Short Sample Solutions to the Sample Exam for
(3rd Year Course 6)
Hilary Term 2011

1. [4]

A *Lattice* is an infinite set of points in space where the environment of any given point is identical to the enivironment of any other point. The lattice points can be written as

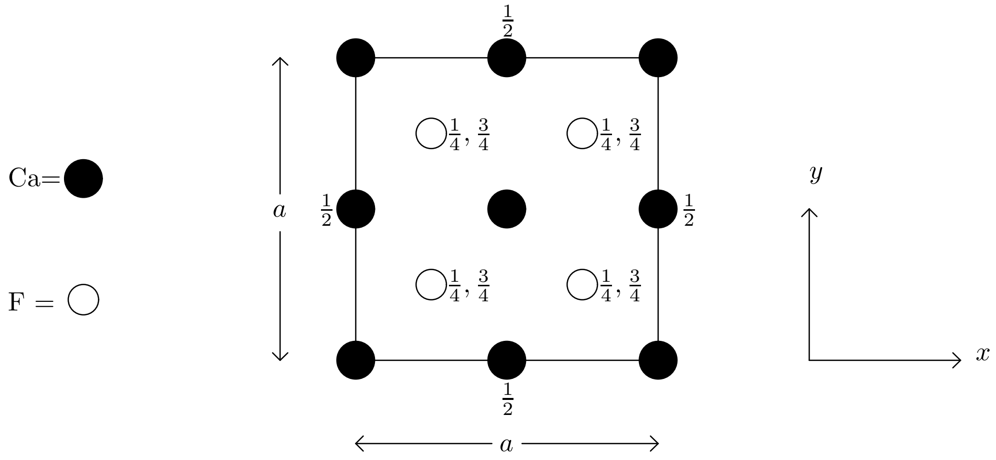
$$\mathbf{R} = n_1\mathbf{a_1} + n_2\mathbf{a_2} + n_3\mathbf{a_3}$$

(here in 3 dimensions) where n_i are integers and $\mathbf{a_i}$ are three linearly independent vectors.

A *basis* is the set of objects (atoms if one is talking about crystal structure) positioned around each lattice point which comprises the unit cell. Note, one can define a basis with respect to a primitive, or conventional unit cell.

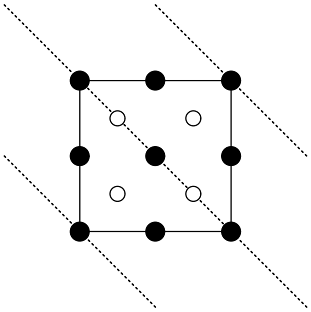
[8]

Plan view of a conventional unit cell of $\mathrm{CaF_2}$:

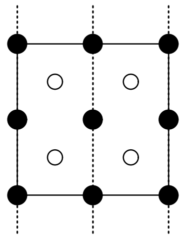


Unlabeled atoms are at $z = 0$ and $z = a$.

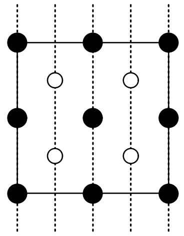
Lattice planes (1 1 0)



Lattice planes (2 0 0)



Lattice planes (4 0 0)



[9]

This is an application of Bragg's law

$$2d_{(hkl)} \sin\theta = \lambda$$

Here $\theta = 21.0$ degrees (the *full* deflection is 42 degrees), and $d_{(200)} = a/2$. Thus we have $a = \lambda/\sin 21^o = .558nm$ the lattice constant for the cubic unit cell.

fcc crystals do not produce a (1 1 0) scattering because of the selection rules (that the three (hkl) indices must be all odd or all even). To see this explicitly we write a basis for the atoms in the FCC unit cell. This basis within the conventional unit cell (ie, with respect to a cubic lattice) is given (in units of the cubic lattice constant) by the four points (x, y, z) given by $\mathbf{R_1} = (0,0,0),\ \mathbf{R_2} = (1/2,1/2,0),\ \mathbf{R_3} = (1/2,0,1/2),\ \mathbf{R_4} = (0,1/2,1/2)$. The structure factor for any incident plane wave with wavevector $\mathbf{k}$ corresponding to miller indices (hkl) will have a factor of

$$S^{fcc}_{(hkl)} = \sum_{d=1}^{4} e^{2\pi i(\mathbf{R_d}\cdot\mathbf{k})} = \sum_d e^{2\pi i(hx_d+ky_d+lz_d)} = 1 + e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}$$

for any fcc structure. As stated above, this sum vanishes unless the three miller indices are all odd or all even. Hence (1 1 0) does not produce a peak.

[4]

Generally the structure factor will be given by

$$S_{(hkl)} = \sum_d f_d\, e^{2\pi i(hx_d+ky_d+lz_d)}$$

where the sum over d is the sum over all atoms in the unit cell, f_d is the form factor for atom of type d and (x_d, y_d, z_d) are the coordinates of atom d in the unit cell.

For Ca, one obtains

$$S^{\text{Ca}}_{(hkl)} = S^{fcc}_{(hkl)} f_{\text{Ca}}$$

For CaF_2 one obtains

$$S^{\text{CaF}_2}_{(hkl)} = S^{fcc}_{(hkl)} \left[f_{\text{Ca}} + 2\cos\left(\frac{\pi}{2}(h+k+l)\right) f_{\text{F}} \right]$$

For X-ray scattering f is positive and roughly proportional to the atomic number Z of the atom ($Z_{\rm F} = 9, Z_{\rm Ca} = 20$, so $f_{\rm Ca}$ is roughly twice as big as $f_{\rm F}$.

For $\mathrm{CaF_2}$ the interference between the Ca and F terms is destructive for (2 0 0) but constructive for (4 0 0). When the interference is destructive, the two terms may very nearly cancel.

The actual observed scattered Xray intensity is proportional to $|S_{hkl}|^2$ times a multiplicity factor (for powder diffraction). This multiplicity factor (8) is the same for (2 0 0) and (4 0 0) and the same for Ca and $\mathrm{CaF_2}$.

Thus

$$\frac{I^{\rm Ca}_{(200)}}{I^{\rm CaF_2}_{(200)}} >> 1 \qquad \text{and} \qquad \frac{I^{\rm Ca}_{(400)}}{I^{\rm CaF_2}_{(400)}} \approx \left(\frac{20}{38}\right)^2$$

(with the last approximation is assuming $f \sim Z$ and assuming that lattice constants of Ca and $\mathrm{CaF_2}$ are similar and assuming that there is no strong dependence of the scattering on wavelength. With the same assumptions one would obtain 100 for the first ratio, although this depends sensitively on the precise values of f and should not be taken too seriously).

2. [6]

A *phonon* is a quantum of vibration in a solid analogous to a photon being a quantum of light. ((begin rant) Using the phrase “quantum of vibrational energy” is discouraged the same way one would not say that a photon is a quantum of light *energy* you just say “a quantum of light”– being that the phonon/photon carries other quantum numbers as well as energy (end rant)).

Phonon dispersion is most easily measured with inelastic neutron scattering. In short, this exploits energy and momentum conservation. A neutron is fired into the crystal with known energy and momentum, it excites a phonon and is measured coming out of the crystal. Assuming a single phonon is excited, the change in neutron energy gives the energy of the phonon and the change in neutron momentum gives the phonon momentum.

[10]

The classical equations of motion for the p^{th} atom are

$$M\ddot{x}_p = F_p = \sum_n C_n(x_{n+p} - x_p)$$

Note, we must have $C_n = C_{-n}$ by Newton’s third law.

Using the usual ansatz $x_p = Ae^{i\omega t - ikpa}$ we obtain

$$-M\omega^2 = \sum_n C_n(e^{-ikna} - 1) = \sum_{n>0} 2C_n(\cos(kna) - 1)$$

Using $1 - \cos(x) = 2\sin^2(x/2)$ we obtain

$$\omega^2 = \frac{4}{M}\sum_{n>0} C_n \sin^2(nka/2)$$

Square-rooting this gives the desired expression. Backing up a step, we write this as

$$\omega^2(k) = \frac{2}{M}\sum_{m>0} C_m(1 - \cos(kma))$$

Now multiplying by $\cos(kna)$ and integrating from $-\pi/a$ to π/a gives

$$\int_{-\pi/a}^{\pi/a} dk\, \omega^2(k)\cos(nka) = \frac{2}{M}\sum_{m>0} C_m \int_{-\pi/a}^{\pi/a} dk(1 - \cos(kma))\cos(nka)$$

Now using the orthogonality of cosines

$$\int_{-\pi/a}^{\pi/a} dk \cos(nka)\cos(mka) = \frac{2\pi}{2a}\delta_{|n|,|m|}$$

we get

$$\int_{-\pi/a}^{\pi/a} dk\, \omega^2(k)\cos(nka) = -\frac{2}{M}\frac{\pi}{a}C_n$$

which gives the desired result.

[4]

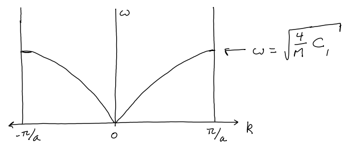
Expand for small kna. We obtain

$$\omega^2 = \frac{4}{M}\sum_{n>0} C_n \sin^2(nka/2) = \frac{1}{M}\sum_{n>0} C_n n^2 k^2 a^2$$

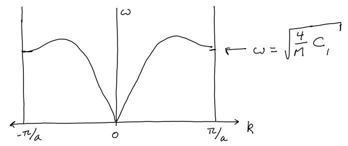
We now use the fact that C_n falls off rapidly with n such that the sum over n converges. We then obtain

$$\omega = k\sqrt{\frac{a^2}{M}\sum_{n>0} C_n n^2}$$

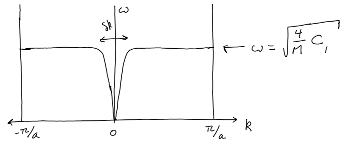
(a)



(b)



(c)



where $\omega = ku$ thus gives the desired result.

$$u = \sqrt{\frac{a^2}{M} \sum_{n>0} C_n n^2}$$

[5]

A sketch of the dispersion curve is given in (a) for $C_1 > 0$ and all other $C_n = 0$. In (b) dispersion curve is shown for $C_1 > 0$ and $C_2 > 0$ with all other $C_n = 0$. In (c) dispersion curve is given where $C_n \sim \exp(-nb)$ where roughly δk is given by $b\pi/a$. (To see this, note that C_n decays at a distance roughly a/b. This form of C_n can also be calculated exactly.). Roughly, inclusion of a nonzero C_n for each n gives an n^{th} fourier mode to the dispersion curve. (Although ω is actually the square root of a fourier series)

3. [6]

The *Fermi Energy* E_F is the chemical potential at zero temperature. Roughly you can think of this as the energy to add the next electron. However, you have to be careful in the case when you have exactly enough electrons to completely fill a band. In this case the chemical potential sits mid-gap at zero temperature. (So more properly it is the average of the energy to add the next electron and the last electron) . The *Fermi Temperature* T_F is just E_F/k_b with k_b Boltzmann's constant.

[13]

The number of electronic states with energy lower than some absolute value of momentum k_0 is given by

$$N(k_0) = 2A \int_{|k|<k_0} \frac{d^2k}{(2\pi)^2} = \frac{2A}{(2\pi)^2}\pi k_0^2.$$

where the prefactor of 2 is from the spin and A is the area (two dimensional volume). With $\epsilon_{k_0} = \hbar^2 k_0^2/(2m)$ we have

$$g = dN/d\epsilon = (dN/dk_0)(dk_0/d\epsilon) = Am/(\pi\hbar^2)$$

which is independent of energy.

$$N = \frac{Am}{\pi\hbar^2}\int_0^\infty dE/(e^{(E-\mu)/k_bT}+1)$$

Using $x = (e^{(E-\mu)/k_bT}+1)$ we have $k_bT\log(x-1)+\mu = E$ so $dE = (k_bT/(x-1))dx$. We then can write

$$N = \frac{Am}{\pi\hbar^2}\int_{e^{-\mu/(k_bT)}+1}^\infty \frac{k_bT}{x-1}dx\frac{1}{x}$$

or

$$\frac{N\pi\hbar^2}{Amk_bT} = \int_{e^{-\mu/(k_bT)}+1}^\infty dx\frac{1}{x(x-1)} = \int_{e^{-\mu/(k_bT)}+1}^\infty dx\left[\frac{1}{x-1}-\frac{1}{x}\right] = \log\left(\frac{x-1}{x}\right)\Big|_{e^{-\mu/(k_bT)}+1}^\infty$$

So

$$\exp\left(\frac{n\pi\hbar^2}{mk_bT}\right) = 1 + e^{\mu/(k_bT)}$$

with $n = N/V$. This quickly simplifies to the desired

$$\mu = k_bT\log\big(\exp(n\pi\hbar^2/mk_bT)-1\big)$$

[6]

Using the result just derived we can take the limit of T becoming small and obtain

$$\lim_{T\to 0}\mu = \frac{n\pi\hbar^2}{m}$$

which defines the fermi energy. Alternately we could use the fact that the density of states is constant. So at $T=0$, we have $N = gE_F = AmE_F/\pi\hbar^2$ which gives the same result.

For a typical three dimensional metal, because the density of electrons is very high, E_F is very large – in the electron volt range, which corresponds to thousands of kelvin – much higher than room temperature. For many purposes room temperature T, being much less than E_F can be approximated as essentially zero. In approximating the Fermi-dirac formula, one does not approximate T as zero, but neglects the dependence of μ on T. In other words, we have

$$\mu = \mu(T=0) + \mathcal{O}(T/E_F)$$

and the correction is neglected (noting that $\mu(T=0)=E_F$). In fact, a more detailed calculation show that the correction to the chemical potential is order $(T/E_F)^2$. To see this we note that the chemical potential at any temperature the first equation given in this problem

$$N=\int_0^\infty dE\frac{g(E)}{e^{(E-\mu)/k_bT}+1}$$

sets the chemical potential. At $T=0$ the fermi factor becomes a step function (and $\mu=E_F$). As the temperature is raised, the step function becomes a smoother step. But close to the fermi energy, the increase of the fermi function above E_F is equal to the decrease below E_F so to linear order in T/E_F there is no change in N for fixed chemical potential, and correspondingly to linear order in T the chemical potential does not change for fixed N.

4. [6]

In simple band theory of electrons (i.e, electrons that do not interact with each other) an insulator occurs when the number of electrons is such that a band is completely filled and there is an energy gap to the next band. Thus there are no low energy excitations of electrons possible and an applied electric field cannot change the velocity of the electrons, hence no current flows and one has an insulator.

[3]

The matrix element between a plane-wave state of momentum k and momentum k' is given by

$$\langle k'|V(x)|k\rangle$$

If the periodic potential is of the form given

$$V(x) = V_0 + V_G\, e^{-iGx} + V_{-G}\, e^{iGx}$$

then the matrix element is nonzero only if $k = k'$ (giving the V_0 term) or

$$k = k' \pm G$$

giving the V_G and V_{-G} terms respectively.

In the nearly free electron model, we are now trying to calculate the energy of a plane wave perturbed by V. Let us try the usual perturbation theory expansion

$$\epsilon_k = \epsilon_k^0 + \langle k|V|k\rangle + \sum_{k' \neq k} \frac{|\langle k'|V|k\rangle|^2}{\epsilon_k^0 - \epsilon_{k'}^0} + \ldots$$

where $\epsilon_k^0 = \hbar^2 k^2/(2m)$.

The leading term $\langle k|V|k\rangle$ gives V_0 independent of k (and is therefore not interesting). The next order term requires that $k' = k \pm G$ (note the sum forbids $k = k'$). However, in order for the term to be significantly large, it must also have a small denominator, i.e., $\epsilon_k \approx \epsilon_{k'}$ which in the 1d model only occurs for $k \approx \pm k'$. The only way this can occur is when k is close to $\pm G/2$ and k' is close to $\mp G/2$. It is thus valid to keep only these two wavevectors in the analysis of the problem as claimed. Note that when k is exactly $\pm G/2$, perturbation theory breaks down because of the divergent denominator and one must resort to *degenerate* perturbation theory. As such, one first solves the problem within the space of states having degenerate energies. This again tells us that we should keep $k = \pm G/2$ to a first approximation.

[10]

We write our Hamiltonian as $H = H_0 + V$ with H_0 being the usual kinetic term and V the potential. We have the ansatz

$$|\psi_k\rangle = A|k\rangle + B|k - G\rangle$$

with the assumption that k is near the zone boundary $G/2$. (Note I have used a different normalization to write a normalized ket rather than just an exponential). We will use

$$H_0|k\rangle = \epsilon_k^0|k\rangle$$

with $\epsilon_k^0 = \hbar^2 k^2/(2m)$ and

$$V|k\rangle = V_0|k\rangle + V_G|k - G\rangle + V_{-G}|k + G\rangle$$

These equations are true for arbitrary k.

We write the schroedinger equation as

$$H|\psi_k\rangle = (H_0 + V)|\psi_k\rangle = \epsilon_k|\psi_k\rangle$$

Using the above equations we then rewrite this as

$$AV_{-G}|k+G\rangle + (A\epsilon_k^0 + BV_{-G} + AV_0)|k\rangle + (B\epsilon_{k-G}^0 + AV_G + BV_0)|k - G\rangle + BV_G|k - 2G\rangle = \epsilon_k\,(A|k\rangle + B|k - G\rangle)$$

At this point, we need to "project" back to our subspace of states which are only those near the zone boundaries $k = \pm G/2$ (i.e, to the space of $|k\rangle$ and $|k-G\rangle$ only). The valid argument for doing this is that given above – that other terms will have energy denominators in perturbation theory and will therefore be much smaller. The mathematical way to do this is to obtain two equations by taking inner products with $\langle k|$ and $\langle k-G|$ to obtain

$$\begin{aligned} (A\epsilon_k^0 + BV_{-G} + AV_0) &= \epsilon_k A \\ (B\epsilon_{k-G}^0 + AV_G + BV_0) &= \epsilon_k B \end{aligned}$$

These can be rewritten as an eigenvalue equation

$$\begin{pmatrix} \epsilon_k^0 + V_0 & V_{-G} \\ V_G & \epsilon_{k-G}^0 + V_0 \end{pmatrix} \begin{pmatrix} A \\ B \end{pmatrix} = \epsilon_k \begin{pmatrix} A \\ B \end{pmatrix}$$

We can calculate the eigenvalue for any k (so long as we keep k close to $G/2$ as we assumed). However, it becomes much easier if we consider only $k = G/2$. We then have $\epsilon_k^0 = \epsilon_{k-G}^0 = \hbar^2 k^2/(2m)$. The eigenvalues of this matrix then simplify to

$$\epsilon_{(k=G/2)} = V_0 + \epsilon_k^0 \pm |V_G|$$

as claimed (where we have used $V_G = (V_{-G})^*$) here.

The first term is the uniform potential that gives just an overall shift of energy (or chemical potential). The second term is the free electron plane wave energy. The final term is the gap that opens up at the zone boundary (full gap is $2|V_G|$) due to the periodic potential. If the number of electrons is such that the band is precisely filled, the size of $|V_G|$ will determine if this is a semiconductor or an insulator. If the band is not precisely filled, we will have a metal (at least in simple band theory approximation).

[6]

Germanium, Silicon, and Diamond all have the same crystal structure with two tetravalent atoms per primitive unit cell – a number which can precisely fill four bands (of two spins each). In the case of diamond, the periodic potential is stronger, so the gap between bands is larger and one obtains an insulator. For Si and Ge, there is still a gap, but it is smaller (hence they are semiconductors). A rough reason why the potential is stronger for carbon is that the Coulomb potential is unscreened by inner atomic shells.