PHYSICAL REVIEW B VOLUME 43, NUMBER 15 15 MAY 1991-II

Electronic structure and core excitons in AlSb as studied by soft-x-ray spectroscopy

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(Received 2 January 1991)

The Al $K\beta$ x-ray-emission and the Al K x-ray-absorption spectra in single crystalline AlSb are reported. A core exciton is observed 0.2 eV below the onset of the Al $1s$-to–conduction-band transition. Its intensity is markedly lower than that of the Al $2p$ exciton in the same compound. This points towards strong dipole selection rules for the formation of core excitons. The corresponding core-exciton recombination radiation could not be identified in the Al $K\beta$ spectrum. Structure in the emission and absorption spectra are discussed in terms of the one-electron densities of states. From all available experimental data, an empirical density of valence states is constructed for AlSb.

I. INTRODUCTION

The electronic properties of most III-V compound semiconductors have been extensively studied by a variety of techniques, and their band structures are among the best known of the semiconductors.[1] A conspicuous exception is AlSb for which optical[1] and photoemission data[2–4] have been reported, mainly for thin-film or polycrystalline samples. Except for two earlier studies,[5,6] it was only recently that spectroscopic ellipsometry[7] and angle-resolved photoemission[8] measurements have been applied to single-crystalline AlSb. These investigations were made possible by the availability of large, high-quality single crystals grown by a recently developed method.[9]

In this study we used these crystals to perform x-ray emission and absorption measurements on AlSb. The information so obtained is complementary to photoemission as it gives the partial (i.e., symmetry resolved) and local (i.e., around a particular element) densities of valence and conduction states. An advantage of this method is the fact that the results yield the bulk electronic properties with little interference from the surface. Here we report on the Al $K\beta$ emission [valence band (VB)$\rightarrow$Al $1s$] and the Al K photoabsorption [Al $1s\rightarrow$conduction band (CB)] spectra, which are related to the partial valence- and partial conduction-band densities with p symmetry around the Al atoms.

An additional motivation for the present investigation was the opportunity to observe core excitons at the Al $1s\rightarrow$CB threshold in the Al K absorption spectrum, and possibly the radiative decay of the same exciton in the Al $K\beta$ emission spectrum. Let us recall that, at threshold, excitonic effects have been observed in various cases. The formation and the radiative decay of core excitons dominate the core absorption and emission spectra in rare gas solids and alkali halides,[10] i.e., in materials with little screening of the Coulomb interaction as expressed by their small dielectric constants. In semiconductors excitonic shifts of the core absorption edges have been observed in a number of cases[11–13] but true *bona fide* core excitons have only been reported in a few instances, mainly involving core to localized surface-state transitions.[14,15] A notable exception are the strong core excitons which dominate the Al $2p$ (Al $L_{2,3}$) absorption threshold in AlSb,[4] the P $1s$ (P K) transition in phosphorus[16] and the C K absorption in diamond.[17] In all these cases only bulk states are involved. The absorption measurements in AlSb have shown furthermore[4] that the states at the bottom of the conduction band which contribute predominantly to the excitons are mainly derived from states centered on Al atoms. It was therefore thought that a comparison of the relative strengths of the the core excitons in the Al K and the Al $L_{2,3}$ absorption spectra in AlSb would yield further information about the symmetry of the excitonic state involved.

Recently, the radiative decay of core excitons has been observed in the L emission spectra of c-Si, a-Si, a-Si:H,[18] and in the Al $K\beta$ emission spectrum of AlAs,[19] which spurred similar investigations for AlSb to be presented below.

II. EXPERIMENTAL DETAILS

The Al $K\beta$ emission spectrum was observed from single crystalline AlSb samples stuck onto a copper anode excited with a 4-kV, 3-mA electron beam. The photoabsorption spectrum was obtained from an absorption screen prepared by depositing a thin layer of AlSb powder onto a 2-μm-thick makrofol foil; the continuous x-ray beam for this experiment was emitted by a gold anode excited by a 2.9-kV, 50-mA electron beam. The AlSb samples were cut from boules grown according to Ref. 9 and they were kept and prepared under argon and inserted into the x-ray tube (emission target) or the spectrometer (absorption screen) under a flow of dry nitrogen to minimize their contact with air.

The x-ray spectra were analyzed step by step in a Johann-type, bent-crystal vacuum spectrometer[20] equipped with a 250-mm curved quartz $10\bar{1}0$ crystal and an Ar-CH$_4$-flow proportional counter as detector. The spectra were scanned with a stepwidth of 0.1 eV. Under these conditions the energy resolution is better than 2×10^{-4} and the precision of the photon energy is ±0.05 eV. An accuracy of the same degree was achieved by measuring the Al K absorption edge of metallic aluminum and using the accepted value of 1559.3 eV to calibrate the energy scale of the spectrometer.

III. RESULTS

In Fig. 1 we show the Al $K\beta$ emission and Al K photoabsorption spectra from crystalline AlSb as a function of transition energy. The same core level, Al 1s, is involved in both cases so the spectra are obtained on a common energy scale. Thus from these experimental data we obtain directly the relative position of the Al 3p valence and conduction states without any further adjustment. In the independent-particle picture the experimental curves correspond to the convolution of the Al p density of states with a Lorentzian distribution of the Al 1s core level which is 0.4 eV wide. The instrument function contributes an additional broadening which has approximately a Gaussian shape of 0.1 eV width, as discussed below.

A. The Al $K\beta$ emission spectrum

The Al $K\beta$ spectrum consists of a strong asymmetric peak I at the highest emission energy followed by a well-separated weaker feature II and a poorly structured region of decreasing intensity labeled III in Fig. 1. The bottom of the emission band lies at about 1549.0 eV. The top of the spectrum which corresponds to transitions from the valence-band maximum (VBM) to the Al 1s level is ill defined due to a "foot" that extends out to ~1562 eV and might be due to the radiative decay of a core exciton in analogy with the AlAs spectrum of Ref. 19.

In order to locate the energy position of the VBM we followed the approach first used by Kraut *et al.*[21] to determine the VBM in III-V compounds with an accuracy of 50 meV from photoemission spectra measured with a resolution of 0.6 eV. Kraut *et al.* fitted their spectrum to an appropriately broadened theoretical density of states (DOS) and used the latter to deduce the position of the VBM in their spectra.

Following this approach we first determined the spectral response function of our experiment by fitting a Fermi function to the high transition energy edge of an Al $K\beta$ emission spectrum of pure Al. It turned out that a perfect fit is achieved by a combined convolution with a Gaussian of 0.1 eV full width at half maximum (FWHM) representing the experimental resolution and a Lorentzian with 0.4 eV FWHM representing the width of the Al 1s core level.[22]

Next we had to obtain a theoretical DOS for AlSb. To our knowledge no calculated DOS for AlSb has been published. We thus capitalized on the canonical nature of the DOS's for all III-V compounds and constructed an empirical DOS in a fashion that could be considered the inverse process of that used by Ley *et al.* to derive critical point energies from photoemission data.[23]

As a starting point we took the DOS of GaSb as calculated by Chelikowsky and co-workers using the empirical pseudopotential method (EPM).[24] We chose GaSb because it already contains the idiosyncrasies typical for the relatively large spin-orbit splitting of the heavy Sb anion. This is in particular the splitting of peak II. Next we identified characteristic structures in the DOS with critical points in the band structure of GaSb. This correlation was used to adjust the DOS to that of AlSb by replacing the GaSb critical-point energies by experimental data obtained for AlSb. The critical-point energies that

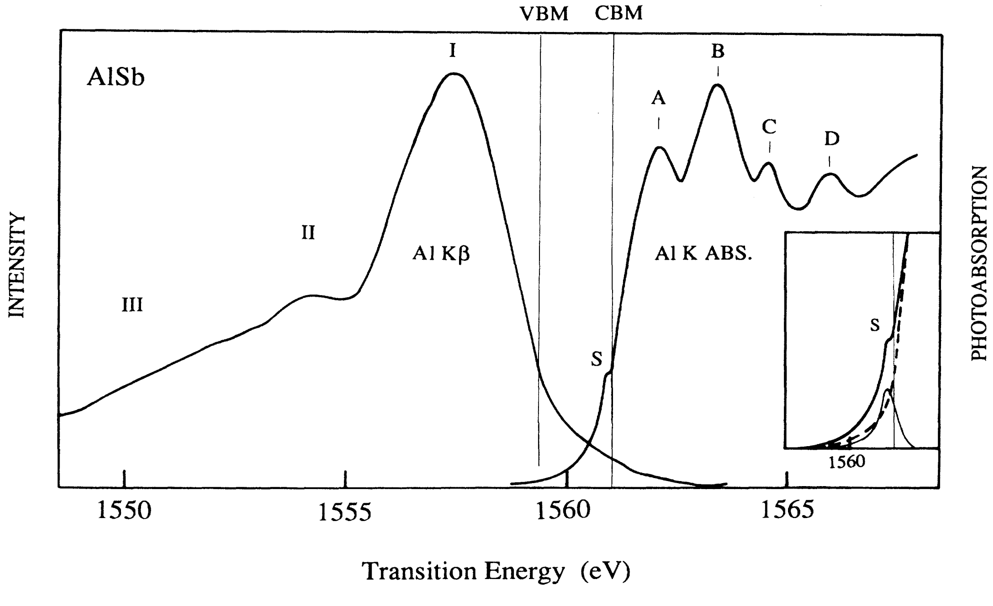

FIG. 1. Al $K\beta$ emission and Al K photoabsorption spectrum from AlSb. The positions of the valence-band maximum (VBM) and the conduction-band minimum (CBM) are indicated. Inset: detail of feature S.

entered in this procedure are listed in Table I.

We used the electroreflectance measurements of Joullie *et al.*[25] to derive from a combination of transition energies the positions of $L_{4,5}$ and L_6. The angle-resolved photoemission measurements of Ehlers *et al.*[8] gave the position of X_6 and $\Sigma_1^{\min}$; the average position of L_6,X_6 (peak II), finally, was taken from the ultraviolet photoemission (UPS) data of Johnson *et al.*[4] After this first step in obtaining the AlSb DOS the "fine-tuning" was performed by adjusting the DOS so as to fit the UPS data. This was accomplished by folding the DOS into a Gaussian of 0.4 eV FWHM to account for the energy resolution of the photoemission experiment. The imaginary part of the hole self-energy was taken into account by a Lorentzian broadening that increased from 0 eV at the VBM over 0.2 eV for peak II to 0.9 eV for peak III. Finally, the intensities of the individual peaks were adjusted to account for differences in the photoemission cross sections. In the final adjustment it turned out that the calculated photoemission spectrum was quite sensitive to the detailed shape of the DOS despite the twofold broadening process.

The final results are given in Fig. 2(a), for the DOS, in 2(b) for the broadened DOS, and in 2(c) for the UPS data. The energies of critical points as used in this adjustment procedure are indicated. The areas under the individual peaks in the DOS are adjusted to the proper electron count, namely 4:2:2 for I:II:III. Next we used peak I of the DOS after convoluting it with a Lorentzian of 0.4 eV FWHM and a Gaussian of 0.1 eV FWHM to determine the position of the VBM in the x-ray emission (XES) spectrum (Fig. 3). The broadened DOS does fit the XES spectrum rather well over most of the high-energy edge of the peak and we place the VBM at 1559.35 eV on the basis of this comparison. It is evident that emission remains beyond that accounted for by the modeled XES; it results from a continuous emission mainly due to bremsstrahlung. Any attempt to fit the extra emission to a single peak superposed on the background that could be interpreted as due to a core exciton decay failed, however. As an alternative interpretation we offer the following.

As the characteristic Al $K\beta$ emission is excited by electrons, it is accompanied by a bremsstrahlung continuum that extends from the electron energy (4 keV) to zero energy and provides thus a background on which the Al $K\beta$ spectrum is superimposed. Because of the high atomic number of Sb this background is much more intense in AlSb than in pure Al, for example. It amounts to about 30% of the peak intensity in the Al $K\beta$ spectrum of Fig. 1 whereas this background is negligible in the Al $K\beta$ spectrum of Al. While the primary bremsstrahlung spec-

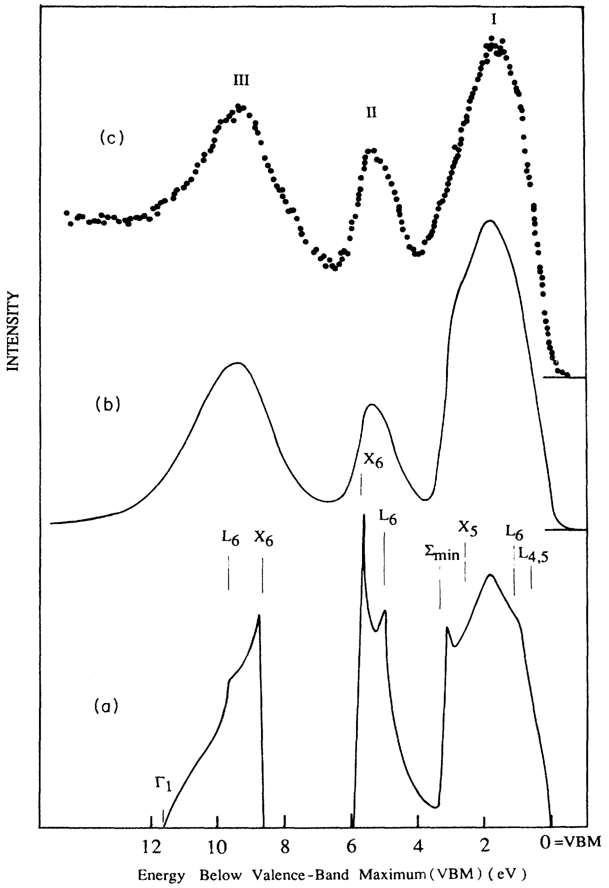

FIG. 2. (a) Empirical density of states (DOS) of AlSb. (b) AlSb DOS broadened so as to model the photoemission spectrum in (c). (c) Experimental photoemission valence-band spectrum of AlSb from Ref. 4.

TABLE I. Energies of critical points in the valence-band structure of AlSb relative to the valence-band maximum (VBM).

Critical point	Peak in DOS	Energy (eV) below VBM	Method	Reference
$L_{4,5}$	I	0.67	Electroreflectance	25
L_6		1.09		
$\Sigma_1^{\min}$		3.3	Angle-resolved UPS	8
L_6	II	5.1	UPS	4
X_6		5.6	Angle-resolved UPS	8
X_6	III	8.8	modeling of UPS	
L_6		9.8	spectrum	This work
Γ_1		11.7	and Al K XES	

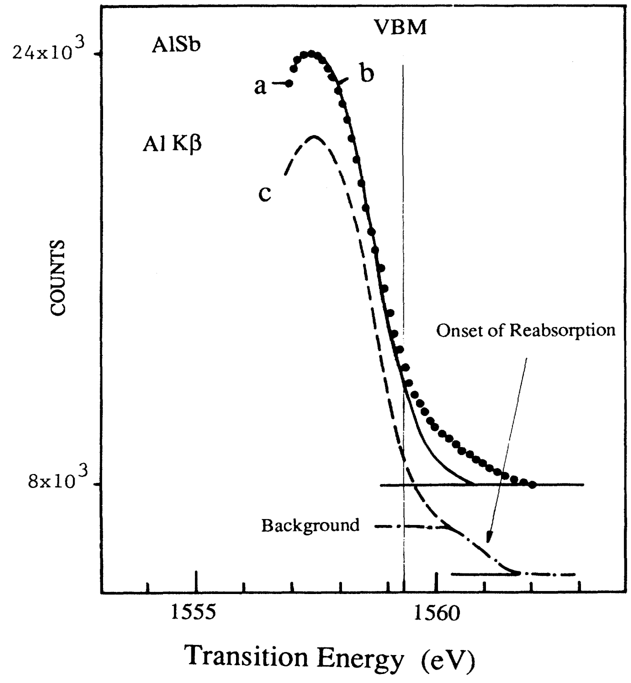

FIG. 3. *a*, Experimental Al $K\beta$ emission spectrum. *b*, AlSb DOS (peak I) broadened as explained in the text. *c*, The Al $K\beta$ emission edge taking into account the calculated DOS and the reabsorption of the bremsstrahlung background. From a comparison of *a* and *b* the position of the VBM in *a* is determined.

trum is structureless on the scale of energies that are of interest here, it may acquire weak structures due to self-absorption in the target material itself. For this reason a step in the bremsstrahlung background is expected at the Al K absorption edge located at about 1561.0 eV in our spectra (compare Fig. 1). The intensity of the background is slightly higher below 1561 eV than above that energy where it is attenuated due to the steeply increasing absorption coefficient of AlSb.

Curve *c* in Fig. 3 models this situation by superimposing the appropriately broadened DOS of peak I on a background that is modulated according to the experimentally determined transmission coefficient. The result reproduces the experimental Al $K\beta$ spectrum near and above the VBM. It shows in particular that the feature observed at 1560.7 eV can be accounted for by the reabsorption effect. Any structure resulting from the decay of a core exciton (see below) is difficult to detect under these circumstances as it would appear in the same energy range. The situation is obviously more favorable in this respect for a low-Z material like AlAs where the bremsstrahlung background is lower and where the emission from a core exciton has reportedly been observed.[19]

Finally, we tried to model the whole Al $K\beta$ emission spectrum. Curve (b) in Fig. 4 was obtained by convoluting the empirical DOS with a Gaussian of 0.1 eV FWHM (resolution) and each peak additionally with Lorentzians of 0.4 (I), 1.0 (II), and 1.3 eV FWHM, respectively, to account for the combined core- and valence-band-hole lifetimes. The decreasing order of peak intensities reflects the decreasing Al $3p$ character of the valence-band states as one goes from the top to the bottom of the valence bands. The Lorentzian broadening and the peak intensities were adjusted to give the best agreement with experiment (compare Fig. 4). This goal is quite well achieved for peaks I and II and less so for peak III. It appears that the ionic gap between II and III is filled in the Al $K\beta$ spectrum. It seems unlikely that electron-hole interaction would cause this redistribution of spectral density without affecting other regions of the spectrum. A more likely explanation is the contribution from a superficial oxygen contamination. In fact, the Al $K\beta$ emission from Al_2O_3 is centered at 1553 eV. By subtracting from the experimental Al $K\beta$ of AlSb an Al_2O_3 contribution with a relative intensity of 5% we obtain the curve presented in Fig. 4. Its general shape is in rather good agreement with the calculated spectrum which shows that the x-ray emission spectrum is well represented by the properly weighted and broadened one-electron DOS. The Lorentzian widths of the individual peaks in the Al $K\beta$ spectrum compare reasonably well with those of the photoemission spectrum if one takes the contribution from the core hole width into account.

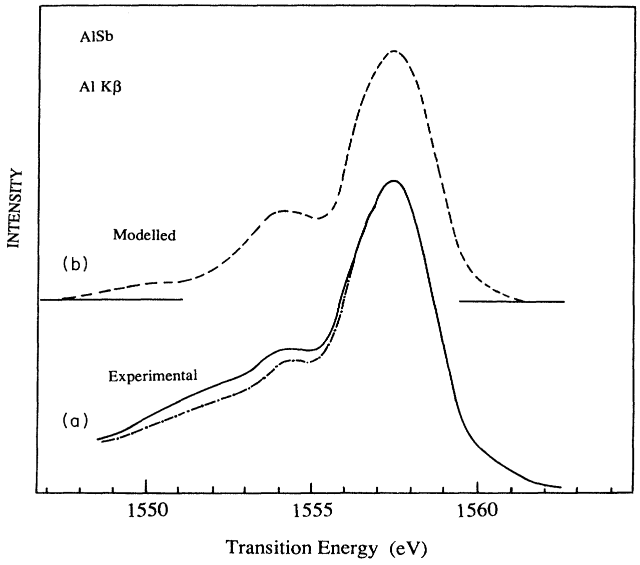

FIG. 4. Measured (a) and calculated (b) Al $K\beta$ emission spectrum. The dashed line indicates a correction in (a) that takes a 5% contribution from a possible Al_2O_3 surface contamination into account.

B. Al K photoabsorption spectrum

The Al K photoabsorption spectrum is shown in Fig. 1. As mentioned earlier, the energy of the VBM is 1559.35 eV on the transition energy scale. In the spirit of a one-electron approximation we expect the Al $1s$ to conduction-band minimum (CBM) transition at $1559.35+E_g=1559.35+1.60\approx1561.0$ eV where E_g is the optical gap of AlSb.[4] As shown in Fig. 1 this point corresponds to the onset of the *main* absorption edge, i.e., neglecting shoulder *S* to be discussed below.

Following the absorption edge, maxima in the absorption cross section are observed at 1.1 (*A*), 2.4 (*B*), 3.6 (*C*), and 5.0 eV (*D*) above CBM. This arrangement of three comparatively intense and closely spaced maxima (*A*, *B*, *C*) and a fourth one (*D*) somewhat further away is in keeping with the canonical density of conduction states as recently calculated by Chelikowsky *et al.* using the EPM, for example.[26] Two of these maxima were earlier observed in the Sb $4d_{5/2}$ absorption spectrum at 1.0 (*A*) and 3.6 eV (*C*).[4] Peaks *B* and *D* were masked by overlapping absorption from the spin-orbit split Sb $4d_{3/2}$ core level. Both observations support an interpretation of structure in the absorption spectrum in terms of the density of conduction states without any recourse to electron-hole interaction.

This is not so for the shoulder *S* which falls into the band gap. After a decomposition as indicated in Fig. 1, *S* corresponds to a peak with an energy of 0.2 ± 0.05 eV below CBM. We identify this peak with the formation of a bound core exciton. Its binding energy (0.2 ± 0.05 eV) agrees with that of the intense core excitons (0.14 eV) observed in the Al 2*p* absorption spectrum in AlSb.[4] The width (FWHM) of the 1*s* core exciton (0.4 eV) is larger than that of the 2*p* exciton (0.2 eV) and it is less intense. The different intensities of the core excitons relative to the conduction-band transitions in the Al *L* and Al *K* absorption spectra reveal that excitonic states with *s* symmetry are preferentially created. Due to their highly localized nature, core excitons form only in conjunction with holes on the Al atoms and not with those on Sb because the bottom of the AlSb conduction band has predominantly Al 3*s* character.

IV. SUMMARY

We have measured the Al $K\beta$ emission and the Al *K* absorption spectrum in single crystalline AlSb. Most of the spectral features are well described in terms of the densities of valence and conduction states, i.e., in a one-electron picture neglecting electron-hole interaction. A notable exception is the observation of a bound core exciton in the absorption spectrum with a binding energy of 0.2 eV. This result confirms earlier observations that transitions from Al core levels lead to the formation of core excitons in AlSb. Spatial and symmetry related selection rules exclude the formation of Sb-related core excitons and govern the relative intensities of Al 1*s* and 2*p* based excitons. The radiative decay of the Al 1*s* core exciton could not be observed due to structure in the underlying bremsstrahlung background. This structure which occurs at the energy of the expected core exciton emission was shown to be due to reabsorption of the bremsstrahlung in the target.

ACKNOWLEDGMENTS

We thank E. Schönherr for the gift of the AlSb single crystal. L.L. greatly appreciates the hospitality of the Laboratoire de Chimie Physique and the financial support, which made his stay possible. The Laboratoire de Chimie Physique is "Unité associée au Centre National de la Recherche Scientifique No. 176." The Laboratoire d'Optique des Solides is "Unité associée au Centre National de la Recherche Scientifique No. 781."

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