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Order, disorder and stability in Be intermetallics for fusion applications

Robin Grimes
Imperial College London, r.grimes@ic.ac.uk

Matthew Jackson
Imperial College London

Patrick Burr
University of New South Wales

Simon Middleburgh
Westinghouse

Imperial College London

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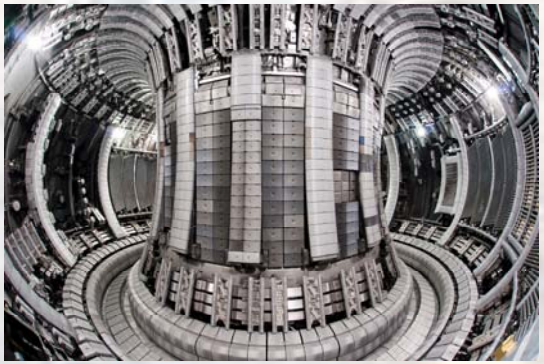
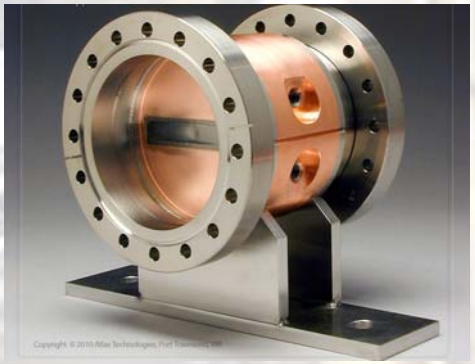


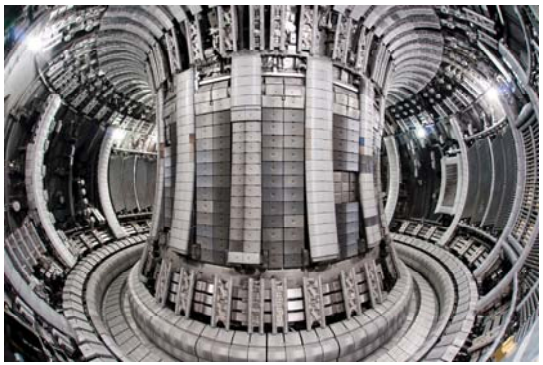
Patrick Burr, Simon Middleburgh, Matt Jackson & Robin Grimes

The issues addressed

- The Results
  - Finding the structure of the binary Fe-Be ε phase
  - Revisiting the binary Fe-Be system:
    Temperature effects and anharmonic contributions
  - Effect of Al additions (ternary Al-Fe-Be system)
  - Order/disorder in Fe-Al-Be intermetallics
  - The structure of $Be_{12}Ti$
  - Non-stoichiometry and defect association in $Be_{12}Ti$ and $Be_{12}V$
- Summary: what has all this atomic scale stuff told us or could tell us?

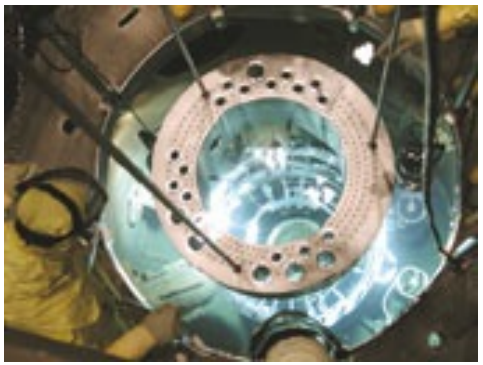
Introduction: Be applications

- Uses: fusion reactors[1], satellite component[2], radiation windows[4], neutron multipliers & reflectors[3].

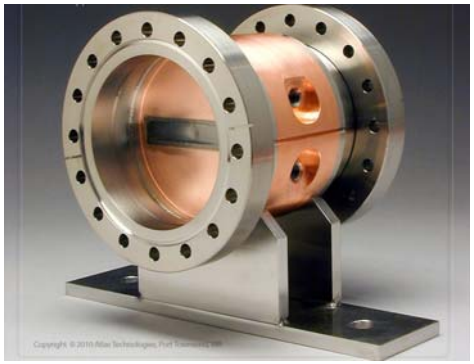


[1]

[2]



[3]



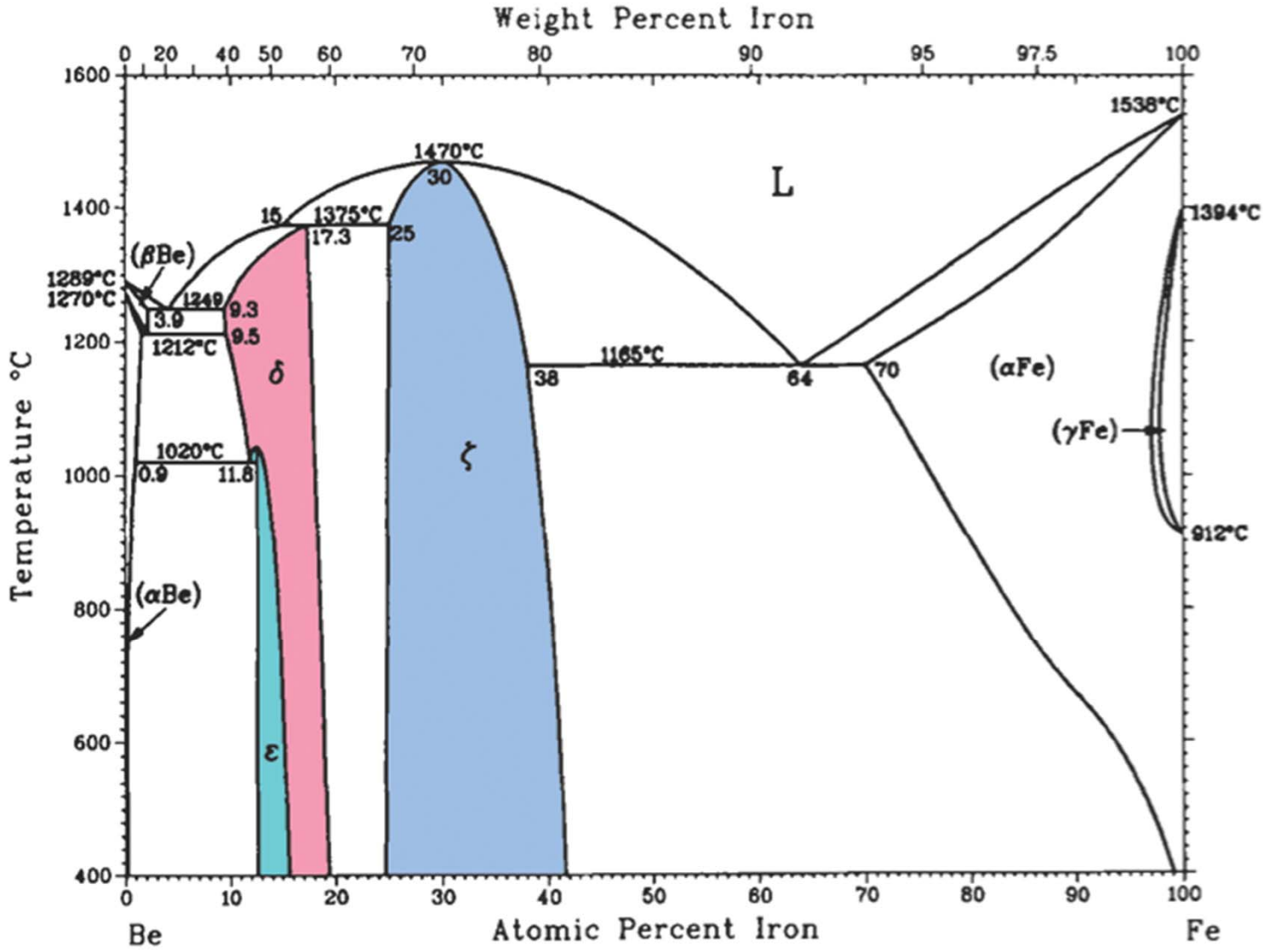
[4]

- Be alloys often contain impurities. Typical alloy composition (in *wt*%):

O	Al	Fe	C	Mg	Si	Tr Met (each)
0.5-2.2	**0.07**	**0.12**	0.12	0.07	0.07	0.04

- $Be_{12}Ti$ and $Be_{12}V$ are alternatives to Be for fusion applications, having adequate neutronic properties but lower tritium retention and swelling, better rad tolerance and improved embrittlement behaviour.

Introduction: Fe-Be system



ζ – $FeBe_2$

δ – $FeBe_5$

ε – $FeBe_{11}$?

Modified from: Okamoto and Tanner, Bull Alloy and Phase Diagrams, **9** (1988) 494-508

Methodology

- All results from Density Functional Theory (DFT)
- Planewave code (Castep)
- PBE exchange-correlation functional
- Cut-off energy 400 eV (550 eV for extrinsic defects)
- k-point spacing <0.03 $Å^{-1}$
- Supercell size 192-216 atoms
- OTF generated Pseudo-potentials from Castep library

Literature on ε phase

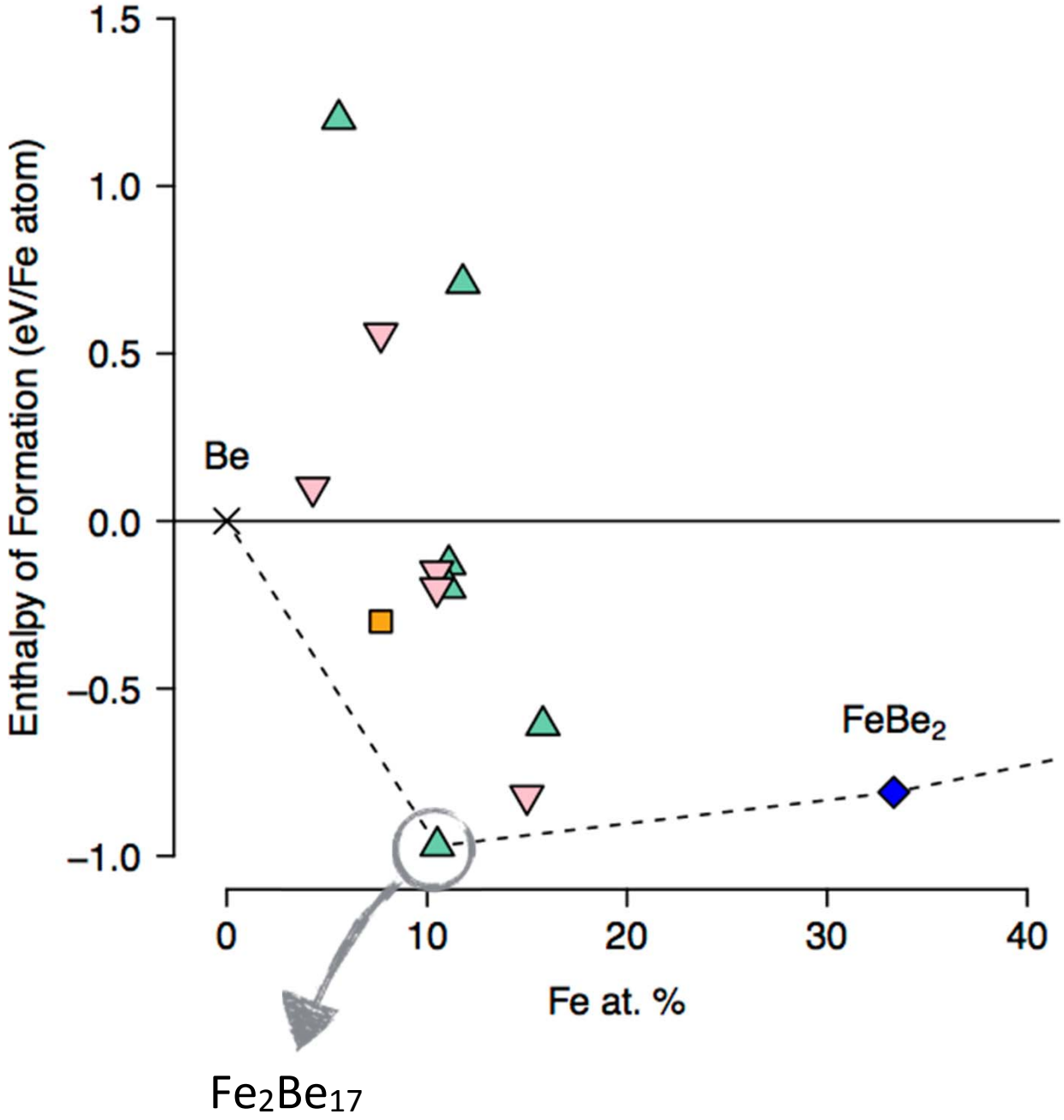
Composition	Crystal class	Prototype structure	Space group	Atoms per unit cell	a (Å)	c (Å)	Reference
$FeBe_9$	—	—	—	—	—	—	†
$FeBe_{11}$	Hex	—	—	18	4.13	10.71	[4]
$FeBe_{12}$	Tetr	$Mn_{12}Th$	I_4mmm	13	4.323	7.253	[5]
$FeBe_{11}$	Hex	—	—	—	4.13	10.71	[12]
$FeBe_x$	Hex	$RhBe_{6.6}$	$P\bar{6}m2$	19*	4.137	10.72	[6]
$FeBe_{11}$	Hex	—	—	—	4.13	10.72	[22]
$FeBe_7$	Hex	—	—	—	7.13	10.99	[7]
$FeBe_{11}$	Hex	—	—	—	7.15	10.72	[8]

[4] Teitel and Cohen, Trans. Am. Inst. Mining, Metall. Pet. Eng. **185** (1949) 285–296.
[5] von Batchelder and Raeuchele, Acta Crystallogr. **10** (1957) 648–649.
[12] Rooksby, J. Nucl. Mater. **2** (1962) 205–211.
[6] Johnson *et al.* Acta Crystalogr. **B26** (1970) 109-113.
[22] Levine and Luetjering, J. Less common Met. **23** (1971) 343–357.
[7] Aldinger and Petzow, p.267 in Beryllium Sci. Technol. Vol. 1, Webster and London (Eds.), Plenum, London, 1979
[8] Jönsson, Kaltenbach and Petzow, Z. für Met. **73** (1982) 534–539.

Simulated structures of ε

Composition	Crystal class	Prototype structure	Space group	Atoms per unit cell	a (Å)	c (Å)	H_f (eV)
Fe_2Be_{17}	Hex	$RhBe_{6.6}$	$P\bar{6}m2$	19	4.10	10.63	−0.97
$FeBe_8$ (1)	Hex	$RhBe_{6.6}$	$P\bar{6}m2$	18	4.09	10.72	−0.13
$FeBe_8$ (2)	Hex	$RhBe_{6.6}$	$P\bar{6}m2$	18	4.10	10.63	−0.20
Fe_2Be_{15}	Hex	$RhBe_{6.6}$	$P\bar{6}m2$	17	4.15	10.45	0.71
$FeBe_{17}$	Hex	$RhBe_{6.6}$	$P3m1$	18	4.11	10.64	1.20
$FeBe_{12}$	Tetr	$Mn_{12}Th$	I_4mmm	13	7.16	4.09	−0.30
$FeBe_{12}$	Hex	Fe_6Ge_6Mg	$P6/mmm$	13	4.15	7.16	0.56
$FeBe_{13}$	Cubic	$NaZn_{13}$	$Fm\bar{3}c$	28	6.98	—	2.66
Fe_2Be_{17}	Hex	Th_2Zn_{17}	$R\bar{3}m$	57	5.41	—	−0.20
Fe_2Be_{17}	Hex	$Ni_{17}Th_2$	$P6_3/mmc$	38	7.11	7.04	−0.15
Fe_3Be_{17}	Cubic	$Be_{17}Ru_3$	$Im\bar{3}$	160	10.99	—	−0.82
$Be_{22}Fe$	Cubic	$Al_{18}Cr_2Mg_3$	$Fd\bar{3}m$	176	11.43	—	0.10

Simulated structures of ε

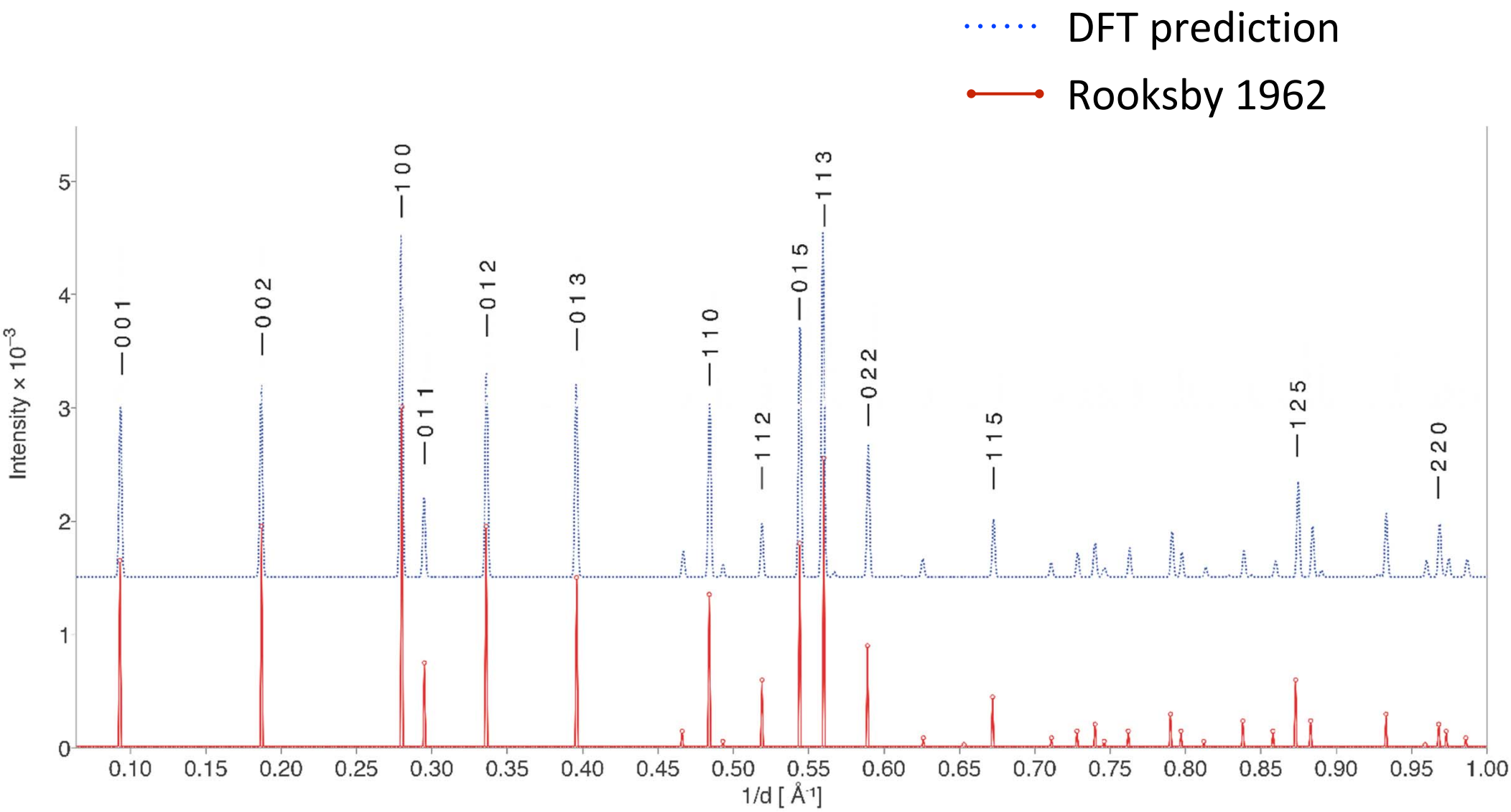


variations on $RhBe_{6.6}$

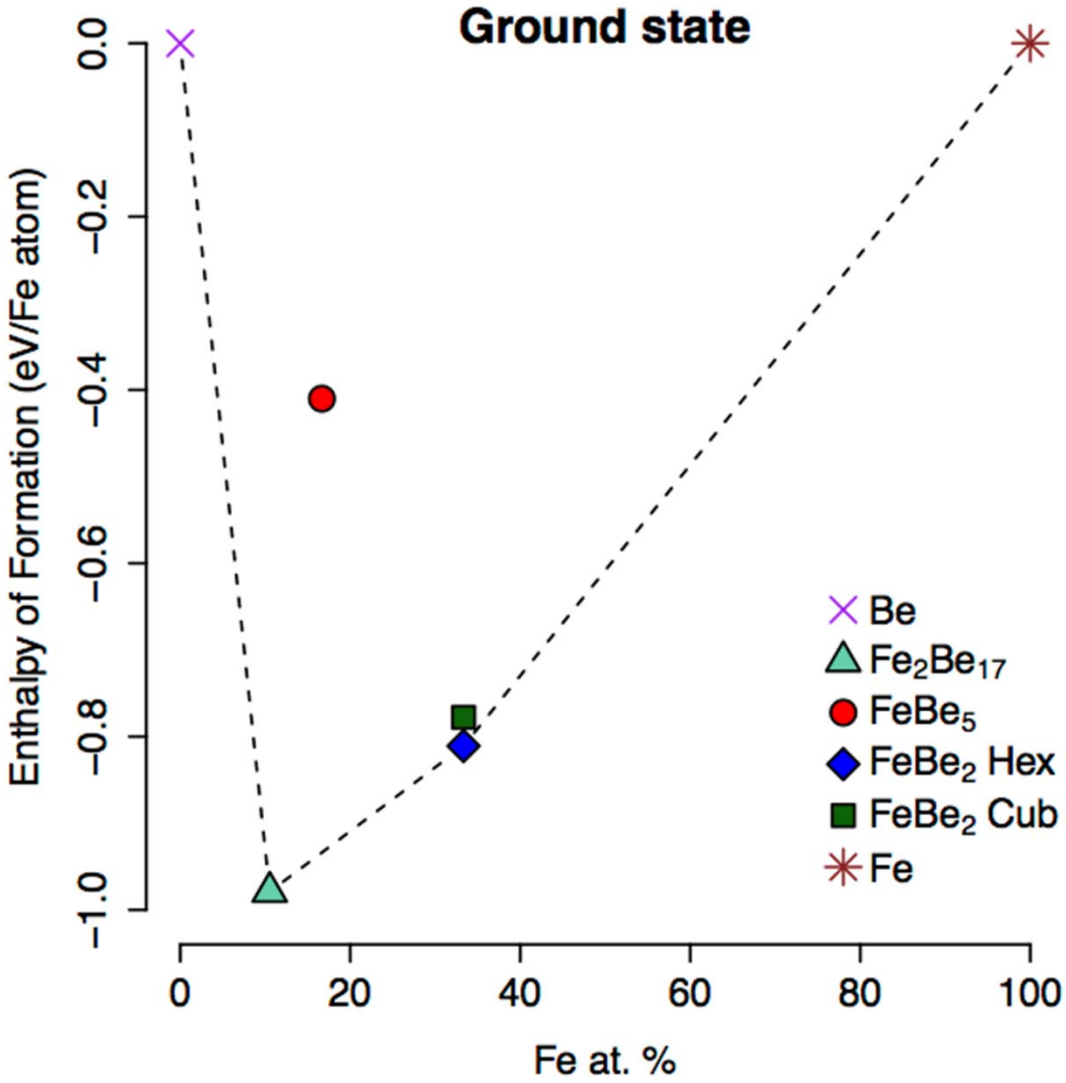
tetragonal $FeBe_{12}$

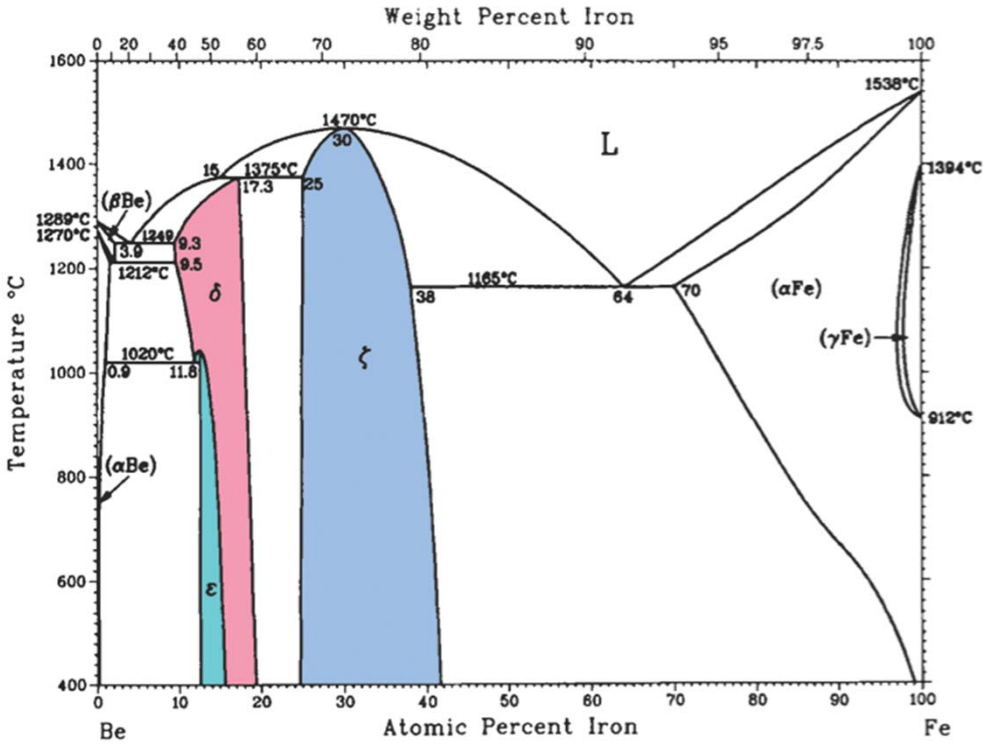
other Be intermetallic structures

Confirming the ε structure

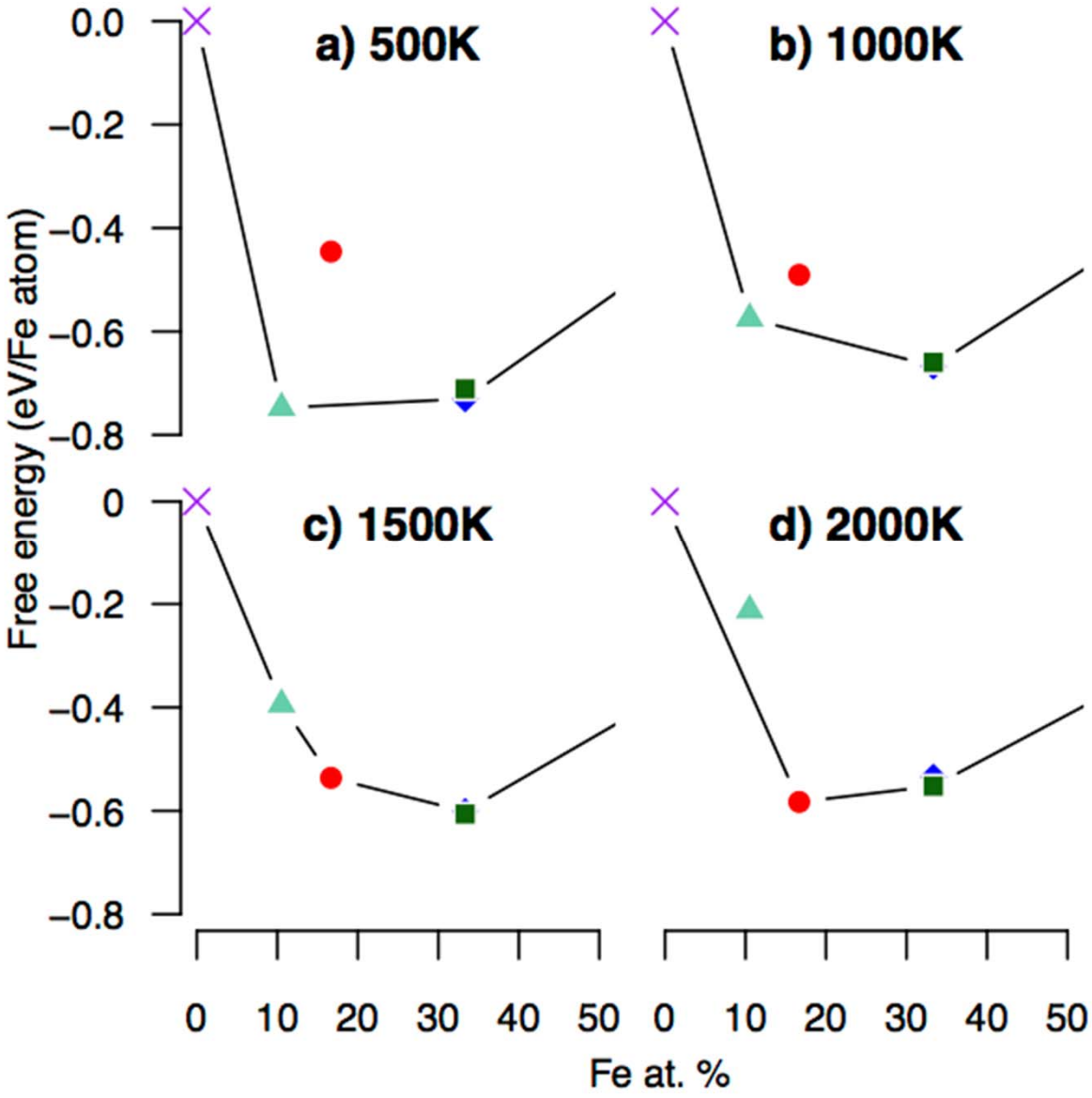


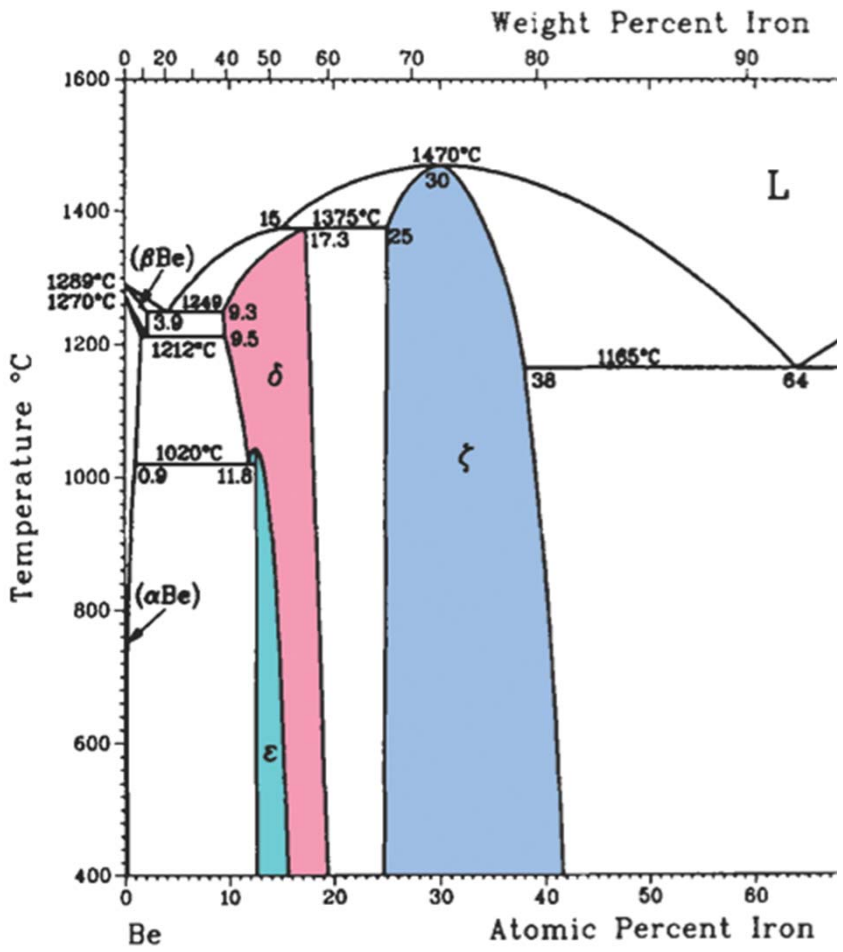
Binary Fe-Be system: ground state





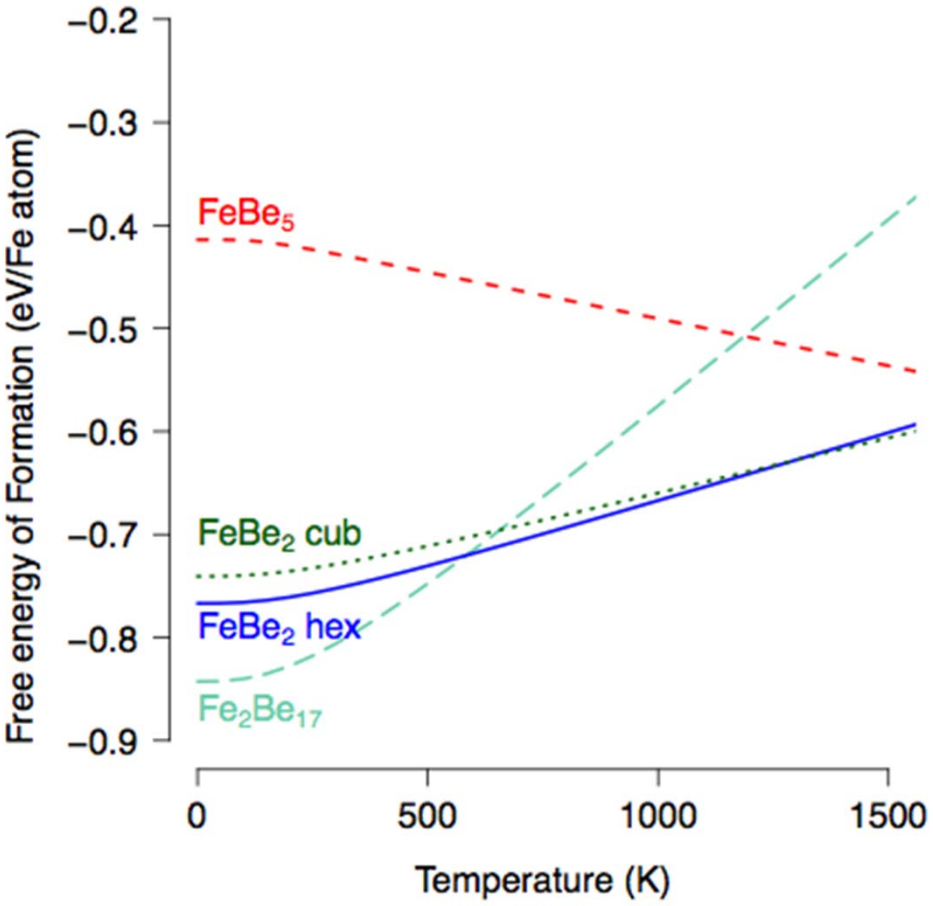
Binary Fe-Be system: temperature effects



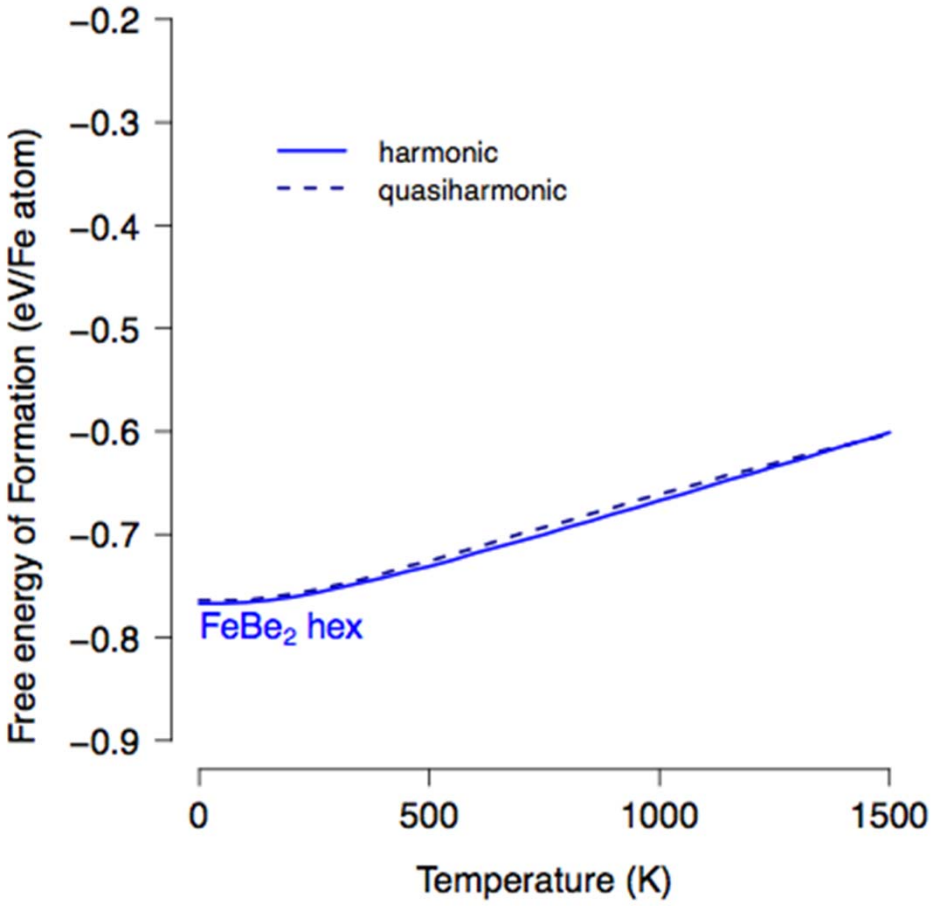


Role of anharmonicity

Harmonic approximation:
Helmholtz free energy



Harmonic vs Quasiharmonic
(Helmholtz vs Gibbs)
for hex-$FeBe_2$



Ternary Al-Fe-Be

Note: Al is insoluble in Be (as is Si)

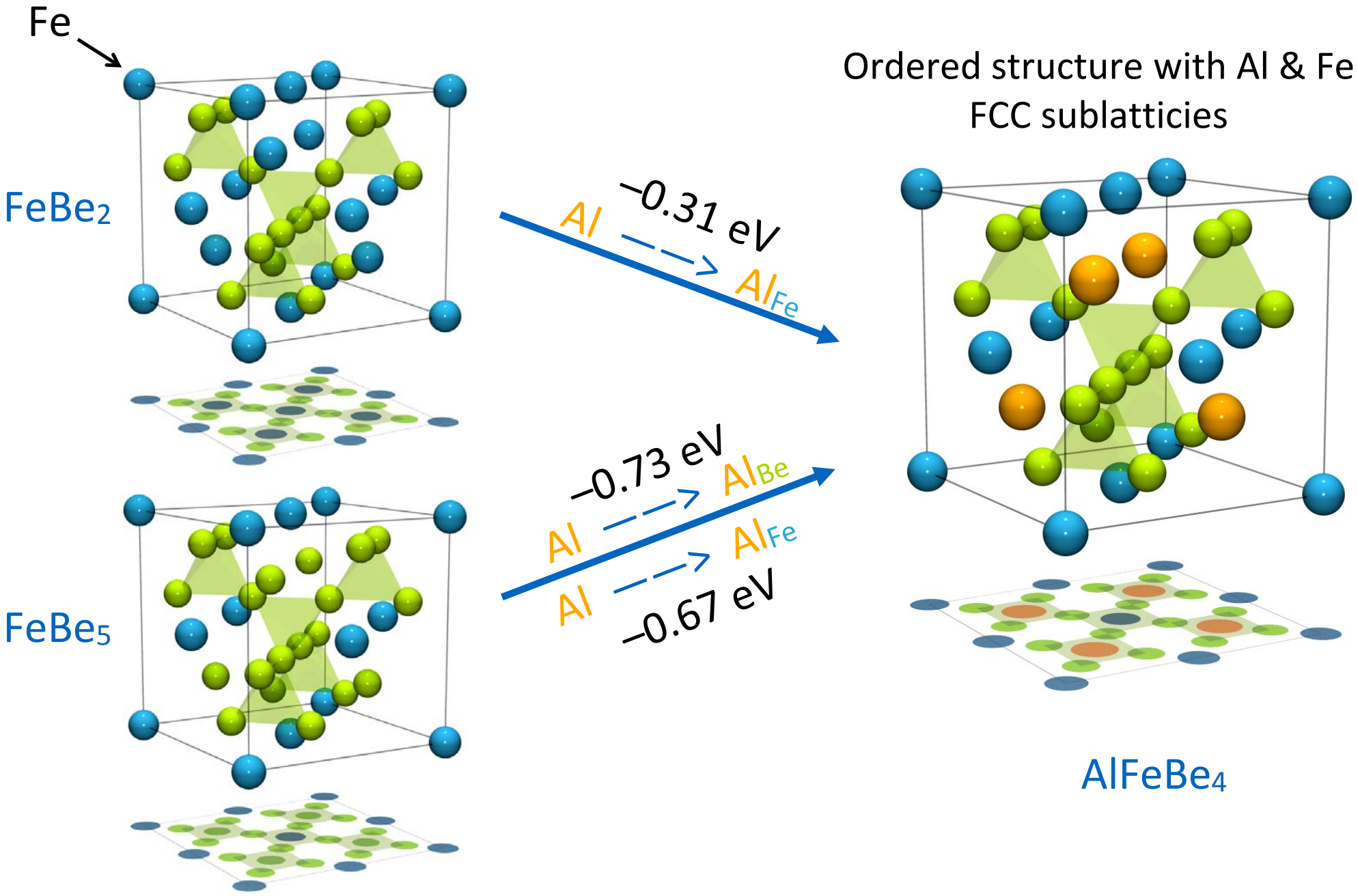
Dilute Al defects stabilise δ-$FeBe_5$ over other phases

	$FeBe_5$	$FeBe_2$	Fe_2Be_{17}
Al_{Be}	**–0.73**	0.79	–0.50
Al_{Fe}	**–0.67**	–0.31	0.27

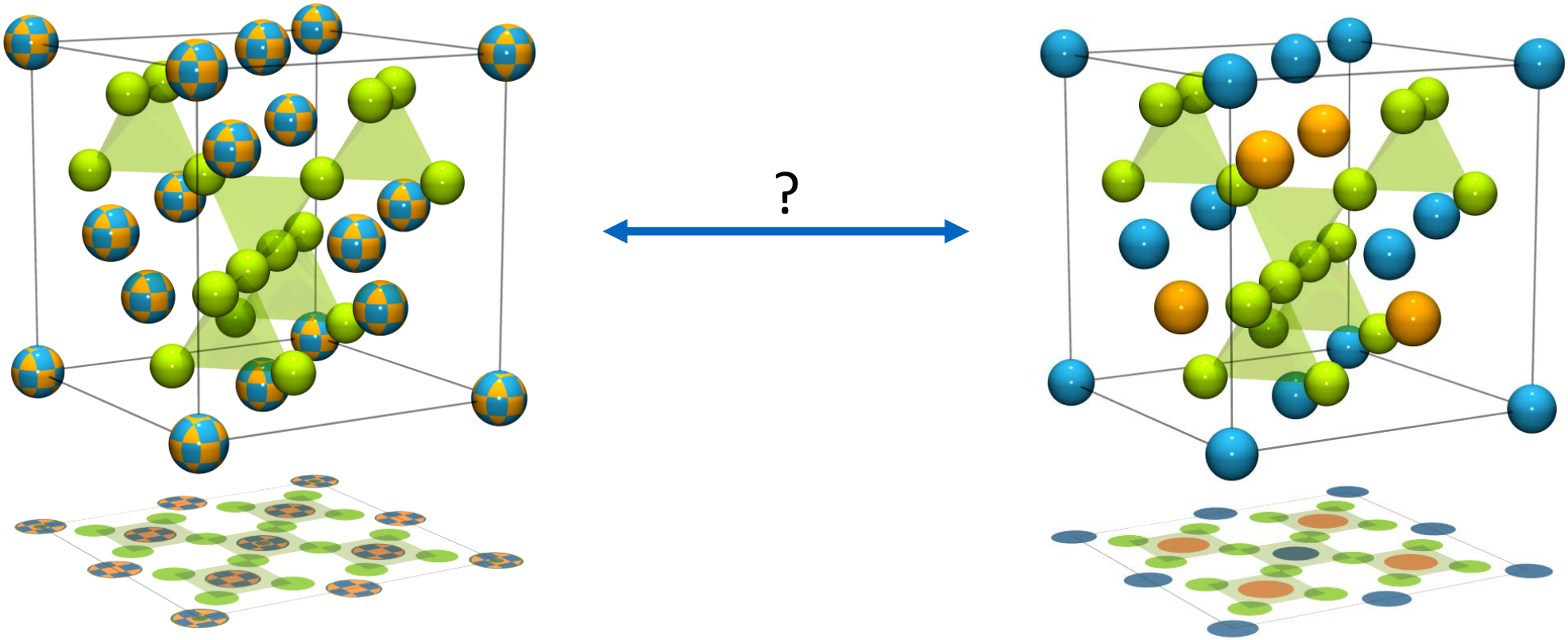
Higher Al concentration cause the formation of $AlFeBe_4$

	$FeBe_5$	$FeBe_2$	Fe_2Be_{17}
$AlFeBe_4$	–0.85	–0.49	–0.33

Ternary Al-Fe-Be



Order-disorder in $AlFeBe_4$

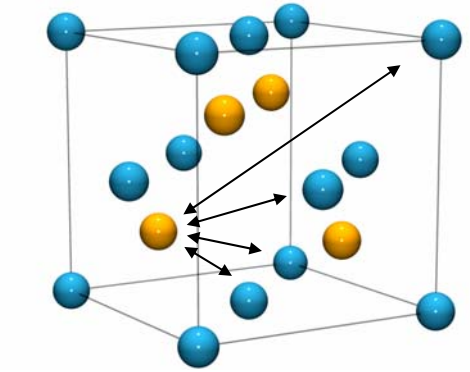


$(AlFe)_2Be_4$

$AlFeBe_4$

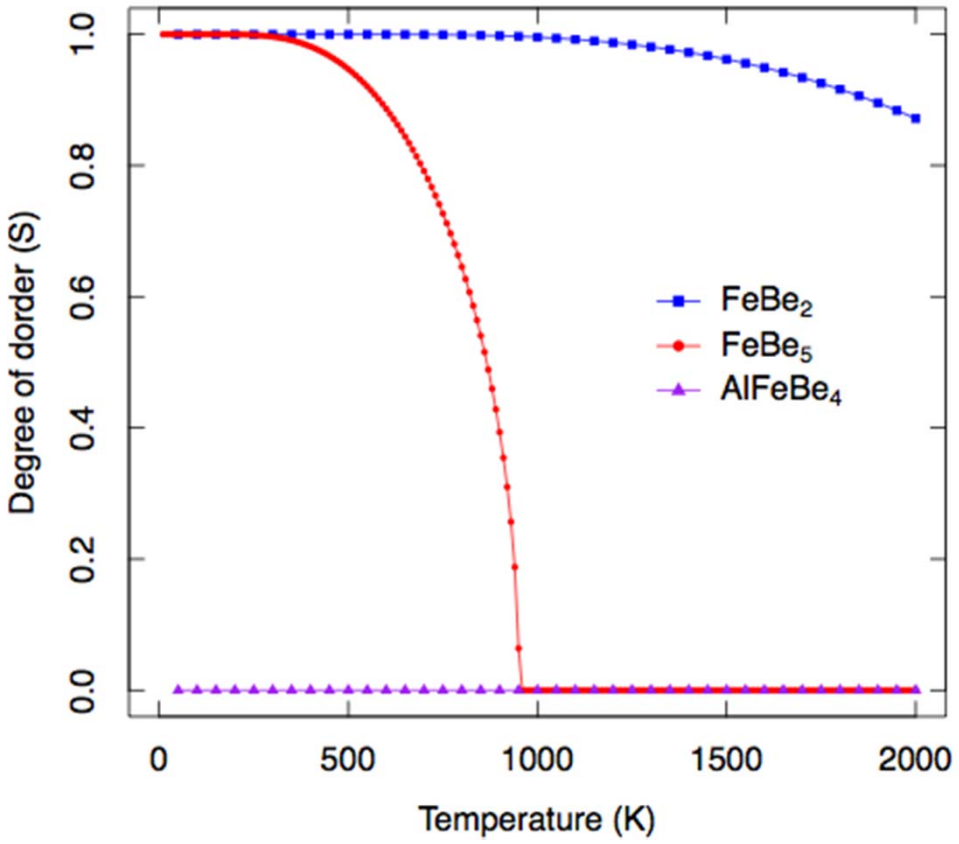
Order-disorder in $AlFeBe_4$

Bragg-Williams approach for disorder in solids is applied by considering the anti-site formation energy



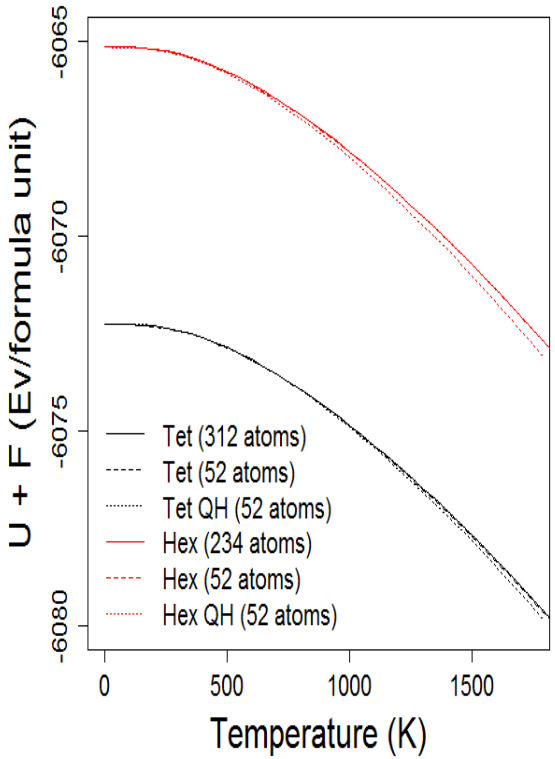
Formation enthalpy (eV)	$AlFeBe_4$	$FeBe_5$	$FeBe_2$
1nn	**–0.06**	0.67	1.99
2nn	**–0.06**	0.65	2.13
3nn	**–0.07**	0.64	2.22
4nn	**–0.11**	0.66	2.14
unbound	0.00	**-1.09**	2.18

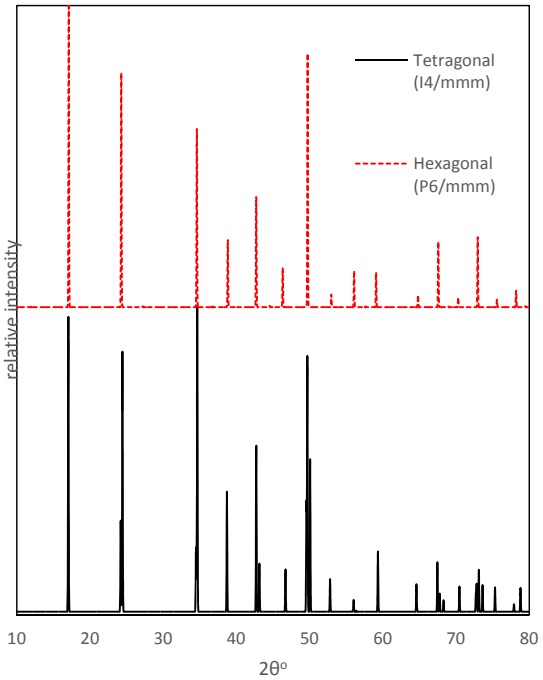
Only stable above ~1000K

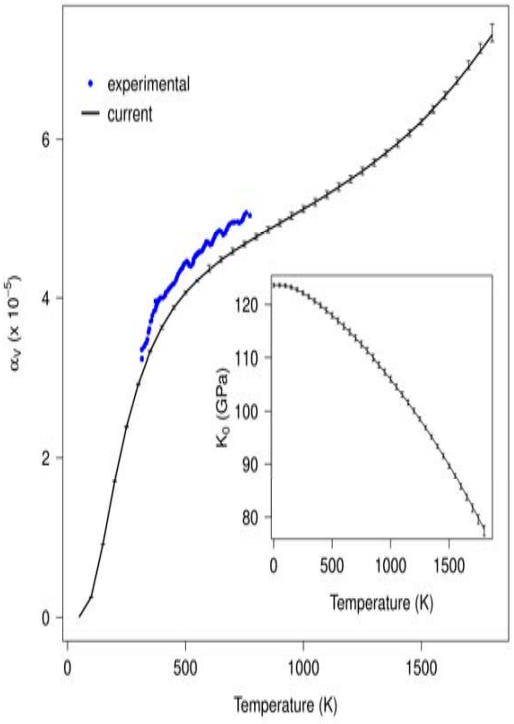


The structure of $Be_{12}Ti$

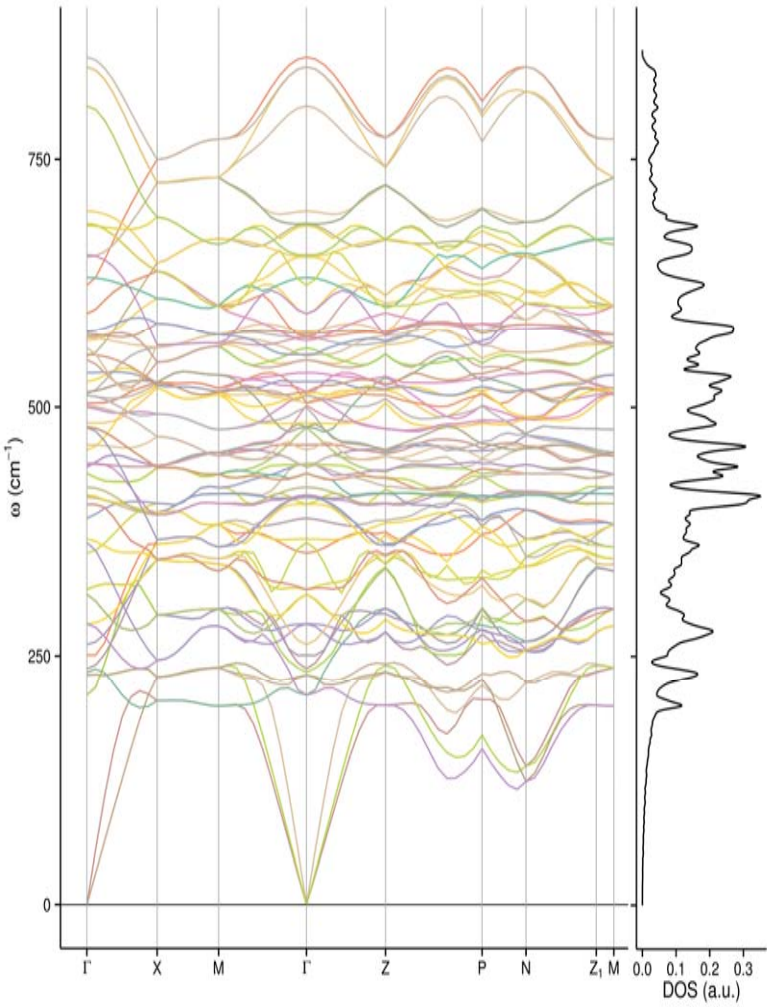
- Two phases reported - I_4/mmm (tetragonal) & P_6/mmm (hexagonal) – very similar aside from position of Ti
- Quasi-harmonic approximation used to evaluate high(er) temperature properties
- Tetragonal shown to be stable over all temperatures investigated



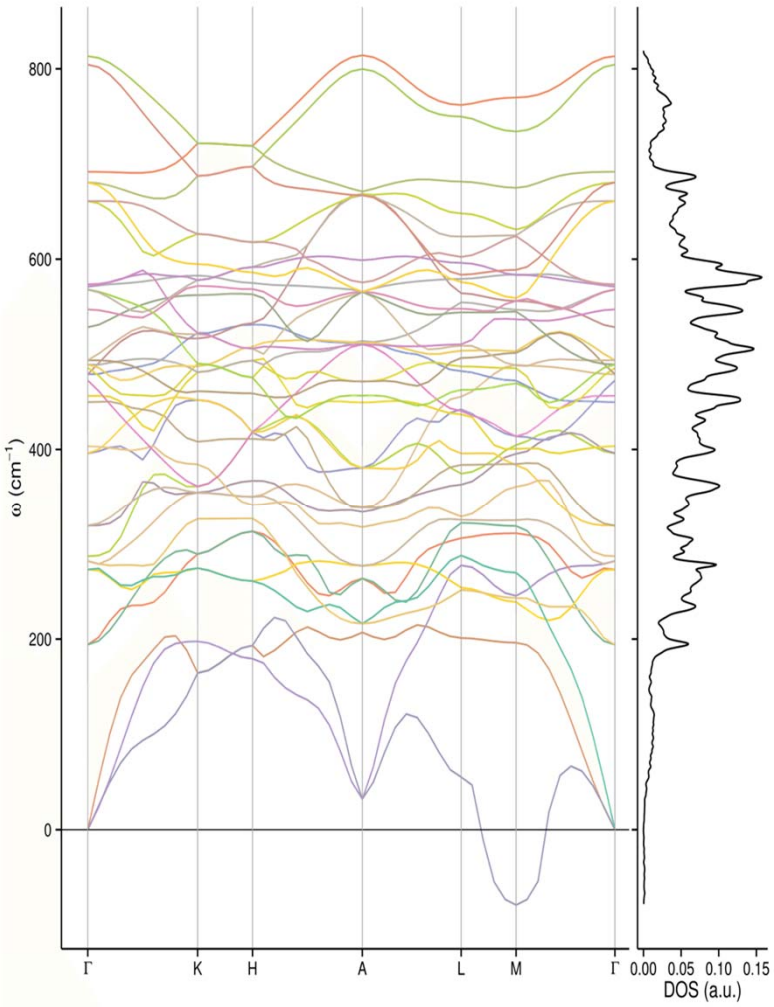




The structure of $Be_{12}Ti$ (Continued)



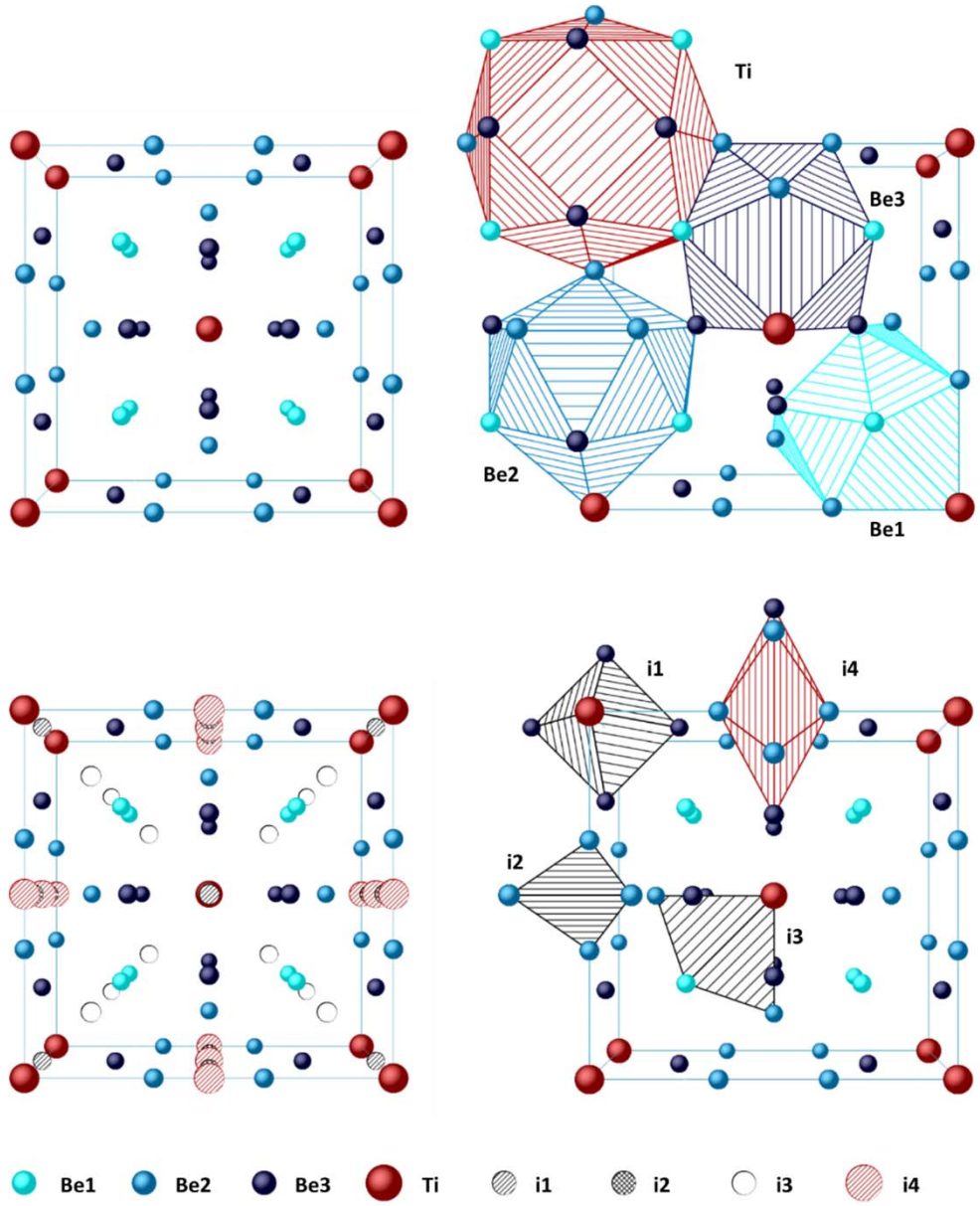
Tetragonal



Hexagonal

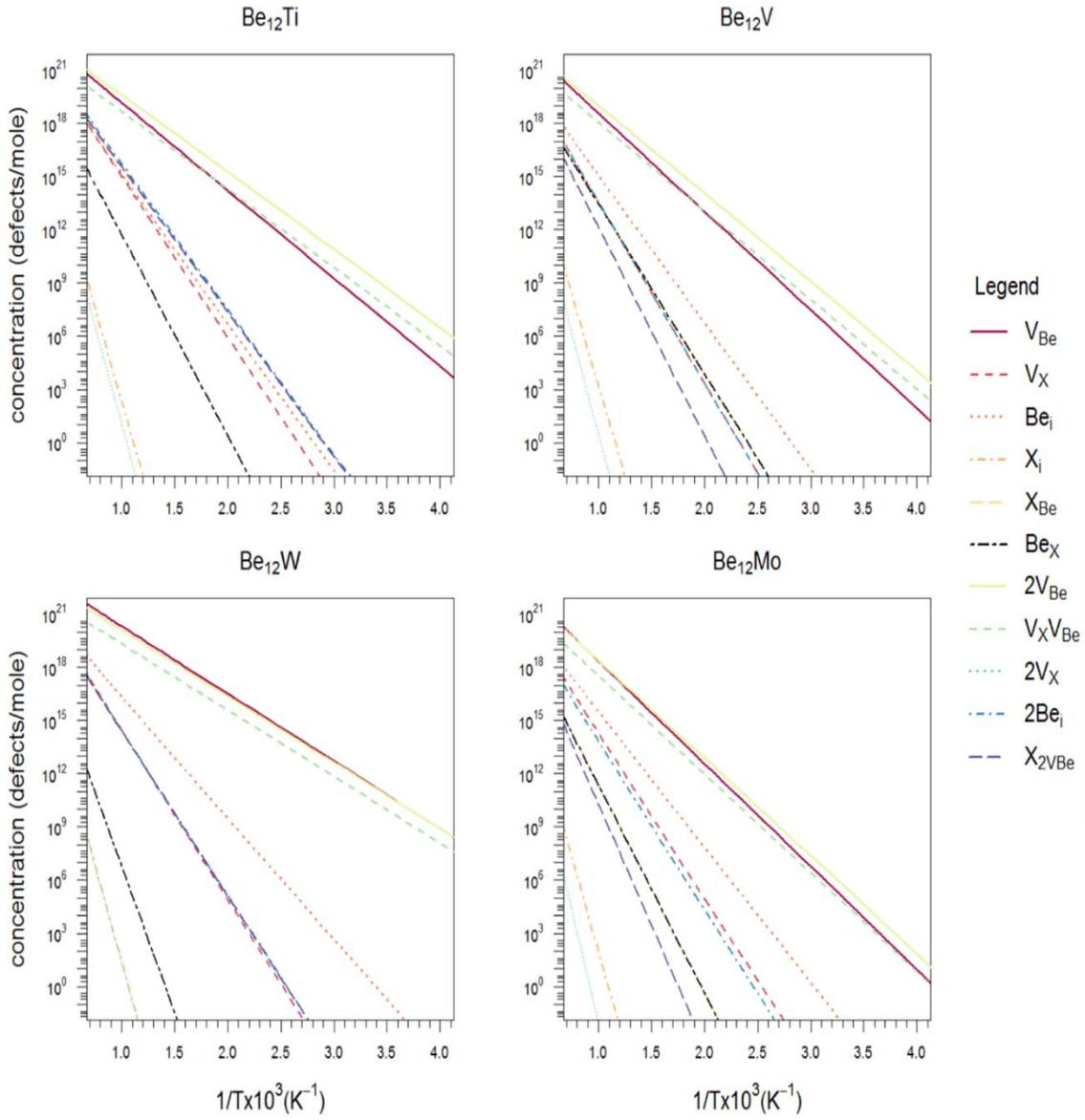
Defects in $Be_{12}Ti,V,W,Mo$

- 1 transition metal site, 3 Be sites
- 4 interstitial sites – one of which is only stable for the transition metal
- V_{be}, V_{Ti}, Be_i Ti_i, Be_X, Ti_{Be} and bound defects investigated



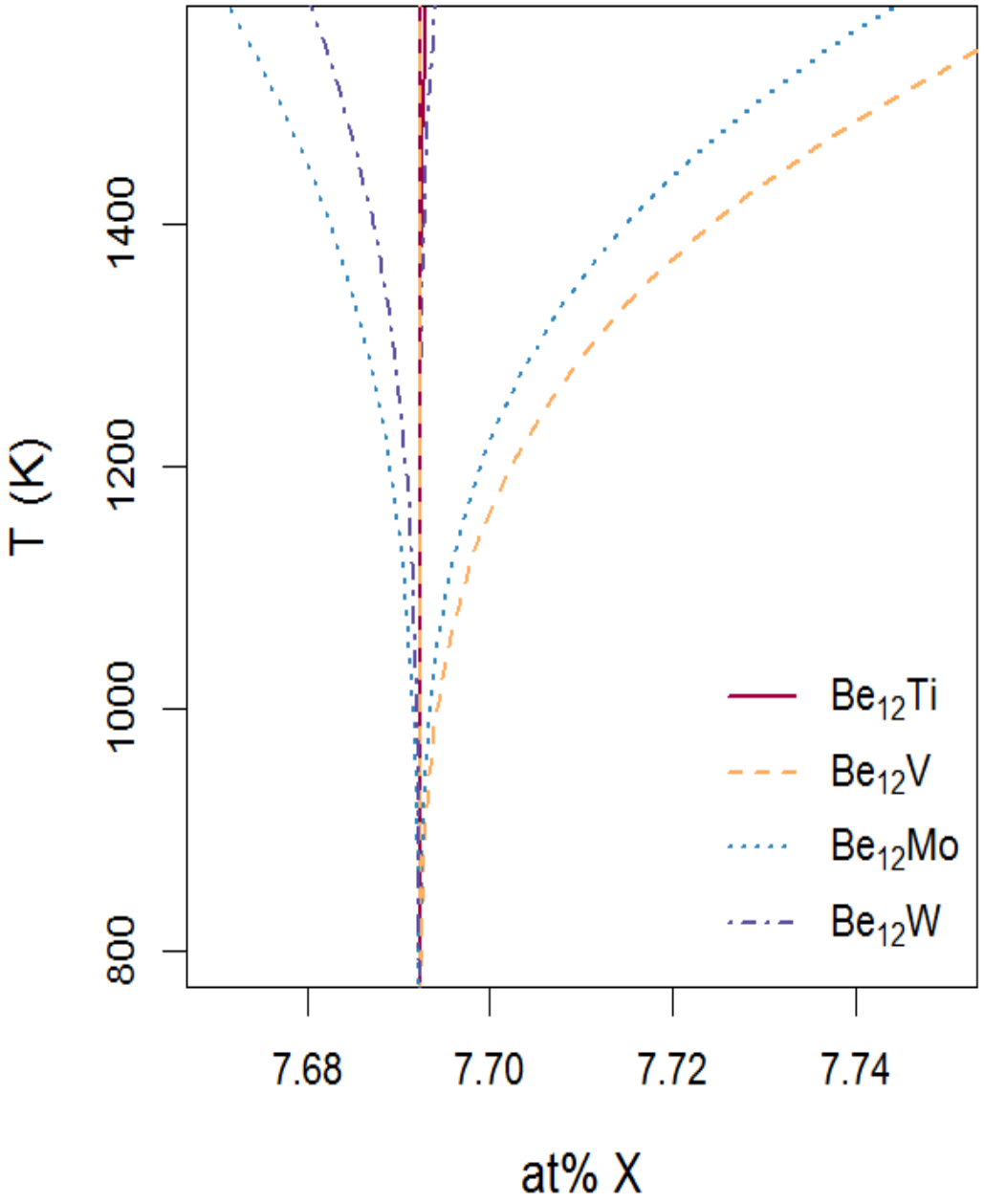
Intrinsic concentrations of defects

- Defect concentrations dominated by V_{Be}, V_{2Be}, V_{BeTi}
- Binding of defects favourable in some cases for $V_{Be}V_{Be}$, Be_iBe_i & Ti_{BeBe}
- Implications for behaviour in reactor – extended defects?



Non-stochiometry

- Very limited nonstochiometry accommodated in $Be_{12}Ti$
- Should manufacture with excess Be
- Varying behaviour for other materials



Summary

- ε-Fe_2Be_{17} is stable only below ~1000K.
- $FeBe_5$ is stabilised by vibrational terms and by Al additions.
- Al is insoluble in Be but readily accommodated in Fe-Be phases (same for Si) and can form disordered $(AlFe)_2Be_4$.
- $FeBe_5$ exhibits an order/disorder transition around 900 K.
- Of the two structures for $Be_{12}Ti$ reported in the literature the tetragonal is more stable up to at least 1800 K.
- $Be_{12}Ti$ & $Be_{12}V$ exhibit very limited non-stoichiometry.
- Defects can bind readily: implications for radiation tolerance?
- Anharmonic contributions are important when investigating lattice expansion and thermal conductivity, but not for the relative stability of these intermetallic phases.