Рабочее совещание по неупругому рассеянию нейтронов
СПЕКТРИНА - 2018
19 - 20 апреля 2018 г ., ПИЯФ НИЦ «КИ», г. Гатчина

Спиновые флуктуации и магнетизм в системах с валентной нестабильностью

П.А. Алексеев

> *Физика как секс: может не давать практических результатов, но это не повод ею не заниматься*
> Р. Фейнман

Все, что интересно, – не просто.
Следствие: когда начинаешь вникать, то получаешь то, чего не ждал…

Рабочее совещание по неупругому рассеянию нейтронов
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Spin fluctuations and magnetism in systems with valence instability

P A Alekseev

Spin fluctuations and magnetism

Rare-earth based compounds with *f*-electron instability

Spin fluctuations are inherent to systems with unfilled and virtually unstable *f*- and *d*- electron shells .

Example – systems based on the f-elements from
the beginning, middle, and end of rare earth series (*Ce*, *Sm*,*Eu*, *Yb*).

"Kondo effect, heavy fermions" Scattering of electrons with spin reversal

"Valence fluctuations" Symbolic presentation $f^{n} \rightleftarrows f^{n-1} + e$ From early 80th...

Commonplace: spin (valence) fluctuations (τ_{sf})– physical reason for the formation of the nonmagnetic ground state (no LRMO and static MM):

$(\tau_{sf})^{-1} > kT$ => effective suppression of the MM on ↓T (HF-, MV-systems)

For selected nonmagnetic systems the formation of semiconducting state with gap ~ 100K is specific!

Also spin-gap and singlet ground state are formed.

This is mixed valence semiconductor or "Kondo insulator" (KI)

Recently KI with magnetic ordering (LRMO) were discovered!

Spin fluctuations is the dynamical effect therefore magnetic neutron spectroscopy is the adequate experimental method

How it was started with neutrons?

from diffraction - to INS

Neutron magnetic form factor – is peculiar to any neutron scattering data

Physical origin of the form factor F(*Q*)

The result of interference of neutron wave scattered (with momentum transfer *Q*) by the electron shell *(in fact – on the magn. moment density,originated from 1) spin and 2) orbital moments of electrons).*

Furrier transform of magnetization density distribution

Forward scattering – no interference, F(0) = 1
Increase of scattering angle or/and neutron energy, (that means increase of the momentum transfer Q) results in F(Q) → 0

Magnetic form factor basically is defined experimentally from:

1) ***Intensity of Bragg peaks in diffraction for ordered state ,***
2) ***In paramagnetic state, form induced moment in external magnetic field by polarized neutron diffraction***

In the most of real cases a dipole approximation (small Q) is used:

$$F(Q)=\langle j_0(Q)\rangle+[(2/g)-1]\langle j_2(Q)\rangle\,,\quad g \text{ – Lande factor}$$

Spin + orbital

Orbital

Spin fluctuations and magnetism

1. Magnetic form factor in intermediate valence state of Sm and Eu

1.1 The form-factor "puzzle" of intermediate valence Sm-ions

For a long time it was not clear, why there is **no evidence** of the presence of "***Sm***$^{3+}$ - like form-factor" in neutron measurements for intermediate valence ***Sm***-based systems - ***SmS*** (**"gold"**) and ***SmB***$_6$, - in spite of the fact that the **average valence** for **Sm** is close to **2.5**

Intramultiplet (ΔJ=0)

$f(Q)=\langle j_0\rangle+C_2\langle j_2\rangle$

$C_2=(2-g_J)/g_J$

Intermultiplet inelastic spin-orbital transitions (**ΔJ≠0**) $C_2 = -1$

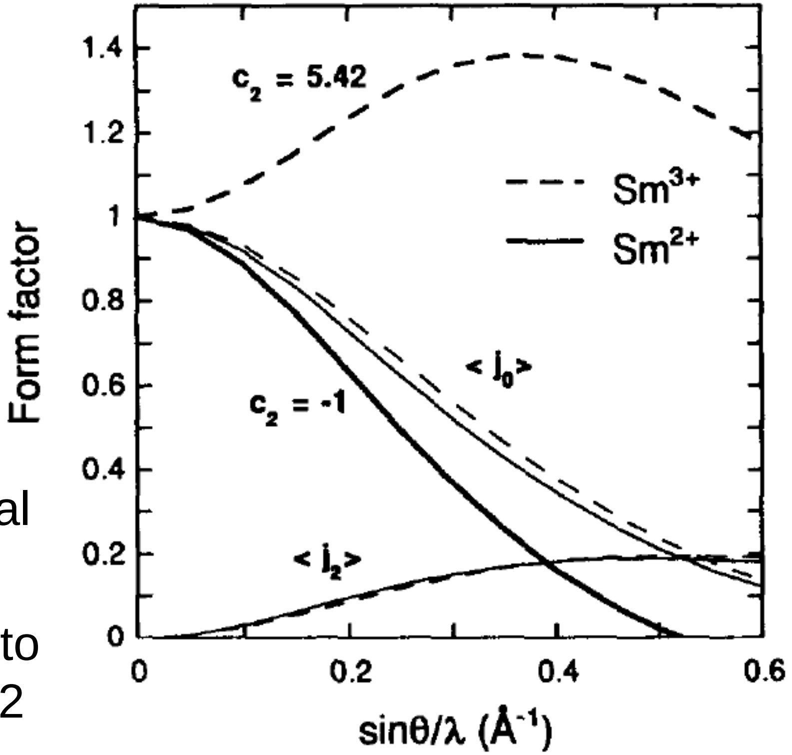
$f(Q)=\langle j_0\rangle - \langle j_2\rangle$

$\langle j_n\rangle$ **-** *are integrals of the product of the 4f radial wave function and spherical Bessel functions of n-order*

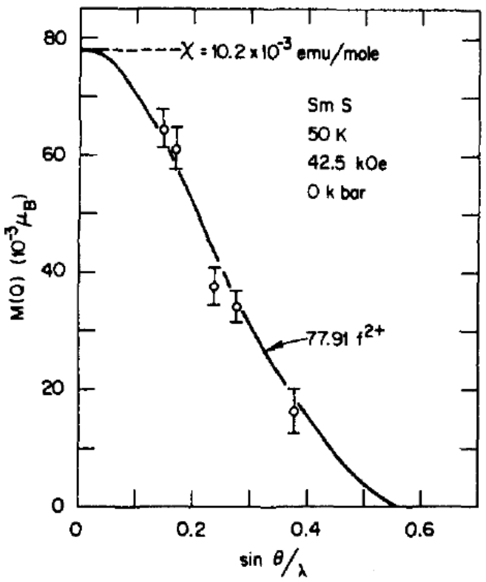
$\langle j_0\rangle$ - associated with both spin and orbital moments,

$\langle j_2\rangle$ - resulted from the orbital moment alone

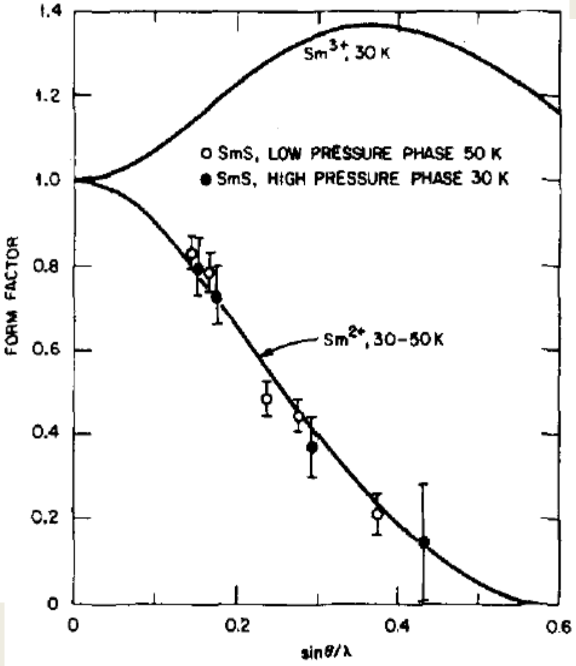
C_2 for Sm^{3+} is very high due to collision of J=5/2, L=5, S=5/2



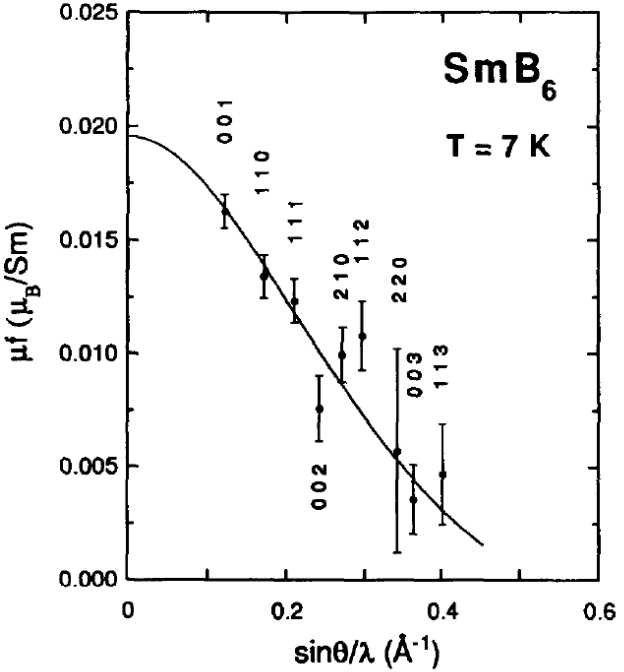
SmS, Sm(Y)S



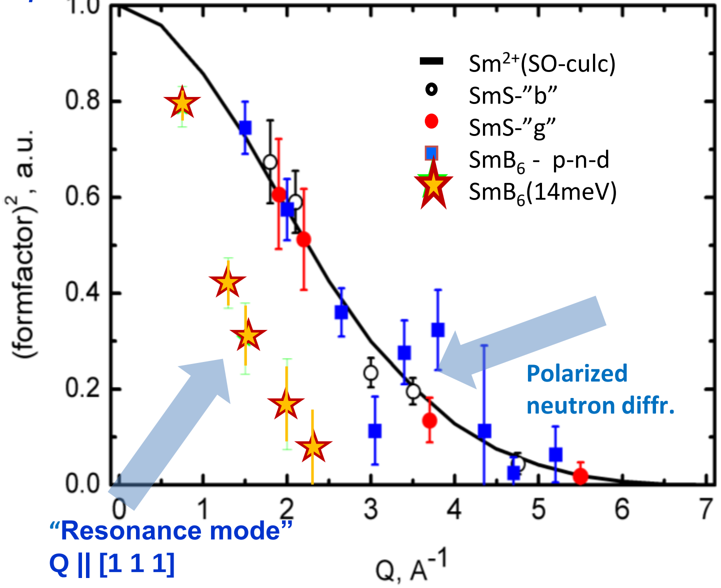
R. M. Moon, W. C. Koehler, D. B. McWhan, and F. Holtzberg, J. Appl. Phys. **49**, 2107 (1978)



J.-X. Boucherle, P. A. Alekseev, B. Gillon, J.-M. Mignot, e.a., Physica B **206–207**, 374 (1994)

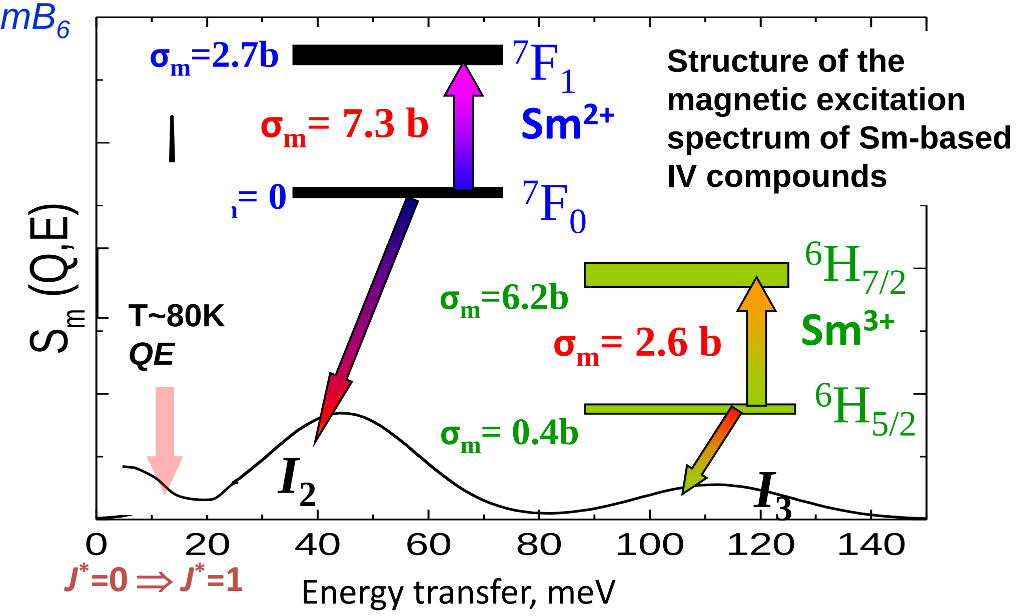


Experimental data for form-factors of SmS and SmB$_6$



Polarized neutron diffr.

"Resonance mode"
Q || [1 1 1]



Structure of the magnetic excitation spectrum of Sm-based IV compounds

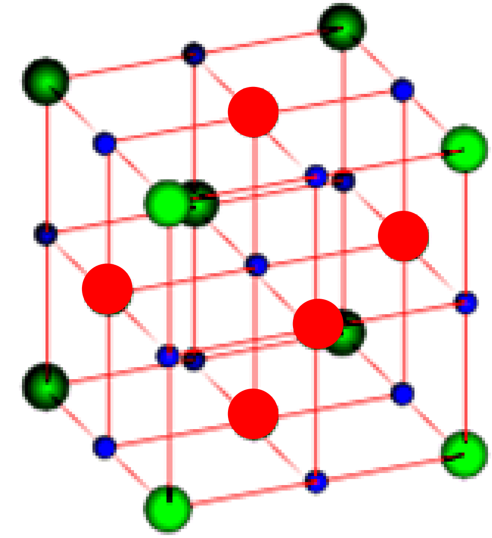
A little more details about INS results for mixed valence systems

Inhomogeneous mixed valence system Sm_3Te_4

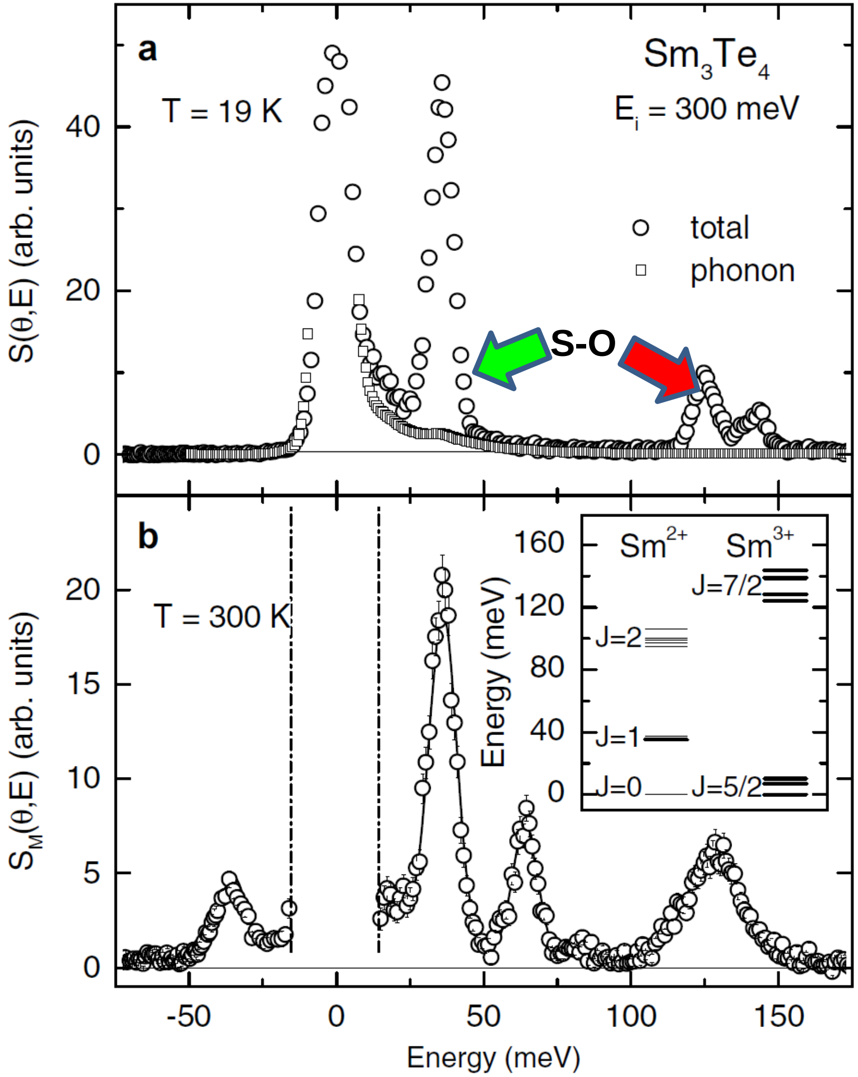
with spin-glass formation below T_g=1.5K

~ 2 : 1

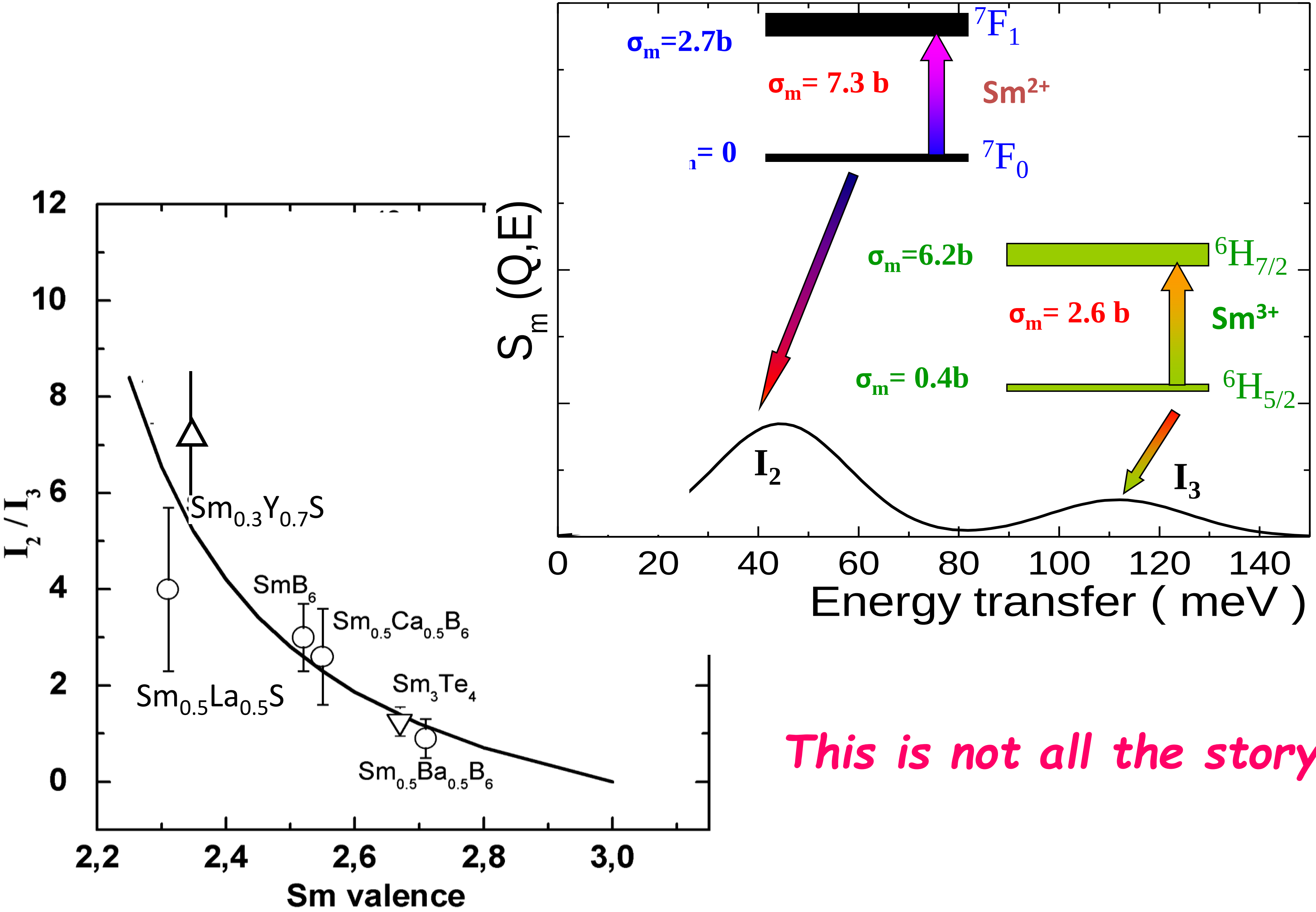
🔴 Sm^{3+} 🟢 Sm^{2+}



Inelastic neutron scattering spectra



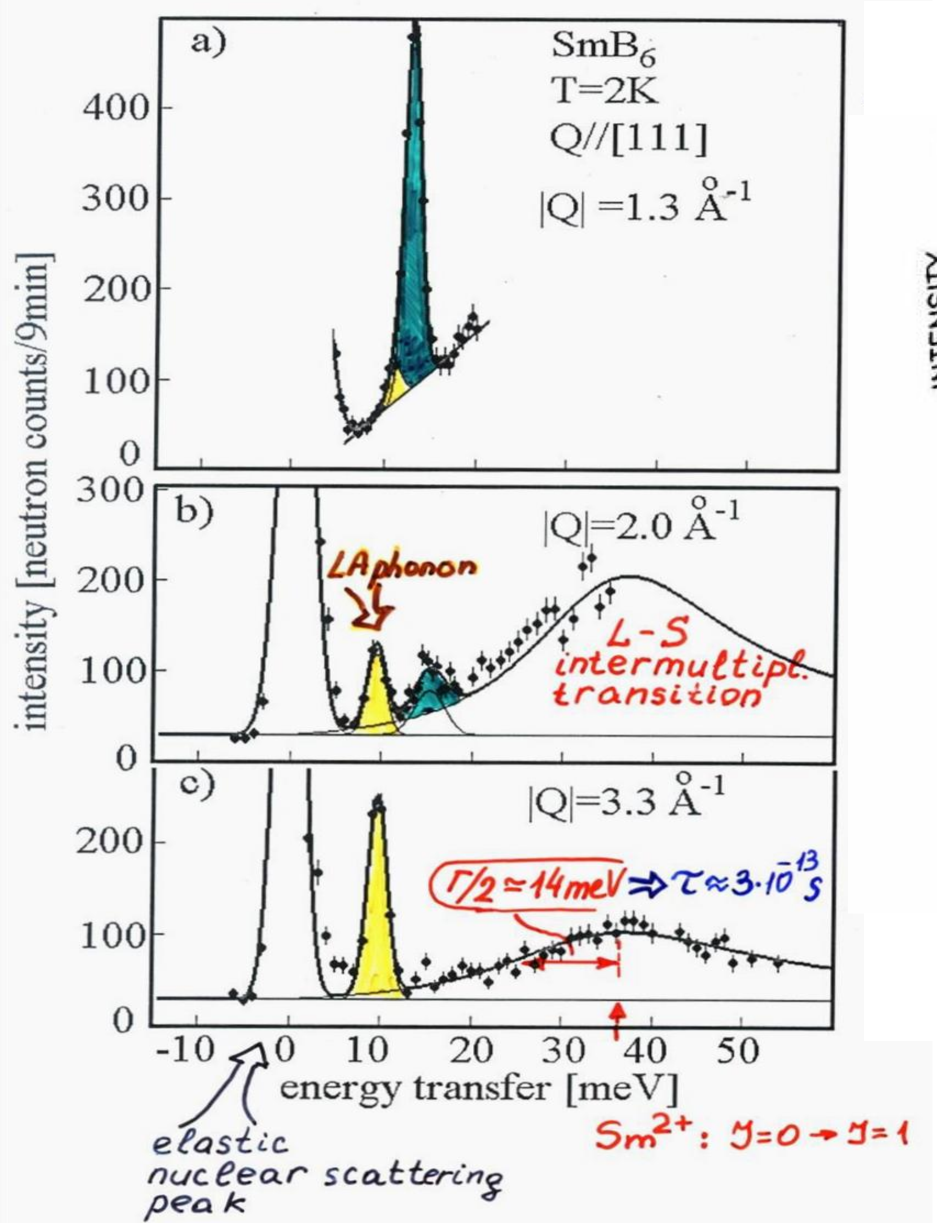
Intermultiplet (spin-orbit) excitations

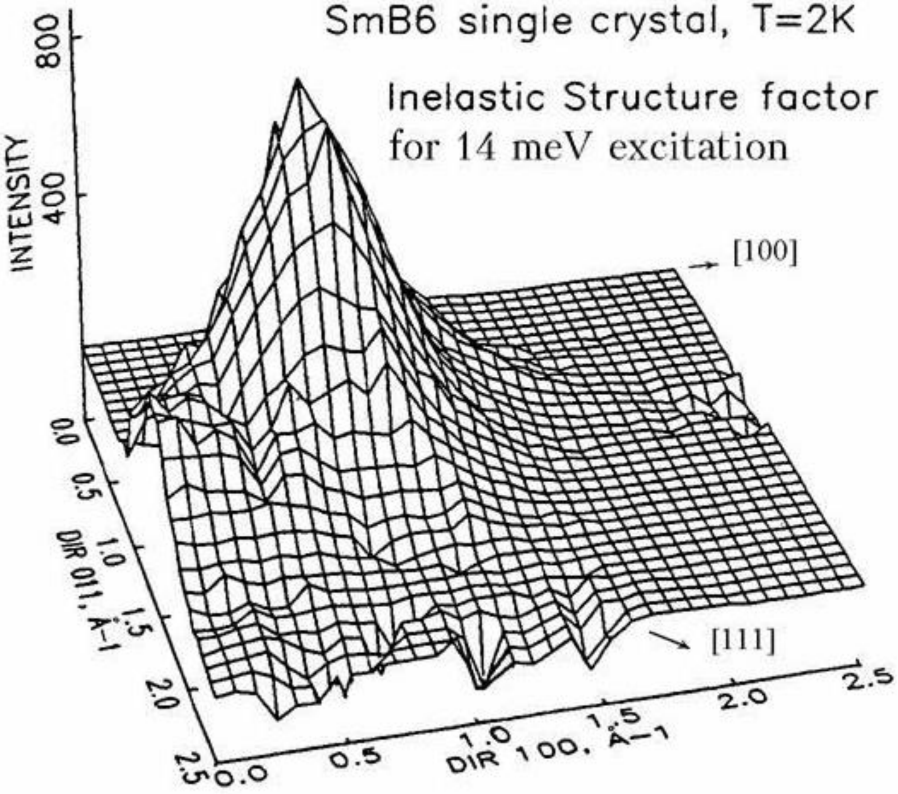


This is not all the story!

Low energy ("resonant") mode in SmB6

$^{154}Sm\,^{11}B_6$ single crystal

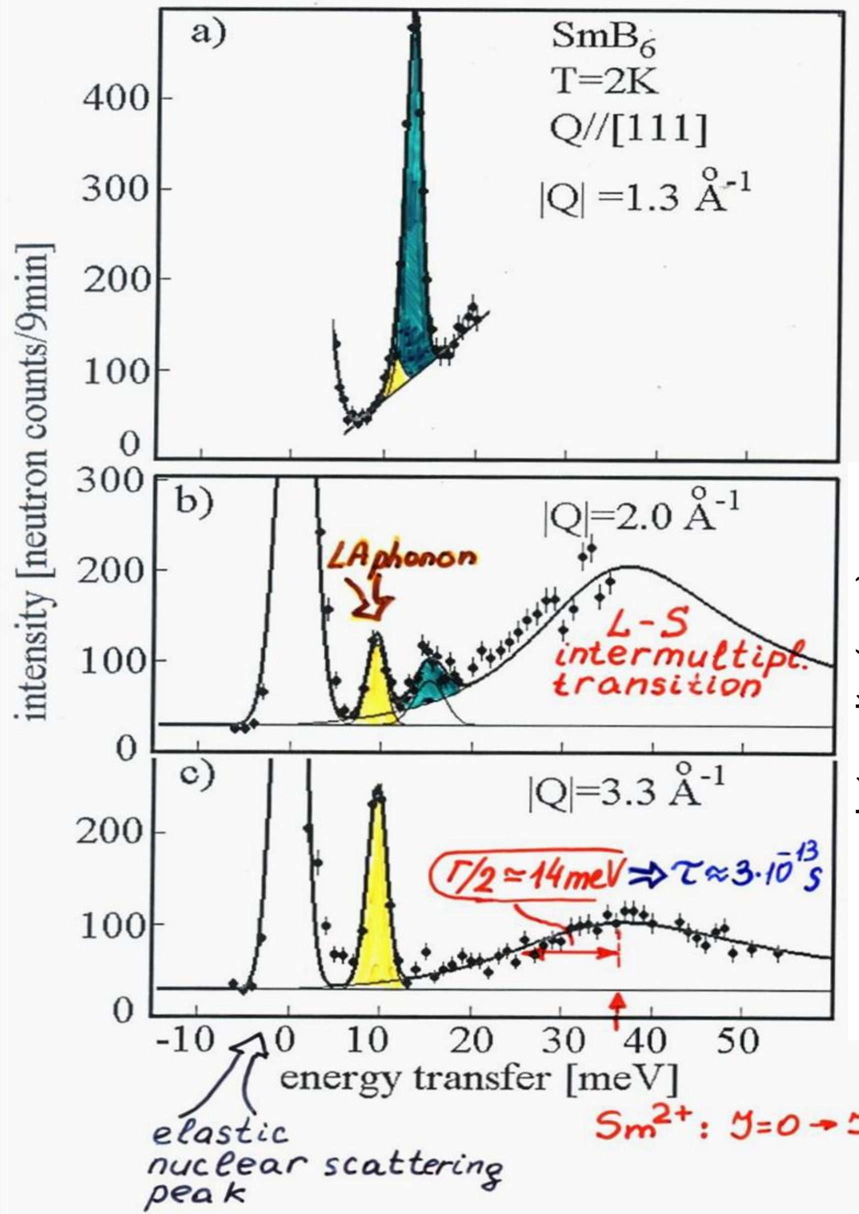


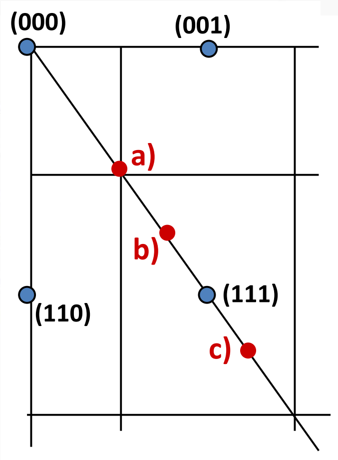


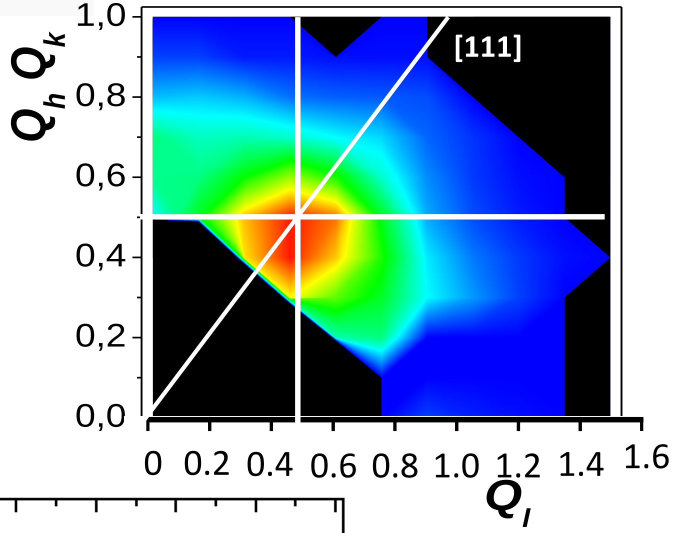
"Map" of inelastic scattering intensity

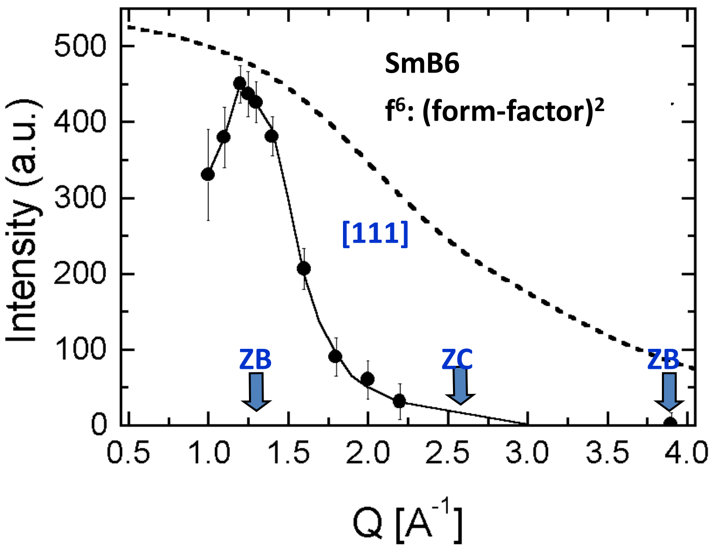
Low energy (“resonant”) mode in SmB6

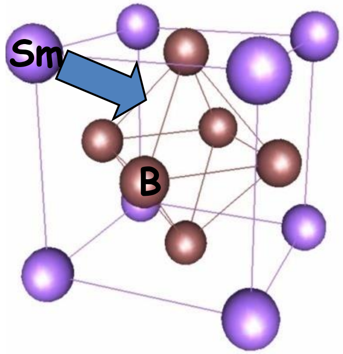
$^{154}Sm\,^{11}B_6$ single crystal





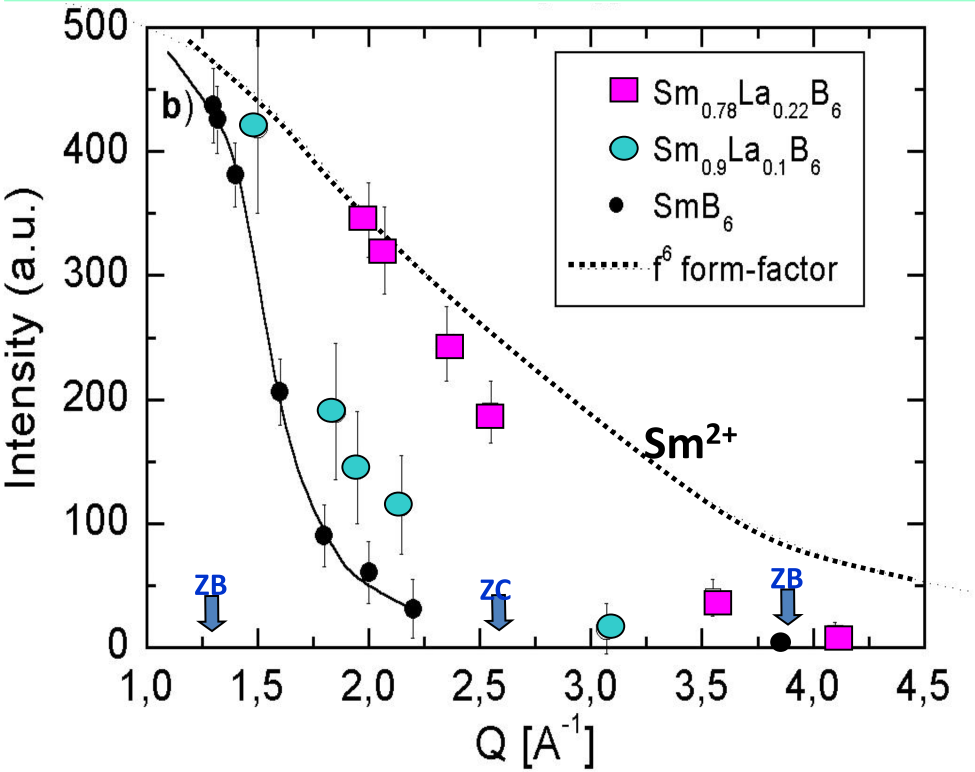


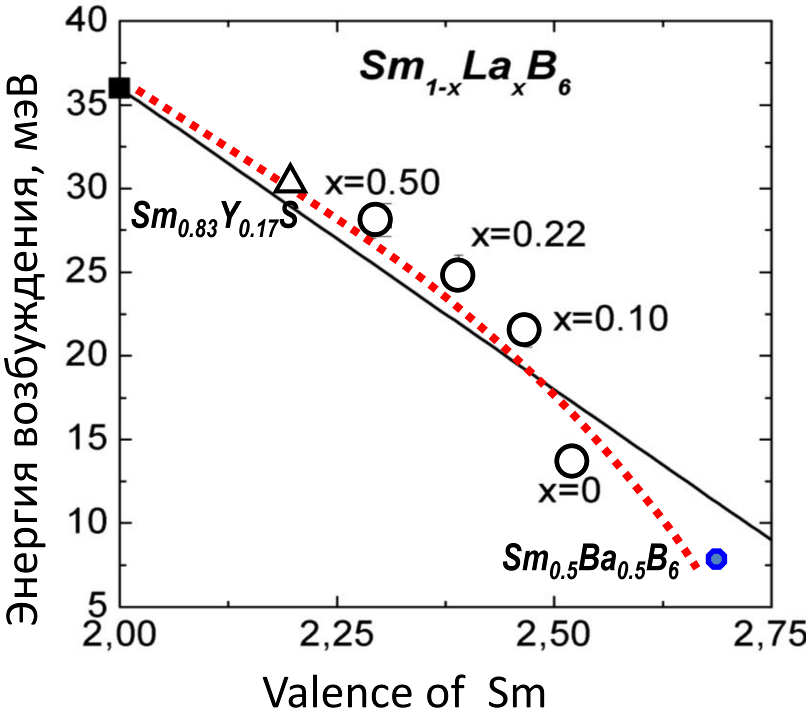




How it is related to the mixed valence?

Low energy ("resonant") mode in SmB6





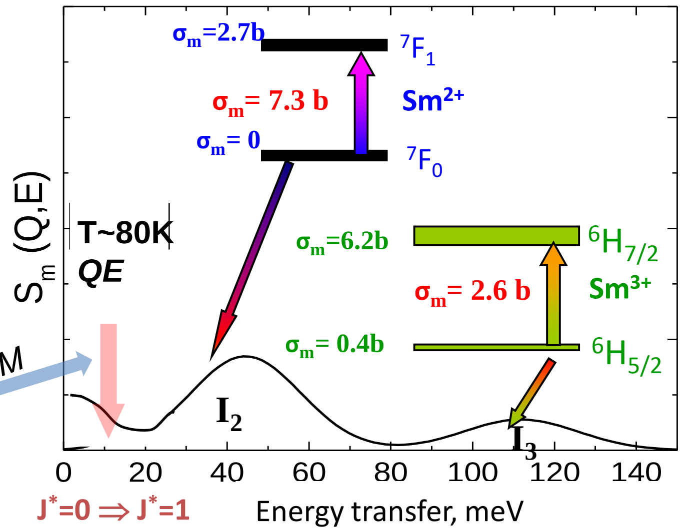
Q-dependence of form-factor with valence change *(along [111] for single crystals)*

Energy - valence correspondence

Does it mean that RM is a " double" of intermultiplet J=0→J=1 (f^6:Sm^{2+}) transition (singlet-triplet) for IV state of Sm !?

"Help" (important detailes) comes from SmS ...

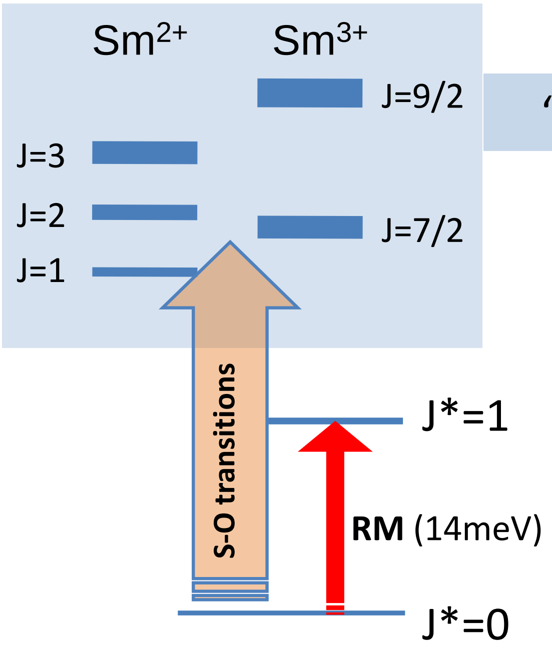
Relation between spectral structure (with corresponding form-factors) and temperature for *SmB$_6$* IV-state *)



Mm=0.8μ_B

Low T — RM

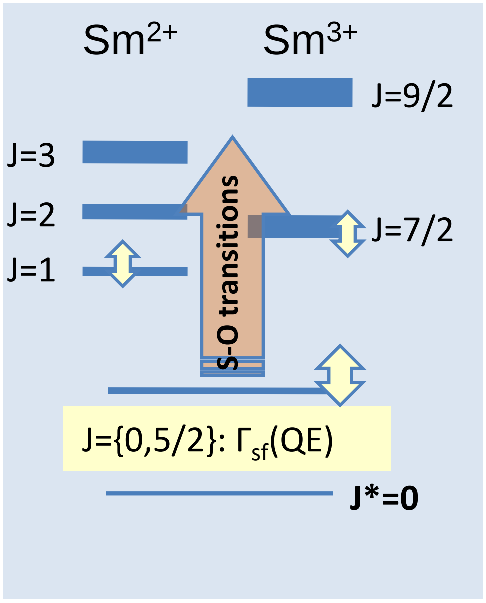
High T (~100K)



"Parent" states Sm^{2+}, Sm^{3+}

SmB$_6$ Kondo insulator

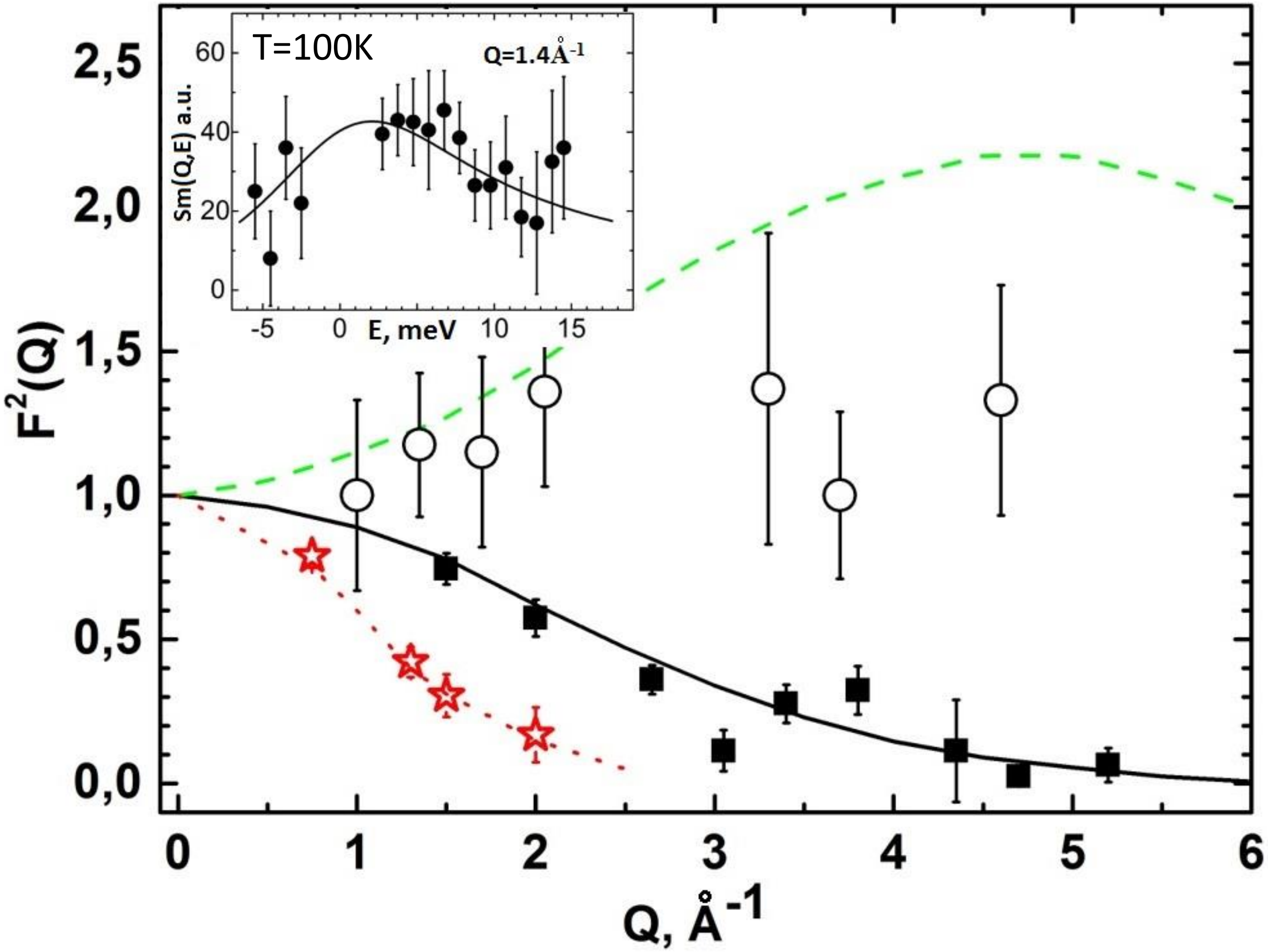
Increase of T



Overdamped RM due to closing of the gap

***) P. A. Alekseev, J.-M. Mignot, P.S. Savchenkov, V.N. Lazukov JETP Letters 103 (10) 636 (2016)**

Summary of low T experimental data for FF of SmB_6 including quasielastic signal at T=100K

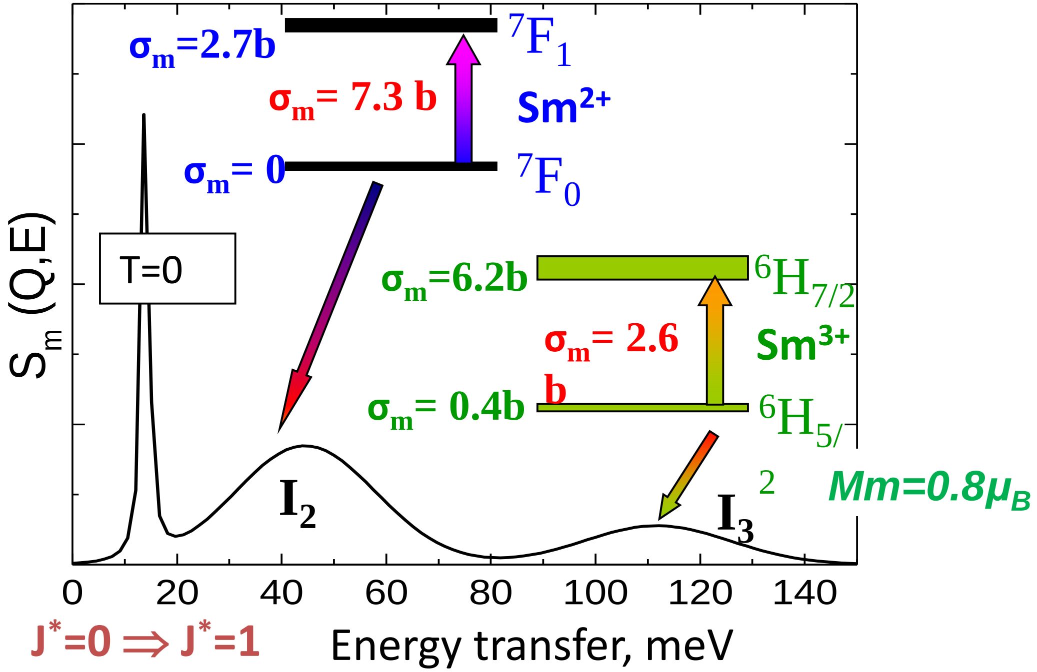


Structure and properties of the ground state wave function of IV state are reflected by form-factor measurements

Form-factor measured depends from type of experiment and conditions of measurements

$$\chi_C^m(T) = (g_J \mu_B^2 / k_B T)\left|\langle m\hat{J}_z m\rangle\right|^2 \exp(-\beta E_m)/Z$$

$$\chi_{VV}^{nm}(T) = 2g_J\mu_B^2 \frac{\left|\langle n\hat{J}_z m\rangle\right|^2}{\Delta_{nm}}\exp(-\beta E_m)/Z$$



For neutron spectroscopy:

$$\chi''(\vec{Q},\omega,T) = \pi\hbar\omega\left[\sum_m f_m^2(\vec{Q},T)P_{mm}(Q,\hbar\omega,T)\chi_C^m(T) + \frac{1}{2}\sum_{m\neq n} f_{mn}^2(\vec{Q},T)P_{nm}(Q,\hbar\omega-\Delta_{nm},T)\chi_{VV}^{mn}(T)\right]$$

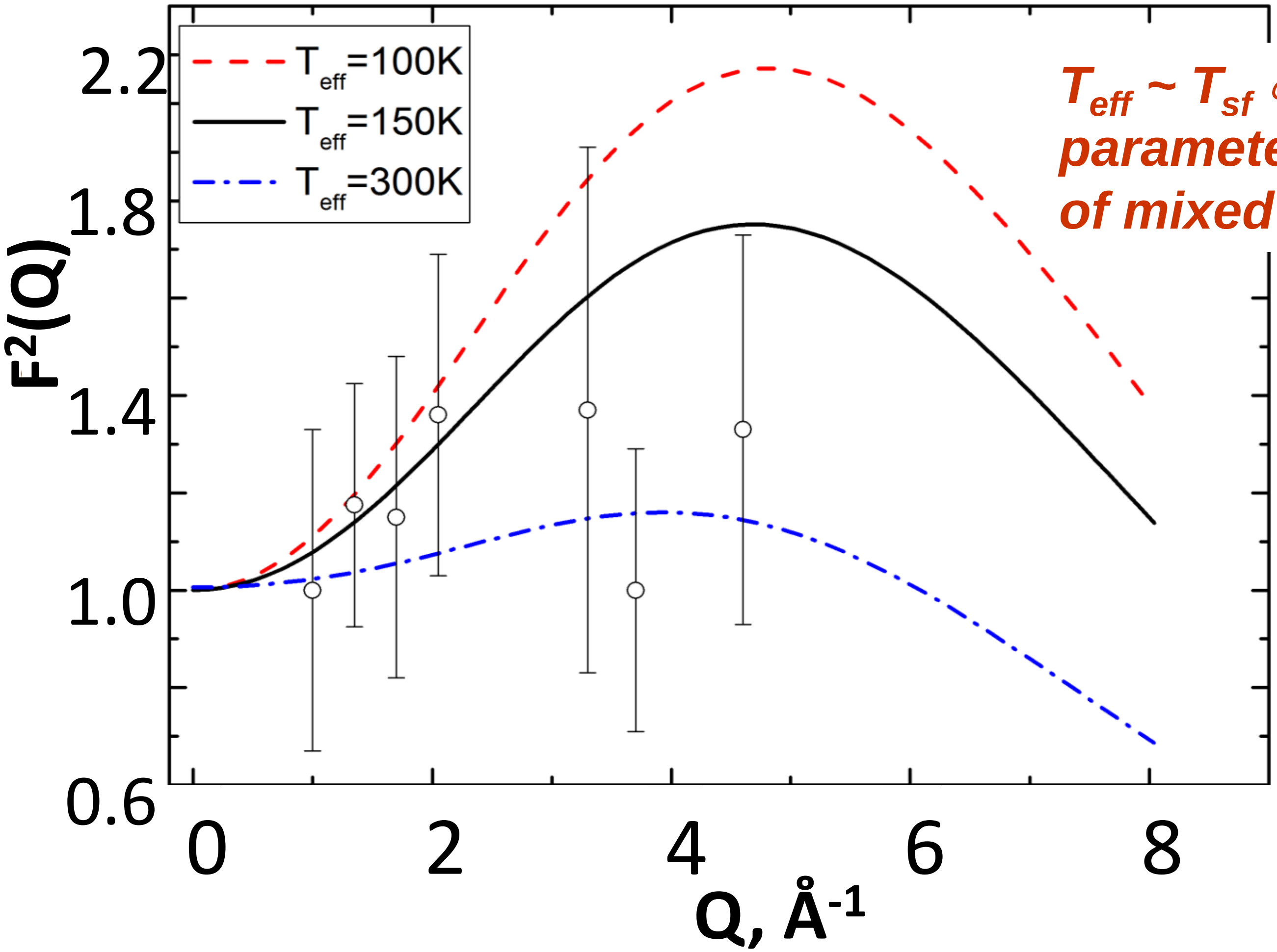
SmB$_6$ at low T : spin gap, - singlet ground state+excitation at 14meV(RM) + Spin-orbitals from Sm^{2+} and Sm^{3+} “parent”= **only Van-Vleck contribution**

SmB$_6$ at high T : spin gap is closed, manifold of “parent” state is available = **quasilestic signal results from Curie contribution**: $T_{eff} \sim T_{sf} \propto (\Gamma_{QE}, \Gamma_{SO})$

$$f_{QE}^2(Q,T) = \sum_i \nu\,\sigma_{2,i}\,\rho_{2,i}(T,J)\,f_{2,i}^2(Q,T) + \sum_i (1-\nu)\,\sigma_{3,i}\,\rho_{3,i}(T,J)\,f_{3,i}^2(Q,T)$$

2, 3 - corresponds to Sm^{2+} and Sm^{3+}, respect.

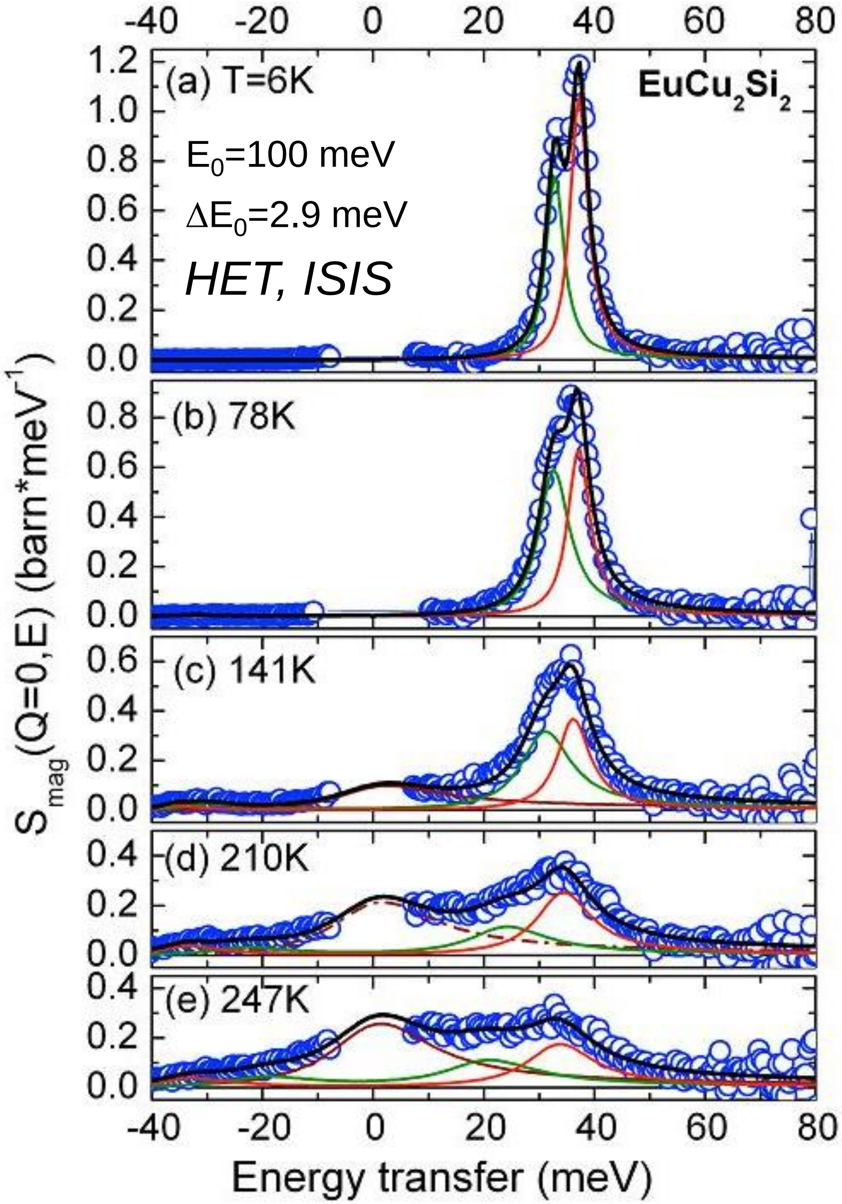
Form factor of QE-signal for SmB_6 (measured at 100K)



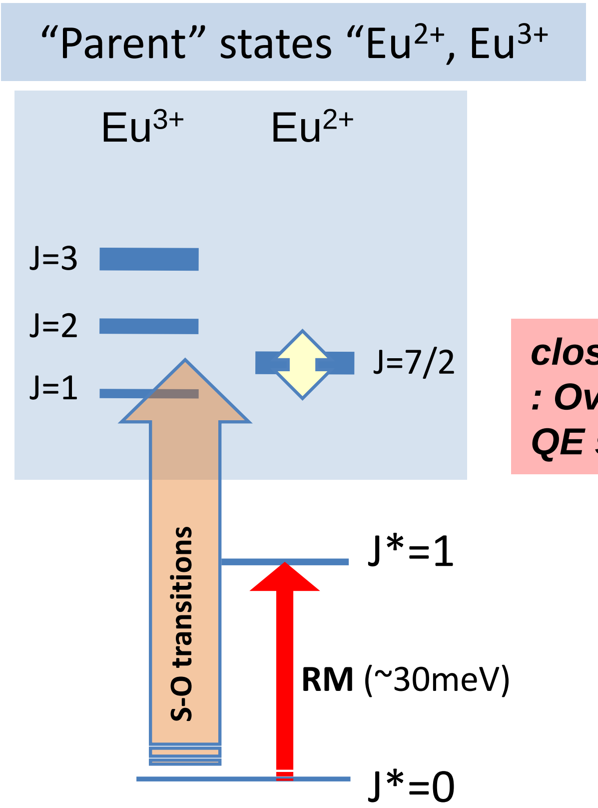
$T_{eff} \sim T_{sf} \propto (\Gamma_{QE}, \Gamma_{SO})$ is a parameter, as well as extent of mixed valence ν

Summary: form-factor measurements in relation to the specific of corresponding spectral function can provide the hint to character of *f*-electron wave function for intermediate valence state

1.2 Form-factors for intermediate valence *Eu*-ions in *$EuCu_2Si_2$* *)



Low T



"Parent" states "Eu^{2+}, Eu^{3+}

Eu^{3+} Eu^{2+}

J=3

J=2

J=1

J=7/2

S-O transitions

J*=1

RM (~30meV)

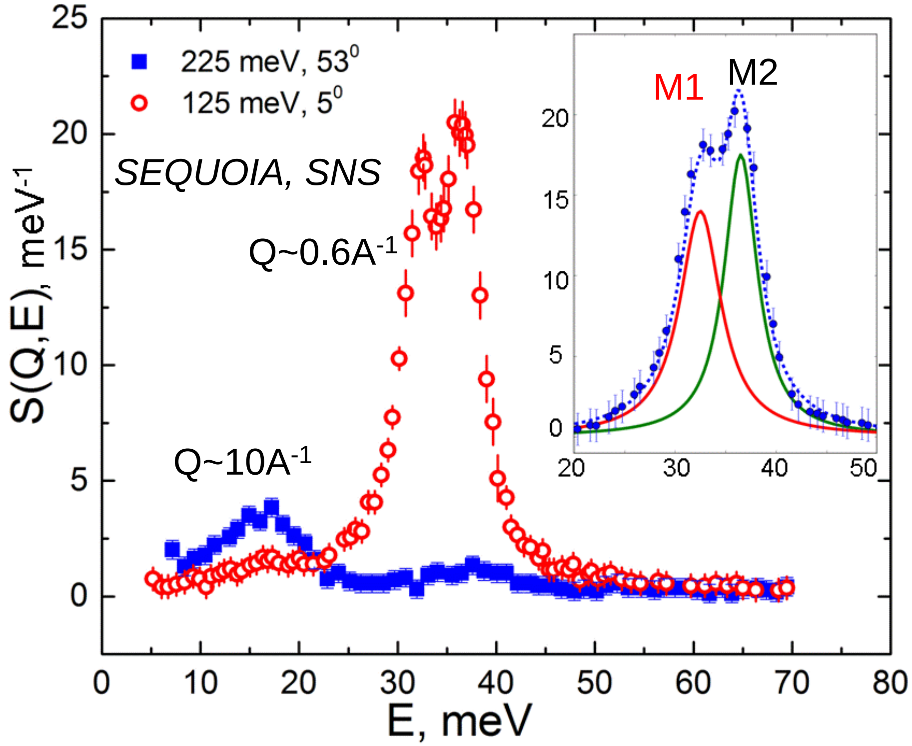
J*=0

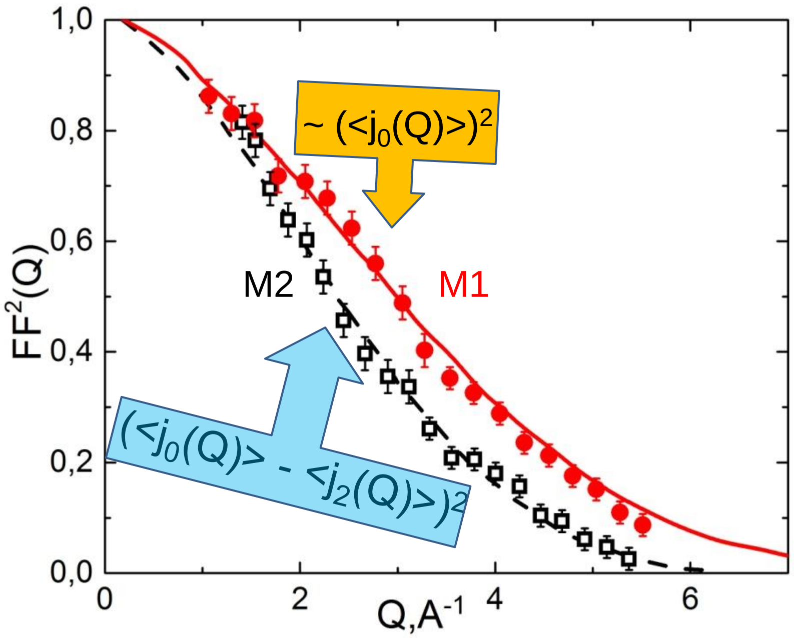
Increase of T

closing of the spin gap
: Overdamped RM
QE signal from J=7/2

***) P S Savchenkov, P A Alekseev, A Podlesnyak, A I Kolesnikov, K S Nemkovski,** *Intermediate-valence state of the Sm and Eu in SmB6 and EuCu2Si2: neutron spectroscopy data and analysis* **J. Phys.: Condens. Mater 30 (5, 7Febr)) (2018) 055801**

$EuCu_2Si_2$





for **M2** form factor $F_{M2}(Q) \sim \langle j_0(Q)\rangle - \langle j_2(Q)\rangle$, SO-excitation
but
for **M1** – form factor is $F_{M1}(Q) \sim \langle j_0(Q)\rangle$), J=S, L=0! **:** ***$f^7$***

Resonant mode (**M1**) carries evidence of the high spin state (f^7) presence at low temperatures for intermediate valence state of Eu
This could be the prerequisite for the development of the magnetism at some point of phase diagram

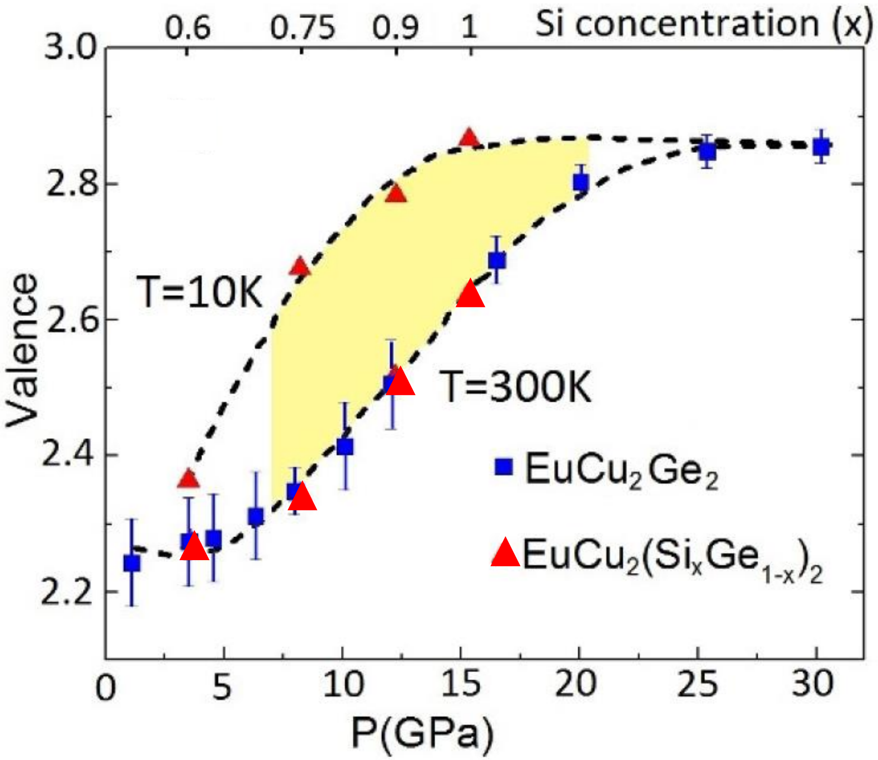
We will omit the quantum mechanics consideration of the ground state wave function of intermediate valence state and its generalization for the case of Sm and Eu as well
(special people exist for that!)

Also not going into very interesting physics for a family of 1-2-2 Eu - based systems…
Just stop at the **$EuCu_2$ $(Si_{1-x}Ge_x)_2$** , for some details of magnetism….

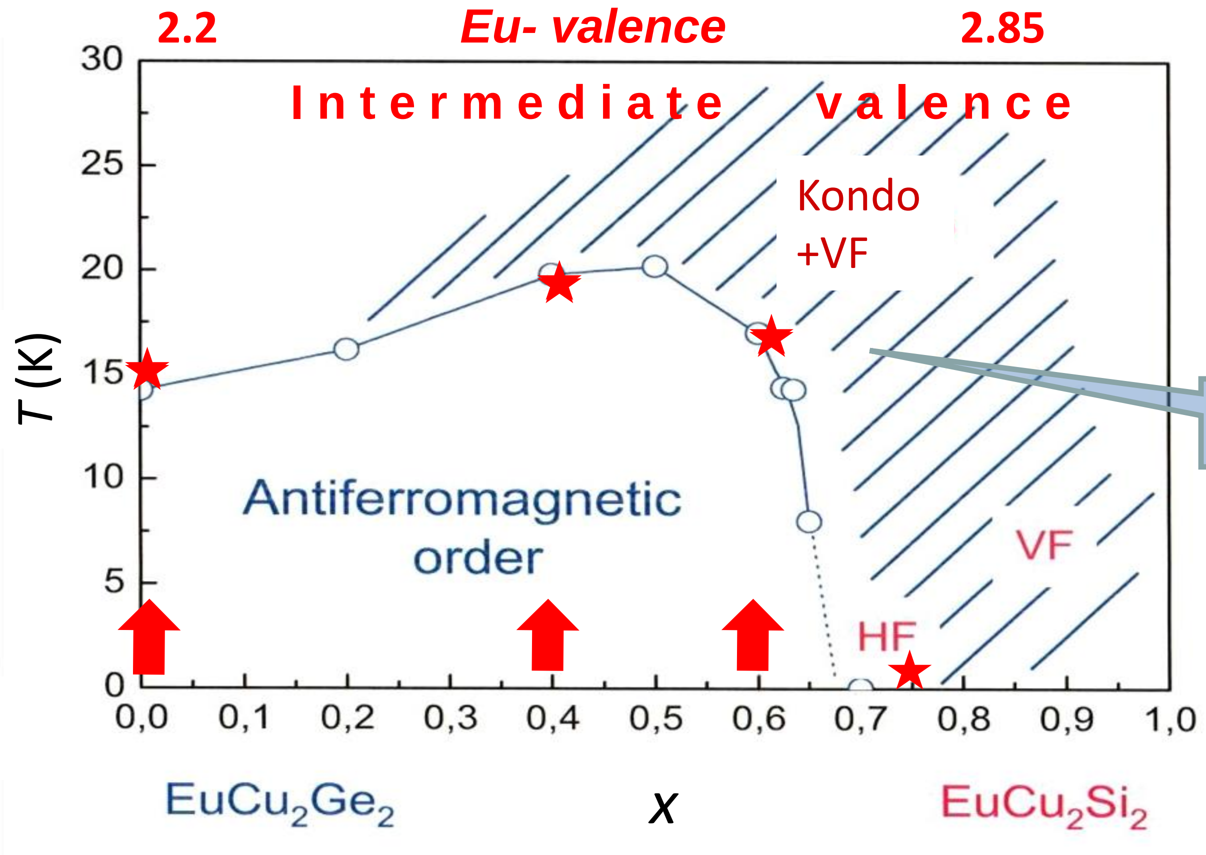
2. Spin fluctuations and long range magnetic order: the case of “strong” (υ ~2.5) and flexible intermediate valence

How the magnetic correlation can survive under these conditions?!

Particular example: Valence is changing in wide range (2^+ - 3^+), staying homogeneous: ***$EuCu_2(Si_xGe_{1-x})_2$***



EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$: magnetic phase diagram



★ Neutron diffraction data

Z. Hossain, C. Geibel, et.al.
*PRB **69** (2004) 014422*

What is the origin of this phase diagram ?

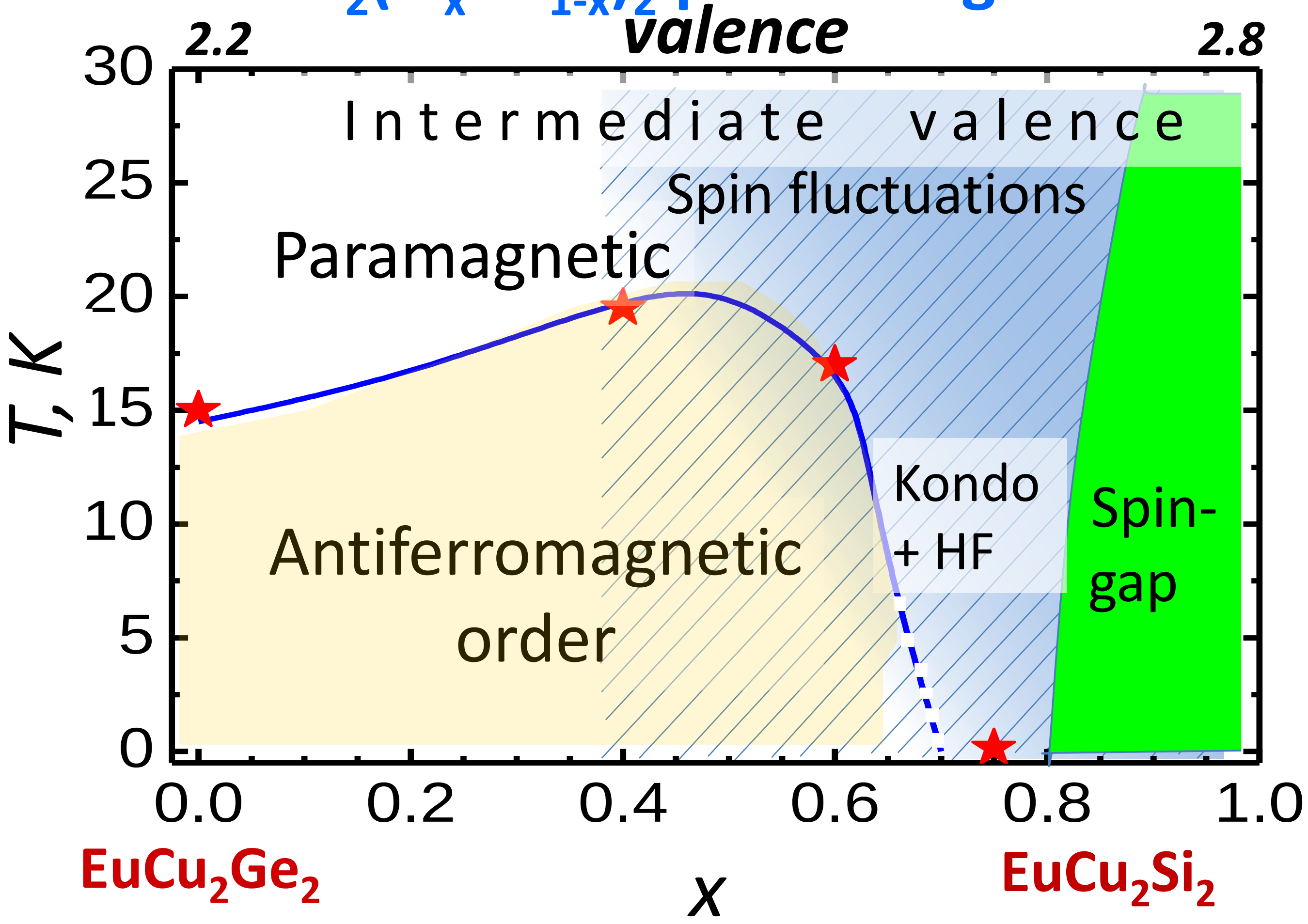
Two “competing” states for intermediate valence Europium:

Eu^{3+} (f^6, like Sm^{2+}) J=0(!),$^7F_0 \rightarrow {}^7F_1$ SO-transition:E=46meV, σ=7.34 barn,

Eu^{2+} (f^7, like Gd^{3+}) J=S=7/2, σ=38.51 barn (NO inelastic excitations)

Then to neutron spectroscopy data: ISIS (HET, MARI) and ILL (IN-4C)

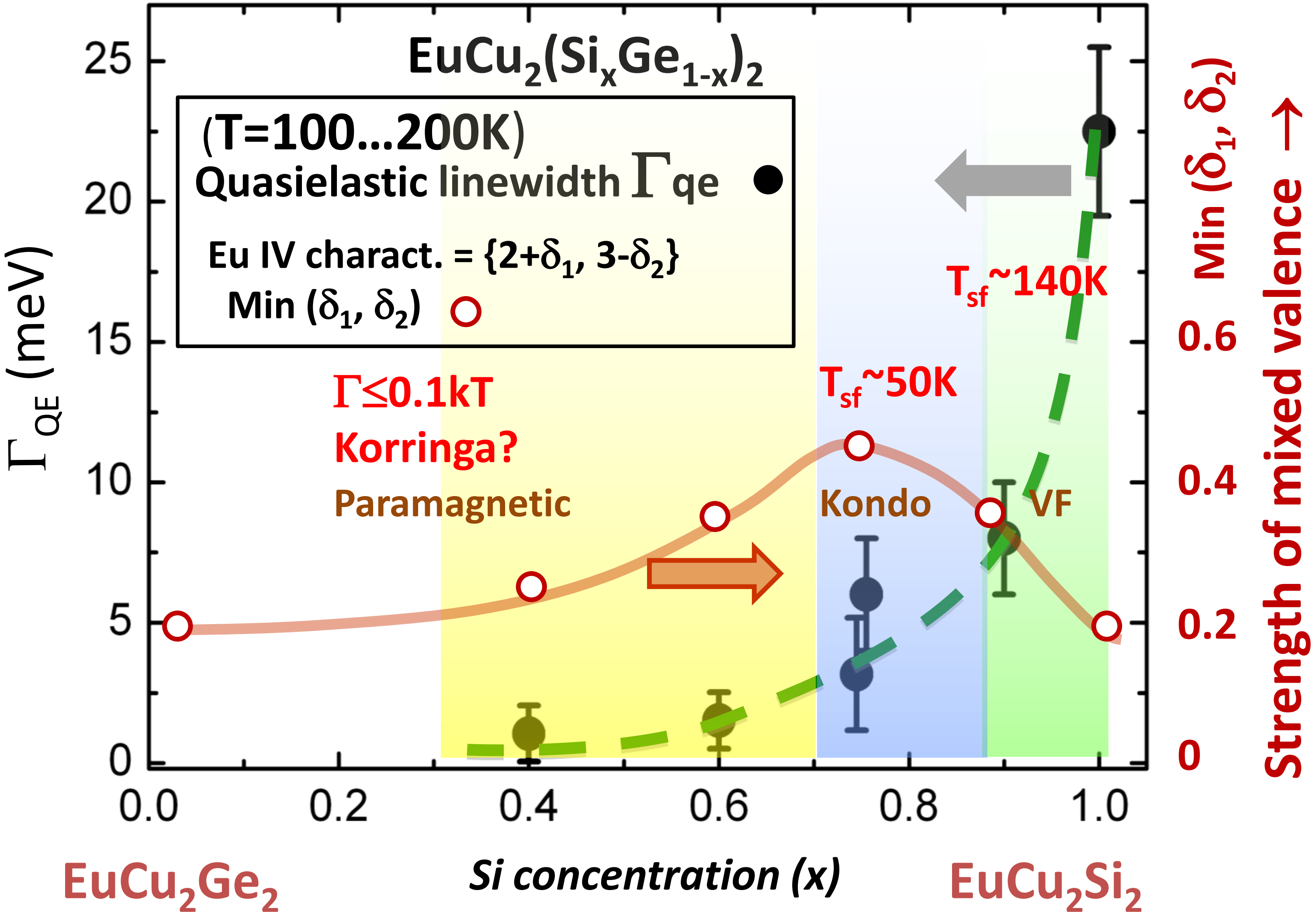
$EuCu_2(Si_xGe_{1-x})_2$ phase diagram



-Some region of x-concentrations appears where LRMO (k=1/3,0,0) coexists with spin fluctuations peculiar to homogeneous IV observed for any x (but NO model !)

-This region verge on HF state similar by spectral characteristics to ones of generic HF systems based on Ce, Yb (BUT "strong" IV !)

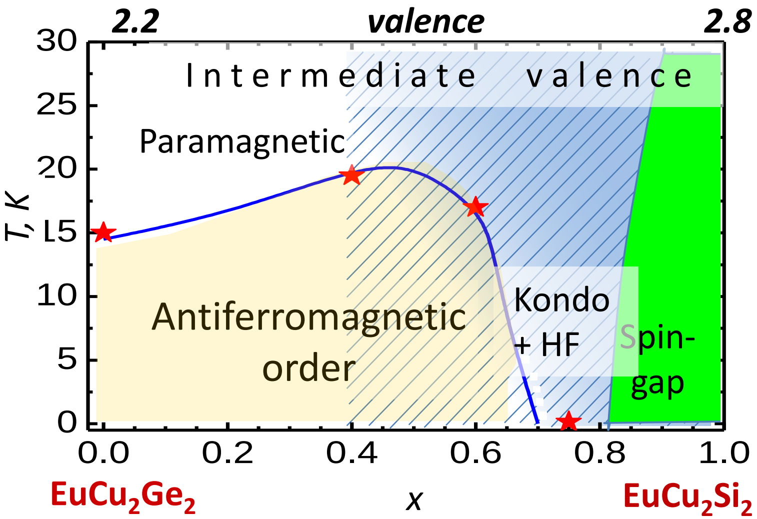
Quasielastic width (T=100…200K) and strength of mixed valence in EuCu$_2$(Si$_x$Ge$_{1-x}$)$_2$



Γ_{QE} steeply decrease with valence decreasing from 2.8 to 2.2 arriving to typical HF – energy range at Ge-concentration close to x ~ 0.75

2.1 *Summary* **IV and LRMO: competition and coexistence**

Formation of the magnetic ground state for IV ***Eu*** is provided by the *rearrangement of the magnetic excitation spectrum* of the system caused by the decrease of valence from **3-δ** down to **2+δ.** Just this rearrangement, probably, is a *background of a sequence of* phase transformations for ***$EuCu_2(Si_xGe_{1-x})_2$*** :



-Moderate spin fluctuations (SF) assist to appearance of **heavy fermion (HF)** state

- Further slowing down of SF result in **LRMO** for reduced moments on ***Eu***.

In some sense – analogy with Ce-based (LRMO-HF) systems, but!!! The valence is very far from integer!

- The elaboration of the adequate physical model is indispensable for understanding of physics behind the coexistence of SF and LRMO.

3. Magnetic impurity effect in Kondo-insulator *)

SmB_6 with Gd^{3+} - impurity (J=S=7/2, concentration from 0.04% up to 5%)

specific heat and *impurity magnetic moment screening* scales systematically in SmB_6

both depends from the exchange constant and electron density of states on E_F -(**$J\eta$**)- which modifies with impurity concentration

$J\eta$ -parameter scaled collapse of *specific heat* ties the low temperature DOS to the reduced impurity moment.
This indicates the involvement of impurity magnetism in the low energy DOS of Gd doped samples

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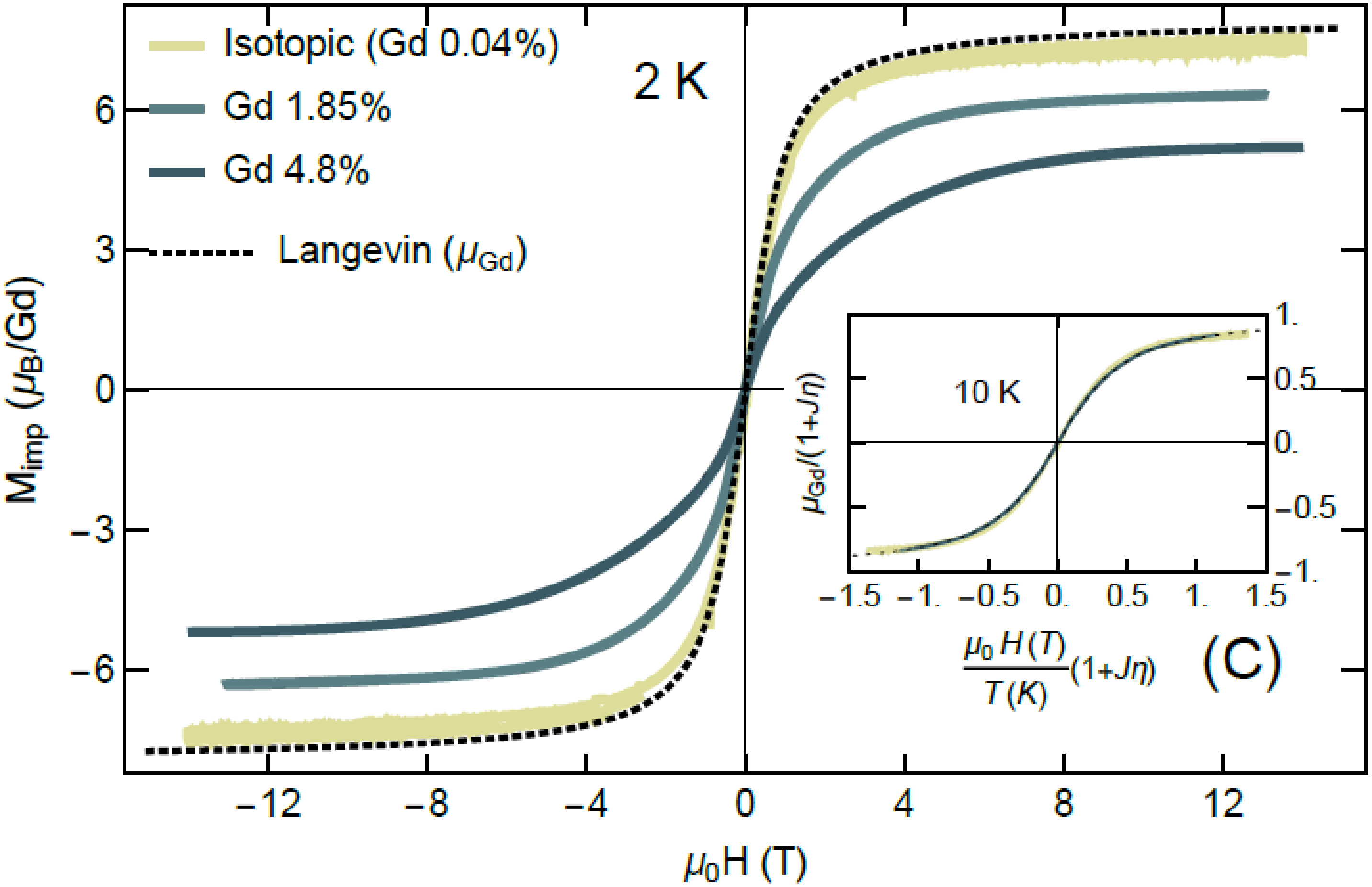
***) W. T. Fuhrman, J. R. Chamorro, P. Alekseev, J.-M. Mignot, et al** *Screened moments and extrinsic in-gap states in samarium hexaboride* , preprint **arXiv:1707.03834, 2017. 2, 2017**

Reduction of the Gd^{3+} effective magnetic moment M_{imp} (μ_B /Gd) in magnetization of SmB_6 with Gd impurity

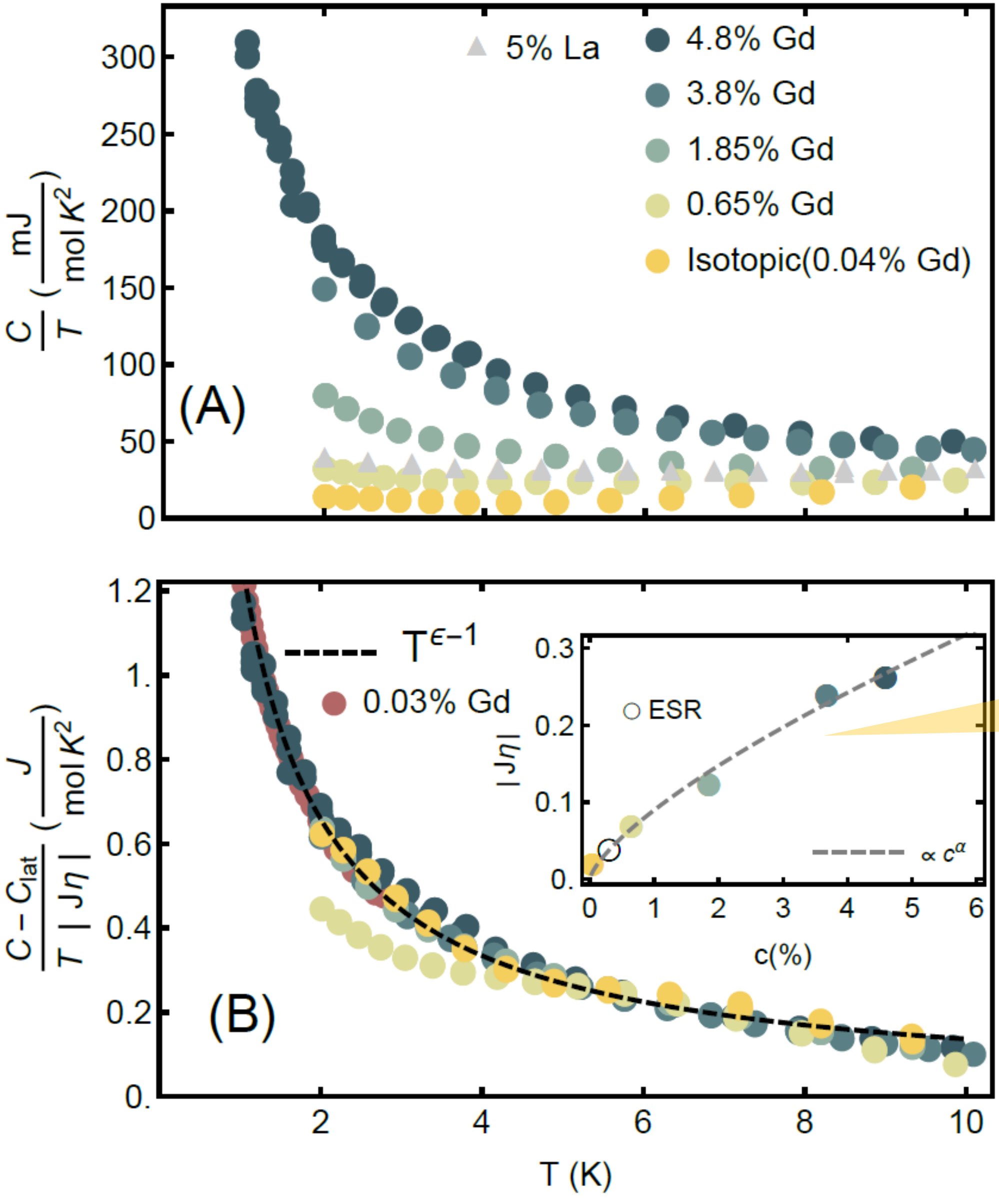


$M(Gd^{3+}) = 7.94\mu_B$

$M_{imp} = 7.74\ \mu_B$, 0.04%Gd
$6.95\mu_B$, 1.85%Gd
$5.84\mu_B$, 4.80%Gd

Kondo screening?!

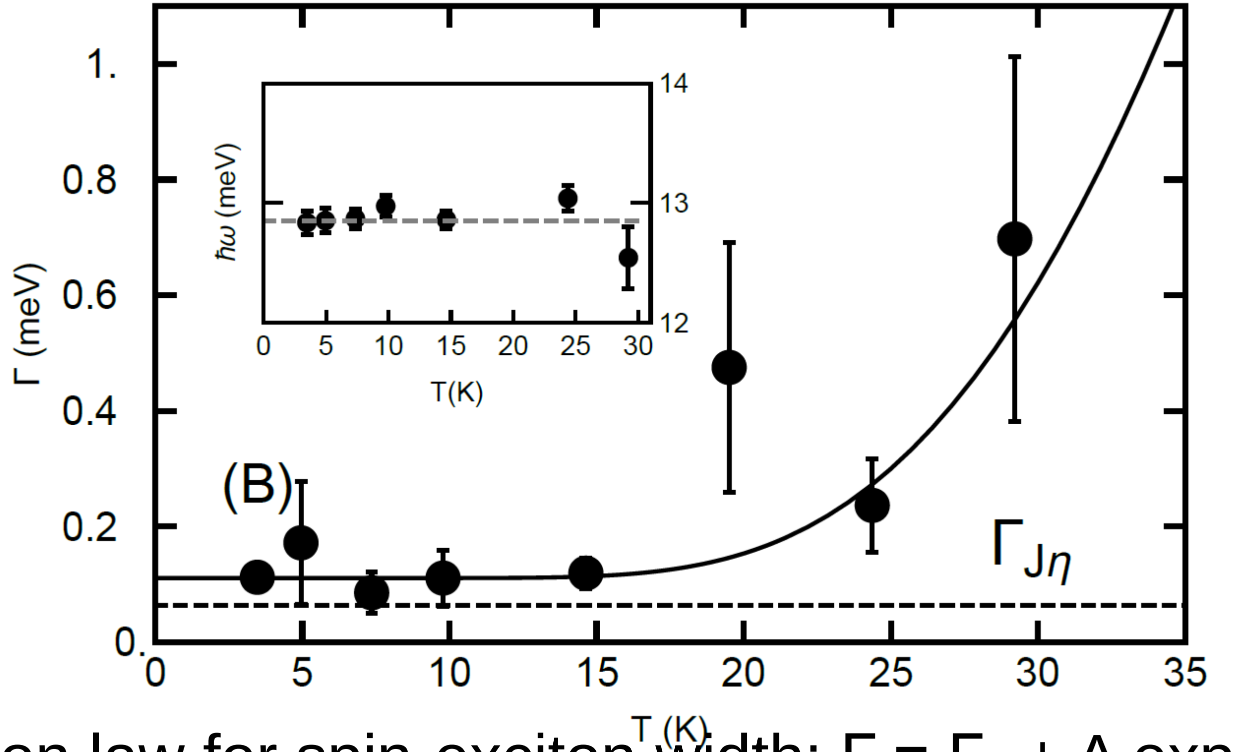
Influence of the Gd impurity on the electronic heat capacity of SmB_6



Jη defined from M_{effGd}(c)

Enhancement of the electronic DOS!?

Relaxation width of resonance mode as function of temperature in SmB6



TRISP data : Experimental resolution ~ 10 μeV

Activation law for spin-exciton width: $\Gamma = \Gamma_0 + A\exp(-\Delta/k_BT)$

A~0.7 eV – band width **Jη** = **-** 0.023

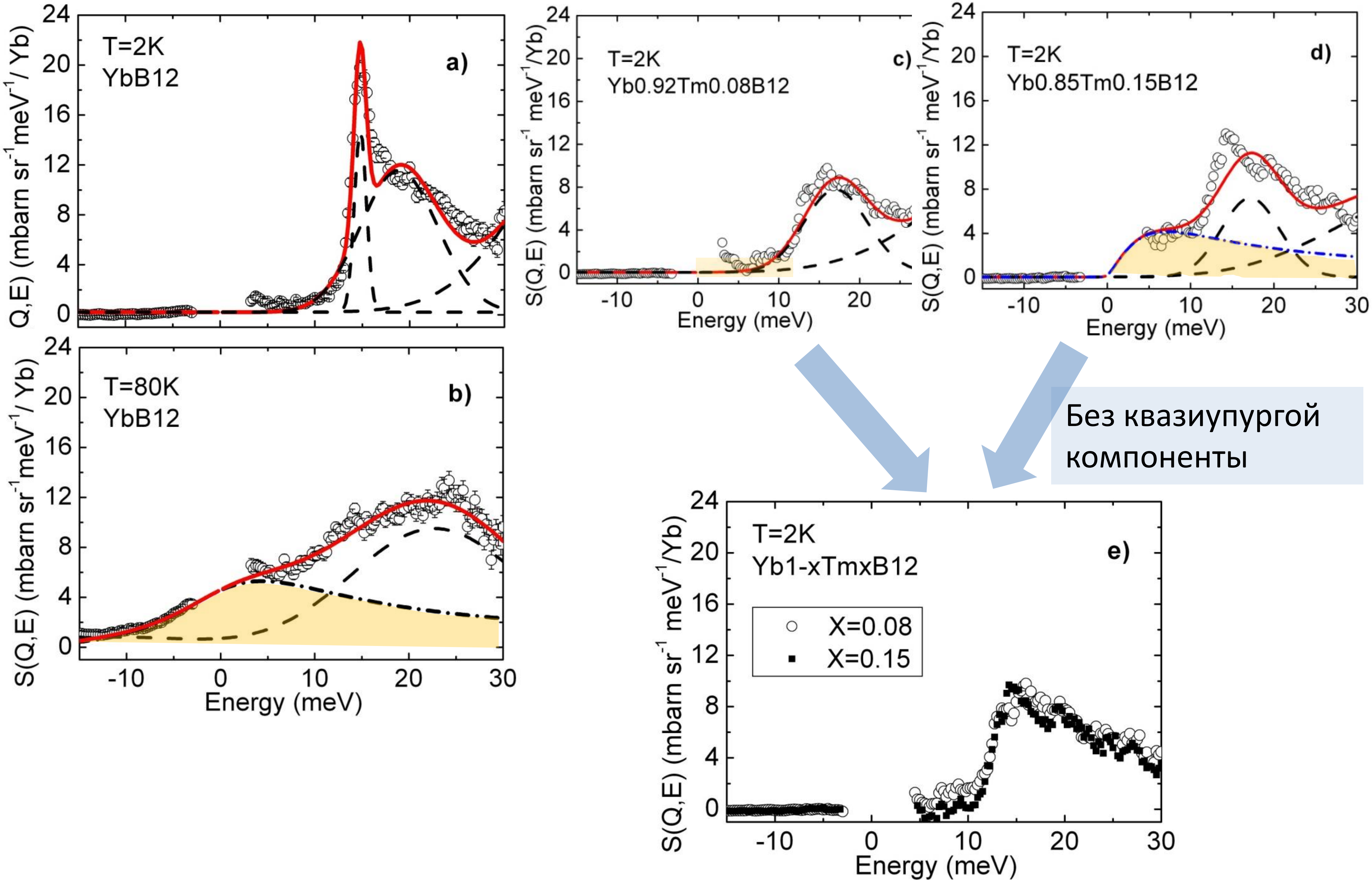
Ω ~Δ =14 meV – mode energy or spin-gap

$\Gamma_0 = \Gamma_{J\eta} = 4\pi(\mathbf{J\eta})^2\,\mathbf{\Omega}$ ~ 0.1meV for Gd: 0.04% ("isotopic pure sample")

Intrinsic width Γ_0 dramatically depends from **Jη** which characterizes impurity effect on the electronic system: just few % of Gd will increase relaxation ~10^2 times

Allow to explain the suppression of RM in *YbB*$_{12}$ by *Tm* - impurity?!

Подавление резонансной моды и переход в режим «квазищели» по мере роста концентрации магнитных ионов Tm



Без квазиупругой компоненты

Spin fluctuations and magnetism in systems with valence instability

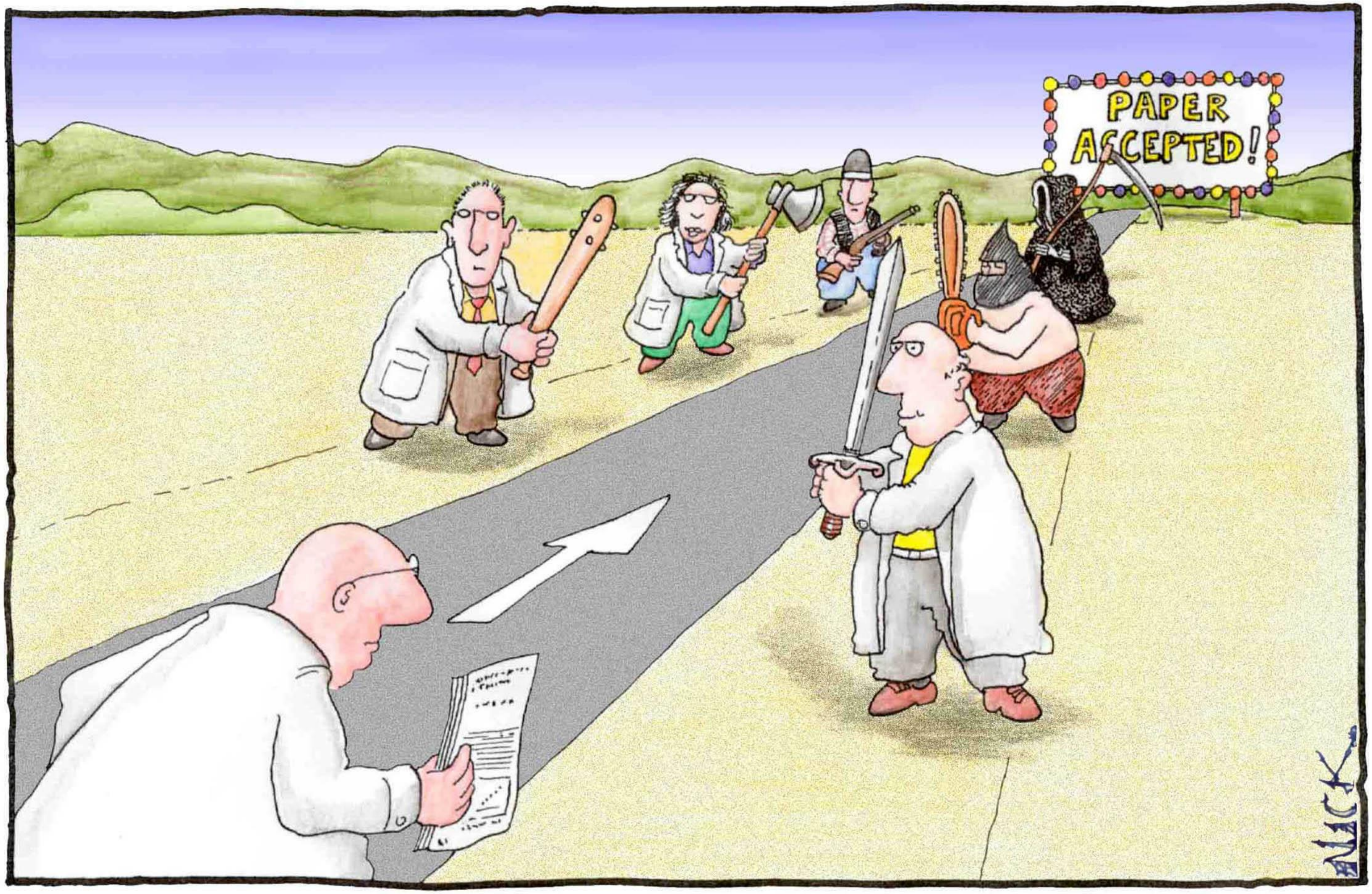
Conclusion

Exotic magnetic behaviour appears as a consequence of the coexistence and competition of different *f*-electron interactions in solids

Neutron spectroscopy – very effective instrument for clarifying the principal features of the exotic magnetic behaviour – that is the way to understanding exotic phenomena….

Благодарю за внимание

Удачи на «Большой дороге» науки!



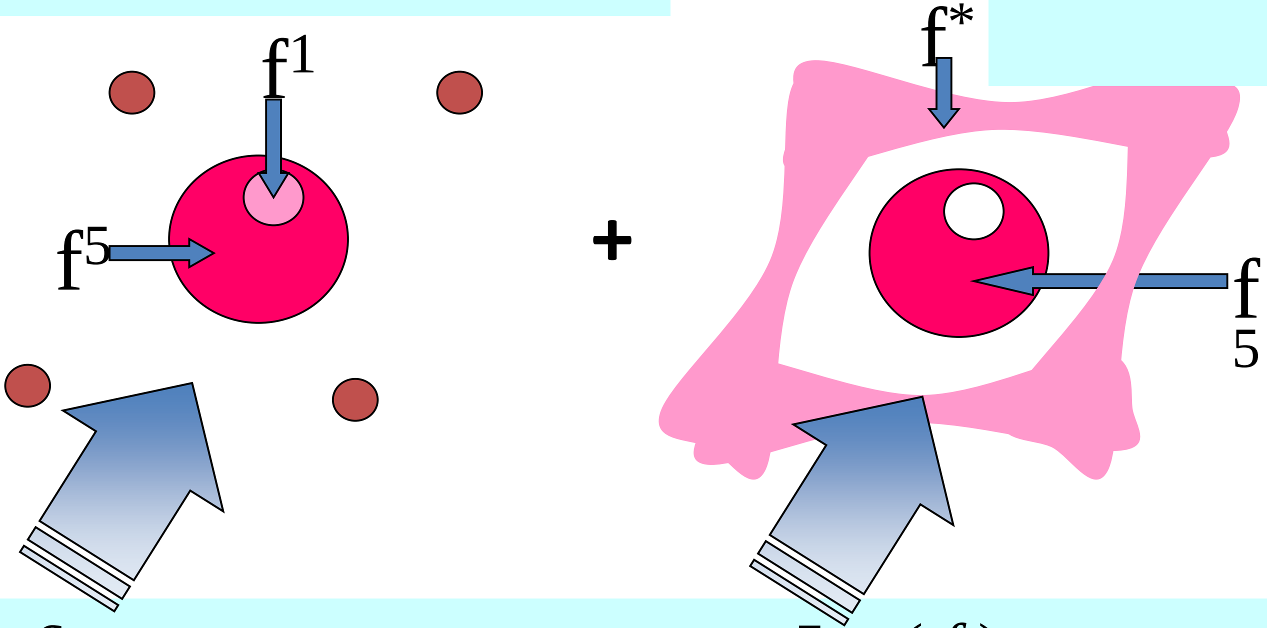
Most scientists regarded the new streamlined peer-review process as ‘quite an improvement.’

RM – low energy symmetry analogue for intermultiplet transition J0→J1 of Sm(2+) or Eu(3+) configuration

Variation of Sm-valence results in the variations of energy and Q-dependence of intensity for RM. Similar effects for Eu valence variation. Such behaviour may be understood on the base of model, which relates the delocalization extent of f-electron and RM energy with Sm-valence value (“excitonic model” of Michshenko & Kikoin)

Total localization of f-electron

Loosely bound state of f-electron and “hole”



$$\alpha \,|\, f^{6} >_{J=0} +(1-\alpha) \,|\, f^{5} B^{(f)} >_{J=0} = \Psi^{g}_{J^*=0}$$

K.W.H. Stevens, J.Phys.C 11 (1978), *K.A. Kikoin,* J.Phys.C 17 (1984)

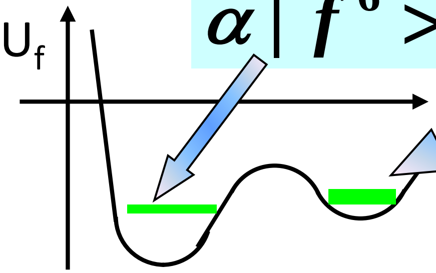
homogeneous MV ground state of "excitonic model"

Loosely bound electron

Sm: $|f^6, {}^7F_0> \longrightarrow |f^6_{J=0}> + |f^5_{J=5/2} \cdot f^*_{j=5/2}> = |\tilde{f}^6, {}^7F_0>$

Transtion to MV state

$$\alpha|f^6>_{J=0} + (1-\alpha)|f^5 B^{(f)}>_{J=0} = \Psi^g_{J^*=0}$$



New ground state wave function

With two types of excitations from singlet ground state:

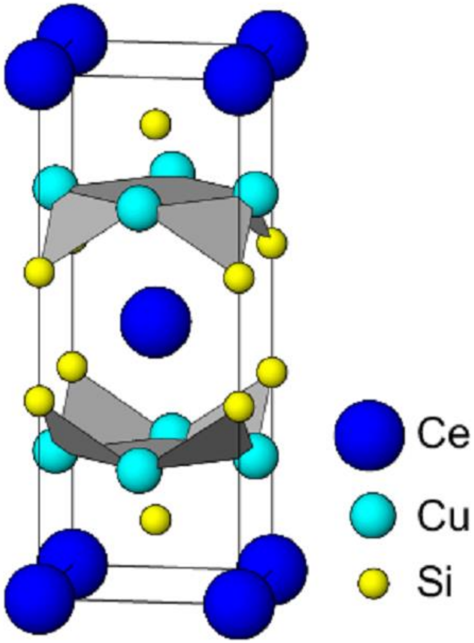
Charge transfer type → **Phonon anomalies: resonance el-ph interaction**

Spin reorientation type → **"resonant" magnetic mode**

2.1 $EuCu_2(Si,Ge)_2$ –IV and LRMO: competition and coexistence

Системы $ReTm_2X_2$ («1-2-2»)

Re = Ba,…Nd, Sm, Eu, Gd…; Tm = Cu, Fe, Ni, Co…; X = P. As. Se. Si. Ge…



Wide class of isostructural compounds, including Cu-free intermetallic superconductors (T_c~30…50K)

Physical properties: moderately anizotropic metals, for *Re = Eu* the combinations are possible:

Long range magnetic order (LRMO)

Superconductivity (T_C~T_N) (SC)

Intermediate valence (IV)

$EuNi_2(Si_{1-x}Ge_x)_2$ LRMO/IV; $EuFe_2(As,P)_2$, $EuFe_2As_2$ LRMO/SC/IV

$EuCu_2(Si,Ge)_2$ – distinguished from others Eu-based systems by the existence of the area of ***heavy fermion*** behaviour between ***LRMO*** and ***IV*** states on phase diagram

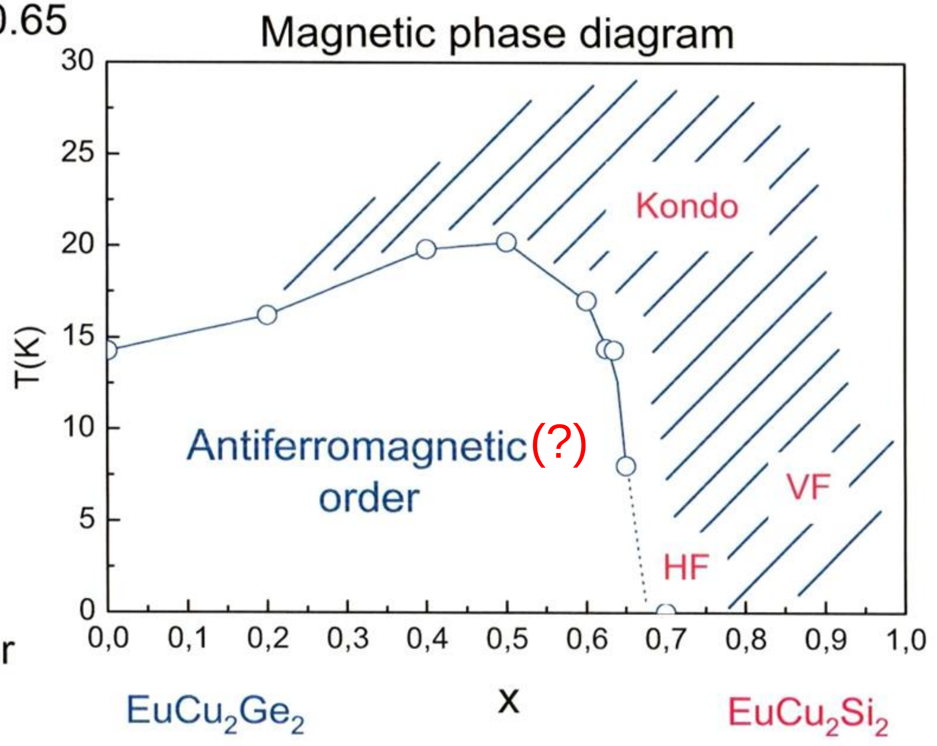
$EuCu_2(Si_xGe_{1-x})_2$ phase diagram (from thermodynamics, transport and X-ray spectroscopy)

*(Z. Hossain et.al. PRB **69** (2004) 014422)*

- Sharp AF-transition until x = 0.65
  - homogeneous AF state
  - no inhomogeneity effect
- Heavy fermion behavior for x ≥ 0.65 *($C(T)$,$\chi(T)$)*
  - Fermi liquid

→ First observation of ***)** heavy fermion behavior in an Eu-compound

- Pronounced Kondo-behavior in resistivity and thermopower for 0.5 < x < 0.9
- Valence fluctuations present even in antiferromagnetic region



(XPS-data)

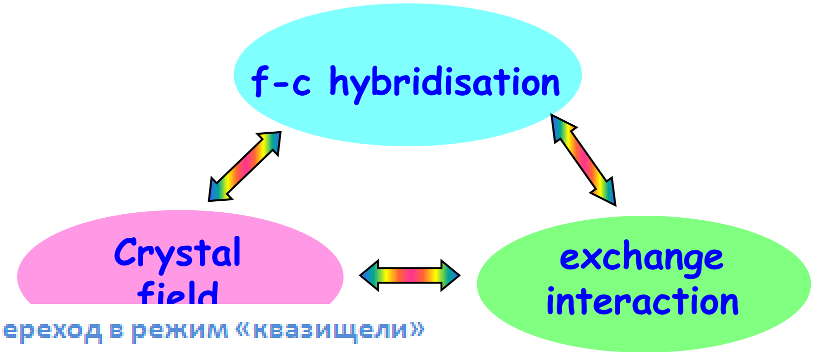
Neutron scattering and complementary spectroscopy studies **)

---

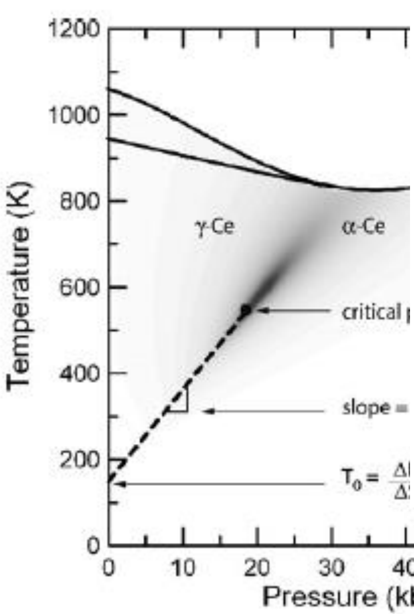
*) The first indication of Kondo behaviour for x >0.7 is in *E.M. Levin, B.S. Kuzhel, O.I. Bodak, e.a. Phys. Stat. Solidi B **161**, 783 (1990)*

**) *K. S. Nemkovski, D. P. Kozlenko, P. A. Alekseev, J.-M. Mignot, e.a., Phys. Rev. B 94 195101 (2016)*

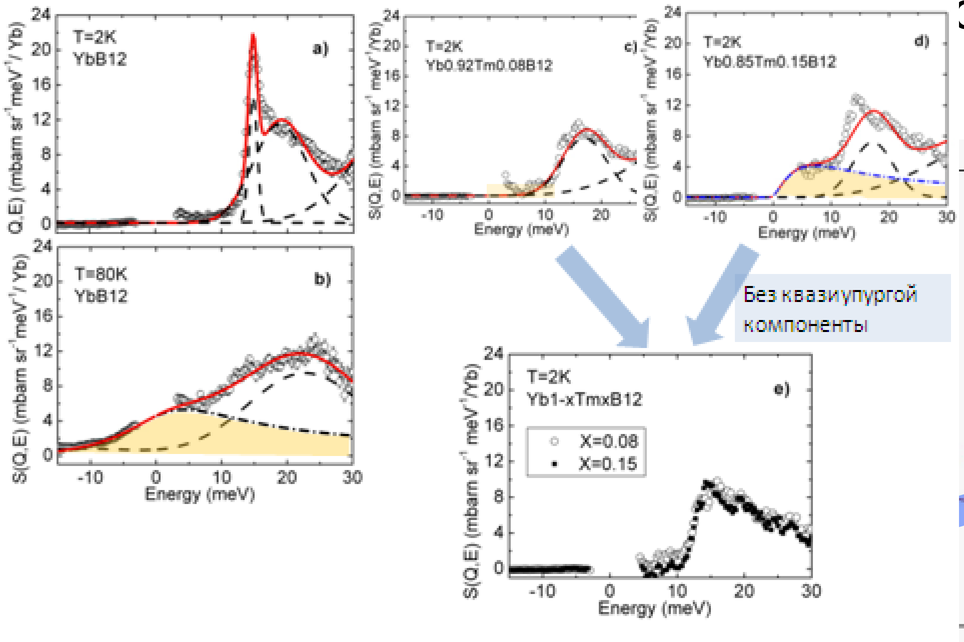
Источник многообразия свойств СКЭС – три взаимодействия.

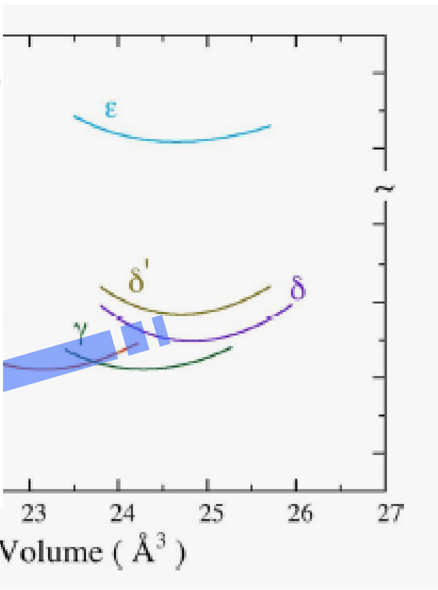


Гибридизация – … ости.



Подавление резонансной моды и переход в режим «квазищели» по мере роста концентрации магнитных ионов Tm





Ce γ - α переход, (Bridgman, 1931*))

ΔV/V~15%

Pu: δ - α, P ~2кбар **)

ΔV/V~25%

---

*)P.W. Bridgman, The Physics of High Pressures, G. Bell and Sons, Ltd., London, 1931, p. 267.

**)"Challenges in Plutonium Science", ed. N.G. Cooper, Los Alamos Science, Number 26, 2000

2.2. Novel insight into Kondo-insulators : the 1-2-10 family

Specific features:

-Magnetic ordering in Ce-based systems (Kondo-insulators) with charge (and spin) gap;

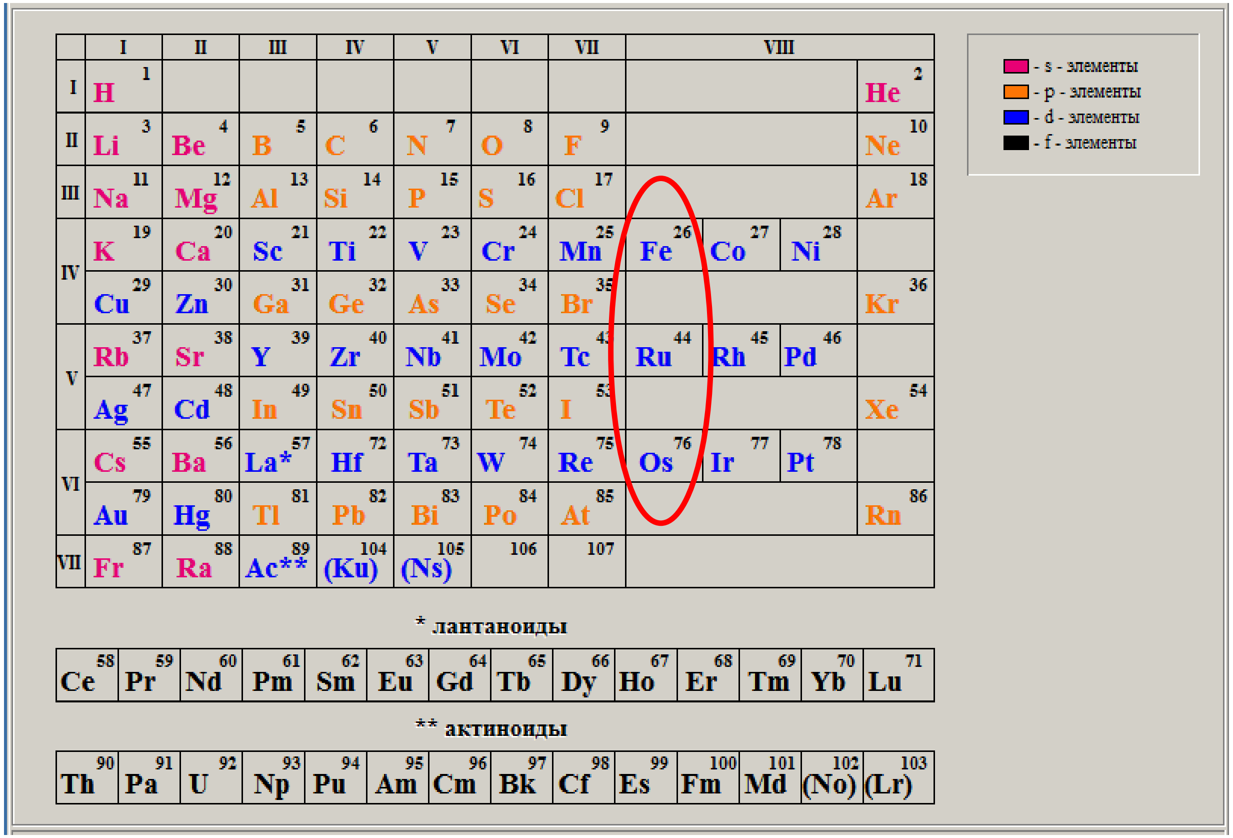
-Relatively *high* T_N for relatively *small magnetic moments*

"1 – 2 – 10 family"

$CeRu_2Al_{10}$ $CeOs_2Al_{10}$ $CeFe_2Al_{10}$

Ce^{3+}

Mixed-valence



	I	II	III	IV	V	VI	VII	VIII
I	H 1							He 2
II	Li 3	Be 4	B 5	C 6	N 7	O 8	F 9	Ne 10
III	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17	Ar 18
IV	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26 Co 27 Ni 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35	Kr 36
V	Rb 37	Sr 38	Y 39	Zr 40	Nb 41	Mo 42	Tc 43	Ru 44 Rh 45 Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53	Xe 54
VI	Cs 55	Ba 56	La* 57	Hf 72	Ta 73	W 74	Re 75	Os 76 Ir 77 Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	At 85	Rn 86
VII	Fr 87	Ra 88	Ac** 89	(Ku) 104	(Ns) 105	106	107	

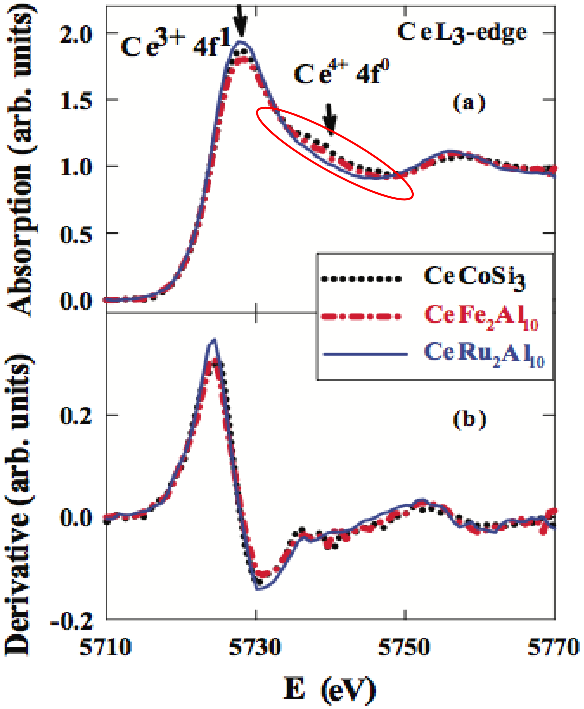
- 🟪 - s - элементы
- 🟧 - p - элементы
- 🟦 - d - элементы
- ⬛ - f - элементы

* лантаноиды

Ce 58	Pr 59	Nd 60	Pm 61	Sm 62	Eu 63	Gd 64	Tb 65	Dy 66	Ho 67	Er 68	Tm 69	Yb 70	Lu 71

** актиноиды

Th 90	Pa 91	U 92	Np 93	Pu 94	Am 95	Cm 96	Bk 97	Cf 98	Es 99	Fm 100	Md 101	(No) 102	(Lr) 103



Adroja, Phys Rev B **87**, 224415 (2013).

«Real» (generic) Kondo insulators

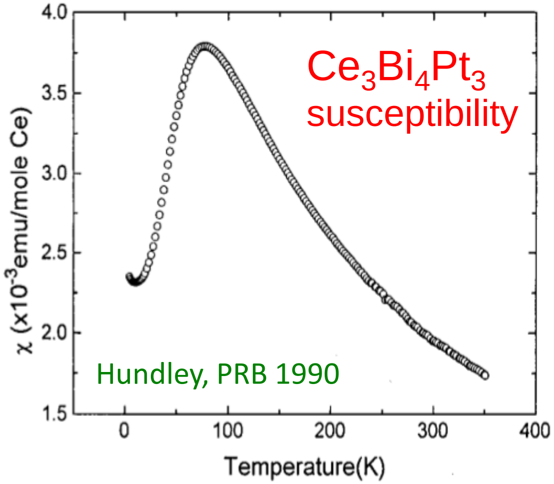
Generally ***nonmagnetic* ground state**

SmB_6, (Sm,Y)S, YbB_{12}

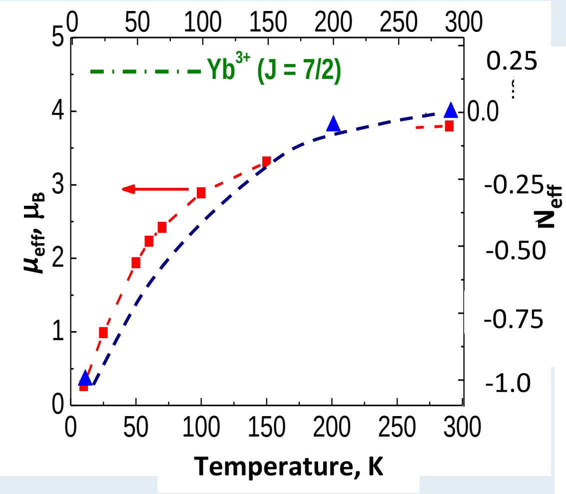
CeNiSn, CeRhSb, $Ce_3Bi_4Pt_3$

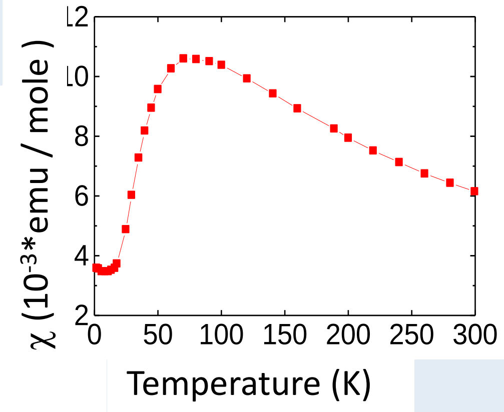
CeT_4Sb_{12}, UFe_4P_{12}, U_2Ru_2Sn …

FeSi (?)

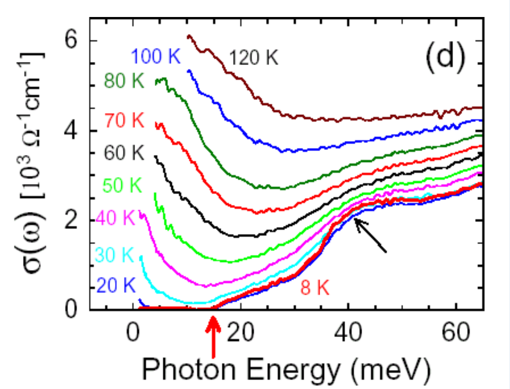


YbB_{12}



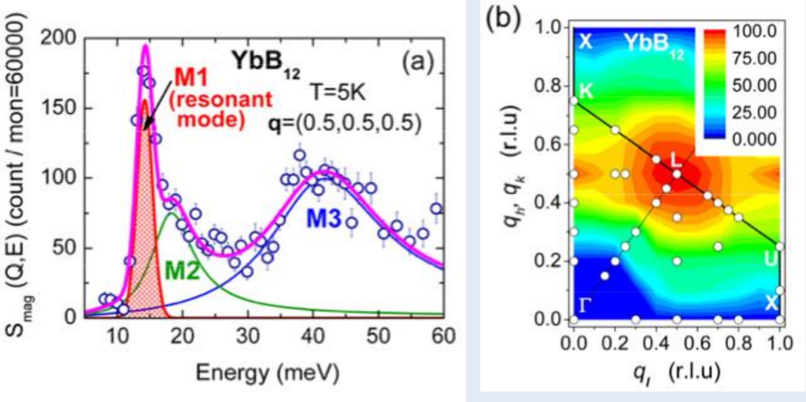


Connection of spin and charge gaps ?!



Dynamical AFM correlations →
Resonance ("exciton") mode

P. Riseborough, JMMM (2001)

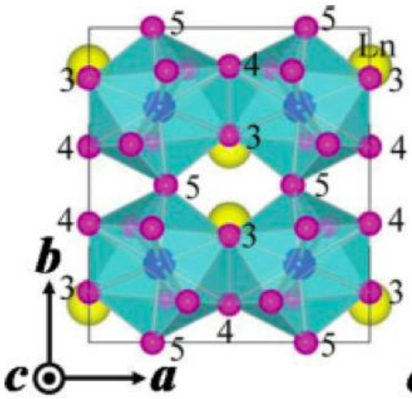


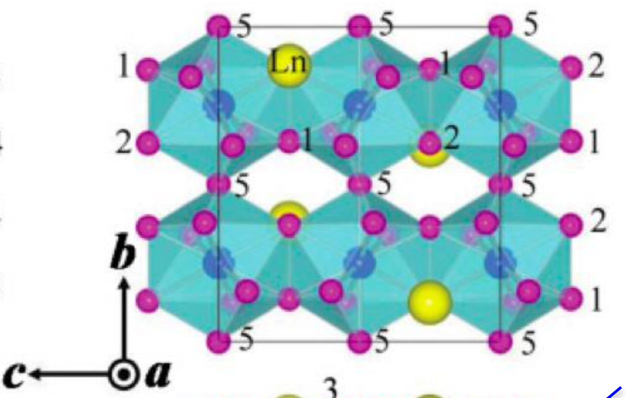
K.S. Nemkovski *et al.*, Physics Procedia **42**, 18 (2013).

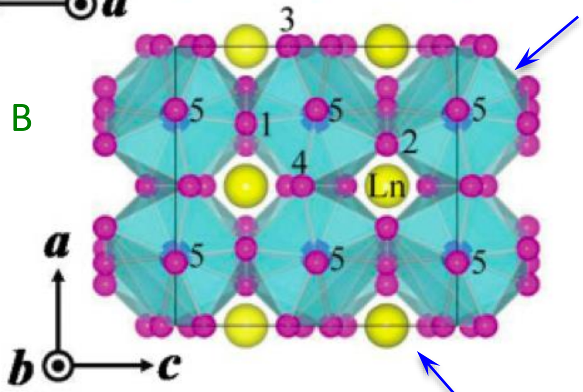
Ln$M_2$$Al_{10}$ crystal structure

***Ln*$M_2$$Al_{10}$** ($M$ = Fe, Ru, Rh, Os,)
Orthorhombic,*Cmcm*

Thiede *et al.* (1998), Muro *et al.* (2009), Nishioka *et al.* (2009)



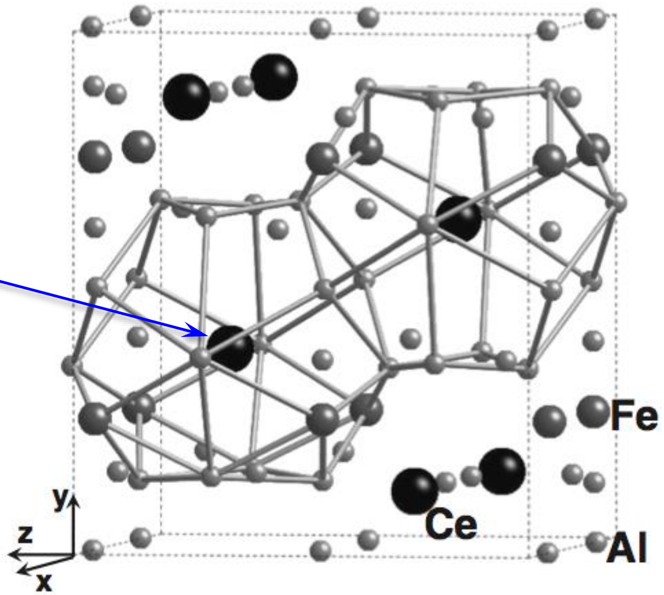




Ru-Al_{10} polyhedra
forming layer in (a,c) plane

H. Tanida et al., Phys Rev B **84,** 115128 (2011).

Ln atoms
in Fe-Al "cage"



$CeFe_2Al_{10}$

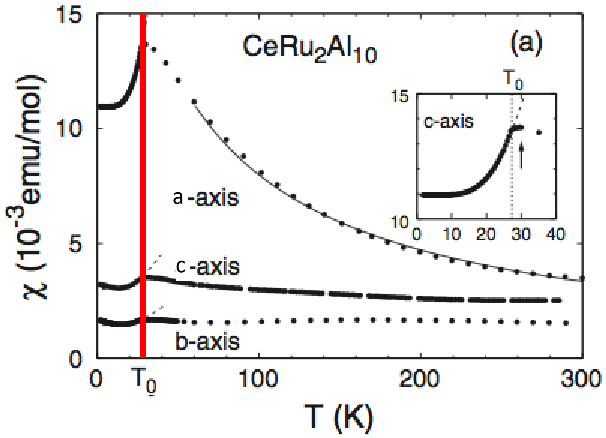
a= 9.016 $Å^{-1}$
b= 10.24 $Å^{-1}$
c= 9.088 $Å^{-1}$

$d_{Ce\text{-}Ce} \approx 5.2$ Å

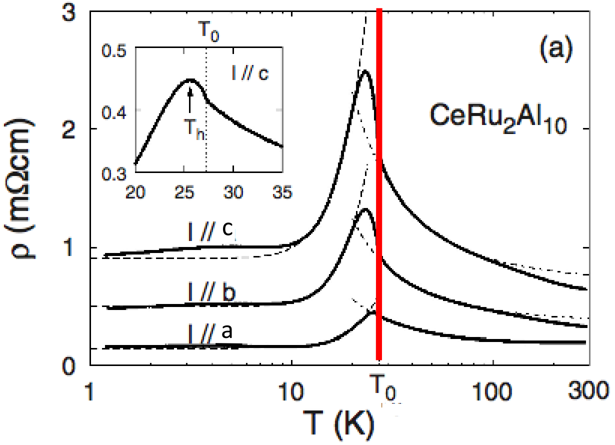
Y. Muro et al., J Phys Soc Jpn **78**, 083707 (2009).

CeRu$_2$Al$_{10}$ - KI + low-T phase transition

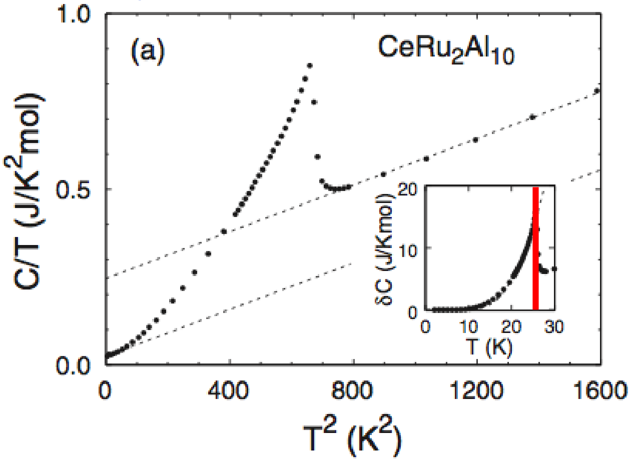
Magnetic susceptibility



Electrical resistivity



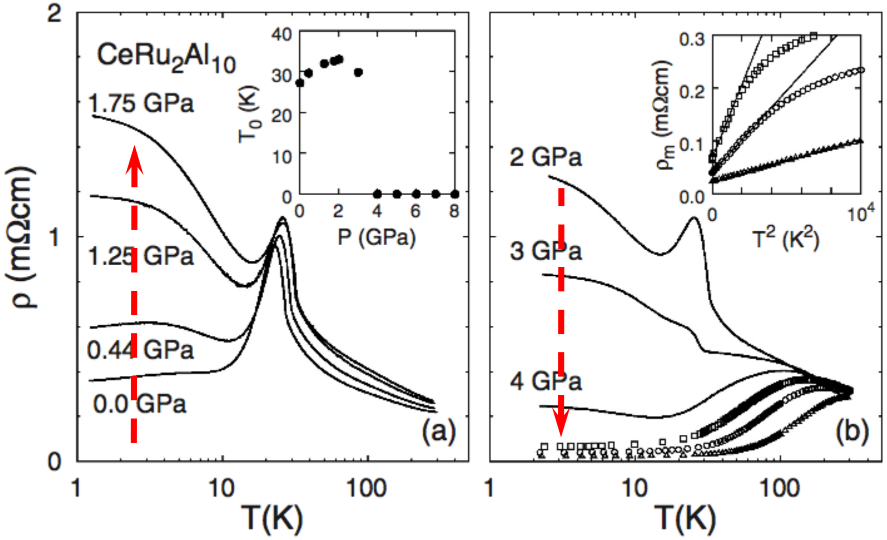
Specific heat



Phase transition at T_0 = 27 K

Strydom, Physica B (2009); Nishioka *et al.*, JPhys Soc Jpn(2009)

High pressure **Kondo insulator → metal**



- Stronger anisotropy (a = easy axis)

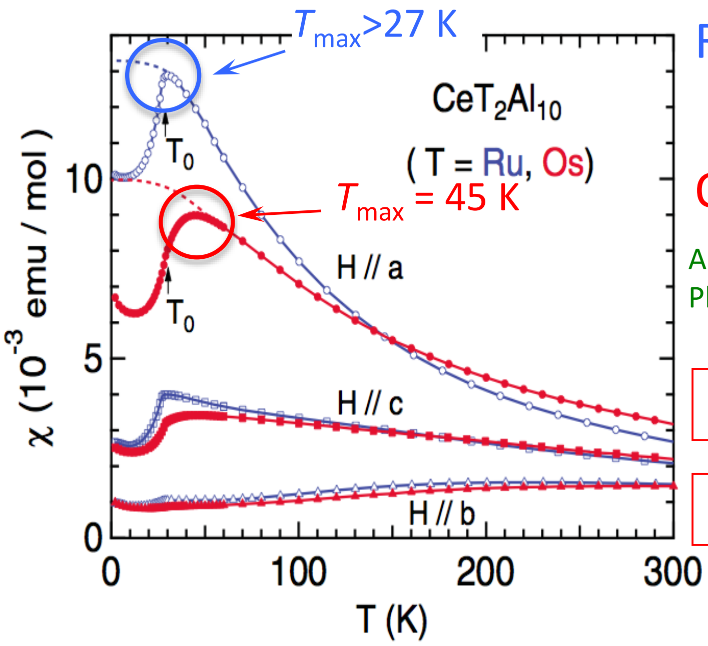
•$\rho(T)$: negative slope, activation law

Ordered phase $T<T_0$

•*Exponential* dependences of χ and C_P :
(Δ ~ 100 K) partial gap opening at the Fermi surface

- Under P : insulating state first enhanced, then suppressed above 2 GPa.

Magnetic order is unconventional



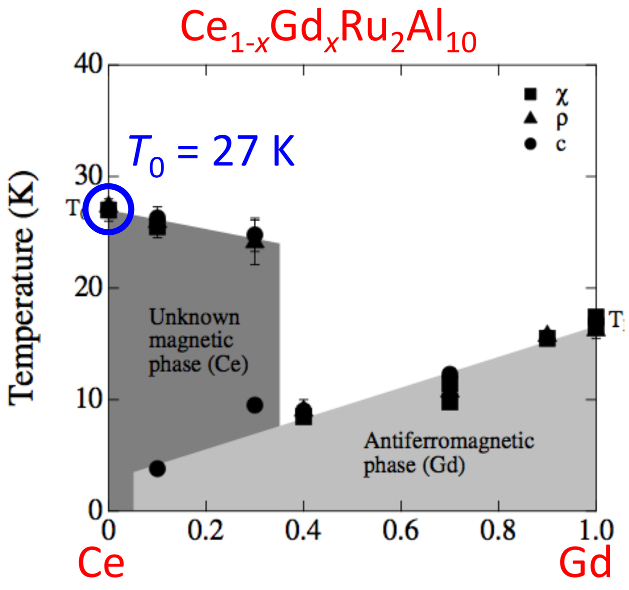
Ru

Os

A. Kondo *et al.*,
Phys Rev B **83**, 180415 (2011).

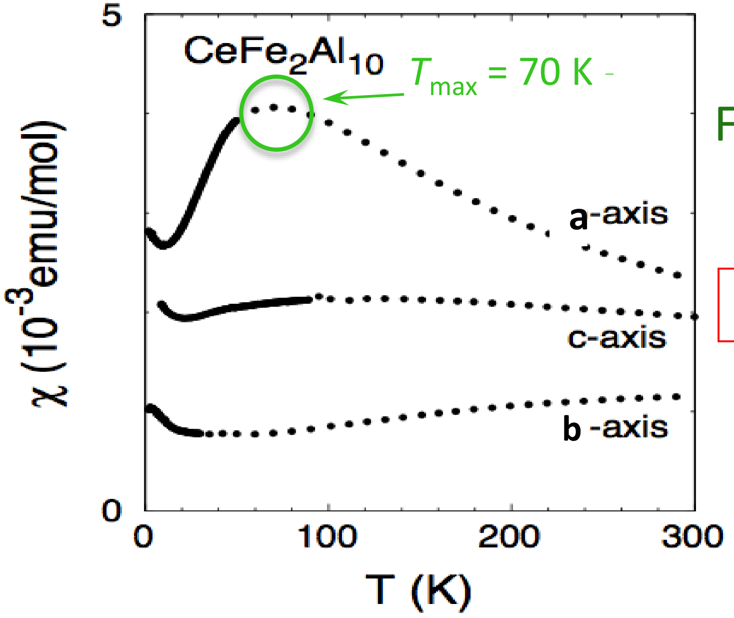
CeRu$_2$Al$_{10}$ - $T_0 \approx 27$ K

CeOs$_2$Al$_{10}$ - $T_0 \approx 29$ K



- Pathologically high ordering temperature, despite large Ce-Ce distances, $d_{Ce\text{-}Ce}$> 5 Å

R. Kobayashi *et al.*,
J Phys Soc Jpn Suppl **80SA**, SA044 (2011).



Fe

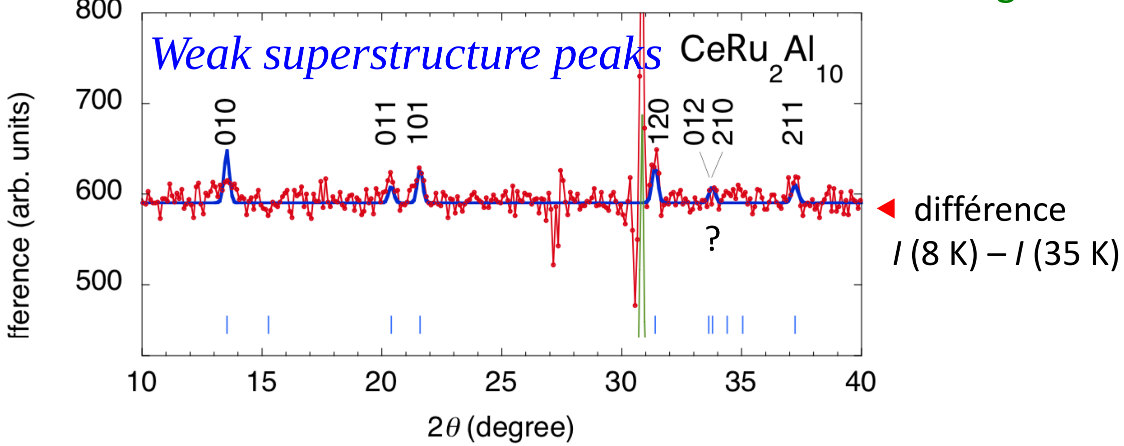
CeFe$_2$Al$_{10}$ – *no magnetic order*

T. Takesaka *et al.*,
J. Phys: Conf Ser **200**, 012201 (2010).

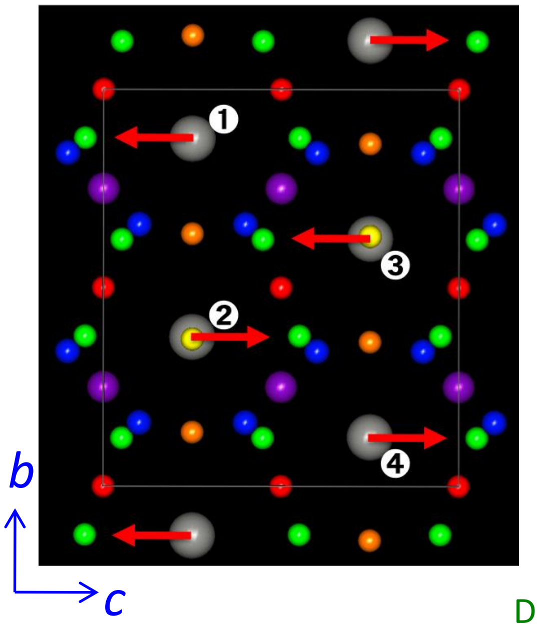
Antiferromagnetic order from neutron diffraction

- J. Robert *et al*, Phys Rev B **82**, 100404(R) (2010).
- J.-M. Mignot *et al.*, J Phys Soc Jpn Suppl **80SA**, 022 (2011)

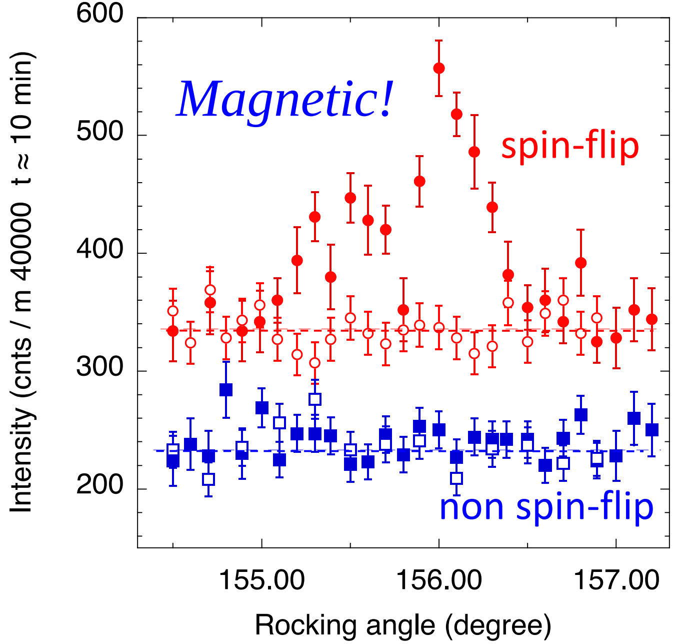
Neutron powder diffraction



Single-crystal diffraction



S.-crystal <u>polarized</u> neutron diffraction $P_0 \parallel Q = (3, 0, 1)$



AFM order

wavevector *k* = (1,0,0)

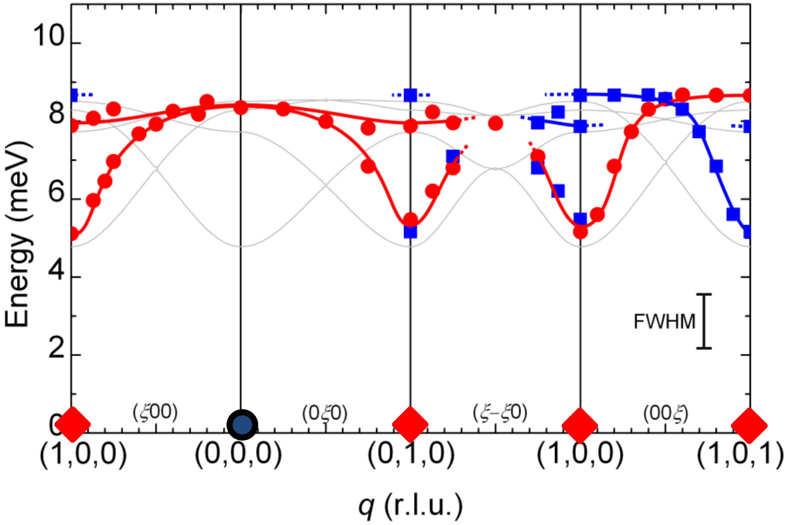
$m_{AF} = 0.34\ \mu_B$

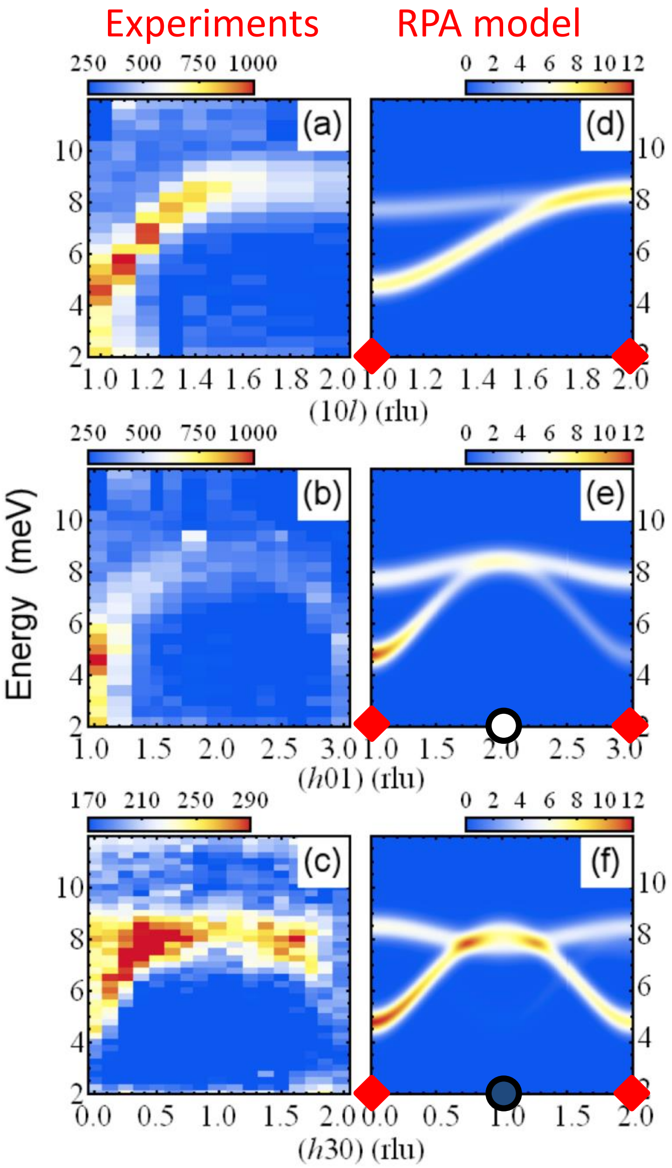
Ce moments $m_{AF} \parallel c$

D.D. Khalyavin et al. (2010); H. Kato et al. (2011) .

Anisotropic magnon picture for $CeRu_2Al_{10}$

J. Robert *et al.*, Phys. Rev. Lett. **109**, 267208 (2012).





RPA calculation *(code: Sylvain Petit)*

Crystal field parameters Strigari, PRB (2012)

$$(B_2^0, B_2^2, B_4^0, B_4^2, B_4^4) = (-1.326, -29.236, +1.013, -1.747, -5.317)\ \mathrm{K}$$

Anisotropic exchange $\mathcal{H}_{i,j} = \sum_\alpha \mathcal{J}^\alpha S_i^\alpha S_j^\alpha$

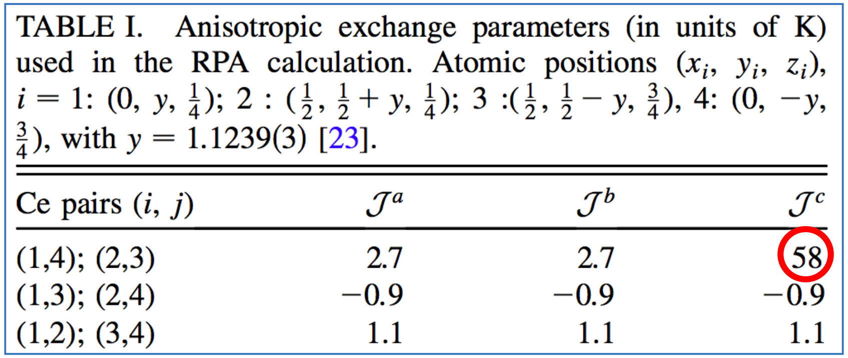


TABLE I. Anisotropic exchange parameters (in units of K) used in the RPA calculation. Atomic positions (x_i, y_i, z_i), $i = 1$: $(0, y, \frac{1}{4})$; 2 : $(\frac{1}{2}, \frac{1}{2} + y, \frac{1}{4})$; 3 :$(\frac{1}{2}, \frac{1}{2} - y, \frac{3}{4})$, 4: $(0, -y, \frac{3}{4})$, with $y = 1.1239(3)$ [23].

Ce pairs (i, j)	$\mathcal{J}^a$	$\mathcal{J}^b$	$\mathcal{J}^c$
(1,4); (2,3)	2.7	2.7	58
(1,3); (2,4)	−0.9	−0.9	−0.9
(1,2); (3,4)	1.1	1.1	1.1

M.M. three times(!) higher than experimental

Direction-selective hybridization?

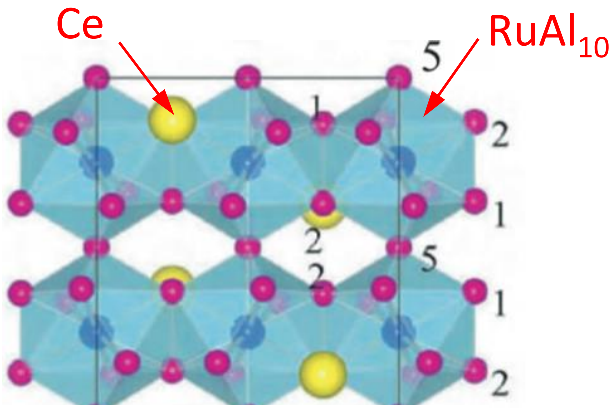
- “Simple” CF + anisotropic exchange model *not* sufficient.

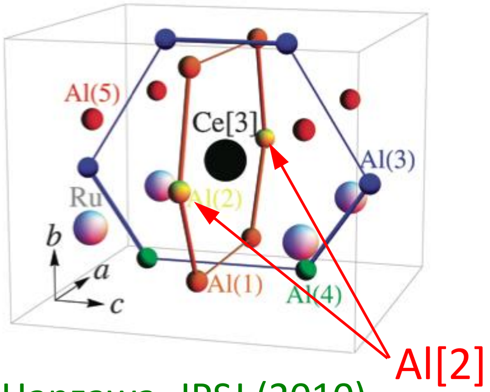
- Role of (anisotropic) “*c-f*” hybridization with Ce ligands ? Sera, JPSJ (2013):

- Structure: maximum deviation from lanthanide contraction occurs along ***a***, negligible along ***b***

- NMR:strong transferred hyperfine field (1158 Oe) at Al[2] site, located along ***a*** direction with respect to Ce site.

Suggestion: hybridization occurs primarily along the *a* direction (Ce–Al[2])





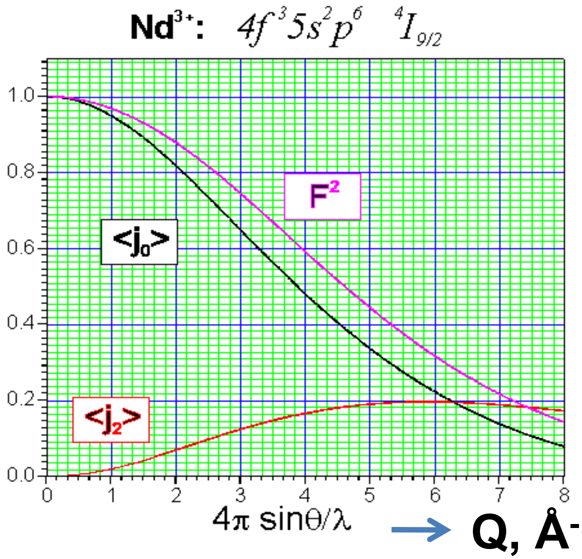
Hanzawa, JPSJ (2010)

Обычно справедливо дипольное приближение, когда

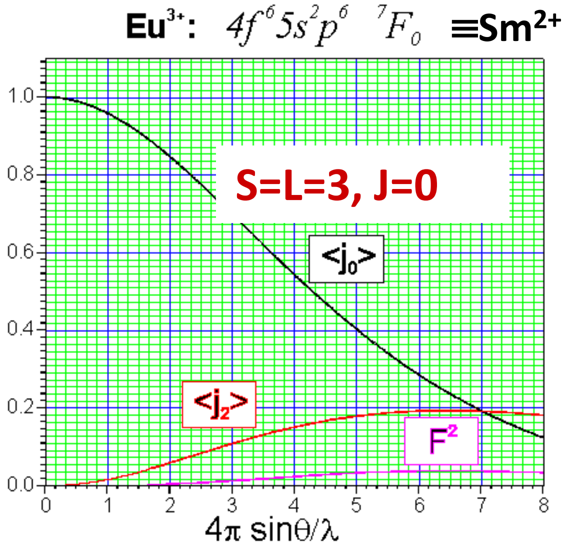
$$F(Q)=\langle j_0\rangle(Q)+[(2/g)-1]\,\langle j_2\rangle(Q)$$

спин+орбита

орбита

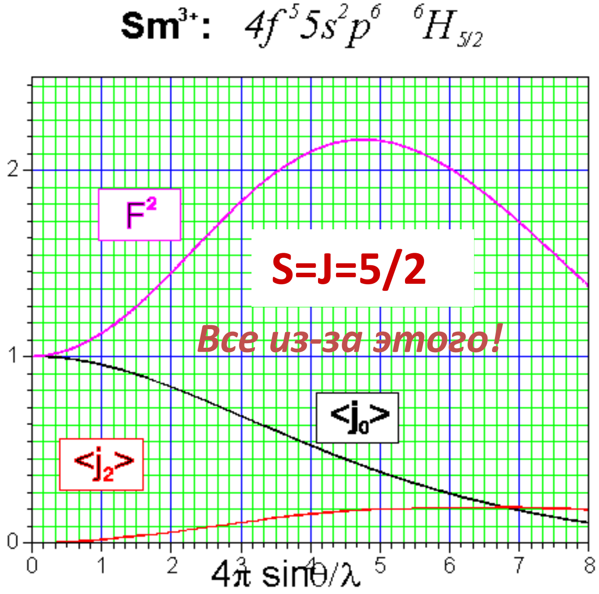


→ **Q, Å^{-1}**



Магнитный момент равен 0!

⟨j$_n$(Q)⟩ are integrals of the product of the spherical Bessel function of order ***n*** and the radial distribution of the electron density, derived from a Dirac-Fock relativistic calculation.



(2-g)/g=6!

Для ПВ-состояния Sm υ≅2.5

Возможно «смешивание» Sm^{2+} и Sm^{3+}состояний из-за «флуктуаций» типа:

Sm^{2+} ⟺ Sm^{3+} + e$^-$

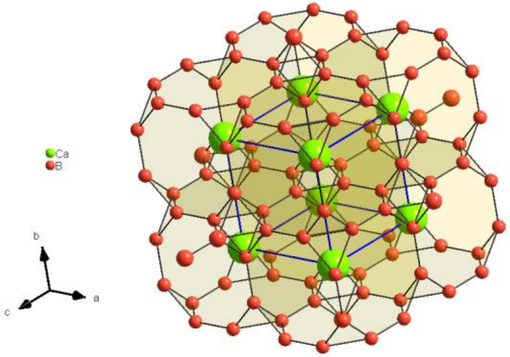
Combined form factor **?!**

Beginning of the story....late 80th

Composite crystal $^{154}Sm^{11}B_6$ V~0.8см^3

KIAE, IPMS, ILL, LLB

03.03.2006 12:21



BCC, a=4.13A

Short introduction:

What are Kondo-Insulators?

What are valence unstable (intermediate / mixed) valence systems?

What is an interest with that?!

What are Kondo-insulators?

“Valence fluctuations” are inherent to systems with unfilled and virtually unstable *f*- и *d*- electron shells .
Example – systems based on the f-elements from
the beginning, middle, and end of rare earth series.

Symbolic presentation $f^{\,n} \rightleftarrows f^{\,n-1} + e$ *From the early 80th…*

“Commonplace”: valence fluctuations (τ_{sf})– physical reason for the formation of the nonmagnetic ground state:

$(\tau_{sf})^{-1} > kT$ => supression of the m.m. on ↓T (like HF-, MV-systems…)

For selected nonmagnetic systems the formation of semiconducting state with gap ~100K is specific!

This is mixed valence semiconductor or “Kondo insulator”

Recently KI with magnetic oredering (LRMO) were discovered!

What are Kondo-insulators!

CeNiSn, $Ce_3Bi_4Pt_3$, $Ce_3Sb_4Pt_3$,CeRhSb,…
SmB_6, SmS(P>6 kbar)
YbB_{12} !

$U_3Sb_4Pt_3$, U_2Ru_2Sn,…

FeSi (?)

"High temperature" limit:
poor metal with local magnetic moment and Kondo-effect

"Low temperature" limit (ground state) :
semiconductor (gap ~100 K) with zero magnetic moment

The most of the Kondo-insulators have fractional occupation of the f-shell *(homogenous mixed valence (MV) state)*

The strong correlations are important both for the spin- and for charge- subsystems.

Specific properties originated from f-electrons and are essentially dynamical effect:
therefore the neutron spectroscopy – is a powerful tool!

What are Kondo-insulators?!

This kind of SCES usually are considered as one “family”...

Perhaps, such treatment is too much simplified?

Indeed!

Neutron spectroscopy (inelastic magnetic neutron scattering) results in discovery of the “resonant mode” phenomenon for mixed valence systems like “Kondo-insulators” and some others...

The most bright examples – MV semiconductors, like:

-SmB_6 и SmS (strong MV), and

-YbB_{12} (weak MV).

The physical result: There are established
two different in nature (but in both cases singlet !)
types of the ground state.

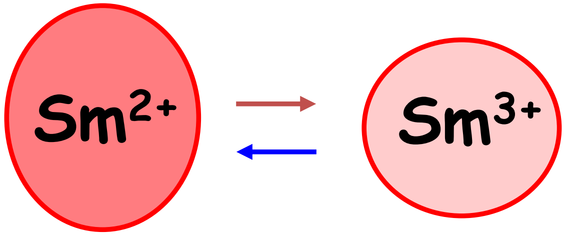
What was initially expected from neutron scattering experiments with MV systems?

Semiconductors with "strong" intermediate valence

Formal (average) valence is far from integer value

SmB_6, SmS "classical" examples

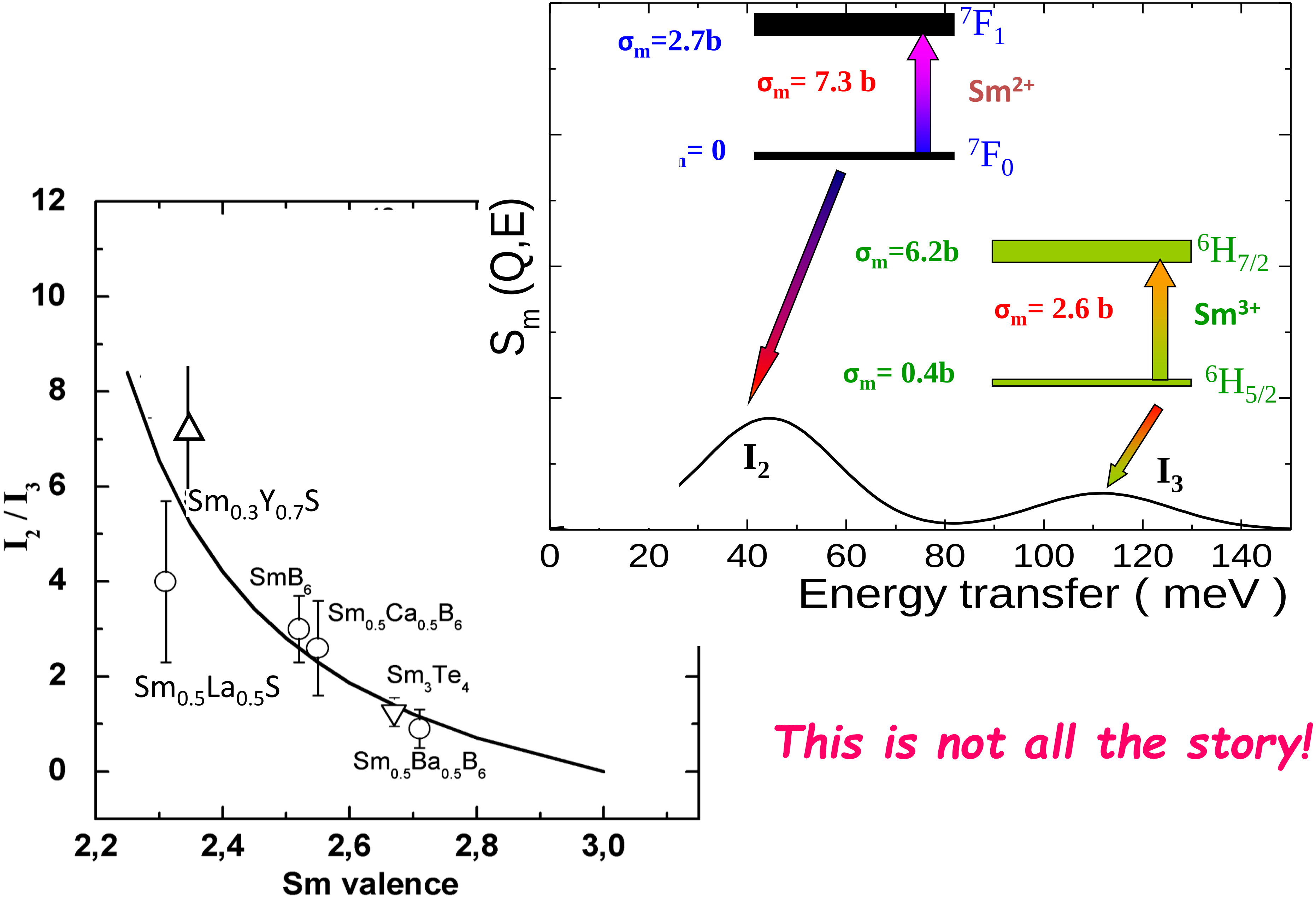
f^6 f^5 + electron in conduction band



What is the structure of the magnetic excitation spectra and its response on the variation of temperature and valence?
One could expect spin-orbit multiplet structure of f6 and f5 configurations to appear…at least!

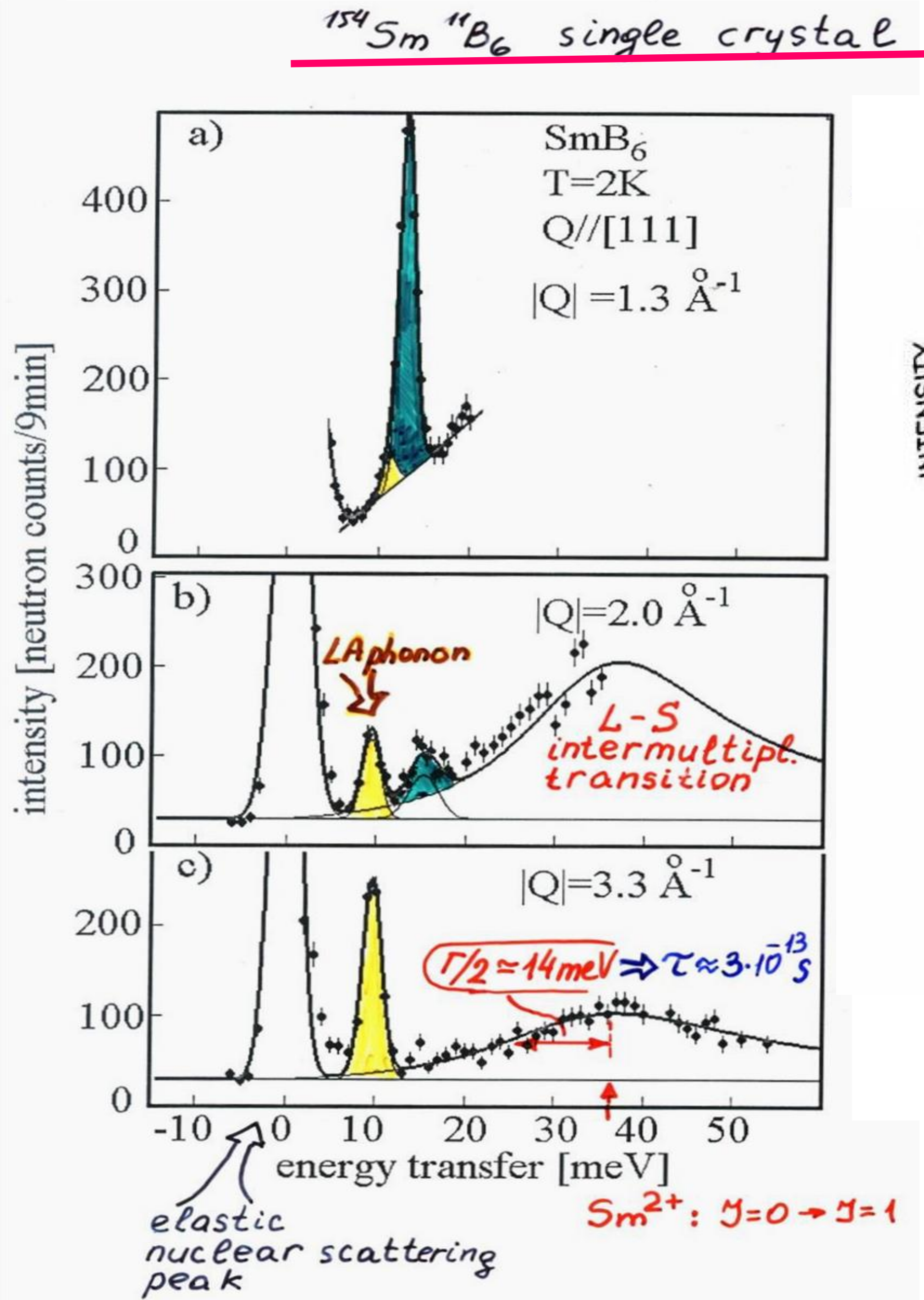
Important – NO CEF effects expected due to valence fluctuation!

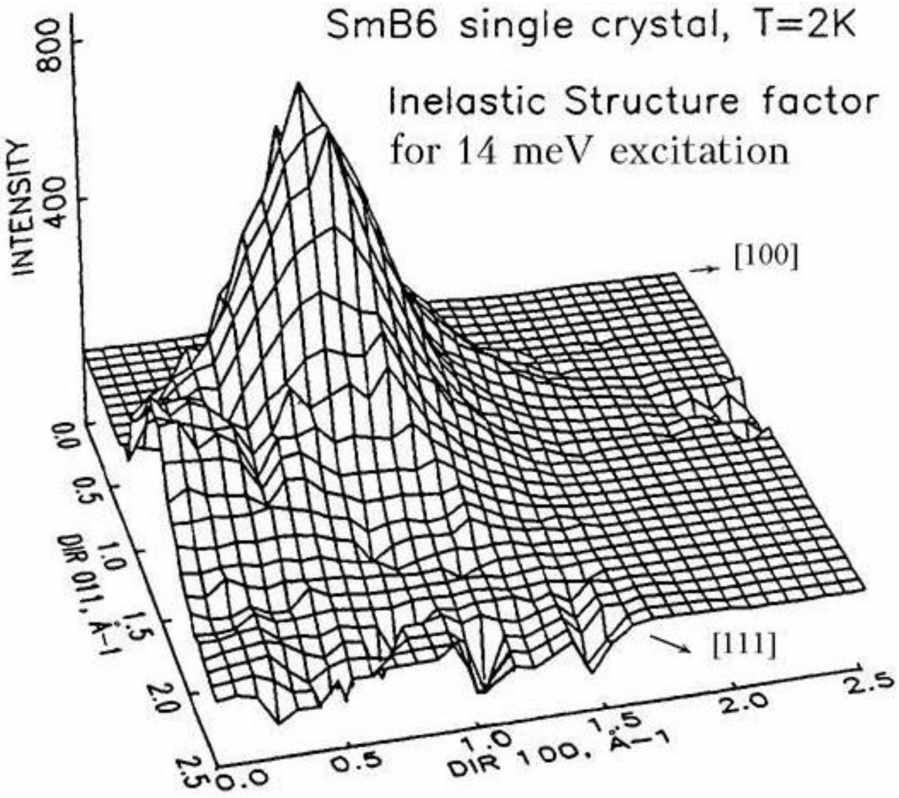
Intermultiplet (spin-orbit) excitations



This is not all the story!

Low energy (“resonant”) mode in SmB6

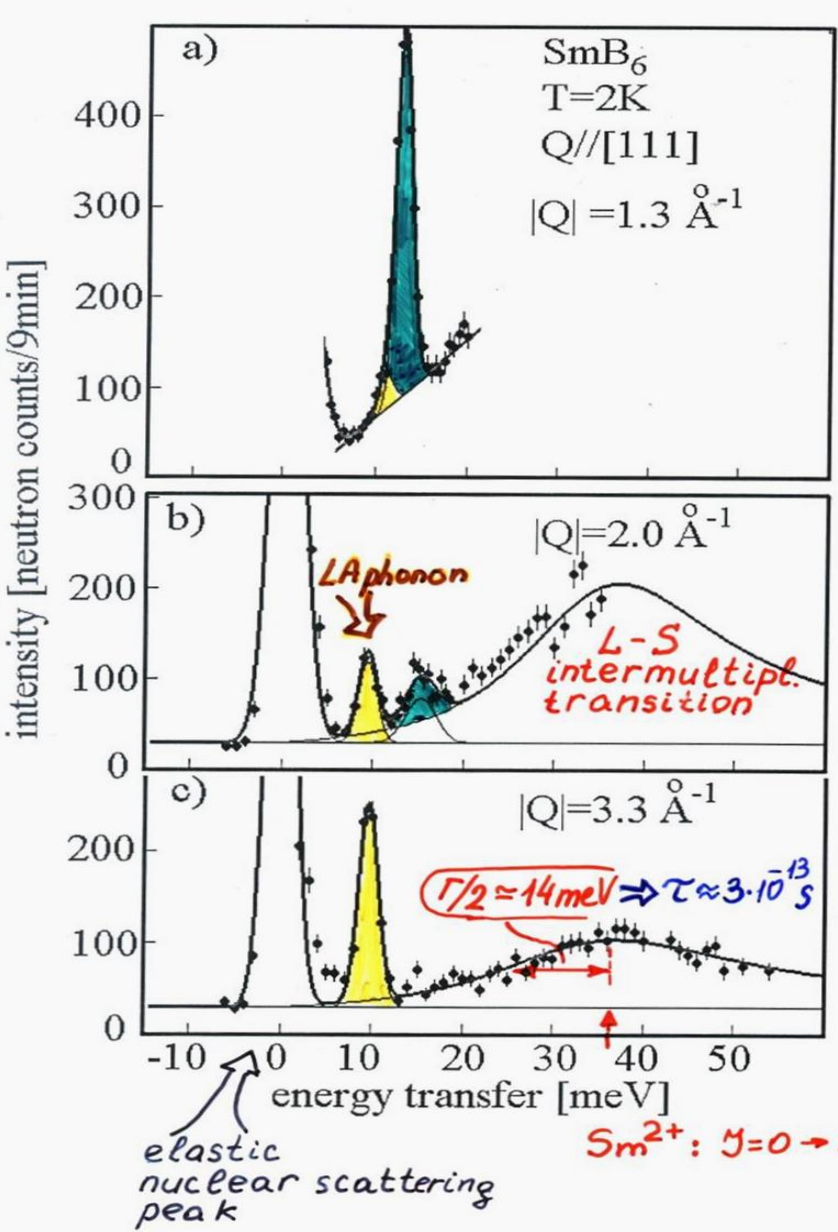




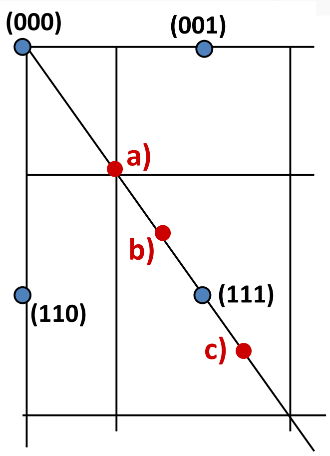
“Map” of inelastic scattering intensity

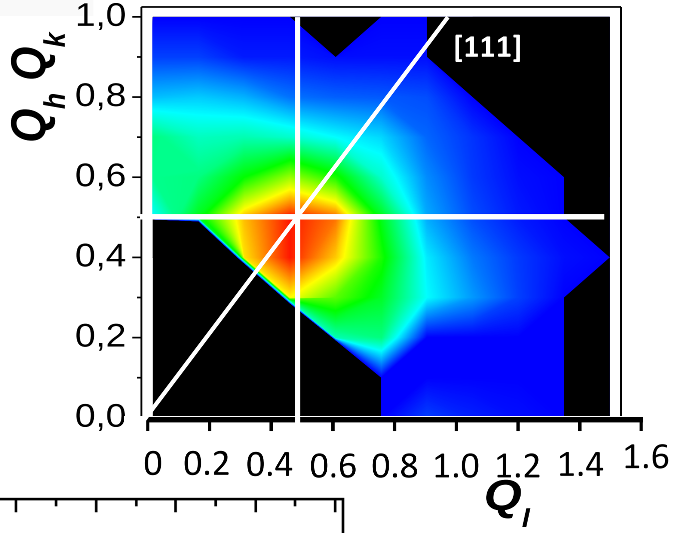
Low energy ("resonant") mode in SmB6

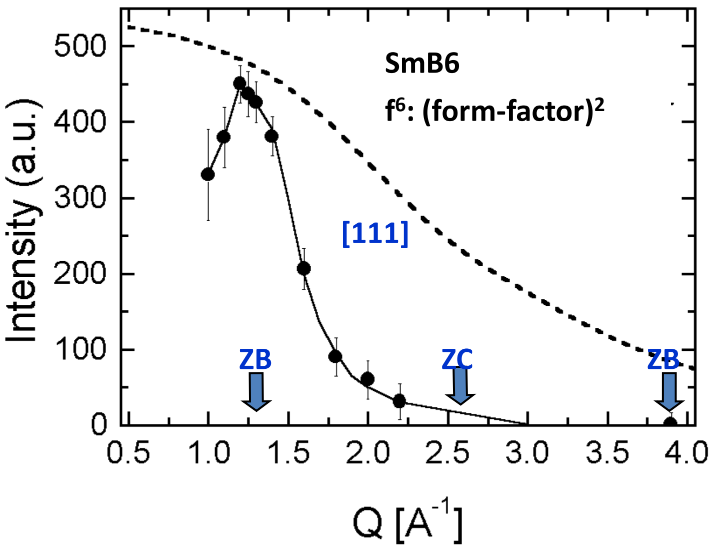
$^{154}Sm\,^{11}B_6$ single crystal

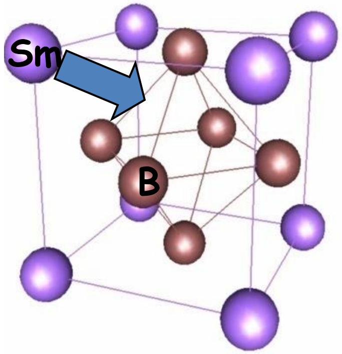


Sm^{2+}: J=0 → J=1









How it is related to the mixed valence?

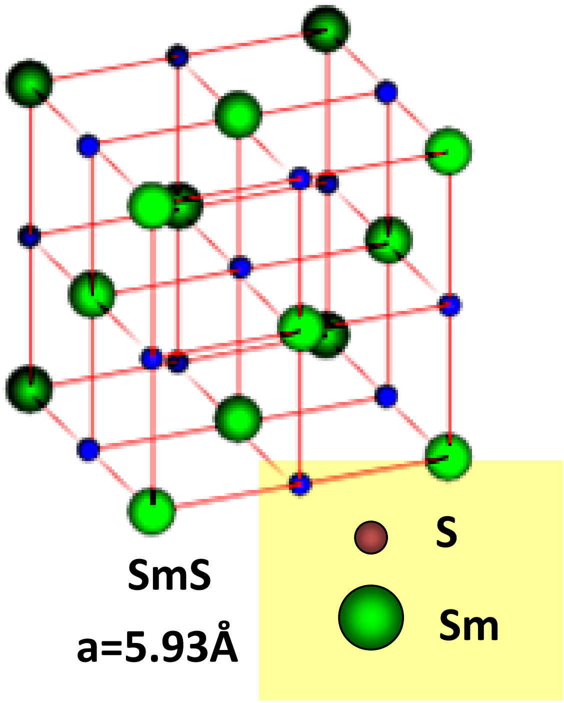
What about an interplay of intermediate valence and magnetism (spin fluctuation vs ordering?)

SmS in IV state is a good model system

In SmS dispersive magnetic excitation for intermultiplet transition *J0→J1* is observed by neutron scattering due to *exchange interaction Sm-Sm*

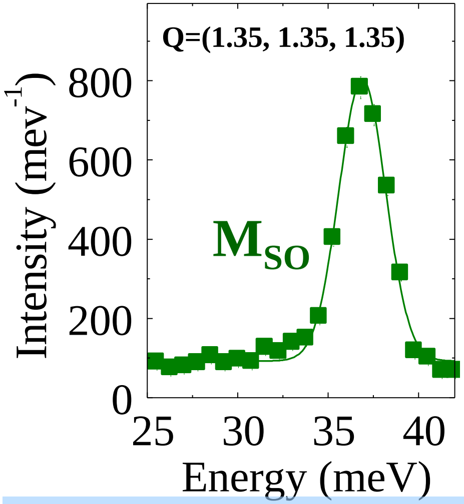
SmS: P = 6 кбар
EPT to “golden” phase, valence~2.7

Sm(Y)S: “chemical pressure ”
with continuous EPT

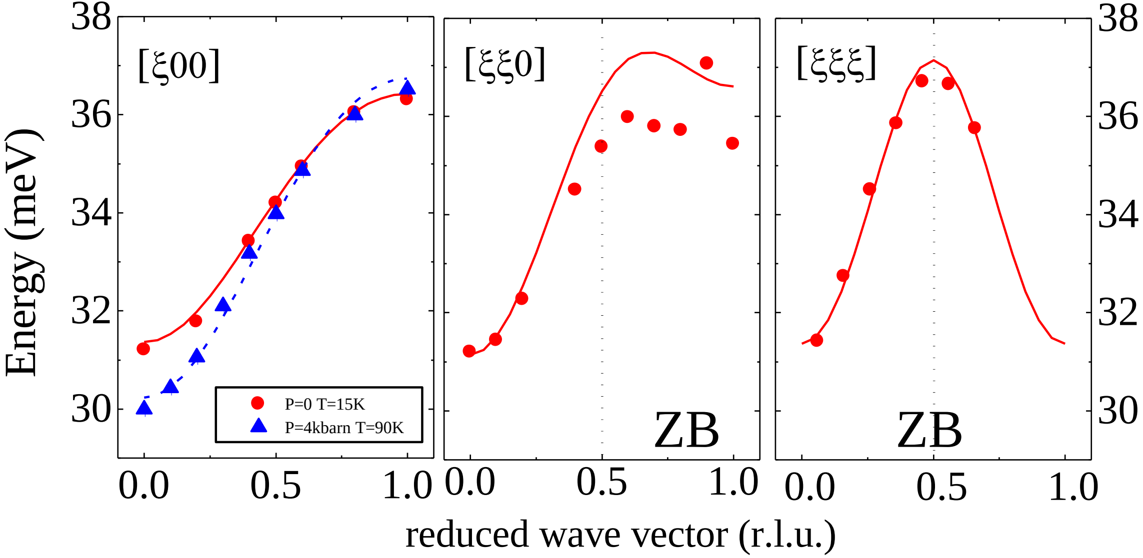


Excitations and Sm-Sm exchange in SmS

Spin-orbit (SO) transition in neutron spectra of SmS

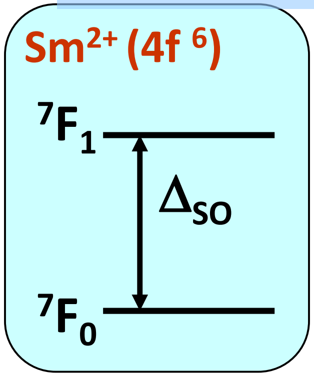


Magnetic excitation dispersion



Model description of a dispersion for SO transition (*S.M.Shapiro e.a., PRL, 1975*)

“induced magnetism”



+

Sm-Sm exchange:

$$J(\vec{q}) = \sum_j J_{ij} \exp\left[i\,\vec{q}(\vec{r}_i - \vec{r}_j) \right]$$

=

$$\hbar\omega_{SO}(\vec{q}) = \Delta_{SO}\left(1 - 16R(T)J(\vec{q})/\Delta_{SO}\right)^{1/2}$$

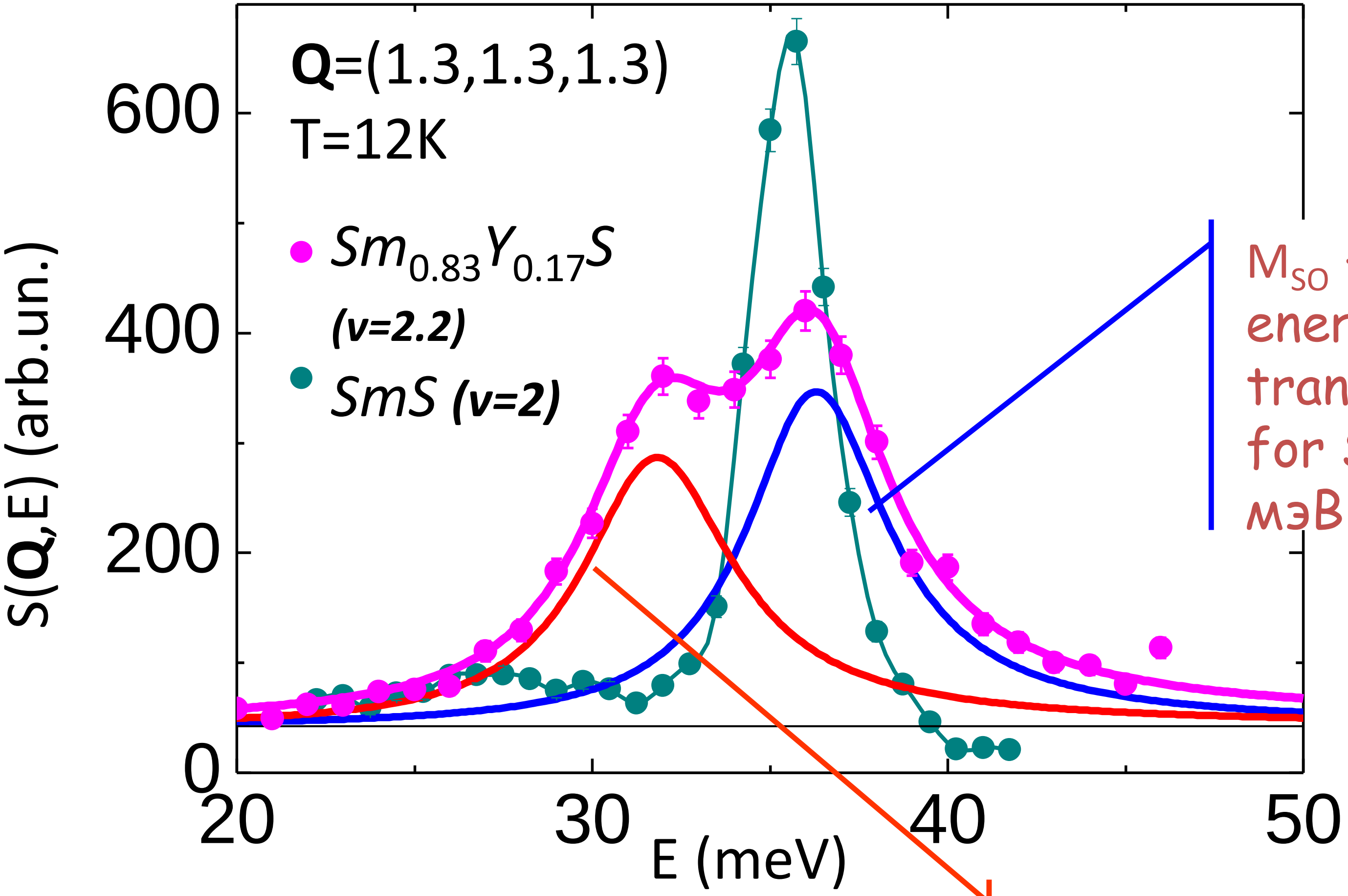
$$R(T) = \frac{1-\exp(-\Delta/kT)}{1+3\exp(-\Delta/kT)}$$

temperature factor

Excange interaction parameters in SmS: $J_1=0.043$ $J_2=0.020$ $J_3= - 0.003$

Magnetic dynamics in Sm(Y)S

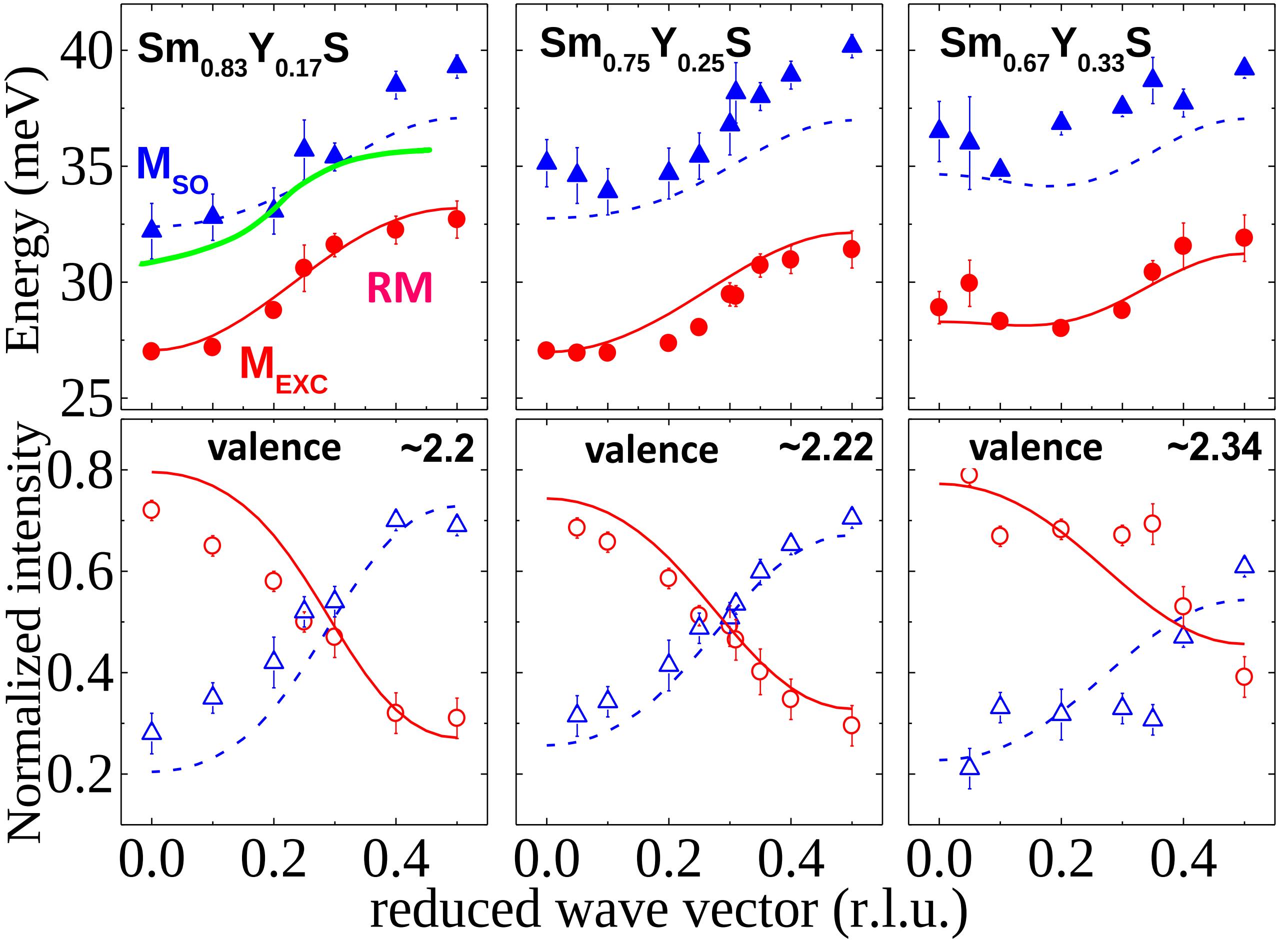
Fine structure of the magnetic excitation spectra in $Sm_{1-x}Y_xS$ single crystal



M_{SO} – close to the energy of SO transition $^7F_0 \rightarrow {}^7F_1$ for Sm^{2+} E ~ 36 мэВ

Another excitation M_{EXC} has an energy E ~ 30 мэВ weakly valence dependent

Dispersion of energies and relative intensities for magnetic peak MSO and Mexc



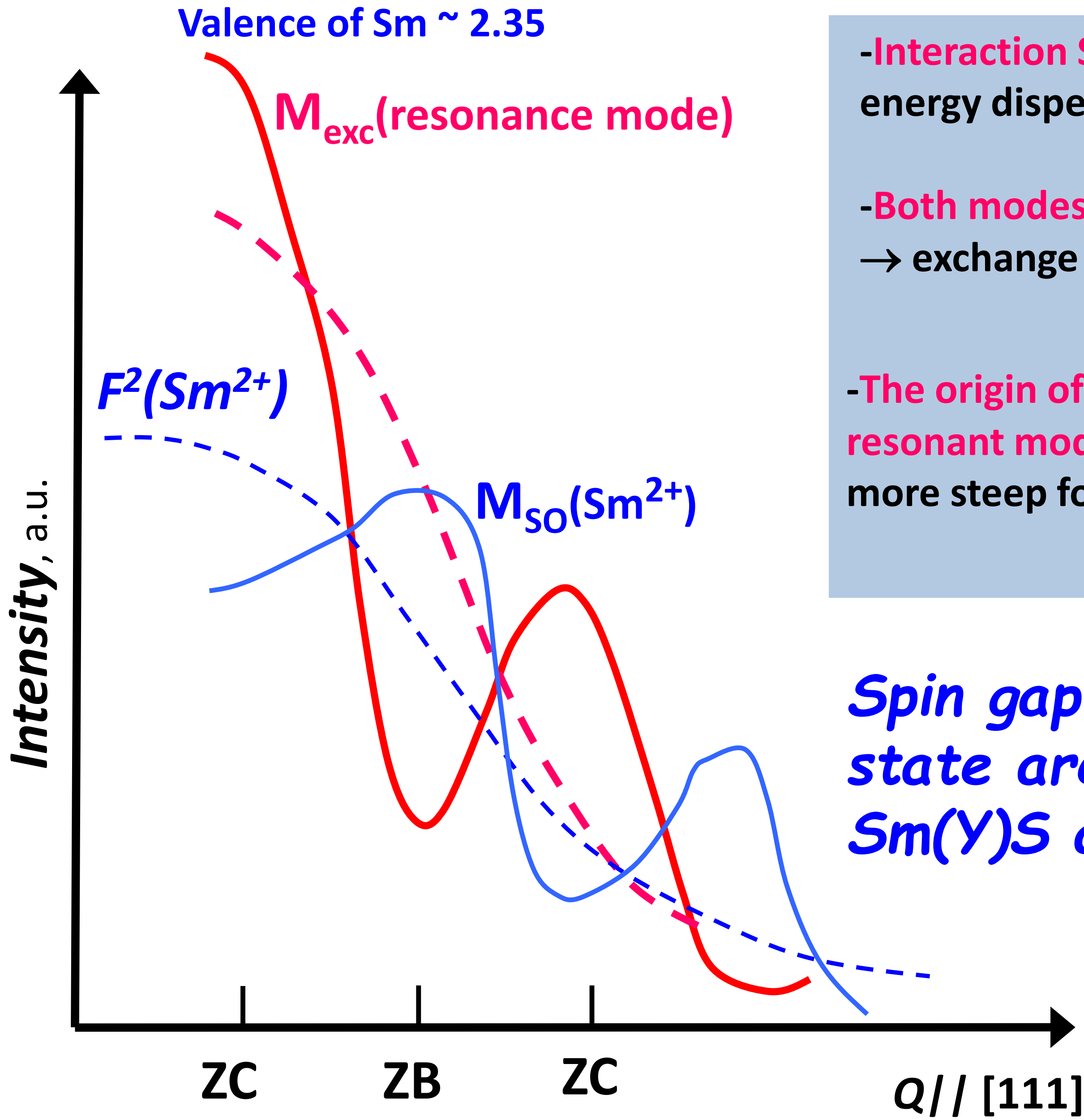
Sm^{2+} → Sm^{3+}

- Dispersion reduced
- Energy minimum is shifted from Γ-point
- M_{EXC} mode becoming dominating in the most of Brillouin zone

$$I_{SO}(I_{EXC}) = \frac{I_{SO}(I_{EXC})}{I_{SO} + I_{EXC}}$$

Introduction of the interaction (hybridization) between M_{SO} and M_{EXC} allows to describe the experimentally observed *E(q) and I (q)*

Intensities of two modes in Sm(Y)S as functions of momentum transfer Q

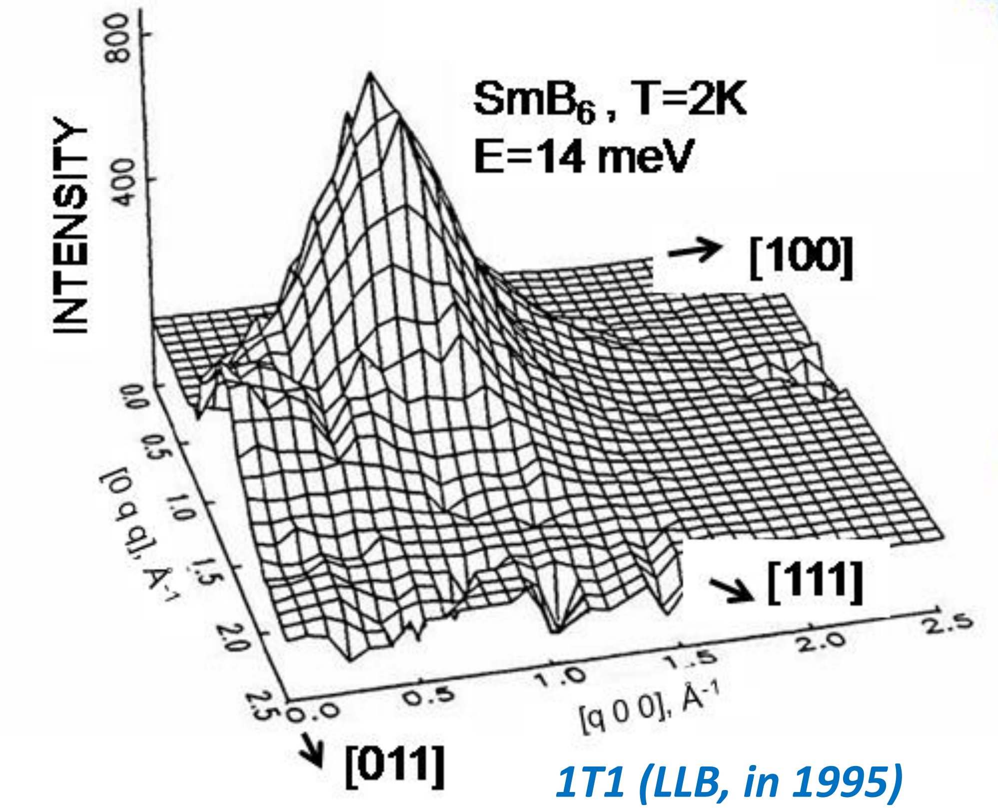


-Interaction Sm-Sm do exists → strong energy dispersion appears

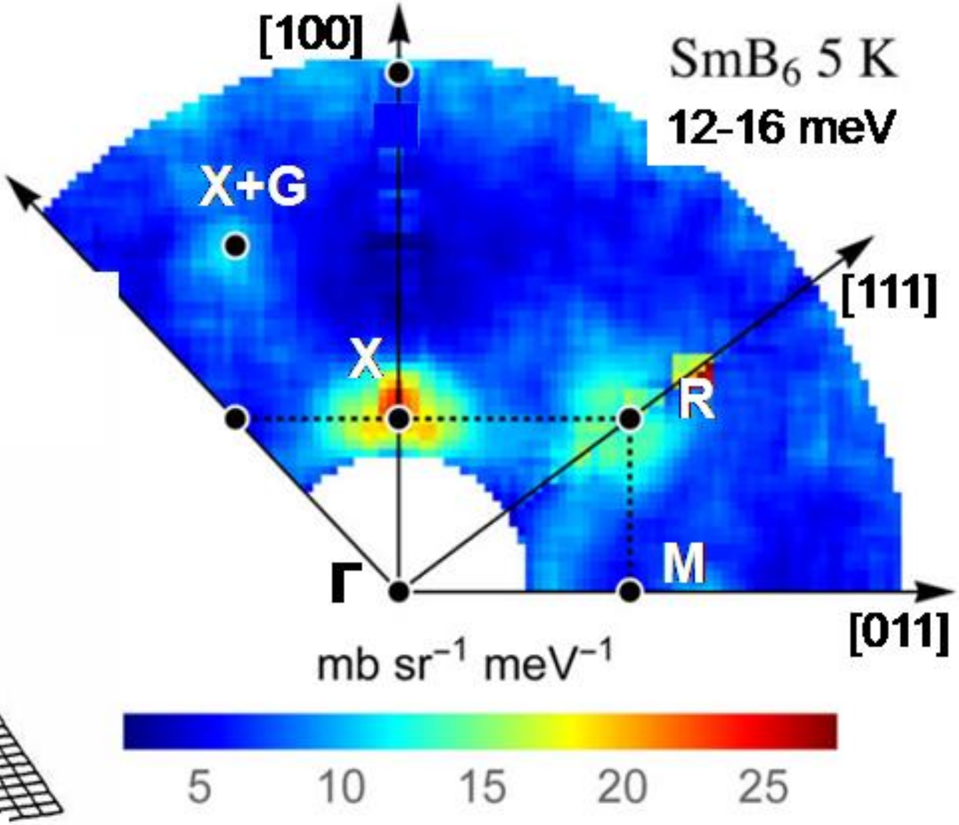
-Both modes are of the same symmetry → exchange of intensity in BZ

-The origin of the exictation M_{exc} identical to resonant mode of SmB6 → more steep formfactor for low energy peak!

Spin gap, singlet ground state are exsiting in Sm(Y)S as well as in SmB_6



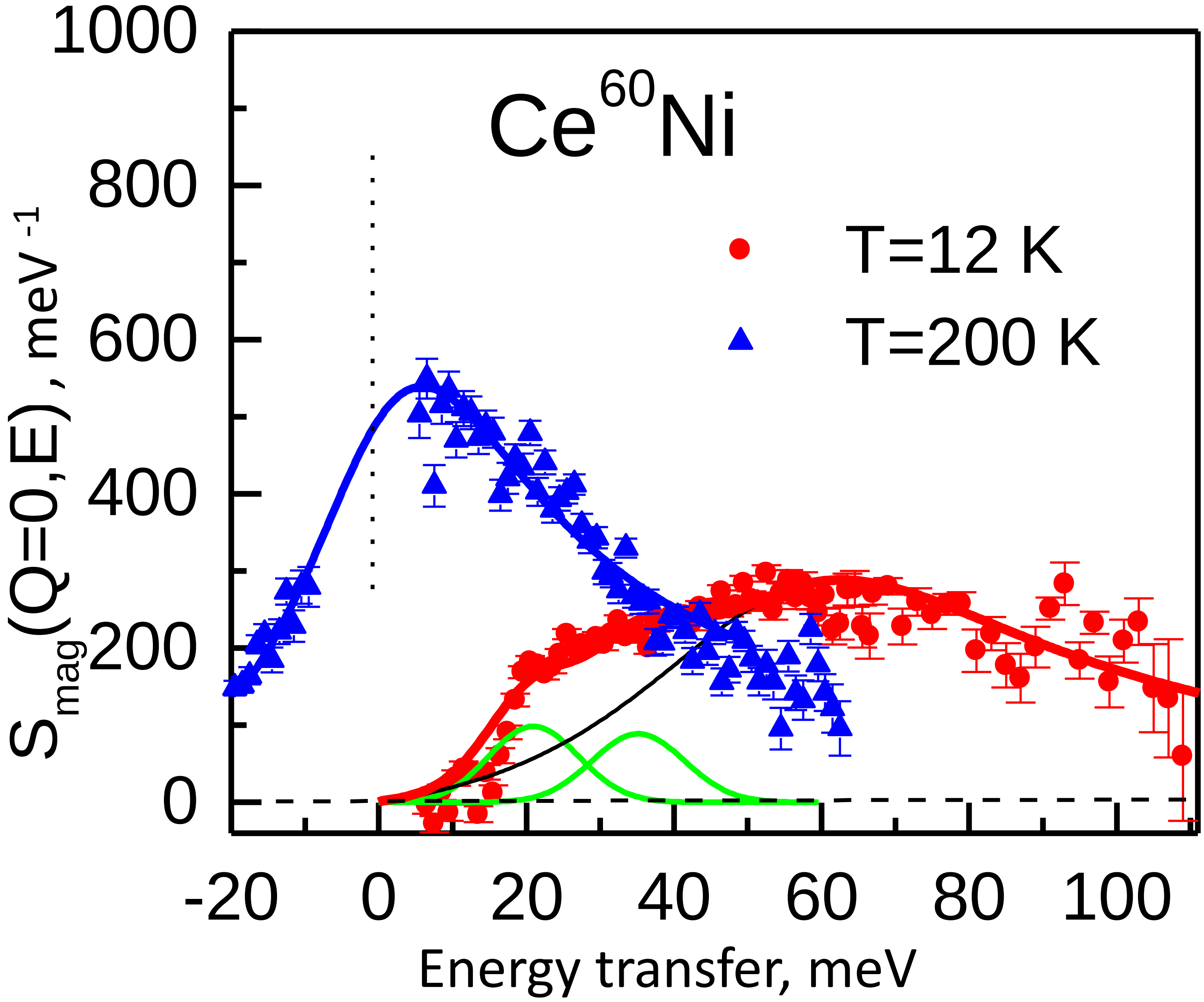
1T1 (LLB, in 1995)



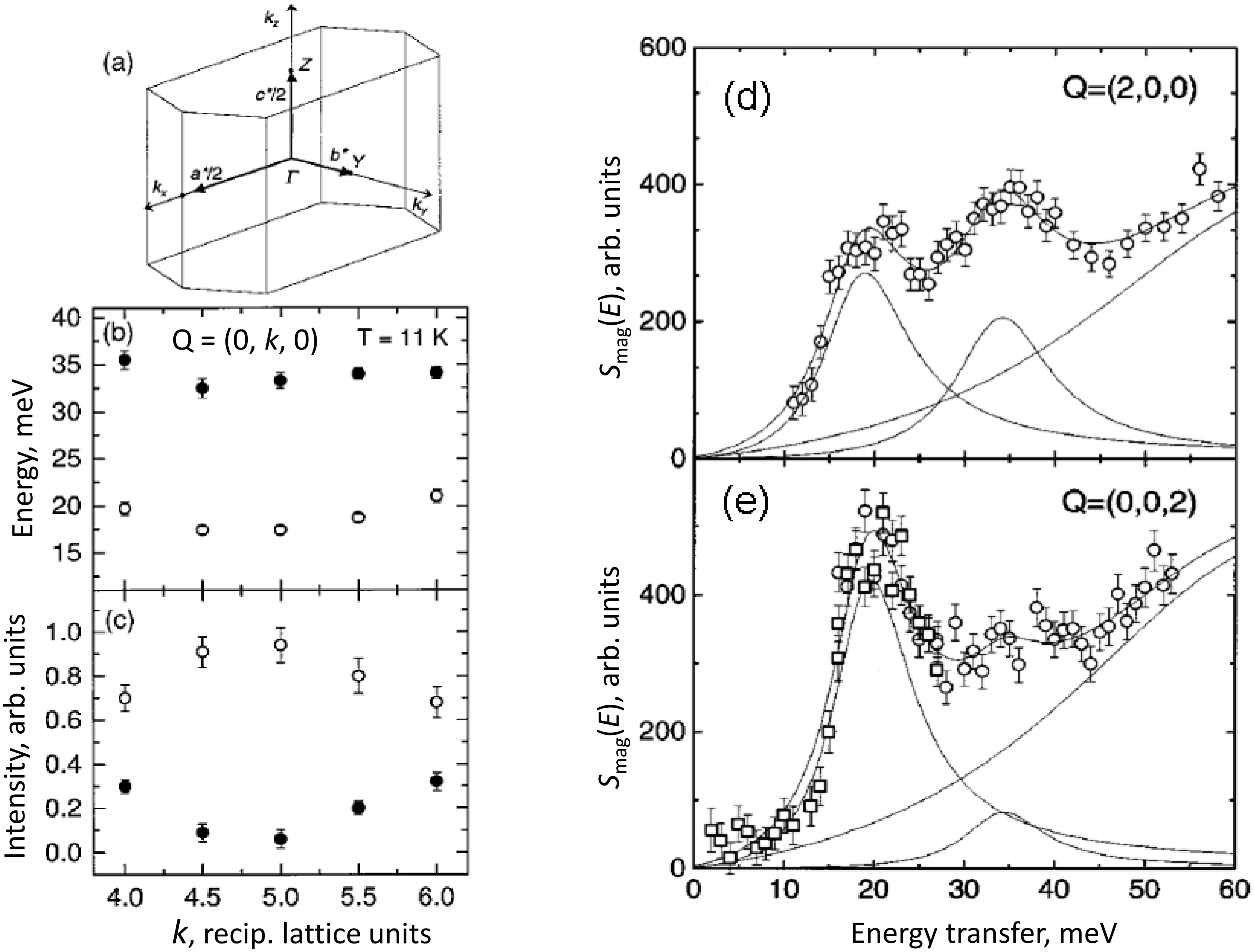
SEQUOIA (SNS) (2015)

Ce-based IV system with spin-gap: CeNi

LaNi –diamagnetic
CeNi – param - Intermediate valence: υ(10K)~3.15
PrNi – ferromag T_C = 21K (“induced” magnetism)
NdNi –ferromag T_C = 31K


Ce^{60}Ni
T=12 K
T=200 K
$S_{mag}(Q=0,E)$, meV^{-1}
1000
800
600
400
200
0
-20
0
20
40
60
80
100
Energy transfer, meV

Magnetic excitation in spin-gap of CeNi spectrum



Spin fluctuations and magnetism

2. “Resonance” mode (RM) in Sm-based intermediate valence systems: single-site and cooperative behaviour

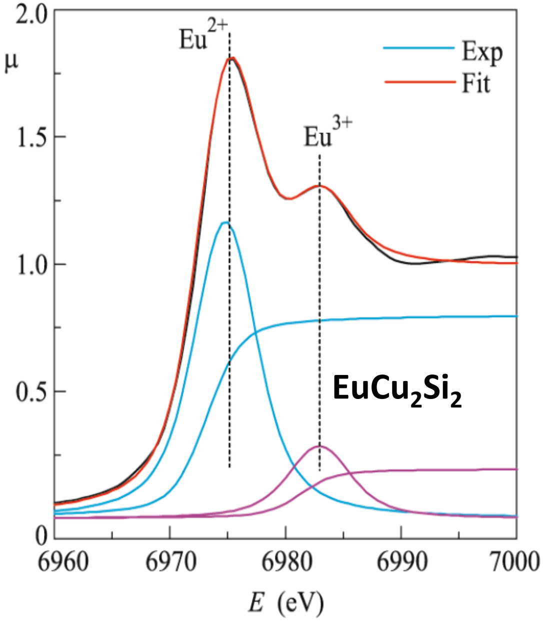
RM appears due to formation of a singlet ground state for intermediate valence compound

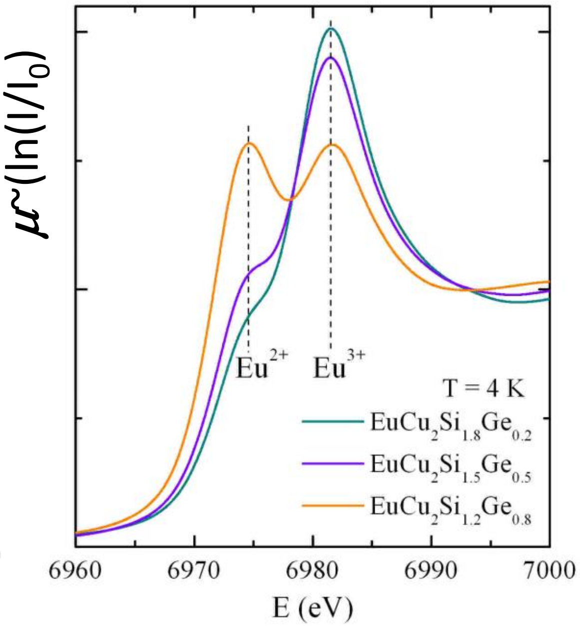
How the magnetic correlation can survive under these conditions?

$EuCu_2(Si_xGe_{1-x})_2$: definition and characterization of valence state

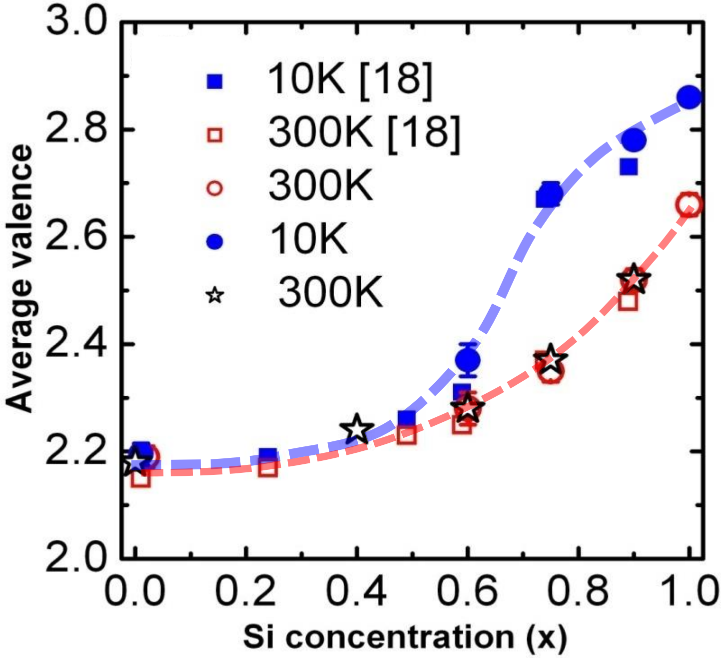
"Fast" and "slow" technique

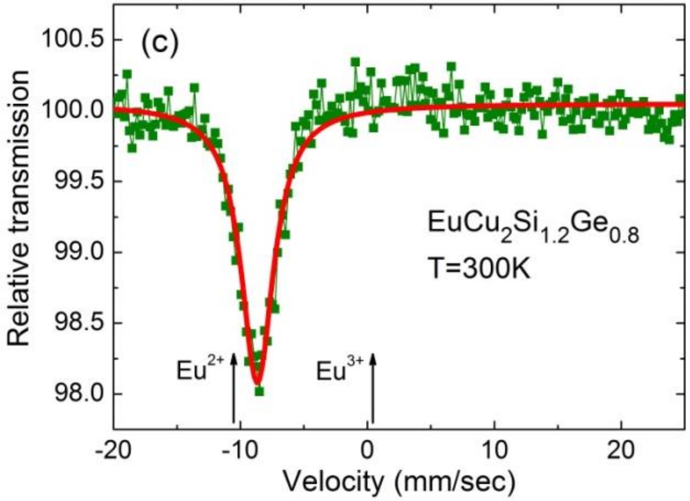
L_3-edge (τ~10^{-15}s): mixed "valence"





Concentration dependence of the "intermediate valence"





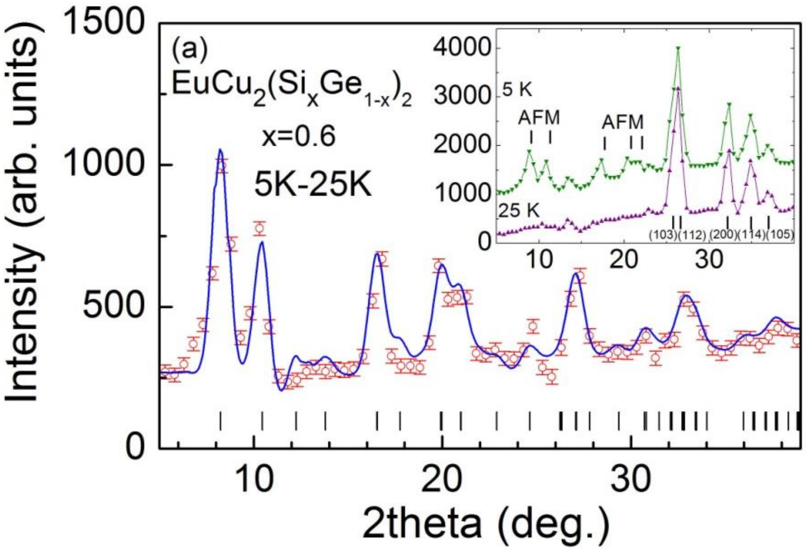
Mössbauer spectroscopy (τ ~ 10^{-8}s): isomer shift - "mixed valence" is homogeneous

[18] ***S. Fukuda et.al.***, Y. Phys. Soc. Jpn. 72, 3189 (2003)

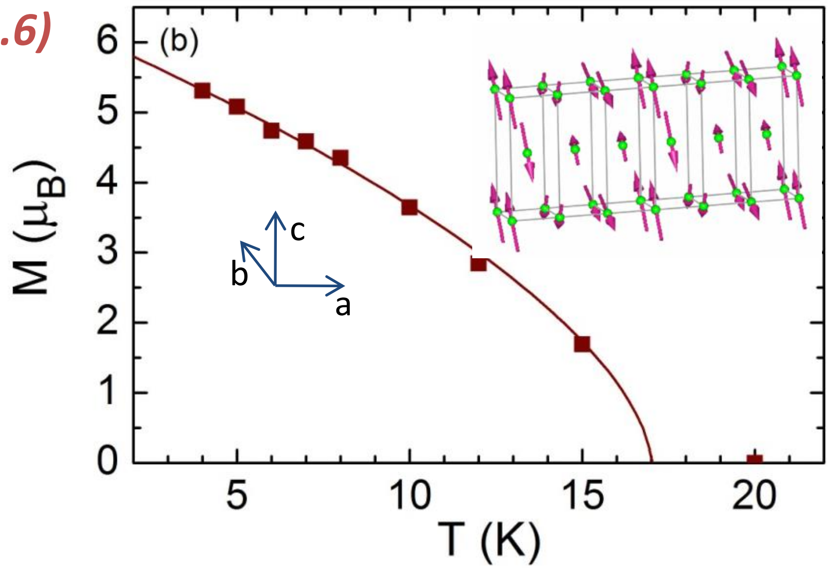
$EuCu_2(Si_xGe_{1-x})_2$: determination of magnetic state

Neutron diffraction (x=0.0, 0.4, 0.6)

Diffractometer 7C2 (“hot” neutron source, LLB), λ=1.121 Å, $2\Theta=3^0 – 40^0$, m_s~0.6g



(x=0.6)



propagation vector ***k*** = (1/3 0 0). The Eu magnetic moments located at positions (0 0 0) and (1/2 1/2 1/2) of the crystal structure have antiparallel orientation. They are located in the (*bc*) planes and oriented at the angles φ = 33° (147°) with respect to crystallographic *c* - axis

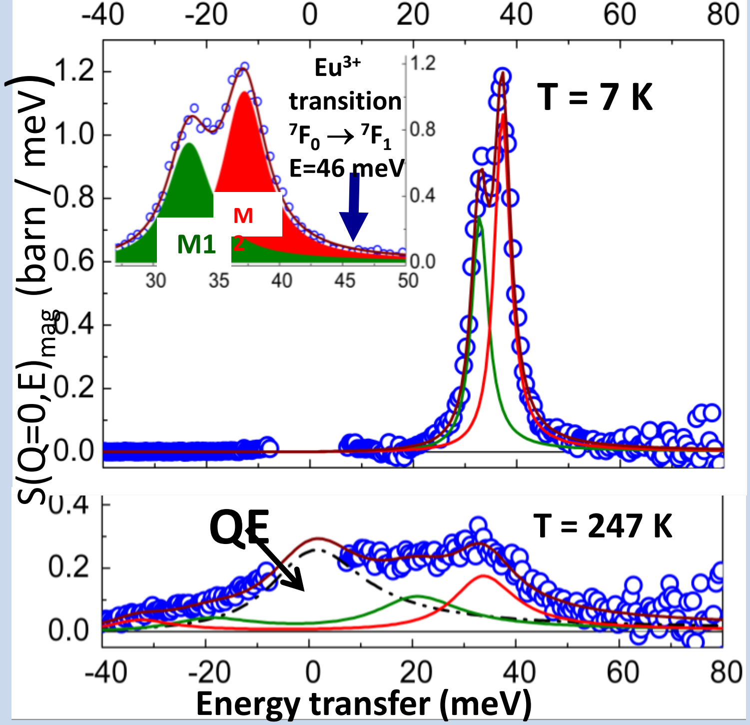
Eu-ion static magnetic moment from the diffraction data at the temperature T=5K.

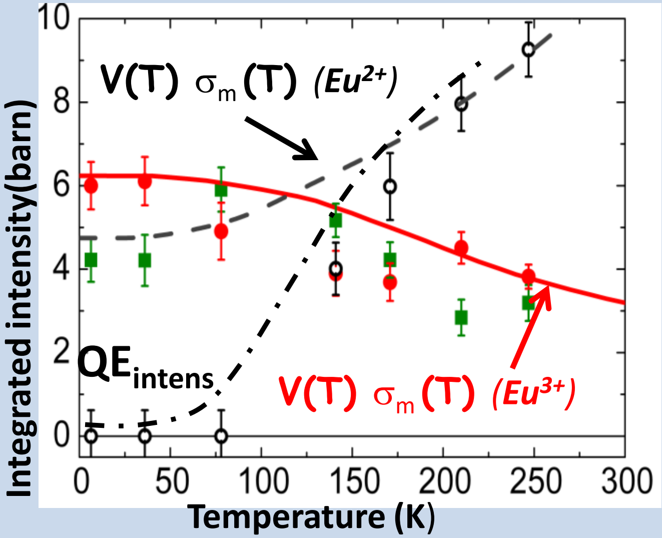
X ($EuCu_2(Si_xGe_{1-x})_2$)	M_x, μ_B	M_y, μ_B	M_z, μ_B	M_{tot}, μ_B	R-factors	T_N,K
0.0: $EuCu_2Ge_2$	3.1	6 .0		6.7(1)	Rp =0.07, Rwp = 0.09	15
0.4: $EuCu_2Si_{0.8}Ge_{1.2}$	3.3	4.1		5.3(1)	Rp =0.09, Rwp = 0.12	19
0.6: $EuCu_2Si_{1.2}Ge_{0.8}$	2.6		4.6	5.3(1)	Rp =0.05, Rwp = 0.07	17

MM (Eu^{2+}) = 7.94μ_B

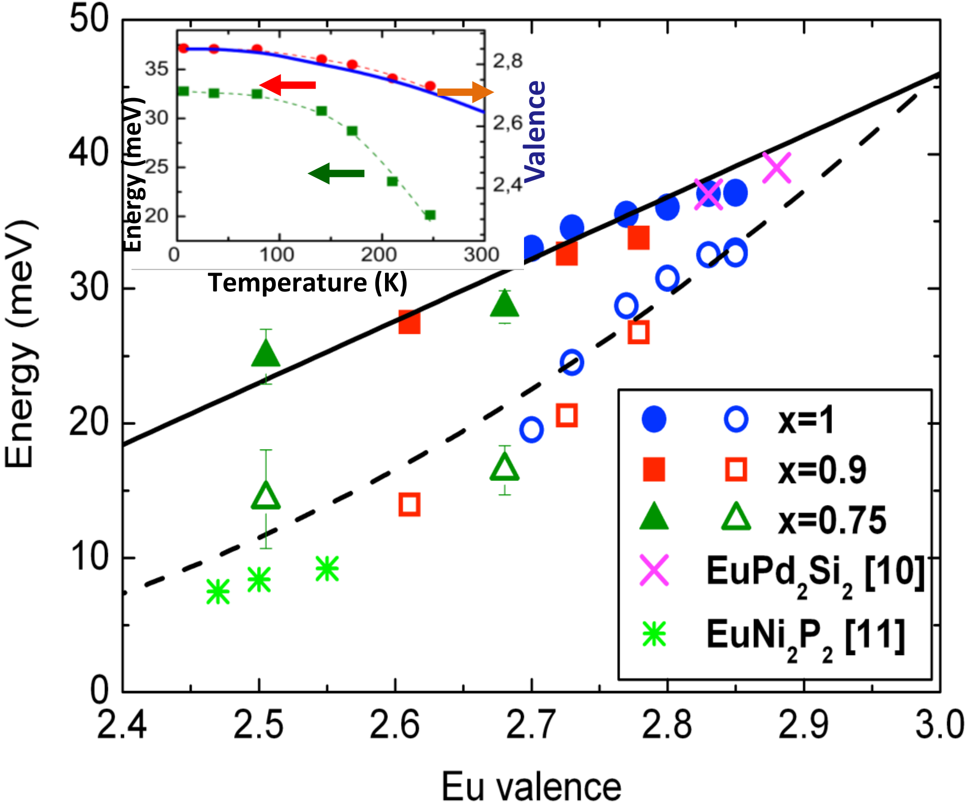
$EuCu_2(Si_xGe_{1-x})_2$: inelastic magnetic neutron scattering

$EuCu_2Si_2$ – neutron data





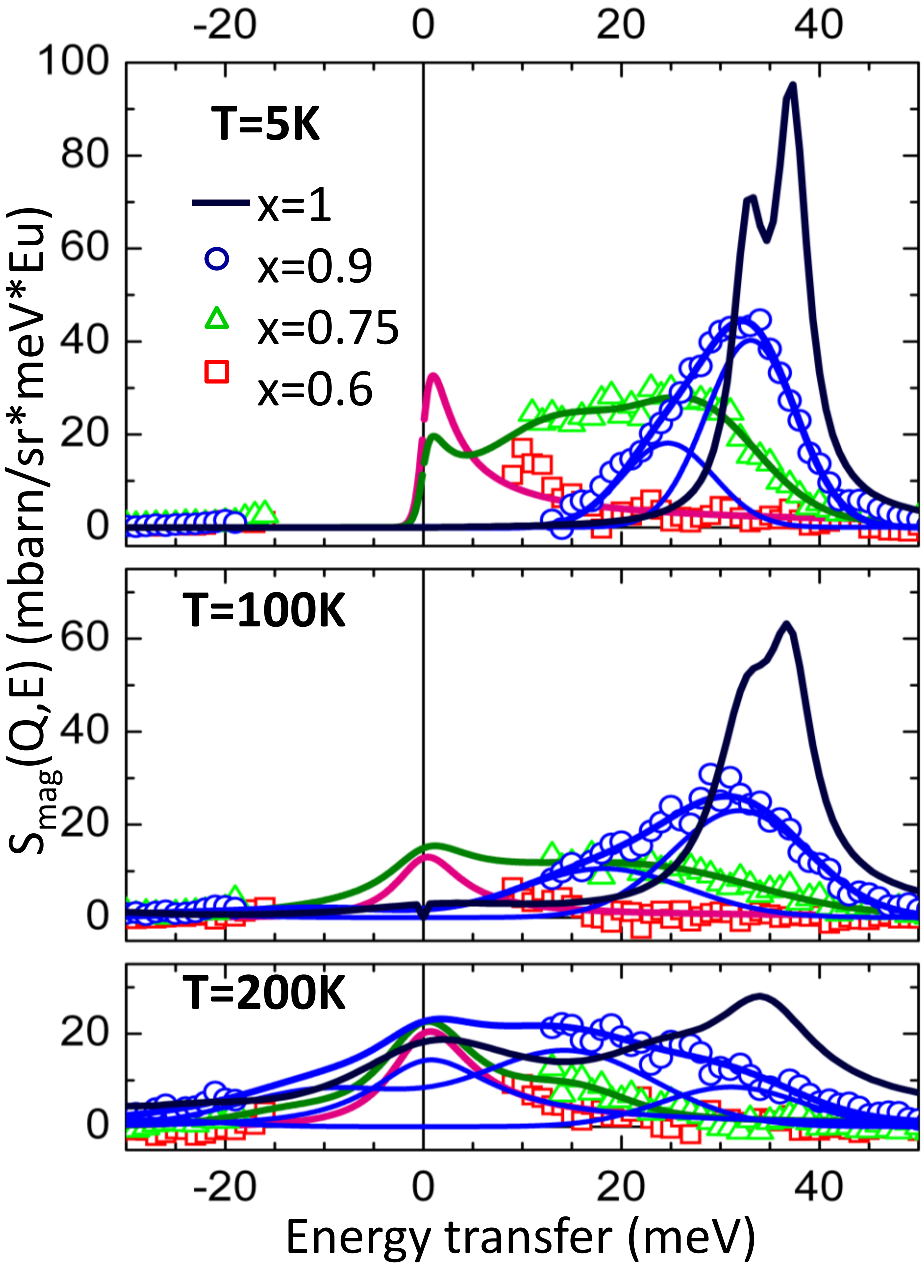
Magnetic excitations in $EuCu_2(Si_xGe_{1-x})_2$



*Decrease of the excitation energy and closing of spin-gap result in **formation of magnetic ground state for IV Eu** at X decreasing to~0.75*

*Eu-Eu interaction is mediated by conduction electrons **not like** in TmSe*

Magnetic excitations in $EuCu_2(Si_xGe_{1-x})_2$



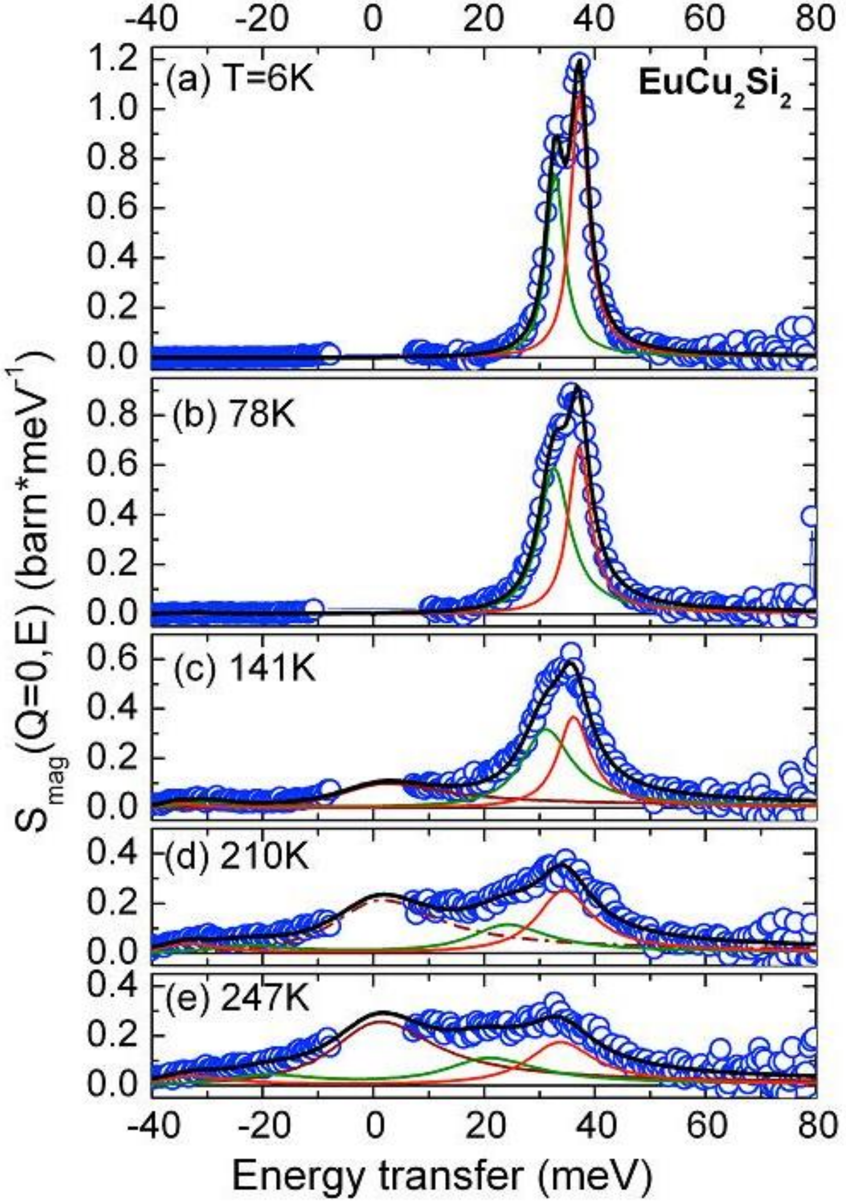
effect of Ge for Si substitution:

- suppression and broadening of both M1 and M2
- further shifting of both M1 and M2 towards low energies;
- appearance of quasielastic scattering signal already at low temperature (at least for x=0.75)

- at x=0.6: inelastic peaks are shifted below 10 meV or suppressed; QE-signal is narrow and exists starting from the low temperature

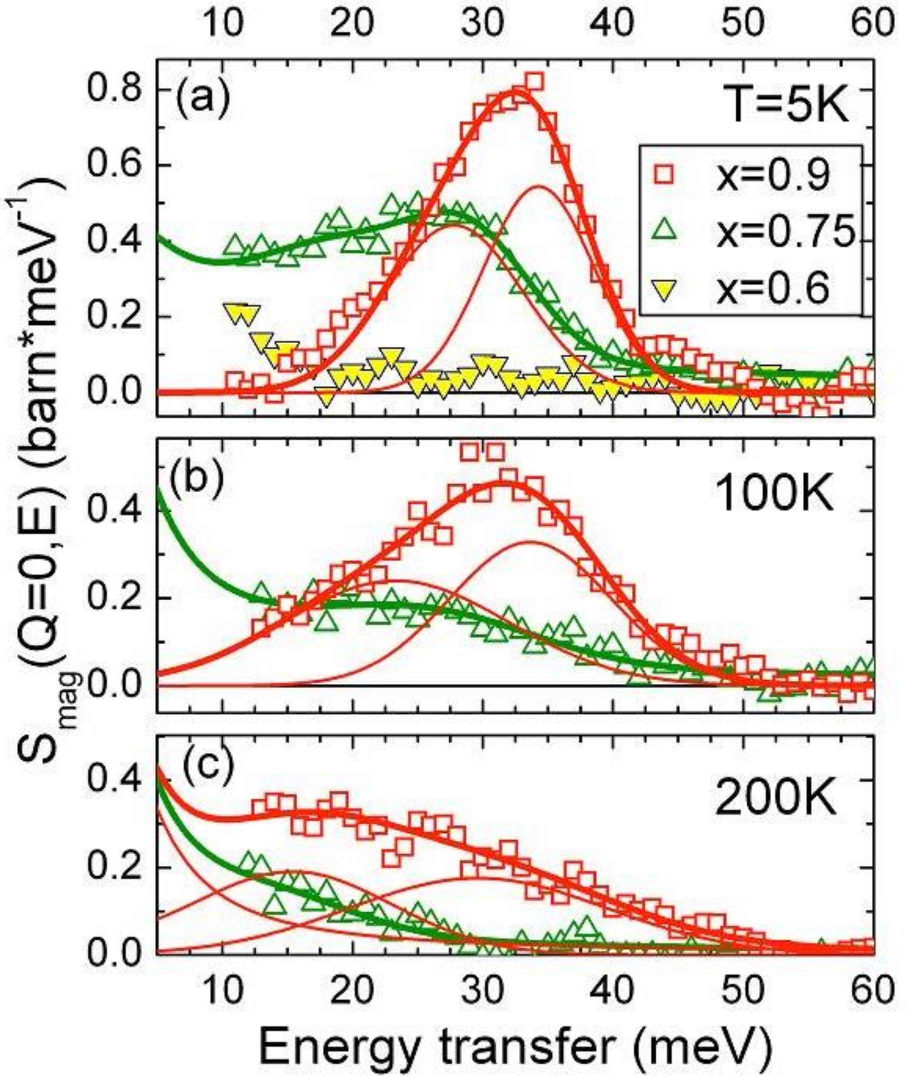
Experimental data for $EuCu_2(Si_{1-x}Ge_x)_2$, TOF spectrometers (HET, MARI) E_0=100meV

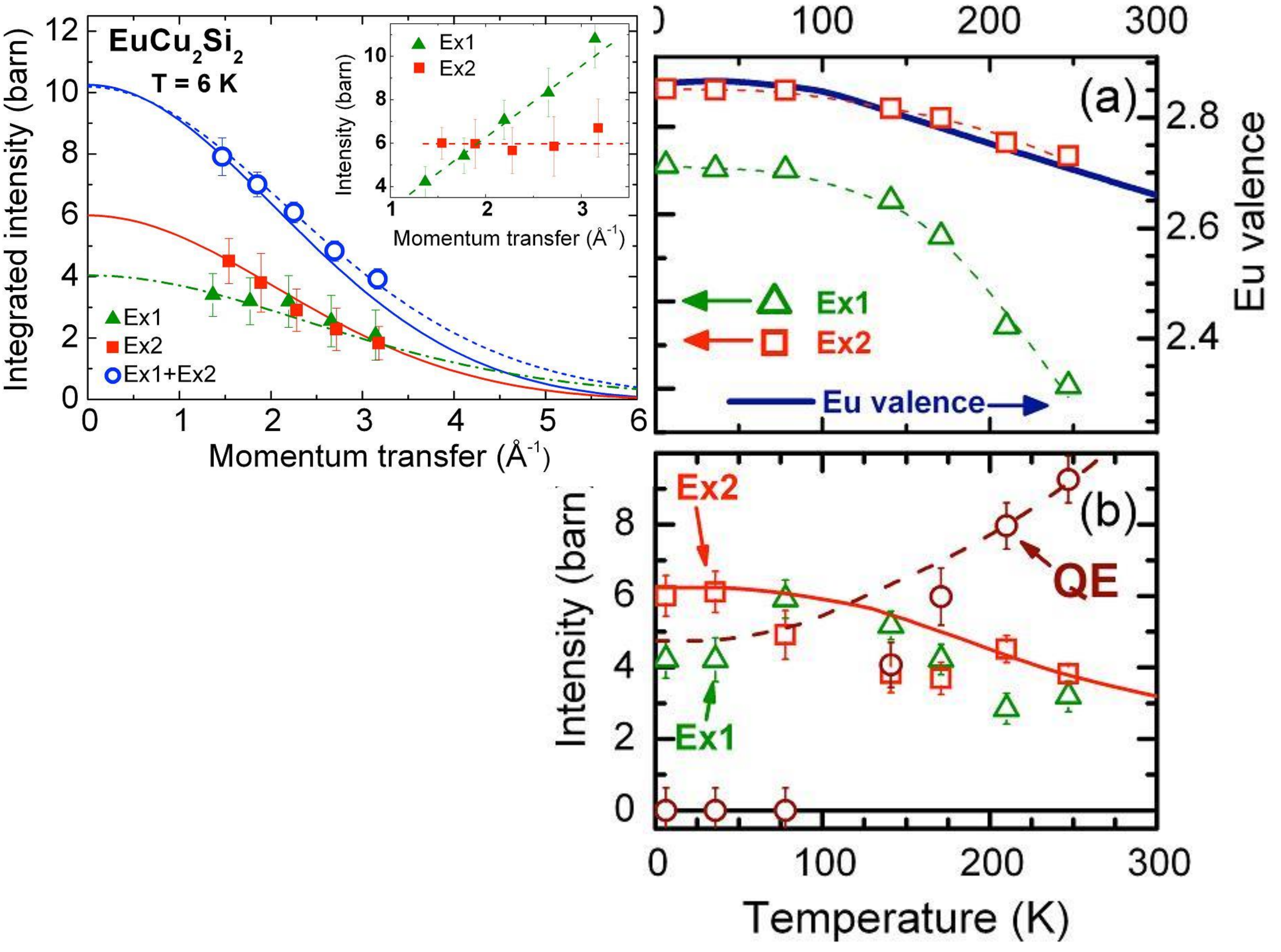
$EuCu_2Si_2$ ΔE_0=2.9 meV



ΔE_0=7.1 (3.7)meV

$EuCu_2(Si_{1-x}Ge_x)_2$




EuCu$_2$Si$_2$
T = 6 K
Integrated intensity (barn)
Momentum transfer (Å^{-1})
0
1
2
3
4
5
6
0
2
4
6
8
10
12
▲ Ex1
■ Ex2
○ Ex1+Ex2
Intensity (barn)
Momentum transfer (Å^{-1})
1
2
3
4
6
8
10
▲ Ex1
■ Ex2
100
200
300
(a)
Eu valence
2.4
2.6
2.8
Ex1
Ex2
Eu valence
(b)
Intensity (barn
0
2
4
6
8
Ex2
Ex1
QE
0
100
200
300
Temperature (K)

3.2 Intermediate valence (IV) and magnetism: TmSe

How the LRO state is formed under the condition of IV state of Tm?
Coherent state appears obviously, but which way it is realized?

The key question is the *origin of "resonance mode" (inelastic excitation) in the spectra of LRO state of TmSe*

> In theoretical approaches to the description of IV state for Tm the existence of two magnetic configurations is supposed simultaneously for f-electrons under the conditions:
> - spacial [**1**,**2**] or
> - time [**3**] coherence for spin fluctuations between two magnetic configurations

By studying the effect of substitution for *Tm* by other ions [**4**] it was shown – the origin of "resonance mode" is single site - this corresponds to the *time coherence* [**3**] as a source of LRO.

1. **A.J. Fedro, S.K. Sinha, in: Valence Fluctuations in Solids, eds. L.M. Falikov, W. Hanke and M.B. Maple (North-Holland, New Yourk, 1981) p. 329**
2. **M. loewenhaupt, E. Holland-Moritz, J. Appl. Phys. 50(11)7456 (1979)**
3. **J. Mazzaferro, C.A. Balsiero, B. Alascio, PRL 47 (1981) 274**
4. **E. Holland-Moritz, JMMM, 38 (1983) 253-263**

3. 2 Transition from heavy fermion to magnetically ordered state on temperature decrease

Spin dynamics CeX_2Si_2
(X=Au, Pd, Rh, Ru)

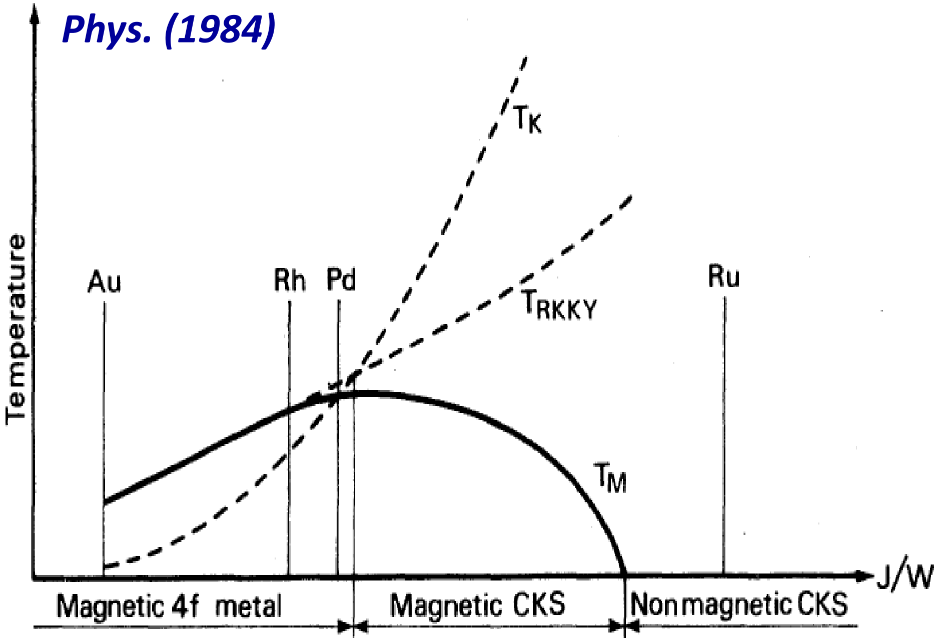
Weak hybridization: $J_{sf} \sim V^2_{sf}/(E_F-E_{4f})$

$T_K \sim \exp\{-N_{EF}(1/|J_{sf}|)\}$

$T_{RKKY} \sim J^2_{sf}$

Doniach's diagram, from

N. B. Brand and V. V. Moshcahlkov, Adv. Phys. (1984)



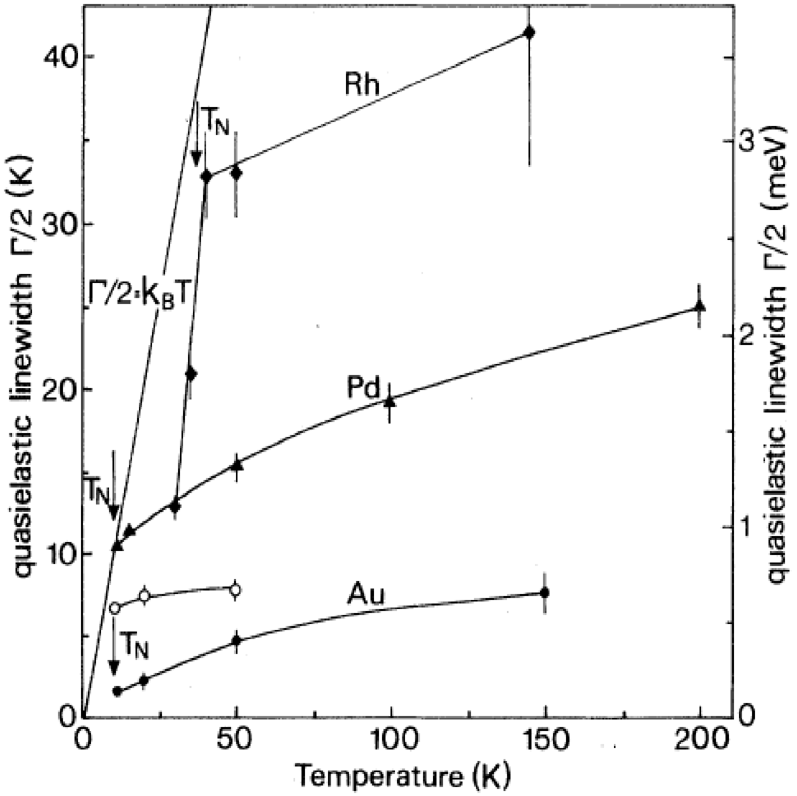


FIG. 5. Quasielastic linewidths vs temperature for $CeAu_2Si_2$ (● Lorentzian, ○ Gaussian), $CePd_2Si_2$ (▲) and $CeRh_2Si_2$ (◆). The arrows indicate the Néel temperatures. The solid lines are guides to the eye.

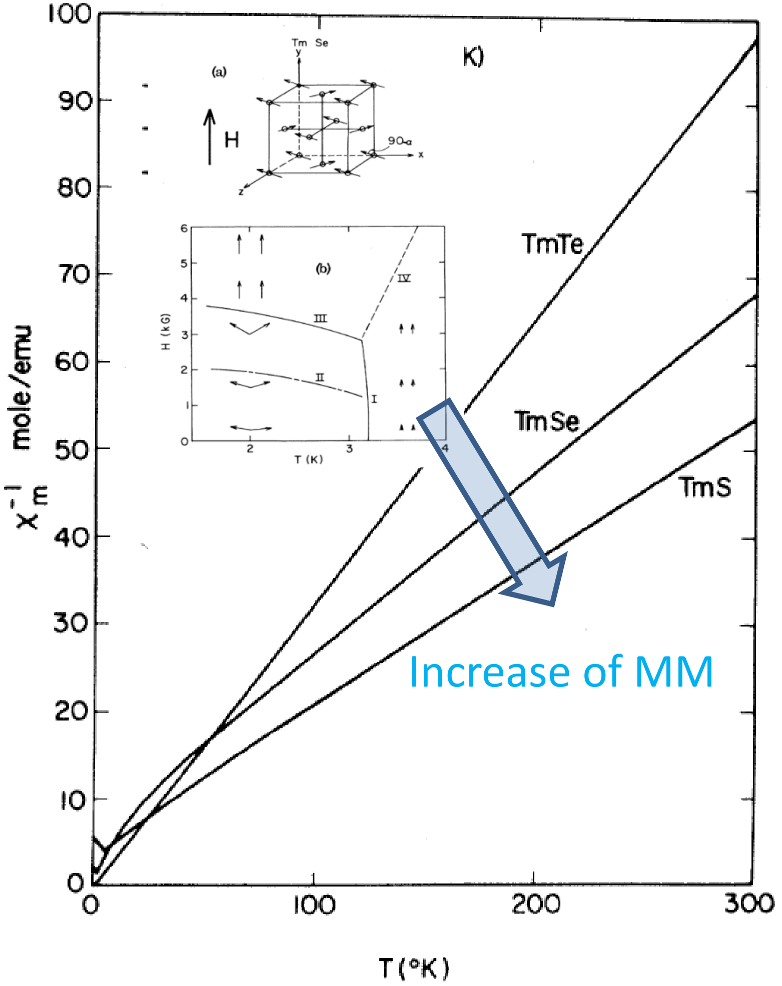
QE-signal exists at some T below T_N!

A. Severing, E. Holland-Moritz, B. Frick, PRB 39 (7) 4164 (1989) etc

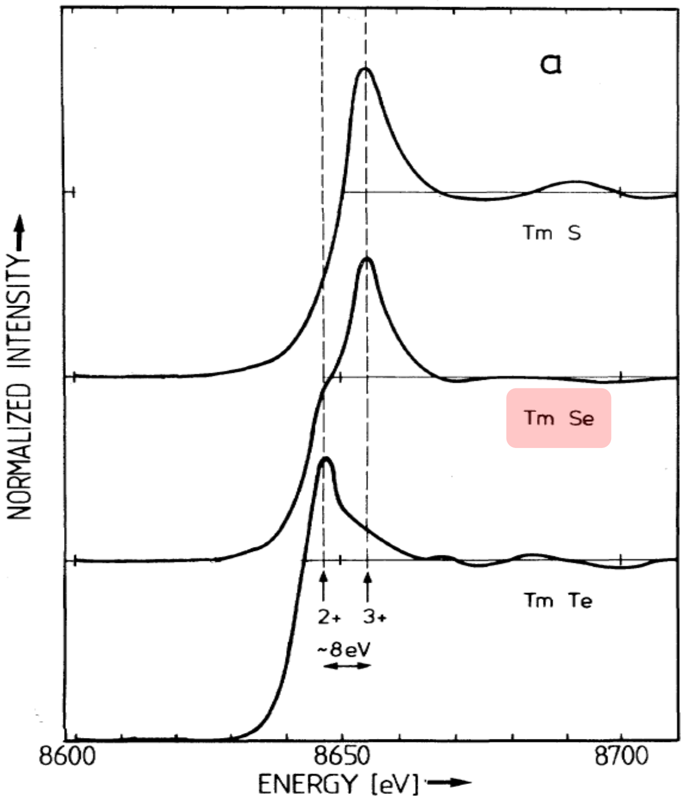
3.2 Intermediate valence and magnetism: TmSe

TmSe (NaCl-type of structure),
valence υ=2.58 , T-independent (XANES, L_3-edge)
T_N=3.5K, AFM I-type, O.M.=1.7μ_B *(Tm^{2+}: J=7/2 (4.5μ_B), Tm^{3+}: J=6 (7.5μ_B)*

L3-edge characterization: TmS (3+); TmSe (IV); TmTe (2+).



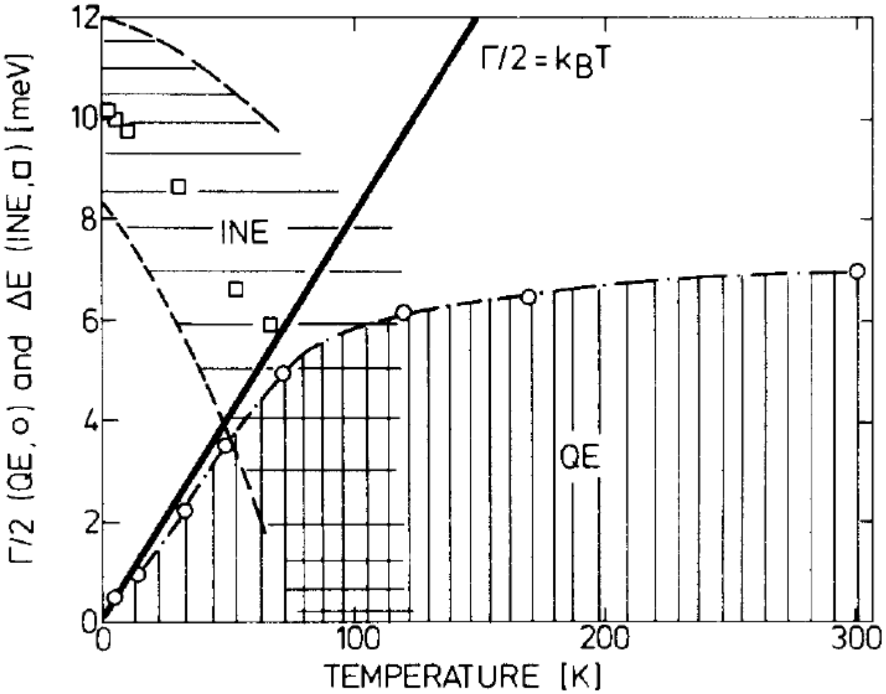
Increase of MM



E. Bucher, e.a. PRB 11 (1) 500 (1975) – magnet susceptibility
H. Bjerrum-Moller, S.M. Shapiro, R.J. Birgeneau, PRL 39 (16) 1021 (1977) magnetic structure
H. Launois, M. Rawiso, E.Holland-Moritz, R.Pott, D. Wolleben PRL 44 (19) 1271 (1980) L3-edge

3.2 Intermediate valence and magnetism: TmSe

Neutron spectroscopy (IMNS) for TmSe



Quaselastic signal disappear at T< T_N =3.5K, Inelastic peak at 10 meV survive !

M. Loewenhaupt, E. Holland-Moritz, J. Appl. Phys.50 (11) 7456 (1979)

“resonance mode” for TmSe: general and specific features

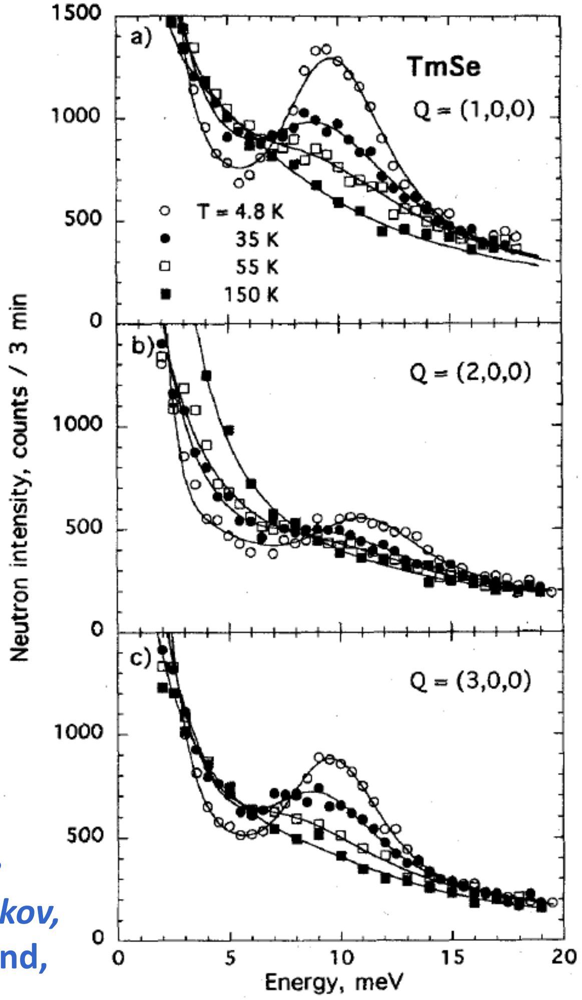


Fig. 7. Neutron scattering spectra of single-crystal TmSe measured in the constant-k_f mode (E_f = 30.5 meV) at fixed scattering vectors $Q = (q, 0, 0)$; (a) $q = 1$, (b) $q = 2$, (c) $q = 3$.

B.H. Grier, S.M. Shapiro, *in: Valence Fluctuations in Solids, eds. L.M. Falikov, W. Hanke, M.V. Maple* (North-Holland, Amsterdam, (1981) p.325

J-M. Mignot, P.A. Alekseev, Physica B 215 (1995) 99-109

Point of view / Summary 2 / Outlook

$CeFe_2Al_{10}$

- **Conventional Kondo insulator.**
- **Resonance-like magnetic exciton mode (SmB_6, YbB_{12})**

$CeRu_2Al_{10}$

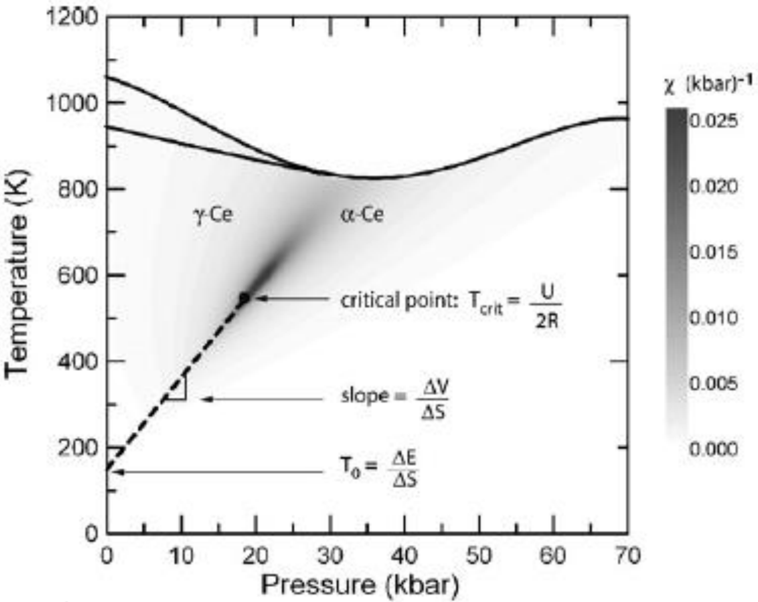
- **Kondo “insulator” (semimetal) + unconventional magnetic order.**
- **Existence of clear dispersive magnon-like modes (consistent with RPA calculations).**

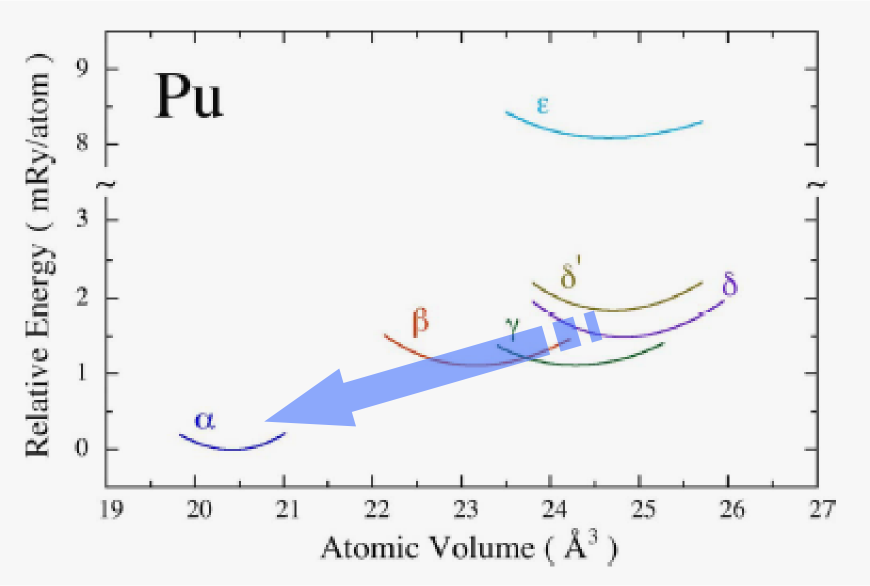
- **Pronounced anisotropy of spin correlations, observed by polarization analysis.**
- **Ordered phase cannot be reduced to the usual competition CEF + RKKY.**

➡ Direction dependent hybridization?

➡ Localized vs. itinerant approach?

Высокие давления и СКЭС





Ce γ - α **переход,** (Bridgman, 1931$^{*)}$)
ΔV/V~15%

Pu: δ - α, P ~2кбар $^{**)}$
ΔV/V~25%

Некторые проблемы физики конденсированных сред, связанные сильными корреляциями электронов:

- описание электронов, балансирующих между делокализацией и локализацией
- учет сильных корреляций, тяжелые квазичастицы
- квантовые критические точки
- необычная (нефононная) сверхпроводимость (текущий рекорд T_c~20K в $PuCoGa_5$)

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*)P.W. Bridgman, The Physics of High Pressures, G. Bell and Sons, Ltd., London, 1931, p. 267.

**)"Challenges in Plutonium Science", ed. N.G. Cooper, Los Alamos Science, Number 26, 2000

Spin fluctuations and magnetism
in rare-earth based compounds with *f*-electron instability

Contents

1. Magnetic form factor in intermediate valence state of Sm and Eu

2. Resonance mode in intermediate valence systems: single-site and cooperative behaviour

3. Spin fluctuations and long range magnetic order:
    - a case of “strong” intermediate valence
    - heavy fermion and Kondo-insulating states