ICTP/UCSB/TWAS
MINIWORKSHOP ON "*FRONTIERS IN MATERIALS SCIENCE*"
15 - 18 May 2001

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"Functional Complexity in Hard & Soft Matter"

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Please note: These are preliminary notes intended for internal distribution only.

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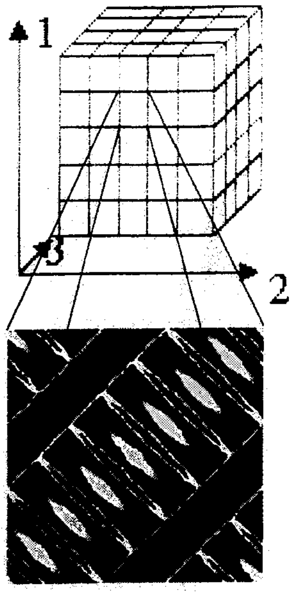
Functional Complexity in Hard & Soft Matter



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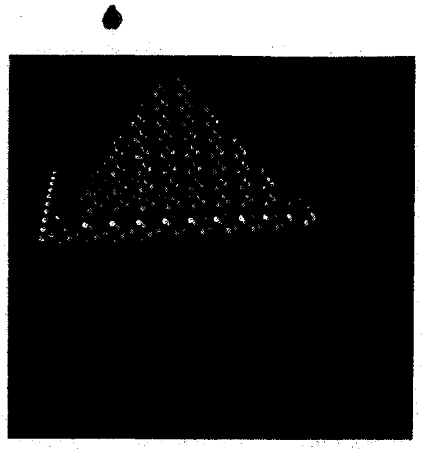

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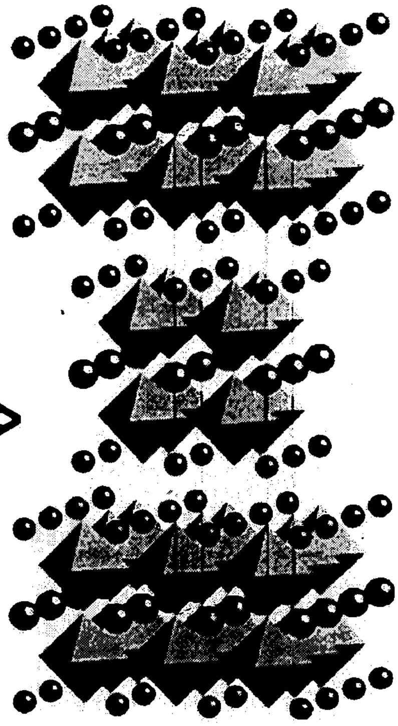


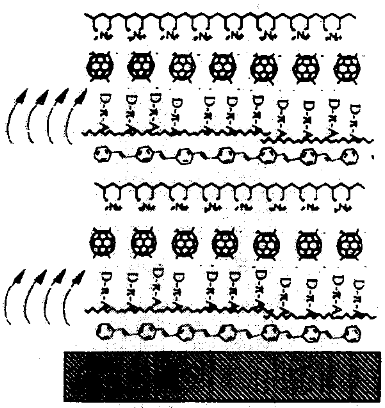
Structural Materials

Electronic Materials

HYBRIDS

Soft Matter

Bio Matter



Leitmotiv — Multiscale Functionality
— Complex (Adaptive) Matter

ALAN BISHOP, MAY 2001

Multiscale Structure and Function from Coexisting Short- and Long-Range Forces

- **Traditional Materials Modeling** $\nearrow$ **Forces $\Rightarrow$ Structure** / $\searrow$ **Different Forces $\Rightarrow$ Function**

- **"Soft " Matter (Inorganic, Organic, Biological)**

  Structure $\rightleftarrows$ **Function** (dynamics)

$\Rightarrow$ **Micro** ? origins of (multiscale) structure

$\downarrow$

Meso ? functionality of multiscale elements (fluctuations *vs.* collective dynamics)

$\downarrow$

Macro ? macroscopic consequences

$\Rightarrow$ **Complex System "Engines" (hierarchical, connected scales)**

$\Rightarrow$ **Nonequilibrium, Nonlinearity, Frustration, Landscapes, Basins of Attraction, Noise, Metastability, Intermittency, Glassiness, Hysteresis, Memory, Global Sensitivity to Local Perturbations, Nonadiabaticity, ...**

$\Rightarrow$ **Tunability of Global (average) Properties $\boxed{\text{AND}}$ Multiscale (spatial – temporal) Functional Textures (e. g., substates, hotspots, ...)**

- **Tunable $\longleftrightarrow$ Electronic/Structural "Polarizability"**

- **Novel "Polarizabilities" from**
  - topological constraints
  - competing interactions
  - multiple timescales

Especially Short – Long Range Forces

2

Competing Short- & Long-Range Interactions (& Entropy) in Hard & Soft Matter

- ***Common Driving Forces for Multiscale Patterns / Dynamics: Contraints & Topology***

e. g.,

with:

- Filamentary Flux Fow in Superconducting Films (PRL **76**, 2985 [1996]) — *N. Jensen*
- Charge-Ordering in Low-D Strongly Correlated Electronic Materials (Organic, Inorganic) (PRL **82**, 4679 [1999]) — *S. Brazovskii, A. Castro-Neto, N. Jensen, B. Stojkovic*
- Charge-Ordering in Polyelectrolytes (PRL **78**, 2477 [1997]) — *N. Jensen*
- Fine-Scale Elastic Textures at Solid-Solid Phase Transformations & Functional (Thin Film) Textures (PRB **60**, R12537 [1999]) — *T. Lookman, A. Saxena, S. Shenoy*

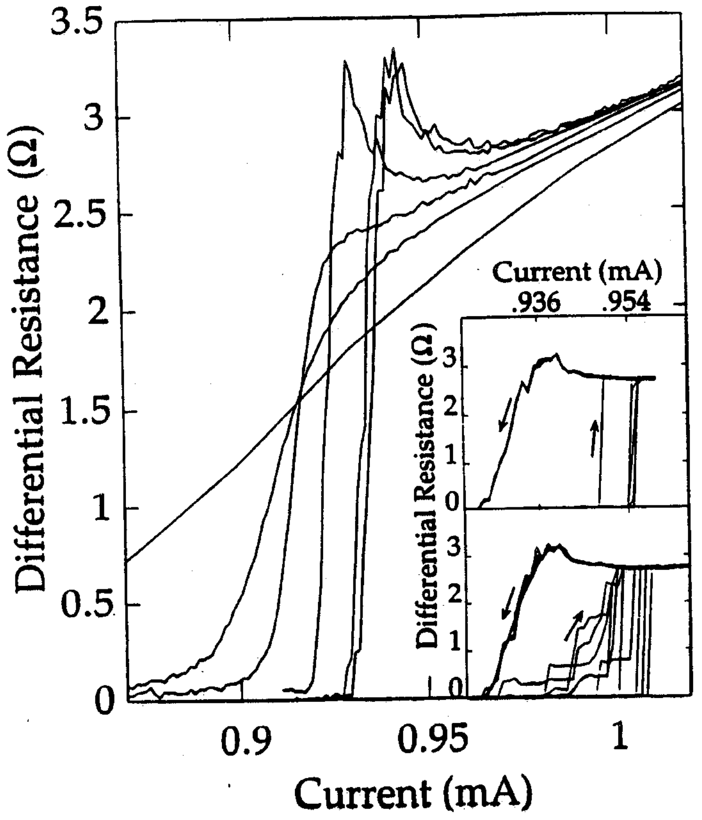
Relaxors; Ferro-Elastic, Magneto-Elastic, Coupling

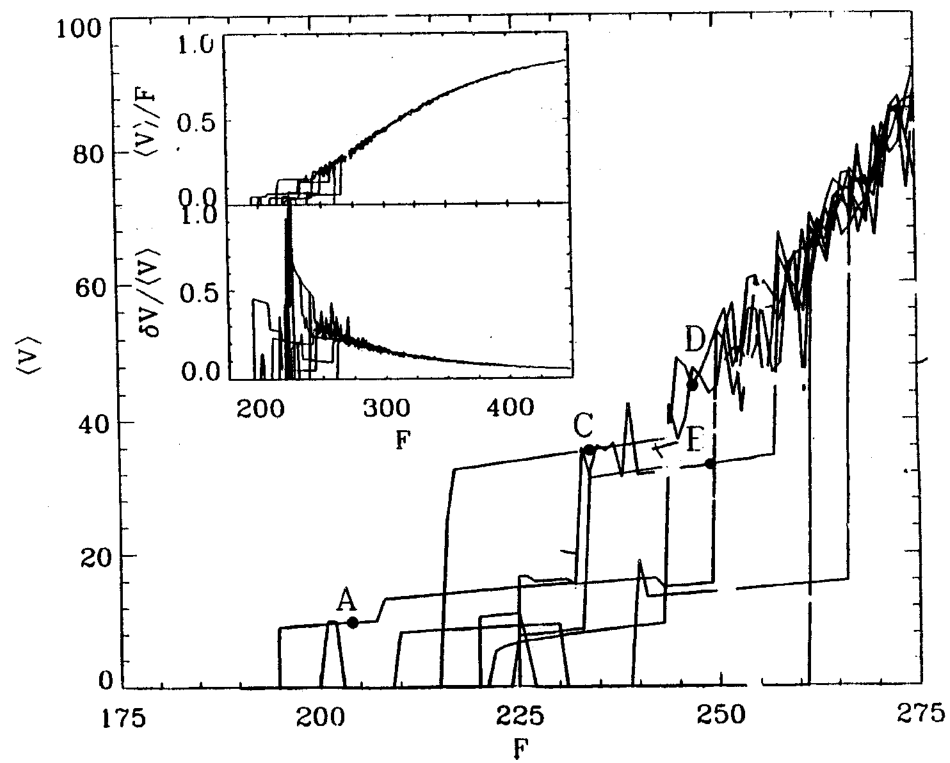
c.f. Seul & Andelman, *Science* **267**, 376 (1995)

DISORDER + MAGNETIC FIELD + CURRENT : NONEQUILIBRIUM FLUX FLOW

Filamentary vortex flow in thin film superconductors

(N. Grønbech-Jensen et al) (1996) **76**, 2985





Experiment

2-dimensional amorphous

$Mo_{77}Ge_{23}$ films (Hellerqvist, Beasley, et al)(1996) PRL

"Plastic". "Filamentary" vortex flow

JJA simulation

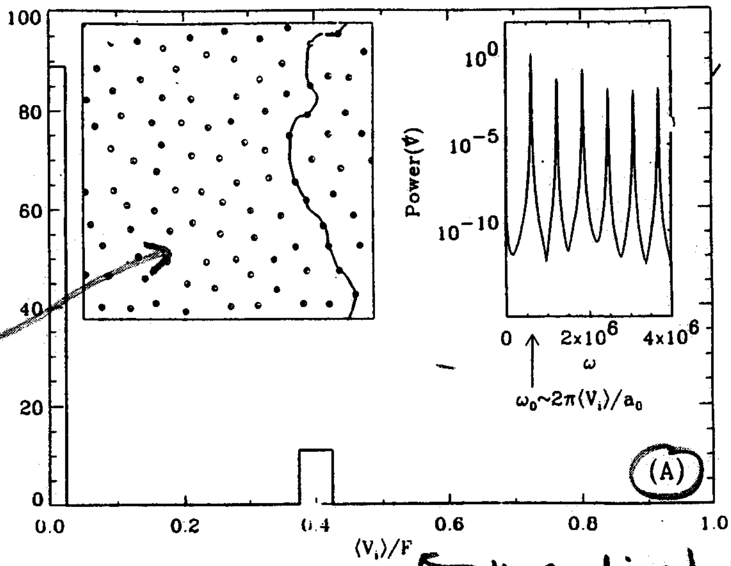
Including long-range interactions

100 vortices ; 500 pinning centers

"steps" ⟷ "filamentary"

N. Grønbech-Jensen et al. (1996) PRL 76, 2985

snapshot of vortices

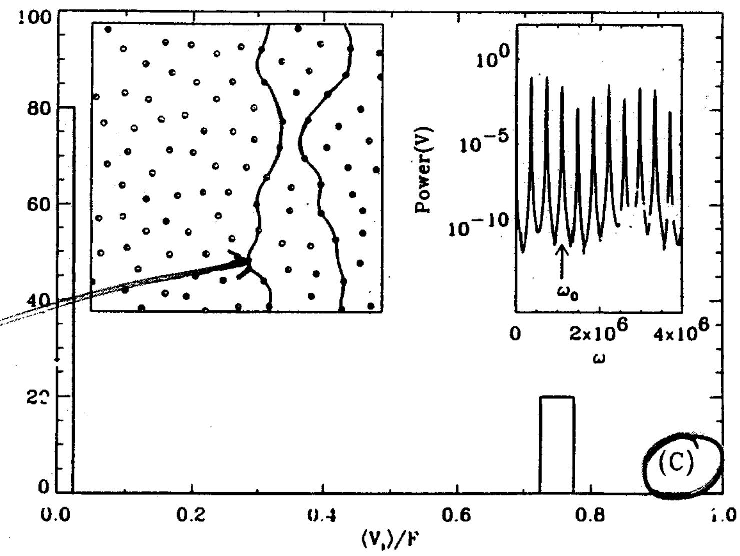


normalized speed

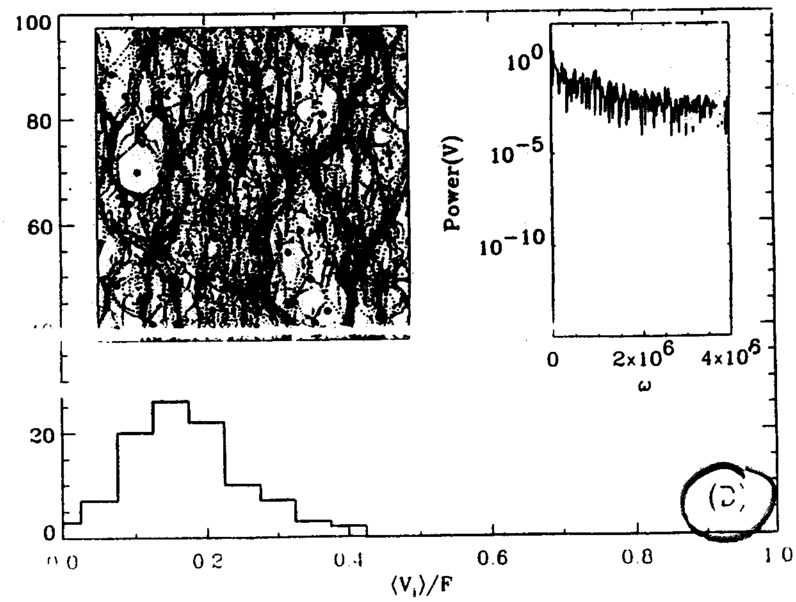
filamentary channel flow

c.f. stress chains, dielectric breakdown ...

vortex flow traces



stick-slip, plastic flow



- NONEQUILIBRIUM FLUX FLOW IN AMORPHOUS THIN-FILM SCS
- LANGEVIN MD WITH LONGRANGE INTERACTIONS & IMPURITY PINNING

ELECTROSTATICS: BUNDLING OF LIKE CHARGED OBJECTS

Theoretical Division, Los Alamos National Laboratory

Long Range Interactions

Ernshaw: Coulomb systems are unstable

Charge Neutrality: Coulomb=Collapse

Short Range Repulsion

Define Geometry

Prevent Coulomb Disaster

Entropy

Thermal Effective Repulsion

Marginal Balance Between Repulsion and Attraction Provides For Sensitive Macroscopic Manipulation

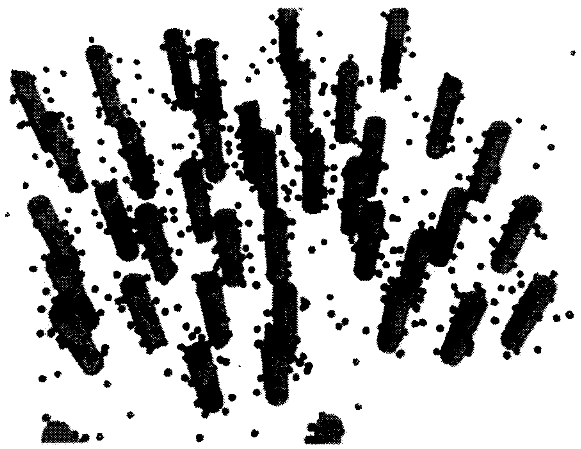
Model System Example:

Like Charged Rods (Polyelectrolyte)

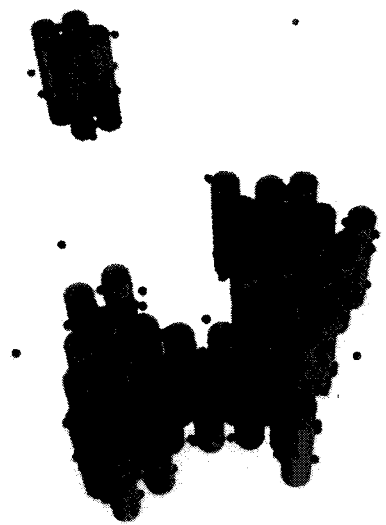
Point Counter Charge (Salt)

Thermal Noise (Room Temperature)

Monovalent Ions (Solvation)



Divalent Ions (Aggregation)



FROM "STRIPES" TO "TWINS"
IN TRANSITION METAL OXIDES

(& MANY OTHER "COMPLEX ELECTRONIC MATERIALS"
- - - LAVES, HEAVY FERMIONS, ORGANIC C-T, WO_3, - - -)

*** INTRINSIC DISORDER ("DIRT") PHYSICS ***
*** — ORIGINS, SIGNATURES, CONSEQUENCES ***

et al
, 57
..41 ('98)
..kovic et al
..L ('99)
, 4679

- **CHARGE (POLARON) LOCALIZATION & MESOSCALE ORDERING**
  (Linear Stripe Segments, etc.)

Polarizability

&

..son et al
, 82, 3288('99)
..g et al
, 80, 3284('98)

- **ENERGY LOCALIZATION IN NONLINEAR LATTICES**
  (Intrinsic Local Modes and Nonadiabaticity)

- **SOLID-SOLID PHASE TRANSFORMATIONS**
  (Fine-scale structure — hierarchical twinning, tweed) subμm – nm

ELASTICITY

..akoy et al
..('99)
, 60, R12537

BIG QUESTION

Is there a (hierarchical) relationship between the 2 faces of TMOs -- ELECTRONIC & ELASTIC multiscale patterns?

YES ⟶ **NEW SCIENCE & TECHNOLOGY OF FUNCTIONAL ELECTRO-ELASTIC MATERIALS**
("Relaxor glasses", "Dielectric breakdown", "Filamentary", "Correlated percolation"...)

Anharmonic Effects in the $A15$ Compounds Induced by Sublattice Distortions

Z. W. Lu and Barry M. Klein
Department of Physics, University of California, Davis, California 95616
(Received 24 April 1997)

We demonstrate that elastic anomalies and lattice instabilities in the $A15$ compounds are describable in terms of first-principles local density approximation electronic structure calculations. We show that at $T = 0$ V_3Si, V_3Ge, and Nb_3Sn are intrinsically unstable against shears with elastic moduli $C_{11} - C_{12}$ and C_{44}, and that the zone center phonons, Γ_2 and Γ_{12}, are either unstable or extremely soft. We demonstrate that sublattice relaxation (internal strain) effects are key to understanding the behavior of the $A15$ materials.

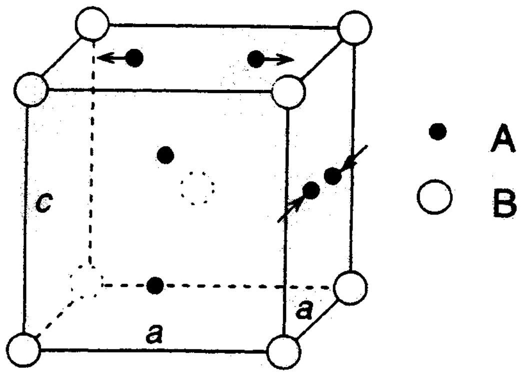


FIG. 1. Schematic diagram of ideal ($c = a$) and tetragonally distorted ($c \neq a$) $A15$ crystal structures (A_6B_2). B atoms form body-centered cube, while A atoms form linear chains on each cube face. Arrows denote allowed internal degrees of freedom (direction of sublattice relaxations) in the tetragonally distorted $A15$ structure.

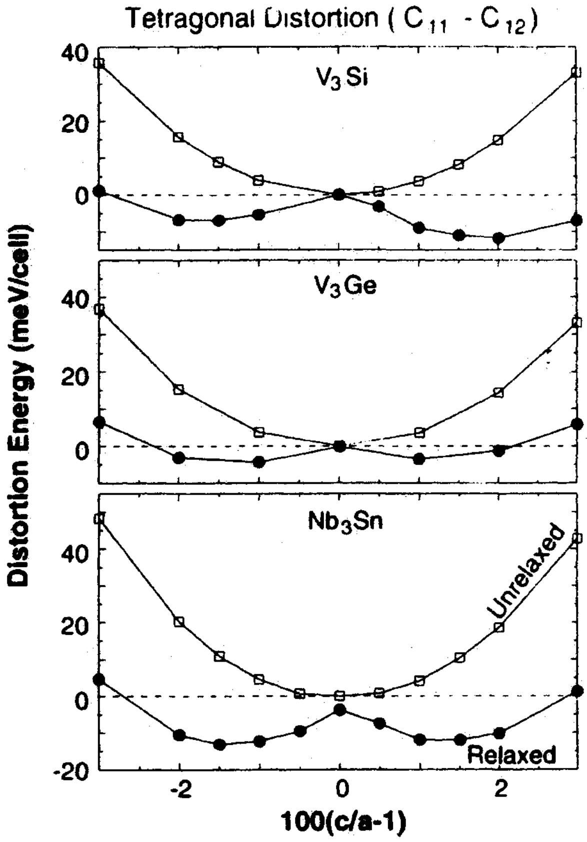


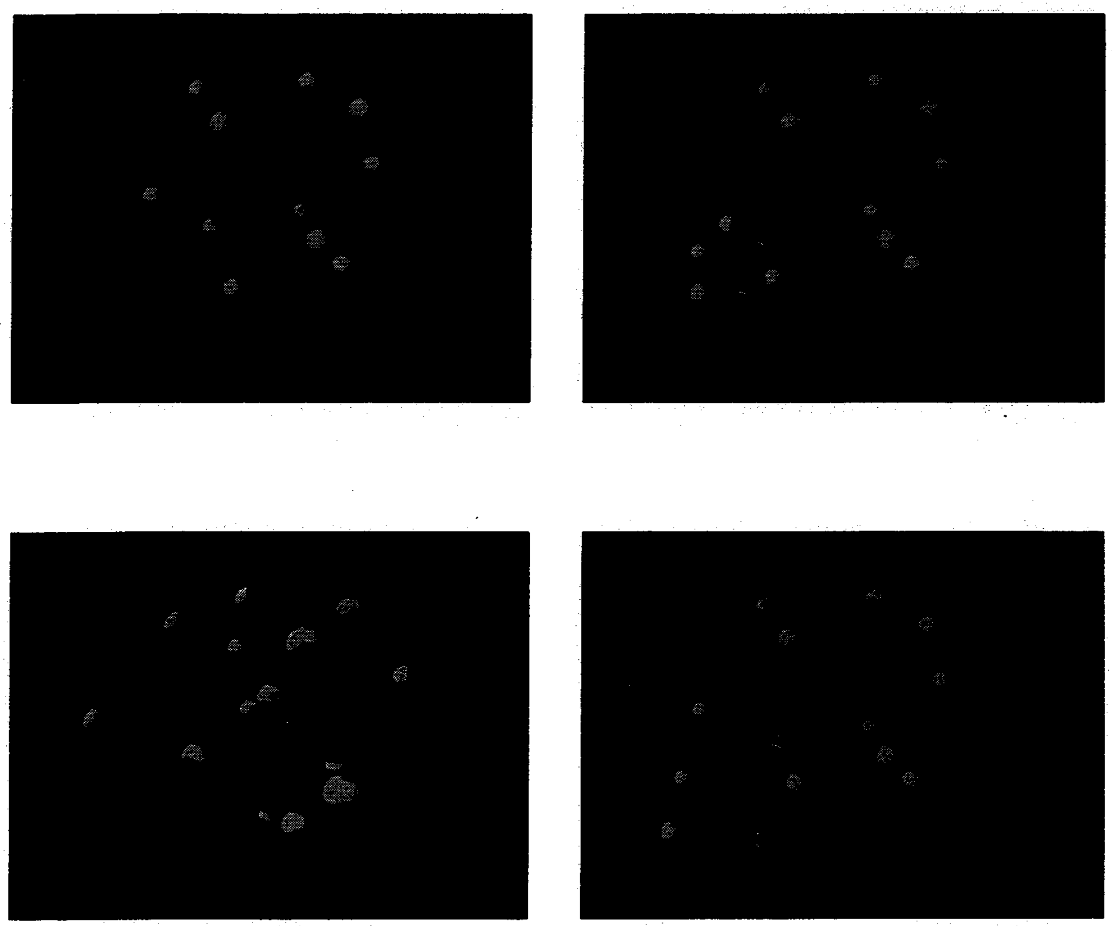
FIG. 3. Distortion energies for tetragonally distorted $A15$ structure and also see the caption of Fig. 2

Linear-Response Calculation of the Electron-Phonon Coupling in Doped $CaCuO_2$

S. Y. Savrasov and O. K. Andersen
Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, 70569 Stuttgart, Germany
(Received 17 June 1996)

Using density-functional linear-response theory, we calculate the electron-phonon interaction for s- and d-wave pairing in the 0.24 hole doped infinite-layer compound $CaCuO_2$. We find $\lambda_{x^2-y^2} \sim 0.3$ to be positive and only slightly smaller than $\lambda_s \sim 0.4$. This suggests that the electron-phonon mechanism *alone* is insufficient to explain the high T_c but could *enhance* another d-wave pairing mechanism. Results of calculated lattice dynamics and transport properties are also presented and discussed. Out-of-plane distortions are found essential for the stability.

ADVANCES IN ELECTRONIC STRUCTURE 8



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"Inhomogeneity"

– a very old and very new topic –

"Extrinsic"

- Impurities
- Disorder
  - -localization
- Disorder & frustration/competition
  - - (spin) glasses

"Intrinsic"

- Feedback mechanisms of
  coupled fields
  (e.g., spin-charge-lattice (-orbital)

⇩

- Strong nonlinearity
- Competing interactions/lengthside/timescales
  (short/long; slow/fast)
  (discrete lattice/long-range)

⇩

- Coherent (nonlinear) structures
  ("intrinsic localization")
  & collective ("mescopic") patterns

⇩

- "Intrinsic disorder," "metastability," "landscapes"
- "Crossover & precursor patterns" not
  "phase transitions"
- Global sensitivity to small/local perturbations

- Multiscale, nonequilibrium processes
- Multiscale, functionality of complex systems
- Mesoscopic organizing principles?

Determination of the Local Lattice Distortions in the CuO_2 Plane of $La_{1.85}Sr_{0.15}CuO_4$

PRL

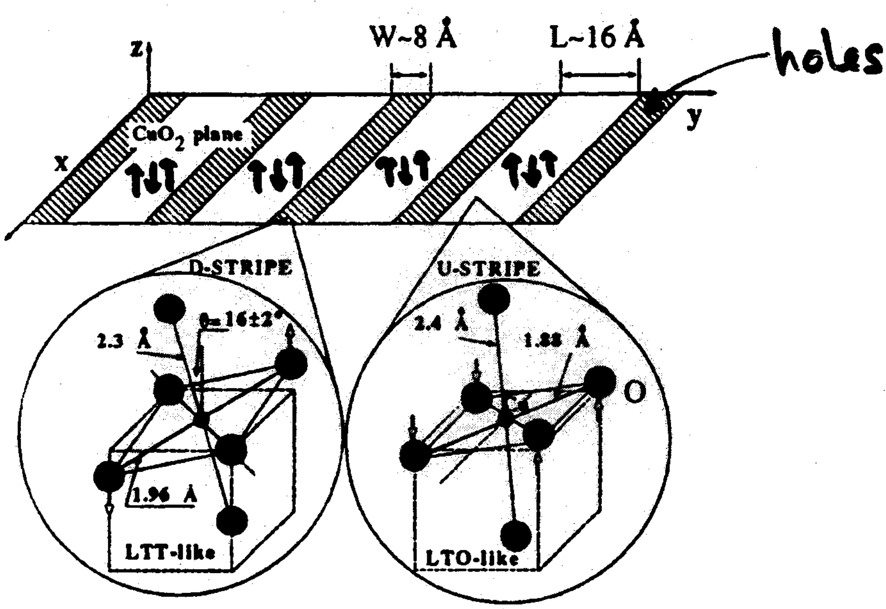
A. Bianconi, N. L. Saini, A. Lanzara, M. Missori, and T. Rossetti
Dipartimento di Fisica, Università di Roma "La Sapienza," P.A. Moro 2, 00185 Roma, Italy

H. Oyanagi, H. Yamaguchi, K. Oka, and T. Ito
Electrotechnical Laboratory, Umezono, Tsukuba, Ibaraki 305 Tsukuba, Japan

(Received 8 June 1995)

The measurement of the Cu-O distances by a local and fast probe, polarized Cu K-edge extended x-ray absorption fine structure (EXAFS) in $La_{1.85}Sr_{0.15}CuO_4$ crystal shows two different conformations of the CuO_6 octahedra below 100 K assigned to two types of stripes with different lattice. This experiment supports a model of "two components" spatially separated in a superlattice of quantum stripes for the anomalous properties of cuprate superconductors.

COMPLEMENTARY DATA FROM NEUTRON { DIFFUSE SCATTERING
PAIR-DISTRIBUTION FUNCTION



Pictorial view of the distorted CuO_6 octahedra, left side, of the "LTT type" assigned to the distorted stripes (D stripes) of width $W \sim 8$ Å and of the undistorted octahedra, right side, of the "LTO type" assigned to the undistorted stripes (U stripes) of width $L \sim 16$ Å.

Yu, Bishop, Gammel et al (1998) (PRB Rapid Comm.) 57, 3241

- Low- and HIGH- ENERGY SIGNATURES OF "STRIPE" MESOSCOPIC PATTERNS (Cuprates, Nickelates ---)
- LOCAL MAGNETOELASTIC COUPLING
- IR, R, $\sigma(\omega)$, $S(q,\omega)$, NMR ...

Issues for Mesoscopic Patterns

- **Origins ?**

STOJKOVIC et al
Phys. Rev. Lett.
82, 4679 (1999)

- **Signatures ?**

EROLES et al
Europhys Lett
50, 540 (2000)

- **Consequences ?**

MARTIN et al

(2000)

Origins

– Competing interactions (lengthscales)

– (Too) many possibilities

- 1-band Hubbard/t - J to nonlinear shell models!
- Needs classification of mechanism/material class

• Quantum

doped Hubbard (1-, 3-band)
t - j, DE ...

intrinsic electronic
tendency toward
nanoscale phase
separation

bootstrapped by
coupling to lattice (≠ "el - ph")
e.g., local buckling / tilting
at localized holes

• (Semi) Classical

directional (d, f) bonding constraints
(c. f. covalent glasses)
and polarizable O

anisotopic elasticity and polarizability

competing
SHORT-range (lattice-scale effects of
doping into AF, CDW, JT, Peierls, ...)
and LONG-range (Coulomb, elastic)
and entropy

landscapes (defects w. r. t. Wigner crystal)
(c. f. vortex patterns, polyectrolytes, ...)

Inhomogeneity-Induced Superconductivity

J. Eroles et al
~~preprint (1999)~~)
Europhys Lett. 50, 540(2000)

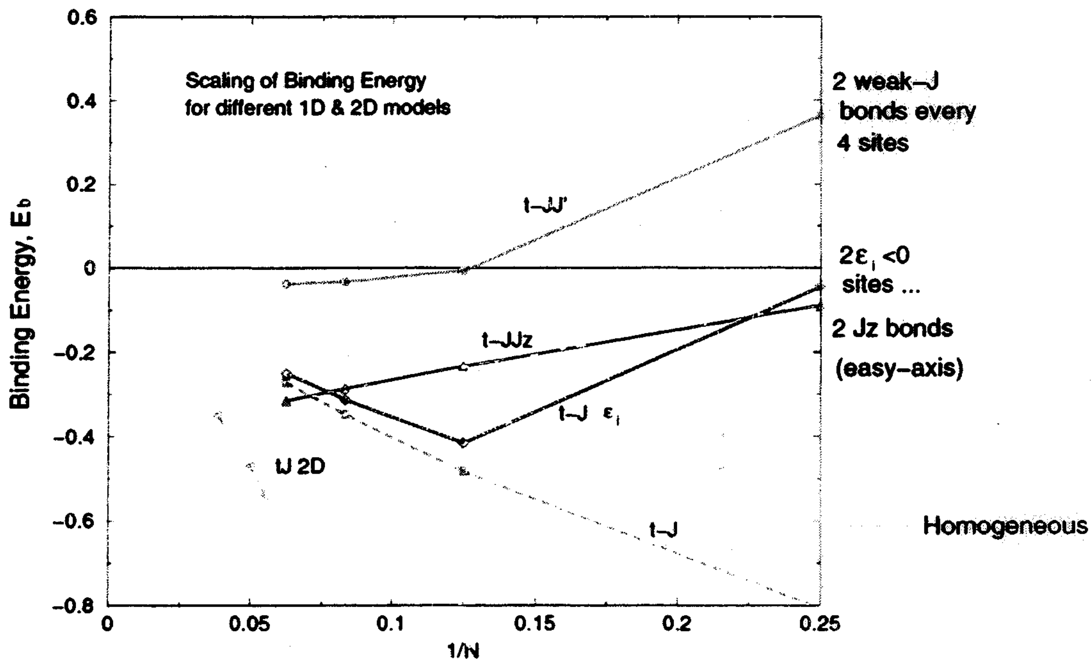
$$H = H_{tJ} + H_{\rm inh}$$

$$H_{tJ} = -t \sum_{\langle i,j\rangle,\sigma} c^\dagger_{i\sigma} c_{j\sigma} + J \sum_{\langle i,j\rangle} (\mathbf{S}_i \cdot \mathbf{S}_j - \frac{1}{4} n_i n_j) \ ,$$

and

$$H_{\rm inh} = \sum_{\langle stripe\ sites\rangle} \delta J_z \ S^z_\alpha S^z_\beta + \frac{\delta J_\perp}{2} \left(S^+_\alpha S^-_\beta + S^-_\alpha S^+_\beta \right)$$

e.g. local Spin-Orbit coupling



$$E_b = (E_{2\ holes} - E_{0\ hole}) - 2(E_{1\ hole} - E_{0\ hole})$$

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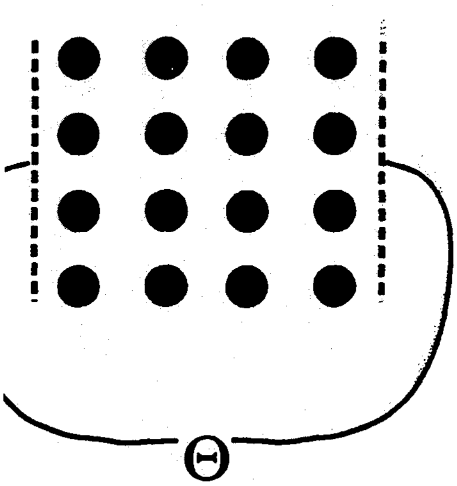
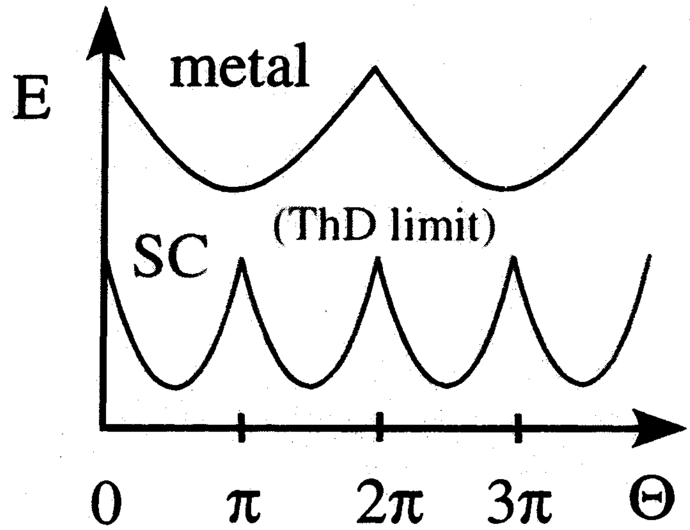
Flux Quantization

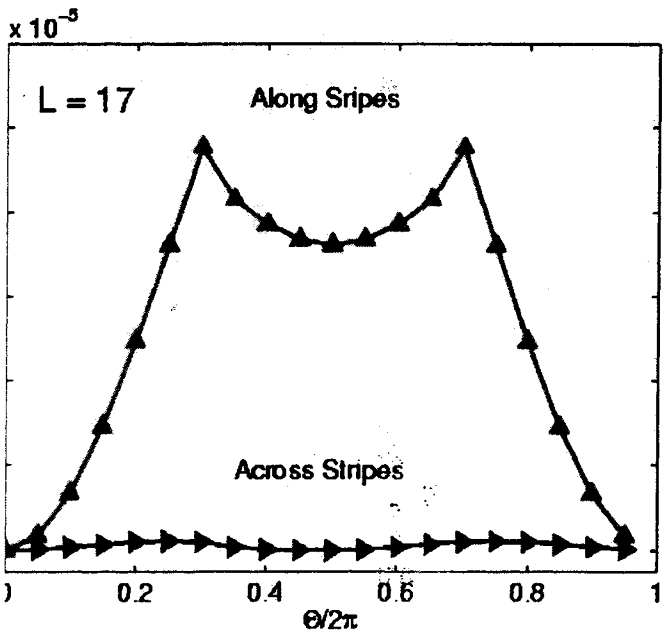
wist:



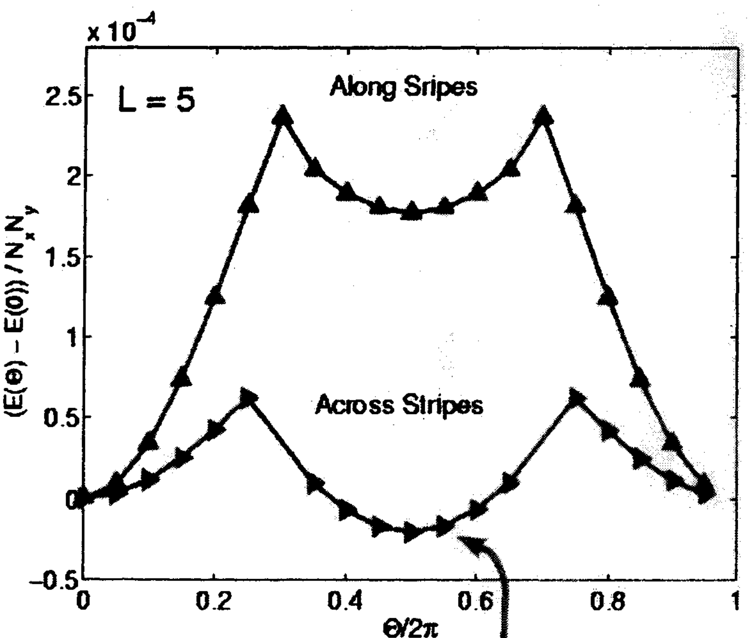


$U = 4\,t,\ V = -\,0.9\,t$

L = 17, x = 6%



L = 5, x = 20%



"Josephson" coupling

ab.js.51a

Stripes and Other Mesoscale Hole-Orderings in (Layered) Transition Metal Oxides

with
B. P. Stojkovic, Z. G. Yu, A. H. Castro Neto, N. Grønbech-Jensen
[PRL 82, 4679 (1999); PRB **62**, 4353 (2000)]
Tabor, Stojkovic, Brazovskii, B : J. Phys. C (2001)

Materials	Doped	Cuprates [Manganites Nickelates]	(+ in-plane/out-of-plane impurities)

MODEL:

- Competing anisotropic short- (spin/charge/valence/orbital /Jahn-Teller/lattice fluctuations)

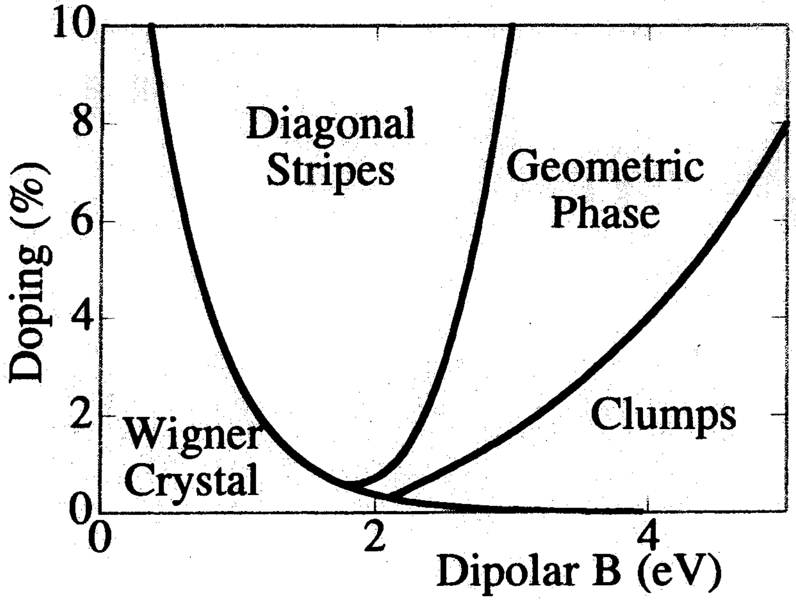
  + long-range (Coulomb, elastic)

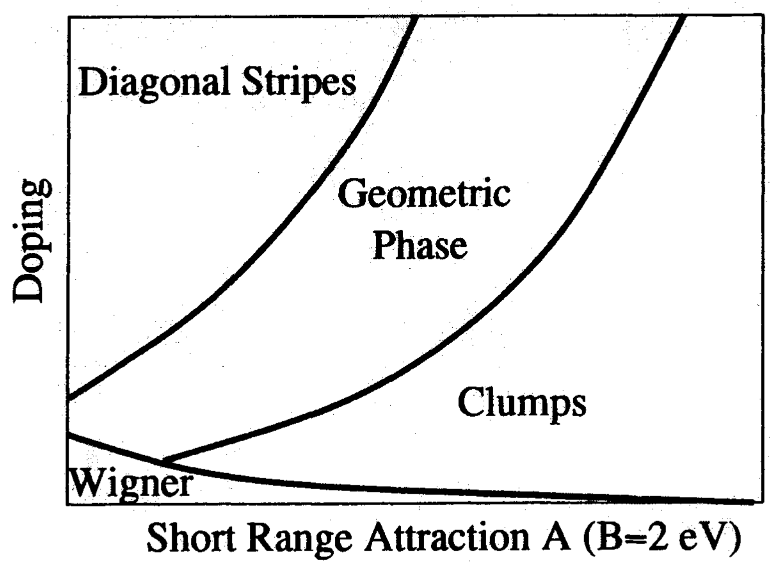
  + impurities

RESULTS:

- Ordering of "defects" with respect to Wigner crystal (not Hubbard) ground state: "Landscape" of states
- Glassy dynamics
- Stripe segments robust

Phase Diagrams

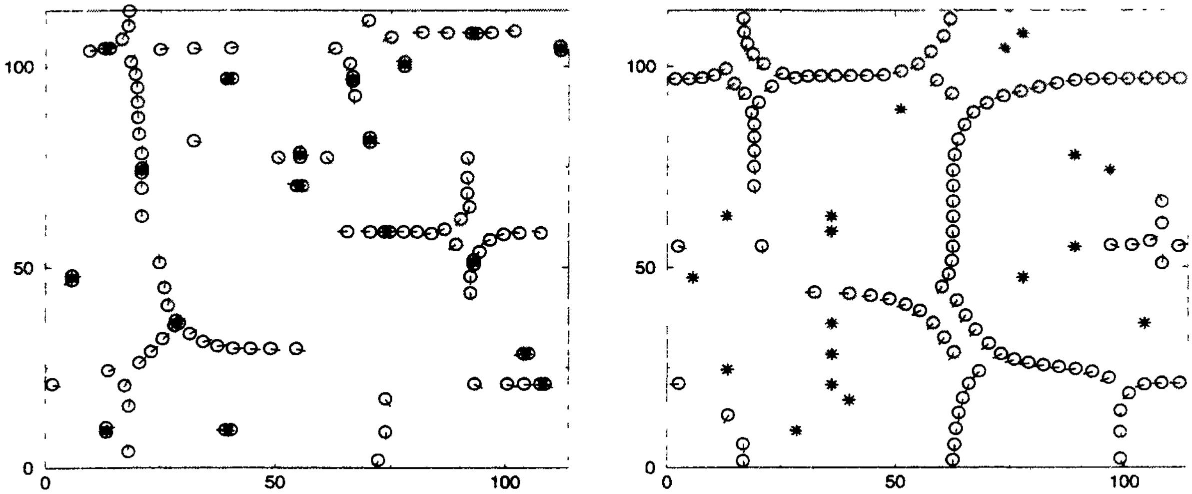




Note: $B = 0 \rightarrow$ only phase separation or Wigner crystal

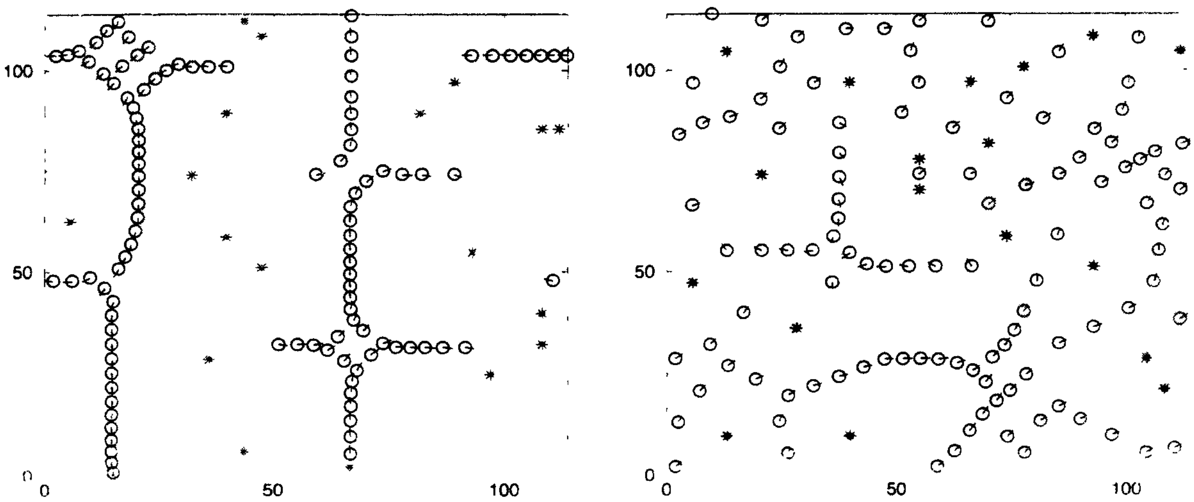
Role of Impurities on Stripe Formation

- **Left**: out-of-plane, pinning impurity (e.g., Sr)
  Right: in-plane, repulsive impurity (e.g., Li)



o HOLE * IMPURITY

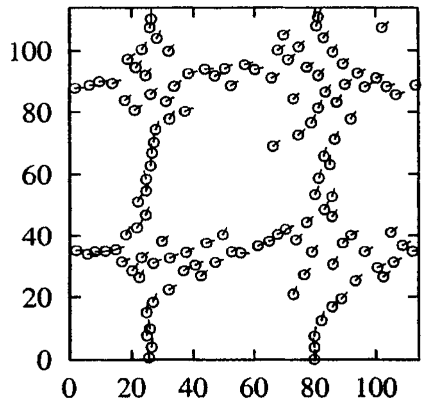
- **Left**: short range uncharged repulsive impurity (e.g., Zn).
  Right: impurity with induced magnetic moment.

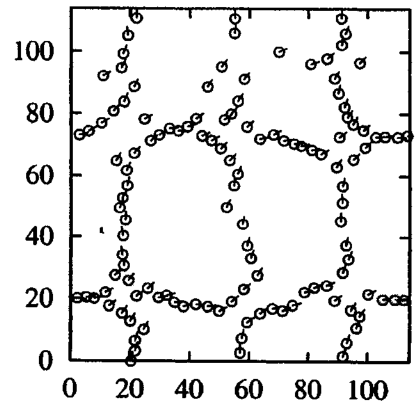


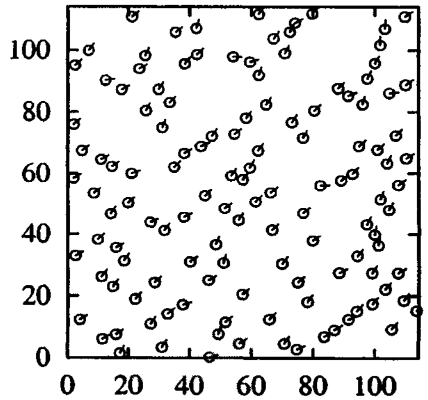
STRIPE SEGMENTS ARE ROBUST → NO LONG-RANGE ORDER, GLASSY, NONLINEAR DYNAMICS

"GLASSY" DYNAMICS : SPATIO-TEMPORAL INTERMITTENCY

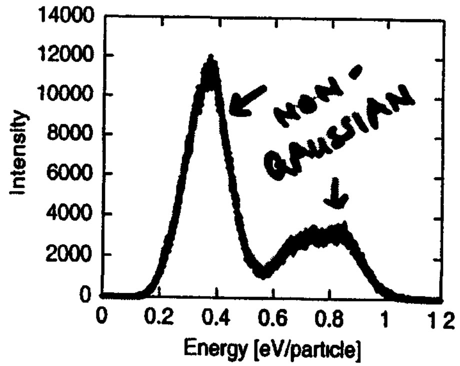
σ
CHARGE
&
MAGNETIC
DIPOLE



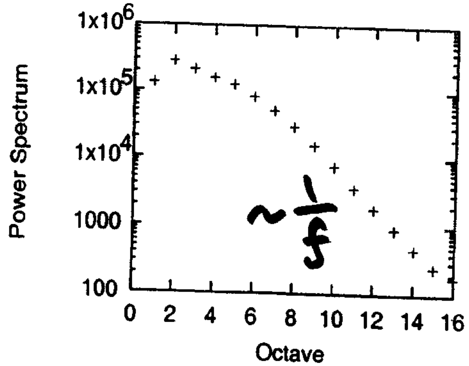




COMPETING BASINS OF ATTRACTION NEAR MELTING(T)
"LANDSCAPES"



INTENSITY OF COMPETING ENERGY STATES



⟨POTENTIAL ENERGY FOURIER COMPONENTS⟩

B. Stojkovic et al

CHARGE-ORDERING IN DOPED BROKEN-SYMMETRY GROUND STATES

(Teber, Stojkovic, Brazovskii, B J. Phys C (2001))

- INTERCHAIN CONFINEMENT ($J_\perp$) + COULOMB

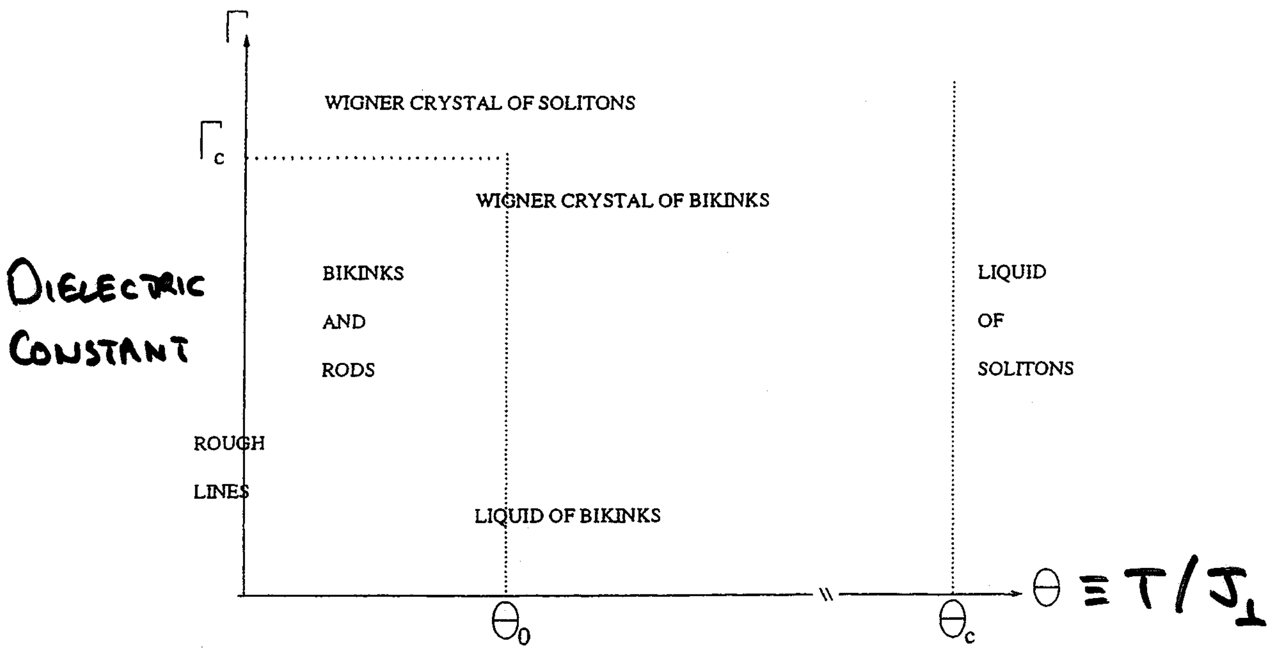
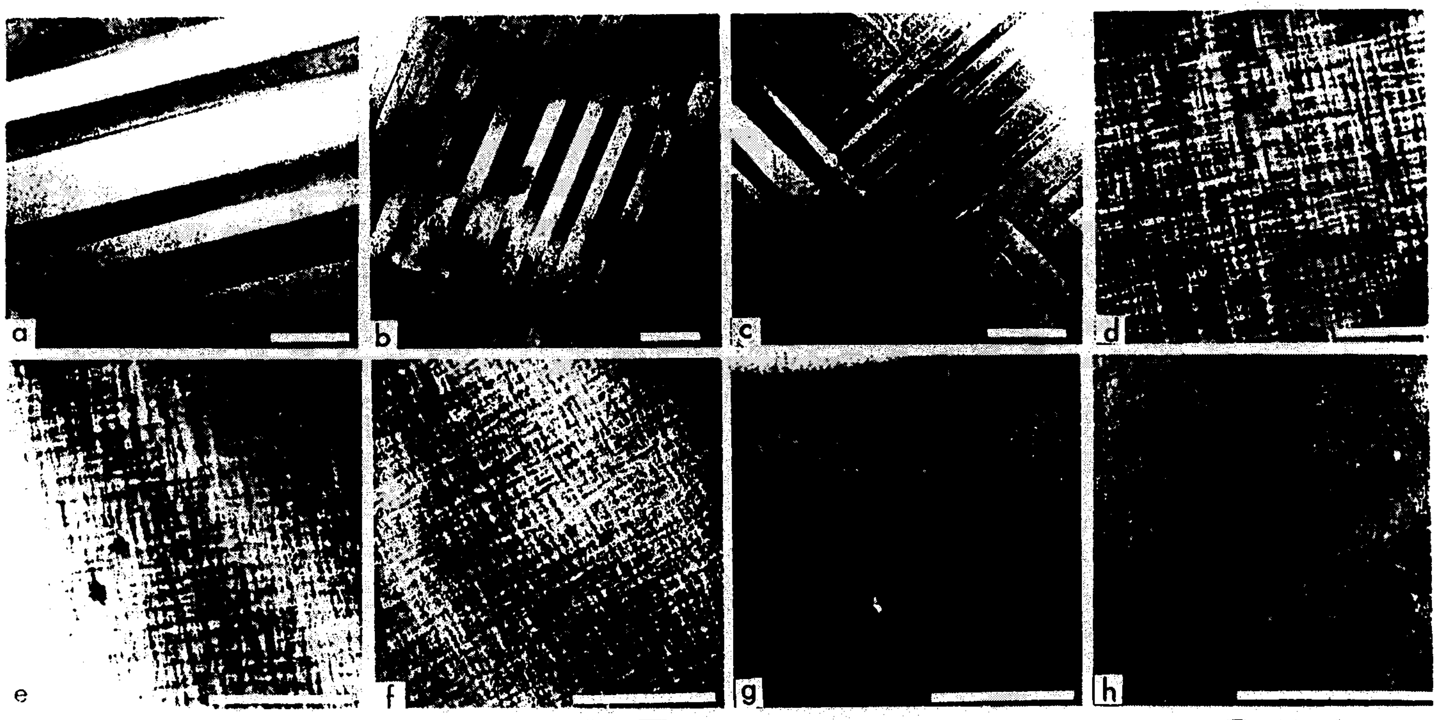
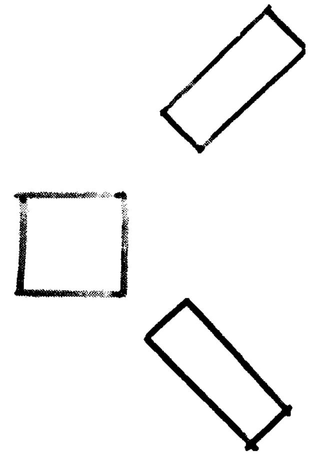


Figure 2. The phase diagram of the 2D model. Θ_c is the confinement transition temperature below which solitons aggregate into bikinks. Θ_0 is the crossover temperature below which bikinks aggregate into growing rods. At $\Theta = 0$ the latter are roughened domain lines perpendicular to the chains when the Coulomb interaction $\Gamma < \Gamma_c$. For $0 < \Theta < \Theta_0$ this confined phase consists of aggregates screened by a liquid or a Wigner crystal of bikinks, depending on the strength of the Coulomb interaction. When $\Gamma > \Gamma_c$ both the lines at $\Theta = 0$ and the aggregates with their screening charges at $0 < \Theta < \Theta_0$ cross over to a deconfined phase, the Wigner crystal of solitons.

(2-FOLD CDW ; D = 2)

"TWIN" and "TWEED" TEXTURES IN PEROVSKITE OXIDES





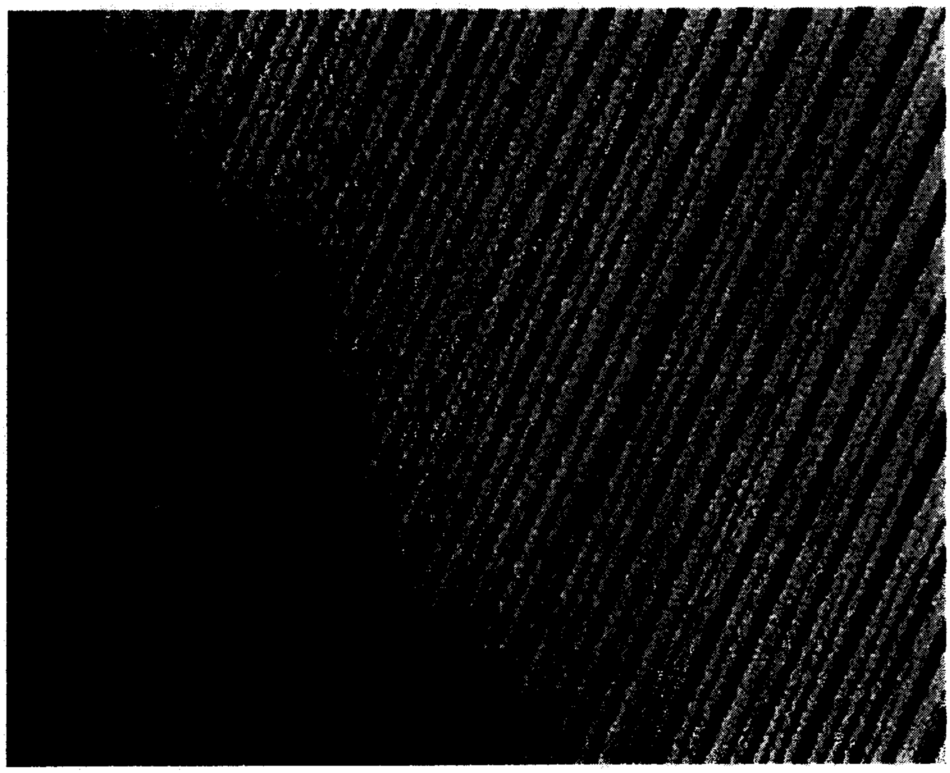
Electron micrographs of {110}-type twin modulations in $YBa_2(Cu_{1-x}Co_x)_3O_{7-\delta}$ with the incident beam parallel to [001]. Length of scale bar: 0·1 μm, compositions from (a) to (h): $x = 0{\cdot}0$, 0·01, 0·02, 0·025, 0·028, 0·03, 0·04 and 0·07.

Salje et al (1990)

HIEARCHICAL "FINE-SCALE STRUCTURE" IN ELASTIC/MARTENSITIC MATERIALS

⟷ MACROSCOPIC "SHAPE-MEMORY"

HTC, CMR.....



Austensite-Martensite Interface

(solid color on left is austensite,
laminated structure is twinned martensite)

Base of Image is 370 microns wide.

Chunhwa Chu and Dick James
University of Minnesota

Cu – 13.95 wt% Al – 3.93 wt% Ni

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MARTENSITIC PHASE TRANSFORMATIONS AND FINE-SCALE STRUCTURE

T

Austenite, $\epsilon = 0$

T_{TW}

Tweed: "strain spin glass"
T_{MS} sensitivity
to composition

"2^{nd} order
transitions"

T_{MS}

Martensite/Twinned, $\epsilon = \pm\epsilon_0$

(e.g. TEM/HREM
Anisotropic thermal expansion
Anomalous elastic constants
Diffuse scattering, ...)

CONCEPTS/MOTIVATION

- **Application of G-L theory to martensitic materials (FePd,NiTi,..): Domain walls as elastic solitons**

- **Strain tensor OP $\rightarrow$ Elastic Compatibility**

- **Textures in terms of Strain $\rightarrow$ materials functionality, constitutive laws**

- **Scientific basis for other ferroelastics**

  Magnetoelastic ($Tb_xDy_{1-x}Fe_2$,**Terfenol**)*Magnetostriction*

  Ferroelectric ($SrTiO_3, BaTiO_3, PZT$) *Electrostriction*

  HTC ($La_xCuO, YBaCuO_7$)

  CMR Manganites($La_xSr_{1-x}MnO_3$) *Magnetoresistance*

  Photoelastic ($Ga_xIn_{1-x}As$)

  ...

- **Techniques: Input and Validation**

  Local imaging (HREM)

  Structure Probes (PDF analysis)

  Neutron Scattering, RUS

ELASTIC COMPATIBILITY

Strain("geometrically linear")

Shenoy et al
PRB $\underline{60}$, R12537('99)

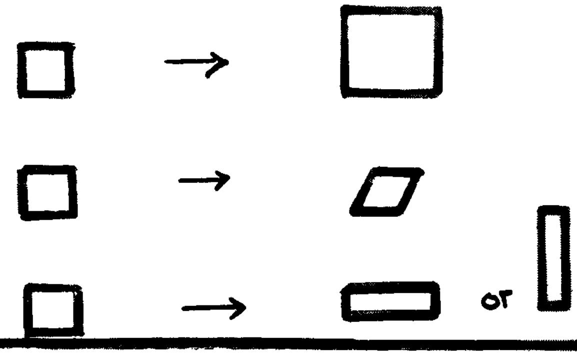
$$\varepsilon_{i,j} = \frac{1}{2}\left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i}\right), \qquad i,j = x,y,z$$

Two dimensions: **Symm:** $\Gamma = A_{1g} \oplus B_{1g} \oplus B_{2g}$

$e_1 = (1/\sqrt{2})(\varepsilon_{xx} + \varepsilon_{yy})$

$e_2 = \varepsilon_{xy}$

$\epsilon = (1/\sqrt{2})(\varepsilon_{xx} - \varepsilon_{yy})$



NOS !
NO
STRAINT

St. Venant Compatibility : $\nabla \times (\nabla \times \overleftrightarrow{\varepsilon})^T = 0$

$$\Delta^2 e_1(r) - \sqrt{8}\Delta_x\Delta_y e_2(r) = (\Delta_x^2 - \Delta_y^2)\epsilon(r),$$

Compression-Shear Free energy

$$F_{cs}(e_1, e_2) = \frac{1}{2}\sum_r [A_1 e_1^2 + A_2 e_2^2] \equiv \sum_r \epsilon(r)\underline{U(|r-r'|)}\epsilon(r')$$

$\dfrac{\cos 4(\theta-\theta')}{|r-r'|^2}$

$$\boxed{U(k) = \frac{\frac{2A_1}{A_2}\left[\frac{(k_x^2-k_y^2)}{k^2}\right]^2}{1 + \frac{8A_1}{A_2}\frac{k_x^2 k_y^2}{k^4}}.}$$

ANISOTROPIC
LONG-RANGE

$$e_1(k) = f(k)\epsilon(k), \quad e_2(k) = g(k)\epsilon(k)$$

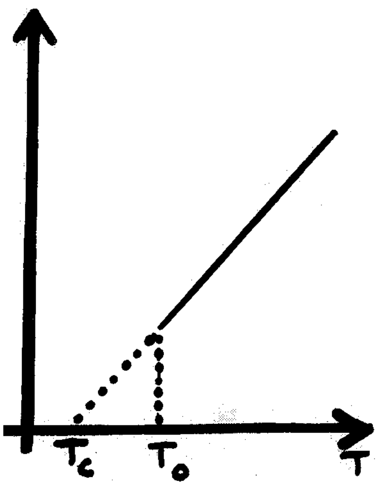
<u>LOCAL</u> LATTICE SYMMETRY HAS <u>GLOBAL</u> CONSEQUENCES ! LANDSCAPE

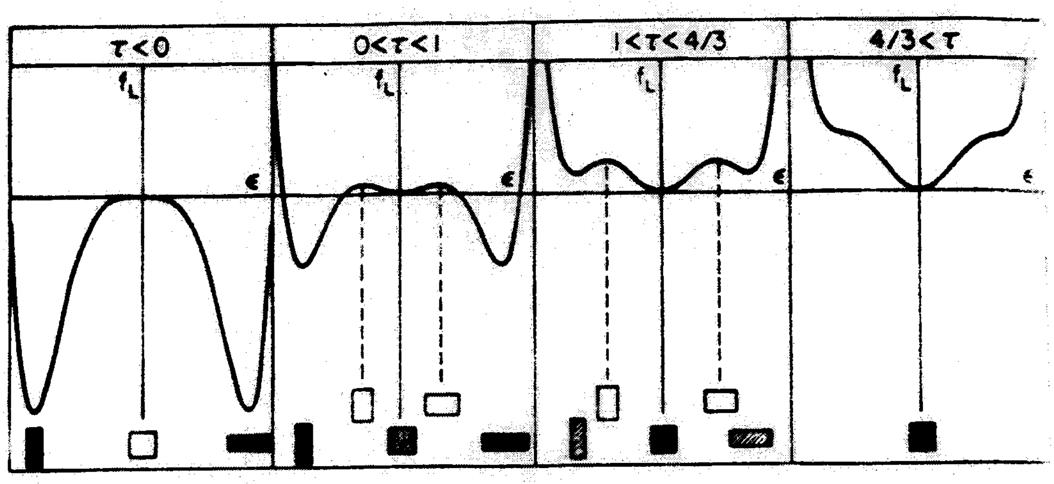
MODEL

$$\boxed{F_{bulk} = F_o(\epsilon) + F_{grad}(\nabla\epsilon) + F_{cs}(e_1, e_2) + F_{dis}(\epsilon) + F_{stress}}$$

$$F_o(\epsilon) = \Sigma_r[(\tau - 1)\epsilon^2 + \epsilon^2(\epsilon^2 - 1)^2]$$

$\tau = (T - T_c)/(T_o - T_c) = 16AC/3B^2, \quad A = C_{11} - C_{12}$





$$F_{grad}(\nabla\epsilon) = \Sigma_r[\tfrac{a}{4}(\nabla\epsilon)^2 + \tfrac{b}{8}(\nabla^2\epsilon)^2]$$

$$F_{dis} = \Sigma_r[A_\eta^{(T)}(r)\tilde{\eta}\epsilon(r)^2 - \tfrac{1}{2}A_\eta^{(p)}\tilde{\eta}(\nabla_x^2 - \nabla_y^2)\epsilon(r)]$$
$$\equiv \Sigma_r[-\alpha\nabla_x^2\epsilon\nabla_y^2\epsilon]$$

$$F_{cs}(e_1, e_2) = \tfrac{1}{2}\Sigma_r[A_1e_1^2 + A_2e_2^2] = \Sigma_{r,r'}\epsilon(r)U(|r - r'|)\epsilon(r')$$

$$F_{stress} = \sigma_\epsilon\bar{\epsilon} + \bar{\sigma}_1 e_1 + \bar{\sigma}_2 e_1$$

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(low T) (high T)

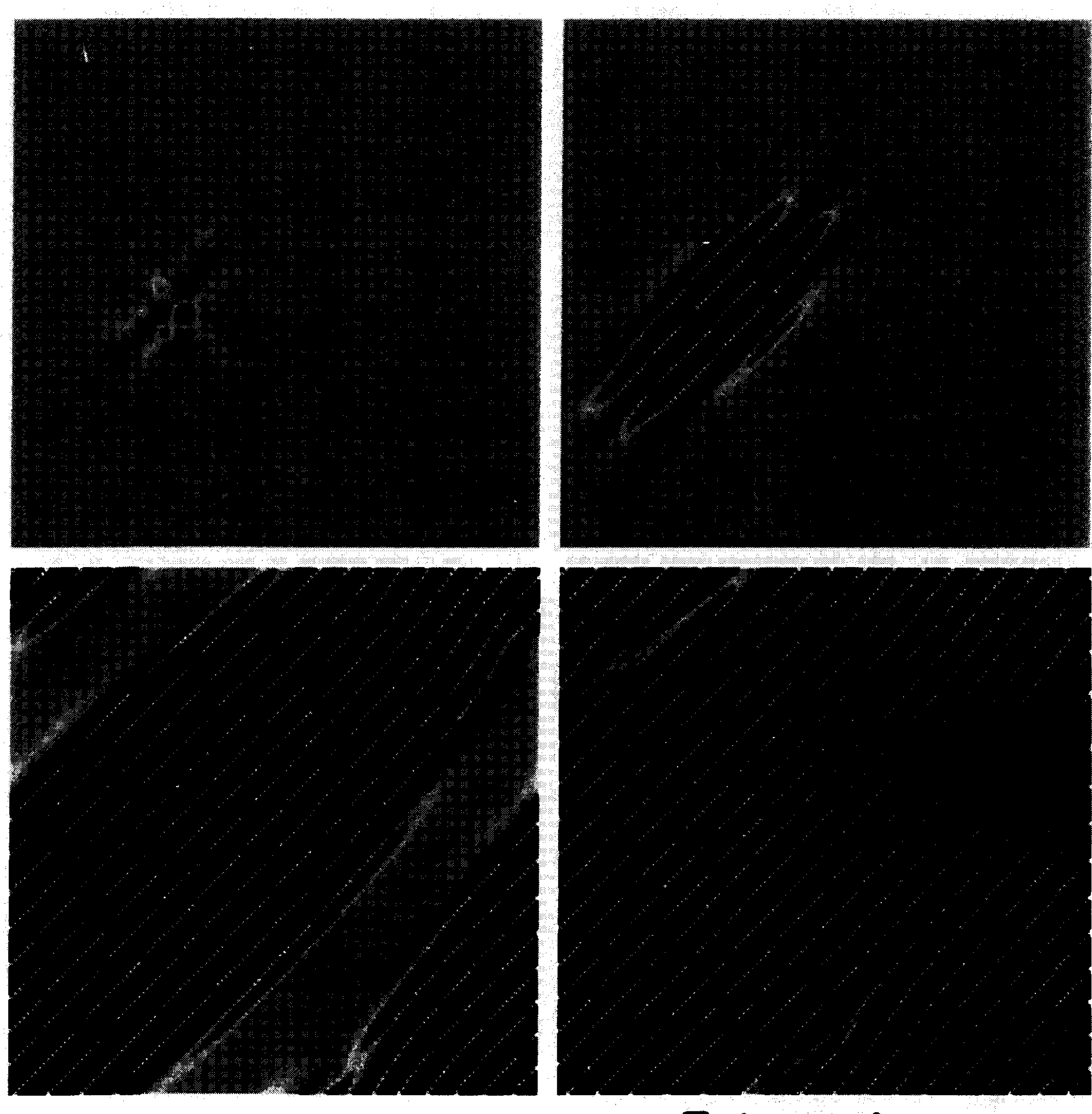
...RMAL NUCLEATION OF MARTENSITE FROM AUSTENITE

ne

t_1 t_2

6

56



t_3 t_4

TWINNING

T. Lookman et al (1998)
PRB 60, R12537 ('99)

GINZBURG-LANDAU MODEL FOR ELASTICITY & SOLID-SOLID TRANSFORMATIO

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Elasticity and Compatibility on a Triangular lattice

$$F = A e_1^2 + T\left(e_2^2 + e_3^2\right) - \frac{1}{3}\left(e_2^2 - 3 e_2 e_3^2\right) + \frac{1}{4}\left(e_2^2 + e_3^2\right)^2$$

$$\frac{+1}{2}\left[\left(\nabla e_2\right)^2 + \left(\nabla e_3\right)^2\right]$$

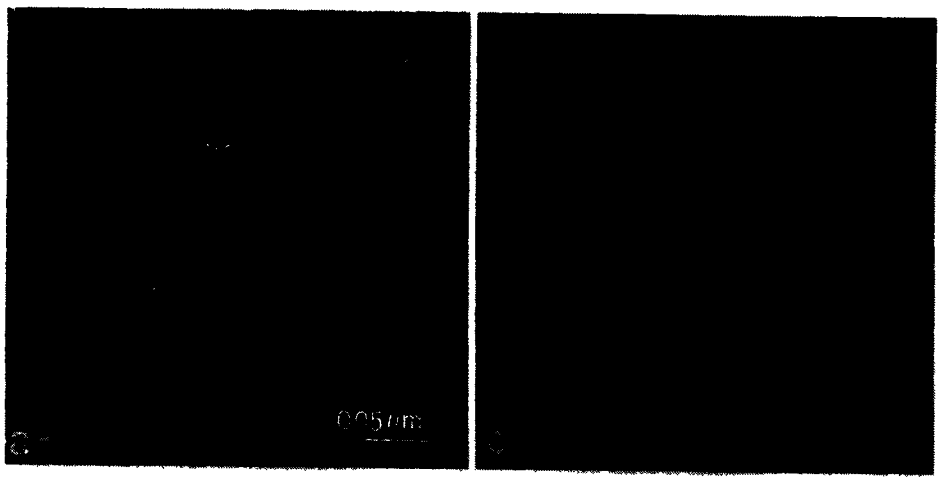
$A = 0$

No Compatibility

$A = 22$

$A = 222$

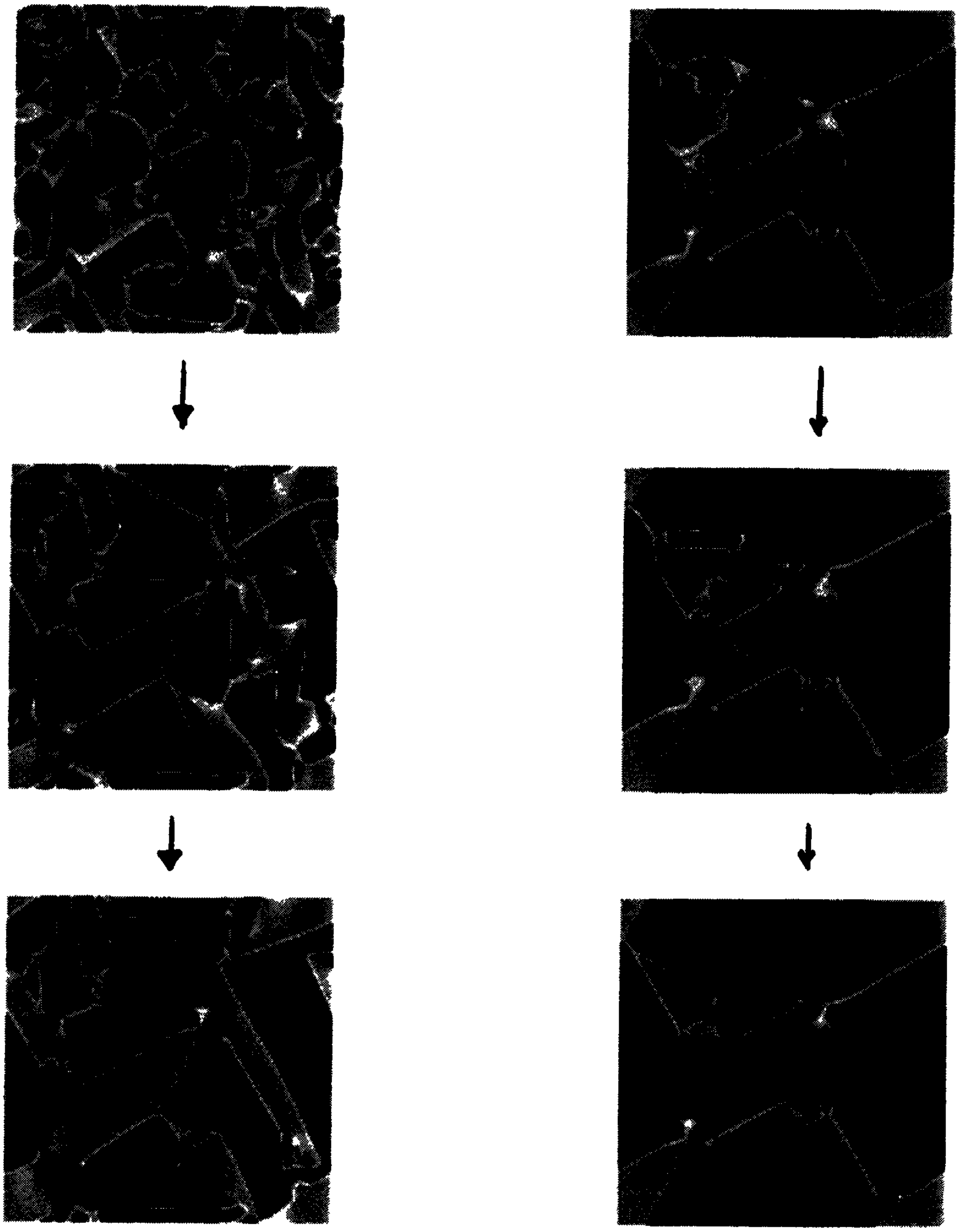
With Compatibility



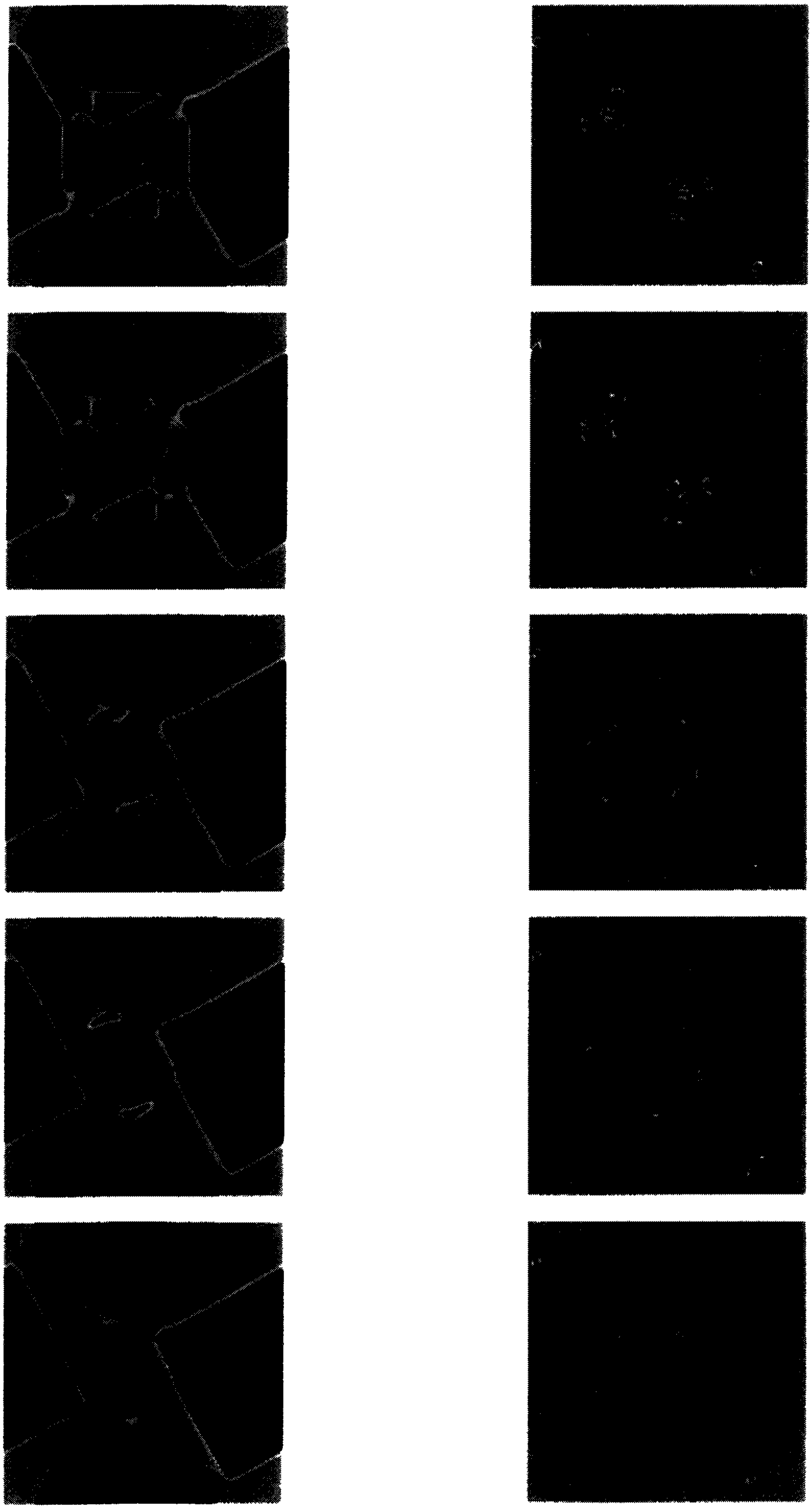
Lead Orthovanadate

Amelinickx and van Tendeloo'86

FORMATION OF NESTED STAR IN LEAD ORTHOVANADATE

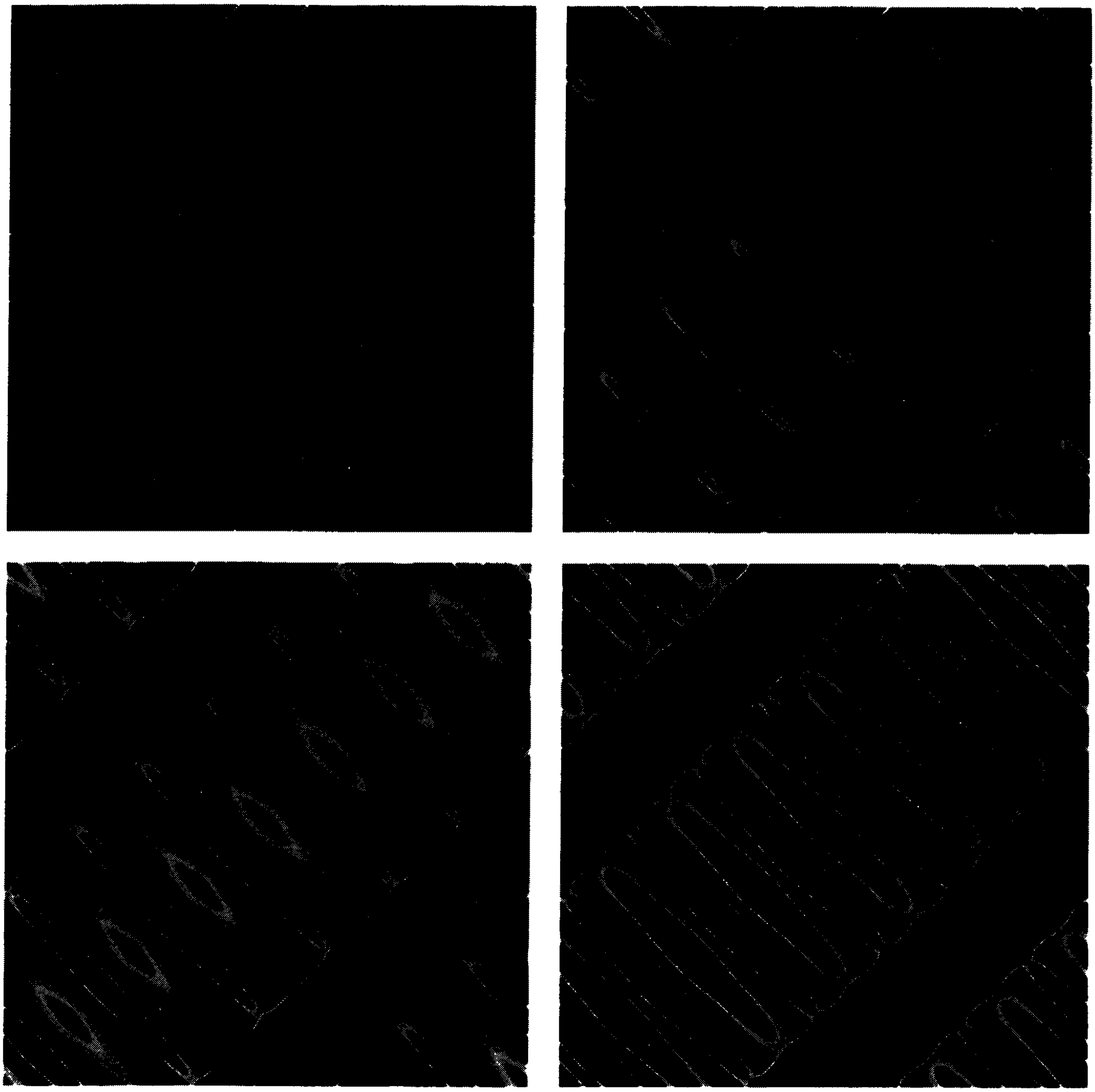


LEAD ORTHOVANADATE: MELTING & VORTICES



$$\boxed{\begin{aligned}\omega = {} & \partial_x e_3 \partial_y e_2 \\ & - \partial_y e_3 \partial_x e_2\end{aligned}}$$

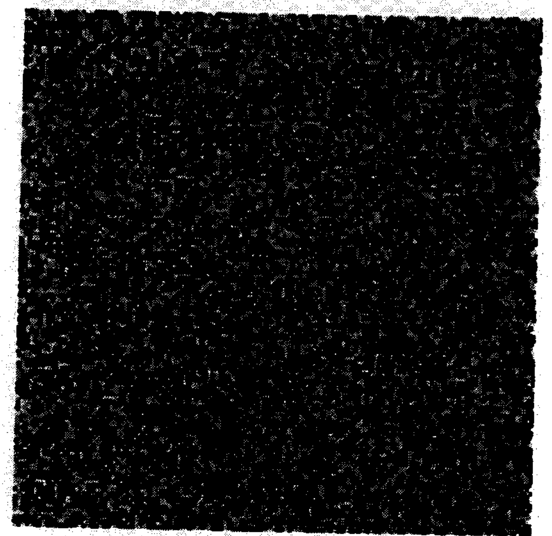
STRESS-INDUCED EVOLUTION OF 2 TWIN GENERATIONS



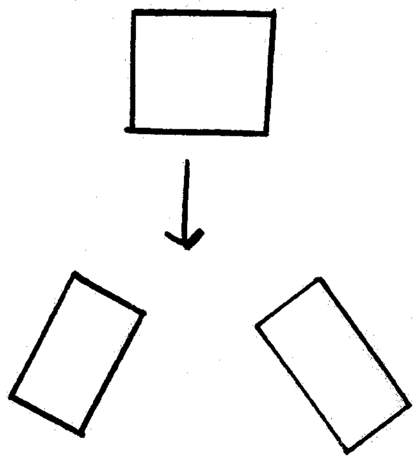
T. LOOKMAN ET AL (1998)
PRB 60, R12537 ('99)

NONLINEAR ELASTICITY

TWEED MICROSTRUCTURE



SOLID-SOLID
PHASE TRANSFORMATION

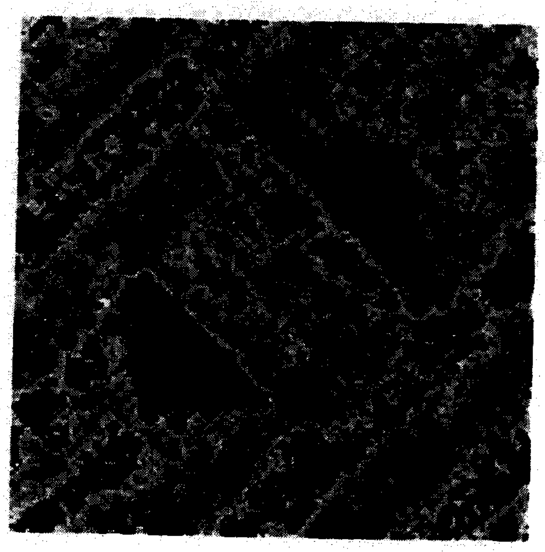


OBAL
NSITIVITY

LOCAL
RTURBATIONS

HARGE
RDERING
↕
NE-SCALE
ATERIALS
EXTURE

IPE
IEMORY
:LES



EMBOSSED PATTERN

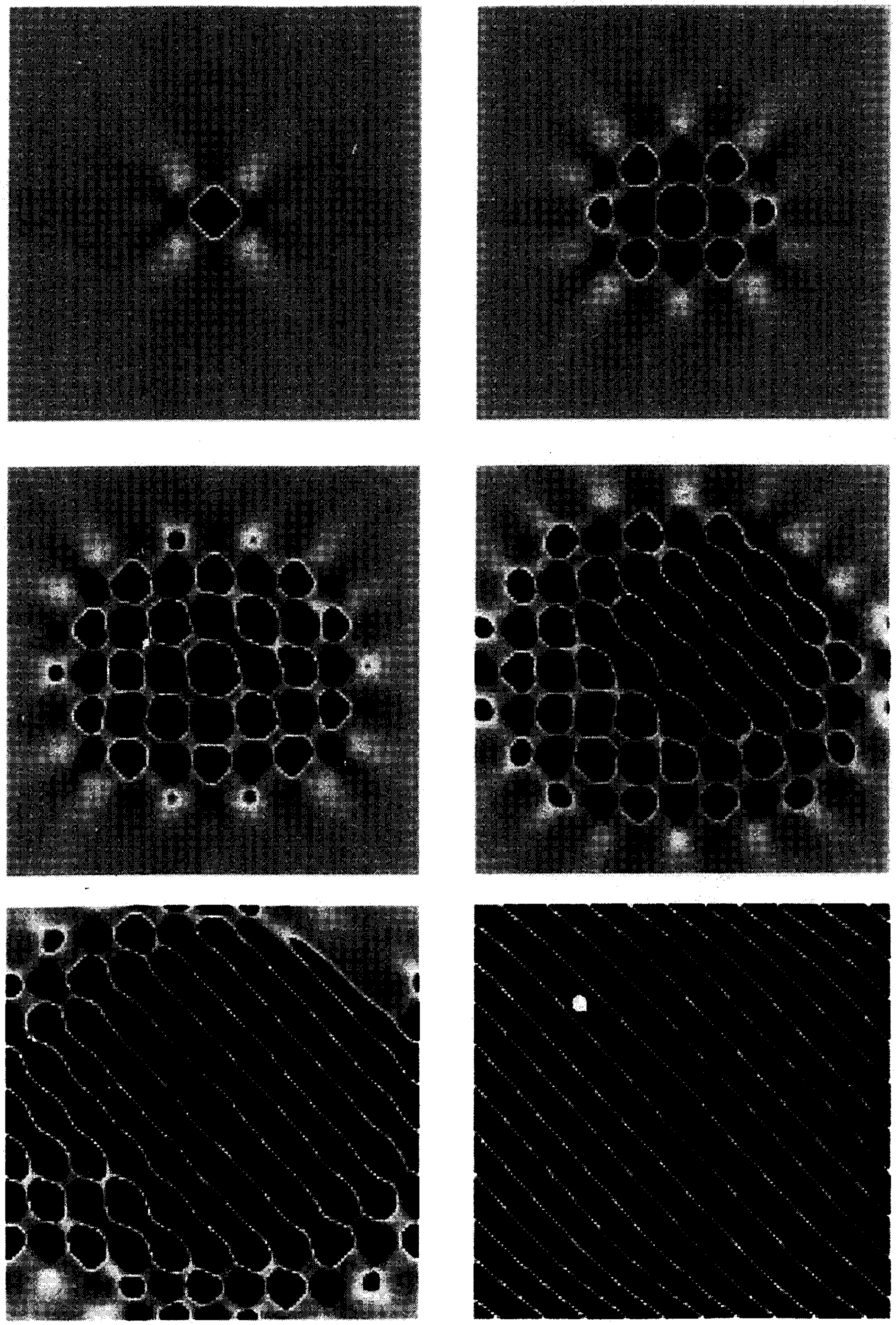
ANISOTROPIC, LONG-RANGE STRAIN COUPLING

from Constrained Ginzburg-Landau Model
(T. Lookman et al, 1998).

(LOCAL) STRESS INDUCED MARTENSITE

$\frac{\sigma_0}{1 + \left(\frac{F}{F_0}\right)}$

...ATION



GLOBAL SENSITIVITY TO LOCAL PERTURBATIONS

INTRINSIC

INHOMOGENEOUS, MULTISCALE TEXTURES IN COMPLEX MATERIALS

- **MATERIALS**

  high temperature Cuprates/Bismuthates
  CMR manganites
  martensites
  ferroelectrics
  chalcogenides
  Laves phase compounds

CHARGE, SPIN, STRAIN ORDERING
n m ϵ

- **STRUCTURAL DISTORTION**

  Strain deformation
  Jahn - Teller (Polaron)
  Buckling

- **GINZBURG-LANDAU MODEL**

  Primary Order Parameters m, n
  Secondary Order Parameter ϵ (Elastic Compatibility)
  Textures in m, n

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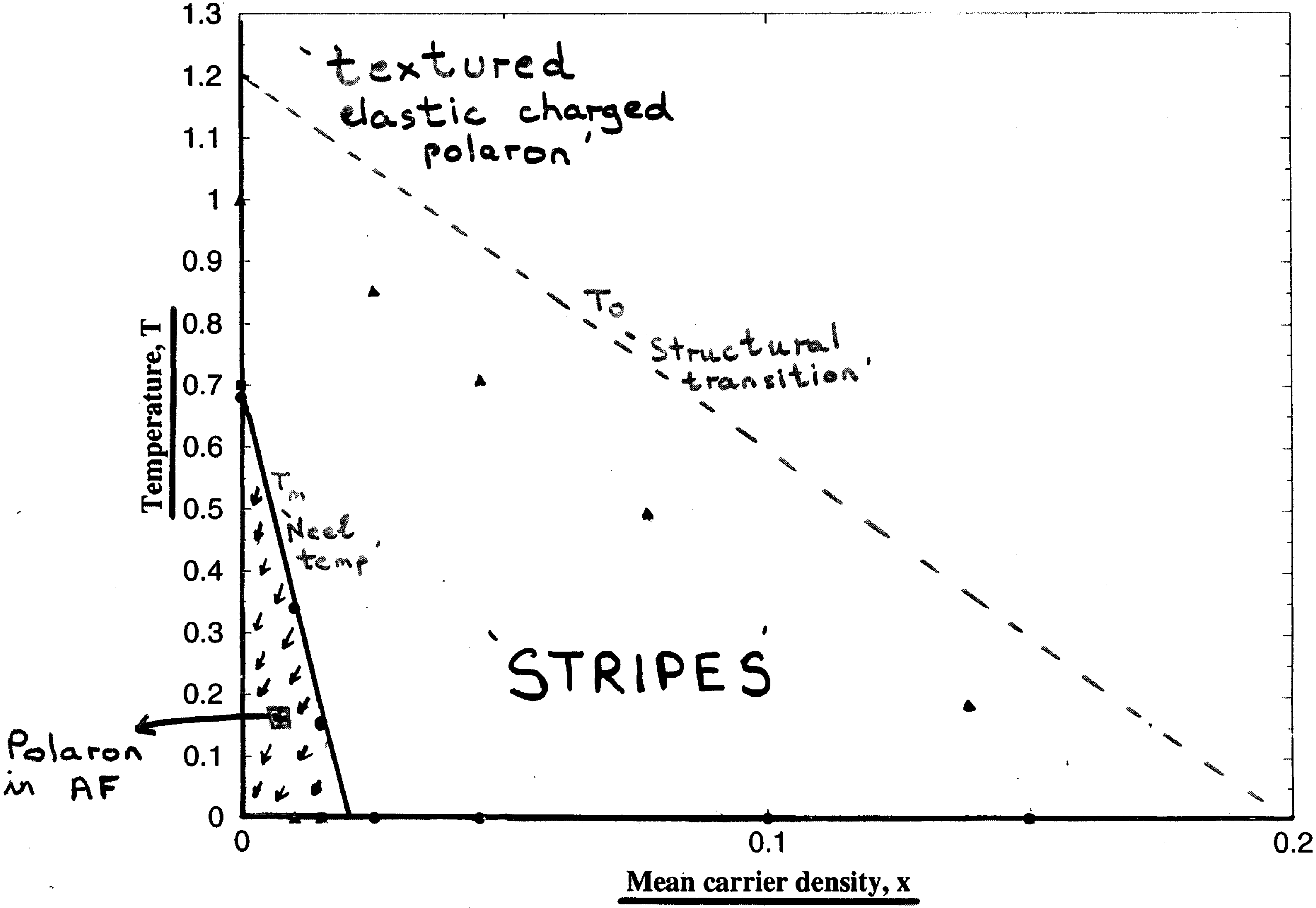
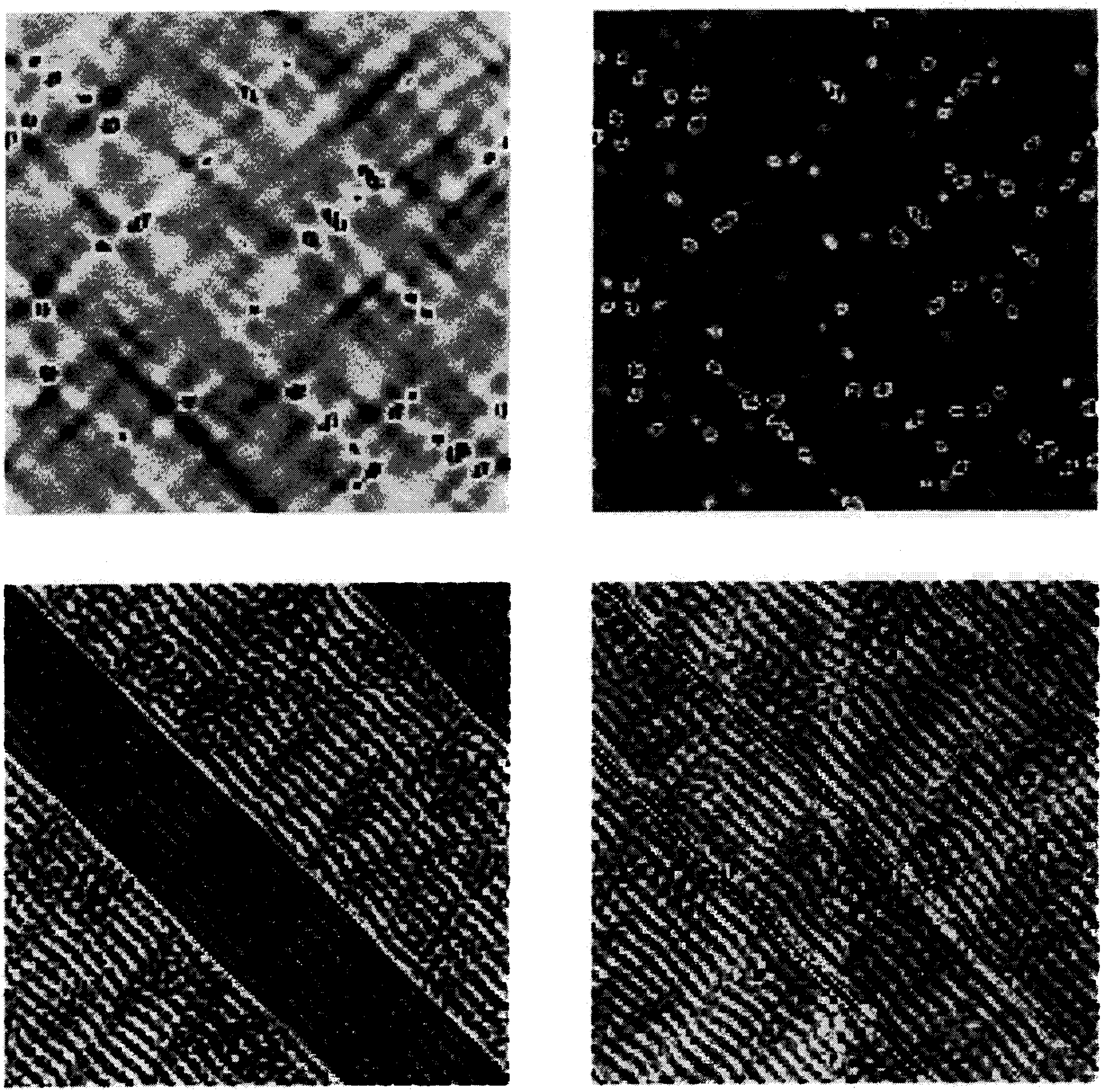
PHASE DIAGRAM FOR 'CUPRATE' MODEL



TEXTURES IN STRAIN AND CHARGE

$> T_0$

$< T_0$

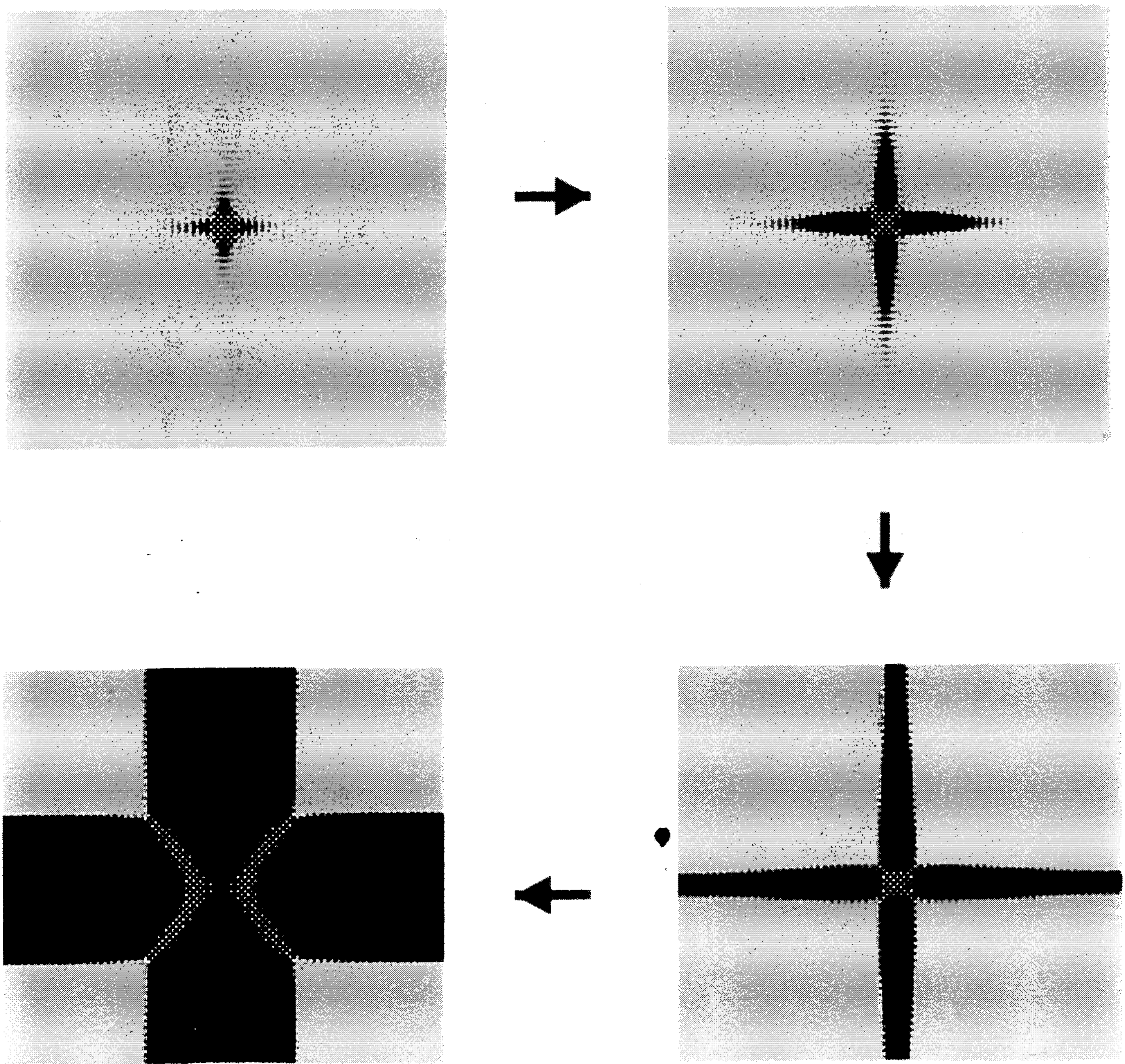


Strain, ε Charge, n

HOLE - LATTICE COUPLING

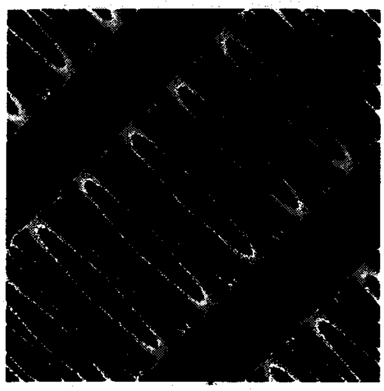
- Charge-strain coupling
- Long-Range, anisotropic lattice distortions from localized charges

e.g. $(\nabla_x^2 - \nabla_y^2)\, n \rightarrow$ "Photocopying"

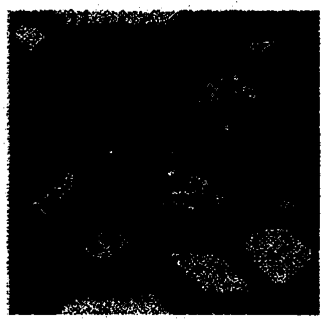


Functional Textures

I. Ferroelastic
(FePd) - ε

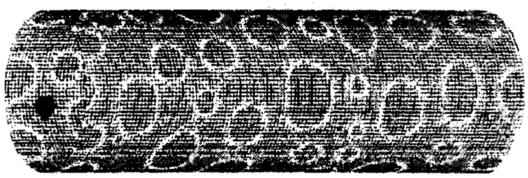


II. Ferroelectric
$SrTiO_3$ (Q) ε
$BaTiO_3$ (P) ε



III. Magnetoelastic
(Terfenol-D) ε

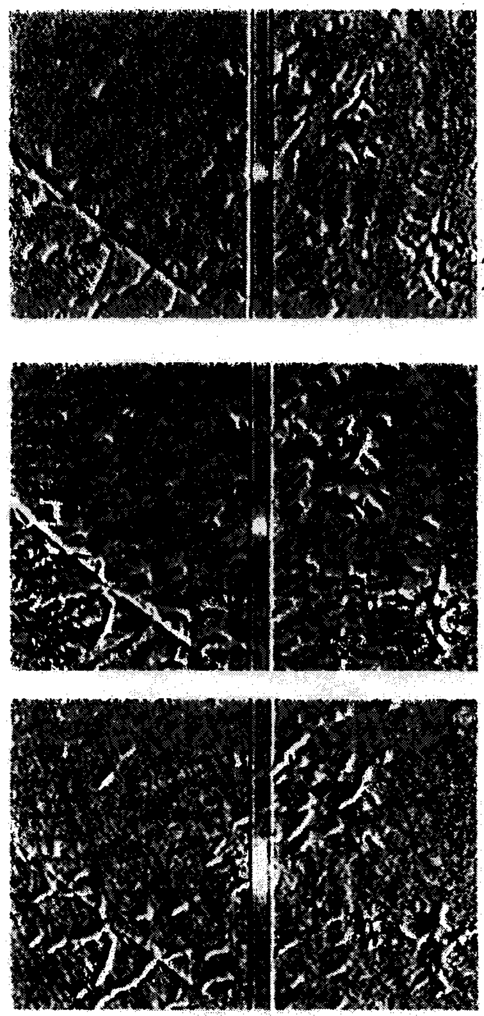
IV. Organic
Microtubules
(soft matter)
phase separation



Miyano, Tokura et al ('99)

Photoinduced Metallic Current Path

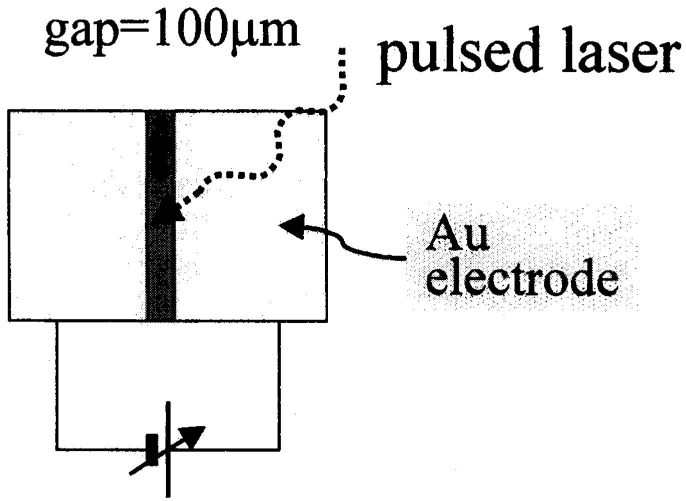
($Pr_{0.7}Ca_{0.3}MnO_3$)



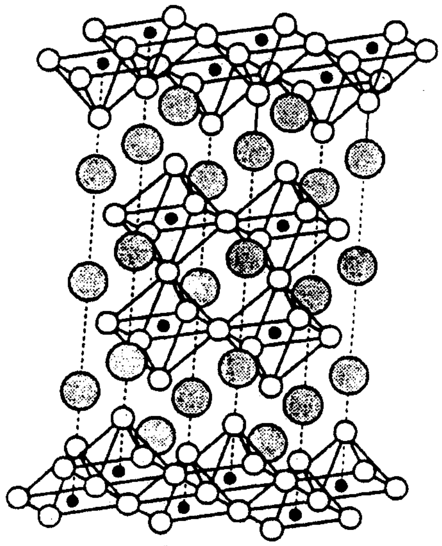
20mA

40mA

150mA

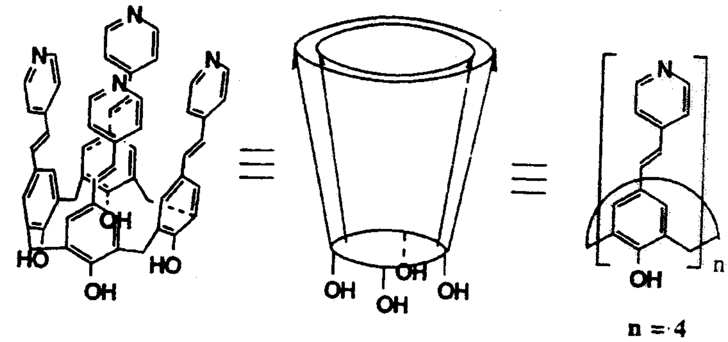


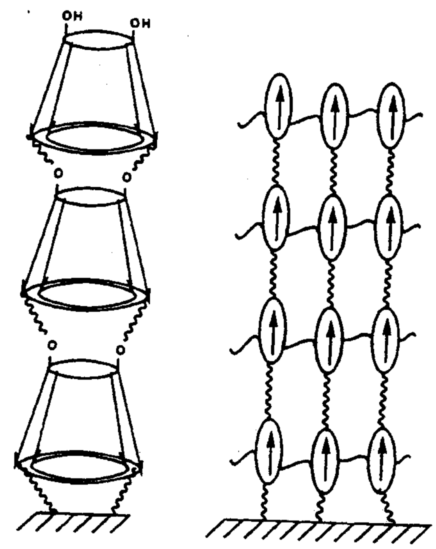
Picture taken at λ=1μm
Image(before the laser) -
Image(after the laser)



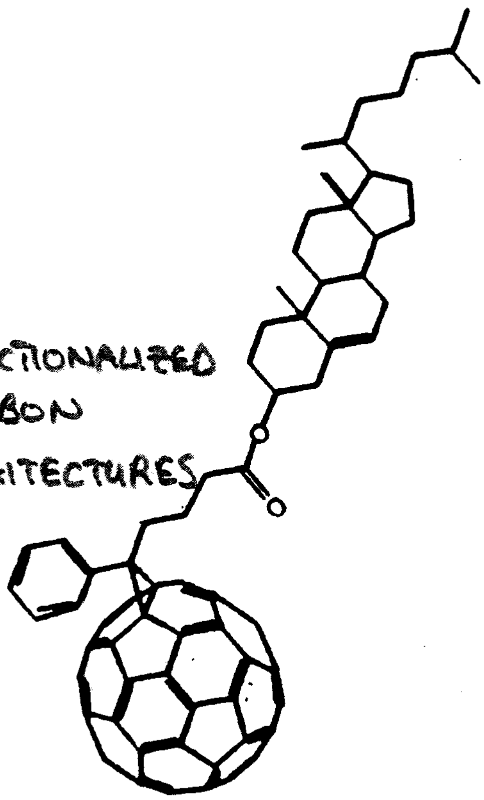
LAYERED PEROVSKITE OXIDES

"SENSITIVITY"
= DEFORMABLE BUILDING BLOCKS
(COMPLEX UNIT CELLS / MOLECULES)
AND CONSTRAINTS





UNCTIONALIZED
ARBON
RCHITECTURES



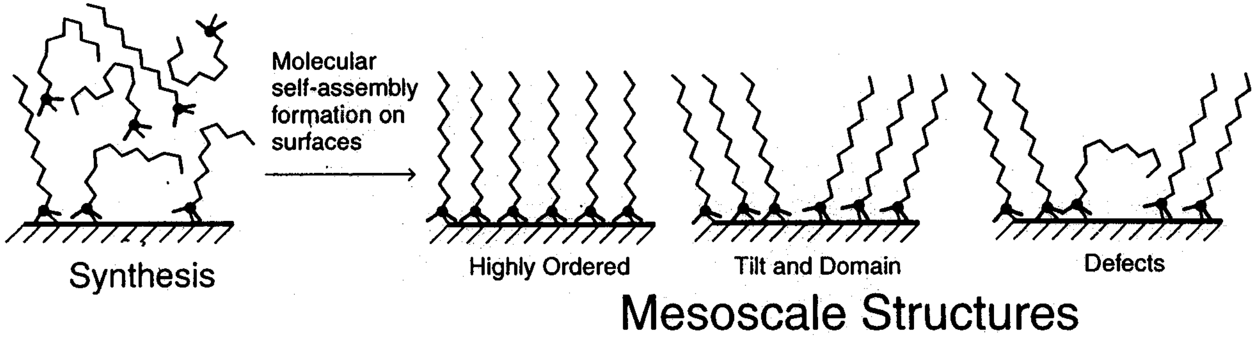
ORGANIC & INORGANIC

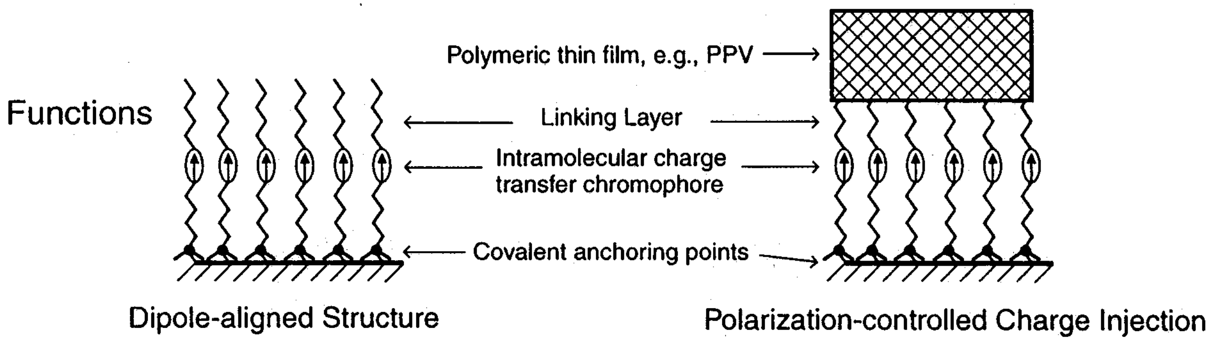
& BIOLOGICAL!

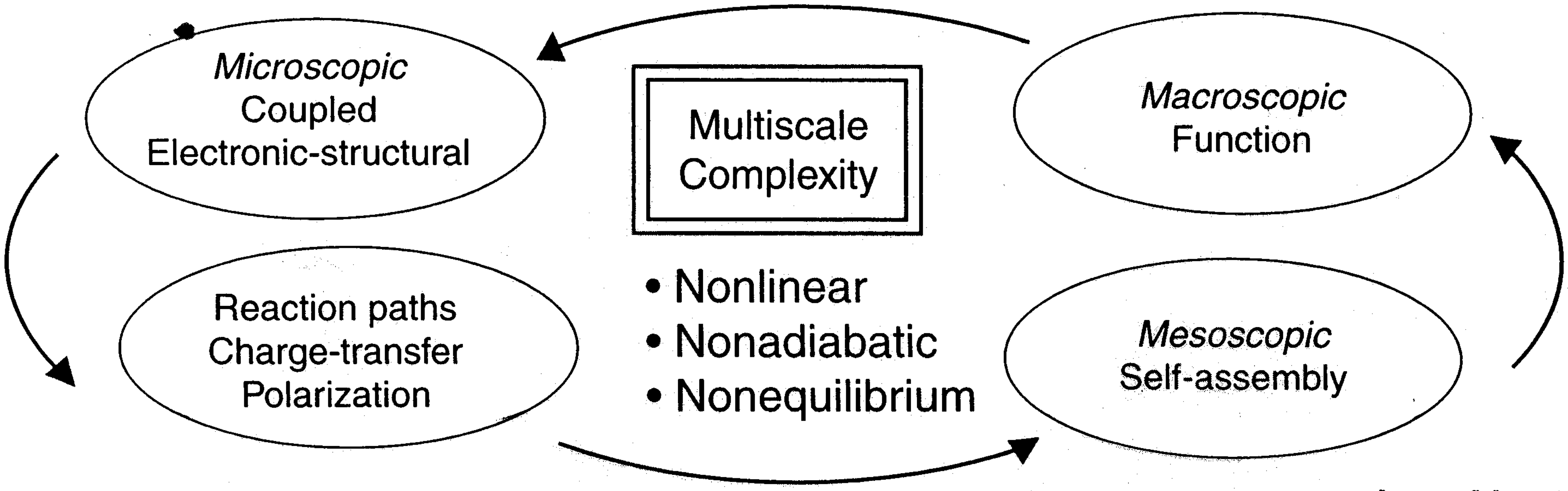
"COMPLEX ELECTRONIC MATERIALS
WITH MULTISCALE FUNCTIONALITY"
"INTRINSICALLY NANOSCALE"

ab.js.2a

Organic Self-Assembly for Optoelectronics







Application of the Au-S Potential

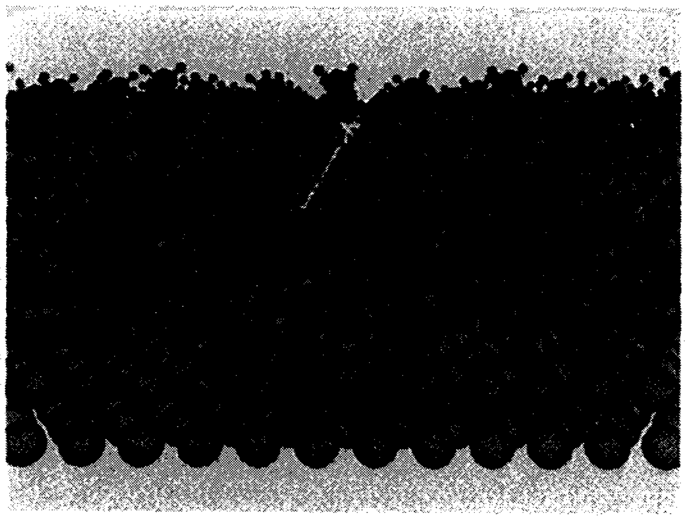
Classical Molecular Dynamics

Time step ~ 1 fs

Thiol diffusion hs-hs > 10 ps

Temporal scale limited by internal vibrations

Spatial scale limited by # of atoms

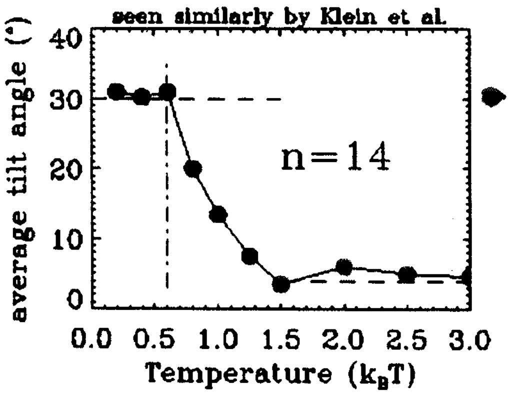


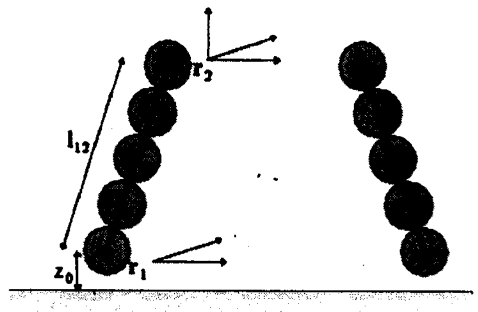
Restricted Brownian Dynamics

Stiff rods, 4 degrees of freedom

Reasonable at low temperature < 300K

More rods, longer 'time'





Beardmore et al, Chem Phys Lett 286, 40 ('98)

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UNDERSTANDING AND CONTROLLING SELF-ASSEMBLY

PROJECT LEADER: BASIL I. SWANSON (CST-1)
Staff: A. N. Parikh (CST-1), N. G. Jensen (T-11), J. D. Kress (T-12), T. A. Zawodzinski (MST-11)
Principal External Collaborators: J. D. Ferraris (Houston), G. Bar (Freiburg), A. L. Plant (NIST)

Aims

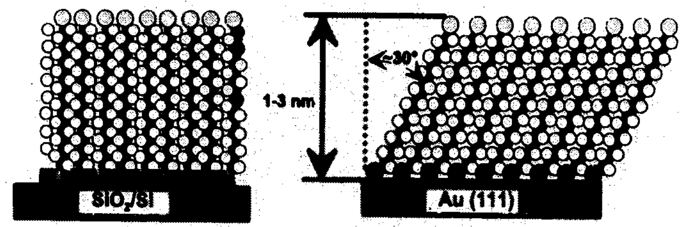
- Toward comprehensive self-assembly mechanisms
- control of structure in self-assembled films
- Extend to mesoscale materials by higher order self-assembly
- Molecular characterization of phase behavior in 3D assembled mesostructures

Selected Highlights

- Self-assembly mechanisms based on ***competition of interactions***, namely vdW, substrate-headgroup, and free energy
- Control over structure and morphology using new ***directed self-assembly approaches***
- New classes of organic-inorganic hybrid materials by ***hierarchical self-assembly***
- Unique ***phase behavior*** in organic-inorganic hybrid materials dues to dimensional and mobility restrictions

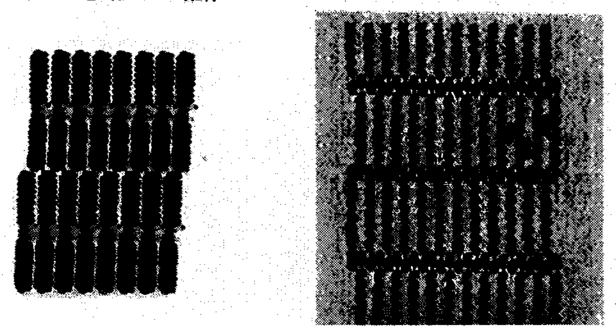
2D Monolayers

$CH_3(CH_2)_nSiO_x/SiO_2/Si$ $CH_3(CH_2)_nSH/Au$



3D organic/inorganic hybrids

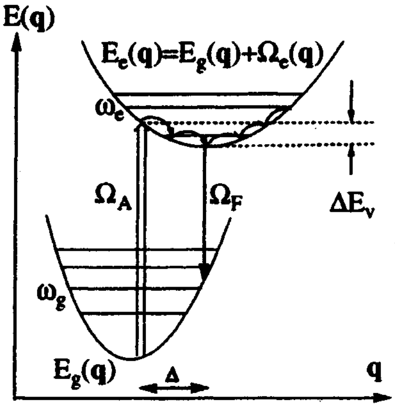
$[CH_3(CH_2)_nSiO_x]_n$ $[CH_3(CH_2)_nSAg]_m$



Excited states dynamics and photochemical reactions in large molecular systems

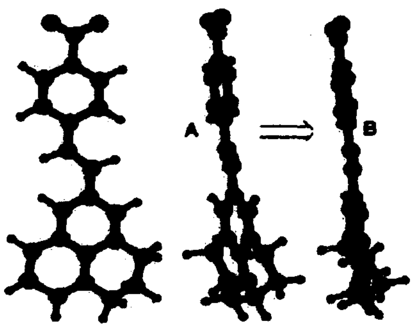
(Sergei Tretiak, Richard L. Martin, Avadh Saxena, and Alan R. Bishop)

Collective Electronic Oscillator Algorithm
(Semiempirical Hamiltonian/TDHF)
(See: Refs. Tretiak, *et al.*, *J. Phys. Chem. B*, 104, 7029 (2000), S. Tretiak, *et al.*, *Science*, **277**, 781 (1997).

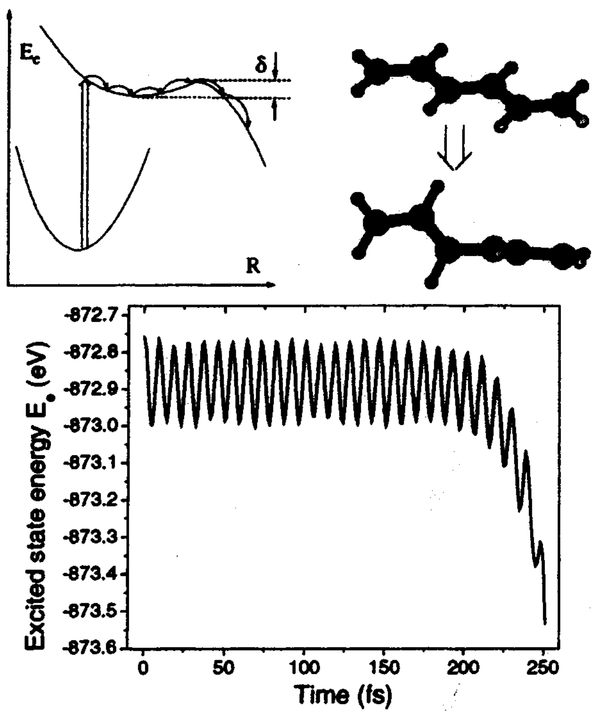


Schematic representation of ESMD propagation. Quantities of interest are excited state energy $E_e(\mathbf{q})$ as a function of nuclear coordinates $\mathbf{q}$, displacements Δ, curvatures ω_e/ω_g, vibrational reorganization energy ΔE_v, vertical absorption Ω_A and fluorescence Ω_F frequencies.

Example Applications:



ESMD geometry relaxation along the excited state surface in a donor-acceptor compound from initial structure (A) to excited state optimal geometry (B)



ESMD simulations of hexatriene photoisomerization.

Important for polar Donor/acceptor compounds, Photoisomerization, electron-hole dynamics/Exciton break-up in conjugated oligomers, *etc, etc.*

Topological Defects & Mesoscopic Phenomena

Examples from 2-D & 3-D Josephson Junction Arrays and Complex Ginzburg-Landau Equations

Multiscale Modeling Strategies

– Micro - Meso - Macro (space, time)

– e.g., topological “defects” as mesoscopic bridges

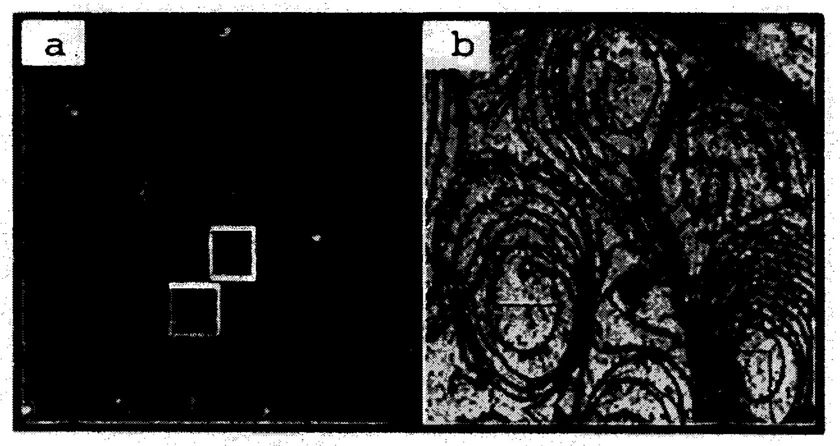
- Elementary building blocks (vortices, etc.)

- Multiple interacting defects
  - “self-organization,” “emergent patterns,” “nonequilibrium/mesoscopic statistical mechanics,” “space-time complexity,” ...

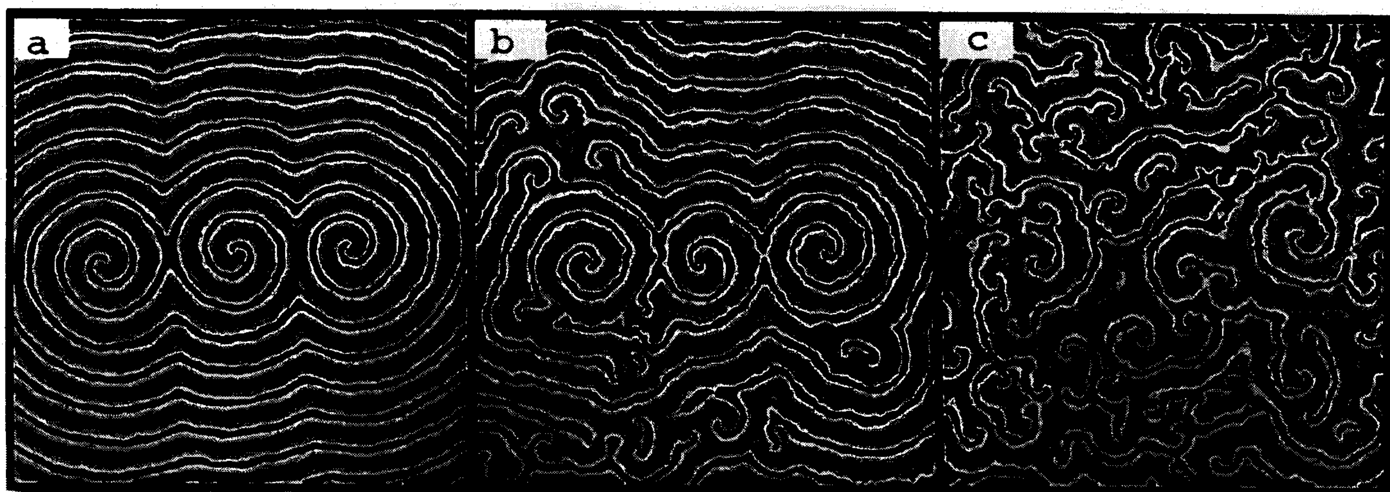
- Competing interactions (long, short, directional, entropic, ...)
  - intrinsic complex spatio-temporal patterns, frustration, landscapes, metastability, glassiness, ...

- Stochastic (colored) noise baths

Spiral Surface Growth



STM Measurements (HTc thin film growth)



(Complex) Ginzburg-Landau Modeling

Frozen Defect states in 2-D Complex Ginzburg-Landau Equation

$$\partial_t A = A - (1 + i\alpha)|A|^2 A + (1 + i\beta)\nabla^2 A.$$

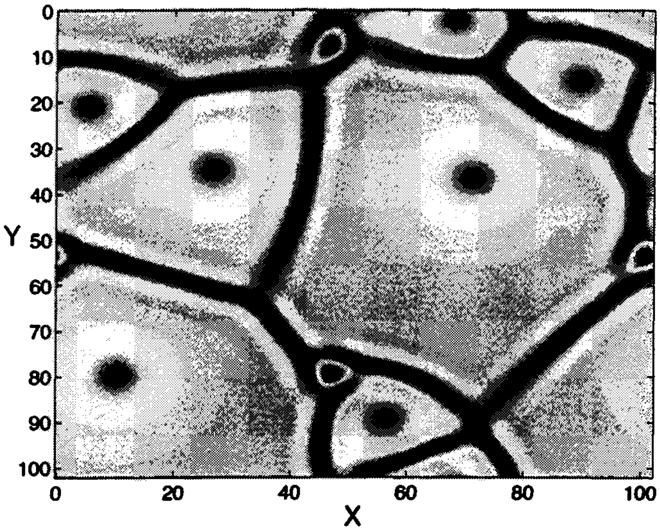


FIG. 1. AMPLITUDE $|A|$ of frozen defect state for $\alpha = 0.8$ and $\beta = -0.7$

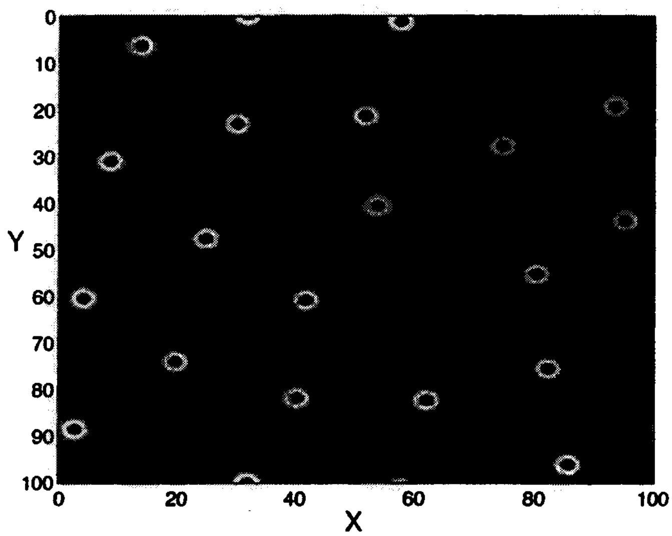


FIG. 3. AMPLITUDE $|A|$ of frozen defect state for $\alpha = 0.8$ and $\beta = -0.1$

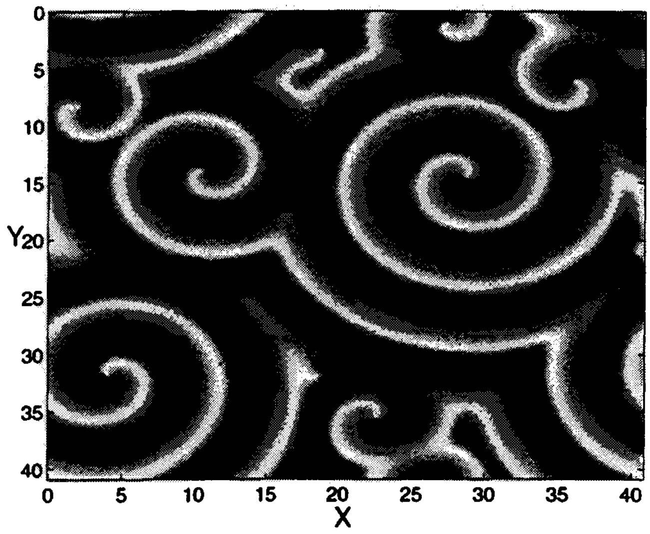


FIG. 2. PHASE. ϕ $[A(x,y) = |A(x,y)|\exp(i\phi(x,y))]$ of frozen defect state for $\alpha = 0.8$ and $\beta = -0.7$

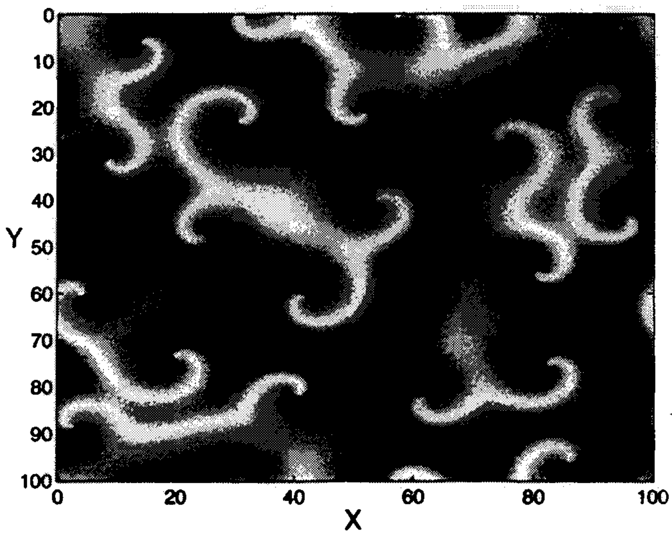


FIG. 4. PHASE of frozen defect state for $\alpha = 0.8$ and $\beta = -0.1$

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Aronson, B, Kramer PRL $\underline{79}$, 4174 ('97)
PRE $\underline{57}$, 5276 ('98)

- DYNAMICS OF VORTEX LINES IN $\underline{3\text{-}D}$ CGL

$$\partial_t A = A - (1+ic)|A|^2 A + (1+ib)\Delta A$$

- TOPOLOGICAL VORTEX FILAMENTS SPONTANEOUSLY $\underline{\text{EXPAND}}$ & $\underline{\text{BEND}}$ (CONTRAST NLS)

$\rightarrow$ SCROLLS, LOOPS, RINGS, KNOTS, ...

- IMPORTANT FOR REACTION-DIFFUSION IN BIOLOGY, CHEMISTRY, CONDENSED MATTER (e.g. Winfree, Chaos $\underline{6}$, 617 ('97))

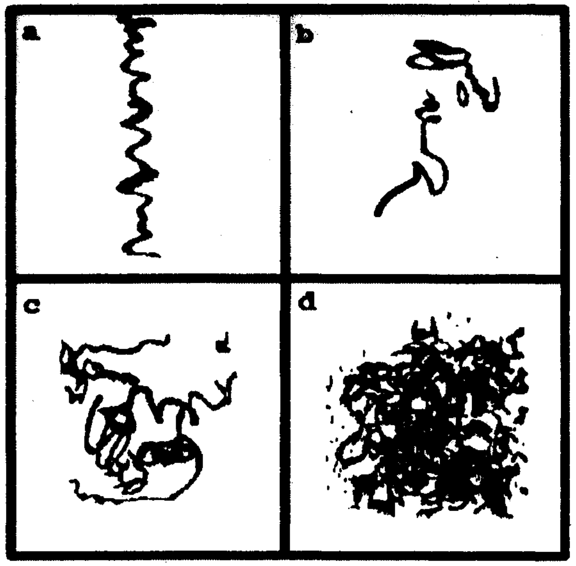


FIG. 3. Instability of a straight vortex filament. 3D isosurfaces of $|A(x,y,z)| = 0.1$ for $\epsilon = 0.02$, $c = -0.03$, shown at four times: 50 (a), 150 (b), 250 (c), 500(d). Similar dynamics is observed also for larger value of ϵ.

VORTEX FILAMENT

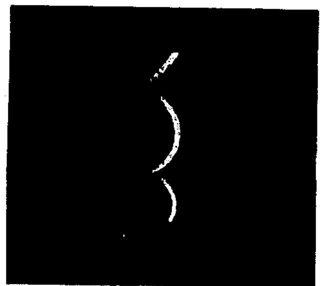


FIG. 10. (a) Stable travelling helix solution, obtained numerically for $\epsilon = 0.3$ and $c = 0.5$.

HELIX

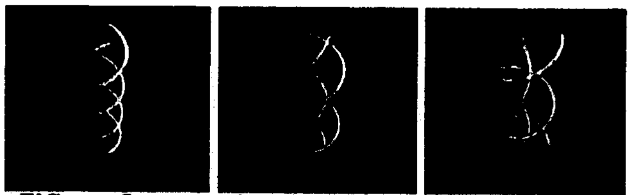


FIG. 11. Sequence of snapshots demonstrating the breakdown of a double helix for $c = 0.5$ and $\epsilon = 0.25$. (a) $t = 60$, (b) $t = 120$ and (c) $t = 240$.

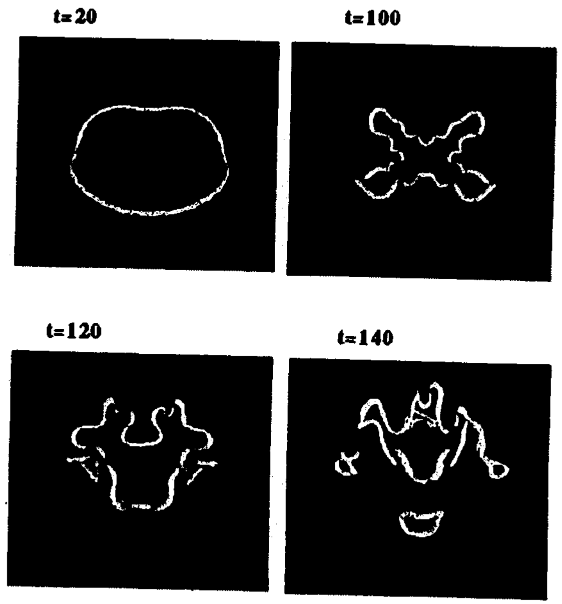


FIG. 6. Sequence of snapshots demonstrating the evol tion of a vortex ring for $\epsilon = 0.2$ and $c = 0.2$.

VORTEX RING

The Promise and Challenge of Multiscale Materials Modeling

The Promise Prediction, Quantifying Uncertainty

- "Multiscale" an old Holy Grail: syntheses - structure - function
- New enabling opportunities:

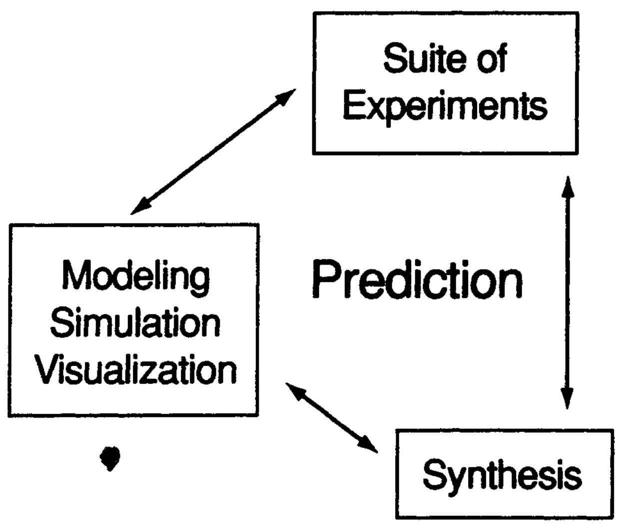
  Qualitative changes in

  - largescale simulation & visualization
  - observational/validation techniques at multiple (space, time) scales
  - synthesis & fabrication: function at multiple scales

The Challenge

- Vertical integration
- Beyond "observation & modeling at multiple scales"
- Integrated, closed-loops of

  Synthesis
  Characterization
  Modeling/Simulation



- Bridging between scales; Stochastic processes
- New modeling frameworks for experiment/simulation

IMPORTANT COMMON ISSUES

- **Prevalence of (hierarchical) CROSSOVERS between global symmetries — intrinsic multiscales ≠ simple critical point**

- **Need to move beyond homogeneous measuring & modeling techniques, single scaling lengths, simple quasiparticles, perturbative concepts ("Lifetimes", "Debye-Waller")**

Stojkovic et al
PRL ('99)
82, 4679
c.f.
Seul & Andelman
Science 267, 476 ('95)
Jensen et al
PRL 78, 2477 ('97)

- **COMPETITION OF SHORT- and LONG-RANGE INTERACTIONS (& ENTROPY)**
  — A TYPICAL source of mesoscopic self-assembly in hard, soft, biological matter
  (liquid crystals, colloids/gels/proteins, macromolecular SA, polyectrolyte SA, flux structure in superconductors, - - - stripes & twins in TMOs - - -)

- **Essential role of DISCRETENESS SCALE in determining mesoscale patterns**

- **Multiscale Materials Science of "Complex Electronic Materials" ≡ Solid State + Chemistry**

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Designing Complex Adaptive Matter
- lessons from nonlinear science -

SomeThemes

- **Structure *vs* Excitations**
  - → What (competing) forces determine structure?
  - → What effective interactions determine excitation (and stability)?
  - → Do lessons from homogeneous patterns apply? (Bloch states, phonons, magnons, ...)

- **Spatio-Temporal Mesoscopic Complexity**
  - → Multiple basins-of-attraction: mesoscopic, (non)equilibrium
  - → Dynamic landscapes
  - → Self-assembly for transient functions,
    e.g., materials morphology plus chemistry;
    mimicking, e.g., biological "rafts" for recognition/transduction

- **Coupled Fields**
  - → Nonlinear, nonadiabatic equations
  - → Multiscale spatio-temporal complexity
  - → Multi - Functionality,
    e.g., spin-charge-lattice (orbital) coupling;
    e.g., electro-elastic materials (organic, inorganic, biological)

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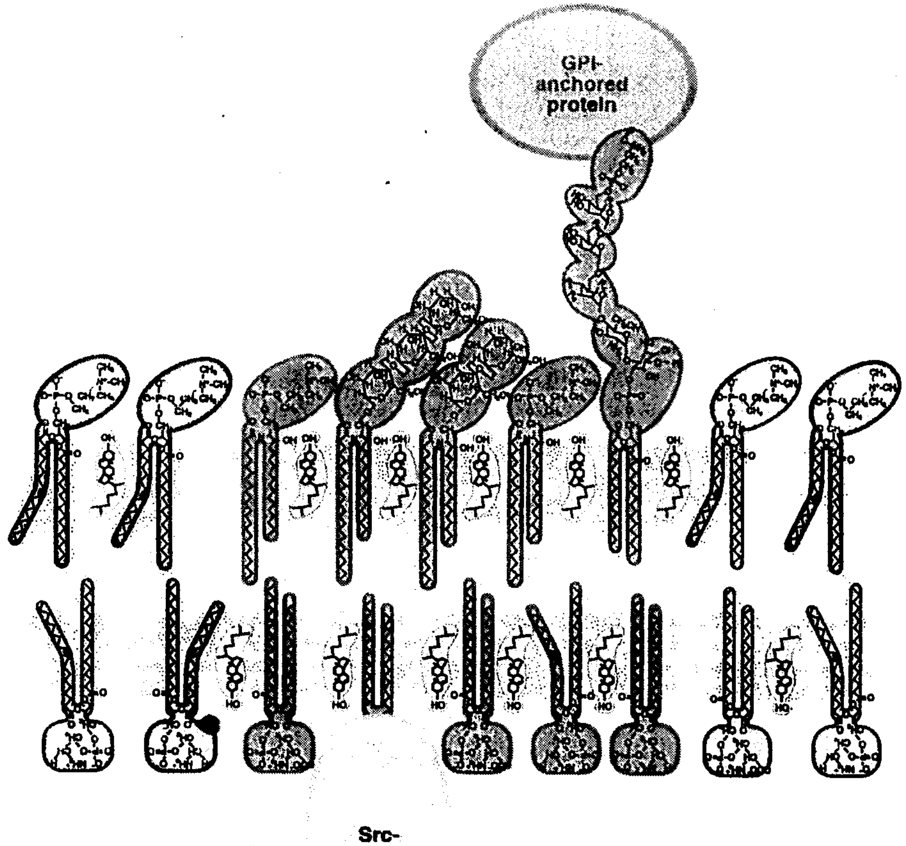

Fig. 1. Model of a raft with two intercalated proteins. A GPI-anchored protein is attached to the exoplasmic leaflet, and a doubly acylated Src-kinase to the cytoplasmic leaflet. Lipids within the liquid-ordered phase are shown as red and in the liquid-disordered phase as blue. Cholesterol, indicated by orange, partitions preferentially into the liquid-ordered phase. The outer leaflet of the raft is enriched in glycosphingolipids and sphingomyelin, and the corresponding inner leaflet is illustrated as containing glycerolipids with predominantly saturated fatty acyls. The degree of acyl chain saturation in the putative inner raft leaflet remains open. The coupling between the exo- and cytoplasmic leaflets is hypothetical; the connecting mechanisms remain to be established, but antibody patching of a GPI-anchored protein leads to copatching of the associated Src-family kinase (85).

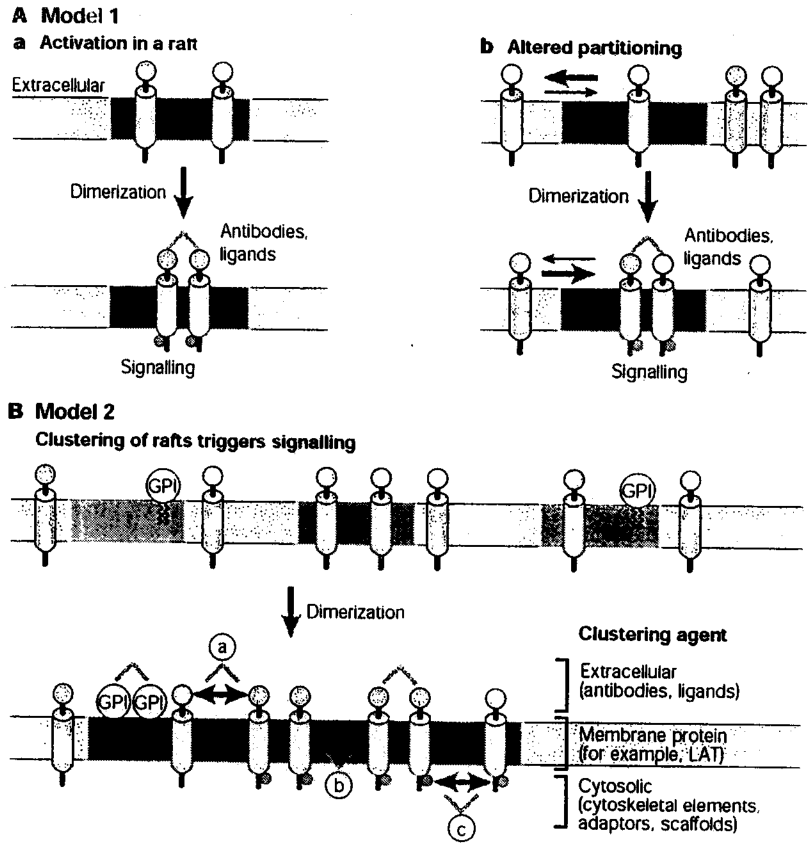

Figure 2 | **Models of how signalling could be initiated through raft(s). A** | In these models, signalling occurs in either single rafts (Model 1) or clustered rafts (Model 2). Following dimerization (or oligomerization) the protein becomes phosphorylated (blue circle) in rafts. In single rafts this can occur by activation **a** | within the raft, or **b** | by altering the partitioning dynamics of the protein. **B** | In the second model we assume that there are several rafts in the membrane, which differ in protein composition (shown in orange, purple or blue). Clustering would coalesce rafts (red), so that they would now contain a new mixture of molecules, such as crosslinkers and enzymes. Clustering could occur either extracellularly, within the membrane, or in the cytosol (a–c, respectively). Raft clustering could also occur through GPI-anchored proteins (yellow), either as a primary or co-stimulatory response. Notably, models 1 and 2 are not mutually exclusive. For instance, extracellular signals could increase a protein's raft affinity (for example, similar to the effect of single versus dual acylation) therefore drawing more of the protein into the raft where it can be activated and recruit other proteins, such as LAT, which would crosslink several rafts.