Solid State Physics

Exam Questions

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1. Determine the basis vectors of the primitive unit cell of the CuCl crystal. What Bravais lattice underlies this lattice? Specify the Cartesian coordinates of the basis vectors and all atoms inside the primitive elementary cell. Determine the space group number for the CuCl lattice. Calculate the volume of a primitive elementary cell.

The primitive unit cell of a CuCl crystal is a simple cubic unit cell, which has lattice points at the corners of a cube with side length

$a = 5,4057$ Å.

Basis vectors of a cubic unit cell:

$\vec{a}_1 = (a, 0, 0)$
$\vec{a}_2 = (0, a, 0)$
$\vec{a}_3 = (0, 0, a)$

Bravais lattice: face centered cubic

There are 8 atoms in the primitive elementary cell, whose Cartesian coordinates are:

Cu_1 : (0.0   , 0.0   , 0.0   )
Cu_2 : (0.0   , 2.7029, 2.7029)
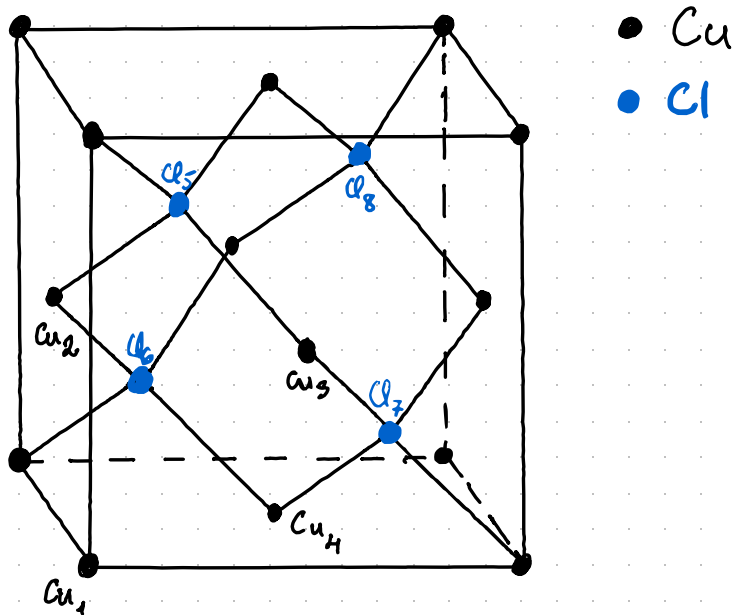Cu_3 : (2.7029, 0.0   , 2.7029)
Cu_4 : (2.7029, 2.7029, 0.0   )

(all of the distances are in Å)

$Cl_5 : (1.3514, 1.3514, 4.0543)$

$Cl_6 : (1.3514, 4.0543, 1.3514)$

$Cl_7 : (4.0543, 1.3514, 1.3514)$

$Cl_8 : (4.0543, 4.0543, 4.0543)$

● Cu

● Cl

Space group :   216. $F\bar{4}3m$

Volume of a primitive elementary cell :

$$\vec{a}_1 = \left(0, \quad \frac{a}{2}, \quad \frac{a}{2} \right)$$
$$\vec{a}_2 = \left(\frac{a}{2}, \quad 0, \quad \frac{a}{2} \right)$$
$$\vec{a}_3 = \left(\frac{a}{2}, \quad \frac{a}{2}, \quad 0 \right)$$

$$\vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) =$$

$$= \left(0, \frac{a}{2}, \frac{a}{2}\right) \cdot \begin{vmatrix} \vec{i} & \vec{j} & \vec{k} \\ \frac{a}{2} & 0 & \frac{a}{2} \\ \frac{a}{2} & \frac{a}{2} & 0 \end{vmatrix} = \left(0, \frac{a}{2}, \frac{a}{2}\right) \cdot$$

$$\cdot \left[\left(0 - \frac{a^2}{4}\right)\vec{i} + \left(\frac{a^2}{4} - 0\right)\vec{j} + \left(\frac{a^2}{4} - 0\right)\vec{k} \right] =$$

$$= \left(0, \frac{a}{2}, \frac{a}{2}\right) \cdot \left(-\frac{a^2}{4}, \frac{a^2}{4}, \frac{a^2}{4}\right) =$$

$$= 0 + \frac{a}{2} \cdot \frac{a^2}{4} + \frac{a}{2} \cdot \frac{a^2}{4} = \frac{a^3}{8} + \frac{a^3}{8} = \frac{a^3}{4}$$

$$V_0 = \left| \vec{a}_1 \cdot (\vec{a}_2 \times \vec{a}_3) \right| = \frac{(5,4057\,\text{Å})^3}{4} \approx$$

$$\approx 39,491\,\text{Å}^3$$

2. Ionic chemical bond - explanation.

Potential energy for ionic interaction. Long-range Coulomb attraction, formulas for calculation. Madelung constant and energy. The nature of the repulsive forces, the formula for calculation. Ionicity of the chemical bond.

In ionic crystals, atoms can be viewed as a set of point charges, such as the Cs and Cl ions in CsCl for example. These ions have incomplete electron shells. In the process of forming an ionic bond, a single valence electron from the outer shell of Cs migrates to the Cl atom. As a result we obtain Cs and Cl ions with completely filled electron shells. The electrons in an ionic crystal are highly localized and found in the valence band. A large amount of energy, more than $8 eV$, is required to transfer an electron to the conducting zone,

are remove it from the Cl atom. This is why
ionic crystals are dielectrics. The interaction
energy between ions i and k can be expressed as:

$$E_{i,k} = \pm \frac{Z_i Z_k c^2}{4 \pi \varepsilon_o r_{i,k}} + \frac{b}{r_{i,k}^m}$$

The first term in the equation represents the
classical Coulomb interaction. Due to the fact
that in ionic crystals the minimum dis-
tance between ions with opposite charge
signs is less than between ions with the
same charge sign, the second term describes
the forces of interionic attraction. This
term is related to repulsion forces and
associated with the overlap of electron
shells of ions and Pauli exclusion prin-
ciple. In the previous equation, Z repre-
sents the dimensionless charges of ions; b
is an unknown parameter; r is the distance
between ions and m must be determined.

The potential energy of ion with number i:

$$E_i = \pm \sum_k \left(\frac{z_i \cdot z_k \cdot e^2}{4\pi \varepsilon_o \cdot r_{i,k}} + \frac{b}{r_{i,k}^m} \right) = -\frac{\alpha_M e^2}{4\pi \varepsilon_o R} + \frac{A^2}{R^m}$$

Here $A = \sum_k \frac{b}{q_{i,k}^m}$ and $\alpha_M = z_i \sum_k \frac{z_k}{q_{i,k}}$ is

called the Madelung constant.

When calculating the Madelung constant, a prob-
lem arises, which is related to the very slow
convergence of this sum. Therefore to calculate
this constant, it is necessary to use the special
mathematical Ewald method. It is based on the
idea of dividing the electrostatic interaction
energy into short- and long-range contributions.
The short-range interactions are computed directly
using a particle-particle term, while the long
range interactions are computed using a particle-
mesh term.

For Na Cl: For CsCl: For Zn S:

$\alpha_M = 1,7476$ $\alpha_M = 1,7627$ $\alpha_M = 1,638$

The total internal energy can be calculated by multiplication of E_i in the previous equation on N (number of atoms).

$$U = N\left(-\frac{\alpha_M e^2}{4\pi \epsilon_0 R} + \frac{A}{R^m}\right),$$

later we replace $\alpha_M \to \dfrac{\alpha_M}{4\pi \epsilon_0}$.

For $T = 0$, atoms are located in equilibrium positions this means that $\dfrac{dU}{dR}\Big|_{R=a} = 0$. Calculation of derivative allows to derive

$$A = \frac{\alpha_M \cdot e^2}{m} \cdot a^{m-1}$$

and substitution to the total internal energy equation we get

$$U = -\frac{N \alpha_M e^2}{a}\left(1 - \frac{1}{m}\right).$$

The compressibility of crystal can be calculated by following:

$$\frac{1}{k} = \frac{1}{V} \cdot \frac{d^2 U}{dV^2}.$$

For NaCl crystal $V = 2Na^2$ then for compressibility:

$$\beta = \frac{18a^2}{(m - Ne^2\alpha_M)}.$$

Using data for NaCl gives $m = 9,4$. This means that the overlapping of the shells leads to a very rapid increase in repulsive forces. For practical measurement of bonding energy the Born - Haber cycle can be used.

The Born - Haber cycle is a cyclic process that relates the lattice energy of an ionic compound to a series of other thermochemical quantities. These quantities can be measured experimentally, and the Born - Haber cycle can be used to calculate the lattice energy of the compound from these measurements.

3. Adiabatic approximation. Explanation and corresponding matematical apparatus.

The adiabatic approximation in quantum mechanics refers to the use of a time-scale separation between fast and slow degrees of freedom to find approximate solutions to the Schrödinger equation as product states. The Born-Oppenheimer approximation, which is used to study molecular electronic structure, assumes that electrons adapt quickly to changes in nuclear geometry and can be solved for fixed nuclear configurations. The adiabatic approximation is also used in the study of vibrational dynamics and in the separation of a Hamiltonian into a system and other methods in condensed matter problems. However, the adiabatic approximation can break down and it is important to understand its limitations in describing time-dependent quantum mechanical processes involving transitions between potential energy sources.

Let us start with Born-Oppenheimer Approximation (BOA).

The general non relativistic Schrödinger equation describing the properties of any substance is as follows

$$\hat{H}\,\Psi = E\,\Psi$$

The wavefunction $\Psi\,(e, R)$ depends on coordinates of all electrons (e) and nuclei (R). $\hat{H}$ - the Hamiltonian can be written in terms of the kinetic energy of the nuclei (N) and electrons (e) and the potential energy for the Coulomb interactions for these particles:

$$\hat{H} = \hat{T}_e + \hat{T}_N + V_{ee} + V_{eN} + V_{NN}.$$

Kinetic energy operator for all electrons in crystal:

Kinetic energy operators for all nuclei:

$$\hat{T}_e = -\frac{\hbar^2}{2 \cdot m}\sum_i \Delta_i$$

$$\hat{T}_N = -\frac{\hbar^2}{2}\sum_n \frac{\Delta_n}{M_n}$$

Potential energy for
interacting electrons:

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0} \sum_{i,j} \frac{1}{r_{ij}}$$

Potential energy for
interacting nuclei:

$$V_{NN} = \frac{e^2}{4\pi\epsilon_0} \sum_{n,m} \frac{Z_n \, Z_M}{R_{n,m}}$$

Potential energy describing the inter-
action of electrons and nuclei:

$$V_{eN} = \frac{e^2}{4\pi\epsilon_0} \sum_{i,J} \frac{Z_J}{R_{i,J}}$$

The total wave function of a many body system can
be represented by a function that depends on
coordinates of all electrons and nuclei in the system.
These coordinates are three-dimensional, so the total
wave function has a large number of parameters:

$$\Psi(\vec{q}, \vec{R}) = \Psi(x_1, x_2, \ldots, x_N, y_1, y_2, \ldots, y_N, z_1, z_1, \ldots, z_{N},$$
$$X_1, X_2, \ldots, X_{N_n}, Y_1, Y_2, \ldots, Y_{N_n}, Z_1, Z_2, \ldots, Z_{N_n})$$

Here x_i, y_i, z_i are the coordinates of electrons and
X_i, Y_i, Z_i are the coordinates of nuclei.

The general Schrödinger equation has a large number
of parameters, proportional to the Avogadro number
(10^{23}). This makes it impossible to solve or even

write down the equation. However, we can simplify the equation by making use of the fact that the mass of electrons is much smaller than the mass of nuclei, meaning that the speed of motion of the electrons is much greater than the velocity of nuclei. This allows us to use the Born–Oppenheimer approximation, which separates the motion of the electrons and nuclei and treats electrons as moving in the field of practically stationary atoms. This allows us to consider the to consider the two subsystems of the crystal separately: the mobile electrons and much slower nuclei". So we get

$$\Psi(\vec{r}, \vec{R}) = \psi(\vec{R}) \cdot \varphi(\vec{r}, \vec{R})$$

practically
immobile
nuclei
(mean field)

for electrons, to
whom nuclei seem
stationary

The kinetic energies described before require us to calculate the derivative of total wavefunction with respect to coordinates of nuclei and electrons

$$\Delta_i \, \underline{\Psi}(r,R) = \Delta_i\left(\varphi(r,R) \cdot \psi(R)\right) =$$

$$= \psi(R) \, \Delta_i \, \varphi(\mu,R)$$

$$\hat{\Delta}_n \, \varphi(\mu,R)\psi(R) = \hat{\nabla}_n \hat{\nabla}_n \, \varphi(\mu,R)\,\psi(R) =$$

$$= \hat{\nabla}_n \left(\varphi(\mu,R) \, \hat{\nabla}_n \, \psi(R) + \psi(R)\,\hat{\nabla}_n \, \varphi(\mu,R)\right) =$$

$$= \hat{\nabla}_n \, \varphi(\mu,R)\,\hat{\nabla}_n\,\psi(R) + \varphi(\mu,R)\,\hat{\Delta}_n\,\psi(R) \; +$$

$$+ \, \hat{\nabla}_n \, \psi(R)\,\hat{\nabla}_n \, \psi(R) + \psi(\mu,R)\,\hat{\Delta}_n \, \varphi(\mu,R) =$$

$$= \varphi(\mu,R)\,\hat{\Delta}_n\,\psi(R) + 2 \cdot \hat{\nabla}_n \, \varphi(\mu,R)\,\hat{\nabla}_n\,\psi(R) \; +$$

$$+ \, \psi(R)\,\hat{\Delta}_n\,\varphi(\mu,R)$$

Substitucting to the equation $\hat{T}_N \, \underline{\Psi}$:

$$\hat{T}_N \, \varphi(\mu,R)\,\psi(R) = -\frac{\hbar^2}{2}\sum_n\left[\varphi(\mu,R)\,\hat{\Delta}_n\,\psi(R) \; + \right.$$

$$\left. + \, 2\hat{\nabla}_n\,\varphi(\mu,R)\,\hat{\nabla}_n\,\psi(R) + \psi(R)\,\hat{\Delta}_n\,\varphi(\mu,R)\right] \cdot \frac{1}{M_n}$$

After substitution to $\hat{H}\underline{\Psi}$, we have :

$$\hat{H}\underline{\Psi} = \psi(R)\,\hat{T}_e \cdot \varphi(\mu,R) + V_{ee}\,\varphi(\mu,R)\,\psi(R) \; +$$

$$+ \, V_{en}\,\varphi(\mu,R)\,\psi(R) - \frac{\hbar^2}{2}\sum_n \frac{1}{M_n}\left[\varphi(\mu,R)\,\hat{\Delta}_n\,\psi(R) + \right.$$

$$+ 2 \hat{\nabla}_n \varphi(u,R) \hat{\nabla}_n \psi(R) + \psi(R) \hat{\Delta}_n \varphi(u,R)] =$$

$$= E \cdot \varphi(u,R) \cdot \psi(R)$$

After reordering:

$$\psi(R) \cdot \hat{T}_e \cdot \varphi(u,R) + V_{ee} \cdot \varphi(u,R) \cdot \psi(R) +$$
$$+ V_{eN} \varphi(u,R) \psi(R) - \frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \left[\varphi(u,R) \hat{\Delta}_n \psi(R) + \right.$$
$$+ 2 \hat{\nabla}_n \varphi(u,R) \hat{\nabla}_n \psi(R) + \psi(R) \cdot \Delta_n \varphi(u,R) \left. \right] +$$
$$+ V_{NN} \cdot \varphi(u,R) \psi(R) = E \cdot \varphi(u,R) \psi(R)$$

This equation can now be split into two parts: one describes the properties of electrons in the field of stationary nuclei and the second one describes the properties of nuclei in the average field created by electrons.

1) $$\psi(R) \cdot \hat{T}_e \cdot \varphi(u,R) + V_{ee} \cdot \varphi(u,R) \psi(R) +$$
$$+ V_{eN} \cdot \varphi(u,R) \cdot \psi(R) = \varepsilon(R) \cdot \varphi(u,R) \psi(R)$$

2) $$\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \left[\varphi(u,R) \cdot \hat{\Delta}_n \psi(R) + 2 \hat{\nabla}_n \varphi(u,R) \hat{\nabla}_n \psi(R) + \right.$$
$$+ \psi(R) \hat{\Delta}_n \varphi(r,R) \left. \right] + V_{NN} \cdot \varphi(u,R) \psi(R) +$$
$$\varepsilon(R) \cdot \varphi(u,R) \psi(R) = E \cdot \varphi(u,R) \psi(R)$$

In the first equation the total energy of electrons $(\mathcal{E}(R))$ plays the role of potential energy for nuclei.

To make use of the normalizing property $\left(\int \underline{\Psi}^*(n,R) \, \Psi(n,R) \, dV = 1 \right)$ we multiply the second equation with $\psi(\vec{n}, \vec{R})^*$, which is followed by integration over the entire crystal with respect to coordinates of electrons $\vec{n}$. So we have

$$-\frac{\hbar^2}{2} \sum_n \frac{1}{M_n} \underbrace{\left[\int \psi(n,R) \, \psi(n,R)^* \, dn^3 \right.}_{(i)} \cdot \hat{\triangle}_n \Psi(R) +$$

$$+ 2 \hat{\nabla}_n \Psi(R) \underbrace{\int \psi(n,R)^* \, \hat{\nabla}_n \psi(n,R) \, dn^3}_{(ii)} +$$

$$+ \Psi(R) \cdot \underbrace{\left. \int \psi(n,R)^* \, \hat{\triangle}_n \psi(n,R) \, dn^3 \right]}_{(iii)} +$$

$$+ V_{NN} \, \Psi(R) \underbrace{\int \psi(n,R)^* \, \psi(n,R) \, dn^3}_{(1)} +$$

$$+ \mathcal{E}(R) \Psi(R) \underbrace{\int \psi(n,R)^* \, \psi(n,R) \, dn^3}_{(i)} =$$

$$= E \, \Psi(R) \int \psi(n,R)^* \, \psi(n,R) \, dn^3$$

Naturally, we assume that wave functions for both (electrons and nuclei) are normalized:

$$\int \psi(n,R)^* \cdot \psi(n,R) \, dn^3 = 1 \; ; \; \int \Psi(R)^* \, \Psi(R) \, dR^3 = 1$$

Simplifying term (i):

$$(i) \int \Psi(u,R)^* \Psi(u,R) \, \hat{\Delta}_n \Psi(R) \, du^3 =$$

$$= \hat{\Delta}_n \Psi(R) \underbrace{\int \Psi(u,R)^* \Psi(u,R) \, du^3}_{=1} = \underline{\underline{\Delta_n \Psi(R)}}$$

Simplifying term (ii):

$$(ii) \int \Psi(u,R)^* \cdot \hat{\nabla}_n \Psi(u,R) \, du^3 = \underline{\underline{0}}$$

The integral (iii) $\int \Psi(u,R)^* \hat{\Delta}_n \Psi(u,R) \, du^3$ is called the integral of nonadiabaticity and it describes the influence of the motion of nuclei on the states of electrons.

Due to the large difference in the masses of electrons nuclei (high electron mobility and slow motion of nuclei) the second order effects are very weak. Meaning $\hat{\Delta}_n \Psi(u,R) \approx 0$.

So the equation for nuclei looks like so:

$$\boxed{\hat{T}_N \Psi(R) + V_{NN}(R) \cdot \Psi(R) = \left(\bar{E} - \epsilon(R)\right) \Psi(R)}$$

The first equation for electrons can be simplified in a similar manner, but this time we multiply by $\Psi(R)^*$ and integrate over the nuclei coordinates $\vec{R}$. This gives us an equation for electrons:

$$\hat{T}_e \cdot \varphi(u,R) + V_{ee}(u) \cdot \varphi(u,R) + V_{eN}(u,R) \cdot \varphi(u,R) =$$
$$= \varepsilon(R) \cdot \varphi(u,R)$$

So, as we can see, the general problem of quantum mechanics for a crystal can be divided into two subtasks / equations (properties of electronic subsystem; description of the motion of nuclei).

It is very important to note that each nucleus moves in the field created by all other nuclei and in the mean field created by all electrons. The energy of electrons plays the role of potential energy for nuclei (partly).

For the equation of the nuclei
$$\hat{T}_N \Psi(R) + U(R) \cdot \Psi(R) = E \Psi(R),$$
where $U(R) = V_{NN}(R) + \varepsilon(R),$

the potential energy can be expanded into
a Taylor power series in the terms of displacement of nuclei with number k from equilibrium positions u_k

$$U = U(0) + \sum_k \frac{dV}{du_k}\Big|_{u=0} \cdot u_k + \frac{1}{2} \sum \frac{d^2V}{du_k \, du_k'}\Big|_{u=0} u_k \, u_k' + \ldots$$

The k-index includes the atom number and the $x, y,$ or z offset direction. In harmonic approximation

$$U = \frac{1}{2} \cdot \sum_k \frac{d^2V}{du_k \, du_{k'}}\Big|_{u=0} \cdot u_k \cdot u_k' = \frac{1}{2} \sum_k \Phi_{kk'} u_k \cdot u_k'$$

$\Phi_{kk'}$ - dynamical matrix or matrix of force constants (elastic coefficients for the spring connecting atoms k and k'). This matrix can be diagonalized using normal coordinates:

$$A_q = \sum_k C_k^q u_k \quad \text{in this case} \quad U = \frac{1}{2} \sum_q \omega^2(q) \cdot A_q^2$$

and Schrödinger equation in normal coordinate representation is

$$-\hbar^2 \frac{\partial^2 \psi^2}{\partial A_q^2} + \frac{1}{2} \sum_q \omega^2(q) \cdot A_q^2 \, \psi_q = 0.$$

Here q is a number of an harmonic oscillator. This can be solved using standard methods of Q.M.