

Max-Planck-Institut für Chemische Physik fester Stoffe

Max-Planck-Institute for Chemical Physics of Solids



Physics of Correlated Matter

Hao Tjeng

highlights, on-going work, future plans

Publications 2012-2015: 161 2015-2018: 187 2018-2021: 224

group leaders:	6+1+1
postdocs:	57
PhD students:	57
tech. staff:	3

Covid: loss of 100 days of beamtime Japan+Taiwan



Steffen Wirth

Simone Altendorf

Zhiwei Hu

STM/STSPCM_02"Hexaborides: materials of
diverse physics"



MBE – thin films PCM_03 "All in-situ studies of topological insulator heterostructures"



Oliver Stockert

Neutron Spectroscopy PCM_05 "Magnetic frustration and quantum criticality in 4*f* materials "



Alexander Komarek

Neutron – crystal growth "Frustration in transition metal compounds" PCM_04



XAS/XMCD PCM_08 "X-ray spectroscopies on transitionmetal oxide based catalysts"



Chun-Fu Chang

XAS/ARPES – thin films "Spin-orbit interaction in 5*d* TM oxides" PCM_0



Andrea Severing (guest – U Cologne)

Neutron/XAS/RIXS/NIXS "Orbital physics in *f*-electron systems" PCM



Hao Tjeng

XAS/NIXS/HAXPES PCM_01 "Orbital imaging and spectroscopy using s-NIXS"

Orbitals: methods and physics

NIXS: non-resonant inelastic scattering (XRS)
HAXPES: hard x-ray photoelectron spectroscopy

orientational dependence \rightarrow direct image of the orbital shape

highlights, work in progress, future plans

- transition metal compounds (magnetism, SST, MIT)
- uranium intermetallics (dual nature of 5*f* electrons)
- measuring (local) charge density of materials ?



non-resonant inelastic x-ray scattering





$$H_{\rm int} = \frac{e^2}{2m_e c^2} \vec{A}^2 + \frac{e}{m_e c} \vec{p} \cdot \vec{A} -$$

dominant at absorption edges

dominant far away from absorption edges

non-resonant inelastic x-ray scattering, x-ray Raman



non-resonant inelastic x-ray scattering



Unveiling *deep states* in UM_2Si_2 family: dual nature of 5*f* electrons







higher multipole transitions reach higher quantum number states
they are at lower energies, further away from continuum states
more excitonic → "deep states"
atomic nature more visible

atomic multiplet structure in intermetallic U compounds
never seen core level XAS/XPS
but visible in NIXS (with high q)

3d	I4/mmm	I4/mmm	I4/mmm	14/mmm
	a=3.945	a=3.908	a=3.970	a=3.981
	c=9.544	c=9.637	c=9.523	c=9.943
	Fe	Co	Ni	Cu
	d _{u-тм} = 3.095	d _{0.7M} = 3.10	d _{u-m} = 3.092	d _{∪.TM} = 3.185
	PP	AF@80K	AF@124,108,40K	AF@106; F@103K
4d	I4/mmm a=4.127 c=9.567 Ru d _{U:TM} = 3.164 HO@17K SC@1.5K	I4/mmm a=4.009 c=10.025 Rh d _{u:™} = 3.209 AF@137K	I4/mmm a=4.230 c=9.873 Pd d _{u=TM} = 3.241 AF@136,≈100,≈75H	
5d	I4/mmm	Р4/nmm	Р4/nmm	I4/mmm
	a=4.121	а=4.076	a=4.192	a=4.224
	c=9.648	с=9.783	c=9.687	c=10.32
	OS	Г	Рt	Au
	d _{∪-™} = 3.179	d _{U-TM} = 3.113	d _{U-TM} = 3.211	d _{∪:тм} = 3.334
	PP	AF@6K	AF@32K	T _m @19К
	AF antiferromagentic, F ferromagnetic, PP Pauli paramagnetic			



Unveiling *deep states* in UM_2Si_2 family: dual nature of 5*f* electrons

$$S(\vec{q},\omega) = \sum_{f} |\langle f|e^{i\vec{q}\cdot\vec{r}}|i\rangle|^2 \delta(E_i - E_f + \hbar\omega)$$

- a spectrum has the initial state $|i\rangle$ and final states $|f\rangle$ as input
- a good fit to the experimental spectrum means that one knows the initial state |i> and final states |f>
- our main goal is to know the initial state $|i\rangle$, e.g. the ground state
- we are actually not so much interested in the final states $|f\rangle$
- but observing that the final states |f > are made up of atomic multiplet states forces us to use an atomic ansatz for the initial state |i>
- this is why it is so important to see the "deep states" in the spectrum



Unveiling *deep states* in UM_2Si_2 family: dual nature of 5*f* electrons

Amorese-Marino-Sundermann-Severing PNAS 2020



- $\Gamma_1^{(1)}$ or Γ_2 singlet or • $\Gamma_2^{(1)}$ $\Gamma_2^{(1)}$ singlet or
- $\Gamma_1^{(1)}$ - Γ_2 quasi-doublet







What to do if one has difficulties to calculate the spectrum ?

$$S(\vec{q},\omega) = \sum_{f} |\langle f| \hat{O}(\vec{q}) |i\rangle|^2 \delta(Ei - Ef + \hbar\omega)$$

Do a sum-rule experiment \rightarrow integrate the spectrum over energy \rightarrow integrated intensity

$$\int S(\vec{q},\omega) \, d\omega = \sum_{f} |\langle f| \, \hat{O}(\vec{q}) \, |i\rangle|^2 = \sum_{f} \langle i| \, \hat{O}(\vec{q}) \, |f\rangle \, \langle f| \, \hat{O}(\vec{q}) \, |i\rangle$$

$$\vec{q} \text{ dependent expectation value of the ground state} = \langle i| \, \hat{O}(\vec{q}) \hat{O}(\vec{q}) | i\rangle$$

$$me \text{ will now do s-NIXS:} = \langle i| \, \hat{O}_{sd}(\vec{q}) \hat{O}_{sd}(\vec{q}) | i\rangle$$

$$\text{there is absolutely no need to know about the final states}$$



s-NIXS

$(s \rightarrow d)$

Max-Planck P01 NIXS beamline PETRA III - Hamburg





direct imaging of orbitals using *s*-NIXS



 $(\mathbf{S} \rightarrow d)$

s-NIXS



Yavas et al., Nat. Phys. 15, 559 (2019)



Amorese et al., PRX 11, 011002 (2021)

Leedahl et al., Nat. Comm. 10, 5447 (2019)



s-NIXS

Leedahl

Spin-state transition in LaCoO₃



Spin-state transition in LaCoO₃



- clear change in *d*-charge density
- within DFT : huge change in band structure
- can DFT reproduce the *d*-charge density ?

this is not about spectra, this is about the charge density for which DFT is supposed to do well ...

s-NIXS

Chang-Dolmantas

Metal-insulator transition in Ti_2O_3







s-NIXS

Chang-Dolmantas

Metal-insulator transition in Ti_2O_3











work in progress Orbital imaging with VB-HAXPES

Takegami PhD-thesis

S.M. Goldberg, C.S. Fadley, and S. Kono, SSC 28, 459 (1978); J. Elect. Spect. Rel. Phen. 21, 285 (1981): PES theory - free atoms



Orbital imaging with VB-HAXPES

work in progress

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Orbital imaging with s-NIXS

Sum-rules for core-level non-resonant Inelastic X-ray Scattering - a tool to observe the one particle density matrix of the electron conduction orbitals

M. Sundermann^{1,2} and M. W. Haverkort³

of the transition is equal to the angular momentum of the shell one excites into $k = l_2$ and there is only one angular momentum transfer possible k' = k. For excitations into the p shell one measures a dipole transition, for excitations into the d shell quadrupole, f shell octupole etc. The integrated intensity measures the operator:

$$T_{n_{1},l_{1}=0,n_{2},l_{2}}^{\dagger}T_{n_{1},l_{1}=0,n_{2},l_{2}} = \sum_{\sigma_{2},m_{2},m_{2}'} \langle R(r)_{n_{2},l_{2}} | j_{k}(qr) | R(r)_{n_{1},l_{1}=0} \rangle^{2}$$

$$\times (-1)^{(m_{2}+m_{2}')} 2(2l_{2}+1)^{3}$$

$$\times \begin{pmatrix} l_{2} \ l_{2} \ 0 \\ 0 \ 0 \ 0 \end{pmatrix} \begin{pmatrix} l_{2} \ l_{2} \ 0 \\ -m_{2} \ m_{2} \ 0 \end{pmatrix} \begin{pmatrix} l_{2} \ l_{2} \ 0 \\ -m_{2}' \ m_{2}' \ 0 \end{pmatrix}$$

$$\times C_{m_{2}'}^{(l_{2})}(\theta_{q}\phi_{q}) C_{m_{2}}^{(l_{2})*}(\theta_{q}\phi_{q}) a_{n_{2},l_{2},m_{2}',\sigma_{2}} a_{n_{2},l_{2},m_{2},\sigma_{2}}^{\dagger},$$

$$(15)$$

which simplifies to:

$$T_{n_1,l_1=0,n_2,l_2}^{\dagger} T_{n_1,l_1=0,n_2,l_2} = \sum_{\sigma_2,m_2,m_2'} \langle R(r)_{n_2,l_2} | j_k(qr) | R(r)_{n_1,l_1=0} \rangle^2 2(2l_2+1)$$

$$\times C_{m_2'}^{(l_2)}(\theta_q \phi_q) C_{m_2}^{(l_2)*}(\theta_q \phi_q) a_{n_2,l_2,m_2',\sigma_2} a_{n_2,l_2,m_2,\sigma_2}^{\dagger},$$
(16)

The operator $a_{n_2,l_2,m'_2,\sigma_2} a^{\dagger}_{n_2,l_2,m_2,\sigma_2}$ measures the hole density matrix, The q dependent prefactor $C^{(l_2)}_{m'_2}(\theta_q\phi_q)C^{(l_2)*}_{m_2}(\theta_q\phi_q)$ creates a function that is proportional to the square of the orbital given by the quantum numbers $l_2 m_2$ and m'_2 , i.e. the density of that orbital (see also Eq. 8). The sum over m_2 and m'_2 thus creates a function proportional to the angular distribution of the hole density. A full angular map of the intensity determines the density matrix of the valence orbital of the edge under consideration.



pre-K-edge XAS

Sundermann

dipole vs. quadrupole









