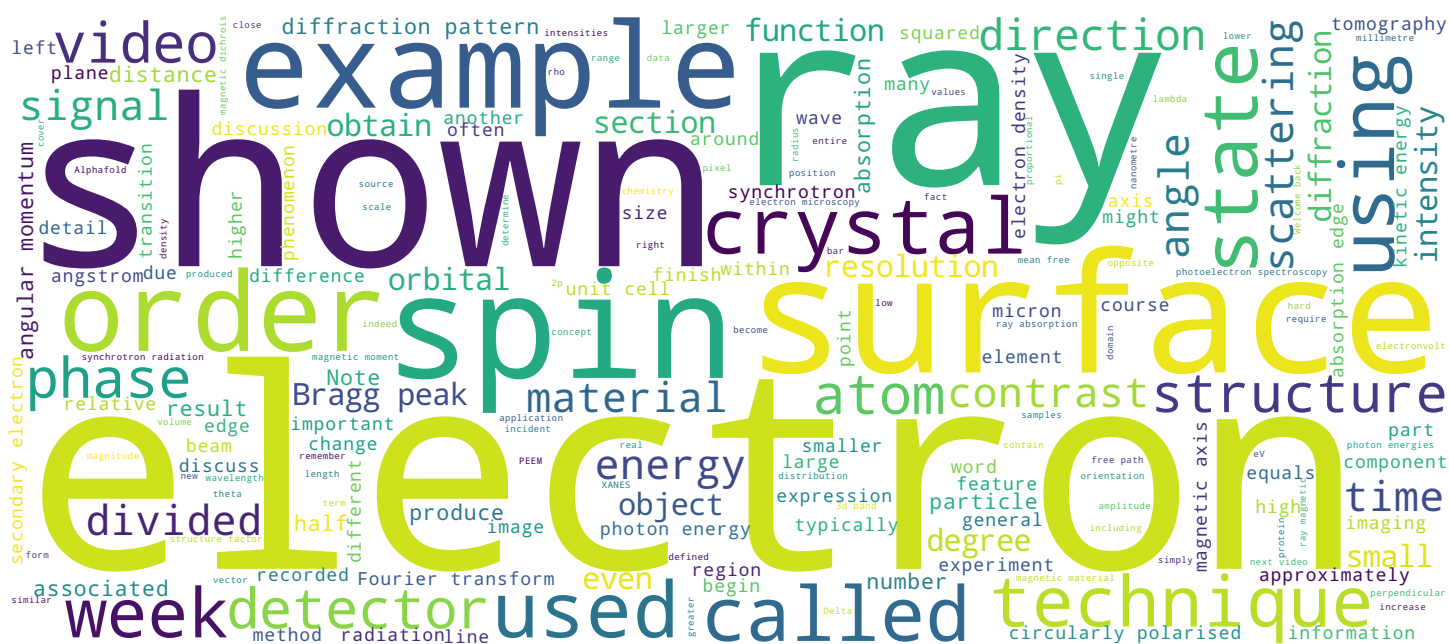


Prof. Philip Willmott



## Search MOOC



## Video



# Contents and objectives of this video



- PEEM intro
- Resolution limits of PEEM
- Magnetic dichroism
- Exchange interaction and ferromagnetism
- XMCD
- XMLD

Hi, again. In this video, we encounter the last variant of XANES to be discussed in this course, namely photoelectron emission microscopy, or PEEM. After some introductory remarks, we will consider magnetic dichroism, which provides magnetic contrast, depending on the polarisation of the incident X-radiation. We'll discover the phenomenon of exchange interaction in ferromagnetism, and finish with a description of both X-ray magnetic circular dichroism and X-ray magnetic linear dichroism.

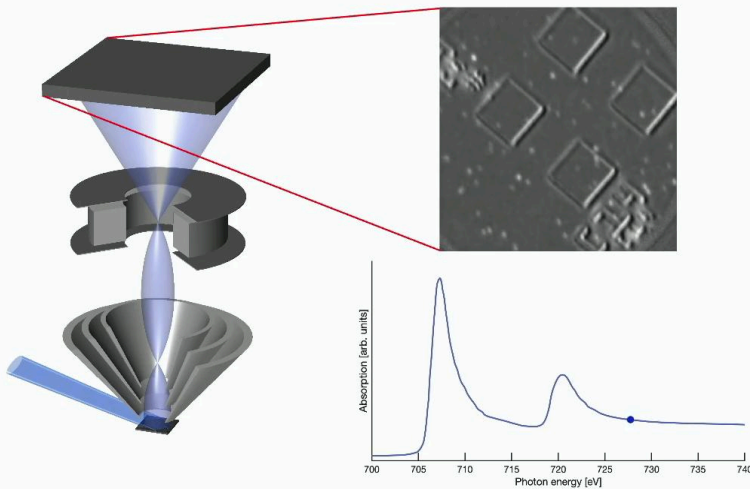
Notes

Summary

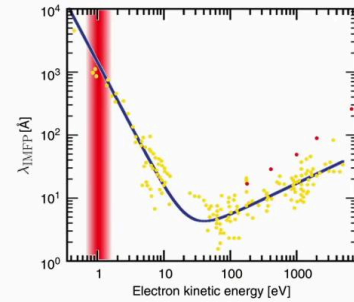


0m 05s

# Introductory comments



- Photoemission electron microscopy (PEEM)
  - Electron microscopy + XANES
    - Full-field imaging, spectromicroscopy
  - Absorption recorded via secondary-electron yield ( $\lesssim$  eV)



- Contrast
  - Chemical shifts
  - Magnetic dichroism

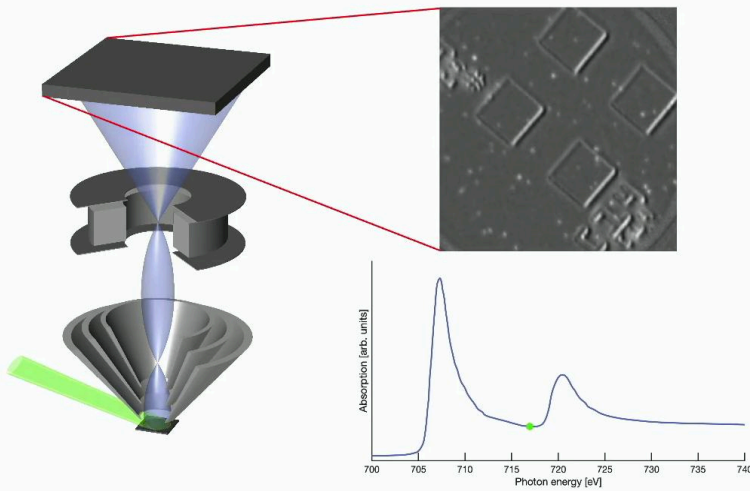
PEEM is a technique that captures the photoelectric emission signal from a relatively large illumination area and images this using electron optics, much as one uses in conventional electron microscopy to form a two-dimensional image of the illuminated surface. The electrons that are captured are low-energy secondary electrons that have been quasi-thermalized through multiple collisions before their emergence from the sample surface. This is in contrast to X-ray photoelectron spectroscopy, discussed next week, which measures the kinetic energy of photoelectrons that have not been inelastically scattered. Contrast in PEEM is achieved either through chemical shifts, PEEM is sensitive to the chemistry of the sample, or through magnetic dichroism. A PEEM experiment essentially consists of tuning synchrotron radiation, illuminating an entire sample in vacuum and imaging the spatial variation of the subsequent secondary-electron yield using the electrostatic and/or electromagnetic lens system. As such, PEEM is a form of spectromicroscopy. Full-field images are recorded at different photon energies, in contrast to STXM, a microspectroscopy technique in which the focused X-ray beam is rastered across the sample.

Notes

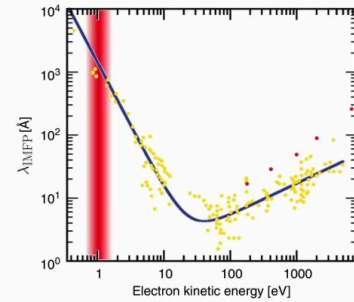
Summary



# Introductory comments



- Photoemission electron microscopy (PEEM)
  - Electron microscopy + XANES
    - Full-field imaging, spectromicroscopy
  - Absorption recorded via secondary-electron yield ( $\lesssim$  eV)



- Contrast
  - Chemical shifts
  - Magnetic dichroism

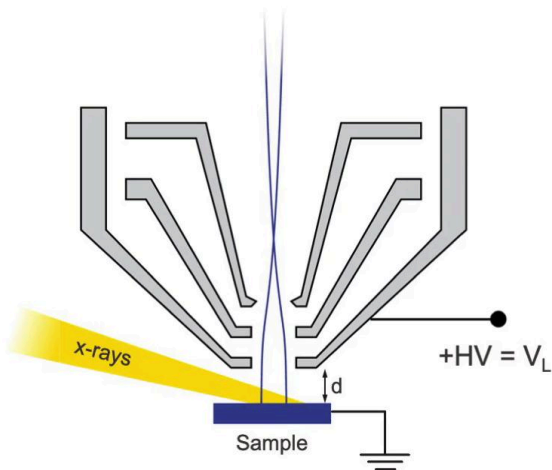
The secondary electrons are imaged using a 2D detector. In contrast to scanning electron microscopy, PEEM does not use a scanned probe electron beam, but instead, the sample surface is uniformly illuminated by the X-rays. The magnified image of the surface can therefore be observed directly and in real time. Stroboscopic time-resolved experiments can therefore be performed using the time structure of the synchrotron down to timescales well below a nanosecond. Because the inelastic mean-free path of the secondary electrons is of the order of several nanometres or more, PEEM is in general, not highly surface-sensitive, although this can be induced by irradiating the sample with X-rays at very glancing angles  $\theta$ , thereby reducing their penetration depth below the sample surface by a factor of  $\sin \theta$ .

Notes

Summary



# Resolution of PEEM



$$\Delta x = \frac{d \Delta \mathcal{E}_e}{eV_L}$$

## Resolution of PEEM

- $\Delta \mathcal{E}_e$  = range of secondary-electron KEs in image plane
- Sample-lens distance  $d \sim 2$  mm
- $V_L \sim 10$  keV
- Accelerating field produces parabolic trajectories
- $\Delta \mathcal{E}_e$  can be reduced using aperture between sample and objective electron lens
  - At cost of reduced signal intensity
- Extrapolate tangents of parabolic trajectories as they enter lens  $\Rightarrow$  1:1 magnification virtual image with resolution  $\Delta x$
- Best  $\Delta x \sim 20$  nm, typically 50 nm

The resolution of PEEM depends on the range of secondary electron energies, the sample lens distance, which is typically a couple of millimetres, and the accelerating voltage from the sample to the first element of the objective electron lens, which is of the order of around 10 keV.

Notes

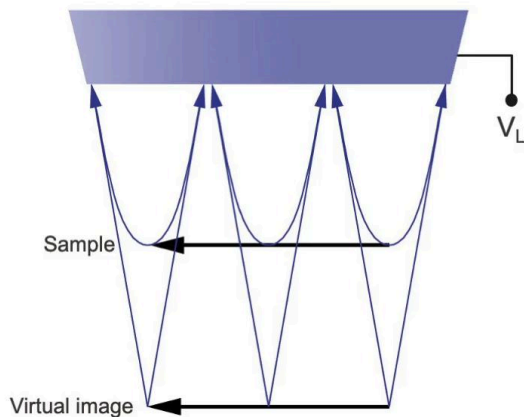
Summary



3m 06s



# Resolution of PEEM



$$\Delta x = \frac{d \Delta \mathcal{E}_e}{e V_L}$$

## Resolution of PEEM

- $\Delta \mathcal{E}_e$  = range of secondary-electron KEs in sample plane
- Sample-lens distance  $d \sim 2$  mm
- $V_L \sim 10$  keV
- Accelerating field produces parabolic trajectories
- $\Delta \mathcal{E}_e$  can be reduced using aperture between sample and objective electron lens
  - At cost of reduced signal intensity
- Extrapolate tangents of parabolic trajectories as they enter lens  $\Rightarrow$  1:1 magnification virtual image with resolution  $\Delta x$
- Best  $\Delta x \sim 20$  nm, typically 50 nm

The electron field,  $V_L$  divided by  $D$ , produces in the electrons a parabolic trajectory with a gradient that depends on how much the transverse component of their kinetic energy is. This can be reduced by using an aperture between the sample and electron optics, but at the cost of signal intensity. If one extrapolates the tangents to the parabolic trajectories as they enter the lens, one obtains a virtual image with a one-to-one magnification and with a resolution  $\Delta x$  given by  $d$ ,  $\Delta \mathcal{E}_e$ , divided by  $e V_L$ . This can be as small as a couple of tens of nanometres, but is more typically around 50 nanometres.

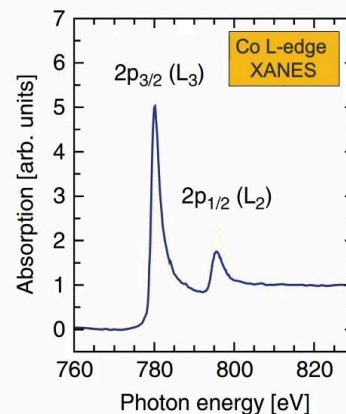
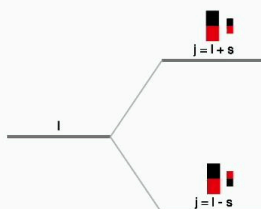
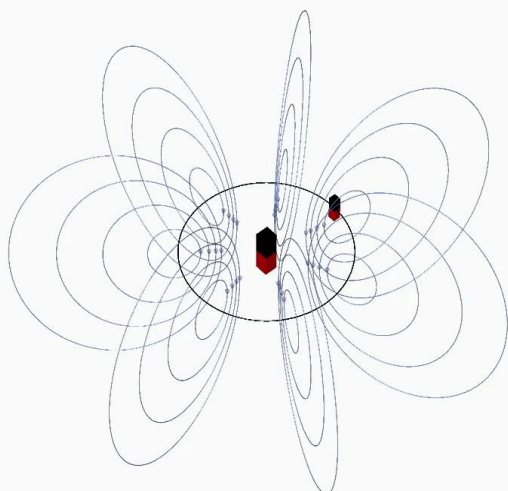
Notes

Summary



# Magnetic dichroism

- Spin selection rules
  - $\Delta s = 0$
- $j = l + s$  has higher energy (lower binding energy) than  $j = l - s$



We now consider the phenomenon of magnetic dichroism in magnetic materials. From our discussions in the first section of this week, you might remember that transitions between states with opposite spin are forbidden. That is, the selection rule,  $\Delta s$  equals zero is observed. Now, this rule isn't entirely strict for condensed matter, but is sufficiently observed to induce dichroism. Now, hopefully you also remember that parallel orbital and spin angular momentum are energetically unfavourable, analogously to two magnets being placed next to each other with their north poles adjacent and south poles adjacent. The quantum state of  $j$ , the total angular momentum, equals  $l + s$ , thus has a higher energy than  $j$  when it's equal to  $l - s$ , and thus, a lower X-ray absorption edge, as it requires less energy to bring an electron in the  $l + s$  state to the unoccupied LUMO than it does the  $l - s$  state. XMCD functions because magnetic materials have an imbalance of electrons with spin up and spin down in the valence band. For example, the transition from a 2p core level to the unoccupied states in a 3d band via the absorption of an X-ray photon will contain two components, one from the 2p half and the other from the 2p three-halves. These are allowed as the change in orbital angular momentum,  $\Delta l$ , is equal to one.

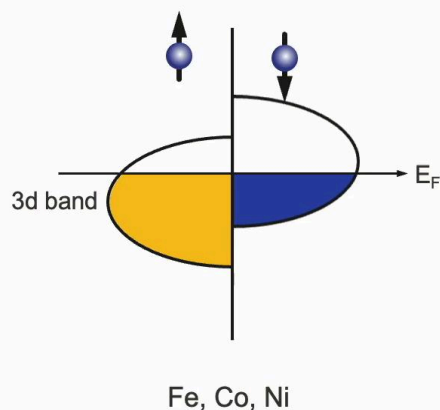
Notes

Summary



4m 19s

# Exchange interaction and ferromagnetism



- Magnetism in ferromagnetic materials due to imbalance between number of spin-up and spin-down states
- Caused by shift in energies of spin-up and spin-down sub-bands
- Result of “exchange interaction”
  - Pauli’s exclusion principle
  - State =  $|n, l, m_l, s, m_s\rangle$
  - If only  $m_s$  different between states  $\Rightarrow$  large spatial overlap
  - $\Rightarrow$  Coulomb repulsion, splitting
  - Splitting  $\sim$  eV

Now, how does the spin imbalance arise to induce ferromagnetism? The Pauli Exclusion Principle states that two electrons with the same spin cannot also have the same spatial wavefunction. This is a consequence of electrons being fermions. Therefore, if the orbits of unpaired outer valence electrons from adjacent atoms overlap, the distributions of their electric charge and space are farther apart when the electrons have parallel spins than when they have opposite spins. This reduces the electrostatic energy of the electrons when their spins are parallel compared to when the spins are antiparallel. Consequently, the parallel spin state is more stable, a bit like the bonding orbital, while the antiparallel state has higher energy. This results in a shift in energies of spin up and spin down sub-bands. The difference in these two states is called the exchange energy.

Notes

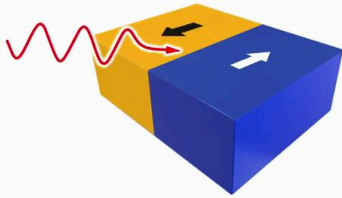
Summary



5m 59s



# Ferromagnetism and x-ray magnetic circular dichroism



- Irradiate with either RCP or LCP
- Spin flips (partially) forbidden
- Absorption depends on
  - Orientation between incident radiation and magnetic domain direction
  - Polarization (LCP or RCP)
  - Spin-orbit core state

Now, how does one obtain image contrast of differently-oriented ferromagnetic domains? This is achieved by using circularly polarised light from which dichroism emerges. Dichroism means two-coloured, and is the phenomenon of a material having an absorption spectrum which changes according to the polarisation of the electromagnetic radiation that is used. Magnetic dichroism describes the dependence of the absorption of a magnetic material on the polarisation of the light used and the relative orientation of an applied external magnetic field. To summarise what we have already discussed in the first section of this week, the intrinsic magnetic moment of an electron is produced by its spin. Note that the direction of the magnetic moment is antiparallel to that of the spin. Electrons always possess spin angular momentum of quantum number  $s$  is equal to plus or minus one-half, and magnitude square root of three quarters multiplied by  $\hbar$ . The orientation of the spin relative to a magnetic field, which is either  $m_s$  plus a half up or  $m_s$  minus a half down, determines it's only two possible orientations.

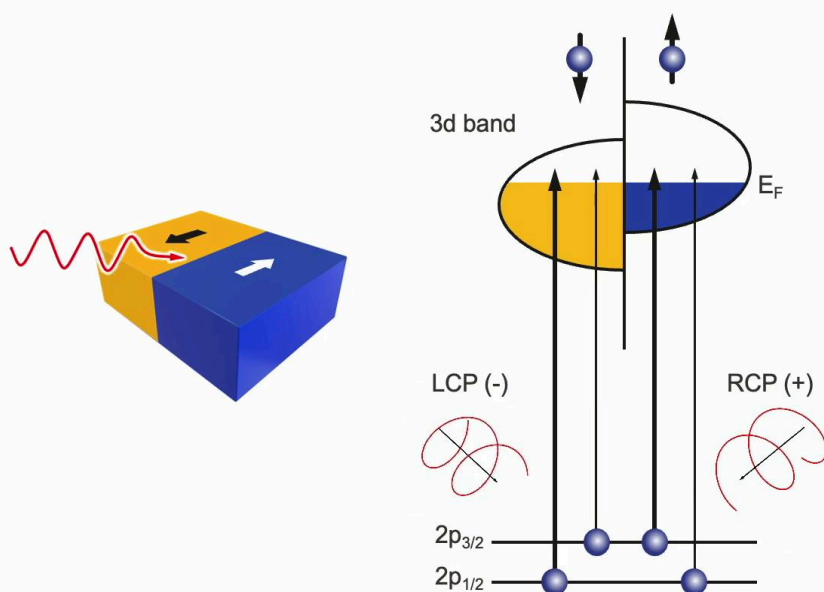
Notes

Summary



7m 05s

# Ferromagnetism and x-ray magnetic circular dichroism



- Irradiate with either RCP or LCP
- Spin flips (partially) forbidden
- Absorption depends on
  - Orientation between incident radiation and magnetic domain direction
  - Polarization (LCP or RCP)
  - Spin-orbit core state

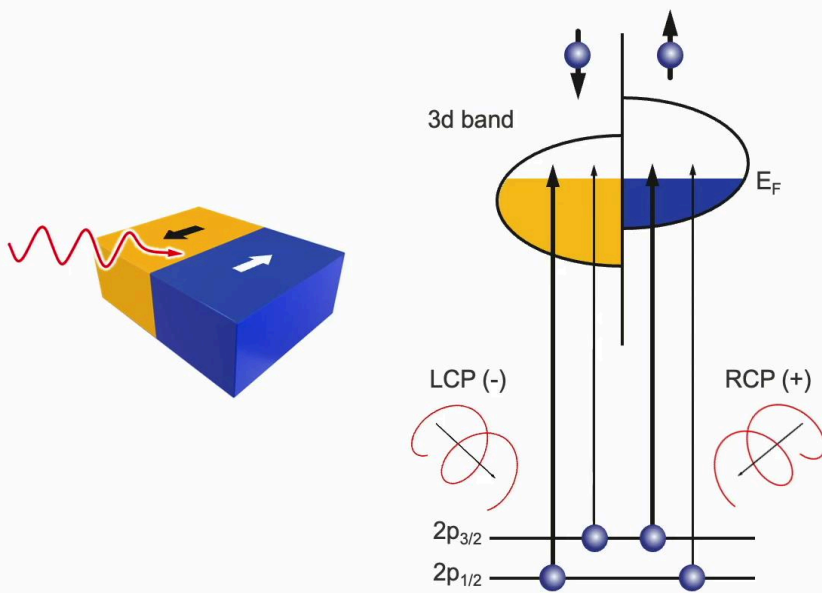
Now, let's consider the transitions from the 2p level to the 3d band. In the case of the blue-coloured domain, there are more occupied 3d states with their spin down than with spin up, hence the magnetisation of this domain is upwards. In other words, the opposite direction to the imbalance in spin states, because remember, the spin direction is opposite to the magnetisation direction. In contrast, the number and density of unoccupied spin-up states above the Fermi level,  $E_F$ , in the 3d band, is greater than for spin down states for the blue domain, and the transition probability for absorption of a photon will thus be greater. In addition, one must take a further selection rule into consideration, which states that for dipole transitions, spin flips are forbidden. To obtain this so-called X-ray magnetic circular dichroism, one uses circularly polarised light. In the case of the blue region, an incident RCP photon, right circularly polarised photon, has its orbital angular momentum pointing forwards, that is, in the direction of propagation, and will preferentially excite the 2p three-halves level over the 2p one-half level. The opposite case arises for left circularly polarised photons, whereby the 2p half states are favoured.

Notes

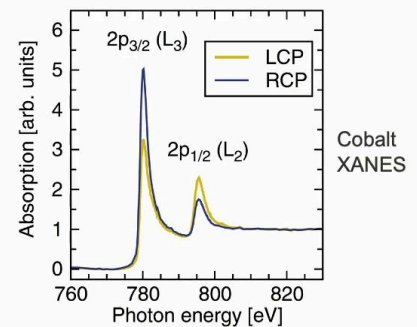
Summary



# Ferromagnetism and x-ray magnetic circular dichroism



- Irradiate with either RCP or LCP
- Spin flips (partially) forbidden
- Absorption depends on
  - Orientation between incident radiation and magnetic domain direction
  - Polarization (LCP or RCP)
  - Spin-orbit core state



Lastly, if we now focus on the gold region with the opposite magnetic orientation to the blue domain, the whole story reverses as the spin down 3d subband is now shifted to higher energies than the spin up subband. By recording PEEM images of ferromagnetic domains with right circularly polarised and left circularly polarised X-rays and dividing the intensities of one image pixel for pixel by those of the other, the domain structure is revealed with maximum contrast.

Notes

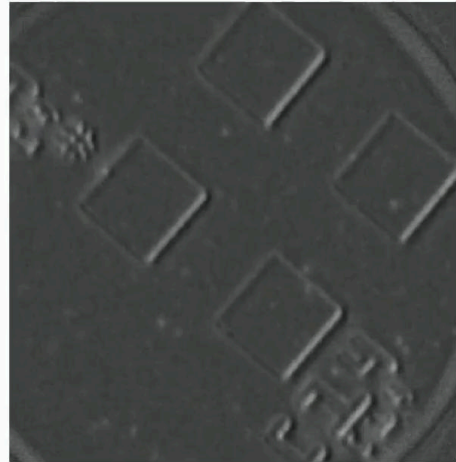
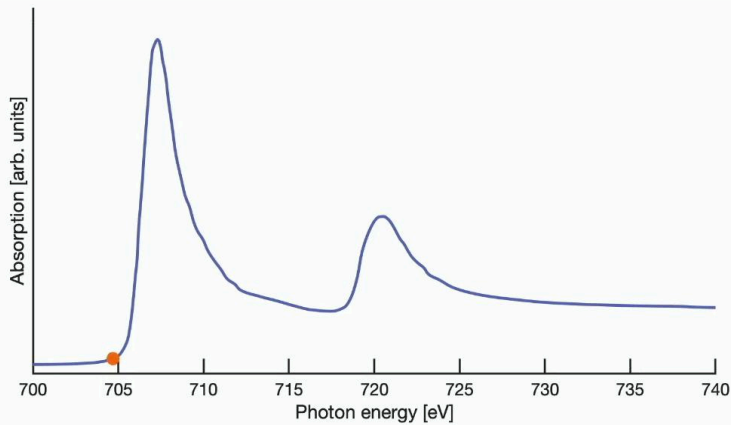
Summary

10m 05s



# Ferromagnetism and x-ray magnetic circular dichroism

Probing iron nanoparticles



A. Fraile Rodríguez *et al.*,  
<https://iopscience.iop.org/article/10.1088/0022-3727/43/47/474006>

An example is shown here of probing iron nanoparticles recorded around the iron L2 and L3 edges between 700 and 740 eV. The particles are brightly lit exactly where the spin orbit split maxima of iron are at 708 and 720 eV.

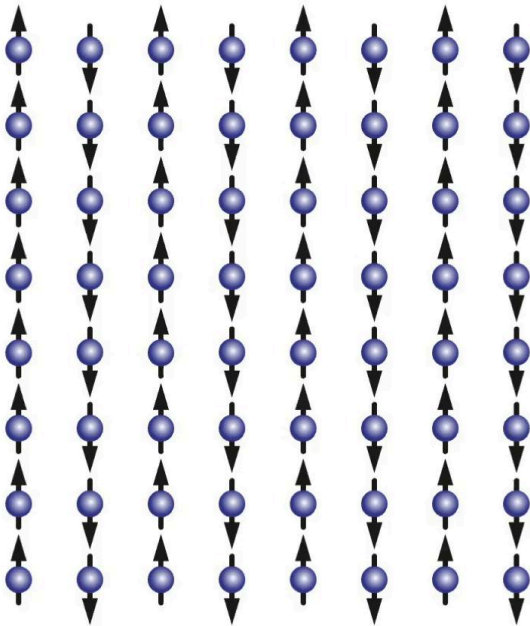
Notes

Summary

10m 39s



# X-ray magnetic linear dichroism



- Antiferromagnets
  - No net magnetic moment
    - Equal and opposite number of spin-ups and spin-downs
  - But have magnetic axis!
- XMLD
  - Spin-orbit coupling  $\Rightarrow$  distortion of spatial distribution of the electron density
  - Provides dichroism depending on whether the linear polarization vector is parallel to or perpendicular to the magnetic axis
  - Effect is smaller than in XMCD
  - $\cos^2\theta$  dependence,  $\theta$  = angle between magnetic axis and linear polarization

We finish our discussion of magnetic dichroism with a brief summary of X-ray magnetic linear dichroism. XMLD is used to investigate the domain structure of antiferromagnetic domains. Such materials are characterised by having antiparallel orientations of neighbouring spin magnetic moments, and thus, no net spin, but nonetheless a defined magnetic axis below a critical temperature known as the Néel temperature.

Notes

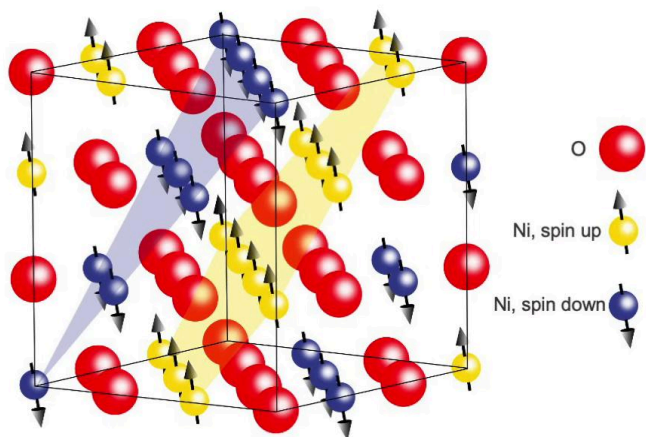
Summary



11m 01s



# X-ray magnetic linear dichroism



- Antiferromagnets
  - No net magnetic moment
    - Equal and opposite number of spin-ups and spin-downs
  - But have magnetic axis!
- XMLD
  - Spin-orbit coupling  $\Rightarrow$  distortion of spatial distribution of the electron density
  - Provides dichroism depending on whether the linear polarization vector is parallel to or perpendicular to the magnetic axis
  - Effect is smaller than in XMCD
  - $\cos^2\theta$  dependence,  $\theta$  = angle between magnetic axis and linear polarization

A simple schematic example is shown here, while the real system of nickel oxide is sketched here. This has a cubic rock salt structure. Below the Néel temperature, the spins of the nickel ions in the 111 crystallographic planes, shown here in blue and yellow, alternate between being all spin up and all spin down. There is therefore no net magnetic moment, but there does exist a magnetic axis given by the spin orientations. XMLD signal arises from the fact that due to spin-orbit coupling, the spatial distribution of the electron density is marginally distorted, providing the necessary dichroism, depending on whether the linear polarisation vector is parallel or perpendicular to the magnetic axis. The effect is usually small and detecting XMLD is more challenging than XMCD. It has a cosine squared theta dependence, where theta is the angle between the polarisation vector of the X-ray light and the magnetic axis of the domain. The maximum XMLD effect therefore occurs when the signal for the polarisation parallel to the magnetic axis is compared to that perpendicular to the axis.

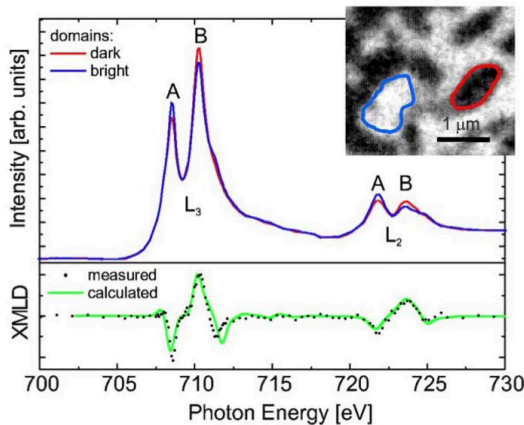
Notes

Summary



11m 36s

# X-ray magnetic linear dichroism



25-nm thin film of  $\text{LaFeO}_3$  grown on  $\text{SrTiO}_3$   
S. Czekaj *et al.*, DOI: [10.1103/PhysRevB.73.020401](https://doi.org/10.1103/PhysRevB.73.020401)

- Antiferromagnets
  - No net magnetic moment
    - Equal and opposite number of spin-ups and spin-downs
  - But have magnetic axis!
- XMLD
  - Spin-orbit coupling  $\Rightarrow$  distortion of spatial distribution of the electron density
  - Provides dichroism depending on whether the linear polarization vector is parallel to or perpendicular to the magnetic axis
  - Effect is smaller than in XMCD
  - $\cos^2\theta$  dependence,  $\theta$  = angle between magnetic axis and linear polarization

An example is shown here on the left of antiferromagnetic domains in thin films of the perovskite material, lanthanum iron oxide, grown on strontium titanate. One sees that the contrast is significantly weaker in XMLD than it typically is in XMCD.

Notes

Summary



13m 01s

## In the next video...



In the next, penultimate, video and the one thereafter, we will conclude this week by discussing extended X-ray absorption fine structure spectroscopy. This technique is important for the study of non-crystalline solids and liquids as it yields element-specific information of the short-range structure of materials. It's thus complementary to diffraction techniques.

Notes

Summary



13m 22s