Photocathode Physics for Photoinjectors Workshop
10/10-14/2010, BNL

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APPLICATIONS OF LASER AND SYNCHROTRON BASED ARPES TO PHOTOCATHODE RESEARCH*

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Applications of Laser and Synchrotron Based ARPES to Photocathode Research

Example: Mechanism of NEA Emission from H:C[100]

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Helpful Discussions:

Phil Allen
Larry Carr
Toni Valla

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a passion for discovery

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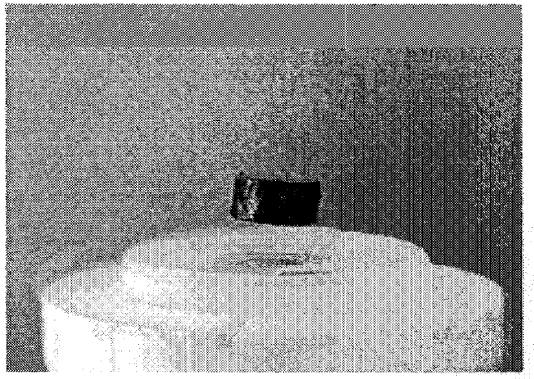
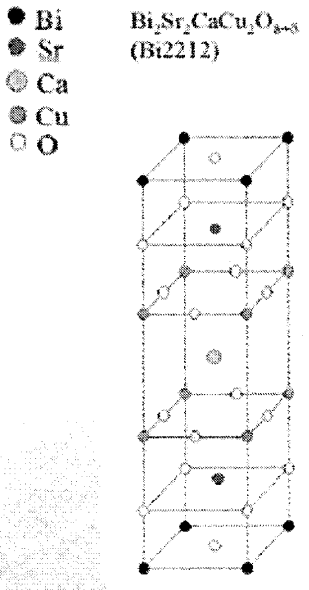
Outline of My Talk

- BNL Electron Spectroscopy – Who We are and What We Do
- A Very Brief Intro to Angle Resolved Photoelectron Spectroscopy (ARPES)
- Relevance to Photocathode Research + Examples
- ARPES at Beamline U13B of NSLS
- Diamond Sample Characteristics, Prep and Handling
- Synchrotron and Laser Based ARPES of Boron Doped, Hydrogen Terminated [100] Diamond
- Summary of Present Results

(Photo)Electron Spectroscopy at BNL

- Correlated Electron Materials
  - Topological Insulators, Graphene (Toni Valla)…
- High T_c Superconductivity (Cuprates, Pnictides…)
- Development of ARPES technique
  - light sources, spectrometers, analysis…





Quantum Mechanics of ARPES

The Spectral Function, A(k,ω), is the probability of finding an electron of energy ω and momentum k when probing the system, in a QM sense. In principle, what is measured is

$$I(k,\omega) \propto \frac{2\pi}{\hbar}\left\langle \psi_f \middle| \vec{A}\cdot\hat{p} \middle| \psi_i \right\rangle A(k,\omega) f(\omega;T) \qquad A(k,\omega) = \frac{1}{\pi}\left|\mathrm{Im}\, G(k,\omega)\right|$$

$$A(k,\omega) = \delta(E_{f,k} - \varepsilon_{i,k} - \hbar\omega)$$ for a non-interacting electron gas

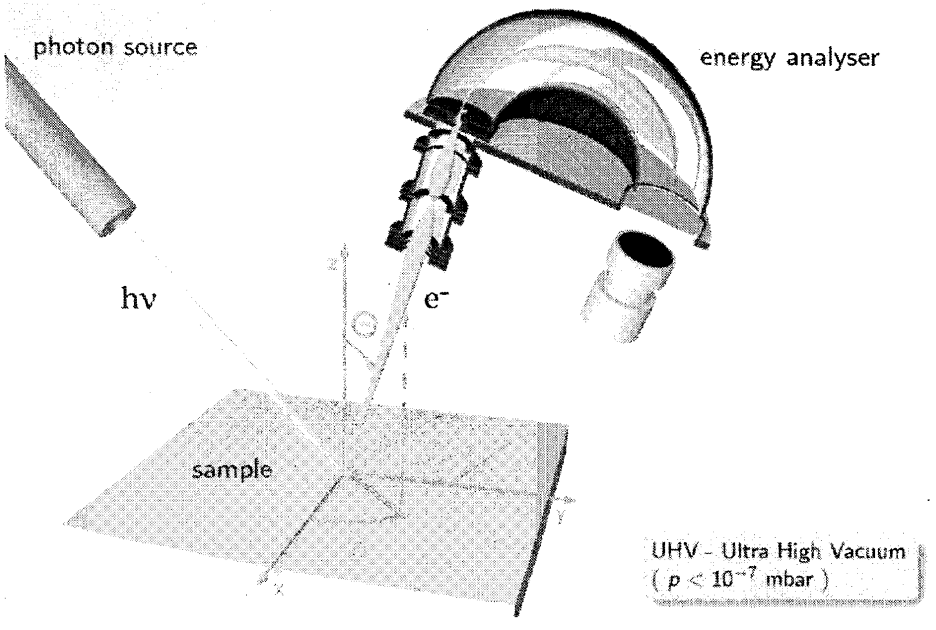
$$A(k,\omega) = \frac{1}{\pi}\frac{\mathrm{Im}\Sigma_k}{(\omega - \varepsilon_{i,k} - \mathrm{Re}\Sigma_k)^2 + (\mathrm{Im}\Sigma_k)^2}$$ for a system with interactions

---

$$\left\langle \psi_f \middle| \vec{A}\cdot\hat{p} \middle| \psi_i \right\rangle$$

Dipole transition matrix elements:
Intensity of photocurrent depends on photon beam polarization, angle of incidence, energy, symmetry of electronic states…

Kinematics of ARPES (For 2D Emission)



Experimentally, we access I(Θ,Φ,KE)

$$KE = h\nu - \phi - E_B$$

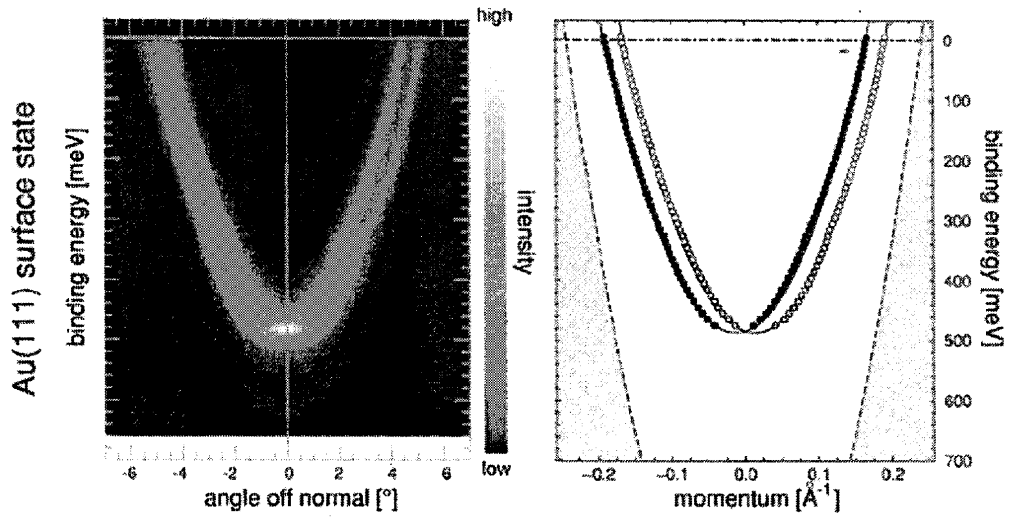
$$\hbar k = \sqrt{2m_e \cdot KE}\,\sin\Theta$$

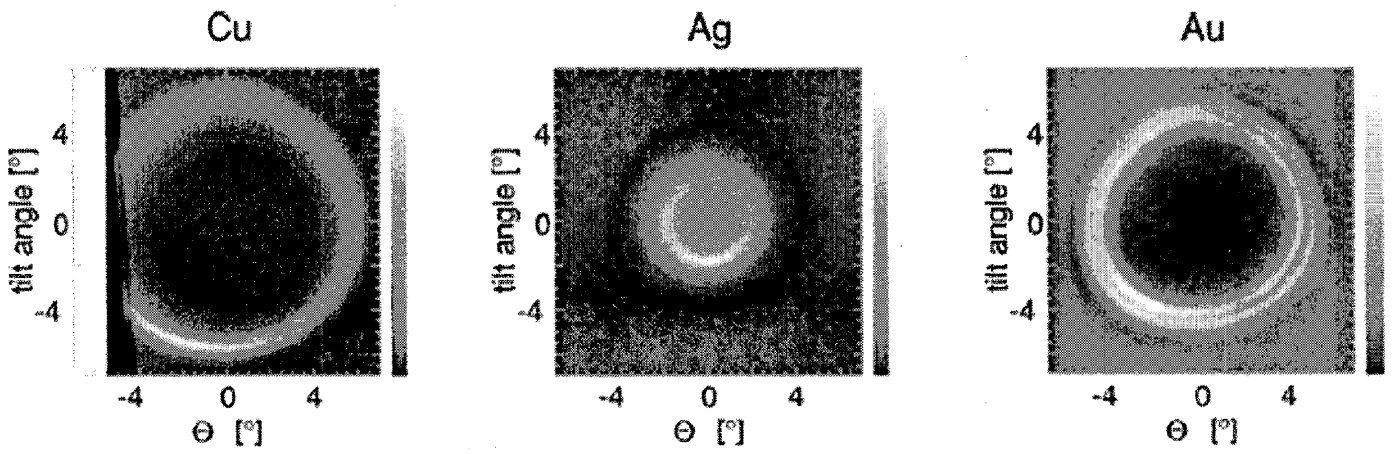
Work backwards from (Θ, KE) to (k, E_B)

Our analyzer takes Θ=±6°, small slices in Φ (~.1°–1°)

Latest Models can take Θ=±30° in one scan!

Example 2 – Metals (He lamp)





PHYSICAL REVIEW B. VOLUME 63. 115415 2001

F. Reinert.* G. Nicolay. S. Schmidt. D. Ehm. and S. Hüfner

Example 1 – Oxide (Synchrotron)

Energy Distribution Curves (EDC's)

Fermi Surface

From momentum distribution curves (MDC's)

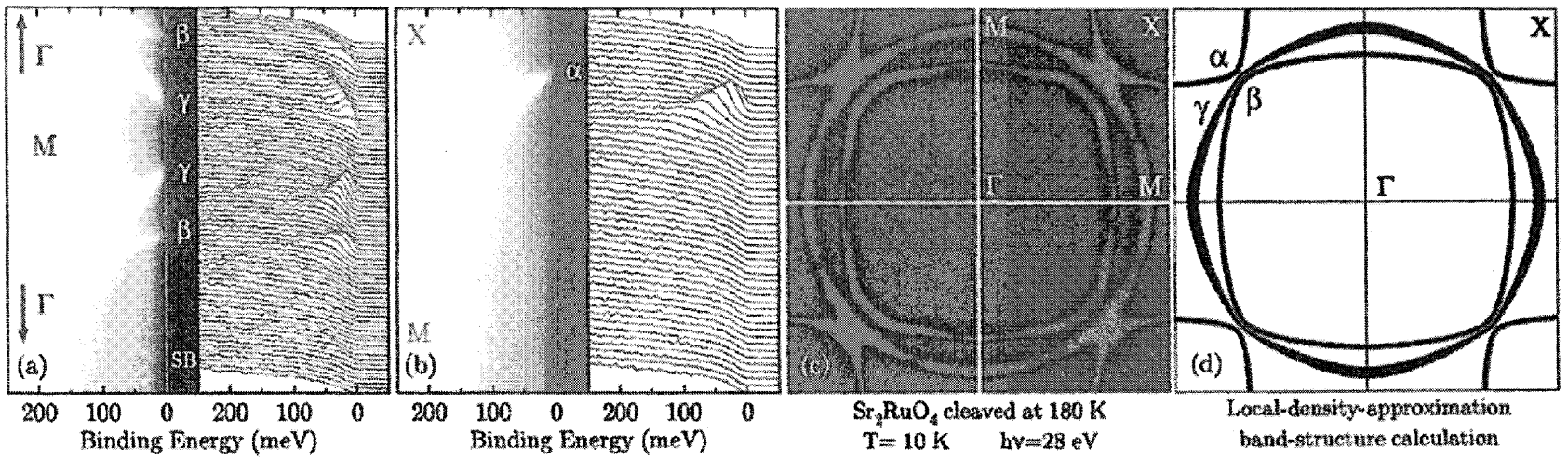


FIG. 9. Photoemission results from Sr_2RuO_4: ARPES spectra and corresponding intensity plot along (a) Γ-*M* and (b) *M*-*X*; (c) measured Fermi surface; (d) calculated Fermi surface (Mazin and Singh, 1997). From Damascelli *et al.*, 2000 (Color).

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Relevance to Photocathodes

Assuming emission is the same at every point illuminated by the photon spot, the total phase space occupied by the photoelectron beam at the surface of the photocathode, on the FS, can be expressed as:

$$V_{phase} \propto W * \Theta \qquad \text{(mm x mrad)}$$

- The proportionality can be made equality by combining ARPES with a photocurrent measurement and photon flux to give an overall scale (Quantum Efficiency).
- For a crystal, the total emittance will generally be a highly nontrivial function of energies and angles.
- For simple systems ARPES gives an "instant" answer

Photoemission at BNL

Synchrotron Based ARPES at U13B

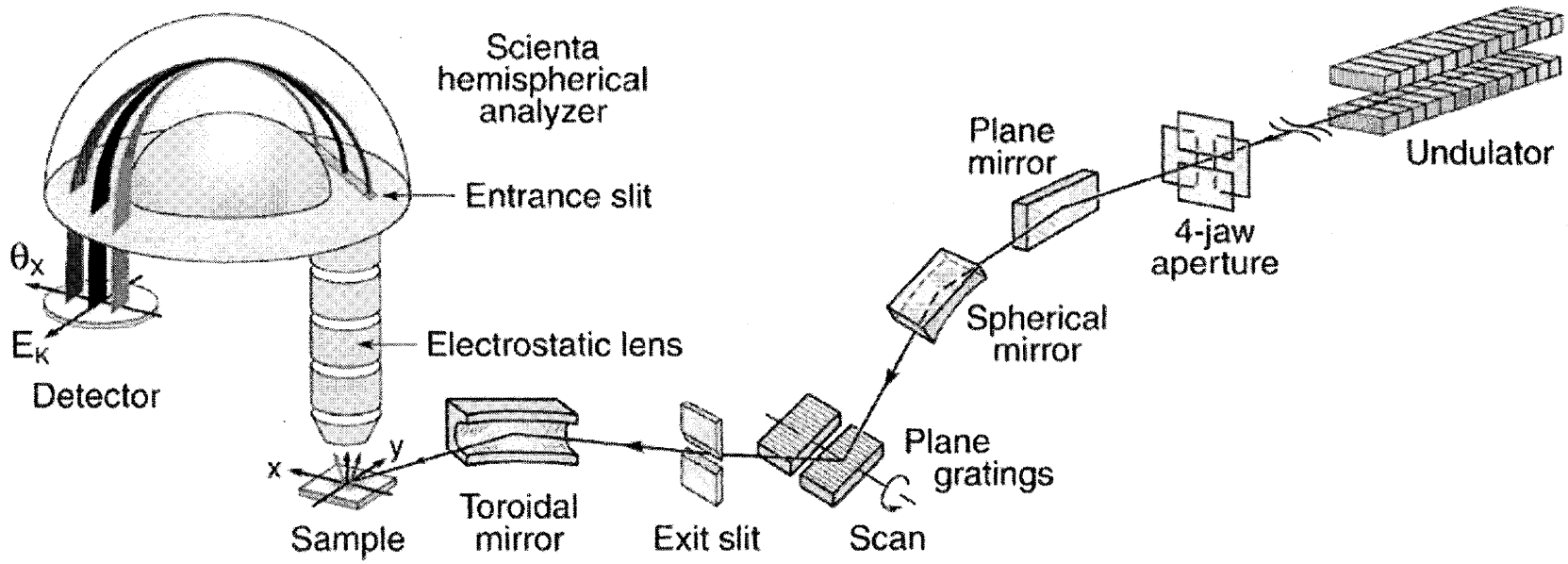
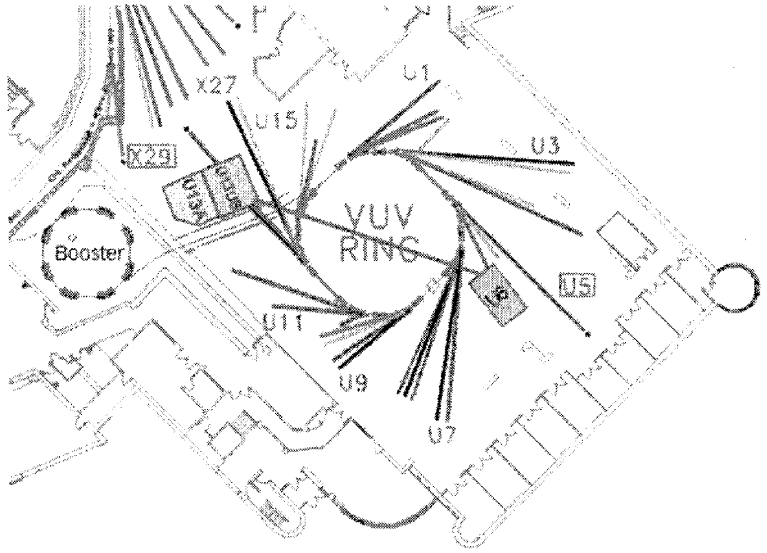


FIG. 6. Generic beamline equipped with a plane grating monochromator and a Scienta electron spectrometer (Color).
(Figure From Damascelli, Hussain & Shen, RMP 75, 473 (2003)

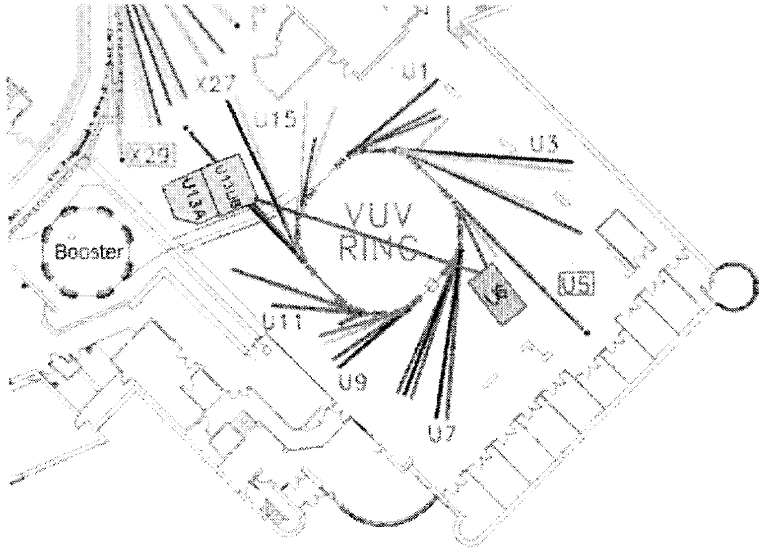
6 eV Laser Based ARPES at U13B

1



6 eV Laser Based ARPES at U13B

1



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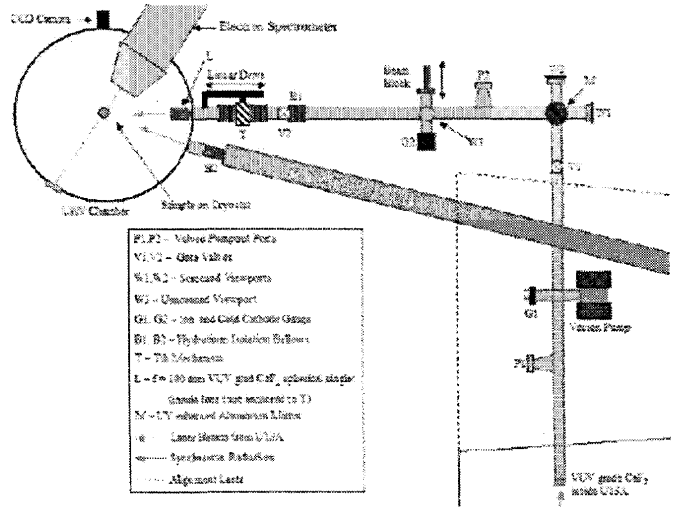
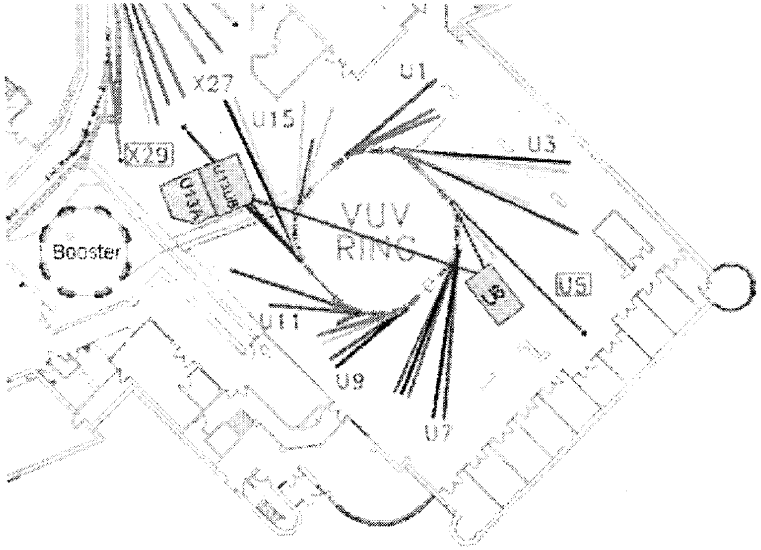


6 eV Laser Based ARPES at U13B

1



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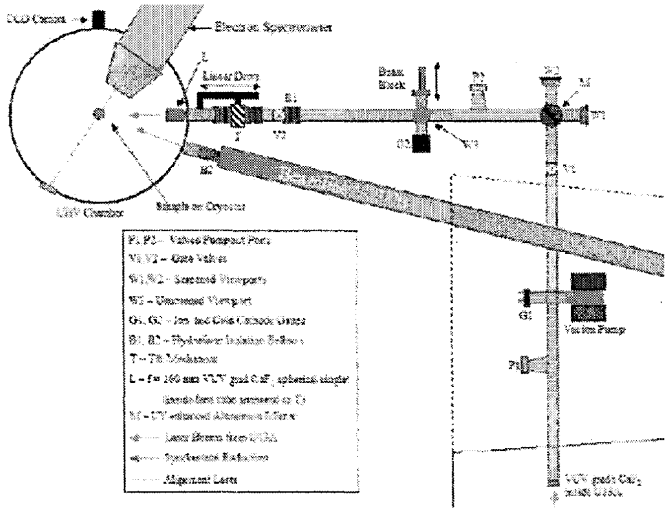

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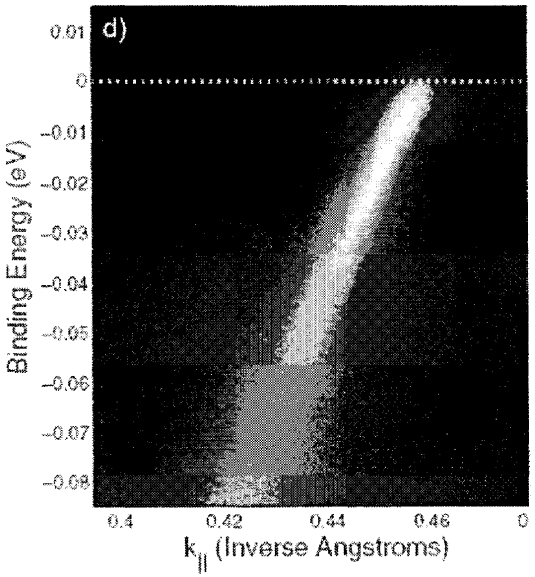
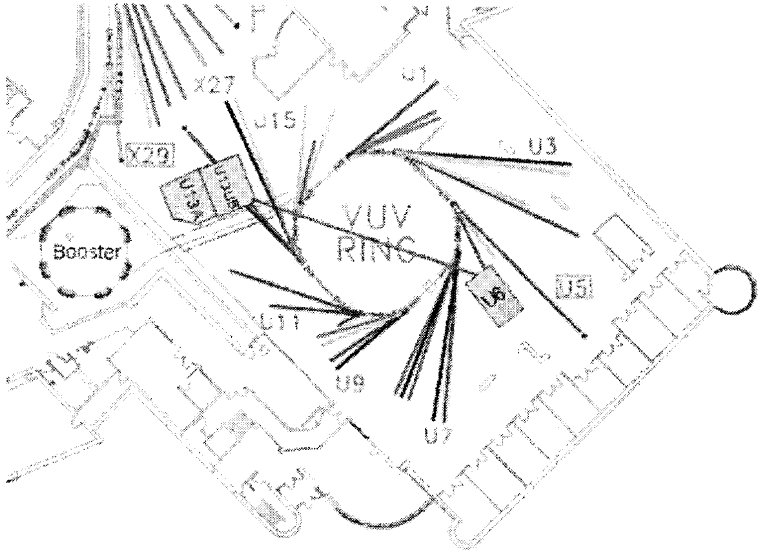
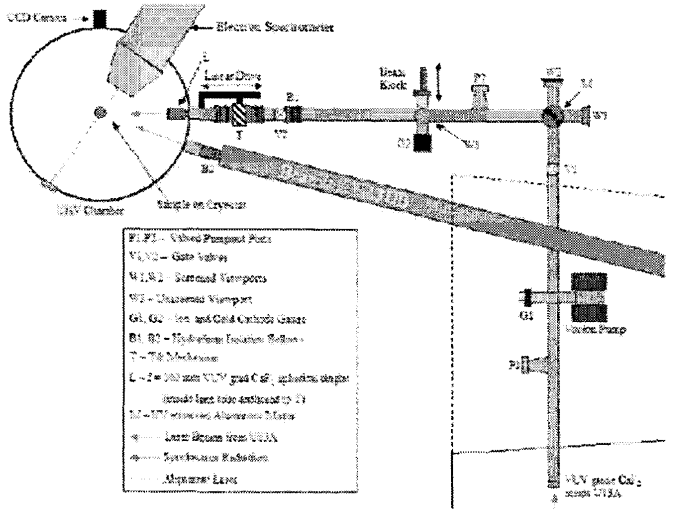


6 eV Laser Based ARPES at U13B

1



2



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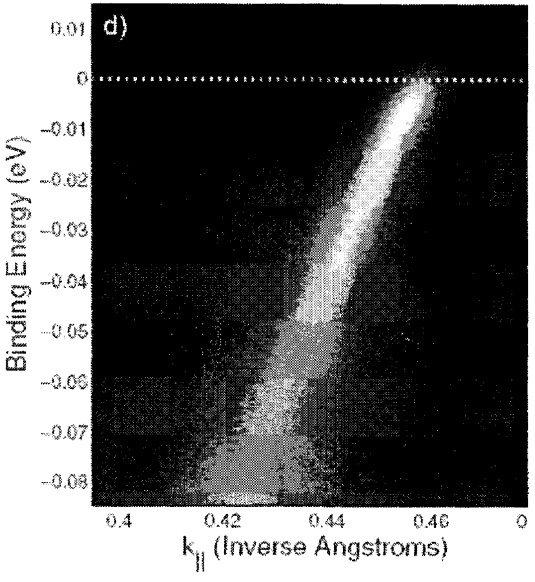

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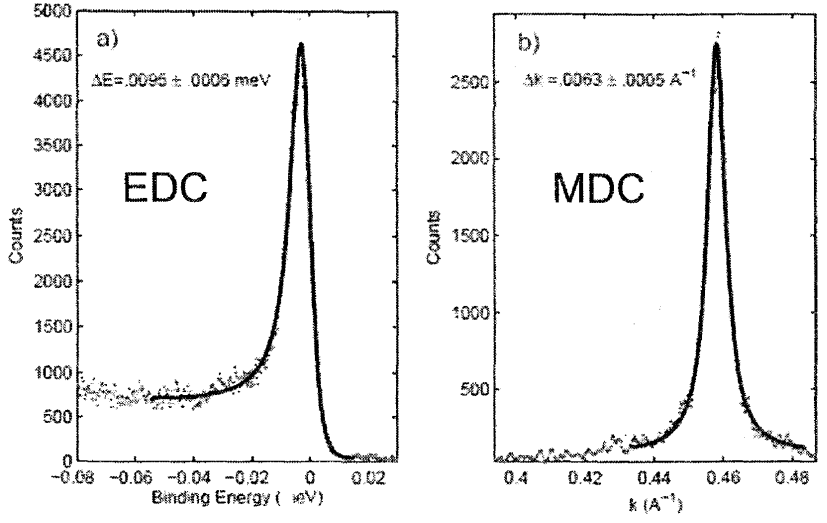
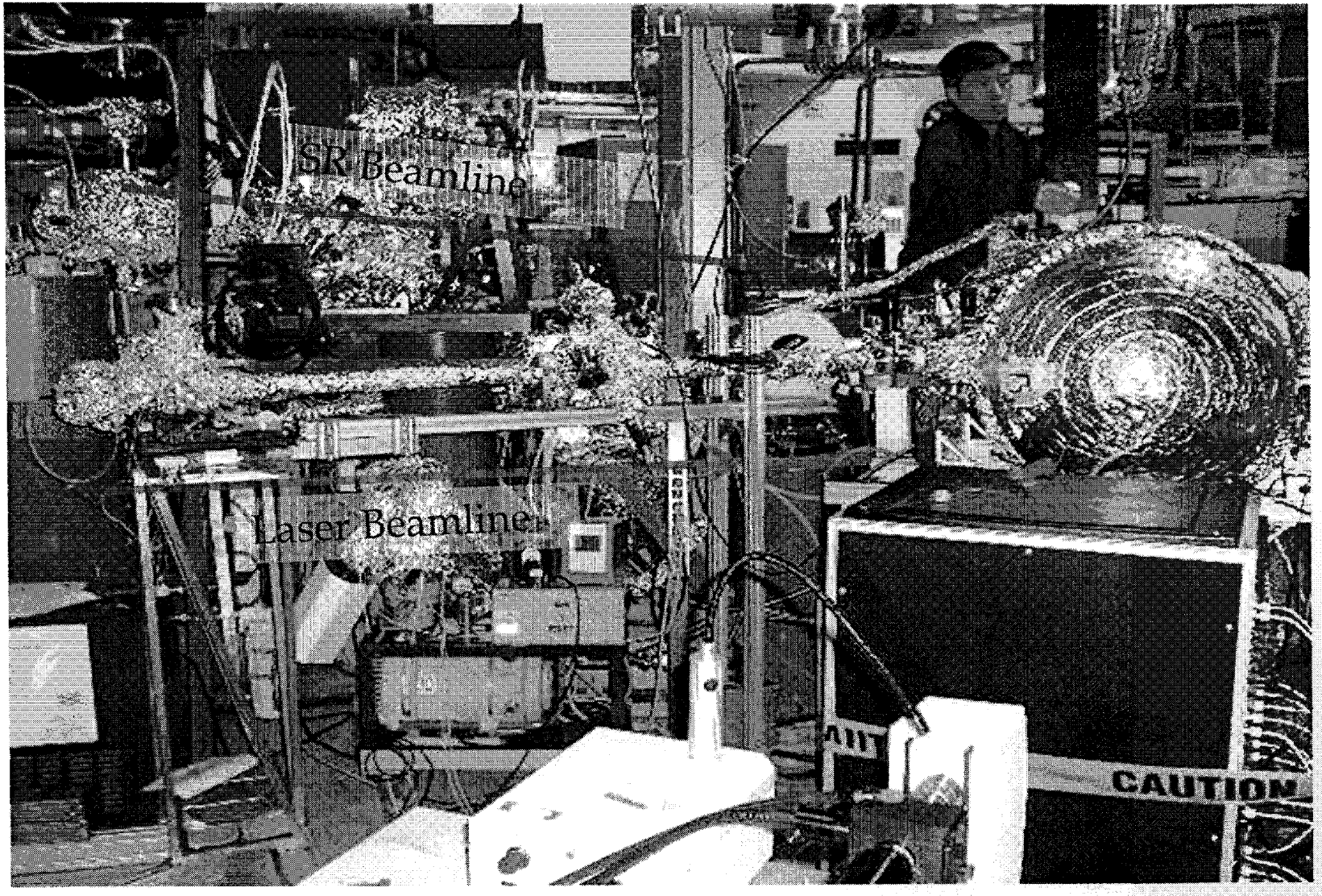
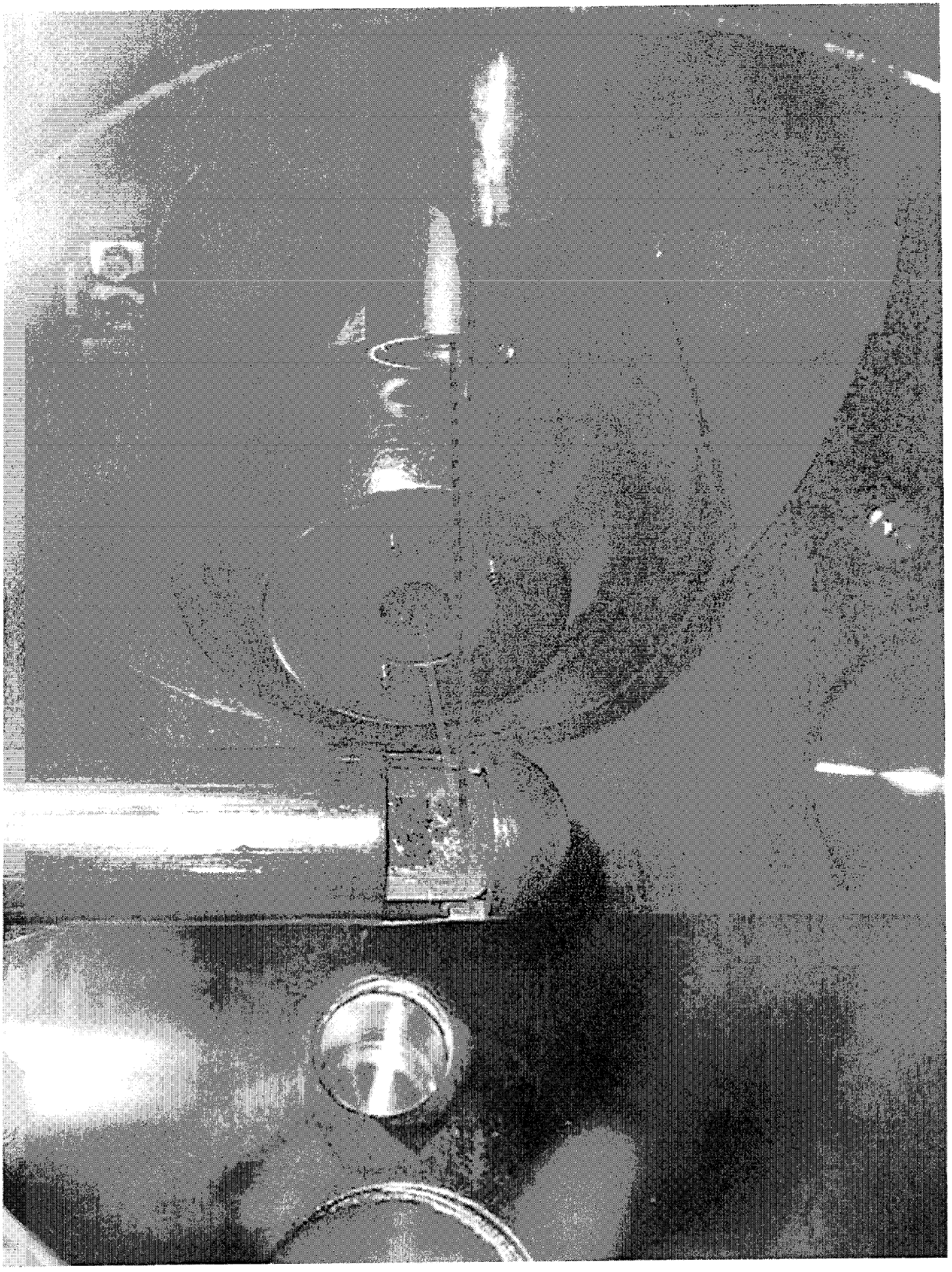
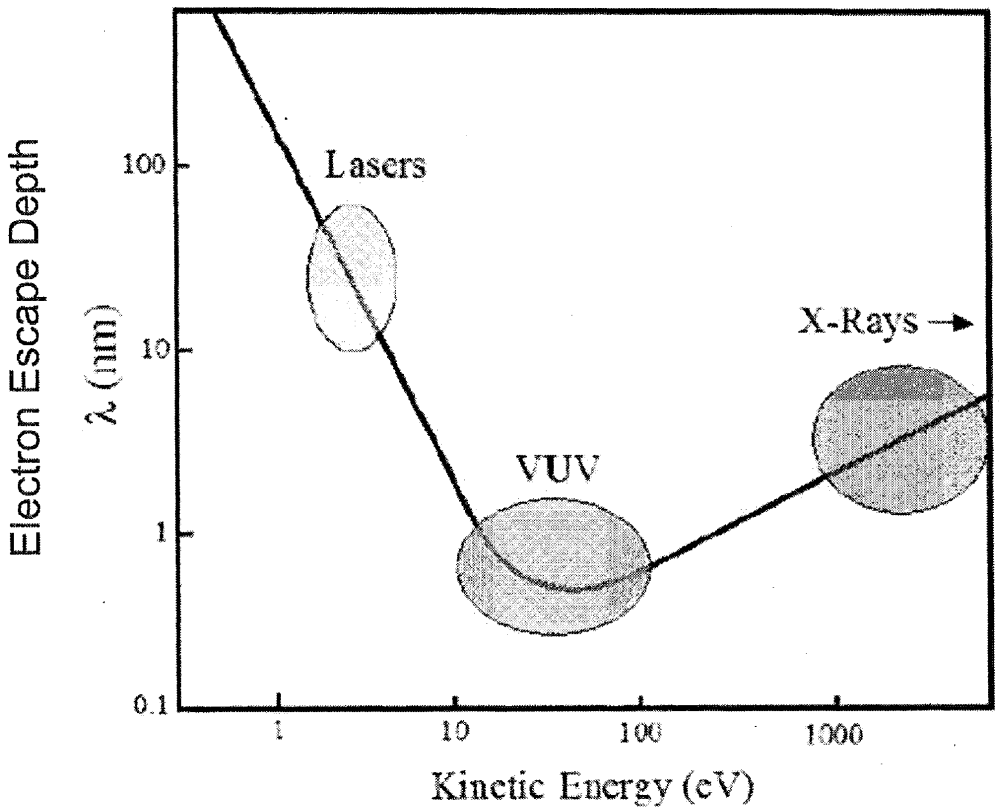



SR Beamline
Laser Beamline
CAUTION



One Reason to Use Both Light Sources

"Universal" Photoelectron Escape Depth Curve

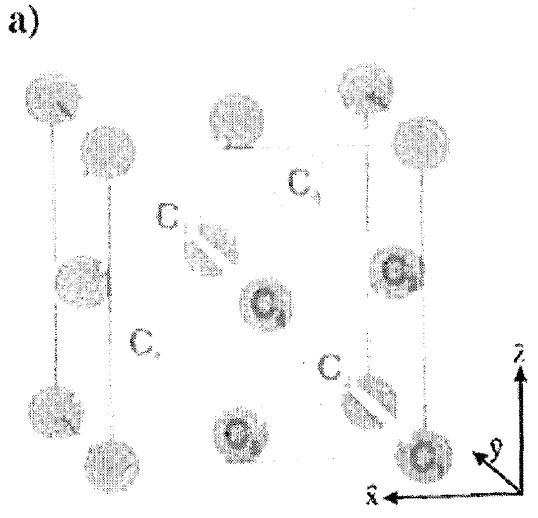


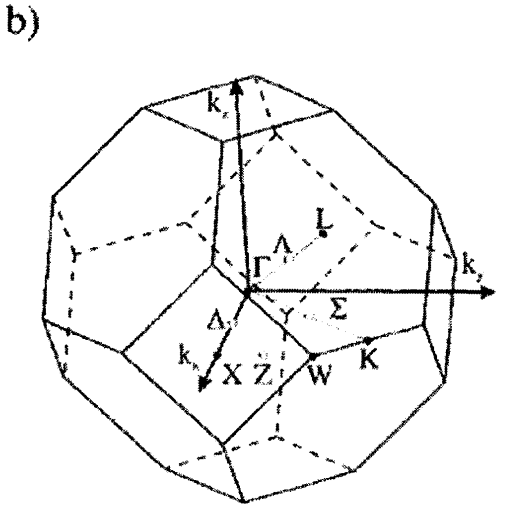
H:C(B)[100] – Hydrogen Terminated, Boron Doped Diamond

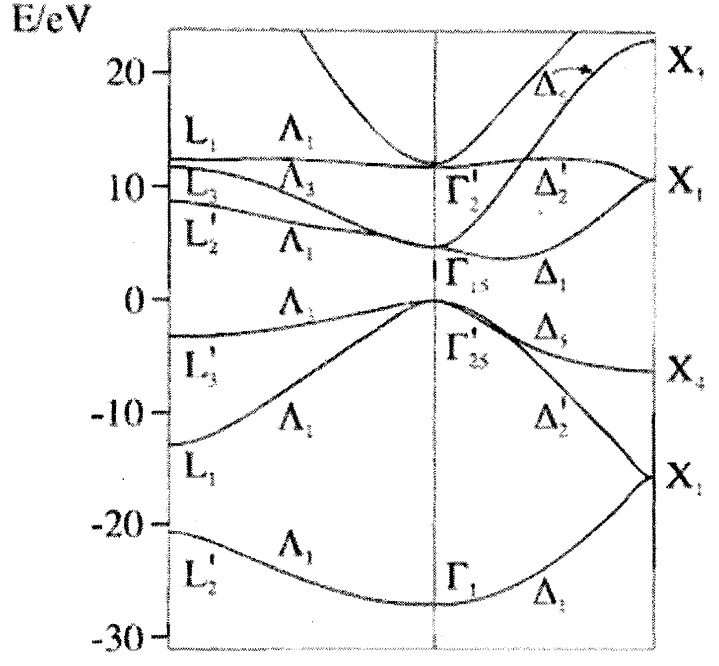
Our Boron Doped Diamond Sample

- Bulk Single Crystal CVD Type IIb (Element 6)
- Dimensions: 3.5 mm^2 X 500 μm thick
- Boron Doping 1-2 x $10^{19}/cm^3$ (~.01% B/C) Sub.
- Confirmed by RT ρ=6 Ωcm, SQUID (No T_c)
- [100] Orientation, H terminated *ex situ*
- *in situ* prep by annealing to 400 ^{0}C with button heater for ~1 hour. Measurements taken at RT
- Most likely unreconstructed surface (LEED)

Crystal, Band Structure and BZ



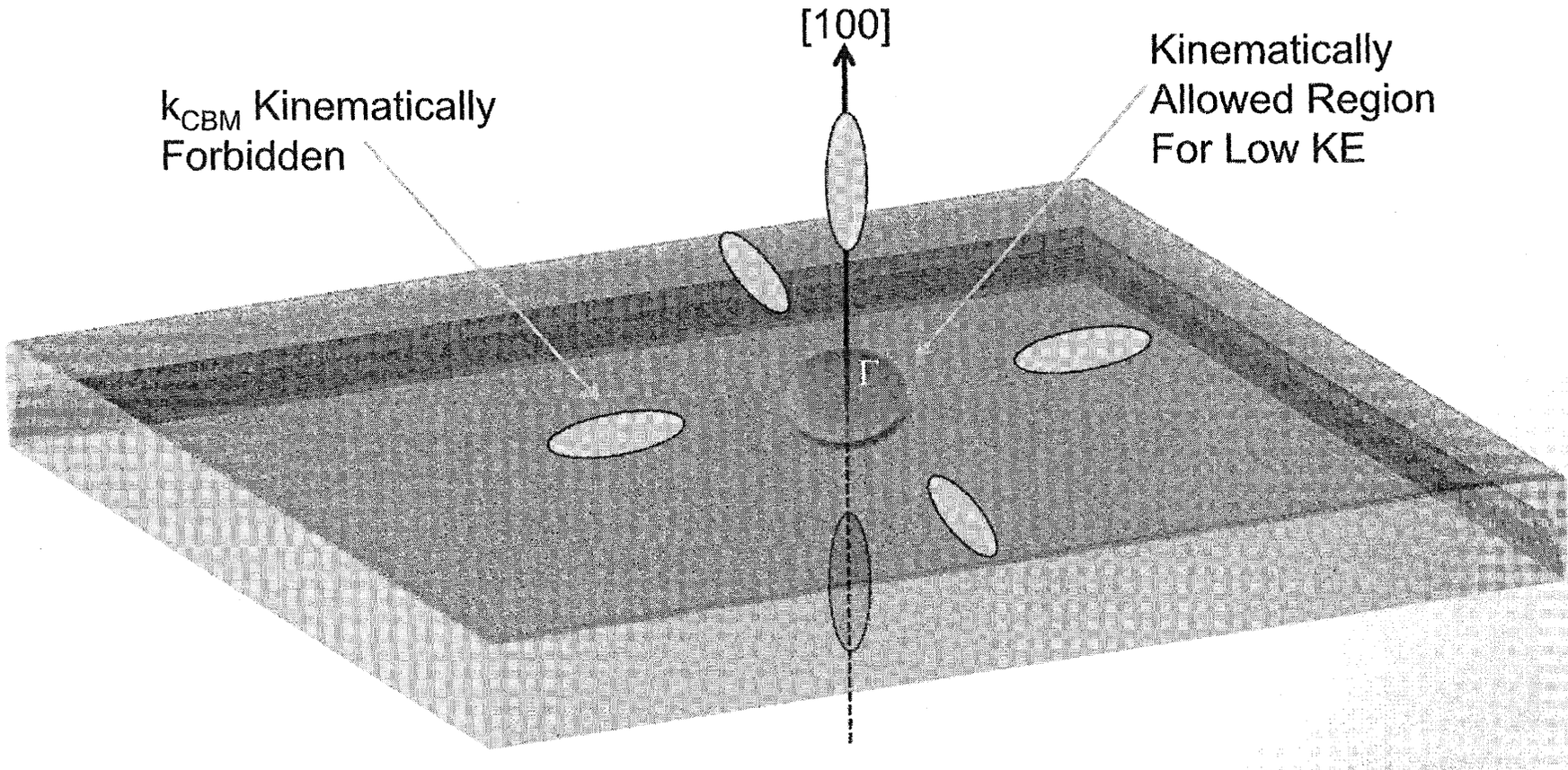




a=3.57 Å Δ_1=1.34 Å^{-1} $k_{max\,||}$~.51 Å^{-1} @ 1 eV KE!

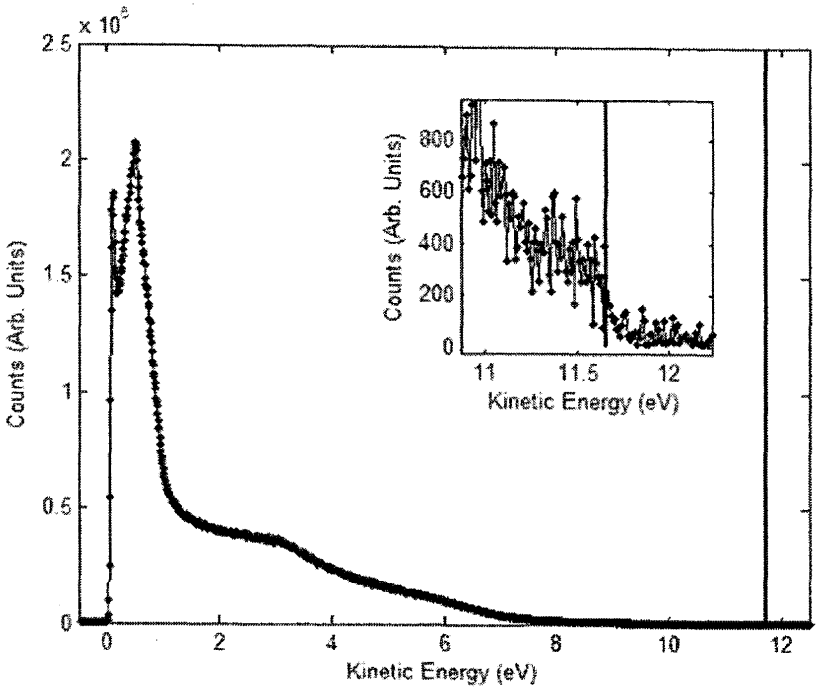
J. Phys. Chem., Vol. 100, No. 26, 1996

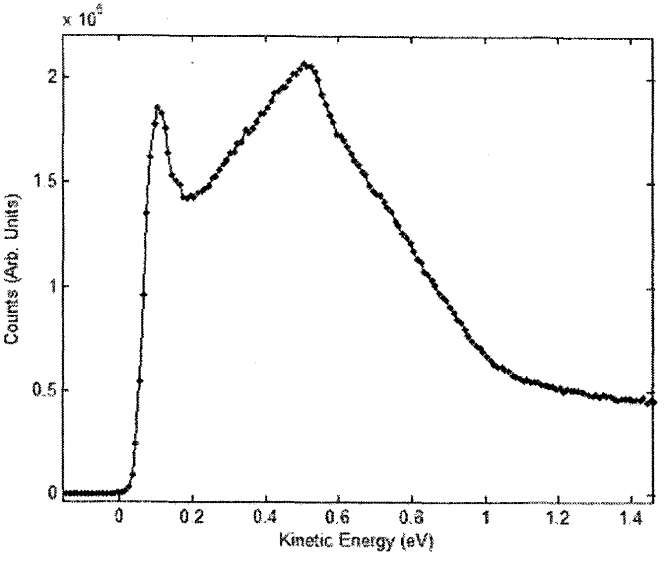
Projection of k-space onto [100] Surface



This is the crux of the problem for NEA Diamond

Synchrotron Measurement of BDD





- Photon Energy 16 eV (p-polarized)
- -10 V Bias between sample and ground
- Fermi Edge Detected (Au referenced) – Past MIT
- Typical features associated with NEA (LE peak…)

Earlier Low Energy PES on Diamond

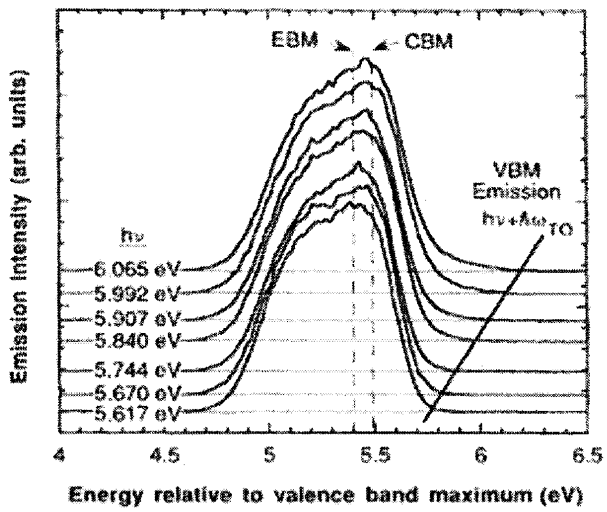


FIG. 4. Electron energy distribution curves referenced to the valence band maximum (VBM) at the excitation photon energies which correspond to peaks and valleys in the total electron yield, at room temperature (EBM, exciton band minimum).

H:C[111] (Bandis & Pate, PRL)
Largele NEA Emission

7 eV Laser, "H"C[100]
Valence Band Emission

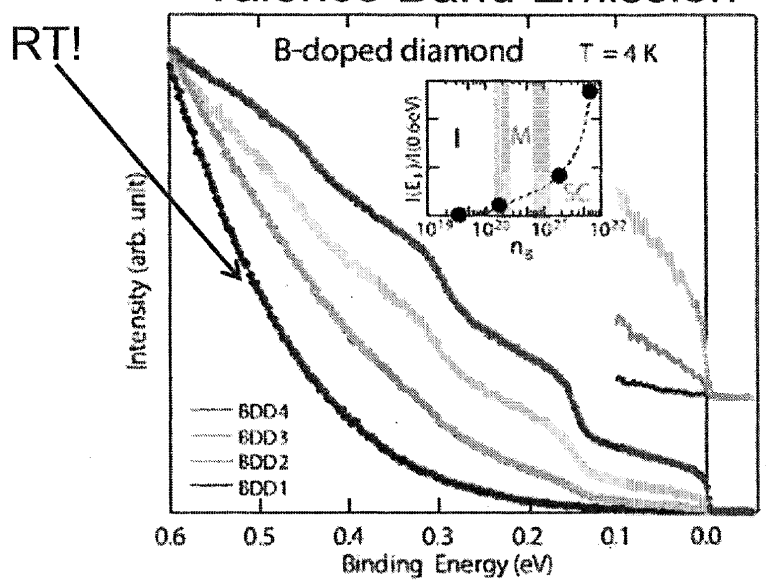


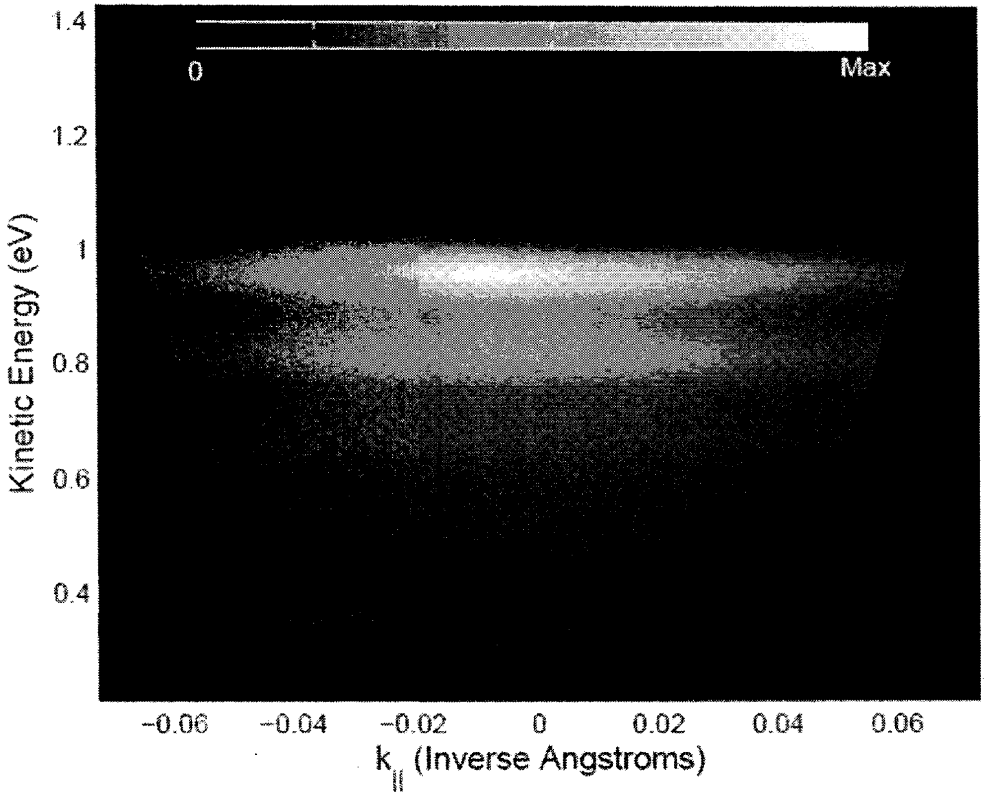
FIG. 2 (color online). The PES results showing the doping dependence of electronic structure for BDD1-4. Near-E_F region for BDD1-BDD3 is magnified in the upper part. The inset shows the intensity at E_F of PES normalized at 0.6 eV, as a function of n_B. I, M, and SC stand for insulator, metal, and superconducting phases as the ground state, respectively.

TABLE I. Characterization of the B-doped diamond samples.

Sample	n_B [cm^{-3}] (B/C%)	Electrical property	Synthesis
BDD1	3.5×10^{19} (0.02)	Insulating	HPHTS
BDD2	1.75×10^{20} (0.10)	Weakly insulating	CVD
BDD3	1.88×10^{21} (1.1)	SC, $T_c = 3.5$ K	CVD
BDD4	6.53×10^{21} (3.7)	SC, $T_c = 5$ K	CVD

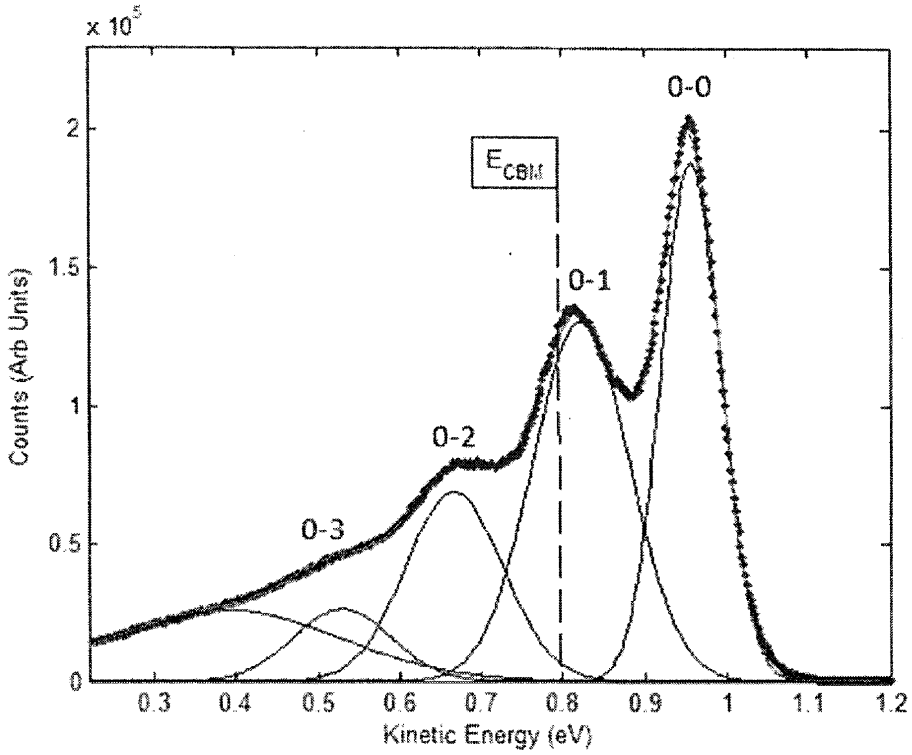
PRL 100, 166402 (2008)

Laser ARPES on BDD at Room Temp



- E_F located at 1.662 eV according to Au reference!
- Very efficient process (scan is short, slits are SMALL)
- KE scale referenced to E_{vac} for NEA material

EDC at Normal Emission



- Data Points
- Total Fit
- Decomposition

χ_{peak} = .955 eV

$\Delta E_{peak} = \hbar\Omega_0 \sim 145$ meV

- Narrow cut around normal emission
- Gaussian fits for all peaks
- *No Background* (e.g. from A_{inc}, "bad" secondaries)

This is (Almost) a Text Book Analysis

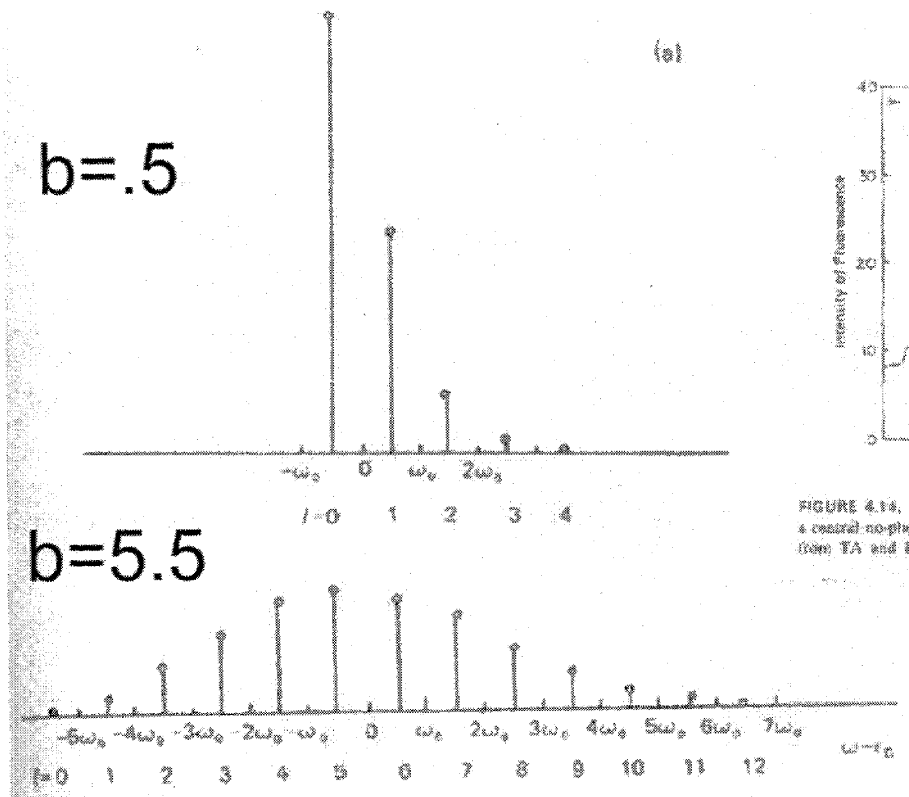


FIGURE 4.10. The spectral function of the independent boson model, Eq. (4.3.13), shown for an Einstein model and two values of coupling constant. (a) For $g = 0.5$, (b) for $g = 5.5$.

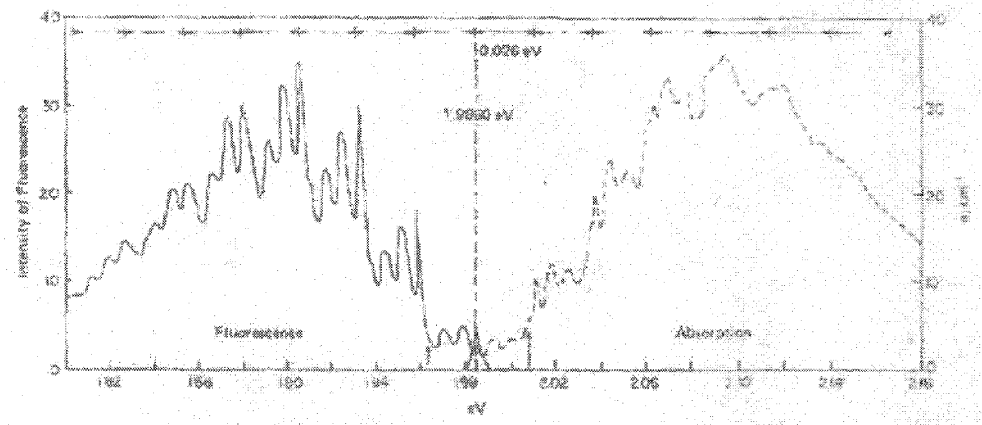


FIGURE 4.14. The fluorescence and absorption at 20 K from an impurity center in ZnTe. The positions of the peak are marked above a central no-phonon line common to both spectra. The LO phonon energy intervals are indicated. The other two peaks in each interval are from TA and LA phonons. *Source:* Dietz *et al.* (1962) (used with permission).

Mahan, "Many-Particle Physics"

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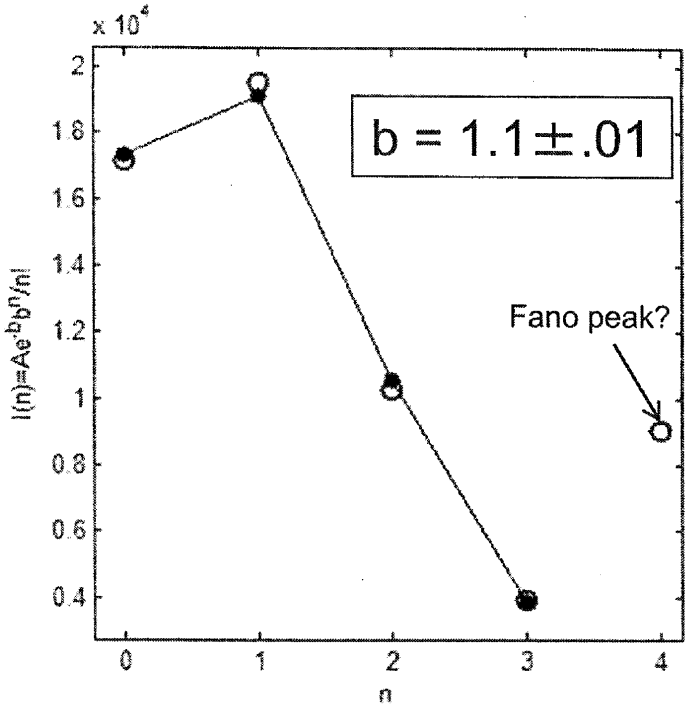
Franck-Condon Analysis



○ Peak Integrated Intensity

● Intensities from F-C Fit

Franck-Condon Factor: $$I(n) = \frac{Ae^{-b}b^n}{n!}$$

n = peak index
b = effective electron-phonon coupling constant
A = overall scale factor

$$E_k = E_{CBM} + \Sigma - n\hbar\Omega_0$$

E_{CBM} = CBM energy
$\Sigma = b\hbar\Omega_0$ is the real part of the electron self energy
$\hbar\Omega_0$ = phonon energy

$$\chi_{eff} = E_{vac} - \left(E_{CBM} + \Sigma\right)$$

Use T=0 theory because $\hbar\Omega_0/k_B$= 1682 Kelvin!
Only optical phonon *emission* can play a role at RT in Diamond

Find the Boson (Optical Phonon)

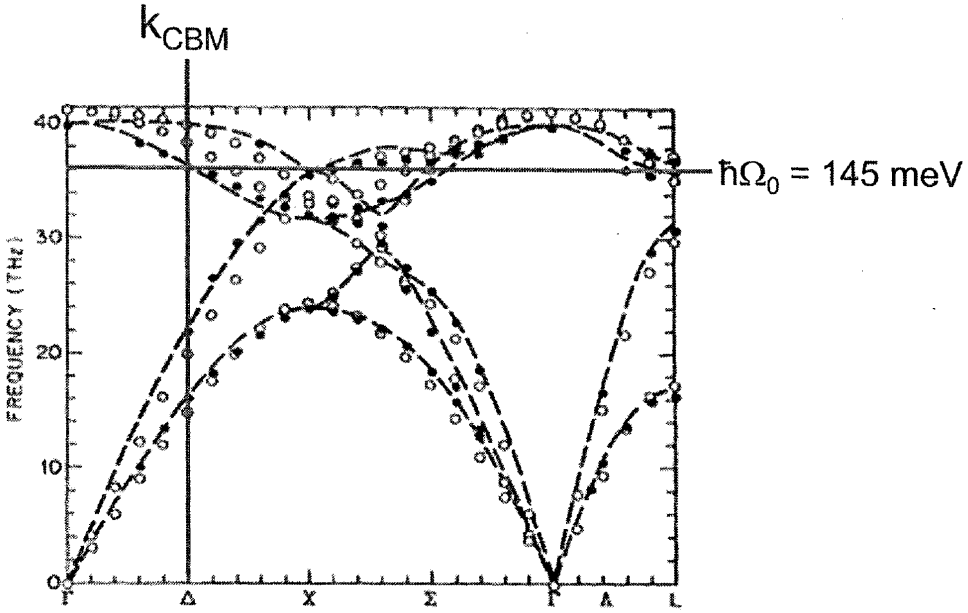


FIG. 2. Phonon dispersion curves for diamond. The open circles and dashes correspond to fits δ_1 and δ_4 in Table I. The solid circles are experimental data from Ref. 14.

E.O. Kane PRB 31, 7865 (1984)

Bulk

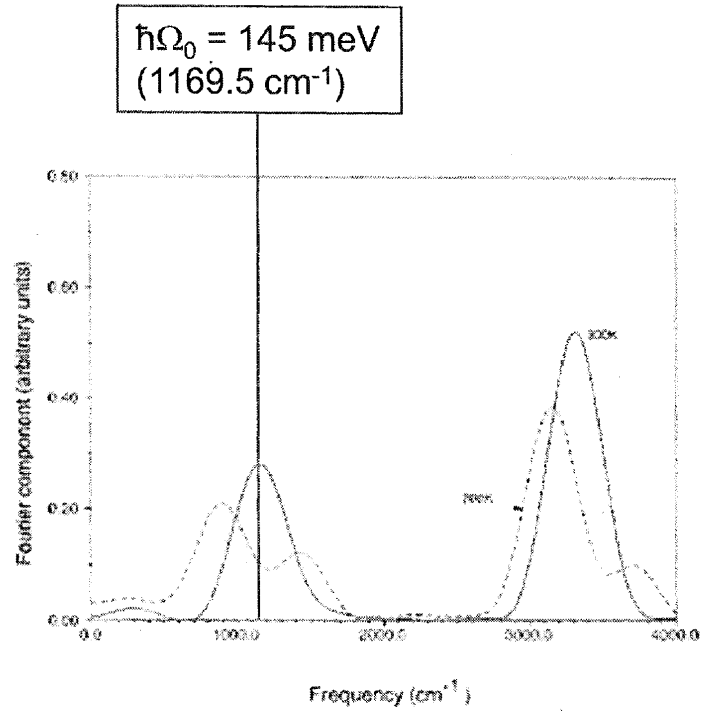
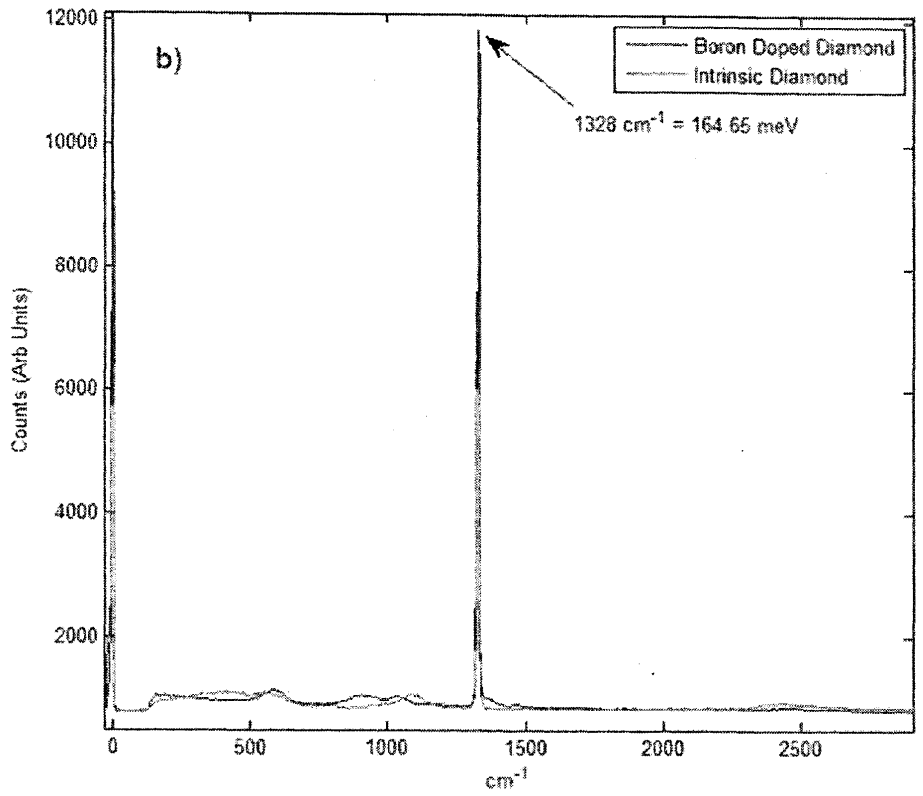


FIG. 4. Vibrational spectra of the C-H bond on the monolayer hydrogen-covered diamond C(100)-(2×1) at 300 K, solid line, and 700 K, dashed line.

PRB 60 16 972

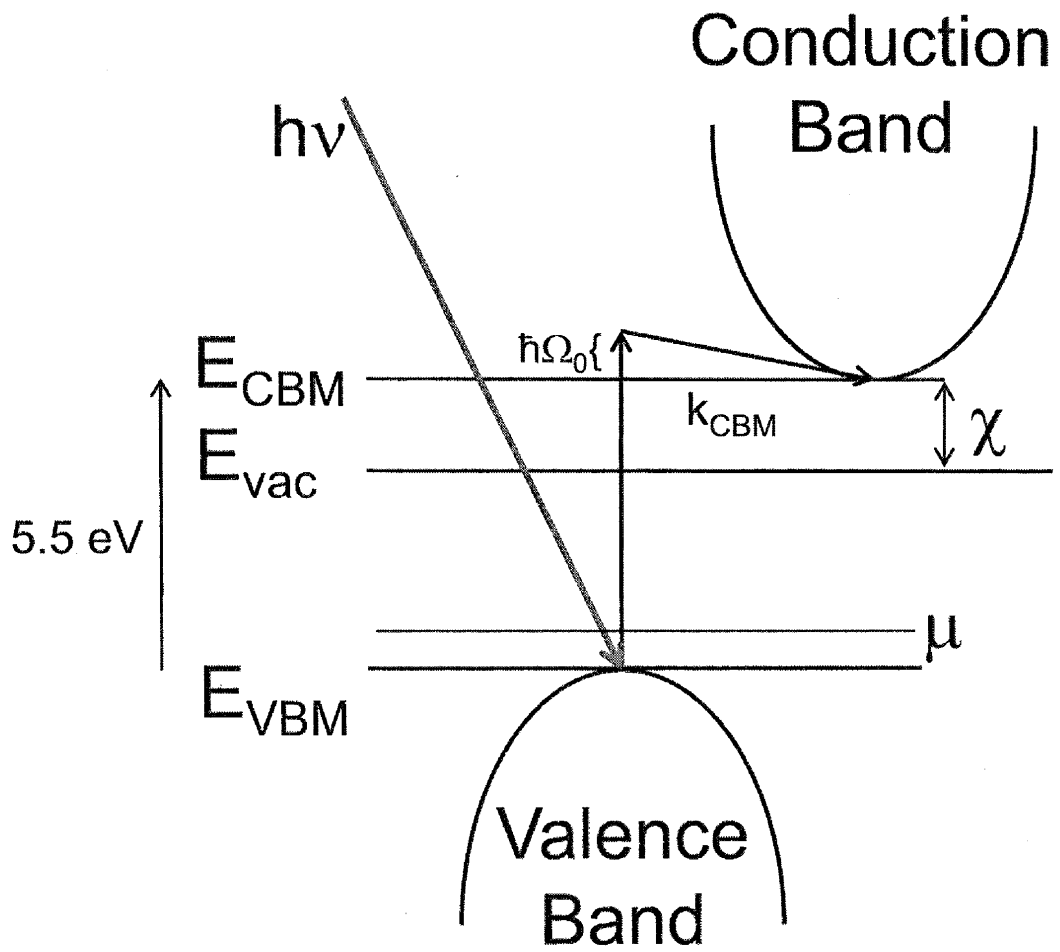
Surface, Zone Center

Our Raman Data

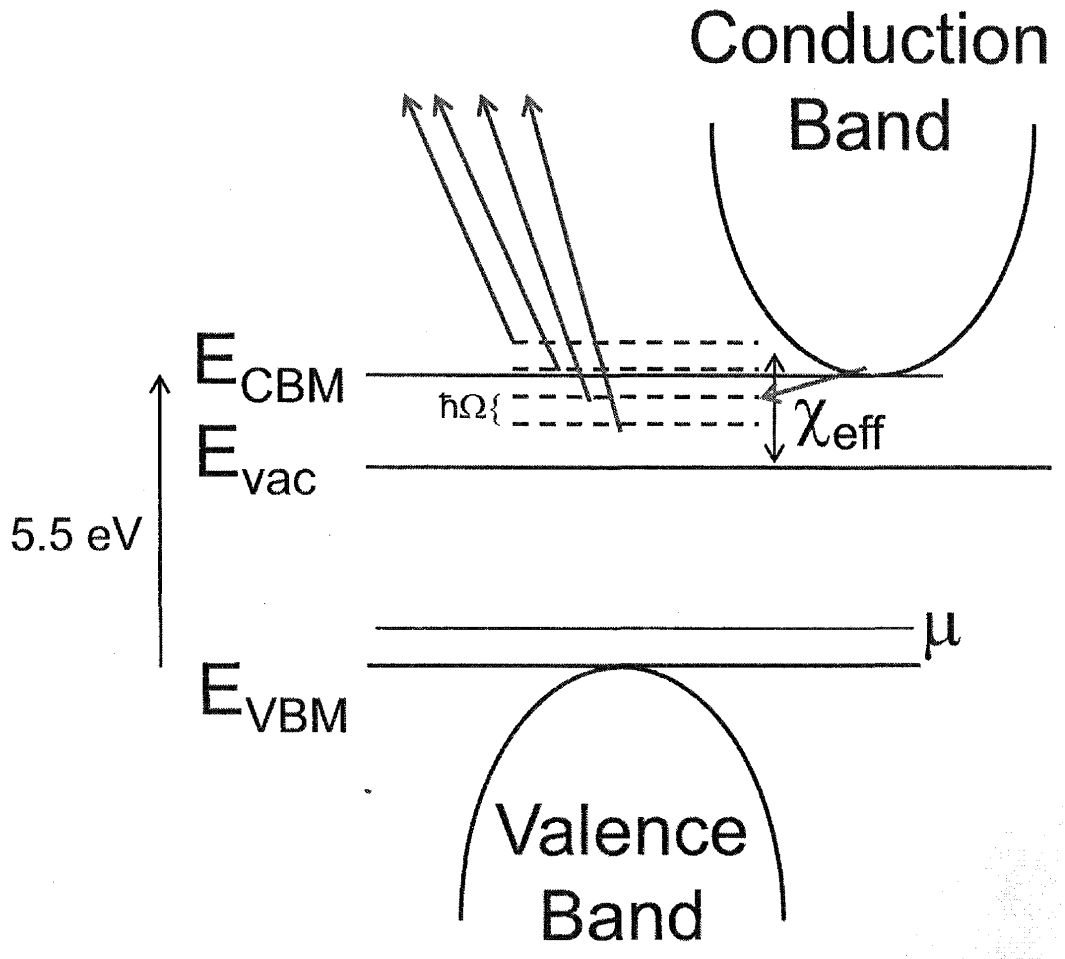


Measurement in the Bulk – Zone Center phonon cannot account for the ARPES data. No significant softening of modes with doping. Cannot account for mode energy we observe in ARPES

Excitation in the Bulk



Emission at the Surface



Quantum Mechanics

In the Franck-Condon picture, the many-body wavefunction of the N electron conduction band state strongly overlaps with the many-body wavefunction of the N-1 electron final state including phonons of momentum k and a free electron in the vacuum.

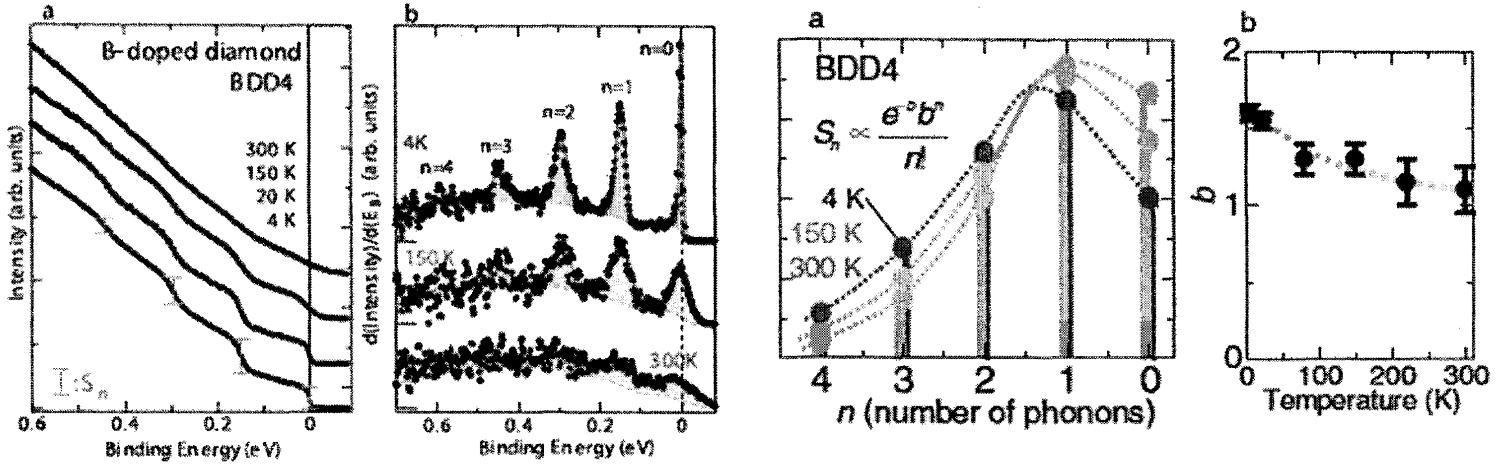
The N electron state, the new "ground state", is metastable due to strong e-ph coupling, inhibition of decay to the original ground state by photon emission (NEA surface) and inhibition of direct emission to the vacuum due to kinematic constraints.

The Surface/Sample is Important for NEA!

Bad Surf?

Difficult Analysis

Same Answer!



We find the SAME e-ph coupling at RT in our .01% B/C sample as they find in a 3.7% sample! With MUCH better data.

Summary & Conclusions

- (Laser) ARPES provides unique information about angle and energy distribution of photoelectrons
- Laser ARPES gives unique insight into how NEA materials work
- ARPES combined with some ancillary measurements gives a *very* complete picture of system electronic physics
- For H:C[100] there is now a clear program for engineering as well as developing analogous systems
- ARPES well suited for identifying "ideal" photocathodes with intrinsically low emittance and high QE

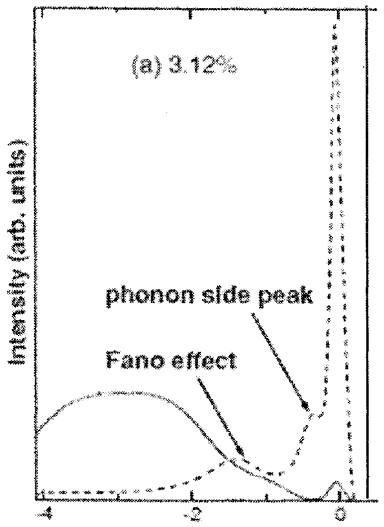
Useful ARPES References

"Photoelectron Spectroscopy, Principles and Applications", Third Edition, Stefan Hüfner, Springer

"Angle-resolved photoemission studies of the cuprate superconductors", Andrea Damascelli, Zahid Hussain, Zhi-Xun Shen, Rev. Mod. Phys. 75, 473 (2003)

"High Resolution ARPES", Stefan Hüfner, Springer

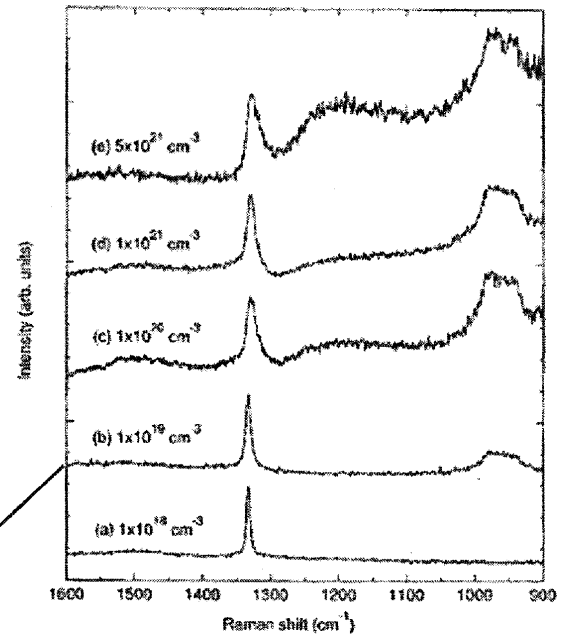
Fano Resonance Effects?

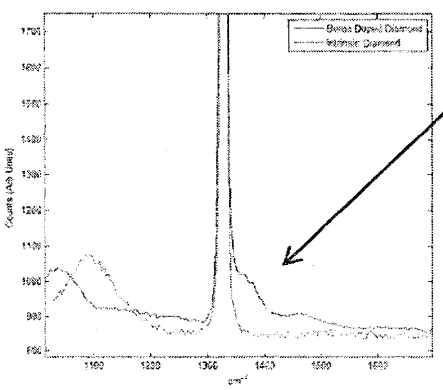


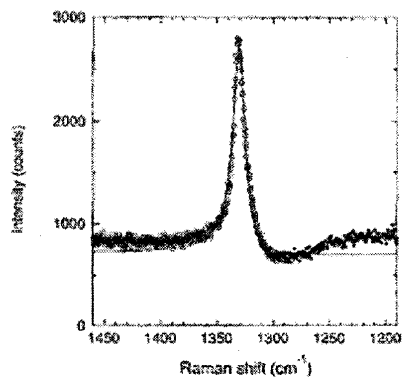
PHYSICAL REVIEW B 77, 045207 (2008)

Coexistence of localization and itineracy of electrons in boron-doped diamond

Raman







Appl. Phys. Lett., Vol. 66, No. 5, 30 January 1995

Synchrotron vs. Laser By the Numbers

U13UB – Undulator + NIM

- <=10^{13} photons/second
- At ~5-10 meV resolution (for bright samples at peak ring current)
- 15-25 eV photon energy
- ~100 μm^2 spot size
- ~10 Angstrom Probing Depth
- >=.01 Inv Angstrom k resolution
- 300 ps to 2 ns pulse duration
- 52.5 MHz rep rate
- Horizontal Polarization
- Lives at a large, communal facility
- Multiple BZ Coverage

6 eV Laser

- ~10^{15} photons/second
- At .5 meV resolution
- ~6.05 eV photon energy
- ~10 μm^2 spot size
- Up to 10 nm probing depth (?)
- >.001 $Å^{-1}$ k resolution
- 2 ps pulses
- 105 MHz rep rate or integer fractions thereof
- Any polarization we want!
- Coherent, Gaussian Beam!
- Can live on a table top!
- ~.62 $Å^{-1}$ max k point reachable