

Calculating Crystal Structure and Lattice Parameters Using X-ray Diffraction

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Abstract

Certain materials, such as Molybdenum and NaCl, have repeating crystal structures with lattice parameters of the order 1-10 Angstroms. It is difficult to observe this spacing on a nanoscopic level, but these properties can be generalised from their macroscopic diffraction properties. X-rays, whose wavelength is of the correct size to interact with the lattices inside the crystals, were directed through a number of different materials, and their lattice parameters and Bravais lattices were calculated from the diffraction pattern they produced. The lattice spacing, d , of NaCl was found to be 2.81Å, and its unit cell was found to be a face-centered cubic structure. An estimate of the value of Planck's constant h , $6.681 \pm 0.12 \times 10^{-34} \text{J} \cdot \text{s}$, was also found using the Duane-Hunt relation.

I. INTRODUCTION

X-rays were discovered by the German physicist Wilhelm Rontgen, in the late 19th century. He was experimenting with electric fields inside vacuum tubes, when he noticed a nearby piece of card coated in barium platinocyanide was starting to fluoresce. At the time, little was known about X-rays - hence their name. In the modern era, they are synonymous with diagnostic imaging, but they also have many uses in physics, particularly the field of X-ray crystallography.

Sir Lawrence and Henry Bragg were the first to discover the potential use of X-rays in detecting the properties of crystals. They found that, when directed through a material with a crystal structure, the X-rays would undergo diffraction, according to a mathematical law which they derived [1]. This law has become known as Bragg's Law

$$n\lambda = 2d \sin \theta \quad (1)$$

The distance between crystal planes d , as found by Bragg's Law, can be related to the Miller indices of the crystals, as well as the type of Bravais lattice (simple cubic, body centered cubic or face centered cubic) that the crystal is comprised of by the following relation:

$$d = \frac{a_0}{\sqrt{h^2 + k^2 + l^2}} \quad (2)$$

This quantity θ is the angle of the incoming X-rays, and particular angles will result in a high intensity of X-ray photons being diffracted. These intensity peaks are the result of electron interactions occurring in the anode - the X-rays transfer their kinetic energy to particular electrons within the atom, and cause those electrons become separated from the atom. It is energetically favourable for the atom to transition out of the excited state, so an electron from a higher energy level drops down to that configuration, and emits the excess energy as an X-ray photon. Different anode materials will generate a set of photons with different frequencies, as they have a unique electron configuration. It can therefore be said that the position of these peaks is a property of both the anode material and the crystal.

Finally, we can use the Duane-Hunt law [2] to equate the calculated wavelength of the emitted photons to their energy.

$$\lambda_{\min} = \frac{hc}{eV} \quad (3)$$

This formula assumes that 100% of the energy is transferred from the electron to the X-ray, so logically it must correspond to the photons of the lowest wavelength. Note that, as we already know the quantities eV , c and λ , we can use this to calculate the value of Planck's constant h .

II. EXPERIMENTAL METHODS

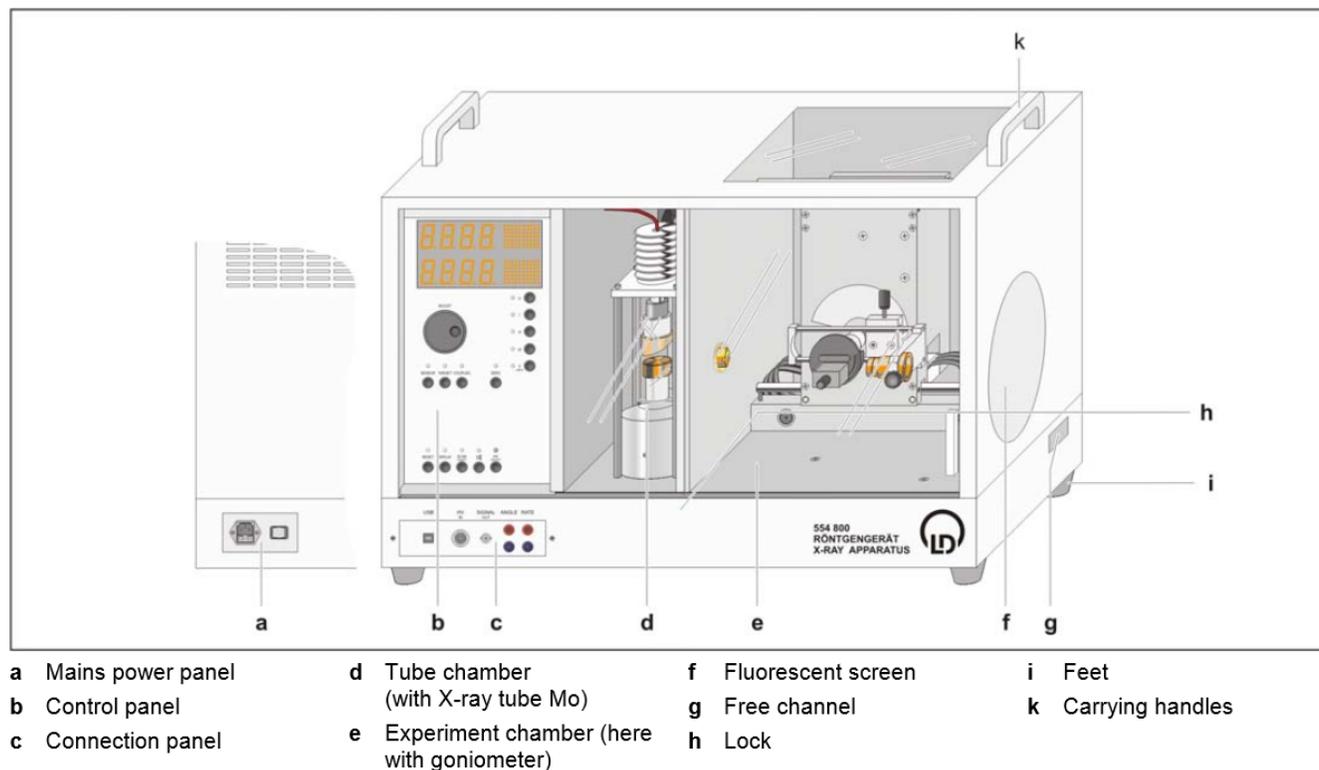


Figure 1: Diagram of the X-ray Apparatus provided by LD Didactic [3]

A Leybold-Didactic X-ray machine (fig. 1) produces X-rays from an X-ray tube, which are sent through a collimator, making them parallel, and then through a sample. The sample can be rotated through a series of angles specified in the data collection software also designed by Leybold-Didactic. The apparatus contains a Geiger-Muller counter at the opposite end from the tube, to measure the intensity of the X-rays that have been diffracted through the sample.

The data from the machine is automatically trans-

ferred to a computer via USB. In addition to changing the sample, the apparatus allows for a filter to be attached to the front of the collimator.

For each part of the experiment, the sample is loaded into the holder and locked in place. The X-ray apparatus software allows for the calibration and setting of limits on the angles through which the sample is tilted, the amount of time for which the scan runs at each angle and the accelerating voltage. In total, the process takes between 20 minutes and 1 hour.

III. RESULTS & DISCUSSION

I. DETERMINATION OF PLANCK'S CONSTANT h

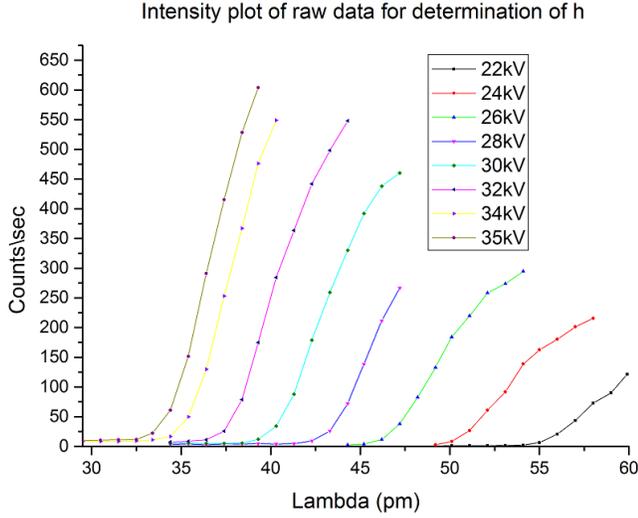


Figure 2: Threshold wavelengths for a series of accelerating voltages

In this part of the experiment, the value of Planck's constant was determined by Duane-Hunt relation. The minimum wavelength of emitted photons was found for a series of accelerating voltages. Then, the electron energy U was calculated for each peak, via the Duane-Hunt relation:

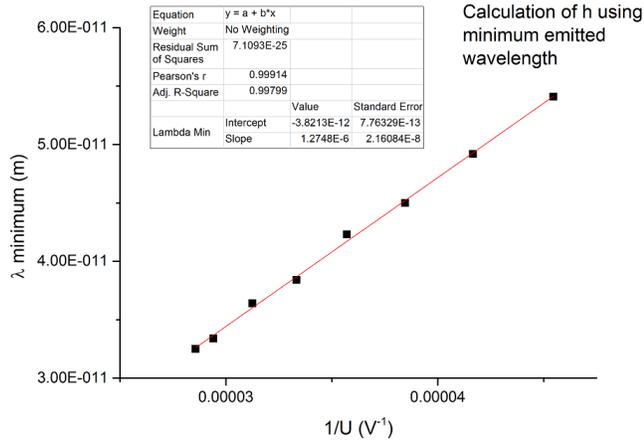


Figure 3: Linear plot of threshold energies against wavelengths

The gradient of this graph is actually the constants hc . So, by dividing our gradient by c , the value of h can be found. The gradient and error were found automatically using the software package 'Origin' by OriginLab. The final value of h was calculated to be $6.681 \pm 0.12 \times 10^{-34} \text{ J} \cdot \text{s}$.

The uncertainty in h is quite low, considering the ease and speed of calculation. To compare, the

photo-transistor method of determining h , which is considerably more laborious, produced a value of $6.32 \pm 0.7 \times 10^{-34} \text{ J} \cdot \text{s}$.

The generally accepted value of h is $6.63 \times 10^{-34} \text{ J} \cdot \text{s}$ [4]. This means that the X-ray diffraction method of measuring h is simultaneously more efficient, more accurate *and* more precise. And, of course, the accepted value of h is within the error permitted by the experimentally determined h .

Possibly the largest source of error in this method of determining h comes from judging where the point λ_{min} is located on the intensity plot. These were measured by eye, and there is a small amount of background intensity on each set of measurements. Combine this with the fact that the angular resolution is quite low, it is difficult to discern the exact starting location of each curve.

II. EFFECT OF ACCELERATING VOLTAGE ON ENERGY SPECTRUM

First, the apparatus was used to demonstrate the effects of increasing the accelerating voltage on the spectrum produced.

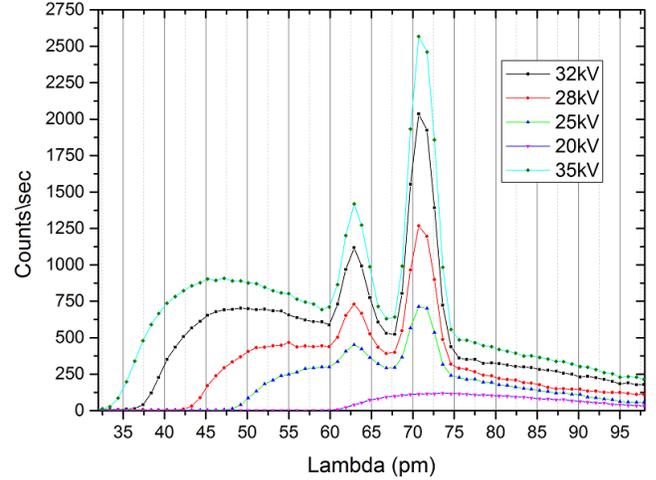


Figure 4: Effect of altering accelerating voltage on intensity of spectrum and presence of characteristic $K\alpha$ and $K\beta$ peaks.

As we can see, as the voltage increases, the minimum wavelength decreases. This is because the electrons that have been accelerated through a higher potential difference have more kinetic energy, which become X-rays of a smaller wavelength (3).

Additionally, at the lowest accelerating voltage, the two characteristic peaks (referred to as $K\alpha$ and $K\beta$) of Molybdenum anode disappear. This is because the energy of the accelerated electrons is smaller than the

binding energy of the electrons in the Molybdenum atoms - so they do not have enough energy to remove those electrons from the atom.

III. MEASUREMENT OF LATTICE SPACING OF NaCl

As mentioned earlier, the characteristic $K\alpha$ and $K\beta$ peaks for Molybdenum only appear only at specific Bragg angles (θ) and hence, at specific values of (λ). If the angle, wavelength and order of diffraction are known, these quantities can be inserted into the Bragg equation to determine the lattice spacing (d) of NaCl.

The angle and wavelength of the first three orders of diffraction ($n = 1, 2$ and 3) were found, allowing a mean value of d (plus a mean error) to be calculated.

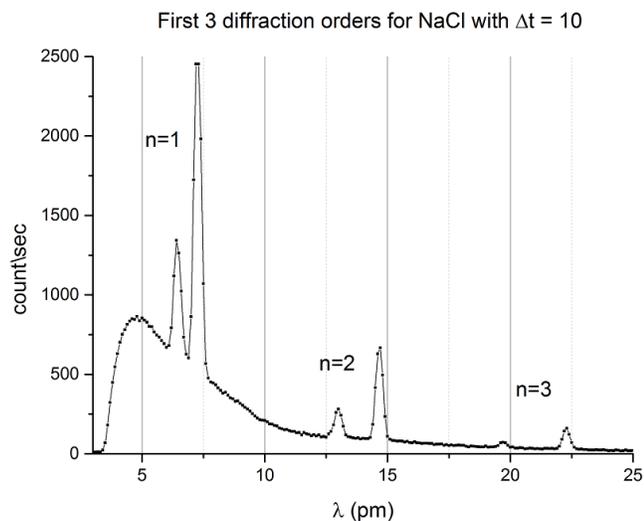


Figure 5: Wavelengths of peak positions for diffraction order $n=1, 2$ and 3 . The $K\alpha$ peaks are the larger ones.

The value of d was found to be $d = 2.82 \pm 0.01 \text{ \AA}$

It should be noted that, this part of the experiment is actually something of a tautology. In order to find the lattice spacing d , the wavelength of the diffracted X-rays is needed - but in turn, d is only calculable for known wavelengths. Initially, the values of λ were generated by LD Didactic's software, however, upon closer inspection, it was found that the software came preprogrammed with a series of d values for different materials!

The value of d was recalculated using known wavelengths of the the $K\alpha$ and $K\beta$ peaks from the University of Leeds Laboratory Manual [5], however, it's entirely possible that those values were also found using Bragg's law for a known d , which would still make the authenticity of the results questionable at best.

IV. MEASUREMENT OF CUBIC STRUCTURE

The cubic structure of a lattice such as NaCl can be represented by its Miller indices (which represent the relative spacing of planes inside the unit cell) and also the type of unit cell (which can be one of simple cubic, face centered cubic and body-centered cubic, and represents how the atoms are packed relative to one another).

We can relate the Miller indices to the d by substituting the Bragg equation (1) into the equation for a cubic system (2). We find the result

$$\sin^2\theta = \left(\frac{\lambda}{2a_0}\right)^2 (nh^2 + nk^2 + nl^2) \quad (4)$$

If we know the quantities a_0 , n and λ , we can calculate the theoretical position of the $K\alpha$ peak for each combination of h , k and l . If we can find our actual peak(s), we can work out which values of h , k and l they correspond to.

Essentially, by applying X-rays from a series of different angles, the X-rays are encountering different parts of the cubic structure - sometimes they penetrate farther, sometimes they are diffracted more, sometimes less.

The values of h , k and l can themselves be related to the type of cubic structure. If the sum of h^2 , k^2 and l^2 is even, then the crystal could be body-centered. If h , k and l are all odd, then it could be face-centered. Therefore, from the positions of the peaks, we can infer the type of Bravais lattice that they are composed of.

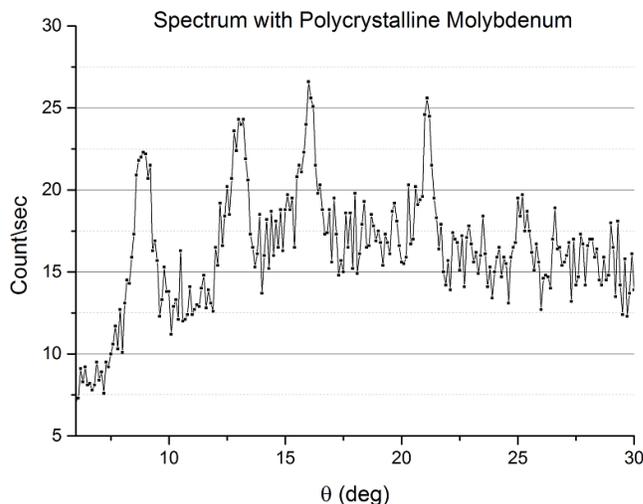


Figure 6: Characteristic $K\alpha$ peaks due to configurations of Miller indices in Molybdenum. A Zr filter was positioned in front of the collimator to remove the more energetic electrons, so no $K\beta$ peaks are visible

For the sample of polycrystalline Molybdenum, four peaks were found to be visible, and all four of

these peaks appeared approximately at the theoretical locations of $K\alpha$ peaks from a body centred cubic structure. It is therefore reasonable to assume that Molybdenum has a body centred cubic (BCC) structure - and indeed, this has been determined experimentally elsewhere [6].

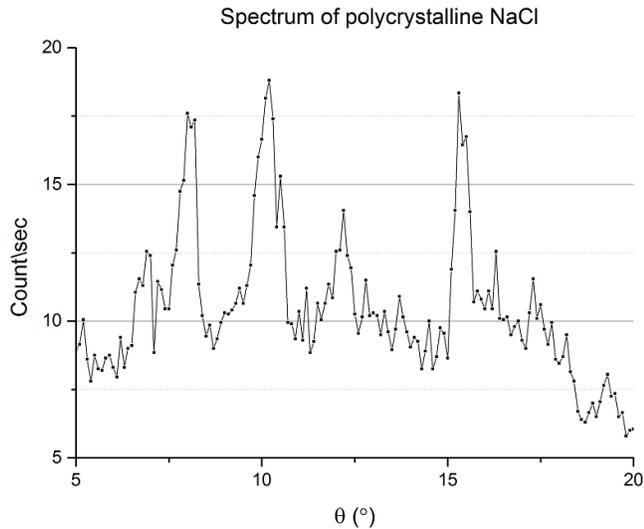


Figure 7: $K\alpha$ peaks due to configurations of Miller indices in NaCl. Again, the lower-frequency $K\beta$ peaks were removed using a Zr filter.

This approach was also taken using a sample of ground NaCl powder. This time, the peaks that were found mostly corresponded to those from a face-centered cubic structure. NaCl actually does have an FCC structure [6], so in this case, our estimation was correct.

There is one small factor in this method that could lead it to give an incorrect result. It does not rule out the possibility that the crystals have a simple cubic (SC) unit cell. However, this structure is very rare in nature, as it has an extremely low packing fraction (0.52%). In other words, the result that we get is not definitive, it is simply an indication of the most likely structure.

IV. REFERENCES

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