Nanoscale Dynamics, Atomic Diffusion

B. Sepiol

Dynamics of Condensed Systems
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Outline

- Our activities
- Benefits from new, brilliant sources

1. Fundamental research
2. New systems

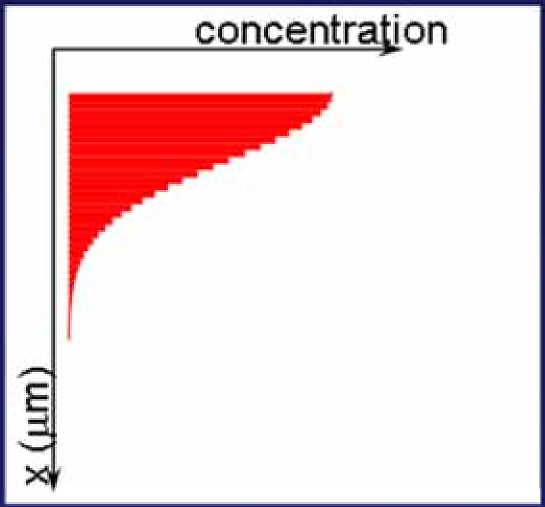
Methods

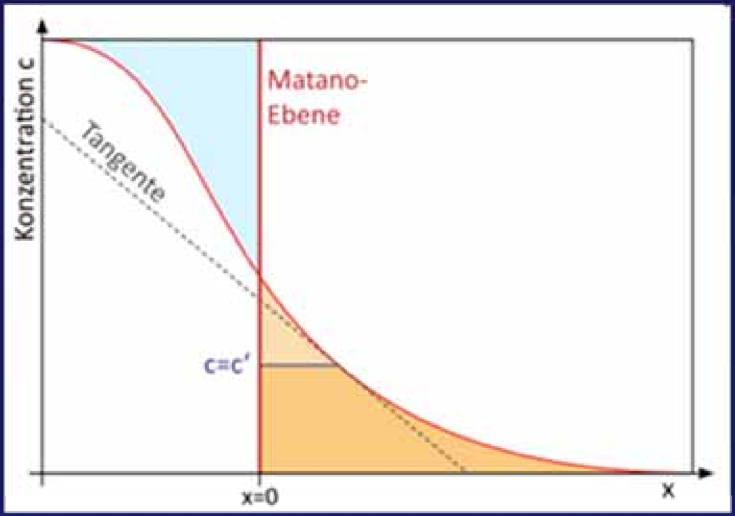
- Mössbauer spectroscopy
- Quasielastic Neutron Scattering
- Nuclear Resonant Scattering – forward,
  grazing incidence and nuclear reflectivity
- Nuclear Inelastic Scattering (NIS)
- X-ray Photon Correlation Spectroscopy

} time and space resolution

Diffusion in solids

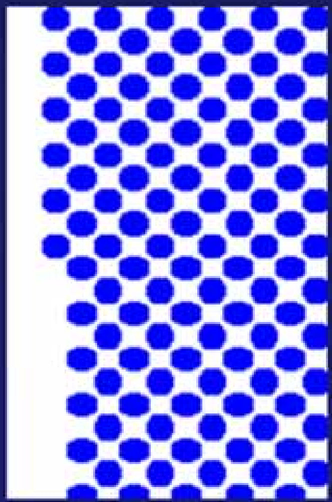
Tracer methods
(macroscopic)

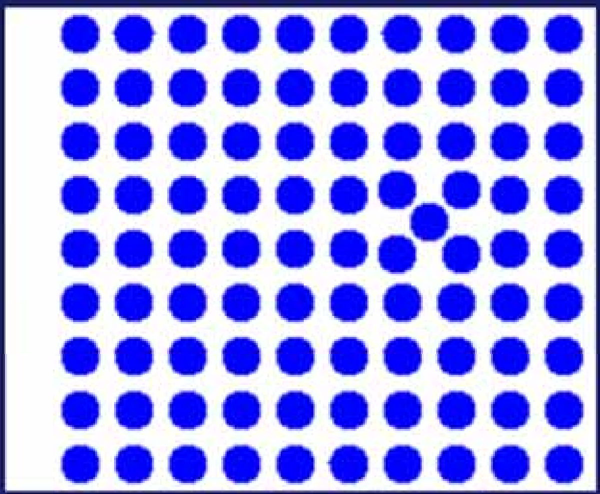




Atomistic methods (microscopic)

Can we determine time-dependence and directions of atomic motion?





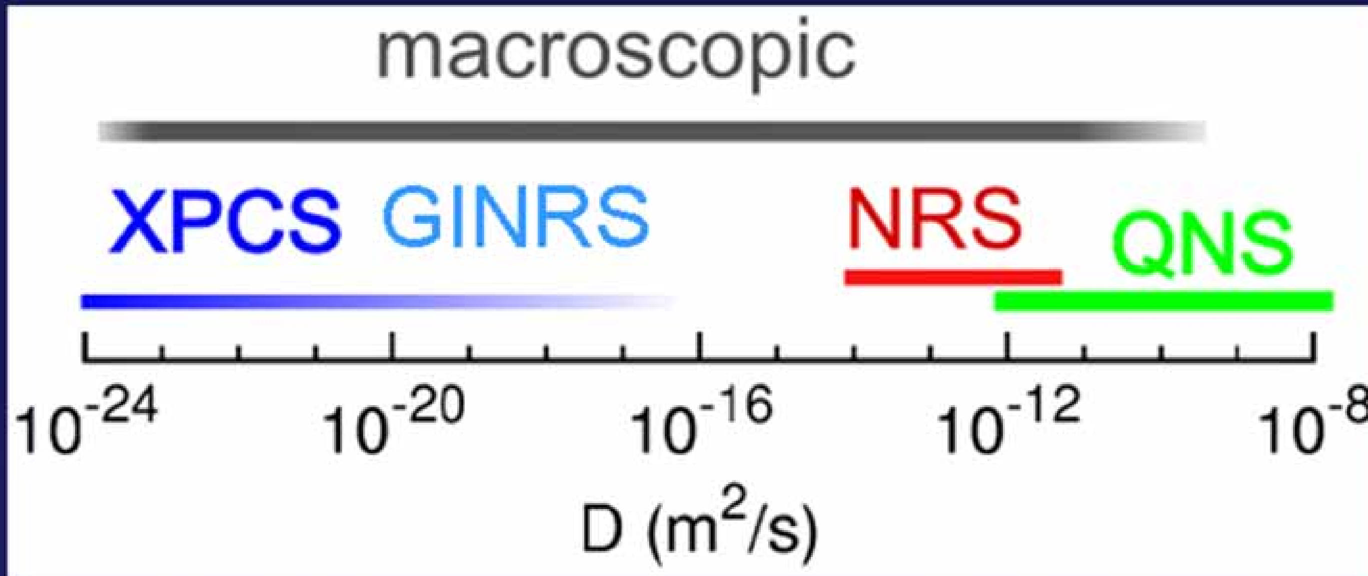
Our primary goal:

overcome limitations of atomistic methods (Mössbauer, QNS, NRS)
to very few elements (^{57}Fe, H, Ni, Co, Ti) and fast diffusion !

(nuclear) reflectivity
„nuclear resonant tracer“

XPCS

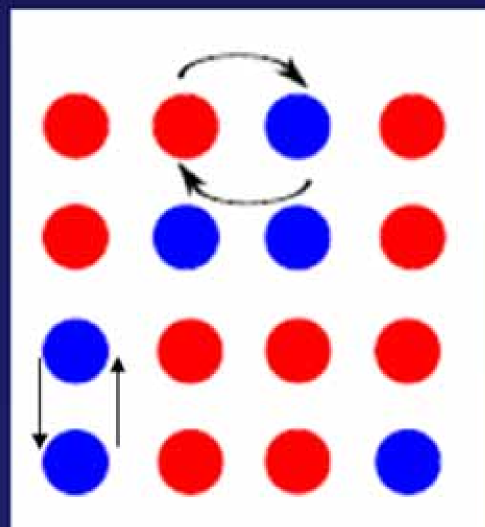
Why is this important?



D [m^2/s]	MSD after 10^5 sec (one day)	Systems
10^{-4}	m	Gases
10^{-9}	cm	Liquids ionic conductors hydrogen in metals
10^{-18}	μm	Solids
10^{-24}	nm	Metals at low/moderate temperatures

$g_2(\boldsymbol{q}, \tau)$ is a pair-correlation function!

Direct consequence: XPCS measures chemical diffusion, not self-diffusion.



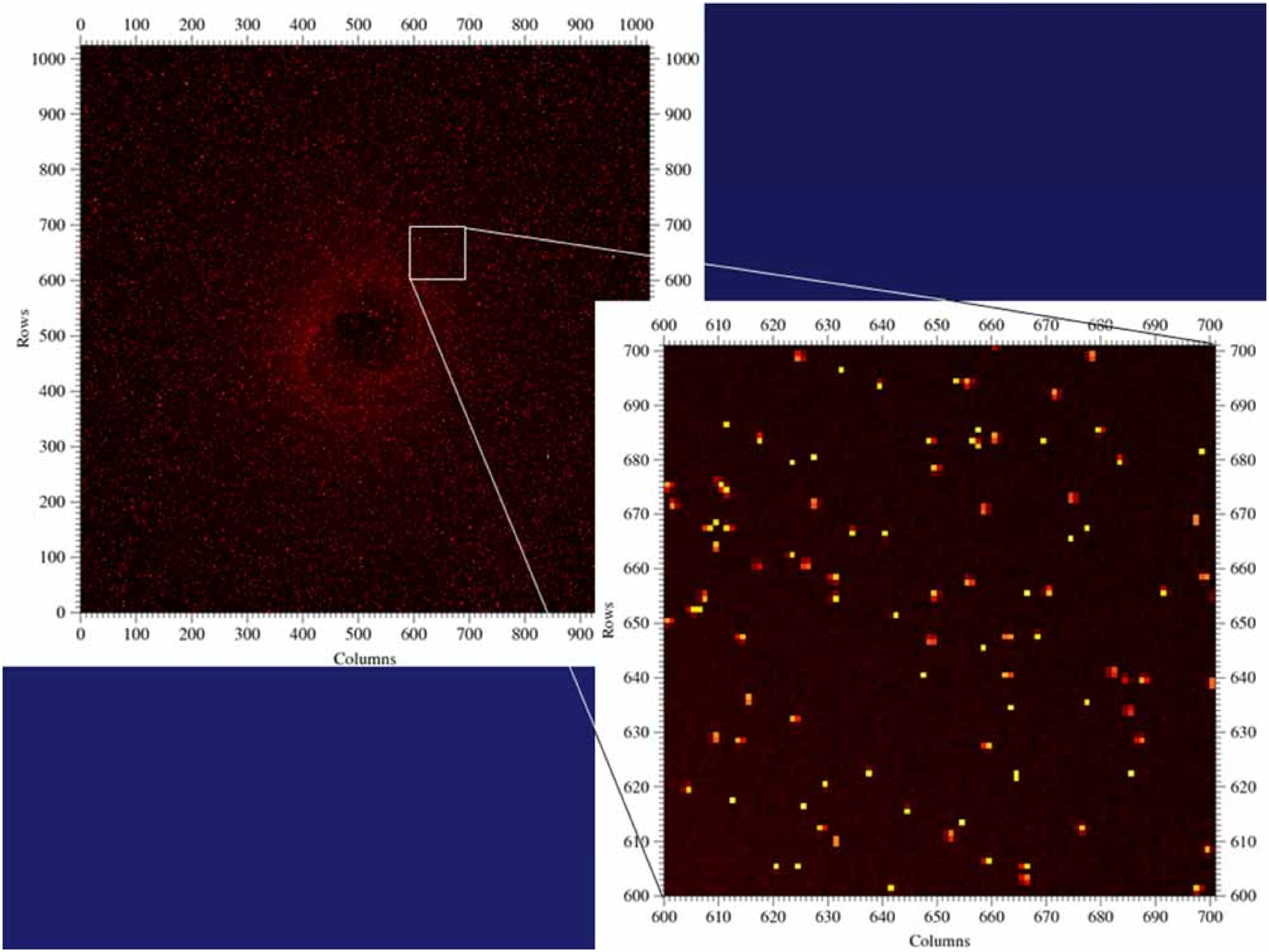
Is atomic-scale XPCS something special?

- Crucial weakness of aXPCS experiments is generally the signal-to-noise ratio

- Multispeckle detection - SNR increases as (number of detector pixel P)$^{1/2}$

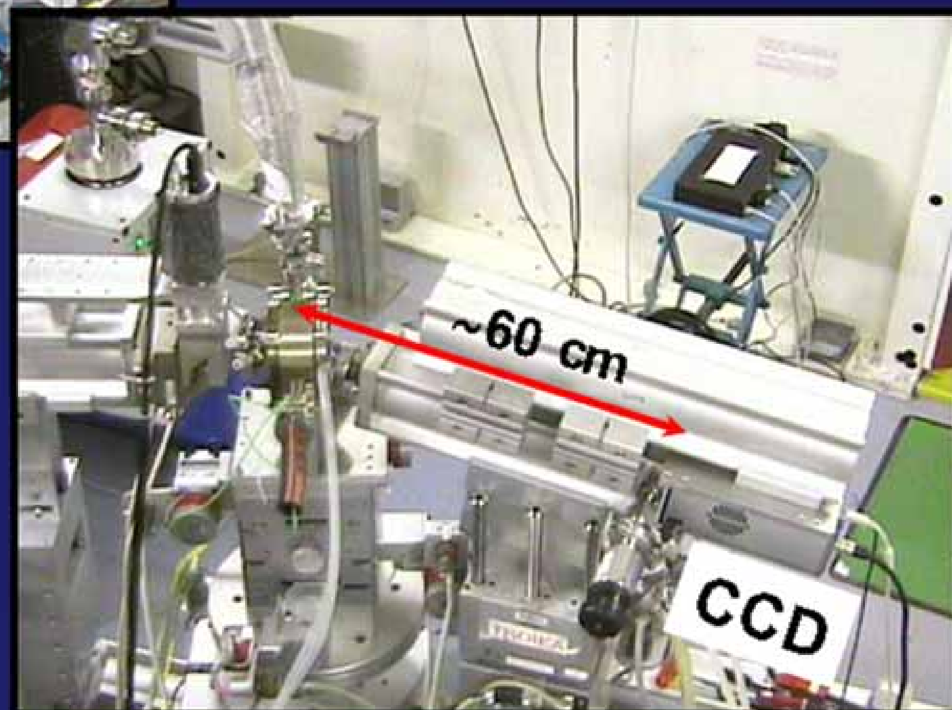
- Crucial importance of a high coherent fraction – Bilderback et al., NJP 12 (2010)

- Fine balance between a beam size (speckle width) and a sample-to-detector distance

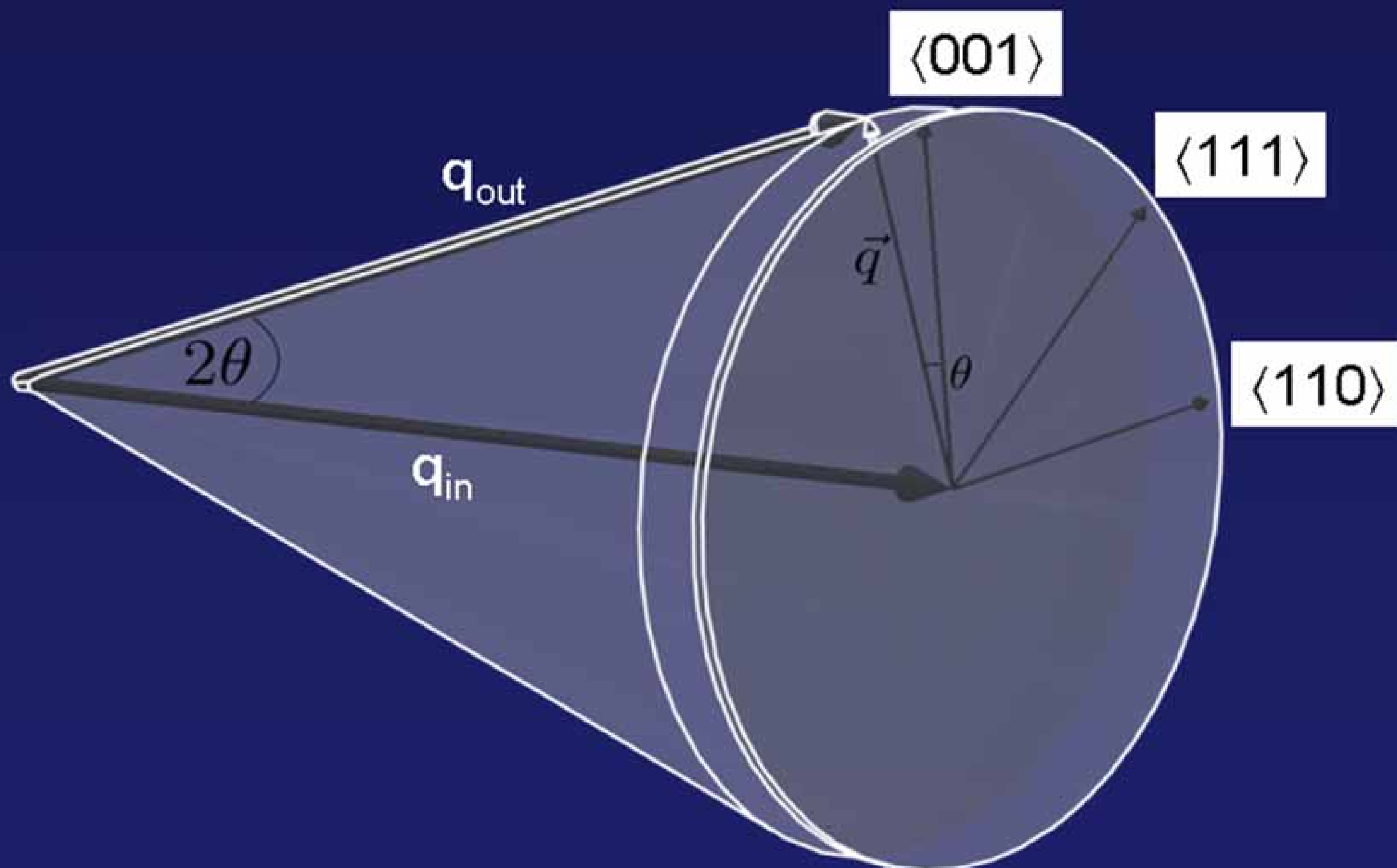


Rows
Columns
Rows
Columns


~120 cm


~60 cm
CCD

The setup



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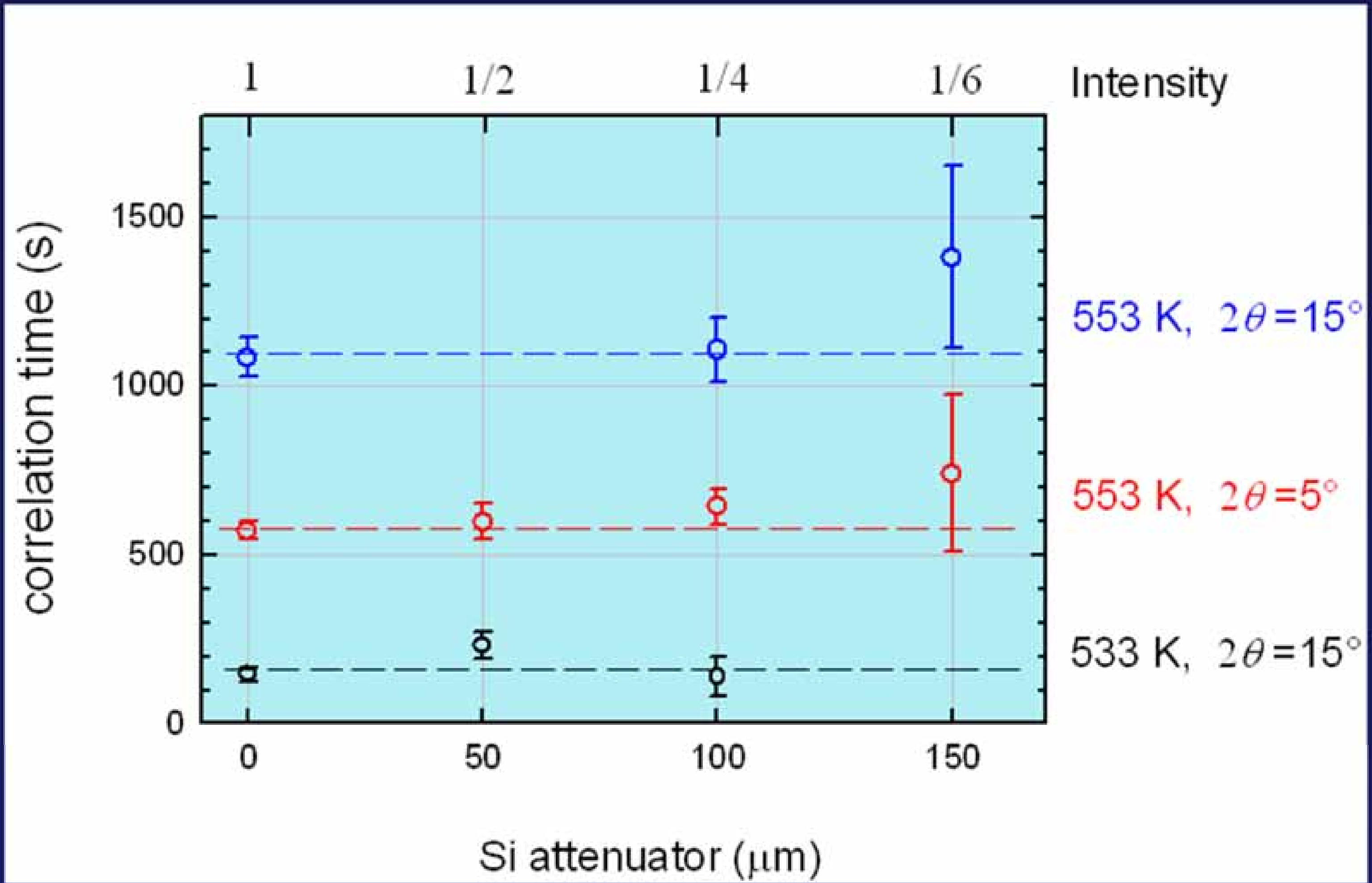
    - 1. Fundamental research
    - 2. New systems

1.1 Impact of photons on atomic dynamics



1
1/2
1/4
1/6
Intensity
correlation time (s)
1500
1000
500
0
553 K, 2θ=15°
553 K, 2θ=5°
533 K, 2θ=15°
0
50
100
150
Si attenuator (μm)

1.2. Beyond a linear regime of scattering theory

Coherent correlation times/quasi-elastic linewidths resulting from the diffusion of atoms on a Bravais lattice

In the limit of weak interactions

P. G. de Gennes, Physica 25, 825 (1959)

S.K. Sinha & D.K. Ross, *Physica* B **149,** 51 (1988

$$\Gamma_{coh}(\vec{q}) = \frac{\Gamma_{inc}(\vec{q})}{S(\vec{q})}$$

Exact formulation of the atomistic diffusion model

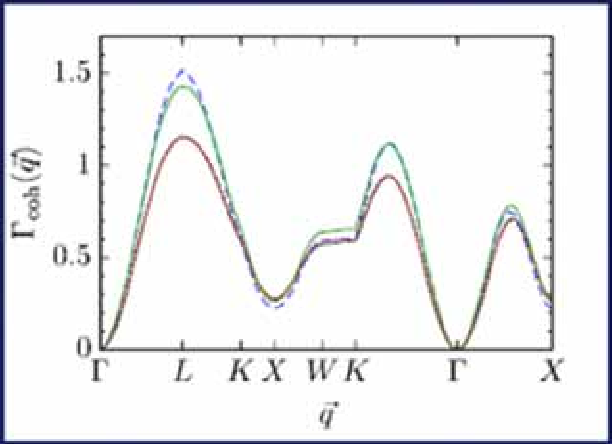
$$\tau(\vec{q}) = \tau_0 \frac{I_{SRO}(\vec{q})}{\left(1 - \sum_i p_i \cos(\vec{s}_i \cdot \vec{q})\right)}$$

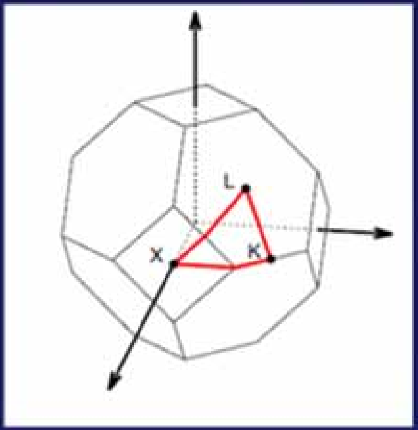
p_i probabilities for jumps, s_i jump vectors, τ_0 mean time between diffusion jumps, $I_{SRO}(\vec{q})$ static scattered intensity

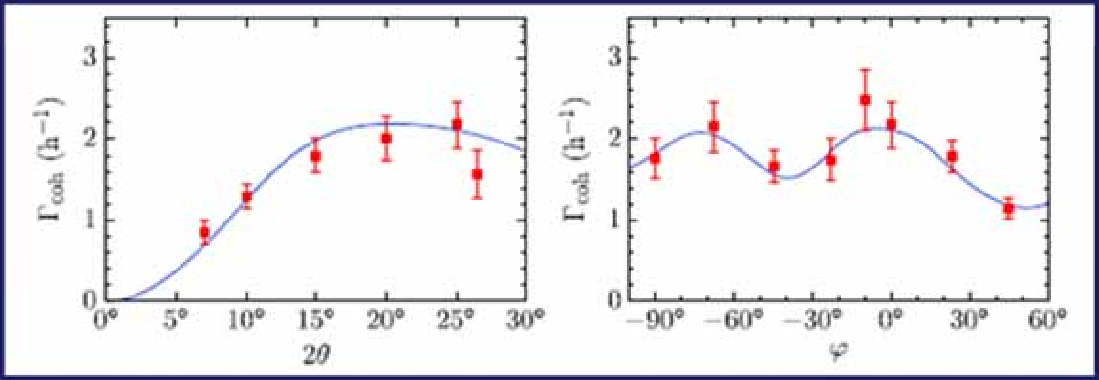
M. Leitner and G. Vogl, "Quasi-elastic scattering under short-range order: the linear regime and beyond", *J. Phys.: Condens. Matter* **23**, 254206 (2011)

The regime of stronger interactions - the deviations from the linear theory contain valuable information about the atomic jump mechanisms

Different transition models (e.g. Metropolis, inverse Metropolis or midpoint model) – different predictions for correlation times







M. Leitner and G. Vogl, *J. Phys.: Condens. Matter* **23**, 254206 (2011); M. Leitner, PhD Thesis 2009, Springer 2011

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2.1 New systems accessible

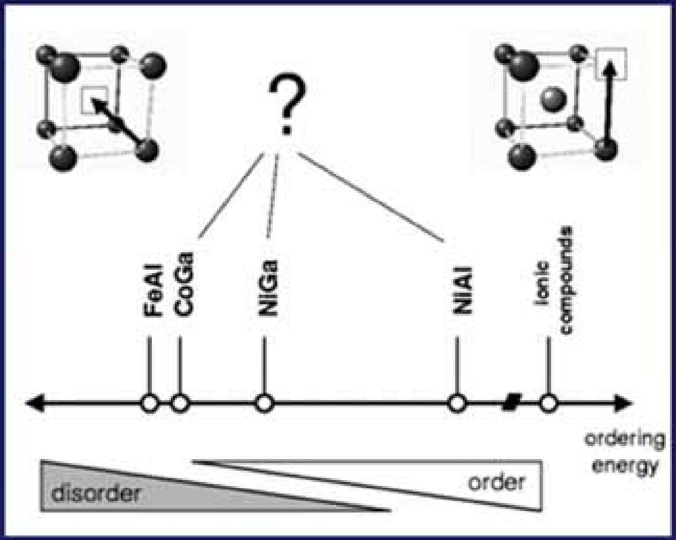
Periodic Table of the Elements

- hydrogen
- alkali metals
- alkali earth metals
- transition metals
- poor metals
- nonmetals
- noble gases
- rare earth metals

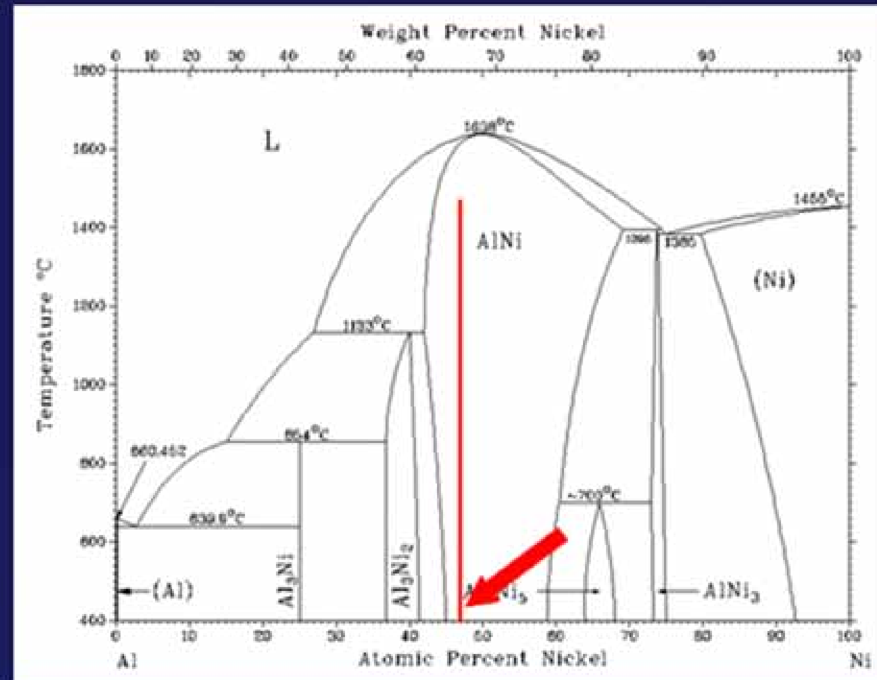
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Unq	105 Unp	106 Unh	107 Uns	108 Uno	109 Une	110 Unn								
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

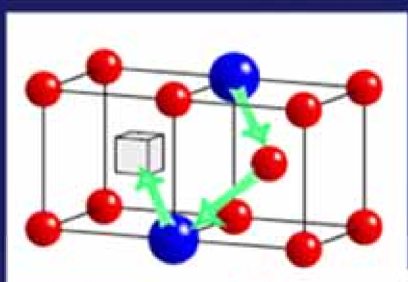
A triple defect system - Al-rich B2 NiAl

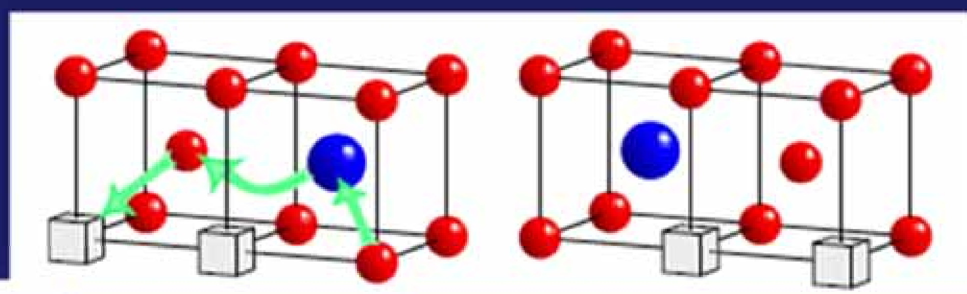
With increasing temperature, the triple defects consisting of two *A*-vacancies and one *A*-ASD are created.

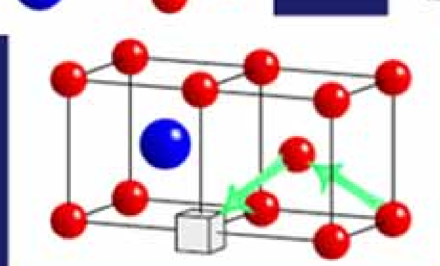


Investigated structure $Ni_{48}Al_{52}$
A very well-ordered system,
less than 10^{-3} defects at 1300K!



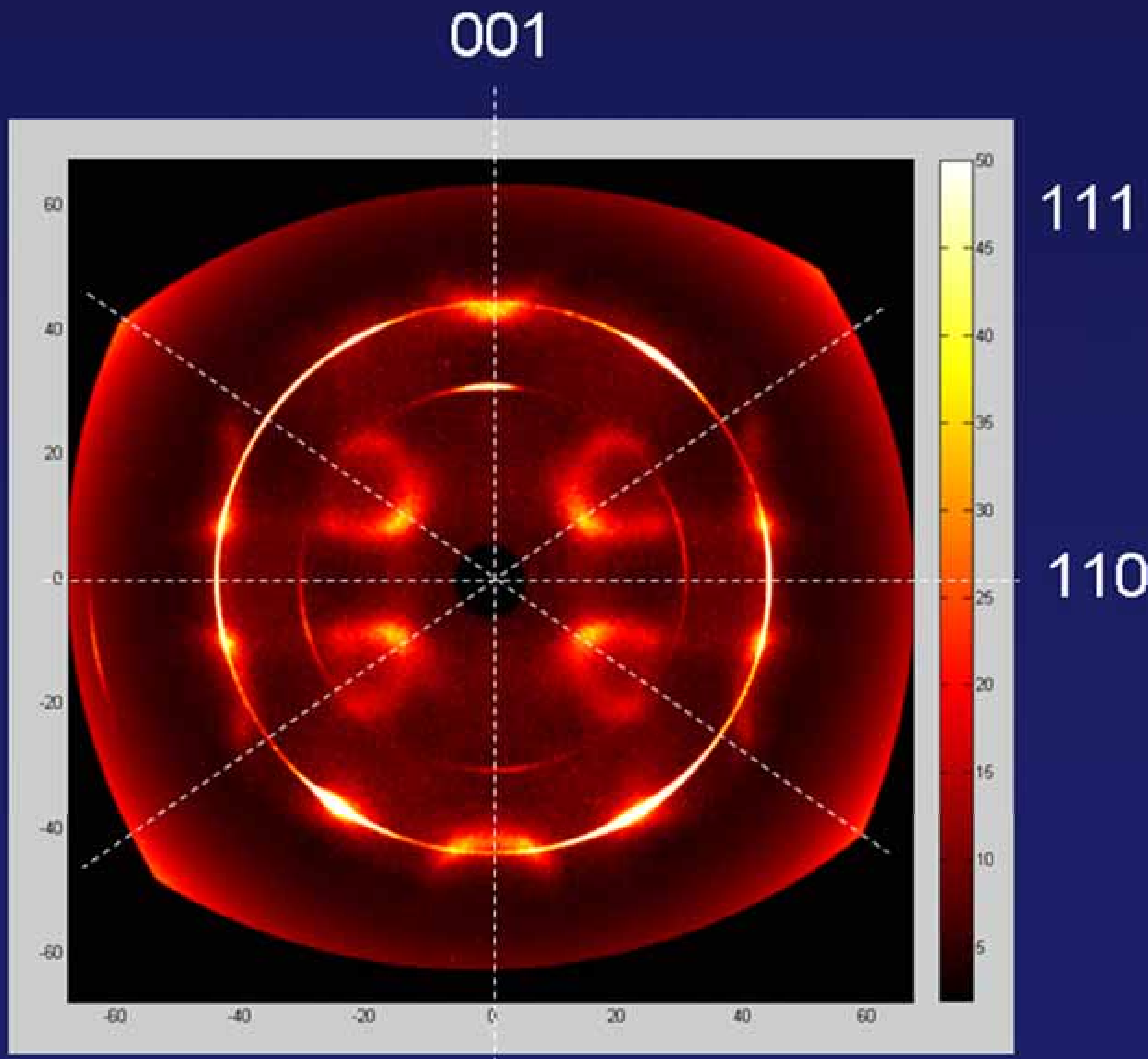


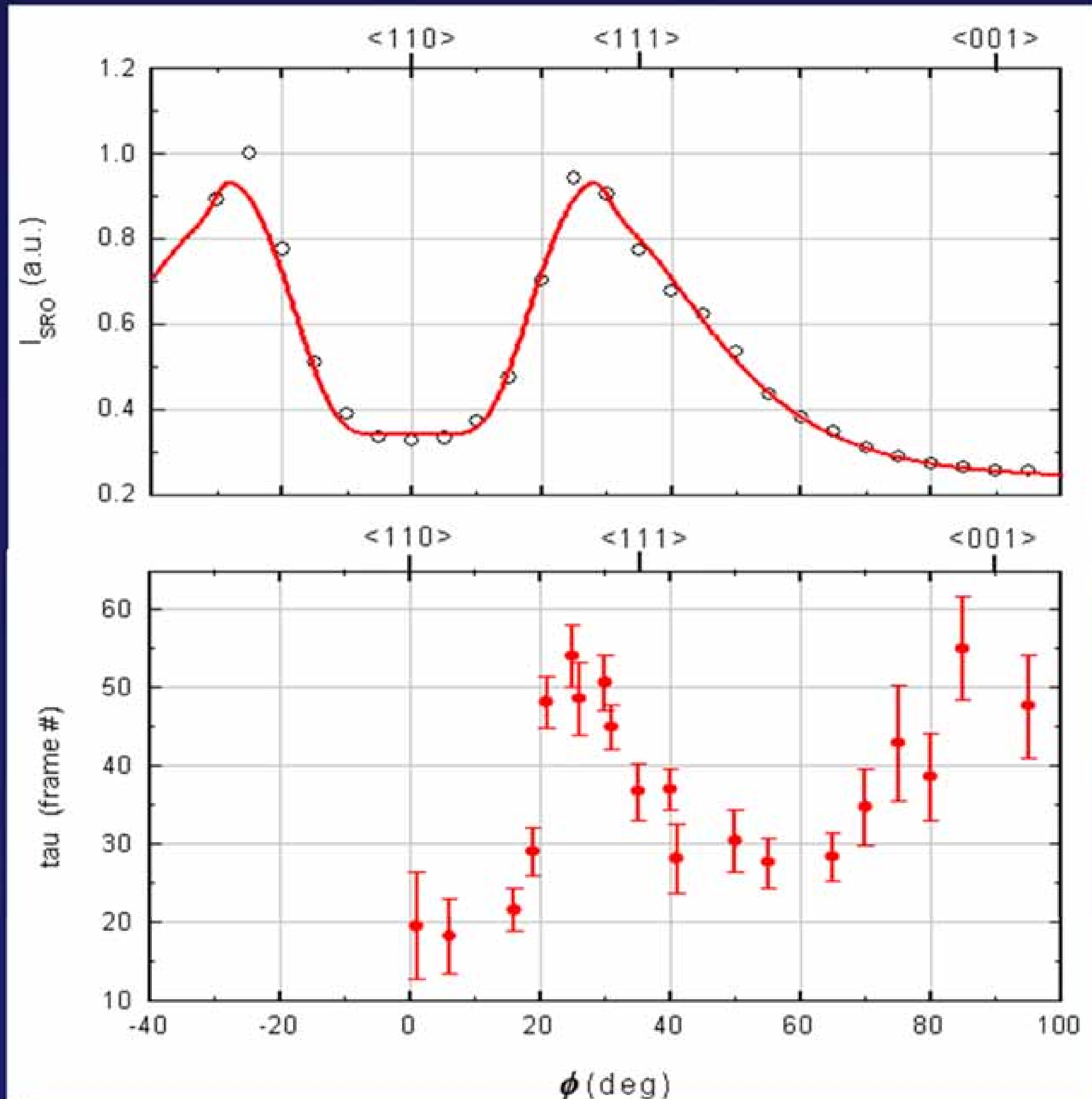




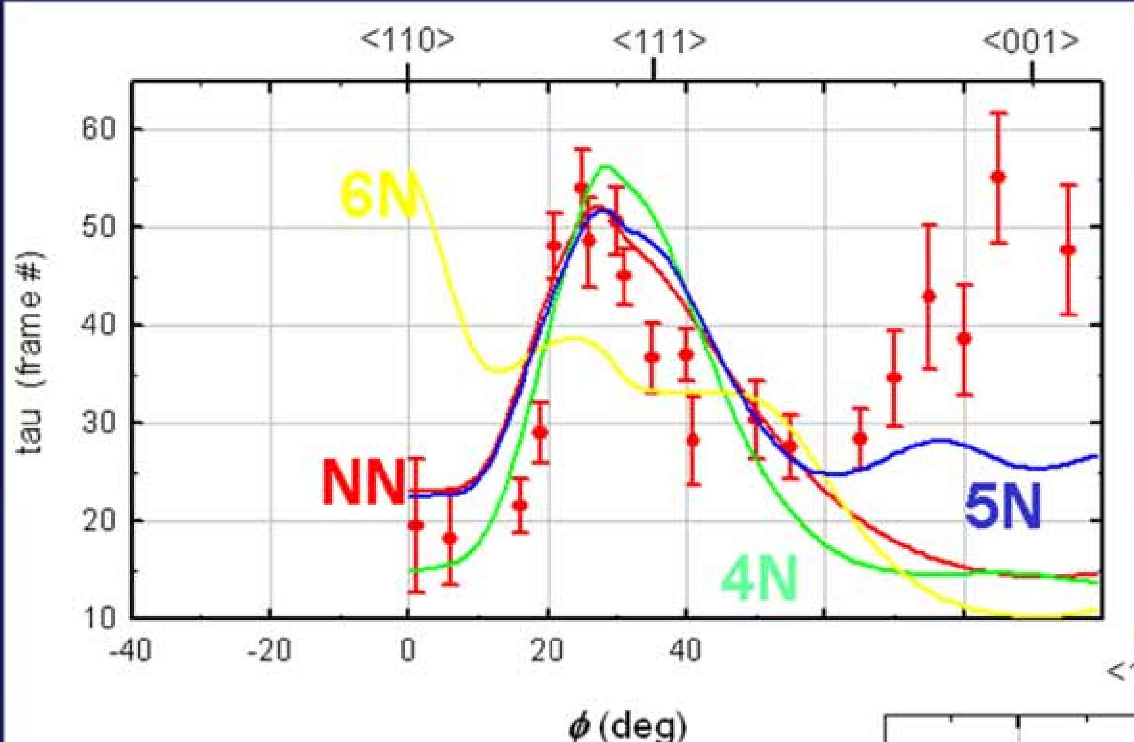
Different jump mechanisms

Diffuse intensity – (110)-oriented $Ni_{48}Al_{52}$

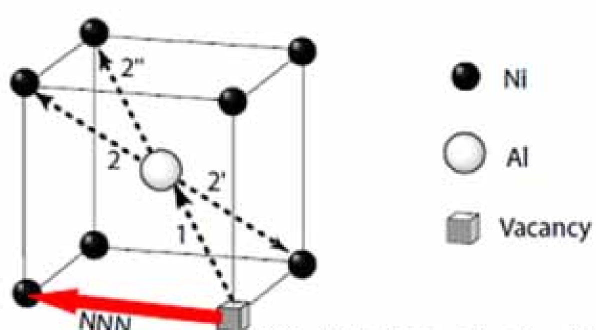


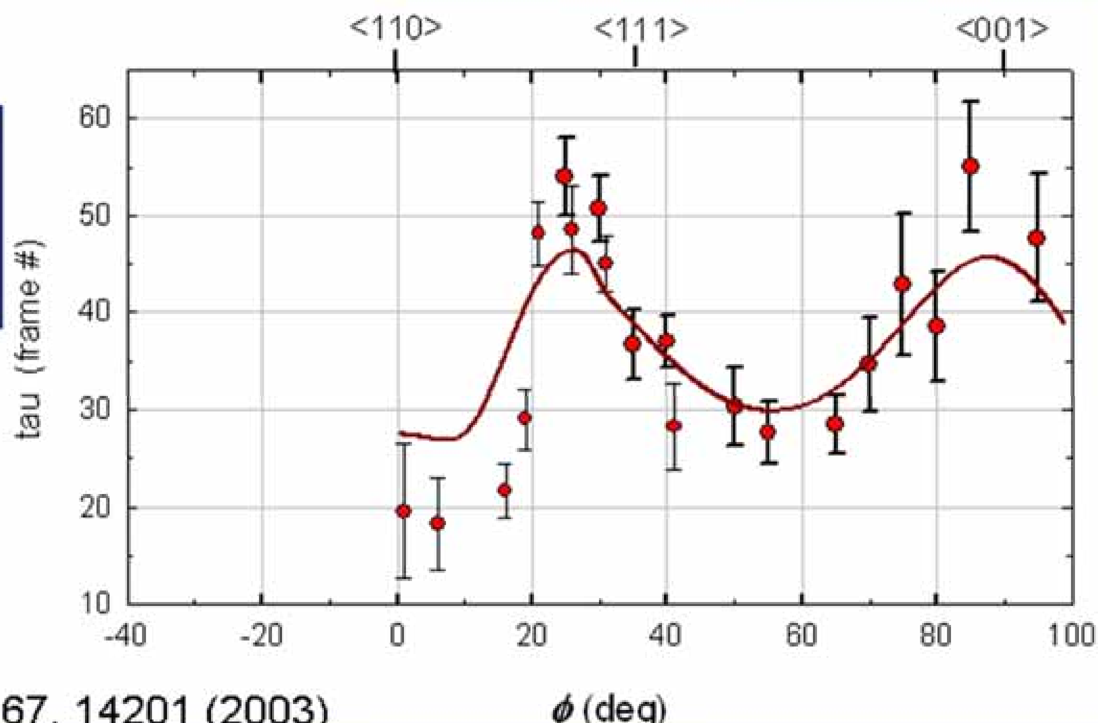


<110>
<111>
<001>
I_{SRO} (a.u.)
tau (frame #)
ϕ (deg)



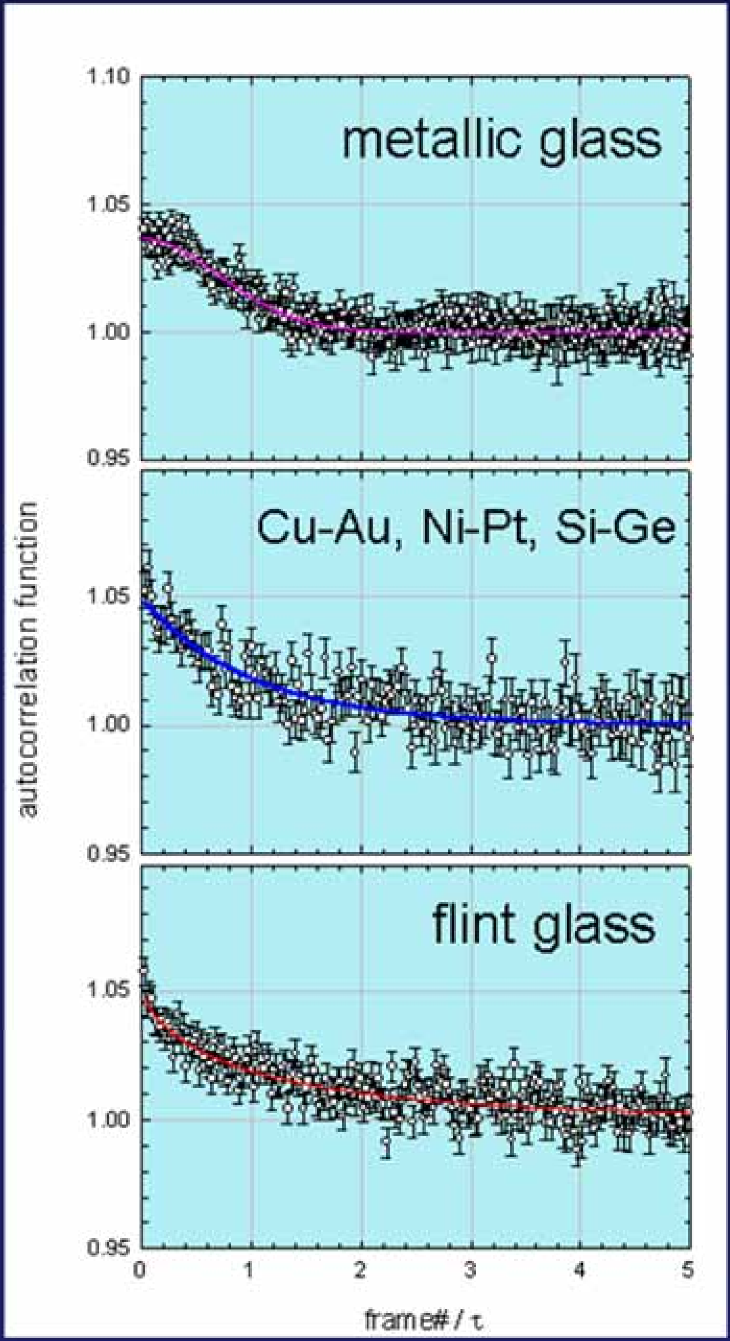
Single-atom jump mechanism
- (100) NNN jump

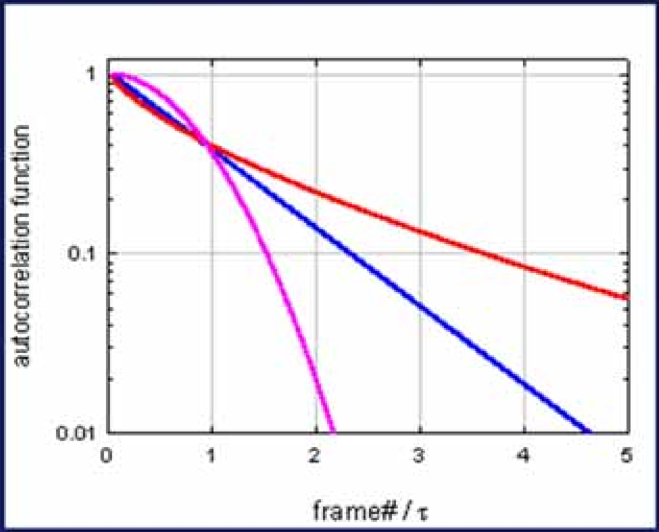




Y. Mishin et al., PRB 67, 14201 (2003)

2.2 Correlation function

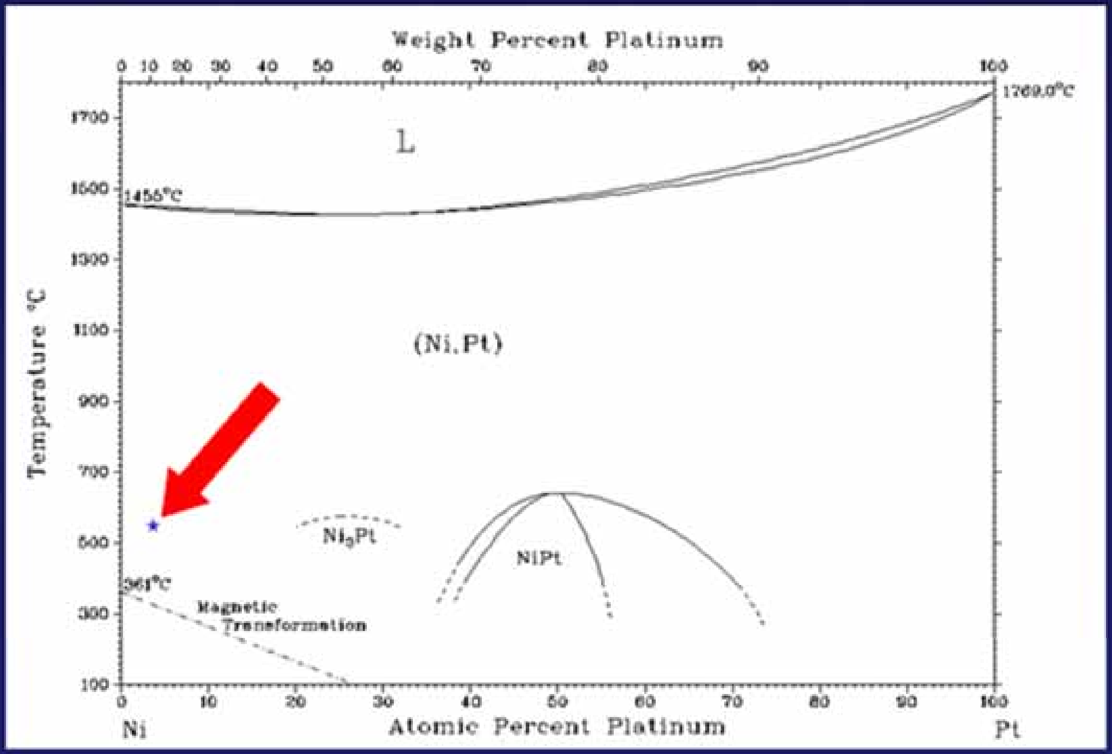




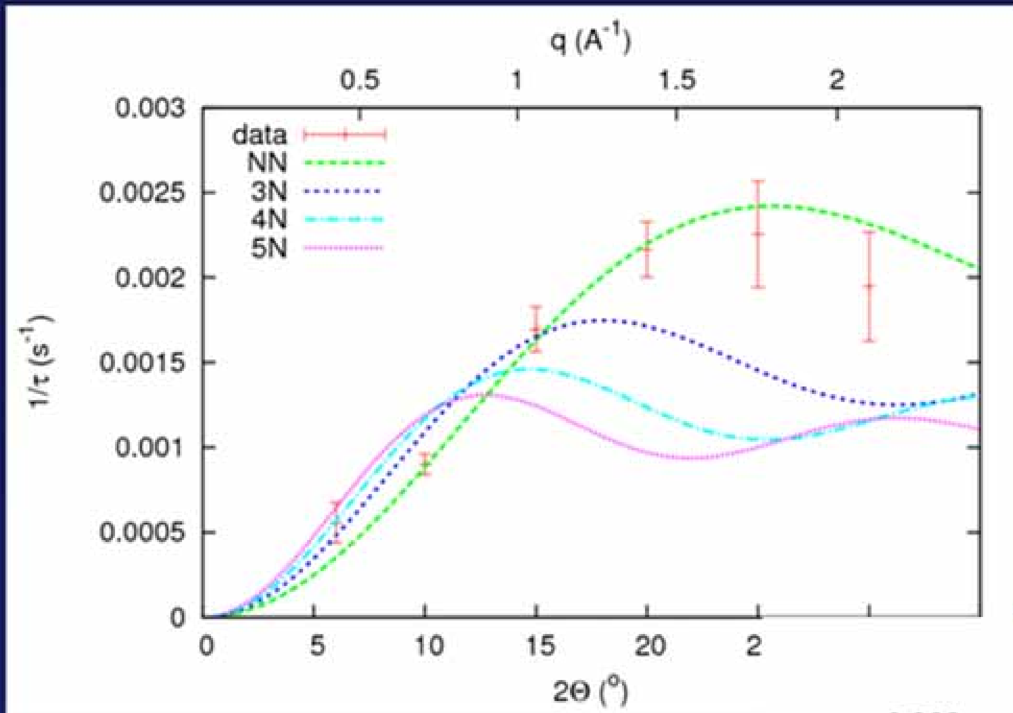
Zr metallic glass – M. Leitner et al., PRB submitted
Cu10at.%Au - M. Leitner et al., NMat 8, 717 (2009)

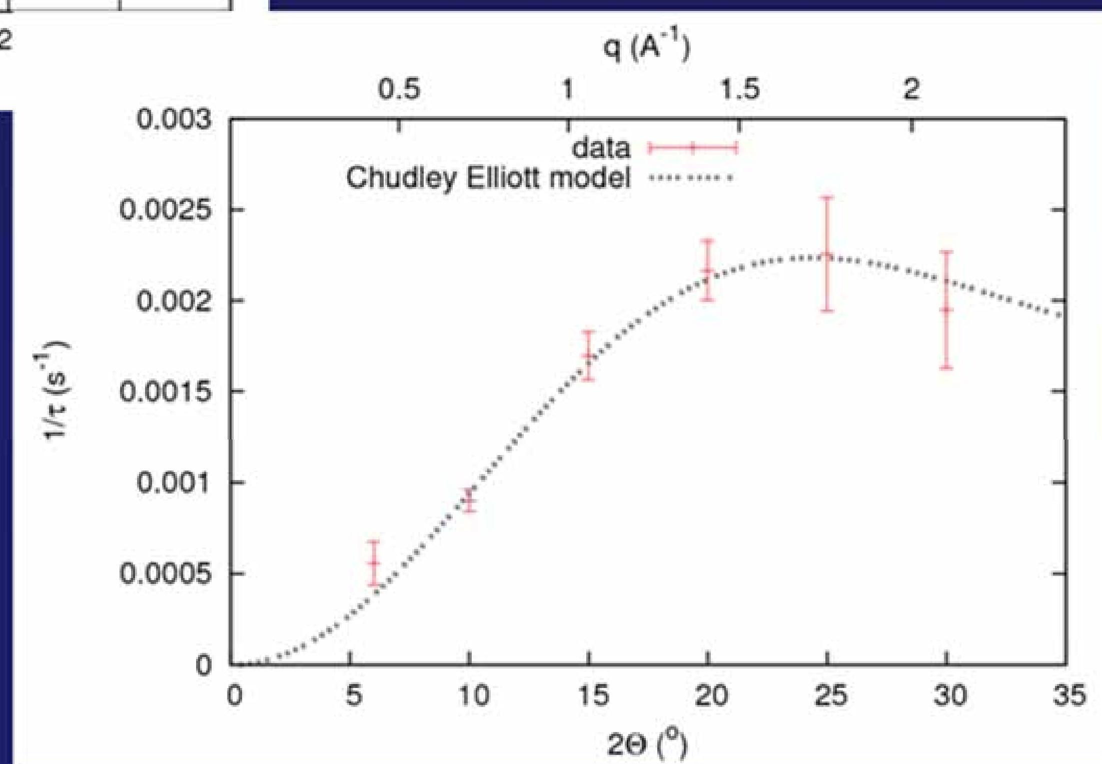
2.3 Impurity diffusion

Ni-3at.%Pt polycrystal @ 830K



M. Stana, Master Thesis 2011

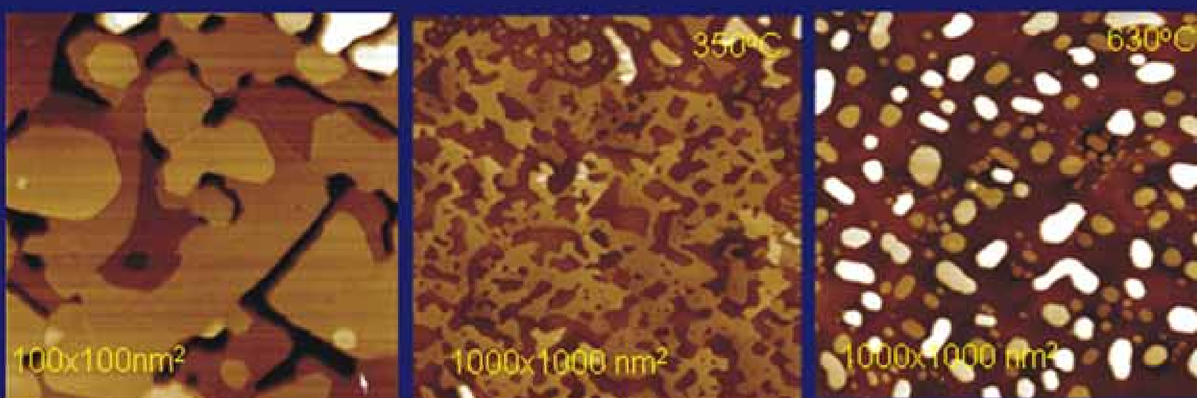

q (A^{-1})
0.5
1
1.5
2
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
data
NN
3N
4N
5N
1/τ (s^{-1})
0
5
10
15
20
2
2Θ (°)

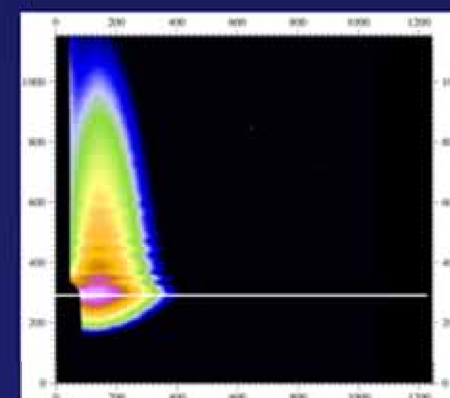

q (A^{-1})
0.5
1
1.5
2
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
data
Chudley Elliott model
1/τ (s^{-1})
0
5
10
15
20
25
30
35
2Θ (°)

2.4 Surface diffusion

Only few methods sensitive to the surface diffusion with space and time resolution: HAS, electron scattering and GINRS

XPCS (GISAXS) L-M Stadler et al., Dynamics of nanoclaster formation on metal oxides





5 ML Au film on $Fe_3O_4(001)$: as prepared and annealed

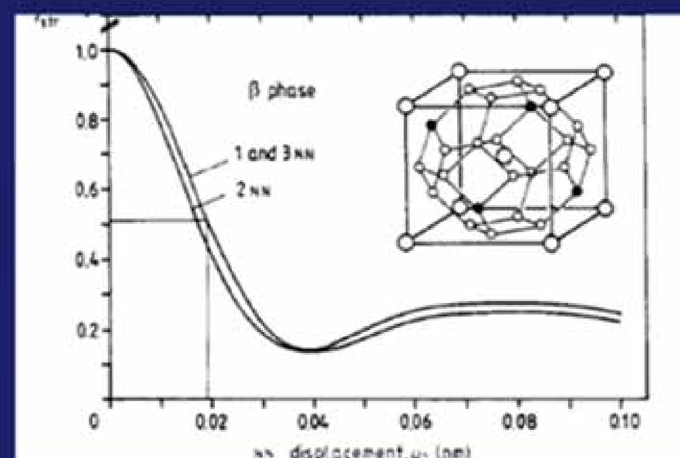
2.5 Hydrogen (Li, C) interstitial diffusion

Diffusing atom is small enough to move between the atoms in the lattice

The scattering does not happen on hydrogen atoms, but on the host-lattice distortions! (fluctuating lattice distortions caused by the diffusion of the interstitials)

1) A. Heidemann, et al., Diffusion of hydrogen in tantalum studied by motional narrowing of Mössbauer lines, *Phys. Rev. Lett.* 36, 213 (1976)

2) F.E. Wagner et al., Influence of interstitial diffusion on the Mössbauer spectra of iron solutes in VD and NbH, J. Phys. F Met. Phys. 14, 535 (1984)



- ✓Impact of photons on atomic dynamics
- ✓Beyond a linear regime of scattering theory
- ✓New systems accessible
- ✓More information can be gained from the correlation function
- ✓Impurity diffusion
- ✓Surface diffusion
- ✓Light interstitials diffusion
- ✓Diffusion under pressure or uniaxial stress