Experiment 2

X-ray fluorescence

X-ray fluorescence (XRF) and X-ray diffraction (XRD) may be used to determine the constituent elements and the crystalline structure of materials.

Introduction

2.1 X-ray fluorescence

XRF refers to the absorption of incident X-rays ($h\nu_0$) resulting in the production of a set of X-rays whose energies ($h\nu_j$) are characteristic of the absorber atom(s) (Z). The characteristic X-rays can therefore be used to identify the atom(s) present in the sample.

The incident X-ray photon ($h\nu_0$) undergoes a photoelectric interaction with a target atom (Z) resulting in the annihilation of the photon and ionization of the target atom. The energy equation is

$$K = h\nu_0 - B$$

where K is the kinetic energy of the photoelectron liberated from the atom and B is its binding energy to the atom. Subsequently, the ionized atom combines with an electron and undergoes a de-excitation to its electrically neutral ground state. X-ray photons, whose energies ($h\nu_j$) are characteristic of the target atom (Z), are produced in the de-excitation. An energy level diagram is shown in figure 2.1. Each level corresponds to the excitation of the atom when a single electron is missing from the otherwise full subshell (nlj). Zero energy corresponds to the ground state of the neutral atom. Level K, corresponds to the binding energy (B_K) of an electron in the K shell. There are three closely spaced L shell levels labelled L_I, L_{II}, L_{III} corresponding to slightly different L shell electron binding energies. If

$$h\nu_0 > B_K$$

then all characteristic X-rays (K series, L series, etc.) are produced. If

$$B_L < h\nu_0 < B_K,$$

then the K series X-rays are not produced.

2.2 X-ray Diffraction

X-ray diffraction is used extensively to determine the structure of crystalline and also of non-crystalline and amorphous materials. For crystalline materials, the directions (θ) and wavelength(λ)

Energy (eV)

K series

10^5

L series

M series

10^4

10^3

10^2

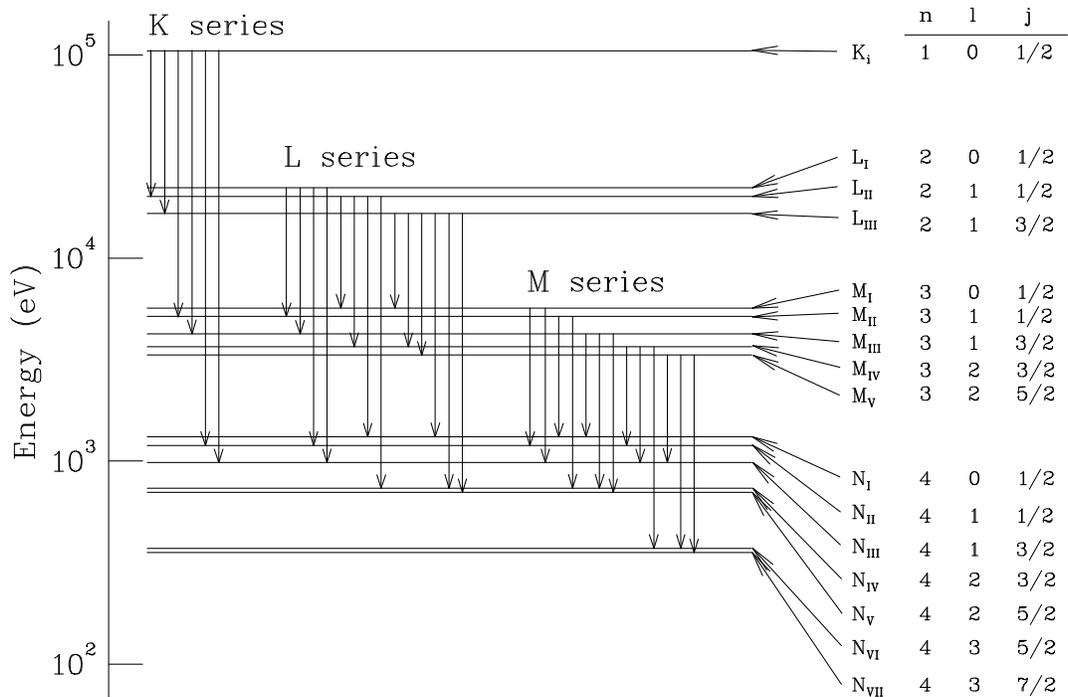|	n	l	j
K_i	1	0	1/2
L_I	2	0	1/2
L_{II}	2	1	1/2
L_{III}	2	1	3/2
M_I	3	0	1/2
M_{II}	3	1	1/2
M_{III}	3	1	3/2
M_{IV}	3	2	3/2
M_V	3	2	5/2
N_I	4	0	1/2
N_{II}	4	1	1/2
N_{III}	4	1	3/2
N_{IV}	4	2	3/2
N_V	4	2	5/2
N_{VI}	4	3	5/2
N_{VII}	4	3	7/2

Figure 2.1: A schematic diagram of the X-ray energy levels.

of the diffracted beams are given by Bragg's Law; with reference to figure 2.2, this is

$$2d \sin \theta = n\lambda$$

where n is the order of diffraction from crystalline lattice planes of spacing d. The equation may be rewritten as

$$2d_n \sin \theta = \lambda$$

where $d_n = d/n$ and the equation now represents first order diffraction from planes d/n. Using Bragg's Law, a measurement of θ and λ for a diffracted beam enables the spacing d_n to be determined. For cubic lattices,

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is the side length of the cubic lattice cell (the lattice constant), and h, k and l are the Miller indices of the lattice planes.

2.3   Apparatus

A diagram of the apparatus is shown in figure 2.3. The incident beam produced by the X-ray machine has its intensity continuously distributed over a range of X-ray photon energy up to a maximum value $= eV$, where V is the X-ray tube voltage.

The incident beam strikes a crystalline powder; the X-rays diffracted from the crystals and those fluoresced from the target atoms are recorded by a Si semiconductor junction photon detector (which is sensitive to photons with energies in the range $\approx 1 \rightarrow 50$ keV) positioned at an angle 2θ relative to the direction of the incident beam. The Si detector produces a single voltage pulse
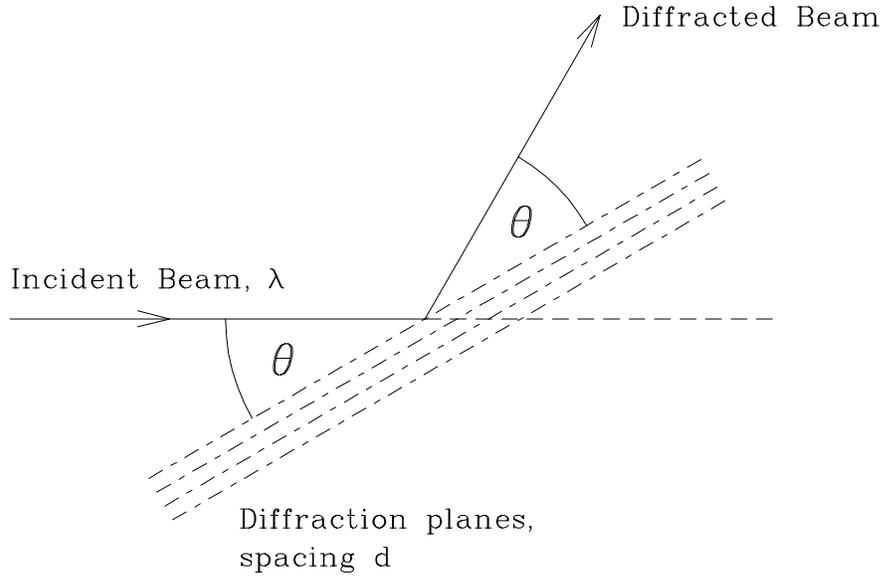
Figure 2.2: Diffraction geometry.

for each photon detected; its amplitude is proportional to the energy of the photon detected. The energy (voltage amplitude) spectrum of X-ray photons produced from the target is recorded by a multichannel analyser (MCA). The spectrum $I(E)$ which is the variation of the number of photons detected, I, with photon energy, E, consists of a series of relatively narrow peaks superimposed on a smoothly varying background. The peaks arise from

- X-rays fluoresced from the target atoms,

- X-rays diffracted from the crystal lattice.

The position of the peak centre on the MCA energy scale equals the corresponding photon energy.

2.4 Energy Dispersive X-ray Diffraction

In this apparatus, the diffraction is observed by measuring $I(E)$ keeping θ constant. Bragg's Law may be rewritten in terms of the diffracted beam photon energy, E, i.e.,

$$2d_n \sin \theta = \lambda = \frac{hc}{E}$$

or,

$$E_{hkl} = \frac{hc}{2 \sin \theta} \cdot \frac{1}{d_{hkl}}. \tag{2.1}$$

hkl are the Miller indices of the planes which produce diffraction of photons of energy E_{hkl}. For a particular value of the diffraction angle r (the detector is positioned at an angle 2θ relative to the incident beam) diffraction from planes with different d_{hkl} values produce diffraction peaks at
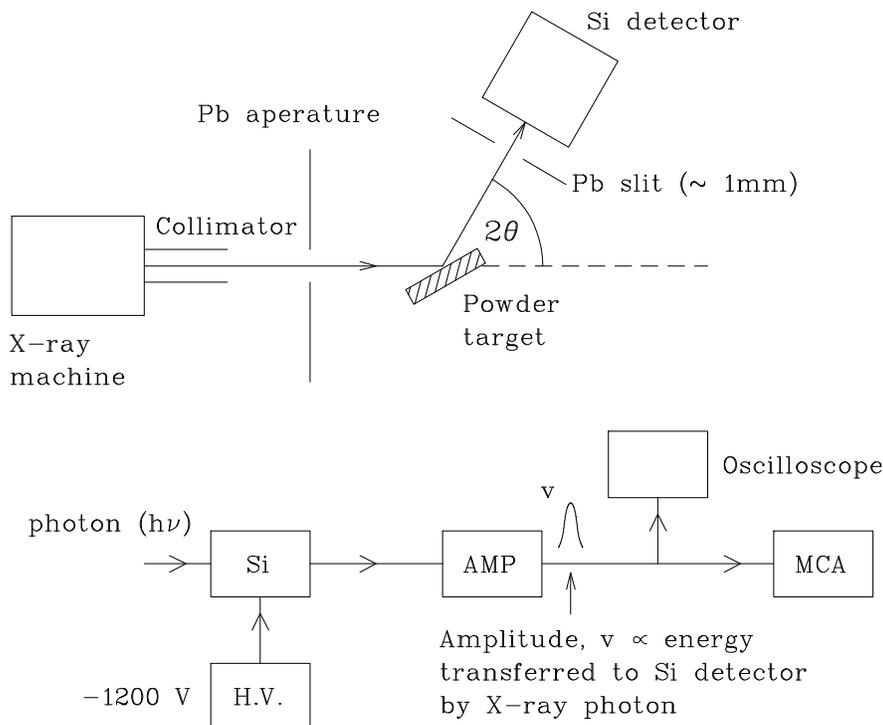
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Figure 2.3: Schematic diagram of apparatus.

energies E_{hkl}, given by equation (2.1). Diffraction peak energies E_{hkl} are a function of θ (Eq. 2.1); XRF characteristic peak energies are independent of θ. In addition, the diffraction peak intensities are normally much weaker than those produced by the characteristic X-rays fluoresced from the target. Either of the above features may be used to distinguish the characteristic X-ray and the diffraction peaks.

Experiment

CAUTION
The instructor will demonstrate the operation of the X-ray machine, the Si photon detector and the multichannel analyser.
Under no circumstances is the apparatus to be operated prior to instruction.
Under no circumstances are adjustments to be made to the target arrangement with the X-ray beam on. The X-ray beam is a radiation hazard.

2.5   Objective

The objective is to identify the constituent elements (using XRF) of the powdered samples.

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2.6 Operation

- **Si Photon Detector**
  The detector is operated at liquid nitrogen temperature. *The detector reverse bias must only be applied to a cold detector, otherwise irreversible damage to the detector will result.*

  Normally, the reverse bias (≈ -1200 V) and the amplifier are already switched on and preset, and no adjustments are necessary. However, if the reverse bias has to be switched ON or OFF, this must be done with the bias voltage potentiometer turned to zero. Do not make any adjustment without first consulting the instructor.

- **X-ray Machine**
  The machine is normally operated at a tube voltage in the range, 20-30 kV, and a current up to a maximum of approximately 15 mA. These values are not at all critical; the voltage range provides an incident X-ray beam spectrum which is reasonably well-matched to that required both for XRF and diffraction.

  <u>Note</u>: The X-ray beam port and shutter must be *closed* and the X-ray tube high voltage switched OFF prior to making any beam-target alignment changes. *This requirement is MANDATORY.*

- **MCA**
  The multichannel analyser (MCA) is normally left switched ON, ready for use. The computer monitor is switched OFF when not in use. The operation of the MCA is by selection from a menu which is displayed, together with the spectrum, on the monitor.

Procedure

2.6.1 Energy Calibration

1. <u>Alignment</u> *(X-ray HV OFF; beam shutter CLOSED)* Position, visually, the energy calibration target into the X-ray beam path (which is determined by the axis of the X-ray beam collimator) and set the Si detector rotatable platform somewhere in the range $2\theta = 45 \to 60°$, relative to the incident X-ray beam path.
   Check visually, but carefully, that the X-ray beam path strikes the target surface centrally and also that the target surface can be seen by the Si detector. The precise value of 2θ is not required; the approximate value ($\pm$ a few degrees) may be helpful in identifying features of the diffraction spectrum. For the calibration, use samples of Zn, Mo and KBr.

2. <u>Spectrum Accumulation</u> *(X-ray HV ON; beam shutter OPEN)*
   Accumulate a "smooth" spectrum in which the peaks are clearly defined (that is, the peak centres can be determined by inspection to $\pm$ 1 channel). The XRF lines due to the main elements in the layer are normally significantly stronger than any diffraction lines. When the accumulation is completed, *CLOSE the beam shutter and turn the X-ray current HV OFF.*

3. <u>Calibration analysis</u>
   Record the channel number (n) for the centre of each XRF peak and identify the peaks with the characteristic energies (E_n) corresponding to the known elements in the calibration target. The energy calibration of the MCA is accurately given by

$$E_n = an + b.$$

The calibration constants (a and b) should be determined by a linear regression analysis and also the data should be plotted. This calibration may be used, without further check, throughout the experiment providing the gain of the Si detector amplifier and the "set-up" of the MCS remain unchanged. Using the calibration, the energies of XRF and diffraction peaks obtained in subsequent spectra may be determined.

4. Diffraction peaks
   Use the d values, with largest intensity, of the calibration samples and an estimated 2θ value, to calculate the E_{hkl} values from Eq. (2.1) where a diffraction peak might be located. Inspect the $I(E)$ spectrum for such (weak) peaks. If one (or more) are found, redo a spectrum at a different ($\pm$ a few degrees) 2θ value and check that indeed the peak energy is a function of θ.

2.7 Analysis of powdered samples

1. Alignment *(X-ray HV OFF; X-ray beam shutter CLOSED)*
   Install the powdered crystalline target and repeat the beam-target-detector alignment described in section 2.6.1, item 1.

2. Spectrum accumulation *(X-ray HV ON, X-ray beam shutter OPEN)*
   Accumulate data and store the resulting spectrum; there should be strong XRF lines present and (maybe) much weaker diffraction lines visible. Change the detector angle by a few degrees and repeat the accumulation; compare with the previous spectrum. The diffraction peaks shift position in the spectrum, the XRF peaks do not. After this provisional classification into XRF and diffraction lines, keep the detector angle fixed and accumulate until a "smooth" spectrum is obtained. A "smooth" spectrum is a very qualitative term which simply means that the centres of the peaks of interest may be determined by visual inspection to approximately $\pm$ 1 channel. It is useful to keep an eye on the X-ray machine current and voltage readings during accumulation *since occasionally the machine trips OFF; if this occurs, restart; if trips persist, call the instructor.* When the accumulation is completed, CLOSE the X-ray beam shutter and turn the X-ray current and HV OFF.

3. Data Analysis

   (a) Determine the energies of the XRF and diffraction peaks (if any).
   (b) Using the characteristics X-ray energy tables, identify the elements in the powdered sample.