How to obtain crystal field parameters ?

Several ways / answers

✓Magnetic :

- Susceptibility fit,
- Specific heat,
- Magnetization curves, different directions, anisotropy
- Magnetic phase diagram (dependence of orientation, anisotropy)

✓Thermal studies

- Specific heat (magnetic contribution to)

✓Neutron Scattering

- Very general useful in most cases widely used

✓Optic

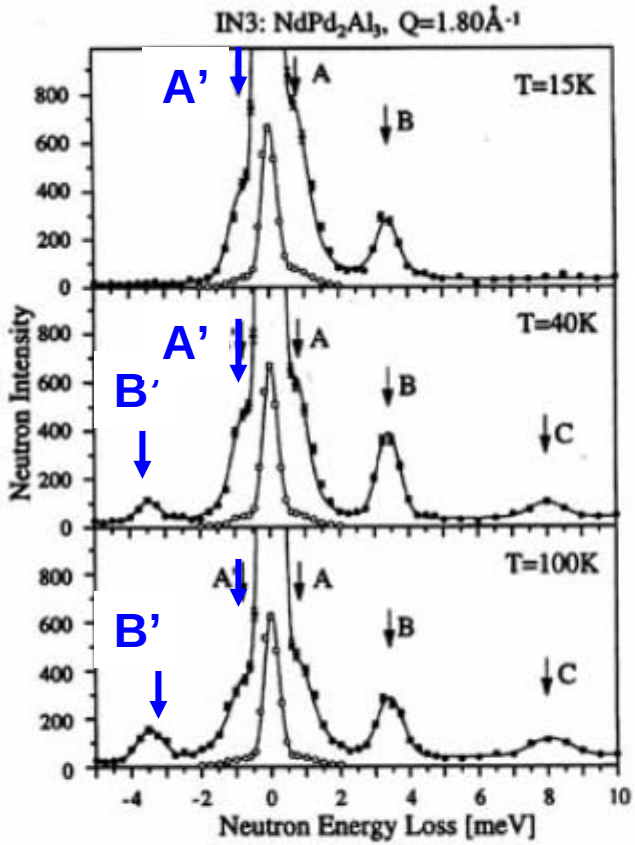
✓Mössbauer spectroscopy

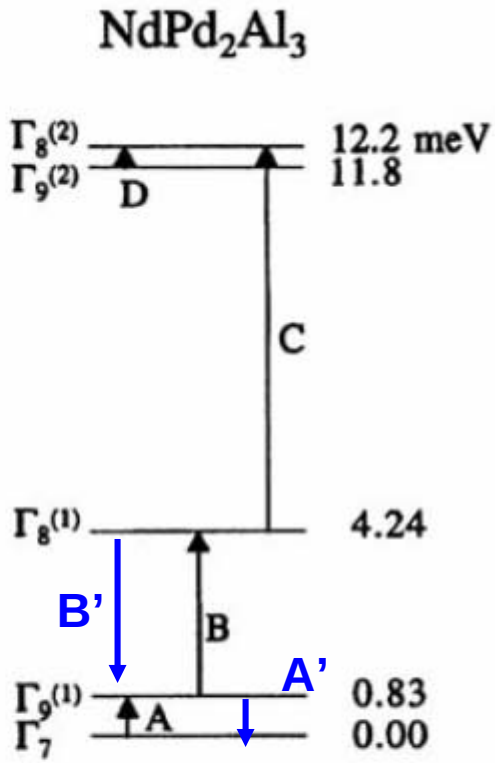
✓X-ray spectroscopy

✓Theoretical structure calculation of charge distribution (DFT…)

✓…

Inelastic Neutron Scattering technique





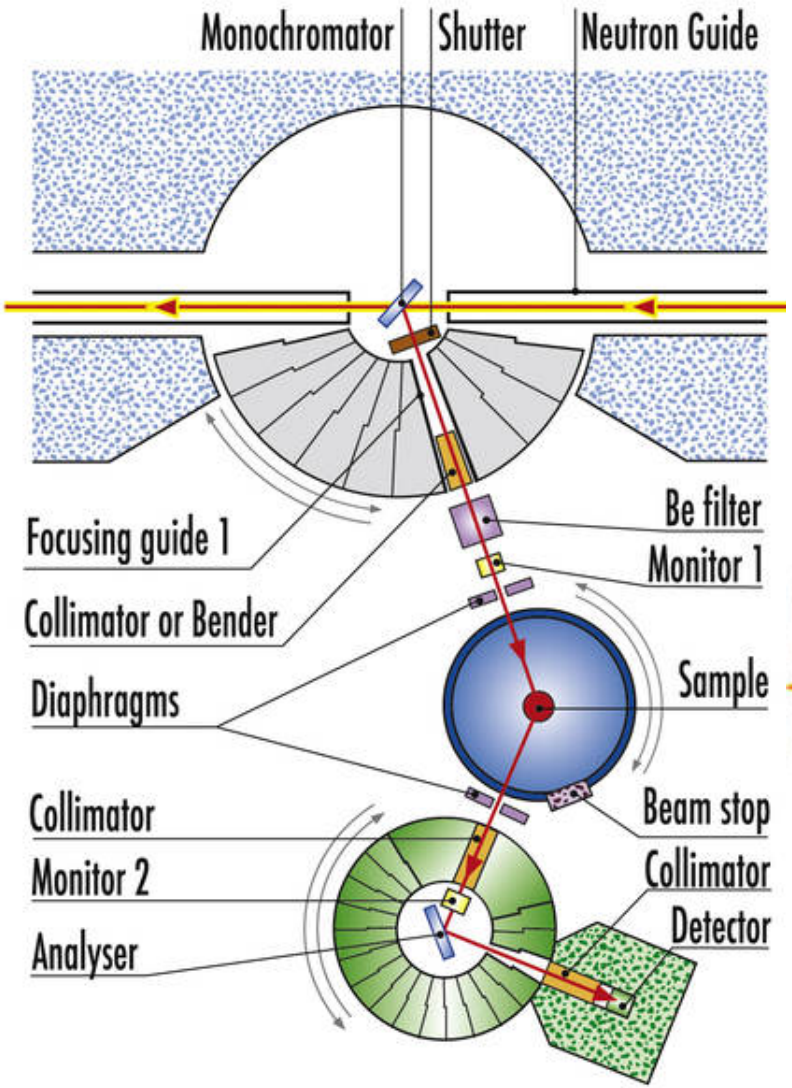
Only A,B,C are possible transitions at very low temperature

Dönni A., Fürrer A., Kitazawa H., Zolliker M.: Neutron Crystalline-Electric-Field Spectroscopy of RPd_2Al_3 (R = Ce, Pr, Nd). J. Phys. Condens. Matter. 9 5921–5933 (1997).

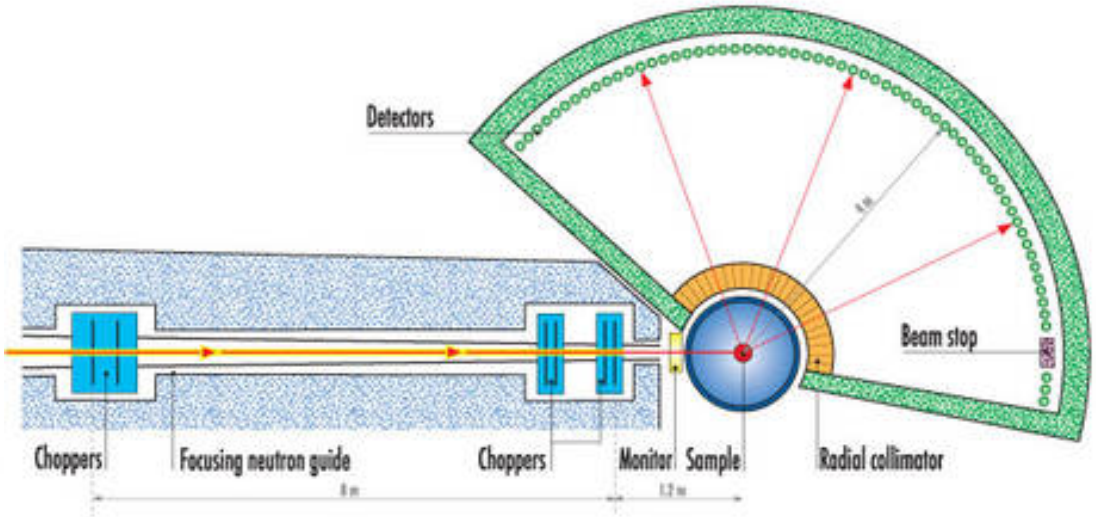
Inelastic neutron spectrometer

NEUTRONS FOR SCIENCE

Triple axis spectrometer



Time of flight instrument



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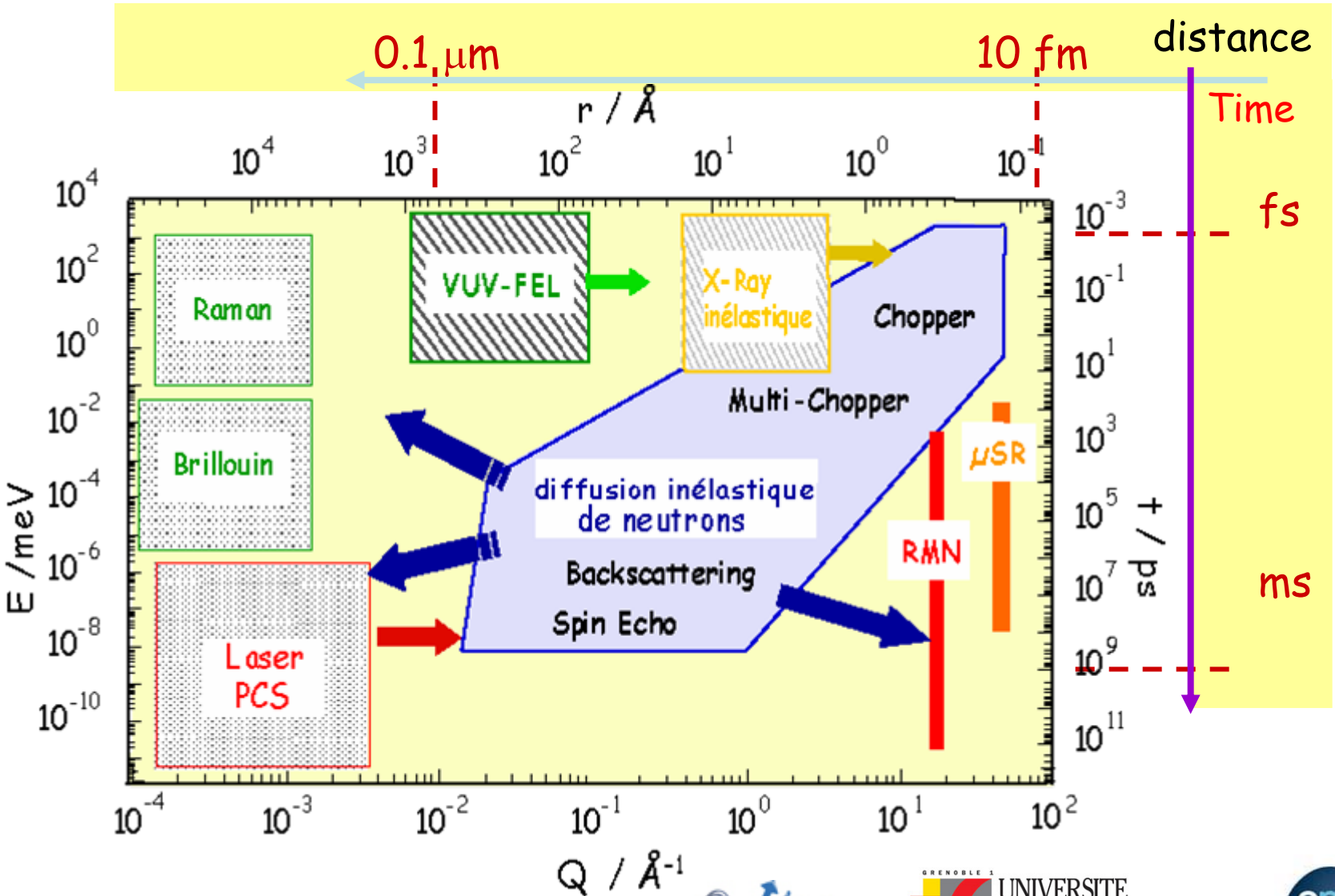
neutrons to probe matter

on large time and distance scales



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Mössbauer spectroscopy

- Hyperfine parameters are sensitive to the charge distribution
- Gd^{3+} pure S state L=0 !! => asphericity comes from surrounding only!

From QS to Vzz

The fitting routine provides the absolute value of the hyperfine field (H_{hf}), the isomer shift δ_{IS}, the quadrupole coupling constant $eQV_{zz} = \Delta E_Q$ and the polar angle θ which defines the direction of H_{hf} with respect to the z-axis of the efg tensor. This axis coincides with the crystallographic c-axis (Fig. 1). The re-

using the relation [11]:

$$B_2^0 = \alpha_J \langle r^2 \rangle_{4f} (1 - \sigma_2) A_2^0, \qquad (1)$$

with $A_2^0 = -\Delta E_Q / [4e(1 - \gamma_\infty)Q]$. The quantity A_2^0 is a universal factor applicable to all isostructural compounds of rare-earths, α_J is the Stevens factor and $\langle r^2 \rangle_{4f}$ is the mean square radius of the 4f wave function, varying from one rare-earth atom to another. σ_2 is a screening coefficient estimated to amount about 0.6 for any rare-earth atom. It describes the modification of the crystal field due to the response of closed shells to the external field. γ_∞ is the Sternheimer antishielding factor of the efg produced by the lattice charges (i.e. the polarization of the core electrons). A value of $\gamma_\infty = -92$ has been derived from $(1-\gamma_\infty)Q = 1.21(3) \times 10^{-26}$ m^2 reported by Barton

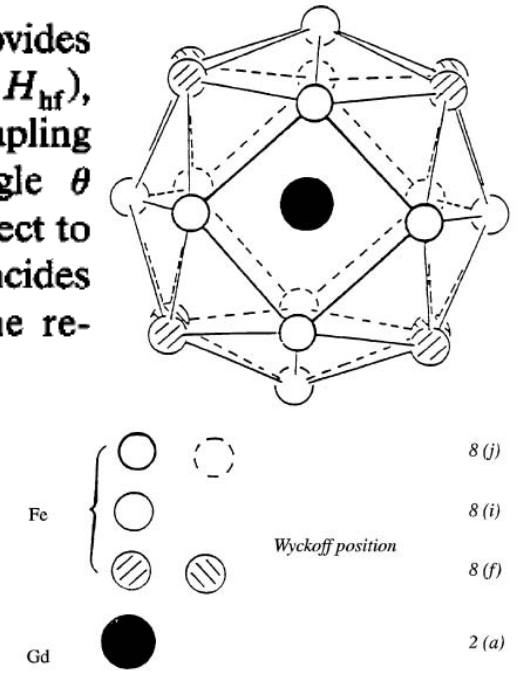


Fig. 3. Local atomic environment around the Gd atom in $GdFe_{11}Ti$.

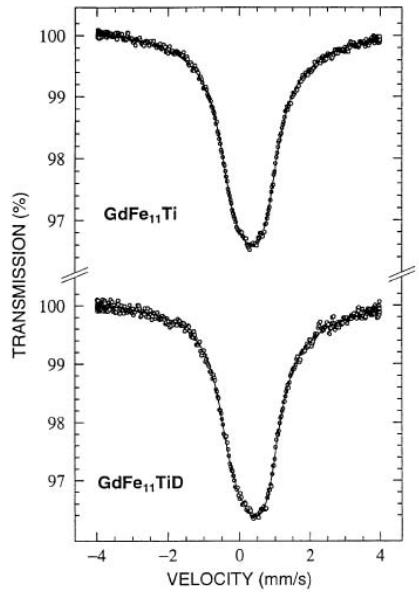


Fig. 4. ^{155}Gd Mössbauer spectra of the $GdFe_{11}Ti$ and $GdFe_{11}TiH_{1-\delta}$ recorded at 4.2 K.

O. Isnard, P. Vulliet, J.P. Sanchez, D. Fruchart, J. Magn. Magn. Mater. 189 (1998) 47-54

Compound	H_{hf} (kOe)	ΔE_Q (mm/s)	V_{zz} (10^{21} V/m^2)	A_0^2 (Ka$_0^{-2}$)	θ^a (°)	δ_{IS} (mm/s)	F W H M (mm/s)
$GdFe_{11}Ti$	175(2)	0.26(5)	0.58(11)	− 50(10)	0	0.26(1)	0.86(2)
$GdFe_{11}TiH_{1-\delta}$	184(2)	0.40(5)	0.89(11)	− 77(10)	0	0.30(1)	0.81(2)

Getting the crystal field parameters from anisotropy coefficient

$$E_R^a = K_{1R}\sin^2\theta + [K_{2R} + K'_{2R}\cos 4\phi]\sin^4\theta + [K_{3R} + K'_{3R}\cos 4\phi]\sin^6\theta, \quad (1)$$

$$K_{1R} = -(3/2)B_{20}\langle O_{20}\rangle - 5B_{40}\langle O_{40}\rangle - (21/2)B_{60}\langle O_{60}\rangle, \quad (2a)$$

$$K_{2R} = (35/8)B_{40}\langle O_{40}\rangle + (189/8)B_{60}\langle O_{60}\rangle, \quad (2b)$$

$$K_{3R} = -(231/16)B_{60}\langle O_{60}\rangle, \quad (2c)$$

$$K'_{2R} = (1/8)B_{44}\langle O_{40}\rangle + (5/8)B_{64}\langle O_{60}\rangle \quad (2d)$$

and

$$K'_{3R} = -(11/16)B_{64}\langle O_{60}\rangle, \quad (2e)$$

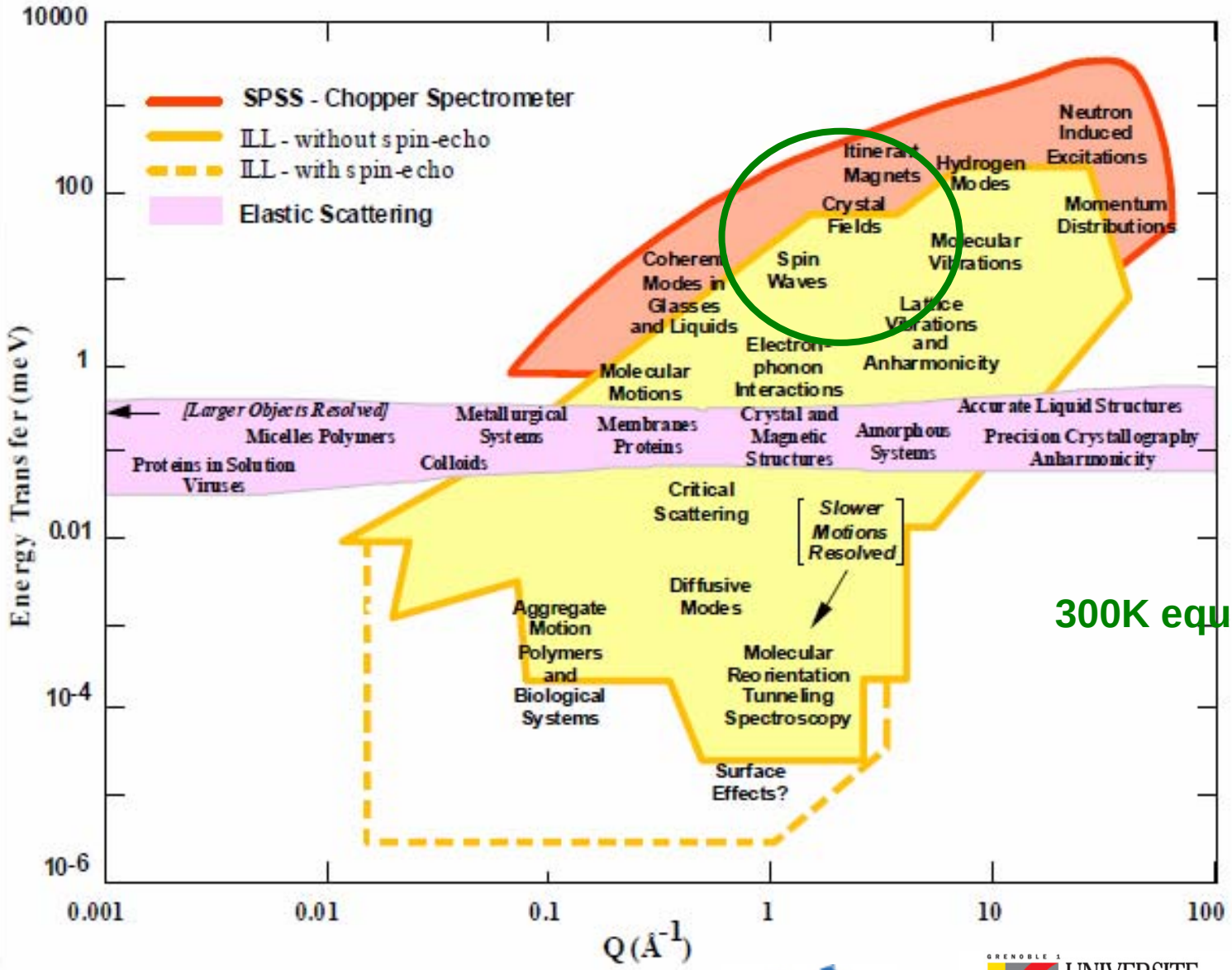
where $\langle O_{nm}\rangle$ are the thermal averages of the Stevens operators [31] and B_{nm} are the crystal field parameters, which depend on the rare-earth ion, and are given by $B_{nm} = \theta_n A_{nm}\langle r^n\rangle$, where θ_n are the single-ion Stevens coefficients, $\theta_2 = \alpha_J$, $\theta_4 = \beta_J$ and $\theta_6 = \gamma_J$, A_{nm} are the crystal field coefficients and $\langle r^n\rangle$ are the average values of the 4f electronic radial distributions.

See articles by

Stevens K W H 1952 *Proc. Phys. Soc.* A **65** 209

Hutchings, M. T. (1964) *Solid state phys., 16,* 227

K.H.J. Buschow and F.R. de Boer (2003) "Physics of Magnetism and materials" Kluver Academic/Plenum publisher



300K equ. 25meV

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