AGH University of Science and Technology

AGH Krakow, Poland

Mössbauer Spectroscopy of Fe-Cr Alloys

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Stainless steels

- Must contain ≥ 10.5% Cr and low content of carbon

- Discoverd in 1900 – 1915 as effort of investigations of many people; Leon Guillet (F), Giesen (GB), Harry Brearley(GB), Hans Goldsmidt (D), Albert Portevin (F), Borchers (D) and Max Mauermann (PL)

Harry Brearly

Albert Portevin

H. Goldsmidt

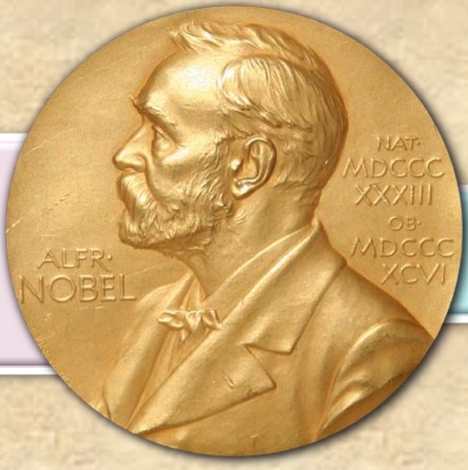
M. Mauermann

Mössbauer Spectroscopy in Fe-Cr Alloys

Two aspects

2007
For GMR

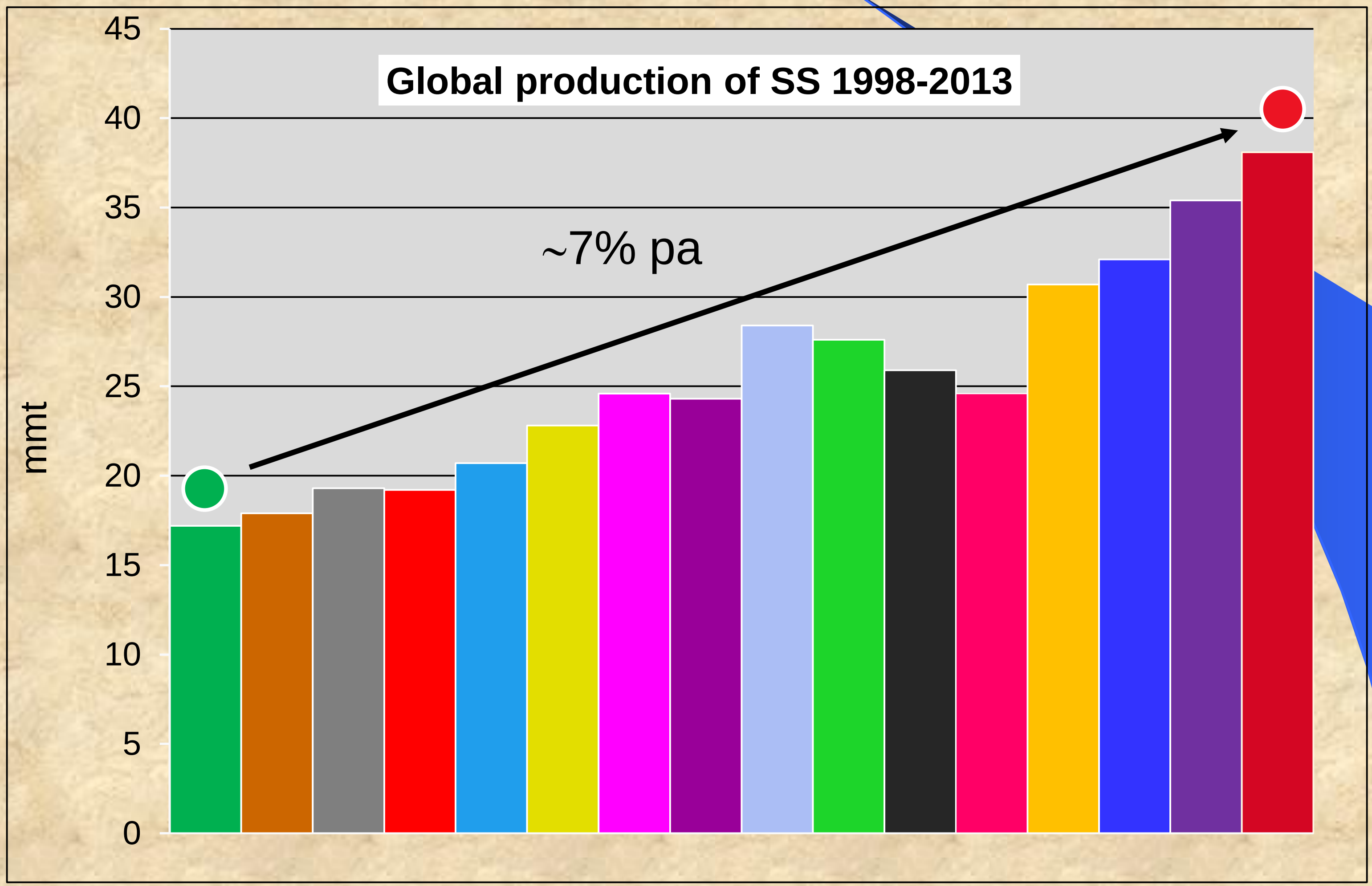
Industrio-
technological



Scientific

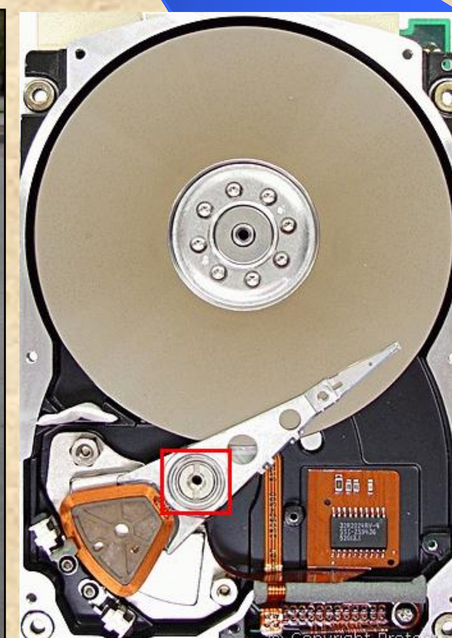
Mössbauer Spectroscopy in Fe-Cr Alloys

• Aspect industrio-technological •



Mössbauer Spectroscopy in Fe-Cr Alloys

• Industrio-technological aspect •

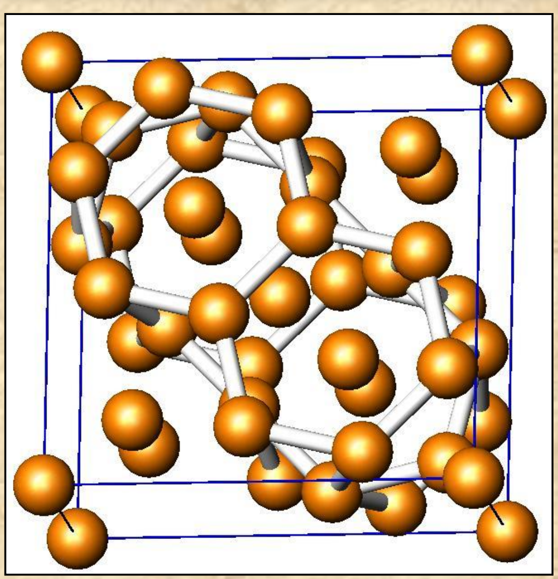


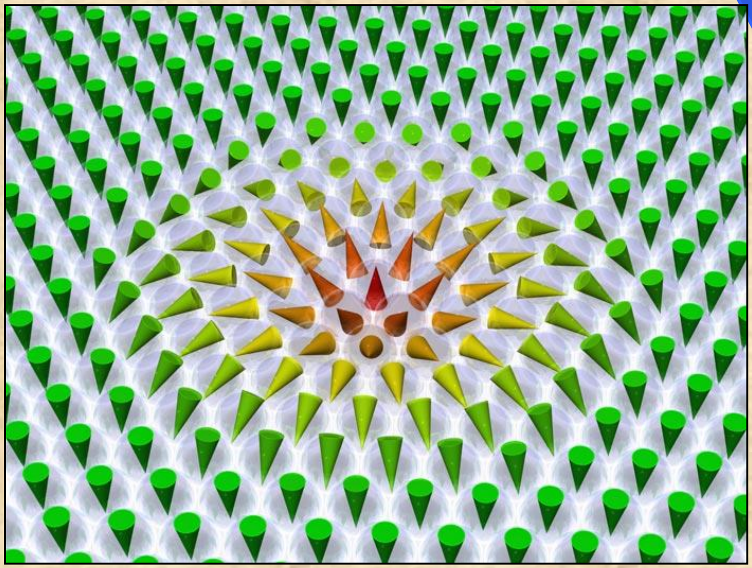
Mössbauer Spectroscopy in Fe-Cr Alloys

• Scientific aspect •

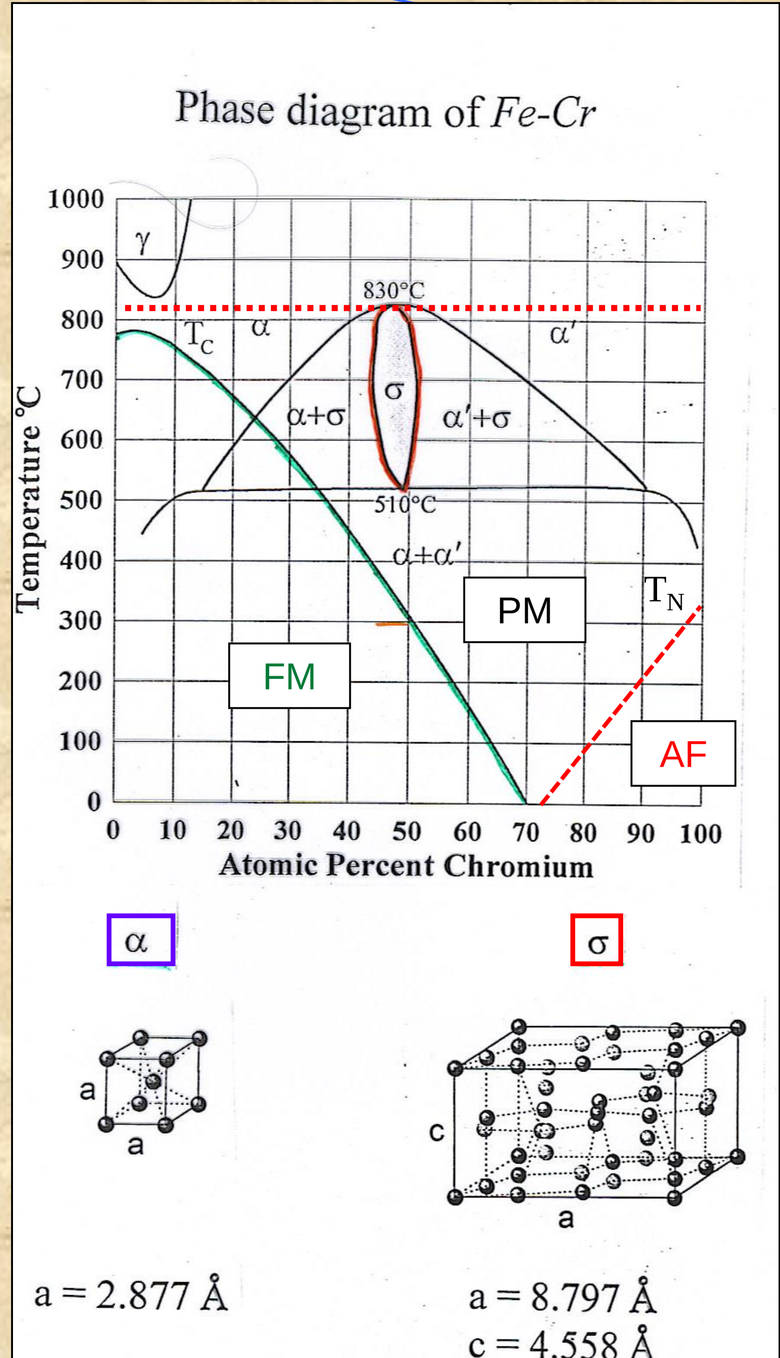
Crystallographic

Magnetic





MS in Fe-Cr Alloys

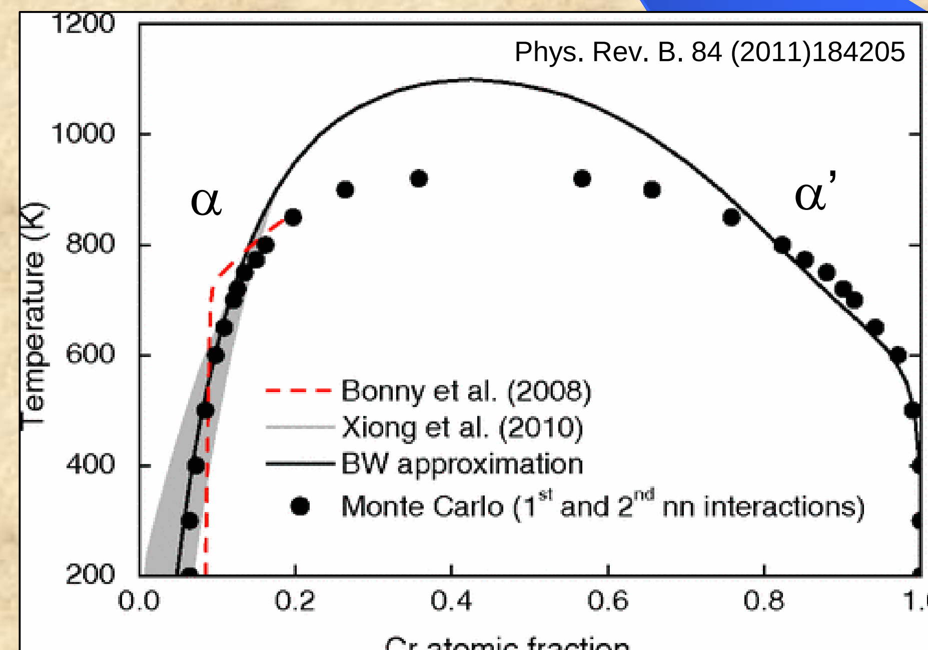


- Crystallographic •

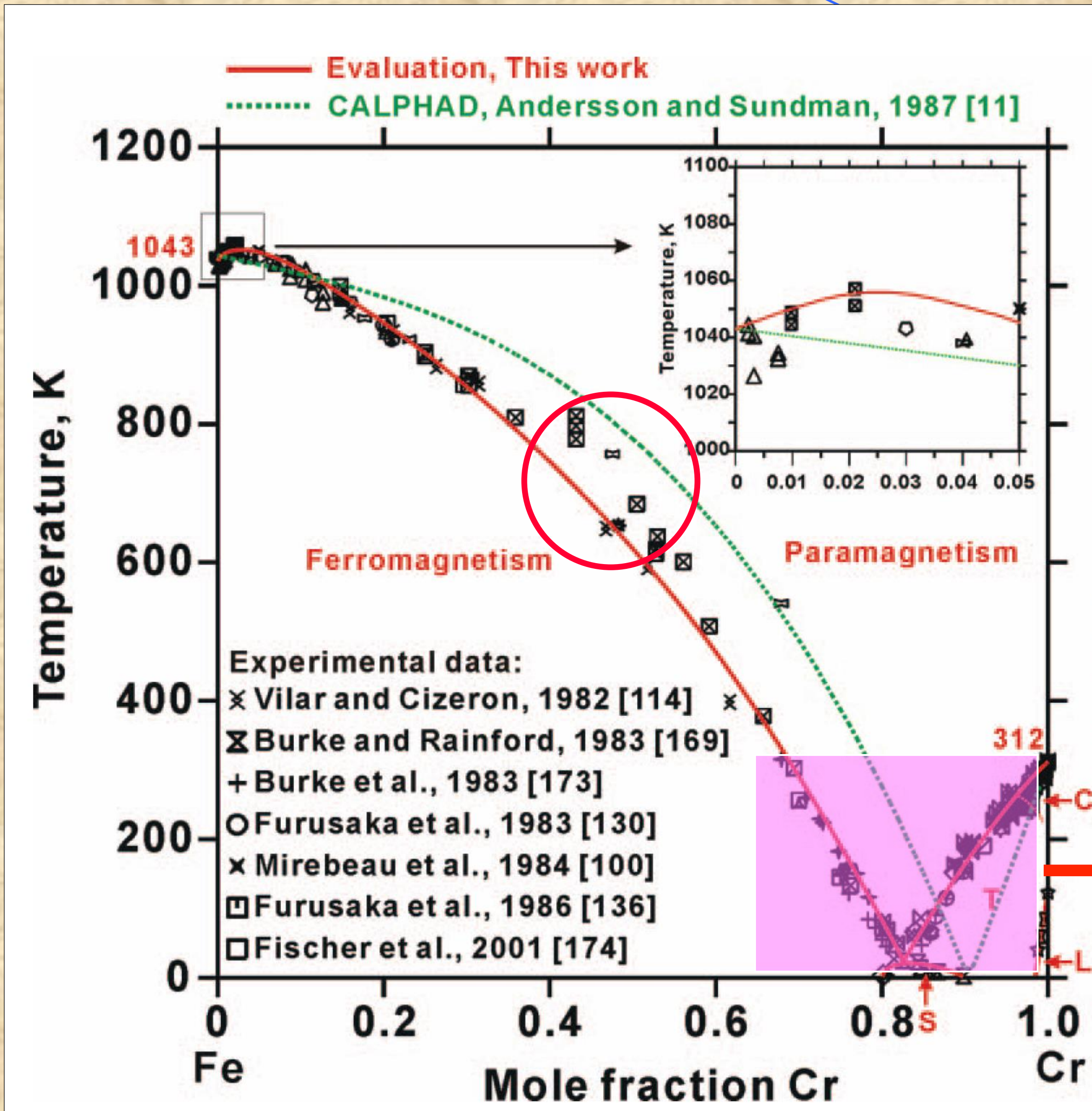
♦ Different phases: **α, α’, γ, σ**

♦ Phase transitions: **α↔γ, α↔σ**

♦ Phase decomposition: **α, α’**

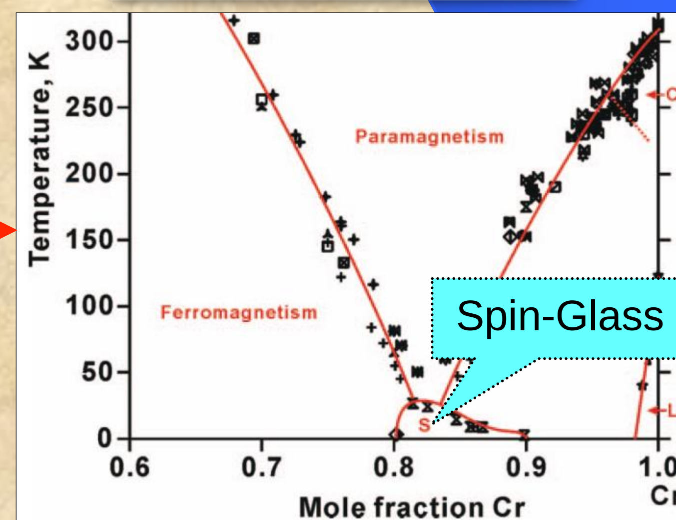


Mössbauer Spectroscopy in Fe-Cr Alloys



Xiong et al., Crit. Rev. Sol. State. Mater. Sci., 35 (2010) 125

- • Magnetic •
- ♦ Ferromagnetism
- ♦ Antiferromagnetism
- ♦ Spin-glass
- ♦ Re-entrence



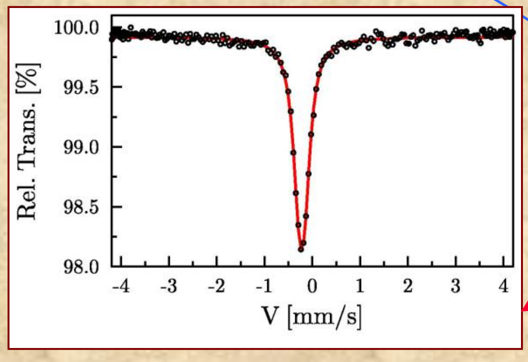
Mössbauer Spectroscopy is one of the most relevant techniques to study Fe-Cr Alloys

- **Spin- and charge-density changes**
- **Identification of α, γ and σ phases**
- **Kinetics of phase formation e. g. $\alpha \rightarrow \sigma$**
- **Short-range ordering (SRO)**
- **Phase decomposition (α, α')**
- **Curie temperature**
- **Néel temperaure**
- **Spin-glass freezing temperature**
- **Re-entrance transition**
- Corrosion
- Texture

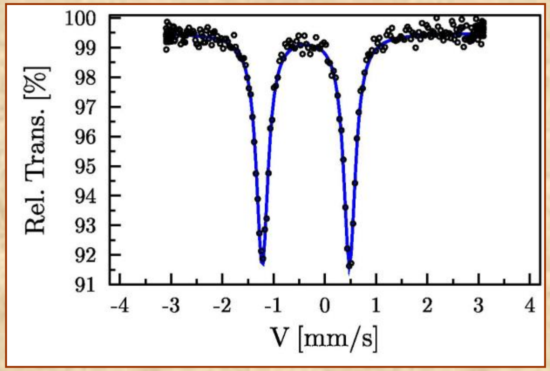
MS and Hyperfine Interactions

$\mathcal{H} = \mathcal{E}0 + \mathcal{E}2 + \mathcal{M}1$

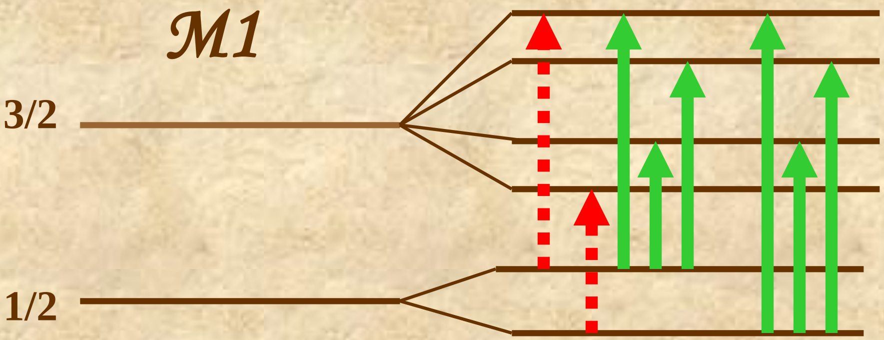
$\mathcal{E}0$

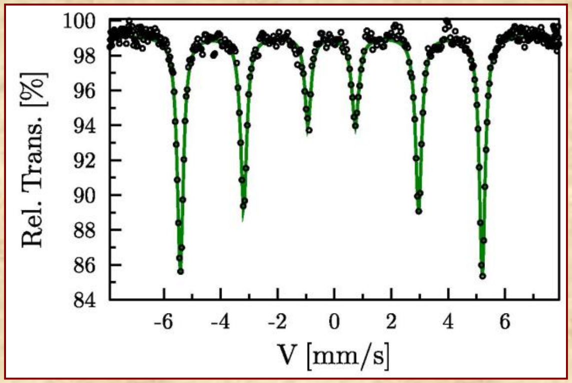


$\mathcal{E}2$

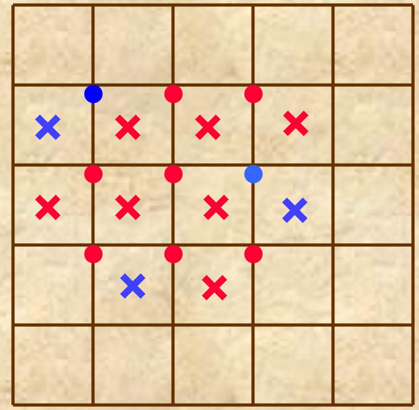


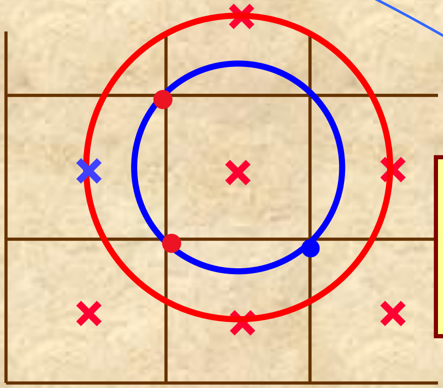
$\mathcal{M}1$





Spin- and charge-density

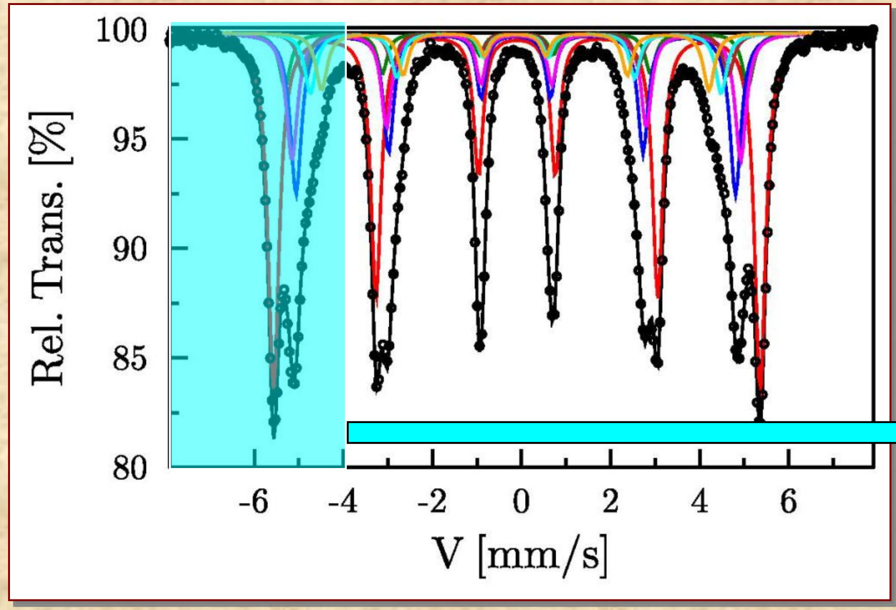


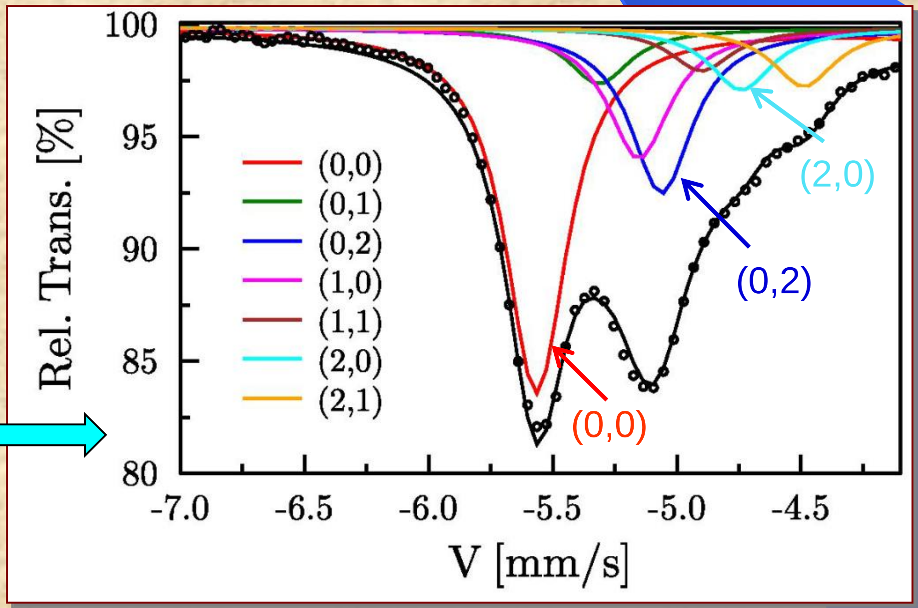


bcc: 1NN=8, 2NN=6

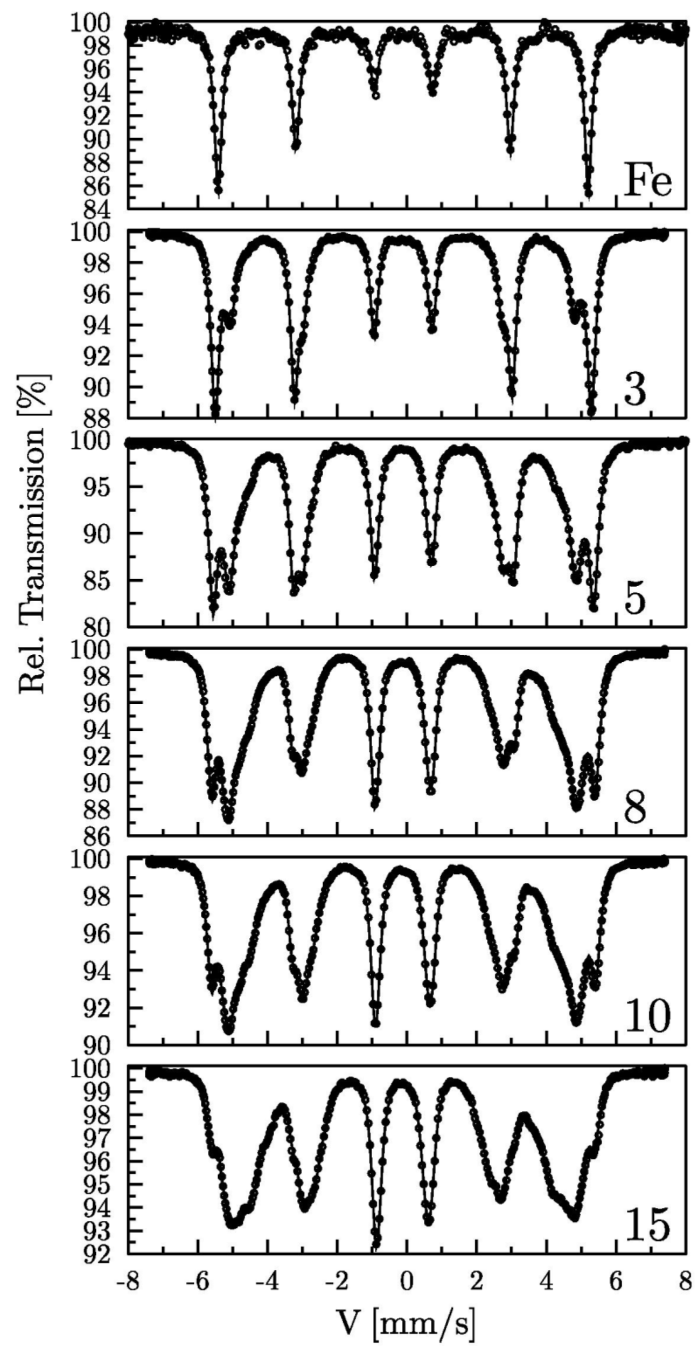
$$P_r(m,n;x) = \binom{8}{m}\binom{6}{n} x^{m+n}(1-x)^{14-m-n}$$

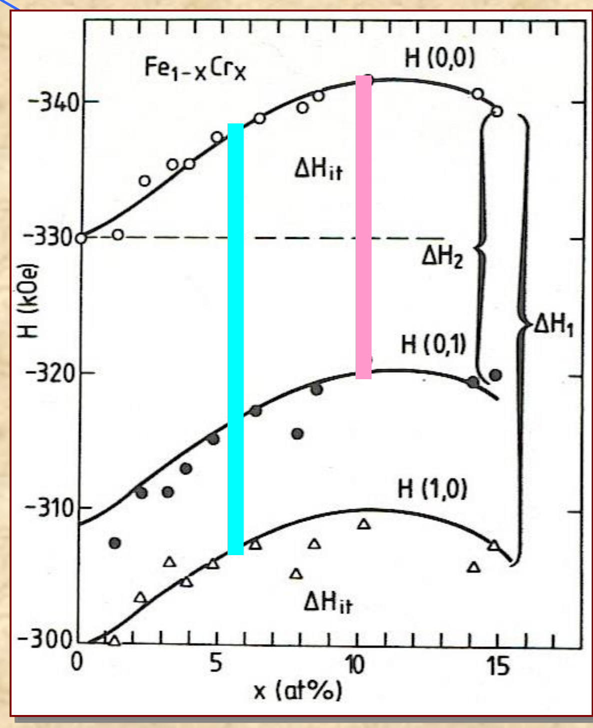
x = 5 at% Cr





Spin & charge





$$\Delta H_1 = 3.2T$$

$$\Delta H_2 = 2.2T$$

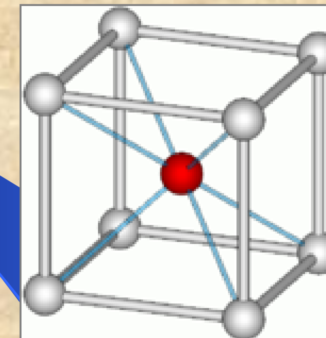
$$H(m,n:x) = H(0,0:x) - m\Delta H_1 - n\Delta H_2$$

Spin- & charge-denisty changes

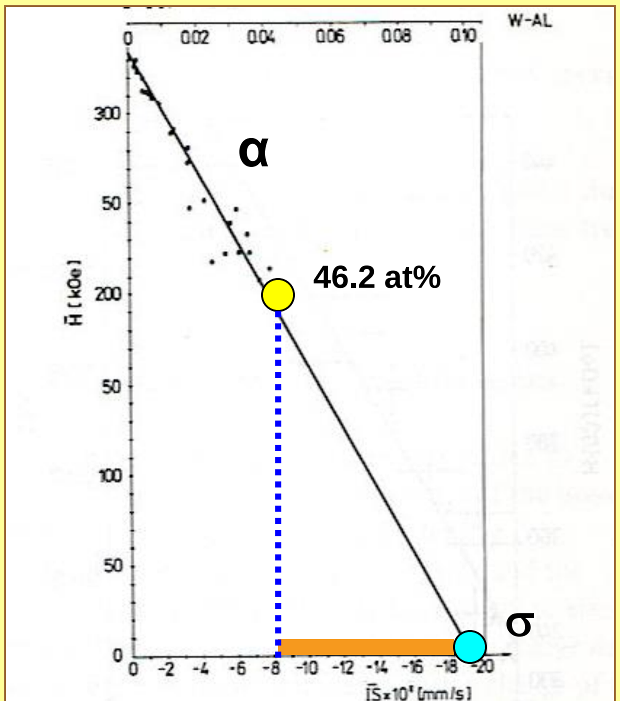
- Local charge-density changes on Fe sites:

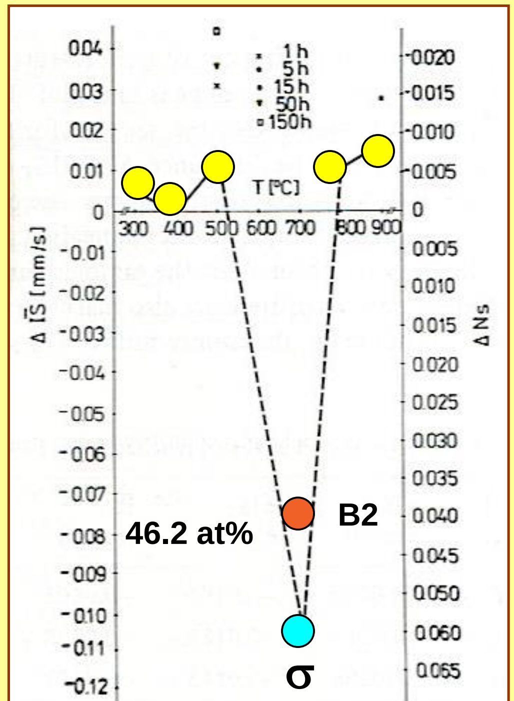
1NN: ΔI_1 = -0.023 mm/s = 0.012 s-electron/Cr atom
2NN: ΔI_2 = -0.007 mm/s = 0.007 s-electron/Cr atom

$q^{\alpha}_{max} \approx 0.04$ e



- Average changes:





$\Delta I = I_{\sigma} - I_{\alpha}$ = -0.11 mm/s $\approx$ 0.06 e

$$\frac{\Delta H_1}{\Delta H_2} \approx \frac{\Delta I_1}{\Delta I_2} \approx 1.5$$

Electrons with spin-up flow from Cr to Fe

SRO in Fe-Cr

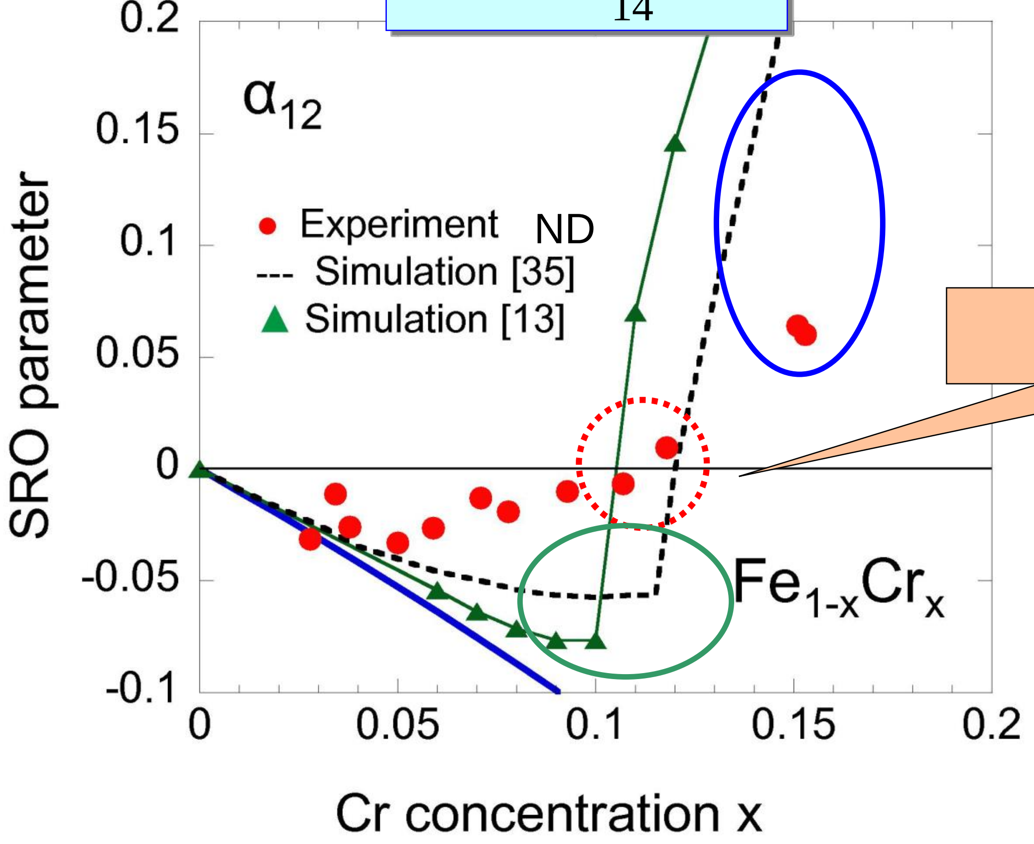
• Cowley SRO parameter, $\alpha_{n:}$

$p_{FeCr}(n)$ – *probability of finding one Cr atom in the n-th shell around a Fe atom*

$$\alpha_n = 1 - \frac{p_{FeCr}(n)}{x} \quad (1)$$

– I. Mirebeau, G. Parette Phys. Rev. B, 82 (2010) 104203**)**

$$\alpha_{12} = \frac{8\alpha(1,0) + 6\alpha(0,1)}{14}$$

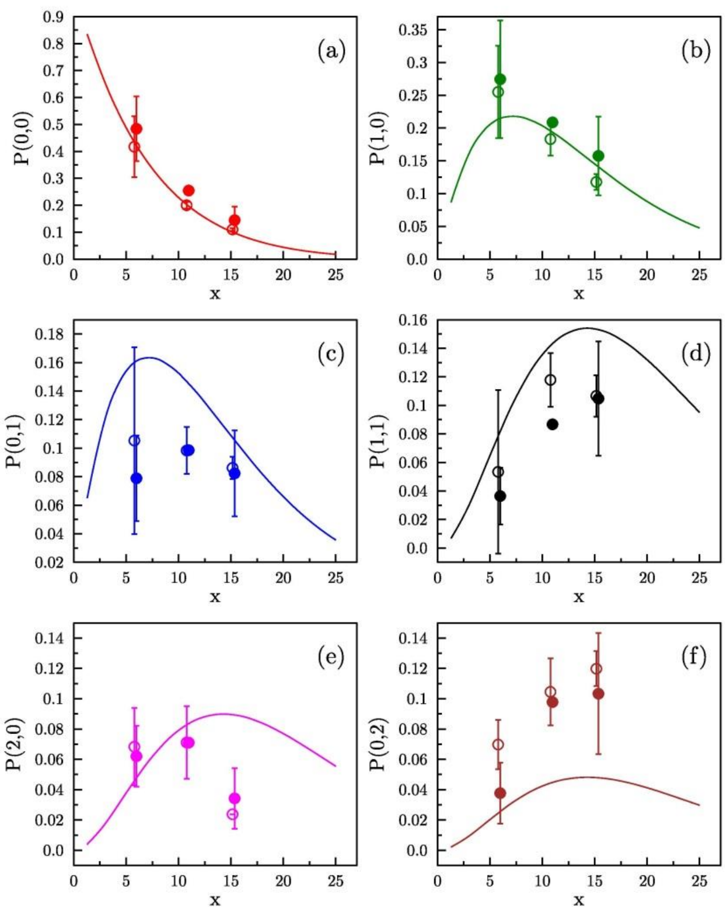


INVERSION

SRO in Fe-Cr - MS

O - cold rolled

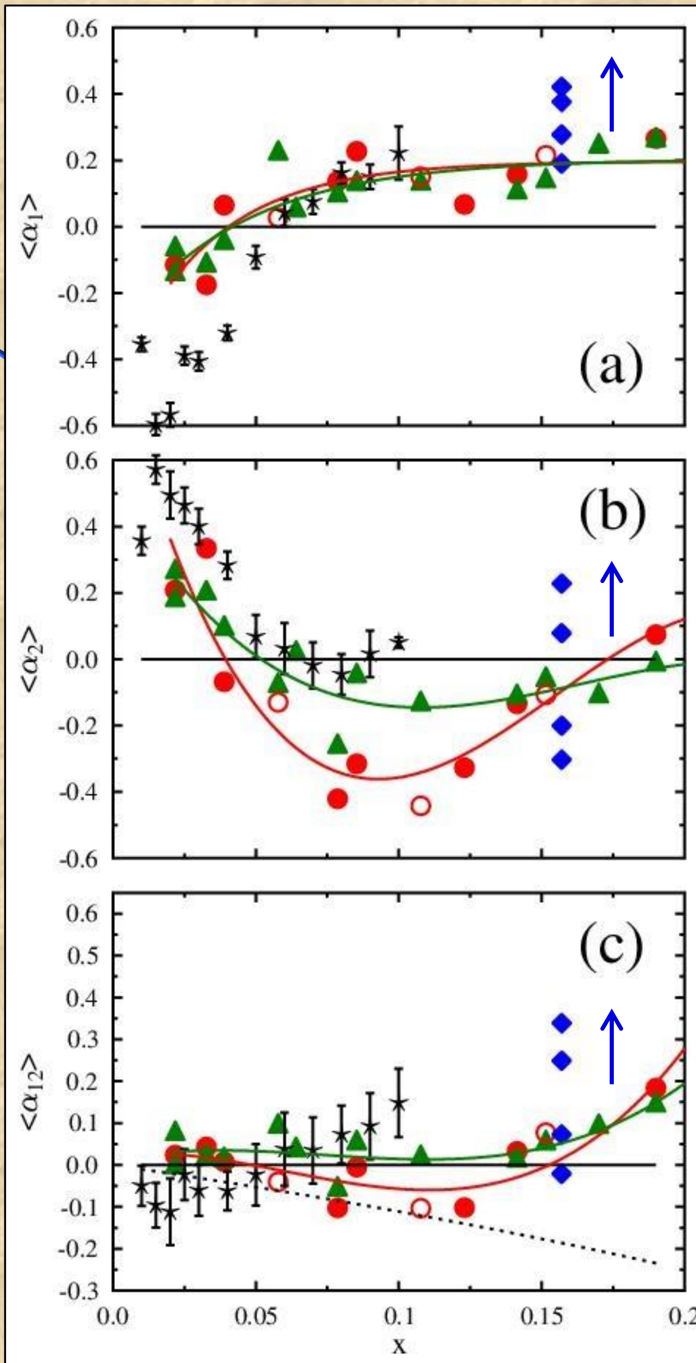
● - quenched



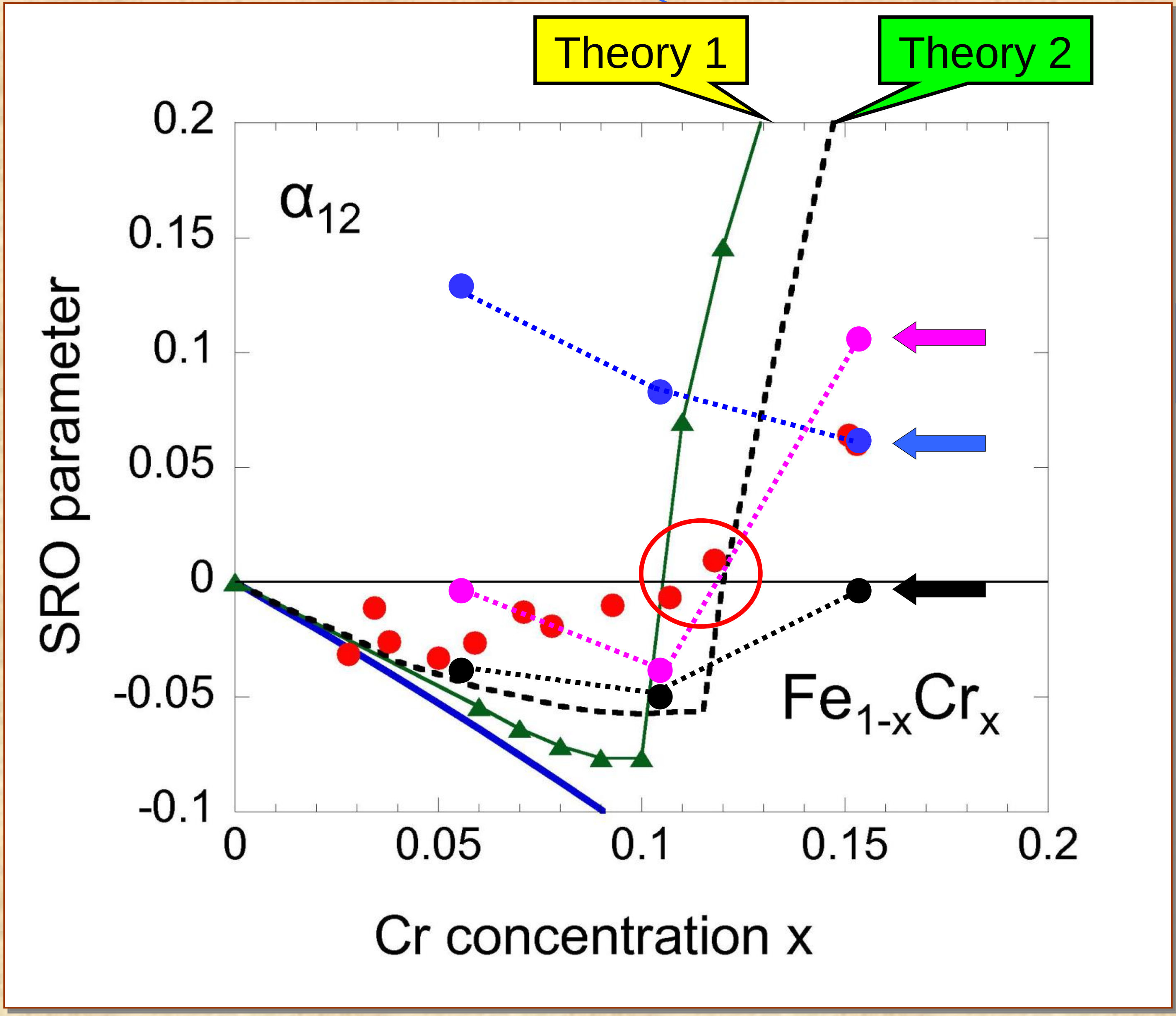
▲ - Q

● - EQ

◆ - IA



SRO in Fe-Cr - MS

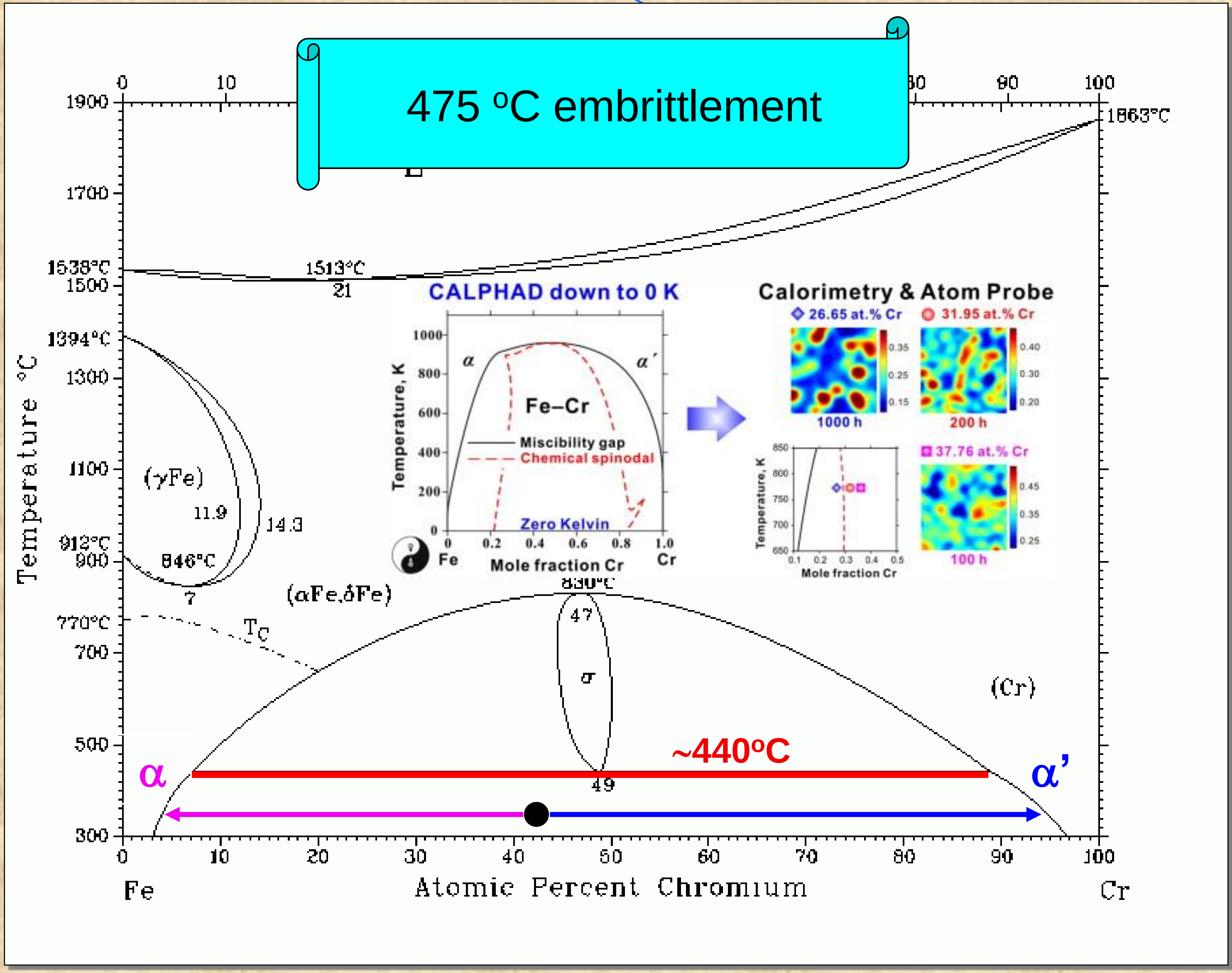


- ND

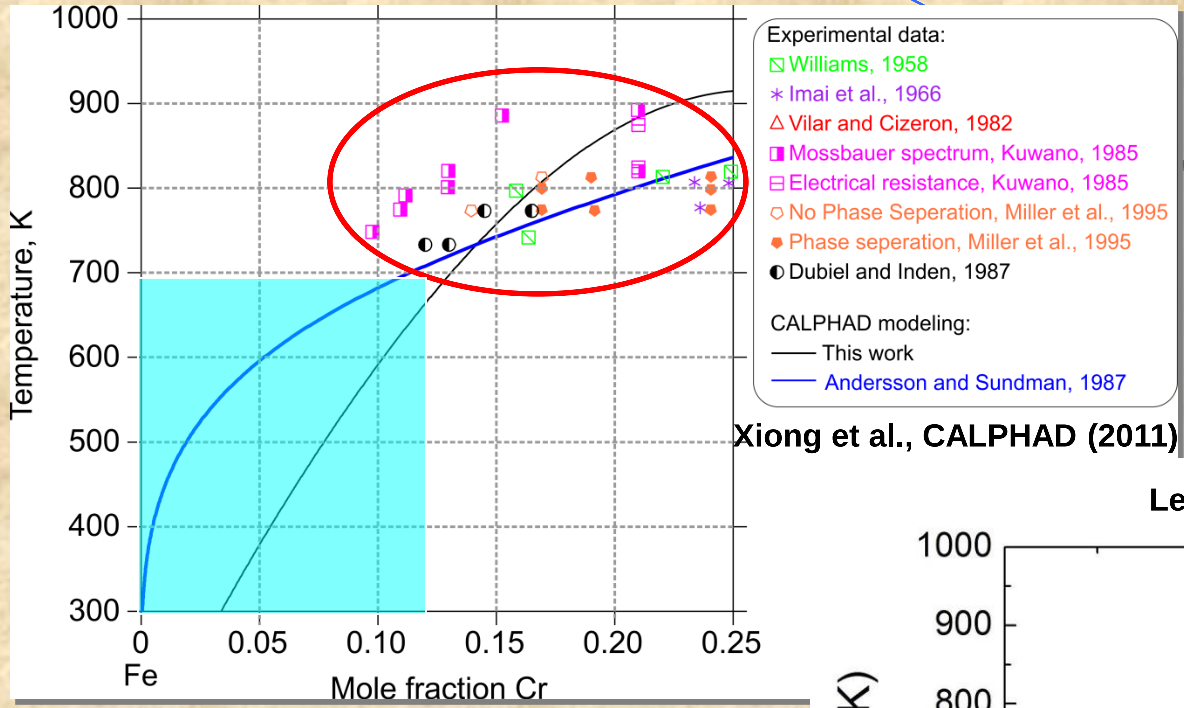
I. Mirebeau, PRB (2010)

- MS (EQ)
- MS (Q)
- MS (CR)

Phase decomposition into α ad α’

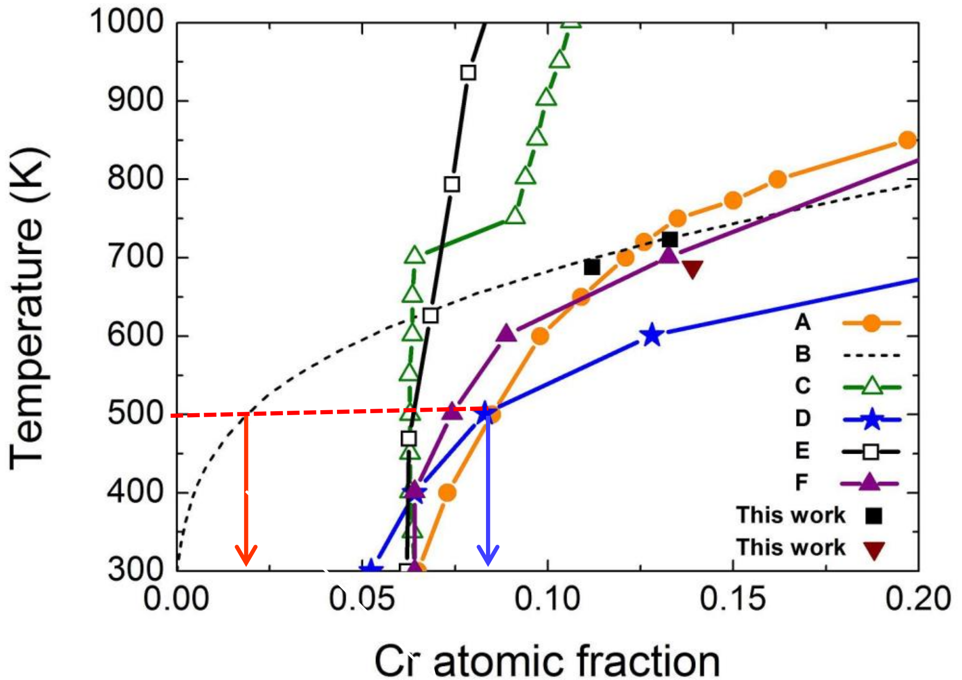


Miscibility gap boundary



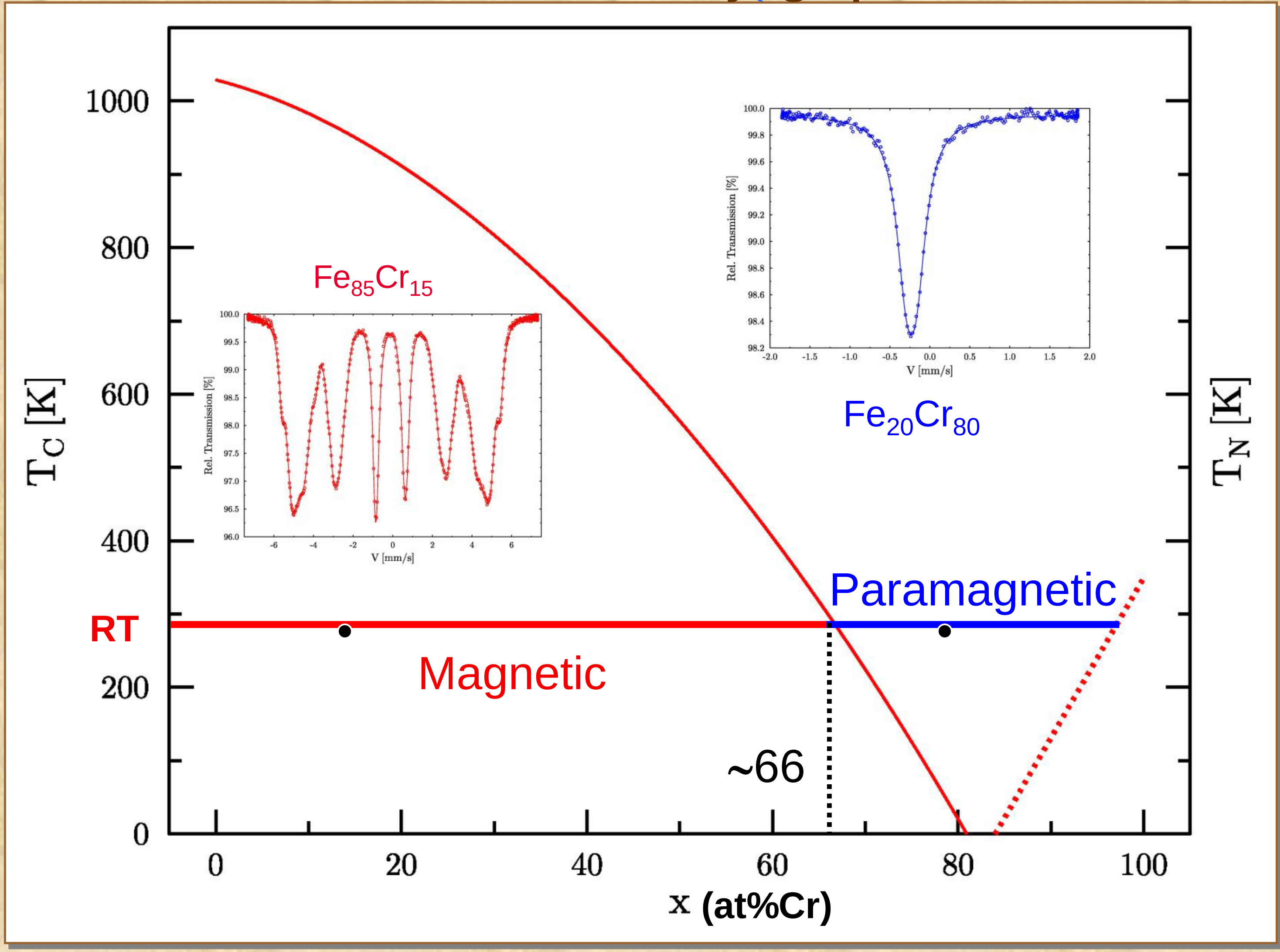
Xiong et al., CALPHAD (2011)

Levesque et al., PRB, 84 (2011) 184205



Phase decomposition into α ad α'

- Borders of miscibility gap



Borders of miscibility gap

S. M. Dubiel & G. Inden, Z. Metallkde, 78 (1987) 544

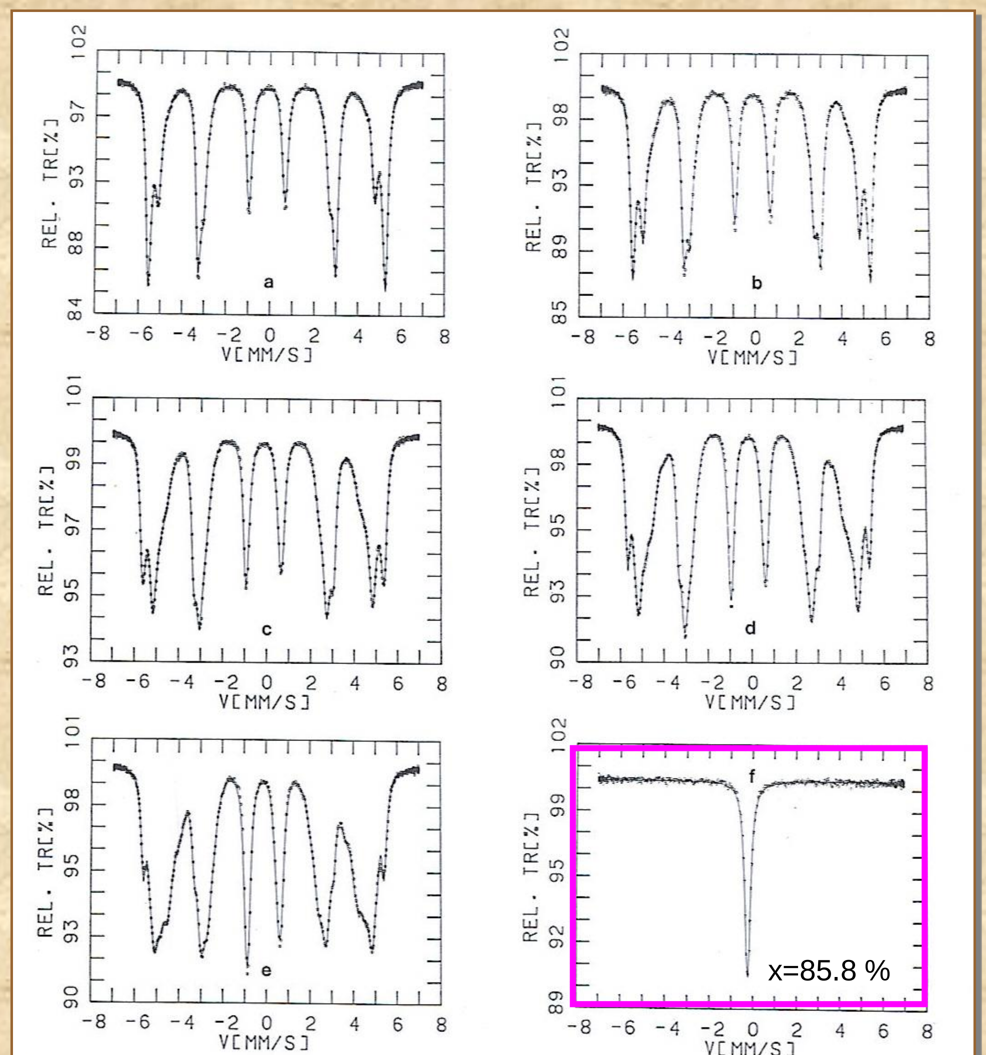
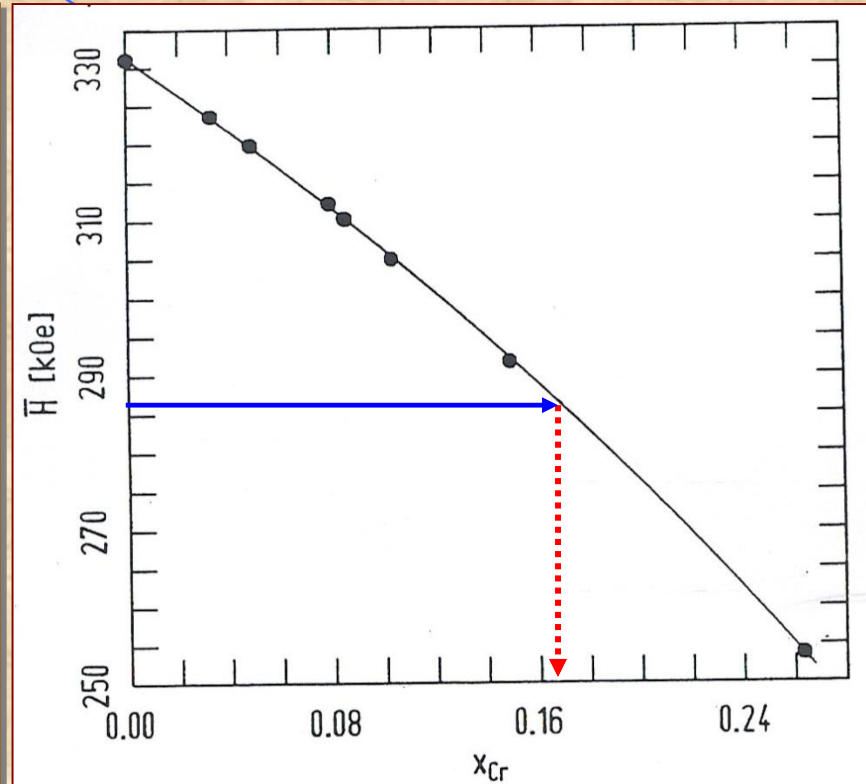


Fig. 3a to f. Room temperature Mößbauer spectra of single phase $Fe_{1-x}Cr_x$ alloys with (a) $x = 0.033$, (b) $x = 0.0485$, (c) $x = 0.079$, (d) $x = 0.103$, (e) $x = 0.149$, and (f) $x = 0.858$. The solid lines represent the fitted spectra.



Borders of miscibility gap

- Annealed samples: (a)15, (b) 20.8, (d) 70.6 at%Cr

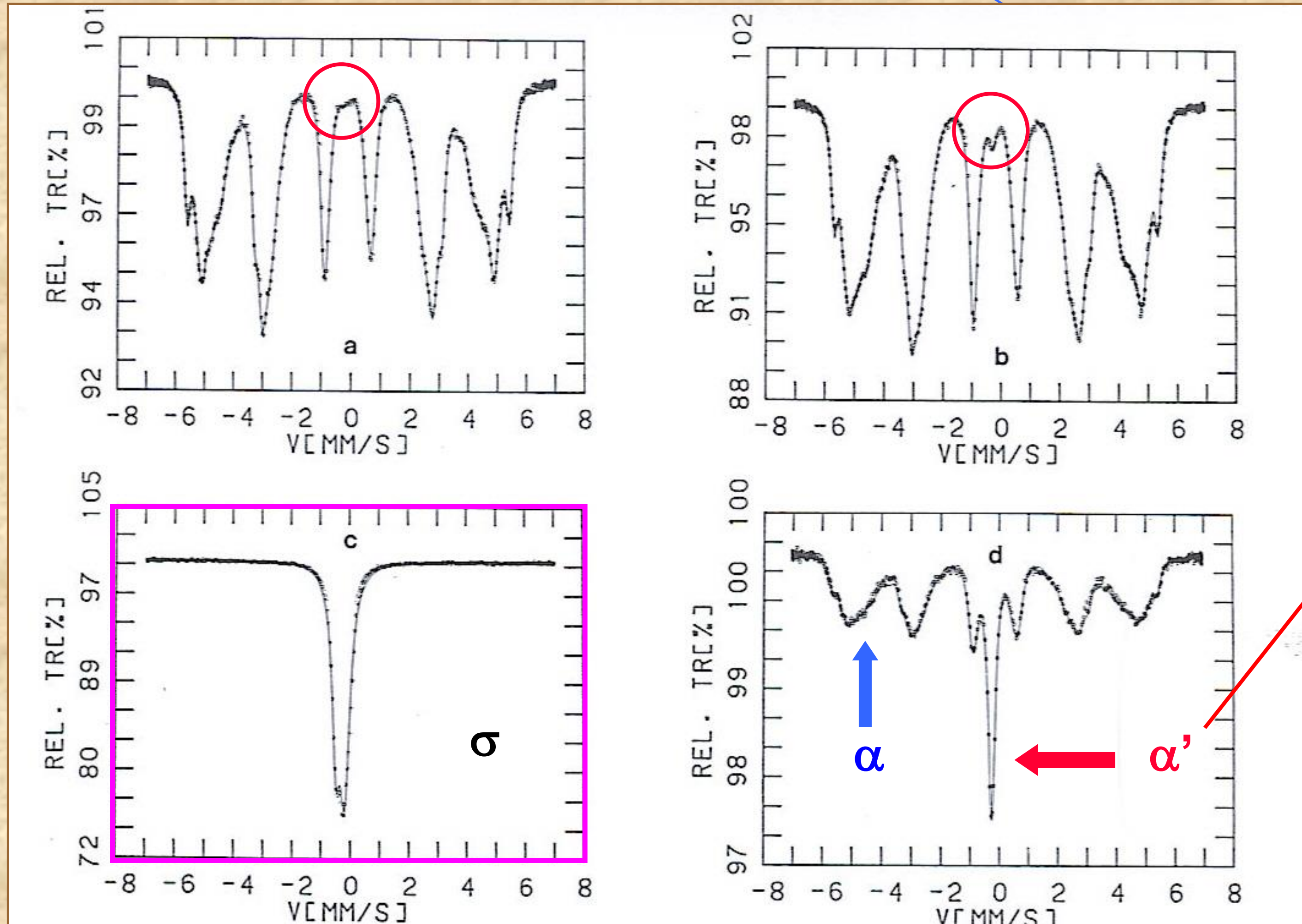
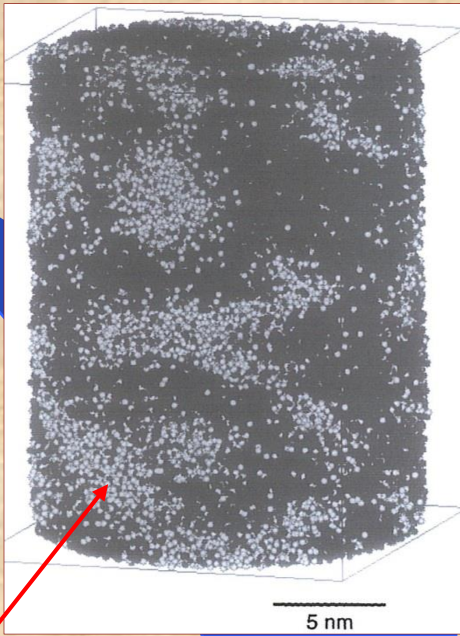


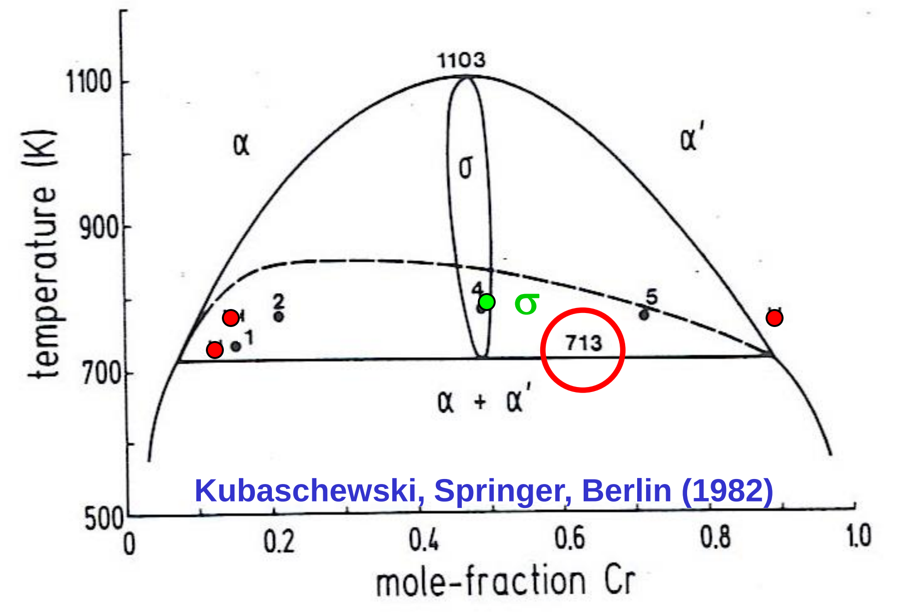
Fig. 8a to d. Room temperature Mößbauer spectra of the long term annealed alloys (a) no. 1, (b) 2, (c) 4, and (d) 5. The spectra (a), (b) and (d) correspond to two-phase states $\alpha + \alpha'$, spectrum (c) corresponds to the σ phase. The solid lines represent the fitted spectra.



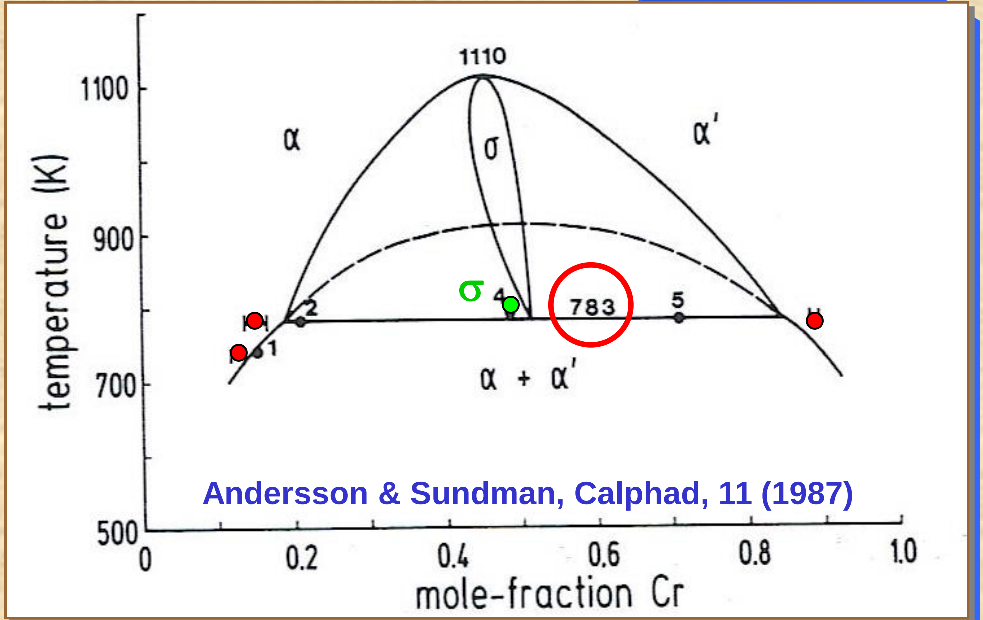
S. M. Dubiel & G. Inden, Z. Metallkde, 78 (1987) 544

Borders of miscibility gap

x (%)	x_α(<N>)	x_α(<H>)	$x_{\alpha'}$
15.0	12.9	12.0	-
20.8	14.3	14.0	-
70.6	15.7	16.5	88.0

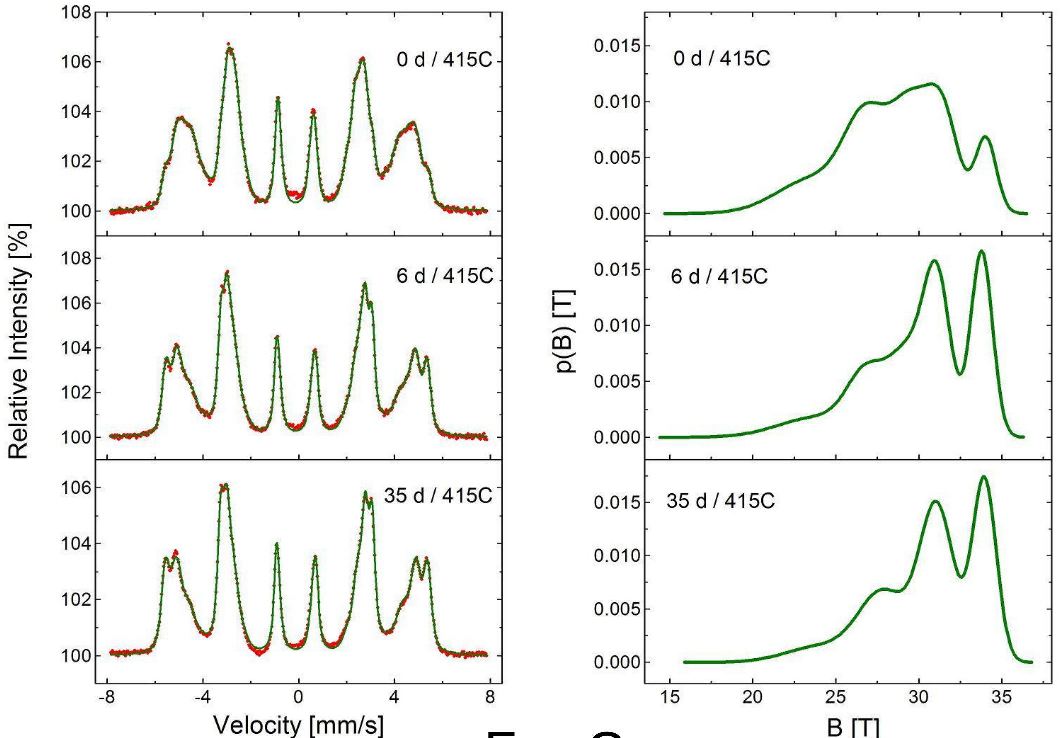


Kubaschewski, Springer, Berlin (1982)

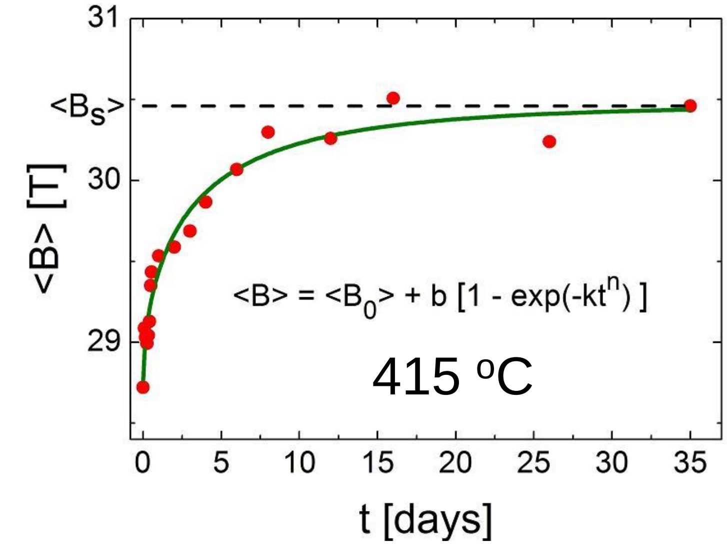


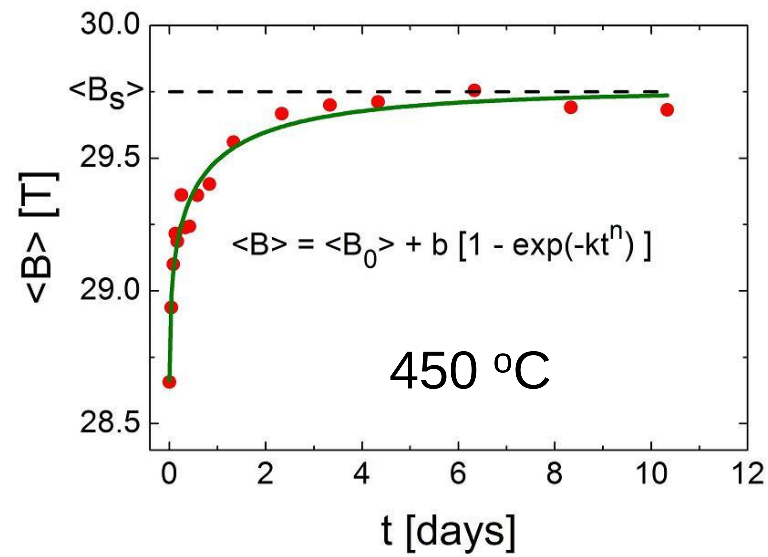
Andersson & Sundman, Calphad, 11 (1987)

Borders of miscibility gap



$Fe_{85}Cr_{15}$

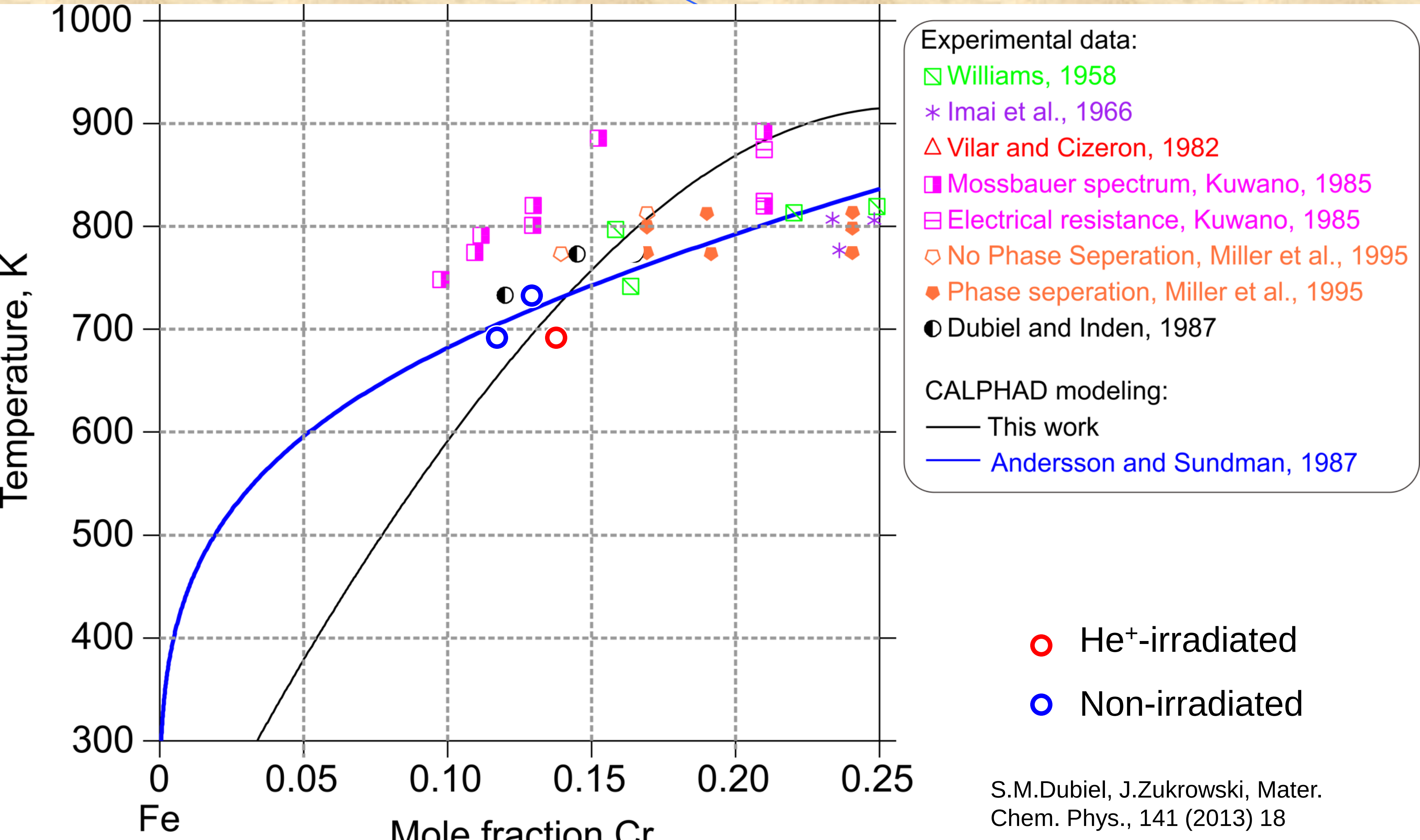




T (^{o}C)	Sample	x_{Cr} (%)
415	NR	11.2(3)
415	IR	13.9(3)
450	NR	13.3(3)

S.M. Dubiel, J. Zukrowski, Mater. Chem. Phys., 141 (2013) 18

Borders of miscibility gap

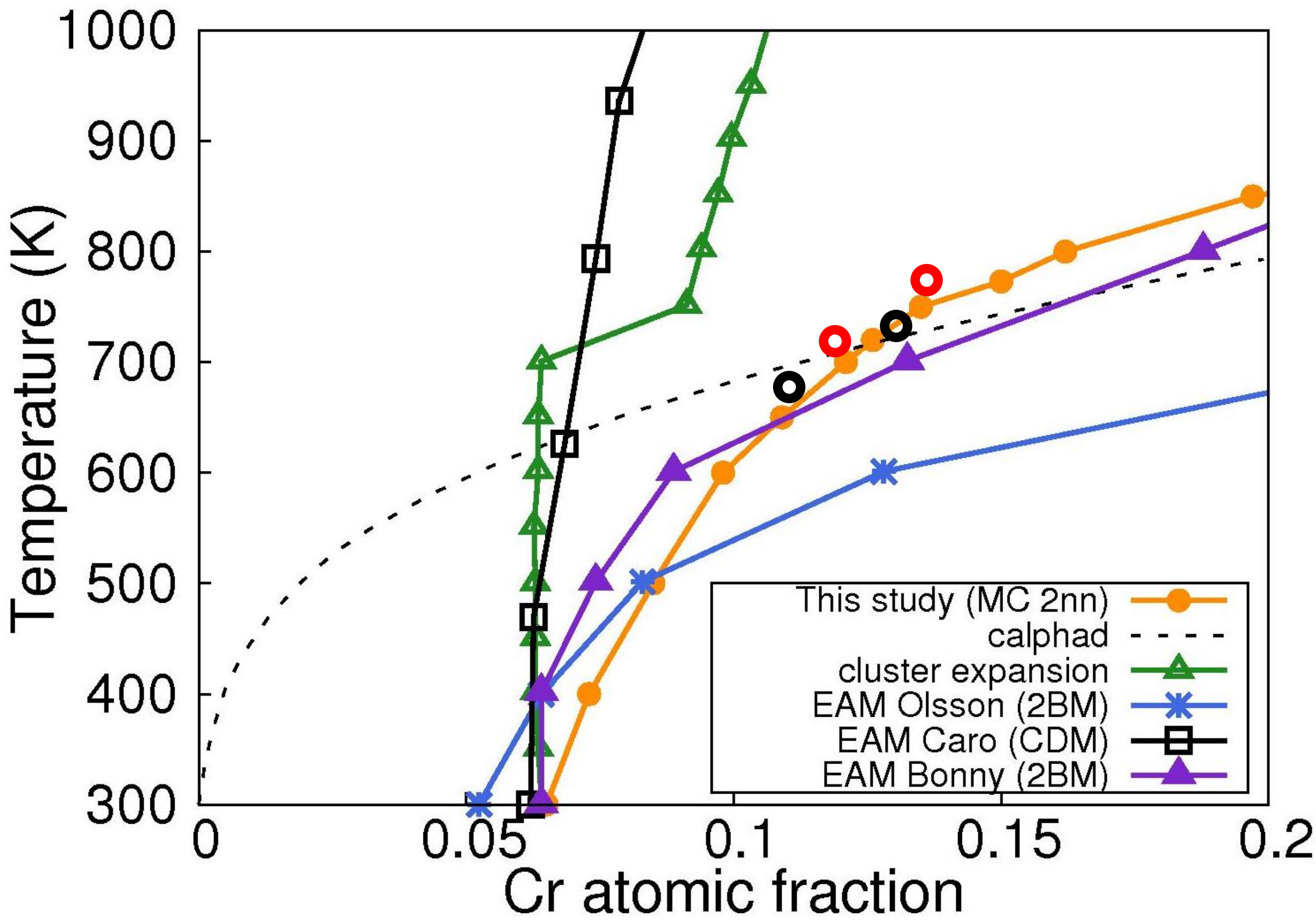


S.M.Dubiel, J.Zukrowski, Mater. Chem. Phys., 141 (2013) 18

Xiong et al., CALPHAD (2011)

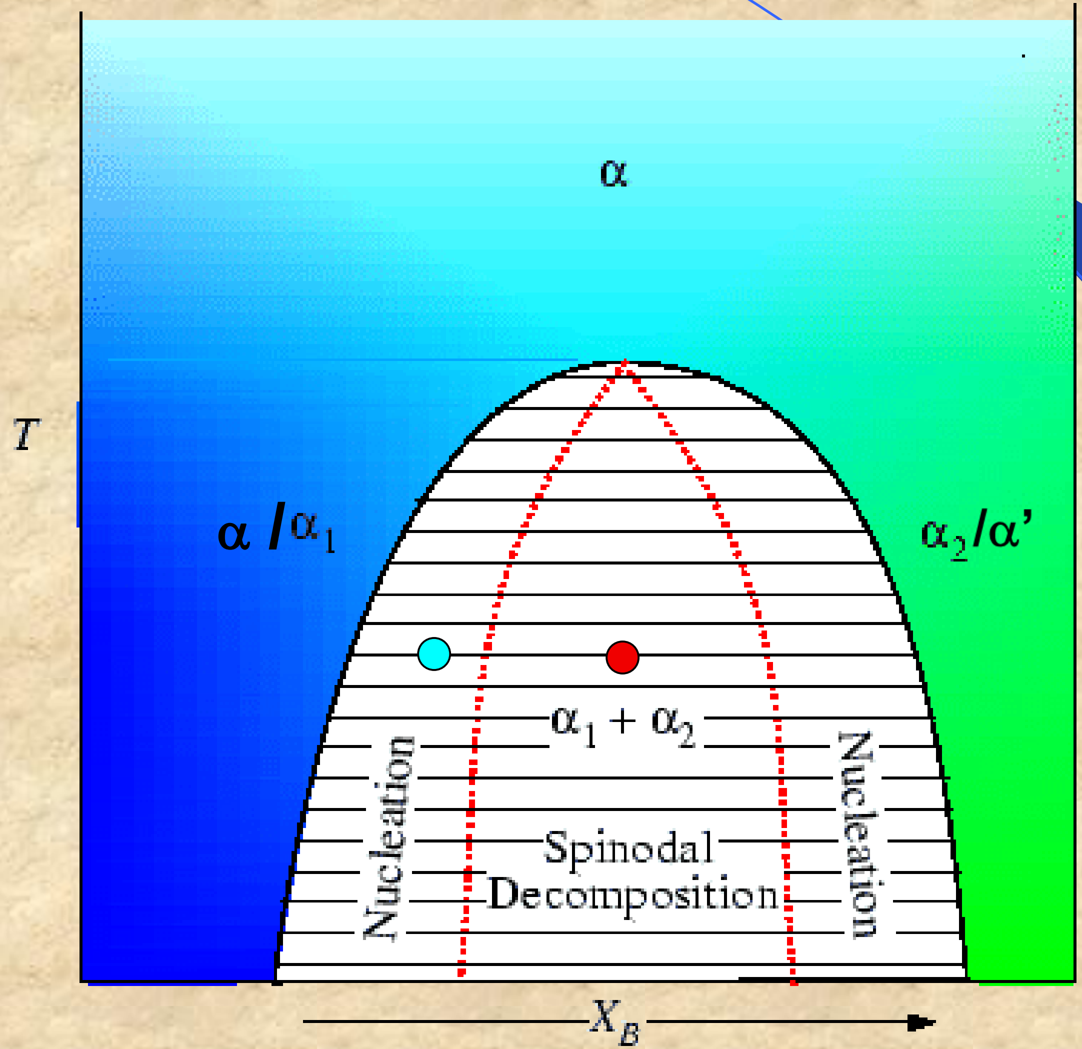
Borders of miscibility gap

M. Levesque *et al.*, PRB, 84 (2011) 184205



Dubiel & Inden (1987); Dubiel & Zukrowski (2013)

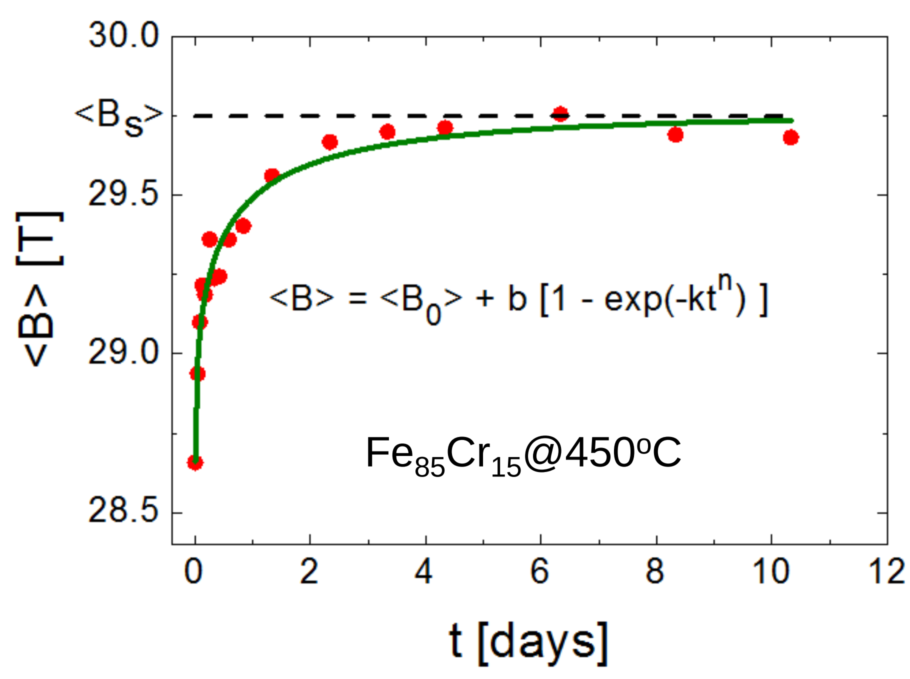
Phase decomposition into α and α’



http://pruffle.mit.edu/3.00/Lecture_32_web/node3.html

Phase decomposition into α ad α'

- Kinetics of decomposition



Arrhenius law

$$k = k_o \exp\left(-\frac{E}{k_B T}\right)$$

$$E = \frac{T_1 T_2}{T_2 - T_1} k_B \ln\left(\frac{k_2}{k_1}\right)$$

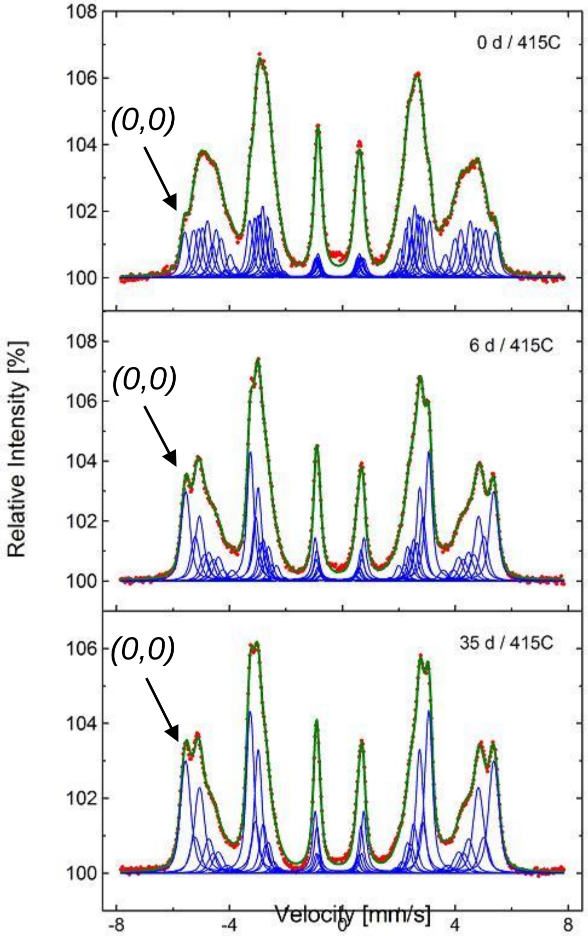
122 kJ/mol

T (^{o}C)	Sample	x_{Cr} (%)	n	k [s^{-1}]
415	NR	11.2(3)	0.6(1)	0.3
415	IR	13.9(3)	1.0(3)	3.9
450	NR	13.3(3)	0.4(5)	2.2

Dubiel & Zukrowski, Mater. Chem. Phys. 141 (2013) 18

Phase decomposition into α ad α'

- Short-range ordering: $Fe_{85}Cr_{15}$@415^{o}C



- Each spectrum was analyzed in terms of 17 subspectra (sextets) corresponding to particular atomic configurations *(m,n)*
- Analysis yielded probabilities of *(m,n)*, *P(m,n)*, based on which the average number of Cr atoms in *1NN*, *<m>*, that in *2NN*, *<n>*, and the one in *1NN-2NN*, *<m+n>*, was determined.
- SRO parameters, α_1, α_2, α_{12}, were next calculated from the following equations:

$$\alpha_1 = 1 - \frac{<m>}{8x}$$

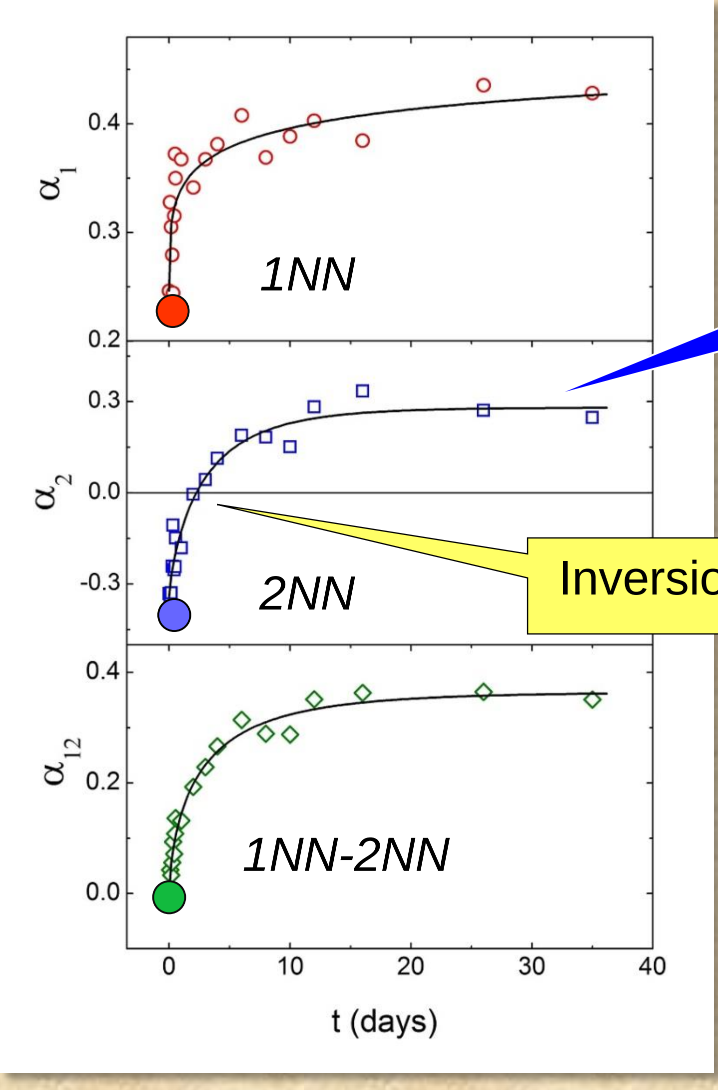
$$\alpha_2 = 1 - \frac{<n>}{6x}$$

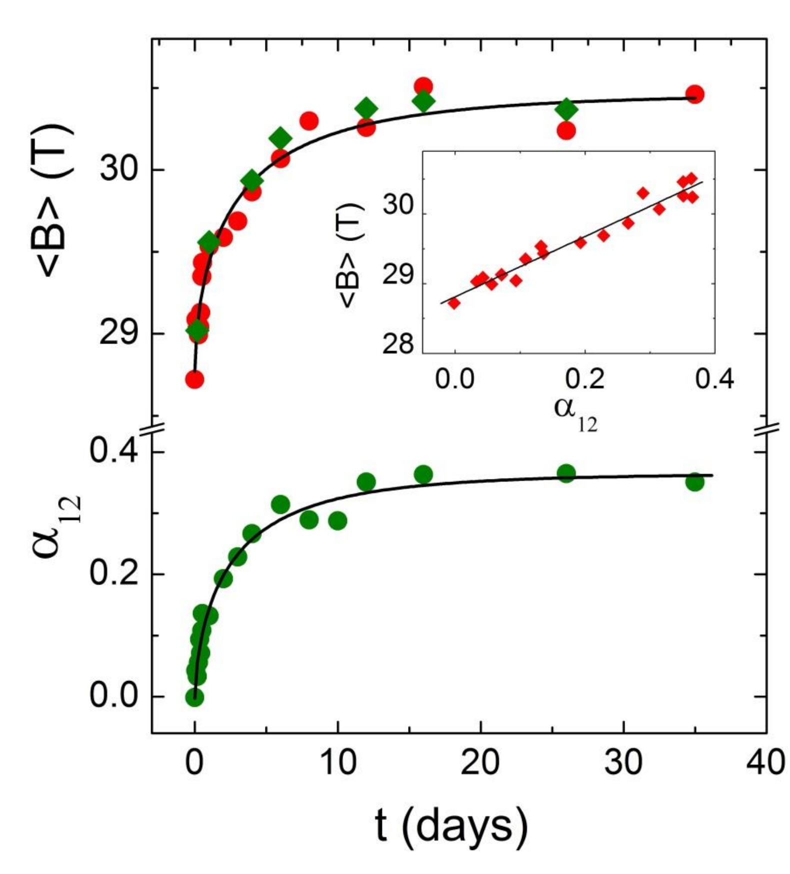
$$\alpha_{12} = 1 - \frac{<m+n>}{14x}$$

Phase decomposition into α ad α'

- Short-range ordering: $Fe_{85}Cr_{15}$ @ 415°C

Solid lines represent best fits in terms of JMAK-like equation, hence α_{12} is linearly correlated with <B>.

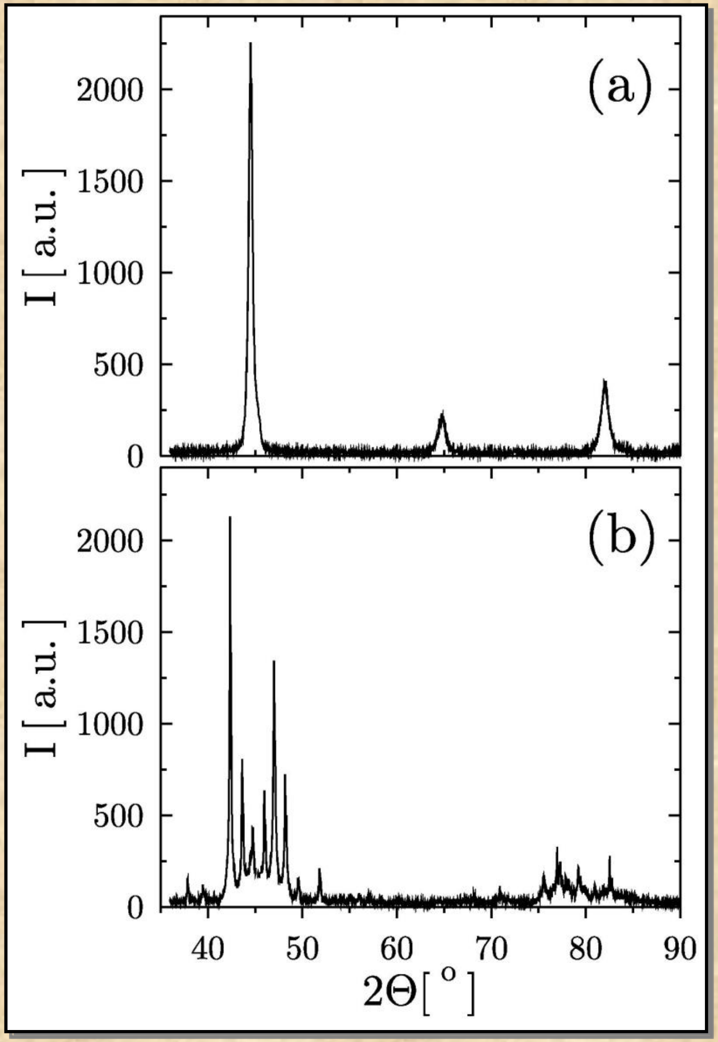




S. M. Dubiel, J. Zukrowski, Acta Mater., 61(2013)6207

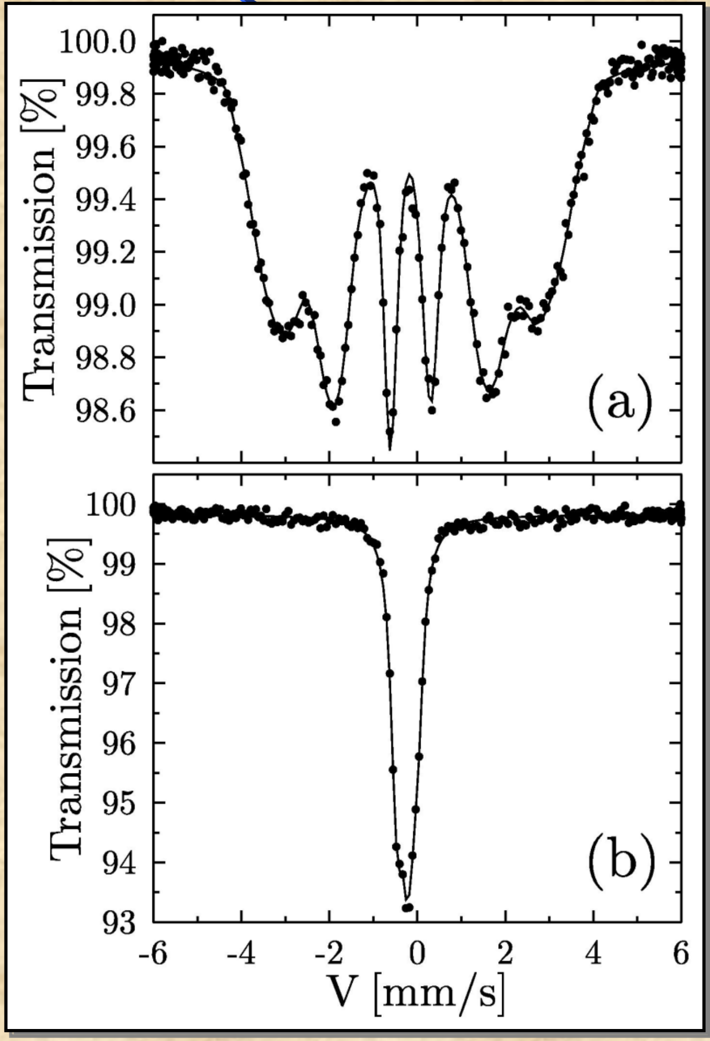
Sigma (σ) phase - identification

XRD • T = 295 K MS



α

σ



σ phase - kinetics

T_a = 700°C

$$A_\sigma = \frac{S_\sigma}{S_\sigma + S_\alpha} 100$$

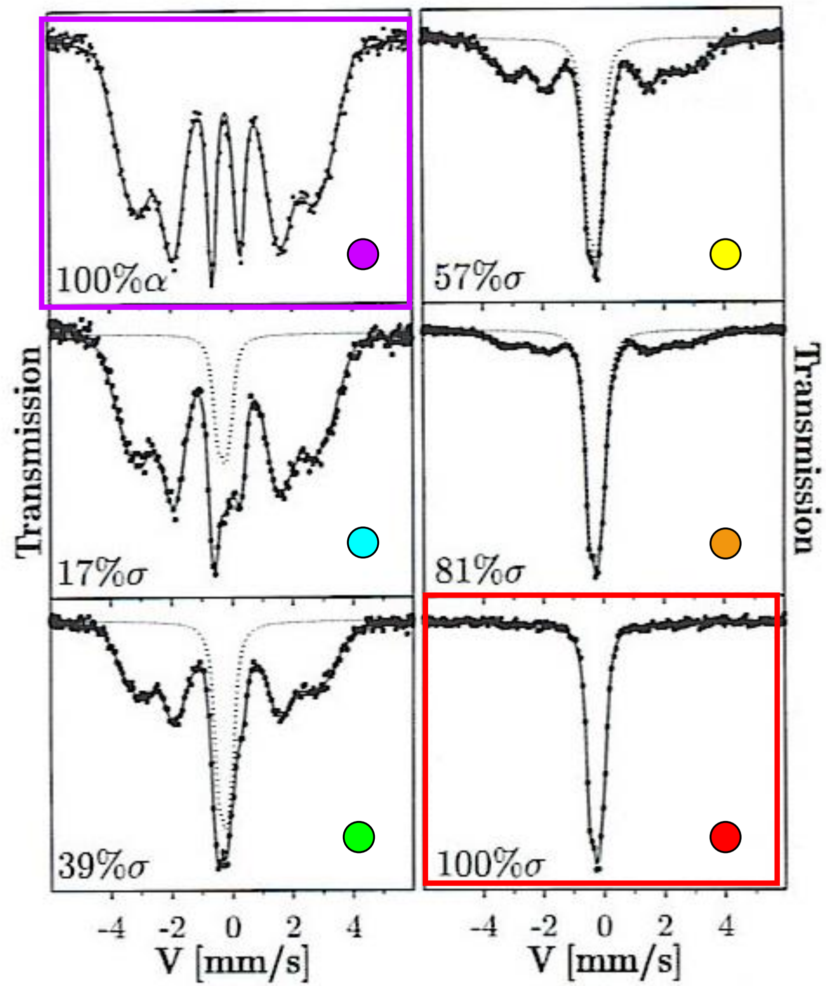


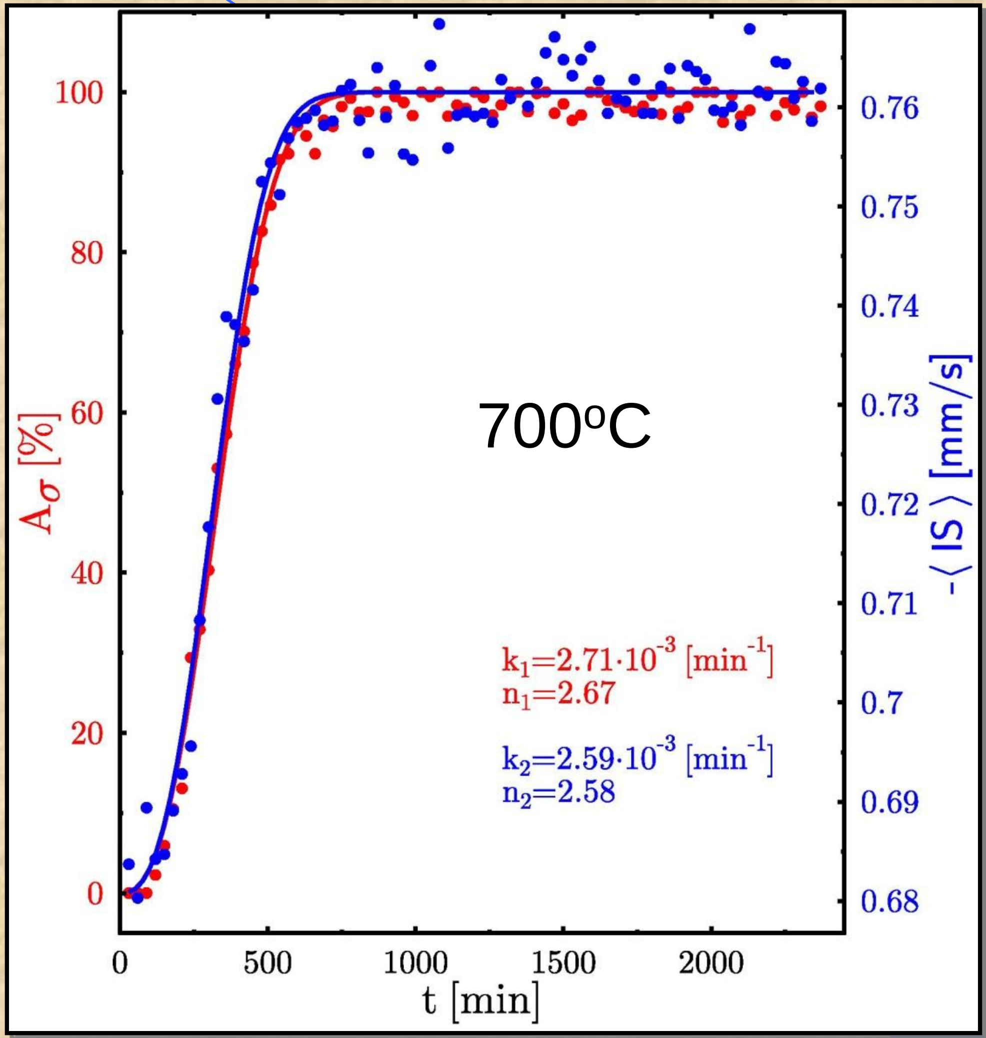
Fig. 1. Room temperature ^{57}Fe Mössbauer spectra recorded on an $Fe_{53.8}Cr_{46.2}$0.3 at% Ti sample with various amounts of the σ-phase formed. Its subspectrum has been marked by a dotted line.

Sigma (σ) phase - kinetics

$$A_\sigma = 100\left[1 - \exp[-kt^n]\right]$$

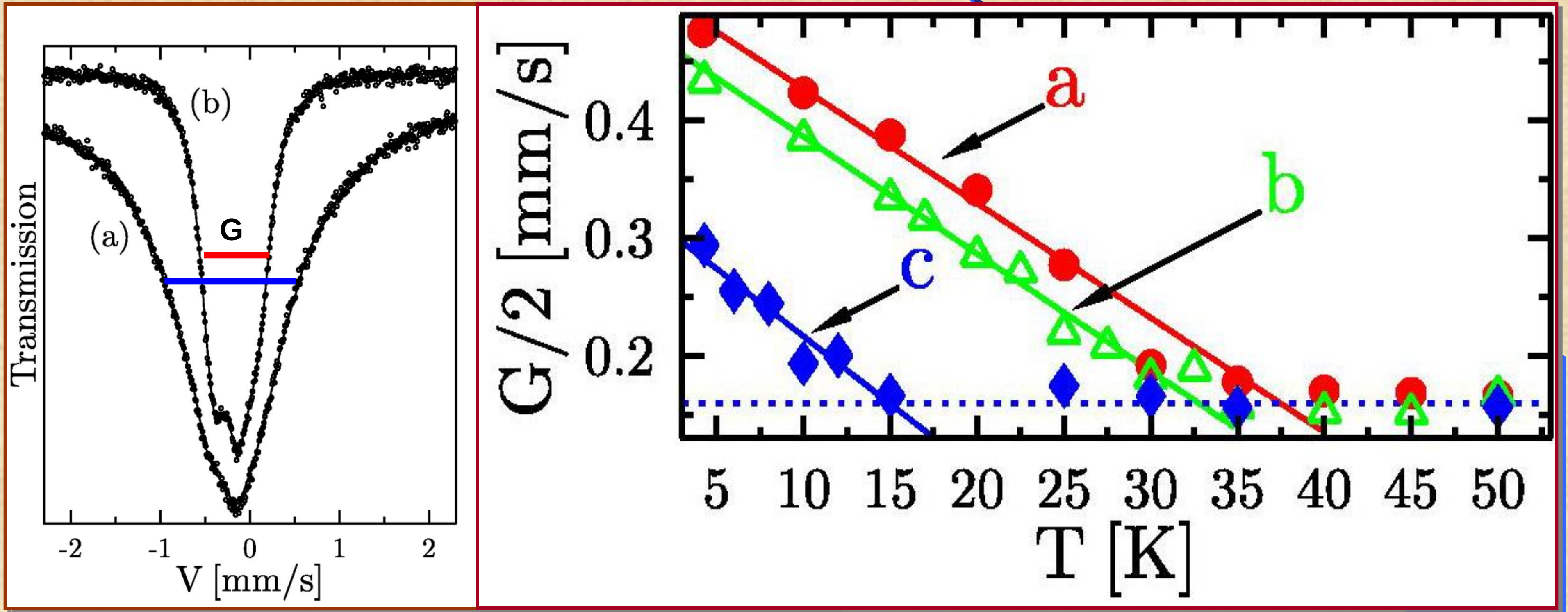
$$k = k_o \exp\left(-\frac{E}{RT}\right)$$

E = 196 ± 2 kJ/mol



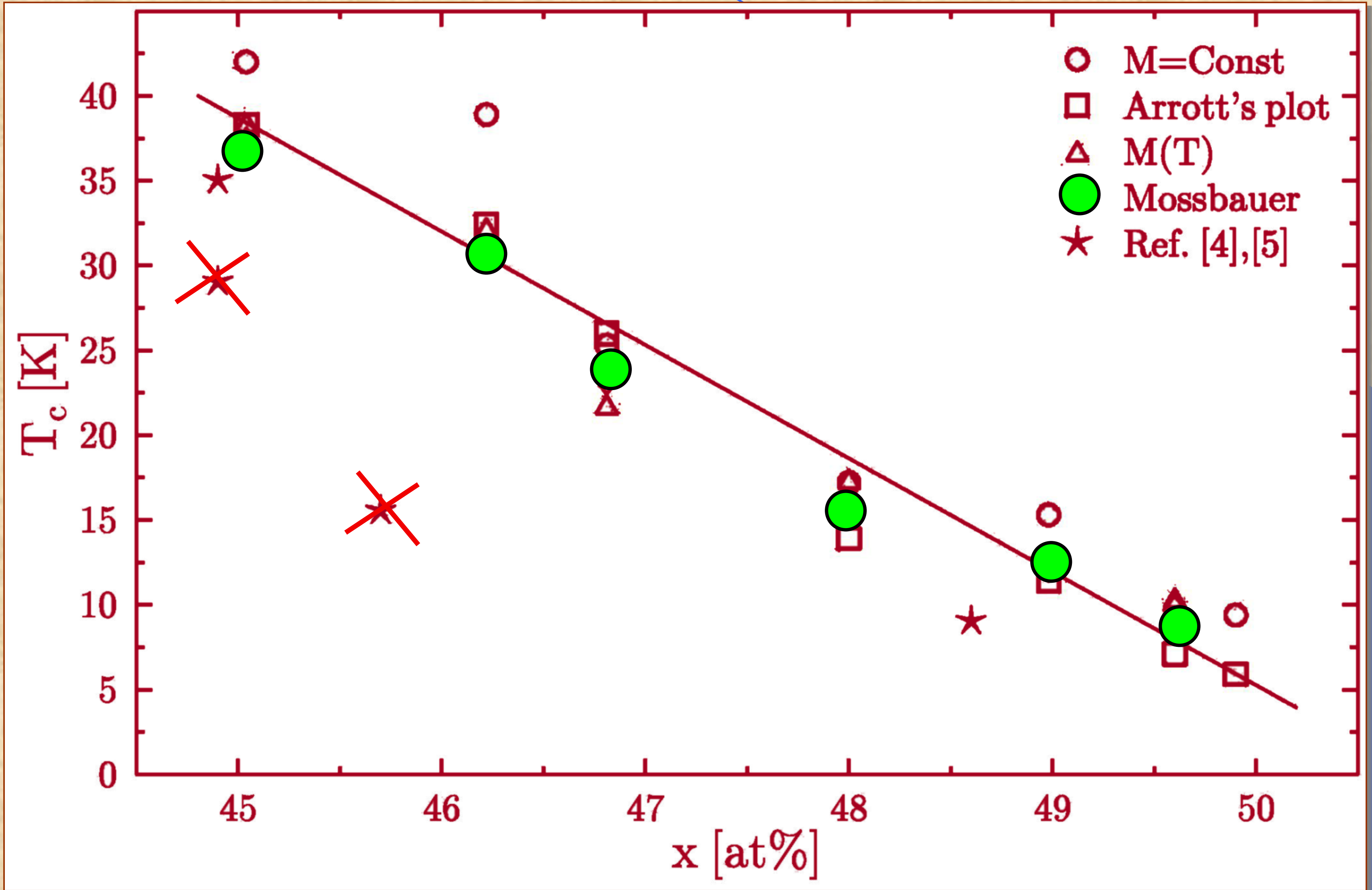
σ phase – Curie Temperature

(a) 4.2 K; (b) 295 K



(a) x = 45.0 (b) x = 46.2 and (c) x = 48.0

σ – Curie Temperature



Summary

Mössbauer Spectroscopy is a very useful techniques to quantitatively investiagte various issues pertinent to Fe-Cr alloys, and in particular:

- Short-rane ordering
- Borders of misceptibility gap
- Kinetics of phase separation
- Sigma-phase identification and its kinetics
- Magnetic ordering temperatures

Acknowledgements

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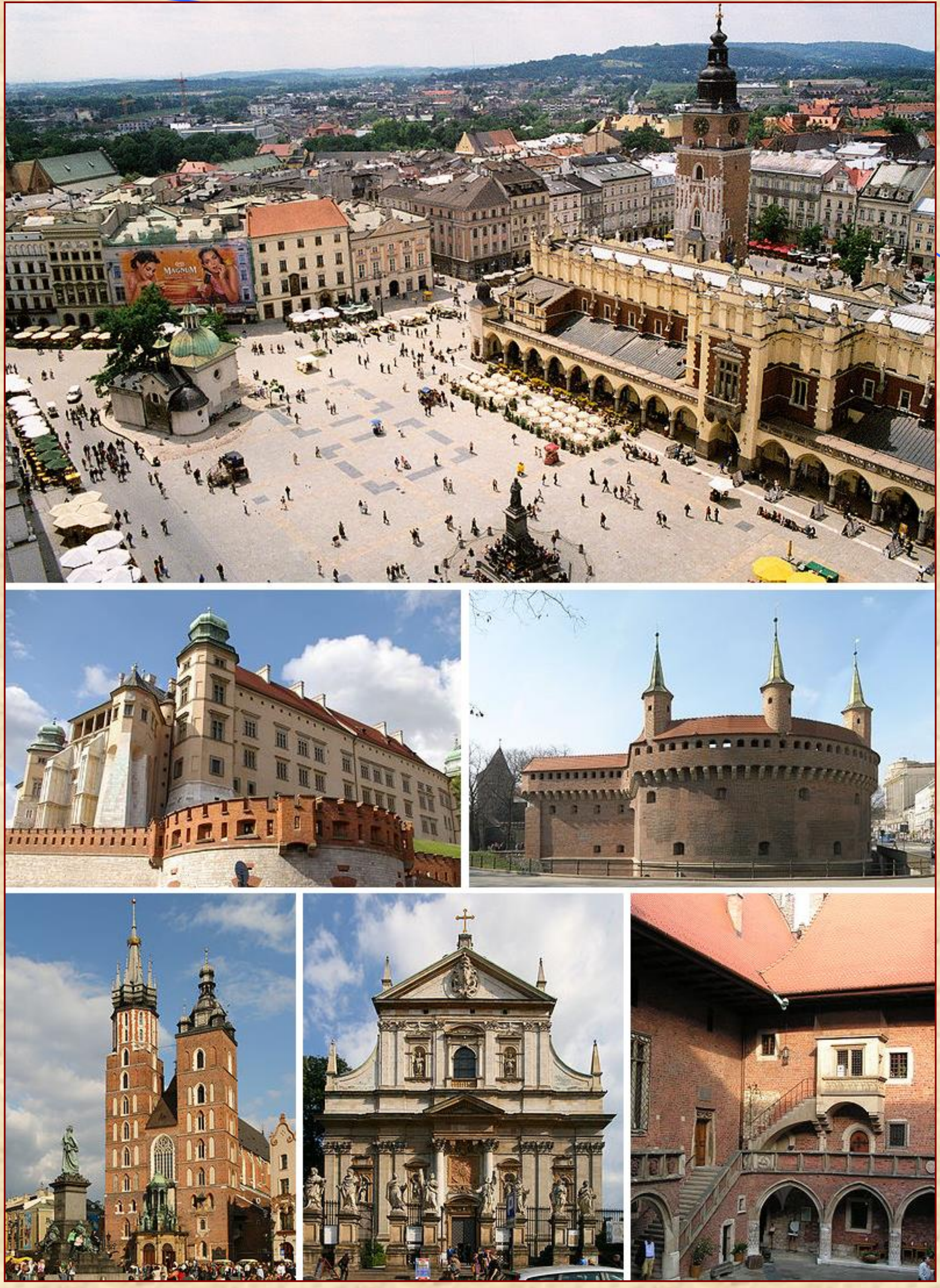
Ministry of Science and Higher Education
Republic of Poland



Thank you for listening!

Mössbauer Effect

Radiation	E [keV]	Intensity	Range* [nm]
γ	14.4	0.11	~20 000
X-K	6.3	0.28	~20 000
X-L	0.7	0.002	
CE-K	7.3	0.79	~10-400
CE-L	13.6	0.08	~20-1 300

* In metallic Fe

Range for He (25 keV) ~225 nm