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Chemisorption geometry on cleaved III-V surfaces: Cl on GaAs, GaSb, and InSb

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Experimental angle-integrated photoemission curves taken on Cl-covered (110) surfaces of GaAs, GaSb, and InSb have been compared to tight-binding calculations of the local density of states. The results clearly demonstrate that the Cl adatoms are bound to the anion substrate atoms rather than to the cation substrate atoms. Some qualitative information is also provided on surface relaxation and on chemisorption bond lengths.

I. INTRODUCTION

The chemisorption of simple gases on (110) surfaces of III-V compounds has been an interesting problem for a long time.[1-3] For example adsorbed atoms or molecules on GaAs(110) have been proposed to be bound either to cation substrate atoms[3] or to anion substrate atoms[2] by different authors. The complexity of the electronic charge redistribution upon formation of the chemisorption bonds prevents one from obtaining reliable predictions on this matter by simple chemical arguments.[1] We show here that the chemisorption site of atomic Cl can be identified by a joint experimental and theoretical study of the local density of states for the outermost atomic planes. The experiments consisted of angle-integrated synchrotron-radiation photoemission measurements on chemisorbed atomic Cl on cleaved GaAs, GaSb, and InSb surfaces. The theory consisted of semiempirical tight-binding calculations of the local density of states for different chemisorption geometries. The best agreement between theory and experiment has been obtained assuming that Cl is bound only to surface anion atoms and not to surface cation atoms. These results agree with the evidence for a similar chemisorption model recently proposed by Mele and Joannopoulos[1] for oxygen molecules on GaAs(110). We have also obtained some evidence that the surface atoms of the substrate are relaxed from their bulk positions in a way similar to the clean GaAs(110) surface.[4]

The experimental work will be described in Sec. II. The theory will be presented in Sec. III and a complete discussion will be carried out in Secs. IV and V.

II. EXPERIMENTAL PROCEDURE AND RESULTS

The experiments have been performed at the University of Wisconsin Synchrotron Radiation Center employing an uv beam line equipped with a vertical, bakable Seya-Namioka monochromator which has a useful spectral range for photoemission experiments: 6–45 eV. The experimental system (base pressure, $P \approx 5 \times 10^{-10}$ Torr) included a double-pass cylindrical mirror electron energy analyzer (operating at a resolution of 200–300 meV) and several sample preparation and characterization facilities. Ultraclean surfaces were obtained by *in situ* cleavage. The cleaved surface was immediately exposed to a Cl atmosphere with pressure in the low 10^{-7} Torr range and residual gas purity monitored by a quadrupole mass analyzer. The Cl coverage was monitored by means of Auger electron spectroscopy and saturation coverage occurred at exposures of $\sim 10^{-4}$ Torr sec. Upon chlorination the surfaces were extremely stable and free of contamination for several days. Photoelectron spectra have been taken at several different photon energies in the range $\hbar\omega = 16-40$ eV and at different photon polarizations. In particular our experimental system enables us to change the photon polarization from s polarization with the electric vector parallel to the surface of the sample to p polarization with the electric vector at 45° with respect to the surface in our geometry *without* modification of the photoelectron collection geometry as described in detail in Ref. 5.

Typical photoemission spectra for GaAs(110) + Cl are shown in Fig. 1 for several photon energies and for both p and s polarization. The three spectral features A, B, and C are due to chemisorbed Cl since they are not present in spectra from the clean surface. In addition the peak positions are nearly the same for several photon energies suggesting that these features are local density-of-states effects. Similar results have been obtained for GaSb(110) + Cl (see Fig. 2) and for InSb(110) + Cl (see Fig. 3). In all three cases the peaks A, B, and C seem to show only weak polarization dependence and photon energy dependence. A comparison of results

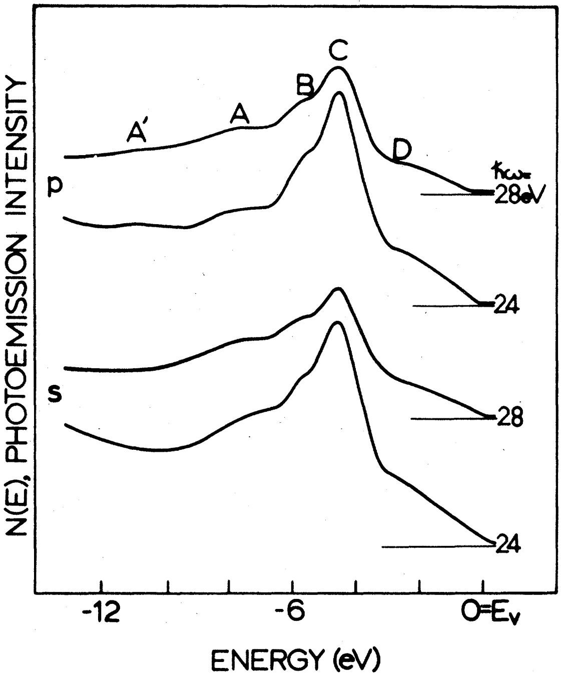

FIG. 1. Experimental photoemission spectra taken at different photon energies and polarizations on Cl-covered GaAs(110).

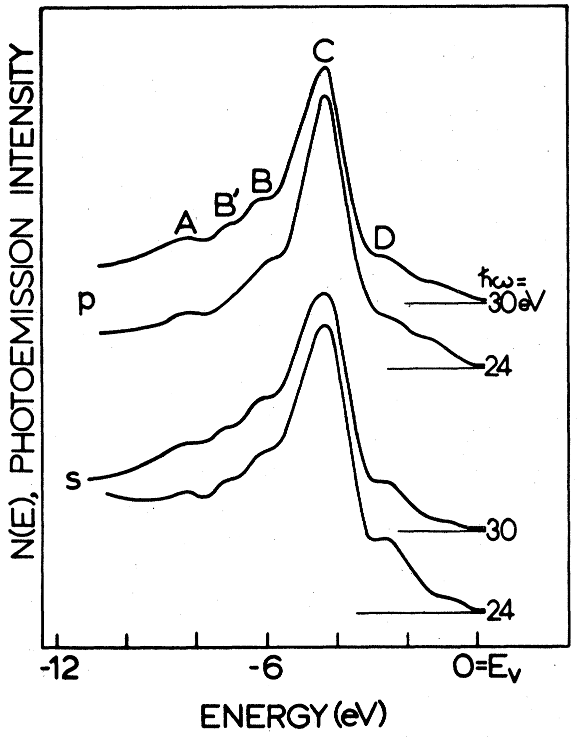

FIG. 2. Experimental spectra for GaSb(110) +Cl similar to Fig. 1.

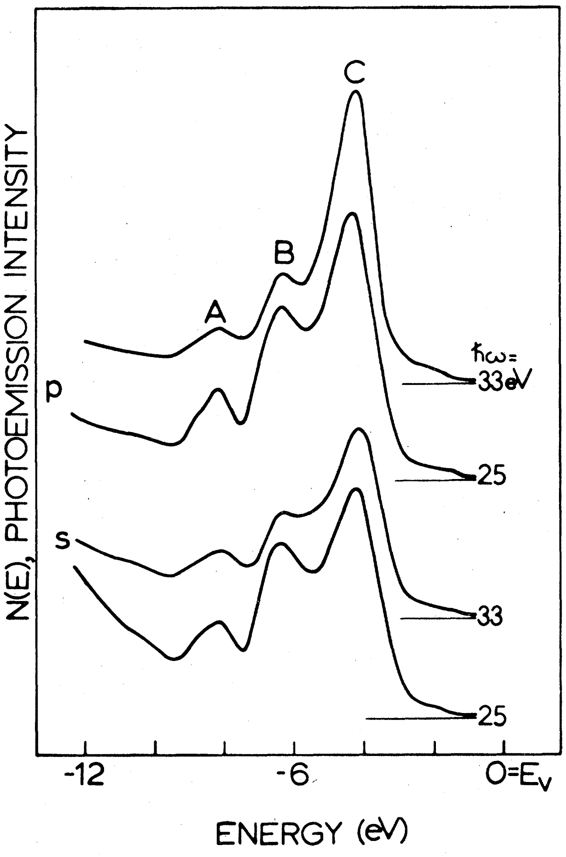

FIG. 3. Experimental spectra for InSb(110) +Cl similar to Fig. 1.

for the three surfaces is shown in Fig. 4 where it is clear that the most prominent Cl peak C is found 4.2–4.6 eV below the top of the valence band, E_v. Additional structure, peaks A', B', and D' is only visible for some of the surfaces. Table I summarizes the binding energies of all the observed photoemission peaks. It is evident from Figs. 1, 2, and 3 that the photon polarization effects are much smaller for these surfaces than for Cl-covered Si or Ge surfaces.[6] The only significant photon polarization effect is the decreased intensity of peak C for InSb(110) +Cl when the polarization is changed from p to s.

In the case of InSb(110) +Cl photoemission data have also been taken in the constant-initial-state (CIS) mode.[5] This consists of monitoring the number of collected photoelectrons while simultaneously scanning the kinetic energy, E, and the photon energy under the condition $E - \hbar\omega = \text{constant}$. The CIS spectra primarily reflect the density of unoccupied states above the vacuum level.[5] Figure 5 shows a series of CIS curves whose initial-state energy has been set to coincide with either peak A or peak B or

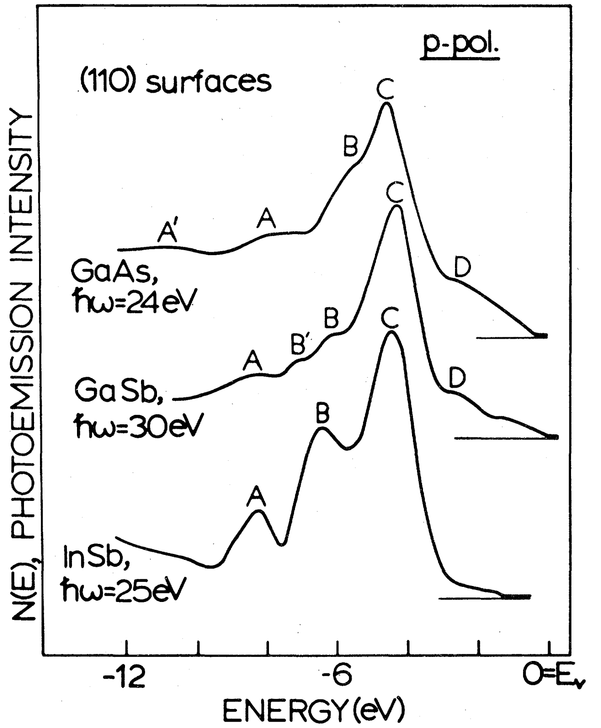

FIG. 4. Direct comparison of the spectra for the three Cl-covered surfaces of GaAs, GaSb, and InSb.

peak C in the spectra of Fig. 3. From these curves it is evident that the Cl adatoms have easily detectable structure as compared to the smooth CIS curves of the clean substrate. In particular three final-state features are visible in Fig. 5 labeled peaks α, β, and γ, whose positions are also shown in Table I.

TABLE I. Experimental energy positions of the spectral peaks for Cl-covered surfaces.[a]

Peak	GaAs(110) +Cl	GaSb(110) +Cl	InSb(110) +Cl
A'	11.3 ±0.5	——	——
A	7.7 ±0.4	8.3 ±0.2	8.15 ±0.3
B	5.6 ±0.3	7.2 ±0.2	6.4 ±0.2
B'	——	6.1 ±0.2	——
C	4.6 ±0.4	4.3 ±0.4	4.2 ±0.3
D	2.0 ±0.4	3.5 ±0.4	——
D'	——	0.7 ±0.4	——
α			6.65 0.3
β			8.35 0.3
γ			10.65 0.3

[a] Energies in eV, measured from E_v.

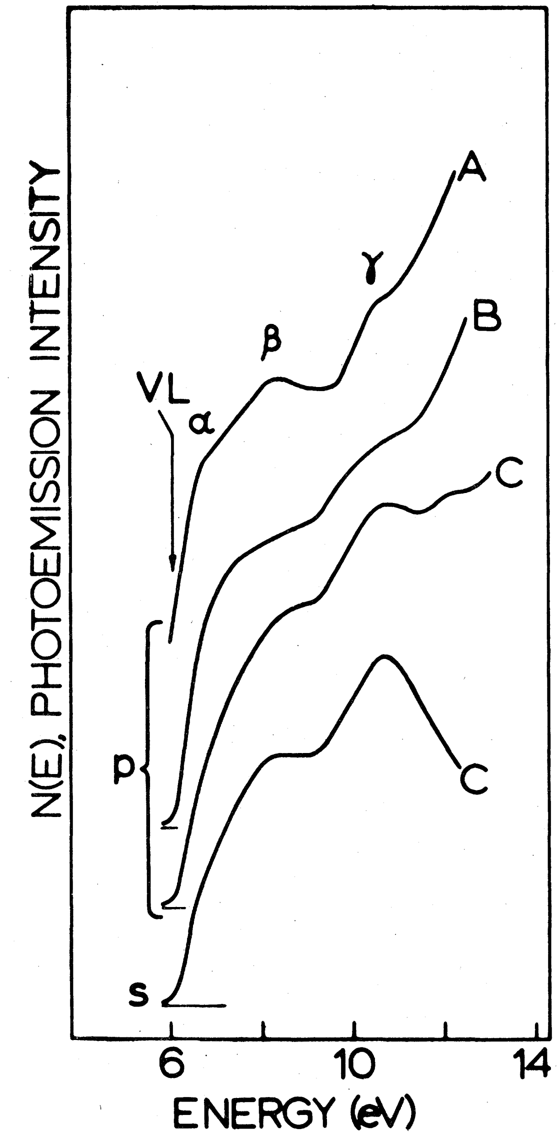

FIG. 5. Constant-initial-state (CIS) energy spectra for InSb(110) +Cl. The labeling of each curve corresponds to the selected initial-state energy (e.g., the initial state of CIS curve C is the energy of peak C which is shown in the photoemission spectra of Fig. 3). A vertical arrow shows the position of the vacuum level (VL).

III. THEORY

A. Details of the theoretical scheme

The calculations of energies, wave functions, and the local density of states have been carried out in an empirical tight-binding scheme. The Cl-covered sample has been simulated by a slab of 12–16 atomic planes with chemisorbed monolayers on both sides.[7,8]

This approach requires a realistic description of the two center integrals, which appear in the secular equation. For tetrahedrally bonded compounds this has been obtained by a Slater-Koster parametrization of the bulk band structure.[9] Using a basis with *s-p* orbitals and neglecting hopping integrals beyond the nearest neighbors one can achieve a realistic description of the valence band and the correct value of the band gap. Spin-orbit coupling can also be included in a simple way and the resulting corrections are non-negligible for the near gap states in Sb compounds.[10] An interesting property of the nearest-neighbor hopping integrals obtained in this way is that they exhibit a simple dependence on the bond length.[11] In the present calculation this hopping-integral versus bond-length dependence has been employed to investigate surface relaxation effects and substrate-absorbate interaction integrals. No direct adatom-adatom interaction has been taken into account since the distances between adatoms (>3.98 Å) are much larger than the Cl-Cl bond length. The neglect of adatom-adatom overlap parameters is also consistent with a nearest-neighbor description of the valence band.[11] A delicate problem in handling binary systems is of course the correct positioning of each constituent's potential in an absolute energy scale. In our case the energy distance between E_v and the vacuum level has been deduced from photoelectric threshold measurements. For the position of the *p* level in free Cl atoms we have employed the value calculated by Herman and Skilman,[12] -12.31 eV.

Some attempt to include self-consistency between the surface charge and potential is important when working on chemisorption problems. Indeed the effects of charge transfer between adatoms and substrate atoms can be much larger than the charge transfer on clean surfaces due to surface relaxation effects. In the case of relaxation on clean surfaces an iterative self-consistent procedure was used (Ref. 7) to determine the dependence of intra-atomic matrix elements on electronic charge transfer. We have used a similar approach in the present calculations and have assumed that the intra-atomic parameters both of Cl adatoms and substrate atoms scale with excess charge in the same way as spectroscopic valence-orbital ionization potentials.[13] This is equivalent to determining the charge-transfer contribution to the energy in terms of the corresponding Coulomb integrals and then iterating to achieve self-consistency. We find a negative charge transfer from the substrate to the Cl adatoms of 0.2–0.3 electrons/atom. As a consequence the binding energy of the *p* level with respect to the vacuum level is decreased by 2.5–3.5 eV in the Cl adatoms. The intra-atomic parameters are also shifted by 0.5–1 eV towards larger binding energies in the substrate atoms of the first plane while no notable modifications are present in the subsequent substrate planes.

B. Theoretical results

In our calculations we have considered different sets of tight-binding parameters and different chemisorption geometries. The results are much more sensitive to the geometry than to the choice of the parameters. Three different geometries have been employed and they are schematically shown in the right-hand side of Fig. 6.

Geometry A. Each Cl atom is bound to an anion substrate atom. Similar to the clean, reconstructed GaAs(110) surface, the substrate atoms are not in their bulk positions.[4] Both anion atoms and cation atoms are displaced in a direction normal to the surface, the anion atoms outside the surface and the cation atoms inside the surface. These displacements are similar to those proposed by Chadi in his bond relaxation model.[4]

Geometry B. The Cl atoms are again bound to substrate anion atoms, but all the substrate atoms are in their bulk positions.

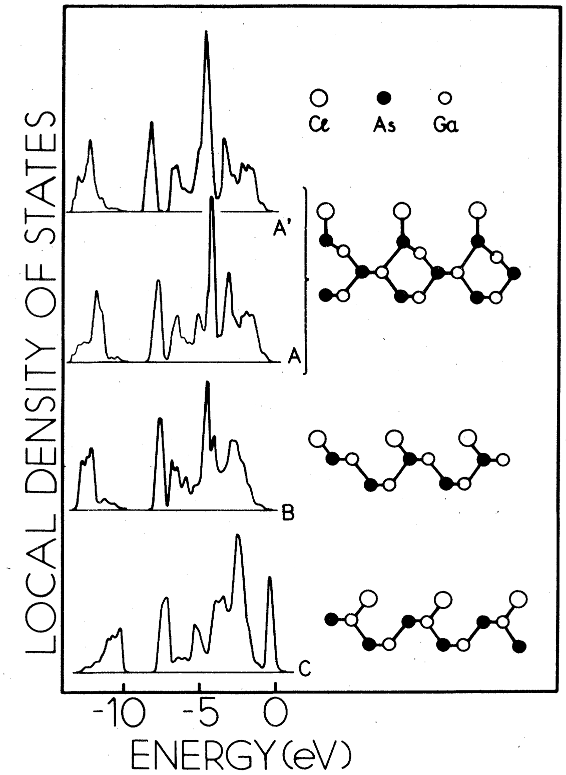

FIG. 6. Theoretical local density of states for GaAs(110) +Cl. Each curve corresponds to a different chemisorption geometry, schematically shown in the right-hand side of the figure and explained in detail in the text. Curve *A'* and curve *A* correspond to the same geometry with two slightly different values of the Cl—substrate-atom bond length, taken equal to the sum of the atomic radii for curve *A* and decreased by 5% for curve *A'*.

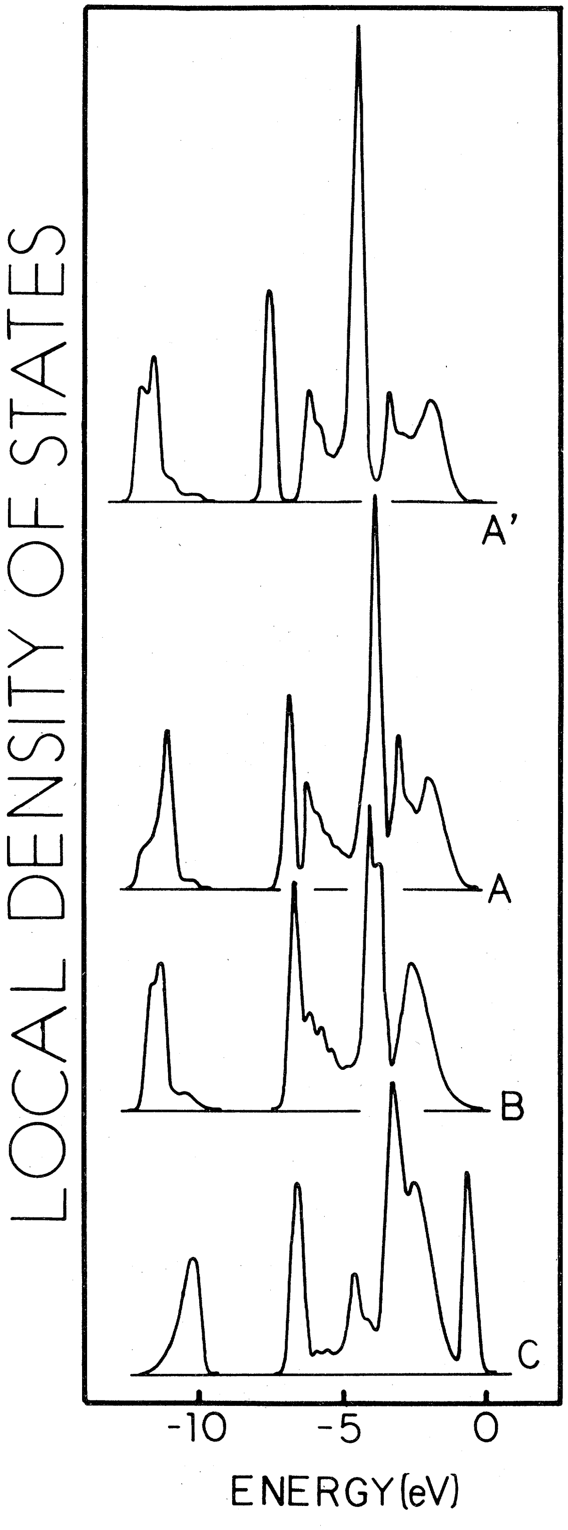

FIG. 7. Theoretical local density of states for InSb(110) +Cl. In this case curve A' corresponds to a chemisorption bond length 10% smaller than the sum of the atomic radii.

Geometry C. The Cl atoms are bound to substrate cation atoms and all the substrate atoms are again in their bulk positions [on the reconstructed clean GaAs(110) surface the Ga atoms would be *inside the crystal*[4]].

For geometry B and geometry C we have taken a bond length between Cl and substrate atoms equal to the sum of the atomic radii. For geometry A we have investigated the effects of modifying the bond length around the above value. Figure 6 shows the calculated density of states of the first two atomic planes for GaAs(110) +Cl. The labeling of each curve indicates the geometry to which it corresponds. Curve A' corresponds to geometry A with a reduction of 5% in the Cl-As bond length with respect to the sum of the atomic radii (used for curve A). Figure 7 shows similar theoretical curves for InSb(110) +Cl. In this case curve A' corresponds to a 10% bond length reduction.[14]

IV. DISCUSSION

The position in energy of the most intense Cl-induced peak immediately demonstrates that the Cl adatoms are bound to substrate anion atoms rather than to substrate cation atoms. Although all the above geometries give an intense peak in the theoretical density of states with prevailing Cl p-like atomic orbital character, for the anion-bonded geometries A and B this peak is located 3.5–4.9 eV below E_v in GaAs(110) +Cl and 4.2–4.5 eV below E_v in InSb(110) +Cl, i.e., close to the experimental positions, 4.6 and 4.3 eV, respectively. Geometry C gives instead a peak in a much shallower position than the experimental one, at 1.5–2.9 eV in GaAs(110) +Cl and at 1.5–3.7 eV in InSb(110) +Cl. This is due to the larger charge transfer in geometry C than in geometries A and B, and to a difference in the binding energy of the p states between anion substrate atoms and cation substrate atoms. For GaAs(110) +Cl for example, the calculated charge transfer from substrate to adatoms is 0.24 electrons/atom for geometry A, 0.22 electrons/atom for geometry B, and 0.32 electrons/atom for geometry C. In the latter case the large extra charge pushes up the energy of the Cl p states with respect to the former two cases. For all three geometries the main Cl-induced peak consists primarily of Cl p states which are mixed with p states of the substrate atom that is bonded to the adatom. The anion p states are deeper in energy than the cation p states and this contribution causes the position of the main peak to be too shallow in geometry C. A similar discussion demonstrates that the Cl chemisorption site on GaSb(110) is also bonded at the anion site. Our identification of the chemisorption site is consistent with the absence of strong photon polarization effects in the experimental spectra. On the clean surface the filled surface states just below the top of the valence band have anion p_z character. Upon formation of Cl-substrate anion bonds these surface states are removed and the anion p_z character is distributed throughout the valence-band region. If the Cl is only bonded to cations as in geometry *C* then the substrate anion dangling bonds are not saturated and the region near E_v retains a strong p_z character. This character should give rise to strong photon-polarization effects like those described in Ref. 6 which are not observed in the present case.

Somewhat better agreement between theory and experiment is obtained with geometry *A* than with geometry *B*. This is emphasized by Figs. 8, 9, and 10 where experimental spectra are directly compared to broadened versions of the local density of states calculated with geometry *A*. For example, the surface relaxation employed in geometry *A* weakens the intensity of the shallowest Cl *p*-like theoretical peak which is quite prominent at 2–3.4 eV in geometry *B* while the experimental curves exhibit rather weak structure there (see Figs. 1 and 6). The predicted atomic-orbital character of the experimental peaks is similar both in geometry *A* and in geometry *B*. For example, for GaAs(110) +Cl the main peak *C* has mainly Cl p_x, p_y character admixed with As p_x, p_y states and a relatively small Ga p_x, p_y contribution. Peak *A* corresponds to the theoretical peak 7.7–8.2 eV below E_v (i.e., in the bulk heteropolar gap which extends from 7 to 10 eV below E_v). The theory predicts the strongest p_z character (Cl + As) for this peak but its weakness in the experimental spectra prevented us from verifying this point by detecting photon polarization effects.[6] Peak *B* corresponds to the theoretical feature around 6.5 eV due to Ga *s* states. The relative intensity of this peak is enhanced with respect to the clean-surface spectra due to a redistribution in energy of the As *p* states formerly present in this region. The broad experimental feature around 2.0 eV below E_v, peak *D*, probably corresponds to a series of theoretical peaks merging together due to substrate atomic orbitals and of a small contribution of Cl *p* electrons. Also note that the experimental peak *A'* (not shown in Fig. 8 but evident in Figs. 1 and 4) corresponds to the theoretical peak 11.3 eV below E_v in geometry *A*. This is yet another independent proof of the formation of Cl substrate anion bonds since the theoretical states at 11.3 eV are As *s* states pushed down in energy from their clean-surface

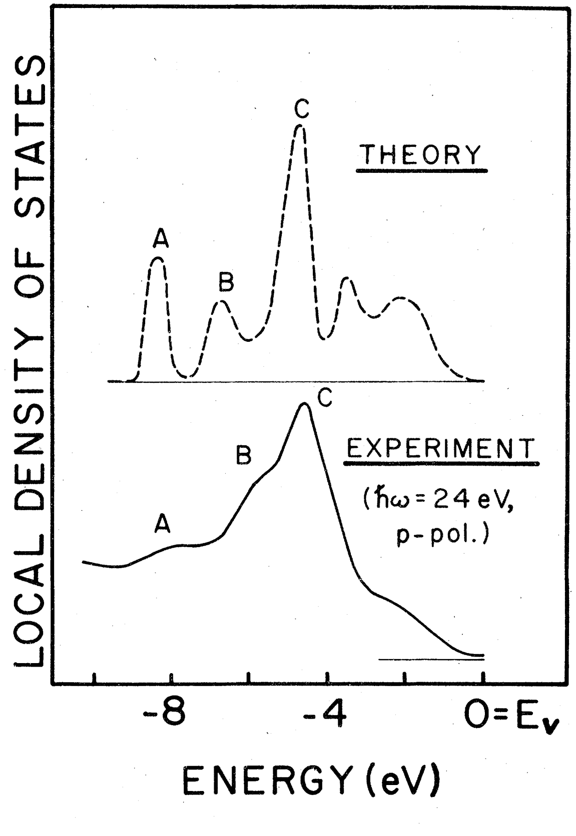

FIG. 8. Comparison between experiment and theory (geometry *A*) for GaAs(110) +Cl.

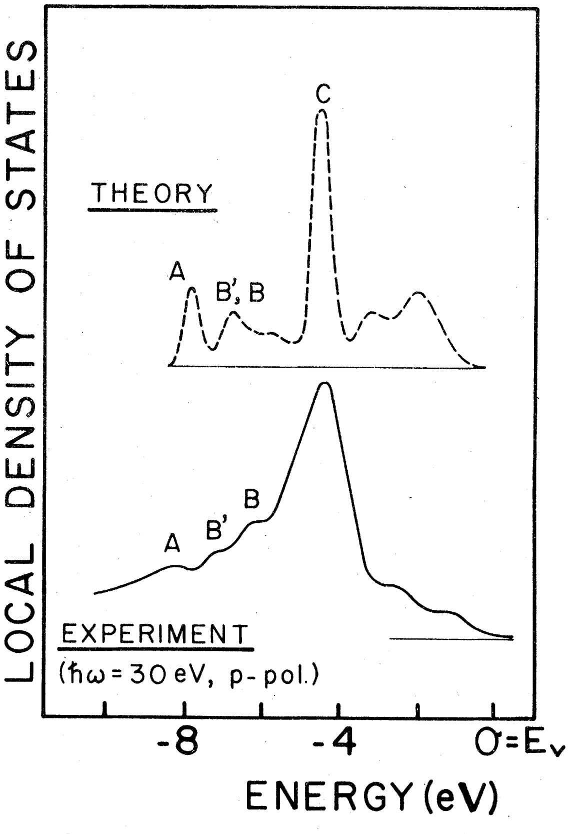

FIG. 9. Comparison between theory and experiment (geometry *A*) for GaSb(110) +Cl.

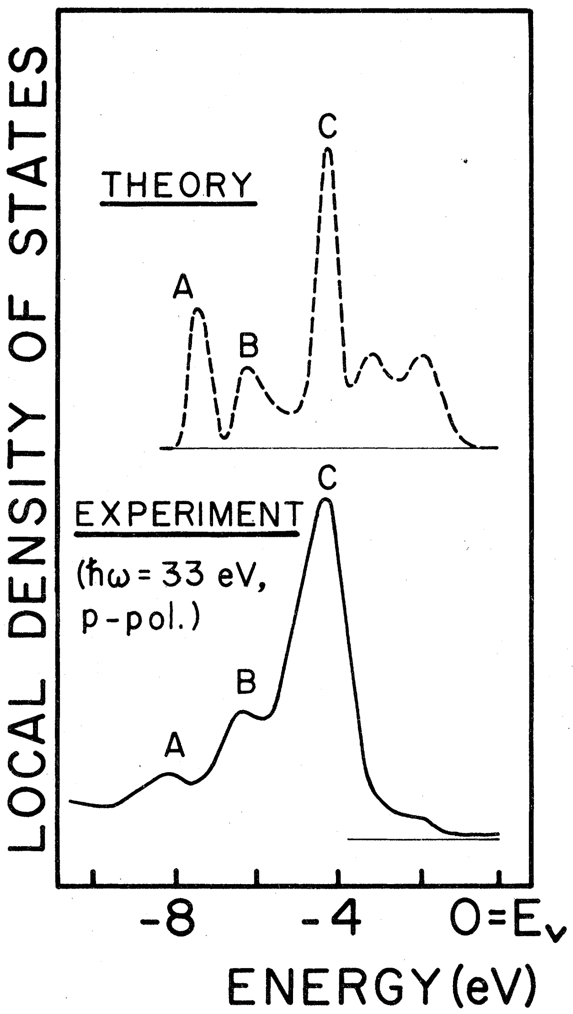

FIG. 10. Comparison between theory and experiment (geometry *A*) for InSb(110) +Cl.

theoretical position when the anion atom is bound to an adatom.

The analysis of the atomic-orbital character of the experimental spectral features in InSb(110) +Cl and GaSb(110) +Cl yields similar results. Note that a theoretically predicted splitting of peak *B* for GaSb(110) +Cl is actually observed in the experimental data (see Fig. 9, peak *B* and *B'*). But the theory does not explain the photon-polarization dependence of peak *C* in InSb(110) +Cl. The experimental results would indicate that some p_z character is present in this peak[6] while only p_x, p_y character is predicted by the theory.

There is some indication that geometry *A* gives better results when the Cl-substrate atom bond length is smaller than the sum of the atomic radii (see curve *A'* in Figs. 6 and 7). For example, the position of the main peak *C* is reproduced with better accuracy by a 5% bond length decrease in GaAs(110) +Cl. An accurate determination of bond lengths is, however, beyond the capabilities of our approach.

V. CONCLUSIONS

The comparison of experimental photoemission spectra with calculated local density of states has clearly demonstrated that the Cl adatoms on cleaved GaAs, GaSb, and InSb surfaces are bound to the anion substrate atoms rather than to the cation substrate atoms. This indicates that the anions are the most chemically active surface atoms in these materials[1] and helps to clarify the issue of chemisorption sites on their surfaces.[1–3] Our results also suggest that the substrate atoms of the Cl-covered surface are displaced from their bulk positions in a way similar to the clean reconstructed GaAs(110) surface.[4] There is some indication that the Cl—substrate-atom bond length is smaller than the sum of the atomic radii of Cl and As.

A *complete* understanding of the Cl chemisorption geometry is of course a more complicated problem whose solution requires many different kinds of experiments such as low-energy-electron-diffraction and angle-resolved photoemission spectroscopy. However, we have demonstrated in this paper that the most important elements of a chemisorption geometry can be deduced by simple angle-integrated photoemission spectra and by elementary theoretical considerations. This approach is attractive for a rapid check of chemisorption sites. It may be the only suitable approach for other systems where the instability of the surface makes a more complete experimental study impossible.

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[13] C. E. Moore, *Atomic Energy Levels*, Nat. Bur. Stand. (U.S.) Spec. Pub. 467, Vol. 2 (U.S. GPO, Washington, D.C., 1948). The details of this approach are given in Sec. III of Ref. 7.

[14] Our approach cannot completely rule out the possibility of more complicated chemisorption mechanisms although they appear less favorable than those here investigated. For example, exchange reactions seem unlikely to occur due to the difference in heat of formation between the new and the old chemical bonds and to the difference in radius between the adatoms and the substrate atoms.