Anomalous XRD

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2023 XRD Summer School August 18th, 2023

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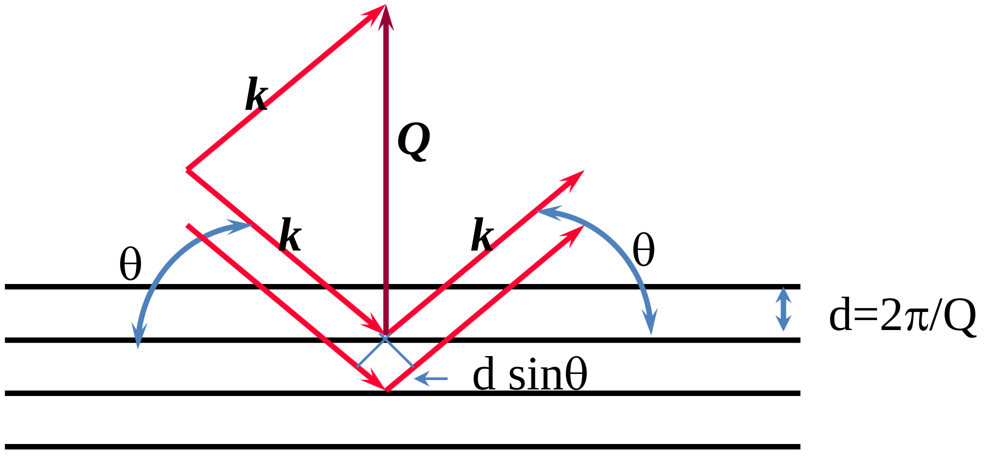
Outline

- Anomalous (resonant) XRD is perfectly normal
- Applications
  - Enhance contrast
  - Phase-selective electronic property
  - Site occupancy
  - Magnetic scattering
- Summary

X-ray diffraction from crystal

Constructive interference of X-ray scattered from atomic plains

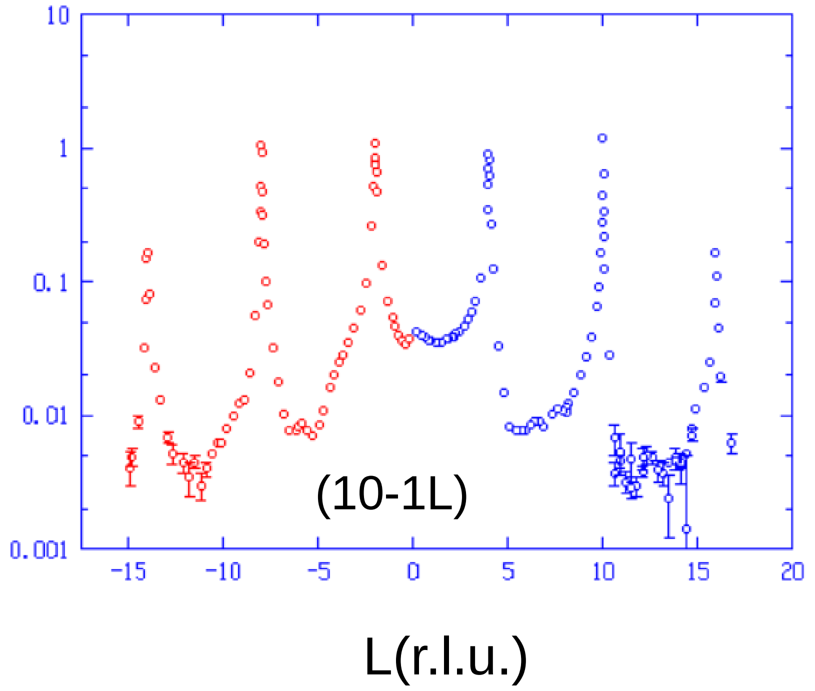


Bragg Condition

$$2d \sin\theta = \lambda = 2\pi/k = 2\pi \, hc \, / \, E$$

$$\mathbf{Q} = \frac{\mathbf{2E}}{\mathbf{12.398}} \; \mathbf{sin\theta}$$

Surface XRD from $LiNbO_3(0001)$



$$F_{hkl} = \sum_n f_n \exp(-M_n) \exp[2\pi i(hx_n + ky_n + lz_n)]$$

Anomalous (resonant) XRD has the ***combined*** *characters of diffraction and spectroscopy with applications for*

- Structure determination
- Magnetism
- *3d* and *f*-electron systems, orbital ordering
- Anomalous Small Angle X-ray Scattering

The differential cross section
for the coherent elastic x-ray scattering on single crystals ($\hbar\omega_k = \hbar\omega_{k'}$ and $E_g = E_f$)
in which the individual atomic scattering amplitudes interfere at different lattice sites n:

$$\frac{d\sigma}{d\Omega} = r_0^2 \left| \sum_n e^{i\boldsymbol{Q}\cdot\boldsymbol{R}_n} f_n(\mathbf{k}, \mathbf{k}', \hat{\epsilon}, \hat{\epsilon}', \hbar\omega_k) \right|^2$$

$r_0 = {e^2}/{mc^2} \approx 2.82 \cdot 10^{-5}$Å: classical electron radius

$f_n(\mathbf{k}, \mathbf{k}', \hat{\epsilon}, \hat{\epsilon}', \hbar\omega_k)$: scattering amplitude of the electrons at site n

$\boldsymbol{R}_n$: position of the n^{th} site

$\boldsymbol{Q} = \boldsymbol{k} - \boldsymbol{k}'$: scattering vector

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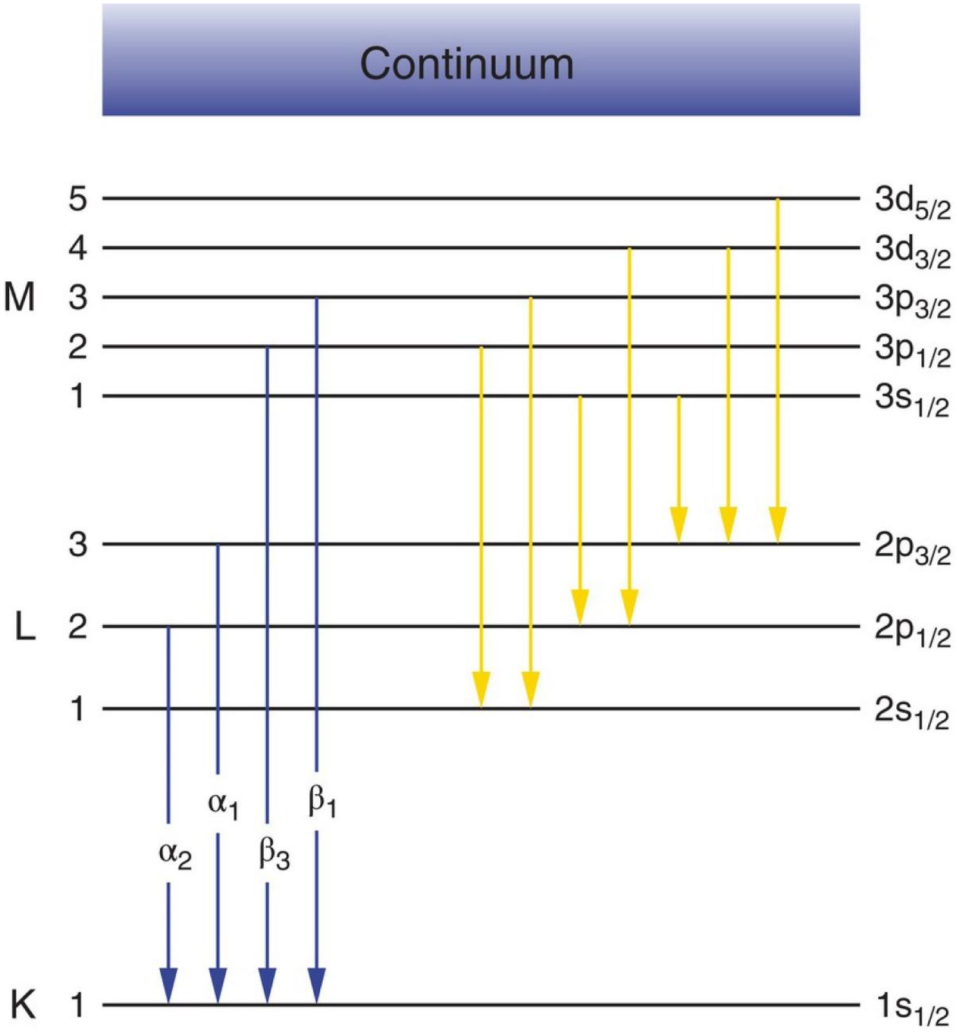
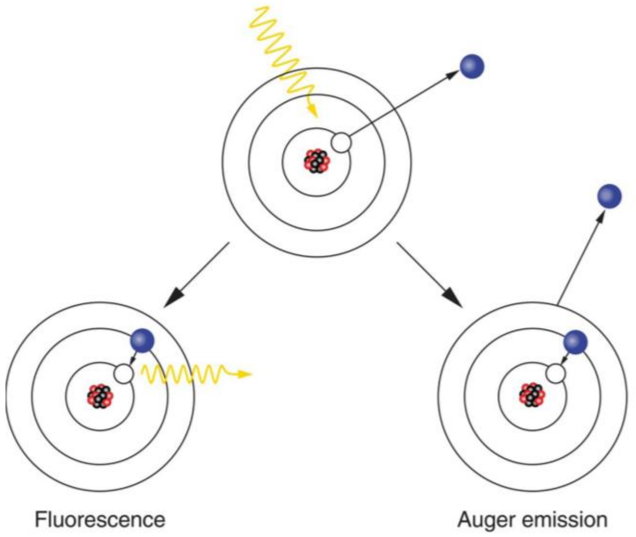
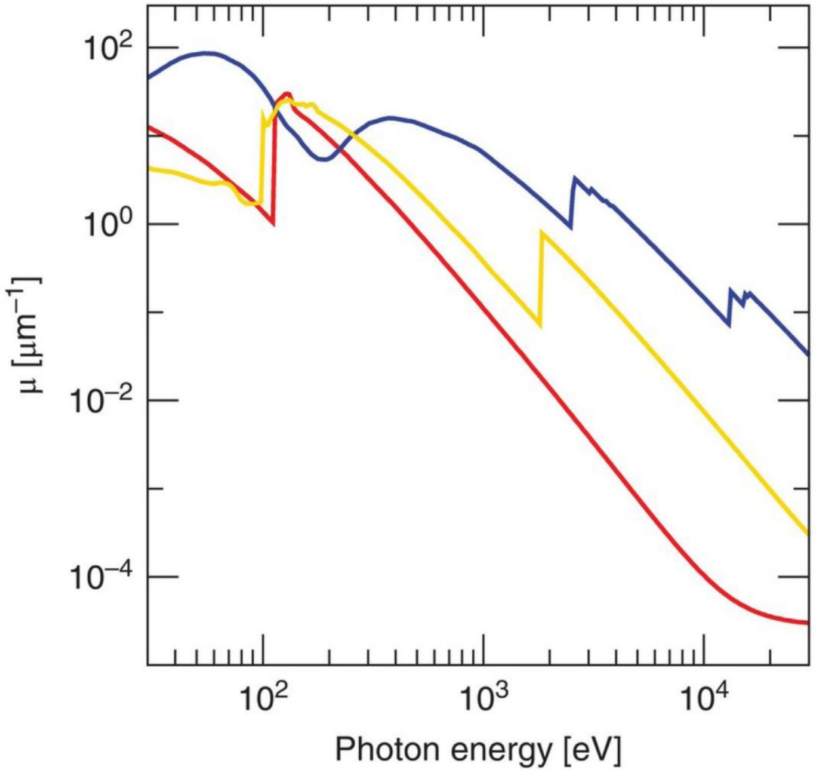
X-ray Absorption







An Introduction to Synchrotron Radiation: Techniques and Applications, Second Edition. Philip Willmott.

$$F_{hkl} = \sum_n f_n \exp(-M_n) \exp[2\pi i(hx_n + ky_n + lz_n)]$$

$$f = f^o + f'(E) + \boldsymbol{if''(E)}$$

Imaginary part implies absorption by the medium proportional to μ/λ

For h = k = l = 0 and one element,

$$F_{hkl} = f * \sum_n \exp(-M_n) \exp[2\pi i(hx_n + ky_n + lz_n)]$$

$$= f * \sum_n \exp(-M_n) = f \; * sf$$

$$I \propto |F_{hkl}|^2 = sf^2 * \{\left(f^0 + f'(E)\right)^2 - \left(f''(E)\right)^2\}$$

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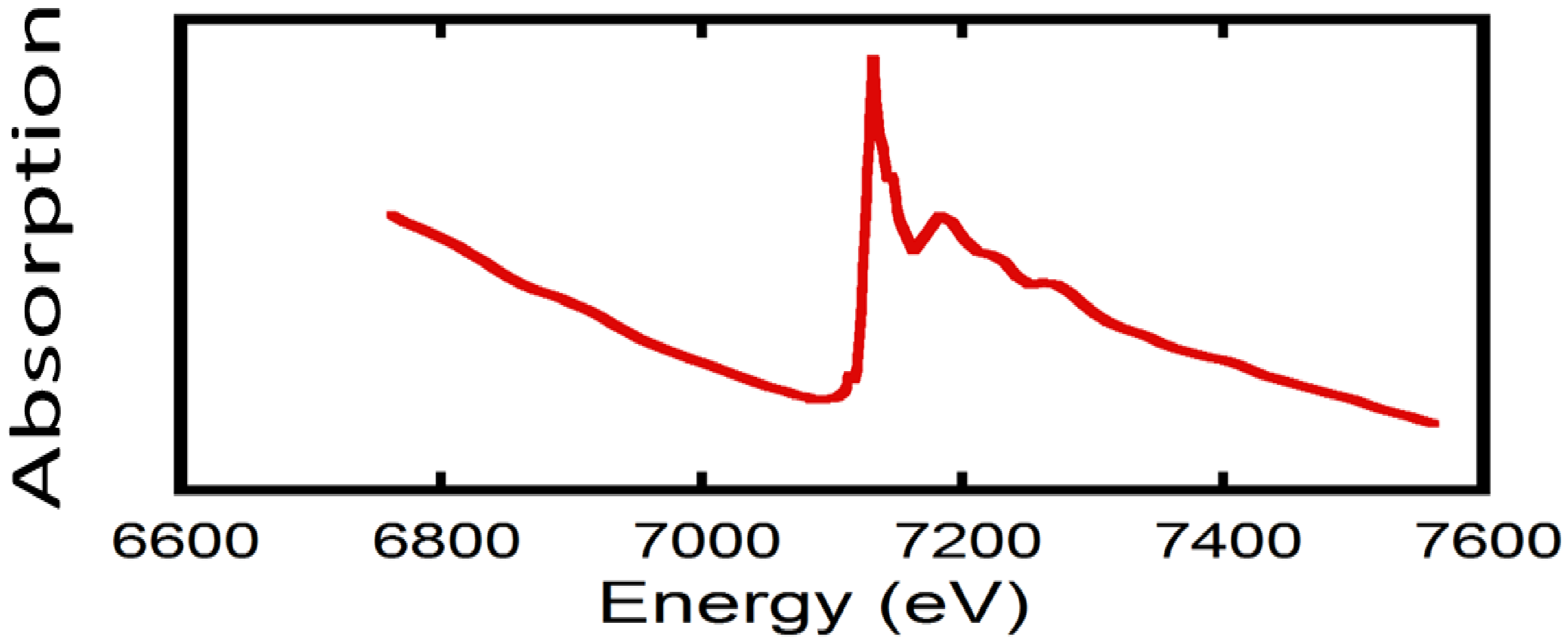
Kramers-Kronig relation

The real part $f'(E)$ of the anomalous scattering factor due to the K electrons can be calculated by absorption data for $f''(E)$

$$f_K'(E) = -\frac{2}{\pi}\int_0^{\infty} \frac{\xi[f''(E)]}{\xi^2 - E^2}\, d\xi$$



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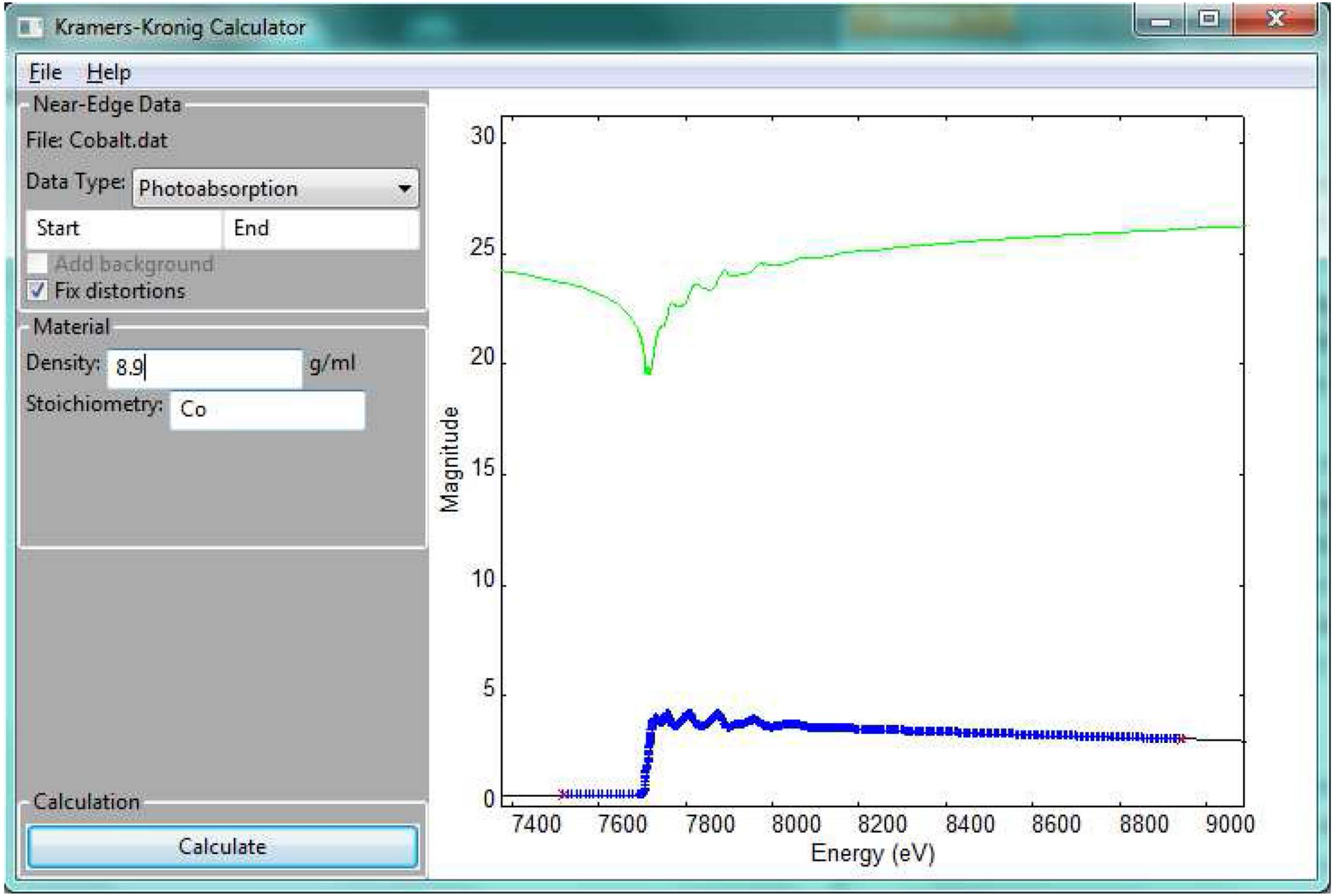
Example calculator, *kkcalc* https://pypi.org/project/kkcalc/



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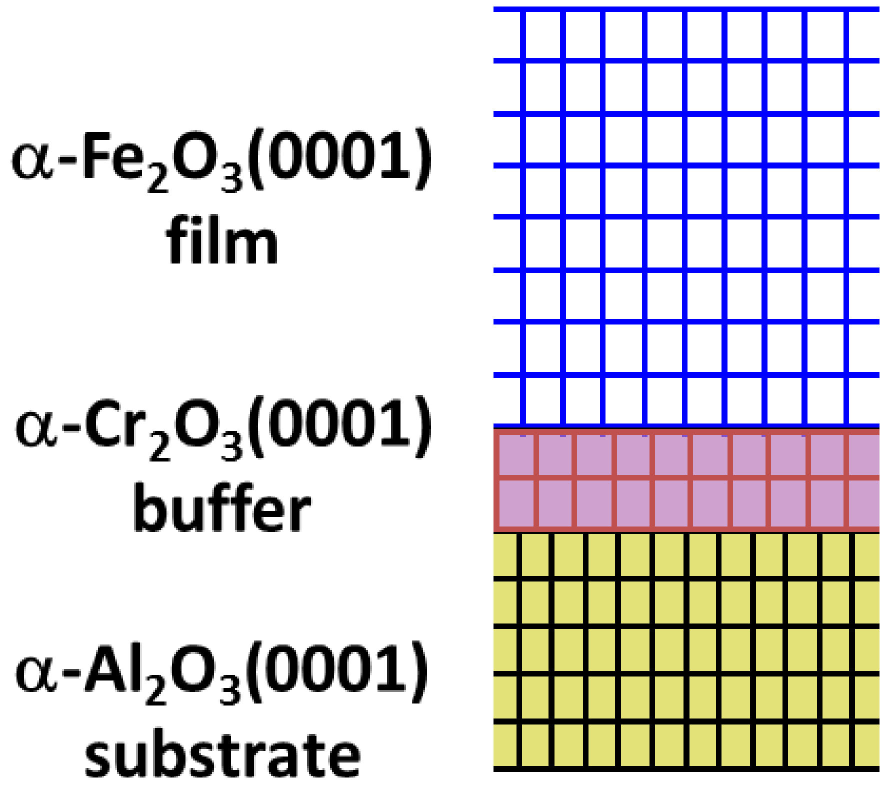
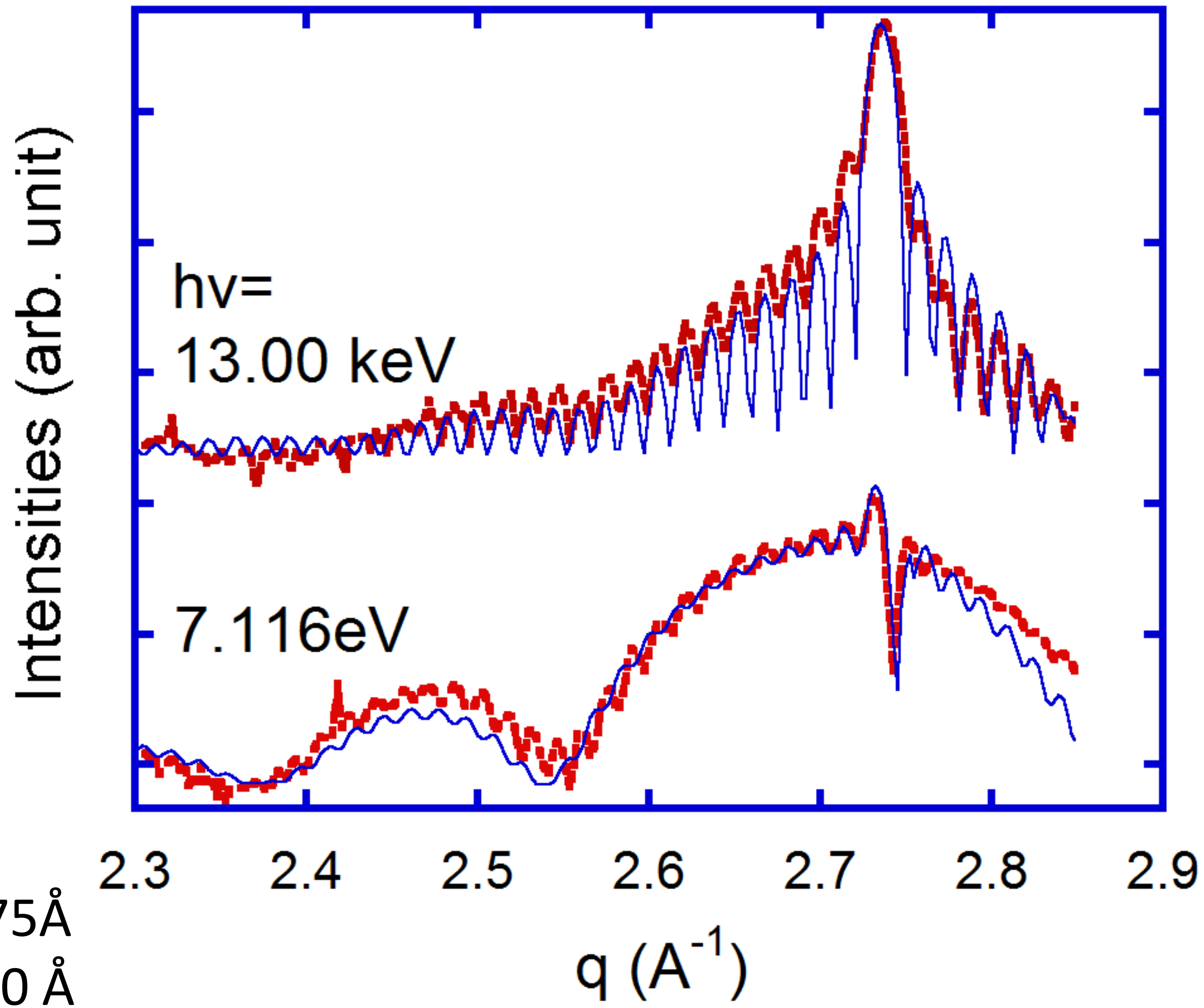
Enhance contrast: buried layer

Thin Solid Films 519 (2011) 5996–5999





Film c = 13.78 Å, 330 Å thick, bulk c = 13.75Å
Buffer c= 13.92 Å, 34 Å thick, bulk c = 13.70 Å
Substrate c = 12.99Å

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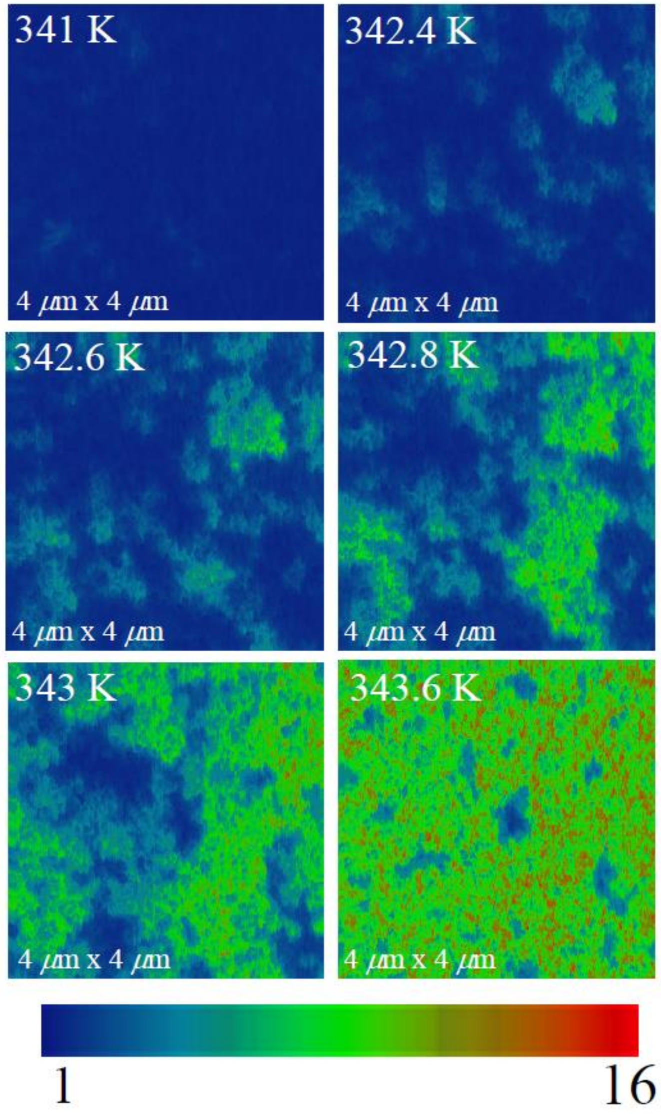
Metal – insulator transitions in VO_2

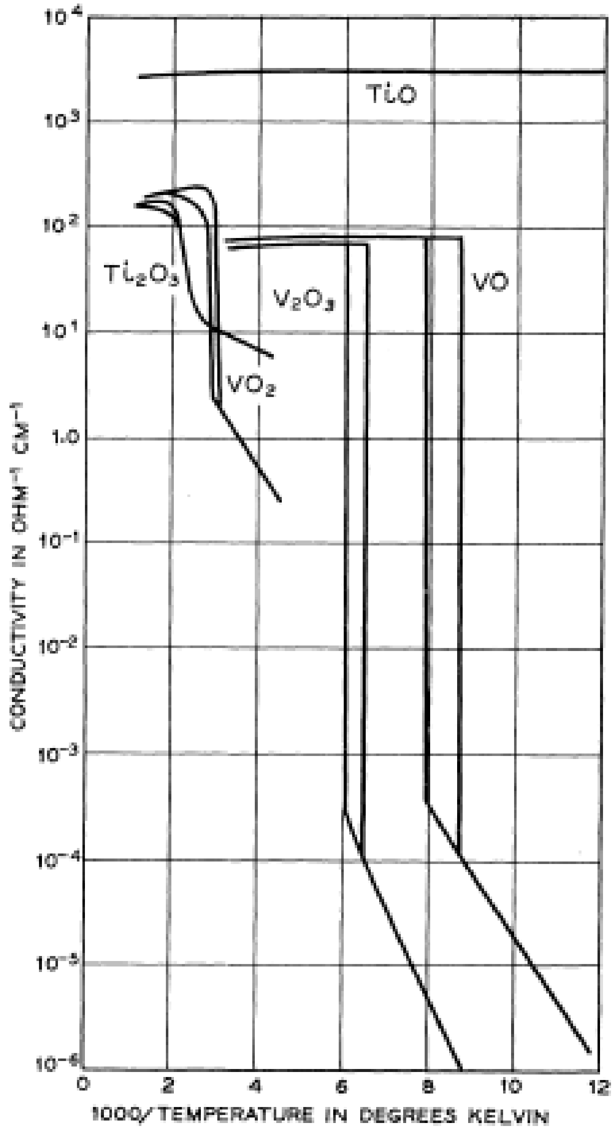
F.J. Morin, PRL3, 34 (1959)



VO_2 341 K : $3d^1$ V^{4+}

First order transition
Accompany structural transition
Doping or strain change T_c

Qazilbash et al., **Infrared** Spectroscopy and Nano-Imaging. Science 318, 1750 (2007).



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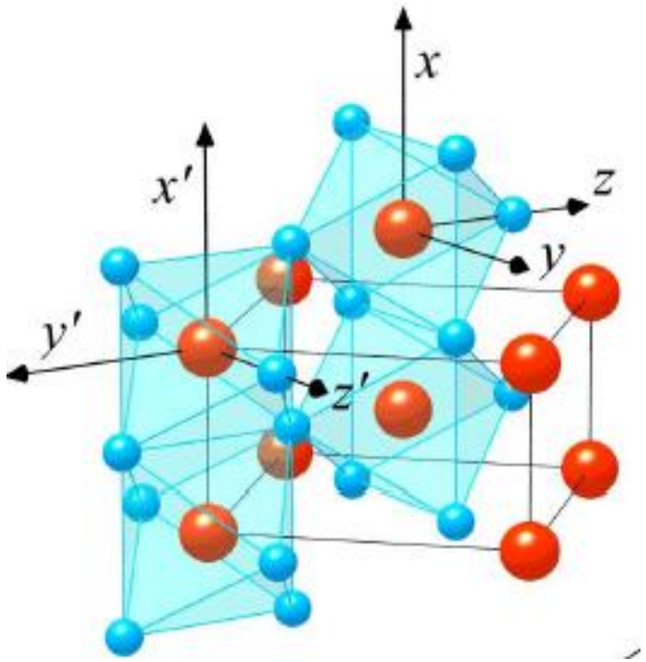
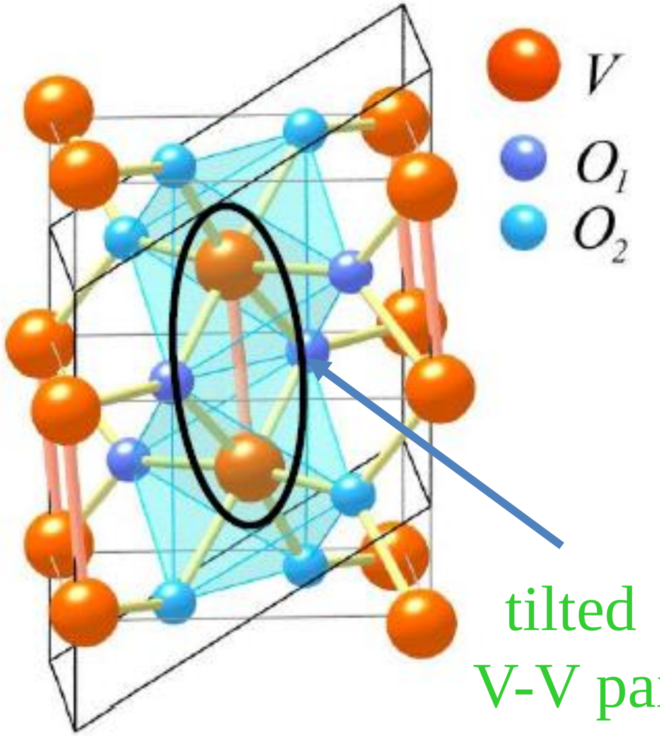
Metallic rutile phase



c_R

Chains of VO_6 octahedra running along c_R

Insulating phase: monoclinic M_1



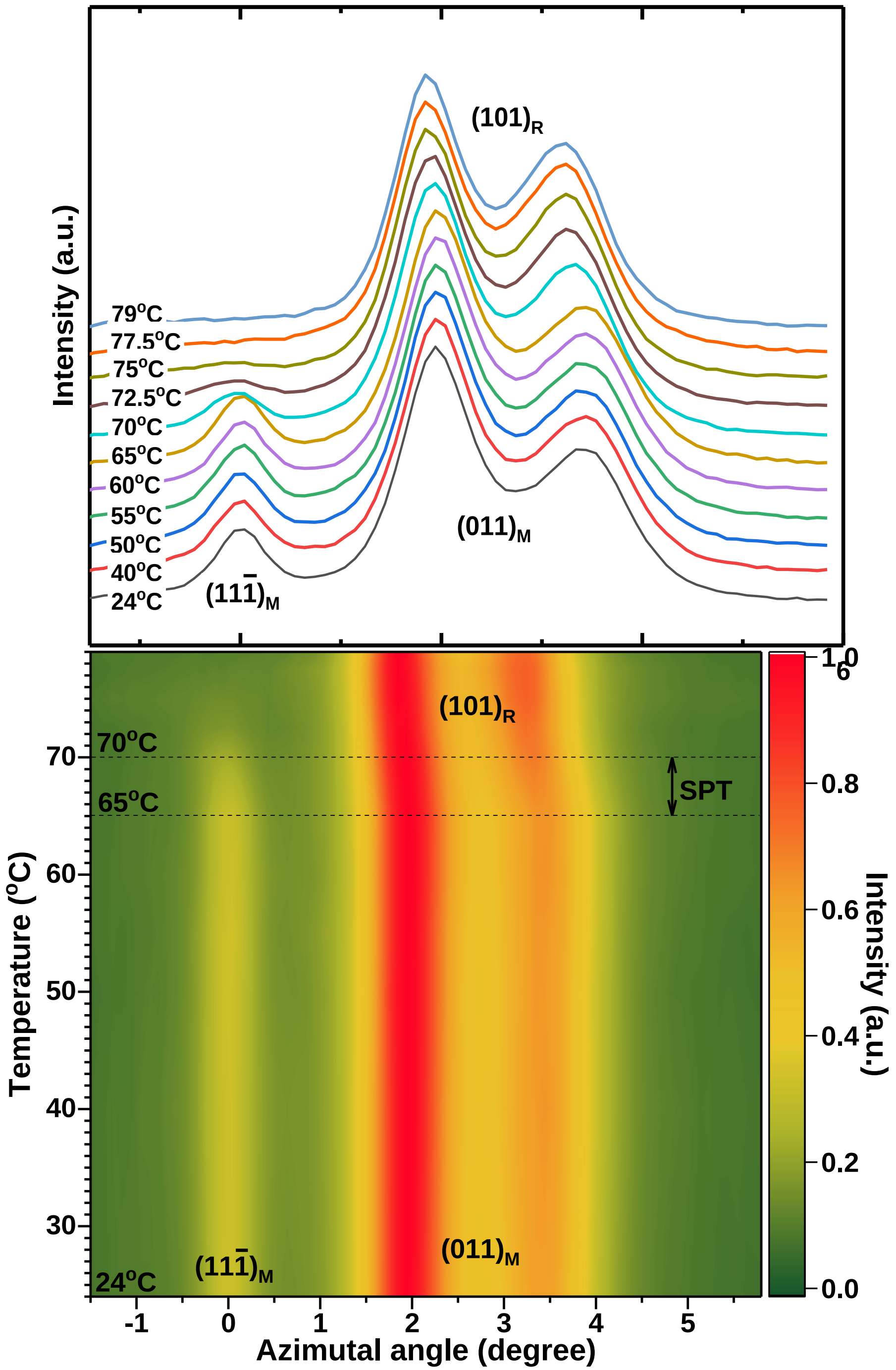
tilted V-V pair

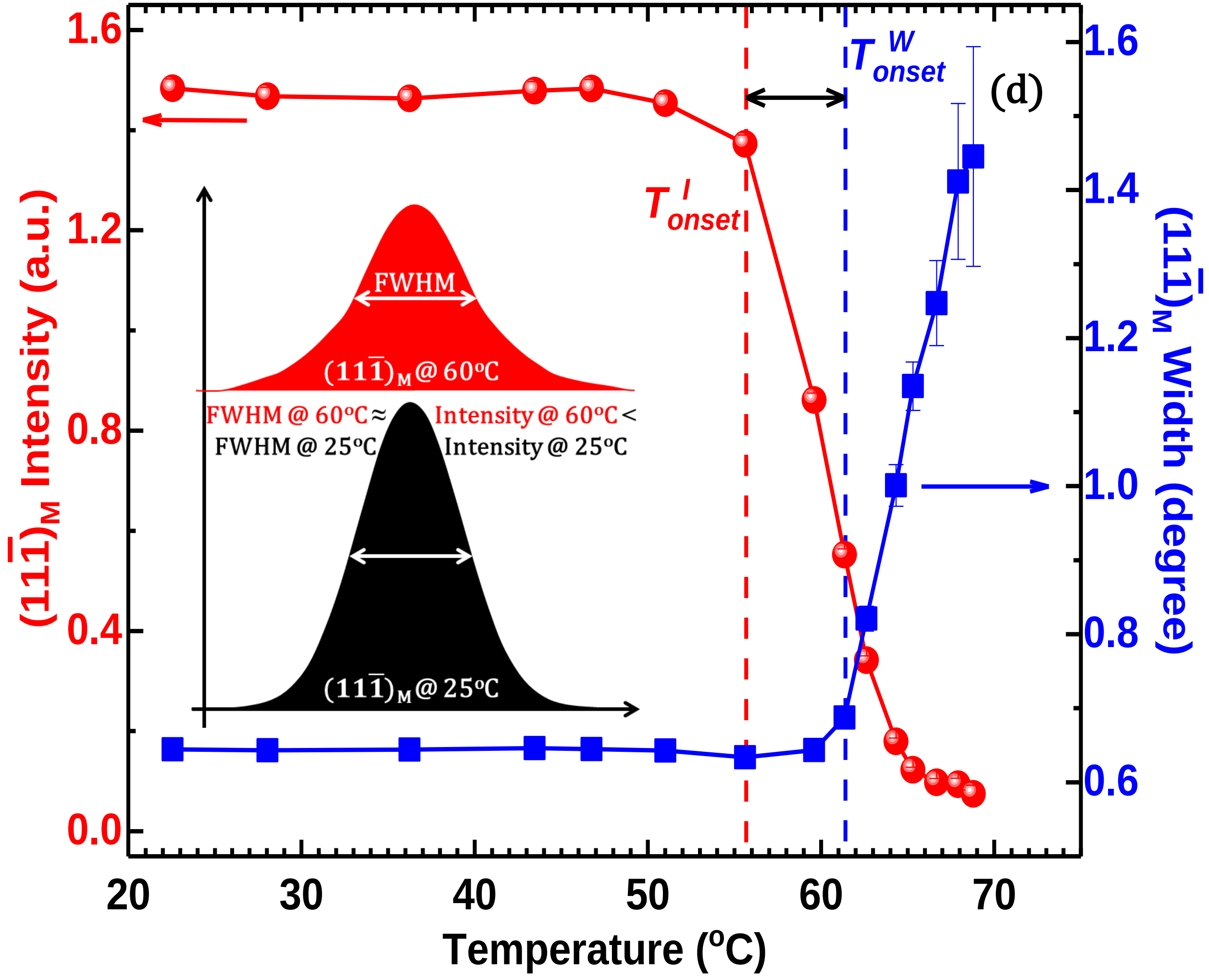
Short V-O2 distance

J.-P. Pouget

Hubbard model

$$H = -\sum_{\langle ij\rangle,\sigma} t_{ij}(c^{+}_{i\sigma}c_{j\sigma} + c^{+}_{j\sigma}c_{i\sigma}) + U\sum_{i} (n_{i\uparrow} - \tfrac{1}{2})(n_{i\downarrow} - \tfrac{1}{2})$$





Kim *et al.*, ACS Applied Electronic Materials 3 (2), 605-610, 2021

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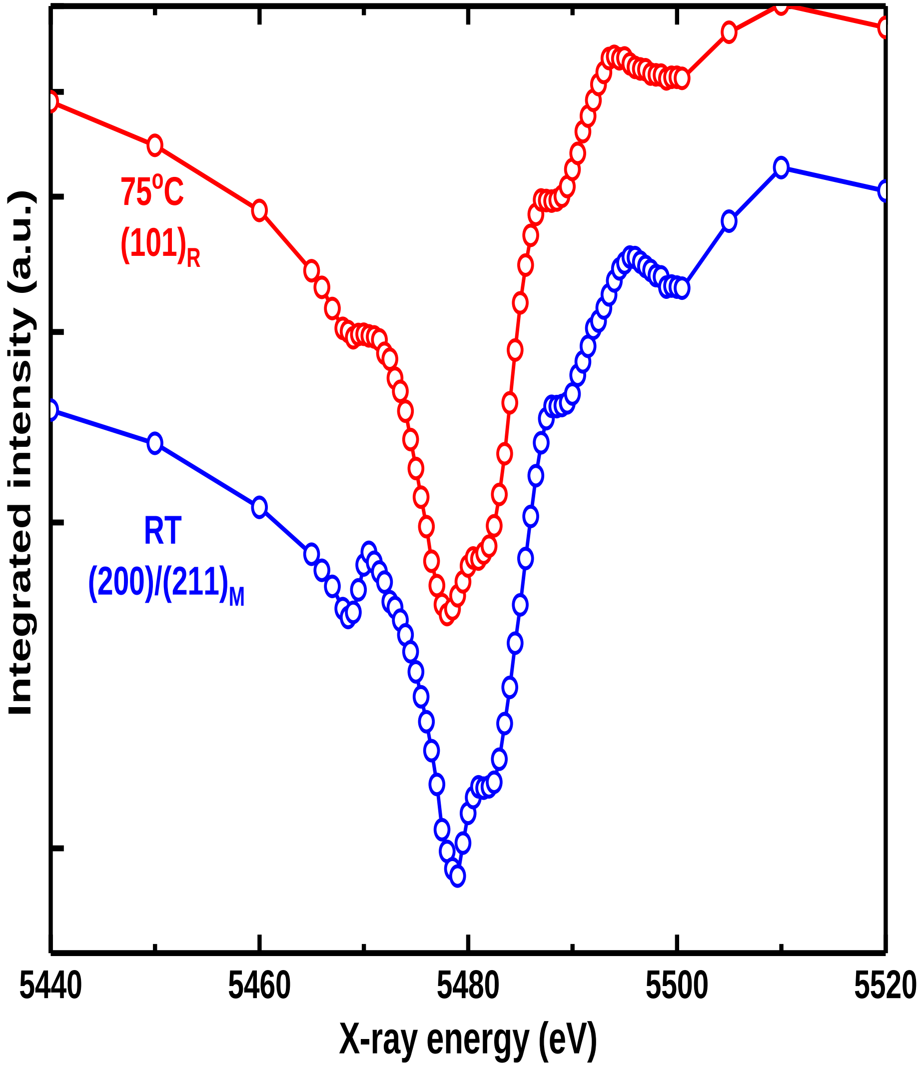
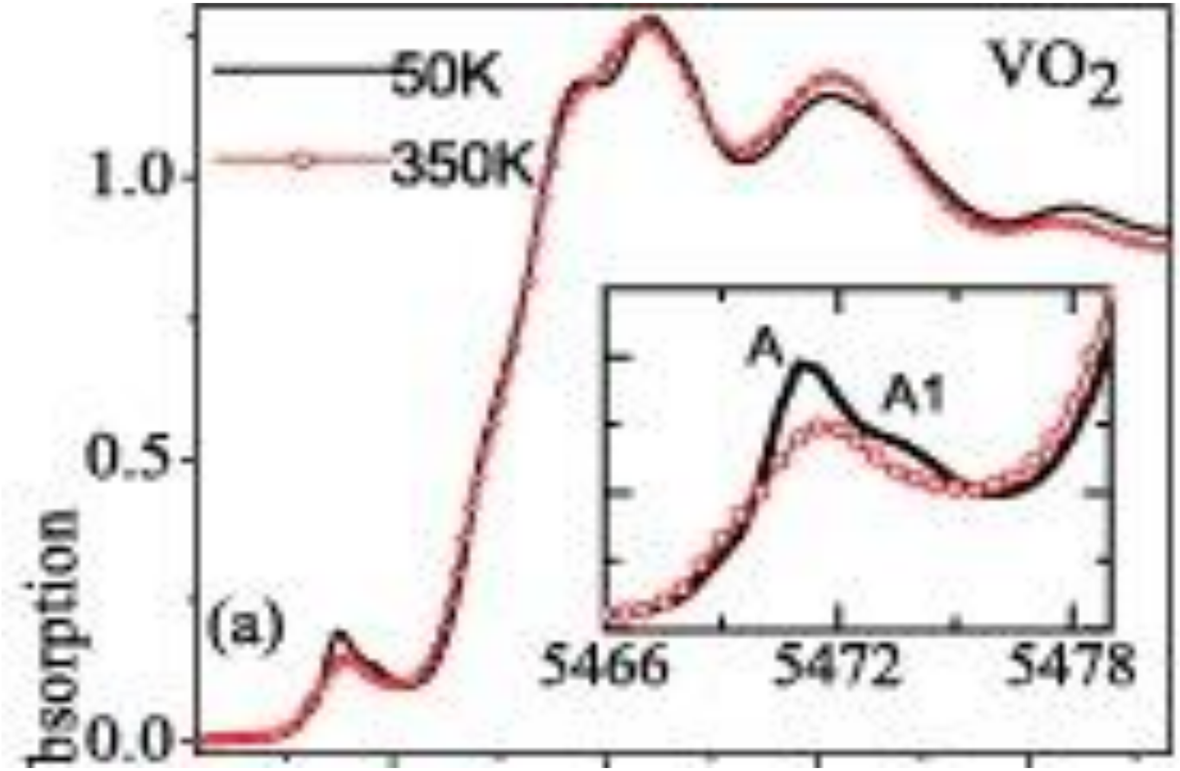
X-ray absorption





C. Marini et al 2013 EPL 102 66004

Reduced dip indicates metallic rutile phase at 75 °C

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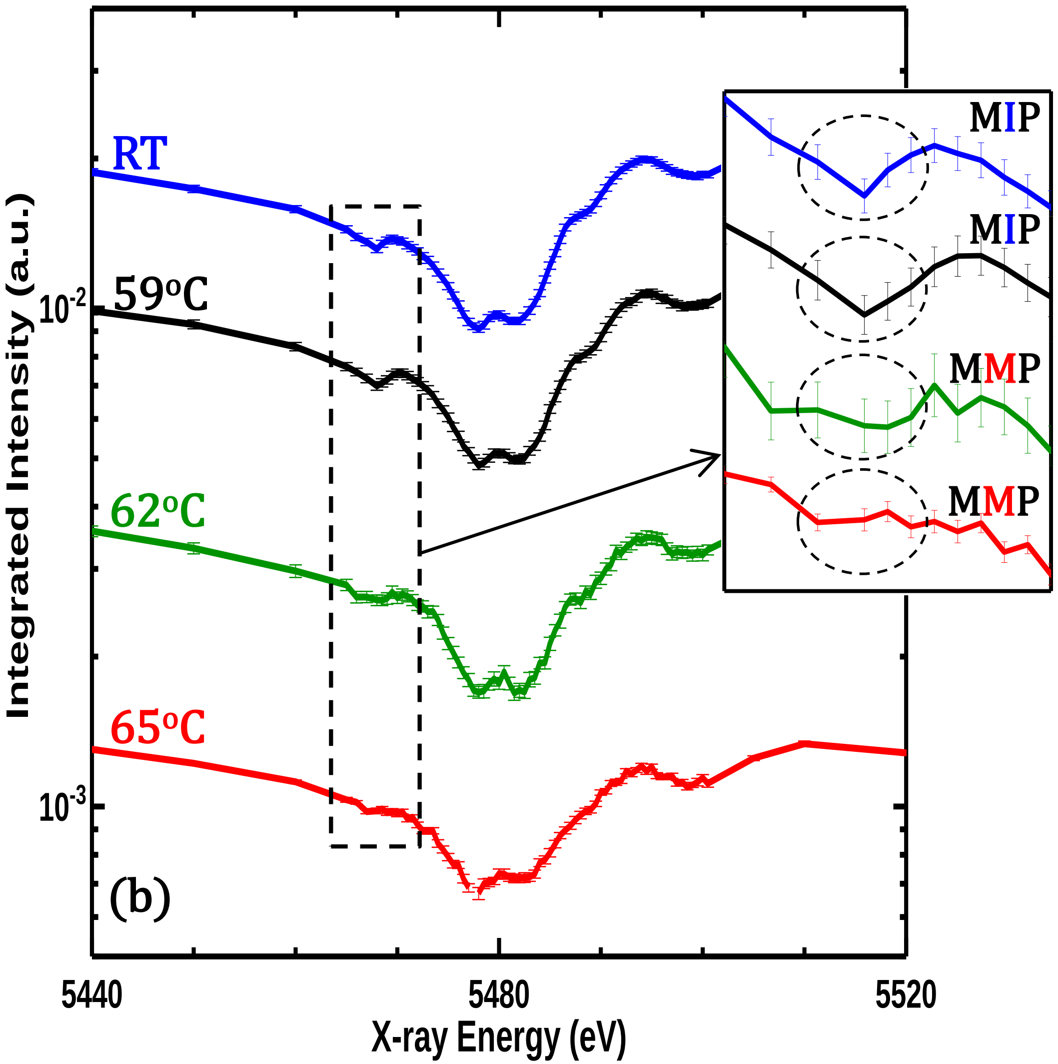

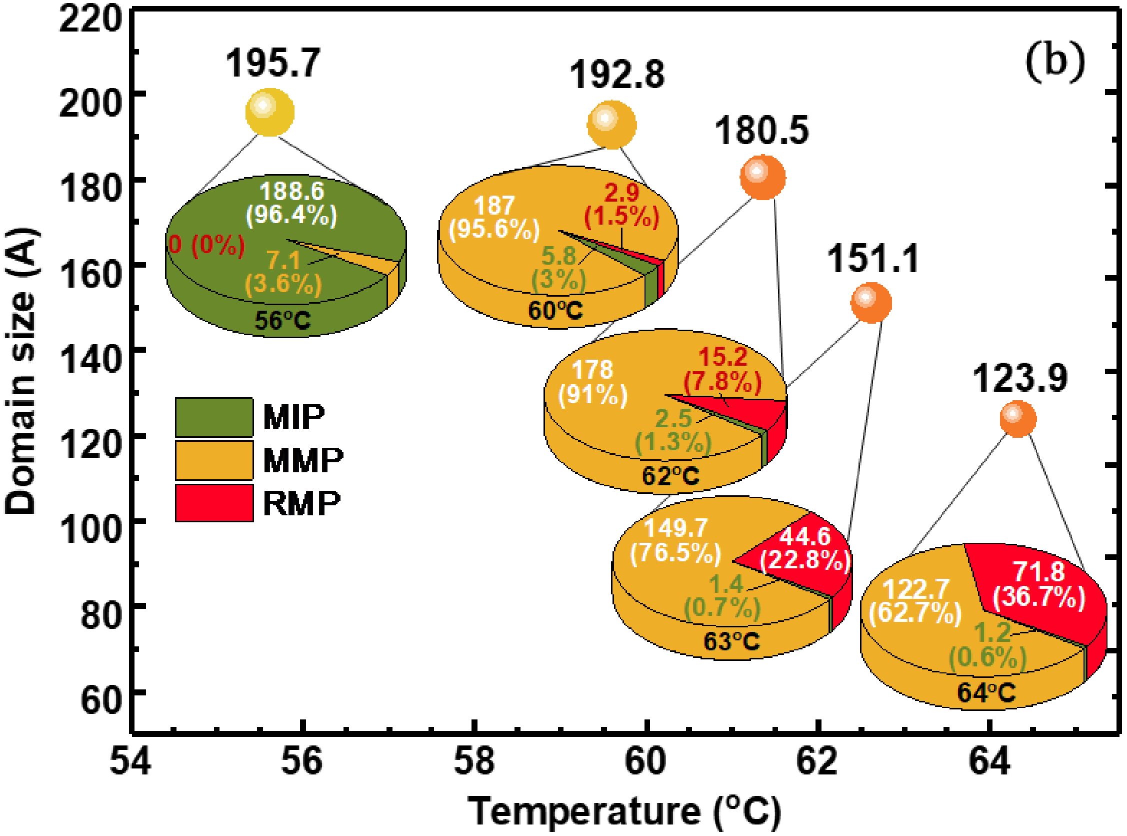

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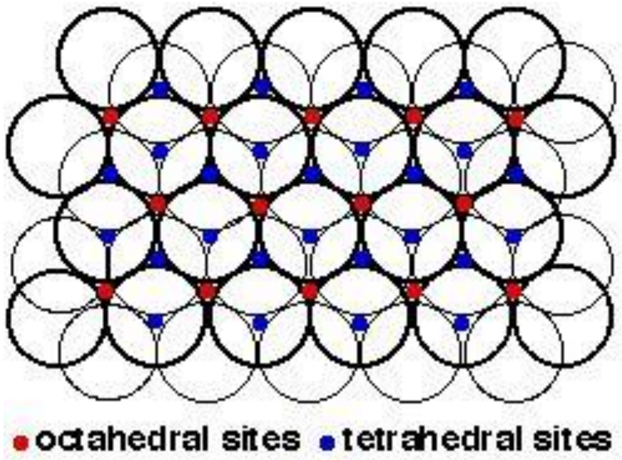
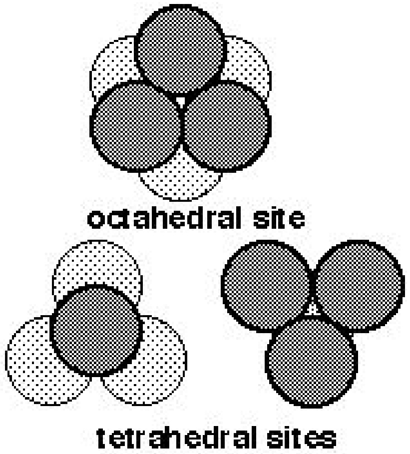
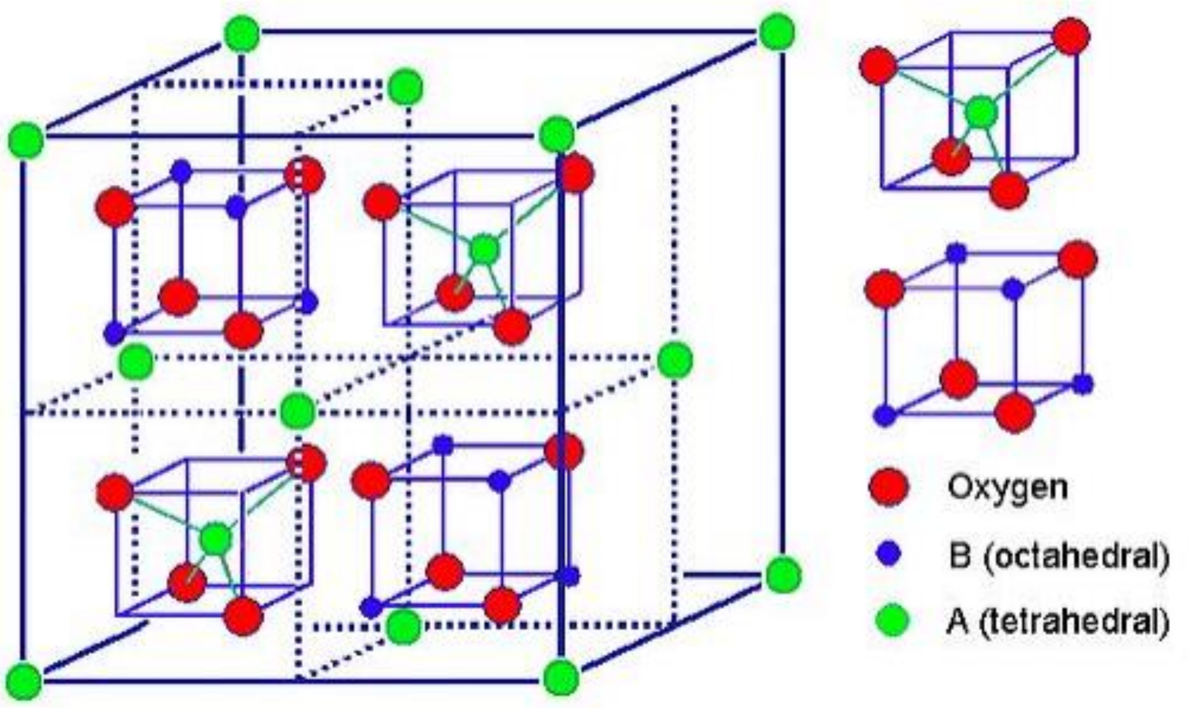
Site occupancy

Cation inversion in spinel $NiMn_2O_4$



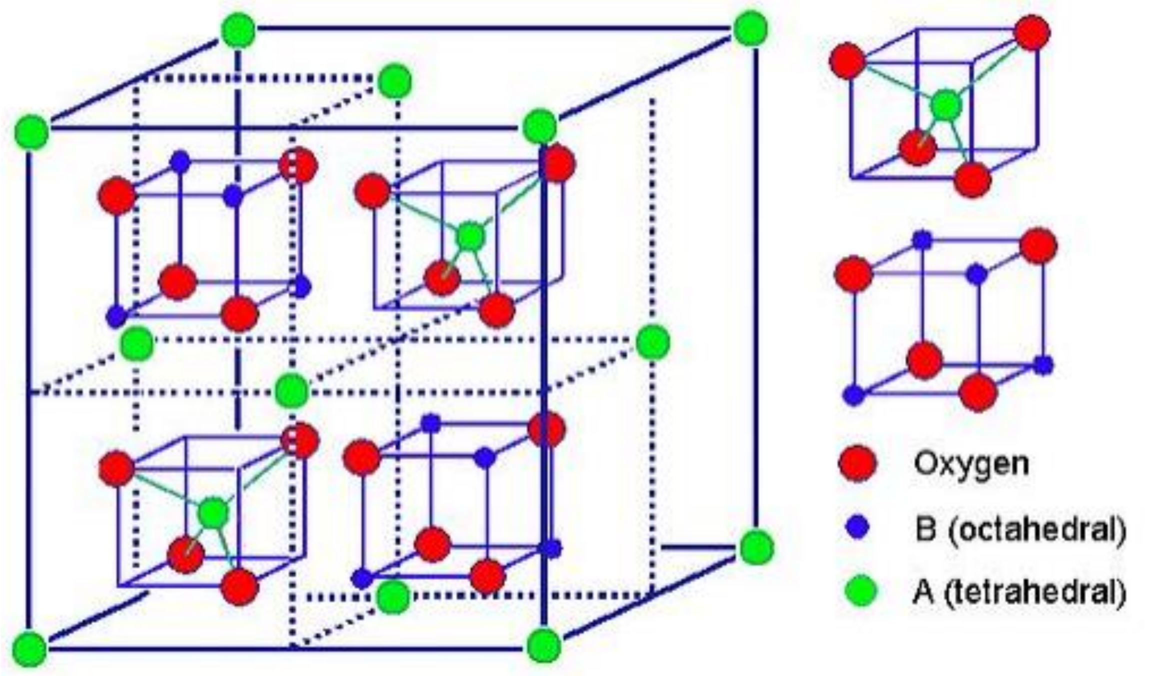




$\nu=0$ $[Ni]_{Td}[2Mn]_{Oh}O_4$ (422) Contribution only from tetrahedral site only

$\nu=1$ $[Mn]_{Td}[Ni,Mn]_{Oh}O_4$ (222) Octahedral only

Tetrahedral sites
(0 0 0), (1/2 1/2 0)
(0 1/2 1/2), (1/2 0 1/2)
(1/4 1/4 1/4), (3/4 1/4 3/4)
(3/4 3/4 1/4), (1/4 3/4 3/4)



$$F_{hkl} = \sum_n f_n \exp(-M_n) \exp[2\pi i(hx_n + ky_n + lz_n)]$$

$$F_{222}^{T} = \sum_n f_T \exp[2\pi i(2x_n + 2y_n + 2z_n)]$$

$$= f_T(e^0 + e^{2\pi i} + e^{2\pi i} + e^{2\pi i} + e^{3\pi i} + e^{7\pi i} + e^{7\pi i} + e^{7\pi i})$$

$$= f_T(1 + 1 + 1 + 1 - 1 - 1 - 1 - 1) = 0$$

(222) Octahedral site only

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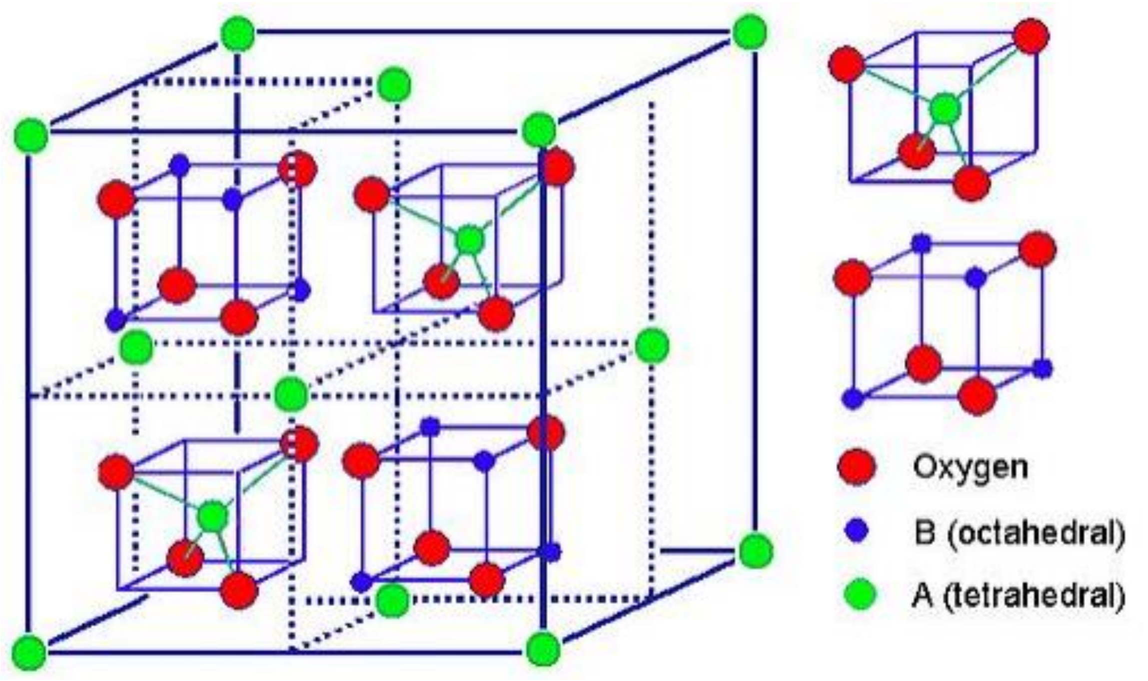
Octahedral sites

(1/8 1/8 5/8), (3/8 3/8 5/8), (1/8 3/8 7/8), (3/8 1/8 7/8)
(5/8 1/8 1/8), (7/8 3/8 1/8), (5/8 3/8 3/8), (7/8 1/8 3/8)
(5/8 5/8 5/8), (7/8 7/8 5/8), (5/8 7/8 7/8), (7/8 5/8 7/8)
(1/8 5/8 1/8), (3/8 7/8 1/8) , (1/8 7/8 3/8), (3/8 5/8 3/8)



$$F_{hkl} = \sum_n f_n \exp(-M_n) \exp[2\pi i(hx_n + ky_n + lz_n)]$$

$$F_{422}^{O} = \sum_n f_O \exp[2\pi i(4x_n + 2y_n + 2z_n)]$$

$$= f_O\{(1 - 1 + 1 - 1) + (1 - 1 + 1 - 1) + (1 - 1 + 1 - 1) + (1 - 1 + 1 - 1)\} = 0$$

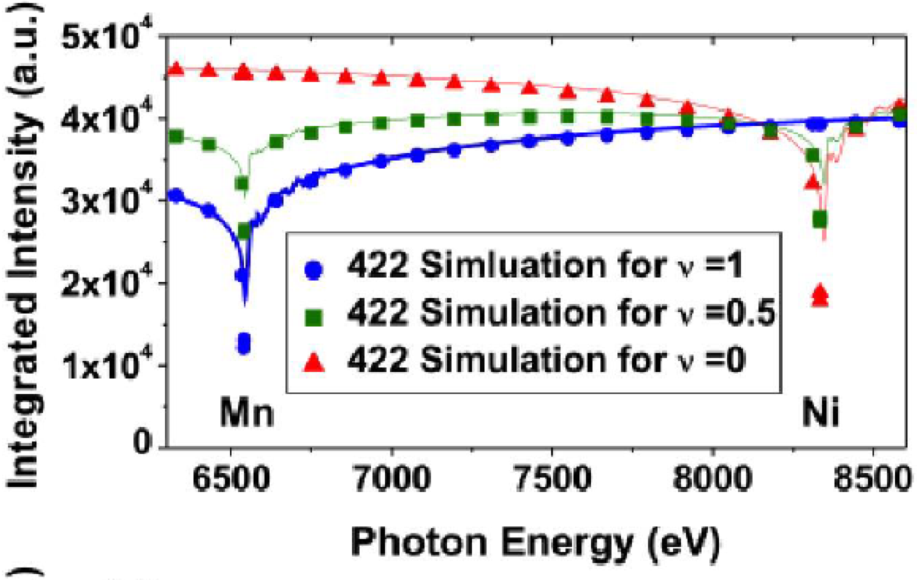
(422) Tetrahedral site only

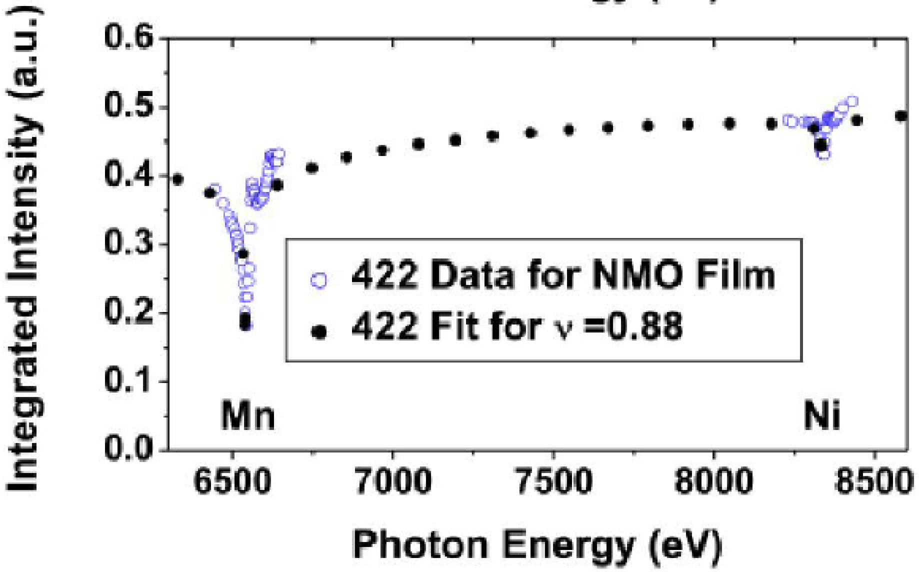
Site occupancy

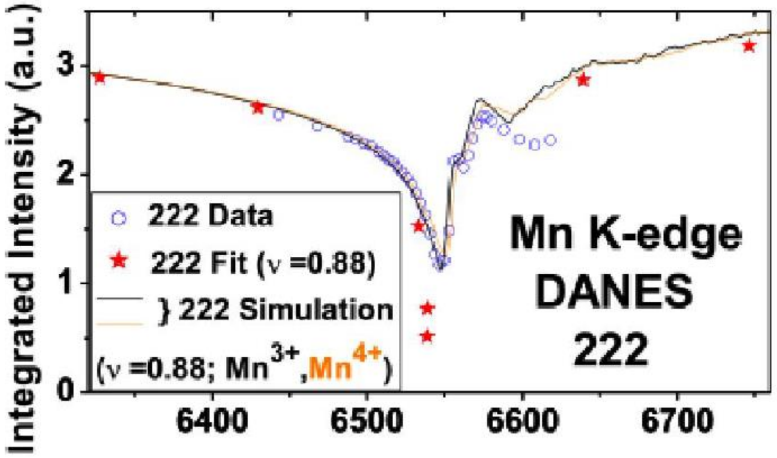
Cation inversion in spinel $NiMn_2O_4$

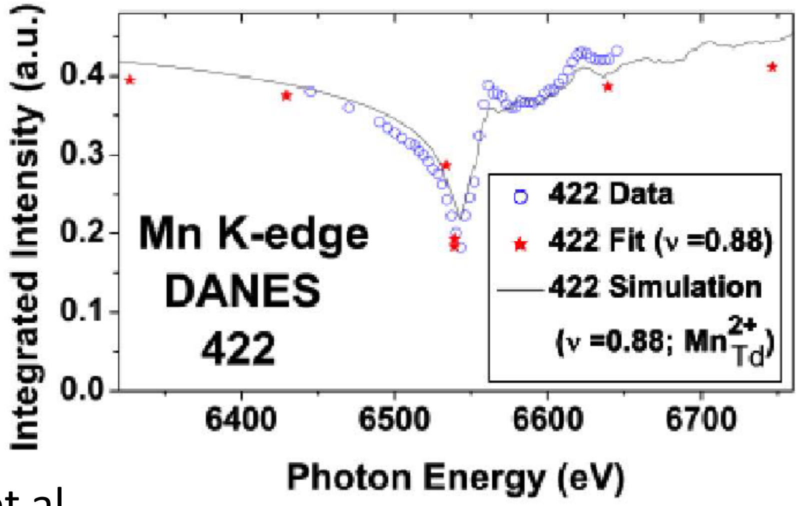
$\nu=0\ [Ni]_{Td}[2Mn]_{Oh}O_4$

$\nu=1\ [Mn]_{Td}[Ni,Mn]_{Oh}O_4$









B.B. Nelson-Cheeseman et al

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Electrons in a quantized electromagnetic field

$$\mathbf{H} = \sum_j \frac{1}{2m}\left(\boldsymbol{P}_j - \frac{e}{c}\boldsymbol{A}(\boldsymbol{r}_j)\right)^2 + \sum_{ji} V(\boldsymbol{r}_{ij}) - \frac{e\hbar}{mc}\sum_j \boldsymbol{s}_j \cdot \nabla \times \boldsymbol{A}(\boldsymbol{r}_j) - \frac{e\hbar}{2(mc)^2}\sum_j \boldsymbol{s}_j \cdot \boldsymbol{E}(\boldsymbol{r}_j) \times \left(\boldsymbol{P}_j - \frac{e}{c}\boldsymbol{A}(\boldsymbol{r}_j)\right) + \sum_{k\lambda} \hbar\omega_k \left((c^+(k\lambda)c(k\lambda) + \frac{1}{2}\right)$$

K.E. of electron in the EM field

Coulomb interaction between electrons

Zeeman energy of electrons with spin s_j

Spin-orbit coupling

Self energy of EM field

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Matter radiation interaction relevant to X-ray scattering

$$H_1 = \sum_i \frac{e^2}{2m} [\boldsymbol{A}(\boldsymbol{r}_i, t)]^2$$

Thomson

$$H_2 = -\sum_i \frac{e^2 \hbar}{2m^2 c^2} \boldsymbol{s}_i \, [\partial_t \boldsymbol{A}(\boldsymbol{r}_i, t) \times \boldsymbol{A}(\boldsymbol{r}_i, t)]$$

Non-resonance Magnetic (10^{-6} of charge)

$$H_3 = -\sum_i \frac{e}{m} [\boldsymbol{A}(\boldsymbol{r}_i, t) \cdot \boldsymbol{p}_i]$$

Spin-orbit coupling

$$H_4 = -\sum_i \frac{e}{m} \boldsymbol{s}_i \cdot [\boldsymbol{\nabla} \times \boldsymbol{A}(\boldsymbol{r}_i, t)]$$

Spin dependent resonance

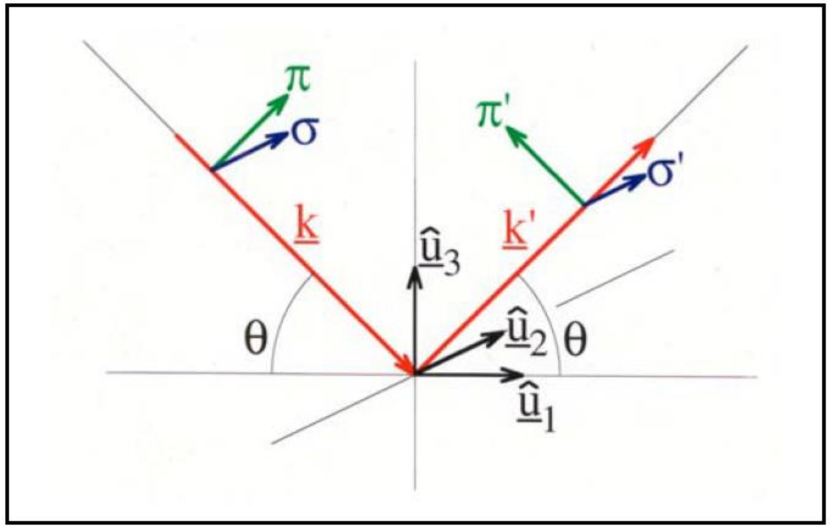
$$f_j'(\omega) + i f_j''(\omega) = \sum_{n,g} \frac{\langle \varphi_g^{(j)} | \hat{H}_3^* + \hat{H}_4^* | \varphi_n \rangle \langle \varphi_n | \hat{H}_3 + \hat{H}_4 | \varphi_g^{(j)} \rangle}{\hbar\omega - (E_n - E_g) + i\frac{\Gamma}{2}}$$

M. Blume, J. Appl. Phys. 57, 3615 (1985)

Elastic cross section for scattering of photon

$$\left.\frac{d\sigma}{d\Omega}\right|_{\varepsilon\to\varepsilon'} = \left[\frac{e^2}{mc^2}\right]^2 \cdot \left| \langle f_C \rangle_{\varepsilon'\varepsilon} + i\frac{\lambda_C}{d}\langle f_M \rangle_{\varepsilon'\varepsilon} \right|^2$$

π/2 phase shift



Polarization dependence

- <fM> for the magnetic part:

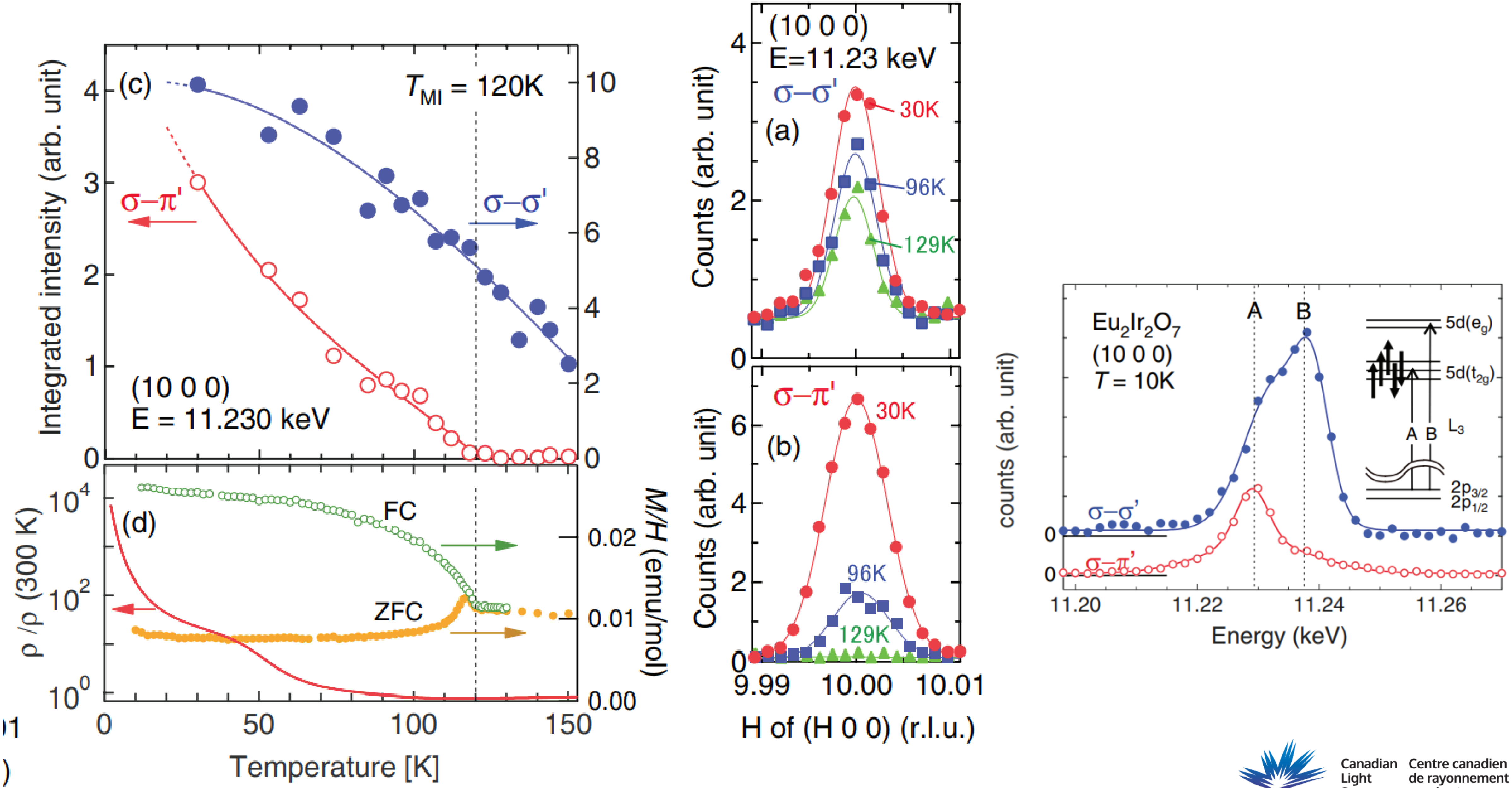
to \ from	σ	π
σ'	$S_2 \cdot \cos\theta$	$[(L_1 + S_1)\cdot\cos\theta + S_3\cdot\sin\theta]\cdot\sin\theta$
π'	$[-(L_1 + S_1)\cdot\cos\theta + S_3\cdot\sin\theta]\cdot\sin\theta$	$[2L_2\cdot\sin^2\theta + S_2]\cdot\cos\theta$

- <fC> for charge scattering:

to \ from	σ	π
σ'	$\rho(\underline{Q})$	0
π'	0	$\rho(\underline{Q})(\cos 2\theta)$

Spin and orbital contributions are different

H. Sagayama et al., PRB 87. 100403



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Further readings

M. Blume, Magnetic scattering of x rays, *Journal of Applied Physics* 57, 3615–3618 (1985)

Resonant X-Ray Scattering in Correlated Systems Y Murakami (ed.) --- Orbital ordering

Anomalous X-Ray Scattering for Materials Characterization- Atomic-Scale Structure Determination, Yoshio Waseda

Magnetism and synchrotron radiation. New trends E. Beaurepaire, H. Bulou, F. Scheurer, J.P. Kappler (eds.)

Luigi Paolasini, Resonant and magnetic X-ray diffraction by polarized synchrotron radiation, *Collection SFN* **13**, 03002 (2014)