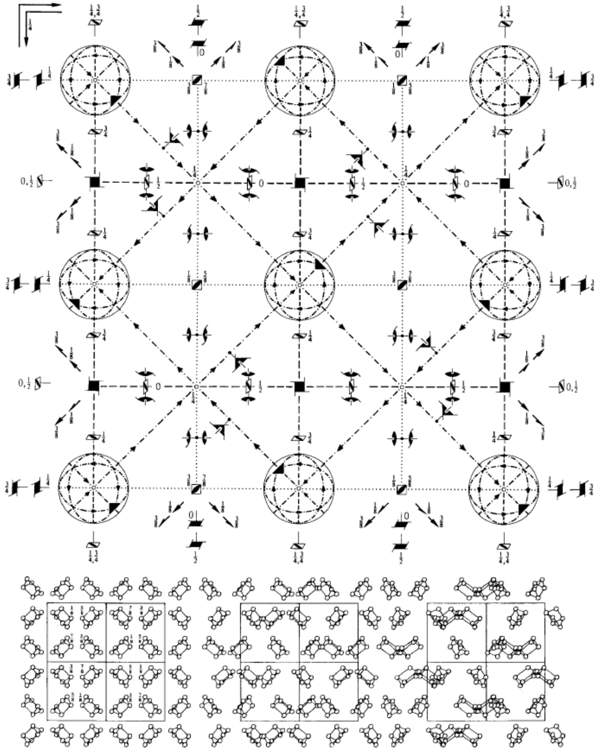
14 Bravais lattices + symmetry elements (centre of symmetry, rotation axes, mirror plane, glide planes, screw axes, inversion axes).

Up to 230 different ways to replicate a finite object in 3-dimensional space.

⇒ ***230 space groups***

$I\,a\bar{3}d$ $\quad O_h^{10}$ $\quad m\bar{3}m$ Cubic

No. 230 $\quad I\;4_1/a\;\bar{3}\;2/d$ Patterson symmetry $I\,m\bar{3}m$



CONTINUED No. 230 $I\,a\bar{3}d$

Symmetry operations
(*given on page* 715)

Generators selected (1); $t(1,0,0)$; $t(0,1,0)$; $t(0,0,1)$; $t(\frac{1}{2},\frac{1}{2},\frac{1}{2})$; (2); (3); (5); (13); (25)

Positions

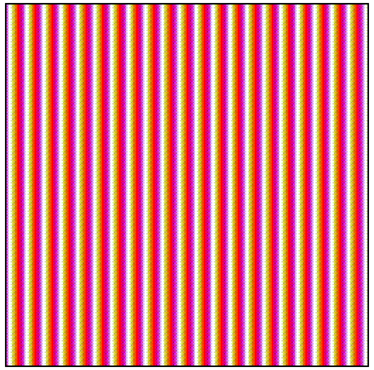
Multiplicity, Wyckoff letter, Site symmetry			Coordinates $(0,0,0)+\ (\frac{1}{2},\frac{1}{2},\frac{1}{2})+$								Reflection conditions (h,k,l permutable)
											General:
96	*h*	1	(1) x,y,z	(2) $\bar{x}+\frac{1}{2},\bar{y},z+\frac{1}{2}$	(3) $\bar{x},y+\frac{1}{2},\bar{z}+\frac{1}{2}$	(4) $x+\frac{1}{2},\bar{y}+\frac{1}{2},\bar{z}$					hkl : $h+k+l=2n$
			(5) z,x,y	(6) $z+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{y}$	(7) $\bar{z}+\frac{1}{2},\bar{x},y+\frac{1}{2}$	(8) $\bar{z},x+\frac{1}{2},\bar{y}+\frac{1}{2}$					$0kl$: $k,l=2n$
			(9) y,z,x	(10) $\bar{y},z+\frac{1}{2},\bar{x}+\frac{1}{2}$	(11) $y+\frac{1}{2},\bar{z}+\frac{1}{2},\bar{x}$	(12) $\bar{y}+\frac{1}{2},\bar{z},x+\frac{1}{2}$					hhl : $2h+l=4n$
			(13) $y+\frac{3}{4},x+\frac{1}{4},\bar{z}+\frac{1}{4}$	(14) $\bar{y}+\frac{3}{4},\bar{x}+\frac{3}{4},\bar{z}+\frac{3}{4}$	(15) $y+\frac{1}{4},\bar{x}+\frac{1}{4},z+\frac{3}{4}$	(16) $\bar{y}+\frac{1}{4},x+\frac{3}{4},z+\frac{1}{4}$					$h00$: $h=4n$
			(17) $x+\frac{3}{4},z+\frac{1}{4},\bar{y}+\frac{1}{4}$	(18) $\bar{x}+\frac{1}{4},z+\frac{3}{4},y+\frac{1}{4}$	(19) $\bar{x}+\frac{3}{4},\bar{z}+\frac{3}{4},\bar{y}+\frac{3}{4}$	(20) $x+\frac{1}{4},\bar{z}+\frac{1}{4},y+\frac{3}{4}$					
			(21) $z+\frac{3}{4},y+\frac{1}{4},\bar{x}+\frac{1}{4}$	(22) $z+\frac{1}{4},\bar{y}+\frac{1}{4},x+\frac{3}{4}$	(23) $\bar{z}+\frac{1}{4},y+\frac{3}{4},x+\frac{1}{4}$	(24) $\bar{z}+\frac{3}{4},\bar{y}+\frac{3}{4},\bar{x}+\frac{3}{4}$					
			(25) $\bar{x},\bar{y},\bar{z}$	(26) $x+\frac{1}{2},y,\bar{z}+\frac{1}{2}$	(27) $x,\bar{y}+\frac{1}{2},z+\frac{1}{2}$	(28) $\bar{x}+\frac{1}{2},y+\frac{1}{2},z$					
			(29) $\bar{z},\bar{x},\bar{y}$	(30) $\bar{z}+\frac{1}{2},x+\frac{1}{2},y$	(31) $z+\frac{1}{2},x,\bar{y}+\frac{1}{2}$	(32) $z,\bar{x}+\frac{1}{2},y+\frac{1}{2}$					
			(33) $\bar{y},\bar{z},\bar{x}$	(34) $y,\bar{z}+\frac{1}{2},x+\frac{1}{2}$	(35) $\bar{y}+\frac{1}{2},z+\frac{1}{2},x$	(36) $y+\frac{1}{2},z,\bar{x}+\frac{1}{2}$					
			(37) $\bar{y}+\frac{1}{4},\bar{x}+\frac{3}{4},z+\frac{3}{4}$	(38) $y+\frac{1}{4},x+\frac{1}{4},z+\frac{1}{4}$	(39) $\bar{y}+\frac{3}{4},x+\frac{3}{4},\bar{z}+\frac{1}{4}$	(40) $y+\frac{3}{4},\bar{x}+\frac{1}{4},\bar{z}+\frac{3}{4}$					
			(41) $\bar{x}+\frac{1}{4},\bar{z}+\frac{3}{4},y+\frac{3}{4}$	(42) $x+\frac{3}{4},\bar{z}+\frac{1}{4},\bar{y}+\frac{3}{4}$	(43) $x+\frac{1}{4},z+\frac{1}{4},y+\frac{1}{4}$	(44) $\bar{x}+\frac{3}{4},z+\frac{3}{4},\bar{y}+\frac{1}{4}$					
			(45) $\bar{z}+\frac{1}{4},\bar{y}+\frac{3}{4},x+\frac{3}{4}$	(46) $\bar{z}+\frac{3}{4},y+\frac{3}{4},\bar{x}+\frac{1}{4}$	(47) $z+\frac{3}{4},\bar{y}+\frac{1}{4},\bar{x}+\frac{3}{4}$	(48) $z+\frac{1}{4},y+\frac{1}{4},x+\frac{1}{4}$					
											Special: as above, plus
48	*g*	..2	$\frac{1}{8},y,\bar{y}+\frac{1}{4}$	$\frac{3}{8},\bar{y},\bar{y}+\frac{3}{4}$	$\frac{7}{8},y+\frac{1}{2},y+\frac{1}{4}$	$\frac{5}{8},\bar{y}+\frac{1}{2},y+\frac{3}{4}$					hkl : $h=2n+1$
			$\bar{y}+\frac{1}{4},\frac{1}{8},y$	$\bar{y}+\frac{3}{4},\frac{3}{8},\bar{y}$	$y+\frac{1}{4},\frac{7}{8},y+\frac{1}{2}$	$y+\frac{3}{4},\frac{5}{8},\bar{y}+\frac{1}{2}$					or $h=4n$
			$y,\bar{y}+\frac{1}{4},\frac{1}{8}$	$\bar{y},\bar{y}+\frac{3}{4},\frac{3}{8}$	$y+\frac{1}{2},y+\frac{1}{4},\frac{7}{8}$	$\bar{y}+\frac{1}{2},y+\frac{3}{4},\frac{5}{8}$					
			$\frac{7}{8},\bar{y},y+\frac{3}{4}$	$\frac{5}{8},y,y+\frac{1}{4}$	$\frac{1}{8},\bar{y}+\frac{1}{2},\bar{y}+\frac{3}{4}$	$\frac{3}{8},y+\frac{1}{2},\bar{y}+\frac{1}{4}$					
			$y+\frac{3}{4},\frac{7}{8},\bar{y}$	$y+\frac{1}{4},\frac{5}{8},y$	$\bar{y}+\frac{3}{4},\frac{1}{8},\bar{y}+\frac{1}{2}$	$\bar{y}+\frac{1}{4},\frac{3}{8},y+\frac{1}{2}$					
			$\bar{y},y+\frac{3}{4},\frac{7}{8}$	$y,y+\frac{1}{4},\frac{5}{8}$	$\bar{y}+\frac{1}{2},\bar{y}+\frac{3}{4},\frac{1}{8}$	$y+\frac{1}{2},\bar{y}+\frac{1}{4},\frac{3}{8}$					
48	*f*	2..	$x,0,\frac{1}{4}$	$\bar{x}+\frac{1}{2},0,\frac{3}{4}$	$\frac{1}{4},x,0$	$\frac{3}{4},\bar{x}+\frac{1}{2},0$	$0,\frac{1}{4},x$	$0,\frac{3}{4},\bar{x}+\frac{1}{2}$			hkl : $2h+l=4n$
			$\frac{3}{4},x+\frac{1}{4},0$	$\frac{3}{4},\bar{x}+\frac{3}{4},\frac{1}{2}$	$x+\frac{3}{4},\frac{1}{2},\frac{1}{4}$	$\bar{x}+\frac{1}{4},0,\frac{1}{4}$	$0,\frac{1}{4},\bar{x}+\frac{1}{4}$	$\frac{1}{2},\frac{1}{4},x+\frac{3}{4}$			
			$\bar{x},0,\frac{3}{4}$	$x+\frac{1}{2},0,\frac{1}{4}$	$\frac{3}{4},\bar{x},0$	$\frac{1}{4},x+\frac{1}{2},0$	$0,\frac{3}{4},\bar{x}$	$0,\frac{1}{4},x+\frac{1}{2}$			
			$\frac{1}{4},\bar{x}+\frac{3}{4},0$	$\frac{1}{4},x+\frac{1}{4},\frac{1}{2}$	$\bar{x}+\frac{1}{4},\frac{1}{2},\frac{3}{4}$	$x+\frac{3}{4},0,\frac{3}{4}$	$0,\frac{3}{4},x+\frac{3}{4}$	$\frac{1}{2},\frac{3}{4},\bar{x}+\frac{1}{4}$			
32	*e*	.3.	x,x,x	$\bar{x}+\frac{1}{2},\bar{x},x+\frac{1}{2}$	$\bar{x},x+\frac{1}{2},\bar{x}+\frac{1}{2}$	$x+\frac{1}{2},\bar{x}+\frac{1}{2},\bar{x}$					hkl : $h=2n+1$
			$x+\frac{3}{4},x+\frac{1}{4},\bar{x}+\frac{1}{4}$	$\bar{x}+\frac{3}{4},\bar{x}+\frac{3}{4},\bar{x}+\frac{3}{4}$	$x+\frac{1}{4},\bar{x}+\frac{1}{4},x+\frac{3}{4}$	$\bar{x}+\frac{1}{4},x+\frac{3}{4},x+\frac{1}{4}$					or $h+k+l=4n$
			$\bar{x},\bar{x},\bar{x}$	$x+\frac{1}{2},x,\bar{x}+\frac{1}{2}$	$x,\bar{x}+\frac{1}{2},x+\frac{1}{2}$	$\bar{x}+\frac{1}{2},x+\frac{1}{2},x$					
			$\bar{x}+\frac{1}{4},\bar{x}+\frac{3}{4},x+\frac{3}{4}$	$x+\frac{1}{4},x+\frac{1}{4},x+\frac{1}{4}$	$\bar{x}+\frac{3}{4},x+\frac{3}{4},\bar{x}+\frac{1}{4}$	$x+\frac{3}{4},\bar{x}+\frac{1}{4},\bar{x}+\frac{3}{4}$					
24	*d*	$\bar{4}$..	$\frac{3}{8},0,\frac{1}{4}$	$\frac{1}{8},0,\frac{3}{4}$	$\frac{1}{4},\frac{3}{8},0$	$\frac{3}{4},\frac{1}{8},0$	$0,\frac{1}{4},\frac{3}{8}$	$0,\frac{3}{4},\frac{1}{8}$			hkl : $h,k=2n,\ h+k+l=4n$
			$\frac{3}{4},\frac{5}{8},0$	$\frac{3}{4},\frac{3}{8},\frac{1}{2}$	$\frac{1}{8},\frac{1}{2},\frac{1}{4}$	$\frac{7}{8},0,\frac{1}{4}$	$0,\frac{1}{4},\frac{7}{8}$	$\frac{1}{2},\frac{1}{4},\frac{1}{8}$			or $h,k=2n+1,\ l=4n+2$
											or $h=8n,\ k=8n+4$ and $h+k+l=4n+2$
24	*c*	2.22	$\frac{1}{8},0,\frac{1}{4}$	$\frac{3}{8},0,\frac{3}{4}$	$\frac{1}{4},\frac{1}{8},0$	$\frac{3}{4},\frac{3}{8},0$	$0,\frac{1}{4},\frac{1}{8}$	$0,\frac{3}{4},\frac{3}{8}$			
			$\frac{7}{8},0,\frac{3}{4}$	$\frac{5}{8},0,\frac{1}{4}$	$\frac{3}{4},\frac{7}{8},0$	$\frac{1}{4},\frac{5}{8},0$	$0,\frac{3}{4},\frac{7}{8}$	$0,\frac{1}{4},\frac{5}{8}$			
16	*b*	.32	$\frac{1}{8},\frac{1}{8},\frac{1}{8}$	$\frac{3}{8},\frac{7}{8},\frac{5}{8}$	$\frac{7}{8},\frac{5}{8},\frac{3}{8}$	$\frac{5}{8},\frac{3}{8},\frac{7}{8}$	$\frac{7}{8},\frac{7}{8},\frac{7}{8}$	$\frac{5}{8},\frac{1}{8},\frac{3}{8}$	$\frac{1}{8},\frac{3}{8},\frac{5}{8}$	$\frac{3}{8},\frac{5}{8},\frac{1}{8}$	hkl : $h,k=2n+1,\ l=4n+2$
											or $h,k,l=4n$
16	*a*	$.\bar{3}.$	$0,0,0$	$\frac{1}{2},0,\frac{1}{2}$	$0,\frac{1}{2},\frac{1}{2}$	$\frac{1}{2},\frac{1}{2},0$	$\frac{3}{4},\frac{1}{4},\frac{1}{4}$	$\frac{3}{4},\frac{3}{4},\frac{3}{4}$	$\frac{1}{4},\frac{1}{4},\frac{3}{4}$	$\frac{1}{4},\frac{3}{4},\frac{1}{4}$	hkl : $h,k=2n,\ h+k+l=4n$

(*Continued on page 715*)

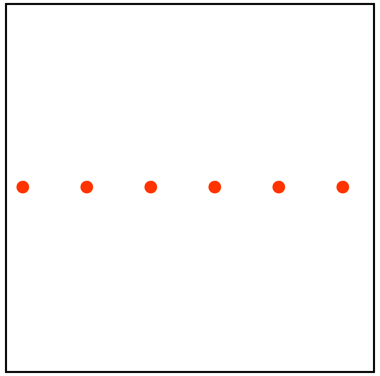
Diffraction

- Laser at slits gives line of diffractions points
  - Repeating units in three dimensions give rise to diffraction pattern
  - Repeating units: Unit cells

a

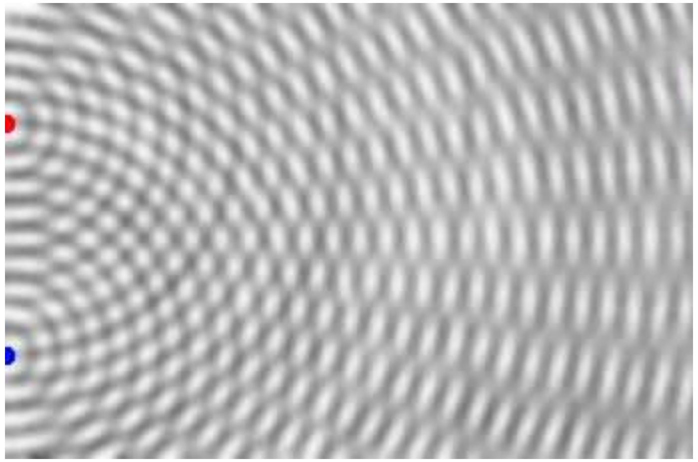


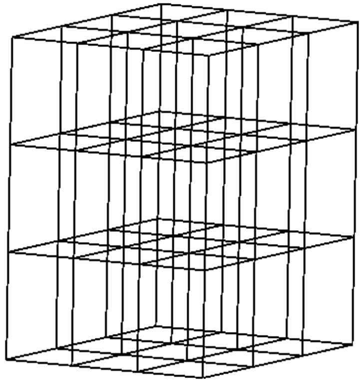
1/a

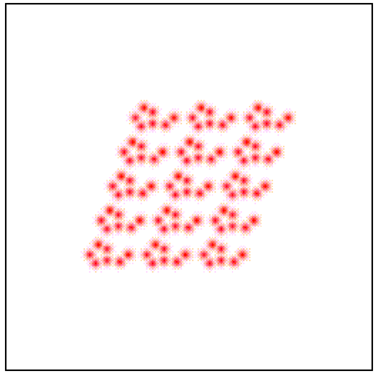


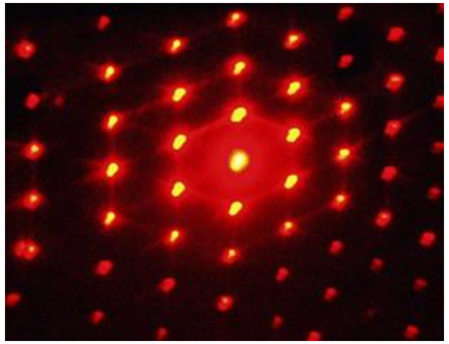
Diffracting object
(Real space)

Measurements
(Reciprocal space)

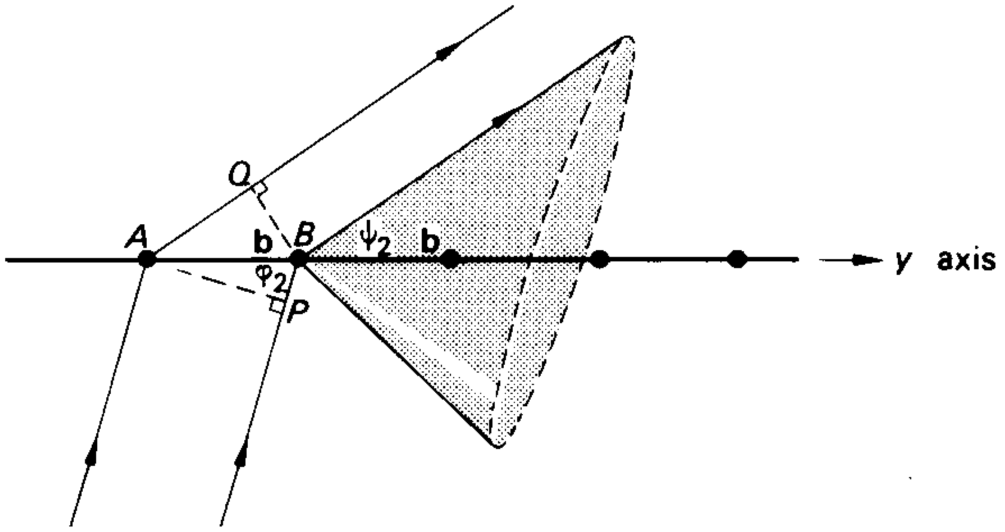








Direction of diffracted beams: Laue's interference condition



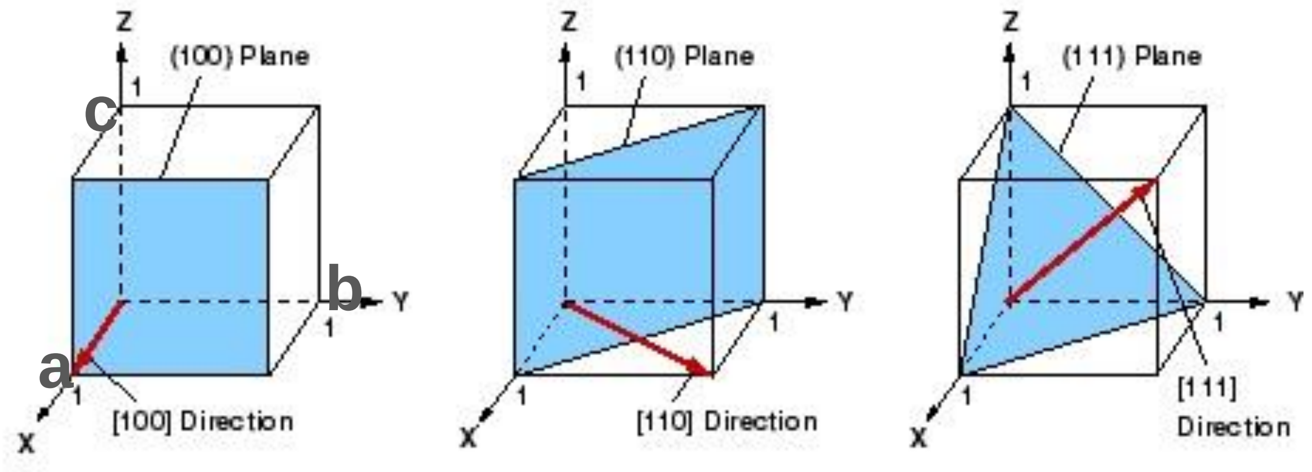
- To get interference (assuming elastic scattering):

  $$AQ\text{-}PB = b(\cos\psi_2 - \cos\varphi_2) = m\lambda \quad (m = \text{integer})$$

- In 3D:

$$\left.\begin{aligned} a(\cos\psi_1 - \cos\varphi_1) &= h\lambda \\ b(\cos\psi_2 - \cos\varphi_2) &= k\lambda \\ c(\cos\psi_3 - \cos\varphi_3) &= l\lambda \end{aligned}\right\} \text{Laue equations}$$

Miller indices

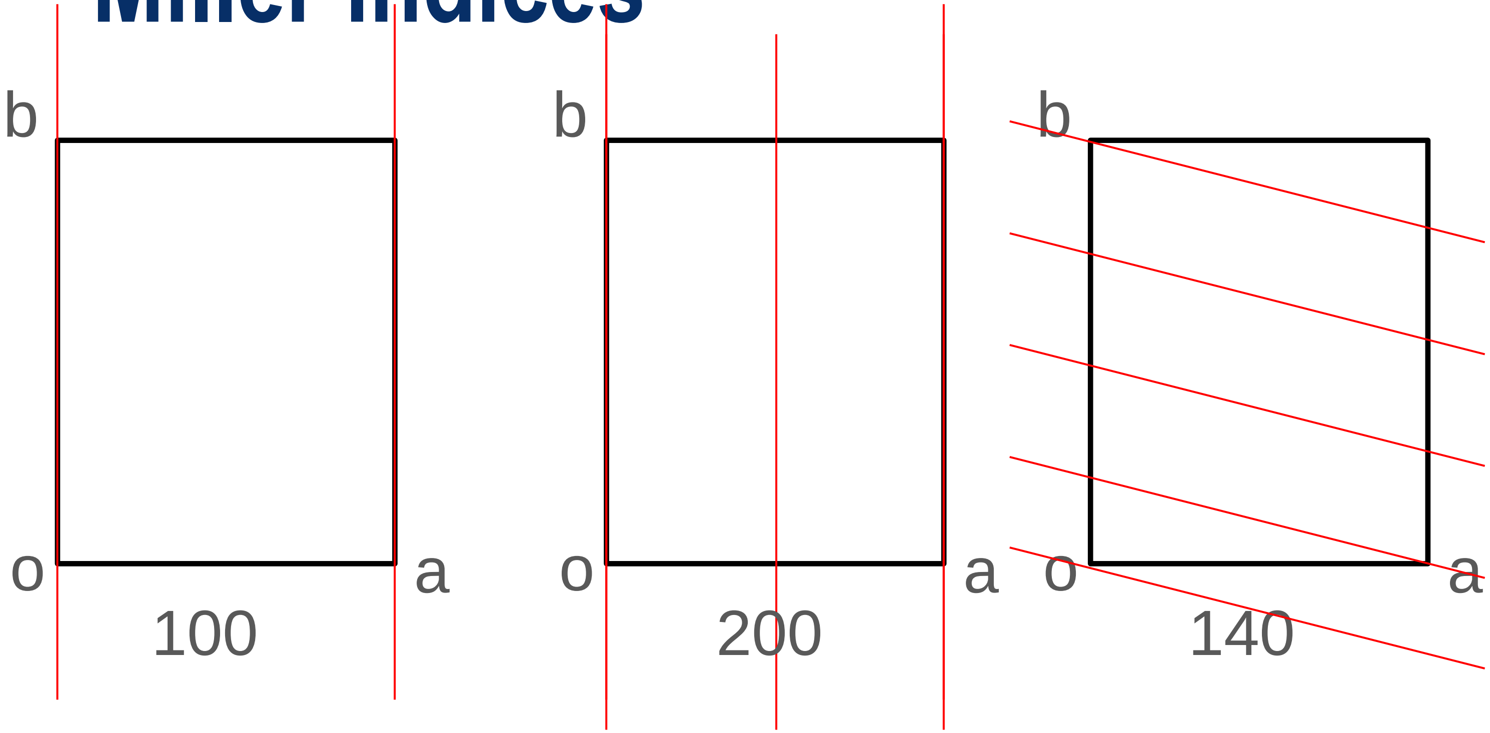


The (*hkl*) plane makes intercepts **a**/*h*, **b**/*k* and **c**/*l* along the x, y, z axes.

The direction [*hkl*] is perpendicular to the (*hkl*) plane.

a,**b**,**c**: Unit cell dimensions

Miller indices

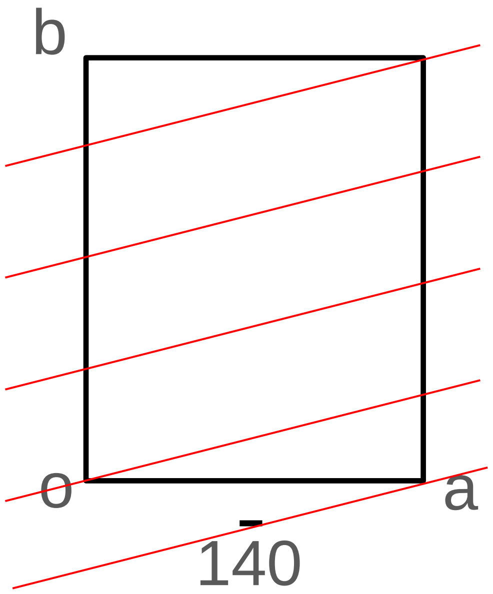


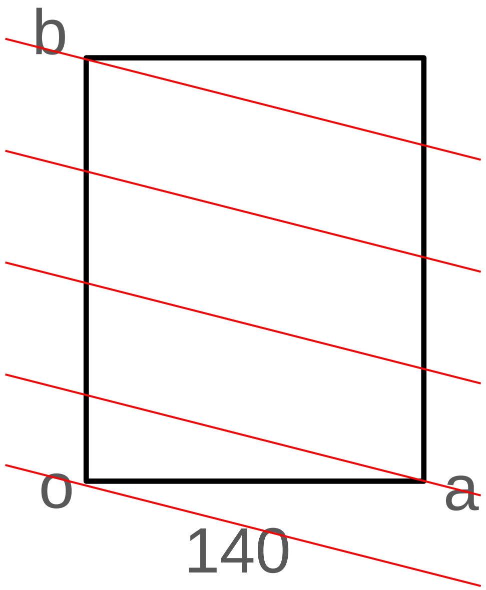
The (*hkl*) plane makes intercepts **a**/*h*, **b**/*k* and **c**/*l* along the x, y, z axes.

The direction [*hkl*] is perpendicular to the (*hkl*) plane.

a,**b**,**c**: Unit cell dimensions

Miller indices



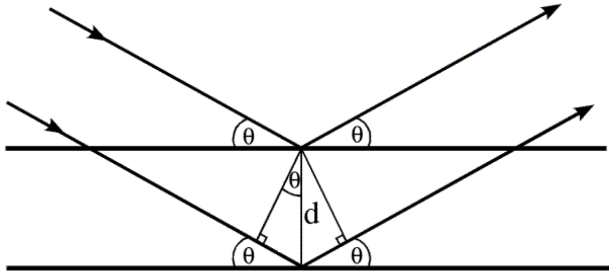


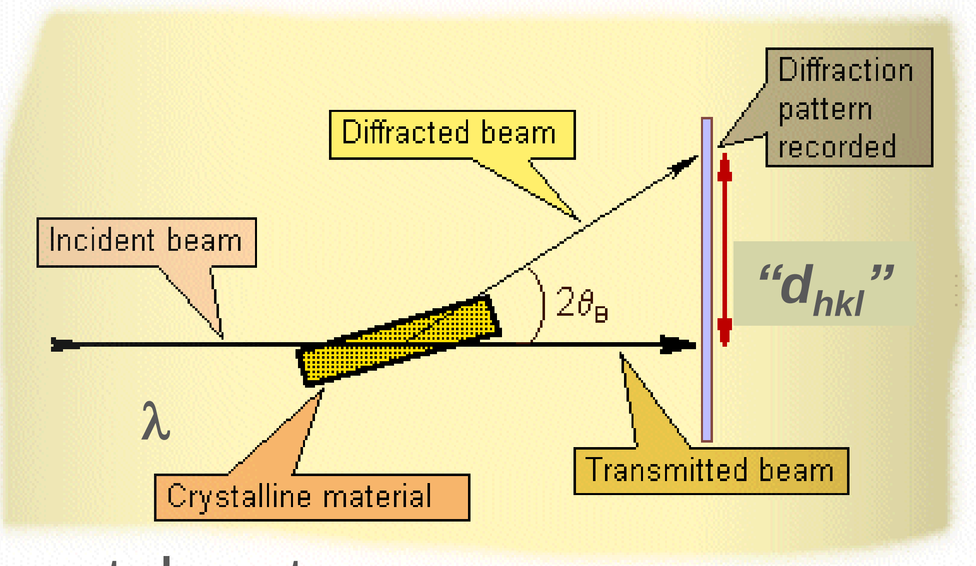
The (*hkl*) plane makes intercepts **a**/*h*, **b**/*k* and **c**/*l* along the x, y, z axes.

The direction [*hkl*] is perpendicular to the (*hkl*) plane.

a,**b**,**c**: Unit cell dimensions

Bragg's law





$$2d_{hkl}\sin\theta = \lambda$$

Ex. Orthorhombic crystal system:

$$d_{hkl} = \frac{1}{\sqrt{(\frac{h}{a})^2 + (\frac{k}{b})^2 + (\frac{l}{c})^2}}$$

Cubic:

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Reciprocal space

Definitions:

a*, **b***, **c***: Reciprocal lattice vectors

$$\mathbf{a}^* = \frac{2\pi}{V_c}(\mathbf{b}\ x\ \mathbf{c});\ \mathbf{b}^* = \frac{2\pi}{V_c}(\mathbf{c}\ x\ \mathbf{a});\ \mathbf{c}^* = \frac{2\pi}{V_c}(\mathbf{a}\ x\ \mathbf{b})$$

V_c = volume of the unit cell

a* perpendicular to the plane containing **b** and **c**
b* perpendicular to plane containing **a** and **c**
c* perpendicular to plane containing **a** and **b**

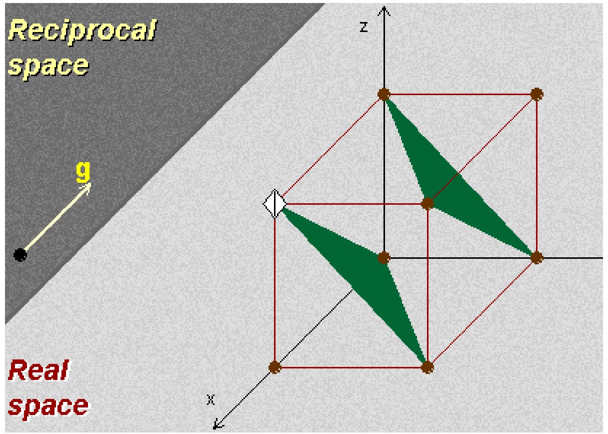
$$\mathbf{a}^*\cdot\mathbf{b} = \mathbf{a}^*\cdot\mathbf{c} = \mathbf{b}^*\cdot\mathbf{a} = \mathbf{b}^*\cdot\mathbf{c} = \mathbf{c}^*\cdot\mathbf{a} = \mathbf{c}^*\cdot\mathbf{b} = 0$$

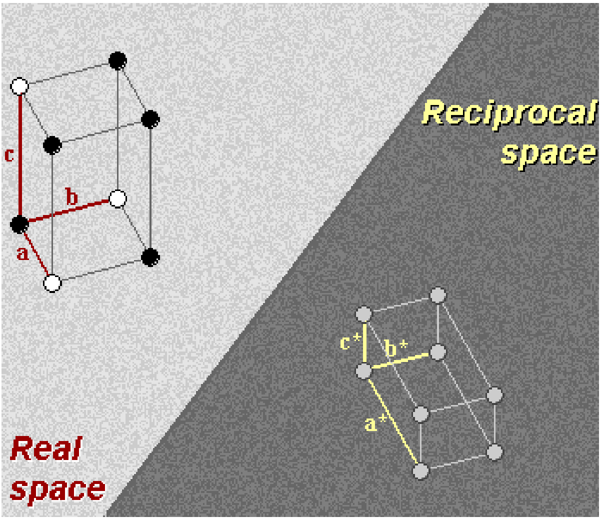
$$\mathbf{a}^*\cdot\mathbf{a} = \mathbf{b}^*\cdot\mathbf{b} = \mathbf{c}^*\cdot\mathbf{c} = 1$$

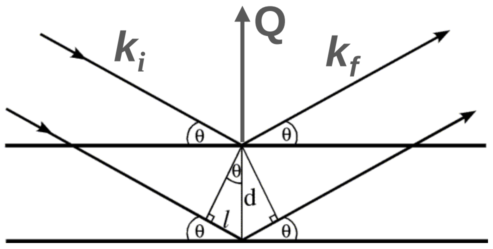
WHY BOTHER WITH THIS???

Real space vs. Reciprocal space

- **Real space**
  - *hkl*: Indices for set of planes
  - ***a***, ***b***, ***c***: Vectors defining unit cell
- **Reciprocal space**
  - $\mathbf{H}_{hkl} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$
  - *hkl*: Coordinates of points
  - **a***, **b***, **c*** : Basal vectors in reciprocal lattice
  - $\mathbf{H}_{hkl} \perp (hkl)$
  - $|\mathbf{H}_{hkl}| = 2\pi/d_{hkl}$







Elastic scattering:
$|\boldsymbol{k}_i| = |\boldsymbol{k}_f| = 2\pi/\lambda$

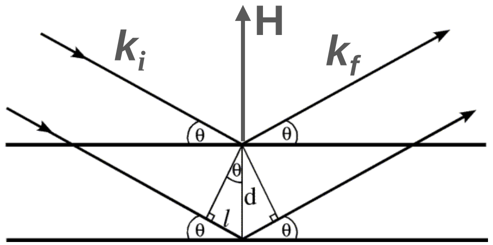
$\mathbf{Q} \equiv \mathbf{k}_f - \mathbf{k}_i$ → $|\mathbf{Q}| = 4\pi \sin(\theta)/\lambda$
the scattering vector

What if $\mathbf{Q} = \mathbf{H}_{hkl}$?
$4\pi \sin(\theta)/\lambda = 2\pi/d_{hkl}$
→ $\lambda = 2\pi d_{hkl}\sin(\theta)$

New condition for constructive interference: $\mathbf{Q} = \mathbf{H}_{hkl}$

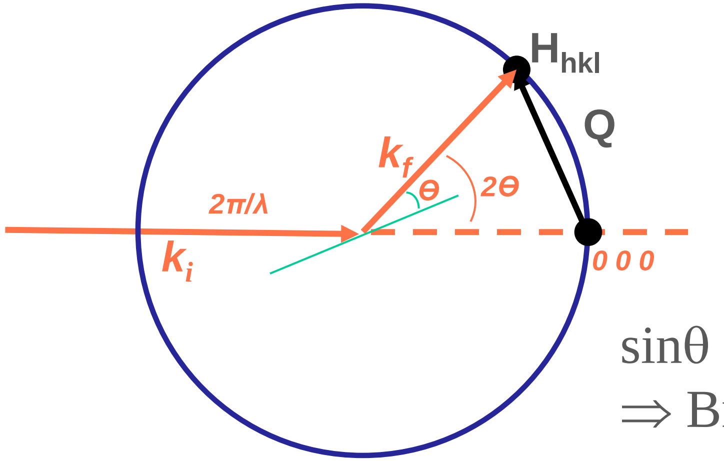
Ewald's sphere construction

Parallel and monochromatic beam

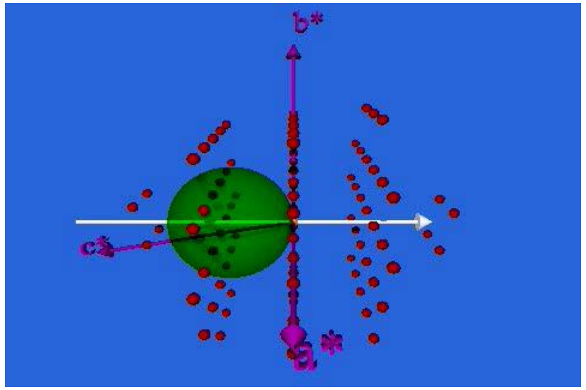


Elastic scattering:

$$|\boldsymbol{k_i}| = |\boldsymbol{k_f}| = 2\pi/\lambda$$



$$\boldsymbol{k_f} = \boldsymbol{k_i} + \mathbf{Q}$$



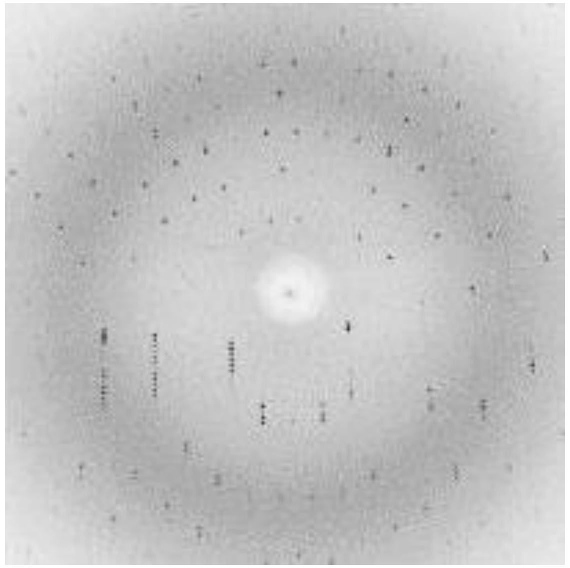
$$\sin\theta = (|\mathbf{Q}|/2)/|\boldsymbol{k}| = (2\pi/2d_{hkl})/(2\pi/\lambda)$$

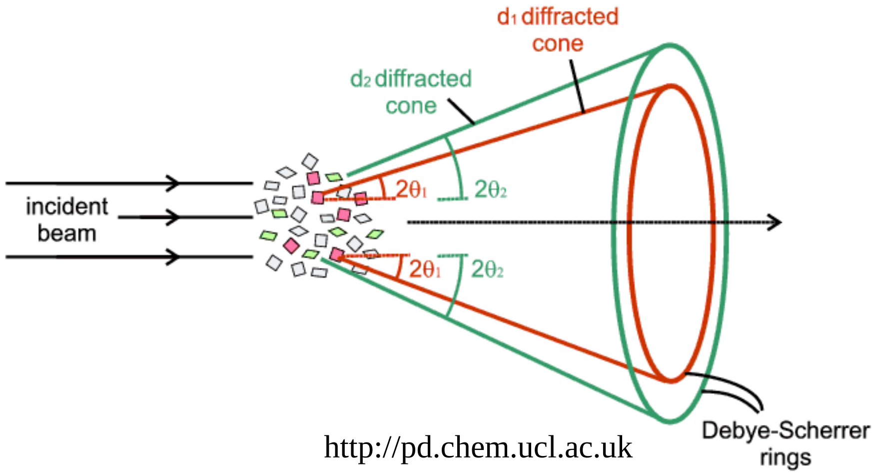
$$\Rightarrow \text{Bragg } (2d_{hkl}\sin\theta = \lambda) \quad (|\mathbf{Q}| = 4\pi \sin\theta/\lambda)$$

When reciprocal lattice point *hkl* on Ewald's sphere ⇒ Bragg's law satisfied for the plane (*hkl*) and Bragg-scattering in that direction.

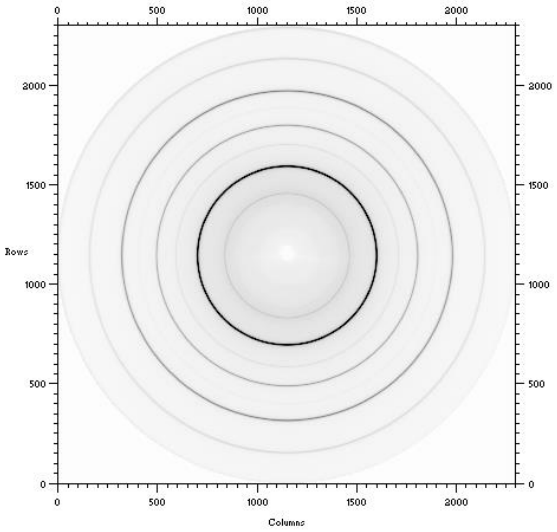
Diffraction patterns

- The reciprocal lattice can be measured
- The positions of the spots (for single crystals) or lines (for powders) are given from Bragg's law



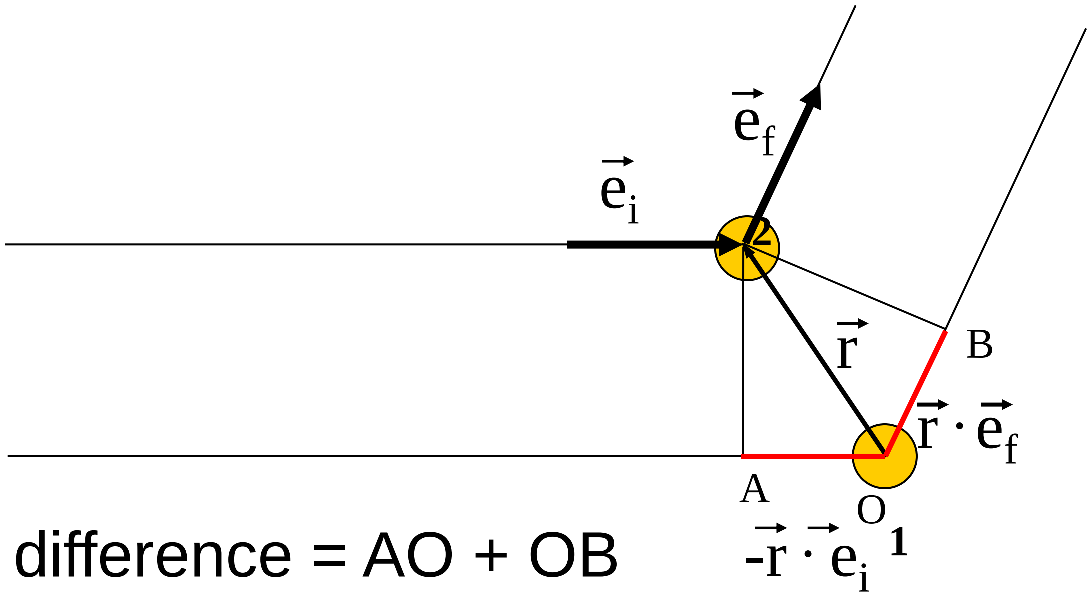


http://pd.chem.ucl.ac.uk



- What about the intensities?

Scattering

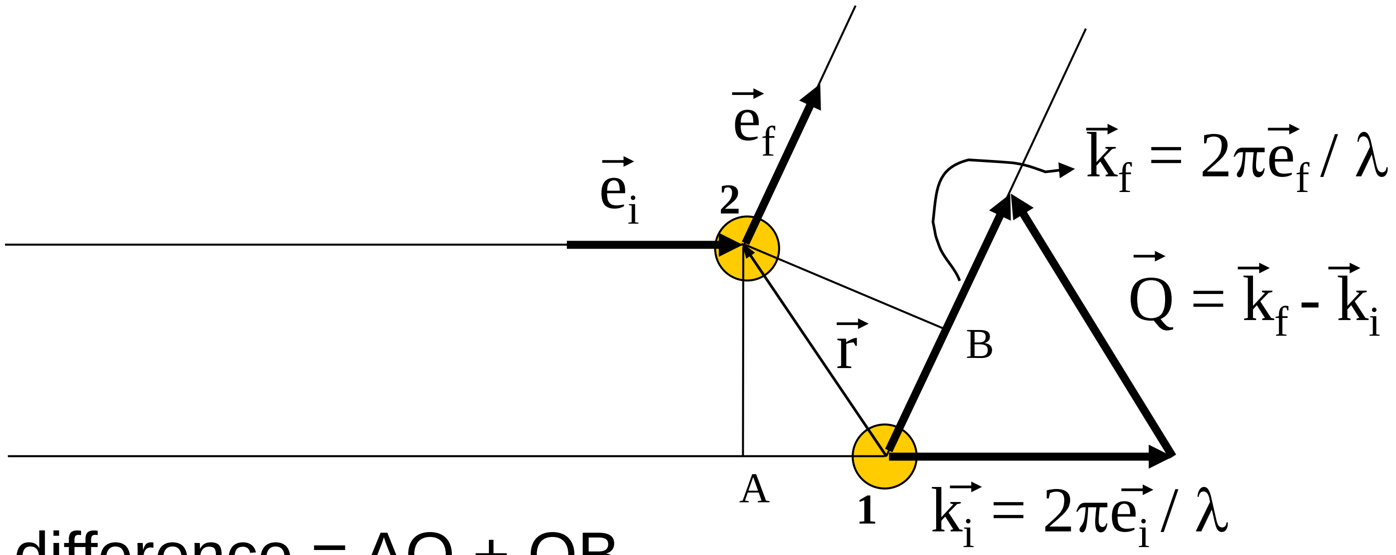


Path difference = AO + OB

$$= (\vec{e}_f - \vec{e}_i)\cdot \vec{r}$$

Phase difference = $\dfrac{2\pi(\vec{e}_f - \vec{e}_i)\cdot\vec{r}}{\lambda}$

Scattering



Path difference = AO + OB

$$= (\vec{e}_f - \vec{e}_i) \cdot \vec{r}$$

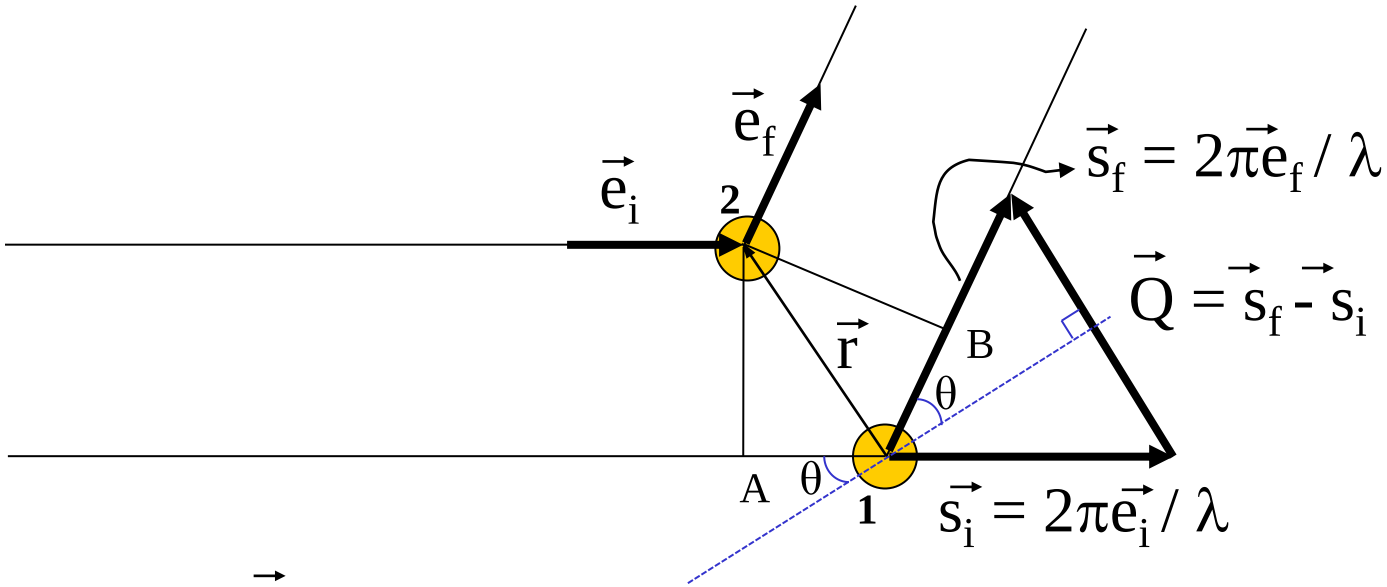
Phase difference $= \dfrac{2\pi(\vec{e}_f - \vec{e}_i)\cdot\vec{r}}{\lambda}$

$$= \vec{Q}\cdot\vec{r}$$

amplitude phase

$$F(\vec{Q}) = \sum_{j}^{N} b_j \, e^{i\vec{Q}\cdot\vec{r}_j}$$

Scattering



Properties of $\vec{Q}$

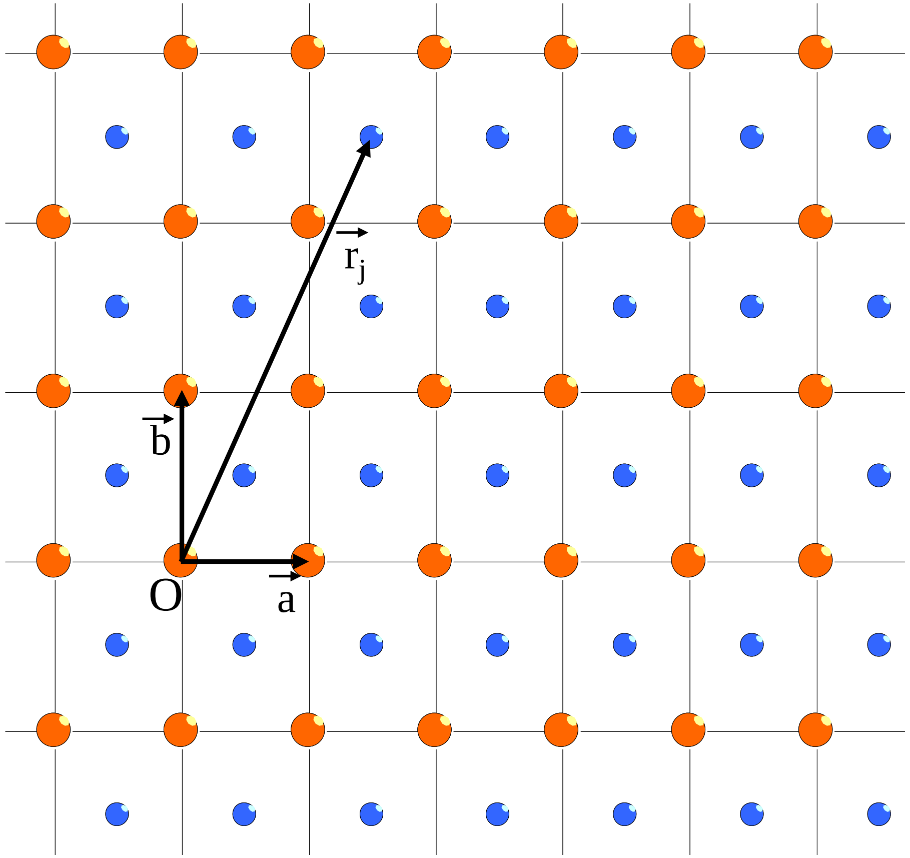
- **Q** is perpendicular to the scattering plane

- |**Q**| = $\frac{4\pi\sin(\theta)}{\lambda} = \frac{2\pi}{d}$

amplitude phase

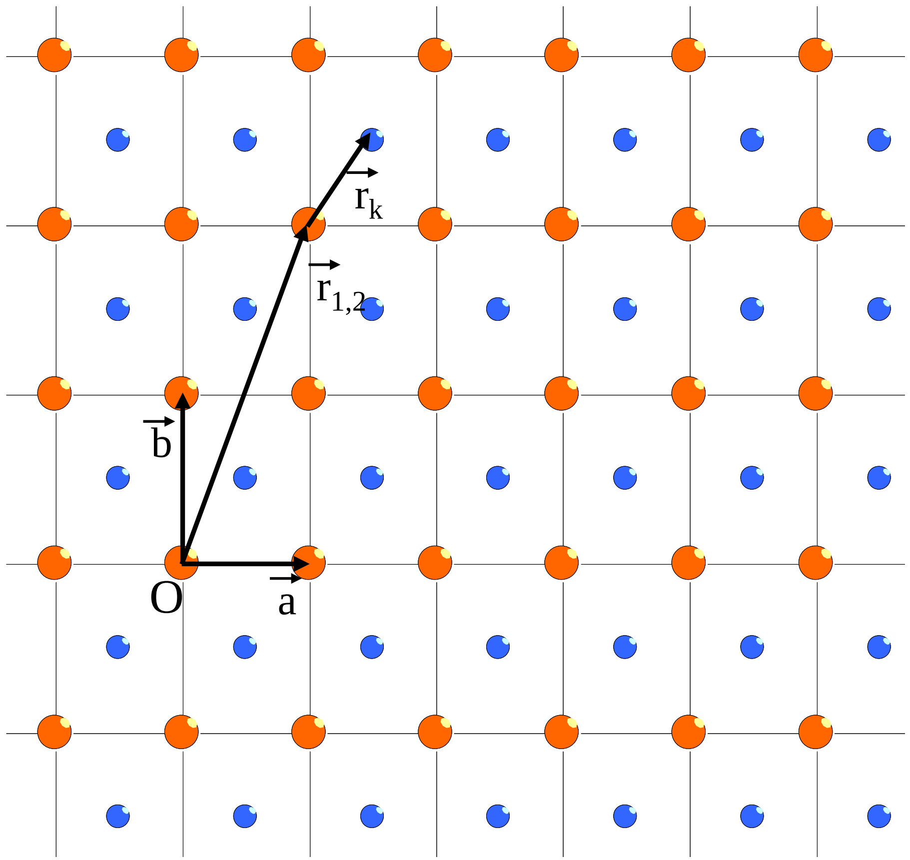
$$F(\vec{Q}) = \sum_{j}^{N} b_j \, e^{i\vec{Q}\cdot\vec{r}_j}$$

Scattering from ideal crystals



$$F(\vec{Q}) = \sum_j^N b_j \, e^{i\vec{Q}\cdot\vec{r}_j}$$

Scattering from ideal crystals



$$F(\vec{Q}) = \sum_j^N b_j \; e^{i\vec{Q}\cdot\vec{r}_j}$$

$$= \sum_{u,v,w=-\infty}^{\infty} \sum_k^n b_k \; e^{i\vec{Q}\cdot(\vec{r}_k+\vec{r}_{uvw})}$$

$$= \sum_{k=1}^n b_k \; e^{i\vec{Q}\cdot\vec{r}_k} \sum_{u,v,w=-\infty}^{\infty} e^{i\vec{Q}\cdot\vec{r}_{uvw}}$$

$$= \sum_{k=1}^n b_k \; e^{i\vec{Q}\cdot\vec{r}_k} \cdot \overbrace{\frac{1}{V} \sum_{h,k,l=-\infty}^{\infty} \delta(\vec{Q}-\vec{Q}_{hkl})}$$

The reciprocal lattice

The structure factor

$$F(\mathrm{Q}) = \sum_j b_j \cdot e^{\mathrm{i}\vec{\mathrm{Q}}\cdot\vec{\mathrm{r}}_j}$$

Neutrons: b_j = scattering length
X-rays: $b_\mathrm{j} = f_{\mathrm{at,j}}$ = atomic form factor

$$F_{hkl} = \sum_{\substack{\text{Unit}\\\text{cell}}} b_\mathrm{j} \cdot e^{2\pi\mathrm{i}(h\cdot\mathrm{x}_\mathrm{j}+k\cdot\mathrm{y}_\mathrm{j}+l\cdot\mathrm{z}_\mathrm{j})}$$

Intensity of scattered beams:

$$\boldsymbol{I \sim |F|^2}$$

Displacement factor (Debye Waller factor, temperature factor):

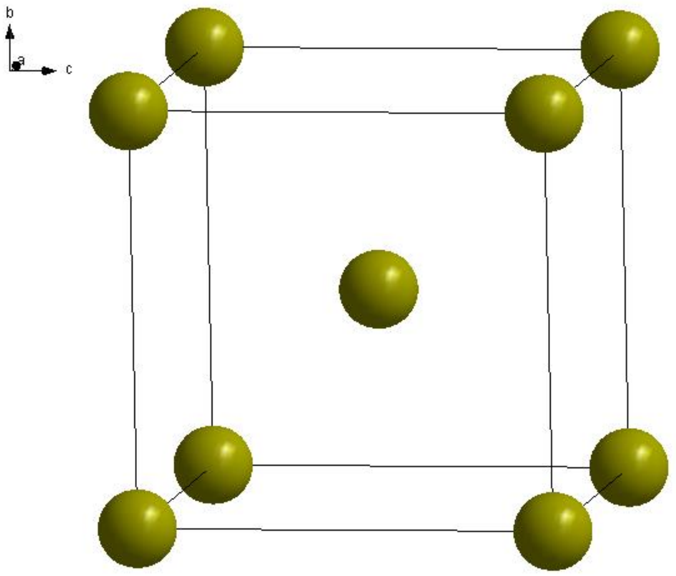
$$T_\mathrm{j} = e^{-W_\mathrm{j}},\ W_\mathrm{j} = 8\pi^2\langle u_j{}^2\rangle\frac{\sin^2\theta}{\lambda^2} = 1/2\,\mathrm{Q}^2\langle u_j{}^2\rangle$$

In total:

$$F_{hkl} = \sum_{\substack{\text{Unit}\\\text{cell}}} b_\mathrm{j} \cdot e^{2\pi\mathrm{i}(h\cdot\mathrm{x}_\mathrm{j}+k\cdot\mathrm{y}_\mathrm{j}+l\cdot\mathrm{z}_\mathrm{j})} \cdot e^{-1/2Q^2\langle u_j{}^2\rangle}$$

Structure factor calculation (joint effort ☺)

Task: Calculate the expression for the structure factor of body-centered cubic Fe.



Fe in 0 0 0 and ½ ½ ½

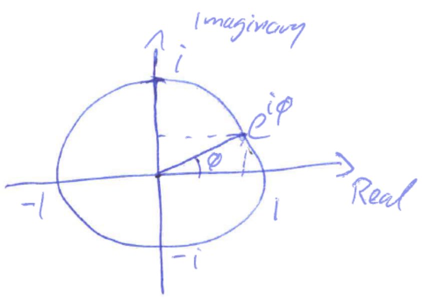
$$F_{hkl} = \sum_j b_j e^{2\pi i (h \cdot x_j + k \cdot y_j + l \cdot z_j)}$$

$$= b_{Fe} e^{2\pi i (h \cdot 0 + k \cdot 0 + l \cdot 0)} + b_{Fe} e^{2\pi i (h \cdot \frac{1}{2} + k \cdot \frac{1}{2} + l \cdot \frac{1}{2})}$$

$$= b_{Fe} \left[1 + e^{i\pi (h+k+l)} \right]$$

$\hookrightarrow = 1, \quad h+k+l = 2n$ (even)

$= -1, \quad h+k+l = n$ (odd)



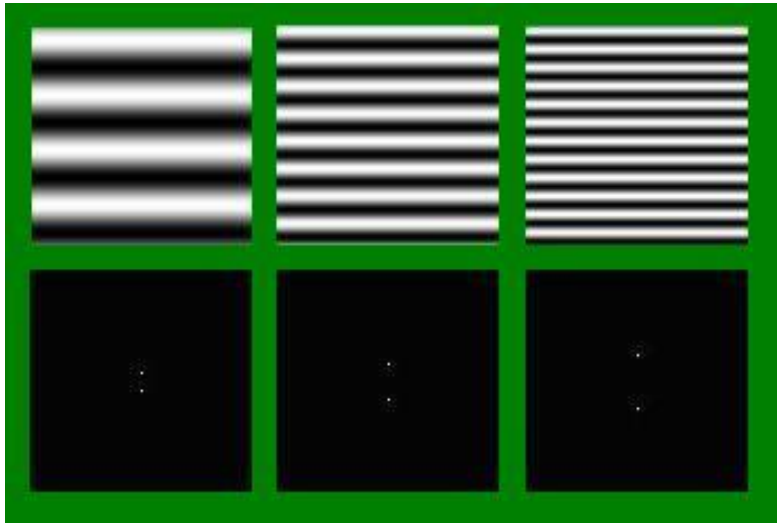
$\Rightarrow h+k+l = 2n: \quad F_{hkl} = 2 b_{Fe}$

$h+k+l = n: \quad F_{hkl} = 0$

The phase problem

Definition

$$FT[f(x)] = \tilde{f}(k) = \int f(x)e^{ikx}dx$$



Inverse Fourier transform:

$$FT^{-1}[\tilde{f}(k)] = \int \tilde{f}(k)e^{-ikx}dk$$

The structure factor is the Fourier transformation of:

- The density of atom cores (scattering lengths) for neutrons
- The electron density for X-rays

The phase problem

$$F_{hkl} = |F_{hkl}|\, e^{i\varphi_{hkl}}$$

$$I_{hkl} \propto |F_{hkl}|^2$$

- The nuclear density:

$$\rho(x,y,z) = \tilde{F}_{hkl} = \frac{1}{V_c} \sum_h \sum_{k=-\infty}^{\infty} \sum_l |F_{hkl}| e^{i\varphi_{hkl}} e^{-2\pi i(hx+ky+lz)}$$

- It is impossible to calculate $\rho(x,y,z)$ as inverse Fourier transformation of the structure factors as long as φ_{hkl} are unknown

$\Rightarrow$ **The phase problem in crystallography**

Methods to solve the phase problem

- **Patterson function**: Fourier transformation of $|F_{hkl}|^2$ without phases:

$$P(u,v,w) = \frac{2}{V_c} \sum_h \sum_{k,-\infty}^{\infty} \sum_k |F_{hkl}|^2 \cos 2\pi(hu + kv + lw)$$

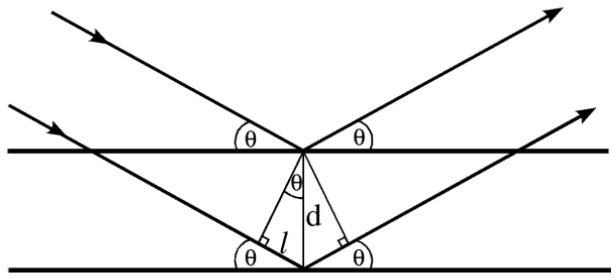
  Self-convolution. Peaks in the Patterson function represent a vector between two atoms; weighted by the product of their scattering power. Used to determine positions of strong scatterers.

- **Direct methods**: Uses statistic relations between observed intensities to guess on phases. Very efficient when scatterers are of similar strength and many independet structure factor amplitues are collected (single crystal)

Most important points

- The condition for constructive interference (Bragg scattering) is given by Bragg's law

$$\lambda = 2d_{hkl}\sin\theta$$



or the condition that the scattering vector **Q** equals a resiprocal lattice vector: $\mathbf{Q} = \mathbf{Q}_{hkl}$ (Laue condition)

Most important points

The scattered wave from a collection of atoms is descibed by the structure factor

$$F(\vec{Q}) = \sum_{j}^{N} b_j \; e^{i\vec{Q}\cdot\vec{r}_j}$$

For atoms in an infinitely repeating lattice, F(Q) is non-zero only when **Q** = $\mathbf{Q}_{\mathbf{hkl}}$

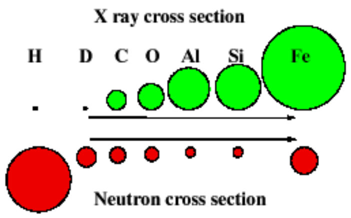
$$F(\vec{Q}_{hkl}) = \sum_{j}^{N} b_j \; e^{2\pi i(hx_j + ky_j + lz_j)}$$

And of course: I ∝ |**F**|^2

Power Neutron Diffraction
vs
Powder X-ray Diffraction

The glory of neutrons

- There is no systematic correlation between atomic number and the scattering length.
  - **Can get information about light and heavy elements simultaneously.**

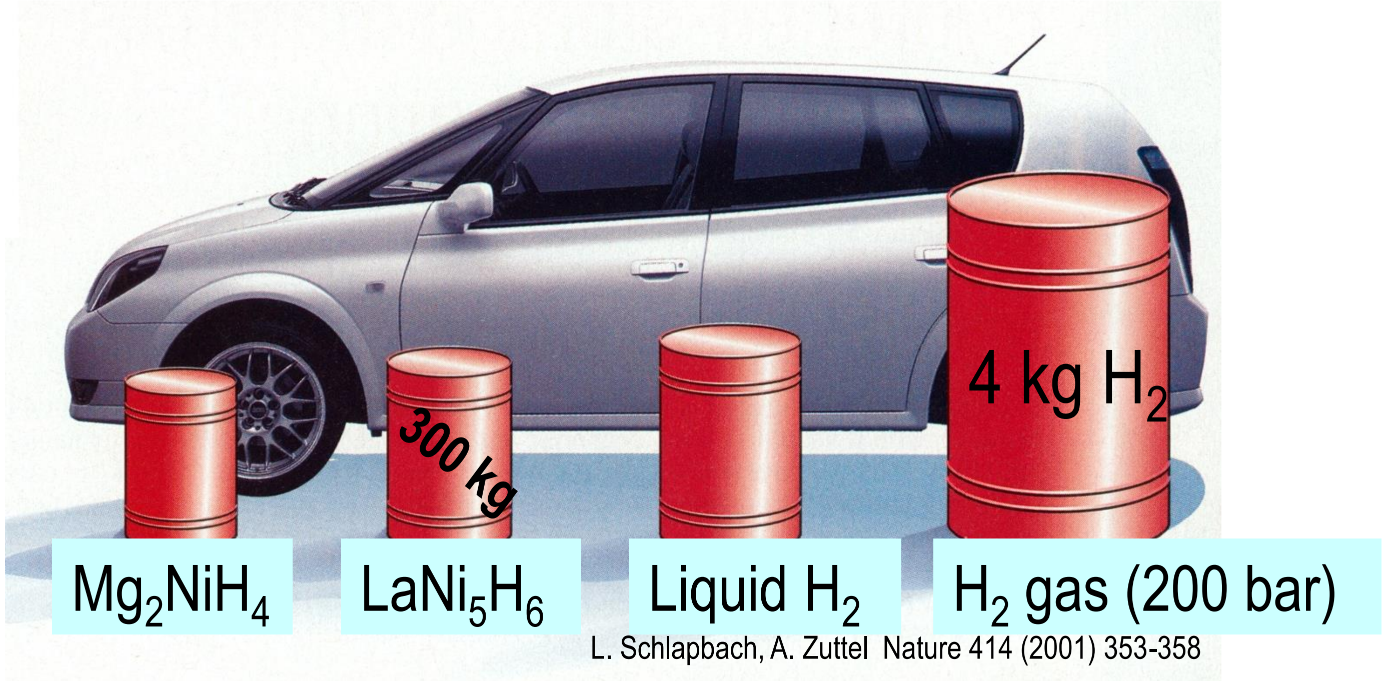


- The neutron interacts weakly with matter.

- The neutron has a magnetic moment.

Metal hydrides

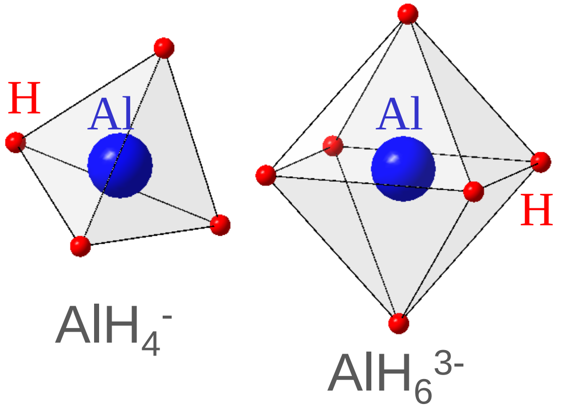
- Materials that contain chemical bonding between metal- and hydrogen atoms.



L. Schlapbach, A. Zuttel Nature 414 (2001) 353-358

$$M_{(s)} + x/2\ H_{2(g)} \leftrightarrow MH_{x(s)} + \text{energy}$$

Alanates



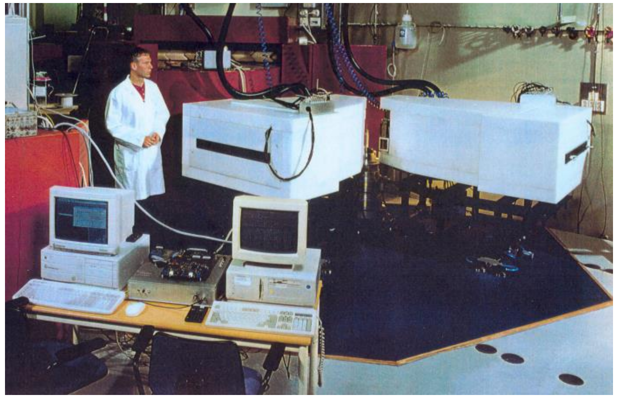
$3\ NaAlH_4$	$\rightleftharpoons$ ($TiCl_3$)	$Na_3AlH_6 + 2\ Al + 3\ H_2$	3.7wt%	~120°C
Na_3AlH_6	$\rightleftharpoons$ ($TiCl_3$)	$3\ NaH + Al + 3/2\ H_2$	1.9wt%	~180°C
NaH	$\rightleftharpoons$	$Na + ½\ H_2$	1.9wt%	425°C

5.6 wt%

B. Bogdanovic, J. Alloys Comp. 253-254 (1997) 1-9.

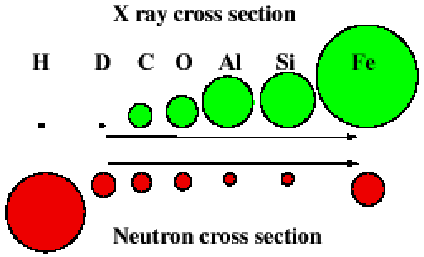
Crystal structure of alanates

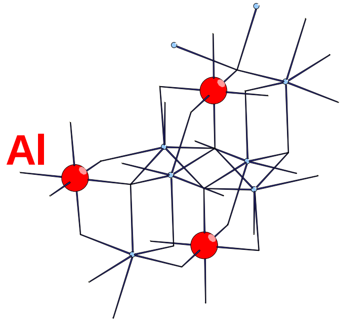
- $NaAlH_4$
- Na_3AlH_6
- $LiAlH_4$
- β-$LiAlH_4$
- Li_3AlH_6
- $KAlH_4$
- $Mg(AlH_4)_2$
- Sr_2AlH_7
- $BaAlH_5$
- Ba_2AlH_7
- Na_2LiAlH_6
- K_2NaAlH_6
- $LiMg(AlH_4)_2$
- $LiMgAlH_6$
- $Ca(AlD_4)_2$
- $CaAlD_5$



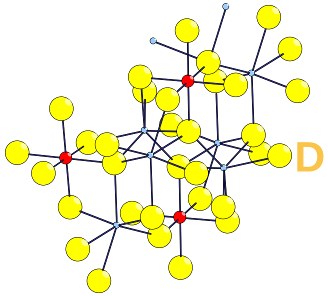
PUS - high resolution diffractometer

The JEEPII reactor





Li_3AlD_6 seen by X-rays



Li_3AlD_6 seen by neutrons

Crystal structure of alanates

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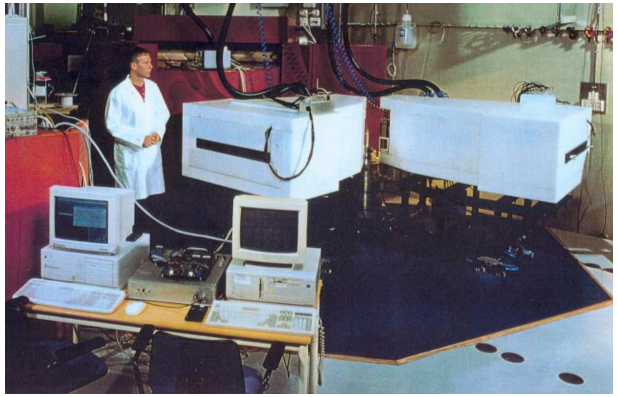
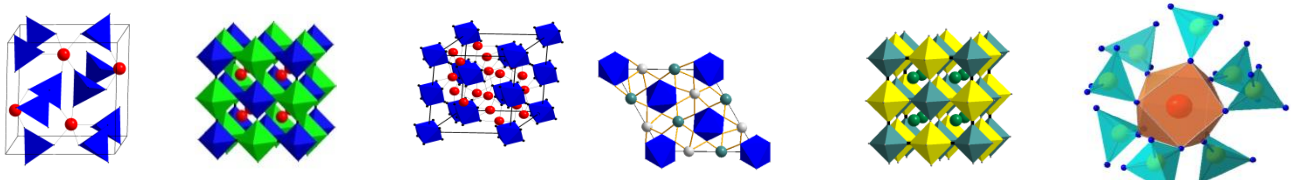
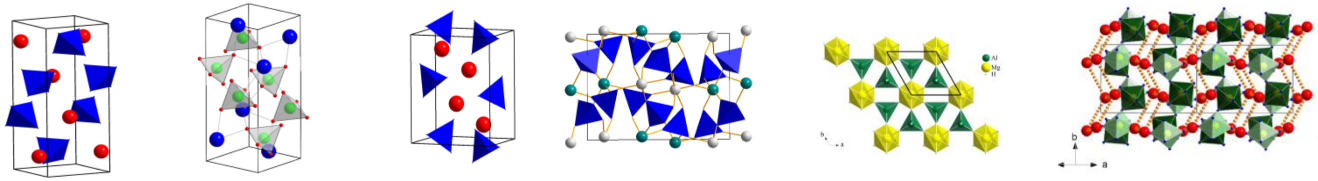
$CaAlD_5$


PUS - high resolution diffractometer


SNBL/ESRF (Grenoble, France)


$LiAlH_4$ Na_2LiAlH_6 Li_3AlH_6 $LiMgAlH_6$ K_2NaAlH_6 $Ca(AlH_4)_2$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The glory of neutrons

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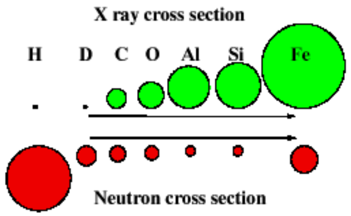
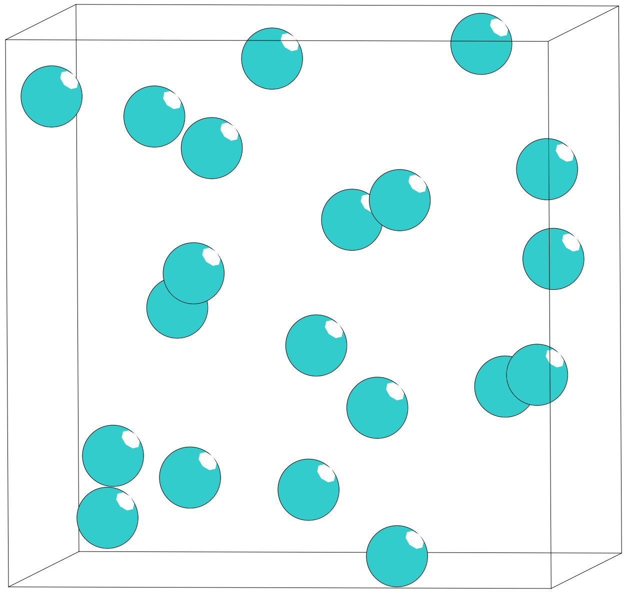


- The neutron has a magnetic moment.

Alloys

β-Mn: Cubic, complex structure, a = 6.31 Å,
Z = 20

$Mn(1)_{12}Mn(2)_8$

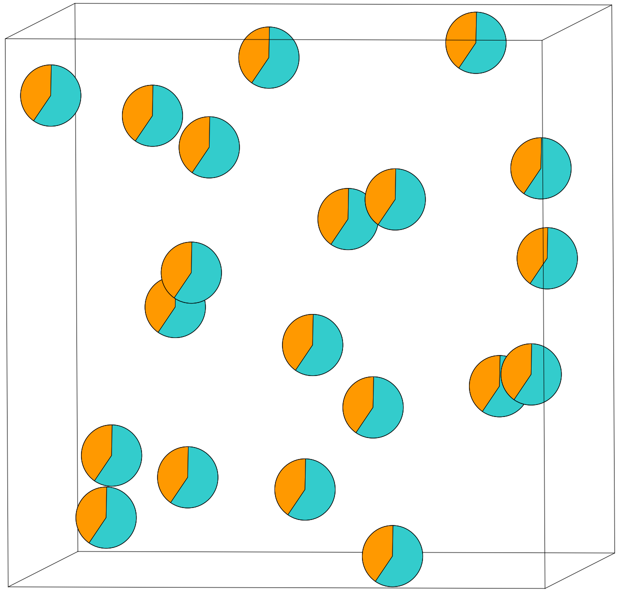


What happens when 40% of the Mn is substituted with Co?

Alloys

β-Mn: Cubic, complex structure, a = 6.31 Å,
Z = 20

$[Mn_{0.6}Co_{0.4}](1)_{12}$ $[Mn_{0.6}Co_{0.4}](2)_8$



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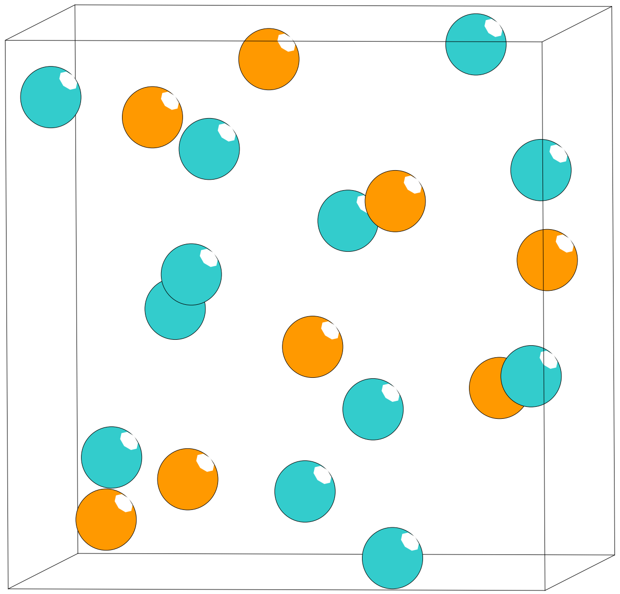
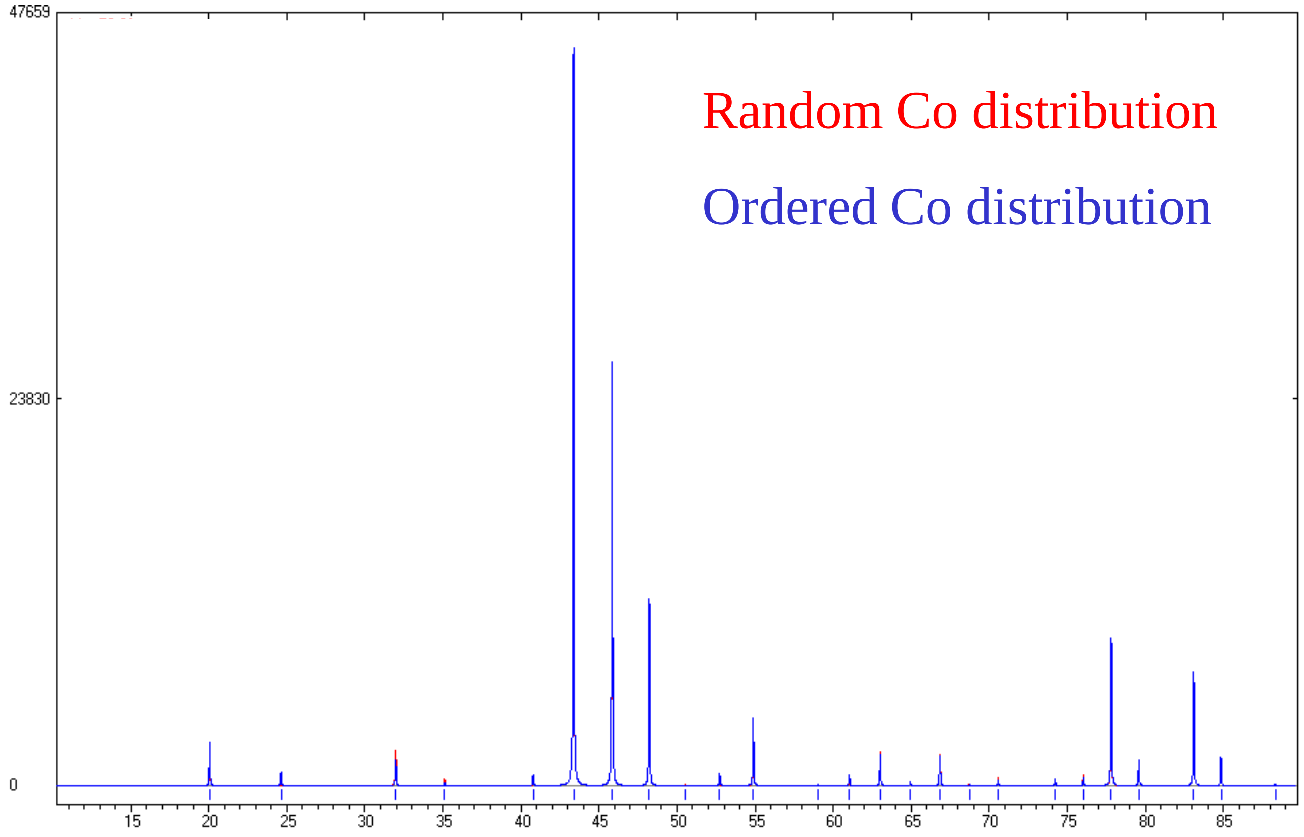


What happens if 40% of the Mn is substituted with Co?

Alloys

Which model is right for $Mn_{0.6}Co_{0.4}$?



X-rays:

Z(Mn)=25

Z(Co)=27

Alloys

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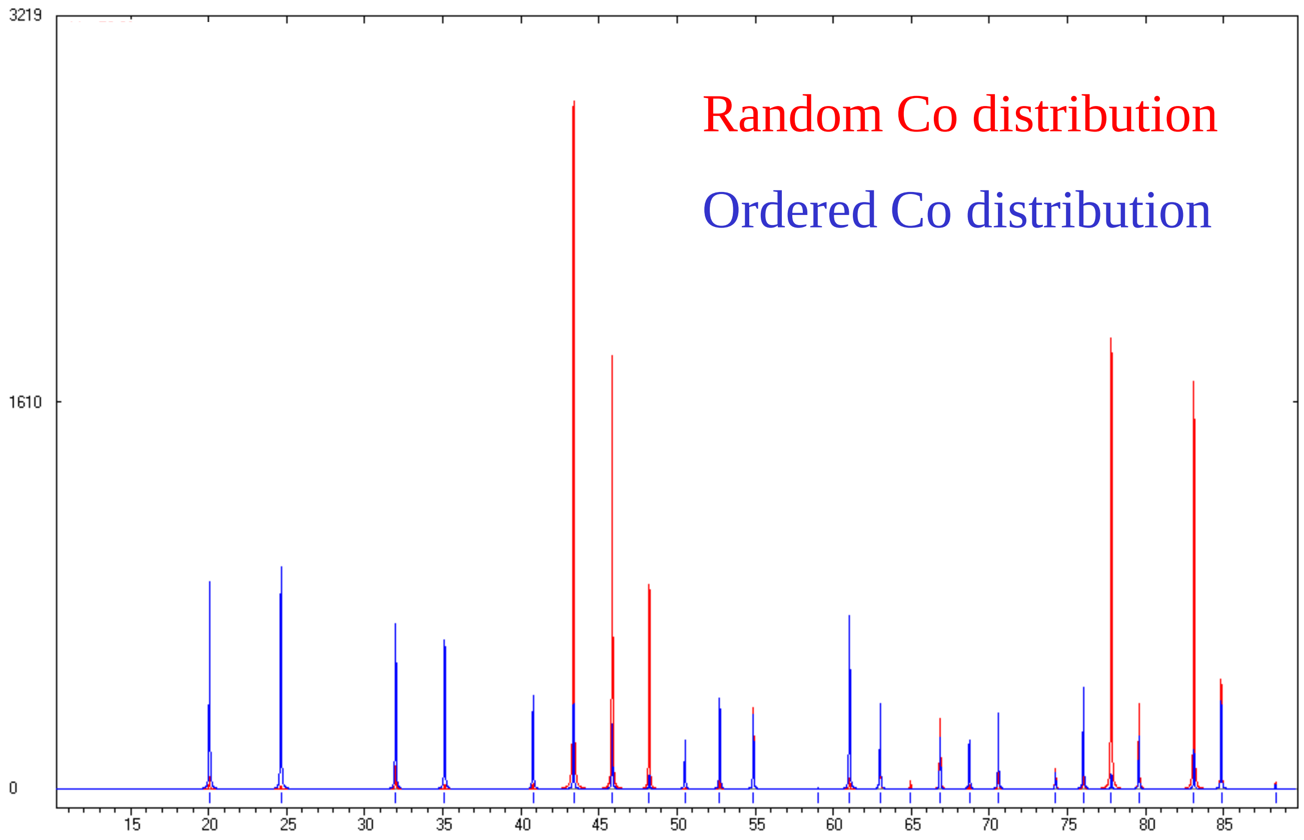


X-rays:

Z(Mn)=25

Z(Co)=27

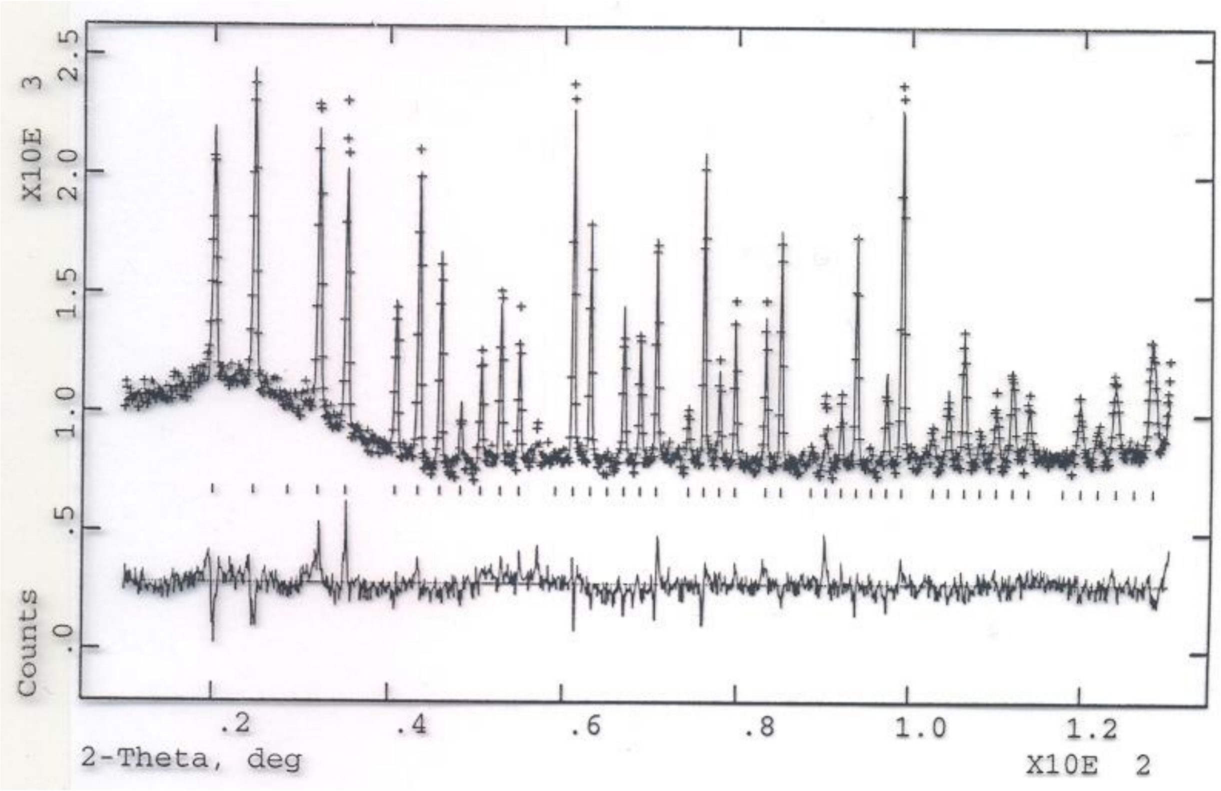
Neutrons:

b(Mn)=-0.373

b(Co)=+0.249

Alloys

Which model is right for $Mn_{0.6}Co_{0.4}$?

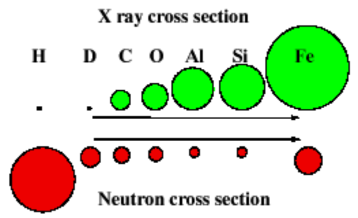


Co selectively occupy the 8-fold position!

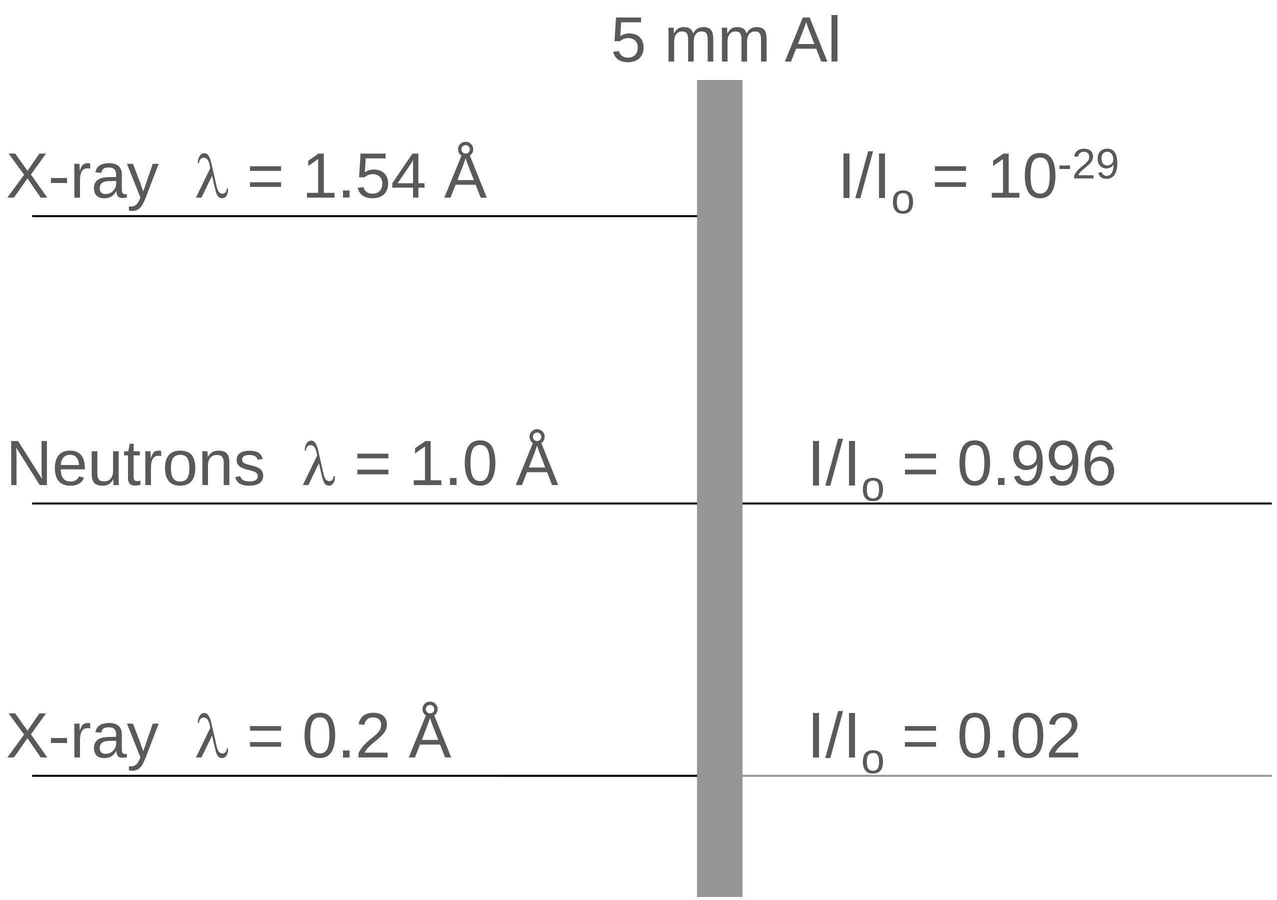
O. B. Karlsen, et al. J. Alloys Comp., 2009, 476 (2009) 9-13

The glory of neutrons

- There is no systematic correlation between atomic number and the scattering length.
  - Can get information about light and heavy elements simultaneously.
  - Can distinguish neighboring elements in the periodic table.
- The neutron interacts weakly with matter.
  - **Complicated sample environment is possible.**
- The neutron has a magnetic moment.



Penetration



Sample environment

- Neutrons can penetrate several millimeters of materials like aluminium and steel.

Sample container (Inconel super-alloy) rated to 3000 bar and 600^{o}C.

Sample environment

- Neutrons can penetrate several millimeters of materials like aluminium and steel.

Furnace

Cryostat

The glory of neutrons

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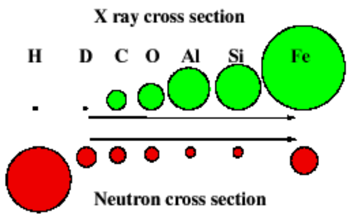
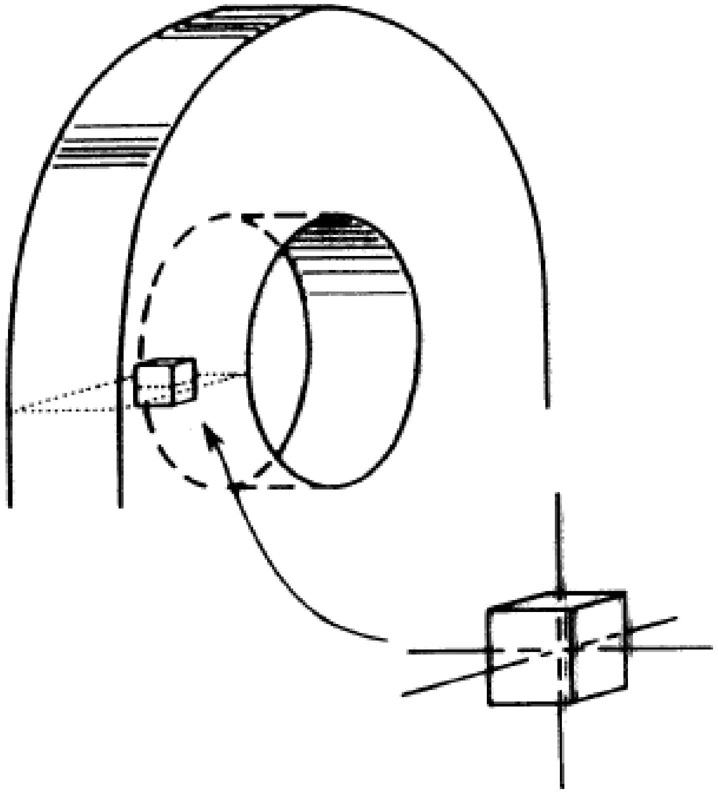
  - Complicated sample environment is possible.
  - **Large samples can be studied.**
- The neutron has a magnetic moment.

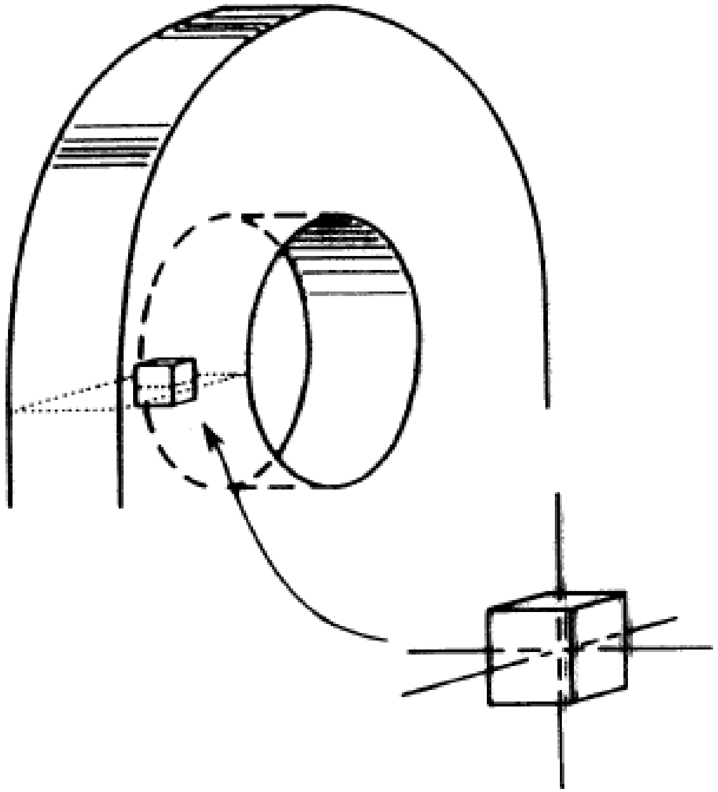


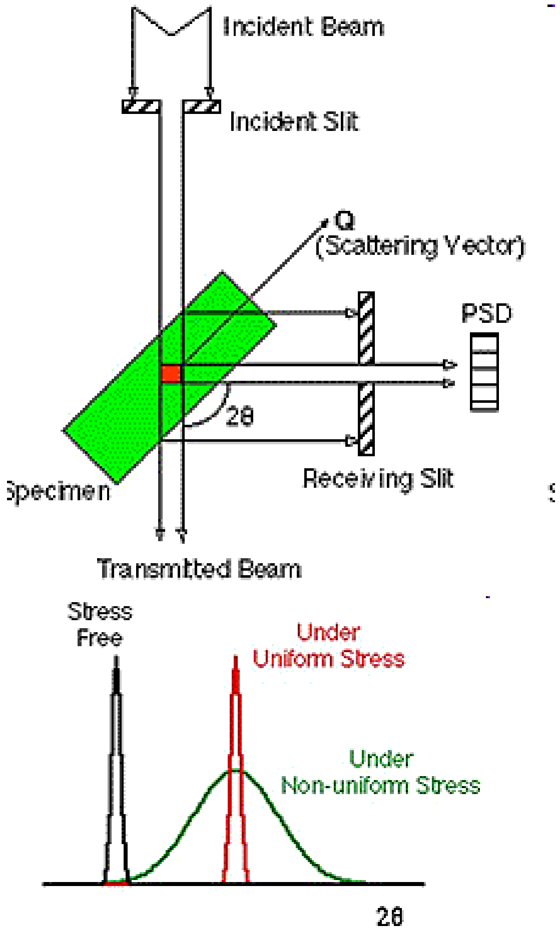
Study of large samples



- How did the machining of the hole influence the material?

Study of large samples





Study of large samples

3D residual stress-field can be mapped in a non-destructive way!

Loading a sample at the NRSF2 instrument at Oak Ridge National Lab (US)

The glory of neutrons

- There is no systematic correlation between atomic number and the scattering length.
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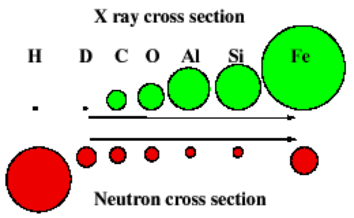
  - Can distinguish neighboring elements in the periodic table.
- The neutron interacts weakly with matter.
  - Complicated sample environment is possible.
  - Large samples can be studied.
  - **Easy interpreations of scattering intensities.**
- The neutron has a magnetic moment.



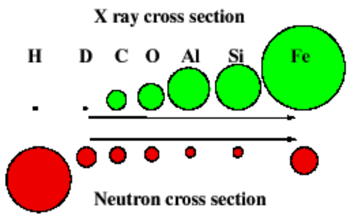
Scattering intensity

$$I = \left|F_K\right|^2 = \left|\sum_i b_i \cdot e^{i(\vec{r}_i \cdot \vec{Q})}\right|^2 = \left|\sum_i b_j \cdot e^{2\pi i(hx_j + ky_j + lz_j)}\right|^2$$

- **Can (usually) neglect effects of multiple scattering and absorption.**

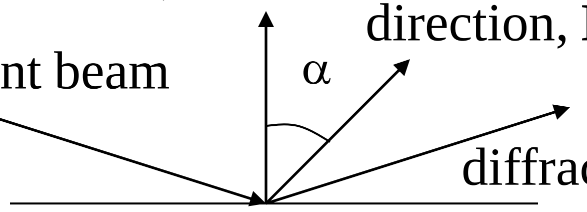
The glory of neutrons

- There is no systematic correlation between atomic number and the scattering length.
  - Can get information about light and heavy elements simultaneously.
  - Can distinguish neighboring elements in the periodic table.
- The neutron interacts weakly with matter.
  - Complicated sample environment is possible.
  - Large samples can be studied.
  - Easy interpreations of scattering intensities.
- The neutron has a magnetic moment.
  - **Can study magnetic ordering.**



Magnetic neutron scattering

- The neutron has a magnetic moment.
- This will interact with the magnetic moment of atoms with unpaired electrons.



$$\vec{F}_{magnetic,hkl} = \sum_i \vec{m}_i f_i \cdot e^{2\pi i(hx_i + ky_i + lz_i)}$$

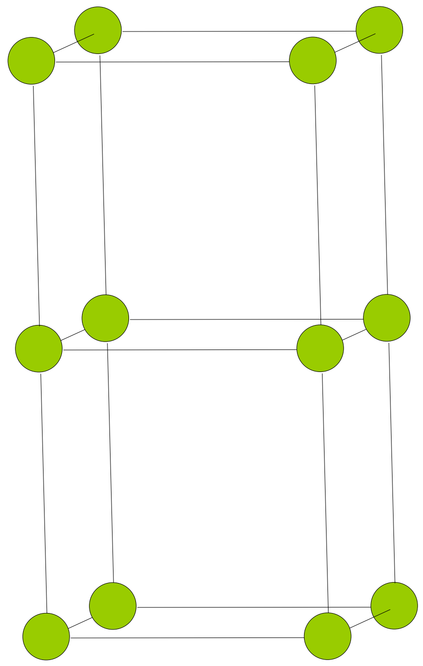
$$\vec{m} = \vec{K}(\vec{K}\cdot\vec{M}) - \vec{M}, \qquad |\vec{m}| = \sin\alpha$$

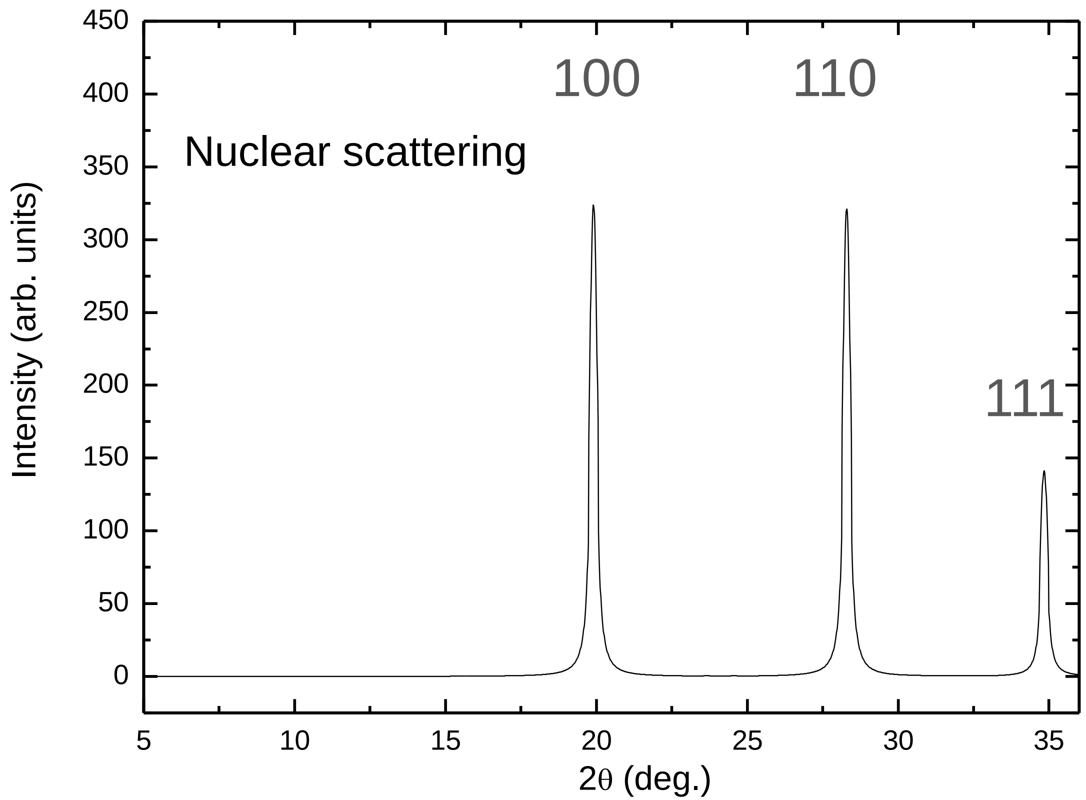
$$|\vec{m}| = 0, \qquad \vec{K} \parallel \vec{M}$$

$$|\vec{m}| = 1, \qquad \vec{K} \perp \vec{M}$$

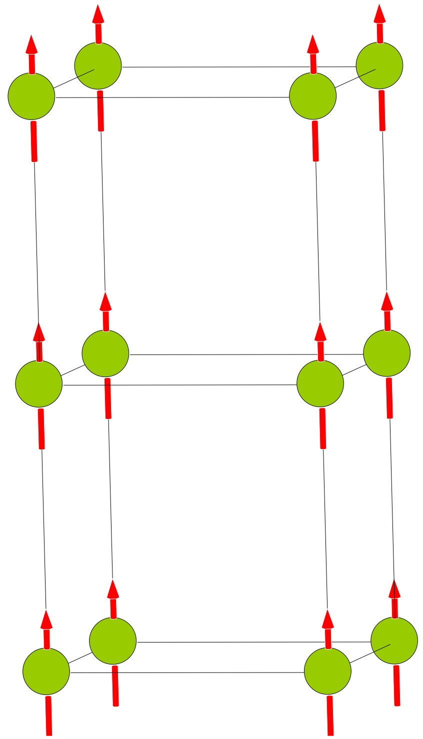
$$I_{hkl} \propto |F_{hkl}|^2 = |F_{nucl,hkl}|^2 + |F_{magnetic,hkl}|^2$$

Magnetic neutron scattering

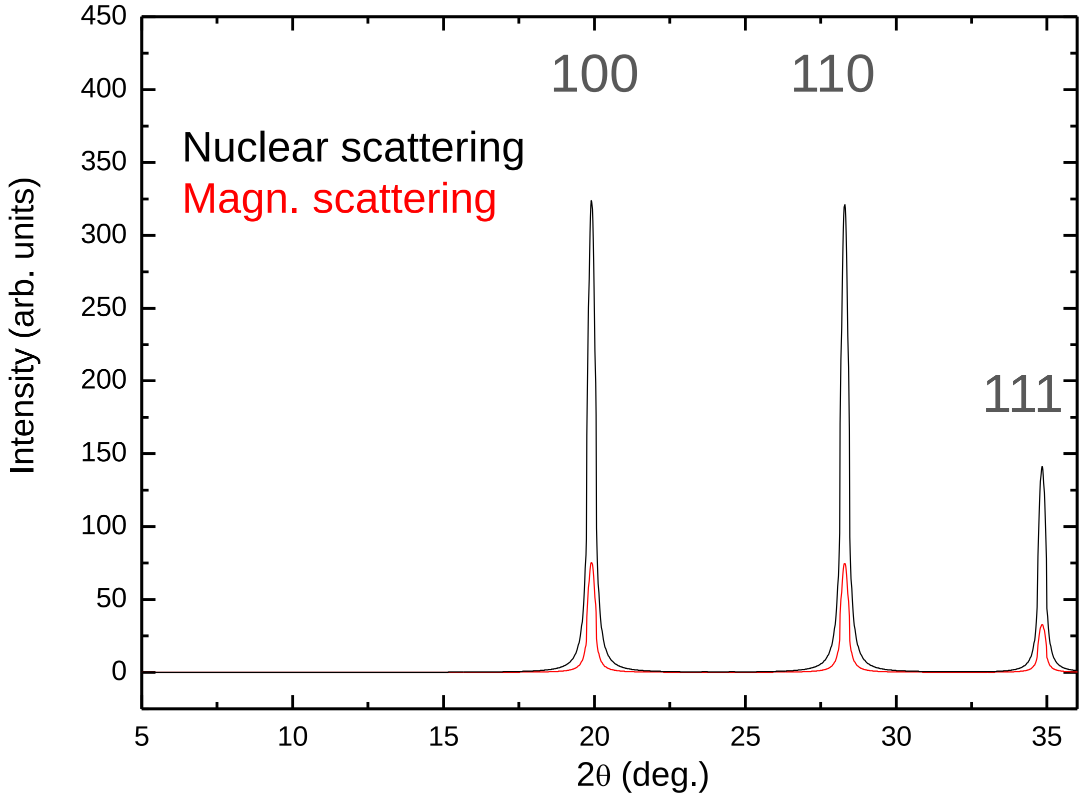




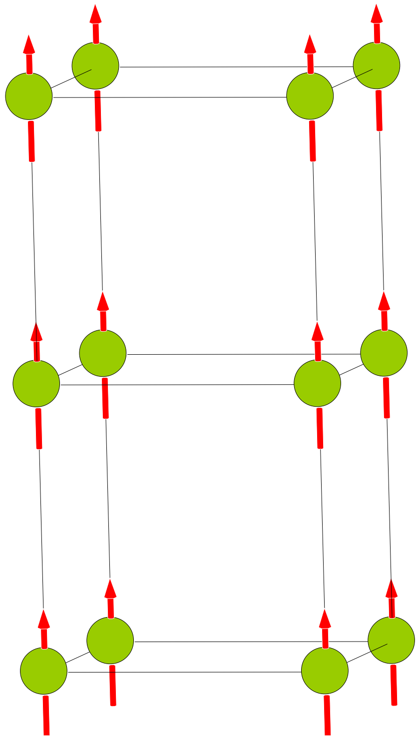
Magnetic neutron scattering

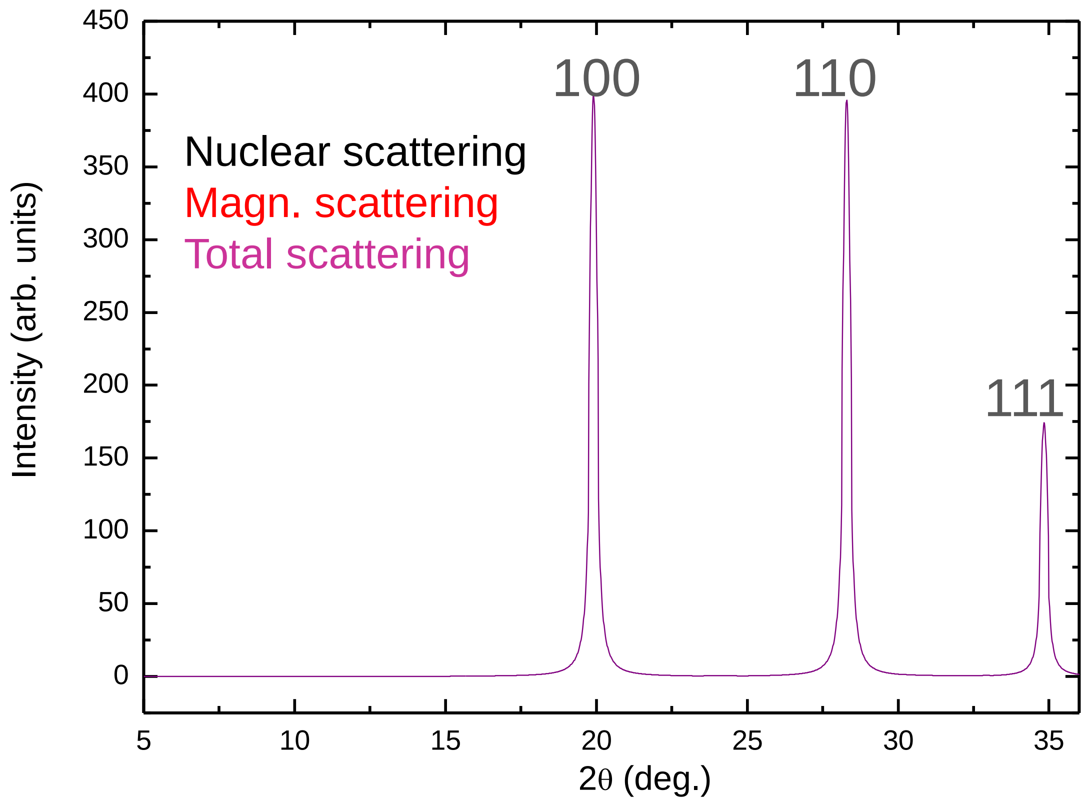


Ferromagnetic



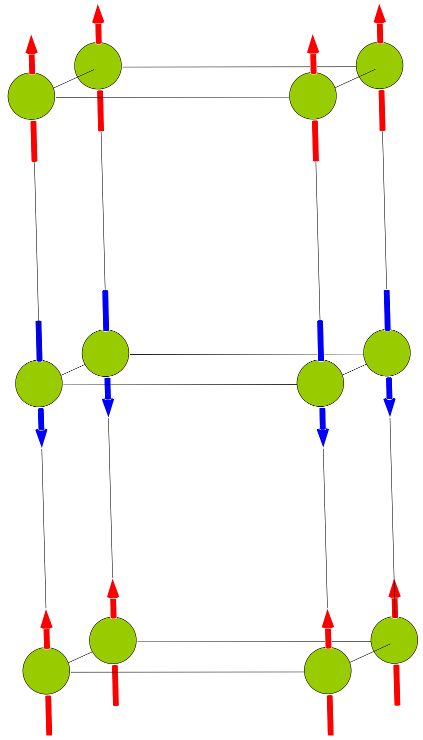
Magnetic neutron scattering

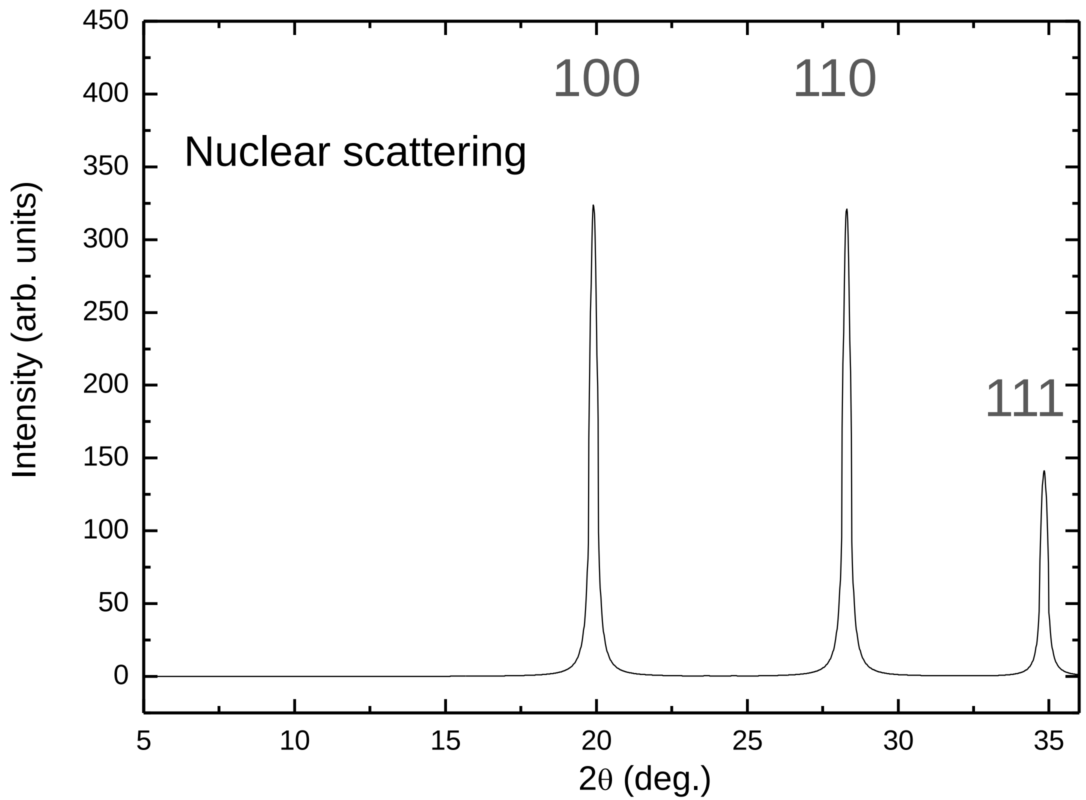




Ferromagnetic

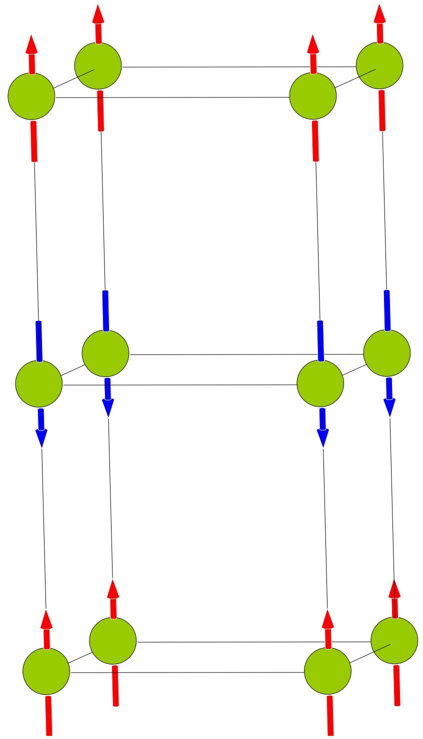
Magnetic neutron scattering

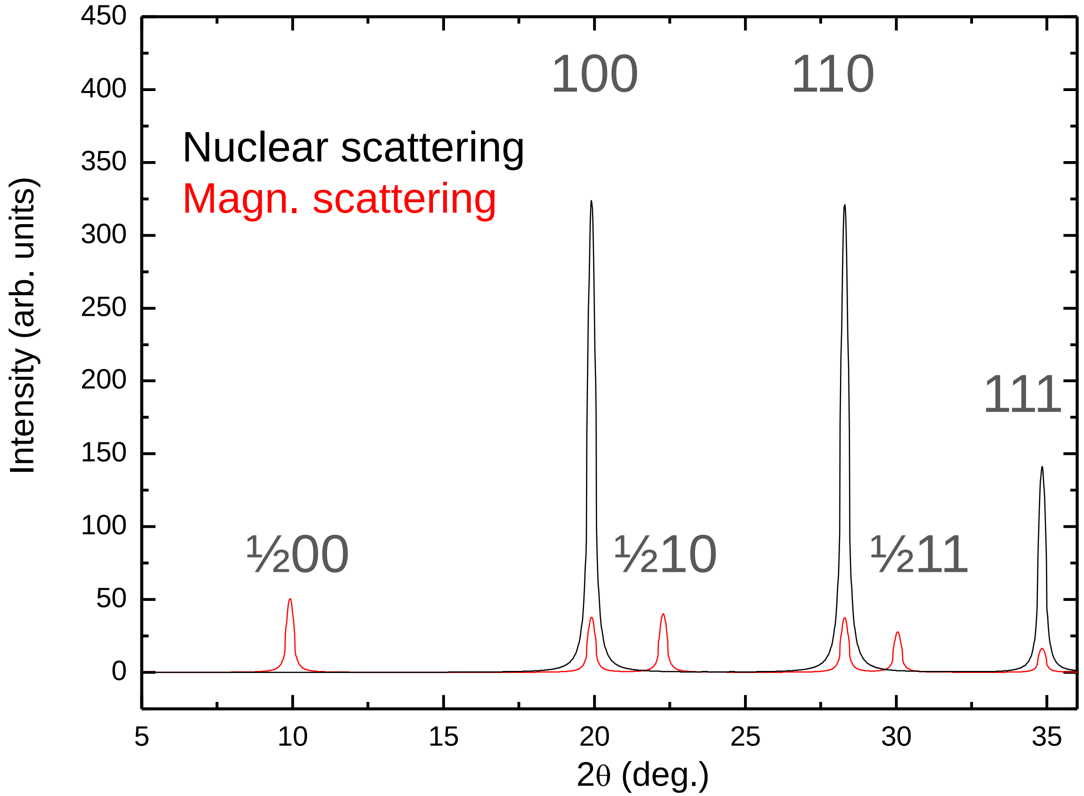




Antiferromagnetic

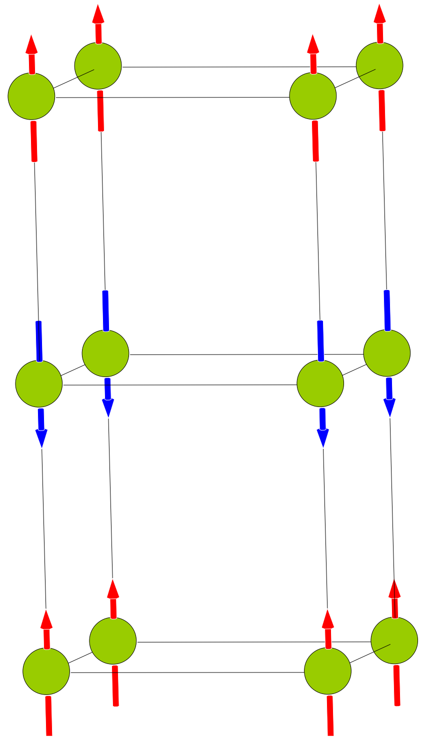
Magnetic neutron scattering



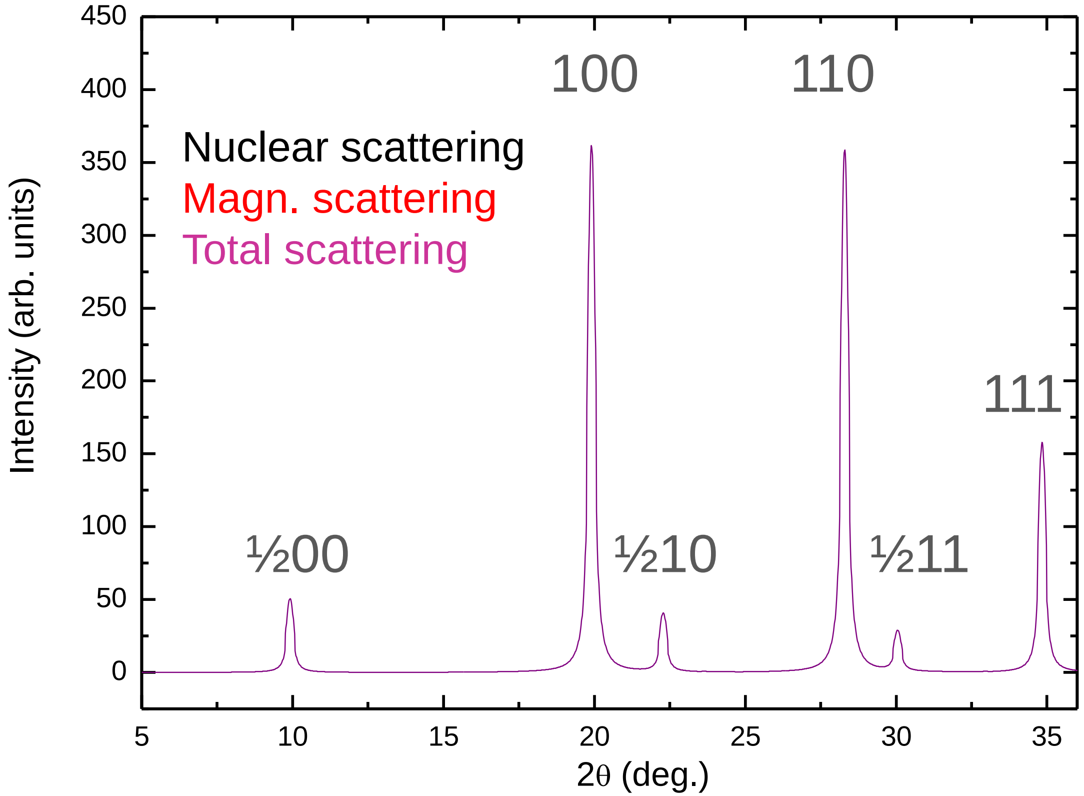


Antiferromagnetic

Magnetic neutron scattering



Antiferromagnetic



Conclusion

Powder neutron diffraction has some major differences from powder X-ray diffraction:

- Different contrast
  - Information about light and heavy elements at the same time.
  - Often good contrast from elements with similar atomic number.
- Weak interactions
  - Scattering from bulk
  - Easy interpreation of intensities
- Magnetic scattering