Novel Electronic and Magnetic Phases in Correlated Spin-Orbit Coupled Oxides
12-15 November 2019, JGU Mainz

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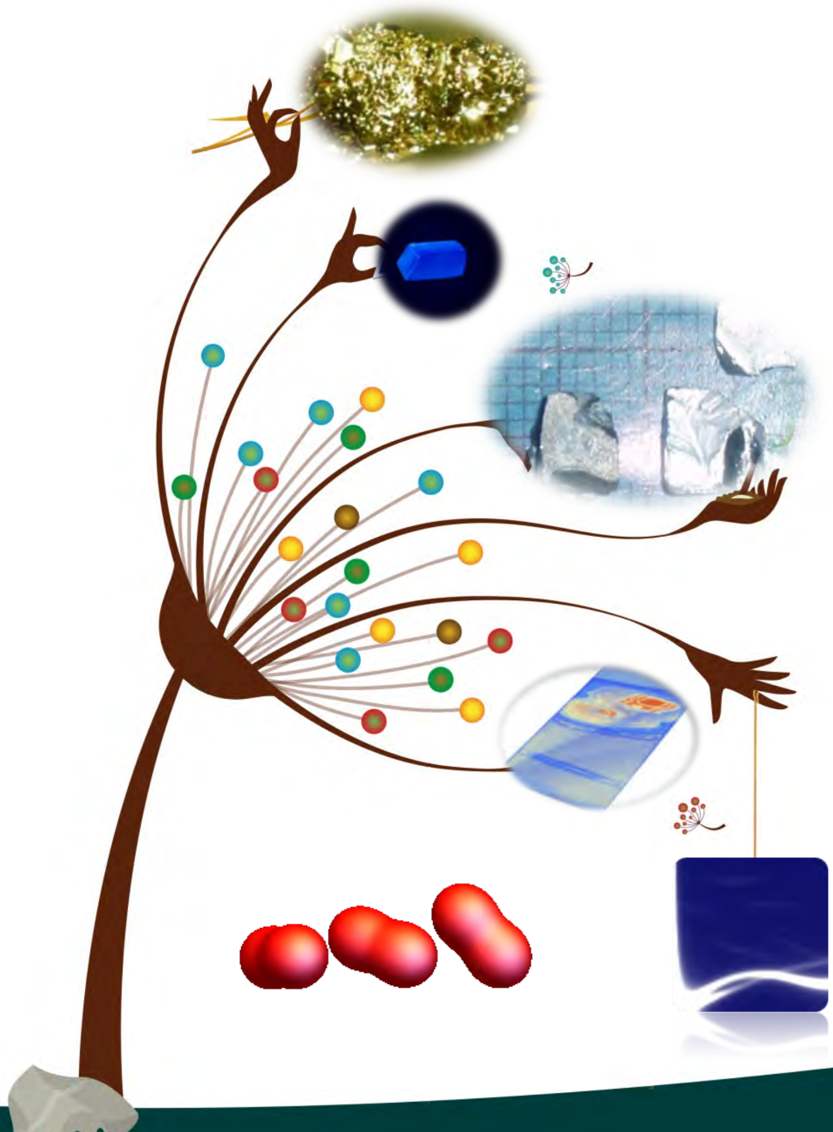
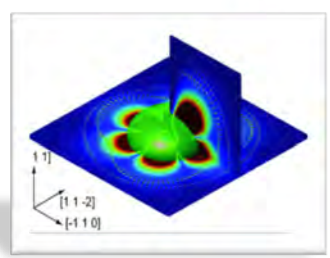
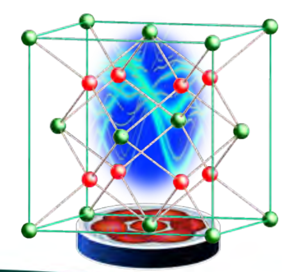


Multipolar order and collective excitations in actinide dioxides

Roberto G. M. Caciuffo





roberto.caciuffo@ec.europa.eu

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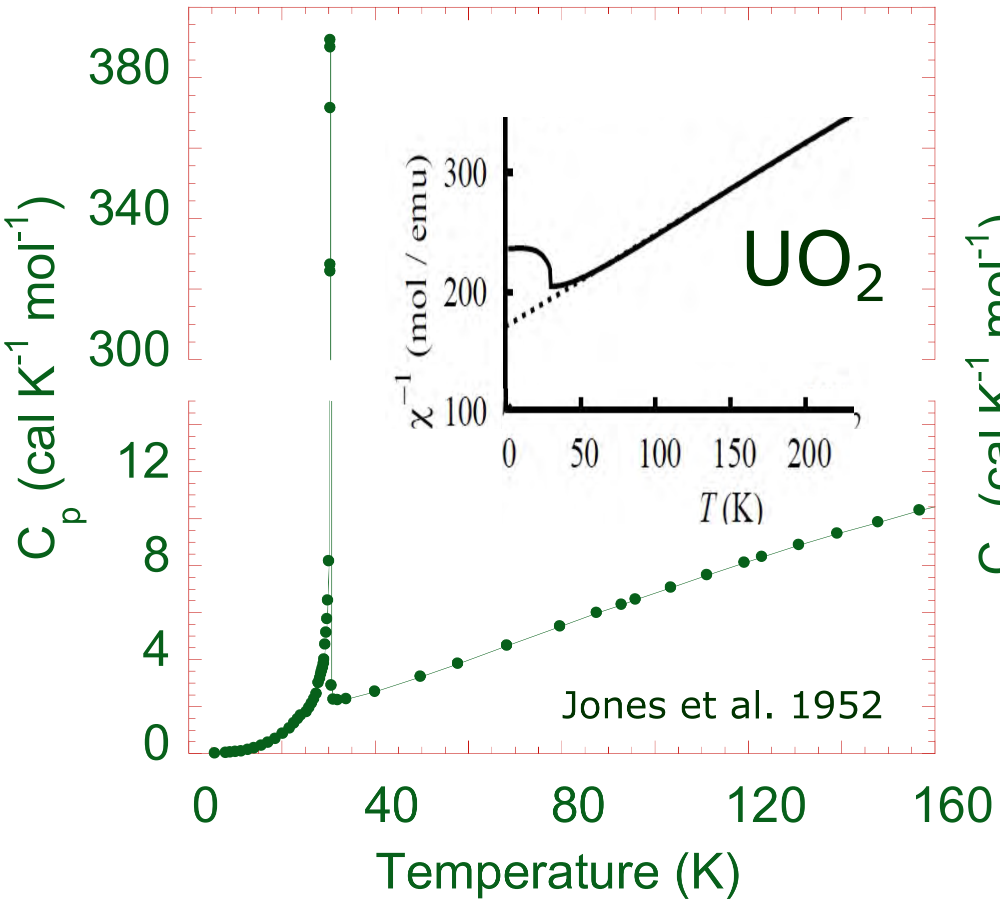
Outline

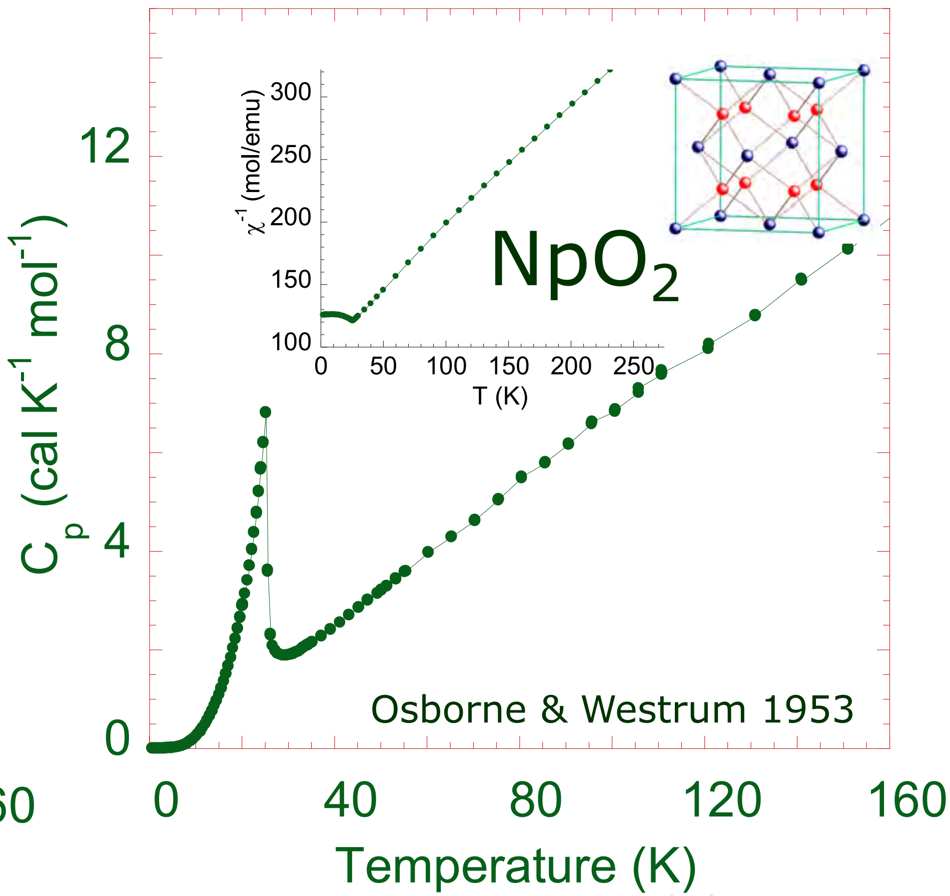
ROBERTO.CACIUFFO@EC.EUROPA.EU

- Ground state and long-range multipolar order in UO_2 and NpO_2
- Lattice dynamics and spin waves
- INS and IXS experiments
- Two-ions quadrupolar interactions
- Observation of dispersive quadrupole waves
- Avoided crossings and mixed modes

AnO_2 1940's-1950's: structure and long-range order

- Fluorite-type structure (Rundle et al., Zachariasen, 1940's)
- Long-range order (Jones et al. 1952, Osborne & Westrum 1953)
- Large gap semiconductors (Willardson et al. 1956)





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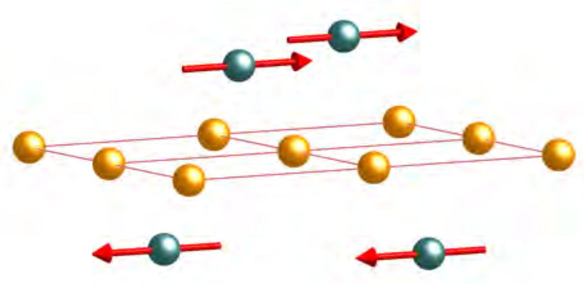
Magnetic Structure of UO_2

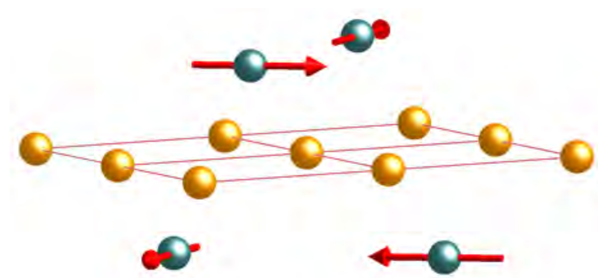
- Neutron diffraction confirms 1st order transition to an AF state in UO_2. (Henshaw & Brockhouse 1957)

- 1-k AF structure is proposed. (Willis & Taylor 1965; Frazer et al. 1965)



1-k

2-k AF structure and internal distortion of the oxygen cage (Faber & Lander 1976)



2-k

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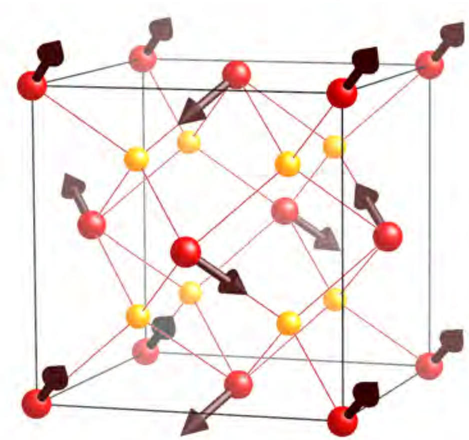
Magnetic Structure of UO_2

Correct magnetic structure proposed by Burlet et al. in 1986:

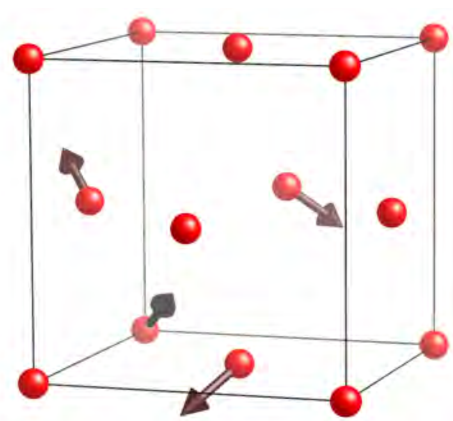
Type I, 3-k transverse structure
<001> propagation vector,
$\mu_0 = 1.74\ \mu_B$

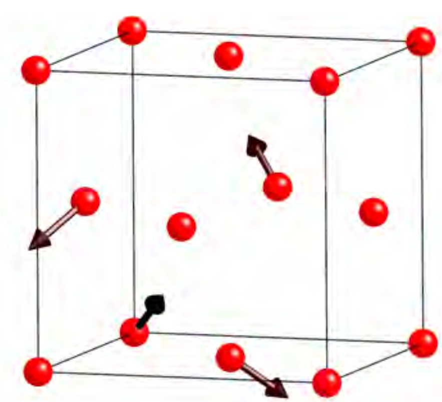
$$\vec{\mu}_n \propto \sum_{j=1}^{j=3} \vec{m}_{k_j} \exp(i\,\vec{k}_j \cdot \vec{R}_n)$$

$$\vec{k}_1 = (1, 0, 0) \text{ etc.}$$

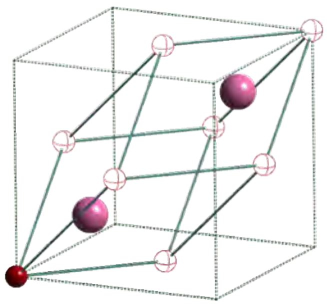


A: $\vec{m}_{100} = (0, 1, 0)$ etc. B: $\vec{m}_{100} = (0, 0, 1)$ etc.





Lattice dynamics of UO_2, inelastic neutron scattering



TA (2×)

LA (1×)

TO1 (2×)

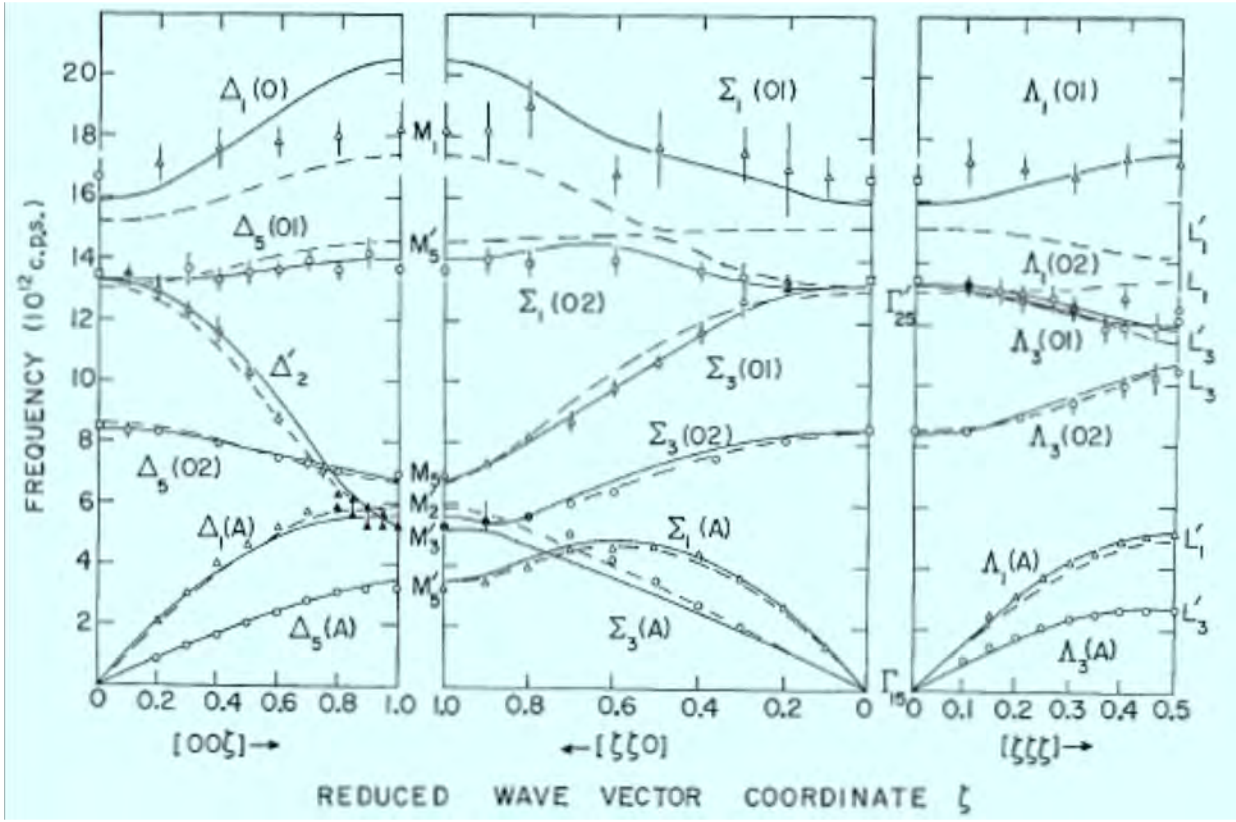
TO2 (2×)

LO1 (1×)

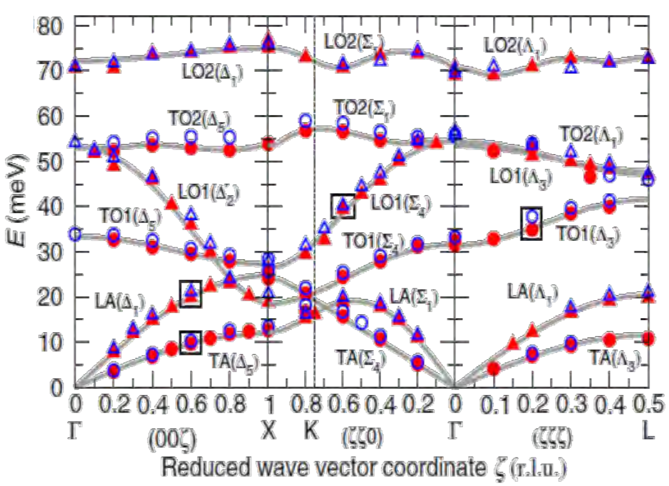
LO2 (1×)

$R_U = (0, 0, 0)$

$R_O = \pm(a/4)(1, 1, 1)$



Dolling, Cowley & Wood, 1965; Cowley & Dolling, 1966 & 1968



J.W.L. Pang et al., PRL 110, 157401 (2013)

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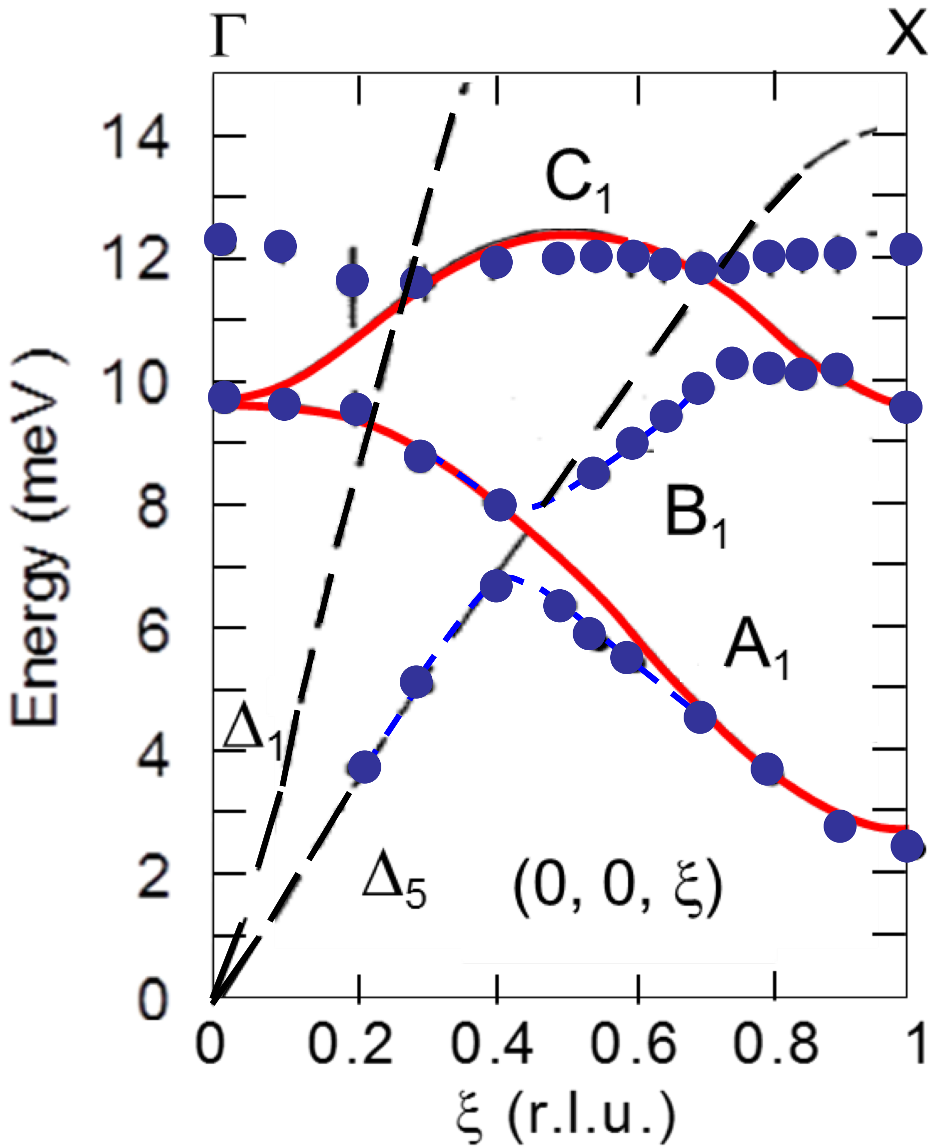
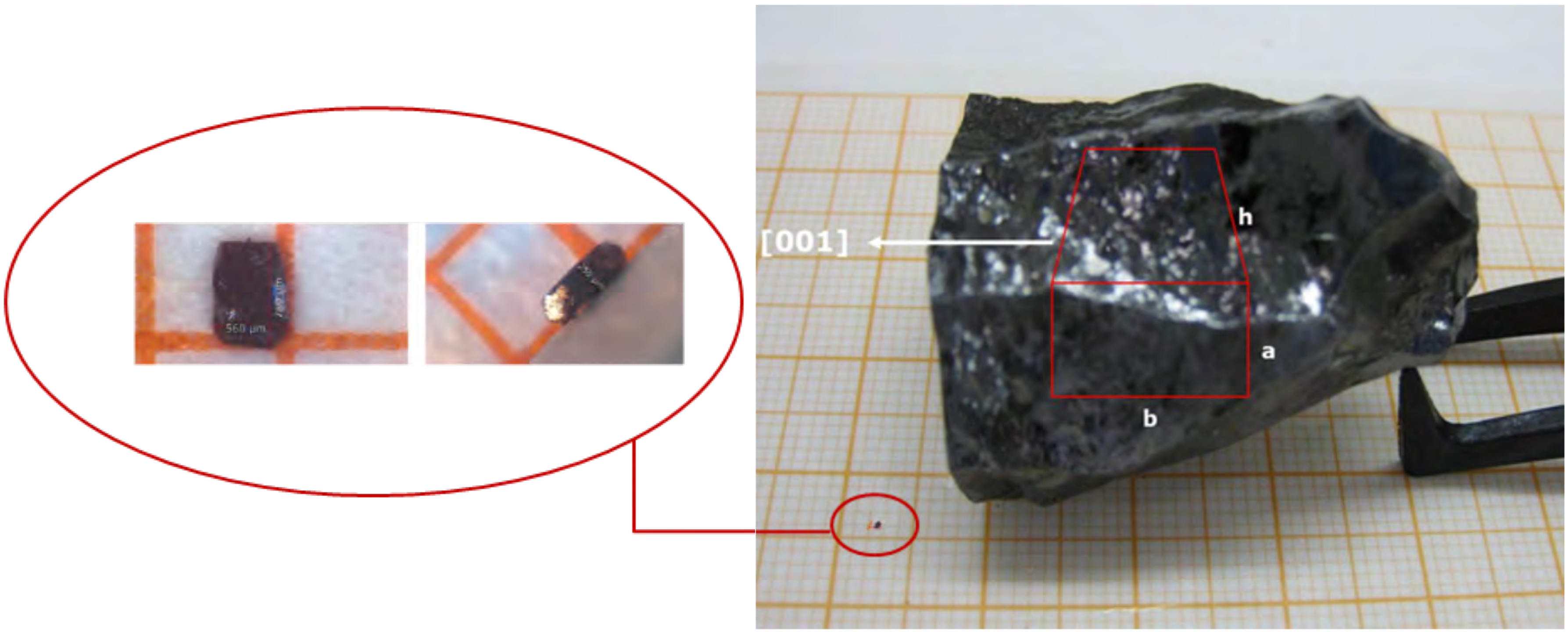
Spin waves in UO_2, inelastic neutron scattering



R. A. Cowley and G. Dolling, Phys. Rev. **167** 464 – 477 (1968)

Lattice dynamics of NpO_2

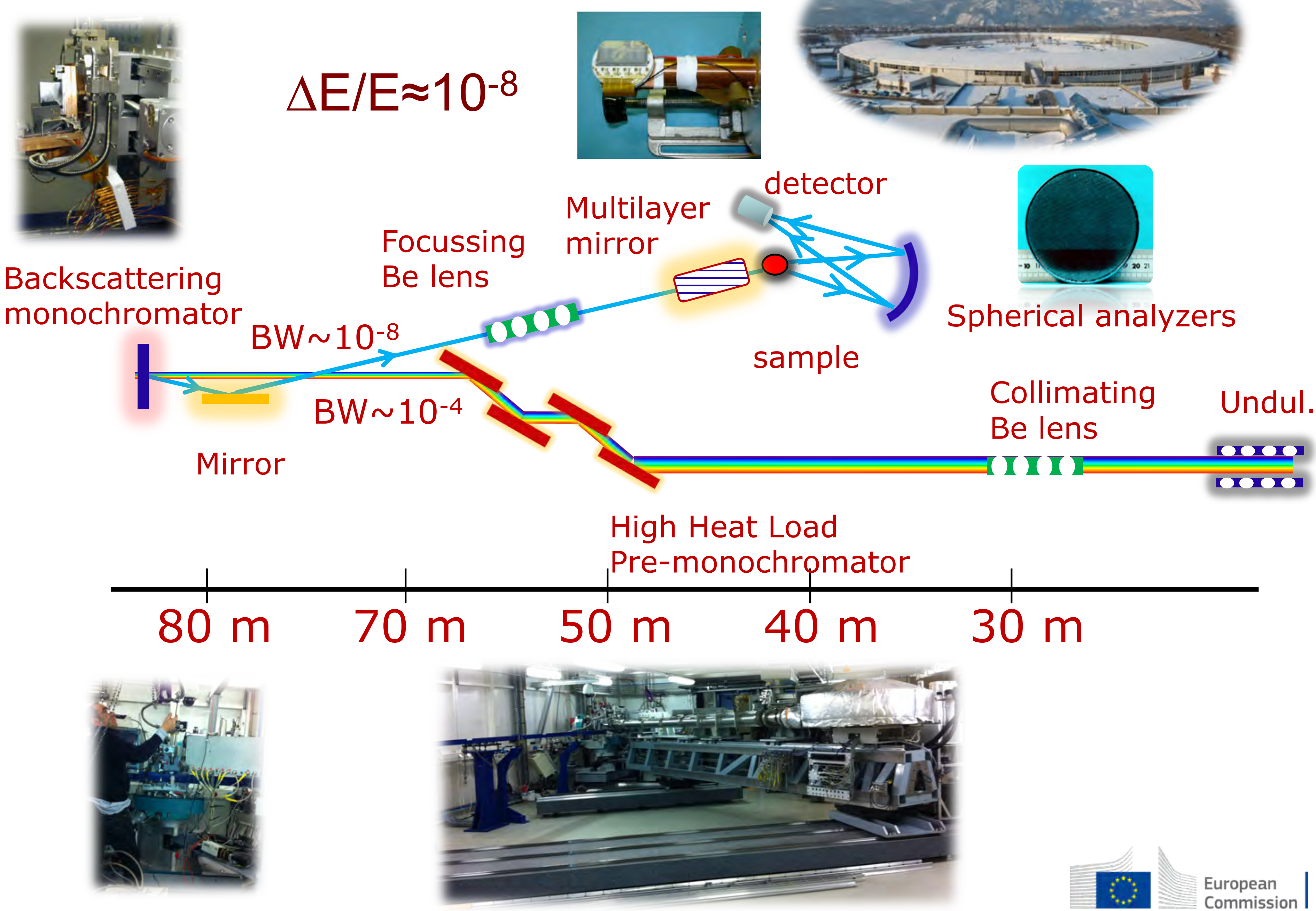
Similar INS measurements have not been done for NpO_2 because of the size of available samples



NpO_2 ~ 1 mg
780×560×250 μm³

UO_2 ~ 99000 mg

Inelastic x-ray scattering at the ESRF



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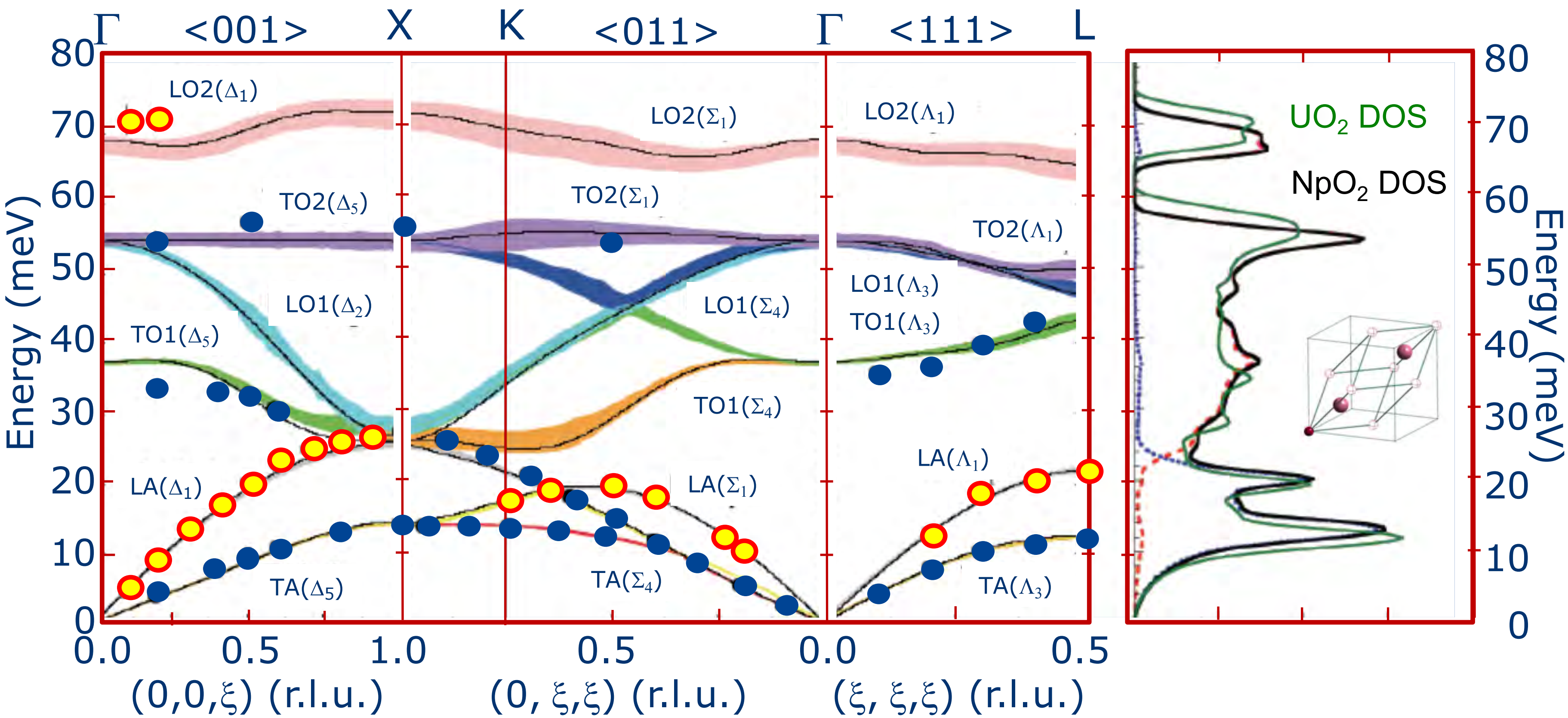
Lattice dynamics in NpO_2 at 300K: inelastic x-ray scattering



P. Maldonado et al., PRB, 93, 144301 (2016)

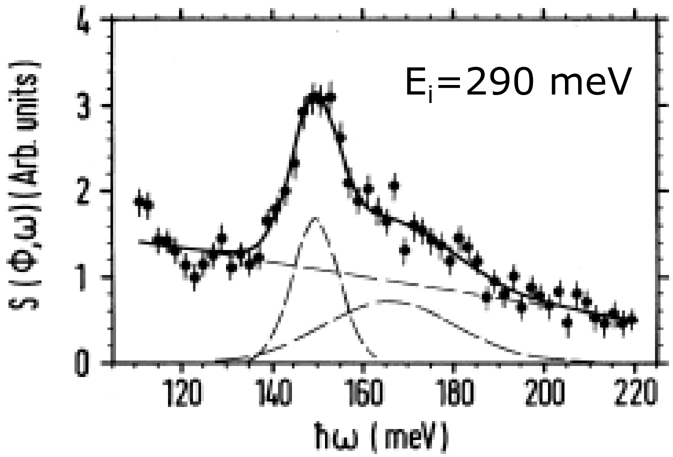
Experimental data compared with phonon frequencies calculated by a "direct method", based on the quasi-harmonic approximation within a DFT framework for the electronic structure (GGA+U; U = 4 eV; J = 0.6 eV)

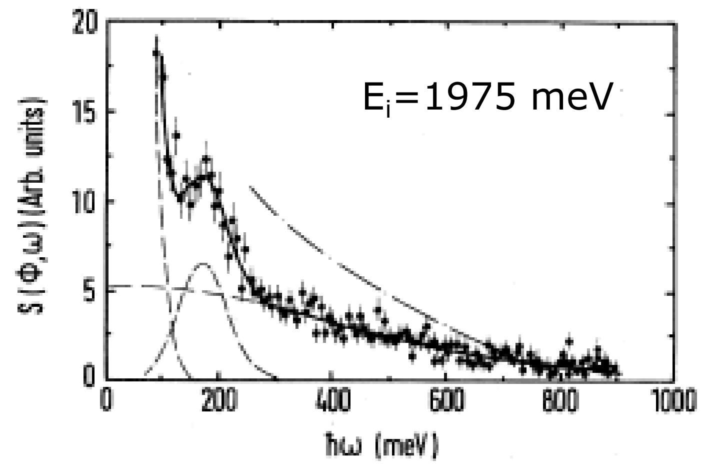
Linewidths: quasi-harmonic approximation + third-order anharmonic terms

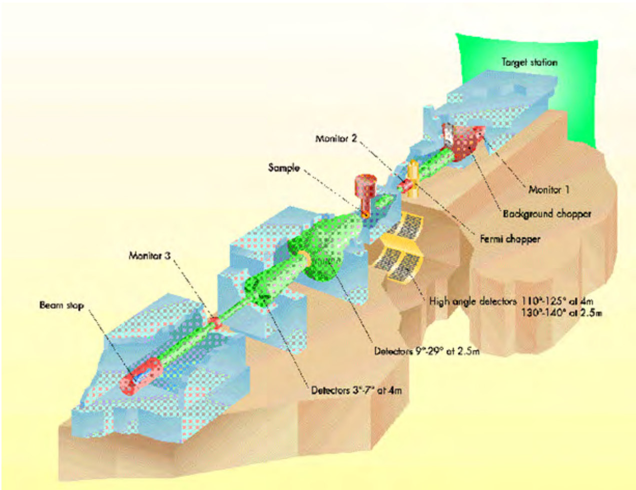
Crystal Field excitations in UO_2

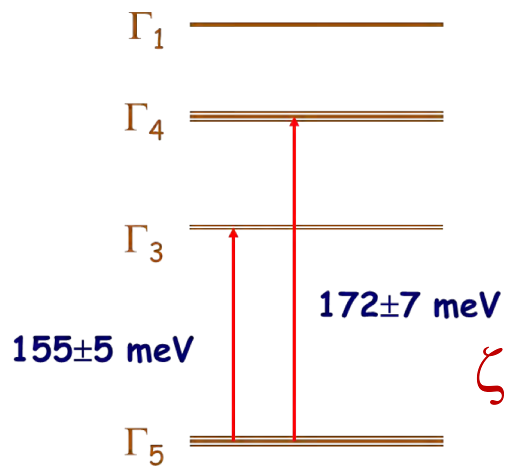
PHYSICAL REVIEW B VOLUME 40, NUMBER 3 15 JULY 1989-II

5f-electron states in uranium dioxide investigated using high-resolution neutron spectroscopy









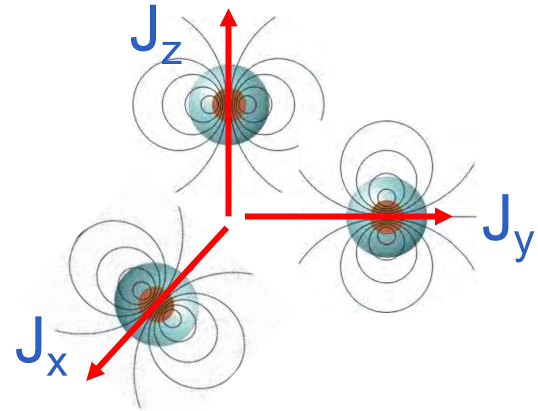
$5f^2$ $^3H_4$

$\zeta_{SO} = 223$ meV

Uranium ions ground state in UO_2

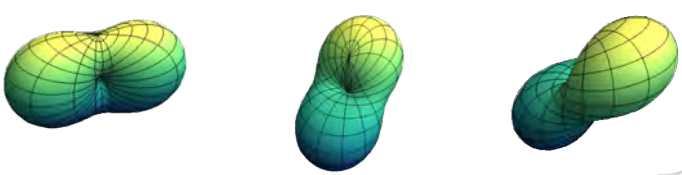
The U^{4+} ground state in the paramagnetic phase of UO_2 is a triplet of Γ_5 symmetry, supporting 8 active degrees of freedom:

- 3 time-odd magnetic dipoles of Γ_4 symmetry



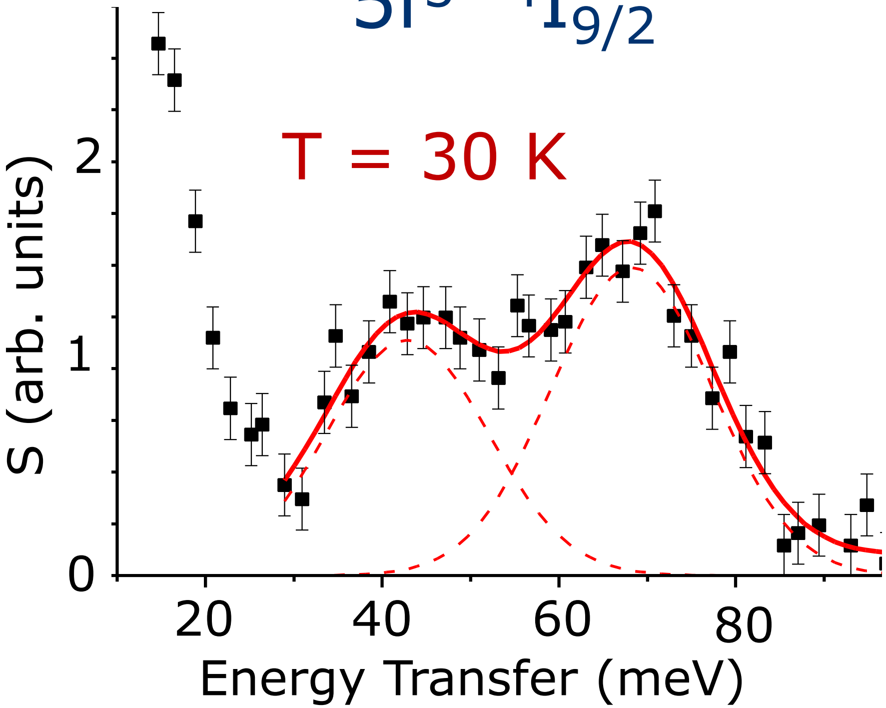
- 2 time-even electric quadrupoles of Γ_3 symmetry transforming as $3z^2$-r^2, x^2-y^2

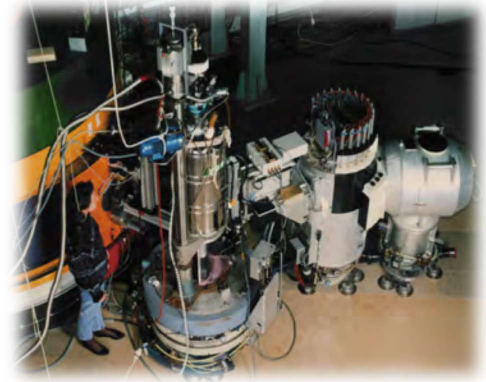
- 3 time-even electric quadrupoles of Γ_5 symmetry transforming as xy, xz, yz

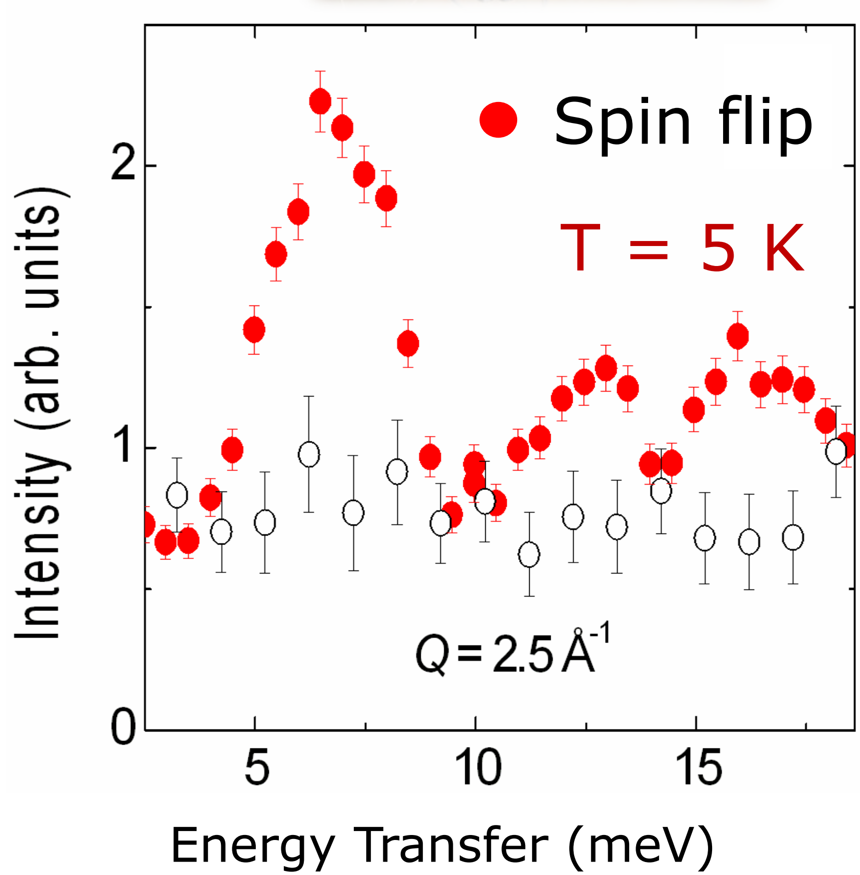


Crystal Field excitations in NpO_2

$5f^3$ $^4I_{9/2}$

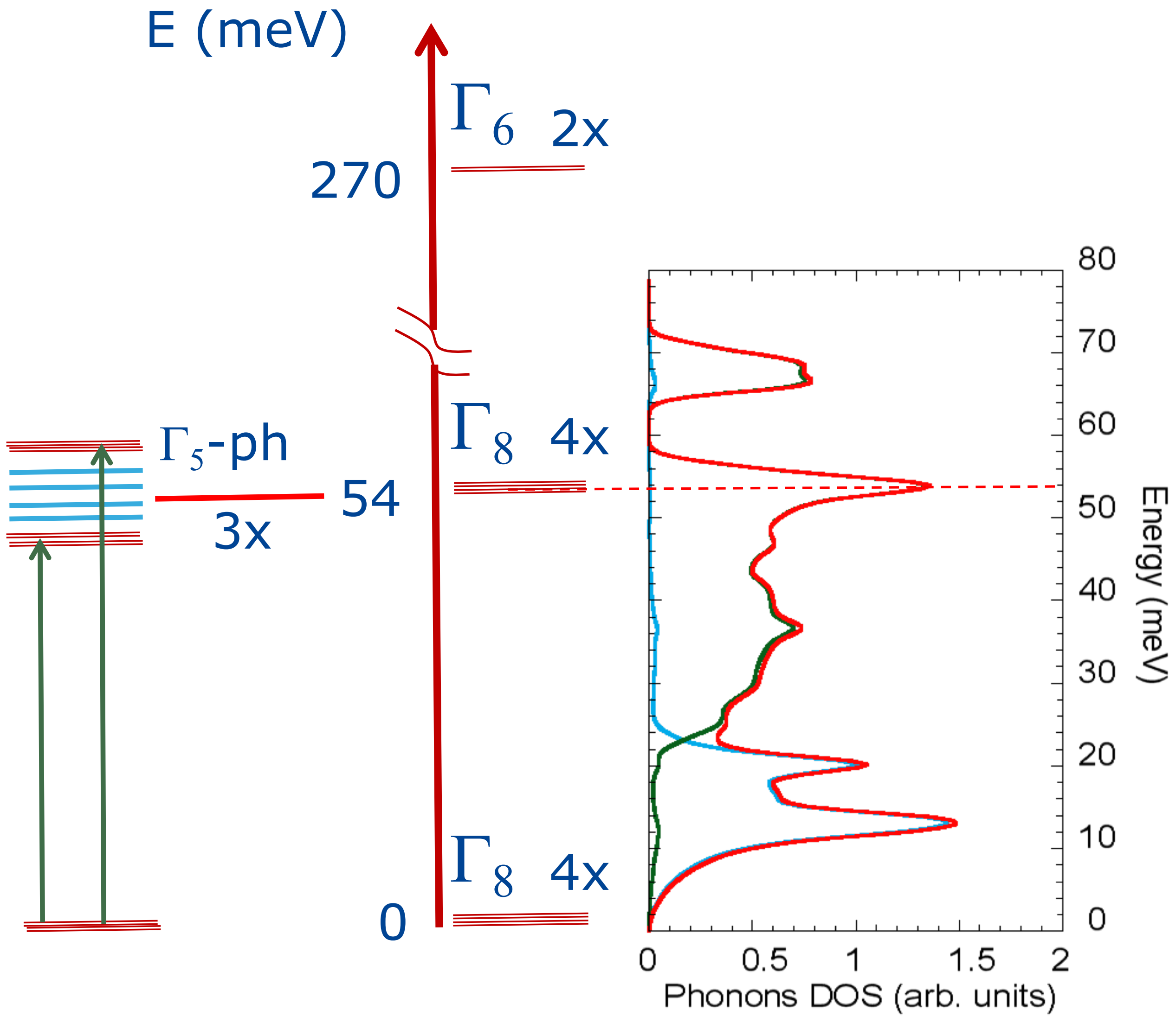






G. Amoretti et al. JPCM **4**, 3459 (1992); N. Magnani et al. PRB **78**, 104425 (2008)

CF-phonons bound state



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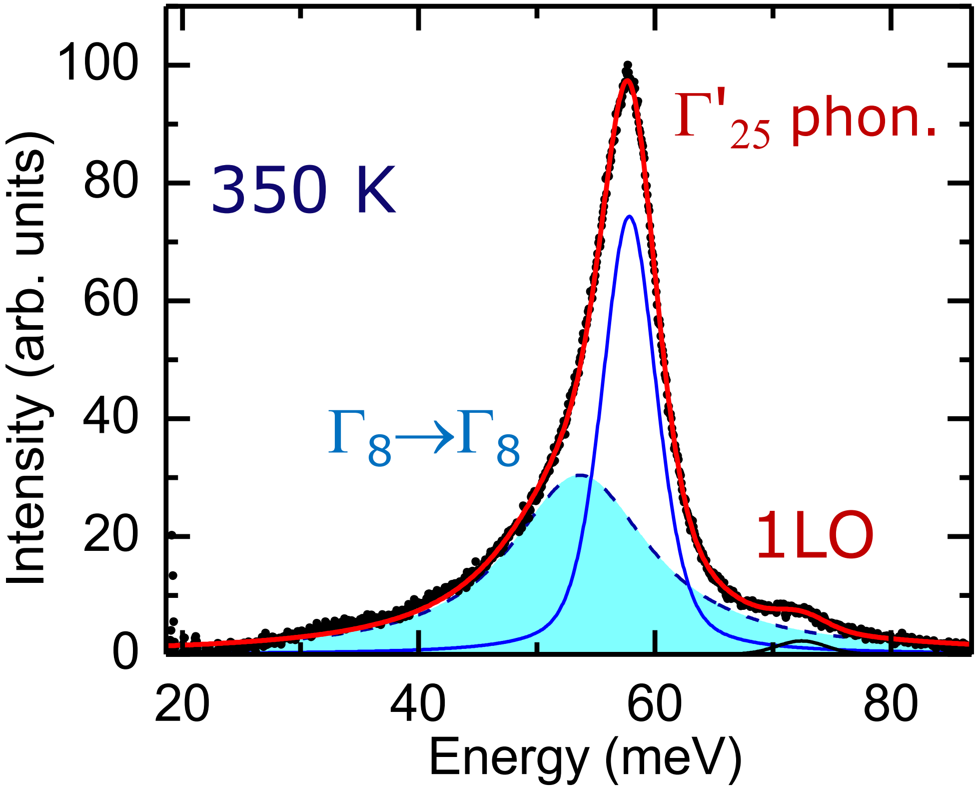
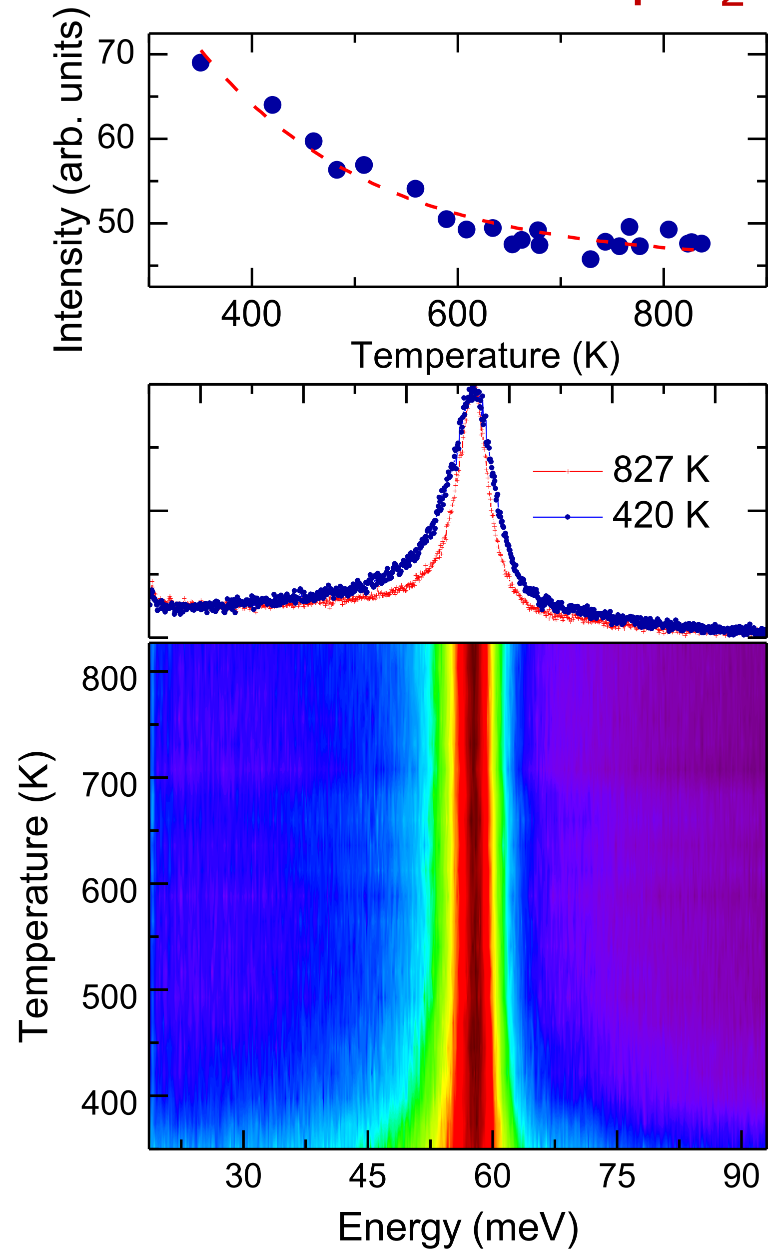
Raman Scattering at high T: bare CF excitation in NpO_2





M. Naji et al., J. Phys. Chem. C **120**, 4799 (2016)

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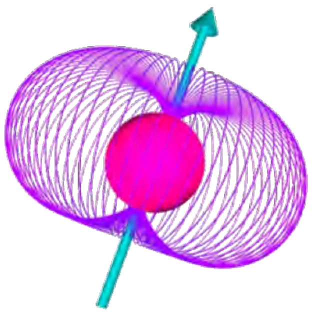
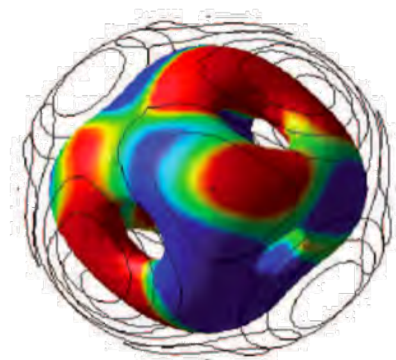
Active degrees of freedom in the Γ_8 Ground State of NpO_2

Time-reversal-even and time-reversal-odd active degrees of freedom up to rank-7

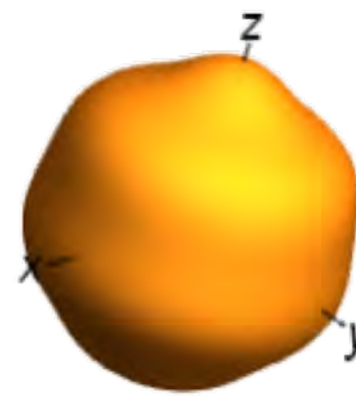


K = 1

K = 3

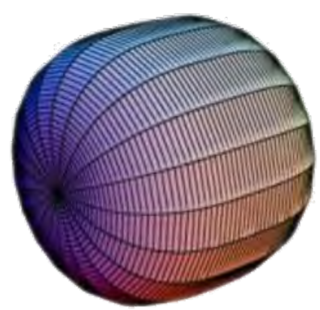


K = 5



K = 7

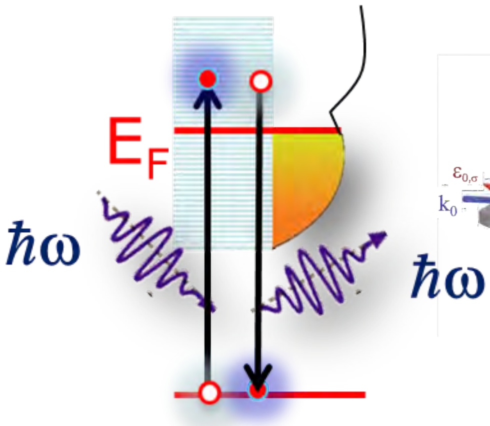
K = 2

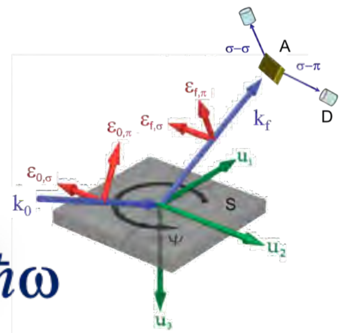


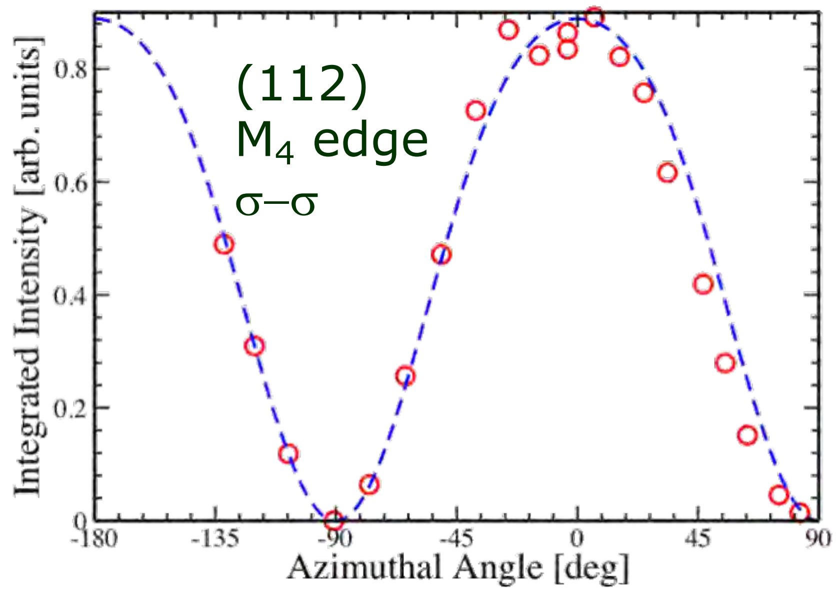
K = 4

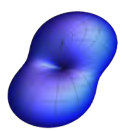
Long-range order of electric quadrupoles in UO_2

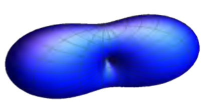
RXS experiments provide direct evidence for the ordering of electric quadrupole moments in UO_2 below T_N

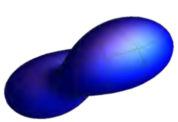


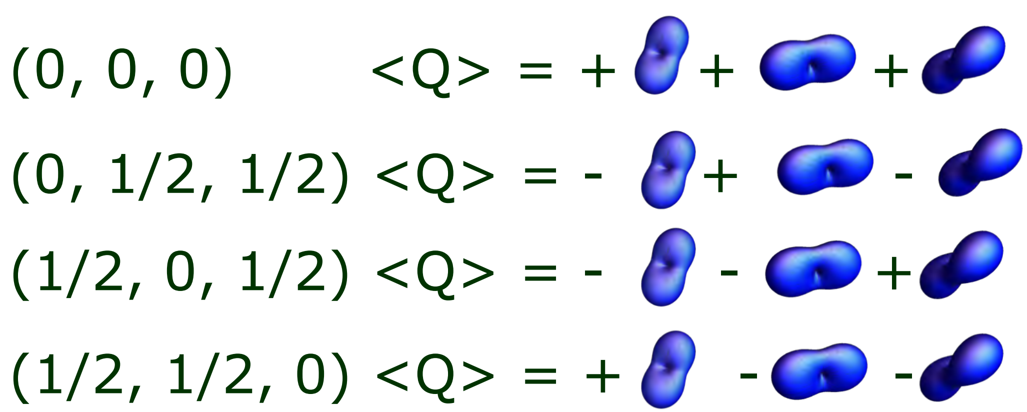




Q_{yz} = 

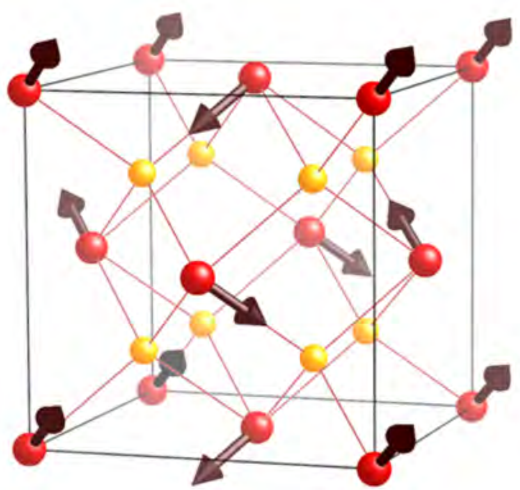
Q_{zx} = 

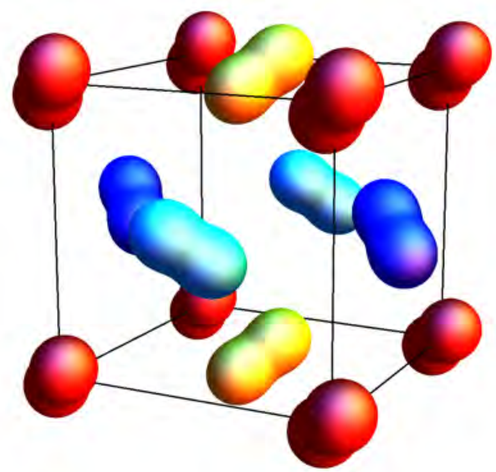
Q_{xy} = 

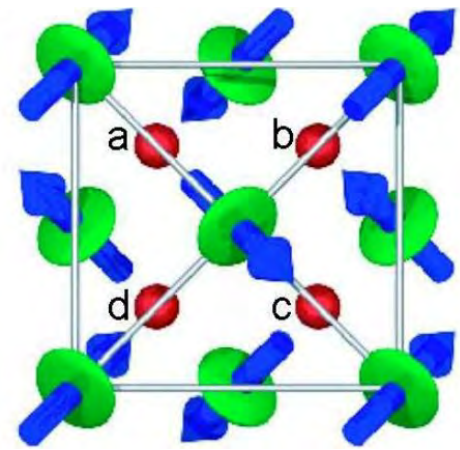


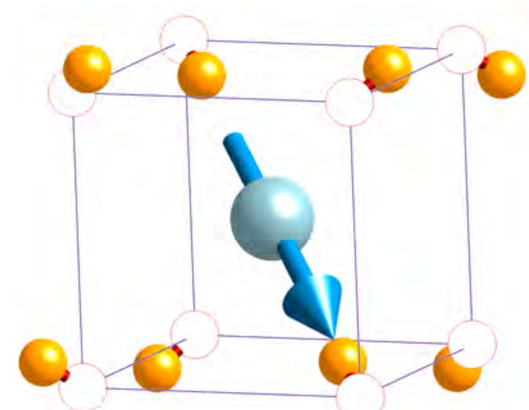
Ordered ground state in UO_2

Transverse 3-k AF order of magnetic dipoles and Γ_5 e-quadrupoles









The U sublattice is simple cubic with

4 atoms in the base

Static 3-k J-T distortion of the O sublattice

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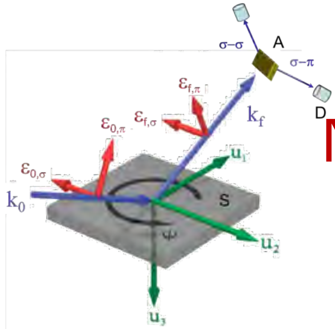
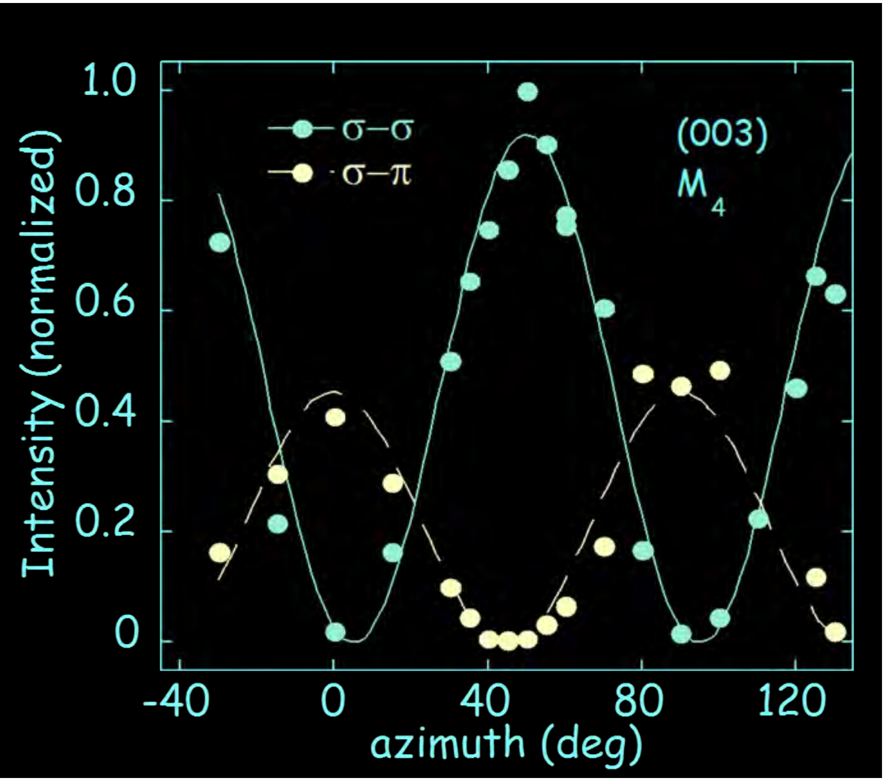


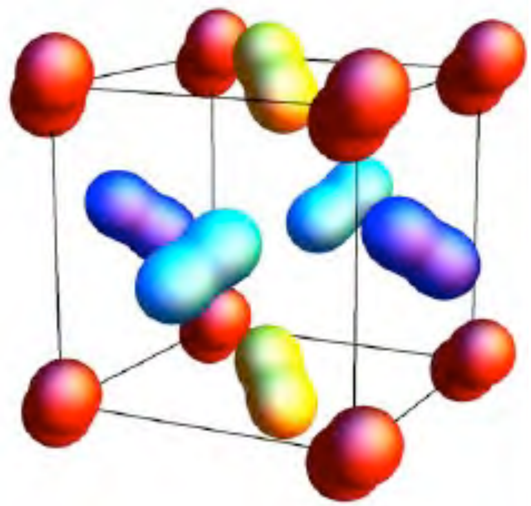
NpO_2: the first example of hidden order

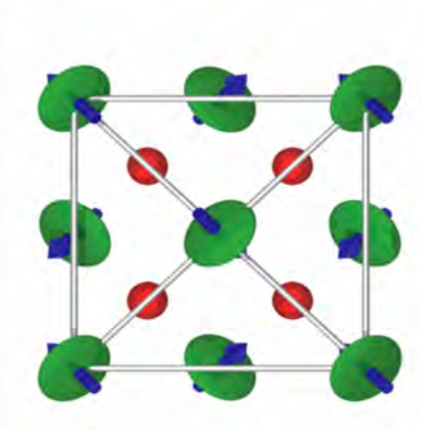
No ordered magnetism and no distortions detected

Longitudinal 3-k structure

Resonant X-Ray scattering







Ordered electric quadrupoles

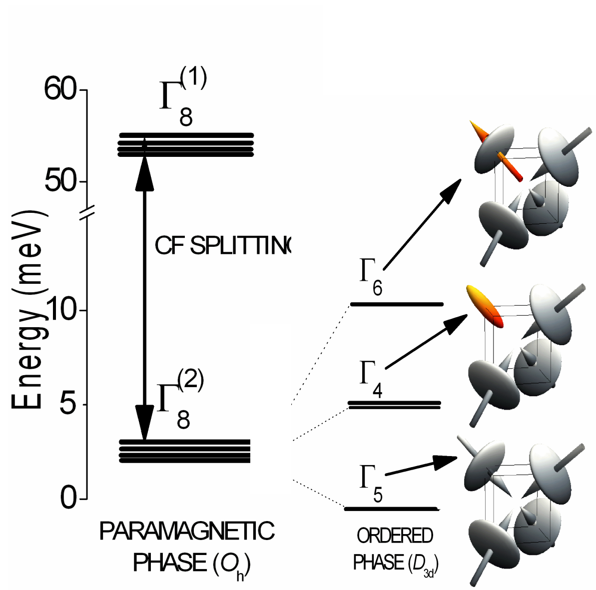
Zero magnetic dipole moment

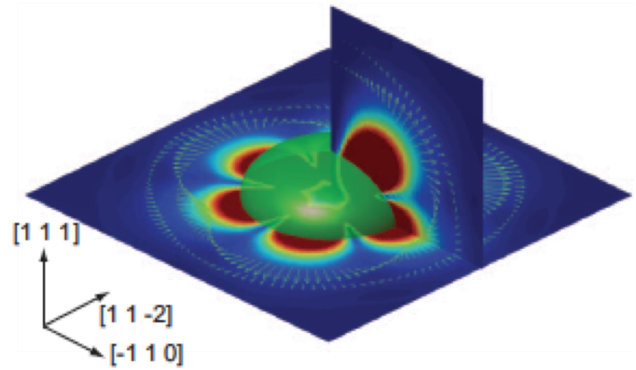
No crystal distortions:

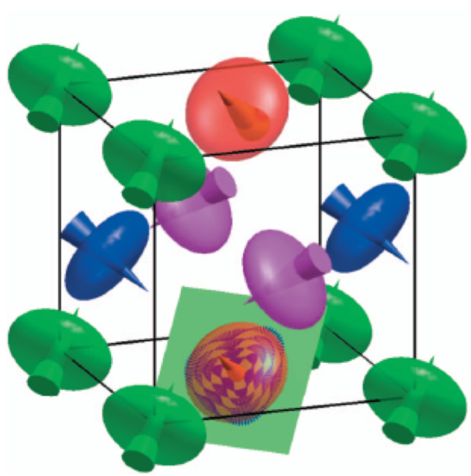
Same atomic positions as in the CaF_2 structure, but different Point Symmetry

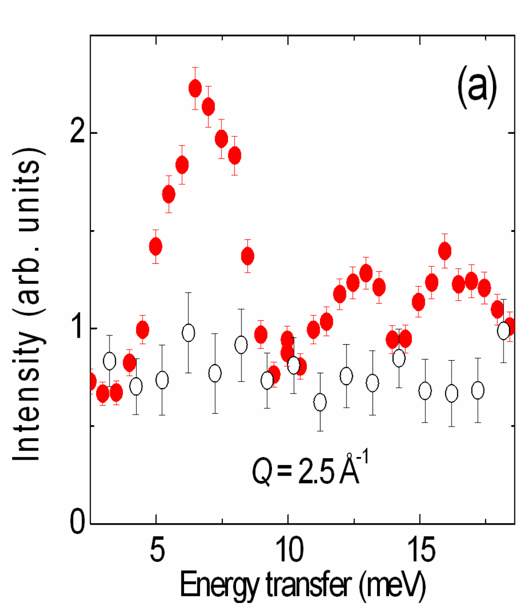
Rank-5 magnetic primary order parameter in NpO_2

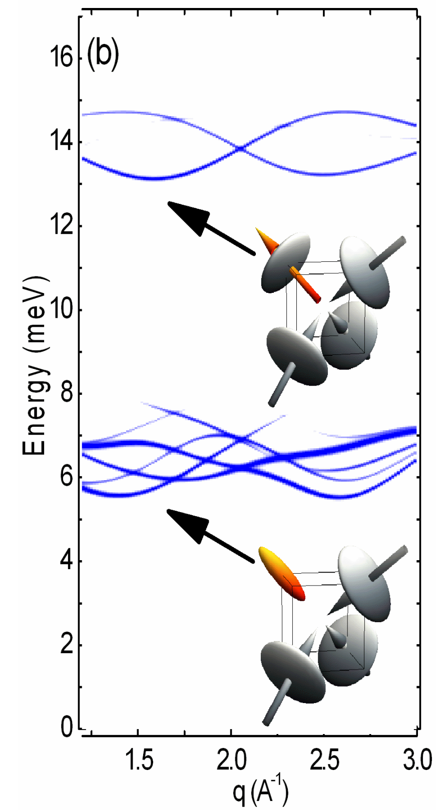
E-quadrupole would split the Γ_8 quartet into two doublets: one low-E peak in INS spectrum



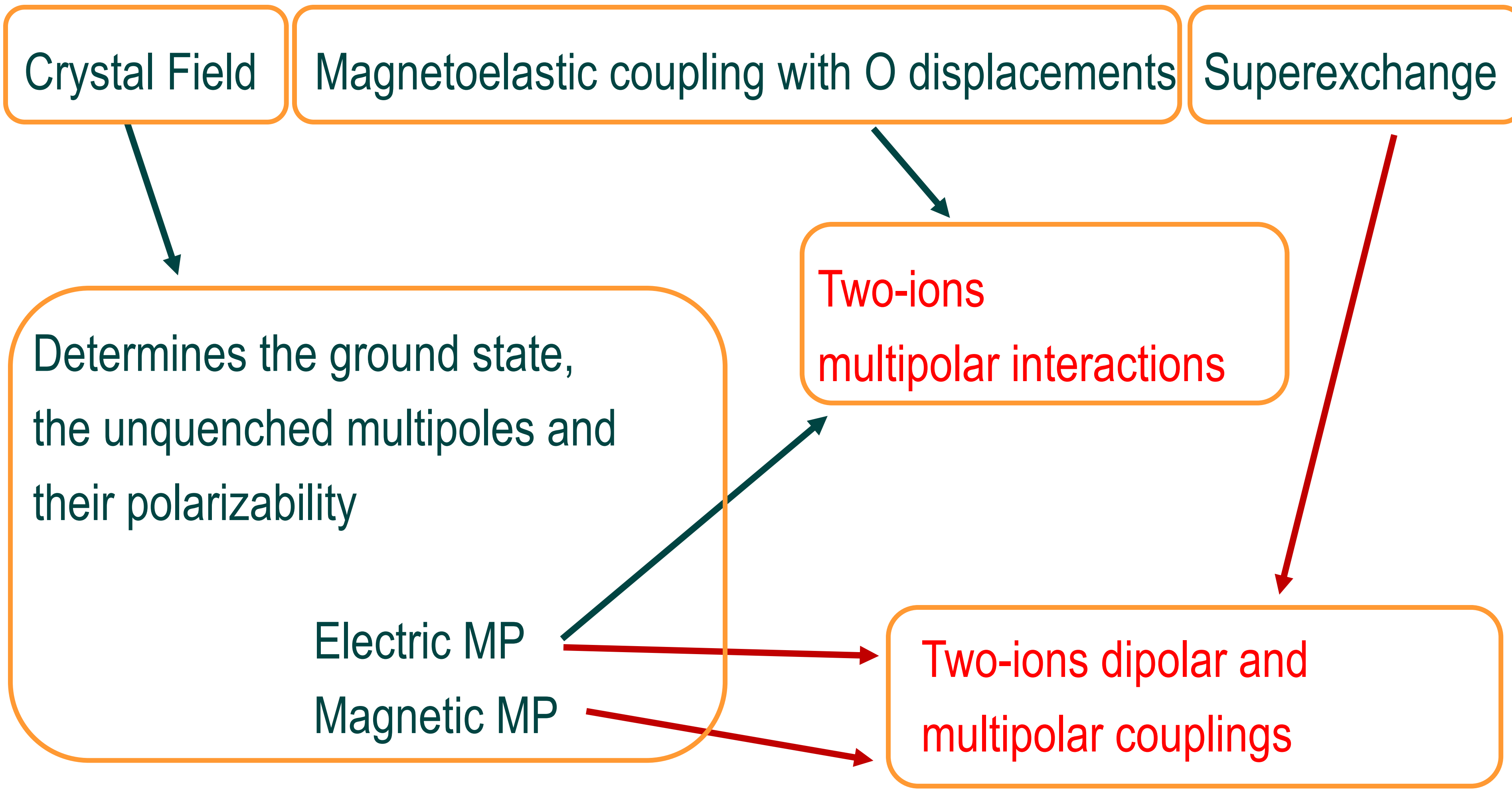








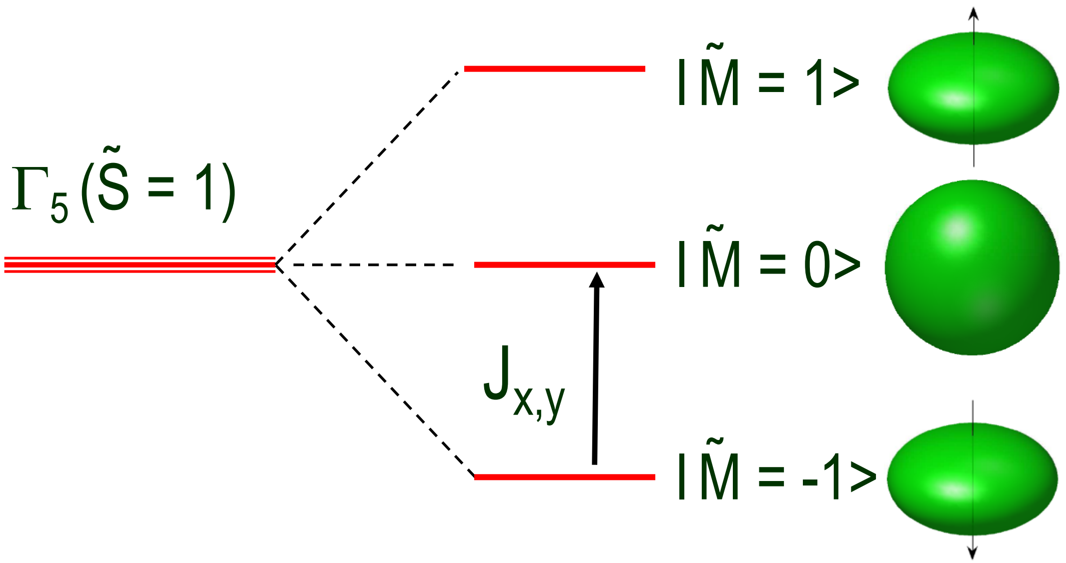
Collective excitations in AnO_2

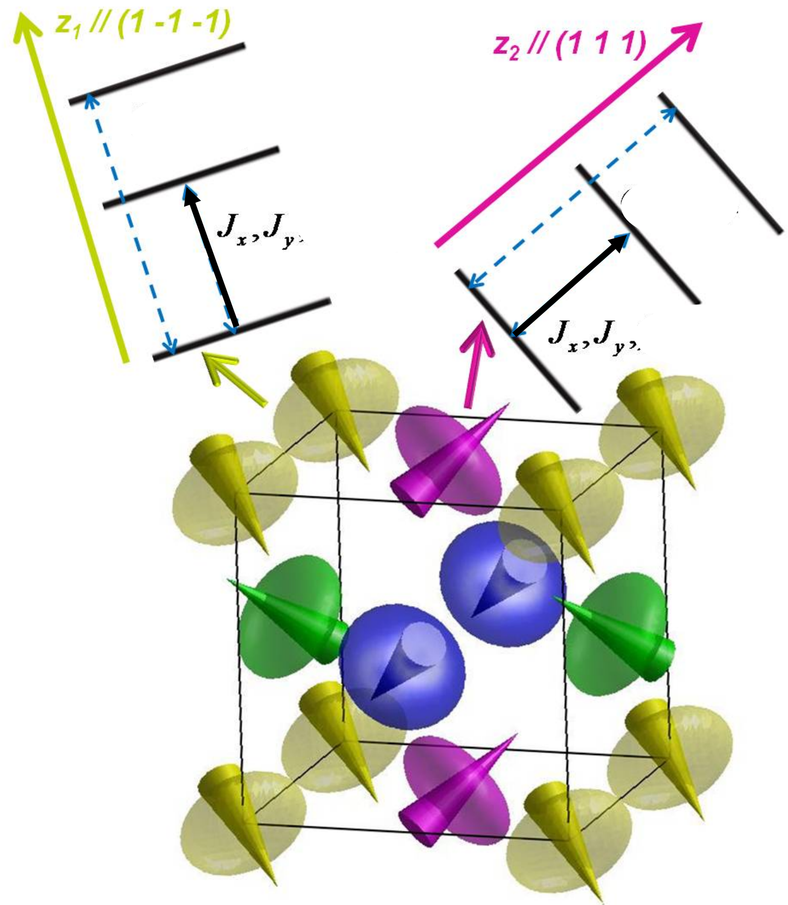


Collective excitations in UO_2

In the ordered phase, the degeneracy of the ground state is removed.

Only one dipolar single-ion excitation is allowed





Two of the eight degrees of freedom (J_x, J_y) fluctuates in time. The others are frozen.

Collective excitations in UO_2

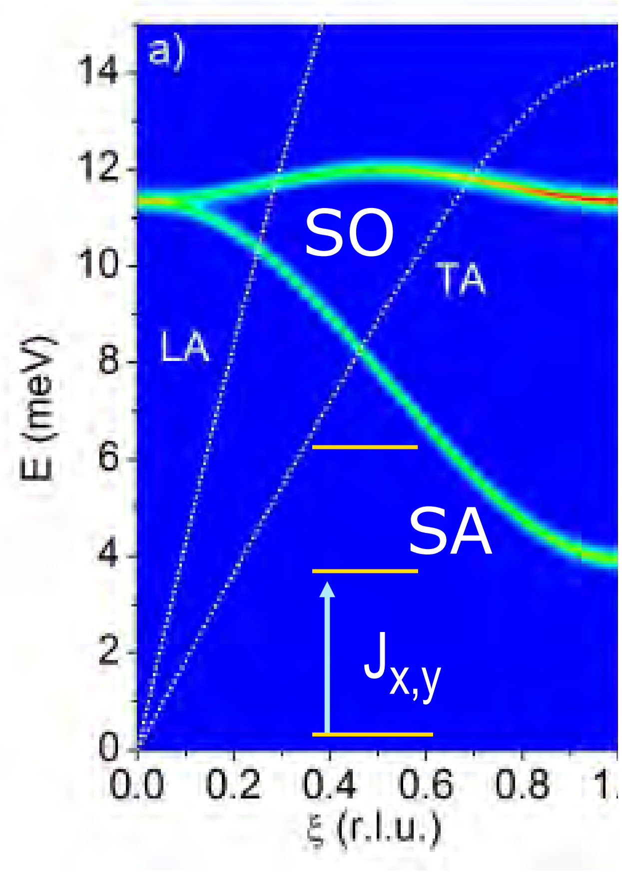
If only anisotropic magnetic exchange interactions were active, 4 propagating branches would be present (in addition to phonons):

4 U sites → 4x1 = 4 excitations branches.

Along the [001] direction

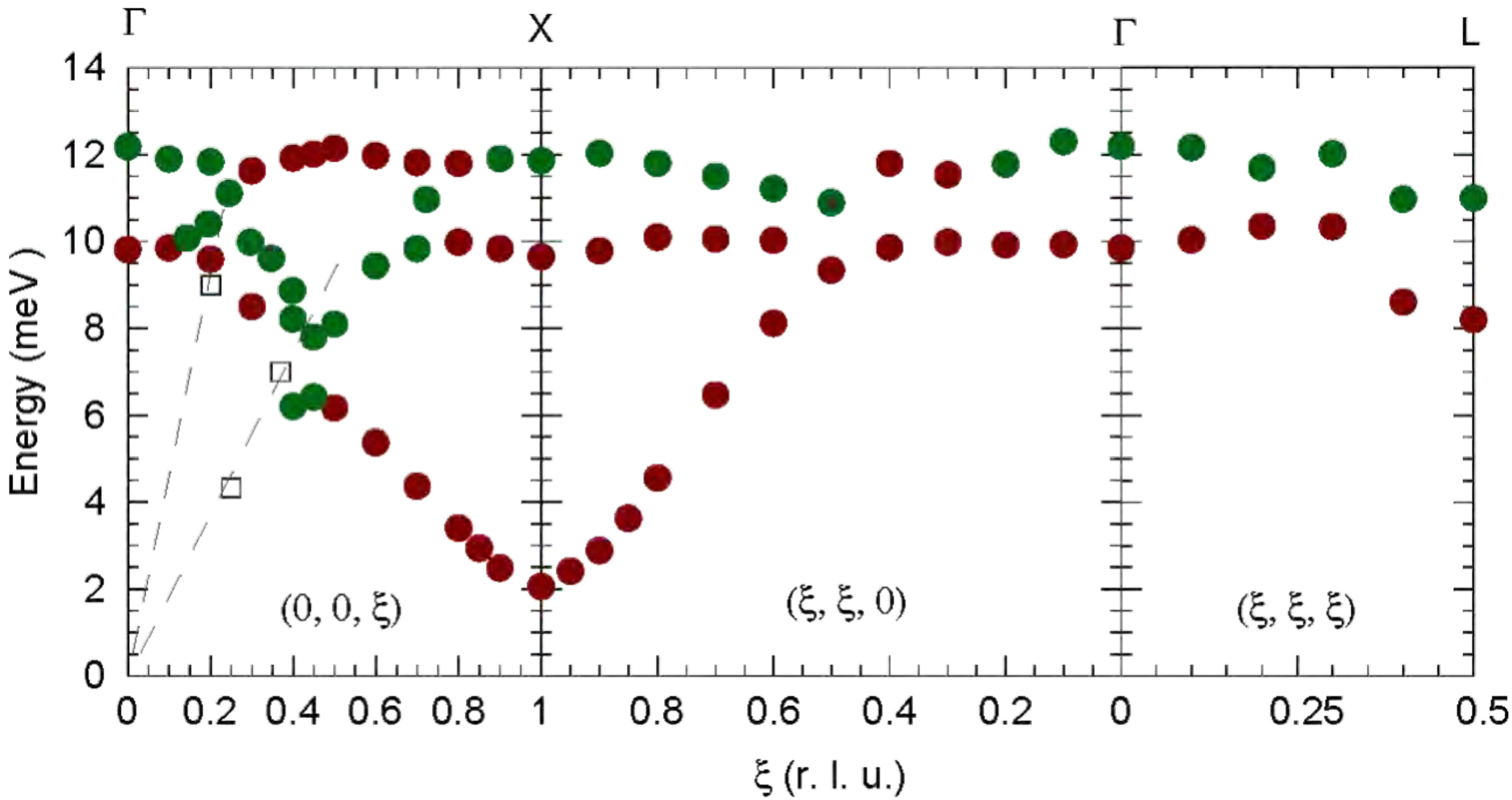
2 degenerate acoustic and

2 degenerate optical spin branches.



UO_2 collective excitations below T_N

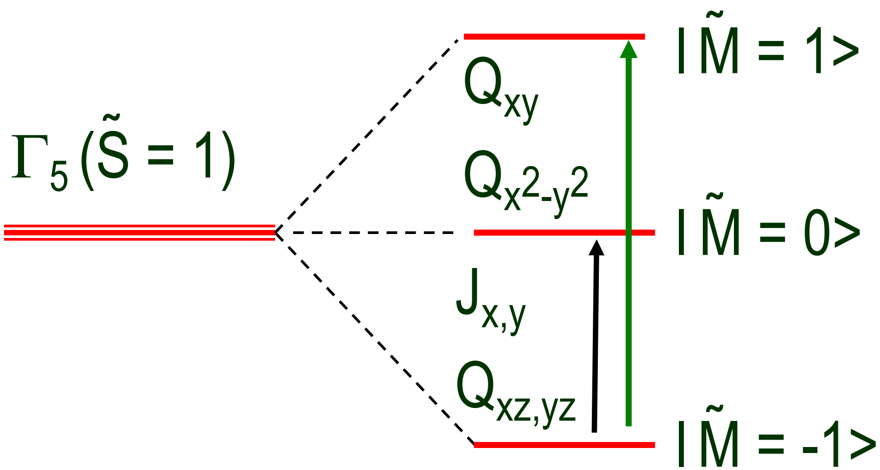
Inelastic neutron scattering

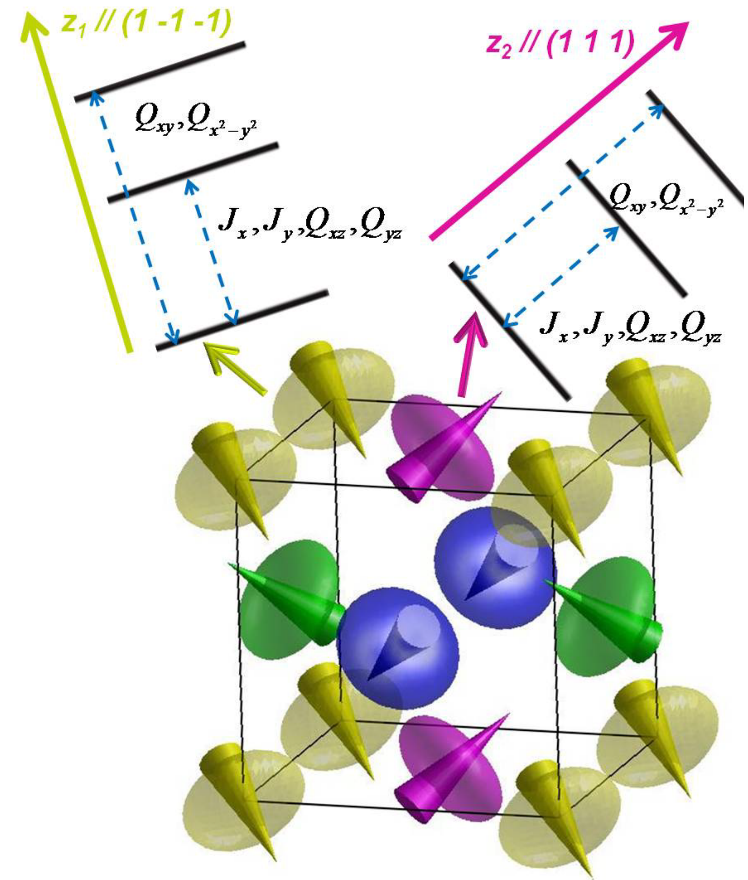


RC et al.
PRB 59, 13892 (1999)
PRB 72, 18441 (2005)
PRB 84, 104409 (2011)

Collective excitations in UO_2

- Quadrupolar transitions (pseudospin flips by 2)





Magnetic dipole + electric quadrupole transitions:

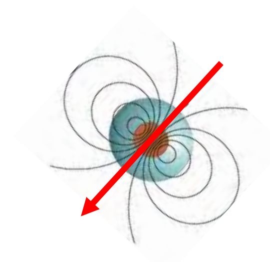
4 U sites → 4x(1+1) = 8 excitations branches

Only J_z and $Q_{3z^2-r^2}$ are frozen degrees of freedom

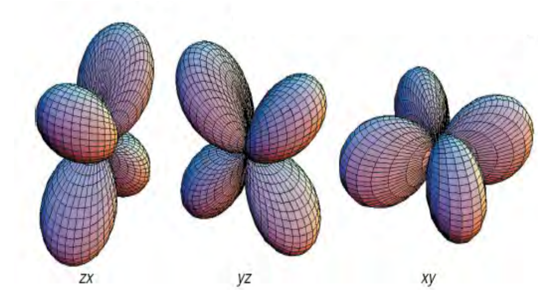
Coupled dynamics of spins, phonons and quadrupoles

Each low-T unit cell provides 60 dynamical variables

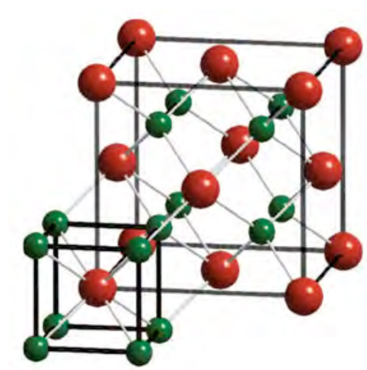
J_x, J_y, J_z Dipoles (3x 4 sublattice = 12)



Q_{xy}, Q_{xz}, Q_{yz} Γ_5 Quadrupoles (3x 4 subl. = 12)



$\Delta \vec{R}_i$ Displacements (3x4x3 = 36)



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Coupled dynamics of spins, phonons and quadrupoles

The microscopic Hamiltonian contains several terms:

$$H = H_{SS} + H_{QQ} + H_P + H_{ME}$$

Spin-spin superexc. — **Quad-quad superexch.** — **Bare phonons** — **Quadr-phonon ME coupling**

<u>The simplest possible model</u> allowing a satisfactory fit to experimental data:

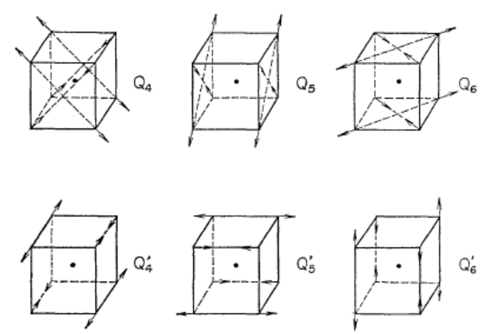
(110) n.n. bond CUBIC ref. frame

$$H_{SS} = J\{S_z(1)\,S_z(2) + d[S_x(1)\,S_x(2) + S_y(1)\,S_y(2)]\}$$

$$H_{QQ} = K^{SE}\{Q^S_{xy}(1)\,Q^S_{xy}(2) + d[Q^S_{yz}(1)\,Q^S_{yz}(2) + Q^S_{xz}(1)\,Q^S_{xz}(2)]\}$$

H_P → **Rigid-ion model**

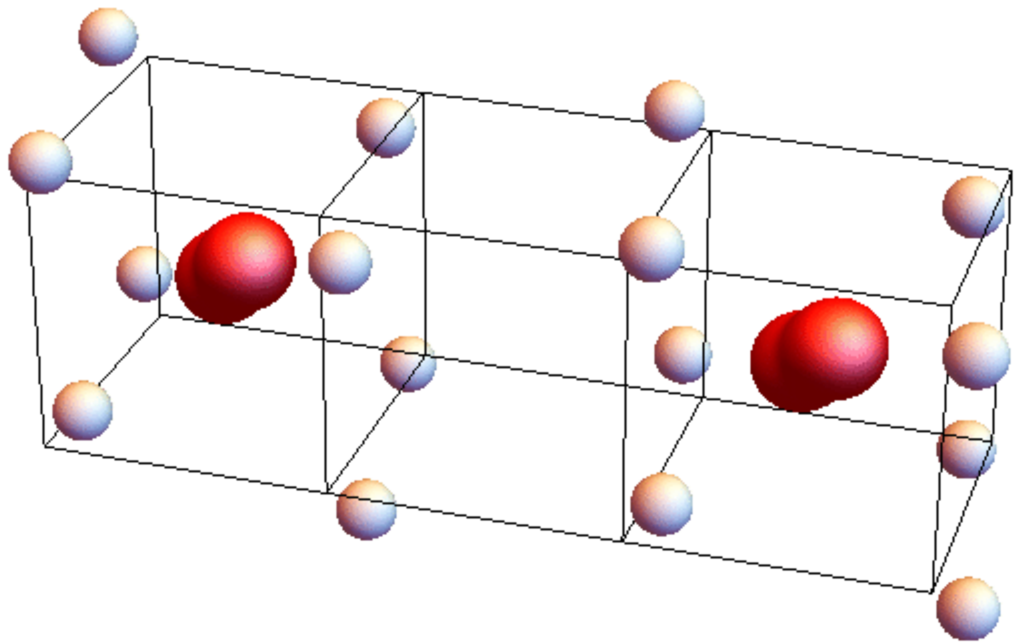
$$H_{ME} = \sum_{\vec{R}} \sum_{\alpha=xy,xz,yz} Q^S_\alpha(\vec{R})[g_A\,\delta_{A,\alpha}(\vec{R}) + g_B\,\delta_{B,\alpha}(\vec{R})]$$



The two normal modes of the cubic oxygen cage having Γ_5 symmetry

Lattice dynamics in UO_2

Retarded (frequency dependent) effective phonon-mediated quadrupole-quadrupole interactions:



$Q_{\alpha}(\mathbf{R})$

$Q_{\alpha'}(\mathbf{R}')$

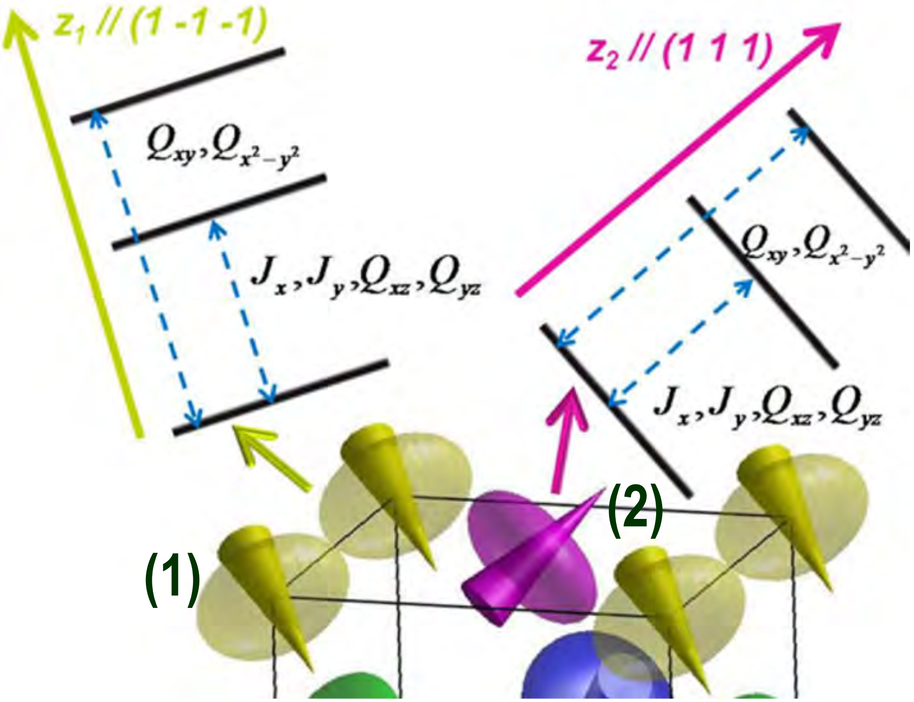
Distortion of the oxygen cubic cage at site R

Corresponds to a super-position of lattice phonons

Distortion of the oxygen cubic cage at site R'

$$K^{ph}_{\alpha,\alpha'}(\mathbf{R},\mathbf{R}';\omega)$$

Mixing of quadrupole and spin waves branches



a) Q_{xy} and $Q_{x^2-y^2}$ fluctuate on site (1)

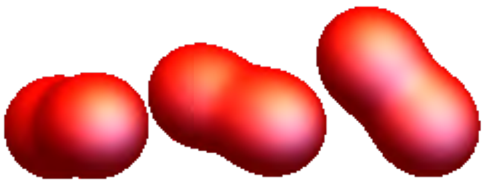
b) The ion in (2) feels a time-dependent quadrupolar field inducing off-resonant oscillations of Q_{xz} and Q_{yz}

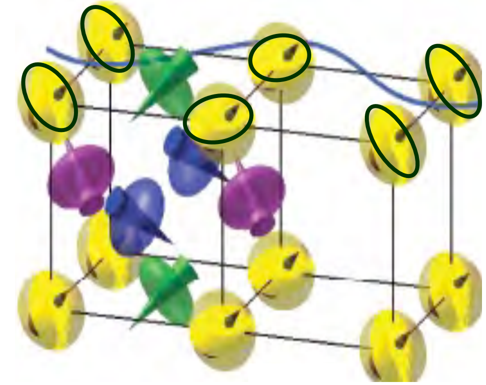
c) As $Q_{xz,yz}$ are locked to $J_{x,y}$, a magnetic oscillation is induced in (2)

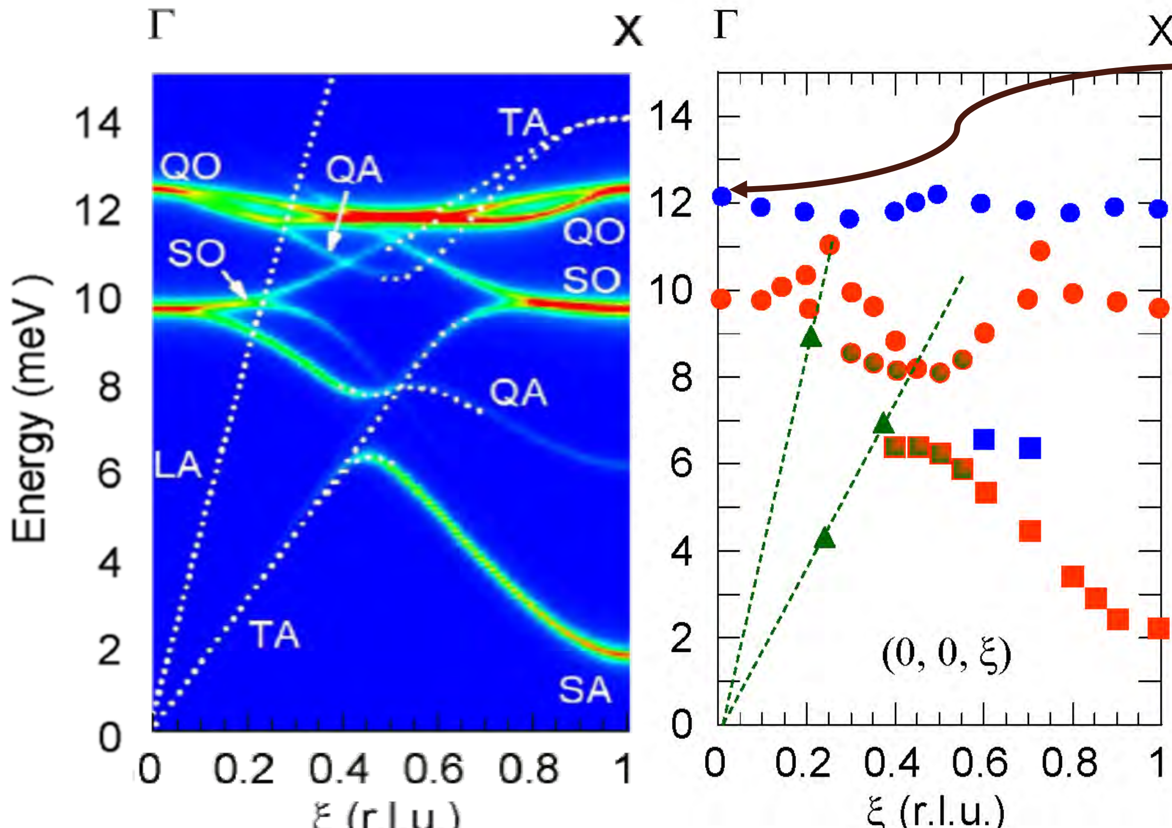
The $\Delta\tilde{M} = 2$ branch gets a magnetic character

Propagating electric quadrupole waves in UO_2

A whole excitation branch in UO_2 is associated with propagating quadrupolar fluctuations driven jointly by magneto-elastic and superexchange multipolar interactions.

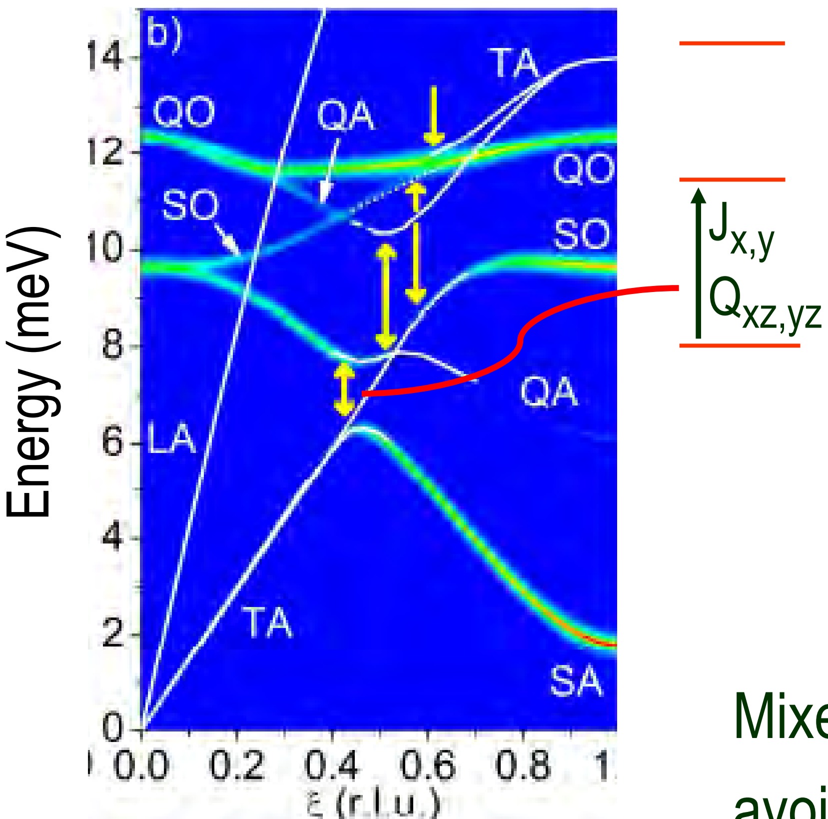






wave-like oscillations of the two locally-ortho-rhombic quadrupoles (Q_{xy}, $Q_{x^2-y^2}$) associated with the precession of a small spin component due to mixing with the spin-wave branch.

Avoided Crossings from spin- phonon- quadrupolar-modes interactions (yellow arrows)



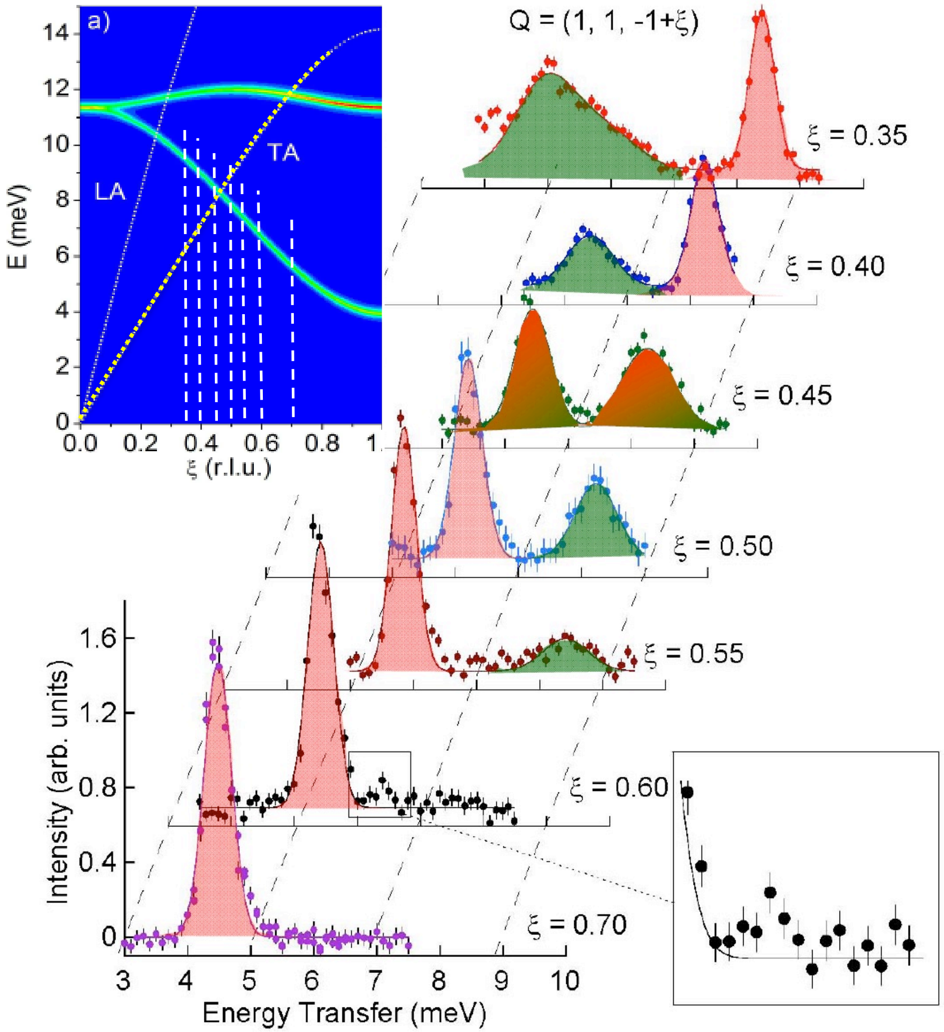
the $Q_{xz,yz}$ quadrupolar operators couple phonons to the (M=-1 → M = 0) excitation and give origin of the AC around 7 meV near $\xi = 0.45$

Mixed spin-phonon character is maximal at avoided crossing positions arising

$$|\Psi_1 > \propto \frac{1}{\sqrt{2}}(SW + TA_1) \qquad |\Psi_2 > \propto \frac{1}{\sqrt{2}}(SW - TA_1)$$

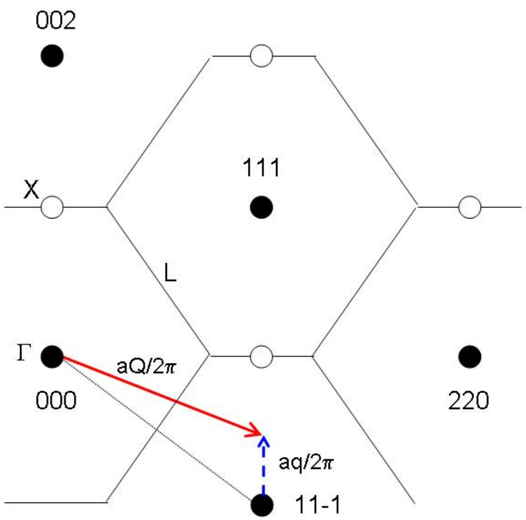
Inelastic neutron scattering experiments

IN14@ILL



Transverse constant-Q scans

$$\mathbf{Q} = \mathbf{G} + \mathbf{q} = (1, 1, -1) + (0, 0, \xi)$$



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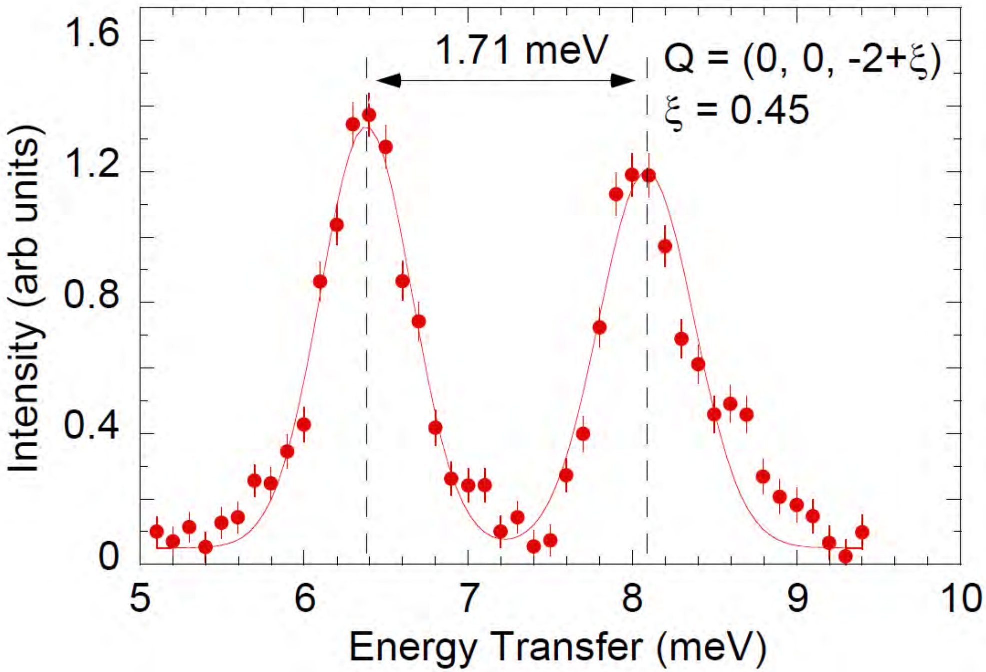
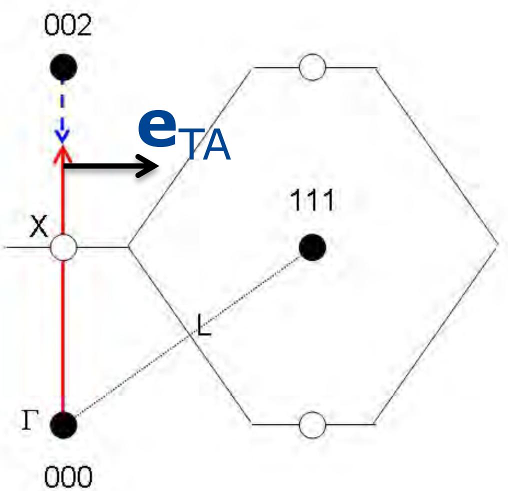
Magnon-phonon avoided crossing at **q** = (0, 0, 0.45)

Longitudinal scan reveals a transverse
50% phonon- 50% magnon mixed mode

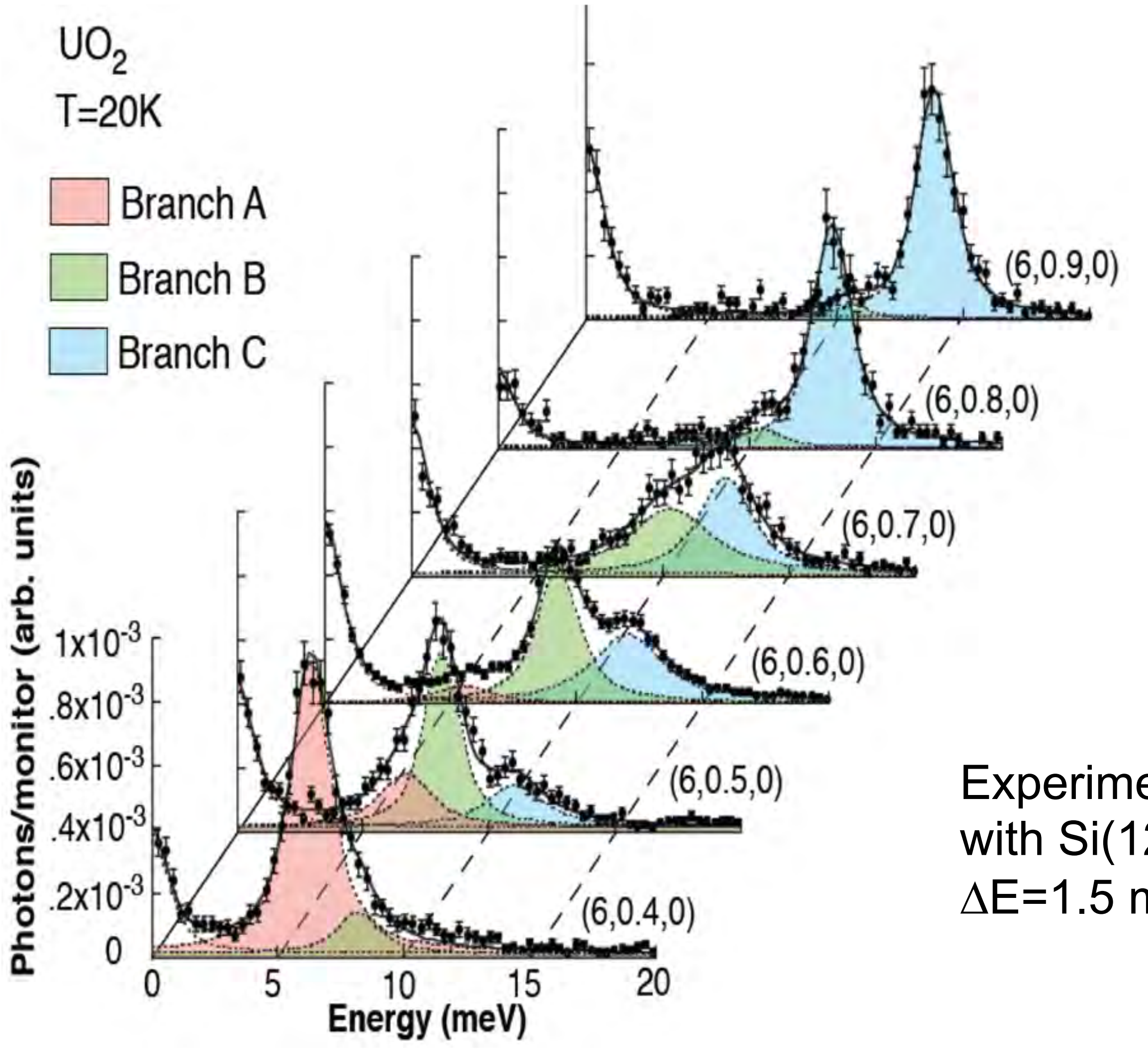
$I_{ph} \propto (\mathbf{Q}\cdot\mathbf{e})^2 = 0$





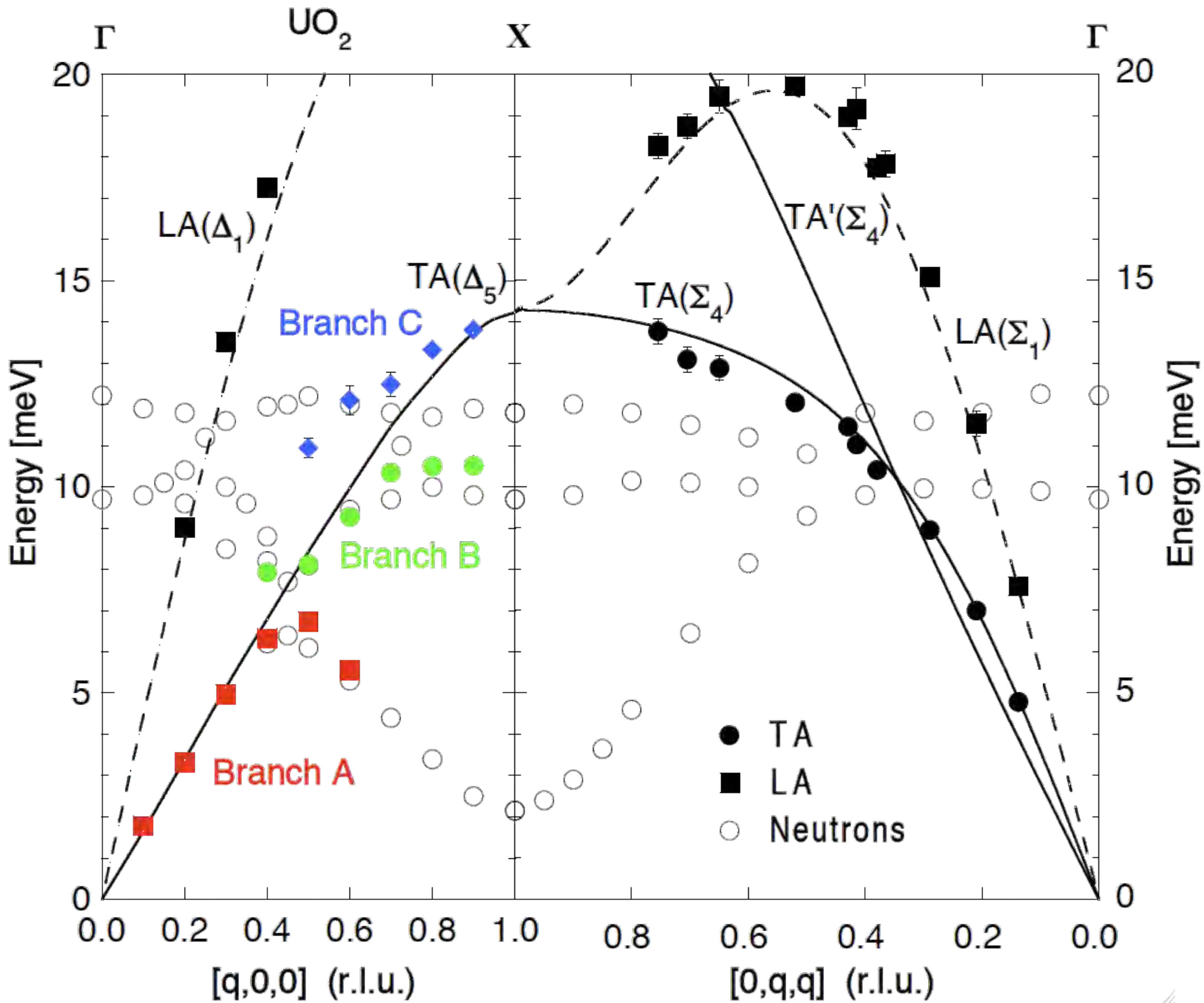
$$| \Psi_1 > \propto \frac{1}{\sqrt{2}}(SW + TA_1) \qquad | \Psi_2 > \propto \frac{1}{\sqrt{2}}(SW - TA_1)$$

UO_2 High-resolution IXS: only phonons are visible



Experiments performed with Si(12 12 12) with $\Delta E=1.5$ meV

IXS, UO_2 @ 10 K:



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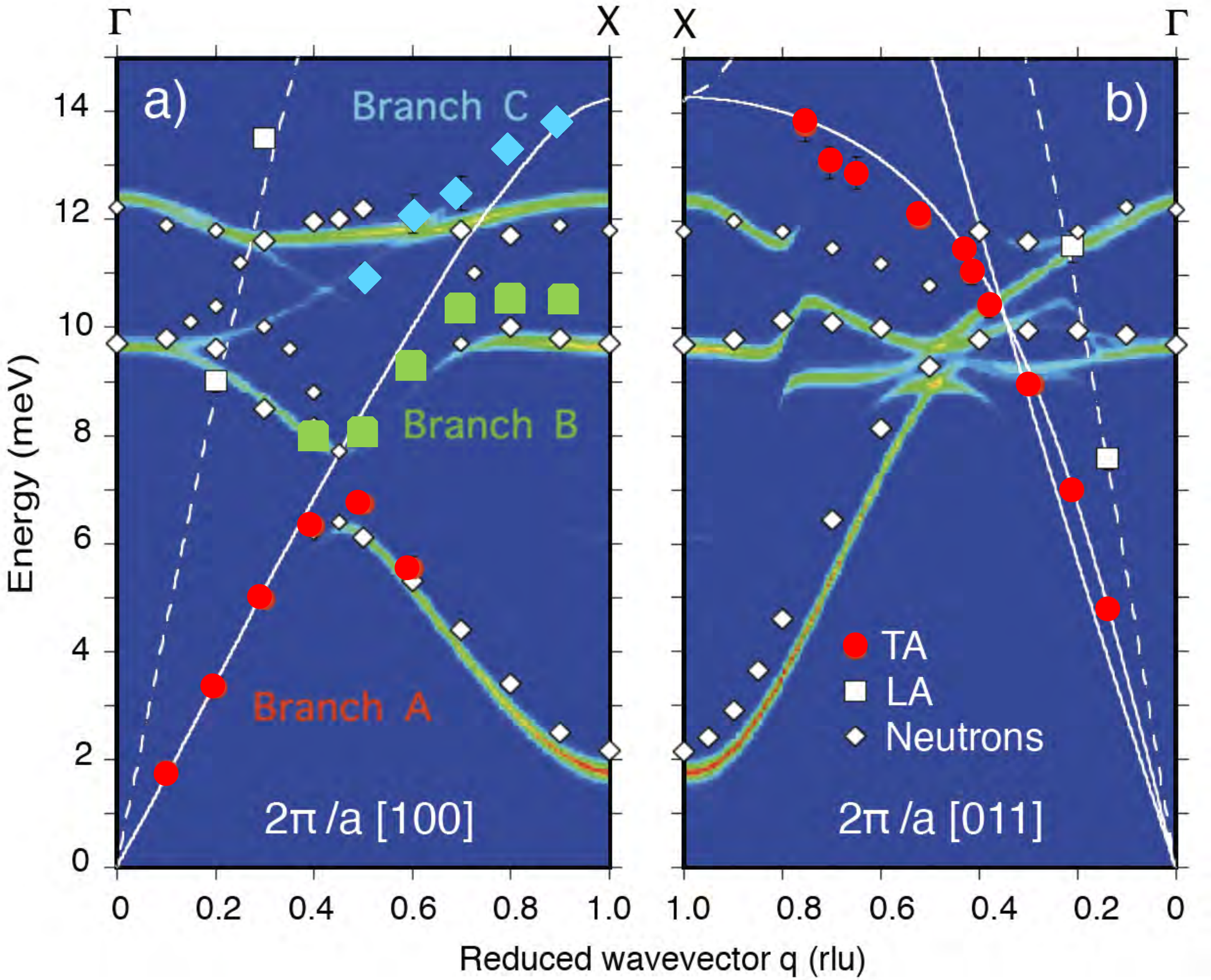
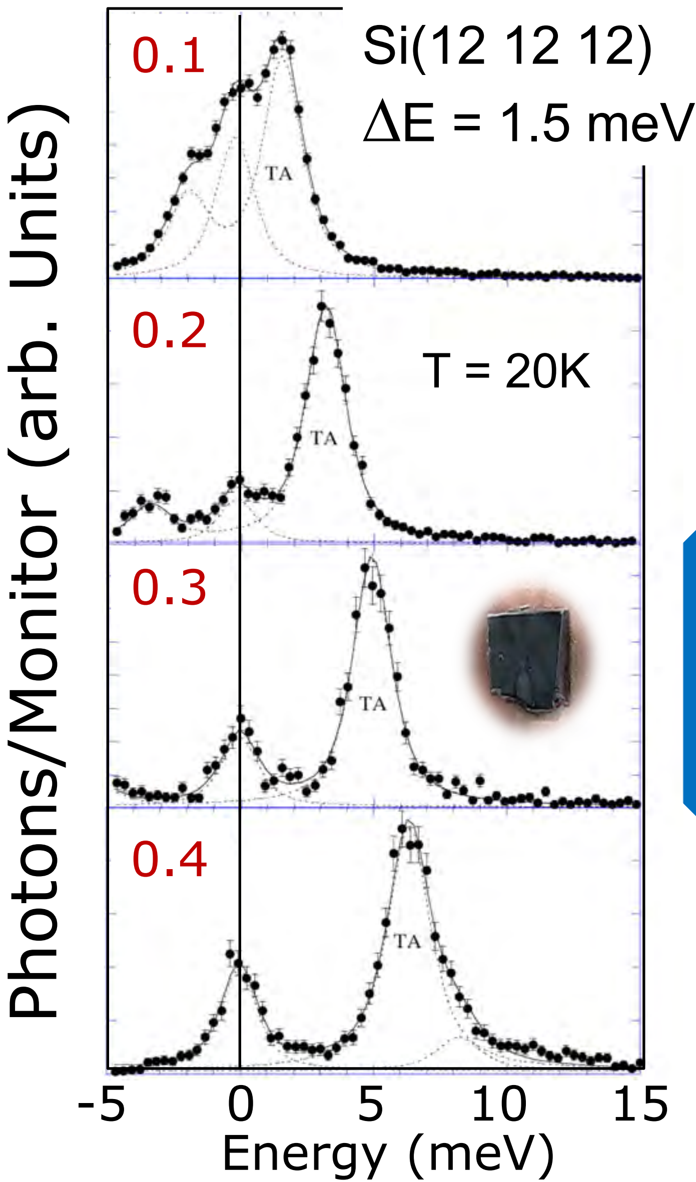
UO_2 IXS:



Γ
X
X
Γ
a)
b)
Branch C
Branch B
Branch A
2π /a [100]
2π /a [011]
TA
LA
Neutrons
Energy (meV)
0
2
4
6
8
10
12
14
0
0.2
0.4
0.6
0.8
1.0
1.0
0.8
0.6
0.4
0.2
0
Reduced wavevector q (rlu)

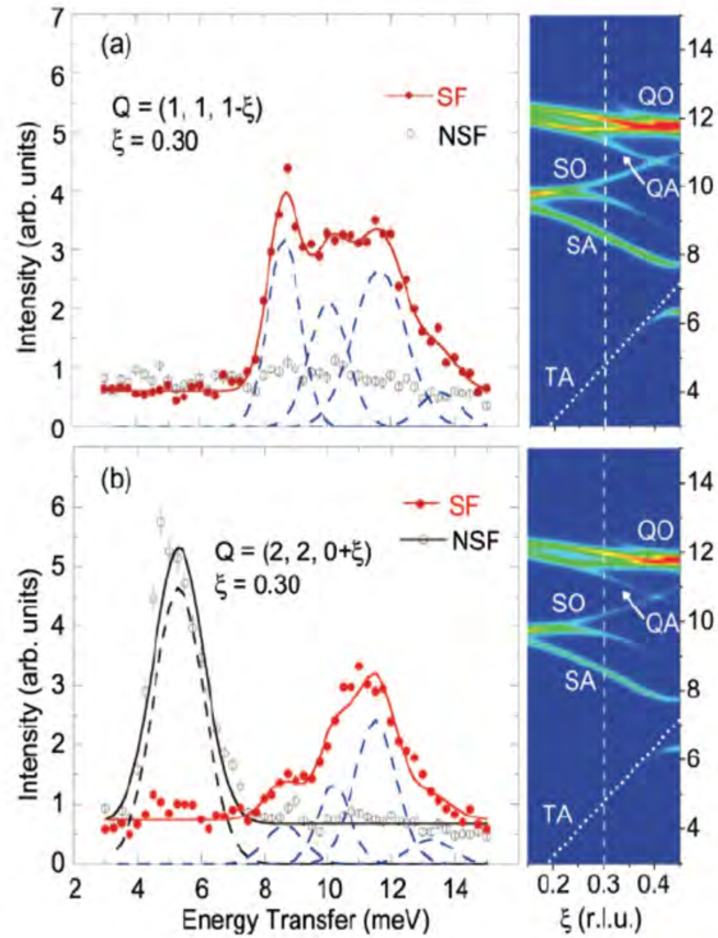
Comparison with experiments: low-q region

(6, 0, 0) + (0,q,0)



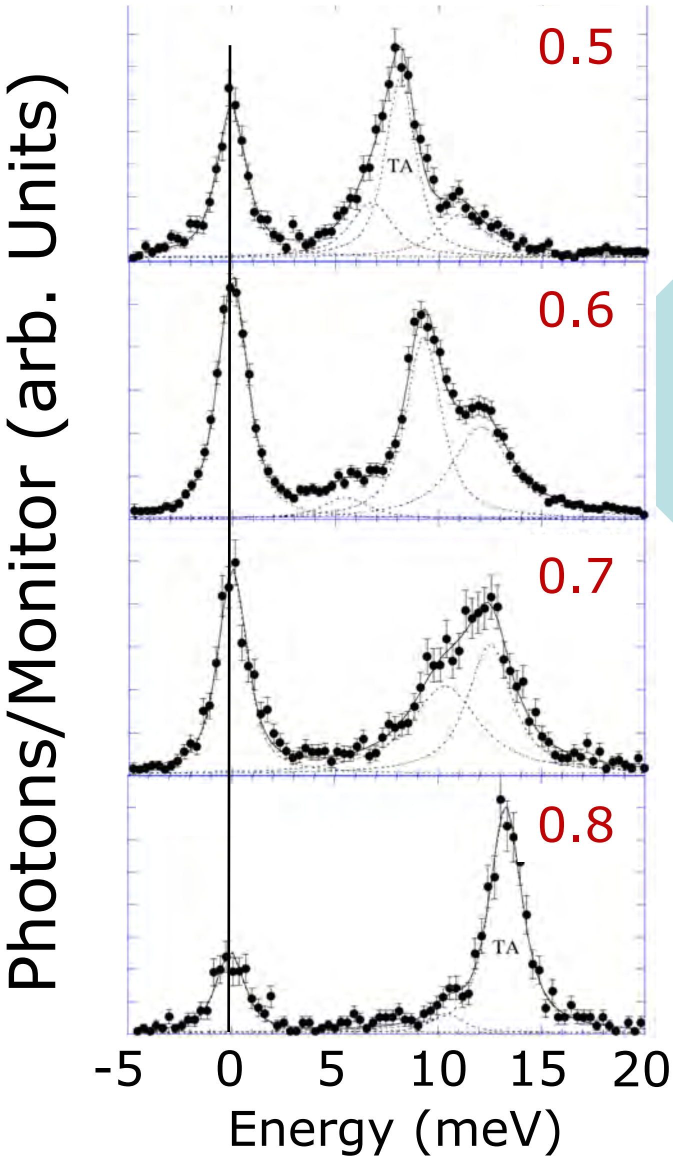
Quadrupolar modes are visible in the INS spectra through the associated spin or vibrational fluctuations.

Polarized neutrons
q=0.3

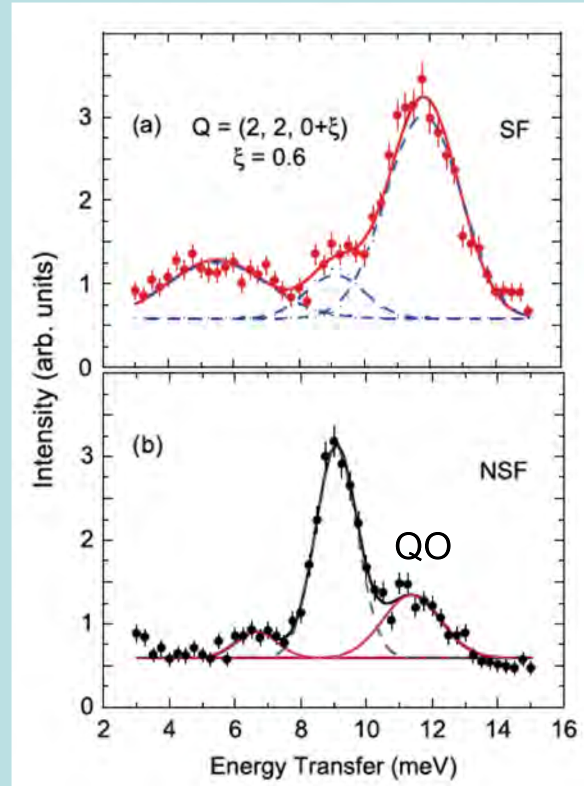


Comparison with experiments: high-q region

(6, 0, 0) + (0,q,0)



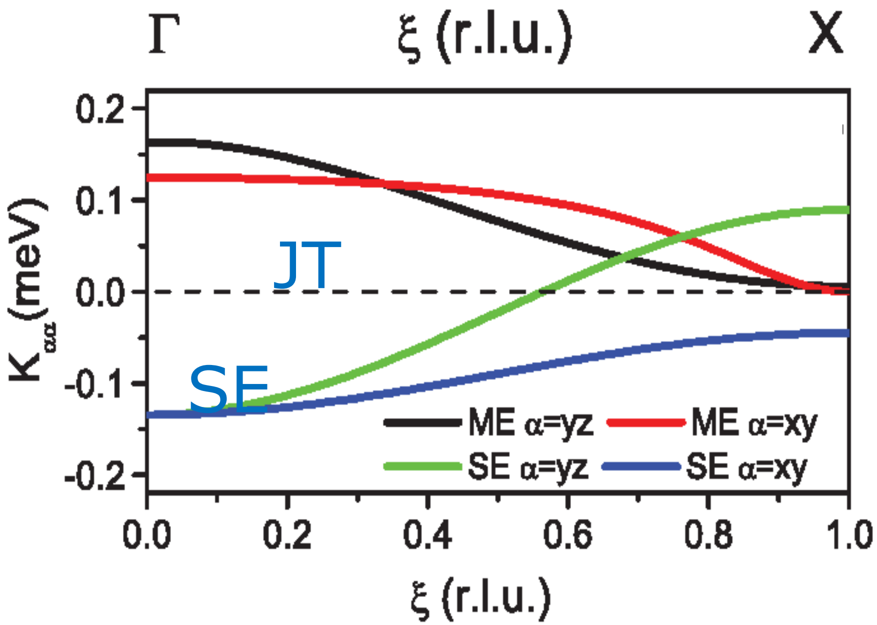
Polarized neutrons q=0.6



Strong TA phonon mixing with QO and SO branches

Jahn-Teller vs. superexchange quadrupole interactions

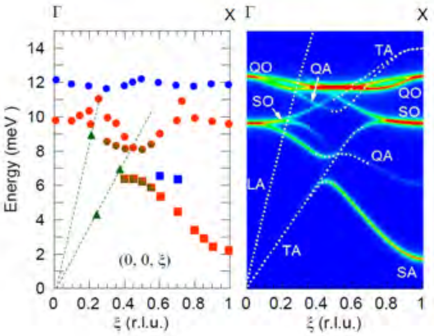
Data on quadrupolar dynamics provide information on the nature of two-ion quadrupolar couplings (superexchange vs Jahn-Teller dilemma).



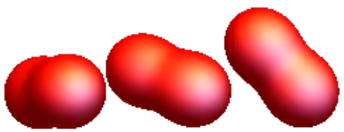
F-transform along Γ–X (q along z) of static Q-Q couplings arising from SE and JT interactions. "αα" means an interaction involving a pair of yz quadrupoles etc..

At the X-point (wavevector for static Q-order) JT QQ coupling is vanishing: static Q-order stabilized by SE quadrupolar interactions

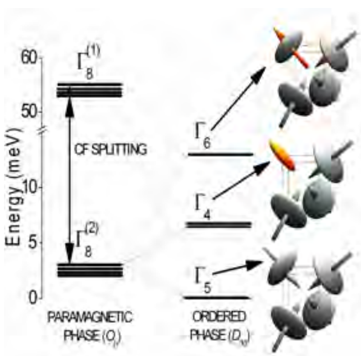
Conclusions

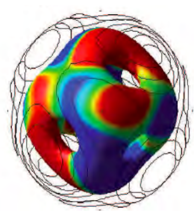


Mixed character of collective excitations in the ordered phase of UO_2 explained by phonon- and electron-mediated two-ions quadrupolar interactions.



Strong anti-crossing observed between TA and SO/QO modes over a wide q-range.





Quadrupolar waves can be detected by INS and IXS through the perturbation induced in the spin and vibrational dynamics.

Reduced phonon lifetimes along the (100) direction and anisotropy effects above T_N.

Phonons dispersion in NpO_2 measured by IXS.

Exotic triakontadipolar primary OP unveiled in NpO_2 by a combination of RXS and INS experiments.

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S. Carretta,

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Dipartimento di Fisica
UNIVERSITÀ DEGLI STUDI DI PARMA


A. Hiess

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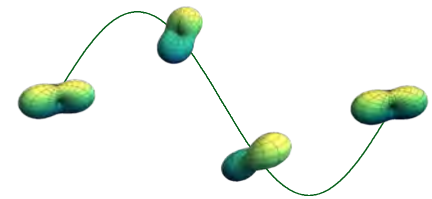


N. Magnani

European Commission

P. Maldonado


P. M. Oppeneer


UPPSALA UNIVERSITET


L.-P. Regnault

cea GRENOBLE


G. H. Lander