Answer All Three Questions

The numbers in square brackets show the provisional allocation of maximum marks per question or part of question.

A module materials booklet, including physical constants if applicable, is attached at the end of the paper.

1. Organic semiconductors **[Part Marks]**
   (a) Explain the difference between singlet and triplet excitons, and give a graphic representation of their spin configurations. **[2]**
   (b) Assuming that singlet and triplet excitons have the same formation probability upon the encounter of an electron and a hole with randomly distributed spins, state the maximum value of the electroluminescence quantum efficiency in an organic LED (OLED) as a fraction of the photoluminescence quantum efficiency. Explain your reasoning. **[2]**
   (c) Three light-emitting diodes (LEDs) emit in the blue (450 nm), in the green (550 nm) and in the red (650 nm) with the same radiometric current efficiency. What is the relation between the luminance of the green LED compared to the others (as perceived by the average human eye) when they are mounted on the same circuit in series with the power supply? **[3]**

(Question continued on next page)

(d) An OLED emits 6000 cd/m^2 when driven in operating conditions at the beginning of its lifetime. If the minimum acceptable luminance performance is 800 cd/m^2 and the ageing can be described by a linear relation with luminance decay rate of 0.1 (cd/m^2)/h when driven at constant current, calculate the expected device lifetime (in hours). Suppose also the operating voltage has to increase by 0.015 V per hour to keep the current constant. What is the operating voltage increase at the end of the useful lifetime? Comment on the relative importance of the decay of luminance vs. the increase of operating voltage in the device ageing in the case of this particular example. Which is the factor that is effectively limiting the device lifetime? **[3]**

(e) Define the open circuit voltage V_{oc} and the fill factor *FF* for a generic organic photovoltaic diode (PVD). What is the significance of the fill factor in terms of the description of the device performance? Are these definitions valid for inorganic PVDs as well? **[4]**

(f) Explain the fundamental processes that lead to charge generation in an excitonic solar cell and the constraints that they put on the materials' selection and device design.

[6]

2. Liquid crystals

   (a) State the two molecular "shapes" for the most common liquid crystals and related typical dimensions. **[3]**

   (b) Describe the nature of the molecular interactions and the type of ordering characteristic of a nematic liquid crystal phase in comparison to that of the crystalline state and that of an isotropic liquid. Give a pictorial representation of this type of (nematic) ordering. **[6]**

   (c) State if the order in the nematic phase is orientational, positional or both. Give the difference with a smectic A phase and with a smectic C phase. **[2]**

   (d) State whether conjugated oligomers can display liquid crystalline properties, or if conjugation and liquid crystalline behaviour are mutually exclusive. Is the answer valid also for conjugated polymers or are there significant differences? **[2]**

   (e) Give two molecular design strategies to give liquid crystalline properties to spherically shaped molecules. **[2]**

   (f) An X-ray diffraction experiment of a liquid crystal (LC) sample has returned the diffraction pattern depicted in figure 1 below with the outer (partial) halo occurring at 'inverse distance' *q1* from the centre of the diffractogram and the inner points at "inverse distance" *q2* from the centre of the diffractogram. Give the name of the LC phase that can be inferred from such details, and a pictorial representation of the molecular ordering, as well as appropriate formulae to calculate the approximate dimensions of the LC molecule. **[5]**

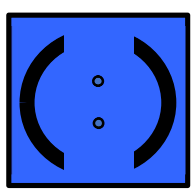

Figure 1.

3. 2D materials

(a) Draw (a portion of) the crystal structure of graphene, including the primitive unit vectors, and give an analytical expression for such vectors as a function of the carbon-carbon distance "*a*". **[4]**

(b) Draw (a portion) of graphene's reciprocal lattice, including the most important symmetry points (*Γ, K, M).* On such a diagram, also indicate the Brillouin zone (e.g. by shading). Give an analytical expression for the (reciprocal) unit vectors, and for the symmetry points above with respect to the centre of the Brillouin zone. **[7]**

(c) Give an analytical expression and a graphic representation for the band dispersion in graphene near K-points. **[4]**

(d) Give the meaning of the symbols in Einstein's energy-momentum relation below. Then show that a massless carrier is expected to display a linear energy dispersion. Give an order of magnitude for an experimentally measured mobility (with appropriate units) of charge carriers in graphene. **[5]**

$$\boxed{E^2 = (pc)^2 + (m_0 c^2)^2}$$

END OF EXAMINATION PAPER

PHAS0058 Physics of Advanced Materials

Materials booklet

Quantity	**formula**
Organic semiconductors	
Charge populations at equilibrium	$p = n_i e^{\frac{E_i - E_F}{kT}}$ and $n = n_i e^{\frac{E_F - E_i}{kT}}$
Luminescence	$l = k_r N = k_r N_0 e^{-kt} = k_r N_0 e^{-\frac{t}{\tau}}$
Photoluminescence Quantum Efficiency	$\eta = \frac{k_r}{k_r + k_{nr}}$
Förster transfer[1]	$k_{ET} \sim \frac{1}{\tau_0}\left(\frac{r_0}{r}\right)^6$
Dexter transfer	$k_{ET} \sim e^{-\frac{2r}{L}}$
Marcus theory	$k = \frac{J^2}{\hbar}\sqrt{\frac{\pi}{\lambda k_B T}}\exp\left(-\frac{\lambda}{4 k_B T}\right)$
Internal Quantum Efficiency of an LED[2]	$\eta_{EL} = \eta_{PL} r_{st} \gamma_{cap}$
Current efficiency	$\eta_{curr} = \frac{Luminance}{J}$
Luminous power efficiency[3]	$\eta_L = \frac{\Phi_L}{VI}$
Current density	$J = nq\mu E$
Space-charge limited current for holes	$J = \frac{9\epsilon_i \mu (V - V_{BI})^2}{8d^3}$

[1] Where $\tau_0 = \frac{1}{k_R + k_{NR}}$ is the experimental PL lifetime

[2] Where r_{st} is fraction of singlets to total excitons

[3] Where Φ_L is luminous flux

Langevin recombination	$B = \frac{q}{\epsilon}(\mu_n + \mu_p)$
Drain current in an FET	$I_D = \frac{W}{L}\mu C_i\left[(V_G - V_0)V_D - \frac{V_D^2}{2}\right]$
Saturation current in an FET	$I_{Dsat} = \frac{W}{2L}\mu C_i(V_G - V_0)^2$
PV fill factor	$FF = \frac{(IV)_{max}}{I_{SC}V_{OC}}$
PV power conversion efficiency[4]	$\eta_{PV} = FF \times \frac{I_{SC}V_{OC}}{P_{light}}$
2D materials	
Rotation matrix	$R = \begin{bmatrix}\cos\theta & -\sin\theta \\ \sin\theta & \cos\theta\end{bmatrix}$
Fermi velocity[5]	$v_F = \frac{1}{\hbar}\frac{\partial E}{\partial k}$
Fermi-Dirac statistics at Fermi energy	$f(E_F, T) = \frac{1}{2}$
Fermi energy at Dirac points	$E(\boldsymbol{k}) = \pm\hbar v_F \boldsymbol{k}$
Einstein energy-momentum relation	$E^2 = (pc)^2 + (m_0c^2)^2$
Carrier density (intrinsic and extrinsic)	$n_i = \frac{\pi}{6}\left(\frac{k_BT}{\hbar v_F}\right)^2 \qquad n_e = \frac{E_F^2}{\pi\hbar^2 v_F^2}$
Fine structure constant	$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c}$
Interband conductivity	$\sigma(\omega) = \frac{\pi e^2}{2h}$

[4] Where P_{light} is illumination power
[5] Approximates to c/300

Intraband conductivity[6]	$\sigma(\omega) = \frac{\sigma_0}{1 + i\omega\tau}$
Absorption	$A(\omega) = \frac{4\pi}{c} Re[\sigma(\omega)]$
Hall effect in a 2D material	$V_H = \frac{I_x B_z}{n_A e}$
Quantum Hall effect[7]	$\sigma = \frac{I_{channel}}{V_{Hall}} = \nu \frac{e^2}{h}$
Ferroelectrics	
Electric dipole potential	$V(\boldsymbol{r}, \boldsymbol{p}) = qd \frac{cos\theta}{4\pi\epsilon r^2}$
Electric dipole field	$\boldsymbol{E} = \frac{3(\boldsymbol{p} \cdot \boldsymbol{r})\boldsymbol{r} - r^2\boldsymbol{p}}{4\pi\epsilon r^5}$
Electric dipole moment	$\vec{\boldsymbol{p}} = q\vec{\boldsymbol{d}}$
Polarisation	$P = \chi E$
Landau theory of phase transitions (Gibbs Energy)	$\mathcal{F}_P = \frac{1}{2}aP^2 + \frac{1}{4}bP^4 + \frac{1}{6}cP^6 + \cdots - EP$
Liquid crystals	
Order parameter	$S = \langle \frac{3\cos^2\theta - 1}{2} \rangle$

[6] Where frequency is given in Hz and τ is the relaxation time in seconds
[7] With ν being the filling factor

Constant	symbol	value
Speed of light in vacuo	c	2.998×10^{8} m s^{-1}
Planck's constant	h	6.626×10^{-34} m^{2} kgs^{-1} (=J s)
Reduced Planck's constant	$\hbar$	$h/2\pi$
Boltzmann's constant	k_B	1.381×10^{-23} m^{2} kgs^{-2} K^{-1} (=J K^{-1})
Electron charge	e	1.602×10^{-19} C
Electron Volt unit	eV	1.602×10^{-19} J
Vacuum permittivity	ε_0	8.854×10^{-12} F/m