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Anomalous Scattering and Resonant X-ray Scattering

What is Anomalous Scattering?

- The classical derivation of the physical basis for anomalous scattering is developed by treating the scattering interaction as a pair of coupled oscillators. One oscillator is the *e* component incident x-ray wave; the other is an electron of the scattering atom treated as a dipole oscillator with frequency equal to the observed value of an absorption edge. This treatment is expounded at length by James (1948), but does not lend itself to an intuitive summary. We will therefore instead try to give a basic description in terms of the scattering cross section of an atom as seen by an incident x-ray photon.
- **When the incident photon has relatively low energy:**
  - The photon is either scattered or not, but is not absorbed as it has insufficient energy to excite any of the available electronic transitions.
  - The scattering cross-section of the atom (or if you like, the probability that the photon is scattered) may be adequately described in using the normal atomic scattering coefficient f_0 only.
  - The photon scatters with no phase delay (imaginary, or *f* ", component is 0).

What is Anomalous Scattering?

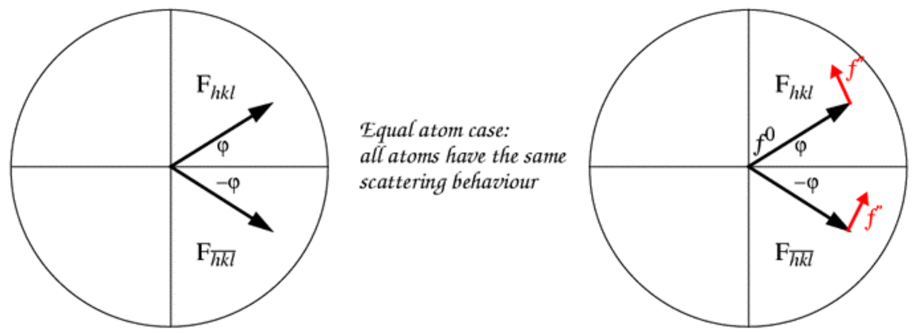
- **When the incident photon has high enough energy:**
  - Some photons are scattered normally.
  - Some photons are absorbed and re-emitted at lower energy (fluorescence).
  - Some photons are absorbed and immediately re-emitted at the same energy (strong coupling to absoption edge energy).
- The scattered photon gains an imaginary component to its phase (f" scattering coefficient becomes non-zero); i.e. it is retarded compared to a normally scattered photon.
- This effect is most easily measured as a function of x-ray energy by noting either the sharp increase in absorption or in fluorescence. The imaginary scattering component f" is proportional to these directly measurable quantities. The real scattering component f' is related to f" via the Kramers-Kronig relationship.

Breaking Friedel's Law

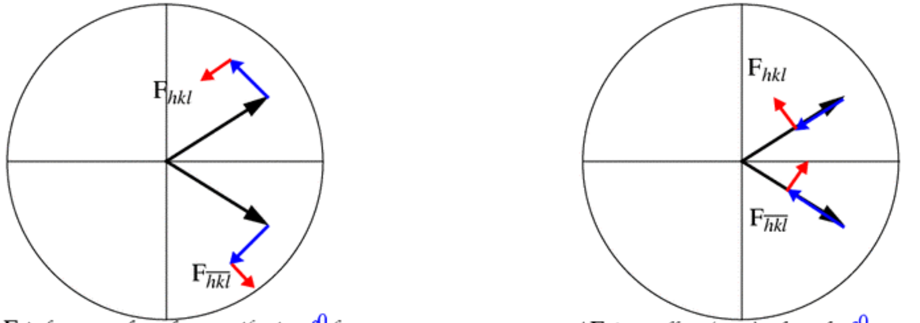
- Friedel pairs are Bragg reflections related by inversion through the origin.
- Friedel's Law states that members of a Friedel pair have equal amplitude and opposite phase.

$$|F_{hkl}| = |F_{\overline{hkl}}| \qquad \varphi_{hkl} = -\varphi_{\overline{hkl}}$$

- Friedel's Law is broken whenever there is anomalous scattering. If all atoms scatter equally, then the amplitudes remain equal but the phase relationship no longer holds.
- This is because the *f* ” term is always positive: if some atoms scatter anomalously and some don't, then both the amplitude and phase relationships are broken.



Equal atom case: all atoms have the same scattering behaviour

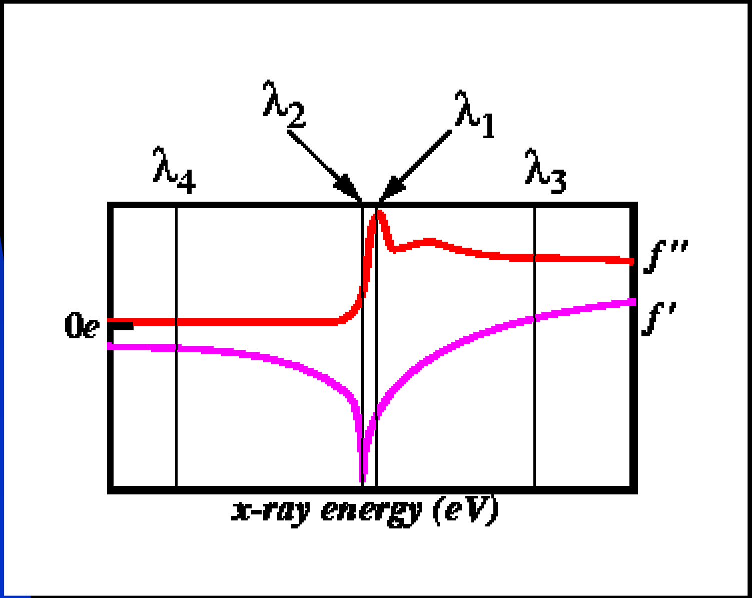


ΔF *is largest when the contribution* f^0 *from the anomalous scattering atoms is* π/2 *out of phase with that of the non-anomalous atoms*

ΔF *is smallest (zero) when the* f^0 *contribution is in phase with that of the non-anomalous atoms*

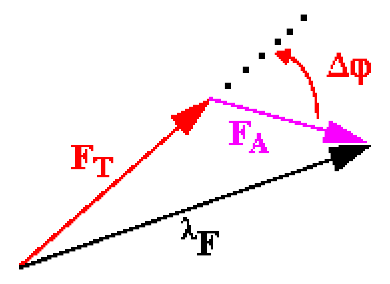
Choosing wavelengths for MAD data collection

- Inspect your EXAFS scan
- Once you have determined the actual scattering factors *f* ' and *f* '' in the energy range of interest for your sample crystal, you need to choose exactly which x-ray wavelengths to use for MAD data collection.
- The largest signal will come from choosing the wavelength with maximal *f* ''
- The second wavelength is usually chosen to have maximal |*f* '|
- Additional wavelengths are chosen at points remote from the absorption edge. Typically they are between 100 eV and 1000 eV from the absorption edge.



MAD phasing

- The basic idea is that if we can locate the anomalous scattering atoms within the unit cell (those contributing to F_A) then we can calculate the corresponding phase angle ϕ_A. The MAD phasing equations can then be used to generate an estimate for $\Delta\phi$ and F_T. In the simplest case we can then estimate the phase of the F_T as $\Delta\phi+\phi_A$.
- A Fourier transform of the amplitudes F_T and phases $(\Delta\phi+\phi_A)$ should yield an electron density map corresponding to all atoms in the structure.

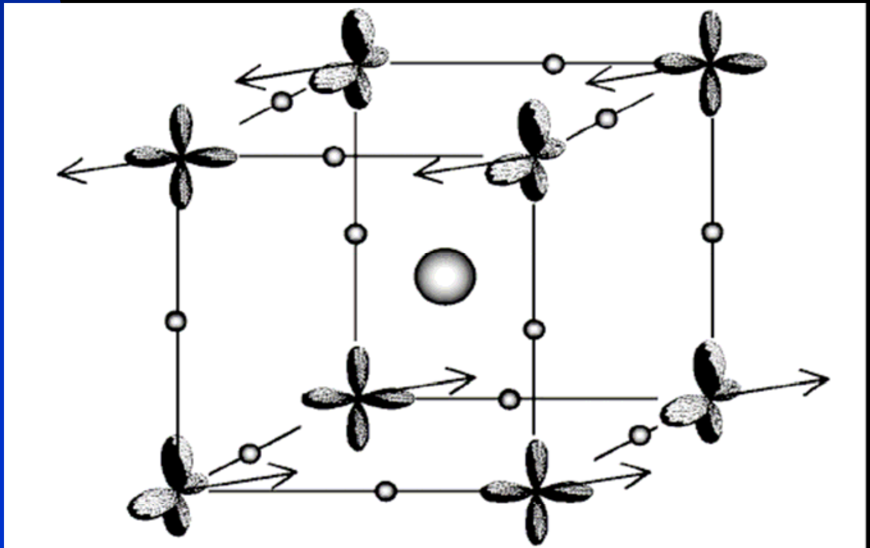


Resonant X-ray Scattering

- RXS is due to a process in which a photon is virtually absorbed by exciting a core electron to empty states, and subsequently reemitted when the excited electron and the core hole recombine. This process introduces anisotropic contributions to the x-ray susceptibility tensor, the amplitude of which increases dramatically as the photon energy is tuned to an atomic absorption edge. In presence of long-range order of magnetic moments, electronic orbitals occupancy or spatially anisotropic valence-electron clouds, the interference of the anomalous anisotropic scattering amplitudes lead to the excitation of Bragg peaks at positions forbidden by the crystallographic space group. For absorbing atoms belonging to the transition-metal series, only the K edge may be of practical use, as the energy of other absorption edges is usually below the cut off for Bragg diffraction.

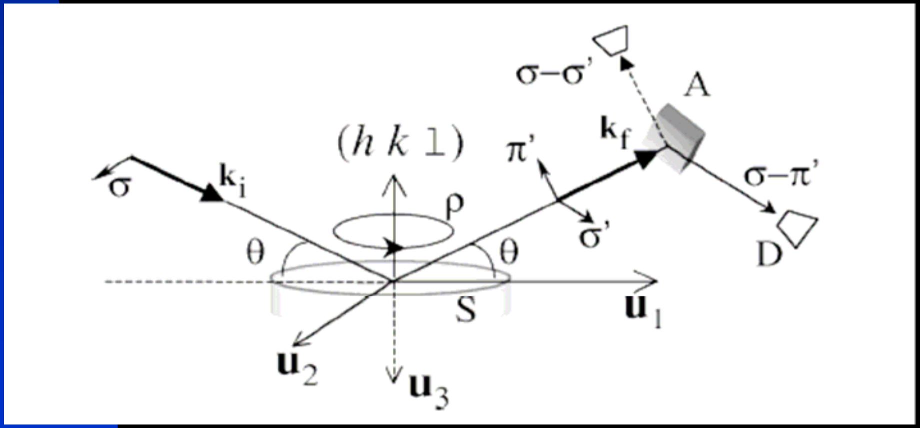
A Case Study: $KCuF_3$

- This system belongs to a class of Mott-Hubbard insulators containing transition-metal ions whose magnetic behavior is largely determined by the structural configuration and the presence of nearly degenerate, partially occupied orbitals. The magnitude and sign of the superexchange interaction depend on the filling of the orbitals, and are therefore indeterminate in presence of degeneracy.
- The empirical Goodenough-Anderson-Kanamori rules, for instance, cannot be applied if the type of occupied orbital is not known. The superexchange Hamiltonian must be generalized, to include the orbital degrees of freedom among with the spin ones. This was done almost thirty yearsago by Kugel' and Khomskii, who proposed a model able to describe the ordering of orbitals by superexchange in substances containing ions with orbital degeneracy, and to predict the corresponding magnetic structure. The KK model shows that symmetry breaking, lifting the electronic degeneracy, leads to magnetic and orbital long-range orders that are closely related, even if they occur at different temperatures.

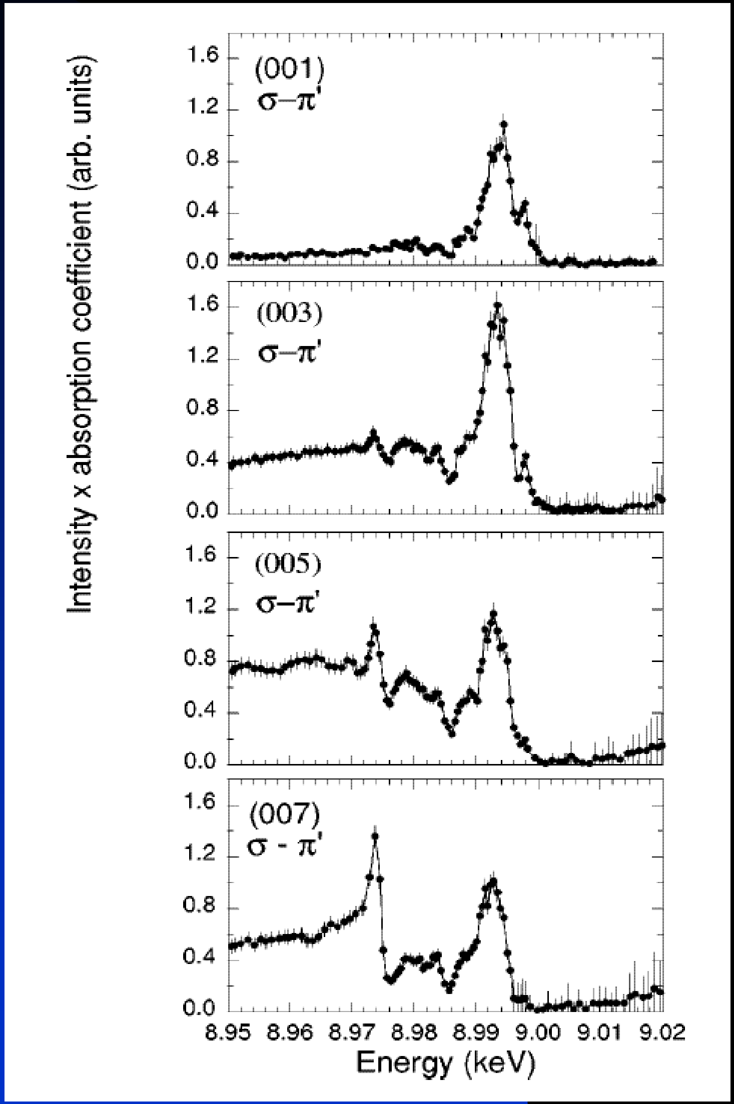


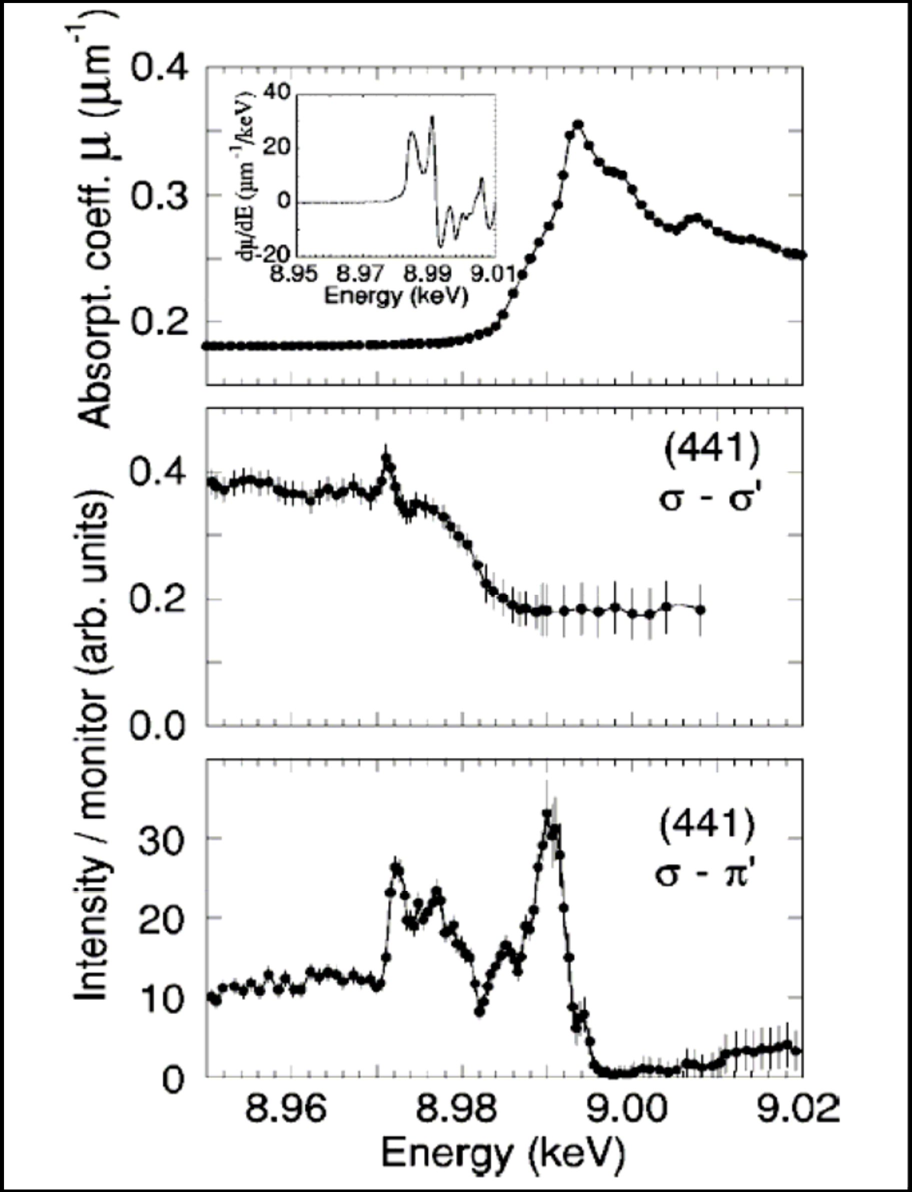
The Experiment

- A photon beam polarized perpendicularlyto the (vertical) scattering plane impinges on the sample *S* and is scattered towards the analyzer crystal *A*.
- The scattered beam componentswith polarization parallel (π') or perpendicular (σ') to the scattering plane can be selected by an appropriate orientation of the analyzer.
- *D* is a standard scintillation detector. Integrated intensities of Bragg peaks are measured as a function of the photon energy for different values of the azimuthal angle ρ, defining the crystal orientation about the scattering vector (*hkl*). The unit vectors $\mathbf{u}_i$ define the reference frame.



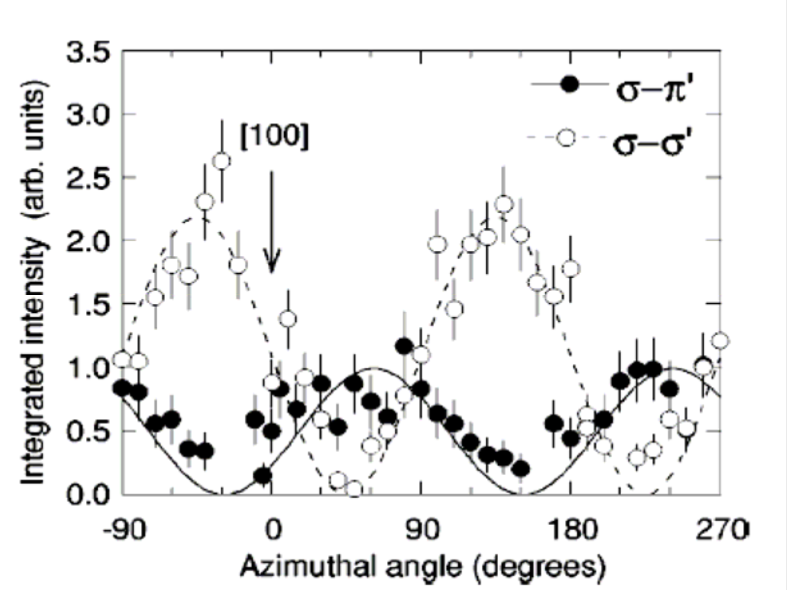
Results


Intensity x absorption coefficient (arb. units)
1.6
1.2
0.8
0.4
0.0
(001)
σ–π'
(003)
σ–π'
(005)
σ–π'
(007)
σ - π'
8.95
8.96
8.97
8.98
8.99
9.00
9.01
9.02
Energy (keV)


Absorpt. coeff. μ (μm⁻¹)
0.4
0.3
0.2
dμ/dE (μm⁻¹/keV)
40
20
0
-20
8.95
8.97
8.99
9.01
Energy (keV)
Intensity / monitor (arb. units)
(441)
σ - σ'
0.4
0.2
0.0
(441)
σ - π'
30
20
10
0
8.96
8.98
9.00
9.02
Energy (keV)

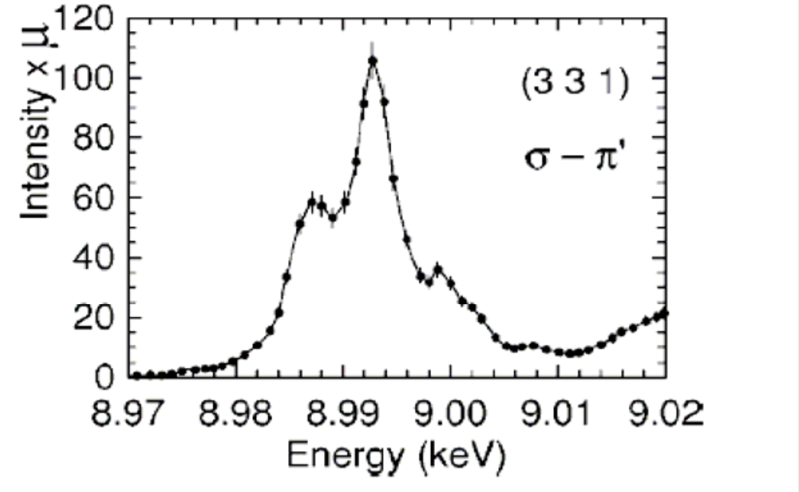
Azimuthal scans

- Azimuthal scans about the (005) magnetic Bragg peak far away from resonance, at *T*=11 K; closed circles correspond to the σ-π’ channel, open circles to σ-σ’. Data points are intensities corrected for absorption. Lines are intensities calculated assuming magnetic moments along the [1 1 0] direction, for a collinear arrangement of spin and orbit moments.



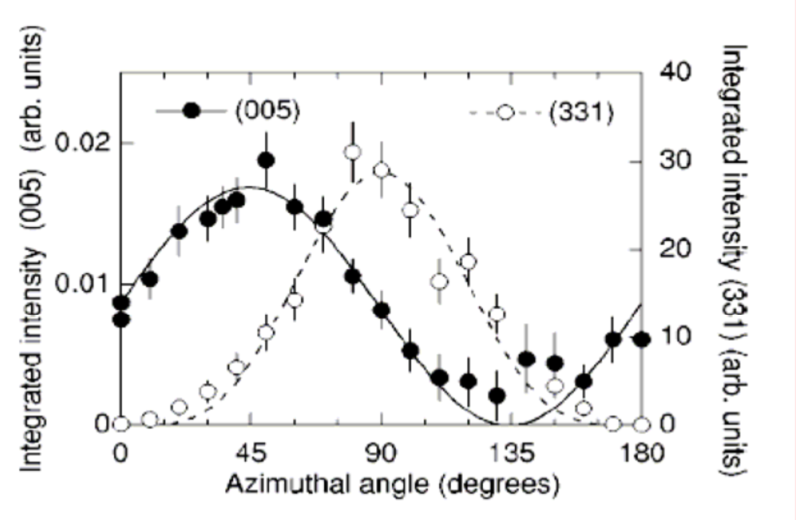
Orbital Ordering

- Energy dependence of σ-π’ intensities of the (331) superlattice reflections, corresponding to long-range ordering of 3*d* Cu orbitals in $KCuF_3$.
- Data were recorded at 12 K, and are corrected for absorption.



Azimuthal scans

- Azimuthal angle dependence of the magnetic (005) (closed circles) and the orbital (331) (open circles) σ-π' intensities.
- Data were taken at 12 K, with incident energy of 8.992 keV and LiF(004) analyzer. The solid lines are the twofold squared sinusoidal curve describing the angular dependence.



Temperature Dependence

- Temperature dependence of the integrated intensity of the (331) orbital ordering peak (triangles) and the magnetic (441) Bragg reflection (circles).
- The qualitative behavior of the orbital order parameter Ψ as a function of temperature, computed in the mean-field approximation is shown in the inset.