Electronic structure of Ge(111) and Ge(111):H
from angle-resolved-photoemission measurements

R. D. Bringans and H. Höchst

Max Planck Institut für Festkörperforschung, Heisenbergstrasse 1, 7000 Stuttgart 80,
Federal Republic of Germany

Angle-resolved-photoemission measurements were made on the annealed (111) surface of germanium and on the same surface with adsorbed hydrogen. Spectra are presented for various values of $\vec{k}_{\parallel}$, the wave-vector component parallel to the surface, for the $[1\bar{1}0]$ and $[\bar{1}\bar{1}2]$ directions, and for photon energies of 16.85 and 21.22 eV. Two surface states at 0.8 and 1.4 eV below the top of the valence band were found in the spectra for the reconstructed Ge(111)-(8) surface. Both states showed only small changes in energy as a function of $\vec{k}_{\parallel}$ but distinct intensity variations. Bulklike states were also found and are compared to $E(\vec{k}_{\parallel})$ curves calculated with a pseudopotential method. The addition of hydrogen to the surface removed the reconstruction and drastically altered the photoemission spectra. A strong hydrogen-induced peak at an average binding energy of about 5 eV showed a similar dispersion to that calculated for Si(111):H by Pandey.

I. INTRODUCTION

The surface properties of semiconductors have recently received a great deal of attention. Of the surfaces studied, the (111) faces of silicon and germanium are particularly interesting because they show strong effects due to surface reconstruction. The ideal (111) surface of the diamond structure has one broken bond per surface atom but despite this apparent simplicity, the Si(111) surface exhibits stable (2×1) and (7×7) superstructures and Ge(111) is seen as either (2×1) or the "Ge(111)-(8)" structure. Metastable (1×1) surfaces also appear to exist for both germanium and silicon. The majority of the work so far has concentrated on Si(111), and there are still many unsolved aspects of the structure and electronic properties of this system. In this paper we concentrate on the (111) surface of germanium and examine its electronic properties using the angle-resolved-photoemission technique. Surface states on Ge(111) have been examined with several experimental techniques and an occupied state has been found in photoemission spectra at energies up to about 1 eV below the top of the bulk valence band.[1−6] Unoccupied surface states have also been revealed by photoelectron partial yield,[7] surface reflectivity,[8,9] and electron-energy-loss measurements.[10] Comparison with calculated surface properties has been difficult because although there have been several calculations for Ge(111)-(1 × 1) (see Ref. 11, for example), none

as yet have been made for the reconstructed surface. The hydrogen-covered surface has also been examined with photoemission[2,3,12] and the simpler symmetry of this surface has allowed a comparison to be made with calculations of the hydrogen induced features.[13]

None of the previous photoemission studies of the Ge(111) surface[1−7,12,14] have examined the angular dependence of the emitted electrons. The angle-resolved results which we present here shed additional light on the form of the electronic states of bulk Ge and of the Ge(111) surface. A direct comparison between experiment and theory can be made for the dispersion in $\vec{k}$ space of the bulk energy bands of Ge. The experimental results also yield detailed information about surface states of the clean Ge(111) surface and of the same surface with adsorbed hydrogen.

Low-energy-electron diffraction (LEED) studies of Ge(111) have shown the cleaved surface to have a (2×1) unit cell at room temperature which transforms irreversibly to the Ge(111)-(8) structure after annealing above about 300 °C.[15−18] The surface transforms to 1×1 after hydrogen adsorption or at temperatures above about 250 °C.[5] The photoemission measurements described here were made on the Ge(111)-(8) surface. The experimentally measured LEED pattern of this surface has been interpreted as being due to a (2×8) (Refs. 16, 17, and 19), (8×8) (Ref. 18), or a centered (2×8) (Ref. 20) reconstruction. In each case the proposed

structure requires more fractional order spots than seen in the experiment and so extinctions due to the precise arrangement must be invoked. The observed pattern is always threefold symmetric and thus requires that the surface has three equivalent domains if the reconstruction is either (2×8) or c-(2×8). The c-(2×8) symmetry suggested by Chadi and Chiang[20] is attractive because it only requires that the $\frac{1}{4}$-order spots be extinguished or too faint to be seen. These authors also propose a surface structure which involves a raising and lowering of surface atoms and which has a structure factor of zero for the $\frac{1}{4}$-order reflections. This structure is similar in character to that now generally accepted for the (2×1) reconstruction of both Si(111) and Ge(111) which consists of alternating rows of "up" and "down" atoms (see, for example, Mark et al.[21]). The c-(2×8) model for Ge(111)-(8), however, has two inequivalent up atom sites and two inequivalent down atom sites suggesting that the occupied dangling bond state for this surface should be split. As will be discussed later, we see two distinct surface states at 0.8 and 1.4 eV below the top of the bulk valence band but further calculations are required before a definite determination of the structure can be made.

The surface sensitivity of the photoemission experiment depends on the electron escape depth. Electrons from the valence band of germanium have a mean free path of about 10 Å at the photon energies of 16.85 and 21.22 eV used here[22] and the photoemission spectra thus contain both bulklike and surfacelike states. In Sec. III we describe a method of calculating the energy and emission angle dependence of spectral features arising solely from bulk states. Comparison with the experimental spectra then enables us to separate purely surface effects from the remainder of the spectrum. Surface and bulk contributions can also be separated to some extent by examining the dependence of spectral features on photon energy, emission angle, and gas adsorption. These aspects will also be discussed.

II. THE EXPERIMENT AND RESULTS

The experiments were made on a single crystal of p-type germanium which had a resistivity of 5×10^{-3} Ω cm. A (111) surface was cut, polished, and acid etched before insertion into the vacuum system and a clean surface was prepared by neon ion bombardment followed by annealing at 800 °C

for 5 min. Heating was carried out by passing a dc current directly through the sample (a plate $0.5 \times 5 \times 10$ mm^3) and could thus be made very quickly. The vacuum chamber had a base pressure in the range of $1 - 3 \times 10^{-10}$ Torr and the effects of surface oxidation could only be seen in the photoemission spectra after several hours. The oxidation could be removed by heating the sample to 700 °C for 30 sec and this process was carried out between each spectrum made on the clean surface (i.e., every 15 min).

After several cycles of ion bombardment and annealing, LEED measurements showed the Ge(111)-(8) pattern seen previously by other authors. The four $\frac{1}{4}$-order spots which surround each $\frac{1}{2}$-order spot in the Ge(111)-(8) pattern were not fully resolved but appeared as streaks. Hydrogen could be adsorbed on the surface by exposing the surface to hydrogen gas in the presence of a tungsten filament held at a temperature of $\simeq$2000 °C. The LEED pattern reverted to (1×1) on exposure to hydrogen. Angle-resolved-photoemission measurements were carried out with a Vacuum Generators ADES 400 spectrometer which was operated with an energy resolution of 0.3 eV and an angular resolution of 3°. The spectra presented here were taken over a range of electron emission angles using unpolarized He I and Ne I photons ($h\nu = 21.22$ and 16.85 eV, respectively).

The geometrical arrangement of the experiment is shown in Fig. 1(a). The incoming photons and outgoing electrons are constrained to lie in a plane perpendicular to the crystal surface, the photon angle being fixed at 45° from the normal. The crystal can be rotated relative to this plane so that emission can occur along any of the directions in the surface. The measured energy and emission angle of the photoelectron fully determine $\vec{k}_{||}$, its wave vector component in the plane of the (111) surface. In reciprocal space, $\vec{k}_{||}$ lies in a plane parallel to the ULW face on the bulk Brillouin zone. Figure 1(b) shows a view onto one of the ULW faces of the Brillouin zone. Two of the symmetry directions of the surface are shown in Fig. 1(a). There are six equivalent $\langle 10\bar{1} \rangle$ directions corresponding to values of $\vec{k}_{||}$ along $L \rightarrow W$ in the bulk Brillouin zone, three equivalent $\langle \bar{1}\bar{1}2 \rangle$ directions corresponding to $\vec{k}_{||}$ along $L \rightarrow U$, and three $\langle 11\bar{2} \rangle$ directions corresponding to $\vec{k}_{||}$ along $L \rightarrow K$.

Photoemission results using 21.2-eV photons are shown for the clean surface as a function of the
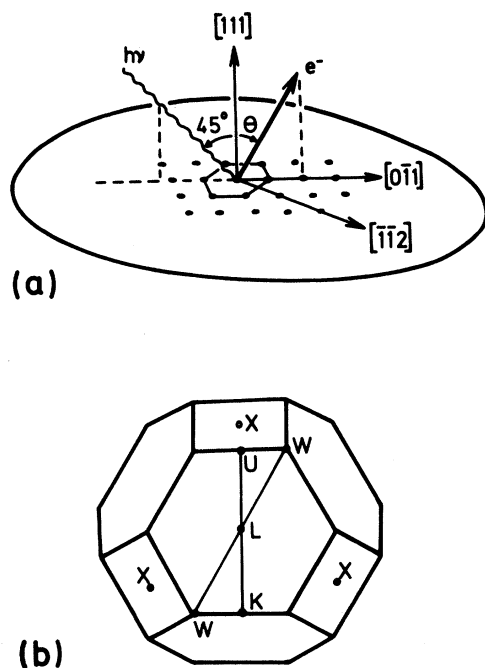
(a)

(b)

FIG. 1. (a) Geometrical arrangement of the experiment. The photon direction is 45° from the normal, and in the plane of the surface normal and the emitted electron. (b) Bulk Brillouin zone viewed along $L \rightarrow \Gamma$.

FIG. 2. Angle-resolved-photoemission spectra of the clean Ge(111)-(8) surface taken with 21.2-eV photons for a series of polar angles θ along the $[1\,\bar{1}\,0]$ direction of the surface.

polar angle θ in Fig. 2 for the $[1\bar{1}0]$ direction and Fig. 3 for the $[\bar{1}\,\bar{1}\,2]$ direction. Energies for all the spectra presented are shown relative to the Fermi energy which is only a few meV above the top of the valence band for the (111) surface of p-type Ge.[6,23] It can be seen immediately that there is considerably more structure in the spectra than expected from the three bulk valence bands present in this energy range. The strong contribution of surface effects to the spectra can also be seen by the large changes which occur when the surface is exposed to hydrogen. The corresponding spectra shown in Figs. 4 and 5 were taken under the same conditions as those in Figs. 2 and 3, respectively, but after an exposure of 10^{-2} Torr sec of hydrogen gas in the presence of a hot tungsten filament. The two peaks centered at about 0.8 and 1.4 eV in the spectra of the clean surface disappear after hydrogen adsorption. As will be discussed later in the following section, this fact provides some of the evidence for the conclusion that they are both surface states. The other major changes with the addition of hydrogen are the increase in intensity of the broad peak centered at 7.5 eV and the appearance of a new peak which disperses between 4 and 5 eV. Photoemission spectra taken with
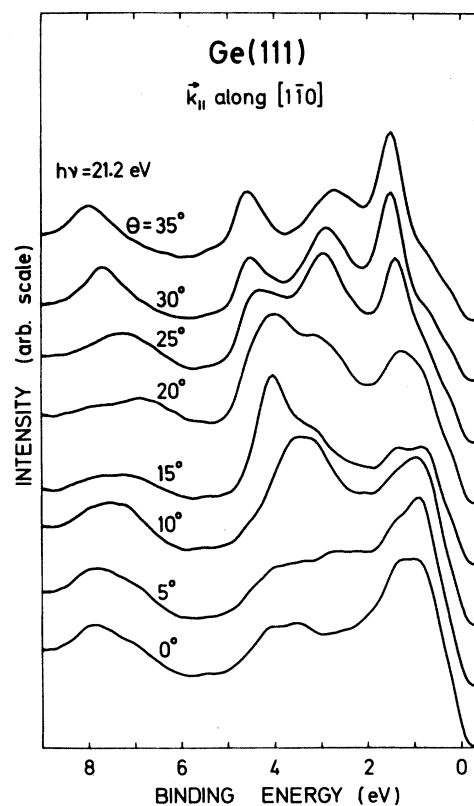
16.85-eV photons are shown for the clean surface in Figs. 6 and 7 for the $[1\,\bar{1}\,0]$ and $[\bar{1}\,\bar{1}\,2]$ directions, respectively.

III. DISCUSSION

The curves in Figs. 2—7 are very complex, and comparison with the calculated spectra must be made for their complete interpretation. A full surface calculation which would require knowledge of the atomic positions of the atoms of the first few layers is beyond the scope of this paper. The approach we have used is to calculate the position in energy and $\vec{k}_{||}$ space of the spectral features expected for purely bulk initial states. Comparison with the photoemission results then reveals information about surface effects.

The calculation of bulk effects was made using the three-step model of photoemission. In this model the event is broken into three independent processes: (i) photoexcitation of an electron from an occupied state to a final state within the crystal,
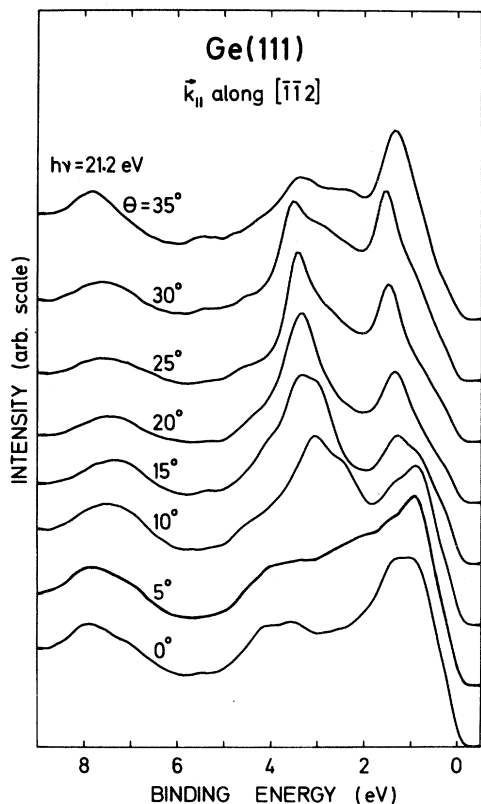
FIG. 3. Angle-resolved-photoemission spectra of the clean Ge(111)-(8) surface taken with 21.2-eV photons for a series of polar angles θ along the $[\bar{1}\bar{1}2]$ direction of the surface.
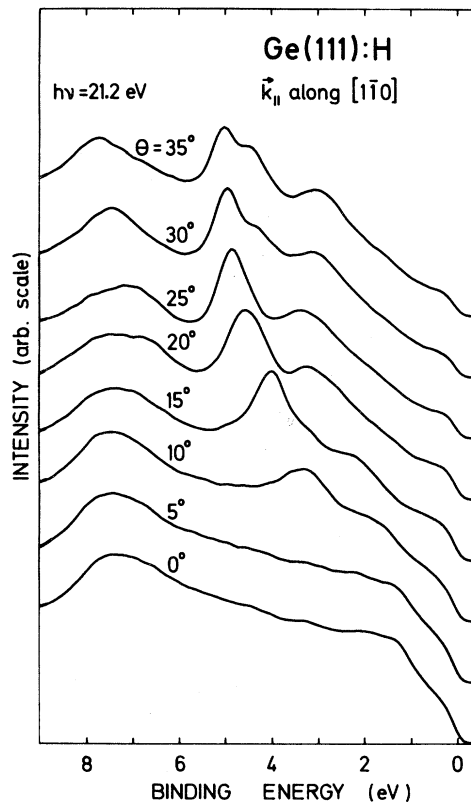
FIG. 4. Angle-resolved-photoemission spectra of the Ge(111) surface after exposure to hydrogen. The measurements were made for a series of polar angles θ along the $[1\bar{1}0]$ direction of the surface using 21.2-eV photons.

(ii) transport of the electron in this final state to the surface, and (iii) transfer through the surface to a free-electron state in the vacuum. The long-range order in the plane of the surface means that $\vec{k}_{\parallel}$ is the same for the initial, final, and photoemitted states to within a reciprocal lattice vector parallel to the surface. The wave vector component along the surface normal, on the other hand, is not conserved exactly due to the loss of periodicity in this direction and because of the finite mean free path of the electron. We will make the assumption that the strong features in the photoemission spectra occur when $k_{\perp}$ is also exactly conserved. This assumption ("direct transition model") has been used successfully to explain the results of angle-resoved photoemission from the noble metals (see, for example, the review by Himpsel[24]).

The aim of the analysis is to determine the occupied states of the system and so with the direct

transition model one must know or make assumptions about the final state to which the electron is photoexcited. The obvious choice of final state is any of the conduction bands from a band-structure calculation which satisfy the energy and wave-vector conservation requirements. It was pointed out by Mahan,[25] however, that the final states which have group velocities along the (outward) direction defined by $(k_{\perp}, \vec{k}_{\parallel})$ will dominate the photoemission spectrum. Electrons with final-state velocities along other directions ("secondary cone" electrons) require a scattering by bulk or surface reciprocal lattice vectors if they are to be detected. Secondary cone emission has been found to make a contribution of order 10% to the photoemission spectrum (see Ref. 24, for example). Using this fact, several authors have taken the final state inside the solid to be a free-electron state. Within this approximation the final state for a fixed value of $\vec{k}$ is
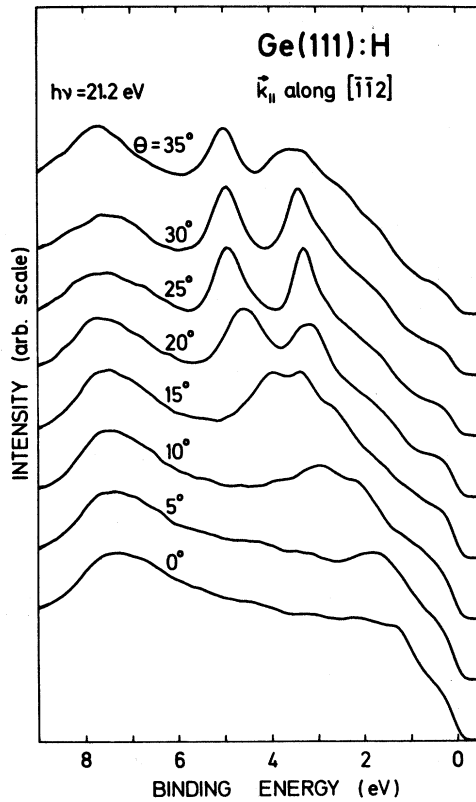
FIG. 5. Angle-resolved-photoemission spectra of the Ge(111) surface after exposure to hydrogen. The measurements were made for a series of polar angles θ along the $[\bar{1}\bar{1}2]$ direction of the surface using 21.2-eV photons.
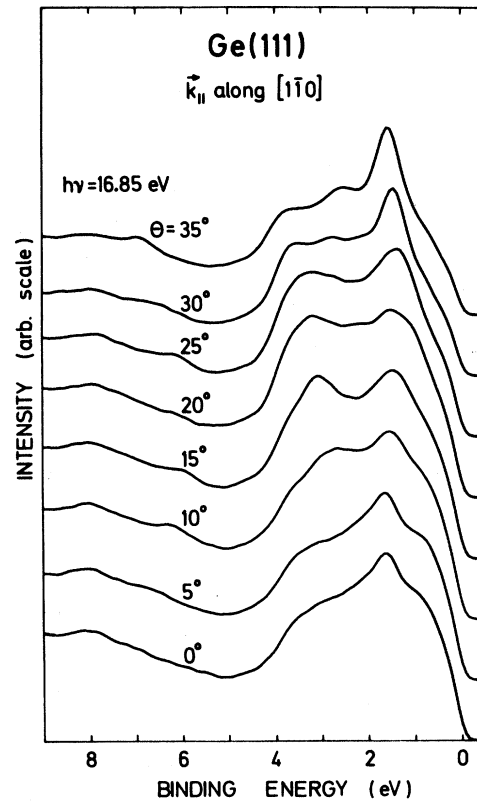
FIG. 6. Angle-resolved-photoemission spectra of the clean Ge(111)-(8) surface taken with 16.85-eV photons for a series of polar angles θ along the $[1\bar{1}0]$ direction of the surface.

$$E(\vec{k}) = \frac{\hbar^2}{2m}(k_\parallel^2 + |\vec{k}_\perp + \vec{G}|^2) - V_0 \ ,$$

where energies are measured relative to the vacuum level, $\vec{k}_\perp$ is within the first Brillouin zone, and V_0 is the inner potential. If only primary cone emission is considered, then the only values of $\vec{G}$ which can contribute are those along the surface normal (i.e., those parallel to $\vec{k}_\perp$). The use of a free-electron final state rather than conduction bands from a band-structure calculation has been justified by Chiang et al.[26] These authors Fourier-analyzed the Bloch final states from a nonlocal pseudopotential calculation for GaAs and found that those having strong components along the emission direction, and thus a high probability of being detected in the experiment, fell very close to the free-electron curve. Chiang et al. concluded that the free-electron final state was a good approximation for photon energies between 25 and 100 eV but their results show the approximation to be

good for all final energies above the vacuum level. Hansson et al.[27] have also shown that the free-electron final state gives the best agreement with experimental results for Si(111)-(7×7) at photon energies between 7.8 and 11.6 eV.

The free-electron final state which we use was calculated using the free-electron mass and its zero was taken at the bottom of the valence band (i.e., V_0 was taken as the sum of the work function and the valence-band width). For each value of $\vec{k}$ there is a line in three-dimensional $\vec{k}$ space of possible initial states. Energy bands were calculated along these (nonsymmetry) lines using a local pseudopotential method with the form factors of Cohen and Bergstresser[28] and then adjusted to fit the results of nonlocal pseudopotential calculations along symmetry directions.[4,29] Possible photoexcitations were found by examining when these initial states and the free-electron final state became separated by the photon energy. The positions of bulk features calculated using this method are shown as
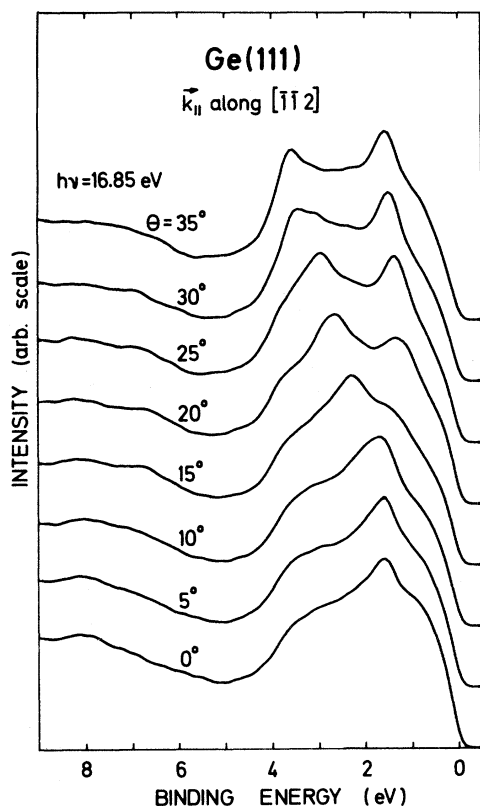
FIG. 7. Angle-resolved-photoemission spectra of the clean Ge(111)-(8) surface taken with 16.85-eV photons for a series of polar angles θ along the $[\bar{1}\,\bar{1}\,2]$ direction of the surface.
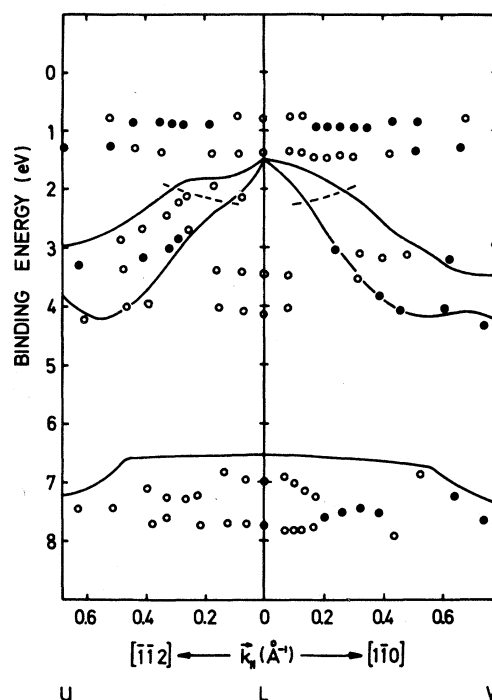

FIG. 8. Positions in energy and $\vec{k}$ space of features in the photoemission spectra measured with 21.2-eV photons. Filled circles correspond to strong peaks and open circles to weaker features. The solid lines show the dispersion calculated from the bulk band structure.

the solid lines in Fig. 8 and are compared with the experimental peak positions for 21.2-eV photons for two of the directions of the (111) surface. Strong peaks in the experimental spectra are shown by filled circles and smaller features by open circles.

For the $[1\,\bar{1}\,0]$ direction, one of the bulk bands agrees well with the experimental dispersion if it is assumed that the absence of structure at small $\vec{k}_{||}$ is due to band gaps in the final state. The dotted line in Fig. 8 shows the locus of points for which the free-electron state touches the zone boundary. The other bands do not agree quite so well with the measured features. Nevertheless, the proximity of the measured dispersion to the calculated bulk values allows us to identify features as being associated with these particular bulk bands. Examination of the hydrogen covered surface also provides additional information about the bands in the surface region. The $E(\vec{k}_{||})$ dispersion of spectral features from both the clean and hydrogen covered surface are plotted together in Fig. 9. Earlier

photoemission investigations of Ge(111) have revealed an occupied dangling bond state at an energy of about 0.7 eV below the top of the valence band.[1-6] States at larger binding energies were assigned by Rowe[3] to back-bond states because the limited sampling depth of the experiment does not allow true bulk states to be seen. The comparison in Fig. 8, however, shows that the departure of the experimental peaks from the bulk dispersion is not large for the upper two valence bands. Whether these states are back bonds or slightly altered bulk states is of course a matter of definition, but it is interesting that these features in the experiment do not show the repeat symmetry of the reconstructed surface but follow the bulk (1×1) bands. In the following discussion we will deal with each of the experimental features in greater detail, beginning with that at the smallest binding energy.

The feature marked 1 and shown as a dotted line in Fig. 9 corresponds to a very weak shoulder at about 0.25 eV below the top of the valence band. In the Ge band structure there are no states at this energy except near Γ and this weak feature probably appears at all values of $\vec{k}_{||}$ due to secondary
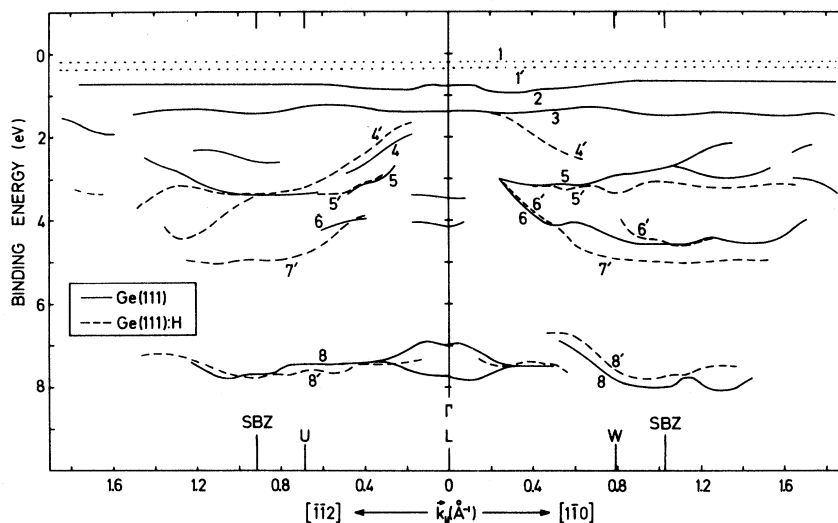
FIG. 9. Positions of features in the $h\nu = 21.2$ eV photoemission spectra as a function of binding energy and $\vec{k}_{||}$ for the clean Ge(111)-(8) surface (solid lines) and the same surface after hydrogen adsorption (broken lines). The dotted lines show the position of a weak shoulder near the top of the valence band.

cone emission from the top of the valence band. A somewhat stronger feature at about 0.4 eV is shown as 1' for the H-covered surface. The weakness of these features, however, makes any determination of position difficult and they will not be discussed further.

The two peaks 2 and 3 which occur at energies of about 0.8 and 1.4 eV, respectively, show variations in energy and particularly in intensity as a function of $\vec{k}_{||}$. They have been assigned to surface states because (i) after H adsorption both peaks disappeared almost completely over the entire range of $\vec{k}_{||}$ and (ii) peaks were found at the same energy in the $h\nu = 16.85$ eV spectra. Surface states have been seen previously in angle-integrated-photoemission experiments at binding energies of 0.7 eV (Refs. 1 and 2) and 0.8 eV (Ref. 3) on Ge(111)-(2×1) and at 0.4 eV (Ref. 2) for Ge(111)-(8). Yield experiments by Guichar et al.[6] have shown surface peaks at 0.7 eV for the (2×1) reconstruction and 0.6 eV for the (8) reconstruction. In all these cases the (single) peak observed was broader than those seen here. The surface peak at 1.4 eV has its maximum intensity at a polar angle of 25 − 30° for He I and Ne I photons and for both the [1 $\bar{1}$ 0] and [$\bar{1}$ $\bar{1}$ 2] directions. For the experimental arrangement used here of a photon incidence angle of 45°, one expects an intensity maximum at 22.5° from a p_z orbital.[30] The 1.4-eV peak would then be interpreted as being due to a dangling bond state. The 0.8-eV peak, which is

well defined only in the He I spectra, has its maximum intensity at about 7°. Eastman et al.[31] found a similar polar angle dependence for two surface states at 0.9 and 1.8 eV on Si(111)-(7×7) using light with mixed polarization. When they made measurements with polarized light however, their results indicated that the 0.9-eV state was dangling bondlike and the other was in the plane of the surface. This result points out the danger of placing a heavy reliance on intensity variations, particularly when unpolarized light is used. With this in mind, it is not possible for us to conclude definitely whether one or both of the surface peaks at 0.8 and 1.4 eV are due to dangling bonds. The possibility that both peaks are associated with dangling bonds cannot be ruled out either however, because (i) both surface state peaks show sixfold symmetry in their intensity and energy position whereas other features show threefold symmetry and (ii) the effect on these states of the bonding of hydrogen to the surface is very strong, removing them almost completely.

The features marked 4, 5, and 6 in Fig. 9 for the clean surface of Ge, are all related to the upper two bulk bands in the Ge valence band. The comparison in Fig. 8 between the experiment and the calculated bands is not exact. The calculations assumed that the direct model of photoemission was correct and that there were no effects due to secondary cone emission. The discrepancy between the experiment and the calculated bands could thus ar-

ise from scattering via surface reciprocal-lattice vectors or could be an intrinsic effect due to surface-induced changes in the strength of the back bonds. In his angle-integrated-photoemission results for Ge(111)-(2×1), Rowe[3] found a peak at 2.8 eV which was strongly dependent on the number of surface steps and assigned it to a back bond. Feature 5 in Fig. 9 shows little dispersion about its mean value of 3.0 and as it departs the most strongly from the calculated bands, it could well correspond to a back bond with altered energy. Feature 6, which agrees well with the calculation, is not altered much after H coverage and is more likely to be due to a genuine bulk effect. Both features 4 for the clean and 4' for the Ge(111):H surface appear to be associated with bulk bands altered by the surface. All of the spectra show a broad peak about 2-eV wide centered at 7.5 eV. At low values of $\vec{k}_\parallel$, this peak has smaller structure superimposed on it at the energies shown in Fig. 8 and at larger $\vec{k}_\parallel$ it sharpens and follows the direct transition band. A strong peak at 7.5 eV has been seen in angle-integrated ultraviolet[4] and x-ray[32] photoemission and measurements and attributed to transitions arising from a very flat band around L in the Brillouin zone.[4] It seems likely, therefore, that at low $\vec{k}_\parallel$ these states are revealed in the present measurements because the (8) reconstruction provides many small surface reciprocal-lattice vectors which cause an angle averaging. One would normally expect primary cone emission to be stronger than a secondary cone effect such as

this but at the point in the Brillouin zone at which the direct transition is possible, the band involved is very steep. Because the intensity of this feature (number 8 in Fig. 9) increases with hydrogen adsorption, at least some of the finer structure may be associated with surface effects.

The hydrogen induced peak 7' is very likely to be due to the Ge—H bond as a calculation for Si(111):H shows a hydrogen state with similar dispersion.[13] This peak has also been seen[3] at 4.9 eV in angle integrated measurements of Ge(111):H. The experimentally determined features for Ge(111):H are shown again in Fig. 10 along with the hydrogen state calculated by Pandey[13] for the silicon surface Brillouin zone and for germanium at the symmetry points of the zone. The comparison reveals that the calculated binding energies for Ge are too small by about 0.3 eV for the band near 5 eV but that the shape of this band is essentially correct. In particular, the region of the Brillouin zone over which the calculation for Si(111):H shows there to be a surface band is the same as the region in which the experimental peak has no counterpart in the clean surface. The good agreement of the experimental and theoretical dispersions for the 5-eV band suggests that the hydrogen atoms are simply bonded to each of the surface layer atoms as assumed in the calculations, with the bond direction normal to the surface. This consideration is not unimportant as there is experimental evidence[33,34] that the situation is more complicated for Si(111).
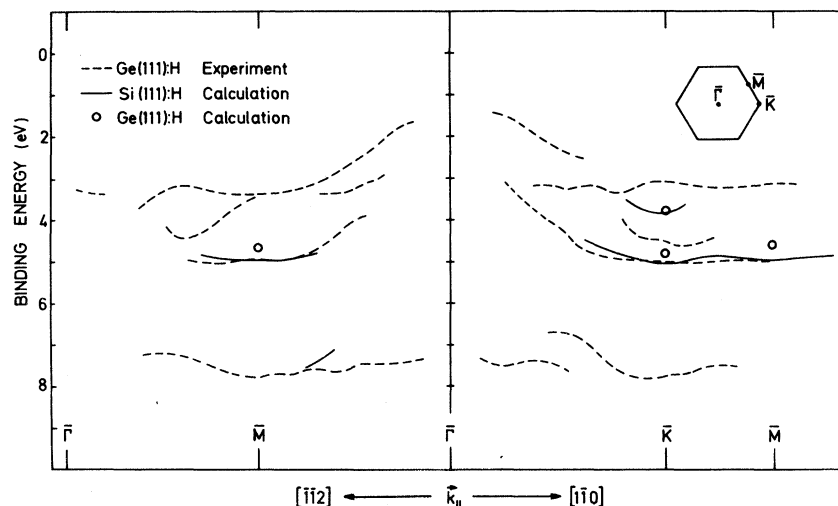

FIG. 10. Positions of features in the $h\nu=21.2$ eV photoemission spectra for Ge(111):H shown as broken lines are compared with the hydrogen associated bands calculated for Si(111):H (solid lines) and Ge(111):H (circles) from Ref. 13. The calculations for silicon are scaled to fit the surface Brillouin zone of germanium.

IV. CONCLUSIONS

Our angle-resolved-photoemission measurements on the Ge(111)-(8) surface have shown surface states at 0.8 and 1.4 eV below the top of the valence band. The results cannot distinguish whether the previously unobserved state at 1.4 eV is associated with a dangling bond or a back bond. A splitting of the dangling bond state was predicted by Chadi and Chiang[20] for a c-(2×8) model of the Ge(111)-(8) reconstruction. Calculations of the amount of splitting expected for this model would be particularly interesting in view of our observations. Features in the photoemission spectra at greater binding energies can be associated with bulk states which are altered slightly by surface effects. The addition of hydrogen removes the surface states and introduces a new state which undergoes a similar dispersion to that predicted by Pandey[13] for Si(111):H.

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