Diffusion in Nanocrystalline Solids

Alan Chadwick
Functional Materials Group
School of Physical Sciences
University of Kent
Canterbury
Kent CT2 7NH, UK

PLAN of the TALK

1. **INTRODUCTION TO NANOCRYSTALLINE SOLIDS**

   What is the reason for interest? Unusual properties. Nanotechnology.

2. **PREPARATION OF SAMPLES**

   How are nanocrystals made? Are samples dependent on the method?

3. **CHARACTERISATION OF SAMPLES**

   How is the size measured? How is the size controlled?

4. **DIFFUSION EXPERIMENTS**

   Techniques. Special problems with nanomaterials.

5. **OVERVIEW OF THE DATA**

   What data are available for nanocrystals

6. **CONCLUSIONS AND VIEW TO THE FUTURE**

ORIGINS

H. Gleiter, Prog. Mater. Sci., 33 (1989) 223.

H. Gleiter, Adv. Mater., 1992, 4, (1992) 474.

H. Gleiter, Acta mater., 48 (2000) 1.

FB Physik,
Gebaude 43,
Universität des Saarlandes,
66041 Saarbrücken, Germany

Institute of Nanotechnology,
Research Center Karlsruhe,
P.O. Box 3640, D-76021, Karlsruhe, Germany

Definition

"A nanostructured (or nanophase) material is one in which one or more dimensions is in the nanometre regime."

Typically <100 nm, more usually <10 nm.

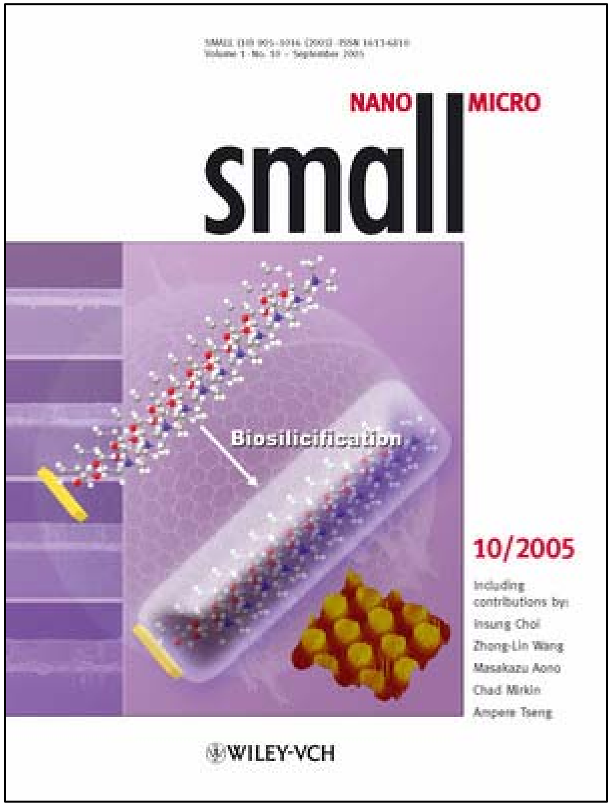
Now of interest to chemists, physicists, materials scientists and biologists.

Quotes

The development of the applications of these materials, *nanotechnology*, features in the forward science planning of most developed countries (e.g. in Foresight plans of the UK, Japan and US) and the US government regards it as *"the next industrial revolution"*.

'Nanocrystals are *terra incognito'* – Joachim Maier

EXAMPLES OF JOURNALS



NANO MICRO

small

Biosilicification

10/2005

Including contributions by:
Insung Choi
Zhong-Lin Wang
Masakazu Aono
Chad Mirkin
Ampere Tseng

WILEY-VCH

Virtual Journal of

Nanoscale Science & Technology

a weekly multijournal compilation of the latest research on nanoscale systems

POSTERS

40 Modelling of Diffusion-Controlled Pattern Formation in Thin Metallic Film Growth on Crystalline Substrates
V. Kuzovkov, E. Kotomin, G. Zvejnieks

41 Calculation of the Effective Diffusion Coefficient for Heterogeneous Media
J.R. Kalnin, E.A. Kotomin, J. Maier, V.N. Kuzovkov

55 Computer Simulation of the Formation of Hollow Nanocrystals
I. V. Belova, G. E. Murch

58 Surface Diffusion and Growth of Alloy Nanoclusters: A Monte Carlo Study S. Heinrichs, M. Einax, W. Dieterich, P. Maass, A. Majhofer

59 Numerical Study of Grain Boundary Diffusion: Size Effects
D. Gryaznov, J. Fleig, J. Maier

63 Diffusion of Nano-Sized Liquid Pb Inclusions in Thin Aluminum Foils
S. Prokofjev, V. Zhilin, E. Johnson, U. Dahmen

67 Enhanced Ionic Conductivity in Heavily Doped Ceria Nanoceramics M. G. Bellino, D. G. Lamas, N. E. Walsöe de Reca

103 Lattice and Grain Boundary Diffusion of Cations in Tetragonal Zirconia
S. Swaroop, M. Kilo, Ch. Argirusis, G. Borchardt, A. H. Chokshi

MATERIALS

1. METALS
2. SEMICONDUCTORS
3. IONIC CRYSTALS
4. POLYMERS
5. BIOLOGICAL SAMPLES

Applications For Nanocrystalline Oxides

As electrolytes

Battery electrolytes

Solid oxide fuel cells (SOFC)

Sensors

As electrodes

Batteries

Photovoltaic devices

As catalysts

Heterogeneous reactions

Absorbers

La Sapienza
Università degli Studi di Roma

KENT
UNIVERSITY OF KENT

School of Chemistry
University of St Andrews

'UNUSUAL PHYSICS AND CHEMISTRY'

1. *DOMAIN SIZE* AT LESS THAN 100nm VARIOUS PROPERTIES OF THE GRAIN ARE AFFECTED. SIZE IS LESS THAN CRITICAL LENGTH FOR MANY PROPERTIES TO BE APPARENT. AN EXAMPLE IS SUPERHARDNESS - THE GRAINS ARE TOO SMALL FOR A FRANK-READ DISLOCATION SOURCE TO BE OPERATIVE. ANOTHER EXAMPLE IS COLOUR.

2. *GRAIN BOUNDARIES* THE SAMPLES ARE RIDDLED WITH GRAIN BOUNDARIES. THUS THERE IS SUPERPLASTICITY AS A COMPRESSED MATERIAL WILL EASILY FLOW AS THE GRAINS SLIDE PAST EACH OTHER. THE FAST GRAIN BOUNDARY DIFFUSION WILL ALLOW QUICK ANNEALING.

3. *HIGH SURFACE AREA* THUS THERE IS ENHANCED CATALYTIC ACTIVITY. NOT SIMPLY AREA BUT DIFFERENT MORPHOLOGY.

4. *UNUSUAL COMPOSITIONS* COMPOSITIONS ARE OFTEN DIFFERENT FROM BULK MATERIALS AS IMPURITIES CAN BE INCORPORATED IN BOUNDARIES.

EARLY EXPERIMENTAL FINDINGS

A. BROAD LINE XRPD

B. REDUCED DEBYE TEMPERATURE

C. ENHANCED SPECIFIC HEAT

D. ENHANCED SOLUTE SOLUBILITY

E. INCREASED THERMAL EXPANSION

F. ENHANCED DIFFUSION

G. CHANGE IN POSITRON LIFETIME

H. MD STUDIES INDICATE A WIDE DISTRIBUTION OF INTERATOMIC SPACINGS IN GRAIN BOUNDARIES

I. REDUCED AMPLITUDE IN EXAFS OSCILLATIONS

COMPARISON OF PROPERTIES

PROPERTY	BULK	GLASS	NANO	SYSTEM
DIFFUSION				
D/m^2s^{-1} at 300K	10^{-39}		10^{-19}	$^{67}Cu/Cu$
	10^{-39}	10^{-36}	$2x10^{-19}$	Ag/Cu
SOLUBILITY/%	$<10^{-4}$		4	Bi/Cu
	10^{-3}		10^{-1}	H_2/Pd
DEFORMATION/%	<0.1		>100	TiO_2
MAGNETISATION /emu/g (4K)	220	213	130	Fe
C_p ELECTRONIC (1-100K)/10^5x J/gm/K	1	~1	1.6	Cu
CARRIER DENSITY /electron per atom	1.24	~1.2	0.6	Cu

IMPORTANCE OF DIFFUSION IN NANOMATERIALS

1. MICROELECTRONICS – nanowires/nanocontacts

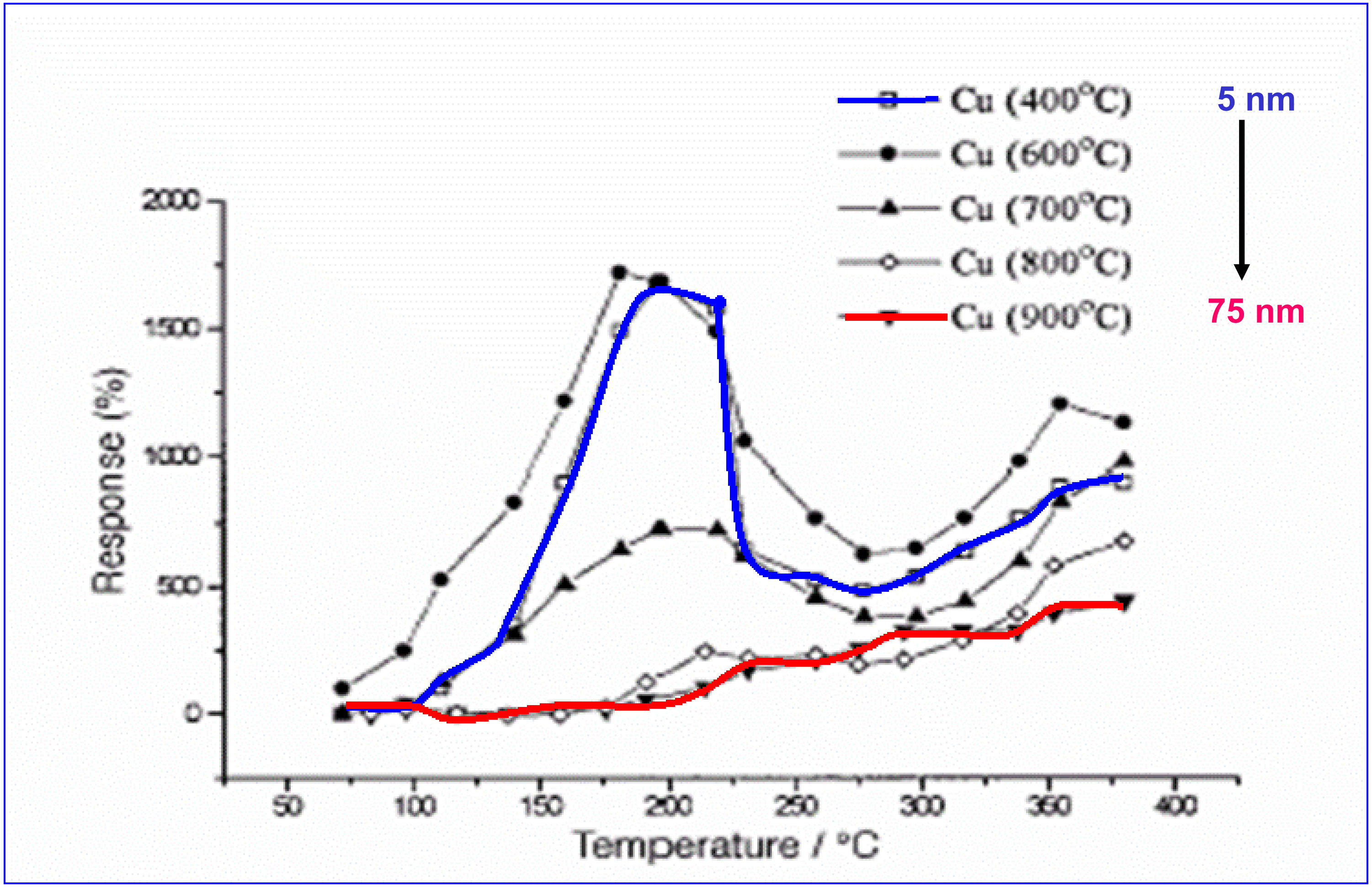
2. CATALYSTS – powder growth/reactant contact

3. CERAMICS – toughness/fatigue

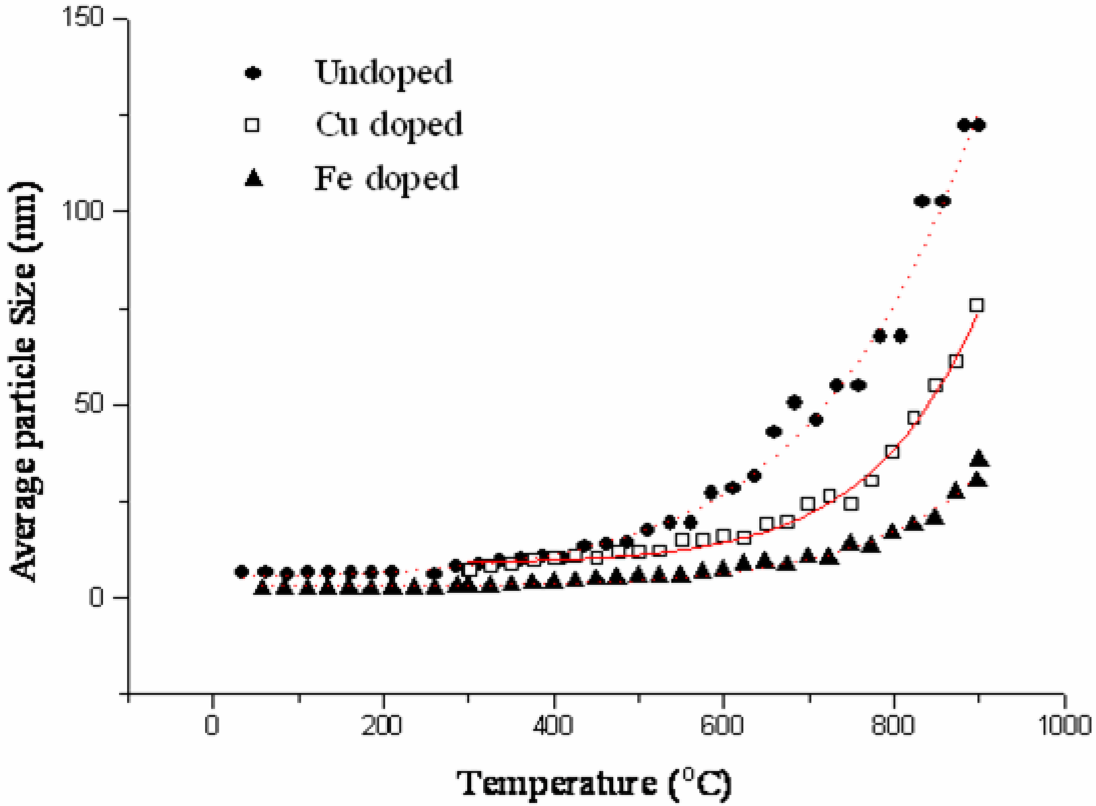
4. SENSORS – aging/hysteresis

5…… Etc,etc,etc

Response of nanocrystalline tin oxide sensor to CO

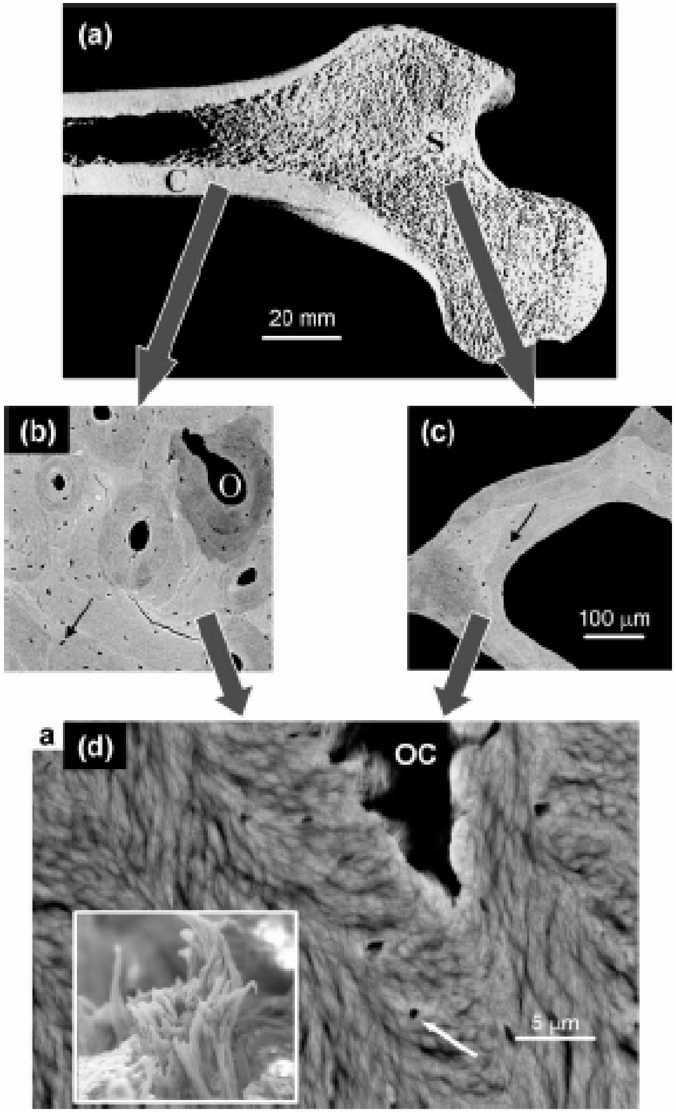


Particle Growth of Tin Oxide



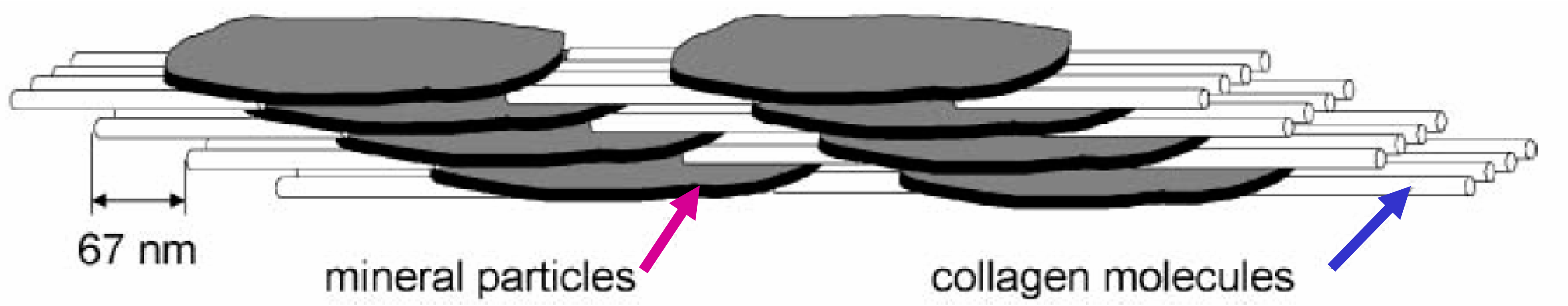
AN EXAMPLE OF DIFFUSION IN NANOCRYSTALLINE

AGE OF ARCHAEOLOGICAL BONES



BONE

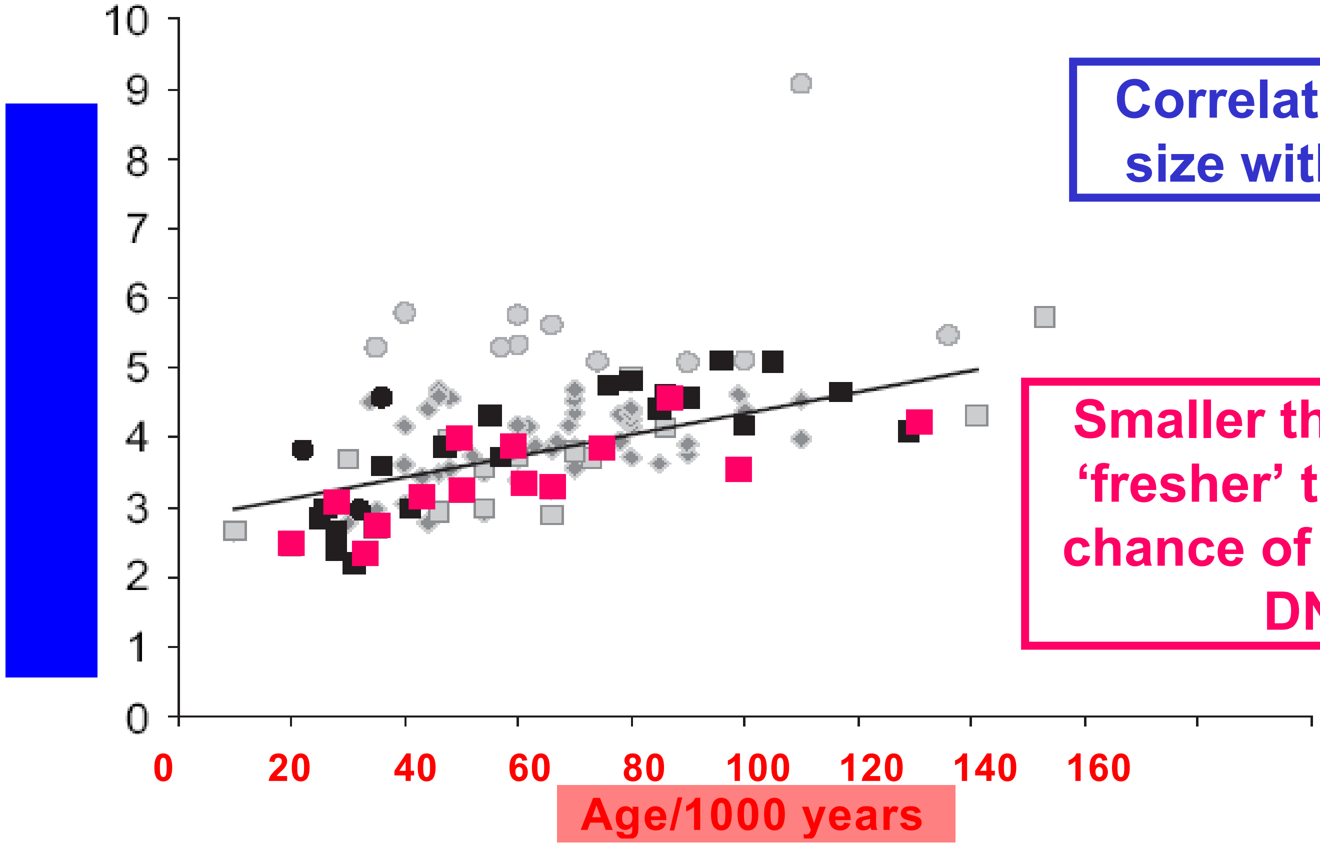
A mineral/organic nanocomposite



calcium hydroxy apatite
2-3 nm thick platelets

biological C/H/O/ polymer chain

Thickness of platelet versus Age
SAXS WAXS data

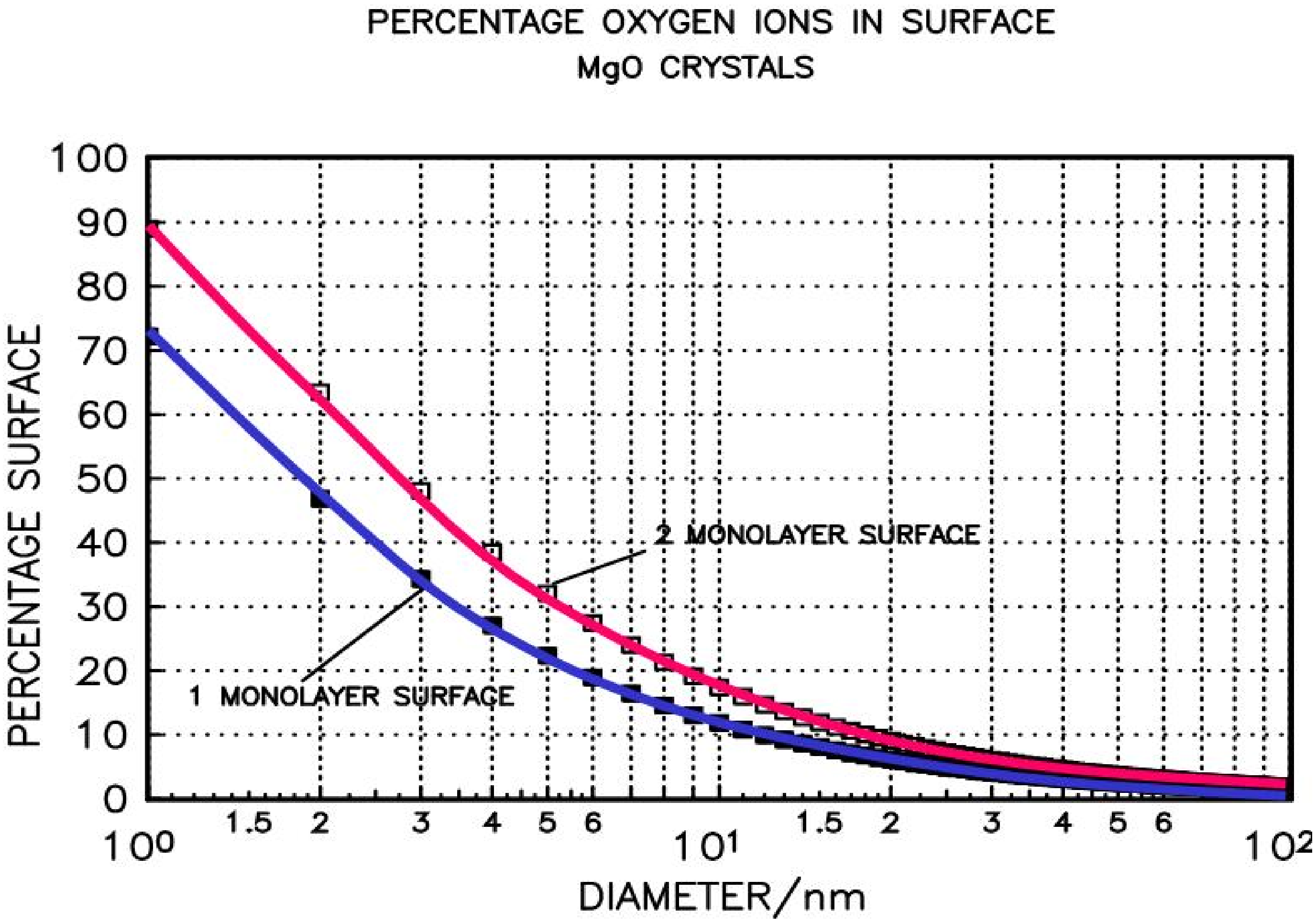


Correlation of size with age

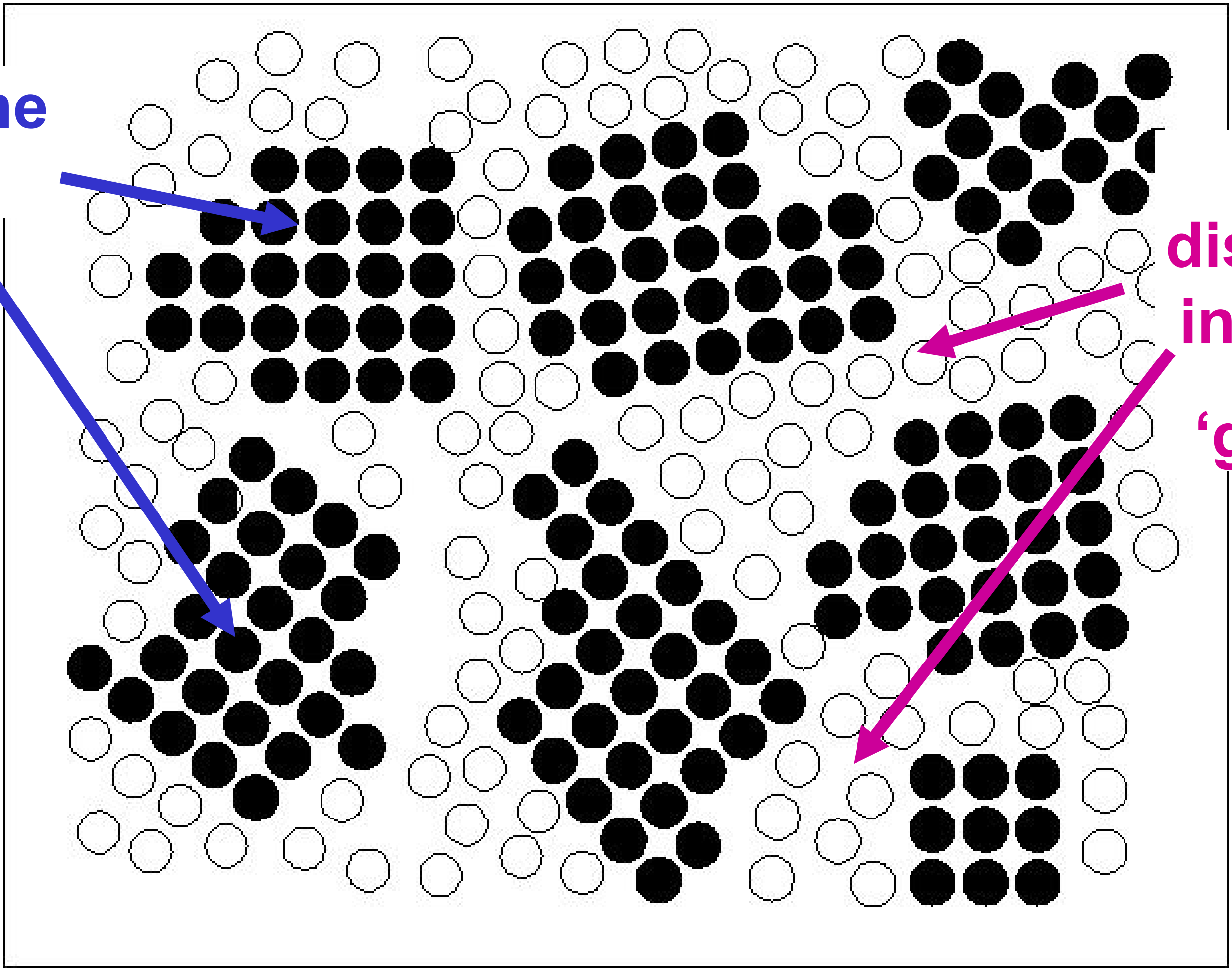
Smaller the size the 'fresher' the bone – chance of extracting DNA

J.C. Hillera, M.J. Collins, A.T. Chamberlain, T.J. Wess; ***Journal of Archaeological Science 31 (2004) 1349***

Percentage Oxygen Ions in the Surface of MgO



Early Picture of Nanocrystals

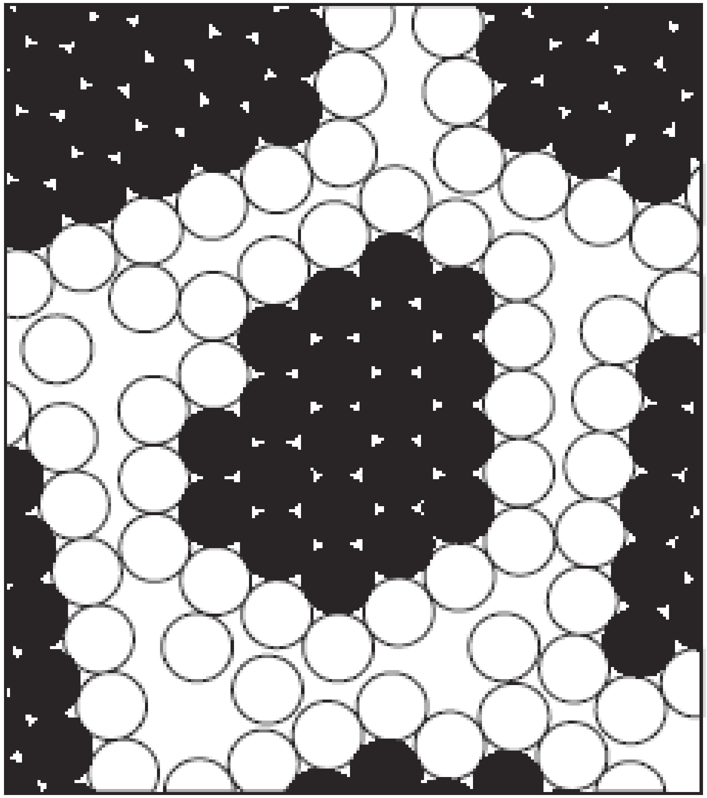


Crystalline grains

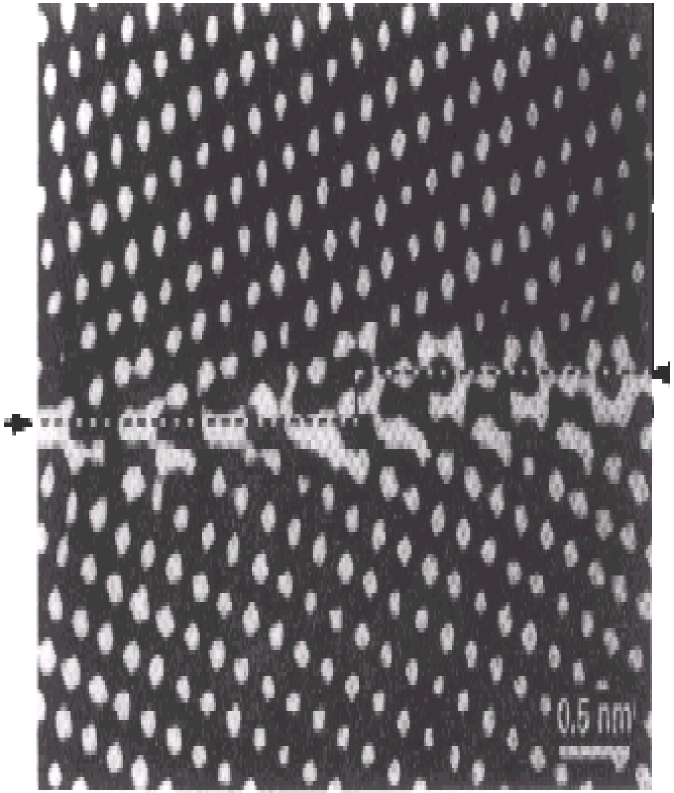
Highly disordered interfaces

‘gas-like’

Two Possible Models for the Interface Between Nanocrystalline Grains



(a) disordered interface



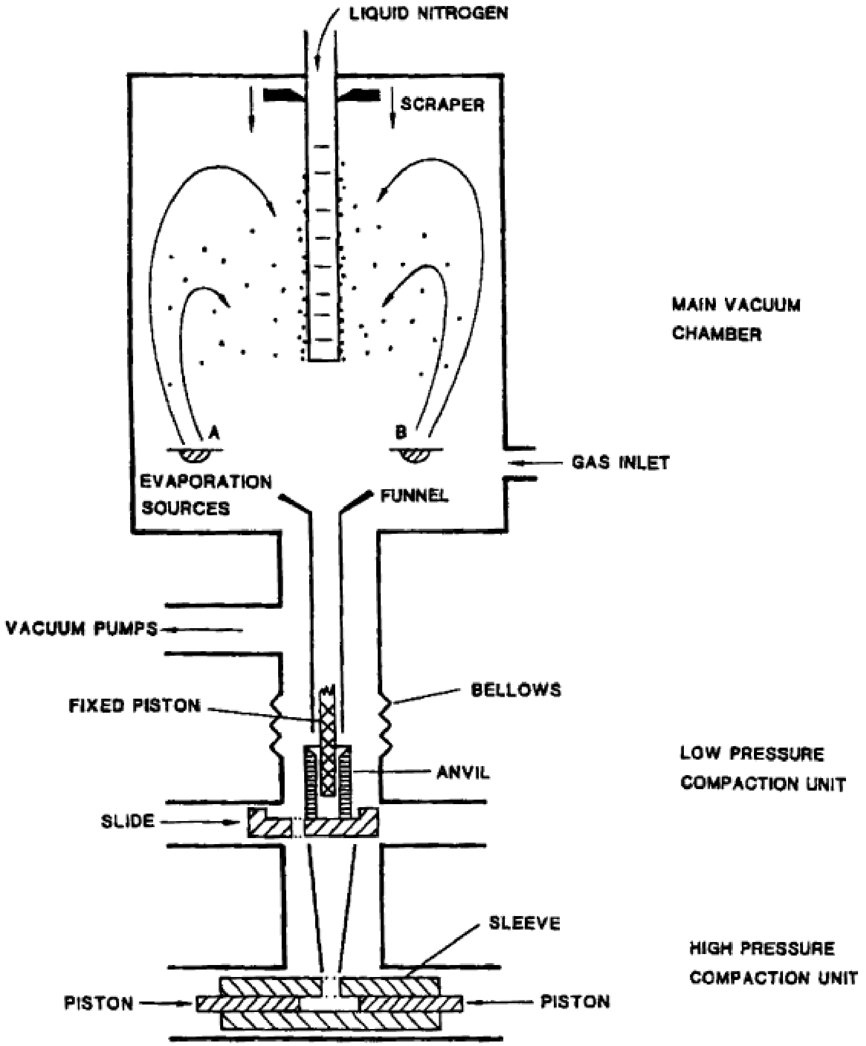
(b) a ‘normal’ grain boundary’

PREPARATION OF SAMPLES

METHODS OF PREPARING NANOCRYSTALS

1. ***Inert gas condensation (IGC) – general/all materials***
2. ***Mechanical attrition – general/all materials***
3. ***Spray pyrolysis – general/mainly inorganics***
4. ***Sol-gel routes – mainly oxides***
5. ***Metal organic vapour deposition – specific materials***
6. ***Sputtering – general/all materials***
7. ***Molecular beam epitaxy (MBE) – general/all materials***

Inert-gas Condensation Facility for Synthesis of Nanocrystalline Particles



Relatively fast

General

Good output

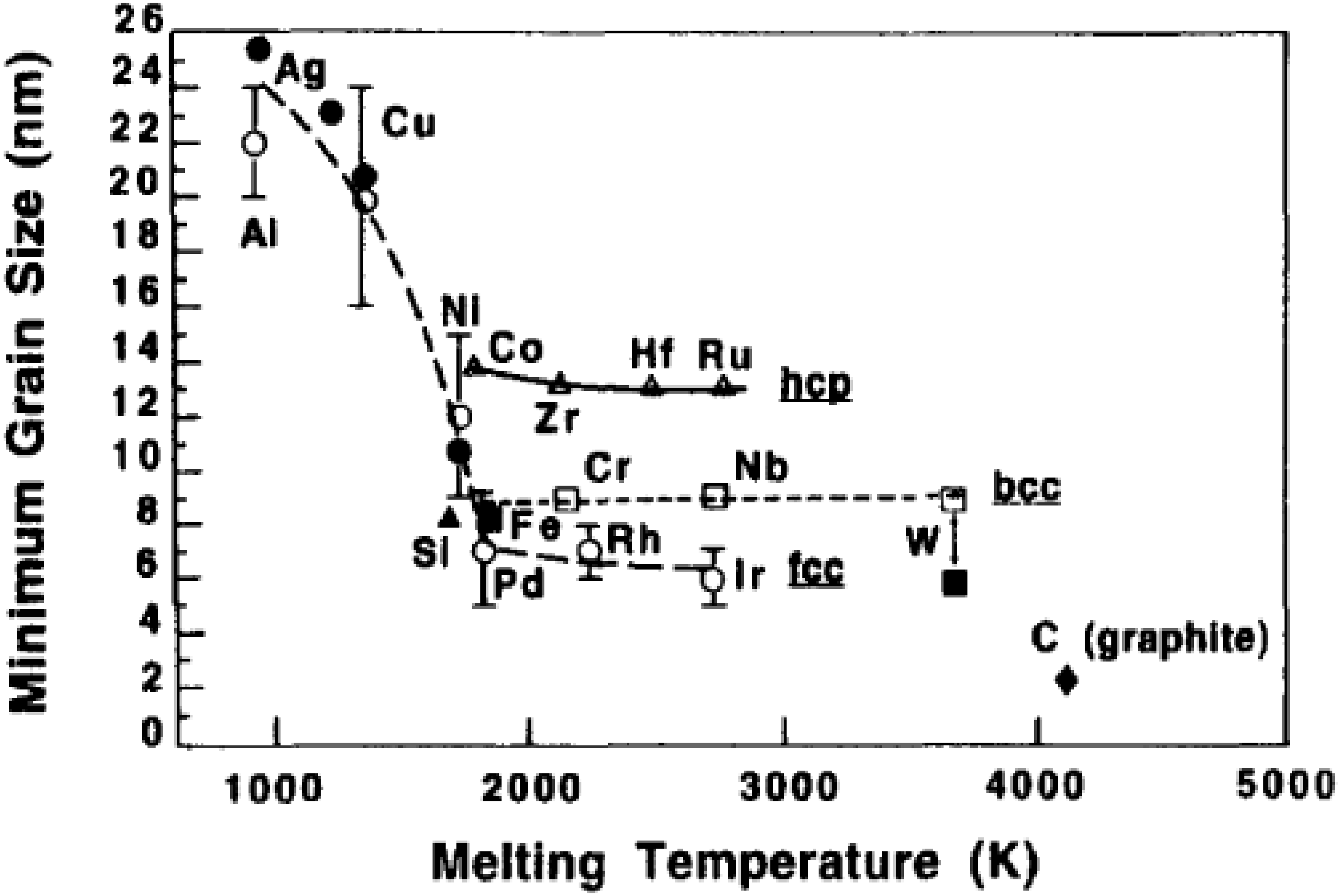
MECHANICAL ATTRITION - HIGH ENERGY BALL MILLING

SPEX

Fast, General, Small quantities

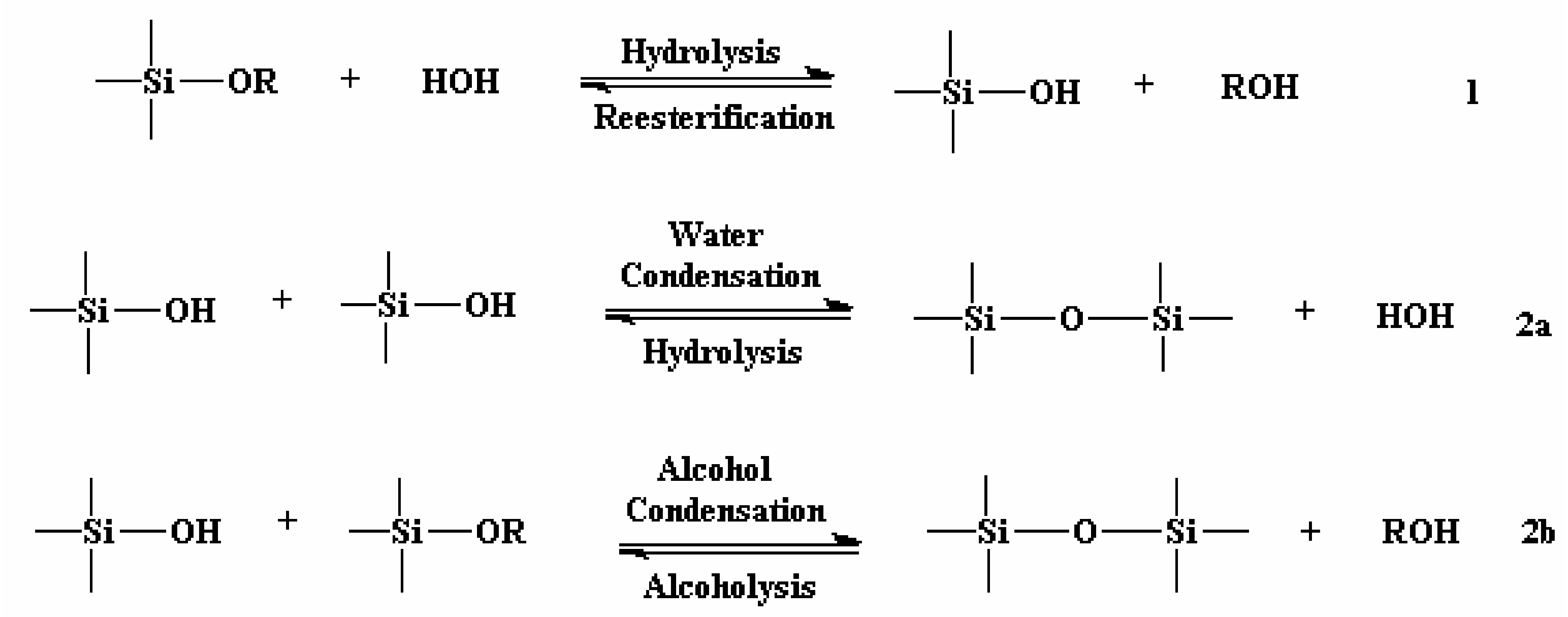
FRITSCH

Variation of Minimum Grain Size With Melting Temperature



SOL-GEL SYNTHESIS

Usually considered for silicon alkoxides



Metal alkoxides can be used and a final calcination step will produce nanoparticle metal oxide

Fast, Good for metal oxides, Small quantities, Expensive

SOL-GEL SYSTEMS

NANOCRYSTALLINE TIN OXIDE

2-3 nm PARTICLES POWDER FROM $SnCl_4.5H_2O$ $+NH_4OH$

NANOCRYSTALLINE ZIRCONIA

’10’ nm PARTICLES POWDER FROM CALCINING $Zr(OH)_4$

5-100nm FILMS ON SAPPHIRE FROM KOSACKI

NANOCRYSTALLINE MAGNESIUM OXIDE

5-10 nm PARTICLES POWDER FROM $Mg(OCH_3)_3$ $+H_2O$

(ZnO, CeO_2, $LiNbO_3$)

CHARACTERISATION OF SAMPLES

CHARACTERIZATION OF NANOMATERIALS

1. **Crystallite size**

   X-ray powder diffraction (XRD)
   Transmission electron microscopy (TEM)
   BET surface area

   (A. Weibel, R. Bouchet, F. Boule'h. P. Knauth, Chem. Mat., (2005) in press.)

2. **Crystallite shape**

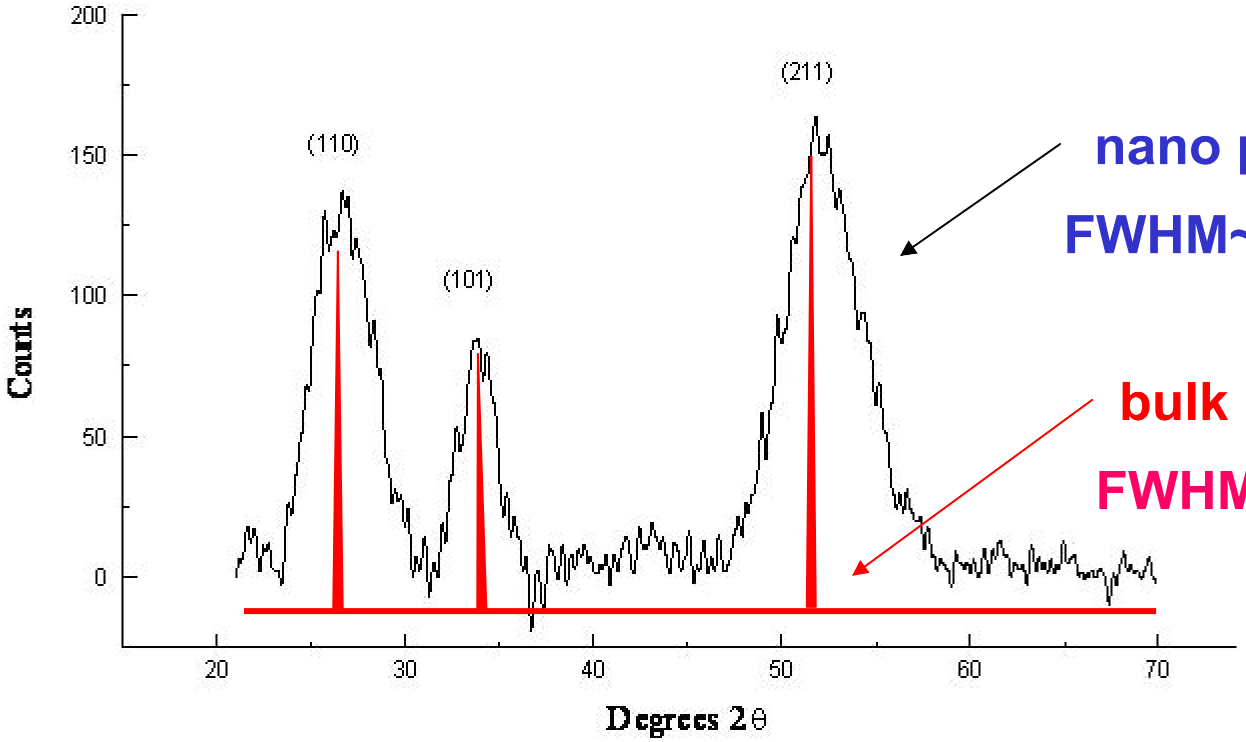
   Small/wide angle X-ray scattering (SAXS/WAXS)
   Transmission electron microscopy (TEM)

3. **Crystallite/sample microstructure**

   Extended X-ray absorption fine structure (EXAFS)
   Transmission electron microscopy (TEM)

Powder Pattern of Sol-Gel SnO_2

Particle size 3 nm



nano powder

FWHM~2 to 3°

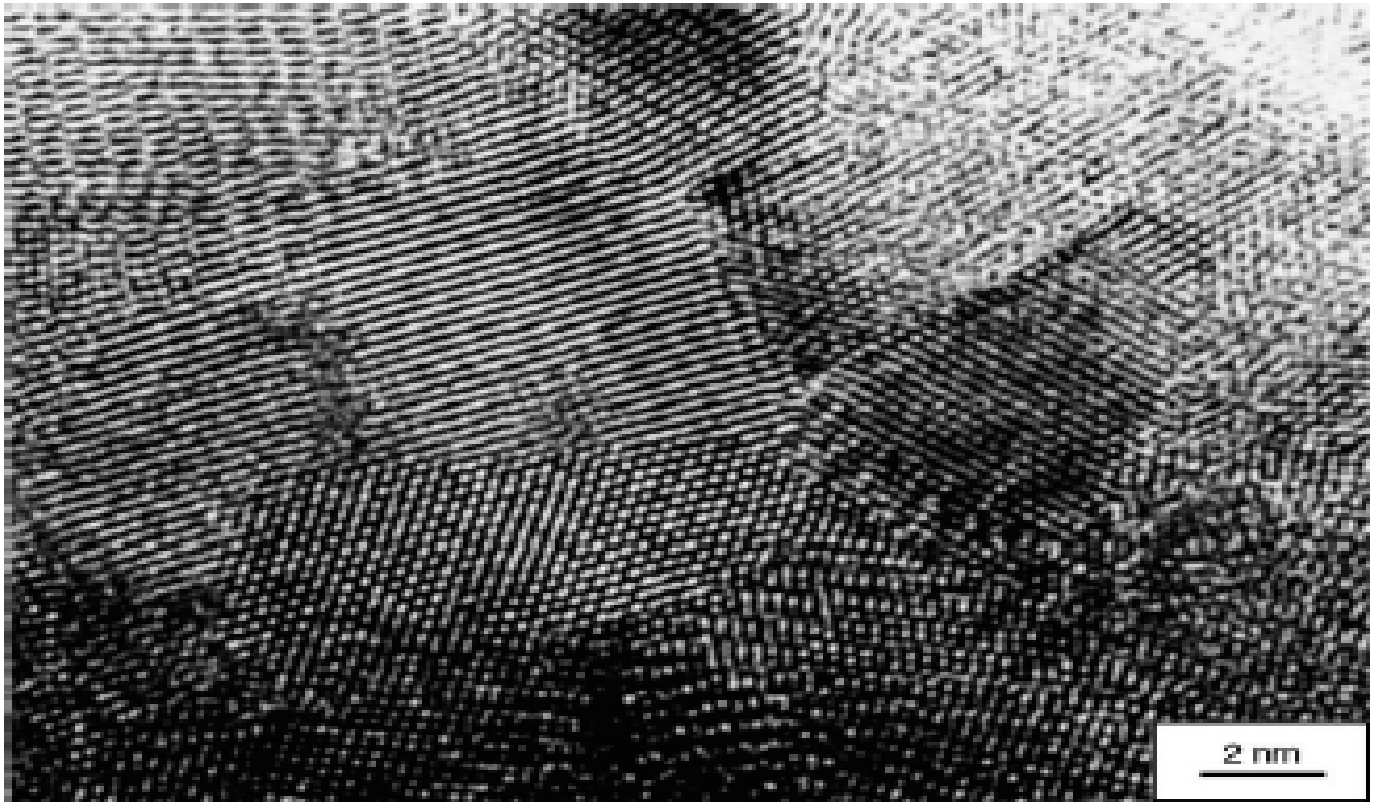
bulk powder

FWHM~0.1 to 0.2°

Scherrer equation

$$s = \frac{k\lambda}{\beta \cos \theta}$$

HRTEM image of a region of nanocrystalline palladium containing a number of grains.



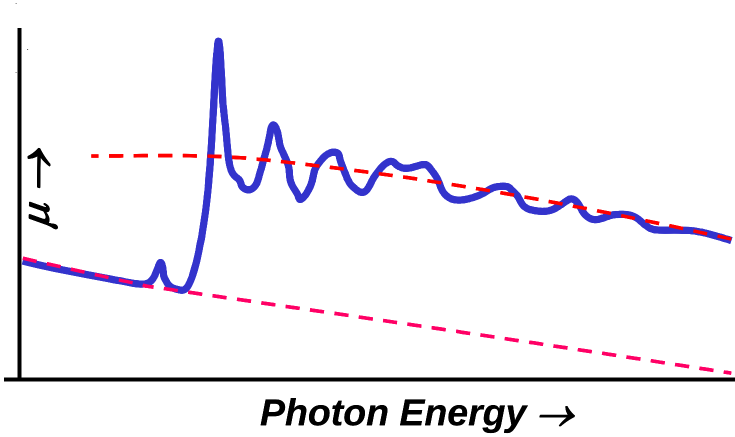
Extended X-ray absorption fine structure (EXAFS)

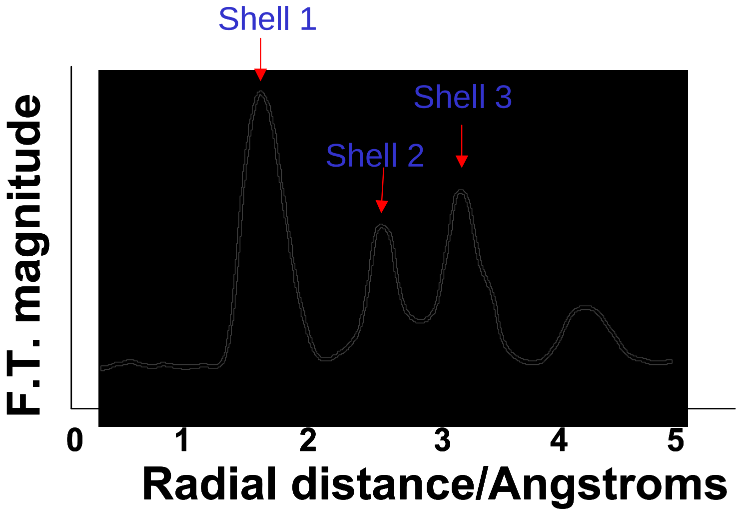
The absorption of X-rays by a sample is measured across the energy range for the photoemission of a core (K or L shell) electron.

Beyond the absorption edge the absorption shows oscillations as a function of incident photon energy.

The oscillations are due to interference between the outgoing photoelectron wave and that part of the wave which is backscattered by neighbours.

The Fourier transform of the absorption coefficient yields a partial radial distribution function around the target atom.





The EXAFS equation

N_j/kR_j^2 amplitude term; depends on N_j number of atoms in shell

$|f_j(\pi)|$ amplitude term; depends of type of atom in shell

$\exp(-2\sigma_j^2k^2)$ amplitude term; EXAFS Debye-Waller factor - σ_j^2 is the mean square variation in R_j

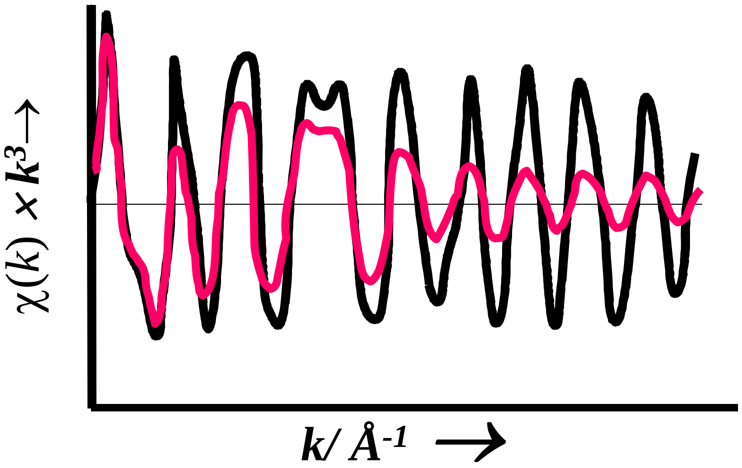
$$\chi(k)=\sum N_j/kR_j^2\,|f_j(\pi)|\,\exp(-2\sigma_j^2k^2)\,\exp(-2R_j/\lambda)\times \sin(2kR_j+\varphi_j+2\delta)$$

Summed over *j* shells

$\sin(2kR_j+\varphi_j+2\delta)$ frequency term; contains R_j and phase shifts

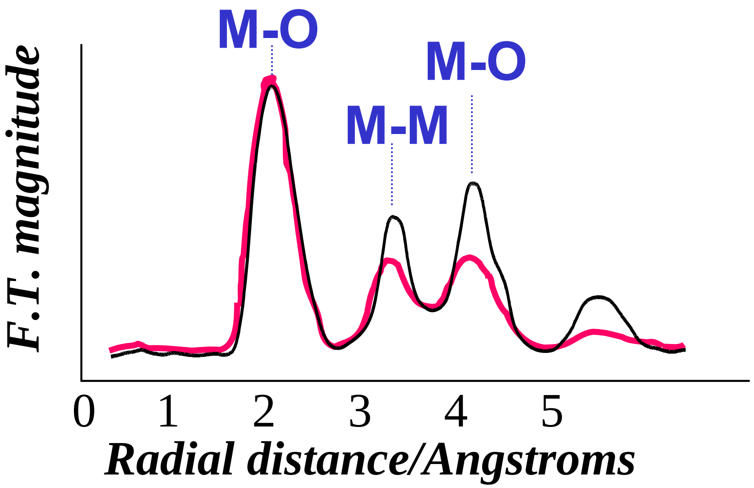
$\exp(-2R_j/\lambda)$ amplitude term; λ is the elastic mean free path of the photoelectron

WHAT DO WE EXPECT FOR THE EXAFS OF NANOCRYSTALLINE SOLIDS?



EXAFS

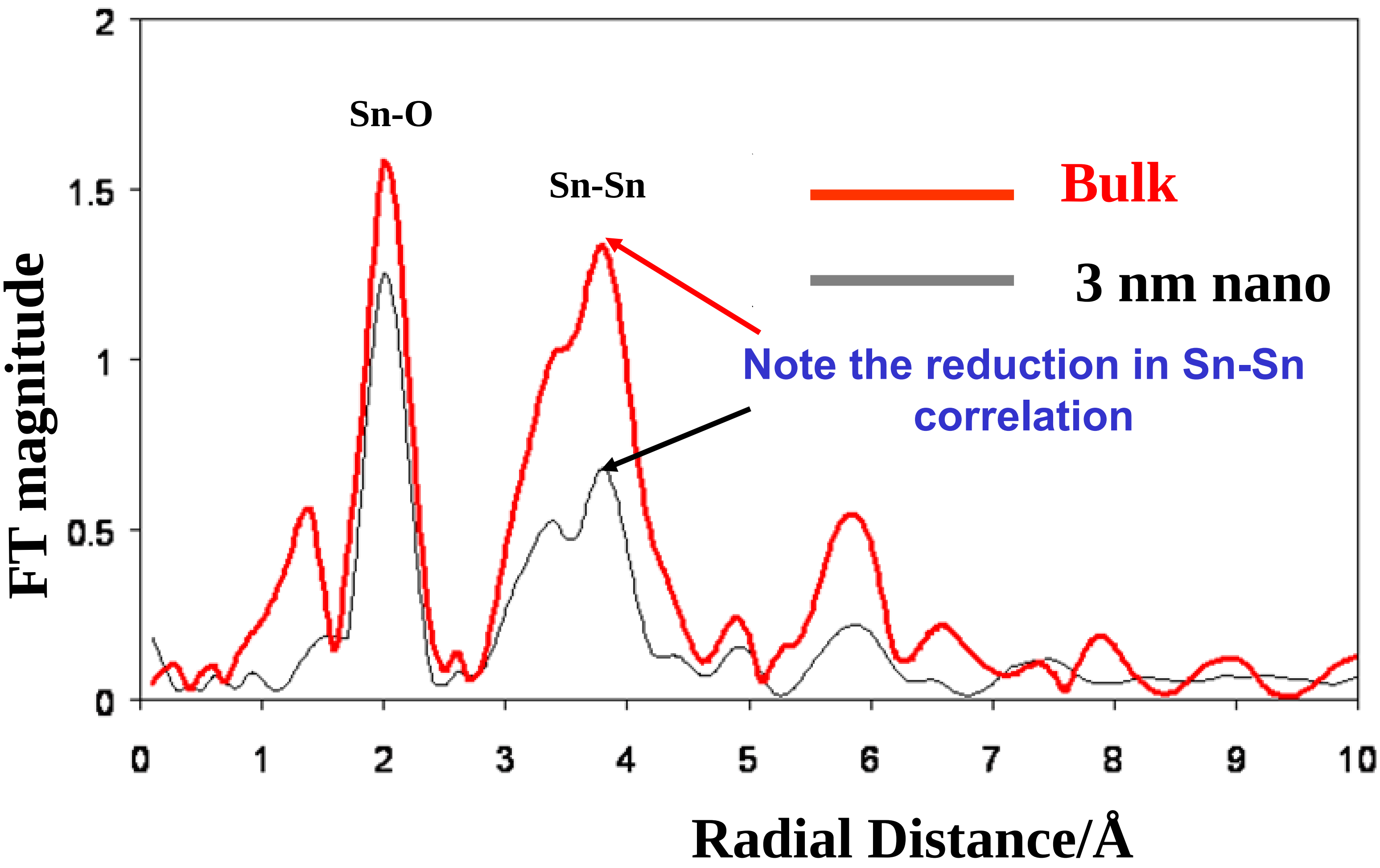
Attenuation of the spectrum due to either size (CN) or disorder (Debye-Waller factor)



Fourier Transform

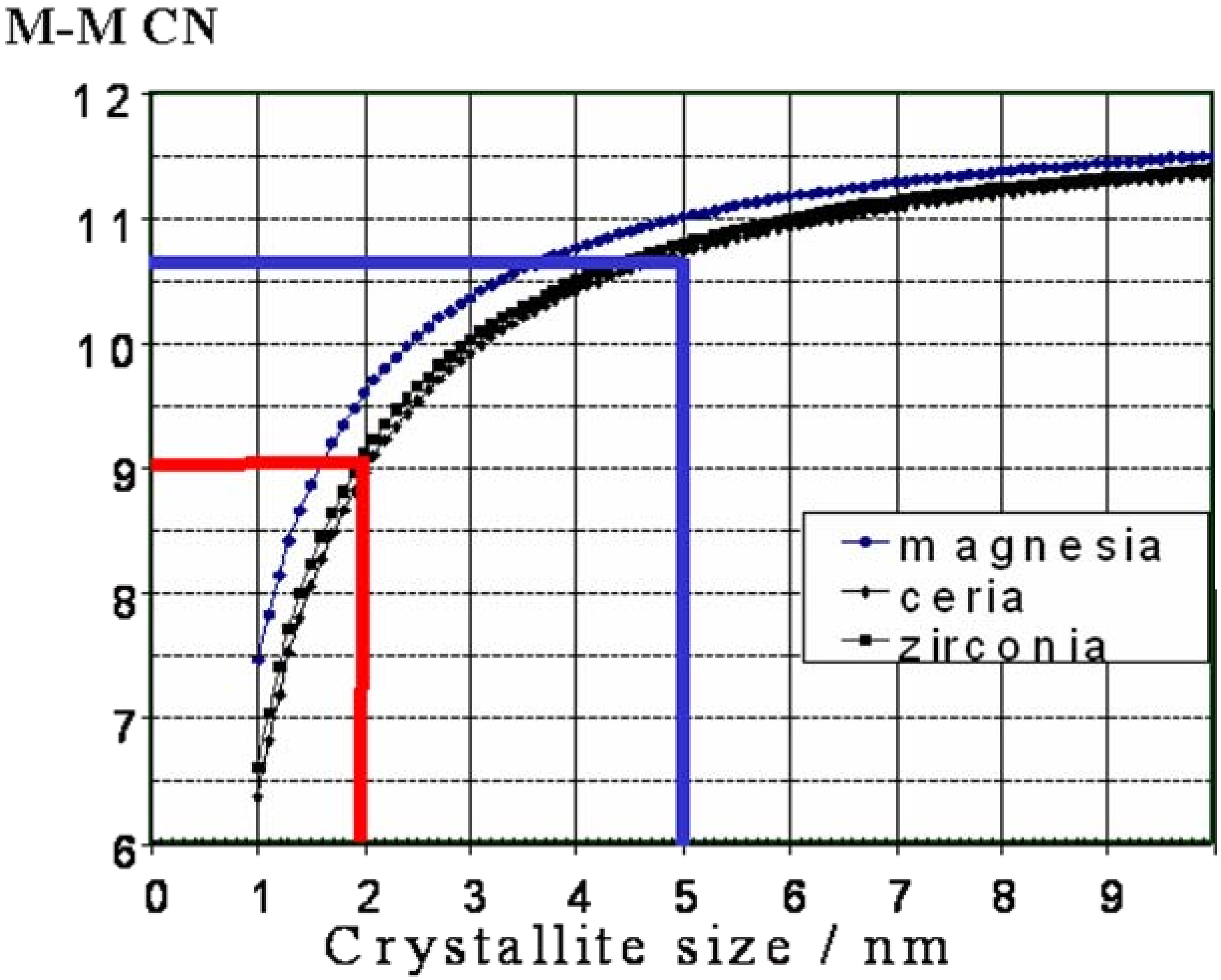
Attenuation of the outer peaks due to either size (CN) or disorder (Debye-Waller factor).

Tin Oxide EXAFS F.T.



Note the reduction in Sn-Sn correlation

M-M coordination number in cubic oxides



EXAFS of 3nm SnO_2

- **The EXAFS is clearly attenuated**
- **Is it due to size?**
- **Is it due to disorder?**

Definitely size and not disorder!

EXAFS EVIDENCE FOR THE MICROSTRUCTURE OF NANOCRYSTALLINE OXIDES

Several systems have now been investigated for sol-gel samples

Simple, binary oxides SnO_2, ZrO_2, CeO_2, ZnO and MgO

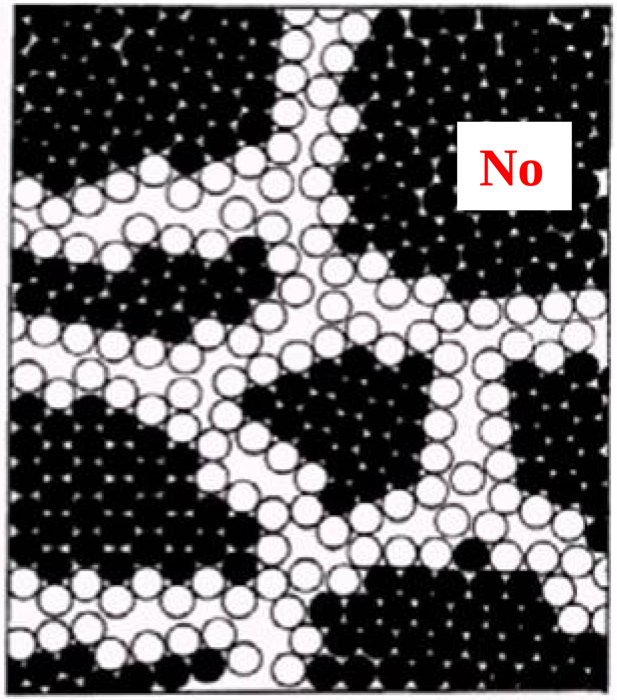
There is no evidence for disorder or amorphous interfaces in these systems (and metals)

Characterization of nanocrystalline oxides by EXAFS spectroscopy
A.V. Chadwick and G.E. Rush, in ‘Nanocrystalline Metals and Oxides’ eds. P.Knauth and J. Schoonman; Kluwer, Boston, 2002.

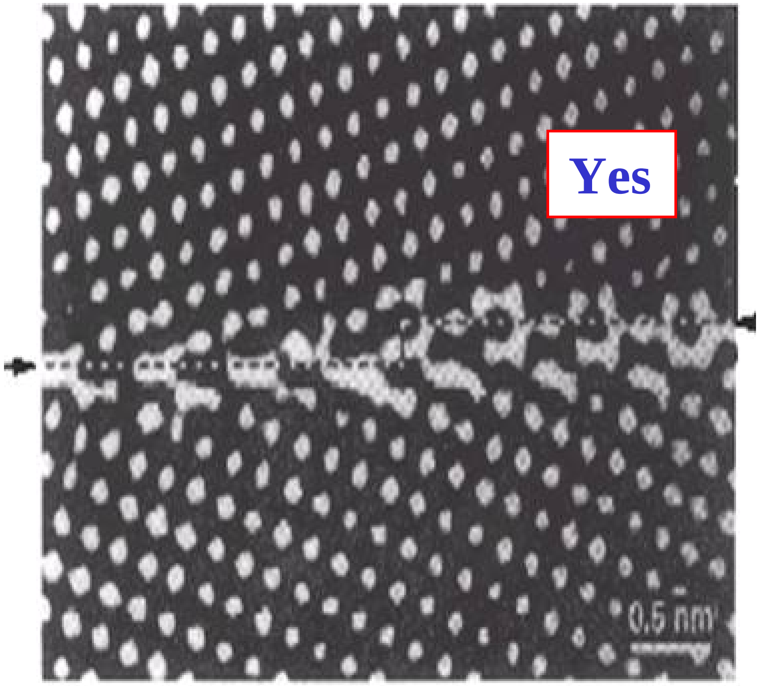
Nature of the nanocrystalline interface

Sol-gel samples (and IGC metals)

Model of boundary in nano oxide



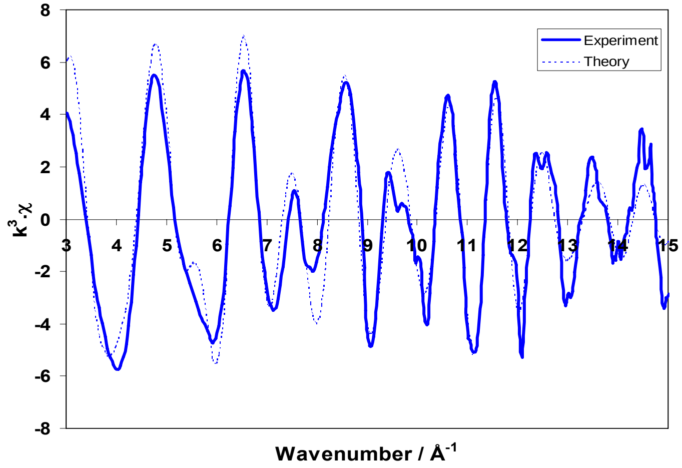
Grain boundary in bulk NiO

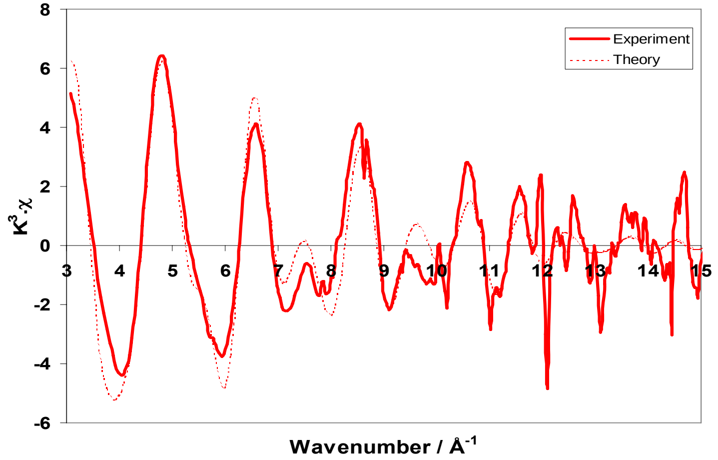


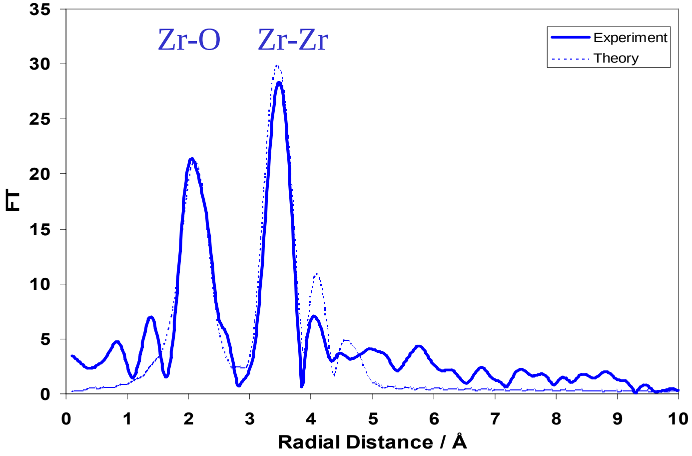
Zr K-edge EXAFS of ZrO_2

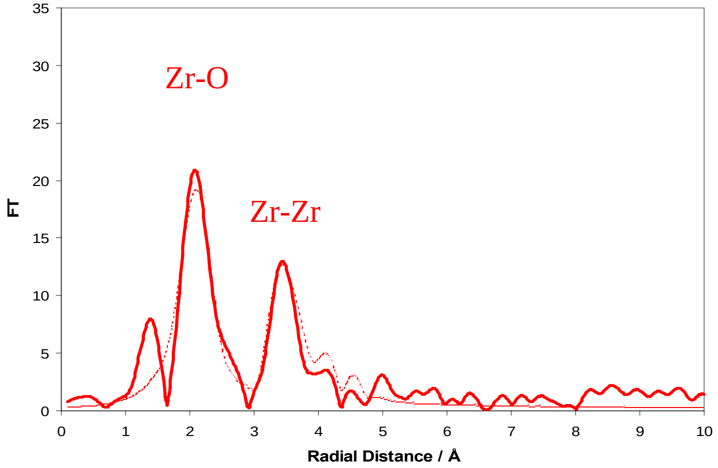
Bulk

Ball milled (14nm)







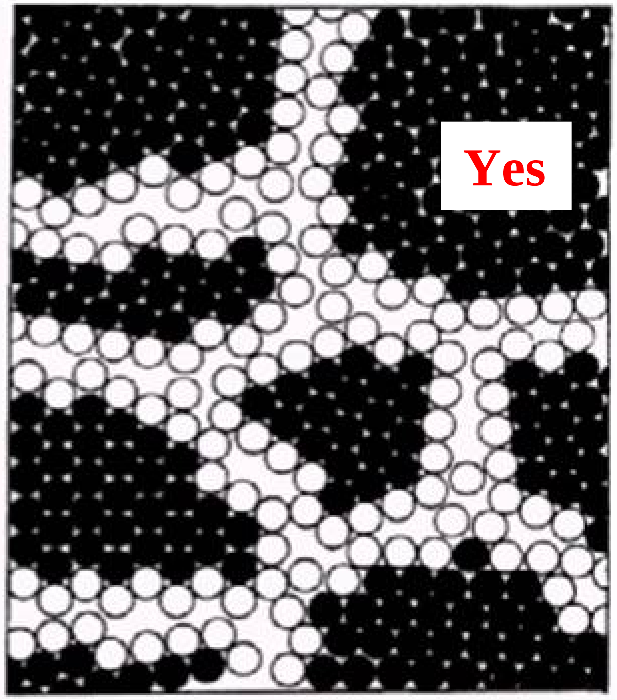


SIMPLE PEAK AREA ANALYSIS:- 50% AMORPHOUS

Nature of the nanocrystalline interface

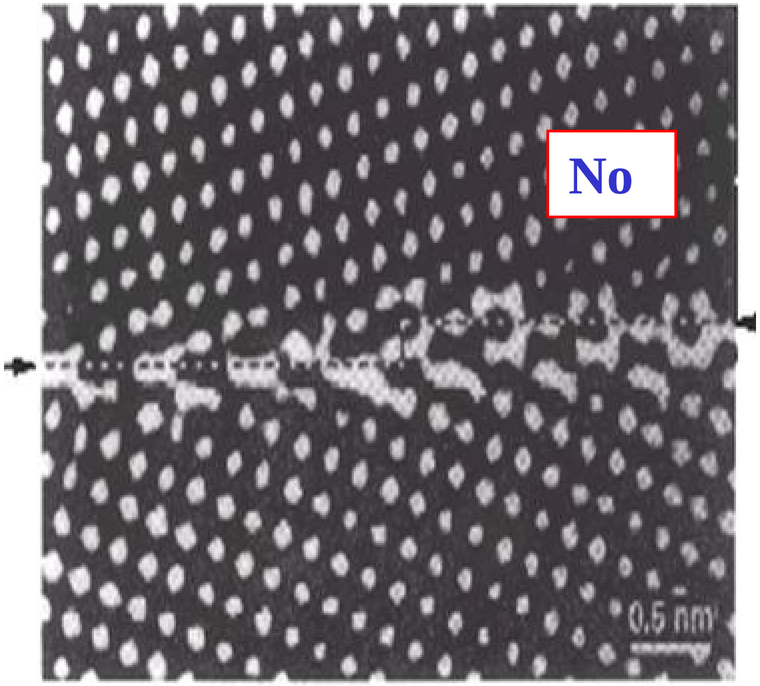
Ball-milled samples

Model of boundary in nano oxide



Yes

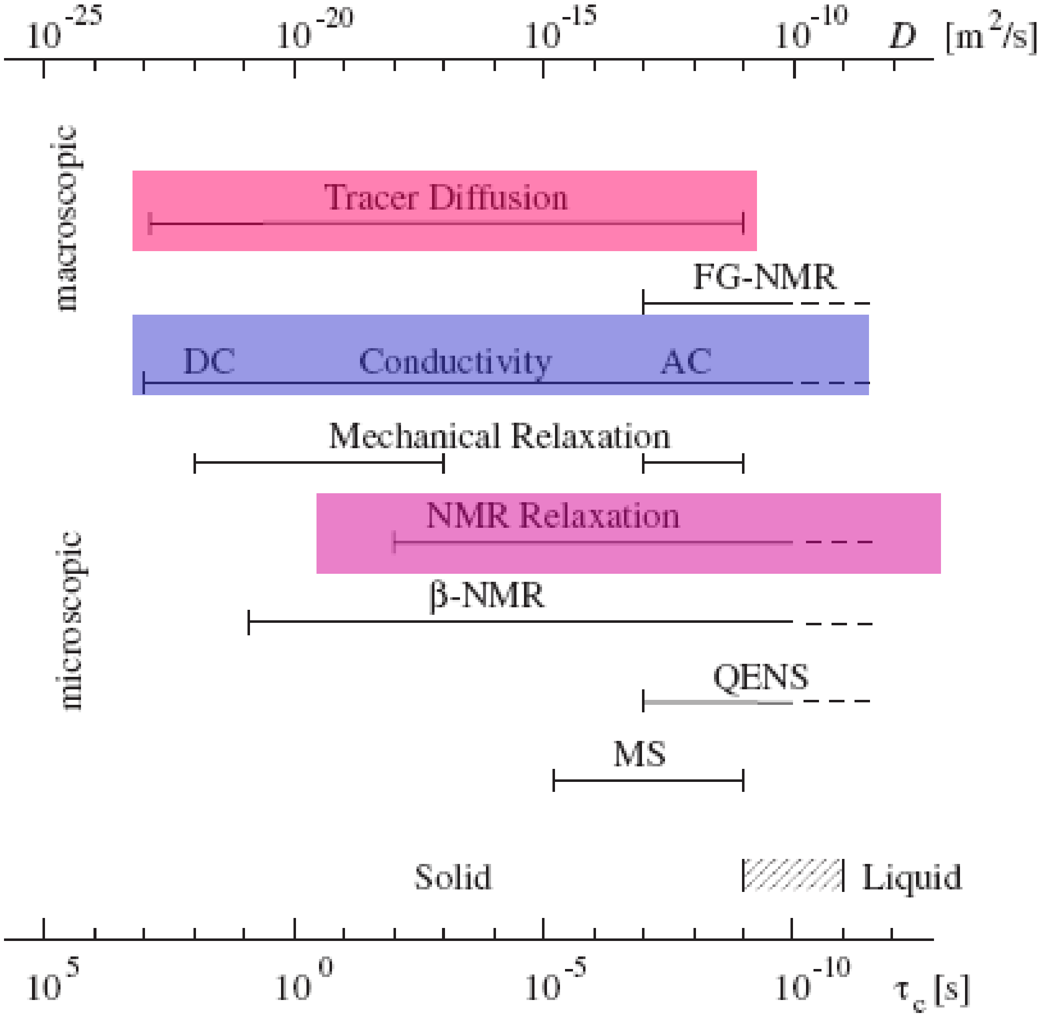
Grain boundary in bulk NiO



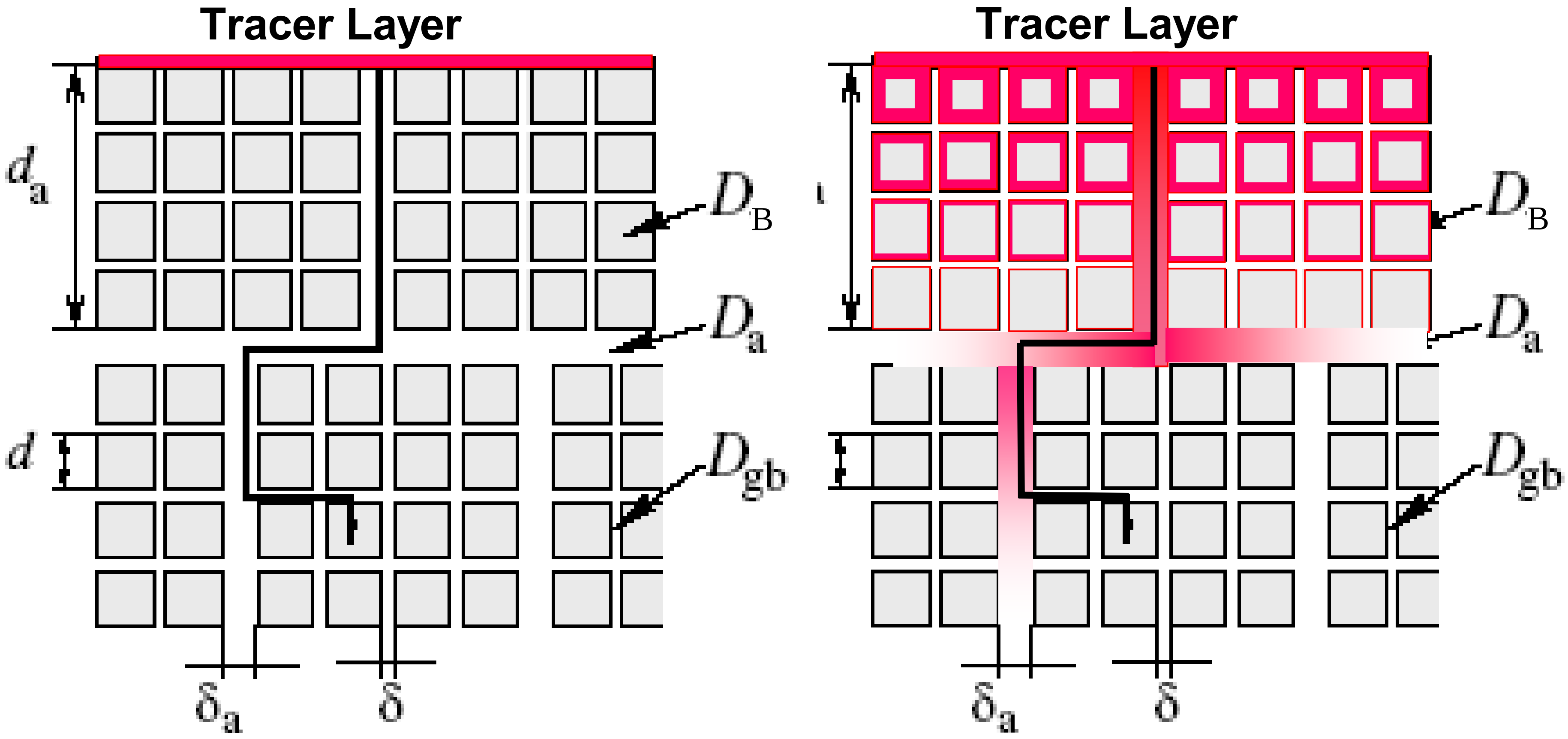
No

DIFFUSION EXPERIMENTS

Diffusion Techniques for Nanomaterials



Tracer penetration in a nanocrystalline compact



Numerical Study of Grain Boundary Diffusion: Size Effects, D. Gryaznov, J. Fleig, J. Maier

SELF-DIFFUSION IN HIGH-DENSITY NANOCRYSTALLINE Fe

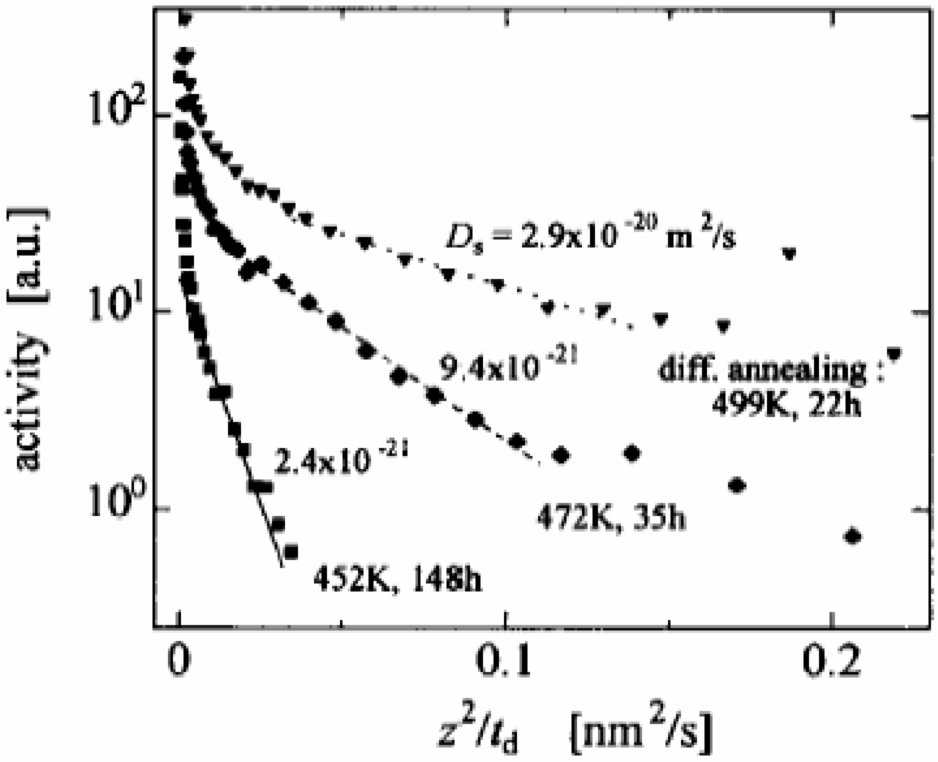
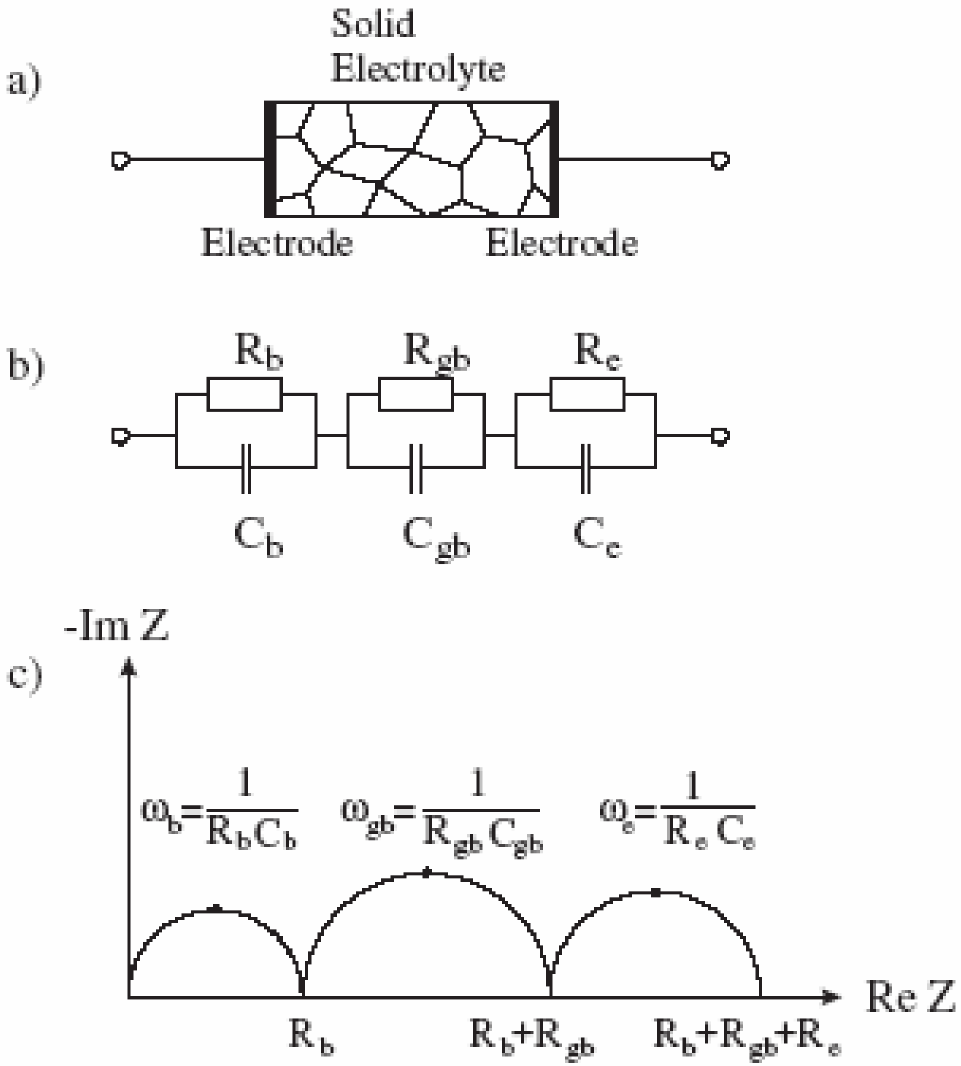


Fig. 2. ^{59}Fe depth profiles observed for high-density n-Fe specimens.

H. Tanimoto, P. Farber, R Würschum, R.Z. Valiev, H.-E. Schaefer, Nanostructured Mater., 12 (1999) 681

AC Impedance Spectroscopy

Measure the sample resistance over a wide frequency range (~1Hz to 1MHz)



NMR Techniques

1. NMR linewidth/line shape

linewidth$\propto$1/D

Micro Li_2O

Micro Li_2O/B_2O_3

Nano Li_2O

Nano Li_2O/B_2O_3

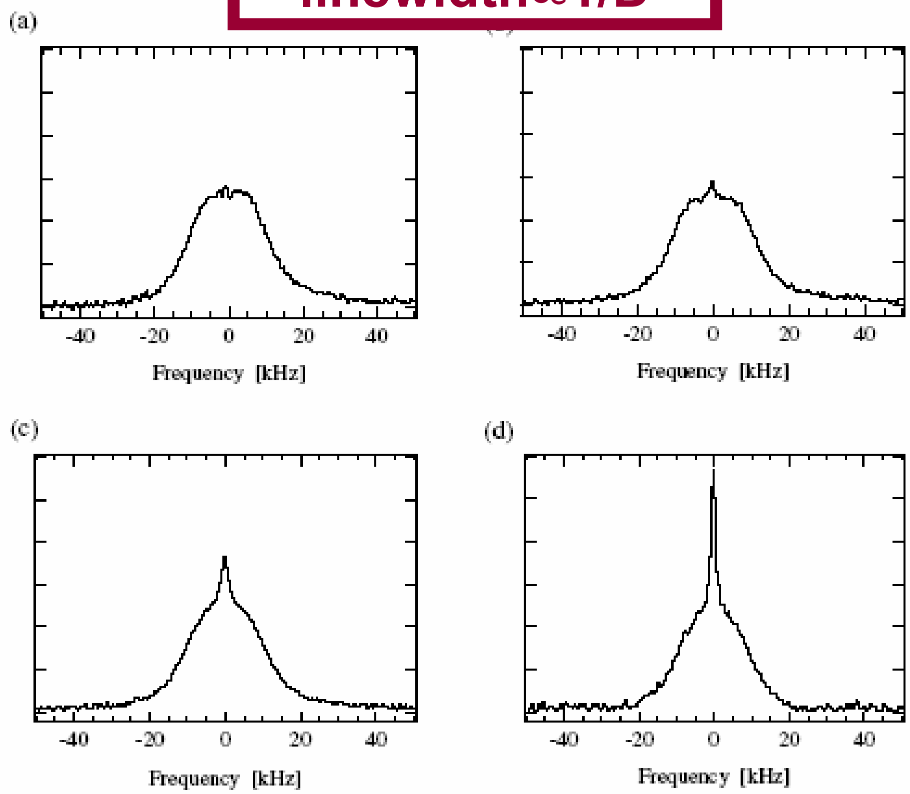


Figure 22. ^{7}Li NMR lineshapes at 58 MHz and 433 K of (a) microcrystalline Li_2O, (b) microcrystalline $(1-x)Li_2O{:}xB_2O_3$, $x = 0.5$, (c) nanocrystalline Li_2O, (d) nanocrystalline $(1-x)Li_2O{:}xB_2O_3$, $x = 0.5$ [140].

Discrimination between bulk and interface is possible

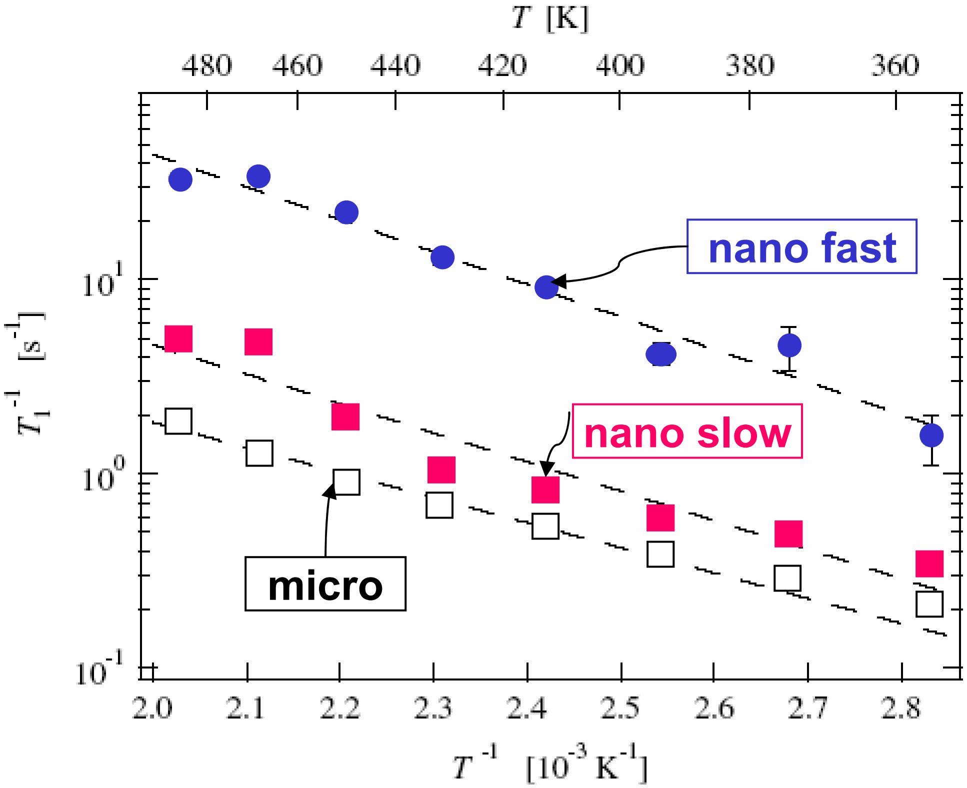
NMR Techniques

2. NMR relaxation times

Diffusion coefficients can be calculated from the spin-lattice relaxation time, T_1. T_1 is determined from the exponential decay of the magnetisation following r.f. pulse.

T_1 is related to the diffusion coefficient, D. If there are diffusion processes with different rates there will be different components in the decay. Thus two D's can be evaluated, fast and slow.

^{7}Li spin–lattice relaxation rates in nano- and microcrystalline $(1 - x)\mathrm{Li_2O}:x\mathrm{B_2O_3}$



Indris S and Heitjans P 2002 *J. Non-Cryst. Solids* 307–310 555–64

OVERVIEW OF THE DATA

OVERVIEW OF DIFFUSION DATA IN NANOMATERIALS

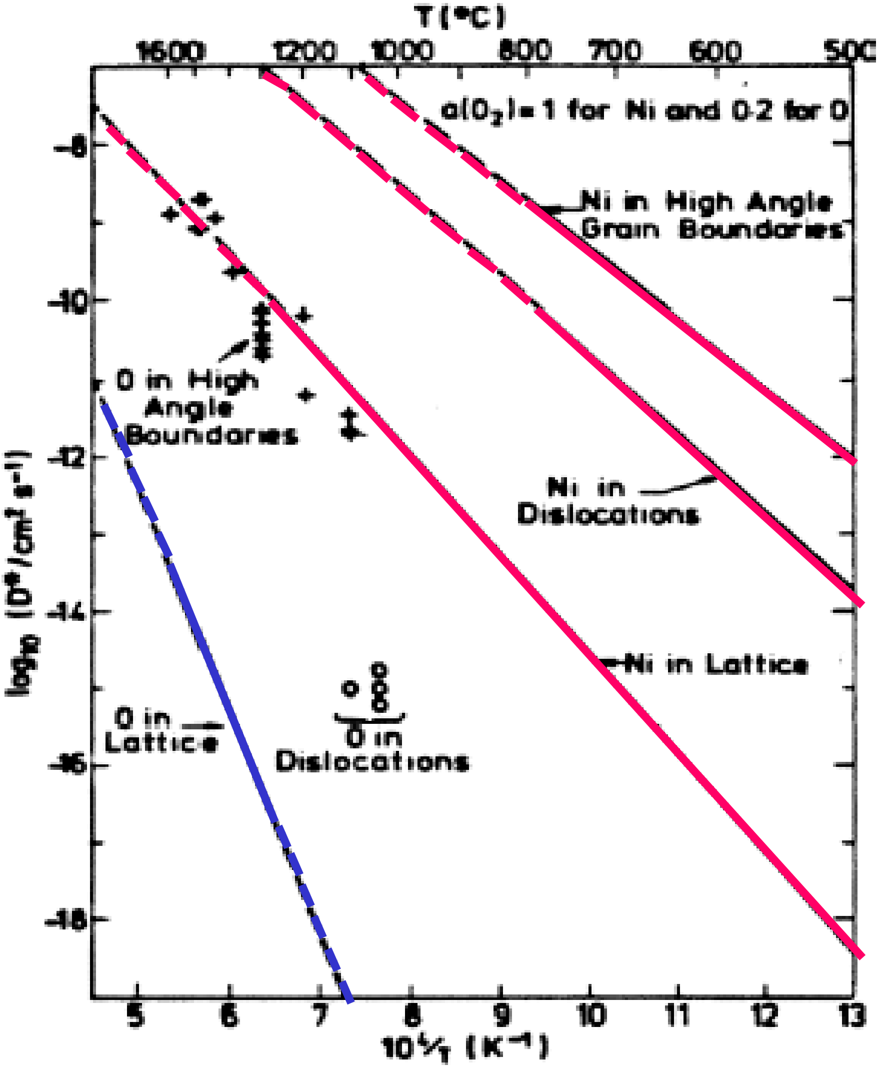
1. Focus on the measurements of diffusion, ignoring creep. Look only at well-defined samples (IGC and sol-gel)
2. Concentrate on metals and simple ionic crystals.
3. It will be an overview, not a comprehensive tabulation of data.

Recent reviews:-
“Diffusion in Nanocrystalline Metals and Alloys-A Status Report”,
R. Würschum, S. Herth, U. Brossmann, *Adv. Eng. Mat*., 5 (2003) 365.

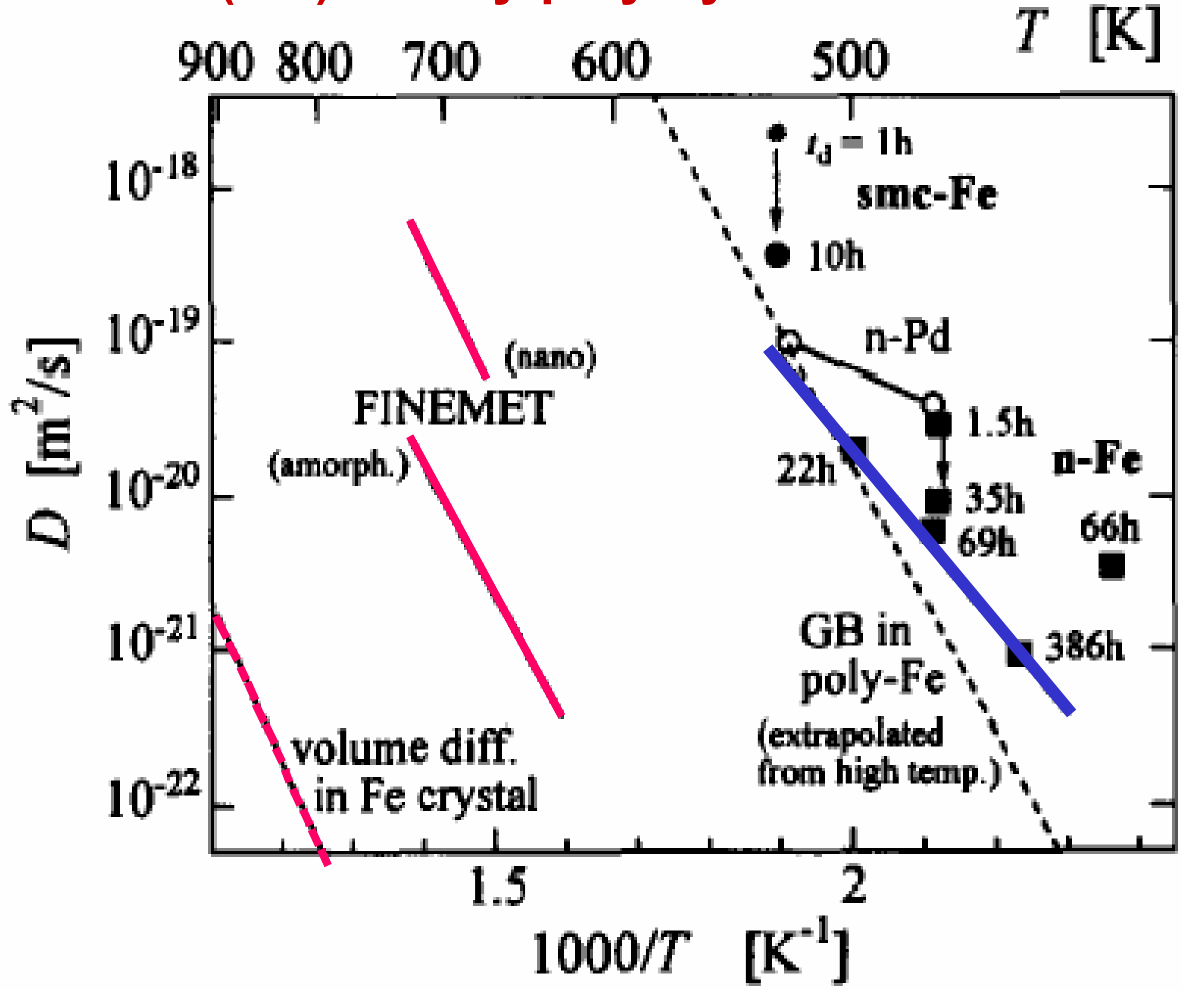
“Diffusion and ionic conduction in nanocrystalline ceramics”
P. Heitjans, S. Indris, *J. Phys.: Condens. Matter* 15 (2003) R1257

Nickel and Oxygen Self-diffusion in Nickel Oxide

Alan Atkinson
(Harwell)

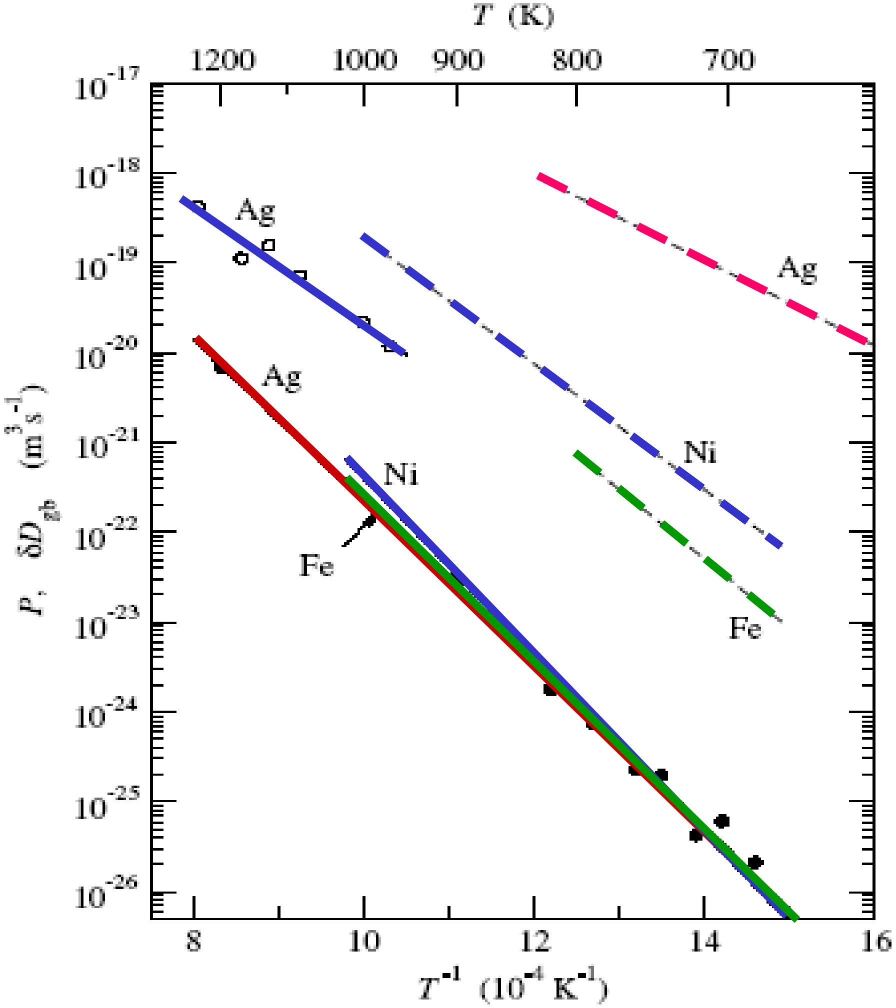


Fe Diffusion Coefficients for Nanocrystalline Metals, Crystalline (c-) Fe, Grain Boundaries (GB) in Poly-polycrystalline Fe and the Finemet Alloys



H. Tanimoto, P. Farber, R Würschum, R.Z. Valiev, H.-E. Schaefer, Nanostructured Mater., 12 (1999) 681

Ag, Fe, and Ni diffusion along nanocrystalline GBs in nanocrystalline Fe – 40wt%Ni alloy. The diffusivities along inter-agglomerate boundaries are shown by dashed lines



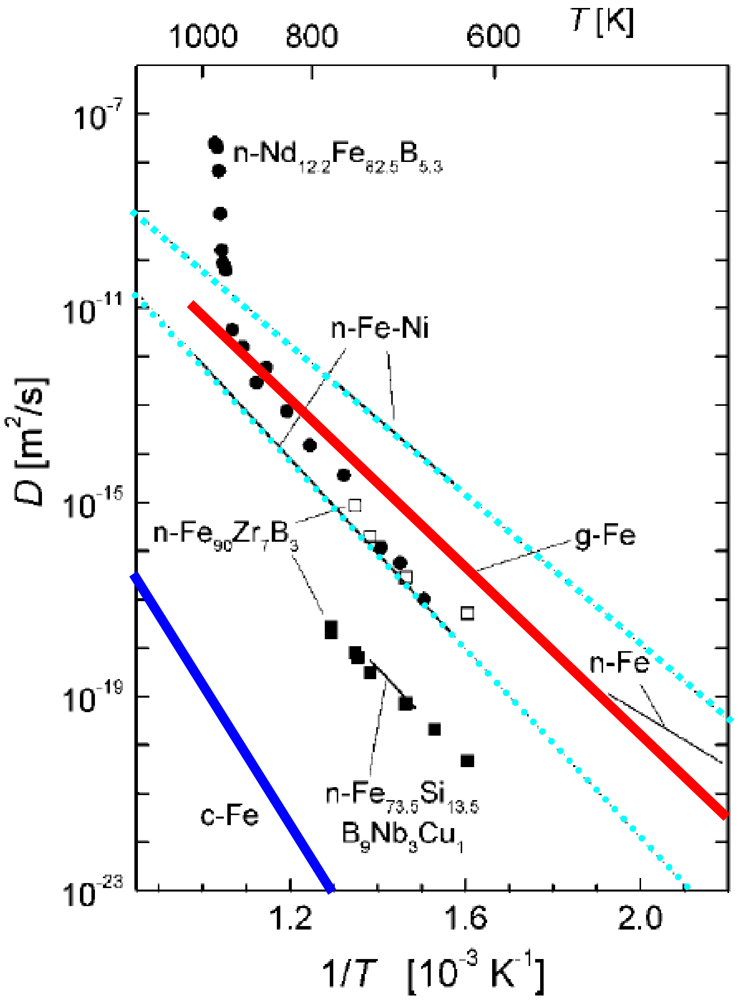
S.V. Divinski, F. Hisker, Y.-S. Kang, J.-S. Lee, Chr. Herzig, Acta Mater., 52 (2004) 645.

Diffusion in nanocrystalline metals

Many of the early experiments yielded tracer diffusion coefficients that were far too high.

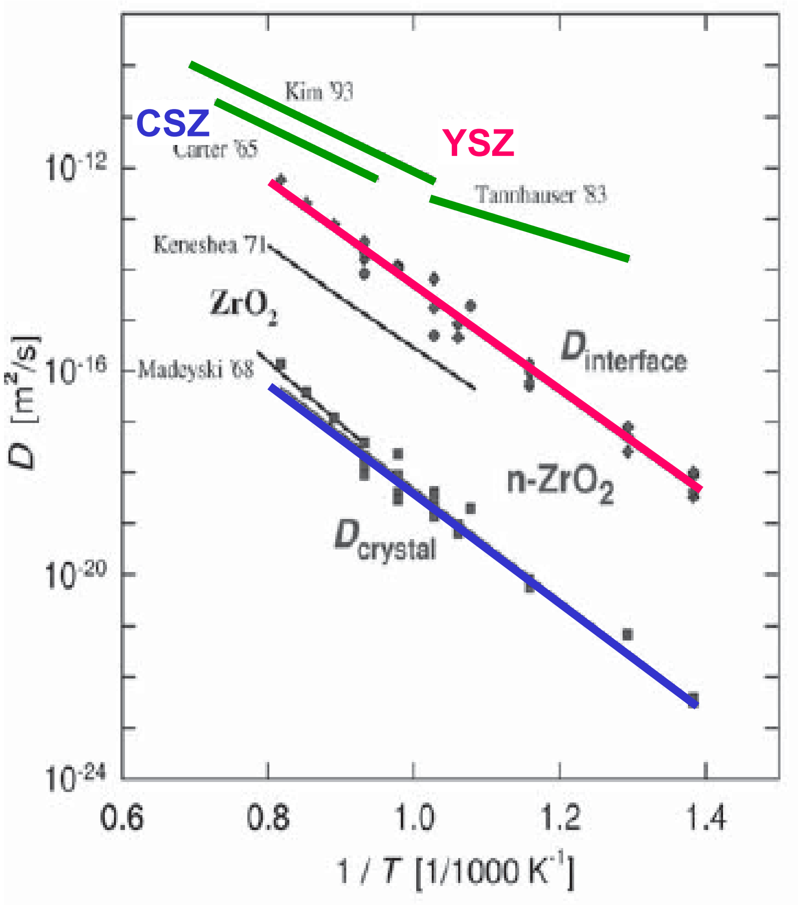
There were problems with *low density samples, pores, grain growth, diffusion induced grain boundary migration*. All yield too fast diffusion.

The current view is that the diffusion is along the boundaries between crystallites. This is similar or slightly faster than normal grain boundary diffusion.



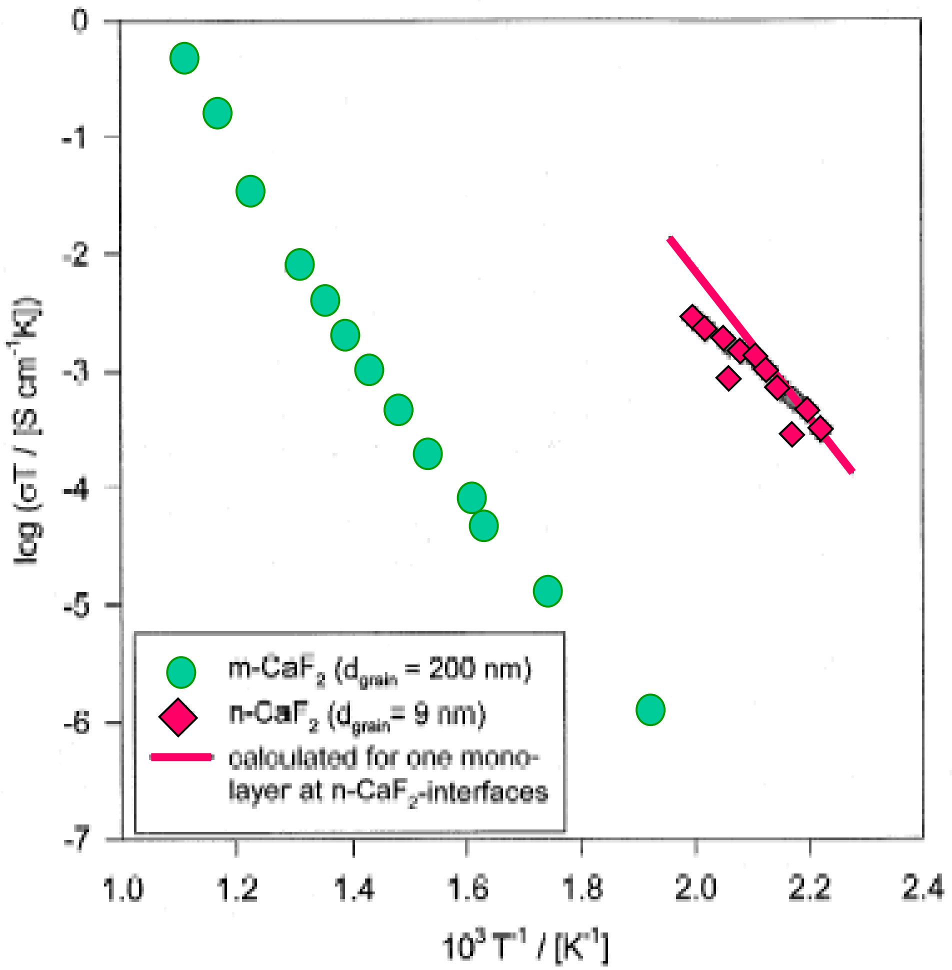
R. Würschum, S. Herth, U. Brossmann, Adv. Eng. Mat., 5 (2003) 365.

^{18}O Tracer Diffusion in Zirconia



Brossmann U, Wurschum R, Sodervall U and Schaefer H-E 1999 *Nanostruct. Mater.* 12, 871

The Conductivities of Nano and Micro-crystalline CaF_2



Puin W, Rodewald S, Ramlau R, Heitjans P and Maier J 2000 *Solid State Ion.* 131 159–64

Maier *et al* (Nature; December 2001)

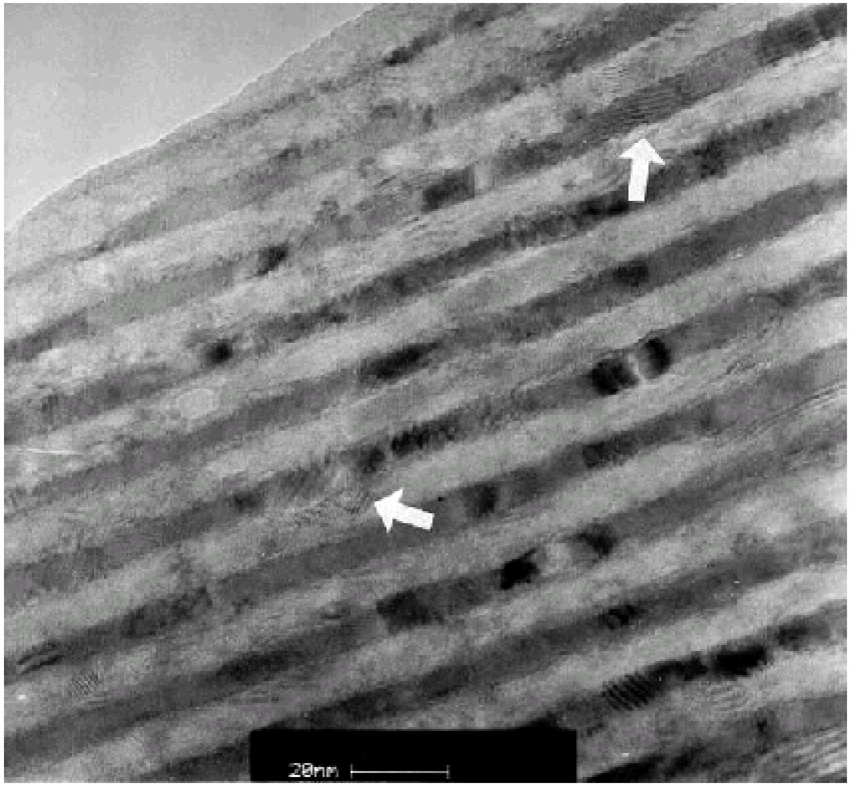


Fig. 1. Typical TEM image of a BaF_2-CaF_2 heterostructure with a period of 18 nm.

Maier *et al* (Nature; December 2001)

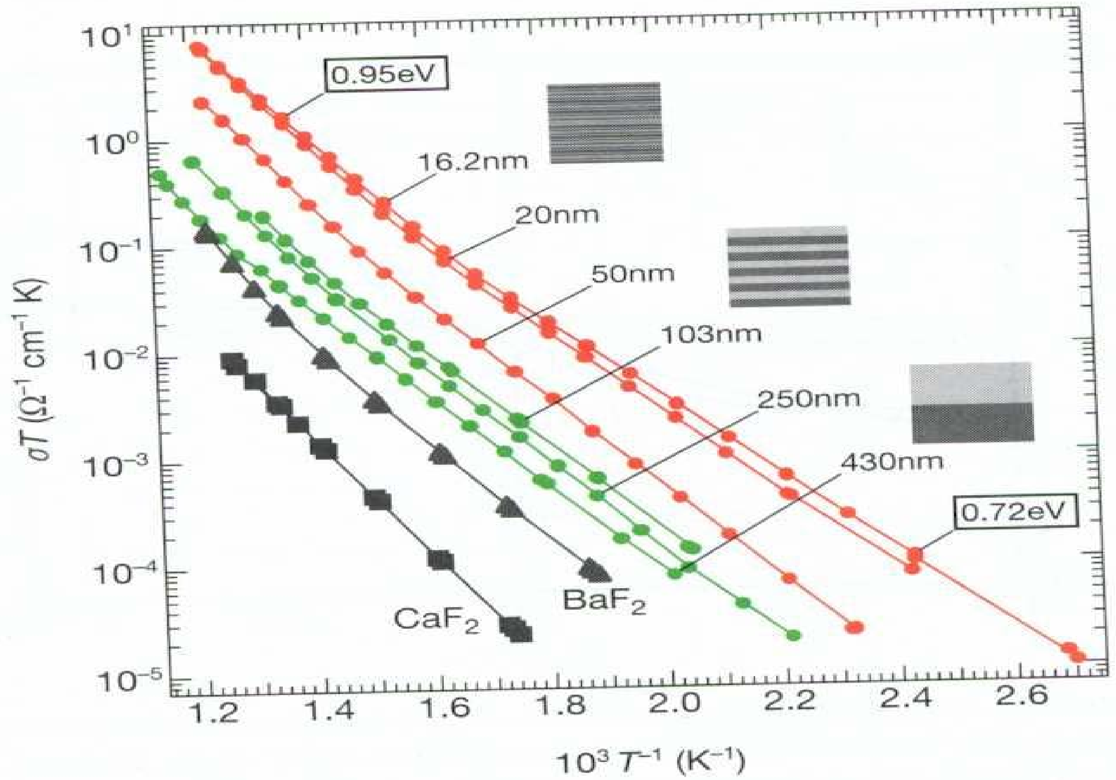
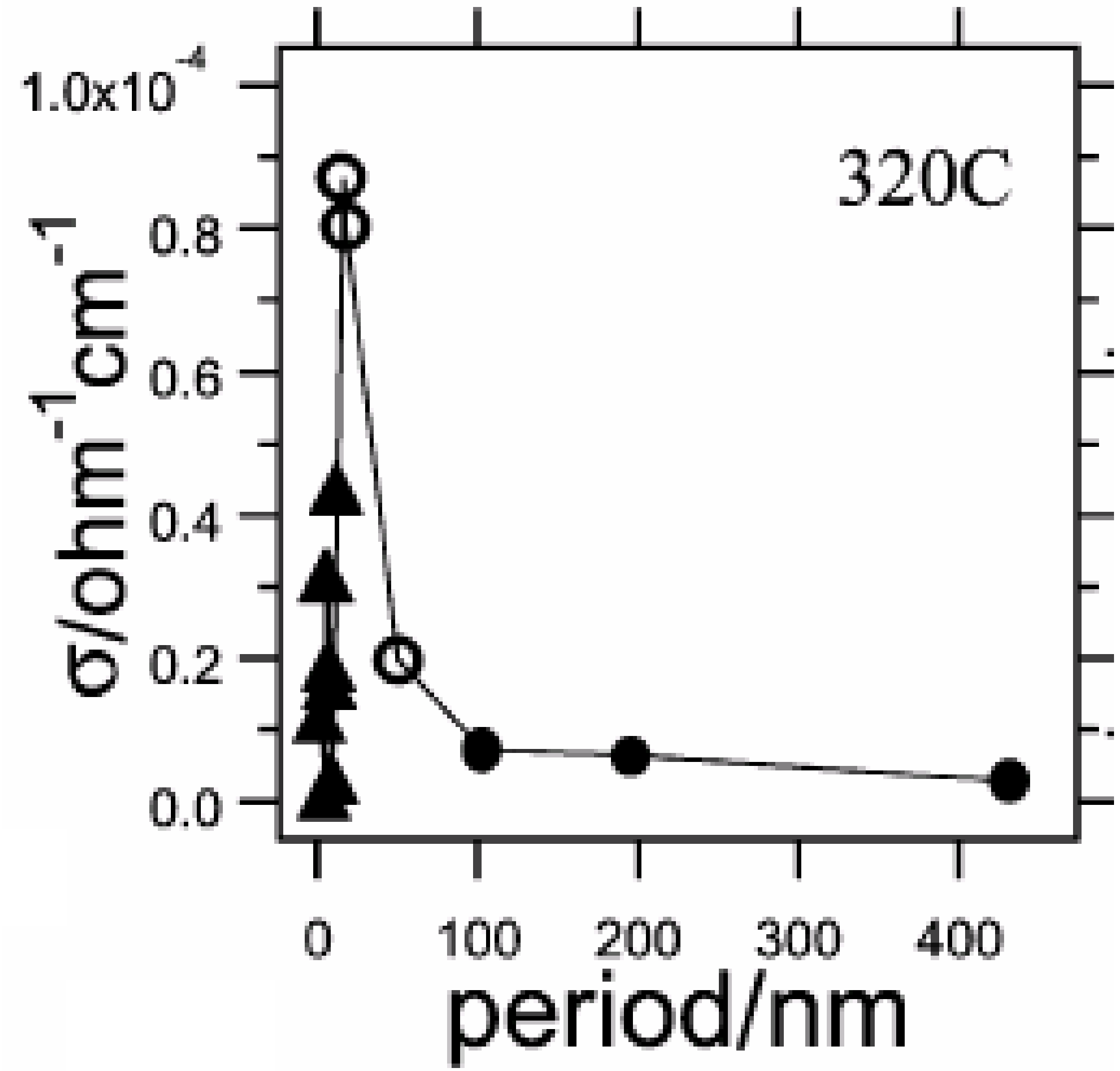


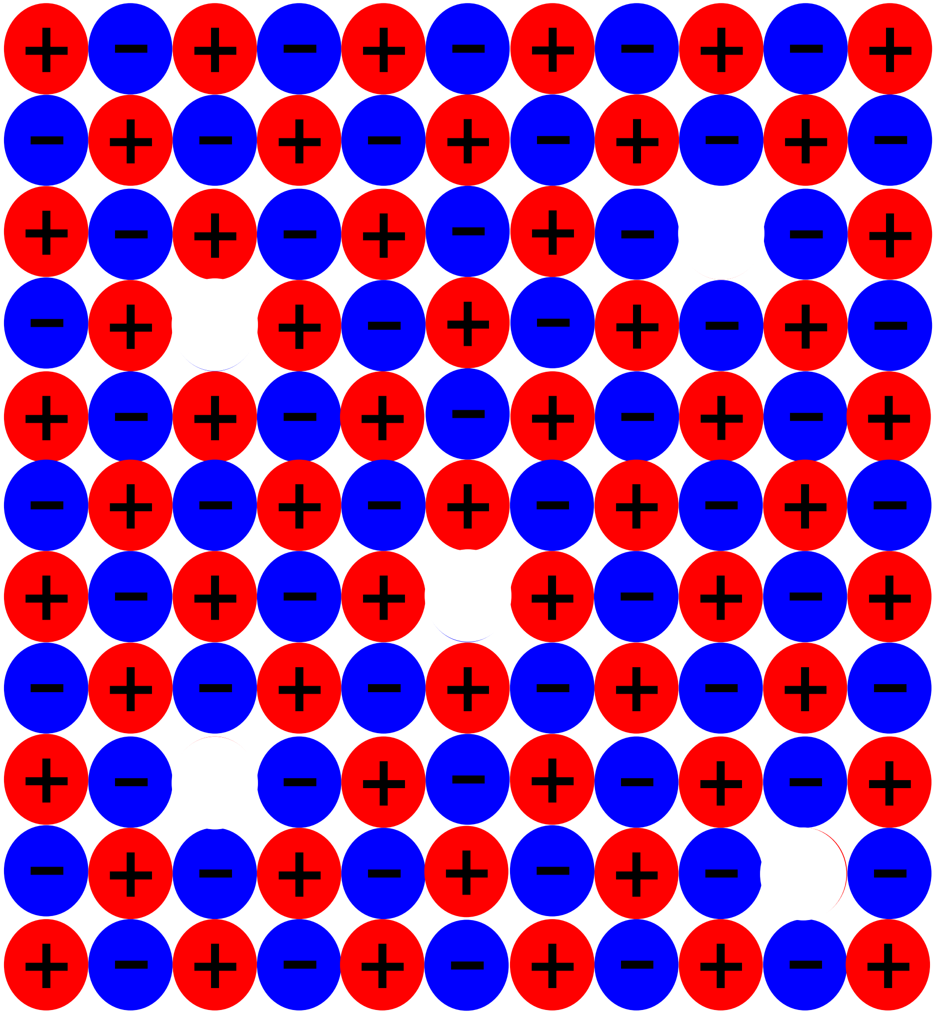
Figure 1 Parallel ionic conductivity of the films. Data are shown for films with various periods and interfacial densities in the 430–16 nm range. We note that the overall thickness is approximately the same in all cases (~500 nm). σ, conductivity; T, temperature. The different colours refer to different site regimes (green: semi-infinite space charge zones; red: finite space charge zones).

N. Sata, K. Ebermann, K. Eberl, J. Maier, Nature, 408 (2000) 946.

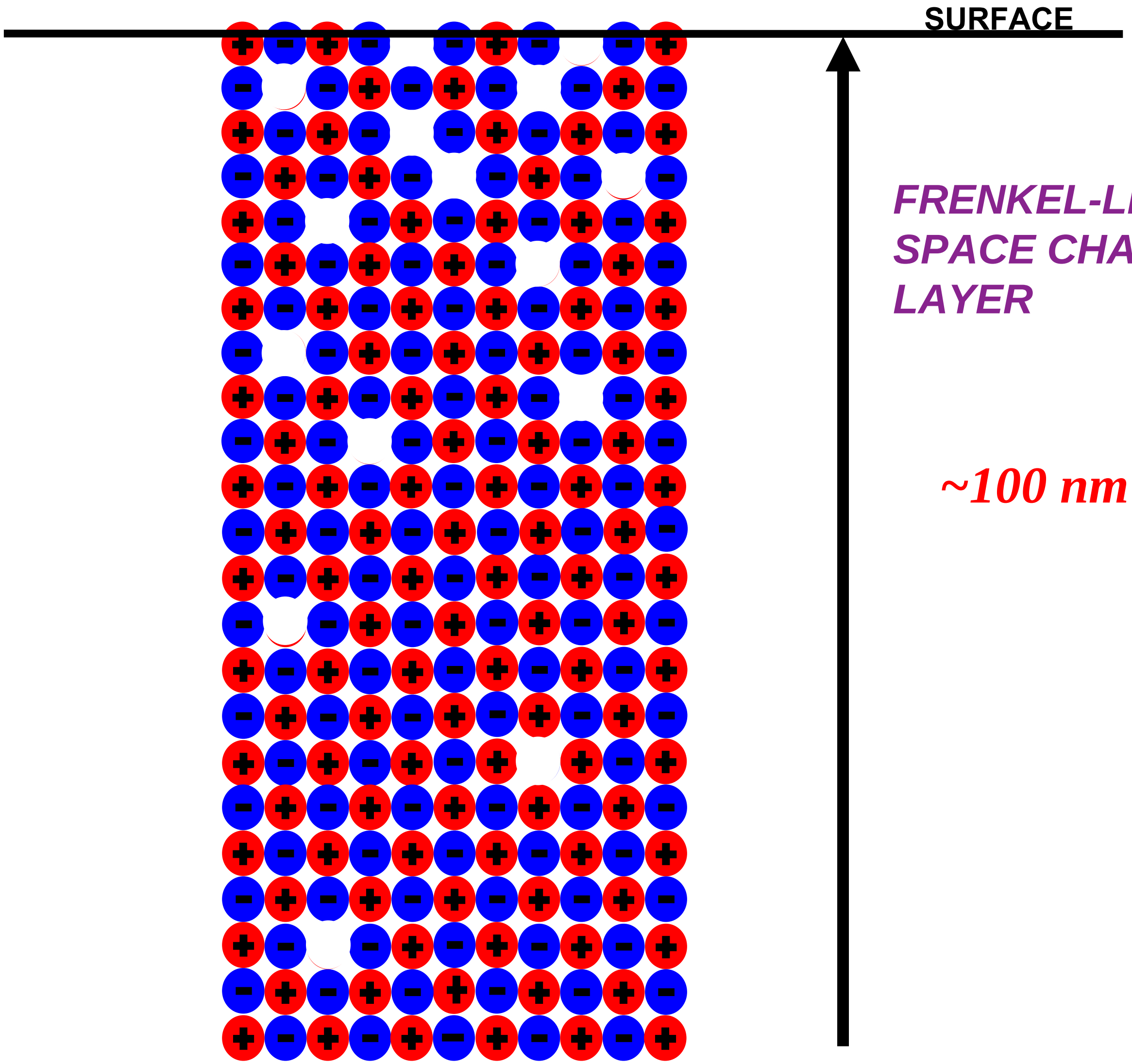


N. Sata, N.Y. Jin-Phillipp, K. Eberl, J. Maier, *Solid State Ionics* 154– 155 (2002) 497– 502

BULK IONIC CRYSTAL



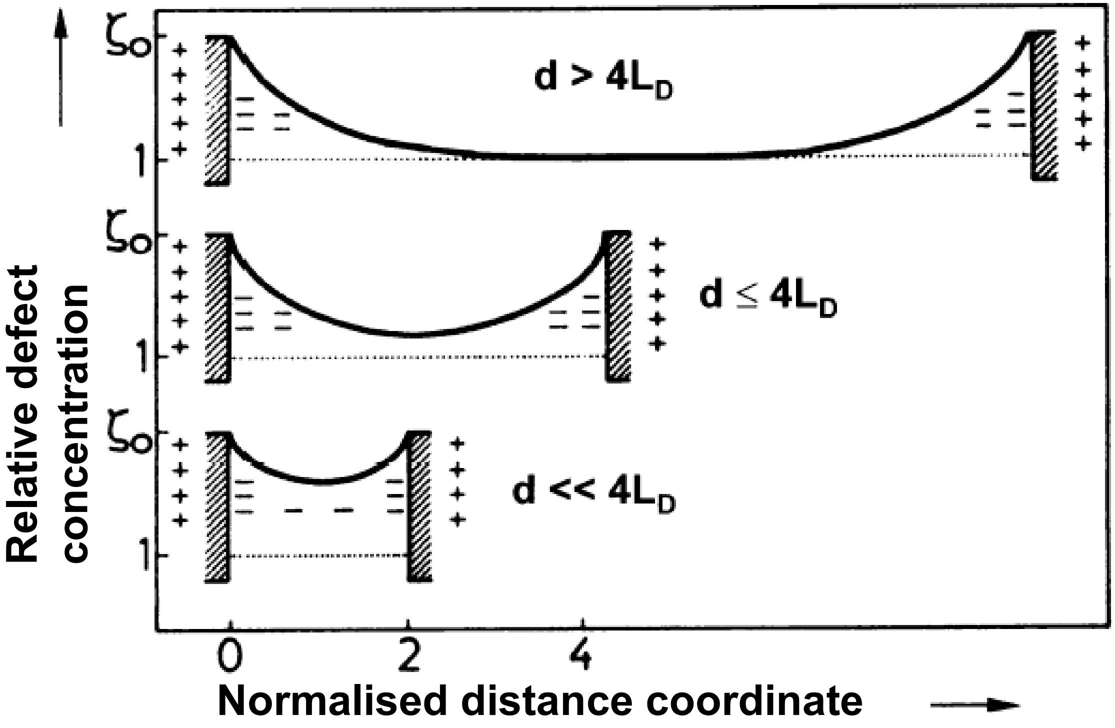
BULK IONIC CRYSTAL WITH SURFACE



FRENKEL-LEHOVEC SPACE CHARGE LAYER

~100 nm

Space Charge Layer *versus* Size



Maier J 1995 *Prog. Solid State Chem.* 23, 171

Maier *et al* (Nature; December 2001)

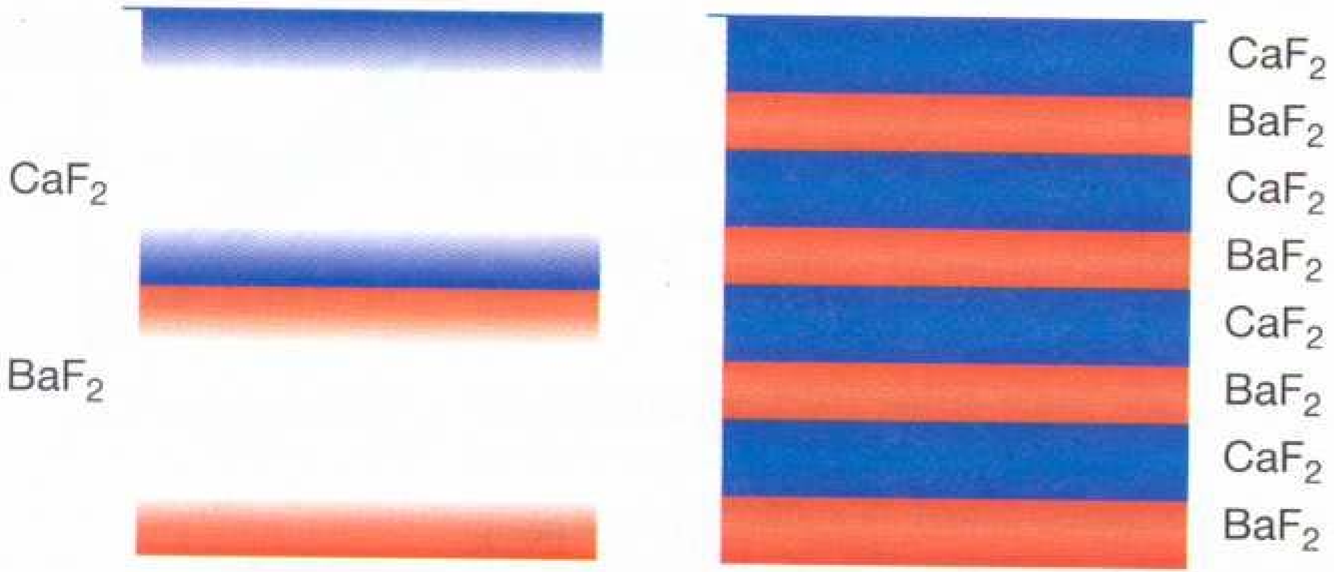


Figure 4 Comparison of conductivity profiles in the semi-infinite space-charge and mesoscale situations. The concentration or (parallel) conductivity profiles are sketched for the semi-infinite space-charge situation (period $> 8\lambda$, left), and for the mesoscale situation (period $< 8\lambda$, right) in which the space-charge regions overlap and bulk values are exceeded even in the centres of the individual layers.

N. Sata, K. Ebermann, K. Eberl, J. Maier, Nature, 408 (2000) 946.

YSZ thin films

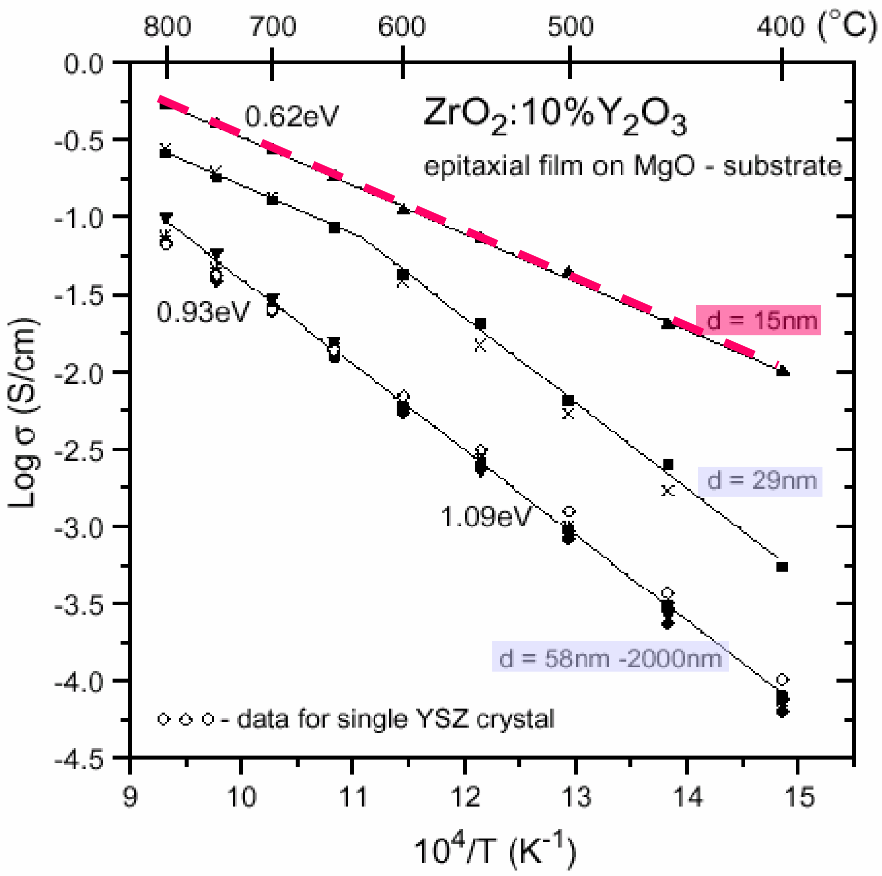


Fig. 7. Temperature dependence of the electrical conductivity determined for epitaxial YSZ thin films with different thicknesses.

I. Kosacki, et al., *Solid State Ionics*, 176 (2005) 1319

WARNING!!!!!

Some oxides, like pure CeO_2, will change stoichiometry as the particle size decreases. Thus an increased conductivity in nanocrystals can be due to a change from ionic to electronic conductivity.

CONCLUSIONS AND VIEW TO THE FUTURE

CONCLUSIONS

1. **The microstructure of nanomaterials depends on the preparation method.**

2. **There are now some good data, but still rather limited.**

3. **The diffusion in nanocrystalline metals is similar (or slightly faster) than along grain boundaries.**

4. **The diffusion in nanocrystalline ionic materials is influenced strongly by grain size; space-charge effects.**

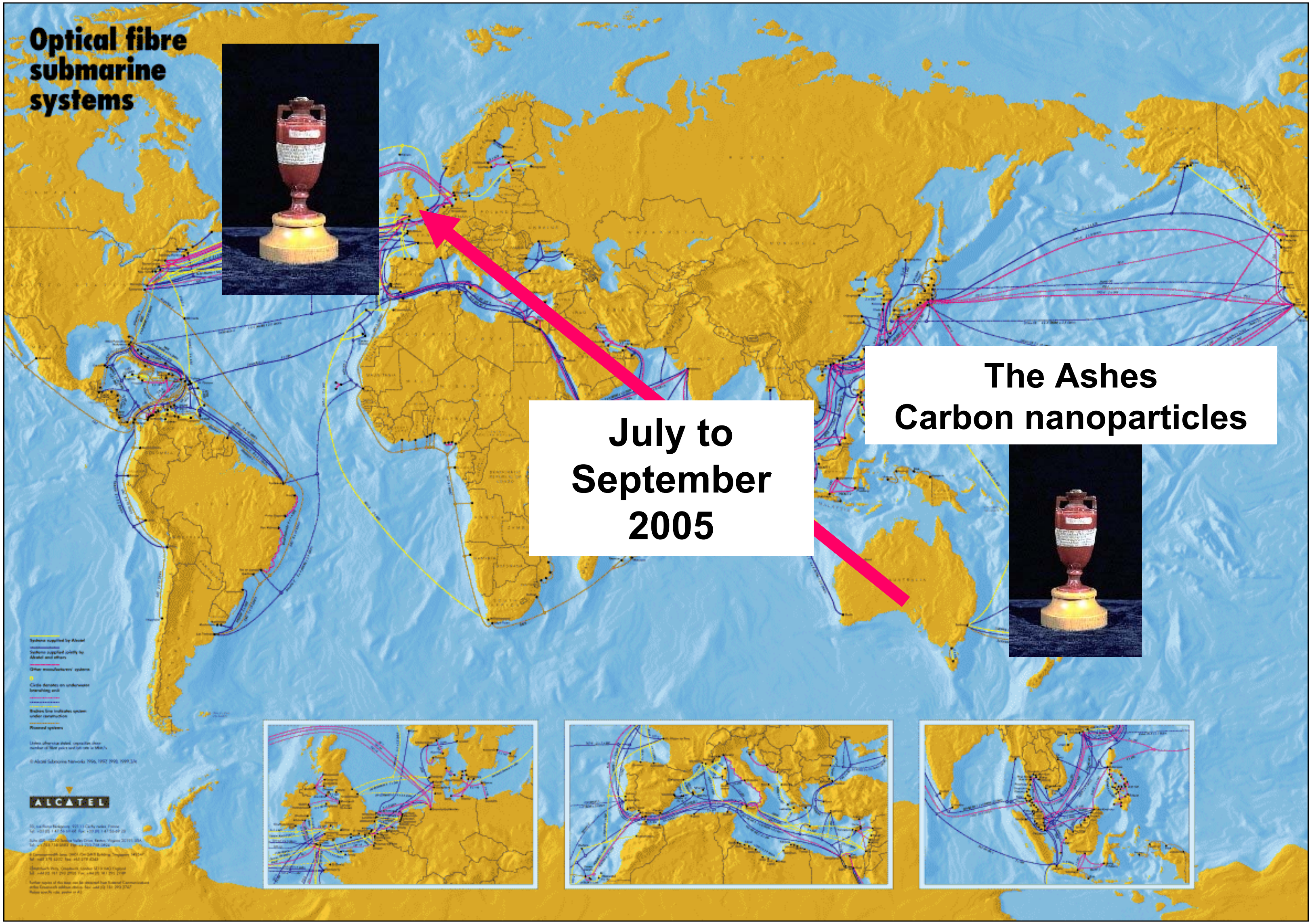
CHALLENGES FOR THE FUTURE

1. **Understanding the precise mechanism of diffusion in the nanomaterials.**

2. **Utilising the properties of nanomaterials; particularly stabilizing the structure at high temperature.**

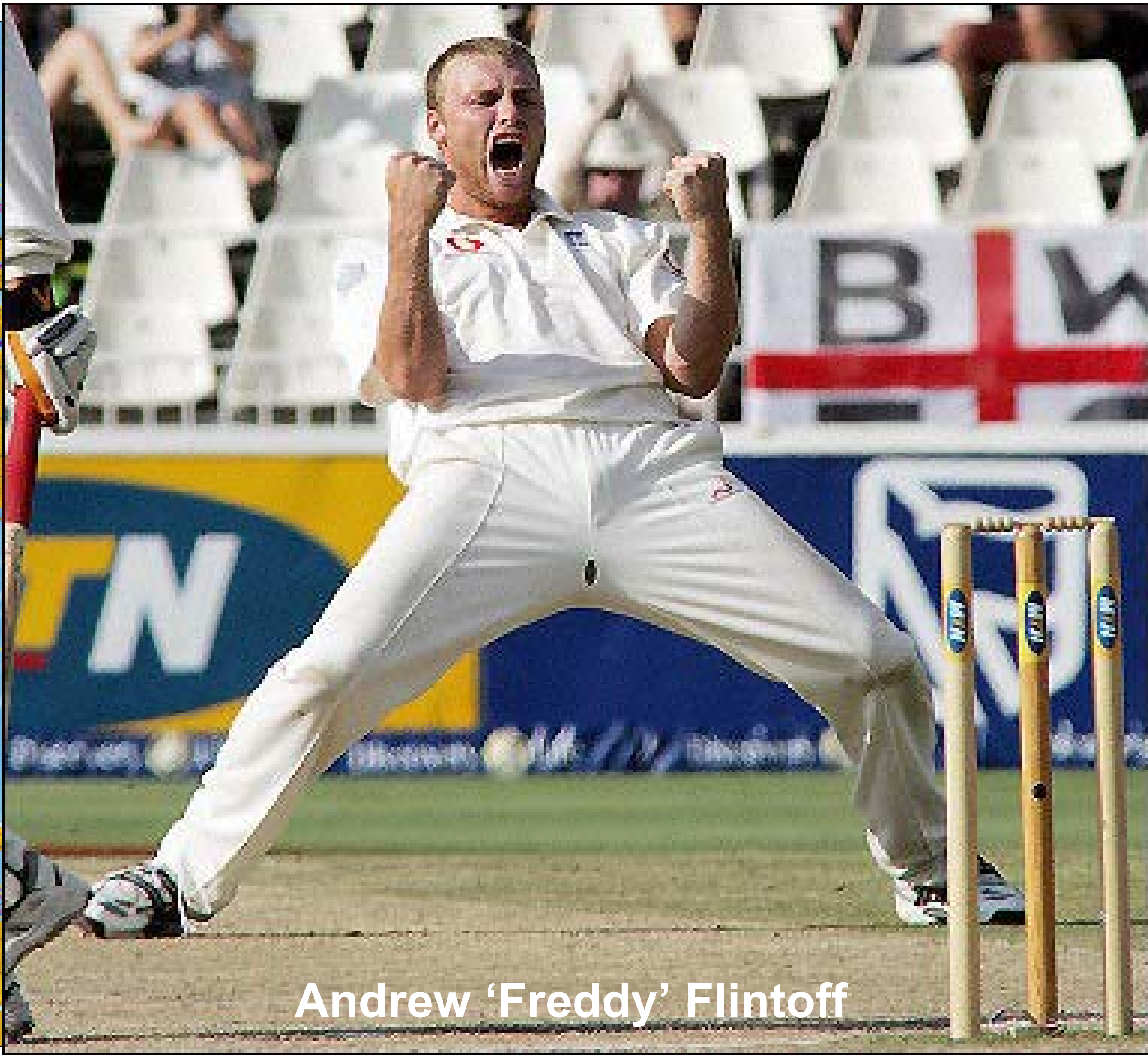
3. **Computer modelling of diffusion in nanomaterials; molecular dynamics.**

THANK YOU FOR YOUR ATTENTION!



July to September 2005

The Ashes
Carbon nanoparticles



Andrew ‘Freddy’ Flintoff