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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 (τ_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 τ_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 CeFe_2 and a RE-rich phase. Annealing the 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 (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

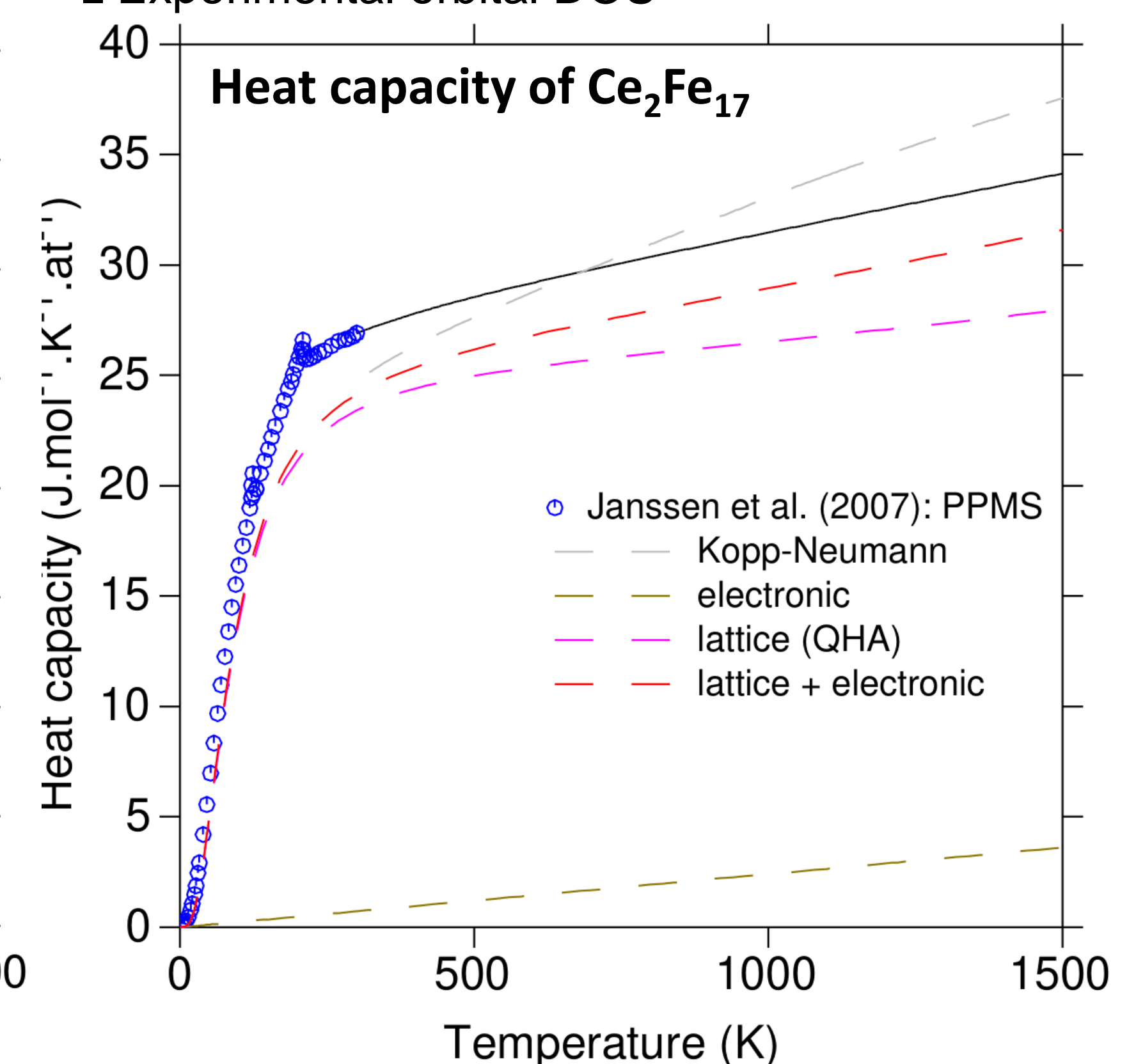
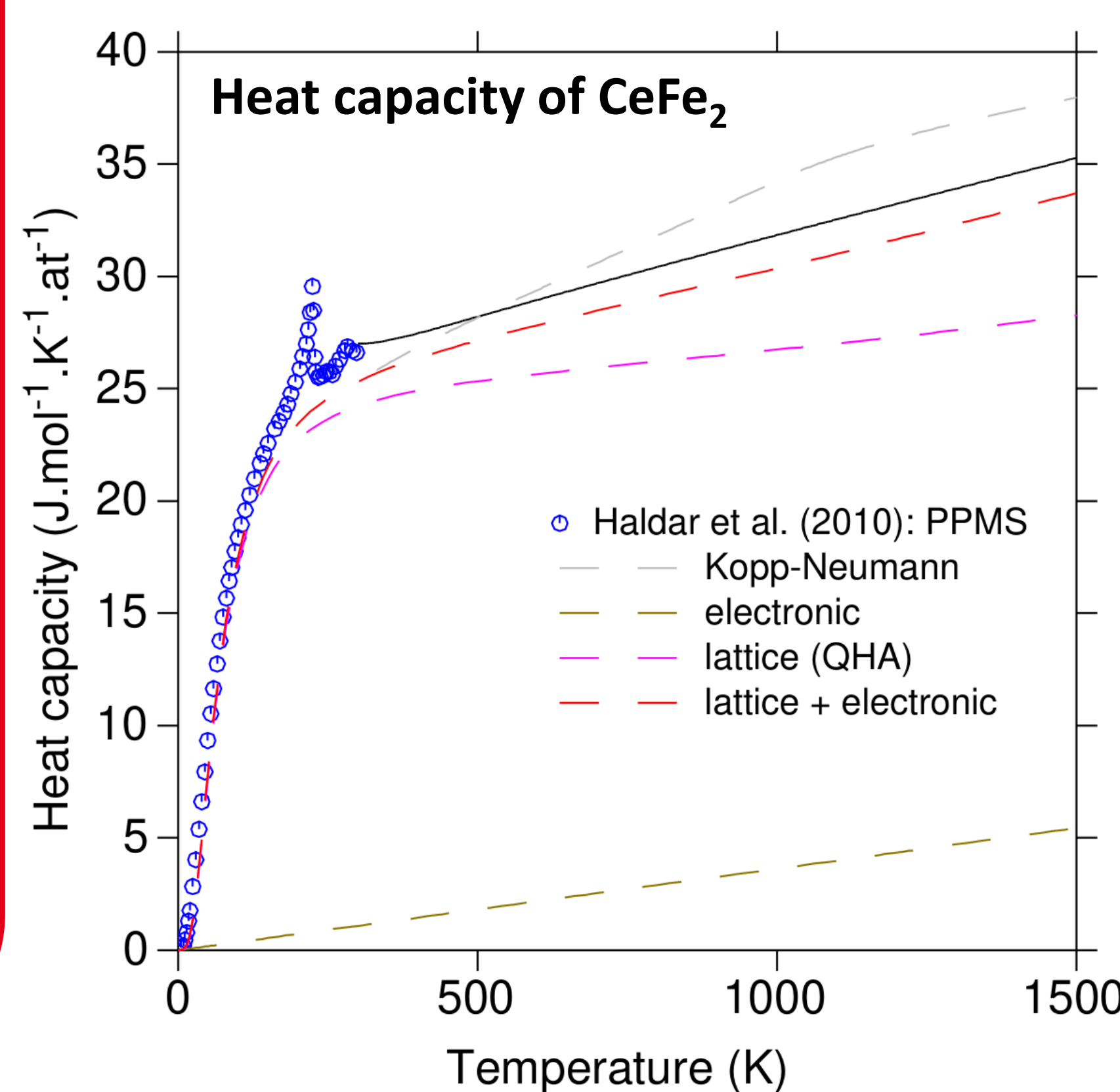
Calculations

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

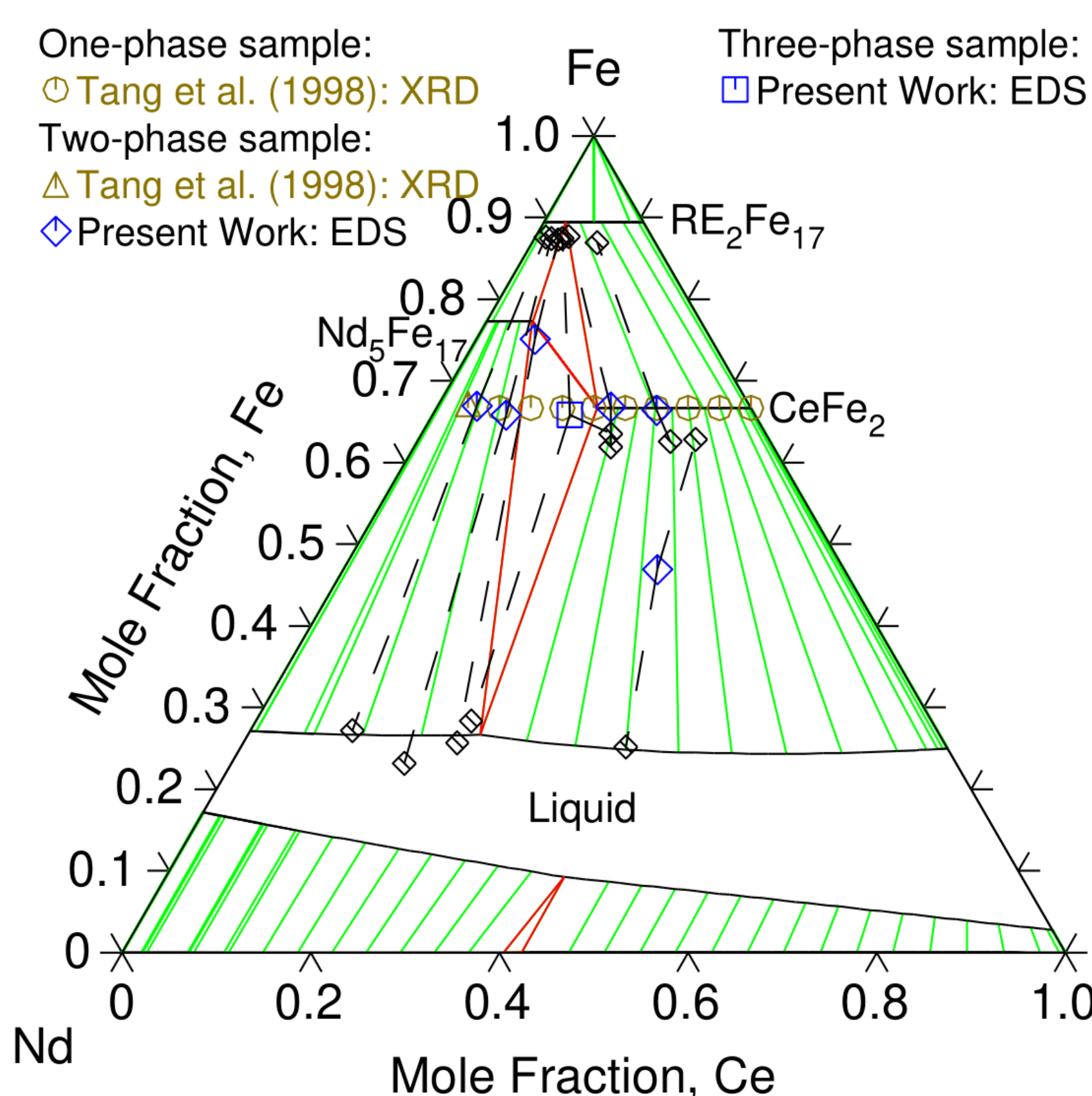
Calculation features:

- CASTEP software
- PAW pseudo-potential method

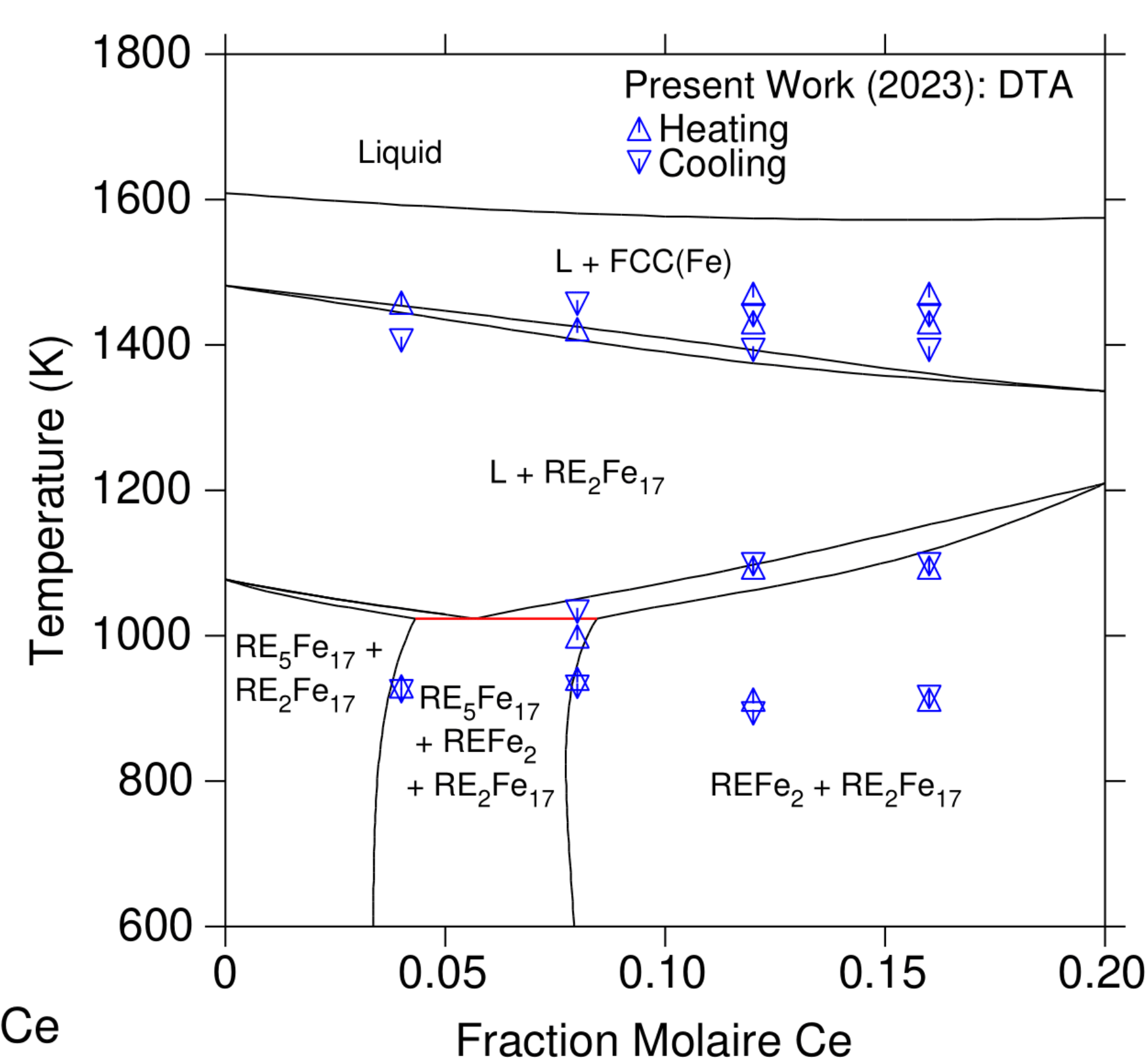
- GGA – PBE
 - Monkhorst-Pack scheme
 - Quasi-harmonic statistical model [2]
 - Electronic contribution : Electron gas model
- Validation:** Comparaison with literature
- Low temperature experimental heat capacities
 - Experimental orbital DOS



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 φ phase:

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

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

- Liquid phase : Ionic liquid model $(C^v)_p(A^{vA}, N^0, V\alpha^{Q-})_Q$
- 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 CeFe_2

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

Application

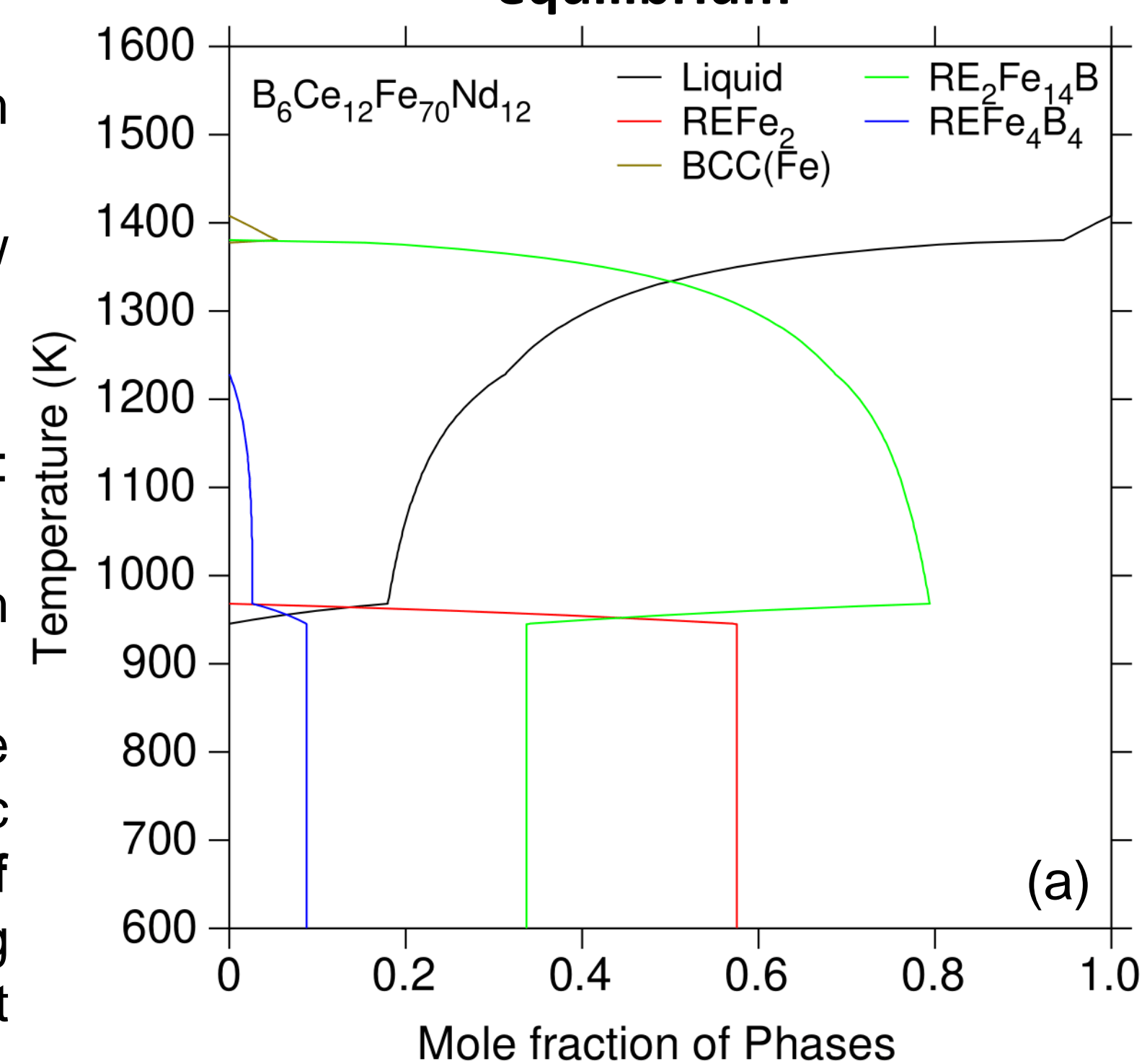
Solidification of a $\text{B}_6\text{Ce}_{12}\text{Fe}_{70}\text{Nd}_{12}$ sample using the database:

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

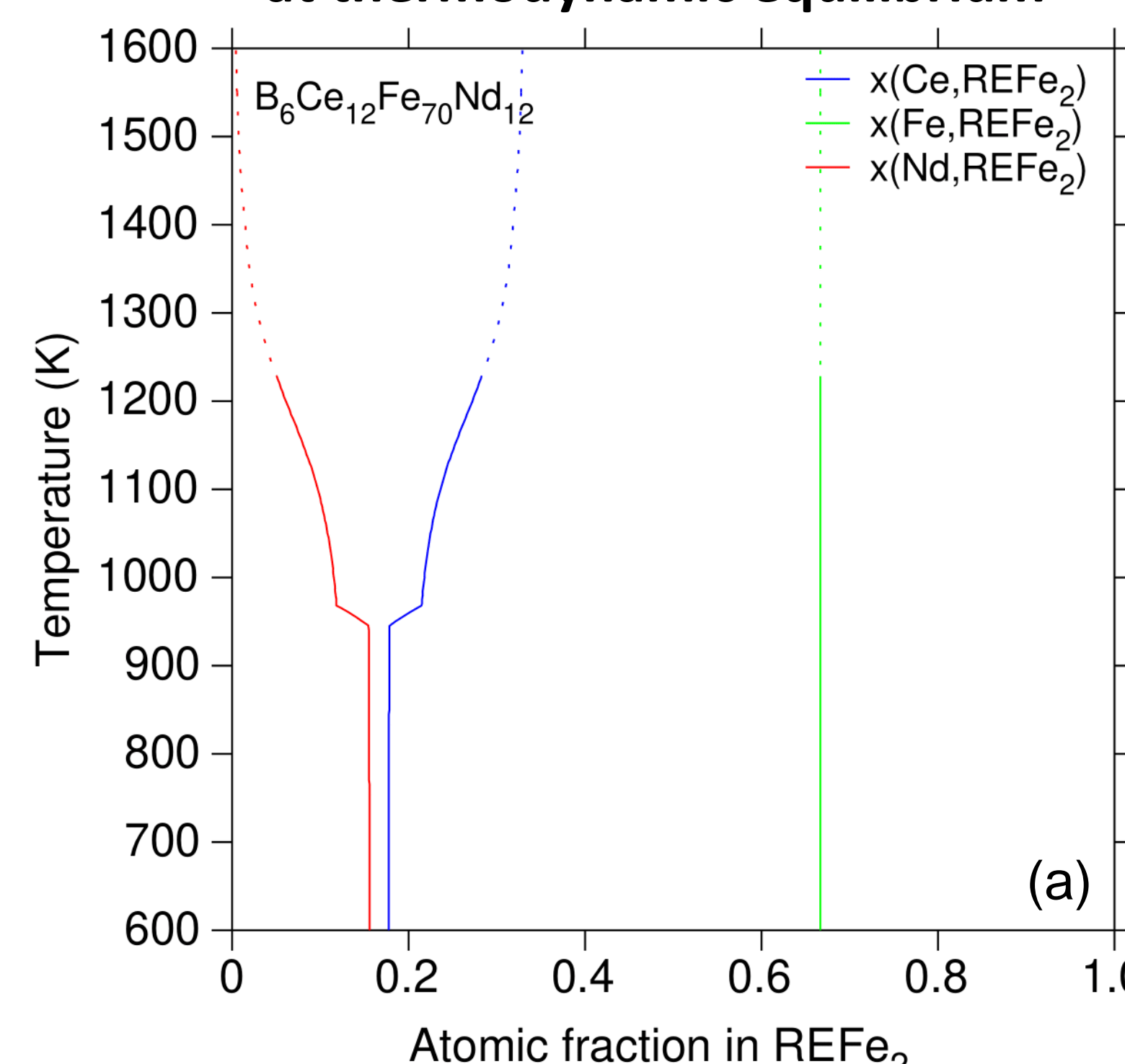
Results of simulation:

- (a) Three phase after cooling: $\text{RE}_2\text{Fe}_{14}\text{B}$, REFe_4B_4 and REFe_2
- (a) Nd-enrichment in REFe_2 which will reduce magnetic performance
- (b) Disparition of the BBC(Fe) phase above 1300 K under thermodynamic equilibrium conditions. **Formation of REFe_2 and a RE-rich phase** during cooling, (b) closer to GB magnet effective compositions

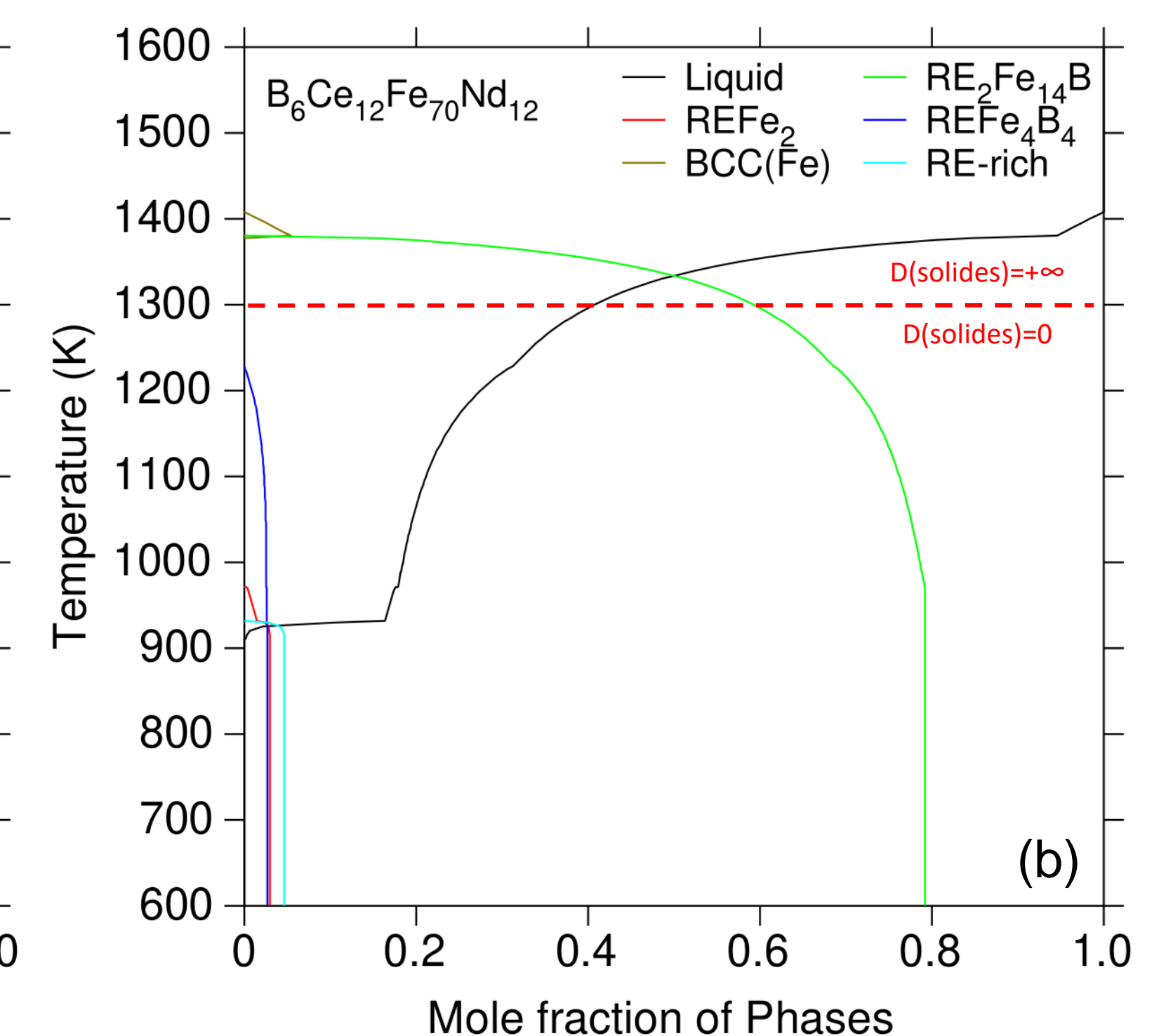
Solidification at thermodynamic equilibrium



Atomic fraction of elements in REFe_2 at thermodynamic equilibrium



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 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.