SURFACE LOCAL - FIELD EFFECT

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Résumé - Afin de déterminer les écarts de la relation de Clausius-Mossotti dus aux changements du champ local près de la surface des cristaux cubiques, nous calculons les propriétés optiques d'un réseau cubique semi-infini de molécules polarisables à l'aide de deux méthodes différentes: l'une est une approche perturbative et l'autre utilise la superposition des modes de volume. Nous discutons les régions de validité de l'approche perturbative. Nous concluons que la surface induit une anisotropie dans la réflexion de la lumière, qui pourrait même être décelée par la spectroscopie différentielle de la reflectivité.

Abstract - In order to determine the deviations of the Clausius-Mossotti relation due to the changes of the local field close to the surface of cubic crystals, we calculate the optical properties of a semi-infinite cubic lattice of polarizable molecules using two different methods: a perturbative approach and the superposition of bulk modes. We discuss the regions of validity of the perturbative approach and we conclude that there is a surface induced anisotropy in the reflectance of light which could be detected by differential reflectance spectroscopy.

I - INTRODUCTION

It is well known than in order to fully understand surface sensitive optical experiments [1] using p-polarized light it is necessary to take into account the non-locality [2] of the dielectric response function. This non-locality appears when there is an interaction mechanism, not included in the average electromagnetic field, which correlates the response of different points of the system. A source of non-locality is the local-field effect, i.e. the interaction between nearby atoms through the microscopic spatial fluctuations of the electromagnetic field.

In order to study the surface effect of the local field in the optical properties of crystals we calculate the microscopic electromagnetic field induced by an external electromagnetic wave in a semi-infinite cubic lattice of point polarizable molecules. In the bulk of this system the difference between the field which polarizes the molecules (local field) and the (average) macroscopic field gives rise to the Clausius-Mossotti relation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} n_0 \alpha \qquad (1)$$

which connects the macroscopic local dielectric function ϵ, and the atomic polarizability α. Here n_0 is the number of molecules per unit

volume. In order to obtain this relation it is assumed that the pola-
rization field $\underset{\sim}{P}$ and the electric field $\underset{\sim}{E}$ are slowly varying func-
tions of position and that the crystal has cubic symmetry. These as-
sumptions break down close to the surface of a crystal.

The correct treatment of the local-field effect near the surface of
crystals might be important in the analysis of experiments such as dif
ferential reflectance between clean and adsorbate covered surfaces /3/,
electroreflectance /4/ and anisotropic surface-plasmon excitation /5/.

Although the model of a semi-infinite cubic array of point polarizable
molecules has been investigated previously /6,7/ , here we present, for
first time, actual numerical results for the reflectance of p-polarized
light which show detectable anisotropy effects for different faces of
a cubic crystal as well as for polarization along different crystalline
directions.

2 - PERTURBATIVE APPROACH

In this section we use the perturbative formalism developed in ref. 8
in order to obtain the optical properties of a crystal taking into ac-
count the local-field effect close to its surface. We consider a semi-
infinite cubic array, in the region $z > 0$, of point polarizable molecu-
les assuming that its bulk is well described by a frequency dependent
local dielectric function $\varepsilon(\omega)$ given by the Clausius-Mossotti relation.
According to ref. 8, in order to obtain the surface impedance, and
therefore all the optical coefficients of the system one has calculate
the surface conductivities $\langle\langle\Delta\sigma_{xx}\rangle\rangle$, $\langle\langle\Delta\sigma_{yy}\rangle\rangle$ and $\langle\langle\Delta S_{33}\rangle\rangle$ which re-
late the excess surface electric current density

$$\underset{\sim}{i} = \int_0^\infty dz\, \Delta \dot{\underset{\sim}{j}}(z) , \tag{2}$$

to the electric and displacement fields at the surface:

$$\dot{i}_k = \langle\langle\Delta\sigma_{kk}\rangle\rangle\, E_k(o) ; \quad k = x \text{ or } y \tag{3}$$

$$\dot{i}_3 = \langle\langle\Delta S_{33}\rangle\rangle\, D_3(o). \tag{4}$$

Here $\Delta\underset{\sim}{j}(z) \equiv \underset{\sim}{j}(z) - \underset{\sim}{j}^o(z)$ where $j(z)$ is the actual current density
of the system and $\underset{\sim}{j}^o(z)$ is the background current density:

$$\dot{\underset{\sim}{j}}^o(z) = \frac{(\varepsilon - 1)}{4\pi i}\, \omega\, \underset{\sim}{E}(z) \tag{5}$$

The surface impedance of the system is then given by Eq. 31 of ref. 8:

$$Z_p = \frac{Z_p^o + 4\pi Q^2 c^2 \langle\langle\Delta S_{33}\rangle\rangle /\omega^2}{1 + 4\pi Z_p^o \langle\langle\Delta\sigma_{xx}\rangle\rangle /c} \tag{6}$$

where Z_p^o is the surface impedance of the background and the subscript
p refers to p polarization. It has been assumed that all macroscopic
fields have a dependance of the form $exp\,i(Qx-\omega t)$ and no y dependance.
Equations (6) and (7) are valid only when the local conductivities
$\langle\Delta\sigma_{xx}(z)\rangle$, $\langle\Delta\sigma_{yy}(z)\rangle$ and $\langle\Delta S_{33}(z)\rangle$, defined by

$$\Delta\dot{j}_k = \langle\Delta\sigma_{kk}(z)\rangle\, E_k(z) ; \quad k = x \text{ or } y \tag{8}$$

$$\Delta\dot{j}_3 = \langle\Delta S_{33}(z)\rangle\, D_3(z) \tag{9}$$

go to zero at a distance $d \ll c/\omega$ from the surface, thus one is able to
ignore the slow variation of the fields along the surface and to

neglect, in the calculation, retardation effects. The equations obey-
ed by each molecule are

$$\underset{\sim}{p_i} = \Gamma \left(\underset{\sim}{E^o} + (1/n_o) \sum_j' \underset{\sim}{p_j} \cdot \nabla \nabla (1/r_{ij}) \right) \tag{10}$$

when i and j number atomic sites, p_i is the dipole moment of the i-th
atom multiplied by n_o, $\Gamma = n_o \alpha$ is the polarizability of the molecules per
unit volume and $\underset{\sim}{E^o}$ is the external field.

Using a plane-wise summation we can rewrite Eq. 10 as

$$\underset{\sim}{p_n} = \Gamma \left(\underset{\sim}{E^o} + \sum_{n=1}^{\infty} \underset{\approx}{U_{nm}} \cdot \underset{\sim}{p_m} \right) \tag{11}$$

where n and m number the crystal planes at z = na and z = ma (a is the
distance between neighboring planes). It is known /9/ that the dipo-
lar interaction U_{nm} between crystal planes decays to zero very rapidly
and it can be neglected whenever $|n-m| \leq N$, where N is a small integer.
We solve Eq. (11) for p_n by matrix inversion and the surface conducti-
vities will be then given by

$$\langle\langle \Delta \sigma_{kk} \rangle\rangle = (-i\omega a / E_k^o) \sum_{n=1}^{\infty} \left[(p_n)_k - \frac{(\varepsilon-1)}{4\pi} \right] \; ; \; k = x \text{ or } y \tag{12}$$

$$\langle\langle \Delta \sigma_{33} \rangle\rangle = (-i\omega a / E_3^o) \sum_{n=1}^{\bar{\infty}} \left[(p_n)_3 - \frac{(\varepsilon-1)}{4\pi} \right] \tag{13}$$

In fig. 1 we show the x-component of the polarization of the surface
planes of an FCC crystal normalized to the Clausius-Mossotti polariza-
tion $(p_n)_x / p_c$, as a function of the plane number n (n=1 corresponds to
the surface) for ε =-5.0. We observe that the behavior of the polari-
zation depends on the orientation of the surface. If the surface has
the (111) orientation the polarization acquires its bulk value just
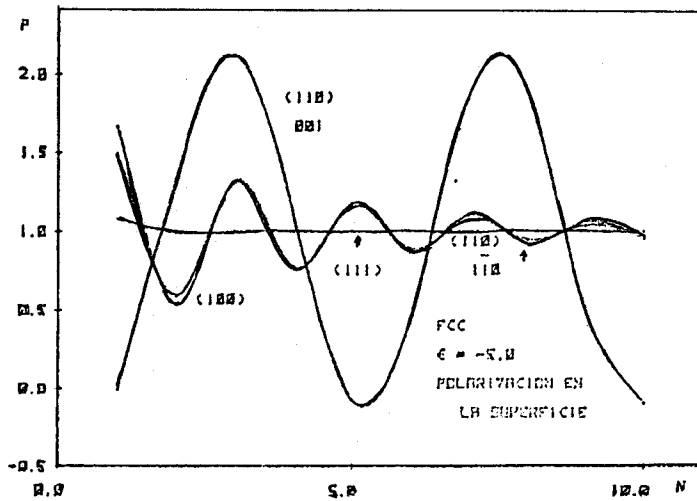after one plane;

Fig. 1 - Normalized polarization as a function of crystal plane number
for different faces (hkl) of an FCC crystal and for different direc-
tions [uvw] of polarization along the surface. Here we chose ε =-5.0.

for the (100) surface, the polarization takes its bulk value after ~10
crystal planes. For the (110) surface there are two non-equivalent
directions for the X-axis. If it points along the [1,1̄,0] direction
the results resemble those for the (100) surface. However, if it

points along the $[0,0,1]$ direction, the polarization has oscillations
around its bulk value and it does not decay. In this case the pertur-
bative method presented above will not be valid.

In order to evaluate the reflectance of the system as a function of
frequency we choose a Lorentzian model for the macroscopic dielectric
function with

$$\epsilon(\omega) = 1 + (\omega_p^2 / (\omega_0^2 - \omega^2 - i\,\omega/\gamma))$$

(14)

In fig. 2a. we show the normalized differential reflectance $\Delta R_p/(R_p^0\,\omega_0 a/c)$
for two orientation of an FCC (110) surface. Here $\Delta R_p = R_p - R_p^0$, R_p and
R_p^0 are the reflectance of p-polarized light of the system and of the
background respectively. We also choose a small lifetime $\gamma = 1/\omega_0$, so
the polarization will always decay rapidly into the bulk due to absorp-
tion processes and the perturbative method will then be valid. We
find that there is a range of values of ω for which $\Delta R_p/R_p$ is of the
order $a\,\omega_0/c$ which becomes $\sim 10^{-3}$ for ω_0 close or within the visible
spectrum. We also find a surface induced anisotropy in the reflec-
tance which is of the same order of magnitude.

We have also found similar changes in the reflectance between different
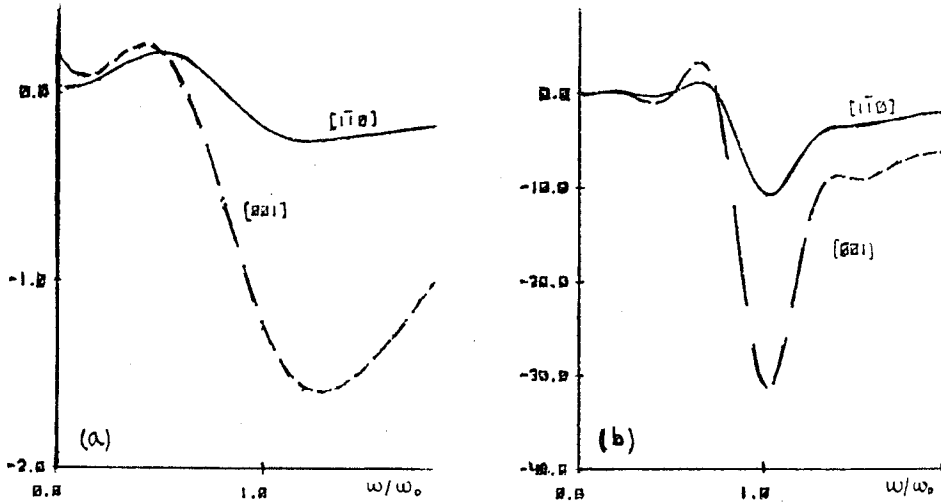faces of the same crystal.

Fig. 2 - Normalized differential reflectance for an FCC (110) surface
versus ω/ω_0 with the X axis along $[1\bar{1}0]$ and $(001]$, $\omega_p = 1\omega_0$ and the angle
of incidence equal to $60°$. (a) $\omega_p\,\gamma$ =1 and (b) $\omega_p\,\gamma$ =100.

3 - SUPERPOSITION OF BULK MODES

When the polarization does not decay to its bulk value near the surface
of the crystal one cannot ignore retardation effects nor the variations
of the macroscopic field along the surface. We have found that in this
case we can write the equations obeyed by the polarization in the follow-
ing form

$$P_n = \Gamma\left[E_n^L + E_n^R + R\cdot P_n + \sum_m W_{nm}\cdot P_m \right]$$

(15)

where E_n^L and E_n^R are the radiation fields that arrive to the n-th plane
traveling to the left from the (n+1)-th plane and traveling to the
right from the (n-1)-th plane respectively (the z axis points to the
right) and $R\cdot P_n$ is the radiation reaction of the n-th crystal plane on
itself. W_{nm} is a short range interaction which can be truncated after

a small number N of neighbor planes, and it differs from the dipole interaction Y_{nm} of the previous section by small terms which become unimportant in the final results.

The right and left-traveling fields obey simple recurrence equations:

$$E^L_{n+1} = (E^L_n + \underset{\approx}{R}^L \cdot \underset{\sim}{p}_n) \, e^{iqa} \tag{16}$$

$$E^R_{n-1} = (E^R_n + \underset{\approx}{R}^R \cdot \underset{\sim}{p}_n) \, e^{iqa} \tag{17}$$

where $\underset{\approx}{R}^L \cdot \underset{\sim}{p}_n$ and $\underset{\approx}{R}^R \cdot \underset{\sim}{p}_n$ are the fields radiated to the left and to the right by the n-th plane, and $exp\,iqa$ is the phase change the fields acquire on traveling the distance a

In an infinite system, the coupled equations (15)-(17) have Bloch-like solutions with a dependence on n of the form $exp\,ikna$, where k obeys one of following dispersion relations:

$$k^2 = \omega^2 \epsilon / c^2 - Q^2 \tag{18}$$

$$1 + [(\epsilon - 1)/2\pi] \sum_{n=1}^{\infty} (W_{om})_{xx} (1 - \cos mka) = 0 \tag{19}$$

$$1 + [(\epsilon - 1)/2\pi] \sum_{n=1}^{\infty} (W_{om})_{33} (1 - \cos mka) = 0 \tag{20}$$

Eq. (18) is the usual macroscopic dispersion relation which has two solutions, while the solutions of Eqs (19) and (20) correspond to 2N transverse and 2N longitudinal microscopic modes, respectively.

In the semi-infinite crystal the solution of Eqs. (15)-(17) is a superposition of the bulk modes shown above, which automatically fulfills Eq. 15 for n>N. The amplitude of each of these modes is determined by the following boundary conditions: (i) the incident field equals the radiation field traveling to the right at the surface, (ii) all the modes inside the crystal decay to the right and (iii) Eq. (15) is obeyed for the first N planes. Once the amplitudes are calculated one obtains the reflected wave as the radiation field traveling to the left at the surface.

In fig. 2b we show the normalized differential reflectance for a transparent material with $\gamma = 100/\omega_0$.

This calculation agrees with the perturbative approach in the region $\omega < \omega_0$ where all the microscopic modes are spatially decaying, but it differs in the region $\omega > \omega_0$ where some of the microscopic modes propagate. We also find a surface induced anisotropy of the same order of magnitude as the one which appears in dissipative materials.

Although the model we used does not correspond to some specific material we expect that in an actual crystal even if the Clausius-Mossotti relation does not hold exactly, the surface induced anisotropy will remain of the same order of magnitude and, therefore it will be detectable with the actual attainable resolution.

We also expect surface induced anisotropy in the dispersion relation of the surface electromagnetic modes of the system and the results of these calculations will be reported elsewhere.

Other effects which might also become important in relation with the surface local-field are: surface reconstruction, surface relaxation, microscopic roughness and adsorbed overlayers. These are now under investigation within the framework of the model used here.

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