A Modified Core-Shell Model of Ferrimagnetic Oxide Nanoparticles

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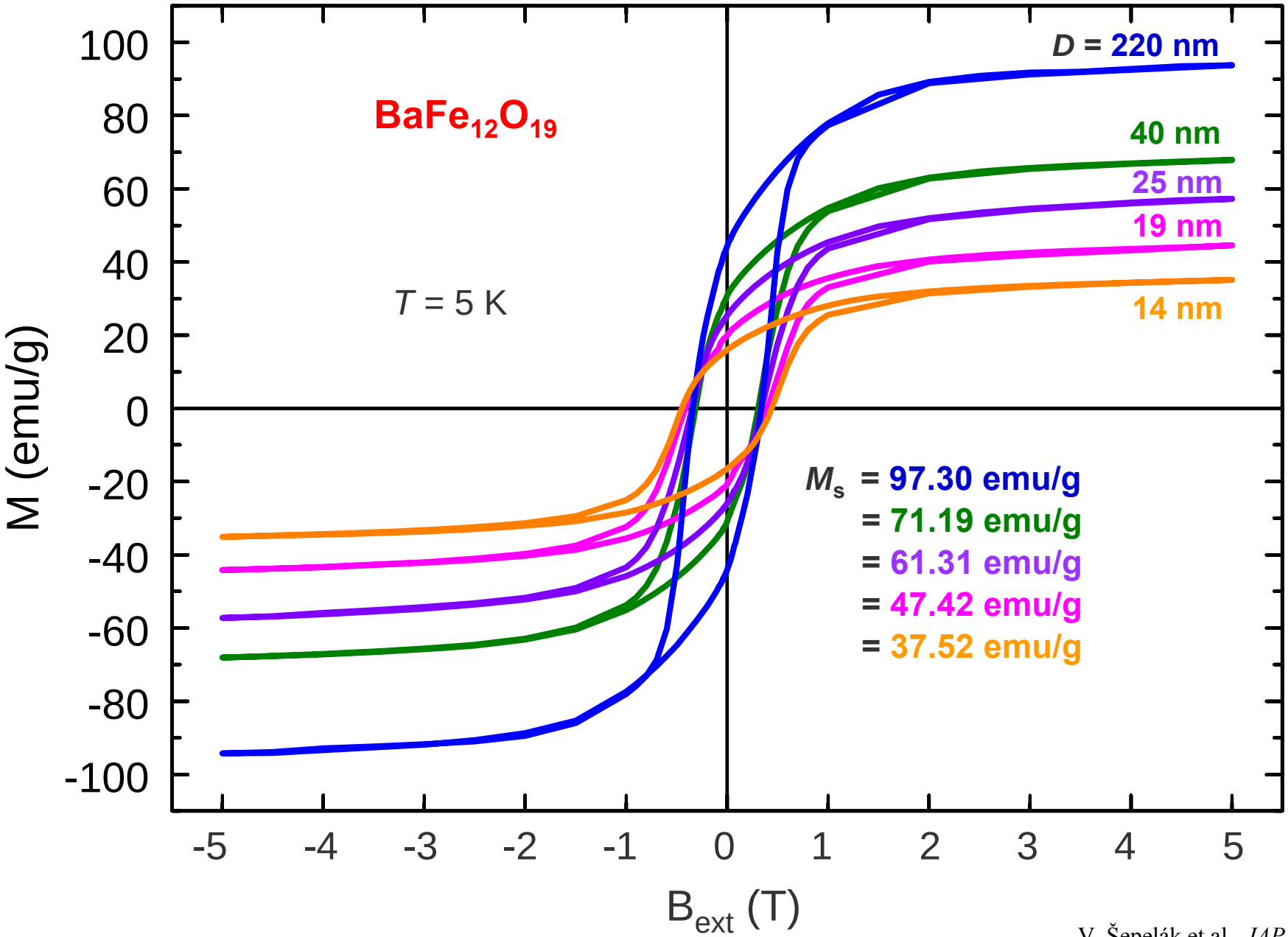
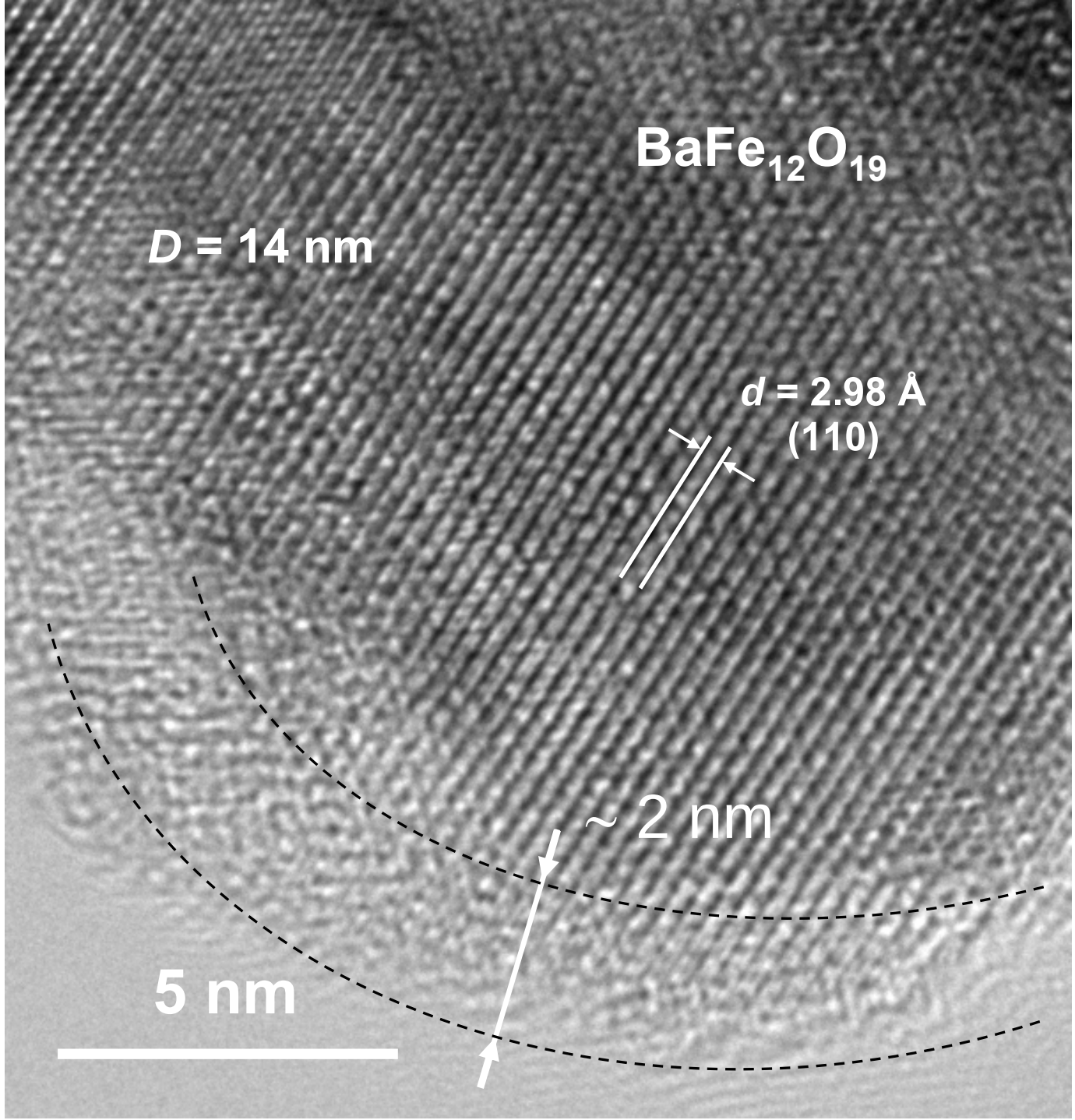
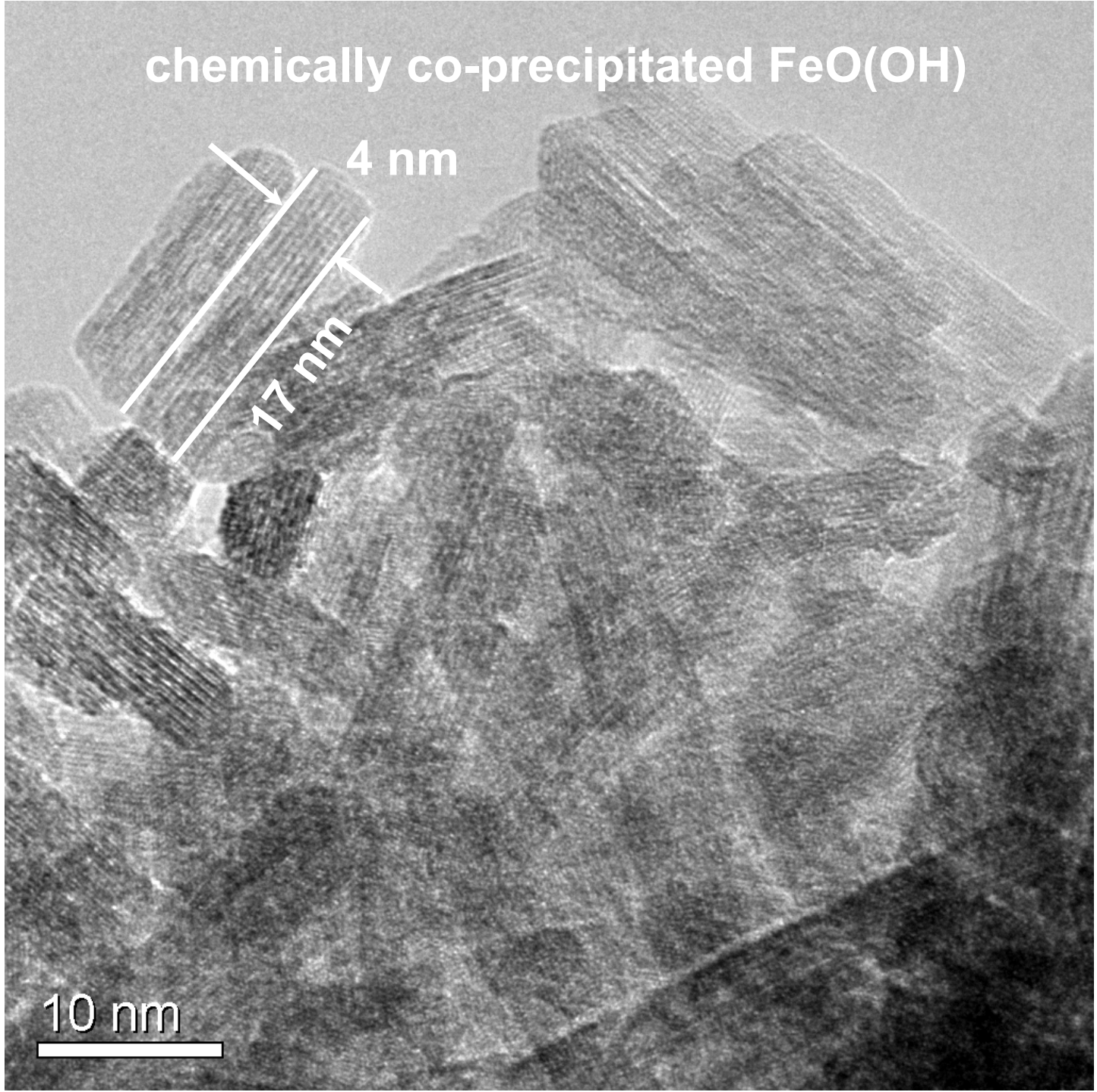
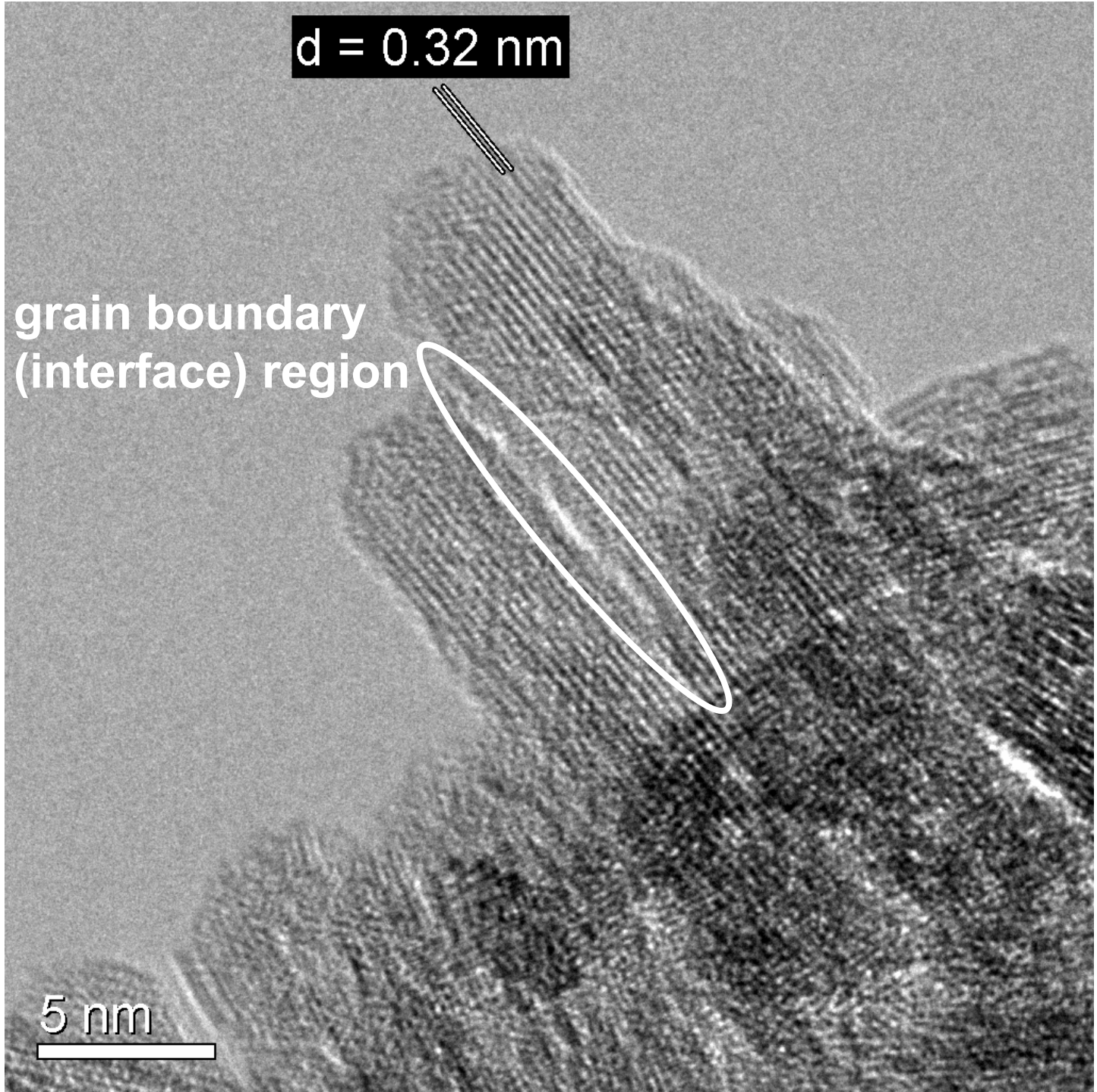
Size-dependent magnetization in nanoscale $BaFe_{12}O_{19}$



V. Šepelák et al., *JAP, in prep.*


$BaFe_{12}O_{19}$
D = 14 nm
d = 2.98 Å
(110)
~ 2 nm
5 nm


chemically co-precipitated FeO(OH)
4 nm
17 nm
10 nm

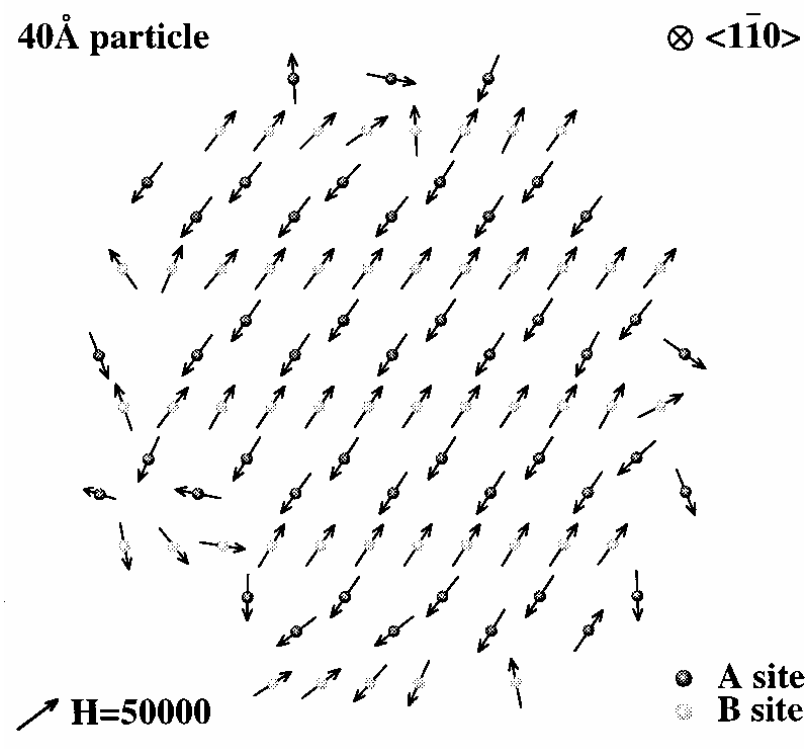

d = 0.32 nm
grain boundary
(interface) region
5 nm

Model of the spin distribution within nanoscale ferrite particle

PHYSICAL REVIEW B VOLUME 59, NUMBER 9 MARCH 1999-I

Atomic-scale magnetic modeling of oxide nanoparticles

R. H. Kodama* and A. E. Berkowitz
Physics Department & Center for Magnetic Recording Research, University of California, San Diego, La Jolla, California 92093
(Received 6 May 1998; revised manuscript received 13 October 1998)

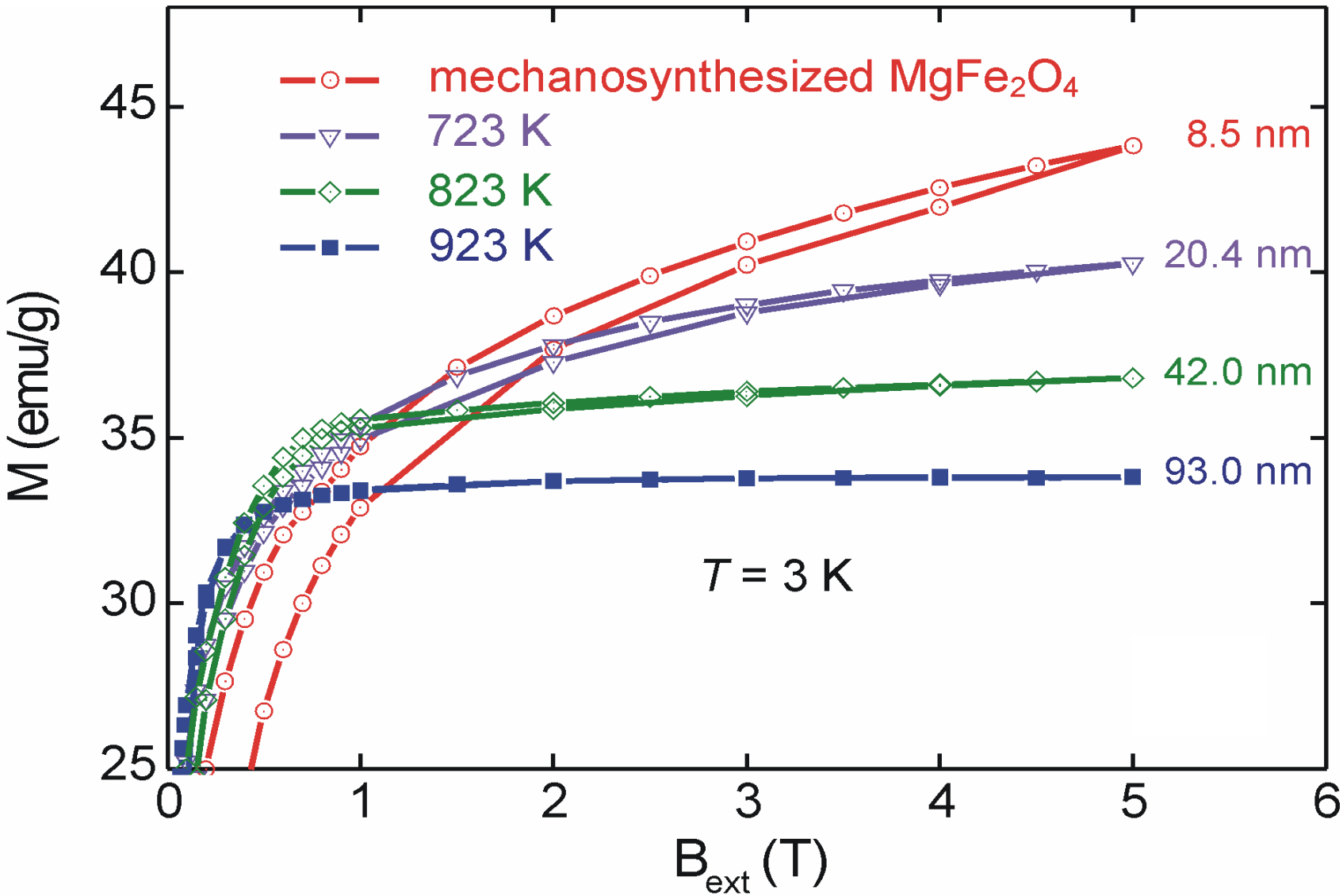


?

Model of a *shell-core structure:*
spin canting is due to broken exchange bonds in the *near-surface layers*

[R.H. Kodama, A.E. Berkowitz, *Phys. Rev. B* **59** (1999) 6321.]

Enhanced magnetization in nanocrystalline $MgFe_2O_4$



V. Šepelák et al., *J. Magn. Magn. Mater.* **316** (2007) e764.

Fundamenal scientific issues in the field of nanocrystalline solids

Explanation of the structure-property relationships in nanomaterials

- elucidation of the fundamental origin of unusual physical and chemical properties of “interface-controlled” materials

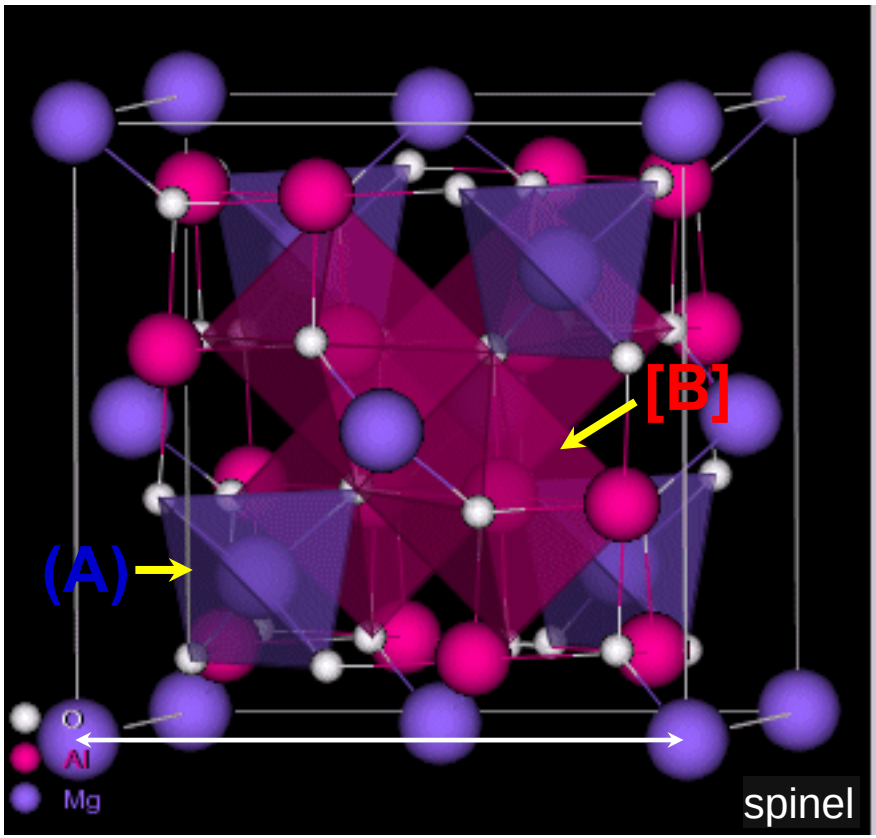
Structural characterization of nanostructures at fine-size (local) scale

- determination of both nonequilibrium ionic distribution and spin configurations in internal interfaces (grain boundary regions) and external surfaces (near-surface layers) of nanoparticles

- characterization of interfaces/surfaces (volume fraction, thickness, …)

Spinel structure

2-3 spinels: $M1^{2+}M2_2^{3+}O_4$



space group Fd3m; cubic unit cell consists of **56 atoms**: **32** anions (O^{2-}) and **24** cations ($M(1)^{2+}$ and $M(2)^{3+}$)

96 interstices between the ions:
64 tetrahedral (A) (8a, 8b, 48f)
32 octahedral [B] (16c, 16d)

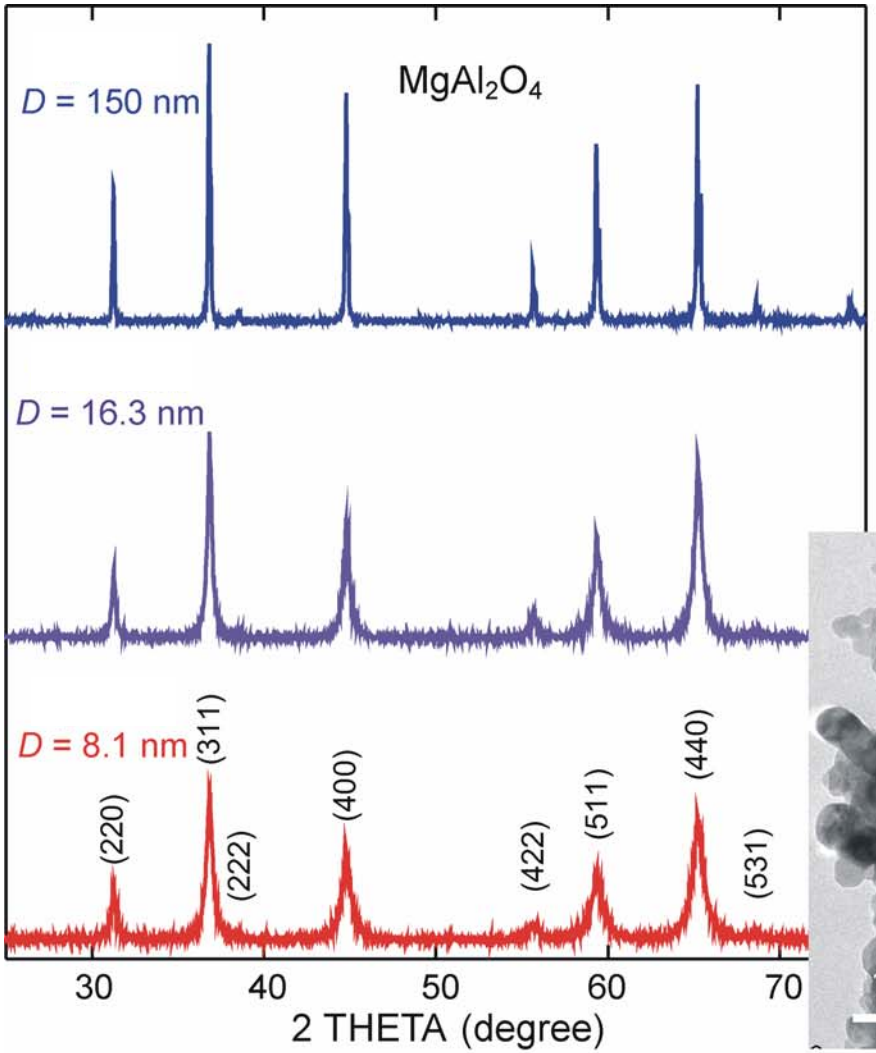
only **24 interstices are occupied** by cations:
8 (A) sites (8a) and **16 [B]** sites (16d)

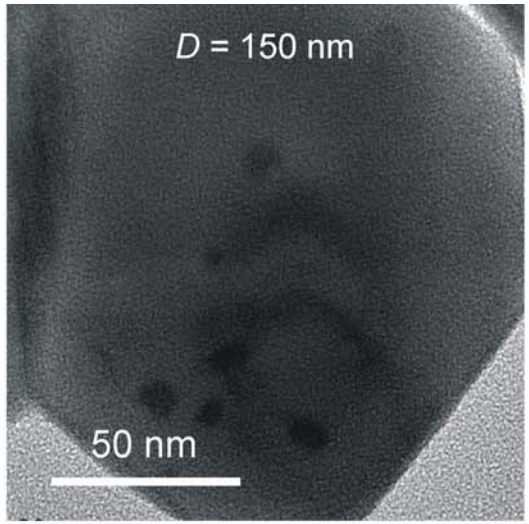
a	unit cell dimension
u	oxygen parameter
λ	**degree of inversion**

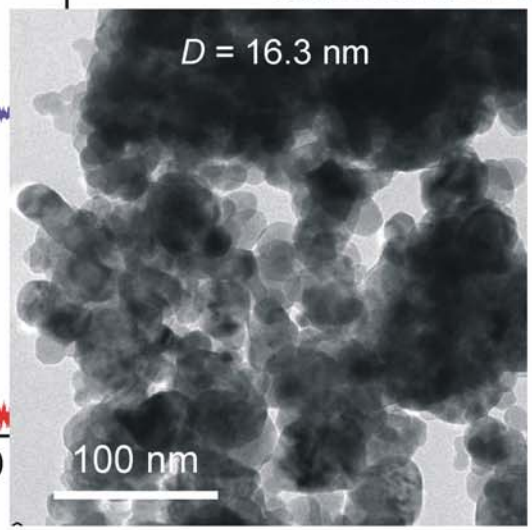
	(A)	[B]	
Spinel ferrites:	$(M_{1-\lambda}\,Fe_{\lambda})$	$[M_{\lambda}\,Fe_{2-\lambda}]$	O_4
Spinel aluminates:	$(M_{1-\lambda}\,Al_{\lambda})$	$[M_{\lambda}\,Al_{2-\lambda}]$	O_4

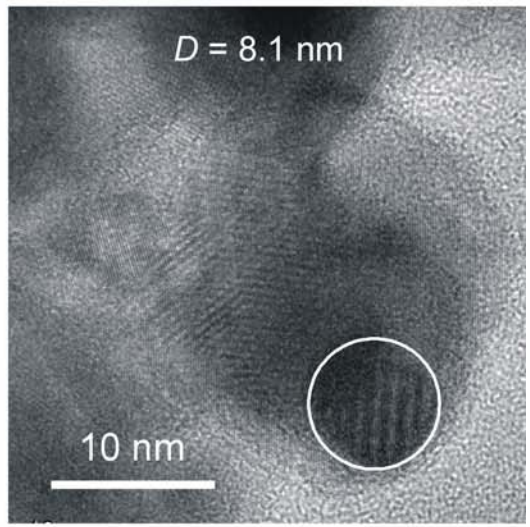
$\lambda = 0$	**normal spinel**
$0 < \lambda < 1$	**partly inverse spinel**
$\lambda = 1$	**inverse spinel**
$\lambda = 2/3$	**random distribution**

From **Macro** to **Nano**



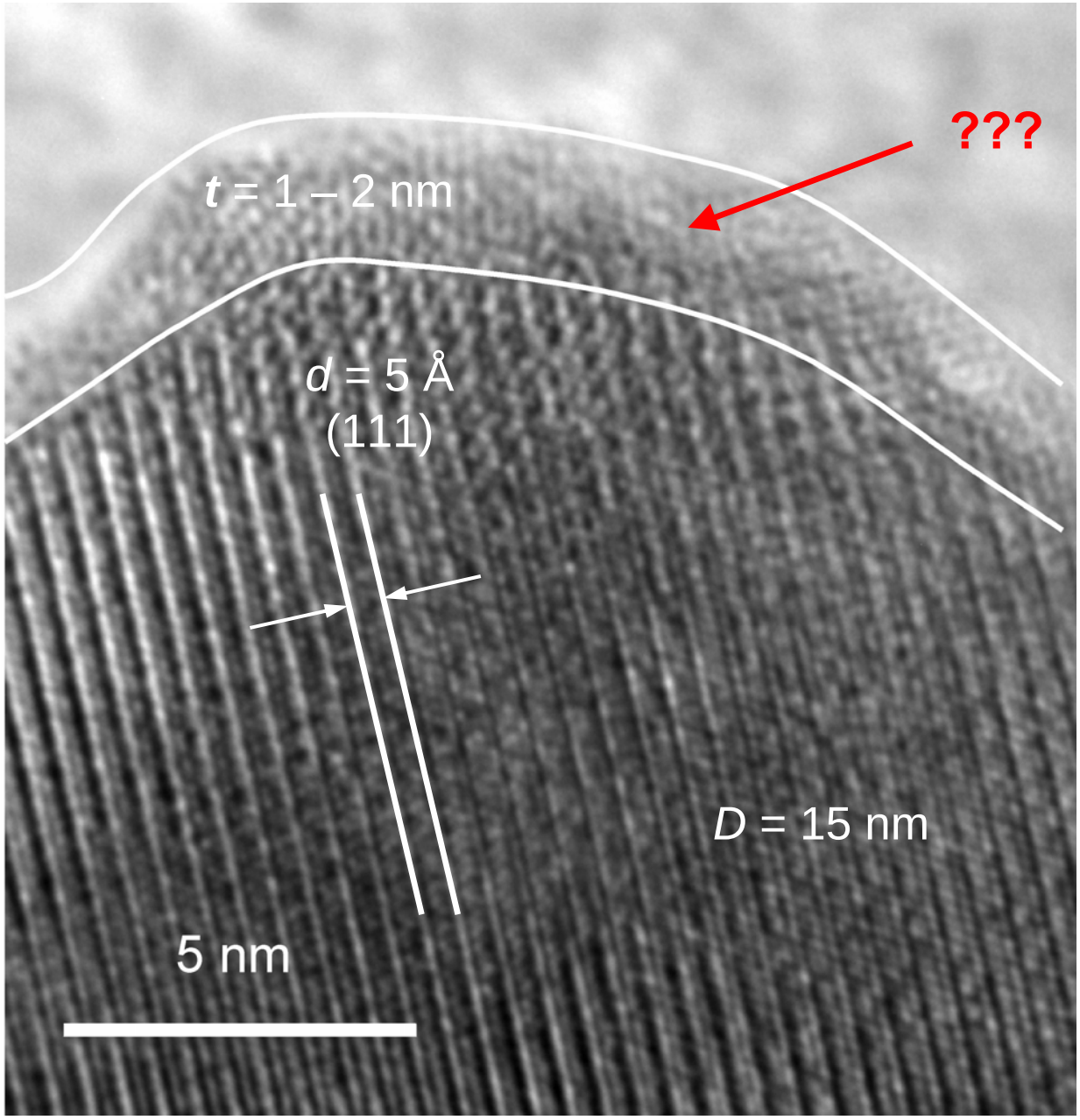






V. Šepelák et al., *Solid State Ionics* **177** (2006) 2487.

The core–shell structure of nanocrystalline spinel oxide

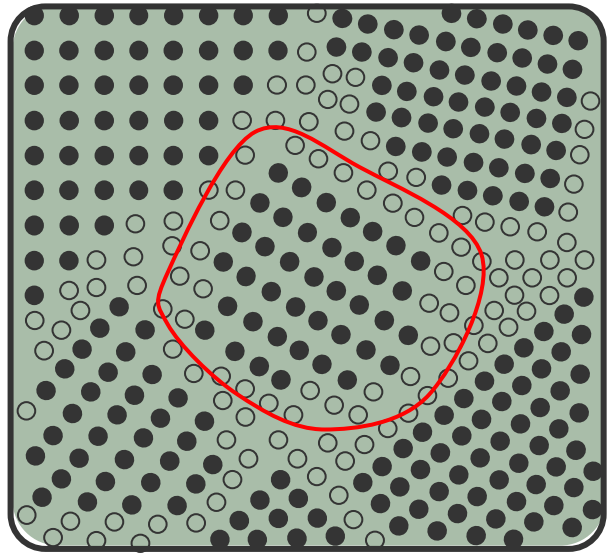


Disordered surface/interface

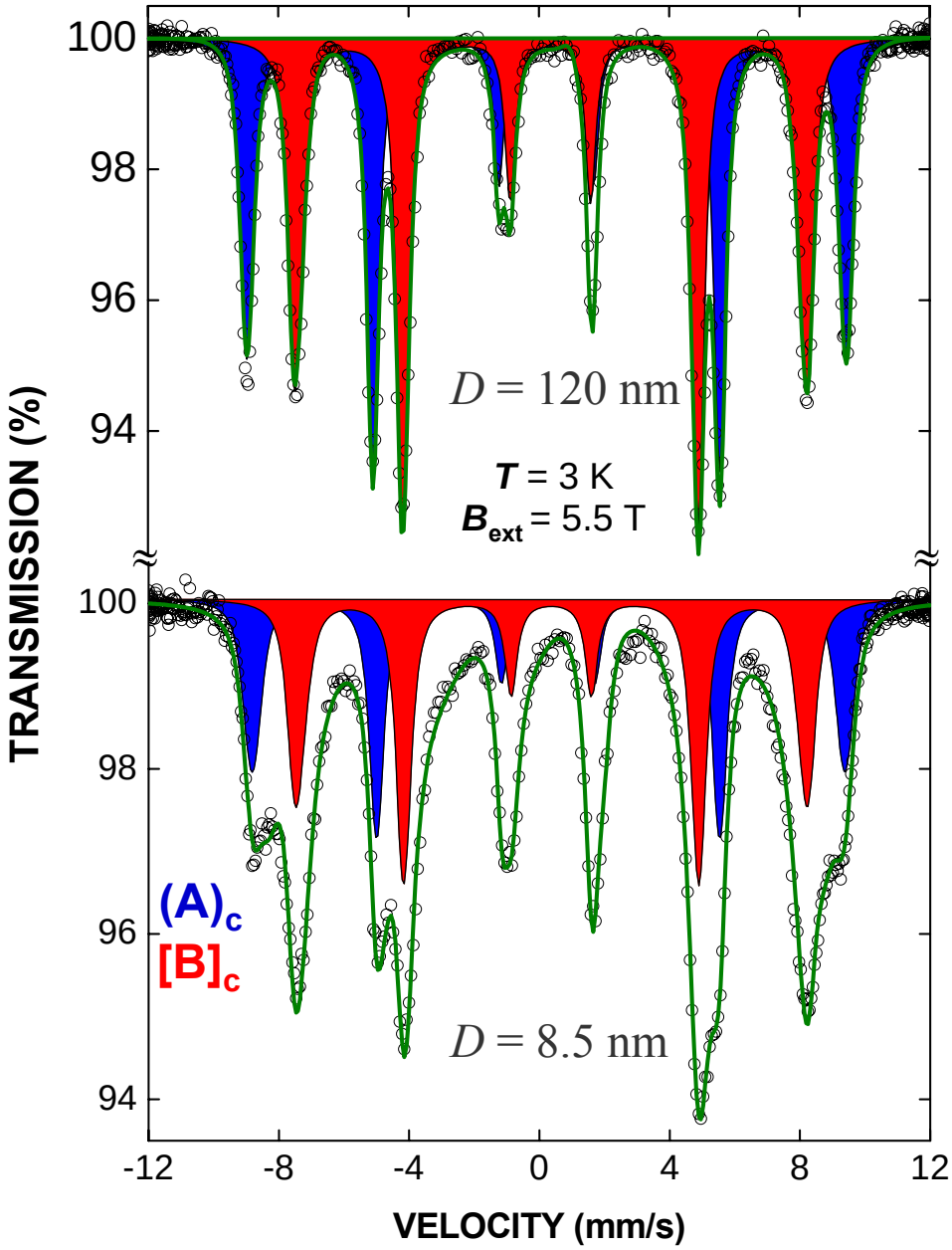
(grain boundary region)

Ordered core

(grain, crystallite)



Ionic and spin disorder in nanoscale spinel $MgFe_2O_4$



bulk $MgFe_2O_4$

$(Mg_{0.10}Fe_{0.90}\uparrow)[Mg_{0.90}Fe_{1.10}\downarrow]O_4$

collinear magnetic structure:

$\Psi_{(A)} = 0°,\ \Psi_{[B]} = 0°$

partly inverse spinel: $\lambda = 0.90$

nanocrystalline $MgFe_2O_4$

core:

$(Mg_{0.10}Fe_{0.90}\uparrow)[Mg_{0.90}Fe_{1.10}\downarrow]O_4$

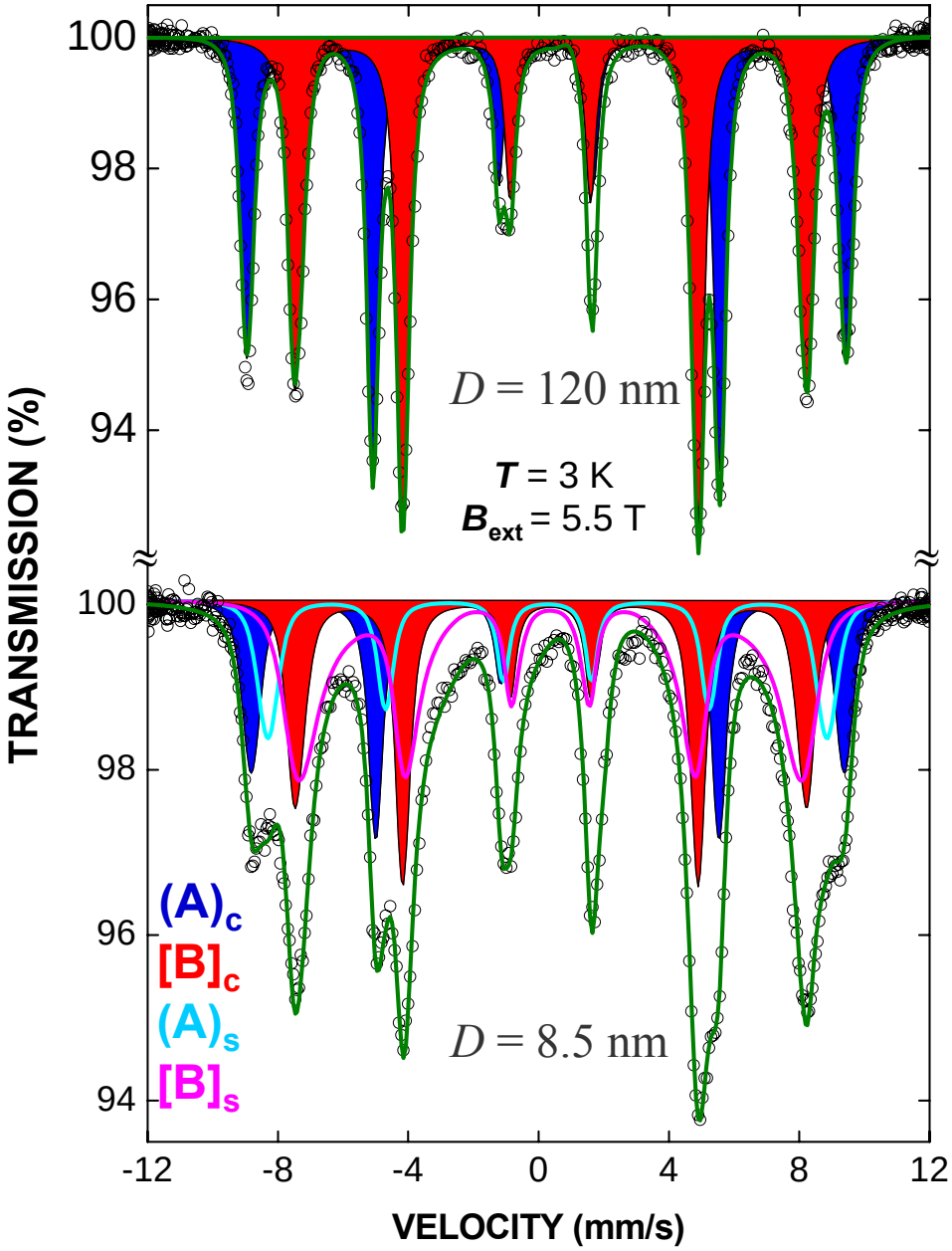
collinear magnetic structure:

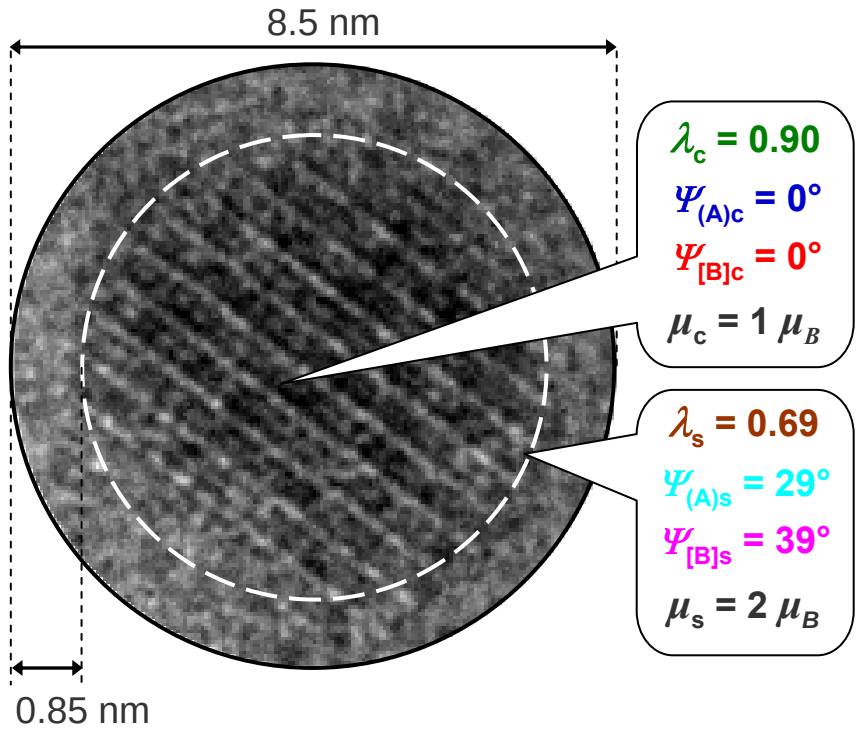
$\Psi_{(A)core} = 0°,\ \Psi_{B]core} = 0°$

partly inverse spinel: $\lambda_{core} = 0.90$

V. Šepelák et al., *Chem. Mater.* **18** (2006) 3057.

Ionic and spin disorder in nanoscale spinel $MgFe_2O_4$





core:

$(Mg_{0.10}Fe_{0.90}\uparrow)\,[Mg_{0.90}Fe_{1.10}\downarrow]\,O_4$

partly inverse spinel: $\lambda_{core} = 0.90$

shell:

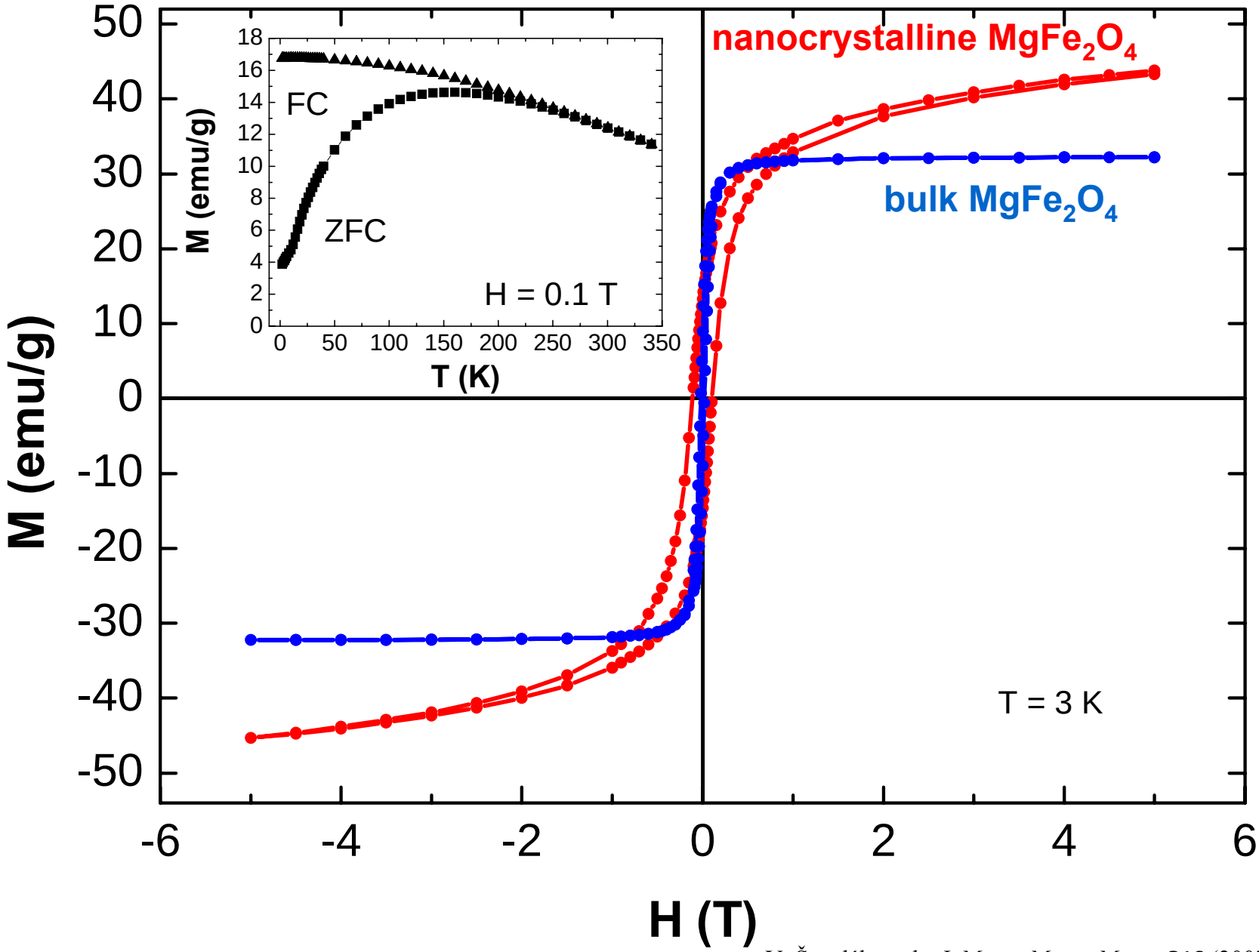
$(Mg_{0.31}Fe_{0.69}\nearrow)\,[Mg_{0.69}Fe_{1.31}\searrow]\,O_4$

$\lambda_{shell} = 0.69$ … nearly random distribution

$\Rightarrow$ ***w*** **~ 50%,** ***t*** **~ 0.9 nm**

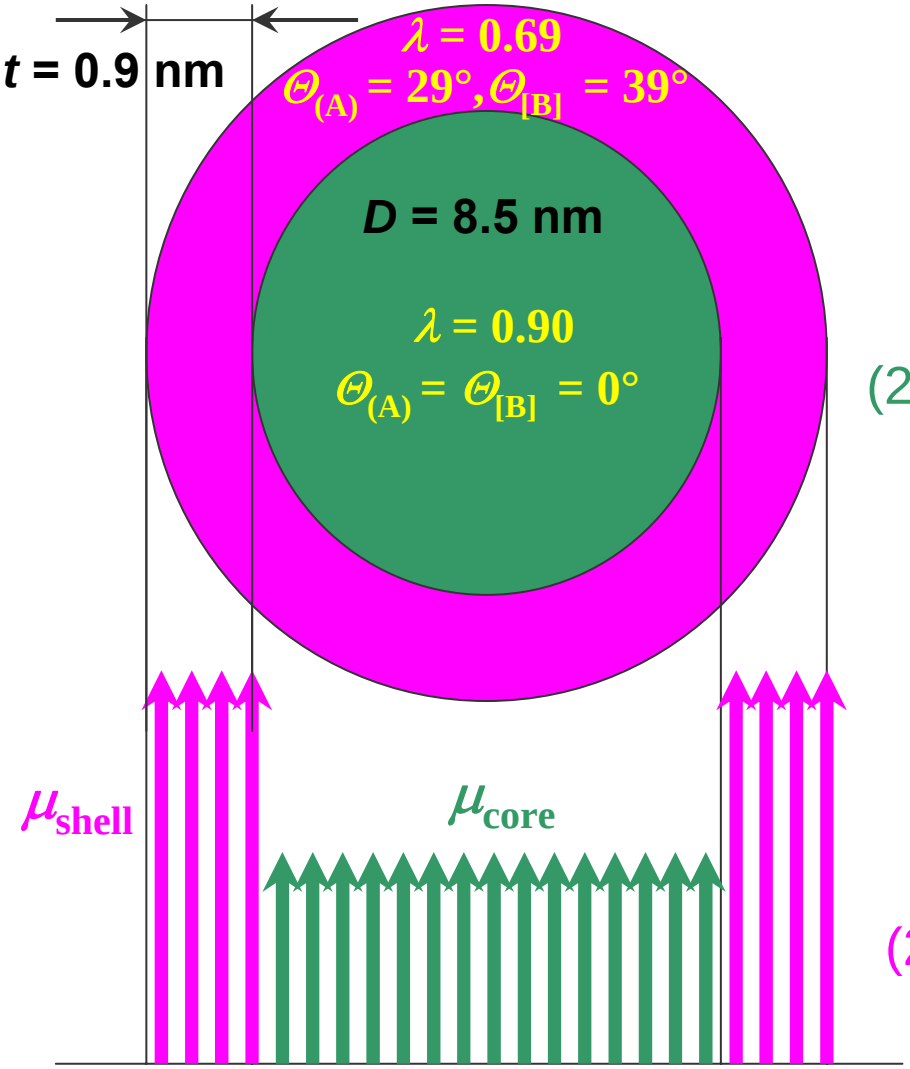
V. Šepelák et al., *Chem. Mater.* **18** (2006) 3057.

Enhanced magnetization in nanocrystalline $MgFe_2O_4$



V. Šepelák et al., *J. Magn. Magn. Mater.* **316** (2007) e764.

"Magnetically active" surface shell in $MgFe_2O_4$ nanoparticles



ordered core:

$$(Mg_{0.1}\,Fe_{0.9}\uparrow)\,[Mg_{0.9}\,Fe_{1.1}\downarrow]\,O_4$$

$$\mu_{core} = \mu_{[B]core} - \mu_{(A)core} =$$

$$(2-\lambda_{core})\mu_{Fe}\cos\Psi_{[B]core} - \lambda_{core}\mu_{Fe}\cos\Psi_{(A)core}$$

$$= 1.1 \times 5\ \mu_B - 0.9 \times 5\ \mu_B = \underline{1\ \mu_B}$$

disordered shell:

$$(Mg_{0.31}\,Fe_{0.69}\nearrow)\,[Mg_{0.69}\,Fe_{1.31}\searrow]\,O_4$$

$$\mu_{shell} = \mu_{[B]shell} - \mu_{(A)shell} =$$

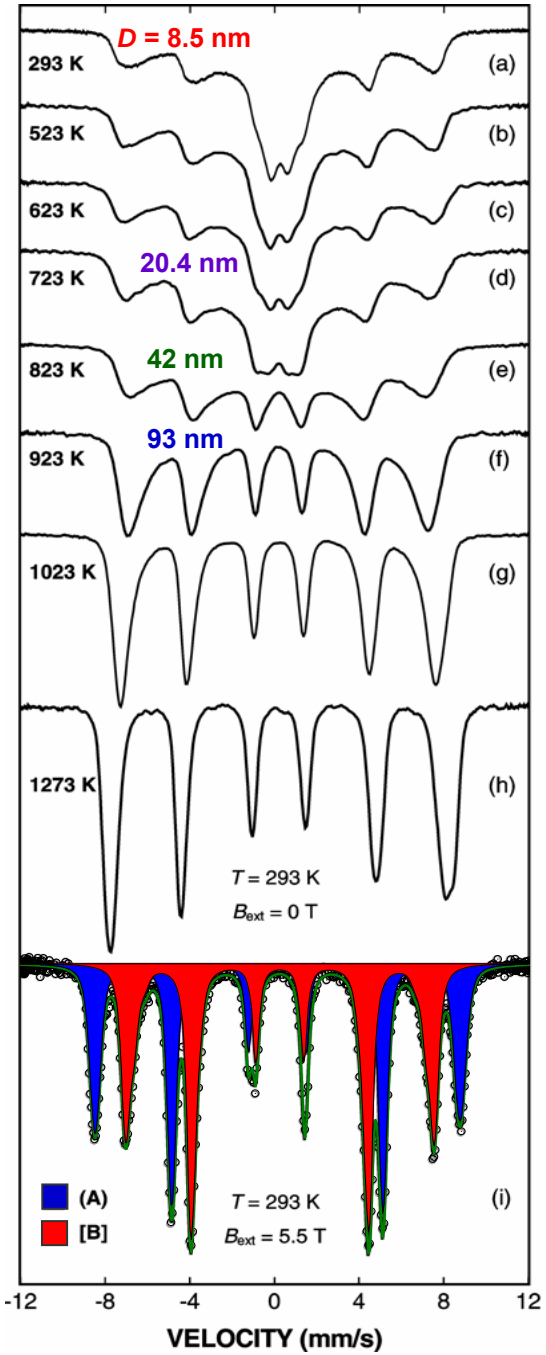
$$(2-\lambda_{shell})\mu_{Fe}\cos\Psi_{B]shell} - \lambda_{shell}\mu_{Fe}\cos\Psi_{(A)shell}$$

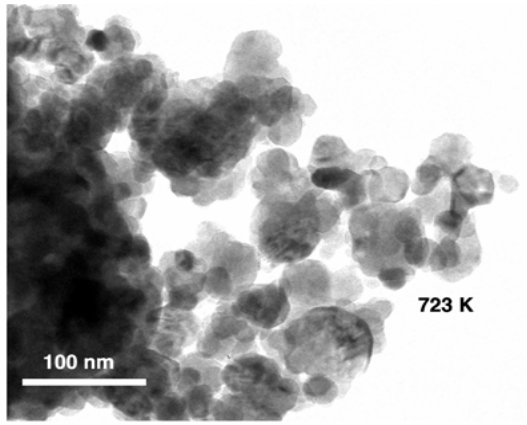
$$\underline{\sim 2\ \mu_B}$$

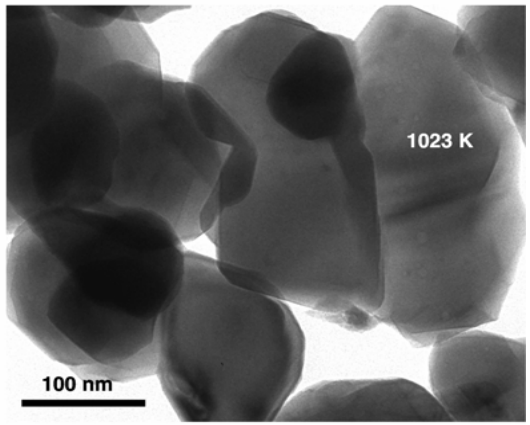
spin canting tends to **reduce** the magnetization

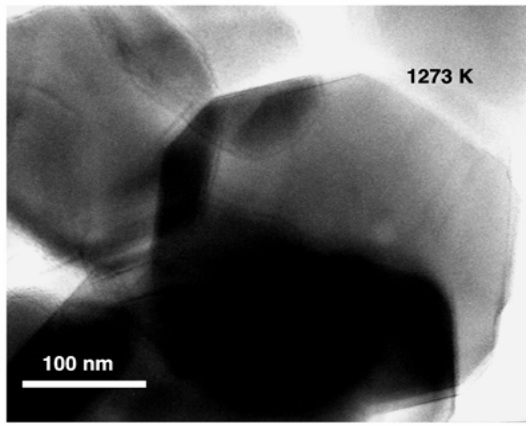
⟷

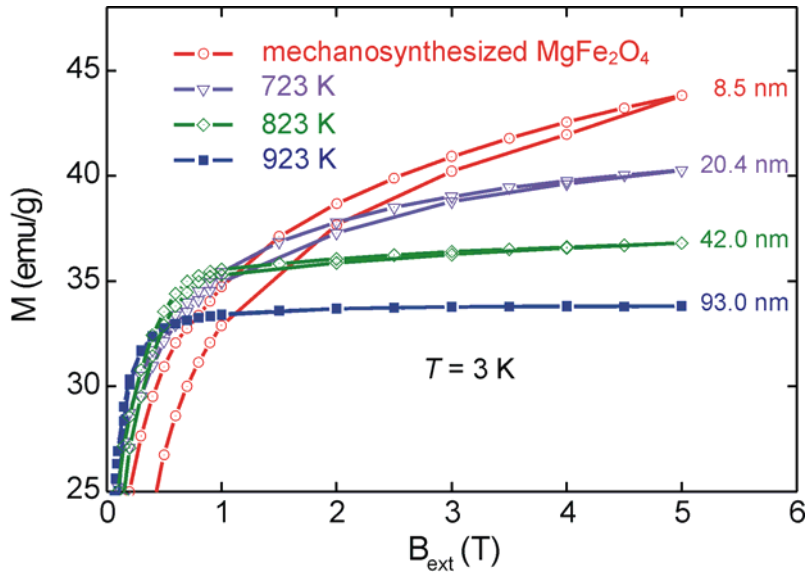
nonequilibrium cation distribution in $MgFe_2O_4$ causes **increase** of the magnetization

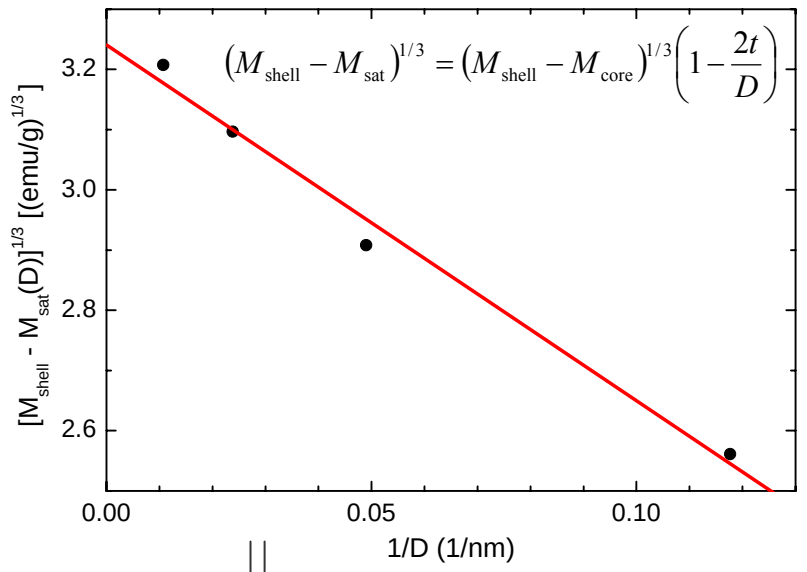








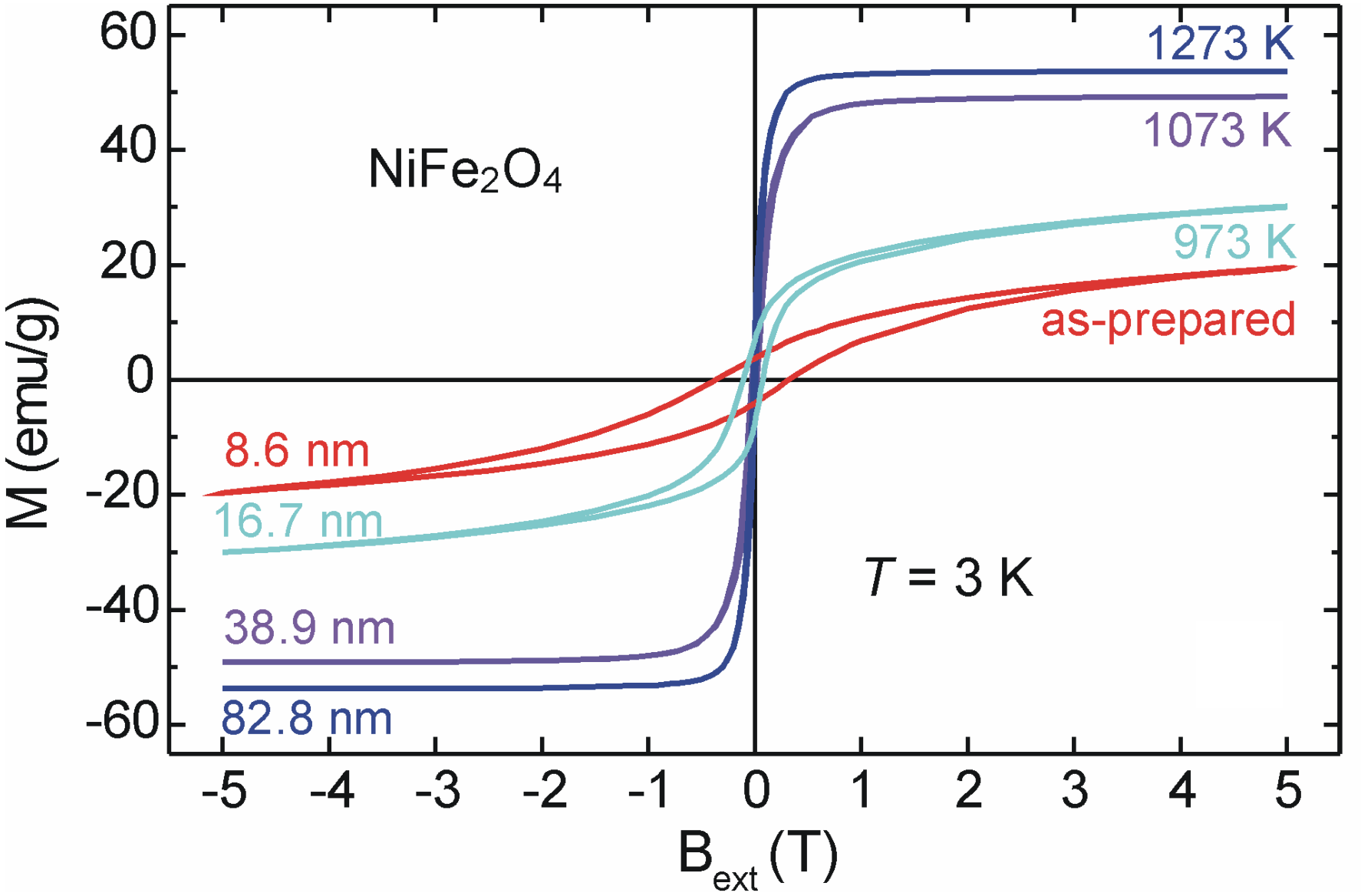




M_{core} = 32.8 emu/g, t = 0.91 nm

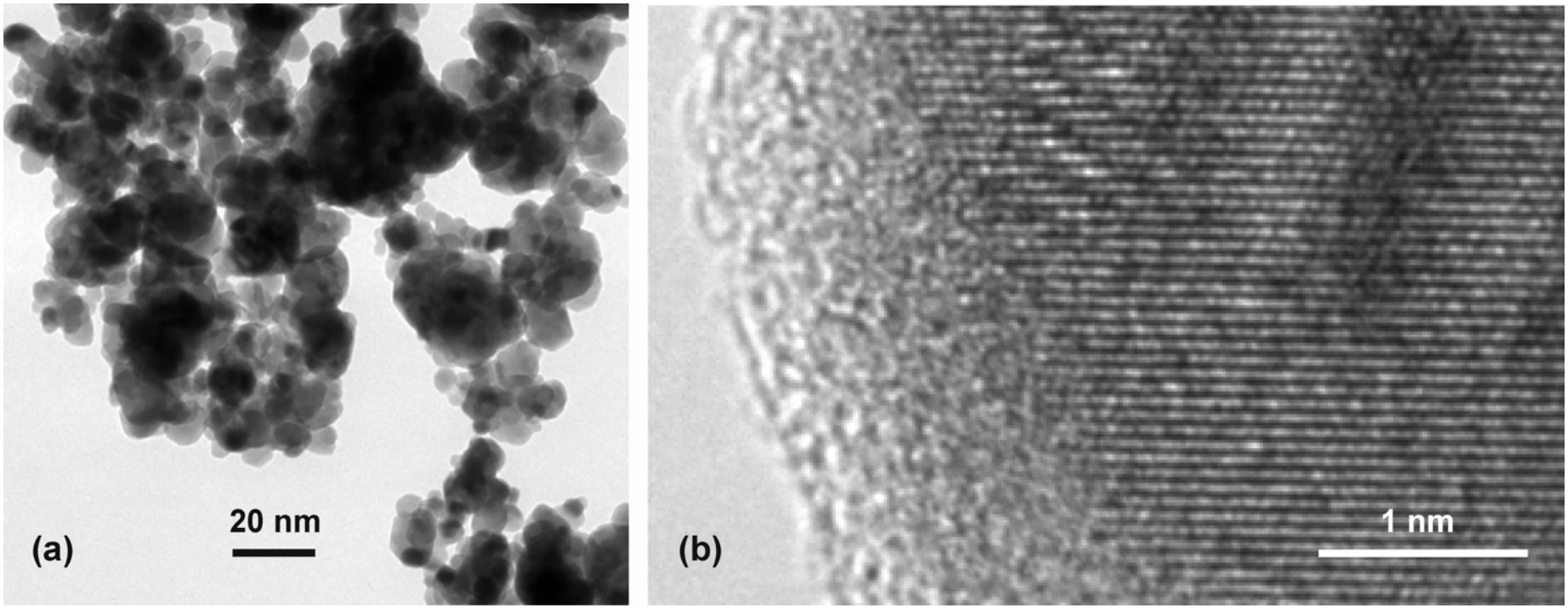
V. Šepelák et al., *Chem. Mater.* **18** (2006) 3057.

Reduced magnetization in nanocrystalline $NiFe_2O_4$

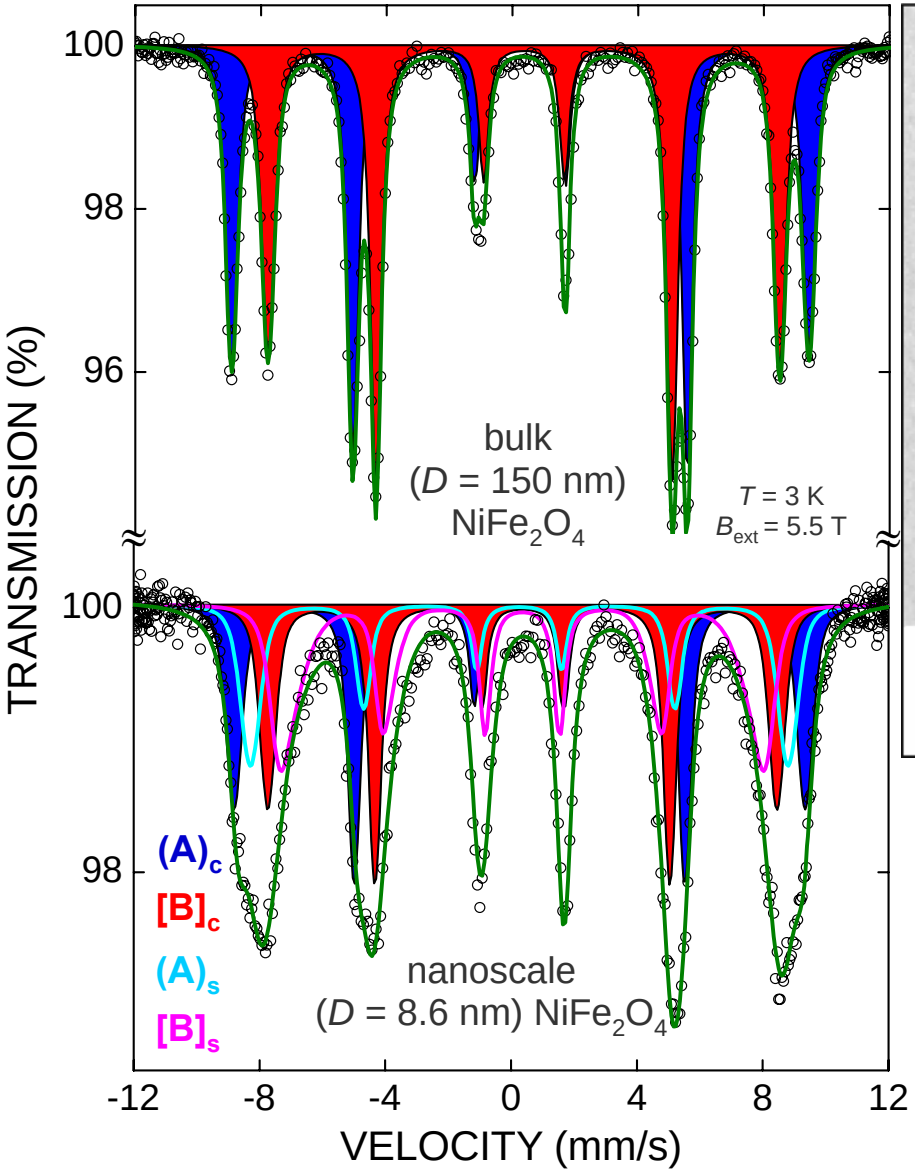


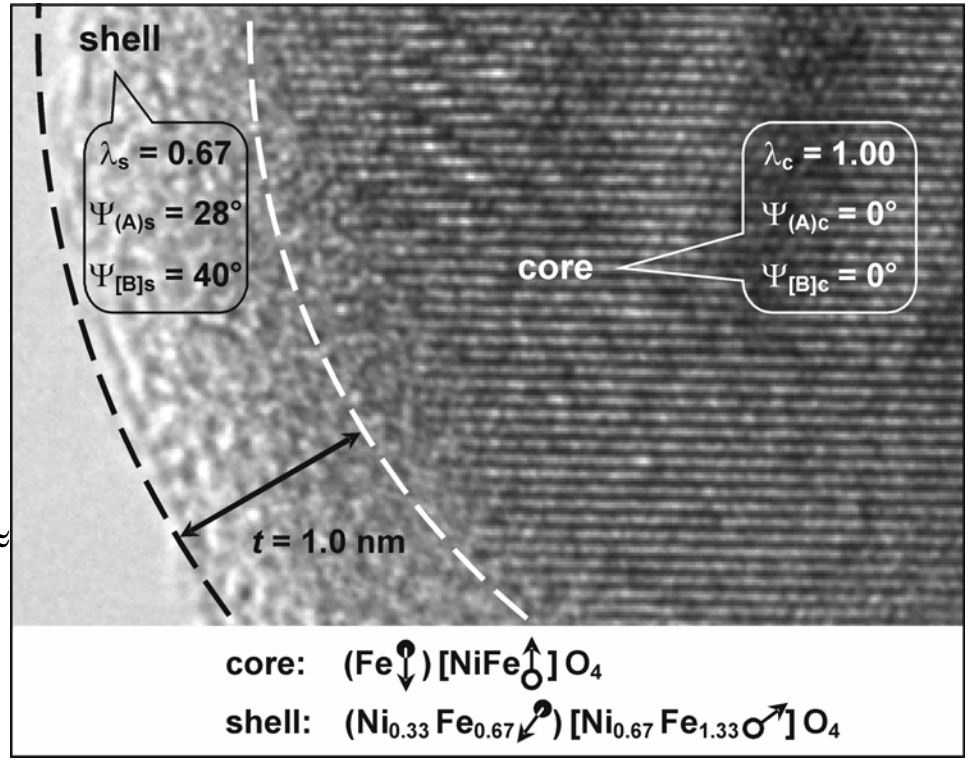
V. Šepelák et al., *J. Phys. Chem. C* **111** (2007) 5026.

The nonuniform core–shell structure of nanocrystalline $NiFe_2O_4$



The nonuniform core–shell structure of nanocrystalline $NiFe_2O_4$





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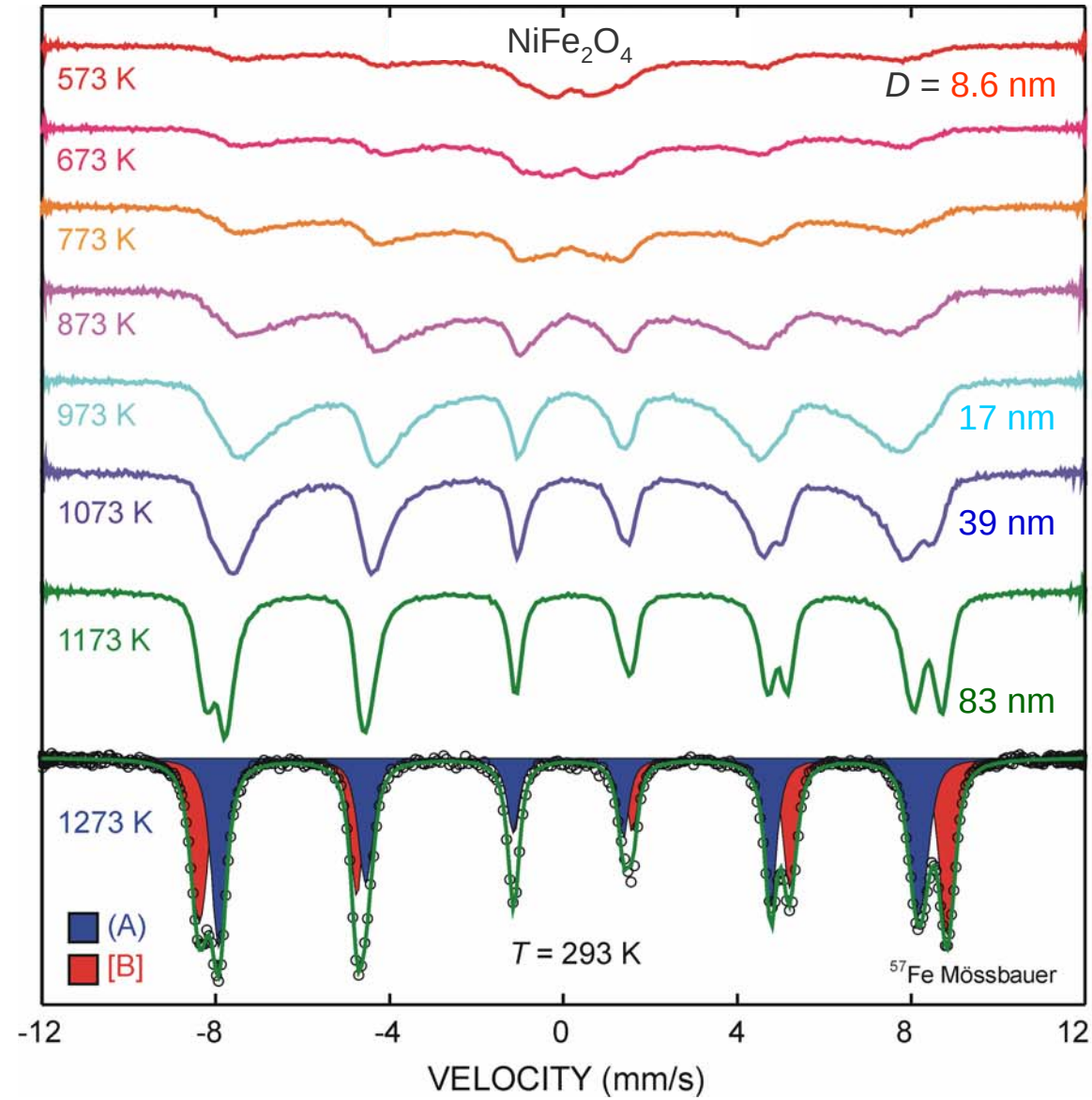
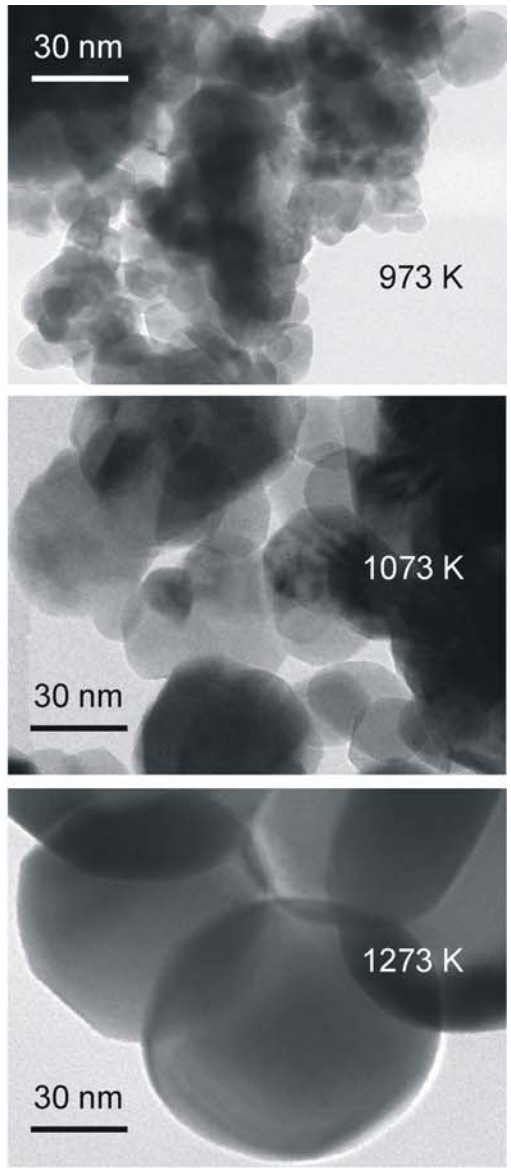
⇒ ***w*** **~ 50%, *t*** **~ 1.0 nm**

V. Šepelák et al., *J. Phys. Chem. C* **111** (2007) 5026.

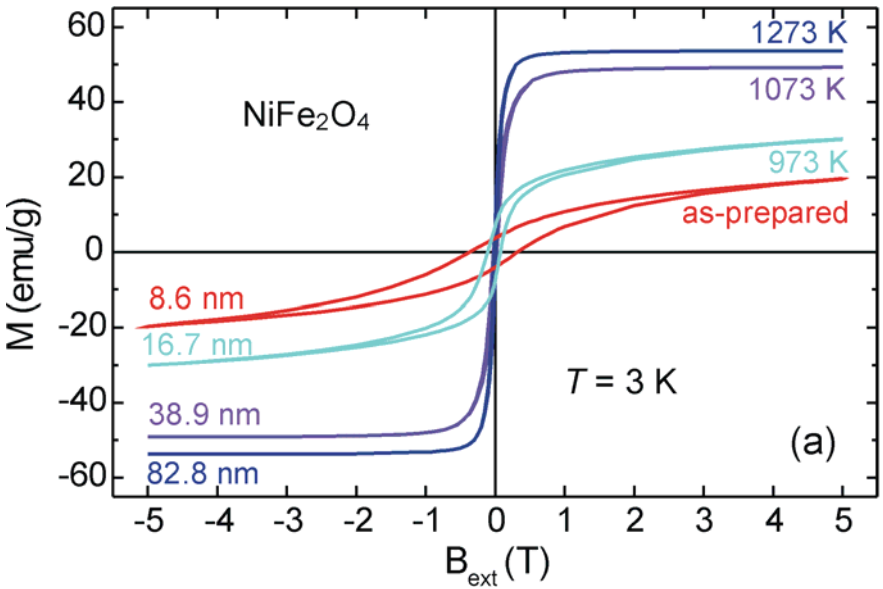
From **Superparamagnetism** to **Ferrimagnetism**

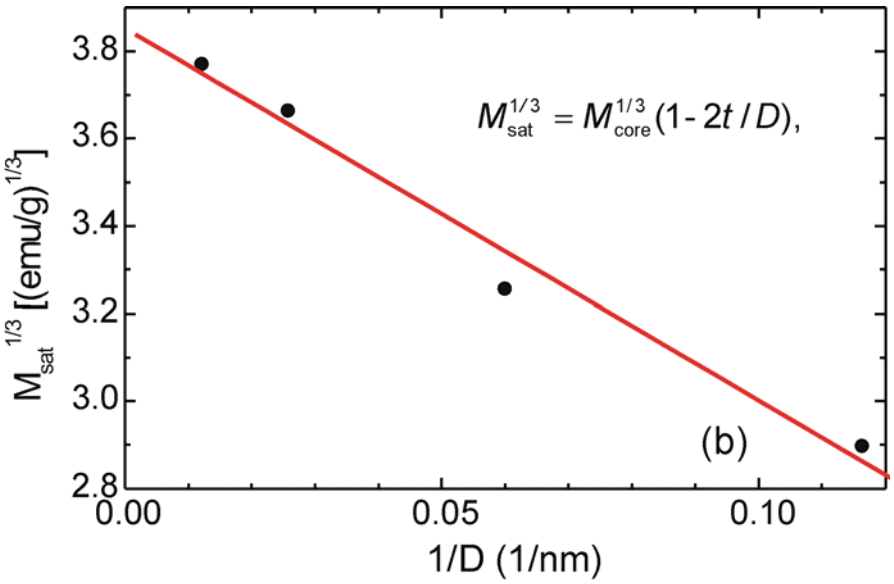




V. Šepelák et al., *J. Therm. Anal. Calorim.* **90** (2007) 93.

Nanoscale $NiFe_2O_4$ particles with **"magnetically dead"** surface shell





spin canting tends to reduce the magnetization

⇕

Nonequilibrium cation distribution causes increase of the magnetization

⇓

M_{core} = 57.2 emu/g, t = 1.1 nm

Features of canted magnetic structures: • Reduced or enhanced nonsaturating magnetization • Reduced or enhanced Néel temperature • Enhanced coercivity • Shift of the hysteresis loop • Magnetization irreversibility

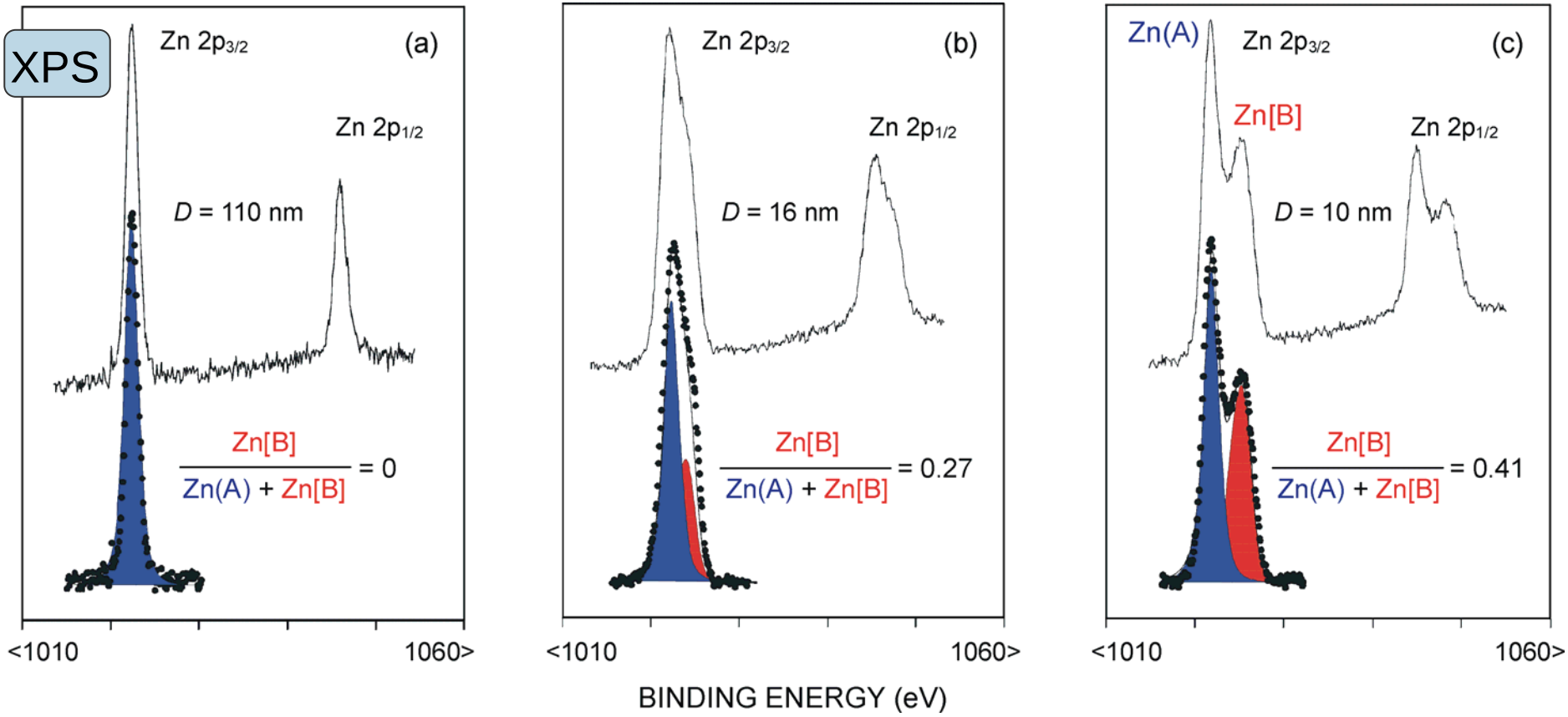
V. Šepelák et al., *J. Phys. Chem. C* **111** (2007) 5026.

Surface structural disorder in nanostructured $ZnFe_2O_4$ spinel

(A) [B] $\lambda = 0$ $\lambda = 0.27$ $\lambda = 0.41$

$(Zn)[Fe_2]O_4 \rightarrow (Zn_{0.73}Fe_{0.27})[Zn_{0.27}Fe_{1.73}]O_4 \rightarrow (Zn_{0.59}Fe_{0.41})[Zn_{0.41}Fe_{1.59}]O_4$

D = 110 nm *D* = 16 nm *D* = 10 nm

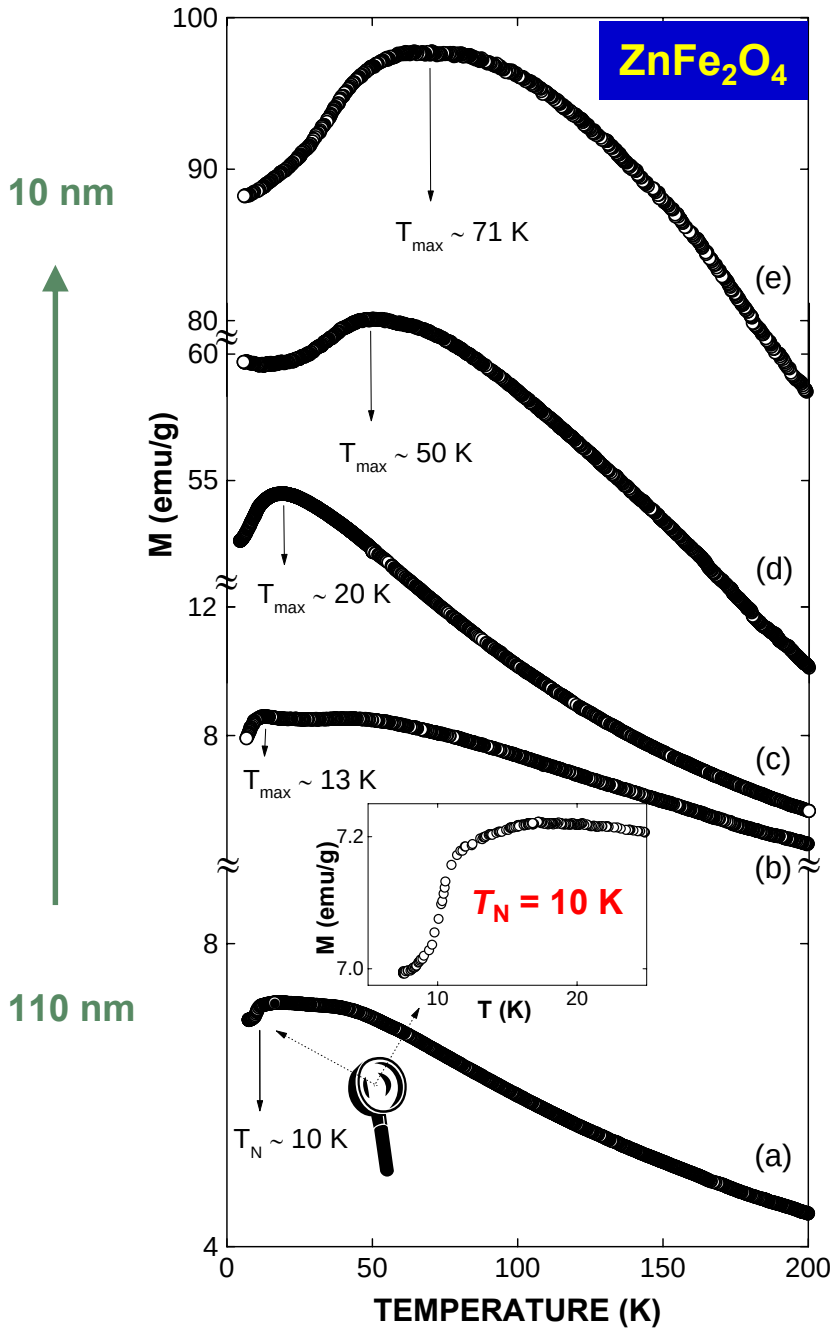


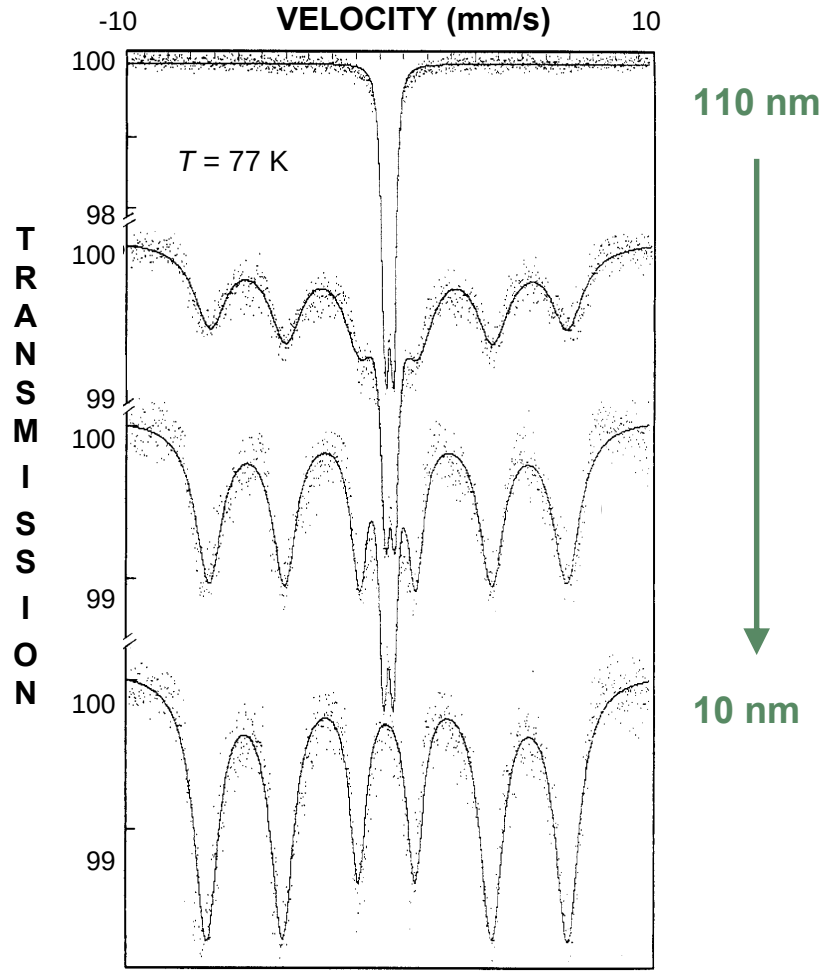
Information depth of the XPS measurements: ~ 6 nm. Conclusions made on the basis of ZnO and Zn_2TiO_4 - the well-known tetrahedrally and octahedrally coordinated zinc compounds, respectively.

V. Šepelák et al., *J. Alloy. Compd.* **434–435** (2007) 776.

Enhanced magnetization and Néel temperature in nanocrystalline spinel ferrite

Enhanced magnetic ordering temperature; T_N ~ 210 K



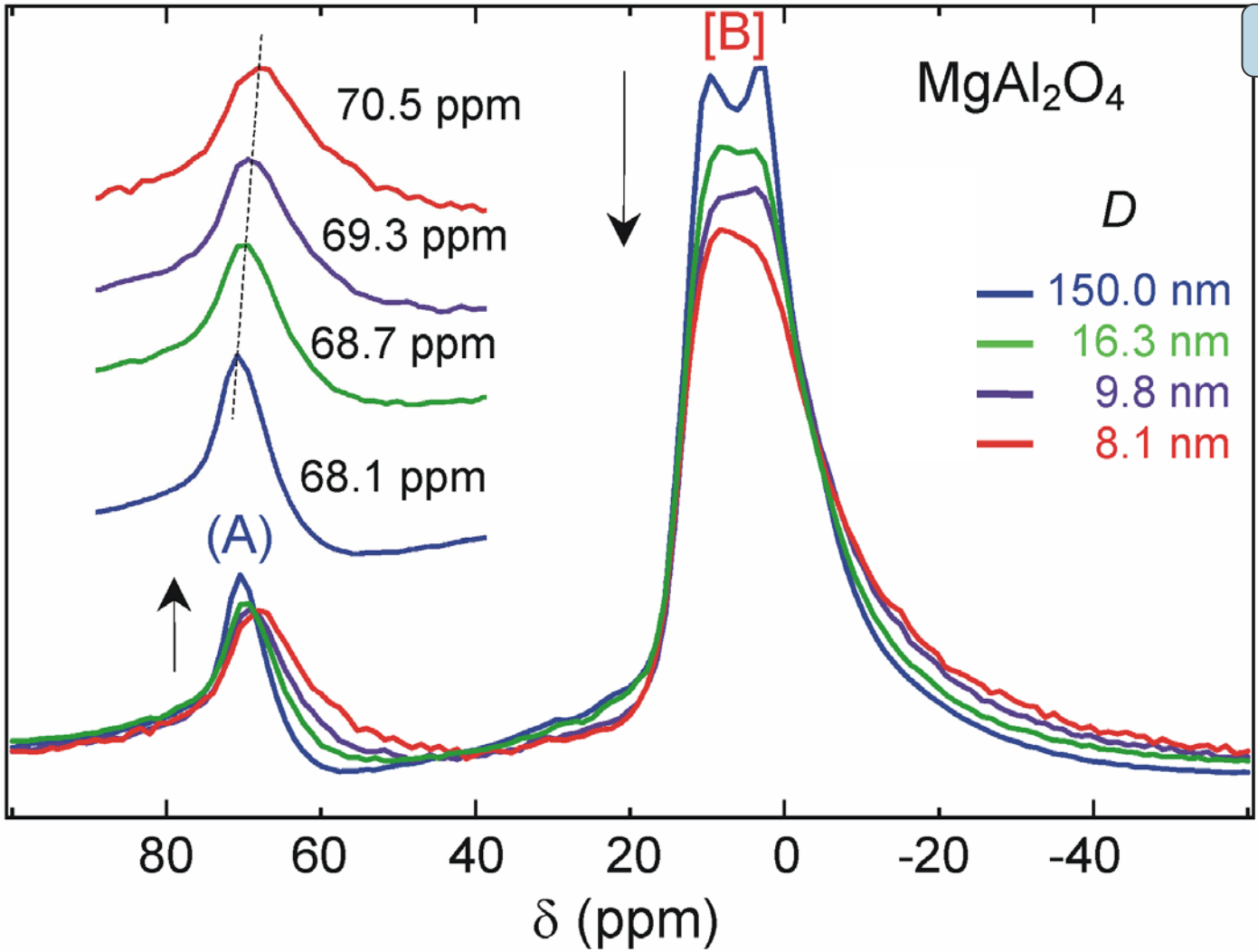


V. Šepelák et al., *Physica B* **234–236** (1997) 617.

Size dependent cation disorder in nanoscale $MgAl_2O_4$ spinel

$\lambda = 0.23$ $\lambda = 0.31$

$$(Mg_{0.77}Al_{0.23})[Mg_{0.23}Al_{1.77}]O_4 \longrightarrow (Mg_{0.69}Al_{0.31})[Mg_{0.31}Al_{1.69}]O_4$$



$$\frac{I_{(A)}}{I_{[B]}} = \frac{\lambda}{2 - \lambda}$$

V. Šepelák et al., *Solid State Ionics* **177** (2006) 2487.

Volume fraction (w) and thickness (t) of interfaces/surfaces in nanocrystalline $MgAl_2O_4$ spinel

$\lambda = 0.23$ $\lambda = 0.31$

$$(Mg_{0.77}Al_{0.23})[Mg_{0.23}Al_{1.77}]O_4 \longrightarrow (Mg_{0.69}Al_{0.31})[Mg_{0.31}Al_{1.69}]O_4$$

$$\lambda = (1 - w)\lambda_c + w\lambda_s$$

	D (nm)	λ	w (%)	t (nm)
Spinel $MgAl_2O_4$	150.0	**0.23**	0	0
	16.3	**0.27**	9.2	0.3
	9.8	**0.30**	16.0	0.3
	8.1	**0.31**	18.3	0.3

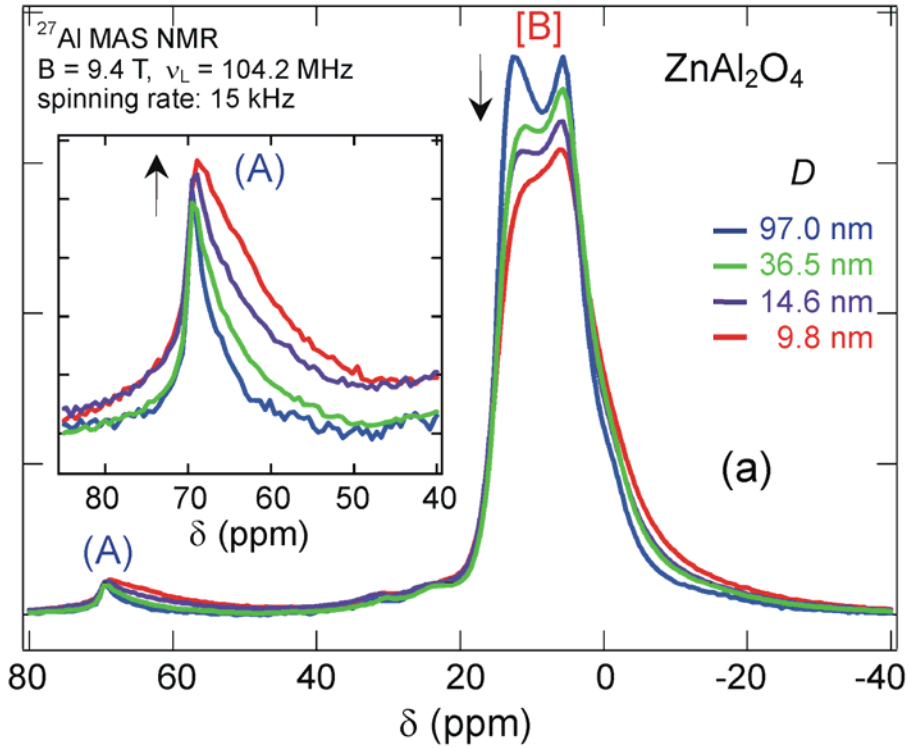
$\lambda = 2I_{(A)}/(I_{(A)}+I_{[B]})$.

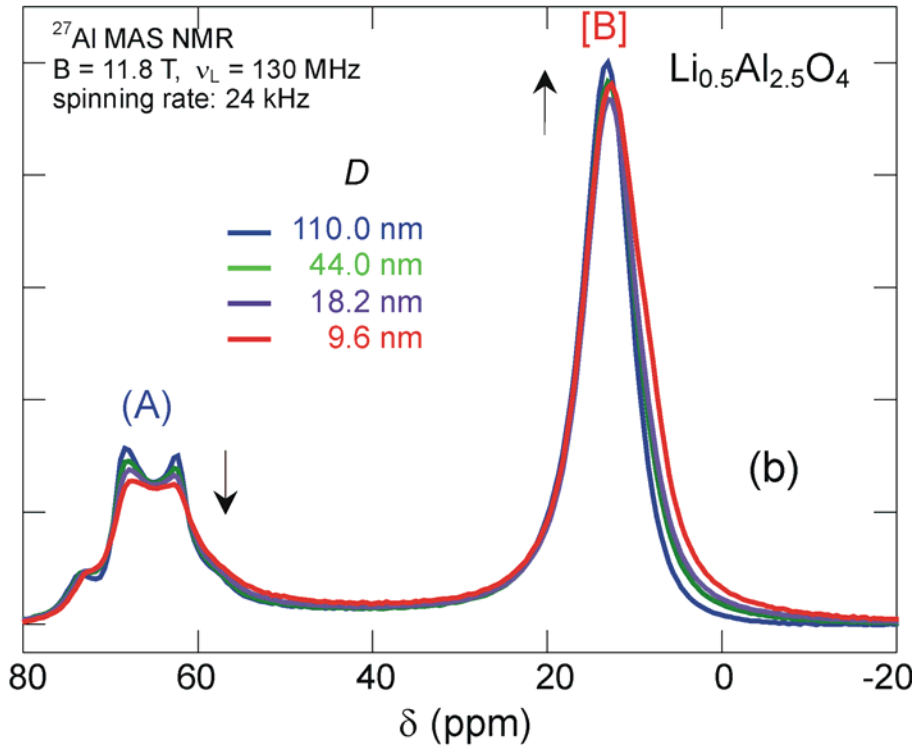
$w = 100[(\lambda-\lambda_c)/(\lambda_s-\lambda_c)]$, where $\lambda_c = 0.23$ and $\lambda_s = 2/3$.

$t = D/2-[(D/2)^3(100-w)/100]^{1/3}$.

V. Šepelák et al., *Current Advances in Materials and Processes* **20** (2007) 1310.

Cation disorder in nanosized $ZnAl_2O_4$ and $Li_{0.5}Al_{2.5}O_4$ spinels





$\lambda = 0.02$

Bulk: $(Zn_{0.98}\,Al_{0.02})\,[Zn_{0.02}\,Al_{1.98}]O_4$

Nano: $(Zn_{0.88}\,Al_{0.12})\,[Zn_{0.12}\,Al_{1.88}]O_4$

$\lambda = 0.12$

$\lambda = 1.00$

Bulk: $(Al_{1.00})\,[Li_{0.5}\,Al_{1.50}]O_4$

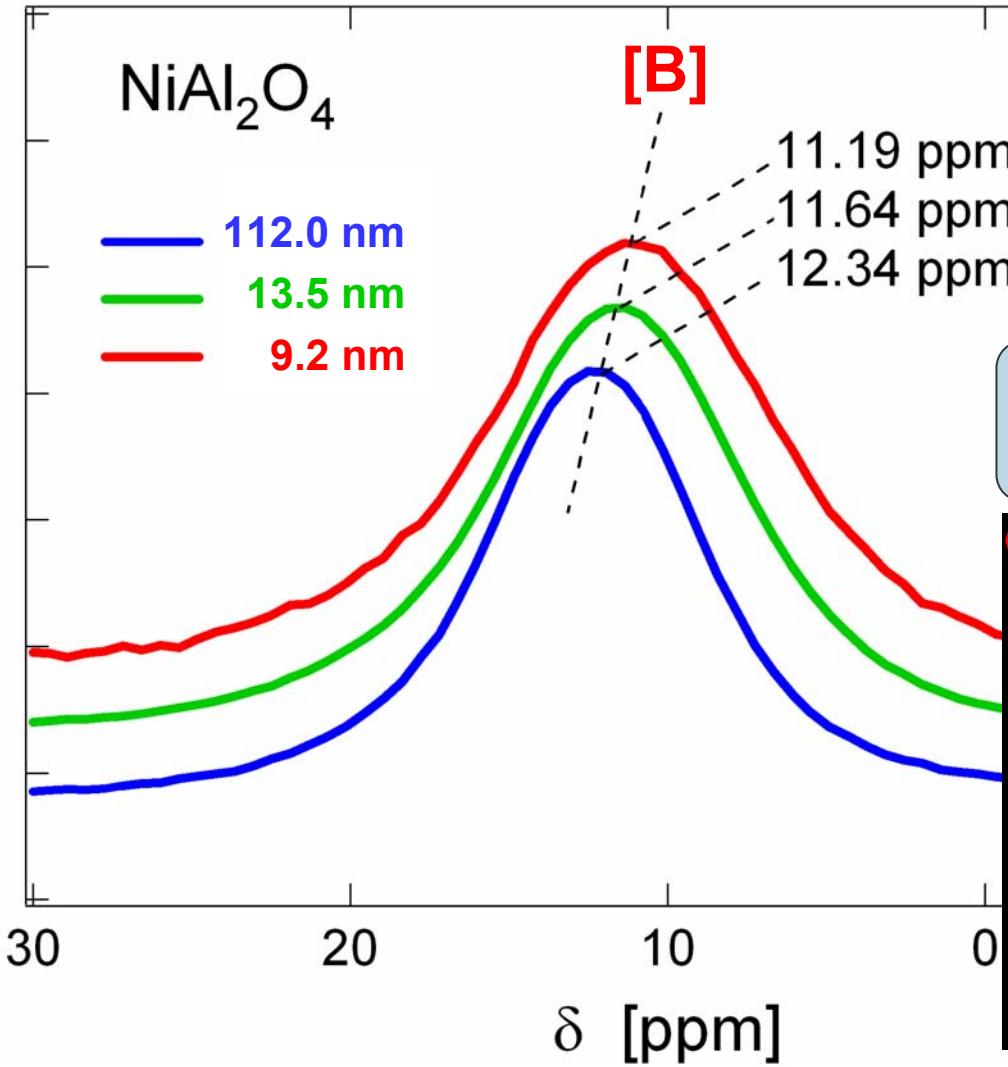
Nano: $(Li_{0.13}\,Al_{0.87})\,[Li_{0.37}\,Al_{1.63}]O_4$

$\lambda = 0.87$

Cation disorder and deformed octahedrons in nanoscale $NiAl_2O_4$ spinel

$\lambda = 0.90$ $\lambda = 0.75$

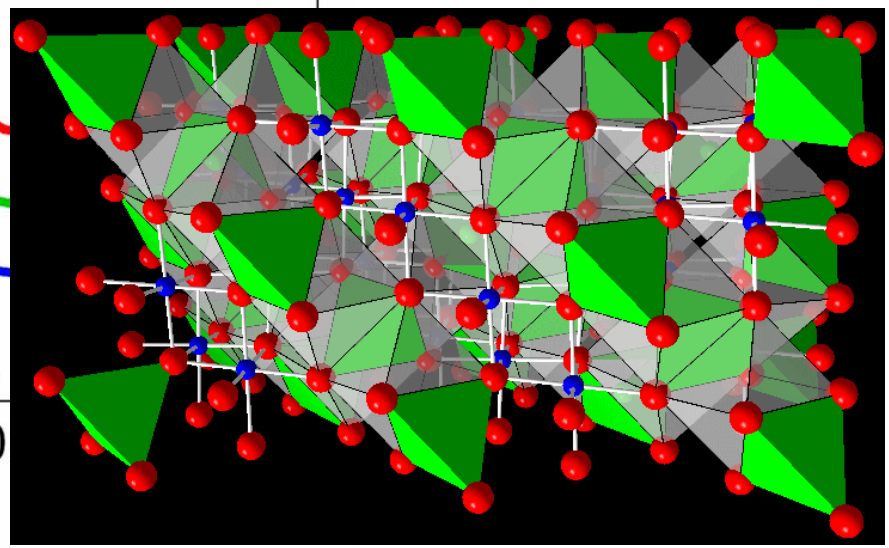
$(Ni_{0.10}\,Al_{0.90})\,[Ni_{0.90}\,Al_{1.10}]O_4 \longrightarrow (Ni_{0.25}\,Al_{0.75})\,[Ni_{0.75}\,Al_{1.25}]O_4$



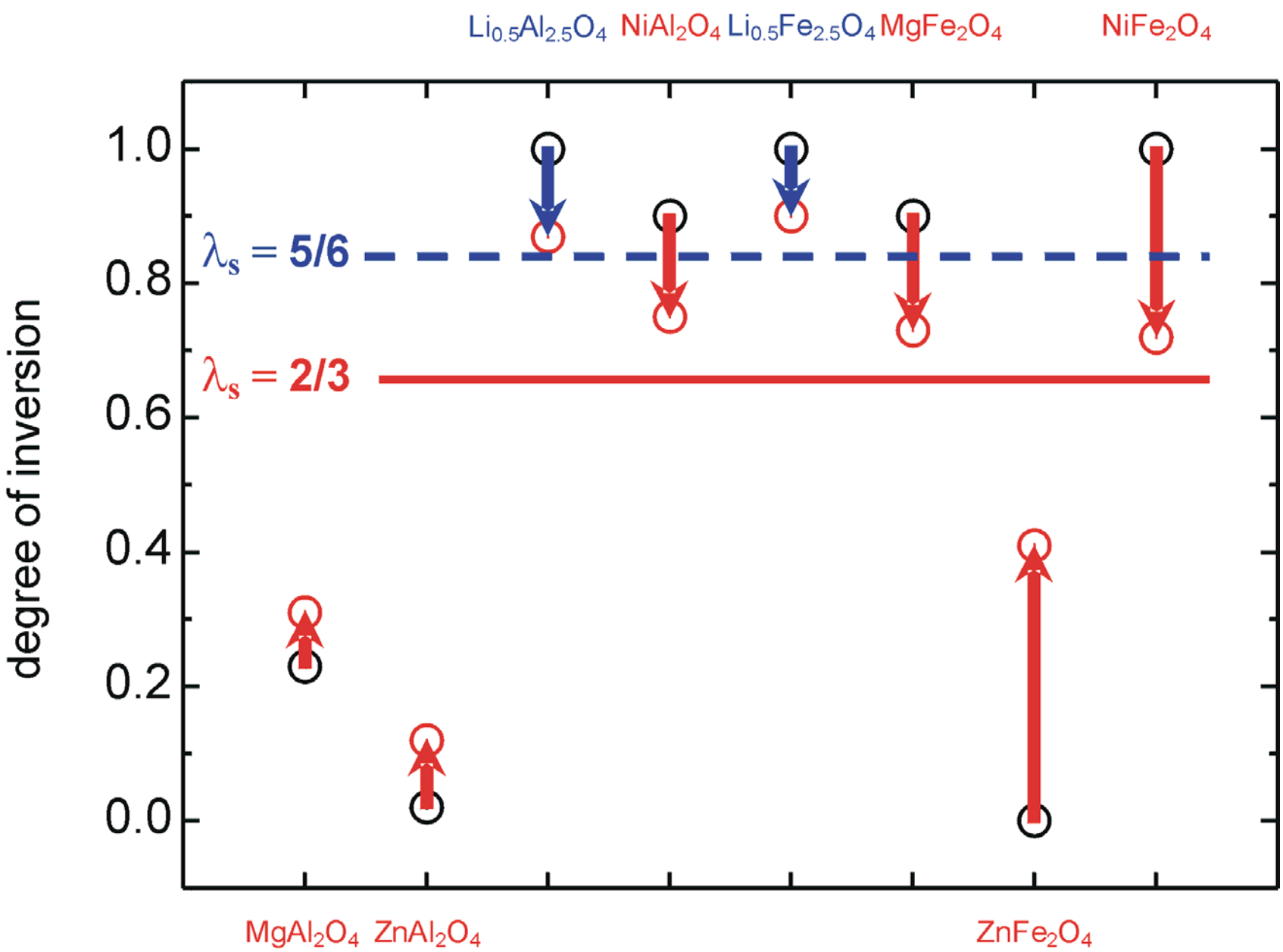
^{27}Al MAS NMR

$\angle$ [B] - O^{2-} - [B] $\neq$ 90°

$\angle$ (A) - O^{2-} - [B] $\neq$ 125°



Cation disorder in nanostructured spinels is directed towards random arrangement



Volume fraction (*w*) and thickness (*t*) of interfaces/surfaces in nanoscale spinel aluminates and ferrites

$$\lambda = (1 - w)\lambda_c + w\lambda_s$$

Spinel	***D*** (nm)	λ	λ_c	λ_s	***w*** (%)	***t*** (nm)
$MgAl_2O_4$	8.1	0.31	0.23	2/3	18.3	0.3
$ZnAl_2O_4$	9.8	0.12	0.02	2/3	15.5	0.3
$Li_{0.5}Al_{2.5}O_4$	9.6	0.87	1.00	5/6	78.0	1.9
$NiAl_2O_4$	9.2	0.75	0.90	2/3	64.3	1.3
$Li_{0.5}Fe_{2.5}O_4$	8.0	0.90	1.00	5/6	60.0	1.1
$MgFe_2O_4$	9.7	0.73	0.90	2/3	72.8	1.4
$ZnFe_2O_4$	10.0	0.41	0.00	2/3	61.5	1.4
$NiFe_2O_4$	8.7	0.72	1.00	2/3	84.0	2.0

$\lambda = 2I_{(A)}/(I_{(A)}+I_{[B]})$ *for 2-3 spinels*; $\lambda = 2.5I_{(A)}/(I_{(A)}+I_{[B]})$ *for 1-3 spinels*.

$w = 100[(\lambda-\lambda_c)/(\lambda_s-\lambda_c)]$.

$t = D/2-[(D/2)^3(100-w)/100]^{1/3}$.

Conclusions

♣ Nanocrystalline complex oxides possess a nonuniform structure consisting of the **ordered nanosized crystallites** surrounded by the **disordered interface/surface regions** (*w* and *t* extend up to about 80% and 2 nm, respectively)

♣ The main structural features of the disordered interface/surface regions in nanooxides are **nonequilibrium cation distribution** and **noncollinear spin arrangement**

♣ Independently of the ionic configuration in the bulk spinel oxides, their particle size reduction leads to the cation redistribution that is directed towards the **random arrangement** (λ = 2/3 (5/6))

♣ The cation order-disorder process is accompanied by the short-range disordering phenomena (e.g., **deformation of polyhedron geometries**)

♣ Nanocrystalline oxides exhibit **unusual properties** (markedly different from those of their bulk counterparts) determined to a large extent by the structure of their interfaces/surfaces

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