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Contribution of the Internal Field to the Anisotropic Optical Reflectance of GaP(110)

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Abstract

This article presents the theory of optical reflection from thin slabs of GaP(110) by means of the discrete dipole model and focusses especially upon the possible implications of this model for the surface induced optical anisotropy. The reflectance of a semi-infinite sample is extracted from slab calculations and compared with experiments. We find that the internal field has a very important role in determining the surface induced optical anisotropy. We also show that the surface sensitivity of such experiments can be estimated to be about five monolayers.

1. Introduction

The surface induced optical anisotropy (SIOA) in cubic systems is one of the most challenging topics in the optics of surfaces. The first experimental observation of this phenomenon was done by Furtak and Lynch [1] for the Ag(110) surface. For similar investigations on semiconductors one had to wait until the eighties. They concerned elemental [2] and III–V [3, 4] semiconductors. Anisotropic differential measurements for GaAs, technologically the most important III–V semiconductor, can be found in [3] and [4]. The present article, however, will focus upon GaP. The key reason for that can be found in the well known article by Huyser *et al.* [5]. Among all III–V compounds studied there, it was the only one shown experimentally to have empty surface states within the gap. Since optical measurements are an important source of information in the study of surface states, the choice of a material where these states show up freely is obvious. The occurrence of empty surface states in the gap is also shown by inverse photoemission experiments on GaP(110) [6].

Two related approaches have been used to clarify the phenomenon of SIOA from the theoretical point of view. The first approach makes use of macroscopic Maxwell's equations and of the non-local dielectric susceptibility. The other approach starts from a discontinuous description, in terms of discrete dipoles, of the crystal optical response, but becomes often mixed with the first one. It is not the place here to give a detailed overview of the vast literature in the field, but a few publications deserve special attention as to the first approach. The first one is the article of Bagchi *et al.* [7], where a perturbative approach using Green's functions was used to solve Maxwell's equations. This method, initially meant for semi-infinite jellium, was extended to treat real (anisotropic) surfaces by Del Sole [8]. Later on Del Sole and Fiorino [9] emphasized the effect of local fields, which can be embodied in the macroscopic dielectric tensor. At first glance the work of Mochan and Barrera [10] should also be classified as a continuous approach, since it is founded on the solution of macroscopic Maxwell's equations. However, they rely so much upon a pure discrete-dipole calculation for determining the macroscopic dielectric tensor, that they also belong to the second group. Also from their work the importance of internal fields became clear. The second approach is mostly based on the work of Wijers and Emmett [11], who recently performed a pure dipole calculation considering only one layer, arriving at the same conclusion.

The rest of the paper contains two parts. The first part (Section 2) treats the optical response of thin slabs of dipoles representing GaP(110). The treatment of electromagnetic interactions is, apart from one minor approximation rigorous. The second part uses the continuous approach and yields relationships between reflectivity and transmittivity of a slab and the reflectivity of a semi-infinite sample (Section 3). This is calculated form them and compared with experimental data (Section 4). The conclusions of this work are outlined in Section 5.

2. Optical response of slabs

2.1. *Description of the configuration*

A description of a basic SIOA setup was already given in Ref. [11]. A beam of electromagnetic radiation impinges upon the surface of a monocrystalline piece of GaP cleaved normally to the [110] direction. In this article only normally incident beams ($\theta = 0$) will be considered. The (110) lattice is spanned by the basis vectors

$$s_1 = (a^c/\sqrt{2},\ 0,\ 0)$$
$$s_2 = (0,\ a^c,\ 0), \tag{1}$$

the x and y directions being parallel to $[1\bar{1}0]$ and [001] respectively. Neither surface reconstruction nor relaxation will be taken into account. The other layers of the slab can be generated from eq. (1) by repeatedly adding

$$\boldsymbol{d} = (\sqrt{2}/4,\ 1/2,\ -\sqrt{2}/4)\,a^c. \tag{2}$$

The minus sign in eq. (2) has been introduced in order to indicate that the slab extends towards the negative-z half-space. The value of the bulk lattice constant a^c (5.4505 Å) is taken from the literature [12]. In this article we adopt the unit cell, consisting of two atoms, one Ga and one P, as the polarizable unit. This choice is known to yield surface optical properties for Si and Ge(110) in good agreement with experiment [10].

Since the surface lattice generated by eq. (1) creates a preferential direction on the surface, it becomes necessary to introduce an azimuthal angle Ω, namely the angle between light polarization and the [001] (y) direction.

As in [11], the incident and reflected beams will be characterized by wave vectors $\boldsymbol{k}$ and $\underline{\boldsymbol{k}}$, which, for normal incidence, are:

$$\begin{aligned} \boldsymbol{k} &= (0, 0, k_z) \\ \underline{\boldsymbol{k}} &= (0, 0, -k_z). \end{aligned} \tag{3}$$

2.2. *Dipole theory for thin slabs*

Dipole theory starts from four basic principles in the case of two-dimensional translationally symmetric systems, as was pointed out already in [11]. It suffices to divide the specimen under consideration into a number of cells with index i, dipole strength $\boldsymbol{p}_i$ and polarizability α_i. Our choice was a rectangular block of height $\sqrt{2}a^c/4$, oriented along the axes introduced before. From Ref. [11] we briefly summarize the results. At first there is the *principle of induction*:

$$\boldsymbol{p}_i = \alpha_i \boldsymbol{E}_{\text{loc},i}.$$

The dipoles $\boldsymbol{p}_i$ give rise to Hertz potentials [13], from which the electric field can be obtained according to:

$$\boldsymbol{Z}_i(\boldsymbol{r}, t) = (\boldsymbol{p}_i/4\pi\varepsilon_0 r) \exp[\mathrm{i}(kr - \omega t)] \tag{5a}$$

$$E_i(\boldsymbol{r}, t) = \nabla(\nabla \cdot \boldsymbol{Z}_i) - (\partial^2 \boldsymbol{Z}_i/\partial^2 t)/c^2, \tag{5b}$$

where $k = \omega/c$. (This holds for a dipole located at the origin.) The external and induced fields have to be combined according to the *principle of superposition*:

$$\boldsymbol{E}_{\text{tot}}(\boldsymbol{r}, t) = \boldsymbol{E}_{\text{ext}}(\boldsymbol{r}, t) + \Sigma_i \boldsymbol{E}_i(\boldsymbol{r}, t). \tag{6}$$

For the reduction of the problem to finite size one needs the principle of *parallel translational symmetry*:

$$\boldsymbol{p}_{qr} = \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{s}_{qr}) \boldsymbol{p}_{00}, \tag{7}$$

where q and r span the surface lattice points $\boldsymbol{s}_{qr}$. This principle needs further comment for the case of a slab. It has to be applied to each layer separately. It reduces the infinitely many unknown dipole-strengths $\boldsymbol{p}_{qr}$ to a single one $\boldsymbol{p}_{00}$ located at the origin $\boldsymbol{r}_i$ of the lattice belonging to the i-plane. The index 00 will be omitted in the following and replaced by the plane index i. Straightforward combination of these principles yields the following system of equations:

$$\boldsymbol{p}_i = \alpha_i[\boldsymbol{E}_{\text{ext},i} + \Sigma_j \mathbf{F}_{ij} \cdot \boldsymbol{p}_j], \tag{8}$$

$$\mathbf{F}_{ij} = (\nabla\nabla + k^2 \mathbf{1}) S_j(\boldsymbol{r}, k)|_{\boldsymbol{r}=\boldsymbol{r}_i}, \tag{9}$$

$$S_j(\boldsymbol{r}, \boldsymbol{k}) = \Sigma'_{qr} \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{s}_{qr}) \exp(\mathrm{i}k|\boldsymbol{r} - \boldsymbol{r}_{j,qr}|)/|\boldsymbol{r} - \boldsymbol{r}_{j,qr}|. \tag{10}$$

The external (incident) field driving the entire process enters eq. (8) as $\boldsymbol{E}_{\text{ext},i}$. Equation (10) defines the lattice sums $\boldsymbol{S}_j(\boldsymbol{r}, k)$. The prime means that in the case $\boldsymbol{r} = \boldsymbol{r}_i$, the term with vanishing denominator must be omitted.

The main problem of the dipole theory is to calculate $\mathbf{F}_{ij}$. The diagonal terms have been studied in detail in [11]. So we can take the intraplanar contribution directly from there:

$$a^3 \mathbf{F}_{ii} = \mathbf{c}_{\text{stat}} + 2\pi \mathrm{i} a[k^2 \mathbf{1} - \boldsymbol{k}_\parallel^{\mathrm{T}} \boldsymbol{k}_\parallel - \boldsymbol{k}_z^{\mathrm{T}} \boldsymbol{k}_z]/(\beta|k_z|), \tag{11}$$

where $a = a^c/\sqrt{2}$ and $\beta = \sqrt{2}$. Symbols $\mathbf{F}_{ij}$, $\mathbf{c}_{\text{stat}}$ or $\mathbf{1}$ represent (3×3) subtensors. Combinations of the type $\boldsymbol{v}^{\mathrm{T}}\boldsymbol{v}$ indicate the corresponding direct product subtensor. Terms of the order $(ak)^3$ have been neglected in the derivation of eq. (11). The value of $\mathbf{c}_{\text{stat}}$ is found according to the method given in [11]:

$$\mathbf{c}_{\text{stat}} = \begin{pmatrix} 4.7901 & 0 & 0 \\ 0 & 0.9060 & 0 \\ 0 & 0 & -5.6961 \end{pmatrix}. \tag{12}$$

Next we have to evaluate the off diagonal terms. For this use is made of the threefold integral transform of Ewald [14]. The generalization of this expression to arbitrary lattices has been done by Litzman [15]. (Please note that in Ref. [15] only eq. (2.11) is correct. Equation (A11) should be the same, but it contains two misprints.) Only the lattice sum $S_j(\boldsymbol{r}, \boldsymbol{k})$ are given here. The application of the differential operator (9) is trivial. We find:

$$S_j(\boldsymbol{r}, \boldsymbol{k}) = (2\pi \mathrm{i}/|\boldsymbol{s}_1 \times \boldsymbol{s}_2|) \sum_{pq} \exp[\mathrm{i}(\boldsymbol{k}_\parallel + \boldsymbol{g}_{pq}) \cdot \boldsymbol{r}] \times \exp(\mathrm{i}\kappa_{qp}|z|)/\kappa_{qp}, \tag{13}$$

$$\kappa_{qp} = (k^2 - |\boldsymbol{k}_\parallel + \boldsymbol{g}_{qp}|^2)^{1/2} \tag{14}$$

where $\boldsymbol{g}_{pq}$ is a vector of the reciprocal surface lattice. It should be noticed that eq. (13) cannot be used for $z = 0$. Also for neighbouring planes it is slowly convergent, but it is still much quicker than direct calculation according to eq. (10). After that it readily approaches the speed of an analytical expression. Once the results of eqs. (11) and (13) are obtained, we are left with a system of $3N$ linear equations in the $3N$ unknowns, the components of the $\boldsymbol{p}_i$'s. The solution is:

$$\boldsymbol{p}_i = \sum_j (\mathbf{A}^{-1})_{ij} \boldsymbol{E}_{\text{ext},j}, \tag{15}$$

where

$$\mathbf{A}_{ij} = \mathbf{1}\delta_{ij}/\alpha_i - \mathbf{F}_{ij}. \tag{16}$$

The dipole strengths $\boldsymbol{p}_i$ together build a complete description of the optical response of the slab upon irradiation by a light wave. The measurable quantities are functions of the $\boldsymbol{p}_i$'s.

2.3. *Remote fields: reflectance and transmittance*

The remote fields can be obtained by applying (13) along the line of calculation shown by eqs. (8)–(10). We find for the reflected and transmitted beam:

$$\boldsymbol{E}^{\mathrm{R}}(\boldsymbol{r}, t) = (2\pi \mathrm{i}/\beta|k_z|a^2)(k^2\mathbf{1} - \underline{\boldsymbol{k}}^{\mathrm{T}}\underline{\boldsymbol{k}}) \times \boldsymbol{P}^{\mathrm{R}} \exp[\mathrm{i}(\underline{\boldsymbol{k}} \cdot \boldsymbol{r} - \omega t)], \tag{17}$$

$$\boldsymbol{E}^{\mathrm{T}}(\boldsymbol{r}, t) = [\boldsymbol{E}_0 + (2\pi \mathrm{i}/\beta|k_z|a^2)(k^2\mathbf{1} - \boldsymbol{k}^{\mathrm{T}}\boldsymbol{k})\boldsymbol{P}^{\mathrm{T}}] \times \exp[\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)], \tag{18}$$

where $\boldsymbol{E}_0 \exp[\mathrm{i}(\boldsymbol{k} \cdot \boldsymbol{r} - \omega t)]$ is the external (incident) field, and:

$$\boldsymbol{P}^{\mathrm{R}} = \sum_j \exp(-\mathrm{i}\underline{\boldsymbol{k}} \cdot \boldsymbol{r}_j)\boldsymbol{p}_j, \tag{19}$$

$$\boldsymbol{P}^{\mathrm{T}} = \sum_j \exp(-\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_j)\boldsymbol{p}_j. \tag{20}$$

Finally we find the complex reflectivity and transmittivity at normal incidence:

$$r = (2\pi \mathrm{i}/\beta|k_z|a^2)k^2(\boldsymbol{E}_0 \cdot \boldsymbol{P}^{\mathrm{R}}/|\boldsymbol{E}_0|), \tag{21}$$

$$t = 1 + (2\pi \mathrm{i}/\beta|k_z|a^2)k^2(\boldsymbol{E}_0 \cdot \boldsymbol{P}^{\mathrm{T}}/|\boldsymbol{E}_0|). \tag{22}$$

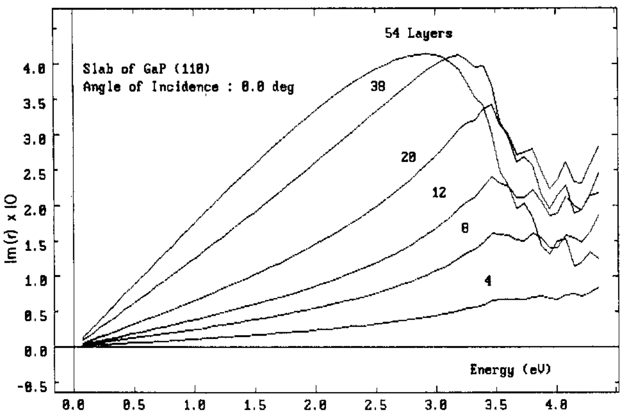

Fig. 1. Imaginary part of the complex reflectivity r of GaP(110) slabs of various thicknesses, computed as explained in the text for light polarized along the [001] direction.

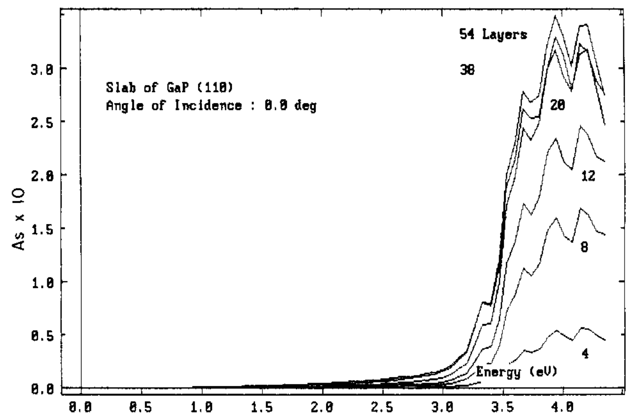

Fig. 2. Absorbance As of GaP(110) slabs of various thicknesses, computed as explained in the text for light polarized along the [001] direction.

3. Reflectance of a semi-infinite crystal

The discrete dipole model treated until now is not suited for the description of semi-infinite systems, hence the results obtained so far cannot be compared with experiments. However the slab in principle can be made so thick that asymptotic conditions are fulfilled in most of its interior. In that case a classical continuous description can be used to extract the required results for a semi-infinite crystal from slab calculations. The basics of such calculations can be found in textbooks as [13], [16] or [17].

Inside the slab, where surface effects are not important, light propagates according to the wavevector q_z given by:

$$q_z = (\omega/c)\varepsilon^{1/2}(\omega). \tag{23}$$

We can find the reflectivity and transmittivity of a slab of depth d by summing the contributions of multiple reflections of waves propagating with wavevector $\pm q_z$. This approach is similar to that of Ref. [18], with the difference that we are here considering field amplitudes (and not their square moduli as in Ref. [18]), in order to fully account also for interference effects, which cannot be neglected in thin slabs. After some algebra we arrive at the relation:

$$r(d) = r + r' \exp(\mathrm{i}q_z d)\, t(d). \tag{24}$$

Here r means the reflectivity of a semi-infinite sample from vacuum to bulk – the required quantity – while r' is the reflectivity from bulk to vacuum. Surface effects are fully included in r and r', according to the approach of Refs [8] and [18]. If one uses eq. (24) for two different layers of thickness d_A and d_B respectively, the reflectance of a semi-infinite crystal turns out to be:

$$r = \{t(d_A)r(d_B) - \exp[\mathrm{i}q_z(d_B - d_A)]t(d_B)r(d_A)\}/ \{t(d_A) - \exp[\mathrm{i}q_z(d_B - d_A)]t(d_B)\}. \tag{25}$$

4. Numerical results and comparison with experiments

In this section we calculate the reflectance of a semi-infinite GaP crystal cleaved normally to the [110] direction. We assume, as it was done in Ref. [10] for silicon and germanium, that all atoms have the same polarizability, which is extracted from the computed bulk dielectric constant [19] according to the Clausius–Mossotti relation. The validity of this procedure is discussed in Ref. [20]; its use is substantiated by the good agreement found with SIOA experiments carried out on Si and Ge (110) natural (i.e., oxydized) surfaces [10, 21]. Obviously the contribution of surface states is completely neglected in this way: the surface affects the optical response and makes it anisotropic only through the internal fields.

Figure 1 shows the imaginary part of the reflectivity as a function of the number of layers. It is commonly known that for very thin dielectric slabs or for a single layer of dipoles the reflectivity becomes almost entirely imaginary in the frequency range where no absorption occurs [22]. This is in agreement with out findings for several layers of dipoles. At low frequencies a fairly linear dependence on ω, hence also on k, can be observed, again in agreement with Ref. [22]. On the high frequency side one observes a decrease of the imaginary part to about one half of the maximum value, when the number of layers is quite big, e.g., 54. This originates from the strong absorption occurring at such frequencies, as can be seen in Fig. 2. The reflectance difference (R90-R00)/ROx is shown in Fig. 3. R90 and R00 are slab reflectances computed for $\Omega = 90°$ and $0°$ respectively, while ROx is the reflectance of a semi-infinite GaP crystal computed according to Fresnel formula. For energy below 3 eV they exhibit a quadratic dependence on ω or k, a feature characteristic for non-absorbing thin slabs. At higher energies we observe again decreasing reflectance difference, much in the same way as shown in Fig. 1. However even for the highest number of layers and within the frequency range of strong absorption, the values are still a factor of three above those of a semi-infinite sample,

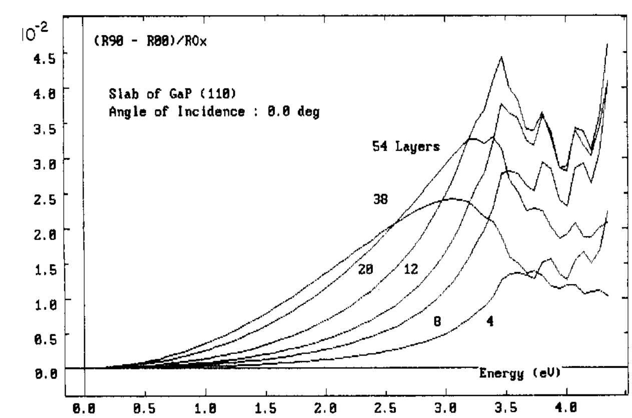

Fig. 3. Reflectance difference calculated for GaP(110) slabs of various thicknesses. R90 (R00) is the reflection coefficient of light polarized along the [1$\bar{1}$0] ([001]) direction, while ROx is the reflection coefficient of a semi-infinite GaP crystal computed according to Fresnel formula.

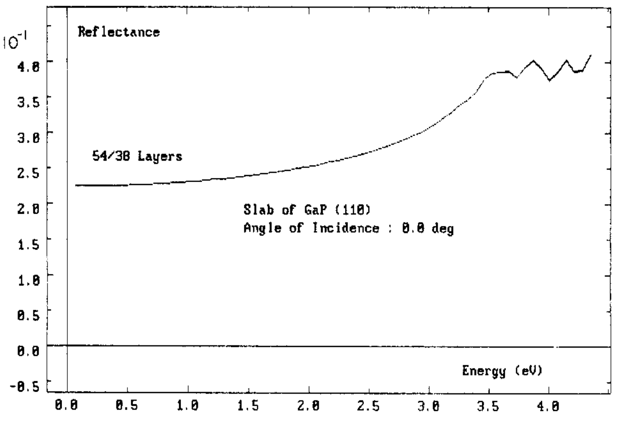

Fig. 4. Reflectance of GaP semi-infinite crystal cleaved normally to the [110] direction, extracted from slab calculations according to equation (25). The curves for light polarized along [1$\bar{1}$0] and [001], and that computed according to Fresnel formula, not accounting at all for surface effects, cannot be distinguished.

as we will show in Fig. 5. This means that the slabs are still not so thick that they can be treated as semi-infinite.

The reflectance of a semi-infinite GaP crystal, computed according to eq. (24) for light polarized parallel and normally to [1$\bar{1}$0], is shown in Fig. 4. It nearly coincides with the result given by Fresnel formula. The curves of Fig. 4 were derived from a pair of slabs of 54 and 38 layers. We have made a series of plots of the reflectance difference (not shown in this article) for the combinations 4/8, 8/12, 12/20, 20/38 and 38/54. The results from the three last combinations are virtually indistinguishable. Results obtained from the 4/8 combination are both in shape and in size incomparable with the others. This means that equation (24), based on the assumption of decoupled surfaces, is reliable already for a very small number of layers, about 10. Therefore we can say that the surface sensitivity of the internal field interactions is of about 5 layers, which is in good agreement with the findings of Mochan and Barrera [10].

Figure 5 shows the final results, i.e. the difference between the reflectances of a semi-infinite GaP(110) sample, measured with light polarized parallel and perpendicular to the [1$\bar{1}$0] direction. The experimental difference, extracted from the data of Ref. [4], taken on the clean GaP(110) surface, is also

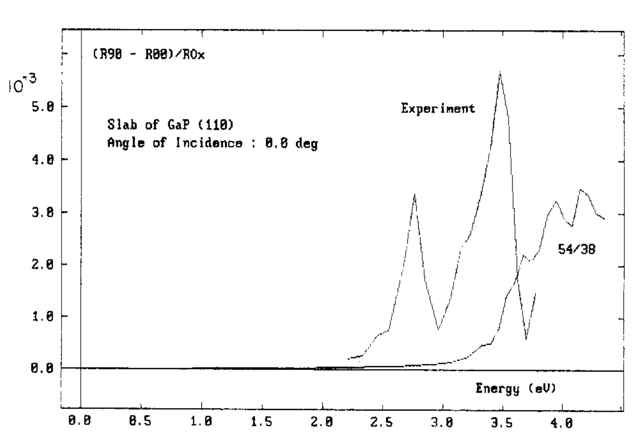

Fig. 5. Computed reflectance difference for a semi-infinite GaP crystal cleaved normally to the [110] direction. R90 (Roo) is the reflection coefficient for light polarized along the [1$\bar{1}$0] ([001]) direction, while ROx has been computed according to Fresnel formula. Experimental data [4] for the clean GaP(110) surface are also shown.

shown. No agreement at all is present between theory and experiment. This is not strange, in view of our neglect of surface states, and in view of the importance of surface states in determining the differential reflectivity of GaP(110), already established in Ref. [19]. Moreover, this result confirms the surface-state origin of GaP(110) differential reflectance. At the same time, it is clear from Fig. 5 that internal field contributions are not negligible as far as SIOA is considered. A better understanding of this phenomenon can come from calculations (presently in progress) similar to the present ones, which however incorporate the peculiarities of the first few layers, by using for them different atomic polarizabilities than in bulk.

5. Conclusions

In this article we have studied the role of the internal field in determining the optical behavior of thin slabs by means of the discrete dipole model. We have shown the feasibility of reflectance and transmittance calculations for slabs in terms of the field emitted by the induced dipoles in response to an external perturbation (the incident wave). One of the advantages of this method is that it does not require the solution of light propagation equations. By using a special transformation we were also able to extract from slab results the reflection coefficient of a semi-infinite crystal. Even though we did not consider the contribution of surface states, we were able to show that the role of the internal field is an essential one, if we are interested in the recently observed phenomenon of surface induced optical anisotropy in cubic crystals.

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