האוניברסיטה העברית בירושלים
The Hebrew University of Jerusalem

High K- nano smart materials

Paul Ben Ishai
The Department of Applied Physics

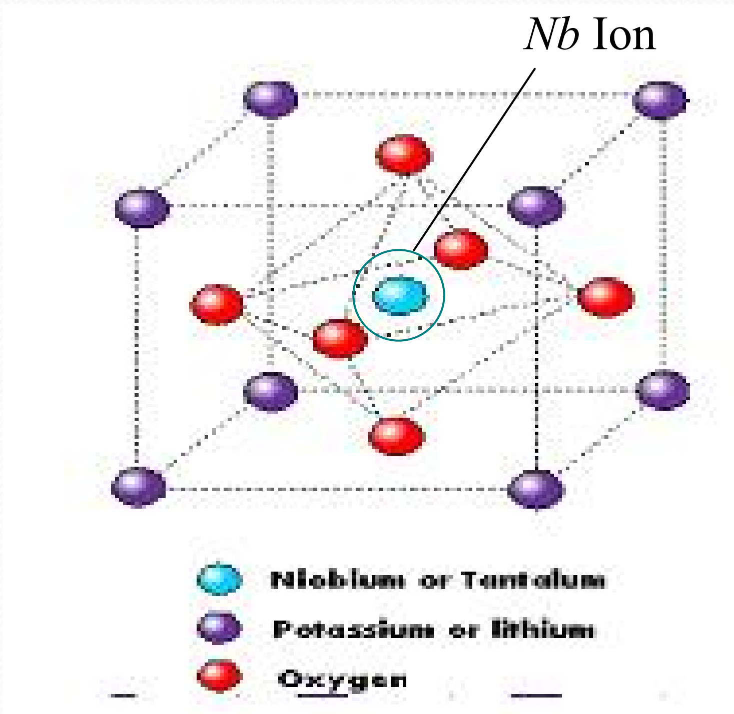
What is High K Nano Smart?

- High K
  - Beyond a great term for Funding Agencies??!!
  - Derived from the world of microelectronic capacitances where ε> 3.9 (Silicon Oxide)
  - Solid state
- Nano
  - Specific dielectric behaviour governed at the nano scale
  - And another great term for the Funding Agencies!!

JOURNAL OF APPLIED PHYSICS VOLUME 89 (2001), 5243

KTN Crystals

$$K_1 Ta_{0.62} Nb_{0.38} O_3$$



Perovskite Structure ABO_3

1959 – S. Triebwasser
$KNbO_3/KTaO_3$

2001 - Y. Girshberg, Y. Yacoby

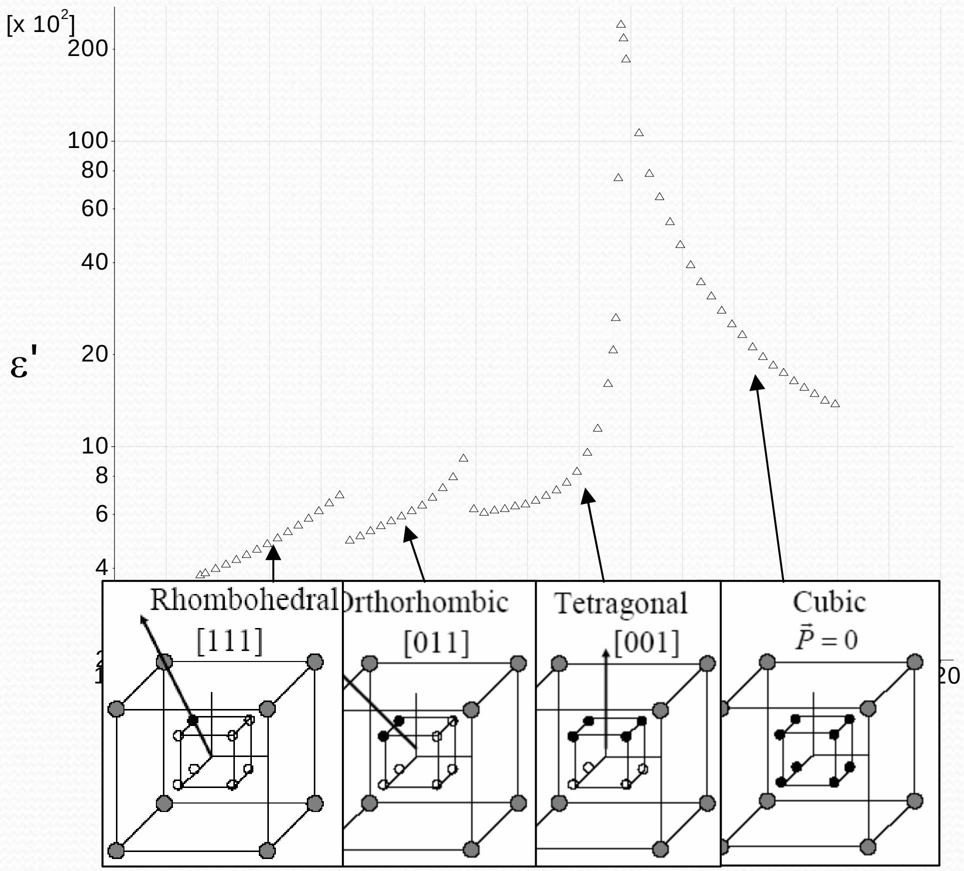
$$\varepsilon_s = \frac{C}{(T - T_0)}$$

High temperature → Low temperature

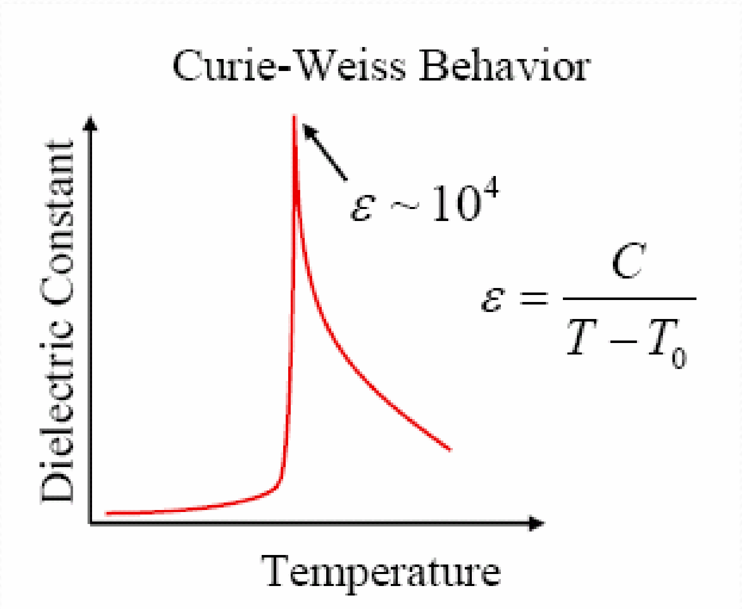
cubic → tetragonal → orthorhombic → rombohedralic

Structural 2nd Order FE Phase Transitions

- Displacement of center ion at low temperatures creates dipole moment



The phase transition is mediated by the interaction between the Nb ion and the Soft-mode phonon of the crystal lattice[1]

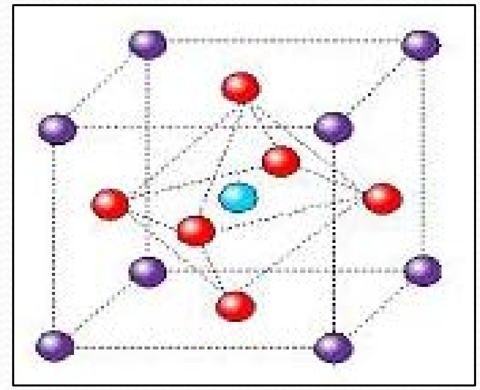


[1] Y. Girshberg and Y. Yacoby, J. Phys. Condens. Mat. **13** (2001), 8817

Soft mode Phonon Models

The simplest model considers the movement of the central ion and its equation of motion

$$m\ddot{x} + \gamma\dot{x} + (K_S - K_L + BT)x = eE_0 \exp(-i\omega t)$$

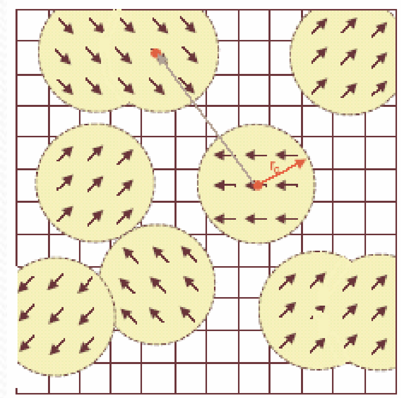


Where

- K_S is the short range harmonic restoring force
- K_L is the long range electrostatic force
- BT is an effective anharmonic restoring force

The resulting susceptibility is

$$\chi = \frac{Ne^2/m}{\overline{\omega}^2 - \omega^2 + i\gamma\omega/m} \quad \text{where} \quad \overline{\omega}^2 = \frac{B}{m}\left(T - \frac{K_L - K_S}{B}\right)$$

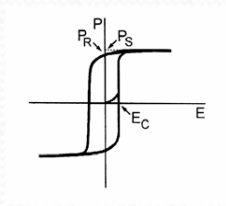
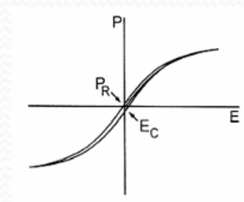
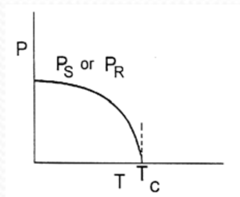
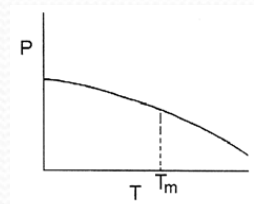
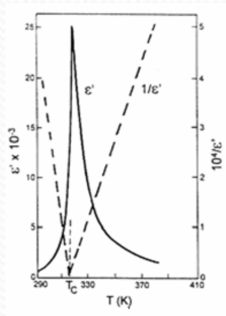
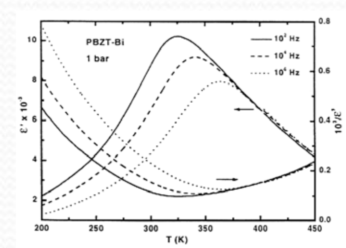


Predicting Curie-Wiess behaviour at

$$T_c = \frac{(K_L - K_S)}{B}$$

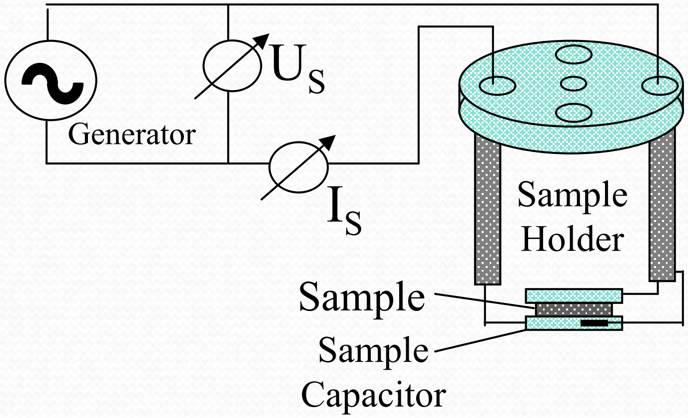
These are highly polarizable lattices, where small concentrations of dopants can have an extraordinary effect!

Relaxors

Ferroelectrics	Relaxors
Macroscopic polarization domains 	Nanoscale polarization domains 
No macroscopic polarization above T_c 	Nanoscale polarization existing above T_m 
•Sharp phase transitions •Curie-Weiss Law obeyed •No frequency dispersion 	•Broad transisition peaks •Divergence from Curie Weiss behaviour •Frequency dispersion in T_m 
• Phase transition with macroscopic symmetry change at T_c	• No structural change at Tm • Critical slowing down of dipolar relaxation below T_m

Methodologies – Broadband Dielectric Spectroscopy

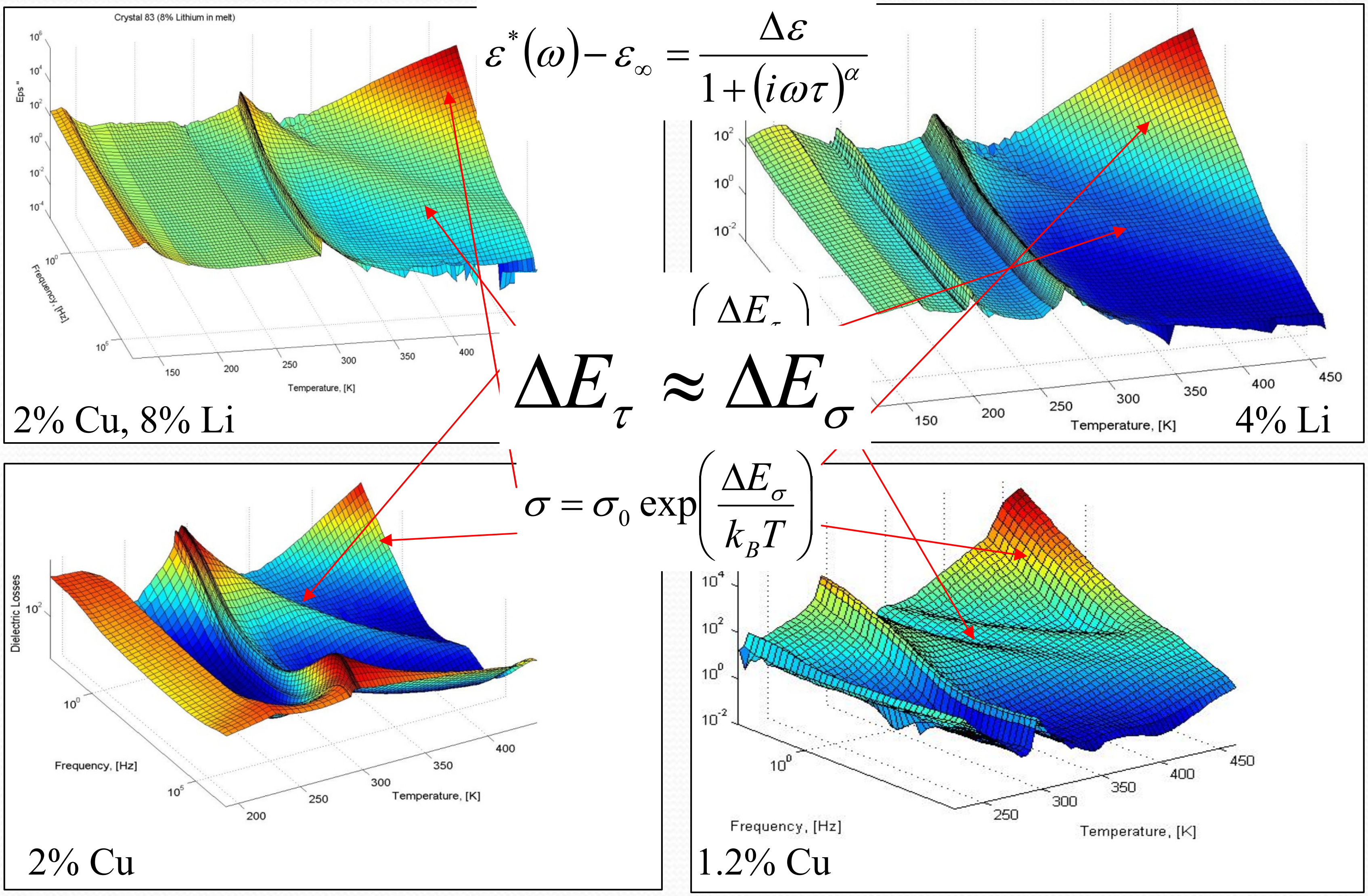
Broad-Band Dielectric Spectrometer BDS 80 **(NOVOCONTROL) in the frequency range 10 mHz – 3 MHz with automatic temperature control by QUATRO Cryosystem (temperature range -150 °C - +400 °C)**



$$Z^*(\omega) = Z'(\omega) + iZ''(\omega) = U_s(\omega) / I_s(\omega)$$

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega) = -i / 2\pi f Z(f) C_0$$

Dielectric Results

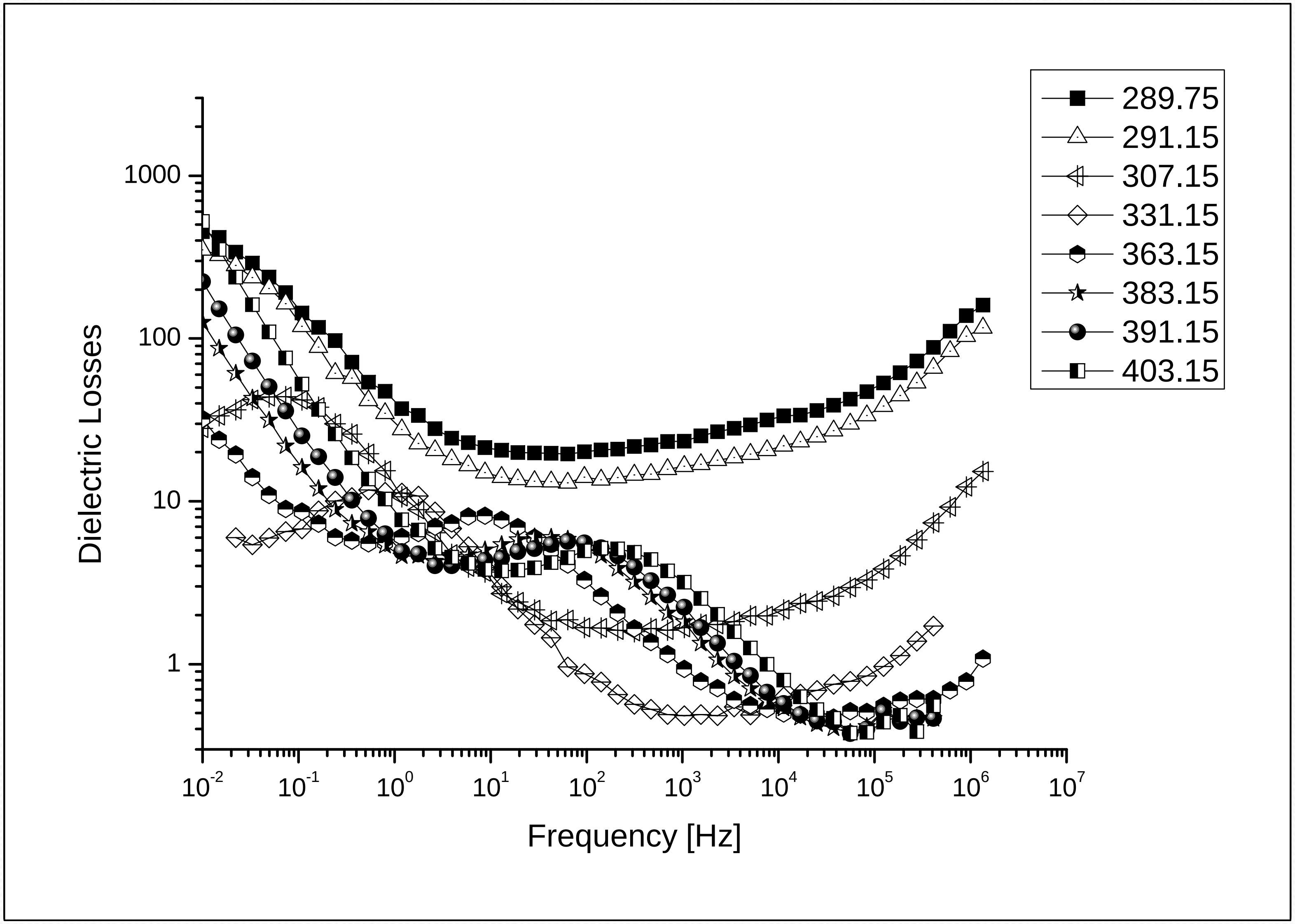


$$\varepsilon^*(\omega) - \varepsilon_\infty = \frac{\Delta\varepsilon}{1 + (i\omega\tau)^\alpha}$$

$$\Delta E_\tau \approx \Delta E_\sigma$$

$$\sigma = \sigma_0 \exp\left(\frac{\Delta E_\sigma}{k_B T}\right)$$

Lithium Series Results



Frequency Impedance Analyzers

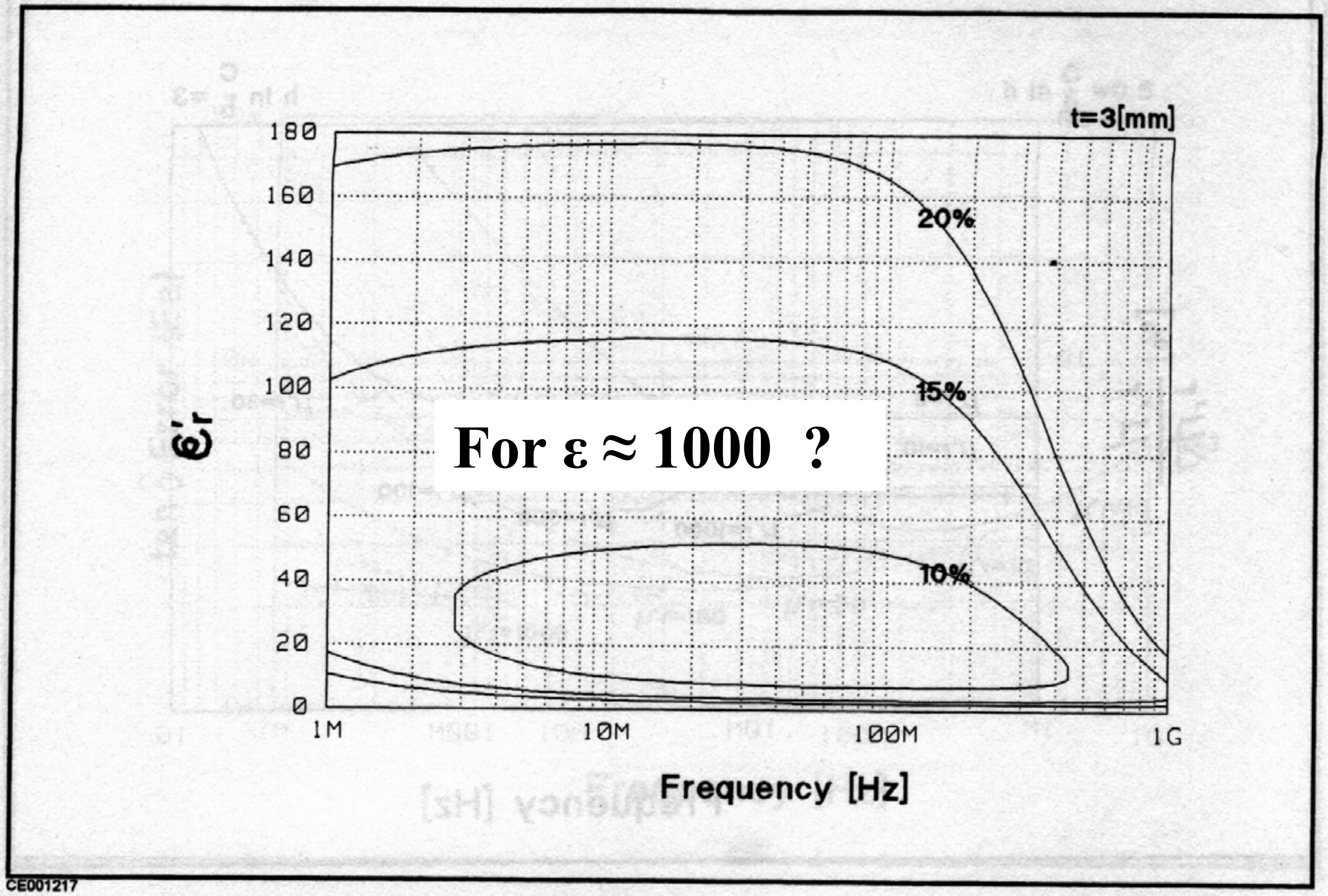


Figure 12-24.
Typical Permittivity Measurement Accuracy (ε_r v.s. Frequency, @thickness = 3 mm)

Smith Chart

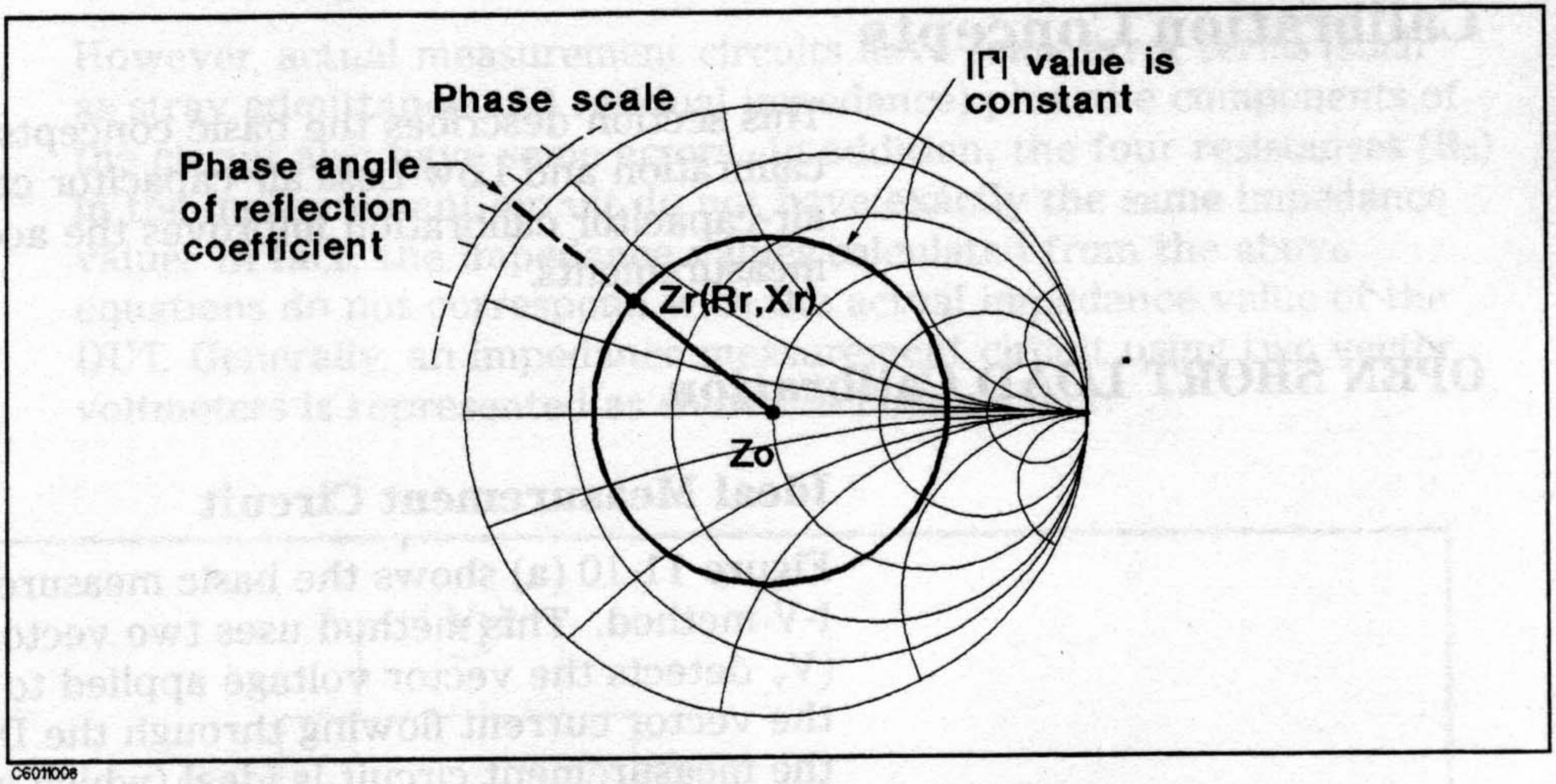
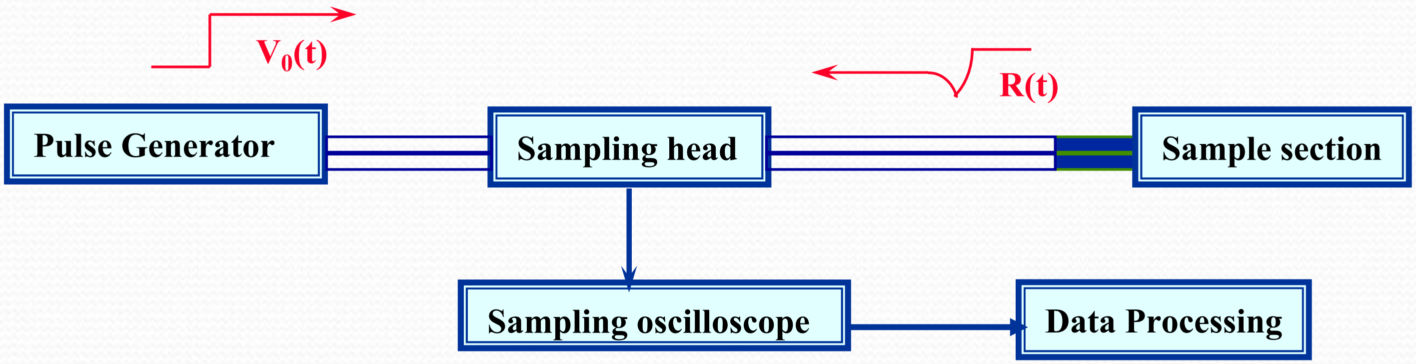


Figure 11-8. Impedance Read-out

TDS measurements

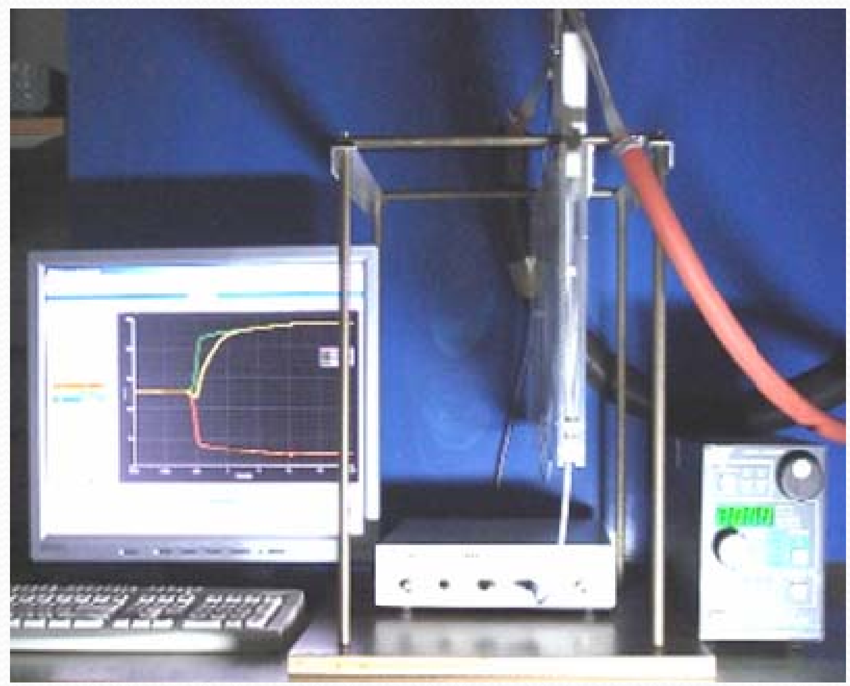


lumped capacitance approximation in time domain:

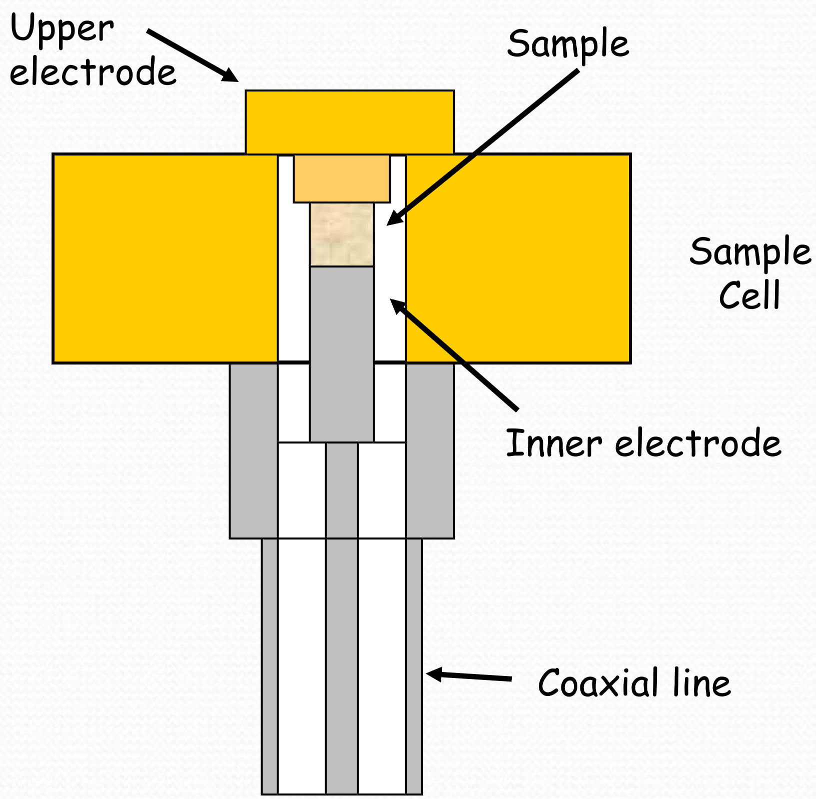
$$Q(t)=C_0\left[\varepsilon_\infty V(t)+\int_0^t \dot{\Phi}(t-t')V(t')dt'\right]$$

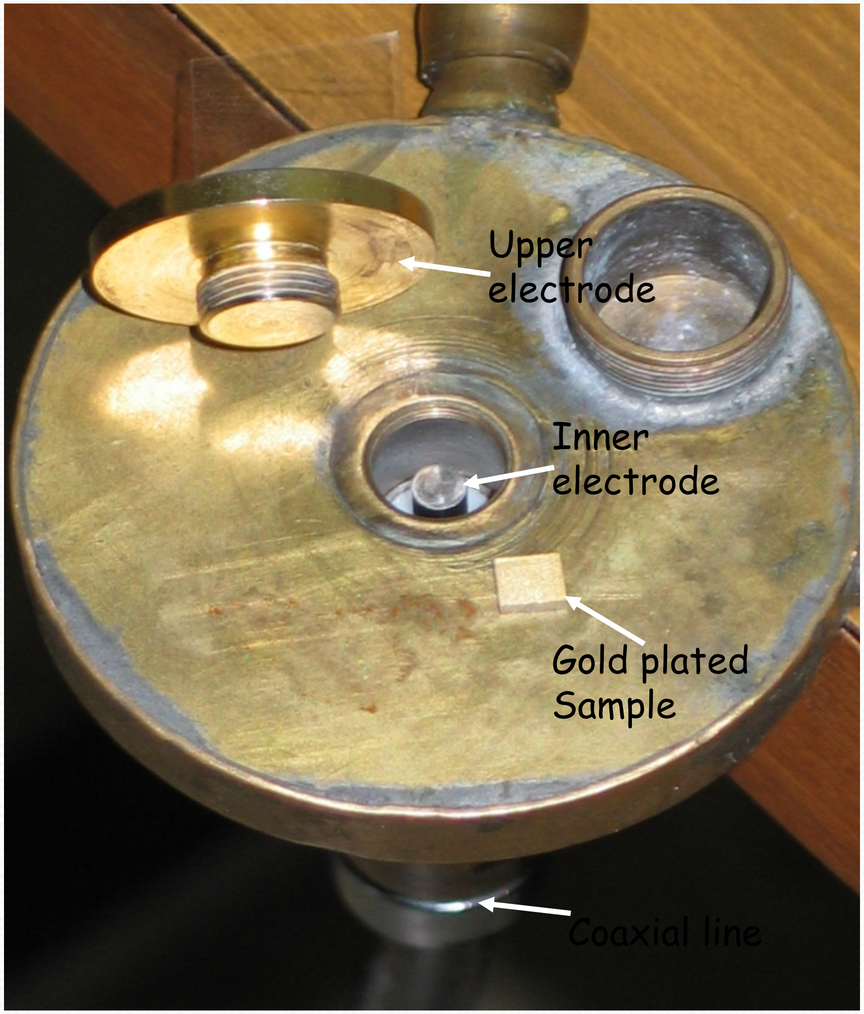
$$\Phi(t)=(\varepsilon_s-\varepsilon_\infty)[1-\psi(t)]$$

$$\psi(t)\cong\Gamma(t)=\frac{\langle\overline{M}(0)\cdot\overline{M}(t)\rangle}{\langle\overline{M}(0)\cdot\overline{M}(0)\rangle}$$

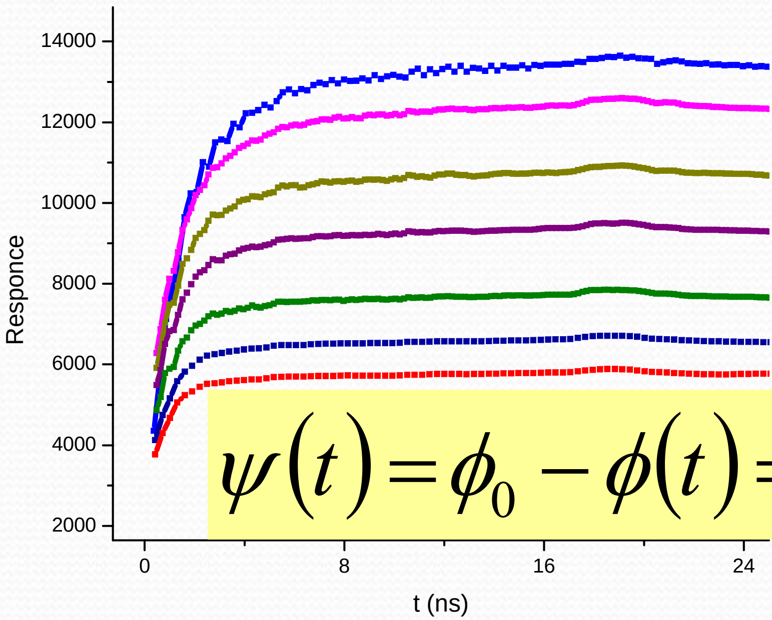


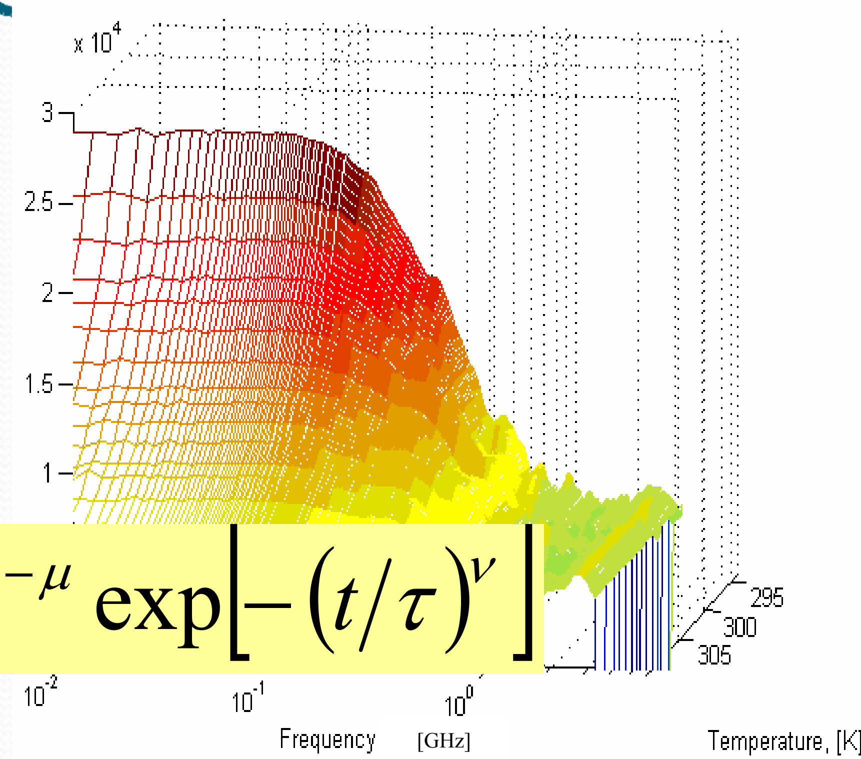
TDS Sample Cell





Typical Results





$$\psi(t) = \phi_0 - \phi(t) = At^{-\mu} \exp\left[-(t/\tau)^{\nu}\right]$$

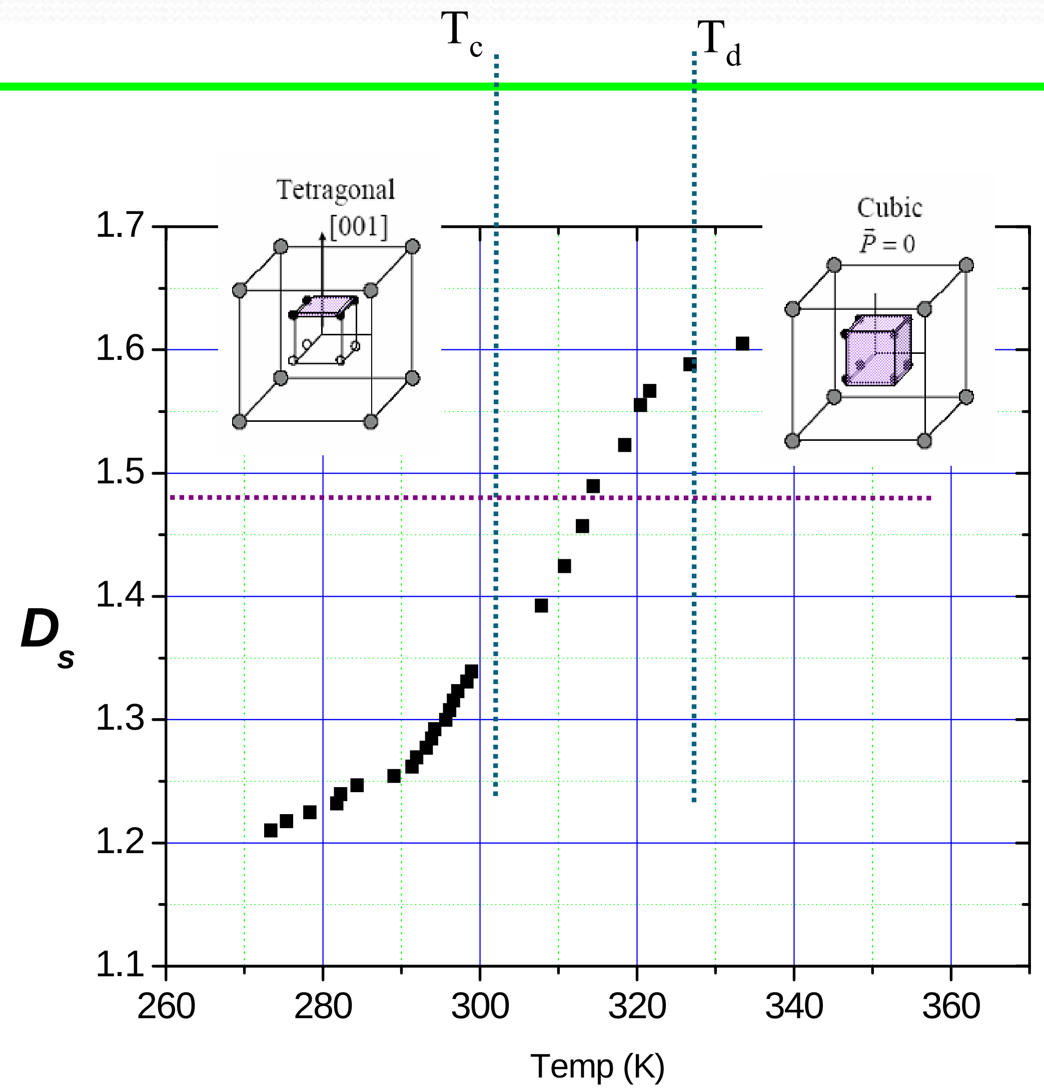
Time domain

Dielectric response function: $\Phi(t)$

Frequency domain Spectrum of dielectric permittivity: $\varepsilon'(\omega)$

Parameters - μ and ν

$$\Psi(t) \sim \exp\left[-\left(t/\tau\right)^{\nu}\right]$$

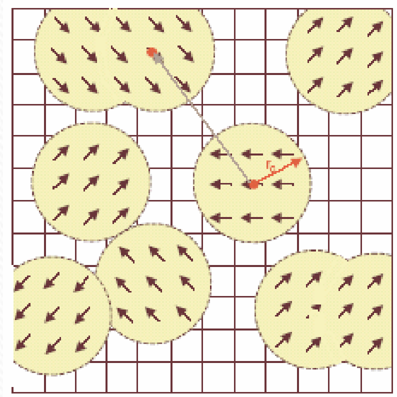


ν - is related to the fractal dimension[1]

$$D_s = d\nu$$

Where d is the dimension of the system

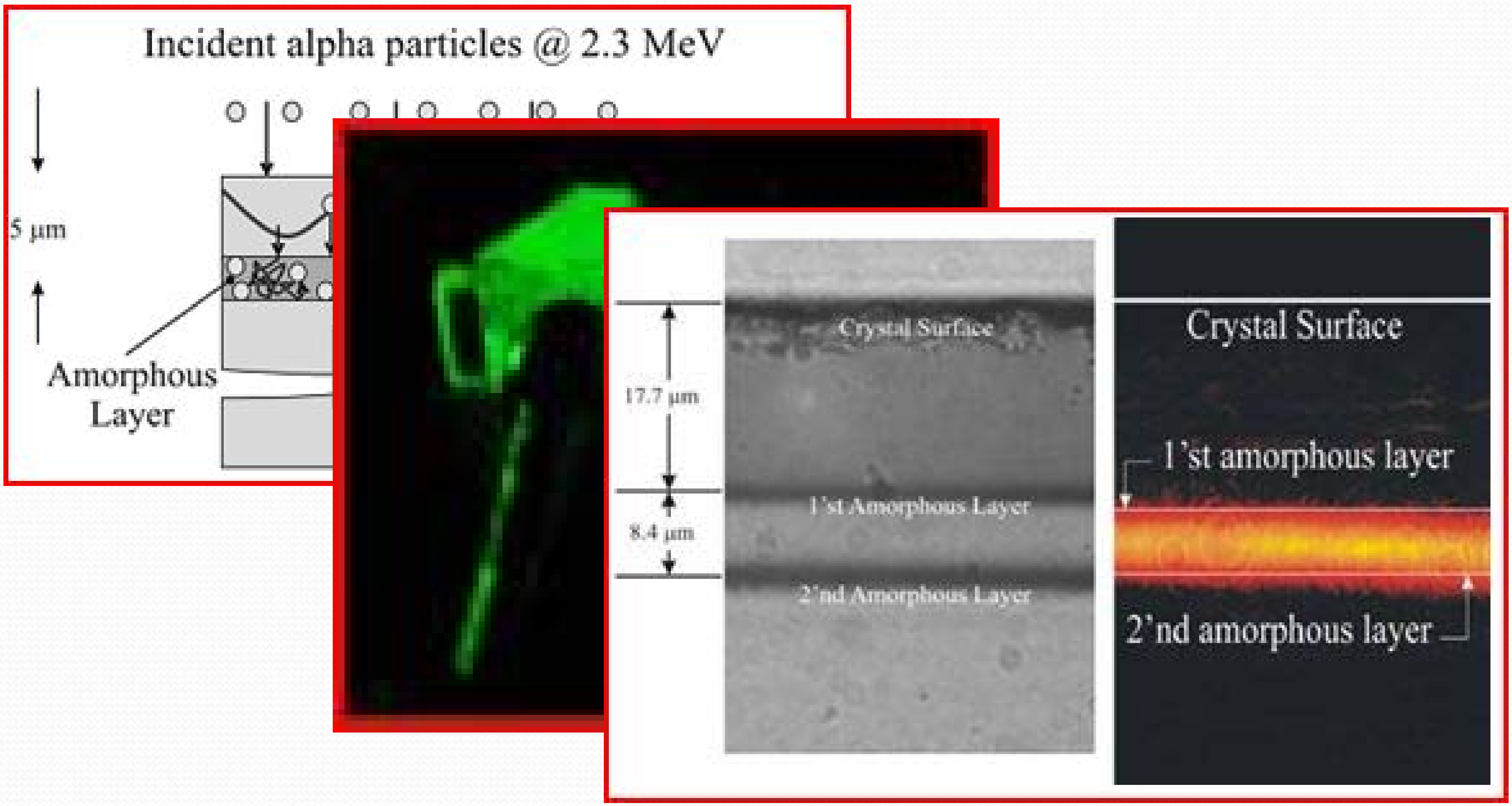
$$d = \frac{[Ta]}{[Nb]} = 1.6$$



[1] Yu. Feldman et al., Phys. Rev. E, 54 (1996), 5420

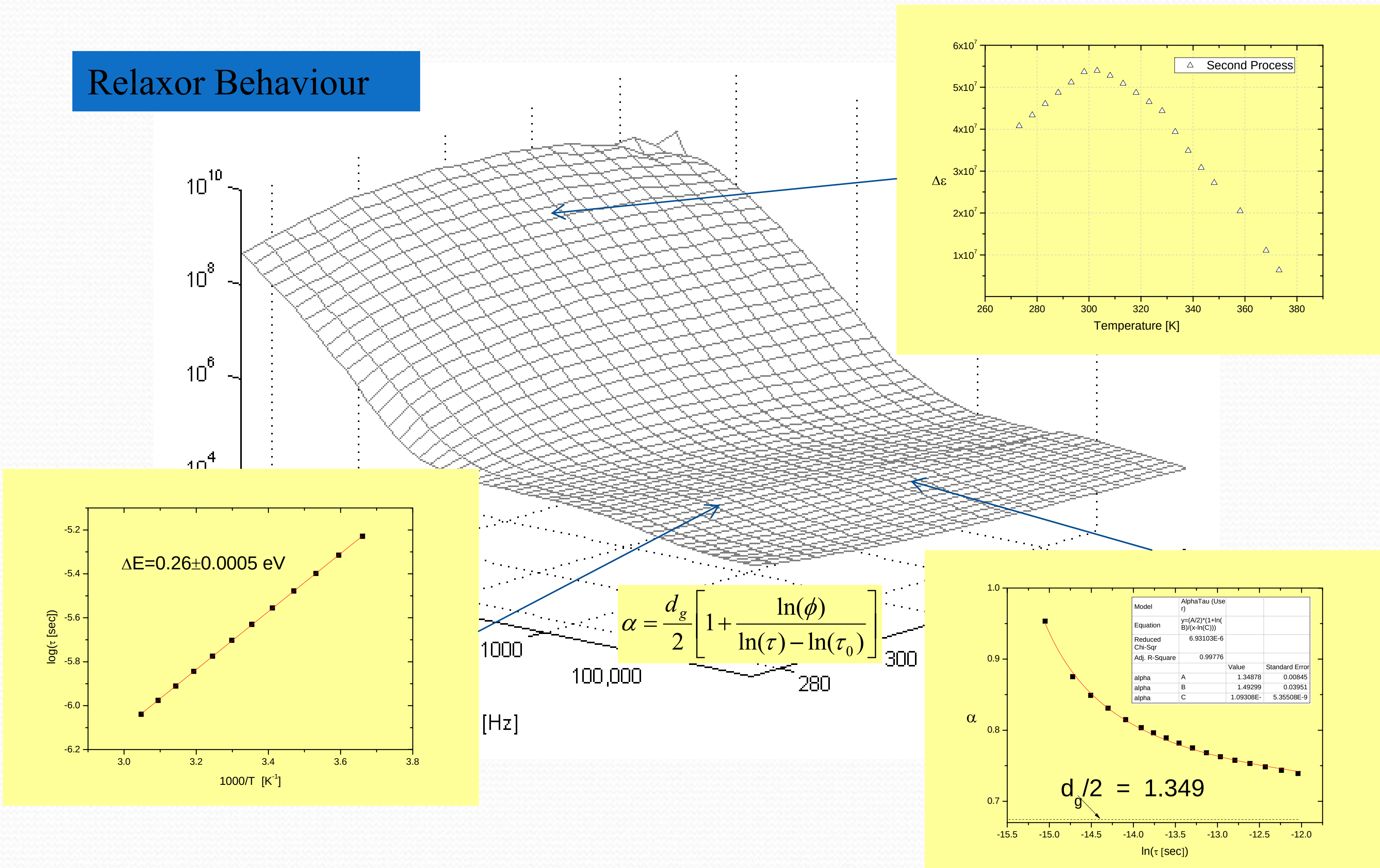
S.E. Lerner, et al., J. Non-Crystall. Sol. **353** (2007), 4422-4427

Using the Nanoscale



The Dielectric Behaviour of the amorphous layer

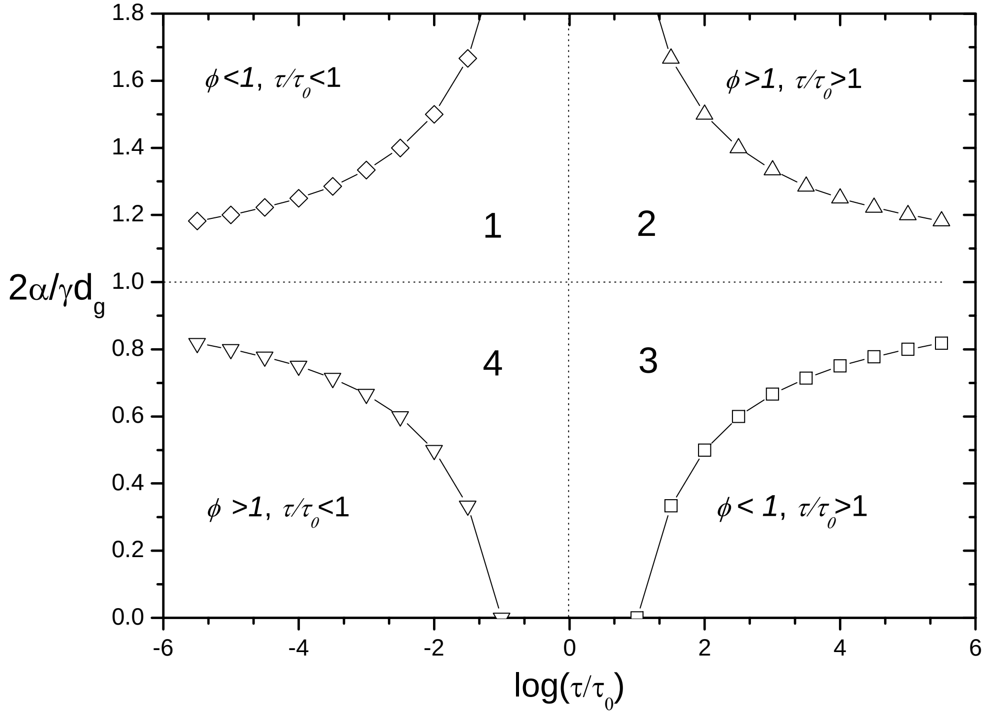
Relaxor Behaviour



$$\alpha = \frac{d_g}{2}\left[1 + \frac{\ln(\phi)}{\ln(\tau) - \ln(\tau_0)}\right]$$

The me

α Is a fractal di … lerlying
Matrix that con … e by using a
diffusion model

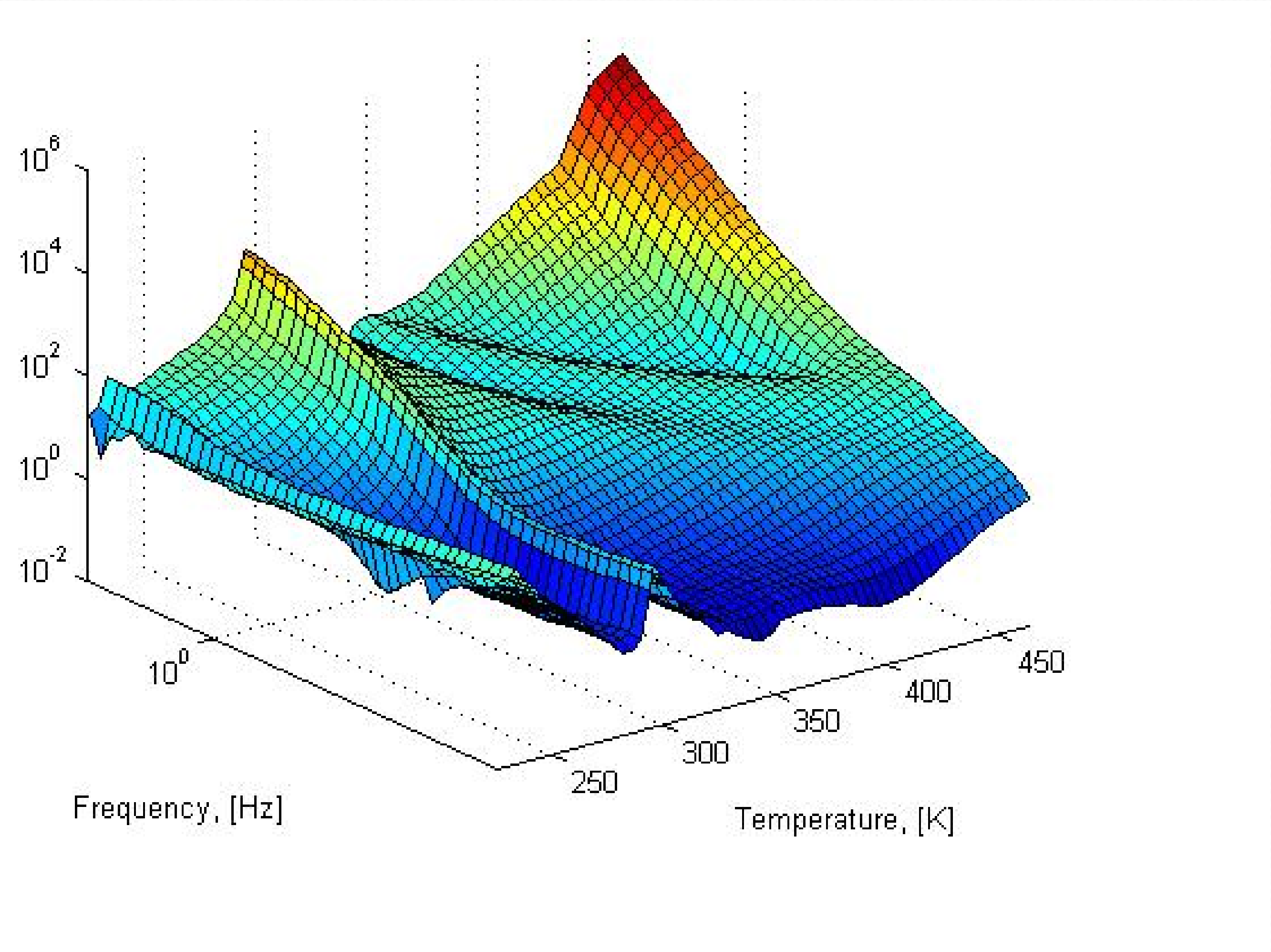


$$\phi = \; \ldots \; /\gamma$$

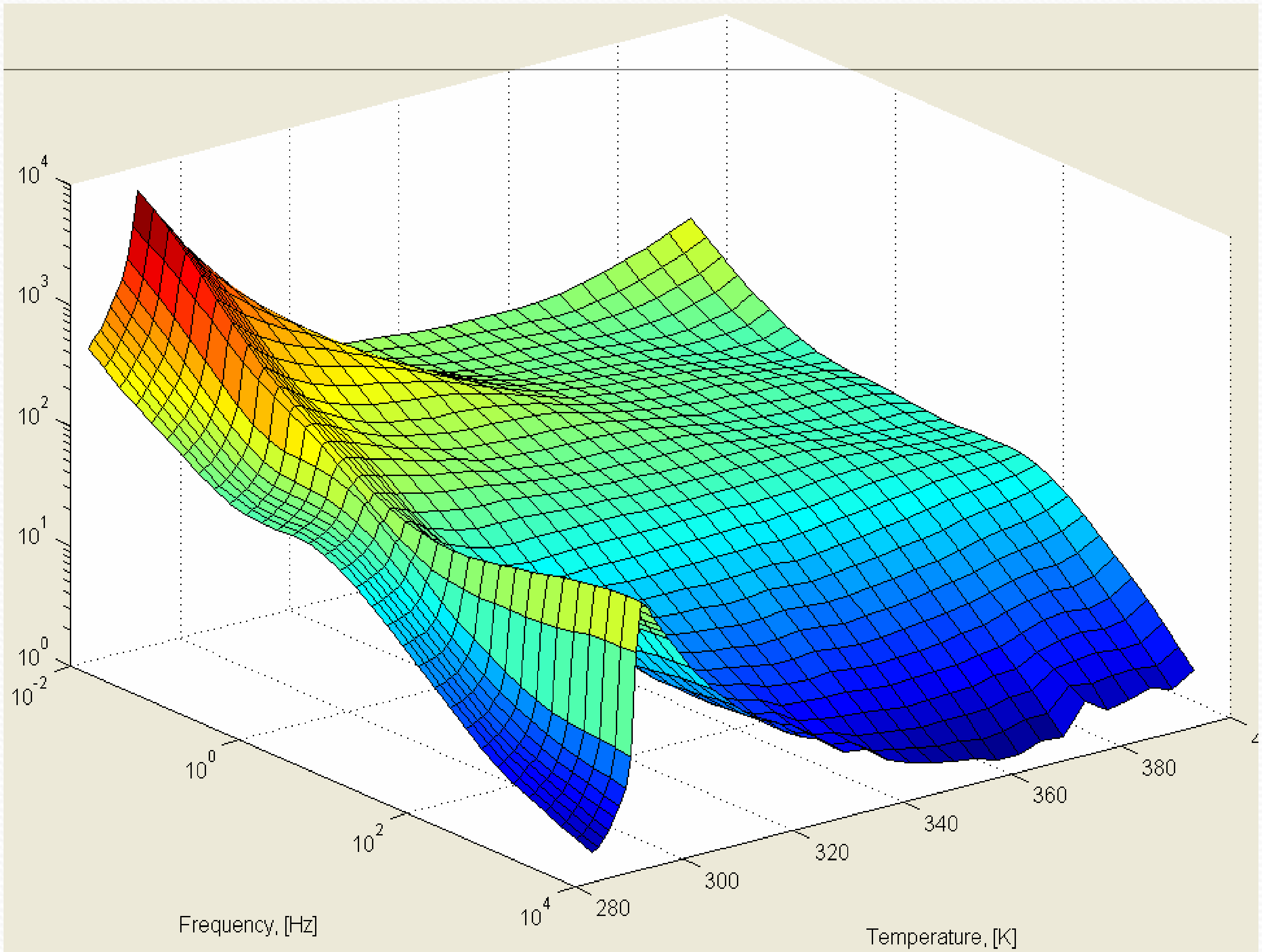
	$\phi>1$		$\phi<1$	
	$\tau > \tau_0$	$\tau < \tau_0$	$\tau > \tau_0$	$\tau < \tau_0$
Dominant feature in Diffusion	Hopping Kinetics (Diffusion length)		Matrix Structure	
Relaxation	Microscopic unit	Mesoscopic cluster	Microscopic unit	Mesoscopic cluster

Ya. E. Ryabov and Yu. Feldman, Physica A **314** (2002), 370

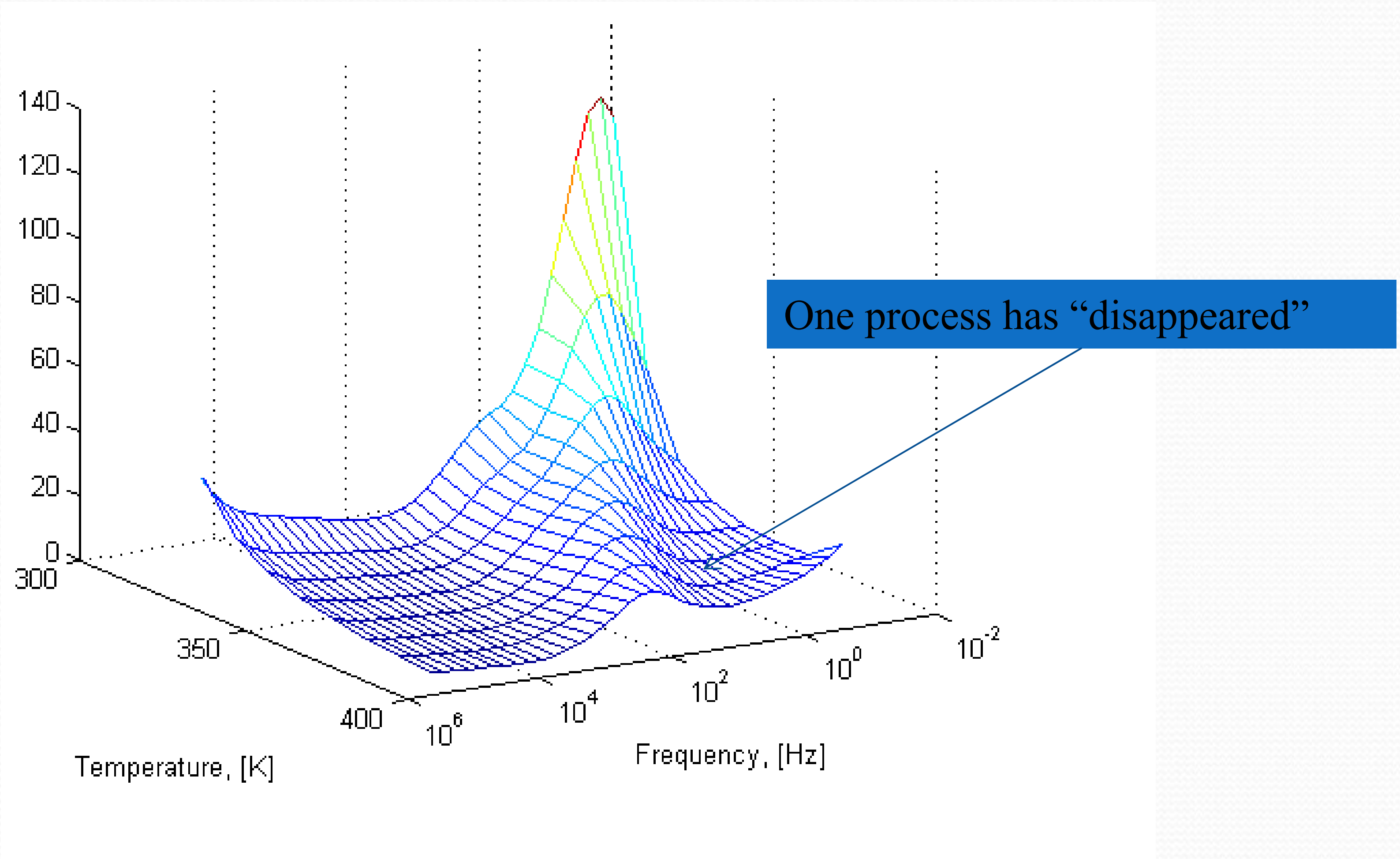
Physics or artifact?



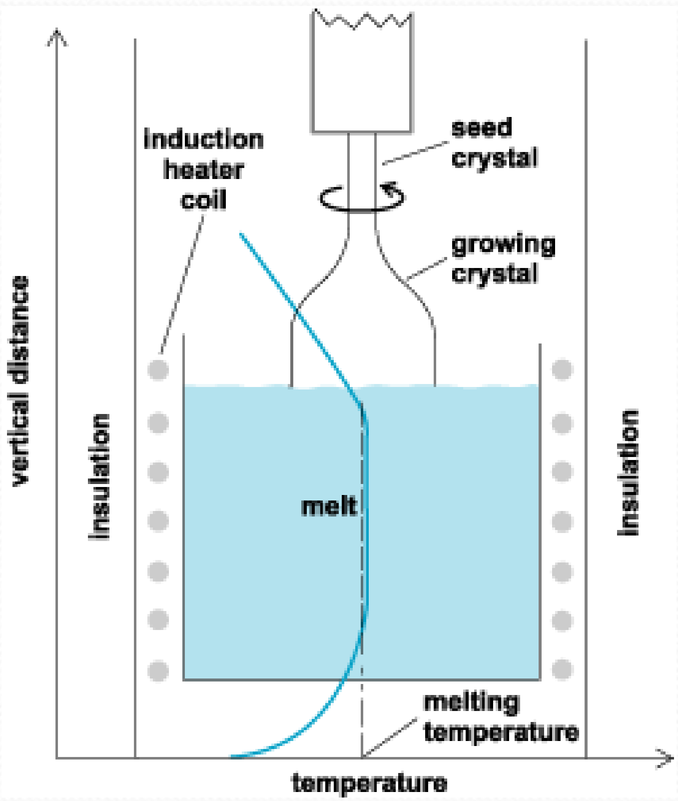
Bad Electrodes or Bad Crystal

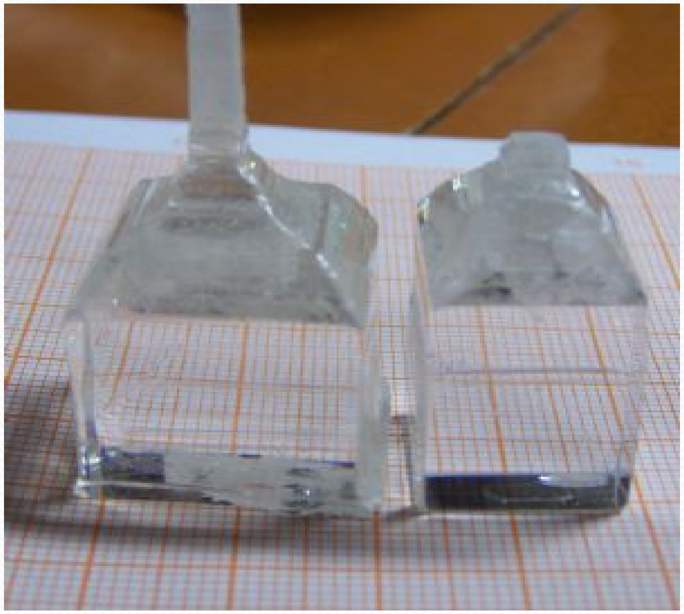


Looking at the “brother”

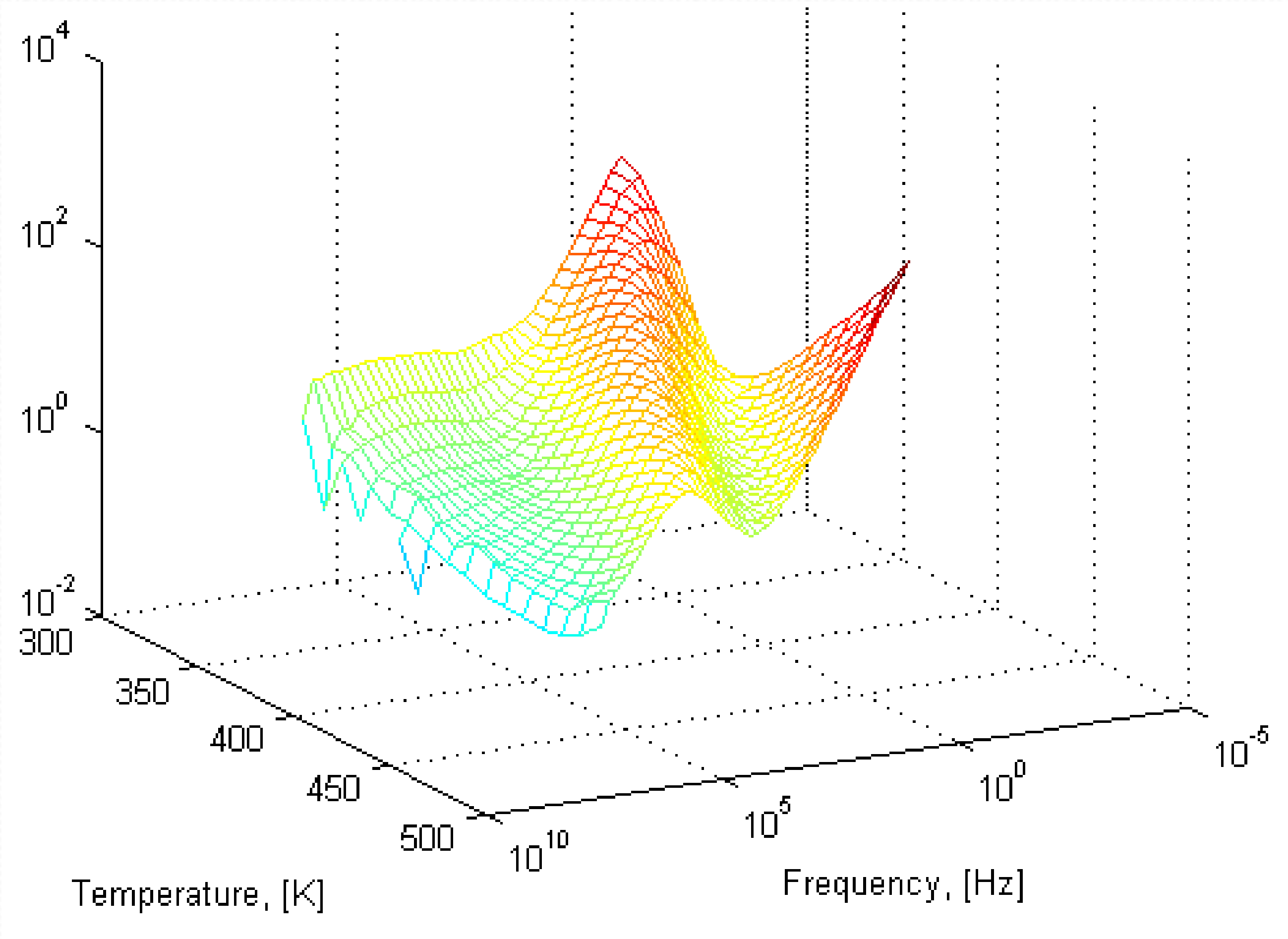


Czochralski crystal growth

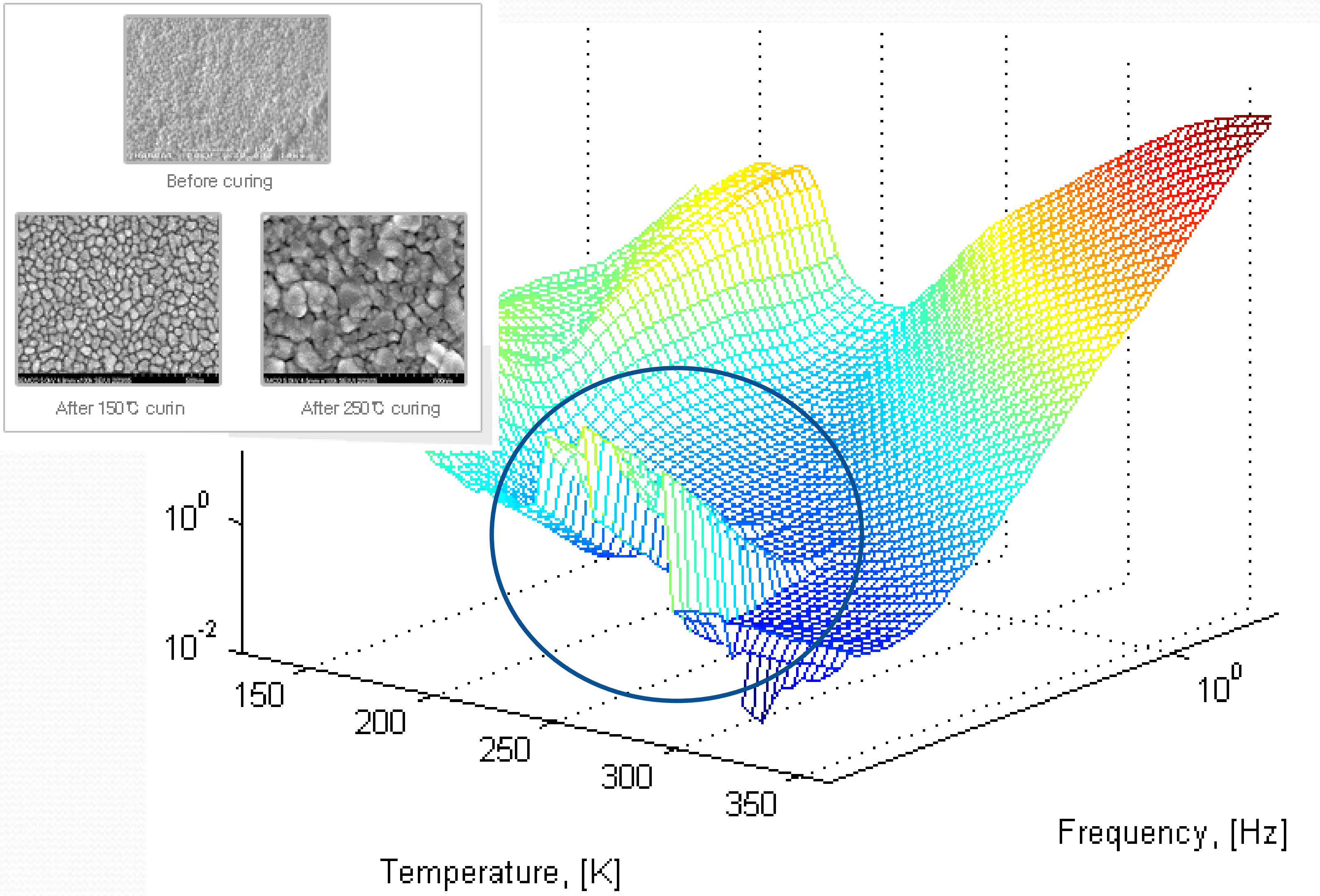




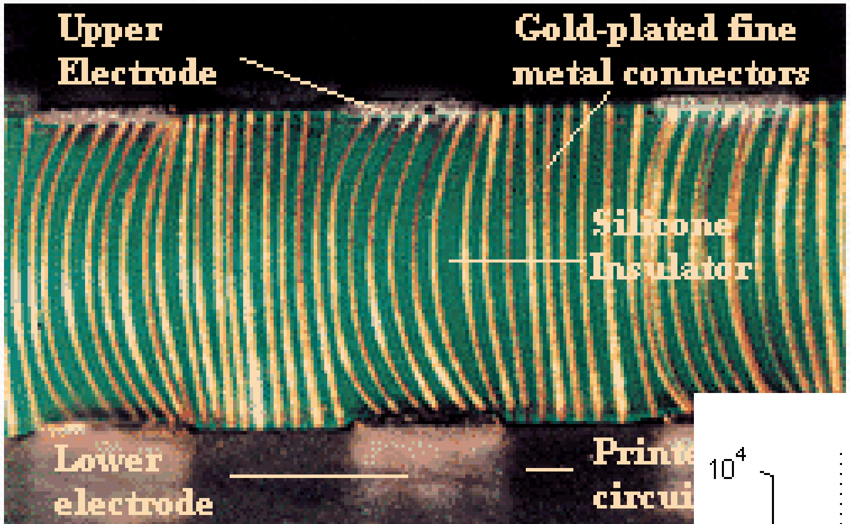
New Crystal – Same composition



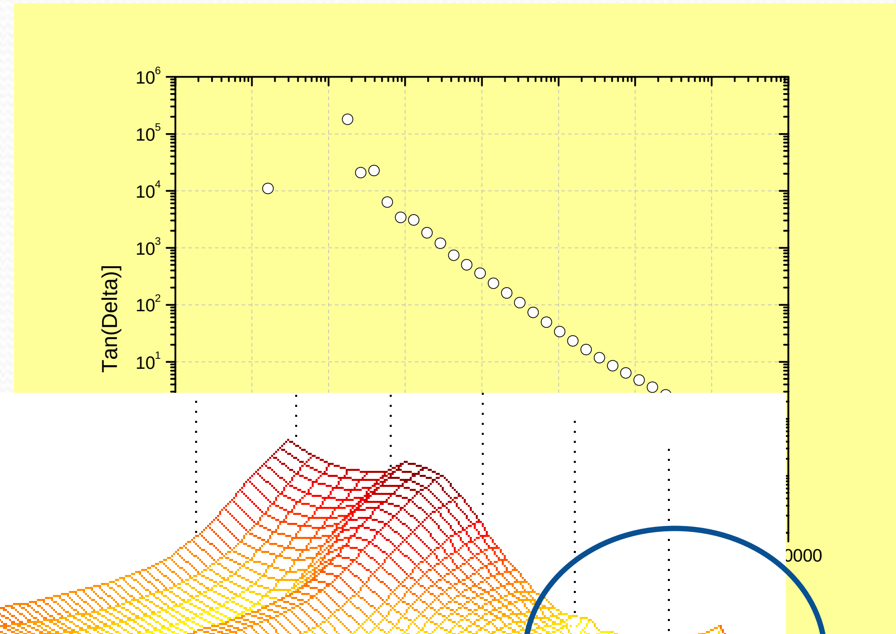
Paste electrodes

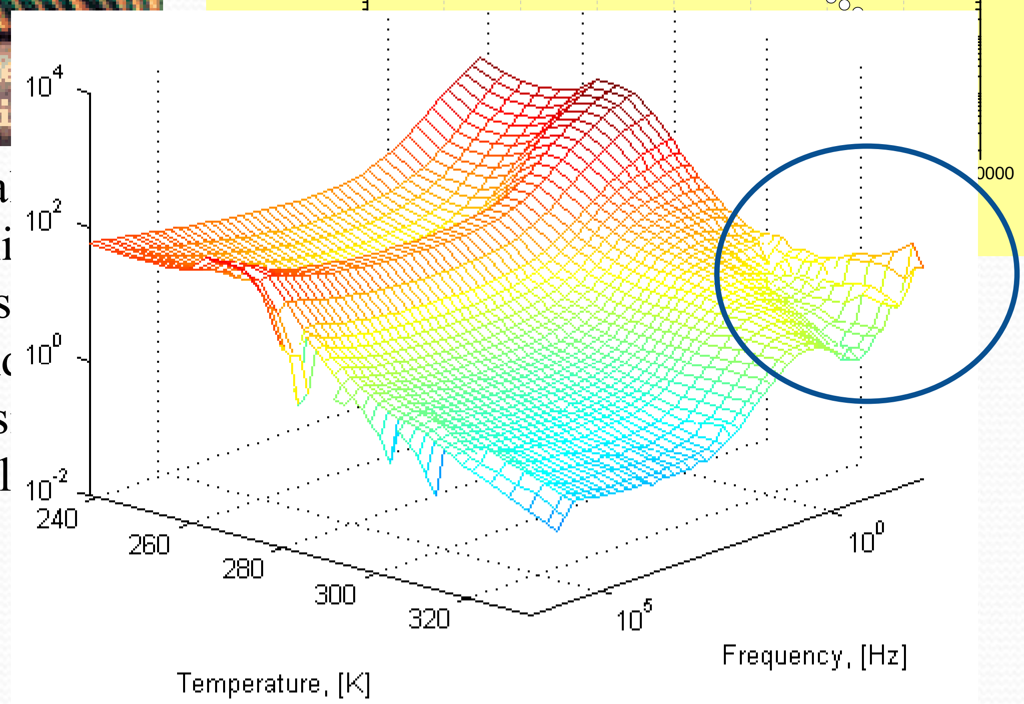


Zebra Electrodes

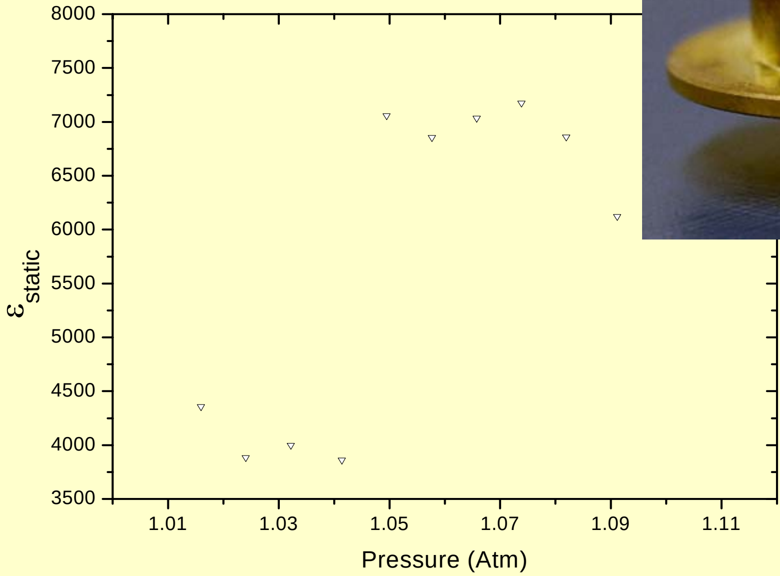


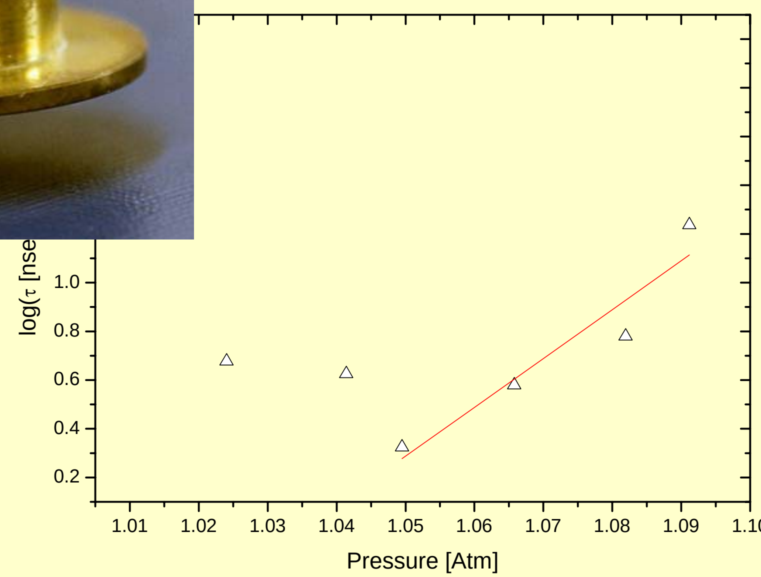
A range of 300 to 2,000 fine meta
per 1 cm2 are embedded in the thi
direction of the transparent s
rubber sheet. The fine metal conc
are gold-plated to ensure low res
and the ability to withstand a rel
high current flow.





Pressure





$$\tau = \tau_0 \exp\left[\frac{\Delta VP}{k_B T}\right]$$

Conclusions

- Never trust your results blindly!!!
- All contacts must be ohmic! (you don't need additional surface effects)
- Axis directions are important.
- Beware of Pressure.