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Origin of surface anisotropies in the optical spectra of III-V compounds

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We present results of *ab initio* calculations of optical spectra of GaP and GaAs (110) surfaces, and show that transitions between bulk single-particle states modified by the crystal truncation account for the largest contribution to above-gap optical anisotropy of these systems.

Surface sensitivity can be achieved in optical measurements by comparison of the optical response of a semiconductor to light of different polarizations.[1-6] In the case of cubic materials such as diamond and zinc-blende semiconductors, in fact, the optical response of the bulk is isotropic, and anisotropy in the optical spectrum must be related to symmetry breaking due to the presence of the surface. The mechanism through which the surface influences the optical response of the system, making it anisotropic, however, has not been greatly investigated. The simplest assumption is to relate anisotropic structures in the surface optical spectrum to optical transitions between surface states. This is certainly true for optical transitions occurring at energies lower than the band gap, which necessarily involve surface states, as in the case of Si(111)-2×1.[1] The situation is more complicated in the case of III-V compounds, where surface states are known to overlap the energy region of bulk states. For this reason the interpretation of anisotropic structures in the optical spectra in terms of transitions between surface states is in this case not so straightforward. A similar problem arises for the interpretation of the above-gap optical anisotropy of Si and Ge (111)-2×1.[2] For these cases the anisotropy observed in differential reflectivity (DR) measurements has been successfully explained within a single-particle approach.[7] The largest contribution was found to come from transitions between bulk states perturbed by the reconstruction-induced structural anisotropy of the surface. A quite different interpretation, based on the surface local-field effect, has been proposed instead for the optical anisotropy of the Si and Ge (110) natural surfaces.[8] However, for these cases a substantial contribution from single-particle transitions has also been found.[7]

In this paper we present a theoretical study, within a single-particle approach, of the anisotropy in the surface optical spectra of III-V semiconductors. In particular we show that the optical anisotropy of the GaAs and GaP (110) clean surfaces is mostly attributed to the perturbation of bulk single-particle states due to the truncation of the crystal. Even if we cannot rule out many-body effects, we show that a single-particle theory is capable of explaining the main features of the observed optical anisotropy. A partial preliminary account of the present work has been given in Ref. 9.

As described in Ref. 7, the calculation of the surface reflectivity in the single-particle approximation requires computation of (i) the bulk and surface energy spectrum, and (ii) the transition probabilities between states of the perfect crystal—defining the bulk dielectric function $\epsilon_b(\omega)$—and the transition probabilities between states of the truncated crystal. Our surface calculations are performed in a repeated-slab geometry, each slab consisting of 15 (110) layers, with the surfaces in the relaxed configuration.[10] The slabs are separated by nine missing layers. The electronic states are determined in the local-density approximation (LDA)[11] using local pseudopotentials and a plane-wave basis set. The X_α expression with $\alpha=1$ is used for the exchange and correlation potential, in order to avoid the underestimates of band gaps resulting from density-functional theory and the LDA. Bulk bands, densities of states, and $\epsilon_b(\omega)$ are found to be in good agreement with those calculated by Wang and Klein,[12] who used norm-conserving pseudopotentials and the LDA with an empirical self-energy correction. In the calculation of the optical spectrum, the off-diagonal elements of the surface dielectric tensor are neglected. Evaluation of their contribution within a generalized three-layer model[7] confirms that this is a very good approximation.[13]

As is well known, the energy spectrum of the truncated crystal is a combination of bulk eigenstates plus extra surface states. The energy position of bulk states is not altered by the presence of the surface; however, this does not imply that the surface does not perturb the bulk wave functions as well. If the experimental technique used to investigate the physical properties of the system is such as to probe the behavior of electron states well inside the crystal, this perturbation does not play a significant role,

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but if a surface-sensitive technique is used, the reduced symmetry of bulk states in the surface region cannot be neglected. In particular, bulk wave functions of the truncated crystal have cubic symmetry well inside the solid, where the atoms are in a cubic environment, but they have the same reduced symmetry of surface-state wave functions near the surface. To illustrate this point, instead of individual wave functions, we consider the behavior of the total charge density. In Fig. 1 we show the contributions of localized surface states [Figs. 1(b) and 1(d)] and bulk states [Figs. 1(a) and 1(c)] to the total charge density of GaAs(110),[14] both in the surface plane [Figs. 1(c) and 1(d)] and in a plane perpendicular to it [Figs. 1(a) and 1(b)]. The breakdown of the cubic symmetry at the surface is particularly evident in Figs. 1(a) and 1(b). It appears that bulk states give rise to the standard bulk charge distribution far away from the surface; near the surface, instead, they are strongly modified by the crystal truncation. On the other hand, Figs. 1(c) and 1(d) show that bulk states give the largest contribution to the total charge density at the surface. One can therefore expect that they will also give a large contribution to the optical anisotropy.

The crucial quantity entering the expression of the surface reflectivity $\Delta R/R$ is the integral over z and z' (where z is the direction perpendicular to the surface) of the slab dielectric susceptibility tensor $\epsilon_{\alpha\beta}(\omega;z,z')$.[15] We shall denote this quantity, which has units of length, $\epsilon_{\alpha\beta}(\omega)$. It is interesting to separate the contributions of optical transitions between bulk and surface states by performing the following decomposition:

$$\epsilon_{\alpha\beta}=\epsilon_{\alpha\beta}^{b\text{-}b}+\epsilon_{\alpha\beta}^{b\text{-}s}+\epsilon_{\alpha\beta}^{s\text{-}b}+\epsilon_{\alpha\beta}^{s\text{-}s}\,.$$

Here the superscripts label a dielectric tensor calculated by considering separately the optical transitions between

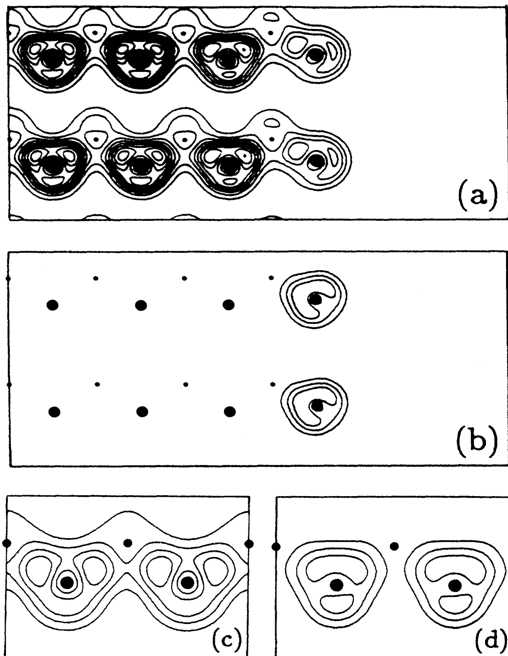

FIG. 1. Charge-density contours for relaxed GaAs(110). (a) and (b) are plotted in the $(1\bar{1}0)$ plane perpendicular to the surface and passing through the surface anions; (c) and (d) are plotted in the (110) surface plane. The contribution of bulk states is shown in (a) and (c); the contribution of localized surface states is shown in (b) and (d). The contours are spaced by 3 electrons per bulk unit cell. The Ga(As) atomic positions are marked by small (big) circles.

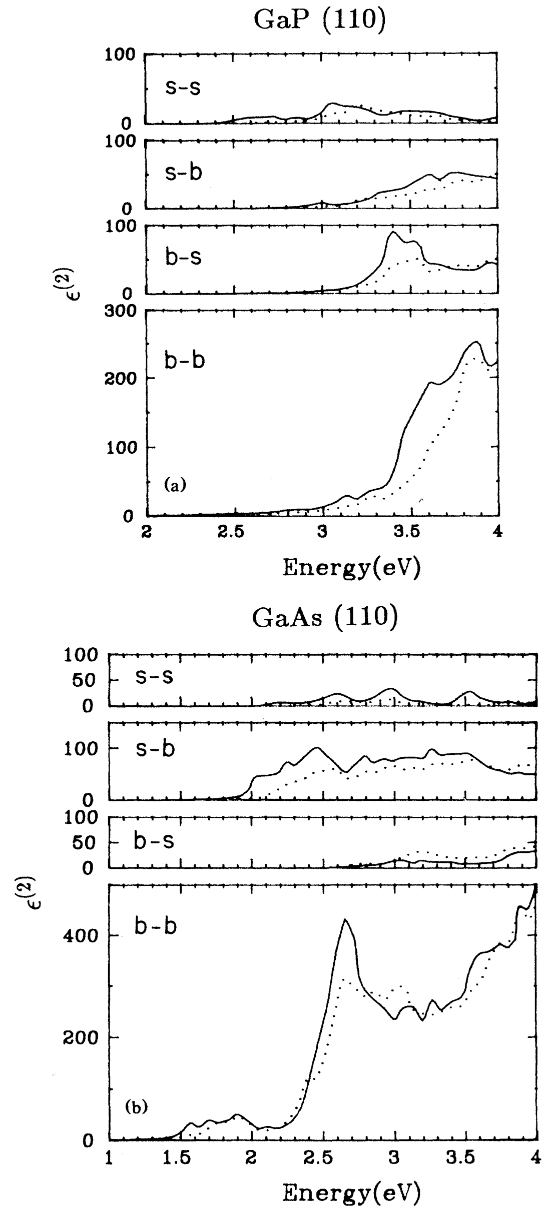

FIG. 2. Contributions to the diagonal components of the imaginary part of the surface dielectric tensor for GaAs and GaP (110), parallel (ϵ_{xx}, solid lines) and perpendicular (ϵ_{yy}, dotted lines) to the direction of the atomic chains in the surface plane. b-b, b-s, s-b, and s-s indicate, respectively, the contributions arising from transitions between bulk states, from bulk to surface states, from surface to bulk states, and between surface states.

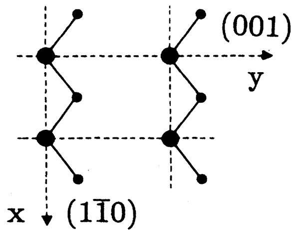

FIG. 3. Sketch of the unit cell of the ideal (110) surface. Solid lines indicate the atomic chains in the surface plane.

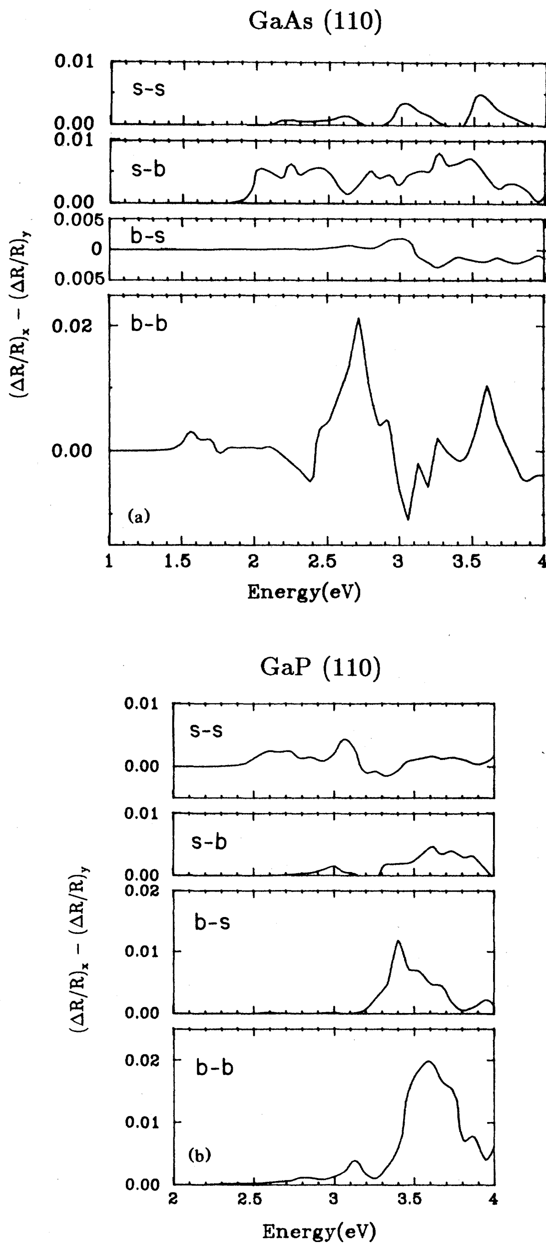

FIG. 4. Contributions to the reflectance anisotropy curves $(\Delta R/R)_x-(\Delta R/R)_y$. Notations are as in Fig. 2. The sum of these contributions is shown in Fig. 5.

bulk states of the truncated crystal (b-b), the transitions from bulk to surface states (b-s), from surface to bulk (s-b), and from surface to surface states (s-s). The result of this decomposition is shown in Fig. 2, where the four contributions to the imaginary part of ϵ_{xx} and ϵ_{yy} are displayed in the energy range of interest for optical spectra [here x and y are the directions parallel and perpendicular to the chains of atoms in the (110) plane, respectively; a sketch of the surface unit cell is shown in Fig. 3 to clarify this notation]. It appears that a large anisotropic contribution comes from the bulk to bulk transitions both for GaAs and GaP (110).

Such an effect is even larger when considering surface reflectivity. In Fig. 4 we show the b-b, b-s, s-b, and s-s contributions to the reflectance anisotropy (RA) $(\Delta R/R)_x-(\Delta R/R)_y$. The sum of all these contributions is shown in Fig. 5. It is apparent that for both GaAs and GaP the largest contribution comes from transitions between bulk states.

In the case of GaAs(110), the main calculated RA structures are at 2.5 (shoulder), 2.7, 3.3, and 3.6 eV; in the following they will be denoted by F_1–F_4. The largest ones (F_2 and F_4) are definitely related to b-b transitions (with a smaller contribution from s-s and s-b transitions in F_4). Besides b-b contributions, F_1 and F_3 contain a s-b term. The deep minimum around 3.1 eV originates from the corresponding minimum in the b-b spectrum of Fig. 4. In GaP(110) the main structures present in our calculated curve are between 2.5 and 2.9 (denoted G_1), at

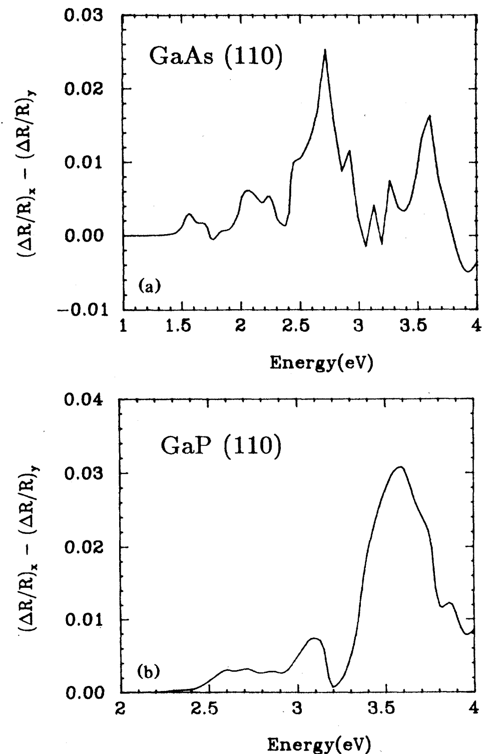

FIG. 5. Total reflectance anisotropy curves for GaAs and GaP (110). The separate contributions to these curves are shown in Fig. 4.

3.1 (G_2), and at 3.6 with a shoulder at 3.7 eV (G_3 and G_4); minima occur at 3.2 and around 3.9 eV. Optical transitions between surface states are responsible for the broad structure G_1 around 2.8 eV and contribute to G_2 together with b-b transitions. The remaining structures appear to be dominated by transitions between bulk states, with smaller contributions from transitions involving surface states as initial and/or final states.

The comparison of the present curves with experimental data can give insight into the physical origin of the measured anisotropy effects. RA spectra for clean GaAs and GaP (110) were measured at low temperatures by Berkovits *et al.*[5,6] We restrict ourselves here to this set of data and do not consider results of DR measurements, which involve several additional complications and uncertainties related to the oxidized surface.

For GaP (Ref. 6), the main experimental peaks are at 2.85 eV (marked S_0), 3.2 eV (marked S'), and 3.55 eV, with minima at 3, 3.4, and 3.7 eV. In order to compare our theoretical results with the experiment, we identify our calculated minima at 3.2 and 3.9 eV with the observed dips at 3 and 3.7 eV, respectively. Correspondingly, our structures at 3.6 eV (G_3) and 3.7 eV (G_4) could be identified with the experimental peaks at 3.2 eV (S') and 3.55 eV, which are therefore attributed to transitions between bulk states. The observed S_0 instead should correspond to our G_1+G_2 structures and is thus assigned to transitions between surface states. It appears that the comparison is on the whole rather satisfactory, although the observed intensities are not well reproduced. A better agreement is obtained in the case of GaAs. The experiment shows main peaks at 2.6 eV (S_1) and 2.8 eV (S_2), and a deep minimum at 3.05 eV. We identify the theoretical peaks F_1 and F_2 with S_1 and S_2, which are thus attributed mostly to transitions between bulk states; the experimental minimum at 3.05 eV corresponds to the calculated minimum around 3.1 eV. Not only the energy, but also the intensity and shape of structures are well described by the calculations.

From our analysis it appears that a large contribution from bulk to bulk transitions is present in all the main above-gap experimental peaks. A similar interpretation of differential reflectivity measurements[16] is less straightforward, as it involves calculations for hydrogen- or oxygen-covered surfaces, and will be presented in a forthcoming paper.[13] Preliminary results confirm that also in that case transitions between bulk states play an important role in anisotropic surface features and are only partly reduced by the subtraction of the chemisorbed surface spectrum.

In summary, we have shown that full *ab initio* calculations of optical RA of GaP and GaAs (110) surfaces allow us to interpret the main above-gap reflectance anisotropy effects as due to transitions between single-particle bulk states perturbed by the crystal truncation.

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