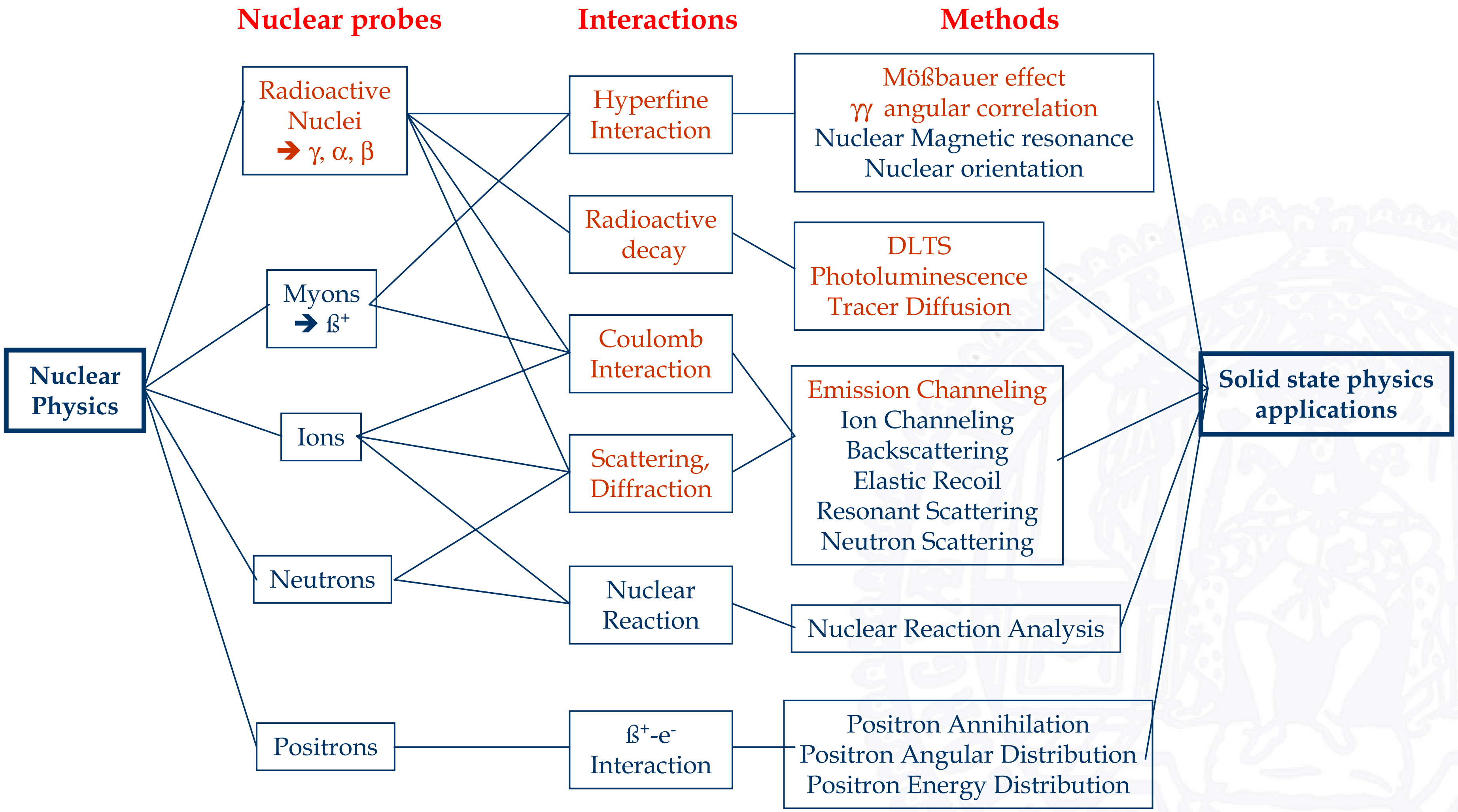
New developments in solid state physics using radioactive ions

A survey by H. Hofsäss

Outline

- Radioactive ion beams for condensed matter physics
- Recent technical and methodical developments
- Possible areas of research (sorted by method):
  - Time Dependant Perturbed Angular Correlation (TDPAC), Mössbauer spectroscopy (MS)
  - Emission channeling (EC)
  - Photo- and Cathodoluminescence (PL/CL), Deep Level Transient Spectroscopy (DLTS)
- Selected examples
  - Phase identification, phase transitions, new phases
  - Diluted magnetic semiconductors , magnetic thin films,
  - High k dielectric materials, optoelectronic materials, photovoltaic materials
  - charge storage materials, diffusion phenomena
- Summary

RIB solid state physics as applied nuclear physics



Nuclear probes

Interactions

Methods

Nuclear Physics

Radioactive Nuclei ➔ γ, α, β

Myons ➔ $ß^+$

Ions

Neutrons

Positrons

Hyperfine Interaction

Radioactive decay

Coulomb Interaction

Scattering, Diffraction

Nuclear Reaction

$ß^+$-e^- Interaction

Mößbauer effect
γγ angular correlation
Nuclear Magnetic resonance
Nuclear orientation

DLTS
Photoluminescence
Tracer Diffusion

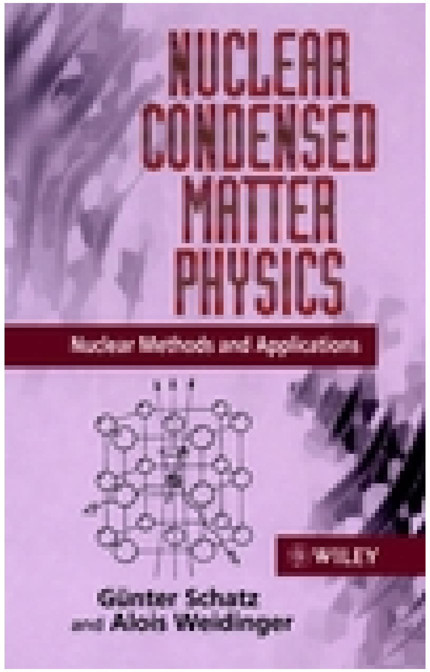
Emission Channeling
Ion Channeling
Backscattering
Elastic Recoil
Resonant Scattering
Neutron Scattering

Nuclear Reaction Analysis

Positron Annihilation
Positron Angular Distribution
Positron Energy Distribution

Solid state physics applications

Textbooks and Reports

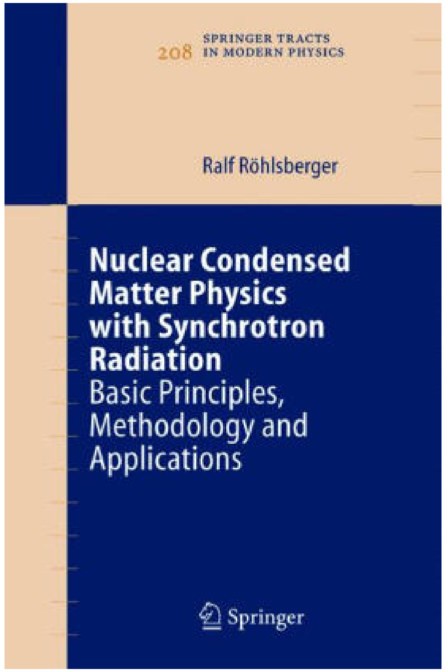


NUCLEAR CONDENSED MATTER PHYSICS

Nuclear Methods and Applications

WILEY

Günter Schatz
and Alois Weidinger



208 SPRINGER TRACTS IN MODERN PHYSICS

Ralf Röhlsberger

Nuclear Condensed Matter Physics with Synchrotron Radiation
Basic Principles, Methodology and Applications

Springer

Komitee für Forschung mit nuklearen Sonden und Ionenstrahlen

Erforschung kondensierter
Materie mit nuklearen
Sonden und Ionenstrahlen
an Großforschungsanlagen
in Deutschland

Status und Perspektiven

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Vol. 208 , 2005

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Berlin, 2003

Some recent review articles

Nuclear probes in life sciences, W. Tröger,
Fakultät für Physik und Geowissenschaften, Universität Leipzig, Germany
Hyperfine Interactions, 120-121 (1999) 117 - 128

A future for nuclear analytical techniques? Why not? P. Bode,
Interfaculty Reactor Institute, Delft University of Technology, Delft, The Netherlands
Analytical and Bioanalytical Chemistry 379 (2004) 181 - 187

Nuclear Resonant Scattering into the New Millennium, R. Rüffer,
European Synchrotron Radiation Facility (ESRF), Grenoble, France
Hyperfine Interactions 141-142 (2002) 83 - 97

Radioactive isotopes in solid state Physics, M. Deicher,
Fachbereich Physik, Universität Konstanz, Konstanz, Germany
Europhysics News (2002) Vol. 33

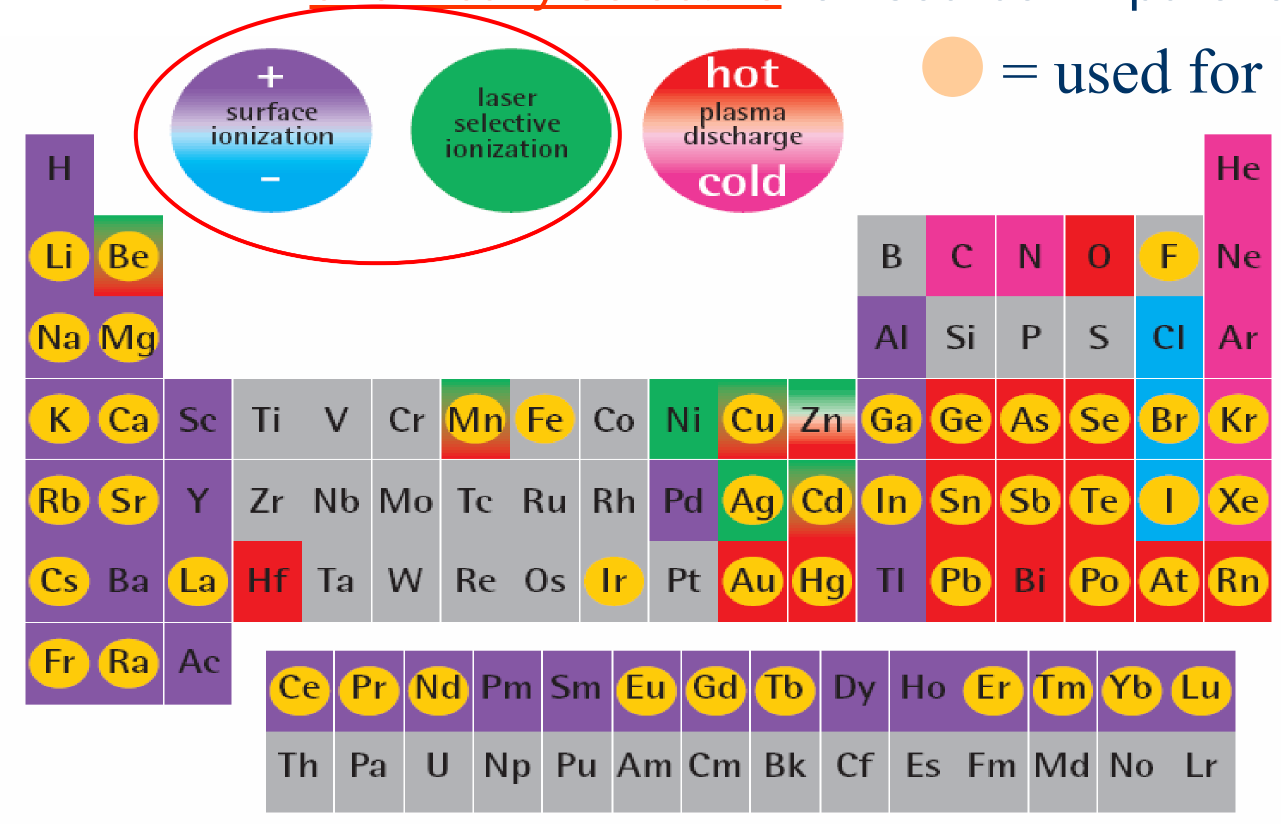
Project Research on the Condensed Matter with Short-Lived Nuclei, M. Seto
Progress report 2002, Materials Science and Radiation effects,
Kyoto University, Research Reactor Institute.

Studies of semiconductors
Th. Wichert, M. Deicher,
Technische Physik, Universität des Saarlandes, Saarbrücken, Germany),
Nuclear Physics A693, 2001, 327-357.

Unique features of radioactive probe atoms and radioactive ion beams

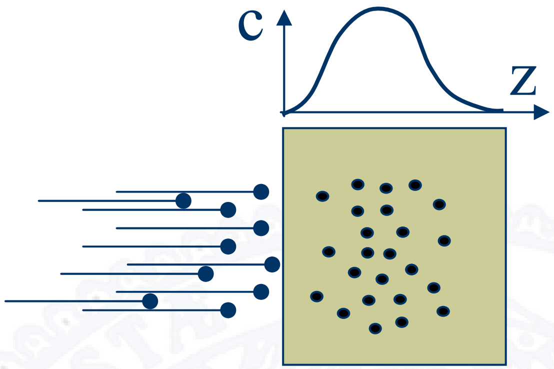
- Large variety of isotopes available at ISOLDE
- chemically selective ion source ➔ pure ion beams

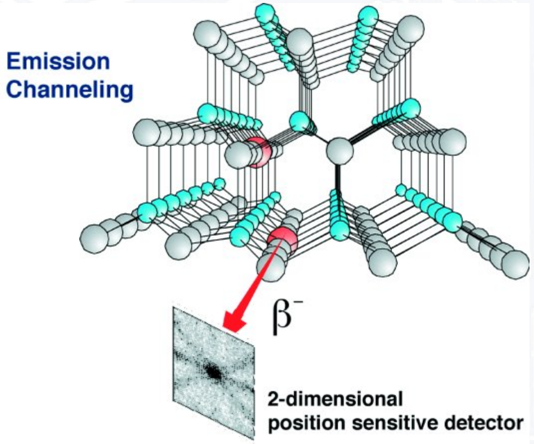
● = used for SSP and life sciences



Unique features of radioactive probe atoms for SSP applications

- **Chemically selective and isotope specific**
- **Extremely good detection limit**
    - among the most sensitive methods,
      no reaction cross section limitation
        - 10^{15} - 10^{18} probes/cm^3
        - 10^{11} - 10^{12} probe atoms
- **Depth distribution and concentration control**
    - Ion energy and ion fluence control
    - Circumventing solubility and diffusion limits
- **Highly local Information**
    - Nucleus-size sensors for **local** magnetic and electric fields
      Electric Field Gradient ~ r^{-3}
      Emission channeling: ~ 0.02 nm position resolution





Why radioactive probes ? Sensitive – Selective - Controllable - Local

Recent technical and methodical developments

TDPAC: Improved efficiency and time resolution, compensation for multiplier drift

- **LYSCO and LUAP Scintillators** : efficient detectors for TDPAC gammas, Efficiency comparable to NaJ,
  Timing < 1ns, energy resolution 7%, chemically robust
- **Fast Digitizer cards**: 1-5 GS/s, real time data analysis

EC: Efficient decay electron imaging

- Position sensitive PAD detectors
- Position sensitive CCD sensors,
  high count rate (> 10 kHz) , low noise, high energy resolution (< 3 keV)

PL/CL: Efficient PL/CL spectroscopy in the UV region

- Compact UV lasers (Diode pumped Nd:YAG, 266 nm, 8mJ/puls, 8ns)
- CCD detectors for UV an soft X-rays

Scintillator crystals for TDPAC

(Developed for advanced PET scanners)

Property	LYSO	LuAP
Density Z_{eff} Stopping Power Attenuation length	7.1 (10% Y) 64 135 1.2	8.3 66 148 1.04
Energy Resolution	~10%	7-9%
Photo Fraction	36%	30%
Light Yield	1.2	~0.5
Decay Time	~40 ns	17 ns
Physically Robust	Hard	Hard
Timing Resolution	<450ps	500ps

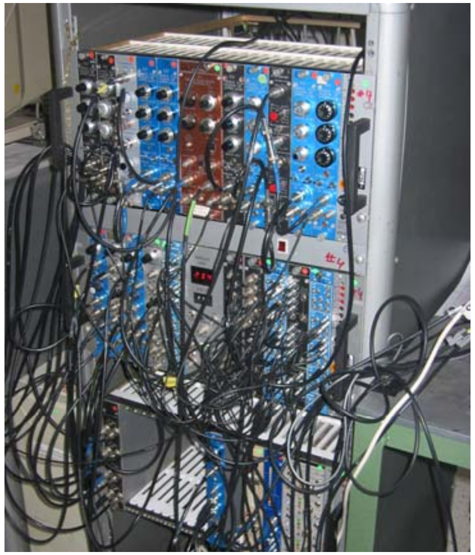
LuAP - $LuAlO_3{:}Ce$

LYSO - $Lu_{2(1-x)}Y_{2x}SiO_5{:}Ce$

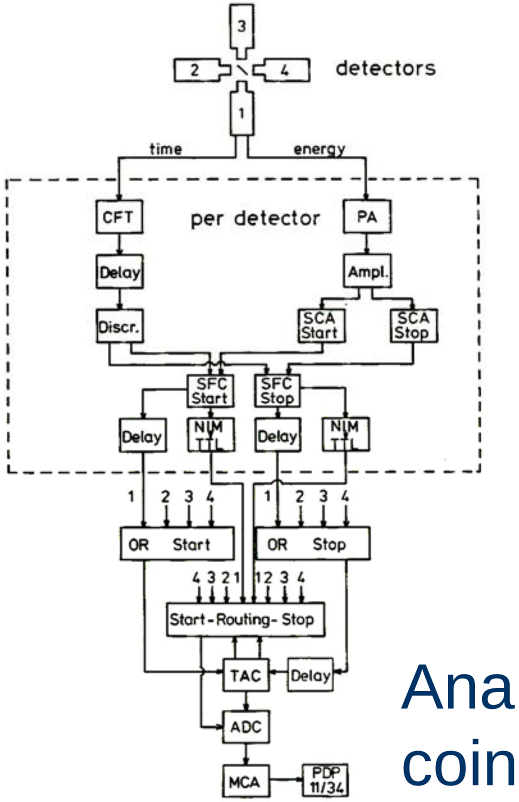
(Source: Photonic materials)

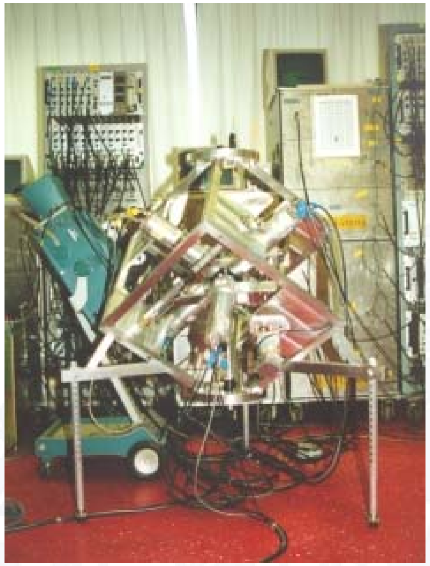
Good Photoefficiency, Light yield, Time resolution, Energy resolution

Conventional TDPAC setup



Source: Univ. Göttingen





Source: Univ. Leipzig

Analog slow-fast coincidence scheme …

… will be replaced by ……

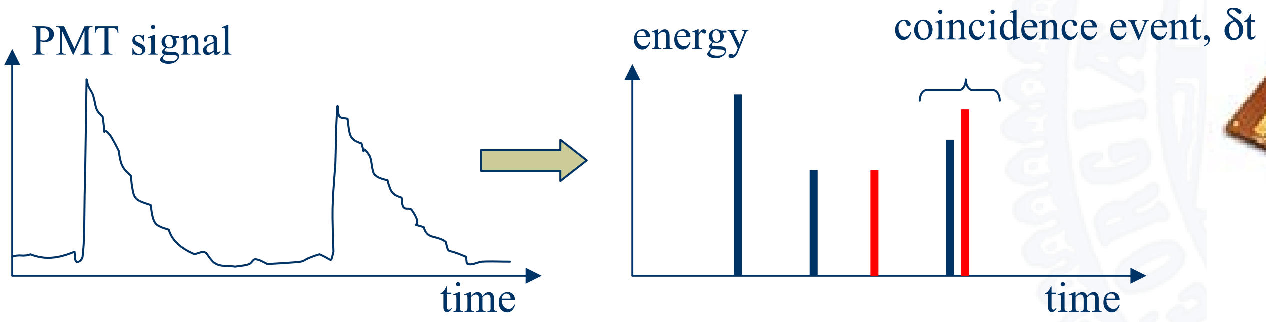
Fast digitizer cards

Applications: RADAR, LIDAR, SATCOM, TOFMS, scanning acoustic tomography, plasma physics, gamma spectroscopy

Commercial systems:

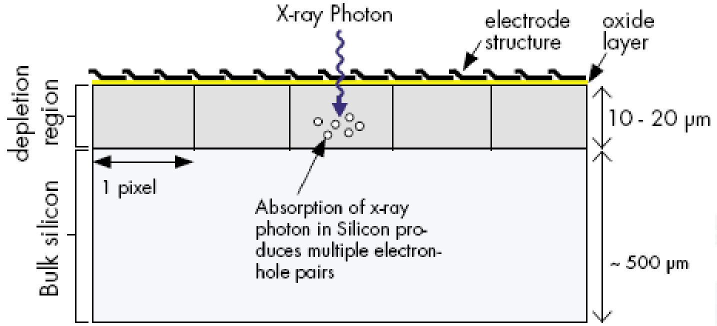
- GaGe compuscope 82 G 2GS/s 8 bit
- GaGe compuscope 85 G 5GS/s 8 bit
- Acqiris DC222 8 GS/s 10 bit
- Acqiris SC240 2GS/s 10 bit (streamer analyzer)
- Acquitek ADC3200 2GS/s 10 bit
- Delphi 2GS/s 8 bit
- EONIC DAR 1.5 GS/s 8 bit

- **Improved timing**
- **Reduced false coincidences**
- **Eliminates PMT drift**
- **Higher count rates**



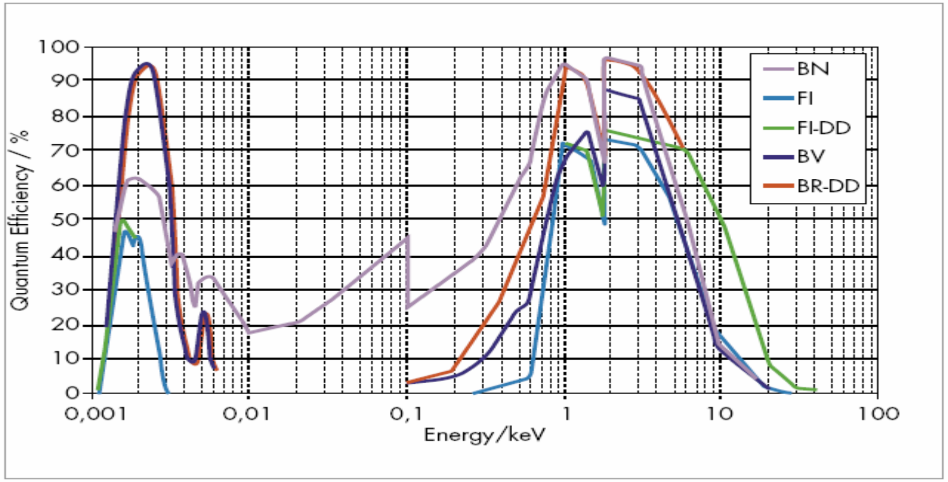
"Blue shift" in optoelectronics - Lasers and CCD detectors for UV light

Diode-pumped, Q-switched pulsed
Nd:YAG laser (LOT-Oriel)
45 mJ at 1064 nm, 100 Hz in 7ns pulses
8 mJ at **266 nm, 100Hz in 8ns pulses**



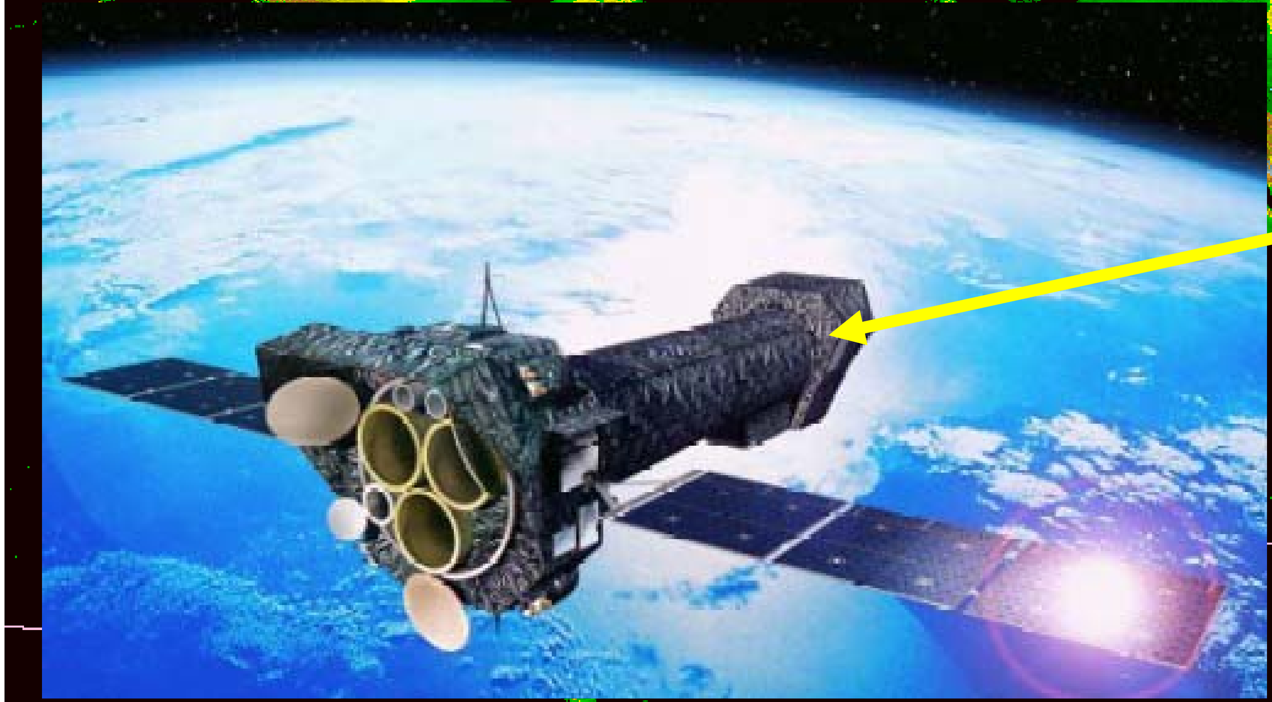
Centurion with SHG/THG module and power supply

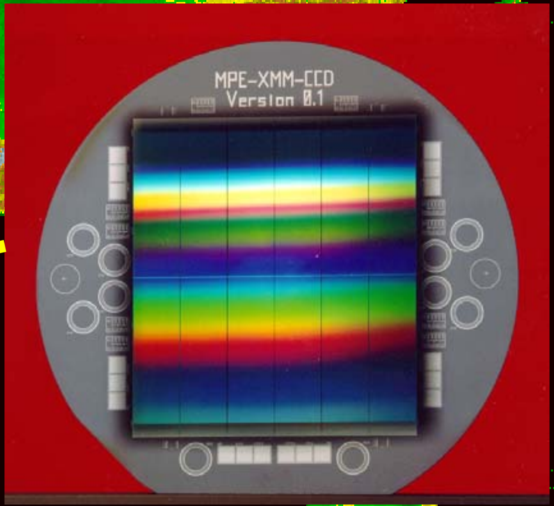
Quantum efficiency of ANDOR CCDs



Efficient UV PL/CL studies on wide band gap materials

X-ray CCD-Sensors for decay electron imaging





12 Modules at
64 x 200 Pixel
3 x 1 cm^2

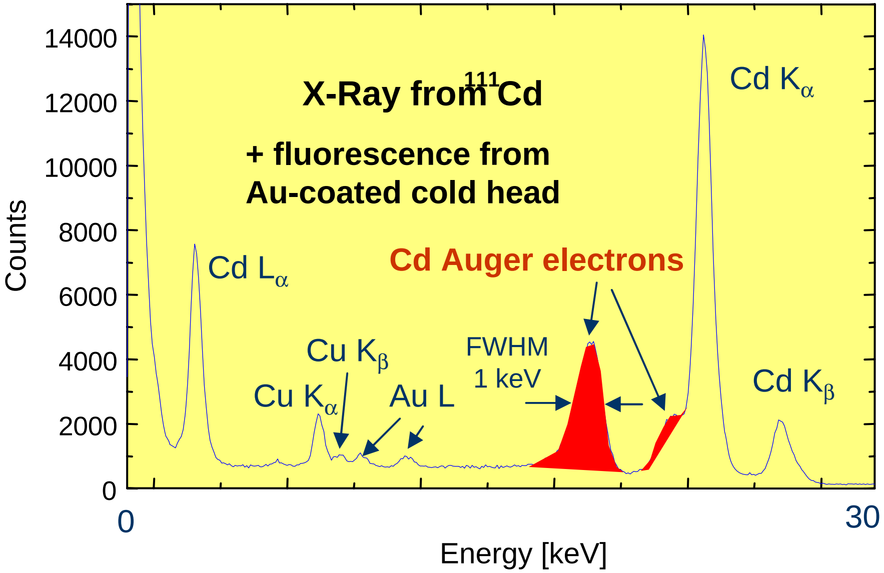
XMM-NEWTON
esa

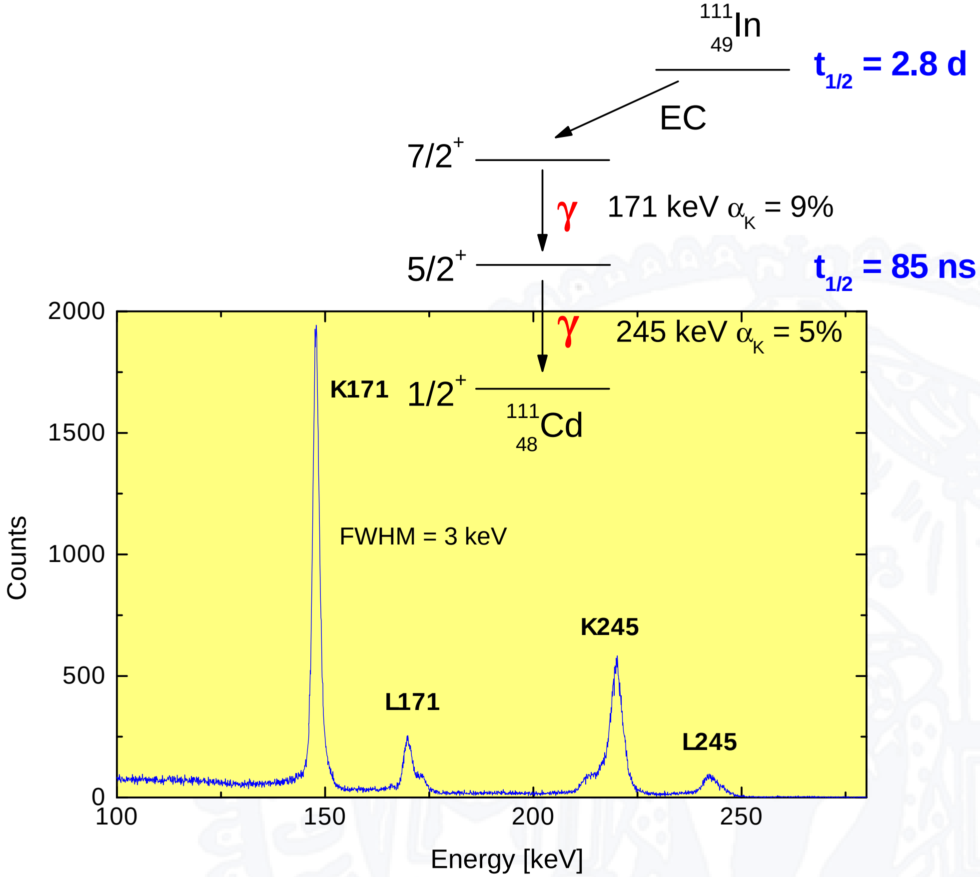
. . . spin-off from X-ray astronomy

X-ray CCD sensor of decay electron imaging spectroscopy

- **64 x 200 Pixel   Pixel size: 150 x 150 μm^2**
- **300 μm pn-CCD from FZ-Si (5 kΩcm)**
- **Noise: 5 e^- ENC (180 K) ;   readout: 4.5 ms**

Semiconductor lab, MPI for Extra-terrestric Physics, Munich





High count rate, low noise, low energies, excellent energy resolution

Possible areas of research

TDPAC and Mössbauer Spectroscopy

Nuclear probes as sensors inside the nanoworld

- Nanopartices, Nanowires, nm-sized layered thin films, Nanocomposite Materials, Macromolecules
- Probe atoms at surfaces and interfaces

Nuclear probes as local magnetic field sensors

- Magnetic properties of clusters and nanocrystalline films
- Heavy fermion systems, Magnetoresistive materials
- Understanding magnetic hyperfine fields in solids

Possible areas of research

TDPAC and Mössbauer Spectroscopy

Understanding advanced materials

- Phase transitions and phase identification
- Impurity defect interactions with light ions H, Li, …
  - Charge storage materials, Li batteries, Ultracapacitors
  - Passivation phenomena in wide band gap semiconductors
- Interface and grain boundary processes , Point defects in intermetallic compounds and alloys, radiation damage effects
- New materials as advanced thin film coatings
- Diluted magnetic semiconductors (TM:ZnO, TM:GaN)
- New high k dielectric materials (Pr_2O_3, HfO_2, . . .)
- Ternary photovoltaic compounds

Life Science

- Biological and pharmaceutical tracer studies

Possible areas of research

Emission channeling

Lattice location studies in UV/VIS optoelectronic materials

- Rare earth elements in wide band gap semiconductors
    - GaN, AlN, ZnO, c-BN, diamond, SiC, sapphire
- Rare earth elements and other color center impurities in Quartz
    - Utilize epitaxial recrystallization of quartz
- Dopant atoms in cubic boron nitride (the “forgotten” III-V semiconductor)

Lattice location and defect interaction of light impurities, Li, Na, ..

- Li diffusion in charge storage materials
- Li diffusion in some wide band gap semiconductors

Lattice location studies in diluted magnetic semiconductors

- Mn doped ZnO and GaN

Lattice location studies in combination with Mössbauer spectroscopy

- Crystalline thin film materials

Towards lattice location of atoms near surfaces

Possible areas of research

PL/CL Spectroscopy of semiconductor materials

UV/VIS optoelectronic materials

- Energy levels of impurity centers
- Annealing of implantation damage
- Transmutation doping studies
- Investigation of Antisite defects, DX centers

DLTS Spectroscopy of semiconductor materials

Detecting deep levels - “the dark matter of semiconductors”

- Identification of deep level centers
- Measuring energy levels
- Correlation to charge carrier lifetimes

Tracer diffusion

Still the most sensitive and most specific way to study diffusion processes

Selected examples

- **Phases and phase transitions in compounds systems:**
  In_2S_3 : a candidate as Li storage material

- **Tracing local environments in complex materials:**
  Phase transition in Mn-oxide

- **Tracing magnetic textures without external B-fields:**
  applications for TDPAC and Mössbauer studies

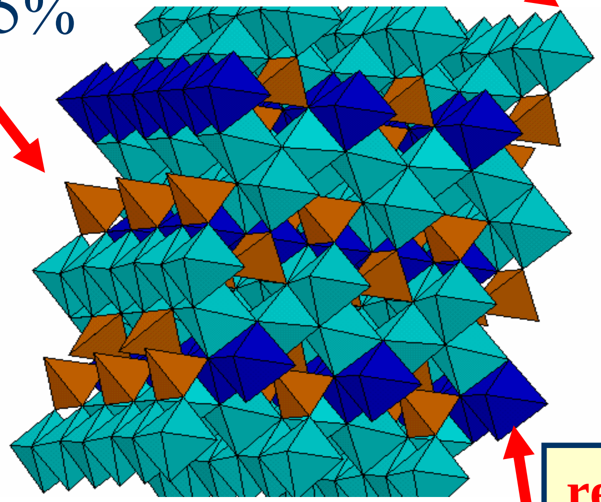
- **MAX Phases:** even more complex future materials; a playground for TDPAC and Mössbauer studies

- **High k dielectric materials**

- **Diluted magnetic semiconductors:**
  Lattice location studies as a key to the local microstructure

Selected examples

β - In$_2$S$_3$



distorted octahedra

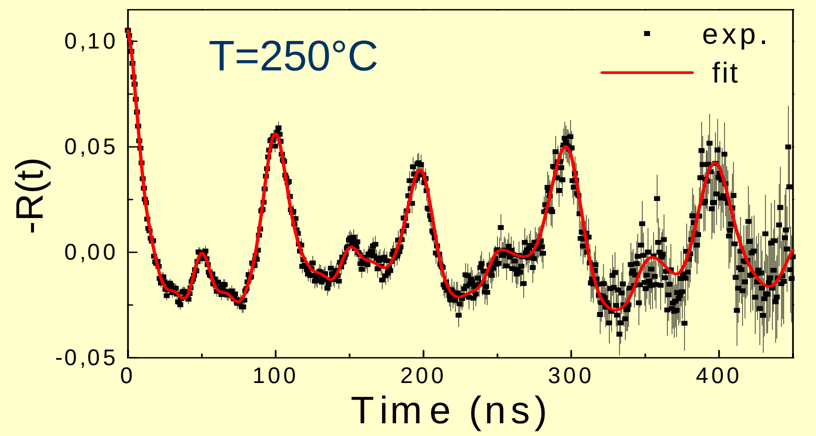
50%

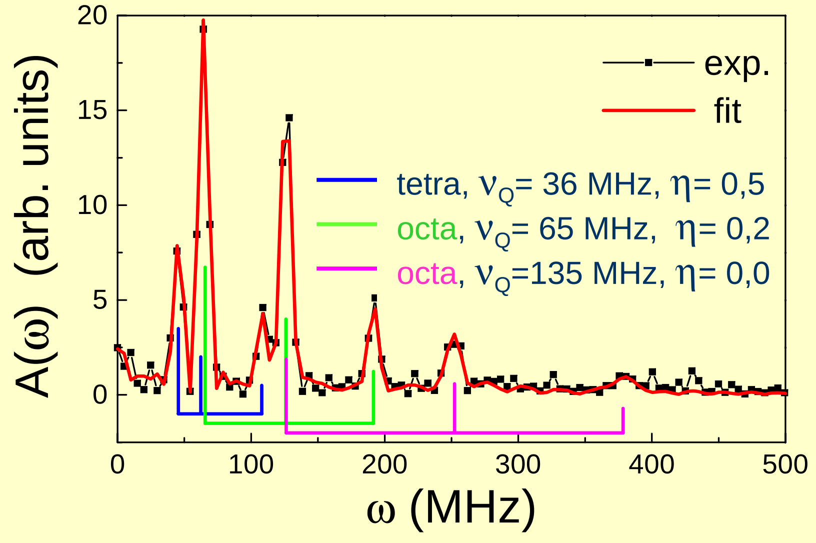
tetrahedra

25%

regular octahedra

25%

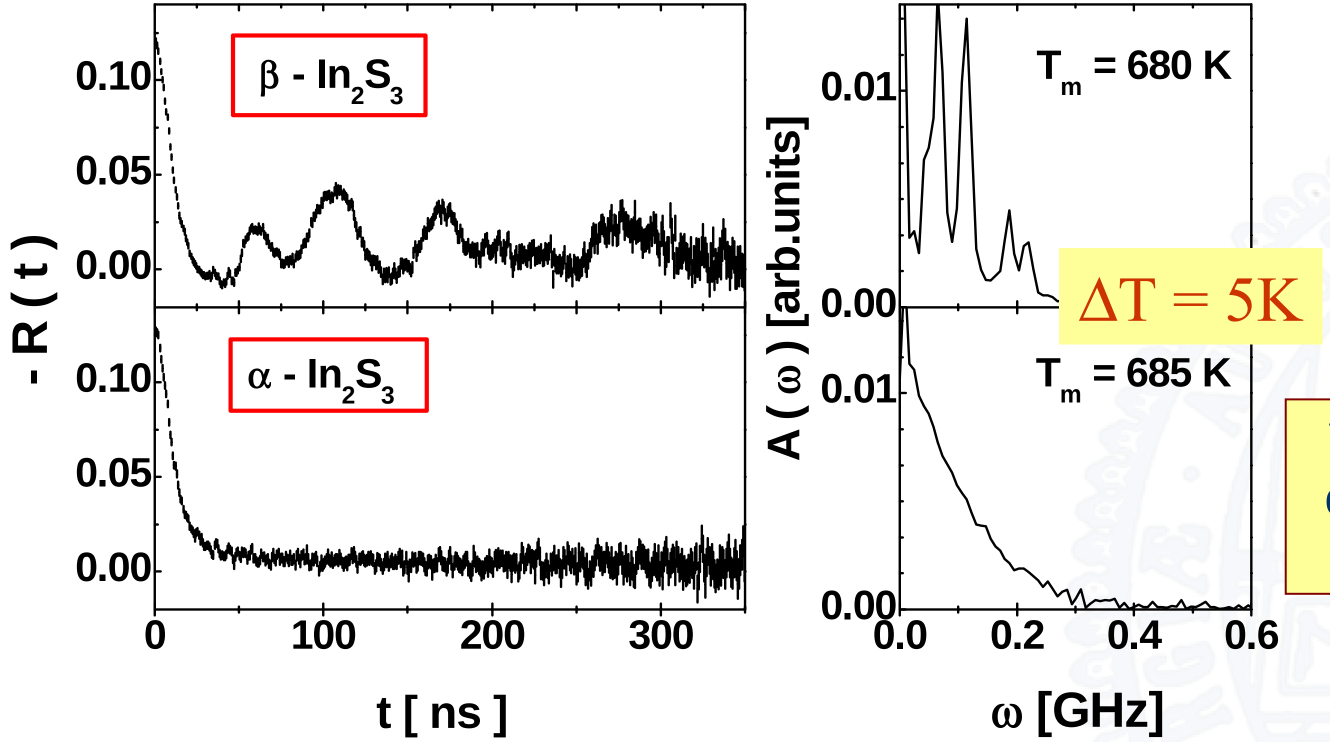




L. Aldon, et al., ***Phys. Rev. B*, 58 (1998)** 11303

Selected examples

$\beta \rightarrow \alpha$ Phase Transition in In_2S_3



$\Delta T = 5K$

Vanishing signature due to highly mobile Indium

Kulinska et al., J. Sol. State Chem. 177 (2004) 109

L. Aldon, et al., Phys. Rev. B, 58 (1998) 11303

Selected examples

Li doped In_2S_3 with mobile Li atoms

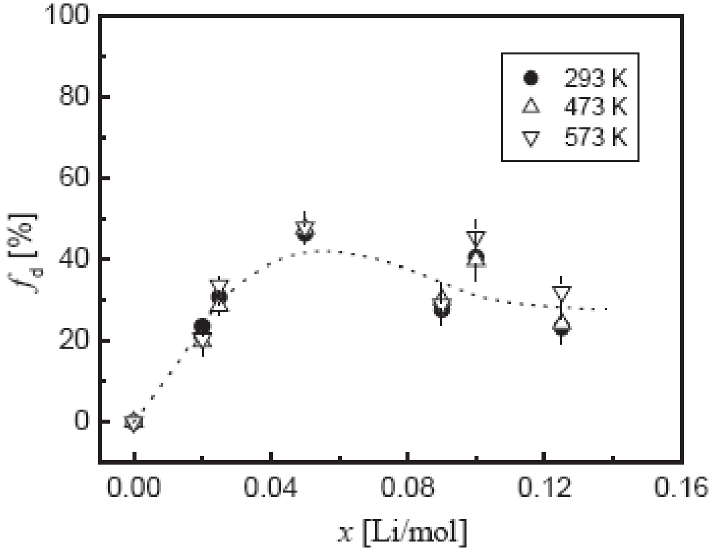


Fig. 6. The change of the dynamic fraction f_d with the Li content x in $Li_xIn_2S_3$.

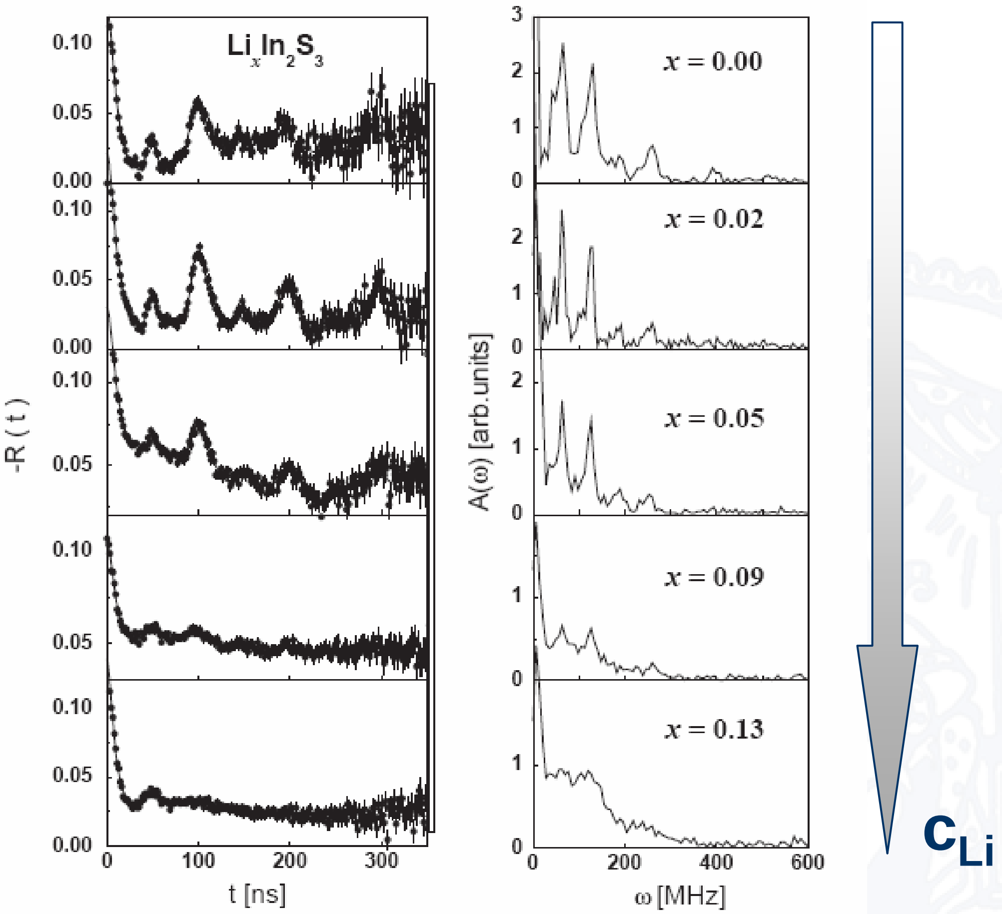
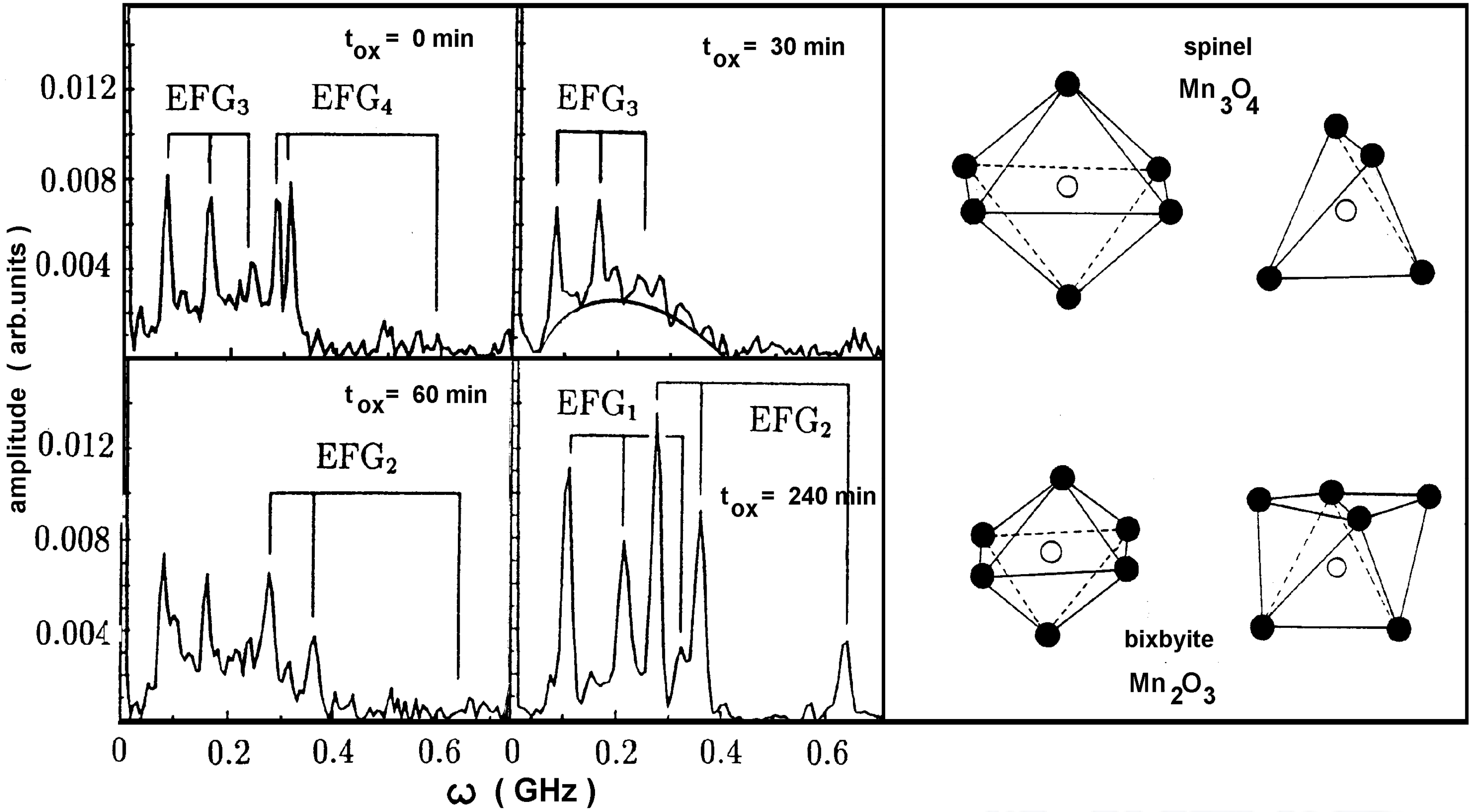


Fig. 4. PAC patterns and Fourier transforms taken at $T_m = 473$ K for ^{111}Cd in $Li_xIn_2S_3$ for different Li contents x.

Kulinska et al., J. Sol. State Chem. 177 (2004) 109

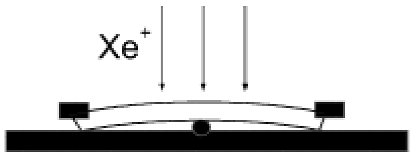
Selected examples

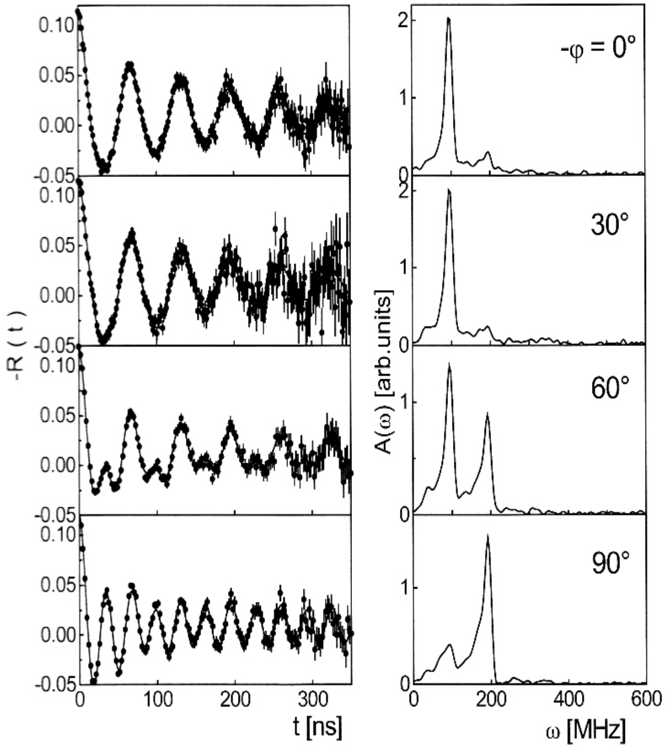
structural phase transition: $Mn_3O_4 \rightarrow Mn_2O_3$



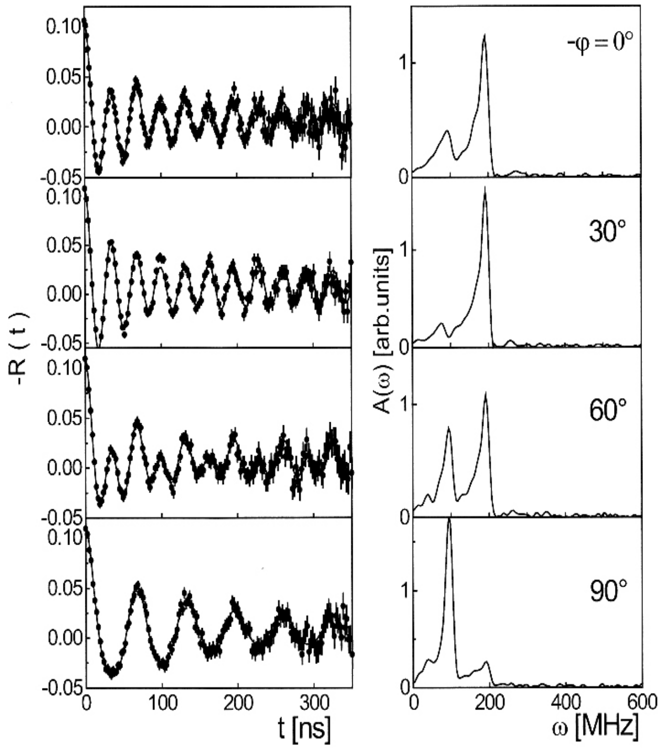
Selected examples

change of the magnetic texture in Ni seen by TDDPAC





Xe-irradiated and bent film

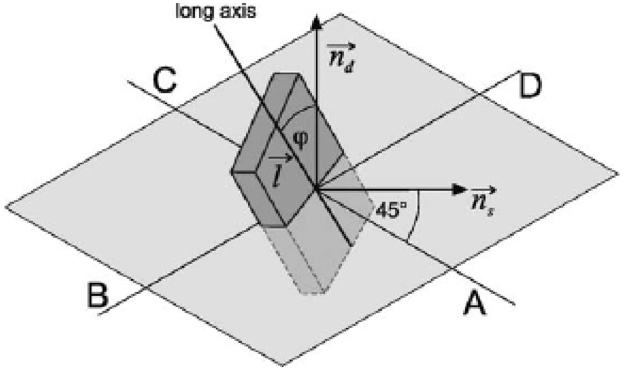


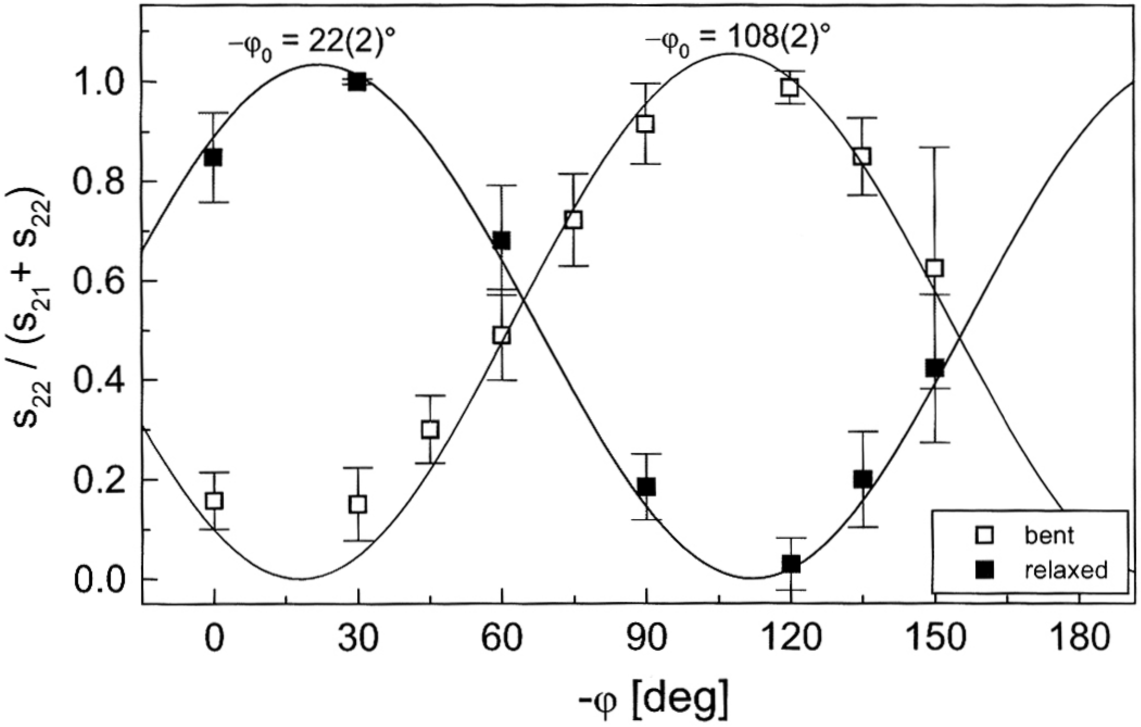
Relaxed film

G.A.Müller, et al., Hyp.Int.**151/152(**2003)223

Selected examples

change of the magnetic texture in Ni seen by TDPAC





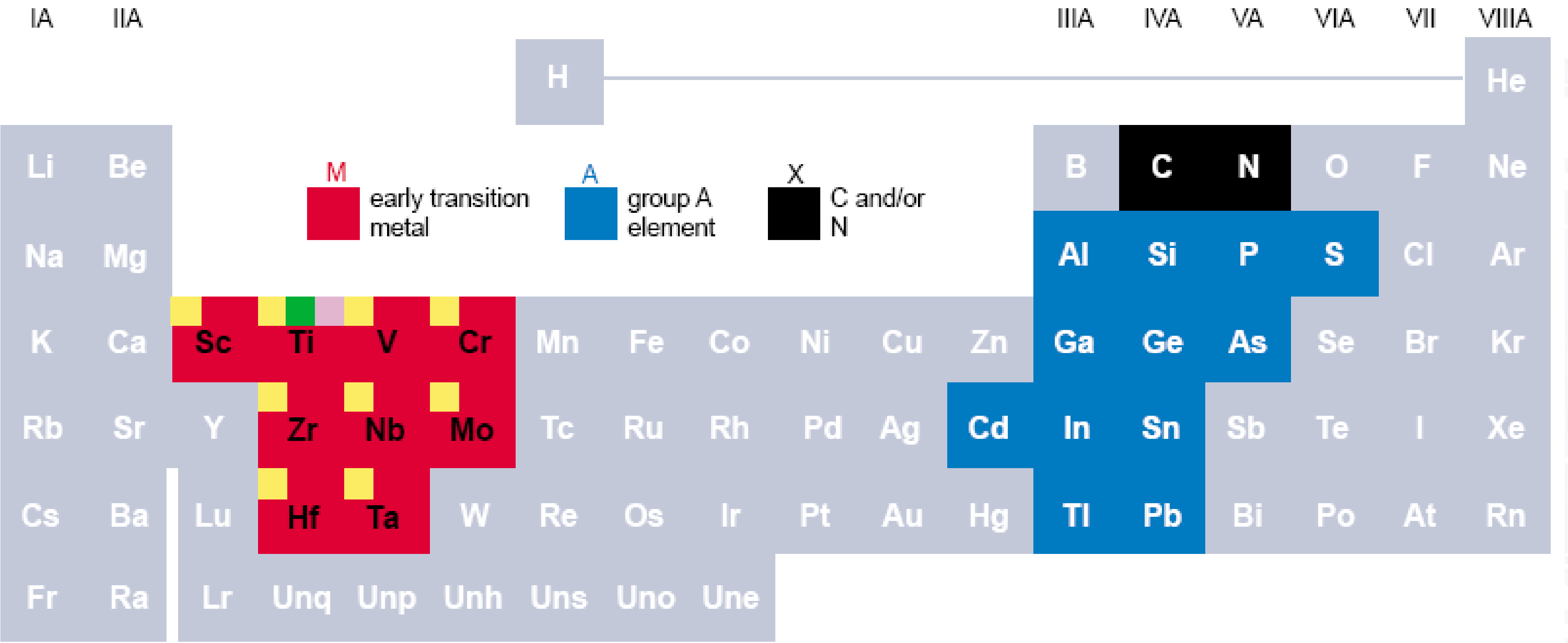
In-plane magnetic texture rotates after relaxation

G.A.Müller, et al., Hyp.Int.**151/152(**2003)223

Selected examples

MAX phases, unique carbide and nitride materials

Michel W. Barsoum and Tamer El-Raghy, American Scientist 89 (2001) 334



Selected examples

- oxidation resistant
- high mechanical strength
- highly conductive
- superior to other metal alloys

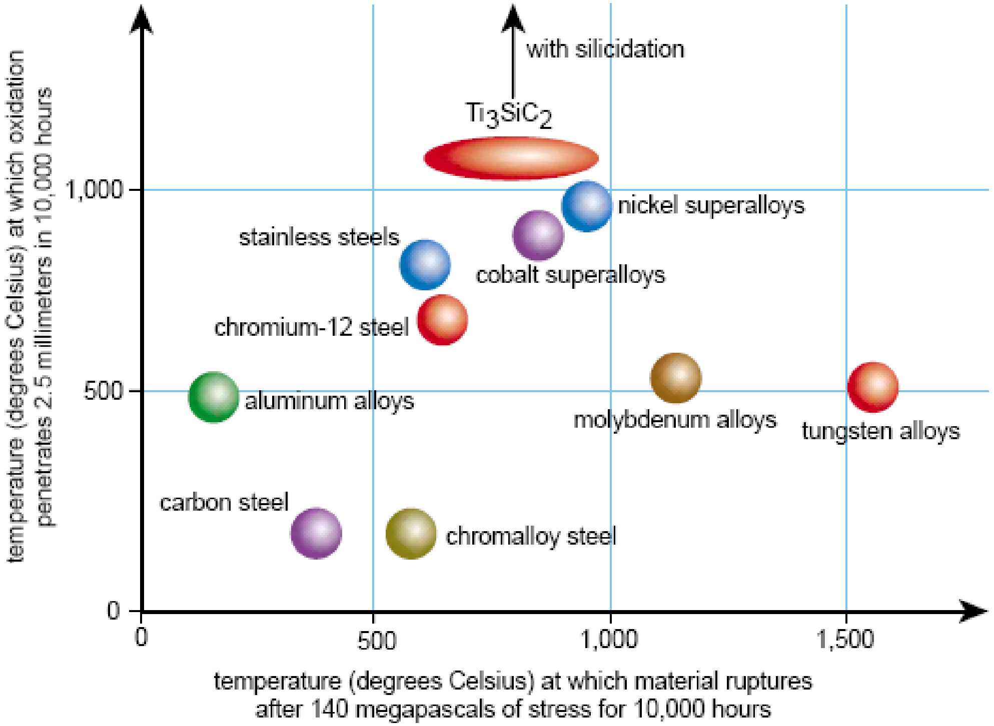
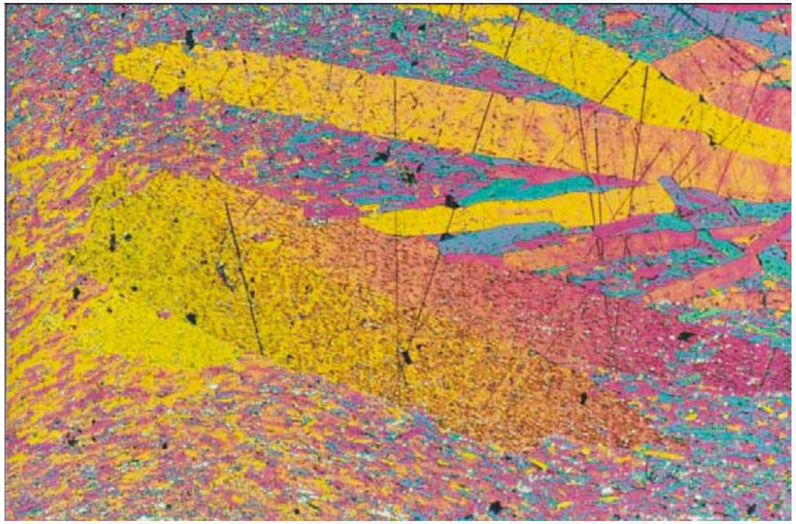
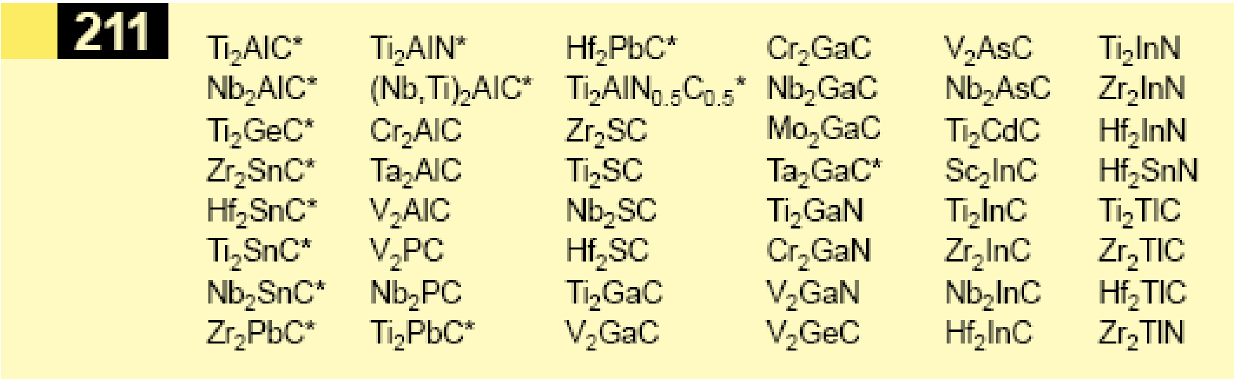


Figure 2. Materials in demanding applications not only must retain their strength, but also need to resist oxidation. The chart shows how some of the most important high-performance alloys stack up against titanium silicon carbide, Ti_3SiC_2. Materials toward the right resist breakage under stress at high temperatures; materials toward the top can reach high temperatures before oxidation attacks the material surface. Titanium silicon carbide exceeds all current materials for oxidation resistance and approaches the nickel superalloys in strength.



Optical micrograph

Selected examples



211

Ti_2AlC^*
Nb_2AlC^*
Ti_2GeC^*
Zr_2SnC^*
Hf_2SnC^*
Ti_2SnC^*
Nb_2SnC^*
Zr_2PbC^*
Ti_2AlN^*
$(Nb,Ti)_2AlC^*$
Cr_2AlC
Ta_2AlC
V_2AlC
V_2PC
Nb_2PC
Ti_2PbC^*
Hf_2PbC^*
$Ti_2AlN_{0.5}C_{0.5}^*$
Zr_2SC
Ti_2SC
Nb_2SC
Hf_2SC
Ti_2GaC
V_2GaC
Cr_2GaC
Nb_2GaC
Mo_2GaC
Ta_2GaC^*
Ti_2GaN
Cr_2GaN
V_2GaN
V_2GeC
V_2AsC
Nb_2AsC
Ti_2CdC
Sc_2InC
Ti_2InC
Zr_2InC
Nb_2InC
Hf_2InC
Ti_2InN
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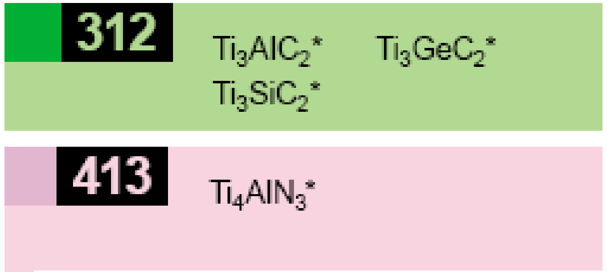
Hf_2TlC
Zr_2TlN

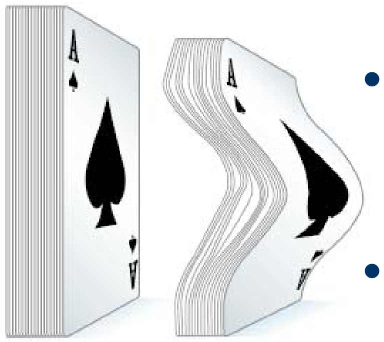


312

$Ti_3AlC_2^*$
$Ti_3SiC_2^*$
$Ti_3GeC_2^*$

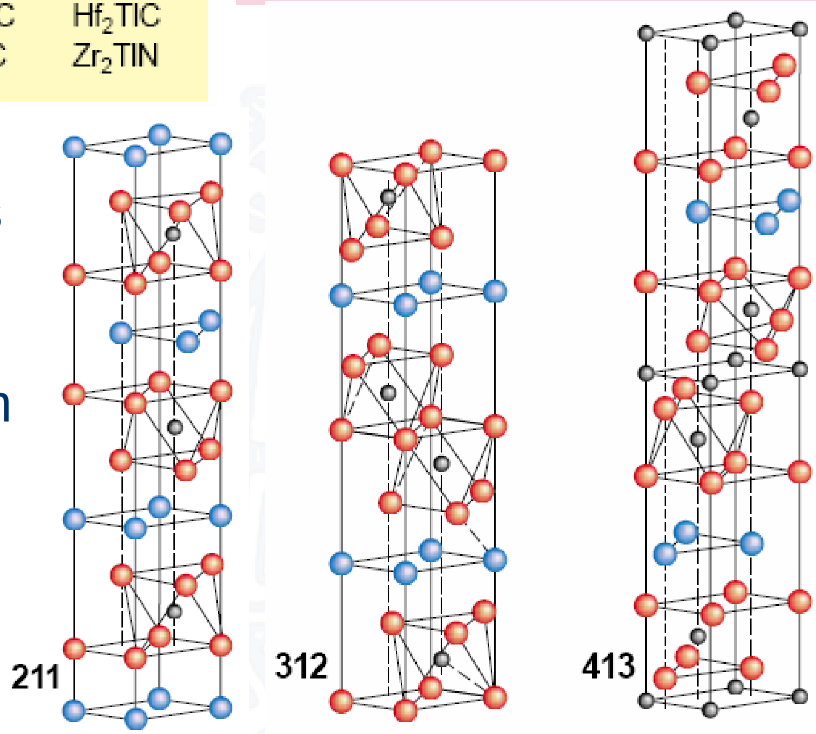
413

$Ti_4AlN_3^*$



- more than 50 compounds need to be explored
- Challenge to grow thin film coatings

- In, Hf and Sn suitable as local probes for TDPAC and MS studies



Selected examples

High k dielectrics on Si: Pr_2O_3, TaO_x, HfO_2, TiO_2

High k gate dielectrics are required for the sub-100 nm MOS structures

- Conventional SiO_2 too thin (e.g. 2 nm) to minimize tunneling currents and out diffusion of boron from the gate.
- A thick layer can be used with high k material to lower the parasitic capacitance between gate and source (drain).

Three types of high k dielectrics:

1. $4 < k < 10$ such as SiN_x;
2. **$10 < k < 100$ such as Ta_2O_5, Al_2O_3, and TiO_2, HfO_2, Pr_2O_3, …**
3. $100 < k$ such as PZT.

Type 2 is most important, e.g. in TFT transistors

Problems to be solved: Interfaces reactions, phase formation, diffusion

Selected examples

High k dielectrics on Si: Pr_2O_3, TaO_x, HfO_2, TiO_2

Problem: Interface SiO_2 formation, crystallinity, phases, interface trap density

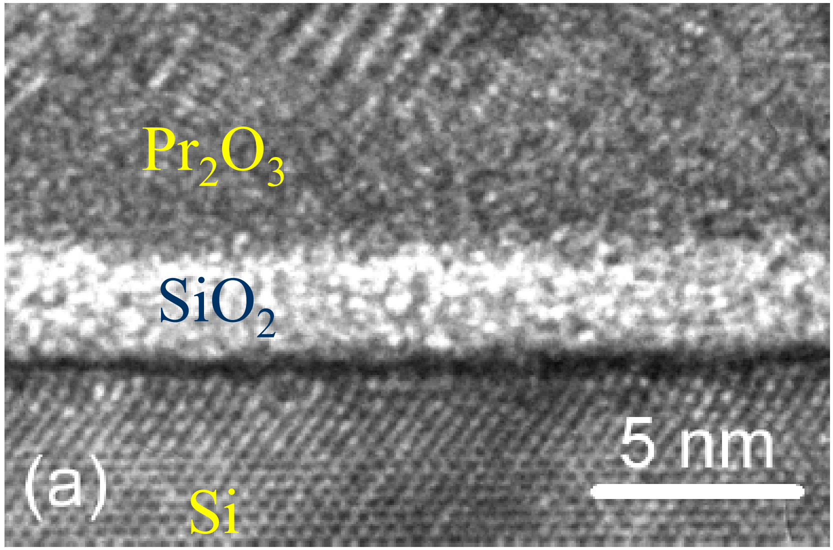
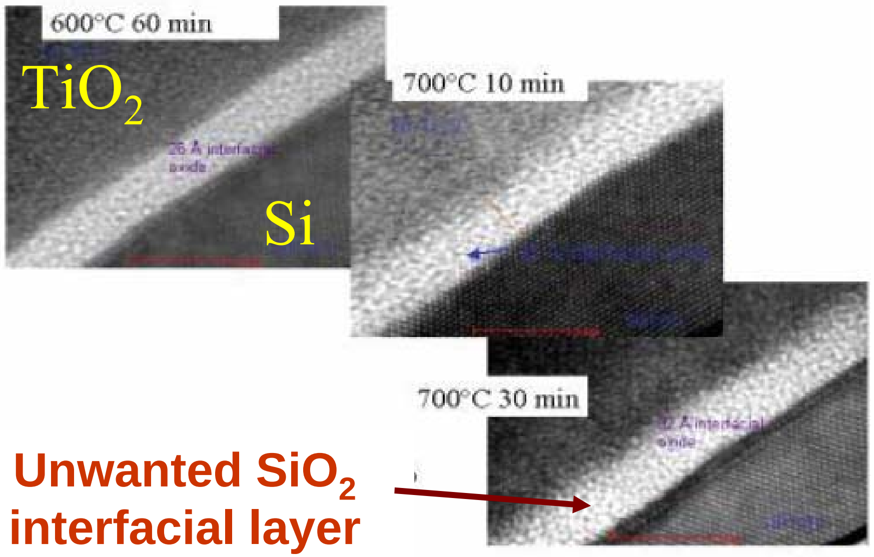


Fig. 3: Cross-sectional TEM images of a Pr_2O_3 film grown on Si(001) without (a) and with (b) a 100 nm thick poly-Si capping layer (grown without leaving the vacuum). The bright amorphous interfacial layer for the film without capping can be attributed to a SiO_x layer due to indiffused oxygen during the contact to air.



Unwanted SiO_2 interfacial layer

(Courtesy of B. Foran of SEMATECH)

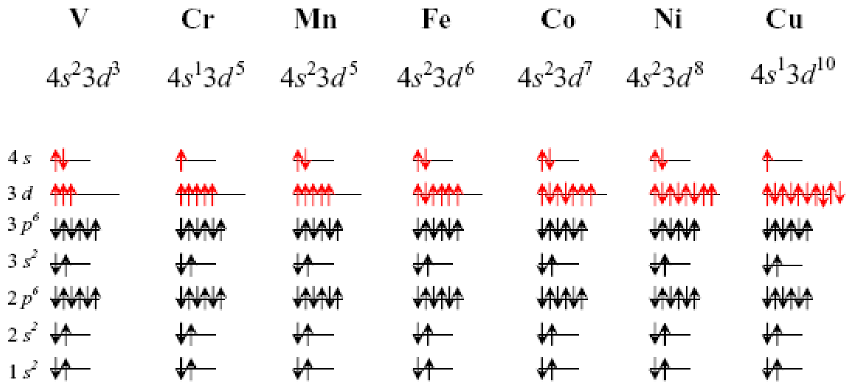
Fissel, JVST B21 (2003) 1765

Osten et al, IWGI 2001, Tokyo

Selected examples

Diluted magnetic semiconductors: TM:ZnO, TM:GaN

C. LIU, F. YUN, H. MORKOC,
JOURNAL OF MATERIALS SCIENCE: MATERIALS IN ELECTRONICS **16** (2005) 555– 597



Electronic configurations of 3d and 4s states

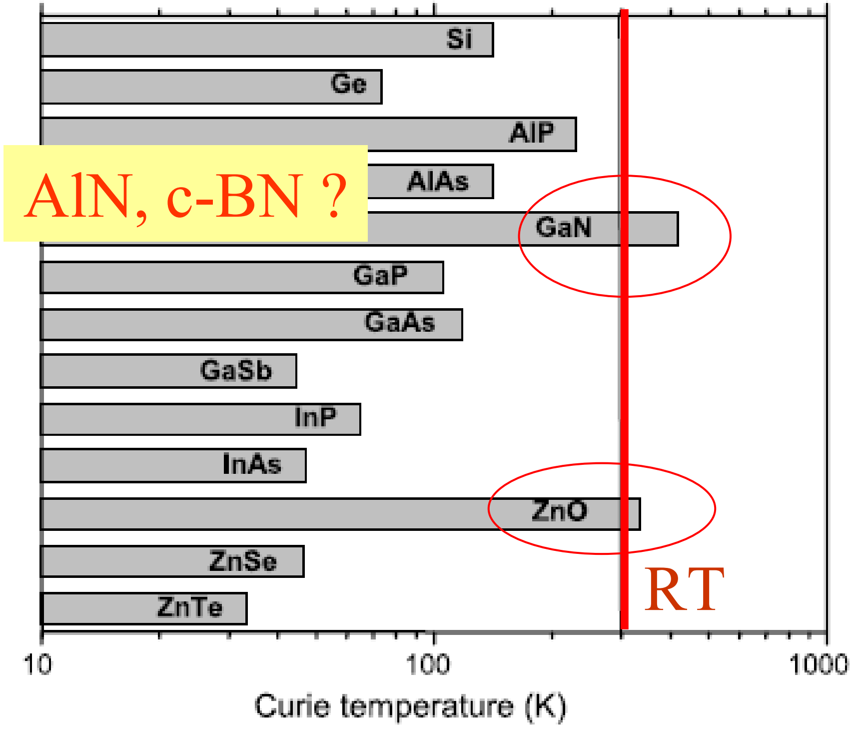
TABLE I Expected oxidation and charge state of some candidate transition metals in ZnO and GaN. Neutral state is referred as the same charge state as that of the cation in the host material, such that Mn^{2+} is the neutral state in ZnO, whereas Mn^{3+} is the neutral state in GaN. The electron configuration for each charge state is given in the first row (after T. Graf *et al.*, ref. 46)

ZnO	$3d^3$	$3d^4$	$3d^5$	$3d^6$	GaN
Acceptor (negative charge)			Cr^+	Mn^+	
Neutral		Cr^{2+}	Mn^{2+}	Fe^{2+}	Acceptor
Donor (positive charge)	Cr^{3+}	Mn^{3+}	Fe^{3+}		Neutral
Double donor (2^+ charge)	Mn^{4+}	Fe^{4+}			Donor

TM atoms: Magnetic impurities with neutral, donor or acceptor character

Selected examples

Diluted magnetic semiconductors: TM:ZnO ; TM:GaN



AlN, c-BN ?

RT

Figure 3 Predicted Curie temperatures as a function of the band gap. Computed values of the Curie temperature T_C for various *p*-type semiconductors containing 5% of Mn and 3.5×10^{20} holes per cm^3. (Reprinted with permission from ref. 3.)

- Required dopant concentration: ~ 5at.%
- No segregation and cluster formation

One of several models…..

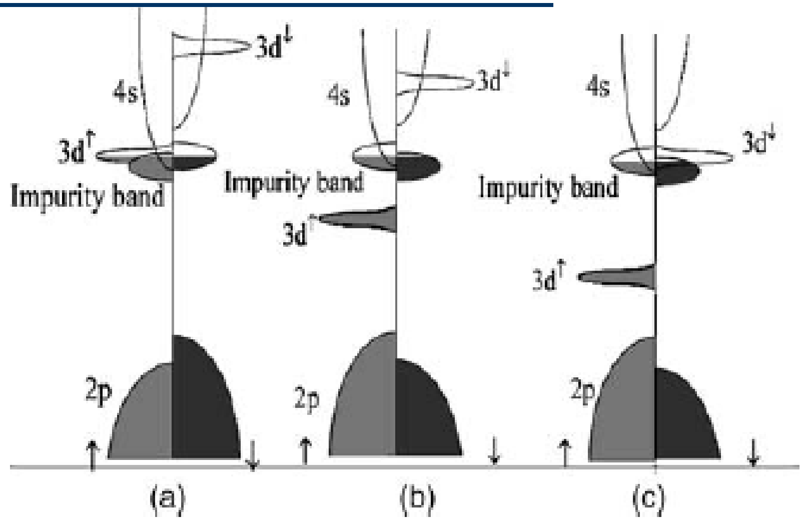
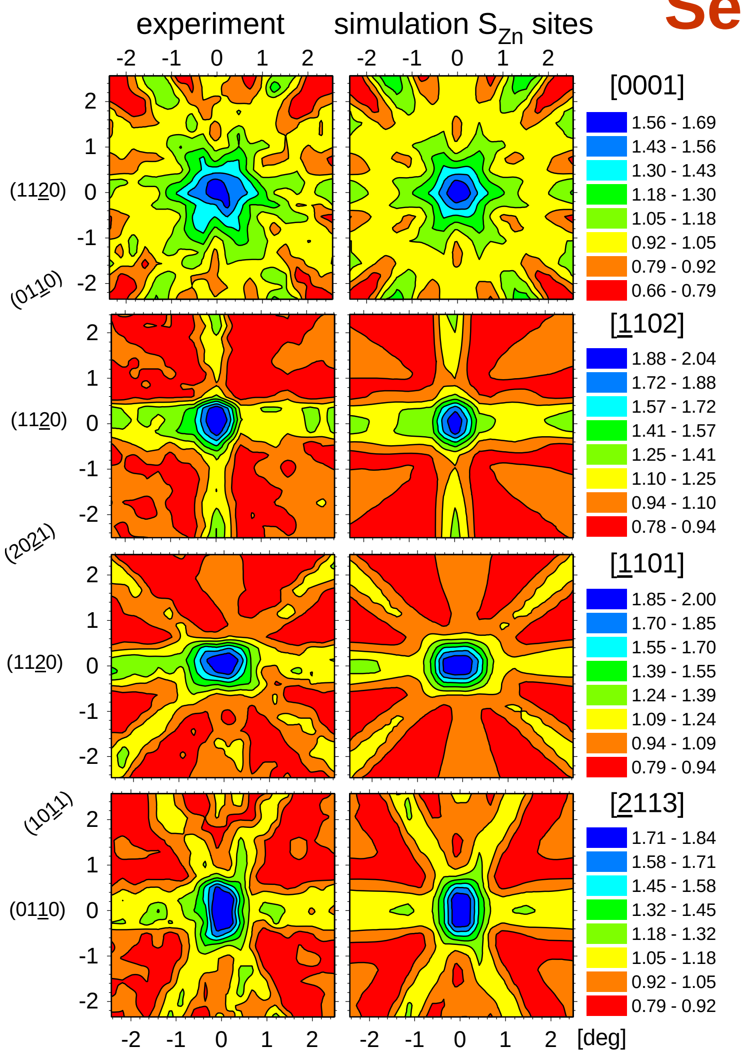


Figure 8 Schematic density of states for (a) TM = Ti, (b) TM = Mn, and (c) TM = Co. The Fermi level lies in a spin-split donor impurity band (after ref. 85). Venkatesan *et al.*

Selected examples



Recent EC studies on: Fe:ZnO

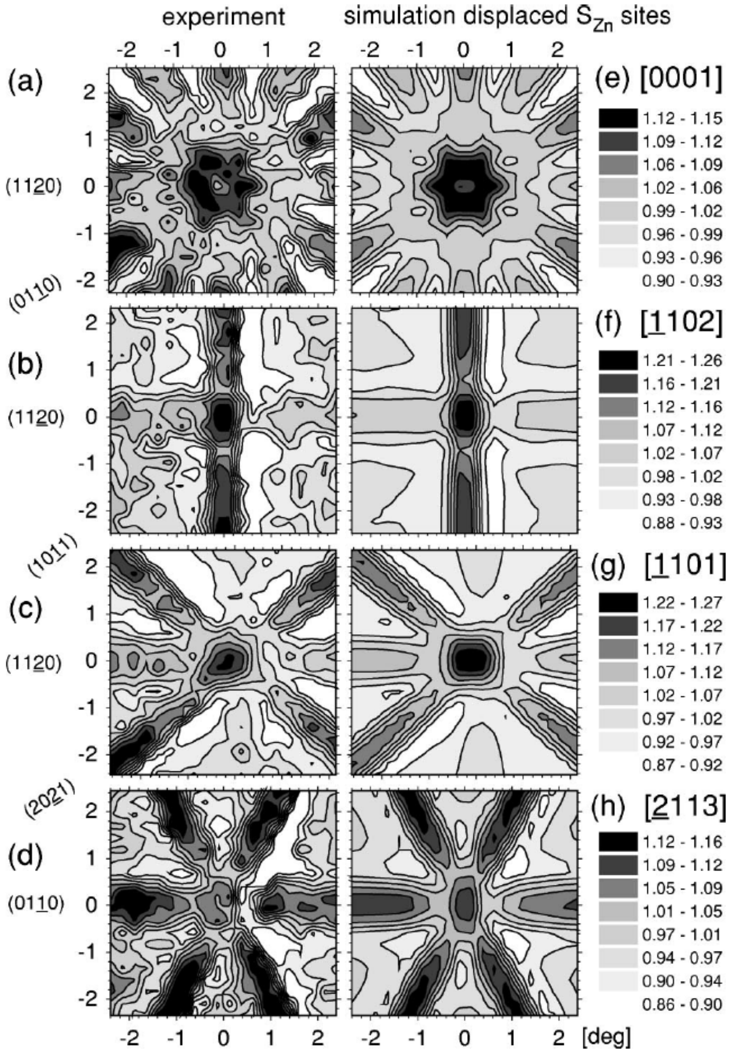
Wahl et al., Appl. Phys. Lett 85 (2004) 4899

^{59}Mn/^{59}Fe($t_{1/2}$ = 44.6 d), $c < 100$ ppm

Fe on substitutional Zn sites
with rms displacement < 0.01 nm

<u>To do:</u> EC studies after doping with stable TM elements up to c ~ 5 at.%

Selected examples



Recent EC studies on: Cu:ZnO

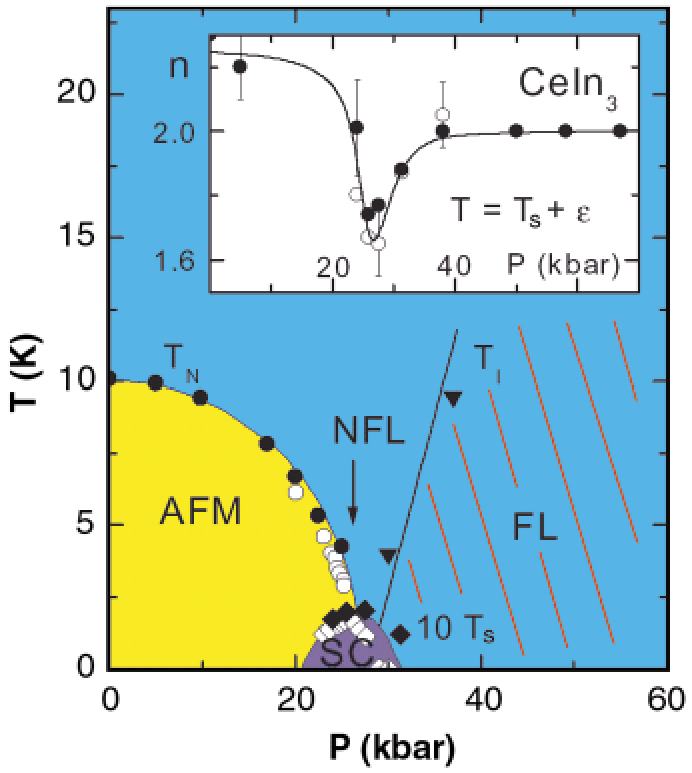
Wahl et al., Physical review B **69**, (2004) 012102

^{67}Cu ($t_{1/2}$ = 61.9 h), c < 100 ppm

Near substitutional Cu with rms displacement of about 0.045 nm

Selected examples

Heavy fermion systems



J.P. Sanchez , CEA-Grenoble, France

(T, P) phase diagram of the anti-ferromagnet CeIn$_3$. T_N and T_I are respectively the Néel temperature and the crossover temperature to the FL regime. The inset shows the pressure variation of the exponent n derived from the low temperature fitting of the electrical resistivity, $\rho = \rho_0 + A_n T^n$. NFL behavior ($n \neq 2$) is observed just at P_c .

Recent TDPAC studies:

Cottenier, Phys. Rev. B 63, 195103 (2001)
Carbonari, Hyp. Int 2001
Tulapurkar, Hyp. Int 1999

Summary

- **Unique features of nuclear probes for solid state studies**
    - Extraordinary good sensitivity and selectivity
      (not achievable with synchrotron radiation resonant scattering)
    - Local probes on a scale of interatomic distances and better
    - Ion implantation provides control of concentration and depth distribution
- **Enhanced efficiency due to technical developments**
    - Highly efficient detectors, Imaging detectors,
    - Fast Digital data acquisition
    - Extended spectral range
    - Quantitative theoretical modelling of complex microstructures
- **Manyfold unexplored areas of research for radioactive probe techniques exist**