

Electron-hole interaction in the d -electron excitations of GeS and SnS

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The excitation energy of the Ge $3d$ and Sn $4d$ electrons in GeS and SnS is consistently 0.7 to 1.7 eV lower than one would expect from a combination of photoemission binding energies and optical interband transitions connecting valence and conduction bands. This, as well as the reversal of the intensity ratio of $d_{5/2}$ and $d_{3/2}$ excitations, is an indication for non-negligible d -hole conduction-electron interactions.

I. INTRODUCTION

In the one-electron model of transitions from core levels to the conduction bands, the excitation energies are given by the difference in binding energies of the core and conduction electrons. When the transition matrix elements are only weakly dependent on the wave vector of the conduction electrons and on the photon energy, the absorption coefficient is represented by the density of states in the conduction band. Absorption measurements on semiconductors performed in the vacuum uv with synchrotron radiation have indeed revealed structure which could be correlated with the density of conduction states.^{1,2}

In past years, there have been discussions as to whether the electron-hole interaction has an important influence on the optical excitations of core electrons. With the advent of reliable core-level binding energies from photo-emission experiments, the influence of the electron-hole interaction may be studied quantitatively. It is now well established that the optical spectra of core excitations in the alkali halides have strong excitonic character with exciton binding energies of several eV,^{3,4} similar to the excitons in the range of valence-band excitations. The absorption thresholds in semiconductors often agree (within 0.1–0.2 eV) with the predictions based on the one-electron model.^{5,6} However, the observed exciton absorption peaks detected by absorption or reflectivity experiments occur at lower energies (~ 1 eV) than those expected by the one-electron model (see Ref. 7 for PbSe and PbTe, Ref. 8 for Se, and Ref. 9 for GaAs). In Si the intensity of the threshold of the $2p$ excitations is enhanced with respect to the one expected from the one-electron model.¹⁰ This indicates the importance of electron-hole interaction also in the core excitations of semiconductors.

In this paper, we present evidence for excitonic effects in the excitations of the Ge $3d$ electrons in GeS crystals and the Sn $4d$ electrons in SnS crystals. Both compounds are layer structures with

a distorted rock-salt structure.¹¹

We proceeded in the following way (see also Fig. 1): The binding energies of the d -electron spin-orbit doublet and the density of states of the valence electrons have been measured with respect to the top of the valence band (TVB) by photoelectron spectroscopy with the He II resonance line of 40.8-eV photon energy. The energies of the main interband transitions between valence and conduction bands have been deduced from optical transmission, electron energy loss, and reflectivity spectroscopy.¹² From a comparison of these data with band-structure calculations for GeS (Ref. 13) it was concluded that these interband transitions [labeled (2,4)(3,5) in Fig. 1] start at valence states

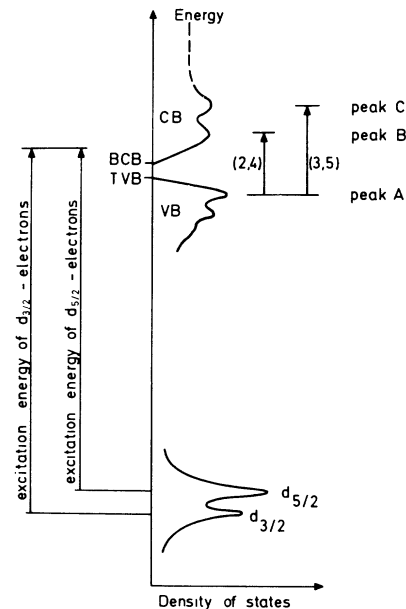


FIG. 1. Schematic diagram, representing binding energies and density of states of the d -electron doublet and the valence and conduction bands, optical interband transitions, labeled (2,4) and (3,5) between valence and conduction states of high density, and excitation energies of the d electrons. TVB: top of the valence bands. BCB: bottom of the conduction bands.

corresponding to the maximum of lowest binding energy of the density of states in the valence band labeled peak *A*. Moreover these interband transitions lead to two maxima in the density of states in the conduction bands.¹² In this way, these two maxima can be located on the scale of binding energies.

We deduce the excitation energies of the *d* electrons from electron-energy-loss spectra, which are proportional to $\text{Im}[-1/\epsilon(\omega)]$. As the energy of the excitations is usually read out from peak positions in $\epsilon_2(\omega)$ spectra, we performed a Kramers-Kronig analysis of $\text{Im}(1/\epsilon)$, which yielded both spectra of ϵ_2 and of the reflectivity *R*. We checked the consistency of the ϵ_2 spectra by comparison of the calculated *R* with the measured reflectivity spectrum for the case of SnS. We have found good agreement. In the one electron model, the excitation energies of the *d* electrons should be the differences between the binding energy of a given maximization in the density of states of the conduction bands and that of the *d* electron doublet. However, we do find considerable reduction of the energy of the Ge-3*d* and Sn-4*d* absorption peaks with respect to the predictions of the one electron model. Excitonic effects are also required to interpret the ratio of intensities observed for the absorption doublet produced by the spin-orbit splitting of the Sn-4*d* state. The fact that no structure due to the density of final conduction states could be identified, is considered as further evidence for the above discussed excitonic effects.

We will present the experimental results in Sec. II, and a detailed discussion in Sec. III.

II. EXPERIMENTAL RESULTS

A. Photoelectron spectroscopy

Angular-integrated photoelectron spectra of the valence bands of GeS and SnS and for photon energies of 21.2 eV, (HeI) 40.8 eV (HeII), and 1486.6 eV ($\text{AlK}\alpha_1$) were already reported in Ref. 14. Figure 2 represents these spectra for the case of SnS. A spectrum containing both valence-band structure and the *d*-electron doublet is presented in Fig. 3. Binding energies of the $d_{5/2}$, $d_{3/2}$ doublets of Sn 4*d* and Ge 3*d* with respect to the top of the valence band are given in Table I. As we will discuss later, the main optical transitions between valence and conduction bands have initial states which correspond to peak *A* in Figs. 1, 2, and 3.

Adding the energy of these interband transitions to the difference of binding energies between peak *A* and the *d* electrons, yields the difference between the binding energies of the maxima of the density of conduction states and the *d* electrons,

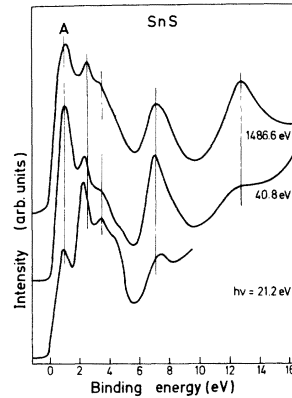


FIG. 2. Angular integrated photoelectron spectra of SnS for different photon energies, in the range of valence-band excitations.

without involving the position of the top of the valence band. Therefore we measured the binding energy difference between the *d*-electron doublets and peak *A* directly (see Table I). In this way we avoid the uncertainty in the identification of the top of the valence band in the photoelectron spectra. A careful estimate of the error of the energy difference between peak *A* and the *d*-electron levels is ± 0.2 eV.

B. Optical spectroscopy of valence-band excitations

ϵ_2 spectra of GeS and SnS in the fundamental absorption range, as obtained from a combined analysis of optical transmission-reflection and electron-energy-loss spectra, have been reported in Ref. 12. Because of the orthorhombic layer structure¹¹ the ϵ_2 spectra for the electric vector parallel to the crystalline directions *a* and *b* are different; *a* and *b* define the cleavage plane. In Ref. 12, the main optical interband transitions, defined by shoulders or peaks in the ϵ_2 spectra, are labeled

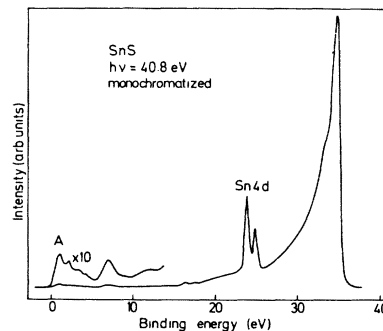


FIG. 3. Angular integrated photoelectron spectra of SnS with valence-band structure and Sn $4d_{5/2}$, $4d_{3/2}$ spin-orbit doublet.

TABLE I. Binding energies (BE) and excitation energies taken from the $\text{Im}(1/\epsilon)$, ϵ_2 , and reflectivity (R) spectra for GeS and SnS.

	BE relative to TVB	BE(<i>d</i>)-BE(<i>A</i>)	$\text{Im}(1/\epsilon)$ peak position	ϵ_2 peak position	R_{calc} peak position	R_{expt} peak position
Ge $3d_{5/2}$	29.61 ± 0.08	28.5 ± 0.2	31.68 ± 0.35	31.33 ± 0.35
Ge $3d_{3/2}$	30.16 ± 0.08	29.05 ± 0.2	31.85 (Ref. 15)			
Sn $4d_{5/2}$	23.80 ± 0.08	23.0 ± 0.2	25.59 ± 0.35	25.24 ± 0.35	25.2 ± 0.35 (sh) ^a	25.65 ± 0.2
Sn $4d_{3/2}$	24.88 ± 0.08	24.1 ± 0.2	26.61 ± 0.35	26.26 ± 0.35	26.37 ± 0.35	26.5 ± 0.2

^ash stands for shoulder.

2 and 3 for polarization parallel to axis *a* and 4 and 5 for polarization parallel to axis *b*. Utilizing a pseudopotential bandstructure calculation for GeS,¹³ the two main structures of highest oscillator strength (transition 2 or 4 and 3 or 5, respectively) have been assigned to transitions over a large volume in *k* space near the Brillouin-zone boundary. The initial states for these transitions are mainly the valence states, which produce peak *A* in the density of states. The final states are 0.8 to 1.8 eV above the bottom of the conduction bands, respectively. They represent two maxima in the density of states of the conduction bands.

For the following discussion, we neglect the anisotropy of 0.2 eV in the transition energies and average these transitions for the two crystalline directions *a* and *b*. We label the averaged transitions (2, 4) and (3, 5) (see Table II).

C. Electron-energy-loss spectroscopy

Electron-energy-loss spectra of thin single-crystal films of GeS and SnS were measured by transmission, as described in Ref. 12. The energy resolution, given by the halfwidth of the no-loss line, was 0.5 eV. As an example, the energy loss function $\text{Im}(1/\epsilon)$ is shown in Fig. 4 in the range of the Sn-4*d* excitation in SnS compound.

The shape and the position of the spectral features in the loss function did not change with the momentum transfer. Such a behavior is expected for excitations from narrow bands of core electrons. No doublet structure was resolved in GeS, probably because of insufficient resolution.

TABLE II. Energies of interband transitions (2, 4) and (3, 5) averaged over polarization directions *a* and *b*, in eV (Ref. 12).

	(2,4)	(3,5)
GeS	3.4 ± 0.1	4.4 ± 0.1
SnS	2.9 ± 0.1	3.9 ± 0.1

The peak positions of $\text{Im}(1/\epsilon)$ for GeS are in good agreement with the electron-energy-loss data of Ref. 15 (see Table I). SnS displays a doublet structure with a separation equal to the spin-orbit splitting observed in the photoelectron spectra. All peak positions of $\text{Im}(1/\epsilon)$ are presented in Table I. For SnS, we performed a Kramers-Kronig analysis of the energy-loss function yielding ϵ_1 , ϵ_2 and the reflectivity R_{calc} , calculated from ϵ_1 and ϵ_2 . The details of this analysis have been given in Ref. 12. $\text{Im}(1/\epsilon)$, ϵ_2 , and R_{calc} are displayed in Fig. 4. The peak positions of the Sn-4*d* excitations in the ϵ_2 spectra are displaced by about 0.35 eV to lower energy with respect to the corresponding peak in the energy-loss spectrum.

Experimentally, we have found no difference in the oscillator strength of the *d*-electron excitation structure in GeS and SnS. Therefore, one may safely assume, that also in GeS the peak position in ϵ_2 is about 0.35 eV lower than the peak position in $\text{Im}(1/\epsilon)$. Peak positions in ϵ_2 are also presented in Table I.

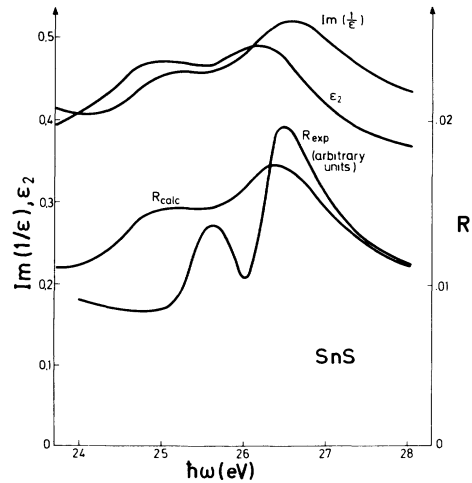


FIG. 4. $\text{Im}(1/\epsilon)$, ϵ_2 , and reflectivity R_{calc} obtained for SnS from the electron energy loss spectra. The measured reflectivity is R_{expt} .

D. Reflectivity spectra in the range of the d -electron excitations

For SnS the reflectivity at near-normal incidence was measured in the vacuum ultraviolet with a resolution of 0.2 eV, utilizing the synchrotron radiation facility of the Deutsches Elektronen Synchrotron (DESY).¹⁶ The measured reflectivity is plotted in Fig. 4 in arbitrary units. Within the experimental error of 0.35 eV, the positions of the higher-energy peaks in R_{expt} and R_{calc} are in agreement.¹⁷

III. DISCUSSION

Transitions from the d -electron levels to the conduction bands of these compounds are symmetry allowed for all bands throughout the Brillouin zone. The conduction-band states are mainly derived from the cation p states (Ge $4p$, Sn $5p$) and to a smaller extent from the sulfur $3p$ states, reflecting the different valence of cations and anions and the ionicity of the compounds.¹⁴ The small dispersion in most of the s -like valence bands^{13, 14} indicates that there is little admixture of s states to the conduction bands. We can therefore safely assume that the matrix elements for transitions from valence to conduction bands do not depend strongly on energy. As mentioned in Sec. I, without d core-hole-electron interaction the excitation spectra should roughly map the density of states in the conduction bands. The spin-orbit splitting of the d electrons should give rise to two contributions to the excitation spectra, displaced by the spin-orbit splitting with an intensity ratio of 6:4, reflecting the multiplicities of the $d_{5/2}$ and $d_{3/2}$ components. The energies of the d excitations should correspond to the energy difference between the d -core states and the regions of high density of states in the conduction bands (indicated as peak B and C , in Fig. 1) as derived from photoelectron and optical spectroscopy. Table III, however, demonstrates that this is not the case. The observed transition energies fall short by energies of about 0.7 and 1.7 eV, with respect to the two maxima B and C in the density of conduction

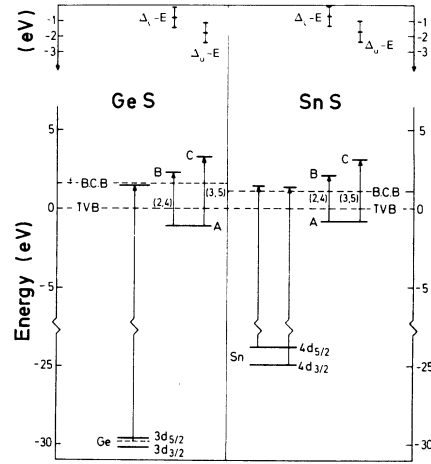


FIG. 5. Binding energies of d electrons and of the peaks A , B , C (see Fig. 1) with respect to the top of the valence band (TVB) and the bottom of the conduction band (BCB). The arrows labeled (2,4) and (3,5) are the average optical interband transitions form Table II, starting at level A . The long arrows, starting at the d levels are the excitation energies, derived from peak positions in spectra of ϵ_2 (Table I). $\Delta_I - E$ and $\Delta_u - E$ are the energy differences between the end points of the long and the two short arrows for each material (see Table III).

states. Even in the case that there were no minimum in the density of states of the conduction bands between the final states B and C , but rather a broad maximum, we would nevertheless have this energy difference of 0.7 to 1.7 eV. This indicates non-negligible electron-hole interaction. However, the energy differences $\Delta_I - E$ and $\Delta_u - E$ cannot be interpreted as binding energies of d excitons. Exciton binding energies are usually defined as the energy difference between exciton energy and the distance in energy between the initial state and the bottom of the conduction band (BCB).

In Fig. 5, the energy of the bottoms of the conduction bands is given together with the binding

TABLE III. E is the energy of the peak positions in ϵ_2 , due to d -electron excitations Δ_I (Δ_u) is the difference in binding energies between the component of the d -electron doublet and peak B (peak C) in the density of states of the conduction electrons (see Fig. 1). The differences $\Delta_I - E$ and $\Delta_u - E$ are expected to be zero in the one-electron model (see text).

	E	$\Delta_I =$ BE(d)-BE(peak B)	$\Delta_u =$ BE(d)-BE(peak C)	$\Delta_I - E$	$\Delta_u - E$
Ge $3d_{5/2}$ {	31.33 ± 0.35	31.9 ± 0.3 {	32.9 ± 0.3 {	-0.82 ± 0.65 {	-1.79 ± 0.65
Ge $3d_{3/2}$ }					
Sn $4d_{5/2}$	25.24 ± 0.35	25.9 ± 0.3	26.9 ± 0.3	-0.66 ± 0.65	-1.66 ± 0.65
Sn $4d_{3/2}$	26.26 ± 0.35	27.0 ± 0.3	28.0 ± 0.3	-0.74 ± 0.65	-1.74 ± 0.65

energies of the d electrons and of peaks A , B , and C . The position of the BCB is determined by the position of the top of the valence band and the transition energy of the fundamental gap, as presented in Ref. 12. (Note that here, for the first time, we make use of the position of the top of the valence band with respect to the d levels and peaks A , B , and C). The apparent final state of the d -electron excitations lies within the error of $\pm 0.4\text{eV}$, at the bottom of the conduction band. This is analogous to the results, observed in the cubic semi-conductors, mentioned in Sec. I^{7,9}. The state of the excited electron must be considered as localized mixing bands over a width of 1–2eV. Therefore, the final states of the (2,4) and (3,5) transitions are not seen in the core absorption spectra but only the spin-orbit splitting of the core states.

There is another argument favoring the excitonic nature of the d -electron excitations. As may be seen from Fig. 4, the intensity ratio 6:4 for $d_{5/2}$ to $d_{3/2}$ excitations is reversed. Similar reversals of intensities of spin-orbit components have been explained for the case of alkali halides and for Ga-3d to surface-state transitions in GaAs by electron-hole exchange interaction (Ref. 18 and 19, respectively). The spin-orbit splitting varies quadratically with the ratio of exchange to spin-orbit coupling constant, while the ratio of intensities of the doublet components varies linearly. Thus for small exchange constants significant changes in the intensity ratio can result with little change in the splitting. The electron-hole exchange interaction

is proportional to the square of the excitonic envelope function at zero distance.¹⁸ The observed reversal of the intensity ratio (Fig. 4) indicates, therefore, a localized excitation. The same argument applies also to the intensity ratio of the spin-orbit components for the transitions from the outermost core levels of the III-V compounds to the conduction bands.²

IV. CONCLUSIONS

Although the electronic band structure of the IV-VI layer compounds is not as well known as that of the tetrahedral semiconductors, experimental data (optical constants, electron energy losses, and photoemission) provide strong evidence for the excitonic character of the d -electron excitations in those materials. It is not possible to explain the absorption spectra for d -electron excitation with the density of states of the conduction bands, as would be expected if no exciton interaction were present.

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¹⁷In Fig. 4, the spin-orbit splitting derived from the experimental reflectivity is 0.85 eV, whereas the spin orbit splitting from the energy-loss spectra is 1.00 eV, in good agreement with the value of 1.08 from photo-emission. The reason for this discrepancy is unknown. However, these discrepancies are too small as to invalidate the conclusions of this paper.

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