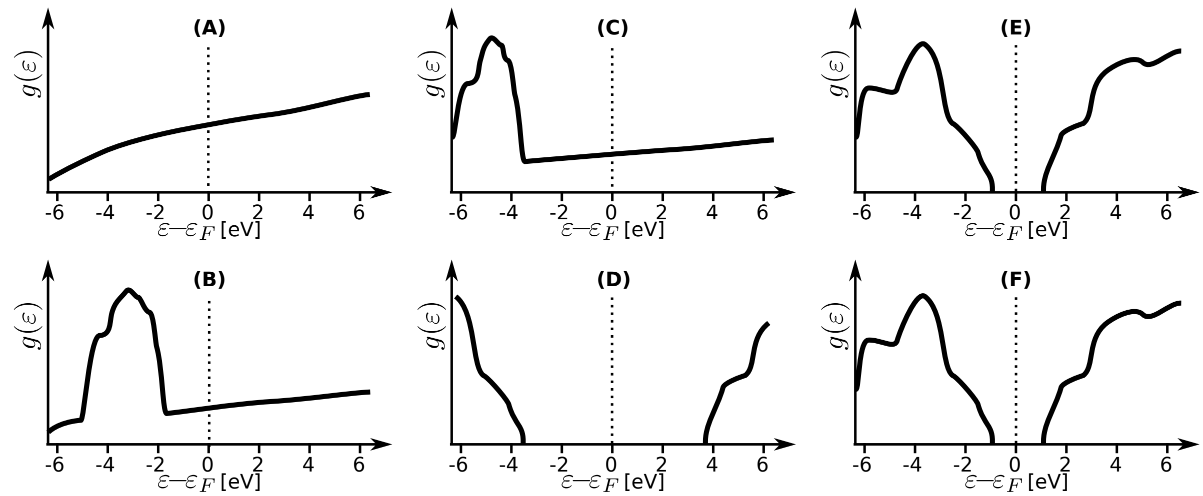
HW10 solution

MTLE-6120: Spring 2023

Due: April 7, 2023

1. **Optical property comparison**

   The density of states of six single-crystalline materials are sketched below. (Note that (E) and (F) are intentionally visually indistinguishable.)



   (a) Identify each material as metallic, semiconducting or insulating.

   (A-C) are clearly metallic, while the rest exhibit a band gap. The band gap is ~ 2 eV for (E-F), and must be semiconductors. The band gap of (D) exceeds 7 eV making it an insulator.

   Note that there is no sharp cut-off in band gap between semiconductors and insulators, with the distinction coming down to whether the material can be effectively doped, depending on the applications. However, 2 and 7 eV are sufficiently far from the border ($\sim 3 - 4$ eV) to make the present cases clear cut.

   (b) Describe the visual appearance of crystals of each material.

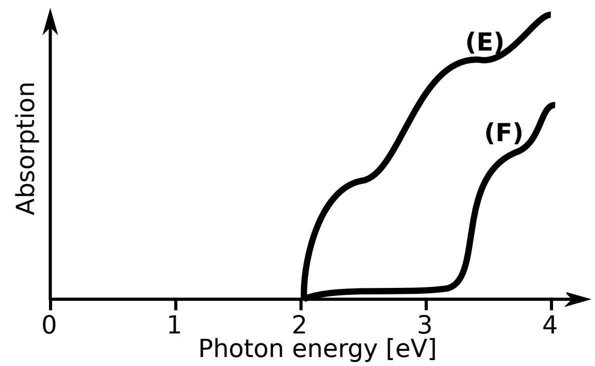
   (A) will be a typical silvery metal. (B) exhibits d-band-like DOS ~ 2 eV below the Fermi level, which makes interband absorption likely at 2 eV. This will lead to stronger absorption of blue light, leading to a yellow or reddish tint like gold or copper. The similar DOS feature in (C) is around 4 eV deep, making the absorption pick up only in the UV, retaining a silvery appearance. (This DOS is qualitatively similar to Ag, in fact.)

   (D) is a high band-gap insulator that cannot absorb visible light, and in the absence of significant defects, must be transparent. (E-F) have a 2 eV gap close to the lower end of the visible spectrum of energy, making them likely to absorb blue light stronger than red light, and likely giving them a reddish hue (in both transmission and reflection).

   (c) What experiment would you perform to distinguish (A) and (C), and why? (Mention the results expected for each.)

   (A) and (C) are both expected to be silvery metals as discussed above because the interband absorption in (C) begins in the UV. Consequently, any spectroscopic technique extending into the UV, *e.g.* UVvis or ellipsometry, should pick up a sudden increase in absorption around 4 eV for (C).

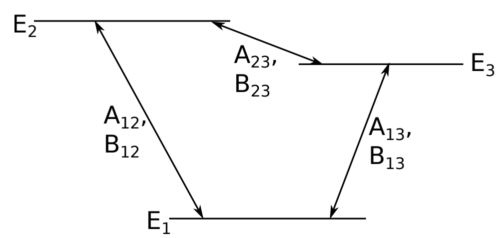
(d) Despite nearly identical density of states, the absorption spectra of (E) and (F) happen to differ as shown below. Explain how this is possible, and what impact will it have on the appearance of these materials.



The immediate increase in absorption from the band gap indicates a direct band gap in (E). The absorption picks up strongly more than an eV above the band gap in (F), indicating an indirect band gap with an interband threshold just above 3 eV. The lower absorption in the visible spectrum ($\sim 1.8 - 3.1$ eV) in (F) will make it closer to transparent, compared to the reddish hue due to blue absorption for (E) discussed above.

2. **Optical pumping and fluorescence**

Consider the minimal three-level system necessary for fluorescence (and lasing) as shown below. A pump light of intensity I_{pump} is tuned to a frequency matching $E_2 - E_1$, and assume the intensities at other frequencies are small enough that stimulated emission is negligible for the other transitions. Assume A and B coefficients for each pair of states as shown.



(a) Write the differential equations governing the kinetics of N_1, N_2 and N_3: the populations (electrons / volume) for the three states.

For each pair of states, there is a rate $AN_{\text{upper}} + BIN_{\text{upper}}$ going from the upper to lower state due to spontaneous and stimulated emission, and a rate BIN_{lower} going form the lower to the upper state due to absorption. This results in

$$\dot{N}_1 = [A_{12}N_2 + B_{12}I_{\text{pump}}(N_2 - N_1)] + A_{13}N_3$$
$$\dot{N}_2 = -[A_{12}N_2 + B_{12}I_{\text{pump}}(N_2 - N_1)] - A_{23}N_2$$
$$\dot{N}_3 = A_{23}N_2 - A_{13}N_3$$

(b) In steady state, find the ratio N_3/N_1 in order to determine the condition for population inversion ($N_3 > N_1$). Find and interpret the $I_{\text{pump}} \to \infty$ limit of this criterion.

In steady state, $\dot{N}_1 = \dot{N}_2 = \dot{N}_3 = 0$, so that

$$0 = [A_{12}N_2 + B_{12}I_{\text{pump}}(N_2 - N_1)] + A_{13}N_3$$
$$0 = -[A_{12}N_2 + B_{12}I_{\text{pump}}(N_2 - N_1)] - A_{23}N_2$$

$$0 = A_{23}N_2 - A_{13}N_3$$

Since we want to compare N_3 and N_1, use the last equation to replace N_2 in favor of N_3 in the second equation (same result if done in first equation). This gives the population inversion criterion:

$$\frac{N_3}{N_1} = \frac{B_{12}I_{\text{pump}}}{A_{13}\left(1 + \frac{A_{12}+B_{12}I_{\text{pump}}}{A_{23}}\right)} > 1$$

In the limit of $I_{\text{pump}} \to \infty$:

$$\frac{N_3}{N_1} = \frac{A_{23}}{A_{13}} > 1$$

which simply means that the spontaneous emission rate from $3 \to 1$ must be slower than that from $2 \to 3$ (which feeds state 3). Therefore, having a forbidden transition (selection rule) is useful to slow down $3 \to 1$.

(c) What is the net power density (rate of energy change per unit volume) absorbed from the pump light into the electrons? Assume that stimulated emission puts energy back into I_{pump} (best case scenario for efficiency), while the energy from spontaneous emission is lost. Just write the answer in terms of instantaneous N_1, N_2, N_3 (don't solve for the Ns).

The net rate per unit volume at which photons are being taken from the pump (absorption - stimulated emission) is $B_{12}I_{\text{pump}}(N_1 - N_2)$. These photons have energy $(E_2 - E_1)$, so the net absorbed power density is $B_{12}I_{\text{pump}}(N_1 - N_2)(E_2 - E_1)$.

(d) Similarly, what is the power density output from the $3 \to 1$ transition (fluorescence)? Again, just express in terms of N_1, N_2, N_3 as needed.

The rate of the fluorescence transition is $A_{13}N_3$ and the photon energy is $E_3 - E_1$, so that the power density emitted is $A_{13}N_3(E_3 - E_1)$.

(e) What is the energy efficiency of the fluorescence process in steady state, and how does it depend on I_{pump}? (This time, solve for the Ns in terms of the A, B parameters and interpret!)

The energy efficiency is the power density emitted / power density absorbed

$$\begin{aligned}
\text{Efficiency} &= \frac{A_{13}N_3(E_3 - E_1)}{B_{12}I_{\text{pump}}(N_1 - N_2)(E_2 - E_1)} \\
&= \frac{A_{13}N_3(E_3 - E_1)}{B_{12}I_{\text{pump}}\left(N_1 - N_3\frac{A_{13}}{A_{23}}\right)(E_2 - E_1)} && \text{last steady state equation} \\
&= \frac{A_{13}\frac{N_3}{N_1}(E_3 - E_1)}{B_{12}I_{\text{pump}}\left(1 - \frac{N_3}{N_1}\cdot\frac{A_{13}}{A_{23}}\right)(E_2 - E_1)} \\
&= \frac{A_{13}\frac{B_{12}I_{\text{pump}}}{A_{13}\left(1+\frac{A_{12}+B_{12}I_{\text{pump}}}{A_{23}}\right)}(E_3 - E_1)}{B_{12}I_{\text{pump}}\left(1 - \frac{B_{12}I_{\text{pump}}}{A_{13}\left(1+\frac{A_{12}+B_{12}I_{\text{pump}}}{A_{23}}\right)}\cdot\frac{A_{13}}{A_{23}}\right)(E_2 - E_1)} && \text{using part (b) solution} \\
&= \frac{A_{23}}{A_{23} + A_{12}} \cdot \frac{E_3 - E_1}{E_2 - E_1}
\end{aligned}$$

The result is independent of the pump power and depends only on the ratio of two A parameters, and the energies. The first factor expresses the fraction of electrons excited to state 2 that end up in state 3 instead of going back to state 1 via spontaneous emission. The second factor accounts for the fact that the energy of the emitted photon is smaller than the absorbed one.