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Chapter 1

Excitons in cuprous oxide

This chapter is devoted to a general description of excitons. One of the keynotes of the chapter is excitonic Bose-Einstein condensation: when the gas, consisting of bosons is at sufficiently low temperature all the particles condense into the lowest accessible quantum state forming a single macroscopic quantum state, resulting in a new form of a matter.

In addition, the optical properties of excitons in cuprous oxide ($\text{Cu}_2\text{O}$) created by photoexcitation are discussed. The absorption spectra show that the excitons in $\text{Cu}_2\text{O}$ can be well understood in terms of the hydrogen atom model with only a slight modification. Finally, it is shown how one can retrieve information on thermodynamic gas parameters from the luminescence spectra.
1.1. General description of excitons.

As mentioned in the introduction, the possibility of the excitation of charges in a crystal lattice, which is not connected with the electrical conductivity of the crystal, was proposed by Yakov I. Frenkel in 1931, [1]. Frenkel suggested that photon absorption may lead to a charge neutral quasi-particle excitation of the electronic system: the exciton, [1, 2].

Using an incident photon, one can excite an electron in a semiconductor to the conduction band, leaving a hole in the valence band. This electron-hole pair may be bounded by Coulomb interaction to form an integer spin particle, called exciton. This system can be modeled as a hydrogen-like atom in which the relative motion of the electron and the hole can be described by an excitonic Bohr radius which is proportional to the square of the principle quantum number. For an excitonic system with elementary charges $e$ in a medium with dielectric constant $\varepsilon$, and reduced mass $\mu$, the ground state Bohr radius is given by:

$$a_B = \frac{\hbar^2}{\mu (e^2/\varepsilon)}, \quad \text{(1.1)}$$

There are two types of excitons which are characterized by the ratio between the excitonic Bohr radius $a_B$ and the lattice constant $l$: Frenkel and Wannier-Mott excitons. Frenkel excitons have a Bohr radius of the order of the lattice constant or smaller. Such exciton is strongly bound and usually localized on one site. The electron and the hole do not move independently. In contrast, a the Bohr radius of a Wannier-Mott exciton is much larger than the lattice constant, therefore it has a smaller binding energy and is delocalized over a number of sites. Both the electron and the hole are mobile. For this type of exciton there are atoms inside the exciton orbit which cause the screening of the Coulomb interaction to $-e^2/\varepsilon r^2$, leading, for instance, Eq. 1.1.

In the excitonic system, the Coulomb interaction binding the electron and the hole decreases the energy of the pair compare to the non-interacting pair. The electron and the hole can be treated as two interacting particles with masses $m_e^*$, $m_h^*$, respectively. The Hamiltonian can be written as [3]:

$$H = -\frac{\hbar^2 \nabla_e^2}{2m_e^*} - \frac{\hbar^2 \nabla_h^2}{2m_h^*} - \frac{e^2}{\varepsilon |r_e - r_h|} + \frac{\hbar^2}{2\mu} \frac{\ell(\ell+1)}{r^2}, \quad \text{(1.2)}$$
where $\varepsilon$ is the lattice dielectric constant, $l$ is the angular momentum quantum number and $r_e$ and $r_h$ are the positions of the electron and the hole, respectively. The corresponding eigen values form a series of exciton energies given by:

$$E_n = E_G - \mu \left( \frac{e^2}{\varepsilon} \right)^2 + \frac{\hbar^2 k^2}{2M} + \frac{\hbar^2 \ell (\ell + 1)}{2 \mu r^2}, \quad (1.3)$$

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}, \quad M = m_e^* + m_h^*$$

Here $E_G$ is the band-gap energy, the second term is the exciton binding energy and the third term is the kinetic energy of exciton of a wave vector $k$. From the Eq. 1.3, a series of sharp peaks can be expected in the exciton absorption spectra (that is, when optical transitions are allowed, see §1.2).

The exciton creation can be described in terms of a band theory. A schematic diagram of an exciton creation and recombination processes is shown in Fig. 1.1. A pure semiconductor has, at zero temperature, no mobile charge carriers. The valence band states are completely filled with electrons and the conduction band is completely empty. Photons with energy $h \nu$ exceeding the semiconductor band-gap $E_G$, create non-equilibrium electrons in the conduction band and the holes in the valence band which can bind into excitons (channel A on Fig. 1.1). Excitons can also be formed directly via the transitions from the valence band to the exciton states (channel B on Fig. 1.1). Once formed in a relatively pure crystal, the excitons behave as mobile particles with a finite lifetime. The thermal relaxation as well as the diffusivity of excitons will be discussed in §2.2.

Excitons may make themselves visible by decaying. The radiative recombination of the electron and the hole back to the ground-state (channel C on Fig. 1.1) produces a photon with an energy:

$$h \nu = E_G - E_{ex}, \quad (1.4)$$

Moreover, the recombination may also take place together with the phonon assistance (channel D):

$$h \nu = E_G - E_{ex} + E_k \pm E_p, \quad (1.5)$$

where $E_k$ is the exciton kinetic energy and $E_p$ is the energy of the phonon and “+“ and “-“ corresponds to anti-Stokes and Stokes processes, respectively. Momentum conservation requires:
Fig. 1.1. Different ways of exciton creation are possible: process A, an electron is excited from the valence band to a conduction band. It may decay either radiatively or non-radiatively to an excitonic state. Process B, direct exciton creation. Process C, direct exciton recombinatio. Process D, phonon-assisted recombination.

\[
\begin{align*}
\vec{k} &= \vec{k}_{\text{photon}} \quad \text{(direct transition)} \\
\vec{k} &= \vec{k}_{\text{photon}} + \vec{k}_{\text{phonon}} \quad \text{(phonon-assisted),} \quad (1.6)
\end{align*}
\]

The direct process can only occur for an exciton with a momentum matching that of the emitted photon, yielding a sharp luminescence line at nearly zero kinetic energy. The phonon-assisted process, on the other hand, samples all of the occupied exciton states for the exciton momentum is easily absorbed by the optical phonon.

It is important to note that the symmetries of the electronic and the vibrational states are crucial to the relaxation properties of the exciton – in particular, their lifetime and scattering rates. A detailed discussion of this can be found in §3.1.3, in particular for the exciton transitions in cuprous oxide.
3.2. Exciton gas as a Bose gas.

The exciton, being composed of two fermions, is an integral-spin particle, i.e. a composite boson. The quantum statistical rules for a boson is that its probability of being scattered into the state of wavevector $k$ is proportional to $1 + f_k$, where $f_k$ is the occupation number of the state. In other words, the likelihood of a boson being scattered into a given state is enhanced by the other bosons already occupying that state. It can be easily shown that this “stimulated” scattering leads to the Bose-Einstein distribution function:

$$f_k = f(E) = \frac{1}{e^{\frac{E-\mu}{k_B T}} - 1}, \quad (1.7)$$

where $E = \frac{\hbar^2 k^2}{2m}$ is the kinetic energy of an exciton and $\mu$ is the chemical potential, which is measured with respect to the total kinetic energy of the exciton at $E=0$ and determined by the condition:

$$\sum_k f_k = N, \quad (1.8)$$

where $N$ is the total number of excitons in the system.

For a macroscopic volume, the number of plane-wave states per unit energy for the ideal non-interacting gas has the form $D(E) = C E^{1/2}$. Therefore, the number of excitons per unit energy is given by the product of the density of states and the occupation number $f(E)$:

$$N(E) = C \frac{E^{1/2}}{e^{\frac{E-\mu}{k_B T}} - 1}, \quad (1.9)$$

If $N$ excitons occupy a volume $V$, then we can determine $C$ from the usual counting of $k$ states, [4]:

$$C = \frac{gV}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{\frac{3}{2}}, \quad (1.10)$$

where $g$ is the spin multiplicity. The constraint Eq. 1.8 may be re-stated as:
In terms of the gas density, \( n = \frac{N}{V} \), we can, finally, write:

\[
N = \int N(E) dE, \quad (1.11)
\]

For a given density and temperature, Eq. 1.12 fixes the chemical potential \( \mu \) of the exciton gas. By defining \( \varepsilon = \frac{E}{k_B T} \) and the dimensionless chemical potential \( \alpha = -\frac{\mu}{k_B T} \), Eq. 1.12 can be written in terms of a dimensionless integral as:

\[
n = \frac{g}{4\pi^2} \left( \frac{2m}{\hbar^2} \right)^{3/2} \int_0^{\infty} \frac{E^{1/2}}{e^{E/\varepsilon - \mu/k_B T} - 1} dE, \quad (1.12)
\]

For a given density and temperature, Eq. 1.12 fixes the chemical potential \( \mu \) of the exciton gas. By defining \( \varepsilon = \frac{E}{k_B T} \) and the dimensionless chemical potential \( \alpha = -\frac{\mu}{k_B T} \), Eq. 1.12 can be written in terms of a dimensionless integral as:

\[
n = n_Q \frac{2}{\pi^{1/2}} \int_0^{\infty} \frac{e^{\varepsilon^{1/2}}}{e^{\varepsilon + \alpha} - 1} d\varepsilon
\]

\[
n_Q = g \left( \frac{mk_B T}{2\pi\hbar^2} \right)^{3/2}, \quad (1.13)
\]

where \( n_Q \) is the “quantum density”, at which the thermal de’Broglie wavelength of the particles equals the inter-particle spacing.

Several examples of the shape of the kinetic energy distribution for a given \( \mu \) and \( T \) are presented in Fig. 1.2. In Fig. 1.2 we plot Eq. 1.9 at a fixed temperature \( T \) as the density of the gas is hypothetically increased. At low densities, the chemical potential is large and negative. This reduces the distribution in Eq. 1.9 to the density-independent shape given classical Maxwell-Boltzman distribution. As we increase \( n \), the chemical potential approaches zero: the spectrum becomes more sharply peaked.

Surprising things happen when more particles are added to the system at a fixed temperature. At some point the density will be reached where \( \mu \) becomes 0. The integral in Eq. 1.12 is still finite. In ideal system, the number of particles in the ground state is proportional to \(-g/\alpha\), where \( \alpha \) is a dimensionless chemical potential. For a realistic volume, the first excited \( k \)-state will also have a large occupation number, but considerably fewer particles than the ground state, due to the sharply peaked distribution function. This effect in which thermodynamic equilibrium of the ideal Bose gas forces a macroscopic number of particles into the lowest state is the Bose-Einstein condensation (BEC).
The phase boundary for BEC of the Bose gas is determined by setting chemical potential in Eq. 1.12 to zero, yielding:

\[ n_{\text{BEC}} = 2,612n_0 = 2,612g \left( \frac{mk_B}{2\pi \hbar^2} T \right)^{\frac{3}{2}}, \quad (1.14) \]

It is obvious from Eq. 1.14, that for a given gas density, Bose-Einstein condensation is expected to be reached at much higher temperatures in an exciton system than in a gas of atoms, due to the light mass of the excitons.

Theories of excitonic condensation (and superfluidity) have been given by Keldysh and Kozlov [5], Haug and Hanamura [6]. The theory of Keldysh and Kozlov [5] discusses the system of the degenerate electrons and the holes of the arbitrary density. At high densities the gas-liquid type phase transition of exciton gas into an electron-hole Fermi liquid is possible - the bound state of a macroscopically large number of electrons and holes, [7-10]. The electron-hole liquid is similar to the metallic hydrogen or alkali metals. Unlike the

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**Fig. 1.2. The shape of the kinetic energy distribution at a fixed temperature (T=10K) but for a different chemical potential values.**
common metals, in the electron-hole liquid not only the electrons but also the holes are Fermi degenerate. At low temperatures the electron-hole liquid transforms to an “excitonic insulator” phase, [5, 11, 12]. In this two-Fermi-liquid state the collective pairing of the electrons and the holes in the vicinity of Fermi surfaces arises. This process is similar to the Bardeen-Cooper-Schreiffer pairing in superconductors (BCS state). This pairing should manifest itself in the appearance of the energy gap around the Fermi surface. In that sense, the excitonic insulator state in the non-equilibrium electron-hole system is a coherent BEC state of the high-density excitons, as the superconducting state is a coherent BEC state of Cooper pairs.

Haug and Hanamura [6] treated the “condensation problem” in the spirit of the Bogoliubov’s model in which excitons are viewed as approximate point bosons with a some interaction with each other. Several assumptions are implicit in this model. Work of Haug and Hamura based on assumption that the excitons have repulsive interaction, otherwise, at increasing densities excitons aggregate into a complex system. As an example, the same problem prevents BEC of a normal gas of hydrogen molecules. Further, the lifetime of the excitons should be longer than time required to establish a true equilibrium with a lattice. And finally, the last assumption is in a negligible interaction between excitons and the radiation field. If the exciton-photon coupling is strong, then the true elementary electronic excitations of the crystals are better described in terms of polaritons [13].

### 3.3. Exciton gas in cuprous oxide.

The optical spectrum of Cu$_2$O is remarkable since all classes of transitions predicted by the theory for exciton spectra are observed in different parts of the energy region. It might therefore not be surprising that cuprous oxide was the favorite semiconductor among many physicists in the pre-silicon era. Cuprous oxide crystallizes in a cubic lattice (lattice constant of 4.3Å) with two molecules per unit cell and space group symmetry $O_h^4$. The side symmetries of copper and oxygen are $D_{3d}$ and $T_d$, respectively, [14]. For convenience the crystal structure is presented in Fig. 1.3a. The band structure of Cu$_2$O contains in total 10 valence bands and 4 conduction bands (Fig. 1.3b shows the lowest two conduction bands, and the highest two valence bands at the zone center), [15]. The direct energy gap between the highest valence and lowest conduction bands is 2.17eV (at T=10K), [16, 17]. The lowest conduction band $\Gamma_6^<$ is formed by Cu 4s orbitals and the highest valence band $\Gamma_7^>$ is formed by Cu 3d orbitals.

Holes and the electrons in these four bands interact through a screened Coulomb interaction and form exciton series in the energy range of visible light.
Fig. 1.3. (a) Crystal structure of Cu$_2$O. Dark grey balls represent oxygen and light grey one - copper. (b) Energy band structure of Cu$_2$O near the zone center. The exciton 1s level lays 150 meV below the first conduction band.

The yellow series are derived from the highest valence band and the lowest conduction band ($V_1$-$C_1$). The green series is related to the gap $V_2$-$C_1$, the blue series to $V_1$-$C_2$ and the indigo series to the gap $V_2$-$C_2$.

For the yellow series the energy gap is direct, but dipole forbidden. To see if a transition can be made we should calculate the absorption coefficient:

$$\alpha \propto \sum_i \langle \Gamma_f | D_i | \Gamma_i \rangle \pi \alpha,$$

where $\Gamma_f$ and $\Gamma_i$ correspond to the final and the initial states, respectively, with parity $\pi$, and $D_i$ proportional to $p_i$ for the dipole operator and to $p_i^2$ for the quadrupole operator, [18]. For the Cu$_2$O the lowest conduction band and the highest valence band have the same positive parity. The dipole operator has a negative parity. When we integrate over the space, the absorption coefficient will therefore always be zero. The quadrupole operator has a positive parity. This means that the matrix element can be non-zero, which is the case for the $V_1$-$C_1$ transition.

For excitonic levels the total parity is determined by the product of the parities of the valence band, the conduction band and the exciton envelope wave function. Since both
valence and conduction bands have a positive parity, the total parity is determined by the
parity of the exciton level. For an excitonic $s$-state, the parity is positive, and the transition
to the ground state is dipole forbidden, but quadrupole allowed. For a $p$-state, the parity is
negative, and the transition to the ground state is dipole allowed.

Due to spin-orbit interaction, every excitonic level is split into a triplet ortho level ($J=1$) and a singlet para level ($J=0$). The corresponding wave functions of the ortho and
para levels can be written as follows:

$$
|O_{-1}\rangle = |\downarrow_e \downarrow_h\rangle \\
|O_{0}\rangle = \left( |\uparrow_e \downarrow_h\rangle + |\downarrow_e \uparrow_h\rangle \right)/\sqrt{2} \\
|P\rangle = \left( |\uparrow_e \downarrow_h\rangle - |\downarrow_e \uparrow_h\rangle \right)/\sqrt{2}, \quad (1.16)
$$

For the 1s exciton state the ortho-paraexciton energy splitting is 12 meV. Because only
transitions between levels can be made when $\Delta J=\pm 1$, decay from any paraexciton state to
the ground state is forbidden for all orders of perturbation. This suggests that theoretically
paraexcitons can live very long. Practically, the lifetime is limited by the defects and
impurities (§2.2 and references therein). For 1s orthoexcitons decay to the ground state is
quadrupole allowed. However, the lifetime of 1s orthoexcitons is mainly limited by
transition to the lower lying paraexciton state and reveal a value around 1,2 ns (§2.1 and
references therein).

Almost 60 years ago Hayashi [19, 20] observed a series of hydrogen-like lines in the
absorption spectrum of solid cuprous oxide which was cooled below the room temperature.
During the same time investigators from Leningrad (St-Petersburg) [21-23] and Strasbourg
[24-27] made more accurate measurements of the wavelengths of these lines over a wide
range of temperatures.

The absorption spectrum of the Cu$_2$O oxide crystal (in [100] crystallographic direction)
at $T=1.2$K is shown in Fig.1.4. Several absorption lines corresponding to transitions to the
ortho exciton $p$-states are clearly observed. All lines are superimposed on a background due
to the tail of the phonon assisted absorption to the conduction band continuum. The spectral
positions of the observed absorption lines are in good agreement the Rydberg equation (Eq.
1.17, see inset Fig. 1.4). The estimated Rydberg constant for the exciton with reduced mass
$\mu=0.34m_e$ [22, 23] in a medium with dielectric constant $\varepsilon=7.2$, [28] $R_y=94$ meV is close to
the one, obtained from the experiment $R_y=97.6$ meV.
Fig. 2.4. Optical absorption versus photon energy in cuprous oxide at 1.2K, showing a series of exciton lines for Cu$_2$O sample of [100] crystal orientation (sample was provided by A. Revcolevschi, University of Paris IV). Inset: empirical fit to the absorption peak position.

\[ E_n = E_G - \frac{\mu (e^2/\varepsilon^2)}{2\hbar^2 n^2}, \quad (1.17) \]

where \( E_G \) is the V$_1$-C$_1$ band gap at \( T=1.2 \) K. As mentioned above, the \( n=1 \) level can not be observed in absorption spectrum, since the transition to this state is only quadrupole allowed. However, one can easily observe \( n=1 \) orthoexciton luminescence (Fig. 1.5). The \( n=1 \) level energy position deviates from the hydrogen model. The \( n=1 \) exciton Bohr radius (7Å) is comparable with the lattice constant (4Å): the screening of the interaction is different then for the higher states giving the binding energy of 150 meV (binding energy at \( n=2 \) state is 90 meV).
The luminescence spectrum of Cu$_2$O at $T=1.2$ K is presented in Fig. 3.5. The sharp band (2.035 eV) is due to direct recombination of the orthoexciton. The broad spectral lines are phonon-assisted orthoexciton lines. Since there are several optical phonons with the appropriate symmetry to participate in the recombination process, each having a different energy, there are several phonon replicas observed in the luminescence spectrum. There are clear lines from phonon-assisted orthoexciton ($\Gamma_5^+$) transitions with the simultaneous excitation of $\Gamma_5^-$ (2,024 eV), $\Gamma_3^-$ (2,026), and $\Gamma_4^-$ (2,020) phonons, [29].

As it mentioned in §1.1, the phonon-assisted process samples all of the occupied exciton states, because the exciton momentum is easily absorbed by the optical phonon. The optical phonon is slightly dependent on the phonon wave vector. For the typical gas temperature of 100 K or less, the exciton wave vectors are small ($k<10^7$ cm$^{-1}$) compared to the Brillouin-zone boundary ($\sim 10^8$ cm$^{-1}$), [30]. The optical-phonon dispersion, as measured by neutron scattering [31], is negligible for these wave vectors. Therefore, the phonon-
assisted processes give an accurate replica of the energy distribution of the excitons. The observed emission band can be described by:

where \( D(E) \sim E^{1/2} \) is the density of exciton states (assuming a quadratic dispersion), and

\[
I(E') = A \int_{-\infty}^{\infty} D(x) f(x) e^{-\frac{(x-E')^2}{\Gamma^2}} dx , \quad (1.18)
\]

\( f(E) \) is either the Maxwell-Boltzmann (classical gas) or Bose-Einstein (quantum gas) distribution function. \( \Gamma \) represents the spectral resolution of the experimental setup. Fitting this equation to the experimentally observed spectrum yields an estimate for the effective exciton temperature and chemical potential. For an ideal, non-condensed, Bose gas the density of bosons is given by Eq. 1.12.

A precise determination of the Cu\(_2\)O samples chemical composition [32] shows that the amount of oxygen and copper usually deviates from a perfect stoichiometric composition. In other words, the samples will contain a certain number of copper and oxygen vacancies. The presence of these vacancies results in three characteristic luminescence bands (Fig. 1.6a): one band centered around 1.35 eV which is attributed to copper vacancies, the two higher energy bands centered around 1.71 eV and 1.51 eV are attributed to oxygen vacancies [32, 33].

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**Fig. 1.6.** (a) Vacancy spectrum of Cu\(_2\)O at T=77K (b) Electronic energy structure of Cu\(_2\)O of [100] orientaton including vacancy states (sample was provided by A. Revcolevschi, University of Paris IV). The excitation wavelength 532 nm (2.33 eV).
Oxygen vacancies $V_O$ can exist in Cu$_2$O in three states: $V_{O^{2+}}$, an unoccupied vacancy with a double positive charge with respect to the lattice; $V_{O^{2+}e}$, a one-electron vacancy, positively charged with respect to the lattice; and $V_{O^{2+}e^+e}$, a two-electron vacancy, neutral with respect to the lattice. The ground levels of these vacancies are situated above the valence band, in the forbidden energy gap, in the order indicated in Fig. 1.6b. It is assumed that the higher energy luminescence band is originating from the $V_{O^{2+}e}$ state. Within the described picture, the possibility of conversion from one type of center into another as a result of two simple processes: the trapping of either electrons or holes from the valence band.

The luminescence line at 1.35 eV (Fig. 1.6a) originates from transitions from the copper vacancy $V_{Cu}$ which is negatively charged with respect to the lattice. The purity of the sample (amount of the vacancy centers) is very critical for certain properties of the exciton gas, in particular to the lifetime of the excitons, as is discussed in §2.2.
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