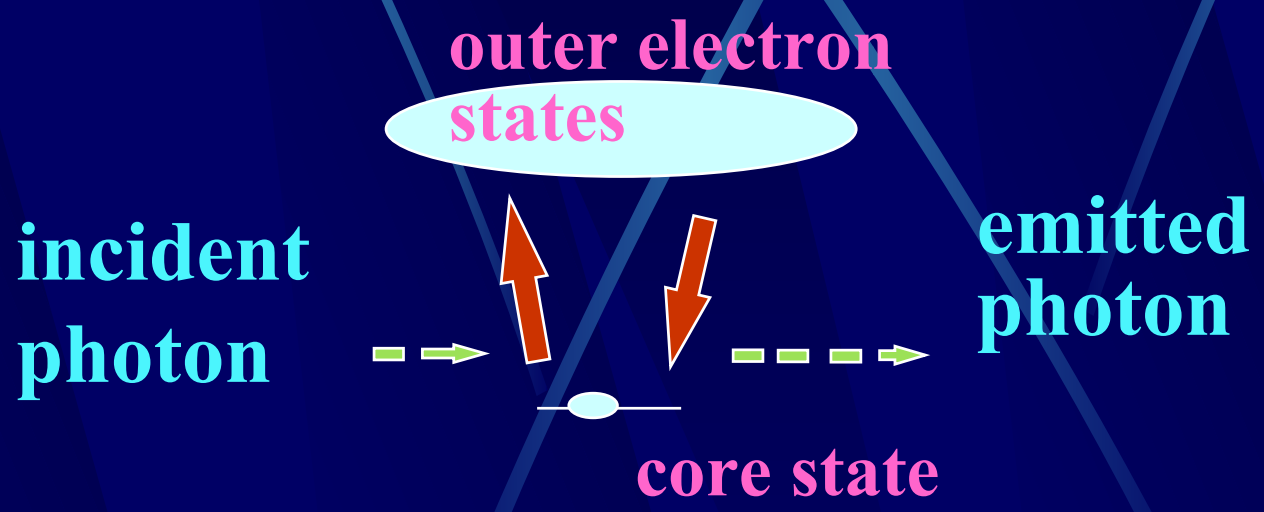
ALS Workshop
October 19, 2004

Magnetic Circular Dichroism of Resonant X-ray Emission Spectroscopy in Rare Earth Systems

RIKEN/Spring-8 and PF-KEK

A. Kotani

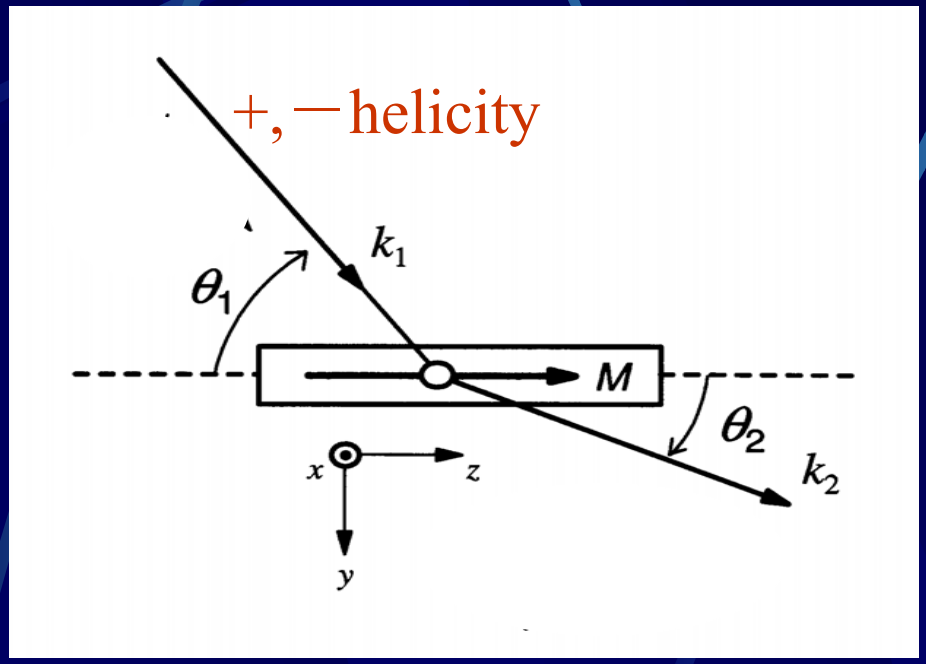
Resonant X-Ray Emission Spectroscopy (RXES)



Coherent second order optical formula:

$$F(\Omega,\omega) = \sum_f \left| \sum_m \frac{\langle f|T_2|m\rangle\langle m|T_1|g\rangle}{E_g + \Omega - E_m + i\Gamma_m} \right|^2 \delta(E_g + \Omega - E_f - \omega),$$

Magnetic Circular Dichroism in RXES (MCD-RXES)



$$\theta_1 = 0$$

Longitudinal Geometry

$$\theta_1 = 90 \text{ deg}$$

Transverse Geometry

$$\Delta F \equiv F^- - F^+$$

1. Longitudinal and Transverse Geometries in MCD-RXES

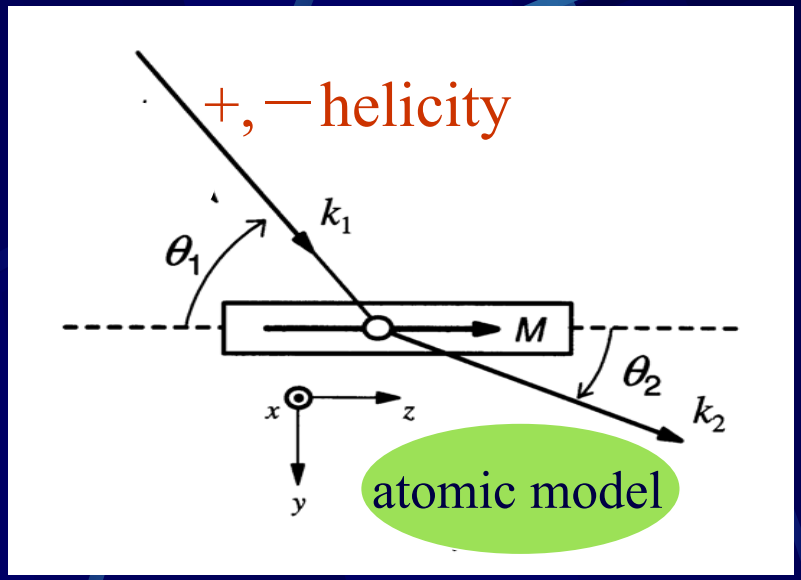
2. Longitudinal Geometry

Excitation spectrum of MCD-RXES:

A powerful tool of high resolution MCD-XAS (XMCD)

3. Transverse Geometry

Longitudinal and Transverse Geometries in MCD-RXES



$$F^{\lambda_1}(\omega_1,\omega_2) = \sum_{f,\lambda_2}\left|\sum_m \frac{\langle f|T_2^{\lambda_2}|m\rangle\langle m|T_1^{\lambda_1}|g\rangle}{E_m - E_g - \omega_1 + i\Gamma_m}\right|^2 \delta(E_f+\omega_2-E_g-\omega_1)$$

$$= \sum_{f,\lambda_2}\sum_m \left|\frac{\langle f|T_2^{\lambda_2}|m\rangle\langle m|T_1^{\lambda_1}|g\rangle}{E_m - E_g - \omega_1 + i\Gamma_m}\right|^2 \delta(E_f+\omega_2-E_g-\omega_1)$$

$$+ \sum_{f,\lambda_2}\sum_{m,m'} \left\{ \frac{\langle f|T_2^{\lambda_2}|m\rangle\langle m|T_1^{\lambda_1}|g\rangle \left(\langle f|T_2^{\lambda_2}|m'\rangle\langle m'|T_1^{\lambda_1}|g\rangle\right)^*}{(E_m - E_g - \omega_1 + i\Gamma_m)(E_{m'} - E_g - \omega_1 - i\Gamma_{m'})} + \text{c.c.} \right\}$$

$$\times\delta(E_f+\omega_2-E_g-\omega_1),$$

$$\Delta F \equiv F^- - F^+$$

$$\Delta F = -\frac{1}{2}\cos\theta_1 \Big[(1+\cos^2\theta_2)$$

$$\times \left(|f_{+1,+1}|^2 + |f_{-1,+1}|^2 - |f_{-1,-1}|^2 - |f_{+1,-1}|^2\right)$$

$$+2\sin^2\theta_2 \left(|f_{0,+1}|^2 - |f_{0,-1}|^2\right)\Big]$$ -- diagonal term

$$-\frac{1}{4}\sin\theta_1 \sin 2\theta_2$$ -- interference term

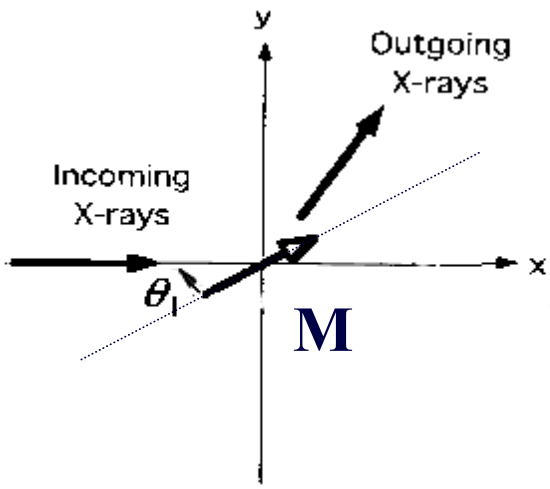
$$\times \Big[(f^*_{-1,0} f_{0,-1} + f^*_{0,-1} f_{-1,0})$$

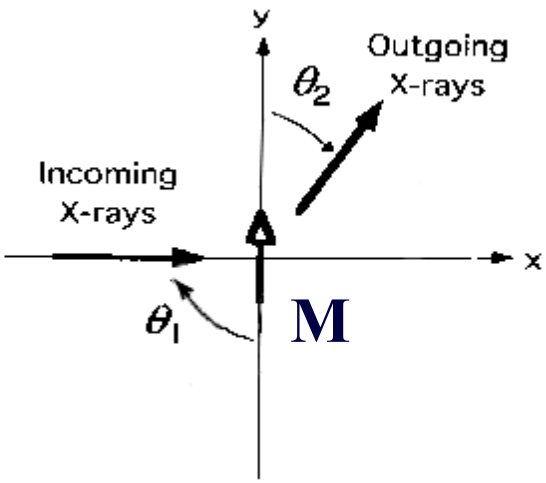
$$-(f^*_{+1,0} f_{0,+1} + f^*_{0,+1} f_{+1,0})$$

$$+(f^*_{-1,+1} f_{0,0} + f^*_{0,0} f_{-1,+1})$$

$$-(f^*_{+1,-1} f_{0,0} + f^*_{0,0} f_{+1,-1})\Big],$$

Longitudinal and Transverse Geometry





Longitudinal Geometry

$\theta_1 \sim 0$

Diagonal term

Transverse Geometry

$\theta_1 = 90$ deg

100% Interference term

θ_2 **- dependence:** $\sin 2\theta_2$

2. Longitudinal Geometry

The case of simple RXES

Excitation spectrum of RXES:

A powerful tool to detect hidden structures in XAS

K. Hamalainen et al. (1991)

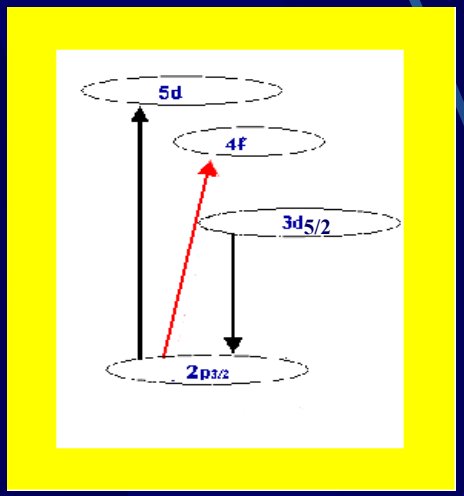
Extension to MCD-RXES

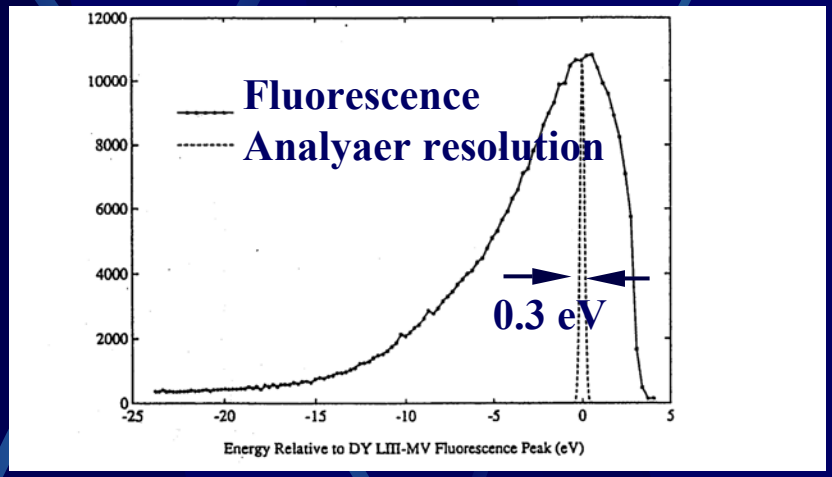
Excitation spectrum of MCD-RXES:

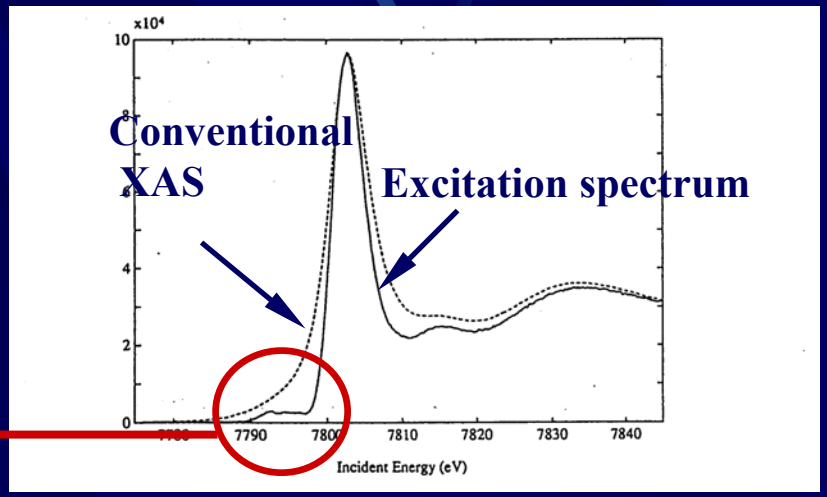
A powerful tool to detect hidden structures in MCD-XAS (XMCD)

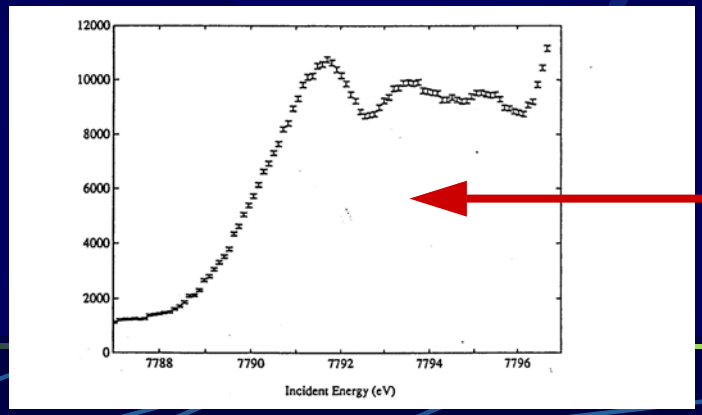
Detection of hidden structure in XAS

Excitation spectrum for $Dy(NO_3)_3$



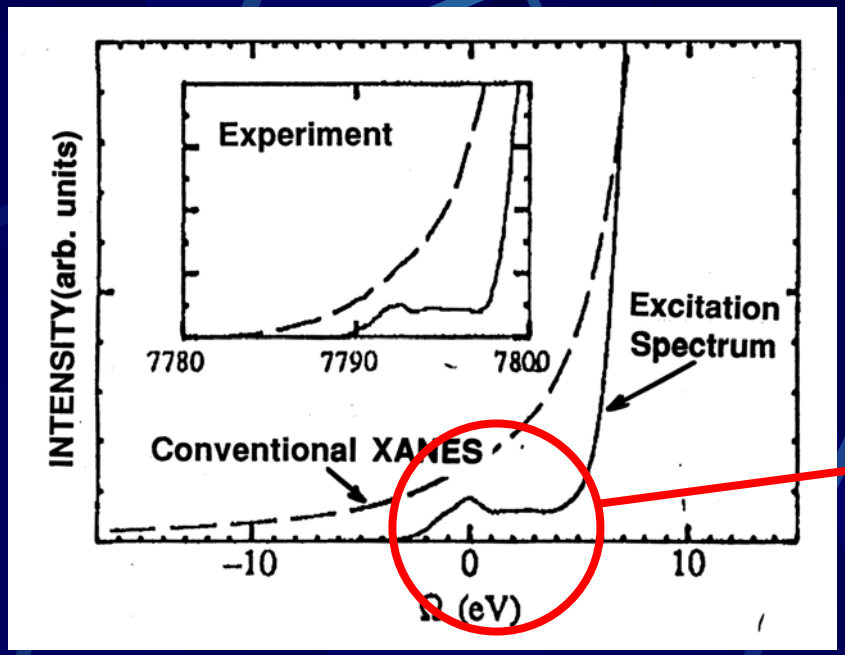


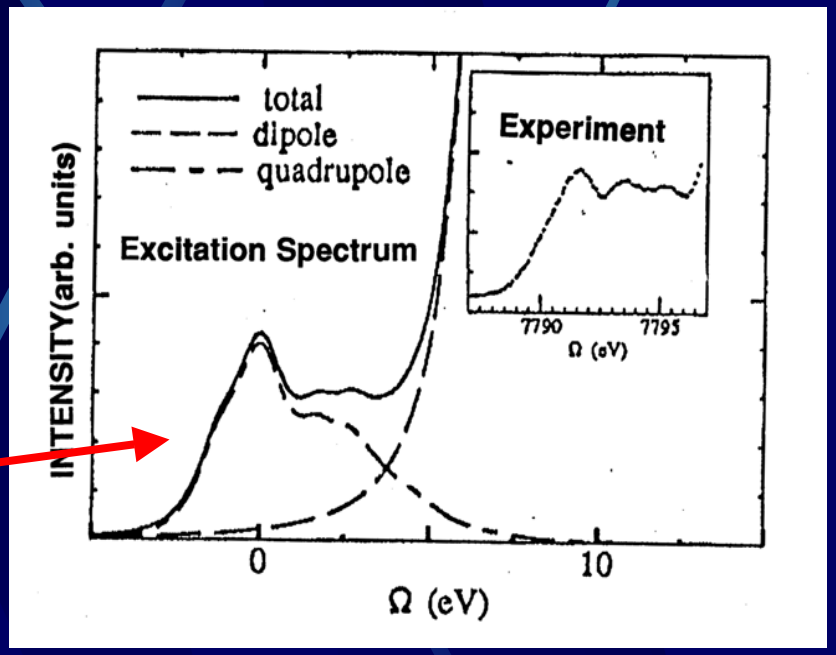




K. Hamalainen et al.
Phys. Rev. Lett. 67, 2850 (1991)

Theoretical calculation





$$S(\Omega,\omega) = \sum_j \left| \sum_i \frac{< j|T_2^\dagger|i >< i|T_1|g >}{E_g + \Omega - E_i - i\Gamma_L} \right|^2 \frac{\Gamma_M/\pi}{(E_j + \omega - E_g - \Omega)^2 + \Gamma_M^2}$$

$\Gamma_L = 2.1$ eV

$\Gamma_M = 0.7$ eV

S. Tanaka, K. Okada and A.Kotani : J. Phys.Soc. Jpn. 63, 2780 (1994)

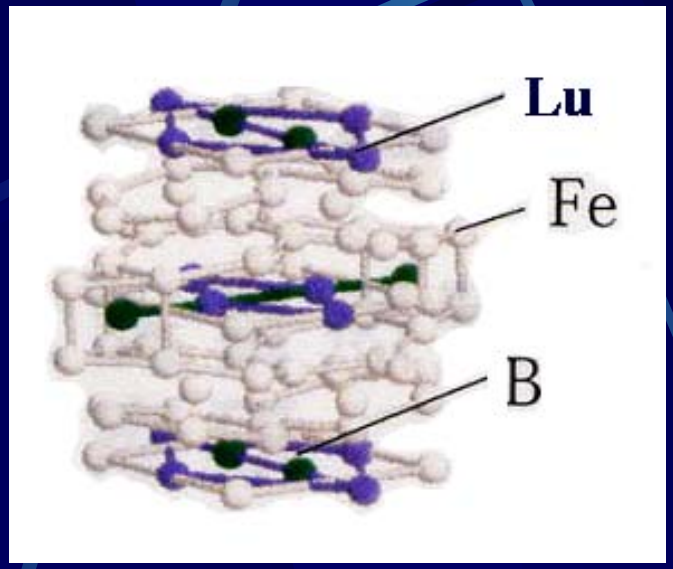
Excitation spectrum of MCD-RXES

A powerful tool to detect hidden structures in MCD-XAS (XMCD)

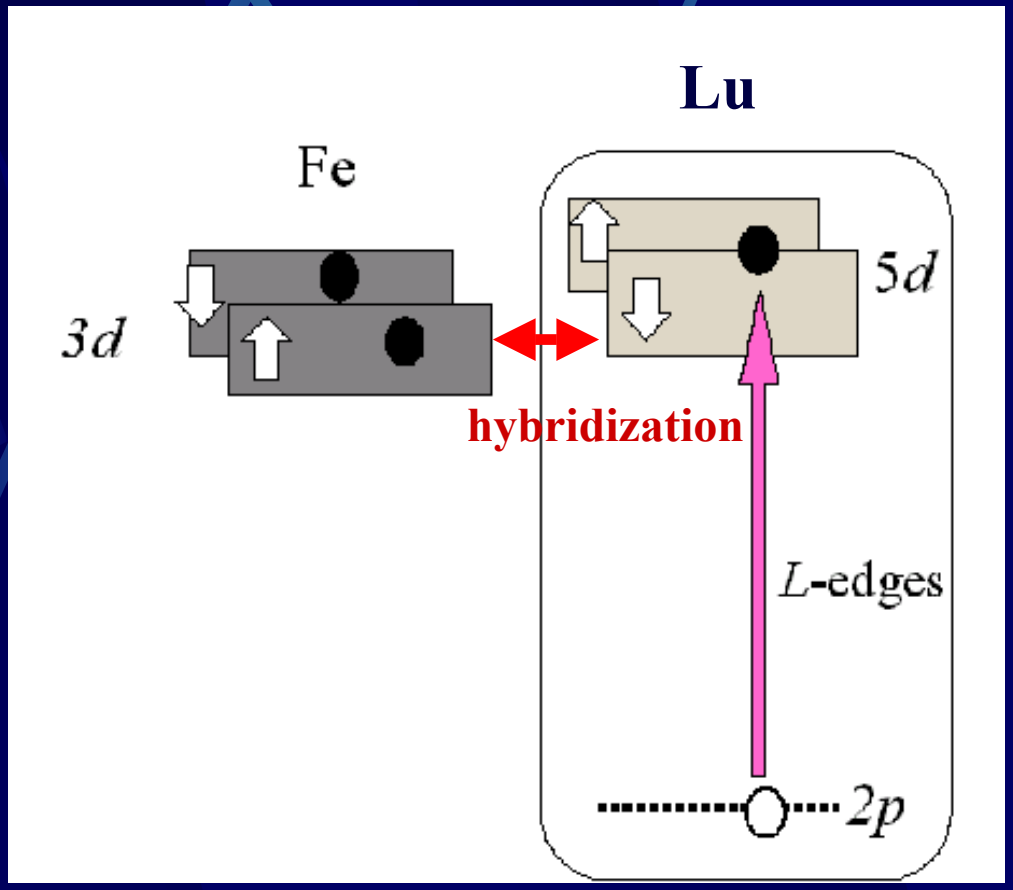
Theoretical calculations on hidden structures in XMCD of

1. ferromagnetic Lu compound
   $Lu_2Fe_{14}B$
2. mixed-valence compound
   $CeFe_2$

XAS and XMCD of $Lu_2Fe_{14}B$



Model

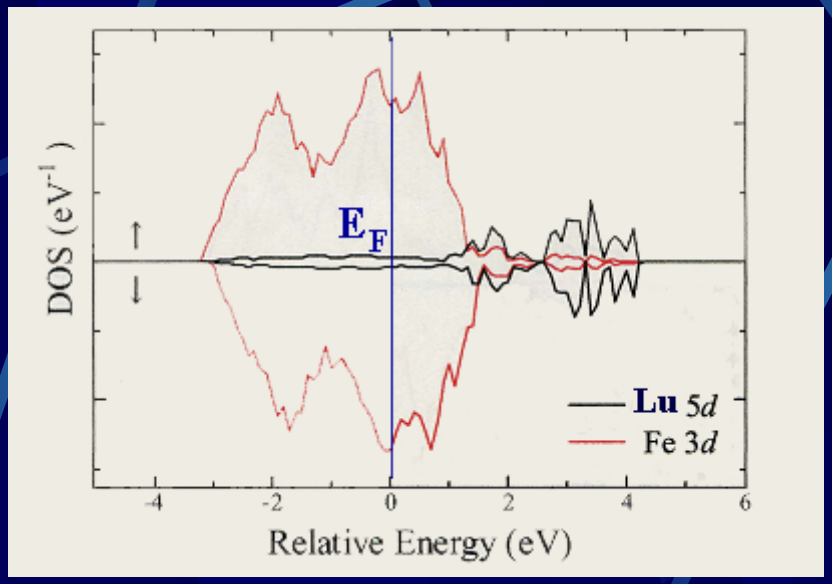


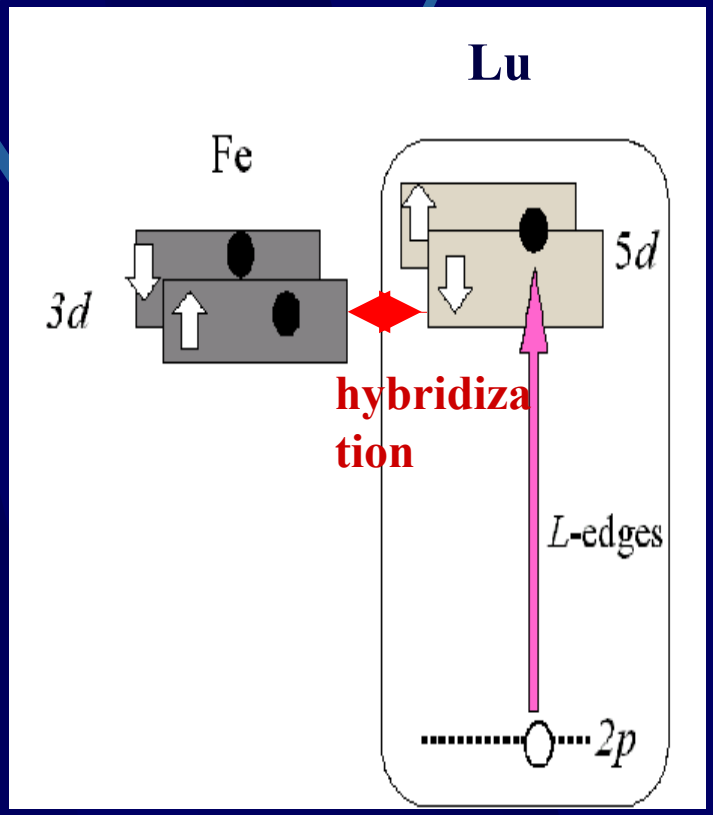
Fe 3d – Lu 5d states :

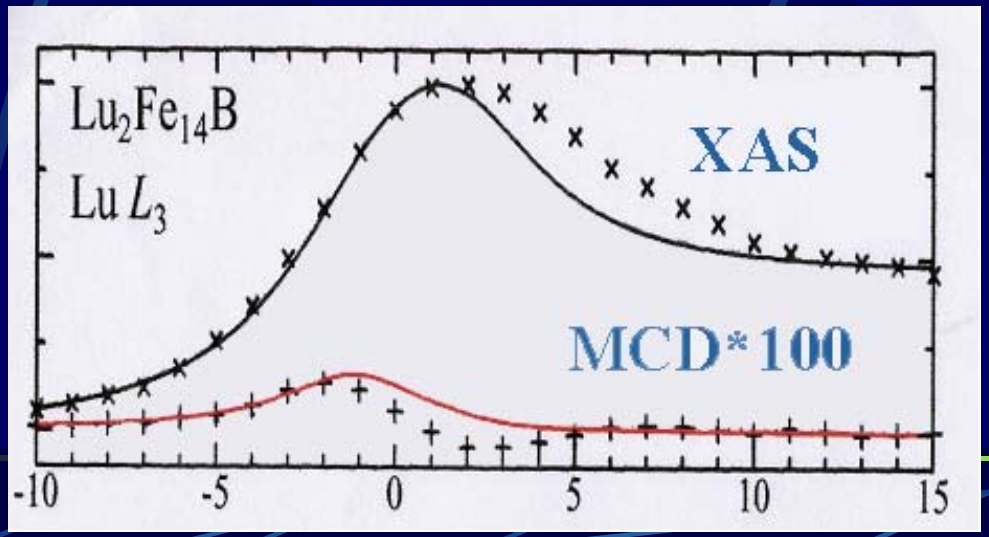
LCAO by tight-binding band calculation

K. Asakura, A. Kotani and I. Harada (unpublished)

XAS and XMCD of $Lu_2Fe_{14}B$

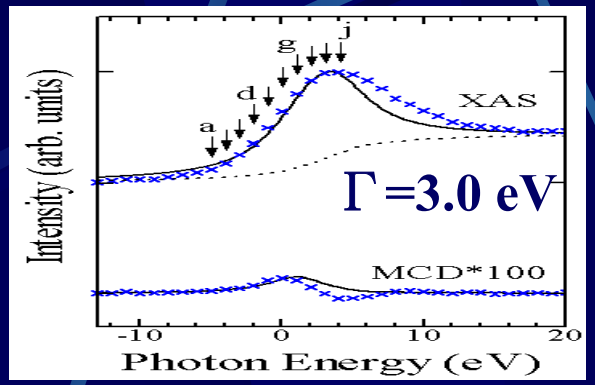




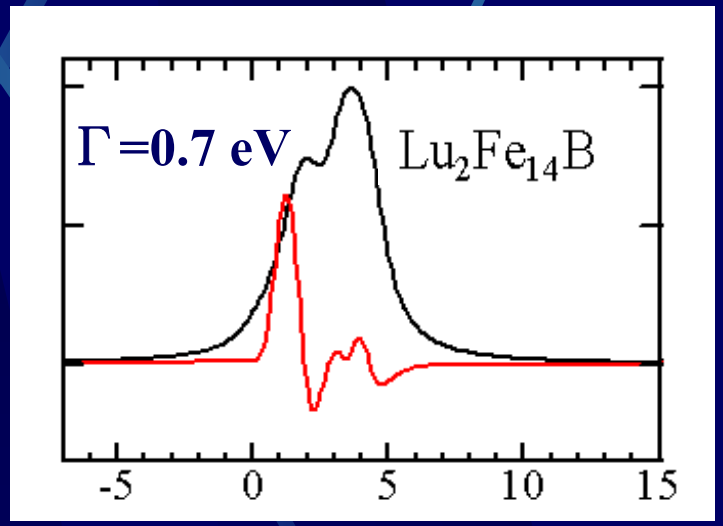


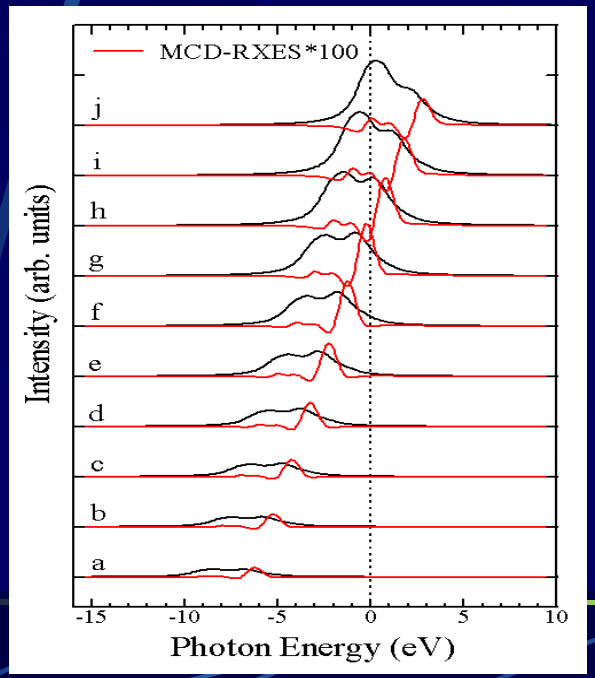
Experiment: J . Chaboy et al., J. Phys. IV FRANCE 7 (1997) C2-449.

RXES and excitation spectrum

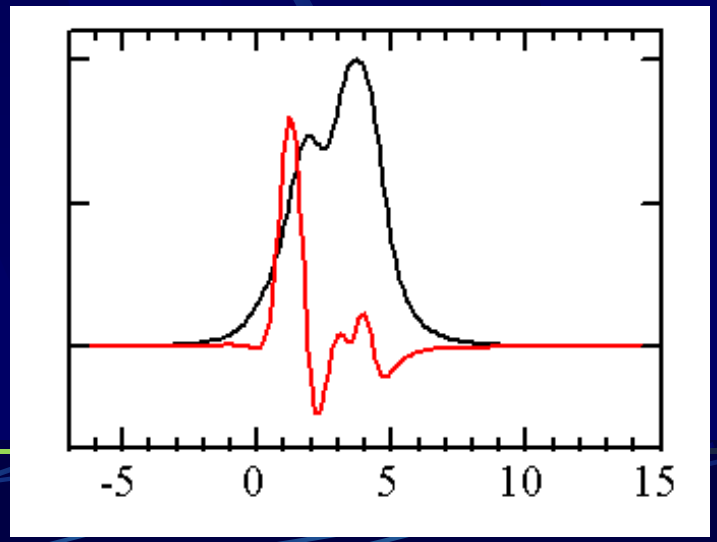


Reduced Γ

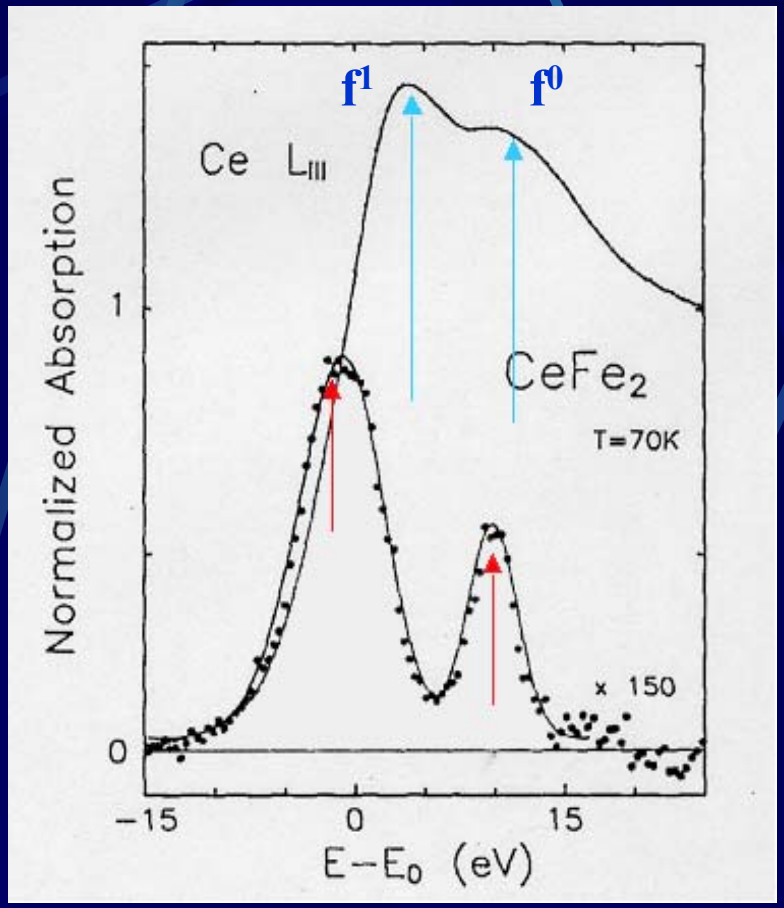




Excitation spectrum



MCD in Ce L_3 XAS of $CeFe_2$



Peak position and the width of XAS differ from those of XMCD.

Experiment: C. Giorgetti et al., Phys. Rev. B 48 (1993) 12732.

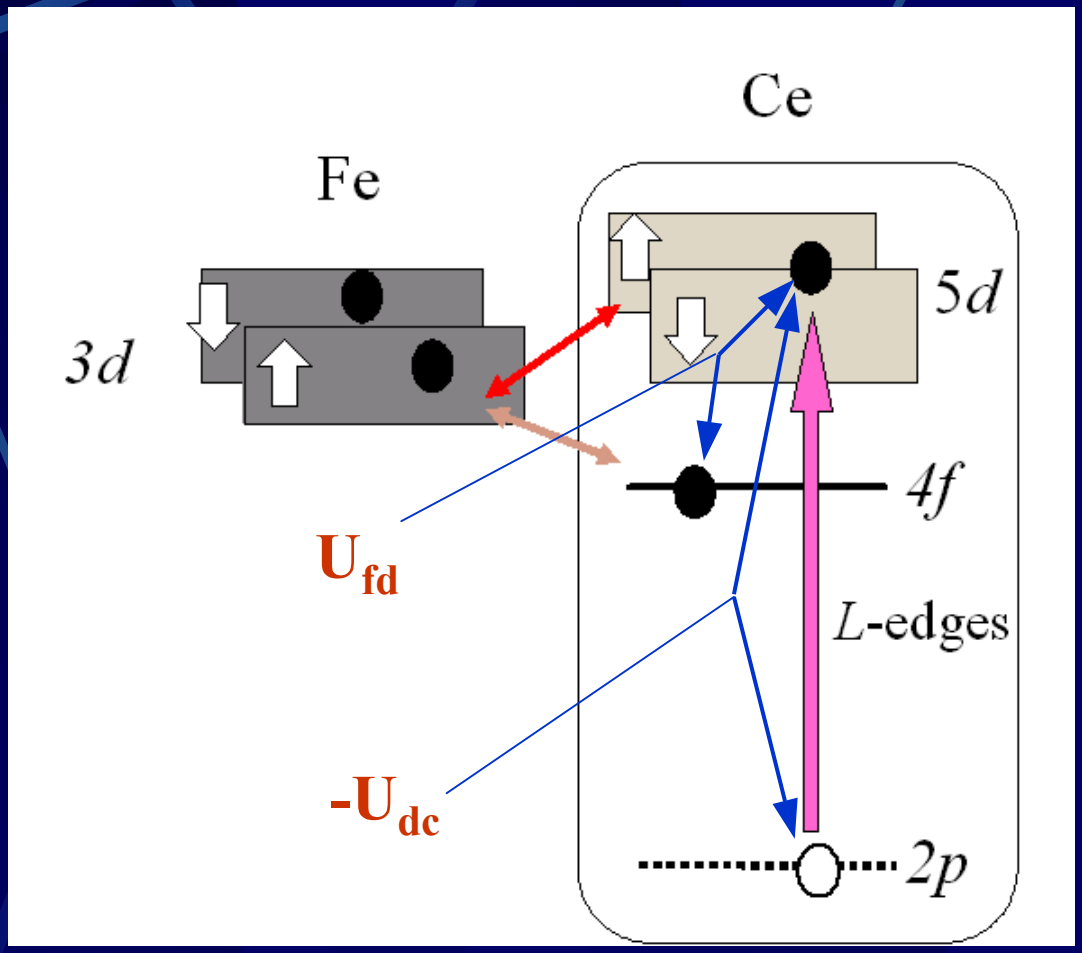
Model

Fe 3d – Ce 5d states :

LCAO for $Ce_{35}Fe_{76}$ cluster model

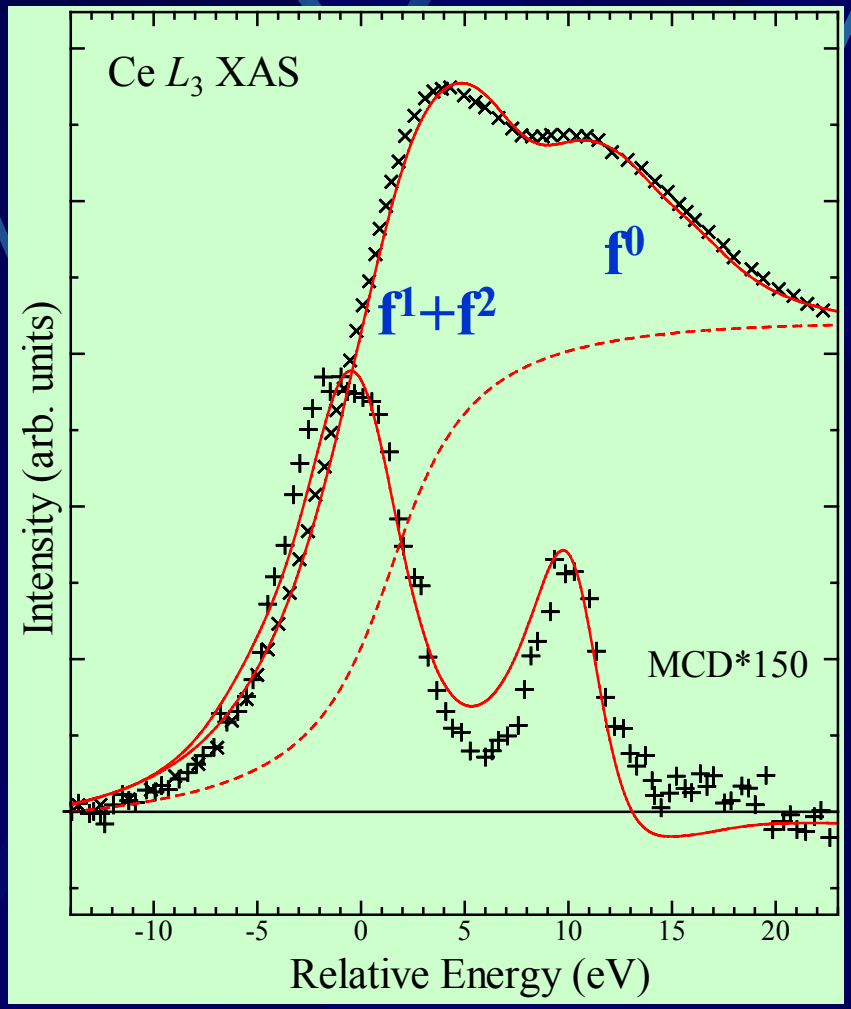
Ce 4f mixed valence effect:

Single impurity Anderson model with $4f^0$, $4f^1$ and $4f^2$ configurations



K. Asakura, K. Fukui, H. Ogasawara, I. Harada, J. C. Parlebas and A. Kotani: J. Phys. Soc. Jpn (2004)

Comparison with Experiments



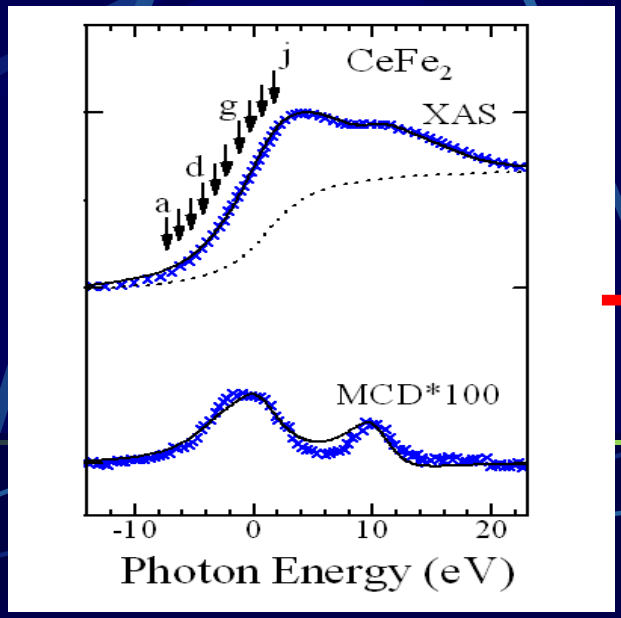
Parameters:

$\varepsilon_f = -0.7$, $U_{dc} = 2.0$ (eV)

$U_{fc} = 10.5$, $U_{fd} = 1.7$

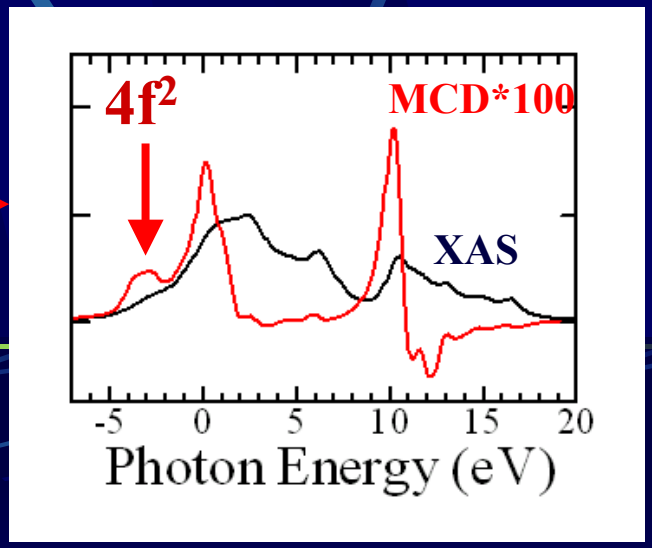
$U_{ff} = 7.5$, $(df\sigma) = 0.35$

Where is $4f^2$?



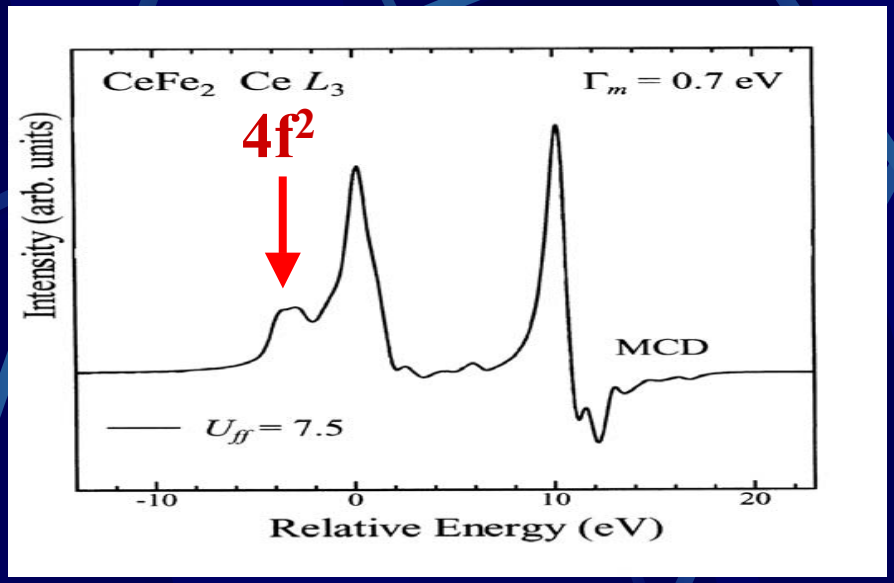
Reduced Γ

Γ =0.7 eV

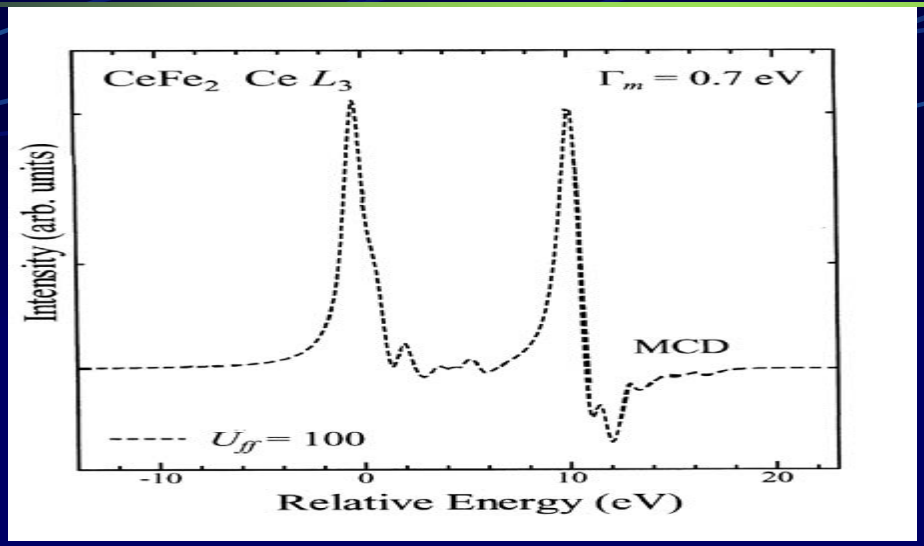


K. Asakura, A. Kotani and I. Harada (unpublished)

Where is $4f^2$?

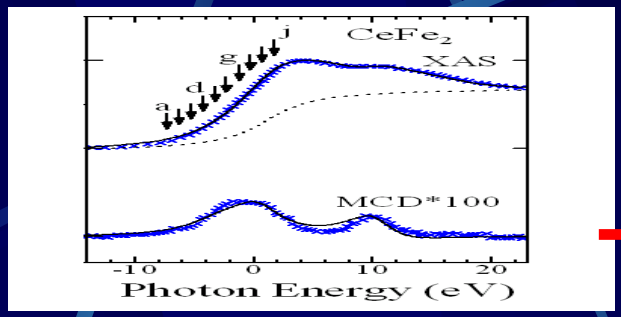


with $4f^2$

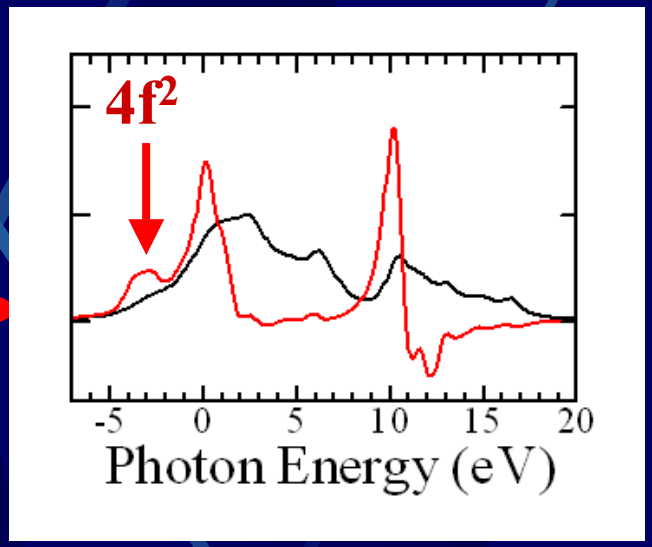


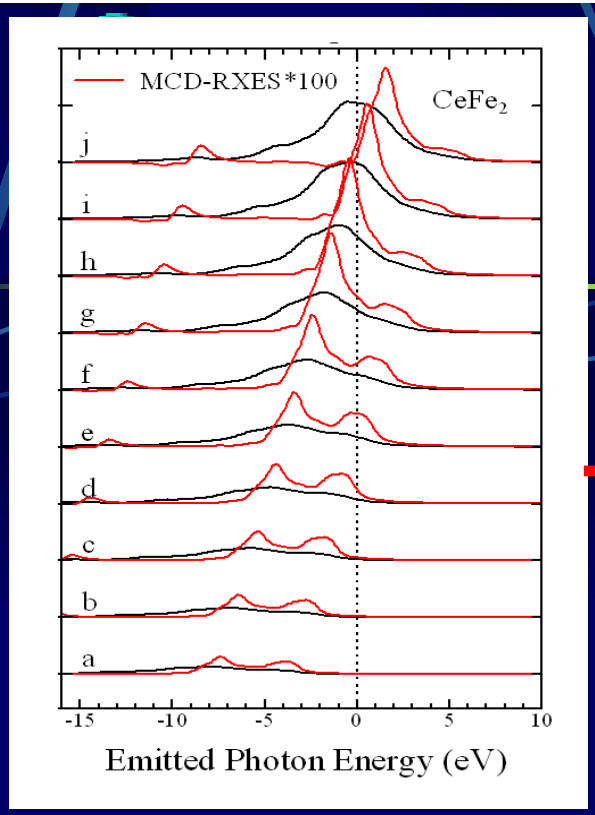
without $4f^2$

Where is $4f^2$?

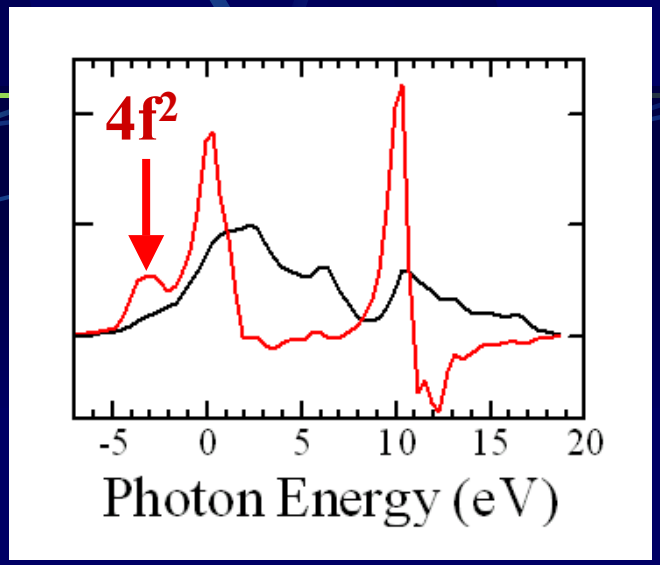


Reduced Γ





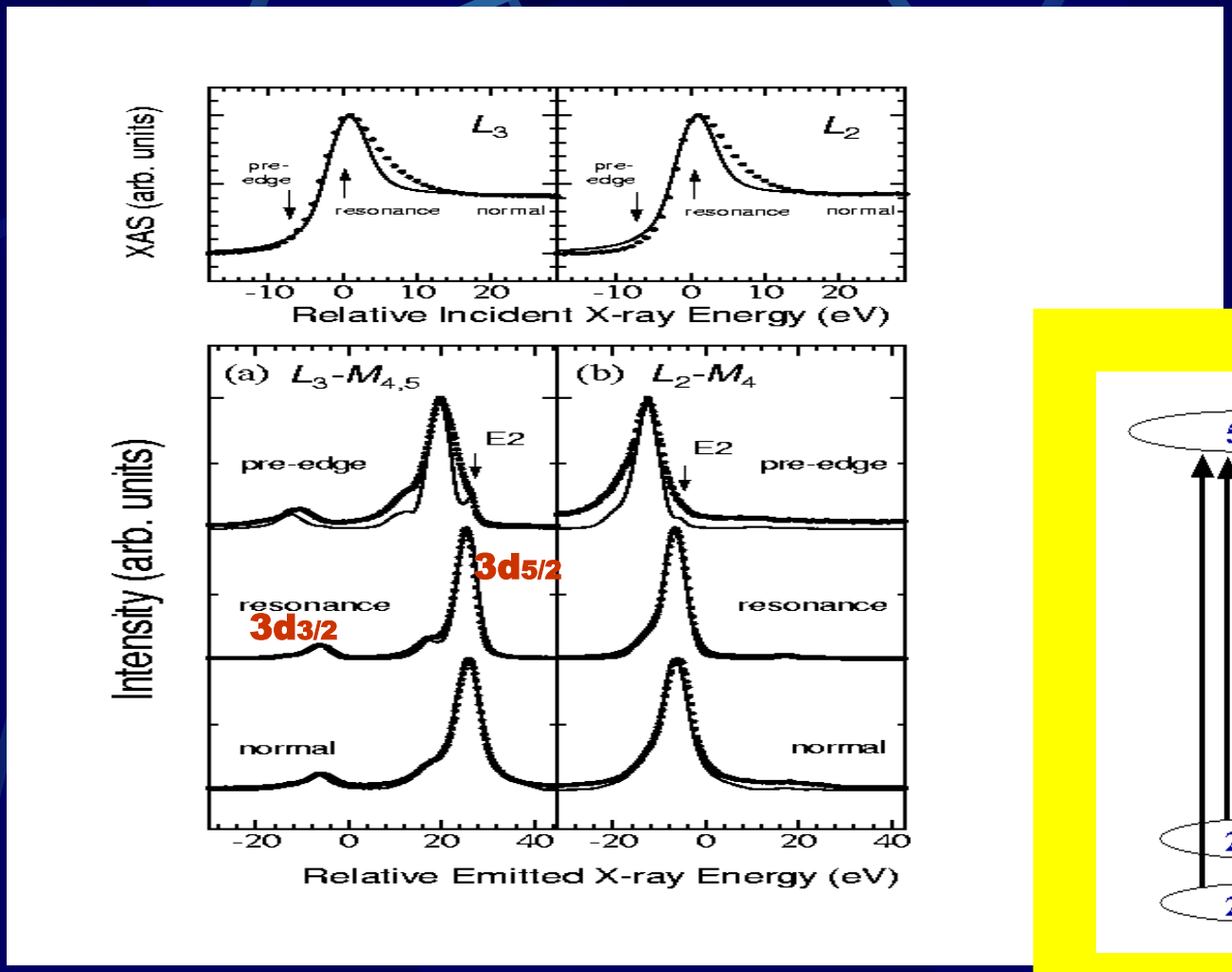
Excitation spectrum

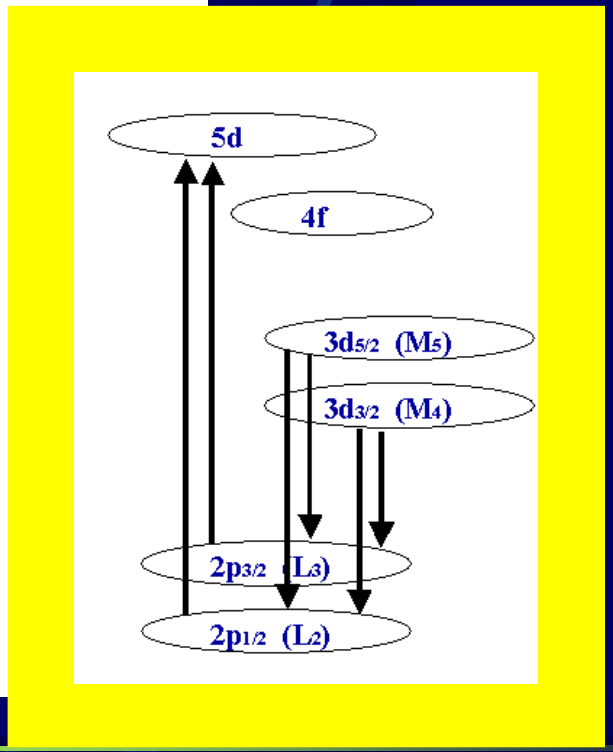


K. Asakura, A. Kotani and I. Harada (unpublished)

3. Transverse Geometry

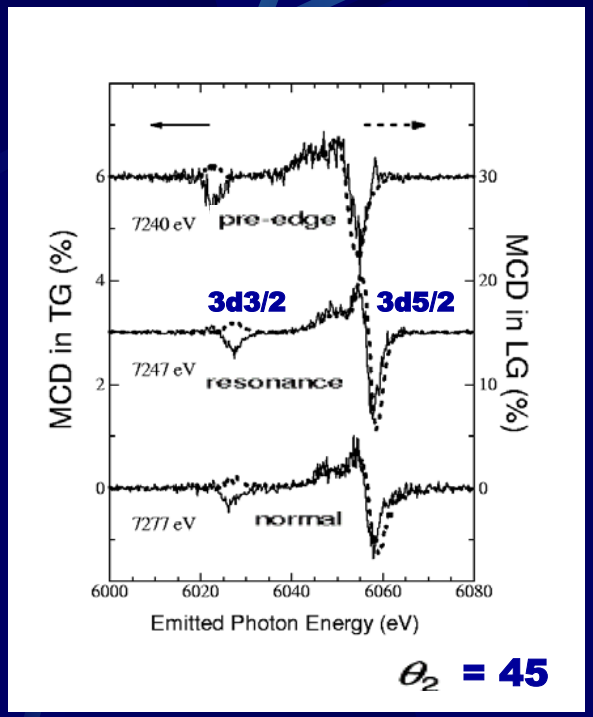
Gd L_{23} XAS and L_{23}-M_{45} RXES in $Gd_{33}Co_{67}$



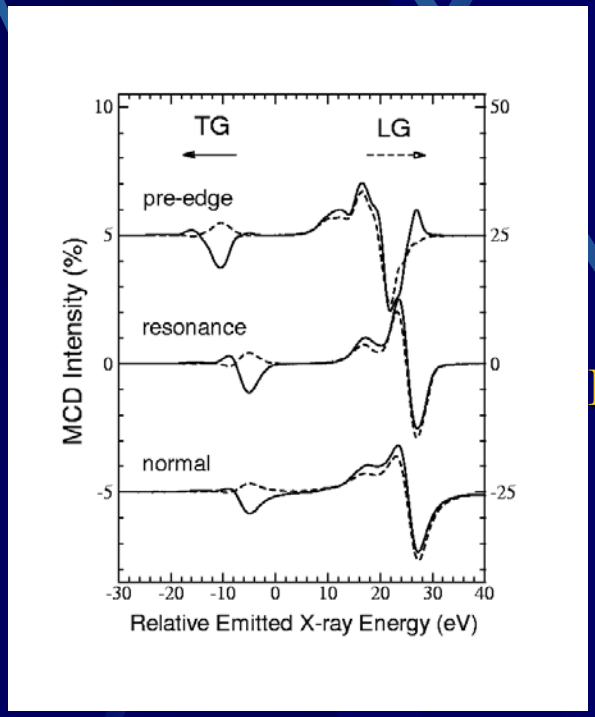


Experiment: Iwazumi et al. Theory: Fukui et al.
J. Phys. Soc. Jpn. 70 (2001) 1230; 70 (2001) 3457.

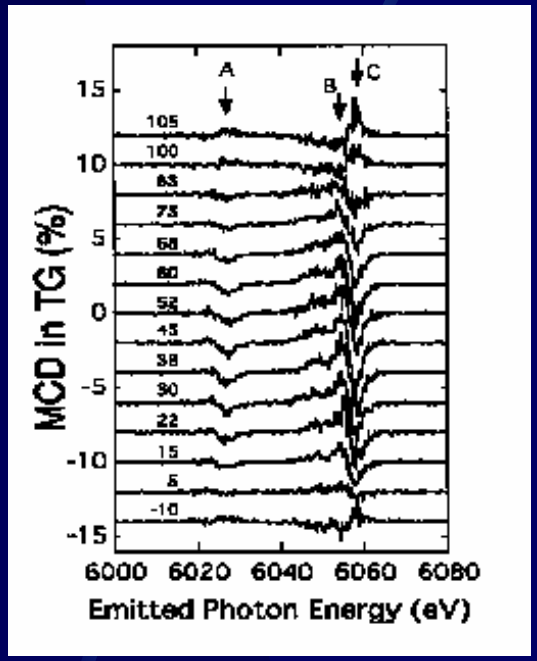
Experiment and Theory



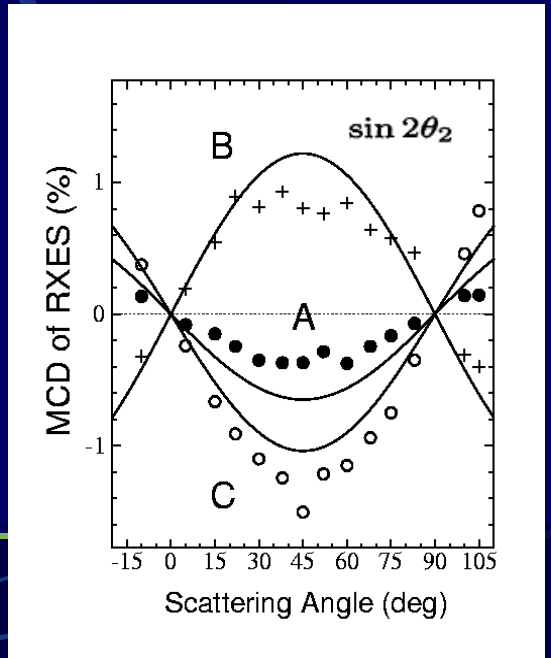
Experiment



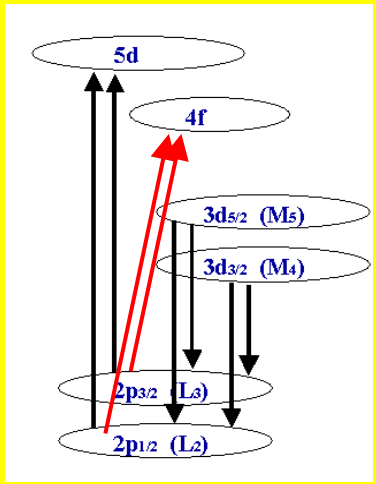
Theory

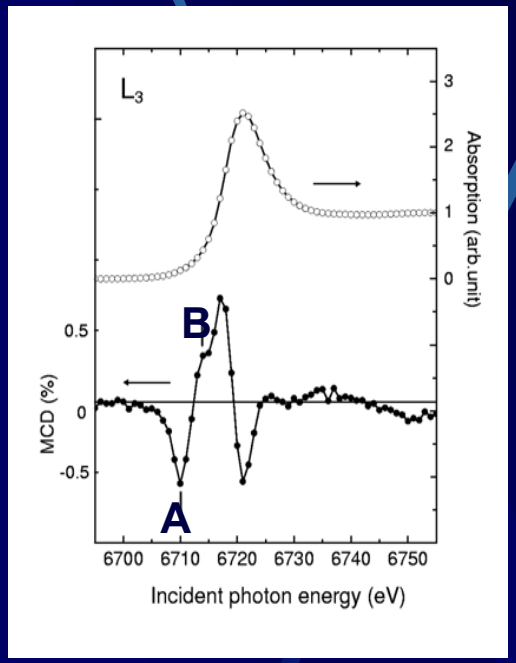


Emission angle dependence



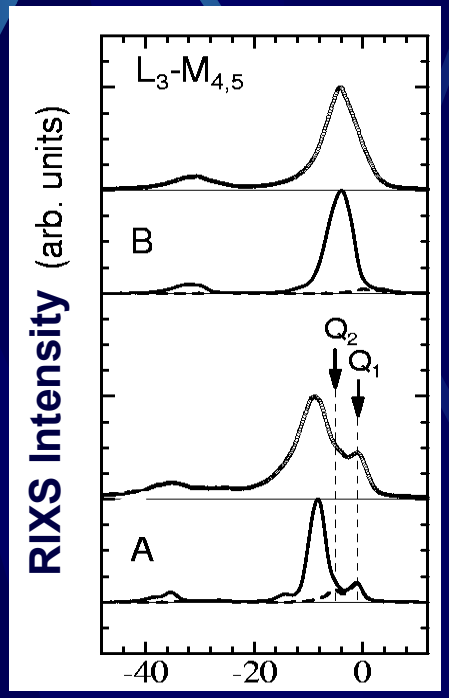
Experiment and Theory (EQ excitation in Sm-Co)

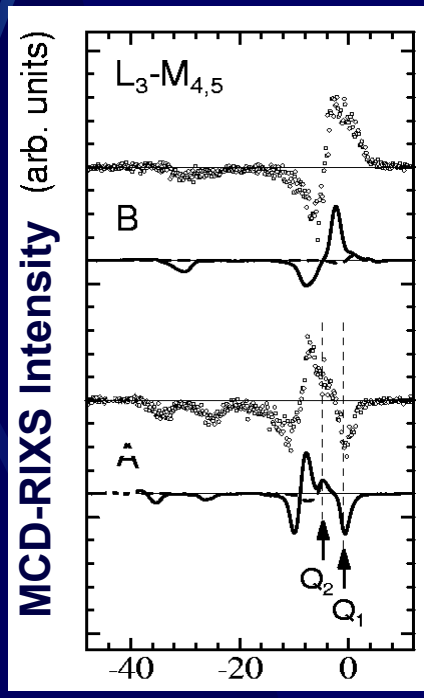




$\theta_1 = 36.9$ deg

$\theta_2 = -35.3$deg





Relative Emitted X-Ray Energy (eV)

Expt: Nakamura et al.
Calc: Fukui and Kotani

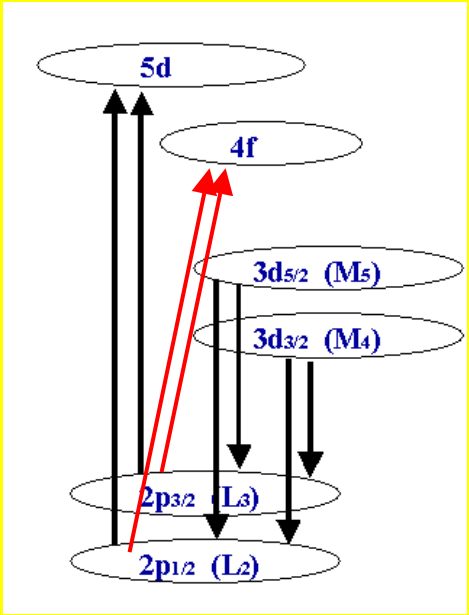
T. Nakamura et al. : Phys. Rev. B 67, 94439 (2003)

Angle Dependence in MCD-RXES by Quadrupole Excitation

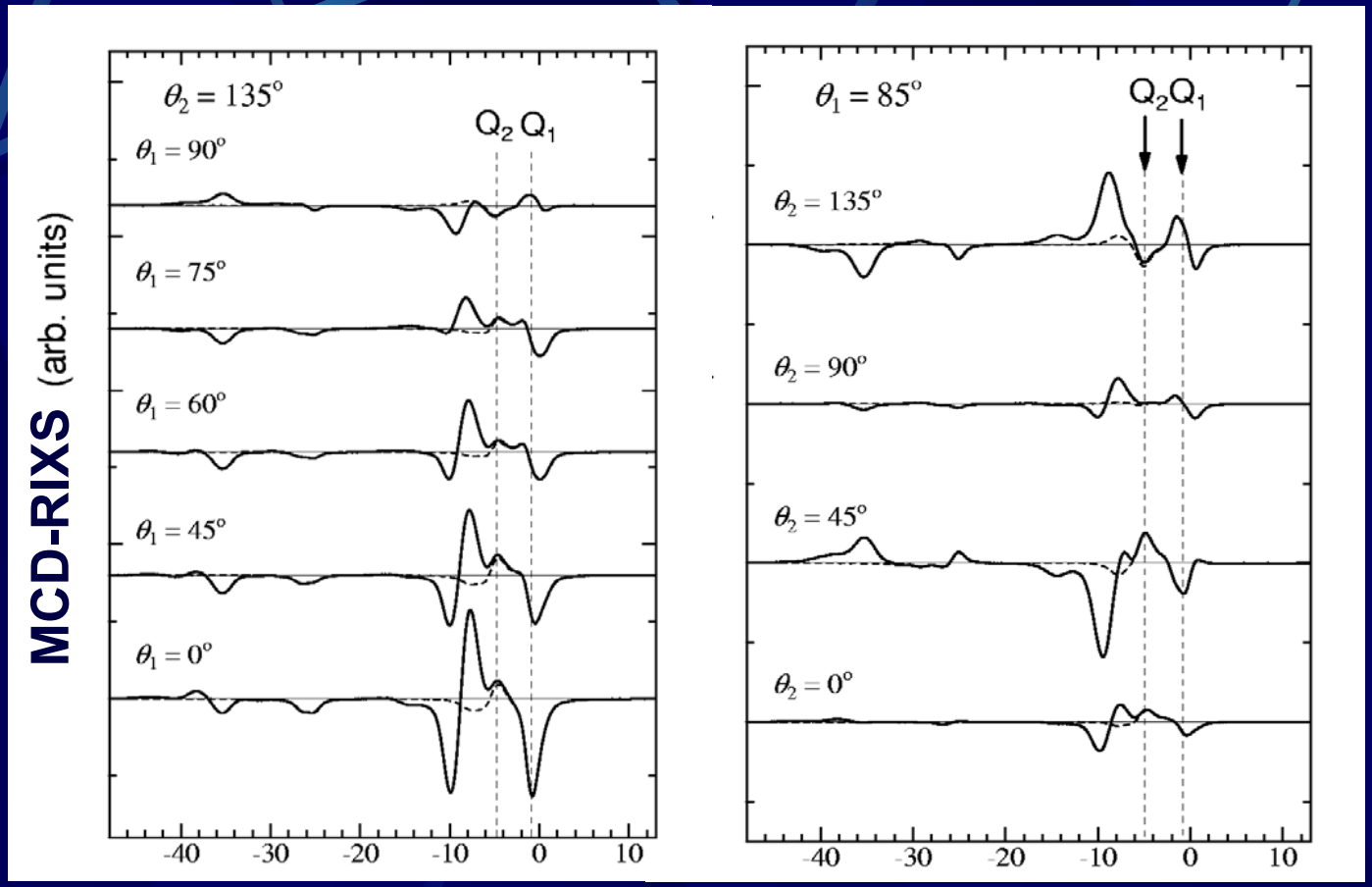
$$\Delta F = -\frac{1}{6}\cos\theta_1 \left\{ \sin^2\theta_1 \left[(\cos^2\theta_2 + 1)F_1 + 2\sin^2\theta_2 F_2 \right] + \cos 2\theta_1 \left[(\cos^2\theta_2 + 1)F_3 + 2\sin^2\theta_2 F_4 \right] \right\}$$
$$- \frac{1}{12}\sin\theta_1 \left[-\sqrt{\frac{1}{2}}(\cos 2\theta_1 + \cos^2\theta_1)\sin 2\theta_2 F_5 + \sqrt{3}\cos^2\theta_1 \sin 2\theta_2 F_6 - \sqrt{\frac{3}{2}}\sin 2\theta_1 \sin^2\theta_2 F_7 \right],$$

where

$$F_1 = |f_{+1,+2}|^2 + |f_{-1,+2}|^2 - |f_{+1,-2}|^2 - |f_{-1,-2}|^2$$
$$F_2 = |f_{0,+2}|^2 - |f_{0,-2}|^2$$
$$F_3 = |f_{+1,+1}|^2 + |f_{-1,+1}|^2 - |f_{+1,-1}|^2 - |$$
$$F_4 = |f_{0,+1}|^2 - |f_{0,-1}|^2$$
$$F_5 = f^*_{+1,+1} f_{0,+2} + f_{+1,+1} f^*_{0,+2} - f^*_{0,+1} f_{-1,+2} + f_{0,+1} f^*_{-1,+2} - f^*_{0,-2} f_{-1,-1} + f_{0,-2} f^*_{-1,-1}$$
$$F_6 = f^*_{+1,0} f_{0,+1} + f_{+1,0} f^*_{0,+1} - f^*_{0,-1} f_{-1,0} + f_{0,-1} f^*_{-1,0}$$
$$F_7 = f^*_{+1,0} f_{-1,+2} + f_{+1,0} f^*_{-1,+2} - f^*_{+1,-2} f_{-1,0} + f_{+1,-2} f^*_{-1,0}$$



Theoretical Prediction



Relative Emitted X-Ray Energy (eV)

K. Fukui and A. Kotani : J. Phys. Soc. Jpn. 73, 1059 (2004).

Conclusion

- **Longitudinal Geometry of MCD-RXES**

  Excitation spectrum of L_3-M_5 MCD-RXES is a powerful tool to detect fine structures of L_3 MCD-XAS beyond the lifetime broadening of the L_3 core hole.

- **Transvers Geometry of MCD-RXES**

  We can measure 100% interference term in the second order optical process.

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