

Answer to the Questions 2019-2020

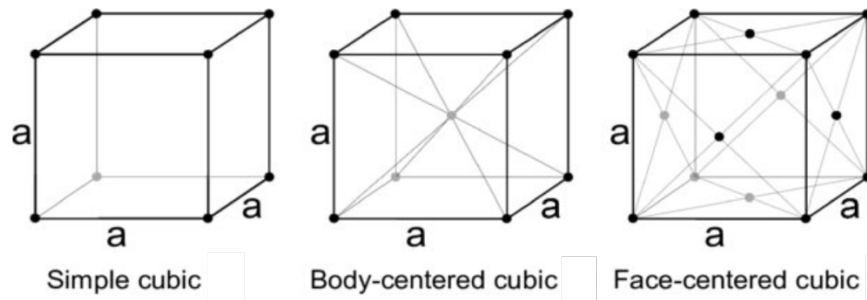
Wednesday, 22<sup>nd</sup> of January 2020, 8:30-11:30 AM

-----The Start of Questions-----


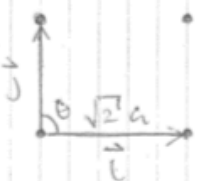
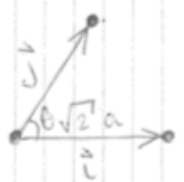
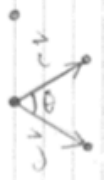
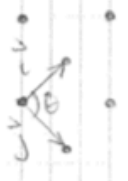
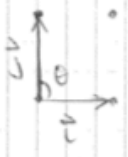
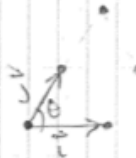
Question 1: Crystal structure (25+3 points)

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A. Cubic Lattice systems has three structures shown below



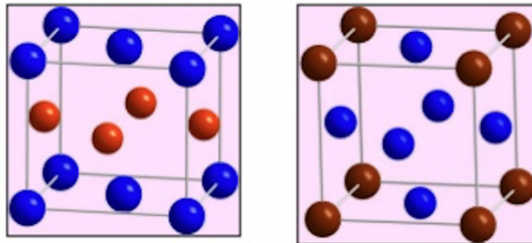
- 1) (9p) Two-dimensional (2D) Bravais lattices can be generated by cutting lattice planes of a 3D Bravais lattice. Determine the 2D Bravais lattices for the (100) (110) and (111) planes of simple cubic, body-centered cubic, and face-centered cubic crystals. Determine the lengths of  $i$ ,  $j$  in the unit of  $a$ , and the angle  $\theta$  between  $i$  and  $j$ .


- 1) SC (100) Square   $\vec{i} = a\hat{x}$   $|\vec{i}| = |\vec{j}| = a$   
 $\vec{j} = a\hat{y}$   $\theta = 90^\circ$
- SC (110) Rectangular   $\vec{i} = \sqrt{2}a\hat{x}$   $|\vec{i}| = \sqrt{2}|\vec{j}| = \sqrt{2}a$   
 $\vec{j} = a\hat{y}$   $\theta = 90^\circ$
- SC (111) Hexagonal   $\vec{i} = \sqrt{2}a\hat{x}$   $|\vec{i}| = |\vec{j}| = \sqrt{2}a$   
 $\vec{j} = \frac{1}{\sqrt{2}}a\hat{x} + \sqrt{\frac{3}{2}}a\hat{y}$   $\theta = 60^\circ$
- BCC (100) is same as SC (100)
- BCC (110) Oblique   $\vec{i} = \frac{1}{\sqrt{2}}a\hat{x} + \frac{1}{2}a\hat{y}$   $|\vec{i}| = |\vec{j}| = \frac{\sqrt{3}}{2}a$   
 $\vec{j} = \frac{1}{\sqrt{2}}a\hat{x} - \frac{1}{2}a\hat{y}$   $\theta \approx 70.53$
- BCC (111) is same as SC (111)
- FCC (100) Square   $\vec{i} = \frac{1}{2}a\hat{x} + \frac{1}{2}a\hat{y}$   $|\vec{i}| = |\vec{j}| = \frac{1}{\sqrt{2}}a$   
 $\vec{j} = \frac{1}{2}a\hat{x} - \frac{1}{2}a\hat{y}$   $\theta = 90^\circ$
- FCC (110) Rectangular   $\vec{i} = \frac{1}{\sqrt{2}}a\hat{x}$   $\sqrt{2}|\vec{i}| = |\vec{j}| = a$   
 $\vec{j} = a\hat{y}$   $\theta = 90^\circ$
- FCC (111) Hexagonal   $\vec{i} = \frac{1}{\sqrt{2}}a\hat{x}$   $|\vec{i}| = |\vec{j}| = \frac{1}{\sqrt{2}}a$   
 $\vec{j} = \frac{1}{\sqrt{8}}a\hat{x} + \sqrt{\frac{3}{8}}a\hat{y}$   $\theta = 60^\circ$

also possible

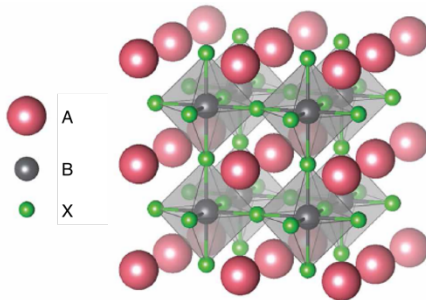
Other combinations  Students, please don't waste your time redrawing the cubes. Just write the answers.

- 2) (6p) Changing the stoichiometry of intermetallic alloy,  $A_xB_y$ , can form different crystal phases. For example, change the ratio of Au (blue ball)/Cu (brown ball) can form the two crystal structures shown below. Identify which one is the AB and which one is the  $AB_3$  phase, Determine the Bravais lattice and number of basis atoms for these two crystals (hint: the atoms in the primitive cell should reflect the stoichiometry).



2) One could take the cubes, so then both are SC   
 $\vec{a}_1 = a\hat{x}$ ,  $\vec{a}_2 = a\hat{y}$ ,  $\vec{a}_3 = a\hat{z}$   
 Left:  $8 \times \frac{1}{8} + 4 \times \frac{1}{2} = 2 \text{ Au}$  &  $4 \times \frac{1}{2} = 2 \text{ Cu} \Rightarrow AB$   
 Right:  $8 \times \frac{1}{8} = 1 \text{ Au}$  &  $6 \times \frac{1}{2} = 3 \text{ Cu} \Rightarrow AB_3$

A perovskite:  $ABX_3$  has a general crystal structure as shown below, where A, B, and X are labeled for different atoms or molecules.



- 3) (4p) Use the idea of repeating environment (say you choose the environment of atom A as the environment to be repeated), identify the Bravais lattice and number and kind of atoms (as A, B, or X) in the basis.

4)

The structure of the perovskite is simple cubic containing 1A, 1B, and 3X atoms at the location of A (0, 0, 0), B (1/2, 1/2, 1/2), and X1 (1/2, 0, 1/2), X2 (0, 1/2, 1/2), and X3 (1/2, 1/2, 0).

- 5) (2p) Calculate the volume of the primitive cell in terms of  $a$  between neighboring X atoms.

$$V = 2\sqrt{2}a^3$$

- 6) (4p) Setup a coordinate system, and calculate the phase factor after summing up  $f_i e^{i\phi_i}$  from the  $i^{\text{th}}$  atom in the basis and determine the scattering intensity by using  $f_A, f_B,$  and  $f_X$ .

A at  $(0,0,0)$   
 B at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$   
 X at  $(\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, 0, \frac{1}{2}), (0, \frac{1}{2}, \frac{1}{2})$

$$S = f_A + f_B e^{i\pi(h+k+l)} + f_X (e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)})$$

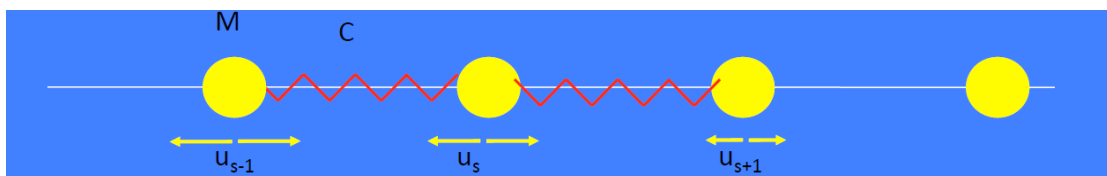
\* all even:  $S = f_A + f_B + 3f_X$   
 \* all odd:  $S = f_A - f_B + 3f_X$   
 \* 1 even 2 odd:  $S = f_A + f_B - f_X$   
 \* 2 even 1 odd:  $S = f_A - f_B - f_X$

$I \propto |S|^2$

- 7) (3p bonus) Some  $ABX_3$  compounds are composed of atoms with very different scattering atomic form factors. For example,  $\text{CH}_3\text{NH}_3\text{PbI}_3$  is a highly efficient candidate for solar cells, where the  $(\text{CH}_3\text{NH}_3)^+$  ion replaces the A atom in the  $ABX_3$  structure. If the scattering from light atoms can be ignored, re-analyze the problem above for this solar cell material. (electronic configurations are H:  $1s^1$ , C:  $2s^2 2p^2$ , N:  $2s^2 2p^3$ , Pb:  $6s^2 6p^2$ , I:  $5s^2 5p^5$ )  
Same as question 5 but omit the contribution from A

**Question 2: Phonons and thermal properties (25+3 points).**

As shown below, consider a linear chain of  $N$  atoms all with mass  $M$ , and force constant  $C$ .



- 1) **(6p)** Calculate and sketch the dispersion relation in the first Brillouin zone for the chain above.

The equation of motion is  $M \frac{d^2 u_s}{dt^2} = C(u_{s+1} + u_{s-1} - 2u_s)$ , which comes from harmonic approx. of an interaction potential. Use solutions of the plane wave form  $u_s = u e^{-i\omega t} e^{isKa}$ , that results in the dispersion relation  $\omega^2 = \frac{2C}{M}(1 - \cos Ka)$ .

- 2) **(6p)** From the dispersion relation, show that the density of modes  $D(\omega) = \frac{2N}{\pi} \frac{1}{\sqrt{\omega_m^2 - \omega^2}}$ , where  $\omega_m$  is the maximum frequency ( $\sin^2 x + \cos^2 x = 1$ ).

The maximum frequency is  $\omega_m^2 = \frac{4C}{M}$ . The number of states in the given interval  $d\omega$  is  $D(\omega)d\omega = 2D(K)dK = \frac{L}{\pi} dK$ , that gives the density of states  $D(\omega) = \frac{L}{\pi} \frac{2}{a} \frac{1}{\omega |\cos \frac{Ka}{2}|} = \frac{2N}{\pi} \frac{1}{\sqrt{\omega_m^2 - \omega^2}}$

- 3) **(6p)** Suppose the optical branch has the form of  $\omega(K) = \omega_0 - AK^2$  near  $K = 0$ , where  $\omega_0$  is a constant. In three-dimension case, show that  $D(\omega) = \left(\frac{L}{2\pi}\right)^3 \frac{2\pi}{A^{\frac{3}{2}}} \sqrt{\omega_0 - \omega}$  for  $\omega < \omega_0$ , and  $D(\omega) = 0$ , for all  $\omega > \omega_0$ .

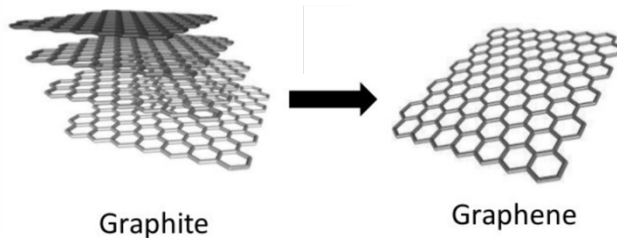
The number of states in 3D in the given interval  $d\omega$  is  $D(\omega)d\omega = D(K)d^3K = \left(\frac{L}{2\pi}\right)^3 d^3K = \left(\frac{L}{2\pi}\right)^3 4\pi k^2 dk$ , where  $k$  is  $|K|$  (absolute value of vector  $K$ ). Required result can be obtained in the same way as for 2)  $D(\omega) = D(k) \left| \frac{d\omega}{dk} \right|^{-1}$ .

- 4) **(3p)** Sketch the dispersion relation in the first Brillouin zone if either the force constant or the mass of atoms changes so that the mono-atomic chain becomes a di-atomic chain. How will the  $\omega(k)$  relationship evolve?

Lattice periodicity is doubled for di-atomic chain in comparison with mono-atomic one, which leads to halving of Brillouin zone (B.Z). Acoustic mode will remain gapless. Optical branch will appear with gap at B.Z. center,

because of anti-phase ionic oscillations. Energy region with no wave-like solutions on B.Z. edges will appear.

- 5) **(4p)** If the number of atoms in the basis increases from 2 to  $n = 3, 4, \dots$ , describe the change to the BZ and how many vibration modes and optical modes can you have if we consider both longitudinal and transverse modes?  
 Kittel p.96:  $N$  unit cells with  $n$  atoms in the primitive cell (all in all  $N \cdot n$  atoms). There are 3 acoustical branches and  $3n-3$  optical branches.
- 6) **(3p bonus)** Consider a simplified model of graphite, which is composed of graphene layers as shown below. The motion of the atoms is restricted to the plane of the carbon layer. Show that the phonon heat capacity in the Debye approximation in the low-temperature limit is proportional to  $T^2$ .



$$E \sim \int_0^{\omega_D} \frac{\hbar\omega}{e^{\frac{\hbar\omega}{k_B T}} - 1} \omega d\omega \sim T^3 \int_0^{x_D} \frac{x^2}{e^x - 1} dx, \text{ where } x_D = \frac{T_D}{T} = \frac{\hbar\omega_D}{k_B T}, \text{ and } x_D \rightarrow \infty \text{ in the}$$

limit of the small temperatures. Therefore the remaining integral could be taken as a constant (could only give exponentially small temperature dependence). Hence the phonon heat capacity is  $C = \frac{dE}{dT} \sim T^2$  at  $T \ll T_D$ .

**Question 3: Free electrons in Copper and its alloys (25+2 points)**

Copper is a typical metal with  $3d^{10}4s^1$  configuration. The Fermi energy of electrons in FCC copper single crystal is 7.0 eV at room temperature. From Hall effect measurements, the electron drift mobility in copper is  $33 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ .

- 1) **(5p)** What is the speed  $v_F$  of conduction electrons with energies around  $E_F$  in copper? By how many times is this larger than the average thermal speed  $v_{th}$  of electrons, if free electrons behave like an ideal gas? (Maxwell-Boltzmann statistics and  $E = 3k_B T/2$ )

The Fermi speed can be obtained from the  $E_F = \frac{1}{2} m_e v_F^2$ , therefore

$$v_F = \sqrt{2 \frac{E_F}{m_e}} = 1.57 \times 10^6 \text{ m/s.}$$

Maxwell - Boltzmann statistics predicts an effective velocity (RMS velocity) which is called “thermal velocity” given by (assume room temperature  $T = 20^\circ\text{C} = 293\text{ K}$ ):

$$\frac{1}{2}m_e v_{thm}^2 = \frac{3}{2}k_B T, v_{thermal} = 1.15 \times 10^5 \text{ m/s, the ratio } \frac{v_F}{v_{thm}} \text{ is more than 10}$$

- 2) **(2p)** Why is  $v_F$  much larger than  $v_{th}$ ?

The difference is the Maxwell-Boltzmann statistics and Fermi-Dirac statistics, which electron should follow due to the Pauli exclusion principle.

- 3) **(3p)** What is the De Broglie wavelength of these electrons? ( $p = \hbar k$  and  $\lambda = 2\pi/k$ )

The De Broglie wavelength is  $\lambda = h/p$  where  $p = m_e v_F$  is the momentum of the electrons.  $\lambda = \frac{h}{m_e v_F} = 4.63 \text{ \AA}$ .

- 4) **(4p)** Will the electrons get diffracted by the lattice planes in copper, given that interplanar separation in Cu =  $2.09 \text{ \AA}$  (try the Bragg’s law here for electrons)?

The inter-planar separation,  $d = 2.09 \text{ \AA}$ . The diffraction Bragg condition is:  $\lambda = 2d\sin\theta$ . Since  $\sin\theta = 1.11 > 1$ , therefore, the electron won’t be diffracted.

- 5) **(3p)** Discuss the main similarities and differences between Drude’s and Sommerfeld’s models for the free electrons. What was added in the latter model for the calculation of specific heat of free electron?

Both of them are gas model, the electrons experiences elastic scattering with time constant  $\tau$ . The Sommerfeld model introduced the FD statistics, therefore correctly counted the energy of each state occupied by individual electron, hence, give rise to the correct specific heat.

- 6) **(4p)** In the electromagnetic field, the force on a charged particle is  $F = q(\mathbf{E} + \mathbf{V} \times \mathbf{B})$ . Calculate and sketch the change of momentum of the electrons due to the electric field  $\mathbf{E}$  for the 3D free electrons in a metal.

The applied electric field  $\mathbf{E}$  cause the shift of center of the Fermi sphere in the  $k$ -space since  $\Delta\mathbf{k} = -\frac{e\mathbf{E}\tau}{k_F}$ , where the  $\tau$  is the scattering constant.

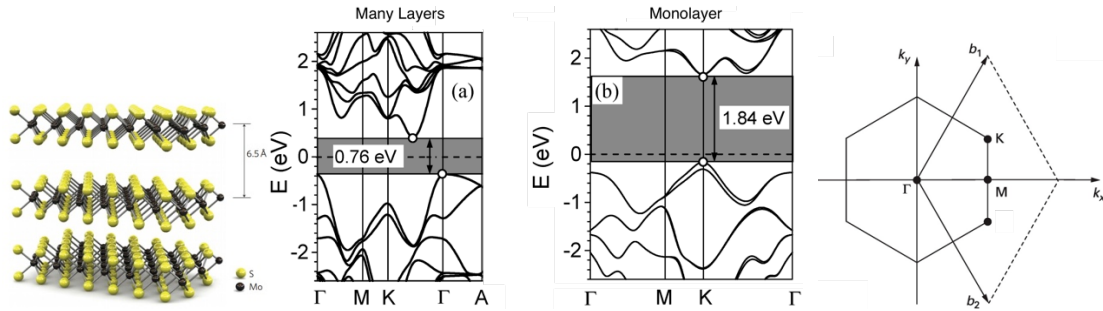
- 7) **(2p bonus)** What will happen to the Fermi sphere above if both  $\mathbf{E}$  and  $\mathbf{B}$  fields are applied.

For the both  $\mathbf{E}$  and  $\mathbf{B}$  field, the  $\mathbf{E}$  field cause the shift of Fermi sphere, and  $\mathbf{B}$

field cause the rotation of  $k_F$  on the surface of Fermi sphere.

- 8) (4p) If FCC lattice constant  $a = 3.597 \text{ \AA}$ , suppose you can make a 2D metal film by cutting a lattice plane of a copper single crystal for the (001) plane, calculate and draw the Fermi surface of your mono-atomic thick Cu film.

**Question 4: Semiconductor, magnetism, and superconductivity (25+2 points)**



Like graphene in question 2(6), a 2D semiconductor can be isolated from a material called  $\text{MoS}_2$  (shown above). The band structure of the system evolves with the number of layers. As shown above, the monolayer  $\text{MoS}_2$  is a 2D system with a hexagonal first Brillouin zone (BZ).

- 1) (6p) From the band structures above for the many-layer and monolayer  $\text{MoS}_2$ , find the location (at which point or between which points of the BZ) of conduction and valence band edge in the first BZ. Identify the size and characteristic of the band gap (direct or indirect) for these two systems.

For the multilayer case, the bottom of CB is between  $\Gamma$  and K point, and the top of VB is at  $\Gamma$  point, gap size is 0.76 eV. Therefore, it is an indirect band gap semiconductor. For the monolayer case, both the bottom of CB is at top of VB are at the K points, it has a 1.84 eV direct band gap.

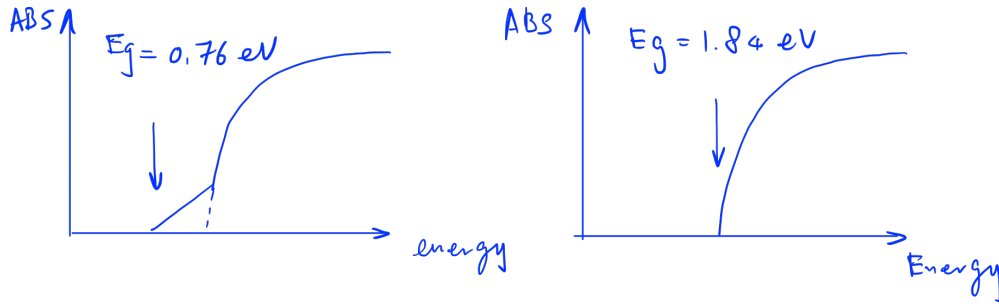
- 2) (5p) Discuss the energy and momentum conservation in the optical absorption of monolayer and many-layer  $\text{MoS}_2$ . Sketch the optical absorption of  $\text{MoS}_2$  near the band edge as the function of the energy of the incident photons for both many-layer and monolayer cases.

For both processes,  $E_i = E_f$  for all the particles involved.

For the direct band gap: (initial state)  $k_{\text{photon}} = (\text{final state}) k_{\text{ele}} + k_{\text{hole}} = 0$

For the indirect band gap: (initial state)  $k_{\text{photon}} = (\text{final state}) k_{\text{ele}} + k_{\text{hole}} + K_{\text{phonon}} = 0$





- 3) **(4p)** From the Newtonian law,  $F = ma = -dU/dx$ , Express the effective mass from the dispersion relationship  $E(k)$ .

From the newton's second law, the mass can be calculated from the  $E(k)$  relationship:  $a = \frac{1}{m}F$ . Since the  $\mathbf{a} = \frac{d}{dt} \mathbf{v}_g$ , where the  $\mathbf{v}_g$  is the group velocity of electrons

$$\mathbf{a} = \frac{d}{dt} (\nabla_{\mathbf{k}} \omega(\mathbf{k})) = \nabla_{\mathbf{k}} \frac{d\omega(\mathbf{k})}{dt} = \nabla_{\mathbf{k}} \left( \frac{d\mathbf{k}}{dt} \cdot \nabla_{\mathbf{k}} \omega(\mathbf{k}) \right),$$

The force gives a rate of change in crystal momentum  $\mathbf{p}$  of the crystal:

$$\mathbf{F} = \frac{d\mathbf{p}_{\text{crystal}}}{dt} = \hbar \frac{d\mathbf{k}}{dt},$$

where  $\hbar = h/2\pi$  is the reduced Planck constant. Combining these two equations yields

$$\mathbf{a} = \nabla_{\mathbf{k}} \left( \frac{\mathbf{F}}{\hbar} \cdot \nabla_{\mathbf{k}} \omega(\mathbf{k}) \right).$$

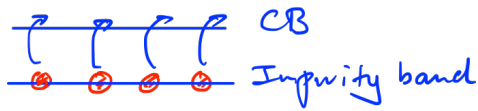
Extracting the  $i^{\text{th}}$  element from both sides gives

$$a_i = \left( \frac{1}{\hbar} \frac{\partial^2 \omega(\mathbf{k})}{\partial k_i \partial k_j} \right) F_j = \left( \frac{1}{\hbar^2} \frac{\partial^2 E(\mathbf{k})}{\partial k_i \partial k_j} \right) F_j,$$

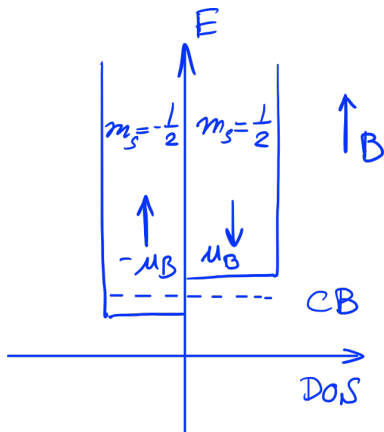
$$\left[ M_{\text{inert}}^{-1} \right]_{ij} = \frac{1}{\hbar^2} \frac{\partial^2 E}{\partial k_i \partial k_j}.$$

- 4) **(6p)** Free electrons can be induced in MoS<sub>2</sub> either by impurity doping or field-effect gating. Sketch the band diagram of having free electron in the conduction band by impurity doping. Sketch the change to the density of states when free electrons a monolayer MoS<sub>2</sub> is subjected to a magnetic field  $\mathbf{B}$ ? Mark the spin quantum number  $S_z$  and magnetic moment on the density of states (hint: monolayer MoS<sub>2</sub> is a 2D system).

Free electron doping to the CB from the impurity band.

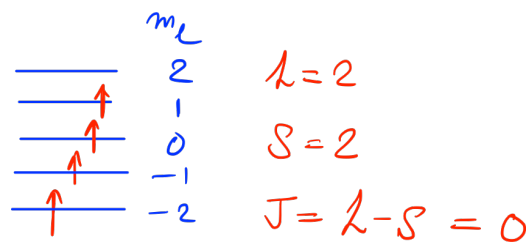


Free electron doped from the impurity band can respond to the  $\mathbf{B}$  field. Due to the 2D nature of MoS<sub>2</sub>, we have the 2D density of states.

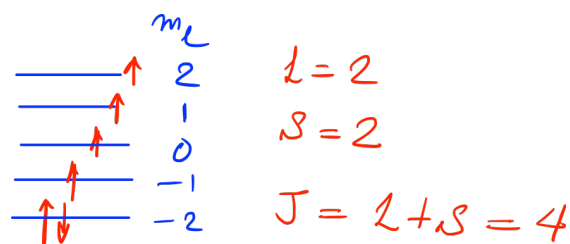


- 5) (4p) Consider MoS<sub>2</sub> as a nonmagnetic matrix, magnetic ions can be doped to induce ordered magnetism in the system. If we choose Cr<sup>2+</sup> (4 electrons in the  $d$  shell), and Fe<sup>2+</sup> (6 electrons in the  $d$  shell) ions as the dopant to MoS<sub>2</sub>. Determine the magnetic configuration  $^{2S+1}L_J$  for these ions using Hund's rule.

<sup>5</sup>D<sub>0</sub>



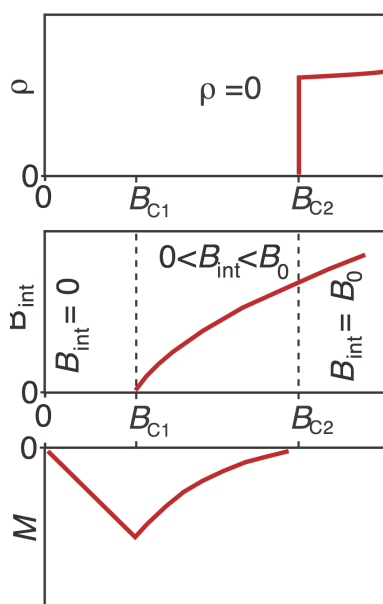
<sup>5</sup>D<sub>4</sub>



- 6) **(2p bonus)** If we dope MoS<sub>2</sub> with a sufficient amount of carriers by field-effect gating, the free electrons eventually turns superconducting. What are the two hallmark physical properties that differentiate a superconductor from any other conductor? If the magnetic lines can pass the monolayer at defects, sketch the magnetization  $M$ , and internal field  $B$  of a monolayer MoS<sub>2</sub> as a function of external field  $\mu_0 H$  applied perpendicular to the plane of MoS<sub>2</sub>.

Zero resistance and zero magnetic field inside a superconductor, namely,  $T < T_c$ ,  
 $R = 0, B = 0$ .

The penetration of the B field can be characterized as follows:



-----The End of Questions-----