

### Answers to exam paper 2001

3. When an external electric field is applied, charge carriers (the charged, mobile species available in the material) respond by accelerating in an appropriate direction. This is a classical picture, but it is adequate. They accelerate until they collide with something, at which time their velocity is randomised again. As a result of this, the carriers drift through the material, carrying current. By solving Newton's law for acceleration for a period  $2\tau$  between collisions, it is possible to show that the mean velocity induced by an applied field  $E$  is

$$v_D = \frac{qE\tau}{m}$$

for carriers with mass  $m$  and charge  $q$ . The current density due to such carriers is  $j = nqv_D = nq^2E\tau/m$  where  $n$  is the density of carriers.

$E_H$  along the  $z$ -axis appears as a result of current flow in a material along the  $y$ -axis in the presence of a magnetic field  $B$  along the  $x$ -axis.

Use the Lorentz formula for the force on a charged particle in the electric and magnetic fields. This is

$$\mathbf{F} = q(\mathbf{E} + \mathbf{v} \times \mathbf{B})$$

and with the electric and magnetic field in the directions specified, this leads to the following relations

$$F_y = qE_y$$

and

$$F_z = qE_z - qv_D B$$

where  $v_D$  is the drift velocity in the  $y$  direction.  $E_z$  is the Hall field, and the total force in the  $z$  direction is zero, since there is no current in that direction. Hence  $E_H = v_D B$ . The current in the  $y$  direction is driven by the force  $F_y$ , and is due to the drift of carriers with velocity  $v_D$ . The current density  $j$  is  $nqv_D$  so  $v_D = j/(nq)$  and thus  $E_H = (nq)^{-1}jB$ . The Hall coefficient  $R_H$  is therefore equal to  $1/nq$ .

The nearly free electron dispersion relation is a perturbed parabolic function ( $E \propto k^2$ ) with discontinuities at the Brillouin zone (BZ) boundaries  $k = \pm\pi/a$ ,  $k = \pm2\pi/a$  etc. The parabolic function is distorted downwards just below the BZ boundary, and distorted upwards just above it. The gradient of the dispersion relation at the boundaries is zero.

From a sketch of the nearly free electron dispersion relation, it should be clear that  $d^2E/dk^2$  is negative below, and positive above a BZ boundary. Thus the effective mass of electrons just below a BZ boundary (i.e. near the top of a band) is negative, while for electrons just above the boundary (i.e. near the bottom of a band) the effective mass is positive.

The drift velocity  $v_D$  is proportional to the inverse effective mass of the electron, so  $v_D \propto d^2E/dk^2$ . The mean drift velocity for electrons in filled band with  $-\pi/a \leq k \leq \pi/a$  is

$$v_D \propto \int_{-\pi/a}^{\pi/a} \frac{d^2E}{dk^2} dk = \left[ \frac{dE}{dk} \right]_{-\pi/a}^{\pi/a}.$$

Since the gradient of the dispersion relation vanishes at the BZ boundary, the mean drift velocity of electrons in the filled region of  $k$ -space  $-\pi/a \leq k \leq \pi/a$  is zero.

We interpret the Hall coefficients of copper and cadmium in the following way. For copper, the Fermi level is near the bottom of a band: the effective mass is positive, the charge of the carrier is negative, and the density of the carriers is (of course) positive. A negative Hall coefficient ( $= 1/nq$ ) is consistent with this picture.

For cadmium, we conclude that the Fermi level must be near the top of a band. A filled band cannot contribute to the transport of charge since the mean drift velocity is zero. A nearly filled band is like a superposition of a filled band and a set of electron holes, each of which behaves like a particle with positive mass and charge. This is a consequence of the fact that the effective mass of the electrons that are missing is negative. The current is then carried by the positively charged holes, and this is consistent with a positive Hall coefficient.

4. A lattice is a set of points in space with translational symmetry, i.e. each point has an identical environment. A basis is a set of atoms that are arranged around each lattice point to make a structure. A unit cell is a volume of space containing lattice points and associated atoms, that can be repeated to fill space and reproduce the desired structure. The conventional cell may contain any number of lattice points, and has a geometry chosen to reflect the symmetry of the structure. The primitive cell, on the other hand, contains strictly one lattice point, and may have a non-intuitive geometry.

The lattice for the diamond structure is face centred cubic, and the basis is a pair of identical atoms, one at a lattice point, and one displaced by a vector  $(\mathbf{a}+\mathbf{b}+\mathbf{c})/4$  from it, where  $\mathbf{a}$ ,  $\mathbf{b}$  and  $\mathbf{c}$  are the lattice vectors of the conventional fcc unit cell. The coordination number is the number of nearest neighbours possessed by each atom, and is equal to 4.

Diamond is transparent at visible wavelengths while tin is opaque. Both have an even number of valence electrons and this means the Fermi level can lie at the top of a band. This is indeed the case, but the band gap above the Fermi level is very different in the two cases. For diamond, the band gap is wide, and photons with visible wavelengths do not have enough energy to raise electrons from the valence band to the conduction band: these photons pass straight through and the material is transparent. For grey tin, the gap is virtually closed (marks given just for saying it is much narrower, or even closed) and so photons can be absorbed. This accounts for the opacity of grey tin.

In white tin, the bands overlap appreciably in the region of the Fermi level, so that white tin, like magnesium, is a conductor of electricity rather than an insulator. It is called a semi-metal. When driven to do so by an applied electric field, the electrons in the solid are able to adjust their wavevectors, such that there is drift and current flows. In insulators, the fact that no empty states lie immediately above the Fermi level means that drift and current flow is not possible.

Napoleon, had he attended a course on solid state (and one which was well ahead of its time) would have known he had to calculate the free energy of grey and white tin and determine the temperature at which they were equal. The first step would be to calculate the cohesive (potential) energy at  $T = 0$ . This could be done using an assumed interatomic pair potential for tin and by evaluating lattice sums for the two structures. Then the kinetic energy and entropic contribution to the free energy would be calculated by performing a normal modes analysis of the lattice vibrations (for example), and summing the free energies contributed by each mode. Marks will be given for describing the essentials of this procedure. One could make approximations along the way, such as using a Debye density of phonon states, but this does not alter the basic procedure Napoleon should have followed. He might have added a  $p\Delta V$  term

to consider the volume change upon making the transition too, though including this term is not expected in answers.

5. The pressure of the free electron gas is given by  $p = -\partial E/\partial V$  where  $E$  is the total energy of the system. We have  $E = N\bar{E}$  where  $N$  is the number of electrons in the solid, and the mean energy  $\bar{E}$  is given in terms of the Fermi energy in the question. So

$$p = -\frac{3N}{5} \frac{\hbar^2(3\pi^2)^{2/3}}{2m} \frac{\partial n^{2/3}}{\partial V}$$

and inserting  $n = N/V$  we get  $p = 2nE_F/5$ .

The Gibbs free energy is  $G = E - TS + pV$  and so at  $T = 0$  this simplifies to  $G = E + pV$ . Since  $E = 3NE_F/5$  and  $pV = 2NE_F/5$ , the chemical potential  $G/N$  is equal to  $E_F$ .

The electron density is  $1/V_p$  where  $V_p$  is the primitive unit cell volume, and then the calculation of the Fermi energy of silver is straightforward and yields a value of  $8.76 \times 10^{-19}$  J or 5.47 eV.

Adding divalent magnesium atoms increases the electron density by one electron per million primitive unit cell volumes, so the increase  $\Delta n$  in the electron density is  $1/(10^6 V_p)$ . The new Fermi energy is

$$E'_F = \frac{\hbar^2(3\pi^2(n + \Delta n))^{2/3}}{2m}$$

We can expand  $(n + \Delta n)^{2/3} \approx n^{2/3}(1 + 2\Delta n/(3n))$  and so we get

$$E'_F \approx E_F(1 + 2\Delta n/(3n))$$

Since  $\Delta n/n$  is  $10^{-6}$  the increase in chemical potential is just  $2 \times 10^{-6} E_F/3$  which is  $3.65 \times 10^{-6}$  eV. Very small!

Silicon in its intrinsic, undoped state has an electronic chemical potential somewhere close to the middle of the band gap. Upon adding small amount of pentavalent impurity, donor electron states are created just below the edge of the conduction band, which at room temperature are ionised, providing mobile electrons in the conduction band. The chemical potential of the electrons is raised to a value a few  $k_B T$  below the conduction band. This is about 0.5 eV above the chemical potential of the intrinsic material. If trivalent impurities are added, they can accept free electrons from the valence band, at room temperature, creating localised electron states and leaving mobile holes in the valence band. The chemical potential of the electrons falls to a few  $k_B T$  above the valence band edge, again about 0.5 eV below the chemical potential of the undoped material. There is thus a great contrast with respect to the case of the perturbation of the electronic chemical potential in metals through adding impurities.