Abstract Submitted
for the New York Meeting of the
American Physical Society
March 24-28, 1980

28

Physics and Astronomy
Classification Scheme
Number 72.40, 72.15

Suggested title of session
in which paper should be placed
Organic Conductors

Junction and Dielectric Characteristics of $(CH)_x$

W. D. GILL, P. M. GRANT, J. MAREK, T. TANI, T. C. CLARKE and G. B. STREET, IBM Research Lab, San Jose, CA 95193--

We report the results of our studies on the frequency dependence of the Schottky barrier properties and dielectric response function of undoped and lightly-doped trans- and cis-$(CH)_x$ in the range 100Hz to 10MHz, and, in addition, measurements of the static dielectric breakdown strength in each isomer. The temperature dependence from -100C to 100C and ageing behavior on exposure to air of the above characteristics are also reported. Strong dispersion of the dielectric constant with both frequency and temperature is observed in trans$(CH)_x$ but not in cis-$(CH)_x$. A large frequency dependence is also found in the reverse bias impedance of Schottky barriers between In and lightly-doped trans-$(CH)_x$. These data will be discussed in terms of various models which have been proposed for the transport properties of semiconducting polymers.

(X) Prefer Standard Session

Signature of APS Member

P. M. Grant
Same name typewritten

IBM Research Laboratory
5600 Cottle Road, K32/281
San Jose, CA 95193

GRANT

Bulletin of the American Physical Society

Volume 25, Number 3, March 1980

PROGRAM OF THE 1980 MARCH MEETING IN NEW YORK, N.Y., 24–28 MARCH 1980

Published for the American Physical Society
by the American Institute of Physics

965 - IBM - 01

monotonically with decreasing temperature, but its temperature dependence is inconsistent with a simple power law or activated conductivity. There is no magnetic field dependence for H<200 Oe, and even in the lowest fields attainable there is no evidence for a superconducting phase transition.

*Supported by NSF Grant DMR79-00830.

AB 10

Resonance Raman Spectroscopy of *cis* and *trans* Polyacetylene,* L.S. LICHTMANN & D.B. FITCHEN, Cornell U., Ithaca, N.Y.--Resonant Raman spectra of cis and trans $(CH)_x$ at 77K for laser excitation wavelengths throughout the visible spectrum are presented. These have been converted to excitation profiles for the resonantly-enhanced carbon-carbon vibrations of both isomers. There is a large enhancement of cis $(CH)_x$ Raman lines with wavelengths near 600nm, corresponding to the electronic absorption at this point. In trans $(CH)_x$, lineshapes and excitation profiles are used to deduce the form of the distribution of conjugation lengths, using simple models for Raman scattering from a linear conjugated molecule of variable lengths. Variations in lineshapes and excitation profiles, and hence of this distribution, with synthetic procedure, film morphology, isomerization procedure, and oxidation or doping of $(CH)_x$ are presented and analyzed in terms of information provided on the nature of the conjugation-limiting bonding defect. The effect of dopants in producing isomerization of cis $(CH)_x$ films is also considered. In addition, the first reported Raman spectra of poly(deuterated acetylene), $(CD)_x$, are presented.

* Work supported in part by the NSF

AB 11 Photoconductivity and Optical Absorption in trans-$(CH)_x$. S. ETEMAD, M. OZAKI, D. L. PEEBLES A. J. HEEGER and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- Detailed measurements of photoconductivity and optical absorption in trans-$(CH)_x$ have been carried out. The photocurrent (I_{Ph}) as a function of energy shows an edge near 1.3 eV with an increase of nearly two orders of magnitude. The higher energy region is characterized by a slower variation; I_{Ph} increases by only about a factor of ten on varying the photon energy from 1.5 eV to 3.0 eV. Similar structure is observed in detailed measurements of the absorption coefficient. The photocurrent has a weak tail at low energies consistent with smearing of the band edge and/o the presence of localized states in the gap. The results will be discussed in terms of the band structure of trans-polyacetylene.

AB 12

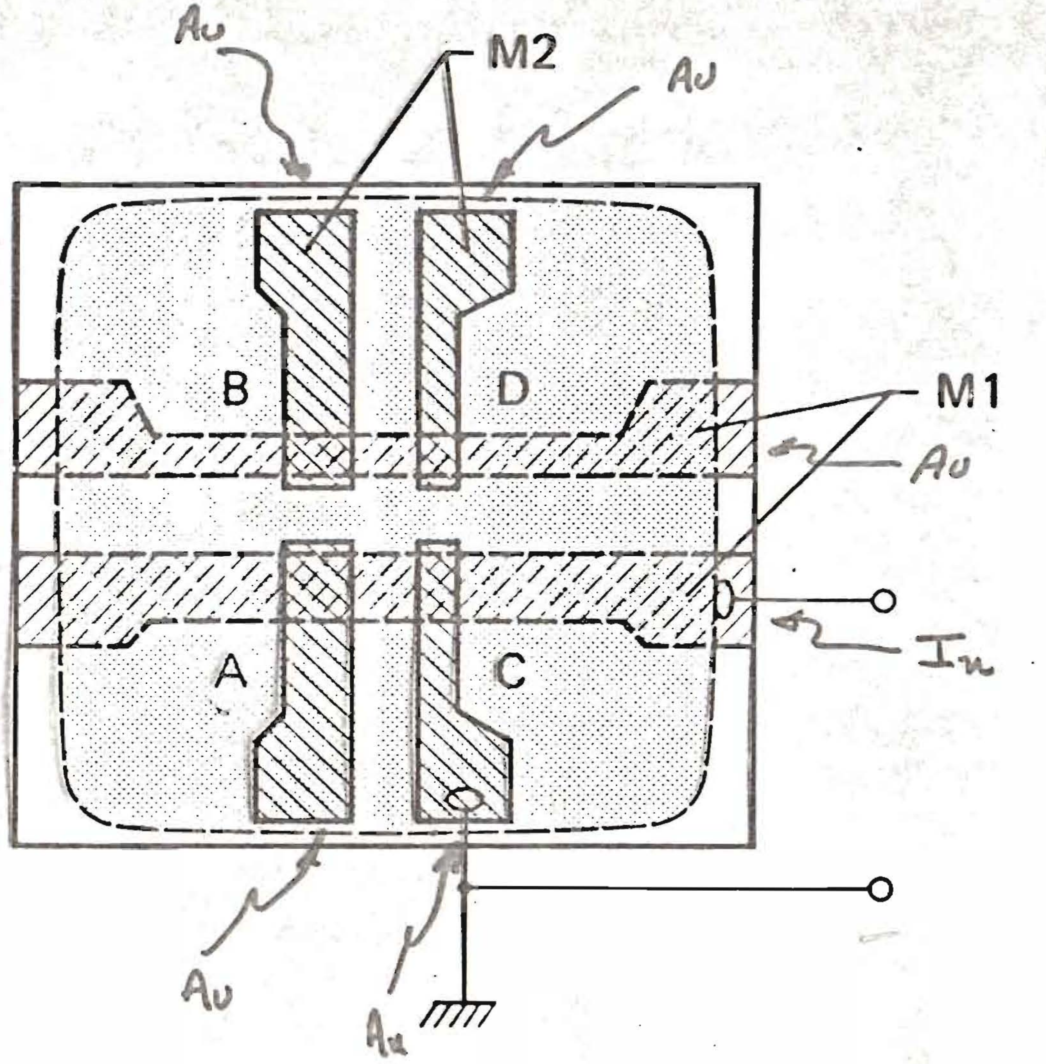
Low Frequency AC Impedance Studies of Doped Polyacetylene. C. K. CHIANG and A. D. FRANKLIN, National Bureau of Standards --Low frequency ac impedance measurements were used to study the inhomogeneous electrical properties of pure and doped polyacetylene. The depression of the impedance spectra of doped polymer suggested that the electrical resistivity can be separated into two parts: the resistance due to polymer chains, and the resistance due to various inhomogenities. These resistances were studies in terms of dopant concentration and temperature. The doping uniformity was also reflected in the frequency distribution of the impedance spectrum.

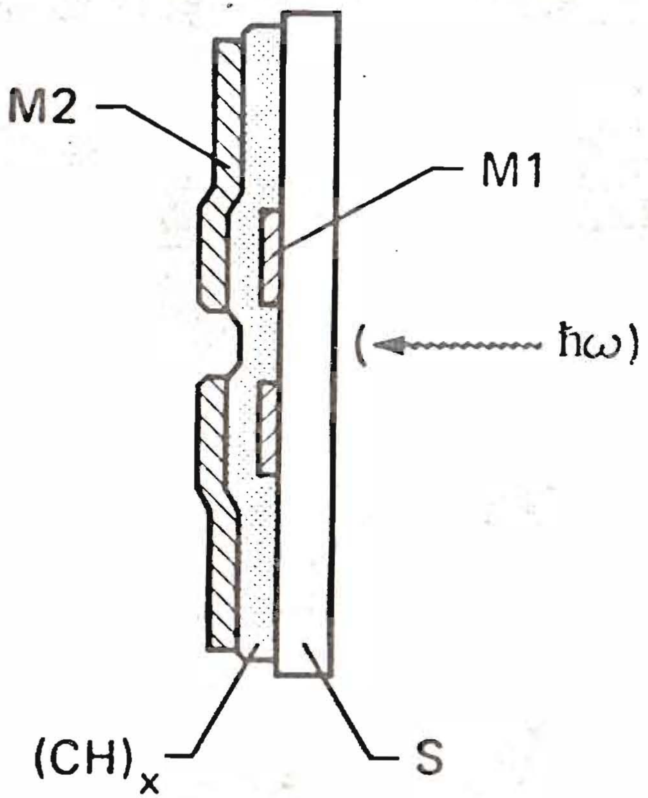
AB 13 Microwave Dielectric Constant and Conductivity of Low-Density Polyacetylene. A. FELDBLUM, A. J. HEEGER, A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA and G. E. WNEK, J. C. W. CHIEN and F. KARASZ, U. of Massachusetts, Amherst, MA -- Samples of polyacetylene in the form of a low-density foam-like material were synthesized by using a gel as an intermediate step. Sample densities were in the range of .1 - .03 g/cm³. The microwave dielectric constant and conductivity were measured as a function of Iodine doping in the range of low dopant concentration ($(CHI_y)_x$, y = .005-.03) using both standing-wave techniques, (single point impedance, two point impedance, and 'semi-finite' sample approximation) and cavity perturbation techniques. Both the dielectric constant and conductivity were found to be reduced from the corresponding values found for as-grown $(CH)_x$ film. The results will be discussed in the context of effective medium theory.

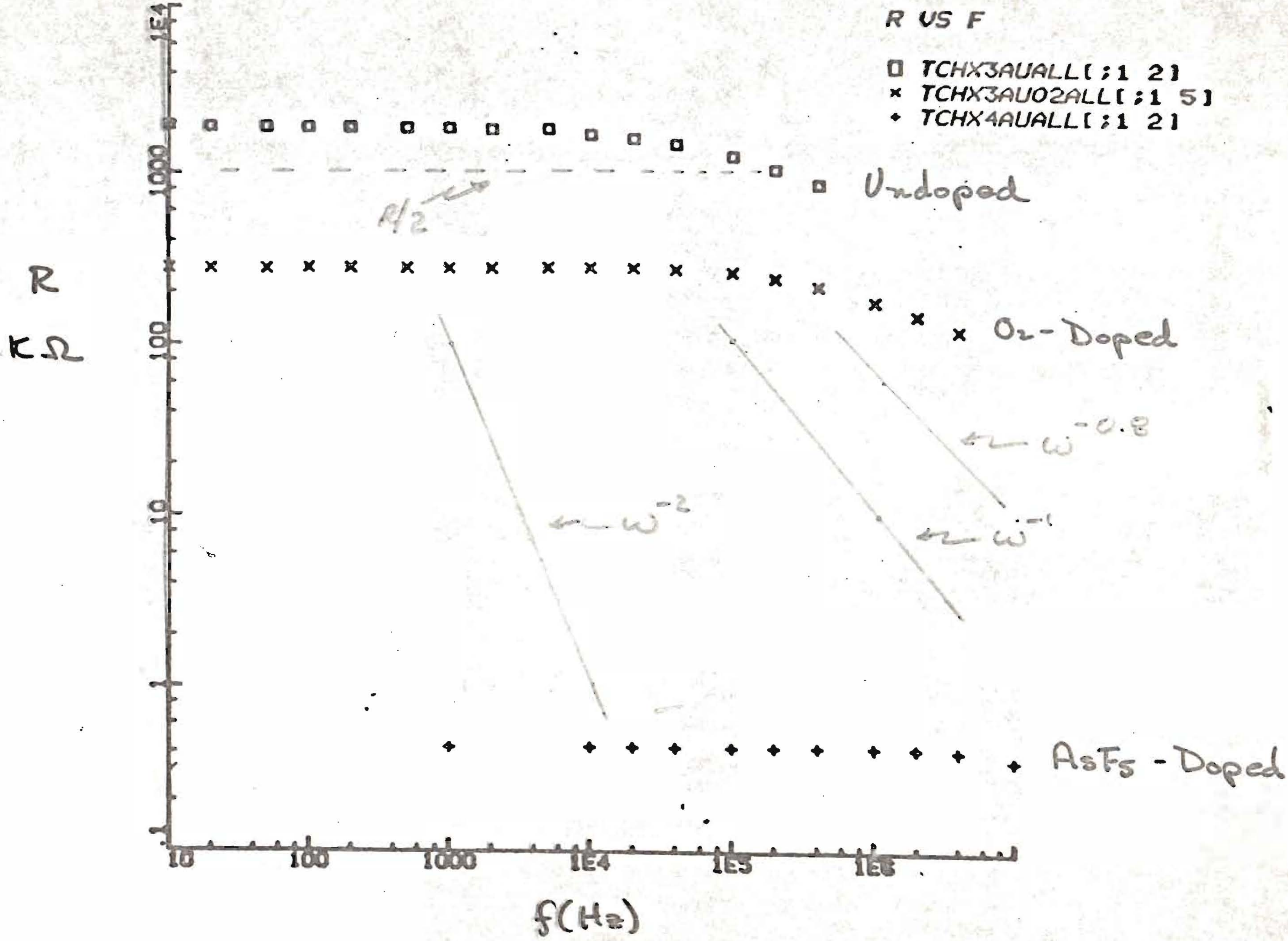
AB 14 Specific Heats of Pure and Doped Polyacetylene. D. MOSES, A. DENENSTEIN, A. PRON, A. J. HEEGER and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- The temperature dependences (0.8 K < T < 7 K) of the specific heats of pure polyacetylene (both cis and trans isomers) and heavily doped metallic $[CH(AsF_6)_{0.1}]_x$ will be reported. The principal motivation of this work was to determine the effects of doping on the electronic and lattice properties of $(CH)_x$. The results for the doped polymer indicate an electronic contribution to C(T) as well as a dramatic change in the lattice contribution. The electronic density of states inferred from the linear term is in agreement with that obtained from susceptibility. Comparison of results from cis and trans starting material indicates isomerization during doping.

AB 15 Junction and Dielectric Characteristics of $(CH)_x$ W. D. GILL, P. M. GRANT, J. MAREK, T. TANI, T. C. CLARKE and G. B. STREET, IBM Research Lab, San Jose, CA 95193-- We report the results of our studies on the frequency dependence of the Schottky barrier properties and dielectric response function of undoped and lightly-doped trans- and cis-$(CH)_x$ in the range 100Hz to 10MHz, and, in addition, measurements of the static dielectric breakdown strength in each isomer. The temperature dependence from -100C to 100C and ageing behavior on exposure to air of the above characteristics are also reported. Strong dispersion of the dielectric constant with both frequency and temperature is observed in trans$(CH)_x$ but not in cis-$(CH)_x$. A large frequency dependence is also found in the reverse bias impedance of Schottky barriers between In and lightly-doped trans-$(CH)_x$. These data will be discussed in terms of various models which have been proposed for the transport properties of semiconducting polymers.

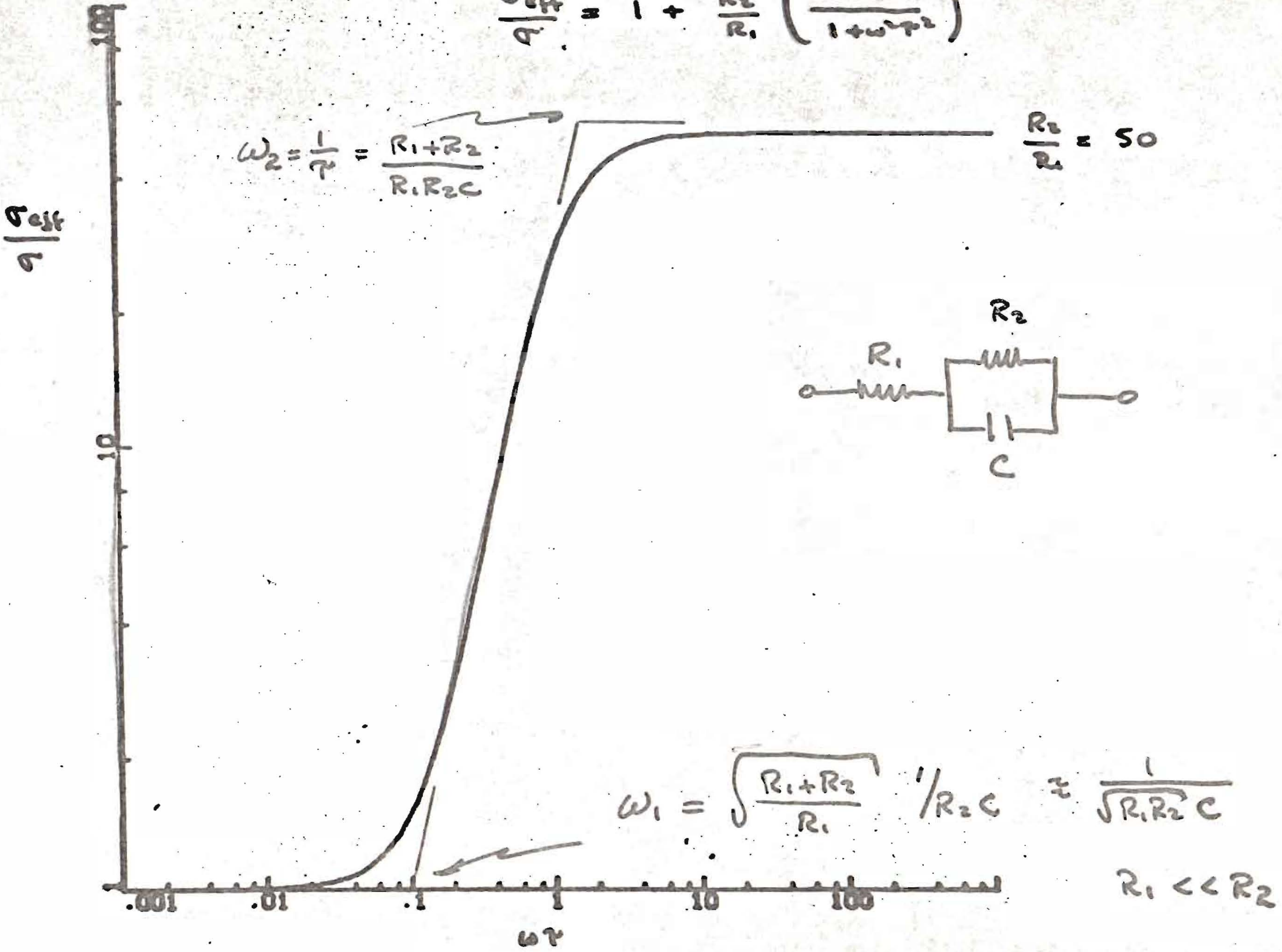
AB 16 Photovoltaic Studies of Polyacetylene Heterojunctions. D. L. PEEBLES, M. OZAKI, B. R. WEINBERGER, A. J. HEEGER and A. G. MAC DIARMID, U. of Pennsylvania, Phila., PA -- Experiments with $(CH)_x$:CdS heterojunctions extend the previous work with $(CH)_x$:ZnS devices. The shape of the photoresponse spectrum and the absolute quantum efficiency below 2.4 eV are similar. The heterojunction diodes have $R_s \sim 200\,\Omega/cm^2$ and exhibit a photoresponse time of less than 0.1 second. Devices can be made either by synthesizing $(CH)_x$ directly onto the CdS, or by pressing a free standing film onto the cleaved surface. C-V measurements imply an acceptor concentration of about 10^{18} cm^{-3} in the as grown $(CH)_x$. The quantum efficiency is greater for more heavily doped CdS in agreement with estimates of the expected increase of the depletion layer in the $(CH)_x$. This implies that the fibrous $(CH)_x$ material can be treated as an effective homogeneous medium.


Au
M2
Au
B
D
M1
Au
A
C
In
Au
Al


M2
M1
(← ħω)
(CH)x
S


R VS F
TCHX3AUALL[;1 2]
TCHX3AUO2ALL[;1 5]
TCHX4AUALL[;1 2]
Undoped
O₂-Doped
AsF₅ - Doped
R/2
ω^-0.8
ω^-1
ω^-2
R
KΩ
1E4
1000
100
10
1
f(Hz)
10
100
1000
1E4
1E5
1E6

$$\frac{\sigma_{eff}}{\sigma} = 1 + \frac{R_2}{R_1}\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right)$$



$\omega_2 = \frac{1}{\tau} = \frac{R_1+R_2}{R_1R_2C}$

$\frac{R_2}{R_1} = 50$

$\omega_1 = \sqrt{\frac{R_1+R_2}{R_1}}\ {}^1\!/_{R_2C} \approx \frac{1}{\sqrt{R_1R_2}\,C}$

$R_1 << R_2$

Influence of Lead Resistance

- Gold Stripe: $\rho_{AU} = 2 \times 10^{-6}\ \Omega \cdot \text{cm}$

  Take: $l = 1\ \text{cm}$, $A = (1\ \text{mm})(2000\ \text{Å})$

  $= 2 \times 10^{-6}\ \text{cm}^2$

  $\therefore R_1 \approx 1\ \Omega$

- Low sample resistance:

  Take $R_2 = 10^3\ \Omega$, $C_2 = 20\ \text{pf}$

  $$\therefore f_1 = \frac{1}{2\pi\sqrt{R_1 R_2}\, C_2}$$

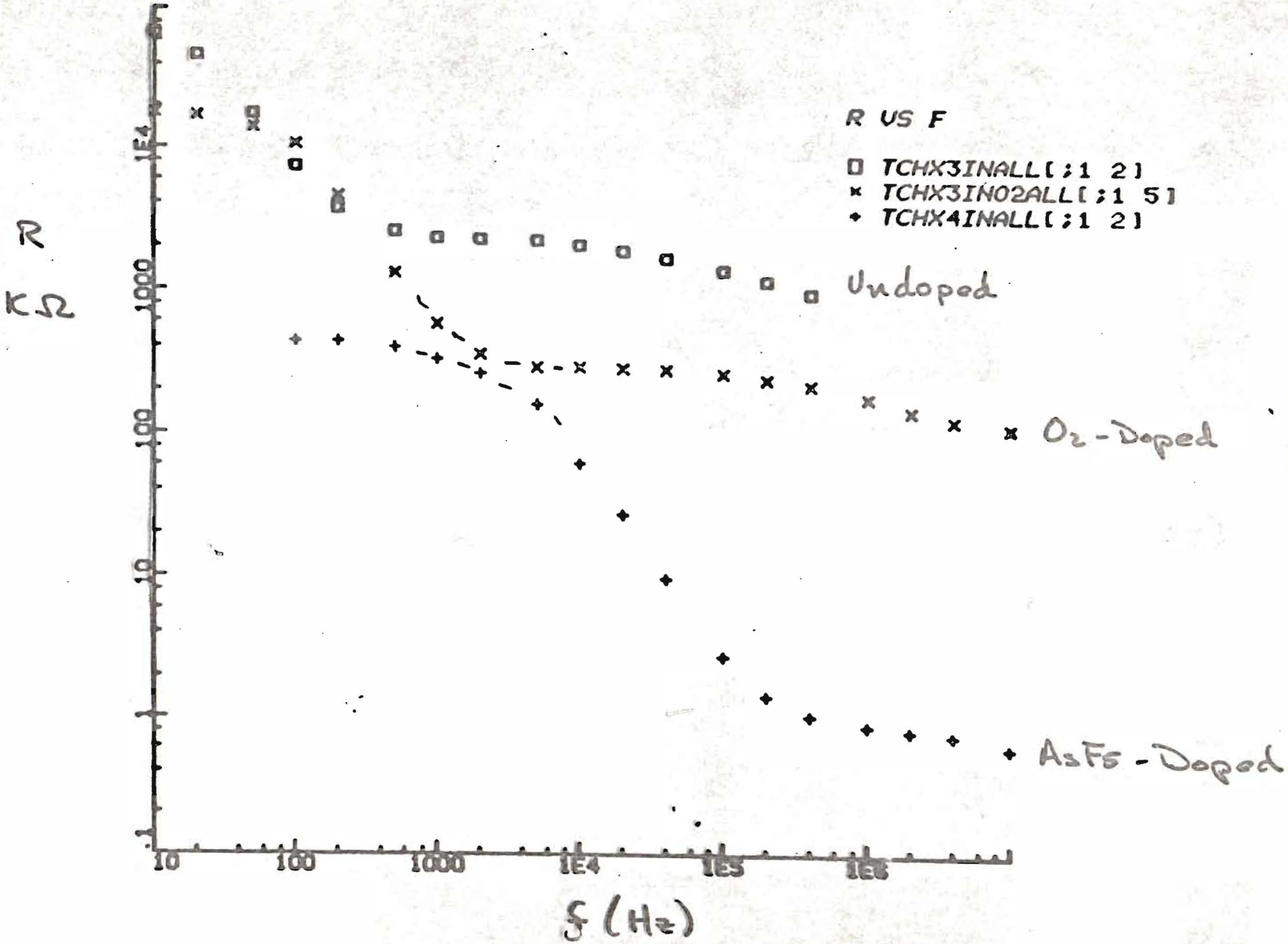
  $= 250\ \text{MHz}$ OK!

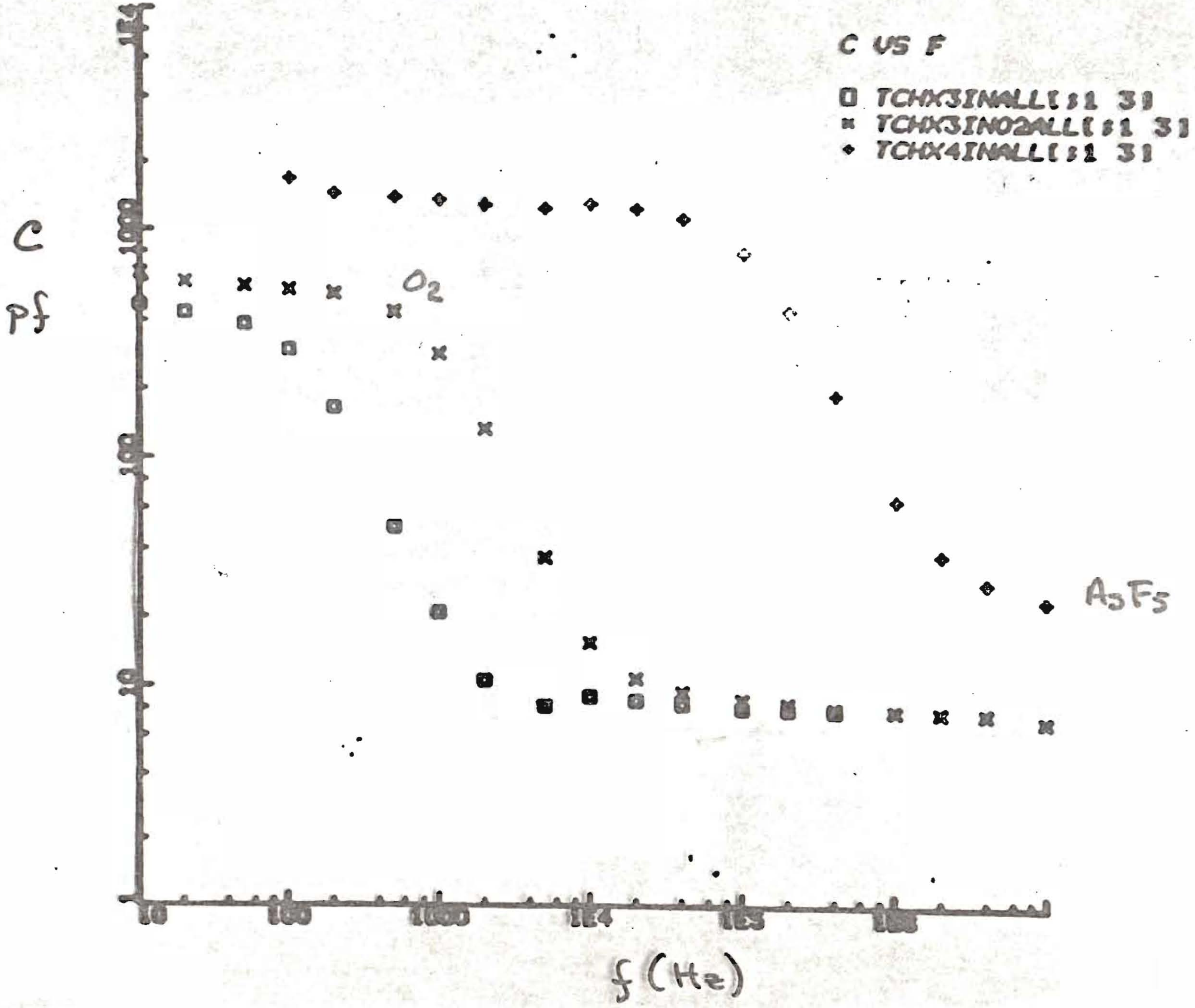
- High sample resistance:

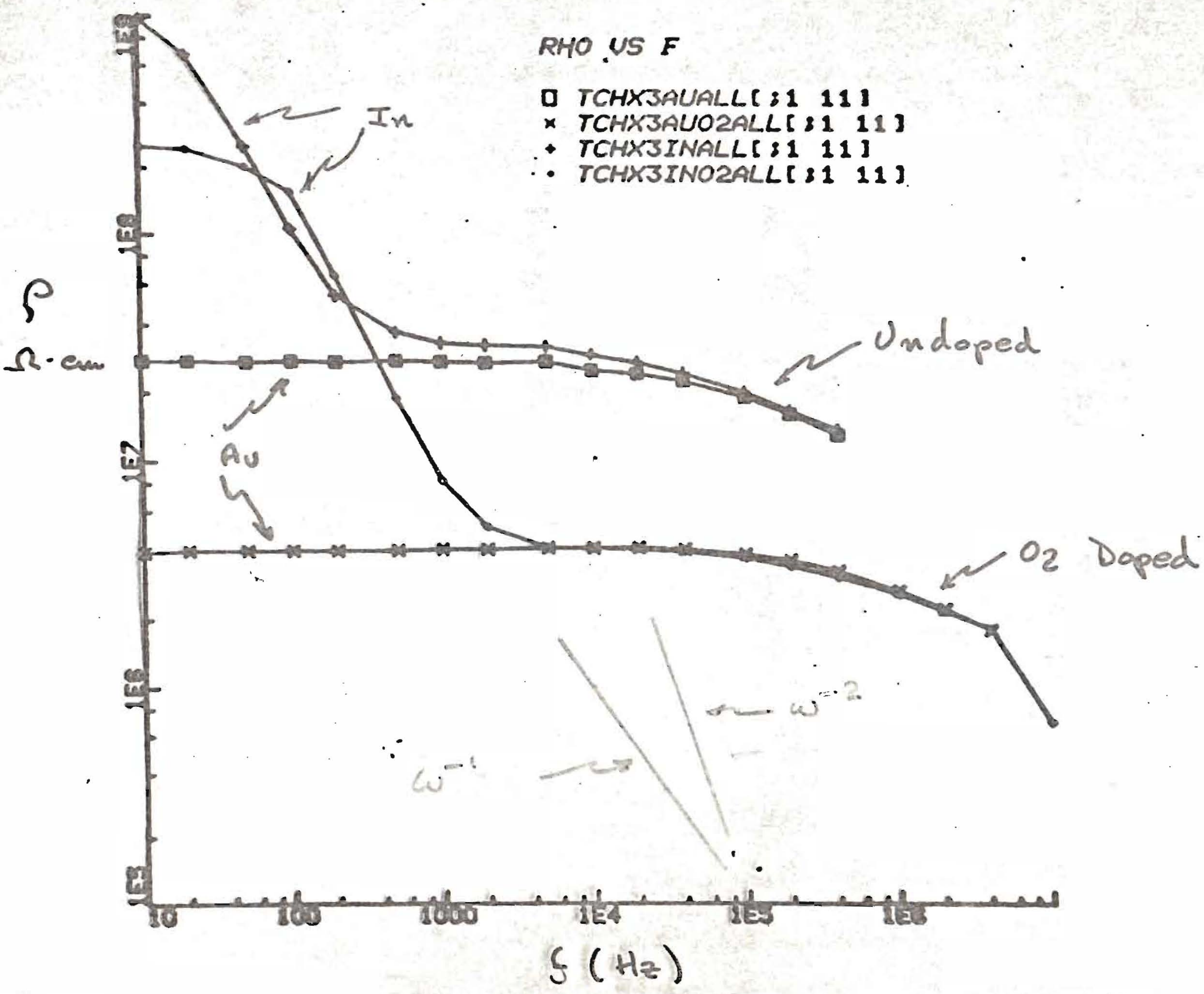
  Take $R_2 = 10^6\ \Omega$, $C_2 = 20\ \text{pf}$

  $\therefore f_1 = 8\ \text{MHz}$!!

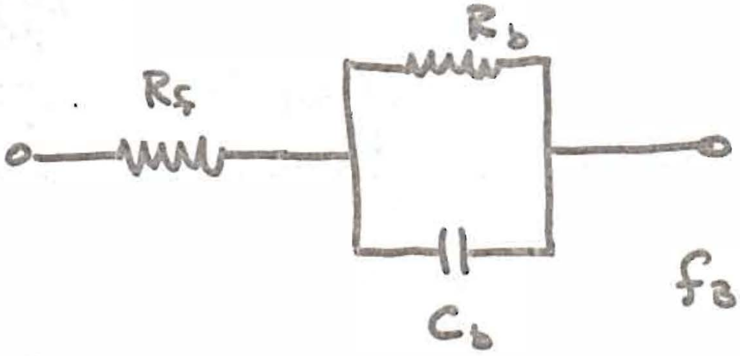
BAD NEWS!
(OR IS IT?)


R VS F
□ TCHX3INALL[;1 2]
× TCHX3INO2ALL[;1 5]
+ TCHX4INALL[;1 2]
R
KΩ
1E4
1000
100
10
1
.1
10
100
1000
1E4
1E5
1E6
f (Hz)
Undoped
O2-Doped
AsF5-Doped


C VS F
TCHX3INALL[;1 3]
TCHX3INO2ALL[;1 3]
TCHX4INALL[;1 3]
1E4
1000
100
10
10
100
1000
1E4
1E5
1E6
C
pf
f (Hz)
O2
AsF5


RHO VS F
□ TCHX3AUALL[;1 11]
× TCHX3AUO2ALL[;1 11]
+ TCHX3INALL[;1 11]
• TCHX3INO2ALL[;1 11]
In
Au
Undoped
O2 Doped
ω^{-1}
ω^{-2}
ρ
$\Omega\cdot$cm
1E9
1E8
1E7
1E6
1E5
10
100
1000
1E4
1E5
1E6
f (Hz)

EFFECT OF DIODE FORWARD RESISTANCE ON FREQUENCY DISPERSION



$$f_B = \frac{1}{2\pi \sqrt{R_f R_b}\, C_b}$$

AsF_5 :

$R_f = 1200\ \Omega$

$R_b = 112\ k\Omega$

$C = 1200\ pf$

$f_B = 11.5\ kHz$

$R_b / R_f = 93$

O_2 :

$R_f = 160\ k\Omega$

$R_b = 28\ M\Omega$

$C = 1000\ pf$

$f_B = 75\ Hz$

$R_b / R_f = 175$

CONCLUSIONS

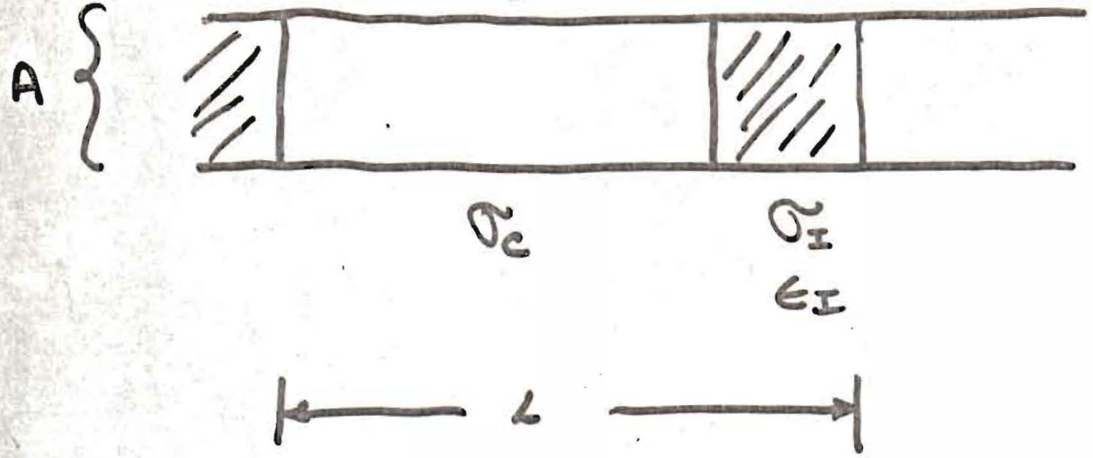
— σ, ϵ ω-independent 0-10 MHz

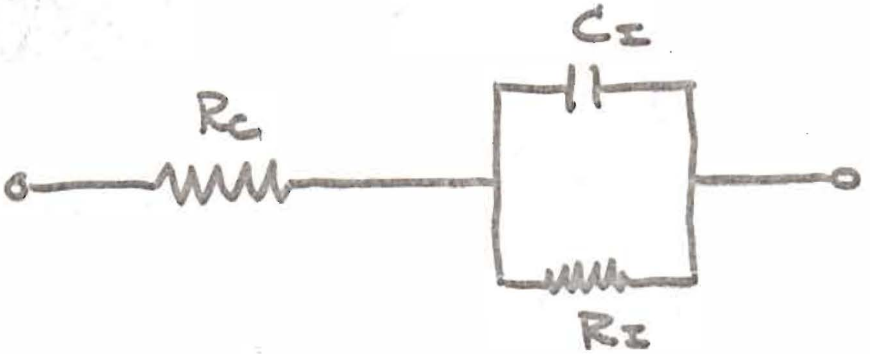
- Semiconductor doping regime
- Carriers may be in extended states

— Indium - t-$(CH)_x$ Schottky Diodes

- ω-dependence due to large forward resistance
- Junction behavior analyzable by simple models

"EXTREME" INHOMOGENEOUS DOPING

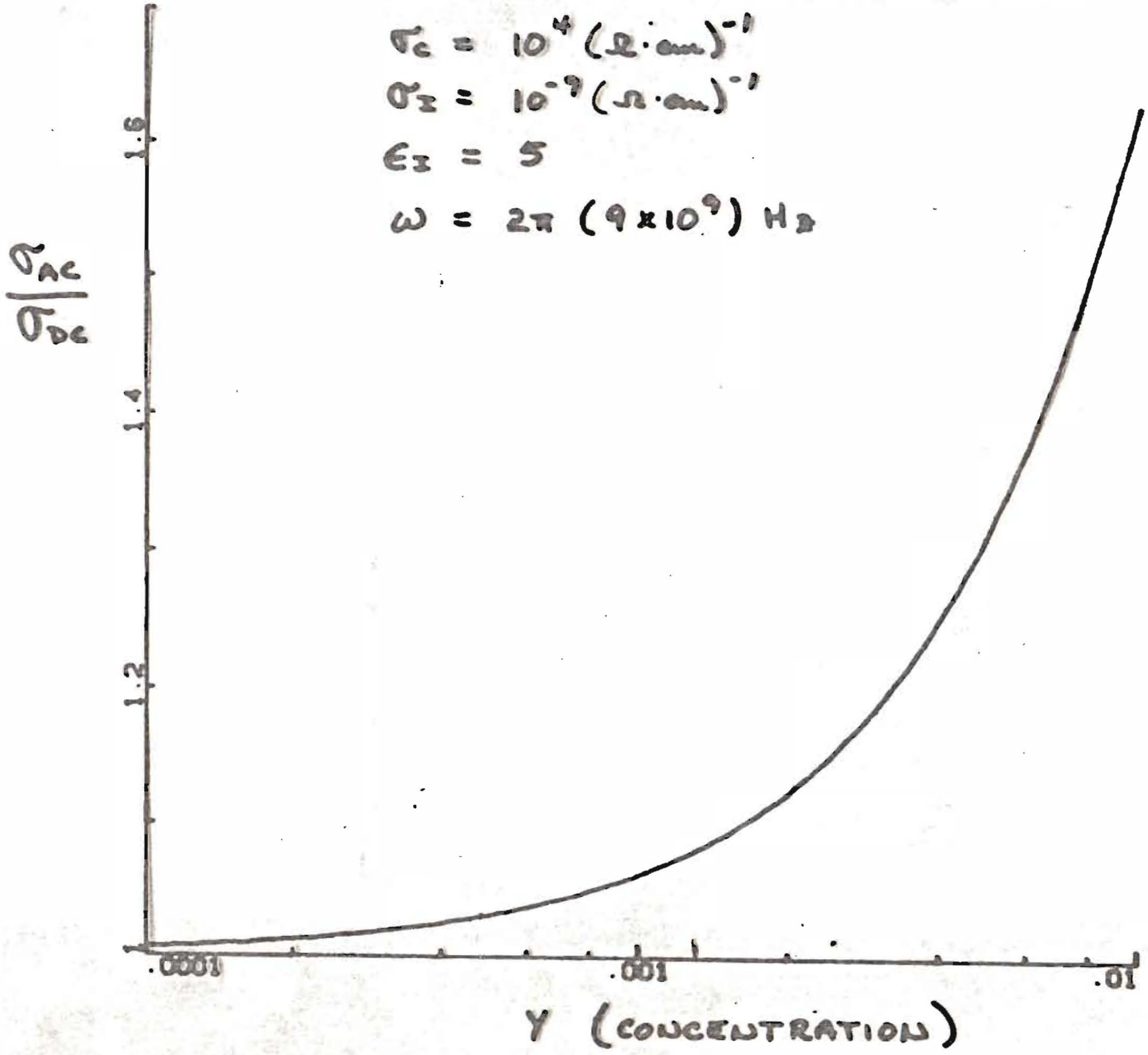


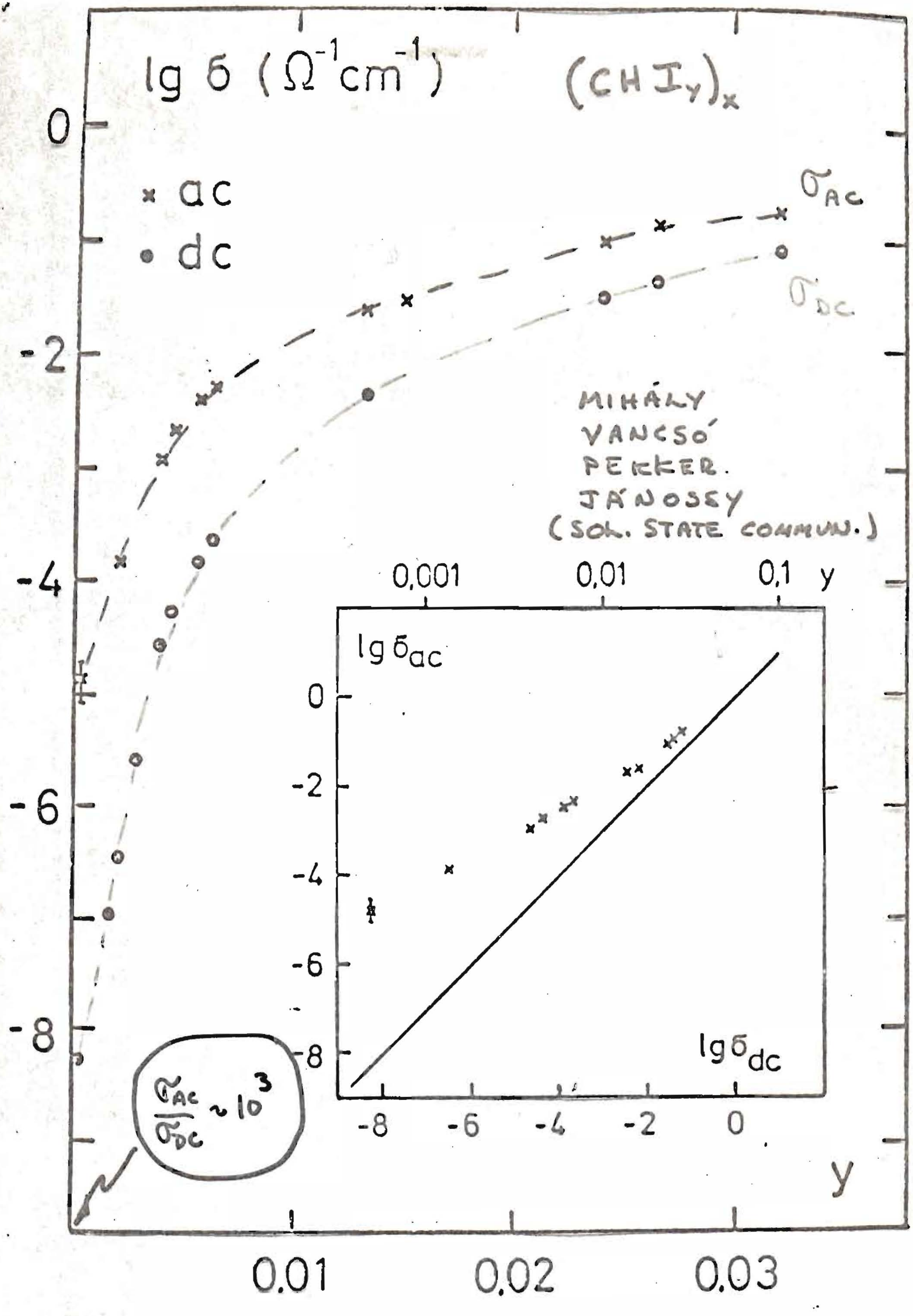


$$\frac{\sigma_{AC}}{\sigma_{DC}} = 1 + \left(\frac{1}{y} - 1\right)\frac{\sigma_c}{\sigma_I}\left(\frac{\omega^2\tau^2}{1+\omega^2\tau^2}\right)$$

$$\tau = \left[1 + \left(\frac{1}{y} - 1\right)\frac{\sigma_c}{\sigma_I}\right]^{-1}\frac{\epsilon_0\,\epsilon_I}{\sigma_I}$$

$$y \equiv \frac{l_c}{L}$$


$\sigma_c = 10^4 (\Omega \cdot cm)^{-1}$
$\sigma_I = 10^{-9} (\Omega \cdot cm)^{-1}$
$\epsilon_I = 5$
$\omega = 2\pi (9 \times 10^9)$ Hz
$\frac{\sigma_{AC}}{\sigma_{DC}}$
1.6
1.4
1.2
.0001
.001
.01
Y (CONCENTRATION)



MIHÁLY
VANCSÓ
PEKKER.
JÁNOSSY
(SOL. STATE COMMUN.)

$\frac{\sigma_{AC}}{\sigma_{DC}} \sim 10^3$