

Topological Crystals: as a New Paradigm

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<http://exp-ap.eng.hokudai.ac.jp/index.html>

MRS, Boston, 26 Nov 2012

Outline

(1) Introduction

(2) Crystal Growth *Covalent wires*

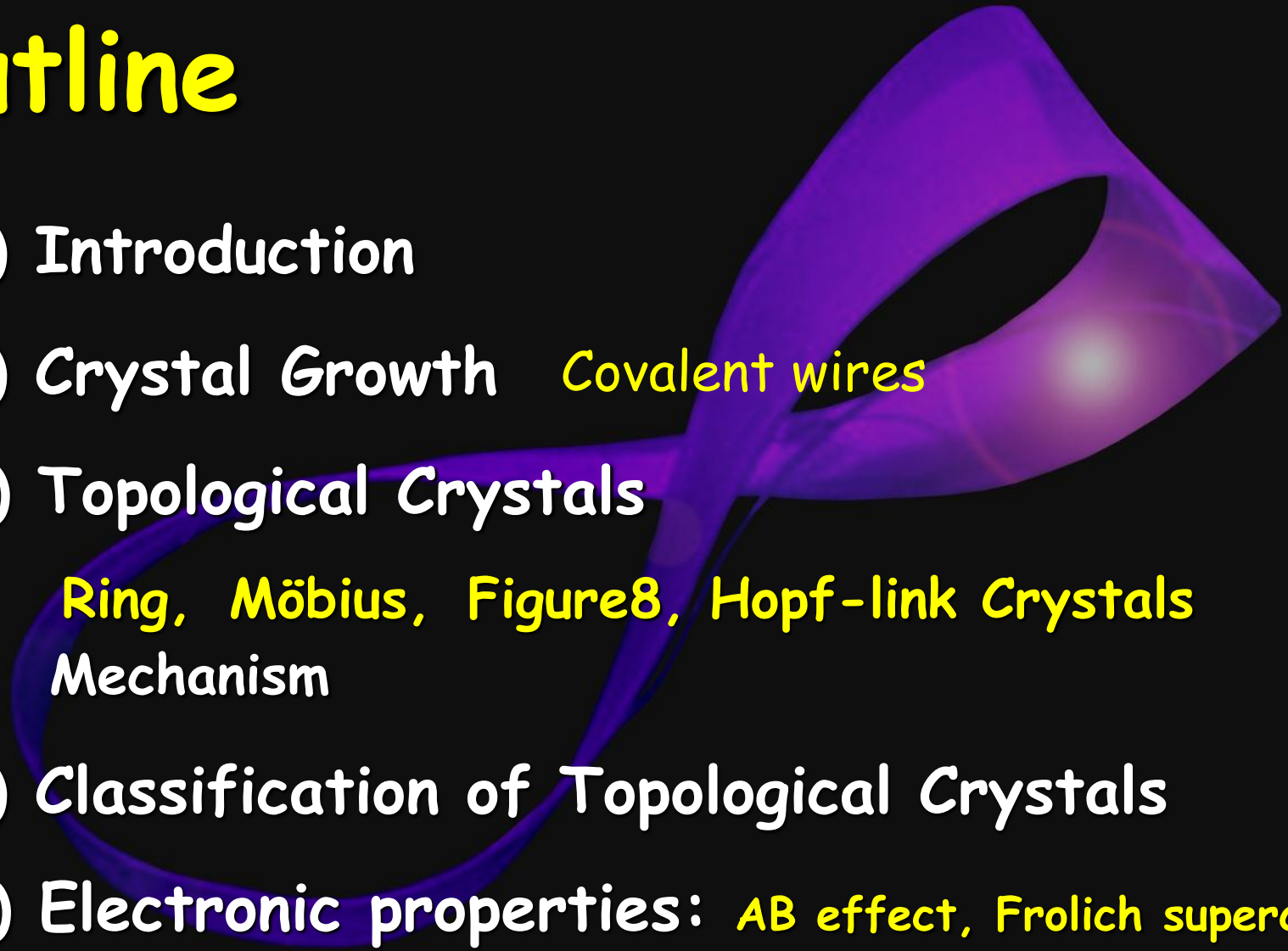
(3) Topological Crystals

Ring, Möbius, Figure8, Hopf-link Crystals
Mechanism

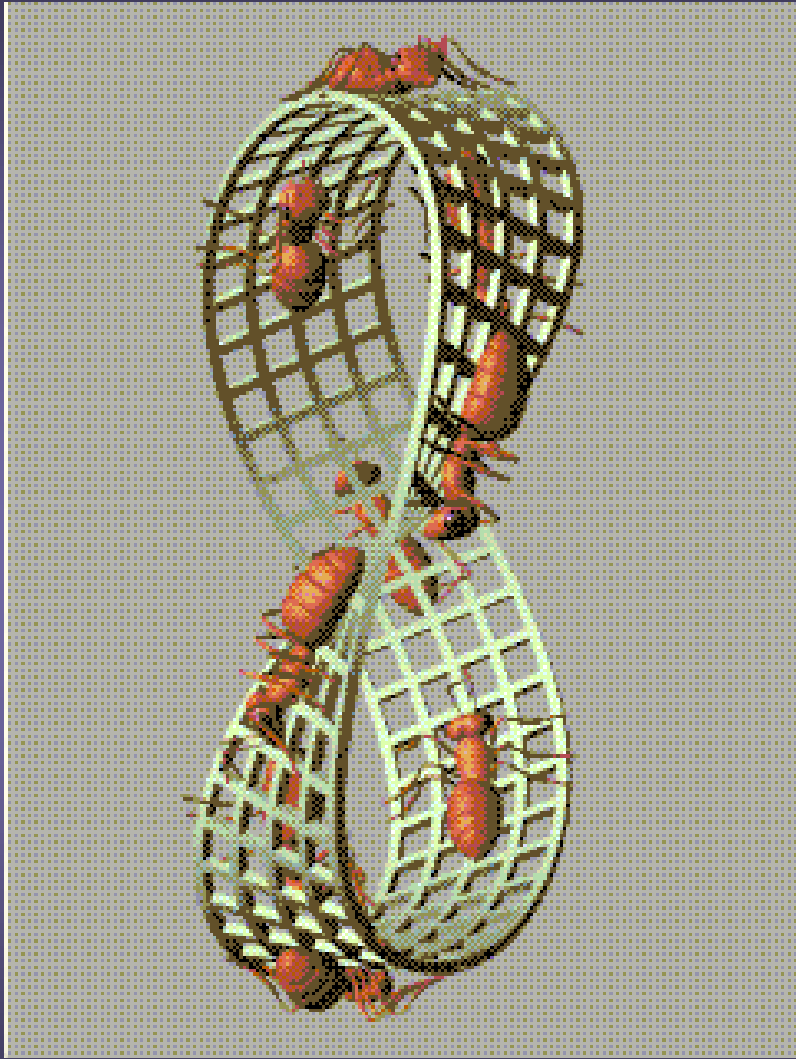
(4) Classification of Topological Crystals

(5) Electronic properties: *AB effect, Frolich supercon.*

(6) Summary



Introduction: Escher's ants



Ants return to the original point
after two laps on Möbius Strips

No distinction between the
Obverse and the **Reverse**

↓
An exotic one-sided world !!

↑
from Artists to Scientists

Ants → Electrons, Spins
Photons, CDWs, Super

Strips → Lattice, Crystal

Möbius Strips II (1963)
by M. C. Escher

Is it Possible ?
What happens ?

Our Goal

1. Topological Crystallography (Ladder)

2. Quantum topological effects in the topological crystals (Ants)

Macroscopic quantum coherence
in nontrivial topological space

Topological gauge fields

Strategy Is it Possible ?



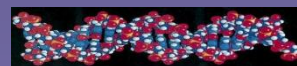
For synthesise of topological crystals

Requirements

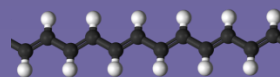
★ One-dimensional wire

Too flexible

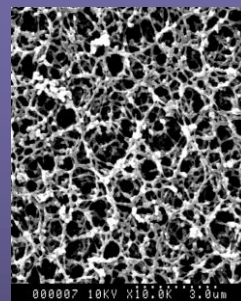
Organic polymer



DNA



$(CH)_x$



$(SN)_x$



★ Rigidity

Inorganic polymer



MX_3, MX_2

Inorganic Covalent wires

Requirement for twisting and bending materials such as Mobius crystals

Semi-flexible !

chain



Typical materials



⋮

⋮



Covalent **Intra**chain

Van der waals force: **Inter**-chain

MX_3 : CDW and Superconductors



Researches in Hokkaido Univ. 35 Years

Discovery of $NbSe_3$ and TaS_3 : Yamaya, Sambongi, Tsutsumi (1977)

Memory Effect of CDW in $NbSe_3$: Ido Oda, Okajima, Sambong (1986)

Ring Crystals in $NbSe_3$: Kawamoto, Okajima, Yamaya, Tanda (1999)

Möbius Crystals in $NbSe_3$ Tanda Tsuneta Inagaki Okajima Yamaya
Hatakenaka

Nature 417 397 (2002)

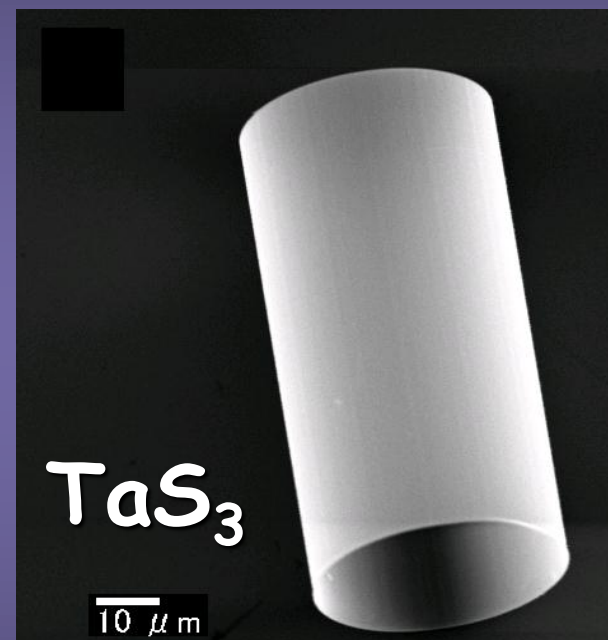
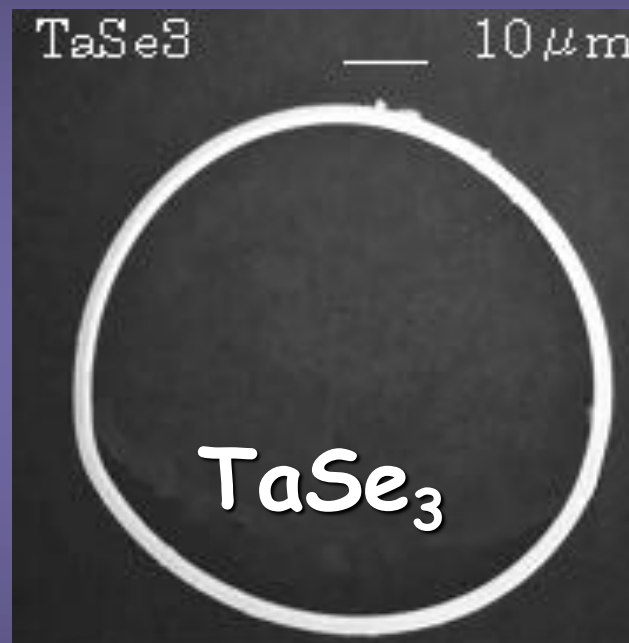
Hopf-link crystals Matsuura, Yamanaka, Hatakenaka, Matsuyama, Tanda
PRB (2006)

Topological quantum Effects in MX_3 : Tsuboa, Matsuura, Kumagai, Tanda
PRB (09,10,11,12)

Chiral CDW in $TiSe_2$: Ishioka, Oda, Ichimura, Tanda PRL (2010,2012)

MX_2 Nanotubes (03,04), Topology change(09,10,11,12)

Ring Crystals



Seamless!!

1999

Synthesize and Condition

**Chemical Vapor
Transportation**
Closed Quartz Tube
<10⁻⁷Torr(initial vacuum)
10 days
Nb, Ta (99.999%),
Se (99.9999%)
Furnace Temperature
600°C~800°C

Starting materials (Nb,
Se) is sealed in an
evacuated ampoule.

1. heating

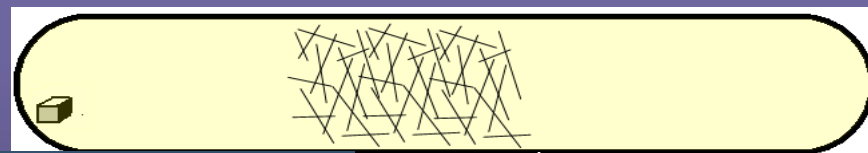
Se Atmosphere

Nb



Quartz Tube

2. transportation



3. final stage



After a few weeks of heating, products are transported to the lowest-temperature end where vapor pressure is also the lowest.

Nonequilibrium condition

Se Atmosphere

Nb



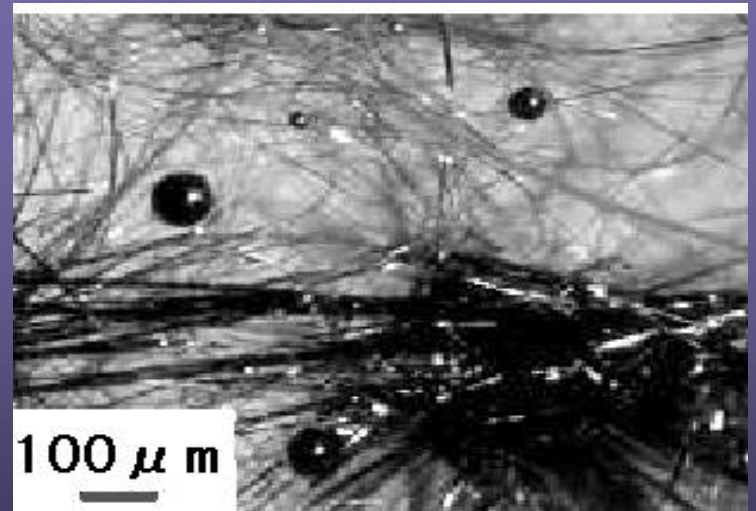
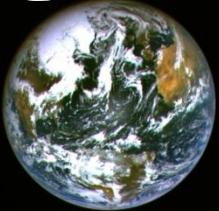
Large Temperature gradient (**more than 150°C**)

Se circulates through

Vapor, mist, liquid droplet

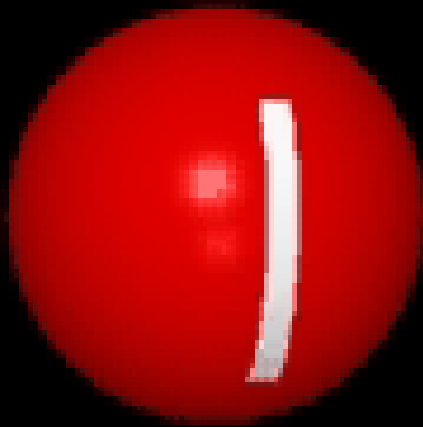


Earth system make
Life polymer
Analogous method

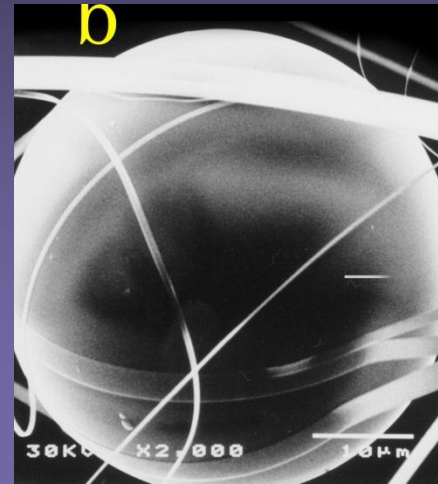


These droplet need for formation of ring crystals.

Formation of Ring Crystals



a growing crystal can eat its own tail.



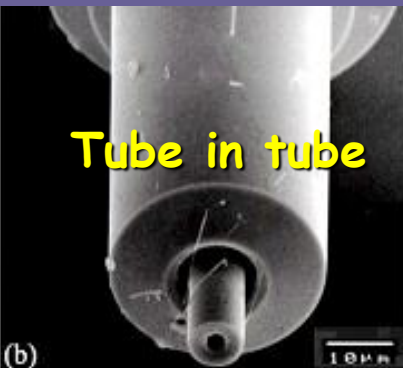
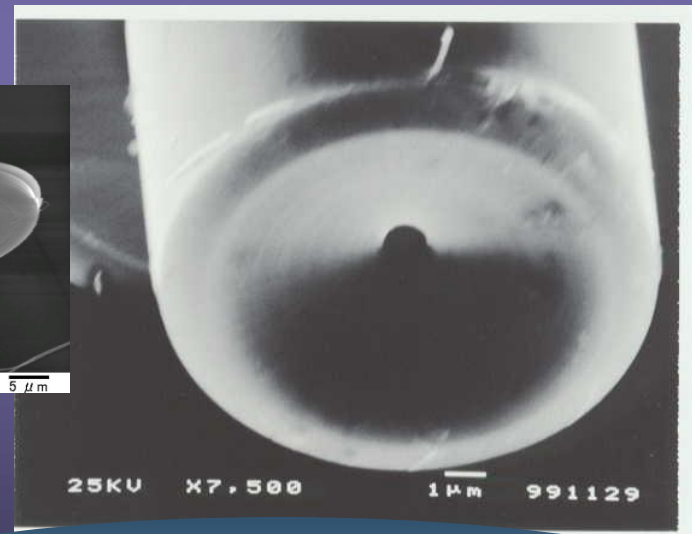
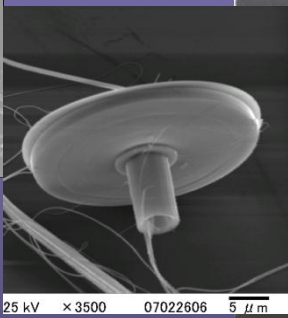
The ribbon-shaped NbSe_3 crystals grown in the viscous Se droplet are bent due to Se surface tension.



NbSe_3 fiber circulate on the equator of Se droplets during growth

Seamless ring

Disks and Tubes Crystals



Hole radius is less than 1 μm !!

CDW Correlation length is 5 μm, which is larger than hole radius!

This system is ideal matter in observation of Interference effect or AB effect of CDW

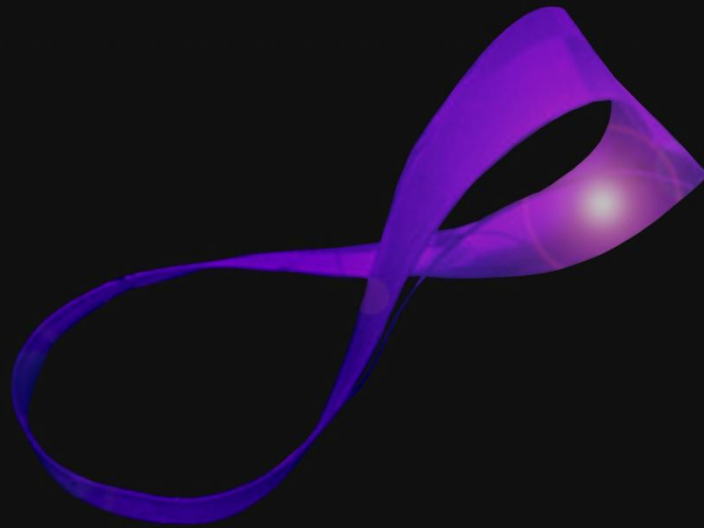
Figure-8 Crystals (2π -twist)

*Knot with Framing
in Math. term*

$+2\pi$ -Twist -Band

-2π -Twist -Band

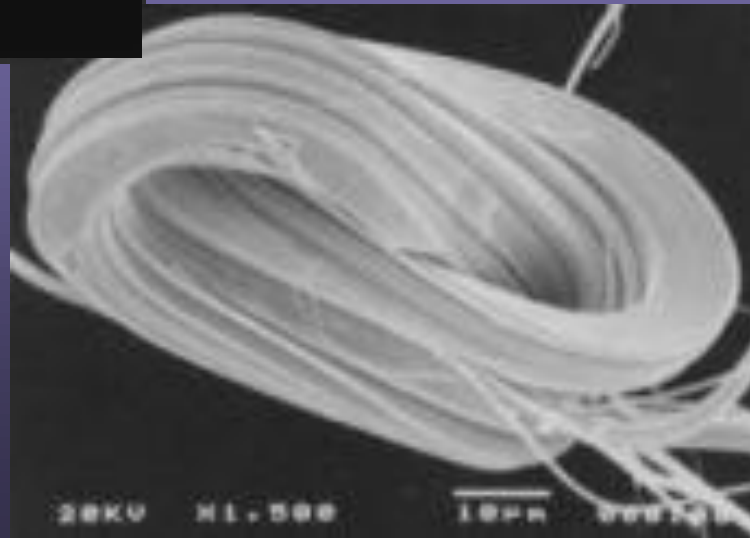
No evidence of breaking
of Chiral Symmetry



Growing 

Self-crossing

Maximum Crystals

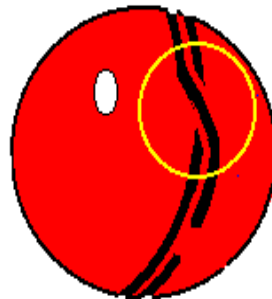


2002 Nature

Mechanism of formation of Figure 8 Crystals (2π twist)



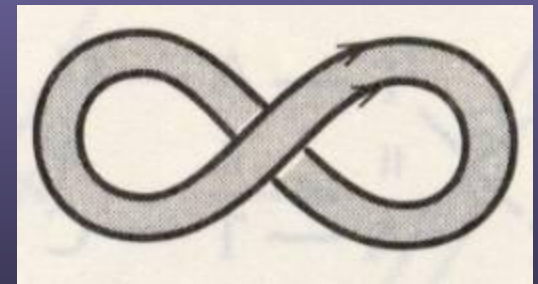
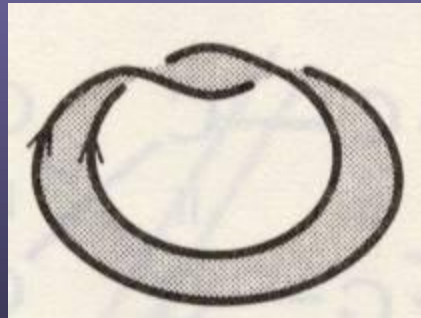
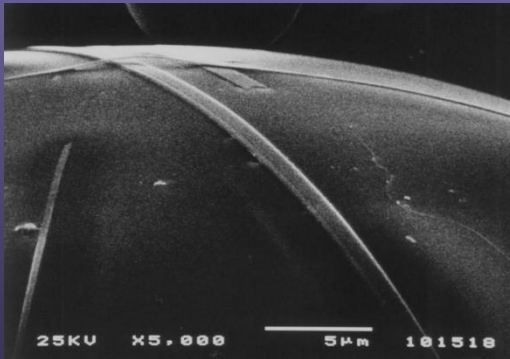
A NbSe₃ crystal band around a droplet two times during its growth



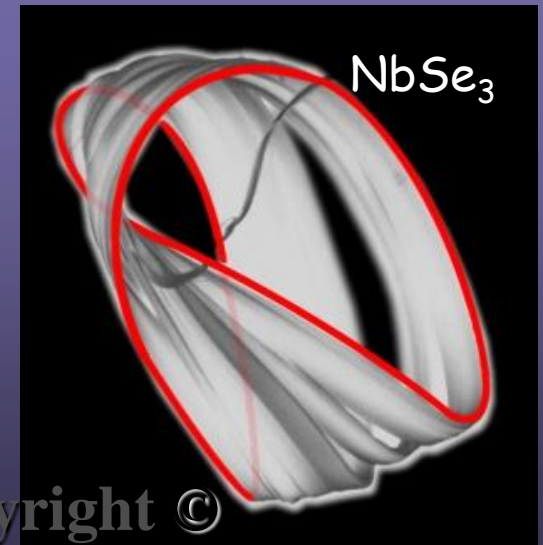
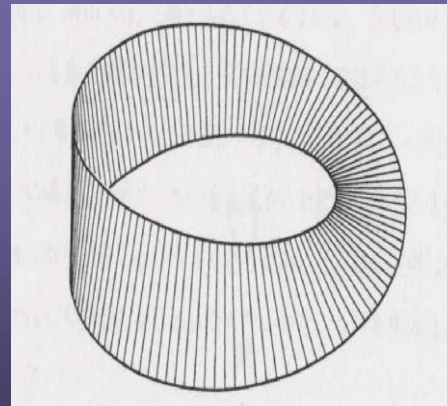
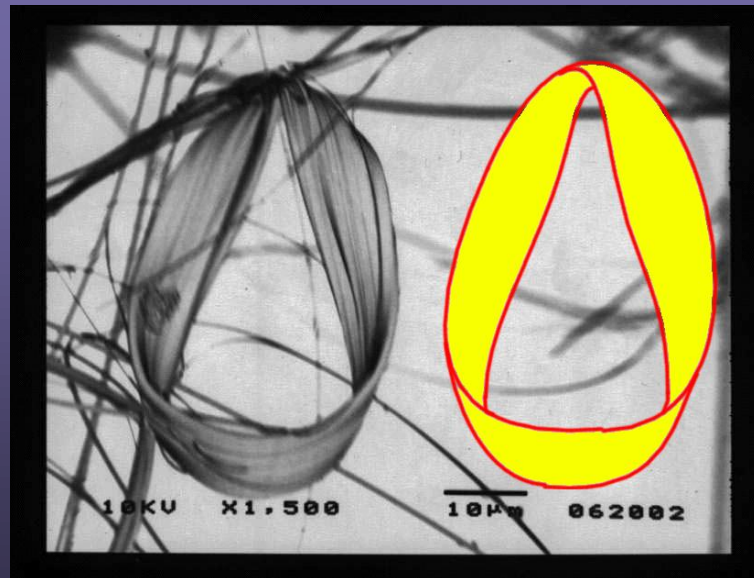
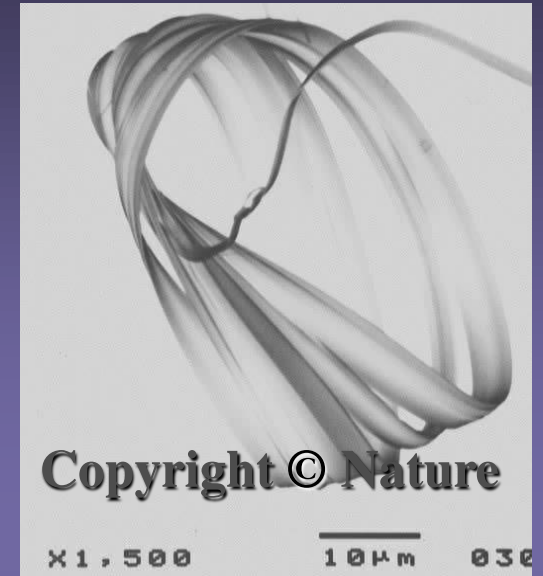
It become to intersect with itself for some reason, and then the both ends coalesce.



The crystal to be to form



Möbius Crystals (π twist)



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Nature

Bending to Twisting

formation mechanism of Mobius crystals

Difficulties \rightarrow twisting shear

Question is how the twisting is introduced without actual shear forces

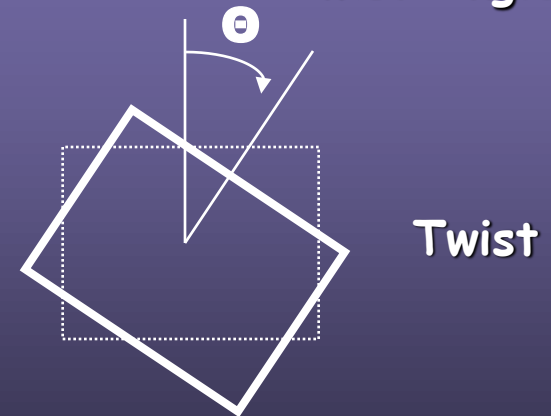
Answer

Crystal symmetry \rightarrow The bending-twisting conversion

Bending \longleftrightarrow Twisting
Compliance

Twist Angle: Θ

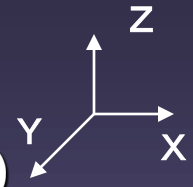
Monoclinic , triclinic



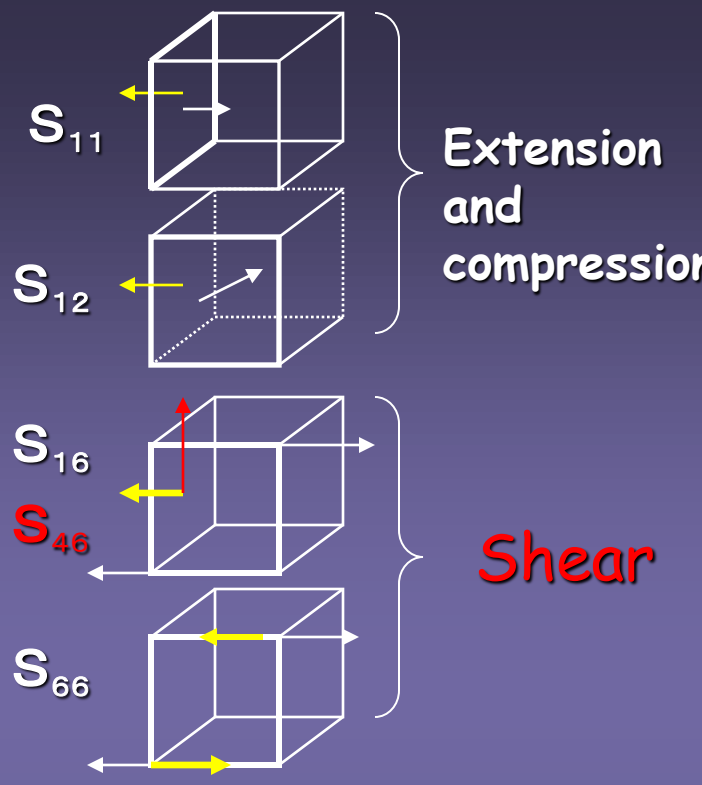
Cross Section

Compliance

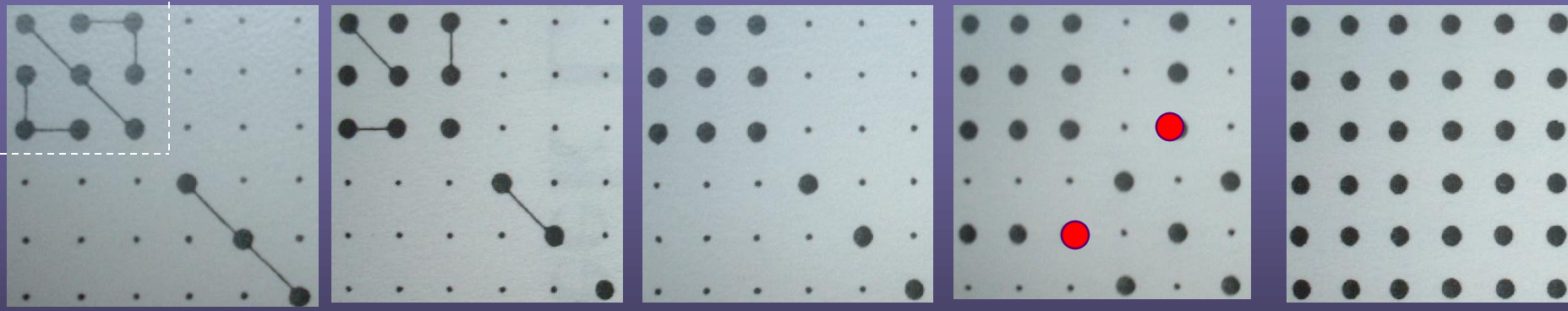
Elasticity (Expansion of Hook's law)
 $X = (1/K) \times F$ $F = kX$



$$\begin{aligned} \epsilon_1 &= s_{11}^E \sigma_1 + s_{12} \sigma_2 + s_{13} \sigma_3 + s_{14} \sigma_4 + s_{15} \sigma_5 + s_{16} \sigma_6 \\ \epsilon_2 &= s_{12} \sigma_1 + s_{22} \sigma_2 + s_{23} \sigma_3 + s_{24} \sigma_4 + s_{25} \sigma_5 + s_{26} \sigma_6 \\ \epsilon_3 &= s_{13} \sigma_1 + s_{23} \sigma_2 + s_{33} \sigma_3 + s_{34} \sigma_4 + s_{35} \sigma_5 + s_{36} \sigma_6 \\ \epsilon_4 &= s_{14} \sigma_1 + s_{24} \sigma_2 + s_{34} \sigma_3 + s_{44} \sigma_4 + s_{45} \sigma_5 + s_{46} \sigma_6 \\ \epsilon_5 &= s_{15} \sigma_1 + s_{25} \sigma_2 + s_{35} \sigma_3 + s_{45} \sigma_4 + s_{55} \sigma_5 + s_{56} \sigma_6 \\ \epsilon_6 &= s_{16} \sigma_1 + s_{26} \sigma_2 + s_{36} \sigma_3 + s_{46} \sigma_4 + s_{56} \sigma_5 + s_{66} \sigma_6 \end{aligned}$$



S_{ab} : Compliance (tensor) Stress: σ
 Strain: ϵ

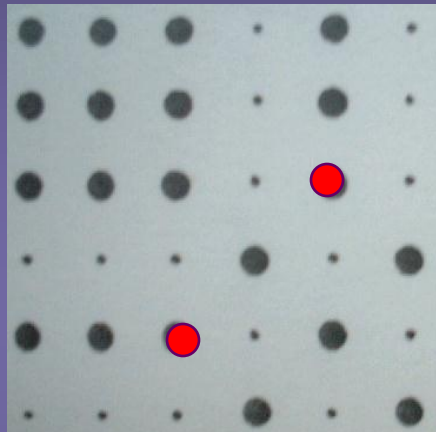


Cubic Tetragonal Orthorhombic Monoclinic Triclinic

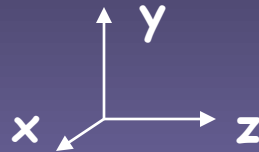
▪ : zero
 ● : nonzero

Lower symmetry

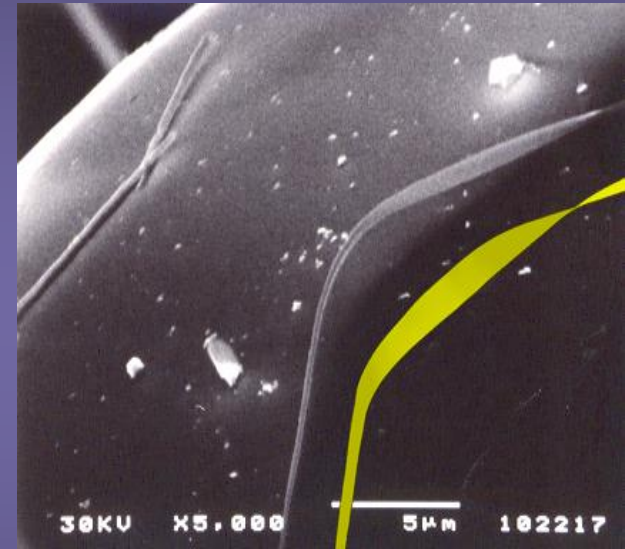
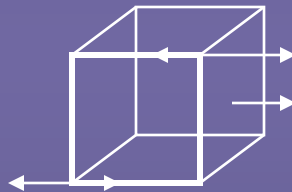
Evidence of Twisting



Monoclinic NbSe₃



S_{35}



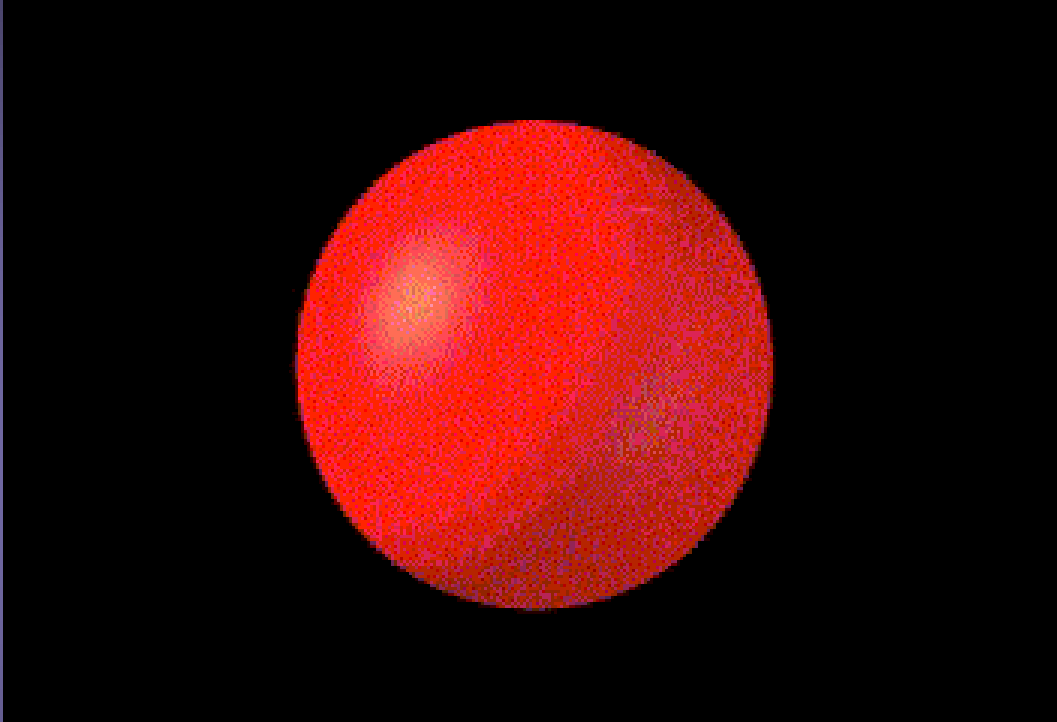
◻: zero

●: nonzero

●: Shear term for Monoclinic

twisting is introduced by bending through this mechanism without actual shear forces during the growth processes along surface

Formation of Möbius Crystals



To form a Möbius strip (1π), a twist is needed to be introduced during spooling.

Can we introduce the concept of topology into crystals ?

Originally, What's Crystal ?



Bragg reflection !

Definition of International Union
of Crystallography (1991)

Definition of Crystals

Snow crystal



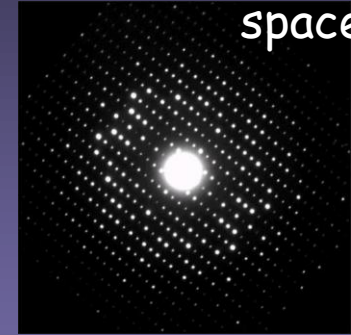
Crystals show Bragg reflection

Bragg reflection of electron beam/X-ray



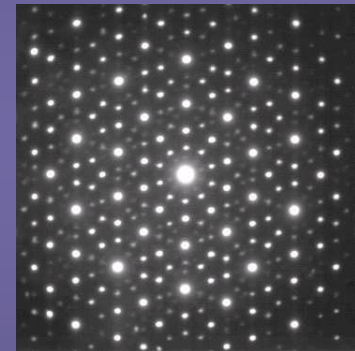
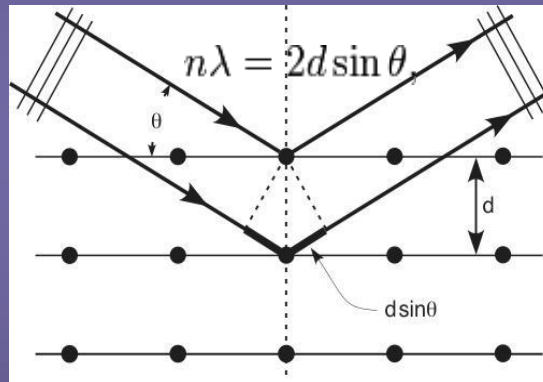
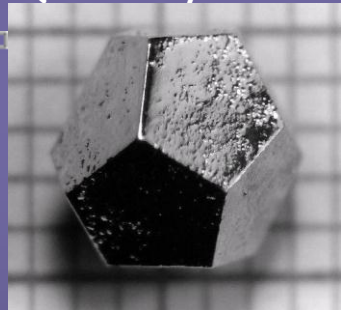
Mathematically, Fourier transform from real space (lattice) to k -space (Bragg spots)

Reciprocal space



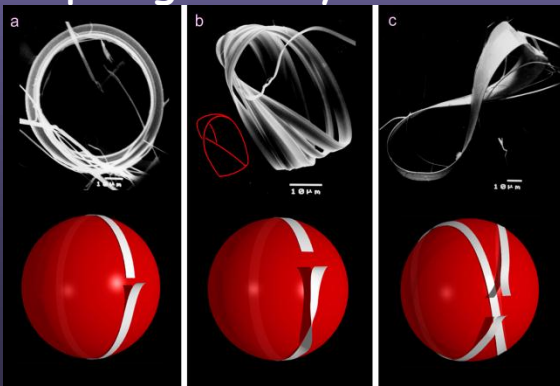
spot

Quasicrystal

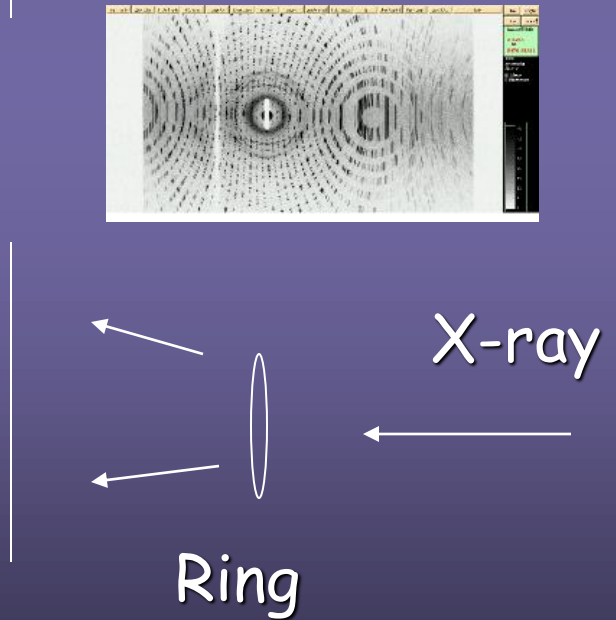
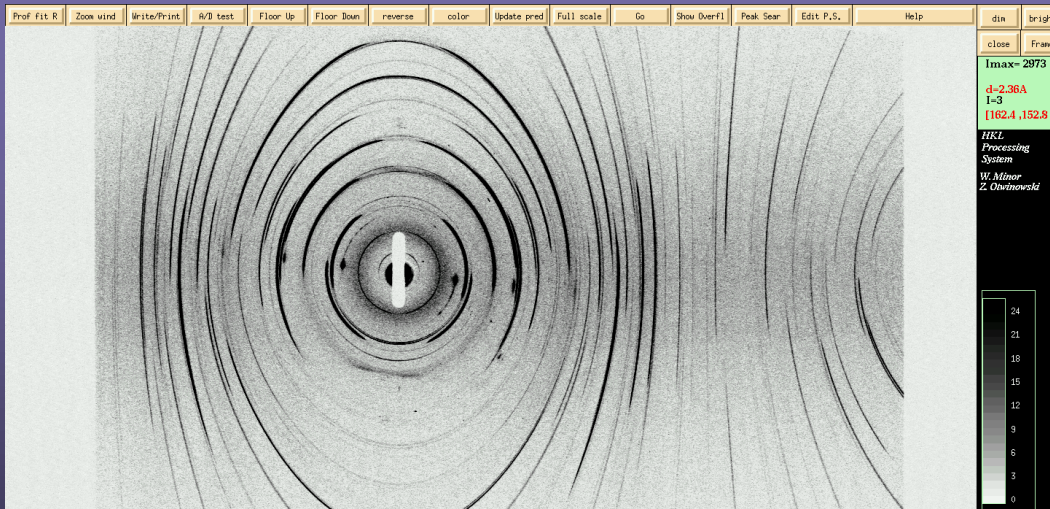
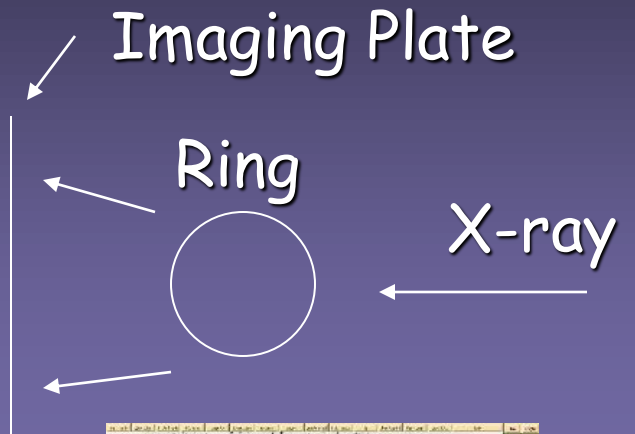
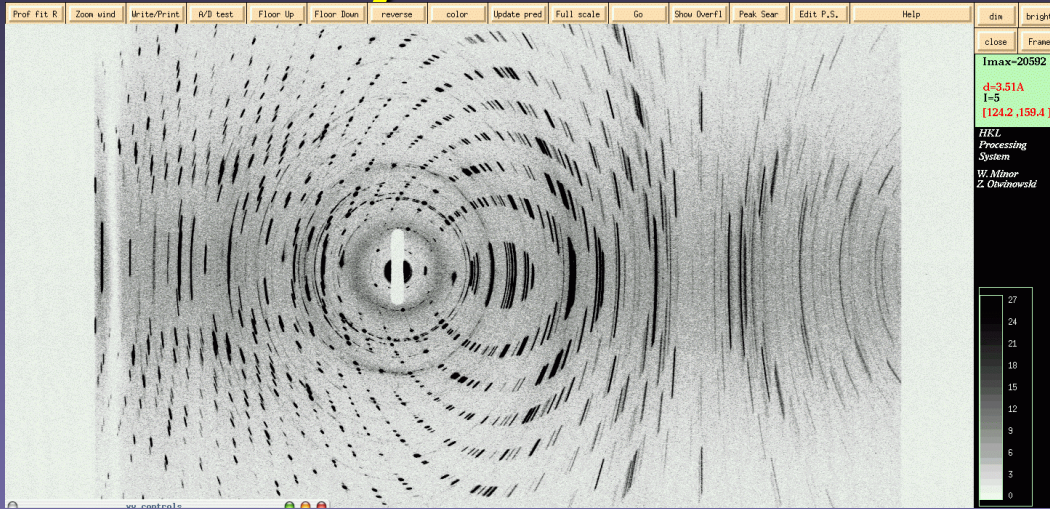


Crystals and quasicrystals show sharp Bragg spots

Topological crystal



X-ray Diffraction: Ring

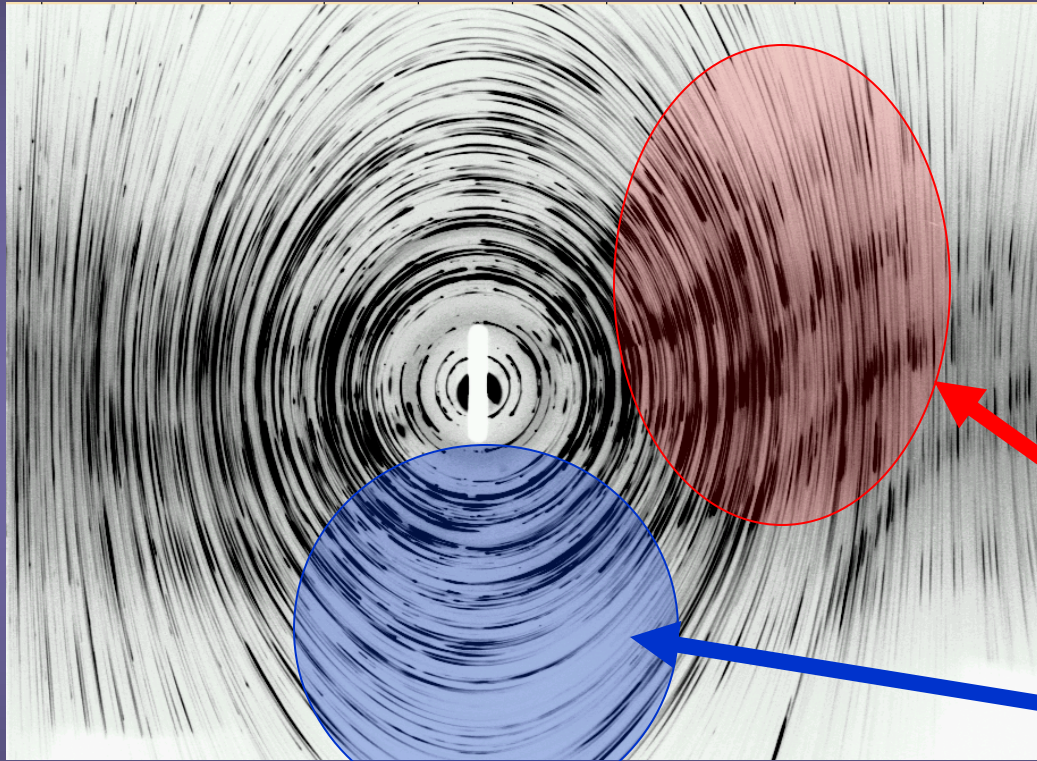


Bragg Ring

Line is homogeneous

Single Crystals !!

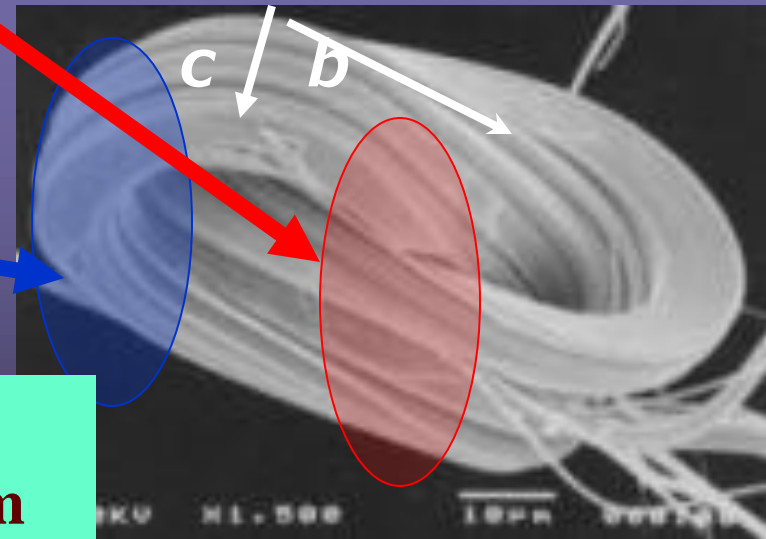
Texture pattern in 8 crystal



K-space

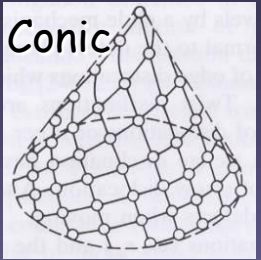
Short strong arcs are diffracted from semi-straight parts

Long weak arcs are diffracted from hair-pin curves

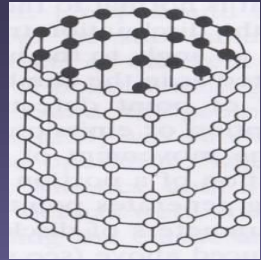


Real space

Classification of Topological Crystals



$\omega = 1/2\pi$
 $\omega^* = 0\pi$



$\omega = 2\pi$
 $\omega^* = 0\pi$

ω : Wedge Disclinations
 ω^* : Twist

ω^* , ω is independent, respectively, due to the topological defect theory of the crystals, as yet. (by Frank)

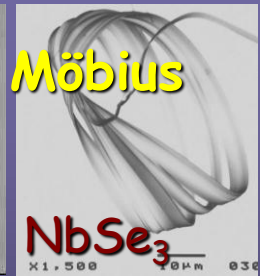
Topological Crystals

New Definition !
 ← Knot Theory →

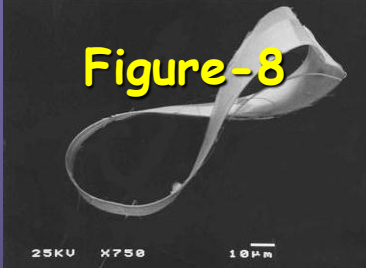
$L_k = (\omega + \omega^*) / 2\pi - 1$
Linking Number



$\omega = 2\pi$
 $\omega^* = 0\pi$
 $L_k = 0$



$\omega = 2\pi$
 $\omega^* = 1\pi$
 $L_k = 1/2$



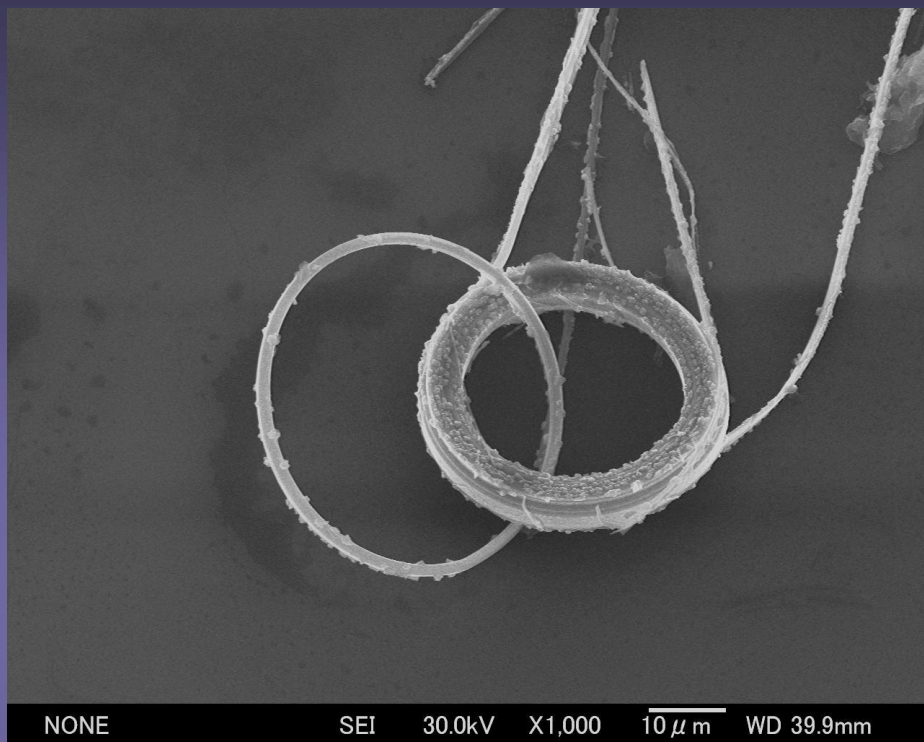
$\omega = 2\pi$
 $\omega^* = 2\pi$
 $L_k = 1$

Global Wedge +
 Global Twisting

Knots Crystals !!

$$\frac{1}{2\pi} \int_{\text{crystal}} f(\omega, \omega^*) dV = L_k$$

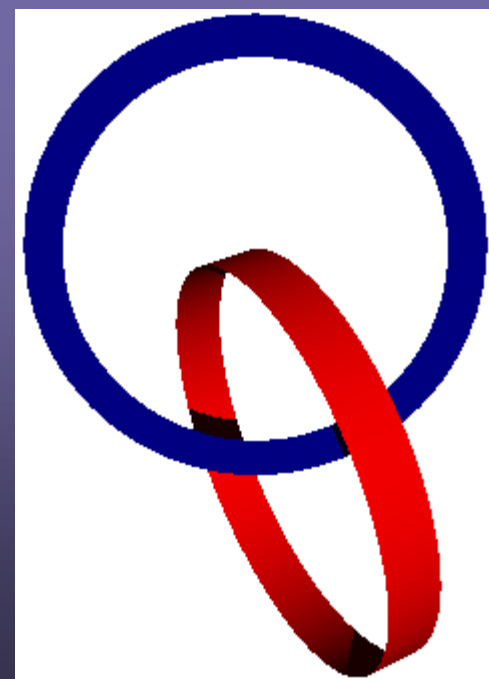
Discover Hopf-Link Crystals



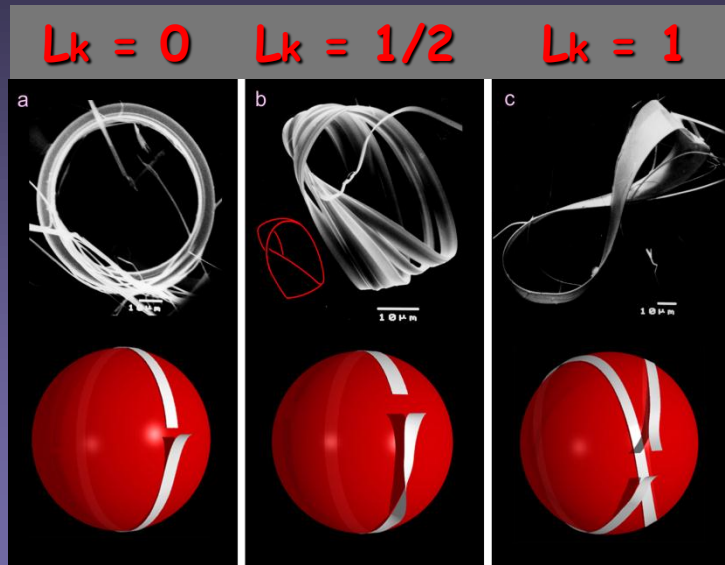
Topologically linked crystals

T.Matsuura, M.Yamanaka, N. Hatakenaka, T. Matsuyama, and S. Tanda, Journal of Crystal Growth 297, 157 (2006).

Hopf-link crystals cannot be categorized by the linking number of Knots crystals and usual point groups → New Classification



Classification By Embedding manifolds



Ring

Mobius

8



Sphere



Klein-Bottle

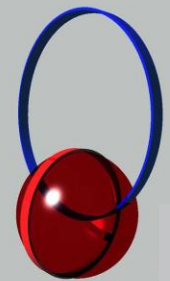


Torus

Hopf-Link Crystals

Matsuura, Matsuyama,
Tanda: JCG (2006)

NONE SEI 30.0kV X800 10 μ m WD 9.4mm



Double-Torus

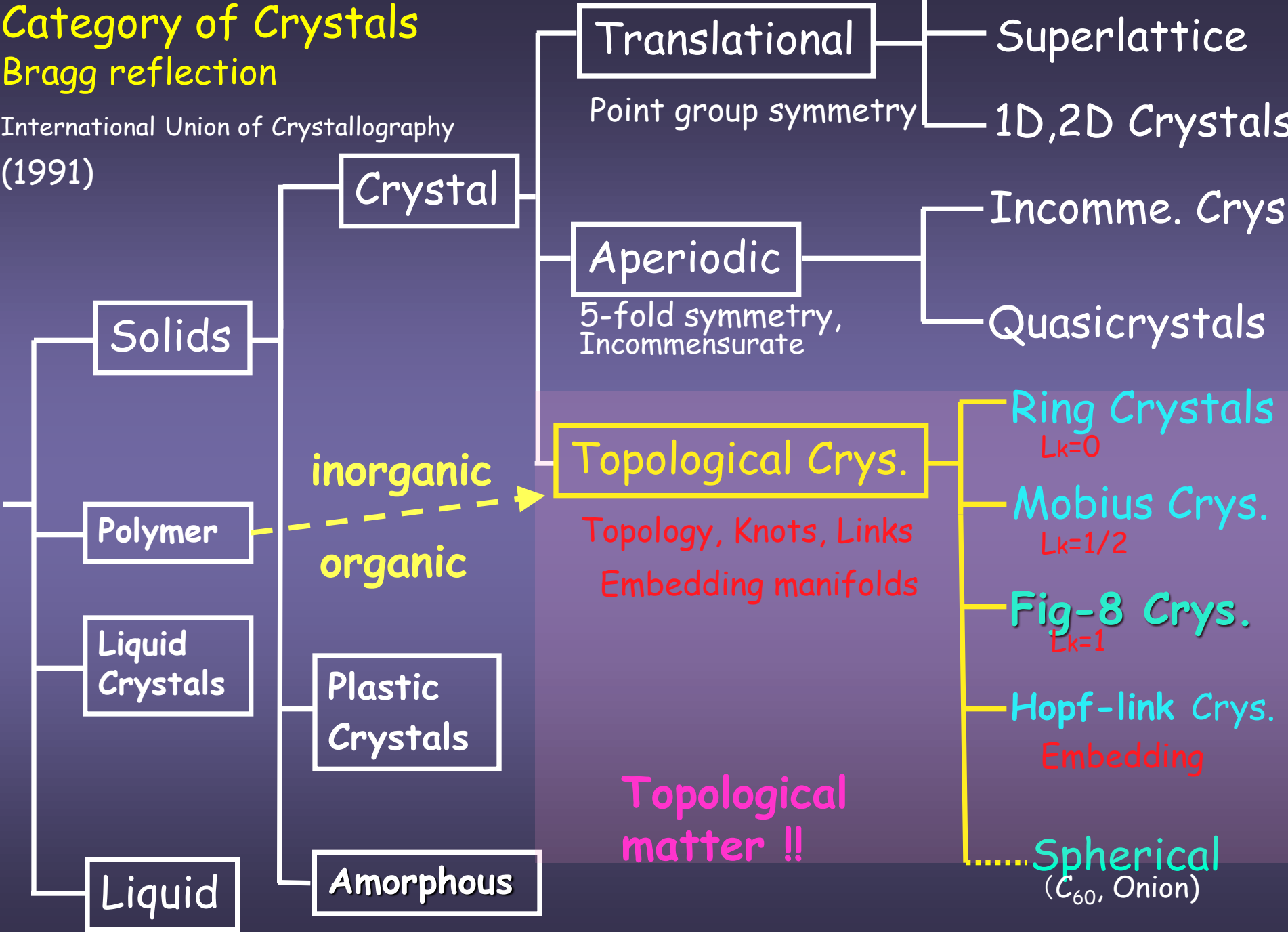
Embedding
manifolds

We propose New Classification with Embedding manifolds

Category of Crystals

Bragg reflection

International Union of Crystallography
(1991)



Translational

Point group symmetry

Superlattice

1D, 2D Crystals

Crystal

Aperiodic

5-fold symmetry,
Incommensurate

Incomm. Crys

Quasicrystals

Solids

Polymer

inorganic

organic

Topological Crys.

Topology, Knots, Links
Embedding manifolds

Ring Crystals

$L_k=0$

Mobius Crys.

$L_k=1/2$

Fig-8 Crys.

$L_k=1$

Hopf-link Crys.

Embedding

Spherical

(C_{60} , Onion)

Topological matter !!

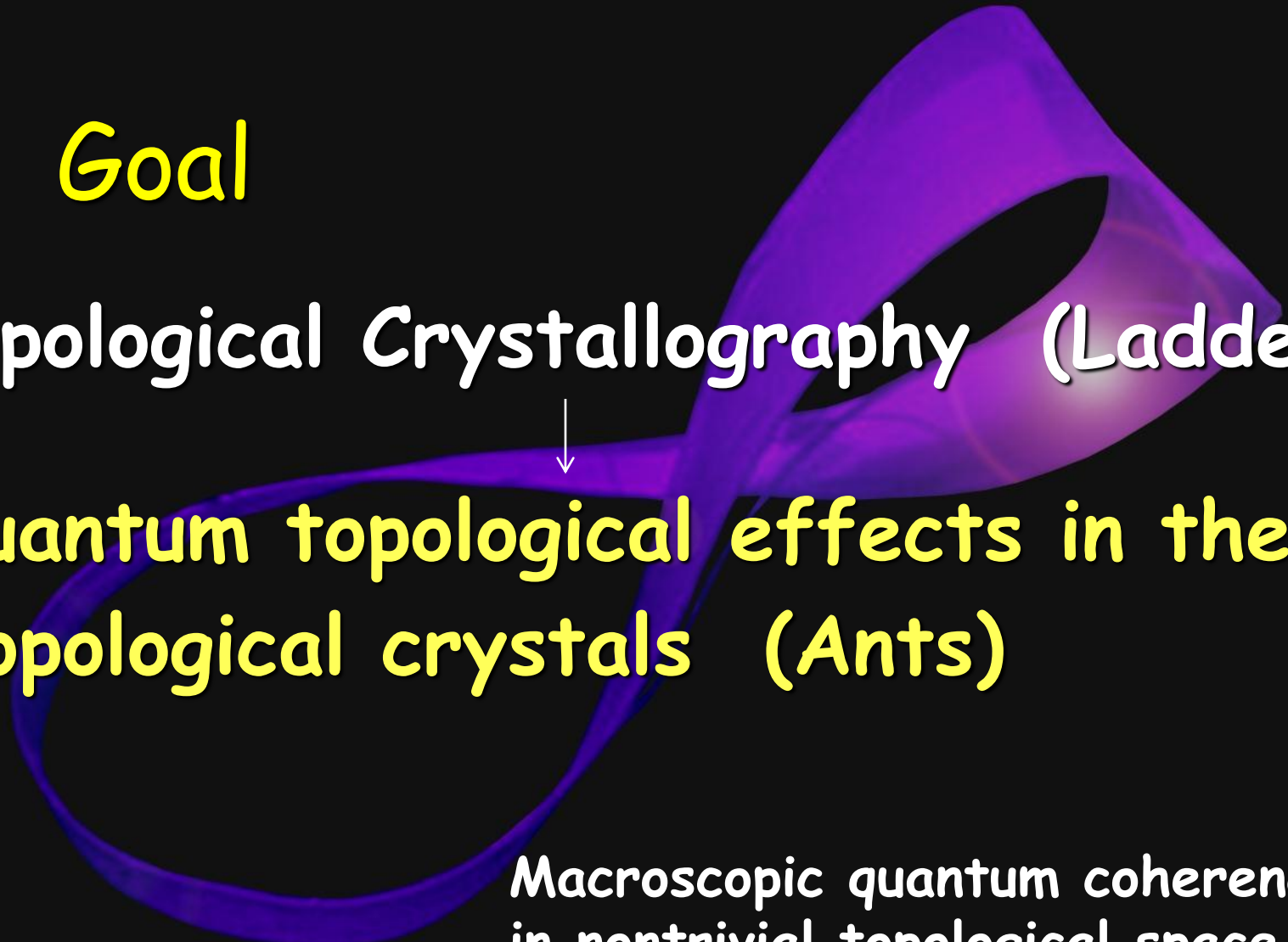
Our Goal

1. Topological Crystallography (Ladder)

2. Quantum topological effects in the topological crystals (Ants)

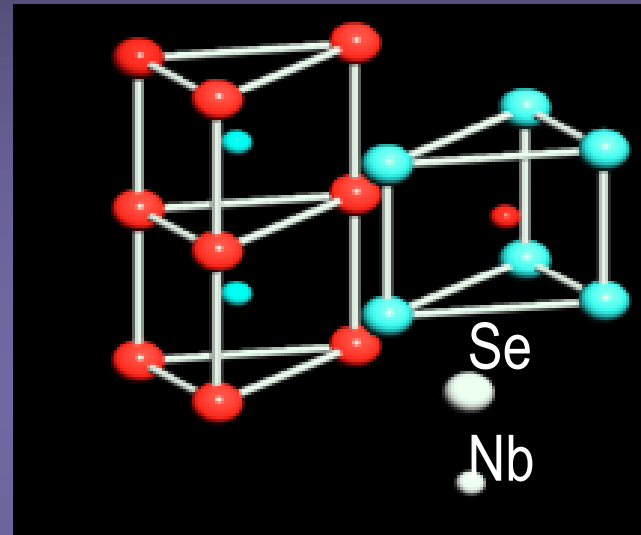
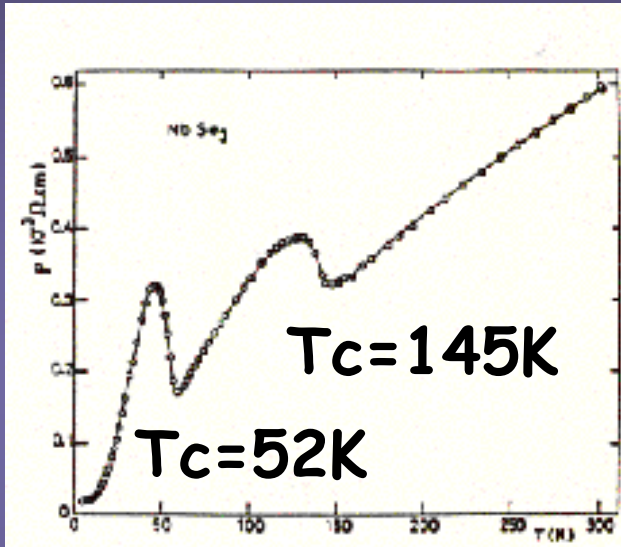
Macroscopic quantum coherence
in nontrivial topological space

Topological gauge fields



NbSe₃ : Charge Density Waves

CDW: Charge-Density-Waves



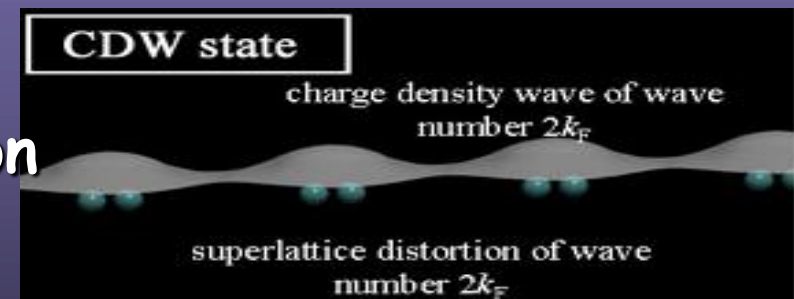
Chain axis

Covalent wires

Fiber structure



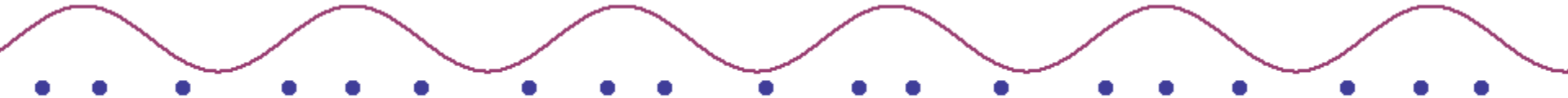
Transition



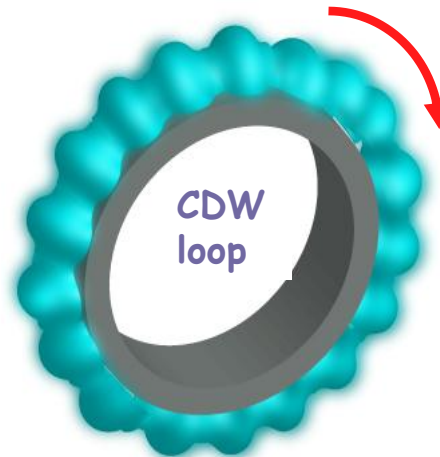
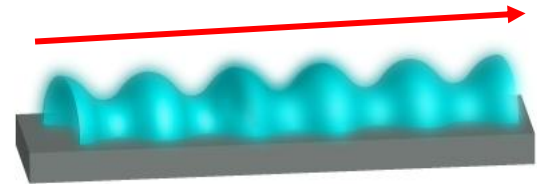
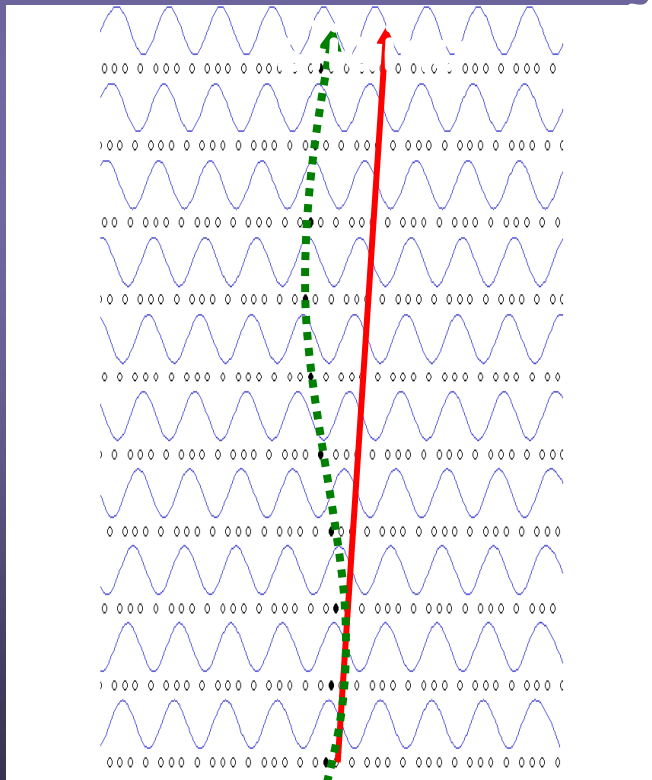
A periodic charge modulation
Macroscopic wave function

Sliding of Macroscopic wave function

Fröhlich superconductors : phason



CDW sliding



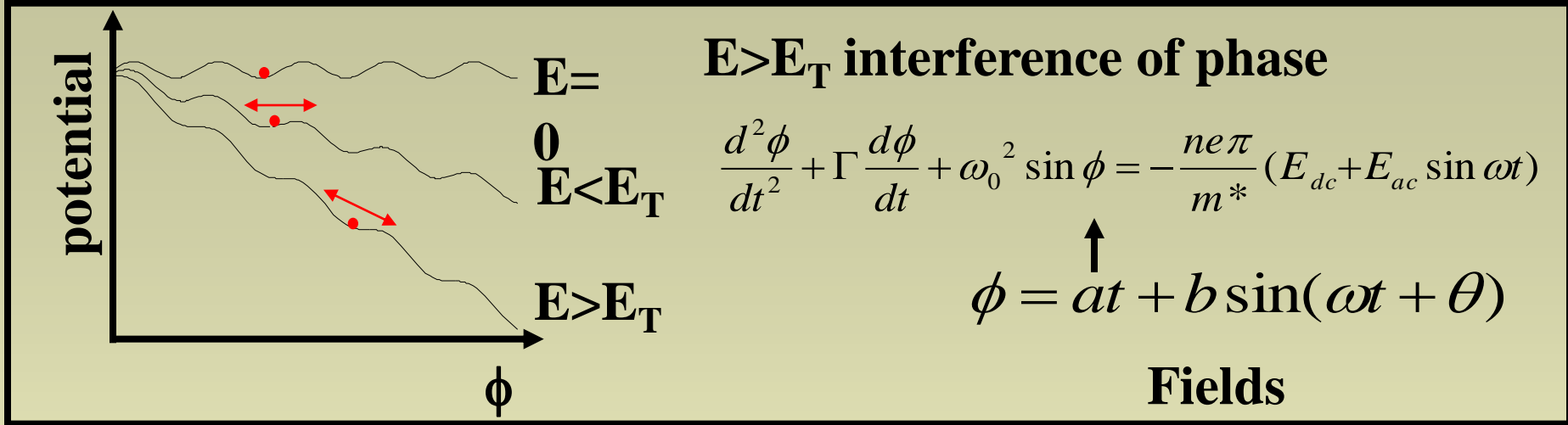
Eternal current

Real space topology

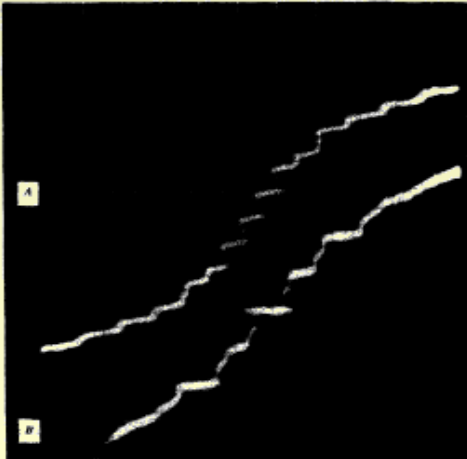
**I. Circulating Sliding Current of CDW
By Shapiro Steps in the Loop**

II. AB-Effect of CDW in the Loop

Shapiro steps (Sliding state)

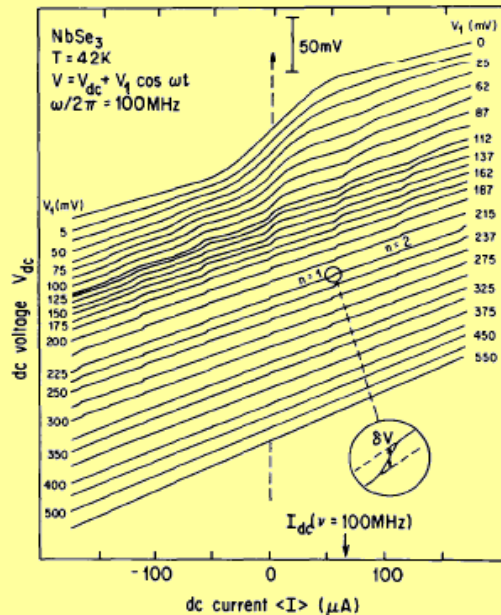


Josephson Junction Shapiro steps

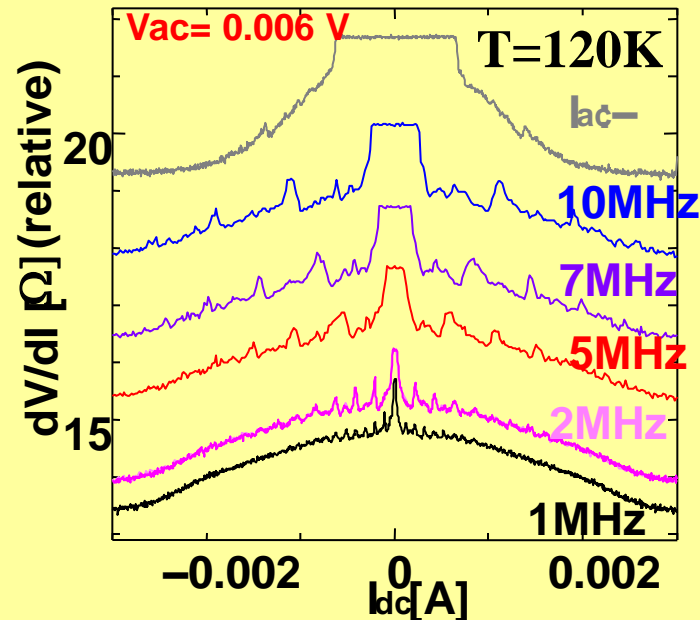


Shapiro, PRL, (1963)

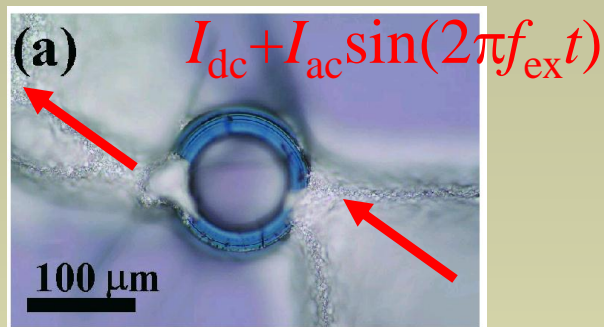
CDW: Shapiro steps : Cut-ring and needle NbSe₃



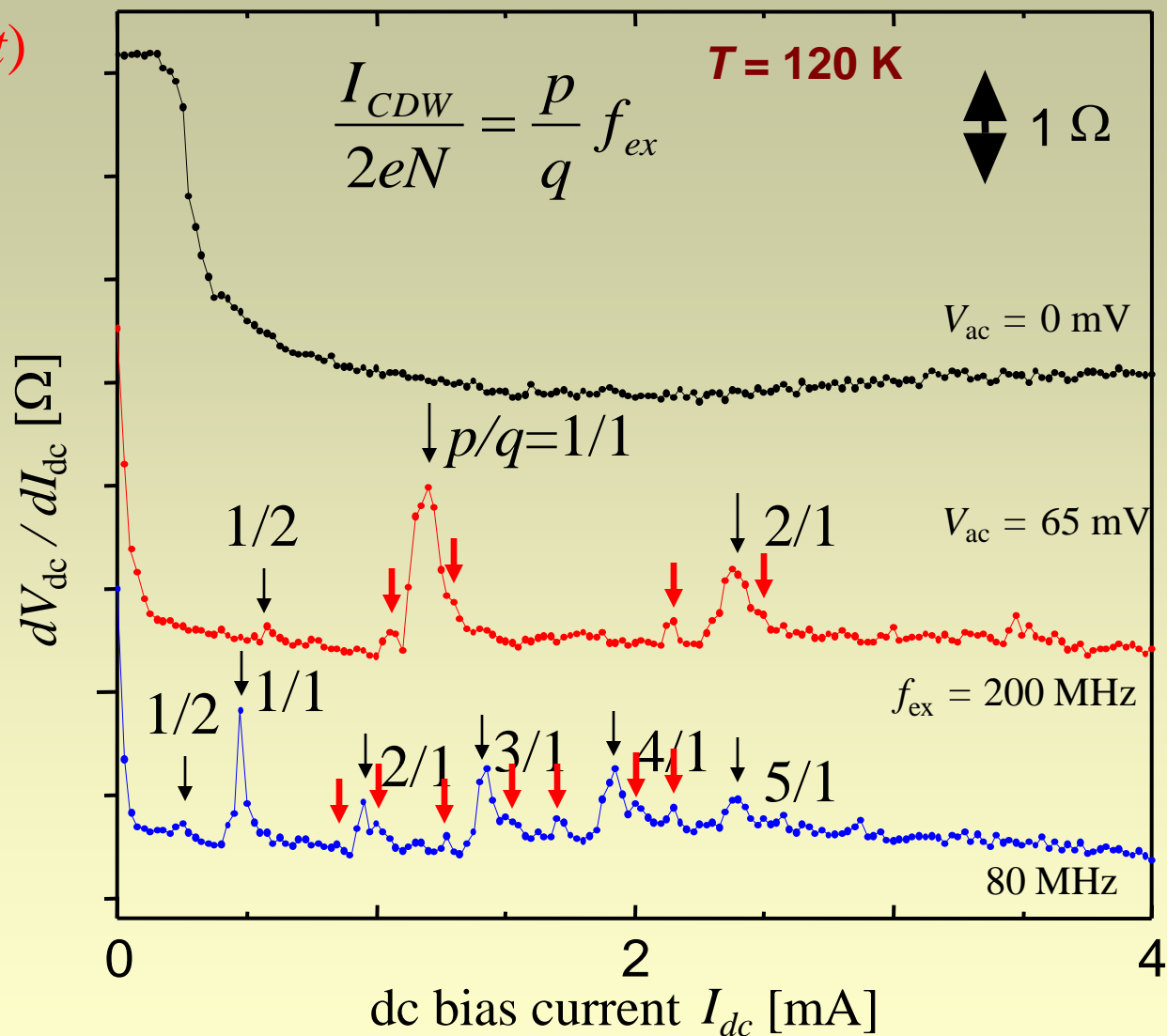
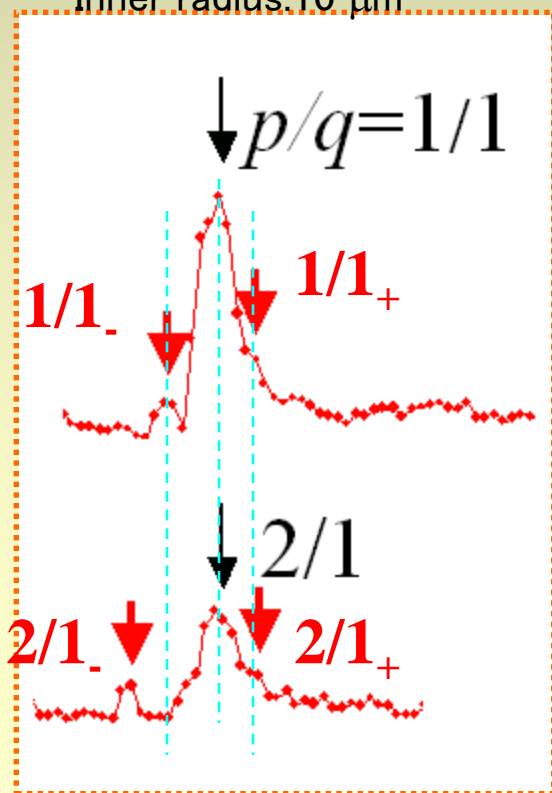
Zettel et.al, SSC, (1983)



★★ Shapiro peaks in CDW loops



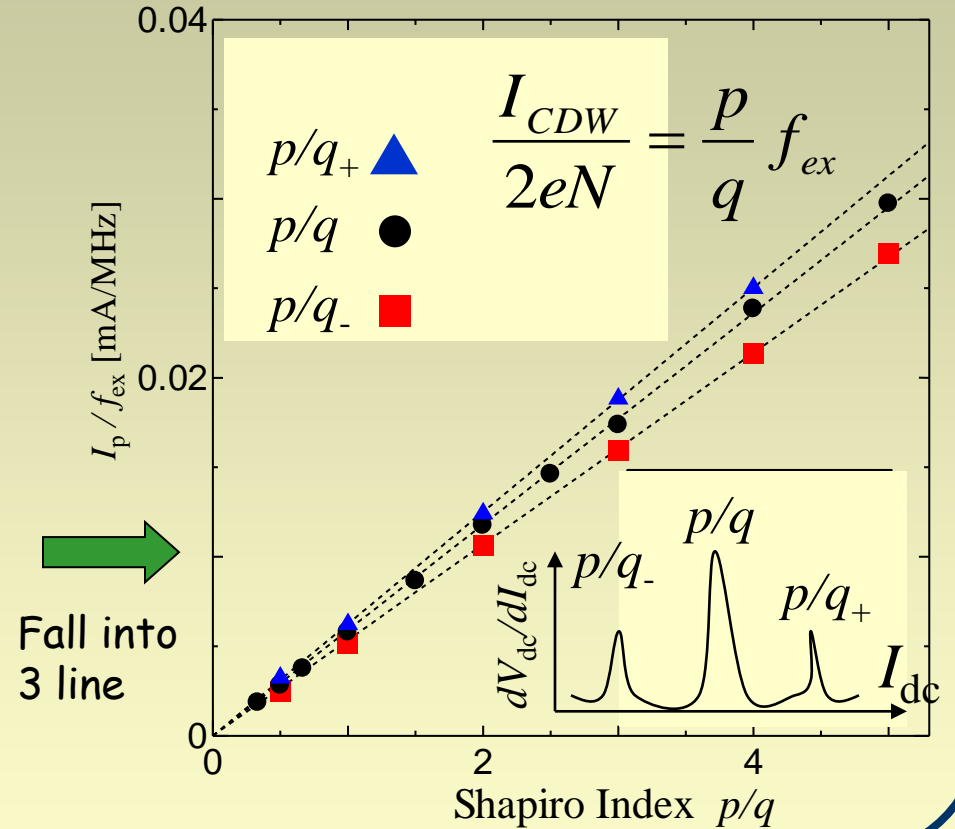
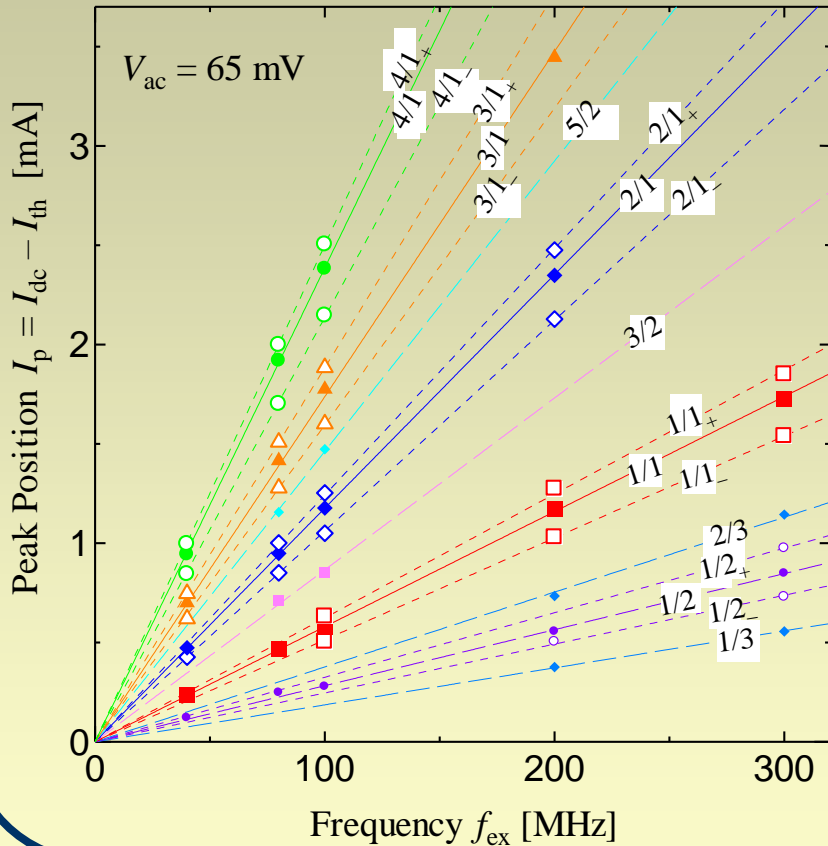
NbSe₃ ring
 Outer radius: 120 μm
 Inner radius: 10 μm



Subpeaks at both sides of Shapiro peaks are observed!

Analysis of peak positions

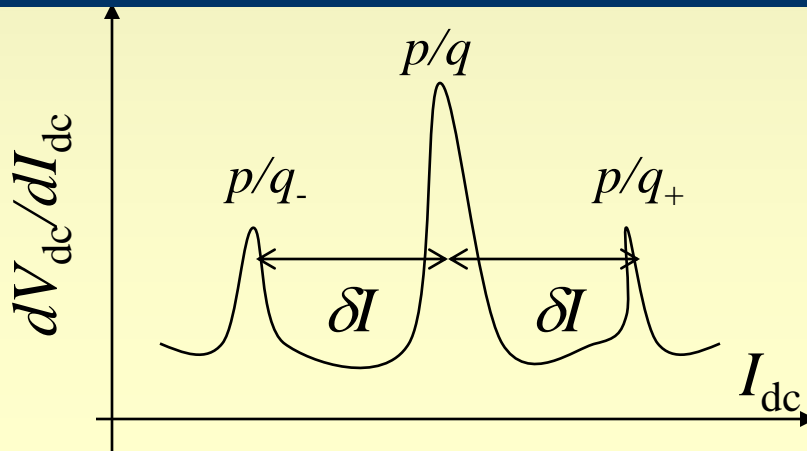
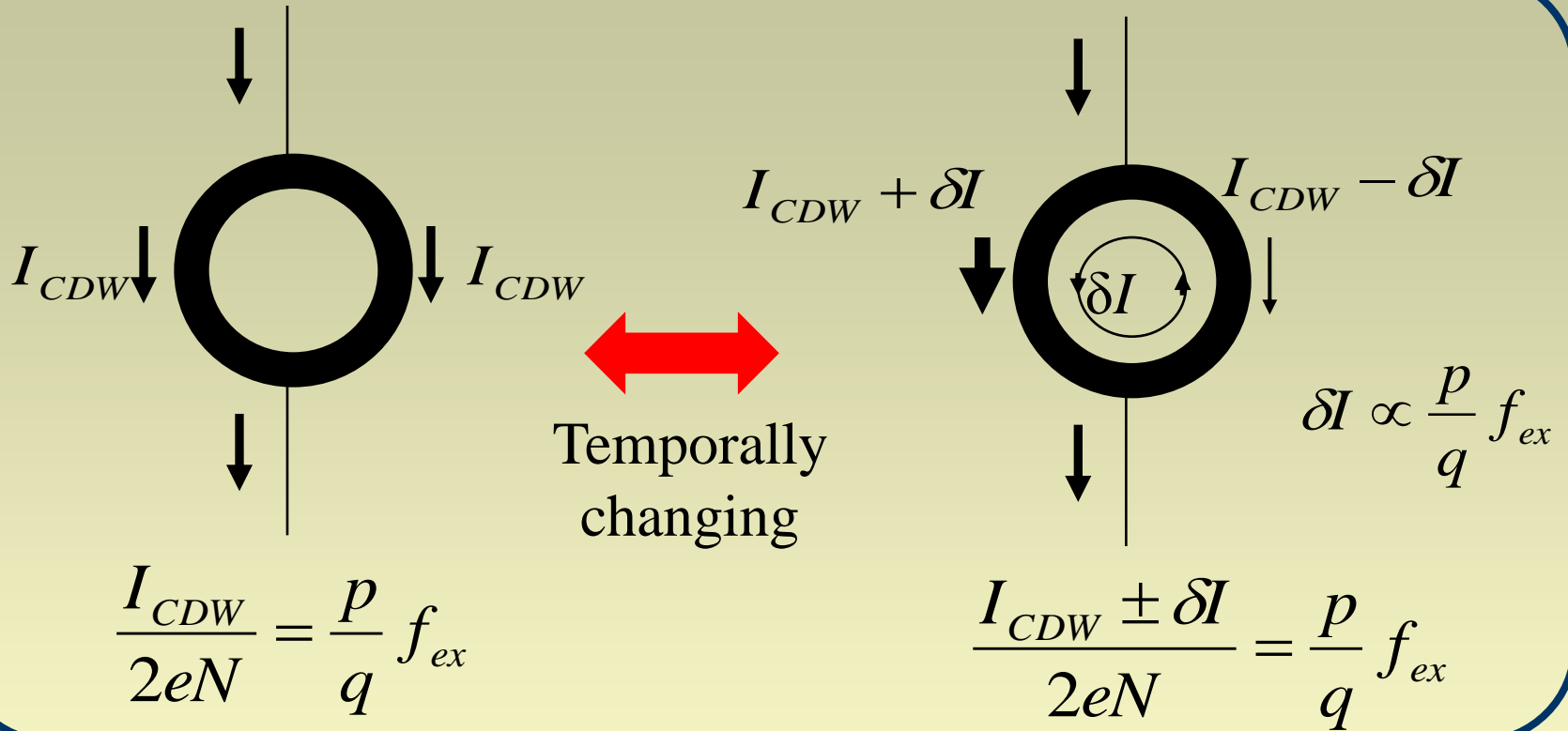
$$f_{\text{ex}} = 40, 80, 100, 200, 300 \text{ MHz}$$



Fall into 3 line

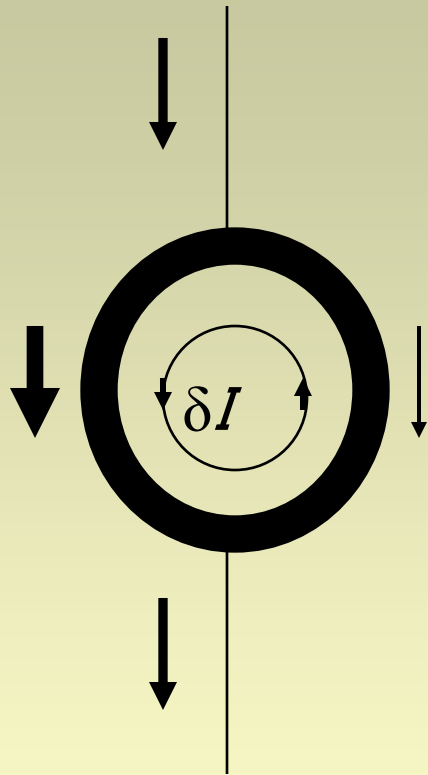
Discovery of Beat peak only in the loop CDW !!

Circulating current



Additional current must exist in the loop CDW

Damping time of Circulating current



If CDW is circulating, the damping time can be estimated by

Circumference: 10^{-4} m

Phason velocity: 10^4 m/s

Circumference / Phason velocity = 10^{-8} s

\gg NbSe₃ Phason damping time: 10^{-11} s

Richard and Chen, Solid State Commun. 86 485 (1993)

Elongation of damping time !!

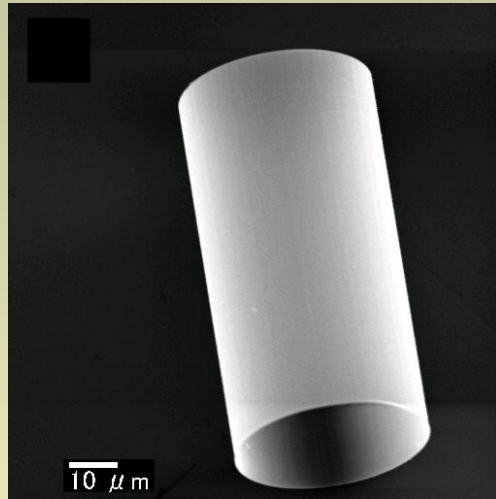
→ Precursor of Fröhlich supercurrent

T. Matsuura, K. Inagaki, and S. Tanda, Phys. Rev. B 79, 014304 (2009).

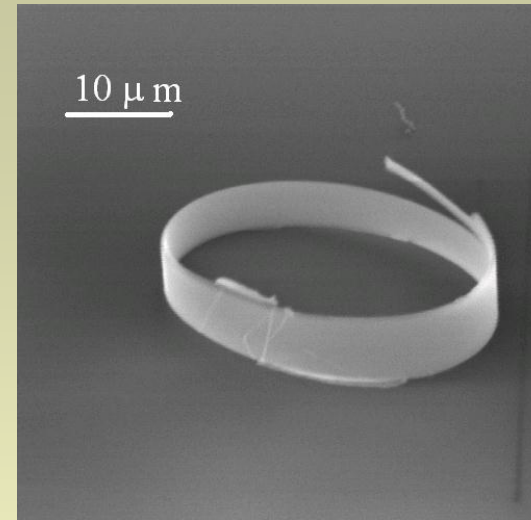
Real space topology

1. Circulating current of CDW
By Shapiro Steps in the Loop
2. AB Effect of CDW in the Loop

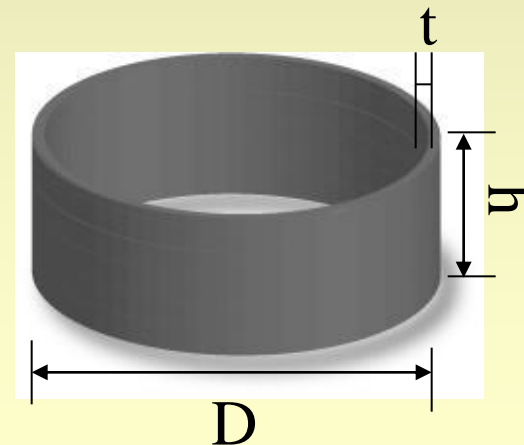
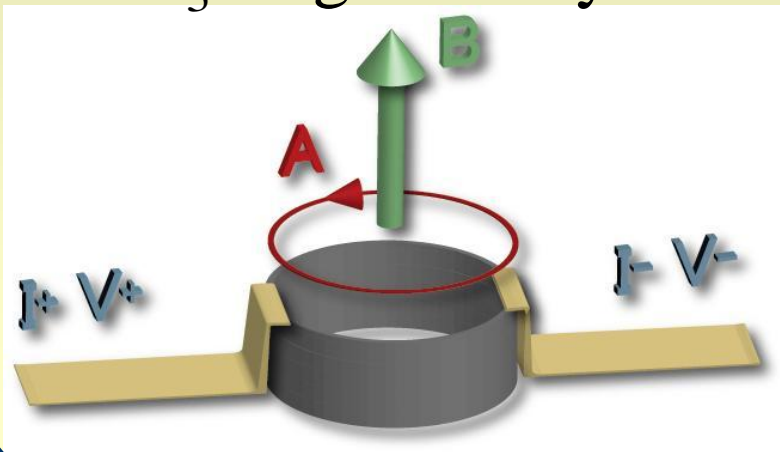
Experimental Setup



FIB cut

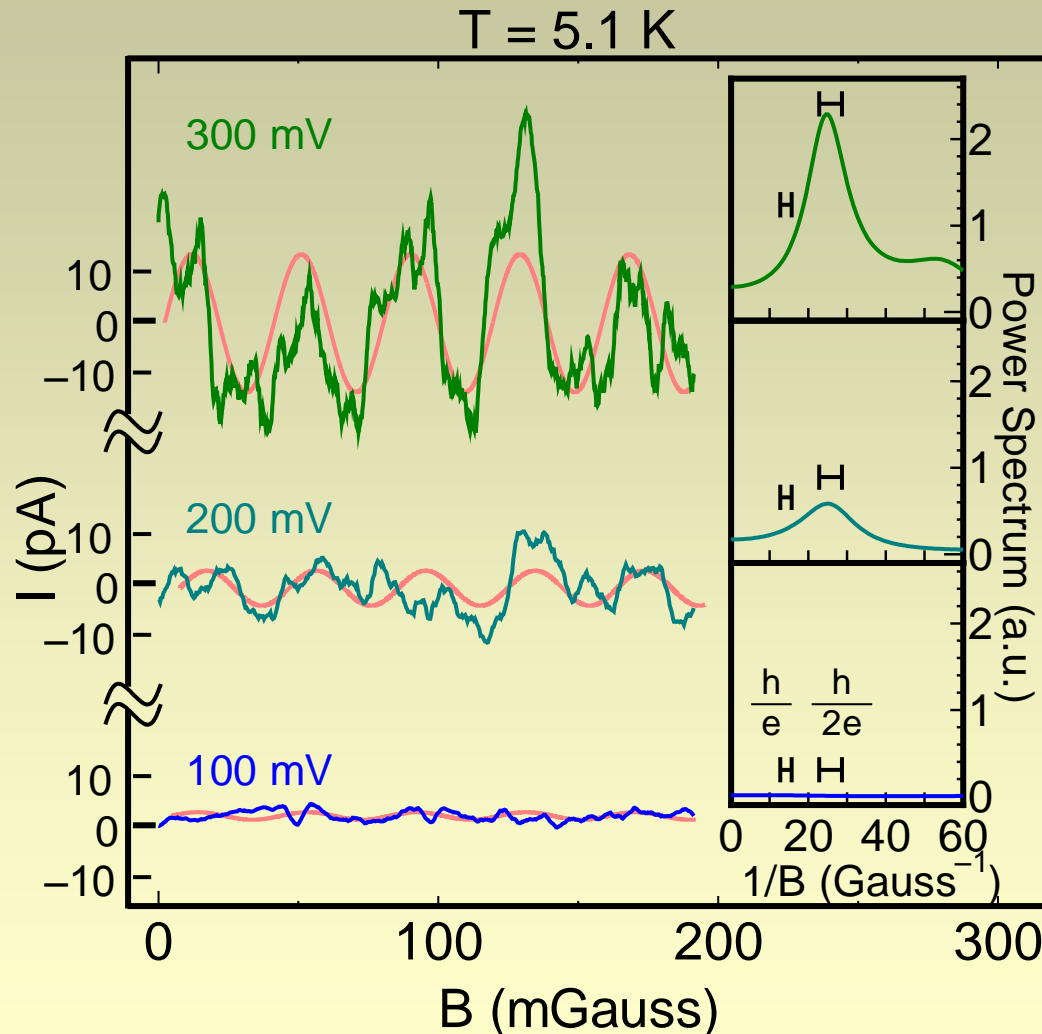


TaS₃ ring/tube crystal



$t \approx 0.1 \mu\text{m}$
 $h \approx 1 \mu\text{m}$
 $D \approx 27 \mu\text{m}$

Result



Periodic oscillations were observed.

Estimation of unit charge

$$\Delta B = \frac{\Phi}{S} = \frac{h}{e^*} \cdot \frac{1}{\pi r^2}$$

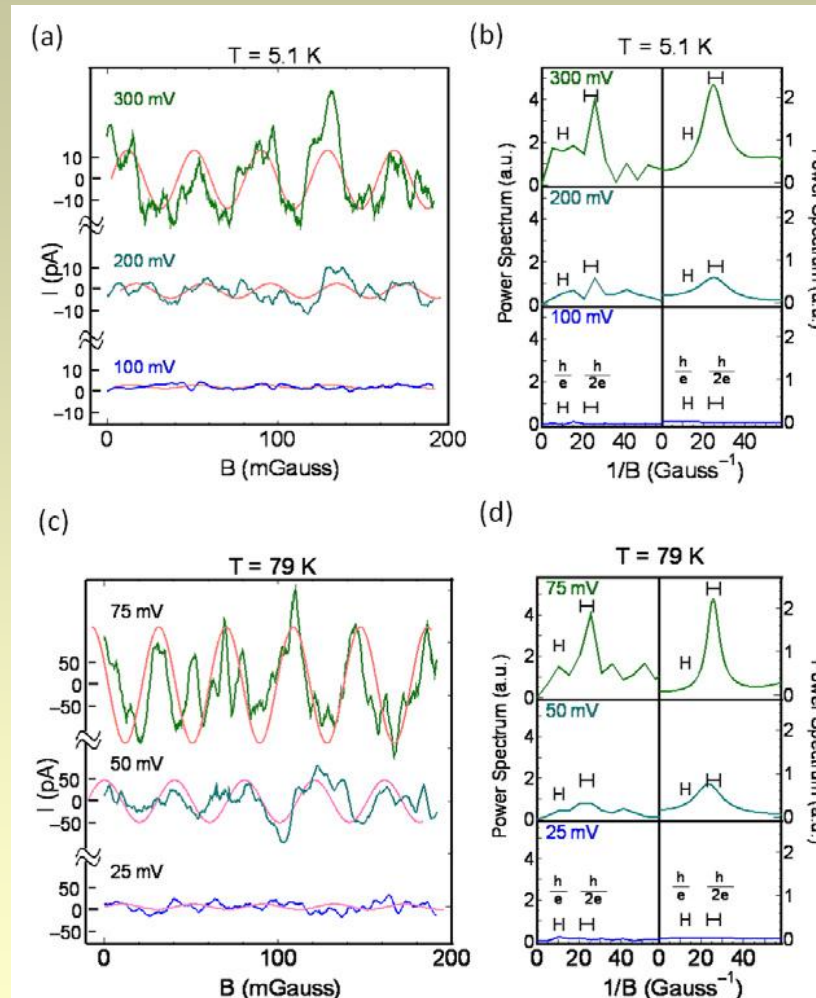
ΔB : The period of the oscillation

S : The area of the ring crystal

Sample	Diameter	Area m ²	Period	Charge
A	27 μm	5.6×10^{-10}	39.7 mGauss	$3.0 \times 10^{-19} \text{ C}$
B	17 μm	2.3×10^{-10}	95.2 mGauss	$3.1 \times 10^{-19} \text{ C}$

Unit charge corresponds to $2e$ ($=3.2 \times 10^{-19} \text{ C}$)

Quantum coherence at temperature of liquid-nitrogen

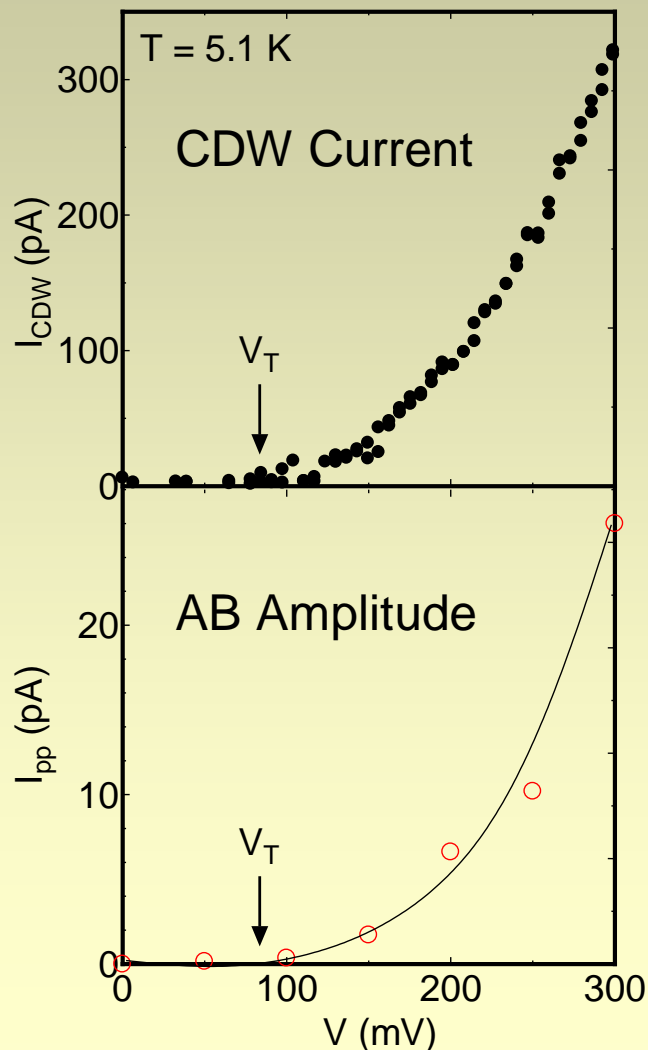


T=5.1K

T=79K

We also observed AB-effect of CDW sliding at 79K in TaS₃ ring crystals !
EPL, 97 (2012) 57011

AB Amplitude

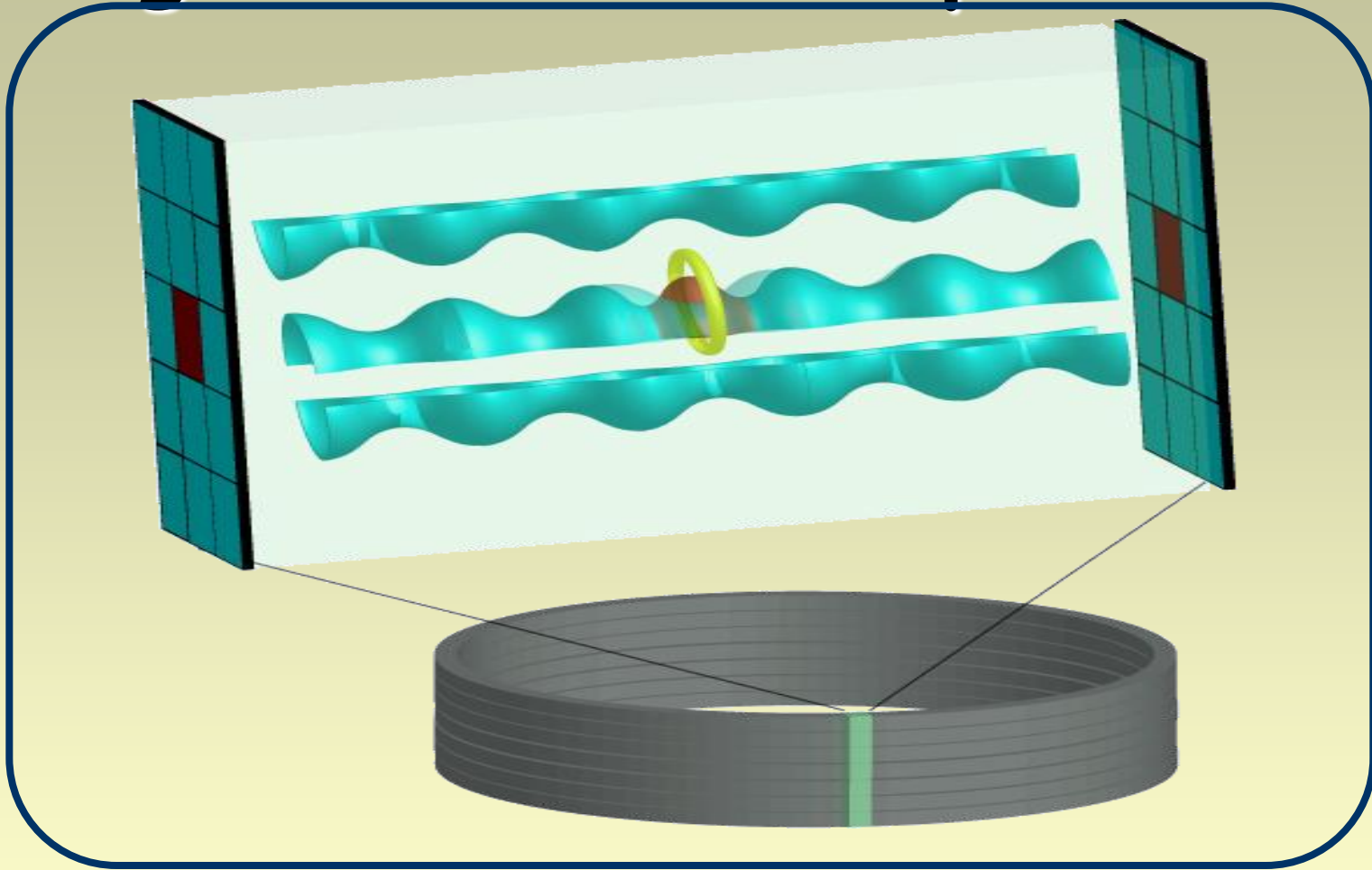


Two curves behave similarly



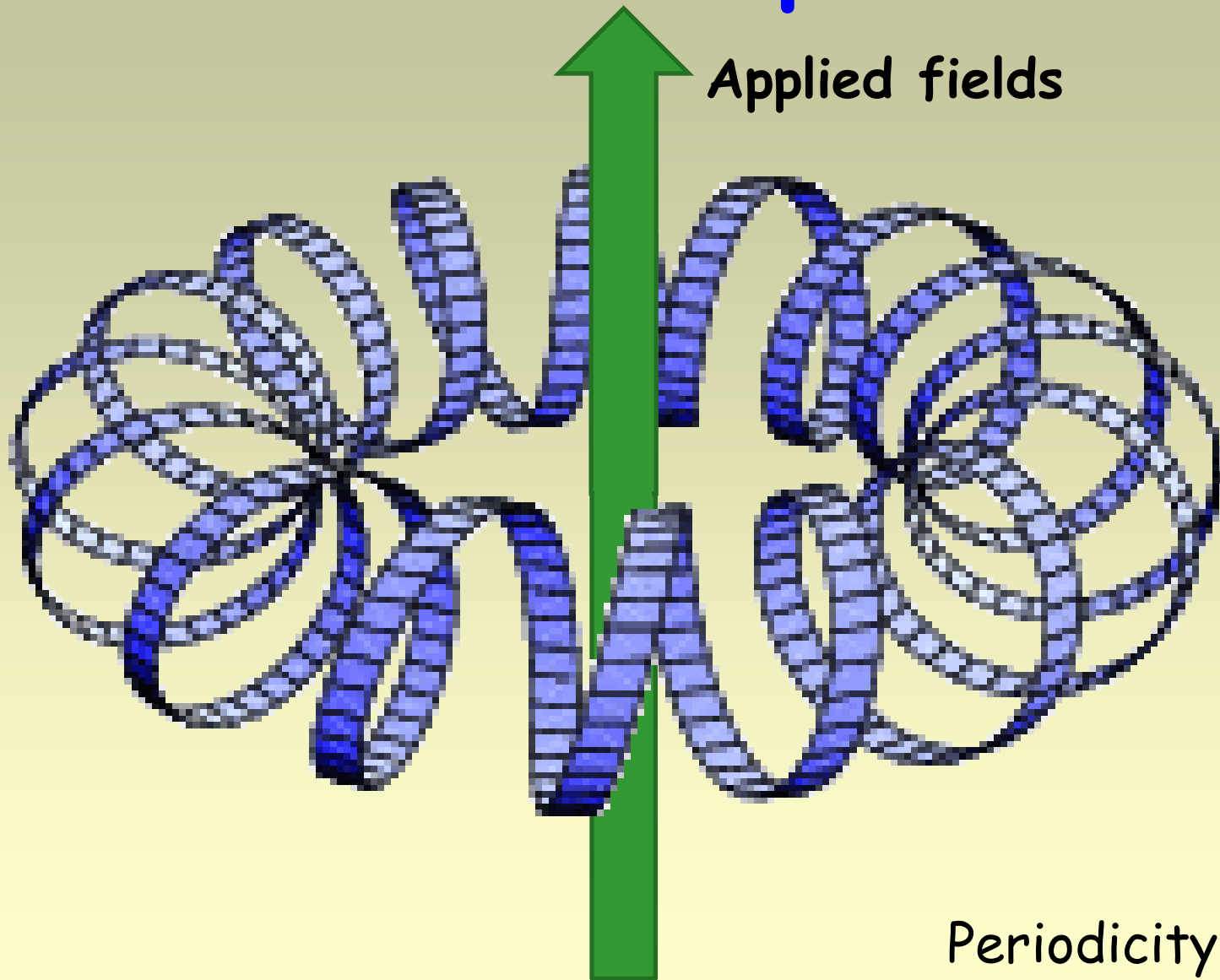
The amplitude of the interference is related with sliding CDW.

Edge dislocation loop : soliton



The dislocation loop of CDW cannot escape from a CDW chain, and provides $2e$ charge.

Quantum Phase Slip in CDW rings



Applied fields

Periodicity $\frac{h}{2e}$

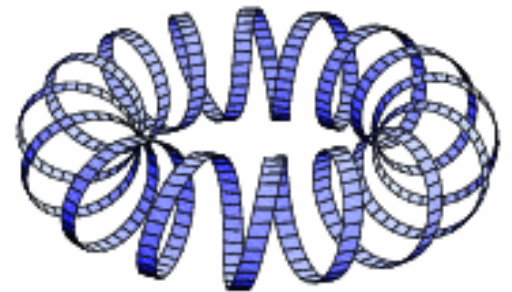
Periodicity $\frac{h}{2e}$

Sliding regime

$$\frac{AB \text{ amplitude}}{CDW \text{ current}} \approx 0.1$$



Ring CDW phase slips



Application of topological crystals

We obtain NbS_3 topological crystals



$T_c=340\text{K}$

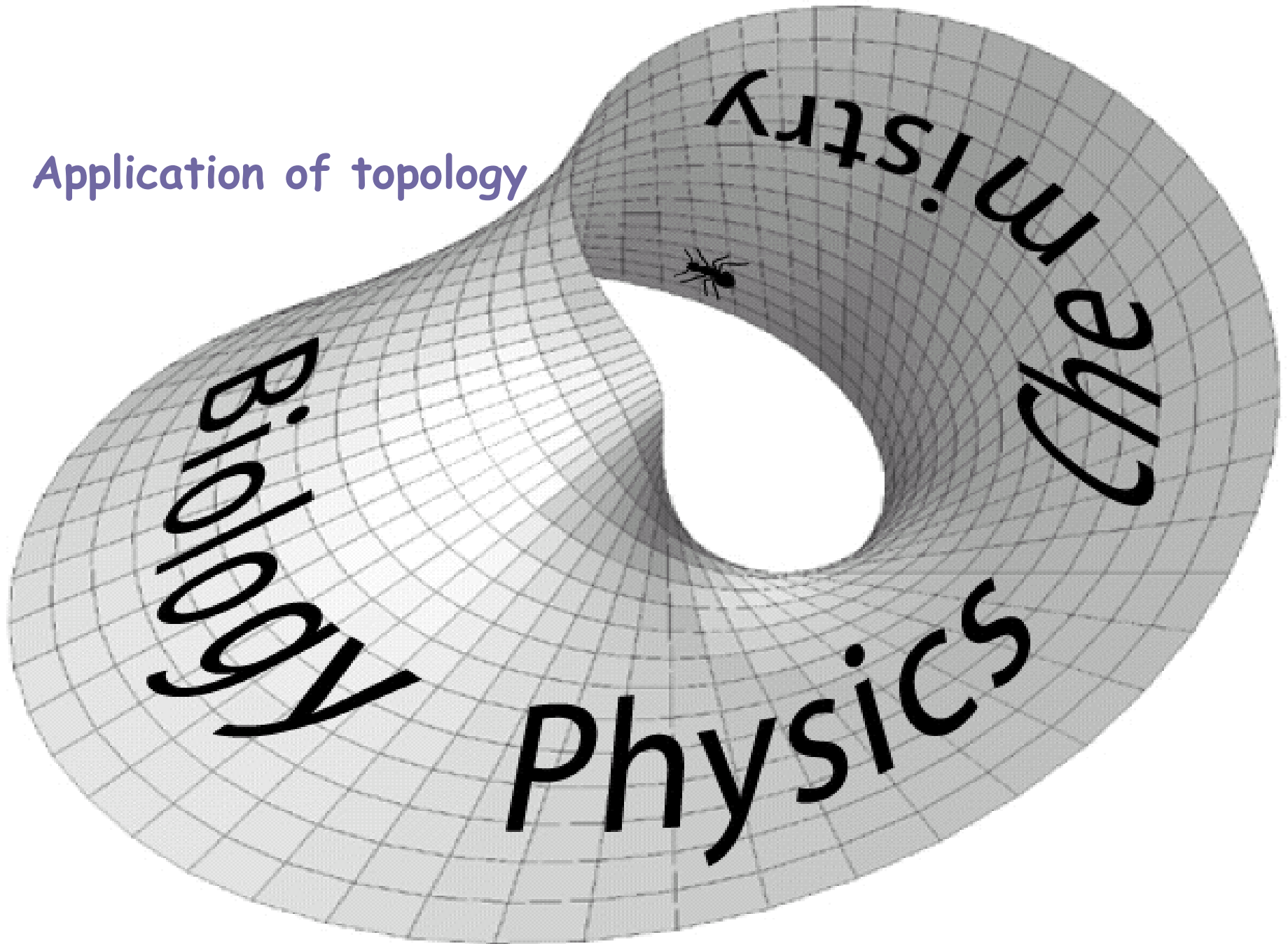
, which have room-temperature Macroscopic-wave function (CDW) !



Room-temperature SQUID



Application of topology



Topology

Biology

chaos



Ribosome

Entanglement
Polymer, Soft-matter

Conformation

RNA, DNA,



Material Science

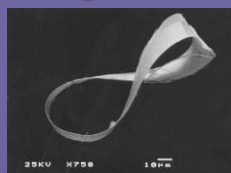
C_{60} , CNT

Organic mat.

Topological Crystals

SDW, CDW

MX_3 , MX_2



Topological Defects

Condensed Matter

p-d-wave

Superconductor

Superconductor

Vortex

He3, texture

Stripes

Topological Insulator

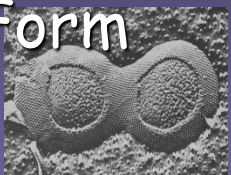
Geometry

Homology

Homotopy

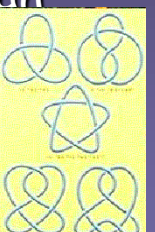
Information

Form



Duality, Non Abelian
Geometry

Knot
theor



Cosmology

Strings

CS Gravity,
Einstein eq.
Black hole



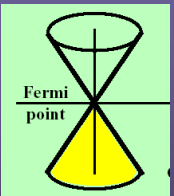
Soliton

Jones eq.

Chern Simon

QHE

Quantum
Anomaly



Spectrum Flow

Helicity

Siberg-Witten

M-Theory

Field Theory

Dirac Monopole
'thoof Monopole

Superconductor

Vortex

He3, texture





Stripes

Topological Insulator

Topology change

Local

Global effects

	Simply connected space : (Cut-ring) 	Multiply connected space :  
Crystals	Cycloid crystals (cut-ring) 	Ring, Mobius, 8, Hopf-link Knots & links crystals Embedding manifold
CDWs	Pinning of CDW at the edge	Frölich superconductor AB effect of CDW
Superconducting vortices	Abrikosov lattice	Cylindrical vortex in ring crystals Knots & Link vortex in 8 crystals

Topology defines the properties of condensed matter

Many Thanks !



色即是空

色=obverse
空=reverse

"Zen": Hakuin (Buddhist)
used Mobius strip in 1758

色=空

Collaboration



AP. Tsuneta Graduate Student
AP. Toshima Graduate Student
AP. Matsuura Appl. Phys of H.U.

Prof. Inagaki Appl. Phys of H.U.

Prof. Yamaya Appl. Phys of H.U.

Dr. Uji National Research Inst. of materials, Japan

Hokkaido
University



Nobel Prize
2010

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Prof. Volovik Helsinki Univ. of Tech., Finland

Prof. Hatakenaka Hiroshima Univ., Japan

Prof. Niemi, Uppsala Univ., Sweden

Prof. Osipov Bogoliubov Institute, Russia

Prof. Matsuyama Nara edu Univ., Japan

Finland

Theory

