Study of the μ phase of Ni-Nb Rietveld analysis, First principle calculations and Calphad approach

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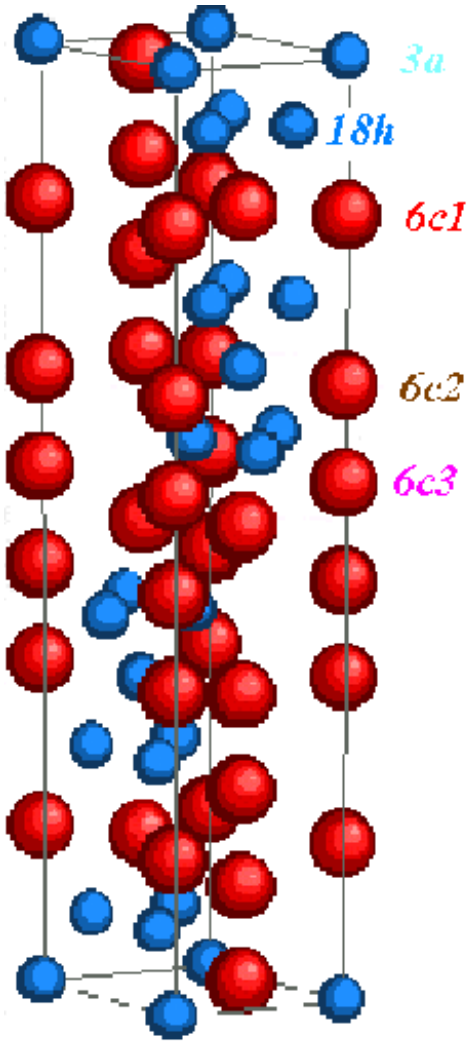
Outline

- The μ phase
- The present study
- Preliminary results
- Perspectives

The mu phase



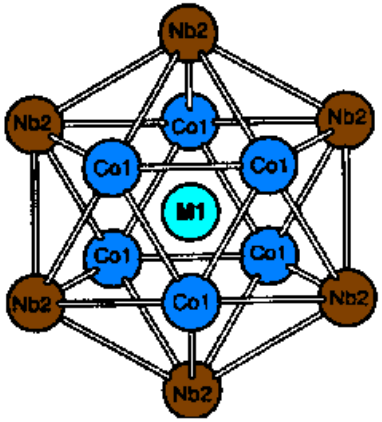
Ideal Structure

Prototype μ	Fe_7W_6				
Space group Pearson symbol	$R\bar{3}m$ $hR13$				
Wyckhoff	3a	6c1	6c2	6c3	18h
Coordination number	12	15	16	14	12
Site occupation	Fe	W	W	W	Fe

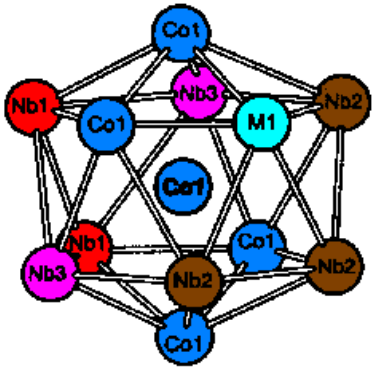
The mu phase

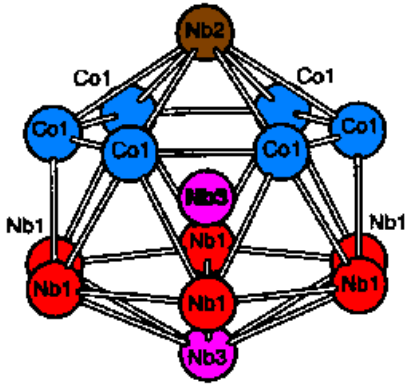
Not stoichiometric

3a
CN 12

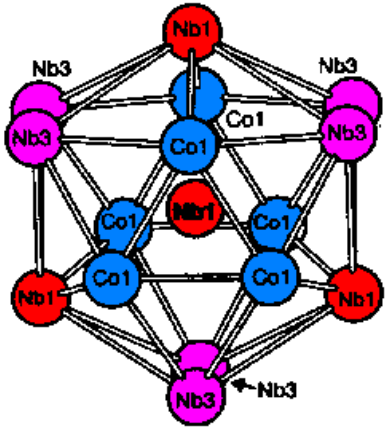


18 h
CN 12

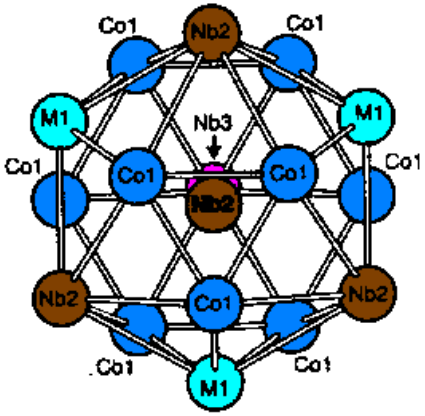




6c3 CN 14



6c1 CN 15



6c2 CN 16

$Co_{6.3}Nb_{6.7}$ V. Wagner, M. Conrad, B. Harbrecht, Acta Cryst. (1995) C15, 1241-1243

The mu phase

Model ?

Crystallography

1995 Wagner *et al.* ($Co_{6.3}Nb_{6.7}$)

in agreement with

1962 Kripryskaya *et al.* (NiTa and NiNb)

$\Rightarrow$ suitable model for NiNb :

$(Ni, Nb)_3\ Nb_6\ Nb_6\ Nb_6\ Ni_{18}$

i.e. $(Ni, Nb)_3\ Nb_{18}\ Ni_{18}$

The mu phase

Available

1996 Bolcavage and Kattner

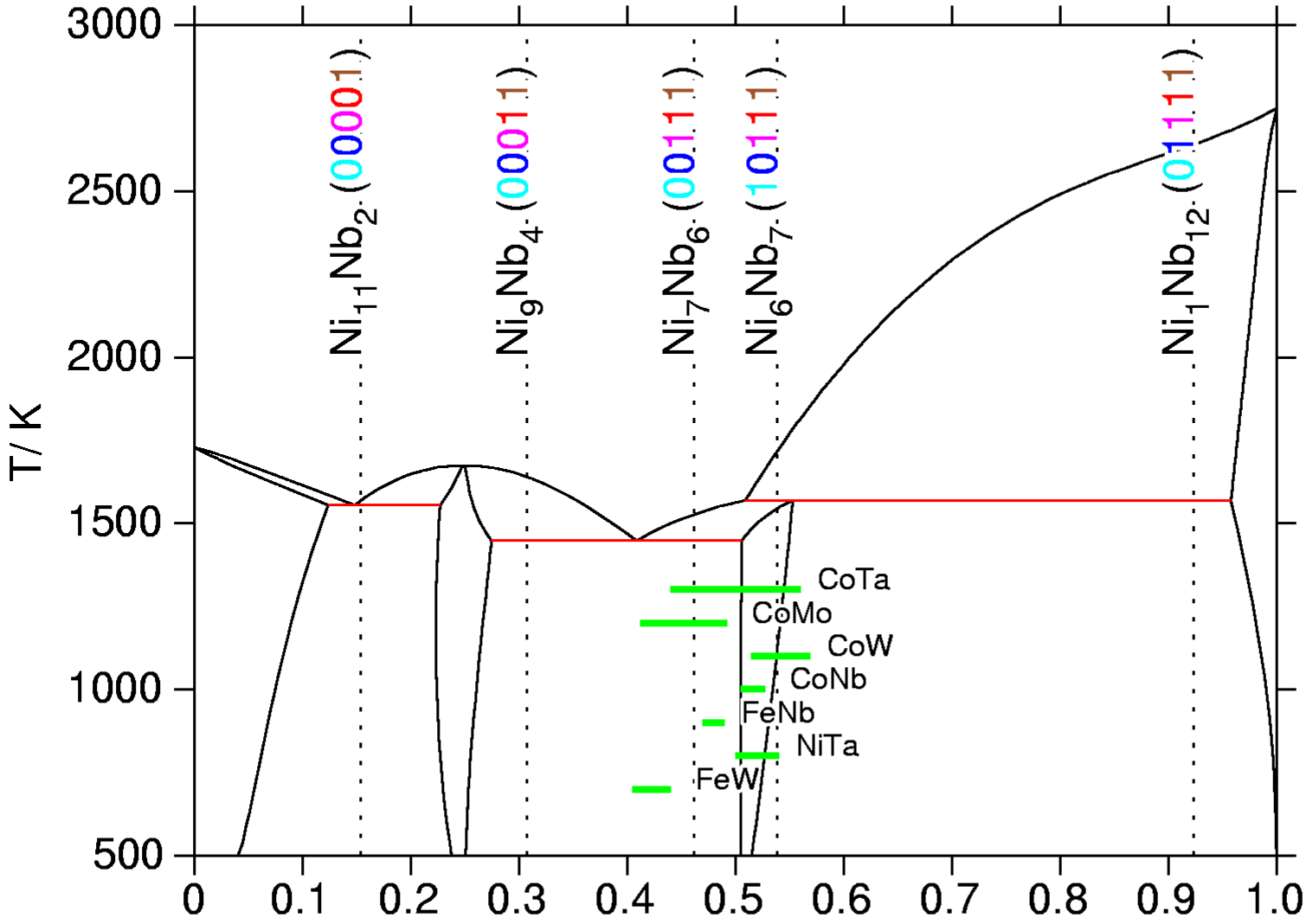
- phase diagram
- CN 12 for 3a and 18h
- compatibility with other descriptions

$\Rightarrow$ $(Ni, Nb)_{21}$ Nb_{18}

$G^{\mu}_{Nb_7Nb_6}$	$magic\ 5kJ/mol$
$G^{\mu}_{Ni_7Nb_6}$	$opt.$
$L^{\mu,0}_{Ni,Nb:Nb}$	$opt.$
$L^{\mu,1}_{Ni,Nb:Nb}$	$opt.$

The mu phase

Composition range



The mu phase

Model?

$(Ni, Nb)_3\ Nb_{18}\ Ni_{18}$

doesn't allow to describe phase diagram

$(Ni, Nb)_{21}\ Nb_{18}$

does describe the phase diagram

doesn't describe the crystallography

cannot describe all the μ phases

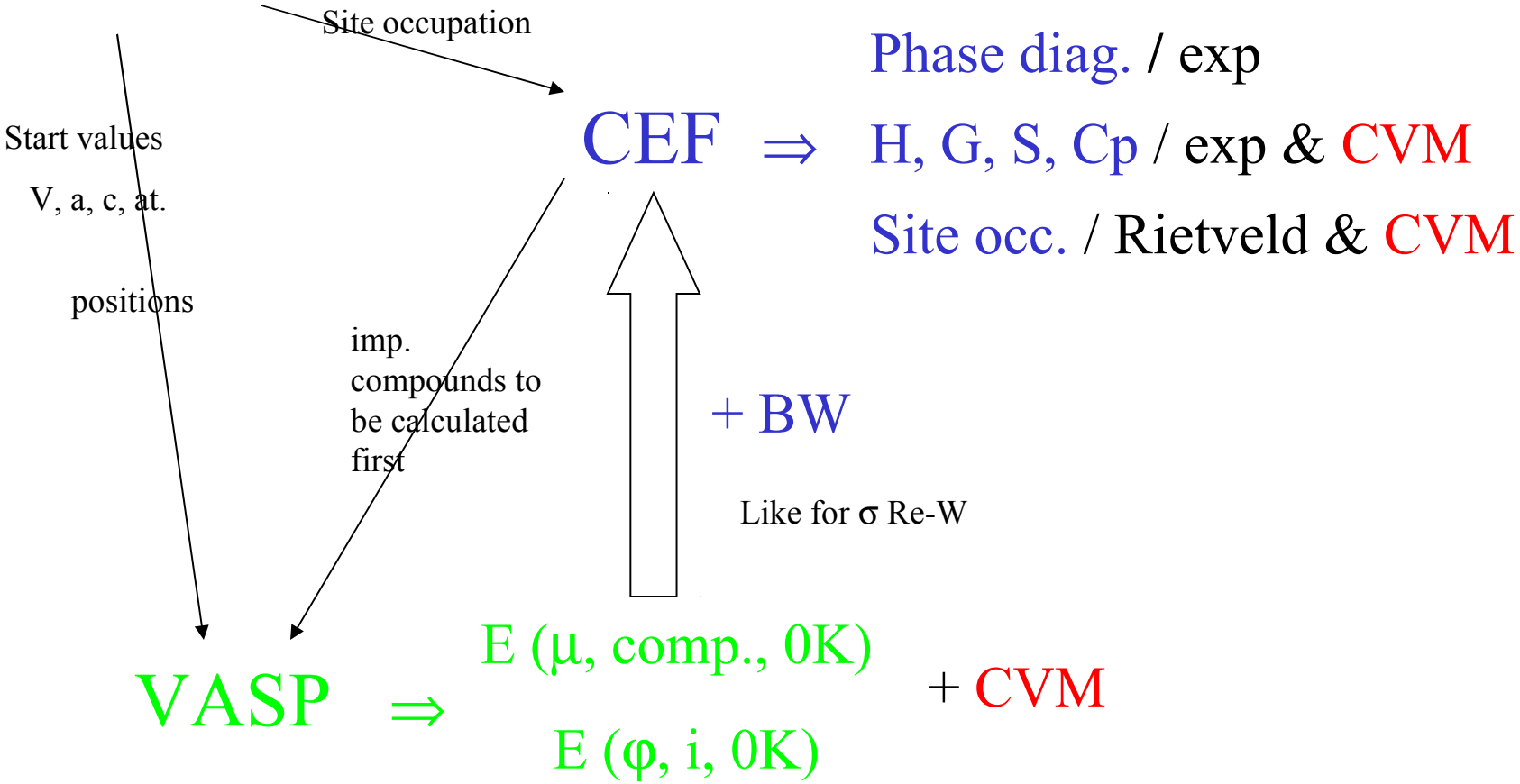
A more complex model is needed.

How to assess easily all its parameters?

The present study

Approach

Rietveld



The present study

VASP

Total Energies computed by Vienna Ab-initio Simulation Package

- **DFA** Density Functional Approximation
- **GGA** Generalized Gradient Approximation
- **non-local optimized ultrasoft pseudopotentials**
- **Full relaxed** (Volume-shape and atomic positions)

For more details: Journal of Alloys and Compounds: Berne, Sluiter, and Pasturel, Theoretical Approach of phase selection in refractory metals and alloys, 334 (2002) 21-33

The present study

C. E. Formalism

$(Nb,Ni)_3\ (Nb,Ni)_{18}\ (Nb,Ni)_6\ (Nb,Ni)_6\ (Nb,Ni)_6$

x : at. composition

y : site fraction

$$G_m^{\mu}(T) - \sum_i x_i^{\mu}\ H_i^{SER}(T_0)$$

$$= \Delta G(x) + \Delta G(y)$$

$$= \sum_i x_i^{\mu}\ \left(G_i^{\mu}(T) - H_i^{SER}(T_0)\right) \Rightarrow \textbf{\textit{Ref}}$$

$$+ \sum_C y_i^1\ y_j^2\ y_k^3\ y_l^4\ y_m^5\ \left(G_C^{\mu}(T) - a_{Nb}\ G_{Nb}^{\mu}(T) - a_{Ni}\ G_{Ni}^{\mu}(T)\right) \Rightarrow \textbf{\textit{Ref}}$$

$$+ R\ T \sum_s \alpha_i^s \sum_i y_i^s \ln y_i^s \Rightarrow \textbf{\textit{id}}$$

$$+ \sum_{\nu} x_{Nb}^{\mu}\ x_{Ni}^{\mu}\ (x_{Nb}^{\mu} - x_{Ni}^{\mu})^{\nu}\ L_{Nb,Ni}^{\mu,\nu} \Rightarrow \textbf{\textit{xs}}$$

The present study

Parameters

Ref. *from VASP*

$\left(G_i^{\mu}(T) - H_i^{SER}(T_0)\right)$ *from VASP*

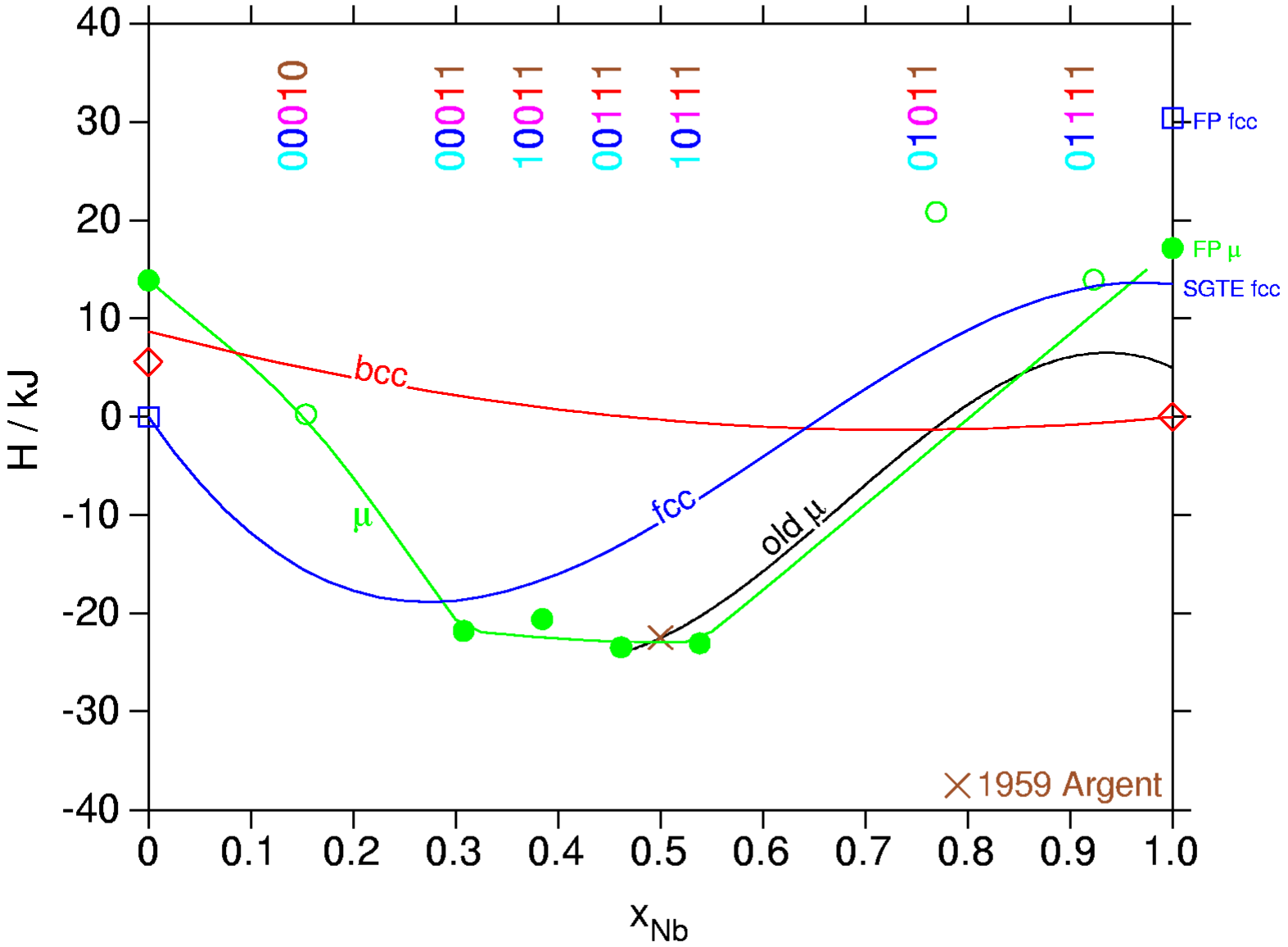
$\left(G_C^{\mu}(T) - a_{\mathrm{Nb}}\ G_{\mathrm{Nb}}^{\mu}(T) - a_{\mathrm{Ni}}\ G_{\mathrm{Ni}}^{\mu}(T)\right)$ *from VASP*

11 available over 32

No xs !

$L_{\mathrm{Nb,Ni}}^{\mu,\nu}$ *zero*

Preliminary results



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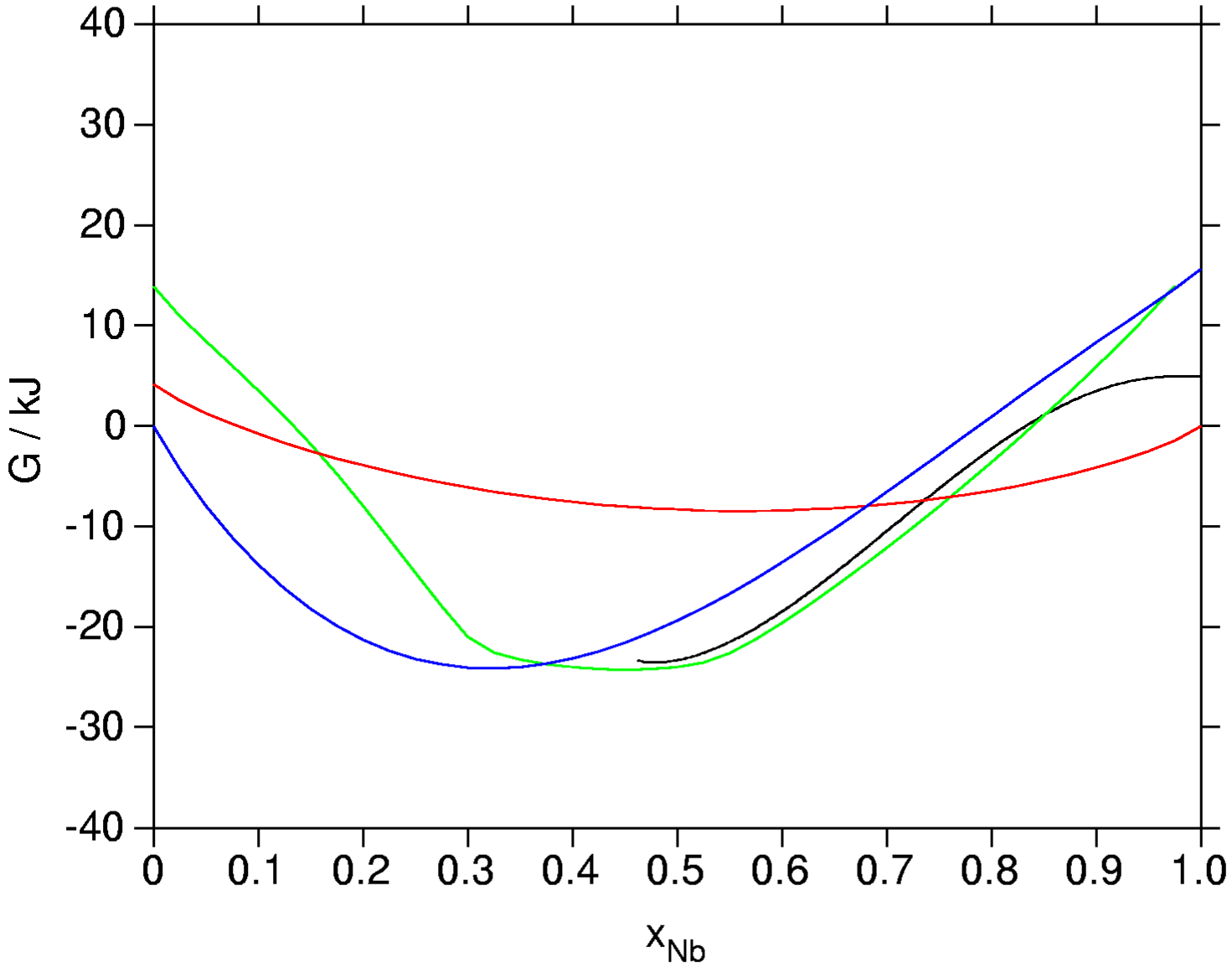

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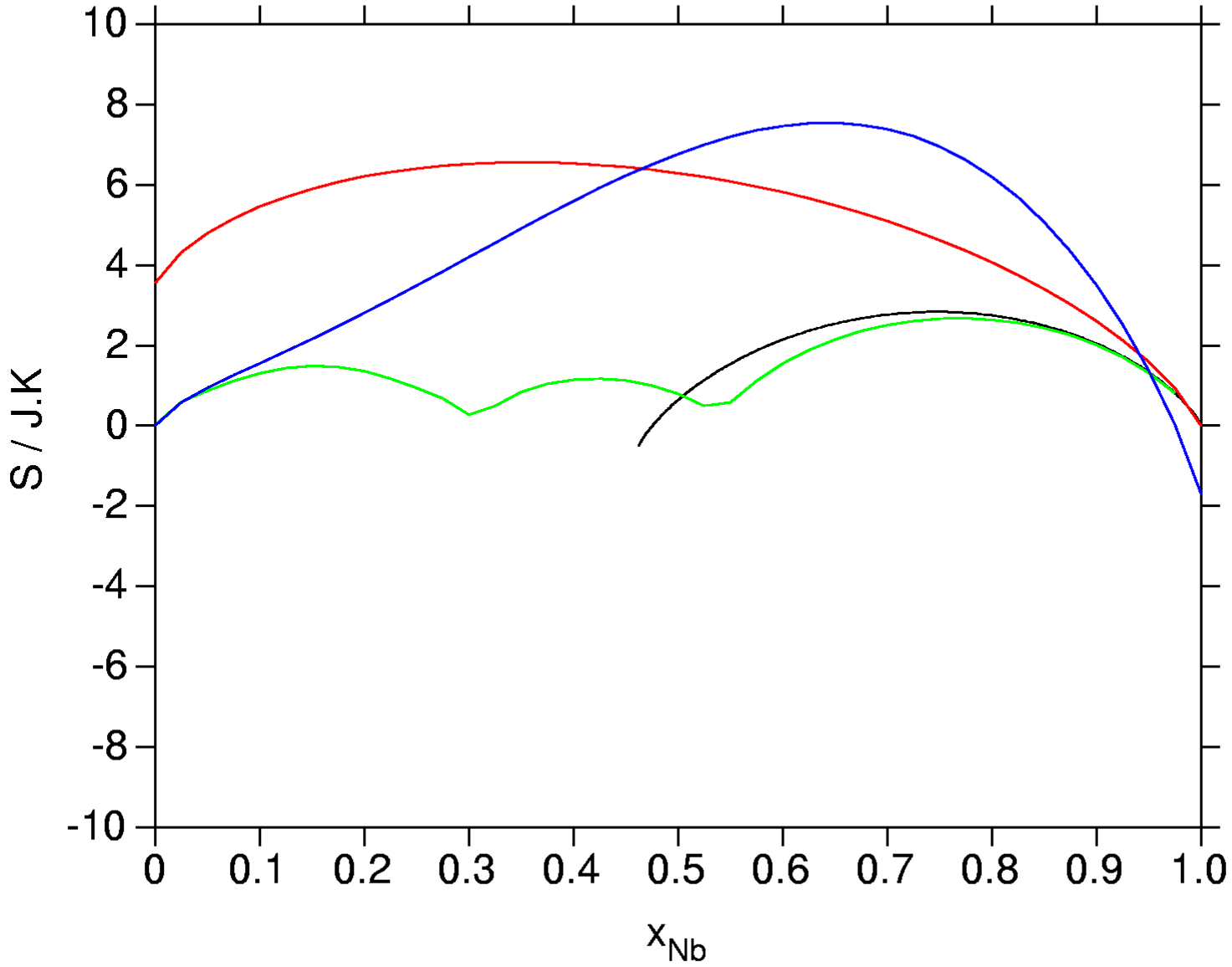

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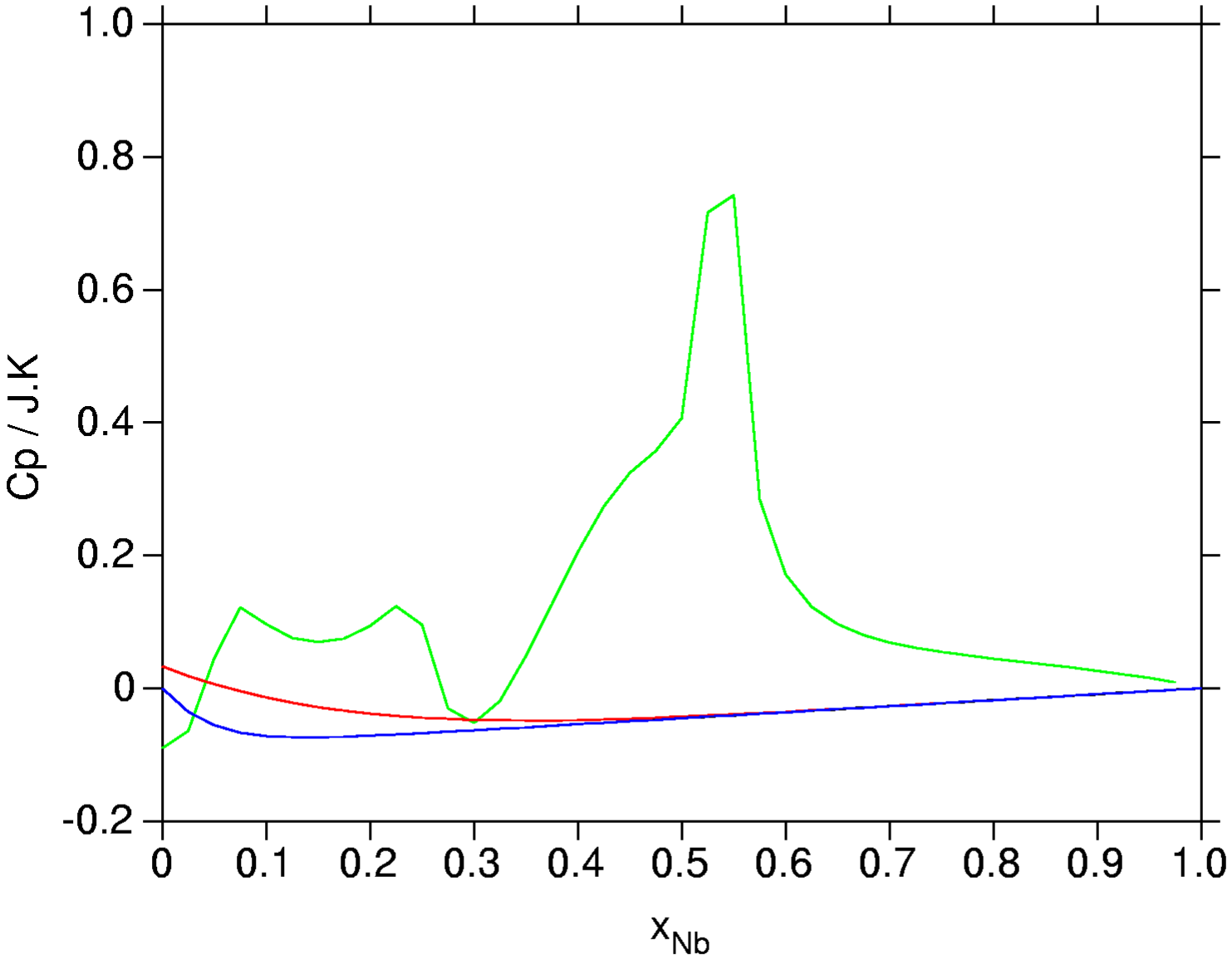
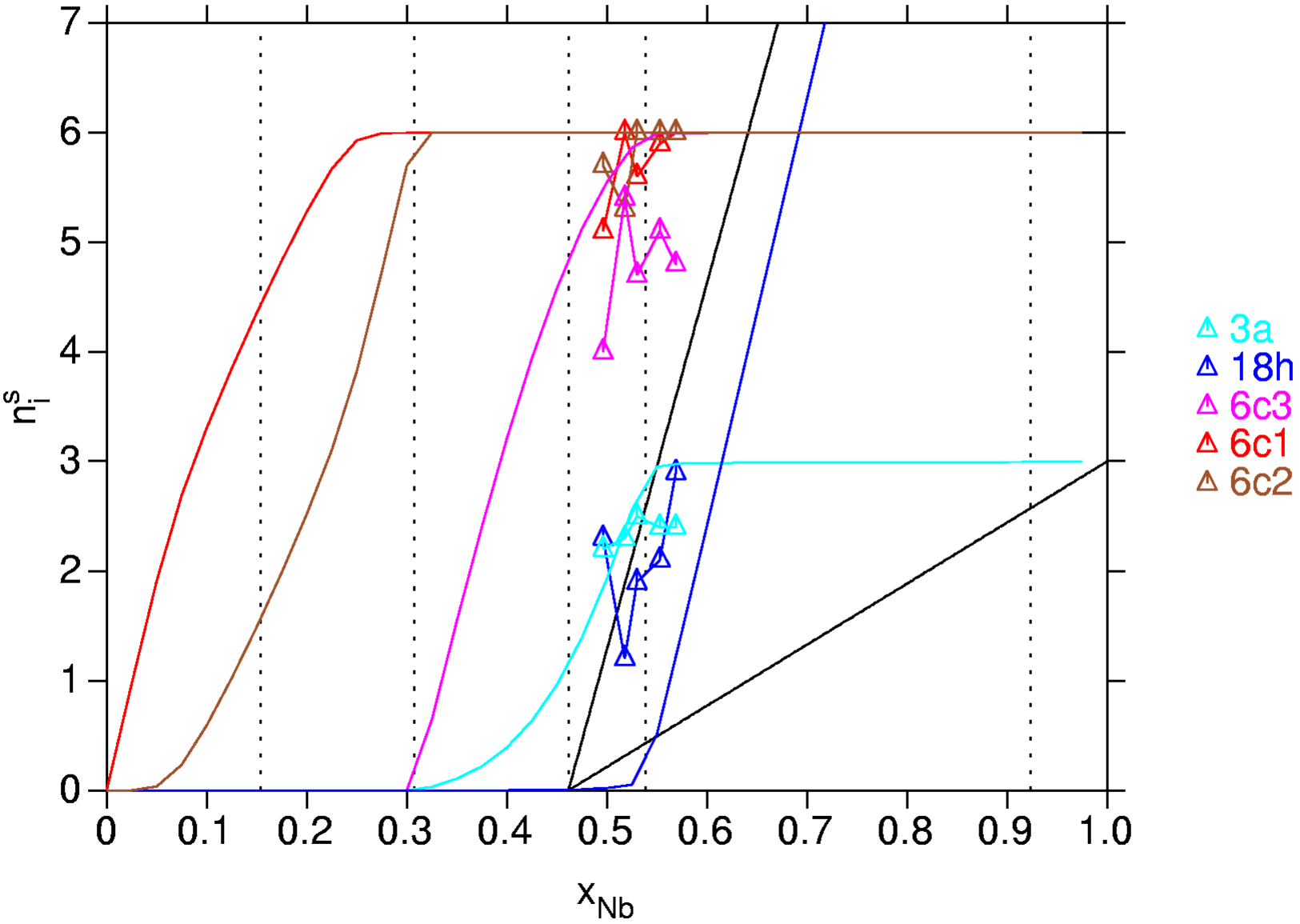
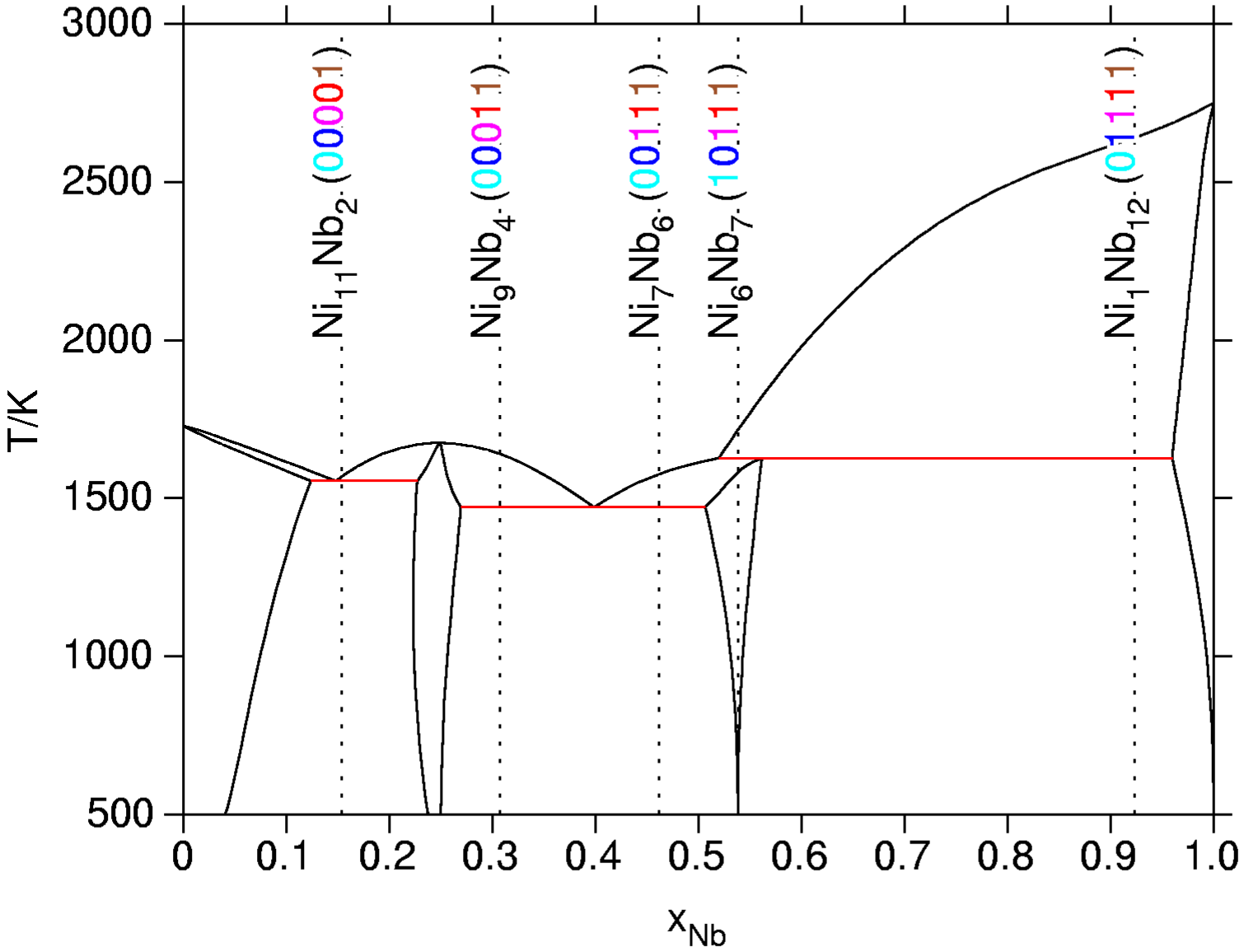


Preliminary results



Preliminary results



Perspectives

- Preliminary results very promising but
  - missing compounds to be calculated
  - comparison of H, G, S, Cp, y with CVM, …
- Application of the approach to
  - other systems
  - other phases
- Revision of lattice stabilities?
  - μ, σ, Laves, …. for pure elements
  - fcc Nb