Characterization of Construction Materials
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Lecture 17
X Ray Diffraction Diffractogram Calculations Part 1

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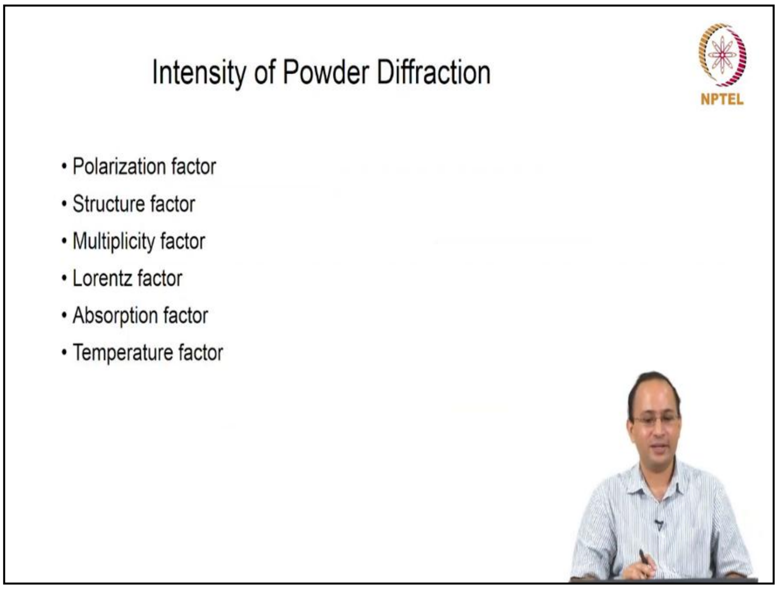

Intensity of Powder Diffraction

- Polarization factor
- Structure factor
- Multiplicity factor
- Lorentz factor
- Absorption factor
- Temperature factor

We will continue our discussion on x-ray diffraction. So, what we have learned so far is starting from how x-rays are generated and how we make use of x-rays to understand the material. Basically we discussed about the characteristic spectrum. Then we discussed about crystallography basics; we did not go in detail but basics of crystallography like lattice are discussed in past few lectures. We looked at unit cell, different crystal systems, and space groups.

Then we talked about diffraction and the Bragg's condition which gives you diffraction. So, you can think of it as constructive interference. There is a condition which has to be met if it is satisfied you get diffraction. So, now we know that you get diffraction from a crystal and that dependence of the plane and incident angle is dictated by two relationships one being Bragg's condition and the other is inter planar spacing

So, when you combine these conditions you can get relationship between incident angle and the diffracting planes. So, we know now if you have an x-ray you will get diffraction from crystal or a poly crystalline material where you have different crystals together. In the last lecture we discussed about what gives rise to the difference in intensity.

So, we can simply understand this by the plotting intensity versus 2Θ and we know that the angular values are obtained from the diffracting planes. Now we talked about what gives rise to the difference in intensities as shown in plot. So, to understand this difference in intensities we need to take into account various factors including structure factor, polarization factor, etc.

So, we also talked about Lorentz factor which is usually combined with the polarization and called as Lorentz polarization factor. Multiplicity factor depends on the planes as some planes are more likely to diffract than others. Some part of the x-rays will be absorbed by the sample so it is important to know about absorption phenomenon and take absorption factor in consideration.

Similarly temperature will affect the thermal vibrations so that also will contribute to disturbance in the intensity. So, in general if you have to write the intensity in simplistic terms where you already know structure factor. It is also know that intensity is directly proportional to the square of structure factor.

Then we also have multiplicity factor M for a given hkl plane. We have Lorentz polarization factor, absorption factor and temperature factor. If you know all these factors you can calculate intensity by using a simple equation

$$\mathbf{I_{hkl} = F^2 M_{hkl} LAT}$$

In some cases you will have one factor dominating the other. This equation is very important and will be used for many calculations later. We know to calculate the structure factor that depends on atomic scattering factors.

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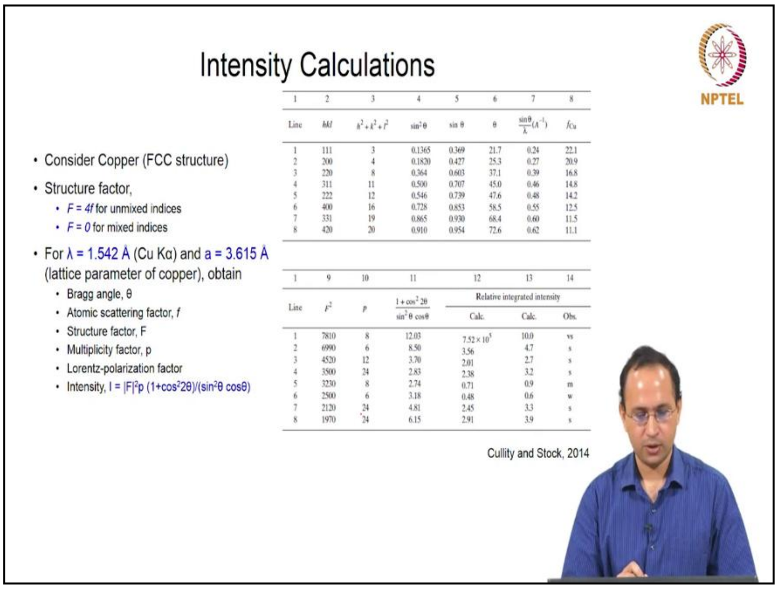

Intensity Calculations

- Consider Copper (FCC structure)
- Structure factor,
    - *F = 4f* for unmixed indices
    - *F = 0* for mixed indices
- For λ = 1.542 Å (Cu Kα) and a = 3.615 Å (lattice parameter of copper), obtain
    - Bragg angle, θ
    - Atomic scattering factor, *f*
    - Structure factor, F
    - Multiplicity factor, p
    - Lorentz-polarization factor
    - Intensity, $I = |F|^2 p\,(1+\cos^2 2\theta)/(\sin^2\theta \cos\theta)$

1	2	3	4	5	6	7	8
Line	*hkl*	$h^2+k^2+l^2$	$\sin^2\theta$	$\sin\theta$	θ	$\frac{\sin\theta}{\lambda}(Å^{-1})$	f_{Cu}
1	111	3	0.1365	0.369	21.7	0.24	22.1
2	200	4	0.1820	0.427	25.3	0.27	20.9
3	220	8	0.364	0.603	37.1	0.39	16.8
4	311	11	0.500	0.707	45.0	0.46	14.8
5	222	12	0.546	0.739	47.6	0.48	14.2
6	400	16	0.728	0.853	58.5	0.55	12.5
7	331	19	0.865	0.930	68.4	0.60	11.5
8	420	20	0.910	0.954	72.6	0.62	11.1

1	9	10	11	12	13	14
				Relative integrated intensity		
Line	F^2	*p*	$\frac{1+\cos^2 2\theta}{\sin^2\theta\cos\theta}$	Calc.	Calc.	Obs.
1	7810	8	12.03	7.52×10^5	10.0	vs
2	6990	6	8.50	3.56	4.7	s
3	4520	12	3.70	2.01	2.7	s
4	3500	24	2.83	2.38	3.2	s
5	3230	8	2.74	0.71	0.9	m
6	2500	6	3.18	0.48	0.6	w
7	2120	24	4.81	2.45	3.3	s
8	1970	24	6.15	2.91	3.9	s

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In the last lecture we took this example of diffraction pattern from this FCC structure copper. We are trying to calculate the intensity and see whether our calculations match the observations. So, the example is just to illustrate the calculation of intensity and structure factor.

We saw that for different conditions, we get different structure factors. So, in this case you see when you have mixed indices the structure factor is zero. So, even though there is a plane depending on hkl you will not see any diffraction. You would not see any diffraction from these planes. For some planes where you have an unmixed indices, you will see diffraction.

This is based on the conditions so now we know the hkl planes where we are getting diffraction. So, you know these planes we have written in the column 2 are hkl 1 1 1, 2 0 0 are the planes where you are getting diffraction based on structure factor calculations. Once we know hkl we can calculate the term $h^2 + k^2 + l^2$. This term is used for Bragg's condition and inter planar spacing for the cubic crystals.

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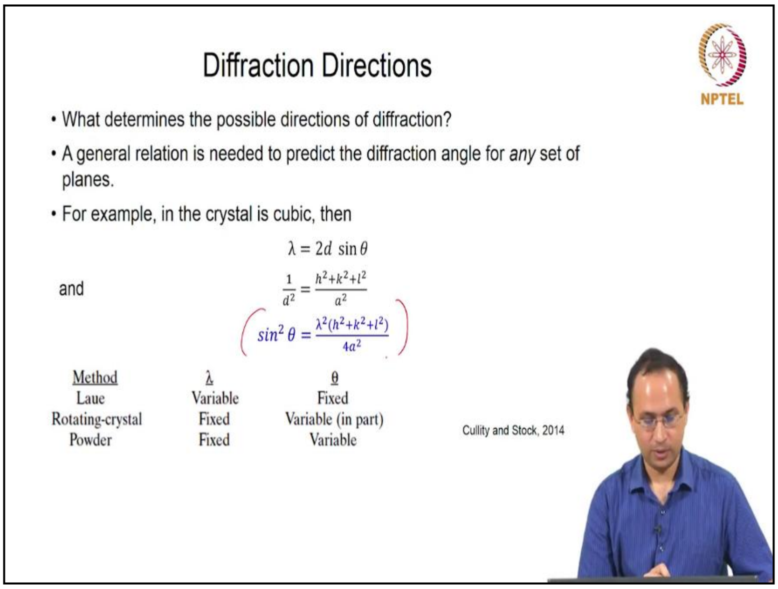

Diffraction Directions

- What determines the possible directions of diffraction?
- A general relation is needed to predict the diffraction angle for *any* set of planes.
- For example, in the crystal is cubic, then

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

and

$$\frac{1}{d^2} = \frac{h^2+k^2+l^2}{a^2}$$

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

Method	λ	θ
Laue	Variable	Fixed
Rotating-crystal	Fixed	Variable (in part)
Powder	Fixed	Variable

Cullity and Stock, 2014

Further to the discussion we can write the equation

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

Or in simpler way it can be written as

$$(h^2+k^2+l^2)/\sin^2 \Theta \ = \frac{4a^2}{\lambda^2}$$

Now since we are talking about the cubic crystal where a is defined as a constant. As we are using monochromatic x-rays λ is fixed so right hand side of equation is a constant. This implies that

$$(h^2+k^2+l^2)\ \alpha\ \sin^2 \Theta$$

This relation is only used for copper which is FCC. For plane 1 1 1 that means $(h^2+k^2+l^2)$ will be 3 and for plane 2 0 0 $(h^2+k^2+l^2)$ it will be 4.

Now we can calculate the value of $\sin^2 \Theta$ that is given by the table as we already have a diffraction pattern. So, once you know these values you can calculate the Θ in degrees. Now, you know the planes and Bragg's angle of diffraction.

As we know to calculate the structure factor, we need to know atomic scattering factor and this scattering factor depends on the term sinΘ by λ. We have f for copper because this depends on sinΘ by λ. So, there is a table and you can use this table to get FCU given by sinΘ by λ.

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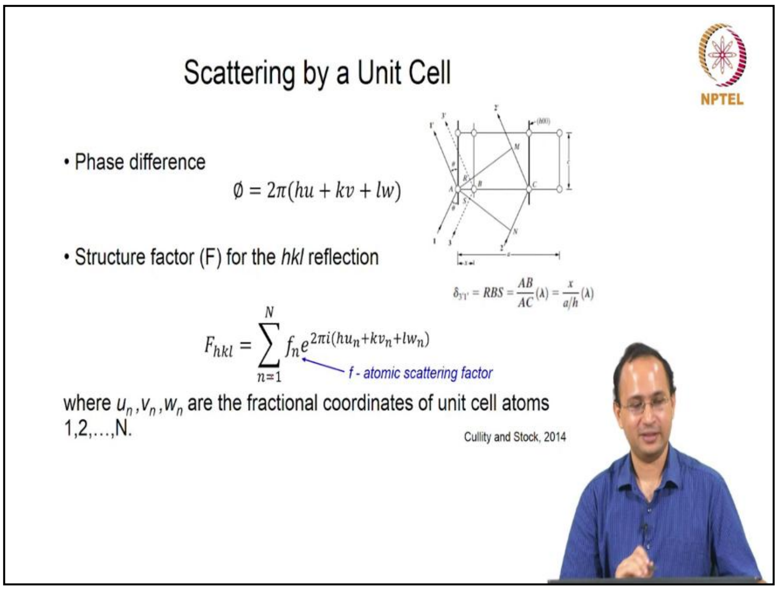

Scattering by a Unit Cell

- Phase difference

$$\phi = 2\pi(hu + kv + lw)$$

- Structure factor (F) for the *hkl* reflection

$$\delta_{3'1'} = RBS = \frac{AB}{AC}(\lambda) = \frac{x}{a/h}(\lambda)$$

$$F_{hkl} = \sum_{n=1}^{N} f_n e^{2\pi i(hu_n + kv_n + lw_n)}$$

f - atomic scattering factor

where u_n, v_n, w_n are the fractional coordinates of unit cell atoms 1,2,…,N.

Cullity and Stock, 2014

To calculate structure factor we use the equation as shown in the above slide which takes in to account various factors such as atomic scattering factor and the fractional coordinates required to know the atomic arrangement.

So now we can calculate the structure factor and once we have the value of F, we can get the value of F^2 or simply can use the relation

$$F^2 = 16f$$

For the planes where F equals to 4f and lot of other planes F is 0. We are calculating square value because the intensity is related to square of the structure factor. Now we have multiplicity factor and the Lorentz polarization factor LP which combines the Lorentz factor and the polarization factor. Now you have all the values, assuming there is no effect of temperature and absorption in this case, we can calculate the intensity which is

$$I = F^2 .P.L$$

So we get the values of calculated intensities and we can simply normalize them to make it easy to assume .For example we can say the values as 10 then we have value as 4.7
You just have to go to this equation you know this you know this you know this let us keep it we do not consider this for now. So, you get the calculated intensities there these ones simply have to multiply see now we can normalize it it is difficult to see so what you can do you can assume this is like you can normalize it and then you can say if it is 10 then this will be 4.7 you can normalize it this x.

So, you get these numbers and thereby line 1 has intensity of 10 counts for an example, line 2 has 4.7. If you look at the intensities of all these lines you can say line 1 is the strongest line then line as obtained by calculations followed by very low intensities such as 0.9 and 0.6. Now if we look at the observed pattern we have VS which means very strong

So, it says that line 1 is the strongest which also matches with your calculated intensity. We have classifications as very strong, strong, medium and, weak. These simple calculations give us the relative intensities. So, now we know the position where we will get diffraction and the intensity of the peaks.

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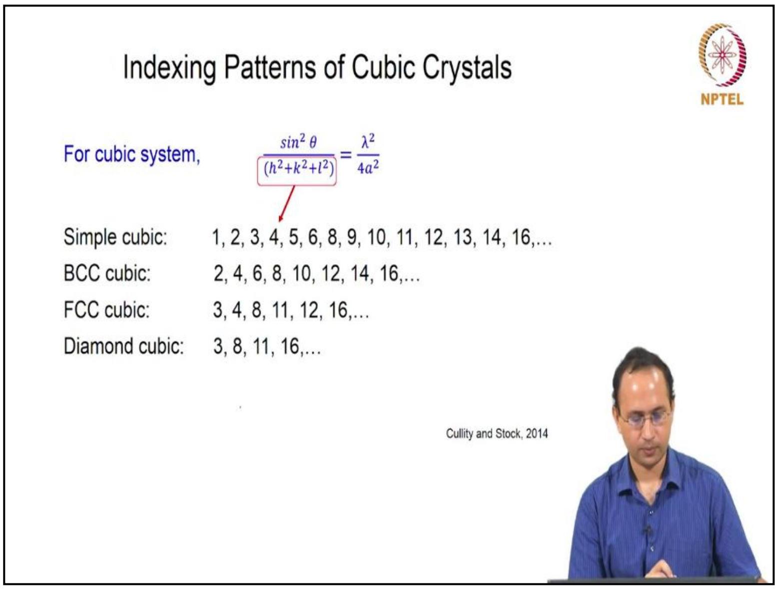

Indexing Patterns of Cubic Crystals

For cubic system, $\frac{\sin^2\theta}{\boxed{(h^2+k^2+l^2)}} = \frac{\lambda^2}{4a^2}$

Simple cubic: 1, 2, 3, 4, 5, 6, 8, 9, 10, 11, 12, 13, 14, 16,…

BCC cubic: 2, 4, 6, 8, 10, 12, 14, 16,…

FCC cubic: 3, 4, 8, 11, 12, 16,…

Diamond cubic: 3, 8, 11, 16,…

Cullity and Stock, 2014

To decide which are the planes or hkl showing diffraction, we need to consider firstly Bragg's condition is met and secondly consider inter planar spacing. As we know for cubic systems, we have

$$\sin^2\Theta/(h^2+k^2+l^2) = \frac{\lambda^2}{4a^2}$$

So, based on this equation we get the possible values of hkl. The value of $h^2+k^2+l^2$ for different cubic systems is mentioned as follows;

Simple cubic:1,2,3,4,5,6,8,9,10,11,12,13,14,16,…

BCC cubic: 2,4,6,8,10,12,14,16,…

FCC cubic: 3,4,8,11,12,16,….

Diamond cubic: 3,8,11,16,….

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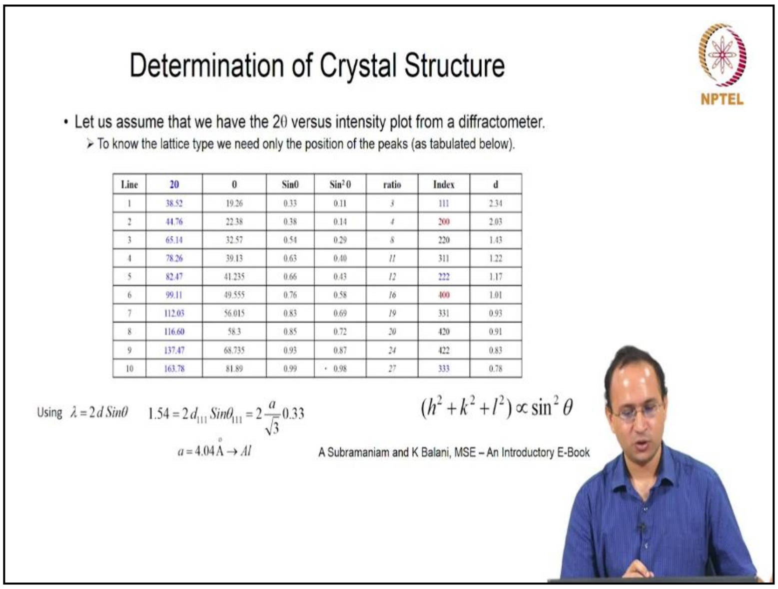

Determination of Crystal Structure

- Let us assume that we have the 2θ versus intensity plot from a diffractometer.
  - ➢ To know the lattice type we need only the position of the peaks (as tabulated below).

Line	2θ	θ	Sinθ	$Sin^2θ$	ratio	Index	d
1	38.52	19.26	0.33	0.11	3	111	2.34
2	44.76	22.38	0.38	0.14	4	200	2.03
3	65.14	32.57	0.54	0.29	8	220	1.43
4	78.26	39.13	0.63	0.40	11	311	1.22
5	82.47	41.235	0.66	0.43	12	222	1.17
6	99.11	49.555	0.76	0.58	16	400	1.01
7	112.03	56.015	0.83	0.69	19	331	0.93
8	116.60	58.3	0.85	0.72	20	420	0.91
9	137.47	68.735	0.93	0.87	24	422	0.83
10	163.78	81.89	0.99	0.98	27	333	0.78

Using $\lambda = 2d\,Sin\theta$ $\quad 1.54 = 2d_{111}\,Sin\theta_{111} = 2\frac{a}{\sqrt{3}}0.33$

$a = 4.04\overset{o}{A} \rightarrow Al$

$(h^2+k^2+l^2) \propto \sin^2\theta$

A Subramaniam and K Balani, MSE – An Introductory E-Book

So finally we want to know how you determine the crystal structure which is an important question to address. Now, you have a diffraction pattern having different values of 2Θ which gives rise to difference in intensities. Now how will you determine the crystal structure from this data. So, if you know the diffraction pattern then you have the values of 2 Θ.

So, let us assume that we have 2 Θ versus intensity plot that is a typical diffraction plot. You have value of 2 Θ which can used to calculate value of Θ. Then you can calculate sin Θ and thereafter can get the value of $\sin^2\Theta$. As we know for cubic systems $h^2+k^2+l^2$ is proportional to $\sin^2\Theta$.

So, we already know the values of $\sin^2\Theta$ expressed in form of decimals. We normalize these decimal points again So as to obtain ratios like 3,4,8,11 etc. Now once you know these ratios it is easy to tell that the structure is FCC by looking for example at ratio such as 3,4,8,11,12. So, now you can write the index values as well for example 4 for plane 2 0 0 and you can calculate the d values for these planes. So, finally let us use this relation Bragg's condition λ equals to 2d sinΘ that will hold at all planes wherever you have diffraction.

Suppose we value of λ is 1.54 angstrom so let us consider the first line of table where we have a d_{11} so it can be written as $2d_{11}\sin\Theta_{11}$. Now since the cubic structure is FCC, d can be expressed in form of lattice parameter by a relation. So from this we can calculate ‘a’ which the lattice parameter is as it is FCC it will be same in all directions.

So, once you know the value of ‘a’ you know that it is aluminium in this case. So, you know the lattice parameter and the type of crystal system. This is a simple example what tells you that you can determine crystal structure as the way Bragg did..

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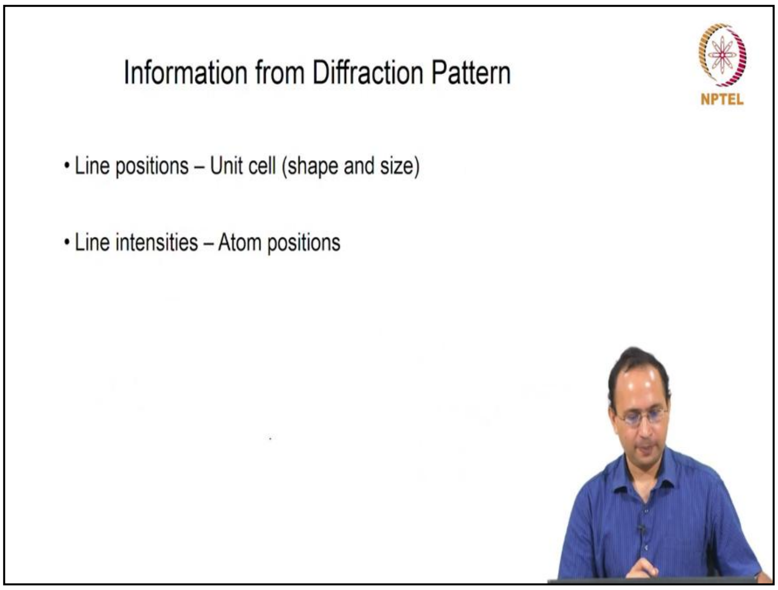

Information from Diffraction Pattern

- Line positions – Unit cell (shape and size)
- Line intensities – Atom positions

So, to summarize we learned about line positions or peak positions which gives information about unit cell, shape and size of unit cell. The shape and size of unit cell dictates the position where you will have diffraction phenomenon. The intensities will depend on the atom positions again you can refer back to our calculation in the last lecture where we calculated that.

So, depending on the atomic position you may not even see a diffraction. So, basically two important things are line positions and line intensities where line positions will tell you about shape and size of unit cell and line intensities tell about atomic position.