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SMR. 628 - 28

Research Workshop in Condensed Matter,
Atomic and Molecular Physics
(22 June - 11 September 1992)

Working Party on:
"Energy Transfer in Interactions with
Surfaces and Adsorbates"
(31 August - 11 September 1992)

# "EELS Study of Surface Plasmon Energy and Dispersion on Ag (001) and Ag (011)

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①

# EELS STUDY OF SURFACE PLASMON ENERGY AND DISPERSION ON Ag (001) AND Ag (011)

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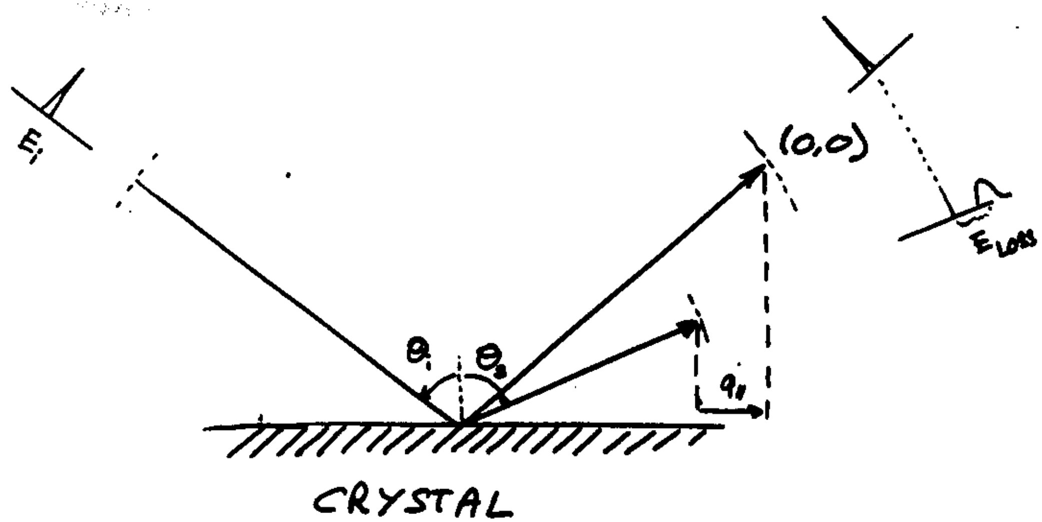
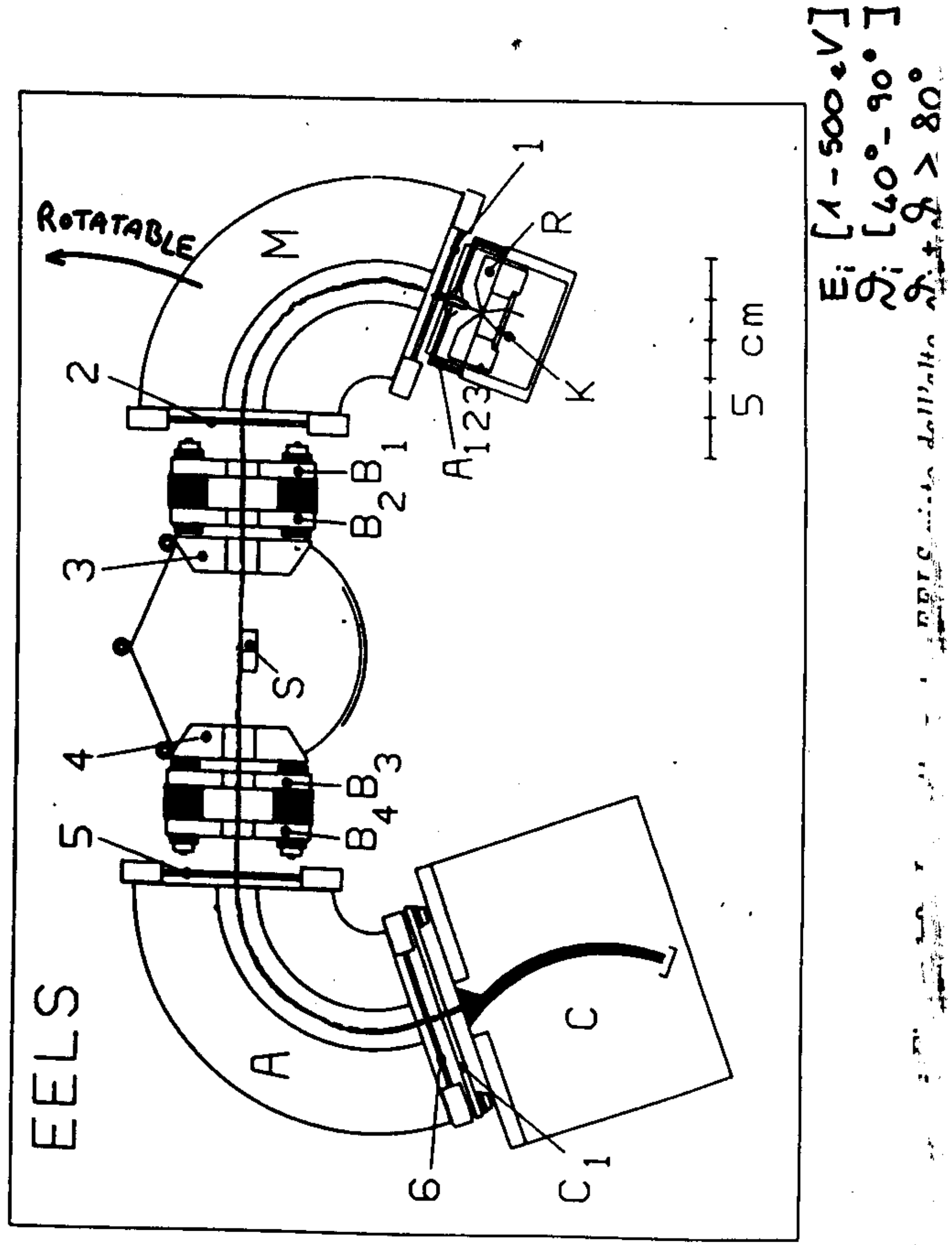
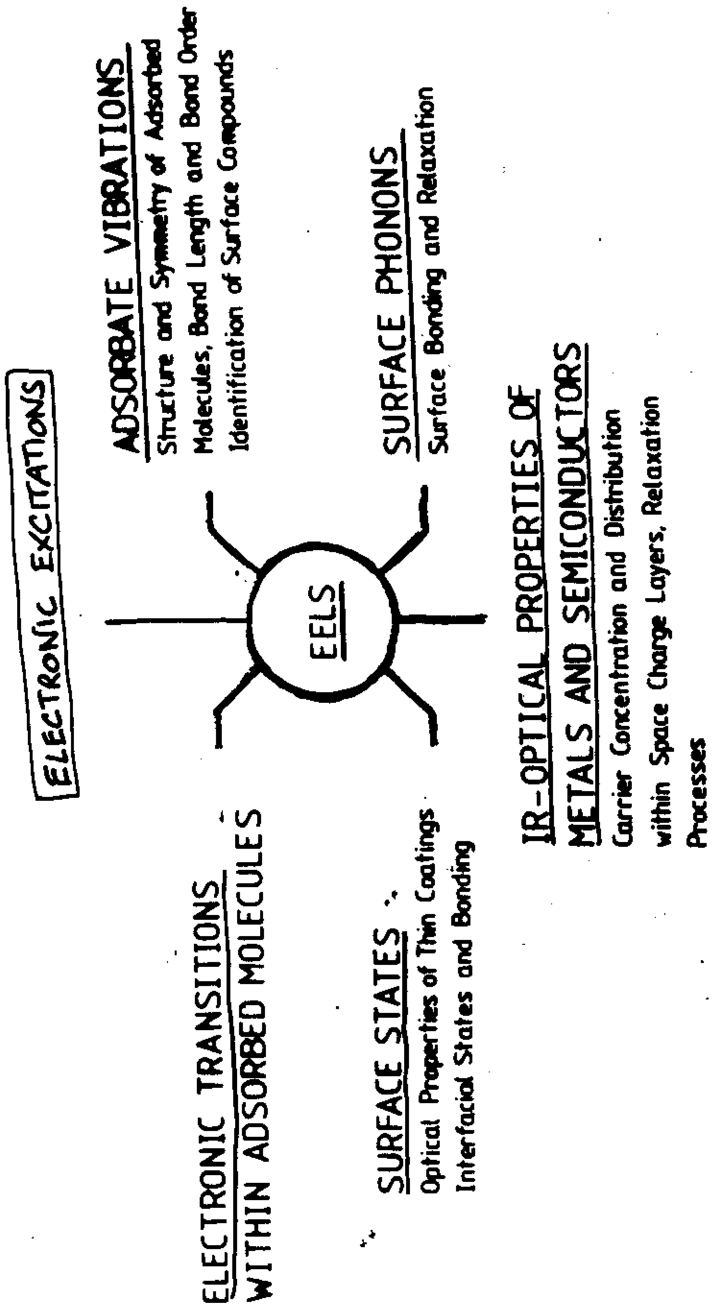
M. LAZZARINO
F. BIGGIO

DIPARTIMENTO DI FISICA - GENOA ITALY

# Low Energy Angle Resolved Electron Energy Loss Spectroscopy






# ELECTRONIC EXCITATIONS

## MOTIVATION:

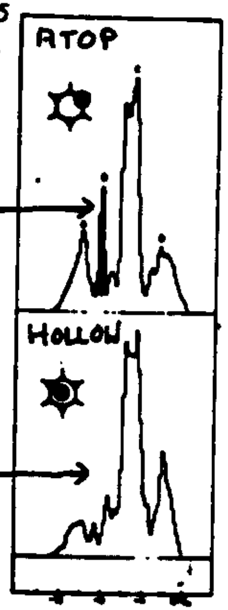
The dynamical response of electrons at a metal surface is related to different chemical and physical properties such as:

- sticking coefficient of incoming molecules
- nature of Van der Waals forces
- energy transfer from excited states
- optical properties
- non-linear surface response
- photoelectric effect

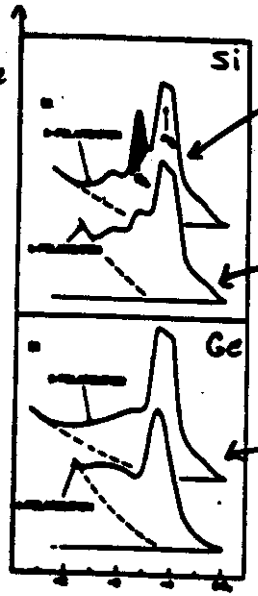
The dynamical response can be investigated by EELS measuring <u>SURFACE PLASMON DISPERSION</u>

## WHAT IF INTENSITIES MUST BE ANALYZED?

QUESTION: WHERE DOES Cl SIT ON Si(111) AND ON Ge(111)?




Schlüter, Rowe, Margaritondo, Ho + Cohen PRL (1976)




FOR Cl/Si SEE $p_z$ PEAK IF $E_\perp \neq 0$

NO PEAK IF $E_\perp = 0$

FOR Cl/Ge SEE NO $p_z$ PEAK IN EITHER POLARIZATION

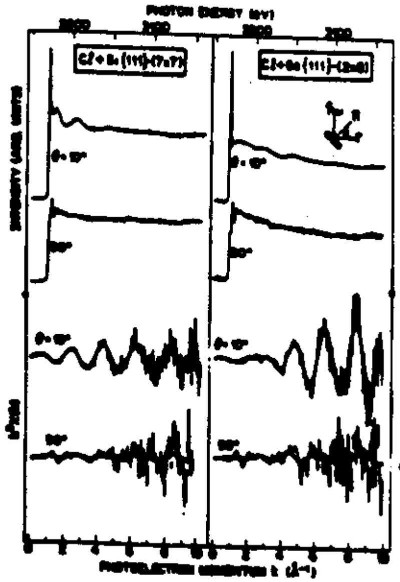
THIS WAS CITED AS EVIDENCE THAT Cl SITS IN THE HOLLOWS ON Ge(111) AND ATOP SITES ON Si.

3-fold site

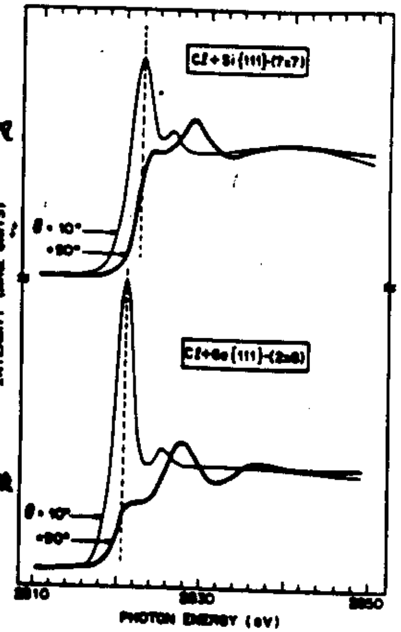
QUESTION: MATRIX ELEM's DIFF'T?

COLLOQ

XAFS EXPERIMENTS (1983) ⇒ SAME SITE ON Si AND Ge: (EXAFS ↔ INTERF. OF OUTGOING e W.F. IN X-RAY ABSORPTION; NEXAFS ↔ DENSITY OF FINAL STATES NEAR EDGE)




CITRIN, ROWE + EISENBERGER (83)




IP(Cl) = 282...

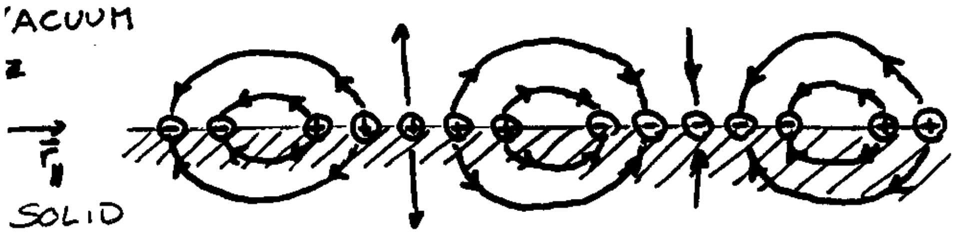
EXAFS POLARIZATION DEPENDENCE + INTERATOMIC DISTANCES ⇒ ATOP SITE IN BOTH CASES

NEXAFS MEASM'T OF UNFILLED STATES CONFIRM GEOMETRY

CONCLUSION: UPS ANALYSIS OF INTENSITIES IS NOT RELIABLE UNLESS MATRIX ELEMENTS EFFECTS ARE KNOWN ⇒ NEED TO KNOW WAVE FN'S AND FIELD

COLLOQ

# SURFACE PLASMON




$$\phi(\vec{r}) = \phi_0 \, e^{i\vec{q}_\parallel \cdot \vec{r}_\parallel} \, e^{-q_\parallel |z|}$$

$$\begin{cases} E_z(z=0^+) = \phi_0 \, q_\parallel \, e^{i\vec{q}_\parallel \cdot \vec{r}_\parallel} \, \cancel{e^{-q_\parallel |z|}} \\ E_z(z=0^-) = -\phi_0 \, q_\parallel \, e^{i\vec{q}_\parallel \cdot \vec{r}_\parallel} \, \cancel{e^{-q_\parallel |z|}} \end{cases}$$

$\vec{\nabla} \cdot \vec{D} = 0$ ($\vec{D}_z$ continuous across surface)

$$\varepsilon(\omega_{sp}) = -1$$

<u>for simple metals</u> $\varepsilon(\omega) = 1 - \frac{\omega_p^2}{\omega^2}$

$$\Rightarrow \omega_{sp} = \frac{\omega_p}{\sqrt{2}}$$

① DISPERSION OF SURFACE PLASMONS

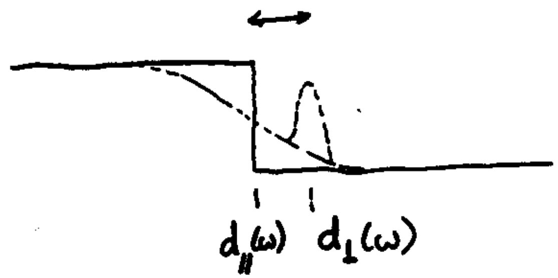
THEORETICAL APPROACH WITHIN JELLIUM MODEL

(P.J. FEIBELMAN 1973, F. FLORES AND F. GARCIA-MOLINER 1972, J. HARRIS AND GRIFFIN 1971)

$$\omega_{sp}(q_\parallel) = \omega_{sp}(0) \left( 1 - \frac{1}{2} d_\perp(\omega) \, q_\parallel + o(q_\parallel^2) \right)$$

$d_\perp(\omega) \equiv$ CENTROID OF INDUCED CHARGE

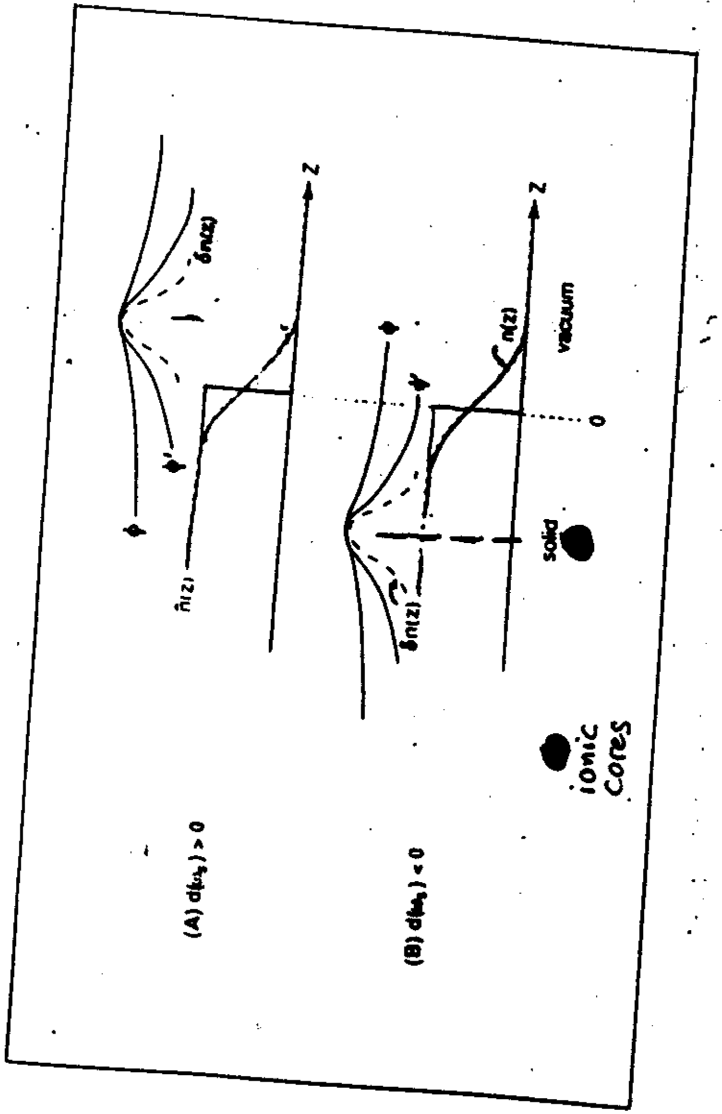
$d_\perp(\omega) > 0$ FOR SIMPLE METALS




PHYSICAL REASON: THE ELECTRON GAS IS MORE COMPRESSIBLE WHERE ITS DENSITY IS LOW (FEIBELMAN '89)

EXPERIMENTAL VERIFICATION ON Na, K, Cs, Mg FILMS BY K.D. TSUEI AND W. PLUMMER (PRL 1989)

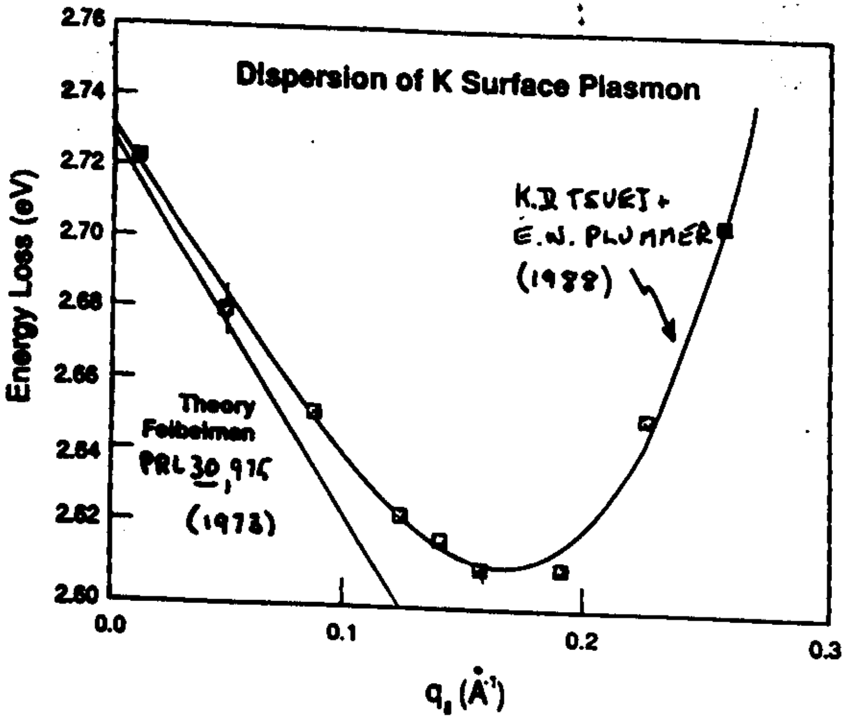
PHYSICAL INTERPRETATION OF SURFACE-PLASMON DISPERSION
( , FEIBELMAN PR 1989)




EXAMPLE:

$$\left.\frac{d\omega_{surf.\ plasmon}}{dq_{\parallel}}\right|_{q_{\parallel}=0} = -\frac{\omega_{sp}}{2}\left[d_{\perp}(\omega_{sp}) - d_{\parallel}(\omega_{sp})\right]$$

$$\omega_{sp} = \frac{\omega_p}{\sqrt{2}}$$




K.D. TSUEI, E.W. PLUMMER, P.J. FEIBELMAN PRL 63, 2256, (1989)

EXP: K.D. TSUEI, E.W. PLUMMER, A. LIEBSCH, K. KEMPA, P. BAKSHI (PRL 1990)

THEORY: BENNETT (1975)

VOLUME 64, NUMBER 1 PHYSICAL REVIEW LETTERS 1 JANUARY 1990

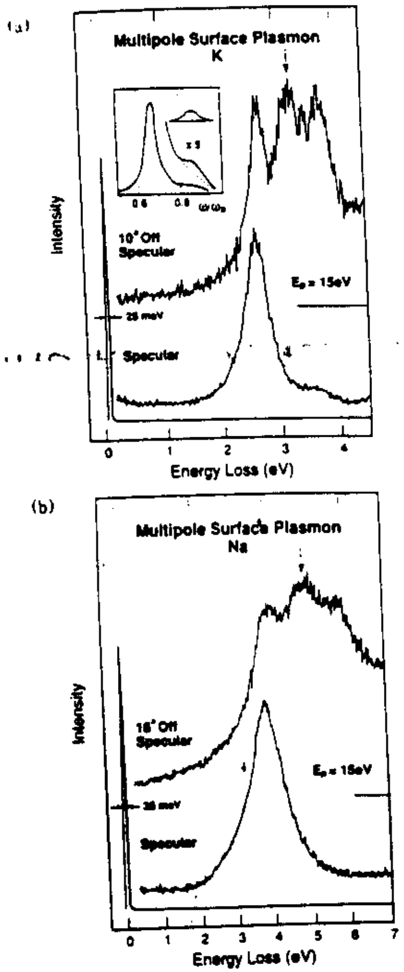



FIG. 1. Electron-energy-loss spectra for (a) K and (b) Na. The bottom curves in (a) and (b) are measurements in the specular direction and the top curves (a) 10° and (b) 16° off of the specular direction. Inset in (a): The calculated loss function Im$g(q,\omega)$ at $q$ = 0.11 Å$^{-1}$.

VOLUME 64, NUMBER 1 PHYSICAL I

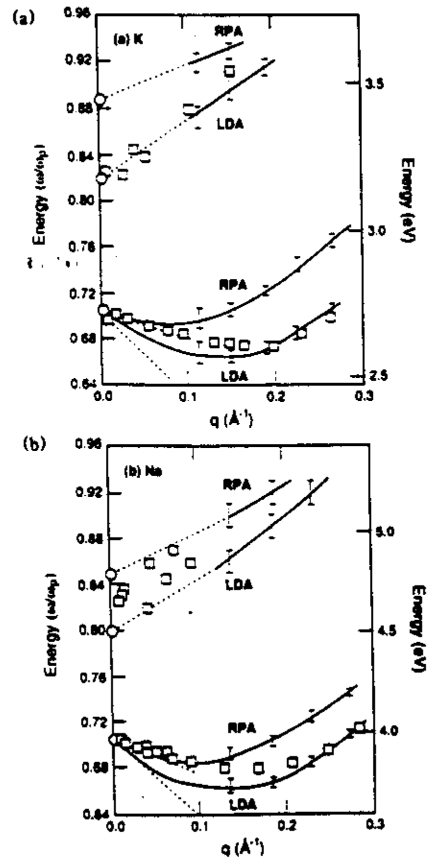



FIG. 2. Momentum dispersion of surface plasmon and multipole plasmon modes for (a) K and (b) Na. The squares ar experimental data, the vertical bars denote the results of the LDA and RPA response calculations, the solid lines are only guide to the eye, the dashed lines are the calculated linea slopes at small $q$ from Eq. (2) with $d(\omega)$ taken from Ref. 17 and the circles denote the $q$ = 0 limits for both modes (Ref 17).

# SURFACE PLASMON IN PRESENCE OF d-electrons

- no theoretical forecast for surface-plasmon dispersion
- transmission experiments on Ag-films:

  $\hbar\omega_p = 3{,}78$ eV $\quad \hbar\omega_{sp} = 3{,}63$ eV

  (Daniels 1967, Zacharias 1970)
- d → sp transition at 3,86 eV (P. Winsemius et al. 1976)
- Low ENERGY EELS on Ag (111)

  $\hbar\omega_{sp}(q_\parallel = 0) = 3{,}69$ eV

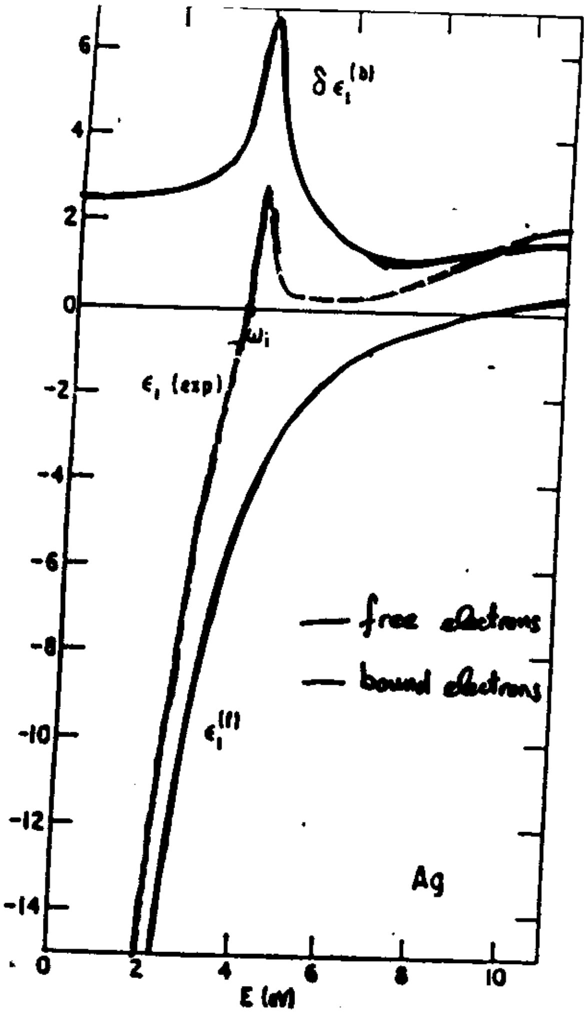
  positive dispersion

  (Contini and Layet SSC 1987)
- Low ENERGY EELS on Ag (111) and Ag (110)

  $\hbar\omega_{sp}$ face and direction dependent

  quadratic dispersion

  (S. Suto, K.D. Tsuei, Plummer PRL '8



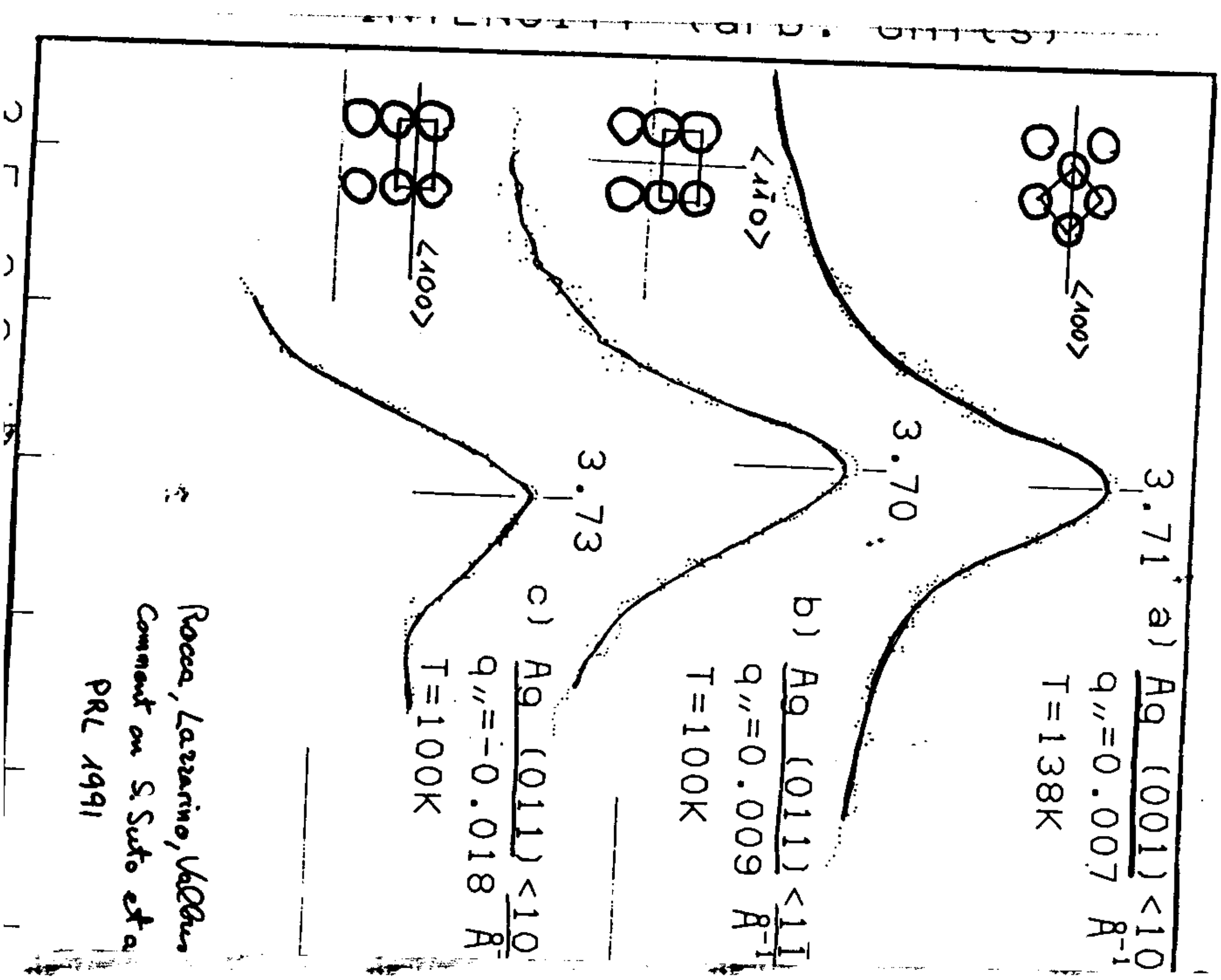

DIELECTRIC CONSTANT FOR Ag:

$\epsilon_1^f$ FREE ELECTRON CONTRIBUTION

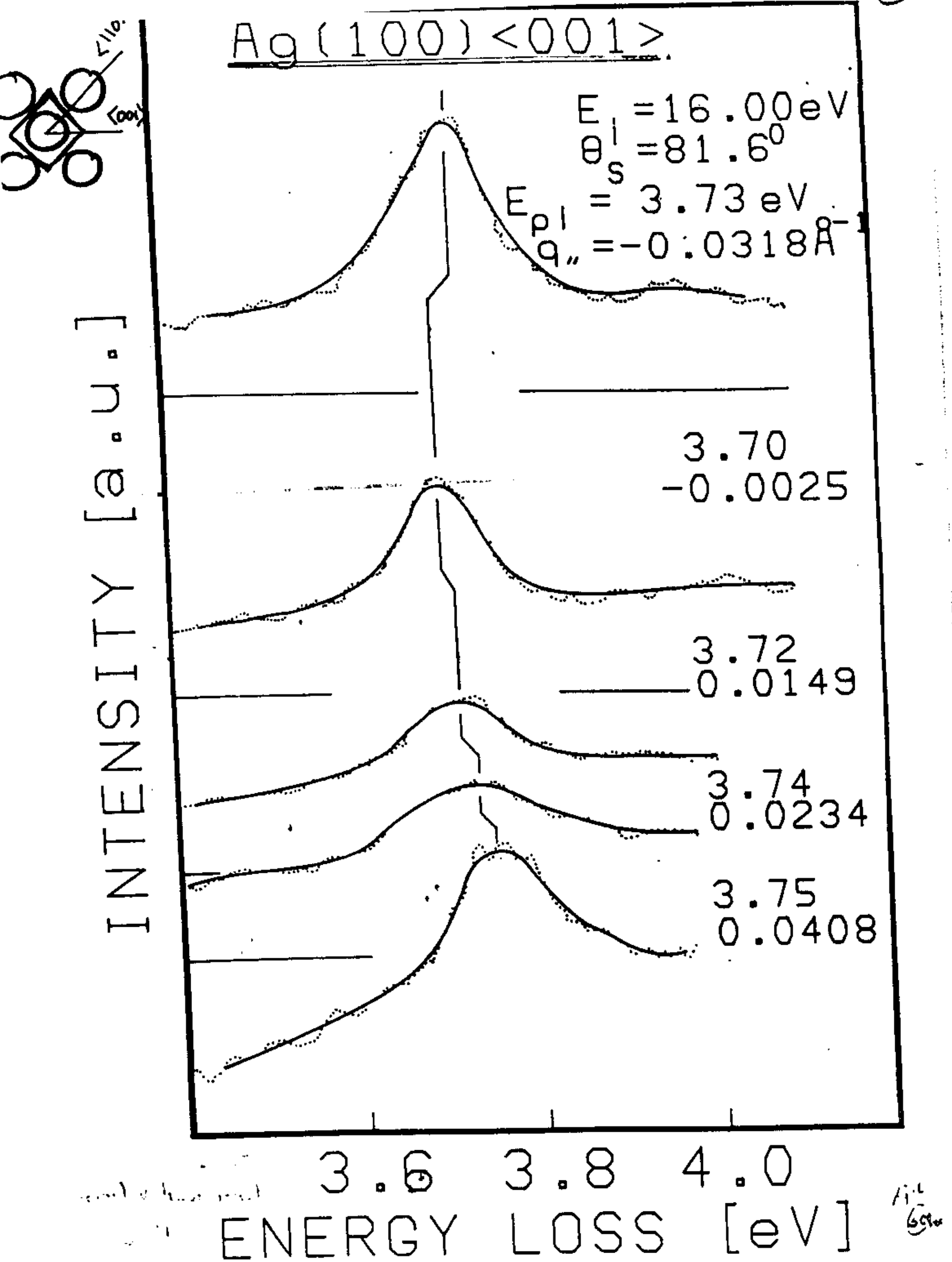
$\epsilon_1^b$ BOUND ELECTRON CONTRIBUTION

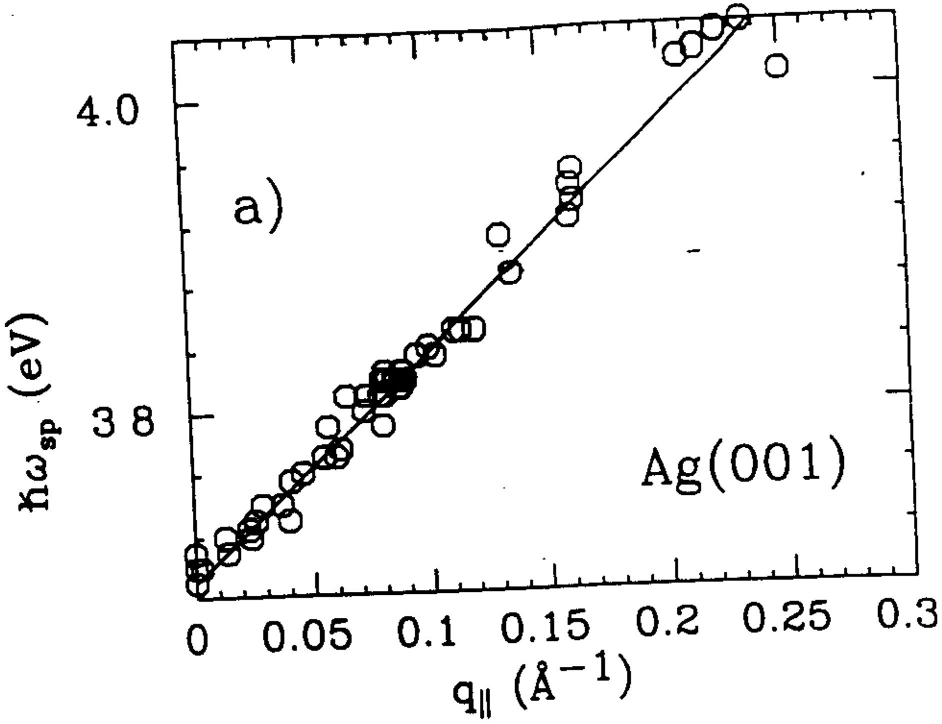
$\epsilon_1 = \epsilon_1^f + \epsilon_1^b$

$\omega_{sp}$ is determined by $\epsilon_1 = -1$




Rocca, Lazzarino, Valbus
Comment on S. Suto et a
PRL 1991

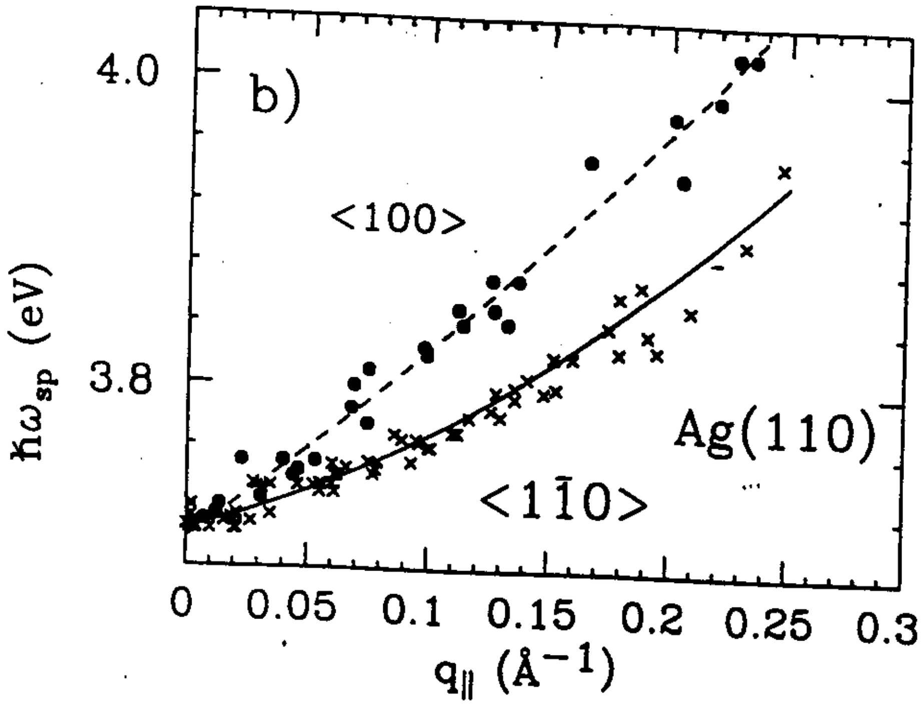


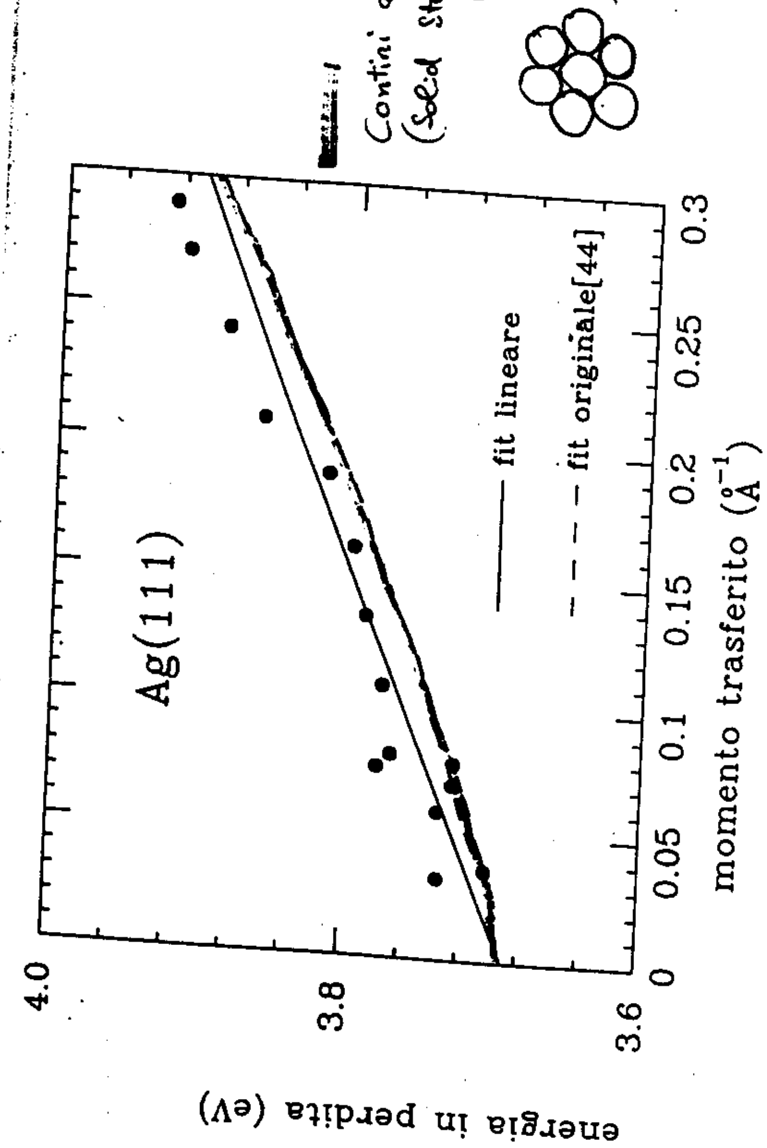

$\hbar\omega_{sp} = 3{,}69\ eV + 1{,}5\ q_{\parallel}\ eV\text{Å}$

Rocca, Valbusa

PRL 1990



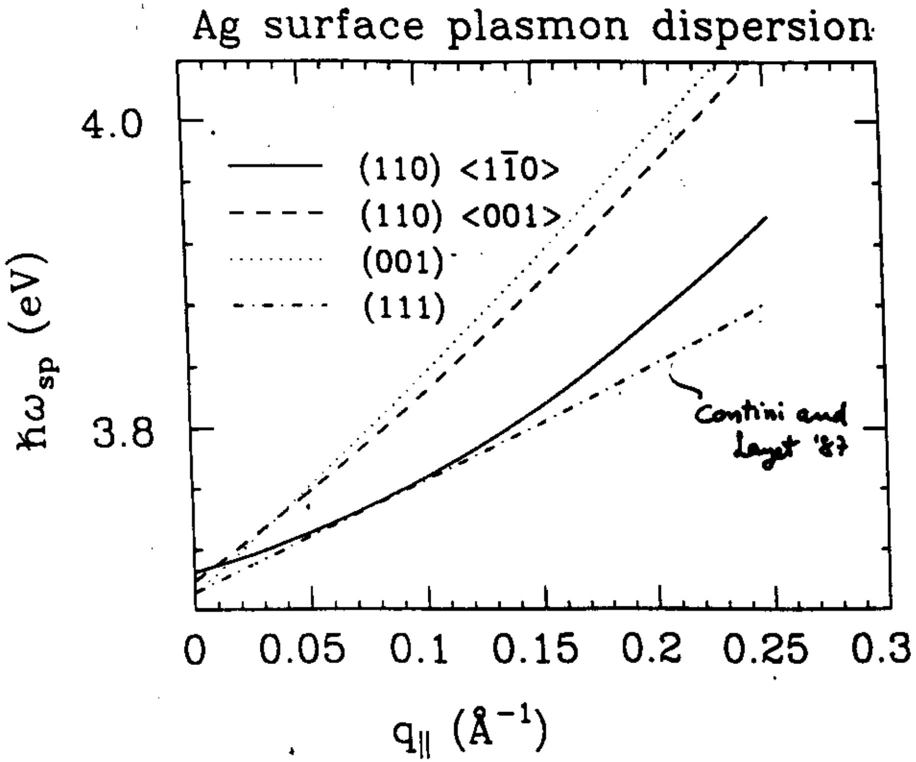

Contini and Layet (Solid State Commun 1987)




Ag(001)

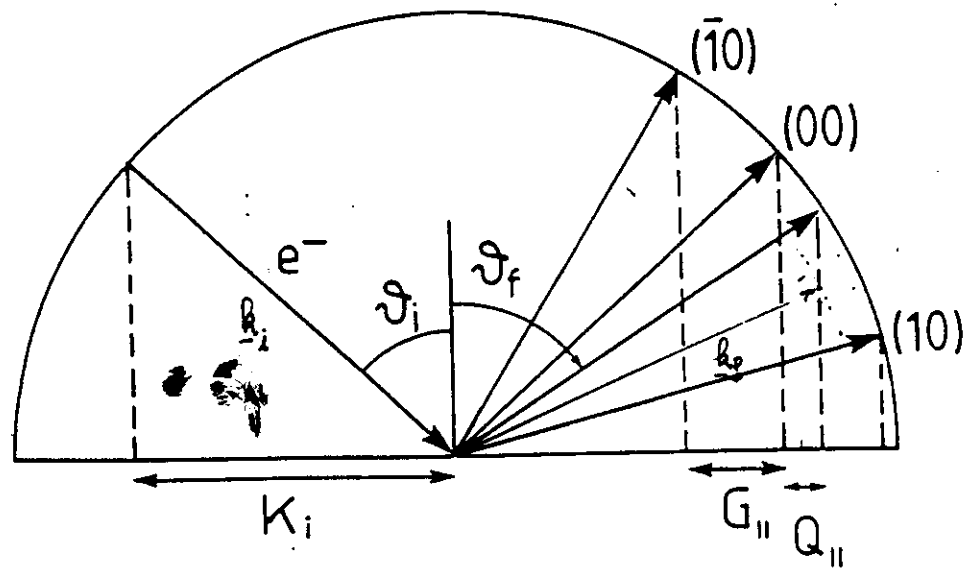
Ag(110)<100> $\hbar\omega_{sp} = 3.70\,eV + 1.13\,q_{\parallel}\,eVÅ + 1.1\,q_{\parallel}^2\,eVÅ^2$ Rocca, Lazzarino, Valbusa (PRL'92)

Ag(110) <1$\bar{1}$0> $\hbar\omega_{sp} = 3{,}70\,eV + 0.42\,q_{\parallel}\,eVÅ + 2.1\,q_{\parallel}^2\,eVÅ^2$



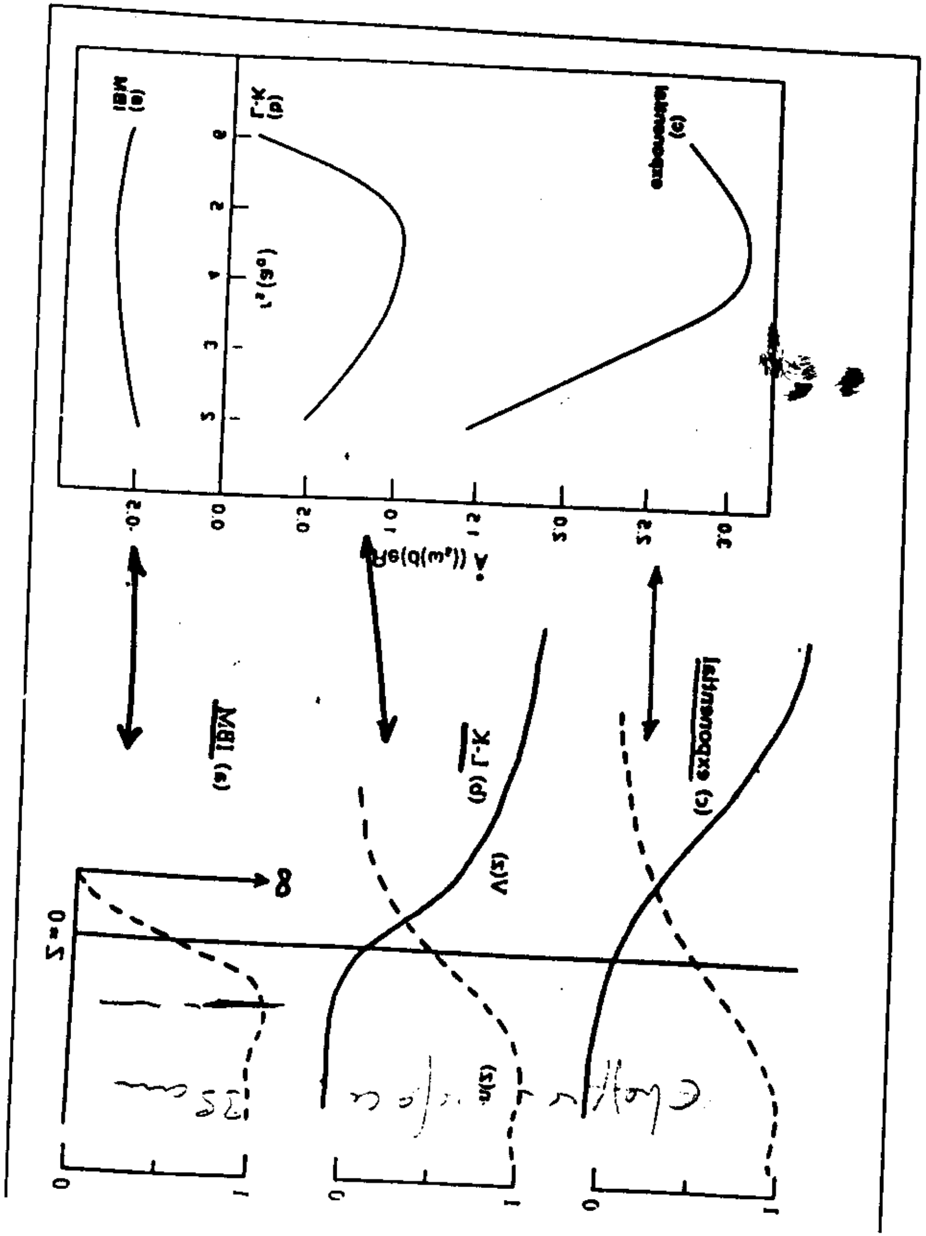

Rocca Lazzarino Valbusa
PRL '92

KINEMATIC OF EXPERIMENT:
ENERGY AND PARALLEL MOMENTUM CONSERVATION




$$E_{Loss} = \left(k_i^2 - k_f^2\right)\frac{\hbar^2}{2m}$$

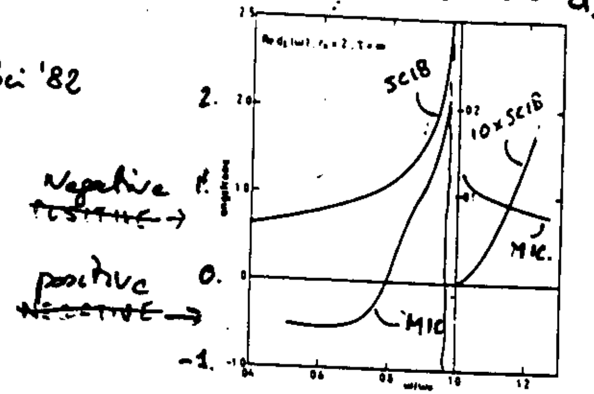
$$q_{\parallel} = \sqrt{\frac{2mE_i}{\hbar}}\left(\operatorname{sen}\theta_i - \sqrt{1-\frac{E_{Loss}}{E_i}}\,\operatorname{sen}\theta_s\right)$$



d(ω) for VARIOUS MODELS (Tsuei PhD Thesis)

P.J. Feibelman, Prog in Surf. Sci '82

"SURFACE POSITION" $d_\perp(\omega)$




QUANTITATIVELY THESE SIMPLIFICATIONS DO A VERY POOR JOB

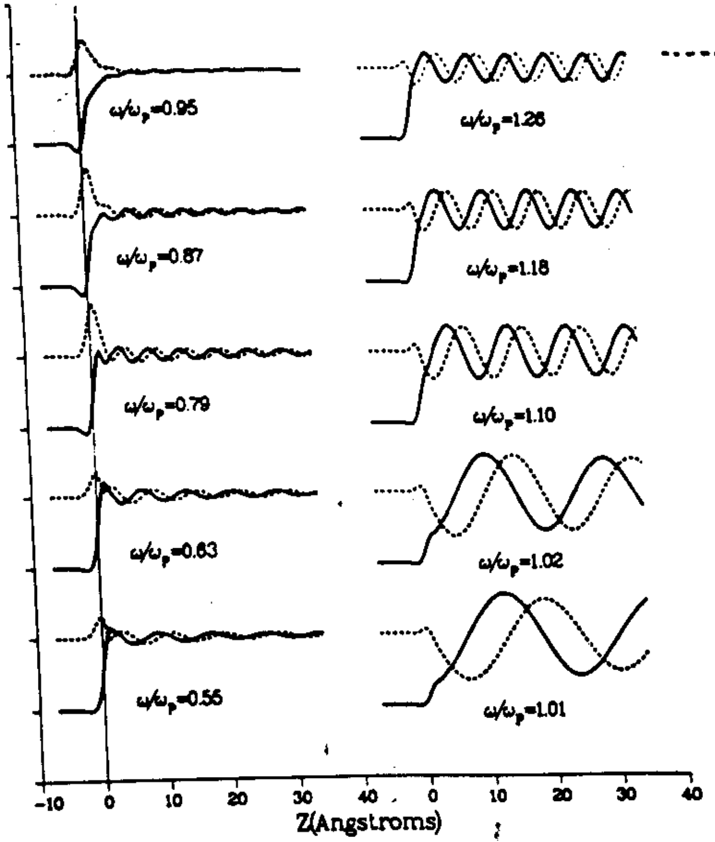
in case of Ag $\frac{\omega_{sp}}{\omega_p} \sim 0.98$

$\Rightarrow$ the electron gas is already compressible at $\omega_{sp}$

2 (Al) FIELDS VS. FREQUENCY, LANG-KOHN GD. STI.

—— → $\mathrm{Re}\left[\frac{E_\perp(z) - E_\perp^{IN}}{E_\perp^{IN} - E_\perp^{OUT}}\right]$

······ → $\mathrm{Im}\left[\frac{E_\perp(z) - E_\perp^{IN}}{E_\perp^{IN} - E_\perp^{OUT}}\right]$




↑ $\omega < \omega_p$

REAL PART LOOKS LIKE "TEXTBOOK TH."
WHAT IS Im PART ?

↑ $\omega > \omega_p$

BULK PLASMON EXCITATION
AMPLITUDE + PHASE ARE SURF. PROPERTIES

at small $q_{\parallel}$ (Feibelman Prog in Surf Sci 1982)

$$\varepsilon(\omega) + 1 - (\varepsilon(\omega) - 1)(d_\perp(\omega) - d_\parallel(\omega))\, q_\parallel = 0$$

$$\Rightarrow \quad \frac{\Delta\omega}{\omega_{sp}} \propto -\frac{1}{\varepsilon_b(\omega_{sp}) + 1}\, d_\perp(\omega_{sp})\, q_\parallel \qquad (*)$$

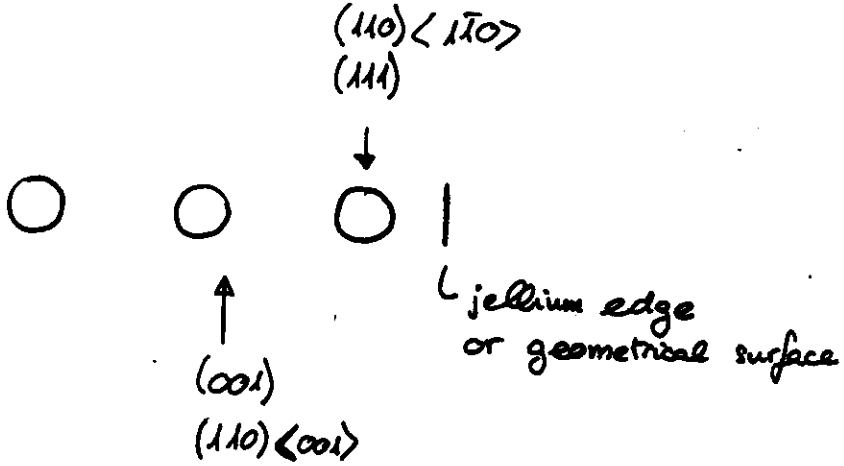
with $\epsilon = \varepsilon_b + \varepsilon_f$ and $\varepsilon_f = -\frac{\omega_p^2}{\omega^2}$ free electron contribution; $\varepsilon_b$ bound electron contribution

for Ag $\varepsilon_b(\omega_{sp}) \simeq 5.3$

| FACE | DIRECTION | SLOPE | $d_\perp(\omega_{sp})$ | $a_\perp$ |
|---|---|---|---|---|
| (111) | | 0.8 eV Å | -1.3 Å | -1.18 Å |
| (001) | | 1,5 eV Å | -2.6 Å | -1.02 Å |
| (110) | <001> | 1.13 eV Å | -1.9 Å | -0,72 Å |
| (110) | <1$\bar{1}$0> | 0.62 eV Å | -0.7 Å | -0,72 Å |

$d_\perp(\omega_{sp})$ as from eq. (*)

$a_\perp$ geometrical surface to ionic cores distance




COINCIDENCE ?

but: independently of model eq (*)

$$d_\perp(111) < d_\perp(001)$$

Similar problematic on Clusters

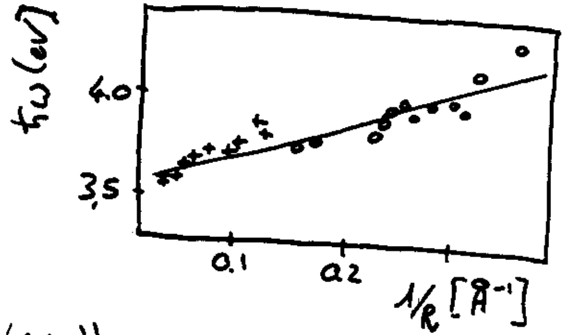
$$\frac{\Delta\hbar\omega}{\hbar\omega_0} = \frac{3}{2+\frac{\varepsilon_d(\omega_0)}{\varepsilon_m}} \; \frac{\mathrm{Re}\left(d_\perp\left(\frac{\omega_0}{\omega_d}\right)\right)}{R}$$

where $\varepsilon_d$ dielectric function of bound electrons
$\varepsilon_m$ " " : of embedding medium (=
$R$ radius of the cluster

(P. Apell, Å. Ljungbert Phys. Scr. 26 (1982) 113

alkali metals $d_\perp < 0 \rightarrow$ red shift

Ag:




blue shift

(J. Tiggesbäumker et al. '92

$$\mathrm{Re}\left(d_\perp\left(\frac{\omega_0}{\omega_d}\right)\right) = -0{,}97\ \text{Å}$$

THEORETICAL INTERPRETATION

$\hbar\omega_p = 3{,}78$ eV

$\hbar\omega_{sp} = 3{,}69$ eV

$\hbar\omega_{d\rightarrow sp} = 3{,}86$ eV

- Plasmon and Surface Plasmon are collective excitations split off the $d \rightarrow sp$ band
- The $d \rightarrow sp$ transition can take place in presence of strong variations of electric fields near to the nuclei

$\Rightarrow$ stronger effect for Ag (001) than for (111)

(Feibelman SSL '92)

ON Ag (110)

MEASUREMENTS ON ELECTRO-CHEMICAL CELL

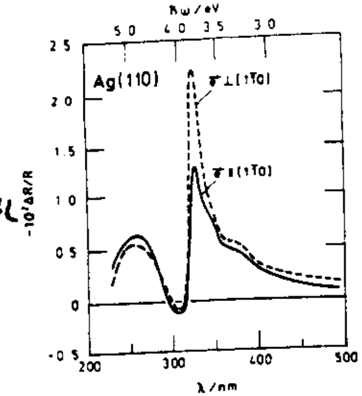



Fig. 2. Normal incidence electroreflectance spectra of Ag(110) in 0.5M $NaClO_4$, for two different crystallographic directions. Potential step is between −0.5 and 0.0 V (SCE).

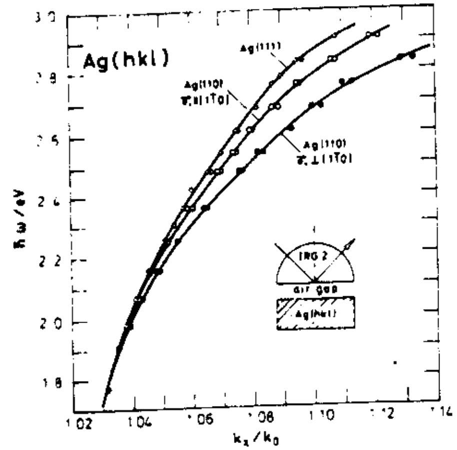
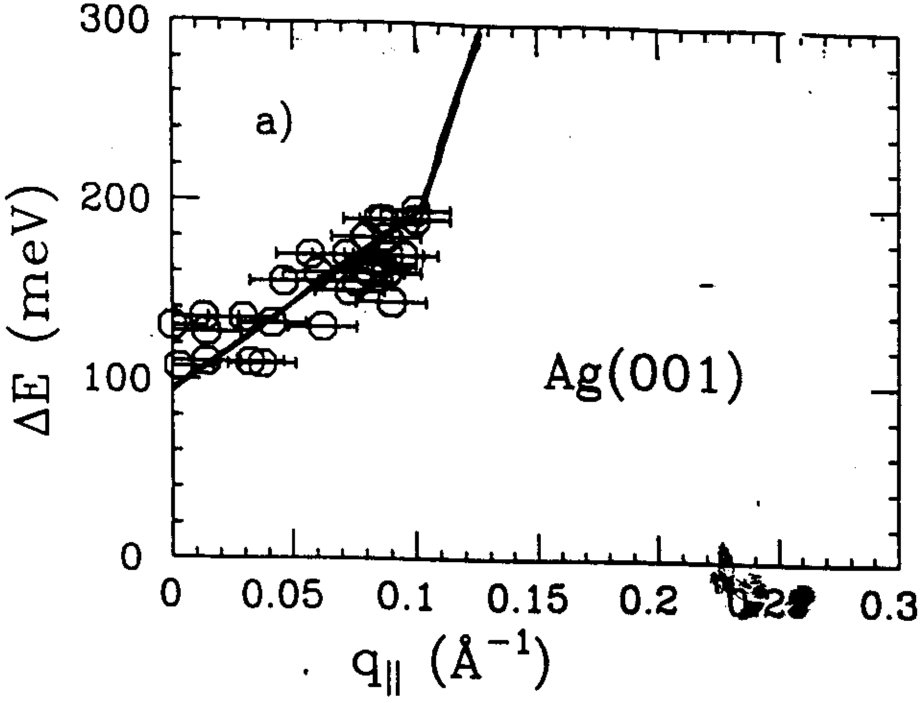


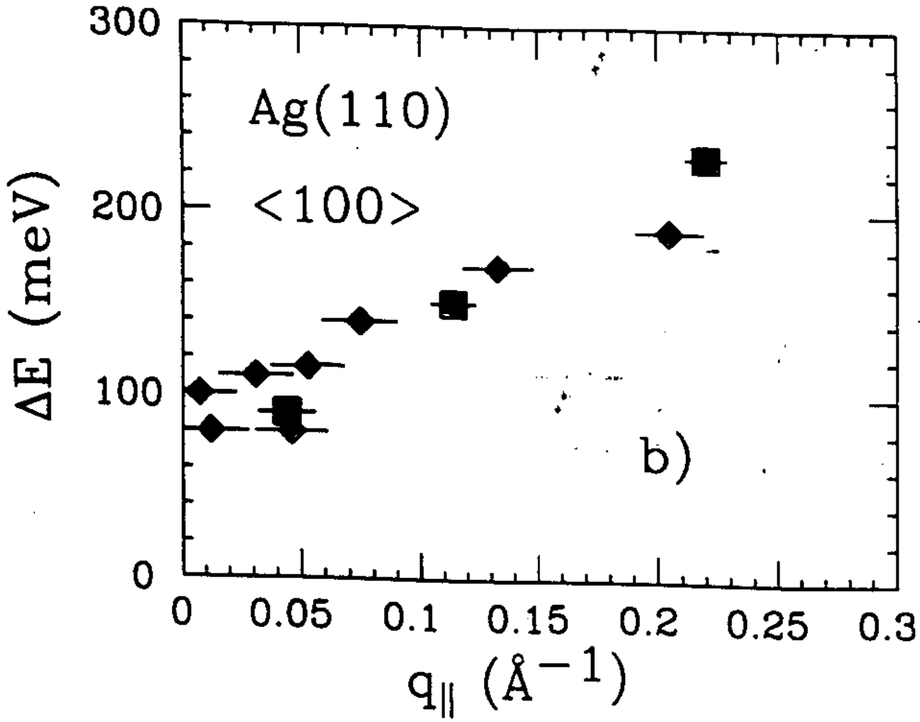

Fig. 3. Surface plasmon dispersion curves for Ag(111) and Ag(110).

Table 1
Real part of the complex dielectric constants of various Ag surfaces; the relative change in optical conductivity, $(\sigma_\perp - \sigma_\parallel)/\sigma_\parallel$, for $\varepsilon_i$ being perpendicular or parallel to $[1\bar{1}0]$ on a Ag(110) surface, is also given

| $\hbar\omega$ (eV) | $\varepsilon'_{Ag(111)}$ | $\varepsilon'_{Ag(110)}$ $\varepsilon_i \parallel [1\bar{1}0]$ | $\varepsilon'_{Ag(110)}$ $\varepsilon_i \perp [1\bar{1}0]$ | $\varepsilon'_{Ag(100)}$ | $10^2\,\Delta\sigma/\sigma_\parallel$ |
|---|---|---|---|---|---|
| 2.07 | −13.00 ± 0.10 | −12.59 ± 0.10 | −12.30 ± 0.10 | −12.5 | −1.62 |
| 2.16 | −11.75 | −11.67 | −11.07 | −11.4 | −3.60 |
| 2.25 | −10.66 | −10.37 | −9.84 | −10.1 | −3.47 |
| 2.36 | −9.53 | −9.17 | −8.51 | −8.7 | −4.72 |
| 2.48 | −8.30 | −8.00 | −7.29 | −7.5 | −5.63 |
| 2.54 | −7.92 ± 0.05 | −7.48 ± 0.05 | −6.78 ± 0.05 | −7.0 | −5.82 |
| 2.61 | −7.40 | −7.00 | −6.14 | −6.4 | −7.48 |
| 2.68 | −6.86 | −6.45 | −5.69 | −5.9 | −7.04 |
| 2.76 | −6.54 | −6.00 | −5.25 | −5.4 | −7.32 |
| 2.83 | −5.97 | −5.42 | −4.58 | −4.9 | −8.78 |
| 2.92 | −5.39 | −4.96 | − | −4.4 | − |

SURFACE PLASMON DAMPING




DAMPING INCREASES ABOVE E = 3,84 eV

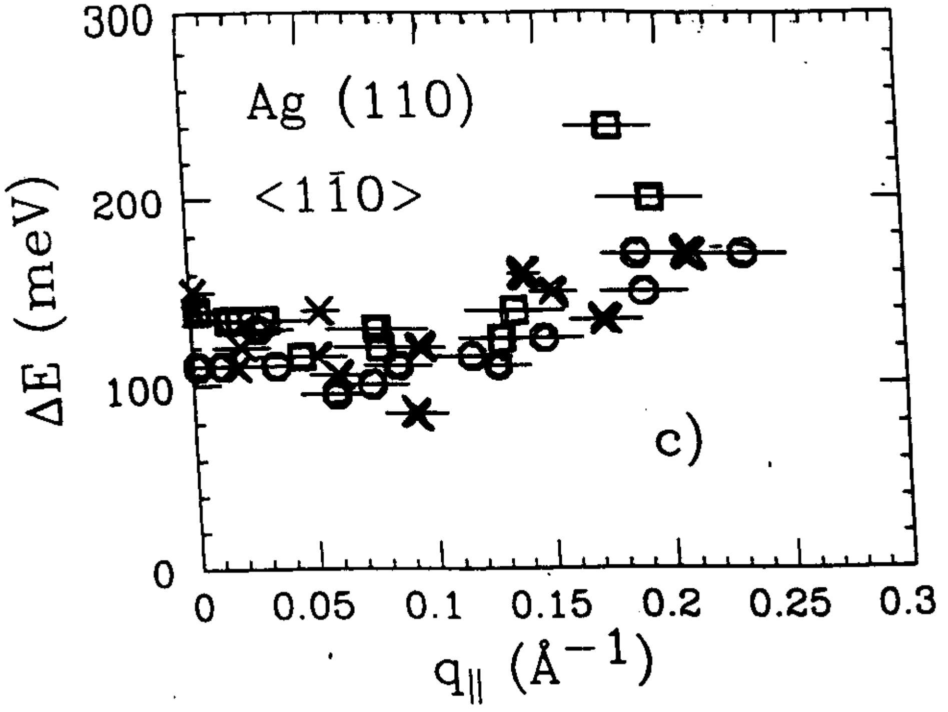
P. WINSEMIUS (J. PHYS F '76)

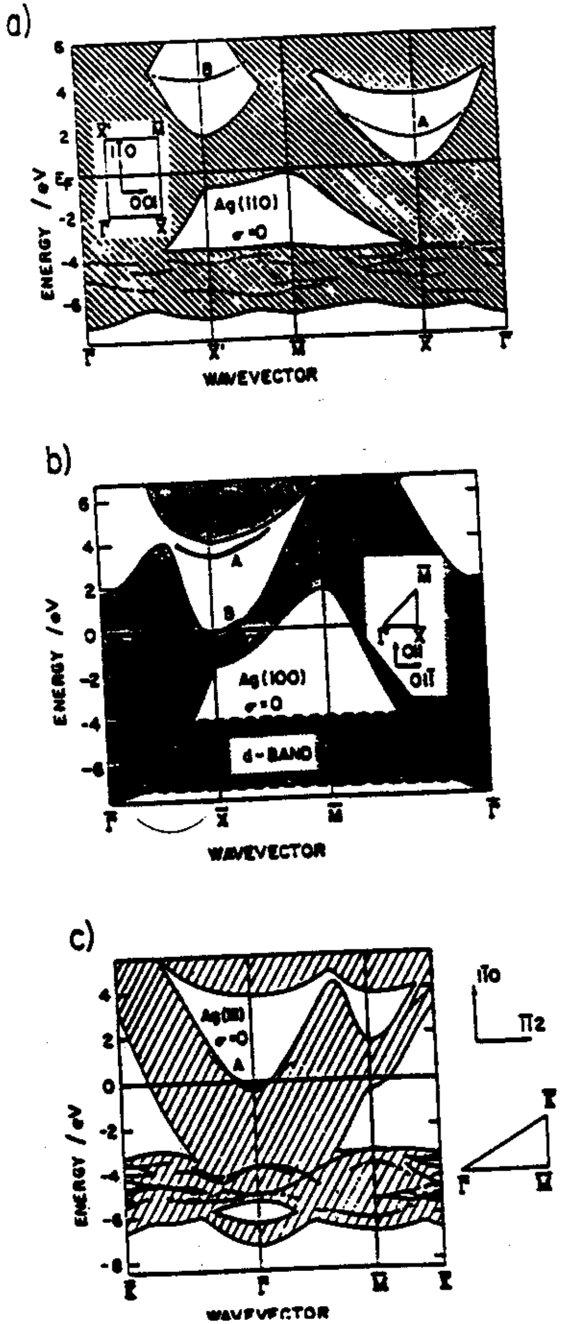
$d \rightarrow E_F$ ONSET 3,86 eV at T = 300K

TOP 3,98 eV

HOWEVER ...

SILVER SURFACES :




(110)

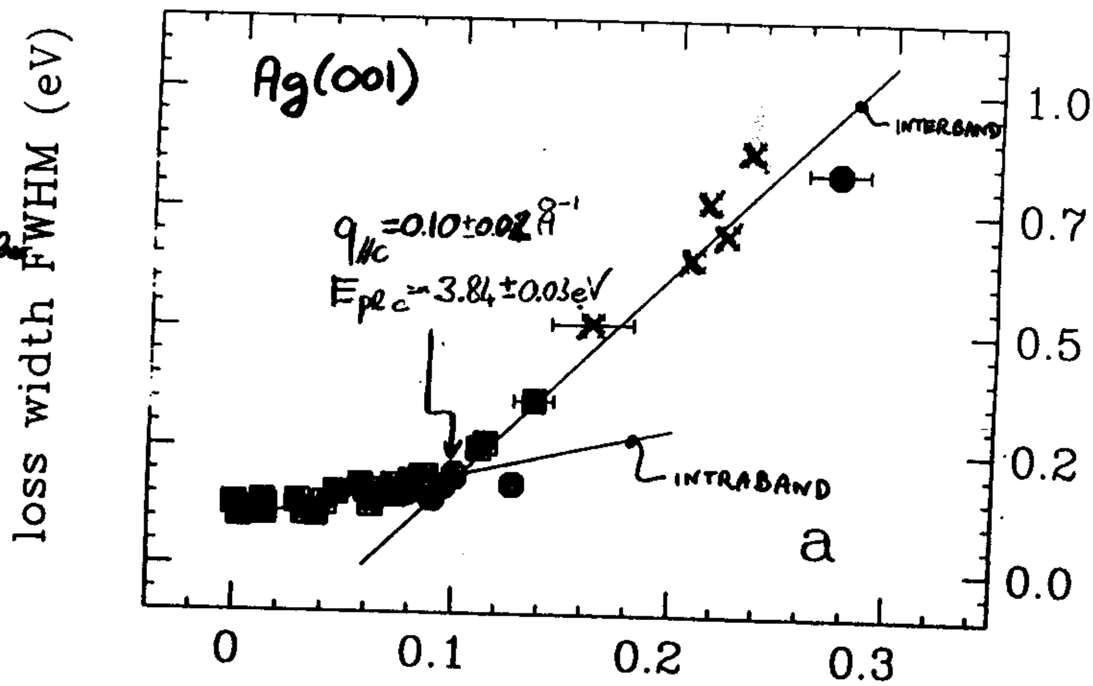
(100)

(111)

K.M. Ho et al
J Electroanal. Chem. 150 (1983) 235

ASMON
'S WIDTH
$q_{//}$

a, Biggio, Vallu
PRB '90)




$E_{sp}$

S: $\Delta E_{Loss} = A + B\, q_{//}$

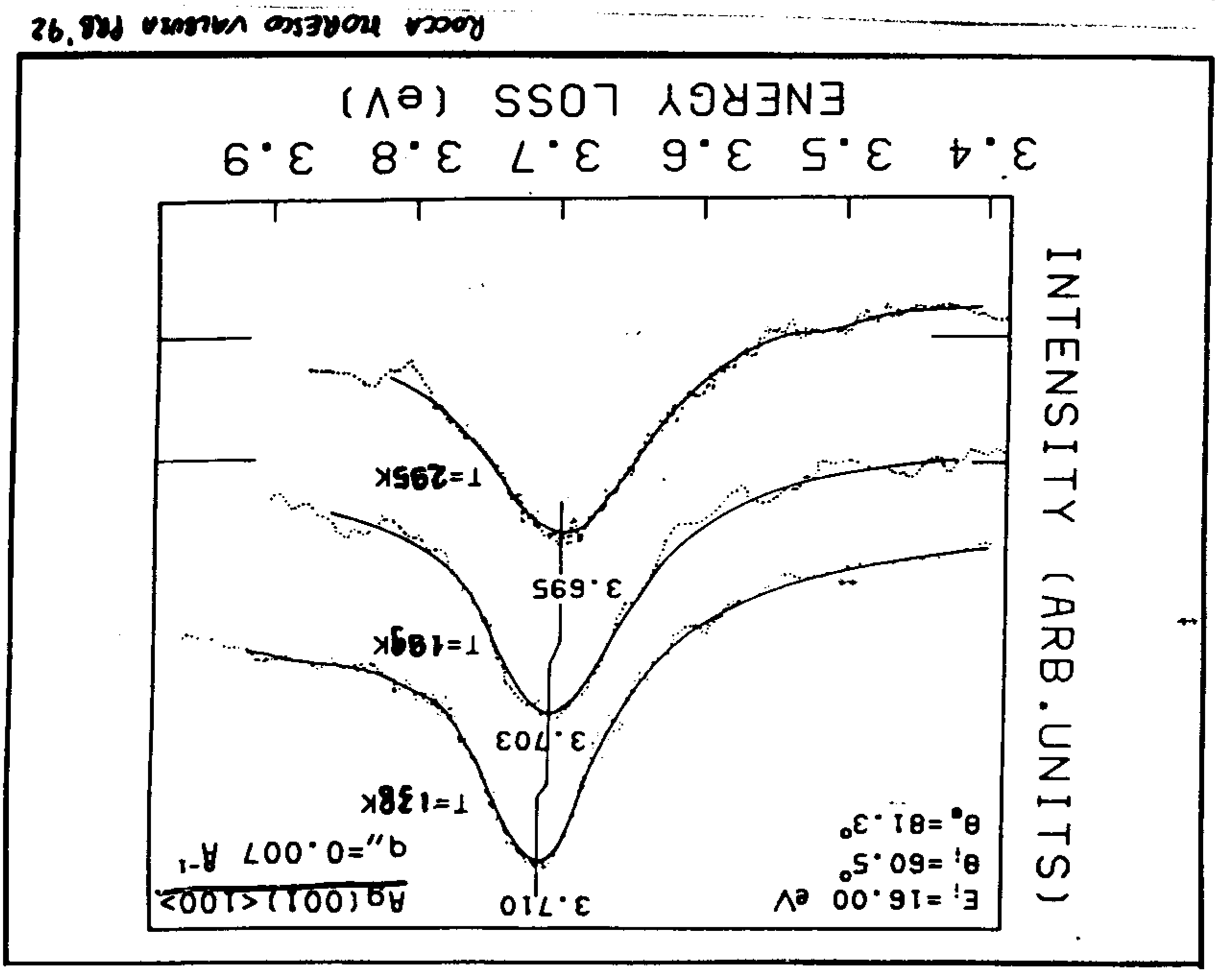
$q_{//} < 0.10$ Å$^{-1}$ A= 0.095±0.01 eV B=1.00±0.15 eVÅ

$q_{//} > 0.10$ Å$^{-1}$ A=-0.26±0.01 eV B=4.6±0.5 eVÅ

} $E_{plc}$ = 3.84±0.03eV

TO EMISSION: (A) SURFACE STATE AT $\bar{X}$ AT 3.8±0.4 eV

(B) SURFACE STATE AT $\bar{X}$ AT -0.1 eV (Reihl et al '84)



DEPENDENCE OF PLASMON FREQUENCY $\omega_{sp}$ ON $T_{CRYSTAL}$:

Ag(001)

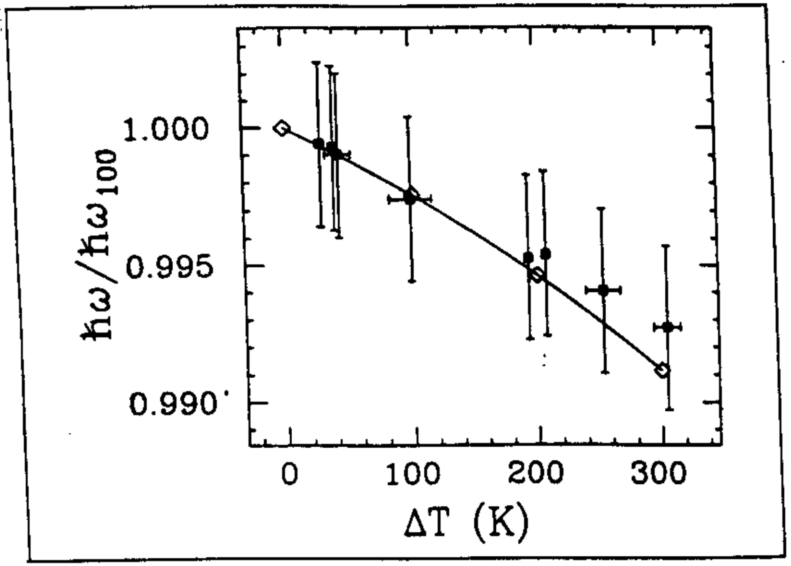



***Figura 3.13:*** *Energia del plasmone in funzione della temperatura, normalizzata a 100 K. Sull'asse x è riportato il valore di* $(T-100)K$. *La linea continua e i rombi rappresentano l'andamento previsto a partire dall'espansione termica del cristallo.*

⇒ PLASMON LOSS SHIFTS WITH T

$\omega_{sp} \propto \sqrt{n}$ : n electron density



DEPENDENCE OF PLASMON LINEWIDTH $\Delta\omega_{sp}$ ON $T_{CRYSTAL}$:

Ag(001)

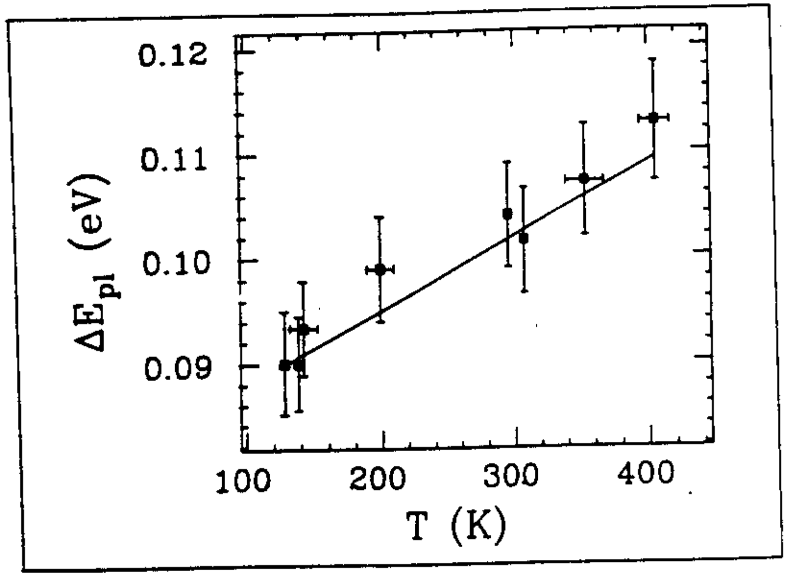


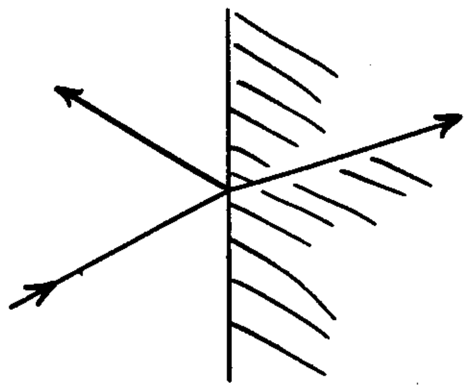

***Figura 3.14:*** *Larghezza del plasmone in funzione della temperatura. La linea continua rappresenta il fit descritto nel testo.*

EFFECT LARGER FOR Ag(011) BECAUSE

$\Theta_D(011) > \Theta_D(001)$

MAIN CONCLUSION:

SURFACE ELECTROMAGNETIC FIELDS



THERE IS STILL PLENTY OF SCIENCE TO UNDERSTAND IN THE PROBLEM OF REFRACTION.