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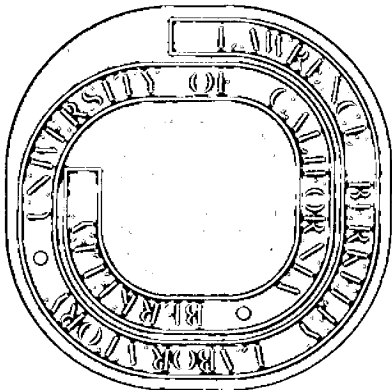
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November 1972

DISCLAIMER

X-RAY PHOTOEMISSION CROSS-SECTION MODULATION IN DIAMOND, SILICON,
GERMANIUM, METHANE, SILANE, AND GERMANE[*]

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Abstract:

The high-resolution XPS valence band spectrum
from a cleaved natural diamond single crystal is reported.
The absence of extrinsic structure allows a reliable
comparison with band theory. The XPS molecular-orbital
spectra of methane, silane, and germane are also given.
The modulation of photoelectric cross sections in the
valence bands of diamond, Si, and Ge are discussed and
compared with atomic XPS cross sections derived from the
spectra of CH_4, SiH_4, and GeH_4.

— — —

The allotropic form of carbon, diamond, is the prototype for Group IV
crystals of the diamond structure. Many calculations of the energy-band structure
have been carried out,[1] yielding results that vary more widely than is the case
for its congeners, silicon and germanium. Thus, it is especially desirable

to determine the positions of the diamond energy bands experimentally. In this

Letter, we report the total valence band density-of-states spectrum of a

cleaved single crystal of diamond. The spectrum was obtained using x-ray

photoemission spectroscopy (XPS) which has recently been employed to yield

total valence-band spectra for silicon and germanium.[2] The diamond spectrum

is compared with theory and with the XPS molecular orbital spectra of CH_4,

SiH_4, and GeH_4.

A diamond single crystal was cleaved in a dry N_2 atmosphere, introduced

into the analyzer chamber of an HP 5950A ESCA spectrometer at 8×10^{-9} Torr, and

irradiated with monochromatized Al $K\alpha_{1,2}$ radiation.[3]

Previous XPS studies of diamond[4,5] on powdered samples yielded valence

band spectra that were not intrinsic, and no detailed comparisons with band

structure theory were possible. In a preliminary experiment on an untreated

diamond single crystal, we observed a valence-band spectrum that was similar

to the previously reported spectra.[4,5] After cleaving the diamond the C(1s)/O(1s)

ratio rose from 4 to 13, and the valence-band spectrum showed no evidence of

oxygen contamination.

The uncorrected spectra I(E) of the diamond valence-band and the

diamond C 1s core region are shown in Fig. 1. Assuming the satellite structure

of the C 1s line to be extrinsic, we corrected the valence-band spectrum

quantitatively for inelastic losses. The corrected spectrum I'(E) is shown

in Fig. 2. This correction does not appreciably affect the valence-band

structure below 25 eV binding energy.

A thin layer of gold was evaporated onto the diamond crystal after

the valence-band measurements were completed, and the separation of the Au $4f_{7/2}$

and the underlying diamond C 1s lines was measured. The binding energy of the

Au $4f_{7/2}$ line relative to the Fermi edge in gold metal was measured to be

84.00 ± 0.01 eV. Using this, the diamond C 1s binding energy relative to the

Fermi level of a thin surface film of gold is 284.44 ± 0.07 eV, in fair

agreement with the value 284.0 ± 0.3 reported by Thomas et al.[4]

There are three peaks in I'(E) as was the case for Si and Ge,[2] which

are also shown in Fig. 2 for comparison. The wider spacing of I'(E) for

diamond is consistent with theoretical expectations[1] and is due to the smaller

lattice constant in diamond. With two atoms per unit cell and four electrons

per atom, diamond has four doubly-occupied valence bands, as indicated in

Fig. 3. These bands produce three peaks in the density of states, $\rho(E)$, with

the top two bands forming a single peak. Labeling the I'(E) peaks as I, II,

and III (Fig. 3), we identify most of peak I with band 1, peak II with band 2,

and peak III with bands 3 and 4.

In a one-electron picture we have, to a good approximation,

$$I'(E) \propto \rho(E)\ \sigma(E,h\nu)\ \rho_e(h\nu - E) \quad .$$

Here $\rho(E)$ is the valence-band and $\rho_e(h\nu - E)$ the continuum density of states,

and $\sigma(E,h\nu)$ is the photoemission cross-section. Taking $\rho_e(h\nu - E)$ as constant

over the valence-band width ΔE, since[6] $h\nu \gg \Delta E$, we have

$$I'(E) \propto \rho(E)\ \sigma(h\nu,E) \quad ,$$

and detailed comparison of I'(E) with $\rho(E)$ would require knowledge of $\sigma(h\nu,E)$.

For molecules, cross-section modulation is readily understood.[7] The

cross section is proportional to the square of the overlap between the initial

one-electron state and the continuum final state of the electron,

$$\sigma(h\nu,E) \propto \left| \langle \psi_i(E) | \chi_f(h\nu - E) \rangle \right|^2 \quad .$$

Taking $\chi_f(h\nu - E)$ as a plane wave, the de Broglie wavelength of an electron

ejected from the valence bands by AlKα radiation is 0.32Å. Thus, the major

contributions to $\sigma(h\nu,E)$ must come from those regions in which $\psi_i(E)$ has a

curvature corresponding to this wavelength; i.e., the atomic-like regions

near the nucleus. The carbon 2s orbital has a larger cross section for

photoemission at this energy than the carbon 2p orbital, because its radial

node makes the 2s wavefunctions' curvatore similar to that of the photoelectron.

Comparison of Figs. 2 and 3 reveals that cross-section modulation is

very important in diamond, Si, and Ge. The valence-electron wavefunctions are

of course eigenfunctions of _linear_ momentum rather than _angular_ momentum because

of the lattice periodicity. Expansion into atomic orbitals therefore extends

over the whole Hilbert space that is orthogonal to the ion cores. However--

especially near the nucleus--the largest contributions to this expansion

come from the ns and np orbitals, where n is the principle quantum number of

the valence electrons in C, Si, and Ge respectively. In this sense band 1

is mostly s-like and bands 3 and 4 are mostly p-like.[8] Band 2 is a mixture of s-

and p-like functions. The variation in the peak area ratio (I + II)/III should

therefore correspond to a similar variation in the atomic-orbital cross-section

ratio $\sigma(s)/\sigma(p)$, as noted earlier for Si and Ge.[2]

To investigate this point more quantitatively we obtained XPS spectra

of the valence regions of the gaseous compounds methane (CH_4), silane (SiH_4),

and germane (GeH_4) in the Berkeley iron-free spectrometer, using a Mg K$\alpha_{1,2}$

x-ray source. The latter two gases were prepared applying the techniques of

Refs. 9 and 10. In all three cases the spectra (Fig. 3 and Table I) exhibit two

peaks which correspond to the (s-like) A_1 level and the (p-like) T_2 level.

An LCAO calculation for the three molecules yields the parentages of

the two levels in terms of the atomic s and p orbitals. From these parentages

and the measured peak intensities we deduced the ratios $\sigma(ns)/\sigma(np)$ listed in

Table II. These ratios show a dramatic change from C to Ge, thus accounting

for the intensity variation of peaks I, II, and III in the valence band

spectra of the elements (a comparison of AlKα and MgKα spectra is valid because

cross-section ratios vary little between these photon energies[11]). In fact

the atomic ratios show more variation because the valence bands in the solids

do not have pure s or p character. Even in the tight binding approach the

states which make up $\rho(E)$ are mixtures of the s and p basis functions for

every value of E. This mixture alone tends to equalize the cross-section over

the valence region. It is thus clear that cross-section modulation can slightly

shift the apparent positions of characteristic features from $\rho(E)$ to $I'(E)$.

At Γ, the center of the Brillouin zone, bands 2-4 all have p character.

Since they all approach Γ'_{25} with zero slope the density-of-states falls rather

sharply at this energy--the top of the valence bands. Thus, in principle,

$E(\Gamma'_{25})$ could be determined rather accurately, without ambiguity due to s,p

mixing or unfavorable structure in $\rho(E)$. By extrapolating down from the

steepest part of the Peak III, we obtained $E(\Gamma'_{25}) = 1.8 \pm 0.3$ eV relative to

$E_F(Au)$.

The peaks in $I'(E)$ should fall at maxima in $\rho(E)$ with small shifts

between the two sets of maxima arising from instrumental broadening of unsym-

metrical peaks and from s/p mixing. The overall increase of s character with

energy below E_F tends to bias $I'(E)$ downward in energy relative to $\rho(E)$. With

these factors considered, we assign the positions of peak I and II as

17.9 ± 0.2 eV and 13.2 ± 0.1 eV below $E_F(Au)$ respectively.

The upper portion of Fig. 3 compares the calculated $\rho(E)$ of Painter,

Ellis, and Lubinsky[12] with our $I'(E)$. Their band structure is shown in the

lower portion of Fig. 3. Since $\rho(E)$ and $I'(E)$ show excellent agreement in the positions of all characteristic features, it is valid to deduce the variation of $\sigma(E)$ over the valence region, as indicated by the broken line in Fig. 3. This line exhibits the smooth decrease from the bottom of the valence band to its top, as expected from the discussion given above. Thus the relative intensities in photoelectron spectra can provide a valuable tool in exploring the atomic origin of different regions in the valence bands of solids.

FOOTNOTES AND REFERENCES

* Work performed under the auspices of the U. S. Atomic Energy Commission.

† On leave from University of Alberta (1971-1972).

†† On leave from University of Bonn, Germany.

‡ In partial-fulfillment of Ph.D.

1. Detailed references to the early literature appear in Refs. 4 and 5 below.

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FIGURE CAPTIONS

Fig. 1. XPS valence band (upper curve) and C 1s core region (lower curve) of diamond.

Fig. 2. a) Corrected valence band spectra I'(E) for diamond, Si and Ge;

b) Molecular orbitals for CH_4, SiH_4, and GeH_4. The $K\alpha_{3,4}$ satellites in these spectra are accounted for in the least-squares computer fit.

Fig. 3. Comparison of the calculated density of states (Ref. 12) with I'(E) for diamond. The broken line gives the cross section modulation as obtained by dividing I'(E) into $\rho(E)$.
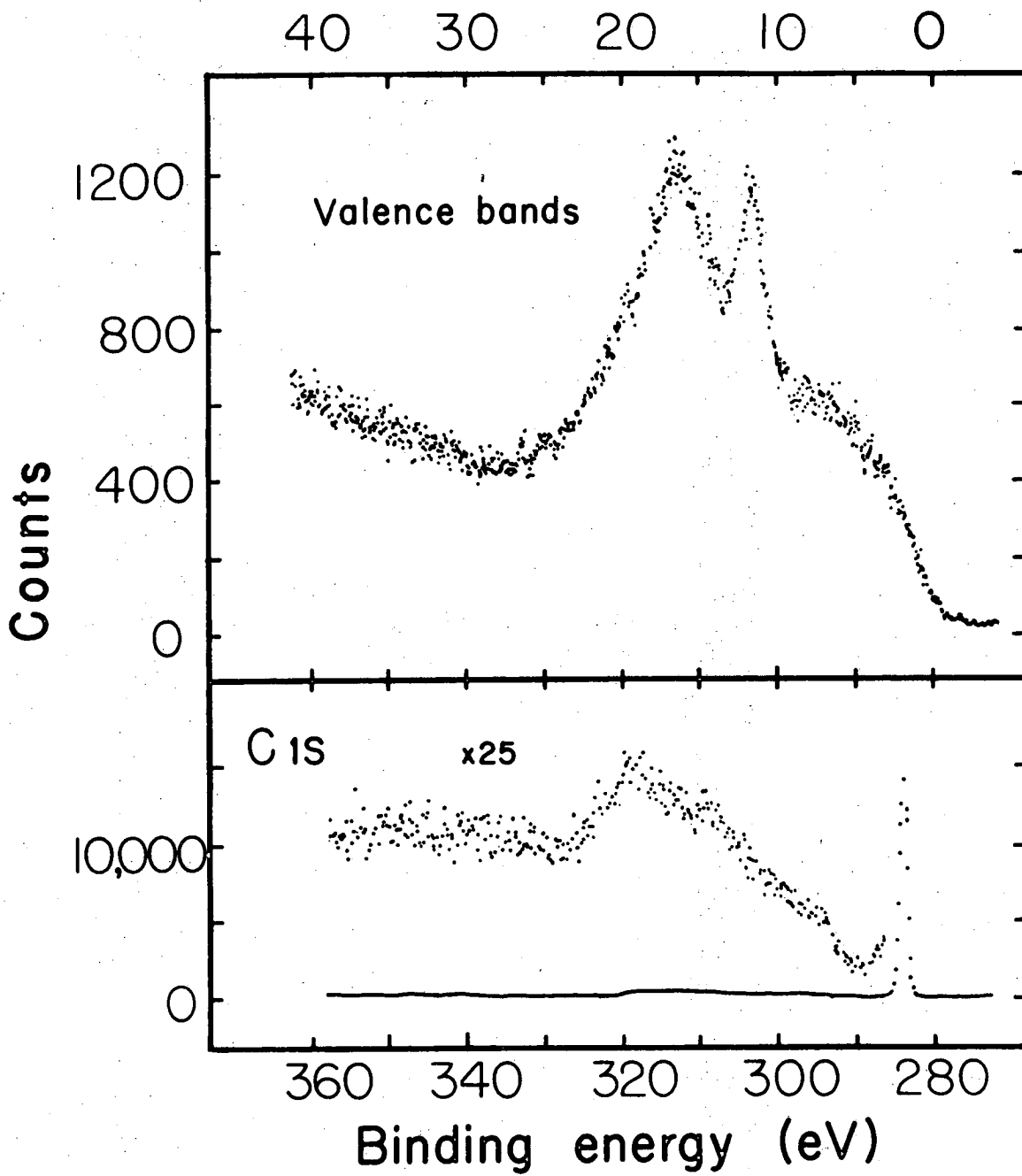
Table I. Binding energies E_B and widths (FWHM) of molecular orbitals of methane, silane, and germane. Energies in eV.

Orbital	CH_4	SiH_4	GeH_4
A_1			
E_B	23.08(4)	18.01(4)	18.46(4)
FWHM	1.71(3)	1.16(6)	1.17(6)
T_2			
E_B	14.5(2)	12.67(4)	12.28(4)
FWHM	2.8(5)	1.69(6)	1.75(6)

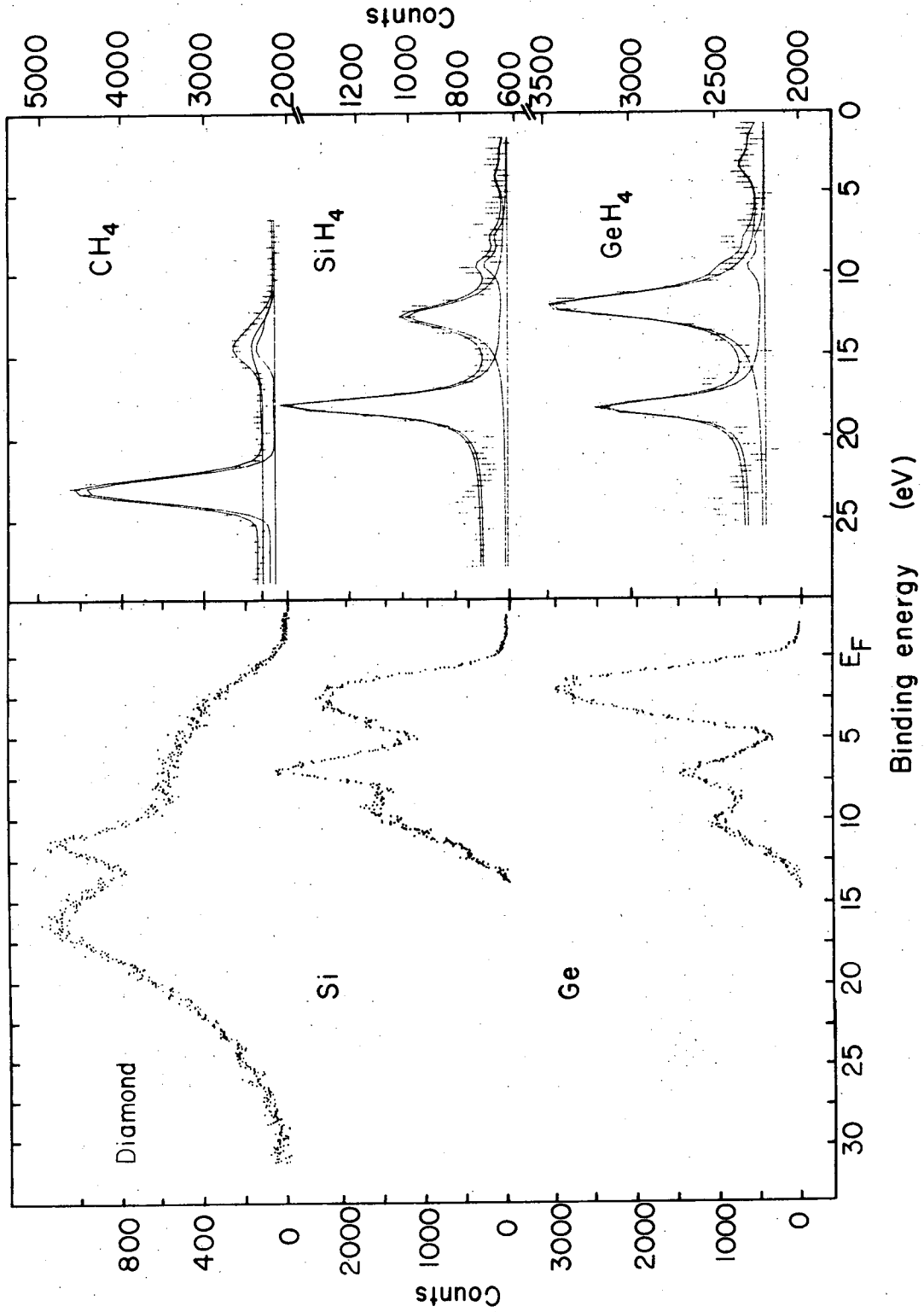*Binding energies were measured using neon as a standard. The Ne 2s peak was assigned a value of 48.72 eV.

Table II. Comparison of the atomic cross section ratio for photoemission $\sigma(s)/\sigma(p)$ with the intensity ratio of peaks I + II to peak III in the valence band spectra of diamond, Si, and Ge.

	$\frac{I + II}{III}$	$\frac{\sigma(s)}{\sigma(p)}$
C	2.9 ± 0.3	12
Si	1.6 ± 0.2	3.4
Ge	0.7 ± 0.1	1.0

Fig. 1

XBL 728-1458

Fig. 2

XBL7211-4391

XBL7211-4364

Fig. 3