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PHYSICAL REVIEW B VOLUME 8, NUMBER 4 15 AUGUST 1973

Energy-Level Spectra of Electrons at the (111), (110), and (100) Surfaces of Silicon and Germanium by Ion-Neutralization Spectroscopy

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(Received 20 February 1973)

Energy-level spectra obtained for the (111), (110), and (100) faces of Si and Ge by ion-neutralization spectroscopy (INS) bear only a superficial resemblance to the bulk density of states for these solids. In particular, the energies of small peaks in the INS-unfold function vary from one surface to another, and also differ from the energies of bulk critical points determined either by theory or by spectroscopies which more nearly yield bulk properties. A similar statement can be made for the width of the degenerate p band, which is narrower at the surface as revealed by INS than it is in the bulk. Thus, the principal conclusion of this paper is that the local density of states (density of states weighted by local-wave-function magnitude) is significantly modulated as one proceeds from the bulk of a solid to its surface. The surface state observed for Si(111) by photoemission as overlapping the top of the valence band is seen in the INS spectra for both the Si(111)1 and Si(111)7 surfaces. The INS spectra for other Si surfaces and for all of the Ge surfaces studied do not show the kind of definitive evidence for a surface state seen in the Si(111) data although we cannot say that such surface states are not present with reduced intensity.

I. INTRODUCTION

The method of ion-neutralization spectroscopy (INS) has been used to determine energy-level spectra of several surfaces each of silicon and germanium. This is the first use of this spectroscopic method in the study of the surfaces of the elemental semiconductors. It is found that the energy-level structures at the various surfaces reflect the gross features of the bulk energy-level structure but differ considerably in detail both from the bulk and among themselves. In particular, what appear to be critical points at the surfaces as indicated by peaks in the INS transition-density functions are found to differ in energy from surface to surface and from bulk critical points predicted by theory[1-4] or observed by other electron spectroscopies.[5-8] Demonstration of this surface modification of bulk band structure depends directly upon the high degree of surface specificity of the INS.

Filled surface states are also in evidence on some of the surfaces studied. On the Si(111)7 and Si(111)1 surfaces, there is evidence for a state which is centered a fraction of a volt below the valence-band edge, and which is not easily identified as a surface-shifted bulk critical point. This state lies close to the position of the state observed by photoemission[9,10] on the cleaved Si(111) face and identified as a surface state. The INS data for other surfaces do not show evidence for such a state of comparable magnitude although a state could well be present at an intensity which makes it not readily distinguishable from other features of the surface local density of states.

The first studies of the ion-neutralization pro-

cess at semiconductor surfaces were performed in our laboratory and published in 1965.[11] Digital data taken at that time for Ge(111) and Ge(100) surfaces were not unfolded to produce the transition-density function $U(\zeta)$ until the method of INS had been developed.[12] When this unfolding was later done, the transition-density functions for these surfaces were found to have peaks, presumed to be due to critical points in the band structure, which did not agree in energy position with theoretical predictions of bulk-critical-point energies. Since we were then just beginning to unfold INS data we thought it prudent to redo the work already done in a contemplated new study of the three cube faces of Si and Ge. This work is that upon which the present paper is based.

The newer INS data produced $U(\zeta)$ functions which agree very well with the analysis of digital data available from the earlier work.[11] However, we did not publish these results immediately because of our inability to unfold the data for one of the surfaces studied, Si(111)7, without resorting to an origin shift of the $F(\zeta)$ function of an amount significantly larger than any required before. We knew this anomaly was not fortuitous but resulted from a specific characteristic of the Si(111)7 surface. We decided not to publish any of our data for semiconductors until we had expended some effort in attempting to understand this effect. The conclusions to which these studies have led us are presented in a companion paper immediately following in this journal.[13] Our studies of chemisorption using INS[14,15] have demonstrated the high degree of surface specificity of INS and have bolstered our confidence in our early conclusion that the differences between our results and bulk theory for these semiconductors are to be attributed to surface modulation of the bulk crystalline band structure.

This paper is organized as follows: In Sec. II we review briefly the nature of the experiment and refer to detailed accounts of the INS method. Sample preparation, surface crystalline structures observed, and how these surface structures were produced are discussed in Sec. III. The principal experimental results are presented in Sec IV. The evidence for surface modulation of the local density of states is discussed in Sec. V and the evidence for the Si(111) surface state in Sec. VI.

II. NATURE OF THE EXPERIMENT

The method of INS used in the present work has been discussed in several earlier publications.[12–17] It is based on the extraction of a so-called transition-density function $U(\zeta)$ as the unfold of a distribution $F(\zeta)$ of paired initial states derived from measured kinetic-energy distribution functions $X(E)$ of electrons ejected in an Auger-type process. E is an energy measured positively upward from the vacuum level and ζ an energy measured positively downward from the Fermi level. This electron-ejection process is that by which a slowly moving positive ion is neutralized when it arrives just outside a solid surface. Examples of such $X(E)$ functions for 5-eV He^+, Ne^+, and Ar^+ ions incident on the Si(111)7 surface are shown in Fig. 1. Note how the structure near the high-energy limit in each curve mirrors that in the other curves indicating that this structure results from initial-state rather than final-state characteristics.

$X_5(E)$ functions for He^+ ions incident on the same Si(111) surface prepared with different surface crystalline superstructures are shown in Fig. 2. These data are further evidence of the high degree of surface specificity of INS. The electron kinetic-energy distribution functions like those of Figs. 1 and 2 are the basic data of the method of INS. The specifics of the method of data reduction are to be found in Refs. 12, 14, and 16.

The apparatus used in the present work was that discussed in Ref. 18 and used in our study of copper and nickel surfaces published in Ref. 19. Thus it does not include the modifications made later.[20] However, the data it produced are of a quality comparable to that of our later work. The degree of reproducibility of data taken repeatedly for the same surface is indicated for He^+ ions on Ge(111)8 in Fig. 3. As expected, we find the greatest variation in the unfold function to occur deep in the band, farthest from the mathematical origin of the

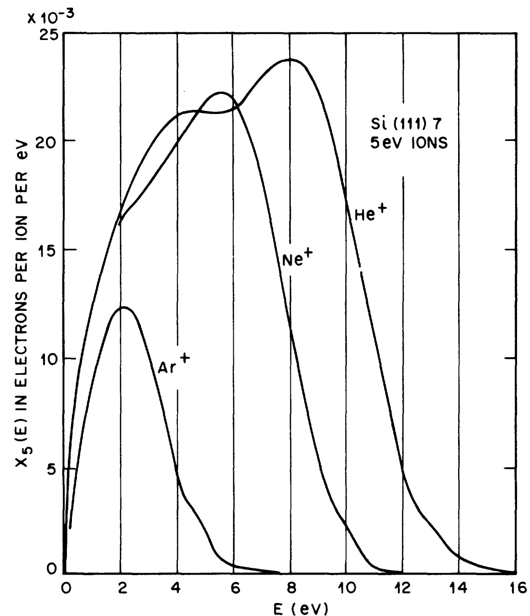

FIG. 1. Kinetic-energy distributions $X_5(E)$ of electrons ejected from the Si(111)7 surface by He^+, Ne^+, and Ar^+ ions of 5-eV incident kinetic energy.

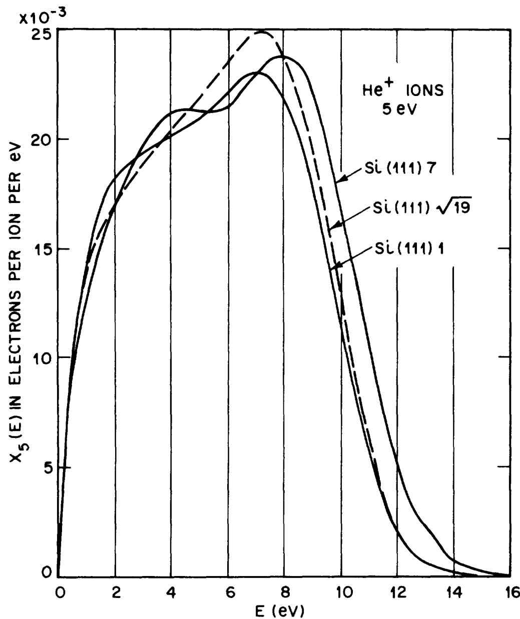

FIG. 2. Kinetic-energy distributions $X_5(E)$ of electrons ejected by 5-eV He^+ ions from three Si(111) surfaces having different surface crystalline superstructures distinguished by differing patterns produced by low-energy electron diffraction (Sec. III).

function. Each of these $U(\zeta)$ functions derive from averaged-kinetic-energy distributions $X(E)$ obtained by adding 10–15 digitalized curves in a multichannel scaler.

Two comparisons of the He^+ data of Fig. 3 are made with other data. In Fig. 3 they are compared with data obtained on the same surface using Ne^+ ions. Over the energy range available to both of these ions we see that every peak and valley of the curve for one ion is faithfully reproduced in that for the other ion. This is clear evidence that the observed structure is to be attributed to local initial-state density in the valence- and surface-state bands and *not* to final states in the conduction band to which the Auger electrons are excited.[12,15]

A second comparison of the $U(\zeta)$ function for He^+ ions on Ge(111)8 of Fig. 3 is that which can be made with the derivative of the fold function $F'(\zeta)$ plotted in Fig. 4. As we have shown in previous publications, particularly Ref. 14, the comparison of the local function F' with the nonlocal function U is, for the general class of function encountered in INS, a definitive test of the correctness of the procedures followed in obtaining U. In particular, this comparison is a direct test of whether or not we have found the correct origin for F. We note that F' of Fig. 4 reproduces accurately, if somewhat less distinctly, all the features of the U functions of Fig. 3. Thus in the language of Ref. 14, each peak feature in U and F' are $b*p$ features, with all $p*p$ features, which depend on peak-height squared, being too small to be seen in F'. All data published in this paper meet this test.

III. SAMPLE AND SURFACE PREPARATION

The materials from which the target samples were cut were the following: All Si samples were cut from a p-type Merck ingot of 350-Ω cm resistivity. The Ge(111) sample came from an n-type ingot of 30–14-Ω cm resistivity pulled at Bell Laboratories. The Ge(110) and Ge(100) samples came from a p-type ingot of 50-Ω cm resistivity also pulled at Bell Laboratories. All samples were cut to the U-shaped form shown in Fig. 2 of Ref. 21 having a 14×7-mm front face. These samples were mounted to legs as shown in Figs. 1 and 3 of Ref. 21. The sputtering filament and shield shown inside the target in these figures were not used in the present work since these electrodes are now supplied at a separate port in the present apparatus (see Fig. 1 of Ref. 19).

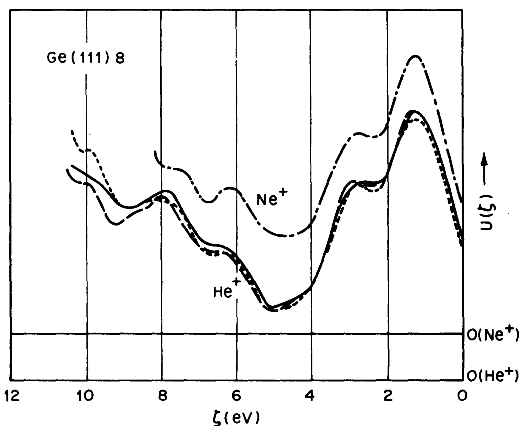

FIG. 3. Transition density or unfold functions $U(\zeta)$ for He^+ and Ne^+ ions incident on the Ge(111)8 surface.

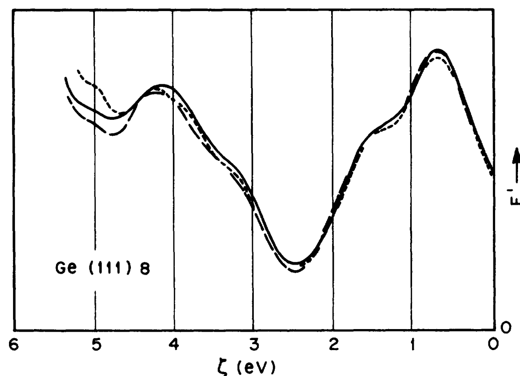

FIG. 4. Plots of three $F'(\zeta)$ functions for He^+ ions in Fig. 3. $F'(\zeta)$ is the derivative of the fold function $F(\zeta)$ of which $U(\zeta)$ is the unfold.

Mechanical polish of each surface was carried through to 0.05-μ Linde abrasive after which each was chemically etched. The Si surfaces and the Ge(111) surface were etched in 20:1::H_2NO_3:HF solution removing approximately 4 μ, after which each sample was immediately immersed in a saturated solution of iodine in methanol and then blotted dry. In the case of Ge(110) and Ge(100) the final etch polish consisted of a 20-min immersion in a saturated solution of bromine in methanol. In all cases the first treatment of the sample in vacuum was a sputtering which removed between 500 and 2000 atomic layers before any heating of the sample was attempted. Subsequent treatments differed from sample to sample and are specified below.

A. Si(111)

In our work with the Si(111) surface we have produced the three distinct superstructures Si(111)1, Si(111)7, and Si(111)$\sqrt{19}$ produced by others.[22–24] Each structure was stable at room temperature, could be reproduced by a well-defined heat treatment, and was characterized both by a distinctive low-energy-electron-diffraction (LEED) pattern and a distinctive $X(E)$ distribution of ejected electrons (Fig. 2).

After the initial sputtering referred to above, performed immediately after installation, a 90-min anneal at 830 °C produced a Si(111)7 pattern which was not uniform over the entire sample face. Further processing involved sputtering to remove an additional 1500 layers, prolonged heating for 17 h at 1110 °C with occasional flashes to 1270 °C. At the end of this treatment we had the Si(111)$\sqrt{19}$ pattern and could recover the Si(111)7 pattern over the entire surface only upon following the prescription given by Van Bommel and Meyer.[25] Although we have no direct evidence in this work bearing on impurities, we see no reason to quarrel with the conclusion of Van Bommel and Meyer[25] that the Si(111)$\sqrt{19}$ pattern is impurity stabilized by a small amount of Ni. Some Ni was undoubtedly present as evaporated material on neighboring surfaces, some of which are in fact made of the alloy nichrome.

After several further sputterings and heatings to 600 °C for long periods and to various temperatures up to 1270 °C for shorter periods, we found it possible to produce each of the three surfaces on demand by the following prescriptions:

(i) Si(111)7 produced by heating for 10–15 min at 600 °C;

(ii) Si(111)1 produced by heating for 10 sec to 830 °C;

(iii) Si(111)$\sqrt{19}$ produced by heating for 5 sec to 1270 °C.

In general, the longer the target had been held at 830 or 1270 °C, the longer the time required at 600 °C to produce the Si(111)7 pattern again. The rate of decrease of target temperature after heating current is reduced to zero is determined by radiation cooling and conduction cooling through the sample supports. We recognize that our prescriptions for obtaining the surfaces studied differ in some details from those given by others.[24,26,27]

B. Si(110)

In agreement with Jona[24] we have found it possible to produce several different LEED patterns on this face of silicon. The two most definite and distinct patterns were Si(100)4×5 and Si(110)5×1. We also saw a Si(110)2×1 pattern but never without a weak admixture of the 4×5 spots. Jona suggests that the 2×1 pattern may be a "step toward the formation of" the 4×5 pattern. Since the INS $X(E)$ function was insensitive to the shift in LEED pattern from predominantly 2×1 to well-developed 4×5, we discuss in Sec. IV results for the 5×1 and 4×5 surfaces only.

Jona[24] found it impossible to establish a recipe for obtaining reproducibly any Si(110) surface structure. We found it possible, however to produce several times each the 5×1 and 4×5 structures as follows. The 4×5 structure was produced by sputtering and heating to a temperature of 1100 °C or higher. The 5×1 pattern was produced from the 4×5 structure by heating the sample for periods of an hour or more at the relatively low temperature of 600 °C. This prescription is somewhat at variance with the observations of Jona. The quality of our 5×1 pattern was not as good as that of the 4×5 pattern. Our final observations were made after a lengthy sequence of sputterings, in which thousands of monolayers of material were removed, and heatings of various durations to a variety of temperatures ranging as high as 1270 °C.

C. Si(100)

The only ordered surface structure we have obtained is Si(100)2, in agreement with earlier work.[22,24] We have not observed the Si(100)4 pattern obtained by Lander and Morrison.[28] Again a lengthy sequence of sputterings and heat treatments was necessary to reach a terminal condition with respect to both LEED pattern and $X(E)$ function. After sputtering we flashed the target to 1235 °C 25 times.

D. Ge(111)

We have observed and studied only one Ge(111) surface structure, namely, Ge(111)8 observed by others[24,28] and attributed to the clean surface. In achieving this surface reproducibly the sample was sputtered seven times, removing a total of 6700

atomic layers of material with various heating periods at temperatures up to 900 °C. The heatings included one at 900 °C for 3 h and another for 16 h at 245 °C. We concluded that a combination of heating at 900 °C and sputtering was required to produce a good Ge(111)8 pattern. Long-period anneals at lower temperatures were not effective in producing the pattern. The data of this paper were taken in the terminal condition in which further sputtering and heating produced no change in $X(E)$ or the LEED pattern.

E. Ge(110)

Only the one pattern labeled by Jona[24] as Ge(110)X was observed in this work. The quality of the pattern was fair at best. All spots observed at 107 eV fit a net formed by superposition of a (110)2 pattern and an identical pattern displaced laterally from the first along the direction of a diagonal by a distance equal to one quarter of that between two integral-order spots.

This Ge(110)X surface was achieved after several sputterings which removed some 13 000 layers, interspersed with many hours of annealing at 600 °C and heatings to temperatures up to the melting point. In fact at one point we heated the sample for 5-sec periods to successively higher temperatures until surface melting occurred at the center of the sample face. No improvement in the LEED pattern resulted. It is interesting that the superstructure of the (110) faces of both Si and Ge are complicated.

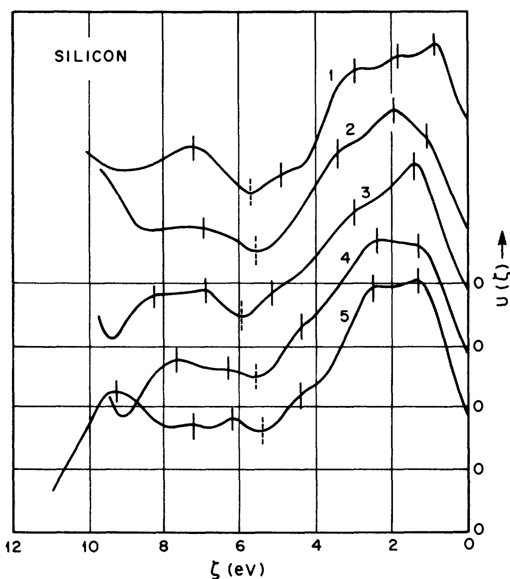

FIG. 5. Transition-density functions $U(\zeta)$ for five faces of silicon. Curve 1: Si(111)7; curve 2: Si(111)1; curve 3: Si(110)5 × 1; curve 4: Si(110)4 × 5; curve 5: Si(100)2.

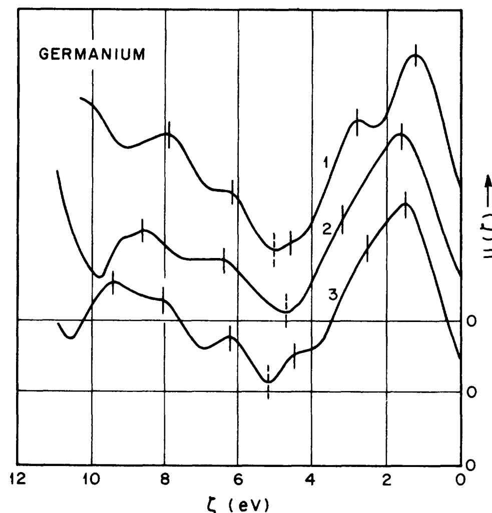

FIG. 6. Transition-density functions $U(\zeta)$ for three faces of germanium. Curve 1: Ge(111)8; curve 2; Ge(110)X; curve 3: Ge(100)2.

F. Ge(100)

We observed one LEED pattern, namely, Ge(100)2, for this face in agreement with previous workers.[22,24,28] Sputtering off 3500 layers plus short heatings to various temperatures as high as 900 °C produced this surface. We did not heat for long periods above 600 °C in order to avoid development of the (111) facets reported by Jona.[24] 3% of the surface at the center of the face was observed, on removal of the sample, to have been melted.

IV. EXPERIMENTAL RESULTS

The basic experimental results of this paper are to be found in Figs. 5 and 6. These are plots of the transition-density function $U(\zeta)$ for five Si and three Ge faces, respectively. The faces are identified in the figure captions. We did not take INS data for the Si(111)$\sqrt{19}$ nor the Si(110)2 × 1 structures. Each $U(\zeta)$ function is the unfold of an $F(\zeta)$ function obtained by the methods of INS. Our standard INS-data-handling procedure, discussed elsewhere in detail,[12,14,15] yielded, in all cases but one, the plotted $U(\zeta)$ functions either without origin shift [Si(111)]1, Si(110)4×5, Si(100)2, Ge(111)8, Ge(110)X] or with a small required origin shift of 0.05 or 0.10 eV toward positive ζ [Si(110)5×1, Ge(100)2]. The origin shifts of 0.1 eV or less required by the latter two surfaces for successful deconvolution of the derived $F(\zeta)$ function are within our previous experience and may or may not be significant in view of possible uncertainty in the magnitude of the debroadening extrapolation.[12,14,15] The exceptional case is the Si(111)7 surface which required an origin shift of the $F(\zeta)$ function of 0.55

eV toward positive ζ before it was possible to produce an unfold, $U(\zeta)$, whose form agreed with $F'(\zeta)$, as discussed earlier. This corresponds to a shift of 1.1 eV in the origin of the $U(\zeta)$ function and to the complete removal of the bulge at the high-energy end of the $X(E)$ distribution for Si(111)7 (Figs. 1 and 2). This requirement has the physical meaning which we discuss in the companion paper following this. For the present it is sufficient to state that the origin-shifted data put the Si(111)7 results on an even footing with the other data in that they result from electrons ejected in the Auger-neutralization process from the principal band of electrons presented to the ion by the semiconductor.[29]

Although the present work is the first in which the method of INS has been applied to semiconductor surfaces and transition-density functions derived from experimental $X(E)$ curves, it is not the first in which ion neutralization at a semiconductor surface has been observed and discussed. Experimental measurements of electron kinetic-energy distributions of Auger-ejected electrons by ions for Si(111), Si(100), and Ge(111) were reported in in 1960.[21] In a companion paper[30] an attempt was made to fit these distributions using a simple theory of the ion-neutralization process starting from parametric forms for the state-density and transition probability variations with band energy. A unique fit was obtained which illuminated several aspects of the ion-neutralization process and yielded a numerical value for the difference between the effective ion-neutralization energy at the ion-surface separation where the Auger process occurs and the ion-neutralization energy in free space. Also, Takeishi and Hagstrum[11] published data on Ge(100) and Ge(111), some of which were later unfolded as indicated in Sec. I.

The previous ion-neutralization measurements referred to above are in general agreement with the present results. First, the unfold of the earlier data on Ge(100)[11] shows all the structure evident in the $U(\zeta)$ functions of Fig. 3 but with somewhat reduced resolving power most likely due to the smaller diameter of the electron-collecting sphere used in the earlier work. It is now possible to interpret the two curves shown in Fig. 13 of Ref. 21 obtained by differing heat treatments. Curve 1 of this figure can now be ascribed to the Si(111)7 structure and curve 2 to the Si(111)$\sqrt{19}$ structure even through the small bulge near the maximum kinetic energy in the present $X(E)$ data for this surface was not evident in the earlier work because of the more primitive point-by-point data-taking procedures and the lower resolving power of the earlier experiment.

The relatively small differences to be seen between the earlier and later Ge(111) results appear also to be interpretable in terms of differences in resolving power of the two experiments. The present work does show, however, that the Si(100) distribution in Fig. 10 of Ref. 21 is incorrectly placed relative to the Si(111) distribution given there and should be shifted by about 1.0 eV to larger electron energy. This error resulted from poor ion focusing for this curve, giving an erroneous vacuum-level cutoff taken as the origin of the function. It was to eliminate this occasionally troublesome possibility that the changes in electron-energy analysis embodied in the apparatus of Ref. 20 were made.

V. SURFACE MODULATION OF THE LOCAL DENSITY OF STATES

We begin the interpretation of our experimental results by pointing out the internal evidence they contain that the surface band structure seen by INS differs from the bulk band structure. By this we mean that the local density of states, defined as the density of states weighted by local-wave-function magnitude, varies significantly as one proceeds from the bulk through the selvedge to the surface. This evidence, internal to the INS experiment itself, is to be found in the fact that, although the general form of $U(\zeta)$ remains the same, the detailed structure in this function varies from crystal face to crystal face. This may be seen in Figs. 5 and 6. The differences among these curves are well outside the limits of error both in the experimental data themselves and in the data-reduction procedure. It is true that plotting on the same ζ scale does not necessarily place the curves properly relative to one another as we shall discuss in detail.

The energy positions of small peaks and the principal minimum in the curves of Figs. 5 and 6, indicated by short vertical lines, are replotted on the graphs of Figs. 7 and 8, respectively, and are listed in Table I. In Figs. 7 and 8 it is perhaps easier to see how successful relative shifts of various amounts between the curves would be in bringing the peak positions into coincidence. All such attempts that we have made have failed to produce coincidence of all important peaks within experimental error. Two such attempts are shown in Figs. 9 and 10. In Fig. 9 the curves for silicon are arranged so the principal minima are aligned vertically above one another. In Fig. 10 the curves for germanium are arranged so that the highest-lying peaks are vertically aligned above one another. In neither case does a better alignment of all the structural features result. We conclude that the peak structures, which we take to indicate band-structure critical points, vary from surface to surface and thus indicate surface and not bulk band structure.

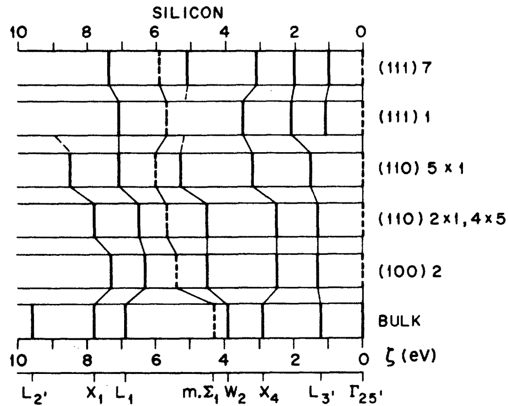

FIG. 7. Graph for silicon of the experimentally determined critical-point energies by INS for the several faces studied (Table I) compared with a set of theoretical critical-point energies for the bulk (top row of Si theoretical results in Table II). The bulk critical points are identified on the lowest scale. A proposed identification of corresponding critical points from one face to the next is indicated by the connecting lines between panels.

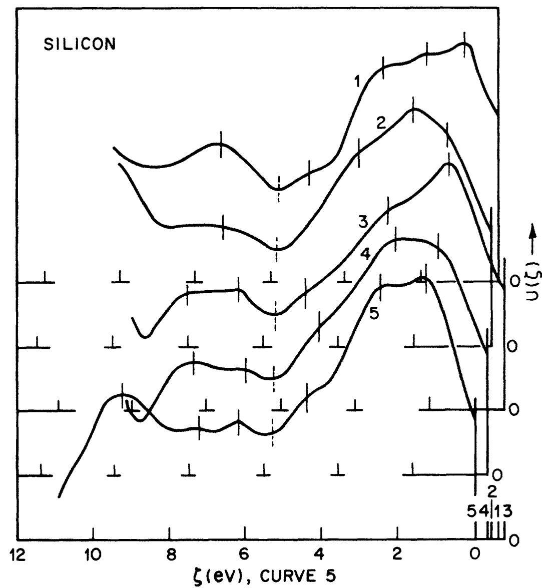

FIG. 9. Plot showing the curves of Fig. 5 shifted relative to one another so as to place the principal minima vertically above one another. Identification of crystal face by curve number is the same as given in the caption of Fig. 5.

The second line of evidence, the external evidence, that INS is showing us the surface local density of states as opposed to the bulk local density of states, comes from a comparison of the INS results with bulk theory and with results of experimental methods which more nearly probe the bulk band structure. In Table II are listed critical-point energies for the valence bands of silicon and germanium derived from theoretical sources indicated in the footnotes to the table. In Figs. 11 and 12 we compare some of our results with theoretical state-density plots for silicon[31] and germanium,[32] respectively. We recognize that the experimental curves should more properly be compared with broadened theoretical curves derived from those of Figs. 11 and 12 by convolution with a broadening Lorentzian or some such function. Such broadening of the theoretical curves would tend to shift the principal minimum to lower energy (larger ζ) bringing theory and experiment into better agreement. Broadening should produce little shift of the principal peaks in the theoretical functions, however. The experimental functions chosen

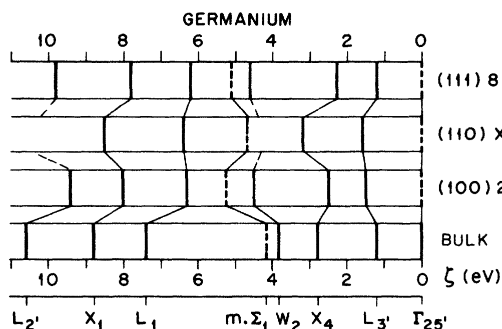

FIG. 8. Graph for germanium of the critical-point energies determined by INS for the crystal faces studied (Table I) compared with those from bulk theory (top row of Ge theoretical results in Table II). Proposed correspondences of critical points are indicated as in Fig. 7.

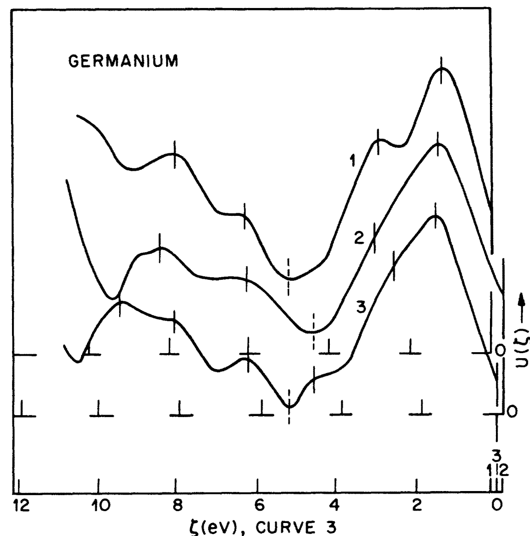

FIG. 10. Plot showing the curves of Fig. 6 shifted relative to one another so that the highest-energy maxima lie vertically above one another.

TABLE I. Surface critical-point energies (ζ in eV) determined from estimated peak positions in the $U(\zeta)$ functions plotted in Figs. 5 and 6. Figures in parentheses refer to the principal minimum.[a]

Si(111)7	Si(111)1	Si(110)5 × 1	Si(110)4 × 5	Si(100)2	Ge(111)8	Ge(110)X	Ge(100)2
1.0	1.1	...	...	...	...	...	...
2.0	2.1	1.5	1.3	1.3	1.3	1.6	1.5
3.1	3.5	3.2	2.5	2.5	2.3	3.2	2.5
5.1	...	5.3	4.5	4.5	4.6	...	4.5
(5.9)	(5.7)	(6.0)	(5.7)	(5.4)	(5.1)	(4.7)	(5.2)
7.4	7.1	7.1	6.5	6.3	6.2	6.4	6.3
...	...	8.5	7.8	7.3	7.8	8.5	8.0
...	...	...	...	...	9.8	...	9.4

[a]The numbers are aligned in rows in accordance with the identification of corresponding levels indicated by the connecting lines between panels in Figs. 7 and 8.

for comparison in Figs. 11 and 12 were those which agree best with bulk theory. Nevertheless, all things considered, Figs. 7, 8, 11, and 12 force us to the conclusion that the detailed structure in bulk-theoretical and surface-experimental curves disagree by amounts which lie outside experimental and presumably also theoretical limits of error. It would also appear that these disagreements are particularly evident deep in the valence band at large ζ values.

We may also compare our results with the results of other electron spectroscopies for which the density-of-states factor in the spectroscopic function should more nearly be that appropriate to the bulk. The photoemission results at $\hbar\omega = 25$ eV (UPS) for cleaved Si(111) and Ge(111) by Grobman and Eastman[8] are compared with our $U(\zeta)$ curves for Si(111)7 and Ge(111)8 in Figs. 13 and 14, respectively. In Fig. 15 we compare two of our silicon functions with transition-density functions obtained by soft-x-ray spectroscopy (SXS). Curve 1 is the SiK spectrum measured by Kern,[33] which shows principally the p valence band. Curve 2 is the Si$L_{2,3}$ spectrum of Crisp and Williams,[34] which resembles closely that published by Weich,[5] and indicates filled s states. The sum of the soft-x-ray spectra of curves 1 and 2 of Fig. 17 should give a total experimental spectrum of the valence bands (see Weich's composite, Fig. 9 of Ref. 5) with which our results (curves 3 and 4) may be compared.

In Fig. 16 we compare two INS results with the transition density function obtained by Amelio[6] by unfolding the kinetic-energy distribution of electrons ejected from the valence band of Si when the ionized cores of surface Si atoms are neutralized in an LVV Auger process. This is one of the two types of electron-ejection processes which underlie the Auger-electron spectroscopy (AES) used for chemical identification of surface atoms. Finally, although we do not reproduce their results here, our $U(\zeta)$ functions for Ge may be compared to the XPS results at $\hbar\omega = 1486.6$ eV of Pollak *et al.*[7] for Ge cleaved in dry nitrogen.

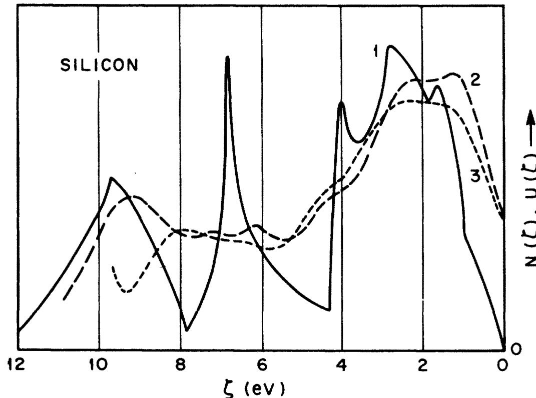

FIG. 11. Comparison of the theoretical state density in the Si valence band from Ref. 31 (curve 1) with the INS transition-density functions $U(\zeta)$ for the Si(100)2 surface (curve 2) and the Si(110)4 × 5 surface (curve 3).

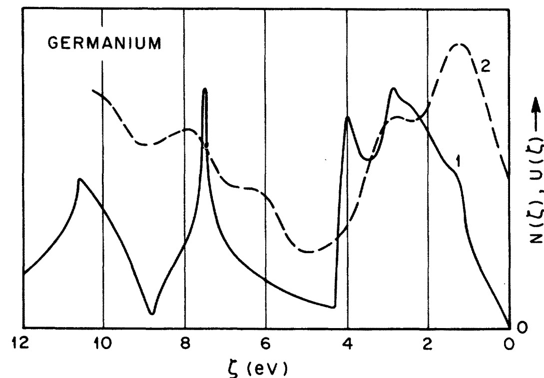

FIG. 12. Comparison of the theoretical state density in the Ge valence band from Ref. 31 (curve 1) with the INS $U(\zeta)$ function for the Ge(100)8 surface (curve 2).

TABLE II. Critical-point energies in eV for the valence bands of silicon and germanium from theory of the bulk band structure.

	$\Gamma_{25'}$	$L_{3'}$	X_4	W_2	$\min\Sigma_1$	L_1	X_1	$L_{2'}$	Γ_1
Si[a]	0	1.2	2.9	3.9	4.3	6.9	7.8	9.6	11.9
	0	1.3	3.0		4.8				
Ge[b]	0	1.2	2.8	3.8	4.1	7.4	8.8	10.6	12.6
	0	1.1	2.6		3.8				

[a]The first row of energies for Si are compromises among the essentially identical theoretical results of Refs 2–4. The second row gives the results of Ref. 1.

[b]The first row of energies for Ge come from Ref. 3, the second from Ref. 1.

We shall not attempt to state in words the detailed differences between the INS and other spectra to be seen in Figs. 13–16. The XPS, AES, and SXS results are observed to be in much better agreement with bulk band theory than are the INS results. This is also true for USP although Grobman and Eastman[8] observe significant differences between their Ge results and bulk theory, possibly as a result of better energy resolution. In any event the differences between the INS results and those of the more bulk-sensitive spectroscopies are taken here as direct evidence that INS is looking at the surface local density of states and that this differs in these materials from the bulk local density of states by the amounts indicated in the above comparisons. The surface p band seems definitely to be narrower than the bulk band as would be expected. It is perhaps 80% as wide as the bulk band. In addition the surface band structure critical points are clearly shifted from the bulk positions.

In view of the surface sensitivity of UPS for

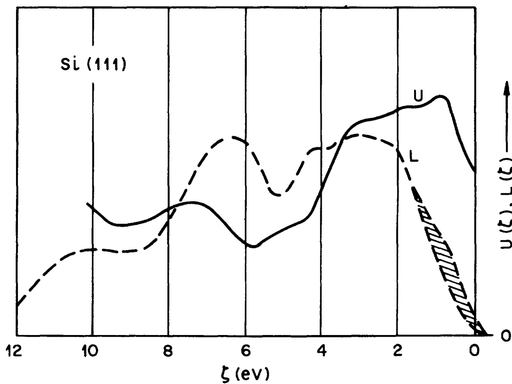

FIG. 13. Graph comparing the UPS spectroscopic function of Grobman and Eastman (Ref. 8) for cleaved Si(111), here labeled $L(\zeta)$, with the $U(\zeta)$ function for Si(111)7. Note that Grobman and Eastman indicate the surface-state contribution to the $L(\zeta)$ curve. Compare with Fig. 1 in Ref. 9.

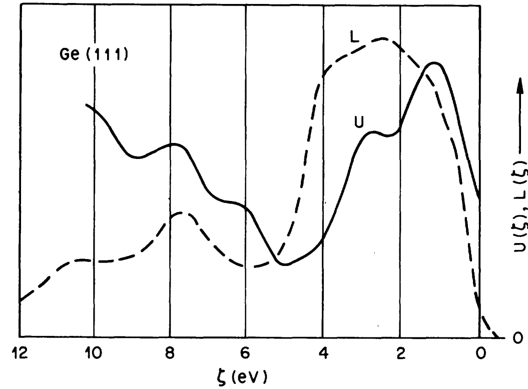

FIG. 14. Graph comparing the UPS spectroscopic function of Grobman and Eastman (Ref. 8) for cleaved Ge(111), $L(\zeta)$, with the $U(\zeta)$ function for Ge(111)8. Here Grobman and Eastman do not specify the surface-state contribution to this function as is done in Fig. 2 of Ref. 9. However, the surface state must account for the small shoulder on the L curve at $\zeta \sim 0.8$ eV which lies on the rapidly rising portion of the U curve.

$\hbar\omega > 20$ eV, one wonders to what extent surface shifts are to be seen in the UPS results. In the kinetic-energy distribution obtained for Si(111) by Grobman and Eastman,[8] for example, and in the surface-state studies[9,10] all features except the surface state are considered to be bulk features even though the method is sufficiently sensitive to reveal the surface state. Adsorption, which removes the surface state, leaves the bulk features intact. This would argue in favor of the interpretation of Grobman and Eastman. Furthermore, it does not appear that the UPS results differ from the theoretical bulk results in the direction of the INS results, as would be expected if they contained a substantial admixture of the surface band spectrum.

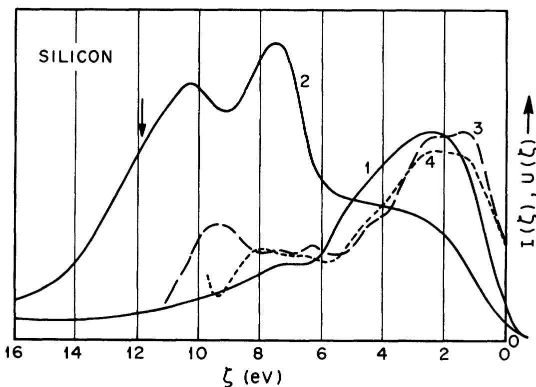

FIG. 15. Graph showing the SiK (curve 1) and Si$L_{2,3}$ (curve 2) soft-x-ray spectra compared to the $U(\zeta)$ functions for Si(111)2 (curve 3) and Si(110)4 × 5 (curve 4). Curve 1 is taken from Ref. 33 and curve 2 from Ref. 34.

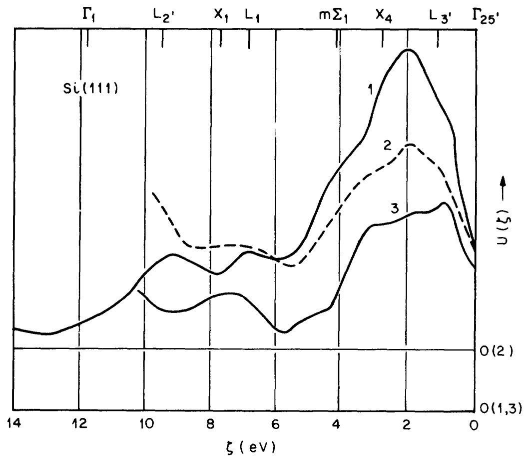

FIG. 16. Comparison of the $U(\zeta)$ function (curve 1), obtained by Amelio (Ref. 6) by unfolding the kinetic-energy distribution of electrons ejected from Si(111) in the LVV core-neutralization Auger process with the INS $U(\zeta)$ functions for Si(111)1 (curve 2) and Si(111)7 (curve 3). Note that curve 2 is plotted to a higher $U=0$ axis than are curves 1 and 3. Amelio's $U(\zeta)$ function (his Fig. 5) extends to $\zeta = 20$ eV but is cut off in this reproduction at 14 eV.

VI. VALENCE-BAND SURFACE STATE ON Si(111) SURFACES

We have been aware for some time that our $U(\zeta)$ functions for the Si(111)7 and Si(111)1 surfaces differed significantly from those for other surfaces in that their broad maxima corresponding to the degenerate p bands have three-peak structures in them as opposed to two such peaks for the other surfaces. This can be seen readily in Figs. 7 and 8 where the peak near $\zeta = 1$ eV for Si(111)7 and Si(111)1 does not appear to have any counterpart for the other surfaces studied. It was not until we saw the recently published photowork,[9,10] however, that it occurred to us that this peak could be interpreted as evidence of a surface state overlapping the valence band. Our $U(\zeta)$ curve for Si(111)7 is compared with photoemission results in Figs. 17 and 18. There arises in any such comparison the question as to what energy is defined by the $\zeta = 0$ point in each spectroscopy. In these figures the UPS and INS results are placed so that the structures observed other than the surface state are in approximate coincidence. This procedure is suspect to the extent that INS is more sensitive to a surface modulation of the density of states than is UPS. However, we have no reason to doubt that the peak near $\zeta = 1$ eV observed by UPS on cleaved Si(111) is a surface-state resonance and that it has also been observed by INS for sputtered and annealed Si(111).

Whether weaker surface-state resonances have been observed by INS on other Si and Ge surfaces is difficult to determine since this matter is intimately tied up with the meaning of the $\zeta = 0$ point. Eastman and Grobman[9] claim to observe such a state on cleaved Ge but it is considerably less intense than that observed for cleaved Si. We really cannot say whether there is or is not evidence for this state in our $U(\zeta)$ function for Ge(111) in Fig.

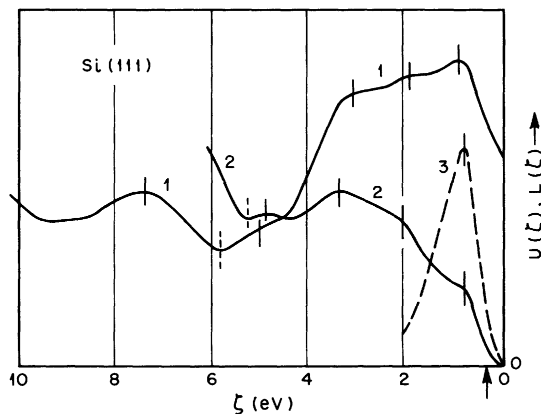

FIG. 17. Comparison of $U(\zeta)$ for Si(111)7 (curve 1) with the kinetic-energy distribution $L(\zeta)$ of electrons ejected from cleaved Si(111) by 20-eV photons (curve 2) published by Eastman and Grobman (Ref. 9). Curve 3 is Eastman and Grobman's optical density of intrinsic surface states. $\zeta = 0$ corresponds to the Fermi-level position determined in the photowork and to the cutoff of the $U(\zeta)$ function in the INS work. The arrow indicates the position of the valence-band top determined by Eastman and Grobman.

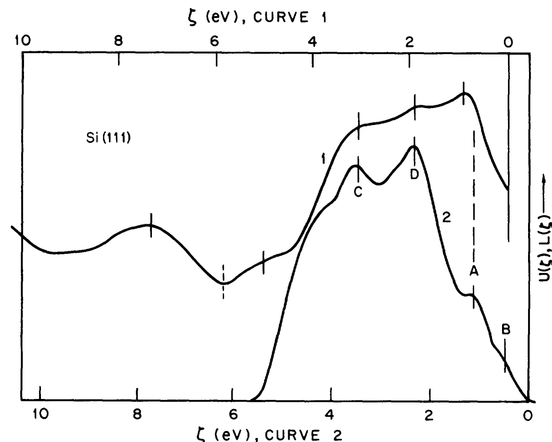

FIG. 18. Comparison of $U(\zeta)$ for Si(111)7 (curve 1) with the kinetic-energy distribution $L(\zeta)$ of photoelectrons (curve 2) determined by Wagner and Spicer (Ref. 10) for cleaved Si(111) using 10.2-eV photons. The designations A, B, C, D for features in curve 2, as well as its ζ scale, are those of Wagner and Spicer. The ζ scale of curve 1 is displaced so as to bring peaks D and C into coincidence with the second and third peaks in $U(\zeta)$ below $\zeta = 0$.

6. We point out again that our evidence for a surface state was obtained for sputtered and annealed Si(111), which has either the 7×7 or the 1×1 surface structure, and that the UPS results are for cleaved surfaces upon which the $\sqrt{3}\times1$ superstructure[35] was undoubtedly present. There is really no *a priori* reason to believe that the cleaved and sputtered-annealed (111) surfaces of *either* Si or Ge should have the same surface-state electronic structure.

We come now to a discussion of two important points. These are (a) the meaning of the $\zeta=0$ point in INS and UPS experiments, and (b) the use of adsorption as a means of distinguishing surface from bulk states. It is clear that the data-handling procedure of INS picks out as $\zeta=0$ that point at which the local density of electrons at the surface (the product of the local density of states, the square of local wave function, and the Fermi-Dirac occupancy function) goes from a zero or relatively low value to the relatively high value characteristic of the filled band. For metals this point must certainly be close to the Fermi level if the density of bulk states is reasonably high there. But for semiconductors this point could be the top of the valence band or the top of a dense band of surface states which need not necessarily be coincident with the Fermi level.

In a sense the data-handling procedure of INS treats a semiconductor as it does a metal in that it produces a step in $U(\zeta)$ at the origin, whereas the state density of a filled band in a semiconductor should vary with energy as $\zeta^{1/2}$ near the band edge. This characteristic of INS distorts, but not seriously, the form of the transition-density function very near the band edge. We have experimented with replacing the first ten points of the $F(\zeta)$ function at the $\zeta=0$ origin with points differing only slightly from the experimental data points but which vary strictly as ζ^2. Such an $F(\zeta)$ unfolds to a $U(\zeta)$ which has an initial $\zeta^{1/2}$ dependence.[36] When this is done it is found that $U(\zeta)$, although rising strictly as $\zeta^{1/2}$, does so so steeply as to be almost indistinguishable from a step. This exercise also makes it clear that any error in locating the true origin by distortion of the initial portions of the $F(\zeta)$ and $U(\zeta)$ functions can amount to no more than 0.1 or 0.2 eV. Whereas it is true that INS could well miss a weak extension of a transition-density function to higher energy (negative ζ) above the large intensity drop which the method finds as origin, its highly surface-selective character will make surface states appear with equal if not enhanced intensity with respect to bulk states.

In UPS work the Fermi level at ϵ_F has been determined as corresponding to the maximum kinetic energy of electrons ejected from an auxiliary metal sample electrically connected to the semiconductor, or ejected from a metal overlay evaporated directly upon the semiconductor surface. This procedure is possible in photoemission because the fastest electrons ejected by a photon of energy $\hbar\omega$ from the Fermi level will be retarded when the voltage between target and collector is $\hbar\omega-\phi_C$ independent of the work function of the target. Here ϕ_C is the work function of the collector. However, the fastest electrons in INS are retarded at a target-collector voltage of $E_i'-\phi_T-\phi_C$ where, E_i' is the effective neutralization energy of the probing ion near the target surface and ϕ_T and ϕ_C the target and collector work functions, respectively. Clearly, an auxiliary metal target can be used to determine the position of the $\zeta=0$ point relative to ϵ_F in INS only if E_i' and the work function at both semiconductor and metal surfaces are known. By intercomparison of UPS and INS data on the semiconductor and an auxiliary electrically connected metal surface it is possible to determine all the necessary parameters. However, this was not done in the present experiment.

In a sense Figs. 9 and 10 represent attempts to determine at least the relative positions of the ζ scales for these surfaces from structure deeper in the band. But we have already pointed out that this cannot really be successful because of the different modulations of the local density of states at the different surfaces. Similar objection can be made to Figs. 17 and 18. We have presented these figures not as definitive relative placements of the INS and UPS curves but to show that it is highly probable that for Si(111) both methods see the same surface state, albeit on surfaces with different atomic superlattices.

The change in the UPS electron-energy distribution upon adsorption of a gas has been used as a means of identifying surface-state resonances. Its success must clearly depend on the fact that UPS ejects electrons from many layers in the solid and thus averages over the entire extent of the surface state whether the surface is clean or has an adsorbate upon it. Under these circumstances disappearance of the surface state should certainly decrease the photoresponse in its energy range. The situation appears to be quite different in INS because of the fact that the method senses a local density of states much more severely restricted to the vicinity of the probing ion outside the solid surface. Disappearance of a surface state must also reduce the magnitude of the wave function at the ion in the energy range of the surface resonance. However, as is discussed in detail in Ref. 15, adsorption of foreign atoms will cause ion neutralization to occur farther from the original metal surface and thus farther out on the tail of a wave function, that of the d band of Ni, for example, which may not have been changed by the act

of adsorption. It is difficult to see how to distinguish these two effects in INS. In addition INS has been shown to be more sensitive than UPS to the surface orbitals of the adsorbate.[17]

Another way to approach this question of the identification of a surface state is to compare spectroscopic functions $U(\zeta)$ from INS, for example, for different clean faces of the same crystal. One might ask, for example, if the differences between two curves in Figs. 5 or 9 could be attributed to the differences in surface-state resonances between the two surfaces of the same substrate. Certainly such a difference curve would reveal the difference in the local density of states at the surface but this would be a far more general definition of the difference in surface-state density than is usually employed.

We point out that the evidence for a filled surface state overlapping the valence band at the two Si(111) surfaces we have studied is in agreement with the theory of Yndurain and Elices.[37] Observation of the theoretical E, k plots in their paper leads one to conclude that the surface states will show a relatively large density near the top of the valence band only for the Si(111) surface, with the densities for Si(110) and Si(100) being considerably weaker. The theoretical E, k curves for Si(111) show a high density about 0.7 eV below ϵ_V and an extension of states at appreciable density to a point 0.3 eV above ϵ_V. Thus if ϵ_F is above this point as expected, this theory would suggest a cutoff at 0.3 eV above ϵ_V in agreement with the value of Erbudak and Fischer[27] for $\epsilon_F - \epsilon_V$ at the Si(111)7 surface.

Two very recent theoretical papers on surface states in Ge and Si should be mentioned. These are the work of Jones[38] for Si and of Elices and Yndurain[39] for Ge. Jones's results differ significantly from those of Yndurain and Elices[37] discussed above and cannot really be said to support a large peak in the surface-state density near $\zeta = 1$ eV in the valence band for Si(111). The theoretical E, k plots of Elices and Yndurain[39] for Ge(111) and (110) faces are similar to those published earlier by them[37] for Si and thus would seem to predict a peak in the surface-state density for Ge(111) near the top of the valence band. As we have seen, the results of neither INS nor UPS show a surface state on Fe(111) of intensity comparable to that on Si(111).

ACKNOWLEDGMENTS

The authors acknowledge with thanks several helpful discussions with J. E. Rowe and E. O. Kane as well as the assistance of P. Petrie in the conduct of these experiments.

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