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Bulk and surface electronic structure of ZnSe(110)

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The valence-electronic structure of the ZnSe(110) surface has been studied by angle-resolved photoelectron spectroscopy using synchrotron radiation. The bulk energy bands along the ΓKX direction have been mapped with use of normal-emission spectra in the 16–70-eV photon-energy range. Off-normal-emission spectra were measured along the $\bar{\Gamma}\bar{X}$, $\bar{\Gamma}\bar{Y}$, and $\bar{\Gamma}\bar{M}$ symmetry lines. Several surface-related structures have been deduced from these data and their dispersions have been determined.

I. INTRODUCTION

Compared to III-V semiconductor surfaces, our knowledge of the electronic structure of II-VI semiconductors is rather poor. A better understanding, especially of the surface electronic structure, may be achieved from systematic, comparative studies of different II-VI compounds. In our previous studies of CdTe(110) (Ref. 1) we found several features in the photoelectron spectra, which we associated with the surface. A more recent parallel study of ZnTe(110) (Ref. 2) has revealed similar surface states and surface resonances (in contrast to "true" surface states, resonances occur outside gaps in the projected density of states). As a continuation of our experimental investigations, we present here a study of ZnSe(110).

Photoemission from ZnSe(110) has been studied earlier by Ebina *et al.*,[3] who reported He I–excited angle-resolved spectra along the $\bar{\Gamma}\bar{X}$, $\bar{\Gamma}\bar{Y}$, and $\bar{\Gamma}\bar{M}$ symmetry lines in the surface Brillouin zone. They found surface resonances at 1.0 eV below the valence-band maximum (VBM) near the $\bar{Y}$ point and at 1.5 eV near the $\bar{X}$ point, as predicted by a calculation of Calandra, Manghi, and Bertoni.[4] They also found a surface state at about 4-eV binding energy at $\bar{\Gamma}$, not present in the calculation. This surface state was later associated with a resonance found at ~3 eV in a calculation by Beres, Allen, and Dow.[5] In this calculation additional, experimentally unconfirmed[3] surface resonances were predicted. Since the experiment was performed at one fixed photon energy, it is justified to suspect that a more extensive study, employing synchrotron radiation, could reveal more information. Indeed, it will be shown here that several additional surface states (resonances) can be identified, some of which are in agreement with the calculation of Beres, Allen, and Dow.[5] Compared to the data of Ebina *et al.*[3] we have very similar spectra for 21-eV photon energy. We also obtain similar band-structure plots, particularly in the $\bar{\Gamma}\bar{M}$ direction. However, except for a state near the $\bar{Y}$ point, at about 3-eV binding energy, our identification of surface-related structures is different from that of Ebina *et al.*[3]

II. EXPERIMENTAL

The experiments were carried out at the toroidal grating monochromator beamline[6] of the MAX storage ring. The ZnSe single crystals, $4\times4\times3$ mm^3 in size, were cleaved in an UHV preparation chamber ($p\approx5\times10^{-10}$ Torr) and transferred to the analysis system ($p\approx1\times10^{-10}$ Torr). This is equipped with a goniometer mounted hemispherical electron energy analyzer, movable around a horizontal and a vertical axis. Low-energy electron diffraction was used for checking the surface orientation. The light, mainly p polarized, was kept at constant incidence angle of 45° relative to the surface normal.

III. RESULTS AND ANALYSIS

A. Normal emission and bulk band mapping

A selection of measured normal-emission spectra in the photon-energy range 18–70 eV is shown in Fig. 1. The rapidly dispersing peaks B and C show the typical behavior of direct transitions and will be identified as such below. The more weakly dispersing peak A is also associated with a direct transition, namely from the uppermost valence band around the center of the Brillouin zone. It reaches its minimum binding energy at 32-eV photon energy, where it becomes degenerate with B. At this point the direct transition occurs at the Γ point and defines zero binding energy for our energy distribution curves (EDC's). There are three peaks, labeled S', $S2(S3)$, and D, respectively, which show no dispersion. They are candidates for surface states (resonances) or nondirect transitions.

For the analysis we first assume direct transitions from valence bands into free-electron-like final bands described by $E=\hbar^2|\mathbf{k}-\mathbf{g}|^2/2m$. With this assumption we can construct an experimental band structure from the peak positions in Fig. 1. The momentum normal to the surface ($\hbar k_\perp$) is calculated using the formula $k_\perp(\text{Å}^{-1})=0.512\sqrt{E_{\text{kin}}+V_0}$, where V_0 is the inner potential and E_{kin} the kinetic energy of the photoelectron. Both are related to the vacuum level and expressed in eV. The best fit to experimental data was found for $V_0=12$ eV. The experimental band structure along the ΓKX direction obtained in this way is shown in Fig. 2, where solid and open circles indicate clear peaks and less-well-defined features, respectively. We have only considered **g** vectors parallel to the surface normal, i.e., [110]. Note that peaks due to transitions into other free-electron bands are then converted into wrong $\mathbf{k}_\perp$ positions by this procedure. These may occur from [111]- and [200]-type **g** vectors, sometimes called "umklapp transitions." In principle they could be brought into correct position if the final bands were known.

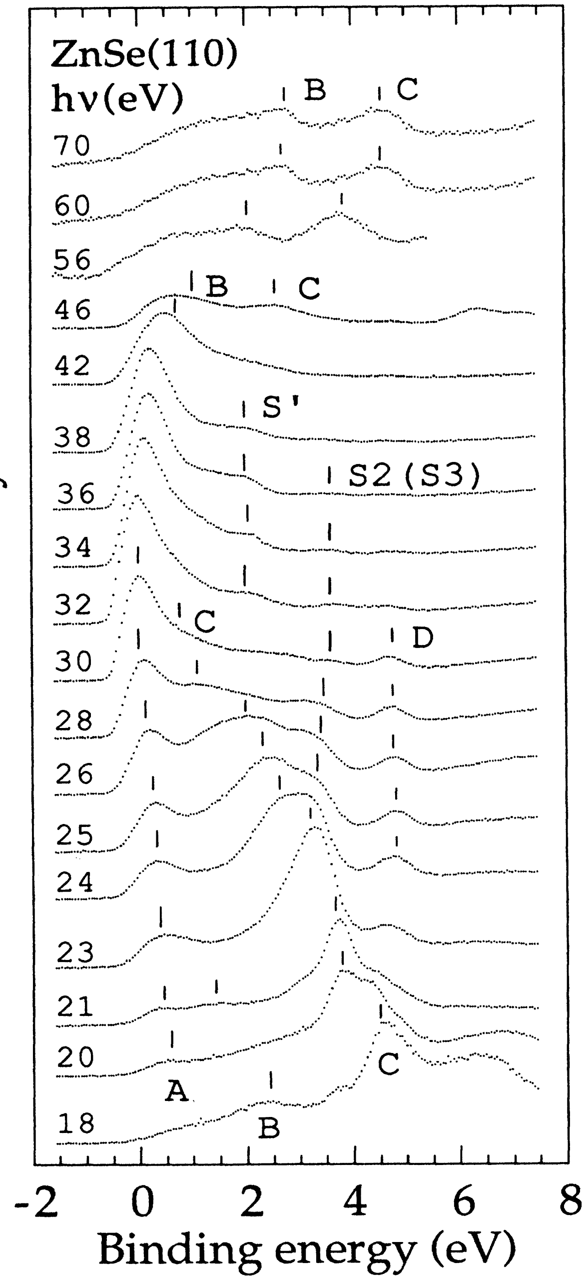

FIG. 1. Normal-emission photoelectron spectra from ZnSe(110) over a wide photon-energy range. The letters are the same as in Fig. 2.

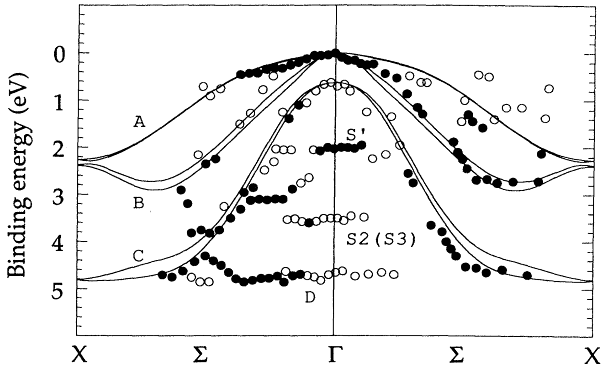

FIG. 2. Experimental (circles) and theoretical (lines) band structure along the Σ (i.e., ΓKX) direction. Solid circles indicate clear peaks and open circles shown less-well-defined structures in the spectra. The letters are the same as in Fig. 1.

As in our earlier work[1,2] on CdTe and ZnTe the valence bands of ZnSe were calculated by a semiempirical relativistic LCAO (linear combination of atomic orbitals) method[7]. By fitting to the experimentally derived energies in Fig. 2, and in particular to the critical energies at Γ, we have obtained the theoretical valence bands shown as solids lines in Fig. 2. It was not possible to obtain a perfect fit all over. So, for instance, the theoretical band *C* has somewhat too small binding energy between Γ and *X*. The energy of the *C* band at the *X* point (X_6) was chosen to agree with the *D* structure as will be discussed below. In principle, one could improve the scheme by including, e.g., second-neighbor interactions, but in view of other approximations (e.g., for the final states) this was not considered very meaningful. The obtained semiempirical band structure was subsequently used to analyze the off-normal-emission data.

From Fig. 2 we conclude that there is a fair agreement between theory and experiment. We find that the spin-orbit splitting at the Γ point is 0.6 eV and the energy at $\Sigma_{\min}$ about 2.9 eV. From the fitted LCAO bands we also obtain extrapolated energies at some critical points. These are compared with values from literature[3,8,9] in Table I.

Structures which do not lie close to the theoretical lines may be due to transitions into other final states than those assumed, i.e., either free-electron bands with **g** vectors not parallel to the surface normal or non-free-electron-like bands (e.g., near-band gaps). There is also the possibility of transitions from regions of high initial density of states ("nondirect transitions"). Finally the unidentified structures may be due to surface-related initial states. These are distinguished by lack of dispersion, since the surface component of the momentum is constant ($\mathbf{k}_\parallel=\mathbf{0}$). One should note, however, that nondirect transitions are also expected to show very little dispersion with $\mathbf{k}_\parallel$. As these often appear at edges of the surface-

TABLE I. Critical-point energies in band structure of ZnSe. Values are given in eV relative to the VBM.

	Γ_7	X_7	X_6	X_6	$L_{4,5}$	L_6	L_6
This work	0.6	2.3	2.4	4.8	0.7	1.2	5.0
Other expt.			2.5[a]	5.25[a],5.3[b]	0.7[b]		5.7[a]
Theory[c]	0.45	1.96	2.17	4.96	0.76	1.04	5.08

[a] Reference 3.
[b] Reference 8.
[c] Reference 9.

projected bulk states and surface states sometimes are tracking these edges, it may in many cases be difficult to distinguish these two possibilities. Around Γ we find three dispersionless features, labeled S', $S2(S3)$, and D at 2.0-, 3.4-, and 4.8-eV binding energies, respectively. They will be studied in some more detail below in connection with the off-normal-emission data and tentative identifications will be given. It is worth pointing out already here that similar structures were also found by us for CdTe(110) (Ref. 1) and ZnTe(110).[2]

B. Off-normal-emission and surface-state dispersions

We have measured off-normal-emission spectra along the $\bar{\Gamma}\bar{X}$, $\bar{\Gamma}\bar{Y}$, and $\bar{\Gamma}\bar{M}$ directions, using three different photon energies, 23, 26, and 29 eV. As an example we show in Fig. 3 a set of spectra obtained with 26-eV photon energy. From these data we have extracted a "band-structure plot," i.e., the binding energies of the peaks are plotted as a function of $\mathbf{k}_{\parallel}$, the surface component of $\mathbf{k}$, the magnitude of which is obtained from $|\mathbf{k}_{\parallel}| = 0.512\sqrt{E_{\text{kin}}}\sin\theta$. The result is shown in Fig. 4 using the same notation as in Fig. 2. As a guide for the interpretation, theoretical transitions were simulated assuming conservation of $\mathbf{k}_{\parallel}$ and including "umklapp" processes with $\mathbf{g}$ vectors of the types [100] and [111]. These transitions are indicated as solid lines in Fig. 4. Again, many of the experimental structures can be associated with the theoretical lines, and are thus attributed to

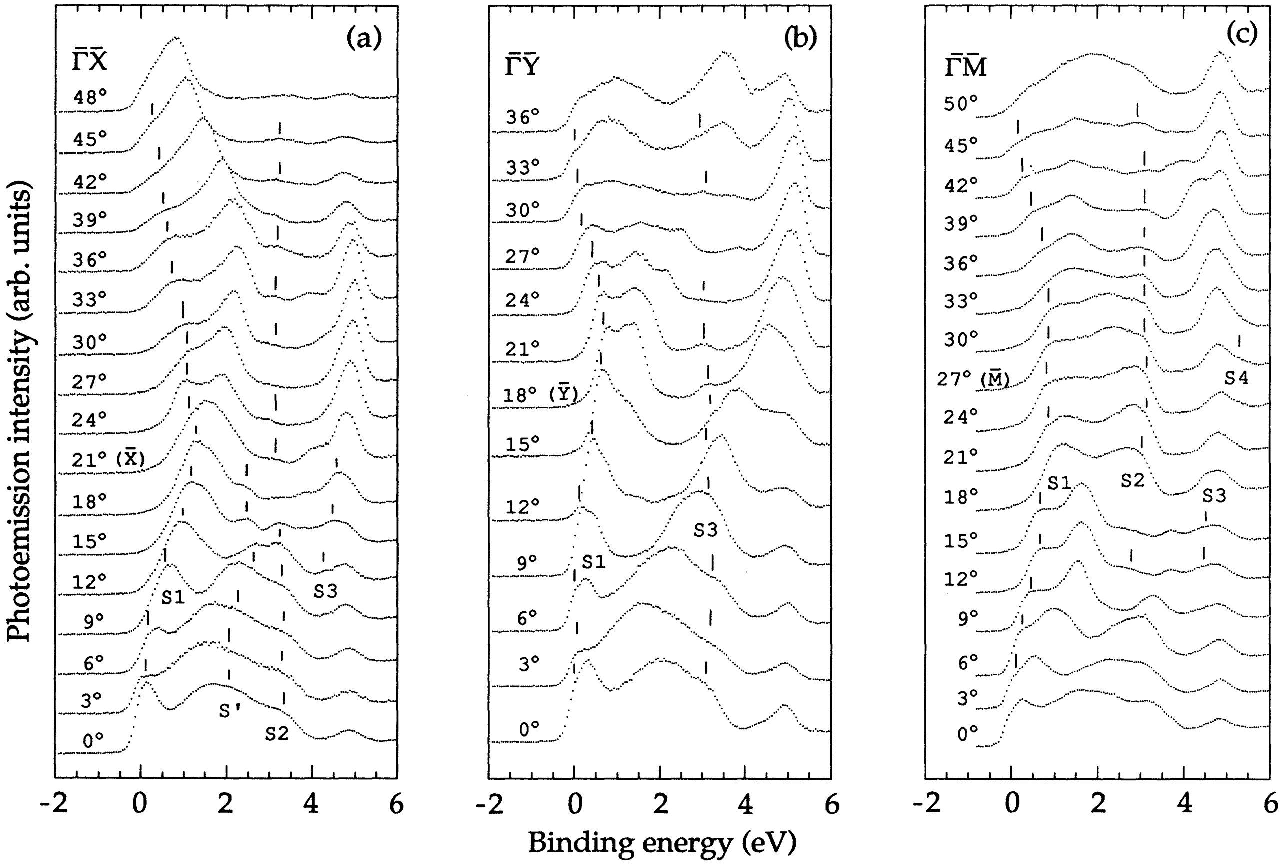

FIG. 3. Off-normal-emission photoelectron spectra at 26-eV photon energy in the (a) $\bar{\Gamma}\bar{X}$, (b) $\bar{\Gamma}\bar{Y}$, and (c) $\bar{\Gamma}\bar{M}$ directions. The EDC approximately corresponding to the Brillouin-zone boundary has been marked in each set. The labels are the same as in Figs. 4 and 5.

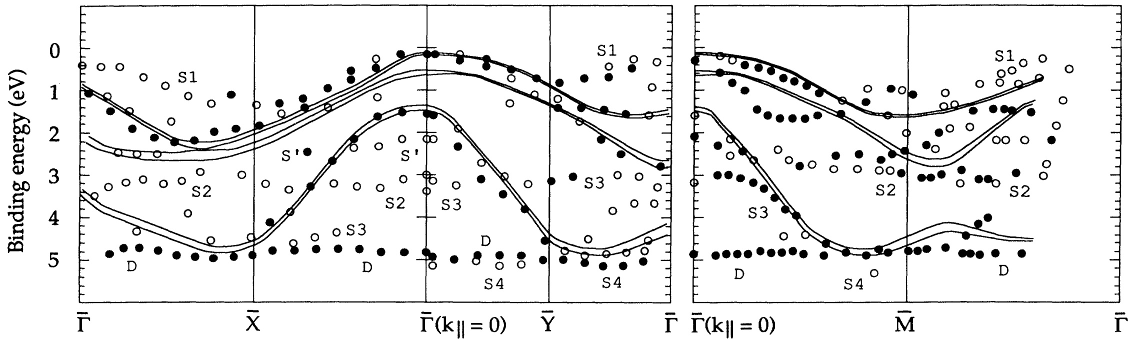

FIG. 4. Experimental band-structure plot at 26-eV photon energy along the $\bar{\Gamma}\bar{X}$, $\bar{\Gamma}\bar{Y}$, and $\bar{\Gamma}\bar{M}$ directions. Solid circles indicate clear peaks and open circles show less-well-defined structures in the spectra. The lines refer to direct transitions in the bulk using LCAO initial bands and final free-electron bands. The letters are the same as in Figs. 3 and 5.

direct transitions in the bulk. Deviations from the simple theory may be due to other final states than assumed (other umklapp processes or non-free-electron bands), lifetime broadening ("density of states" structures), or due to emission from surface states or resonances.

Structures not reproduced by the calculations are the ones labeled $S1$, $S2$, $S3$, $S4$, S', and D. In Fig. 5 we have plotted the positions of these structures, as observed at three different photon energies, 23, 26, and 29 eV. Different symbols are used for the three photon energies. Solid and open symbols refer to clear and faint structures, respectively. The dotted region in this figure shows the calculated projected bulk states, with the dot density indicating the density of states. It was obtained from the LCAO calculation which was fitted to the normal-emission bulk bands as described above. This means that the surface-emission peaks, to be discussed below, will be related to the correct bulk band energies. This is an advantage compared to the situation where the experimental surface-related features are related to pure theoretical bands.

Structure D at about 4.8-eV binding energy shows a small dispersion in all **k** directions. It is interpreted as originating from the high-density-states region at the low edge of the valence band. We have found the corresponding structures for ZnTe(110) (Ref. 2) and CdTe(110).[7] They can be reproduced in our calculations by introducing large broadening in the final state. As in the case of ZnTe, we find in the region of the band edge a surface state $S4$ which emerges below the band edge in the region of $\bar{M}$. Also halfway between $\bar{\Gamma}$ and $\bar{Y}$ we find a peak well below the band edge, probably due to the same $S4$ state. Due to the strong overlap with the relatively wide density-of-states peak, $S4$ is difficult to trace throughout the Brillouin zone. For ZnTe we have observed[10] the same feature around $\bar{\Gamma}$ and $\bar{X}$, but only as a shoulder on the density-of-states peak D.

Also the remaining structures $S1$, $S2$($S3$), and S' have their counterparts in CdTe (Ref. 1) and ZnTe,[2] and are surface induced. This conclusion is based on the observation that the corresponding dispersion curves have the periodicity of the surface Brillouin zone and are insensitive to changes in photon energy. $S1$ runs below the upper band edge, with a similar dispersion as the edge

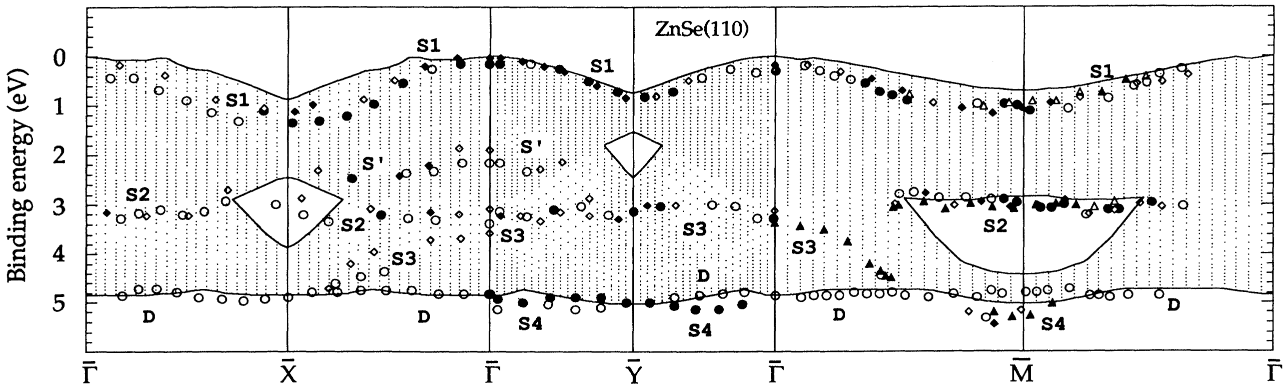

FIG. 5. Surface-related structures as observed at 23-eV (△), 26-eV (○), and 29-eV (◇) photon energies. Solid circles indicate clear peaks and open circles show less-well-defined structures in the spectra. The letters are the same as in Figs. 3 and 4. The hatched area shows the projected density of bulk states as obtained from a LCAO calculation.

and is therefore assigned as a surface resonance. Also $S2$, $S3$, and S' can be described primarily as surface resonances. Near $\bar{X}$ and $\bar{M}$ the $S2$ peaks appear, however, to be located in a gap, which justifies the more strict assignment as a true surface state. It is recognized that around $\bar{M}$ the $S2$ state is very close to the band edge, which calls for some caution regarding the assignment. It is worthwhile to repeat that the band edges are determined from a semiempirical band structure, based on fitting to normal-emission data. Therefore, we consider their location quite reliable.

IV. SUMMARY

By use of a model with direct bulk transitions to free-electron final bands, and in the spirit of our previous studies on other II-VI compounds, we have interpreted both normal and off-normal photoemission spectra from ZnSe(110). The critical energies at the Γ, X, and L points in the bulk Brillouin zone are estimated from the adjustment of the parameters in a semiempirical LCAO band calculation to fit the experimental data. By comparison with calculations of the surface electronic structure by Beres, Allen, and Dow,[5] we suggest that the observed $S1$, $S2$, $S3$, and $S4$ states have their counterparts in the calculated states $A4$ and/or $A5$, $A3$, $C2$, and $C1$, respectively. The most apparent discrepancies between our results and the calculations are that $S4$ ($C1$) near the $\bar{M}$ point is lower than the projected bulk density of states and S' is not predicted at all. It should be mentioned, however, that a similar state has been found experimentally for GaAs(110) (Ref. 11) and InSb(110),[12] and also predicted by calculations on GaAs(110).[13] Comparison with III-V compounds in this context is interesting, since they show, despite significantly lower ionicity, very similar geometric surface relaxations as the II-VI systems.[14]

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[1] H. Qu, J. Kanski, P. O. Nilsson, and U. O. Karlsson, J. Electron. Spectrosc. Relat. Phenom. **52**, 149 (1990); H. Qu, J. Kanski, P. O. Nilsson, and U. O. Karlsson, Vacuum **41**, 610 (1990).

[2] H. Qu, J. Kanski, P. O. Nilsson, and U. O. Karlsson, Phys. Rev. B **43**, 9843 (1991).

[3] A. Ebina, T. Unno, Y. Suda, H. Koinuma, and T. Takahashi, J. Vac. Sci. Technol. **19** (3), 301 (1981).

[4] C. Calandra, F. Manghi, and C. M. Bertoni, J. Phys. C **10**, 1911 (1977).

[5] R. P. Beres, R. E. Allen, and J. D. Dow, Phys. Rev. B **26**, 769 (1982).

[6] U. O. Karlsson, J. N. Andersen, K. Hansen, and R. Nyholm, Nucl. Instrum. Methods A **282**, 553 (1989).

[7] H. Qu, P. O. Nilsson, J. Kanski, and L. Ilver, Phys. Rev. B **39**, 5276 (1989).

[8] D. E. Eastman, W. D. Grobman, J. L. Freeouf, and M. Erbudak, Phys. Rev. B **9**, 3473 (1974).

[9] J. R. Chelikowsky and M. Cohen, Phys. Rev. B **14**, 556 (1976).

[10] H. Qu, J. Kanski, P. O. Nilsson, and U. O. Karlsson, Proceedings of the 11th European Conference on Surface Science, edited by J. L. de Segovia and F. Flores [Surf. Sci. (to be published)].

[11] A. Huijser, J. van Laar, and T. L. van Rooy, Phys. Lett. **65A**, 337 (1978).

[12] C. Janowitz, R. Manzke, H. P. Barnscheidt, H. Carstensen, and M. Skibowski, *Proceedings of the 19th International Conference on the Physics of Semiconductors*, edited by W. Zawadzki (Institute of Physics, Polish Academy of Sciences, 1988), p. 761.

[13] S. B. Zhang and M. L. Cohen, Surf. Sci. **172**, 754 (1986).

[14] F. Bechstedt and R. Enderlein, *Semiconductor Surfaces and Interfaces* (Akademie-Verlag, Berlin, 1988), p. 270.