X-Ray Diffraction Crystallography

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1 abstract

The experiment presented in this paper was done in Waterloo University. We are performing X-ray diffraction experiment which is a popular technique to identify the identity of an unknown substance by producing a unique pattern for every substance. In this experiment, we are trying to identify the identity of an unknown metal. The metal was found to be Aluminum with miller indices of: (111),(200),(220),(311), (222),(400),(420) and with a lattice parameter = 3.93591 $\mathring{A}$ and so the Bravice lattice shape was found to be FCC.

2 Introduction

Studying the crystal lattice, we find that the most prominent characteristic of the crystals is its symmetry, in which the cells arrangement in the crystal lattice are periodic and they repeat themselves. In my paper, I will discuss the periodicity of the crystal lattice and how to determine its crystalline structure. One way to study the crystalline structure is to study the light that diffracts from the crystal. The diffraction happens only in certain directions as it happens for the light that diffracts from a diffraction grating. With studying the pattern and the intensity of these diffracted beams, we can know more about the structure that causes this diffraction pattern. There are three type of rays used in these diffraction experiments: X-rays, Neutron and Electrons diffraction. The mathematical analysis of these three techniques is similar so we will just consider the X-Rays diffraction case. After a brief discussion how the X-rays are generated and discussing some of X-ray properties, we will discuss the theory Bragg's law for x-ray diffraction that caused by the Crystal planes. Finally, I will represent an experiment I did in which I am applying this theory to determine the identity of an unknown metal.

2.1 The rays used to study the crystal structure

For the rays to be suitable to study the crystal structure in the solid form, we need its wavelength to be comparable with the atomic distances between the atoms which is around $10^8 cm$, so the used rays should be in the same order of the magnitude to obtain useful information about the crystal structure. So when rays are diffracted from the crystal plans, they form unique patterns which we can analyze to obtain information about the crystal structure. As we mentioned earlier, we can use different kinds of photons in these diffraction experiments, like X-rays, Neutrons and Electrons. Although they differ in their energy and in their wavelengths, still the mathematical aspects are

almost the same. The diffraction angles of these photons depend mainly on the elementary structure of the material and the photons' wavelengths. The photon's energy is determined using this relationship:

$$E = h\nu = \frac{hc}{\lambda} \tag{1}$$

Such that,

h is planck's constant 6.62×10^{-27}

ν is the frequency

c is the speed of light $3 \times 10^{8} m/s$

and so from this relation, we can write the wavelength of x-ray as:

$$\lambda(\mathring{A}) = \frac{12.4}{E(KeV)} \tag{2}$$

From this relation we see that the energy photon in the range 10-50 KeV, gives wavelength in the range of 0.4-1.2 $\mathring{A}$.

Referring to figure 1, we can see the range of x-rays takes in the Electromagnetic spectrum.

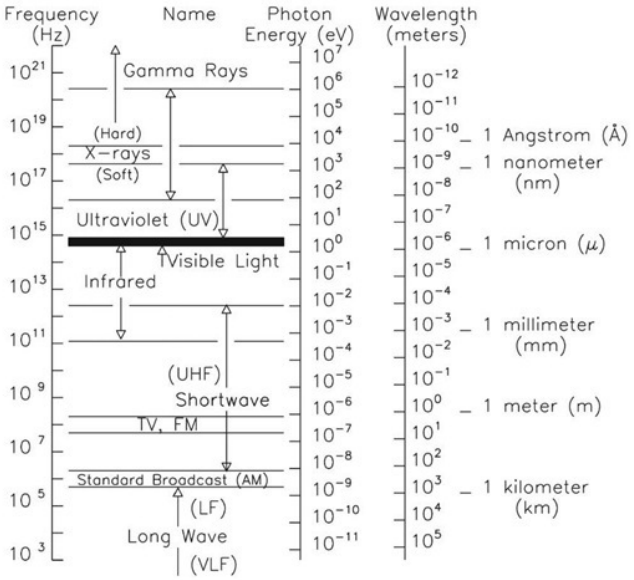

Figure 1: The spectrum of electromagnetic radiation

2.2 Generation of X-Rays

X-rays were discovered in the summer of 1895 by the German scientist Wilhelm Conrad Roentgen. Roentgen was interested in generating Cathode rays and by coincidence when he observed a fluorescent glow of crystals on a table near his tube. From this moment, he dedicated his life to study the properties of this mysterious rays that causes this glowing effect and he called it X-rays. This discovery was met with interest in the science community, not soon enough and it was used in the medical field. Fifteen years later with little known about these mysterious rays, in 1912, the German physicist Max Von Laue discovered the diffraction of X-rays by crystals. "Von Laue designed an experiment in which he placed a copper sulphate crystal between an X-ray tube and a photographic plate. His assistants, Walter Friedrich and Paul Knipping, carried out the experiment. After a few initial failures, they met with success on 23 April, 1912. X-rays passing through the crystal formed the pattern of bright spots that proved the hypothesis was correct." [1]

As shown in figure 2 X-rays can be generated when metallic cathode filament is heated and electrons are ejected and move away from the filament. Electrons are accelerated through a potential to a metal target where some of the energy is emitted as X-ray photons. One example of a material that is used for the metal target is tungsten.

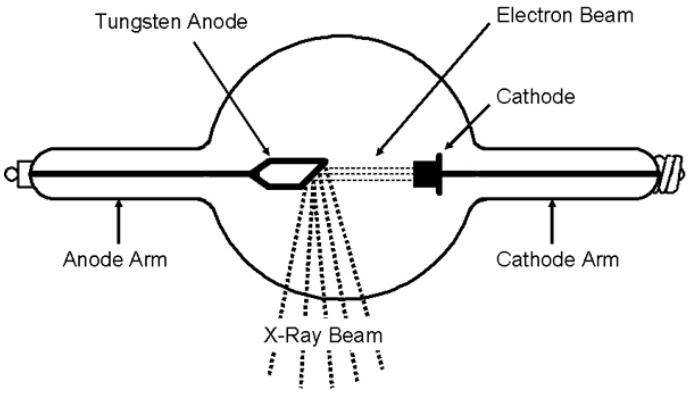

Figure 2: X-ray generator tube diagram

The X-rays are produced either by bremsstrahlung where the energy of the electron is lost as it is affected by the nucleus and produces an x-ray and it's continuous as shown in figure 3, or the electron ejects an inner electron from an atom and an x-ray is emitted as an electron at a high shell fills the lower shell. These x-rays are then emitted as a beam towards the target and they are called characteristic x-rays. Characteristic x-rays are

the main source that is used for the investigation of crystal structure by x-ray diffraction.

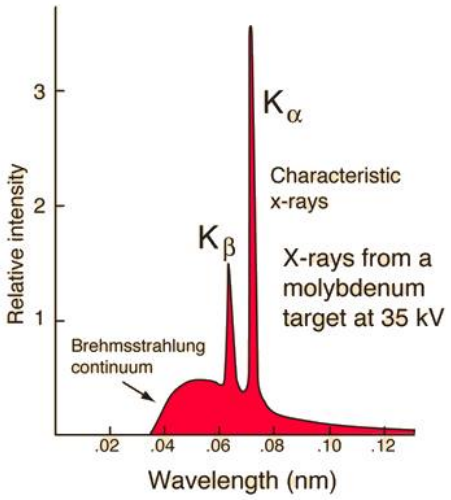

Figure 3: X-ray generator tube diagram

2.3 X-ray diffraction experiment to determine the identity of an unknown metal

One of the basic method used to study the structure of crystals, is Laue Method. In this method, we fix the incident angle θ of the beam and we vary the wavelength. This is achieved by placing the crystal at a fixed position and then directing it towards the x-rays source. On the other side, there is a film that receives the diffracted beam and so we can get the diffraction pattern that allows us to study the crystal structure as shown in figure 4.

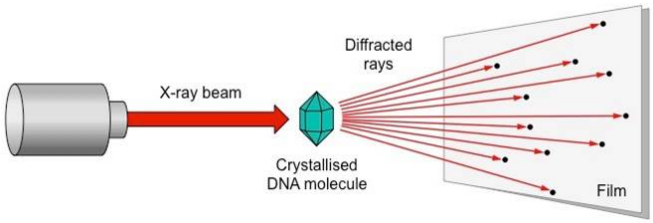

Figure 4: studying the diffraction pattern to determine the structure of the substance

The method we are using in this experiment is called the Diffractmeter method which is considered relatively advanced and recent, where the diffraction pattern data is being

registered digitally and then plotted later, instead of using imaging films. This method uses a fixed wavelength λ, but the incident beam angle θ varies. This is require a monochromatic x-ray source with a known wavelength, and to do that, a crystal is used to filter x-rays. As shown in figure 5, the sample is being projected to the x-ray beam that passed through the required optics to condition the primary X-ray beam to the required wavelength, beam focus and size. The sample is placed on the Goniometer where it rotates with a constant velocity around its axis. The diffracted beam is being received by the detector and then the data will be obtained for further analysis.

In this experiment, an unknown metal wire will be examined using this technique. The data we are obtaining will be 2θ Bragg's angle vs the intensity of the diffracted beam. We will be studying this pattern to identity Bragg's peaks, and then accordingly, we will be able to determine the miller indices and its lattice spacing wich will allow us to determine the identity of the metal.

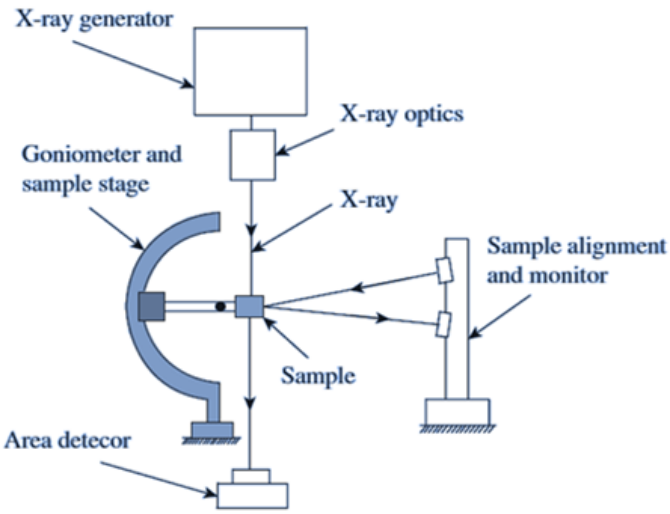

Figure 5: Used method diagram

3 THEORETICAL BACKGROUND [2]

To get a sharp peak in the intensity of the scattered x-rays radiation, the X-rays should be reflected by the atoms in one plane, and the reflected rays from the successive planes should interfere constructively.

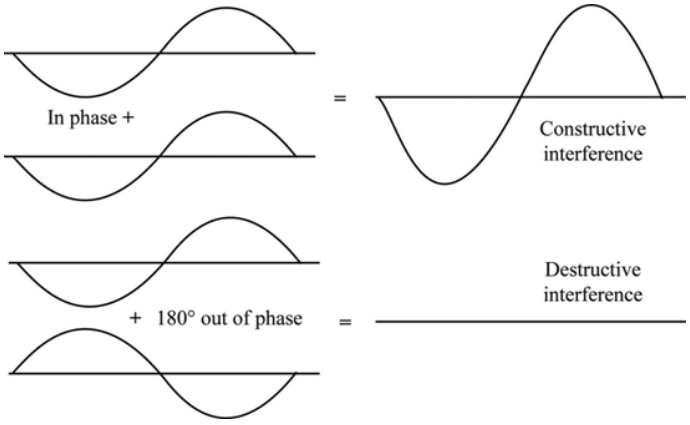

Figure 6: Constructive interference vs destructive interference

Referring to figure 6, to get a constructive interference, the two diffracted rays should be in phase, that means that the deference between the diffracted rays from the successive planes should be equal multiple integer number of the wavelength.

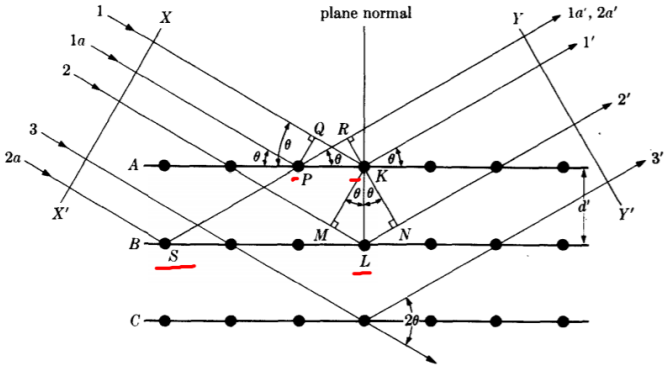

Figure 7: Diffraction from the crystal lattice

Referring to figure 7, the difference between ray 1 and 2, is the distance **ML** + **LN**

$$ML + LN = d'sin\theta + d'sin\theta \tag{3}$$

the path difference is equal to a whole number n of wavelengths:

$$n\lambda = 2d'sin\theta \tag{4}$$

where n = 1,2,3..

d' is interplanar spacing

λ is the wavelength

θ is the diffraction angle

This equation is called Bragg's law and it was first introduced by W. L. Bragg. So for diffraction to occur, this condition must be satisfied. In the experiment, we found Bragg angles θ for the sample, now it's possible to determine the crystalline structure of the sample. For cubic structure, we will assign indices to each peak position, those indices are called Miller indices, hkl. We know that the cubic crystal relation:

$$d_{hkl} = \frac{a_o}{\sqrt{h^2 + k^2 + l^2}} \tag{5}$$

In our experiment, we need to determine the lattice constant a_o for every peak in the sample.

Then we substitute Bragg's law in the above equation, we get:

$$\lambda = \frac{2a_o sin\theta}{\sqrt{h^2 + k^2 + l^2}} \tag{6}$$

Then:

$$sin^2\theta = (\frac{\lambda^2}{4a^2})(h^2 + k^2 + l^2) \tag{7}$$

Such that $(\frac{\lambda^2}{4a^2})$ is constant So for all the Bragg angles we obtained, we divide $sin^2\theta$ by set of integers to get a common quotient which is the value of $(\frac{\lambda^2}{4a^2})$. Now we divide $sin^2\theta$ by the quotient we got for each Bragg peak to get the integers of $h^2 + k^2 + l^2$.

(hkl)	$h^2 + k^2 + l^2$	SC	BCC	FCC
100	1	✓	×	×
110	2	✓	✓	×
111	3	✓	×	✓
200	4	✓	✓	✓
210	5	✓	×	×
211	6	✓	✓	×
220	8	✓	✓	✓
300, 221	9	✓	×	×
310	10	✓	✓	×
311	11	✓	×	✓
222	12	✓	✓	✓
320	13	✓	×	×
321	14	✓	✓	×
400	16	✓	✓	✓
410, 322	17	✓	×	×
411, 330	18	✓	✓	×
331	19	✓	×	✓
420	20	✓	✓	✓
421	21	✓	×	×

Figure 8: Indexing Cubic Crystals

Using table 8 [3], now we can identify the Braivais lattice, whether it's primitive, Face Centered Cubic (FCC) or Body-Centered Cubic (BCC).

Finally, now we can determine our best value lattice parameter a_o

$$a_o = \frac{\lambda\sqrt{h^2 + k^2 + l^2}}{2sin\theta} \tag{8}$$

4 EXPERIMENTAL DESIGN AND PROCEDURE

4.1 Description of the apparatus

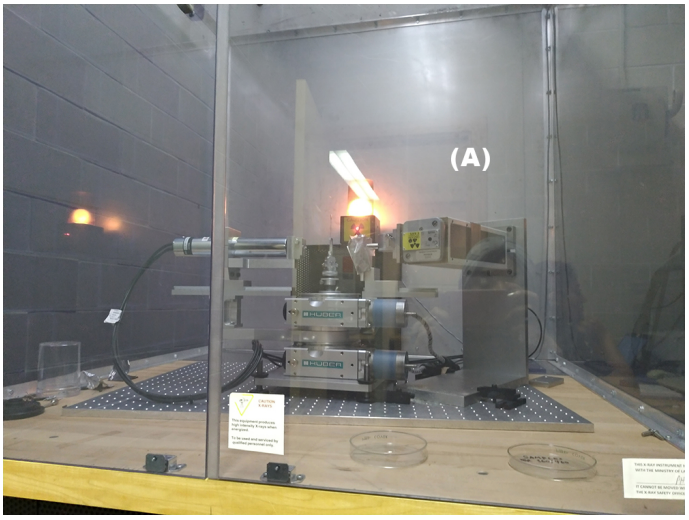

Figure 9: apparatus components

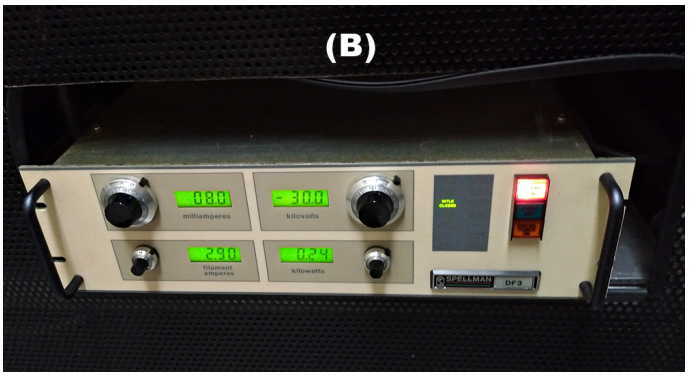

Figure 10: apparatus components

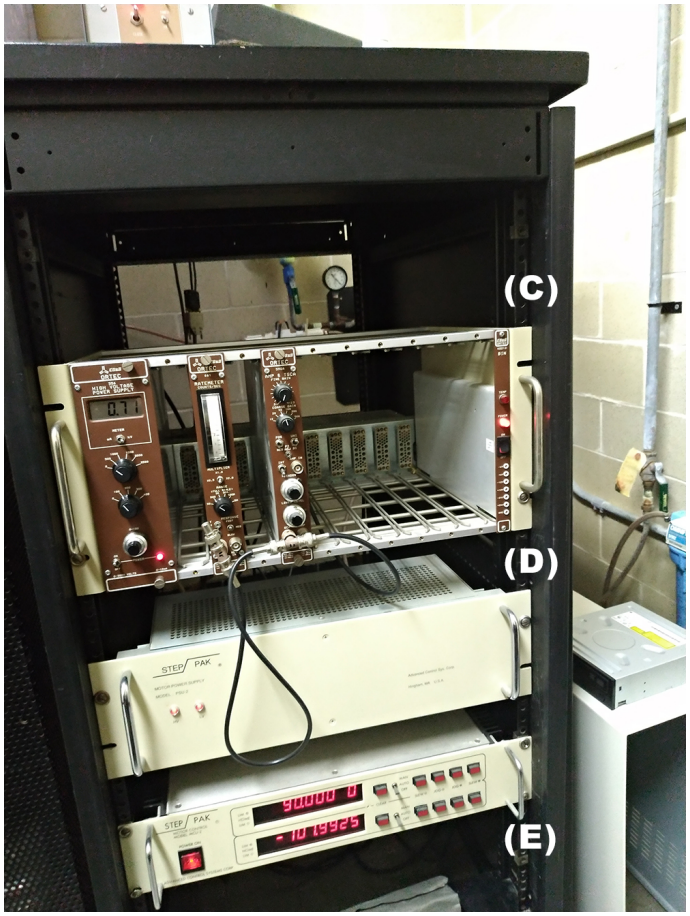

Figure 11: apparatus components

The used apparatus consists of :

A) The experiment area, contains the detector, the source and the sample holder.

B) The filament source power supply.

C) The detector high voltage supply.

D) The stepper motor power supply.

E) Step Pak motor control model MCU-2.

F) (Not shown in the picture) The x-ray shutter control box.

4.2 Description of the experimental procedure

There are two parts for this experiment. For the first part, we were provided with a sample of a metallic wire in order to determine Bragg Angles so we can calculate

the lattice Spacing of the metal. For the second part, we were provided with a powder sample to determine Bragg Angles, and so we can determine its crystalline structure and its lattice parameter. We started by adjusting the power supplies to the right settings as written in the provided lab manual, then we placed the sample on the goniometer.

Then we used the Lab's PC to obtain the data, the system used is Linux, we opened the terminal and used "twoc" program. We started by testing the stepper motor command, we moved the detector to a position at 10 degrees. However, we had some troubles calibrating the stepper motor to align with the program command so we had to reset the system multiple times.

After we calibrated the detector position, we were ready to start the scan. We performed the scan from 10 to 120 degrees using 1100 data points, which is 0.1° for each step. So each point was exposed to the rays for 4 seconds. As shown in figure 12, we could see the peaks while performing the experiment. We collected the data points for the two samples provided.

Figure 12: Linux system, using 'twoc' program on terminal

5 ANALYSIS

5.1 Method of Analysis and Presentation of Results

The used software showed us real-time data from what was happening in the XRD, and after plotting the data using Python, we obtained the following graph.

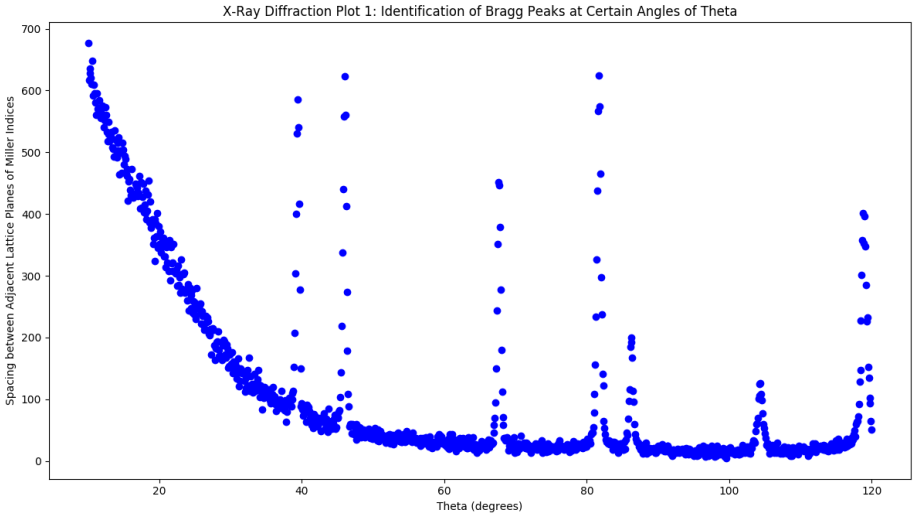

Figure 13: Plot of the diffraction angle 2θ vs intensity

2θ	Bragg's Angle θ	$Sin^2(\theta)$	$h^2+k^2+l^2$	hkl	a_o	Structure
39.4	19.7	0.1136332	3	111	0.396096	SC,FCC
46	23	0.1526708	4	200	0.394588	All
67.6	33.8	0.3094648	8	220	0.391951	All
81.7	40.85	0.4278219	11	311	0.390892	SC,FCC
86.2	43.1	0.466863	12	222	0.39083	All
104.4	52.2	0.6243449	16	400	0.390247	All
118.8	59.4	0.7408768	20	420	0.400529	All

Figure 14: Metal sample data

After we determined the approximate lattice parameter a_o, we can identify the metal using the data given in Appendix 5 in Cullity textbook as shown in table 15. The metal is Aluminum with an error difference is 3%.

Element	Type of Structure	Temp. (°C)	Lattice parameters (Å*)			Distance of closest approach (Å*)
			a	*b*	*c* or axial angle	
Ac Actinium	FCC, A1		5.311			3.755
Al Aluminum	FCC, A1	25	4.0497			2.8636
Am Americium, α*	Hex., La type	20	3.4681		11.240	3.4505
Sb Antimony	Rhomb., A7	25	4.5069		α = 57° 6′27″	2.906
As Arsenic	Rhomb., A7	22.5	4.1319		α = 54° 8′	2.507
Ba Barium	BCC, A2	25	5.013			4.341
Be Beryllium, α*	HCP, A3	R.T.	2.286		3.584	2.2257
Bi Bismuth	Rhomb., A7	25	4.736		α = 57° 14′	3.071
B Boron*	Tetrag.	R.T.	8.80		5.05	

Figure 15: Metals with their lattice parameter's values From cullity textbook

5.2 Discussion of results

In Figure 5.1, we can see that at certain points, there are peaks that stand out from the rest of the graph. Those points are as follow: At: (θ; Miller indices); (19.7; 111) (23;200) (33.8; 220) (40.85; 311) (43.1; 222) (52.2; 400) (59.4; 420)

6 CONCLUSION

In conclusion, I think X-ray diffraction was a success as we succeeded in identifying the metal be Aluminum with miller indices of: (111),(200),(220),(311), (222),(400),(420) and with a lattice parameter = 3.93591 $\AA$ and so the Bravice lattice shape was found to be FCC.

References

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