

Inelastic x-ray scattering from phonons at the ESRF: recent results and perspectives.

Michael Krisch

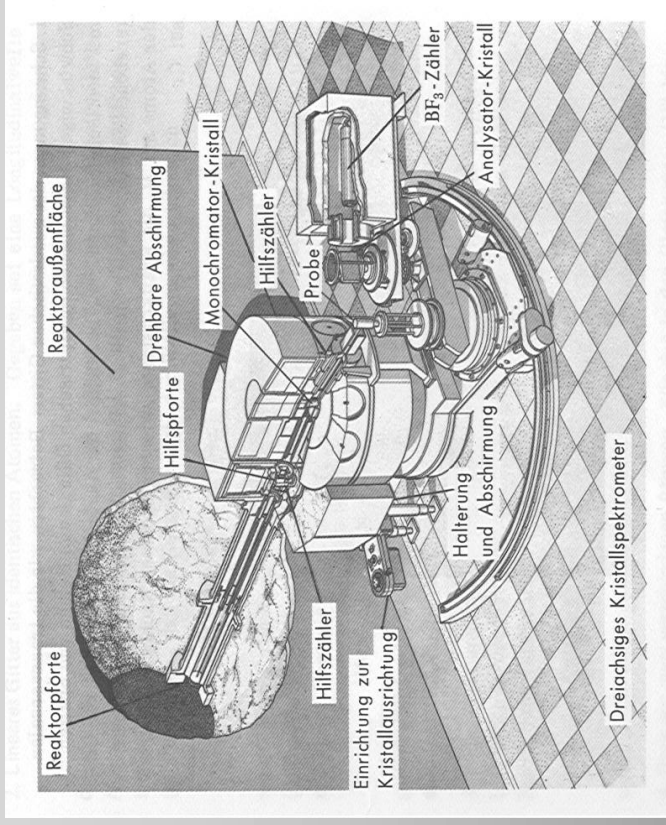
European Synchrotron Radiation Facility



Outline

- Introduction
- Examples
- Perspectives
 - Determination of density of states
 - Phonons from surfaces

INS and IXS



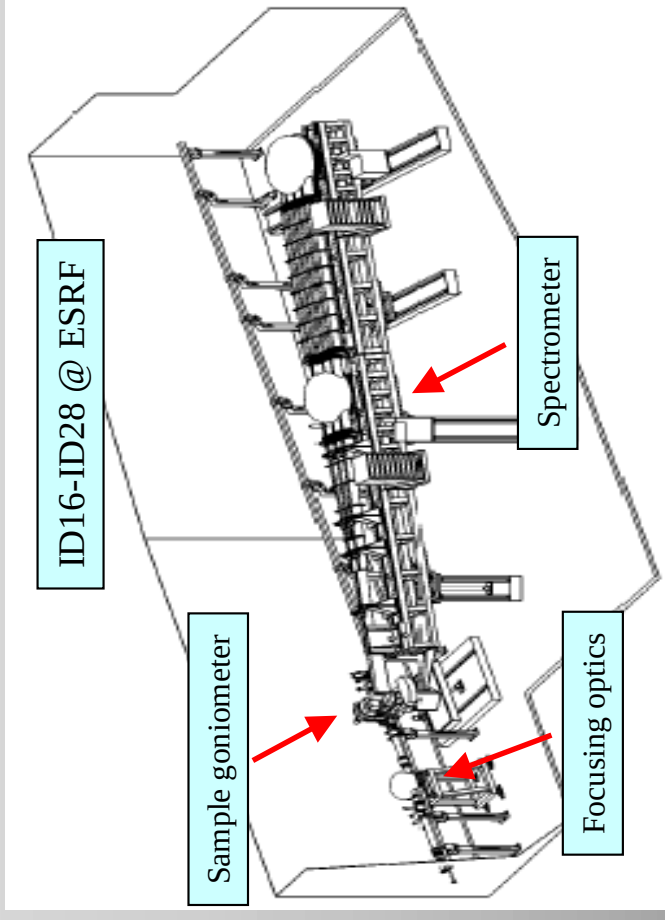
Brockhouse; 1955

Thermal neutrons:

$$E_1 = 25 \text{ meV}$$

$$k_1 = 38.5 \text{ nm}^{-1}$$

$$\Delta E/E = 0.01 - 0.1$$



Burkel, Dörner and Peisl (1987)
Sette, Krisch (1994)

Hard X-rays:

$$E_1 = 18 \text{ keV}$$

$$k_1 = 91.2 \text{ nm}^{-1}$$

$$\Delta E/E \leq 1 \times 10^{-7}$$

Why X-rays?

- **No kinematic limitations:** E independent of Q
- **Small sample volumes:** $10^{-4} - 10^{-5} \text{ mm}^3$

- **Study of disordered and polycrystalline systems at small Q**
- **“difficult” materials, surfaces**
- **Very high pressure**

Experimental set-up

Monochromator:

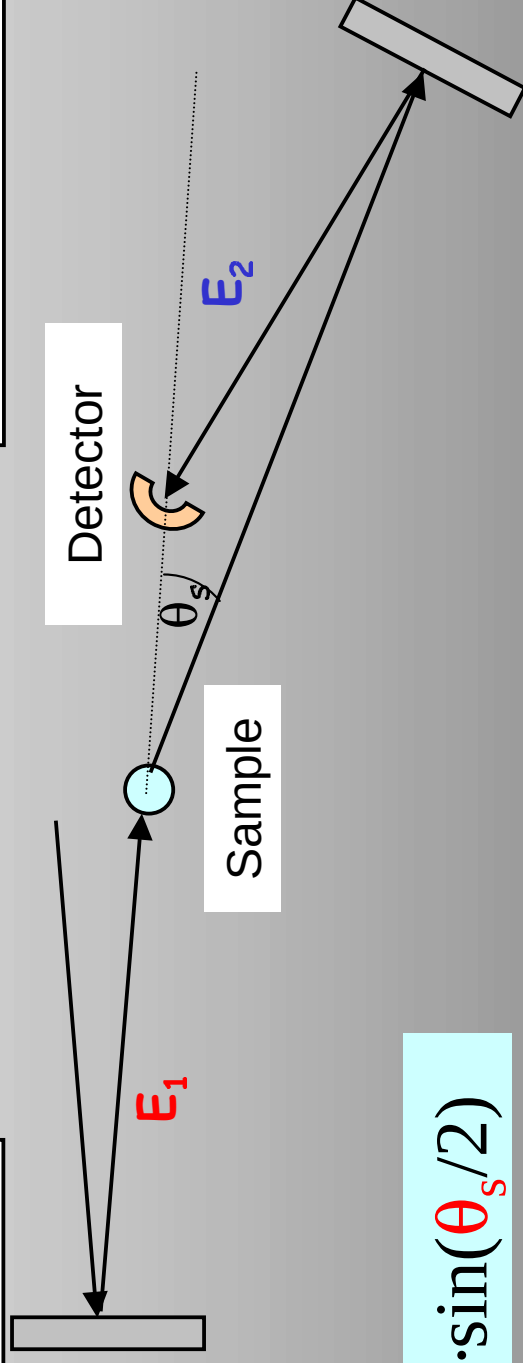
Si(n,n,n), $\theta_b = 89.98^\circ$
n=7-13

λ_1 **tunable**

Analyser:

Si(n,n,n), $\theta_b = 89.98^\circ$
n=7-13

λ_2 **constant**



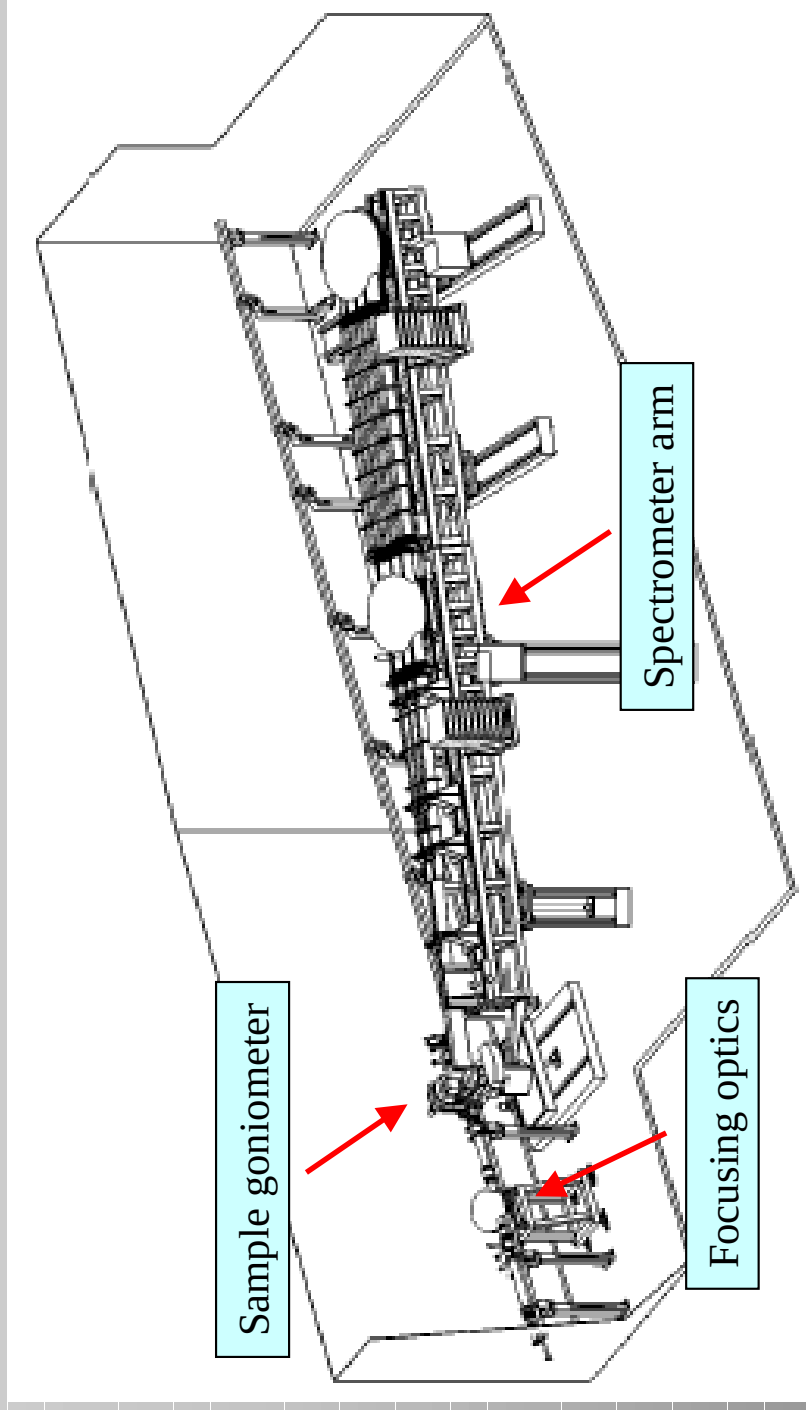
$$Q = 4\pi/\lambda \cdot \sin(\theta_s/2)$$

$$\lambda = 2 \cdot d(T) \sin\theta_B$$

$$\Delta d/d = \Delta E/E = -\alpha(T) \cdot \Delta T \quad (\alpha = 2.58 \cdot 10^{-6} \text{ at RT})$$

Beam size: 30 (250) x 70 μm^2 (hor. x vert.)

IXS spectrometer on ID28



Reflection	ΔE [meV]	$Q_{\max}(7)$ [nm^{-1}]
(7 7 7)	7	64
(8 8 8)	5.5	73
(9 9 9)	3.0	82
(11 11 11)	1.7	100
(13 13 13)	0.9	119

Selection of investigated systems

Liquids and glasses

- **Water** (P,T)

- liquid metals (Na, Si, Ge, Sn, Ga, ..)

- a-SiO₂.

- Quantum liquids (H₂, D₂, He³, He⁴)

Small samples (at ambient pressure)

- C¹², C¹³, GaN, AlPdMn, ZnMgY, **C**, CoSb₃, ..

- NbSe₃, **Pu**

- Superconductors (**Nd**_{1.86}**Ce**_{0.14}**CuO**_{4+δ}, LaSrCuO₄, HgBa₂CuO₄, **MgB**₂)

High pressure studies

- **Fe**, FeS, FeO, FeSi, CH₄-H₂O (polycrystals)

- **Co**, Zn, Mo, Cs, SmS, MgO (single crystals)

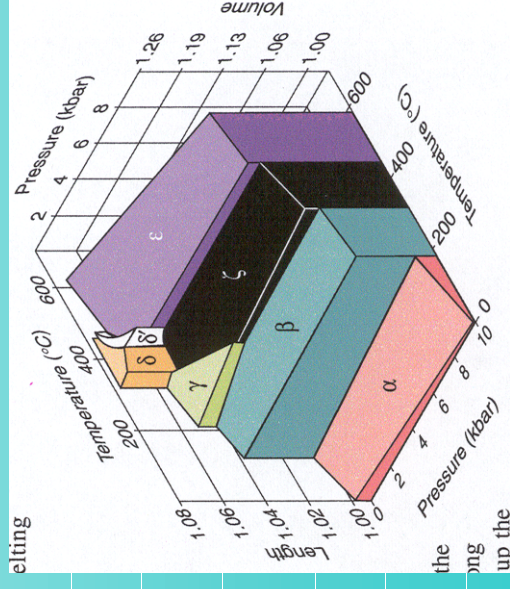
Phonon dispersion of fcc δ -Plutonium

J. Wong¹, M. Krisch², D.L. Farber¹, F. Occelli¹, A.J. Schwartz¹, T.-C. Chiang³, M. Wall¹,
C. Boro¹, and R. Xu³; *Science* 301, 1078 (2003).

¹Lawrence Livermore National Lab, ²ESRF, ³University of Illinois at Urbana-Champaign

Pu is the most unusual and fascinating element.

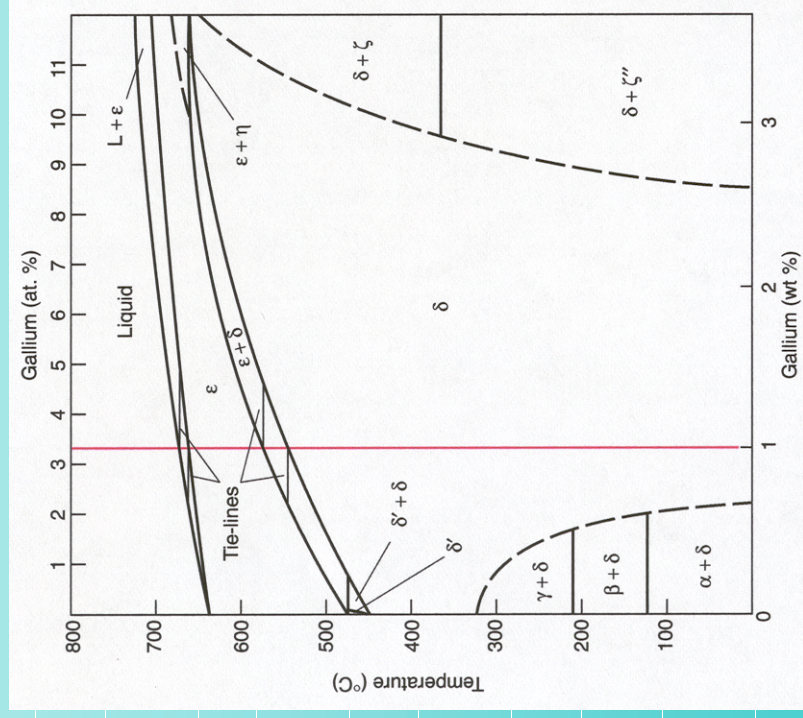
- Multitude of unusual properties
- central role of the 5f electrons
- radioactive and highly toxic



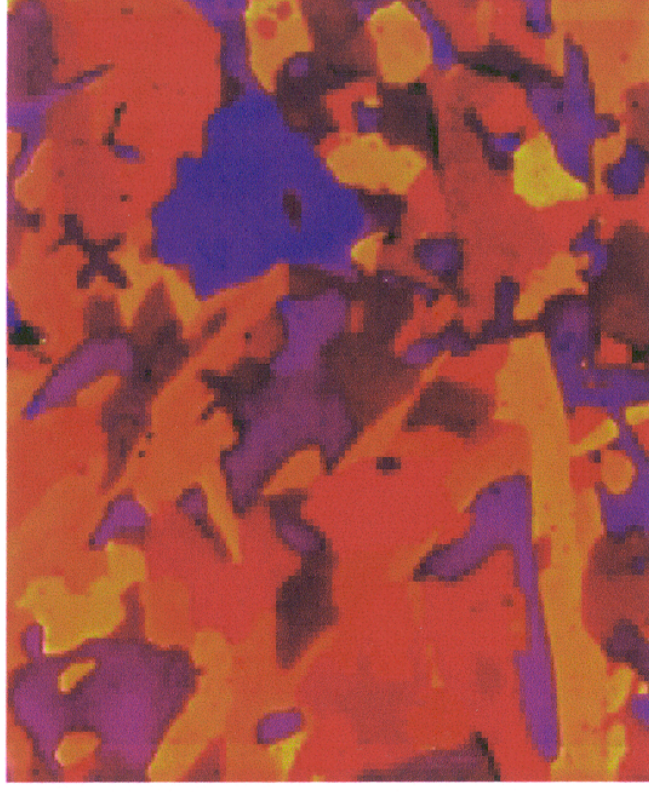
Hardly any data on elasticity and phonons !

Phase diagram and sample morphology

Pu (Ga) phase diagram



Preparation of fcc Pu-Ga (0.6 wt%) alloy by a strain enhanced recrystallisation technique.



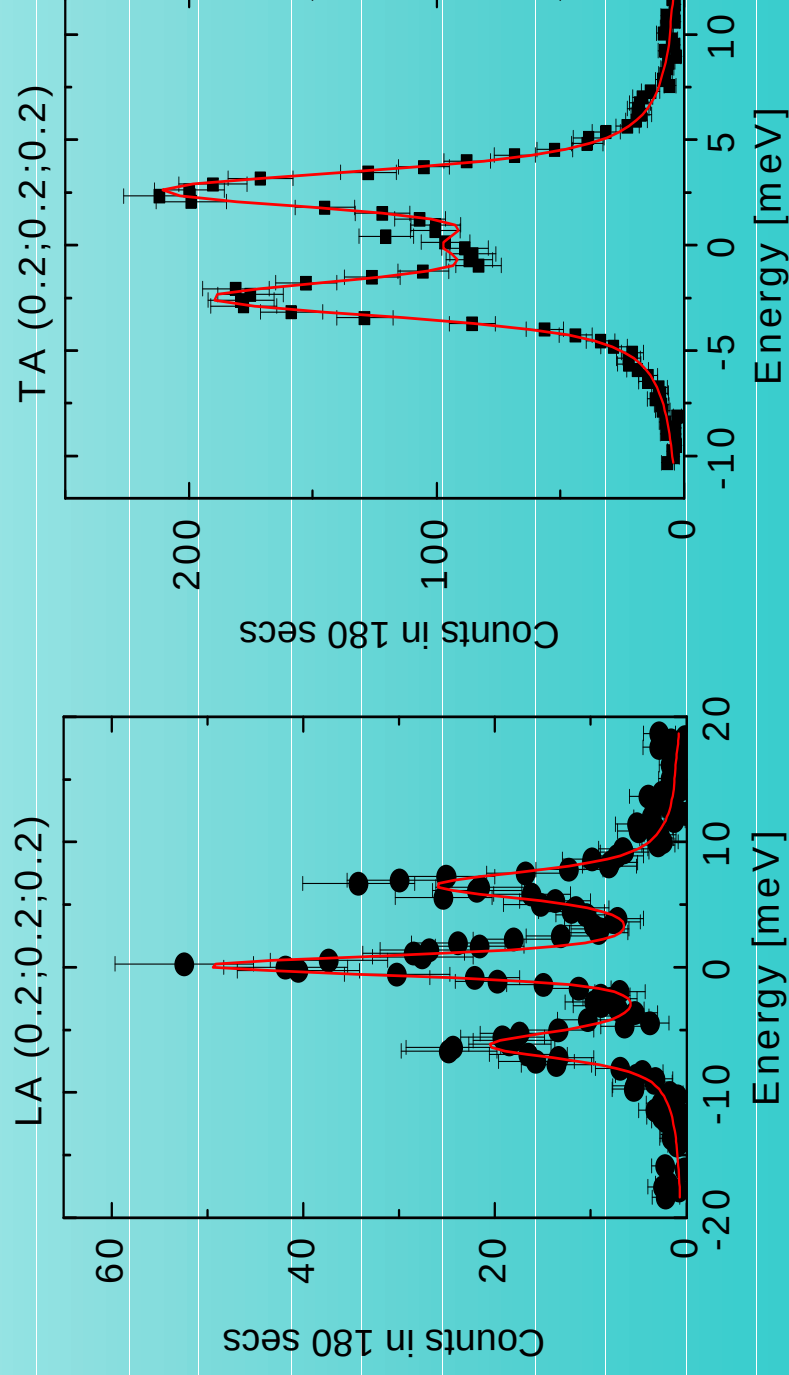
typical grain size: 90 μm
foil thickness: 10 μm

J.C. Lashley et al.; Los Alamos Science 26, 226 (2000)

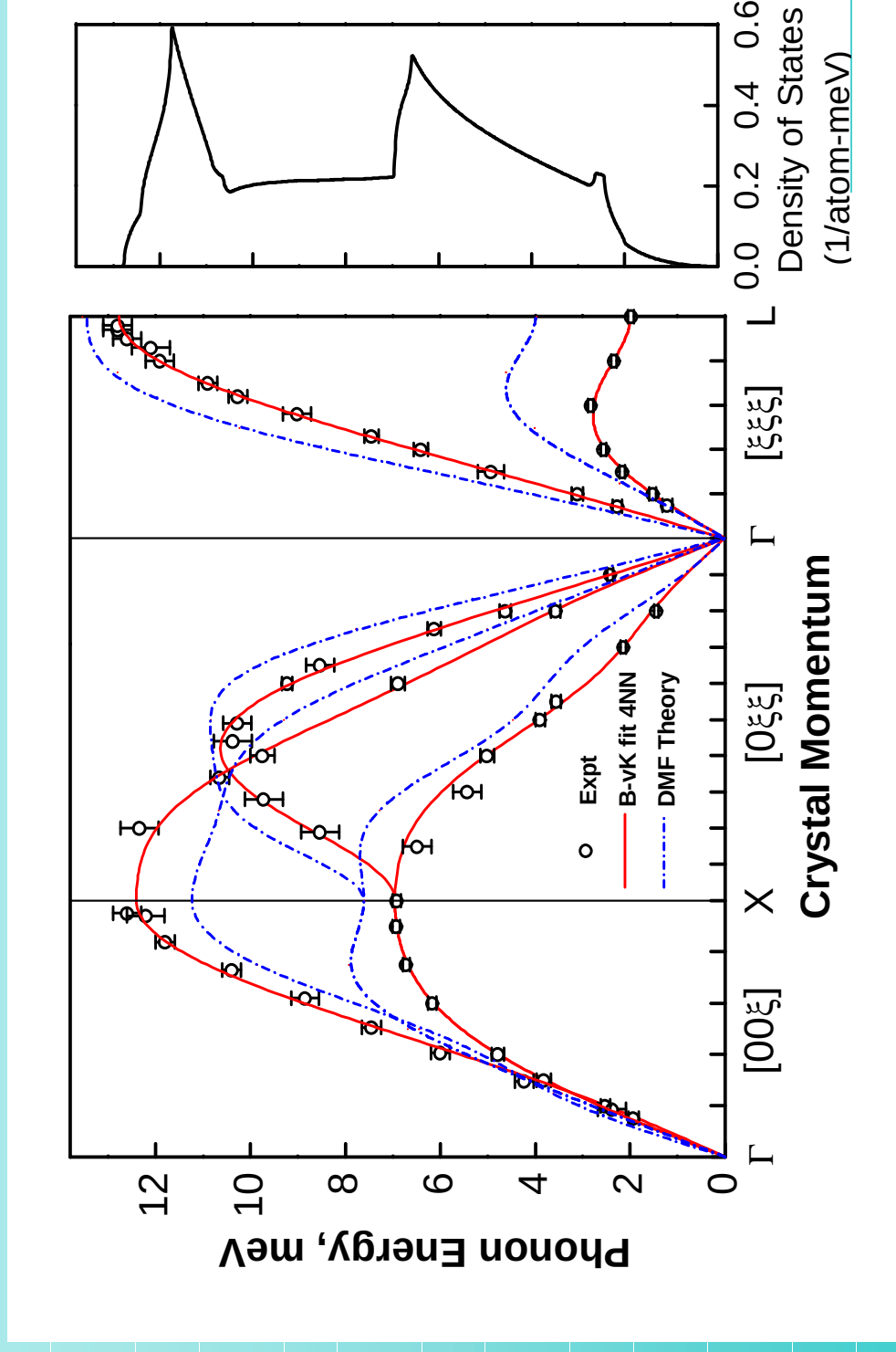
The IXS experiment

ID28 at ESRF

- Energy resolution: 1.8 meV at 21.747 keV
- Beam size: 20 x 60 μm^2 (hor. x vert., FWHM)
- On-line diffraction analysis



Experiment versus Theory



Dynamical mean field calculations: X. Dai et al.; Science 300, 953 (2003)

Main Results

- **elastic constants**

$$C_{11} = 35.3 \pm 1.4 \text{ GPa}$$

$$C_{12} = 25.5 \pm 1.5 \text{ GPa}$$

$$C_{44} = 30.53 \pm 1.1 \text{ GPa}$$

$$- 2C_{44} / (C_{11} - C_{12}) = 6$$

- excellent agreement with ultrasound results.

(*H.M. Ledbetter and R.L. Momet; Acata Metall. 24, 891, 1976*)

- δ -Pu-Ga is the most elastically anisotropic fcc metal known.

- **Born-von Karman force constant model fit**

- good convergence, if fourth nearest neighbours are included.
- interplanar force constants
- phonon density of states
- lattice specific heat, ...

Main Results (bis)

- **Phonon curve anomalies**

- kink in the $T_1[011]$ branch (as in Th)
 δ' and ε at high T
- soft-mode behaviour of $T[111]$ branch (as in Th, γ -Ce, La)
proximity of structural phase transition
(-> monoclinic α' phase at 163 K)

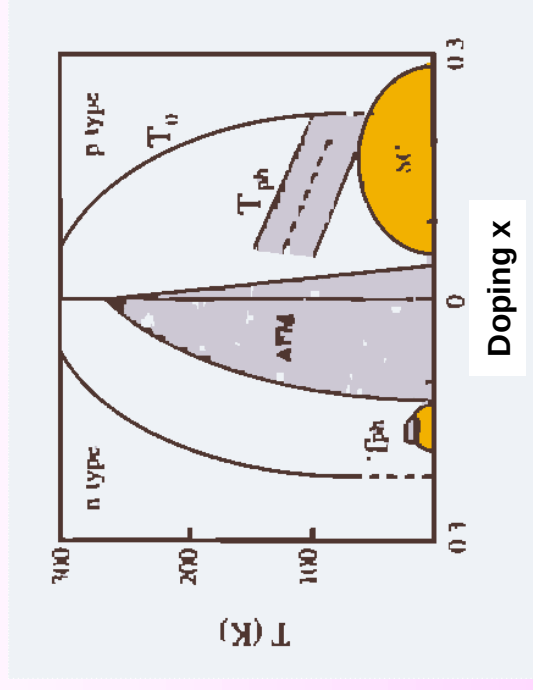
- **Good qualitative agreement with DMF theory**

=> experiment provides stringent test of theory

Phonon dispersion in $\text{Nd}_{1.86}\text{Ce}_{0.14}\text{CuO}_{4+\delta}$

M. D'Astuto et al.; Phys. Rev. Lett. 88, 167002 (2002)

Electron-phonon coupling in e⁻-doped high TC superconductors?



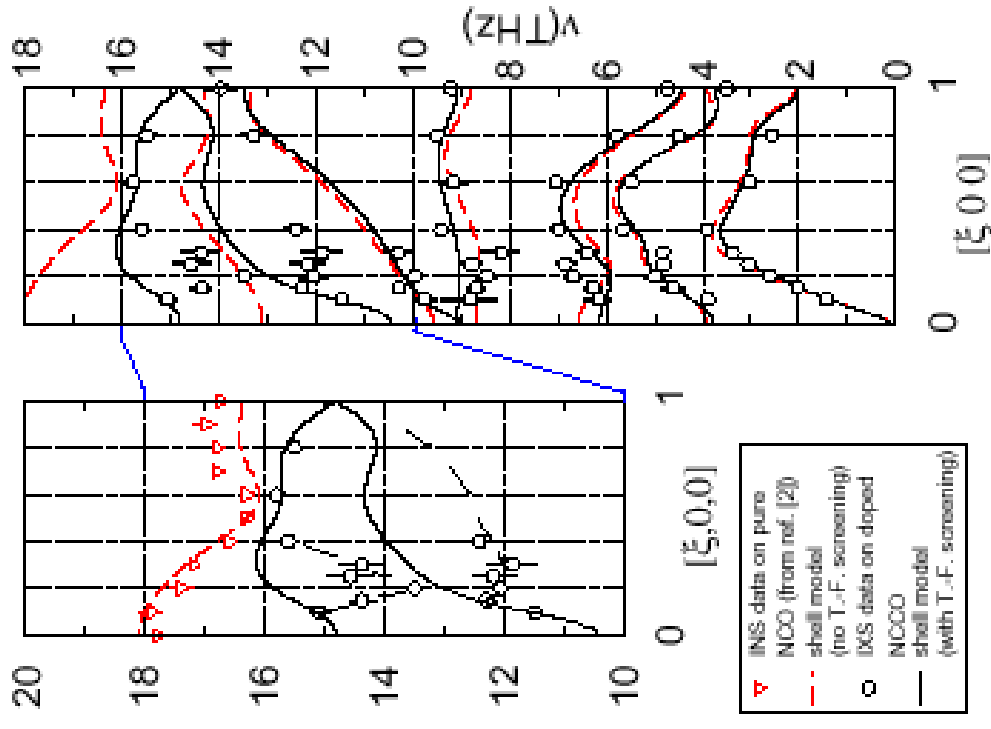
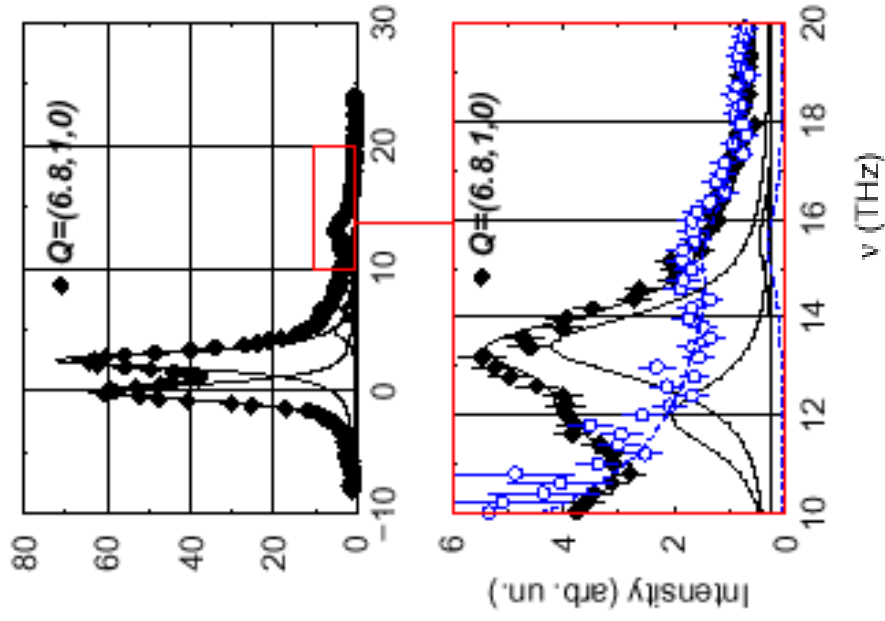
Z.-X. Shen (2001)

explanation for electron-hole asymmetry

- Angle-resolved photoemission: discontinuity of the quasi-particle dispersion
- INS in p-doped systems ($\text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4$): anomalous dispersion of LO branch

$T = 15 \text{ K}$

$V = 5 \cdot 10^{-3} \text{ mm}^3$



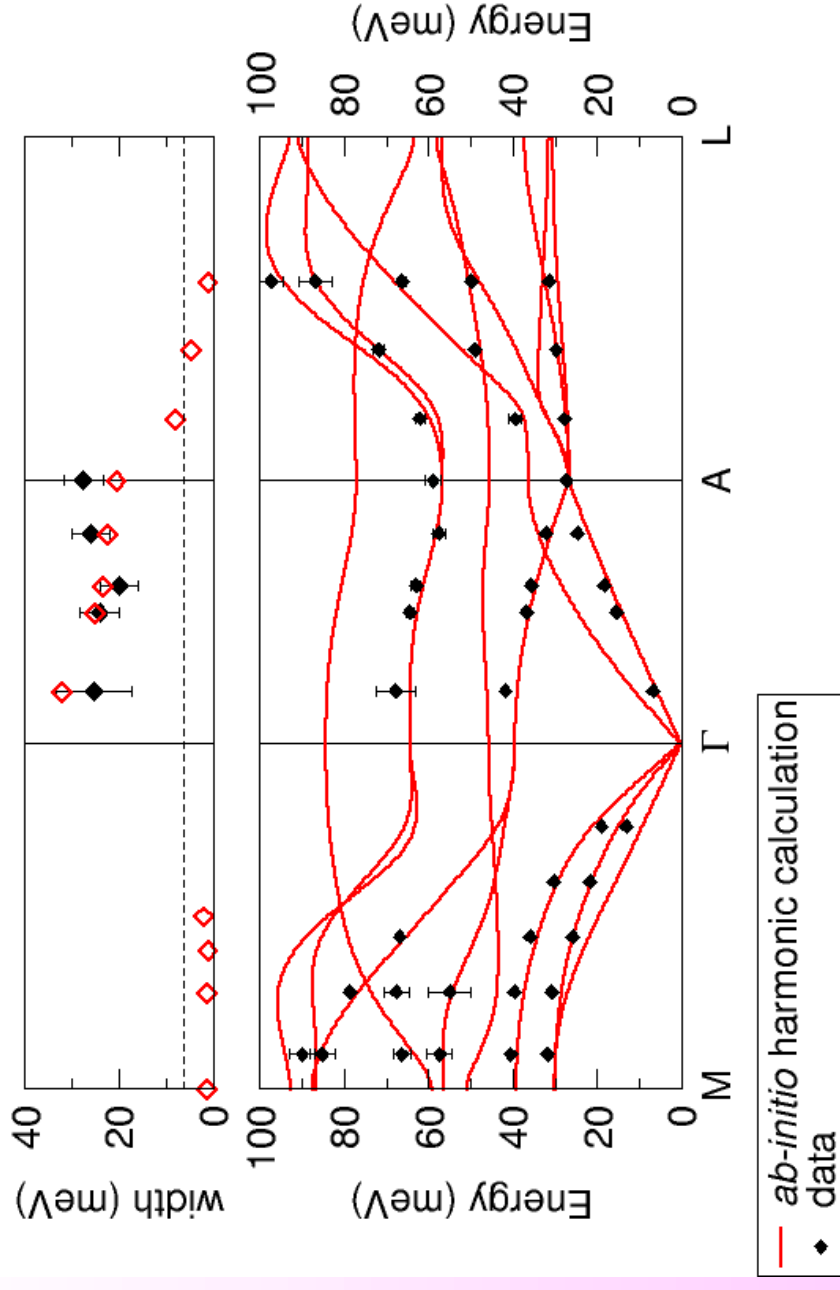
- Renormalisation of the highest LO branch.
- Anomalous dispersion of the LO branch.

$\Rightarrow$

Electron-phonon coupling as well in n-doped cuprates.

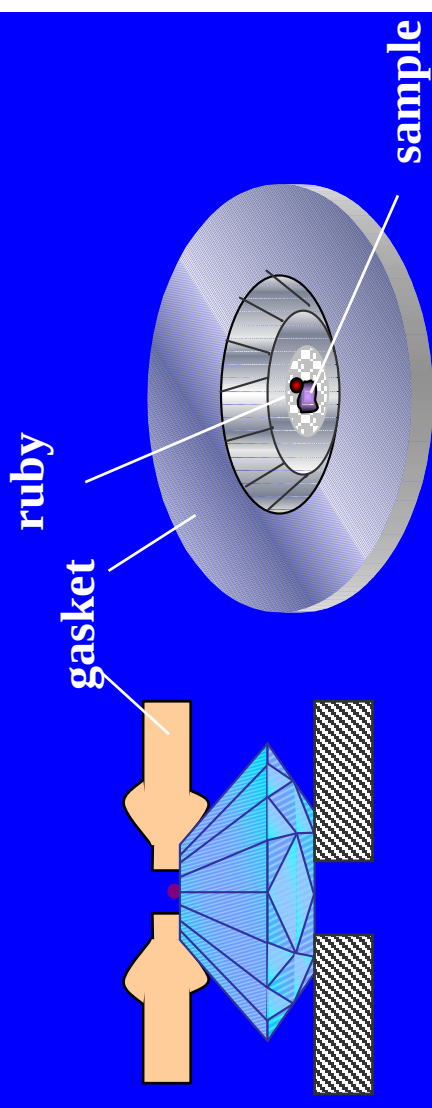
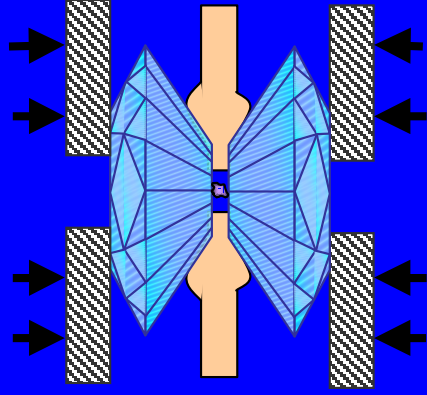
Phonon dispersion and lifetime in MgB₂

A. Shukla, M. Calandra, M. d'Astuto et al. *Phys. Rev. Lett.* **90** (2003)



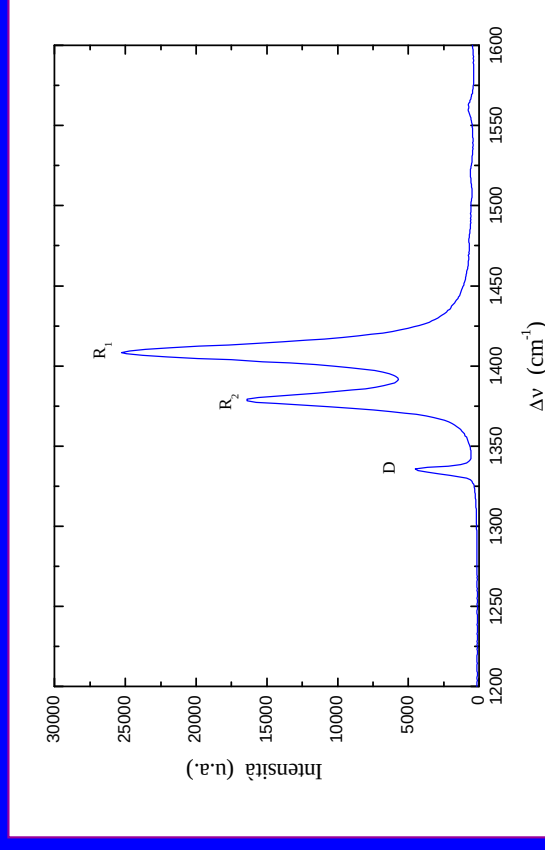
Experimental determination of the e⁻-ph coupling constant $\lambda(q)$

High pressure applications: the diamond anvil cell

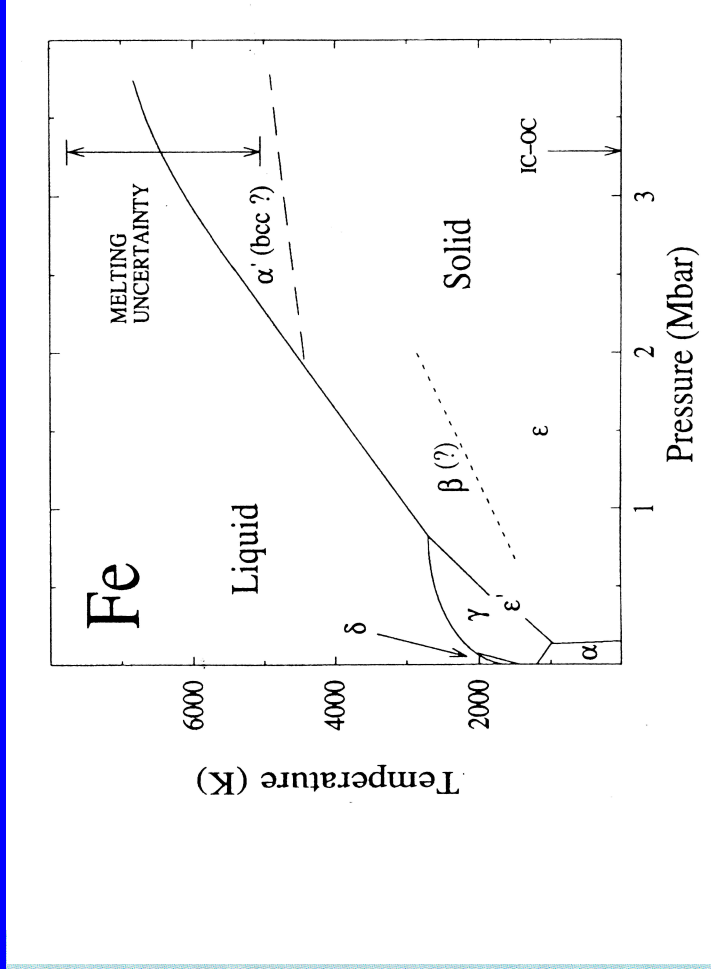
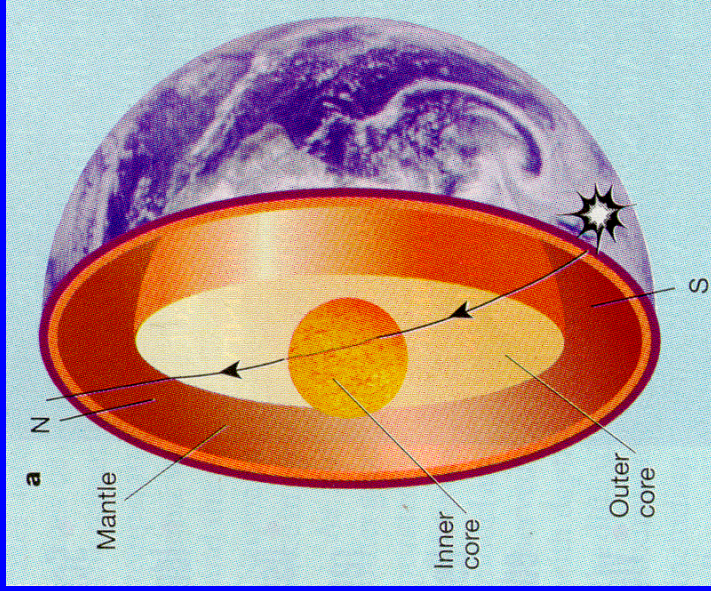


Pressure determination by Ruby fluorescence

Sample size: 50 μm ; $t=20\text{ }\mu\text{m}$
Sample volume: $4 \times 10^{-5}\text{ mm}^3$
X-ray beam size: $25 \times 60\text{ }\mu\text{m}^2$ (FWHM)



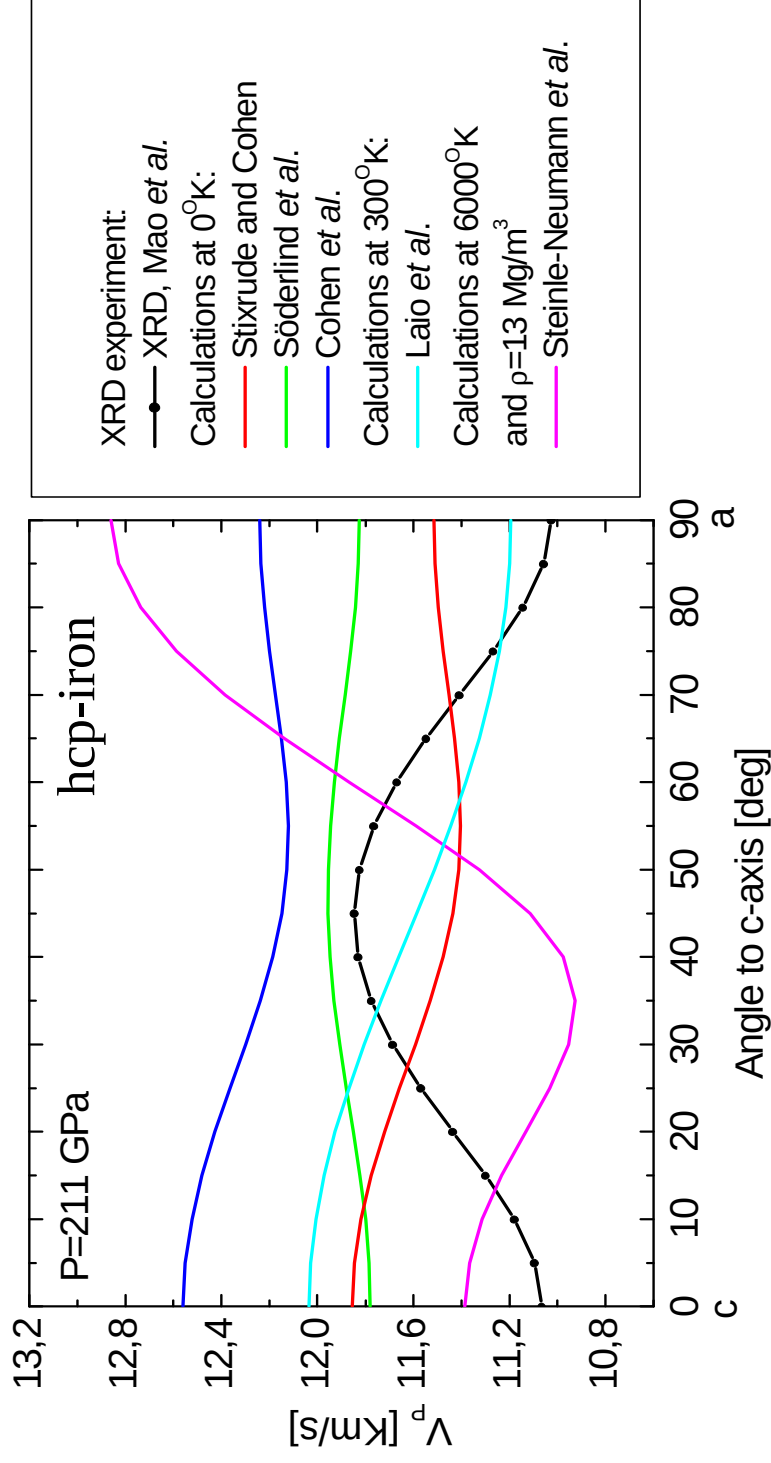
Geophysical applications of IXS



Determination of sound velocities

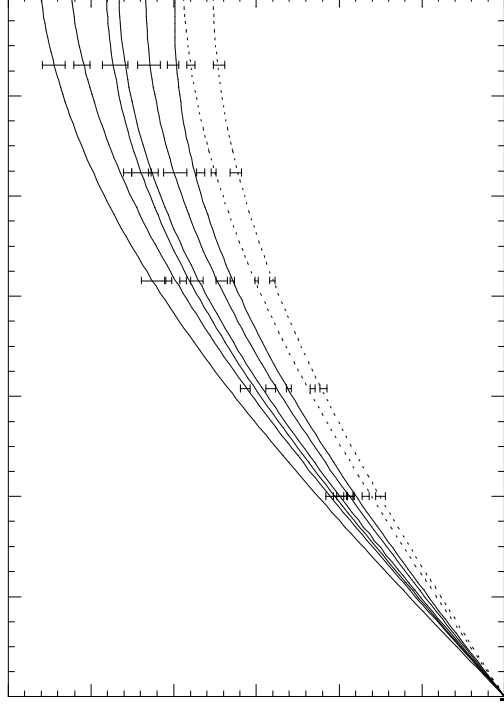
- Comparison with seismic results
- Geochemical models

Anisotropy in sound propagation

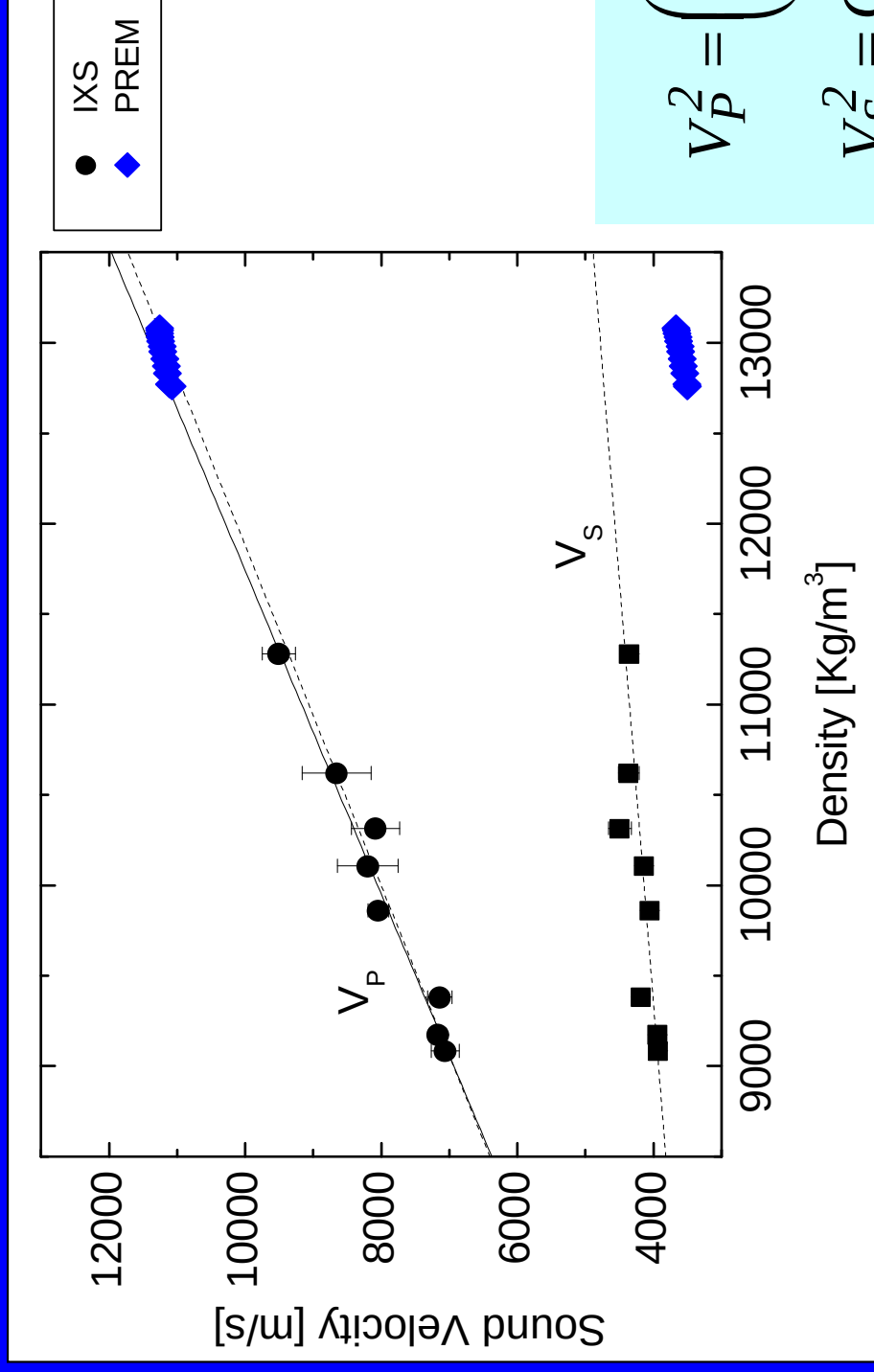


Urgent need for experimental result !!!

Polycrystalline ε (hcp)-Eisen



Density dependence of V_P and V_S

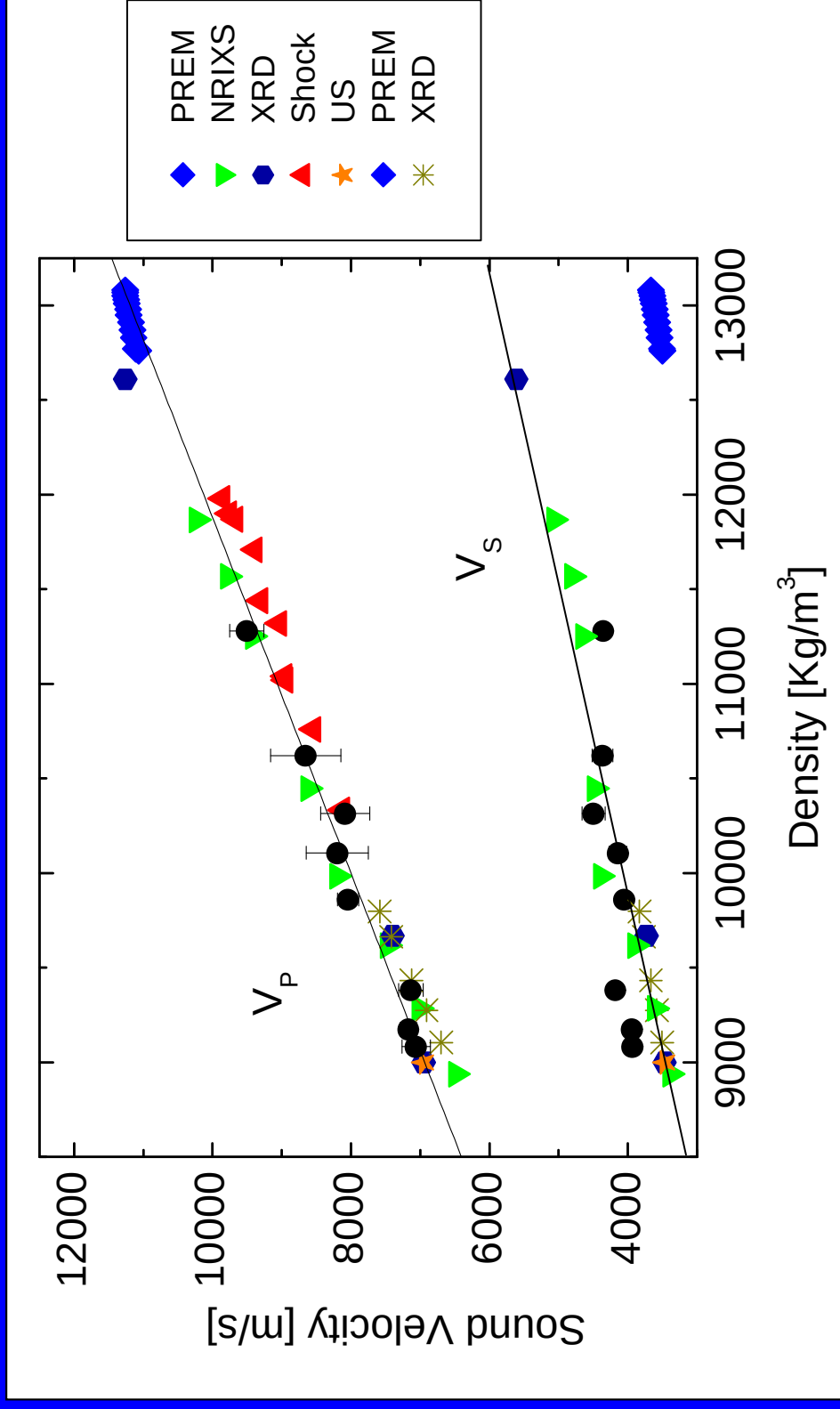


$$V_P^2 = \left(K + \frac{4}{3} G \right) / \rho$$

$$V_S^2 = G / \rho$$

D. Antonangeli et al; Earth and Planetary Science Letters 225, 243 (2004)

Comparison with other experimental results



Conclusions

- Good agreement of different experimental results.
 - “benchmark” for theoretical approaches.
- Shock experiments yield systematically lower results for V_p .
 - $V_p(\rho, \mathbf{T})$
 - ϵ -iron V_p too low with respect to PREM.
 - different iron phase?
 - light elements?
- Strong temperature effect for V_s .
 - strong T-dependence of shear modulus G close to melting.
(*Laio et al.; Science 287, 1027, 2000*)
 - Partial melting of inner core?

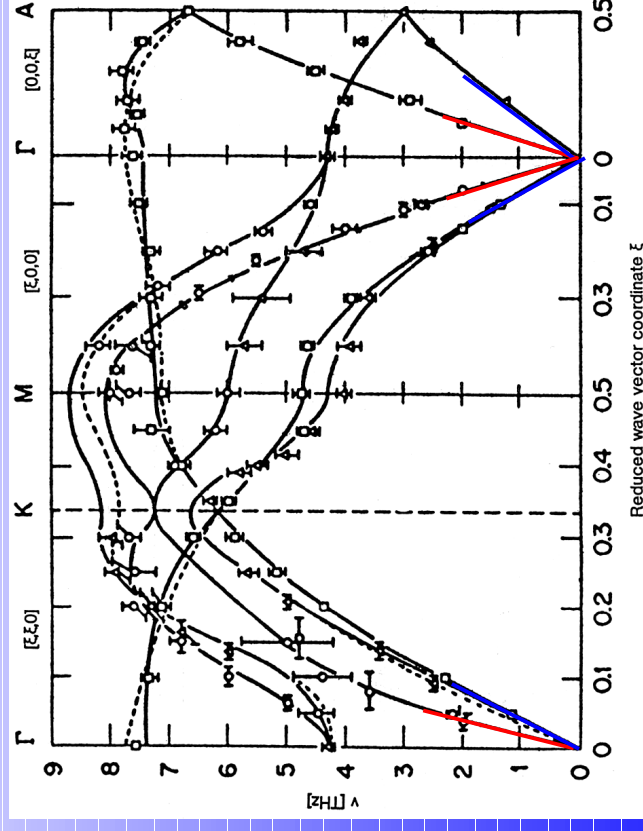
Studies on polycrystals:

- Orientational average (V_P)
- No direct determination of V_S

Single crystals:

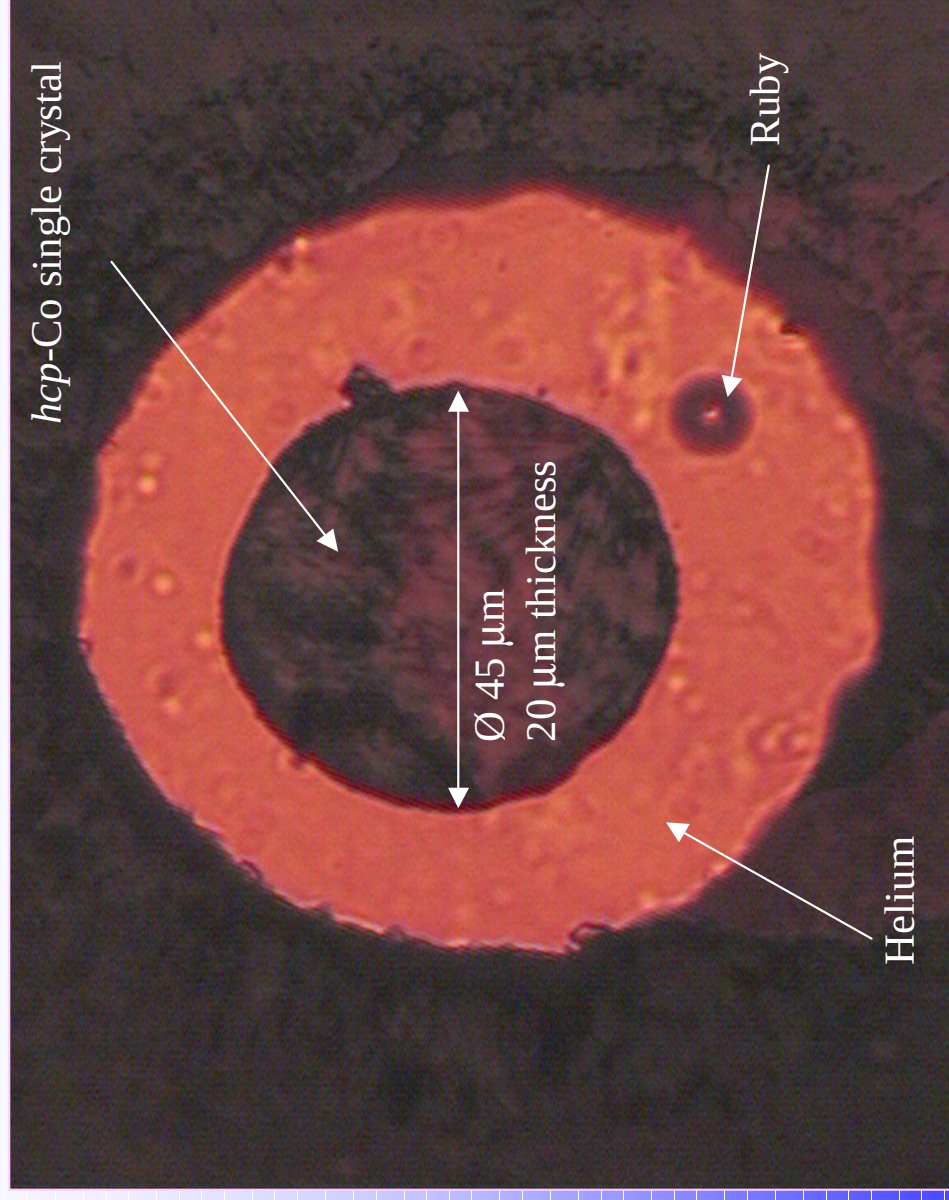
- complete elasticity tensor

hcp-Co



D. Antonangeli et al. Phys. Rev. Lett. 93, 215505 (2004)

Cobalt single crystal in DAC



Sample preparation: C. Aracne, D. Farber, F. Occelli (LLNL, USA)

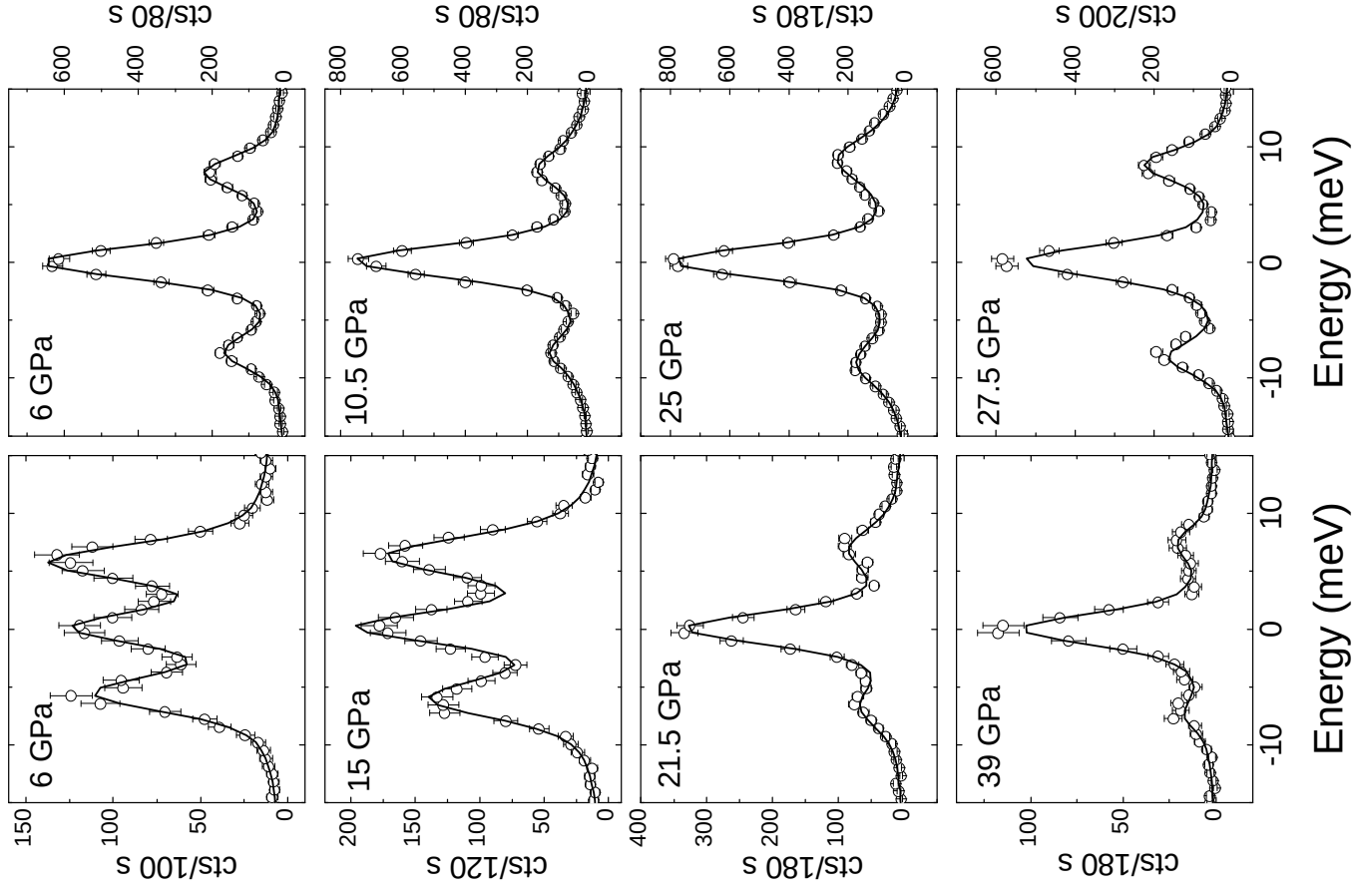
Gas loading: B. Couzinet (Paris) and D. Gibson, M. Hanfland (ESRF)

LA(100)

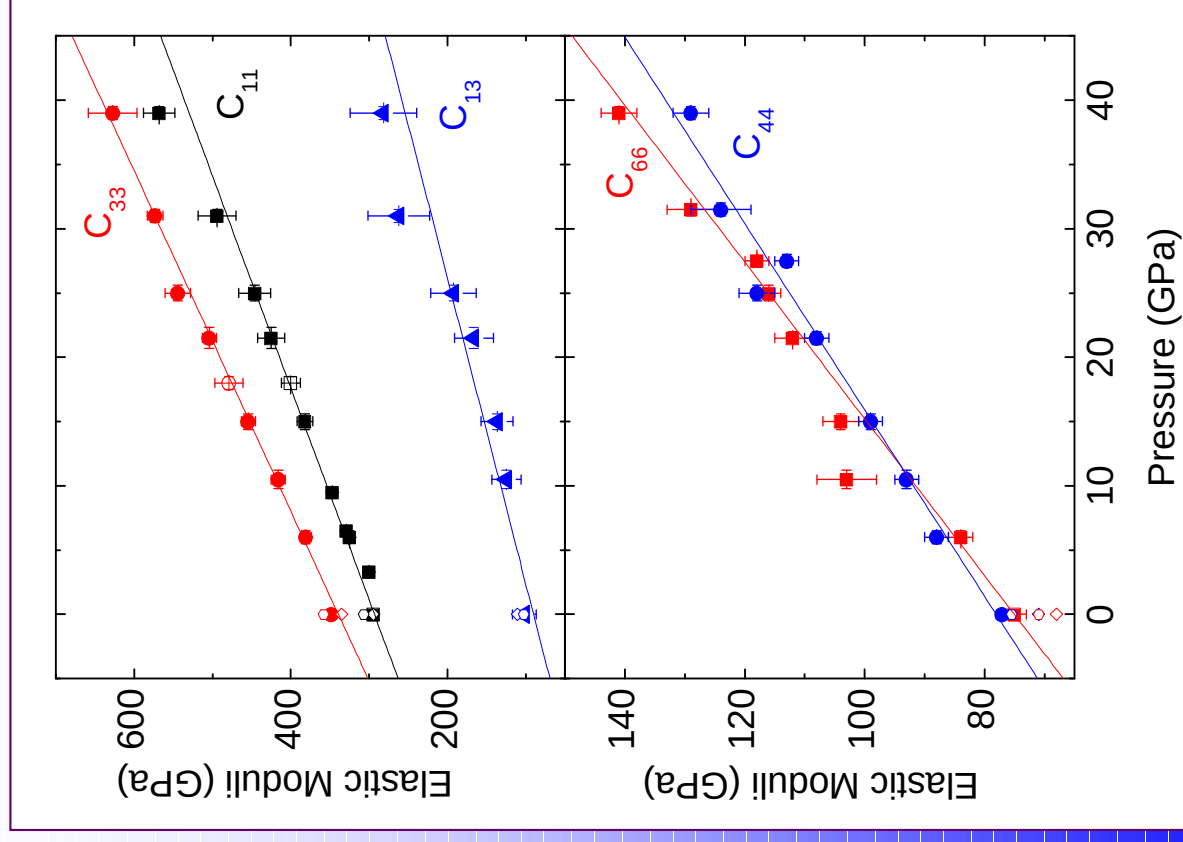
Q(1.05; 0; 0)

TA(110)_{<001>}

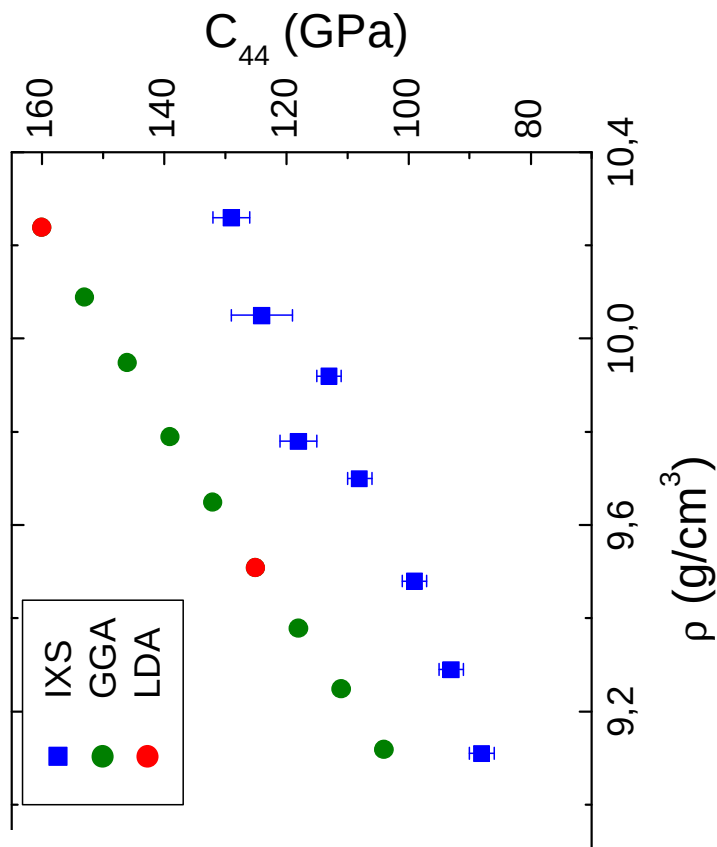
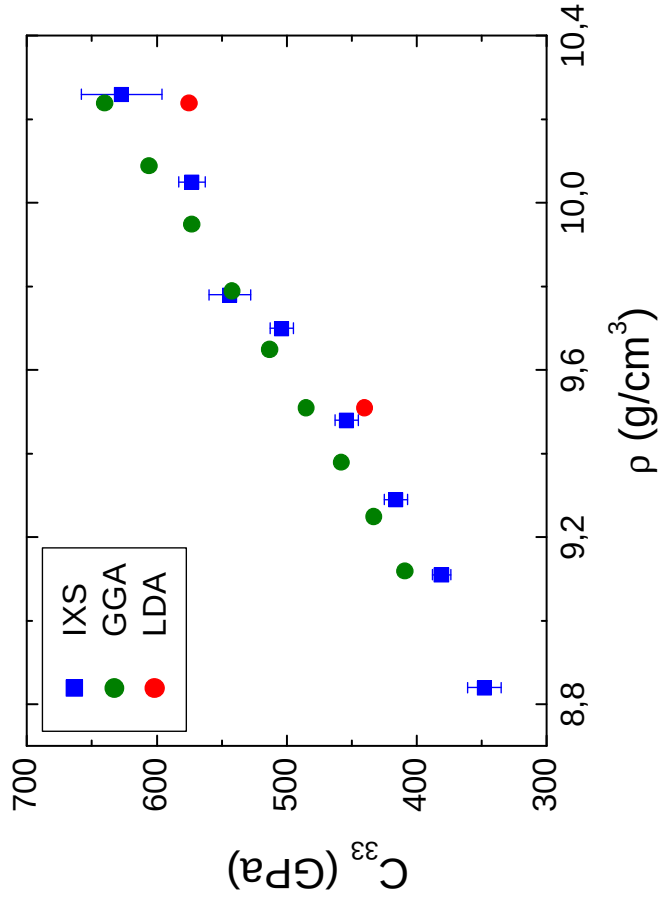
Q(0.075; -0.15; 2)



Pressure evolution of elastic moduli

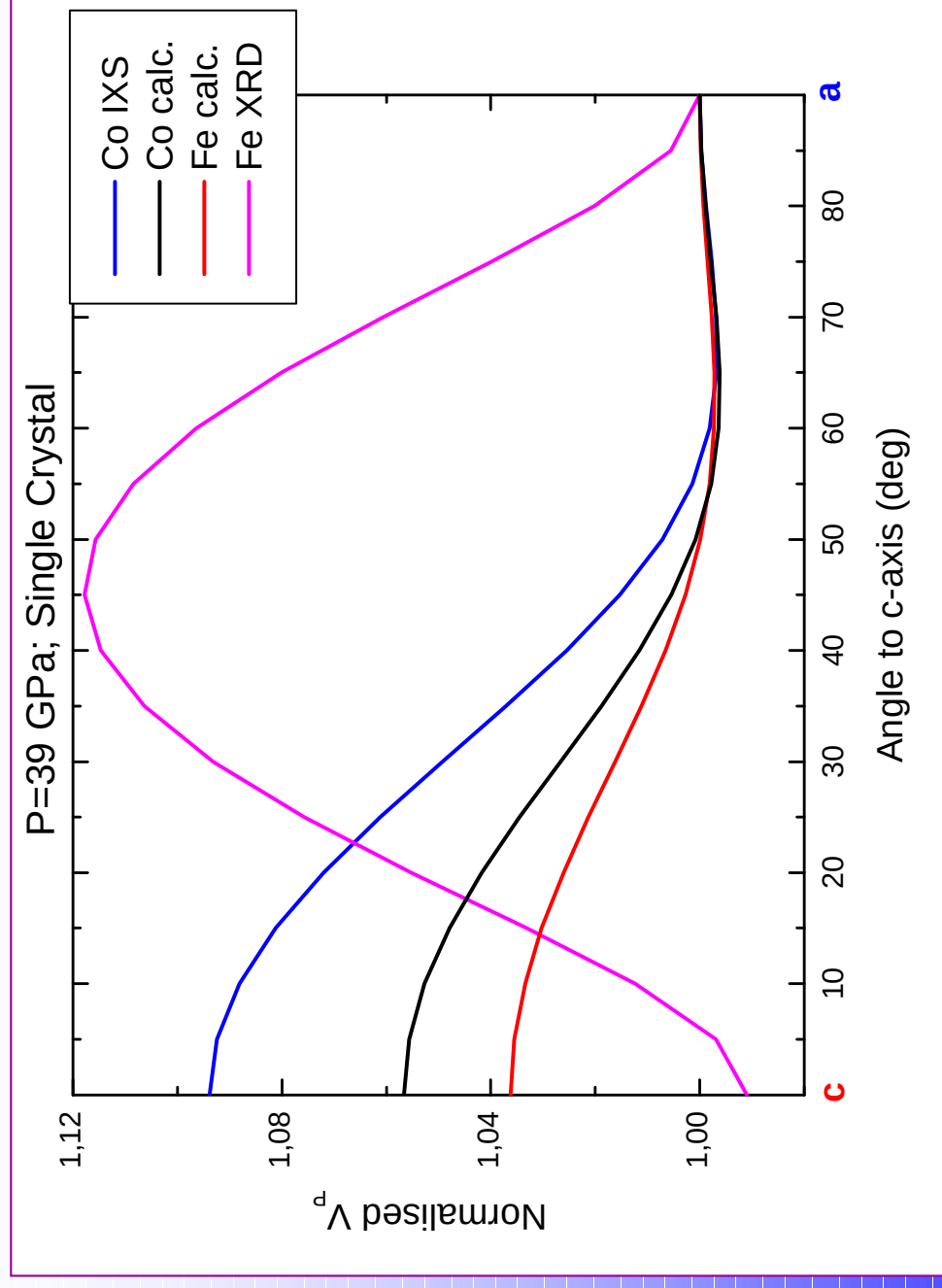


Comparison with Theory



Calculations: Steinle-Neumann et al., Phys. Rev. B 60, 791 (1999)

Comparison: Cobalt <-> Iron



Calculations: Steinle-Neumann et al., *Phys. Rev. B*, **60**, 791 (1999)

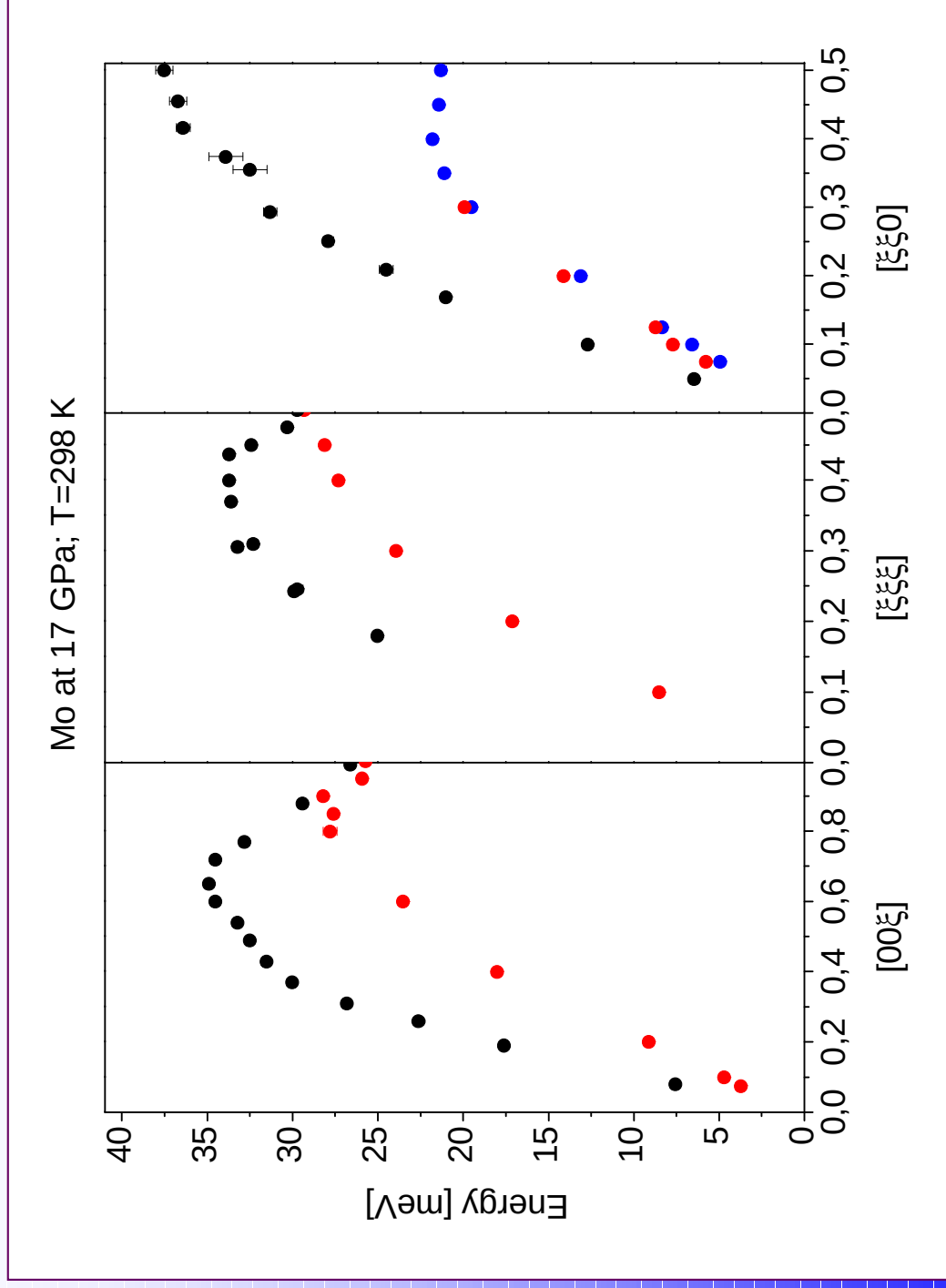
XRD: Mao et al., *Nature*, **396**, 741 (1998)

Conclusions

- Experimental determination of C_{ij} 's with a few % accuracy.
- Reasonable agreement between experiment and theory:
 - choice of pseudo-potential
 - electron exchange and correlation
 - choice of applied strains
- Shape of the V_p variation correctly reproduced.
- ΔV_p (0° - 90°) ∇P .
- Co und Fe: very similar elastic properties ≤ 40 GPa.
- XRD measurements ???

Phonon dispersion of Molybdenum

(D. Farber, M. Krisch, F. Occelli, A. Beraud et al.)



Determination of the phonon density of states

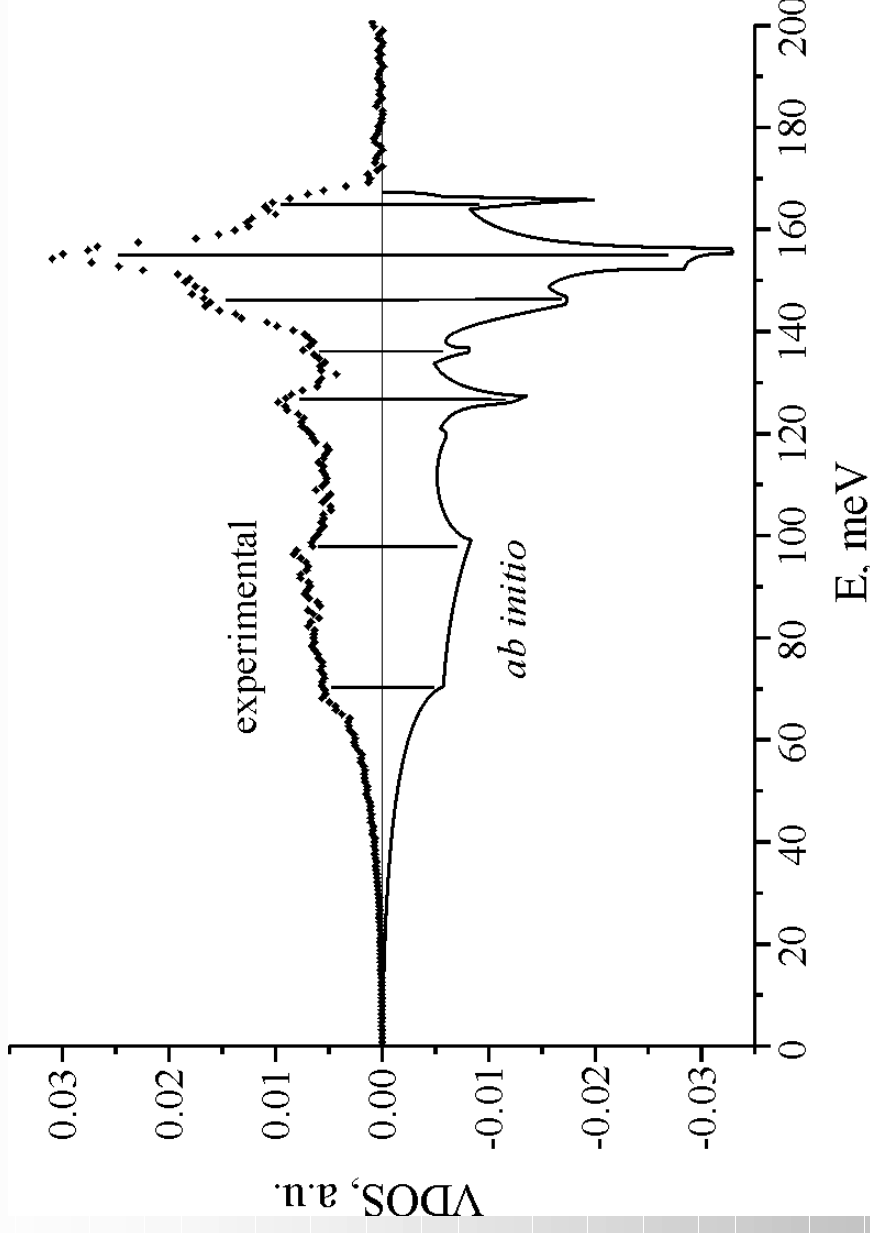
A. Bosak and M. Krisch

- Incoherent inelastic neutron scattering
 - sample volume: 10^{-4} mm^3
 - $f(Q)$ versus b
- Nuclear inelastic scattering
 - no need of Mössbauer isotope

Prerequisites

- Uniform sampling of the Brillouin zone
- Mutual annihilation “selection rule” -terms

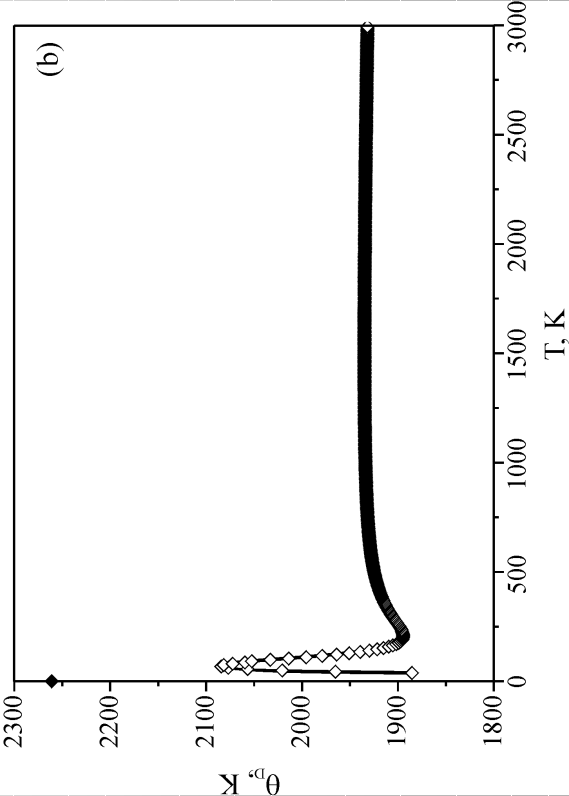
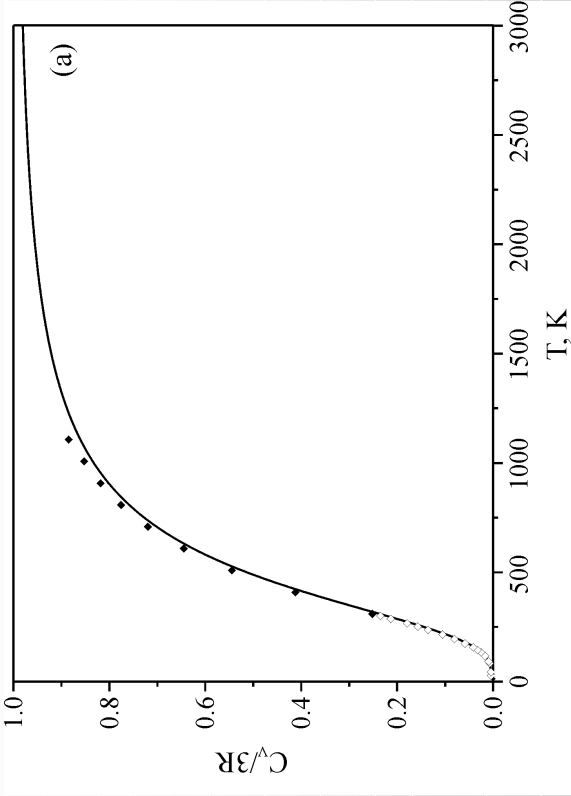
Test case: polycrystalline diamond



- $\Delta E = 3 \text{ meV}$
- Sum of 10 IXS spectra ($45 \text{ nm}^{-1} < Q < 60 \text{ nm}^{-1}$)

Ab initio calculations: P. Pavone et al., Phys. Rev. B 48 (1993) 3156

Results



Parameter	X-VDOS	Other results
Θ_D high T	1930 K	1860 K
Θ_D low T	2250 K	2240 K
V_D	13550 m/s	13455 m/s [4]

References

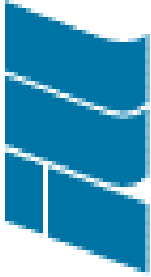
- [1] A.C. Victor, J. Chem. Phys. 36 (1962) 1903
- [2] W. DeSorbo, J. Chem. Phys. 21 (1953) 876
- [3] Specific heat: non-metallic solids. Eds. Y.S. Touloukian, E.H. Buyco, IFI/Plenum New York – Washington 1970.
- [4] E.S. Zouboulis *et al.*, Phys. Rev. B 57 (1998)

Perspectives

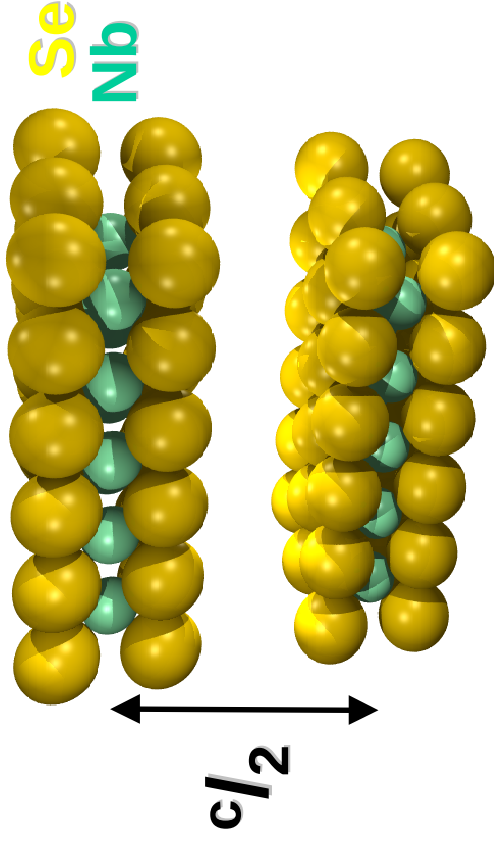
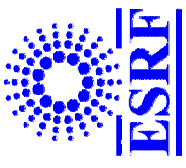
- High pressure studies
- XVDOS (V_D) + IXS (V_P) + Diffraction (B)
=> single crystal elastic constants
- Combining X-VDOS, INS and NIS
 - extract partial VDOS in multi-component systems

Surface IXS on 2H-NbSe₂

B. Murphy¹, H. Requardt², J. Stettner¹, M. Müller¹,
M. Krisch², W. Press^{1,3}.

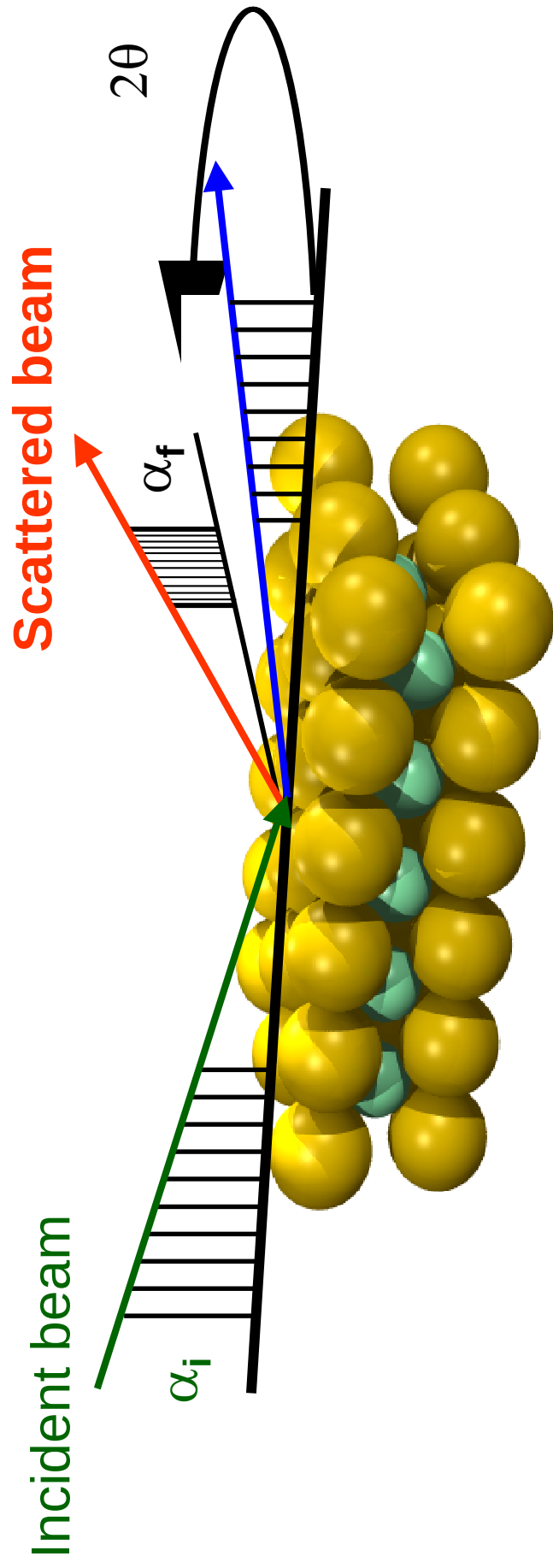


¹University of Kiel, ²ESRF, ³ILL



- Layered hexagonal structure ($a=3.443 \text{ \AA}$, $c=12.547 \text{ \AA}$)
- 2-D like behaviour
- Formation of a charge-density wave below $T_C = 33 \text{ K}$

Grazing Incidence Scattering

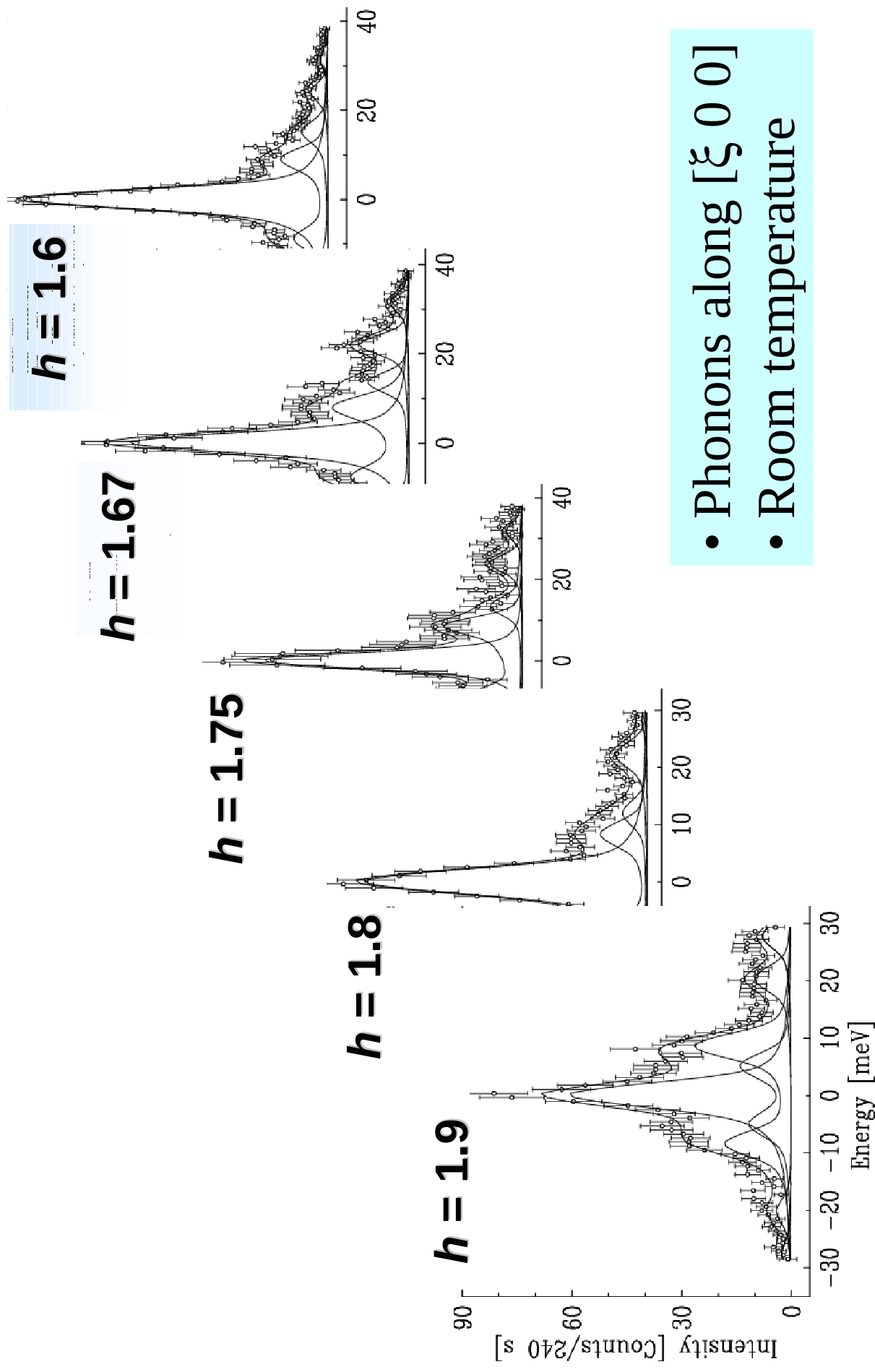


NbSe₂ @ 15.817 keV ($\alpha_c = 0.18^\circ$)

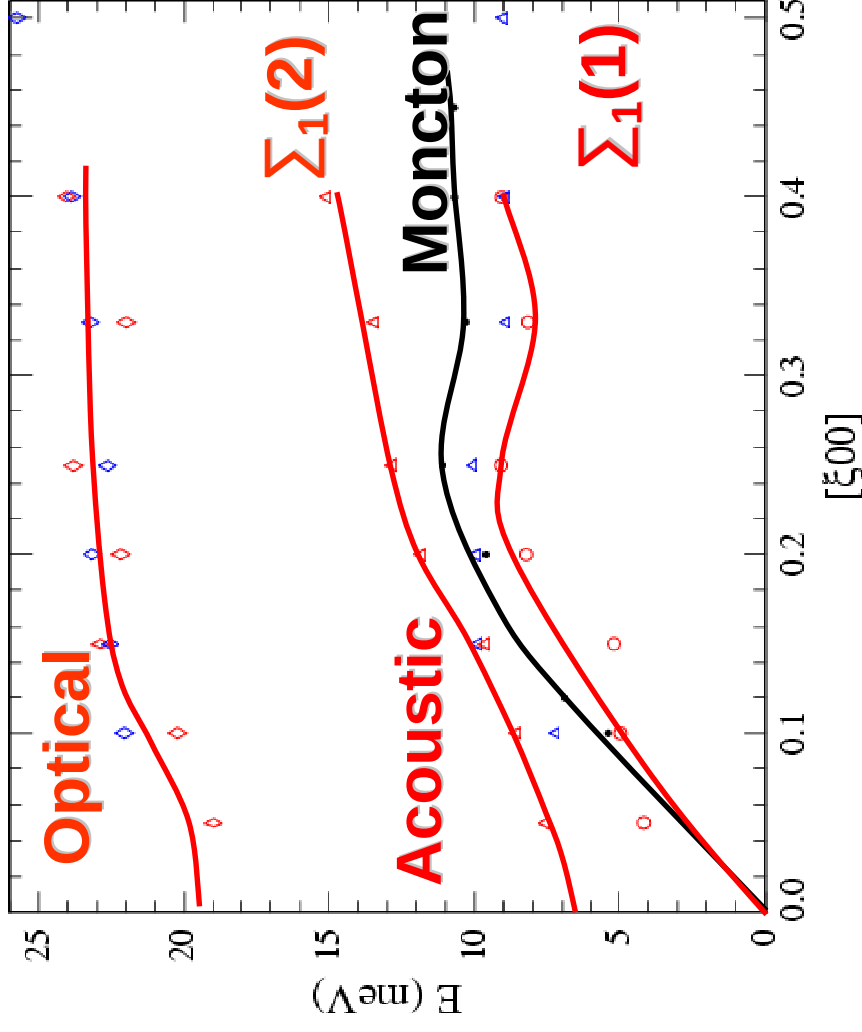
$\alpha_i = \alpha_c - 0.03^\circ$, penetration depth: ~ 23 Å

Energy resolution: 5.5 meV

First X-ray Surface Phonon Spectra



Surface Phonon Dispersion Curve



Differences between surface and bulk dynamics

- Evidence of phonon softening already at RT
- Temperature dependent study

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University of Krakow:	K. Parlinski