

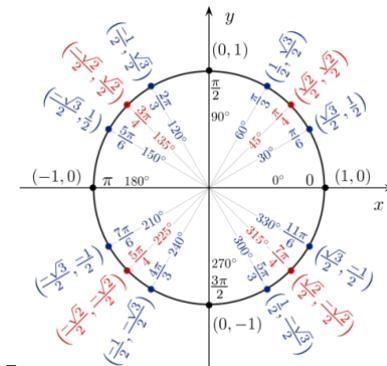
MSE 238 – Preliminary Exam sheet – status week 5

Reminder on Mathematics:

- Euclidean geometry
 - The following notation will be used: $\mathbf{a} = \begin{pmatrix} a_x \\ a_y \\ a_z \end{pmatrix}$
 - The magnitude (or norm) of a vector: $\|\mathbf{a}\| = \sqrt{a_x^2 + a_y^2 + a_z^2}$
 - Scalar (or dot) product: for two vectors in the **orthonormal basis $\mathbf{i}, \mathbf{j}, \mathbf{k}$** , we have: $\mathbf{a} \cdot \mathbf{b} = a_x b_x + a_y b_y + a_z b_z$
 - $\mathbf{a} \cdot \mathbf{b} = \|\mathbf{a}\| \|\mathbf{b}\| \cos(\alpha)$ where α is the angle between the two vectors.
 - The cross product of two vectors forming an angle α is a vector perpendicular to these vectors, with the magnitude: $\|\mathbf{a} \times \mathbf{b}\| = \|\mathbf{a}\| \|\mathbf{b}\| \sin(\alpha)$
 - In an orthonormal basis $(\mathbf{i}, \mathbf{j}, \mathbf{k})$, the Cross product of two vectors \mathbf{a} and \mathbf{b} is:
- $$\mathbf{a} \times \mathbf{b} = (a_y b_z - a_z b_y) \mathbf{i} + (a_z b_x - a_x b_z) \mathbf{j} + (a_x b_y - a_y b_x) \mathbf{k}$$
- **Line:** Parametric equation of a line passing by two points A and B: $L = \left\{ \mathbf{M} = \begin{pmatrix} x \\ y \\ z \end{pmatrix} \text{ such that } \exists \lambda \in \mathbb{R} \ \mathbf{AM} = \lambda \mathbf{AB} \right\}$
- **Plane:**
 - A plane is defined by 3 points $A = \begin{pmatrix} x_A \\ y_A \\ z_A \end{pmatrix}$, $B = \begin{pmatrix} x_B \\ y_B \\ z_B \end{pmatrix}$ and $C = \begin{pmatrix} x_C \\ y_C \\ z_C \end{pmatrix}$ or a point A and a normal $\mathbf{n} = \begin{pmatrix} n_x \\ n_y \\ n_z \end{pmatrix} = \begin{pmatrix} a \\ b \\ c \end{pmatrix}$
 - This can be expressed in a simple way as: $P = \left\{ \mathbf{M} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, \mathbf{AM} \cdot \mathbf{n} = 0 \right\}$
 - One can extract the linear equation: for $(a, b, c, d) \in \mathbb{R}^4$, $P = \left\{ \mathbf{M} = \begin{pmatrix} x \\ y \\ z \end{pmatrix}, ax + by + cz - d = 0 \right\}$
- **Angles**
 - The angle between two vectors can be calculated from the dot or the cross products.
 - Angle between a line and a plane: Complementary of the angle between the line direction and the normal of the plane.
 - Angle between two planes: Angle between their normals:
- Volume formed by three vectors: $V = \vec{a} \cdot (\vec{b} \times \vec{c}) = \vec{b} \cdot (\vec{c} \times \vec{a}) = \vec{c} \cdot (\vec{a} \times \vec{b})$

Complex Numbers

- **Exponential form:** $z = r \cos \theta + i r \sin \theta = r e^{i\theta}$
- For $z \in \mathbb{C}$, $z = r e^{i\theta}$, $z^* = r e^{-i\theta}$
- $|e^{i\theta}| = 1 = \sqrt{x^2 + y^2}$, with $x = \cos \theta$ and $y = \sin \theta$
- $\cos(x) = \frac{e^{ix} + e^{-ix}}{2}$ and $\sin(x) = \frac{e^{ix} - e^{-ix}}{2i}$
- Unity circle is shown to the right.



Crystalline State:

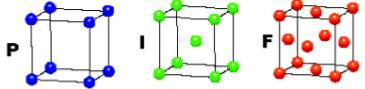
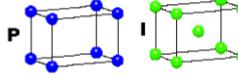
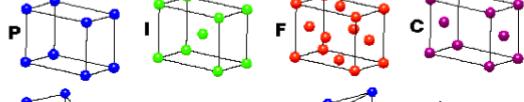
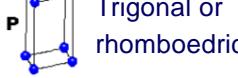
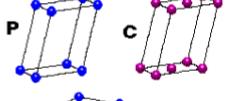
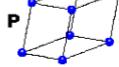
Materials in a crystalline state are organized into ordered arrangements of atoms. The chemical composition of the material forms a motif, that is placed at prescribed positions on a lattice called the Bravais Lattice.

The Bravais lattice is expressed mathematically as an infinite set of points with translational symmetry along three axis that form a vector basis. Choosing an origin O, one can write

$$\mathcal{B} = \{P, \mathbf{OP} = n_1 \mathbf{a} + n_2 \mathbf{b} + n_3 \mathbf{c}, (n_1, n_2, n_3) \in \mathbb{Z}^3\}$$

The vectors (a, b, c) are the primitive vectors of the Bravais lattice.

One can distinguish **7 crystal systems**, that reflect the symmetry of the crystal. **14 Bravais lattices**:

Cubic	$a = b = c$ $a = b = g = 90^\circ$	
Tetragonal	$a = b \neq c$ $a = b = g = 90^\circ$	
Orthorhombic	$a \neq b \neq c$ $a = b = g = 90^\circ$	
Hexagonal	$a = b \neq c$ $a = b = 90^\circ; g = 120^\circ$	
Monoclinic	$a \neq b \neq c$ $a = g = 90^\circ \neq b$	
Triclinic	$a \neq b \neq c$ $a \neq b \neq g$	
		$a = b = c$ $a = b = g \neq 90^\circ$
		7 classes / 14 Bravais
		P : primitive
		I : centered
		F : face centered
		C : base centered

Cells and basis

- To represent crystals, we use different types of unit cells. The conventional unit cell is the most commonly used as it exhibits the highest symmetry of the crystal. They can however contain several motifs.
- Primitive unit cells are cells with one motif.

Coordination Number

- Number of closest neighbors, ie when spheres are in contact in a hard sphere model.
- For crystals with different atoms in the motif and notably for ionic crystals, the coordination number counts the closest atoms of different nature.

Hard Sphere model

- A first intuitive representation of crystals can be obtained by considering atoms as hard spheres packed into 3D geometrical forms; From basic geometric and vectorial consideration of the unit cell, one can calculate key properties of materials such as density and packing fraction (of free volume).
 - Density: $\rho = \frac{N_{\text{atoms per cell}} \times m_{\text{atoms}}}{V_{\text{cell}}}$
 - Packing fraction: c or $p = \frac{N_{\text{atoms per cell}} \times V_{\text{atoms}}}{V_{\text{cell}}}$
- The number of atoms per cell must be evaluated carefully as each atom is shared with other neighboring cells.
- Direction and planes of high density are defined where atoms are organized in a dense manner where they are in contact with each other.

Interstitial sites and Ionic / covalent crystals

- The notion of interstitial sites in metals can be used to estimate what the crystal structure could be of ionic crystals.
 - First Pauling Rule: For two atoms (NaCl, ClCs, ZnS etc...), the first Pauling rule establishes a formula that defines the coordination number depending on the ratio of the radius of the cation to the one of the anion: $\rho = \frac{r_+}{r_-}$
 - Based on the hard sphere model, it predicts that if the cation is too small, anions get too close to each other which lead to an unstable structure due to repulsive forces.
 - At the limit of stability, geometric consideration can give a condition on the ratio to have a certain coordination, in other words a certain number of cations surrounding an anion (and vice versa).
 - The formula is given by: $\rho = \frac{r_+}{r_-} = \sqrt{\frac{12}{12 - CN}} - 1$, where CN = coordination number
 - For $0.1547 < \rho < 0.2247$, CN = 3 ; Type of void: triangular planar
 - For $0.2247 < \rho < 0.4142$, CN = 4 ; Type of void: Tetrahedral
 - For $0.4142 < \rho < 0.7320$: CN = 6 ; Type of void: Octahedral
 - For $0.7320 < \rho < 1$: CN = 8 ; Type of void: Cubic

Crystal symmetries

- There are an infinite possibilities of Bravais lattices as the lattice parameters (vector norms and angles) can be chosen arbitrarily.
- The combination of the motif symmetry and the translational symmetry associated to the Bravais Lattice imposes restrictions on the type of symmetries a crystal (motif + Bravais lattice) can have.

- For a crystal to have a rotational symmetry of angle θ for example, translational symmetry indeed brings severe restrictions, as we can only have the following values for θ : $\frac{2\pi}{1}, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}$.
- A symmetry operation** is an action that leaves an object unchanged.
- A symmetry element** is a part of the object that doesn't move during the operation: a point, a line, a plane, an entire object.
- There are two kinds of symmetry operations:
 - Travel symmetry operations:**
 - Glide plane: *Action*: Reflect through a plane then translate parallel to it;
 - Screw axis: *Action*: Rotation by $360/N$ around an axis and translation along the axis
 - Point symmetry operations:**
 - Identity (1)**: *Action*: inversion through a point; *Symmetry element*: entire object
 - Inversion ($\bar{1}$)**: *Action*: inversion through a point; *Symmetry element*: a point
 - Rotation (N)**: *Action*: N -fold rotation around an axis ($360/N$); *Symmetry element*: a line
 - Mirror plane or reflection (m)**: *Action*: Reflection through a plane; *Symmetry element*: a plane
 - Rotoinversion (\bar{N})**: *Action*: Rotation +Inversion; *Symmetry element*: a point

Point Group:

- Points group are a set of symmetries associated to a 2D object (or motif), that verifies certain rules.
- A *Group* is a very important mathematical construction. A set G of objects is a group if it is **closed under an operation ***: for any $x, y \in G$, $x * y \in G$.
- A Group is a mathematical construction that satisfies the following properties:
 - Identity (fixed point) – There is an element e in G , such that for every $x \in G$, $e * x = x * e = x$
 - Inverse – For every x in G there is an element $y \in G$ such that $x * y = y * x = e$
 - Associativity – The following identity holds for every $x, y, z \in G$: $x * (y * z) = (x * y) * z$
- Point Group Symmetry
 - Closure: The combination of symmetry operators is a symmetry operator in the group.
 - All symmetry operators have an inverse, some are their own inverse.
 - Identity is part of all the Point group symmetry.
 - Associativity is respected
- Order (or cardinal) of a group:** number of symmetry elements in the group.
- In 2D there are 10 point groups when we restrict to the 1,2,3,4 and 6 fold rotational symmetries. Combined with the 5 2D Bravais lattices, we obtain 17 “Plane groups” that characterize the possible symmetries of a 2D crystal.
- In 3D, there are 32 points group, and 14 possible Bravais Lattices. This results in 230 “Space groups”:
- For all crystals with one atom per motif, the space group corresponds to the point group of the conventional cell geometry. The atom being considered spherical, it conserves all other symmetries.

Crystal directions and planes, Miller indices

- Crystal directions are lines that pass through at least two lattice points. The direction can be defined by an origin (all lattice point can be an origin) and the coordinate of the other point in the lattice basis.
- The coordinates, which are relative integers, represent the Miller indices.
- Crystal planes pass through three lattice points and are also defined by Miller indices.
- Miller indices can vary depending on the basis used. Conventional cells are used by default to determine Miller indices.
- In the cubic system, in the orthonormal basis $\mathcal{B}(O, \mathbf{x}, \mathbf{y}, \mathbf{z})$, the equation of an (hkl) plane that intercepts the axis at points $A\left(\frac{a}{h}, 0, 0\right); B\left(0, \frac{a}{k}, 0\right); C\left(0, 0, \frac{a}{l}\right)$ where a is the edge of the cube, is given by:

$$\mathcal{P}^{(hkl)} = \{(x, y, z) \in \mathbb{R}^3 / hx + ky + lz = a\}$$
- In the cubic system, for a lattice parameter (or cube edge) a , the distance between parallel crystal planes $d_{(hkl)}$ is given by:

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

Reciprocal space

- For a Direct lattice space $(O, \mathbf{a}, \mathbf{b}, \mathbf{c})$, we define the Reciprocal Lattice $(O, \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$ such that:

$$\begin{array}{l} \overrightarrow{a^*} \cdot \overrightarrow{a} = 2\pi \\ \overrightarrow{a^*} \cdot \overrightarrow{b} = 0 \\ \overrightarrow{a^*} \cdot \overrightarrow{c} = 0 \end{array} \quad \begin{array}{l} \overrightarrow{b^*} \cdot \overrightarrow{a} = 0 \\ \overrightarrow{b^*} \cdot \overrightarrow{b} = 2\pi \\ \overrightarrow{b^*} \cdot \overrightarrow{c} = 0 \end{array} \quad \begin{array}{l} \overrightarrow{c^*} \cdot \overrightarrow{a} = 0 \\ \overrightarrow{c^*} \cdot \overrightarrow{b} = 0 \\ \overrightarrow{c^*} \cdot \overrightarrow{c} = 2\pi \end{array}$$

- The reciprocal lattice, or reciprocal space, is the set of points: $\mathcal{R} = \{P, \mathbf{OP} = n_1 \mathbf{a}^* + n_2 \mathbf{b}^* + n_3 \mathbf{c}^*, (n_1, n_2, n_3) \in \mathbb{Z}^3\}$.

- The reciprocal basis, from these considerations, is constructed as follow: $\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{V}$; $\mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{V}$; $\mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{V}$, where V is the volume formed by the $(\mathbf{a}, \mathbf{b}, \mathbf{c})$ vectors: $V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})$.
- A definition of Miller indices: Miller indices (hkl) represent the indices of the planes in the direct lattice that are orthogonal to the vector $h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ in the reciprocal lattice.
- By construction, the distance between parallel crystal planes is given by: $d_{(hkl)} = \frac{2\pi}{\|N_{(hkl)}^*\|}$ where $N_{(hkl)}^*$ is a vector of coordinates (h, k, l) in the reciprocal basis $(O, \mathbf{a}^*, \mathbf{b}^*, \mathbf{c}^*)$.

– Monoclinic:	$d_{hkl} = \frac{1}{\sqrt{\left(\frac{h^2}{a^2} + \frac{l^2}{c^2} - \frac{2hl}{ac} \cos\beta\right) \frac{1}{\sin^2\beta} + \frac{k^2}{b^2}}}$
– Orthorhombic:	$d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}$
– Tetragonal:	$d_{hkl} = \frac{1}{\sqrt{\frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2}}}$
– Hexagonal:	$d_{hkl} = \frac{1}{\sqrt{\frac{4}{3} \frac{a^2}{h^2 + k^2 + hk} + \frac{l^2}{c^2}}}$
– Cubic:	$d_{hkl} = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}}$

Diffraction

- Interference phenomena can occur when a X-ray beam is shun upon a crystal. Crystal planes act as scatterers and a Bragg law can be obtained that linked the angle of incidence, the wavelength and the distance between crystal planes, in order to observe a peak of interference.
- **Bragg law**: $2d_{(hkl)} \sin(\theta) = n\lambda$, where $\frac{\pi}{2} - \theta$ is the angle of incidence with the normal to the plane, n is an integer defining the order of the interference, and λ the wavelength of the incident beam.
- **Laue condition**: a condition for constructive interference where the difference of the diffracted wave vector \mathbf{k}_1 and the incident wave vector \mathbf{k}_0 verifies: $\mathbf{K} = \mathbf{k}_1 - \mathbf{k}_0 \in \mathcal{R}$ where \mathcal{R} is the reciprocal space. In other words, for a given illumination direction given by \mathbf{k}_0 , interference peaks will be measured along directions (\mathbf{k}_1) for which the vector representing the difference between the two wave vectors belongs to the reciprocal space.

B = Solids

Hg = Liquids

Kr = Gases

Pm = Not found in nature

1	1 H 1.00794	2	2 He 4.002602
3	4 Li 6.941	4 Be 9.012182	
11	12 Na 22.989770	12 Mg 24.3050	
	3	4	
	5	6	
	7	8	
	9	10	
	11	12	
	13	14	
	15	16	
	17		
	18		
5	6 B 10.811	7 C 12.0107	8 O 14.00674
13	14 Al 26.581538	9 F 15.9994	10 Ne 18.9984032
14	15 Si 28.0855	11 P 30.973761	12 S 32.066
15	16 Cl 35.4527	17 Ar 39.948	
16	17 He 4.002602		
17			
18			
19	20 Ca 44.955910	21 Ti 47.867	22 V 50.9415
K 39.0983	Sc 40.078	Ti 51.9961	Cr 54.938049
37	38 Sr 85.4678	39 Zr 88.90585	40 Nb 91.224
Rb 85.4678	Y 87.62	Zr 92.90638	Nb 95.94
42	43 Mo (98)	44 Ru 101.07	45 Rh 102.90550
43	42 Tc (98)	46 Pd 106.42	47 Ag 196.56655
44	45 Ru 101.07	48 Ag 112.411	49 Cd 114.818
45	46 Rh 102.90550	50 In 118.710	51 Sn 121.760
46	47 Pd 106.42	52 Sb 127.60	53 Te 127.60
47	48 Ag 196.56655	54 I 126.90447	54 Xe 131.29
48	49 Cd 112.411	55 Te 131.29	
49	50 In 114.818	56 At (210)	
50	51 Sn 118.710	57 Rn (222)	
51	52 Sb 121.760	58 Po (209)	
52	53 Te 127.60	59 At (209)	
53	54 Xe 131.29	60 Rn (222)	
54	55 Te 126.90447	61 Pm (145)	62 Sm 150.36
55	56 At (209)	62 Pm (145)	63 Eu 151.964
56	57 Rn (222)	63 Eu 151.964	64 Gd 157.25
57	58 Ce 140.116	64 Gd 157.25	65 Tb 158.92534
58	59 Pr 140.50765	65 Tb 162.50	66 Dy 164.93032
59	60 Nd 138.9055	66 Dy 167.26	67 Ho 168.93421
60	61 Pm 144.24	67 Ho 167.26	68 Er 173.04
61	62 Sm 151.964	68 Er 168.93421	69 Tm 173.04
62	63 Eu 151.964	69 Tm 173.04	70 Yb 173.04
63	64 Gd 157.25	70 Yb 173.04	
64	65 Tb 158.92534		
65	66 Dy 162.50		
66	67 Ho 164.93032		
67	68 Er 167.26		
68	69 Tm 168.93421		
69	70 Yb 173.04		
70			
71	72 Lu 174.967	73 Hf 178.49	74 Ta 180.94.79
72	73 Lu 174.967	75 Hf 178.49	76 Ta 183.84
73	74 Lu 174.967	77 Hf 178.49	78 Ta 186.207
74	75 Lu 174.967	79 Hf 178.49	80 Ta 190.23
75	76 Lu 174.967	80 Hf 178.49	81 Ta 192.217
76	77 Lu 174.967	81 Hf 178.49	82 Ta 195.078
77	78 Lu 174.967	82 Hf 178.49	83 Ta 196.56655
78	79 Lu 174.967	83 Hf 178.49	84 Ta 200.59
79	80 Lu 174.967	84 Hf 178.49	85 Ta 204.3833
80	81 Lu 174.967	85 Hf 178.49	86 Ta 207.2
81	82 Lu 174.967	86 Hf 178.49	87 Ta 208.58038
82	83 Lu 174.967	87 Hf 178.49	88 Ta (209)
83	84 Lu 174.967	88 Hf 178.49	89 Ta (210)
84	85 Lu 174.967	89 Hf 178.49	90 Ta (222)
85	86 Lu 174.967	90 Hf 178.49	91 Ta (222)
86	87 Lu 174.967	91 Hf 178.49	92 Ta (222)
87	88 Lu 174.967	92 Hf 178.49	93 Ta (222)
88	89 Lu 174.967	93 Hf 178.49	94 Ta (222)
89	90 Lu 174.967	94 Hf 178.49	95 Ta (222)
90	91 Lu 174.967	95 Hf 178.49	96 Ta (222)
91	92 Lu 174.967	96 Hf 178.49	97 Ta (222)
92	93 Lu 174.967	97 Hf 178.49	98 Ta (222)
93	94 Lu 174.967	98 Hf 178.49	99 Ta (222)
94	95 Lu 174.967	99 Hf 178.49	100 Ta (222)
95	96 Lu 174.967	100 Hf 178.49	101 Ta (222)
96	97 Lu 174.967	101 Hf 178.49	102 Ta (222)
97	98 Lu 174.967	102 Hf 178.49	103 Ta (222)
98	99 Lu 174.967	103 Hf 178.49	104 Ta (222)
99	100 Lu 174.967	104 Hf 178.49	105 Ta (222)
100	101 Lu 174.967	105 Hf 178.49	106 Ta (222)
101	102 Lu 174.967	106 Hf 178.49	107 Ta (222)
102	103 Lu 174.967	107 Hf 178.49	108 Ta (222)
103	104 Lu 174.967	108 Hf 178.49	109 Ta (222)
104	105 Lu 174.967	109 Hf 178.49	110 Ta (222)
105	106 Lu 174.967	110 Hf 178.49	111 Ta (222)
106	107 Lu 174.967	111 Hf 178.49	112 Ta (222)
107	108 Lu 174.967	112 Hf 178.49	113 Ta (222)
108	109 Lu 174.967	113 Hf 178.49	114 Ta (222)
109	110 Lu 174.967	114 Hf 178.49	115 Ta (222)
110	111 Lu 174.967	115 Hf 178.49	116 Ta (222)
111	112 Lu 174.967	116 Hf 178.49	117 Ta (222)
112	113 Lu 174.967	117 Hf 178.49	118 Ta (222)
113	114 Lu 174.967	118 Hf 178.49	119 Ta (222)
114	115 Lu 174.967	119 Hf 178.49	120 Ta (222)
115	116 Lu 174.967	120 Hf 178.49	121 Ta (222)
116	117 Lu 174.967	121 Hf 178.49	122 Ta (222)
117	118 Lu 174.967	122 Hf 178.49	123 Ta (222)
118	119 Lu 174.967	123 Hf 178.49	124 Ta (222)
119	120 Lu 174.967	124 Hf 178.49	125 Ta (222)
120	121 Lu 174.967	125 Hf 178.49	126 Ta (222)
121	122 Lu 174.967	126 Hf 178.49	127 Ta (222)
122	123 Lu 174.967	127 Hf 178.49	128 Ta (222)
123	124 Lu 174.967	128 Hf 178.49	129 Ta (222)
124	125 Lu 174.967	129 Hf 178.49	130 Ta (222)
125	126 Lu 174.967	130 Hf 178.49	131 Ta (222)
126	127 Lu 174.967	131 Hf 178.49	132 Ta (222)
127	128 Lu 174.967	132 Hf 178.49	133 Ta (222)
128	129 Lu 174.967	133 Hf 178.49	134 Ta (222)
129	130 Lu 174.967	134 Hf 178.49	135 Ta (222)
130	131 Lu 174.967	135 Hf 178.49	136 Ta (222)
131	132 Lu 174.967	136 Hf 178.49	137 Ta (222)
132	133 Lu 174.967	137 Hf 178.49	138 Ta (222)
133	134 Lu 174.967	138 Hf 178.49	139 Ta (222)
134	135 Lu 174.967	139 Hf 178.49	140 Ta (222)
135	136 Lu 174.967	140 Hf 178.49	141 Ta (222)
136	137 Lu 174.967	141 Hf 178.49	142 Ta (222)
137	138 Lu 174.967	142 Hf 178.49	143 Ta (222)
138	139 Lu 174.967	143 Hf 178.49	144 Ta (222)
139	140 Lu 174.967	144 Hf 178.49	145 Ta (222)
140	141 Lu 174.967	145 Hf 178.49	146 <br