

## Materials 200B, Winter 2008, Homework 3

Due in class on Tuesday Jan. 29th

Please turn in the two questions in separate answer packages since Alison and Bharat will grade one each.

### QUESTION 1

This question reviews some of what we've covered throughout the quarter so far, and is in the style of a mid-term question. The number in square brackets gives the number of points for each sub-part.

In the first row transition metals, both the  $4s$  and  $3d$  electrons are considered to be valence electrons. The  $4s$  and  $3d$  electrons have similar energies in the atoms, and their corresponding bands overlap in the solids.

- (a) What is the electronic structure of an isolated Ni atom? What is the total number of valence electrons?[1]
- (b) Sketch the radial part of the wavefunctions for  $3d$  and  $4s$  atomic orbitals in a hydrogen atom as a function of distance from the nucleus. Indicate clearly which orbital extends furthest from the nucleus. [1]
- (c) Sketch electronic energy level diagrams for (i) an isolated Ni atom, (ii) a pair of Ni atoms separated by the bonding distance, (iii) three Ni atoms separated by the bonding distance, and (iv) a sample of bulk, solid Ni. You need only show the  $4s$  and  $3d$  valence electrons. (HINT - you should use your result from part (b) to estimate the strength of the interaction between neighboring  $4s$  electrons, and neighboring  $3d$  electrons. It's safe to assume that the wavefunctions in a Ni atom are not too different from those in a hydrogen atom). [3]
- (d) Using your sketches, explain why bulk, solid Ni is a good conductor of electricity. [1]
- (e) The room temperature resistivity of Ni is  $6.84 \times 10^{-8} \Omega m$ . Taking the electron mobility to be  $0.00185 \text{ m}^2/\text{Vs}$ , calculate the number of electrons per cubic meter that contribute to the conductivity. [1]
- (f) The density of Ni is  $8.90 \text{ g/cm}^3$ , the atomic mass of Ni is  $58.69 \text{ g/mole}$  (and there are Avagadro's number of Ni atoms in a mole of Ni). How many Ni atoms are there in a cubic meter? [1]

- (g) Using your answers to parts (e) and (f), calculate the number of electrons per atom of nickel that contribute to the conductivity. Explain why this number is not an integer, given that only the  $s$  electrons are delocalized enough from the parent atoms to be able to contribute to the conductivity. Also, based on your result, work out how many  $d$ -electrons there must be per atom in metallic Ni. [2]
- (h) In *magnetic* metals, the  $d$ -electron band splits into a lower energy band which is occupied by the up-spin electrons, and a higher energy band for the down-spin electrons. The magnitude of the magnetic moment is determined by the difference between the numbers of up- and down-spin  $d$  electrons. In Ni, all 5 of the up-spin  $d$  bands are filled (i.e. there are 5 up-spin electrons per Ni atom). How many down-spin  $d$  bands are filled? What do you expect the magnitude of the magnetic moment to be in Ni (in units of electronic magnetic moments per atom)? [2]

## QUESTION 2

- (a) In class we showed that the lowest energy orbital in a chain of  $1s$  orbitals was at  $k = 0$ , and that the highest orbital was at  $k = \pm\frac{\pi}{a}$ . Proof that all orbitals in a periodic solid can be described by a  $k$  value that lies within a range of size  $\frac{2\pi}{a}$  (e.g. from  $0$  to  $\frac{2\pi}{a}$ , or from  $-\frac{\pi}{a}$  to  $+\frac{\pi}{a}$ ). The easiest way to do this is to show that the coefficients,  $c_k = e^{ikna}$  are the same for  $k$  and  $k + \frac{2\pi}{a}$ .
- (b) Work out the band structure (that is the energy versus  $k$  diagram) for a linear chain of  $1s$  orbitals spaced a distance  $a$  apart, but this time make the unit cell be of size  $2a$ , containing 2 atoms. (I realize that this is a bit silly, because this system is physically the same as the example we did in class where we considered only one atom per unit cell but you'll find that it's instructive!) This time your unit cell will contribute two bands, one from the intra-unit cell bonding combination, and one from the intra-unit cell antibonding combination. And your range of  $k$  values will be from  $-\frac{\pi}{2a}$  to  $+\frac{\pi}{2a}$ . You'll need to work out how the intra-unit cell bonding and anti-bonding combinations change their energy as a function of  $k$ .

Compare your resulting picture to the standard result (with only one atom per unit cell) that we obtained in class, particularly in light of part (a) of this question.

How would your picture change if the two atoms within the unit cell were different from each other?

- (c) Sketch the band structure for a 2-dimensional square lattice of  $s$  orbitals, along the following directions in  $k$ -space:

$$\begin{aligned}(k_x, k_y) &= (0, 0) \text{ to } \left(\frac{\pi}{a}, 0\right) \\(k_x, k_y) &= \left(\frac{\pi}{a}, 0\right) \text{ to } \left(\frac{\pi}{a}, \frac{\pi}{a}\right) \\(k_x, k_y) &= \left(\frac{\pi}{a}, \frac{\pi}{a}\right) \text{ to } (0, 0)\end{aligned}$$

These are the so-called *high symmetry lines* in  $k$ -space.