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## **Phase equilibria and solubility limits in the B-Ce-Fe-Nd system**

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## Context

- Powerful permanent magnets are polycrystalline material of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  phase ( $\tau_1$ ).
- Ce-substituted Nd-Fe-B permanent magnets present poor magnetic properties.
- Magnetic performance of Ce-substituted Nd-Fe-B magnets can be enhanced through a **better control of grain boundary (GB) compositions**.
- Especially in the **Multi Main Phase (MMP)** approach:
  - Two type of  $\tau_1$  phases are synthesized separately : one with 100 at.% Nd and another which is a mixture 50 at.% Nd and 50 at.% Ce. They are crushed, the two powders are then mixed in various proportions and sintered.
  - Several phases are present at GB including  $\text{CeFe}_2$  and a RE-rich phase. Annealing the  $\text{CeFe}_2$  phase allows to obtain more continuous GB, screening short range coupling between adjacent grains [1].

## Objectives

- Develop a thermodynamic database of the (Ce-Nd)-Fe-B elements by using the CALPHAD method to optimize the fabrication process
- This will required on and GB phases ( $\text{REFe}_2$ , RE-rich, etc.) to:
  - Study their stabilities and range of solubilities
  - Measure their transition temperatures
  - Compute their specific heats and formation enthalpies

## Results

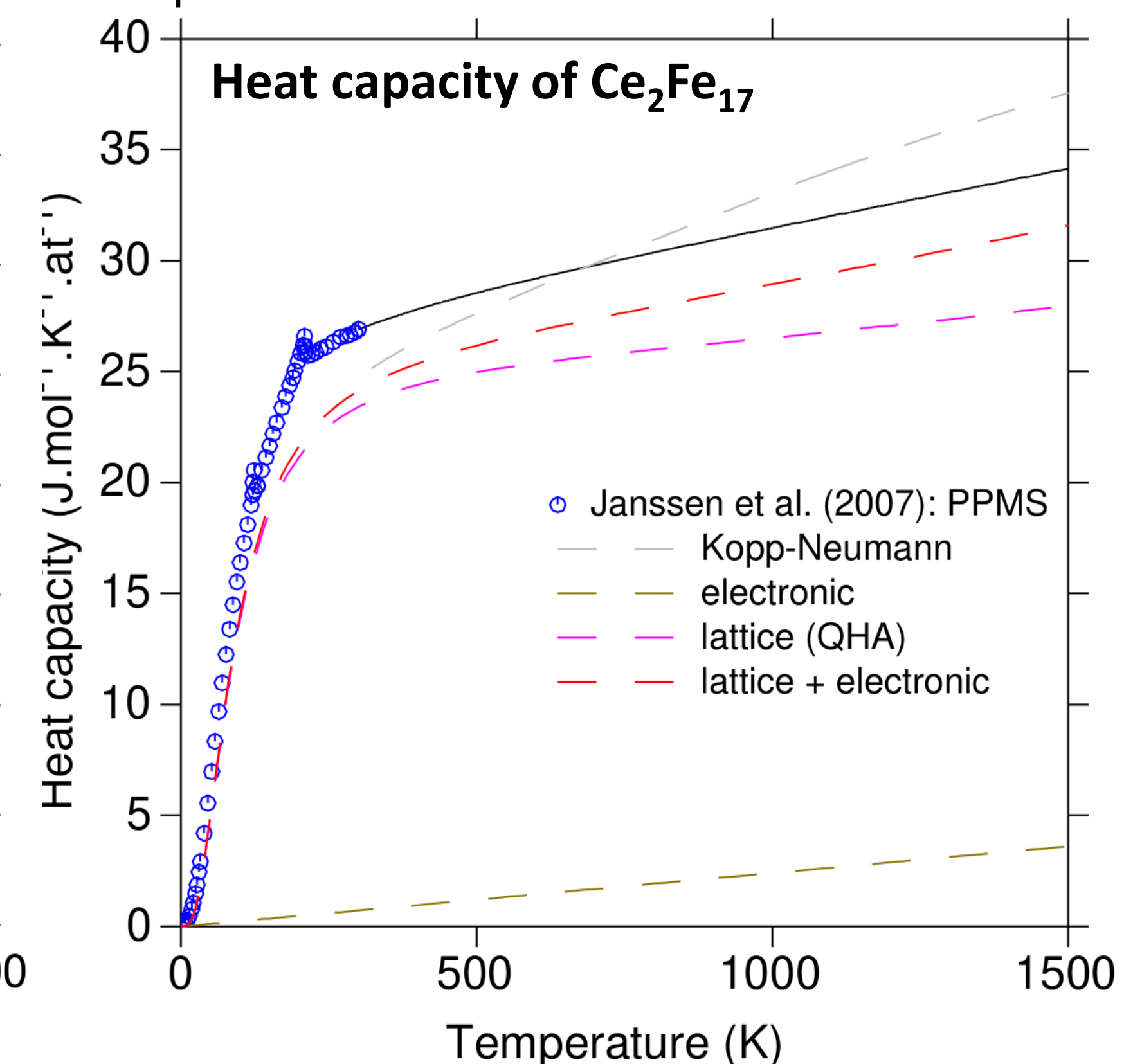
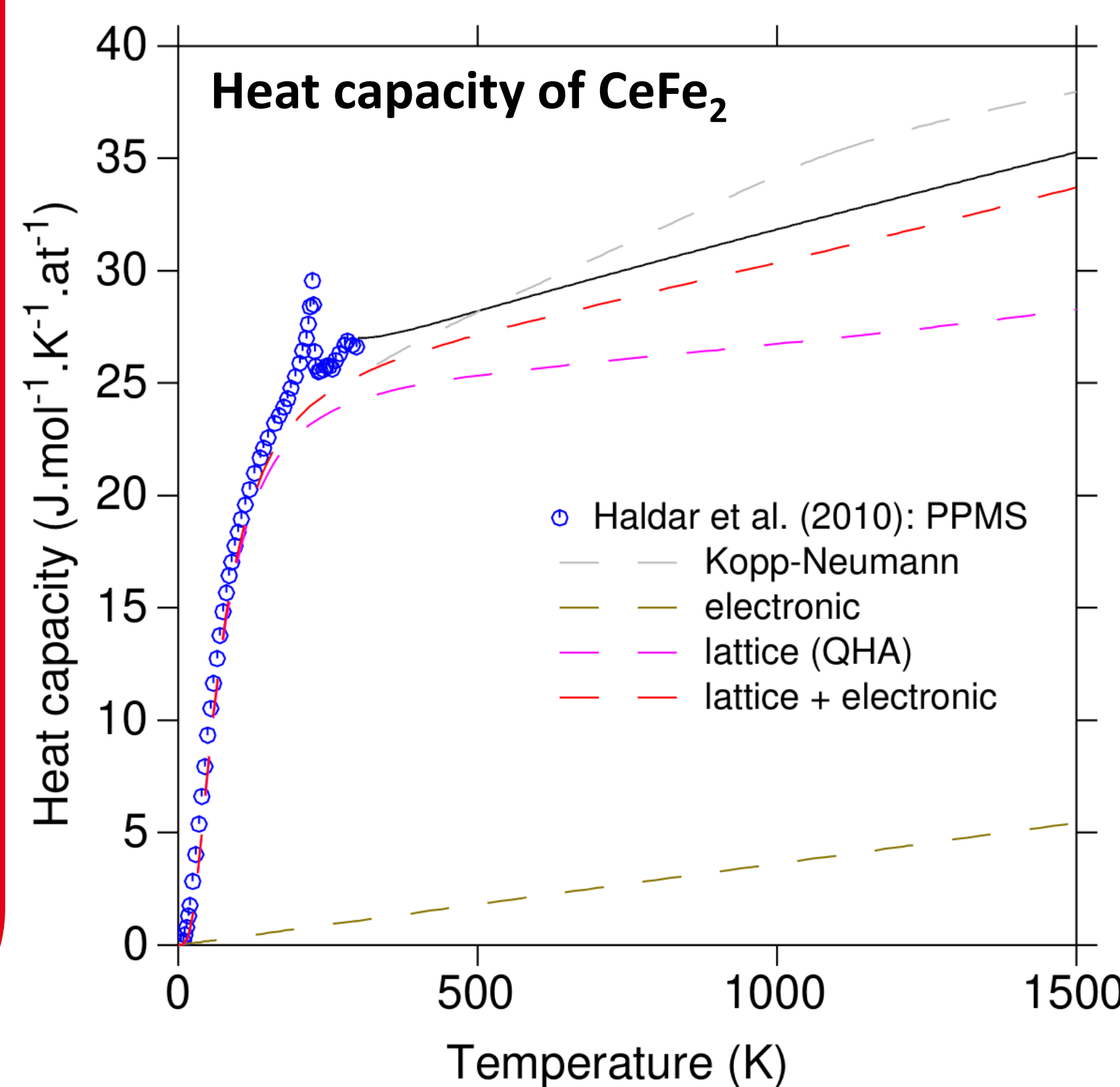
### Calculations

To support the development of the CALPHAD database, DFT simulations were performed to calculate heat capacities of some complex compounds.

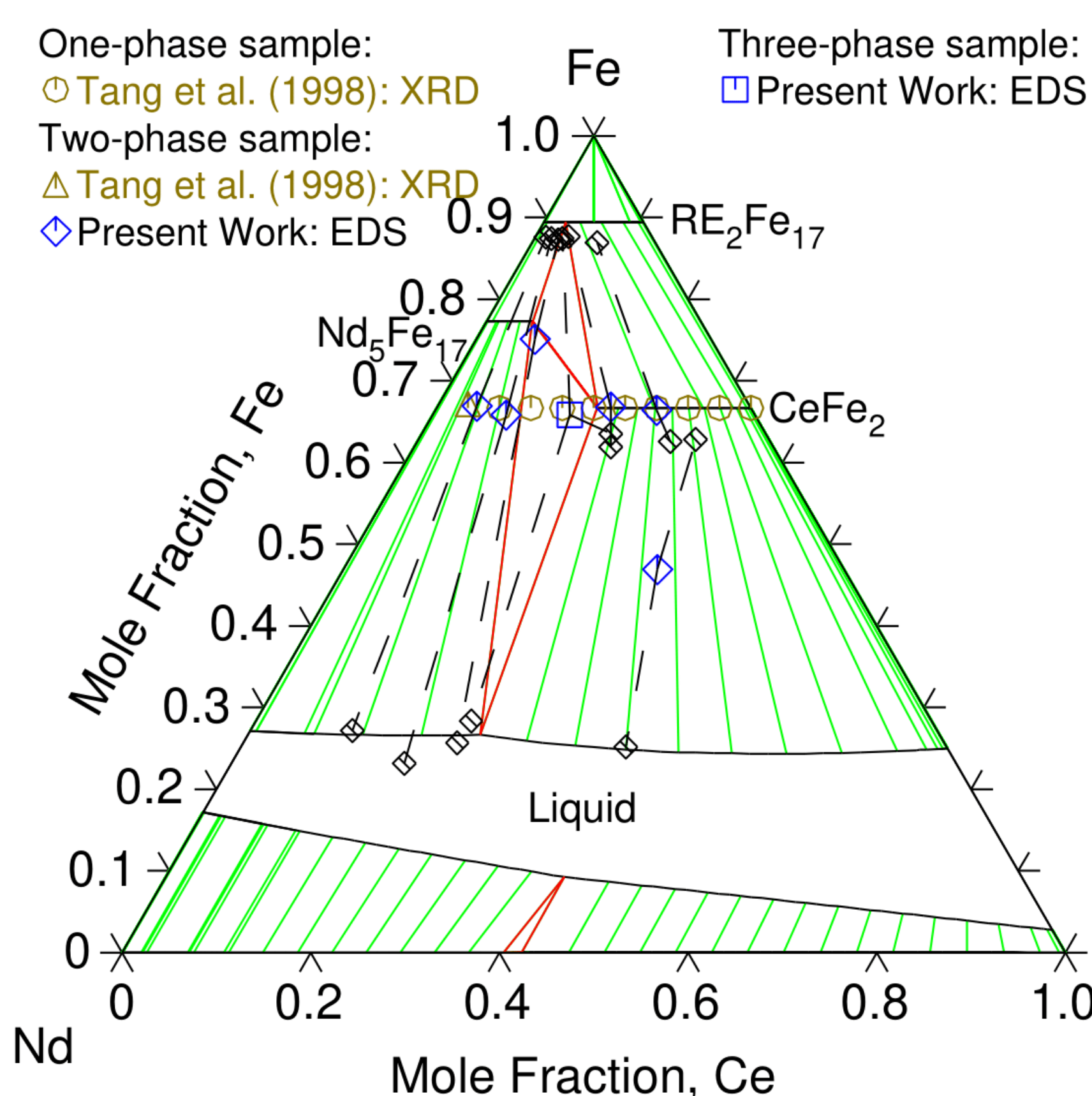
Calculation features:

- CASTEP software
- PAW pseudo-potential method

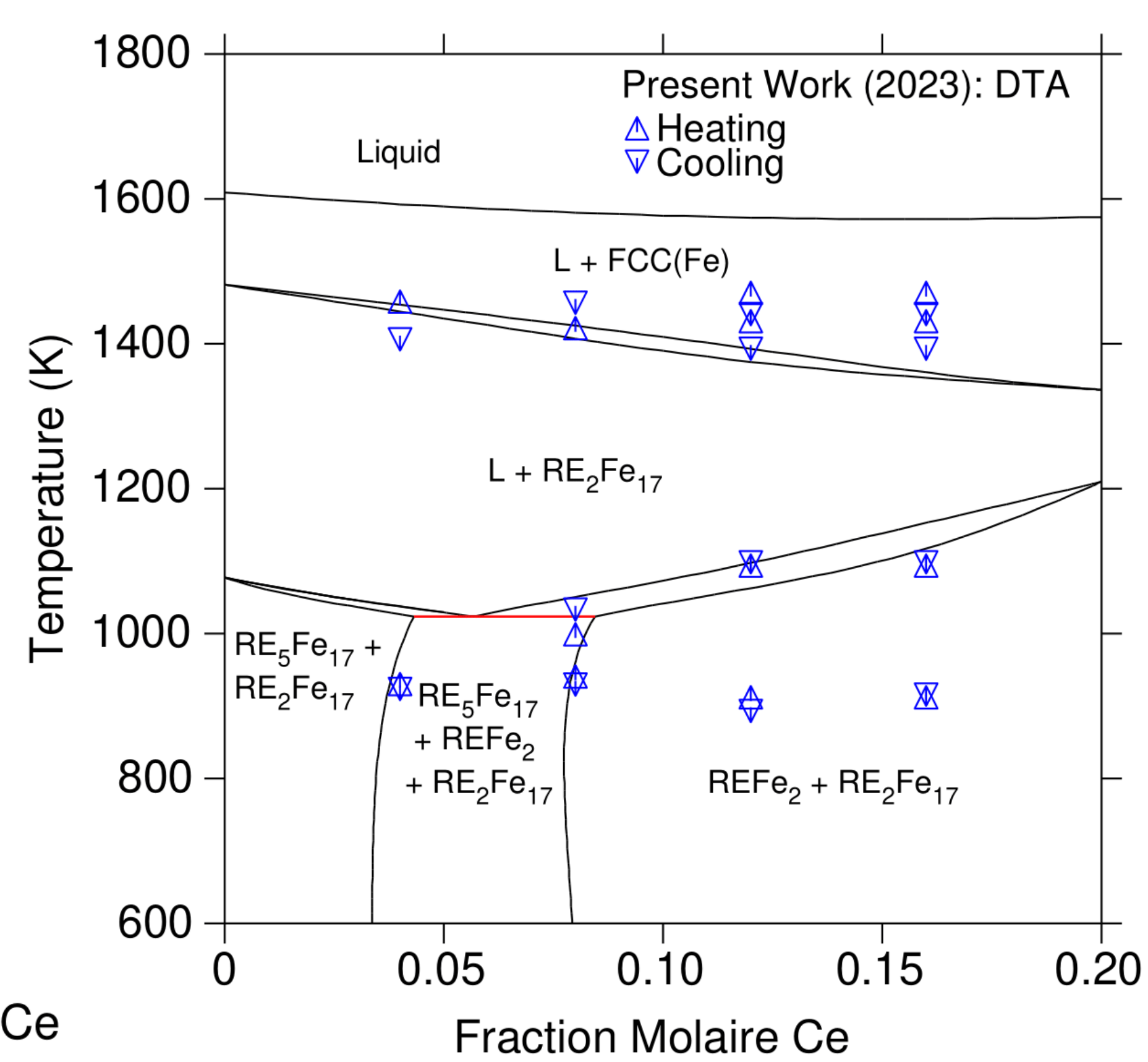
- GGA – PBE
  - Monkhorst-Pack scheme
  - Quasi-harmonic statistical model [2]
  - Electronic contribution : Electron gas model
- Validation:** Comparaison with literature
- Low temperature experimental heat capacities
  - Experimental orbital DOS



### Phase diagram of Ce-Fe-Nd at 1023 K



### Isopleth of Ce-Fe-Nd at 80 at.% Fe



### Thermodynamic model: The CALPHAD approach

General expression for the Gibbs energy of a  $\varphi$  phase:

$$G_m^\varphi = \sum_i x_i G_i^\varphi + RT \sum_i x_i \ln x_i + \text{ex} G_m^\varphi + \text{phy} G_m^\varphi$$

Reference state energies, Ideal entropy of mixing, Excess free energy, Physical phenomena energy (ex: magnetism)

- Liquid phase : Ionic liquid model ( $C^{vc}$ )<sub>p</sub>( $A^{vA}$ ,  $N^0$ ,  $V\alpha^{Q-}$ )<sub>Q</sub>
- End-member interaction parameters : Redlich-Kister-Muggianu

### Thermal analysis

Measured solubilities in the intermetallics after heat treatment (10 days at 1023 K):

- Solid solution  $(\text{Ce,Nd})_2\text{Fe}_{17} \rightarrow \text{RE}_2\text{Fe}_{17}$
- 43.6 at.% Nd in  $\text{CeFe}_2$

Comparison DTA/calculation : Good results at 80 %at. Fe

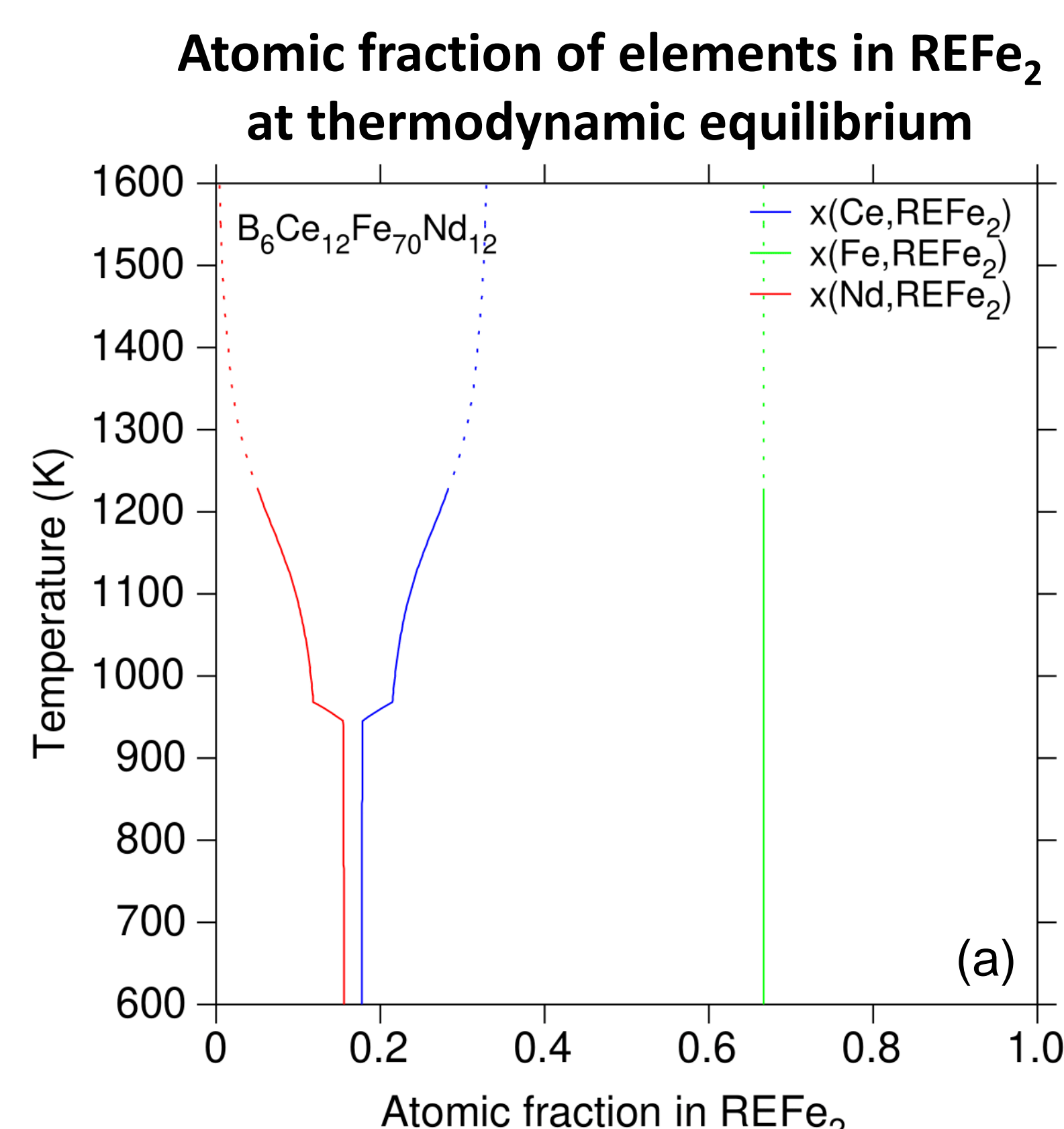
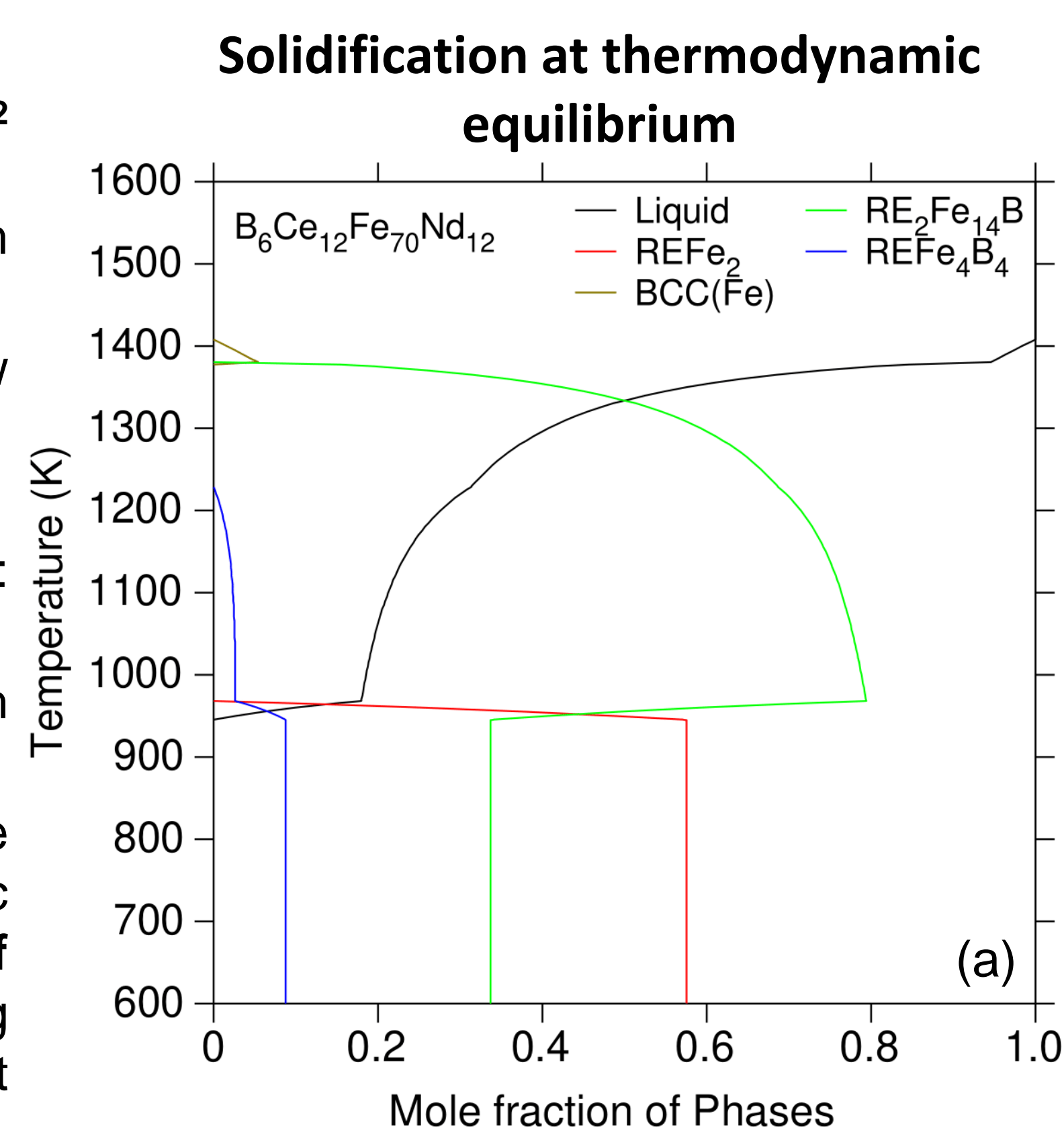
## Application

Solidification of a  $\text{B}_6\text{Ce}_{12}\text{Fe}_{70}\text{Nd}_{12}$  sample using the database:

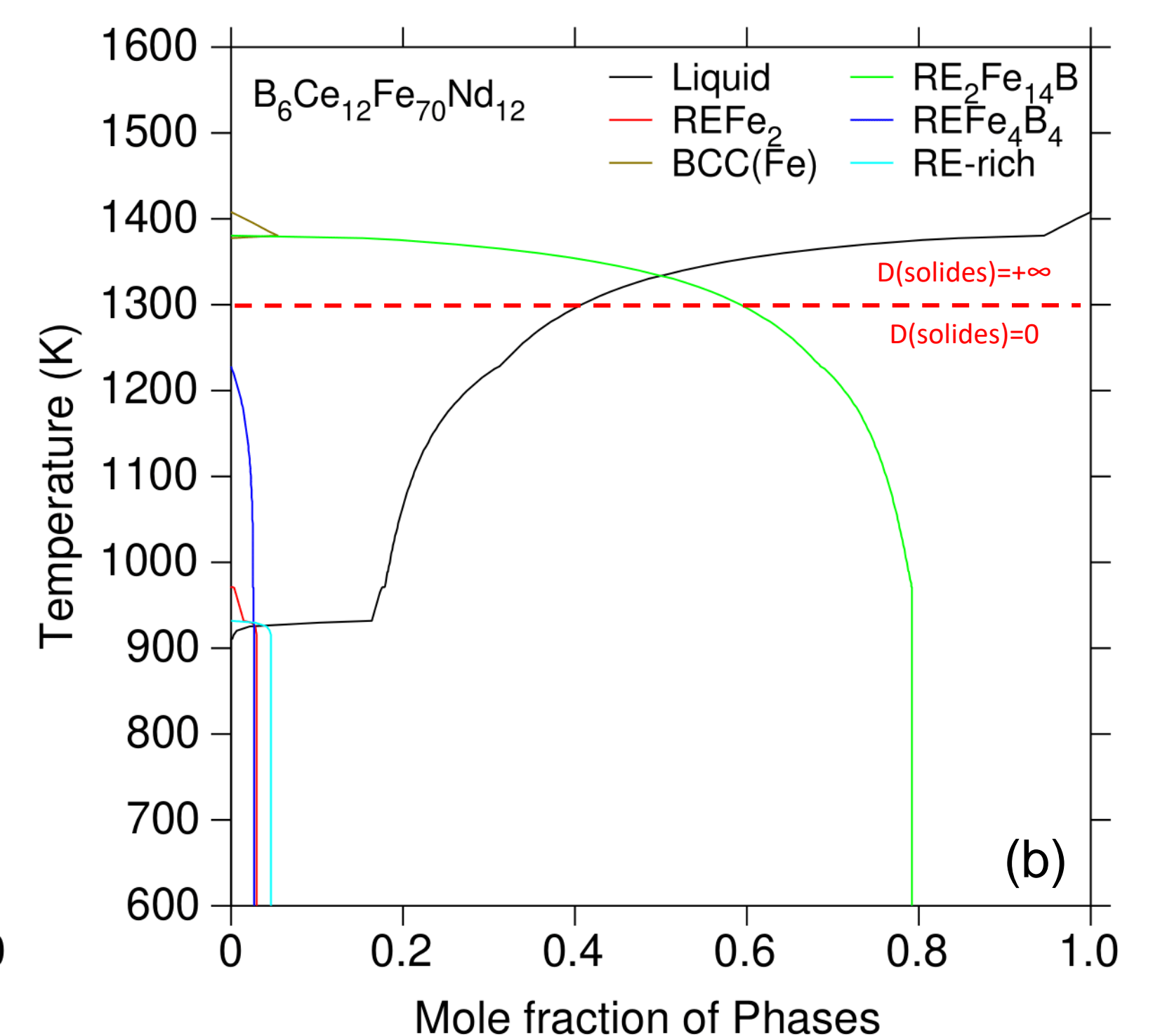
- (a) Thermodynamic equilibrium (Lever conditions)
- (b) Without diffusion in solids below 1300 K (Scheil-Gulliver conditions)

Results of simulation:

- (a) Three phase after cooling:  $\text{RE}_2\text{Fe}_{14}\text{B}$ ,  $\text{REFe}_4\text{B}_4$  and  $\text{REFe}_2$
- (a) Nd-enrichment in  $\text{REFe}_2$  which will reduce magnetic performance
- (b) Disparition of the BCC(Fe) phase above 1300 K under thermodynamic equilibrium conditions. **Formation of  $\text{REFe}_2$  and a RE-rich phase** during cooling, (b) closer to GB magnet effective compositions



### Solidification without diffusion in solids below 1300 K



## Conclusions

A thermodynamic database of the B-Ce-Fe-Nd system is under development. This computational tool will allow to **predict stable phases** and their thermodynamic properties for any compositions and temperatures.

The database can be associated with other multi-physics codes to **simulate composition evolutions within the main  $\text{RE}_2\text{Fe}_{14}\text{B}$  grain and the GB** during successive heat treatments. Other physical phenomena are controlling this evolution such as: diffusion, GB type, interfacial interactions, etc. and will required further dedicated modelling.

## Perspectives

Adding to the database :

- Other RE elements Dy, La, Pr
- Oxygen (traces in permanent magnets)
- Hydrogen (use in decrepitation processes)
- Other GB control elements : Co, Cu, Ga

[1] Y. Zhang, T. Ma, J. Jin, J. Li, C. Wu, B. Shen, M. Yan, Effects of  $\text{REFe}_2$  on microstructure and magnetic properties of Nd-Ce-Fe-B sintered magnets, Acta Materialia. 128 (2017) 22–30.

[2] J.L. Fleche, Thermodynamical functions for crystals with large unit cells such as zircon, coffinite, fluorapatite, and iodoapatite from *ab initio* calculations, Phys. Rev. B. 65 (2002) 245116.