

Written exam of Condensed Matter Physics - July 12th 2022
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Exercise 1. Sodium chloride (NaCl) is a face-centered cubic (fcc) lattice with a Na-Cl atom basis. The NaCl lattice can be regarded as two interpenetrating fcc primitive lattices displaced by $\mathbf{d} = \frac{a}{2}(\hat{x} + \hat{y} + \hat{z})$, where a is the side of the conventional unit cell (see the right panel of Fig. 1) and \hat{x} , \hat{y} , \hat{z} are the unit vectors of the corresponding Cartesian axes.

1. [3 points] Given that the mass density of NaCl is $\rho = 2.16 \times 10^3 \text{ kg/m}^3$, and known the masses of Na ($M_{\text{Na}} = 3.82 \times 10^{-26} \text{ kg}$) and Cl ($M_{\text{Cl}} = 5.89 \times 10^{-26} \text{ kg}$) atoms, calculate the side of the conventional unit cell a .
2. [8 points] The graphs in the central and right panels of Fig. 1 show the phonon dispersion curves along the Γ -K direction of the first Brillouin zone (the central panel reports the entire dispersion curves, the right panel displays an enlarged view of the acoustic phonon branches near the Γ point). Determine the average sound velocity $v_{\Gamma\text{-K}}$ associated to the given direction, within the Debye model. Determine the Debye temperature Θ_D of the sound modes, assuming that $v_{\Gamma\text{-K}}$ can be taken as the average sound velocity v_D within the Debye model.
3. [4 points] Evaluate the specific heat c_v at the temperatures $T = T_1 = 10 \text{ K} \ll \Theta_D$ and $T = T_2 = 600 \text{ K}$, assuming that only sound modes contribute at $T = T_1$ and that complete equipartition is achieved at $T = T_2$.

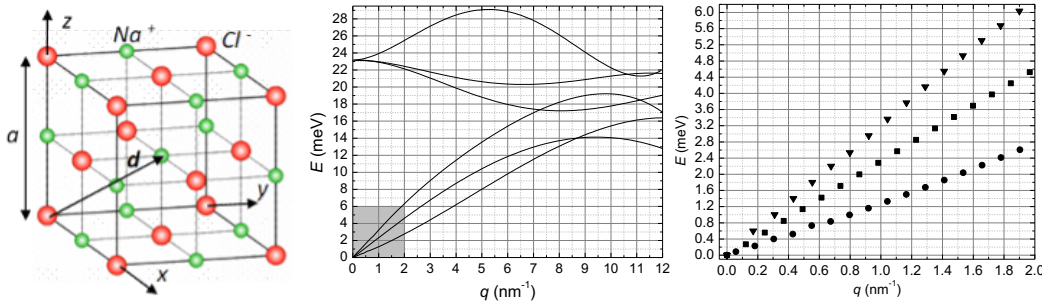


Fig. 1.

Exercise 2. Consider a two-dimensional honeycomb lattice (see left panel of Fig. 2) with lattice parameter $a = 0.425 \text{ nm}$, whose inequivalent sites are occupied by two different atoms, A and B, respectively. Both atoms have outermost s -type orbitals, with atomic energies $\varepsilon_A = -3.65 \text{ eV}$ and $\varepsilon_B = -4.15 \text{ eV}$, respectively. Assume that the electron bands of the given system can be described within the tight-binding approximation, with nearest-neighbor transfer integral $\gamma = 0.75 \text{ eV}$. All other transfer integral and all overlap integral are negligible. Two electrons per unit cell are present.

1. [5 points] Determine the tight-binding expression of the valence and conduction band, $\varepsilon_v(\mathbf{k})$, and $\varepsilon_c(\mathbf{k})$, where $\mathbf{k} = (k_x, k_y)$ is the two-dimensional wave vector.
2. [5 points] Calculate the values of the bands at the high-symmetry points Γ, K, M of the first Brillouin zone (see right panel of Fig. 2, the side of the hexagonal first Brillouin zone is $b = \frac{4\pi\sqrt{3}}{9a}$).
3. [5 points] Show that the maximum of the valence band and the minimum of the conduction band are located at one of the high-symmetry points, and determine the band gap E_g .

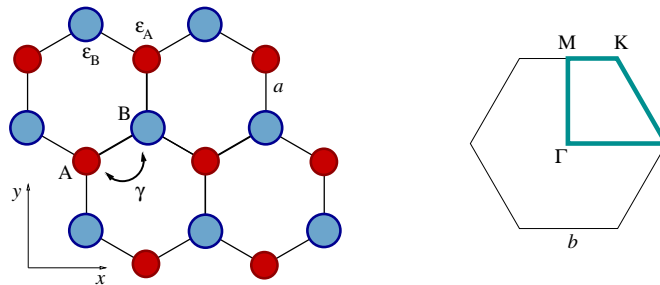


Fig. 2.

[Note that 1 eV corresponds to an energy of $1.602 \times 10^{-19} \text{ J}$; the Planck constant is $\hbar = 1.055 \times 10^{-34} \text{ J}\cdot\text{s}$; the Boltzmann constant is $\kappa_B = 1.381 \times 10^{-23} \text{ J/K}$].

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Exercise 1.

1. For NaCl, in a conventional unit cell with volume a^3 we have 4 (i.e., $\frac{1}{8} \times 8 + \frac{1}{2} \times 6$) Na and Cl atoms. Consequently

$$a = \left[\frac{4(M_{\text{Na}} + M_{\text{Cl}})}{\rho} \right]^{1/3} = 0.564 \text{ nm.}$$

The volume Bravais lattice point density is

$$n = \frac{4}{a^3} = 2.23 \times 10^{28} \text{ m}^{-3},$$

and the volume atomic density is $\mathcal{N} = 2n = 4.46 \times 10^{28} \text{ m}^{-3}$.

2. Taking the ratio between the phonon energy and the wavevector in the linear region of the dispersion curves, one obtains

$$\begin{aligned} E(q = 1.5 \text{ nm}^{-1}) = 2.00 \text{ meV} &\Rightarrow v_{t1} = 2025.7 \text{ m/s}, \\ E(q = 1.5 \text{ nm}^{-1}) = 3.44 \text{ meV} &\Rightarrow v_{t2} = 3484.2 \text{ m/s}, \\ E(q = 1.5 \text{ nm}^{-1}) = 4.81 \text{ meV} &\Rightarrow v_{\ell} = 4871.9 \text{ m/s}, \end{aligned}$$

as the velocity of the two transverse and of the longitudinal sound modes. Then,

$$v_{\Gamma-\kappa} = \left[\frac{1}{3} \left(\frac{1}{v_{t1}^3} + \frac{1}{v_{t2}^3} + \frac{1}{v_{\ell}^3} \right) \right]^{-1/3} = 2699 \text{ m/s.}$$

Hence,

$$\Theta_D = \frac{\hbar v_D}{\kappa_B} (6\pi^2 n)^{1/3} = 227 \text{ K},$$

where, according to the text, v_D was identified with $v_{\Gamma-\kappa}$.

3. The low-temperature specific heat of the crystal is dominated by the sound modes, so at $T = T_1 = 10 \text{ K}$ we can write

$$c_v(T_1) = 234 \left(\frac{T_1}{\Theta_D} \right)^3 n \kappa_B = 6.23 \times 10^3 \text{ J/(K} \cdot \text{m}^3).$$

At $T = T_2 = 600 \text{ K}$ the text suggests that complete equipartition is achieved, therefore we can use the Dulong-Petit formula $c_v(T_2) = 3\mathcal{N}\kappa_B = 6n\kappa_B = 1.85 \times 10^6 \text{ J/(K} \cdot \text{m}^3)$.

Exercise 2.

1. Let $\mathbf{h} \equiv a(\frac{\sqrt{3}}{2}, \frac{1}{2})$, $a(-\frac{\sqrt{3}}{2}, \frac{1}{2})$, $a(0, -1)$ be the vectors that locate the three neighboring B atoms of an A atom taken as the origin, and

$$\Gamma_{\mathbf{k}} \equiv \gamma \sum_{\mathbf{h}} e^{i\mathbf{k}\cdot\mathbf{h}} = 2\gamma e^{iak_y/2} \cos\left(\frac{\sqrt{3}ak_x}{2}\right) + \gamma e^{-iak_y}.$$

with $\Gamma_{-\mathbf{k}} = \Gamma_{\mathbf{k}}^*$. Then, the coefficients of the linear combination of atomic orbitals of A and B atoms that contribute to the valence and conduction band, b_A and b_B , obey the set of equations

$$\begin{cases} (\varepsilon_A - \varepsilon_{\mathbf{k}}) b_A - \Gamma_{\mathbf{k}} b_B = 0, \\ -\Gamma_{\mathbf{k}}^* b_A + (\varepsilon_B - \varepsilon_{\mathbf{k}}) b_B = 0, \end{cases}$$

that admits nontrivial solutions only if the energy $\varepsilon_{\mathbf{k}}$ fulfills the eigenvalue equation $\varepsilon_{\mathbf{k}}^2 - (\varepsilon_A + \varepsilon_B)\varepsilon_{\mathbf{k}} + \varepsilon_A\varepsilon_B - |\Gamma_{\mathbf{k}}|^2 = 0$. Thus,

$$\varepsilon_{\mathbf{k}} = \frac{\varepsilon_A + \varepsilon_B}{2} \pm \sqrt{\left(\frac{\varepsilon_A - \varepsilon_B}{2}\right)^2 + |\Gamma_{\mathbf{k}}|^2}.$$

The conduction band is the solution with the + sign, the valence band is the solution with the - sign.

2. We have

$$|\Gamma_{\mathbf{k}}|^2 = 4\gamma^2 \cos^2\left(\frac{\sqrt{3}ak_x}{2}\right) + 4\gamma^2 \cos\left(\frac{3ak_y}{2}\right) \cos\left(\frac{\sqrt{3}ak_x}{2}\right) + \gamma^2 \equiv G_{\mathbf{k}}.$$

The coordinates of the high symmetry points of the first Brillouin zone are: $\Gamma = (0, 0)$, $K = b\left(\frac{1}{2}, \frac{\sqrt{3}}{2}\right)$, $M = b\left(0, \frac{\sqrt{3}}{2}\right)$. Then,

$$G_{\mathbf{k}=\Gamma} = 9\gamma^2 = 5.0625 \text{ eV}^2, \quad G_{\mathbf{k}=K} = 0, \quad G_{\mathbf{k}=M} = \gamma^2 = 0.5625 \text{ eV}^2$$

Hence

$$\varepsilon_v(\mathbf{k} = \Gamma) = -6.16 \text{ eV}, \quad \varepsilon_v(\mathbf{k} = K) = -4.15 \text{ eV}, \quad \varepsilon_v(\mathbf{k} = M) = -4.69 \text{ eV},$$

and

$$\varepsilon_c(\mathbf{k} = \Gamma) = -1.64 \text{ eV}, \quad \varepsilon_c(\mathbf{k} = K) = -3.65 \text{ eV}, \quad \varepsilon_c(\mathbf{k} = M) = -3.11 \text{ eV}.$$

3. Since under the square root in the expression for the conduction and the valence bands there is the sum of two squares, the maximum of the valence band and the minimum of the conduction band correspond to the minimum of $|\Gamma_{\mathbf{k}}|^2 \equiv G_{\mathbf{k}} \geq 0$. This is located at the K point, where $G_{\mathbf{k}=K} = 0$, hence

$$E_g = \varepsilon_c(\mathbf{k} = K) - \varepsilon_v(\mathbf{k} = K) = \varepsilon_A - \varepsilon_B = 0.5 \text{ eV}.$$