Crystallography and ordering

Nathalie Dupin
nathdupin@wanadoo.fr

Calcul Thermodynamique

SATA / Giens Peninsula / 2017
The goal of this lecture is to understand how the crystallographic data can help the Calphad thermodynamic modelling.
The goal of this lecture is to understand how the crystallographic data can help the Calphad thermodynamic modelling whatever the phase.
The goal of this lecture is to understand how the crystallographic data can help the Calphad thermodynamic modelling whatever the phase and in particular to model ordering.
Outline

- Crystallography
  - Experimental data
  - Nature of the phase
  - Sublattice model
  - + DFT

- A same model for different structures
  - interstitials
  - metallic ordering
  - Interstitials and metallic ordering

- Conclusion
Crystal structure data

Fig. 7a. Mg$_{33.3}$Cu$_{66.6}$ recuit 20 jours à 500°C (K$_4$Cu)
Fig. 7b. Mg$_{37.9}$Cu$_{62.1}$ non recuit (K$_4$Cu)
Fig. 7c. Mg$_{33.4}$Ni$_{66.6}$ recuit 22 jours à 480°C (K$_4$Cu) avec indication des raies utilisées pour le calcul du paramètre a.
Crystal structure data

Fig. 7a. Mg$_{33.3}$Cu$_{66.8}$ recuit 20 jours à 500°C (K$_2$Cu)
Fig. 7b. Mg$_{37.8}$Cu$_{62.4}$ non recuit (K$_2$Cu)
Fig. 7c. Mg$_{33.4}$Ni$_{66.6}$ recuit 22 jours à 480°C (K$_2$Cu) avec indication des raies utilisées pour le calcul du paramètre de la maille cubique de MgCu$_2$ en fonction de la composition (at.% Mg) et de la température (1 Å = 10^{-10} m).
Crystal structure data

**Table III.**—Alloy A (5 per cent. Mg).
(Face-centred cubic.)

<table>
<thead>
<tr>
<th>Radiation</th>
<th>$h$ $k$ $l$</th>
<th>Intensity</th>
<th>$d/n$ observed</th>
<th>$d/n$ calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>* $K_\beta$</td>
<td>111</td>
<td>V.W.</td>
<td>4.186</td>
<td>4.043</td>
</tr>
<tr>
<td>* $K_\alpha$</td>
<td>111</td>
<td>V.W.</td>
<td>4.029</td>
<td>4.043</td>
</tr>
<tr>
<td>$K_\beta$</td>
<td>111</td>
<td>M.</td>
<td>2.089</td>
<td>2.089</td>
</tr>
<tr>
<td>$K_\alpha$</td>
<td>111</td>
<td>St.</td>
<td>2.098</td>
<td>2.098</td>
</tr>
<tr>
<td>$L_\alpha$ (tungsten)</td>
<td>100 (2)</td>
<td>W.</td>
<td>1.820</td>
<td>1.817</td>
</tr>
<tr>
<td>$K_\alpha$</td>
<td>100 (2)</td>
<td>St.</td>
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<td>1.817</td>
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<td>$K_\alpha$</td>
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<td>St.</td>
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<td>1.284</td>
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<td>$L_\alpha$ (tungsten)</td>
<td>131</td>
<td>W.</td>
<td>1.093</td>
<td>1.096</td>
</tr>
<tr>
<td>$K_\alpha$</td>
<td>131</td>
<td>St.</td>
<td>1.094</td>
<td>1.095</td>
</tr>
</tbody>
</table>

**Note.**—Lines of $\beta$ phase are marked with an asterisk (*).
Crystal structure data
Crystal structure data

Table 4
Atomic coordinates and atomic displacement parameters of the Rh₆₁₉Te₂₅ compounds (0.15 < x < 0.80) as refined in the I2/m space group

<table>
<thead>
<tr>
<th>Atom</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy × site multiplicity</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh₁₁₁₅Te₂₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te(1)</td>
<td>0.339(2)</td>
<td>0</td>
<td>0.374(1)</td>
<td>4</td>
<td>1.12(6)</td>
</tr>
<tr>
<td>Te(2)</td>
<td>0.337(3)</td>
<td>0</td>
<td>0.878(1)</td>
<td>4</td>
<td>1.12(6)</td>
</tr>
<tr>
<td>Rh(1)</td>
<td>0.036(5)</td>
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<td>0.251(1)</td>
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<tr>
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<td>0</td>
<td>0</td>
<td>0.553(3)</td>
<td>1.02(1)</td>
</tr>
<tr>
<td>Rh(3)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>empty</td>
<td></td>
</tr>
<tr>
<td>Rh₁₂₁₅Te₂₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te(1)</td>
<td>0.338(1)</td>
<td>0</td>
<td>0.368(6)</td>
<td>4</td>
<td>1.6(7)</td>
</tr>
<tr>
<td>Te(2)</td>
<td>0.333(1)</td>
<td>0</td>
<td>0.879(7)</td>
<td>4</td>
<td>1.6(7)</td>
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<tr>
<td>Rh(1)</td>
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<td>Rh(2)</td>
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<td>0</td>
<td>1.11(4)</td>
<td>1.6(1)</td>
</tr>
<tr>
<td>Rh(3)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>empty</td>
<td></td>
</tr>
<tr>
<td>Rh₁₃₁₅Te₂₅</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te(1)</td>
<td>0.343(7)</td>
<td>0</td>
<td>0.3669(4)</td>
<td>4</td>
<td>1.7(6)</td>
</tr>
<tr>
<td>Te(2)</td>
<td>0.355(1)</td>
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<td>0.8797(4)</td>
<td>4</td>
<td>1.7(6)</td>
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<td>0.261(5)</td>
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<td>1.9(1)</td>
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<td>Rh(2)</td>
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<td>0</td>
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<tr>
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<td>0.5</td>
<td>0</td>
<td>empty</td>
<td></td>
</tr>
<tr>
<td>Rh₁₄₁₅Te₂₅</td>
<td></td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te(1)</td>
<td>0.338(1)</td>
<td>0</td>
<td>0.3773(6)</td>
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<td>2.45(1)</td>
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<td>0.8689(6)</td>
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<td>Rh(1)</td>
<td>−0.019(1)</td>
<td>0</td>
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</tr>
<tr>
<td>Rh(2)</td>
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<td>0</td>
<td>2.24(1)</td>
<td>1.2(1)</td>
</tr>
<tr>
<td>Rh(3)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>1.12(3)</td>
<td>1.2(1)</td>
</tr>
<tr>
<td>Rh₁₅₁₅Te₂₅</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Te(1)</td>
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<td>0.3808(3)</td>
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<td>0.88(6)</td>
</tr>
<tr>
<td>Te(2)</td>
<td>0.3420(6)</td>
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<td>0.8824(4)</td>
<td>4</td>
<td>0.88(6)</td>
</tr>
<tr>
<td>Rh(1)</td>
<td>0.0166(9)</td>
<td>0</td>
<td>0.2411(5)</td>
<td>4</td>
<td>0.93(8)</td>
</tr>
<tr>
<td>Rh(2)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.93(8)</td>
<td>0.93(8)</td>
</tr>
<tr>
<td>Rh(3)</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.61(2)</td>
<td>0.93(8)</td>
</tr>
</tbody>
</table>

Fig. 3. Perspective view of the Rh₁₁₁₅Te₂₅ structures (x>0.5). The gray sphere corresponds to the octahedral sites filled by rhodium (Rh(3)) beyond the Rh₁₁₁₅Te₂₅ composition (see Fig. 2 for details of the other rhodium position). Larger open circles are Te atoms.
Crystallographic information

Of interest for the thermodynamic modelling

⇝ Nature of the phase: prototype, StrukturBericht
   ⇒ continuous model, phase name

⇝ Number of sites, multiplicity
   ⇒ sublattice model

⇝ Site occupancy
   ⇒ species to consider in the modelling
   ⇒ can be fitted

⇝ Volume
   ⇒ can be fitted
Continuous modelling

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure type</th>
<th>Pearson symbol</th>
<th>Space group No.</th>
<th>Material search</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Cu,Ni)</td>
<td>Cu</td>
<td>cF4</td>
<td>225</td>
<td></td>
</tr>
</tbody>
</table>

Continuous modelling is obvious when there is a continuous solution.

Cu and Ni: prototype Cu ⇒ substitutional model: (Cu,Ni)

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Bibliographic data

Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski, 1990, #1442-1446, Chakrabarti D.J., Chen S.W., Chang Y.A.
Continuous modelling is obvious when there is a continuous solution.

Cu and Ni:
- prototype Cu
  ⇒ substitutional model: (Cu,Ni)

\[
G^\text{fcc} = x_{Cu} G^\text{fcc}_{Cu} + x_{Ni} G^\text{fcc}_{Ni} + RT (x_{Cu} \ln x_{Cu} + x_{Ni} \ln x_{Ni}) + x_{Cu} x_{Ni} L^{fcc}_{Cu,Ni}
\]
Continuous modelling

<table>
<thead>
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Continuous modelling

Continuous modelling may be less obvious when there is a miscibility gap.

(Cu) and (Co) ht: prototype Cu
⇒ substitutional model: (Cu,Co)
Continuous modelling

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⇒ substitutional model: (Cu,Co)

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<tr>
<th>Phase</th>
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<tr>
<td>(Cu)</td>
<td>Cu</td>
<td>cF4</td>
<td>225</td>
<td>Search</td>
</tr>
<tr>
<td>(Co) ht</td>
<td>Cu</td>
<td>cF4</td>
<td>225</td>
<td>No Data</td>
</tr>
<tr>
<td>(Co) rt</td>
<td>Mg</td>
<td>hP2</td>
<td>194</td>
<td>No Data</td>
</tr>
</tbody>
</table>

Bibliographic data
Continuous modelling

The reciprocal solubility can also be limited due to intermediate phases. (Al) and (Cu): prototype Cu ⇒ substitutional model: (Al,Cu)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure type</th>
<th>Pearson symbol</th>
<th>Space group No.</th>
<th>Material search</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAl₂</td>
<td>CuAl₂</td>
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<td>140</td>
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<td>Cu₁₁₅Al₇</td>
<td>Cu₁₁₅Ge</td>
<td>hP6</td>
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<td>No Data</td>
</tr>
<tr>
<td>Cu</td>
<td>Cu</td>
<td>cF4</td>
<td>225</td>
<td>No Data</td>
</tr>
<tr>
<td>Cu₉₇Al₄</td>
<td>Cu₉₇Al₄</td>
<td>cP52</td>
<td>215</td>
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</tr>
<tr>
<td>Cu₄Al</td>
<td>Au₄Al</td>
<td>cP20</td>
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<td>CuAl</td>
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Bibliographic data

Binary Alloy Phase Diagrams, II Ed., Ed. T.B. Massalski,1990,1,141-143,Murray J.L.
Continuous modelling

The reciprocal solubility can also be limited due to intermediate phases. (Al) and (Cu): prototype Cu ⇒ substitutional model: (Al,Cu)

<table>
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<tr>
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<td>CuAl₂</td>
<td>CuAl₂</td>
<td>c112</td>
<td>140</td>
<td>Search</td>
</tr>
<tr>
<td>Cu₁₅Al₆ h₁t</td>
<td>Cu₁₇₂₅Ge</td>
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<td>Cu</td>
<td>cF4</td>
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<tr>
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<tr>
<td>Cu₄Al h₁t</td>
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<td>cP20</td>
<td>198</td>
<td>No Data</td>
</tr>
<tr>
<td>CuAl h₁t</td>
<td>CuAl</td>
<td>mS20</td>
<td>12</td>
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</tr>
<tr>
<td>Cu₁₃₂₄Al₁₆ h₁t</td>
<td>Cu₃₁₂₄(Cu₀₆₈₂₄Al₄₃₂₄Al₁₆</td>
<td>hR156</td>
<td>160</td>
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<td>Cu₅Al₄ h₁t</td>
<td>Cu₅Zn₈</td>
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<td>217</td>
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</table>
Continuous modelling

It is recommended to use the same model for phases having the same crystallographic structure.
Continuous modelling

It is recommended to use the same model for phases having the same crystallographic structure.

- It is obvious when similar composition, similar elements, known continuous solubility.
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- It is not obvious - but recommended to be able to treat multicomponent cases - when different compositions in simple systems, very different crystallographic parameters, no reciprocal solubility.
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ex: CsCl/NiAl
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- It is not recommended when no common elements, no possible solubility, very different interactions.
  ex: CsCl/NiAl

Using a phase name related to the crystallographic structure may avoid names losing their meaning when considering different systems. BCC\_A2 is $\alpha$ or $\delta$ for Fe, $\beta$ for Ti, $\gamma$ for U.
Laves phases

<table>
<thead>
<tr>
<th>Phase</th>
<th>Structure type</th>
<th>Pearson symbol</th>
<th>Space group No.</th>
<th>Material search</th>
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<tr>
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<td>cF24</td>
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<tr>
<td>Cu</td>
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<td>[Search]</td>
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</tbody>
</table>

Bibliographic data
Laves phases

<table>
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<th>Structure type</th>
<th>Pearson symbol</th>
<th>Space group No.</th>
<th>Material search</th>
</tr>
</thead>
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<td>hP2</td>
<td>194</td>
<td></td>
</tr>
<tr>
<td>MgCu₂</td>
<td>MgCu₂</td>
<td>cF24</td>
<td>227</td>
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<tr>
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<tr>
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<td>Mg₂Cu</td>
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<td>70</td>
<td></td>
</tr>
</tbody>
</table>

**Acta Crystallogr. C,1984,40,.1-5,Ohba T., Kitano Y., Komura Y.**

**Preparation**  
Synthesis: No data.  
Starting materials: No data.

**Crystal Structure**  
**X-ray Diffraction**  
**Properties**

**Crystal Structure (Published)**

**Niggli-reduced cell**

**Crystallographic data**  
Cell parameters:  
a = 0.49738 nm, b = 0.49738 nm, c = 0.49738 nm,  
α = 60°, β = 60°, γ = 60°  
Cell volume: 0.08701 nm³

**Crystal Structure (Standardized)**

**Crystallographic data**  
Cell parameters:  
a = 0.7034 nm, b = 0.7034 nm, c = 0.7034 nm,  
α = 90°, β = 90°, γ = 90°  
Cell volume: 0.3480 nm³  
Cell density (calculated): 5.78 Mg m⁻³  
Z: 8

**Atom coordinates**

<table>
<thead>
<tr>
<th>No</th>
<th>Site notation</th>
<th>Atom</th>
<th>Multiplicity</th>
<th>Wyckoff</th>
<th>Site symmetry</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
</tr>
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<tbody>
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<td>Cu</td>
<td>16</td>
<td>c</td>
<td>-3m</td>
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<td>0</td>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
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<td>Mg</td>
<td>Mg</td>
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**Bibliographic data**

Laves phases

Crystallography

Sublattice Model

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Preparation

Synthesis  No data.
Starting materials  No data.

Crystal Structure

Crystal Structure (Published)

Niggli-reduced cell

Crystallographic data

Cell parameters  
- \(a = 0.49738 \text{ nm}, b = 0.49738 \text{ nm}, c = 0.49738 \text{ nm},\)
- \(\alpha = 60^\circ, \beta = 60^\circ, \gamma = 60^\circ\)

Cell volume  0.08701 nm³

Crystal Structure (Standardized)

Crystallographic data

Cell parameters  
- \(a = 0.7034 \text{ nm}, b = 0.7034 \text{ nm}, c = 0.7034 \text{ nm},\)
- \(\alpha = 90^\circ, \beta = 90^\circ, \gamma = 90^\circ\)

Cell volume  0.3480 nm³

Cell density (calculated)  5.78 Mg m⁻³

Z  8

Atom coordinates

<table>
<thead>
<tr>
<th>No</th>
<th>Site notation</th>
<th>Atom</th>
<th>Multiplicity</th>
<th>Wyckoff</th>
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\(\Rightarrow (\text{Cu})_2(\text{Mg})\)
Laves phases

<table>
<thead>
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<th>Phase</th>
<th>Structure type</th>
<th>Pearson symbol</th>
<th>Space group No.</th>
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<td>Mg2Cu</td>
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<td>70</td>
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Crystallography and ordering

**MgCu2**

<table>
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<tr>
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<th>Pearson symbol</th>
<th>Space group</th>
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<td>cF24</td>
<td>Fd-3m</td>
<td>22</td>
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</tbody>
</table>

*Standardiz


**Preparation**

**Synthesis**
No data.

**Starting materials**
No data.

**Crystal Structure**

**X-ray Diffraction**

**Properties**

**Crystal Structure (Published)**

- **Niggli-reduced cell**

**Crystallographic data**
- Cell parameters: $a = 0.49738\text{ nm}$, $b = 0.49738\text{ nm}$, $c = 0.49738\text{ nm}$,
- $\alpha = 60^\circ$, $\beta = 60^\circ$, $\gamma = 60^\circ$
- Cell volume: $0.08701\text{ nm}^3$

**Crystal Structure (Standardized)**

**Crystallographic data**
- Cell parameters: $a = 0.7034\text{ nm}$, $b = 0.7034\text{ nm}$, $c = 0.7034\text{ nm}$,
- $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$
- Cell volume: $0.3480\text{ nm}^3$
- Cell density (calculated): $5.78\text{ Mg m}^{-3}$
- $Z = 8$

**Atom coordinates**

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<th>No</th>
<th>Site notation</th>
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<th>Multiplicity</th>
<th>Wyckoff</th>
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<th>x</th>
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<tbody>
<tr>
<td>1</td>
<td>Cu</td>
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<td>c</td>
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**+ homogeneity range $\Rightarrow (\text{Cu,Mg})_2(\text{Cu,Mg})$**
Laves phases

$$(\text{Cu},\text{Mg})_2(\text{Cu},\text{Mg})$$

$$G_{C15}^{C15} = y_{16c}^{Cu} y_{16c}^{Cu} G_{Cu:Cu}^{C15} + y_{16c}^{Cu} y_{8b}^{Mg} G_{Cu:Mg}^{C15} + y_{16c}^{Mg} y_{8b}^{Cu} G_{Mg:Cu}^{C15} + y_{16c}^{Mg} y_{Mg}^{8b} G_{Mg:Mg}^{C15}$$

$$+ RT \left( 2 \sum_{i} y_{i}^{16c} \ln y_{i}^{16c} + \sum_{i} y_{i}^{8b} \ln y_{i}^{8b} \right)$$

$$+ y_{16c}^{Cu} y_{16c}^{Mg} \sum_{j} y_{j}^{8b} L_{C15}^{Cu,\text{Mg}:j}$$

$$+ y_{8b}^{Cu} y_{8b}^{Mg} \sum_{i} y_{i}^{16c} L_{C15}^{i:Cu,\text{Mg}}$$
Laves phases

\[(Cu, Mg)_2(Cu, Mg)\]

\[
x_i = \frac{2}{3} y_{16c}^i + \frac{1}{3} y_{8b}^i
\]

\[
y_i^{8b} = 3x_i - 2y_{16c}^i
\]
Laves phases

$$(\text{Cu},\text{Mg})_2(\text{Cu},\text{Mg})$$
Laves phases

\[ \text{Cu}_2\text{Mg} \quad \text{C}15 \]

\[ \text{Zn}_2\text{Mg} \quad \text{C}14 \]

\[ \text{Ni}_2\text{Mg} \quad \text{C}36 \]

Cu\textsubscript{2}Mg is the prototype for the C15 Laves phases.

The Laves phases are a family of intermetallic phases appearing in many binary and ternary systems.

They have all often been modelled with a 2SL model with reciprocal substitution in order to describe their range of homogeneity.

The C14 is often identified in multicomponent alloys of industrial interest.

U. Kattner et al., Calphad XLII

Nathalie Dupin (CT)  Crystallography and ordering  SATA / Giens Peninsula / 2017
Laves phases

Cu₂Mg is the prototype for the C15 Laves phases.

The Laves phases are a family of intermetallic phases appearing in many binary and ternary systems.

They have all often been modelled with a 2SL model with reciprocal substitution in order to describe their range of homogeneity.

The C14 is often identified in multicomponent alloys of industrial interest.

C14: \((A,B)_2(A,B)\) or \((A,B)_3(A,B)(A,B)_2\)?
Laves phases

The C14 often appears as an extension of a binary phase in temperature and composition along an almost constant composition line, ...
Laves phases

1969 Gladyshevskii E.I.

... as a ternary phase,
Laves phases

1969 Gladyshevskii E.I.

\[ (\text{Ni},\text{Si})_6(\text{Nb})_4(\text{Ni},\text{Si})_2 \]
Laves phases

1969 Gladyshevskii E.I.

\[ \Rightarrow (\text{Ni})_6(\text{Nb},\text{Si})_4(\text{Ni})_2 \]

\[ \Rightarrow (\text{Ni},\text{Si})_6(\text{Nb})_4(\text{Ni},\text{Si})_2 \]
Laves phases

1969 Gladyshevskii E.I.

Experimental site occupancies are not directly from diffraction patterns. Assumptions are made. Critical assessment is also needed for these data.

\[
\Rightarrow (\text{Ni})_6(\text{Nb},\text{Si})_4(\text{Ni})_2
\]

\[
\Rightarrow (\text{Ni},\text{Si})_6(\text{Nb})_4(\text{Ni},\text{Si})_2
\]
Laves phases

... but also with different homogeneity range topology.
Laves phases

... but also with different homogeneity range topology.

Laves phases

Fig. 8. Occupation of the atomic sites for the $\tau_3$-phase as a function of the Al-content.

© ASM International 2009. Diagram:

Laves phases

Compilations may reinterpret original data. Original data are safer for crystallography also.
Laves phases

\[(\text{Al, Ni, Ti})_2(\text{Al, Ni, Ti})\] is not a good model for the C14 phase.

⇒ \[(\text{Al, Ni, Ti})_3(\text{Al, Ni, Ti})(\text{Al, Ni, Ti})_2\]
Laves phases

Based on its limited non-stoichiometry in some systems and on partial or bad site occupancies experimental results, the C14 has often been modelled with two sublattices only, like the C15.

However, in order to describe properly the C14, MgZn$_2$-type, phase, 3 sublattices are needed to allow different occupations for the 3 crystallographic sites.
Laves phases

For decades simplified models have been used because of computers limitations and the impossibility to assess all the compounds.

These simplications were made grouping together similar crystallographic sites. It is still interesting to use them in some cases.

However they may oversimplify phases presenting large multicomponent area. Nowadays that DFT can help, models close to the crystallography are recommended.
μ Phase

Fe-Mo-Ta Phase Diagram (1992 Raghavan V.)

Published phase label | Formula | Prototype | Pearson symbol
--- | --- | --- | ---
(Fe) rt | Fe | W | cl2
α | | | Im-3m
Mo5.1Fe7.9 rt | Mo5.08Fe7.92 | W5Fe7 | hP39
Fe7Mo6,μ | | | R-3m
Ta7Fe6 | Ta6.5Fe6.5 | W6Fe7 | hP39
FeTa,μ | | | R-3m
(Ta,Mo) | Ta0.5Mo0.5 | W | cl2
(Mo,Ta) | | | Im-3m
(TaFe2,MoFe2,rt) | MoFe2 | MgZn2 | hP12
Fe2(Mo,Ta) | | | P63/mmc
μ Phase

Fe-Mo-Ta Phase Diagram (1992 Raghavan V.)

Mo$_{5.1}$Fe$_{7.9}$ and Ta$_7$Fe$_6$ prototype $W_6Fe_7$ ⇒ same model.
μ Phase

Prototype μ

<table>
<thead>
<tr>
<th>Prototype μ</th>
<th>Fe₇W₆</th>
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<tbody>
<tr>
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</tr>
<tr>
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<td>Coordination number</td>
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<tr>
<td>Site occupation</td>
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Crystallography + DFT

Nathalie Dupin (CT)

Crystallography and ordering

SATA / Giens Peninsula / 2017
### Phase

#### Crystallography and ordering

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<tr>
<th>Prototype $\mu$</th>
<th>Fe$_7$W$_6$</th>
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<tr>
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<tr>
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<tr>
<td>Wyckhoff</td>
<td>$3a$ $6c1$ $6c2$ $6c3$ $18h$</td>
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**μ Phase**

Prototype $\mu$ | Fe$_7$W$_6$
--- | ---
Space group | $R3m$
Pearson symbol | $hR13$
Wyckhoff | 3a 6c1 6c2 6c3 18h
Coordination number | 12 15 16 14 12
Site occupation | Fe W W W Fe

Crystallography + DFT

Nathalie Dupin (CT)
μ Phase

Prototype μ
Fe$_7$W$_6$

Space group
R3m
hR13

Wyckhoff
3a 6c1 6c2 6c3 18h

Coordination number
12 15 16 14 12

Site occupation
Fe W W W Fe

Crystallography and ordering
SATA / Giens Peninsula / 2017

Nathalie Dupin (CT)
The CEF 5SL using the 32 compounds from VASP and the CEF 4SL using the 16 compounds from VASP are very close to CVM.

The CEF 3SL using 8 compounds from VASP 8 is far from CVM for low Nb content. It will not work properly for all systems.
A same model for different structures

- Interstitials
- Metallic ordering
- Interstitials and metallic ordering
\((M, M')(C, \Box)\)

\[\Rightarrow C\text{-Cu-Ti: } (Cu, Ti)(C, \Box) \text{ both A1 and B1}\]
The continuous modelling between metallic solutions and carbides is based on crystallographic consideration. This continuity is experimentally observed in very few systems.
Different crystallography  Interstitials

\( \text{U(C, C}_2, \square) \)

![Graph showing temperature vs. composition for U(C, C\(_2\), \square) at \( x_C = 0.5 \)]

![Graph showing heat capacity vs. temperature for U(C) at 1500 and 3000K]

Nathalie Dupin (CT)
Crystallography and ordering
SATA / Giens Peninsula / 2017 17 / 29
Zr$_3$(O,□)(O,□)(O,□)

2001 Liang et al.: $\alpha$ and $\alpha'$
$\text{Zr}_3(\text{O},\square)(\text{O},\square)(\text{O},\square)$

2001 Liang et al.: $\alpha$ and $\alpha'$
$\text{Zr}_3(\text{O,□})(\text{O,□})(\text{O,□})$

2001 Liang et al.: $\alpha$ and $\alpha'$
Metallic ordering
Metallic ordering

A2

B2

L2₁
Metallic ordering
Metallic ordering

A2

B2

L2₁

A3

D0₁₉

Fe

Ti

Fe

Al

Ni

A1

L1₂

L1₀
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, $G(y^s_i)$, using the CEF, function of the site occupation of the different sublattices, $y^s_i$. 
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, $G(y^s_i)$, using the CEF, function of the site occupation of the different sublattices, $y^s_i$.

\[(A,B)(A,B)(A,B)(A,B)\text{ fcc based}\]

\[
\begin{align*}
&\implies y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)} \text{ A1} \\
&\implies y_i^{(1)} = y_i^{(2)} = y_i^{(3)} \neq y_i^{(4)} \text{ L1}_2 \\
&\implies y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)} \text{ L1}_0
\end{align*}
\]
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, \( G(y_i^s) \), using the CEF, function of the site occupation of the different sublattices, \( y_i^s \).

\[
(A,B)(A,B)(A,B)(A,B) \text{ bcc based}
\]

\[
\begin{align*}
\Rightarrow & \quad y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)} \quad \text{A2} \\
\Rightarrow & \quad y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)} \quad \text{B2} \\
\Rightarrow & \quad y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} \neq y_i^{(4)} \quad \text{D0}_3 \text{ or } \text{L2}_1 \\
\Rightarrow & \quad y_i^{(1)} = y_i^{(3)} \neq y_i^{(2)} = y_i^{(4)} \quad \text{B32}
\end{align*}
\]
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, $y_i^s$.

\[(A,B)(A,B)(A,B)(A,B) \text{ hcp based} \]

$\implies y_i^{(1)} = y_i^{(2)} = y_i^{(3)} = y_i^{(4)} \ A3$

$\implies y_i^{(1)} = y_i^{(2)} = y_i^{(3)} \neq y_i^{(4)} \ D0_{19}$

$\implies y_i^{(1)} = y_i^{(2)} \neq y_i^{(3)} = y_i^{(4)} \ B_{19}$
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, \( G(y^s_i) \), using the CEF, function of the site occupation of the different sublattices, \( y^s_i \).

\[
G(y^s_i) = \sum_{ijkl} y_i^{(1)} y_j^{(2)} y_k^{(3)} y_l^{(4)} G_{ijkl} + RT \sum_s a^s \sum_i y_i^s \ln y_i^s + G^{xs}
\]

Relations between the parameters of \( G(y^s_i) \) are to be imposed so that the disorder can become stable. This is obtained taking into account the symmetries of the lattices.
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, \( G(y^s_i) \), using the CEF, function of the site occupation of the different sublattices, \( y^s_i \).

It is in general splitted into two contributions.

\[
G(y^s_i) = G^{\text{dis}}(x_i) + \Delta G^{\text{ord}}(y^s_i)
\]

This is not a requirement. It allows easier management of big databases, avoiding to introduce the CEF for systems without significant ordering.

\[
G^{\text{dis}}(x_i) = \sum_i x_i G^{\text{dis}}_i + RT \sum_i x_i \ln x_i
\]

\[
+ \sum_{i,j} x_i x_j L^{\text{dis}}_{i,j} + \sum_{i,j,k} x_i x_j x_k L^{\text{dis}}_{i,j,k}
\]
Metallic ordering

The Gibbs energy of the different phases of a same family can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, $y_i^s$.

It is in general splitted into two contributions.

$$G(y_i^s) = G^{\text{dis}}(x_i) + \Delta G^{\text{ord}}(y_i^s)$$

The ordering part itself is the difference of two terms, expressed in the CEF, allowing it to cancel when the phase is disordered.

$$\Delta G^{\text{ord}}(y_i^s) = G^{\text{ord}}(y_i^s) - G^{\text{ord}}(y_i^s = x_i)$$

The relations allowing the phase to disorder are to be imposed between the parameters defining $G^{\text{ord}}(y_i^s)$. They can easily be related to the crystallographic symmetry of the lattice.
The Gibbs energy of the different phases of a same family can be described with a single expression, $G(y_i^s)$, using the CEF, function of the site occupation of the different sublattices, $y_i^s$.

It is in general splitted into two contributions.

$$G(y_i^s) = G^{\text{dis}}(x_i) + \Delta G^{\text{ord}}(y_i^s)$$

The ordering part itself is the difference of two terms, expressed in the CEF, allowing it to cancel when the phase is disordered.

$$\Delta G^{\text{ord}}(y_i^s) = G^{\text{ord}}(y_i^s) - G^{\text{ord}}(y_i^s = x_i)$$

In order to use this formalism in Thermo-Calc the following command has to be given in G_E_S

```plaintext
AMEND_PHASE_DESCRIPTION ord DIS_PART dis
```
A2/B2 modelling

To be able to describe the 2nd order transition between the A2, B2 and L2₁ phases in the ternary system Al-Fe-Ti, the A2 and B2 phases have to be described with 4SL in Fe-Ti.
bcc ordering
bcc ordering
bcc ordering
**bcc ordering**

From crystallographic symmetry, the following configurations are equivalent.
bcc ordering

From crystallographic symmetry, the following configurations are equivalent.

B2 configurations
bcc ordering

From crystallographic symmetry, the following configurations are equivalent.

D0₃ configurations
bcc ordering

From crystallographic symmetry, the following configurations are equivalent.

B32 configurations
**bcc ordering**

The fact to assign the same Gibbs energy to equivalent configurations allows the disordered phase to be stable. This stands for Gibbs energy of the stoichiometric compounds as well as for interaction parameters.

In Thermo-Calc software, there is an option - B - where the equality of the Gibbs energy of the equivalent configurations of the irregular tetrahedron constituting the bcc lattice is built in.

The use of DFT estimates for the compounds that are not stable is recommended. However, up to the quaternary compounds, a cluster expansion on the 1st and 2nd neighbours bonds can be used as first approximation for extrapolation.
fcc ordering

The fcc ordering is more simple as the lattice is built on regular tetrahedra.
fcc ordering

From crystallographic symmetry, the following configurations are equivalent.
**fcc ordering**

From crystallographic symmetry, the following configurations are equivalent.

$L1_2$ configurations
fcc ordering

From crystallographic symmetry, the following configurations are equivalent.

$L1_0$ configurations
A1/L12 modelling

Different crystallography
Metallic ordering

A1/L12 modelling

Rastogi & Arc
Chellman
Chellman & A
Gentry & Fine
Maheshwari i
Hornbogen &
Watanabe et
Li & Ardell
08Gwy
34Fin
37Ale
31Sch
42Phi
52Tay
72Tay
83Nas
84Rob
87Hil
88Bre
90Jia
91Ver
93Col

A1

L12

L10

T/K

x(Ni)
Interstitial and metallic ordering

The E$_2^1$ $\kappa$ phase, stable in Al-Fe-C for instance, should be described with the same model as all these crystallographic structures, considering ordering between metallic elements and between C and vacancies.
Conclusion

The knowledge of the crystallography of the phases is key for a good thermodynamic modelling.

To estimate properly the configurational entropy of phases showing large homogeneity range, it is important to use a model close to the crystallography.

Such models are in general more complex but the parameters assessment can be tremendously simplified by the use of DFT estimates for metastable configurations.
Bibliography


http://nathdupin.free.fr/public/Lectures/TCSAB-10years.pdf