Importance of resonances in surface-electronic-state spectroscopy: (110) surfaces of ZnSe and ZnTe

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The angle-resolved photoemission spectrum of the ZnSe(110) surface is reexamined, with several of its prominent features (in particular, the previously unexplained one near − 4 eV) assigned to resonant one-electron surface states. The empty surface states observed in the electron-energy-loss spectra of ZnSe and ZnTe are interpreted as Zn $3d$ surface Frenkel excitonic resonances, caused by the final-state electron-hole interaction.

I. INTRODUCTION

Recently Ebina *et al.* performed an angle-resolved photoemission (ARP) study of the (110) surface of ZnSe,[1] from which they were able to extract features of the (occupied) surface-state dispersion curves $E(\bar{k})$. Some of these features were found to be in agreement with the surface-state calculation of Calandra *et al.*[2] but others were not. Here we present calculations of dispersion curves for the resonant and bound surface states of ZnSe and ZnTe, and show that some discrepancies between the observations and previous theory appear to be resolved by a more complete treatment of the resonant states within the bulk bands.

Ebina, Asano, and Takahashi,[3] using electron-energy-loss spectroscopy, have also observed empty surface states in ZnSe and ZnTe. Our calculations indicate that the lowest empty one-electron surface-state band should lie at considerably higher energy than the lowest state observed by Ebina *et al.* but that the Zn $3d$ Frenkel core exciton[4] at the surface[5,6] is a resonance at an energy near their measured energy-loss peak.

The two types of resonances, intrinsic one-electron surface-state resonances and Frenkel excitonic resonances, are thus predicted to play major roles in determining the surface electronic spectra of semiconductors such as ZnSe and ZnTe.

II. METHOD OF CALCULATION

Our calculations employ a substantially better tight-binding model than those used in previous theoretical work— the sp^3s^* model of Vogl *et al.*[7] This model has a history of successes in many different areas, including the theories of bulk point[8] and extended[9] defects in a variety of semiconductors, core excitons in the bulk[4] and at the surfaces of III-V semiconductors,[5,6] surface-defect levels and Schottky-barrier heights,[6,10] and semiconductor surface states.[11] The energies of the bound and resonant surface states at a given surface planar wave vector $\bar{k}=(k_1,k_2)$ are determined using this model as follows.

First the bulk Green's function G_0 is obtained from the analytic representation[12]:

$$G_0(\vec{x},\vec{x}';\bar{k}E)=-2\pi i\sum_{k_3}\psi(\vec{x};\bar{k},k_3)\psi^{\dagger}(\vec{x}';\bar{k},k_3^*)\times\mathrm{sgn}(x_3-x_3')/v_3(\bar{k},k_3)\,, \tag{1}$$

where the notation is explained in Ref. 12.

Second, the perturbation matrix

$$V\equiv H-H_0 \tag{2}$$

is evaluated, where H_0 is the Hamiltonian matrix for the perfect crystal and H is the Hamiltonian after (i) the bonds are cut between a pair of adjacent (110) planes to form a pair of surfaces, and (ii) the surface atoms are allowed to relax in the fashion characteristic of (110) zinc-blende surfaces.[13]

Finally, the energies of bound and resonant surface states are calculated by means of the "effective-Hamiltonian" technique[12]: Let H_{eff} be

defined by

$$E - H_{\text{eff}} = G_0(E)^{-1} - V \ , \tag{3}$$

where $G_0(E)$ is the bulk Green's function within the subspace of the perturbation. One can readily calculate the eigenvalues E_i of H_{eff}:

$$H_{\text{eff}}\xi_i(E) = E_i(E)\xi_i(E) \ . \tag{4}$$

In a gap at fixed $\bar{k}$, H_{eff} is Hermitian and the condition for a surface bound state is

$$E_i(E) = E \ . \tag{5}$$

Within the bulk bands (at fixed $\bar{k}$), H_{eff} is non-Hermitian, but the condition for a resonance is

$$\text{Re}[E_i(E)] = E \ . \tag{6}$$

Details of the method will be given in a longer article.

III. OCCUPIED SURFACE STATES

Our predictions for bound and resonant surface states at the (110) surfaces of ZnSe and ZnTe are shown in Figs. 1 and 2. Much of the resonance structure and the states A_1' and A_2' were not reported in previous theoretical studies of these materials. Figure 1 also contains the features inferred from the ARP measurements for the occupied surface-related states at the ZnSe(110) surface. There is rather good agreement when one bears in mind that the theory contains sizable quantitative uncertainties at energies far from the band gap; e.g., the resonance predicted at approximately -12.5 eV could easily lie 1 to 2 eV higher. Notice that we are able to locate bound and/or resonant surface-state bands at all planar wave vectors on the boundary of the surface Brillouin zone.

The experimental features near $\bar{\Gamma}$ and $\bar{X}$ at approximately -11 eV are naturally explained by our predicted A_2 resonance at $\simeq -12.5$ eV. The strong features near $\bar{\Gamma}$ at approximately -4 eV, along both $\bar{\Gamma}\bar{X}'$ and $\bar{X}\bar{\Gamma}$, can be associated with our predicted C_2 resonance at $\simeq -3$ eV. These features were not explained by the previous calculation.[2] The features near $\bar{X}'$ and $\bar{X}$ in this energy range appear to be associated with the same resonance.

Near $\bar{\Gamma}$, just under the valence-band edge, we predict an A_4 band of resonances with initial downward dispersion along both $\bar{\Gamma}\bar{X}'$ and $\bar{X}\bar{\Gamma}$, in agreement with the measurements. (A_4 and A_5 appear to hybridize along $\bar{X}\bar{\Gamma}$.) These states below the valence-band edge had also been regarded as a discrepancy between the earlier theory and the data.[1] The same resonance can explain the data near $\bar{X}'$ and $\bar{X}$, just under the valence-band maximum.

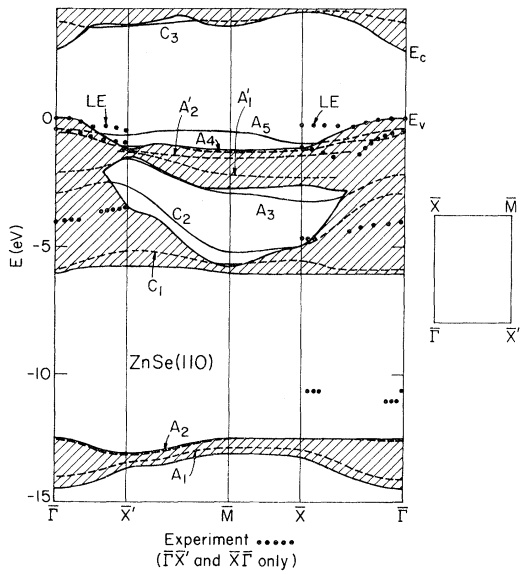

FIG. 1. Predicted energies (in eV) of surface bound states (solid lines) and surface resonances (dashed) for the (110) surface of ZnSe, as functions of the planar wave vector $\bar{k} = (k_1, k_2)$. The surface Brillouin zone is shown to the right; $\bar{\Gamma}$ is the origin, $\bar{k} = (0,0)$. The bulk bands are shaded. E_v and E_c are the valence- and conduction-band edges. The experimental features identified with bound and resonant surface states in Ref. 1, along the two symmetry lines $\bar{\Gamma}\bar{X}'$ and $\bar{X}\bar{\Gamma}$, are indicated by the dotted lines. LE labels the leading edge of Ref. 1.

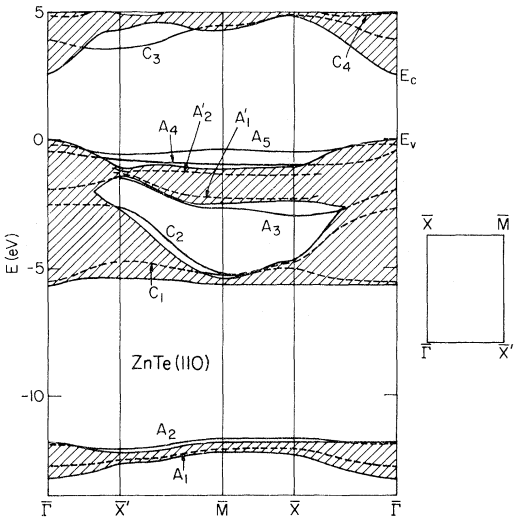

FIG. 2. Predicted bound and resonant surface states for ZnTe(110).

Finally, the leading edge[1] in the measurements may be due to both the valence-band edge and the bound and/or resonant surface states that are predicted to lie at $\simeq -0.5$ eV with respect to the valence-band edge. In the data, the surface band appears to emerge from the valence band as $\bar{k}$ increases away from Γ. The predicted surface-state band shows similar behavior, since it exhibits less dispersion than the top of the valence band.

There are several remaining features in the predicted dispersion curves that were not reported in the measurements. It would be interesting to see whether any of these features are strong enough to be seen in future experiments.

IV. UNOCCUPIED SURFACE STATES AND FRENKEL CORE EXCITONS

Our prediction for the lowest unoccupied surface-state band is dramatically different from that of the previous calculation,[2] in that we predict the minimum to lie approximately 1 eV above the conduction-band edge for both ZnSe and ZnTe, rather than at the edge.

We believe that the difference between our predicted unoccupied one-electron surface states and the data[3] occurs because the final-state electron-hole interaction is omitted from the one-electron description of these excitations. Using the same theory that yields the intrinsic surface states, plus a table of atomic energies for constructing the central-cell electron-hole interaction potential for a hole localized in the Zn $3d$ shell, we can also calculate the Zn $3d$ surface core excitons.[4–6] We find that they lie 0.4 and 0.8 eV above the conduction-band edge for ZnSe and ZnTe, respectively. (These materials are thus different from the Ga-V compounds, for which the predicted and observed surface excitons lie within the gap.)

We interpret the empty surface states observed in the energy-loss measurements[3] as surface Frenkel excitons, which are analogous to impurity states[5] and which are determined by both surface and bulk bands. Our results thus predict that no transitions to Frenkel exciton states within the band gap will be observed for the Zn $3d$ excitations of electron-energy-loss spectroscopy, for either ZnSe(110) or ZnTe(110). These predictions are in accord with the measured loss peaks.[3]

V. CONCLUSIONS

We have calculated the surface bound states and surface resonances as functions of the planar wave vector $\bar{k}$ for the (110) surfaces of ZnSe and ZnTe. The results for ZnSe are in good agreement with the measurements of Ebina *et al.*[1] Several discrepancies between experiment and previous theory appear to be resolved by a more complete treatment of the surface resonances.

Our results emphasize a central principle: *Surface resonances are as important as surface bound states.*

We predict that the Zn dangling-bond surface-state band has its minimum well above the conduction-band edge for both materials. This result is in agreement with the experimental finding that there are no intrinsic surface states within the band gap of either material.

Finally, we identify the observed electron-energy-loss peaks for the (110) surfaces of ZnSe and ZnTe with Frenkel surface-core-excitonic resonances lying above the conduction-band edge.

ACKNOWLEDGMENTS

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