σ-Phase, its Properties and its Relevance to Stainless Steels

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STAINLESS STEEL HISTORY

- 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), Philip Monnartz (D), Portevin (F), Borchers (D) and Max Mauermann (PL)

1912: English metallurgist Harry Brearley invents SS in his search for an alloy to protect cannon bores from erosion. The first commercial production of SS occurs in August, 1913.

1915: During World War I, SS is used to manufacture valves for aircraft engines.

1919-1923: Sheffield cutlers start regular production of SS cutlery, surgical scalpels and tools.

1924: The first SS roof makes an appearance in America.

1928: The brewery industry installs the first SS fermenting tank.

1929: The first SS tanker is used for transporting 3,000 gallons of milk.

1929-1930: The Chrysler Building's top seven arches are clad in SS. This New York City landmark is one of the world's most recognized skyscrapers.

1931: The first SS railway carriage appears in the US. Also, Rolls Royce produces the first SS radiator grill and emblem.

1933: SS kitchen sinks and furniture are introduced.

1950: SS is used with increasing frequency for car accessories.

1954: The first SS underwater TV camera is made.

1963: The first SS razor blades are produced.

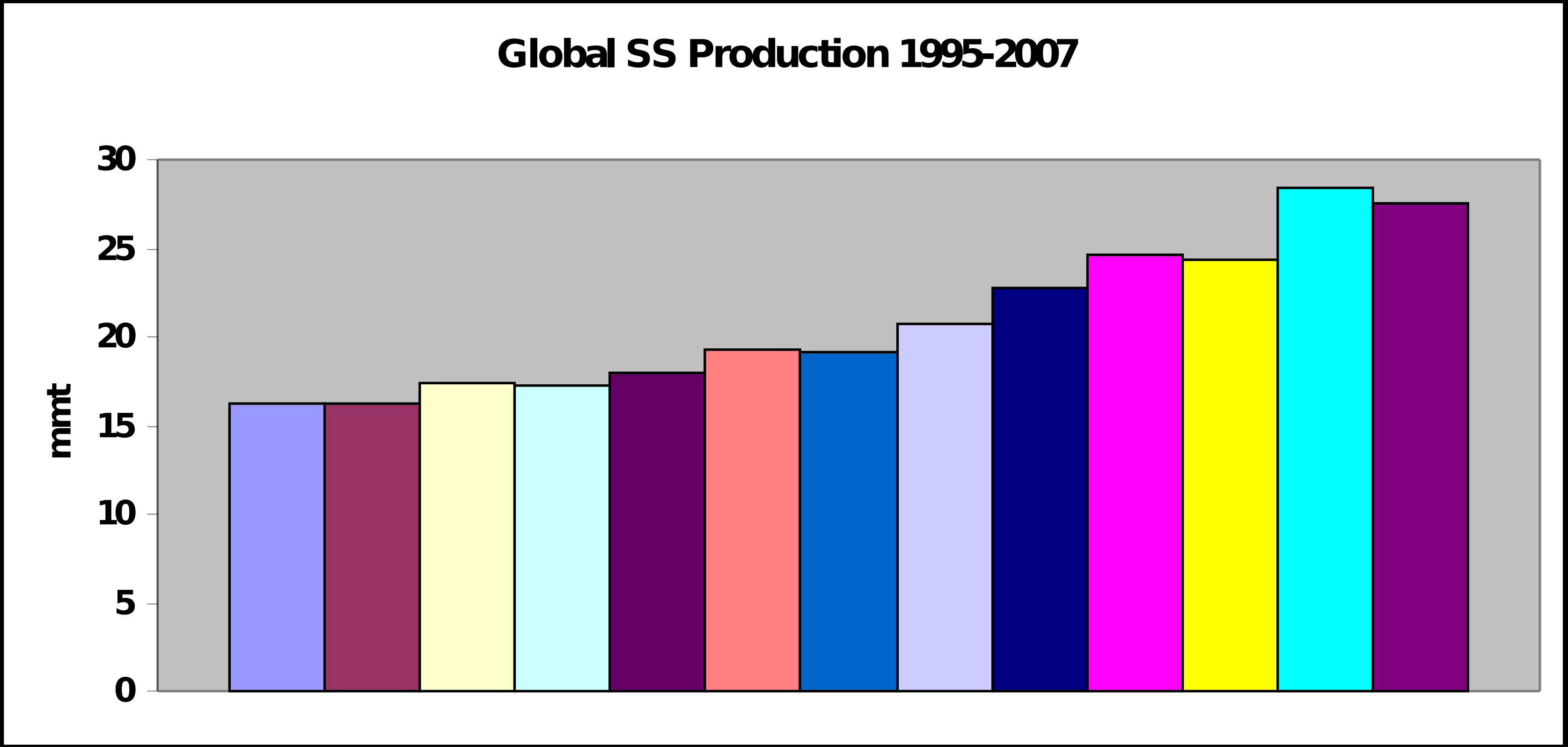
1969: The first men on the moon (Apollo 11) are taken there by a SS Saturn V Rocket.

2000: Grey Feather Toy Creations introduces bird toys constructed exclusively with SS

STAINLESS STEELS FAMILY

- Austenitic and Super Austenitic SS (grades: 304, 316, 321, 347); typically: 18%Cr and 10%Ni, known also as 18/10 SS (70% of all SS)
- Duplex and Super Duplex SS 50/50 mix of ferrite and austenite (grades: 2205, 2324, 2327, 2328, 2377); 19-28%Cr, 7%Ni and ≤ 5%Mo
- Ferritic SS; 10-29%Cr, few % of Mo, W, Ni (Fe-29Cr-4Mo; Fe-29Cr-4W;Fe-29Cr-2Ni)
- Martensitic SS; 12-14%Cr, ≤ 2%Ni, ≤ 1%Mo

STAINLESS STEELS PRODUCTION



Increase from ~16 to ~27 mmt (~75 bln $)

EXAMPLES OF INDUSTRIAL USE

- Oil Refineries and Pipelines

EXAMPLES OF INDUSTRIAL USE

• Power Plants, Heat Exchangers Gas Turbines and Boilers

EXAMPLES OF INDUSTRIAL USE

- Buildings and Constructions

EXAMPLES OF INDUSTRIAL USE

- Motobikes, Cutlery and Watches

THE PROBLEM

Precipitation of the σ-phase that causes degradation of many useful properties

- decrease of ductility and impact toughness
- increase of embrittlement
- decrease of corrosion resistance
- increase of hydrogen-induced embrittlement and cracking

PRECIPITATION

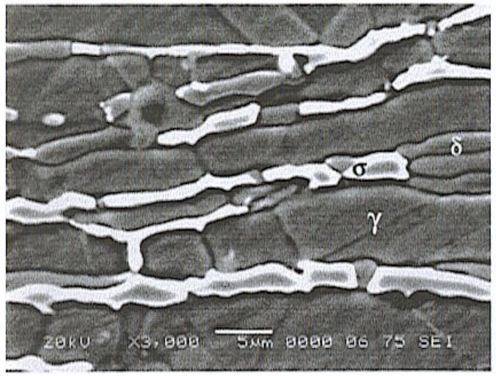


Fig. 7 – SEM micrograph of the base metal annealed at 850 °C.

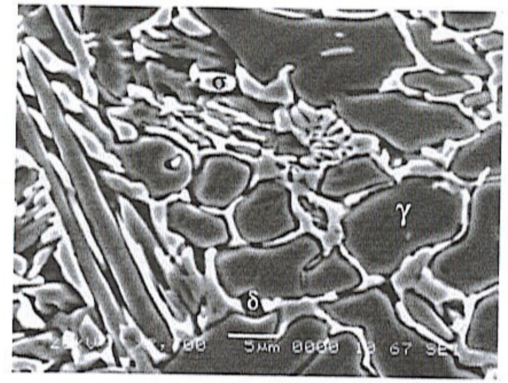


Fig. 5 – SEM micrograph of the weld metal annealed at 850 °C

B

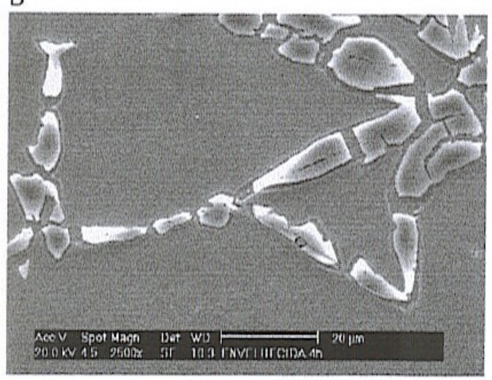


Fig. 1 – Micrographs of a sample aged at 850 °C for 4 h, showing the presence of the sigma phase at the grain boundaries.

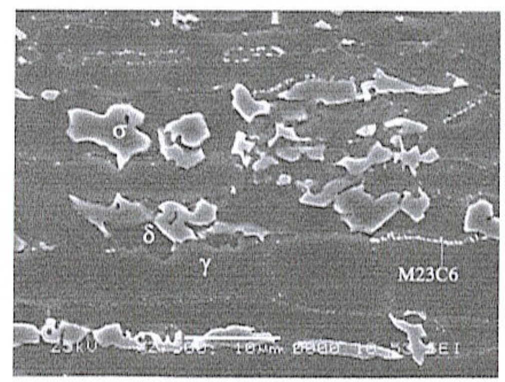
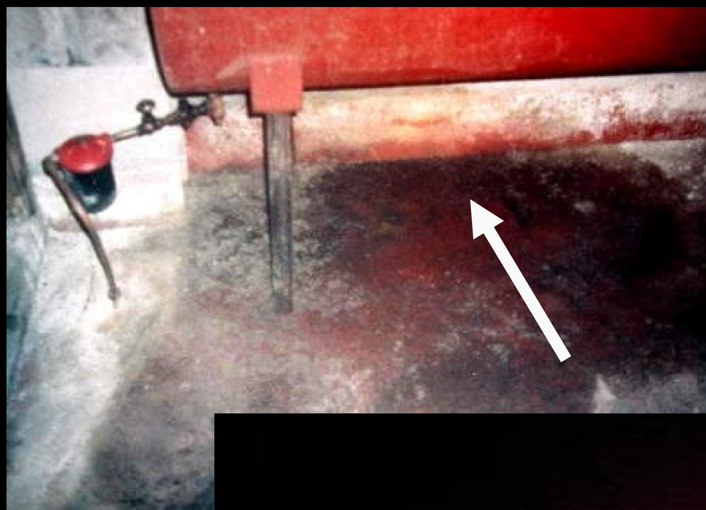


Fig. 6 – SEM micrograph of the HAZ annealed at 850 °C.

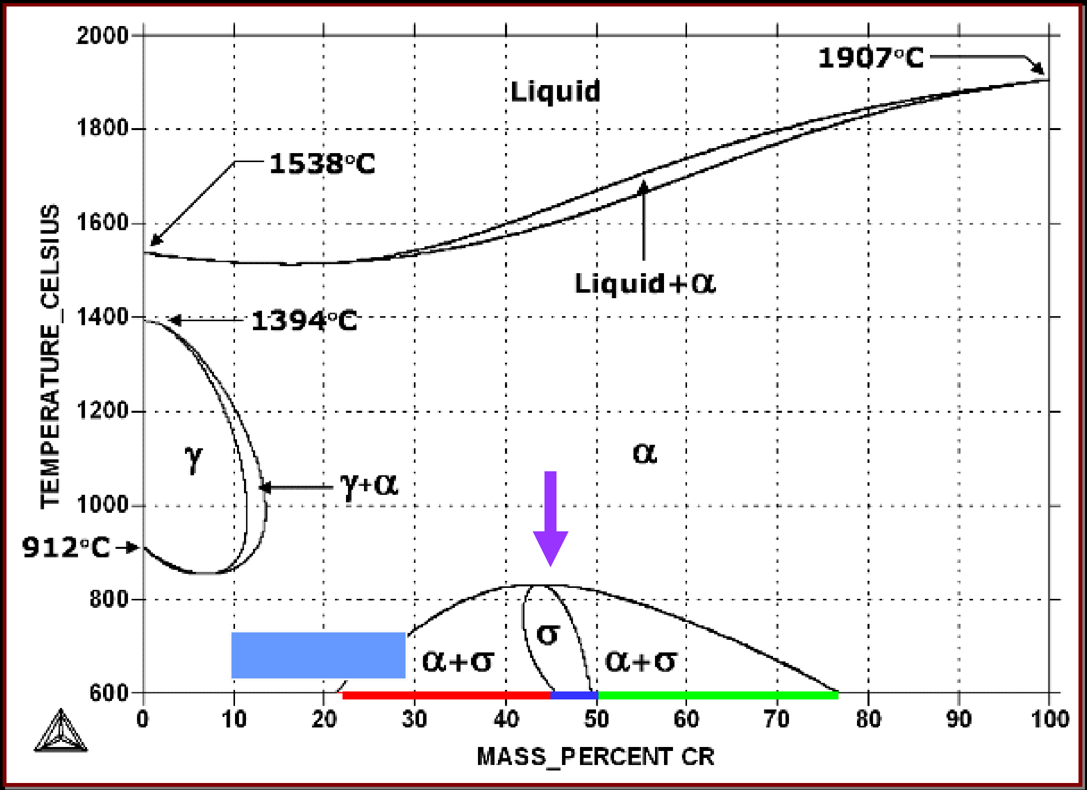
Mater. Charact., 59 (2008) 503; superferric SS (Fig.1); duplex SS (Figs. 5-7)

FAILURES & LEAKAGES

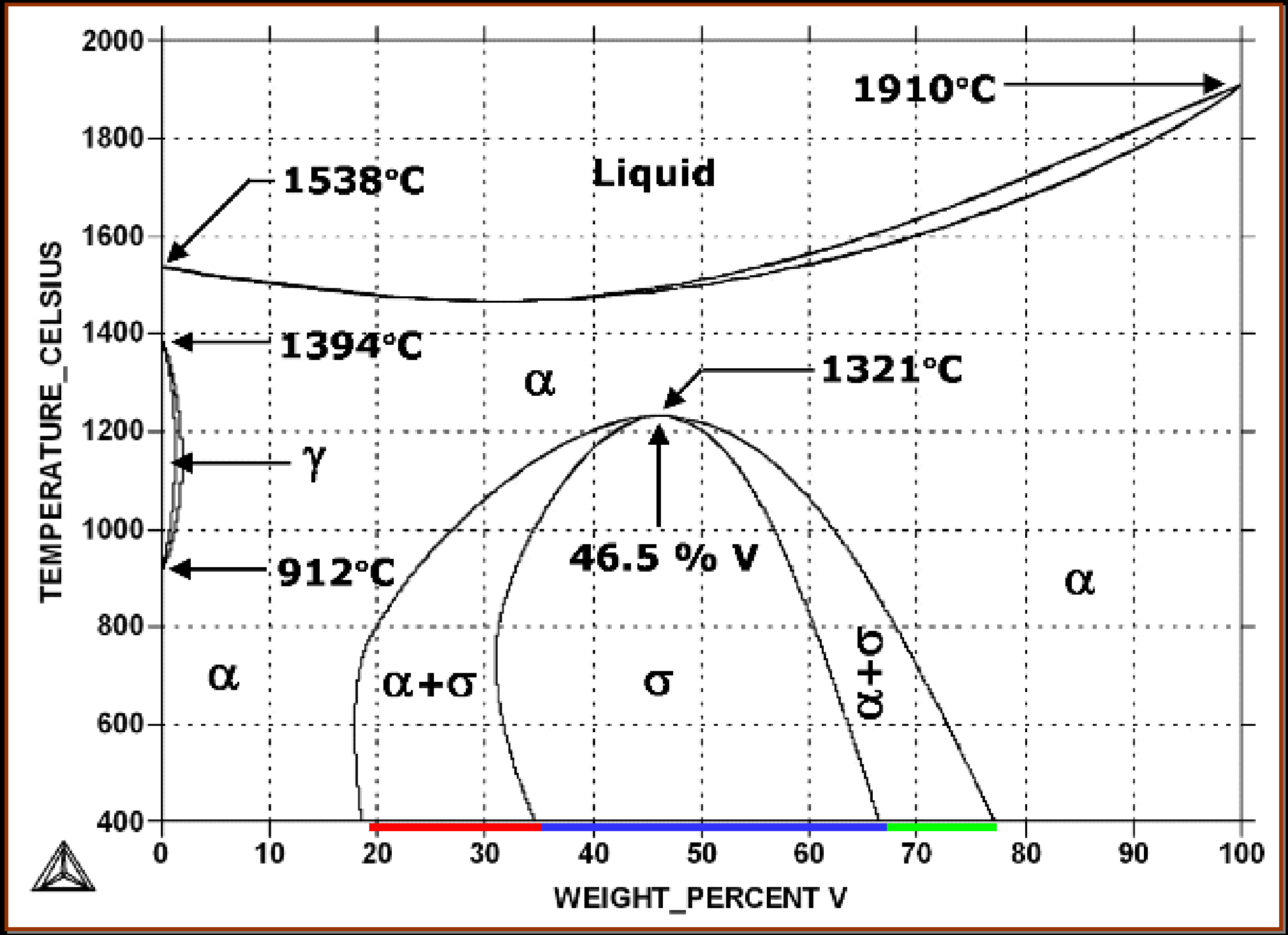


SIGMA - PHASE FAMILY

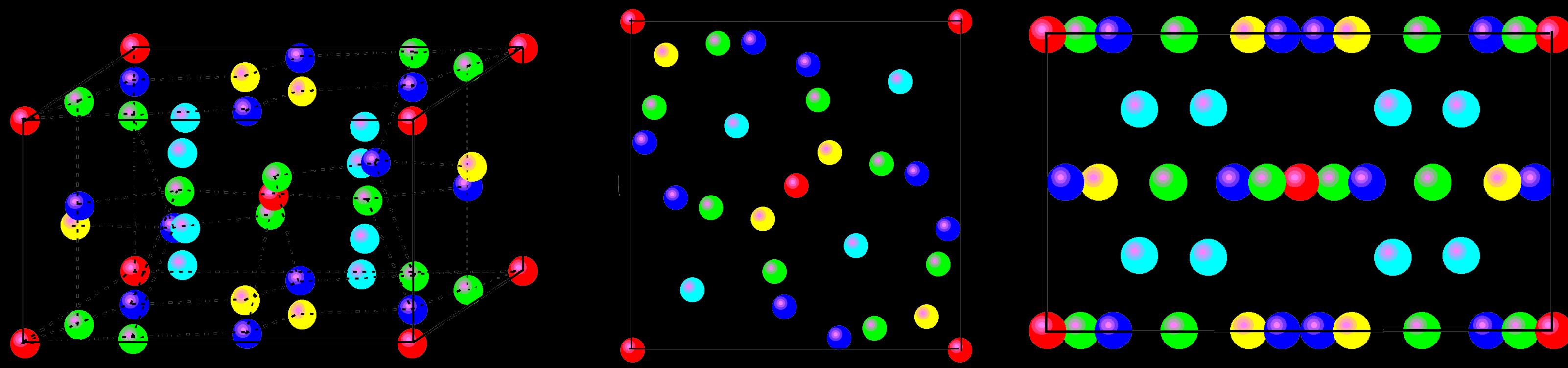
- 53 cases in binary alloys e.g. FeCr, FeNb, FeTa, FeV, FeMo, FeTc, FeRe

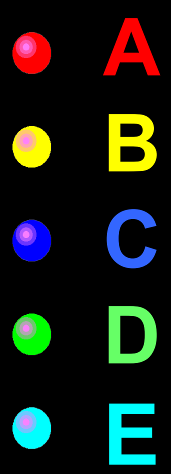


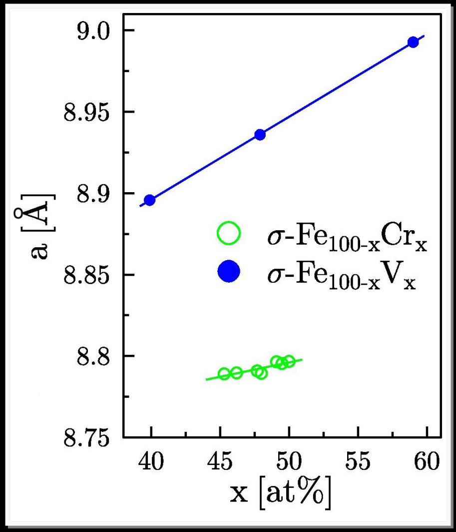
PHASE DIAGRAM - FeV SYSTEM

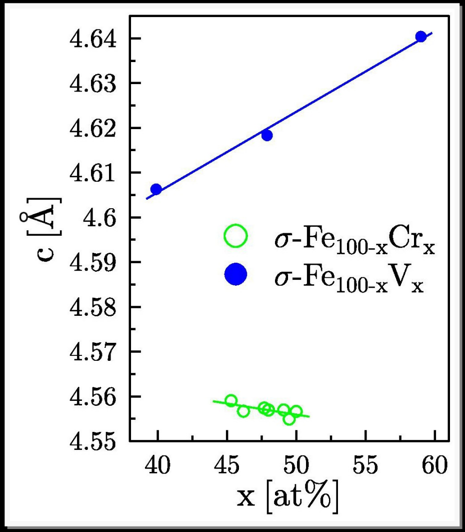


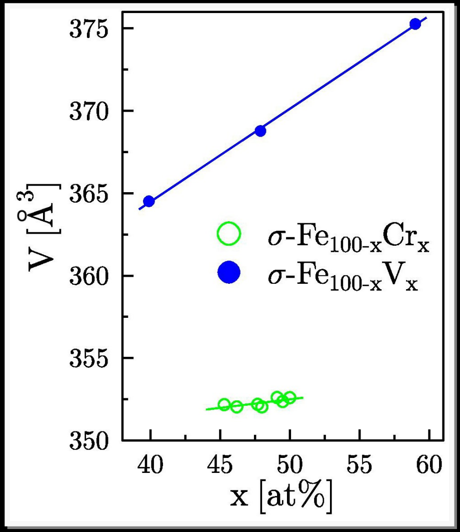
STRUCTURE – UNIT CELL









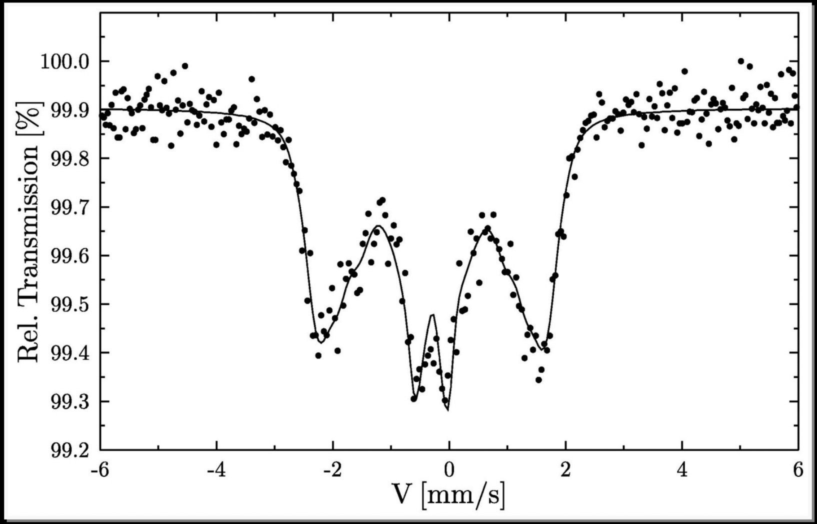


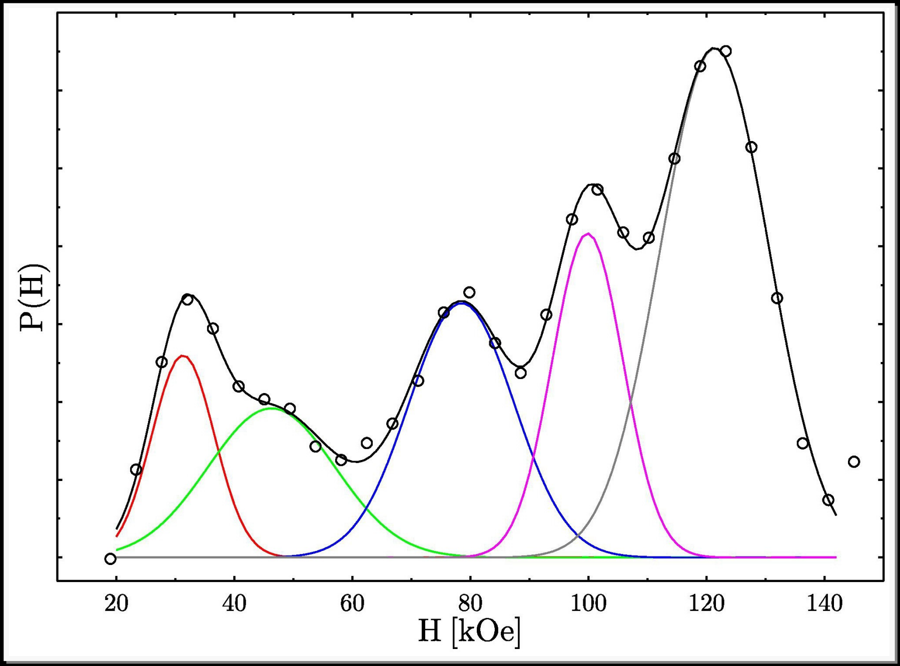
STRUCTURE – SITES

No	Site	CN	ON	<d>[nm]
1	I/A	12	2	0.2508
2	II/B	15	4	0.2701
3	III/C	14	8	0.2652
4	IV/D	12	8	0.2526
5	V/E	14	8	0.2638

STRUCTURE – SITES OCCUPANCY

- Mössbauer spectroscopy (σ-FeCr) B_a = 13.5 T



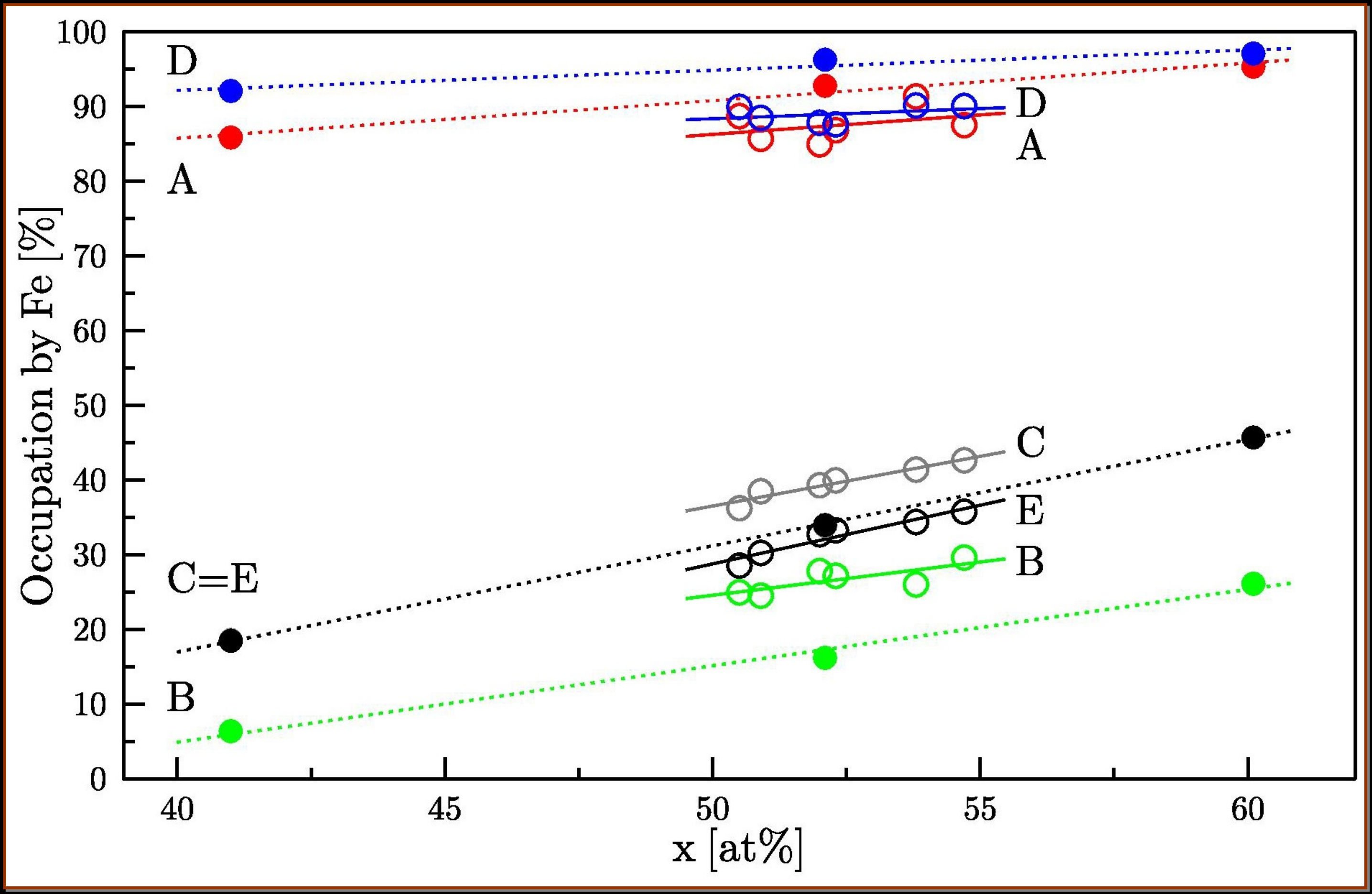


→ **Five different sites occupied by Fe atoms**

J. Cieslak, M. Reissner, S. M. Dubiel, W. Steiner, PSS(a), 205 (2008) 1794

STRUCTURE – SITES OCCUPANCY

• Neutrons (σ-FeCr and σ-FeV)



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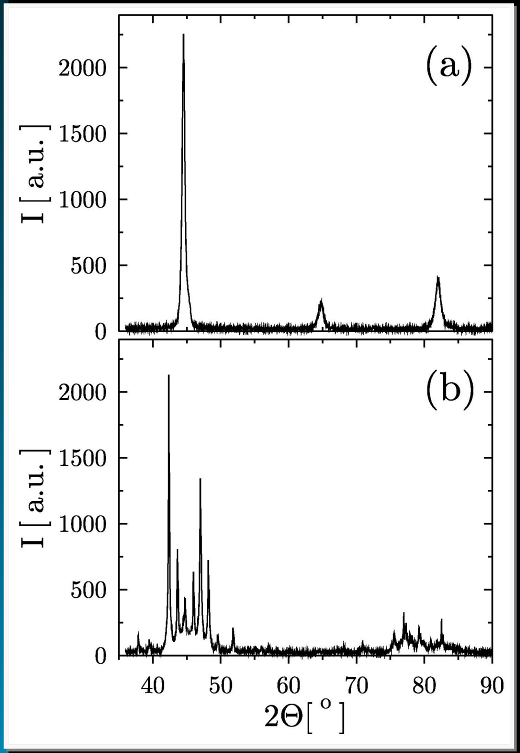
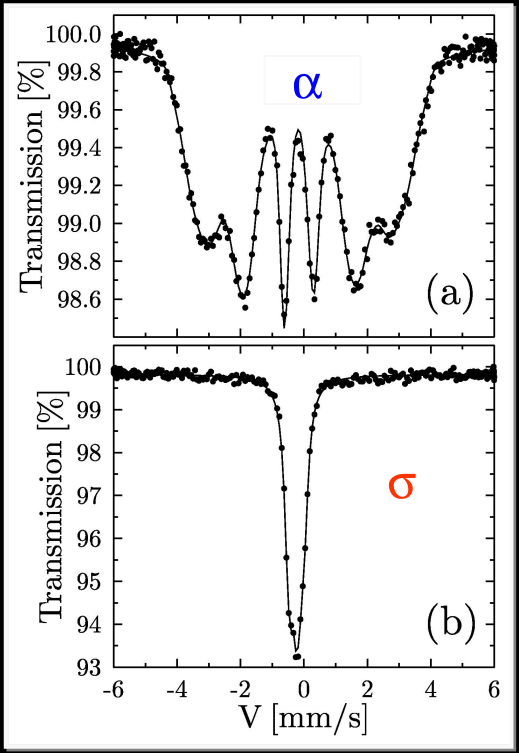
IDENTIFICATION OF SIGMA

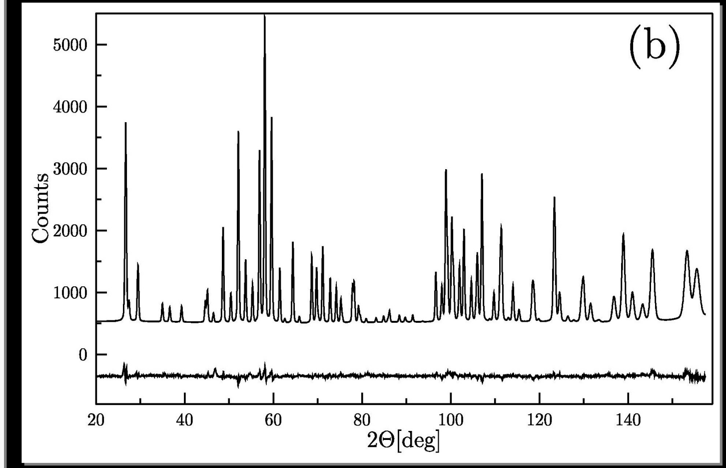
XRD

MS





NEUTRONS



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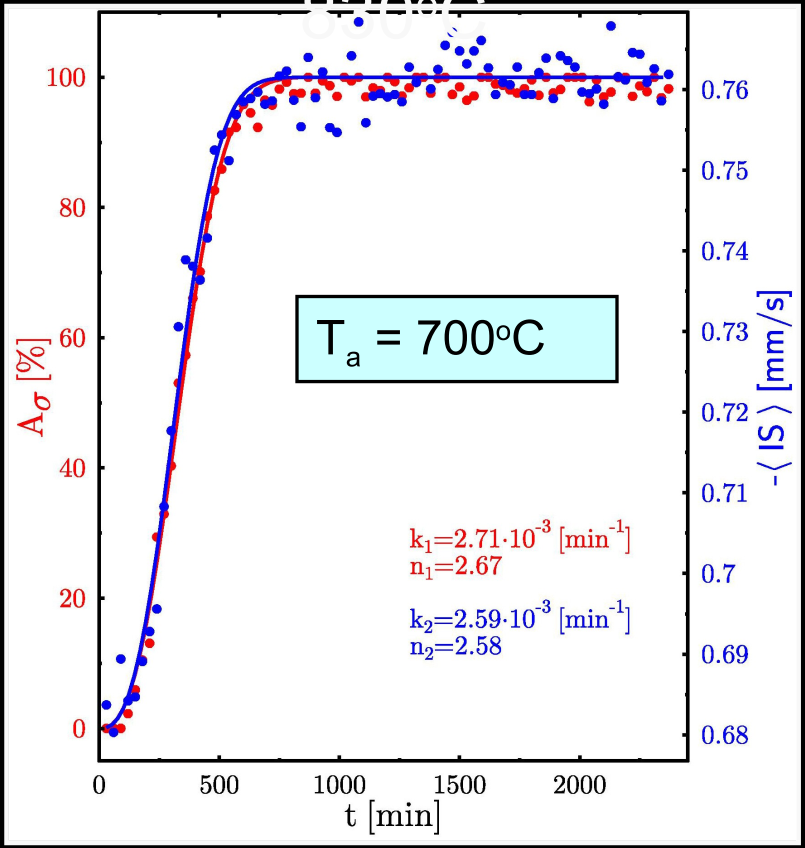
$\Delta IS = IS_\sigma - IS_\alpha \approx$ -0.1 mm/s $\approx$ 0.05 e

TRANSFORMATION KINETICS

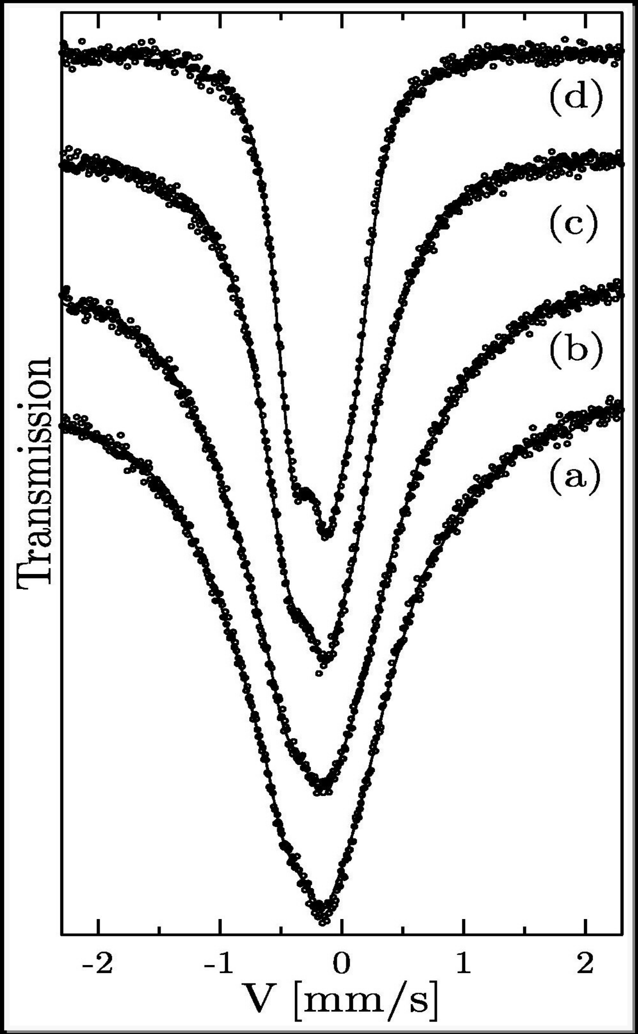
- σ-FeCr; Isothermal annealing at ~ 530 ≤ T_a ≤ ~ 830°C



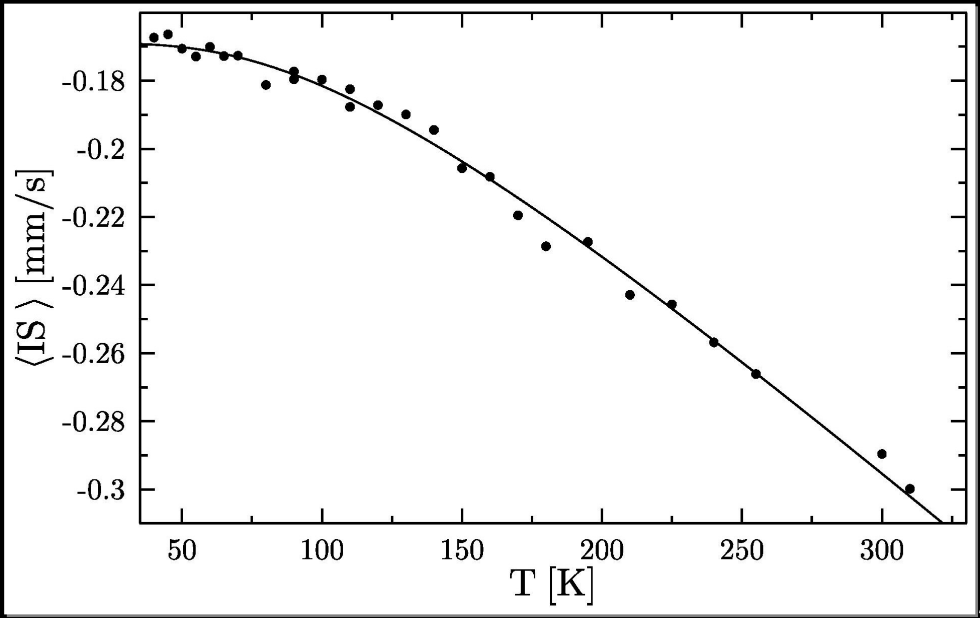
Johnson-Mehl-Avrami equ.

E = 196 ± 2 kJ/mol

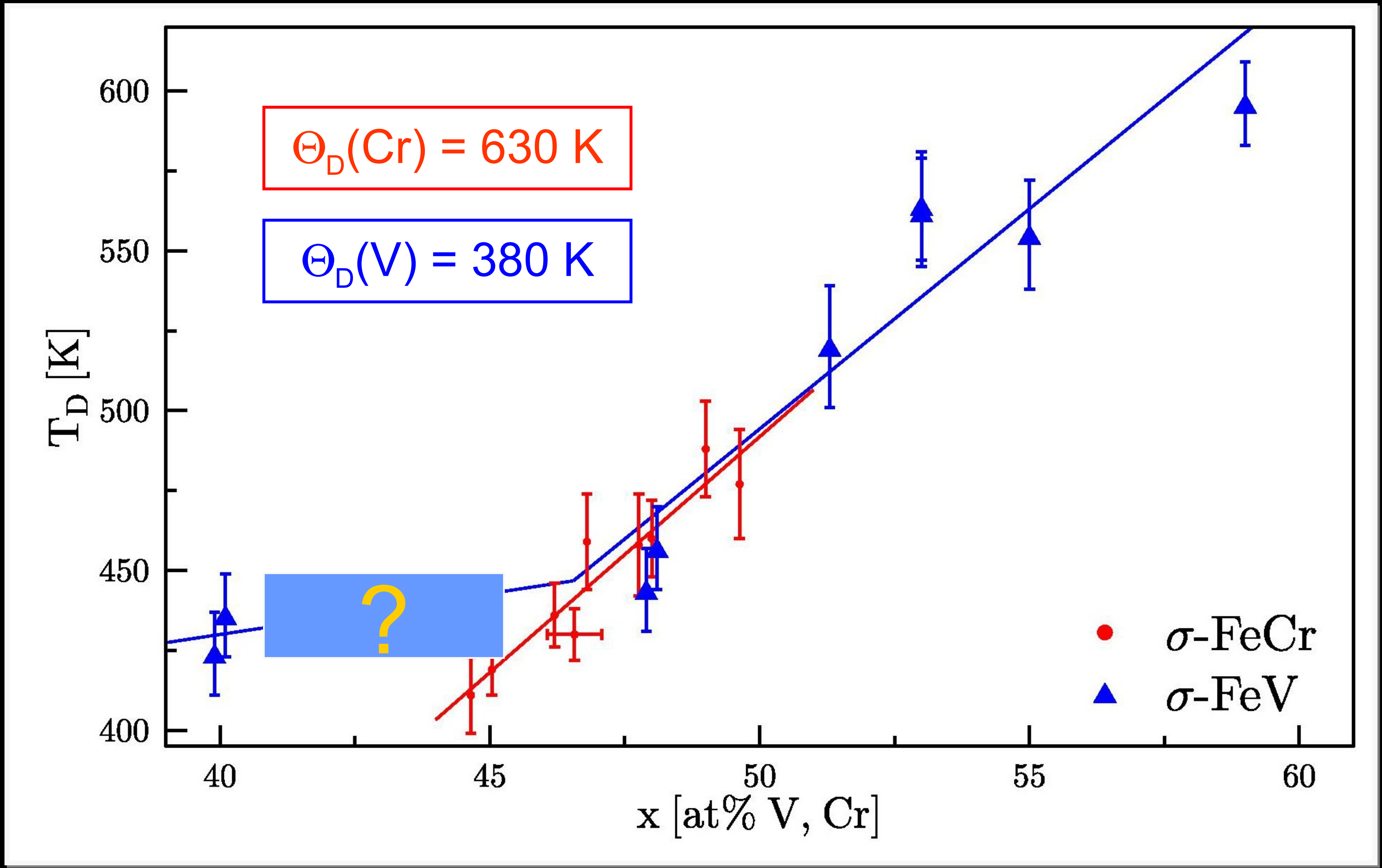
DEBYE TEMPERATURE



- σ-FeCr   4.2 K ≤ T ≤ 60 K

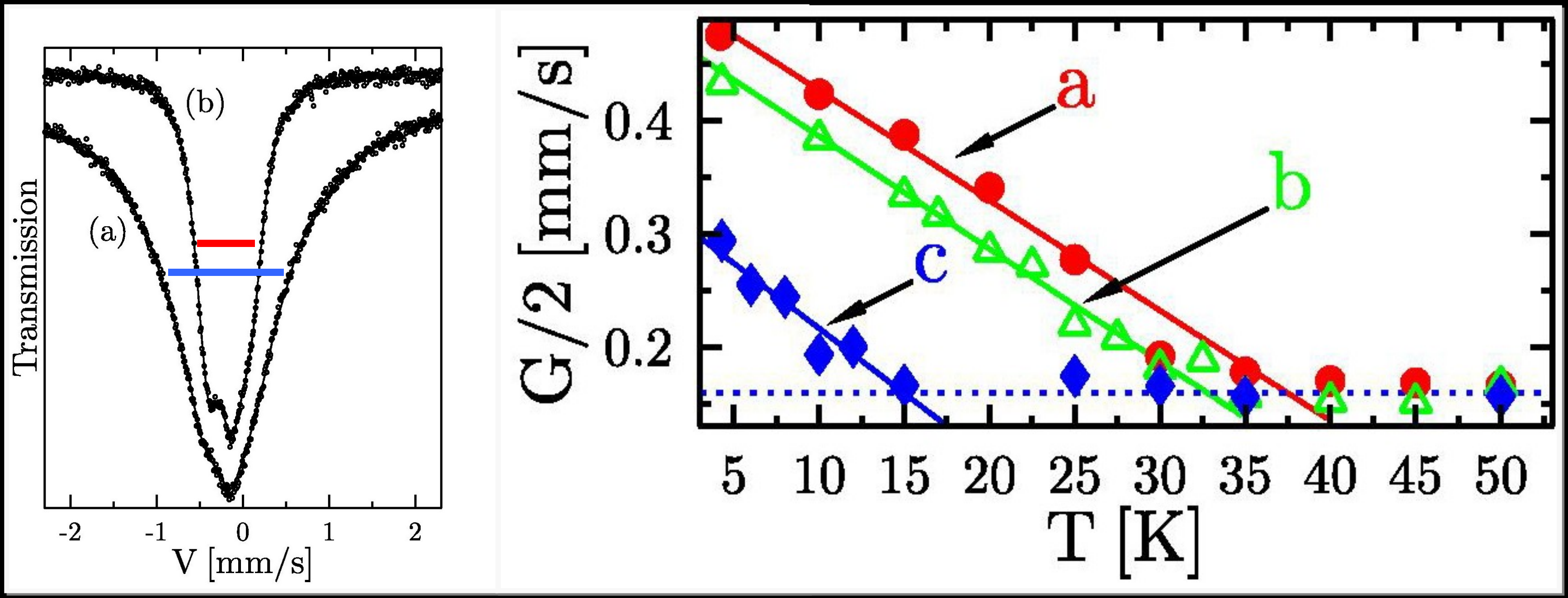


DEBYE TEMPERATURE



CURIE TEMPERATURE

- Mössbauer effect (σ-FeCr)

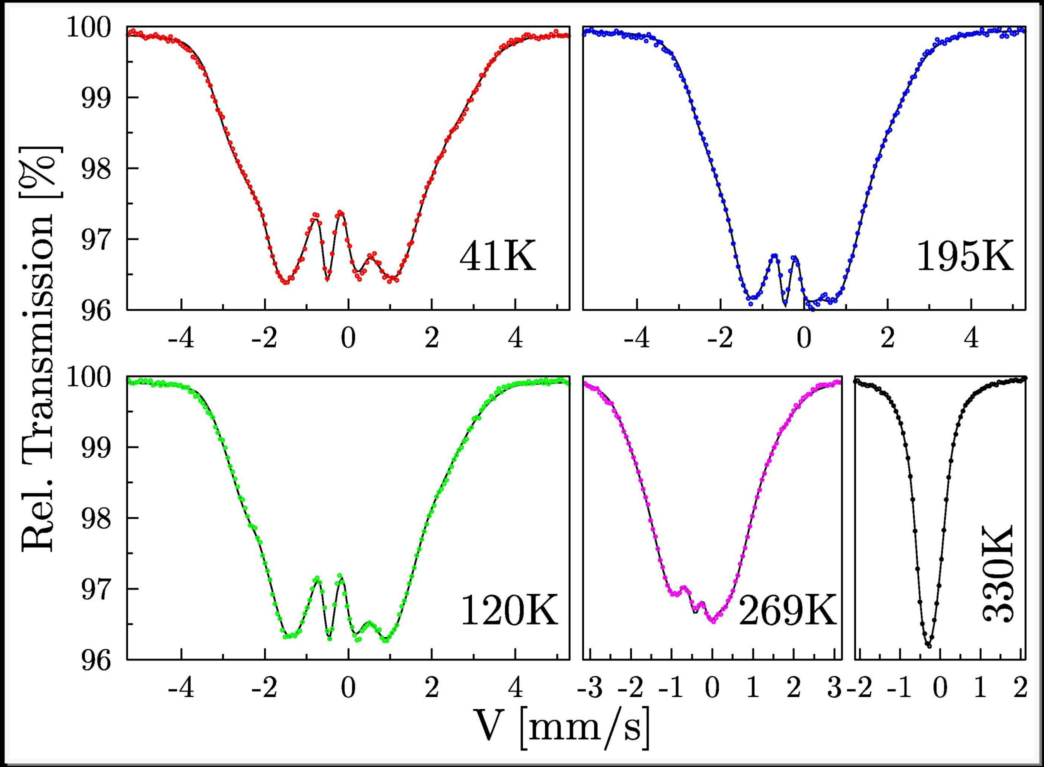


(a) 4.2 K; (b) 295 K (a) x = 45.0, (b) x = 46.2 and (c) x = 48.0

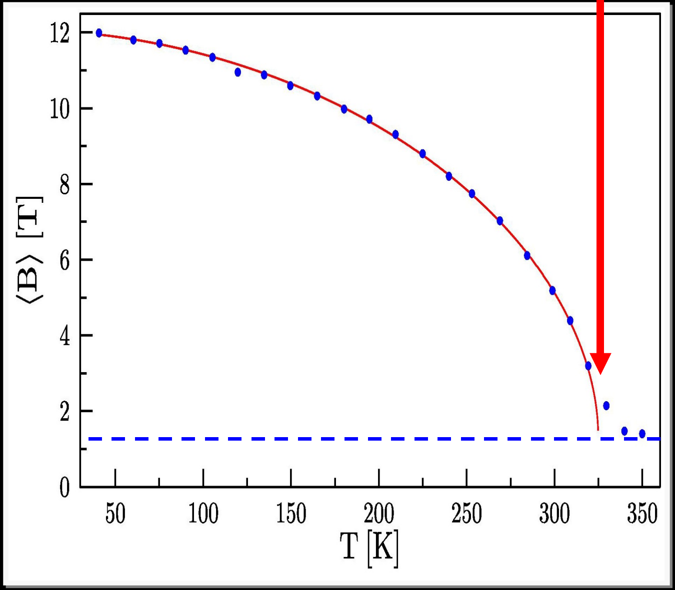
J. Cieslak et al., J. Magn. Magn. Mater., 272-276 (2004) 534

CURIE TEMPERATURE

- Mössbauer effect (σ-FeV_{34})



T_C = 323 K



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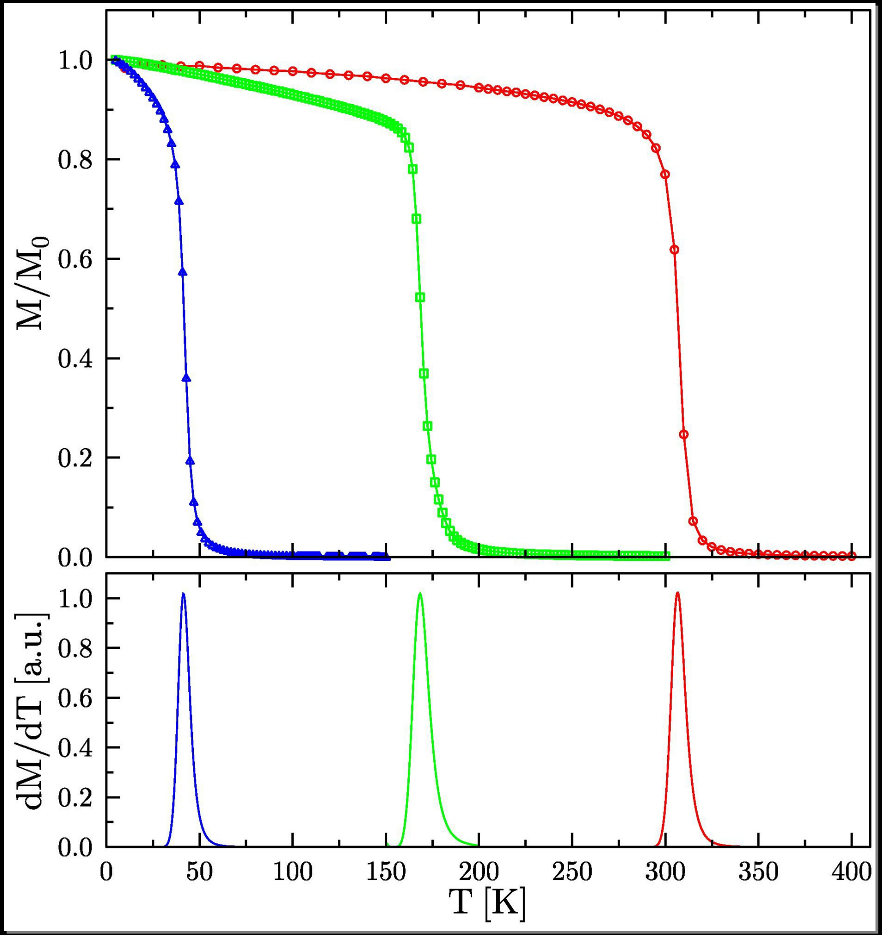
CURIE TEMPERATURE

- Magnetization vs. T - σ-FeV_x

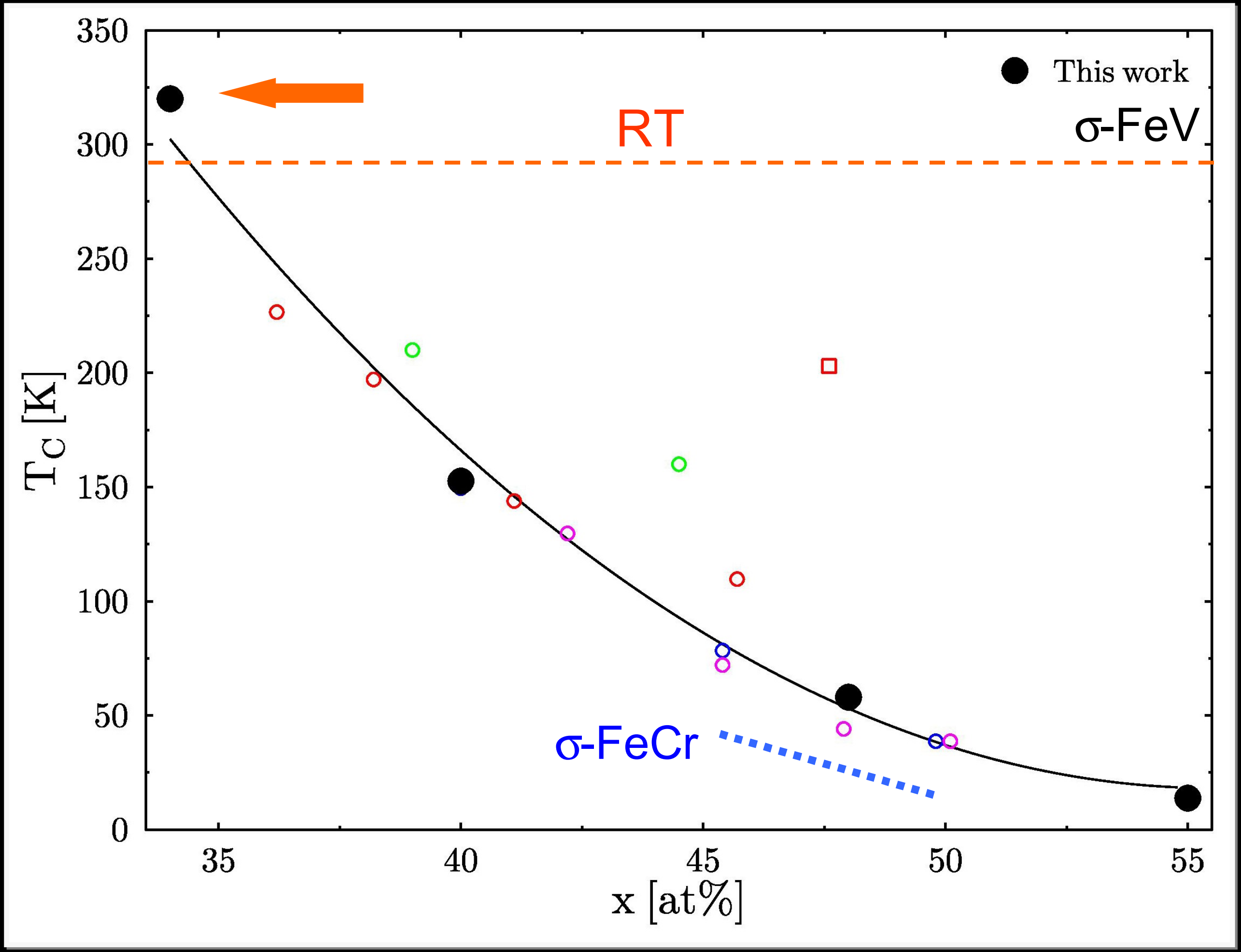


X = 34.4

X = 39.9

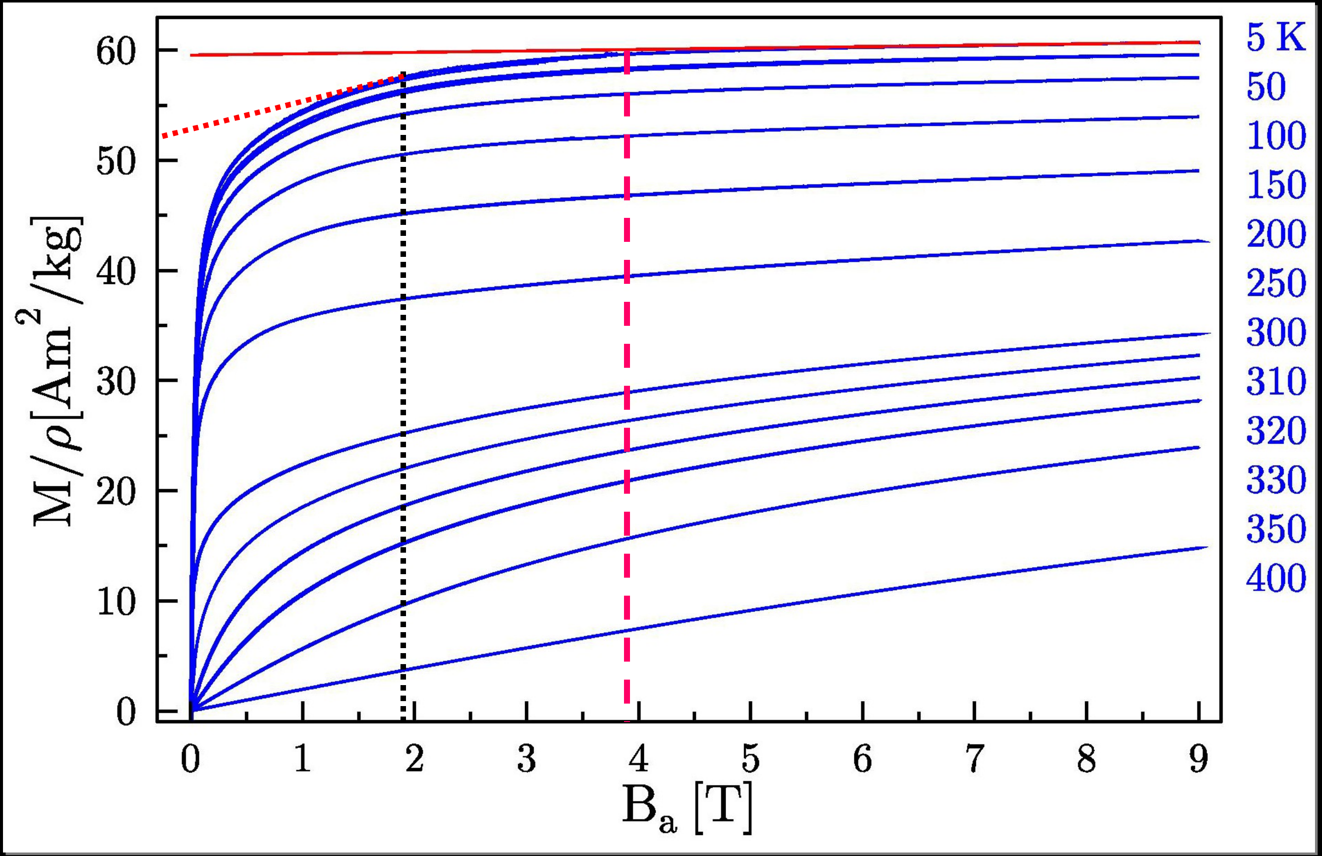
X = 47.8

CURIE TEMPERATURE



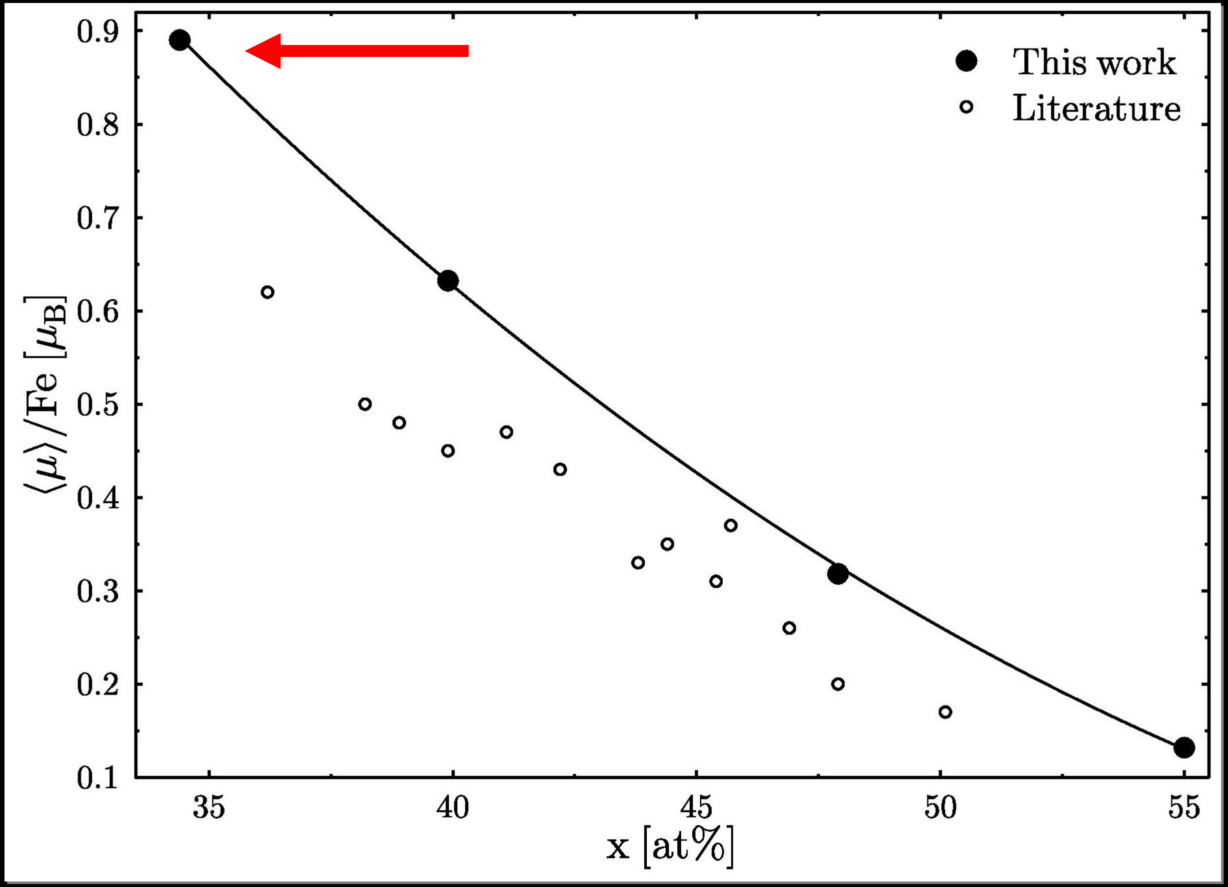
MAGNETIC MOMENT

- Magnetization vs. B_a - σ-FeV

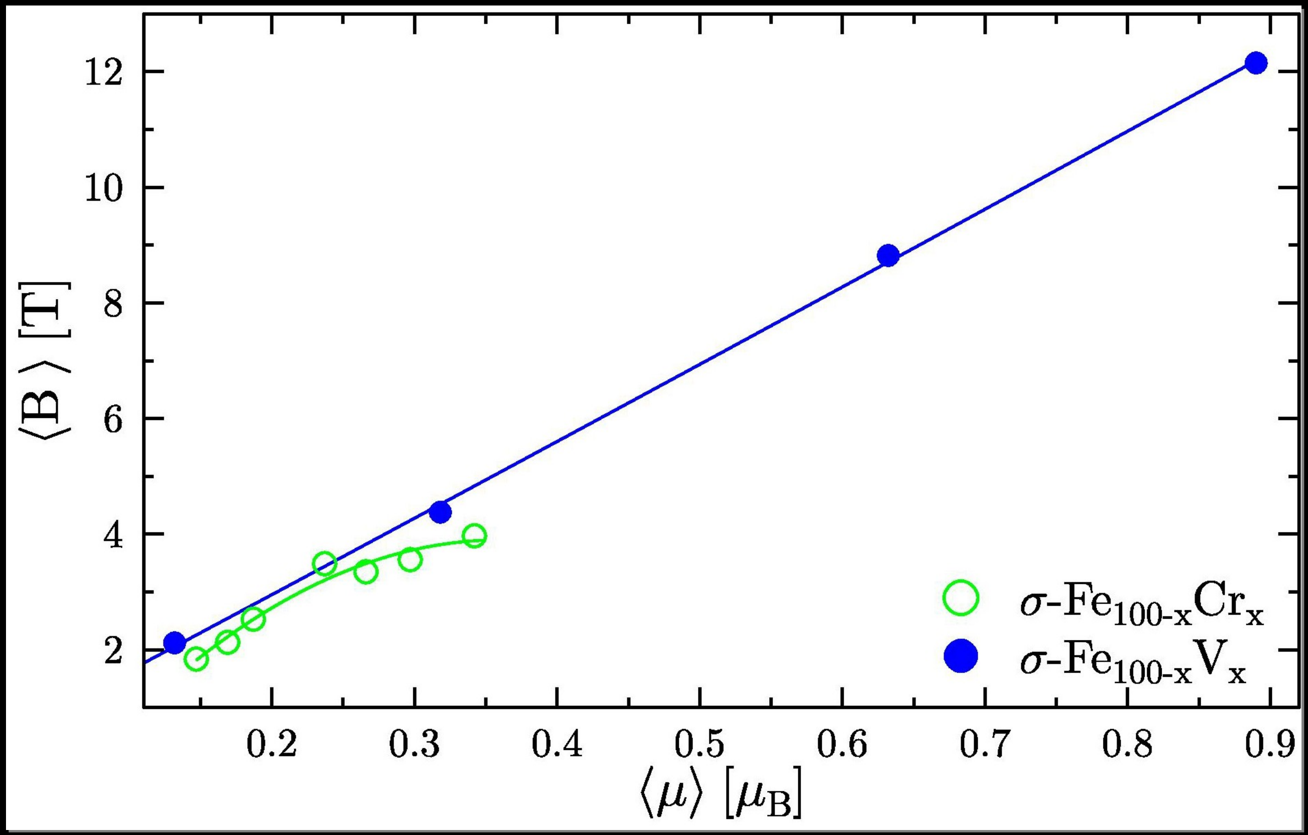


MAGNETIC MOMENT

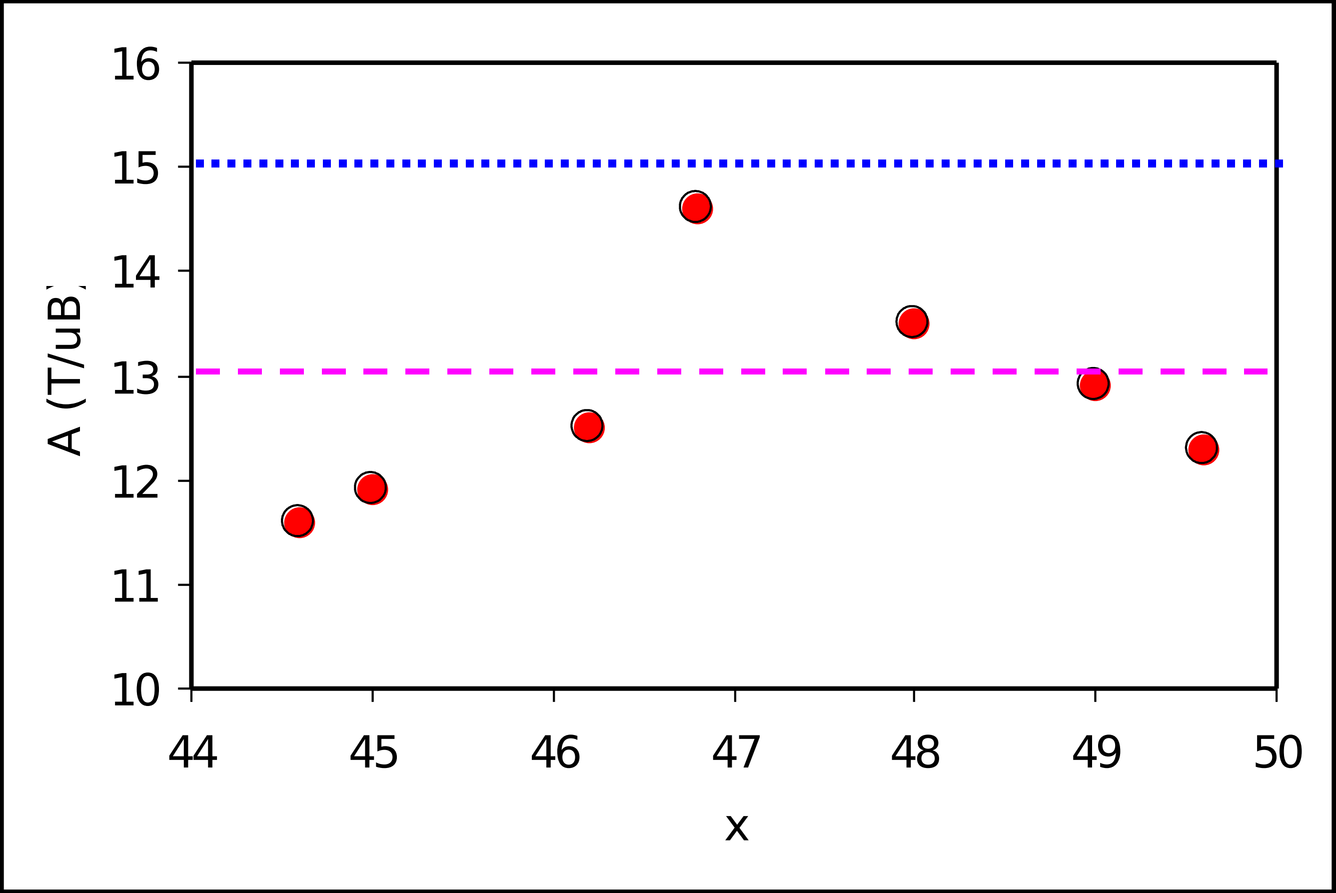
- σ-FeV_x



B - μ RELATIONSHIP

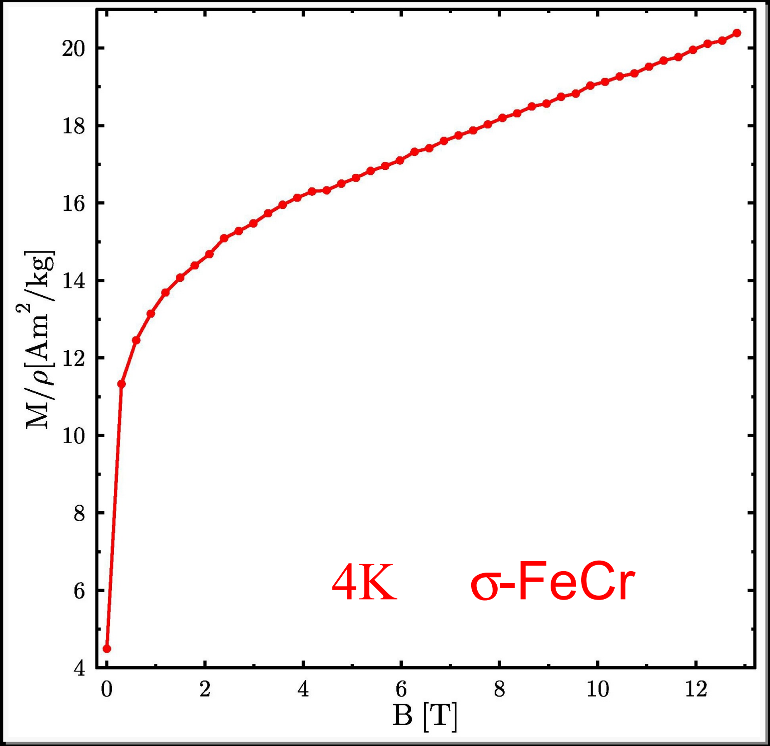


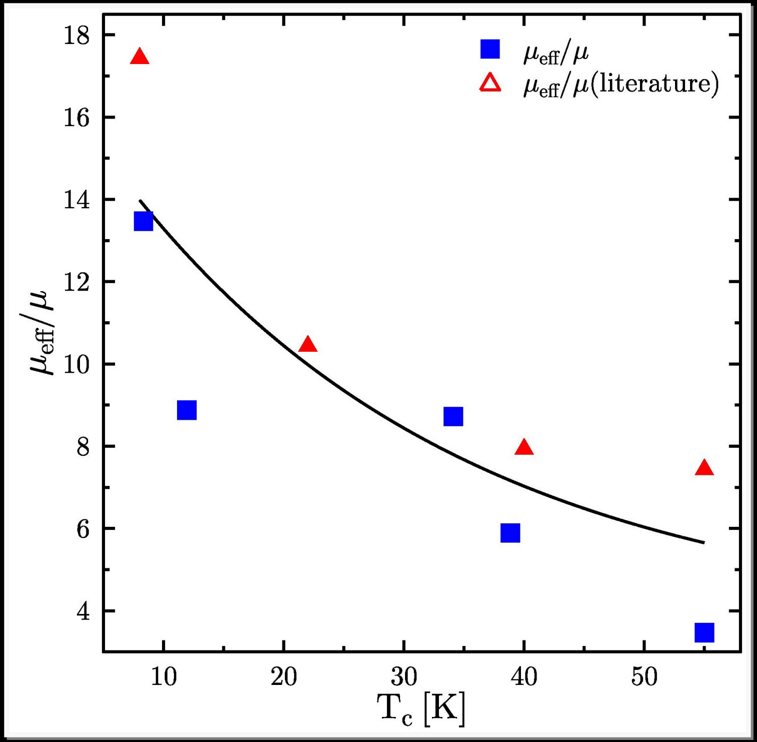
COPULING CONSTANT, *A*



MAGNETISM OF SIGMA

- Rhodes-Wohlfarth plot





→ **Itinerant character of magnetism**

CONCLUSIONS

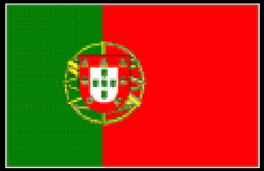
- Sigma-phase in Fe-Cr and Fe-V based alloy systems can be quantitatively studied by MS

- Following characteristics relevant to the phase can be investigated:

  - ▷ Its identification and determination of relative amount
  - ▷ Determination of the transformation kinetics
  - ▷ Determination of the Curie and Debye temperatures

Acknowledgement

- Benilde F. O. Costa, UC, Coimbra



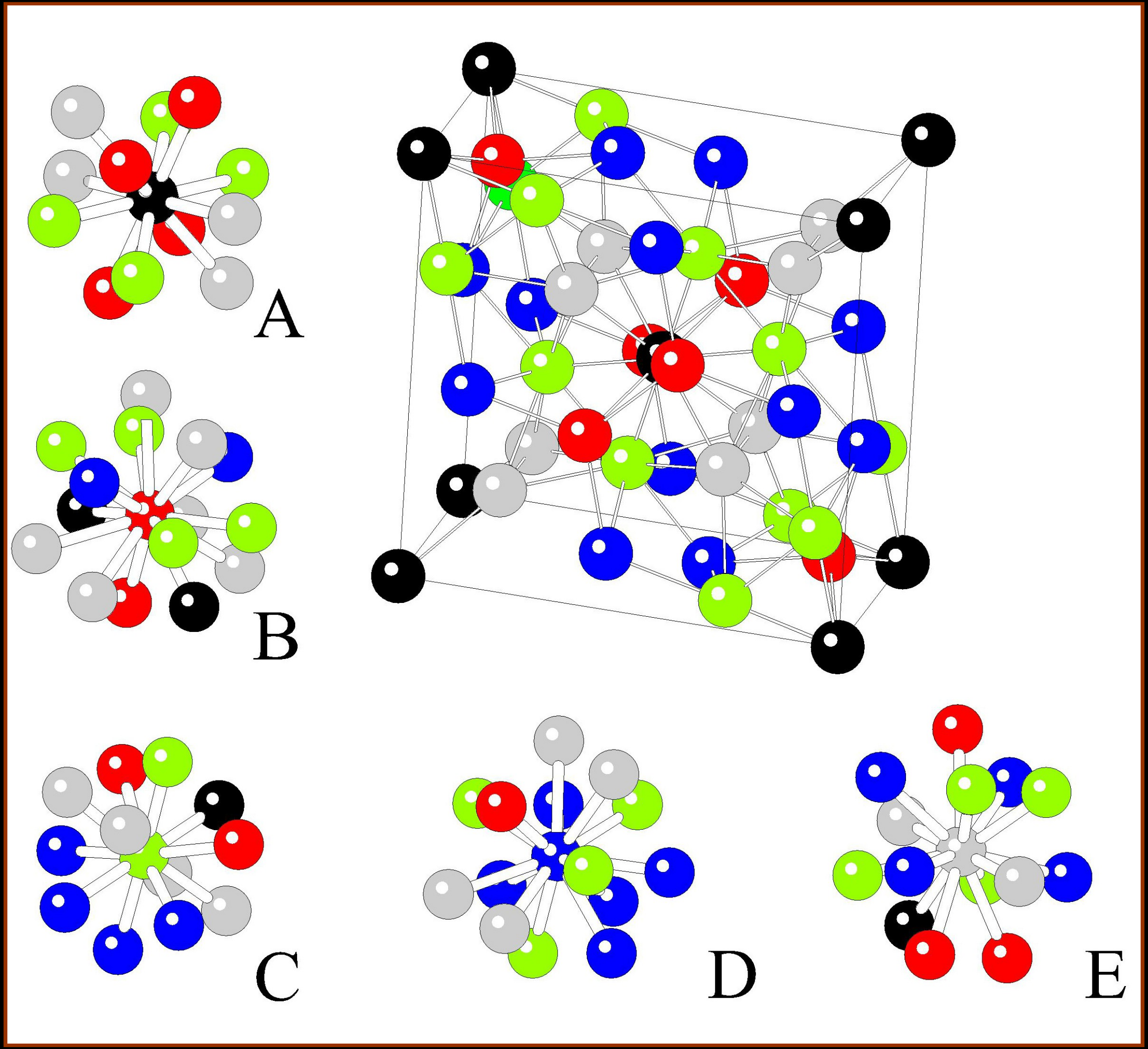
- Michael Reissner, TU, Wien

- Walter Steiner, TU, Wien
- Jakub Cieslak, AGH, Krakow

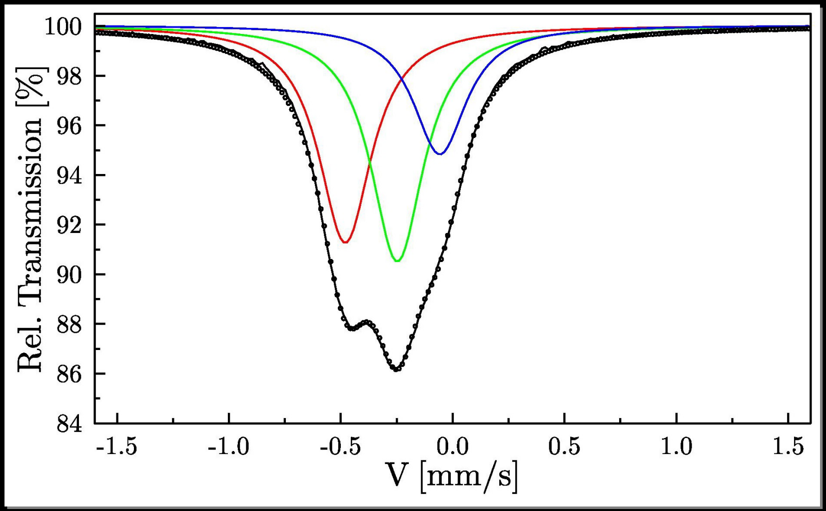
Thank you for your attention

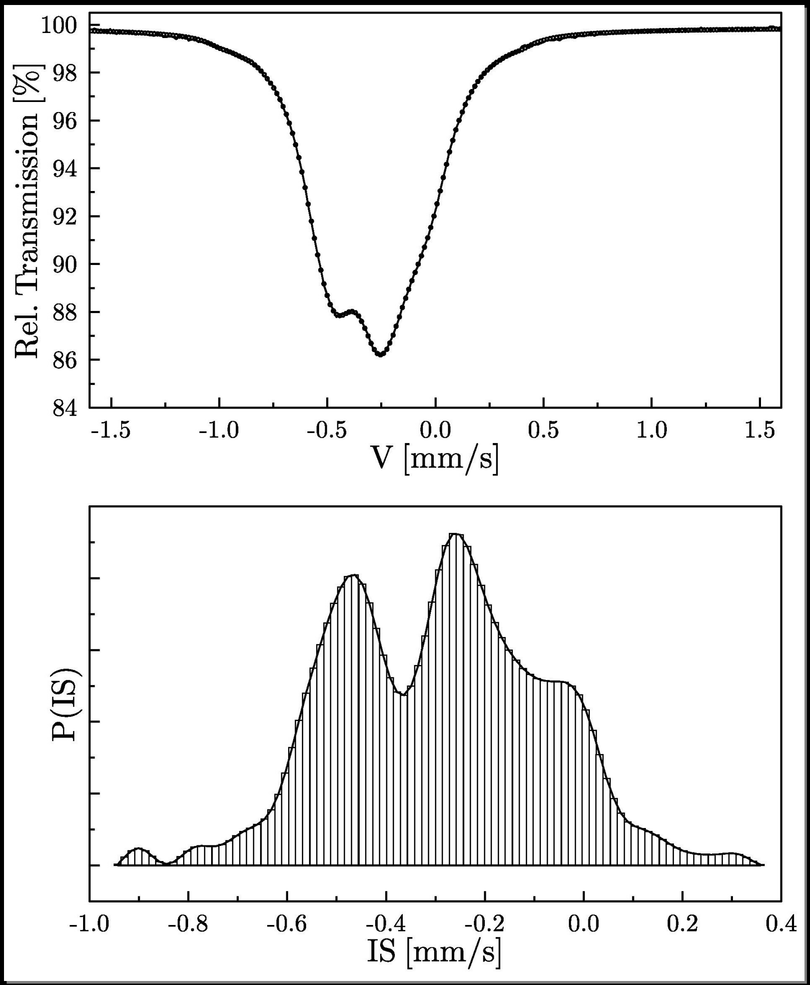
The 1st oil refinery in the world (1856), Ulaszowice (Galicia, Poland)

SPECTRAL PARAMETERS



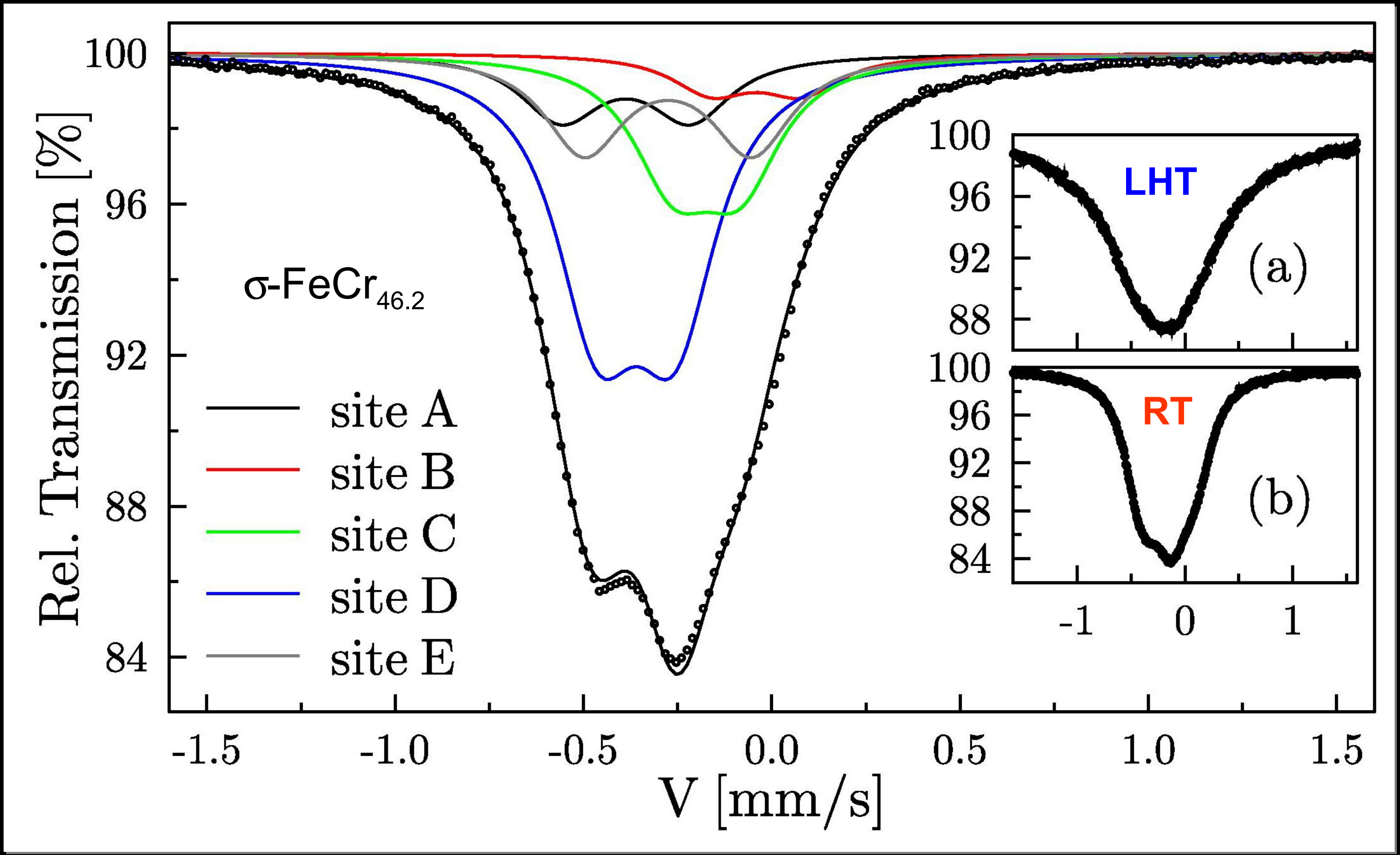
SPECTRAL PARAMETERS





σ-$FeCr_{46.2}$ at RT

SPECTRAL PARAMETERS



J. Cieslak et al., J. Phys.; Condens. Matter, 20 (2008) 235234

SPECTRAL PARAMETERS

Neutrons & Theor. [1]				Exper. [2]			[3]	
Site	Prob. %	IS* mm/s	QS mm/s	IS* mm/s	QS mm/s	Prob. %	IS* mm/s	Prob. %
A	11.3	-0.27	0.34	-0.13	0.11	24.45	-0.45	19.7
B	6.4	0.075	0.24	-0.18	0.52	32.6	+0.08	16.6
C	20.5	-0.24	0.18	-0.18			-0.35	19.3
D	44.9	-0.06	0.21	-0.13	0.11	24.45	-0.06	17.8
E	17.0	-0.17	0.45	-0.35	-	18.5	-0.18	26.5

*** Relative to bcc-Fe**

[1] J. Cieslak & al., J Phys CM, 20 (2008); [2] A. Gupta et al., Hyp. Int., 54 (1990); [3] own data