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INTERNATIONAL CENTRE FOR THEORETICAL PHYSICS
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**SMR. 767 - 5**

**MINIWORKSHOP ON STRONG CORRELATIONS AND QUANTUM CRITICAL PHENOMENA**
**(4 - 22 July 1994)**

# DOPED ONE-DIMENSIONAL TRANSITION METAL OXIDES

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# SOME CONCEPTS THAT HAVE BEEN VISITED

—

SPIN LIQUIDS

✓ SPIRAL STATES NEAR MIT

✓ "NEARLY" AFM FERMI LIQUID

✓ LARGE / SMALL FERMI SURFACES

MAGNETIC POLARONS

⋮

## 1D Mott-Hubbard Systems

**Quantum spin liquids**

**s=1/2 Ungapped with $\xi = \infty$**

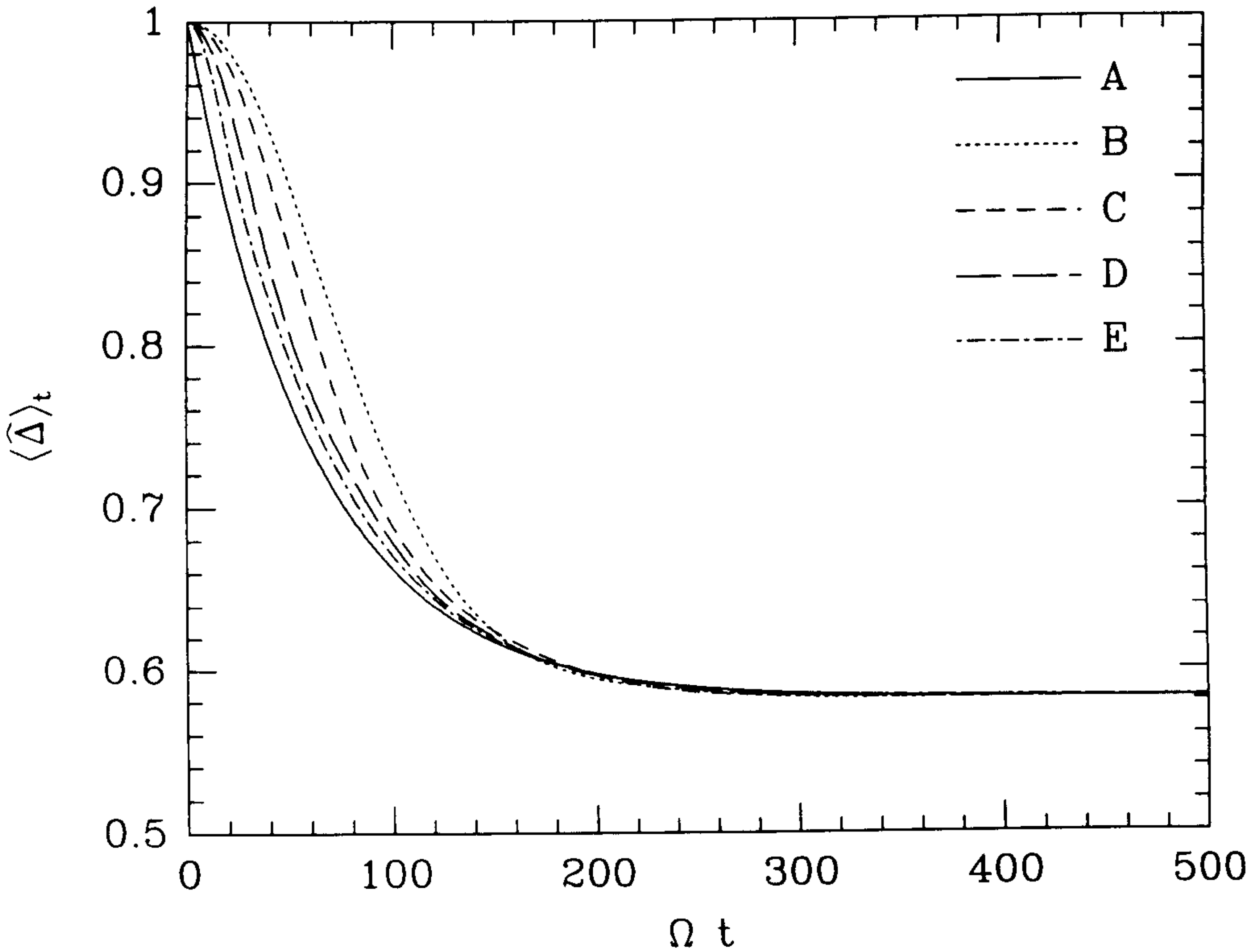
**s=1 gapped with $\xi \sim 6$**

- **Symmetry of lattice.**
- **Not on the threshold of ordering**
- **Charge and spin gap.**

**Quantum liquids**

**Superconductors**
**Haldane 1D AFM**
**FQHE**

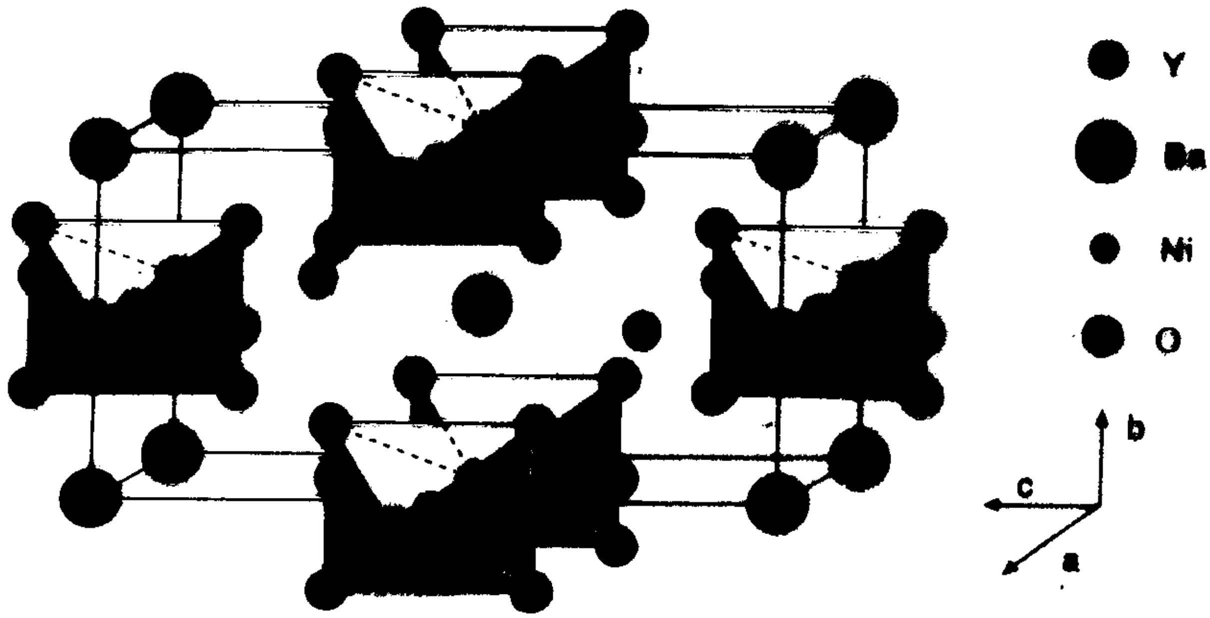
* • **1D provides the unique opportunity to dope a quantum spin liquid** *



1
0.9
0.8
0.7
0.6
0.5
0
100
200
300
400
500
$\langle\hat{\Delta}\rangle_t$
$\Omega$ t
A
B
C
D
E


Fig 2

$Y_2BaNiO_5$






$Ni^{2+}$ $d^8$ $S=1$

$(Cu^{2+}$ $d^9$ $S=1/2)$

$Y_2^{3+}Ba^{2+}Ni^{2+}O_5^{--}$

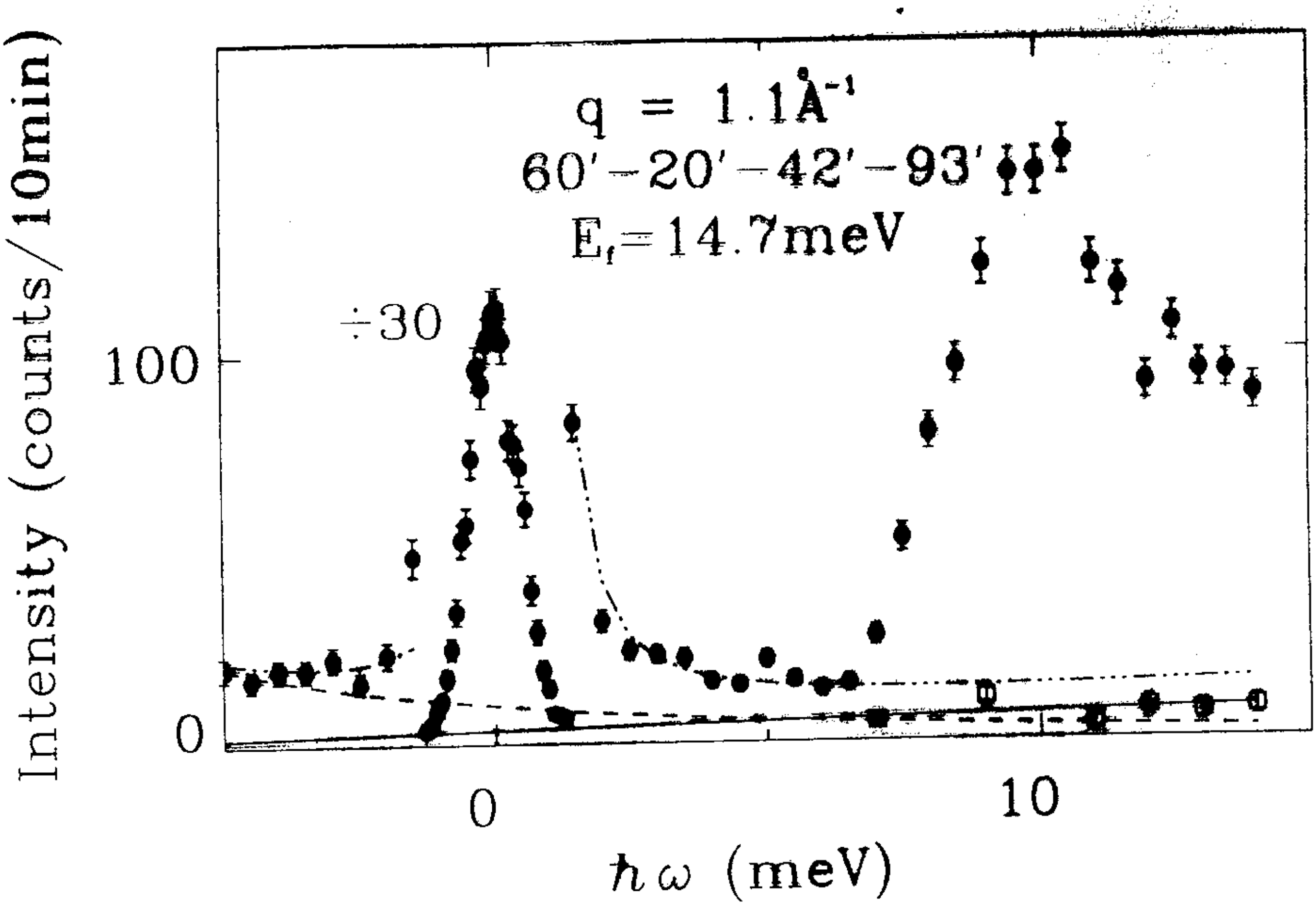
$6 + 2 + 2 - 10 = 0$

**How do we know if it is a quantum liquid?**

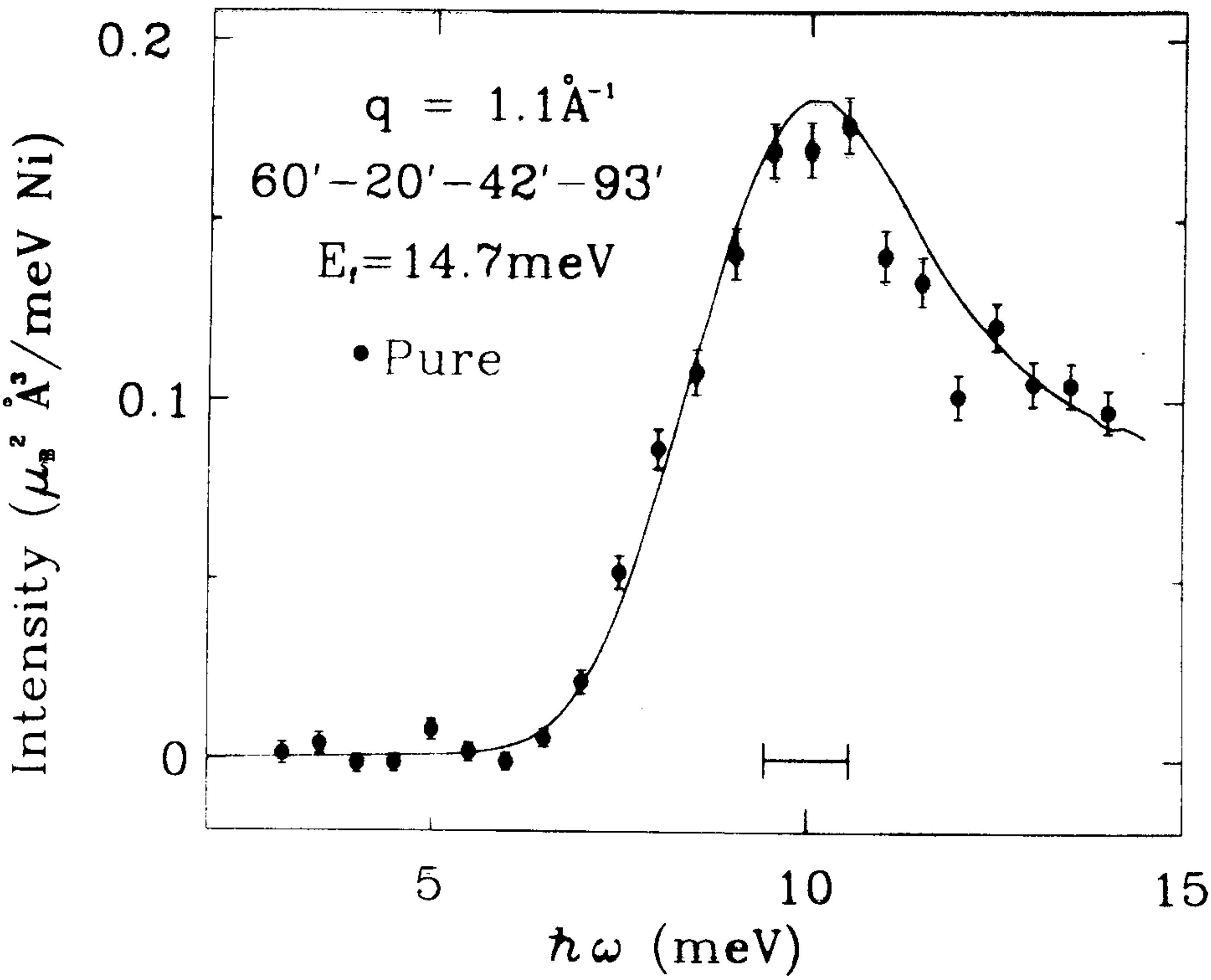
⇒ • **Liquid Structure Factor.**

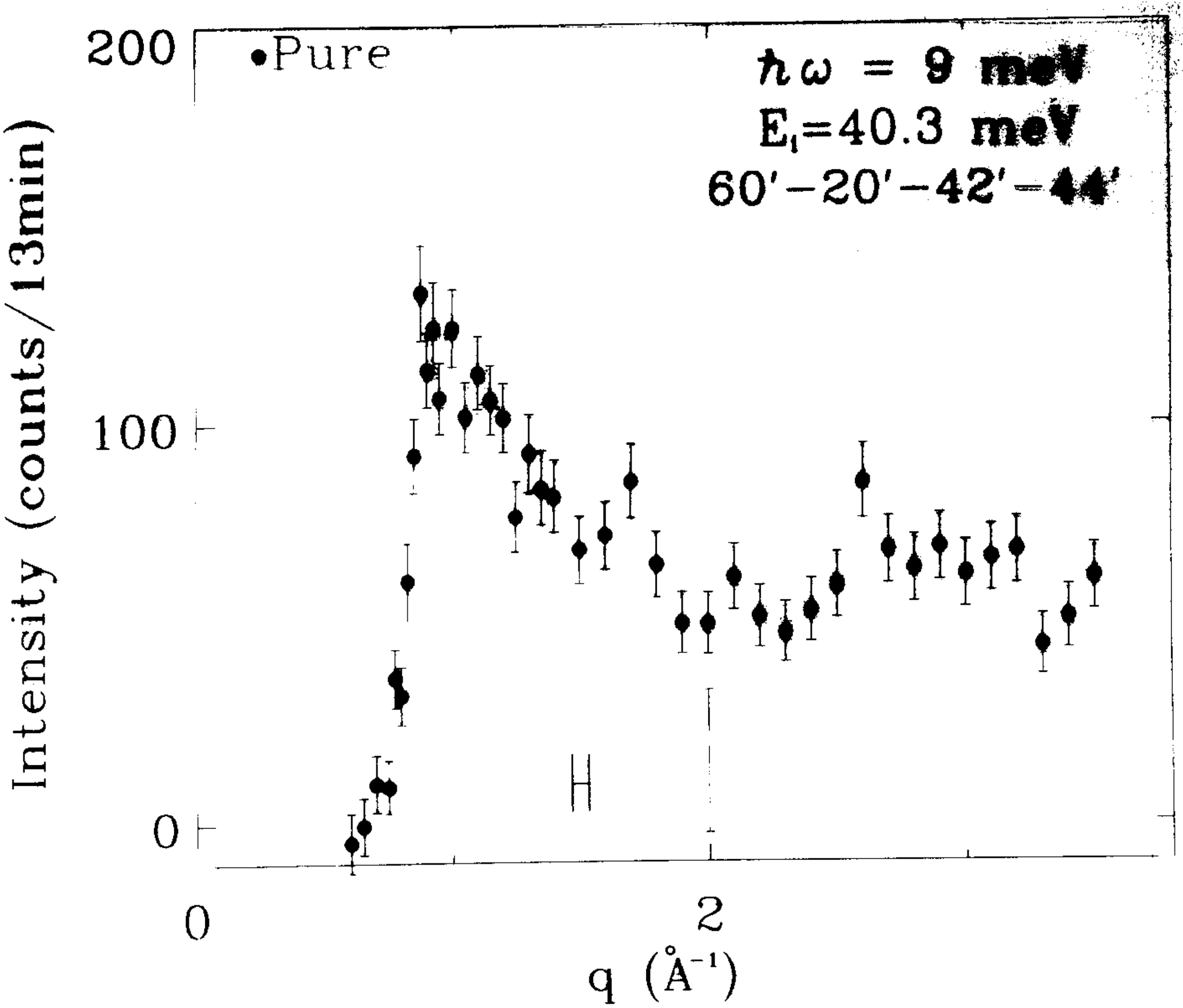
**How can we measure the structure factor directly?**

• **Neutron Scattering.**



q = 1.1Å⁻¹
60′–20′–42′–93′
$E_f$=14.7meV
÷30
100
0
0
10
Intensity (counts/10min)
ħω (meV)

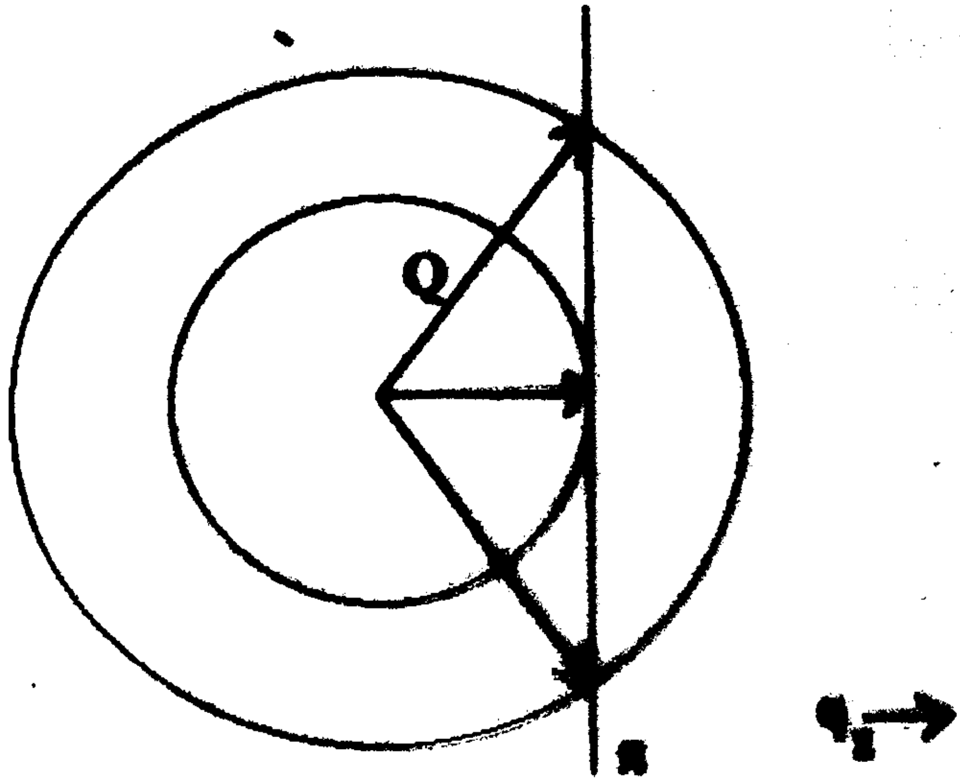

0.2
0.1
0
q = 1.1Å⁻¹
60′−20′−42′−93′
E_f=14.7meV
• Pure
Intensity (μ_B² Å³/meV Ni)
5
10
15
ħω (meV)



200
100
0
•Pure
ħω = 9 meV
E_i=40.3 meV
60'−20'−42'−44'
Intensity (counts/13min)
0
2
q (Å⁻¹)


J

$\hbar\omega = \Delta$




<u>Powder Average of 1D Structure Factor</u>

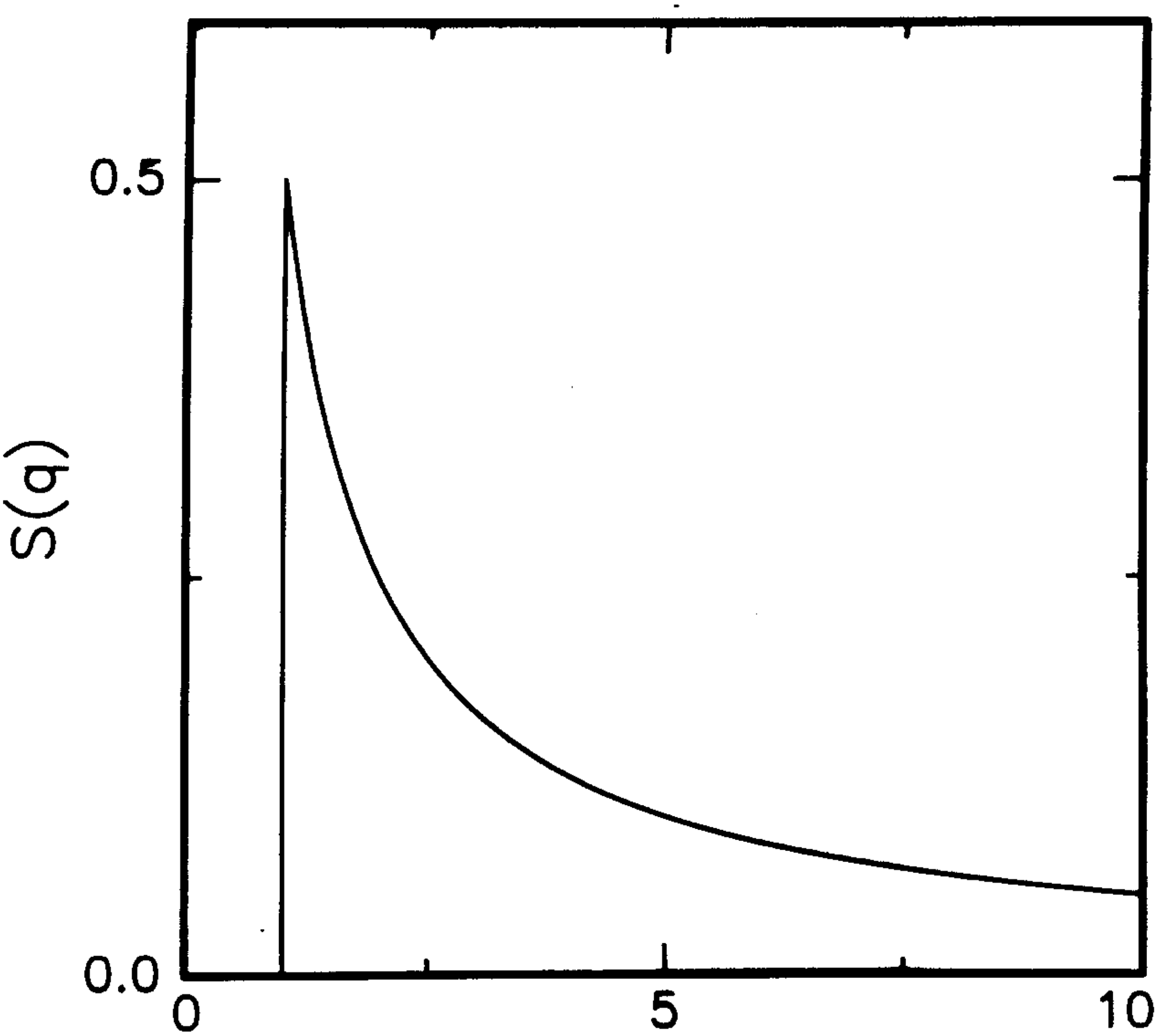
$$S(q) = \frac{1}{4\pi}\int d\Omega_q\ \delta(q_{\parallel} - \pi)$$

$$S(q) = \frac{1}{2}\int_{-1}^{1} d\cos\theta\ \delta(q\cos\theta - \pi)$$

If $q < \pi$, $\underline{S(q) = 0}$

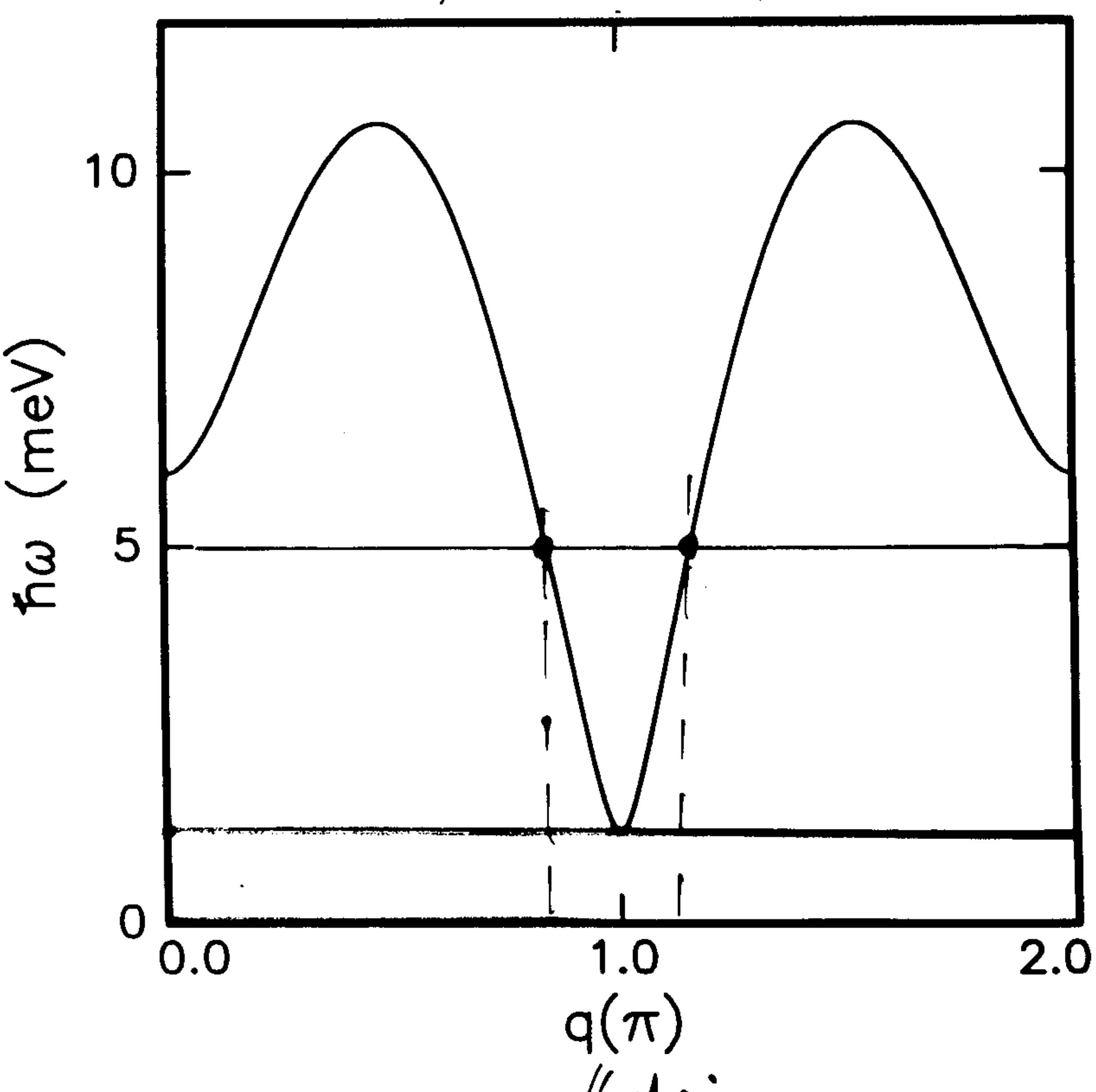
If $q > \pi$,

$$S(q) = \frac{1}{2}\left[\frac{d\, q\cos\theta}{d\cos\theta}\right]^{-1} = \boxed{\frac{1}{2q}}$$


0.5
0.0
S(q)
0
5
10
q(π)

All info about 1-D system is present in POWDER!

$\hbar\omega$ fixes discrete set of $q_{\parallel}$, which together with nominal $Q$, determine $\langle S(Q)\rangle_{powder}$ exactly!




// chain

$$\langle S(Q)\rangle\Big|_{\hbar\omega_0} = \sum_{\hbar\omega(q_i)=\hbar\omega_0} \Theta(Q-q_i)\,\frac{\partial q}{\partial \hbar\omega(q)}\Big|_{q_i} M^2(q_i)$$

# Fitting the Neutron Data

**Start with the single-mode structure factor**

$$S^{\perp,p}(q,\omega) = -\frac{2}{3}\frac{V}{(2\pi)^3} \frac{g^2\langle H\rangle}{\hbar\omega_{\perp,p}(q_p)} (1-\cos(q_p a)) \delta(\hbar\omega - \hbar\omega_{\perp,p}(q_p))$$

**Consistent with numerical simulations and NENP experiments.** **S. Ma, et al. PRL 69, 3571 (1992)**

**V Volume per Ni.** **$g = 2$**

**$\langle H\rangle$ is the ground state energy per spin.**

**$q_p$ is the component of q along the chain.**

# Dispersion Relation NENP

$$\omega_{\perp,p}(q_p) =$$

$$\left[\Delta^2_{\perp,p} + v^2 \sin^2(q_p a) + A_{\perp,p} \cos^2(q_p a/2)\right]^{1/2}$$

S. Ma, et al. PRL 69, 3571 (1992)

For $Y_2 BaNiO_5$:

$\Delta_\perp$ = 9.11 ± 0.2 meV

$\Delta_{\parallel}$ = 16.6 ± 0.3

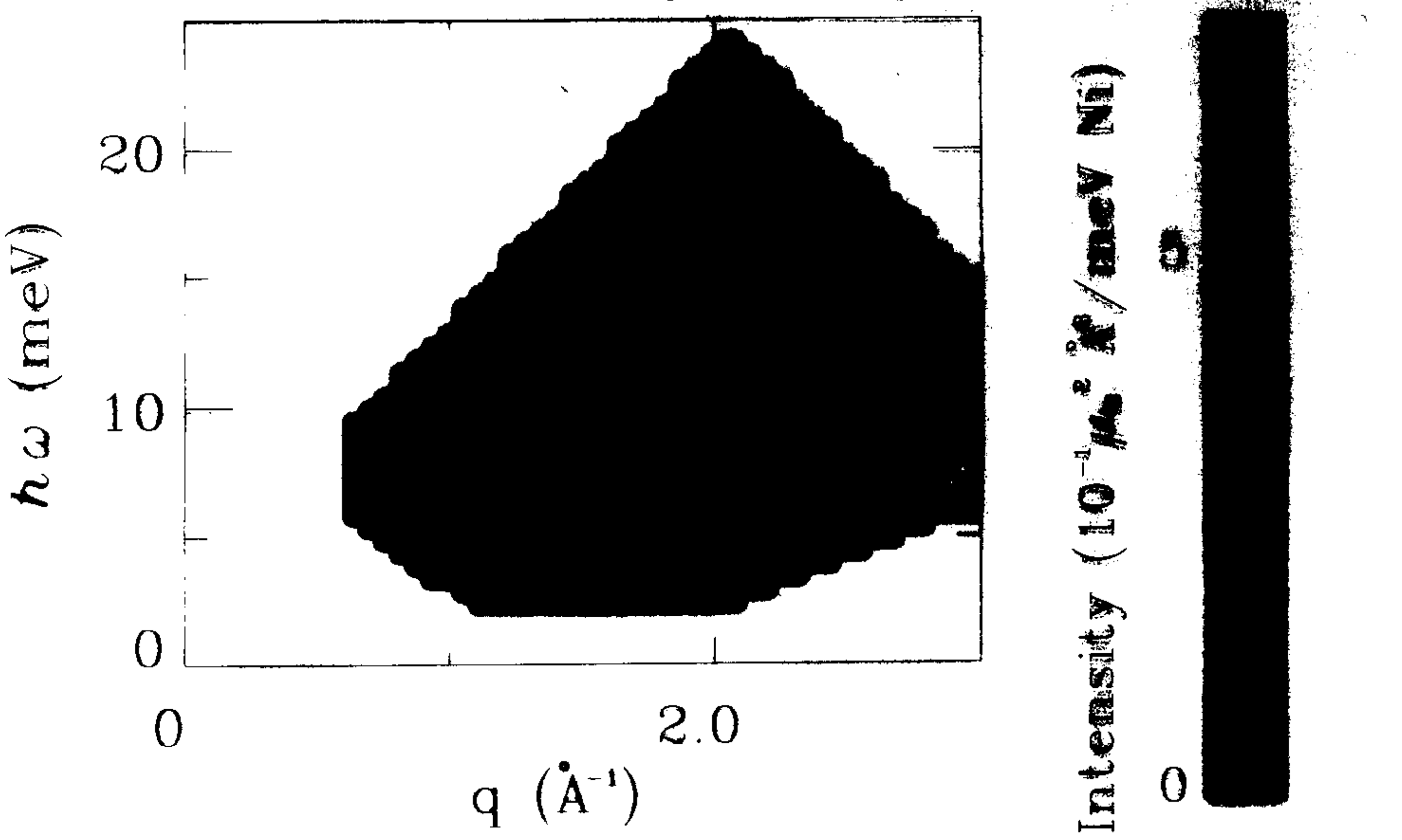
$v$ = 54 ± 15 meV ≃ J

(assuming A = 0)

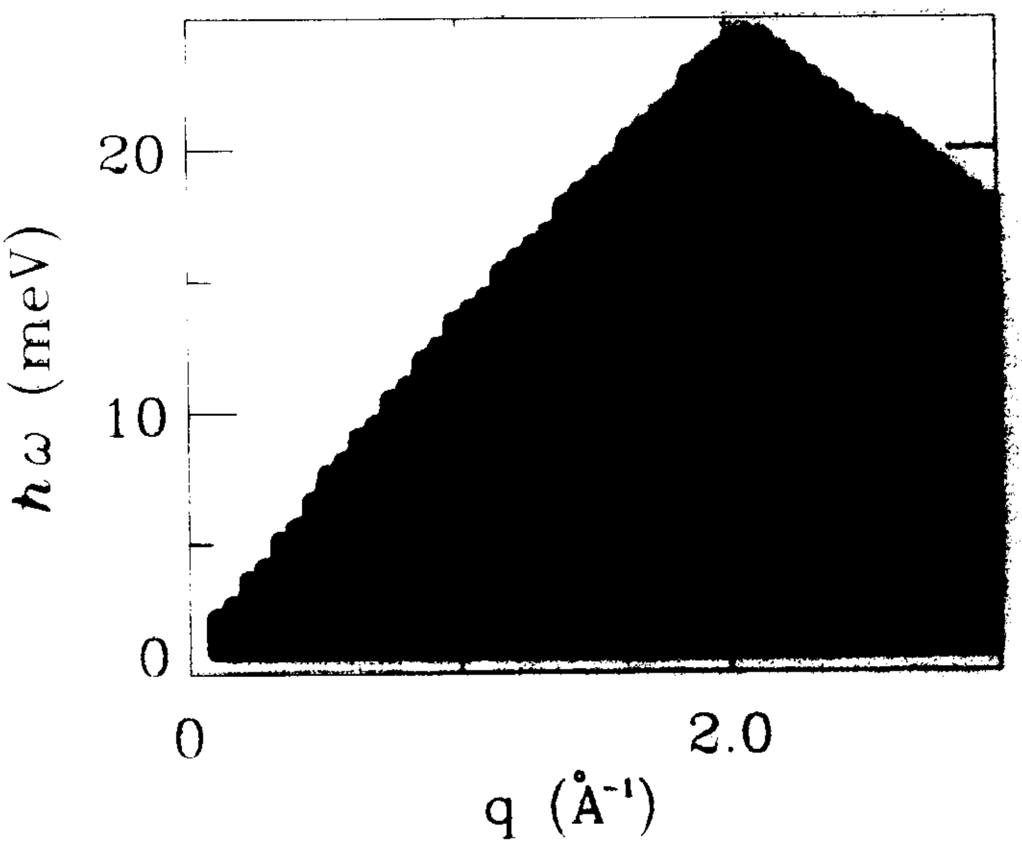
N.B. bulk value for J ≅ 50 meV

$\langle \mathcal{H} \rangle$ = 40 ± 15 meV

Data For $Y_2BaNiO_5$




Fit For $Y_2BaNiO_5$

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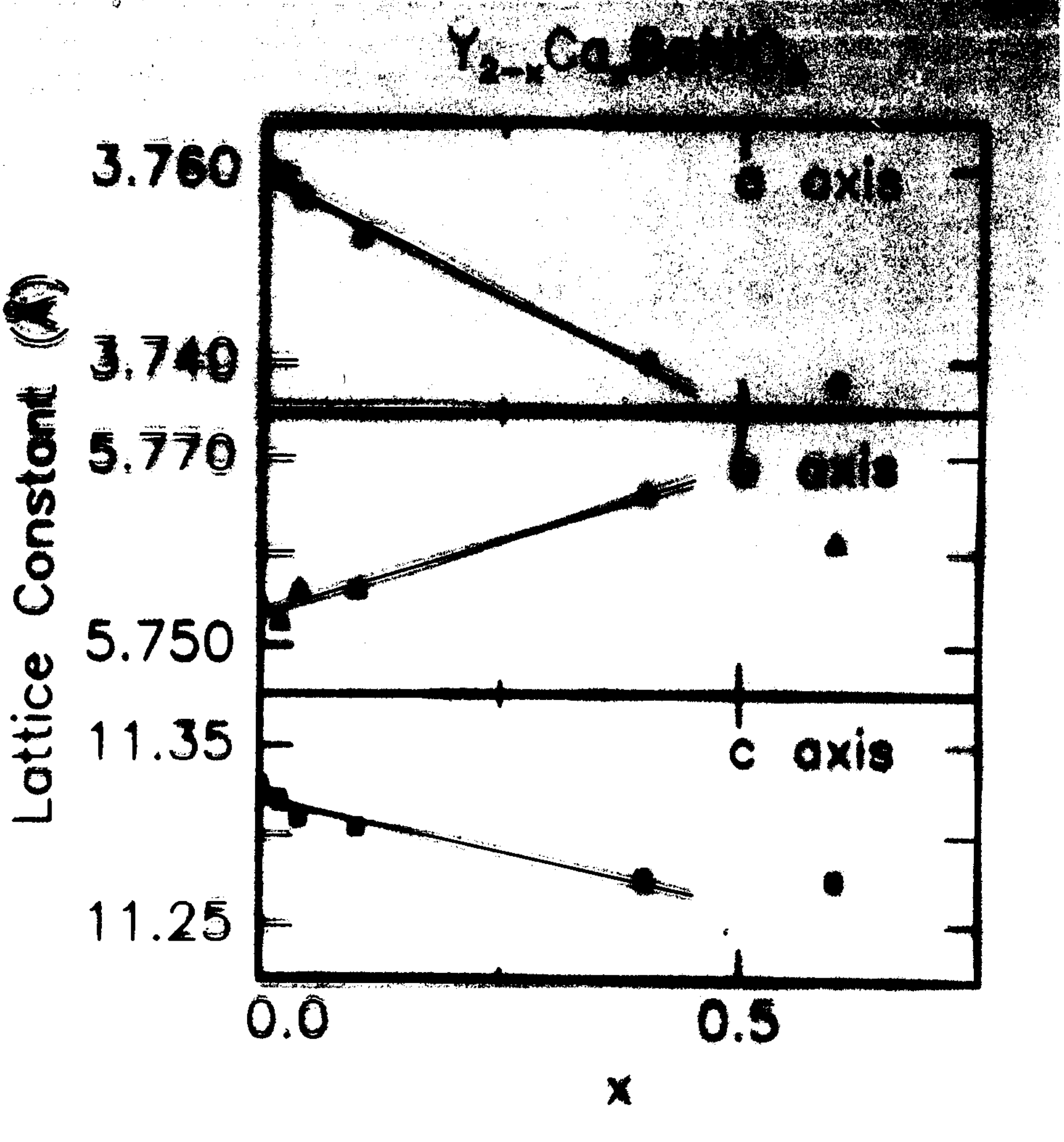
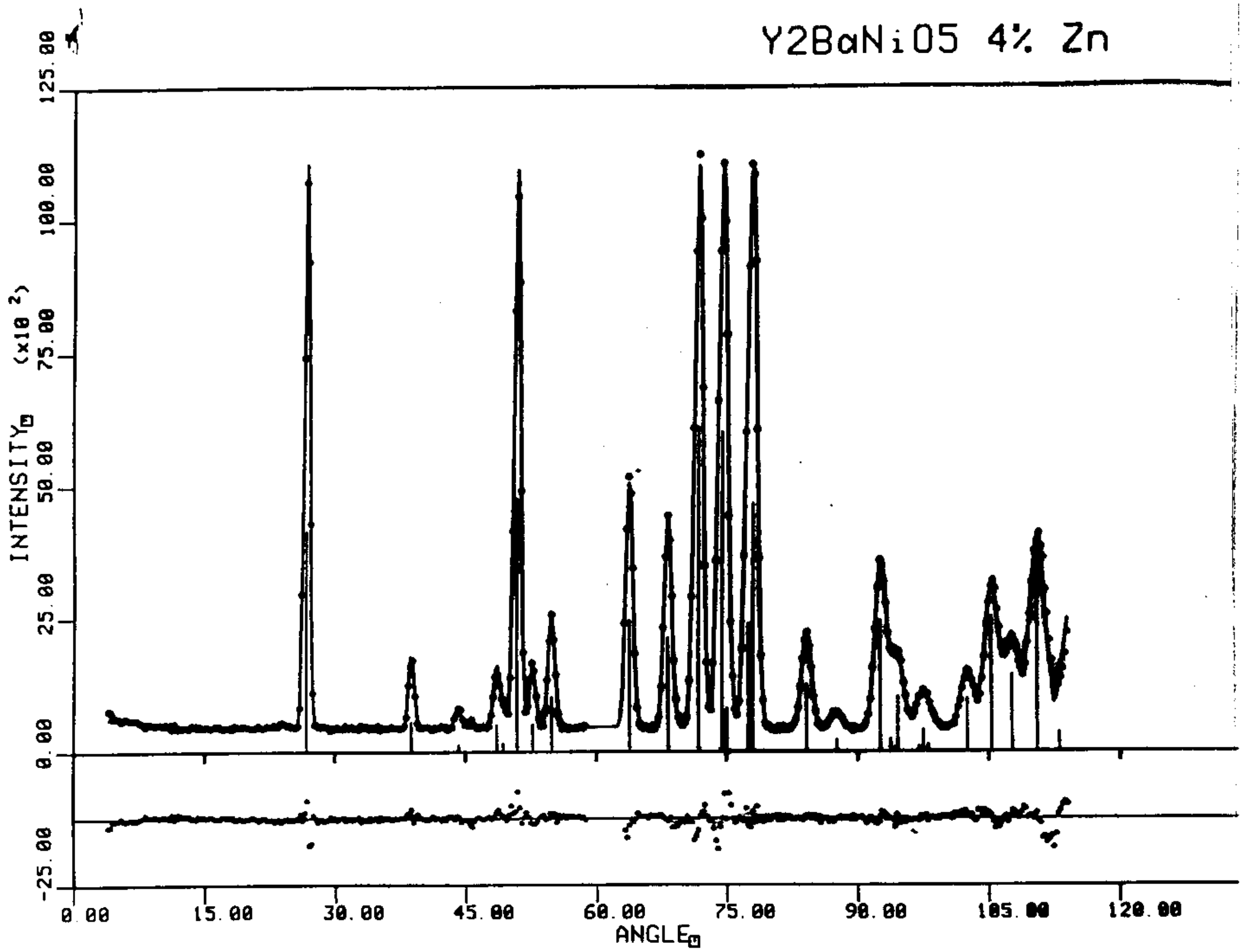
## Neutron Activation [illegible]

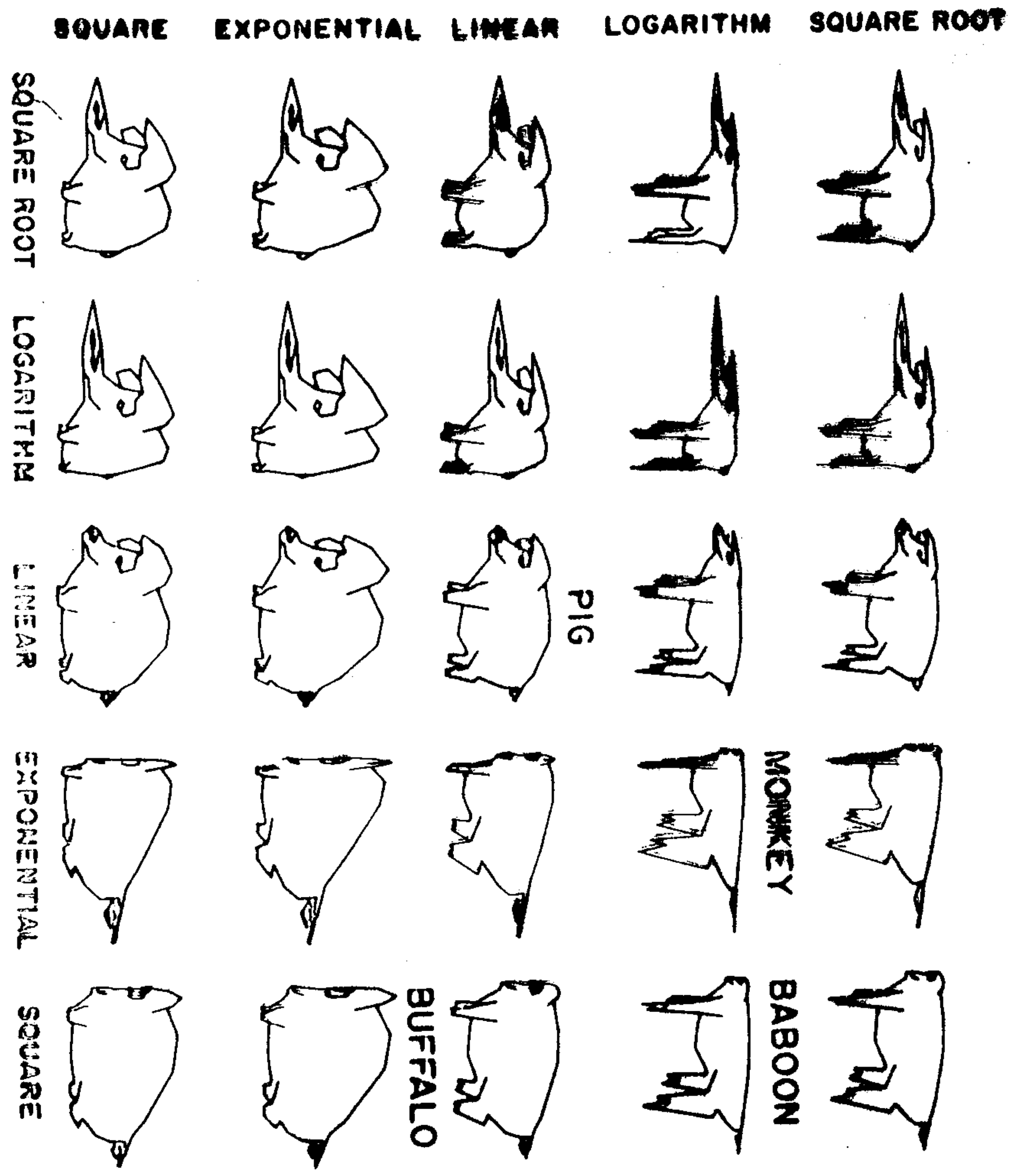
| Sample | Y | Ba | [illegible] | [illegible] |
|---|---|---|---|---|
| Ca 0.04 | 1.95 | 0.99 | 0.99 | [illegible] |
| ± | 0.03 | 0.015 | [illegible] | .01 |
| Ca 0.10 | 1.90 | 0.99 | 0.99 | [illegible] |
| ± | .05 | 0.04 | .03 | 0.01 |
| Zn 0.04 | 2.00 | 1.02 | 0.94 | [illegible] |
| ± | 0.05 | 0.04 | .03 | .01 |

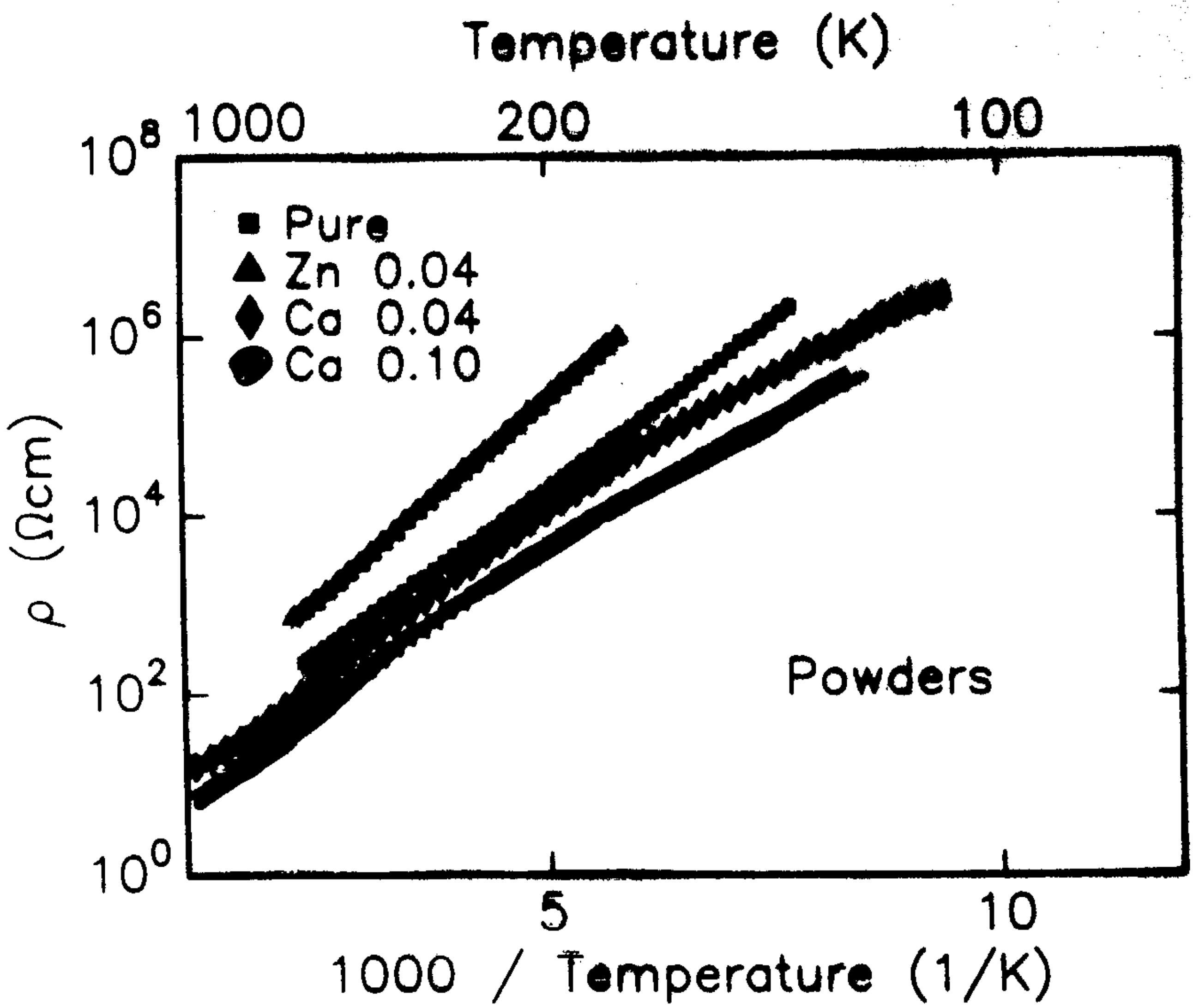


$Y_{2-x}Ca_xBaNiO_5$
a axis
b axis
c axis
3.760
3.740
5.770
5.750
11.35
11.25
Lattice Constant (Å)
0.0
0.5
x

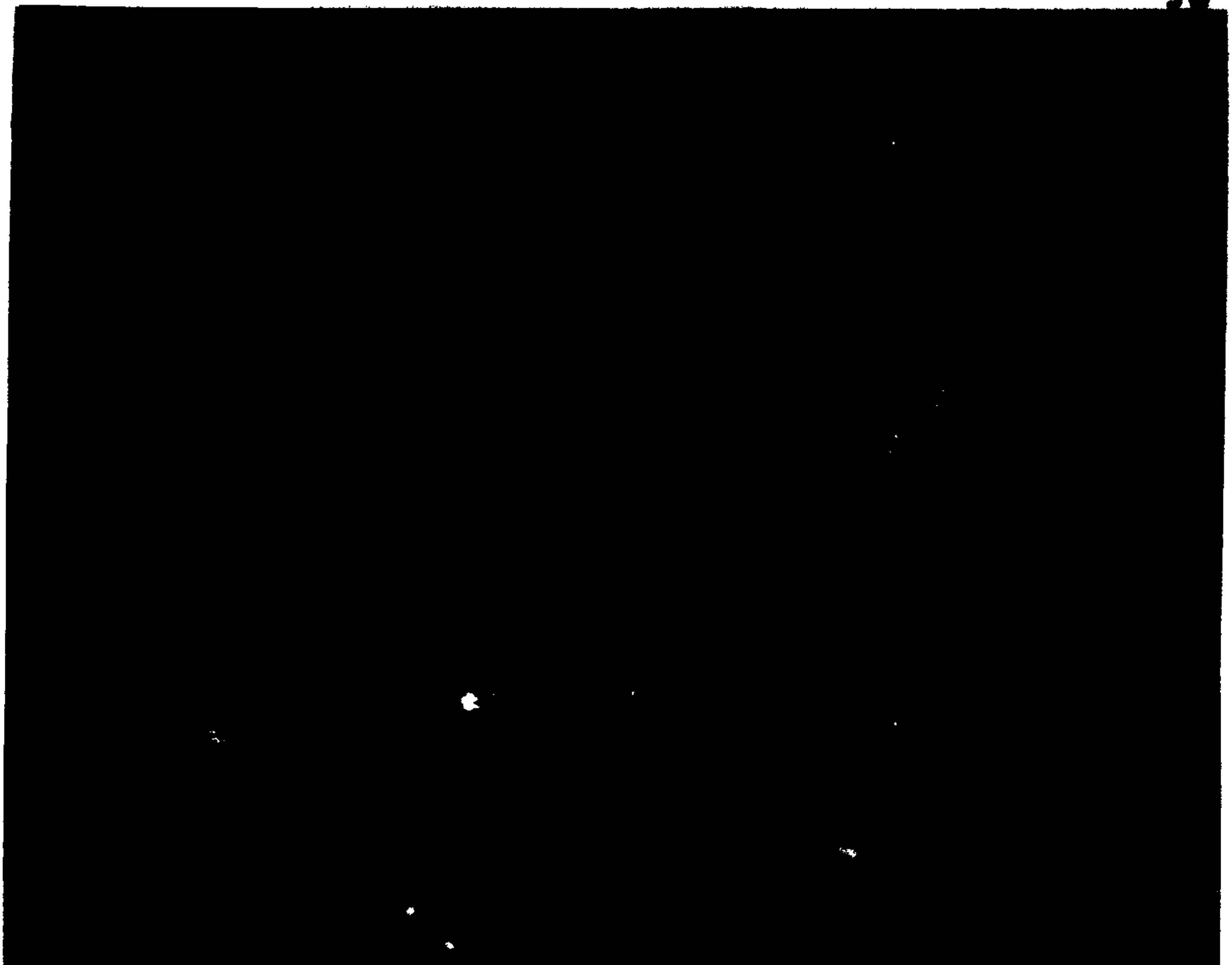
34136

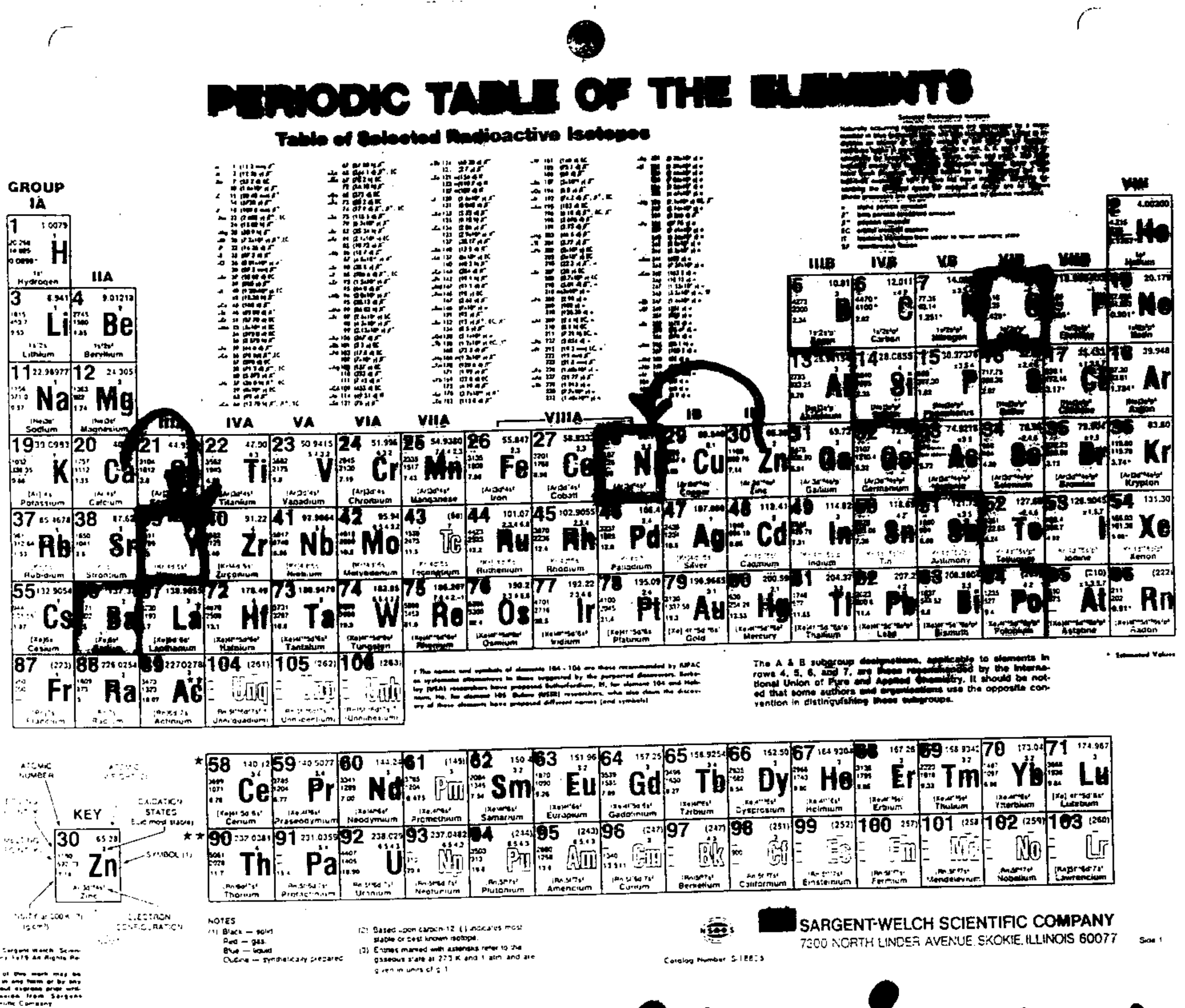

Y2BaNiO5 4% Zn
INTENSITY
(x10 2)
125.00
100.00
75.00
50.00
25.00
0.00
-25.00
0.00
15.00
30.00
45.00
60.00
75.00
90.00
105.00
120.00
ANGLE


SQUARE
EXPONENTIAL
LINEAR
LOGARITHM
SQUARE ROOT
SQUARE ROOT
LOGARITHM
LINEAR
EXPONENTIAL
SQUARE
PIG
MONKEY
BABOON
BUFFALO



Temperature (K)
1000
200
100
$10^8$
$10^6$
$10^4$
$10^2$
$10^0$
Pure
Zn 0.04
Ca 0.04
Ca 0.10
$\rho$ ($\Omega$cm)
Powders
5
10
1000 / Temperature (1/K)






$Ni^{2+}$ $d^{8}$ $S = 1$

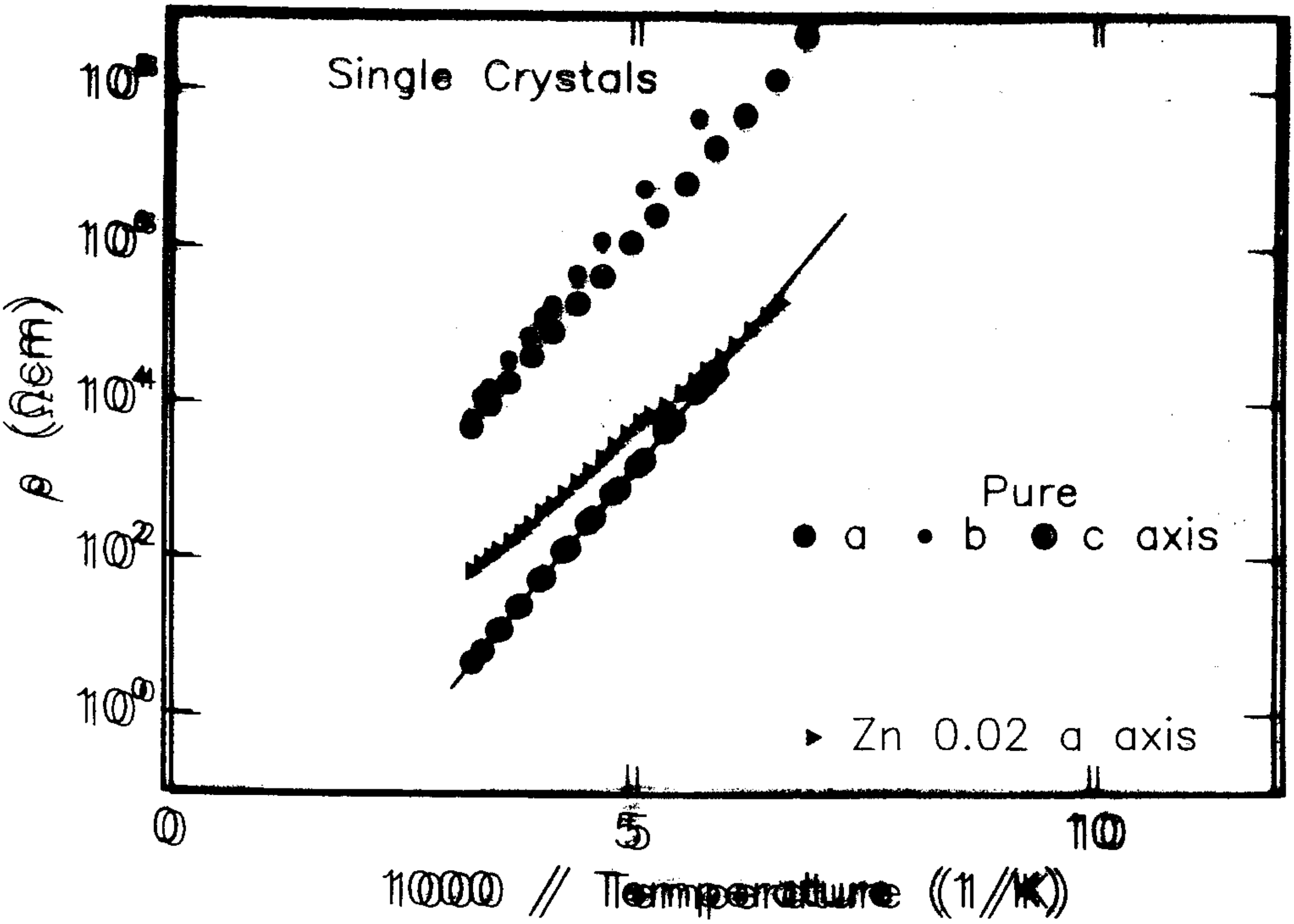
$Zn^{2+}$ $d^{10}$ $S = 0$

$Ca^{2+(-1)} = Ca^{1+}$

$Y^{2+}$

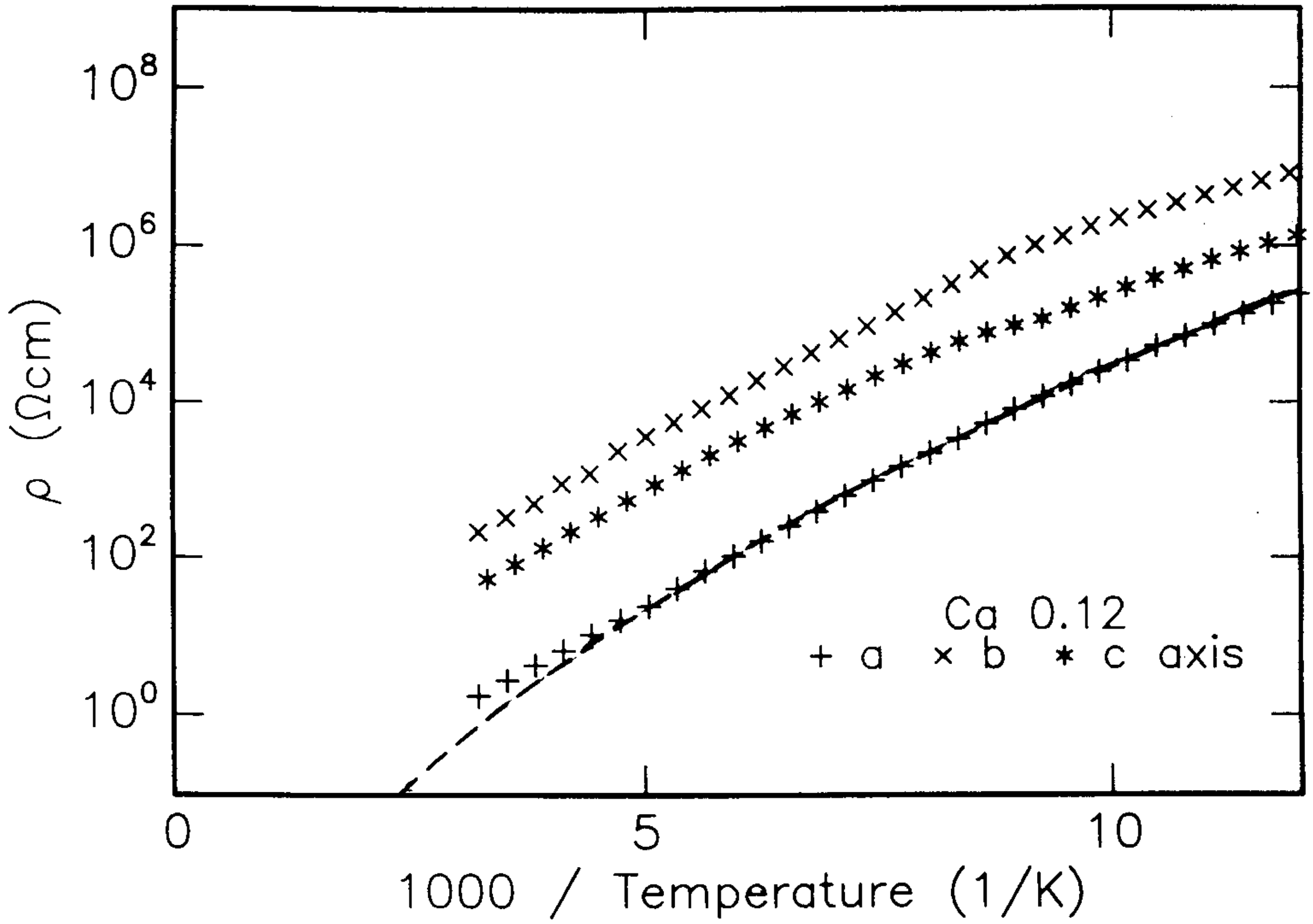
$$\rho = \rho_0 \exp(\Delta_g / kT)$$

$$\Delta = 0.6\,eV$$




Zn "blocks" activated hopping along chains

32



$10^8$
$10^6$
$10^4$
$10^2$
$10^0$
ρ (Ωcm)
Ca 0.12
+ a × b ∗ c axis
0
5
10
1000 / Temperature (1/K)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## Variable Range Hopping in 1D

**Hopping between states with distributions in energy and space.**

**Transition probability**

$$w_{ij} = w_0 \exp\left(-\frac{2R}{\lambda} - \frac{W}{k_B T}\right)$$

**$\lambda$ is the localization length**

**assume constant density of states, g**

**one state in** $W = 1/Rg$

**Find extremum in exponent for most probable hopping distance $R_a$**

$$R_a = \left(\frac{\lambda}{2k_B T}\right)^{1/2}, \quad w_a = \left(\frac{2k_B T}{g\lambda}\right)^{1/2}$$

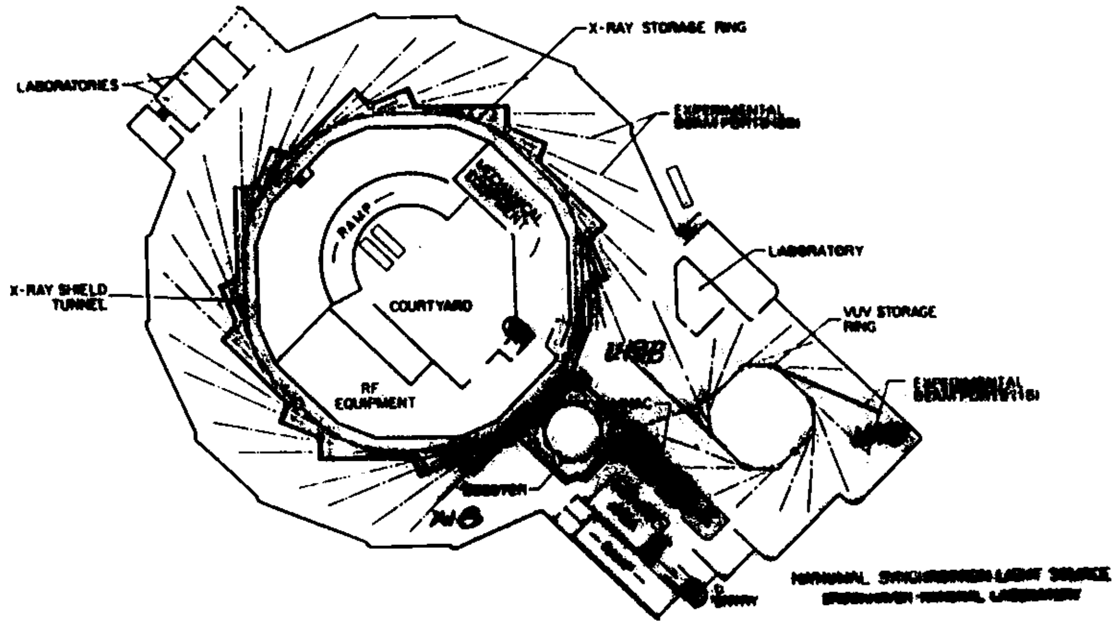
$$\boxed{\rho = \rho_0 \exp\left(\frac{T_0}{T}\right)^{1/2}, \quad T_0 = \frac{8}{g\lambda k_B}.}$$

$T_0 = 4.5\,eV$ ✓

$$\rho \approx \exp\left(\frac{T_0}{T}\right)^{\frac{1}{d+1}}$$

Where are the carriers?

DO NOT AFFIX OVERLAYS ALONG THIS SURFACE




E-9148 (6-85)
AT&T BELL LABORATORIES

AT&T

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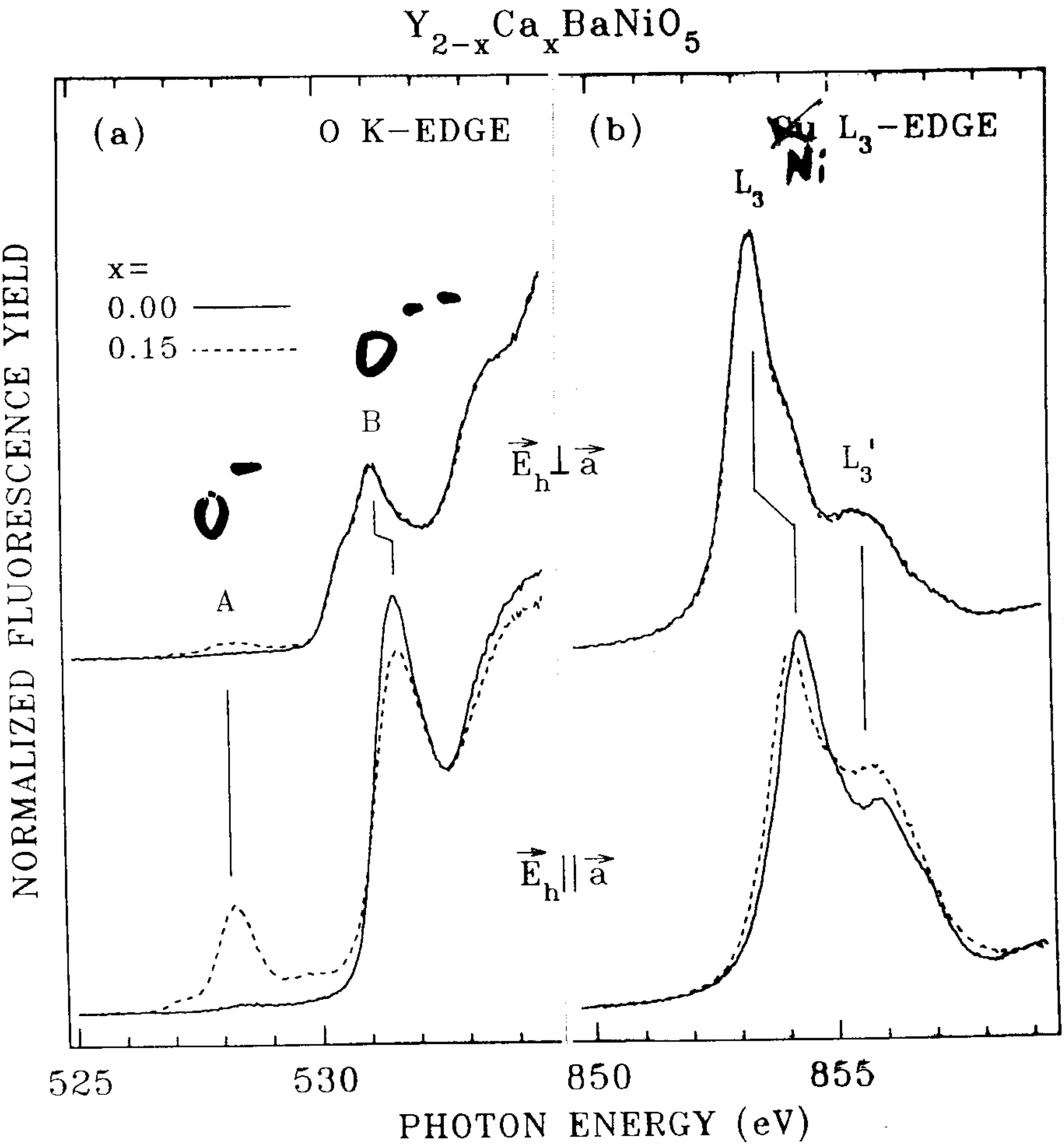
(41)

J.-H. Park und C.T. Chen




O – Ni – O – Ni – O

a

w. ...

1) CROSS-OVER FROM

$\exp \Delta_g / 2k_B T$

for pure & Zn-doped
( $\Delta_g$ = 0.3 - 0.6 eV )

to

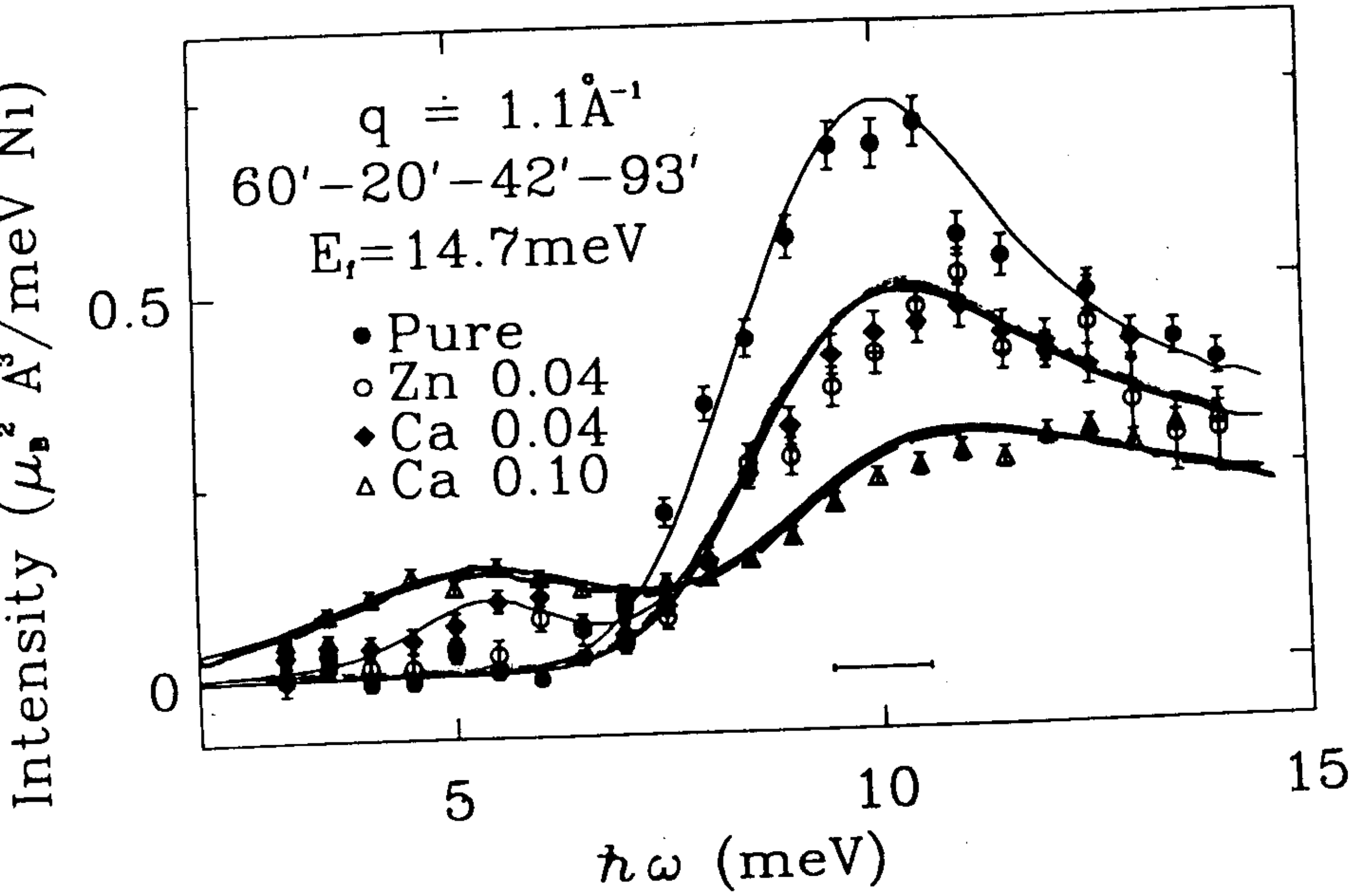
$\exp -(T_0/T)^{1/2}$

with $T_0 \simeq 4.5$ eV
for Ca-doped

2) $O^{--}$ to $O^{-}$

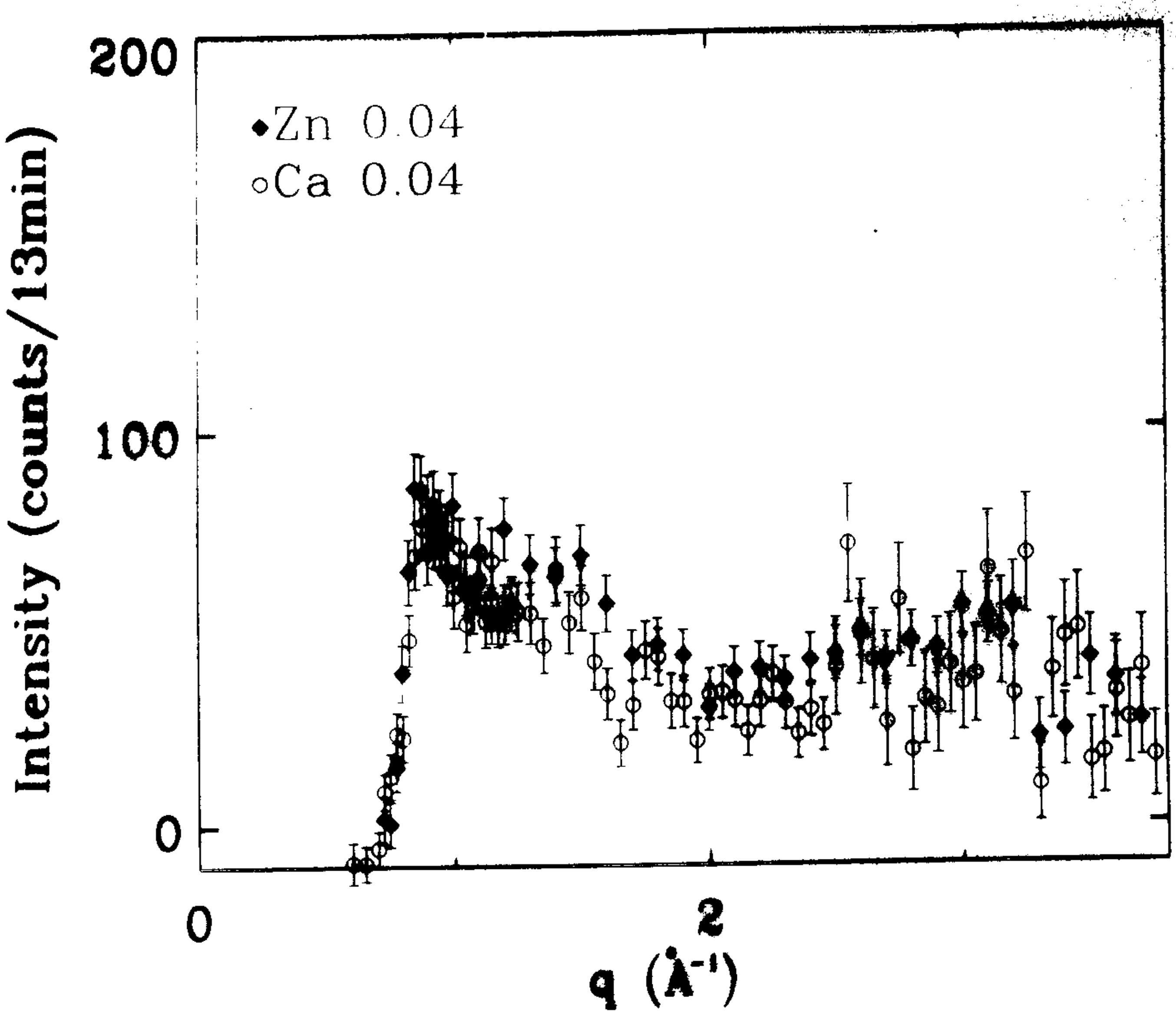
hole motion
// chains

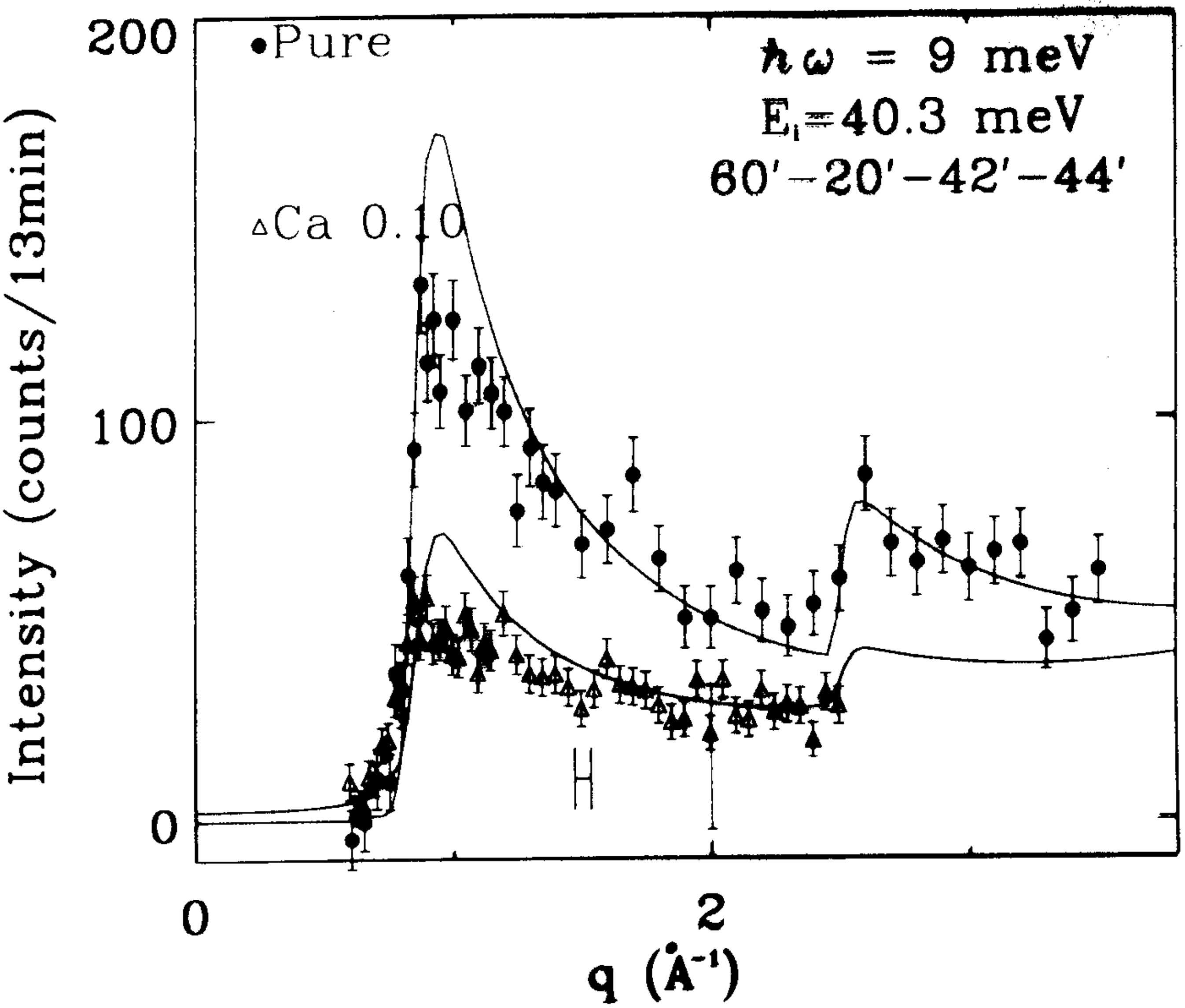
holes more on O
than on Ni



q ≐ 1.1Å$^{-1}$
60′–20′–42′–93′
$E_f$=14.7meV
Pure
Zn 0.04
Ca 0.04
Ca 0.10
Intensity ($\mu_B^2$ Å$^3$/meV Ni)
0.5
0
5
10
15
$\hbar\omega$ (meV)


FIGURE 5


200
100
0
Intensity (counts/13min)
◆Zn 0.04
○Ca 0.04
0
2
q (Å⁻¹)



•Pure
△Ca 0.10
$\hbar\omega$ = 9 meV
$E_i$=40.3 meV
60'−20'−42'−44'
200
100
0
Intensity (counts/13min)
0
2
q (Å$^{-1}$)

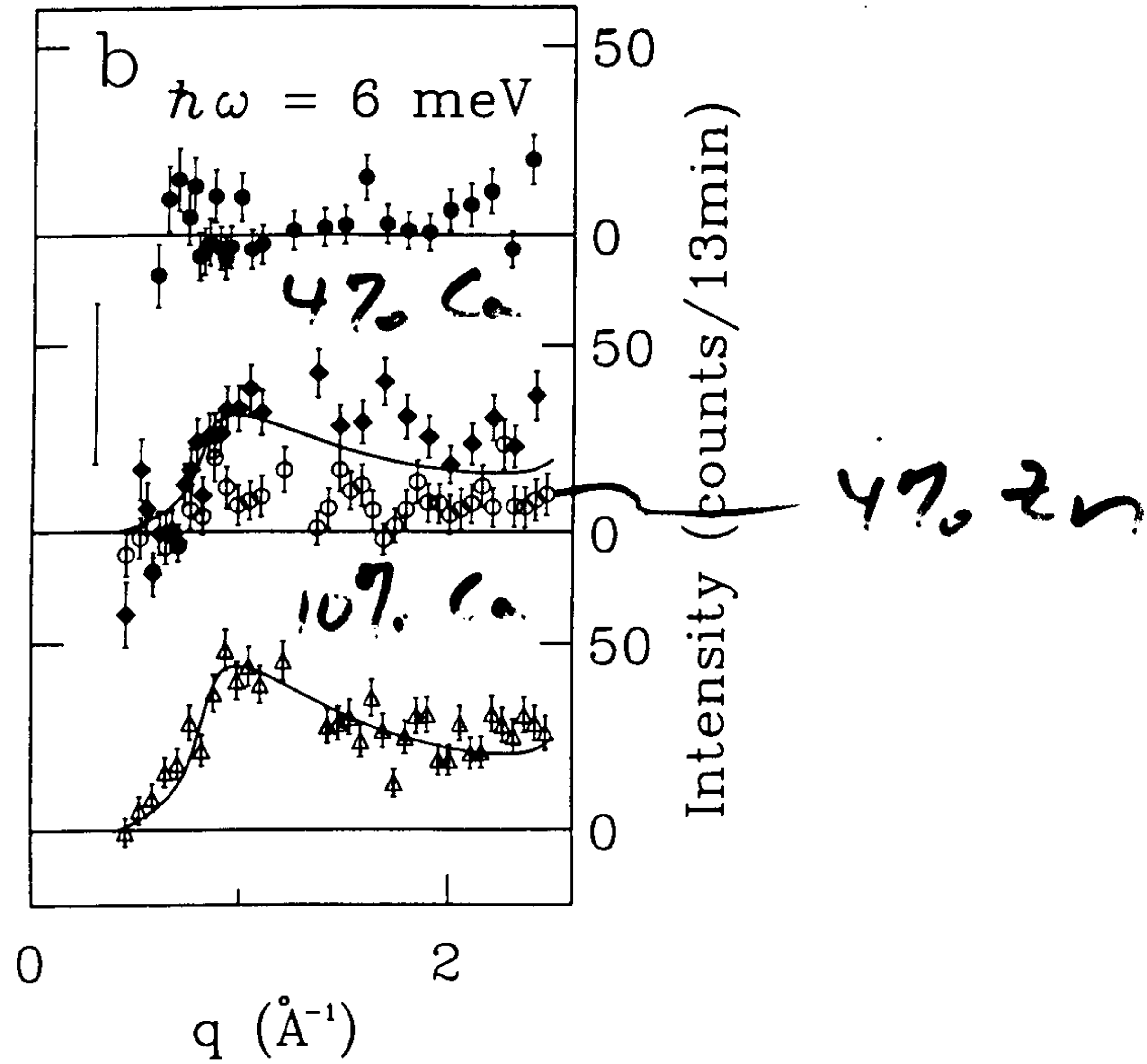
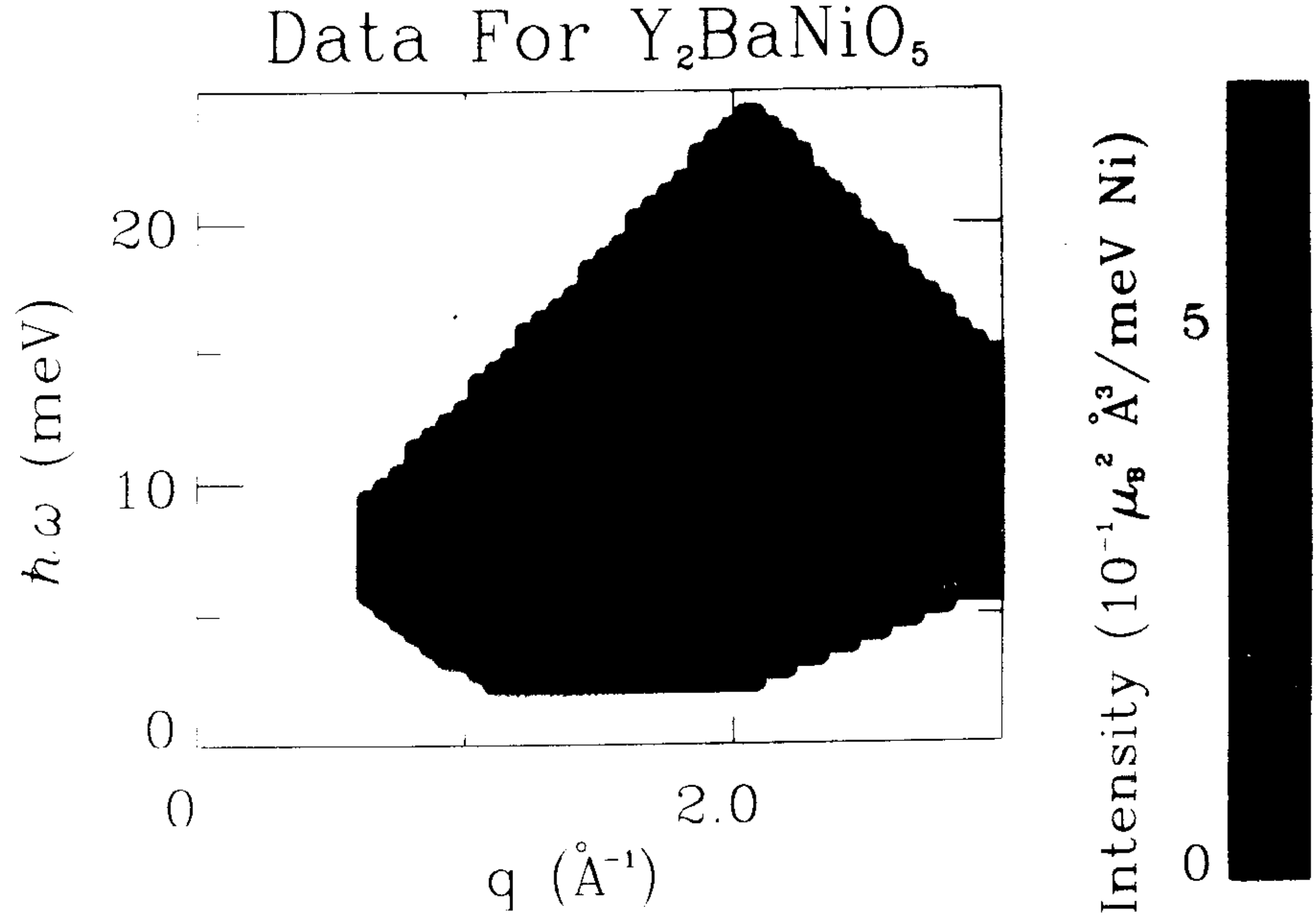
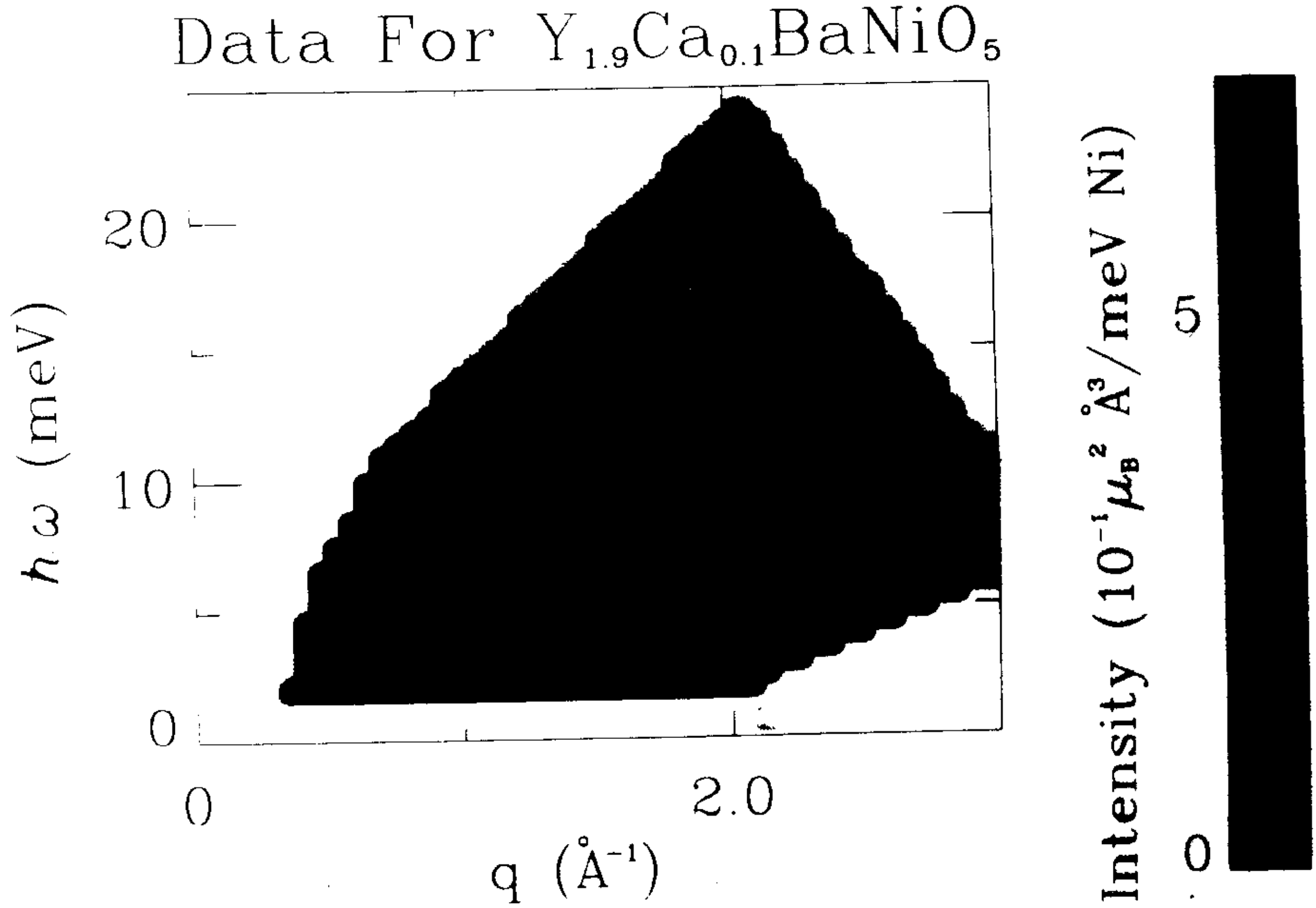

b
ħω = 6 meV
50
0
4% Ca
50
4% Zn
0
10% Ca
50
0
Intensity (counts/13min)
0
2
q (Å$^{-1}$)

FIGURE 4b


Data For $Y_2BaNiO_5$
$\hbar\omega$ (meV)
0
10
20
0
2.0
q ($\mathring{A}^{-1}$)
Intensity ($10^{-1}\mu_B^2\,\mathring{A}^3$/meV Ni)
0
5


Data For $Y_{1.9}Ca_{0.1}BaNiO_5$
$\hbar\omega$ (meV)
0
10
20
0
2.0
q ($\mathring{A}^{-1}$)
Intensity ($10^{-1}\mu_B^2\,\mathring{A}^3$/meV Ni)
0
5

At $\hbar\omega \gtrsim 10$ meV

CHAIN CUTTING
$\equiv$
CHAIN DOPING

At $\hbar\omega \lesssim 10$ meV

NEW STATES FOR CHAIN DOPING BUT NOT FOR CUTTING

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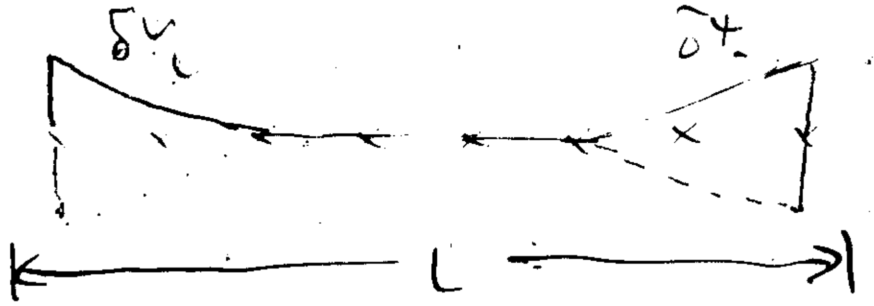
CHAIN CUTTING
$\equiv$
BOX QUANTIZATION
$\oplus$
DISTRIBUTION OF BOX SIZES

C.F. FINITE SIZE EFFECTS

What does this mean?

<u>Consider Ground State first</u>

$\overline{\Psi}_\infty$




$— \; = \;$ e.g. $\langle n_i \cdot n_{i+1} \rangle - \overline{\langle n_i \cdot n_{i+1} \rangle}$

$\therefore \; \Psi_L \approx \mathrm{Proj}_L(\Psi_\infty) + \delta\psi_\ell \otimes \delta\psi_r$

2 fold degenerate   2 fold degenerate

$\Rightarrow$ possible ground states are singlets & triplets because

$\langle \Psi_L | H | \Psi_L \rangle$ couples $\delta\psi_\ell$ & $\delta\psi_r$

$\rightarrow$ expect $\omega = 0$ "excitation" for triplet

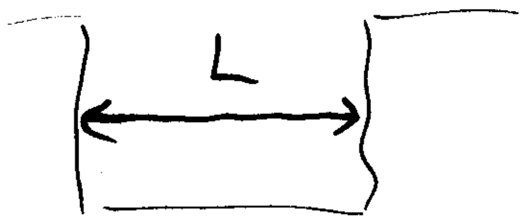
$\Rightarrow$ Curie tail + $S=1$ Schottky

AND THE EXCITED STATES —

for $L=\infty$, like particles in a Relativistic Field theory

$$E = \sqrt{k^2+m^2}$$

for finite $L$, like particles in a Box of size $L$.




But what boundary conditions?

ORTHOGONALITY TO $\Psi_L$

$$\langle \psi_e | \psi_L \rangle = 0$$

$\Rightarrow$ $\psi_e = 0$ at walls of box


$$\delta q = 2\pi / La$$

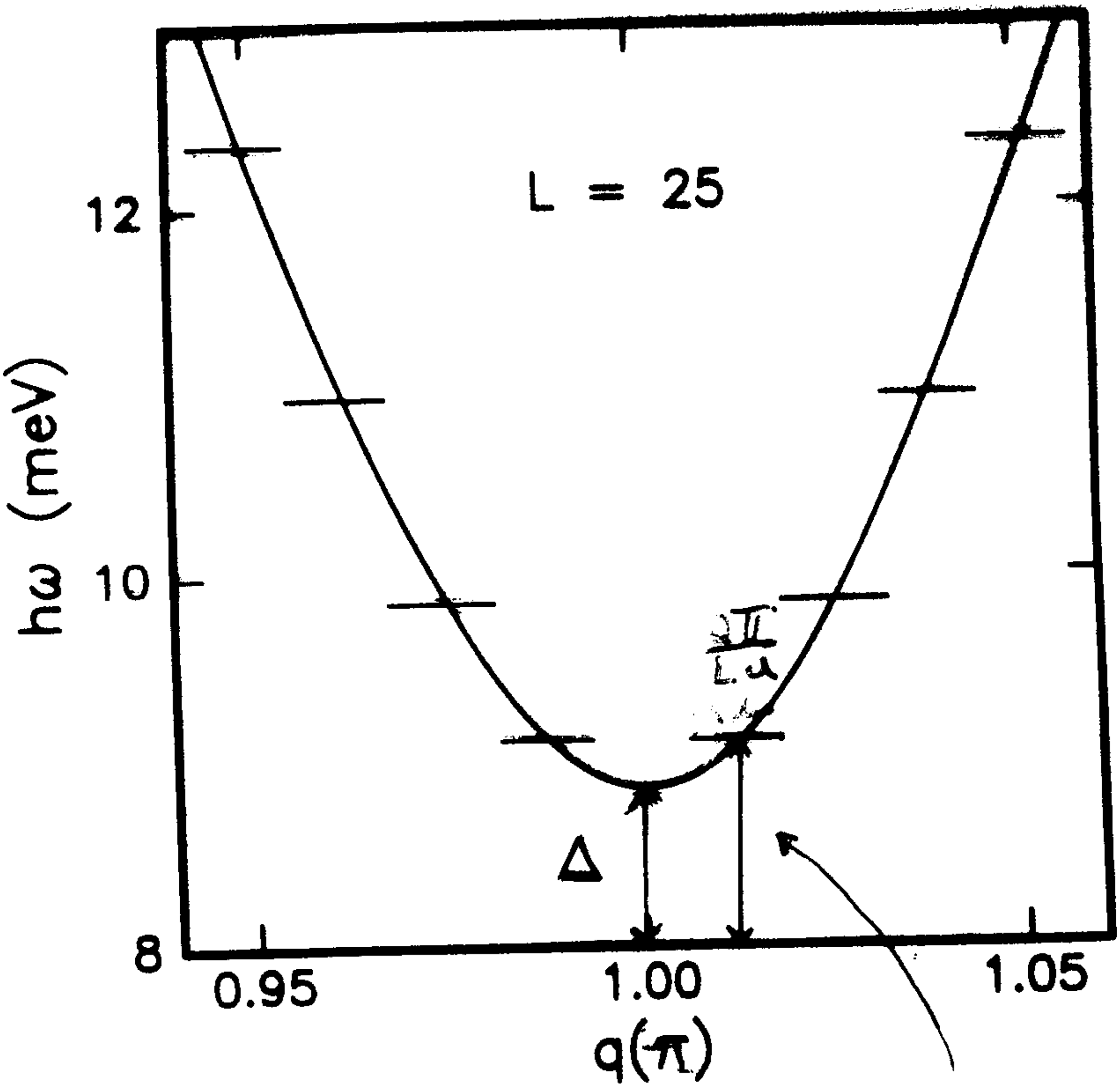
$$\Delta_L = \left( \Delta^2 + v^2 \sin^2 (\pi - L^{-1}) \right)^{1/2}$$

$$\left.\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right|_L = \left.\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right|_{L=\infty,\ \Delta_L} \otimes \exp - \frac{1}{2} \frac{q^2}{(\delta q)^2}$$

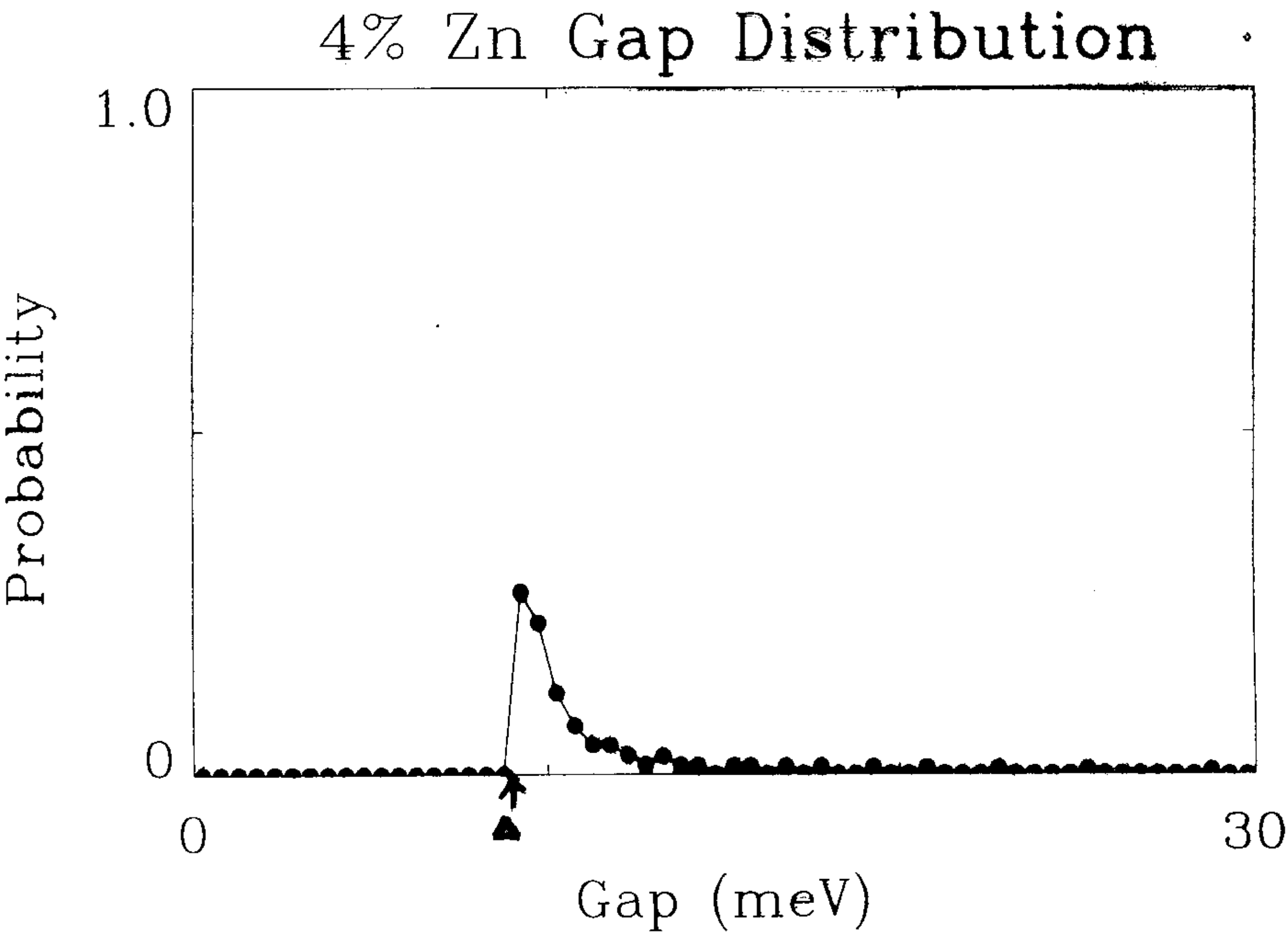
and

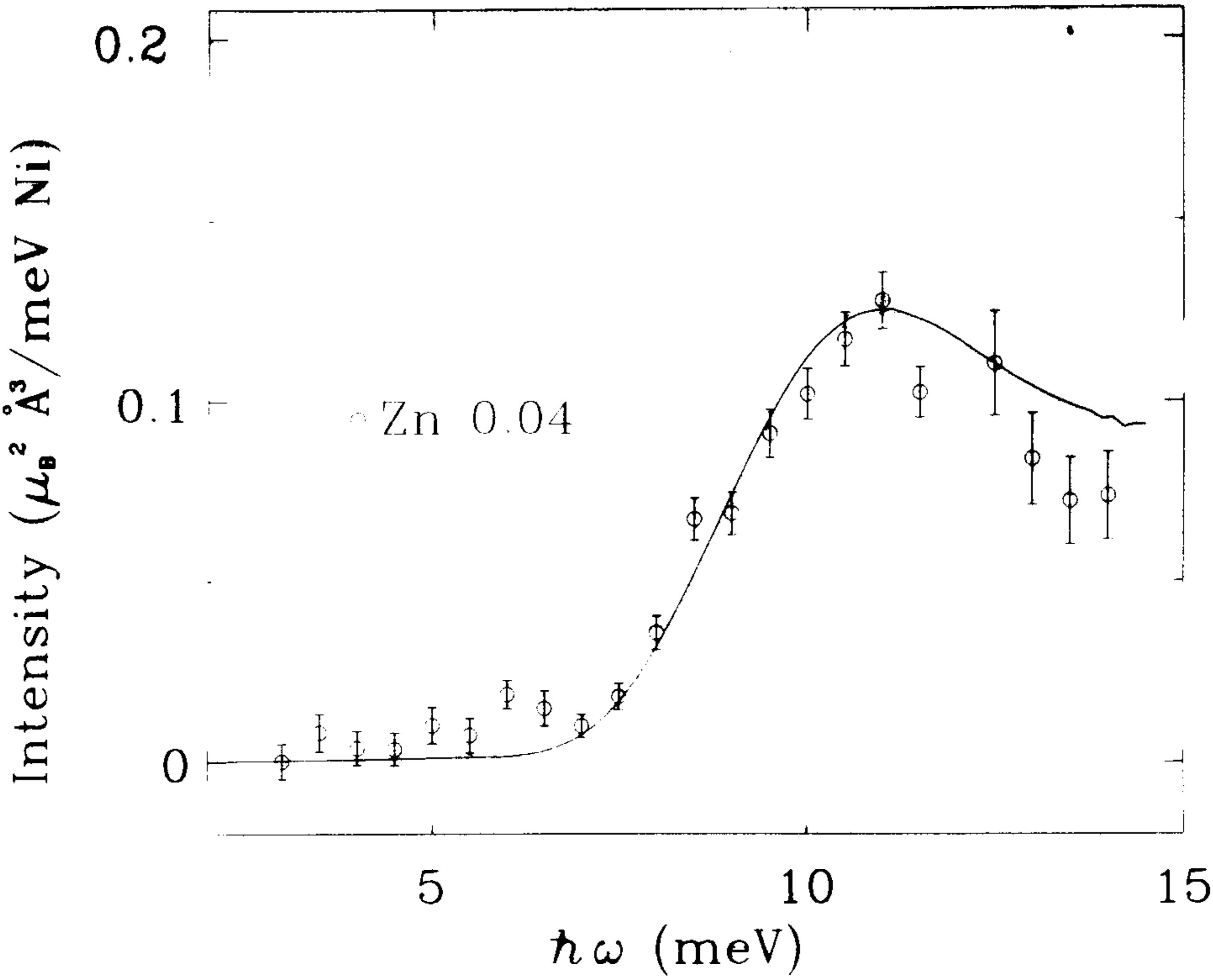
$$\left.\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right|_c = \sum_L \left.\frac{\partial^2 \sigma}{\partial \Omega \partial \omega}\right|_L \underbrace{L c^2 (1-c)^L}_{\text{prob. that a given site belongs to a Ni chain of length } L}$$

S.R. White and D.A. Huse Phys.Rev. B 48, 3844 (1993)

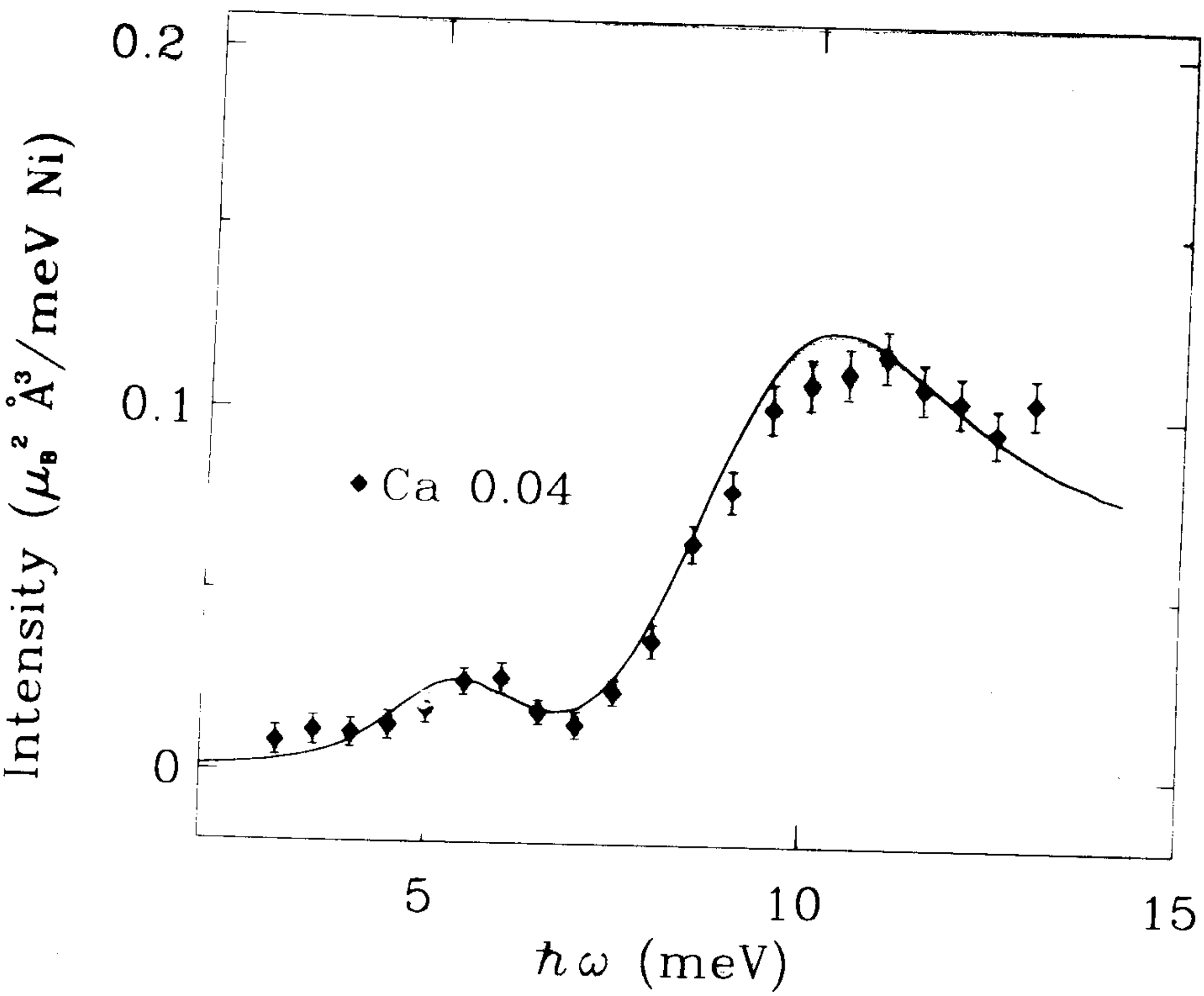


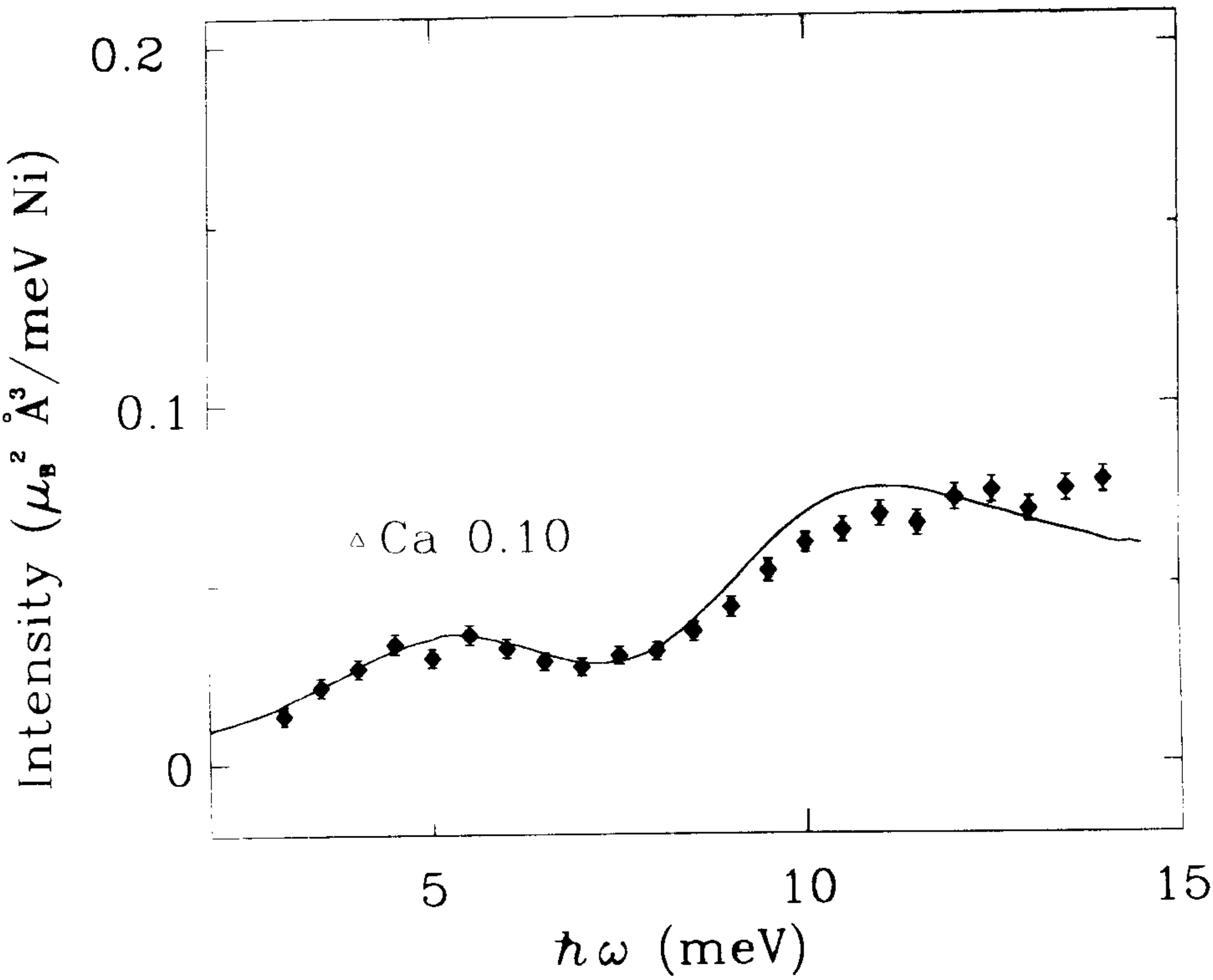

$\sqrt{\Delta^2 + V^2 \sin^2\left(\pi - \frac{\pi}{L}\right)}$


4% Zn Gap Distribution
1.0
0
Probability
0
30
Gap (meV)

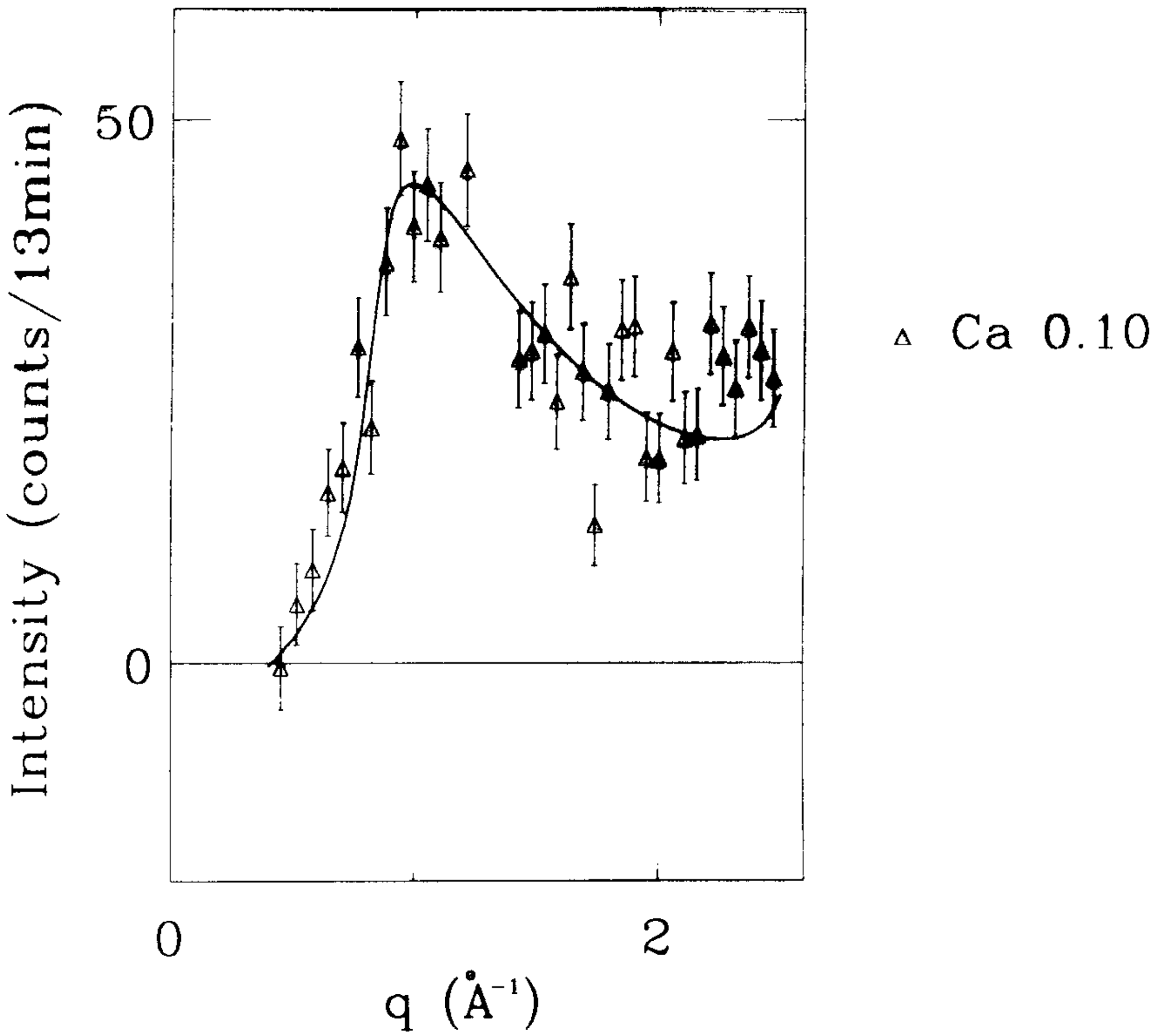


Intensity ($\mu_B^2$ Å$^3$/meV Ni)
0.2
0.1
0
Zn 0.04
5
10
15
$\hbar\omega$ (meV)


Intensity ($\mu_B^2$ Å$^3$/meV Ni)
0.2
0.1
0
Ca 0.04
5
10
15
$\hbar\omega$ (meV)



0.2
0.1
0
Intensity ($\mu_B^2$ Å$^3$/meV Ni)
△ Ca 0.10
5
10
15
$\hbar\omega$ (meV)


Intensity (counts/13min)
50
0
0
2
q (Å$^{-1}$)
Ca 0.10

# Modelling Sub-Gap Resonance

## Harmonic Oscillators

## With Spatial extent $\xi$

$$S_l^{\perp,p}(q_p,\omega)=\frac{V}{(2\pi)^3}$$

$$\left[1+2\sum_{l=1}^{\infty}(-1)^l\exp(-l/\xi)\frac{\cos(lq_p a)}{l^{1/2}}\right]$$

$$\frac{2}{\pi}\frac{\langle m^2\rangle}{3\hbar}\;\frac{\omega\omega_0\Gamma}{(\omega^2-\omega_0)+(\omega\Gamma)^2}$$

# Gap Resonance Fitting Parameters

| Ca Conc | $\omega_0$ (meV) | $\Gamma$(meV) | $\xi$ (a) | $\langle m^2\rangle$ ($\mu_B^2$) |
|---|---|---|---|---|
| 0.04 | 5.5 ±0.3 | 1.4 ±0.2 | > 10 | 11.3 ±3.0 |
| 0.10 | 5.7 ±0.3 | 4.4 ±0.2 | 4 ± 1 | 12.2 ±3.0 |

If $\langle m^2\rangle = g2\ S(S+1)$, and $g=2$

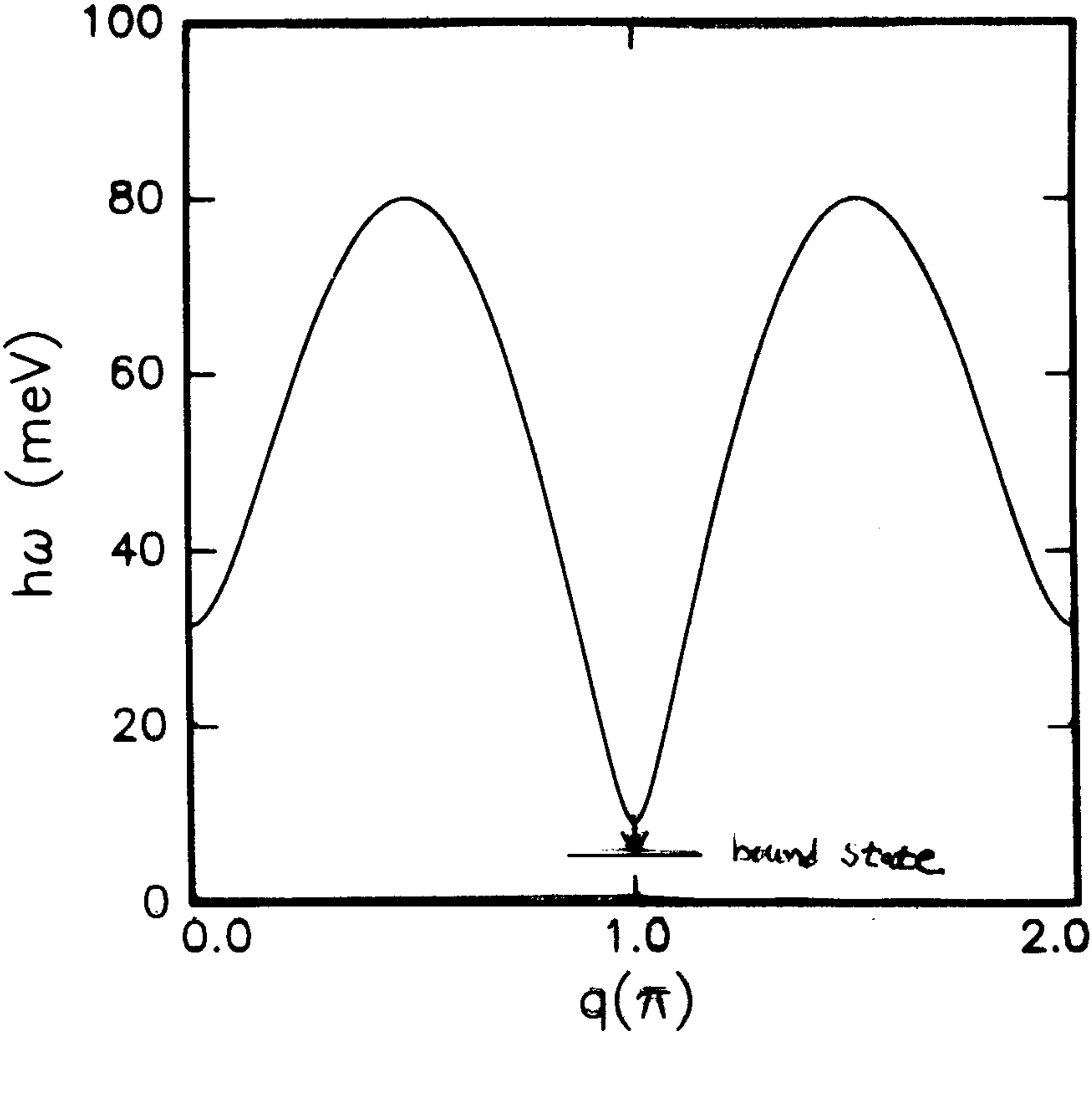
$1 < S < 3/2$

For spin 1/2 $\langle m^2\rangle = 3\ \mu_B^2$ Hole

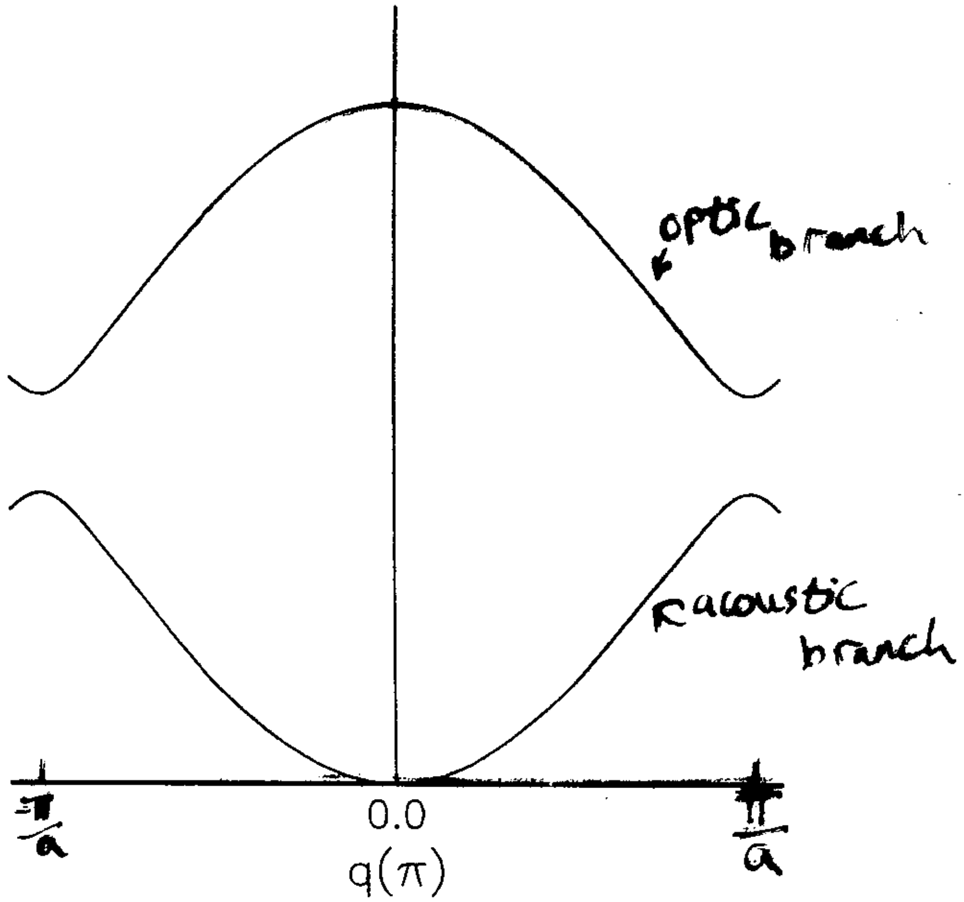
For spin 1 $\langle m^2\rangle = 8\ \mu_B^2$

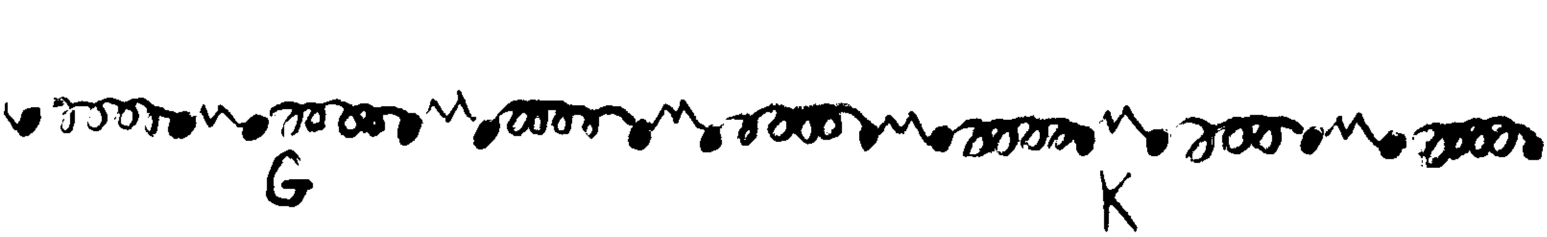
For spin 3/2 $\langle m^2\rangle = 15\ \mu_B^2$

- Disturbance introduced by carriers >> s=1/2 introduced by carriers !!


100
80
60
40
20
0
0.0
1.0
2.0
hω (meV)
q(π)
bound state

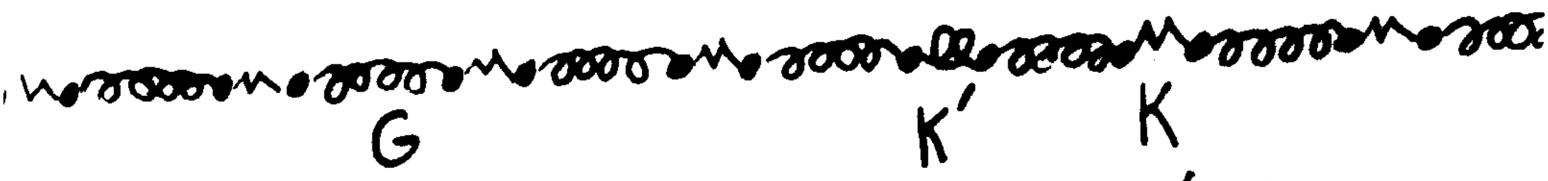
Diatomic Chain
Phonon Dispersion Relation



# Bound State
# Properties

$K' < K$

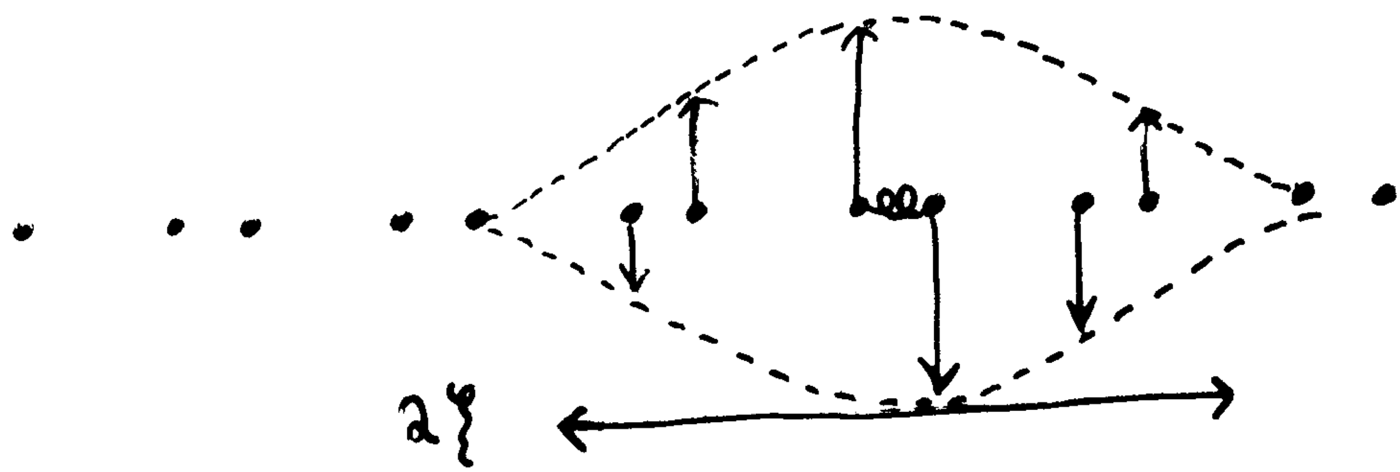



$q = \pi$ $\qquad \omega' = \sqrt{\dfrac{2K'}{M}}$ $\qquad$ as $K' \to K$, $\omega' \to \omega$

Spatial Extent

$$\xi = -a\left[\ln\left(\frac{K'/K}{2 - K'/K}\right)\right]^{-1}$$

as $K' \to K$, $\xi \to \infty$




As more 'defective' springs are added, a continuum of banded bound states will appear

$$\Gamma/\Delta E \to \sim 1$$

## How is the Optic Phonon model relevant to Spin Chains

$O^{2-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$

| | | | | |
|---|---|---|---|---|
| S=1 | S=1 | S=1 | S=1 | S=1 |

J

$O^{2-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$-$O^{1-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$-$O^{2-}$-$Ni^{2+}$

| | | | | |
|---|---|---|---|---|
| S=1 | S=1 | S=1 | S=1 | S=1 |

J'

$$J'_{Ni\text{-}Ni} \neq J_{Ni\text{-}Ni}$$

**Open Questions:**

1. **Role of Carrier Hopping**
2. **Why Effective decoupling at higher $\omega$?**

## Summary

- $Y_2BaNiO_5$ is a 1D, spin 1, AF consistent with the Haldane conjecture.

- Zn Doping
  Finite Size Effects - Box Quantization
  Seen for the first time for a Haldane chain
  . Probe Quantum Mechanics on a Mesoscopic length scale

- Ca doping :

  i) introduces holes onto the NiO chains

  ii) finite size effects

  iii) Holes modulate superexchange to produce new bound states , as in the optic phonon model.

# CONCLUSIONS

(1) WE ACTUALLY HAVE A
(1D !) SPIN LIQUID HOST
FOR CARRIERS & FINITE SIZE
CONFINERS. FIND MAGNETIC
POLARONS !

(2) WE HAVE A ("NEARLY") AFM
FERMI LIQUID WITH A
"SPIRAL" STATE NEAR IMT,
HOWEVER, RELATION TO AFMI
UNCLEAR

(3) 1 2 3-D OXIDES
SEEM TO PROVIDE
EXCELLENT REALIZATIONS
OF HOPES FOR
2-D OXIDES ...