

ments.

A forthcoming paper will contain further details of the various proofs and calculations mentioned here together with an examination of the finer details of the spectrum and a review of relevant experiments.

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Photoemission Valence-Band Densities of States for Si, Ge, and GaAs Using Synchrotron Radiation*

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We present experimental valence-band optical densities of states for Si, Ge, and GaAs obtained from ultraviolet photoemission energy distribution curves obtained at about 25 eV of photon energy. The width of the upper two valence bands of Si and the positions of several energy-band minima for the second and third valence bands of Ge and GaAs have been accurately determined. Comparing the above-mentioned band edges with theoretical calculations based on optical data, we find good agreement for Si and observe significant differences for Ge and GaAs.

Spectroscopic energy-level overviews of the valence-band density of states of semiconductors are of general interest, both theoretically and experimentally. We present high-resolution ultraviolet photoemission spectroscopy (UPS) spectra using photon energies of $\lesssim 25$ eV which give overviews of the entire ~ 12 -eV-wide valence bands of Si, Ge, and GaAs. From these spectra, we obtain "optical densities of states" (ODS) which show overall agreement with theoretical¹ densities of states. Also, the positions of several energy-band minima with respect to the valence band edge, E_v , have been accurately determined for the first time from these studies.²

For Si we obtain $E_v - \Sigma_{1\min} = 4.7 \pm 0.2$ eV, in

good agreement with calculation, while for Ge we obtain $E_v - \Sigma_{1\min} = 4.5 \pm 0.2$ eV, i.e., about 0.5 eV larger than current calculated values. For GaAs we find $E_v - \Sigma_{1\min} = 4.1 \pm 0.2$ eV and $E_v - X_3 = 6.8 \pm 0.2$ eV, both values being about 0.4 eV larger than current calculated values.

These currently available theoretical band calculations are primarily tied to optical measurements and so are only dependent on valence band-conduction band separations. Also, the main structure in $\epsilon_2(\omega)$ which has been fit involves only the upper valence bands within a few eV of E_v , the valence band edge. Our results present new data giving absolute valence-band energy positions over a wide energy range below E_v . This

type of data, when combined with optical data, should contribute to the refinement of crystal potentials for semiconductors.

Photoemission energy distribution curves were obtained using a two-stage cylindrical-mirror electron energy analyzer and synchrotron radiation from the 240-MeV electron storage ring at the University of Wisconsin's Physical Sciences Laboratory. For Ge, the data presented here were taken at the Cambridge Electron Accelerator using the same photoemission spectrometer. In the present work, the total instrumental resolution varied from 0.2 to 0.4 eV in the 20- to 26-eV photon energy range, and signal-to-noise ratios were 100:1 or better. The samples were single crystals of 5- Ω cm ($\sim 10^{15}$ cm $^{-3}$) *n*-type Si, 4- Ω cm ($\sim 4 \times 10^{14}$ cm $^{-3}$) *n*-type Ge, and lightly doped *n*-type GaAs. Crystals 4 to 6 mm long and 2×2 mm in cross section were cleaved (with some faceting) in ultrahigh vacuum ($\lesssim 5 \times 10^{-10}$ Torr) and (111) faces of Si and Ge and the (110) face of GaAs were studied. For Si and Ge the Fermi energy E_F was obtained by measuring E_F for a metal film evaporated onto the cleaved crystal *in situ*. For Si and Ge the valence-band edge E_v was determined from the band bending (which determines $E_F - E_v$) corresponding to the known bulk doping.³ The valence-band edge for GaAs was determined by extrapolation of the edge of the photoelectron energy distribution curve to zero emission intensity (which occurs at about 0.1 eV above E_v because of the finite resolution of the spectrometer).

In order to determine the extent to which valence-band positions are reflected in such high-energy photoemission spectra, we have performed a model calculation for Ge based on the usual three-step picture of the photoemission process.⁴ The starting point was an empirical pseudopotential-method band calculation⁵ of both the valence bands and conduction bands (final states) over the entire energy range involved in 25-eV optical transitions. This calculation used the Cohen-Bergstresser⁶ pseudopotential coefficients. The valence-band density of states as well as photoemission spectra were then obtained (including the effect of pseudopotential matrix elements) from a computer program due to Janak which employs a modified version of the Gilat-Raubenheimer k -space integration method.⁷ This program assumes direct optical transitions and includes the effects of hole-lifetime broadening, transport to the surface, and escape. The secondary electron distribution and hole lifetimes were determined using Kane's random- k method⁸

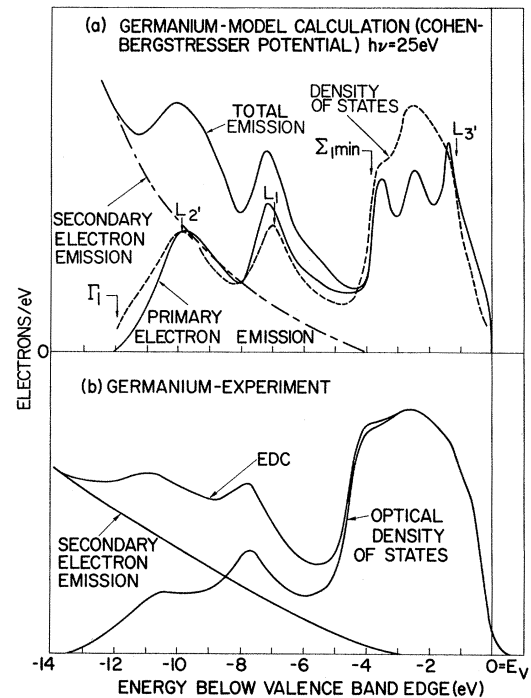


FIG. 1. (a) Comparison between the photoemission primary and total emission for a model calculation for Ge and the density of states $N(E)$ for the same calculation. (b) Illustration of the subtraction of a secondary electron distribution for a Ge photoemission distribution at $h\nu=25$ eV to obtain the primary electron distribution or "ODS."

and assuming a yield of 1% at $h\nu=9$ eV. The correlation of structure in the valence-band density of states with that in the calculated photoemission spectra is seen in Fig. 1(a), where we show the primary, secondary, and total electron energy distributions for $h\nu=25$ eV as well as the density of states $N(E)$ for this model calculation.

The features in $N(E)$ corresponding to the band edges L_3' , Σ_{1min} , and Γ_1 , as well as the critical points L_1 and L_2' , are seen in the primary photoelectron spectrum in the same position as in the density of states. Our calculations show that this correspondence is maintained for these features for other values of $h\nu$ in the 20- to 25-eV energy range. Other features, such as the peak in $N(E)$ at -2.6 eV (near the critical point X_4), change position ($\lesssim 0.4$ eV) because of direct transition effects as $h\nu$ varies. Structureless secondary electron distributions, similar to that shown in Fig. 1(a), were calculated for all $h\nu$ in the 20-25-eV range.⁹

The calculation described above indicates that a reasonable overall view of $N(E)$ can be obtained

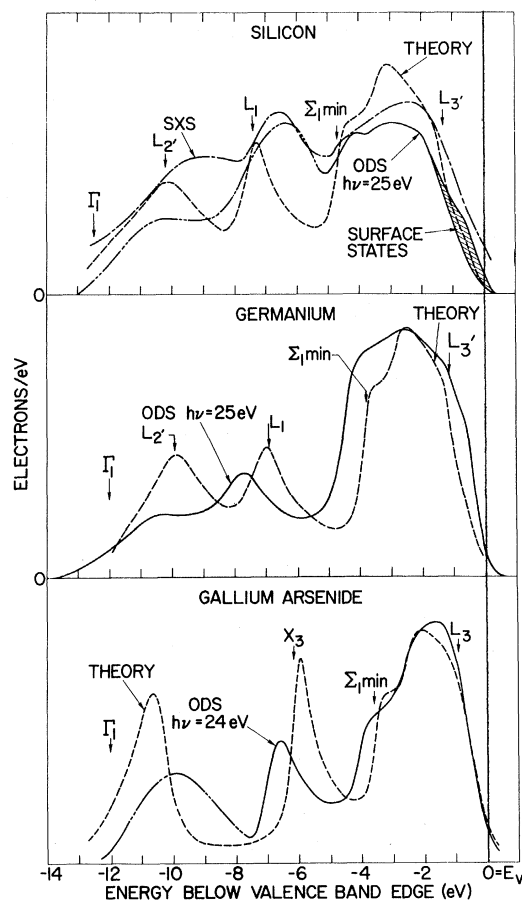


FIG. 2. Comparison of our ODS's for Si, Ge, and GaAs and lifetime-broadened empirical pseudopotential-method densities of states (Ref. 12). The SXS density of states for Si is also presented. Critical-point positions indicated correspond to the theoretical curves.

from a high-energy photoemission energy distribution curve by subtracting a structureless secondary electron spectrum of the shape shown in Fig. 1(a) from the total emission curve.¹⁰ Such a procedure is illustrated in Fig. 1(b) for Ge at $h\nu = 25$ eV. The resulting experimental optical density of states for Ge shows structure attributable to primary emission and hence the overall valence-band structure as in the model calculation, but does not include the undesirable skewing caused by secondary electron emission.

Optical densities of states for Si, Ge, and GaAs determined in the above-mentioned manner for $h\nu = 25$, 25, and 24 eV, respectively, are given in Fig. 2 as solid lines.¹¹ The dashed curves $N(E)$ are densities of states obtained from the Cohen-Bergstresser⁶ (Ge and GaAs) and Saravia² (Si) pseudopotential coefficients and the empirical pseudopotential method. In order to simulate

lifetime broadening, these $N(E)$ curves were convolved with a Lorentzian function of full width at half-maximum varying from 0.25 eV at E_v to 0.75 eV at $E_v - 12$ eV. In the case of Si, we also show (dash-dotted curve) a soft-x-ray spectroscopy¹³ (SXS) "density of states." As the position of E_v is not known accurately in SXS, we have positioned this curve to coincide with our ODS near E_v .

Using the ODS's in Fig. 2, and other photoemission data for $h\nu < 24$ eV, we have been able to determine the absolute values for critical point locations with respect to E_v given in Table I. This was done by observing the relation of critical point locations in the $N(E)$ calculations in Fig. 2 to elements of structure in the $N(E)$ curve and making the same correspondence for the ODS curves. For example, $\Sigma_{1\min}$ corresponds to the center of the sharp drop in emission at the bottom of the upper two valence bands. The best-defined experimental edges are $\Sigma_{1\min}$, the L_1 edge for Ge, and the X_3 edge for GaAs.¹⁵

In Table I we also present the values for selected critical points in Si, Ge, and GaAs determined by Cohen and Bergstresser,⁶ as well as the results of a paper by Zucca *et al.*¹⁴ for GaAs. The discrepancies between experiment and theory in Table I are not surprising in view of the fact that these calculated values were fitted to optical data and were not fitted to lower-energy valence-band positions. Other band calculations¹ which were also fitted to optical data consistently predict values for $E_v - \Sigma_{1\min}$ which differ by at least 0.5 eV from our experimental value for Ge and which are smaller by 0.4–0.8 eV in GaAs, while generally agreeing reasonably well for Si. Likewise, values of $E_v - X_3$ for GaAs are typically 0.4 to 0.6 eV smaller than we have obtained.

In summary, our results illustrate the use of photoemission at high energies for obtaining overviews of the valence-band density of states as well as accurate positions of band minima for semiconductors. Band structure calculations which fit both $\epsilon_2(\omega)$ data and such photoemission-determined valence-band data should more accurately represent absolute energy locations of both valence and conduction bands.

Measurements extending this photoemission technique to higher photon energies are now in progress, and should permit a more accurate determination of critical points in the lowest valence bands and the X_1 - X_3 valence-band gap for the heteropolar semiconductors, since primary and secondary electron emission for these bands

TABLE I. Critical-point energies below E_v (eV).

	L_3'	$\Sigma_1 \min^a$	L_1	L_2'	Γ_1
Si Expt		4.7 ± 0.2	6.4 ± 0.4	...	12.4 ± 0.6
Theory ^b	1.3	4.7	7.4	...	12.5
Ge Expt	1.1 ± 0.2	4.5 ± 0.2	7.7 ± 0.2	10.6 ± 0.4	12.6 ± 0.3
Theory ^b	1.1	3.8	6.9	9.9	12.0
	L_3	$\Sigma_1 \min$	X_3^d	Γ_1	
GaAs Expt	0.8 ± 0.2	4.1 ± 0.2	6.8 ± 0.2	11.9 ± 0.6	
Theory ^b	0.9	3.6	6.15	12.3	
Theory ^c	0.9	3.2	6.3	12.0	

^aFrom $h\nu \lesssim 15$ eV data; see text.

^bRef. 6.

^cRef. 14.

^dRef. 15.

can be more precisely separated at higher energies.

The assistance of J. Freeouf in obtaining the Ge data is greatly appreciated. We wish to thank J. F. Janak, A. R. Williams, and V. Moruzzi for providing us with some of the computer codes used in this paper. We also acknowledge the able assistance of members of the Physical Sciences Laboratory storage-ring group, and the staff of the Cambridge Electron Accelerator.

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¹There is an extensive literature dealing with semiconductor band structure information. We have compared the experimental critical point positions discussed in the present paper with many of the values given in the references listed by F. Herman *et al.*, in *Methods in Computational Physics*, edited by B. Alder, S. Fernbach, and M. Rotenberg (Academic, New York, 1968), Vol. 8, pp. 193-249, as well as more recent calculations. A detailed comparison and reference list will be presented in a future extension of the present paper.

²There have been numerous earlier UPS measurements of valence-band structure of semiconductors [e.g., W. E. Spicer and R. C. Eden, in *Proceedings of the Ninth International Conference on the Physics of Semiconductors, Moscow, 1968* (Nauka, Leningrad, U.S.S.R., 1968), Vol. 1, p. 61; W. E. Spicer, J. Res. Nat. Bur. Stand., Sect. B 397 (1969), and references therein]. Previous measurements have usually been limited to the upper two valence bands because of the limited photon energy range, i.e., LiF window cutoff at 11.6 eV. In recent papers L. R. Saravia and L. Casamayou [J. Phys. Chem. Solids **32**, 1075, 1541 (1971)] have related certain features in the energy bands of Si and Ge to such low-energy photoemission experiments

via large-scale computer calculations. In this paper we show that UPS measurements at higher energies (~ 25 eV) permit overviews of valence-band structure, i.e., density-of-states information, to be obtained in a manner similar to that used in x-ray photoemission spectroscopy.

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⁹The primary/secondary electron emission ratio is highly insensitive to the assumed hot electron scattering rate, which was determined by fitting to the quantum yield of 1% at $h\nu=9$ eV.

¹⁰This procedure is similar to that used when nondirect transitions are assumed. However, we have justified it for obtaining principal band features for the case of direct transitions, which are evident in UPS data up to at least $h\nu=28$ eV.

¹¹Note the primary structure in the Si curve is markedly weaker than for Ge and GaAs. We believe this is due to a poorer quality cleaved Si surface (but not contamination).

¹²The ODS curves in Fig. 2 are broken by dots in the region where they are less certain because of secondary electron and, in the case of Si, possible contamination effects.

¹³Curve 1 of the lower part of Fig. 9 in the article by G. Wiech in *Soft X-ray Band Spectra*, edited by D. J. Fabian (Academic, New York, 1968), p. 59.

¹⁴R. R. L. Zucca *et al.*, Solid State Commun. **8**, 627 (1970).

¹⁵We use X_3 as a convenient label for our experimental

lower edge for band 2 since X_3 lies lower than L_2 in most band calculations for GaAs. However, this lower edge could be at L_2 .

Far-Infrared Surface Resistance of Cu:Fe; Dynamics of a Kondo System*

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The frequency- and temperature-dependent surface impedance of a Kondo system Cu:Fe has been measured in the far infrared using sensitive transmission-line techniques. Good agreement is found with our numerical calculation of the surface impedance from the Nagaoka equations provided that coherent potential scattering effects are included.

Although the existence of anomalous behavior in the resistivity of systems like Cu:Fe, Au:Fe, and Cu:Ni is to be expected from various theories of the Kondo effect, the qualitative differences in, for example, the dc resistivity of these systems is still unexplained.^{1,2} To obtain a better understanding of the basic scattering processes present we have studied the Kondo anomaly in the far-infrared surface resistance of copper containing 850 ppm iron impurities (Cu:Fe). For frequencies ω typically greater than the Kondo temperature T_K , so that $\hbar\omega > k_B T_K$, a fairly successful comparison is made with our numerical results for the surface resistance calculated from the Bloomfield-Hamann-Nagaoka (BHN) theory^{3,4} if a large value of coherent potential scattering at the magnetic impurity sites is included.

As discussed by several authors, a potential scattering term added to the spin-dependent exchange scattering term of the Kondo Hamiltonian produces an interference effect with severe effects on transport properties.⁵ In the resistivity, for example, the phase shifts rather than the amplitudes for the two processes are additive, so that (roughly) $\rho_{dc} \sim 1 - \cos 2\delta_v \cos 2\delta_{ex}$. A potential phase shift δ_v giving small values of $\cos 2\delta_v$ thus reduces drastically the classic Kondo anomaly of a rise in resistance at low temperatures; a negative value even inverts this behavior.

The interesting question is whether δ_v (in this model) is large enough ($\approx \pi/4$) to account for the qualitative difference in the observed resistivities. Unfortunately, a satisfactory theory for temperatures or frequencies below T_K does not exist, and detailed fitting of the resistivity for $T < T_K$ as indicated in Fig. 1 is problematic. Be-

cause of difficulties with background subtractions, it is also difficult to obtain the phase shift from fitting the resistivity for $T > T_K$. In the present experiment we instead probe the frequency dependence of the scattering in the infrared surface impedance for photon energies large enough ($\hbar\omega > k_B T_K$) for the BHN theory to be valid. By varying the temperature, we can then perform differential measurements which eliminate the background. Even so the experiment is a rather delicate one.

The Cu:Fe alloy was prepared by melting high-grade copper and iron in an aluminum crucible under argon atmosphere and quenching it in water. It was then cold rolled into foils about 15 μm thick and carefully etched. Chemical analysis and dc resistivity measurements at different sections of the foils yielded an iron concentration of

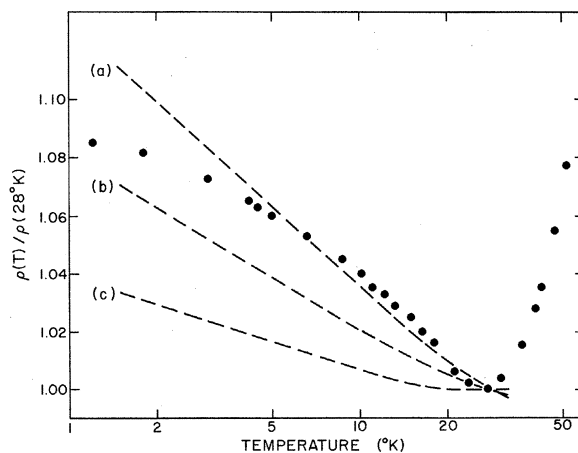


FIG. 1. dc resistivity versus temperature of Cu:Fe (850 ppm). The dashed curves are the predictions of the BHN theory with potential phase shifts of (a) $|\delta_v| = 37.5^\circ$, (b) 40° , and (c) 42.5° , with $T_K = 16^\circ\text{K}$.