# . UNIVERSITY OF OSLO

## Faculty of Mathematics and Natural Sciences

**Final exam: MEF 3000 / MEF 4000 – Functional materials**
**Day/time/place: Monday 11. December, kl. 15.30 – 18.30**
**Duration: 3 hours**
**The set of tasks is on: 4 pages (3 tasks)**
**Appendix: Useful constants, The periodic table of elements**
**Allowed aids: Calculator**
**Language: English**

**Note:**
Control that the set of tasks is complete before you answer the questions.

**Task 1: (34 %)**

**Given the following information:**

| | | |
|---|---|---|
| $P4mm$ | | |
| $a = 3.995$ Å, $c = 4.034$ Å | | |
| | | |
| Ba | 1a | $z = 0$ |
| Ti | 1b | $z = 0.6$ |
| O | 1b | $z = 0$ |
| O | 2c | $z = 0.5$ |

*(The structure is somewhat simplified from the real structure.)*

In the table for this space group the following information is given about the positions.

**Positions**

Coordinates

Multiplicity,
    Wyckoff letter,
        Site symmetry

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | g | 1 | x, y, z | -x, -y, z | -y, x, z | y, -x, z |
| | | | x, -y, z | -x, y, z | -y, -x, z | y, x, z |
| 4 | f | .m. | x, ½, z | -x, ½, z | ½, x, z | ½, -x, z |
| 4 | e | .m. | x, 0, z | -x, 0, z | 0, x, z | 0, -x, z |
| 4 | d | ..m | x, x, z | -x, -x, z | -x, x, z | x, -x, z |
| 2 | c | 2m m. | ½, 0, z | 0, ½, z | | |
| 1 | b | 4m m | ½, ½, z | | | |
| 1 | a | 4m m | 0, 0, z | | | |

(a) For this structure, give the following:
- Its crystal system = Tetragonal
- Bravais lattice = Primitive
- Corresponding pointgroup = 4mm
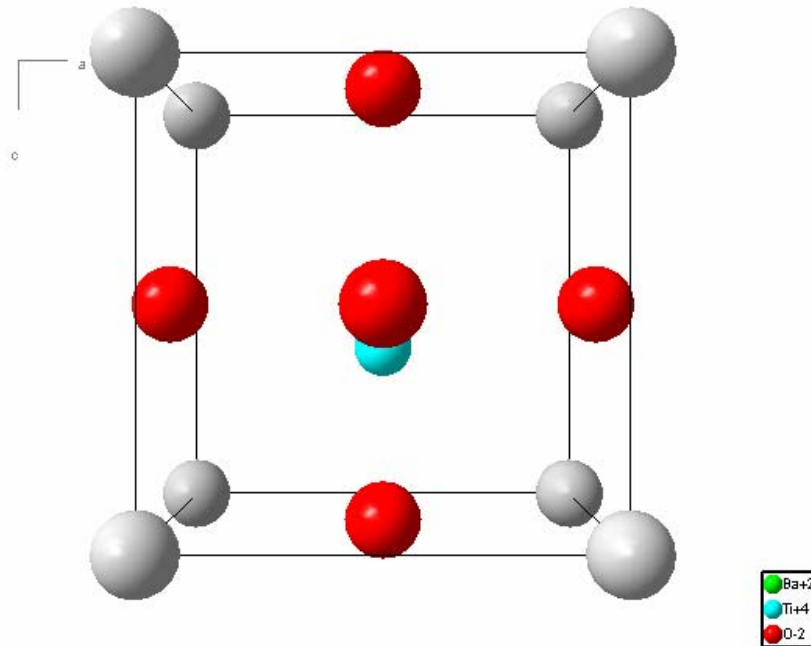- Chemical formula = $BaTiO_3$
- Number of formula units in cell = 1

(b) Give the coordinates for all of the atoms within the unit cell.

Ba: (1, 0, 0), (0, 1, 0), (0, 0, 1), (0, 0, 0), (1, 1, 0), (0, 1, 1), (1, 0, 1), (1, 1, 1)
Ti: (0.5, 0.5, 0.6)
O: (0.5, 0.5, 0), (0.5, 0.5, 1), (0.5, 0, 0.5), (0.5, 1, 0.5), (0, 0.5, 0.5), (1, 0.5, 0.5)

Sketch the structure as a projection on the **ac** plane. Please use the appended grid.



Note : The structure above is given with a depth perspective. This is not required, but it is required to note atoms that cover each other.

(c) Assume that the structure as given represents a ferroelectric material.

Draw a curve/loop that shows the polarisation versus external electric field for a ferroelectric material. Note the positions for remanent polarisation, saturation polarisation and coercivity. (The point for coercivity is not mentioned in the book and thus given as a bonus. Think about the analogy to magnetic materials.)

**Saturation ($P_s$)**
**Remanence ($P_r$)**
**Coercivity ($E_c$)**
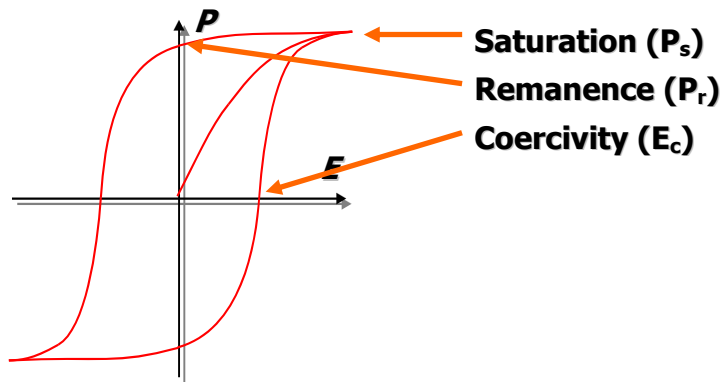
If a structure is ferroelectric, is it then also pyroelectric?

Yes

What does it mean that a material is pyroelectric?

The electrical polarization of the material is affected by a change in temperature.

(d) Reason weather the material will show second harmonic generation if it were exposed to laser light.

What is second harmonic generation?

You send in electromagnetic radiation(eg light) with frequency $f_1$. After passage through the material the radiation contains the frequency $2f_1$ ( $2f_1$ is the 2nd harmonic of $f_1$)

What condition must be met to have this property?

It must be non-centrosymmetric. $BaTiO_3$ should thus be able to show second harmonic generation.
If you answer that the material must be nonlinear, that is also correct. [see text book page 339, page 351, page 461, page 462]

(e) What type of magnetic properties will the material have, e.g., is it dia-, para-, ferro-, or anti-ferro magnetic?

$Ba^{2+}$ $d^0s^2$, $Ti^{4+}$ $d^0s^0$, no unpaired electrons, thus diamagnetic.

If all the $Ti^{4+}$ is replaced by $Mn^{4+}$, what will then happen with the magnetic properties of this material?

Has a $Mn^{4+} = d^3$ situation, there are unpaired electrons and the structure gives a possibility of superexchange which gives a antiferromagneic ordering.

**Task 2: (33 %)**
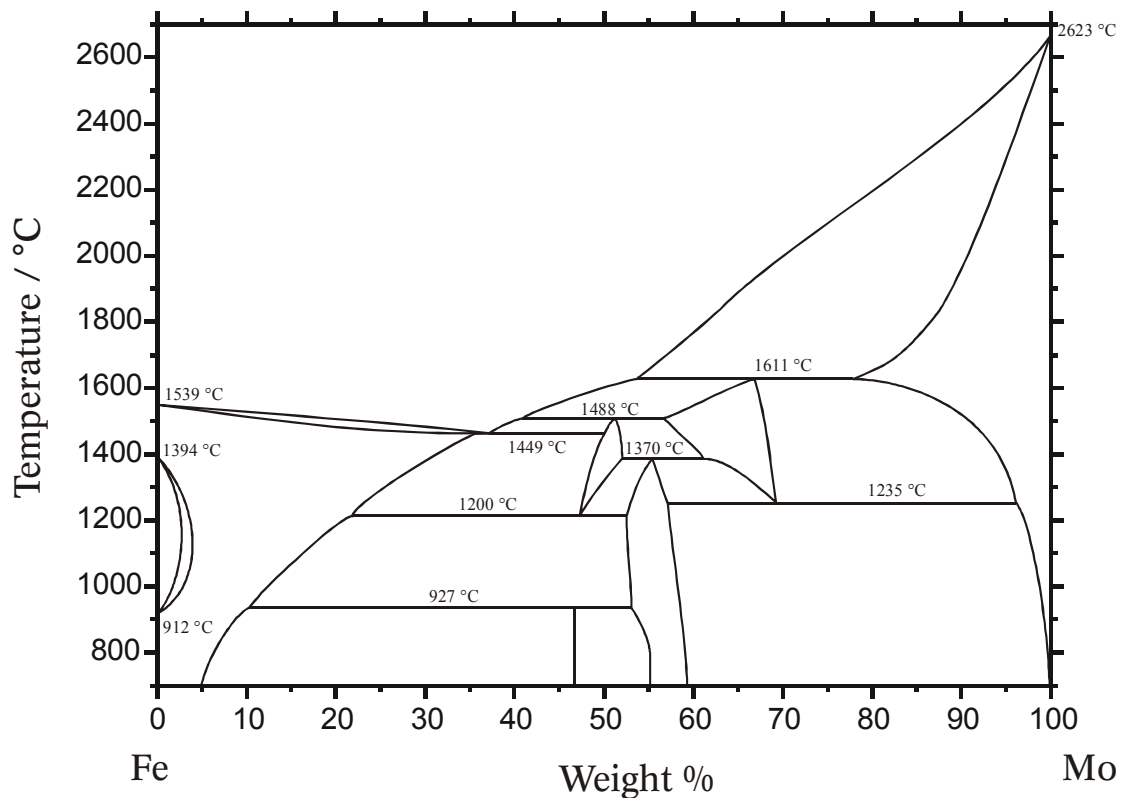


(a)  Examine the phase diagram for the system iron – molybdenum. Mark all the singular phases on the diagram and name them. Use one of the appended phase diagrams.
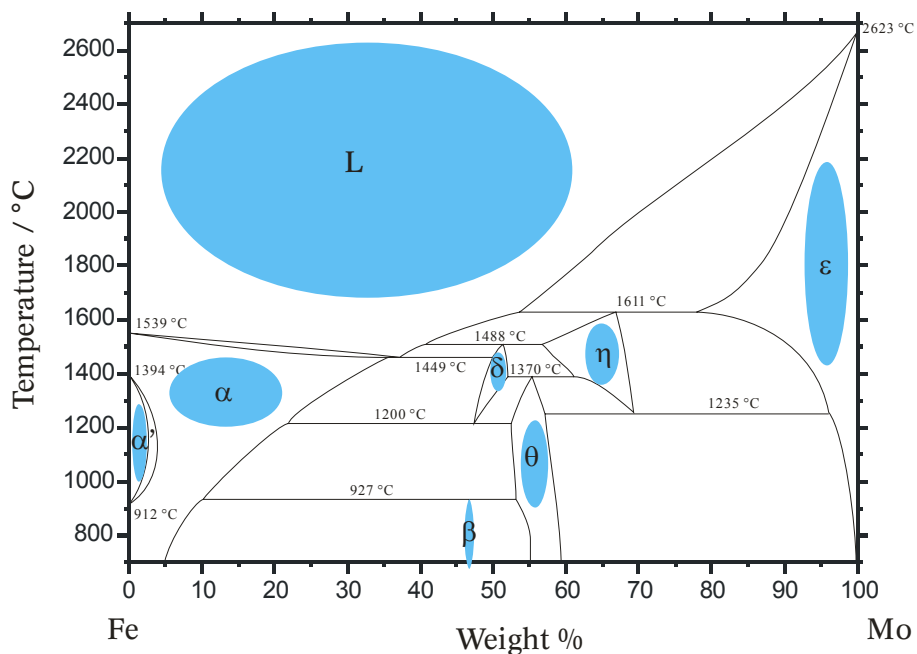


(b)  The phase diagram Fe – Mo shows many reactions that run at given temperatures. Identify the invariant reactions (mark them by a circle and a number on the phase diagram) and write their reaction equations (refer to the numbers you have given on the phase diagram). Use the Gibbs condensed phase rule (P + F = C + 1) to argue that

the reactions are invariant.
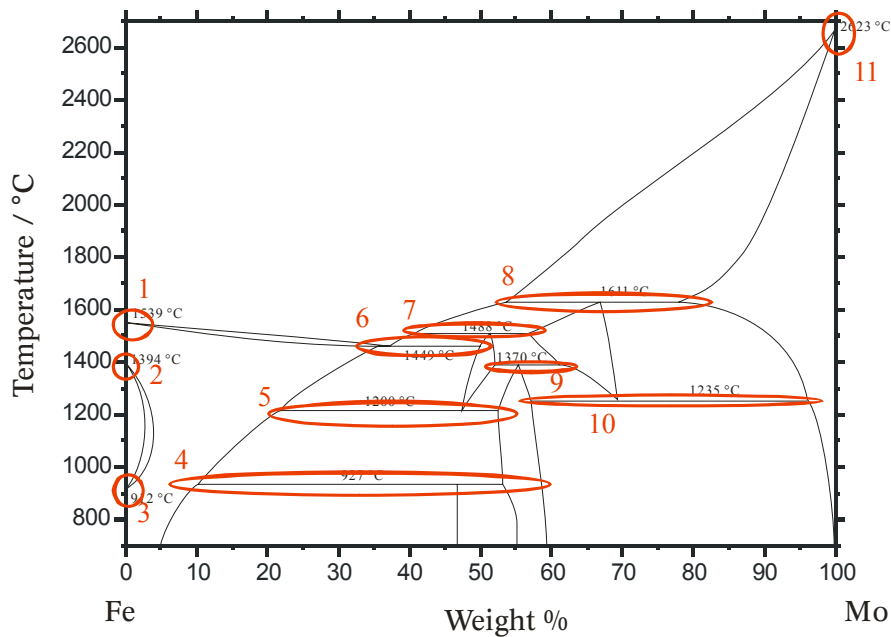


Invariant reactions with one components present (P = 2 and C = 1 gives F = 0):

1: Solidification (or melting): L → α
2: Phasetransition: α → α'
3: Phasetransition: α' → α
11: Solidification (or melting): L → ε

Invariant reactions with two components present (P = 3 and C = 2 gives F = 0):

4: Peritectoid: α + θ → β
5: Eutectoid: δ → α + θ
6: Eutectic: L → α + δ
7: Peritectic: L + η → δ
8: Peritectic: L + ε → η
9: Peritectoid: δ + η → θ
10: Eutectoid: η → θ + ε

(c) Sketch the cooling curve (temperature versus time) for a sample with 65 Wt% Mo that is cooled from 2000 °C down to 800 °C. Assume thermodynamic equilibrium under the whole process. Write the reactions that occur.

L

L→ ε
L + ε → η   L → η

η

η → θ
η → θ + ε

ε → θ
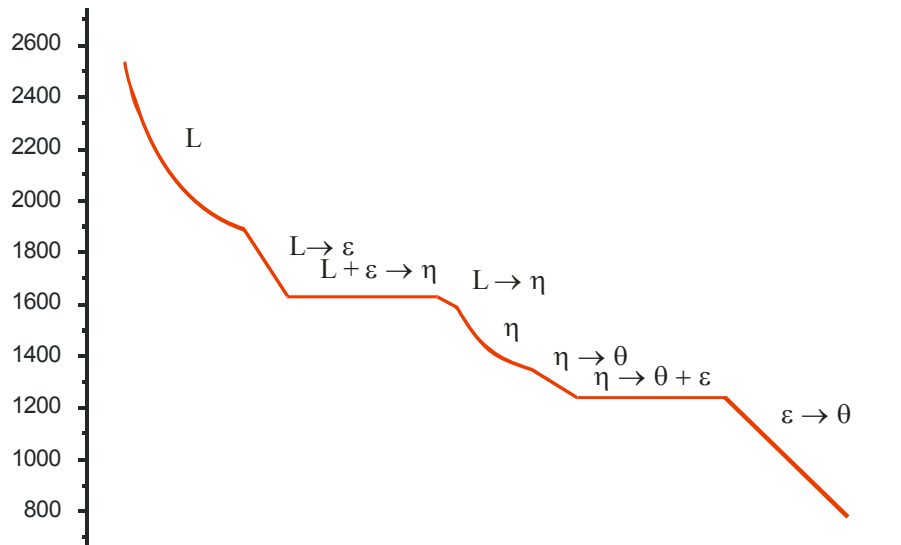
(d) Assume that we have a diffusion pair consisting of a piece of Fe and a piece of Mo that is squashed together and heated to 1300 °C for a long time so that they diffuse into each other. In one end there is pure Fe and in the other there is pure Mo, while the concentration varies between the ends. Draw a schematic picture of how the concentration varies from one end to the other. Please use one of the appended phase diagrams to draw an axis for the concentration.

Mo

Weight %

Weight %

Temperature / °C

Fe

Distance

| Fe | α' | α | δ | θ | η | ε | Mo |
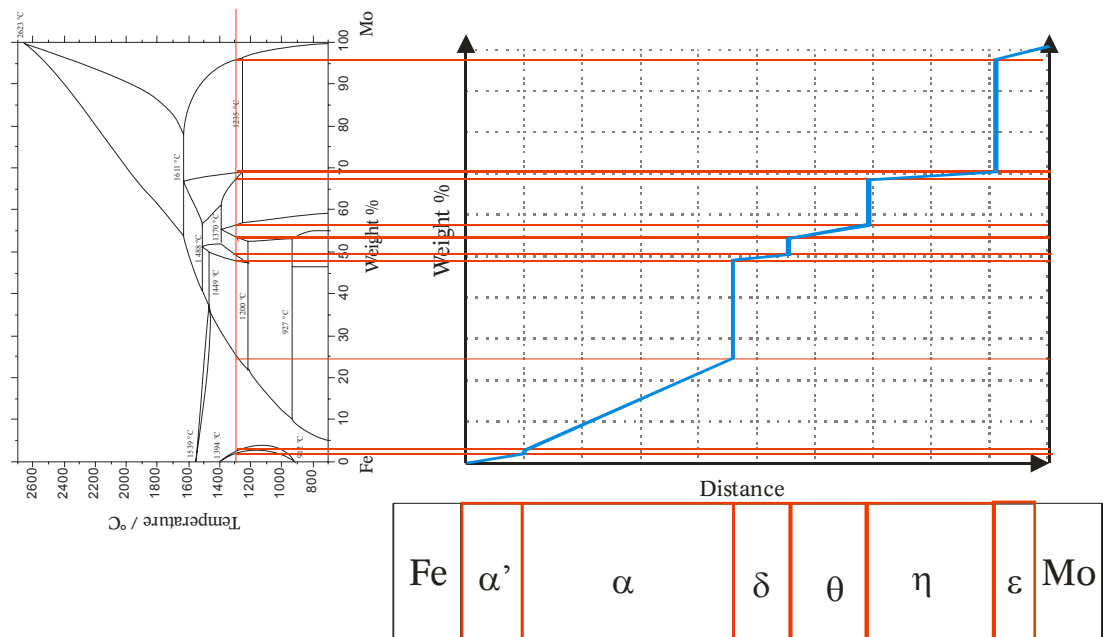
The shape of the curves in the solid solution regimes is probably not linear, but rather curved. The main point of this task is to identify that several new phases will be formed between the Fe and Mo end members, and that the concentration goes in steps between the different phases.

(e) What factors contribute to large solid solubility of two solid compounds (answer very shortly)?

**Task 3 (33%)**

(a) What is the difference between a semiconductor and a semimetal?

(b) The Fermi-Dirac distribution function is given by
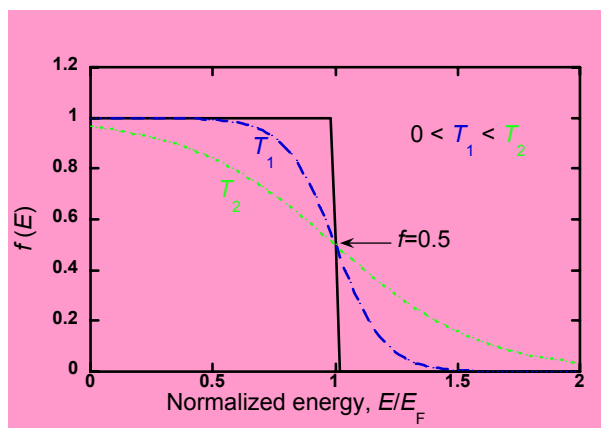
$$f(E) = \frac{1}{1 + \exp\left(\dfrac{E - E_F}{kT}\right)}$$

where the symbols have their usual meaning.

What is the meaning of the symbols?

Sketch the function



( Fig 2. 31 p. 50  text book)

Tell very shortly what the equation expresses.

Show the identity
$$f(E_F + \Delta E) = 1 - f(E_F - \Delta E)$$
and express with words it's meaning.

We write out the left hand side by inserting into function $f$

$$f(E_F + \Delta E) = \cfrac{1}{\exp\left(\cfrac{E_F + \Delta E - E_F}{kT}\right) + 1} = \cfrac{1}{\exp\left(\cfrac{+\Delta E}{kT}\right) + 1}$$
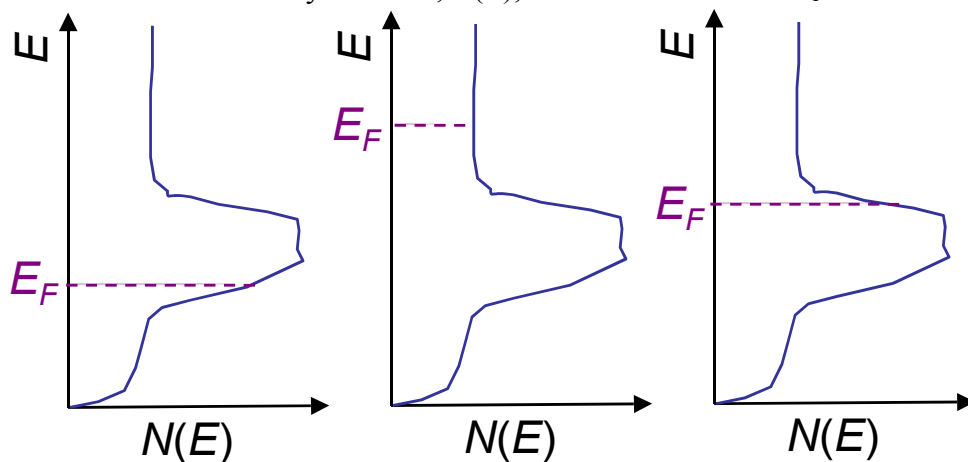
Then the right hand side

$$f(E_F + \Delta E) = \cfrac{1}{\exp\left(\cfrac{E_F + \Delta E - E_F}{kT}\right) + 1} = \cfrac{1}{\exp\left(\cfrac{+\Delta E}{kT}\right) + 1}$$

We see left hand side and right hand side are identical , QED.

'$1 - f(E_F - \Delta E)$' is the probability that a state at an energy $\Delta E$ less than $E_F$ is vacant. This is equal to the probability that a state located at $\Delta E$ above the Fermi level is occupied.

(c)  Below is shown the density of states, $N(E)$, for three metals and $E_F$ at 0 K.



For which metal will the Femi energy $E_F$ (=$E_F(T)$ =chemical potential) change the least with temperature and why?

For each case (Left, Middle Right) will $E_F$ increase or decrease with temperature and why?

(Hint: The number of electrons pr. volume unit does not vary with temperature)

$n_e$= density of electrons, it is constant

We have $n_e = \int\limits_0^\infty N(E) f(E) dE$ [eq 3c-1]

Where $N(E)dE$ is the number of states with energy between $E$ and $E+dE$ pr vol.

At $T$=0 K $f$ is a simple step function and $n_e = \int\limits_0^{E_F} N(E) dE$ [eq 3c-2]

At a finite temperature $f(E)$ has the specific symmetry property given in problem

b). In the present context; If $N(E)$ don't vary around $E_F$ then states above $E_F$ and those below will contribute equally to the integral [eq 3c-1]. Thus $E_F$ is constant if and only if $N(E)$ is constant or symmetric around $E_F$. If we for the left case metal assume erroneously that $E_F$ is constant, then the integral in eq 3c-1 will be larger with increasing temperature and will be larger than that in eq3c-2. , -because there are more states above $E_F$ than below $E_F$ in equal energy distance from $E_F$. Thus $E_F$ must be reduced, to keep $n_e$ constant, and $E_F$ will decrease with temperature. We will thus have

$$\left.\frac{\partial E_F}{\partial T}\right|_{left} < 0 \approx \left.\frac{\partial E_F}{\partial T}\right|_{middle} < \left.\frac{\partial E_F}{\partial T}\right|_{right}$$

The absolute value of the $E_F$ variation is smallest for the case in the middle.
Comment:
The relevant differences in the curves for $N(E)$ is its slope around $E_F$. Consider the case to the left where this slope is positive. The essential parts are contained in the Fig below
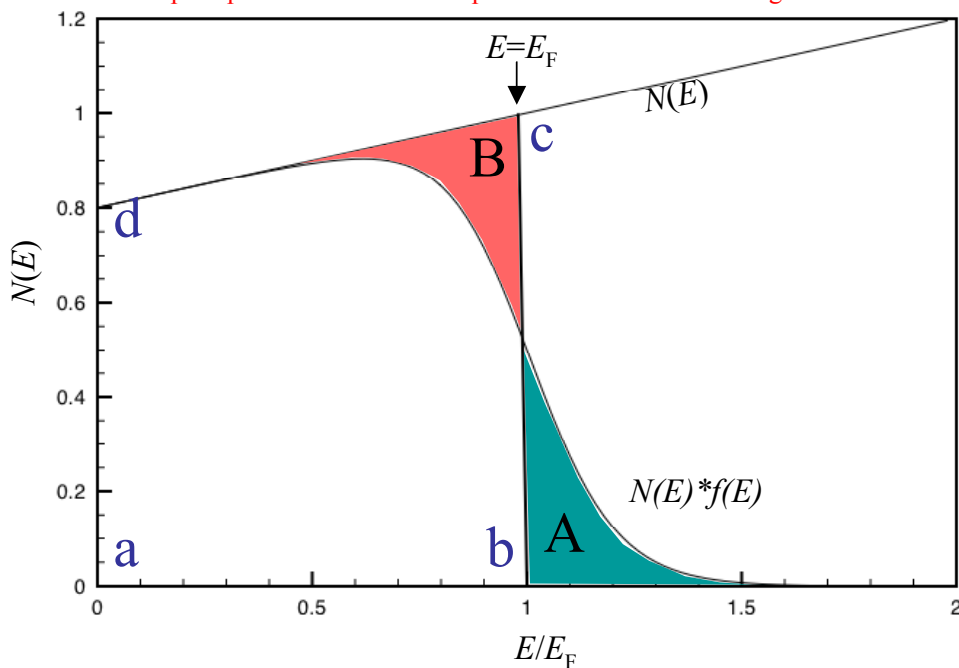


The density of electrons at $T=0$ is given by eq 3c-2, the trapezoid abcd $=n_e$. If we erroneously assume $E_F$ is constant, then the integral of eq 3c-1 is $n_e$+A-B. We see this that is larger than $n_e$ because A>B. To get a smaller value we must let $E_F$ be smaller than it is for $T=0$.

(d) Light can be scattered when propagating through materials. Different scattering processes have been given different names.

What is the origin of Brilloin scattering?
scattering is from phonons  (acoustic phonons = low energy phonons)

What is the origin of Raman scattering?
scattering is from phonons (optical phonons = high energy phonons)

What is the origin of Reyleigh scattering?
scattering from particles (assumed insulator)  much smaller than the wave length of the light.

Comment: For Rayleigh scattering, see text book p. 452-453. It describes elastic scattering, i.e. scattering

with no change of photon energy. The two other scattering processes are mentioned only in lectures and their notes; so they are optional knowledge. They are inelastic scattering processes. For optical phonons the change in photon energy is readily observable optically (thus the name )  and Raman scattering is used in spectroscopy to identify molecules and materials.