A First-principles Study on Fe Substituted $Cr_{23}C_6$

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ABSTRACT

$Cr_{23}C_6$ and its various solid solutions is a dominating phase in the creep-resistant steels. Although understanding its behavior with r espect to elevated temperature properties is important and a great deal of work has been done the thermodynamic properties of Cr_{23} C_6 and its solid solutions is not sufficiently studied. First-principl es calculation is done by the all-electron full potential linearized a ugmented plane-wave method (FLAPW) within the generalized g radient approximation. The calculated ground state equilibrium la ttice parameter is 10.57 Å and 10.56 Å for nonmagnetic $Cr_{23}C_6$ a nd ferromagnetic $FeCr_{22}C_6$ respectively, where Fe atom prefers to substitute the 4a site. The formation enthalpy of $Cr_{23}C_6$ is calculat ed to be 1.82 kJ atom-mol^{-1} higher than the lowest formation ent halpy of $FeCr_{22}C_6$.

Creep Resistant Steel

Steam Power Plant
Efficiency ~42 %

Temperature 600 °C
Pressure 30 MPa

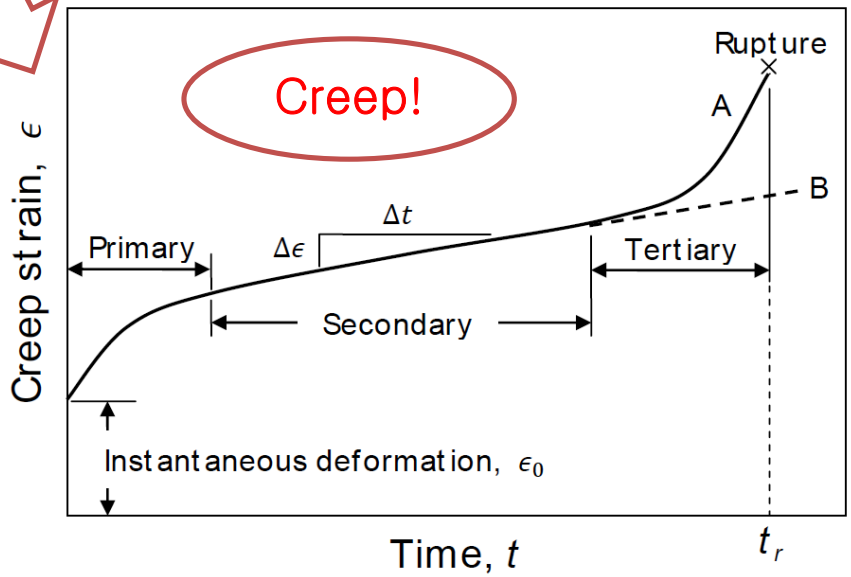
High T, P

Goal
Efficiency 45 %

Temperature 650 °C
Pressure 120 MPa

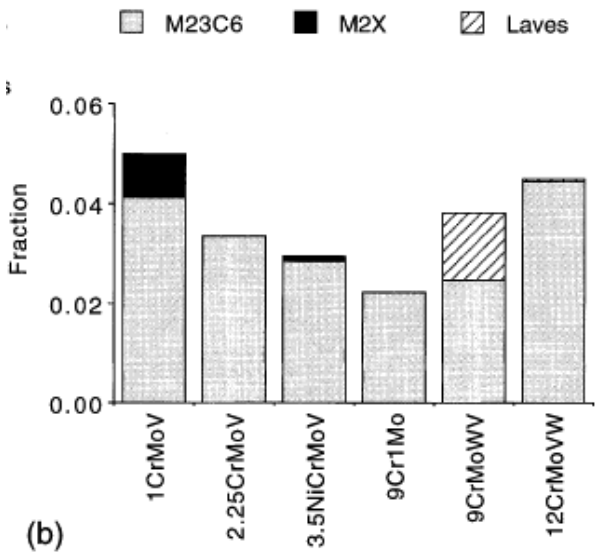
Control Measure	Increase in Efficiency / %
Reduction of condenser pressure by 50 %	1.5
60 °C increase in steam temperature	1.4
Use of double reheat	1
20 % increase in steam pressure	0.3
Reducing excess air by 10 %	0.25
10 °C decrease in flue gas temperature	0.25

Anticipated efficiency improvements for changes in power plant operating conditions
[Wachter and Ennis, 1995]



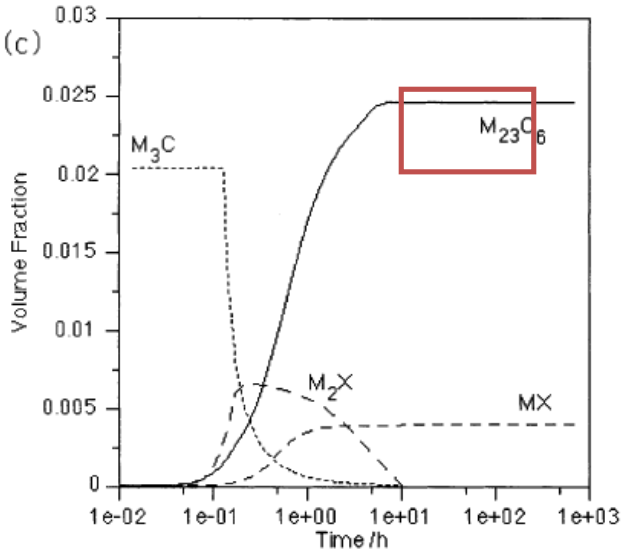
Typical creep curve at elevated temperature.
[Callister, 2007; Dieter, 1998]

$M_{23}C_6$ in Power Plant Steels

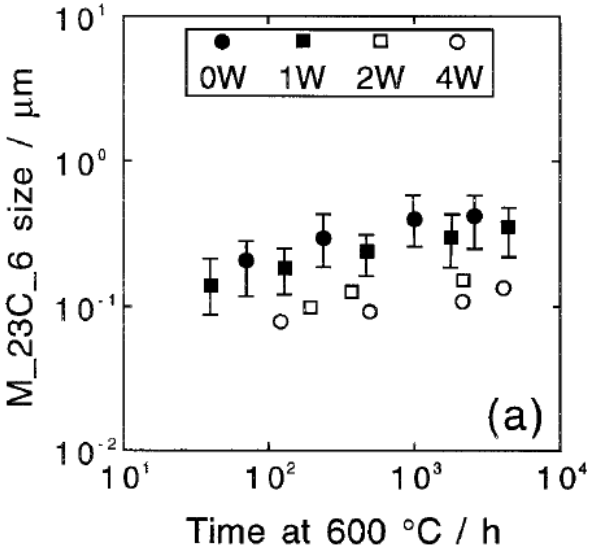


Equilibrium fractions of carbides in some common power plant steels (MTDATA, SGTE database, 565 °C)

[Bhadeshia, 2001]



The predicted evolution of precipitate volume fractions at 600 °C for 10CrMoV
[Robson and Bhadeshia, 1997]



Fe-0.1C-9Cr-0.5Mn-0.3Si wt% steel, tested in creep at 600 °C [Abe].

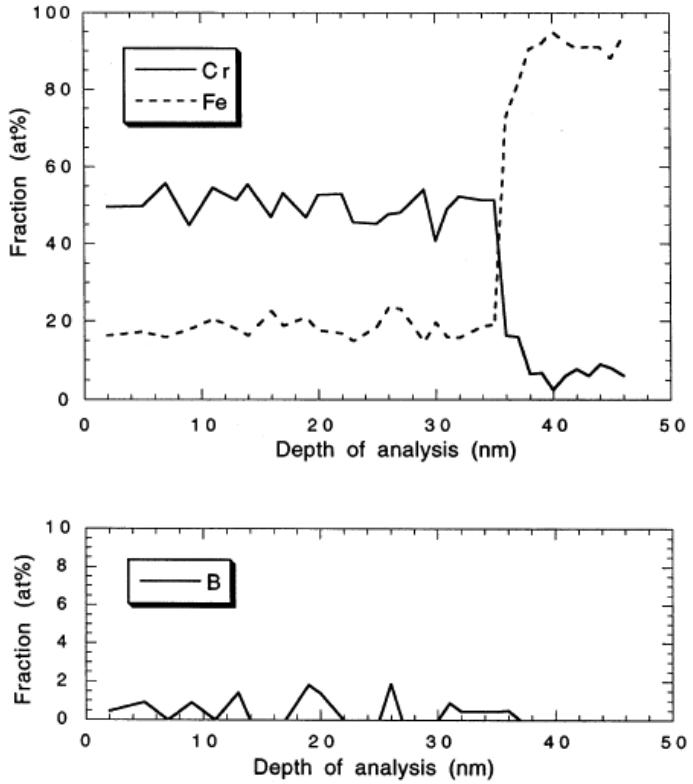
- The volume fraction of $M_{23}C_6$ dominates and does not decrease after a long time.
- The size of $M_{23}C_6$ particles increase.

→ $M_{23}C_6$ is the majority carbide in creep-resistant steels and coarsens in creep condition.

Fe and B in $M_{23}C_6$

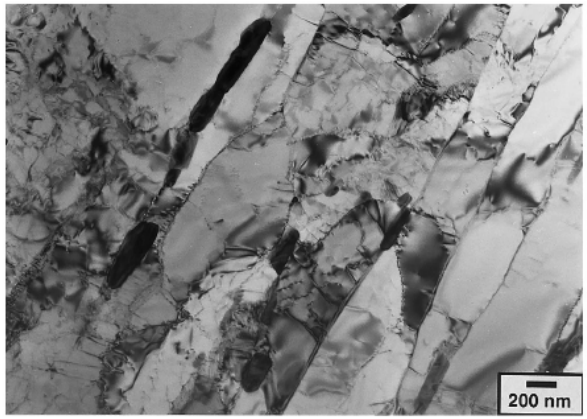
Chemical composition of investigated steels (wt. %)

	Fe	Cr	Mn	Ni	Co	Mo	W	V	Nb	C	B	N
CD2	bal.	9.5	0.9	0.1	1.0	0.5	1.8	0.21	0.04	0.06	0.004	0.05



	Fe	Cr	B
FB4	18.8 ± 0.5	50.4 ± 0.8	0.50 ± 0.08
CB1	18.1 ± 0.9	47.4 ± 1.2	0.99 ± 0.23
CB1	19.4 ± 1.0	50.4 ± 1.3	0.52 ± 0.19
CB2	17.5 ± 1.3	51.5 ± 1.9	1.8 ± 0.5
CD2	17.4 ± 0.9	50.2 ± 1.3	0.41 ± 0.13

Concentration profiles across a carbide/matrix interface in steel FB4.



Typical microstructure of a martenstitic 9-12% Cr steel in the tempered condition. (TEM)

[Hättestrand and Andrén, 1999]

- $M_{23}C_6$ is observed in grain boundaries
- 50 at% of Cr and 18 at% of Fe in $M_{23}C_6$ (Atom Probe Field Ion Microscope)
- Boron is evenly dissolved in $M_{23}C_6$ (Atom Probe Field Ion Microscope)

Calculation Parameters

- FLAPW method
- Generalized Gradient Approximation
- Calculated Systems

  $Cr_{23}C_6$ $Fe_{23}C_6$

  $Fe^{4a}Cr_{22}C_6$ $Fe^{8c}Cr_{22}C_6$ $Fe^{32f}Cr_{22}C_6$ $Fe^{48h}Cr_{22}C_6$
- Calculated energies are at 0 K and zero pressure
- ΔH_f : Formation enthalpy per atom of $Cr_xFe_yC_pB_q$
- E(X) : Calculated ground state energy of X
- N : Number of atoms, x+y+p+q

$$\Delta H_f(Cr_xFe_yC_pB_q)$$

$$= \{E(Cr_xFe_yC_pB_q) - xE(Cr) - yE(Fe) - pE(C) - qE(B)\}/N$$

E. Wimmer, H. Krakauer, M. Weinert, and A. J. Freeman, *Phys. Rev. B* **28**, 864 (1981).
M. Weinert, E. Wimmer, and A. J. Freeman, *Phys. Rev. B* **26**, 4571 (1982).
Perdew, J. P., Burke, K., Ernzerhof, M., *Phys. Rev. Let.* **77**,3865 (1996).
S.-W. Seo, Y. Y. Song, R. Rahman, I. G. Kim, M. Weinert, and A. J. Freeman, *J. Magnetics* **14**, 137 (2009).

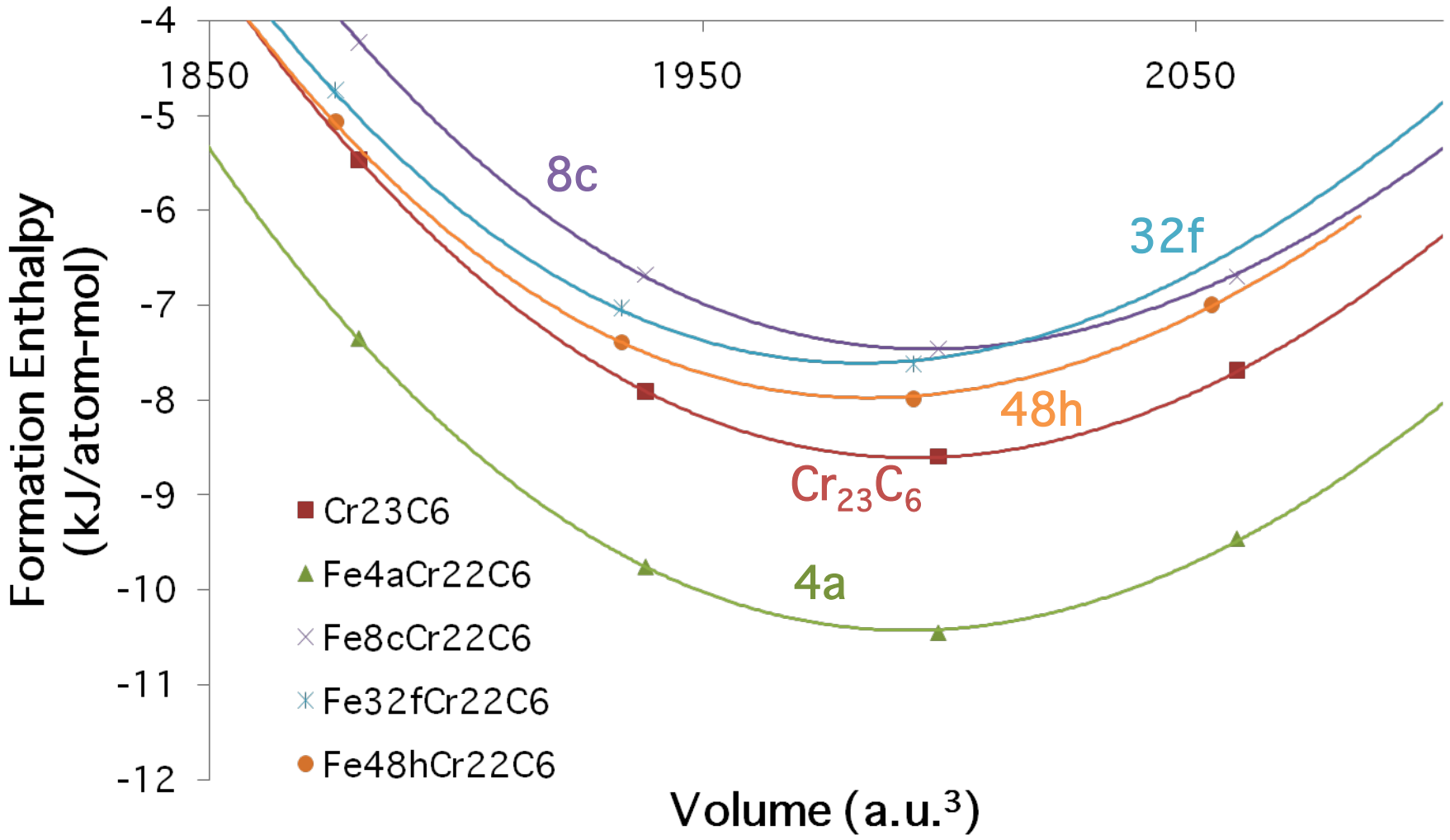
Crystal Structure of $Cr_{23}C_6$

- Cr1(4a)
- Cr2(8c)
- Cr3(32f)
- Cr4(48h)
- C(24e)

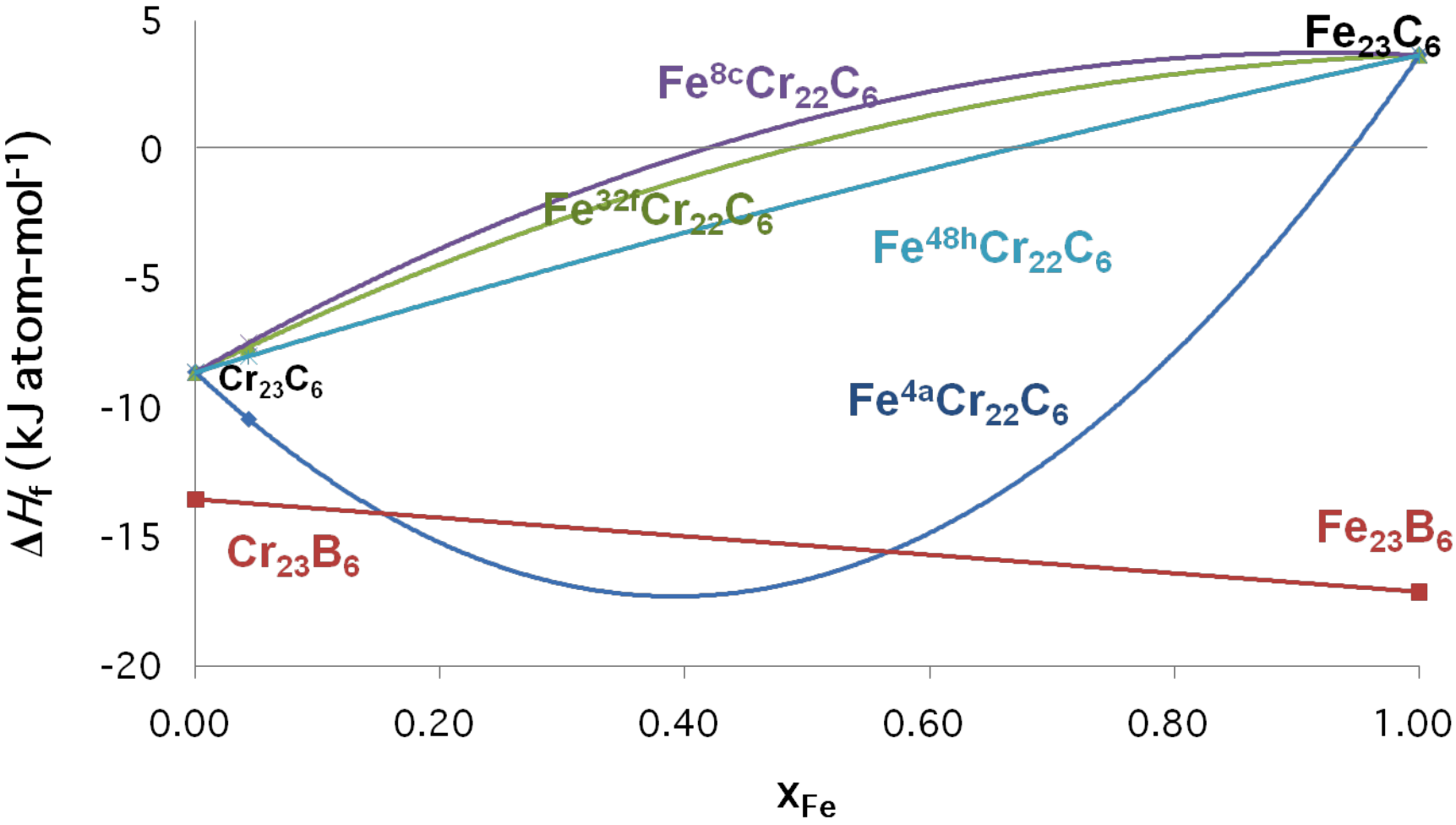
$Fm\bar{3}m$

	Relaxed (Calculated)			Bowman, 1972		
a (Å)	10.57			10.66		
	x	y	z	x	y	z
Cr1(4a)	0	0	0	0	0	0
Cr2(8c)	0.25	0.25	0.25	0.25	0.25	0.25
Cr3(32f)	0.381	0.381	0.381	0.385	0.385	0.385
Cr4(48h)	0	0	0.34	0	0	0.35
C(24e)	0.276	0.276	-0.276	0.275	0.275	-0.275

Volume versus Enthalpy

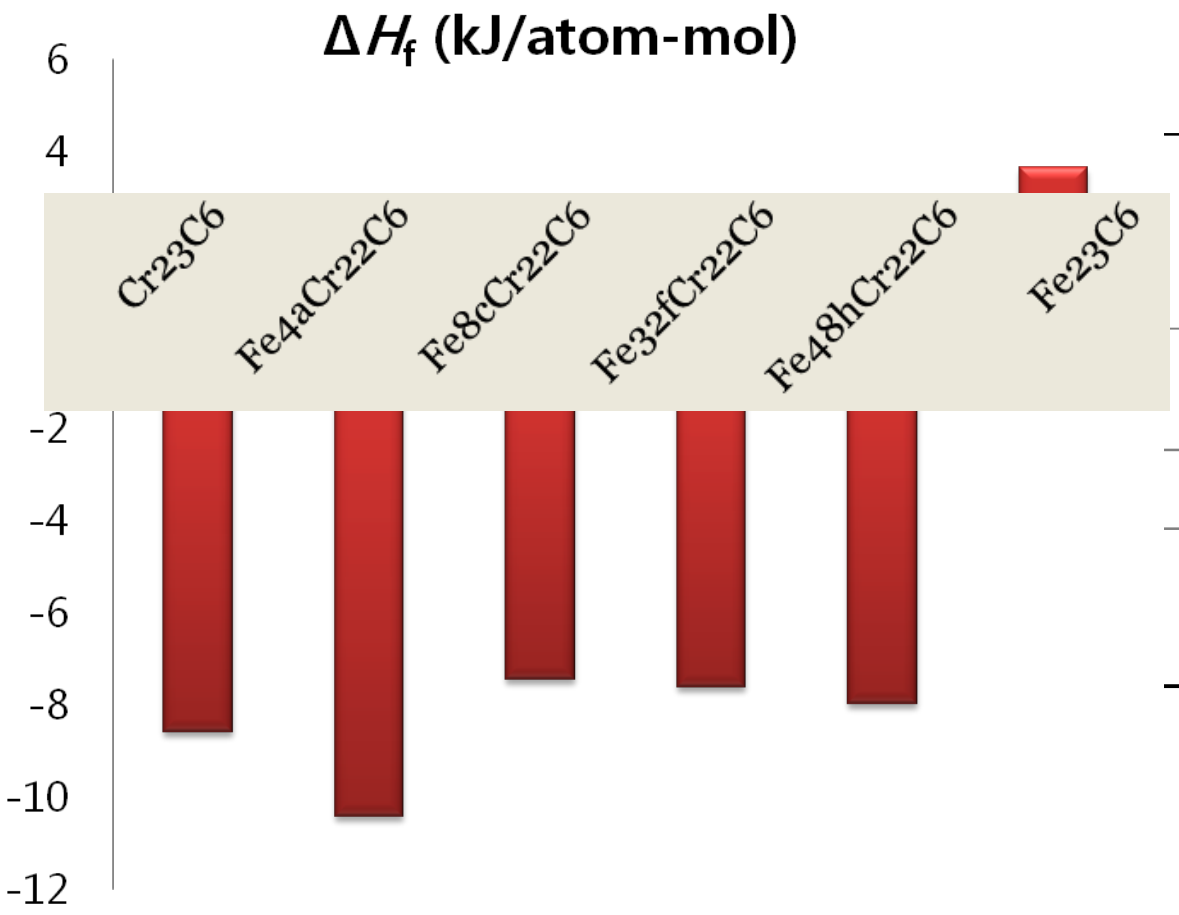


Fe Concentration versus Enthalpy



- Fe prefers to substitute Cr1(4a) site in $M_{23}C_6$

Calculated Formation Enthalpy



	ΔH_f/ kJ atom^{-1} mol^{-1}
$Cr_{23}C_6$	-10.98 (1)
	-8.18 (2)
	-9.65 (3)
	-8.75 (4)
$Fe^{4a}Cr_{22}C_6$	-10.65 (4)
$Fe_{23}C_6$	11.98 (5)
	4.39 (2)

(1) *Kleykamp, 2001

(2) Sandberg *et al.*, 2008

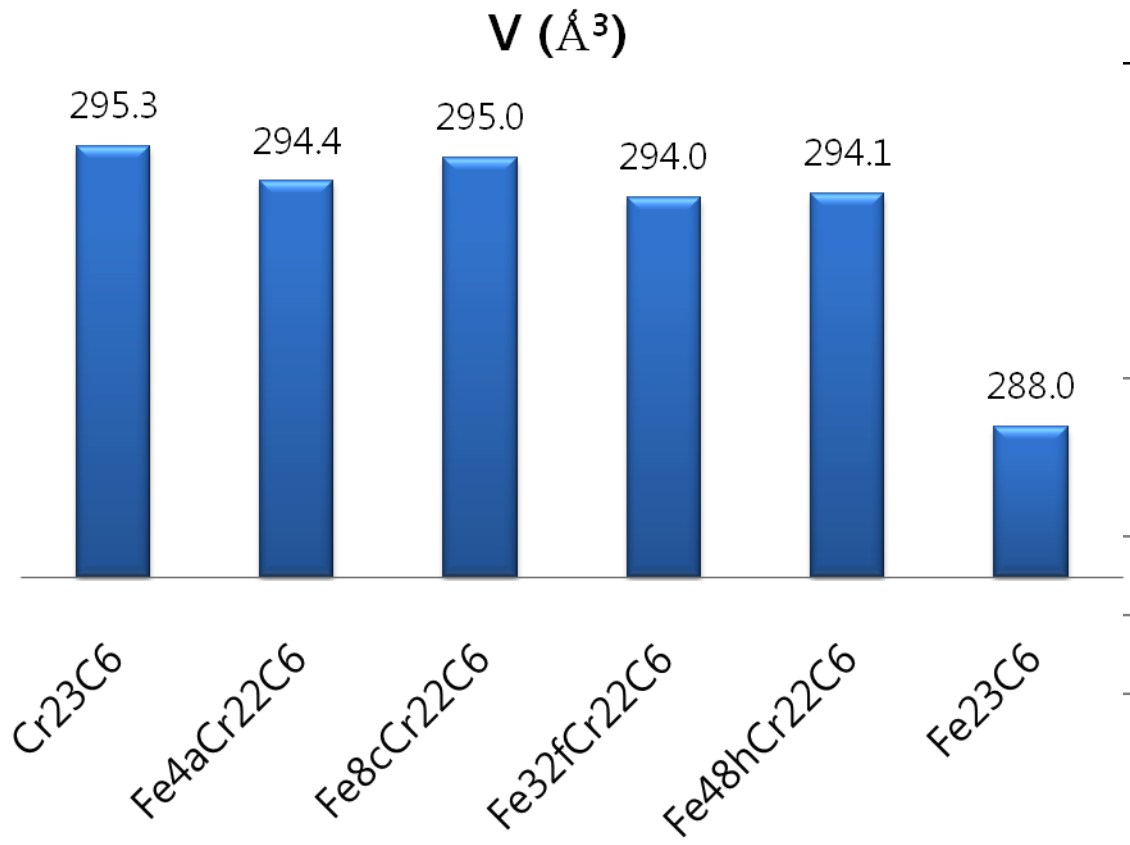
(3) Chao, 2008

(4) Henriksson *et al.*, 2008

(5) *Guillermet and Grimvall, 1992

➡ Fe concentration increases

Calculated Volume of $M_{23}C_6$



	a / Å	*B* / GPa
$Cr_{23}C_6$	10.66 (1)	
	10.90 (2)	275
	10.56 (3)	294
	10.53 (4)	298
$FeCr_{22}C_6$	10.65 (5)	
	10.90 (2)	278
$Fe^{4a}Cr_{22}C_6$	10.55 (3)	
$Fe_{23}C_6$	10.63 (2)	276

(1)* Yakel, 1987

(2) Xie *et al.*, 2005

(3) Henriksson *et al.*, 2008

(4) Chao, 2008

(5)* Villars and Calvert, 1991

➡ Fe concentration increases

CONCLUSION

- Fe substitution to $M_{23}C_6$
  - Prefers to substitute to Cr1(4a) site.
  - Stabilizes up to about 6 Fe atoms.
  - Decreases the unit cell volume of $M_{23}C_6$.
  - Nonmagnetic $Cr_{23}C_6$ becomes Ferromagnetic $Fe_xCr_{23-x}C_6$
- Future Work
  - Substitution of B in C site : $M_{23}(B,C)_6$