Nanocrystalline Iron Based Alloys

E.Burzo
Faculty of Physics, Babes-Bolyai University Cluj-Napoca Romania

1. Sm-Fe-Si alloys
2. Fe_3C and Fe_2B compounds
   - crystal structure
   - magnetic properties
   - band structure calculations

Iron based magnets with rare-earths

R-Fe systems:

RFe_2, RFe_3, R_6Fe_{23}, R_2Fe_{17}

no RFe_5 phases are formed

R_2Fe_{17}

-Low Curie temperatures, $T_c < 477$ K for Gd_2F_{17}

-High magnetization $M_{Fe} \cong 2.1\text{-}2.2$ μ_B/atom

-Planar anisotropy

Rhombohedral structure: $R\bar{3}m$ space group

Sm:6c, Fe:6c, 9d, 18f, 18h

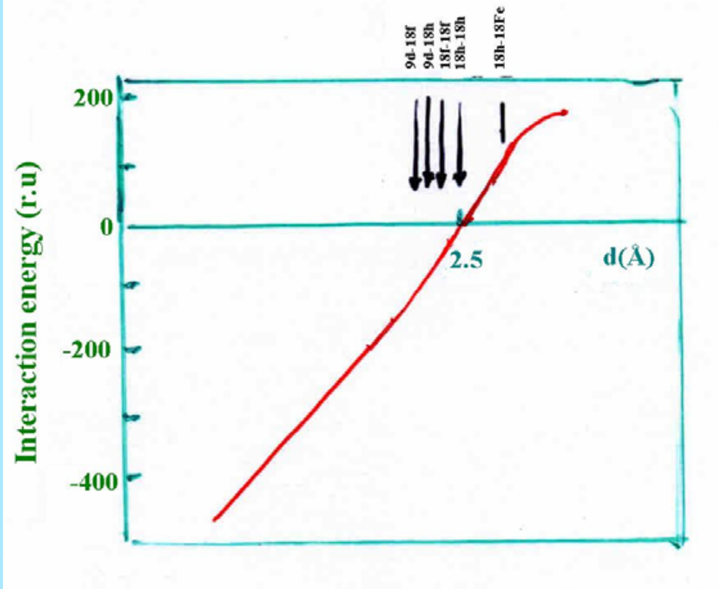
different local environments

Increase T_c values by:

- replacement of iron involved in negative exchange inteactions
- increase volume: interstitial atoms (C,N)

Uniaxial anisotropy

Fe(9d)-Fe(18f)	2.439 Å	negative
Fe(9d)-Fe(18h)	2.467 Å	negative
Fe(18f)-Fe(18f)	2.490 Å	negative
Fe(18h)-Fe(18h)	2.501 Å	
Fe(18h)-Fe(18f)	2.641 Å	positive
Fe(18h)-Fe(6c)	2.660 Å	positive



d< 2.50 Å negative exchange interactions, (-)J_{Fe-Fe}

d > 2.50 Å positive exchange interactions, (+) J_{Fe-Fe}

(+)J_{Fe-Fe} > (-) J_{Fe-Fe}

↓

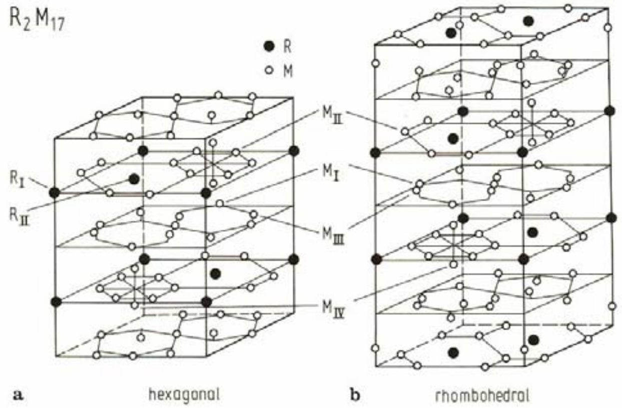
parallel alignment of Fe moment

↓

considerable magnetic energy is stored

↓

Low Curie temperatures



$P6_3/mmc$ $R\bar{3}m$

Atom	Site	Coordinates
R_I	2b	$\pm(0, 0, 1/4)$
R_{II}	2d	$\pm(1/3, 2/3, 3/4)$
M_I	6g	$\pm(1/2, 0, 0; 0, 1/2, 0; 1/2, 1/2, 0; 1/2, 0, 1/2; 0, 1/2, 1/2; 1/2, 1/2, 1/2)$
M_{II}	12j	$\pm(x, y, 1/4; \bar{y}, x-y, 1/4; y-x, \bar{x}, 1/4; \bar{y}, \bar{x}, 1/4; x, x-y, 1/4; y-x, y, 1/4); x=1/3; y=0.968$
M_{III}	12k	$\pm(x, 2x, z; 2\bar{x}, \bar{x}, z; x, \bar{x}, z; \bar{x}, 2\bar{x}, 1/2+z; 2x, x, 1/2+\bar{z}; \bar{x}, x, 1/2+z); x=1/6; z=0.984$
M_{IV}	4f	$\pm(1/3, 2/3, z; 2/3, 1/3, 1/2+z); z=0.109$

Atom	Site	Coordinates
R	6c	$\pm(0, 0, z); \quad z=1/3$
M_I	9d	$\pm(1/2, 0, 1/2; 0, 1/2, 1/2; 1/2, 1/2, 1/2)$
M_{II}	18f	$\pm(x, 0, 0; 0, x, 0; x, x, 0); \quad x=0.283$
M_{III}	18h	$\pm(x, x, z; x, 2x, z; 2\bar{x}, \bar{x}, z); \quad x=1/2, z=0.148$
M_{IV}	6c	$\pm(0, 0, z); \quad z=0.094$

For $TbCu_7$-type structure having P6/mmm-space group

1. Sm-Fe-Si alloys

Preparation. Crystal structure

High energy ball milling and annealing

$Sm_2Fe_{17-x}Si_x$; $Sm_2Fe_{17-x}Si_xC$ $R\bar{3}m$ for T_a>850 ^oC

Metastable $Sm_{1-s}(Fe,Si)_{5+2s}$ P6/mmm type structure

s = 0.22 $TbCu_7$ T_a= 650 ^oC-850 ^oC

s = 0.33 Sm_2Fe_{17}

s = 0.36-0.38 $SmFe_9$ (new)

Carbonation: mixture of alloys and $C_{14}H_{10}$ powders 420 ^oC in vacuum

Atom		s = 0 1/5	s = 0.22 $TbCu_7$	s = 0.33 2/17	s = 0.36 1/9
1Sm(1a)	1-s	1	0.78	0.66	0.64
2Fe(2c)	2(1-3s)	2	2	0	0
6Fe(6l)	6s	0	0	2	2
3Fe(3g)	3	3	3	3	3
2Fe(2e)	2s	0	0.44	0.66	0.72

$R_{1-s}M_{5+2s}$

P6/mmm

Grain sizes:

$SmFe_{9-y}Si_y$: 22-28 nm

$SmFe_{9-y}Si_yC$: 18-22 nm

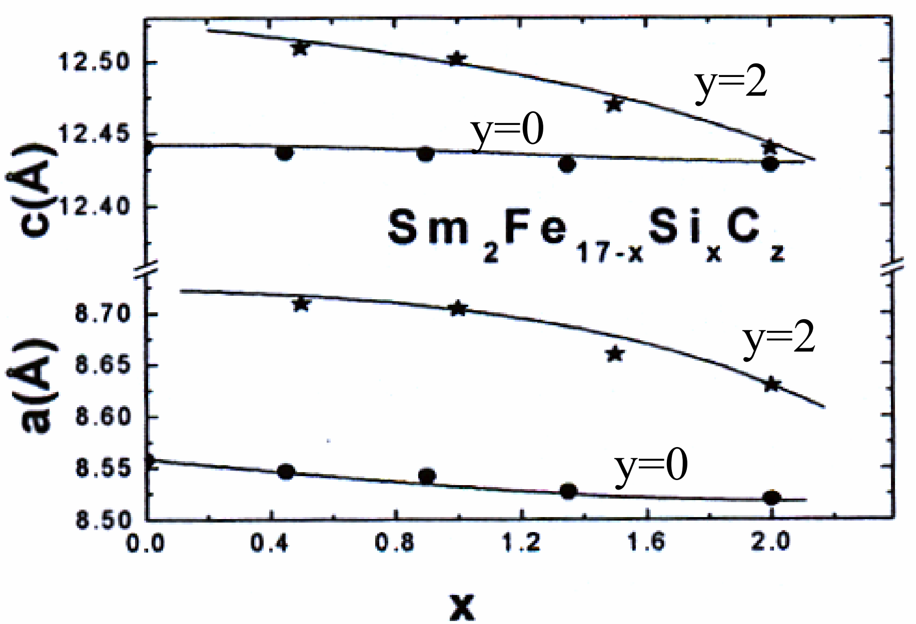
$Sm_2Fe_{17-x}Si_xC_2$:18-25 nm

Rietveld analysis of $Sm_{1-x}(Fe,Si)_{5+2s}$

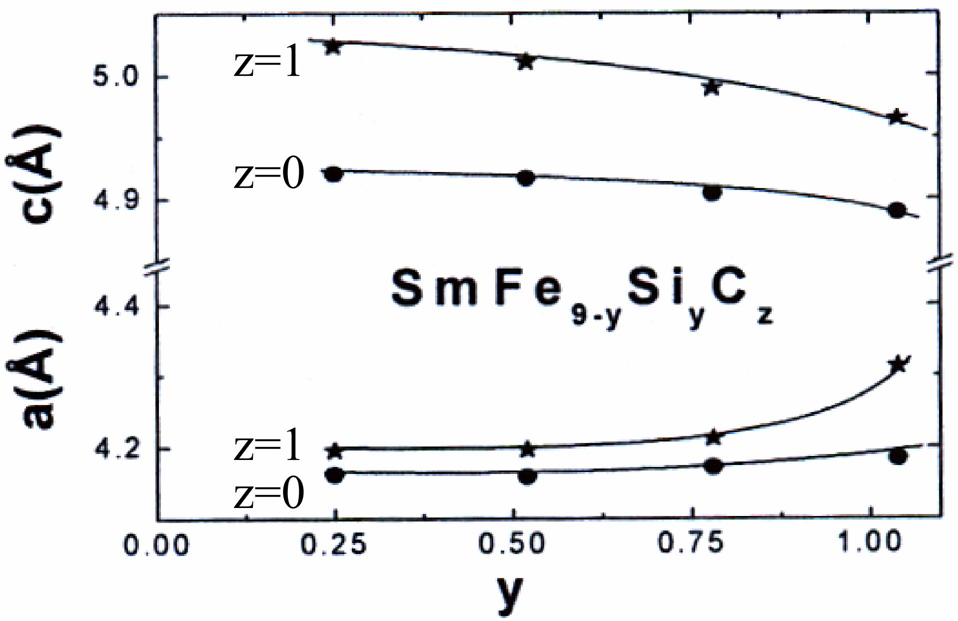
C 3f sites (1/2,0,0); (0,1/2,0); (1/2,1/2,0)

Sm at (0,0,0) is occupied by 0.64-0.62 atoms

Si 3g sites

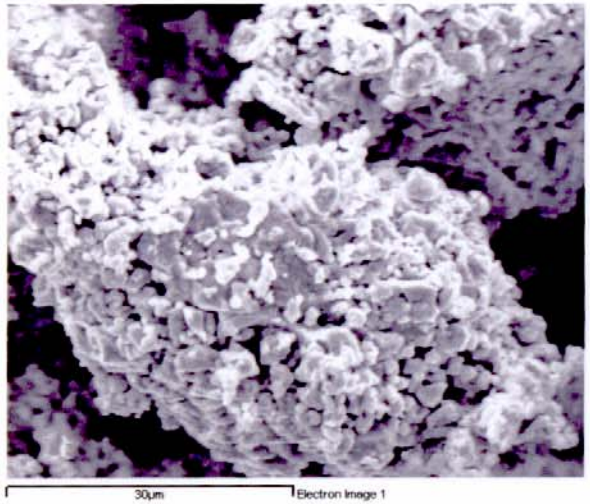


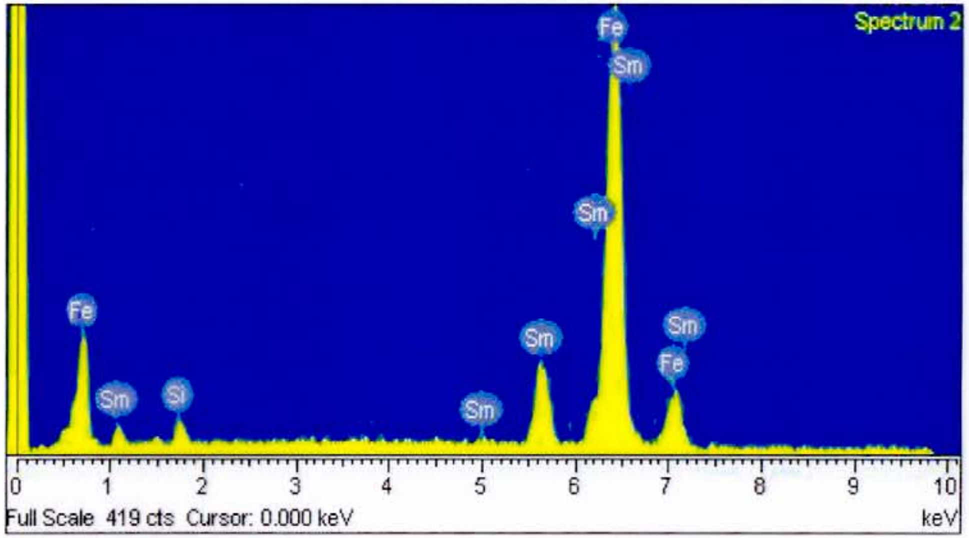
c(Å)
a(Å)
12.50
12.45
12.40
8.70
8.65
8.60
8.55
8.50
0.0
0.4
0.8
1.2
1.6
2.0
x
y=2
y=0
y=2
y=0
$Sm_2Fe_{17-x}Si_xC_z$



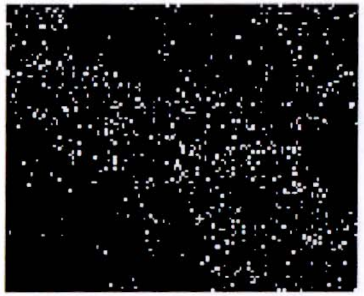
c(Å)
a(Å)
5.0
4.9
4.4
4.2
0.00
0.25
0.50
0.75
1.00
y
z=1
z=0
z=1
z=0
$SmFe_{9-y}Si_yC_z$

Electron microscopy:
distribution of elements
particle dimensions

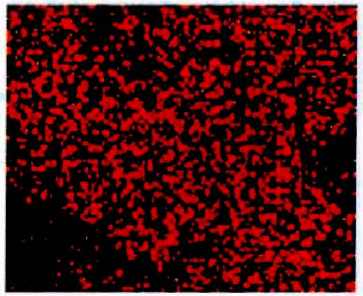




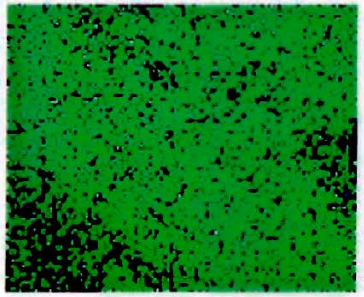
$SmFe_{8.75}Si_{0.25}$



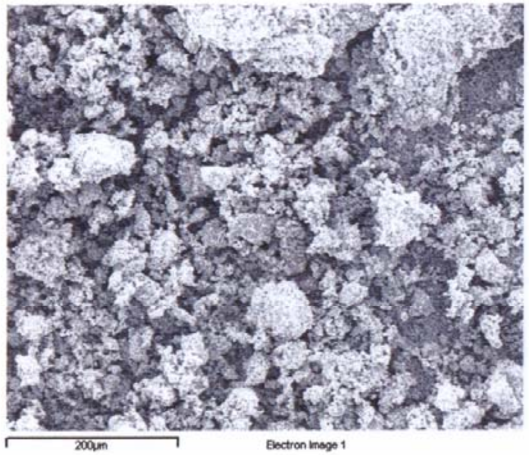
Silicon Ka1

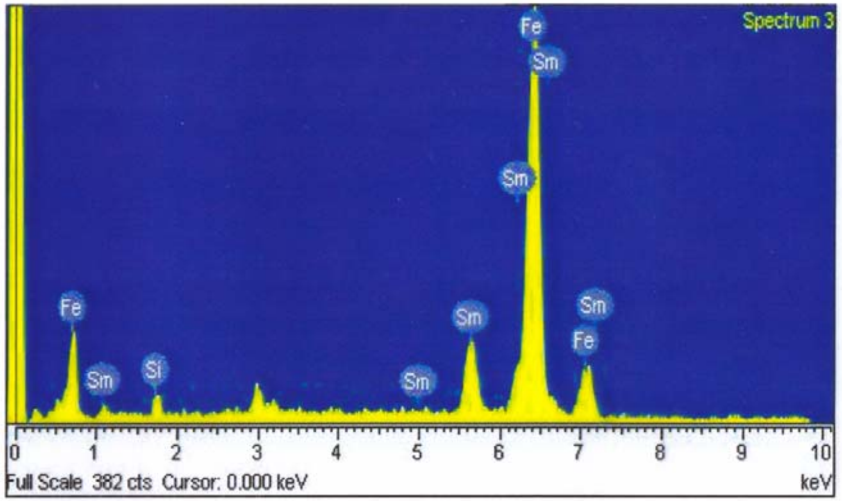


Samarium La1

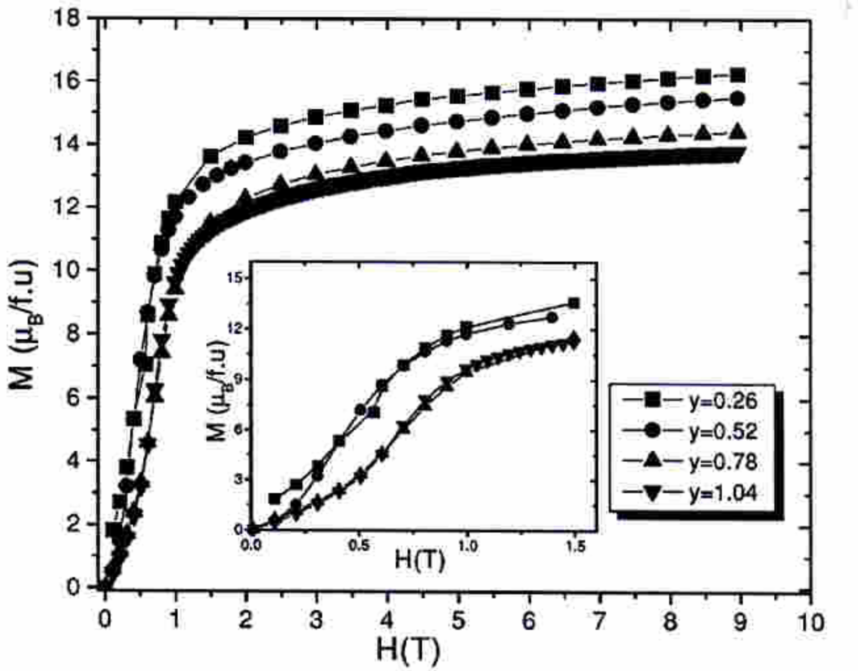


Iron Ka1

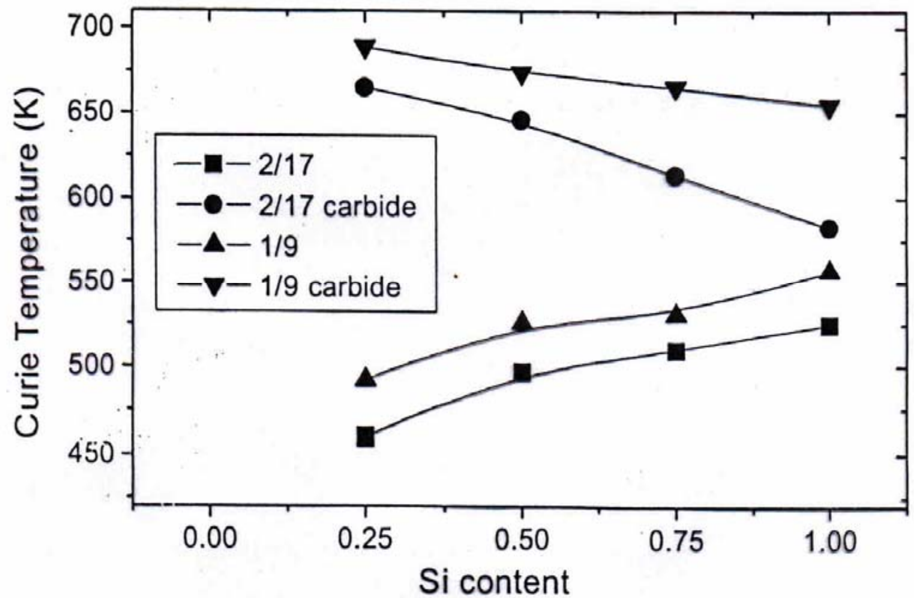




Element	App	Intensity	Weight%	Weight %	Atomic%
	Conc.	Corrn.		Sigma	
Si K	0.95	0.5091	1.36	0.22	3.20
Fe K	101.84	1.0335	72.25	1.07	85.24
Sm L	35.57	0.9884	26.39	1.07	11.56
Totals			100.00		



M (μB/f.u)
H(T)
y=0.26
y=0.52
y=0.78
y=1.04

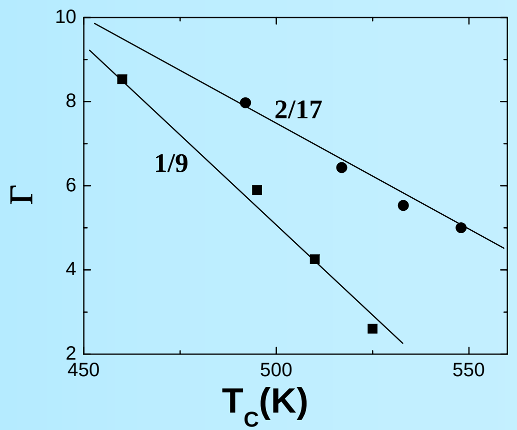


Curie Temperature (K)
Si content
2/17
2/17 carbide
1/9
1/9 carbide

Curie temperature: effect of Si

- T_c increases by Si substitution in noncarbonated samples
- T_c decreases in carbonated sample

Volume effects:



$$\Gamma = \frac{1}{\kappa T_C}\frac{dT_C}{dp} = \frac{d\ln T_C}{d\ln v}$$

Localized moment of iron moments

$$\Gamma = \frac{5}{3} + 2\frac{d\ln J_{eff}}{d\ln v} + \frac{5}{8}\frac{k_B N_o g^2 I}{S(S+1)J_{eff}^2 I_b} T_c$$

$\Gamma = a - bT_C$ **a = 34.5** **a =47.5**

2/17 phases **1/9 phases**

b =0.054 K^{-1} **b = 0.06 K^{-1}**

$$\gamma = \frac{d\ln J_{eff}}{d\ln v}$$

16.4 **2/17**

22.9 **1/9**

Iron moments show a rather high degree of localization

Intrinsic magnetic properties

Magnetic measurements: H ≤ 9T T≥4.2 K

•initial magnetization curves

- inflection typical for pinning effects coherent precipitates with matrix

impede the motion of domain walls

•Band structure calculations: LMTO-LDA method

M_{Sm}=-0.66 μ_B/atom

$M_{Fe}(6c) > M_{Fe}(18h) \cong M_{Fe}(18f) > M_{Fe}(9d)$

•Mean magnetic moment of Fe in field of 9T

increases with Si content

Noncarbonated: 1.50 μ_B (y=0.25); 1.75 (y=1.0)

Carbonated: 1.88μ_B (y=0.25); 1.97 (y=1.0)

Asymmetric filling of Fe 3d band by Si3p electrons

Technical parameters

Uniaxial anisotropy is induced in 1:9 phase

2:17 phase

Coercive fields $SmFe_{9-x}Si_xC$

X = 0.25	H_c=1.2 MA/m	T_a=750 ^oC
x = 0.50	H_c = 1.04MA/m	T_a=800 ^oC

The maximum in H_c values:

- Too low T_a hinders the complete solid-state reaction for forming a perfect metastable phase responsible for magnetic hardening
- Increasing T_c

- number of surface defects of hexagonal P6/mmm phase is reduced H_c ↗

- the domain size increases H_c ↘

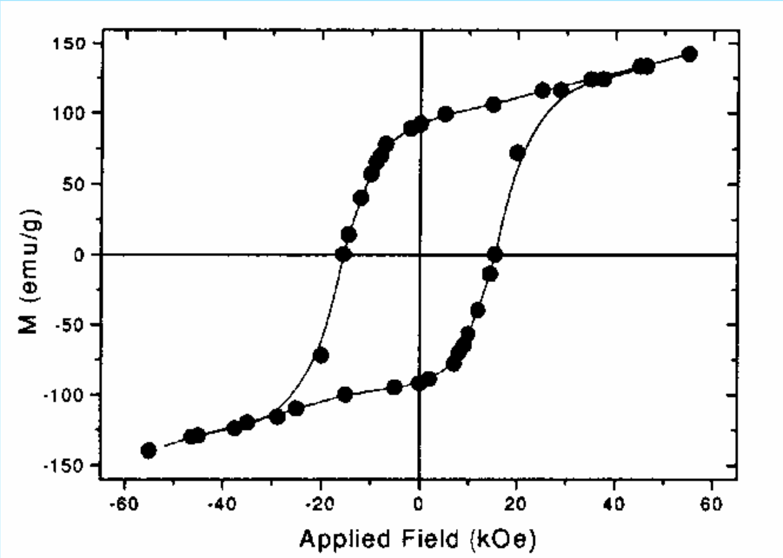
Curie temperature increases

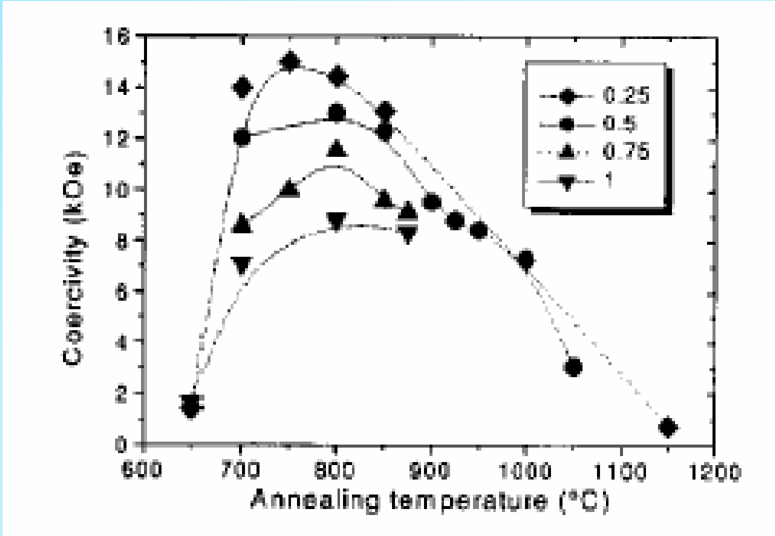
$T_c \cong 700$ K for $SmFe_{8.75}Si_{0.25}C$

Remanent induction

$B_r \cong 0.80\ B_s$

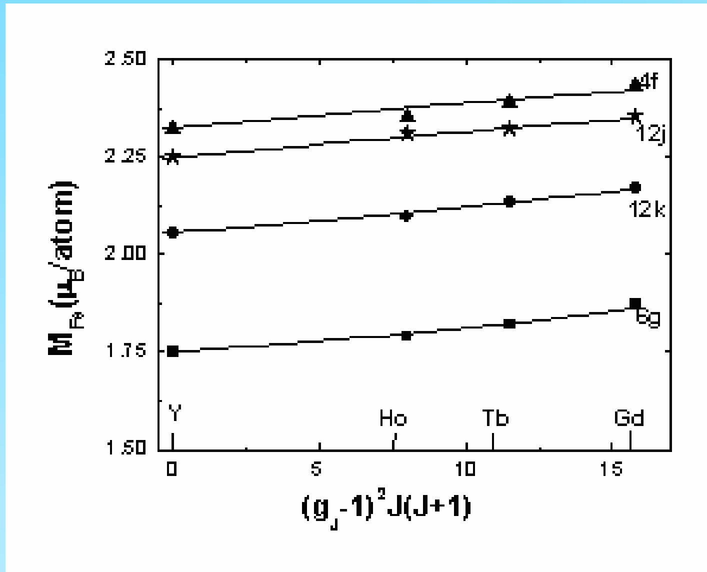
High energy product is expected with a smaller temperature coefficient than Nd-Fe-B alloys

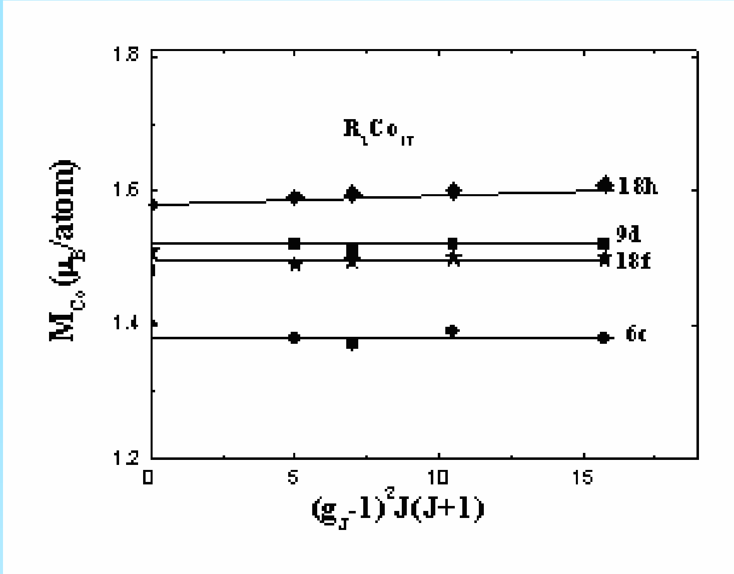




Exchange interactions 4f-5d-3d path

R_2Fe_{17} $M = Fe, Co$





$M_{Co} = M_M(0) + \alpha G$

$M = Fe$ $\alpha = 4 \cdot 10^{-4}\ \mu_B$

$M = Co$ $\alpha \cong 10^{-5} \mu_B$

Co localized moment

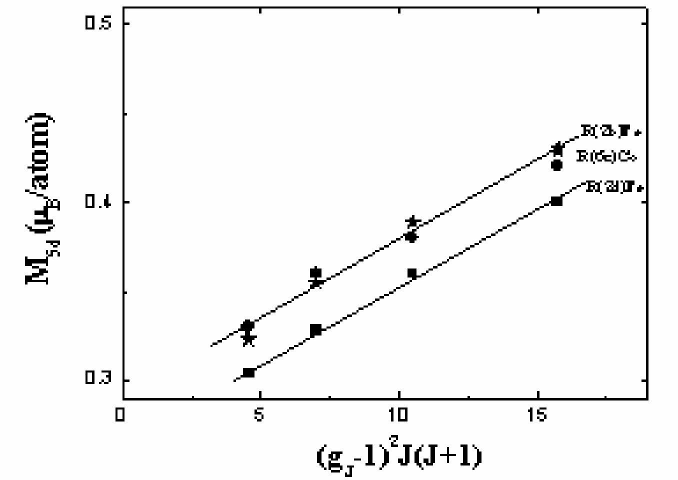
Fe 95% 3d electrons in narrow d band

5 % itinerant electrons

Compound	Magnetic moments (μ_B)				
	Sm(6c)	Fe(6c)	Fe(9d)	Fe(18f)	Fe(18h)
Sm_2Fe_{17}	-0.66	2.50	1.70	2.20	2.20

$$M_{5d} = M_{5d}(0) + \beta G$$

$\beta = 1 \cdot 10^{-2}\ \mu_B$ for M = Fe and Co



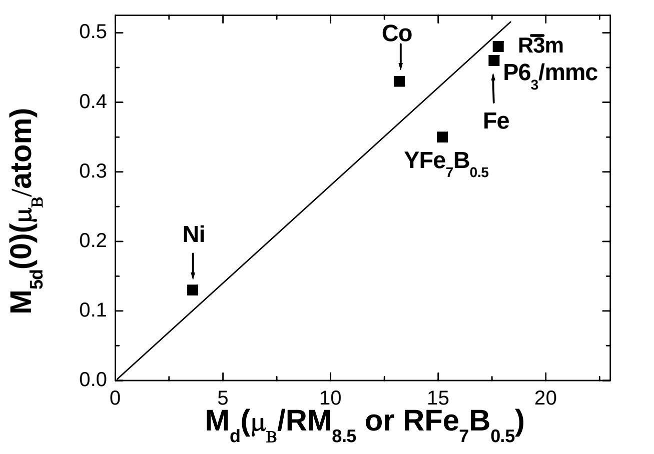
βG-intra atomic 4f-5d exchange interaction $G = (g_J-1)^2 J(J+1)$

$M_{5d}(0)$-short range exchange interactions 5d-3d; 5d-5d

$$H = -2J_{3d-5d} S_{5d}(0) \sum_i S_{3di}(0) - 2J_{5d-5d} S_{5d}(0) \sum_j S_{5dj}$$

Molecular field model

$$M_{5d}(0) = gM_{Fe}$$



$g = 0.028(4)$

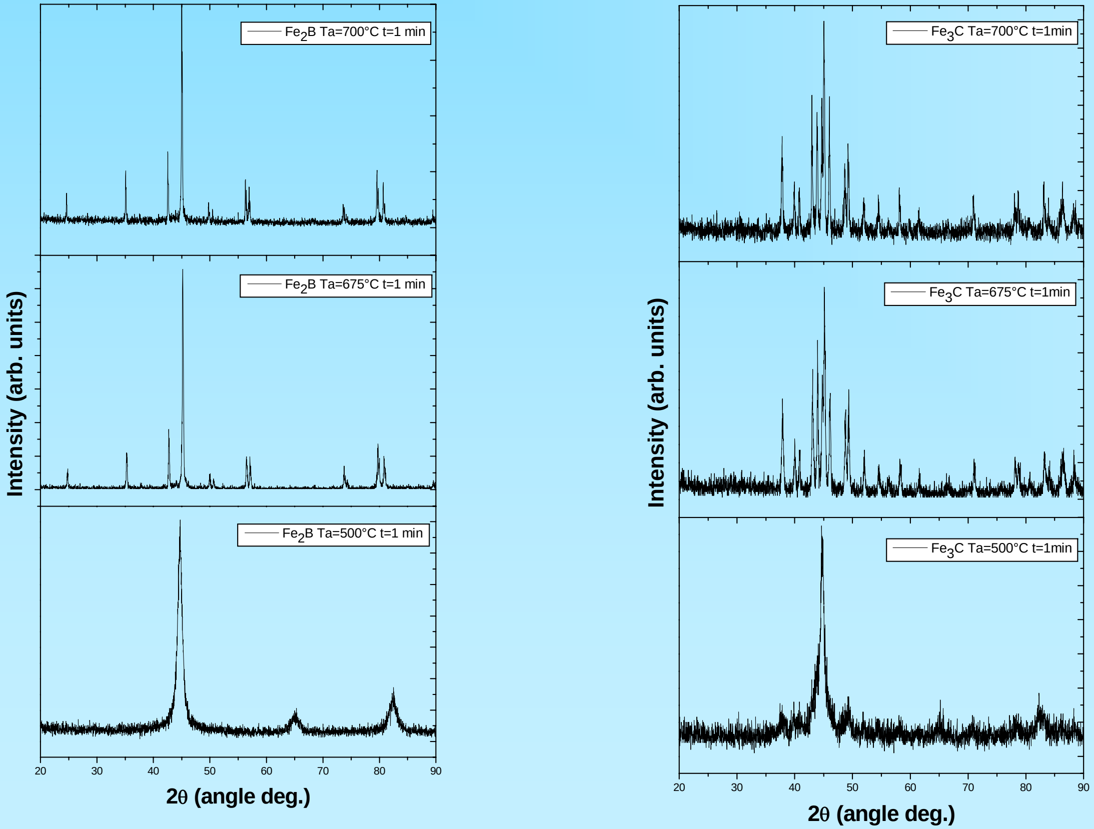
2. **Nanocrystalline Fe_2B and Fe_3C compounds**

Preparation:

Homogenization of the mixture: bulk iron and carbon and boron powder (2 hr)

High energy ball milling 5 hrs

Thermal treatment at 500 ^{o}C – 700 ^{o}C, 1 – 20 minutes



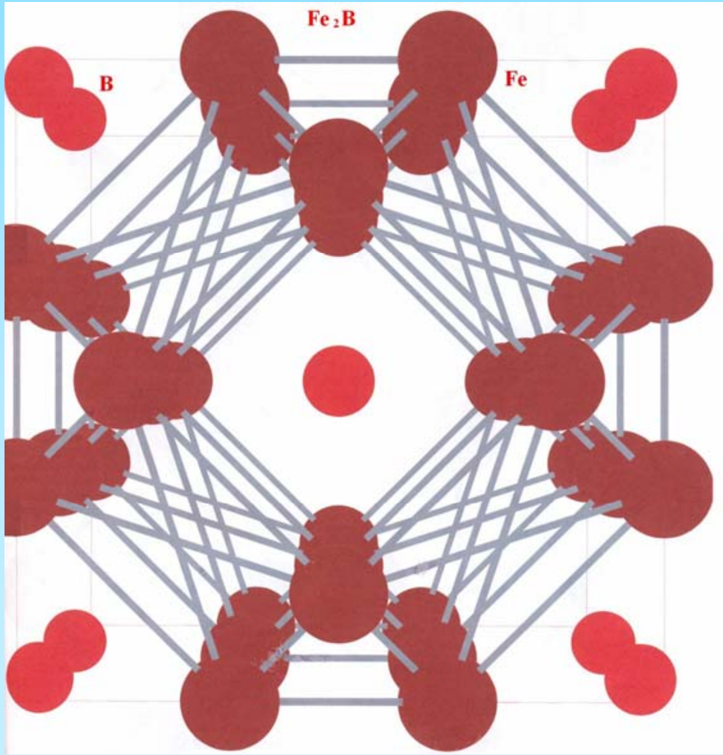
Optimum annealing temperature

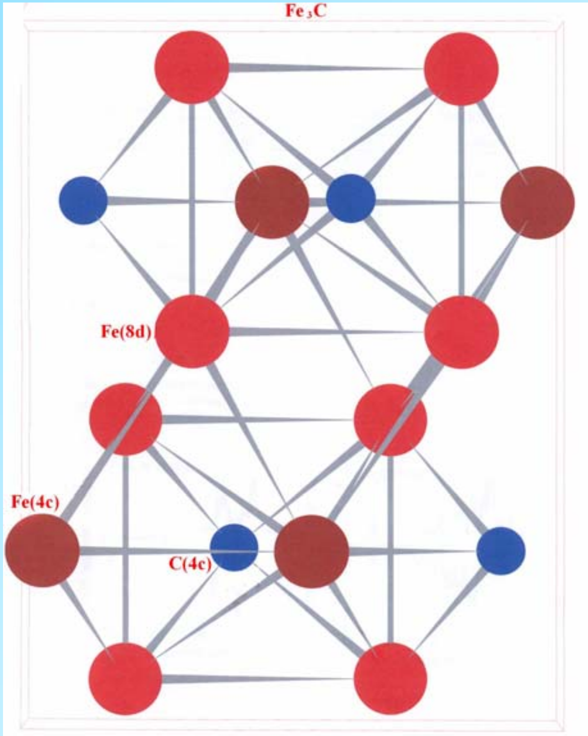
675 °C for Fe_2B

700 °C for Fe_3C

Table 1 Lattice parameters

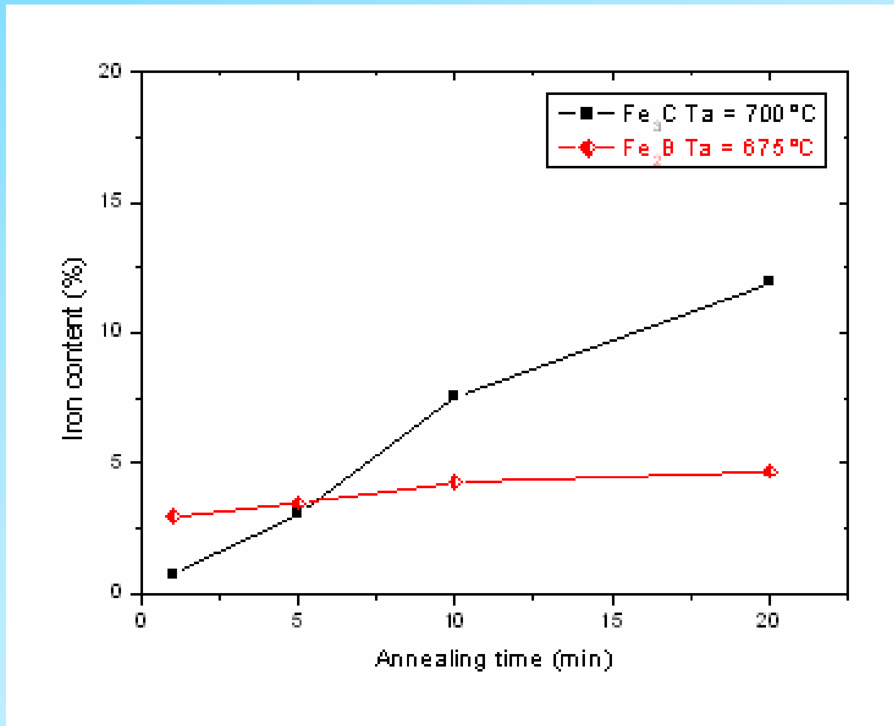
Nanocrystalline sample	Space group	Lattice constant (Å)			<d> (nm)
		a	b	c	
Fe_2B	I4/mcm tetrag.	5.113(2)	5.113(2)	4.246(1)	53.5
Fe_3C	Pnma orth.	5.086(4)	6.752(3)	4.523(2)	70





Crystal structures

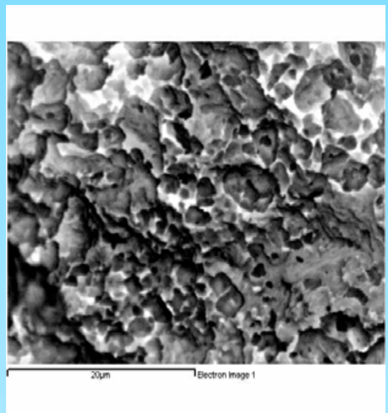
Iron content as function of annealing time

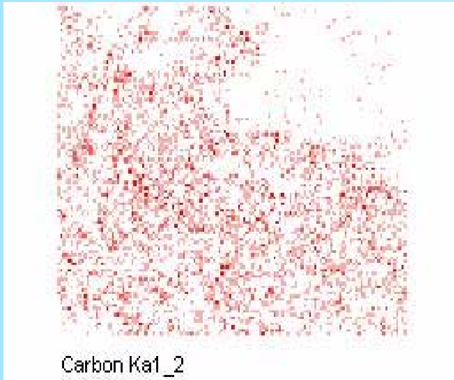


Electron microscope

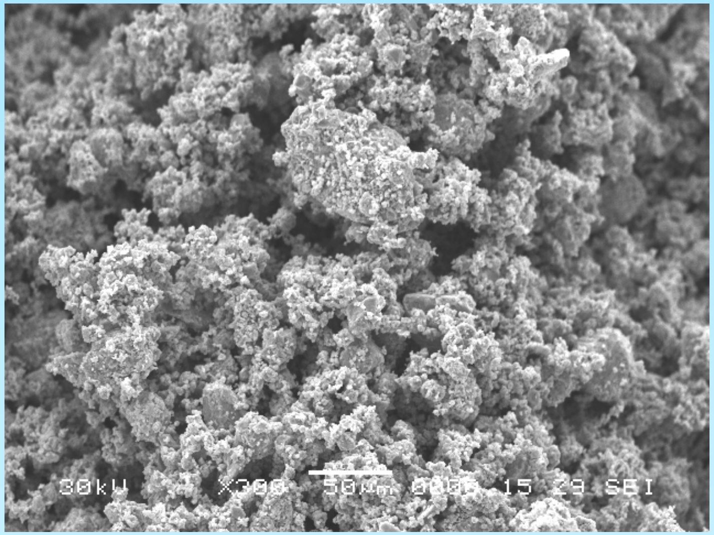
Random distribution of constituting elements

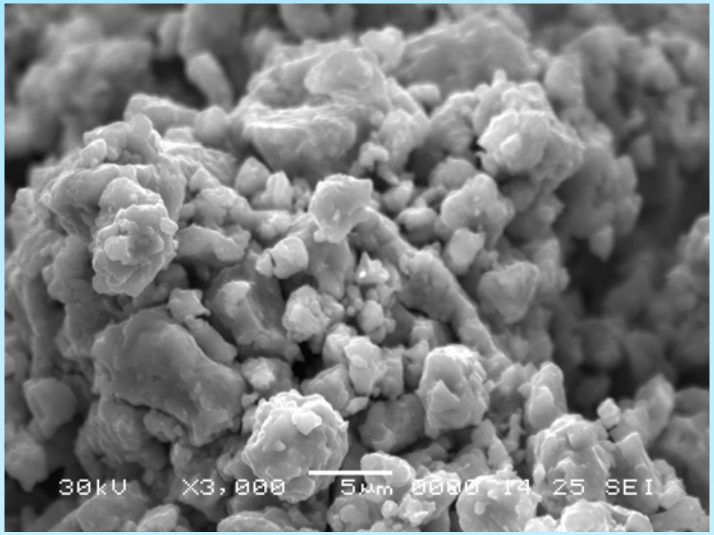
Confirmation of formation of structures

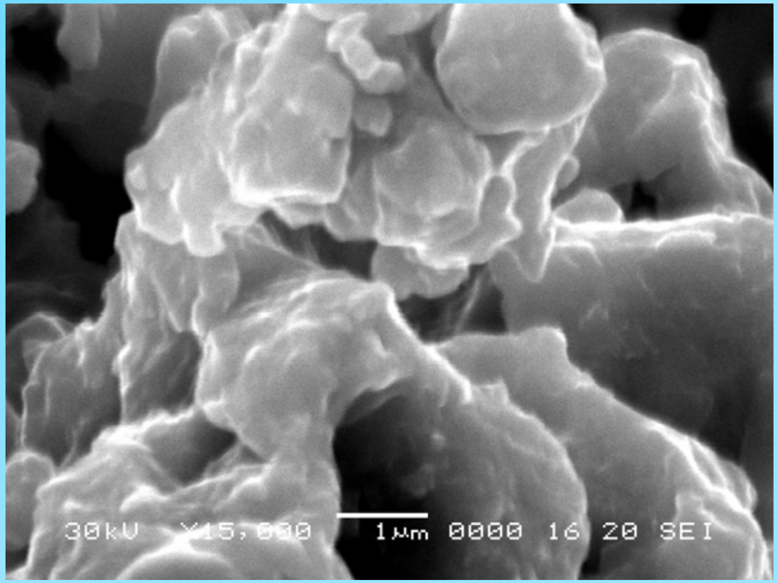


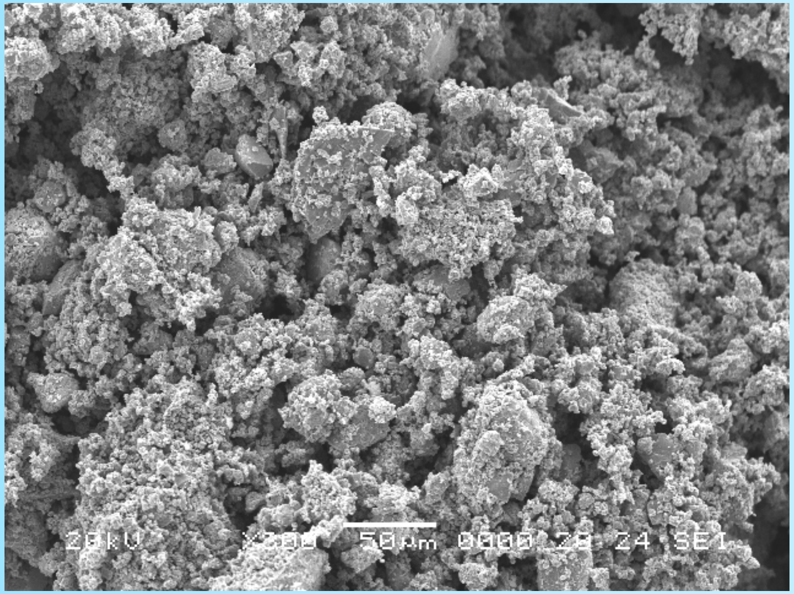


Fe_3C

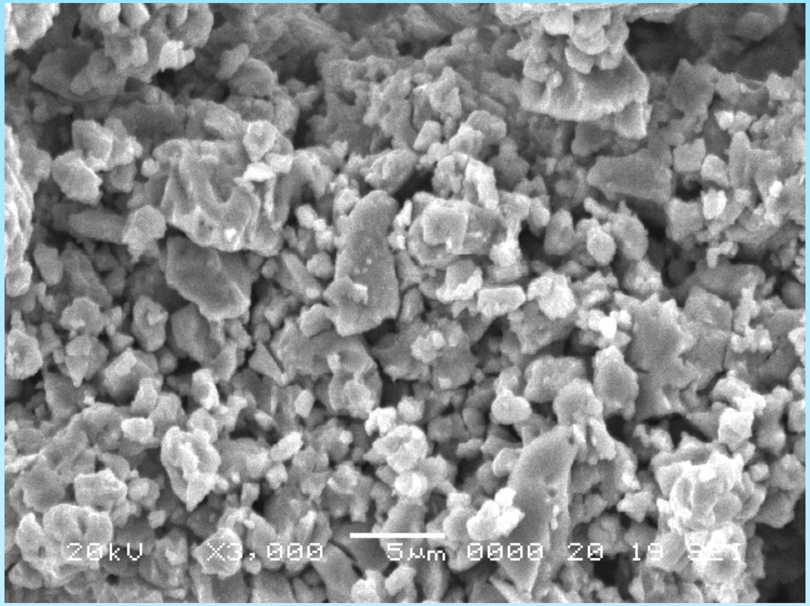


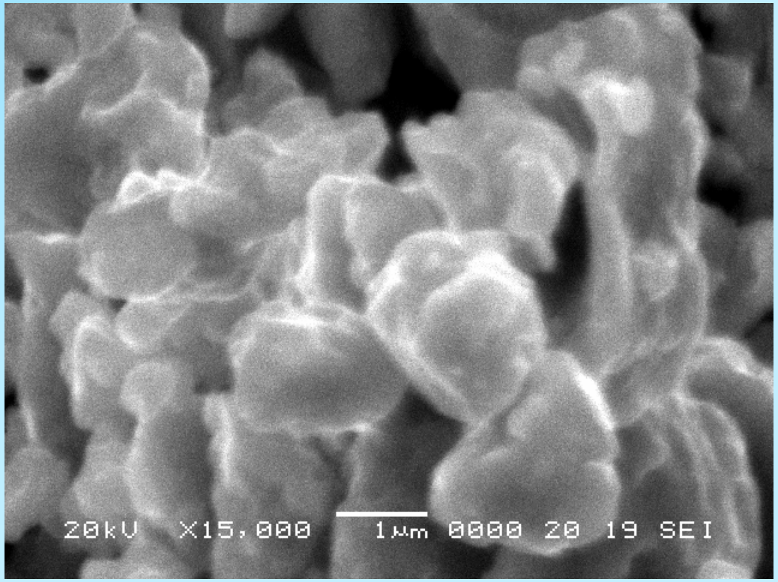



30kV X15,000 1μm 0000 16 20 SEI


20kV X300 50μm 0000 20 24 SEI

Fe_3C


20kV X3,000 5μm 0000 20 19 SEI


20kV X15,000 1μm 0000 20 19 SEI

Magnetic measurements

Magnetization isotherms at 4.2 K: sample thermally treated at 500 ^{o}C

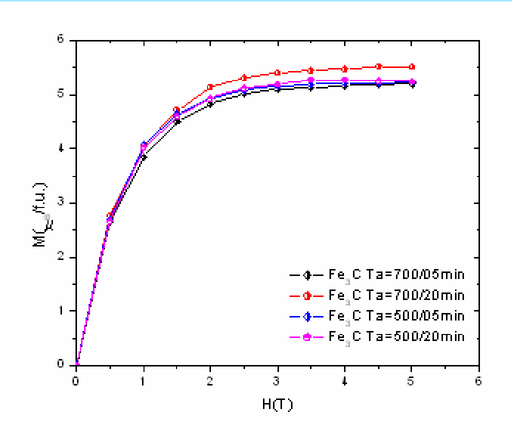
magnetization decrease as function of t_a

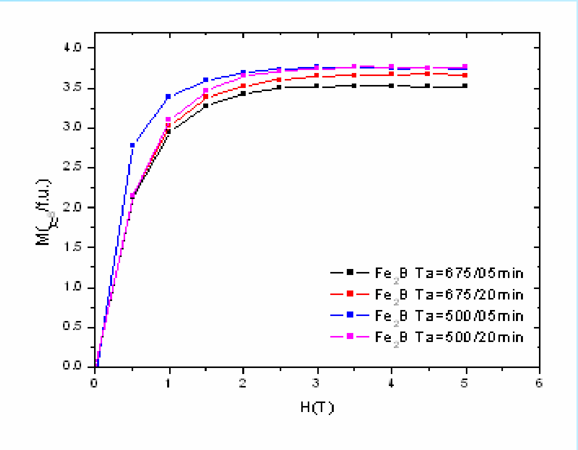
formation of Fe_2B, Fe_3C phase

Sample treated at optimum temperature (675 ^{o}C Fe_2B, 700 ^{o}C Fe_3C)

magnetization increase as function of t_a

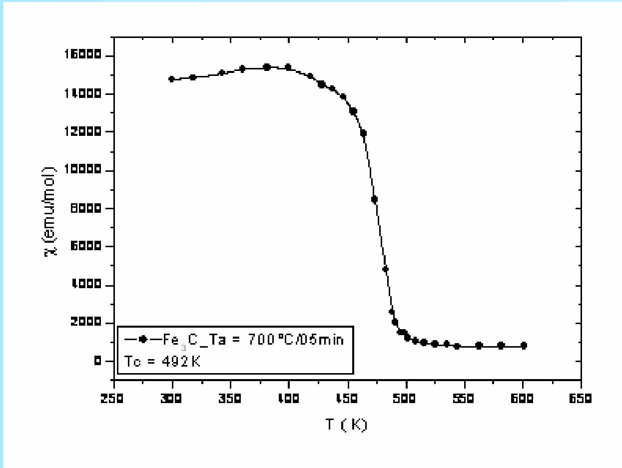
precipitation of iron





Feromagnetic ordering

Sample	Magnetic moments (μ_B/Fe atom)	T_C (K)
Fe_2B	1.78	912
Fe_3C	1.83	492



Transition from ferromagnetic to paramagnetic phase

⇓

no other phases are present

Band structure calculations

Fe_2B

Sample	Atom	M	band	$M(\mu_B)$	M (μ_B/f.u.)	
					Computed	Experimental
Fe_2B	Fe8h	1.815	s	-0.0005	3.513	3.550
			p	-0.025		
			d	1.840		
	B4a	-0.12	s	-0.022		
			p	-0.107		

$M_{orb} = 0.06\ \mu_B$ smaller than $0.08\ \mu_B$ in pure Fe

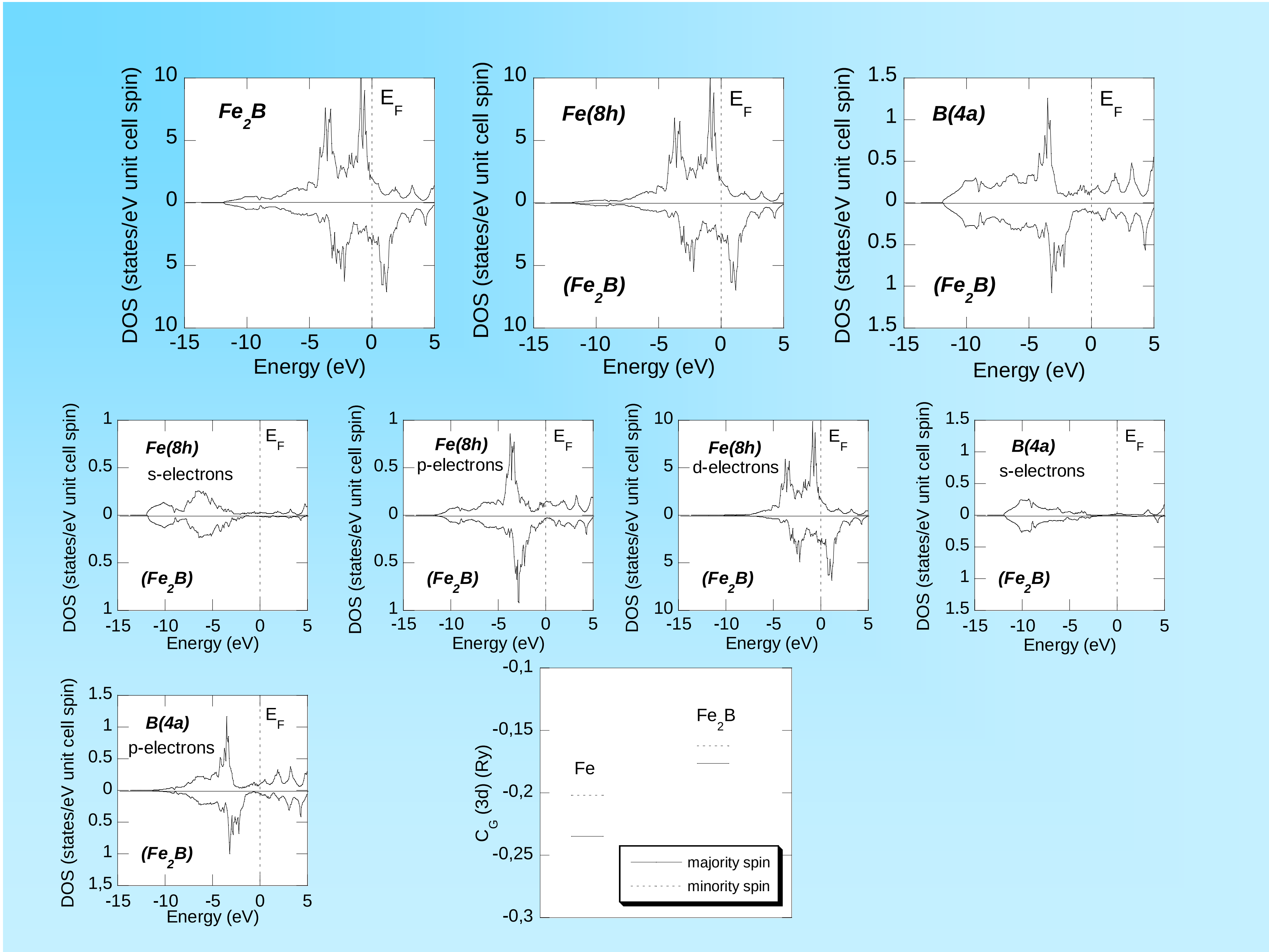
Hybridization effects Fe3d-B2p

⇓

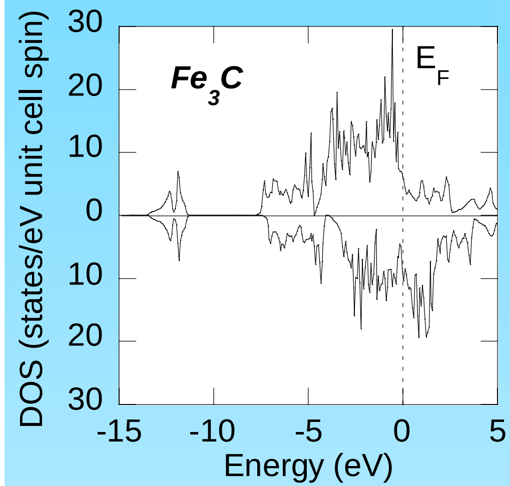
induced polarization at B site

band filling of Fe3d minority band

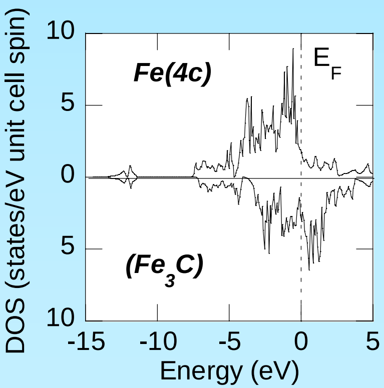
The exchange splitting is diminished as compared to iron metal

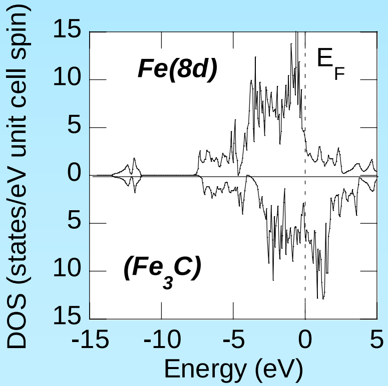

Fe2B
Fe(8h)
B(4a)
(Fe2B)
EF
DOS (states/eV unit cell spin)
Energy (eV)
Fe(8h) s-electrons
Fe(8h) p-electrons
Fe(8h) d-electrons
B(4a) s-electrons
B(4a) p-electrons
CG (3d) (Ry)
Fe
Fe2B
majority spin
minority spin

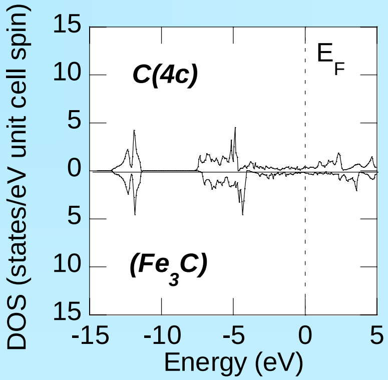
Fe_3C

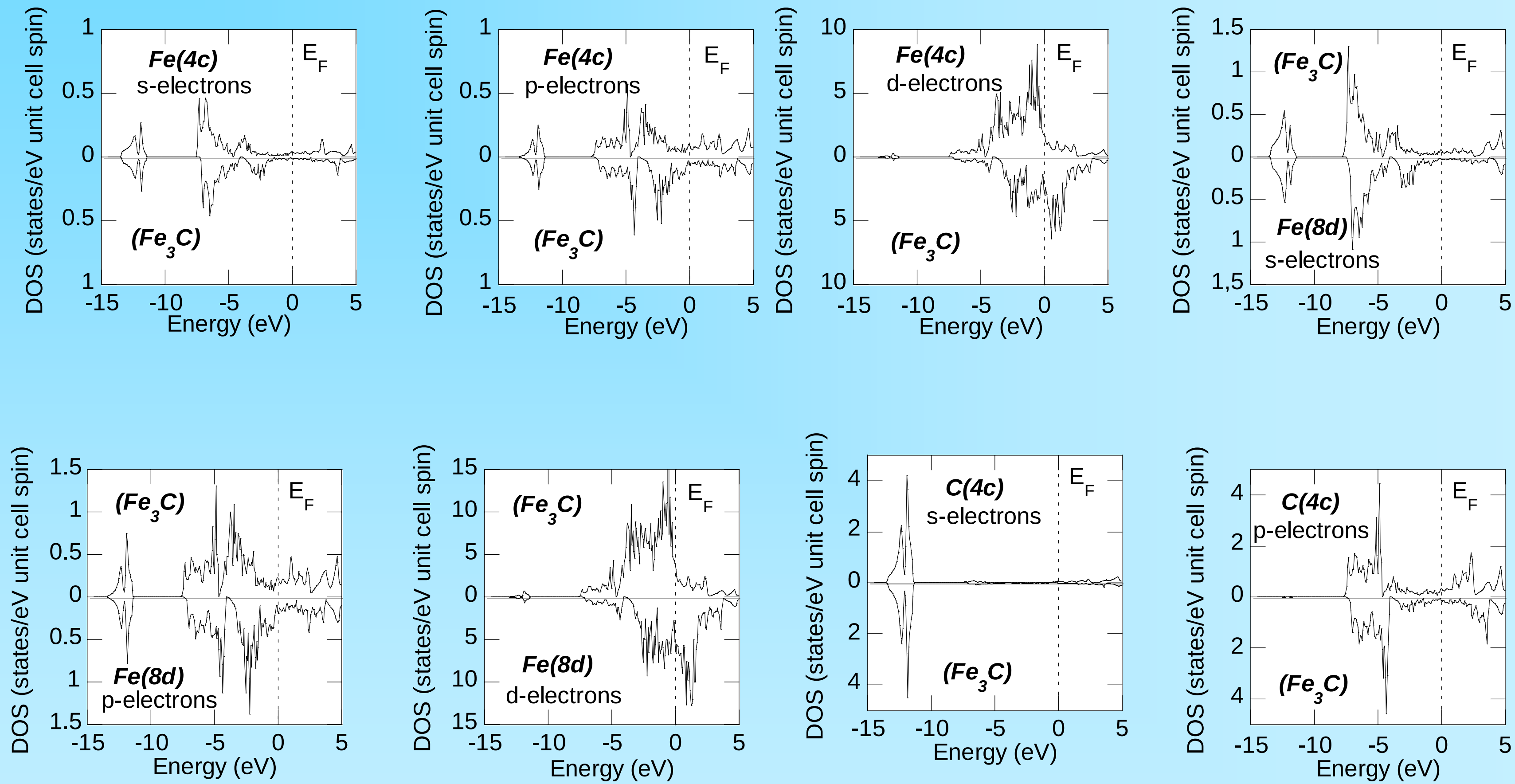


Sample	Atom	M (μ_B)	band	M(μ_B)	M (μ_B/f.u.) Computed	M (μ_B/f.u.) Experimental
Fe_3C	Fe4c	1.815	s	-0.003	5.49	5.51
			p	-0.016		
			d	1.836		
	Fe8d	1.908	s	-0.004		
			p	-0.019		
			d	1.931		
	C4c	-0.126	s	-0.012		
			p	-0.129		



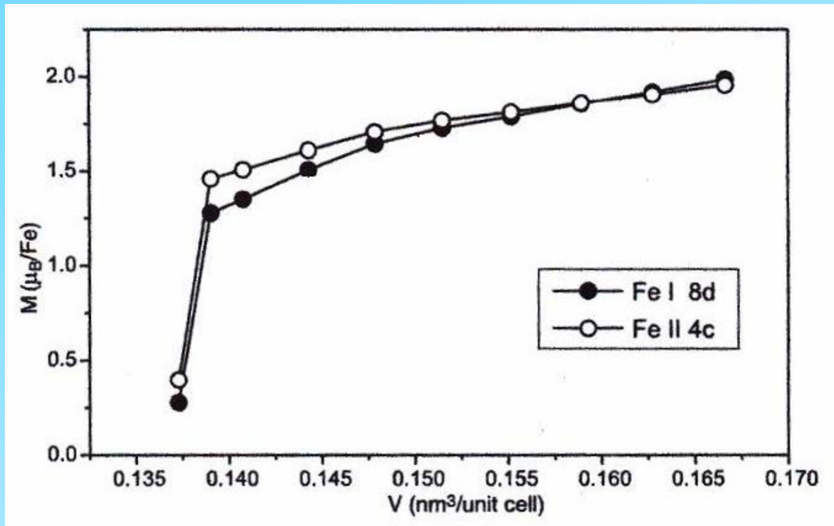




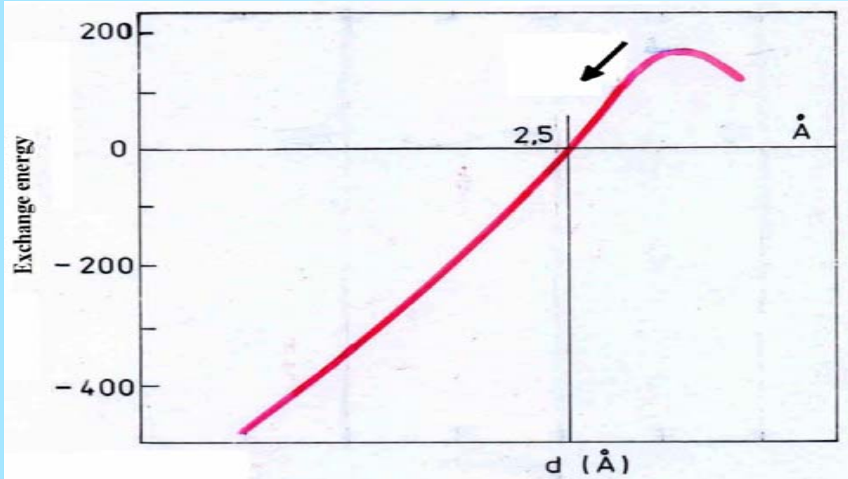


Fe(4c)
s-electrons
(Fe3C)
EF
DOS (states/eV unit cell spin)
Energy (eV)
Fe(4c)
p-electrons
(Fe3C)
EF
Fe(4c)
d-electrons
(Fe3C)
EF
(Fe3C)
Fe(8d)
s-electrons
EF
(Fe3C)
Fe(8d)
p-electrons
EF
(Fe3C)
Fe(8d)
d-electrons
EF
C(4c)
s-electrons
(Fe3C)
EF
C(4c)
p-electrons
(Fe3C)
EF

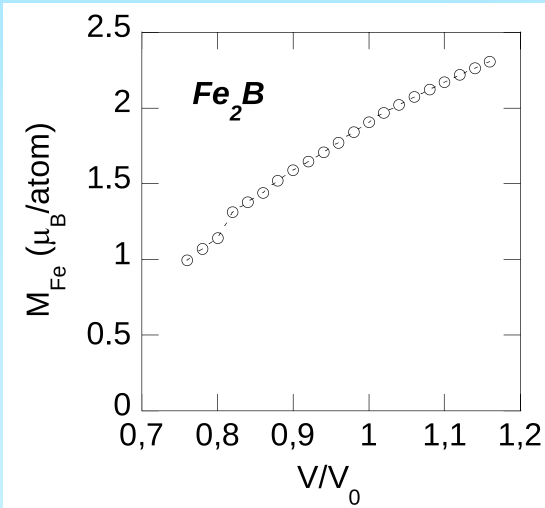
Iron moments sensitive to the volume cell (distances between iron atoms)



Moments vs. volume



Néel-Slater curve



Thank you very much for your attentions.