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# LOCAL-FIELD AND EXCITONIC EFFECTS ON OPTICAL PROPERTIES OF CRYSTAL SURFACES

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The general theory of local-field effects on optical properties of crystal surfaces is developed. Reflectivity is calculated using the local representation of the dielectric tensor, including electron-hole interaction. Application is made to the (001) surface of a simple-cubic crystal.

## I. Introduction

The optical properties of crystal surfaces have been the object of extensive experimental investigation [1-4], but only recently their theoretical understanding is becoming satisfactory [5,6]. The importance of local-field effects has been stressed by classical (Lorentz-Lorenz) calculations [7], while large excitonic effects at surfaces are expected [8-10]. In spite of this, there is no theory giving a comprehensive account of local-field and excitonic effects on surface optical properties. The aim of this communication is to develop such a theory, describing local-field effects via the macroscopic non-local dielectric tensor, and including excitonic effects in the generalized contact-exciton picture of Hanke and Sham [11]. We will show the feasibility of these calculations and their relevance in the case of a simple-cubic crystal with nearest-neighbour interactions and surface states [9].

## II. Macroscopic Non-local Dielectric Tensor

The equation of propagation for the Fourier-transformed electric field $\vec{E}(\vec{q}_{/\!/}k_z)_{\vec{G}_{/\!/}}$ in presence of a semi-infinite crystal ( occupying the half-space z>0) can be written as:

$$-(\vec{q}_{/\!/}+\vec{k}_z+\vec{G}_{/\!/})\times(\vec{q}_{/\!/}+\vec{k}_z+\vec{G}_{/\!/})\times\vec{E}(\vec{q}_{/\!/}k_z)_{\vec{G}_{/\!/}}$$

$$=\frac{\omega^2}{c^2}\Sigma_{\vec{G}'_{/\!/}}\int_{-\infty}^{\infty}dk'_z\,\overleftrightarrow{\varepsilon}(\vec{q}_{/\!/}k_zk'_z\omega)_{\vec{G}_{/\!/}\vec{G}'_{/\!/}}\cdot\vec{E}(\vec{q}_{/\!/}k'_z)_{\vec{G}'_{/\!/}}\ , \tag{1}$$

where $\vec{q}_{/\!/}$ is the surface-plane component of the light wave-vector, $\vec{k}_z$ and $\vec{k}'_z$ are perpendicular to the surface and $\overleftrightarrow{\varepsilon}(\vec{q}_{/\!/}k_zk'_z\omega)_{\vec{G}_{/\!/}\vec{G}'_{/\!/}}$ are the Fourier-components of the microscopic dielectric tensor. The 2-dimensional periodicity has been taken into account through the 2-dimensional reciprocal lattice vectors $\vec{G}_{/\!/}$. We define the field components $\vec{E}(\vec{q}_{/\!/}k_z)_0$, with $|k_z|$ smaller than a cut wave-vector $k_c \gg \omega/c$, as macroscopic, and microscopic the others. We eliminate the latter from eqs.(1), and find the propagation equation for the macroscopic field $\vec{E}_M(\vec{q}_{/\!/}z)$:

$$\vec{\nabla} \times \vec{\nabla} \times \vec{E}_M(\vec{q}_{/\!/} z) = \frac{\omega^2}{c^2} \int_{-\infty}^{\infty} dz' \overleftrightarrow{\varepsilon}_M(\vec{q}_{/\!/}, z, z', \omega) \cdot \vec{E}_M(\vec{q}_{/\!/} z') \ . \tag{2}$$

The macroscopic non-local dielectric tensor $\overleftrightarrow{\varepsilon}_M(\vec{q}_{/\!/}, z, z', \omega)$ has Fourier-components (limited at $|k_z|, |k_z'| < k_c$) given by:

$$\overleftrightarrow{\varepsilon}^F_M(\vec{q}_{/\!/}, k_z, k_z', \omega) = \overleftrightarrow{\varepsilon}(\vec{q}_{/\!/}, k_z, k_z', \omega)_{00} - \Sigma_{\vec{G}_{/\!/}} \int d\tilde{k}_z \Sigma_{\vec{G}_{/\!/}'} \int d\tilde{k}_z'$$
$$\vec{\varepsilon}^{L}(\vec{q}_{/\!/}, k_z, \tilde{k}_z, \omega)_{0\vec{G}_{/\!/}} \tilde{\varepsilon}^{LL}(\vec{q}_{/\!/}, \tilde{k}_z, \tilde{k}_z', \omega)^{-1}_{\vec{G}_{/\!/}\vec{G}_{/\!/}'} \varepsilon^{L\rightarrow}(\vec{q}_{/\!/}, \tilde{k}_z', k_z', \omega)_{\vec{G}_{/\!/}' 0} . \tag{3}$$

Here $\varepsilon^{\rightarrow L}$ ($\varepsilon^{L\rightarrow}$) is the right-hand (left-hand) longitudinal component of the microscopic dielectric tensor, while $\tilde{\varepsilon}^{LL}(\vec{q}_{/\!/}, k_z, k_z', \omega)_{\vec{G}_{/\!/}\vec{G}_{/\!/}'}$ is its longitudinal-longitudinal component defined in the subspace of microscopic fields.

Local-field effects are formally absent from eq.(2), being embodied in the macroscopic dielectric tensor. This is the generalization to finite crystals of the bulk macroscopic dielectric constant of Adler and Wiser [13], and reduces to the latter a few layers inside the crystal [12], provided $k_c$ is chosen smaller than the half-width of the bulk Brillouin Zone in the direction perpendicular to the surface.

## III. Reflectance and Ellipsometry

The solution of eq.(2) has been carried out in [5] and [6], to first order in $\omega d/c$ (d is the depth of the surface-perturbed layer), giving the surface contribution to reflectivity coefficient, $\Delta R$:

$$\Delta R_s/R_s = 4\frac{\omega}{c}\cos\theta \ \mathrm{Im}(\Delta\tilde{\varepsilon}_{Myy}/(\varepsilon_M - 1)) \tag{4}$$

for s-light incident in the xz-plane, and

$$\Delta R_p/R_p = 4\frac{\omega}{c}\cos\theta \ \mathrm{Im} \frac{(\varepsilon_M - \sin^2\theta)\Delta\tilde{\varepsilon}_{Mxx} + \varepsilon_M^2 \sin^2\theta \overline{\Delta\varepsilon^{-1}_{Mzz}}}{(\varepsilon_M - 1)(\varepsilon_M \cos^2\theta - \sin^2\theta)} \tag{5}$$

for p-light. $\theta$ is the angle of incidence, $\varepsilon_M$ the bulk macroscopic dielectric constant, and $(i, j \neq z)$

$$\Delta\tilde{\varepsilon}_{Mij} = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \left[\varepsilon_{Mij}(z,z') - \delta_{ij}\delta(z-z')\varepsilon_M(\omega)\right] -$$
$$\int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} dz'' \int_{-\infty}^{\infty} dz''' \varepsilon_{Miz}(z,z') \varepsilon^{-1}_{Mzz}(z',z'') \varepsilon_{Mzj}(z'',z'''), \tag{6}$$

$$\overline{\Delta\varepsilon^{-1}_{Mzz}} = \int_{-\infty}^{\infty} dz \int_{-\infty}^{\infty} dz' \left[\varepsilon^{-1}_{Mzz}(z,z') - \delta(z-z')/\varepsilon_M(\omega)\right] , \tag{7}$$

where $\varepsilon^{-1}_{Mzz}(z,z')$ is the inverse kernel of $\varepsilon_{Mzz}(z,z')$, and the dependence on $\vec{q}_{/\!/}$ and $\omega$ has been suppressed. Similar equations, analogous to those of [6], can be given for internal reflectivity.

This solution can be extended to the case of ellipsometry [5,12]. Writing the relative change (reflected to incident) of the polarization ratio as:

$$E_p^r E_s^i/(E_s^r E_p^i)=\mathrm{tang}\psi\exp(i\Delta),$$

we find the surface contribution: $\delta\Delta=\mathrm{Re}\mu$, $\delta\mathrm{tg}\psi=-\mathrm{tg}\psi_0\mathrm{Im}\mu$, where

$$\mu=-2\frac{\omega}{c}\cos\theta(\varepsilon_M-1)^{-1}(\varepsilon_M\cos^2\theta-\sin^2\theta)^{-1}\{A^2\Delta\tilde{\varepsilon}_{Mxx}+(\sin^2\theta-\varepsilon_M\cos^2\theta)\Delta\tilde{\varepsilon}_{Myy}+$$
$$\varepsilon_M{}^2\sin^2\theta\overline{\Delta\varepsilon_{Mzz}^{-1}}-\Delta\tilde{\varepsilon}_{Mxy}A\left[(E_p^i/E_s^i)(A\cos\theta-\sin^2\theta)-(E_s^i/E_p^i)(A\cos\theta+\sin^2\theta)\right]$$
$$+\Delta\tilde{\varepsilon}_{Myz}\varepsilon_M\sin\theta\left[(E_p^i/E_s^i)(A\cos\theta-\sin^2\theta)+(E_s^i/E_p^i)(A\cos\theta+\sin^2\theta)\right]\}, \qquad (8)$$

$A = (\varepsilon_M-\sin^2\theta)^{1/2}$, and

$$\Delta\tilde{\varepsilon}_{Myz}=\int_{-\infty}^{\infty}dz\int_{-\infty}^{\infty}dz'\int_{-\infty}^{\infty}dz''\Delta\varepsilon_{Myz}(z,z')\varepsilon_{Mzz}^{-1}(z',z''). \qquad (9)$$

The off-diagonal components of the macroscopic dielectric tensor make $\mu$ dependent on the polarization ratio $E_p^i/E_s^i$ of the incident wave.

## IV. Local Representation

For sake of simplicity, we consider the case of a surface with enough symmetry that the z-axis is a principal axis of the non-local dielectric tensor. An example of such a surface is the (001)surface of a simple-cubic crystal considered in next Section. In this case the off-diagonal terms $\varepsilon_{Miz}(z,z')$ vanish, and $\Delta\tilde{\varepsilon}_{Mii}(i=x,y)$ can be related to the longitudinal components of the microscopic dielectric tensor [12]. We use the local representation of the longitudinal dielectric response [11] including exchange, and we find, after tedious matrix algebra [12]:

$$\Delta\tilde{\varepsilon}_{Mii}=\lim_{q_z\to 0}\{-(4\pi e^2/\Omega_0)\Sigma_{ss'}f_s^i S_{ss'}(\omega)f_{s'}^{i*}\exp\left[iq_z(R_z+R_z')\right]+(\varepsilon_M-1)/2iq_z\}, \qquad (10)$$

where $\Omega_0$ is the unit cell volume, the index s(as well as s') labels couples of valence-conduction Wannier functions $\phi_\mu$ and $\phi_\nu$, centered respectively at $\vec{R}_z$ and $\vec{R}+\vec{R}_z$, $f_s^i$ is the i-component of the dipole matrix element, and the matrix $S(\omega)$ is given by:

$$S(\omega) = (N^{-1}(\omega)-V)^{-1} \quad . \qquad (11)$$

The polarizability matrix $N(\omega)$, including electron exchange interaction, is defined by eq.(2.46) of [11], while V is given by eq.(3.11) of [11].

A similar treatment can be developed for $\overline{\Delta\varepsilon_{Mzz}^{-1}}$, giving [12]:

$$\overline{\Delta\varepsilon_{Mzz}^{-1}}=\lim_{q_z\to 0}\{(4\pi e^2/\Omega_0)\Sigma_{ss'}f_s^z S_{ss'}(\omega)f_{s'}^{z*}\exp\left[iq_z(R_z+R_z')\right]+(\varepsilon_M^{-1}-1)/2iq_z\}. \qquad (12)$$

The cut wave-vector $k_c$ does not appear in final formulas eqs.(10) and (12), as might be expected.

## V. (001) Surface of a Simple-cubic Crystal

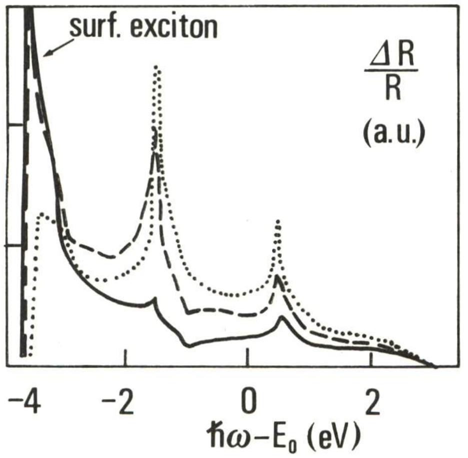


Fig.1. Normal incidence reflectivity of a simple-cubic crystal, computed according to one-electron theory (...), including excitonic (---) and local-field (——) effects

We apply eqs.(4) and (10) to the (001) surface of a simple-cubic crystal. We consider a flat p-like valence band and a s-like conduction band with nearest-neighbour interactions, $\beta$ [9]. Central-cell electron-hole (e-h) interaction $V^{x}$ is considered, while the Coulomb interaction $V_{ss'}$ is exactly accounted for, giving a central-cell term V and dipolar interactions, that we sum layer by layer according to [14]. We choose such parameters to obtain bulk excitonic and local-field effects of the same order as those computed for diamond [11], namely $\beta$=0.5 eV, $2V-V^{*}$=-0.4 eV and $(8/3)\pi f^2/\Omega_0$=0.8 eV. Then we invert analytically the matrix $N^{-1}-V$ and compute normal incidence reflectivity (Fig.(1)) as function of $\hbar\omega - E_0$, being $E_0$ the average bulk gap. The one-electron curve below the bulk gap (at -3 eV) is proportional to the density of surface state, showing the step-like singularity at the onset (-3.5 eV). Logarithmic singularities are also evident at -1.5 eV (saddle point) and 0.5 eV (surface band top). A strong distortion is generated by inclusion of excitonic and local-field effects, which increase surface exciton binding energy and oscillator strength.

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