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

R. G. Cavell†, S. P. Kowalczyk, L. Ley††, R. A. Pollak‡,
B. Mills, D. A. Shirley, and W. Perry

Department of Chemistry and
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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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.

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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,

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

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 <u>linear</u> momentum rather than <u>angular</u> 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 unsymmetrical 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.

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FOOTNOTES AND REFERENCES

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††On leave from University of Bonn, Germany.

‡In partial-fulfillment of Ph.D.

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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

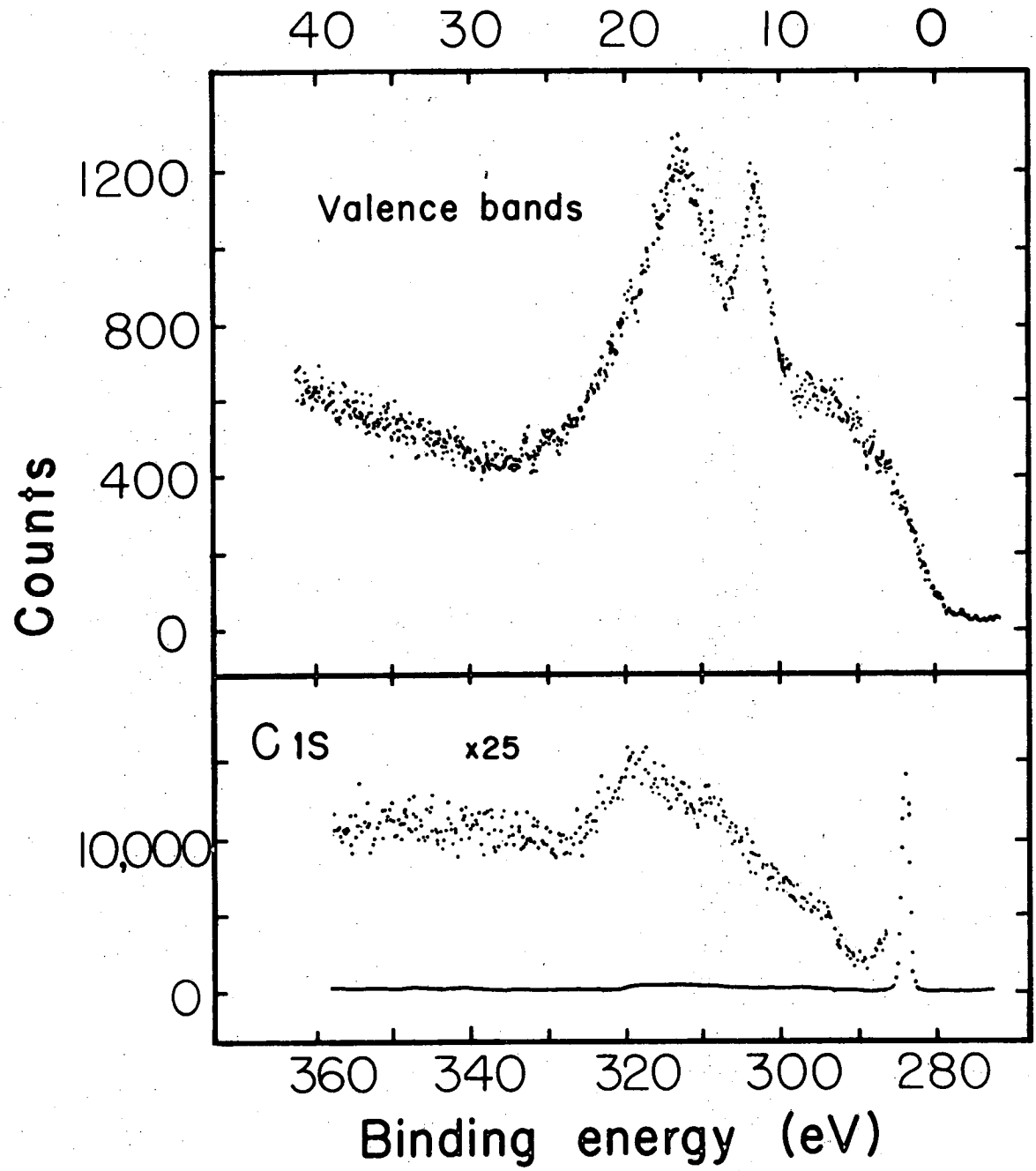

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Fig. 1

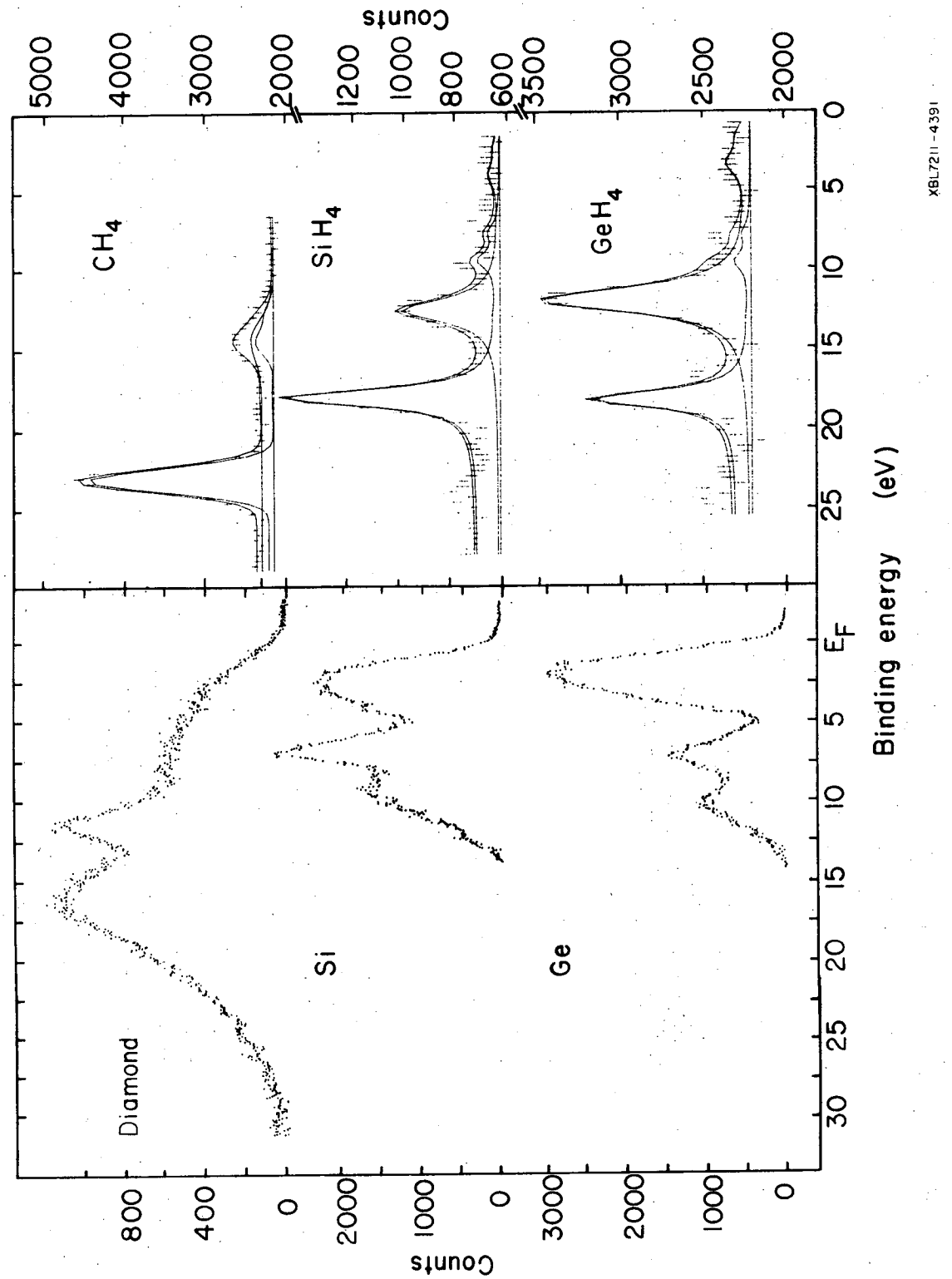
Counts
5000
4000
3000
2000
1200
1000
800
600
3500
3000
2500
2000
CH4
SiH4
GeH4
0
5
10
15
20
25
Binding energy (eV)
EF
Diamond
Si
Ge
30
800
400
0
2000
1000
0
3000
2000
1000
0
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Fig. 2

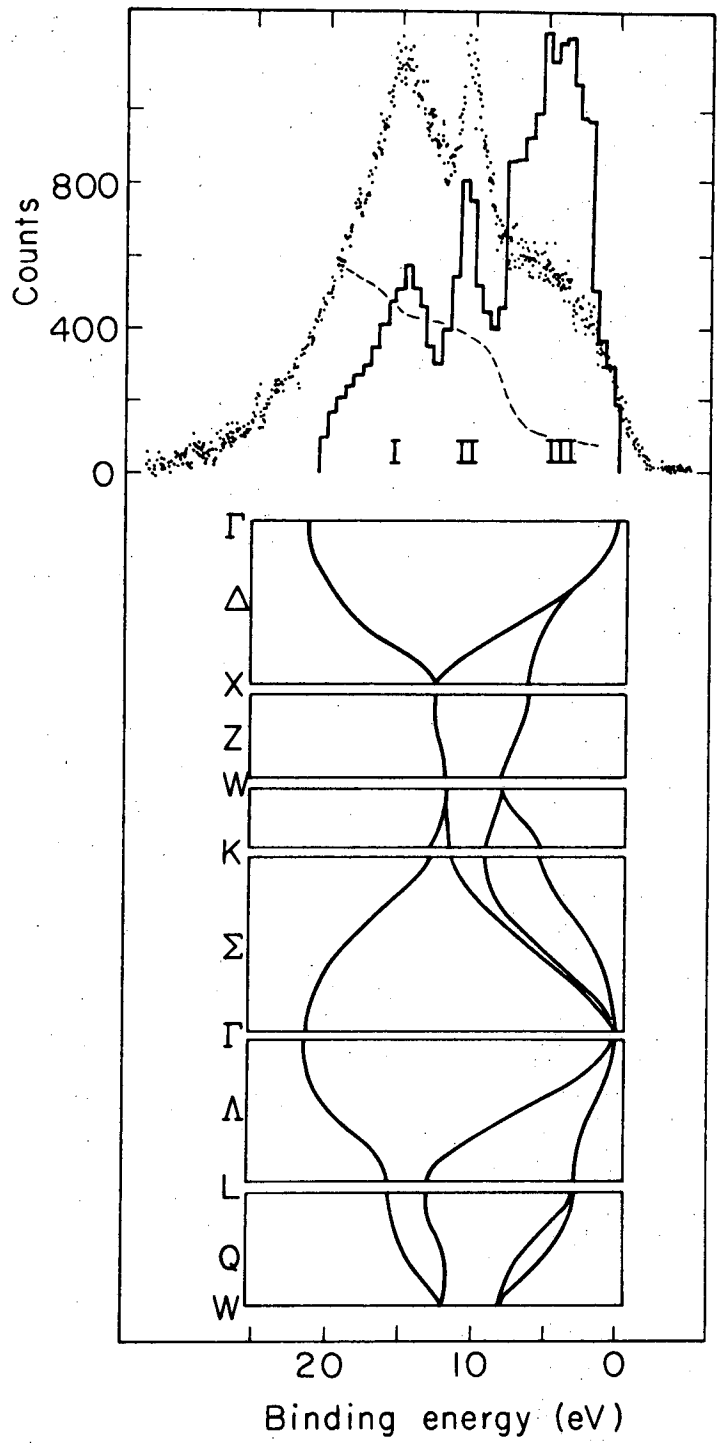

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Fig. 3

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