

Composition dependence of the valence-band states in III-VI and IV-VI solid solutions

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We report on a study of the valence-band states in $\text{GaS}_x\text{Se}_{1-x}$ compounds and in $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ compounds by photoemission spectroscopy using linearly-polarized synchrotron radiation. The changes of the valence-states binding energies with x are always smooth but much larger for $\text{GaS}_x\text{Se}_{1-x}$ than for $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$. For the $\text{GaS}_x\text{Se}_{1-x}$ family some of these effects are related to the "cationic" or "anionic" character of the corresponding valence-band states while the anomalous behavior observed for the states at the top of the valence band appears related to composition-induced changes in their atomic-orbital character.

I. INTRODUCTION

We have investigated the binding energy and the atomic-orbital character of the valence-band states in $\text{GaS}_x\text{Se}_{1-x}$ and $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ solid solutions in the range $x=0$ to 1. The study has been carried out by photoemission spectroscopy with linearly polarized synchrotron radiation. For both series of compounds we have found that the measured binding energy of the valence-band states changes with x , the composition parameter. This dependence on x is smooth and continuous. For $\text{GaS}_x\text{Se}_{1-x}$ the atomic-orbital character of each state is the most important factor in determining magnitude and direction of the x dependence of its binding energies. A similar correlation has not been found for $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ compounds where all the binding energies exhibit much weaker dependence on x than for $\text{GaS}_x\text{Se}_{1-x}$ compounds.

Extensive photoemission investigations¹⁻⁶ and theoretical studies^{2,5,7-11} have recently clarified to a great extent the nature of the electronic states in different families of layer compounds. Detailed results have been obtained in particular for groups III and IV layered chalcogenides.¹⁻¹¹ In the present article we extend these investigations to a particularly interesting kind of materials in these families, the ternary solid solutions GaSe-GaS and $\text{SnS}_2\text{-SnSe}_2$. The main goals of our investigation were the following. First we wanted to search for possible discontinuities in the dependence on composition of the valence-band states. The possible presence of discontinuities for $\text{GaS}_x\text{Se}_{1-x}$ compounds was suggested by Raman¹² and optical¹³ data and it was primarily associated with stacking effects. The stacking geometry changes

from ϵ/γ stacking to β stacking as the composition parameter, x , increases.¹² This change, for example, strongly influences the Raman-active modes.¹² The observed discontinuities¹³ in the changes of the optical data with x suggested that the electronic states are also influenced by the stacking geometry. However, our present study gives negative results and shows no discontinuities in the shift in energy of the valence-band states with x . The second goal was to determine the sensitivity of each valence-band state to the kind of anion atoms forming the crystal. This sensitivity was expected to be directly related to the atomic character of the state.¹³ It appeared, therefore, a good probe of theoretical predictions^{2,5,7-11} of the atomic-orbital character in GaSe , GaS , SnSe_2 , and SnS_2 . This verification has been very successful for the III-VI compounds but less satisfactory for the IV-VI compounds and we shall see that some theoretical problems still remain for the latter materials.

The remainder of this article will be divided in four sections. Section II will describe the experiments and their results. Sections III and IV will discuss the results for $\text{GaS}_x\text{Se}_{1-x}$ and for $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$. Section V will summarize our conclusions.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The experiments consisted of taking ultraviolet photoemission energy distribution curves (EDC's) on seven distinct compounds in each of the two families at different photon energies and photon polarizations. The single crystals have been grown by the technique of the chemical transport reactions with iodine. After

reaction of the elements mixed in stoichiometric ratio the compounds were chemically transported forward and backward in the silica glass crucible, several times, in order to improve the homogeneity. The last transport was slackened by decreasing the temperature gradient, so that large flaky crystals grew in a few days. Typical growth temperatures are 800 °C for Ga compounds and 600 °C for Sn compounds. Usually, a larger quantity of iodine, added as transport agent (5 mg/cm³), resulted in wider and thicker crystals.

Mixed crystals of GaS_xSe_{1-x} could also be grown from the melt by the Bridgman-Stockbarger technique. The prereacted compound was sealed in a crucible with a bent tip. The melt at 1040 °C is cooled down from the tip forward at a rate of a few mm/h. In order to grow single crystals of Sn compounds, it is preferable to start with a melt richer in the metal (Sn) because of the incongruent melting of the stoichiometric compound. Heat treatments of the solidified ingots improve the quality of the single crystal.

The photoemission spectra were taken using photons emitted by the storage ring Tantalus I of the University of Wisconsin Synchrotron Radiation Center. A monochromatic beam was obtained with a vertical, bakable Seya-Namioka monochromator. We routinely took data at many different photon energies in the range 17–30 eV for each compound. The peak positions of the valence-band spectra in the EDC's of these materials depend on the photon energy in the lower part of this photon energy. We observed that this dependence becomes weaker as the photon energy increases. All the peaks reach their asymptotic position below 23–24 eV. In the case of GaSe and SnS₂, in particular, we observed no change in the spectral peak positions when the photon energy changed in the range 24–40 eV. Therefore we based the discussion of our data on the assumption that the spectra in the upper part of our photon energy range correspond to the density of states.^{1,5}

The experimental chamber was equipped with a double-pass cylindrical mirror electron energy analyzer. The samples were cleaved *in situ* and the pressure was always kept below 8×10^{-11} Torr (base pressure: 3.5×10^{-11} Torr). The contamination rate at these pressures for these extremely unreactive materials is negligible.^{1,4}

The geometry of the experimental chamber enabled us to change the polarization angle, p , between the sample normal and the electric field of the radiation without modifying the photoelectron collection geometry. The angle p could be selected in the range 47.7°–90° with an accuracy $\pm 0.5^\circ$. The photoelectron collection geometry was such that the acceptance cone of the analyzer included the sample normal. More details about the experimental geometry have been given in Ref. 14.

Figure 1 shows typical EDC's for GaS_xSe_{1-x} compounds. Here the dashed lines correspond to a polarization angle $p = 90^\circ$ (s polarization) and the solid lines to polarization angles of 75°–79° (p polarization). These spectra were taken at a photon energy of 22 eV (curves 3 and 6) or 19 eV (curves 1, 2, 4, and 5). The three upper curves 4, 5, and 6 were taken on GaS and the three lower curves 1, 2, and 3 on GaS_{0.2}Se_{0.8}. The general appearance of these spectra is similar for these two compounds as well as for all other compounds in this family. Five EDC features

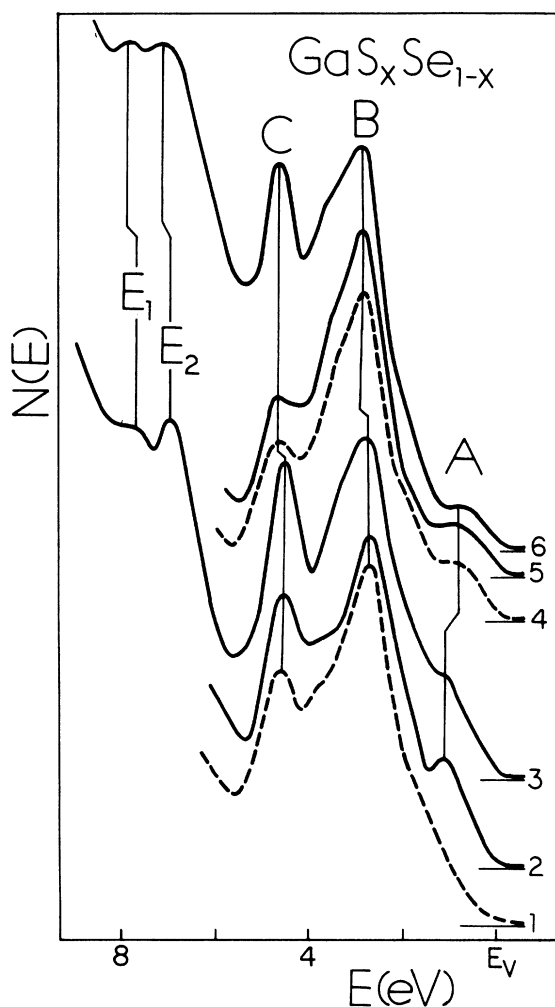


FIG. 1. Photoelectron energy distribution curves (EDC's) taken on two compounds in the GaS_xSe_{1-x} series. Curves 1, 2, and 3 were taken on GaS_{0.2}Se_{0.8} and curves 4, 5, and 6 were taken on GaS. The photon energy was 19 eV for curves 1, 2, 4, and 5 and 22 eV for curves 3 and 6. The two dashed lines, curves 1 and 4, were taken with a polarization angle $p = 90^\circ$ (s polarization), i.e., with the electric vector of the photon parallel to the sample surface (xy plane). All other curves were taken with p -polarized photons and the angle p was 79° for curves 2 and 5, and 76.5° and 75° for curves 3 and 6.

are visible, peaks A , B , C , E_1 , and E_2 . It is evident from curves 1 and 2 that peak A is strongly polarization dependent in $\text{GaS}_{0.2}\text{Se}_{0.8}$. It has almost no intensity when s -polarized photons are used. The same polarization effect cannot be observed for GaS , curves 4 and 5. All other compounds in this family do exhibit a weaker peak A for s polarization than for p polarization but this polarization effect becomes more pronounced as x decreases. Figure 2 shows the dependence of this photon polarization effect on p for GaSe .¹⁴ These data of Fig. 2 are consistent with a $\cos^2 p$ dependence of the intensity of peak A and the interpretation of this dependence will be discussed in Sec. III.

Typical spectra for the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ family are shown in Fig. 3. Curves 1, 2, 3, and 4 in this figure correspond to $x = 0.9, 0.7, 0.3,$ and 0.1 . No strong polarization effects were observed for this series of compounds in agreement with earlier findings^{4,5} for SnS_2 . The curves shown in Fig. 3 were all taken with $p = 90^\circ$. Once again the general appearance of the spectra is similar for all the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ compounds and it corresponds to the well-known EDC's published^{4,5} for SnS_2 . Four features can be identified, peaks A , B , C , and D .

In Figures 1 and 3 one observes small but detectable shifts in energy of the EDC peaks as x changes.

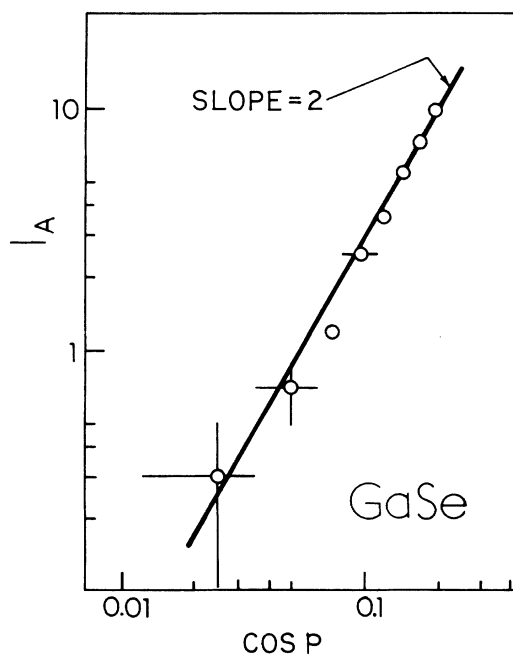


FIG. 2. Intensity of peak A in GaSe (in arbitrary units) plotted as a function of the cosine of the polarization angle p . The data were taken at a photon energy of 23 eV and the intensity of peak A was corrected for the tail of peak B . A straight line with slope 2 is superimposed for comparison upon this log-log plot.

The position of the EDC peaks is referred here to the top of the valence band as determined by a linear extrapolation of the EDC upper edge. The experimental peak positions are plotted in Fig. 4 as a function of x for both the $\text{GaS}_x\text{Se}_{1-x}$ series and the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ series. Note that the zero of the energy scale for each of the five $\text{GaS}_x\text{Se}_{1-x}$ peaks and of the four $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ peaks has been arbitrarily shifted in Fig. 4. This was done to facilitate the comparison of the x dependence of different peaks. It is evident from the plots of Fig. 4 that the x dependence of the binding energies does not exhibit detectable discontinuities. The experimental points are consistent with a linear dependence of the binding energy on x . This is emphasized by the straight lines seen in Fig. 4 which correspond to least-squares fits of the data. The slopes of these lines are listed in Table I.

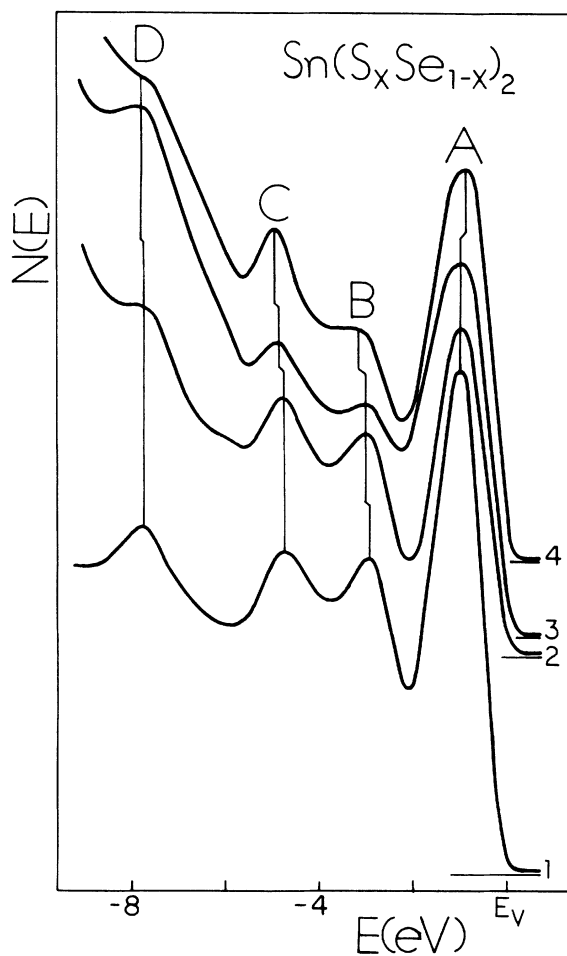


FIG. 3. Photoelectron EDC's taken on four compounds in the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ series. All the curves were taken at a photon energy of 25 eV and with $p = 90^\circ$ (no photon polarization effects have been observed for these materials). The crystal composition for curves 1, 2, 3, and 4 was $\text{SnS}_{1.8}\text{Se}_{0.2}$, $\text{SnS}_{1.4}\text{Se}_{0.6}$, $\text{SnS}_{0.6}\text{Se}_{1.4}$, and $\text{SnS}_{0.2}\text{Se}_{1.8}$.

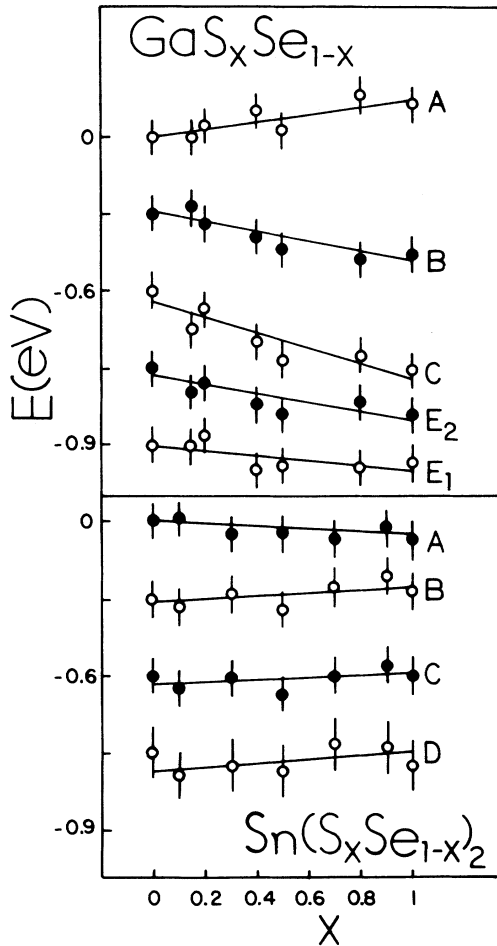


FIG. 4. Plot of the EDC peak positions as a function of x for the two series of materials under investigation. The energy of each of the five $\text{GaS}_x\text{Se}_{1-x}$ peaks and of the four $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ peaks has been referred to a different reference energy. This has been done to emphasize the different behavior of the different peaks.

TABLE I. Slopes ($\Delta E/\Delta x$) determined by linear least-squares fit of the data plotted in Fig. 4.

Crystal family	Peak	Slope (eV)
$\text{GaS}_x\text{Se}_{1-x}$	A	0.14
	B	-0.21
	C	-0.26
	E_2	-0.18
	E_1	-0.10
$\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$	A	-0.05
	B	0.05
	C	0.05
	D	0.06

III. DISCUSSION OF THE $\text{GaS}_x\text{Se}_{1-x}$ SPECTRA

The discussion of our spectra will be based on some of the already established properties of the binary compounds GaSe and SnS_2 . A detailed discussion of the valence-band properties of these materials based on their theoretical band structures was recently presented in Ref. 1 for GaSe and in Ref. 4 for SnS_2 . We summarize here the results of Ref. 1 that are most relevant to our present discussion.

The band structure of GaSe includes three groups of bands 0–8 eV below E_v . The first group below E_v is primarily due to bonding Ga–Ga states containing Se p_z orbitals (π bands). Together with the Ga–Ga antibonding states these Ga–Ga bonding states give rise to the forbidden gap. These p_z -like orbital correspond to peak A in the GaSe spectra. The second group of bands originates from p_x, p_y states in the Ga–Se bond. These bands give rise to peaks B and C in the GaSe spectra. The bands at the bottom of this second group are quite dispersive and their zone-boundary energies essentially overlap the Γ -point energies of the third group of bands.² This third group of bands is due to essentially nonbonding Ga s orbitals and it corresponds to the spectral peaks E_1 and E_2 .

The data of Figs. 1 and 4 show no discontinuities in the dependence on x of the peak positions in $\text{GaS}_x\text{Se}_{1-x}$. This suggests that the clear discontinuities found in the optical data¹³ are related to conduction-band effects. We observe that the conduction-band states are more likely to be affected by stacking effects than those in the valence band. We see in Figs. 1 and 4 that the dependence on x is different for the different $\text{GaS}_x\text{Se}_{1-x}$ EDC peaks. The most dramatic difference is between peak A which shifts upwards as x increases and all other peaks which shift downwards. Detailed optical data presented by Schlüter *et al.*¹³ suggest that a strong dependence on x should correspond to a strong anionic character of the peak. We shall see now that this simple rule explains some of the differences between the x dependence of different peaks but it is not sufficient to explain the peculiar behavior of peak A.

The presence of "mostly anionic" or "mostly cationic" peaks in the density of states is related to the nonionicity of some of the chemical bonds in GaSe-like compounds. All the materials in $\text{GaS}_x\text{Se}_{1-x}$ crystallize in the same structure as GaSe except for changes in the stacking geometry of the layers.^{7,8} This structure becomes unstable upon charge transfer leading to a completely ionic $\text{Ga}^+(\text{S}_x\text{Se}_{1-x})^-$ configuration.⁷ In particular the Ga–Ga bonds perpendicular to the layers (z direction) must be covalent in character.^{7,8} On the contrary the anion-cation bonds are mostly ionic in character.^{7,8} Depeursing⁸ has recently demonstrated that an increase in the ionicity of the anion-cation bonds causes a downwards shift of

the density of states peaks related to this bond, e.g., peak *B*. This is confirmed by our present results since the ionicity of the anion-cation bonds increases while changing composition from GaSe to GaS. The same effect should not be found in peaks with cationic character. For example peaks E_1 and E_2 have a strongly cationic character^{7,8} and are mostly due to Ga *s* electrons. Table I correspondently shows that the *x* dependence of peaks E_1 and E_2 is weaker than that of the mostly anionic peaks *B* and *C*. The dependence on *x* still observed for peaks E_1 and E_2 confirms the recent theoretical prediction by Depeursing⁸ that these peaks have some anionic component in addition to the predominant cationic components.

Differences between "cationic" and "anionic" peaks do not explain the difference between the *x* dependence of peak *A* and of all other peaks. For example the anionic components are comparably strong in peak *A* and in peak *B*^{1,7,8} but they move in opposite directions as *x* increases. We propose that the peculiar behavior of peak *A* is related to *changes* in its atomic-orbital character induced by changes in *x*. This hypothesis is supported by the observed photon-polarization effects. We have seen that peak *A* is much weakened in GaSe when the angle ρ is increased towards its 90° limit. This effect was observed and analyzed in detail for different III-VI compounds^{1,15} and similar effects were observed and analyzed in ZnIn₂S₄ (Ref. 16) and in chemisorbed overlayers on silicon and germanium surfaces.¹⁷ It was demonstrated¹⁵⁻¹⁷ that this polarization effect is due to a strong p_z character of the corresponding valence-band states. The results shown in Fig. 2 are actually consistent with the somewhat stronger assumption that the initial states of the photoemission process are p_z -like and the final states of the optical excitation nearly-plane waves.¹⁴ These assumptions give indeed a $\cos^2\rho$ polarization dependence as seen in Fig. 2. A p_z character of peak *A* in GaSe is also in excellent agreement with the theoretical predictions of different authors.^{7,8} The theory shows⁷ that peak *A* is due to Ga p_z states (Ga-Ga bonding) and to Se p_z states (nonbonding) while the p_x and p_y states (Ga-Se bonding) are found at energies at least 1 eV below these p_z states. We have seen, however, that when *x* increases the above polarization effect tends to disappear. Earlier experiments actually demonstrated¹ that weak polarization effect are present for GaS both in peaks *A* and *B*. This indicates that as the composition changes from GaSe to GaS the p_z states at the top of the valence band become increasingly mixed with the deeper p_x and p_y states. At the same time the plots of Fig. 4 show that the average distance between the p_z and p_x, p_y states increases by almost 0.4 eV.

This mixing could be explained at least by two different causes, crystal-field interaction and interlayer interaction. A crystal-field interaction mixing would

be forbidden at high-symmetry points of the Brillouin zone but it is allowed in lower symmetry regions in *k* space. This implies that large contributions in the angle-integrated EDC's arise from low-symmetry regions of the extended zone scheme and this in agreement with recent angle-resolved photoemission results for GaS.¹⁸ Another possible cause of the observed mixing between p_z and p_x, p_y states is the interaction between atoms in adjacent layers. A bigger overlap between their orbitals has been theoretically predicted¹⁹ as the composition changes from GaSe to GaS. The overlap should induce changes in the upper valence-band states consistent with our findings. These effects actually involve states at the *A* point of the Brillouin zone as well as states at the Γ point and this emphasizes the limits of the two-dimensional character in our crystals. In summary our results indicate that contrary to GaSe the top of the valence band in GaS does not have a clear p_z character but a mixed atomic-orbital character involving all kinds of *p* states.

IV. DISCUSSION OF THE RESULTS FOR $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$

Similar to what we did in Sec. III for GaSe our discussion of the SnS_2 - SnSe_2 solid solutions will be based on some of the known properties of the SnS_2 valence band. The band structure of SnS_2 and the corresponding valence-band properties were discussed in detail in Ref. 4. We summarize here the results of that discussion. The band structure of SnS_2 exhibits two different groups of bands in its top 8 eV. The first group below E_v includes the bands due to the *p* electrons of the ionized sulphur atoms. These states give rise to peaks *A*, *B*, and *C* in the SnS_2 spectra. The second group of bands is due to Sn *s* orbitals and it is associated with the spectral peak *D*—although this identification is only partially satisfactory as we shall discuss below.

It is evident from Fig. 4 and from the slopes listed in Table I that the dependence on *x* of the valence-band binding energies is much weaker for the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ family than for the $\text{GaS}_x\text{Se}_{1-x}$ family. There are also less dramatic differences between the behavior of different states. This is not surprising since the chemical bonds in the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ compounds are more ionic in character than those in the $\text{GaS}_x\text{Se}_{1-x}$ compounds.⁵ As matter of fact the CdI₂-like structure typical of these IV-VI solid solutions would not be *a priori* unstable as the GaSe structure for a completely ionic $\text{Sn}^{2+}(\text{S}_x\text{Se}_{1-x})_2^-$ configuration.

The rather strong ionic character of the chemical bonds, however, does not prevent some cationic component from being present in the valence band of the $\text{Sn}(\text{S}_x\text{Se}_{1-x})_2$ compounds. The theory^{5,9,11} predicts Sn *s*-like states to be found in SnS_2 and

SnSe₂ at energies ≥ 5.5 eV from the top of the valence band, i.e., below the anion *p*-like states. It is commonly assumed⁴⁻⁶ that these states give rise to the photoemission peak *D* in Fig. 3 although no satisfactory explanation was obtained until now for the ~ 1.4 -eV discrepancy between theoretical and experimental binding energies. The other three peaks in the EDC's of Fig. 3 all correspond to theoretical peaks^{5,7,9-11} with anion *p*-like character. The difference between "cationic" and "anionic" states, therefore, cannot explain the *x* dependence we observe for Sn(S_xSe_{1-x})₂ in Fig. 4 and in Table I. In fact we see that peak *A* has a different dependence on *x* with respect to all other peaks although it has an anionic character similar to peaks *B* and *C*. On the contrary we do not see much difference between the behavior of the mostly cationic peak *D* and that of the anionic peaks *B* and *C*.

The current band-structure calculations seem somewhat insufficient to explain the observed *x* dependence for Sn(S_xSe_{1-x})₂. This is due in part to the small magnitude of the composition induced changes in the binding energy. These changes are of the order of 0.5 eV which is equal to or better than the best agreement currently obtained between theoretical and experimental binding energies for IV-VI compounds.^{5,11} Further theoretical calculations appear therefore necessary to explain the data of Fig. 4 and Table I for this family. The current theoretical calculations, however, do qualitatively reproduce one of the features in our data. We observe that the total width of the upper valence band (peaks *A*, *B*, *C*, and *D* which do not include the deeper anion *s* states) exhibits a small decrease, ~ 0.06 eV, as the composition changes from SnSe₂ to SnS₂. This is consistent with the results of Fong and Cohen's band-structure calculations¹⁰ as well as with those of Schlüter and Schlüter⁹ and of Murray and Williams.¹¹

V. SUMMARY

We have found that the smooth dependence on *x* of the valence-band binding energies observed for GaS_xSe_{1-x} compounds is primarily related to two factors. The first of these factors is the cationic or anionic character of the state. Peaks in the EDC's for which the theory predicts a strong cationic character in GaSe depend less on *x* than the anionic peaks with the exception of peak *A* whose behavior is somewhat anomalous. This is in agreement with the optical

data analysis by Schlüter *et al.*¹³ As to the anionic peaks the theory establishes a link between the *x* dependence of some of them and the increase in ionicity of the Ga anion bonds as the composition changes from GaSe to GaS. A second factor influences the *x* dependence of the states at the top of the valence band. This is a change in the atomic-orbital character of these states as *x* increases. Photon-polarization effects in the EDC's taken for different values of *x* demonstrate this change. We conclude that the strong *p_z* character at the top of the GaSe valence band becomes a mixed *p_z* and *p_x,p_y* character in GaS.

The small but detectable composition-induced binding-energy shifts observed for Sn(S_xSe_{1-x})₂ compounds cannot be explained with the above approach. In particular we did not find a simple correspondence between the anionic or cationic character of a given peak and its behavior as *x* changes. The reproduction of this behavior seems somewhat beyond the limits of the current theoretical calculations although the theory does correctly predict an increase in the upper valence-band width as *x* decreases. We observe in general that more detailed band-structure calculations of the intermediate compounds would be required for a complete explanation of our experimental findings. These calculations should also clarify the possible role of effects such as the spin-orbit splitting which were not explicitly considered in our present discussion.

In summary the current theoretical calculations need some improvement in the case of the IV-VI family compounds. We emphasize instead that the theoretical description of the electronic states in III-VI compounds^{7,8} appears now satisfactory and able to explain the many and detailed photoemission results obtained in these materials.

ACKNOWLEDGMENTS

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