[1.11] (a) For an f.c.c. structure, $a = 2\sqrt{2}r$.

$a = 2 \times \sqrt{2} \times 0.1246 = 0.3524\,\text{nm}.$

(b) Weight of one atom = $58.71/6.02\times10^{23} = 9.752\times10^{-23}$ g. Since there are 4 atoms per unit cell of volume a^3,

$$\text{Density} = \frac{4\times9.752\times10^{-23}}{(0.3524\times10^{-9})^3} = 8.91 \text{ Mgm}^{-3}.$$

[1.12] MgO has a NaCl-type structure with Mg^{2+} cations and O^{2-} anions occupying two interpenetrating f.c.c. sub-lattices. The ratio of the ionic radii $r/R = (0.065/0.14) = 0.46$ which fits into the *r*/*R* band 0.414 – 0.732 which have a maximum coordination number of 6. Each Mg^{2+} cation is octahedrally coordinated with six larger O^{2-} anions and vice versa. MgO is stoichiometric and the unit cell contains 4 cations and 4 anions.

[1.13] Let H be the origin, HB the x-axis, HC the y-axis.

For ABC:

	x	*y*	*z*
intercepts	1	1	0.5
reciprocals	1	1	2

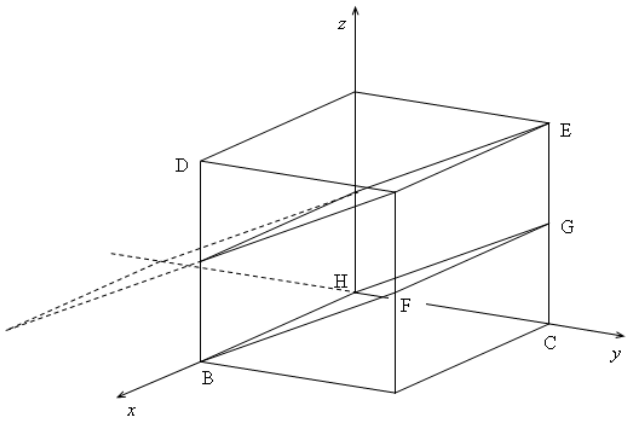
Hence Miller index = (112)

For BCED,

	x	*y*	*z*
intercepts	1	1	∞
reciprocals	1	1	0

Hence Miller index = (110)

For BFGH, to find the intercepts displace the plane upward by half a unit as shown:



	x	*y*	*z*
intercepts	∞	-1	0.5
reciprocals	0	-1	2

Hence Miller index = $(0\bar{1}2)$

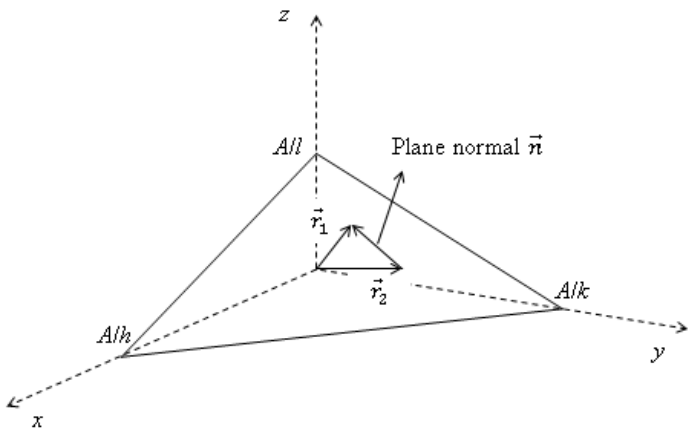
[1.14] The equation of a plane is $\frac{x}{a}+\frac{y}{b}+\frac{z}{c}=1$ where *a*, *b* and *c* are intercepts with the *x*, *y* and *z* axes respectively. For the (*hkl*) plane, since its intercepts are proportional to the reciprocals of *h*, *k* and *l* (say *A*/*h*, *A*/*k*, *A*/*l* where *A* is a constant), its equation is:

$$\frac{x}{(A/h)}+\frac{y}{(A/k)}+\frac{z}{(A/l)}=1$$

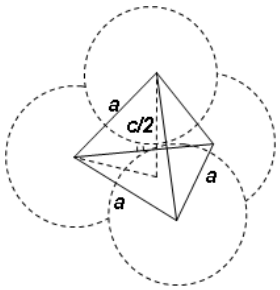
This can be written as a dot product between two vectors $\vec{n}=(h,k,l)$ and $\vec{r}=(x,y,z)$:

$$\vec{n}\bullet\vec{r}=A. \qquad (*)$$

In eqn. (*), $\vec{r}=(x,y,z)$ is the position vector of any arbitrary point on the plane, and so this equation says that no matter where this point is, the projection of $\vec{r}$ on the direction of $\vec{n}$ must be a constant *A*. This can only happen if $\vec{n}$ is the normal direction of the plane. To see this, let $\vec{r}_1$ and $\vec{r}_2$ be two points on the plane, and so $(\vec{r}_1-\vec{r}_2)$ is a vector lying on the plane. Then, making use of eqn. (*), it is easy to show that $\vec{n}\bullet(\vec{r}_1-\vec{r}_2)=0$, which means that $\vec{n}=(h,k,l)$ is normal to $(\vec{r}_1-\vec{r}_2)$ and hence is the normal direction of the plane.



[1.15] In the h.c.p. unit cell in Figure 1.15b, an atom in the middle layer sits on the interstice between three atoms in the bottom layer, and these 4 atoms form a regular tetrahedral arrangement:



The side length of the tetrahedron is *a*, and its height is *c*/2, where *c* is the height of the entire h.c.p. unit cell. For a regular tetrahedron, (height)/(side length) = $\sqrt{2/3}$, and so $c/(2a) = \sqrt{2/3}$, which gives $c/a = 2\sqrt{2/3} = 1.633$.

[1.16] Along [110] in b.c.c., there is one atom per a distance of $\sqrt{2}a$. Hence the linear density is $1/(\sqrt{2}a)$ or 0.707/*a*. Along [111] in the same structure, there is one atom per $\sqrt{3}a/2$, i.e. linear density is $2/(\sqrt{3}a)$ or 1.15/*a*. [111] is denser than [110].
Along [110] in f.c.c., there is one atom per $\sqrt{2}a/2$, so linear density is $\sqrt{2}/a$ or 1.414/*a*. Along [111], there is one atom per $\sqrt{3}a$, and this gives a linear density of $1/(\sqrt{3}a)$ or 0.577/*a*. In this case, [110] is denser than [111].

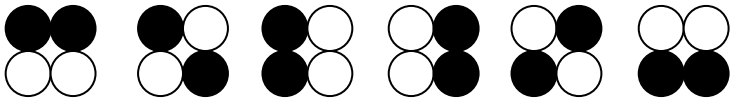
[1.17] On (110) in b.c.c., there are $4\times\frac{1}{4}$ corner atoms and 1 centre atom. The plane measures $\sqrt{2}a$ by *a*. So planar density is 2 atoms per $\sqrt{2}a^2$, or $1.414/a^2$.
On (100) in b.c.c., there are $4\times\frac{1}{4}$ corner atoms. The plane measures a^2, and so planar density is $1/a^2$. The (110) plane is therefore denser.
On (110) in f.c.c., there are $4\times\frac{1}{4}+2\times\frac{1}{2}=2$ atoms. Planar density is $1.414/a^2$.

On (100) in f.c.c., there are $4\times\frac{1}{4}+1=2$ atoms. Planar density is $2/a^2$. The (100) plane is denser.

[1.18] Each unit cell of f.c.c. contains 4 atoms. From $4r=a\sqrt{2}$, lattice constant of Cu is $a=4\times0.128/\sqrt{2}=0.362\,\text{nm}$. Therefore, density $\rho=\frac{4\times0.0635}{6.023\times10^{23}\times(0.362\times10^{-9})^3}$ = 8890 kgm^{-3}.

Chapter 2

[2.1] There are 6 ways:



[2.2] $dS=C_p\frac{dT}{T}$, so

$$\Delta S=\int_{T_1}^{T_2}C_p\frac{dT}{T}=\int_{T_1}^{T_2}(22.64+6.28\times10^{-3}T)\frac{dT}{T}=\int_{300}^{1358}(\frac{22.64}{T}+6.28\times10^{-3})dT$$

$$=22.64\times\ln\left(\frac{1358}{300}\right)+6.28\times10^{-3}(1358-300)=40.8\,\text{J mol}^{-1}\,\text{K}^{-1}$$

[2.3] The solid/liquid line for typical metals is a vertically sloping forward line. For Bi and Ga this solid/liquid line slopes backwards. The reason for this change is that increasing the pressure for a typical metal will lead to liquid metal freezing. For Bi and Ga these metals expand on freezing and hence increasing pressure will lead to fusion.

[2.4] 100g of Au-Ag contains 40g of Au and 60g of Ag.
40g of Au contains 40/197 = 0.20305 mole or 1.2229×10^{23} atoms.
60g of Ag contains 60/108 = 0.55556 mole or 3.3461×10^{23} atoms.

Mole fraction of Au = 0.20305/(0.20305+0.55556) = 26.8%
Mole fraction of Ag = (100- 26.8) = 73.2%

With the Stirling formula, entropy of mixing,

$$S = k[N \ln N - n \ln n - (N - n) \ln(N - n)]$$

N = (1.2229 + 3.3461)×10^{23} = 4.569×10^{23} atoms
n = 1.2229×10^{23} Au atoms
(N-n) = 3.3461×10^{23} Ag atoms

$$S = 1.38062 \times [4.569 \times \ln(4.569 \times 10^{23}) - 1.2229 \times \ln(1.2229 \times 10^{23}) - 3.3461 \times \ln(3.3461 \times 10^{23})] = 3.66 \text{ J K}^{-1}$$

[2.5] (a) Using the relationship $(\text{At}\%)_x = \dfrac{(\text{Wt}\%)_x A_y}{(\text{Wt}\%)_x A_y + (\text{Wt}\%)_y A_x} \times 100$

(i) Cu60%-Zn40%: $(\text{At}\%)_{\text{Zn}} = \dfrac{40 \times 63.55}{40 \times 63.55 + 60 \times 65.39} \times 100 = 41.23$ at. %

(ii) Cu90%-Al10%: $(\text{At}\%)_{\text{Al}} = \dfrac{10 \times 63.55}{10 \times 63.55 + 90 \times 26.98} \times 100 = 20.24$ at. %

(iii) Cu80%-In20%: $(\text{At}\%)_{\text{In}} = \dfrac{20 \times 63.55}{20 \times 63.55 + 80 \times 114.82} \times 100 = 12.15$ at. %

(b) In terms of (e/a) ratio, the compositions are:

(i) Cu-41.23at%Zn = $\dfrac{(58.77 \times 1\text{electron}) + (41.23 \times 2\text{electrons})}{100\text{ atoms}} = 1.4$

(ii) Cu-20.74at%Al = $\dfrac{(79.26 \times 1\text{electron}) + (20.74 \times 3\text{electrons})}{100\text{ atoms}} = 1.4$

(iii) Cu-12.15at%In = $\dfrac{(87.85 \times 1\text{electron}) + (12.15 \times 3\text{electrons})}{100\text{ atoms}} = 1.24$

The significance of the (e/a) ratio is that 1.4 gives the primary solid solubility of favourable elements in copper, silver or gold.

Indium is different in that the size factor of indium in copper is borderline to unfavourable and hence the solubility limit falls short of the requirement of 20 at.%.

[2.6] Simple cubic cell: volume = a^3; number of atoms per cell = 1; (volume/atom) = a^3.

Hexagonal cell: volume = $3\sqrt{2}a^3$; number of atoms per cell = 6; (volume/atom) = $\dfrac{a^3}{\sqrt{2}}$.

% volume change = $\frac{a^3 - a^3/\sqrt{2}}{a^3} \times 100\% = 29\%$.

[2.7] A tie line drawn at 1250ºC shows the liquid contains 32%Ni, the solid 45%Ni and the amount given by the lever rule is

$\frac{45-40}{45-32} = 38\%$ for the liquid;

$\frac{40-32}{45-32} = 62\%$ for the solid.

[2.8] Taking the maximum α-solid solubility to be 19% Sn, the eutectic composition to be 63% and the maximum β-solid solubility to be 2.5%Pb, then the

$$\% \alpha = \frac{97.5-63}{97.5-19} \times 100\% = 43.9\%$$
$$\% \beta = \frac{63-19}{97.5-19} \times 100\% = 56.1\%$$

[2.9] Cu, Ni, Ag are all isostructural (FCC) but their sizes vary. The lattice constants of pure Cu and Ni are respectively 0.361 and 0.352 nm, hence they differ by only about 2.5%. According to the "size factor" criterion, extended solubility between Cu and Ni is expected. The lattice constant of pure Ag is 0.409 nm which is 13.3% larger than that of Cu. The "size factor" is therefore less favourable for extended solubility between Cu and Ag.

[2.10] It is the relative valency effect. Cu has an electronic configuration of $3d^{10}4s^1$ and Zn $3d^{10}4s^2$. The valency of Zn is therefore higher and so Zn would tend to be the solute.

[2.11] The size of the interstitial site $\left(\frac{1}{2}, \frac{1}{4}, 0\right)$ has a radius 36 pm or 0.29*r*, where *r* is the radius of the Fe atom, and the $\left(0, 0, \frac{1}{2}\right)$ site has a radius of 19 pm or 0.154*r*. The reason the smaller site is occupied is that it has 2 nearest neighbour Fe atoms which can be pushed away more easily than the 4 Fe atoms surrounding the tetrahedral $\left(\frac{1}{2}, \frac{1}{4}, 0\right)$ site.

[2.12] (a) Using the lever rule, the amount of Fe_3C is $\frac{0.80-0.025}{6.67-0.025}=11.7\%$.

The amount of α-phase is $\frac{6.67-0.80}{6.67-0.025}=88.3\%$.

(b) Using the lever rule, the amount of Fe_3C is $\frac{0.20-0.025}{6.67-0.025}=2.6\%$.

The amount of pearlite is $\frac{0.20-0.025}{0.80-0.025}=22.6\%$

Chapter 3

[3.1] $\lambda = KR^{-n}$ => $\log\lambda = \log K - n\log R$. So from the two conditions, we have
$\log 100 = \log K - n\log 0.1$ or $2 = \log K + n$, and
$\log 10 = \log K - n\log 60$ or $1 = \log K - 1.778n$
Solving gives n = 0.36, K = 43.66.

[3.2] Planes with higher planar densities are slower to advance. The planar densities of the (110) and (100) planes have been worked out in Qs. [1.17] in Chapter 1. Those for (111) can be worked out in a similar way. The results are summarised as follows:

f.c.c.:

Plane	Planar density	Growth speed
(111)	$2.309/a^2$	Slowest
(110)	$1.414/a^2$	Highest
(100)	$2/a^2$	Medium

b.c.c.:

Plane	Planar density	Growth speed
(111)	$0.577/a^2$	Highest
(110)	$1.414/a^2$	Slowest
(100)	$1/a^2$	Medium

[3.3] In melt-spinning, a narrow stream of molten metal drips onto the rim of a water-cooled spinning wheel and is made to solidify at a cooling rate of ~10^6 K/s. The cast metal is in the form of a ribbon typically tens of microns thick.

In a typical atomisation method, a stream molten metal impacts with a stream of high-pressure gas or water. The cooling rate is on the order of 10^3 K/s, and the cast product is in the form of powder or particles. Oxygen contamination can be severe if water stream is used.

[3.4] See equation (3.8) in text. This assumes that (i) the partition coefficient at the liquid-solid interface is constant, (ii) the liquid is well mixed so there is no concentration gradient, and (iii) the solid diffusion is slow.

[3.5] (i) See derivation of equation (3.8) in text. Alternatively, consider solidification of the melted zone happening at x (between 0 and 1). The depletion of solute in the purified zone from 0 to x is $\int_0^x [c_o - c_s(x')]dx'$. The remaining melted zone from x to 1 is enriched by this amount of solute, hence the solute concentration in the melted zone is

$$c_L = c_o + \frac{1}{(1-x)}\int_0^x [c_o - c_s(x')]dx' = \frac{1}{(1-x)}\left(c_o - \int_0^x c_s(x')\,dx' \right).$$

At the solidification front at x, partition coefficient k is the ratio of the solute concentrations in solid and liquid, i.e. $k = c_s(x)/c_L(x)$.

So $kc_L = \frac{k}{(1-x)}\left(c_o - \int_0^x c_s(x')\,dx' \right) = c_s(x)$.

Rearranging and differentiating give $(1-k)c_s(x) = (1-x)\frac{dc_s(x)}{dx}$, the solution of which is

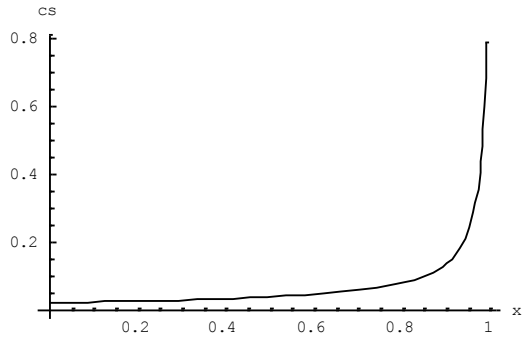
$c_s(x) = kc_o(1-x)^{k-1}$.

(ii) The impurity content at $x = 0.5$ is given by

$c_s = kc_o(1-x)^{k-1} = 10^{-5} \times 10^{-6}(1-0.5)^{-1} = 2 \times 10^{-11}$.

[3.6] The impurity content in solid is given by

$c_s(x) = kc_o(1-x)^{k-1} = 0.25 \times 0.1 \times (1-x)^{0.25-1} = 0.025 \times (1-x)^{-0.75}$



[3.7] At such small compositions, reading off from the phase diagram is not very accurate – it is better to use the Scheil equation: $c_s(x) = kc_o(1-x)^{k-1}$. The partition coefficient *k* is defined as $k = c_S / c_L$ where c_S is composition of the solid and c_L is that of the liquid. For a eutectic reaction, the composition of the liquid just before reaching T_E is just the eutectic composition, i.e. $c_L = 12.6\%$. Composition of α phase at T_E is $c_S = 1.65\%$. Hence, $k = c_S / c_L = 1.65/12.6 = 0.131$.

The composition of the initial solid formed is given by c_s at $x = 0$, i.e. $c_s(0) = kc_o$

At $c_o = 0.2\%$ Si overall, the composition of the first solid formed is $kc_o = 0.131 \times 0.2 = 0.026\%$Si.

At $c_o = 0.5\%$ Si overall, composition of first solid is $0.131 \times 0.5 = 0.066\%$Si.

[3.8] This question is similar to Qs. [3.7] above, with $c_L = 33$, $c_S = 5.65\%$. Hence, $k = c_S / c_L = 5.65/33 = 0.171$.

The composition of the initial solid formed is $c_s(0) = kc_o = 0.171 \times 2 = 0.342\%$

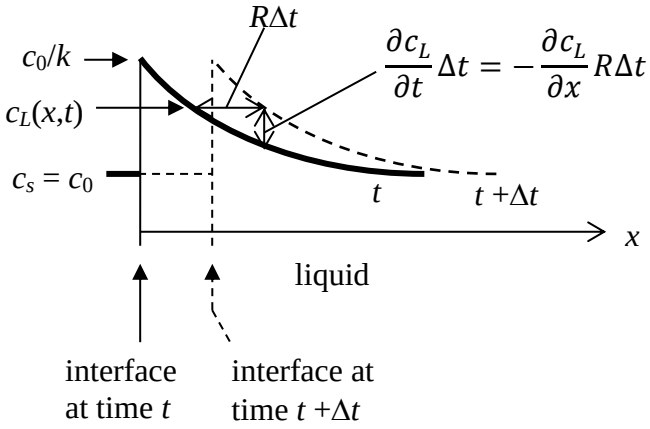
[3.9] Metallic glasses are amorphous in structure and do not have dislocations which are crystalline defects. Their yield strength is therefore high, and on impact, e.g. with a golf ball, they do not absorb as much energy as ordinary crystalline metals, since there is no dislocation movement as energy dissipation mechanism.

[3.10] See derivation of equation (3.2) in text, but now, ΔG_v is treated as positive, i.e. the absolute value of the phase energy change for solidification.

[3.11] See derivation of equation (3.2) in text.

[3.12] The Gibbs-Thomson equation becomes the equation for r_c in Question [3.10] by recognizing that $\Delta G_v = \Delta G/V$, which is the case, since ΔG_v is the free energy of the new phase per unit volume.

[3.13] The steady-state concentration profile in liquid is shown below:



Because of the steady state, the profile at time $t + \Delta t$ is simply that at t displaced rigidly to the right by a distance $\Delta x = R\Delta t$, where R is the speed of interface. Geometry consideration gives:

$\frac{\partial c_L}{\partial t}\Delta t = -\frac{\partial c_L}{\partial x} R\Delta t$ or $\frac{\partial c_L}{\partial t} = -R\frac{\partial c_L}{\partial x}$ …(1)

Fick's second law (see Chapter 7) is: $\frac{\partial c_L}{\partial t} = D\frac{\partial^2 c_L}{\partial x^2}$

Substituting in eqn. (1) gives: $D\frac{\partial^2 c_L}{\partial x^2} + R\frac{\partial c_L}{\partial x} = 0$

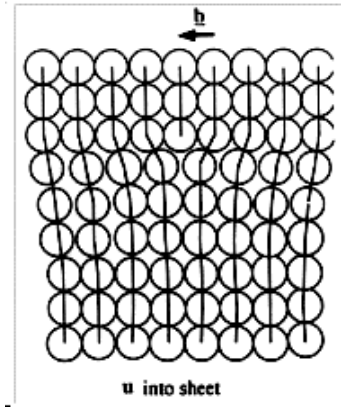
Solution is of the form: $c_L = A + B\exp\left(-\frac{Rx}{D}\right)$

Boundary conditions $c_L(0) = c_0/k$ and $c_L(\infty) = c_0$ are satisfied with $A = c_0$ and $B = c_0(1-k)/k$.

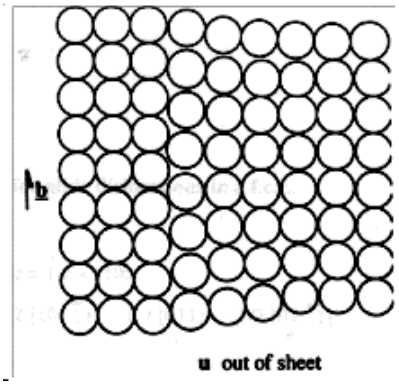
Hence, $c_L(x) = c_0\left[1 + \frac{(1-k)}{k}\exp\left(-\frac{Rx}{D}\right)\right]$.

Chapter 4

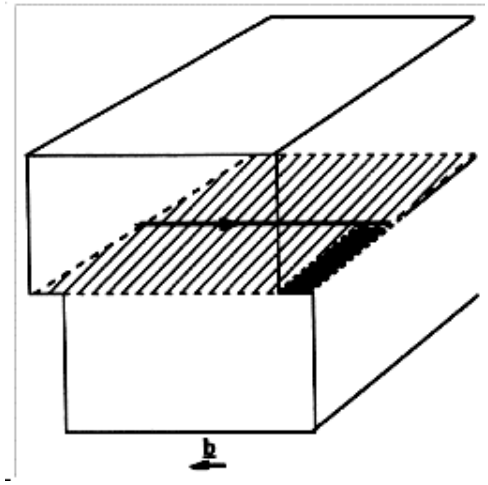
[4.1]



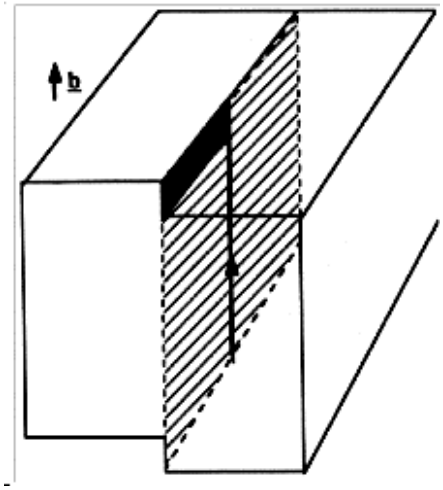
[4.2]



[4.3]



[4.4]



[4.5] The smallest perfect lattice translation vector = ½<110>

$= 1/2[110]; \quad 1/2[1\bar{1}0]; \quad 1/2[101]; \quad 1/2[10\bar{1}]; \quad 1/2[011]; \quad 1/2[01\bar{1}].$

[4.6] The Burgers vector of the dislocation is $1/2[1\bar{1}0]$ and its glide plane normal is $\underline{n} = [11\bar{1}]$. The line direction $\underline{u}$ of the screw direction is $[1\bar{1}0]$ (parallel to $\underline{b}$) and the line direction of the edge dislocation is $\underline{n} \times \underline{b} = [112]$.

[4.7] The slip planes $\underline{n}$ for f.c.c. metals are {111}. The four {111} planes in a cubic system are $(111), (\bar{1}11), (1\bar{1}1)$ and $(11\bar{1})$. The Burgers vector of a dislocation must lie in

its slip plane. $\therefore \underline{b}\cdot\underline{n}=0$. Thus the ½[101] dislocation can glide on the $(\bar{1}11)$ and $(11\bar{1})$ planes.

[4.8] The line direction $\underline{u}=[101]\times[1\,\bar{1}\,\bar{1}]=[12\bar{1}]$.

[4.9] Of the most widely spaced {110} planes, ½[111] can glide on $(1\bar{1}0)$, $(10\bar{1})$ and $(01\bar{1})$.

[4.10] (a) $a/2[111]+a/2[1\,\bar{1}\,\bar{1}]\rightarrow a[100]$
(b) $a/6[11\bar{1}]+a/3[112]\rightarrow a/2[110]$
(c) $1/6[\bar{2}023]+1/6[20\bar{2}3]\rightarrow[0001]$

[4.11] (a) $|\underline{b}|=(a/2)\sqrt{1^2+1^2+1^2}=a\sqrt{3}/2$
(b) $|\underline{b}|=(a/6)\sqrt{1^2+1^2+2^2}=a/\sqrt{6}$

[4.12] The magnitudes of the vectors are irrelevant in this question, therefore we can put $\underline{a}=[11\bar{1}]$ and $\underline{b}=[11\bar{2}]$.

$$\cos\theta=\frac{\underline{a}\cdot\underline{b}}{|\underline{a}||\underline{b}|}=\frac{1+1+2}{\sqrt{3}\sqrt{6}}=\frac{4}{\sqrt{18}}\qquad\therefore\theta=61.9^\circ$$

Pole of plane $\underline{n}=\underline{a}\times\underline{b}=\begin{vmatrix}\underline{i}&\underline{j}&\underline{k}\\1&1&\bar{1}\\1&1&\bar{2}\end{vmatrix}=-\underline{i}+\underline{j}$

$\therefore\underline{n}=[\bar{1}10]$

[4.13] (i) Read-Shockley equation for the energy of tilt boundary: $E=E_o\theta(A-\ln\theta)$, where θ = angle of tile, $E_o=\mu b/4\pi(1-\nu)$ and $A=\ln(b/r_o)$ where b = Burgers vector, r_o = core radius.

(ii) $A-\ln\theta\approx1$ when $\ln(b/r_o\theta)\approx1$, or $1.3/\theta\approx2.72$ if $b/r_o=1.3$. Hence, the factor ($A-\ln\theta\approx1$) can be dropped when $\theta\sim$ 0.5 rad or 30º.