24 Electron Diffraction

INTRODUCTION

The dualism of radiation as wave and particle led de Broglie (1924) to conclude that electrons possess wave as well as corpuscular properties. Electrons should, therefore, obey de Broglie equation,

$$\lambda = h / mv \qquad \ldots(1)$$

where, λ = wavelength, h = Planck's constant, m = mass, v = velocity. We know that

$$KE = 1/2\ mv^2 = Ve \qquad \ldots(2)$$

where v = potential difference through which the electron beam has been excited and e is the charge on the electron. Combining equations 1 and 2 and substituting the standard values of h, m and e we get

$$\lambda = \sqrt{\left(\frac{150}{V}\right)} \times 10^{-8} \text{ cm} \quad \text{or} \quad \lambda = \frac{12}{\sqrt{V}} \times A$$

C. J. Davison and **I. H. Germer** showed the phenomenon of diffraction of electrons by nickel crystal.

PRINCIPLE

Electrons can be accelerated to precisely controlled energies by applying a known potential difference. When accelerated through 10 keV, they acquire a wavelength of 12 pm which makes them suitable for molecular diffraction investigations. **Electron diffraction** studies generally utilize electrons with energies of the order of 40 keV. Since electrons are charged, they are scattered strongly by their interaction with electrons and nuclei of atoms of the sample. Hence, they **cannot be used for studying molecules in the gaseous state** held on surface and in thin films. The application to surfaces, which is called **low energy electron diffraction** (LEED), is a major use of the technique. Electron diffraction technique is applicable to very small solid samples and so may be used when single-crystal X-ray diffraction is impractical or powder **diffraction** is too complex to interpret. A sample size of about 10^4 unit cells can be used for electron diffraction studies on solids, which is several million times smaller than for X-ray crystallography.

SCATTERING INTENSITY AND SCATTERING ANGLE

Consider diatomic molecule AB to study electron diffraction theory. The atom A lies at the origin and B at a distance r away (Fig. 1). The orientation of the molecule AB is specified by **angles** α **and** ϕ. The incident electron beam **enters parallel** to Y-axis and **diffraction** occurs through an angle 0. The interference between the wave scattered from A and B depends on the difference between the lengths of the paths they traverse. Draw from B a

perpendicular BN on to the diffracted direction and a perpendicular BM on to the undiffracted direction to calculate the **path difference** δ. When M and N are in phase the path difference is

$$\delta = AN - AM \qquad ...(3)$$

Because PM is perpendicular to AY and PN is perpendicular to the diffracted beam.

$$\delta = AN - AM = AP\cos(\theta + \phi - 90) - AP\cos(90 - \phi)$$

Since $AP = r\sin\alpha$, so $\delta = r\sin\alpha\,[\sin(\theta + \phi) - \sin\phi]$

$$\delta = 2r\sin\alpha\cos\left(\phi + \frac{\theta}{2}\right)\sin\frac{\theta}{2} \qquad ...(4)$$

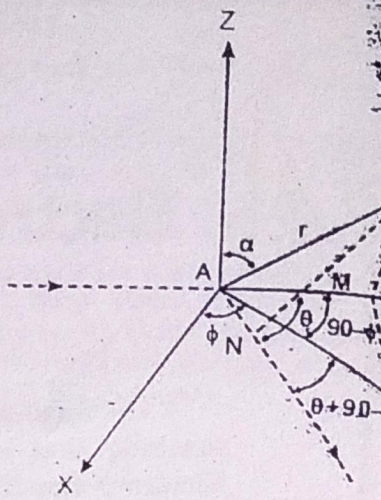

Fig. 1. Scattering of electrons by a diatomic molecule.

In order to **add waves that differ in phase and amplitude**, it is necessary to add them vectorically. The difference in phase between two scattered waves is $(2\pi/\lambda)\,\delta$. Assuming the atoms A and B identical, the resultant amplitude at P is,

$$A = A_0 + A_0 \cdot e^{2\pi i\delta/\lambda} \qquad ...(5)$$

where A_0 is called **atomic form factor for electron scattering** and depends on the nuclear charge of the atom. The intensity of radiation is proportional to square of the amplitude or in this case to $A\bar{A}$. Hence

$$I = A\bar{A} = A_0^2\,[1 + e^{-2\pi i\delta/\lambda}]\,[1 + e^{2\pi i\delta/\lambda}]$$

$$= A_0^2\,[2 + e^{-2\pi i\delta/\lambda} + e^{2\pi i\delta/\lambda}]$$

$$= 2A_0^2\left[1 + \cos\frac{2\pi\delta}{\lambda}\right] = 4A_0^2\cos^2\frac{\pi\delta}{\lambda}$$

To obtain scattering intensity of a randomly oriented group of molecules, it is essential to average the expression for the intensity at one particular orientation (α, ϕ) over all possible orientations. The differential element of the solid angle is $\sin\alpha\,d\alpha\,d\phi$ and the total solid angle of the sphere around AB is 4π. Thus the average scattering intensity is given by

$$I_{av} = \frac{4A_0^2}{4\pi}\int_0^{2\pi}\int_0^{\pi}\cos^2\left[2\pi\frac{r}{\lambda}\sin\frac{\theta}{2}\sin\alpha\cos\left(\phi + \frac{\theta}{2}\right)\right]\sin\alpha\,d\alpha\,d\phi$$

On integration, we get

$$I_{av} = 2A_0^2\left(1 + \frac{\sin sr}{sr}\right) \text{ where } s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2} \qquad ...(6)$$

For a more complex molecule, the resultant intensity is calculated by **Wierl equation**.

WIERL EQUATION

When a beam of electrons strikes a jet of molecules, two types of collisions occur.

(i) Elastic collisions produce atomic and molecular **coherent scattering.**

(ii) Inelastic collisions result in **incoherent scattering.** Atomic coherent scattering as well as incoherent scattering are responsible for the steeply falling background while molecular coherent scattering is responsible for the appearance of concentric

rings on a photographic plate. The coherent scattering is represented by Mark and Wierl (1930) equation.

When the molecule consists of a number of atoms, we sum over the contribution from all rs, and find that the total intensity has an angular variation, given by the Wierl equation :

$$I(\theta) = \sum_{ij} f_i f_j \frac{\sin sR_{ij}}{sR_{ij}}, \quad s = \frac{4\pi}{\lambda} \sin \frac{1}{2}\theta$$

re λ is the wavelength of the electron in the beam and θ is the scattering angle. The tron scattering factor, f is a measure of the intensity of electron scattering powers of the ms. The Wierl equation indicates the appearance of diffraction pattern caused by a lecule in a path of electron beam. $I(\theta)$ can be calculated only at discrete, equally spaced ues of scattering angle. However, Wierl equation does not allow the direct calculation of ernuclear distance from the measurement of $I(\theta)$ at various values of diffraction angle.

lecular representation of electron diffraction pattern using extended Wierl uation.

To calculate the molecular structure, Wierl equation is given by

$$I(\theta) = K \sum_{i=2}^{N} \sum_{J=1}^{i-1} f_i f_j \int_0^{\alpha} P_{ij}(r) \frac{\sin sR}{sR} dr \qquad ...(7)$$

ere $I(\theta)$ = intensity at diffraction angle θ, K (= 1) is experimental constant, f_i = form factor atom i, $P_{ij}(r)$ = probability distribution of the vibrational variation in the distance between oms i and j. $s = \frac{4\pi}{\lambda} \sin\left(\frac{\theta}{2}\right)$ is scattering angle in dependence of the wavelength.

Equation 7 is modified to

$$P_{ij}(r) = d(r - r_{ij}) \qquad ...(8)$$

The equation 8 assumes the interatomic distance to be constant and thus the molecule said to be rigid. Replace the form factor f_i by an atomic property A_i in the equation 7.

$$I(\theta) = \sum_{i=2}^{N} \sum_{j=1}^{i-1} A_i A_j \frac{\sin sR_{ij}}{sR_{ij}} \qquad ...(9)$$

Atomic properties such as atomic number, partial atomic charge or atomic polarizability llow to code 3*D* molecular representation of electron diffraction pattern.

MEASUREMENT TECHNIQUE

In a typical gas phase electron diffraction apparatus, electrons are emitted from a hot lament and then accelerated using a potential of about 50,000 volts. Then they pass hrough the stream of gas and on to a **fluorescent screen.** The wavelength of electrons ccelerated through a potential difference V is

$$\lambda = h/(2m_e \text{ eV})^{1/2}$$

For an accelerating potential difference of 40 kV, the wavelength is 6·1 pm. The gaseous ample presents all possible orientations of atom-atom separation to the electron beam. The iffraction of *X*-rays by a crystal depends upon the spacing between the layers while the *iffraction of electrons by gaseous molecules* depends upon the distances between the atoms n a molecule. The resulting **diffraction pattern** consists of a series of concentric ndulations on a background with an intensity that decreases steadily with increasing

scattering angle. The undulations are ascribed to molecular scattering that is the [illegible] defined scattering from the nuclear positions. The background is due largely to [illegible] scattering. One way of levelling the total intensity and hence to emphasize the undulations is to insert a rotating heart-shaped disk in front of the screen.

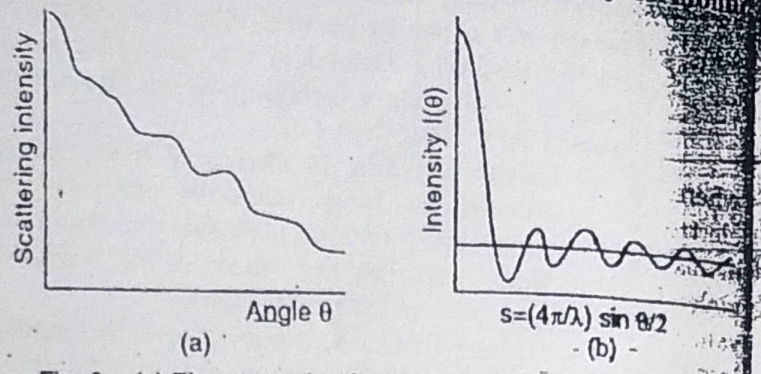

Fig. 2. (a) The scattering intensity consists of a smoothly varying background with undulation superimposed. (b) The undulations are emphasized if a sector is rotated in front of the screen and then $I(\theta)$ plotted against $s = (4\pi/\lambda) \sin \theta/2$.

Since the gaseous molecules are randomly oriented relative to the electron beam, the diffraction pattern, like that of an *X*-ray powder photograph, consists of concentric rings. There is enough background scatter of the electron beam with the result that diffraction bands are only poorly resolved. Recent techniques, have however greatly improved the resolution of bands.

It is possible to calculate electron scattering from a pair of nuclei separated by a distance R_{ij} and oriented at definite angle to the incident beam. The overall diffraction pattern is then calculated by allowing for all possible orientations of a pair of atoms. This procedure amounts to integration overall possible orientations. The final expression obtained for the diffraction intensity is

$$I_{ij}(\theta) = 2f_i f_j \{(1 + \sin R_{ij})/sR_{ij}\}$$

where $s = -(4\pi/\lambda) \sin\left(\frac{\theta}{2}\right)$, λ = wavelength of electron beam, θ is the scattering angle, $f_i f_j$ are the scattering factors of the ith and jth atoms. They determine the scattering power of the atoms (Fig. 2). If a molecule consists of a number of atoms, the total intensity is given by **Wierl equation** (described earliar).

The electron diffraction pattern gives the distance between all possible pair of atoms in the molecule (not just to these bonded together). When there are only a few atoms, the peaks can be analysed quickly and the analysis proceeds by assuming a geometry and calculating the intensity pattern by using Wierl equation. The best fit is then taken as the actual molecular geometry.

ELUCIDATION OF STRUCTURE OF SIMPLE GAS PHASE MOLECULES

Electron diffraction studies are useful for evaluating bond lengths and bond angles in simple gaseous molecules. The accuracy of bond length obtained from electron diffraction studies is comparable to that obtained from *X*-ray diffraction studies for simple molecules. The accuracy exceeds to ± 2 pm (**Table 1**). However, as the number of atoms in the molecules increases, the reliable information (viz., spacings of the resolved diffraction rings) is not enough to evaluate all the necessary **structural parameters.** The number of electron diffraction rings observed is usually much less than the number of *X*-ray diffraction spots observed in the *X*-ray crystal study. This shows that difficulties lie in the path of structure determination by electron diffraction. However, many molecular structures have been determined by this method.

Table 1. Bond lengths and bond angles in some compounds.

Compound	Bond	Bond length, pm	Geometry	Compound	Bond	Bond length pm	Bond angle
CCl_4	Cl—Cl	285	Tetrahedral	C_2H_4	C—C	133	H—C—H 115·5°
$GeCl_4$	Ge—Cl	208	Tetrahedral	CH_3Cl	C—H	111	H—C—H 110°
$TiCl_4$	Ti—Cl	218	Tetrahedral	$(CH_3)_3P$	C—P	185	C—P—C 98·8°
SF_6	S—F	158	Octahedral	Cl_2O	O—Cl		Cl—O—Cl 111°

Exercise. *Calculate bond length in CCl_4*

Solution. CCl_4 exhibits tetrahedral geometry. The scattering equation is given by

$$\frac{I}{K} = \Sigma i \Sigma j \psi_i \psi_j \frac{\sin ij}{\chi_{ij}} \quad ...(10$$

where I = Intensity of the scattered electron beam, K = constant, ψ = scattering factor of eac particular atom for electrons, χ_{ij} is defined in terms of I_{ij} which is the distance betwee centres of atoms designated as i and j. Thus

$$\chi_{ij} = 4\pi I_{ij} \frac{\sin \theta/2}{\lambda} \quad ...(1$$

where λ is the equivalent wavelength of the electron. On applying the scattering equation case of CCl_4, we get

$$\frac{I}{K} = Z_C^2 + 4Z_{Cl}^2 \times 12Z_{Cl}^2 \frac{\sin Cl - Cl}{\chi_{Cl-Cl}} + 8Z_C Z_{Cl} \frac{\sin \chi_{C-Cl}}{\chi_{C-Cl}}$$

The term Z_C^2 is the scattering due to carbon (Z is the atomic number of carbon), $4Z_C^2$ produced by 4 Cl atoms. The third term is due to the scattering by each pair of Cl ato There are 12 such pairs possible. Similarly the fourth term is due to scattering betw carbon and chlorine atoms (there are eight such individual terms being involved). in Z_C^2 : $4Z_{Cl}^2$ the I_{ij} is zero. So χ_{ij} is zero and $\sin Z_{ij}/\chi_{ij}$ must be unity. χ_{C-Cl} in the fourth term sho be equal to $\sqrt{(3/8)}\, x_{C-Cl}$ because the C—Cl is $\sqrt{(3/8)}Cl - Cl$ due to tetrahedral structur the molecule.

Thus, $$\frac{1}{K} = 6^2 + 4 \times 17^2 + 12 \times 17^2 \frac{\sin x}{x} + 8 \times 6 \times 17 \frac{\sin \sqrt{(3/8x)}}{\sqrt{(3/8x)}}$$

The value of $1/K$ is obtained by substituting various arbitrary numerical values of x 0 to 50. The results are then plotted on a curve. The first and second terms make a cons contribution, these may be neglected. The first three scattering maxima for CCl_4 have found to be at x = 7·75, 13·90 and 20·60 respectively. The wavelength λ of the electron can be determined from the accelerating potential. The quantity $\sin(\theta/2)\lambda$ for the first maxima given by CCl_4 vapour were calculated to be 0·217, 0·380 and $0{\cdot}555 \times 10^8$ respect Applying equation (10), we get

$$7{\cdot}75 = 0{\cdot}217 \times 10^{-8} \times 4 \times 3{\cdot}1415 \times l\,; \quad \therefore \quad l = 2{\cdot}81 \times 10^{-8}\ \text{cm}$$

$$13{\cdot}90 = 0{\cdot}380 \times 10^{-8} \times 4 \times 3{\cdot}1415 \times l\,; \quad \therefore \quad l = 2{\cdot}91 \times 10^{-8}\ \text{cm}$$

$$20{\cdot}60 = 0{\cdot}555 \times 10^{-8} \times 4 \times 3{\cdot}1415 \times l\,; \quad \therefore \quad l = 2{\cdot}95 \times 10^{-8}\ \text{cm}$$

On comparing these values with the maximum scattering determined experimentally the Cl—Cl bond length has been found to be 285 pm. The C—Cl bond length should, therefore be $\sqrt{(3/8) \times 2{\cdot}85} = 174$ pm. The experimental value, 176 pm is in agreement with this value.

ELECTRON DIFFRACTION STUDIES OF SOME COMPOUNDS

Structural Studies. Brockway and Gross suggested tetrahedral structure of $Ni(CO)_4$ by electron diffraction method. The internuclear distances, Ni—C and C—O bond distances have been found to be 182 ± 3 pm and 115 pm respectively. The small distance suggests a resonance structure for nickel carbonyl in which Ni—C bond partake of single and double bond character. C—O bond length indicates it to be of the same type as CO and are tetrahedrally disposed about the nickel atom in $Ni(CO)_4$.

- Electron diffraction studies indicate $AlCl_3$ to be dimeric containing two tetrahedra showing an edge. It is at the centre being surrounded by Cl atoms occupying the corners of the tetrahedra.
- **Hedberg and Schomaker have proposed a bridged structure** for the compound in which the bridging $H - B$ bond distance is 133·4 pm, terminal H—B bond distance is $118{\cdot}7 \pm 3$ pm and $B - B$ distance is $177 \pm 1{\cdot}3$ pm. The terminal H—B bond distance value agrees well with the single bond value 113 pm.
- Studies of **cis and trans**-dichloro and dibromo ethylene indicate that the scattering atoms, halogens are much closer in cis form than in *trans* form.
- Ring structure suggested for triazo group ($—N_3$) and diazo group (—N=N—) in aliphatic compounds by **parachor** measurements have been proved incorrect by diffraction studies. Methyl azide and diazomethane have linear structures.

Determination of Interatomic Distances by Electron Diffraction Studies.

- The interatomic distances determined by diffraction studies are usually in good agreement with those obtained by **Pauling's additivity rule** *which states that the bond distance A-B is equal to the arithmetic mean of the distance A-A and B-B.* For example, C—C distance in diamond is 154·2 pm and Cl—Cl distance in Cl_2 is 198·8 pm. The arithmetic mean of these (171·5) pm is almost equal to C—Cl distance 176·6 pm found in CCl_4.

The interatomic distance in CO_2, N_2O, carbon suboxide and cyanogen shows the existence of resonance. For example, C—O distance in CO_2 is 115 pm compared to additive value 124 pm for double bond and 111 pm for a triple bond which indicates resonance between three possible structures.

$$O^-—C{\equiv}O^+ \longleftrightarrow O{=}C{=}O \longleftrightarrow O^+{\equiv}C—O^-$$

LOW ENERGY ELECTRON DIFFRACTION (LEED) AND STRUCTURE OF SURFACES

Low energy electron diffraction is one of the most informative technique for determining the arrangement of atoms close to the surface. LEED is generally electron diffraction but the sample is now the **surface of a solid.** The use of low-energy (10 to 200 eV) electrons corresponding to wavelengths in the range 100 to 400 pm ensures that the *diffraction is caused only by atoms on and close to the surface.* The **experimental arrangement** used for LEED experiment consists of sample container, electron gun, grids and phospher screen. The

trons diffracted by the surface layers are detected by fluorescence they produce on the phosphor screen 3).

ucture of Surfaces.

The LEED pattern portrays the **two-dimensional** ucture of the surface. It is possible to measure the kness of surface layer and also to infer some details out the vertical locations of the atoms by studying the fraction intensities which depend on the energy of the ctron beam. Note that :

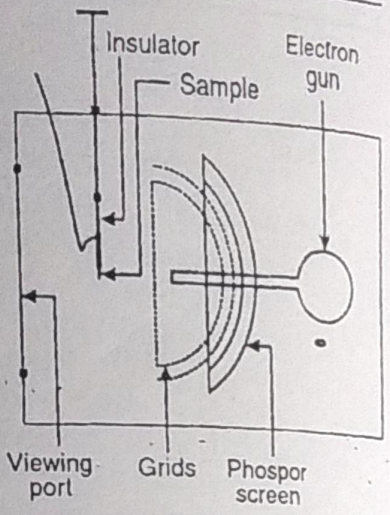

Fig. 3. A schematic diagram of the apparatus used for LEED experiment.

- **LEED pattern is sharp** if the surface is well ordered for long distances compared with the wavelength of the incident electrons. Generally, sharp patterns are obtained for surfaces ordered to depths of 20 nm or more.
- Diffuse LEED patterns shows the poorly ordered surface or the presence of impurities.
- If the LEED pattern does not correspond to the pattern expected by extrapolation of the bulk surface to the surface, then either reconstruction of the surface has occurred or there is order in the arrangement of an adsorbed layer.
- The surface of a crystal has exactly the same form as a slice through the bulk. LEED experiments indicate that metal surfaces are simply the truncations of the bulk lattice but the distance between the top layer of atoms and the one below is contracted by about 5%.
- Reconstruction occurs in ionic solids. Consider LiF. The Li^+ and F^- ions close to the surface lie on slightly different planes.

Refined LEED technique provides detailed information about the structure of a surface close to the point of attachment of CH_3C- **to the (110) surface of rhodium** at 300 K and the changes in positions of rhodium atoms that accompany chemisorption (Fig. 4). Semiconductors have surfaces reconstructed to a depth of several layers.

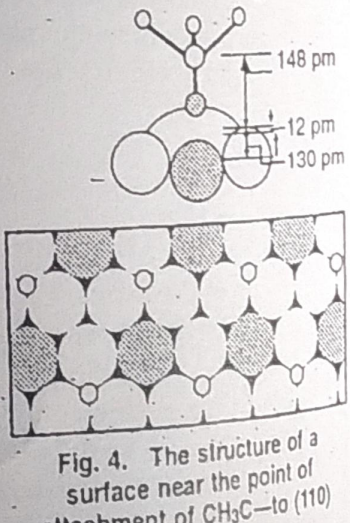

Fig. 4. The structure of a surface near the point of attachment of CH_3C- to (110)

Notations to Express the Arrangement of Atoms at a Surface. *An arrangement of atoms corresponding to the bulk unit cell is known as* **substrate structure** and is denoted by (1×1). Hence the substrate structure of (111) face of a metal M would be represented as $M(111) - (1 \times 1)$. An adsorbed species A which has the same structure would be designated by $(1 \times 1) - A$. For example, a monolayer of oxygen atoms on the (111) face of Si can be denoted Si (111) – (1×1) – O.

- A surface structure with a unit cell side that is twice as large as the unit cell side of the substrate surface is given by (2×2).
- In general, the relative size would be designated by $(n \times m)$. The surface atoms form a lattice that can be rotated with respect to the substrate. For instance, a surface structure

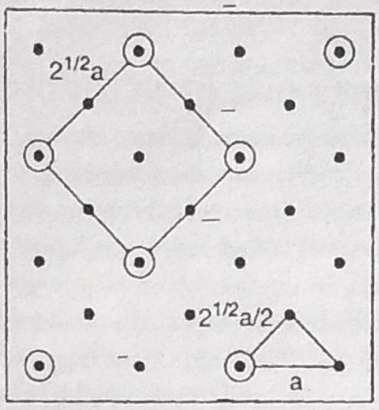

Fig. 5. Designation $(2^{1/2} \times 2^{1/2})$ R45° of adsorbed surface layers.

rotated by 45° would be indicated R 45° as in $(2^{1/2} \times 2^{1/2})$ R 45° illustrated in Fig. 5.

APPLICATIONS OF LEED.

LEED pattern may be used to assess the defect density of a surface. The pattern is affected by the presence of terraces, steps and kinks in a surface. The samples can be obtained by cleaning a crystal at different angles to a plane of atoms. Only terraces are produced when the cut is parallel to the plane and the density of steps increases as the angle of cut increases. The additional structure in LEED patterns shows that the steps are arrayed regularly.

SHORT ANSWER QUESTIONS

1. *Why electrons can not be used for studying interiors of solid samples?*
Ans. Because electrons are charged, these are scattered strongly by their interaction with electrons and nuclei of atoms of the sample.

2. *List some techniques for studying surface composition.*
Ans. (i) Low-energy electron diffraction, (ii) Scanning electron and scanning probe (scanning tunnelling and atomic force) microscopy, (iii) High vacuum and ionization techniques, (iv) Auger electron, vibrational and energy loss-spectroscopy, (v) Surface-extended X-ray absorption fine structure spectroscopy.

MULTIPLE CHOICE QUESTIONS

1. An electron beam passing through an evacuated region can be focussed by means of
(a) Magnetic field only (b) Electric field only
(c) Magnetic or electric field (d) None

2. Electrons, when accelerated through 10 keV, require a wavelength of
(a) 12 pm (b) 10 pm (c) 20 pm (d) 50 pm

3. Electron diffraction studies generally utilize electrons with energies of the order of
(a) 10 keV (b) 40 keV (c) 50 keV (d) 30 keV

4. The diffraction of electrons by gaseous molecules depends upon the
(a) Distance between the atoms in a molecule
(b) Spacing between the layers
(c) Orientation of electron beam
(d) All

5. If a molecule consists of a number of atoms, the total intensity is given by
(a) de Broglie equation (b) Wierl equation
(c) Laue method (d) Debye equation

6. Wierl equation shows the appearance of diffraction pattern caused by
(a) Solids (b) Liquids
(c) Molecule in the path of electron beam (d) All

7. One of the most informative technique for determining the arrangement of atoms clos to the surface is
(a) Low-energy electron diffraction (b) Auger electron spectroscopy
(c) Scanning electron microscopy (d) Molecular beam technique

8. LEED pattern portrays
(a) Three dimensional structure (b) Two dimensional structure
(c) Complicated structure (d) Depth structures

9. Interpretation of LEED data is
(a) Much more complicated than the interpretation of bulk *X*-ray data
(b) Easier than *X*-ray diffraction studies
(c) Easier than scanning microscopy
(d) None

10. A mono layer of oxygen atoms on the (111) face of silicon would be denoted by
(a) $(1 \times 1) - O$ (b) $Si(111) - (1 \times 1) - O$
(c) $2^{1/2} \times 2^{1/2} - Si$ (d) $Si(1 \times 1) - O$

ANSWERS

1. (c) 2. (a) 3. (b) 4. (a) 5. (b) 6. (c) 7. (a) 8. (b) 9. (a) 10. (b)