The Equi-Entropy Criterion (EEC) for the 3rd generation thermodynamic databases

Bo Sundman

OpenCalphad, 9 Allée de l'Acerma, 911 90 Gif-sur-Yvette, France

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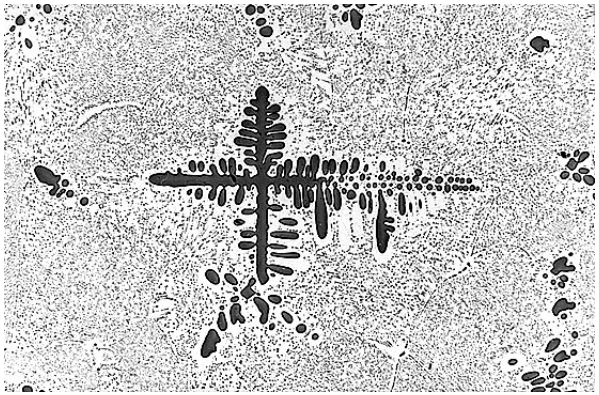
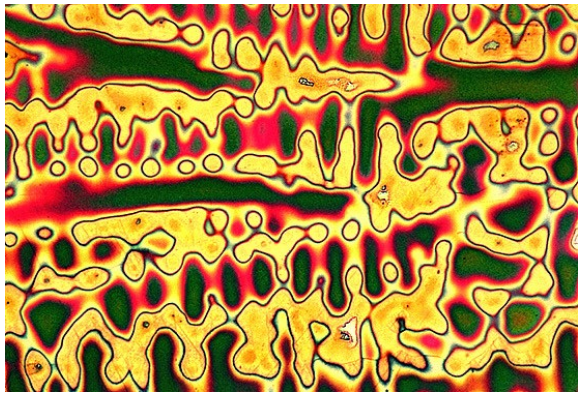
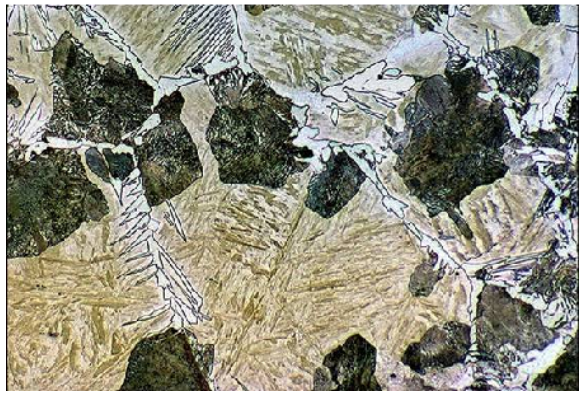
Why I got interested in materials science

Studying engineering at KTH I was enchanted by microstructures like this:

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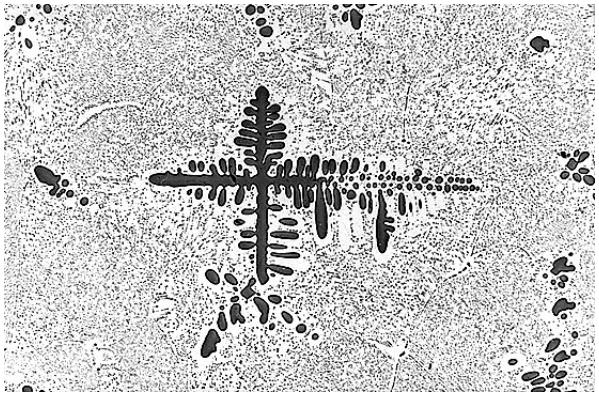
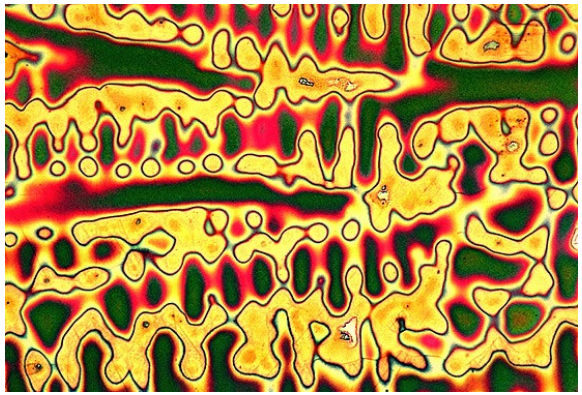
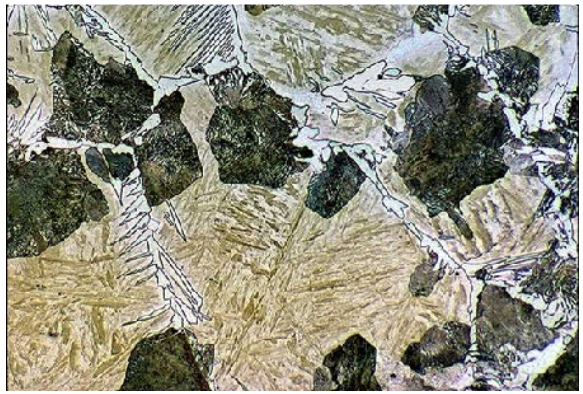

At that time, early 1970, I did not like computers which looked like this in 1975:

So I thought materials science was too complicated for computers, one could only study materials by experimental work.

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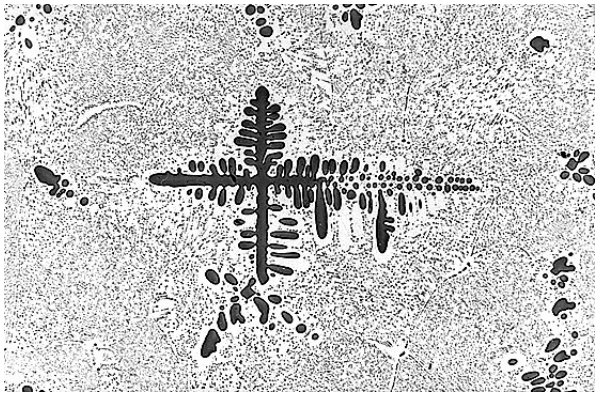
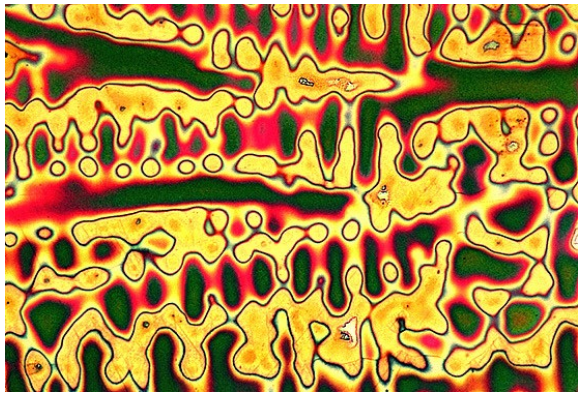
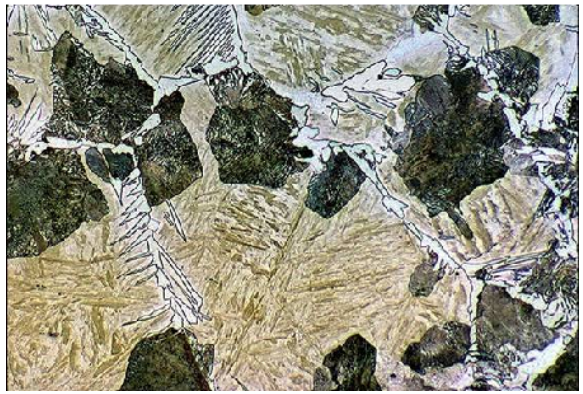

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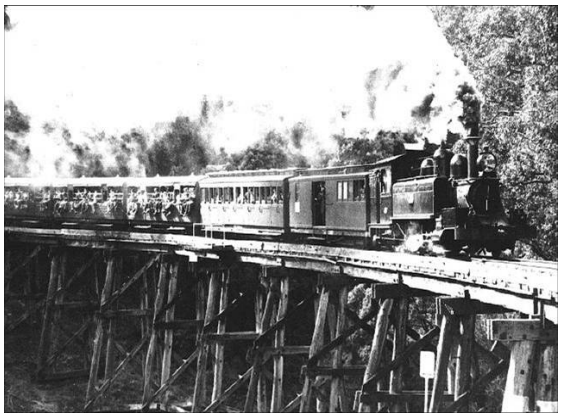

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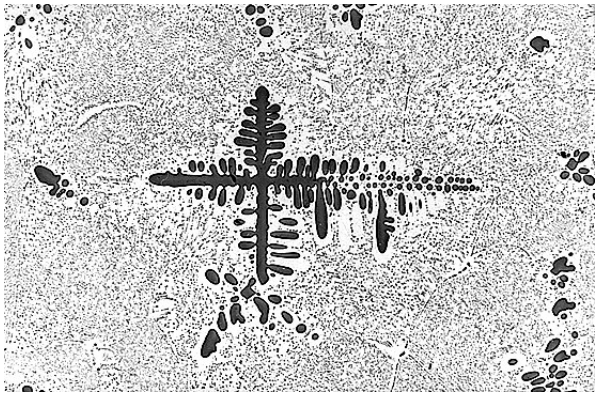
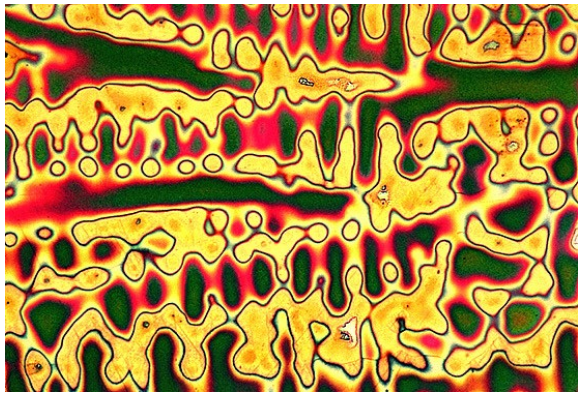
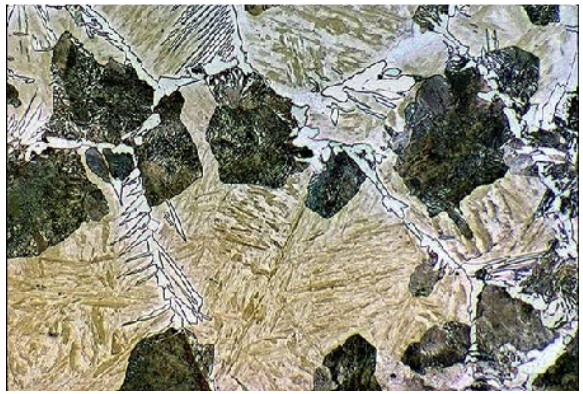

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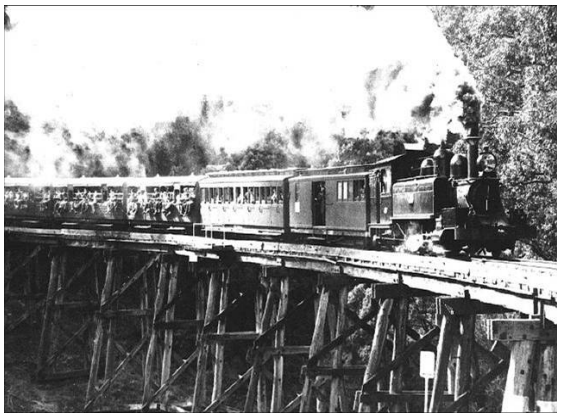
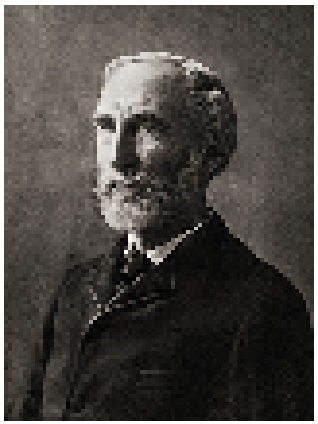
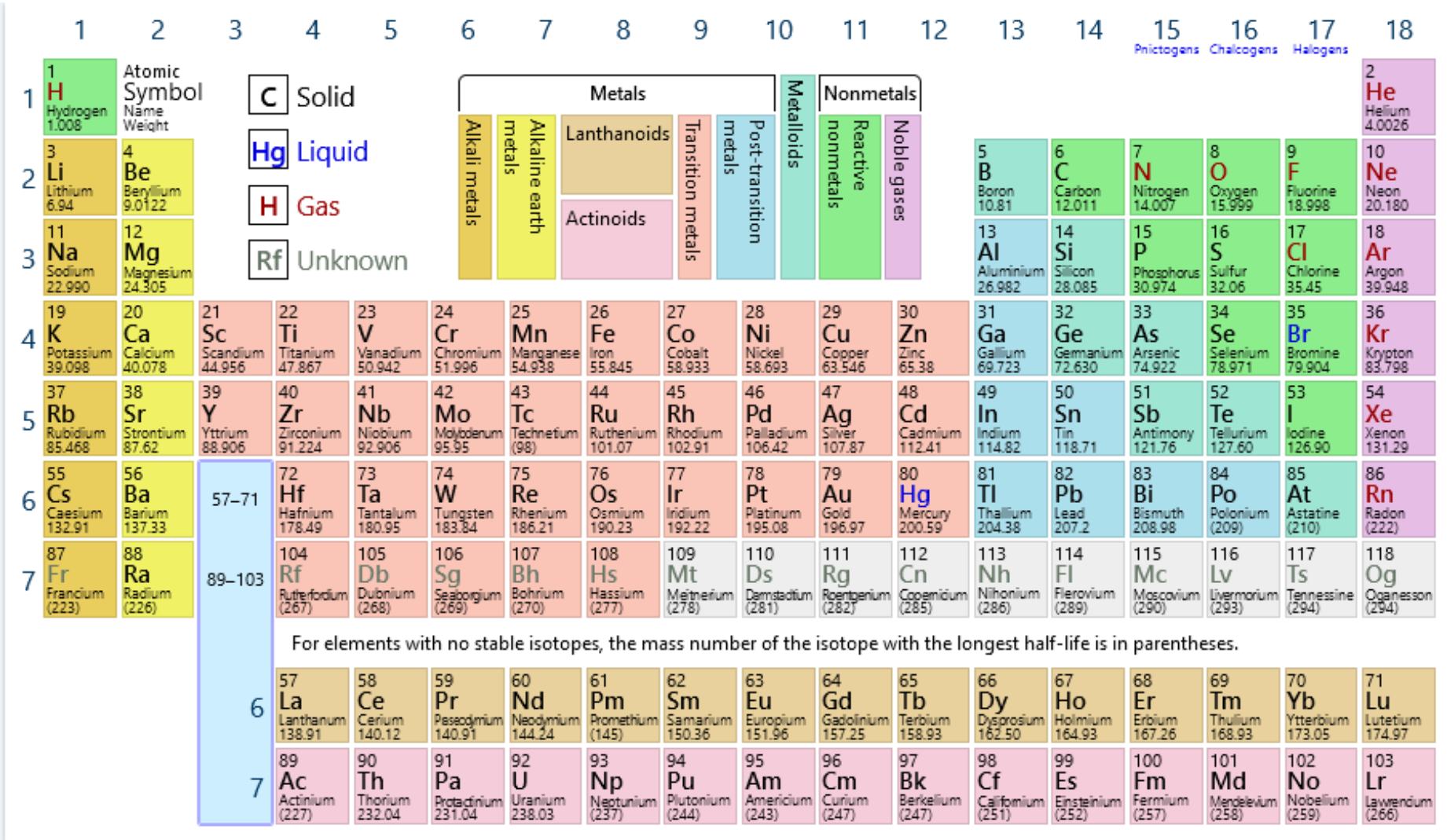




Like most students I did not like thermodynamics, this complex set of relations between properties such as temperature, heat, pressure etc, developed by J W Gibbs, explained by Mats Hillert.

Thermodynamics is valid in the whole universe we know

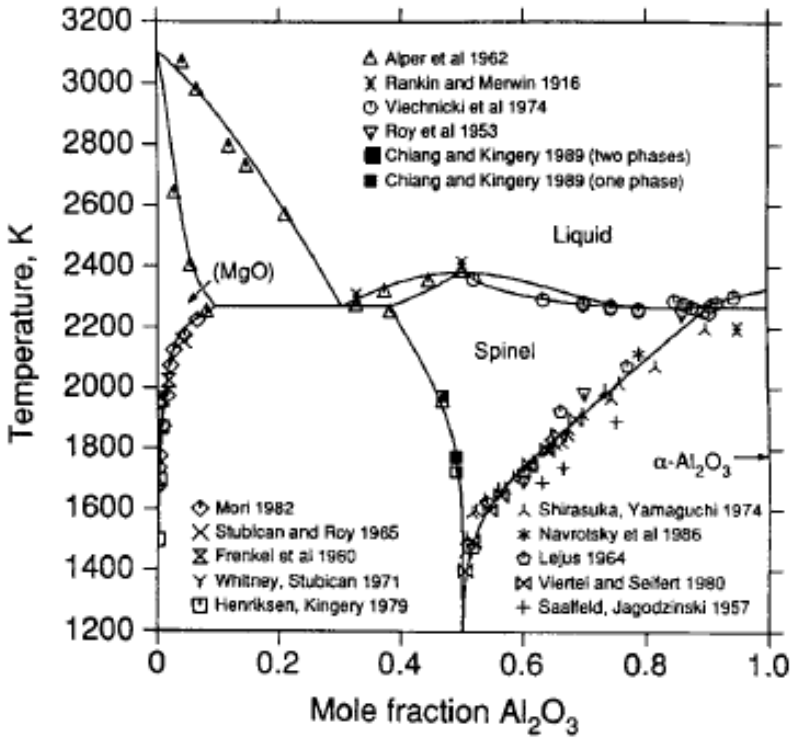
Each element has unique thermodynamic properties

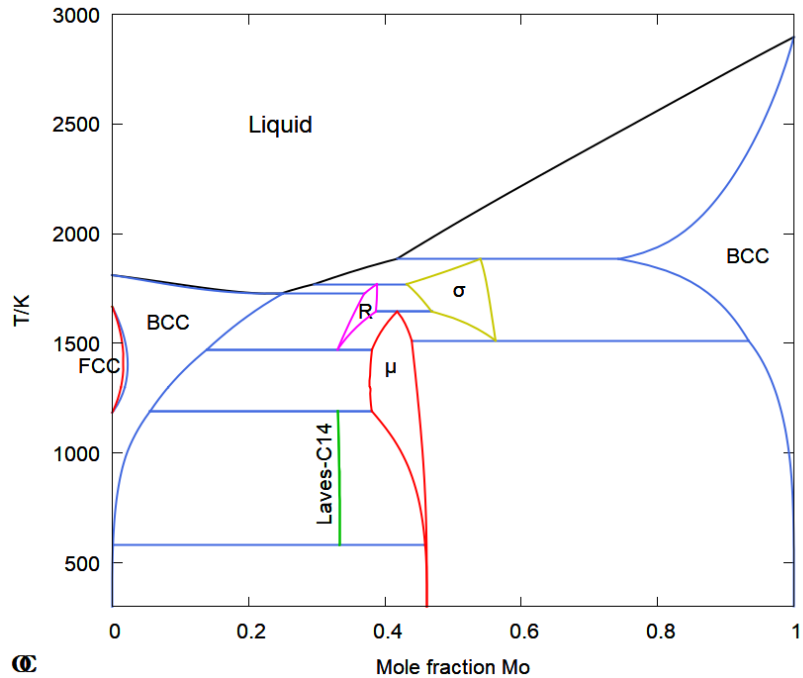


The elements have many different crystalline structures as solids and at higher T most elements transform to a liquid and at even higher to a gas. A few elements, such as H, N, O are gas already at ambient T but become liquid and solids at low T.

Phase diagrams and thermodynamics go well together

For more than 100 years **phase diagrams**, as the two below for the systems Al_2O_3-MgO and Fe-Mo, have been used to understand which phases are stable in materials at different compositions and temperatures.





Originally the phase diagrams were determined by experiments, as shown in the left figure, but when computers were becomming available in the 1970 some scientists started to develop models to calculate phase diagrams using thermodynamic data. The thermodynamic properties of the different elements are important for phase diagrams and for all kinds of processes in materials science.

and thermodynamics is perfectly fitted to computers $\cdots$

In thermodynamics we have:
extensive state variables such as the volume, V, the amount of an element A, N_{A}, the electric charge, Q, etc and
intensive state variables or potentials, such as the temperature, T, the pressure, P, the chemical potential of element A, μ_{A}, the electric potential, E, etc. At equilibrium an intensive property has the same value independent of the size of the system.

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The entropy, related to the heat capacity and the enthalpy, H, of a system, is an elusive property.

For a strict derivation of all thermodynamic relations you can choose between several 1000 textbooks that explain these in different ways.

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The key feature of Calphad was that Larry Kaufman, who started it in 1973, understood that one must have a set of unary Gibbs energies for the pure elements in their metastable allotropes, for example $G_{\rm Cr}^{\rm FCC}$, $G_{\rm Ni}^{\rm BCC}$ etc., so called **lattice stabilities**.

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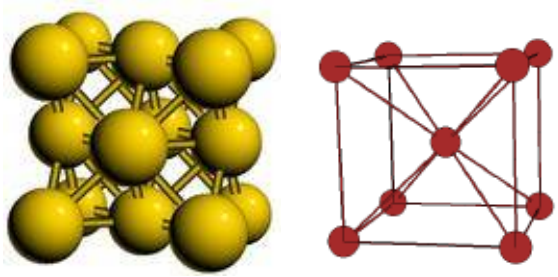
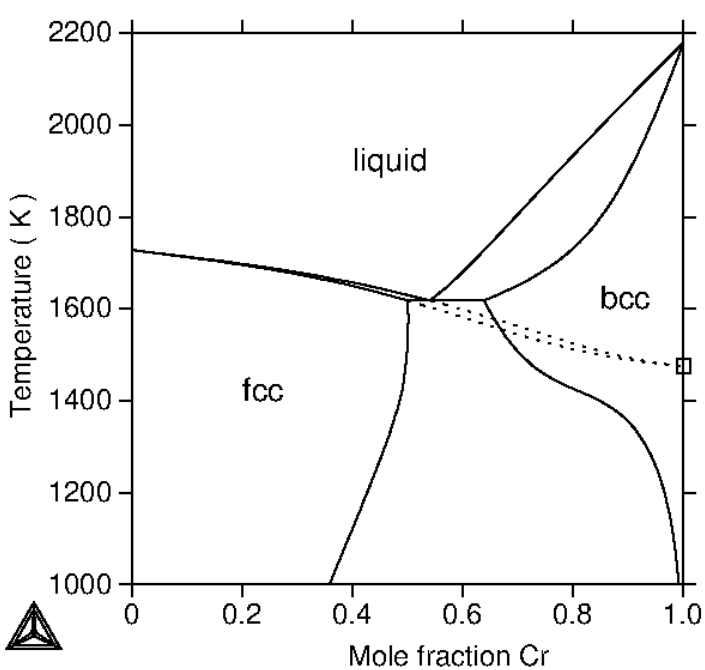
This was in contrast with other eminent scientists who considered that the metastable allotropes could be adjusted for each system - the dilute school.
The metastable allotropes of an element are often assumed to have the same heat capacity as the stable phase for the element, i.e. the lattice stabilities are Gibbs energy expressions linear in T:

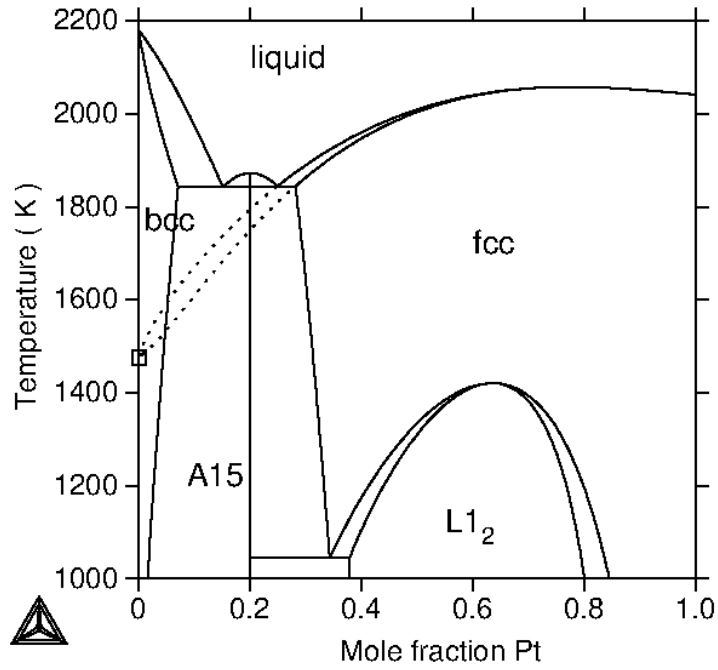
$$ {}^{\circ}G_{\mathrm{A}}^{\alpha} - {}^{\circ}G_{\mathrm{A}}^{\beta} = a + bT \qquad (1) $$



How the lattice stability of FCC-Cr was estimated 1970

The two figures below show how one can estimate the melting T of an metastable FCC Cr by extrapolate the experimental liquidus curve from Cr-Ni and Cr-Pt. Together with an estimate of the melting entropy this gives the lattice stability of the metastable FCC Cr.





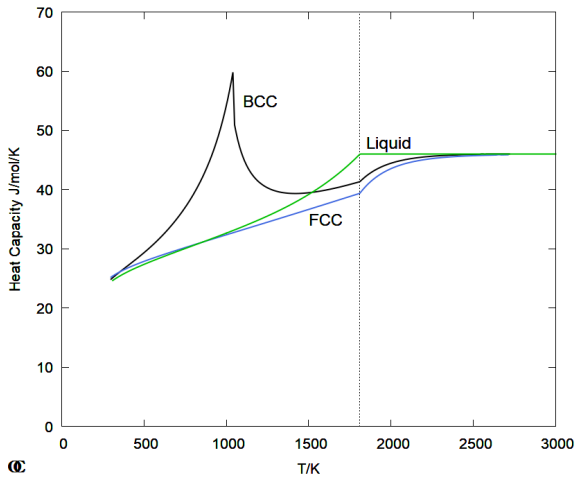
Today such values can be calculated by DFT but some of them, such as FCC Cr, is **mechanically unstable** and the DFT value is meaningless. In other cases the original lattice stabilities fit well with such calculations.

Contributions to the heat capacities of the pure elements

A linear T difference between the Gibbs energy of the allotropes of an element works for many elements but not for a few, such as Fe, due to the ferromagnetic transition of BCC-Fe. A separate phenomenological model for the ferromagnetism was proposed by Inden in 1978 depending on two properties, the Curie temperature, T_C, and the Bohr magneton number, β.

- $$G_{\mathrm{Fe}}^{\mathrm{BCC}} - H_{\mathrm{Fe}}^{\mathrm{SER}} = a + bT + cT\ln(T) + G^{\mathrm{magn}} + \cdots$$
  $$T_{C\,\mathrm{Fe}}^{\mathrm{BCC}} = 1043$$
  $$\beta_{\mathrm{Fe}}^{\mathrm{BCC}} = 2.22$$

where SER is the reference state for A at 298.15 K and 1 bar. T_C and β varies with the composition of the phase.



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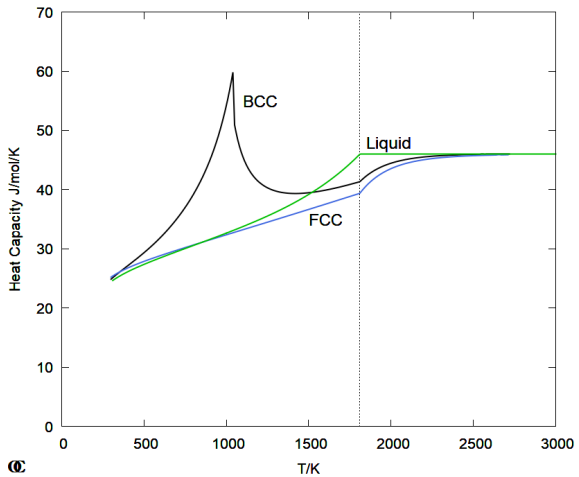

where SER is the reference state for A at 298.15 K and 1 bar. T_C and β varies with the composition of the phase.

The heat capacity data above 298.15 K for the pure elements together with a magnetic model treating T_C and β as composition dependent parameters was included in the SGTE unary database 1991. This greatly improved extrapolations and transformed Calphad to Computational Thermodynamics.

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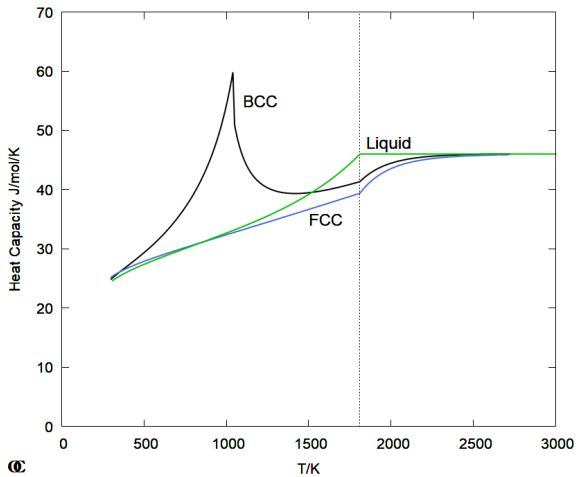

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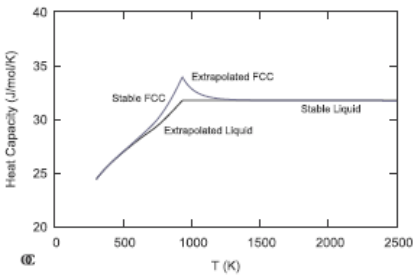
The break point in the heat capacity at the melting T (vertical dashed line) was a quick fix to avoid that the solid phases becomes stable if its heat capacity is extrapolated to high T.

Extrapolated heat capacities for the pure elements

When the heat capacity was added in 1991 there were some new problems. A breakpoint was introduced at the melting T, and the solid was extrapolated to approach the liquid heat capacity, here for pure Al:



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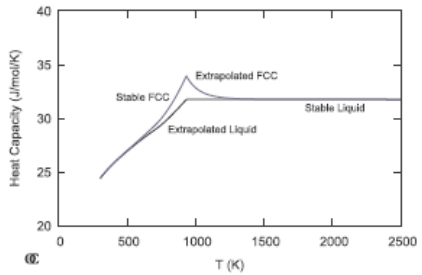

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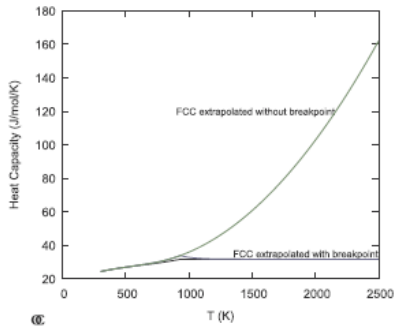
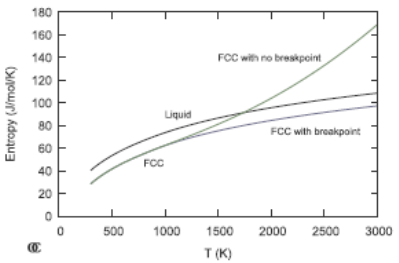
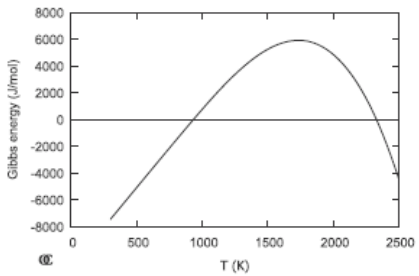


(b) Heat capacity extrapolated



(c) Entropy



(d) Difference G(fcc)-G(liquid)

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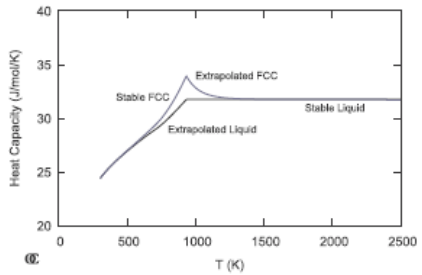

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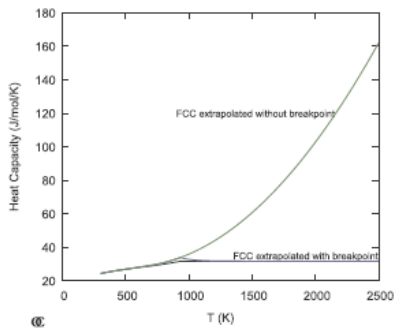

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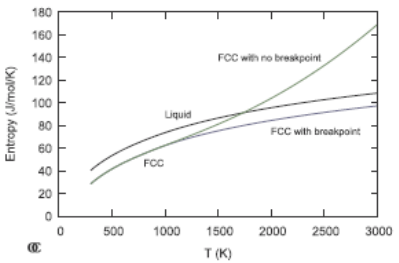

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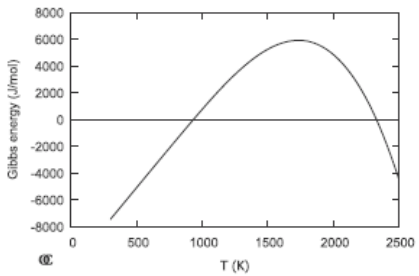

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To prevent this an "Equal Entropy Criteria" (EEC) can be introduced in the software.
The idea with EEC is that a solid phase with entropy higher than the liquid at the same T must be **mechanically unstable**.

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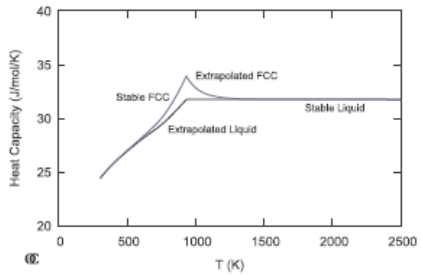

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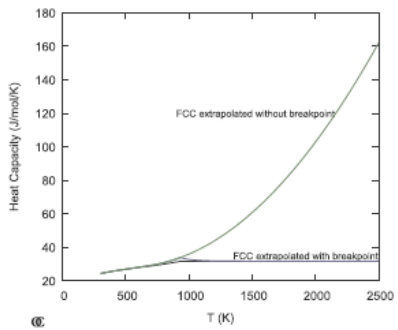

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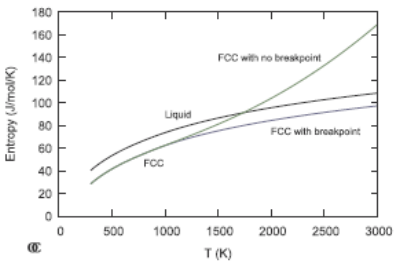

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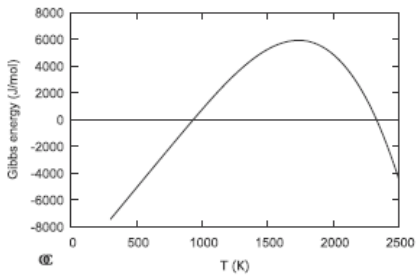

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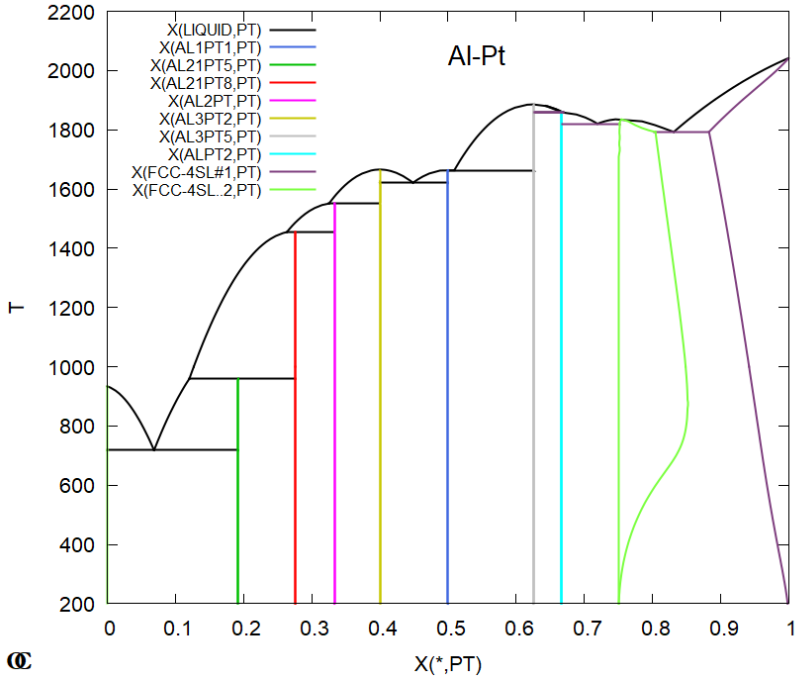
For a pure element or compound this is related to the "entropy catastrophy" but EEC is applied to solution phases in multicomponent systems comparing the entropy of phases at the same T but with different compositions.

Al-Pt without break point in heat capacity with or without EEC

In the Al-Pt system there is an FCC based ordered $L1_2$ phase stable above 1800 K.



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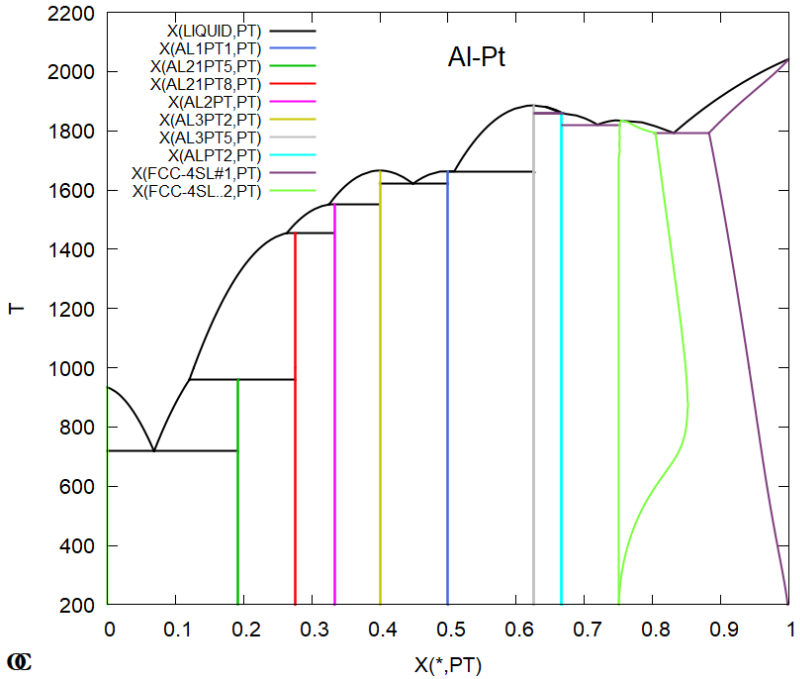

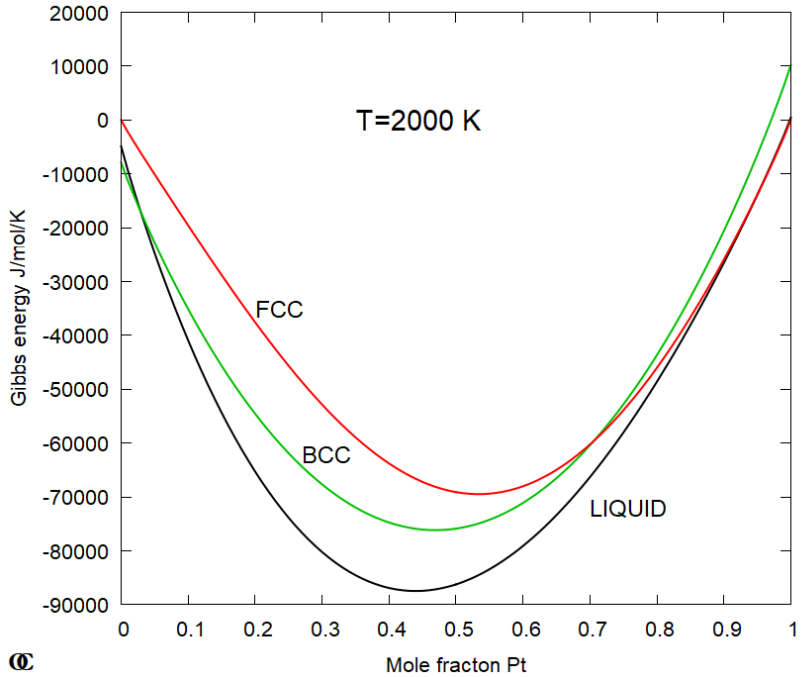

If the heat capacity of Al is not restricted the Gibbs energy curves for FCC, BCC and Liquid at $T = 2000$ K will look like this across the system, using FCC as reference state. The end points of the curves are the lattice stabilities for the pure elements and at the Al-side BCC has lower Gibbs energy than the liquid.

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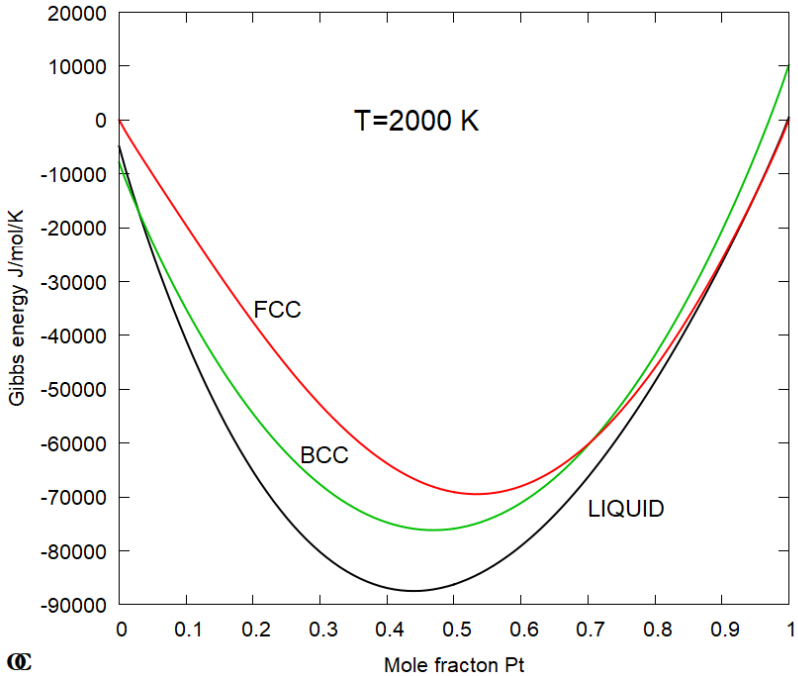

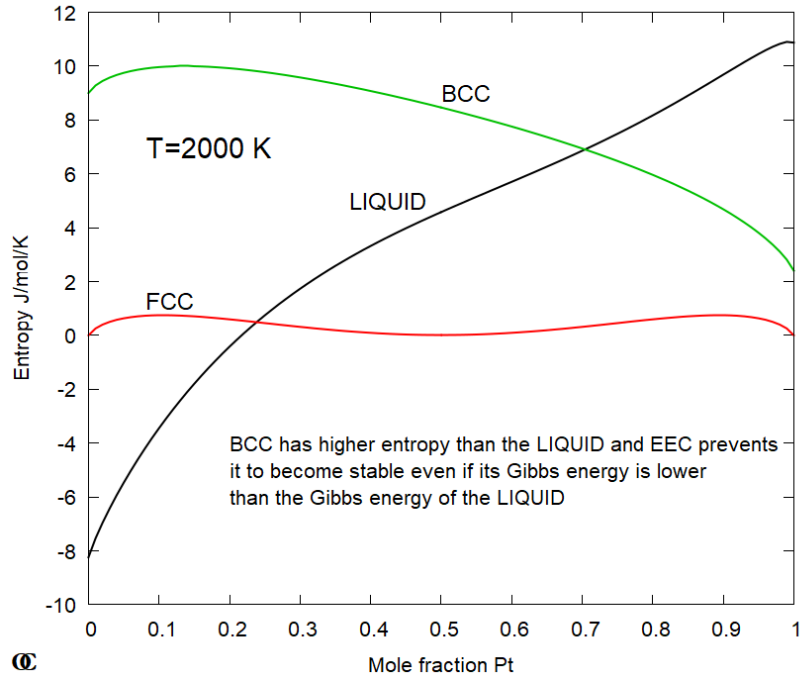

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But this is due to the extrapolated heat capacity of pure Al as confirmed by the fact the entropy of FCC and BCC is higher than that of the liquid on the Al-rich side. EEC will prevent BCC from beoming stable by testing this.

The new unary database

The EEC proposal is part of a project to develop a new unary set of data to improve the extrapolations from the SGTE 1991 database. Other things which will be considered are:

1. The heat capacity is extended down to 0 K using an Einstein model together with a polynomial in T with powers ≥ 2.
2. Perfectly crystalline phases will have entropy zero at $T = 0$ K.
3. A two-state model is used to describe the liquid and the amorphous phases with a single Gibbs energy function.
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There are several commercial and free software packages using the SGTE 1991 unary database, for example Thermo-Calc, FactSage, Pandat but also some free software such as OpenCalphad, pyCalphad and Thermochimica.

Solution models and assessments

In addition to the pure element data various models have been developed to describe how the Gibbs energy varies with the constitution of the phase.
Calphad use mean-field models normally with ideal configurational entropy because it works very well for extrapolations to multi-component systems. It started with a regular substitutional models with excess parameters, sublattice models for phases with LRO, associated models in liquids, ionic models, quasichemical models, etc.

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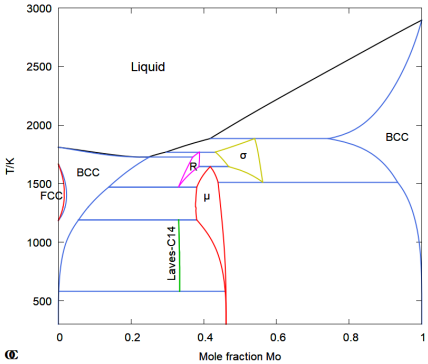
In binary and ternary systems SRO can be very important but in systems with 5-10 elements the number of SRO clusters increase so rapidly that none of them has a significant probability.
For binary system with strong SRO such as FCC in Au-Cu, Al-Ni, Fe-Pt, HCP in Al-Ti and BCC in Al-Fe etc. there are accurate assessments including an approximate SRO description. They extrapolate well to higher order systems.

Creating databases

The assessed model parameters can be combined to databases in order to calculate multicomponent phase diagrams and chemical potentials for use in simulations. Usually assessments of all binary and the most important ternary systems are sufficient to make reliable extrapolations to multi-component systems with 5-15 elements. Most high quality databases are commercial because collecting, verifying and often amend the assessments are a very time consuming effort requiring long experience.

Calphad is engineering

A Calphad database provides information for many properties, not just the phases, their Gibbs energy, heat capacity but also the chemical potentials, magnetic transitions, chemical ordering, sometimes volumes etc.



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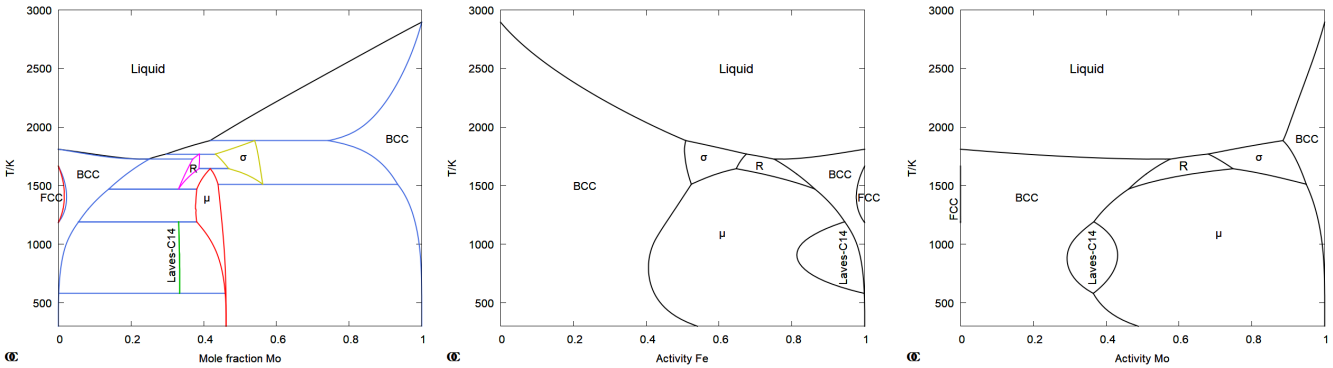

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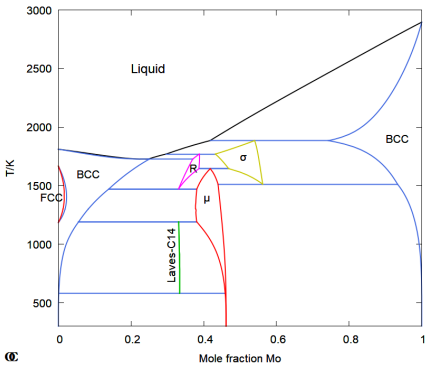

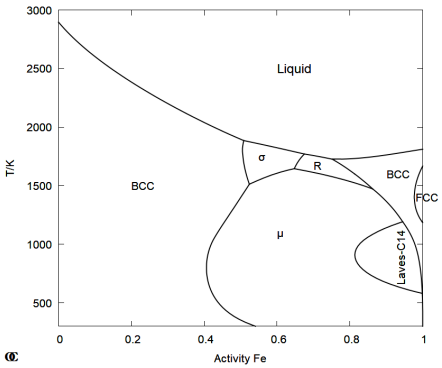

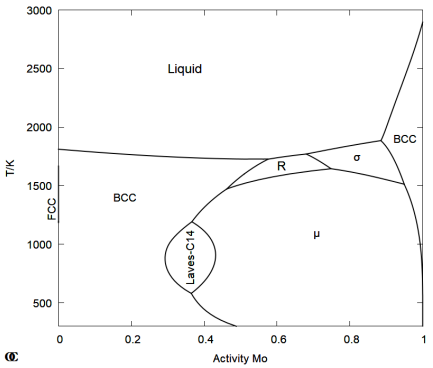

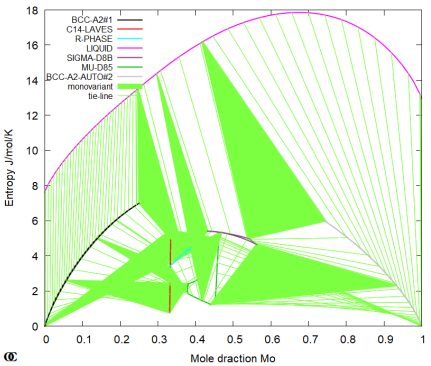

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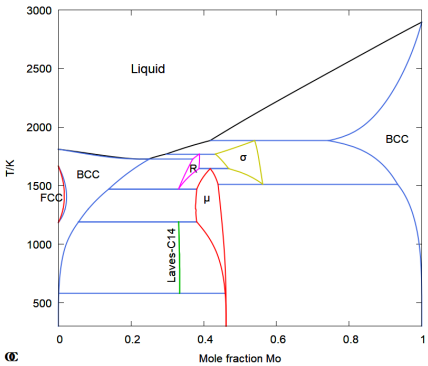

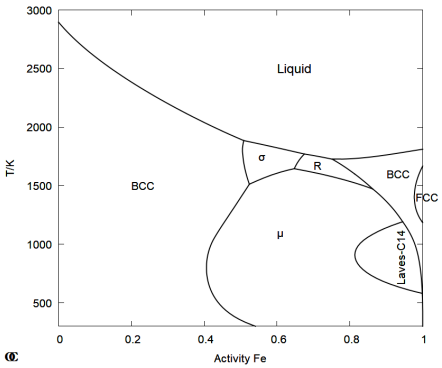

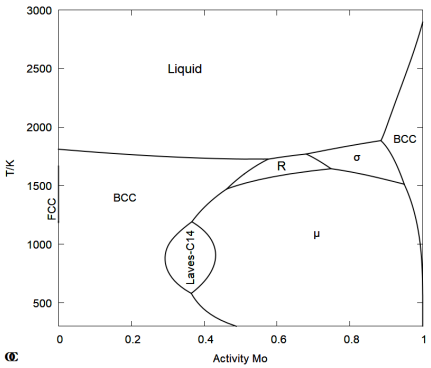

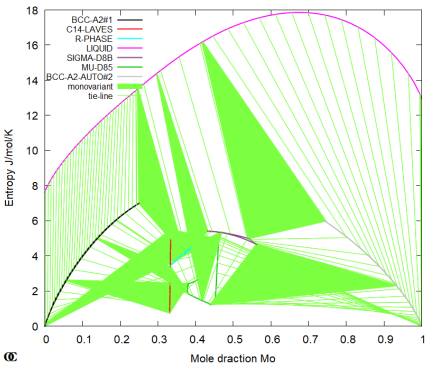

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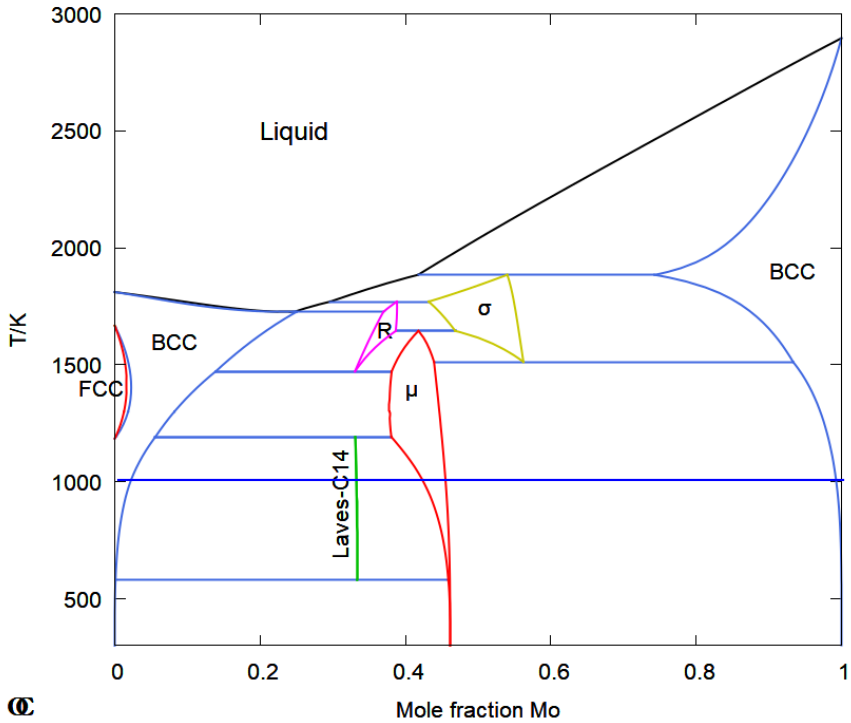
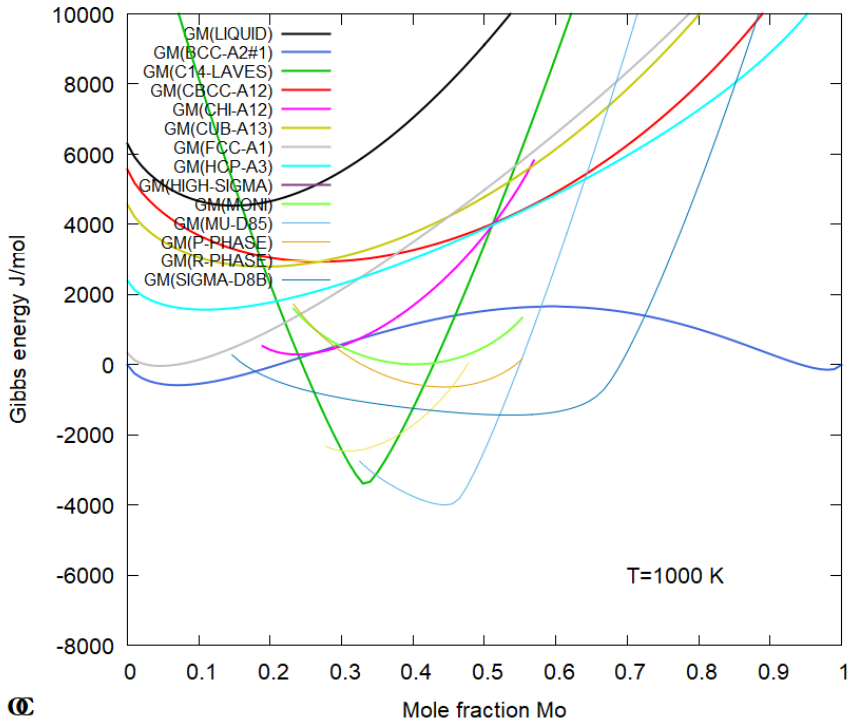
But Calphad is not sufficient to describe the microstructure because that is part of the history of the heat treatments of the alloy. For that kinetic data and models are needed.

The data behind the phase diagram?

To calculate a phase diagram with the Calphad method one must have Gibbs energy expressions for all phases, normally across the whole composition range. The end points of such curves are the lattice stabilities and the curves in Fe-Mo has been calculated from a thermodynamic database. The first set of curves are for $T = 1000$ K. A very small part of these Gibbs energy curves represent stable states.





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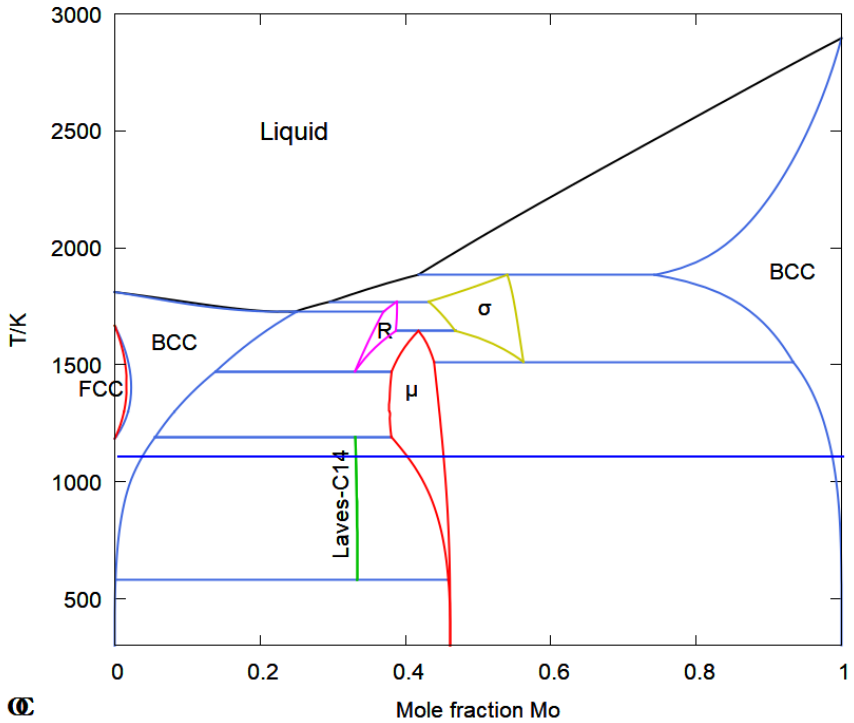

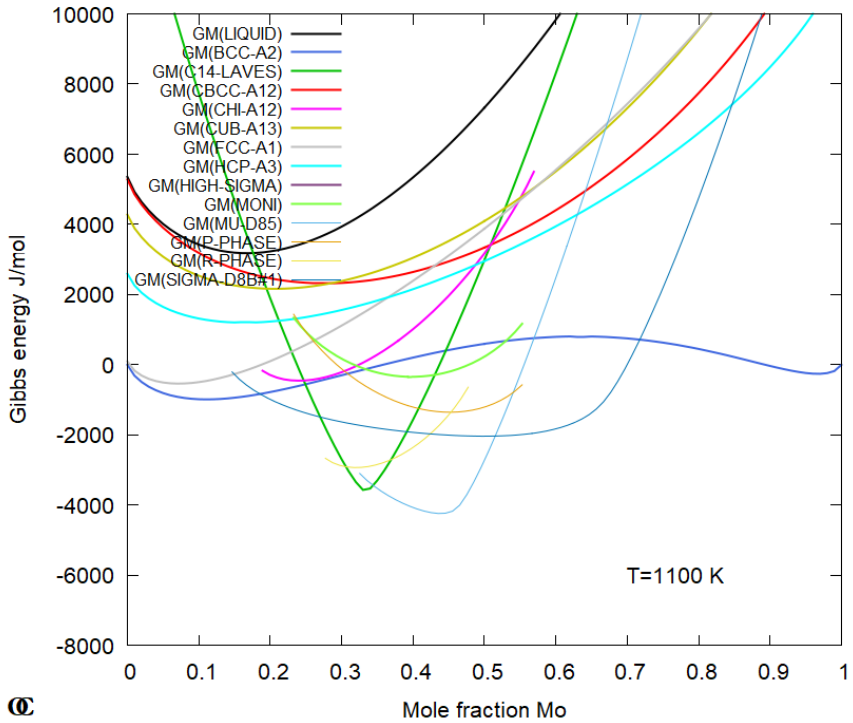

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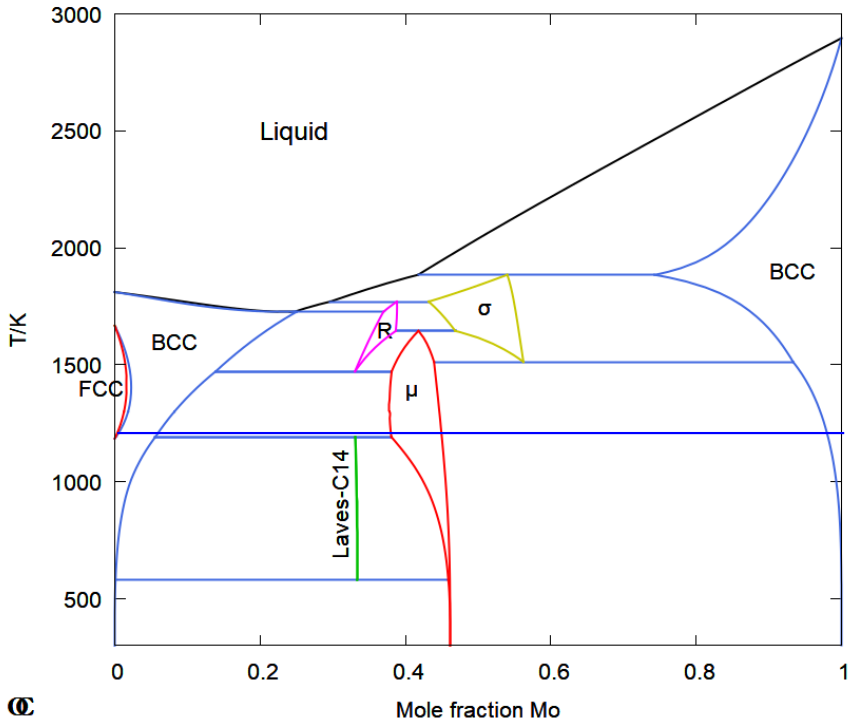

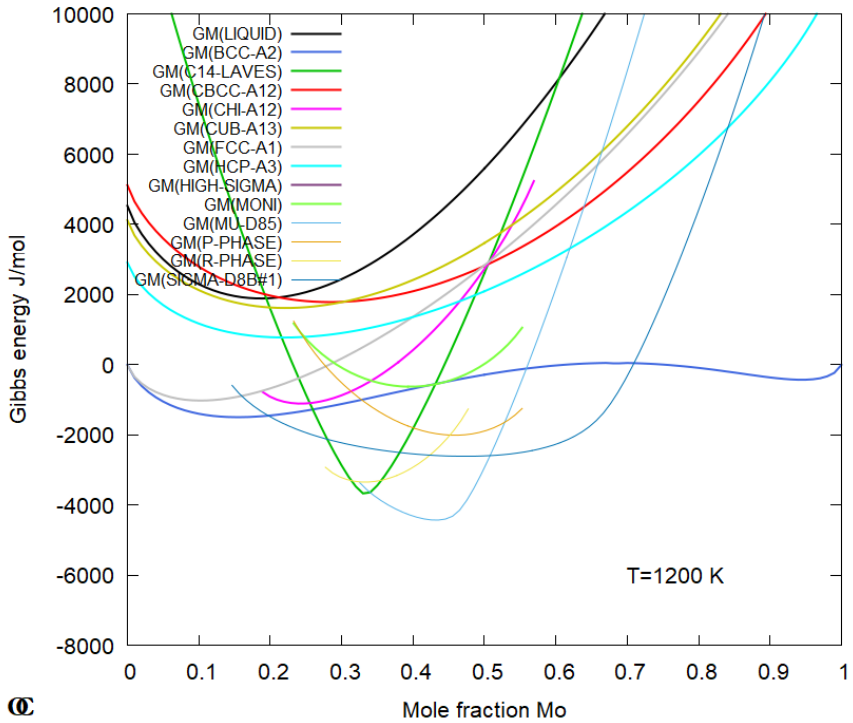

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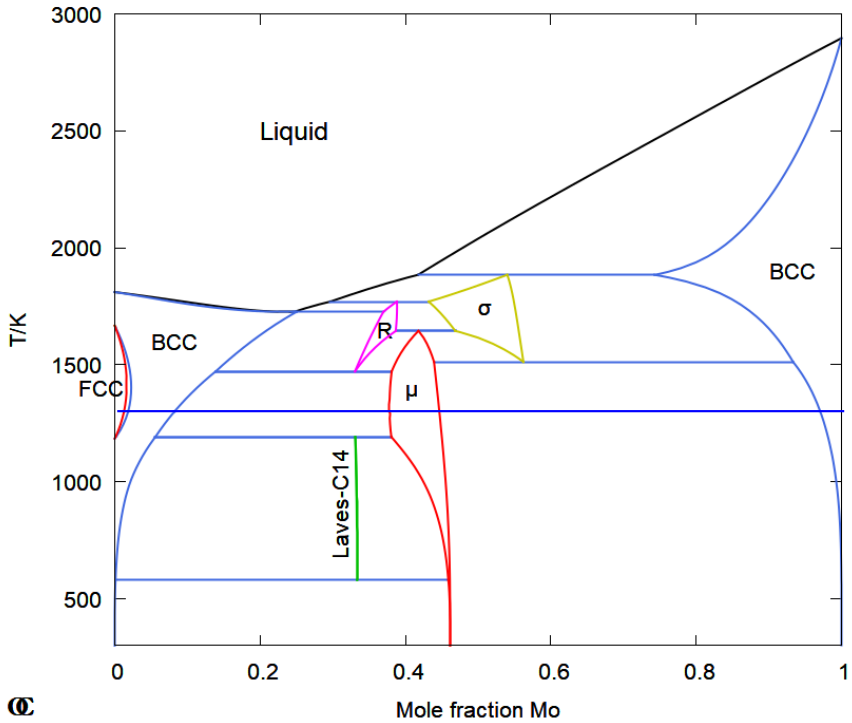

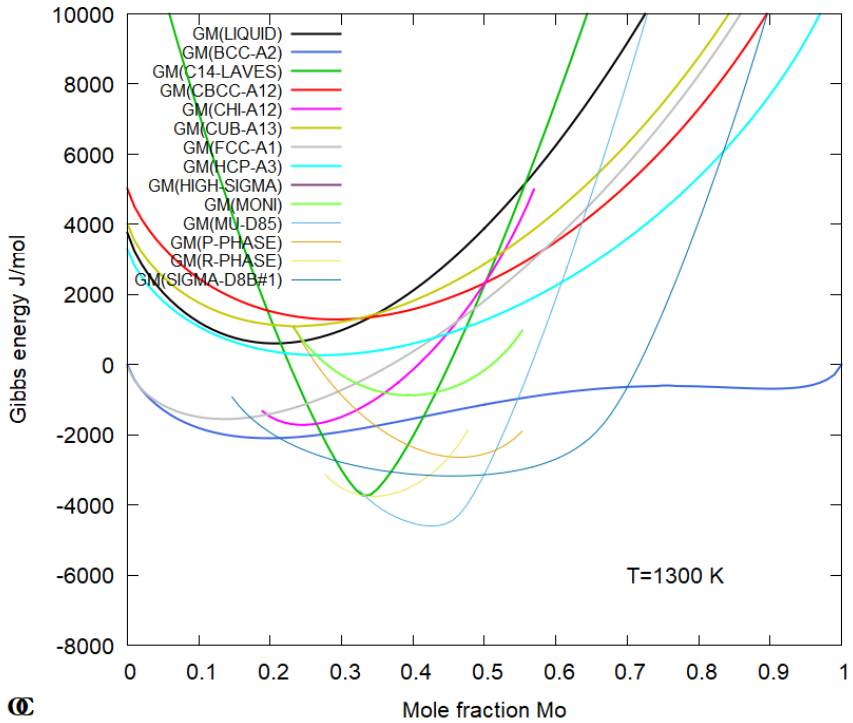

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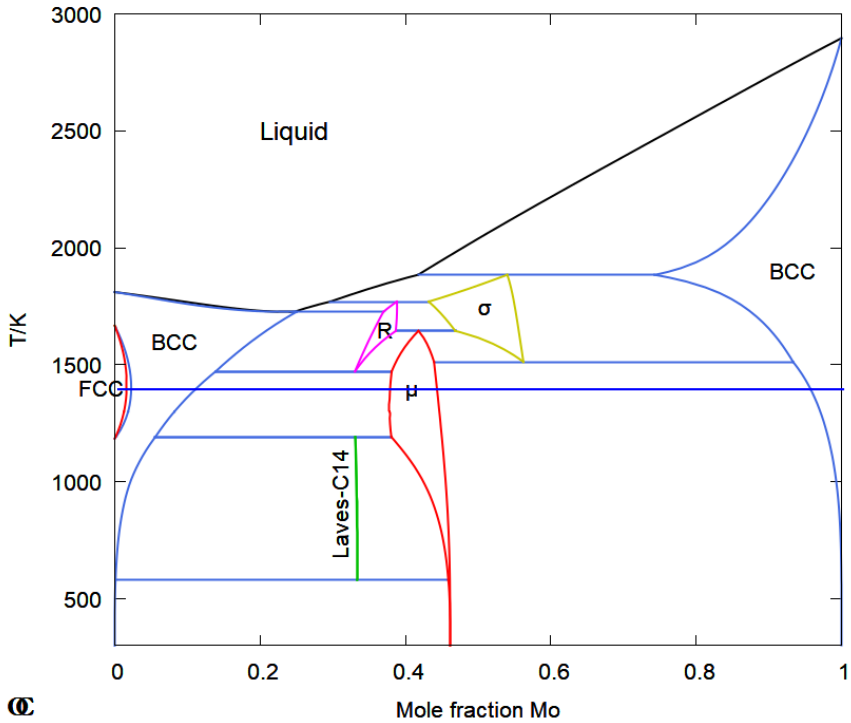

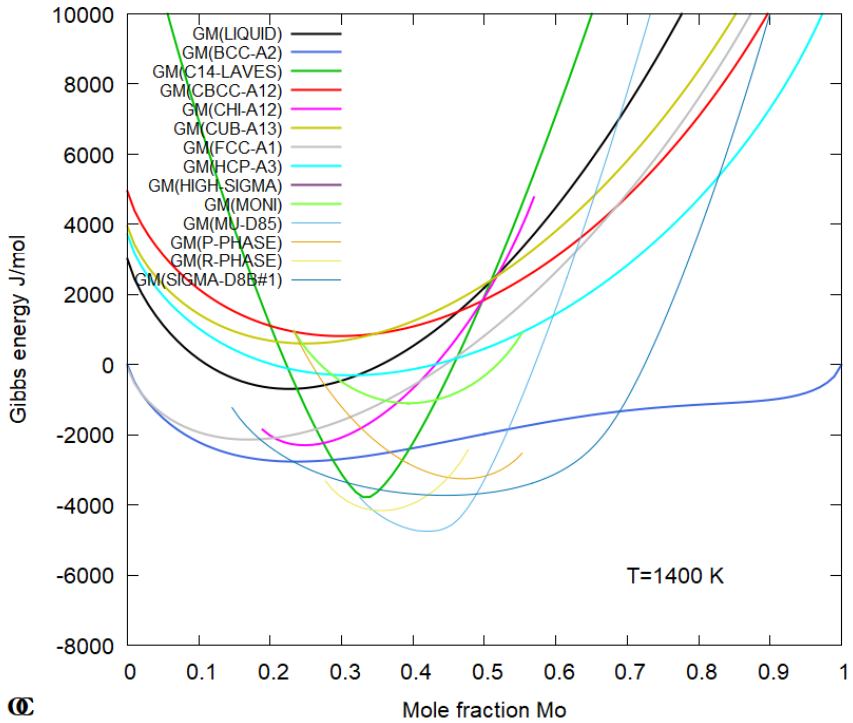

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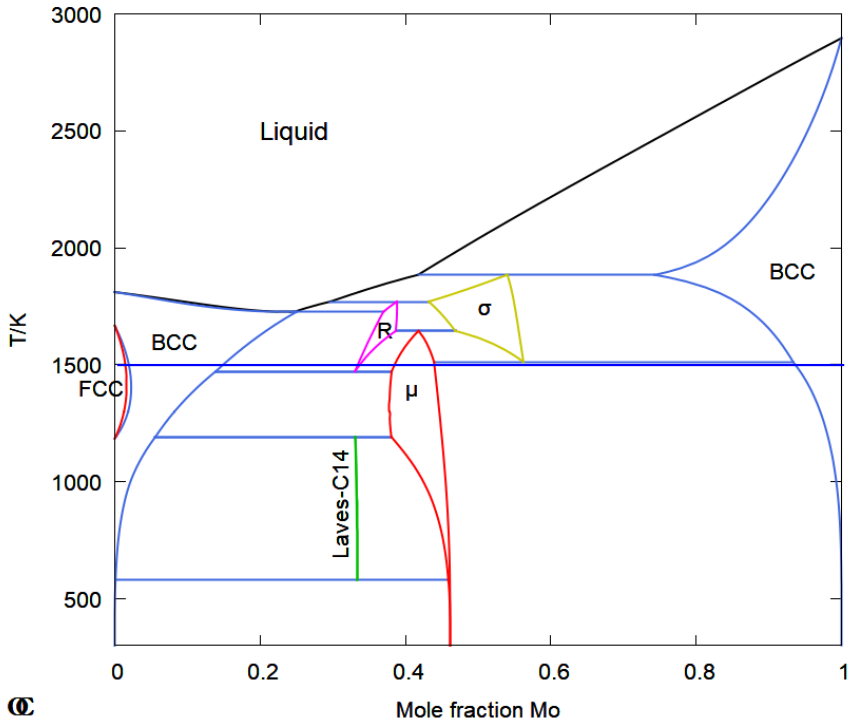

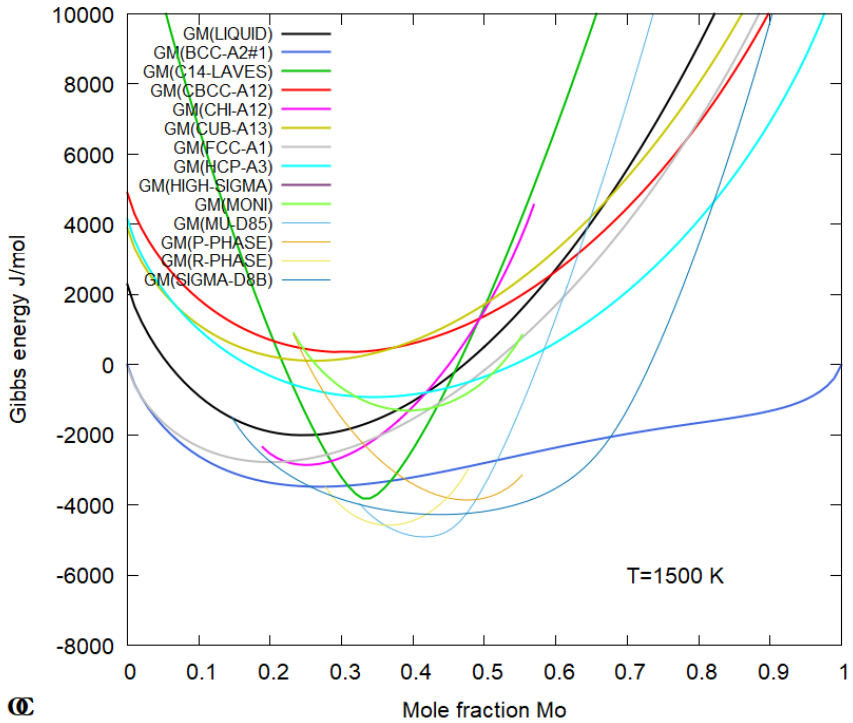

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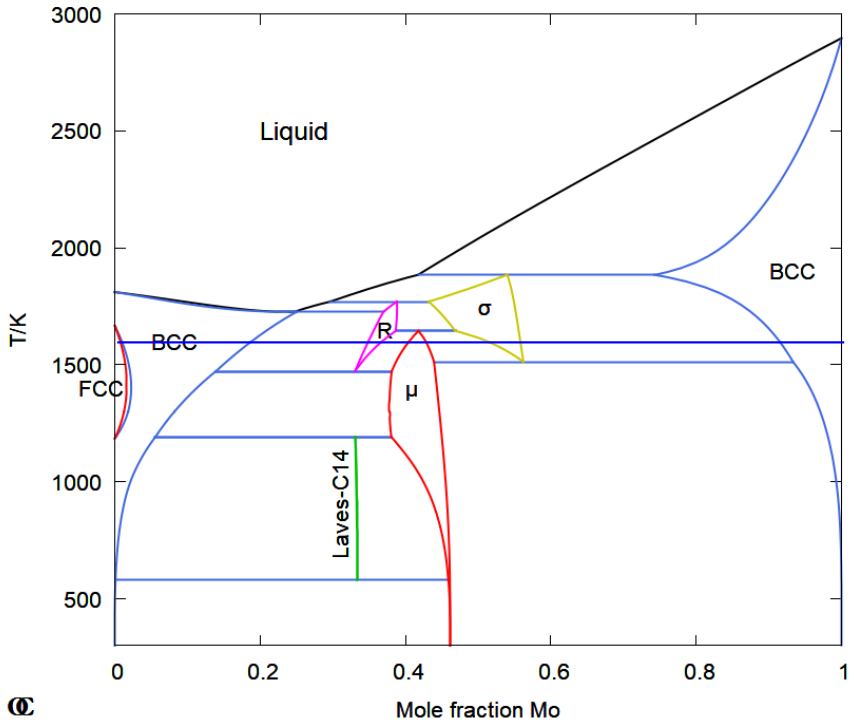

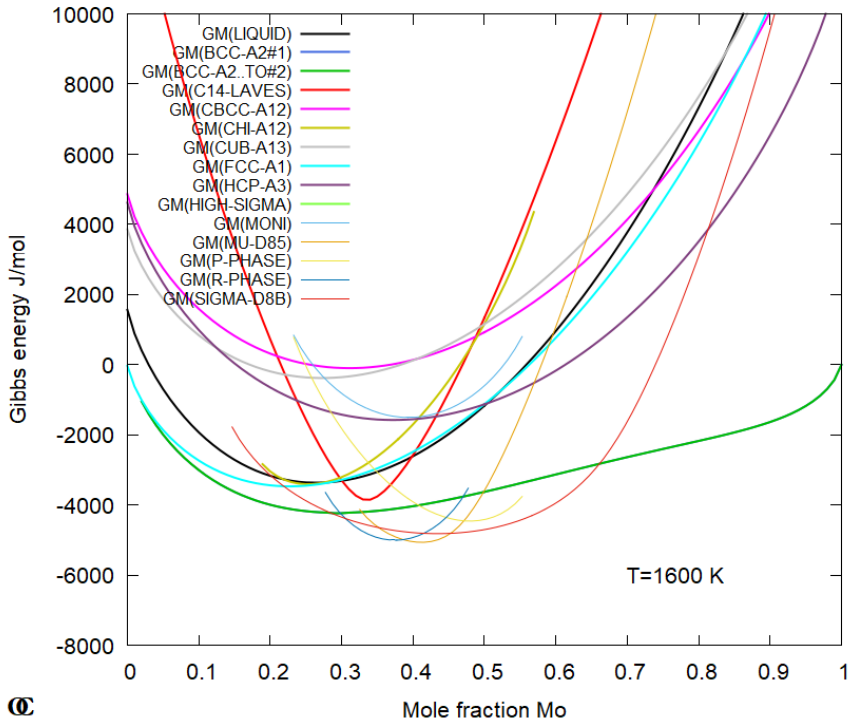

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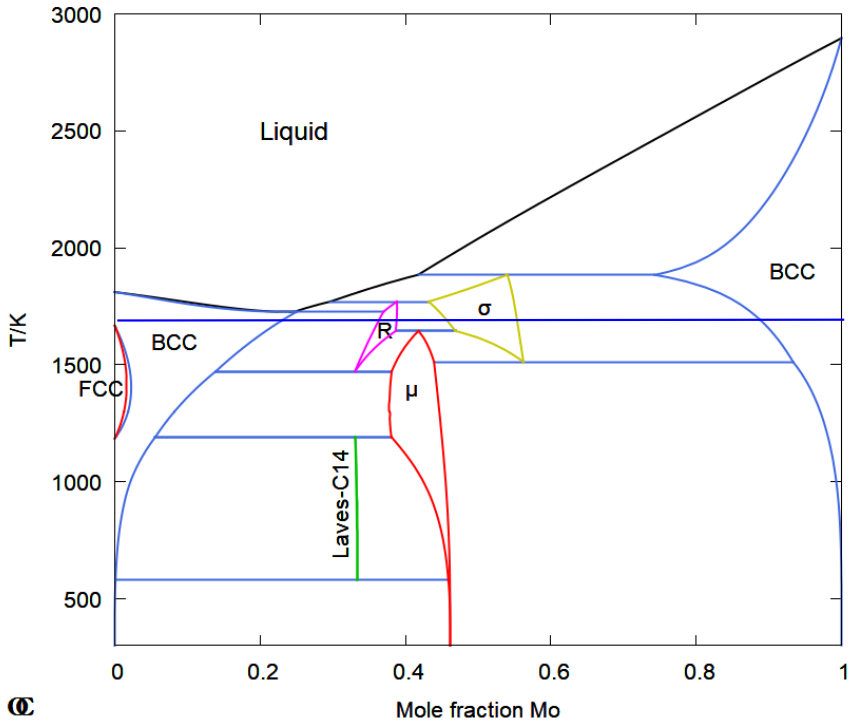

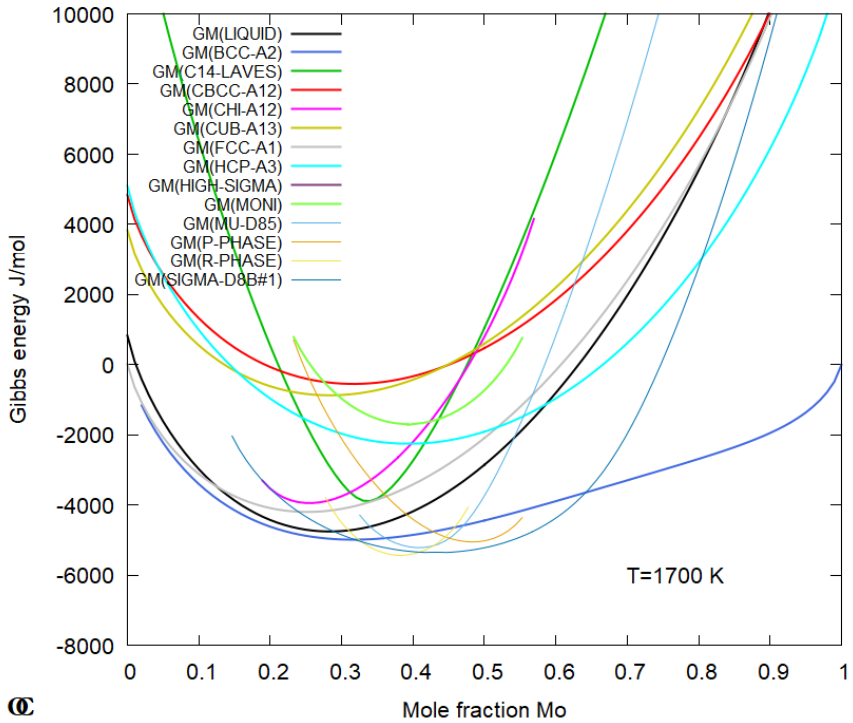

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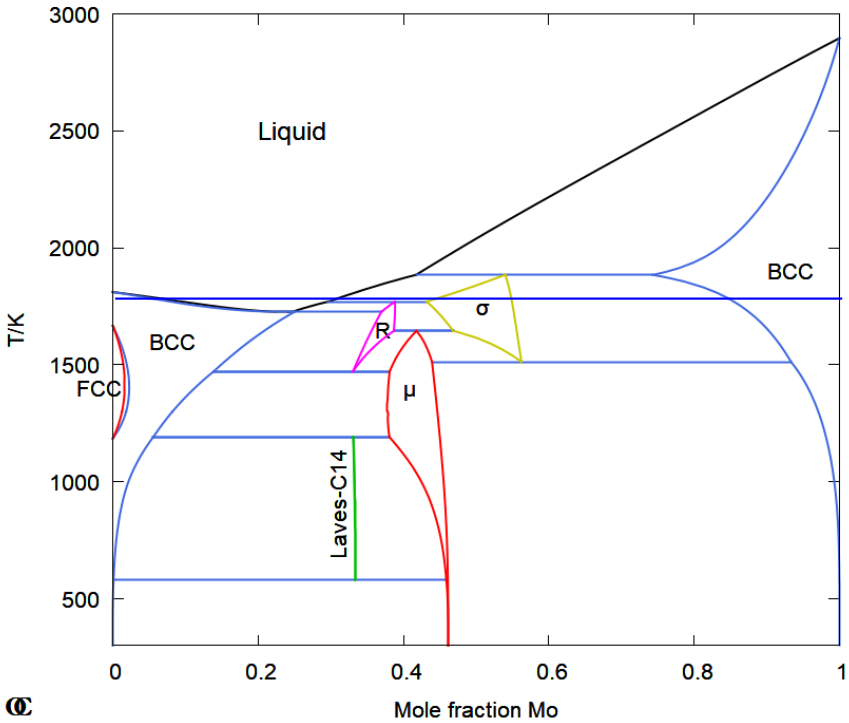

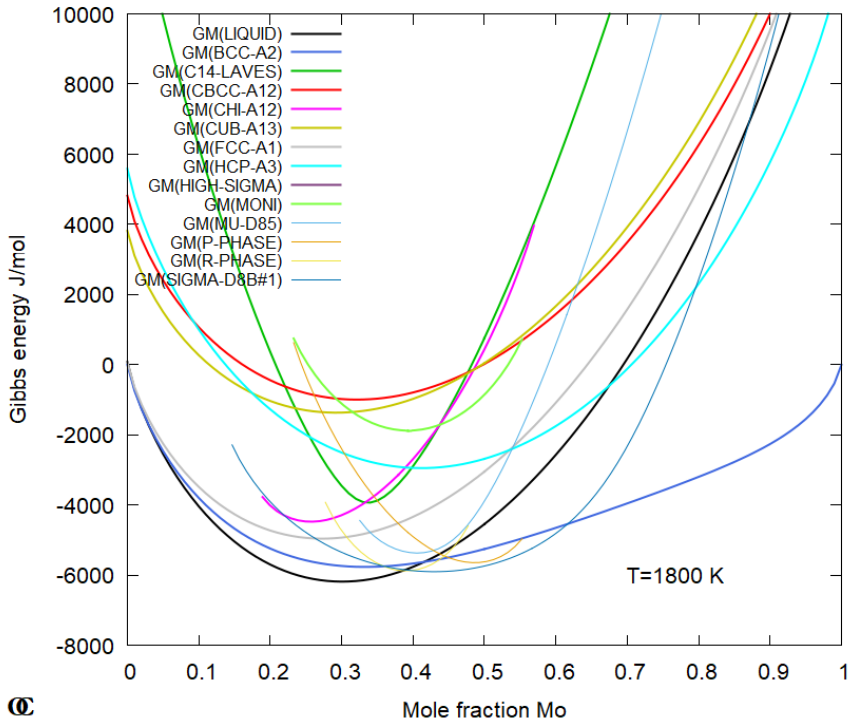

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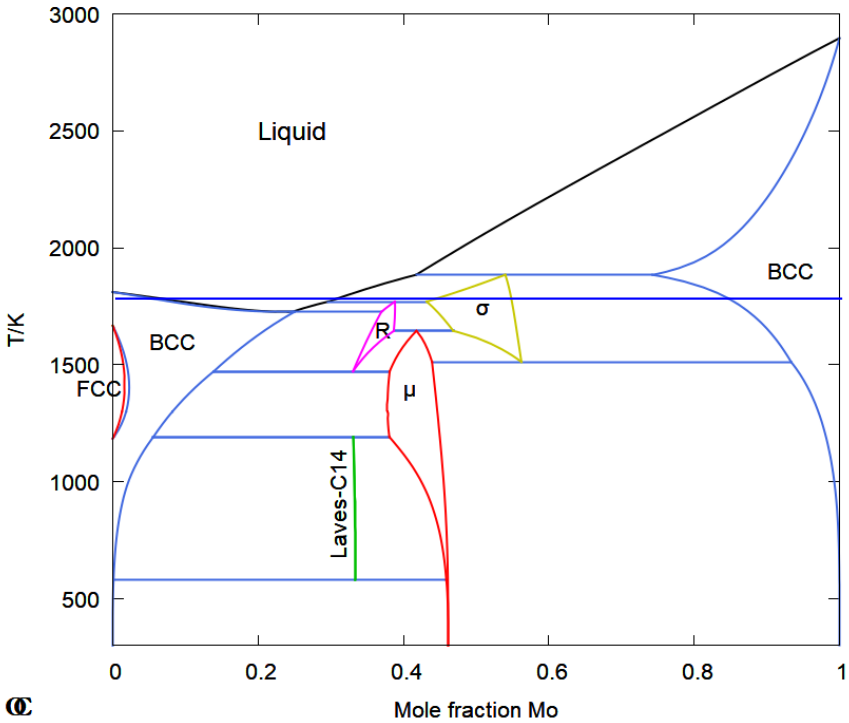
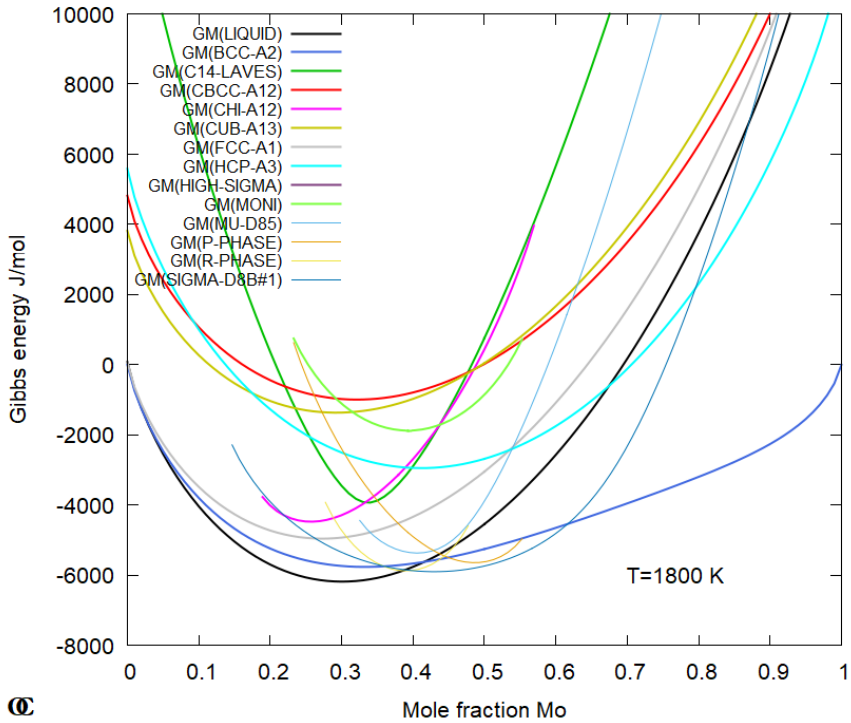


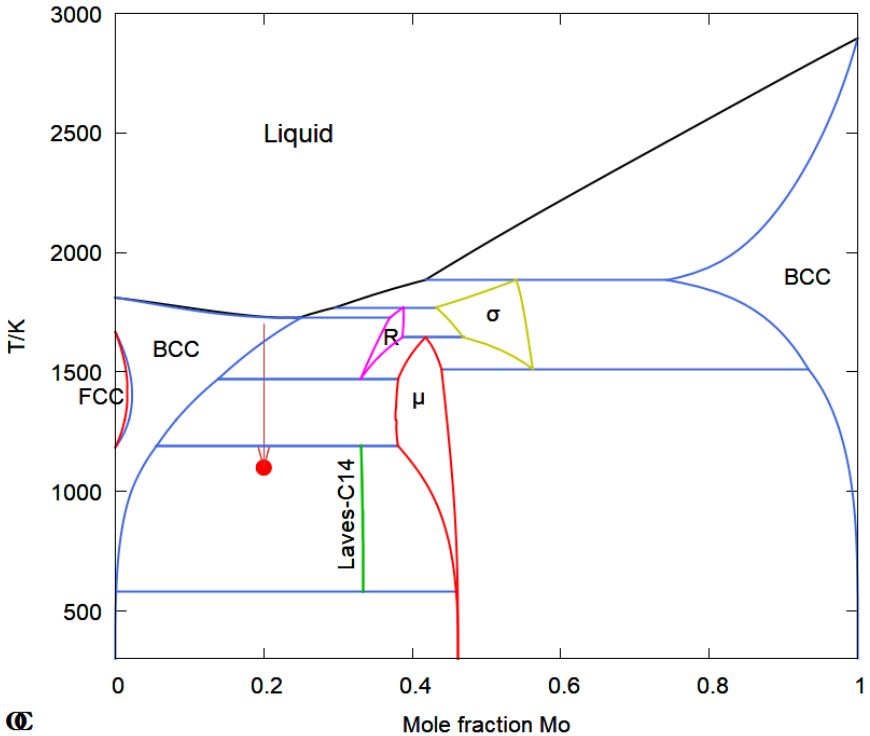


What is the use of the curves outside the stable ranges?

SIMULATE PHASE TRANSFORMATIONS

Phase transformation step 1: nucleation of a new phase

Quenching an Fe-Mo alloy with $x_{\mathrm{Mo}} = 0.20$ from 1700 to 1100 K.



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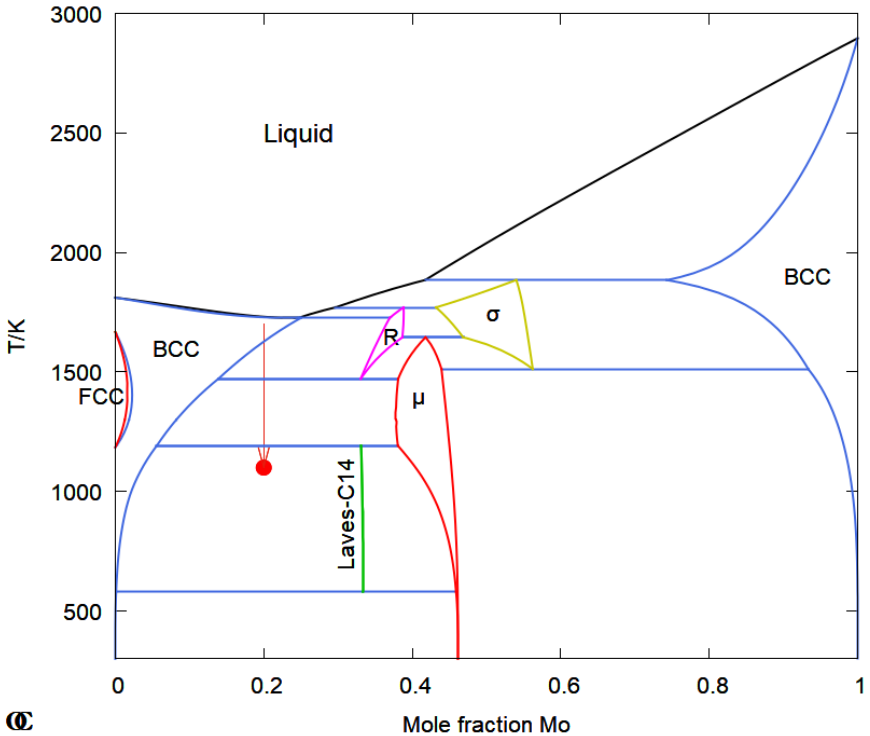

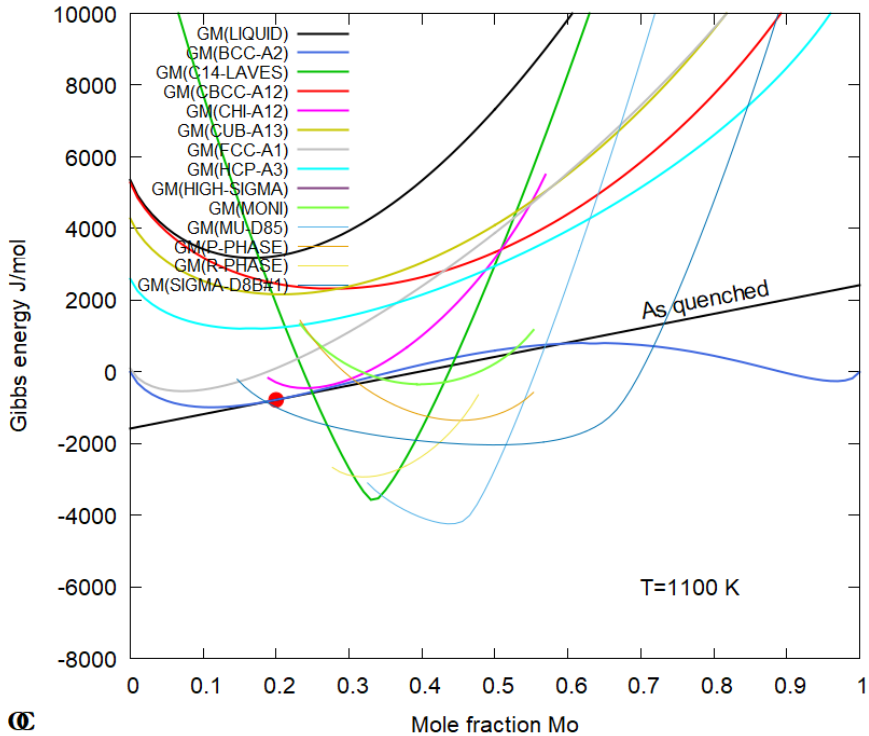

As quenched, and before any nucleation, this tangent with the red dot on the Gibbs energy curve for BCC describes the metastable state of the system at 1100 K.
There are several phases with Gibbs energy curves below this tangent and they can all nucleate.

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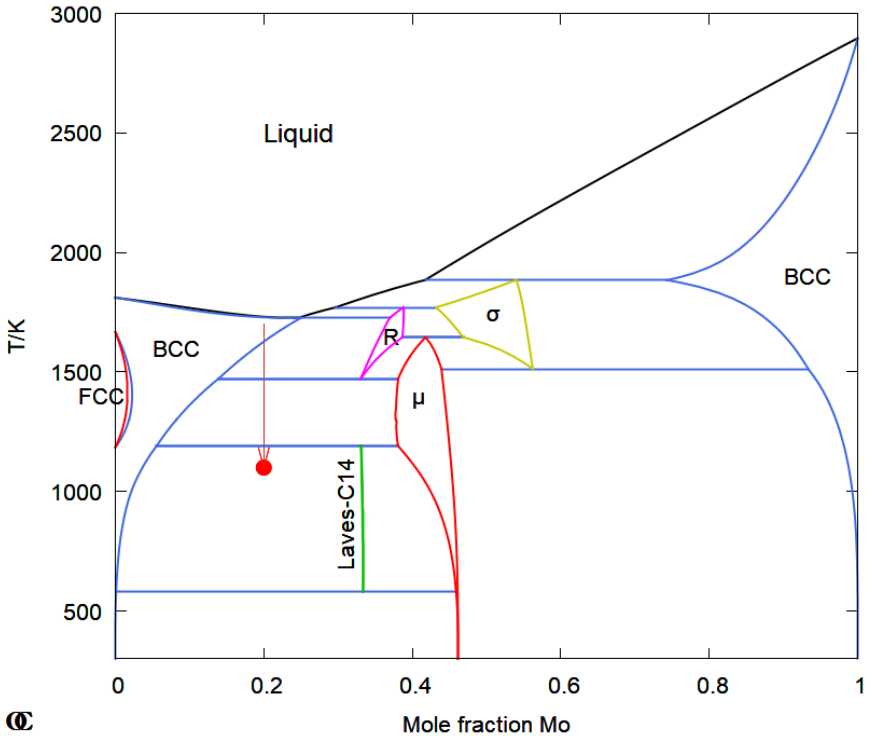

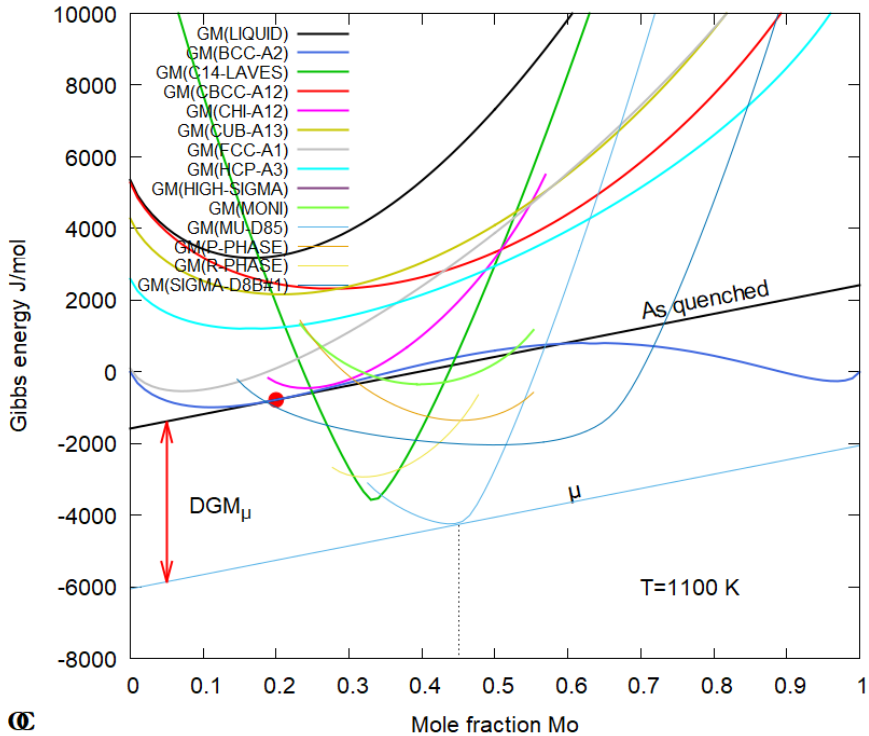

The driving force for nucleation of a new phase is found as a tangent on the Gibbs energy curve for the phase **parallel to the metastable BCC tangent**, here shown for the μ phase. This is the largest driving force, DGM$_\mu$.
The parallel tangent construction indicate also the most favoured composition of the nucleus of μ.

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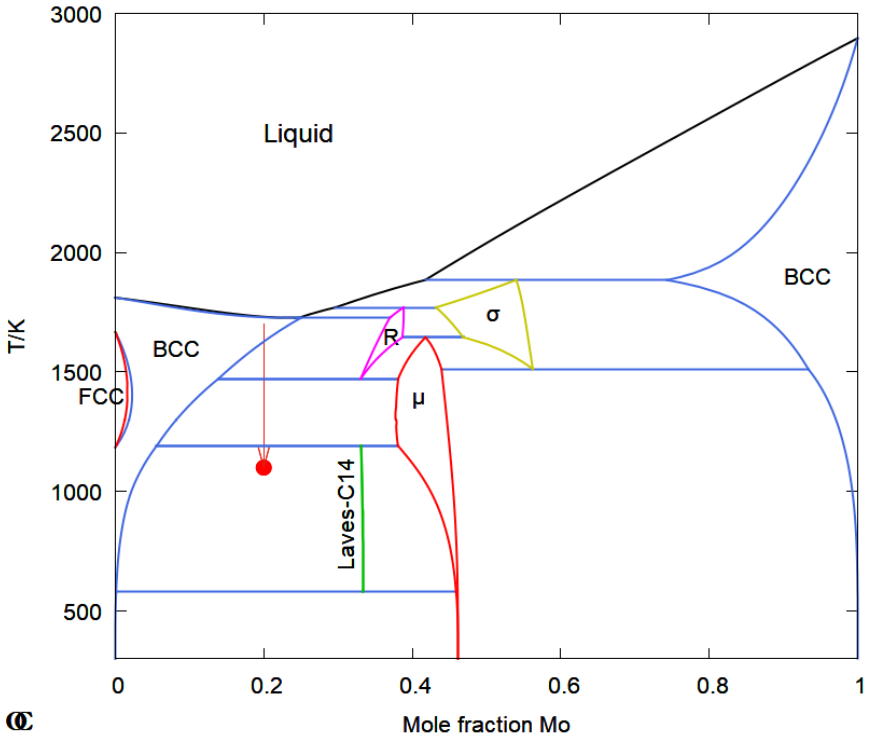

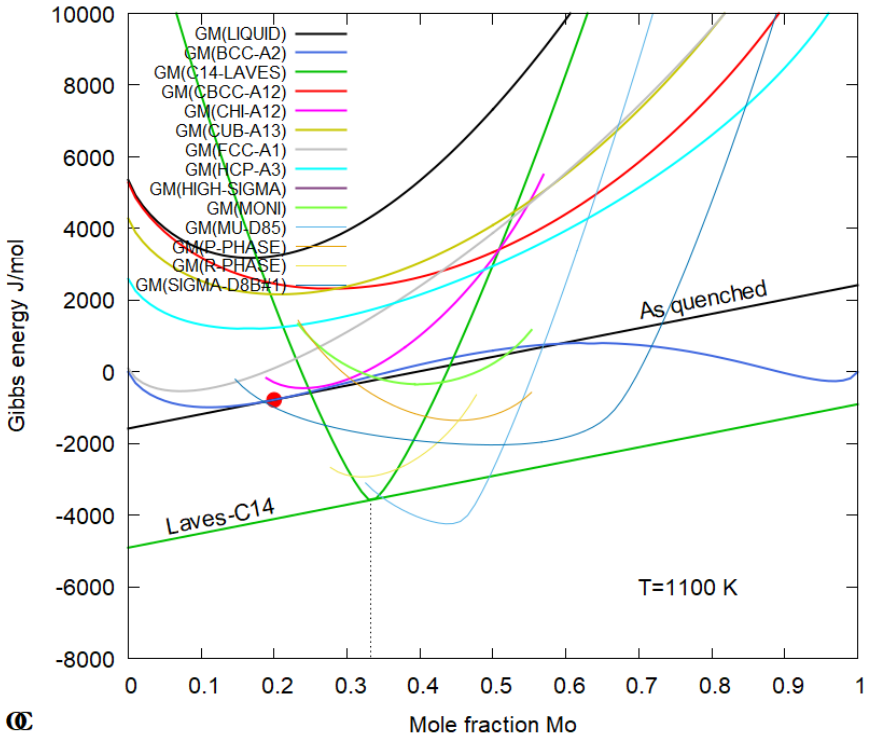

The Laves phases has a smaller driving force, although according to the phase diagram it should become stable.

Phase transformation step 1: nucleation of a new phase

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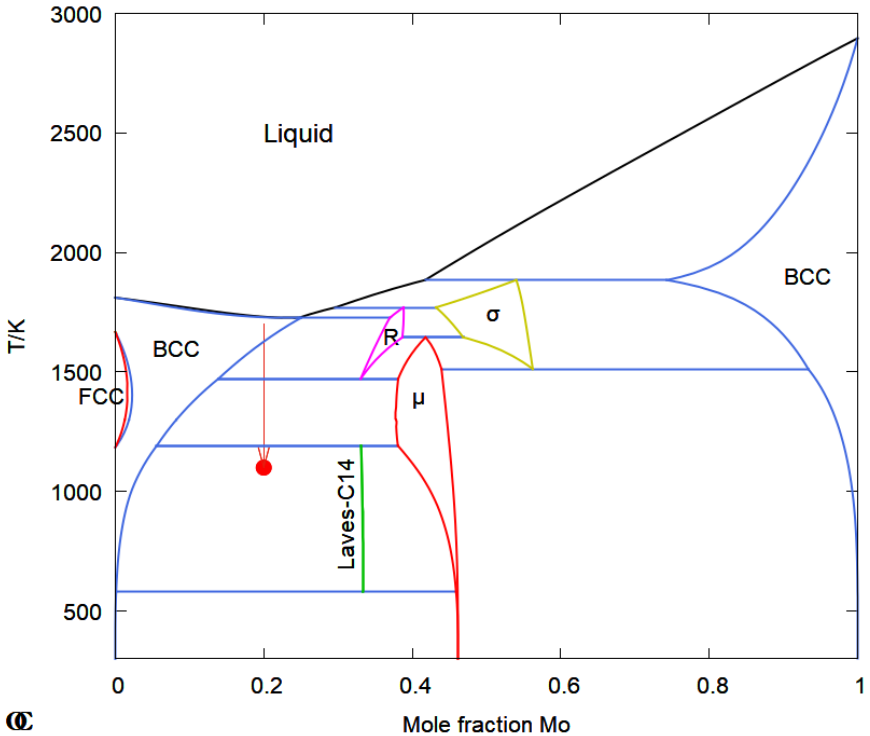

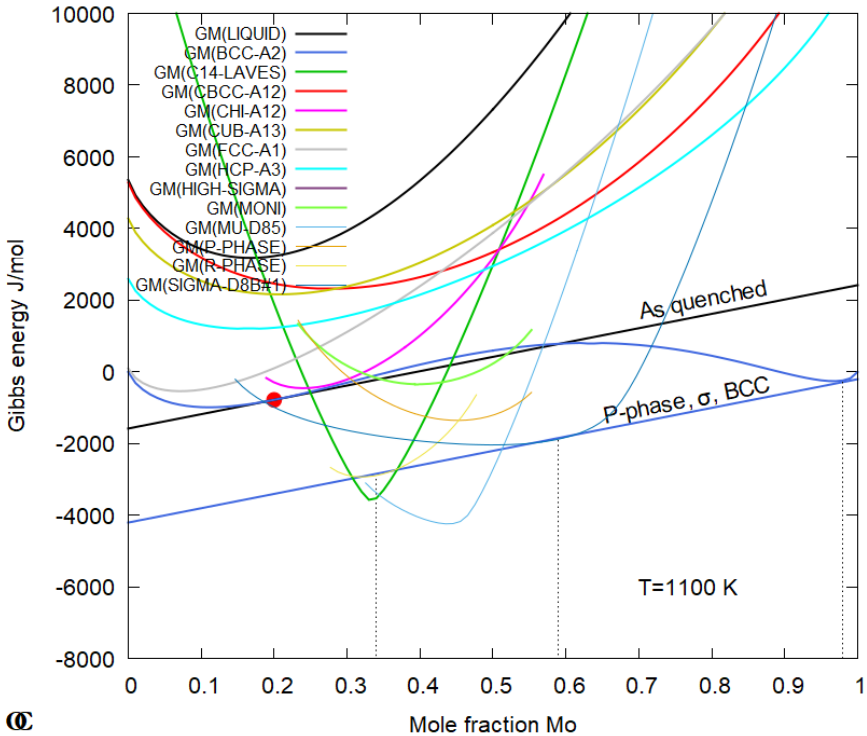

There are several phases with almost the same driving forces, including an Mo-rich BCC phase.

Phase transformation step 1: nucleation of a new phase

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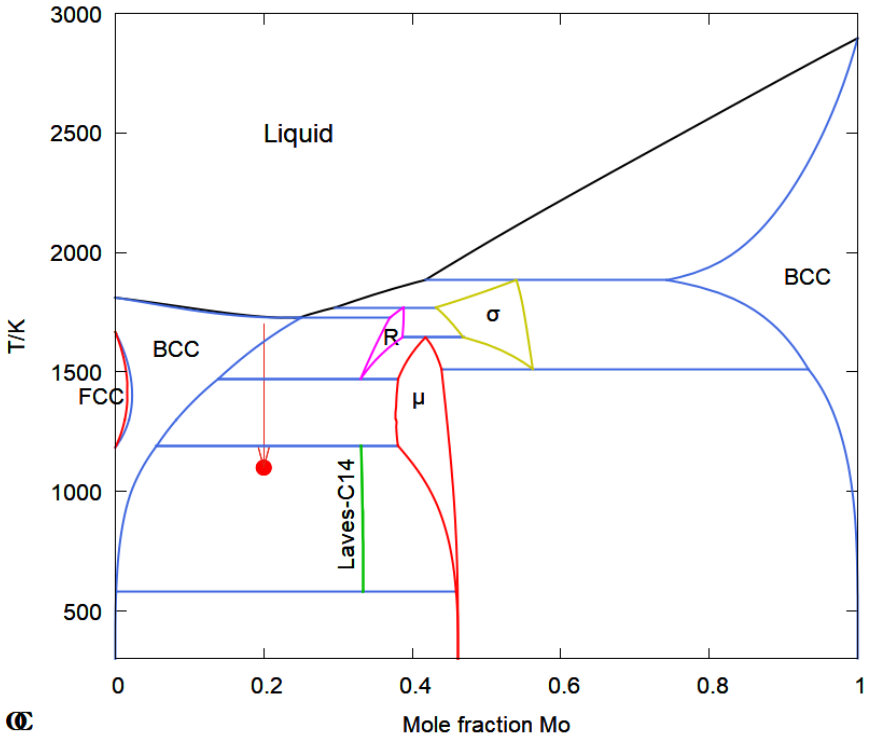

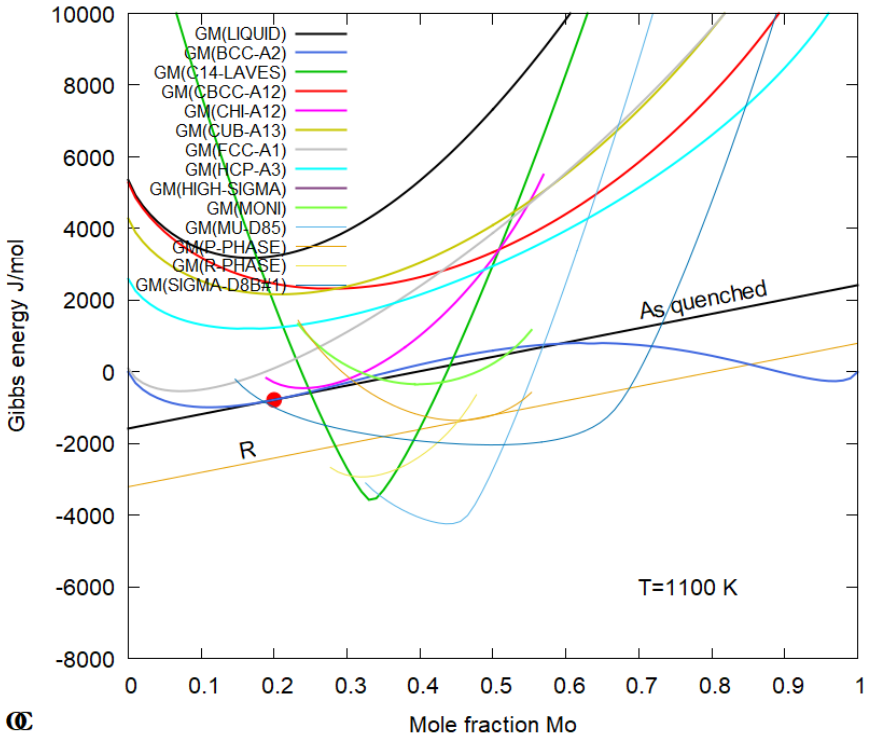

The driving force for the R phase.

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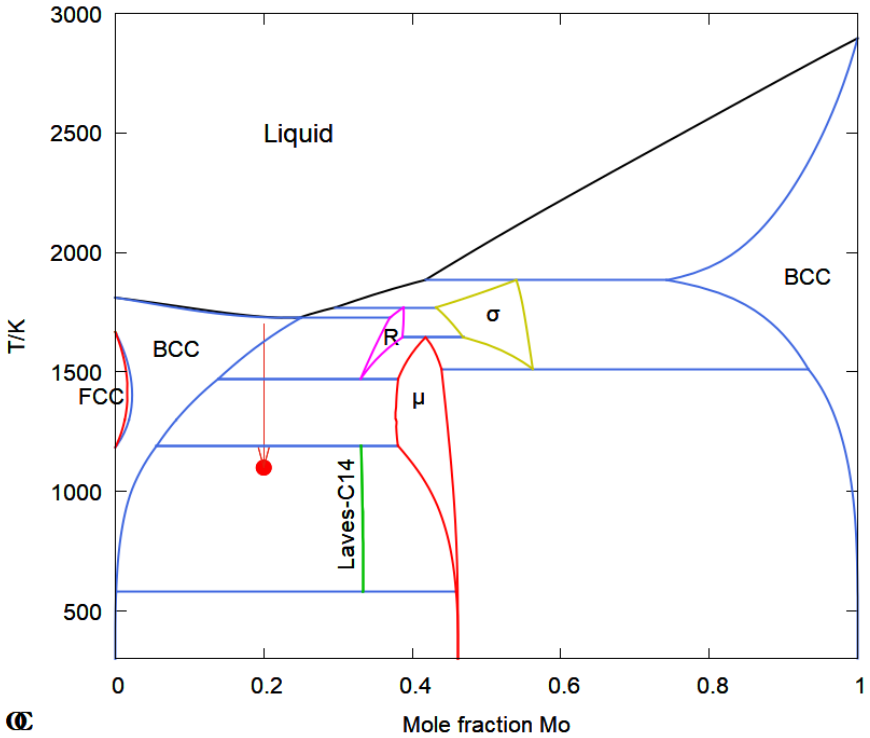

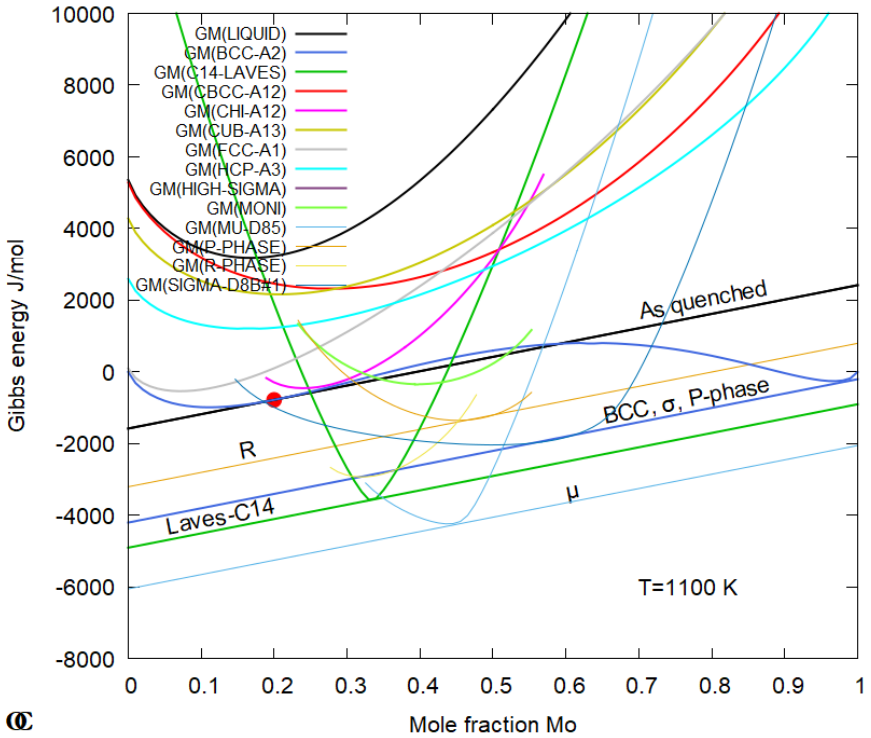

All driving forces plotted together.

Phase transformation step 1: nucleation of a new phase

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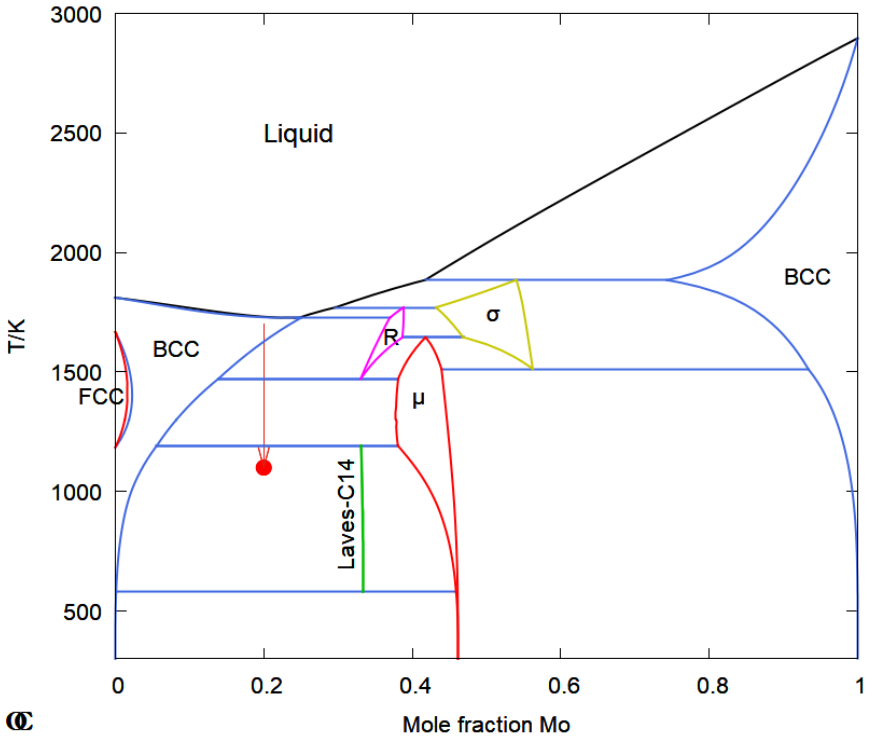

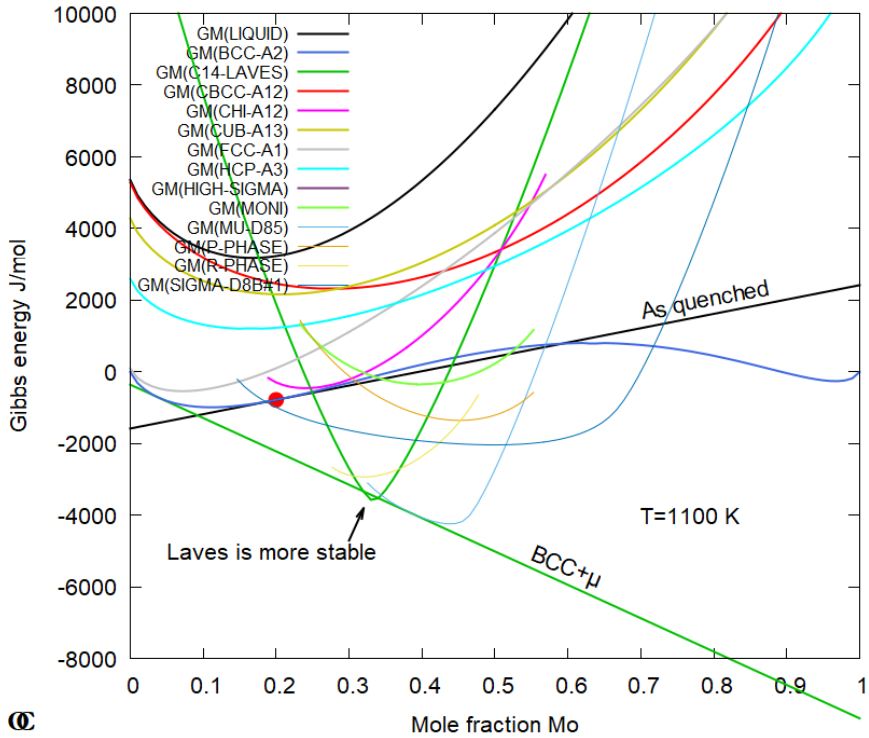

This common tangent construction between BCC and μ phase indicates it is a metastable equilibrium.

If μ or Laves or both are nucleated is decided by the surface energies and the kinetic model. The kinetic model may nucleate the Laves phase at the interface between the BCC and the growing μ phase.

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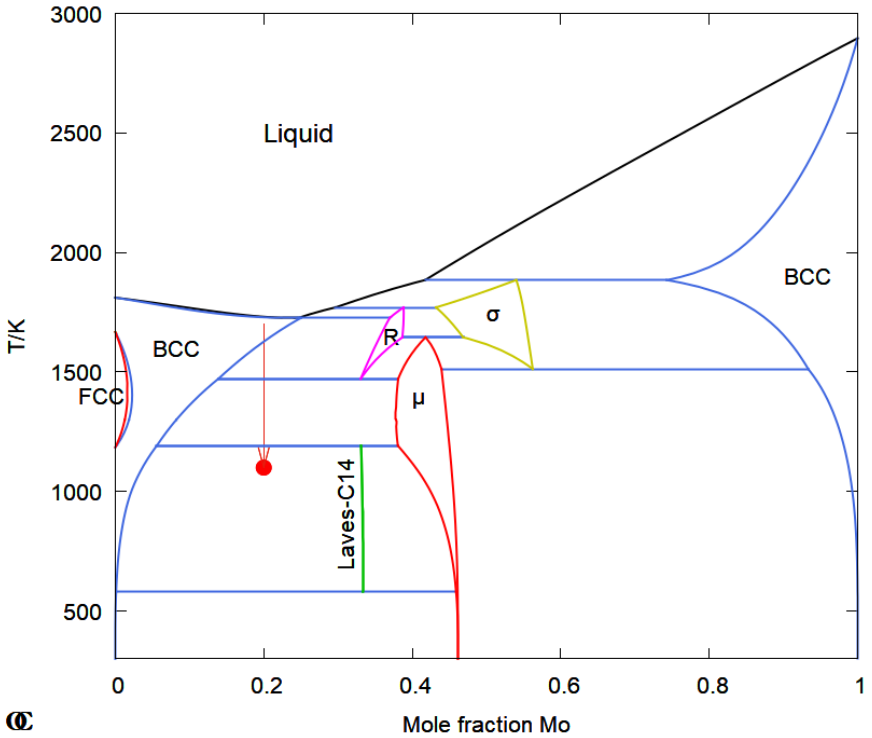

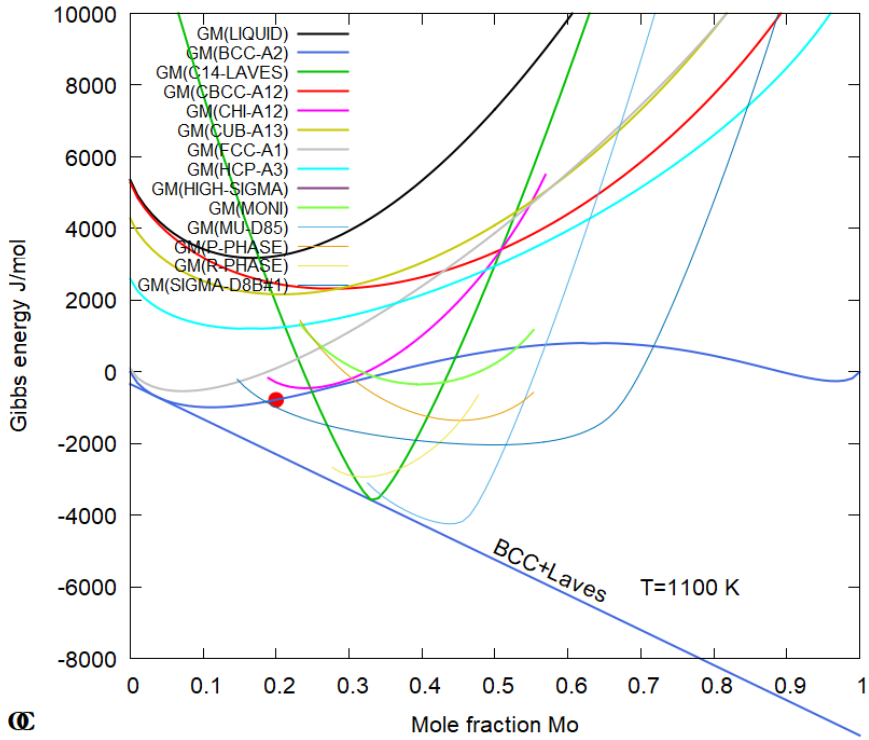

This common tangent construction between BCC and Laves phase is the stable state as in the phase diagram.

It is important to use thermodynamic data in a simulation which reproduces the phase diagram.

Phase transformation step 1: nucleation of a new phase

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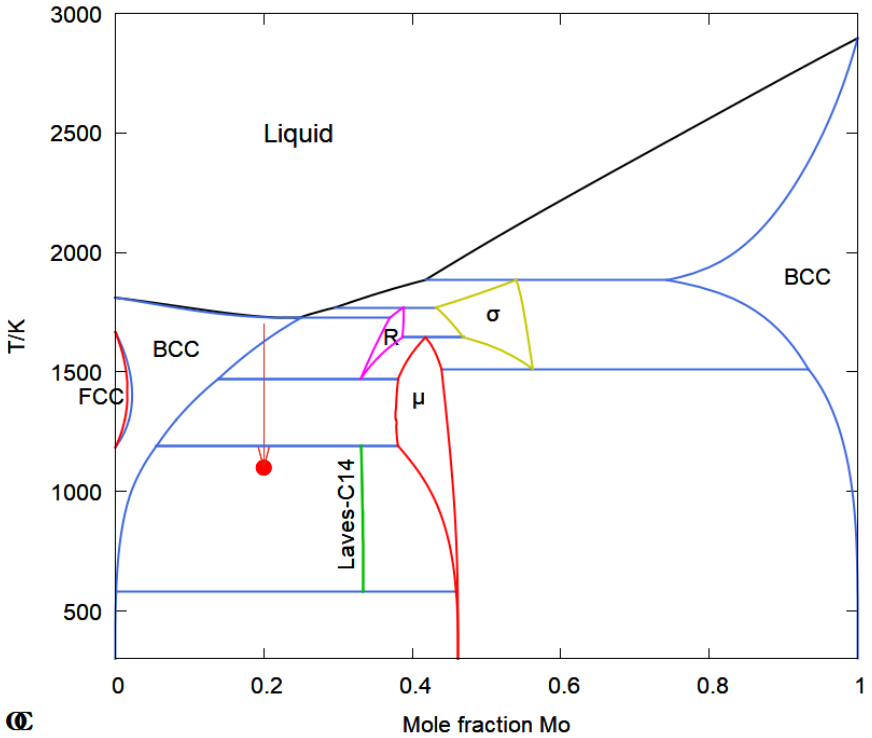
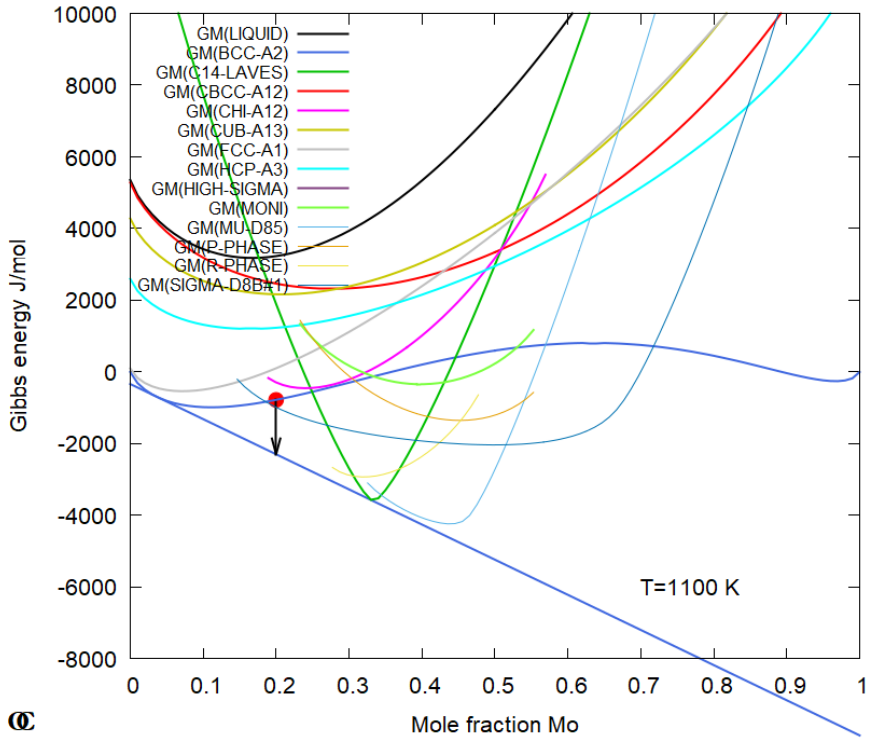
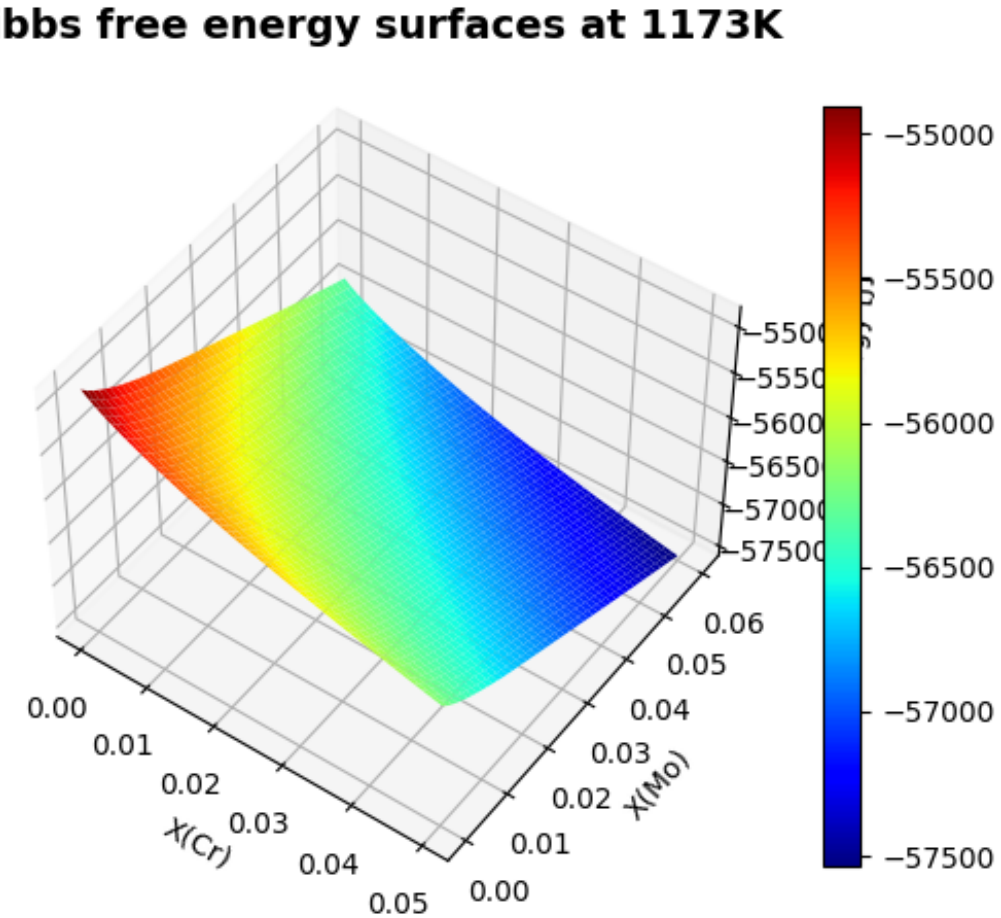




The total change in Gibbs energy for the transformation is indicated.
Thermodynamics gives the initial state, the driving forces for the nucleation of the phases to form and the final total change in energy.
During the transformation it provides the gradients in chemical potentials for the diffusion which, together with mobilities, change the composition of the phases.

Extrapolation of Gibbs energy surfaces in 3D

The Fe-Mo example is for a binary system but the Gibbs energy surfaces for a multi-component system are extrapolated to as many dimensions as one has components.



The driving forces for all metastable phases are calculated together with the stable set of phases. They are needed also when calculating phase diagrams.

Calculating an equilibrium

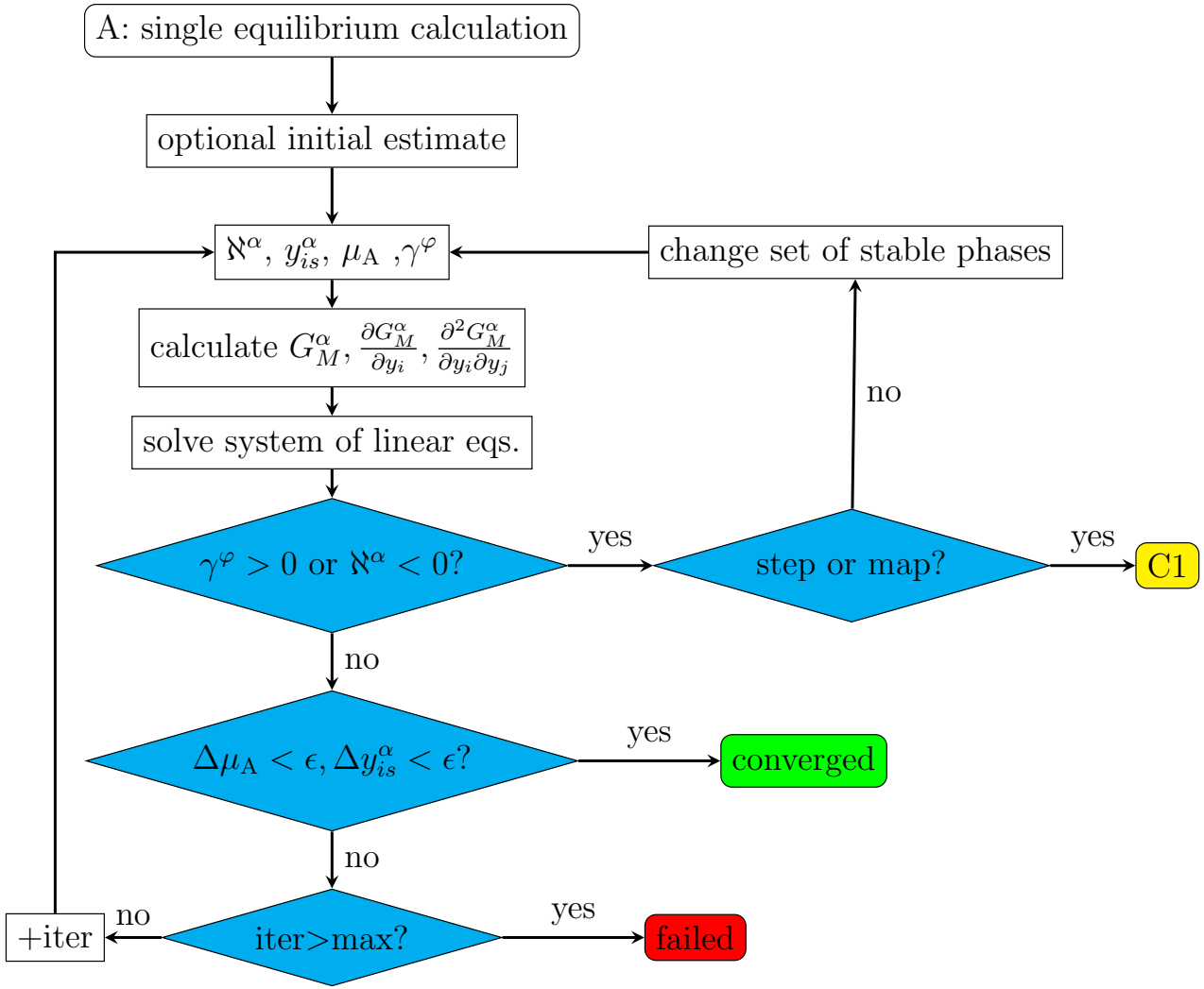


Figure 1: Flowchart of algorithm A to calculate a single equilibrium.

This algorithm, published by Hillert 1981, is used in many thermodynamic softwares.

Conditions allowed for equilibrium calculations

The type of conditions which can be used to calculate the equilibrium is important. In TC and OC one can use:

- T, P and overall composition in moles, N_{A}.
- $T, P, N = 1$ and overall mole or mass fractions of alloy elements
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- The amount of a phase (useful for phase diagram calculations)

Several free and commercial thermodynamic software can use any mix of all these conditions and this is related to the fact they calculate second derivatives of G_M in the minimization algorithm.

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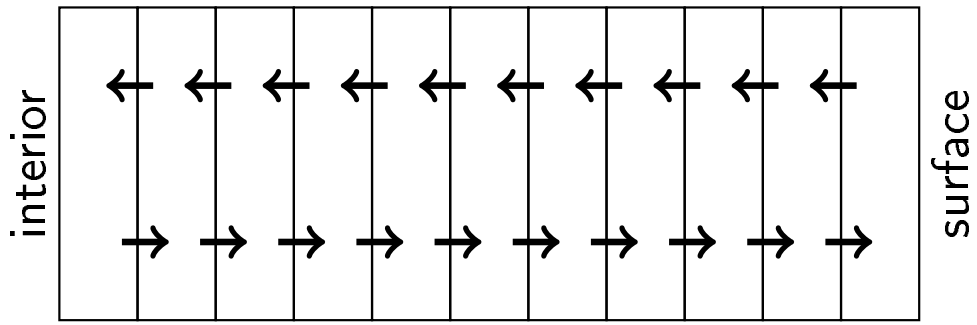
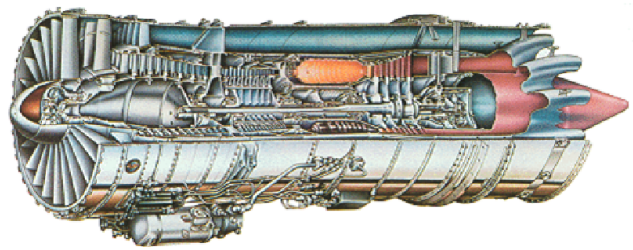
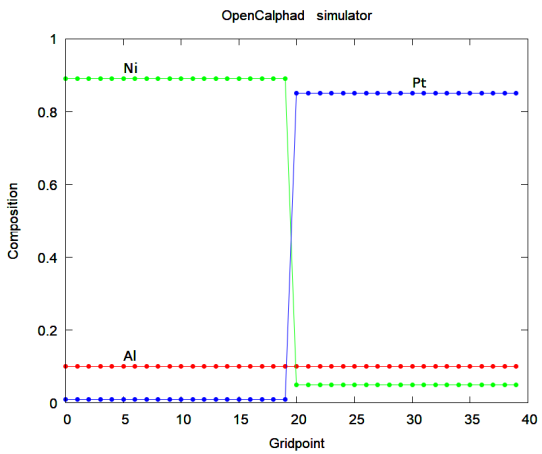
To simulate a phase transformation in a system one can divide it into a grid and the **local equilibrium assumption** to calculate the chemical potentials in each grid point separately. These are used together with mobilities to move the atoms between the grid points.

Phase transformation step 2: ternary diffusion Al-Ni-Pt in FCC in 1D

A very simple 1D diffusion model for a turbine blade made of Al-Ni and coated with a thin layer of Pt. The stable phase is FCC with different kinds of ordering using a 4 sublattice CEF model. 40 gridpoints are used and at the left and right boundaries the system is closed. The simulation $T = 1073$ with the initial profile below.







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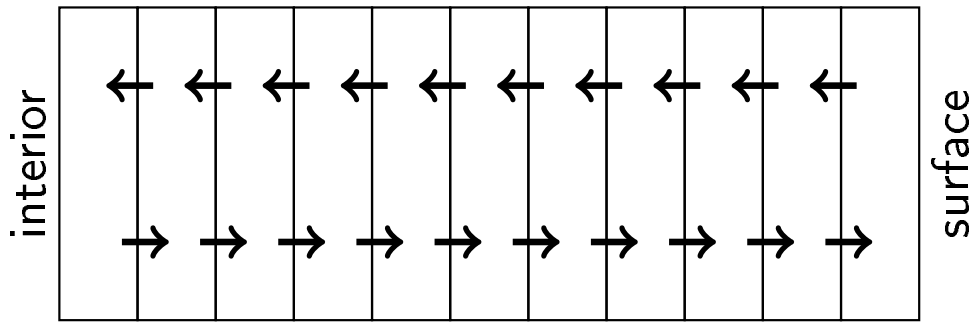
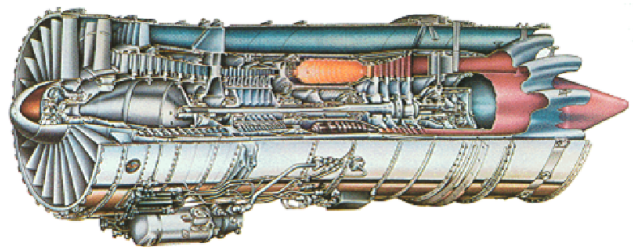
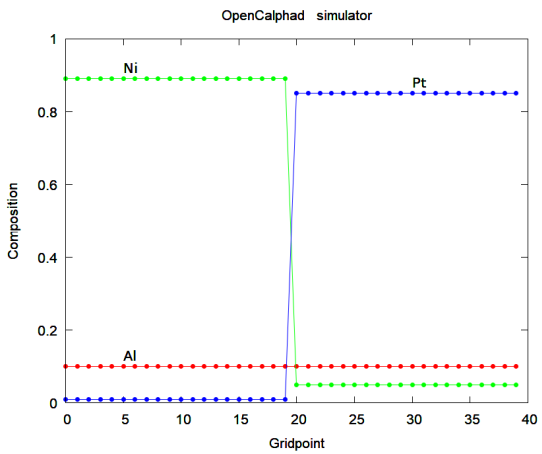
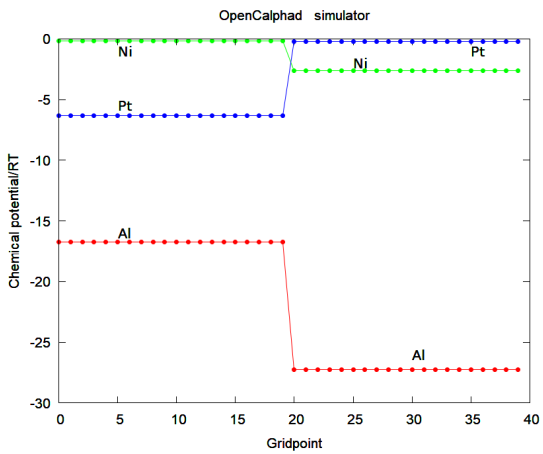




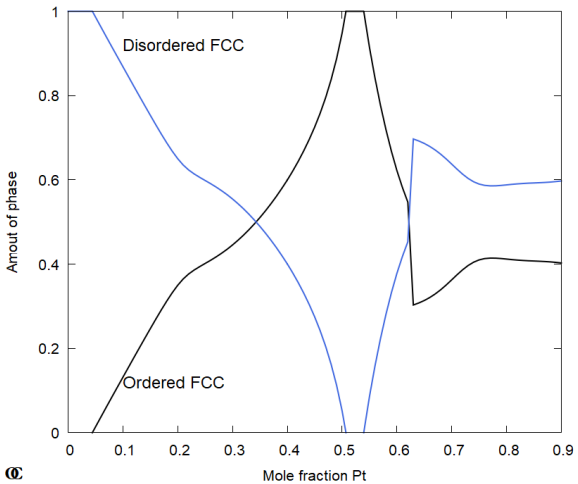




This right figure has the chemical potentials. Pt lowers the chemical potential of Al and that will force Al to diffuse to the surface to form a protective layer of Al_2O_3.

Phase transformation step 2: ternary diffusion Al-Ni-Pt in FCC in 1D

Calculating the stable phases at $T = 1073$ with x(Pt) varying from 0 to 0.9 gives the amount of phases as shown below



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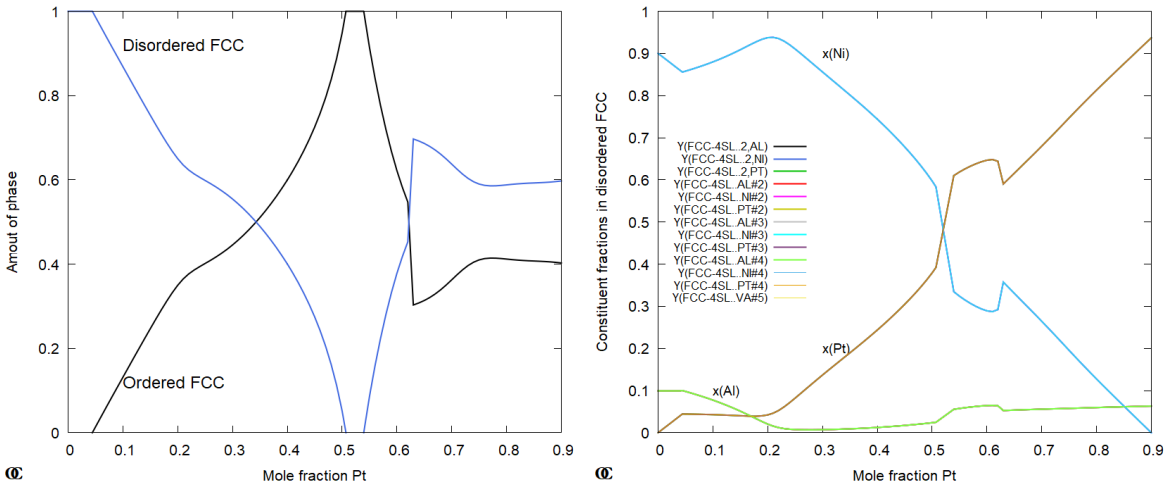

The variation of the constitution of the disordered FCC from the same calculation is shown in this plot. It verifies that the disordered FCC is really disordered.

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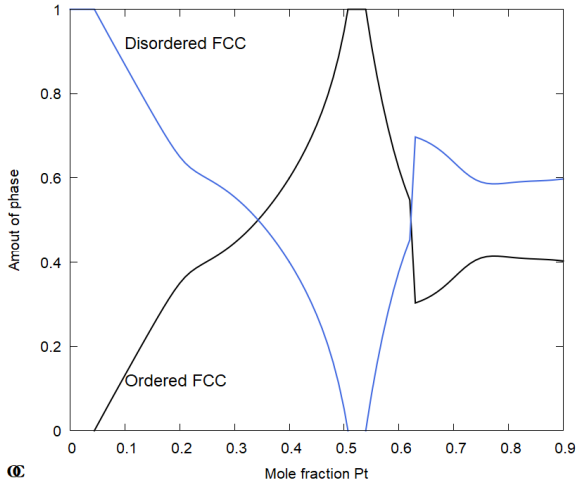

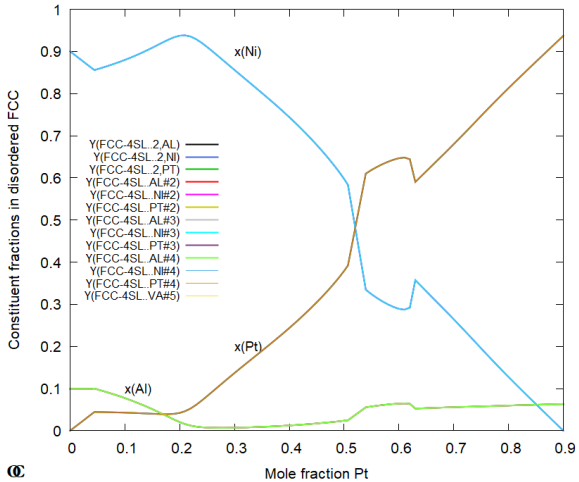

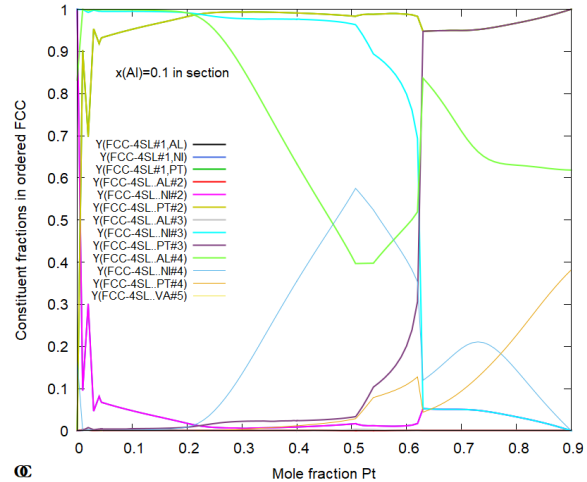

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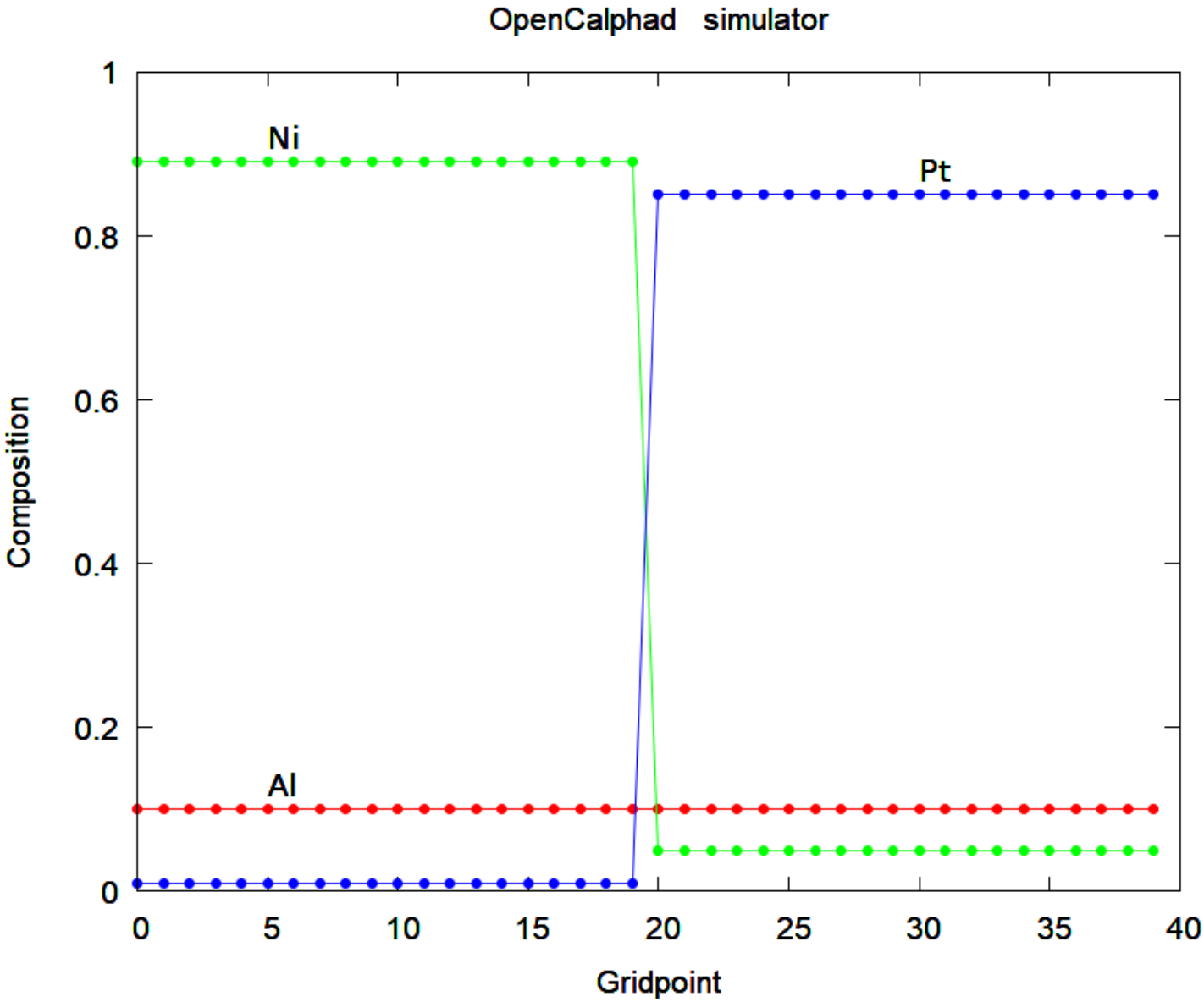
In the ordered phase the ordering change depending on the composition. At each end it is $L1_2$, in the center close to $L1_0$.

The difference between the disordered FCC and the ordered forms is very small and the diffusion is simulated as in a single phase region.

Simulation 2: Concentration profiles at different time steps



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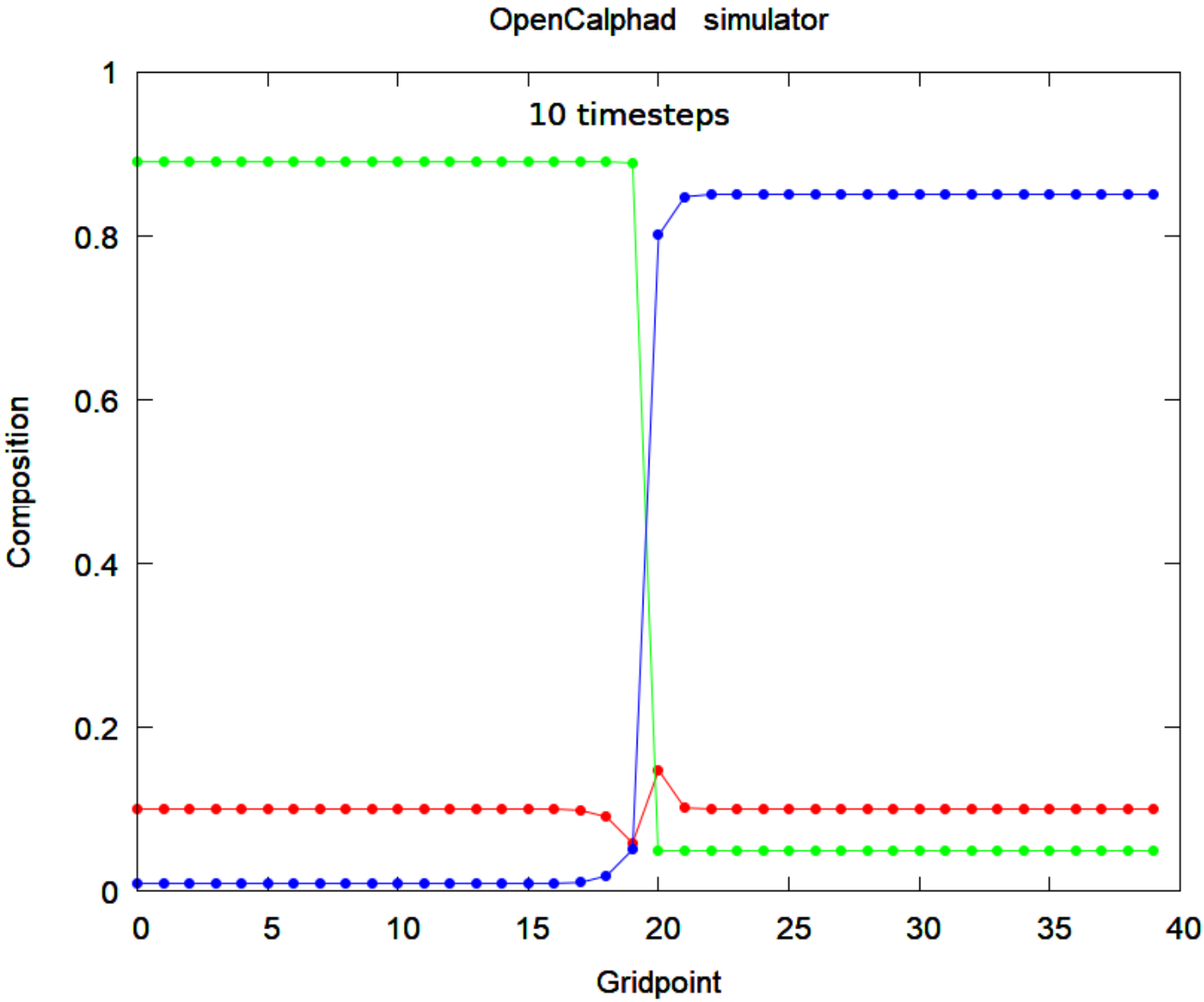

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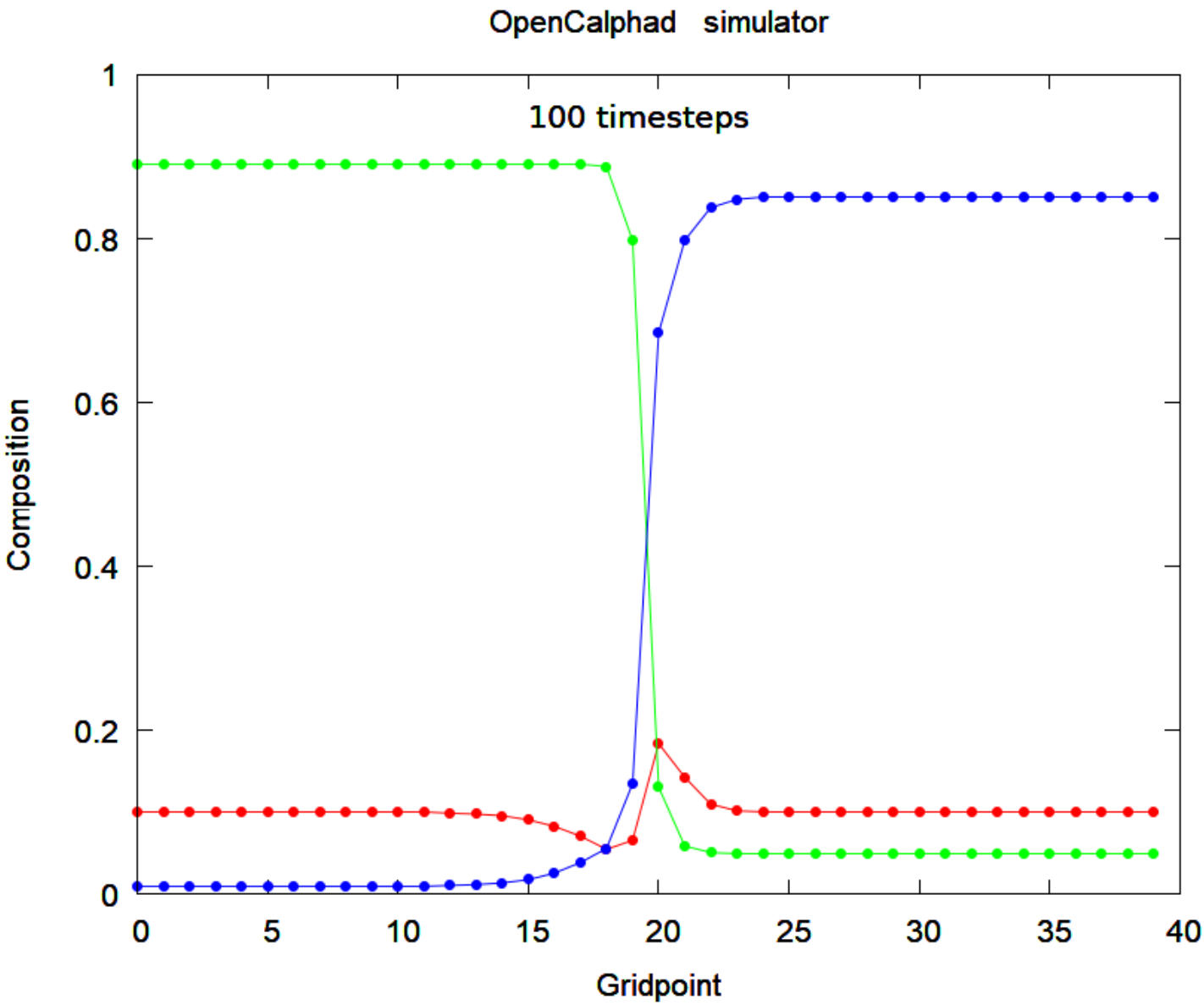

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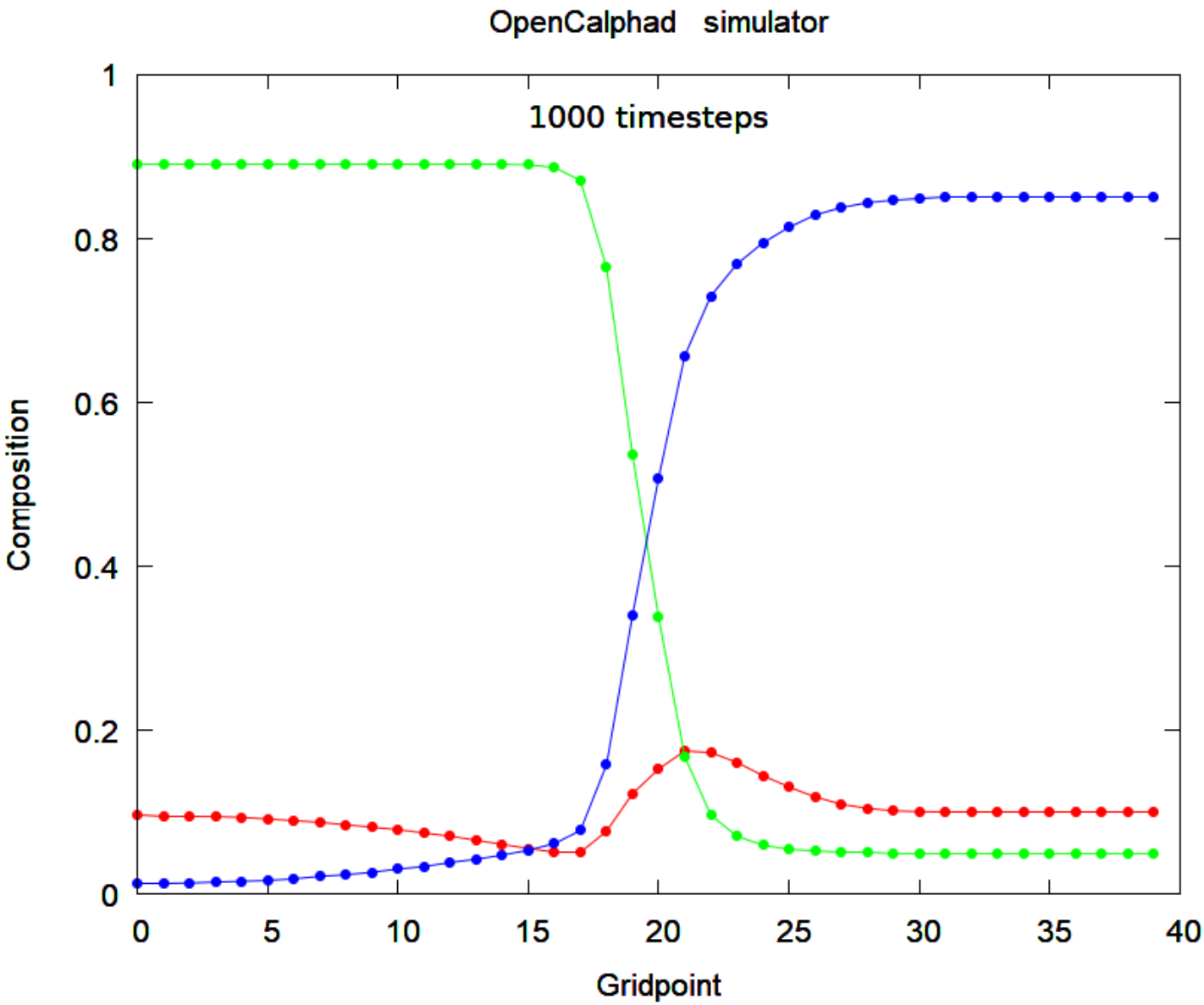

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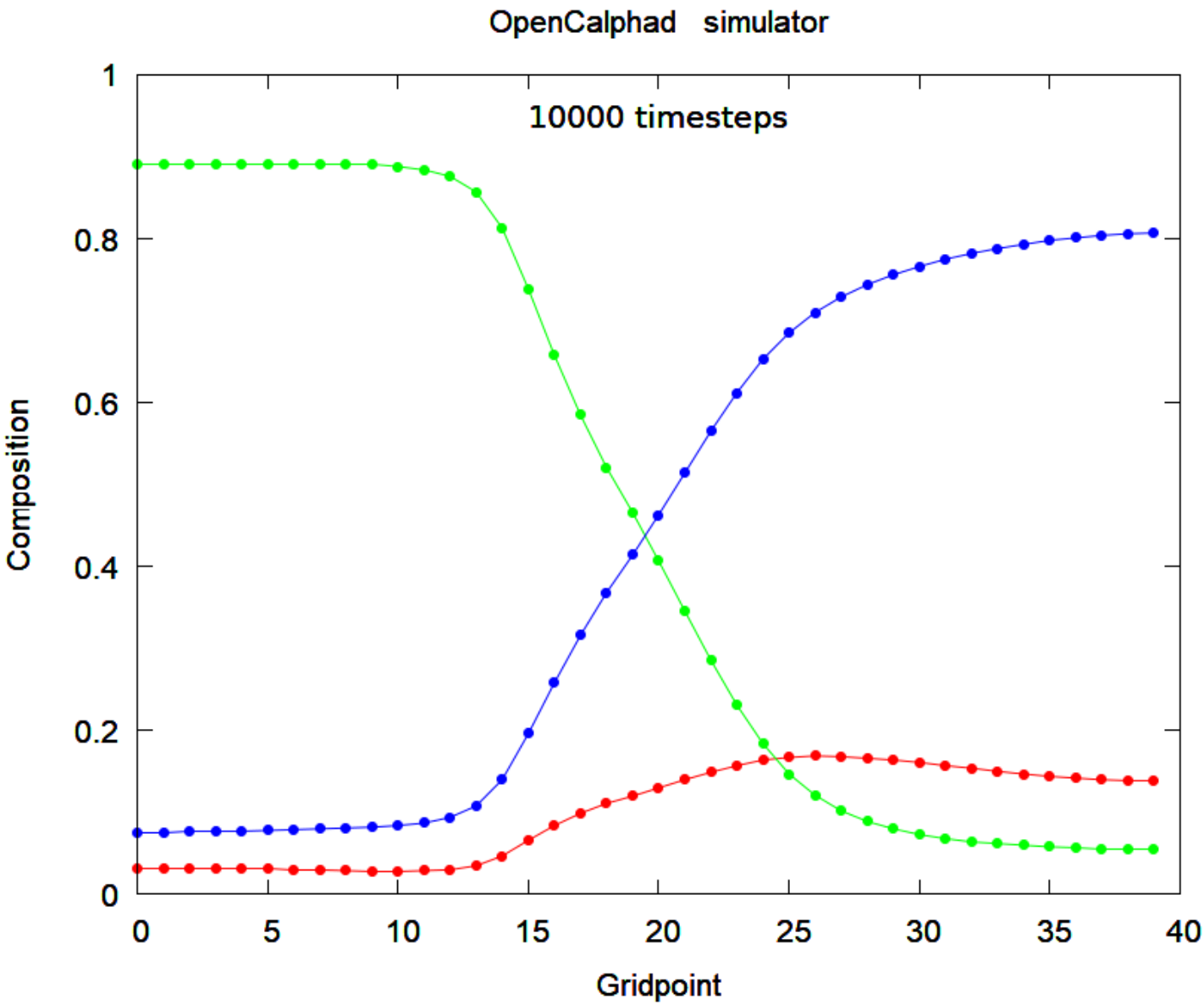

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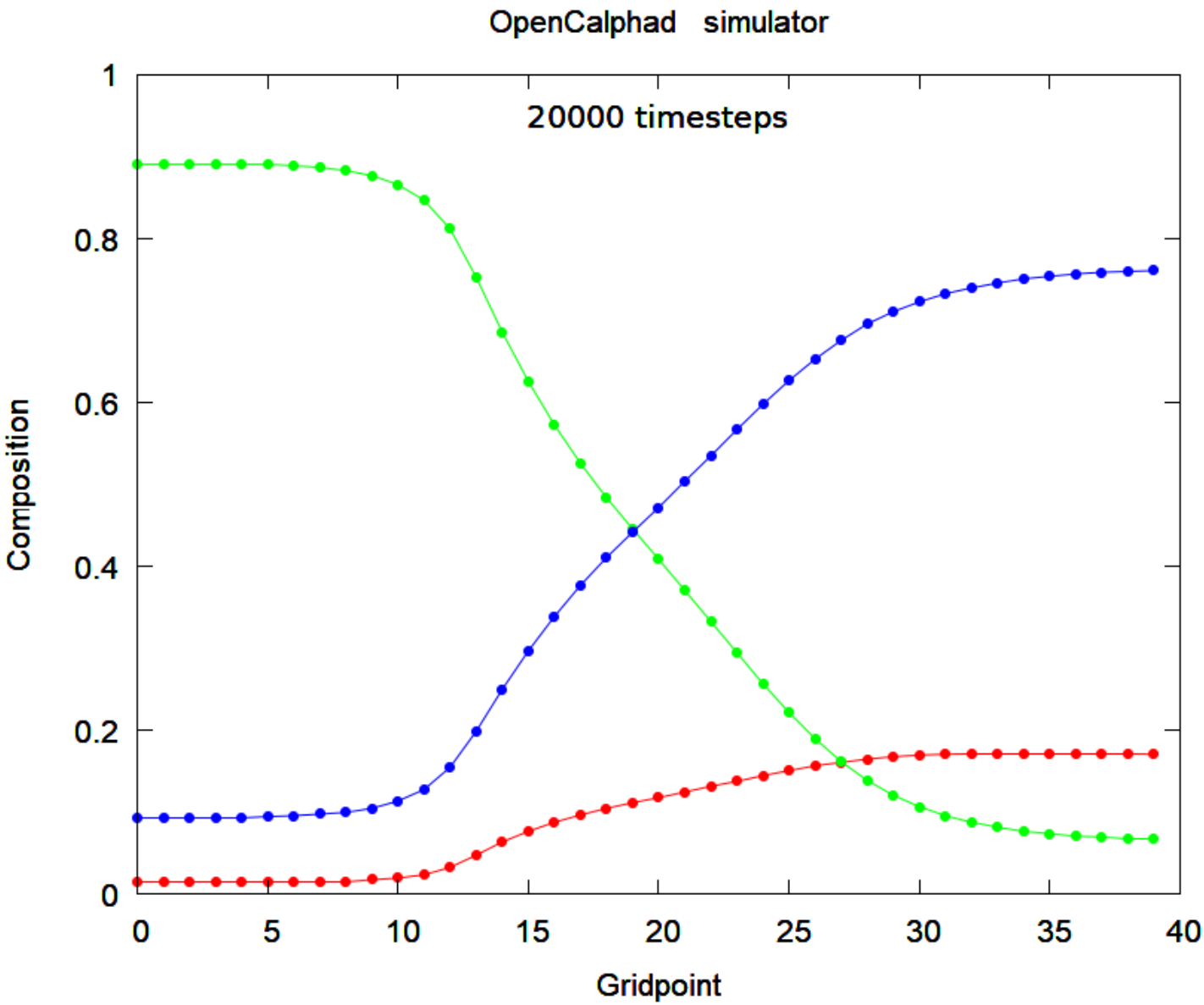

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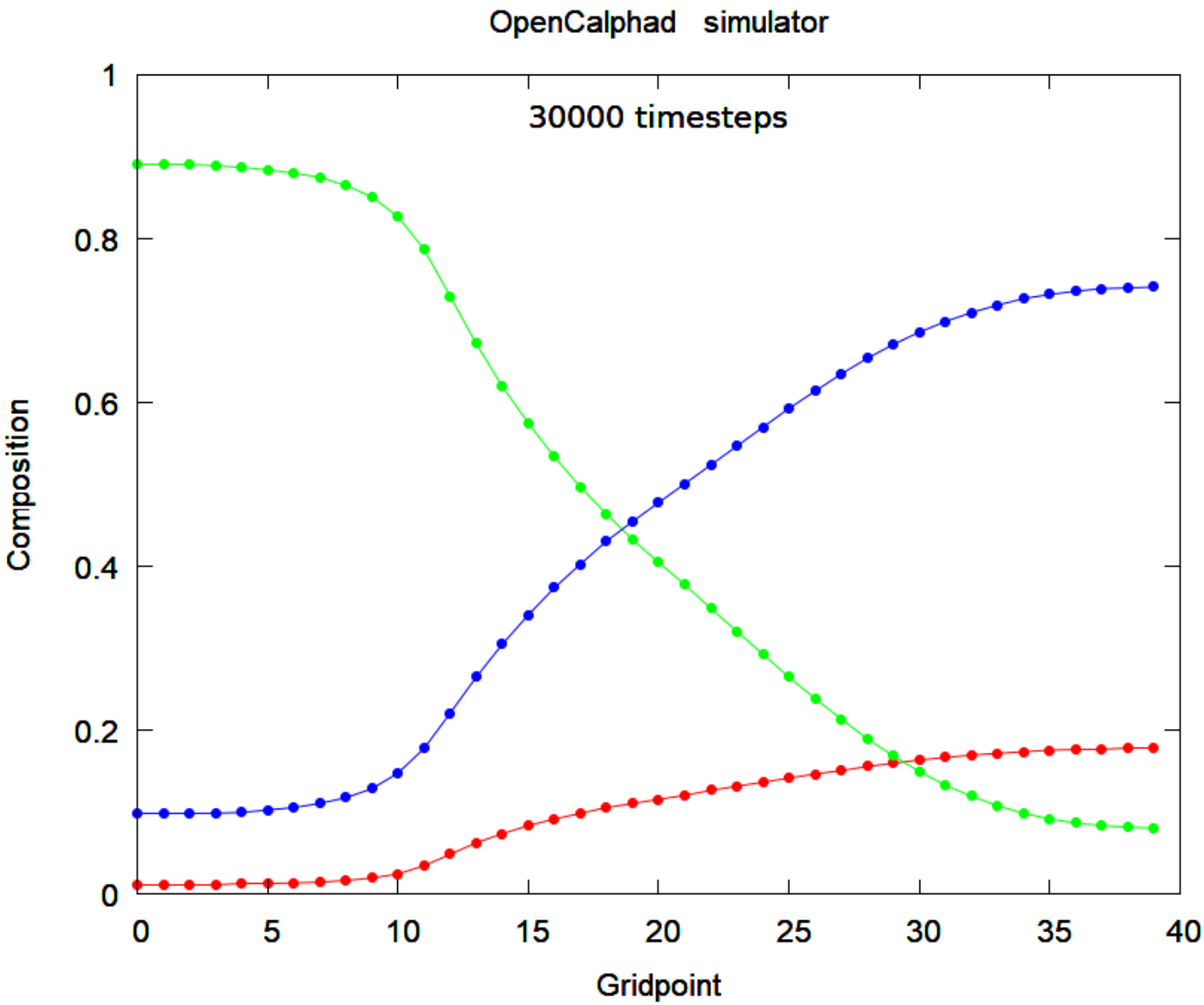

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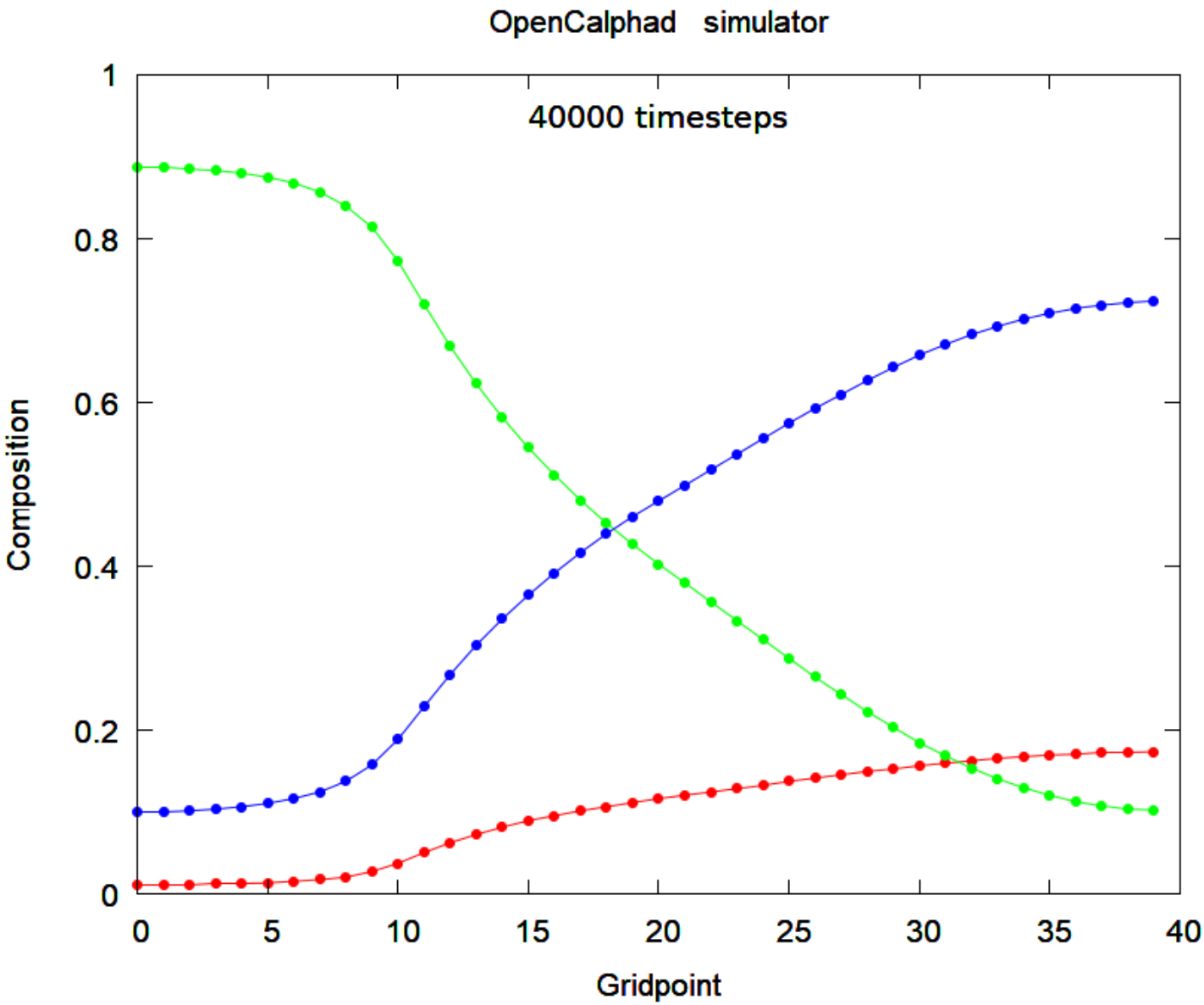

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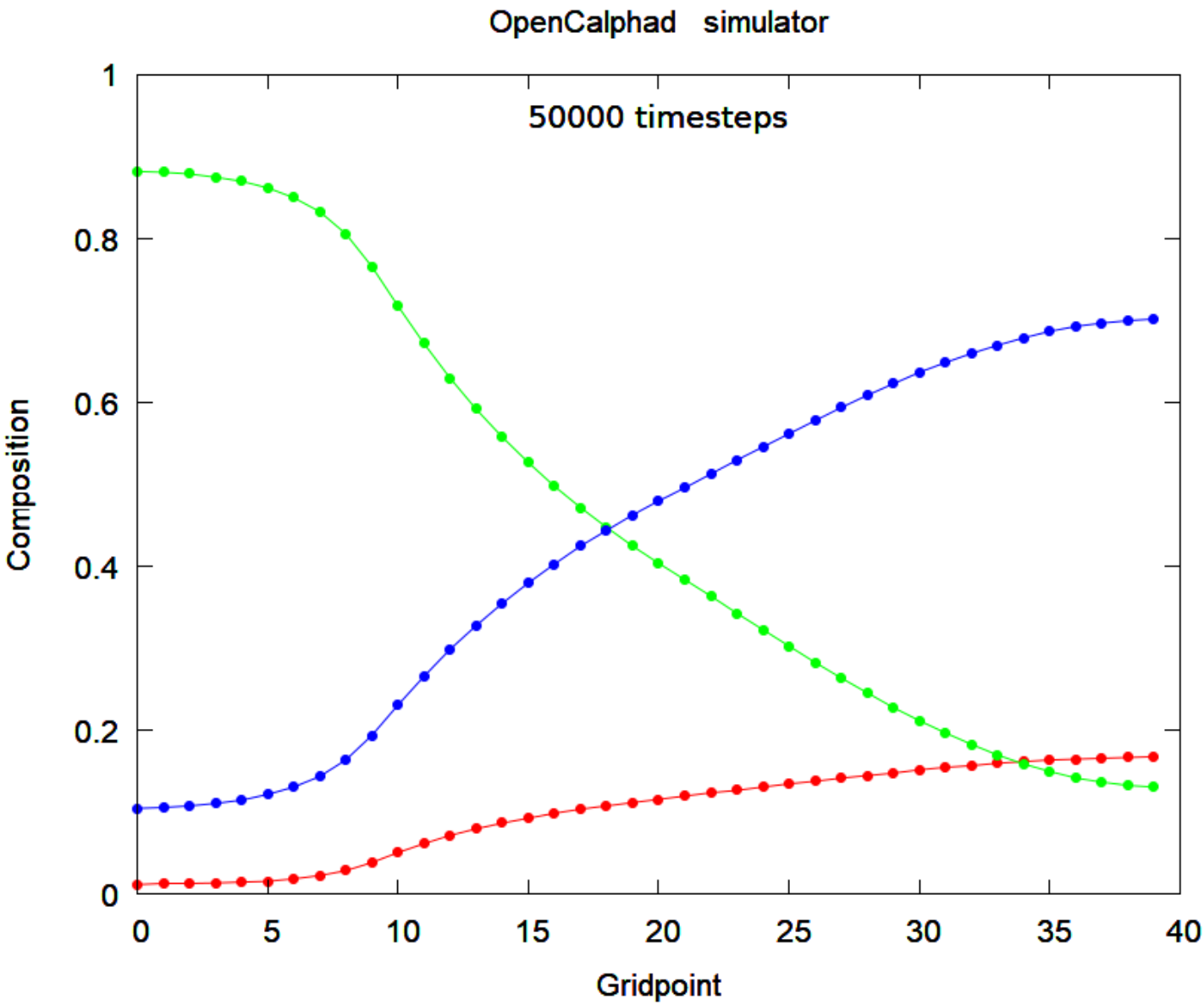
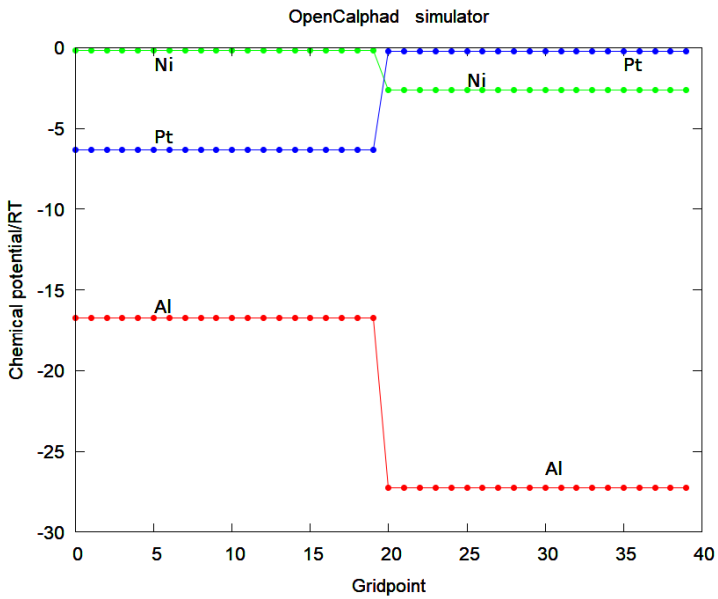
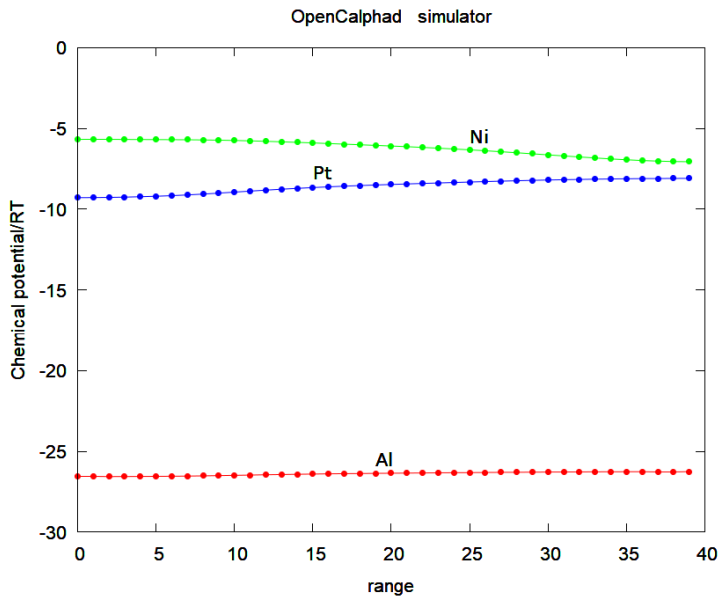


Simulation 2: Chemical potentials profiles, inital and at 50000 timesteps





The gradients in the chemical potentials drives the diffusion.
The Al profile is almost flat after 50000 timesteps and it is maybe time to add a new coating or replace the turbine blade.

This simulation depends on extrapolated Gibbs energy surfaces in order to calculate the chemical potentials for a wide range of stable and metastable compositions.

Phase diagram calculation use Zero Phase Fraction (ZPF) lines

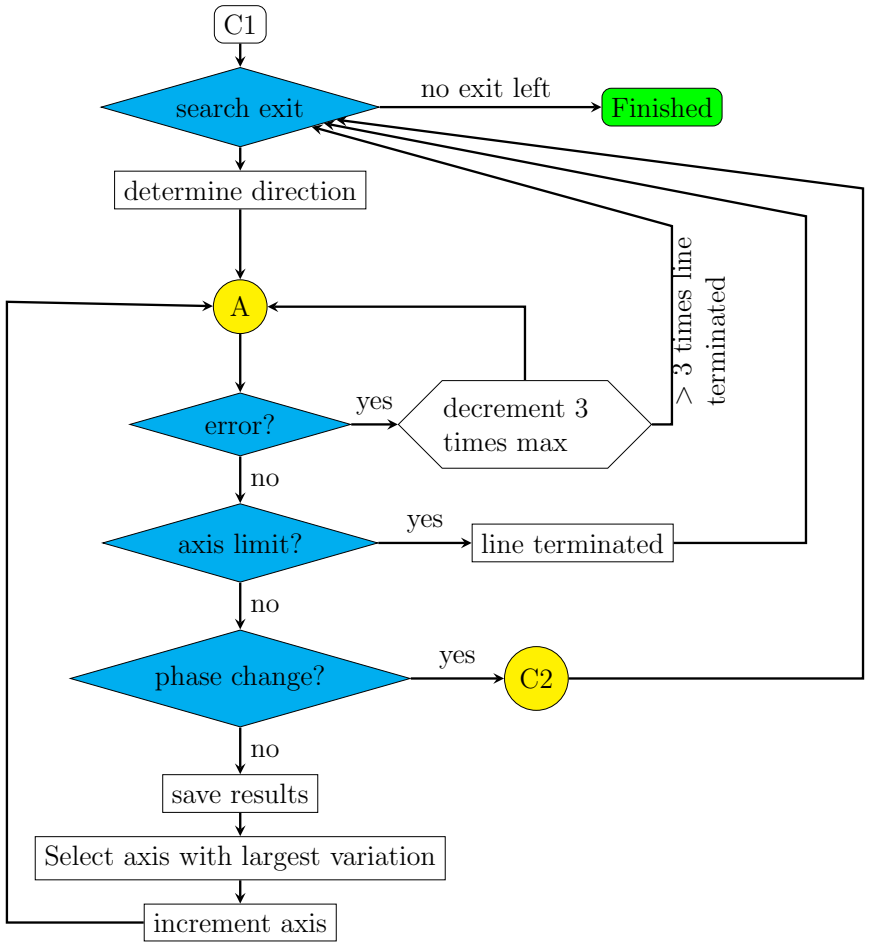
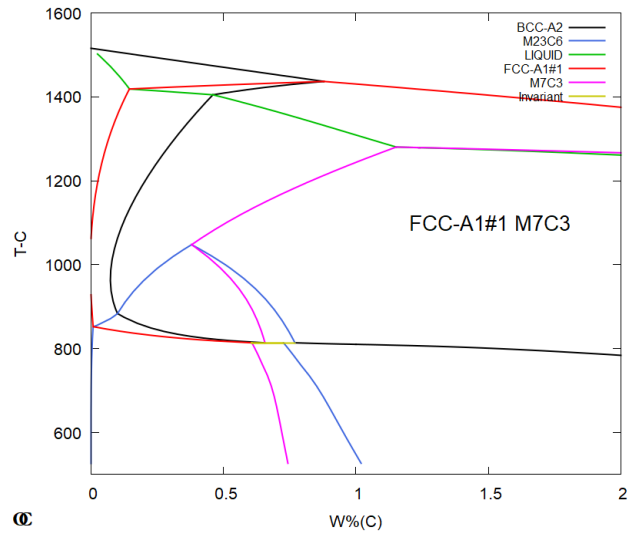


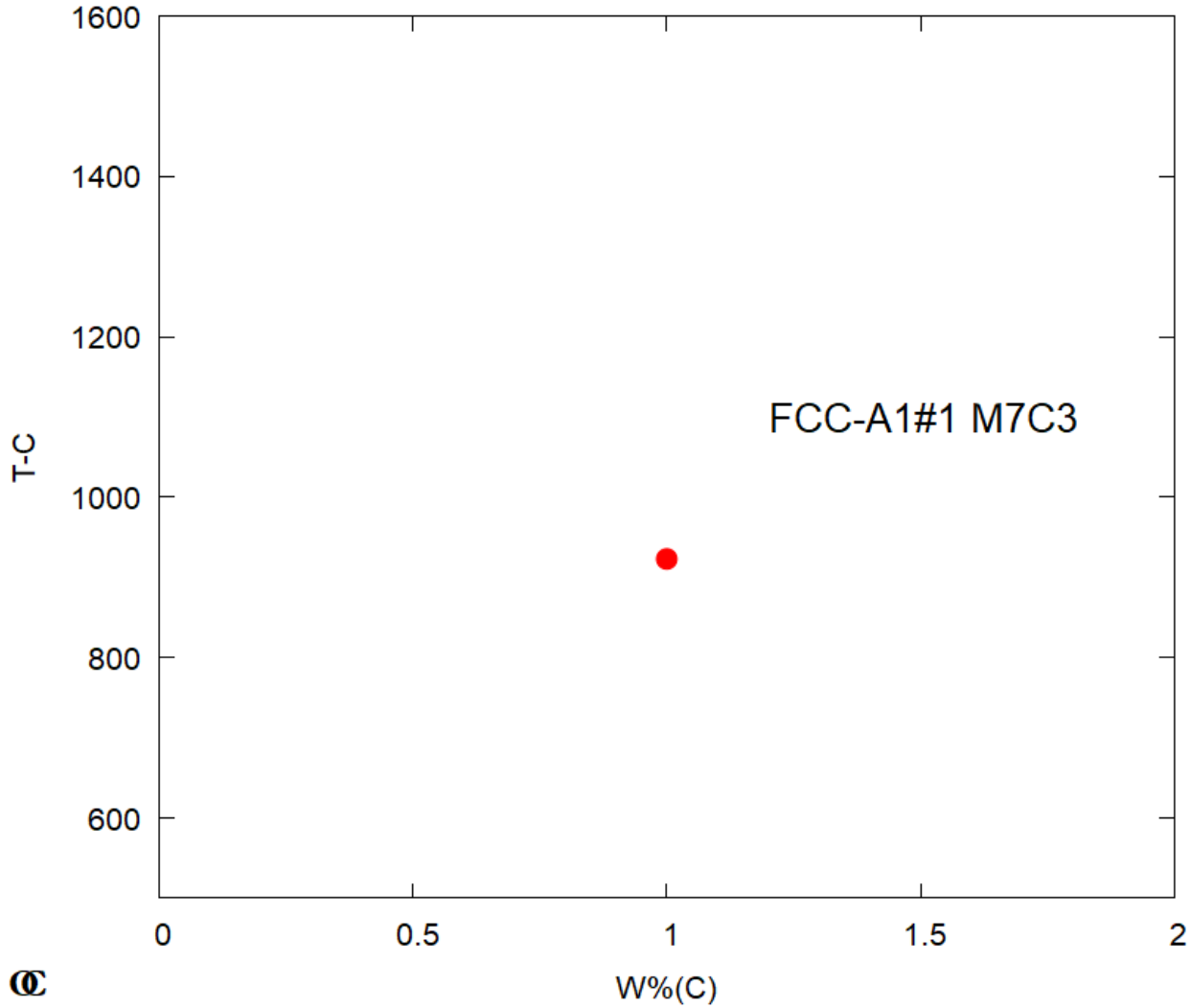
Figure 1: Flowchart of algorithm C1 to follow equilibria along lines using algorithm A to calculate each equilibrium and call algorithm C2 when algorithm A finds a change of the set of stable phases.



The lines in the phase diagram are calculated as ZPF lines by Algorithm C1.
Each line starts and ends with a change of the set of stable phases or axis limit.

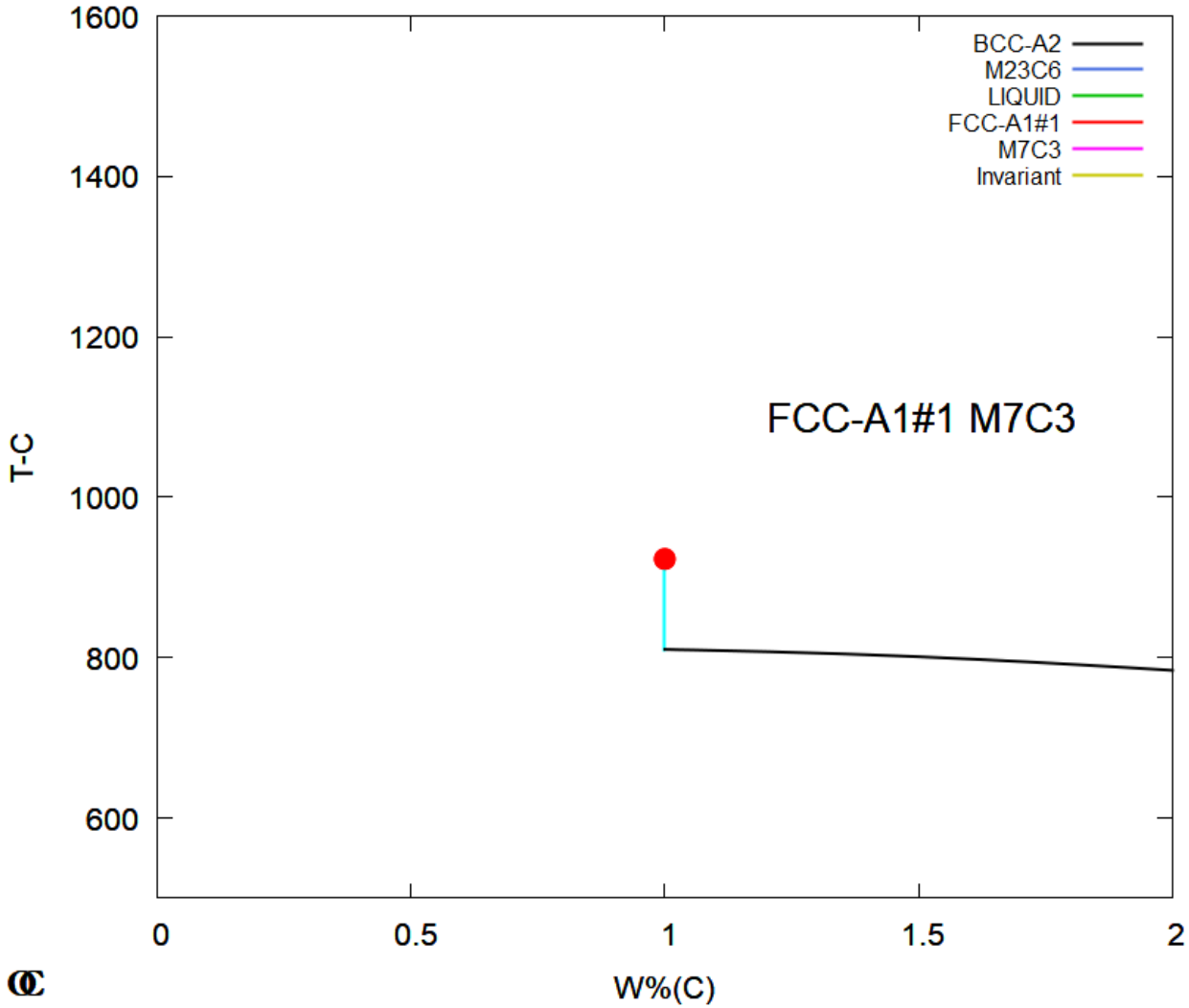
B Sundman, N Dupin and B Hallstedt, Calphad, **75** (2021) 102330

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



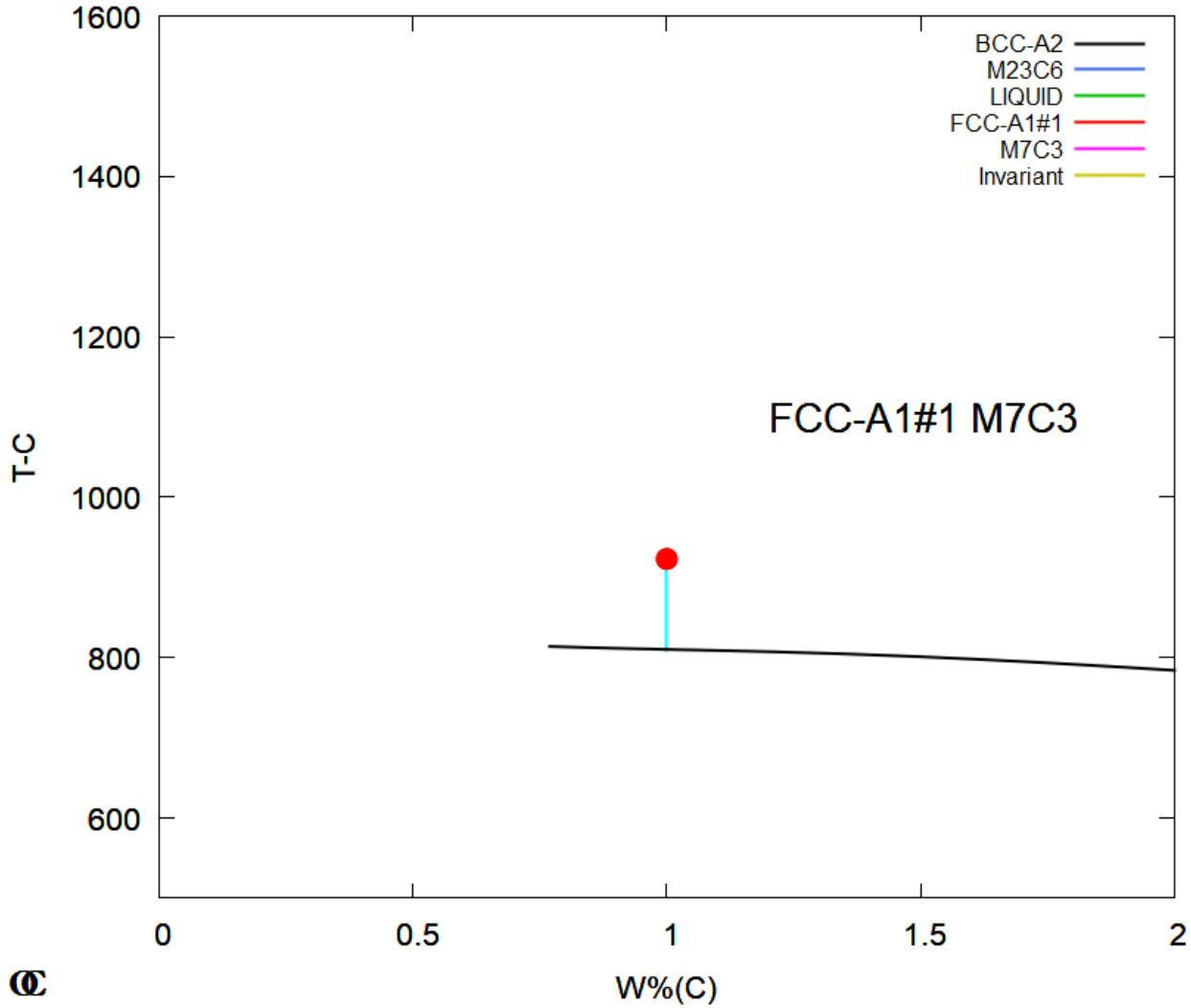
Initial start point with FCC and M7C3 stable. Except in the singlephase regions the phase compositions are outside the plane of the diagram, no tie-lines.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



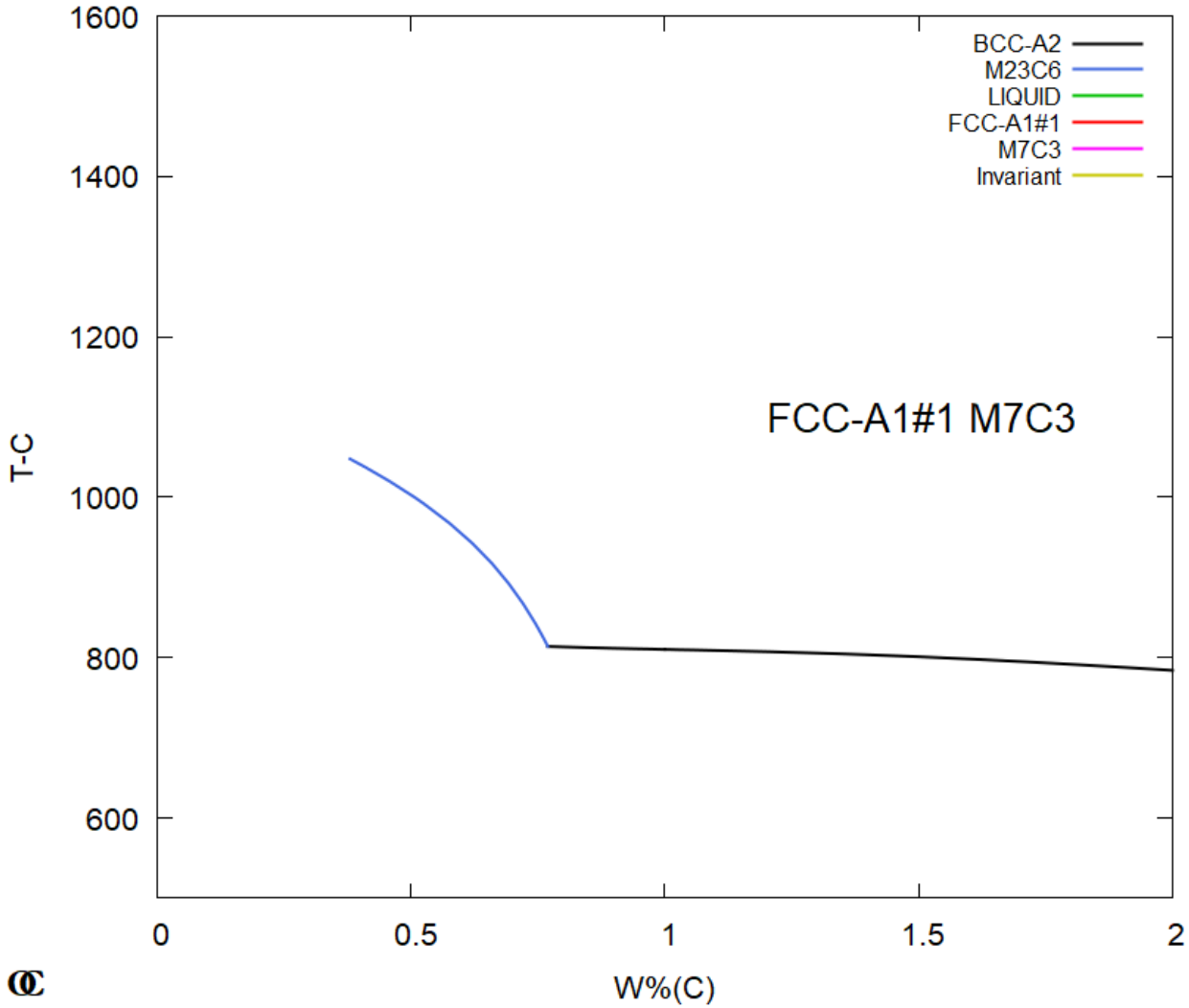
Lowering T makes the BCC phase stable. Two exits are generated and one with BCC as fix with zero amount and FCC and M7C3 as stable is followed to the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



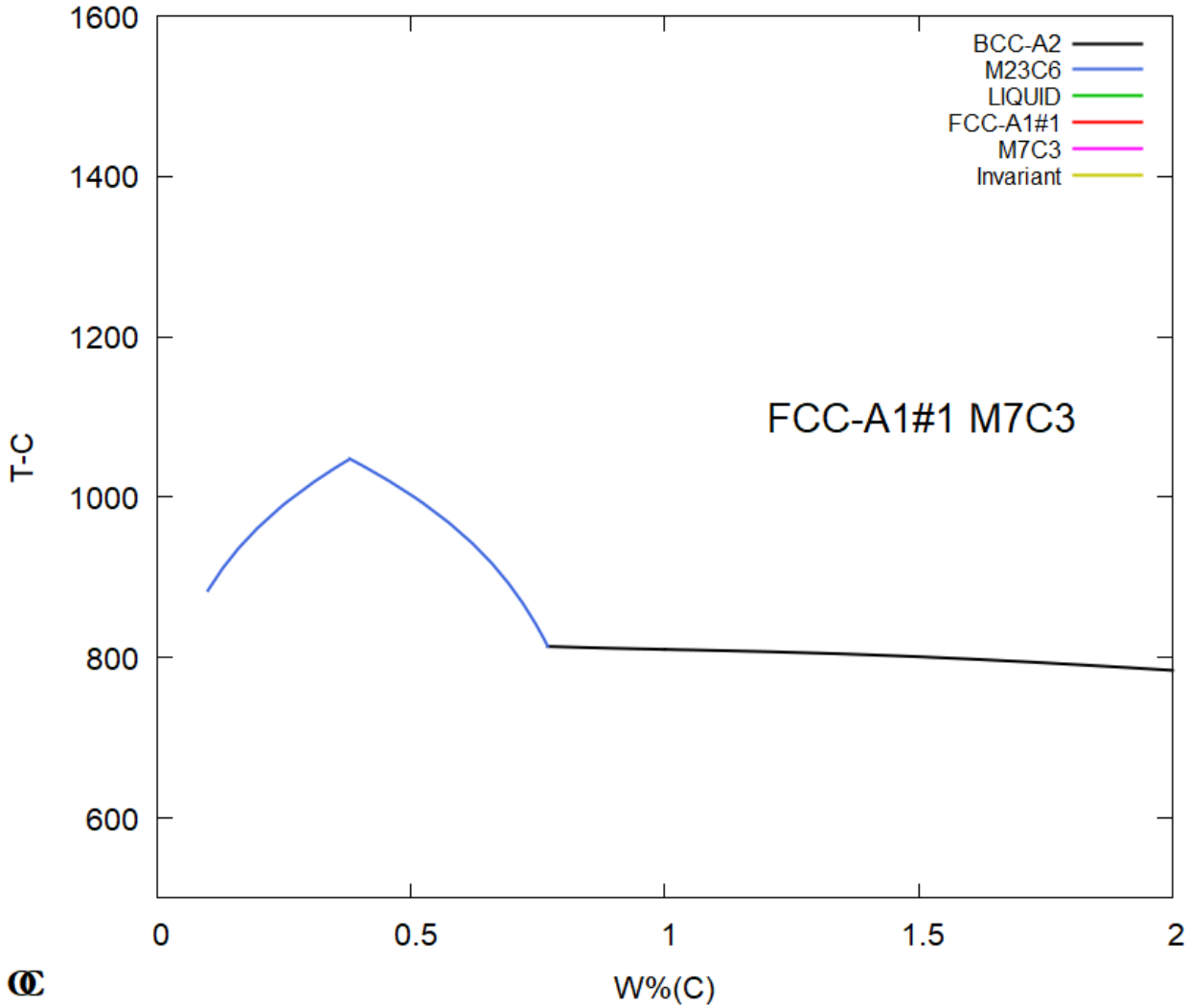
The other exit with BCC as fix and FCC and M7C3 as stable ends when M23C6 becomes stable. This is an invariant equilibrium with 4 stable phases. A node is generated with 8 exits (one already found). Invariants in iso-pleths are complicated.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



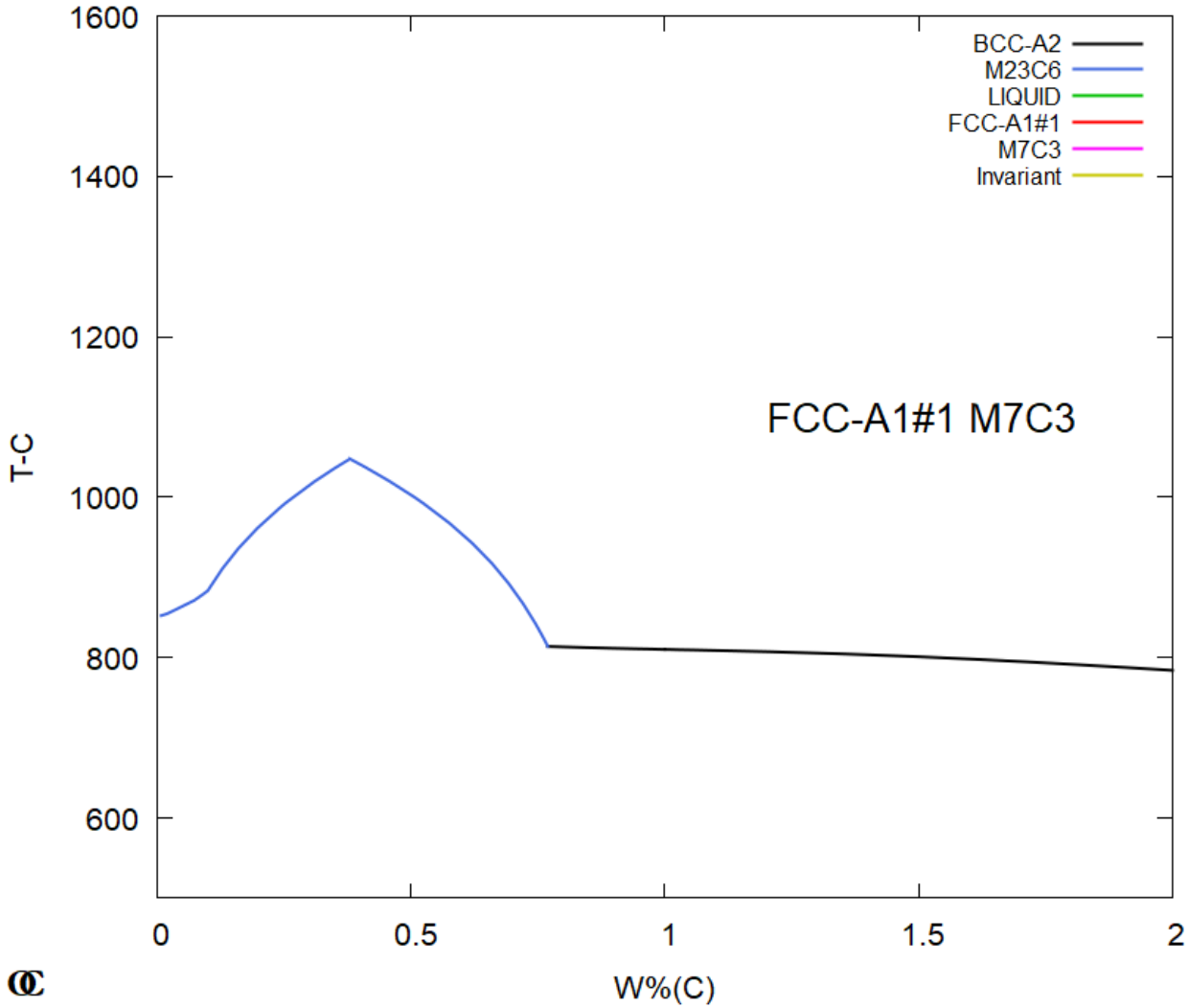
One of the exits from the invariant with M23C6 as fix and FCC and M7C3 as stable gives this line until the M7C3 is no longer stable. A node point is generated with 4 exits. Most nodes in an iso-pleth represent 2 lines crossing, i.e. 4 exits.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



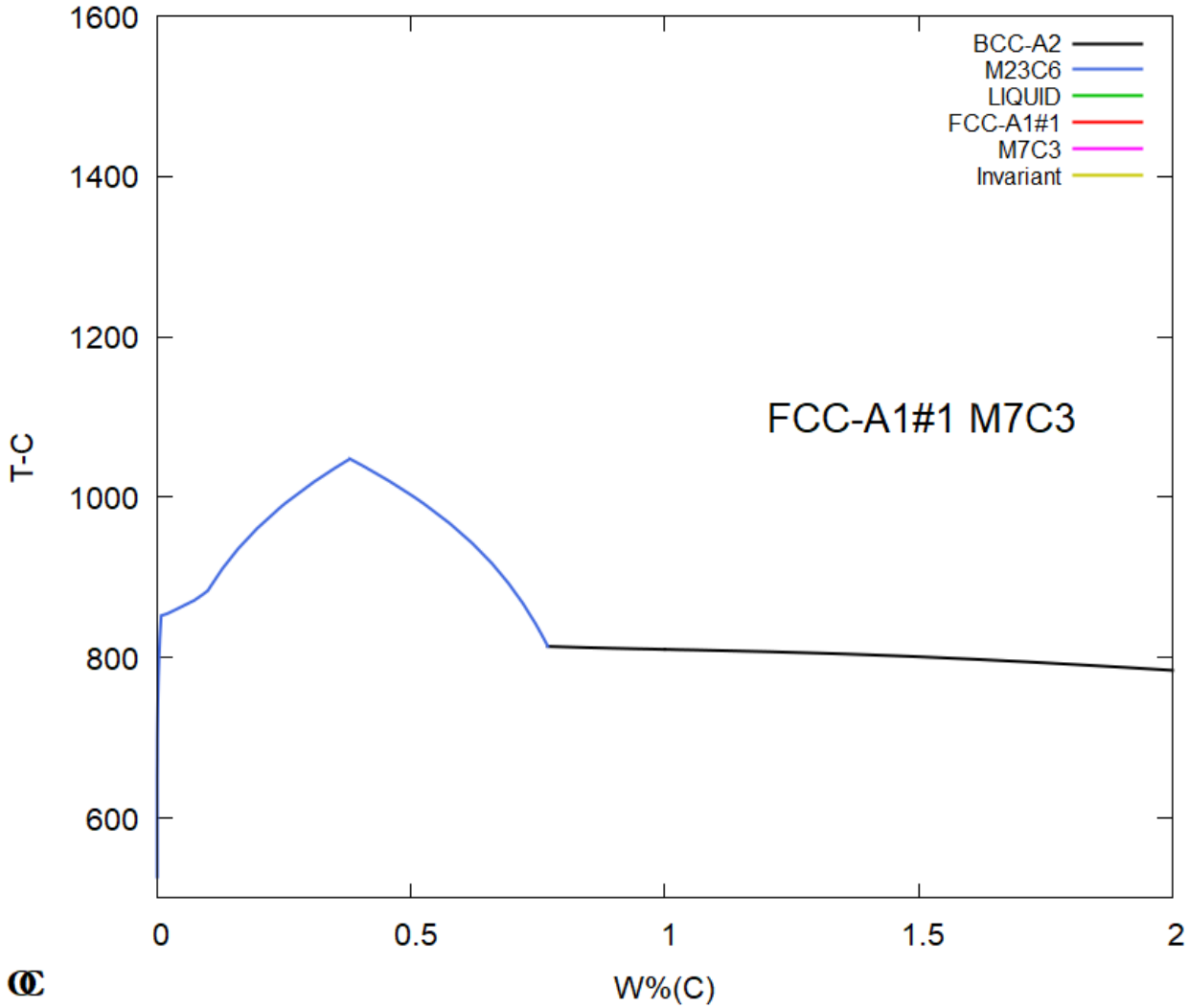
One exit from the last node with M23C6 as fix and FCC as stable is followed and the line ends when BCC becomes stable again. A new node point with 4 exits is generated (one marked as already found).

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



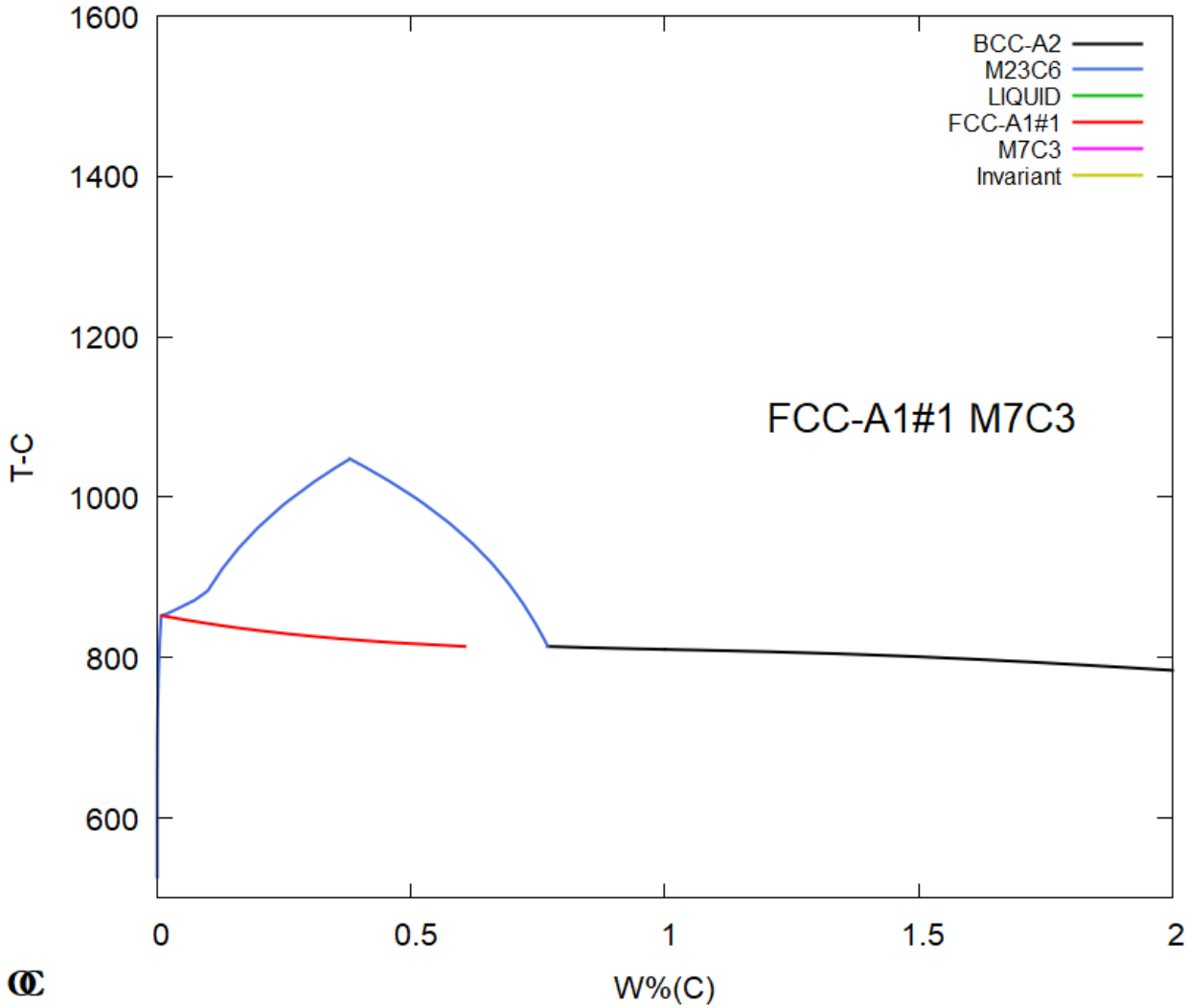
The line with M23C6 as fix and FCC and BCC as stable is followed and ends when FCC is no longer stable. A node point with 4 exits is generated (and as always one of the exits is marked as found).

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



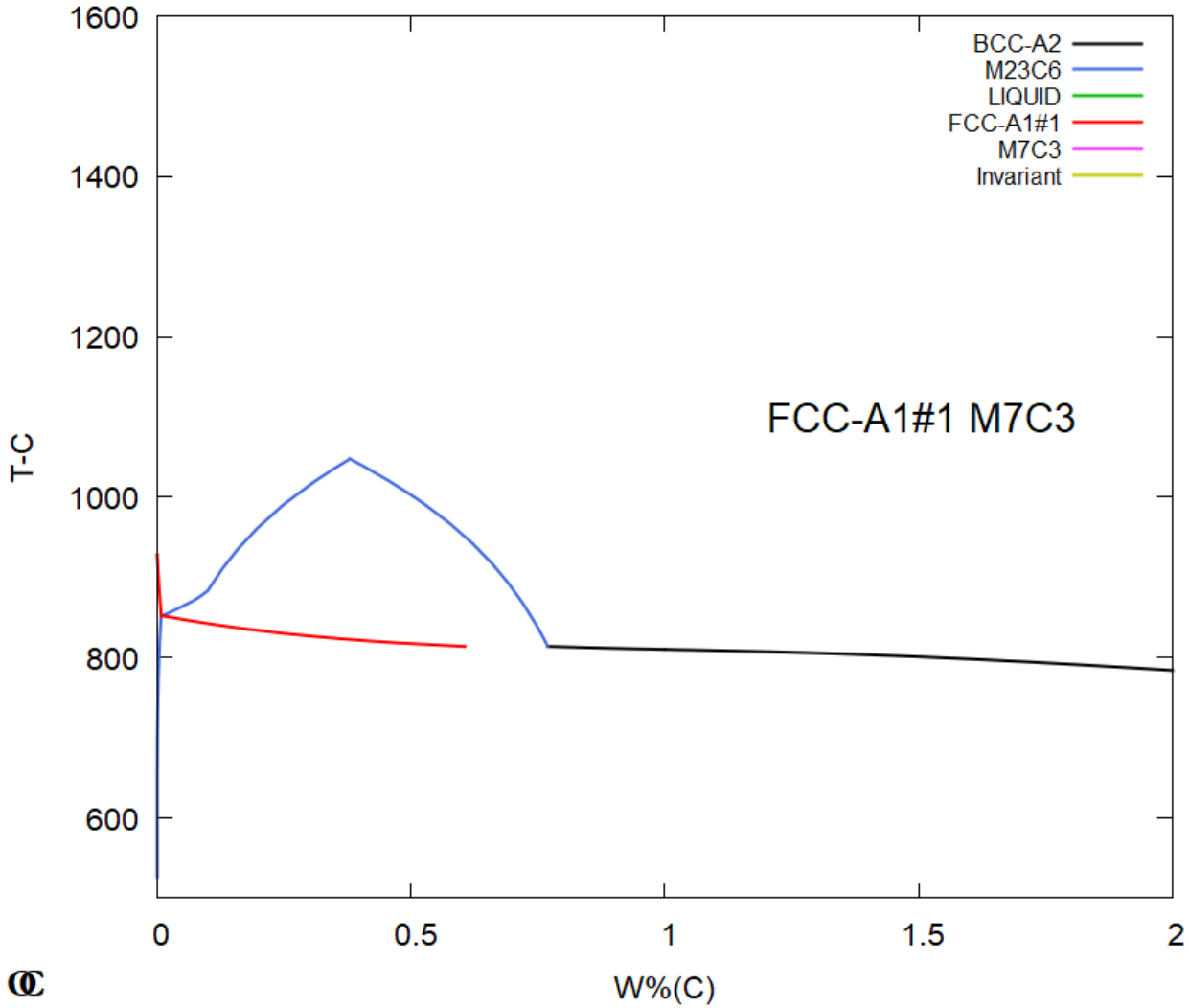
The exit with M23C6 as fix and only BCC as stable is followed close to the Fe-13%Cr composition. It ends the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



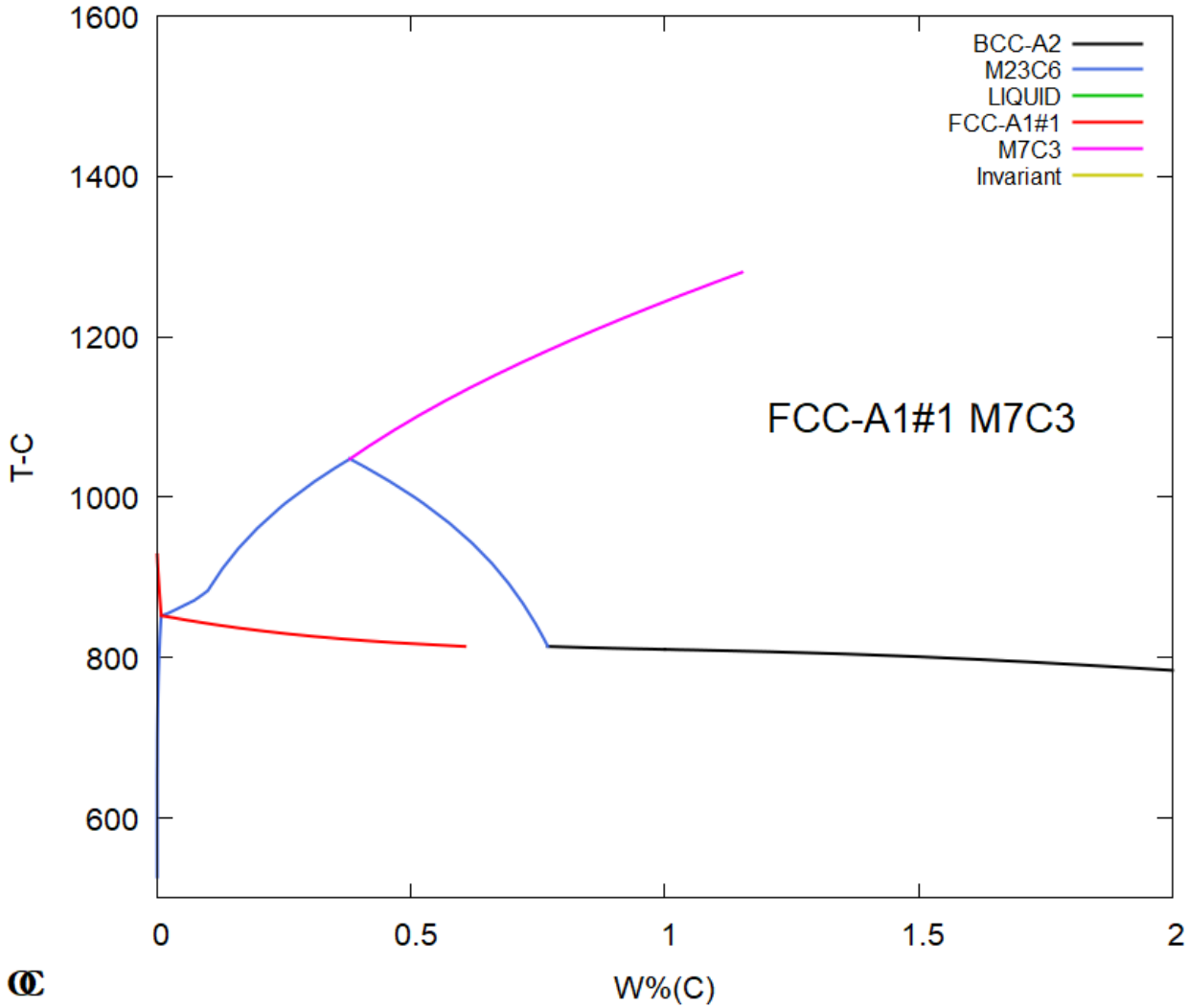
Another exit from the same node with FCC as fix and BCC and M23C6 as stable is followed and the line ends when M7C3 becomes stable, i.e. at the invariant already found. The corresponding exit is removed from the invariant.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



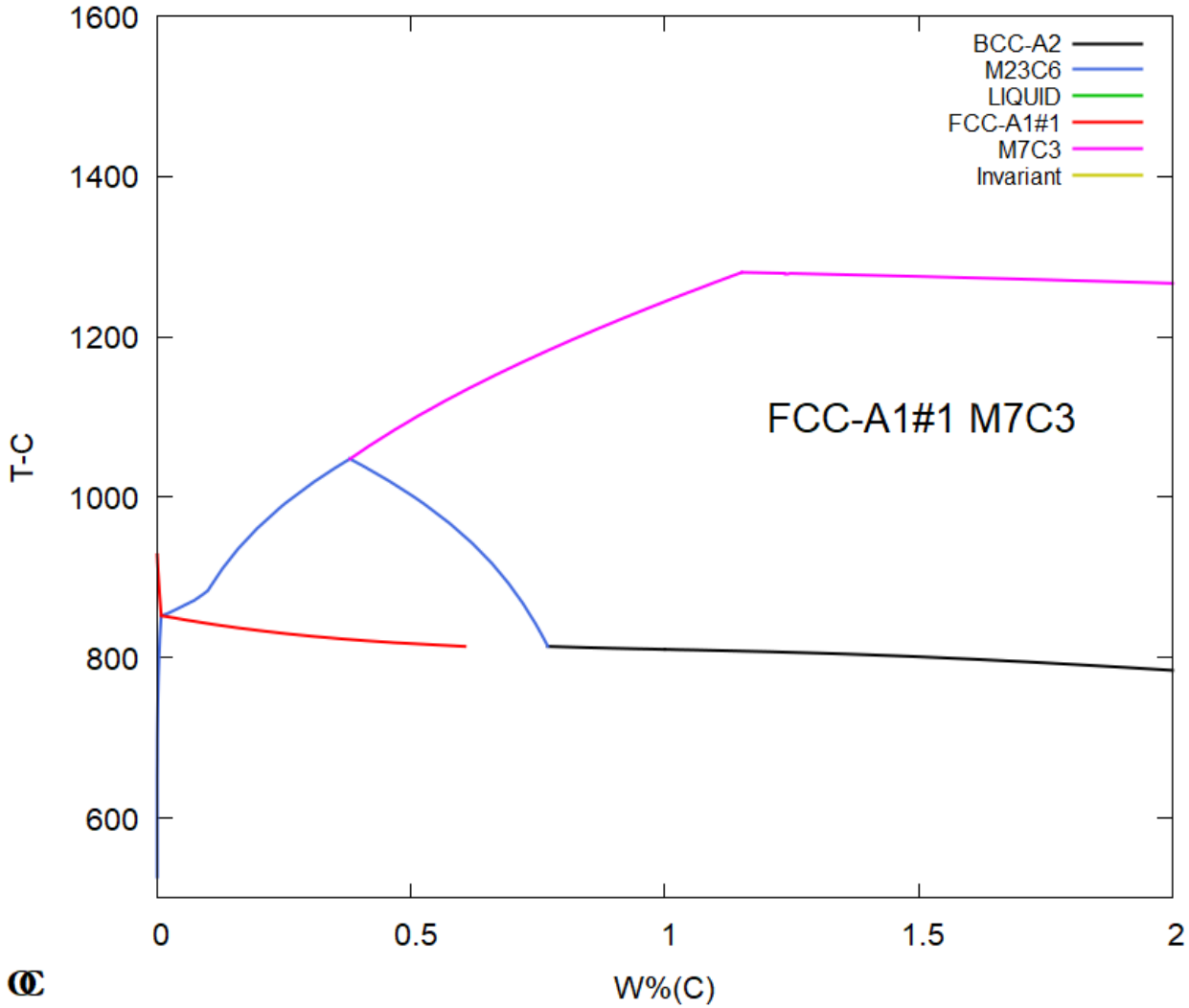
The final exit from the last node with FCC as fix and BCC as stable is followed until it ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



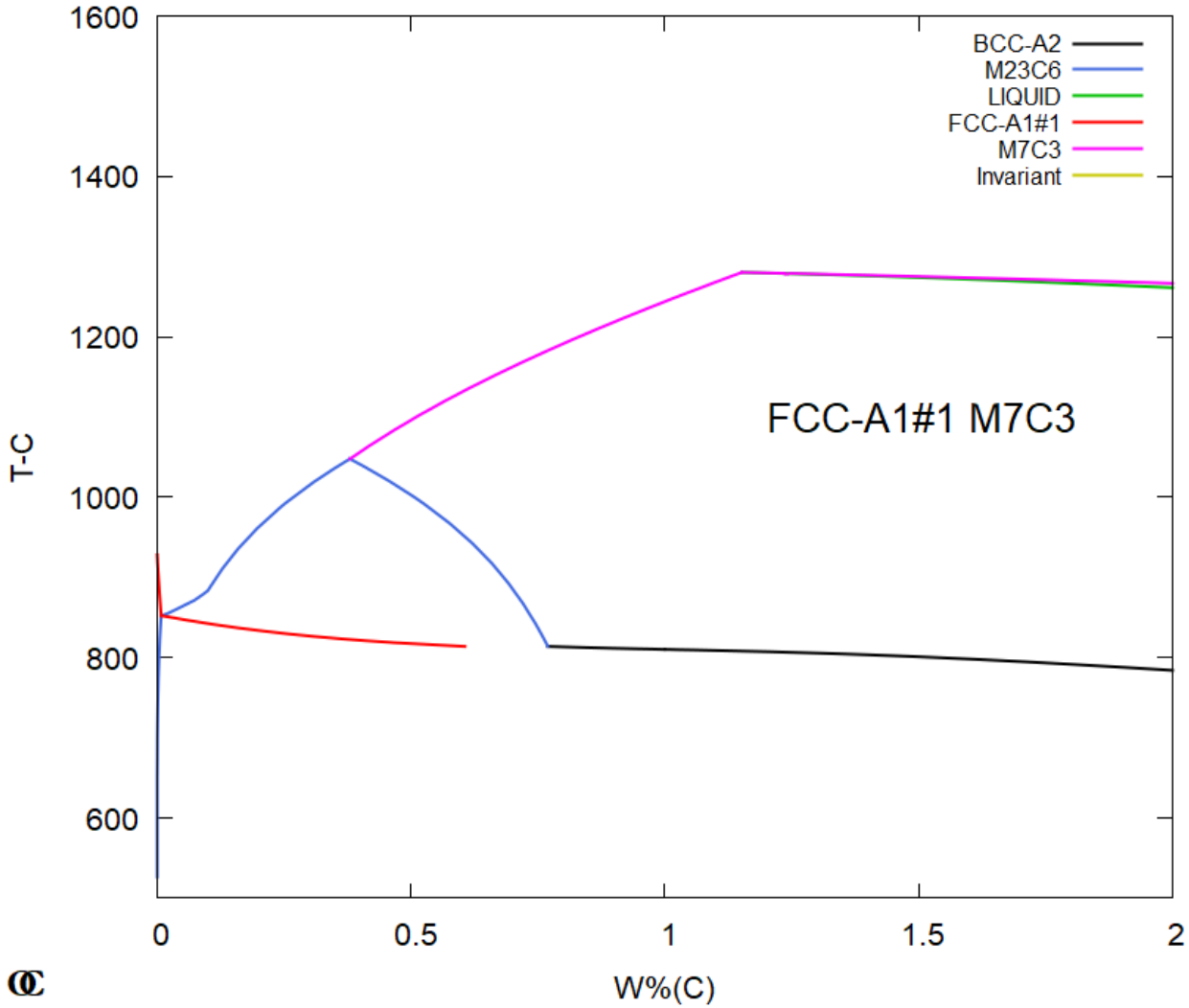
An exit from a previous node with M7C3 as fix and FCC as stable is followed until the liquid becomes stable. As usual a node point with 4 exits is generated.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



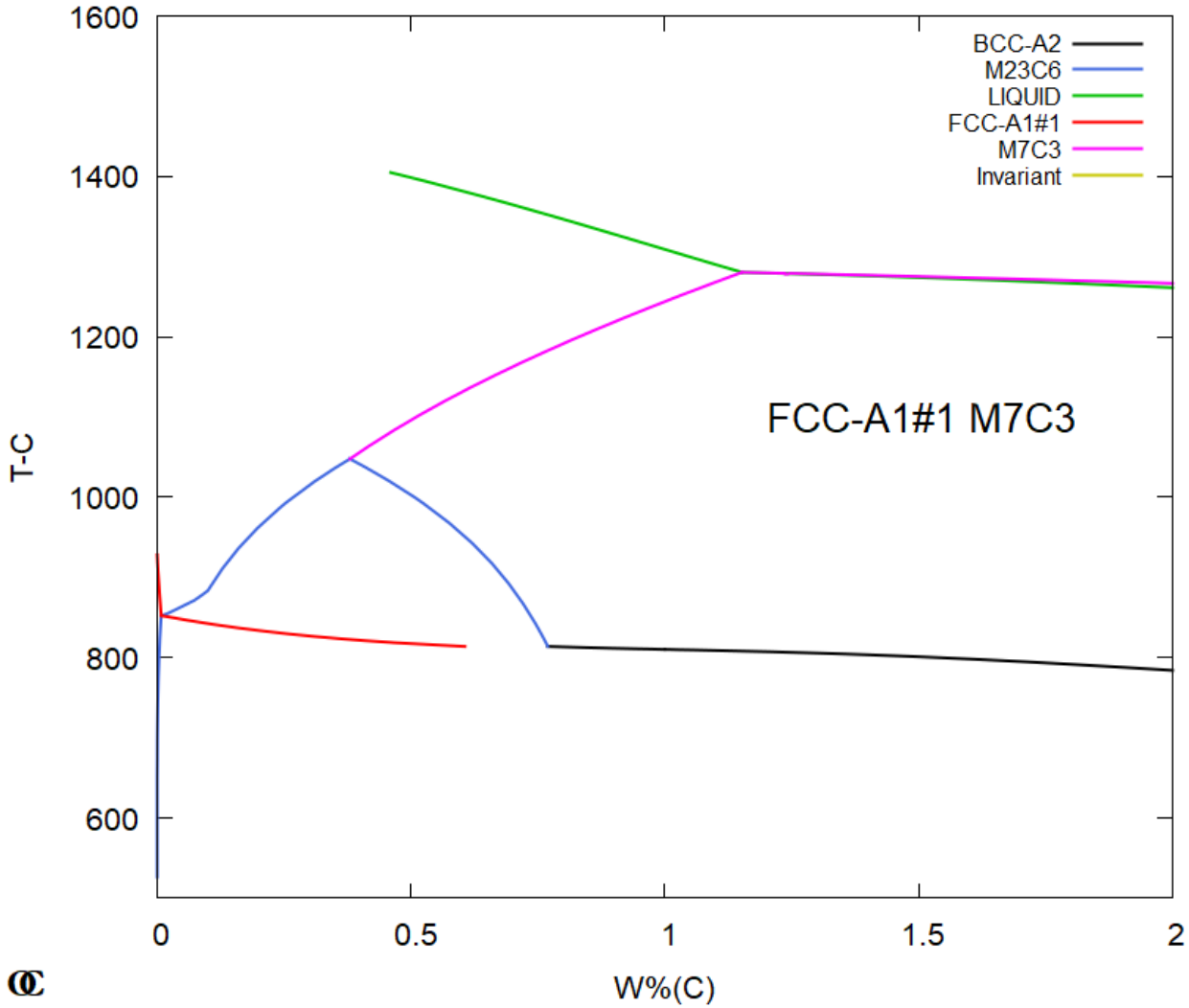
This line has liquid as fix and FCC and M7C3 as stable. It ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



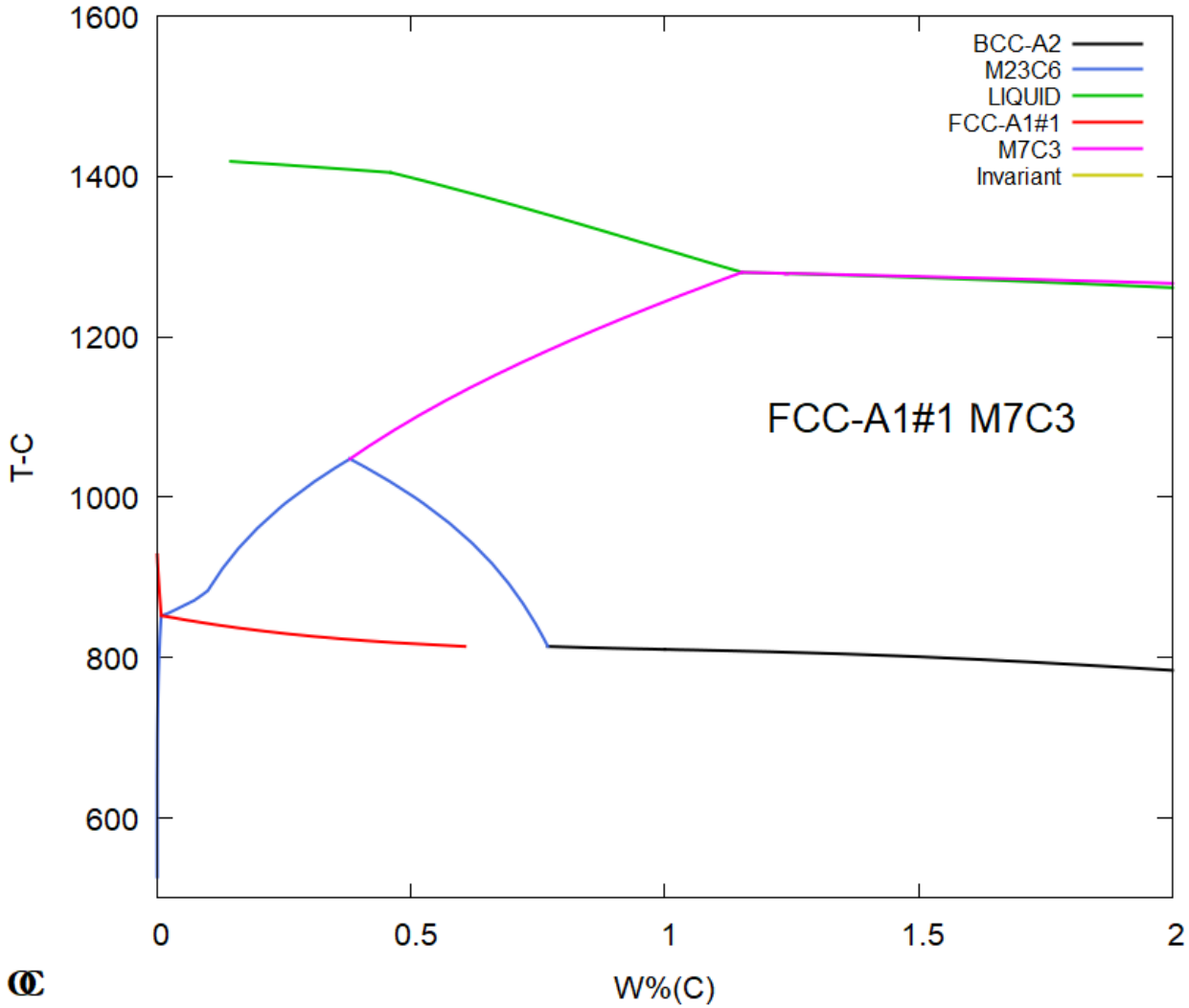
Another exit from the same node has M7C3 as fix and liquid and FCC as stable. It is very close to the prevous line and ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



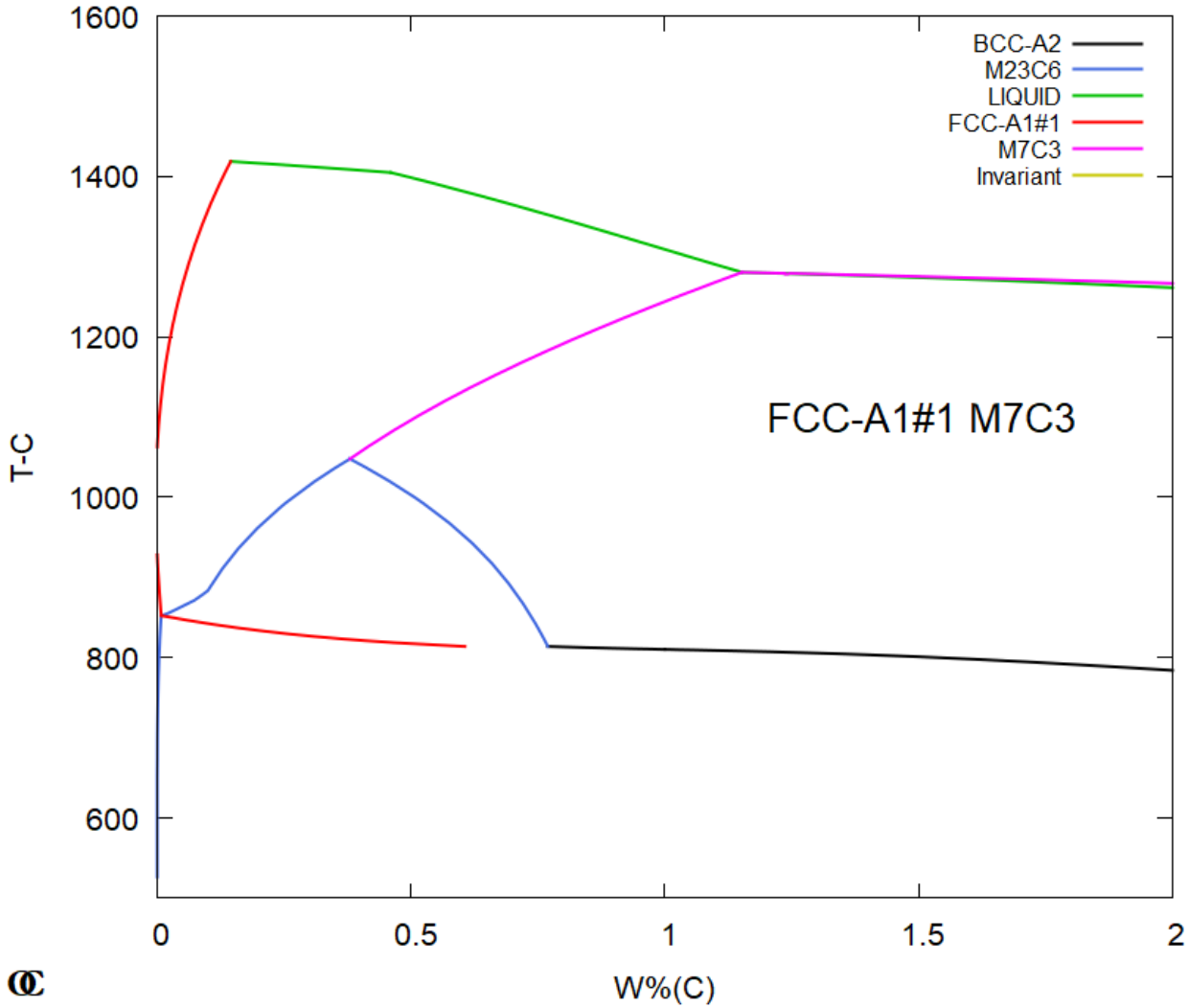
The last exit from this node has the liquid as fix and FCC as stable. The line ends when the BCC becomes stable. A node with 4 exits is generated. No big surprise.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



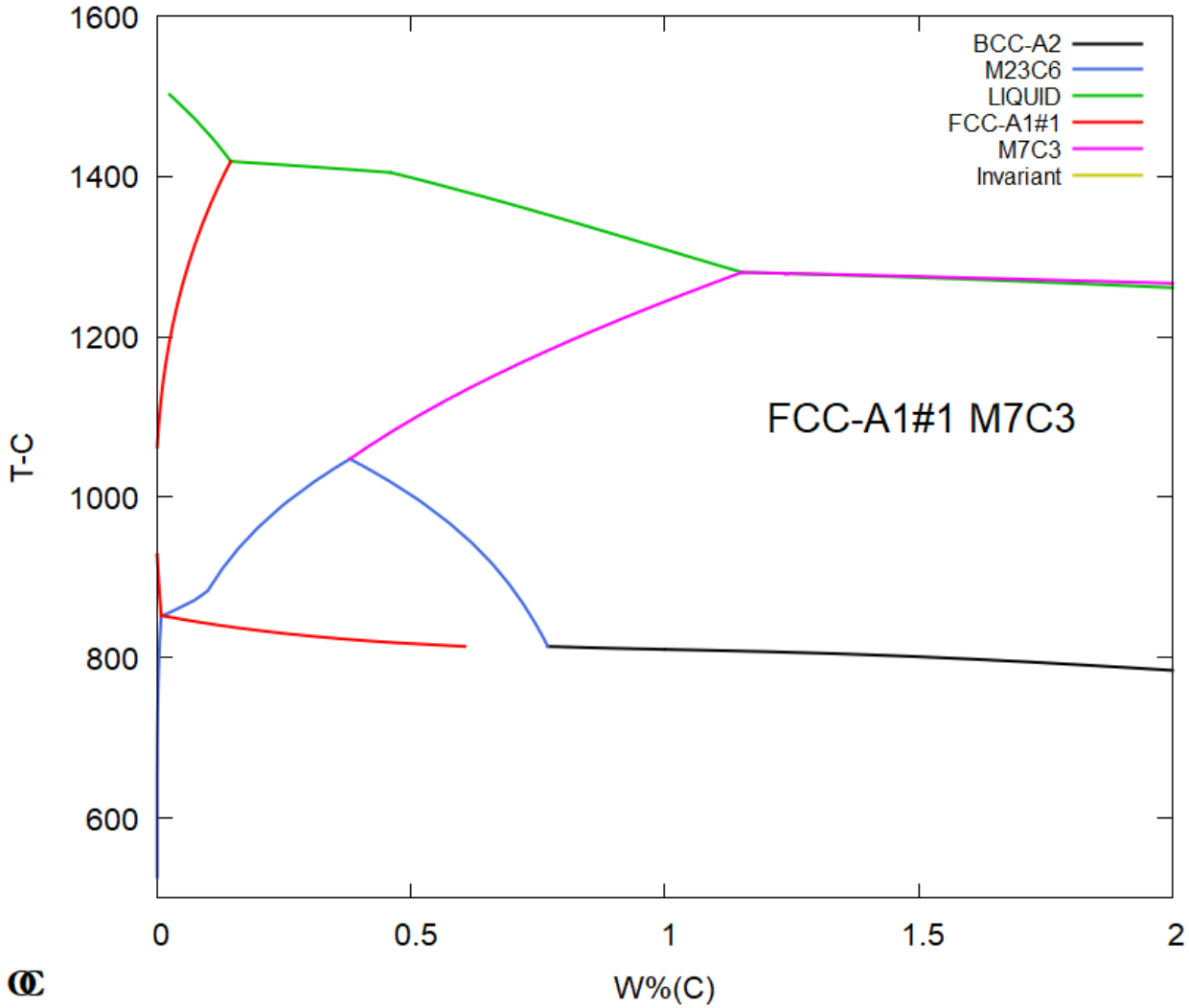
At the new node the exit with liquid as fix and BCC and FCC as stable is used to calculate this line. It ends when FCC is no longer stable. A node with 4 exits is generated.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



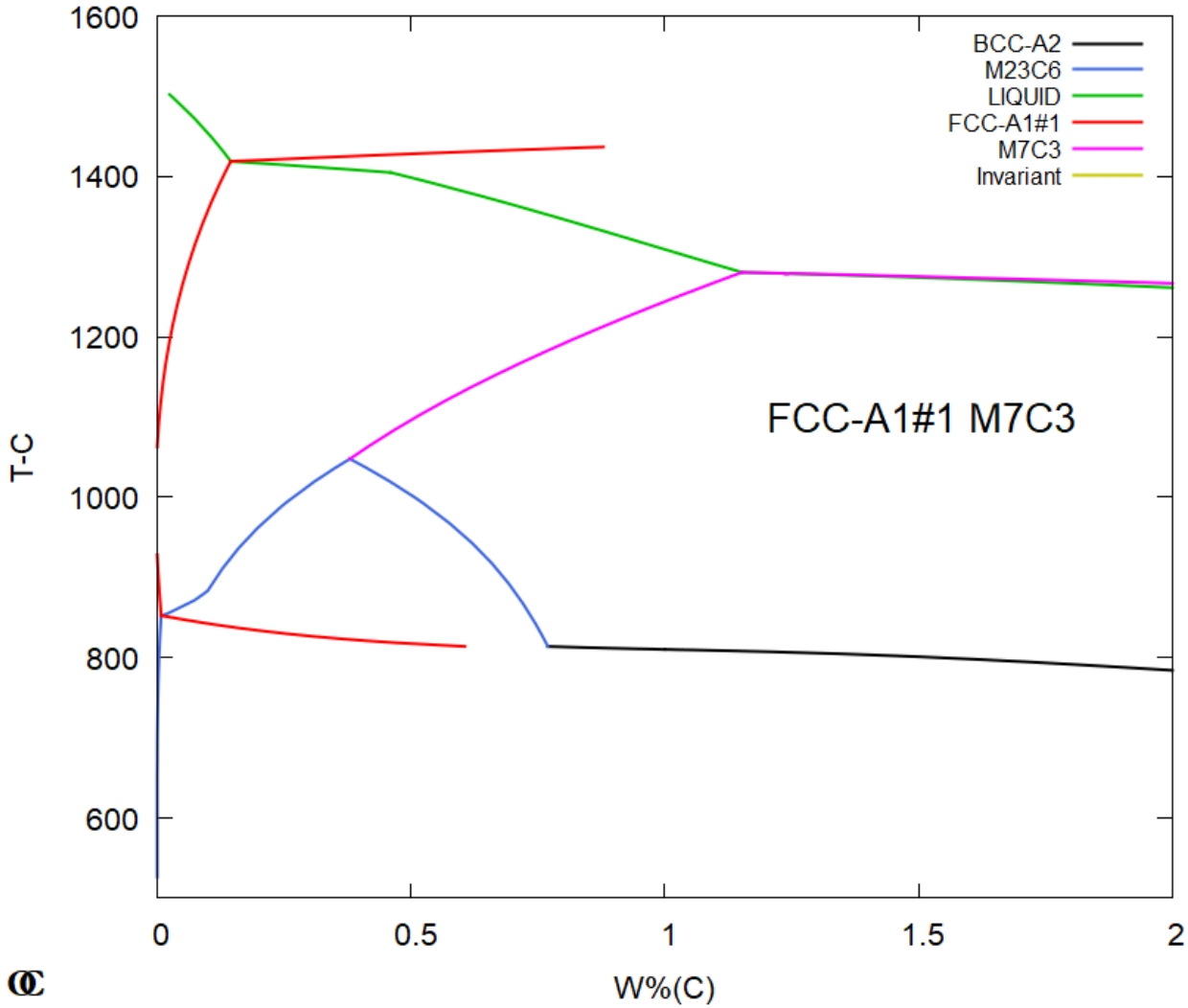
This line has FCC as fix and BCC as stable. It ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



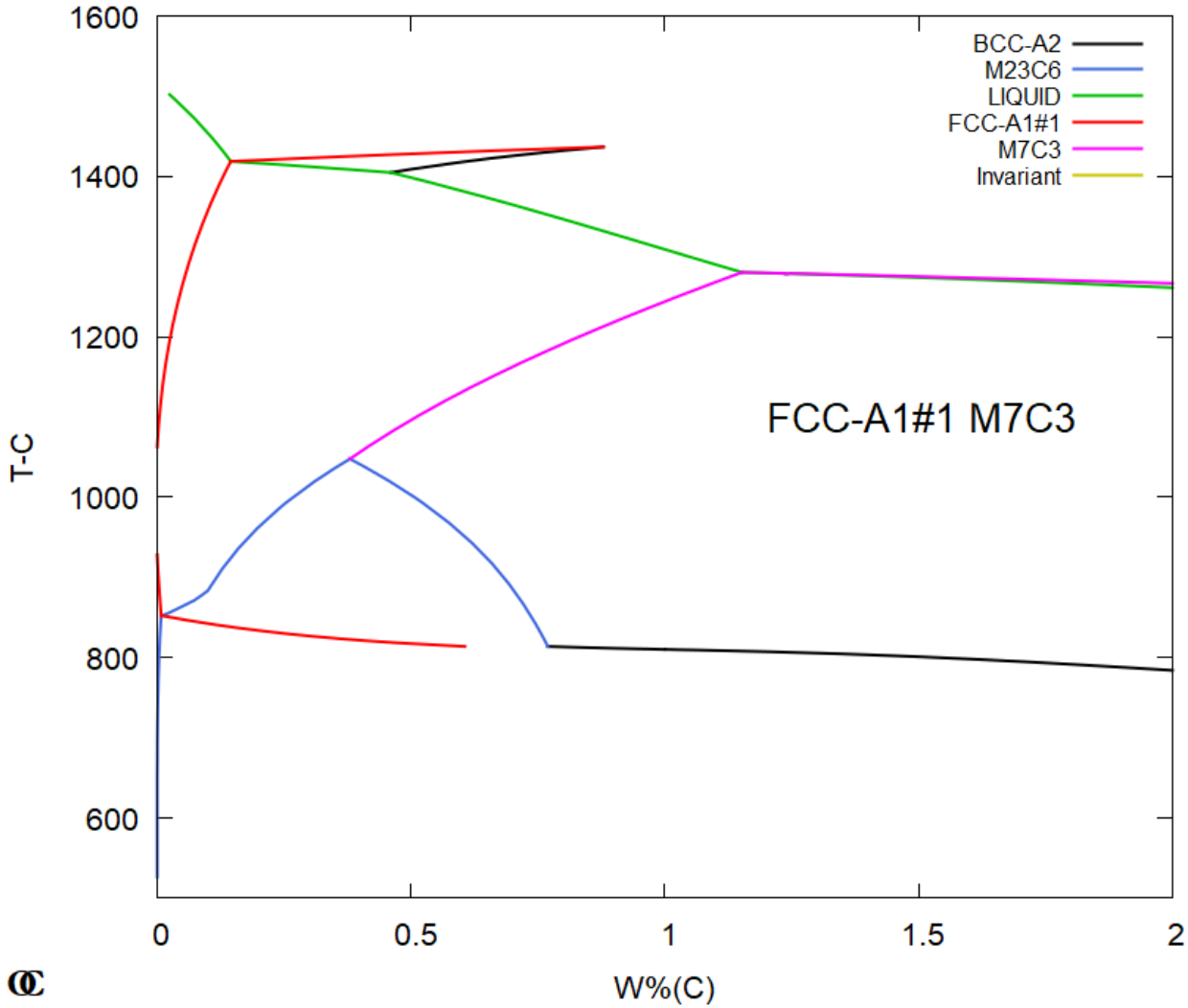
This line has liquid as fix and BCC as stable. It ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



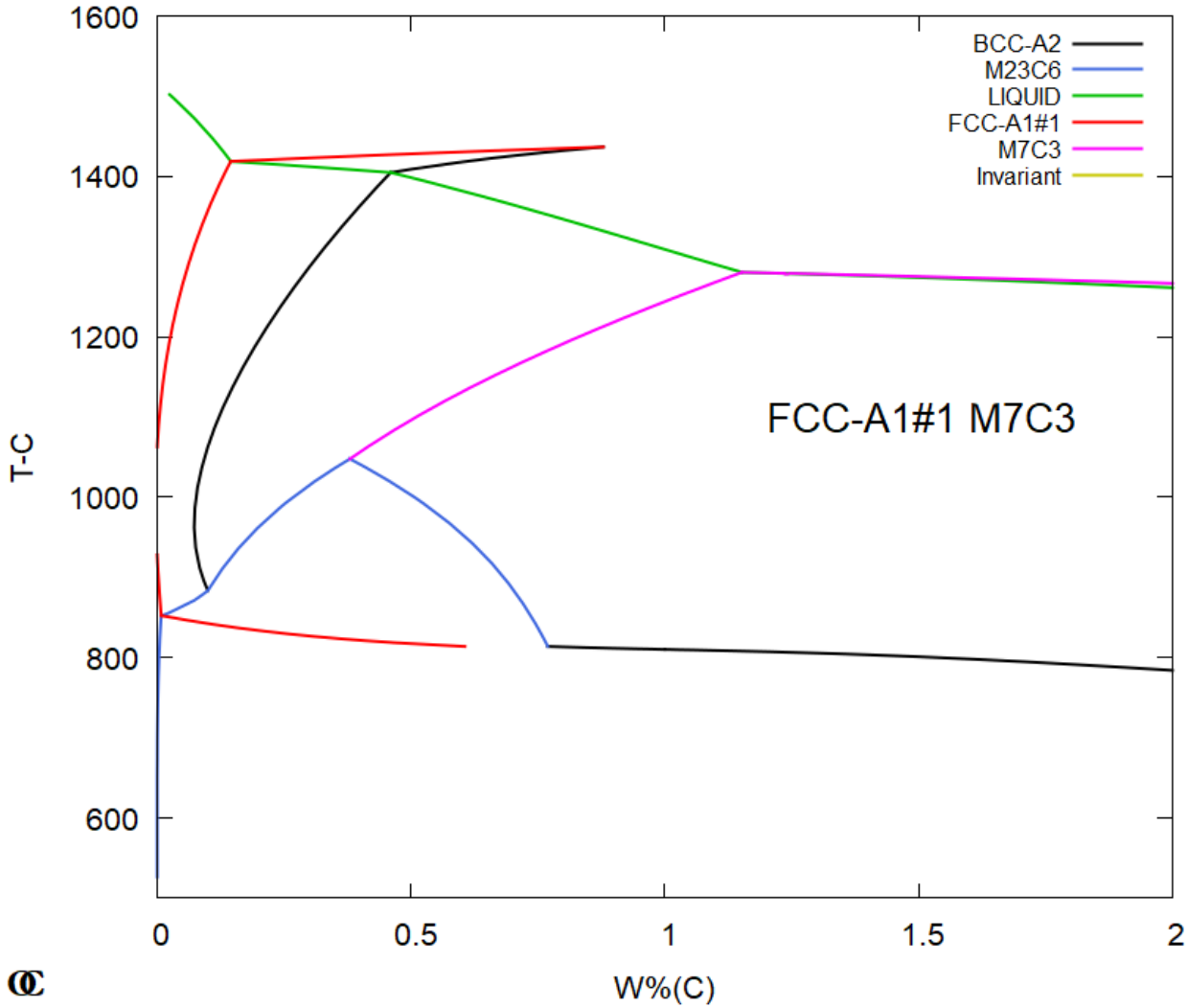
From the same node this exit has FCC as fix and liquid and BCC as stable. It ends when BCC is no longer stable. A node with 4 exits is generated.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



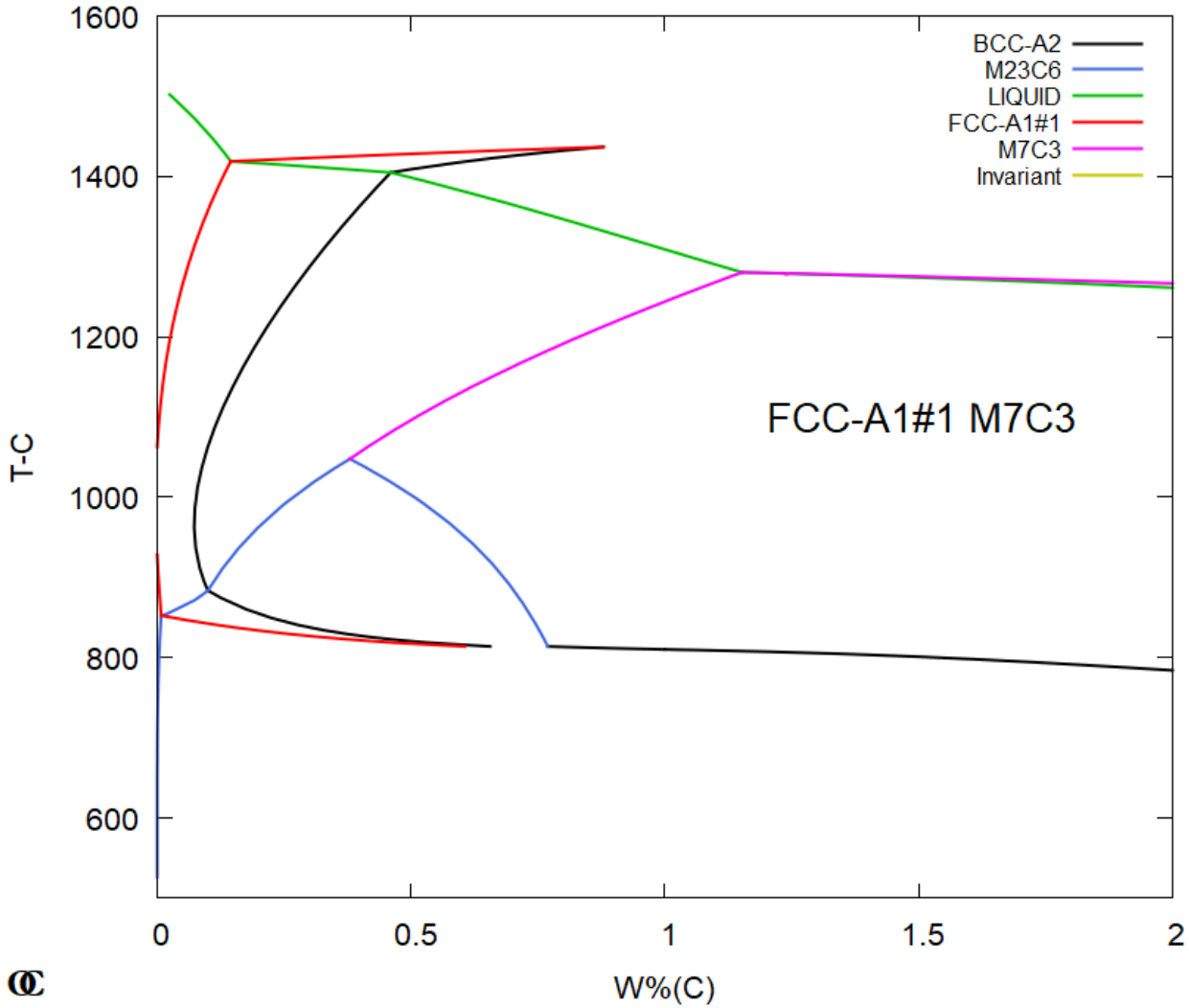
From the new node an exit with BCC as fix and liquid and FCC as stable gives this line. It ends at an already known node and the corresponding exit is removed. This line closes the 3 phase region with FCC, BCC and liquid stable.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



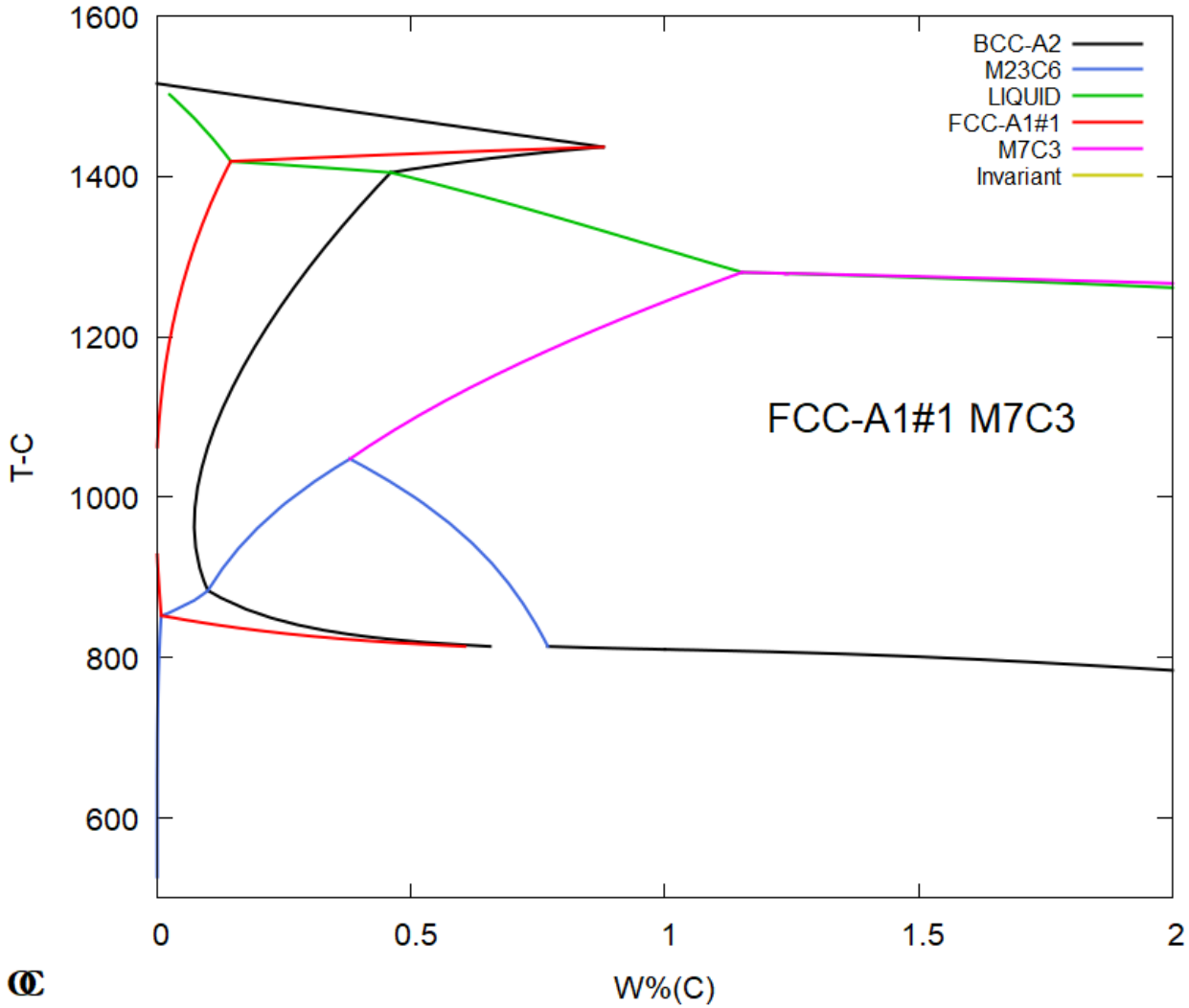
The final exit from this node with BCC as fix and FCC as stable is followed. The line ends when M23C6 becomes stable at an existing node and the corresponding exit is removed. This line closes the region with a single FCC phase.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



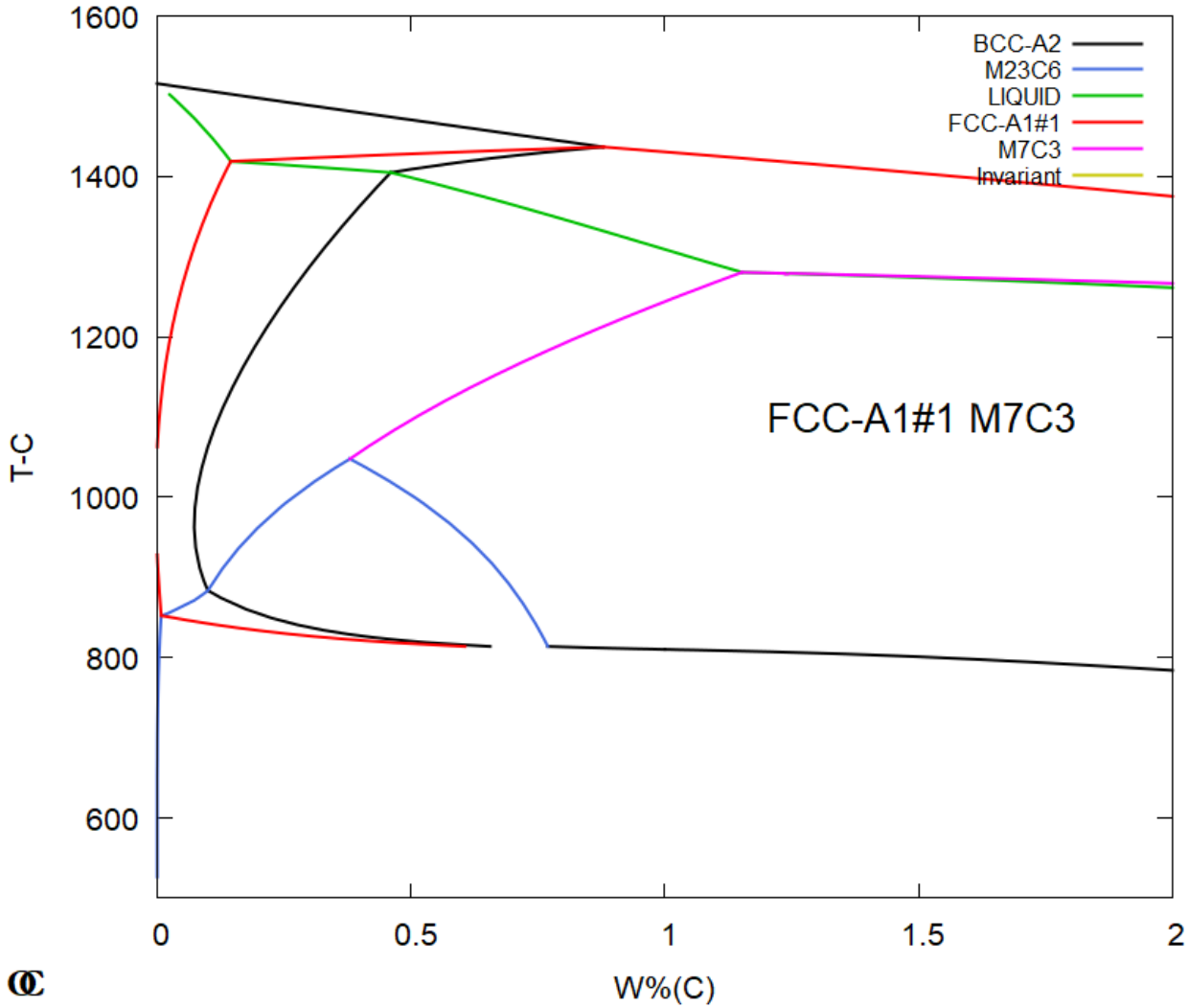
An exit from the last node with BCC as fix and FCC and M23C6 as stable is followed and ends when M7C3 becomes stable, i.e. at the invariant. The corresponding exit is removed.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



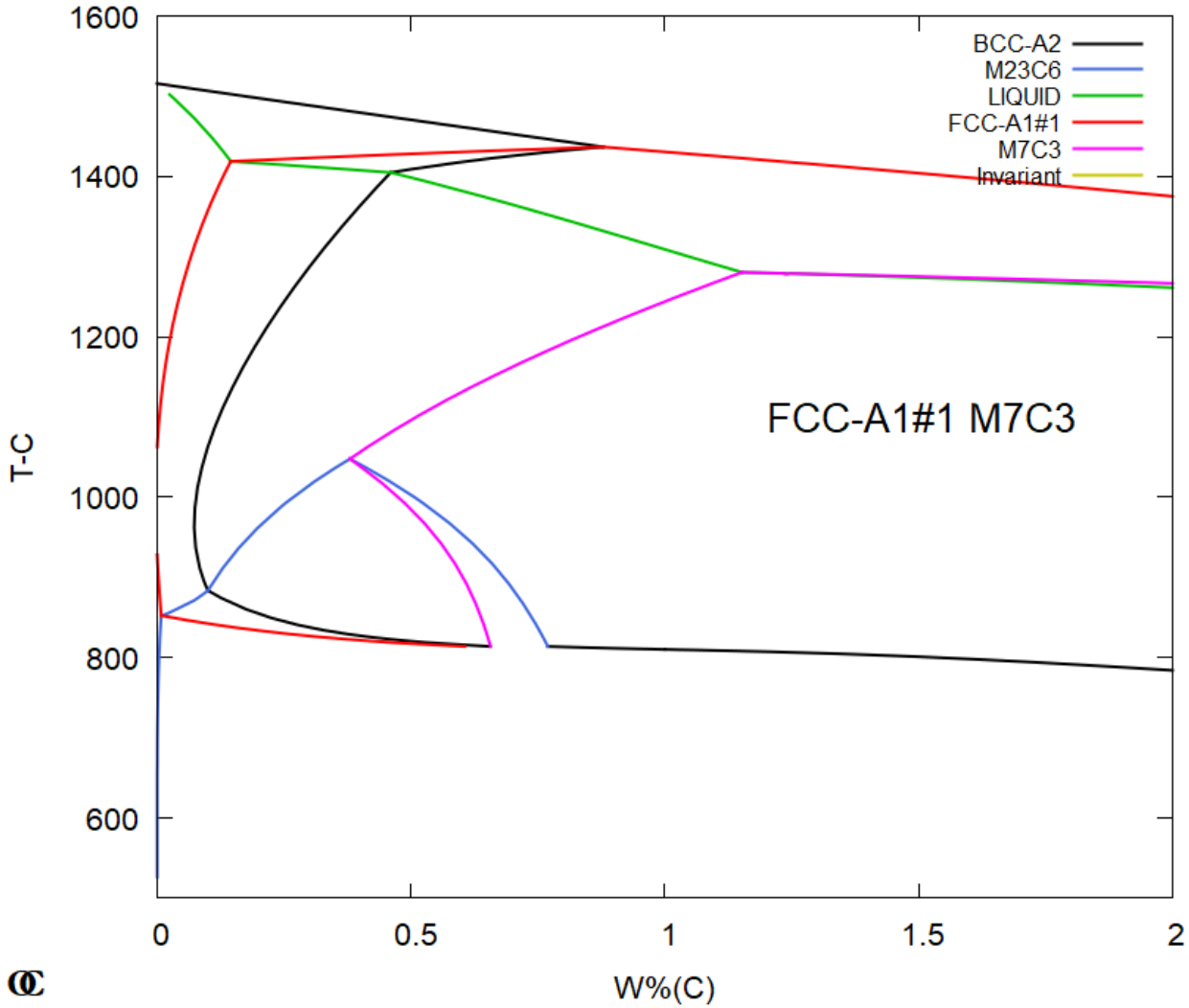
This line is calculated with BCC as fix and liquid as stable. It ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



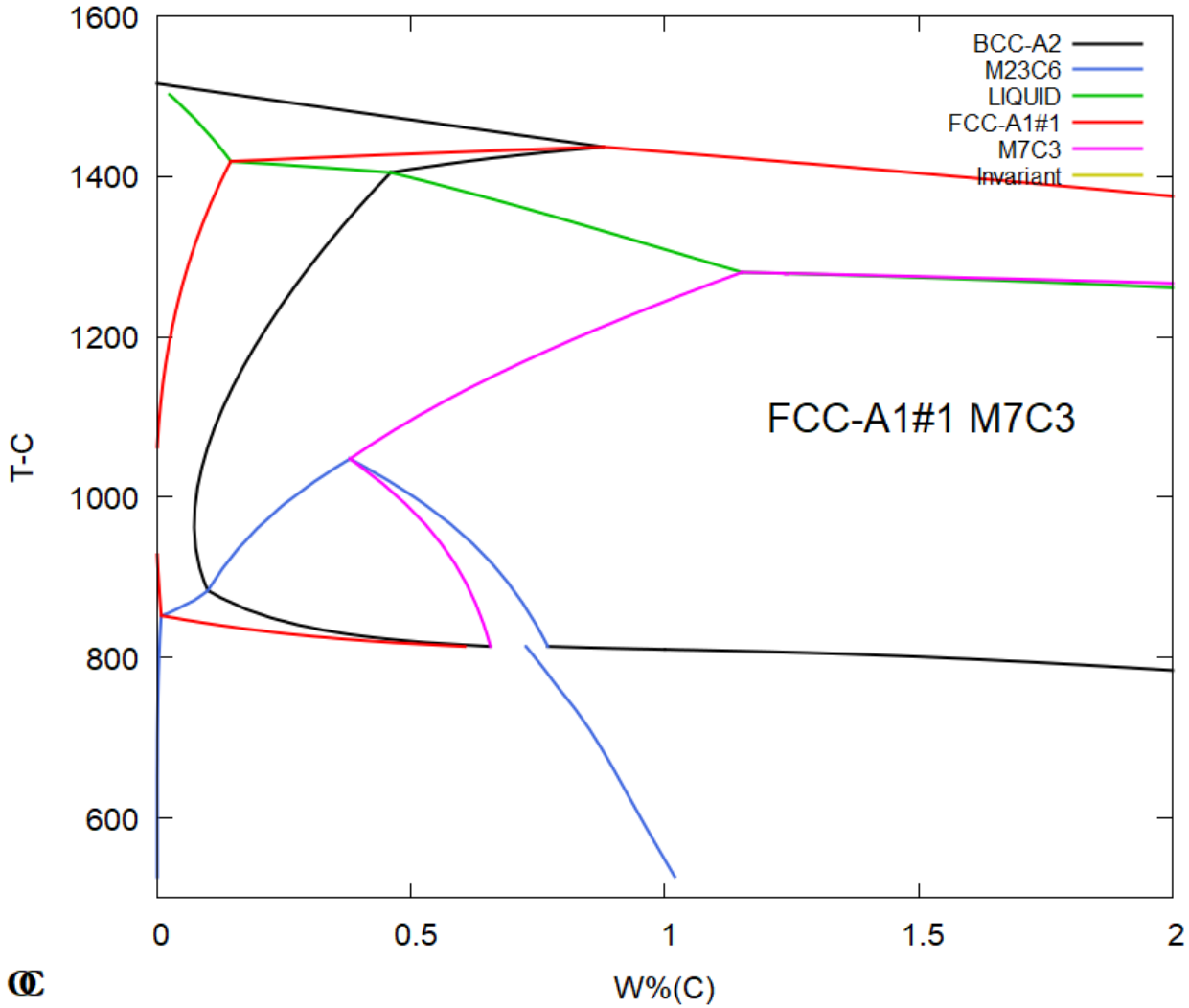
The liquidus line with FCC as fix and liquid as stable ends at the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



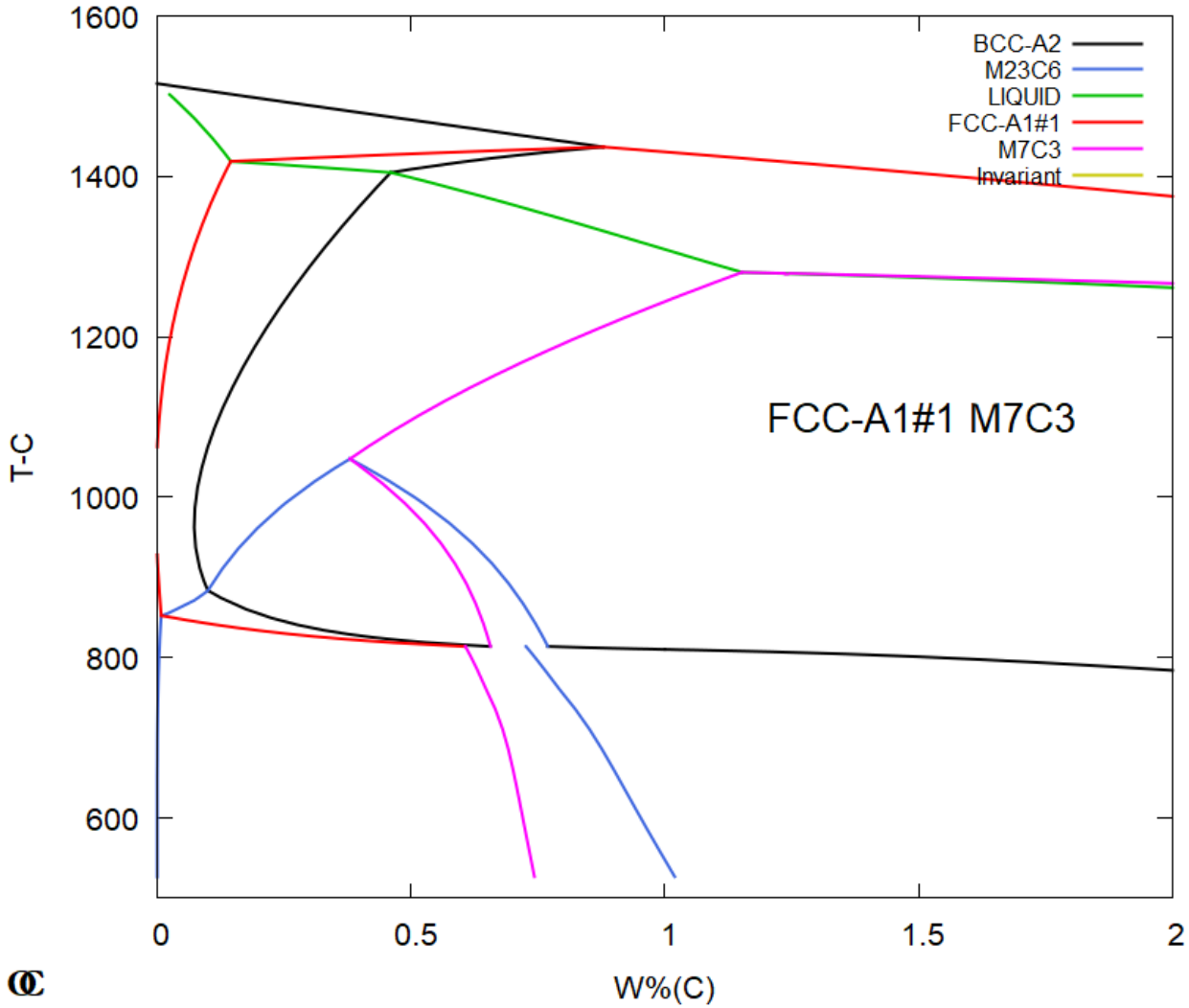
The final exit from this node with M7C3 as fix and FCC and M23C6 as stable gives this line. It ends when BCC becomes stable i.e. at the invariant equilibrium. The corresponding exit is removed.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



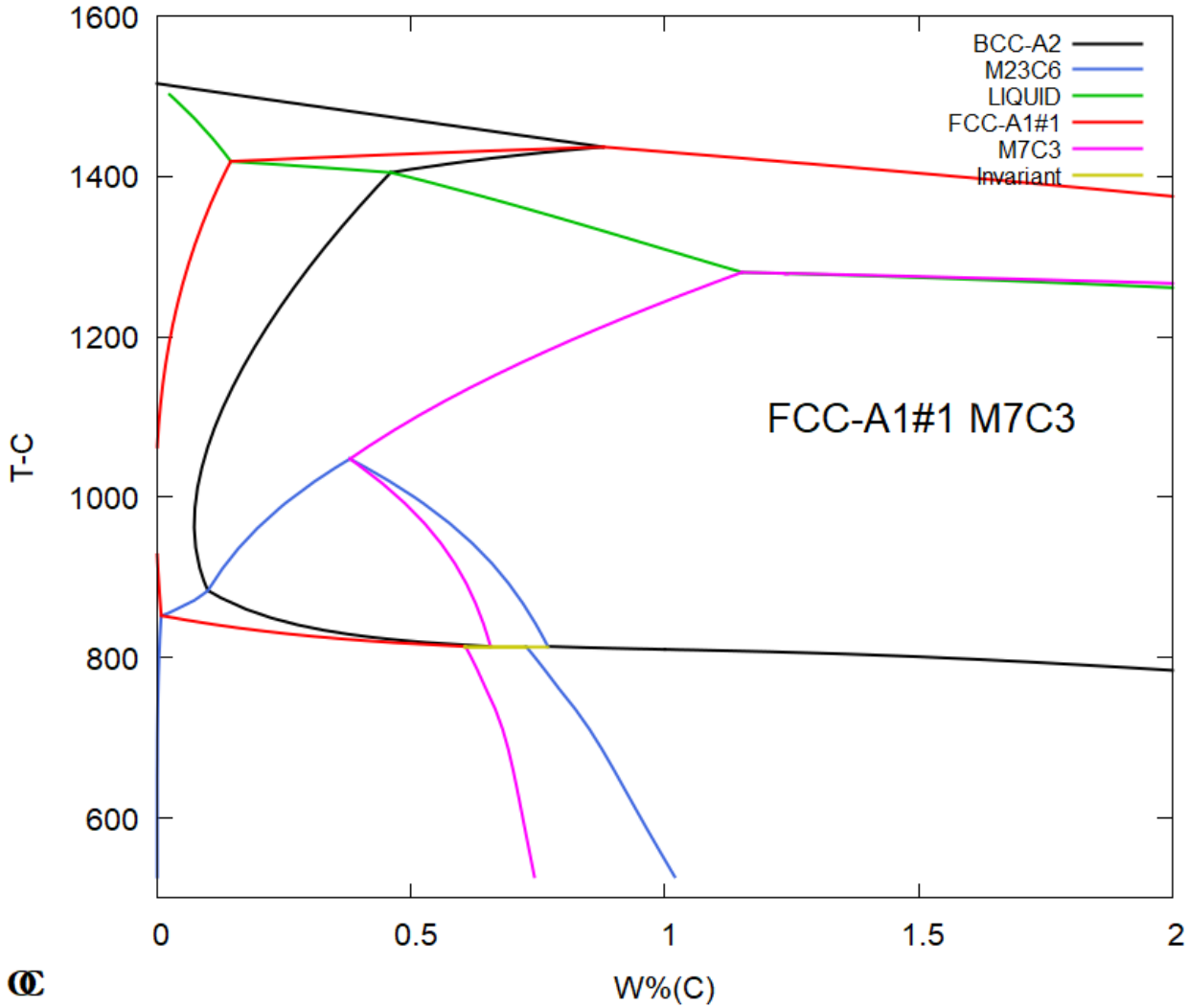
A remaining exit from the invariant with M23C6 as fix and BCC and M7C3 as stable is followed to the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



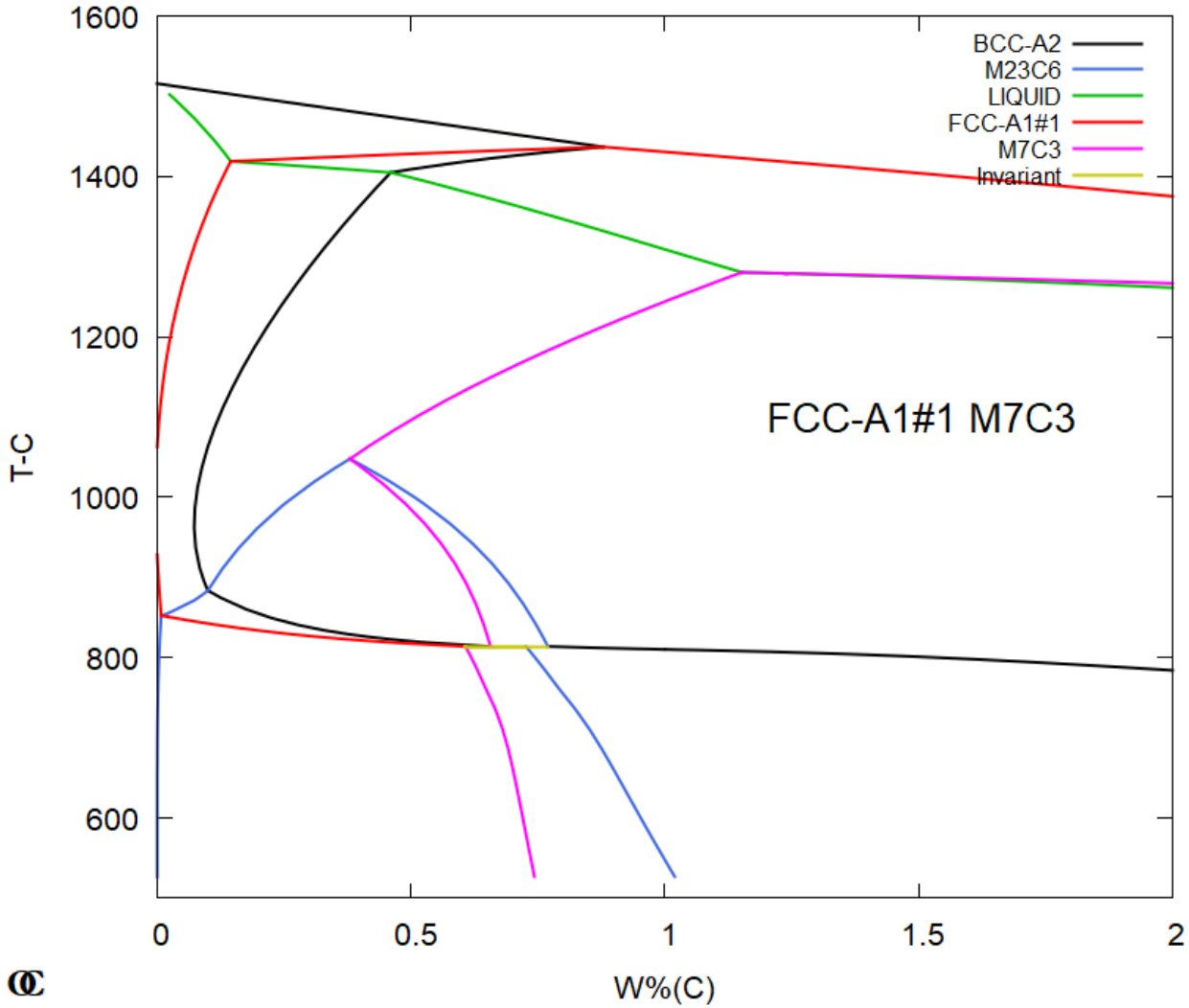
Another exit from the invariant with M7C3 as fix and M23C6 and BCC as stable is followed to the axis limit.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



The final exit follows the line with FCC as fix and BCC and M7C3 as stable gives this line which ends at the axis limit. It is almost identical to the first calculated line. The invariant is drawn.

How the mapping algorithm works for an iso-pleth Fe-13 w/o Cr-C



More details can be found in
B Sundman, N Dupin and B Hallstedt, Calphad, **75** (2021) 102330

Thermodynamic databases

The databases are the essential part of Calphad. But it is a tedious, slow and expensive work to develop high quality thermodynamic databases. For steels we have worked more than 30 years but still cover mainly the iron-rich corner for some 20 elements.

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In a good database all binary and most ternary systems should have model parameters with references to assessments based on experimental or theoretical data. As shown for Fe-Mo system the model parameters provides important information for metastable states where there are little or no experimental or theoretical data.
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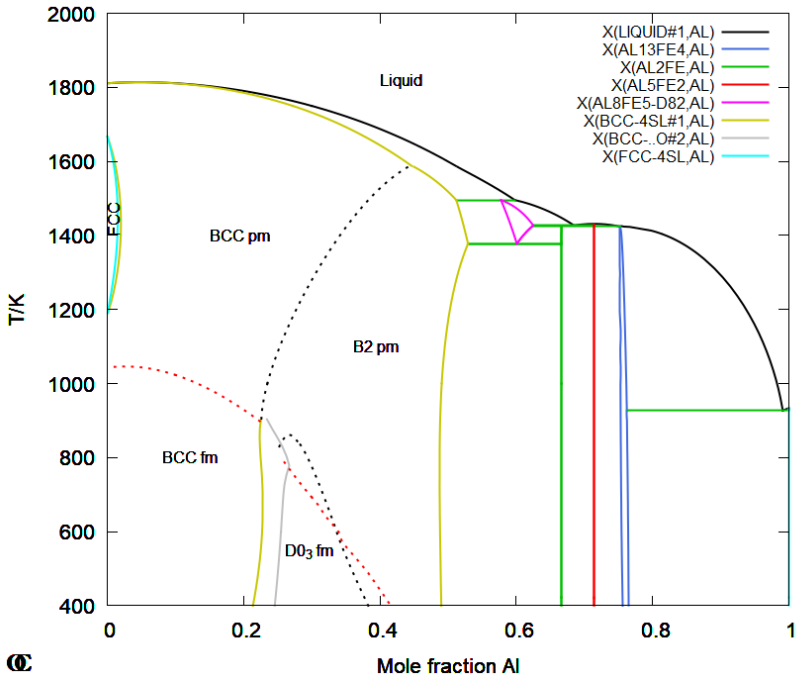
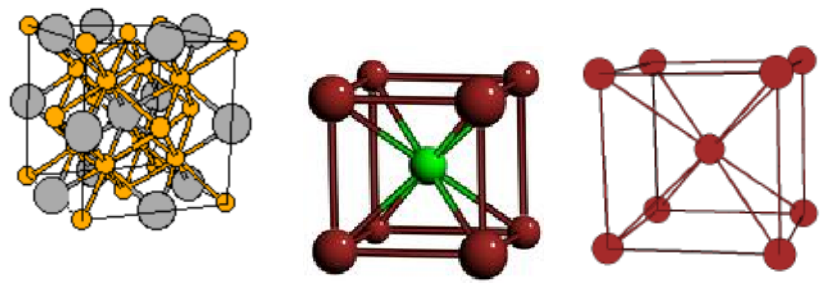
The database manager is a very important person.

Models for crystalline phases

Models are always approximate and has to be selected with care.
The Compound Energy Formalism (CEF) with sublattices and ideal mixing on each sublattice can handle most solid phases, including an approximate SRO contribution.
For physicists the lack of SRO has always been a problem to accept Calphad. But it seems that CEF models are now accepted for many intermetallics because when you already have LRO the SRO contribution is very small. But some of the assessments done by physicists do not treat the disordered state correctly and extrapolate badly.





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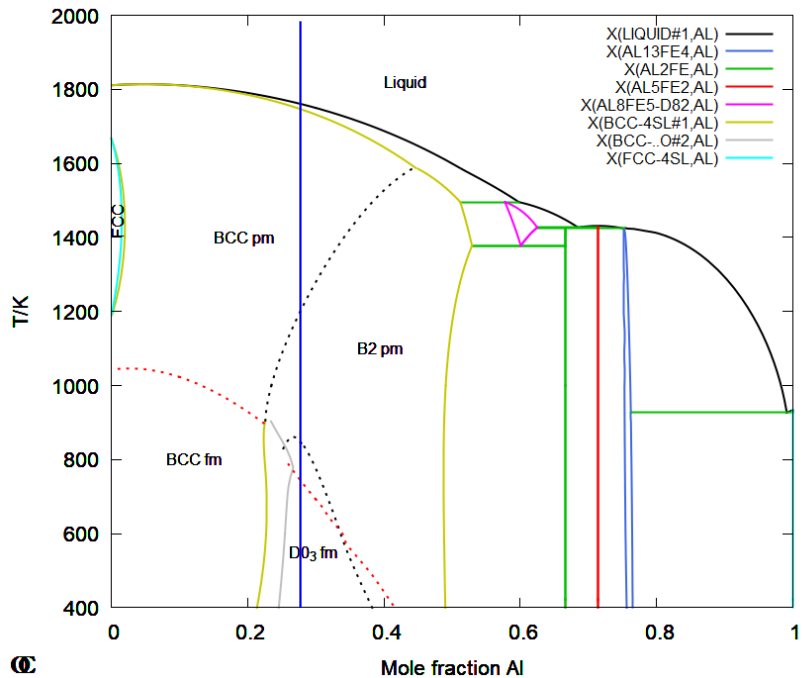

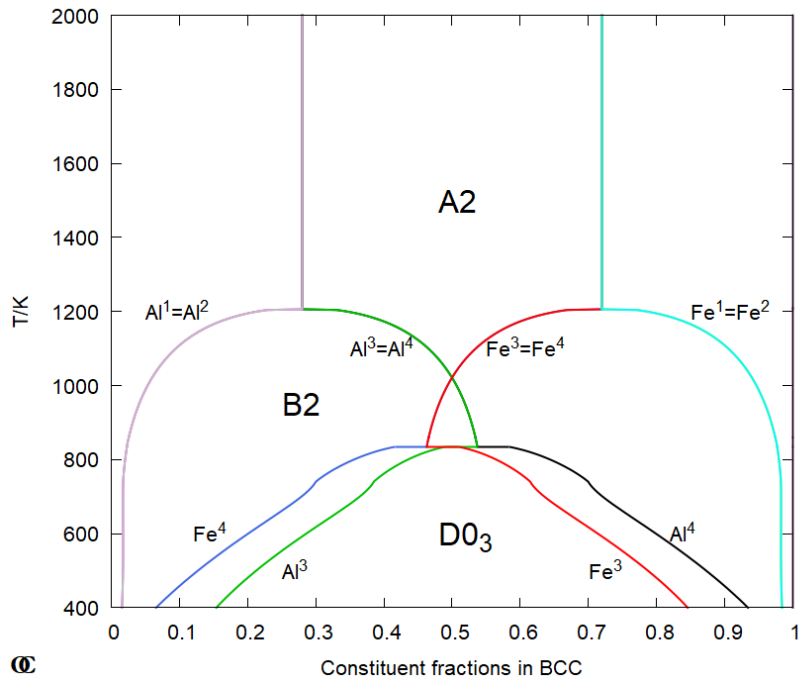

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Recently a modification of CEF, EBEF, has been proposed to simplify the use of DFT data and may improve multi-component extrapolations for intermetallics.
The magnetic model was included already in the SGTE unary 1991 and has been very important to extrapolate data for steels. The work on a new unary will extend the Calphad models down to 1 K and may improve many things. But new models such as EEC may make extrapolations less easy to control.

Models for the liquids with and without SRO

- The regular solution model with ideal configurational entropy. Works well for multi-component metallic liquids and similar.
- The associated model. It is useful in binary and some ternary systems but extrapolates badly to higher order systems.
- The Temkin model for ionic solutions, treating SRO as LRO. Works well for molten salts, oxides and similar systems with strong SRO.
  (When Hillert 1970 introduced the 2-sublattice model for C dissolved in austenite he used a Temkin model and not CVM because he knew SRO was insignificant.)
- The partially ionic 2 sublattice liquid model (I2SL), extends the Temkin model with vacancies (for metallic liquids) and neutrals. It works well with metals and stongly ionic liquids but has problems with some multi-component extrapolations.
- The Modified Quasichemical Model (MQM) use a quasichemical model with 2 bonds/atom, i.e. a one dimensional chain. It works well with weak SRO and extrapolates well to higher order systems. But or strong SRO the configurational entropy may become negative.
- The MQM with Quadruplet Approximation (MQMQA) merges MQM with the Temkin model in an attempt to handle both strong LRO and weak SRO.

Calphad is the link between theory, experiments and applications

There are annual Calphad meetings and at my first meeting in 1979 almost half of the participants were experimentalists and most of them could not understand how anyone could be interested in calculating something they could measure.

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There are still many experimentalists at the Calphad meetings and most DFT experts have realized that the the energy differences between stable and metastable states are too small to calculate, one must at least use experimental phase diagram data. The use of SRO is not important when extrapolating to multi-component systems because the number of clusters will be so high that each has insignificant probability. The use of Calphad databases and methods in simulations for research and industry is growing.

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Recent computational techniques such as AI or ML predict properties of materials based on a large amount of experimental and theoretical information without the use of models for the individual phases. They can not extrapolate as Calphad and do not provide data for simulations. But they can indicate systems which should be properly assessed for example in High Entropy Alloys (HEA).

End of lecture

Thanks for listening ...

... but there is still a lot of work to do ...

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