Condensed matter physics 2013
Solutions for Exercise 4

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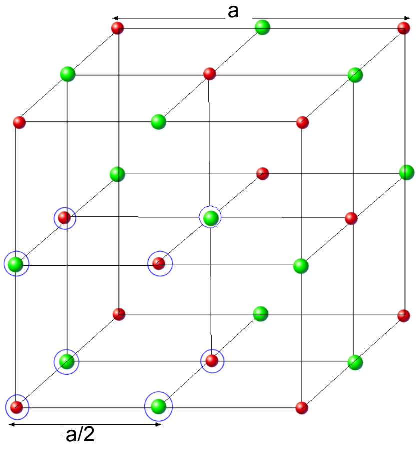
Problem 14

The figure below shows a unit cell of the KCl fcc lattice where the different colours represent the different atoms and the inter-atom distance (nearest neighbours) is $a/2$.



The definition of the structure factor is

$$S(\vec{K}) = \sum_j f_j(\vec{K}) e^{-i\vec{K}\cdot\vec{x}_j}$$

with the atomic scattering factors (or atomic form factors) $f_j(\vec{K})$ (essentially the Fourier transform of the electron density of a single atom). For simplicity we assume that the form factor is independent of $\vec{K}$ and identical for identical atoms, i.e. $f_j = f^+$ for K and $f = f^-$ for Cl. Then we can write:

$$S(\vec{K}) = \sum_j f_j e^{-i\vec{K}\vec{\xi}_j}$$

where $\vec{K}$ are reciprocal lattice vectors. The atom positions $\vec{\xi}_j$ can be found using the figure above (in units of $a/2$):

$$\vec{\xi}_1 = \begin{pmatrix} 0 \\ 0 \\ 0 \end{pmatrix} \qquad \vec{\xi}_2 = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \qquad \vec{\xi}_3 = \begin{pmatrix} 1 \\ 1 \\ 0 \end{pmatrix}$$

$$\vec{\xi}_4 = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \qquad \vec{\xi}_5 = \begin{pmatrix} 0 \\ 1 \\ 1 \end{pmatrix} \qquad \vec{\xi}_6 = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$\vec{\xi}_7 = \begin{pmatrix} 1 \\ 0 \\ 1 \end{pmatrix} \qquad \vec{\xi}_8 = \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}$$

The position with indices $2, 4, 6$ and 8 are, for example, K atoms, while $1, 3, 5$ and 7 are Cl atoms. The components of $\vec{K}$ take on half-integer values in units of $4\pi/a$, or integer values in

$2\pi/a$, so that the arguments of the exponential function becomes $-i\vec{K}\cdot\vec{\xi}_j = -i\frac{2\pi}{a}\begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix}\cdot\frac{a}{2}\vec{\xi}_j = -i\pi\begin{pmatrix} h_1 \\ h_2 \\ h_3 \end{pmatrix}\cdot\vec{\xi}_j = -i\pi\vec{h}\vec{\xi}_j$ with $h_{1,2,3}\in\mathbb{Z}$

The individual terms can be directly calculated:

$j=1$: $e^{-i\pi\vec{h}\vec{\xi}_1} = e^0 = 1$

$j=2$: $e^{-i\pi\vec{h}\vec{\xi}_2} = e^{-i\pi h_1}$

$j=3$: $e^{-i\pi\vec{h}\vec{\xi}_3} = e^{-i\pi(h_1+h_2)}$

$j=4$: $e^{-i\pi\vec{h}\vec{\xi}_4} = e^{-i\pi h_2}$

$j=5$: $e^{-i\pi\vec{h}\vec{\xi}_5} = e^{-i\pi(h_2+h_3)}$

$j=6$: $e^{-i\pi\vec{h}\vec{\xi}_6} = e^{-i\pi h_3}$

$j=7$: $e^{-i\pi\vec{h}\vec{\xi}_7} = e^{-i\pi(h_1+h_3)}$

$j=8$: $e^{-i\pi\vec{h}\vec{\xi}_8} = e^{-i\pi(h_1+h_2+h_3)}$

$\Rightarrow S(\vec{h}) = f^+[1+e^{-\pi i(h_1+h_2)}+e^{-\pi i(h_2+h_3)}+e^{-\pi i(h_1+h_3)}]+f^-[e^{-\pi i h_1}+e^{-\pi i h_2}+e^{-\pi i h_3}+e^{-\pi i(h_1+h_2+h_3)}]$

If all h_p are even the exponents are multiple of 2π and one obtains

$$S(\vec{k}) = f^+[1+1+1+1]+f^-[1+1+1+1] \propto (f^+ + f^-)$$

If all h_p are odd, the sums of two h_p are even and give multiples of 2π, while the terms containing one or three h_p are odd multiples of π. This yields

$$h_i = 2n_i + 1, n_i \in Z$$

$$S(\vec{k}) = f^+[1+1+1+1]+f^-[-1-1-1-1] \propto (f^+ - f^-)$$

If h_i contains both, odd and even terms the -1 and $+1$ compensate each other:

$$S(\vec{k}) = f^+\cdot 0 + f^-\cdot 0 = 0$$

If we assume that we have ideal ionic binding between the atoms the occupations of the atomic orbitals in KCl are the same for both atomic species, i.e. K$^+$: 3s^{2}3p^6 and Cl$^-$: 3s^{2}3p^6. Assuming that the charging of the atoms does not significantly change the orbitals, we therefore would expect that the scattering cross sections of the atoms are also identical:

$$f^+ = f^-$$

Therefore, we will only obtain reflections from lattice planes with even indices. The ones with odd or with a mixture of odd and even indices are not allowed due to destructive interference.

For NaCl the structure is the same as for KCl, but the population of the atomic orbitals is not the same for the different atoms, i.e. Na$^+$: 2s^{2}2p^6 and Cl$^-$: 3s^{2}3p^6. Therefore $f^+\neq f^-$ and reflections are allowed for lattice planes with all indices odd or all even. Only those with a mixture of odd and even have destructive interference.

Problem 15

In a three dimensional isotropic medium (approximation!) Young's modulus E (not to be confused with an energy!) is defined by the (macroscopic) relative length change $\Delta L/L$ as a result of a force F exerted on an area A: $F/A = E \cdot \Delta L/L$. We can describe the same change in the length by an effective spring constant f, which yields $F = f\Delta L$. If we reduce our view to a single unit cell, we can insert $A = a^2$ and $L = a$ and find $E = f \cdot L/A = f/a$. Inserting the given value for E yields $f = 30\,\mathrm{N/m}$.

The above derivation of a spring constant is for a deformation along one axis. Vibrations take place in all three dimensions and we already assumed an isotropic medium, i.e. f is the same in all directions. Therefore we obtain three degrees of freedom which are excited by temperature to an energy of $\frac{1}{2}k_BT$. From the equipartition theorem we thus obtain for the average energy of the motion in the harmonic potential that corresponds to f:

$$E_{vib} = \frac{1}{2} f < |\vec{r}|^2 >= \frac{3}{2} k_B T$$

$$\sqrt{< \vec{r}^2 >} = \sqrt{\frac{3k_BT}{f}}$$

At $T = 300\,\mathrm{K}$:

$$\sqrt{< \vec{r}^2 >} = 0.2\,\mathring{A}$$

At $T = 1687\,\mathrm{K}$:

$$\sqrt{< \vec{r}^2 >} = 0.48\mathring{A}$$

The Lindemann Criterion states that at the melting temperature the root mean square of the vibration amplitude is a universal fraction C of the inter-atomic distance a: $\sqrt{< \vec{x}^2 >} = Ca$. Here we find

$$C = \frac{\sqrt{< \vec{x}^2 >}}{a_0} = \frac{0.48}{3.13} = 0.15$$

i.e. 15% of the atomic distance. We note that we made some very rough approximations in the calculations (a and E along [111], but neglected other directions, ...). Often the values lie around 30%.

Problem 16

Referring to an FCC lattice, the basis of diamond is 000; $\frac{1}{4}\frac{1}{4}\frac{1}{4}$. Thus

$$S_{basis} = \; 1 + e^{-i(\pi/2)(v1+v2+v3)}$$

The total structure factor is

$$S(v1v2v3) = \; S_{lattice} \cdot S_{basis}$$

For the FCC lattice we have the sites 000; $0\frac{1}{2}\frac{1}{2}$;$\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$. Thus

$$S_{lattice} = \; Nf[1 + e^{-i(\pi)(v2+v3)} + e^{-i(\pi)(v1+v3)} + e^{-i(\pi)(v1+v3)}]$$

The result is given by the product

$$S = \; Nf[1 + e^{i(\pi)(v1+v2)} + e^{i(\pi)(v1+v3)} + e^{i(\pi)(v2+v3)}][1 + e^{i(\pi)(v1+v2+v3)/2}]$$

Problem 17

We will discuss two ways to obtain the Debye-Waller factor. For the one required in the posed problem, we assume that the positions of the atom positions are ‘blurred’ by the temperature to a Gaussian distribution with a standard deviation σ. This can be described in the following way: The lattice is given by a sum of Dirac-Delta functions:

$$g(\vec{r}) = \sum \delta(\vec{r} - \vec{r}_j),\ \vec{r}_j \in \mathbf{G}$$

each of which is broadened by folding with a normalized Gaussian shape function:

$$w(\vec{r}) = N e^{-\frac{|\vec{r}|^2}{2\sigma^2}} = \frac{1}{(\sigma\sqrt{2\pi})^3} e^{-\frac{x^2+y^2+z^2}{2\sigma^2}}$$

The mean square expectation value, $< r^2 >$, of the deviation r of the atom from its lattice position is given by

$$< r^2 >= \int_0^\infty \int_0^\pi \int_0^{2\pi} r^2 \cdot w(r) \cdot r^2 \sin(\theta) dr d\theta d\phi = \sqrt{\frac{2}{\pi}} \frac{1}{\sigma^3} \underbrace{\int_0^\infty r^4 e^{-\frac{r^2}{2\sigma}} dr}_{3\sqrt{\frac{\pi}{2}}\sigma^5} = 3\sigma^2$$

(integrals in spherical coordinates and wikipedia.org/wiki/Lists_of_integrals for the final integral)

The distribution of the atomic position around a lattice site is then given by $w * g$, where $*$ denotes the convolution. To obtain the electron density, in addition one has to convolute this with the electron density of a single atom ρ_{at} (the convolution is associative and we assume that the atoms do not overlap):

$$\rho = \rho_{\text{at}} * w * g$$

The scattering amplitude is essentially the Fourier transform of the electron density:

$$\begin{aligned} A(\vec{q}) &= \mathcal{F}(\rho_{\text{at}} * w * g) = \mathcal{F}(\rho_{\text{at}}) \cdot \mathcal{F}(w) \cdot \mathcal{F}(g) \\ &= f_j \cdot \mathcal{F}(w) \cdot \sum \delta(\vec{q} - \vec{k}_j),\ \vec{k}_j \in \text{reciprocal lattice} \end{aligned}$$

(Here we use that the Fourier transform of a convolution is the product of the individual transformations, the definition of the atomic form factor f_j, and that the transform of the direct lattice is the reciprocal lattice.) The Fourier transform of a Gaussian function is again a Gaussian:

$$\mathcal{F}\left(\frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{x^2}{2\sigma^2}}\right) = e^{-\frac{\sigma^2 q_x^2}{2}}$$

Therefore we find

$$\mathcal{F}(w) = e^{-\frac{\sigma^2}{2}(q_x^2+q_y^2+q_z^2)} = e^{-\frac{1}{2}\sigma^2 q^2} = e^{-\frac{1}{6}<r^2>q^2}$$

This is the additional factor mentioned in the script, page 2.20. The Debye-Waller factor reads

$$D(\vec{q}) = |\mathcal{F}(w)|^2 = e^{-\frac{1}{3}<r^2>q^2}$$

.

We now discuss a second derivation of the Debye-Waller factor (see lecture). This time we perform a time average of the atom motion. Inserting the position of an atom $\vec{x}(t) = \vec{x}_j + \vec{r}(t)$ into the expression of the structure factor and averaging in time yields:

$$A(\vec{q}\,) = f_j \cdot e^{-i\vec{q}\cdot\vec{x}_j} \cdot < e^{-i\vec{q}\cdot\vec{r}(t)} > \equiv A_0(\vec{q}\,) \cdot < e^{-i\vec{q}\cdot\vec{r}(t)} >$$

The exponential function can be written as a Taylor expansion and the time average can be performed over the individual parts:

$$< e^{-i\vec{q}\cdot\vec{r}(t)} >=< 1 - i\vec{q}\cdot\vec{r}(t) - \frac{1}{2}(\vec{q}\cdot\vec{r}(t))^2 + ... >\approx< 1 - \frac{1}{2}(\vec{q}\cdot\vec{r}(t))^2 >$$

The last step uses that $< \vec{q}\vec{r} >= \vec{q} < \vec{r} >= 0$ (motion around equilibrium position). The time average of the second term can be obtained as follows:

$$< \frac{1}{2}(\vec{q}\cdot\vec{r}(t))^2 >=< \frac{1}{2}q^2r^2\cos^2(\theta) >= \frac{1}{2}q^2 < r^2 >< \cos^2(\theta) >$$

where θ is the angle between the two vectors $\vec{q}$ and $\vec{r}$, which takes on all values between 0 and 360° randomly (thermal motion). The averaging is done easiest in spherical coordinates:

$$< \cos^2(\theta) >= \frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}\cos^2(\theta)\cdot\sin(\theta)d\theta d\phi = \frac{1}{3}$$

.

Inserting above yields the Debye-Waller factor:

$$D(\vec{q}) = \frac{|A|^2}{|A_0|^2} = e^{-\frac{1}{3}<r^2>q^2}$$

Problem 18

The goal is to estimate the mean square value of the atomic vibrations. The assumption is that the atoms reside in a confining harmonic potential determined by the characteristic frequency ω. This is related to the displacement as follows: For a harmonic oscillator the equation of motion is

$$m\ddot{u} = -uk$$

with k the ‘spring constant’. This can be solved using the Ansatz

$$u(t) = u_0\sin\omega t$$

$$\Rightarrow -mw^2u = -uk$$

$$\Rightarrow k = mw^2$$

The average potential energy reads (it is not necessary to explicitly evaluate the averaging):

$$\overline{E}_{pot} = \frac{1}{2}k < u^2 >= \frac{1}{2}m\omega^2 < u^2 >= \frac{3}{2}k_BT$$

The last step is due to the fact that at reasonably high temperatures every degree of freedom (three directions in three dimensions) obtains $\frac{1}{2}k_BT$ due to thermal excitation.

From this we obtain

$$< u(t)^2 >= \frac{\frac{3}{2}k_BT}{\frac{1}{2}m\omega^2} = \frac{3k_BT}{m\omega^2},$$

which can be inserted into the Debye-Waller factor (see problem 17):

$$I = I_0e^{-\frac{1}{3}G^2<U(t)^2>}$$

$$I = I_0e^{-\frac{k_BT}{m\omega^2}G^2},$$

where $G = |\vec{G}$ is the amplitude of the scattering vector in the reciprocal lattice.

Inserting the numbers given in the problem:

$m_{\mathrm{Cu}} = 0.0635\,\mathrm{kg/mol} = 1.05 \times 10^{-25}\,\mathrm{kg/atom}$

$a = 3.61$ Å

$\omega = 10^{14}\,\mathrm{s}^{-1}$

$T = 4\,\mathrm{K}$ or $T = 300\,\mathrm{K}$

$G_{[110]} = \frac{2\pi}{a}\sqrt{2} = 2.46 \times 10^{10}\,\mathrm{m}^{-1}$

Therefore:

$T = 4\,\mathrm{K}$: $\frac{I}{I_0} \approx 1.00$

$T = 300\,\mathrm{K}$: $\frac{I}{I_0} \approx 0.998$

At first sight, it seems not worth to perform XRD experiments at low temperatures because the intensity is not improved significantly for this scattering vector. However, for higher indices in the reciprocal lattice, this is not correct anymore. For example:

$G_{[666]} = \frac{2\sqrt{3\times 6^2}\pi}{a} = \frac{12\sqrt{3}\pi}{a} = 1.81 \times 10^{11}\,\mathrm{m}^{-1}$

$T = 4\,\mathrm{K}$: $\frac{I}{I_0} \approx 0.998$

$T = 300\,\mathrm{K}$: $\frac{I}{I_0} \approx 0.879$