Solution to HS's problem 1

Heat capacity of a two-dimensional electron gas

GaAs/AlGaAs heterostructure (see Marder Section 19.5):

$$n = 10^{11} \text{ cm}^{-2}, \qquad \varepsilon = \frac{\hbar^2 k^2}{2m^*}, \qquad m^* = 0.067 m_e \tag{1}$$

The present situation corresponds to the case (a) of the previous problem 6.5 in Marder, i.e. the gas is purely two-dimensional in the sense that only the $(p = 1)$ band needs to be considered, and $\vec{k}$ is a two-dimensional vector with the length $k = \sqrt{k_x^2 + k_y^2}$. The most important quantity is the Fermi energy, which is determined by evaluating N at zero temperature:

$$n = \frac{N}{A} = \int_{k \le k_{\mathrm{F}}} D_{\vec{k}} d\vec{k} = \frac{2}{(2\pi)^2} \int_0^{k_{\mathrm{F}}} 2\pi k \, dk = \frac{k_{\mathrm{F}}^2}{2\pi} \quad \Rightarrow \quad k_{\mathrm{F}} = \sqrt{2\pi n} \tag{2a}$$

The same result is obtained by using that, according to problem 6.4 or equation (6.35), $D(\varepsilon) = m^*/\pi\hbar^2$ in the two-dimensional case:

$$n = \int_0^{\varepsilon_{\mathrm{F}}} D(\varepsilon) \, d\varepsilon = \frac{m^* \varepsilon_{\mathrm{F}}}{\pi\hbar^2} \quad \Rightarrow \quad \varepsilon_{\mathrm{F}} = \frac{n\pi\hbar^2}{m^*} \quad \text{or} \quad k_{\mathrm{F}} = \sqrt{2\pi n} \tag{2b}$$

Introducing the numbers, and using that $k_{\mathrm{F}} = 1 \text{ Å}^{-1}$ corresponds to a Fermi energy $\varepsilon_{\mathrm{F}} = 3.81$ eV when the mass is m_e, then we get

$$k_{\mathrm{F}} = 0.793 \cdot 10^{-2} \text{ Å}^{-1}, \qquad \varepsilon_{\mathrm{F}} = \frac{(0.793 \cdot 10^{-2})^2}{0.067} 3.81 \text{ eV} = 3.58 \text{ meV} \tag{3}$$

This Fermi energy corresponds to a Fermi temperature $T_{\mathrm{F}} = \varepsilon_{\mathrm{F}}/k_{\mathrm{B}} = 41.5$ K.

1) $T = 1$ K is much smaller than the Fermi temperature and the heat capacity may be determined by the leading order expression (6.77)

$$c_V = \frac{\pi^2}{3} D(\varepsilon_{\mathrm{F}}) k_{\mathrm{B}}^2 T = \frac{\pi}{6} \frac{T}{T_{\mathrm{F}}} k_{\mathrm{F}}^2 k_{\mathrm{B}}, \qquad \text{as} \quad D(\varepsilon_{\mathrm{F}}) = \frac{m^*}{\pi\hbar^2} = \frac{k_{\mathrm{F}}^2}{2\pi\varepsilon_{\mathrm{F}}} = \frac{k_{\mathrm{F}}^2}{2\pi k_{\mathrm{B}} T_{\mathrm{F}}} \tag{4}$$

In the case of a sample with the area $A = 1 \text{ cm}^2$ the result is

$$C_V(\text{el}) = A \, c_V = A \frac{\pi}{6} \frac{1}{41.5} (0.793 \cdot 10^6 \text{ cm}^{-1})^2 \times 1.38066 \cdot 10^{-23} \text{ J/K} = \underline{1.1 \cdot 10^{-13} \text{ J/K}} \tag{5}$$

The explicit result is $C_V(\text{el}) = A\pi m^* k_{\mathrm{B}}^2 T/(3\hbar^2)$. Hence, the small value of C_V is not due to the low electron density n but to the two-dimensionality of the system and the small effective mass.

2) In order to estimate the phonon contribution to the heat capacity we shall use the Debye model (Section 13.3.2 in Marder). The Debye temperature of GaAs is $\Theta_D = 344$ K (which value is not changed much when some of the Ga ions are replaced by Al ions). Using (13.70), (13.75) in Marder (2.Ed.) and

$$\int_0^\infty \frac{x^4 e^x}{(e^x - 1)^2} \, dx = \frac{4\pi^4}{15} \quad \Rightarrow \quad c_V = \frac{12\pi^4}{5} n_A k_{\mathrm{B}} \left(\frac{T}{\Theta_D}\right)^3 \quad (T \ll \Theta_D) \tag{6}$$

According to Table 2.5 (page 27) in Marder, GaAs has the zincblende structure ($\sim$ diamond structure) with the lattice parameter $a = 5.63$ Å. In this structure there are 8 atoms per unit cell, and the density of atoms is $n_A = 8/a^3 = 4.48 \cdot 10^{22}$ cm^{-3}. [The mean atomic mass (periodic table) is $(69.72 + 74.92)/2 = 72.3$ u, implying a mass density $\rho = 5.38$ g cm^{-3}]. Assuming $V = 1$ cm^3 and $T = 1$ K, the phonon contribution becomes

$$C_V(\text{ph}) = \frac{12\pi^4}{5} \times 4.48 \cdot 10^{22} \times 1.38066 \cdot 10^{-23} \left(\frac{1}{344}\right)^3 \text{ J/K} = \underline{3.55 \cdot 10^{-6} \text{ J/K}} \quad (7)$$

which is much larger than the electronic contribution. Utilizing that $C_V(\text{el}) \propto T$ and $C_V(\text{ph}) \propto T^3$, the temperature T_0 at which the two contributions are equal, is determined by (T_0 in K)

$$1.10 \cdot 10^{-13} \, T_0 = 3.55 \cdot 10^{-6} \, T_0^3 \quad \Rightarrow \quad T_0 = \underline{1.8 \cdot 10^{-4} \text{ K}} \quad (8)$$

A more fair comparison would be to consider a film of thickness ~ 100 μm, i.e. $A = 1$ cm^2 and $V = 10^{-2}$ cm^3, in which case $T_0 = 1.8$ mK, a temperature within an accessible range (however, the reduction of the size of the sample makes it more difficult to determine the heat capacity).

11.2 Zinc in copper

Copper is a monovalent fcc and zinc a divalent hcp (not fcc) metal. At a small concentration of Zn^{++}, the crystal structure is fcc until the Fermi surface touches some point on the edge of the Brillouin zone:

(a) In the nearly free electron approximation, the Fermi wave vector is (nearly) determined as in the free electron case,

$$n = \int_{|\vec{k}| \leq k_F} D_{\vec{k}} d\vec{k} = \frac{2}{(2\pi)^3} \int_0^{k_F} 4\pi k^2 dk = \frac{1}{3\pi^2} k_F^3 \quad \Rightarrow \quad k_F = \left(3\pi^2 n\right)^{1/3} \quad (1)$$

Defining c to be the concentration of Zn^{++} ions and a to be the lattice parameter of the fcc lattice, then the electron density is

$$n = \frac{4}{a^3}[(1-c) + 2c] = \frac{4}{a^3}(1+c) \quad \Rightarrow \quad k_F = \left[\frac{12\pi^2}{a^3}(1+c)\right]^{1/3} = \frac{4.9109}{a}(1+c)^{1/3} \quad (2)$$

(b) The primitive unit vectors of the face-centered cubic lattice are, (2.2):

$$\vec{a}_1 = \frac{a}{2}(1,1,0), \qquad \vec{a}_2 = \frac{a}{2}(1,0,1), \qquad \vec{a}_3 = \frac{a}{2}(0,1,1) \quad (3)$$

and the corresponding primitive vectors of the reciprocal lattice are

$$\vec{b}_1 = 2\pi \frac{\vec{a}_2 \times \vec{a}_3}{\vec{a}_1 \cdot \vec{a}_2 \times \vec{a}_3} = \frac{2\pi}{a}(1,1,-1), \quad \vec{b}_2 = \frac{2\pi}{a}(1,-1,1), \quad \vec{b}_3 = \frac{2\pi}{a}(-1,1,1) \quad (4)$$

The boundaries of the 1. Brillouin zone are established by the planes perpendicular to $\pm \vec{b}_i$ at the distance $k_1 = |\vec{b}_i|/2$ from the origin. Hence the shortest distance from the origin to the zone boundaries is

$$k_1 = \frac{|\vec{b}_i|}{2} = \frac{\pi\sqrt{3}}{a} = \frac{5.4414}{a} \quad (5)$$

$k_F(c = 0)$ is smaller than k_1, and $k_F(c)$ becomes equal to k_1 at the zinc concentration $c = c_1$

$$4.9109(1 + c_1)^{1/3} = 5.4414 \quad \Rightarrow \quad c_1 = \underline{0.36} \tag{6}$$

The experimental phase diagram (see Fig. 4 in Chapter 21 of Kittel) shows a transition from fcc to bcc, for increasing c values, at about the Zn concentration determined here.

(c) The primitive unit vectors of the body-centered cubic lattice are, (2.3):

$$\vec{a}_1 = \frac{a}{2}(1, 1, -1), \qquad \vec{a}_2 = \frac{a}{2}(1, -1, 1), \qquad \vec{a}_3 = \frac{a}{2}(-1, 1, 1) \tag{7}$$

and the corresponding primitive vectors of the reciprocal lattice are

$$\vec{b}_1 = \frac{2\pi}{a}(1, 1, 0), \quad \vec{b}_2 = \frac{2\pi}{a}(1, 0, 1), \quad \vec{b}_3 = \frac{2\pi}{a}(0, 1, 1) \tag{8}$$

Notice, that the reciprocal of the bcc lattice is fcc, and equivalently, that the reciprocal lattice of fcc is the bcc lattice.

In the case of bcc there are 2 atoms per cubic unit cell, hence

$$n = \frac{2}{a^3}(1 + c), \quad k_F = \left[\frac{6\pi^2}{a^3}(1 + c)\right]^{1/3} = \frac{3.8979}{a}(1 + c)^{1/3} \tag{9}$$

The shortest distance from the origin to the boundaries of the 1. Brillouin zone is

$$k_2 = \frac{|\vec{b}_i|}{2} = \frac{\pi\sqrt{2}}{a} = \frac{4.4429}{a} \quad \text{and} \quad k_2 = k_F \quad \text{when} \quad c = c_2 = \underline{0.48} \tag{10}$$

Once again, this is about the right Zn concentration at which the Cu-Zn alloy system shows a change of crystal structure (from bcc to a complex γ structure).

If the atomic density is assumed to stay constant at the transition fcc $\rightarrow$ bcc, the Fermi wave vector is the same on each side of the phase line, but the lattice parameter a is changed, $a_{bcc} = (1/2)^{1/3} a_{fcc} = 0.794\, a_{fcc}$. The cubic lattice parameter a also changes (increases) gradually with the Zn concentration, in between the phase lines, since $n_{Cu} = 1.33\, n_{Zn}$, however, all the possible variations of a have no influence on the arguments above. β-brass is the alloy with $c = 0.5$, and it shows an order-disordered phase transition at about 470 °C, which we are going to discuss later on.

Citation from Kittel: "Why is there a connection between the electron concentrations at which a new phase appears and at which the Fermi surface makes contact with the Brillouin zone? We recall that the energy bands split into two at the region of contact on the zone boundary [Marder, Chapter 8, (8.24)]. If we add more electrons to the alloy at this stage, they will have to be accommodated in the upper band or in states of high energy near the zone corners of the lower band. Both options are possible, and both involve an increase of energy. Therefore it may be energetically favorable for the crystal structure to change to one which can contain a Fermi surface of larger volume (more electrons) before contact is made with the zone boundary. In this way H. Jones made plausible the sequence of structures fcc, bcc, γ, hcp with increasing electron concentration."