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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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SMR. 628 - 30

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)

"Bortolani - Mills Paradox on Cu (001)"

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Bortolani – Mills Paradox

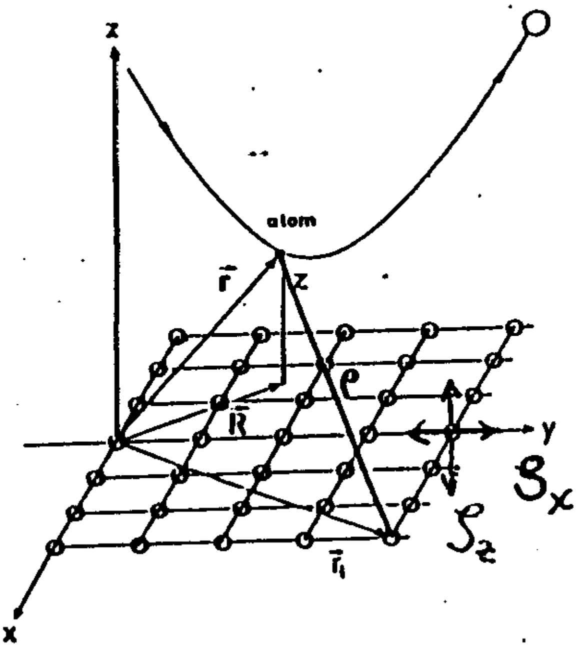
on Cu(001)

N.S. Luo, P. Ruggerone, G. Benedek

J. Ellis, A. Reichmuth, J.P. Toennies

Motivation

Dynamics of One-Phonon Inelastic Scattering



assume Tang-Toennies

atom-atom potential

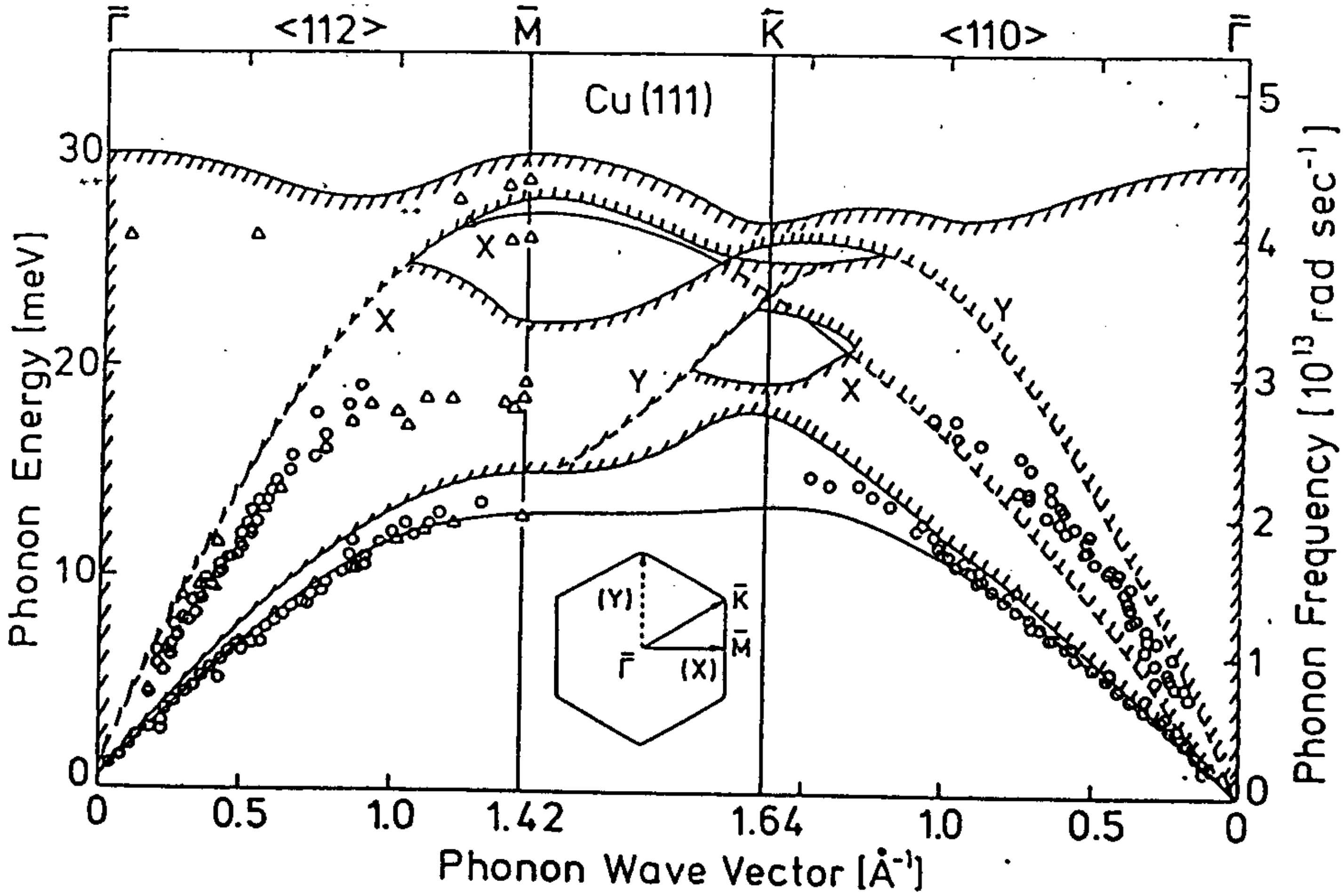
$$V(\rho) = A \cdot \exp(-b\rho) - f_6(b,\rho) \cdot \frac{C_6}{\rho^6}$$

$$\frac{d^2R}{dE \cdot d\Omega} \propto \sum_{Q,j} \frac{|+i\beta\underline{\zeta_z}(Q,j) + Q\underline{\zeta_x}(q,j)|^2}{\omega(Q,j)} \left| \left\langle \chi_f(z) \left| \frac{\partial V_0}{\partial z} \right| \chi_i(z) \right\rangle \right|^2 \cdot \exp\left(-\frac{Q^2\bar{z}}{\beta_0}\right) \cdot n\left(\omega(Q,J)\right)$$

Eichenauer, Harten, Toennies and Celli, J.Chem.Phys. 86, 3693 (1987)

Inelastic He atom scattering is also coupled with electronic oscillations. ?

Bortolani – Mills Paradox on Cu(111)



Data fitted	Bulk force constants[a)]	Surface force constants[b)]	Reference
EELS △	β_1^b=27.0	$\beta_{\parallel}^s$=0.85 β^b $\beta_{\perp}^s$=1.0 β^b	Hall et al.
HAS ○	α_1^b=-0.20, β_1^b=31.34, δ_1^b=-0.49 α_2^b=-0.32, β_2^b= 0.11, δ_2^b=-0.47 etc.	$\beta_{\parallel}^s$=0.33 β_1^b $\beta_{\perp}^s$=1.59 β_1^b	Bortolani et al.

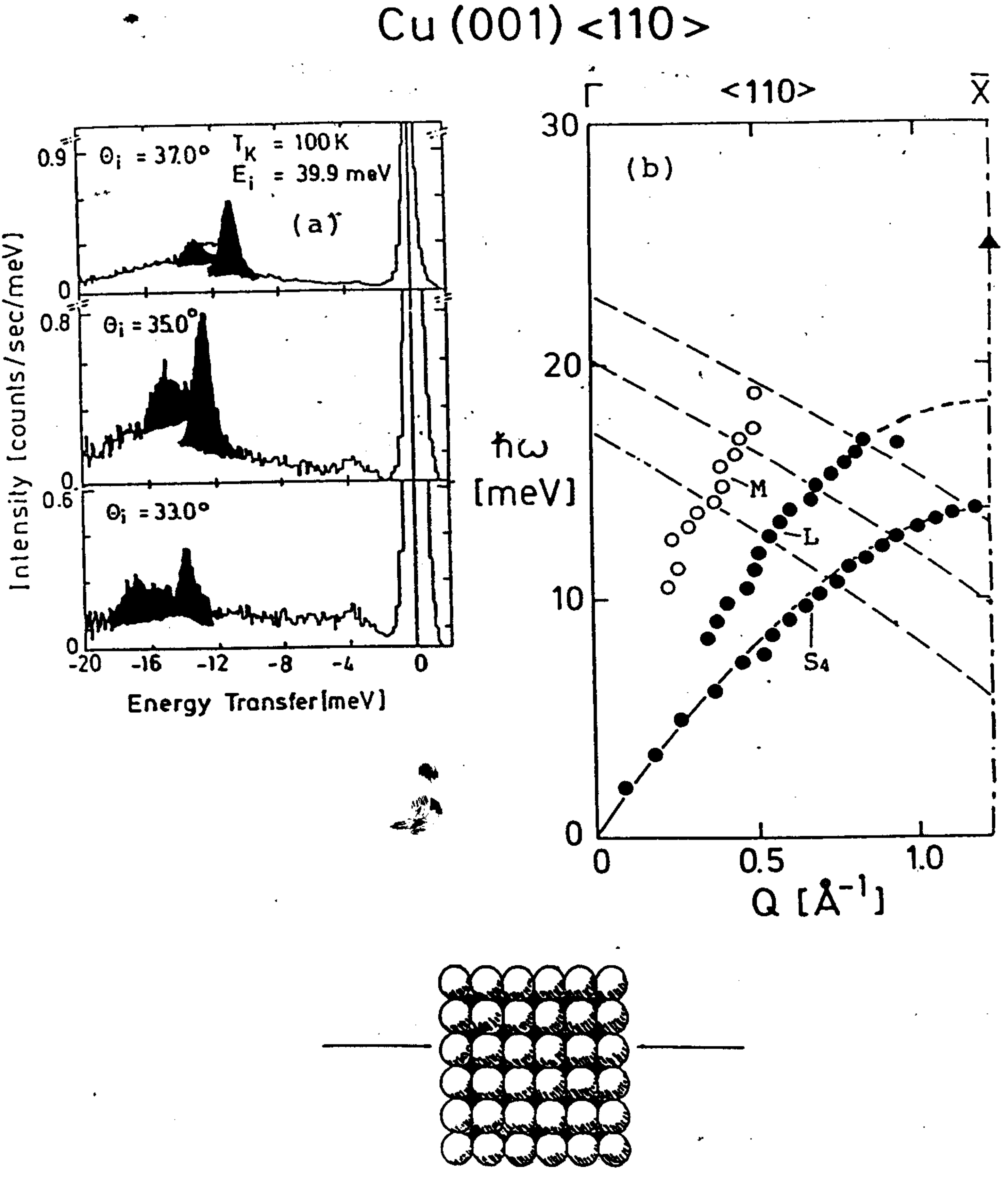
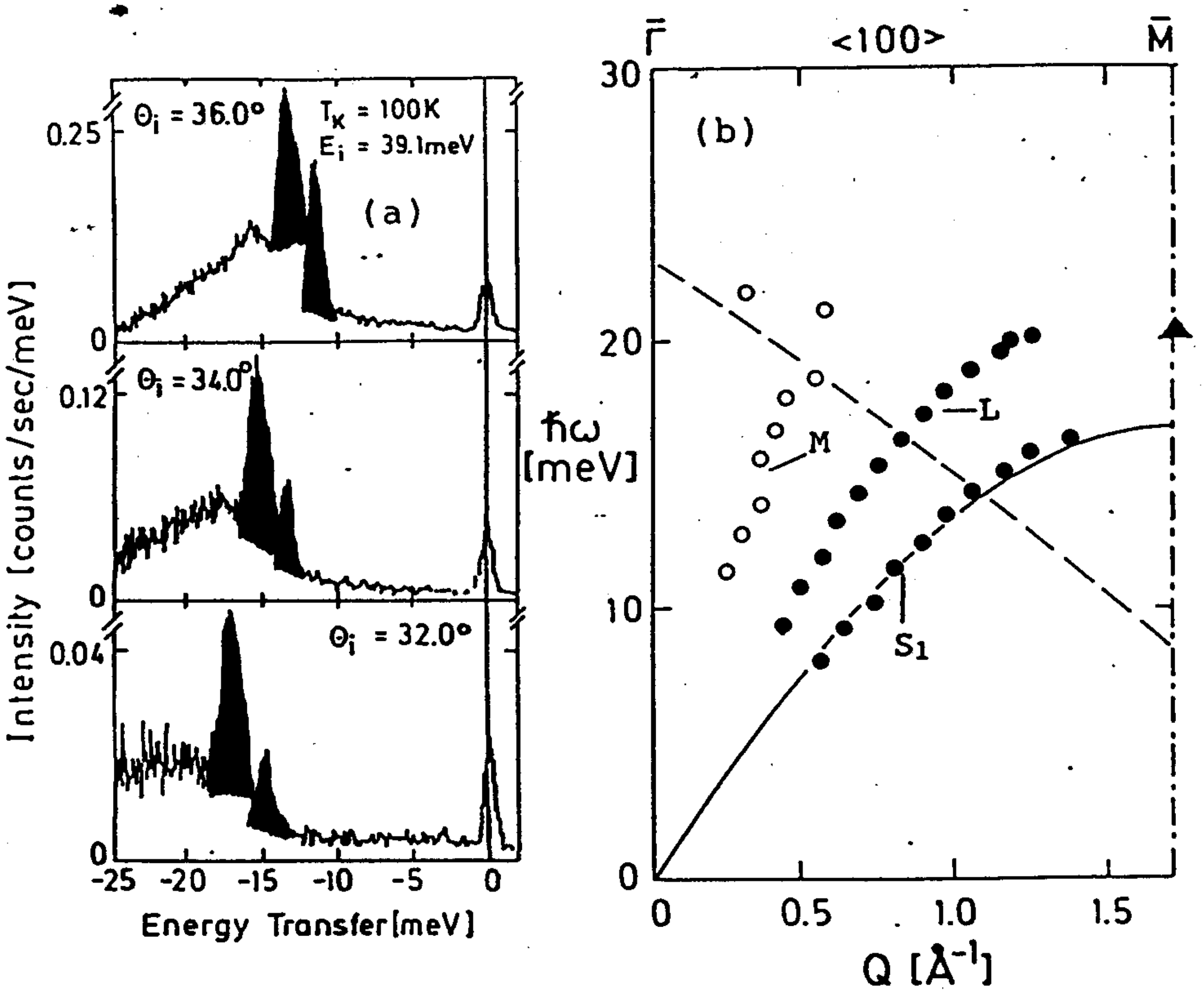

Cu (001) <110>
Γ
<110>
X̄
(a)
(b)
Θi = 37.0°
TK = 100 K
Ei = 39.9 meV
Θi = 35.0°
Θi = 33.0°
Intensity [counts/sec/meV]
Energy Transfer [meV]
ħω [meV]
Q [Å⁻¹]
M
L
S4

Fig.1

Cu (001)<100>



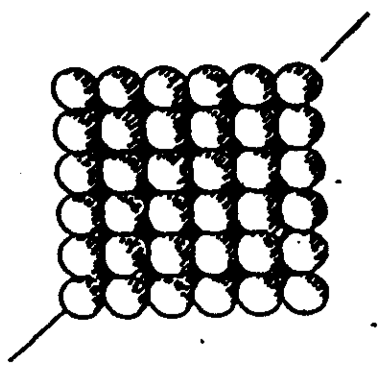
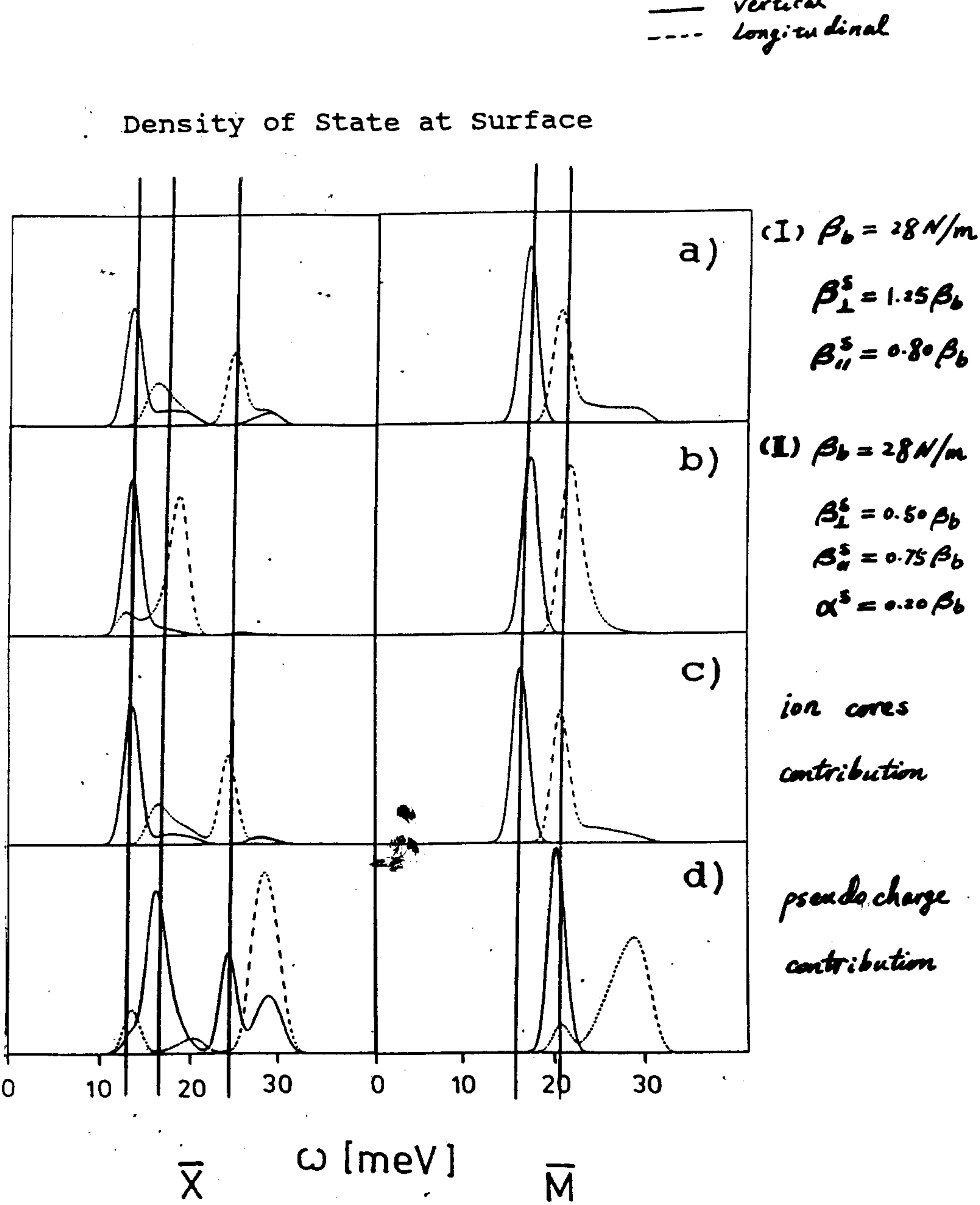


Fig.2

Density of State at Surface



Questions from HAS experiment

1. Why is there ~~the~~ anomaly of longitudinal resonance on Cu surface?

   "Due to additional contribution from electron ossilations" by Kaden, et al on Cu(111)

2. Why is this anomaly much magnified on Cu(001)?

3. Why is this anomaly very strong along $\bar{\Gamma}\bar{M}$ direction, whereas very small along $\bar{\Gamma}\bar{X}$ diretion?

One-Phonon Inelastic Scattering of He atom

(I) Old theory

$$\frac{d^2R}{dE\,d\Omega} \propto \sum_{\vec{Q},j} |F_a|^2 \cdot \frac{\left|\langle \chi_f(z) \left| \frac{\partial V_0}{\partial z} \right| \chi_i(z)\rangle\right|^2}{\omega(\vec{Q},j)} \cdot \underbrace{\exp\left(-\frac{Q^2}{Q_c^2}\right)}_{\text{cut-off factor}} \cdot \underbrace{n(\omega(\vec{Q},j))}_{\text{Bose Einstein factor}}$$

Eichenaur, Harten, Toennies and Celli, J. Chem. Phys. 86, 3693 (1987)

$$F_a = -i\beta u_z(\vec{Q},j) + \vec{Q}\cdot u_x(\vec{Q},j)$$

(II) New theory

$$\frac{d^2R}{dE\,d\Omega} \propto \sum_{\vec{Q},j} |F_a + F_d + F_g|^2 \cdot \frac{\left|\langle \chi_f(z) \left| \frac{\partial V_0}{\partial z} \right| \chi_i(z)\rangle\right|^2}{\omega(\vec{Q},j)} \cdot \exp\left(-\frac{Q^2}{Q_c^2}\right) \cdot n(\omega(\vec{Q},j))$$

$$F_d = \frac{1}{2}\sum_j \left[\beta \Delta C_{dz}(j) + iQ\Delta d_x(j)\right]\cdot \exp(-i\vec{Q}\cdot\vec{R}_j)$$

$$F_g = \frac{1}{2}\sum_j \beta \Delta C_{gz} \cdot \exp(-i\vec{Q}\cdot\vec{R}_j)$$

from pseudocharge multipole model

The Pseudocharge Multipole Expansion Method

Total energy

$$E = E_i + E_e[n],$$

$$E_e[n] = F[n] + \int w(\vec{r})n(\vec{r})d^3r$$

Expand interstitial electron density

$$n(\vec{r}) = \sum_l n_l(\vec{r})$$

$$n_l(\vec{r}) = \sum_{j,\Gamma k} c_{\Gamma k}(lj)Y_{\Gamma k}(\vec{r} - \vec{r}_{lj}).$$

→ coupled to atomic motion

The equations of motion of nuclei and electron degrees of freedom are:

$$m\ddot{u}_\alpha(l) = -\sum_{l'\beta} \underline{R_{\alpha\beta}(ll')}u_\beta(l') - \sum_{\Gamma}\sum_{l'j'k} \underline{T_{\alpha k}(\Gamma; ll'j')}\Delta c_{\Gamma k}(l'j')$$

$$m_\Gamma \Delta\ddot{c}_{\Gamma k}(lj) = -\sum_{l'\alpha} \underline{T_{\alpha k}(\Gamma; l'lj)}u_\alpha(l') - \sum_{\Gamma' l'}\sum_{j'k'} \underline{H_{kk'}(\Gamma\Gamma'; ljl'j')}\Delta c_{\Gamma' k'}(l'j')$$

Solve with m_Γ=0 (Born-Oppenheimer approximation)

$$E = E_0 + \frac{1}{2}\sum_{\substack{l\alpha \\ l'\beta}} \underline{\phi_{\alpha\beta}(ll')}\, u_\alpha(l)\, u_\beta(l')$$

$$+ \frac{1}{2}\sum_{\Gamma}\sum_{\substack{ljK \\ l'\alpha}} \left[\underline{\phi_{K\alpha}(\Gamma; l'lj)}\, u_\alpha(l')\, \Delta C_{\Gamma K}(lj) + \underline{\phi_{\alpha K}(\Gamma; ljl')}\, u_\alpha(l')\, \Delta_{\Gamma K}(lj) \right]$$

$$+ \frac{1}{2}\sum_{\Gamma\Gamma'}\sum_{\substack{ljK \\ l'j'K'}} \underline{\phi_{KK'}(\Gamma\Gamma'; ljl'j')}\, \Delta C_{\Gamma K}(lj)\, \Delta_{\Gamma' K'}(l'j')$$

$$\phi_{\alpha\beta}(ll') = \frac{\partial^2 E}{\partial u_\alpha(l)\, \partial u_\beta(l')}$$

ion – ion

$$\phi_{\alpha K}(\Gamma; l'lj) = \frac{\partial^2 E}{\partial u_\alpha(l')\, \partial C_{\Gamma K}(lj)}$$

$$= \int d^3\vec{r}\, \frac{\partial}{\partial u_\alpha(l')} \cdot \frac{\delta E}{\delta n(\vec{r})} \cdot Y_{\Gamma K}(\vec{r} - \vec{r}(lj))$$

ion – pseudo charge

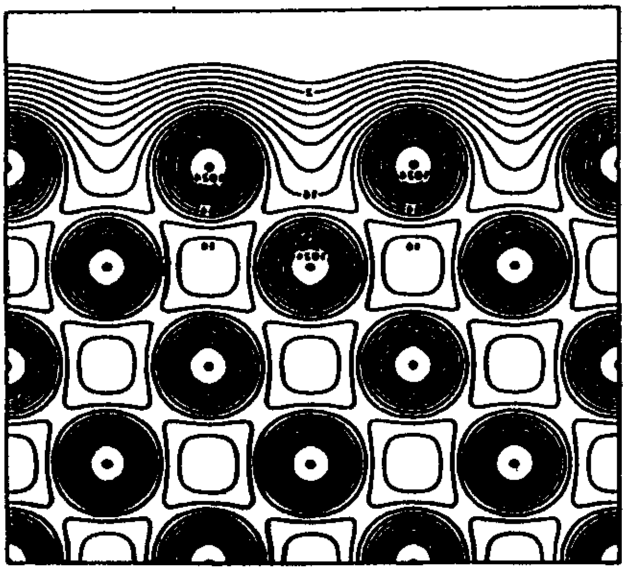
$$\phi_{KK'}(\Gamma\Gamma'; ljl'j') = \frac{\partial^2 E}{\partial C_{\Gamma K}(lj)\, \partial C_{\Gamma' K'}(l'j')}$$

$$= \iint d^3\vec{r}\, d^3\vec{r}\,'\, \frac{\delta^2 E}{\delta n(\vec{r})\, \delta n(\vec{r}\,')}\, Y_{\Gamma K}(\vec{r} - \vec{r}(lj))\, Y_{\Gamma' K'}(\vec{r}\,' - \vec{r}(l'j'))$$

pseudo charge – pseudo charge

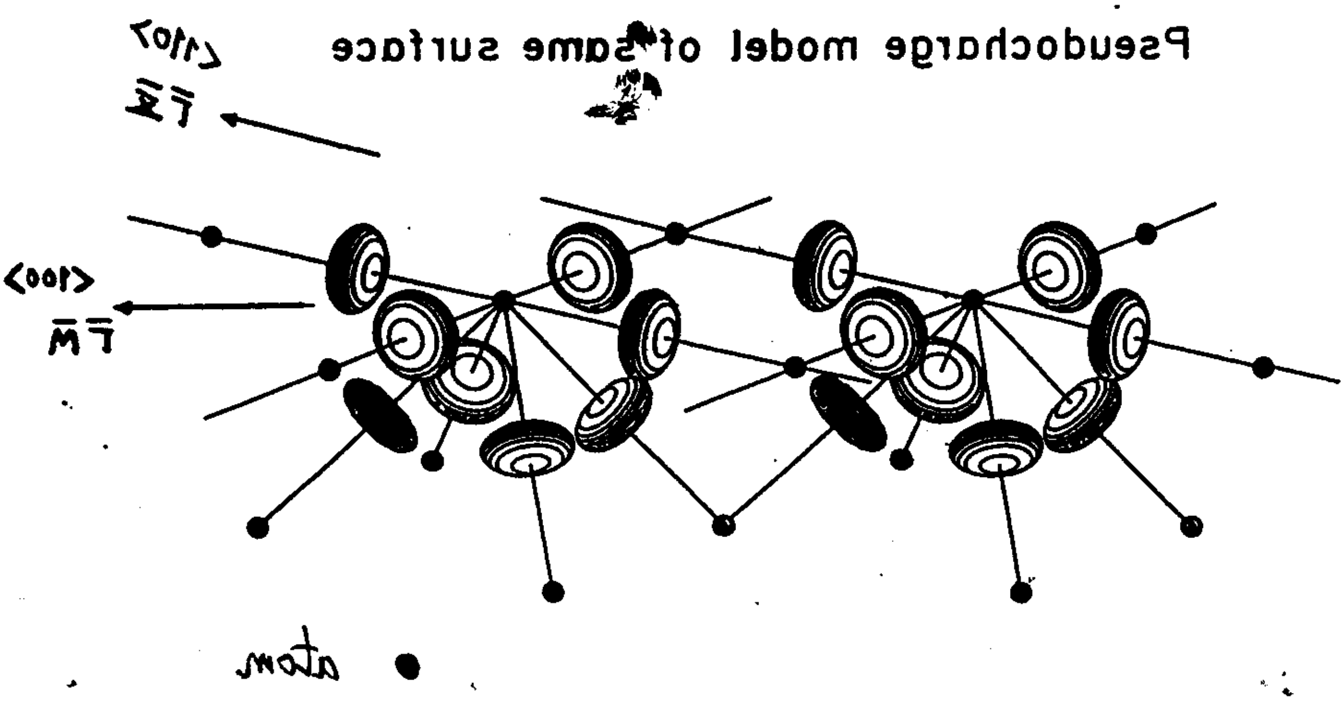
Evidence for Pseudocharges from First Principles Calculations

Self-consistent local-orbital method

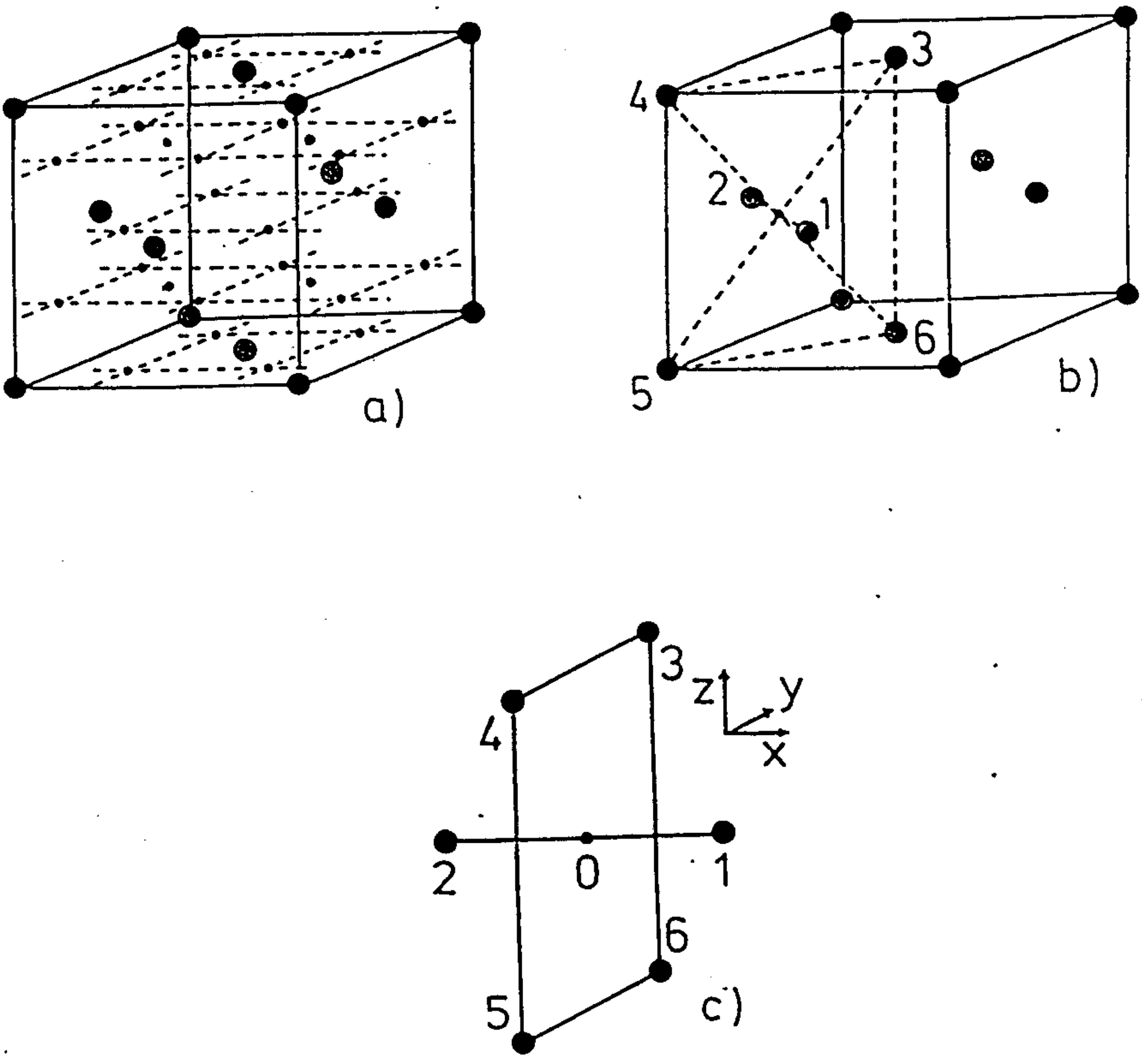


Smith, Gay and Arlinghaus, Phys. Rev. B21, 2201 (1980)

Pseudocharge model of same surface

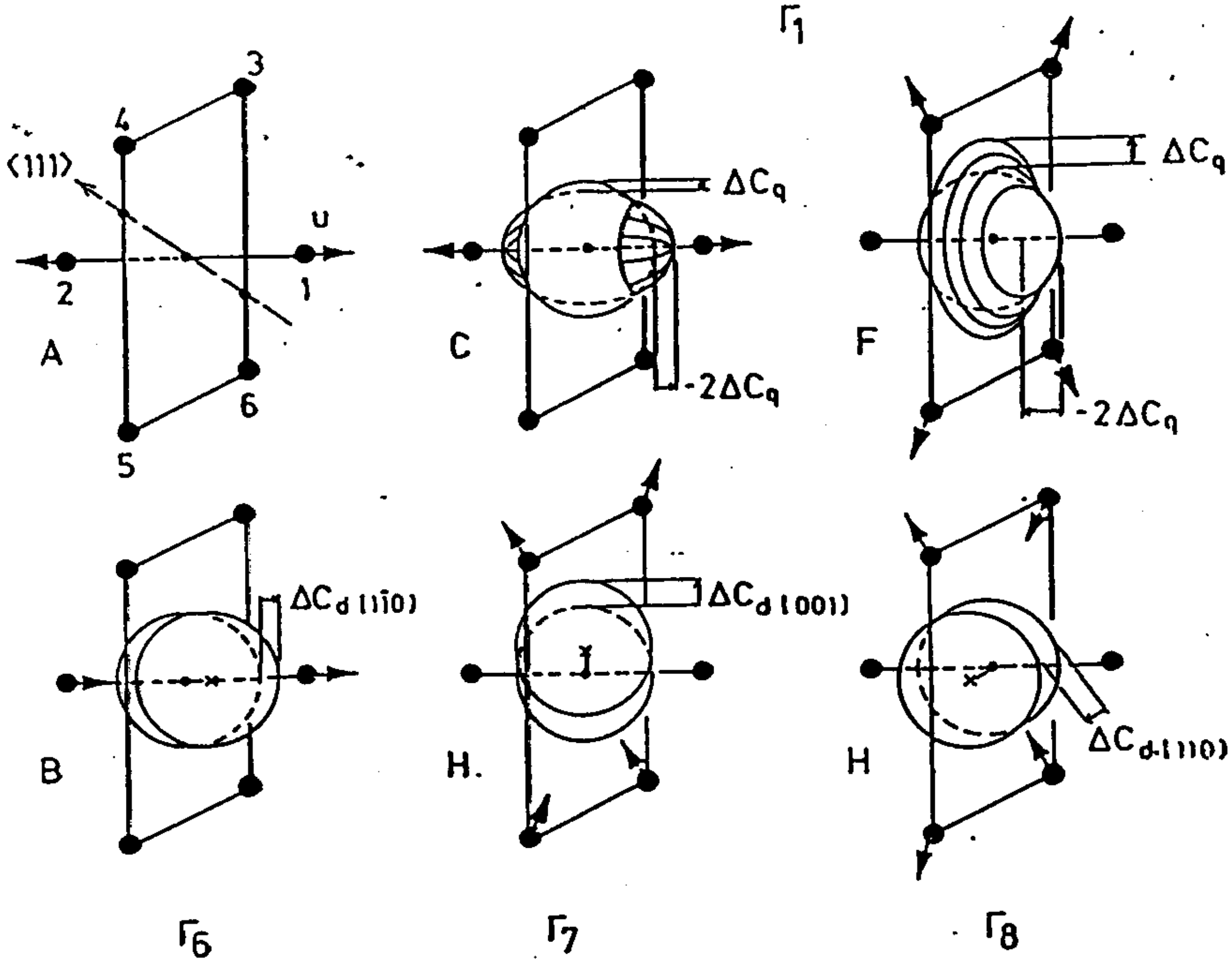


Pseudocharge Positions

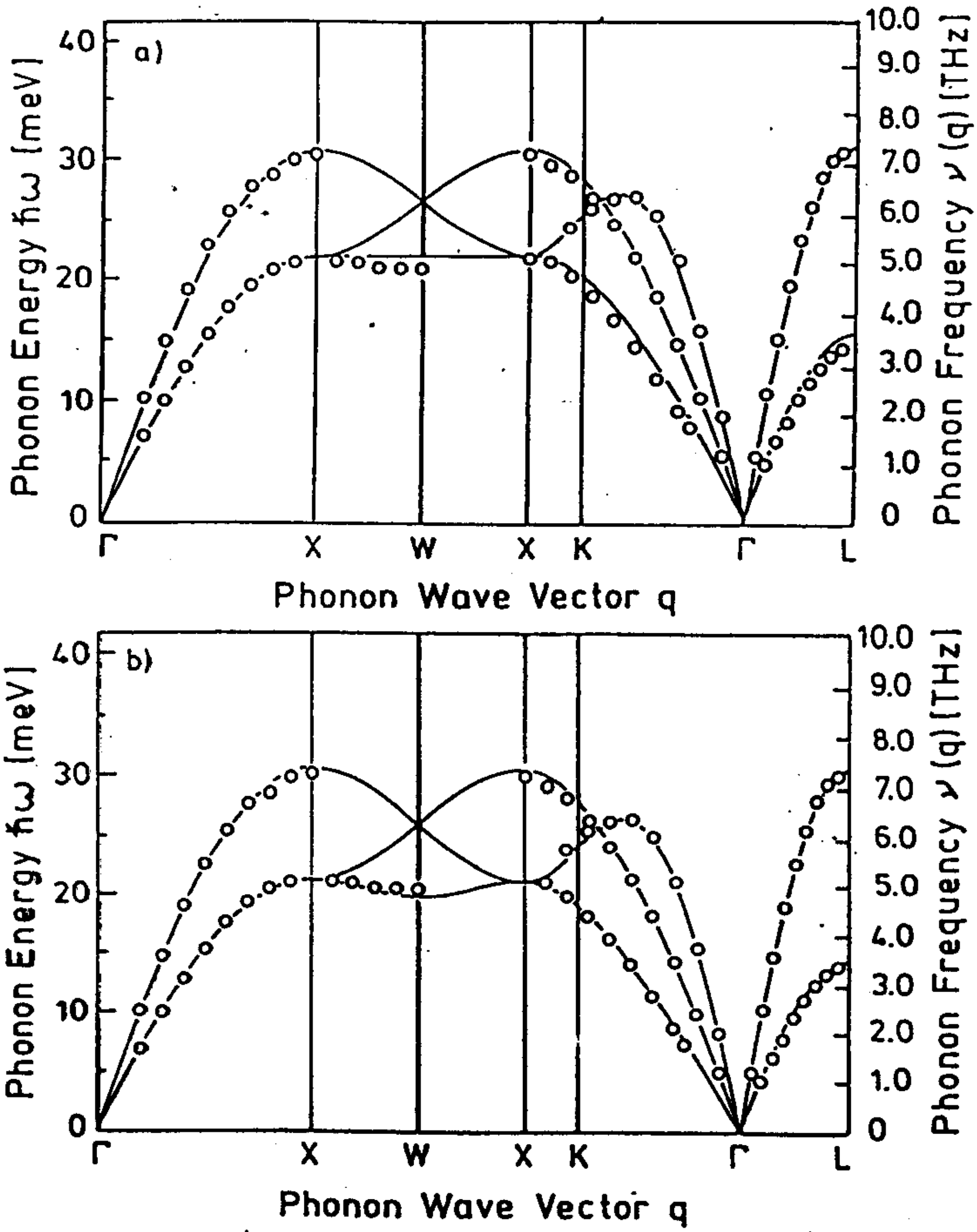


D_{2h}

Couplings



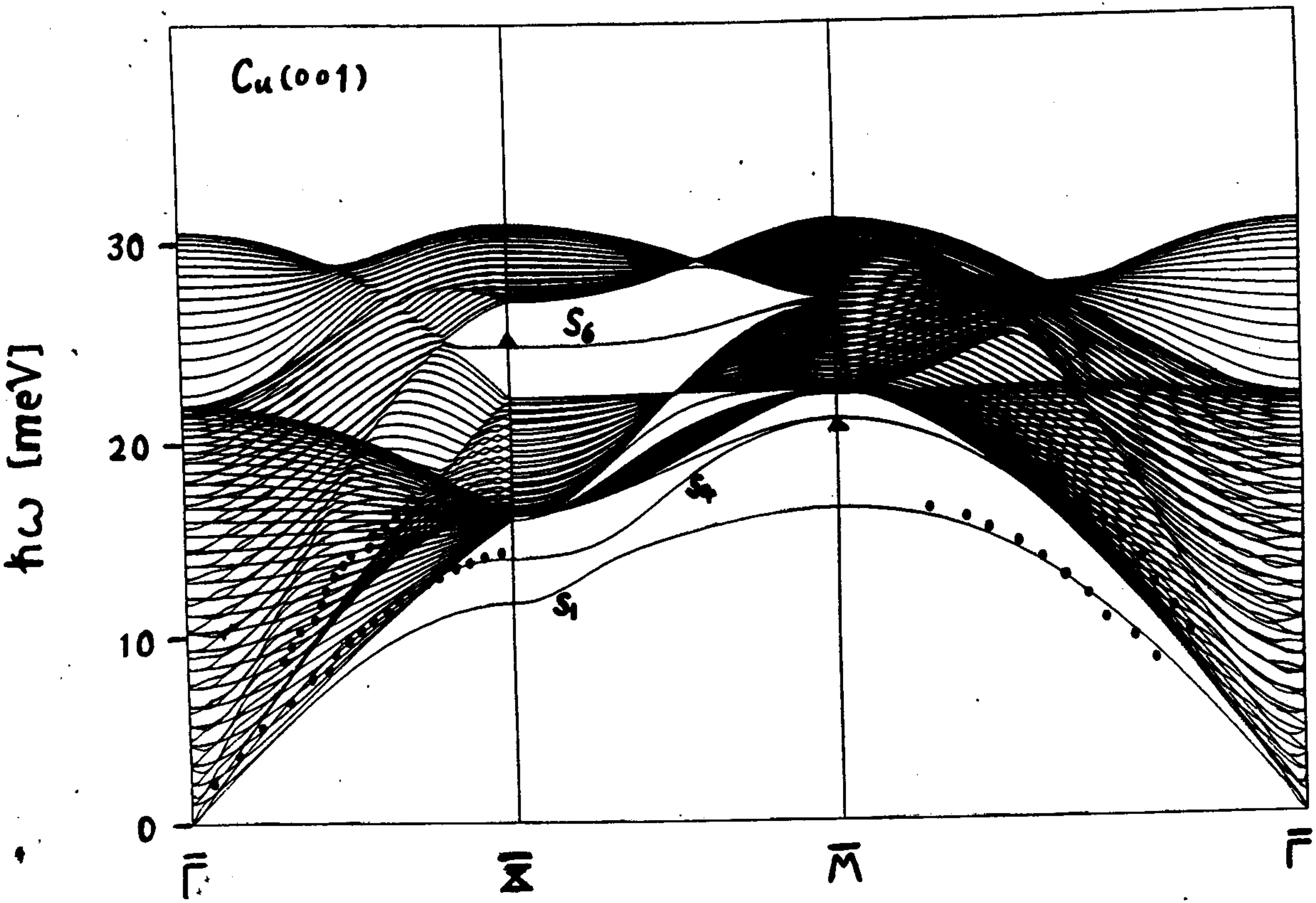
Bulk Phonon



C_{11} (fit) $= 1.73 \cdot 10^{11}\ N/m^2$ (1.68)

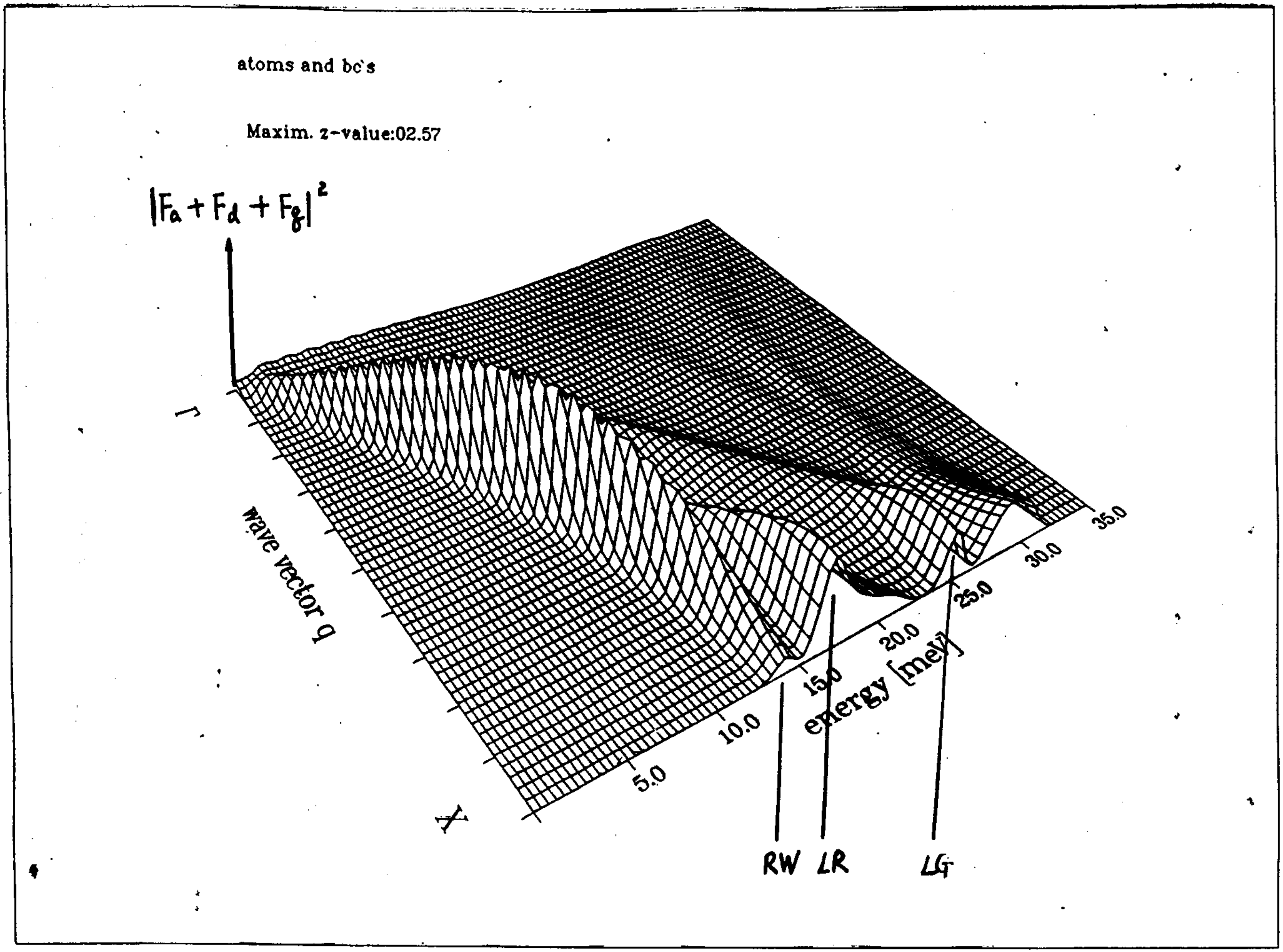
C_{12} (fit) $= 1.14 \cdot 10^{11}\ N/m^2$ (1.21)

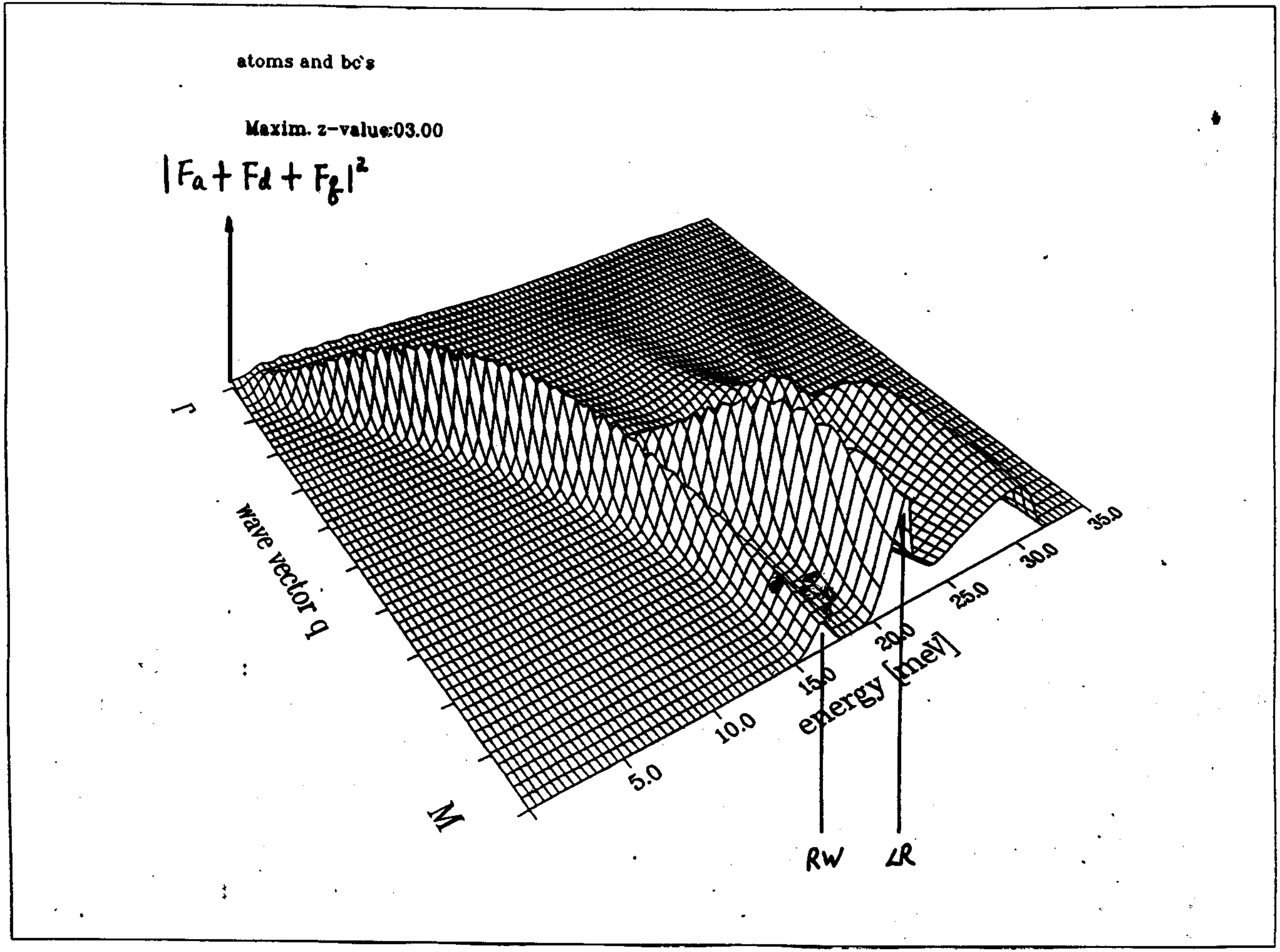
C_{44} (fit) $= 0.83 \cdot 10^{11}\ N/m^2$ (0.75)



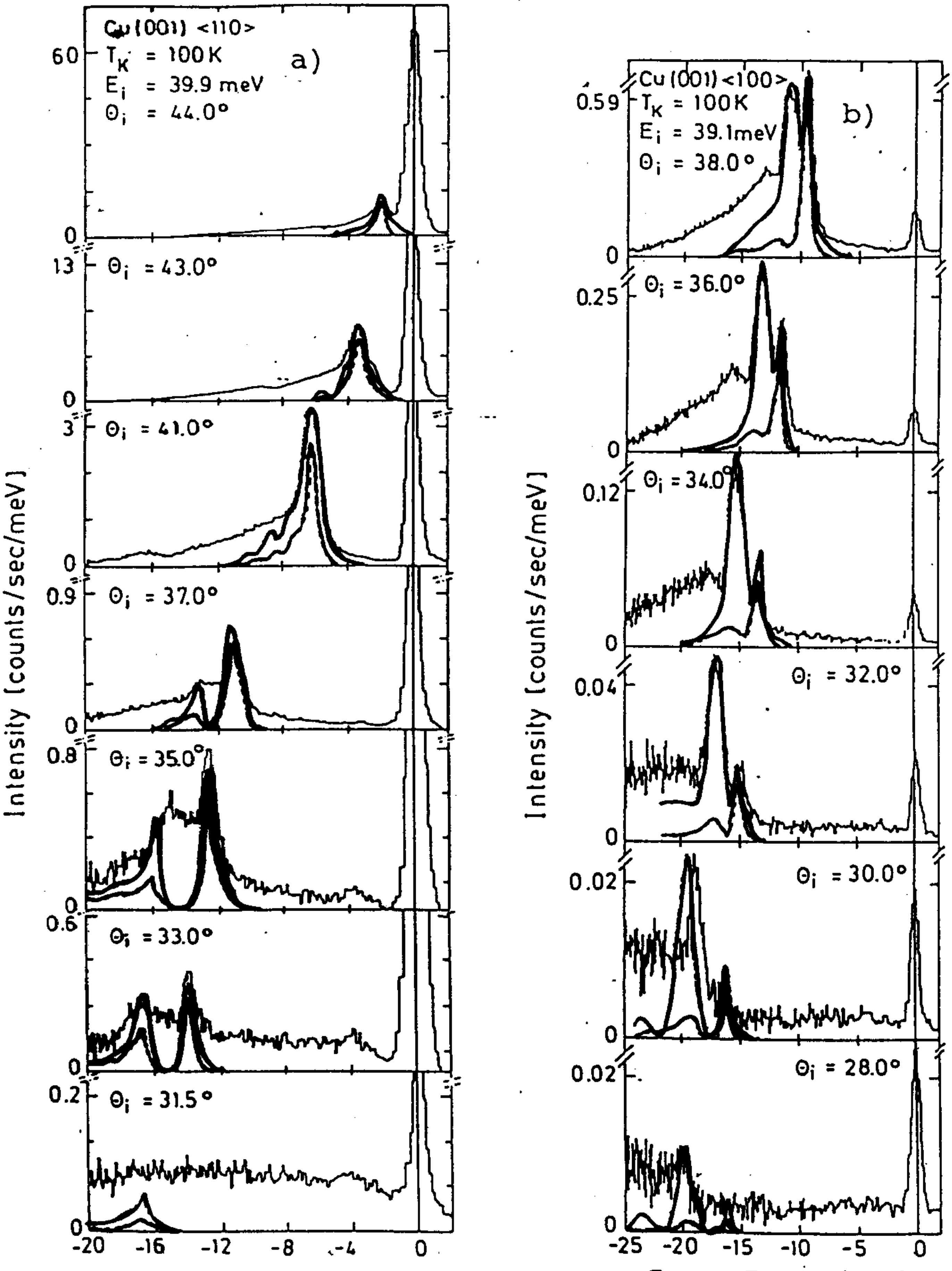
at surface $\Delta B = -0.98$ N/m

$\Delta C = +9.6$ N/m


atoms and bc's
Maxim. z-value:02.57
$|F_a + F_d + F_g|^2$
Γ
wave vector q
X
5.0
10.0
15.0
20.0
25.0
30.0
35.0
energy [meV]
RW
LR
LG



atoms and bc's
Maxim. z-value:03.00
$|F_a + F_d + F_g|^2$
Γ
wave vector q
M
5.0
10.0
15.0
20.0
25.0
30.0
35.0
energy [meV]
RW
LR



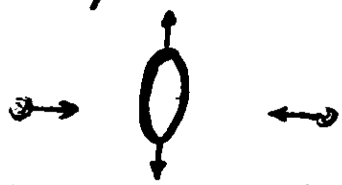
Cu(001) <110>
T_K = 100K
E_i = 39.9 meV
Θ_i = 44.0°
a)
Θ_i = 43.0°
Θ_i = 41.0°
Θ_i = 37.0°
Θ_i = 35.0°
Θ_i = 33.0°
Θ_i = 31.5°
Intensity [counts/sec/meV]
Energy Transfer [meV]
Cu(001) <100>
T_K = 100K
E_i = 39.1meV
Θ_i = 38.0°
b)
Θ_i = 36.0°
Θ_i = 34.0°
Θ_i = 32.0°
Θ_i = 30.0°
Θ_i = 28.0°
Intensity [counts/sec/meV]
Energy Transfer [meV]

Fig.13

Explanation

① Pseudocharge oscillations coupled with atomic vibration

for longitudinal



<u>quadrupolar has large vertical oscillation</u>.

for RW

this effect is very small

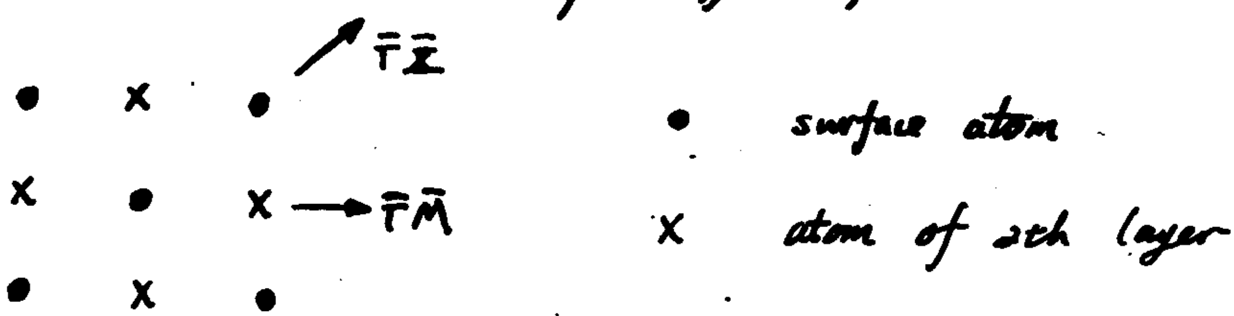
②.	Cu(001)	Cu(111)	Cu bulk
	8 NN	9 NN	12 NN
at 1th layer	4 NN	6 NN
at 2th layer	4 NN	3 NN

Cu(001) has more change of electron density.

<u>∴ the anomaly is magnified</u>

③ For Cu(001), $\bar{\Gamma}\bar{X}$, $\bar{\Gamma}\bar{M}$

there are anisotropic effect from structure



The surface longitudinal vibration along $\bar{\Gamma}\bar{M}$ is much softer than that along $\bar{\Gamma}\bar{X}$.

∴ along $\bar{\Gamma}\bar{M}$ the atomic vibration and pseudocharge oscillations have more surface densities than that along $\bar{\Gamma}\bar{X}$ So the anomaly along $\bar{\Gamma}\bar{M}$ is larger