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Pandat 软件

第一期优化培训教程

第四讲

2020年7月5日

CompuTherm, LLC
8401 Greenway Blvd, Middleton, WI, USA
http://www.computherm.com

答疑

1. Pandat数据库中很强调大小写吗，我发现元素在开始定义ZN，之后参数中写成Zn就会提示错误，而且大小写还得和POP文件中的一样，否则又会提示找不到该成分？
2. Tieline是连接线的本意吗？还是定义的专有名词？
3. 2 1 1 和 2 0.666 0.3333 有区别吗？
4. TDB文件里面描述一个相需要哪些函数呢，比如一个相两个点阵，每个点阵两个原子，**按照排列组合的话G函数和L函数有很多个，里面有哪些是必须输入的吗，还是说所有的都得输入进去？** 这个体系中纯组元的吉布斯能表达式可以怎么获得，发现设置待优化参数时，液相到1阶，fcc相到2阶，hcp相却只有0阶。这一块有什么讲究吗？
5. 上午这个Al-Zn体系 的FCC和bcc相都只有一个亚点阵，没有包括间隙亚点阵，是这个体系特殊，还是说和正常的没有什么区别？

亚点阵模型(Sublattice model)

Atoms in crystalline solids – occupy different type of **sublattices**
Sublattices represent LRO – modify entropy and excess Gibbs energy

Example:

$(A,B)_p(C,D)_q$

p,q – ratio of sites on the two sublattices (smallest possible integer numbers)
A,B,C,D – constituents (in CEF)

液相或置换型固溶体: 一个亚点阵 (A,B,C,D)

计量化合物: 一个亚点阵 (A_pC_q) 或 多个亚点阵 $(A)_p(C)_q$

多亚点阵固溶体相: $(A,B)_p(C,D)_q$

间隙固溶体，置换固溶体

Compound Energy Formalism(CEF)

亚点阵模型(Sublattice model)

$(A,B)_p(C,D)_q$ ： $i = A,B\ldots;\quad j = C,D\ldots$

$$G^{\varphi} = \sum_{i,j} y_i^I \cdot y_j^{II} \cdot G_{i:j}^{0,\varphi} + pRT\sum_i y_i^I \ln y_i^I + qRT\sum_j y_j^{II}\ln y_j^{II} + G^{ex,\varphi}$$

$$\Downarrow \qquad\qquad \underbrace{\qquad\qquad}$$

$${}^{\mathrm{ref}}G \qquad\qquad {}^{\mathrm{conf}}G$$

溶液模型(一个亚点阵，(A,B,C…))

$$G^{\varphi} = \sum_i y_i \cdot G_i^{0,\varphi} + RT\sum_i y_i \ln y_i + G^{ex,\varphi}$$

$G_i^{0,\varphi}$: endmember 值，必须要给出。

无值时默认为0， 通常是不合理的。

CaO-MgO TDB 文件

```
Element          Ca                          Fcc     40.078        5736     41.588 !
Element          Mg                          Hcp     24.305        4998     32.671 !
Element          O          1/2_MOLE_O2(G)           15.999        4341     102.52 !
Species             CaO                          Ca1O1 !
Species             MgO                          Mg1O1 !
```

CaMgO_TwoLiquid.tdb

CaMgO_ASSModel.tdb

```
$ CaO and MgO are components
Element          CaO                         Halite  56.077        0      38.100 !
Element          MgO                         Halite  40.304        0      26.95 !
```

CaO-MgO_LIQOX.tdb

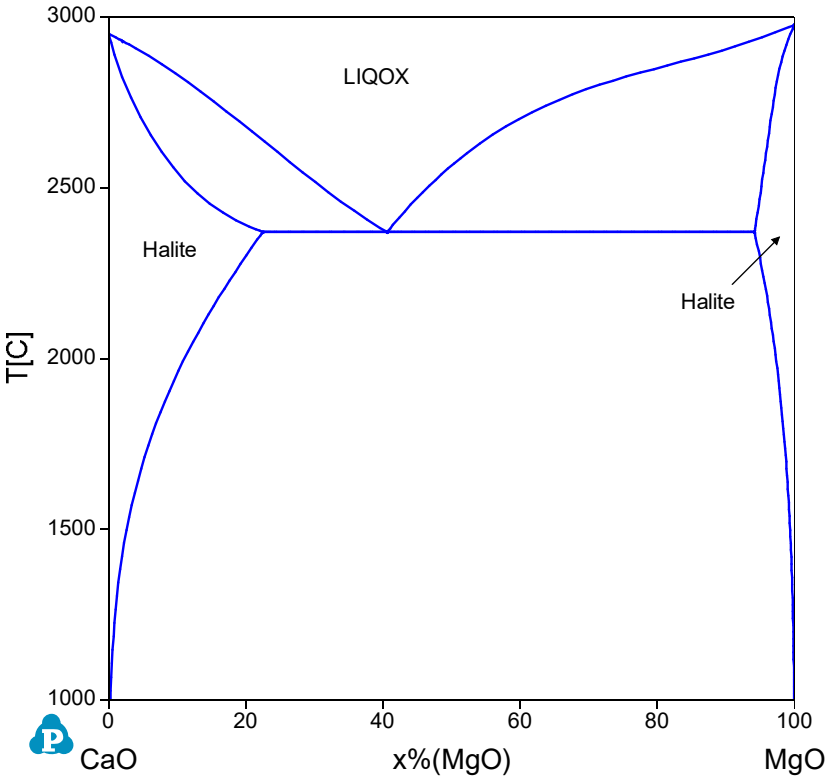
```
Phase LIQOX % 1 1 !
Constituent LIQOX :CaO,MgO:!
    Parameter G(LIQOX,CaO;0) 298.15  GLIQCAO; 6000 N!
    Parameter G(LIQOX,MgO;0) 298.15  GLIQMGO; 5100 N!
    Parameter L(LIQOX,CaO,MgO;0) 298.15  -3381.86;  6000 N !
    Parameter L(LIQOX,CaO,MgO;1) 298.15  -25707.1;  6000 N
```

CaMgO_TwoLiquid.tdb

```
Phase Liquid:L % 1 1 !
Constituent Liquid:L :Ca,CaO,Mg,MgO,O:!
    Parameter G(Liquid,Ca;0) 298.15   +GLIQCA; 6000 N !
    Parameter G(Liquid,Mg;0) 298.15   +GLIQMG; 6000 N !
    Parameter G(Liquid,O;0) 298.15    +GLIQO; 6000 N !
    Parameter G(Liquid,CaO;0) 298.15  +GLIQCAO; 6000 N !
    Parameter G(Liquid,MgO;0) 298.15  +GLIQMGO; 6000 N !
    Parameter G(Liquid,Ca,Mg;0) 298.15    -32322.4+16.7211*T; 6000 N !
```

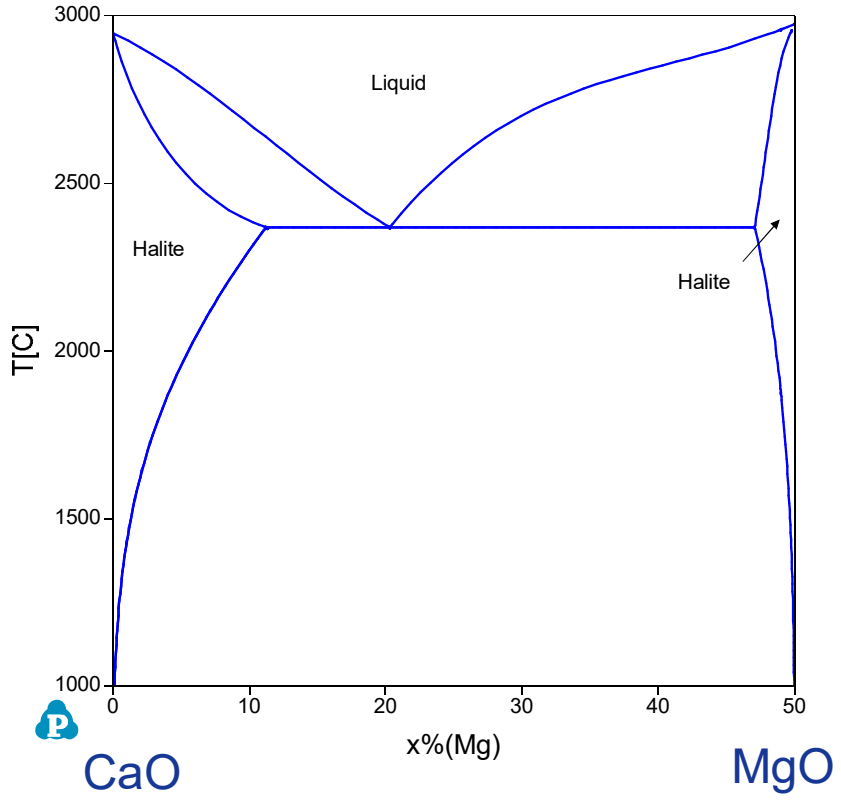
CaMgO_ASSModel.tdb

CaO-MgO 相图



CaO-MgO_LIQOX.tdb

CaO-MgO 体系中的二元相图



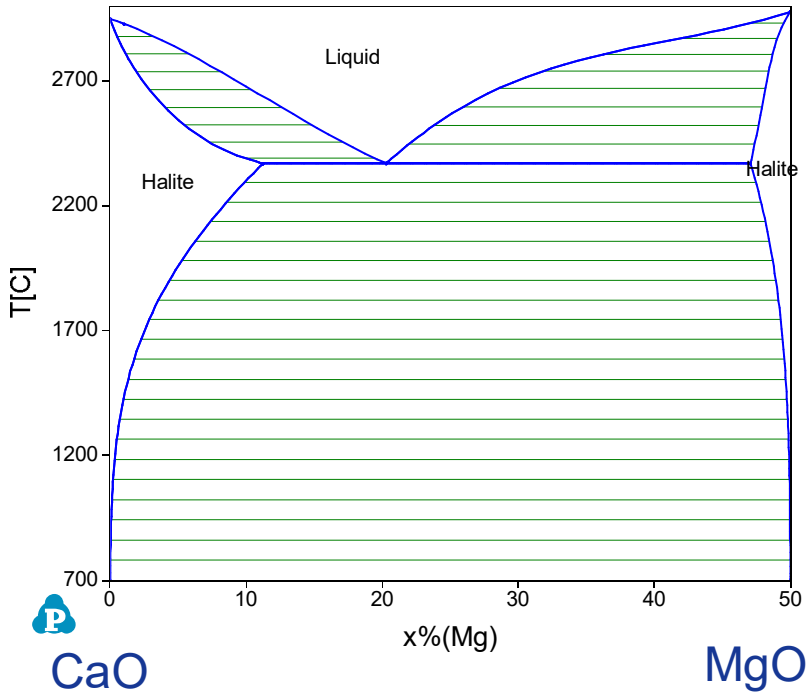
CaMgO_TwoLiquid.tdb CaMgO_ASSModel.tdb

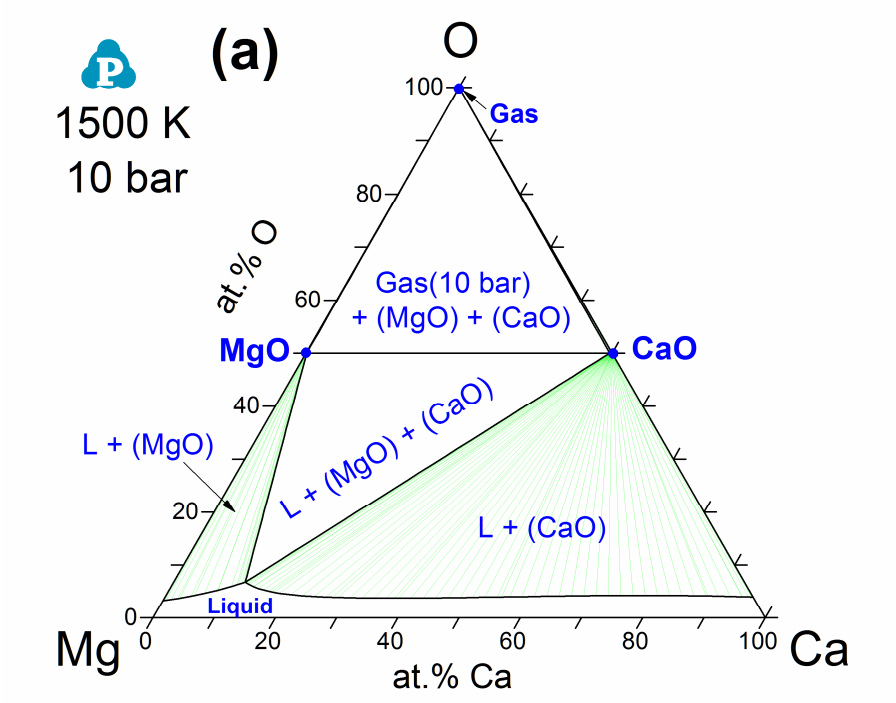
Ca-Mg-O 体系中的准二元相图

Pseudo binary phase diagram

S.-M. Liang, R. Schmid-Fetzer, Complete thermodynamic description of the Mg-Ca-O phase diagram including the Ca-O, Mg-O and CaO-MgO subsystems, J. Eur. Ceram. Soc., 38 (2018) 4768-4785.

Tie-Line (结线)


Liquid
Halite
Halite
2700
2200
1700
1200
700
T[C]
0
10
20
30
40
50
x%(Mg)
CaO
MgO


(a)
1500 K
10 bar
O
Gas
Gas(10 bar)
+ (MgO) + (CaO)
MgO
CaO
L + (MgO)
L + (MgO) + (CaO)
L + (CaO)
Liquid
at.% O
100
80
60
40
20
0
Mg
Ca
at.% Ca

亚点阵模型(Sublattice model)

$(A,B)_p(C,D)_q$ ： $i = A,B\ldots;\quad j = C,D\ldots$

$$G^{\varphi} = \sum_{i,j} y_i^I \cdot y_j^{II} \cdot G_{i:j}^{0,\varphi} + pRT\sum_i y_i^I \ln y_i^I + qRT\sum_j y_j^{II} \ln y_j^{II} + \quad G^{ex,\varphi}$$

$$\Downarrow \qquad\qquad \underbrace{\qquad\qquad\qquad\qquad\qquad\qquad}$$

$$^{\mathrm{ref}}G \qquad\qquad\qquad\qquad\qquad\qquad ^{\mathrm{conf}}G$$

计量化合物 每个亚点阵只有一个组元。$(A)_p(C)_q$

$$y_i = 1; y_J = 1 \qquad G_{ApCq}(T) = G_{A:C}^{0,\varphi}$$

计量化合物模型

计量化合物 A_pC_q 作为体系金属间相

$(A)_p(C)_q$ $pA + qC = A_pC_q$ $G_{ApCq}(T) = G^{0,\varphi}_{A:C}$

$$\Delta G = G_{A_pC_q} - pGA - qG_C = \Delta H - T\Delta S$$

$$\Longrightarrow \quad G_{A_pC_q} = \Delta H - T\Delta S + pG_A + qG_B$$

浮动参考态

$$G_{A_pC_q} = \mathbf{A + BT} + pG_A + qG_B$$

$$C_p(A_pC_q) = pC_p(A) + qC_p(B)$$ **Neumann–Kopp rule**

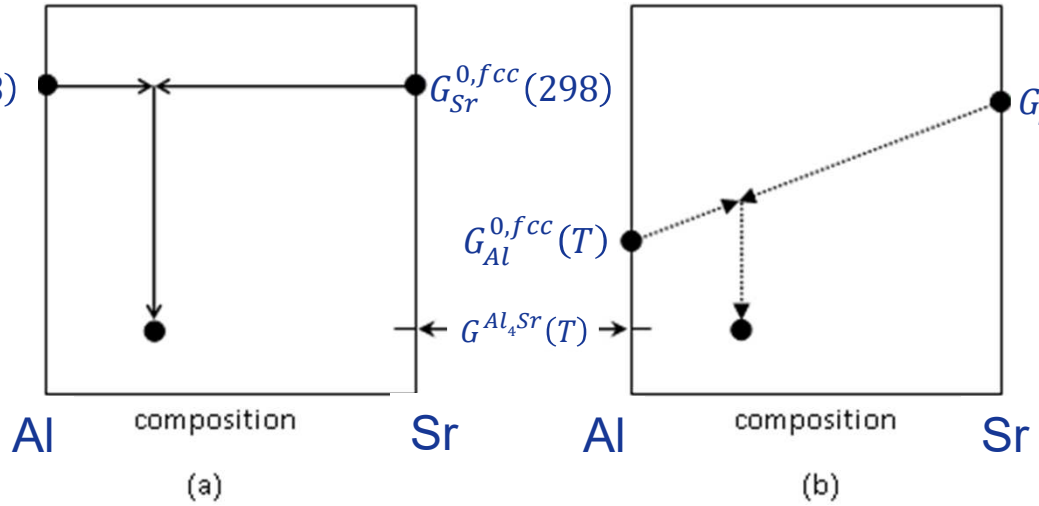
计量化合物 A_pC_q 是系统组元(component)

$$G_{ApCq}(T) = A + BT + CT\,lnT + DT^2 + ET^3 + FT^{-1} + \ldots$$

浮动参考态 vs 绝对参考态

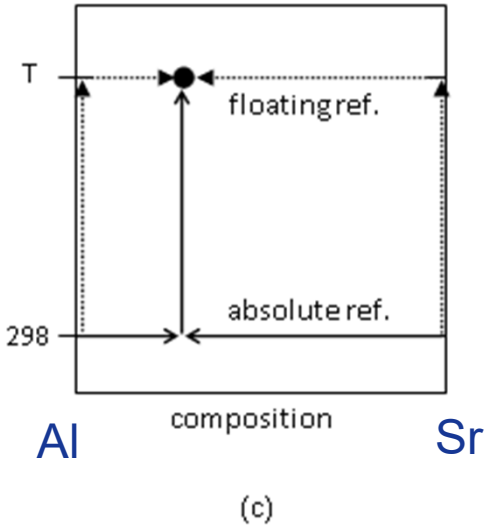
绝对参考态:

Absolute
reference state



浮动参考态

Floating
reference
state



浮动参考态 vs 绝对参考态

Al_4Sr为例

浮动参考态 (Floating reference state)

$$G^{Al4Sr}_{Al:Sr}(T) = -26701 + 4.118T + 0.8\,G^{0,fcc}_{Al}(T) + 0.2\,G^{0,fcc}_{Sr}(T)$$

```
Parameter G(Al4Ca, Al:Ca; 0)  298.15  -26701+4.118*T
                    +0.8*GFCCAL+0.2*GFCCSR; 6000 N !
```

-26701 J/mol-atoms = enthalpy of formation (T-independent)

-4.118J/mol-atoms K= entropy of formation(T-independent)

绝对参考态 (Absolute reference state)

常数

$$G^{Al4Sr}_{Al:Sr}(T) = a + bT + cTln(T) + dT2 + \cdots + 0.8G^{0,fcc}_{Al}(298K) + 0.2G^{0,fcc}_{Sr}(298K)$$

a, b ; determined from(but not equal to) enthalpy and entropy at 298.15K

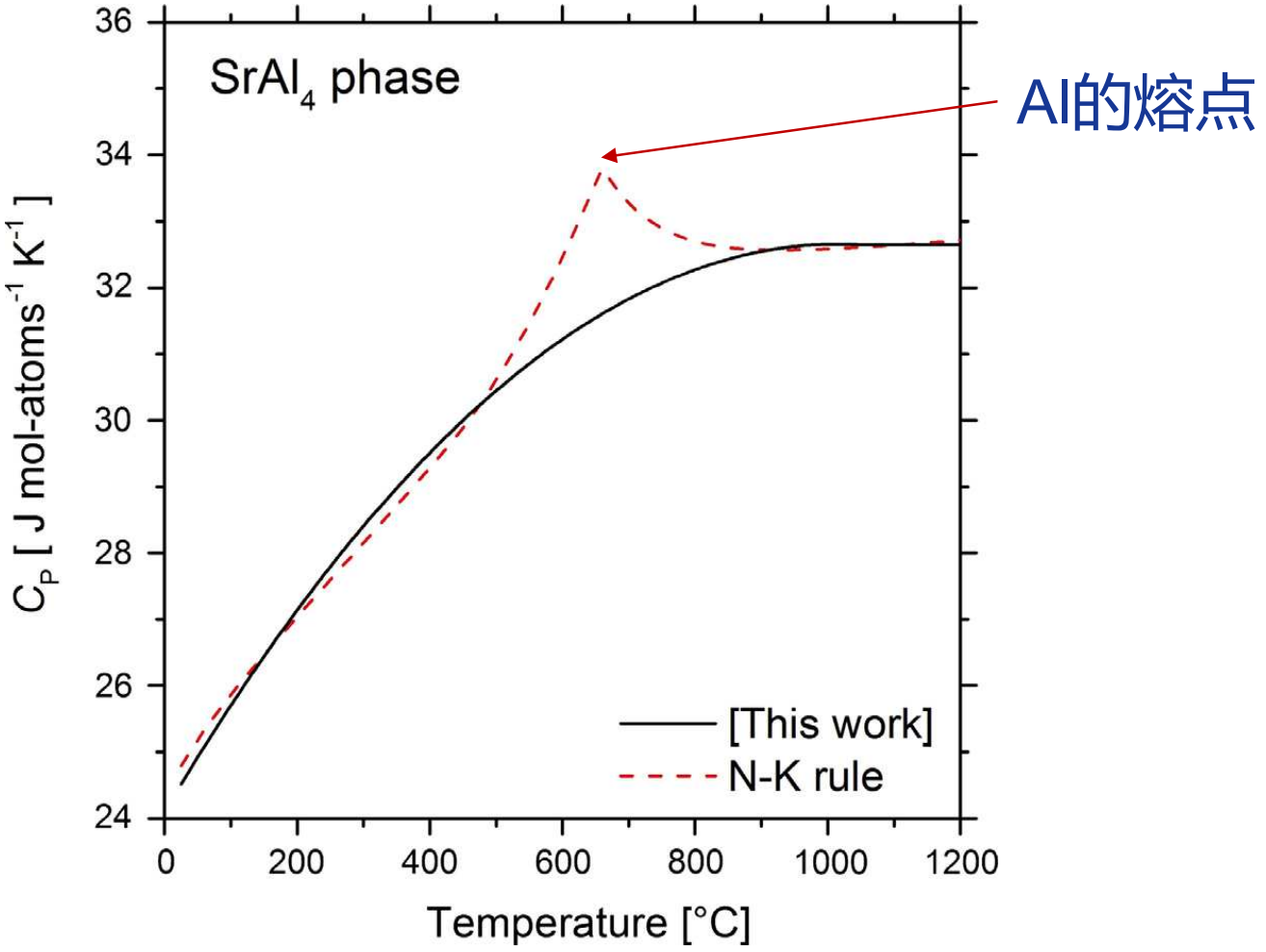
c, d, … ; determined from experimental C_p of Al_4Sr

$G_{MxNy}(T)$ = A + BT + CT *ln*T + DT^2 + ET^3 + FT^{-1} + . . .

```
Parameter G(AL4SR,AL:SR;0)  298.15 -177788+535.06*T
                -94.4169*T*LN(T)-0.0534*T**2+6.93E-06*T**3;
```

S.-M. Liang, et al., Key experiments and thermodynamic revision of the binary Al–Sr system, J. Alloys Compd., 610 (2014) 443-450.

浮动参考态 vs 绝对参考态



S.-M. Liang, et al., Key experiments and thermodynamic revision of the binary Al–Sr system, J. Alloys Compd., 610 (2014) 443-450.

多亚点阵固溶体相

φ 相: $(A,B)_p(A,B)_q$

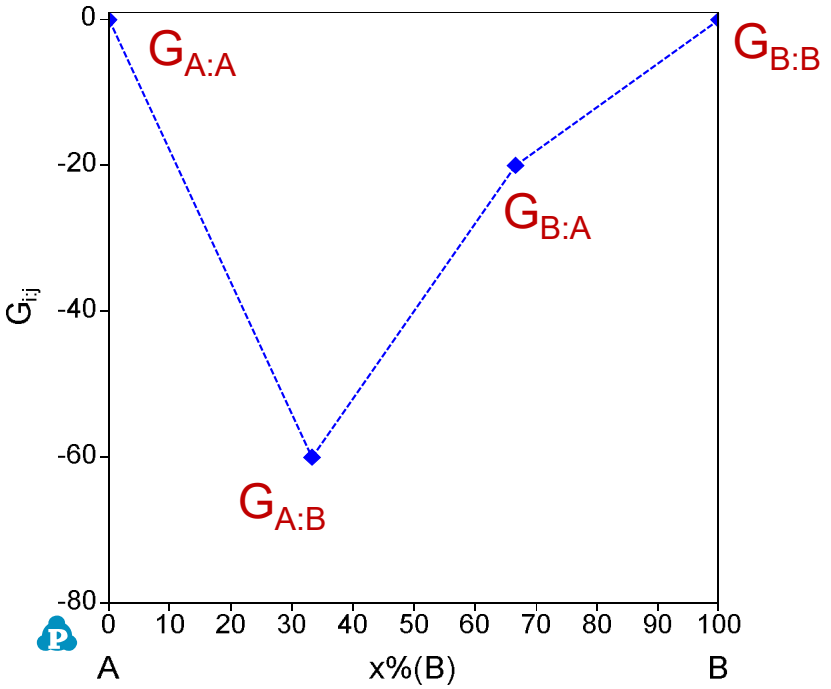
$$G^{\varphi} = \sum_{i,j} y_i^I \cdot y_j^{II} \cdot G_{i:j}^{0,\varphi} + pRT \sum_i y_i^I \ln y_i^I + qRT \sum_j y_j^{II} \ln y_j^{II} + G^{ex,\varphi}$$

⇩

$${}^{\mathrm{ref}}G$$

Endmember 值:

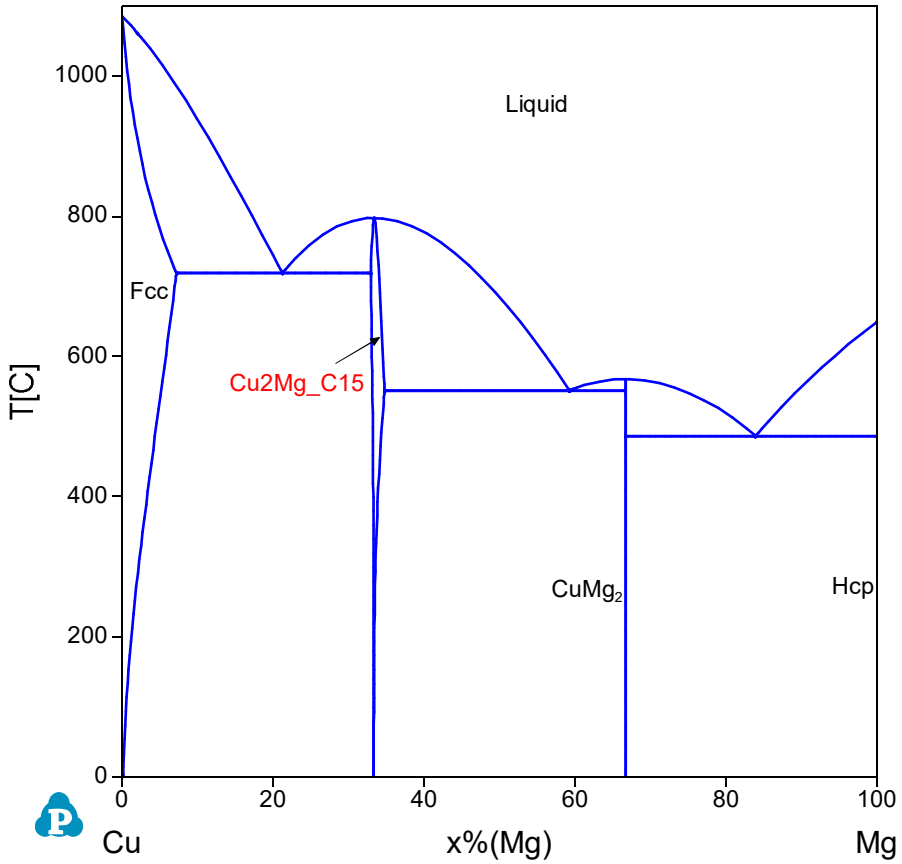
- $G_{A:A}^{0,\varphi}$: φ相 全部为 A原子
- $G_{B:B}^{0,\varphi}$: φ相 全部为 B原子
- $G_{A:B}^{0,\varphi}$; φ相 为 A_pB_q
- $G_{B:A}^{0,\varphi}$; φ相 为 B_pA_q



$$G^{ex,\varphi} = y_A^I y_B^I \cdot y_A^{II} \cdot L_{A,B:A}^{\varphi} + y_A^I y_B^I \cdot y_B^{II} \cdot L_{A,B:B}^{\varphi}$$

$$+ y_A^{II} y_B^{II} \cdot y_A^I \cdot L_{A:B,A}^{\varphi} + y_A^{II} y_B^{II} \cdot y_B^I \cdot L_{B:A,B}^{\varphi}$$

Cu-Mg 相图



Cu2Mg_C15:
(Cu, Mg)2(Cu,Mg)1

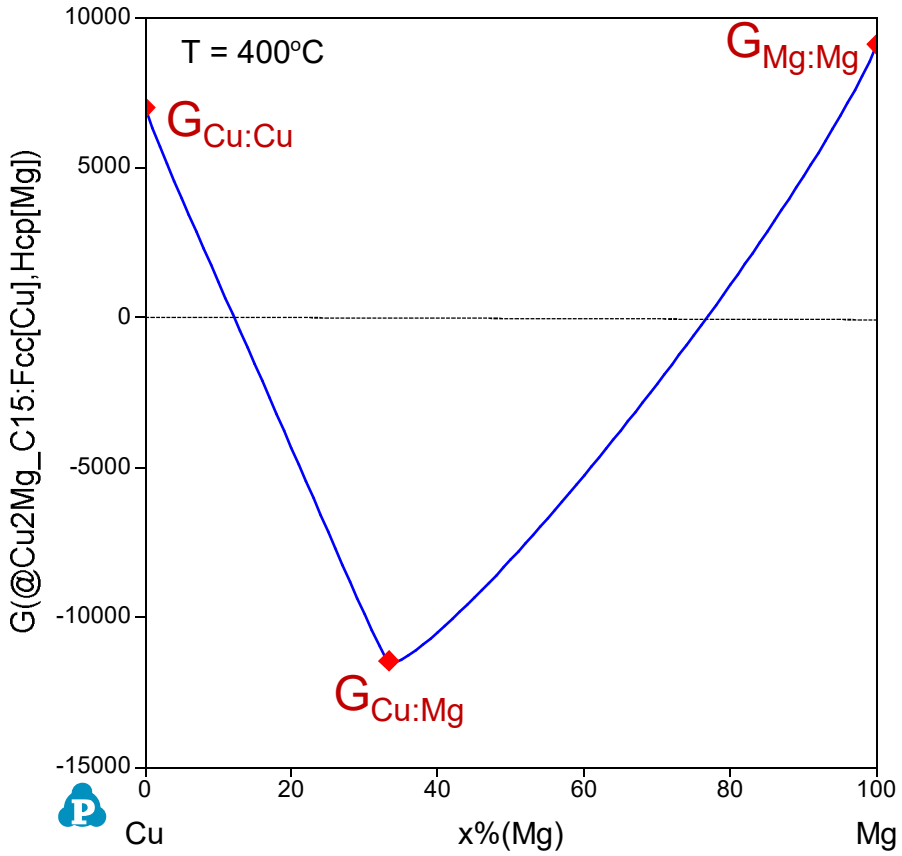
$G^{C15}_{Cu:Cu}$ = 21014.88+3*GHSERCU.

$G^{C15}_{Mg:Mg}$ = 27357.33+3*GHSERMG

$G^{C15}_{Cu:Mg}$ = -54690.99+364.73085*T
-69.276417*T*LN(T)
-5.1925E-4*T**2+143502*T**(-1)

$G^{C15}_{Mg:Cu}$ =+105000-
16.5*T+2*GHSERMG+GHSERCU

Cu-Mg 相图



Cu2Mg_C15:
(Cu, Mg)2(Cu,Mg)1

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-5.1925E-4*T**2+143502*T**(-1)

$G^{C15}_{Mg:Cu}$ =+105000-
16.5*T+2*GHSERMG+GHSERCU

多亚点阵置换型固溶体相

选择原则：

- 晶体结构，原子占位
- 模型尽可能简单
- 参数尽可能少
- 应用

晶体结构信息

Strukturbericht Designation

https://homepage.univie.ac.at/michael.leitner/lattice/struk/index.html

Strukturbericht Designation	Crystal Type
A	Elements
B	AB compounds
C	AB_2 compounds
D	A_mB_n compounds
E, F, G, H ··· K	More complex compounds
L	Alloys
O	Organic compounds
S	Silicates

Fcc_A1; Bcc_A2; Hcp_A3
Bcc_B2;
C14; C15; C36

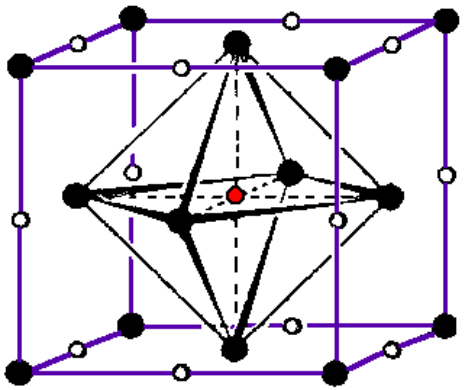
Pearson Symbol

Fcc_A1: cF4; Bcc_A2: cI2; Hcp: hP2

Space Group

间隙固溶体: 亚点阵

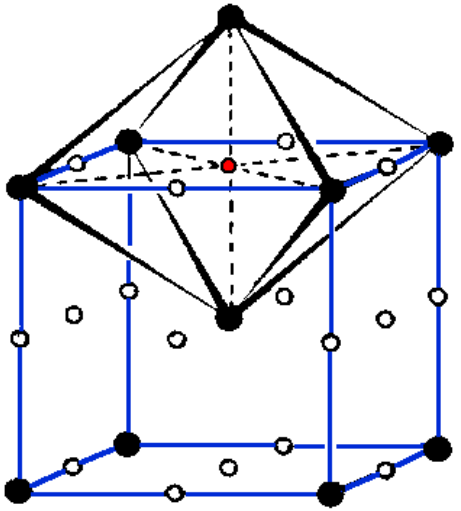
M = metal, I = interstitial , Va = vacancy (M)*x*(**Va**,I)*y*



fcc cF4 A1 phase sublattice model (M)1(**Va**,I)1

Void： 12/4 + 1 = 4

Fcc cF4 = 4 atoms/cell → 4/4 = 1 octahedral void/atom



bcc cI2 A2 phase sublattice model (M)1(**Va**,I)3

Void： 12/4 + 6/2 = 6

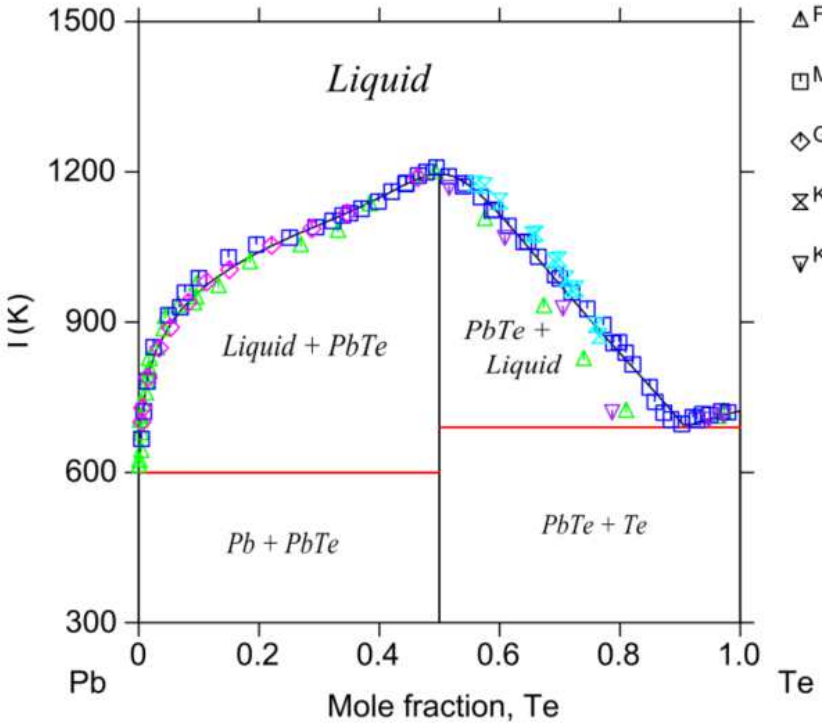
bcc cI2 = 2 atoms/cell → 6/2 = 3 octahedral voids/atom

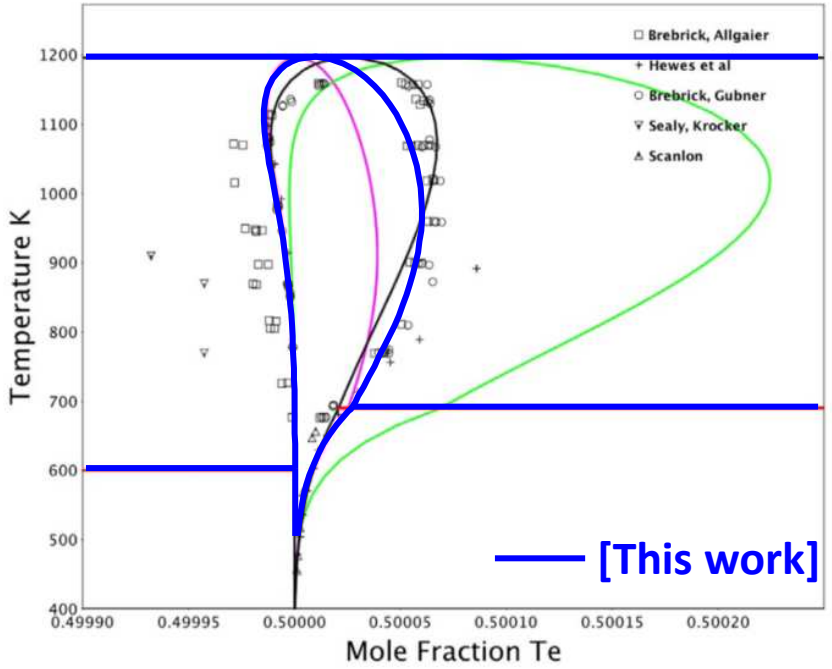
hcp hP2 A3 phase sublattice model (M)1(**Va**,I)0.5

1 void/atom but only half filled

亚点阵模型选择原则

计量化合物还是有固溶度化合物

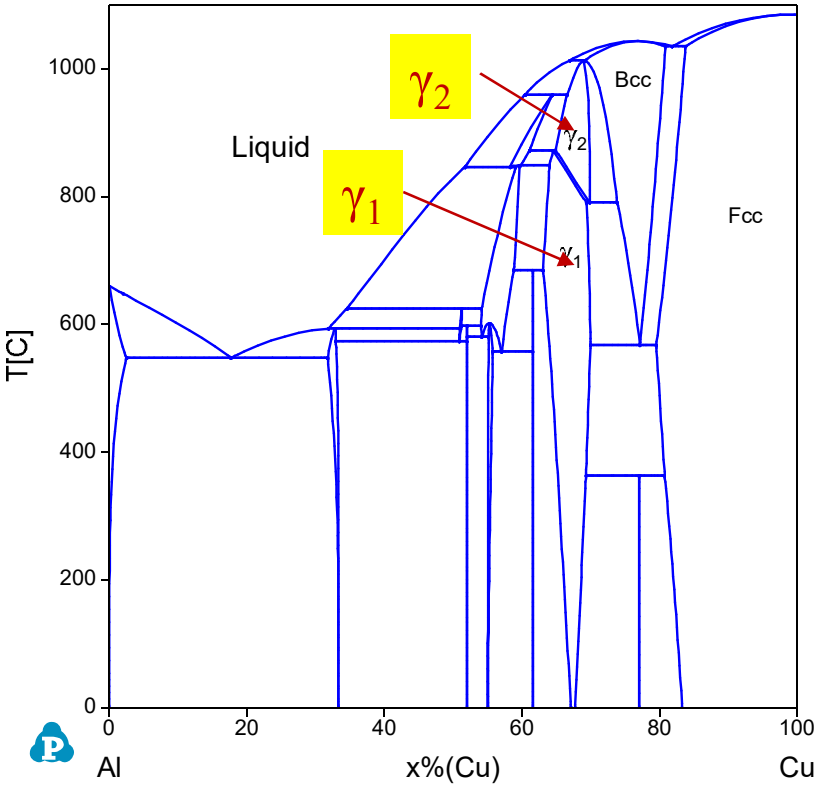


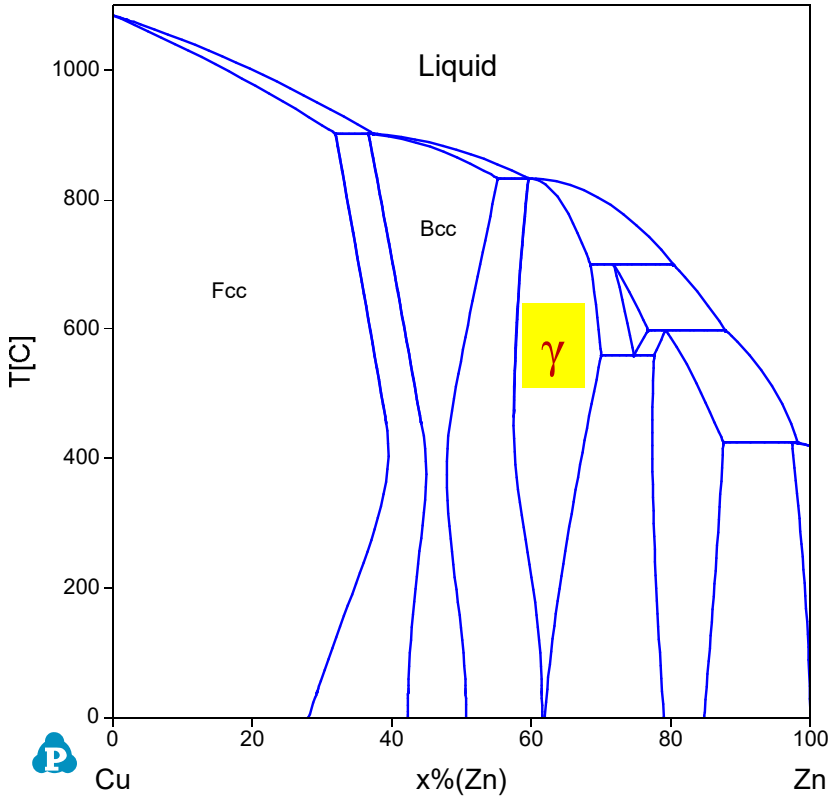


5SL: (Pb,Va,Va-2)(Te,Va,Va+2)(Va)(Va,e^-)(Va,h^+)

2SL: (Pb,Va)(Te,Va)

Al-Cu-Zn 体系中的 γ 相



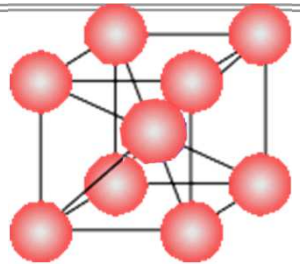


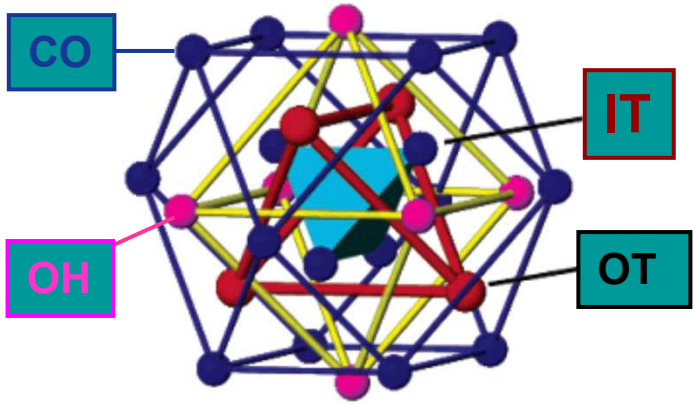
Challenge: model selection of the γ_2 phase

Crystal structure: **cI52 , *I-43m***

Two clusters with 26 atoms
as BCC structure.

IT : Inner tetrahedron. (4 atoms)
OT: Outer tetrahedron. (4 atoms)
OH: Octahedron. (6 atoms)
CO: Cuboctahedron. (12 atoms)





possible atomic Distribution Models

	Max (at.% Cu)	IT 4	OT 4	OH 6	CO 12	
A	38	Zn	Cu	Cu	Zn	Ideal Cu_5Zn_8
B	15 – 85	Zn	Cu	(**Cu**,Zn)	(Cu,**Zn**)	**Cu-Zn**
C	61 – 100	(Al,Cu)	Cu	Cu	(Al,Cu)	**Al-Cu**
B+C		(Al,Cu,Zn)	Cu	(**Cu**,Zn)	(Al,Cu,Zn)	**Al-Cu-Zn**

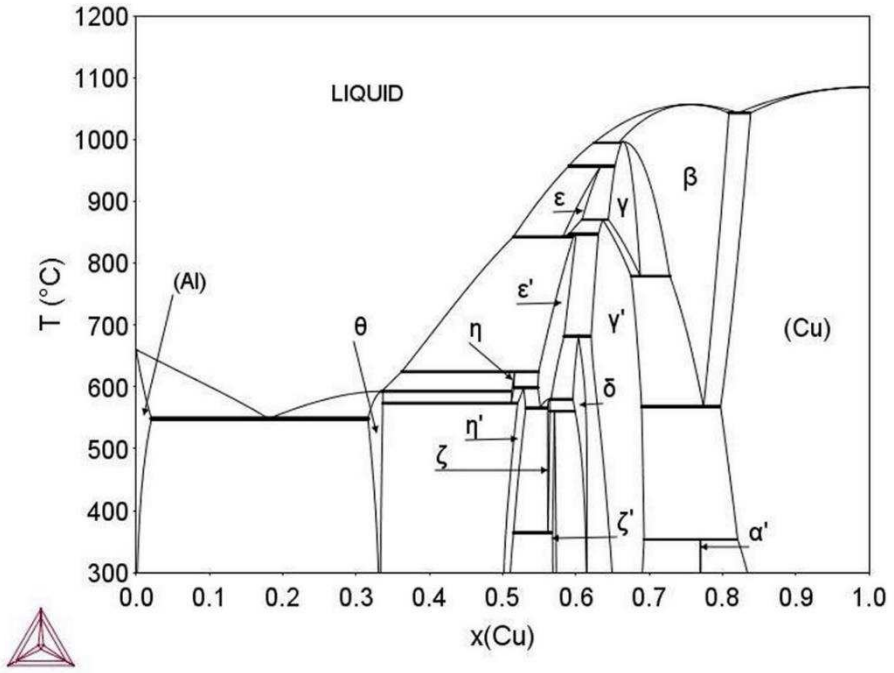
→ **(Al,Cu,Zn)4** **(Cu)4** **(Cu,Zn)6** **(Al,Cu,Zn)12** **18 end members**

Combine **IT** & **CO** ➔ **(Cu)4 (Cu,Zn)6 (Al,Cu,Zn)16 : 6 end members**

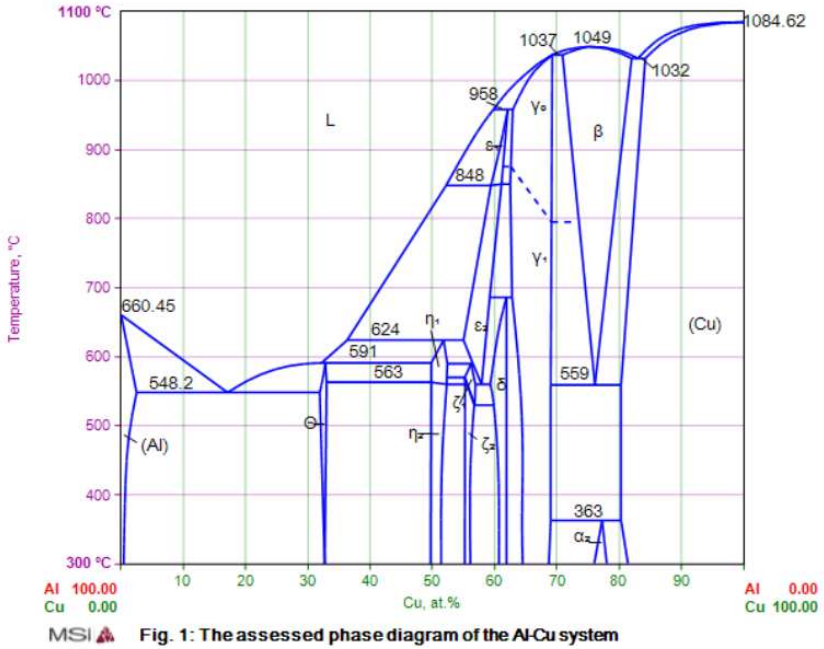
S.-M. Liang, R. Schmid-Fetzer, Thermodynamic assessment of the Al–Cu–Zn system, Part III: Al–Cu–Zn ternary system, Calphad, 52 (2016) 21-37.

亚点阵模型选择原则

计算Al-Cu相图



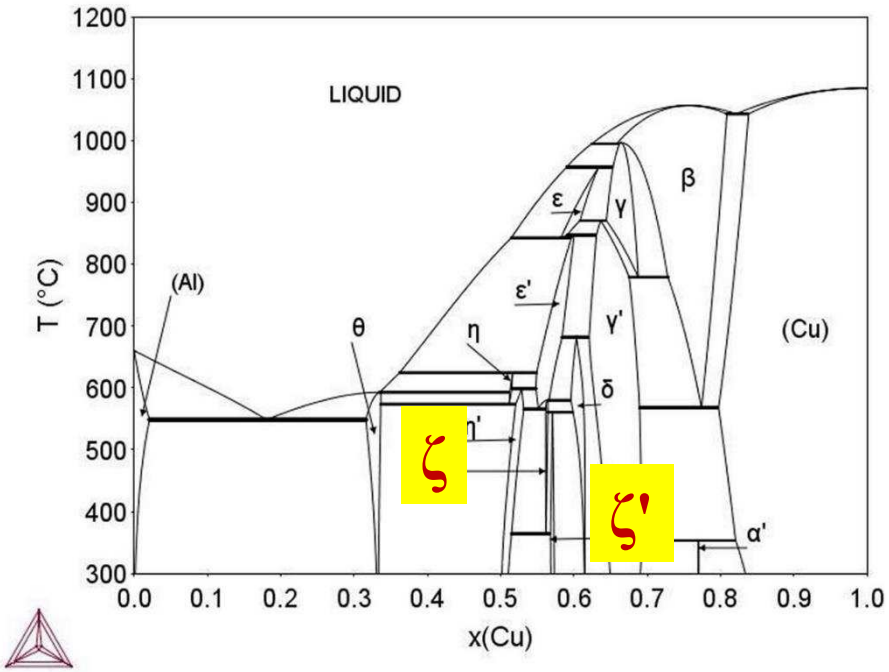
实验Al-Cu相图



计算相图和实验相图吻合得非常不错

亚点阵模型选择原则

计算Al-Cu相图



ZETA

$(Cu)_3(Cu,Va)_3$

$(Al,Cu)_2(Al)_4$

4个亚点阵

12 个参数

ζ

$^{0}G^{AL3CU4\_HT}_{Cu:Cu:Al:Al} = -104590.1 + 9.8592*T + 6*G^{HSER}_{Al} + 6*G^{HSER}_{Cu}$

$^{0}G^{AL3CU4\_HT}_{Cu:Cu:Cu:Al} = +25000 + 4*G^{HSER}_{Al} + 8*G^{HSER}_{Cu}$

$^{0}G^{AL3CU4\_HT}_{Cu:Va:Al:Al} = +25000 + 6*G^{HSER}_{Al} + 3*G^{HSER}_{Cu}$

$^{0}G^{AL3CU4\_HT}_{Cu:Va:Cu:Al} = -70004.62 - 18.7960*T + 4*G^{HSER}_{Al} + 5*G^{HSER}_{Cu}$

$^{0}L^{AL3CU4\_HT}_{Cu:Cu:Al,Cu:Al} = -133424.9+7.0310*T$

$^{1}L^{AL3CU4\_HT}_{Cu:Cu:Al,Cu:Al} = 390000$

$^{0}L^{AL3CU4\_HT}_{Cu:Va:Al,Cu:Al} = -133424.9+7.0310*T$

$^{1}L^{AL3CU4\_HT}_{Cu:Va:Al,Cu:Al} = 390000$

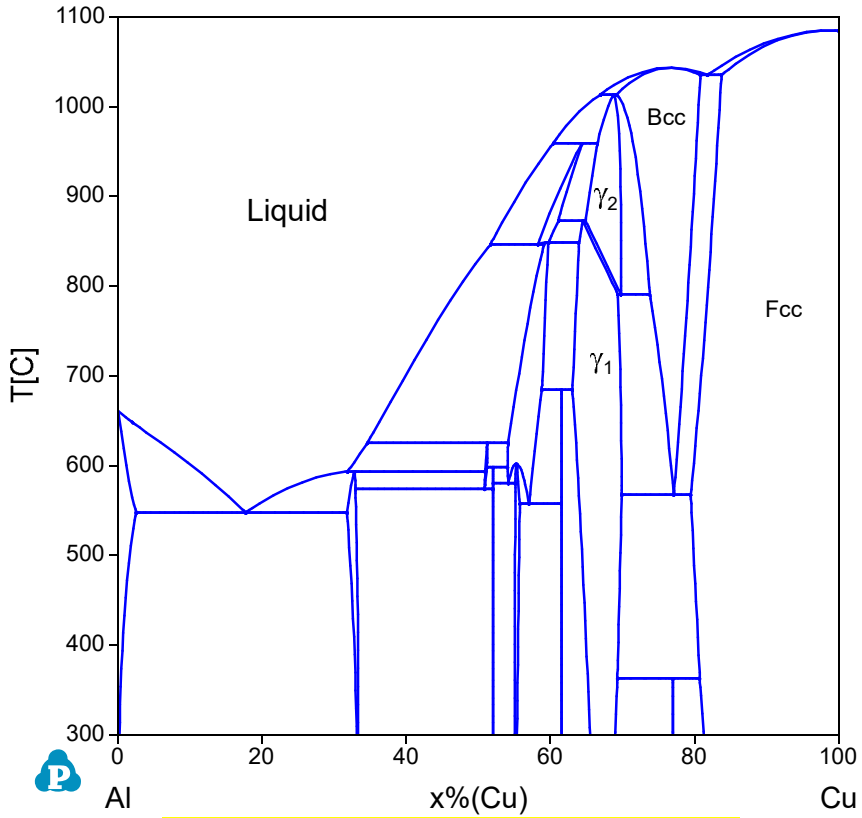
$^{0}L^{AL3CU4\_HT}_{Cu:Cu:Va:Al:Al} = -557902.2+184.57*T$

$^{1}L^{AL3CU4\_HT}_{Cu:Cu,Va:Al:Al} = -300000$

$^{0}L^{AL3CU4\_HT}_{Cu:Cu:Va:Cu:Al} = -557902.2+184.57*T$

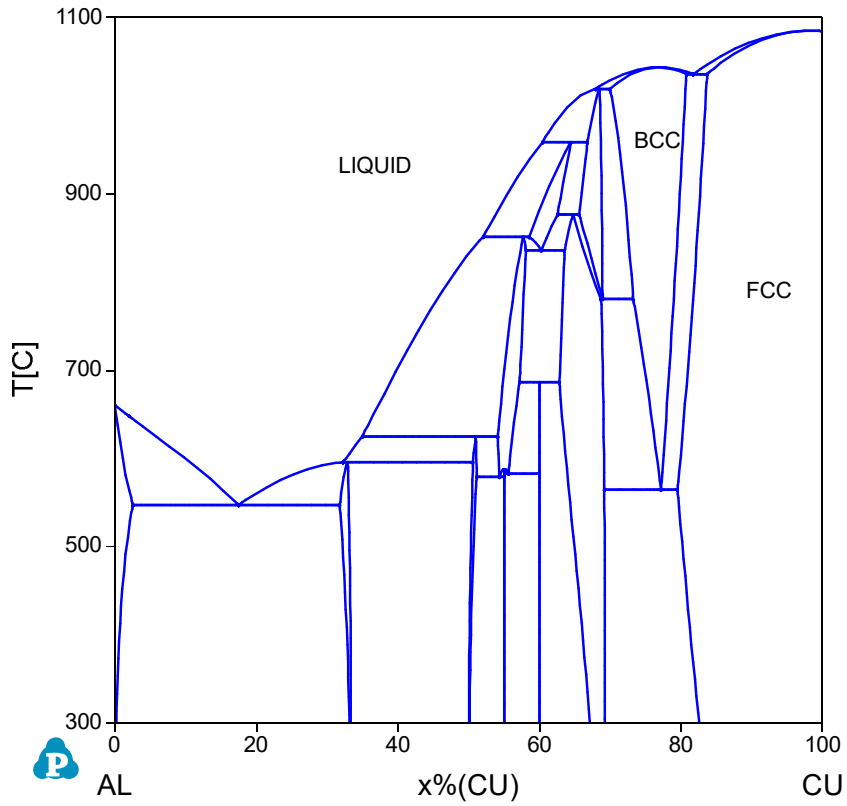
$^{1}L^{AL3CU4\_HT}_{Cu:Cu,Va:Cu:Al} = -300000$

亚点阵模型选择原则



ζ: (Al,Cu)9(Cu)11

S.-M. Liang, R. Schmid-Fetzer, Thermodynamic assessment of the Al–Cu–Zn system, part II: Al–Cu binary system, Calphad, 51 (2015) 252-260.



ζ: (Al)9(Cu)11

V.T. Witusiewicz, U. Hecht, S.G. Fries, S. Rex, The Ag–Al–Cu system: Part I: Reassessment of the constituent binaries on the basis of new experimental data, J. Alloys Compd., 385 (2004) 133-143

Questions?