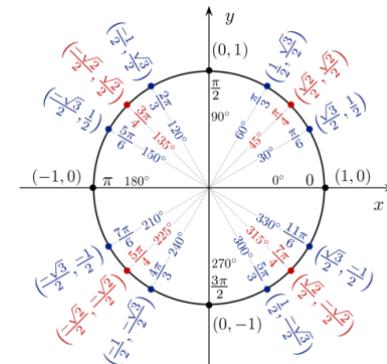


## MSE 238 – Preliminary Exam sheet – status week 4

### 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  $\alpha$  is the angle between the two vectors.
  - The cross product of two vectors forming an angle  $\alpha$  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:

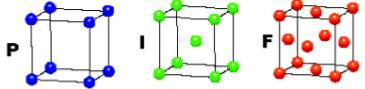
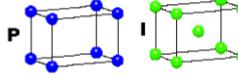
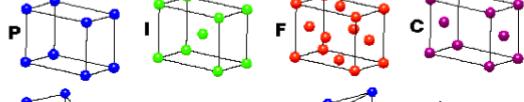
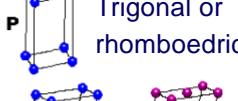
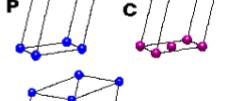
Materials in a crystalline state are organized into ordered arrangements of atoms. The chemical composition of the material forms a motif, that is placed at prescribed positions on a lattice called the Bravais Lattice.

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	$a = b \neq c$ $a = b = 90^\circ; g = 120^\circ$	 Trigonal or rhomboedric
Monoclinic	$a \neq b \neq c$ $a = g = 90^\circ \neq b$	
Triclinic	$a \neq b \neq c$ $a \neq b \neq g$	
		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  $\theta$  for example, translational symmetry indeed brings severe restrictions, as we can only have the following values for  $\theta$ :  $\frac{2\pi}{1}, \frac{2\pi}{2}, \frac{2\pi}{3}, \frac{2\pi}{4}, \frac{2\pi}{6}$ .
- 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:  

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

B = Solids      Hg = Liquids      Kr = Gases

Pm = Not found in nature

1		18									
H		He									
1.00794	2	4.002602									
<b>1</b>	<b>H</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>	<b>11</b>
<b>Li</b>	<b>Be</b>	<b>6,941</b>	<b>9,012182</b>	<b>13</b>	<b>14</b>	<b>15</b>	<b>16</b>	<b>17</b>	<b>18</b>	<b>19</b>	<b>20</b>
<b>Na</b>	<b>Mg</b>	<b>22,989770</b>	<b>24,3050</b>	<b>3</b>	<b>4</b>	<b>5</b>	<b>6</b>	<b>7</b>	<b>8</b>	<b>9</b>	<b>10</b>
<b>K</b>	<b>Ca</b>	<b>39,0983</b>	<b>40,078</b>	<b>21</b>	<b>22</b>	<b>23</b>	<b>24</b>	<b>25</b>	<b>26</b>	<b>27</b>	<b>28</b>
<b>Rb</b>	<b>Sr</b>	<b>85,4678</b>	<b>87,62</b>	<b>38</b>	<b>39</b>	<b>40</b>	<b>41</b>	<b>42</b>	<b>43</b>	<b>44</b>	<b>45</b>
<b>Cs</b>	<b>Ba</b>	<b>132,90545</b>	<b>137,327</b>	<b>55</b>	<b>56</b>	<b>71</b>	<b>72</b>	<b>73</b>	<b>74</b>	<b>75</b>	<b>76</b>
<b>Fr</b>	<b>Ra</b>	<b>(223)</b>	<b>(226)</b>	<b>87</b>	<b>88</b>	<b>103</b>	<b>104</b>	<b>105</b>	<b>106</b>	<b>107</b>	<b>108</b>
<b>Lr</b>	<b>Rf</b>	<b>(223)</b>	<b>(262)</b>	<b>57</b>	<b>58</b>	<b>59</b>	<b>60</b>	<b>61</b>	<b>62</b>	<b>63</b>	<b>64</b>
<b>La</b>	<b>Ce</b>	<b>138,9055</b>	<b>140,116</b>	<b>140,50765</b>	<b>144,24</b>	<b>145</b>	<b>150,36</b>	<b>151,964</b>	<b>157,25</b>	<b>158,92534</b>	<b>162,50</b>
<b>Ac</b>	<b>Th</b>	<b>232,0381</b>	<b>232,0381</b>	<b>89</b>	<b>90</b>	<b>91</b>	<b>92</b>	<b>93</b>	<b>94</b>	<b>95</b>	<b>96</b>
<b>Pa</b>	<b>U</b>	<b>231,03588</b>	<b>238,0289</b>	<b>(237)</b>	<b>(244)</b>	<b>(243)</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>
<b>Np</b>	<b>Ds</b>	<b>(261)</b>	<b>(262)</b>	<b>(263)</b>	<b>(262)</b>	<b>(265)</b>	<b>(266)</b>	<b>(269)</b>	<b>(272)</b>	<b>(277)</b>	<b>(277)</b>
<b>Uut</b>	<b>Uup</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>
<b>Uuh</b>	<b>Uuo</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>	<b>(277)</b>
<b>57</b>	<b>58</b>	<b>59</b>	<b>60</b>	<b>61</b>	<b>62</b>	<b>63</b>	<b>64</b>	<b>65</b>	<b>66</b>	<b>67</b>	<b>68</b>
<b>La</b>	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	<b>Er</b>
<b>89</b>	<b>90</b>	<b>91</b>	<b>92</b>	<b>93</b>	<b>94</b>	<b>95</b>	<b>96</b>	<b>97</b>	<b>98</b>	<b>99</b>	<b>100</b>
<b>Ac</b>	<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>
<b>(237)</b>	<b>(244)</b>	<b>(243)</b>	<b>(247)</b>	<b>(247)</b>	<b>(247)</b>	<b>(247)</b>	<b>(251)</b>	<b>(251)</b>	<b>(252)</b>	<b>(252)</b>	<b>(259)</b>
<b>101</b>	<b>102</b>	<b>103</b>	<b>104</b>	<b>105</b>	<b>106</b>	<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>
<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>
<b>100</b>	<b>101</b>	<b>102</b>	<b>103</b>	<b>104</b>	<b>105</b>	<b>106</b>	<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>
<b>101</b>	<b>102</b>	<b>103</b>	<b>104</b>	<b>105</b>	<b>106</b>	<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>
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<b>104</b>	<b>105</b>	<b>106</b>	<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>
<b>105</b>	<b>106</b>	<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>
<b>106</b>	<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>
<b>107</b>	<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>
<b>108</b>	<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>
<b>109</b>	<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>
<b>110</b>	<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>
<b>111</b>	<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>
<b>112</b>	<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>
<b>113</b>	<b>114</b>	<b>115</b>	<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>
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<b>116</b>	<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>
<b>117</b>	<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>
<b>118</b>	<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>
<b>119</b>	<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>	<b>130</b>
<b>120</b>	<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>	<b>130</b>	<b>131</b>
<b>121</b>	<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>	<b>130</b>	<b>131</b>	<b>132</b>
<b>122</b>	<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>	<b>130</b>	<b>131</b>	<b>132</b>	<b>133</b>
<b>123</b>	<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>	<b>130</b>	<b>131</b>	<b>132</b>	<b>133</b>	<b>134</b>
<b>124</b>	<b>125</b>	<b>126</b>	<b>127</b>	<b>128</b>	<b>129</b>	<b>130</b>	<b>131</b>	<b>132</b>	<b>133</b>	<b>134</b>	<b>135</b>
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<b>150</b>	<b>151</b>	<b>152</b>									