

Dipole-allowed generation of the yellow-series excitons in Cu₂O due to an applied electric field

A. R. H. F. Ettema and J. Versluis

TU Delft, Department of NanoScience, Lorentzweg 1, 2628 CJ Delft, The Netherlands

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The electron bands of Cu₂O near the band gap have been calculated for the undistorted cubic crystal with O_h symmetry and a tetragonally distorted case with C_{4v} symmetry. The tetragonal structure has a distortion of the linear Cu crystal field that represents the structure of a polarized crystal in an electric field. The symmetry of the bands changes in such a way that the dipole forbidden transition of the yellow series excitons in the undistorted cubic structure becomes dipole allowed in the tetragonal structure. The energy of the excitons becomes lower in the polarized crystal. These changes in the band gap properties make it possible to create an exciton trap in thin Cu₂O films with a scanning tunneling microscopy tip while the excitons can be resonantly created with a laser via a dipole allowed transition.

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The excitons in Cu₂O have gained much attention during the last decade because of the prosperity of exciton Bose-Einstein condensation (BEC) in Cu₂O. The small mass $m_{ex} = 2.7m_0$, the small bohr radius of 7 Å, the large binding energy of 150 meV, and the long lifetime of 10 μs make the exciton system in Cu₂O a promising candidate to achieve BEC.^{1,2}

Besides the excitons in Cu₂O, the exciton system in AlGaAs multiple quantum well structures has progressed fast during the last year with respect to BEC.³ With the observation of high-density exciton lakes in in-plane potential traps, whereby the photoluminescence experiments show that the quasi-two-dimensional excitons form a statistically degenerated Bose gas.⁴ A macroscopically ordered state is observed in the luminescence ring that has a fragmentation pattern of circular structures that forms a periodic array over lengths up to 1 mm.^{5,6}

Despite the prosperous characteristics of the exciton system in Cu₂O and AlGaAs quantum wells, BEC has not been realized due to the difficulty to create sufficient excitons in order to reach the critical density needed for BEC.^{7,8} The long radiative lifetime in Cu₂O is related inversely proportional to the oscillator strength of the corresponding transition. One of the main problems in achieving the critical density in Cu₂O is given by the symmetry of the conduction-band minimum (CBM) and the valence-band maximum (VBM). The symmetry of the electron bands does not allow a dipole transition from the VBM to the CBM.⁹ Therefore different kinds of techniques have been used to circumvent this problem. In various studies the exciton properties were examined as a function of applied stress.¹⁰⁻¹² By applying stress to the semiconductor host lattice the band gap is reduced and excitons diffuse into the region of lowest energy. Although the para- and orthoexcitons show a strong mixing and the exciton energy levels show some dispersion upon stress, the bands remain in a dipole forbidden symmetry.

The yellow series excitons in Cu₂O can be formed resonantly via a quadrupole transition, a two-photon process, or a one-photon absorption accompanied with the absorption or emission of an optical phonon.¹³⁻¹⁵ It is obvious that the transition probability is strongly reduced by the simultaneous interaction of two particles with a valence-band electron in order to create an exciton.

Once approaching high exciton densities in Cu₂O, the kinetics of this exciton system become complicated due to the Auger decay process at high densities.¹⁶⁻¹⁸ This decay process occurs with a constant rate but is strongly density dependent. In order to overcome the decay rate of the excitons, an efficient and fast exciton generation process seems to be even more imperative to reach sufficient exciton densities for BEC.

In this paper we present results from band structure calculations and a group theory symmetry analysis which show that the symmetry problem to create the excitons via a dipole transition can be lifted with the Stark effect caused by an applied electric field. The electric field polarizes the crystal and distorts the crystal field of the Cu atoms resulting in a removal of the inversion symmetry. The distortion in this study is applied along the (100) axis of the crystal but the distortion can be applied in any other direction including (110) and the (111) direction. By making use of group theory compatibility tables the appropriate representations can be found for similar distortions in other directions. The energy, symmetry, and degeneracy of the bands are, due to the distortion, changed in such a way that the transition between the VBM and the CBM becomes dipole allowed. Moreover, the band gap decreases slightly by the applied field which makes it possible to create the yellow exciton series resonantly via a dipole transition and collect the excitons in a trap if thin Cu₂O films are subjected to the inhomogeneous electric field of a scanning tunneling microscopy (STM) tip.

The calculations in this study were performed using the full potential linearized augmented plane-wave (FLAPW) method of the WIEN2K code.¹⁹ This code solves the Kohn-Sham equations inside the atomic spheres and augments the numerical radial wave functions with plane waves outside the spheres. The basis set of orbitals is split in core states and valence states at an energy of 6 Ry. For the atoms in Cu₂O the O 1s, Cu 1s, 2s, and 2p form the core states that are treated inside the sphere only with a spherical potential. The radii of the muffin-tin spheres were taken 1.7 Å for both atoms. The electron-electron interactions are calculated within the generalized gradient approximation (GGA).

Without external electric field the compound Cu₂O has a cubic structure with the Cu atoms forming an fcc lattice, the

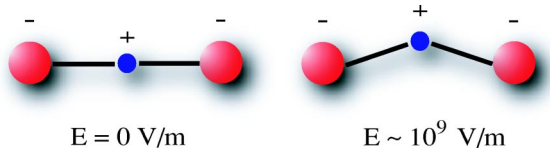


FIG. 1. (Color online) Electric-field-induced ionic polarization.

Cu atoms occupy the positions $(0,0,0)$, $(1/2,1/2,0)$, $(1/2,0,1/2)$, and $(0,1/2,1/2)$. The oxygen atoms form a bcc lattice and occupy the positions $(1/4,1/4,1/4)$ and $(3/4,3/4,3/4)$. The unit-cell axis has a length of 4.26 Å, the number of Cu_2O units is 2 ($Z=2$) and the space group is $Pn\bar{3}m$ (O_h^4).²⁰ The copper atoms are in a linear coordination surrounded by two oxygen atoms. This linear metal atom coordination is rather unusual and has only been observed for Ag_2O and Pb_2O . The linear coordination of Cu indicates that the Cu $3d_{z^2}$ states play a dominant role in the bonding mechanism. The oxygen atoms are in a tetrahedral coordination surrounded by four Cu atoms.

If Cu_2O is subjected to an external field the lattice polarizes; the fcc Cu lattice is shifted with respect to the bcc O lattice. The Cu atoms are then pulled out of the O-Cu-O axis (Fig. 1) and the quadrupole crystal field is symmetry broken. The structure of cuprite transforms under influence of an electric field in that of the tetragonal space group $P4_2nm$ (C_{4v}^4 , the Cu atoms occupy position $4c$ $(1/4,1/4,1/4 + \delta)$, $(1/4,3/4,3/4 + \delta)$, $(3/4,1/4,3/4 + \delta)$, $(3/4,3/4,3/4 + \delta)$, and the O atoms are at position $2a$ $(0,0,0)$ and $(1/2,1/2,1/2)$. The displacement δ was taken 0.1 in fractional coordinates and correspond to an externally applied electric field in the (001) direction in the order of 10^9 V m^{-1} if a relative dielectric constant of $\epsilon_r = 7.11$ is used.²¹

The calculated band structures in Fig. 2 show the three-fold degeneracy of states at the valence-band maximum in Γ of the cubic structure. The symmetry of the VBM is Γ_5^+ , while the symmetry of the CBM is Γ_1^+ . When an external electric field is applied to the crystal the ionic polarization will force the atoms in a tetragonal crystal structure of C_{4v} symmetry. This externally applied electric field splits off one band with symmetry Γ_4 , the valence-band maximum becomes twofold degenerate with symmetry Γ_5 . The CBM changes from Γ_1^+ in O_h to Γ_1 in C_{4v} .

The electric field has a strong influence on the optical properties of Cu_2O near the band gap. The WIEN2K package is capable to calculate the optical-absorption coefficient via the momentum matrix elements $M_i = \langle n' \vec{k}_i | \vec{p} \cdot \vec{e}_i | n \vec{k}_i \rangle$ between all band combinations for each k point. From this calculation the absorption coefficient of cubic Cu_2O goes to zero as the center of the Brillouin zone (BZ) is approached. In the C_{4v} symmetry case this absorption coefficient remains at a value of $\alpha \sim 1000 \text{ cm}^{-1}$ near the absorption edge which is comparable to one-tenth of the absorption of GaAs.²²

It is well known that local-density approximation band-structure calculations tend to underestimate the band gap. Also in this calculation the band gap is smaller than the experimentally determined values. The underestimation of the band gap in Cu_2O in this calculation is nearly solely due to the large dispersion of the lowest conduction band. Due to the larger dispersion of the band in the calculation the number of states per energy interval is underestimated. Therefore the underestimation of the band gap leads to an underestimation of the final density of states $|n' \vec{k}_i\rangle$ in the dipole matrix element M_i .

The WIEN2K code has an option for the “scissors method” in order to make the optical properties more comparable in energy with results from optical experiments. This method shifts the valence bands and conduction bands in energy. In the results presented here we adjusted the band gap to 2.0 eV.

In order to examine the possibilities for a dipole transition the symmetry of the final state needs to be an irreducible representation of the direct product between the initial-state representation and the representation of the $e\vec{E} \cdot \vec{r}$ dipole operator. In the cubic case the symmetry representation of the dipole operator is Γ_4^- . The irreducible representations of the direct product are

$$\Gamma_5^+ \otimes \Gamma_4^- = \Gamma_2^- \oplus \Gamma_3^- \oplus \Gamma_4^- \oplus \Gamma_5^-.$$

The representation of the conduction-band minimum (Γ_1^+) is not an element of the direct product therefore from symmetry arguments it is clear that the transition of the Γ_5^+ valence state to the Γ_1^+ conduction-band state is not dipole allowed.

From the data in Table I it becomes clear that there is only one case in which the dipole transition is allowed: for the

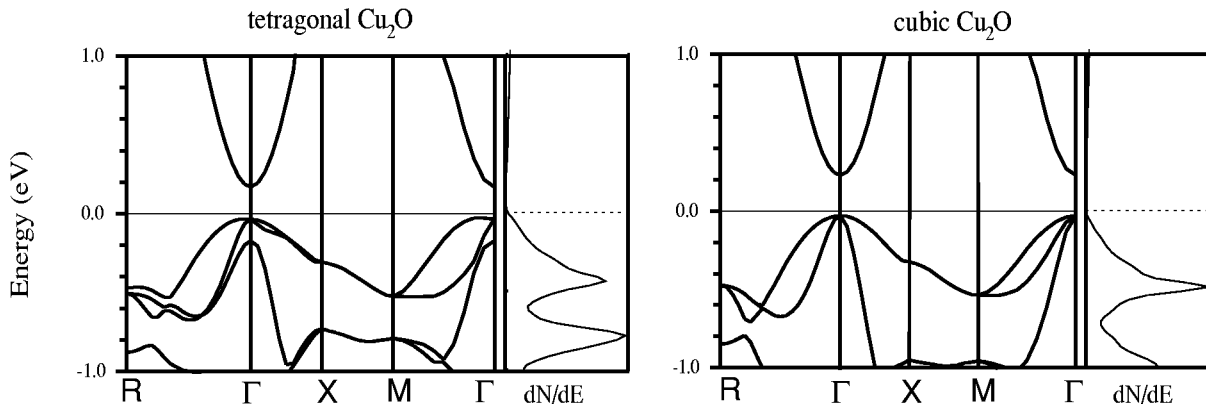
FIG. 2. Band structures of Cu_2O in an electric field (tetragonal Cu_2O) and without electric field (cubic Cu_2O).

TABLE I. Symmetry of the initial state, dipole operator, their direct product and the symmetry of a dipole allowed final state without time-inversion symmetry.

	No perturbation (O_h)	Strain field (D_{4h})	Electric field (C_{4v})
Initial state	Γ_5^+	Γ_5^+, Γ_4^+	Γ_5, Γ_4
Dipole operator(s)	$\Gamma_4^-(x,y,z)$	$\Gamma_2^-(z), \Gamma_5^-(x,y)$	$\Gamma_1(z), \Gamma_5(x,y)$
Direct product(s)	$\Gamma_5^+ \otimes \Gamma_4^- = \Gamma_2^- \oplus \Gamma_3^- \oplus \Gamma_4^- \oplus \Gamma_5^-$	$\Gamma_4^+ \otimes \Gamma_2^- = \Gamma_3^-$ $\Gamma_4^+ \otimes \Gamma_5^- = \Gamma_5^-$ $\Gamma_5^+ \otimes \Gamma_2^- = \Gamma_5^-$ $\Gamma_5^+ \otimes \Gamma_4^- = \Gamma_1^- \oplus \Gamma_2^- \oplus \Gamma_3^- \oplus \Gamma_4^-$	$\Gamma_4 \otimes \Gamma_1 = \Gamma_4$ $\Gamma_4 \otimes \Gamma_5 = \Gamma_5$ $\Gamma_5 \otimes \Gamma_1 = \Gamma_5$ $\Gamma_5 \otimes \Gamma_5 = \Gamma_1 \oplus \Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$
Final state	Γ_1^+	Γ_1^+	Γ_1

VBM and light with its polarization in the xy plane while the distorting electric field is along the z axis (see Fig. 3).

Following Elliott⁹ and taking the electron spin into account a similar table as Table I can be compiled with the symmetry representations of the initial states, the dipole operators, the direct product (possible final states) and the conduction-band minimum in Cu_2O for the cases of no perturbation, a strain field, and an external applied electric field. The data in Table II show that the only dipole allowed transitions can be found in the C_{4v} symmetry (electric-field distorted case).

The excitons in Cu_2O have been subject of interest since the first observation in 1950 by Hayashi and Katsuki.²³ Since then more studies appeared and in the last decade the excitons in Cu_2O were studied more extensively in attempts to achieve BEC. The prosperous material properties make Cu_2O a good candidate to achieve BEC at relatively high temperatures, however, the main difficulty remains the gen-

eration of sufficiently high exciton densities. The symmetry is an important factor to control the effectiveness of the generation of excitons in Cu_2O . In an experiment of Brahms and Cardona²⁴ the manipulative effect of an electric field ($10\text{--}100 \text{ keV cm}^{-1}$) on the optical transition of the yellow-series excitons has been shown. Although this experimental study did not interpret the findings with theoretical arguments, it establishes the effect of symmetry breaking on the optical transition of the yellow-series exciton and suggests the reduction of the band gap with increasing field from the phonon-assisted lines. The observations of Brahms and Cardona are in full agreement with the results presented here. The symmetry breaking of the electric field lifts the constraints for the dipole transition across the band gap. The band-structure calculations show a splitting of the VBM and an absorption coefficient similar to that of GaAs near the absorption edge. The group theory analysis explains that in both cases (with and without spin-orbit interaction) strain has no effect on the optical transition and the yellow series can only be generated resonantly with an electric field.

Although the generation of the yellow-series excitons can be achieved through an optical dipole transition, the nonzero oscillator strength reduces the lifetime of the corresponding exciton to the same extend. The electric-field manipulation in the generation of the exciton gas should therefore only be applied during the buildup of the exciton density and be switched off if the maximum density is achieved.

The energy dependence of the band gap with the electric field means that the excitons will diffuse to the place in the Cu_2O film where the electric field is strongest. Similar as in experiments where the excitons diffuse to an area in the crystal where the band gap was reduced by mechanical strain.¹⁶

We presented the results from band-structure calculations and a group symmetry analysis of the electron bands around the band gap of Cu_2O in the natural cubic structure and of a tetragonal distorted structure of Cu_2O that reflects the polarization state of Cu_2O in an electric field. The changes in the band structure upon distortion due to an externally applied electric field has consequences for the exciton condensation in Cu_2O . The reduction of the band gap opens the possibility to confine the excitons in a potential well. The change in symmetry allows a dipole transition in the tetragonal phase

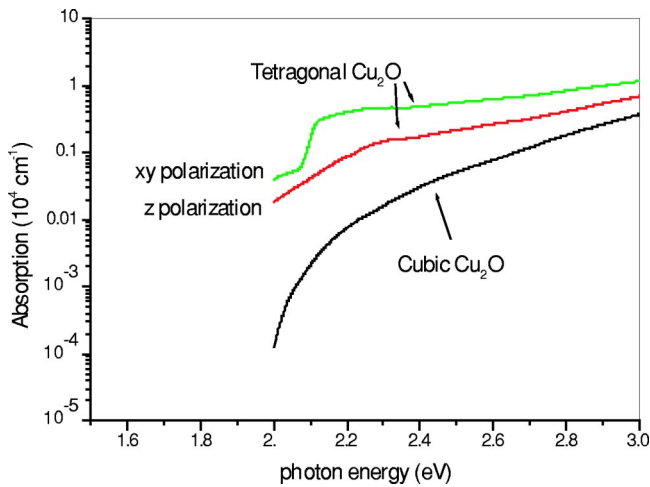


FIG. 3. (Color online) The optical absorption of the undistorted cubic phase and the tetragonal distorted phase representing Cu_2O in an electric field. The optical absorption of cubic Cu_2O becomes zero in the limit of approaching the band edge. The tetragonal case has absorption curves for the xy polarized light and z polarized light, for both polarizations the absorption is dipole allowed at the band edge. The step in the curve of the xy polarization is due to the addition of absorption from a second valence band.

TABLE II. Symmetry of the initial state, dipole operator, their direct product and the symmetry of a dipole allowed final state with time-inversion (spin) symmetry.

	No perturbation (O_h)	Strain field (D_{4h})	Electric field (C_{4v})
Initial state(s)	Γ_7^+ (yellow series) Γ_8^+ (green series)	$\Gamma_7^+, \Gamma_7^+, \Gamma_6^+$	$\Gamma_7, \Gamma_7, \Gamma_6$
Dipole operator(s)	$\Gamma_4^-(x,y,z)$	$\Gamma_2^-(z), \Gamma_5^-(x,y)$	$\Gamma_1(z), \Gamma_5(x,y)$
Direct product(s)	$\Gamma_7^+ \otimes \Gamma_4^- = \Gamma_7^- \oplus \Gamma_8^-$ $\Gamma_8^+ \otimes \Gamma_4^- = \Gamma_6^- \oplus \Gamma_7^- \oplus \Gamma_8^-$	$\Gamma_6^+ \otimes \Gamma_2^- = \Gamma_6^-$ $\Gamma_6^+ \otimes \Gamma_5^- = \Gamma_6^- \oplus \Gamma_7^-$ $\Gamma_7^+ \otimes \Gamma_2^- = \Gamma_7^-$ $\Gamma_7^+ \otimes \Gamma_5^- = \Gamma_6^- \oplus \Gamma_7^-$	$\Gamma_6 \otimes \Gamma_1 = \Gamma_6$ $\Gamma_6 \otimes \Gamma_5 = \Gamma_6 \oplus \Gamma_7$ $\Gamma_7 \otimes \Gamma_1 = \Gamma_7$ $\Gamma_7 \otimes \Gamma_5 = \Gamma_6 \oplus \Gamma_7$
Final state	Γ_6^+	Γ_6^+	Γ_6

that is forbidden in the cubic phase which is an important step in the creation of a large number of excitons. Both properties are important in achieving BEC in this system. The application of an electric field with an STM tip on a thin

Cu_2O film creates a potential well for the excitons where a high exciton density can be generated resonantly via a dipole transition by illuminating the film with laser light of a suitable wavelength.

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