fact the case, this class of materials forms a new and interesting addition to the list of ferroelectrics.

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Core Excitons and the Soft-X-Ray Threshold of Silicon*

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The photoabsorption coefficient in crystalline Si is computed in the 100-eV region (L_{II}, L_{III}) on the basis of core excitons, using an adaptation of the effective-mass theory. The line shape is in good agreement with experiment, and, using experimental evidence from the phosphorus impurity in Si as to the central-cell correction, we find the absolute value to be compatible with experiment.

The absorption spectrum of semiconductors in the extreme ultraviolet and soft-x-ray region has recently been investigated in detail using synchrotron radiation as a continuum source.[1] In particular, very high-resolution measurements of the $L_{II,III}$ absorption threshold of crystalline silicon have been performed.[2,3] The inadequacy of the one-electron theory to reproduce the sharp rise in absorption at the threshold energy, even if account is taken of the $\vec{k}$ dependence of momentum matrix elements,[4] has been pointed out, as well as the need for a theoretical investigation including the effect of the electron-hole interaction.[3-5]

The purpose of the present Letter is to carry out an analysis of the role of Coulomb interactions at this soft-x-ray threshold; we believe that, despite the various simplifications used in the following, the present calculation provides evidence for important excitonic effects in core electron transitions to the conduction band.

Absorption transitions from the $2p$ levels in Si begin at about 100 eV. A simple picture of the final state of a transition from a $2p$ core state can be obtained by starting with a description of the ground state of the crystal in terms of antisymmetrized localized atomic wave functions for the core electrons (equivalent to Bloch functions, since the shells are filled), and of the usual Bloch representation for the valence electrons.

When an impinging photon removes one of the $2p$ electrons, the corresponding hole is a very localized and "heavy" positive charge, which, far from the origin, appears to be pointlike. If we neglect, as is customary in semiconductors,[6,7] exchange effects in comparison with the Coulomb term in the electron-hole interaction, the situation is, except in a region very close to the excited atom, similar to a donor-impurity problem, in which an extra nuclear charge is introduced into the crystal. One can therefore use an effective-mass approximation for the excited

electron, while describing the hole in the tight-binding limit. This intuitive argument can be formally justified by carrying out the usual derivation of the effective-mass exciton theory,[6] replacing everywhere the hole wave function with an atomic state and taking proper account of its localization. Accordingly, screening effects are included, far from the excited atom, in the static dielectric constant.

One then recovers the familiar hydrogenlike spectrum, with a ground-state binding energy[8] $R = 30$–40 meV. The theory of optical transitions to exciton states in the effective-mass approximation,[9] predicting a series of discrete lines at $\hbar\omega = E_g - R/n^2$ with strength decreasing as n^{-3}, and a continuum enhanced near threshold, can also be extended to our case; it is appropriate to replace the anisotropic inverse-mass tensor near the Δ_1 conduction-band minima with an "average" scalar inverse mass μ^{-1}.

At this point, it is important to remember that the lifetime of the exciton state is rather short, being essentially equal to the radiative and Auger lifetime of the deep hole. Therefore, it is to be expected that the discrete lines will not be resolved.

Ignoring for the moment the actual structure of the Si conduction band, i.e., the degeneracy of the six Δ_1 valleys and the anisotropy of the inverse-mass tensor, as well as central-cell corrections, we compute the threshold absorption $\alpha(\hbar\omega)$ by convoluting the discrete and continuum contributions[10] with a Lorentzian of half-width Γ, that is,

$$\alpha(\hbar\omega) = |\vec{p}|^2\left[\frac{4\pi^2e^2}{m^2c\omega}\sum_n |F_n(0)|^2 \frac{\Gamma/2\pi}{[\hbar\omega - (E_g - R/n^2)]^2 + \Gamma^2/4} + \frac{e^2}{m^2c\omega}\left(\frac{2\mu}{\hbar^2}\right)^{3/2}\int_{E'>E_g} (E' - E_g)^{1/2}|F_{E'}(0)|^2 \frac{\Gamma/2\pi}{[\hbar\omega - E']^2 + \Gamma^2/4}\,dE'\right]. \quad (1)$$

Here $|\vec{p}|^2$ is the absolute square of the momentum matrix element between the $2p$ atomic function and the Bloch function at the bottom of the conduction band, and $|F(0)|^2$ is the absolute square of the envelope function at the origin, i.e.,

$$|F_n(0)|^2 = \frac{1}{\pi n^3}\left(\frac{2\mu R}{\hbar^2}\right)^{3/2} \quad (2)$$

for the discrete states, and

$$|F_{e'}(0)|^2 = \pi\gamma[e^{\pi\gamma}/\sinh(\pi\gamma)] \quad (3)$$

for the continuum states, where

$$\gamma = [R/(E' - E_g)]^{1/2}. \quad (4)$$

In order to take into account the spin-orbit splitting of the $2p$ core level into the L_{III} and the L_{II} states, we further superimpose the spectrum (1) with an analogous one, shifted[11] by 0.6 eV and weighted by a factor $\frac{1}{2}$.

The line shape computed on the University of Rochester IBM 360-65 for $\Gamma = 0.1$ eV and $R = 0.04$ eV is shown in Fig. 1 as the dashed curve which has been normalized to the observed[12] (solid line) optical density curve at -0.1 eV in this figure. It has been shown[13] that this value of the hole lifetime broadening provides a good fit to the emission spectrum associated with the $2p$ hole. Despite our simplifying assumptions, which will be discussed in the following, the agreement between the theoretical and the experimental line shape is quite satisfactory. For smaller values of Γ the $n = 1$ exciton peak is not completely smeared out and appears as a little bump on the

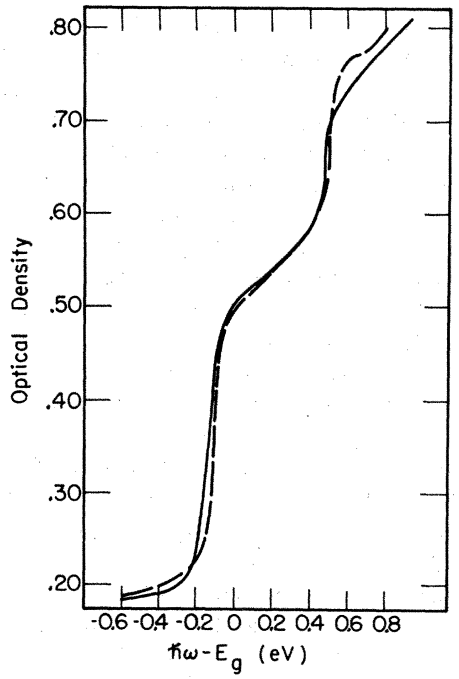

FIG. 1. Solid line, experimental optical density of Si near the $L_{II,III}$ edge (Ref. 12). Dashed line, theoretical line shape (present work).

low-energy side. On the other hand, if Γ is made larger, the steepness of the increase of Γ near threshold is accordingly reduced. Good agreement with the data is obtained for Γ between 0.09 and 0.12 eV, and this is consistent with the value suggested from emission data in Ref. 13. If the experimental linewidth in the experiments of Ref. 12 were too large, small structure predictable for $\Gamma < 0.09$ eV might not have been observable, so that smaller values of Γ cannot absolutely be ruled out. If one does not invoke excitons at all, by removing the first term from the right-hand side of Eq. (1), and the Sommerfeld factor from the second term, the computed shape bears no resemblance to that which is observed.[4]

It is not possible, however, to ignore the deviations from the simple effective-mass theory in a more ambitious calculation aiming at the prediction not only of the shape but also of the height of the absorption shoulder shown in Fig. 1. This is because the absorption coefficient (1) is proportional to the absolute square of the envelope function at the origin, that is, the region in which the validity of the effective-mass approximation breaks down, so that the expressions Eqs. (2) and (3) are no longer adequate. The amount of deviation from (2) is expected to be particularly large for $n=1$, and in Eq. (3), for E' very close to E_g. It is indeed known[14] by analysis by ENDOR data that in the case of the phosphorus donor in Si the actual $|F(0)|^2$ for the ground state exceeds the effective-mass value by a factor of about 10. (For Si, $Z=14$, for P, $Z=15$, so that the conditions are quite analogous.)

Bearing this in mind, we estimated the height of the first absorption shoulder in Fig. 1, corresponding to the onset of the L_{III} absorption, using for the matrix element of p the value obtained from the full zone $\vec{k}\cdot\vec{p}$ procedure as given by Ref. 13, and the more accurate calculation of Ref. 4, which are in substantial agreement with each other. Taking proper account of the degeneracies of the initial and final states, one obtains an absorption coefficient enhancement from the background (associated with transitions of the valence electrons) of 10^3–10^4 cm^{-1} if the effective-mass expressions Eqs. (2) and (3) are used. If a correction of the order of magnitude 10 discussed above is included for the lowest discrete state as well as for the continuum states immediately above the gap (for which the wave functions are large at the origin), the result is in semiquantitative agreement with the enhancement of $\sim 6\times 10^4$ cm^{-1} observed experimentally.

In order to discuss the role of the simplifying assumptions, it is important to remark that the main feature of the computed curve, i.e., the appearance of a steep absorption shoulder within a tenth of an eV, is essentially independent of the details of the density of states used, since the shoulder is mainly contributed by the $n=1$ peak and the continuum very close to the band gap, where the band structure is parabolic. Far from the threshold region, we expect the computed curve to differ from the experimental one, because the nonparabolicity would be reflected in a changed density of states, and because the central-cell corrections would become smaller and smaller, implying a decrease of absorption with respect to that obtained by Eq. (1), normalized to experiment by the extra factor of order 10 discussed above.

Furthermore, the relative contribution of the $n>1$ levels with respect to the $n=1$ level is actually given by a factor much smaller than $1/n^3$, since the first peak is enhanced by central-cell corrections. However, since the contribution of higher peaks is already small when evaluated according to Eq. (1), this correction does not affect the computed curve. The valley-orbit interaction can also be ignored, its effect consisting only of a negligible modification of the binding energy for the $n=1$ exciton.

In conclusion, it has been shown that a simple extension of the effective-mass theory to optical transitions from core states provides good agreement with the observed line shape and a reasonable estimate for the absolute value of the absorption coefficient. It is difficult to see how this line shape could be reproduced without taking Coulomb interactions into account. We therefore believe that the present calculation provides evidence for the importance of excitonic effects in the $L_{II,III}$ absorption threshold of Si.

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X-Ray Photoemission Valence-Band Spectra and Theoretical Valence-Band Densities of States for Ge, GaAs, and ZnSe†

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The first high-resolution valence-band x-ray photoemission spectra for Ge, GaAs, and ZnSe are compared with pseudopotential density-of-states calculations. The general agreement between the experimental and theoretical results is quite good. For ZnSe the photoemission spectrum shows the Zn $3d$ states to be higher in energy than the lowest valence-band s state. In order to obtain this ordering of states in the theoretical calculation, a pseudopotential with an explicit energy dependence is required.

Much theoretical and experimental effort has been devoted to the study of the band structures of tetrahedrally coordinated semiconductors because of their numerous applications. Most earlier measurements (optical spectroscopy, transport properties, etc.) have been useful in yielding information concerning electronic properties near the Fermi energy. Only recently have there been any experimental data (e.g., soft-x-ray spectroscopy) which yield information about the density of states in regions near the bottom of the valence band.

We report here the first high-resolution x-ray photoemission spectra for all valence bands in the isoelectronic series Ge, GaAs, and ZnSe. These experimental results are compared with theoretical valence-band density-of states calculations using the empirical pseudopotential method (EPM).[1] Since the lattice constants and ion cores are essentially constant for the series, the band spacings are used to obtain information about the increasing ionicity from purely covalent Ge to the more ionic ZnSe. The experimental results also yield information about the asymmetric part of the pseudopotential.

High-purity single crystals were cleaved in a dry-nitrogen atmosphere immediately before insertion into the spectrometer vacuum ($\sim 8\times10^{-9}$ Torr). The spectra were obtained on an HP 5950A electron spectrometer using monochromatized Al $K\alpha$ x rays (1486.6 eV). The possibility of using this method to study the valence-band