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THE DOUBLE CELL TECHNIQUE: A DISCRETE DIPOLE APPROACH TOWARDS SURFACE OPTICS

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A local model based on the discrete dipole model has been developed in order to treat internal field effects at the surface of dielectric systems. The central part of the model is the double cell technique in which we match a freely chosen surface layer to the underlying bulk described by normal modes. We calculate the bulk and surface contributions to the anisotropic reflectance of the (1 1 0) surface of GaP obtaining results as good as the best delocalised treatments.

WE DEVELOPED a local method, based on the discrete dipole approach, to calculate the optical response of a semi-infinite dielectric, taking into account in an exact way local field effects of both bulk and surface. As such the theory is an extension of the one described in [1], where slab results are converted into semi-infinite quantities using a continuum description for the bulk. The central part of the model is the double cell technique, in which we match a freely chosen surface layer to the underlying bulk described by normal modes. This way, we preserve the flexibility of the two-slab approach [1] as far as the structural and electronic properties of the surface are concerned, while no further assumptions are needed to incorporate the bulk behaviour into the model. This makes the interpretation of the theoretical calculations much more transparent. Furthermore, the double-cell technique makes it possible to distinguish between surface local field effects [1–3] and bulk phenomena which are sensitive to spatial dispersion (e.g. birefringence in cubic crystals [4, 5]. Finally, a substantial improvement in processing speed has been achieved as compared to the two-slab method [1].

In order to test the validity of the double-cell technique we will calculate the internal field contribution to the surface induced optical anisotropy (SIOA) of the (1 1 0)-surface of GaP. SIOA has recently become an important tool in the investigation of semiconductor surfaces [6–14]. We will show that for a sufficiently large surface area, our results converge to those of the two-slab method [1] and we will see to what extent the bulk contributes to the anisotropy signal. As in [1] we need only three basic assumptions, or principles, to get started: the induction principle, the superposition principle and the parallel translation symmetry. All further steps are mathematical and the final solution is an exact one within the limits of the assumptions and numerical precision. The information about the physical system enters through a limited number of spatial coordinates locating the dipoles and an equal amount of polarizability tensors. As a natural result problems involving dielectric constants or boundary conditions will be avoided. Using the above mentioned principles in combination with the microscopic Hertz-potential formalism, yields for an arbitrary collection of dipole lattice planes, obeying the same parallel translation symmetry, the general description:

$$\mathbf{p}_i = \overleftrightarrow{\alpha}_i \left[\mathbf{E}_{\text{ext},i} + \alpha_0^{-1} \sum_j \overleftrightarrow{f}_{ij} \cdot \mathbf{p}_j \right], \tag{1}$$

$$\overleftrightarrow{f}_{ij} = a^3 [\nabla \nabla^T + k^2 \overleftrightarrow{1}] S_j(\mathbf{r}, \mathbf{k})|_{r=r_i}, \tag{2}$$

$$S_j(\mathbf{r}, \mathbf{k}) = \sum_{n,m}{}' \exp(i\mathbf{k}^T \mathbf{s}_{nm}) \frac{\exp(ik|\mathbf{r} - \mathbf{r}_{j,nm}|)}{|\mathbf{r} - \mathbf{r}_{j,nm}|}. \tag{3}$$

α_0 is a normalisation unit for the polarizability and has been defined as $4\pi\varepsilon_0 a^3$. The prime in equation (3) denotes that the term with vanishing denominator has to be omitted. The coordinate system is chosen such that every lattice plane is oriented in the xy-direction and $\hat{z}$ points in the direction of the upper half-space. The parallel translational symmetry is governed by two vectors $\mathbf{s}_1 = a(1, 0, 0)$ and $\mathbf{s}_2 = a(\alpha, \beta, 0)$ which span the lattice plane. We can then select an arbitrary number of lattice planes, each having a local origin at the characteristic site $\mathbf{r}_j$. An arbitrary site is given by $\mathbf{r}_{j,nm} = \mathbf{r}_j + n\mathbf{s}_1 + m\mathbf{s}_2$ (n, m integers). We define the incident wavevector $\mathbf{k} = (k_x, k_y, k_z)$ and its length $k = |\mathbf{k}|$, required by the scalar planar lattice sums $S_j(\mathbf{r}, \mathbf{k})$, $\mathbf{a}^T\mathbf{b} = \mathbf{a} \cdot \mathbf{b}$ the scalar improduct, $\mathbf{ab}^T$ the

direct product tensor or dyad of two vectors **a** and **b**, and for any arbitrary vector $\mathbf{u} = (u_x, u_y, u_z)$ its reflected counterpart $\underline{\mathbf{u}}$ as $\underline{\mathbf{u}} = (u_x, u_y, -u_z)$.

To the characteristic site $\mathbf{r}_j$ belong: the polarizability tensor $\overleftrightarrow{\alpha}_j$, the external field $\mathbf{E}_{\text{ext},j}$ and the characteristic dipole strength $\mathbf{p}_j$. Calculation of the interaction tensors $\overleftrightarrow{f}_{ij}$ requires three different transformations of the $S_j(\mathbf{r}, \mathbf{k})$: interplanar far, interplanar near and intraplanar. Far interplanar sums are used if $|z_i - z_j|$ exceeds a and yield the $\overleftrightarrow{f}_{ij}$ according to Ewald's threefold integral transform [15]:

$$\overleftrightarrow{f}_{ij} = \sum_{p,q} \overleftrightarrow{d}_{pq} \exp\,(\mathrm{i}\mathbf{k}_{pq}(\mathbf{r}_i - \mathbf{r}_j)), \quad (z_i > z_j)$$

$$\overleftrightarrow{d}_{pq} = \frac{2\pi\mathrm{i}a}{\beta} \frac{(k^2\overleftrightarrow{1} - \mathbf{k}_{pq}\mathbf{k}_{pq}^T)}{\kappa_{pq}} = \overleftrightarrow{d}_{pq}(\mathbf{k}_{pq}),$$

$$\mathbf{k}_{pq} = (\mathbf{k}_{pq}^{\parallel}, \kappa_{pq}), \quad \kappa_{pq} = (k^2 - \mathbf{k}_{pq}^{\parallel 2})^{1/2}, \tag{4}$$

with $\mathbf{k}_{pq}^{\parallel} = \mathbf{k}_{\parallel} + \mathbf{g}_{pq}^{\parallel}$ and $\mathbf{g}_{pq}^{\parallel}$ being a surface reciprocal lattice vector. If $z_i < z_j$ one has to replace in equation (4) $\overleftrightarrow{d}_{pq}$ by $\underline{\overleftrightarrow{d}}_{pq} = \overleftrightarrow{d}_{pq}(\underline{\mathbf{k}}_{pq})$. For the intraplanar and interplanar near ($|z_i - z_j| \leqslant a$) lattice sums one needs a generalization of Ewald's onefold integral transform [1, 16]. The intraplanar sum governing the interaction of the characteristic dipole with its own plane will be written as $\alpha_0^{-1}\overleftrightarrow{c}$. These integral transforms have also been studied in [17, 18] and approximate expressions for $\overleftrightarrow{c}$ can be found in [1, 19].

Next, two cells will be defined each obeying the same parallel translational symmetry. The surface cell contains N_S characteristic dipoles to be chosen arbitrarily. This cell can take into account the influence of surface reconstruction, relaxation and surface states. The bulk cell, containing N_B characteristic dipoles, has to be chosen such that it yields the correct bulk optical properties. The bulk characteristic dipoles are located at $\mathbf{r}_{v,V} = \mathbf{r}_v^B + Vd_B\hat{\mathbf{z}} + d_S\hat{\mathbf{z}}$, where $d_{B(S)}$ represents the height of the bulk (surface) cell. By convention $\mathbf{r}_1^B = \mathbf{0}$. Indices i, j refer to the surface cell. Indices V, W refer to the Vth respectively the Wth bulk cell and indices v, w refer to positions inside those bulk cells.

The double cell technique starts from the bulk normal modes, defined as:

$$\mathbf{p}_{v,V} = \sum_{m=1}^{M} v_m \mathbf{u}_{mv} \mathrm{e}^{\mathrm{i}q_m aV}.$$

M defines the number of normal modes of which only the 2 lowest ones will be used. The q_m's represent the refracted wavevectors, the $\mathbf{u}_{mv}$ the normal mode strengths. Values of q_m and $\mathbf{u}_{mv}$ can be found through a generalization of Litzman's procedure [18, 20]. The computational effort reduces drastically if the bulk cell can be reduced to the elementary bulk cell by means of:

$$\mathbf{u}_{mv} = \mathrm{e}^{\mathrm{i}\mathbf{k}_m\mathbf{r}_v^B}\mathbf{u}_m, \quad \mathbf{k}_m = (\mathbf{k}_{\parallel}, q_m),$$

where $\mathbf{u}_m$ is shorthand for $\mathbf{u}_{m1}$. The validity of this commensurability theorem will be discussed in [16]. The q_m's follow from the secular determinant:

$$\det\,(\overleftrightarrow{a}(\mathbf{k}_m)) = 0, \tag{5}$$

and the normal mode strengths $\mathbf{u}_m$ from the secular equation:

$$\overleftrightarrow{a}(\mathbf{k}_m)\mathbf{u}_m = 0. \tag{6}$$

The explicit expression for $\overleftrightarrow{a}(\mathbf{k}_m)$ has been found to be for the particular case of GaP(1 1 0):

$$\overleftrightarrow{a}(\mathbf{k}_m) = \alpha_0^{-1}\Bigg[\overleftrightarrow{\alpha}_B^{-1}\cdot\alpha_0 - \sum_{w=1}^{2}{}' \mathrm{e}^{\mathrm{i}\mathbf{k}_m\mathbf{r}_w^B}\overleftrightarrow{f}_{1w}^B + \sum_{w=1}^{2}\mathrm{e}^{\mathrm{i}\mathbf{k}_m\mathbf{r}_w^B}\Bigg[\sum_{p,q}\Bigg(\frac{\overleftrightarrow{d}_{pq}\mathrm{e}^{-\mathrm{i}\mathbf{k}_{pq}\mathbf{r}_w^B}}{1 - \exp\,(\mathrm{i}(q_m - \kappa_{pq})d_B} + \frac{\underline{\overleftrightarrow{d}}_{pq}\mathrm{e}^{-\mathrm{i}\underline{\mathbf{k}}_{pq}\mathbf{r}_w^B}}{1 - \exp\,(-\mathrm{i}(q_m + \kappa_{pq})d_B)}\Bigg)\Bigg]\Bigg].$$

Here $\overleftrightarrow{\alpha}_B$ represents the bulk polarizability tensor and $\overleftrightarrow{f}_{1,w}^B$ represents the interaction tensor between the two lattice planes of the original bulk cell. Continuing the derivation we find two sets of equations: one set for characteristic dipoles from the surface cell $\mathbf{p}_j$ (j: 1, . . . , N_S) and one for the coefficients of the 2 normal mode strengths v_m. The last ones obey:

$$-\sum_{j=1}^{N_S}\mathrm{e}^{-\mathrm{i}\mathbf{k}\mathbf{r}_j}(\mathbf{g}_m^{\infty T}\overleftrightarrow{d}_{00})\mathbf{p}_j - |\mathbf{g}_m^{\infty}|^2 v_m = \mathbf{g}_m^{\infty}\mathbf{E}_0,$$

$$\mathbf{g}_m^{\infty} = \frac{\overleftrightarrow{d}_{00}\mathrm{e}^{-\mathrm{i}k_z d_S}}{1 - \exp\,(\mathrm{i}(q_m - k_z)a)}\sum_{w=1}^{2}\mathrm{e}^{\mathrm{i}(q_m - k_z)z_w^B}\mathbf{u}_m. \tag{7}$$

Whereas a characteristic dipole belonging to the surface cell gives rise to the equation:

$$\sum_{j=1}^{N_S}(\overleftrightarrow{\alpha}_i^{-1}\delta_{ij} - \alpha_0^{-1}\overleftrightarrow{f}_{ij}^S)\mathbf{p}_j - \sum_{m=1}^{M}\underline{\mathbf{g}}_m^i v_m = \mathbf{E}_i,$$

$$\underline{\mathbf{g}}_m^i = \sum_{v=1}^{2}\sum_{p,q}\frac{\underline{\overleftrightarrow{d}}_{pq}\mathrm{e}^{\mathrm{i}\underline{\mathbf{k}}_{pq}(\mathbf{r}_i - \mathbf{r}_{Bv})}}{1 - \exp\,(\mathrm{i}(q_m + \kappa_{pq})a)}\mathrm{e}^{\mathrm{i}\mathbf{k}_m\mathbf{r}_{Bv}}\mathrm{e}^{\mathrm{i}\kappa_{pq}d_S}\mathbf{u}_m. \tag{8}$$

Equations (7)–(8) yield a perfectly solvable system of $(3N_S + 2)$ equations, which upon solution produces all $\mathbf{p}_j$'s and v_m's. The essence of the method is to increase N_S (by adding bulk planes) such that those 2 normal modes suffice for convergence. To obtain from those solutions the semi-infinite reflection coefficients

is done by using:

$$r = \left(\frac{ik^2}{2\varepsilon_0 \beta k_z a^2}\right)\left(\frac{\mathbf{E}_0 \cdot \mathbf{P}^R}{|\mathbf{E}_0|}\right),$$

$$\mathbf{P}^R = \sum_{j=1}^{N_S} e^{-i\mathbf{k}\mathbf{r}_j}\mathbf{p}_j + e^{ik_z d_S}\sum_{m=1}^{2} \times \left[\sum_{w=1}^{2} \frac{e^{i(q_m + k_z)z_{Bw}}}{1 - \exp(i(q_m + k_z)a)}\right] v_m \mathbf{u}_m. \quad (9)$$

We will now specify the configuration for the particular case of the (1 1 0)-surface of GaP. The polarizable unit for bulk and surface contains one Ga atom and one P atom. We limit ourselves here to bulk-truncated GaP and we choose $\alpha = 0$, $\beta = \sqrt{2}$ and $\mathbf{d} = (a/2)(1, \beta, 1)$. The surface lattice plane generates all other planes in this case by repeatedly adding $\mathbf{d}$. The bulk cell contains two characteristic dipoles and has height a. The bulk lattice constant is $a^c = \beta a$ and has for GaP the value 5.4505 Å. The surface and bulk electronic structure of the semiconductor enter the calculation through the polarizabilities, which were derived from RPA surface and bulk dielectric constants [1, 21] using the Lorentz–Lorenz relation. Only the first three layers of the surface cell have polarizabilities different from the bulk. Surface reconstruction has been incorporated only by taking into account the rotation relaxation of 27.5° [22].

Equation (5) yields the two values for q_m which control the bulk behaviour. Since, they are essentially wavevectors, they can be compared to q_F, the Fresnel wavevector. Figure 1 shows for both values of m the quantity $|(q_m - q_F)/q_F|$. The result is apparently different from zero, but the deviations from Fresnel behaviour are very small in the optical region (of the order 10^{-5}), which proves that our normal mode decomposition is indeed capable of describing the optical response of the bulk within the discrete dipole approach and thus offers a discrete analogue of the usual continuum approaches [23, 24]. Furthermore, we also see in Fig. 1 that the two values of m produce a different curve, so even though we have isotropic bulk polarizabilities, the bulk internal fields give rise to an anisotropy. The reason for this is the following. Arguments about optically isotropic behaviour of cubic crystals rely upon simple static cubic symmetry. In reality however, this symmetry becomes distorted by the electromagnetic wave itself. As a result the orientation of the beam with respect to the bulk unit cell should play a role. From equation (5) it is immediately clear that this is indeed the case. In Fig. 2 we plot the anisotropy in the refractive index ($\Delta n = n[\bar{1}\,1\,0] - n[0\,0\,1]$), as a function of the photon energy $\hbar\omega$. We find that for an energy of 1 eV the anisotropy is about 5.0×10^{-6} or the same order of magnitude as the one experimentally observed for Si(1 1 0) in [4], proving that the phenomenon of birefringence in cubic crystals is indeed largely due to bulk internal field effects. In the discrete approach this phenomenon arises naturally; similar nonlocal descriptions are not so straightforward [5], because they need an expansion of the dielectric function $\varepsilon(\omega, k)$ in terms of k. Finally, as to the bulk behaviour we would like to comment on the mode strengths $\mathbf{u}_m$. The two optical normal modes $\mathbf{u}_m$ turn out to be polarized exactly along the $(1\,\bar{1}\,0)$ and (1 0 0) direction for perpendicular incidence. These modes are excited exclusively by electromagnetic waves of the same polarization, a fact which cannot be deduced from equation (5) as such.

In order to test the convergence behaviour of the double-cell method we calculated the reflectance anisotropy (RA) of the clean GaP (1 1 0)-surface as a function of the number of layers in the surface cell.

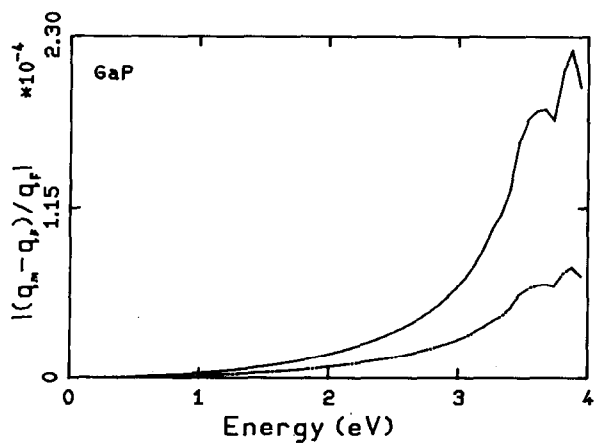

Fig. 1. Bulk anisotropy of the q_m's (see text). Plotted: $|(q_m - q_F)/q_F|$. Solid curve: p-polarization; chain-dotted curve: s-polarization.

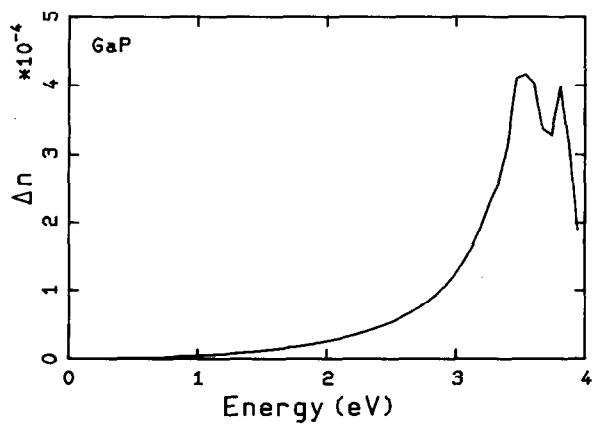

Fig. 2. Bulk anisotropy in the refractive index ($\Delta n = n[\bar{1}\,1\,0] - n[0\,0\,1]$).

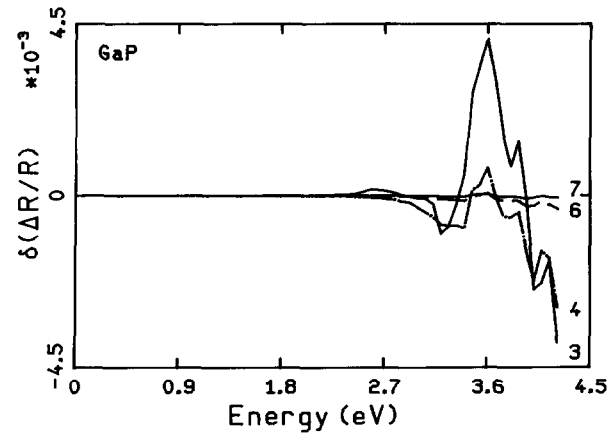

Fig. 3. Convergence of the anisotropic reflectance of the (1 1 0)-surface of GaP. Plotted: $AR(N_S = \infty)$-$AR(N_S = N_S)$ for N_S = 3, 4, 6 and 7.

The RA is defined as $(R_{90} - R_0)/R_F$. The reflectances R_{90} with respect to R_0 belong to polarizations of the incoming light beam along the $(1\,\bar{1}\,0)$ with respect to (0 0 1) direction, R_F will be the classical Fresnel value. Figure 3 shows plots of the difference $(RA(\infty)$-$RA(N_S))$ for several values of N_S. The value $RA(\infty)$ corresponds to the RA obtained for N_S = 18, whereas the $RA(N_S)$ have been obtained for values of N_S varying from 3, 4, 6 through 7. It is clear that the effective range of the internal field has to be about 7 layers, most in agreement with the conclusions arrived at in [1].

Figure 4 shows the total RA for GaP(1 1 0). The results have been obtained by means of the double cell technique, using 18 dipoles in the surface cell. It appears that the bulk anisotropy effect (Fig. 2.) does not contribute substantially to the SIOA spectrum; the bulk signal is about 1% of the surface one. The same AR has been calculated as well by means of the two slab method [1], but the results are virtually indistinguishable, confirming in yet another way the validity of the asymptotic continuation approach. Furthermore, we have obtained a substantial gain in processing speed compared to the two-slab method; the memory requirements are about 4 times smaller and the computing time is reduced by a factor 16.

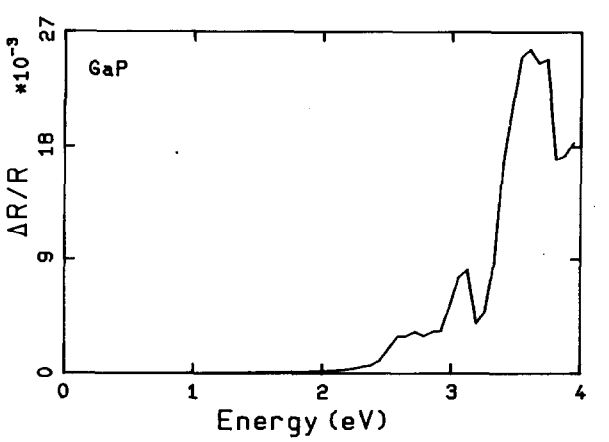

Fig. 4. Theoretical AR for the GaP(1 1 0) surface.

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