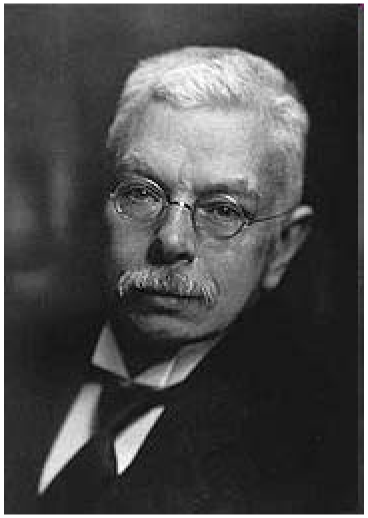
Electron Spin Resonance in High Magnetic Fields

Sergei Zvyagin

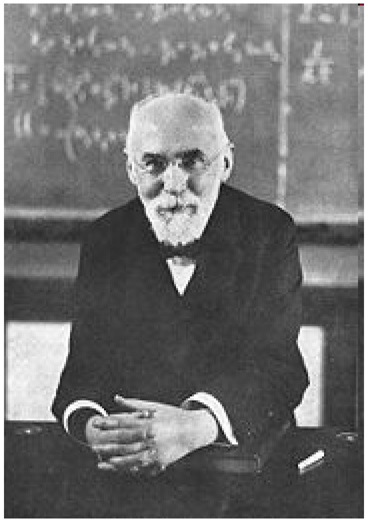
Dresden High Magnetic Field Laboratory (HLD)
Helmholtz Zentrum Dresden – Rossendorf
Dresden, Germany

Historical Perspective

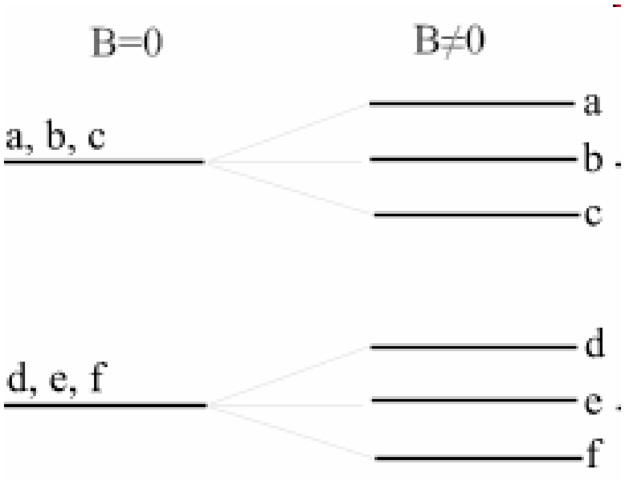


Pieter Zeeman

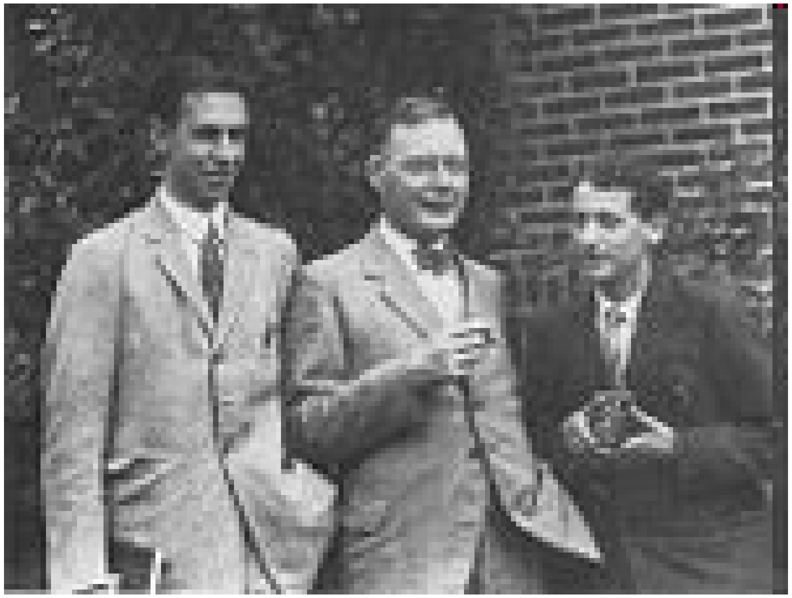
1902: Nobel Prize in Physics for discovery of the Zeeman effect

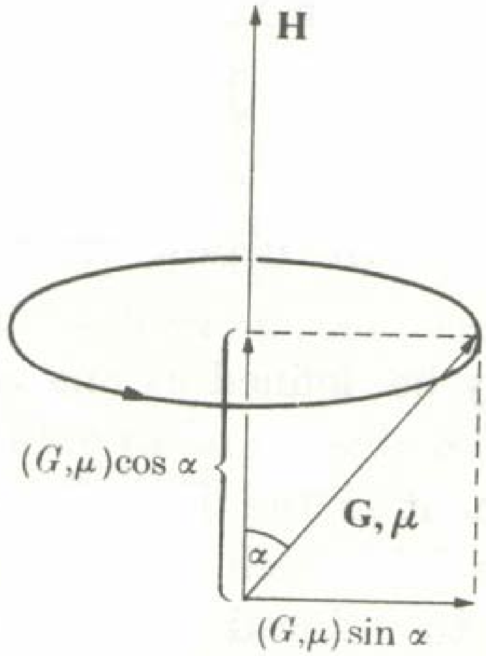


Hendrik Lorentz



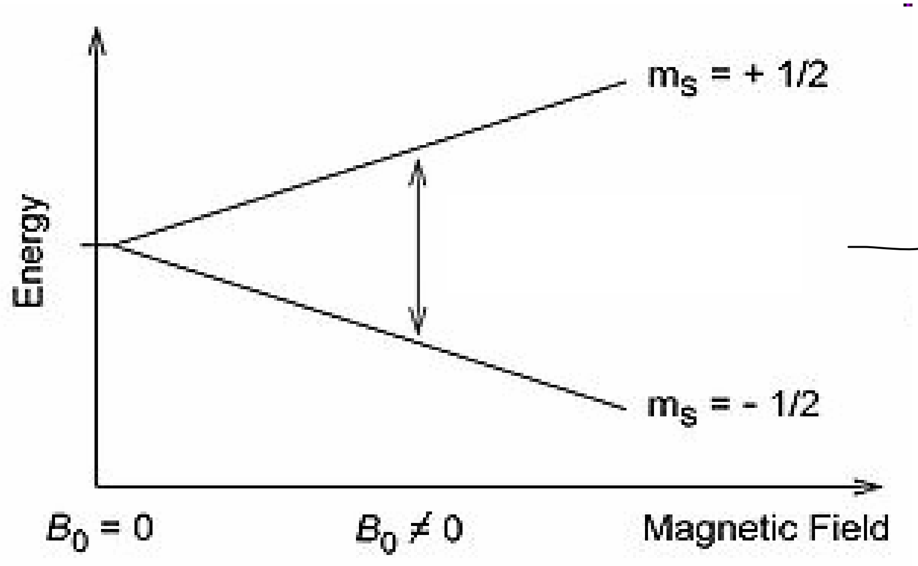
1925: *Uhlenbeck* and *Goudsmit* link the electron magnetic moment with the concept of electron spin angular moment

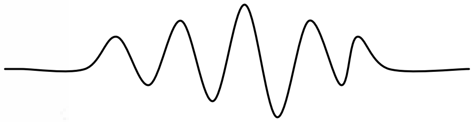




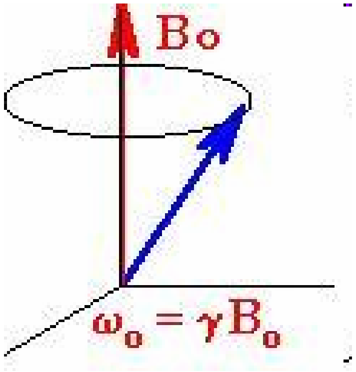
$$\mu = \gamma\, G$$

1938: *Rabi* studied transitions between spin levels induced by an oscillating magnetic field





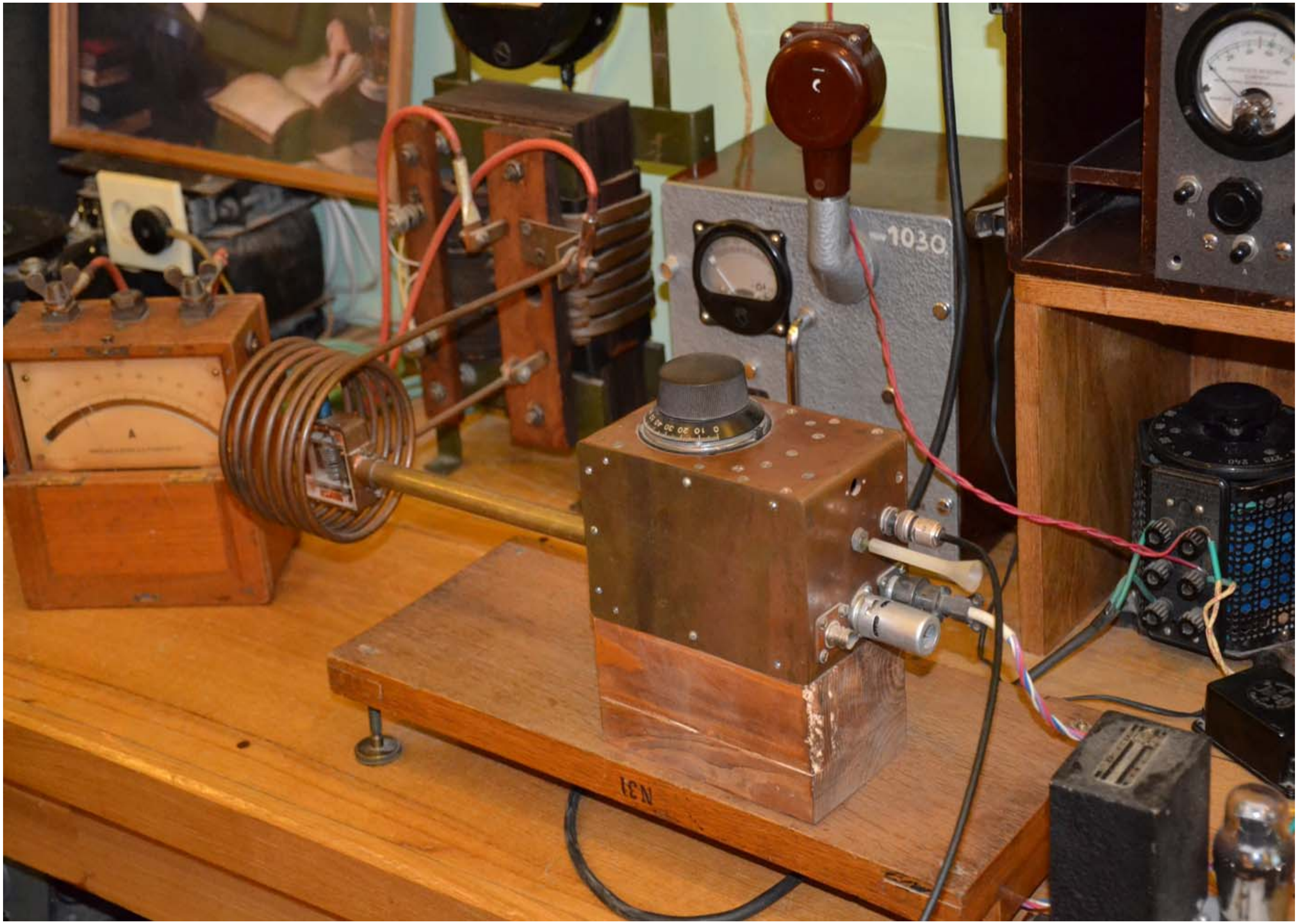
$\Delta E = h\nu_0$



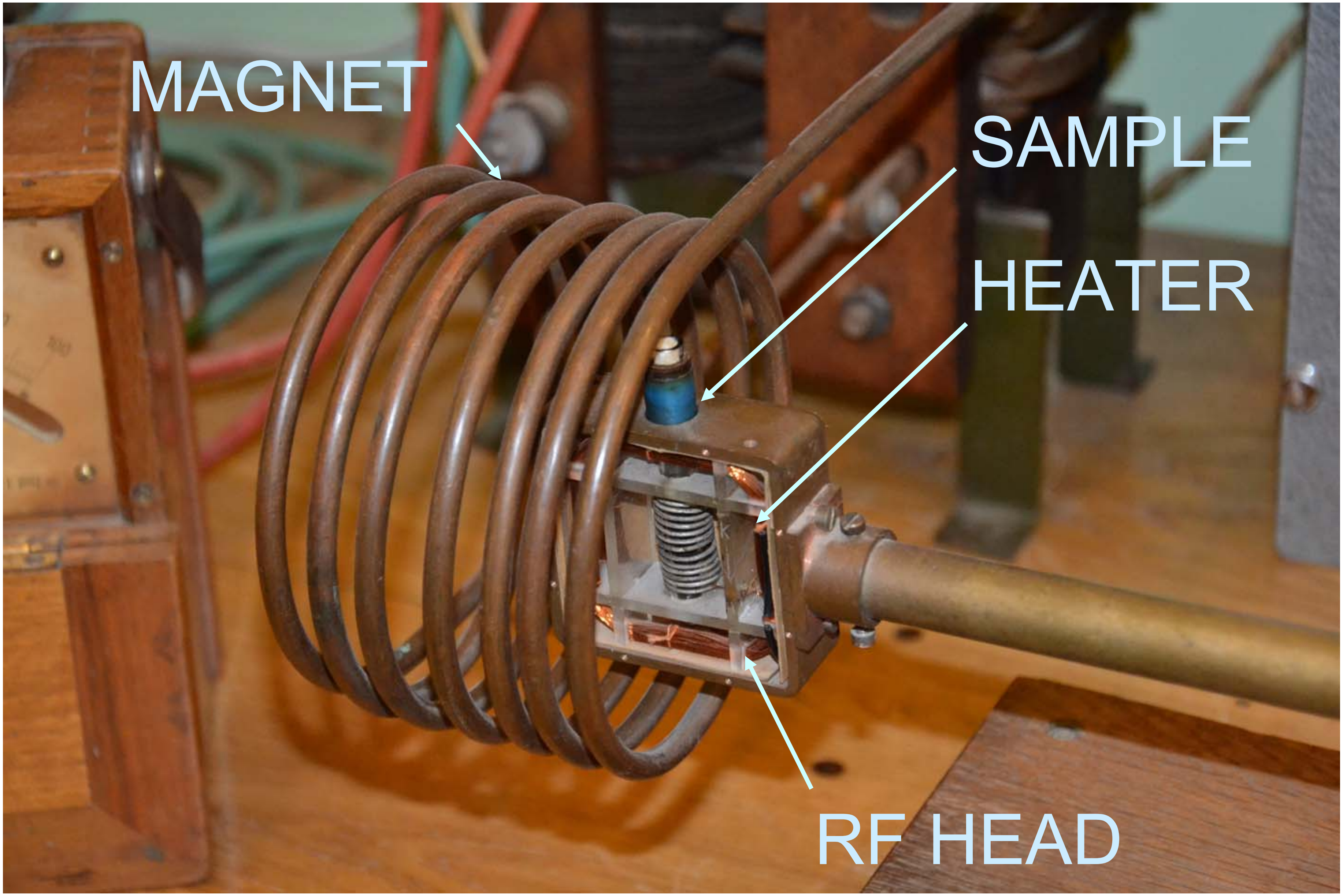
1944: discovery of EPR by *Evgeny Zavoisky* (Kazan University, USSR)

1946: further development of EPR by *Brebis Bleaney* (Oxford University, UK)

First EPR spectrometer



10 MHz, 7.5 Oe



1950s: rapid development of microwave technology (radar techniques)

50-60s: Major contributions toward the ESR spectrum interpretation (laser technologies)

Late 50s: pioneering high-field ESR works of M. Date in Japan

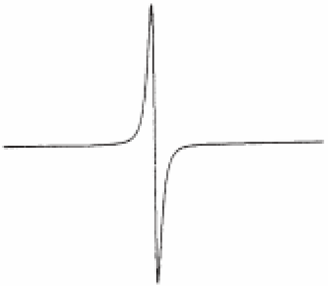
60-70s: ESR in USSR, France and Germany

90s: ESR in UK, USA, Hungary, Italy, etc.

ESR = Electron Spin Resonance =
EPR = Electron Paramagnetic Resonance =
EMR = Electron Magnetic Resonance

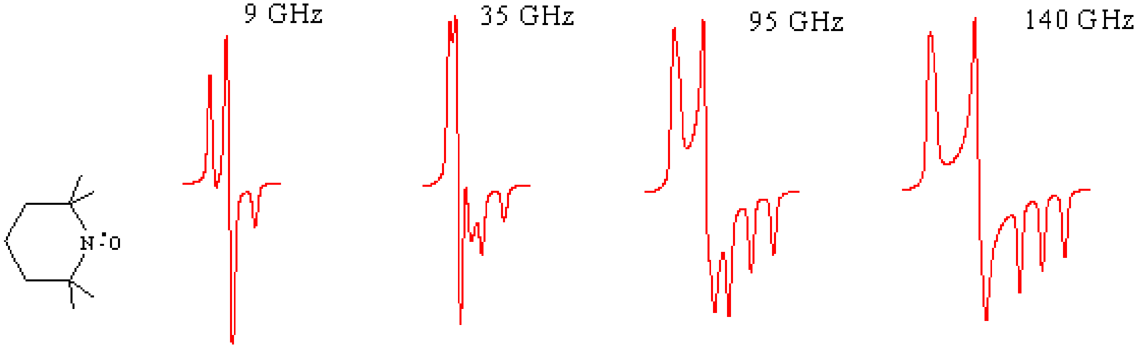
Commercially available
spectrometers:
1-2 GHz (L-band)
2-4 GHz (S-band)
8-10 GHZ (X-Band)
35 GHz (Q-band)
95 GHz (W-band)
263 GHz (mm-wave)

Fixed parameters: frequency
Variable parameters: field, temperature, angle

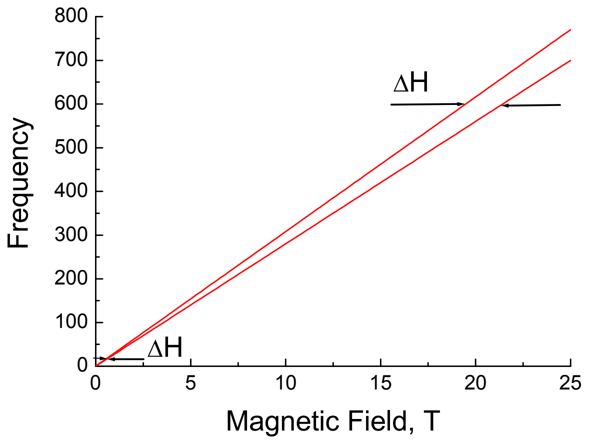


Lack of commercially-available multi-frequency ESR spectrometers

1. Better *g*-factor resolution in powders



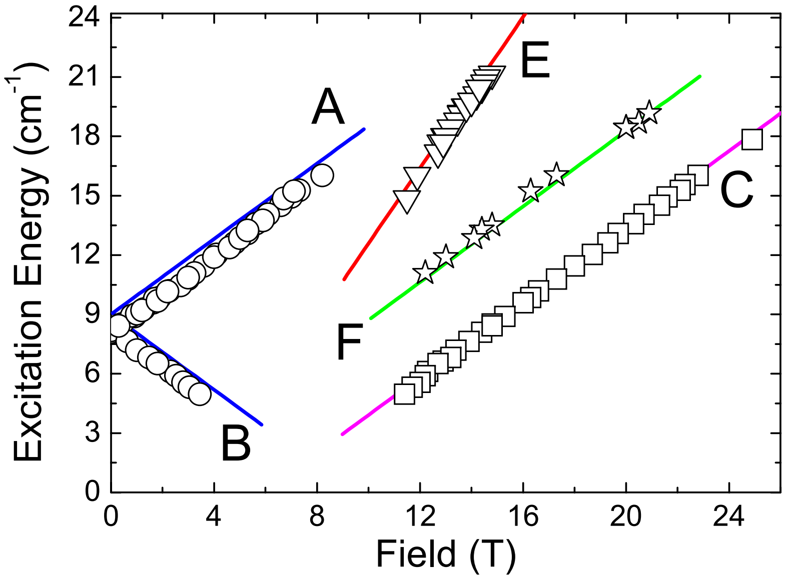
EPR spectra of a nitroxide radical as a function of frequency



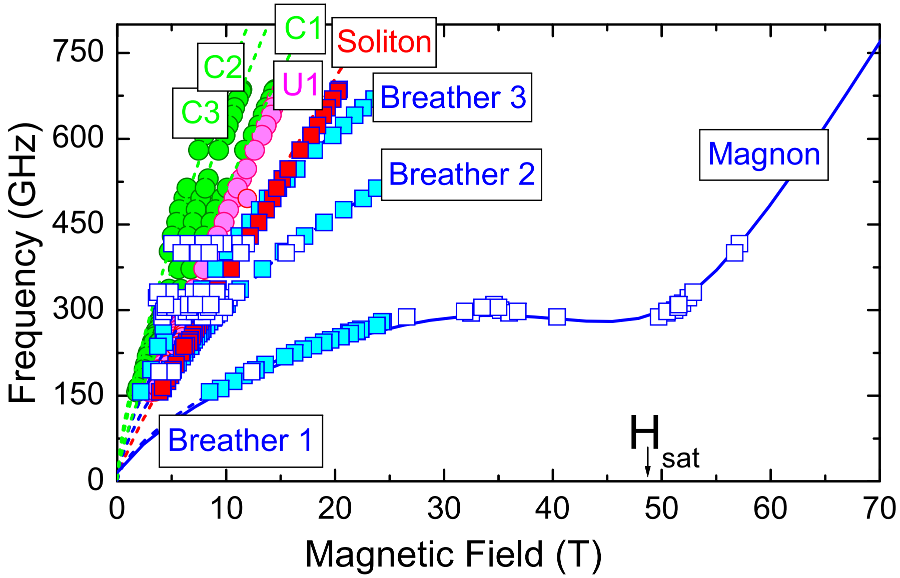
Strong needs of high-frequency and field ESR techniques

Why high-field and multi-frequency?

2. Excitations with a finite zero-field splitting
3. Excitations with nonlinear frequency-field dependences

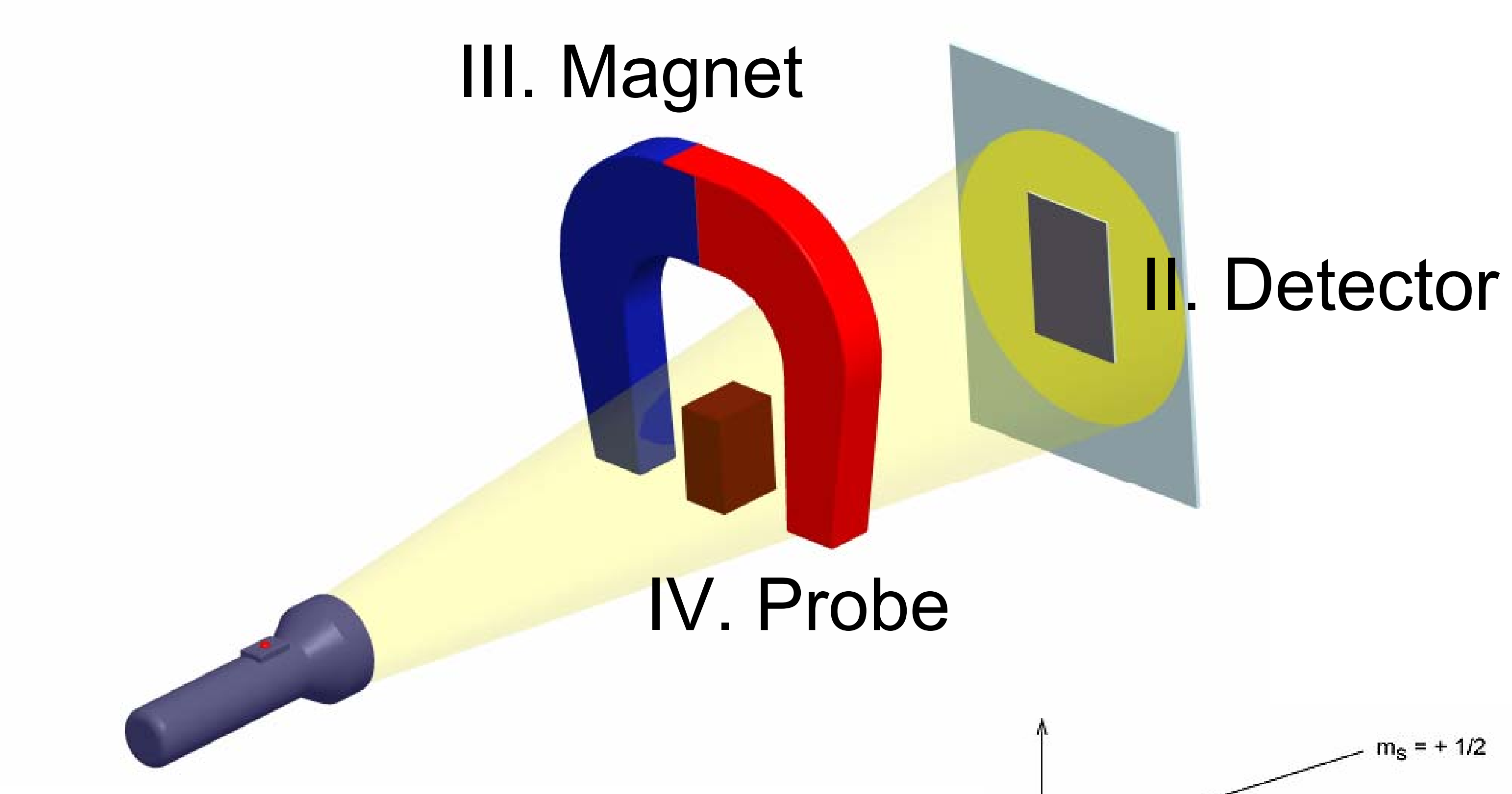


S=1 chain material DTN



S=1/2 chain material Cu-PM

Strong needs of high-field and multi-frequency ESR techniques

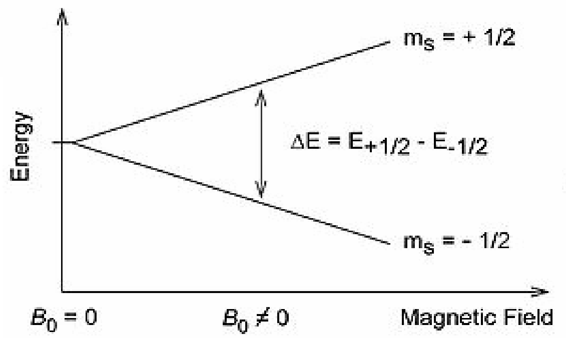


III. Magnet

II. Detector

IV. Probe

I. Radiation source,
cm, mm, sub-mm range

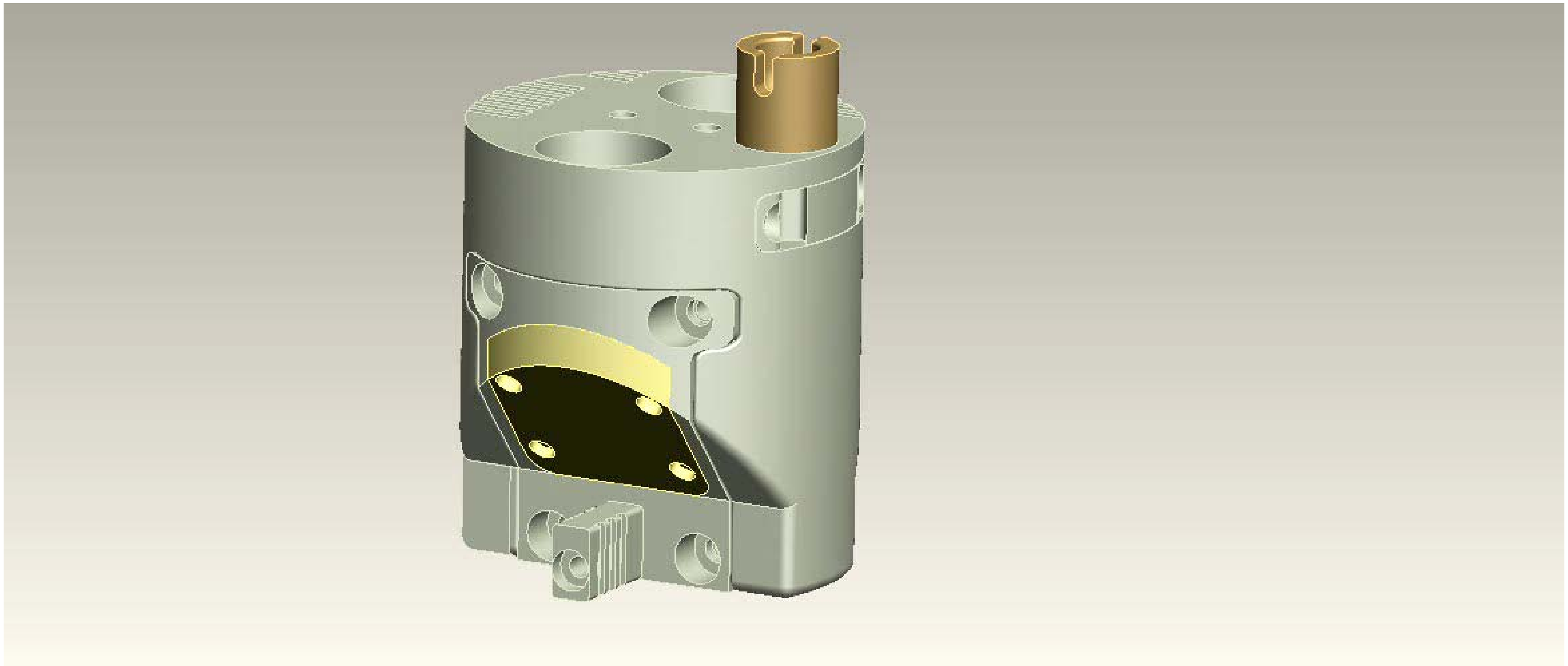


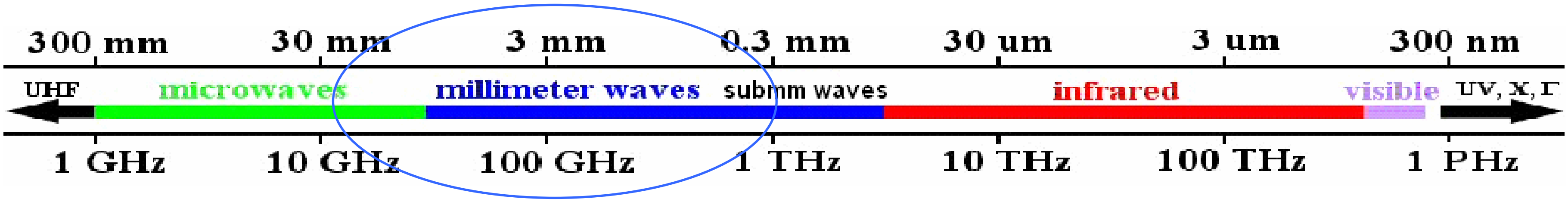
Multi-frequency ESR spectrometers:
using oversized wave-guides and quasi-optical approaches .


07/23/2010


07/23/2010

ESR spectrometer sample-holder





10 – 1000 GHz - 5 – 50 K

❑ Possibility of working with small samples (at least one dimension can be be $\sim\lambda/2$: 300 GHz → d=0.5 mm)

❑ High spectral resolution (~ 10^{-4} - 10^{-5}) and sensitivity (10^{9} – 10^{12} spins)

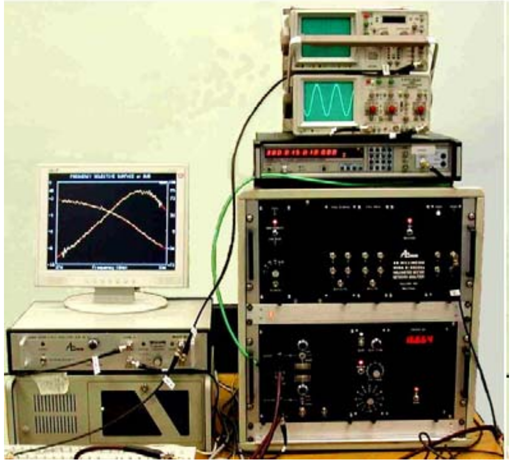
❑ ESR in high magnetic fields is possible (no principle limitations; HLD: 63 T pulsed field routinely available)

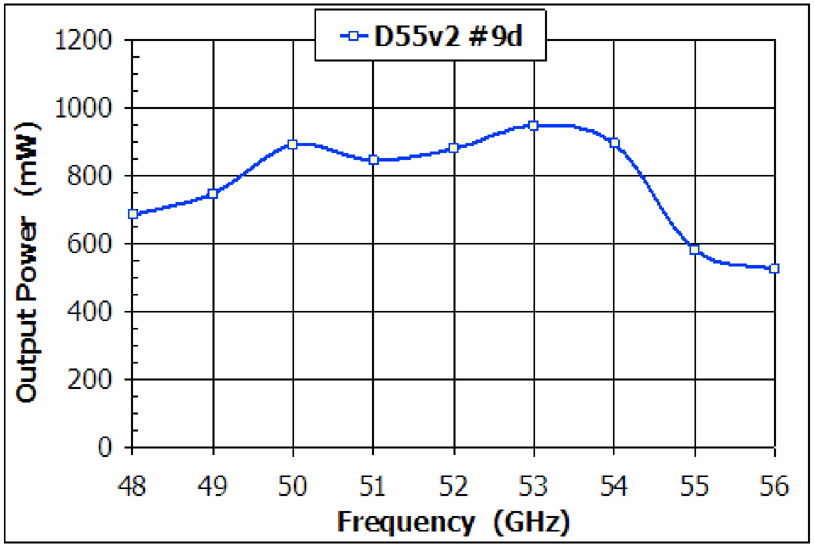
❑ Deutoration is not needed

❑ Extendable frequency range

Solid-state generators

VDIs, Gunn-diodes, IMPATT-diodes, MVNA



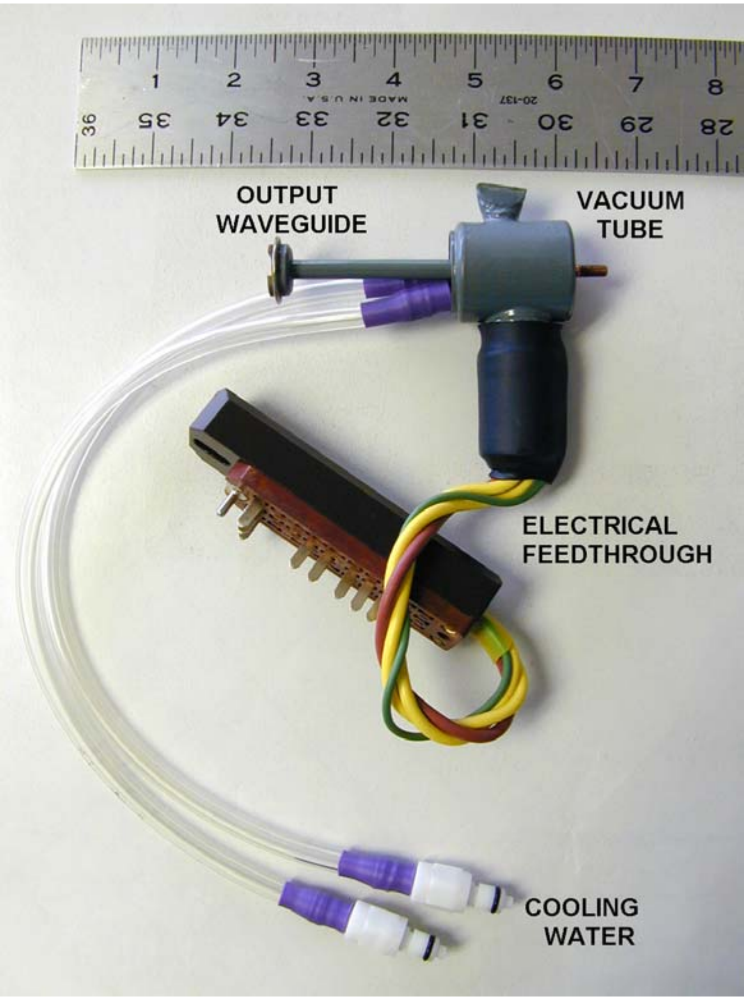


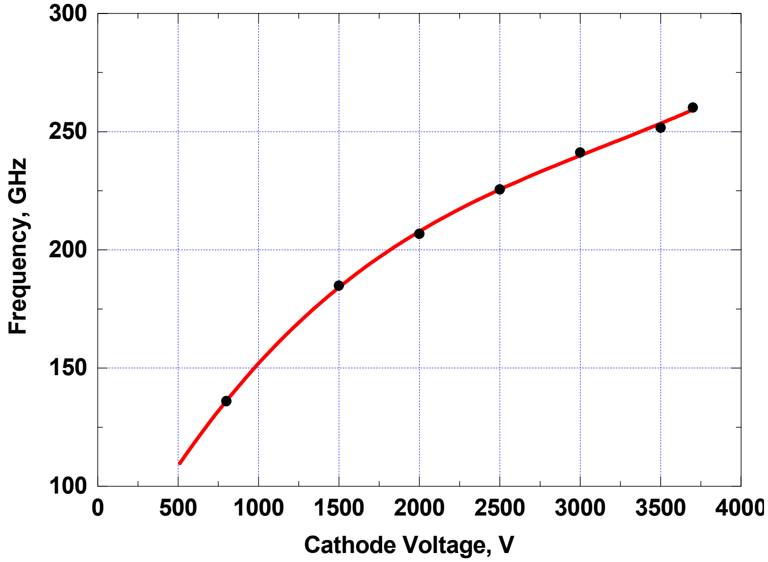
- •Approx. up to 700 GHz
- •Advantages: easy-to-operate, stable, low phase noise

www.virginiadiodes.com
www.millitech.com
www.abmillimetre.com

Backward-wave oscillators

(30 – 1300 GHz / set of 12 BWOs)





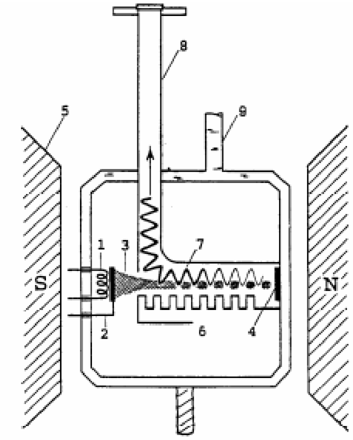
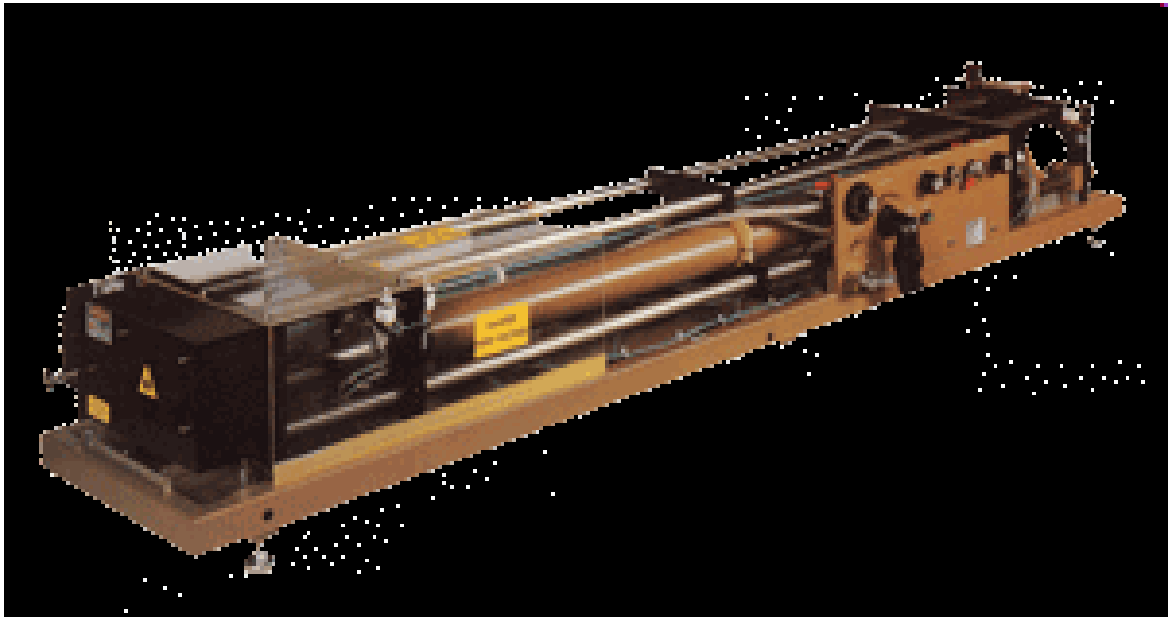


Fig. 3.2. Schematic diagram of backward wave oscillator: *1* – heater, *2* – cathode, *3* – electron beam, *4* – collector (anode), *5* – permanent magnet, *6* – slowing system, *7* – electromagnetic wave, *8* – waveguide, *9* – water cooling

Optically pumped molecular laser

0.25 to 7.5 THz

Producer: Edinburgh Instruments

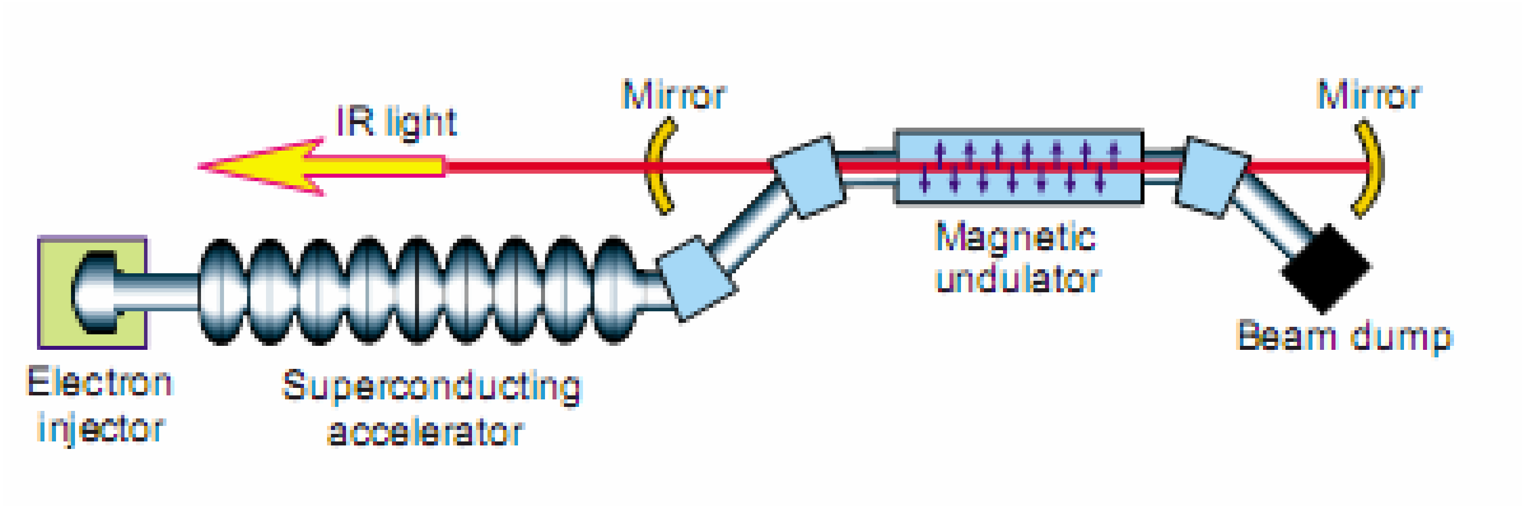


Advantages: several frequencies available, high output power

Concerns: poor stability

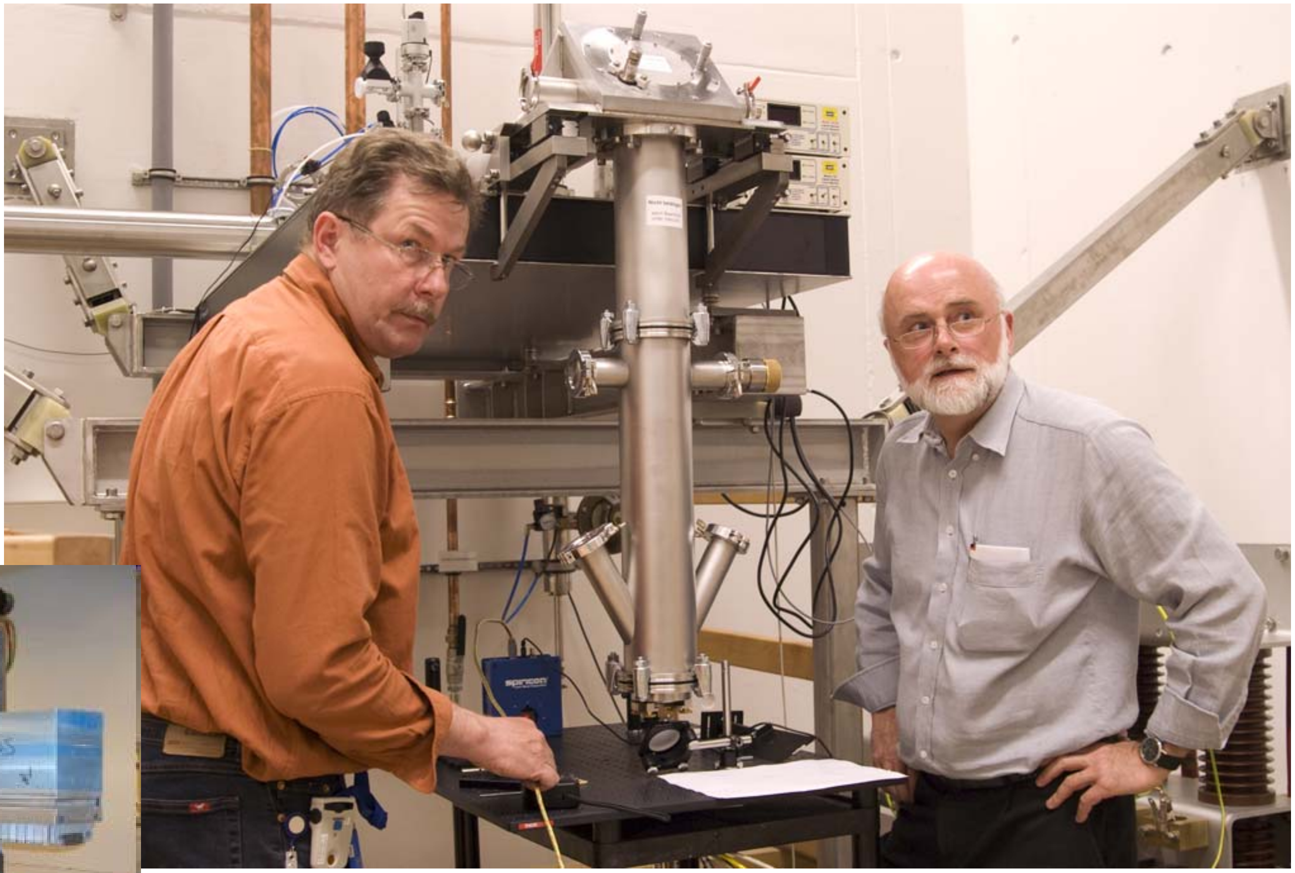
www.edinst.com/fir.htm

Free-electron laser



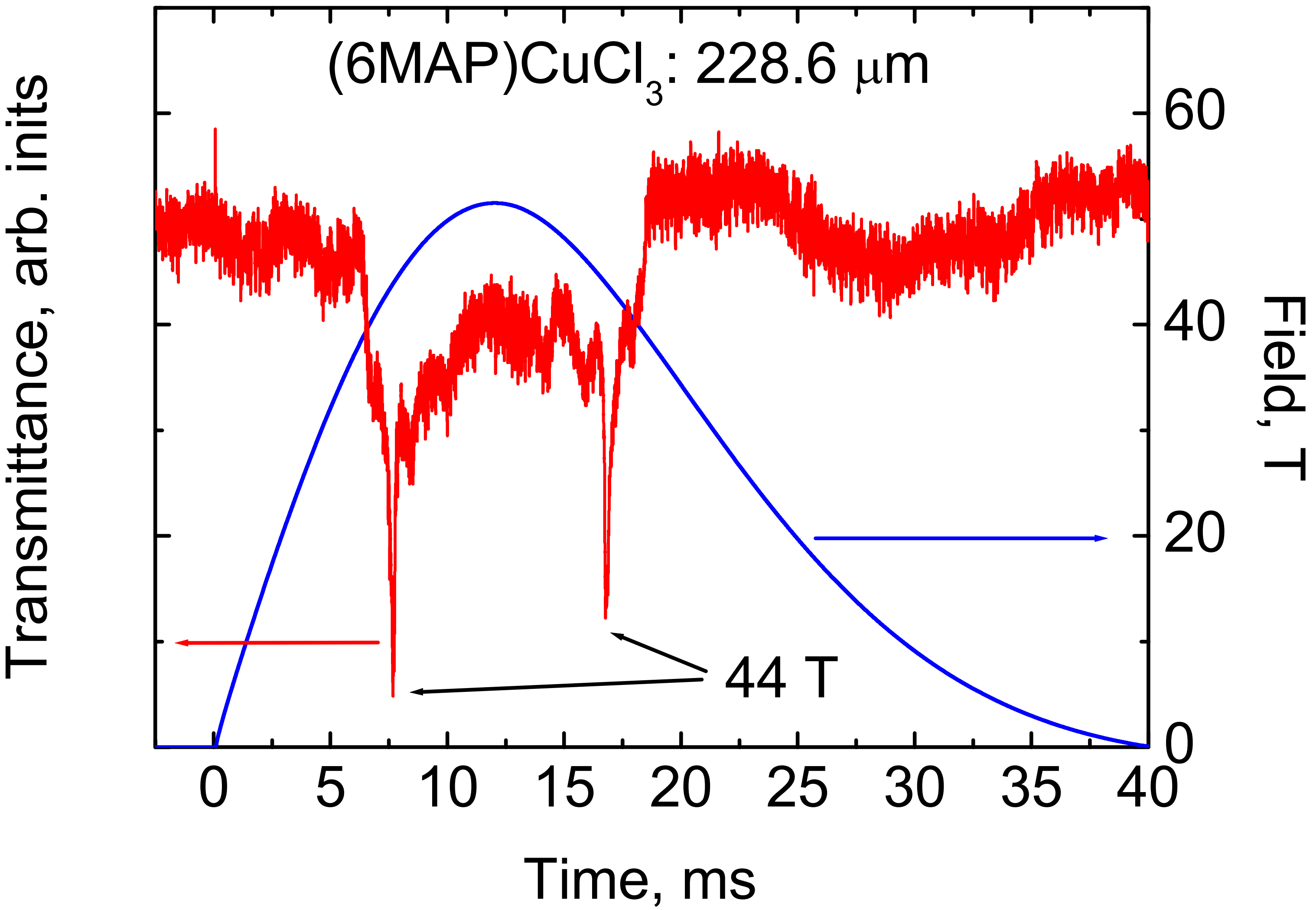
Advantages: tunability, high output power

Free-electron Laser at RZ Dresden-Rossendorf
1.2 – 75 THz, quasi-CW mode

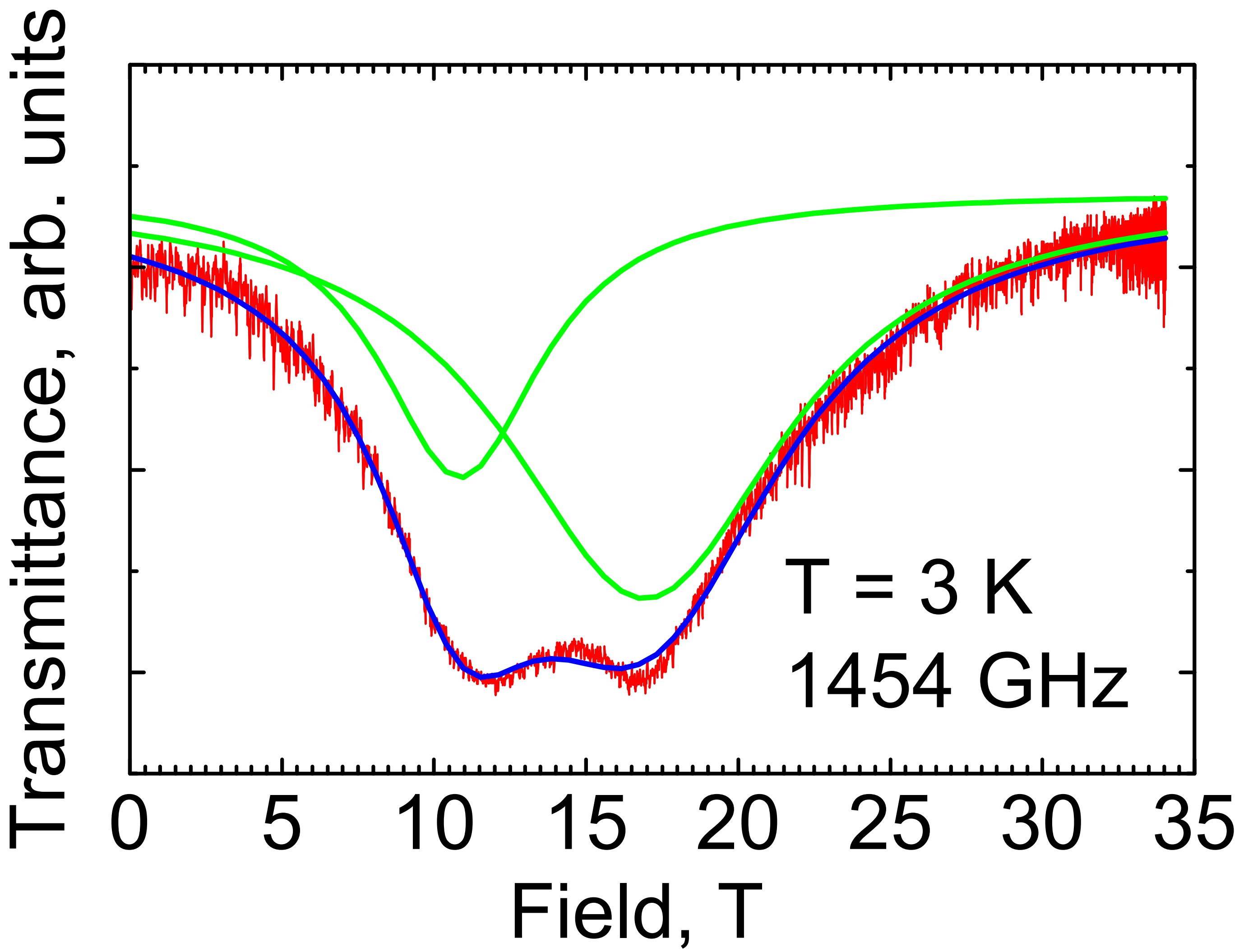


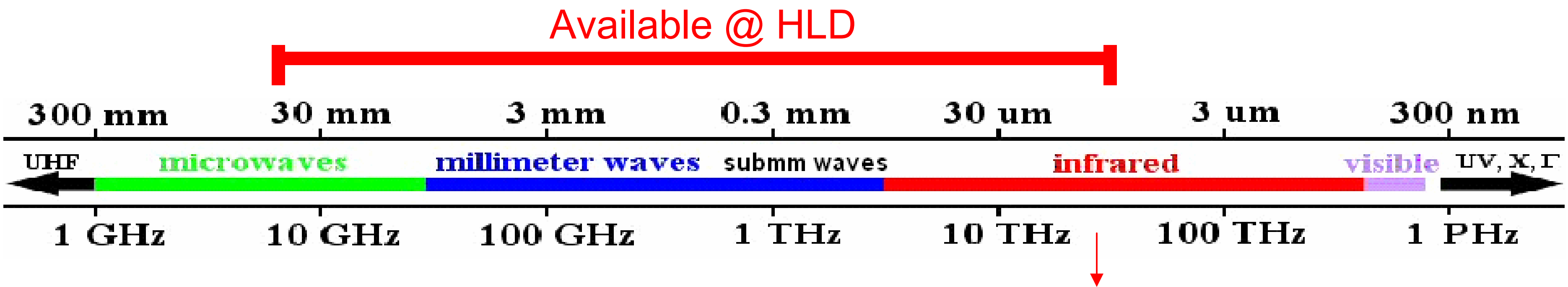
S.Z. et al., RSI 80, 073102 (2009)

Pulsed-field FEL ESR in (6MAP)CuCl3

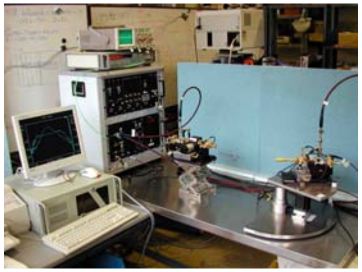


Pulsed-field FEL ESR in YMnO3



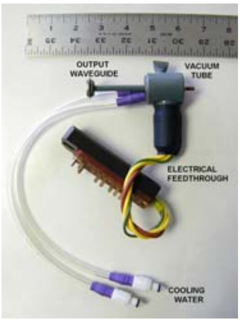


X-band Bruker
9 GHz



Microwave Network Analyzer
30 – 1000 GHz

Free Electron Laser @ ELBE
1.2 – 75 THz



Backward Wave Oscillators
30 – 1300 GHz

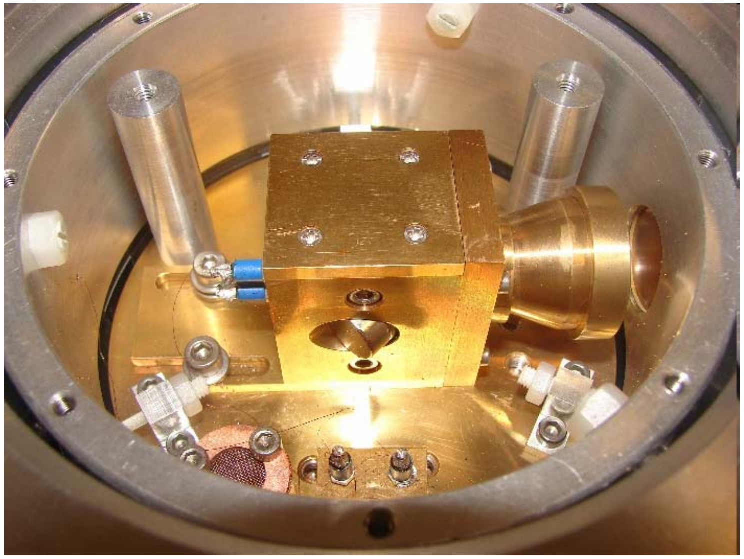
Gunn/Schottky Diodes
22 – 300 GHz

Frequency: 9 GHz – 75 THz

Temperatures: down to 1.4 K
(0.3 K in progress)

Magnetic Field: up to 16 T (SCM)
and 63 T (pulsed-field)

Detector
n-InSb hot electron bolometer (“QMC Instruments”)

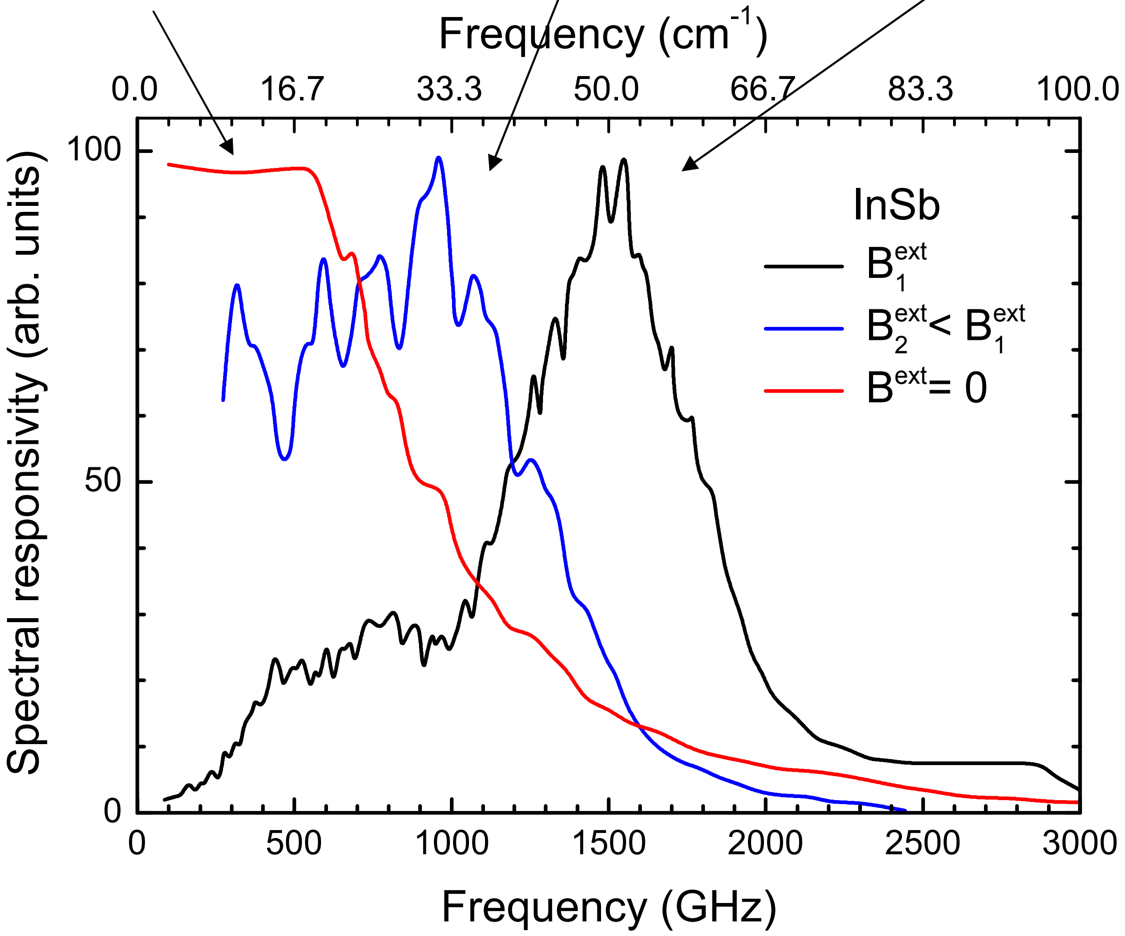


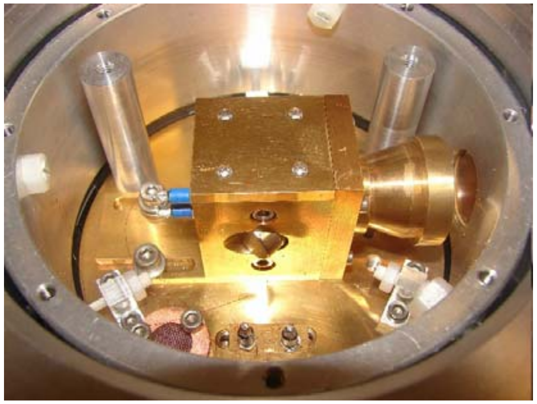
- *www.terahertz.co.uk*

Inhomogeneously detuned

Homogeneously detuned

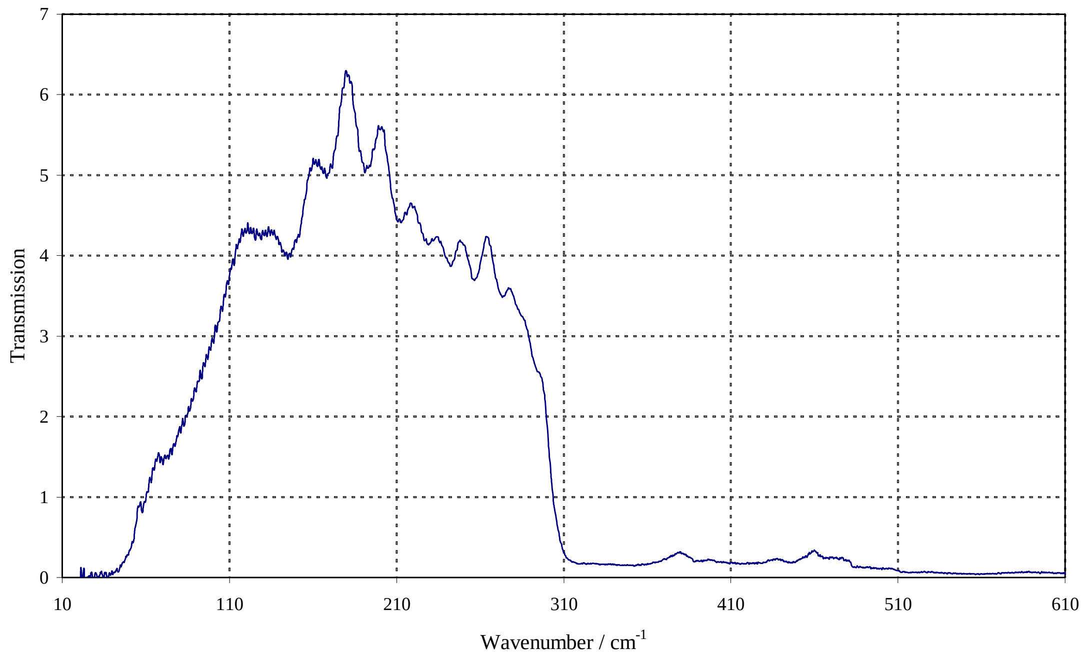
Original Response



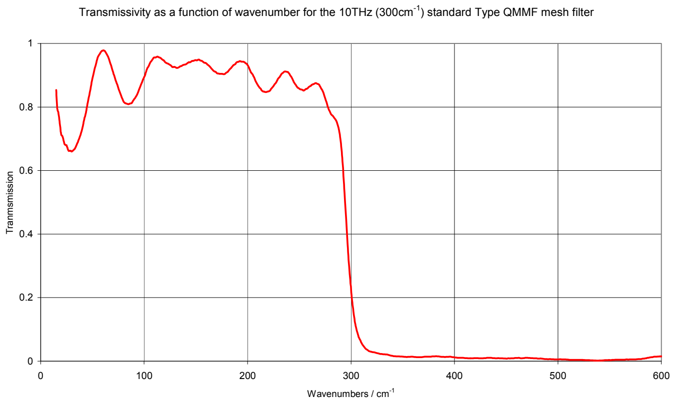


Ga:Ge bolometer ("QMC Instruments")

Ga:Ge bolometer + low-pass filter

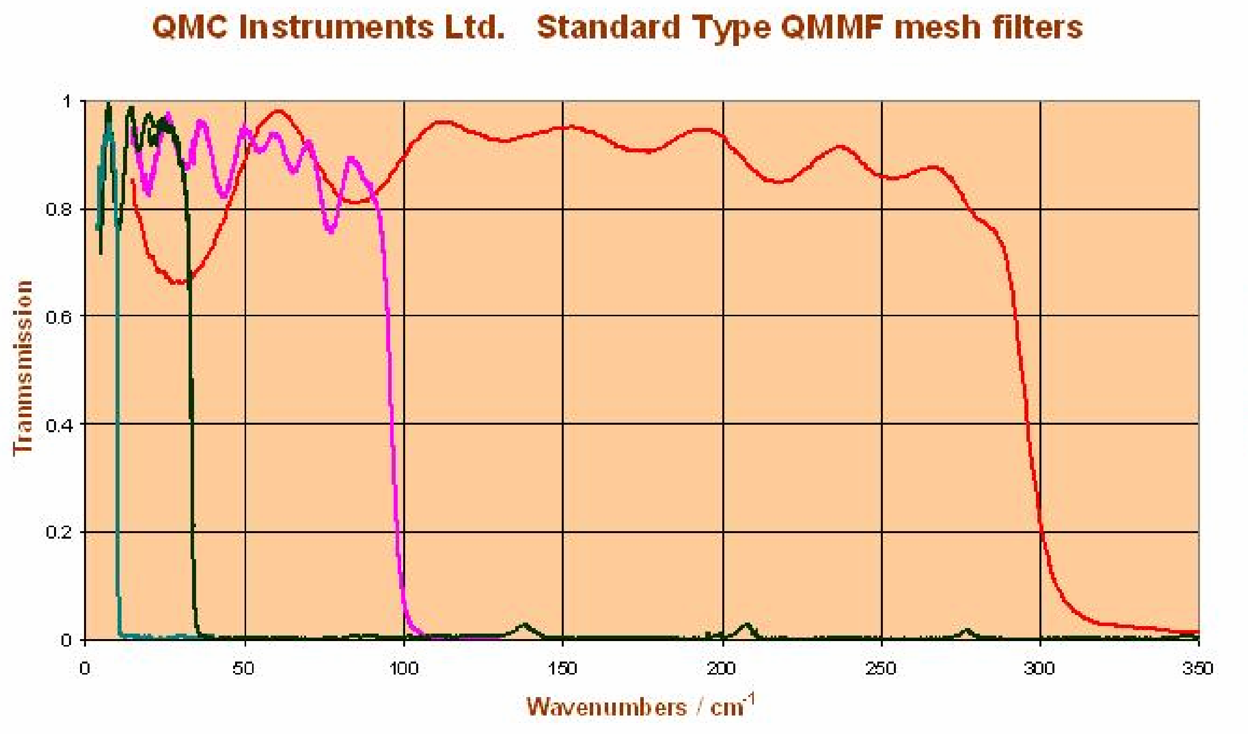


Low-pass filter



M.F. Kimmitt, Far-Infrared techniques

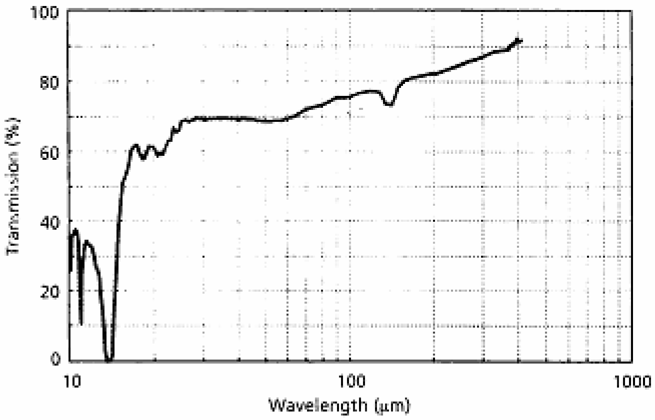
Materials for filters



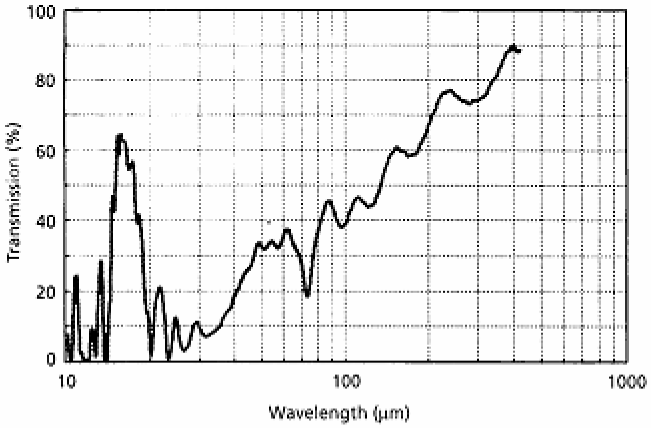
www.oxford-instruments.com
www.tydex.ru
www.terahertz.co.uk

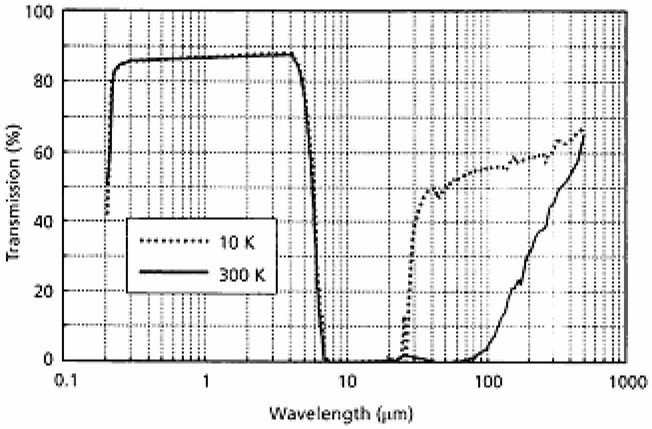
Materials for windows

Polythene

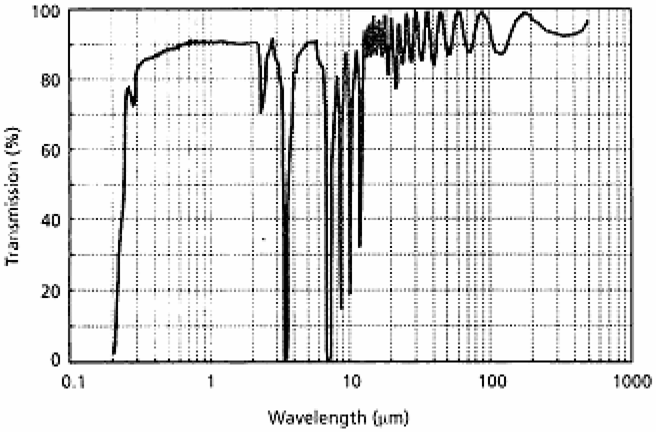


Mylar





Sapphire

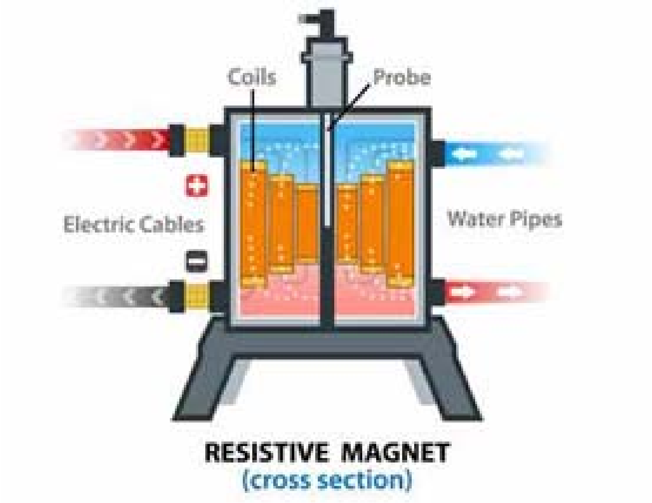


Polypropylene

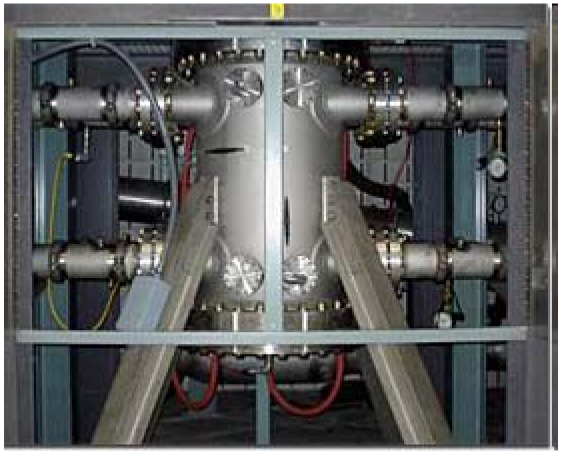
Magnets

Superconducting magnets
Up to **22 T**

Resistive magnets
Up to **35 T**, Tallahassee,
Nijmegen, Grenoble,
Sendai]



Hybrid magnets
Up to **45 T**,
Tallahassee



www.oxford-instruments.com

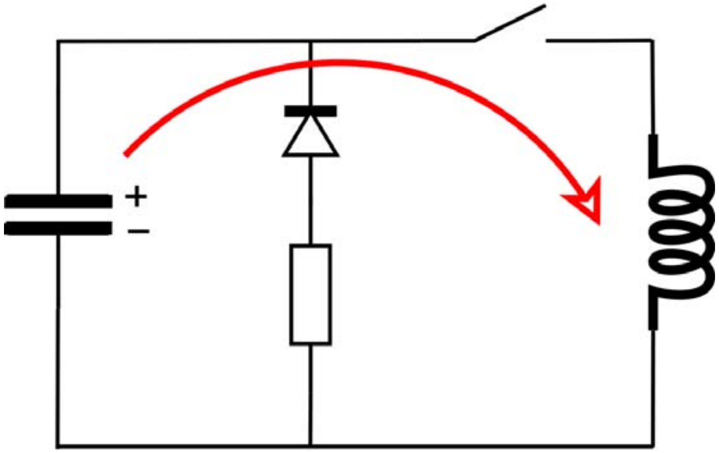
www.magnet.fsu.edu

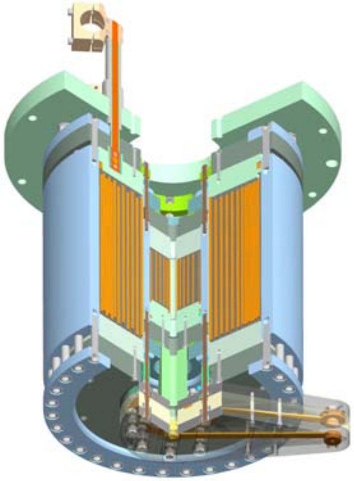
Pulsed-field magnets

up to **100 T** (multi-turn nondestructive): Los-Alamos (100.75 T), Toulouse, Dresden, etc.

up to ca **300 T** (single-turn destructive): Los Alamos, Toulouse, Tokyo

up to **2800 T** (flux-compression): Sarav (Russia)





Nondestructive magnet (pulse duration – up to 200 - 300 ms)

Destructive single-turn magnet (pulse duration ~ 10 us)

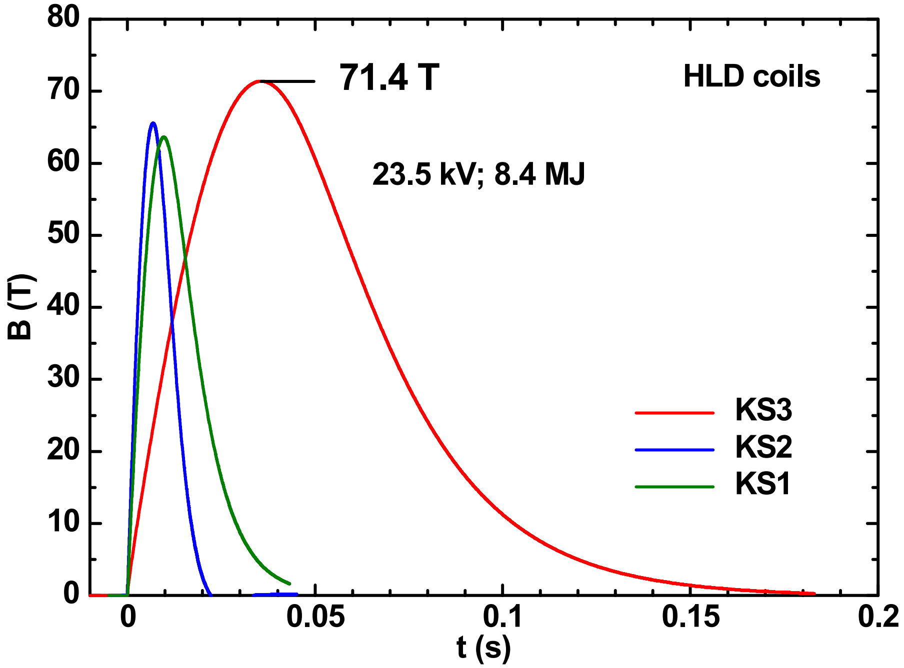
Flux compression by explosives in Sarov, Russia ⇒ 2800 T.

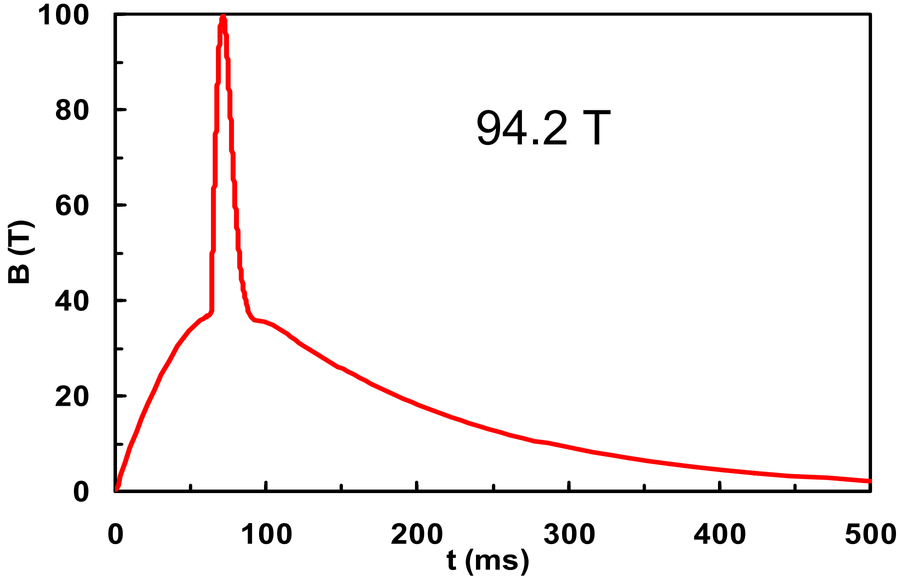
Dresden High Magnetic Field Laboratory (HLD) at HZ Dresden – Rossendorf

Since Summer 2008
Pulsed Field **User** Facility

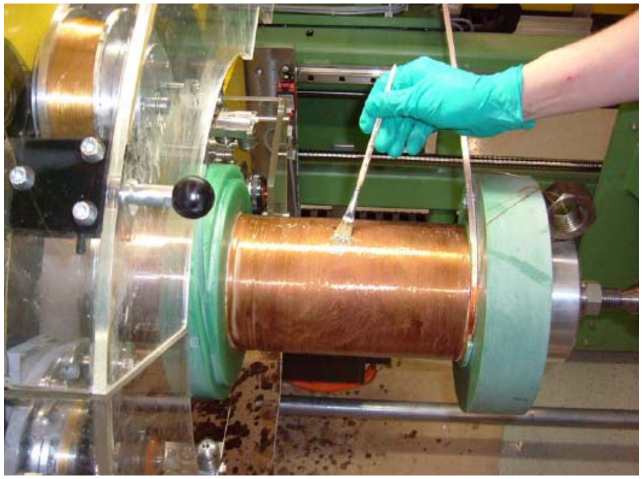
Since January 2009 a part of the consortium
European High Magnetic Field Laboratory
Grenoble, Nijmegen, Toulouse, and Dresden

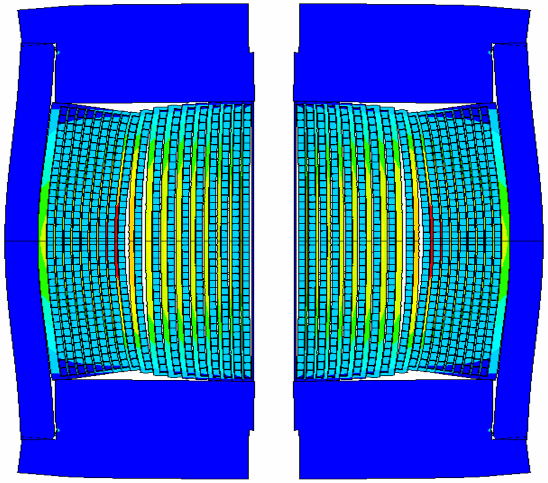
Pulsed-field techniques available at HLD:
- ☐ El. Transport
- ☐ ESR
- ☐ Ultrasound
- ☐ Magnetization
- ☐ Magnetostriction
- ☐ NMR (in progress)
- ☐ Field record: 94.2 T


71.4 T
HLD coils
23.5 kV; 8.4 MJ
KS3
KS2
KS1
B (T)
t (s)
0
10
20
30
40
50
60
70
80
0
0.05
0.1
0.15
0.2


94.2 T
B (T)
t (ms)
0
20
40
60
80
100
0
100
200
300
400
500

- Extremely high Lorentz force ($F = j \times B$) leads to huge mechanical stress in the magnet
- Thermal shock: $Q = \int R(T(t),B(t))I^2(t)dt$
- Dynamic effects: eddy current ~ dB/dt;
- mechanical inertial effects
- Electric fields: operational voltage of
- 10 - 24 kV





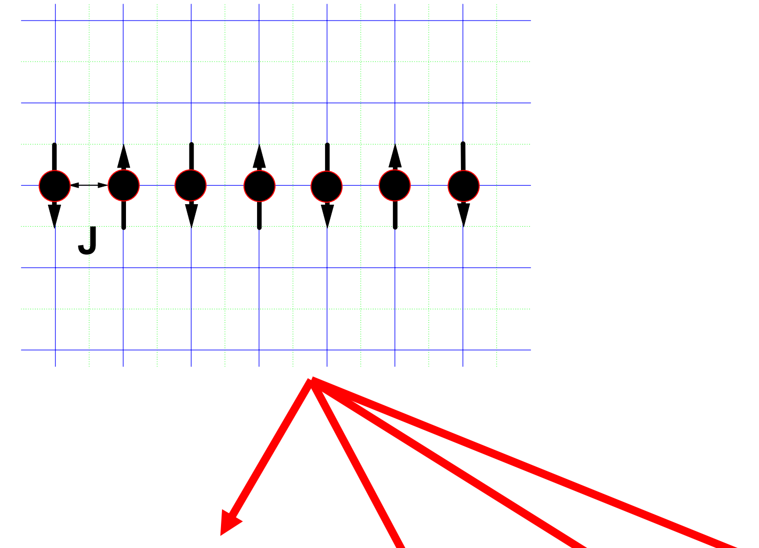
How much energy is 50 MJ?

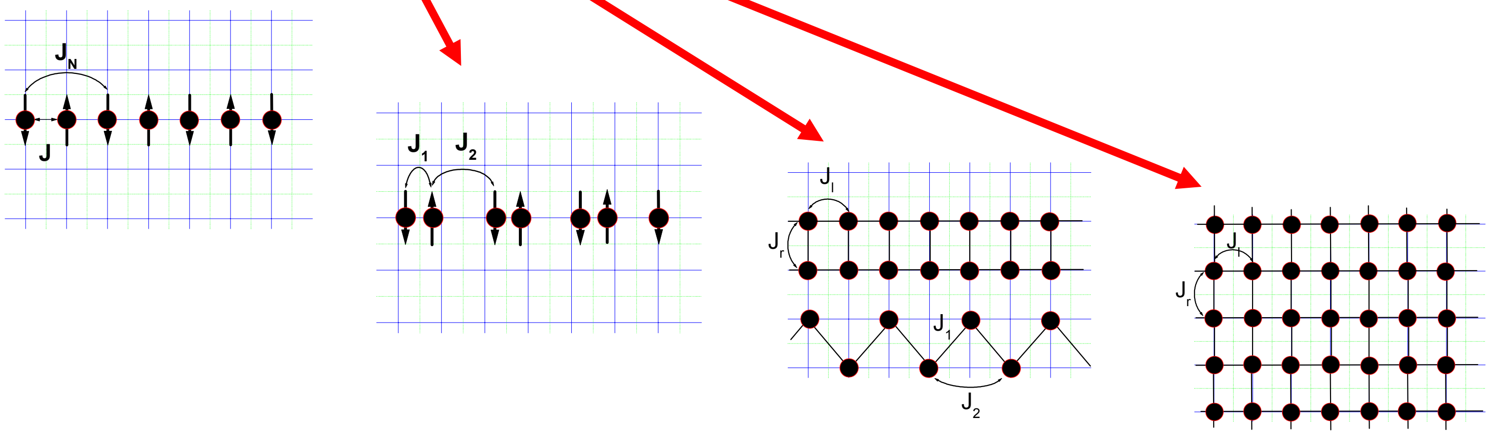
60 tons going at
150 km/h

Let’s talk about applications

ESR as a tool to study magnetic excitations in low-D quantum systems

Diversity of low-D magnets





, etc.

Three reasons to study low-dimensional magnets

1. Ideal ground for testing various theoretical concepts.
2. Understanding the role of quantum fluctuations which are significantly enhanced in low-D systems
3. Extending models to more complex systems (superconductivity, heavy-fermions, etc.)

Outline of the “scientific” part of the talk

Brief review of our ESR experiments with some examples relevant to previous presentations. Among them:

- ☐ Spin dynamics in spin-1/2 Heisenberg AF spin chains
- ☐ Spin dynamics in spin-1 quantum chains with anisotropy
- ☐ On-going projects on frustrated magnets (Cs_2CuBr_4, azurite)

Spin dynamics of S=1/2 Hesienberg AFM chains in magnetic fields

M. Ozerov, J. Wosnitza – Dresden HMF Lab/HZDR, Dresden, Germany
E. Čižmár – Safarik University, Koisice, Slovakia
J. Krzystek - NHMFL, Tallahassee, USA

Samples:
R. Feyerherm, HZB-ME, Berlin, Germany

Theory:
O. Kolezhuk – Institute of Magnetism, Kiev, Ukraine
S.R. Manmana – UC, Boulder, USA
F. Mila – EPFL, Lausanne, Switzerland

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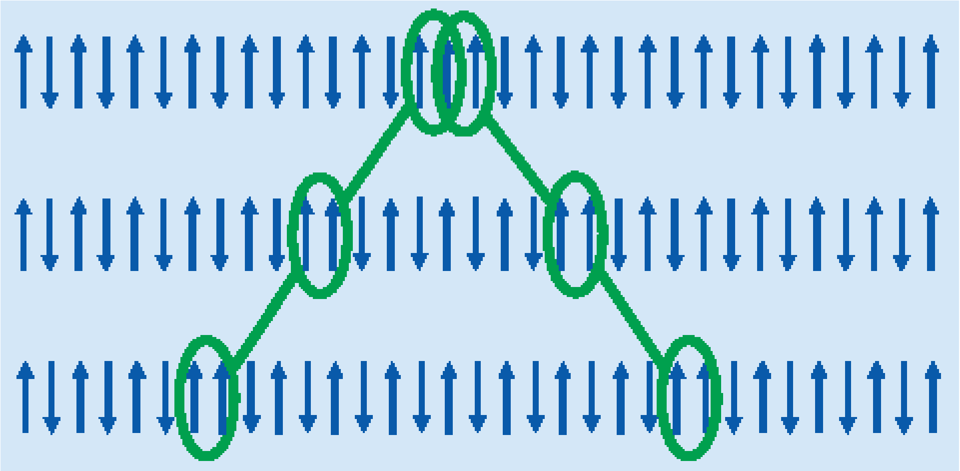
1. *S.A. Zvyagin, A.K. Kolezhuk, J. Krzystek, and R. Feyerherm, PRL. **93**, 027201, 2004*
2. *S.A. Zvyagin, A.K. Kolezhuk, J. Krzystek, and R. Feyerherm, PRL **95**, 017207, 2005*
3. *S.A. Zvyagin, E. Čižmár, M. Ozerov, J. Wosnitza, R. Feyerherm, S.R. Manmana, and F. Mila, PRB **83**, 060409(R), 2011*

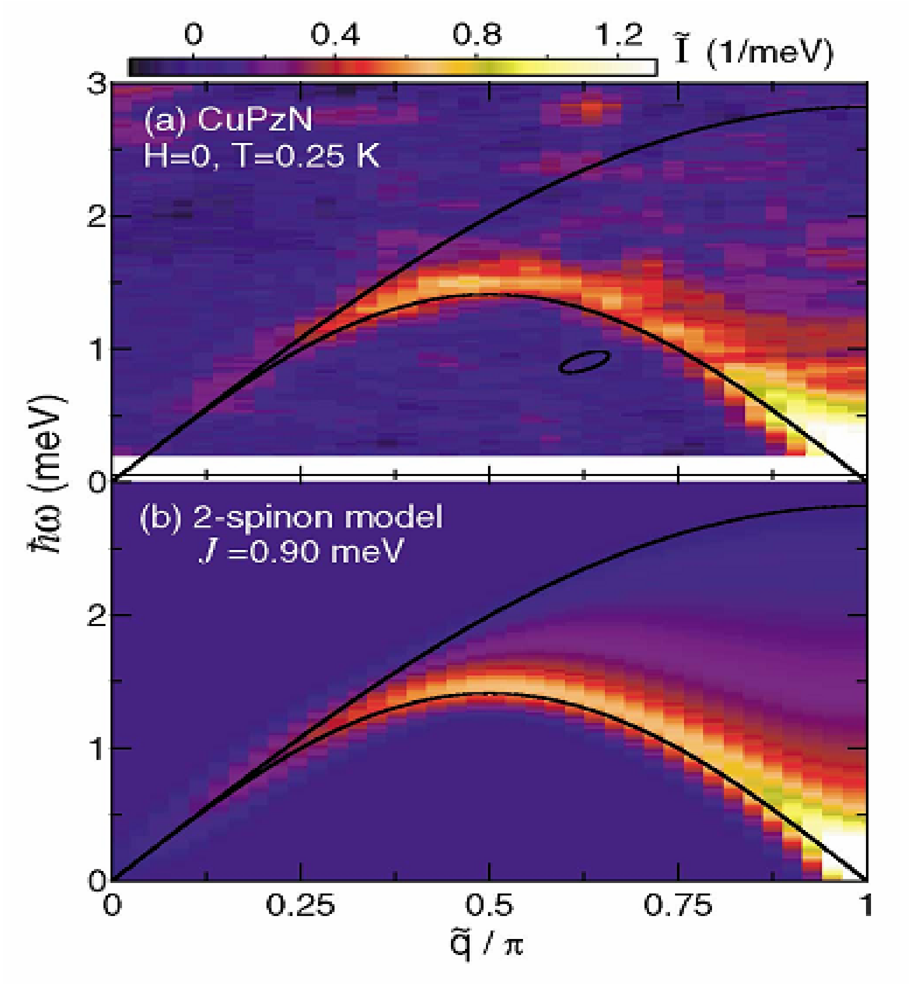
Uniform S=1/2 Heisenberg chain – the simplest spin-chain model system

The excitation spectrum is formed by spinons

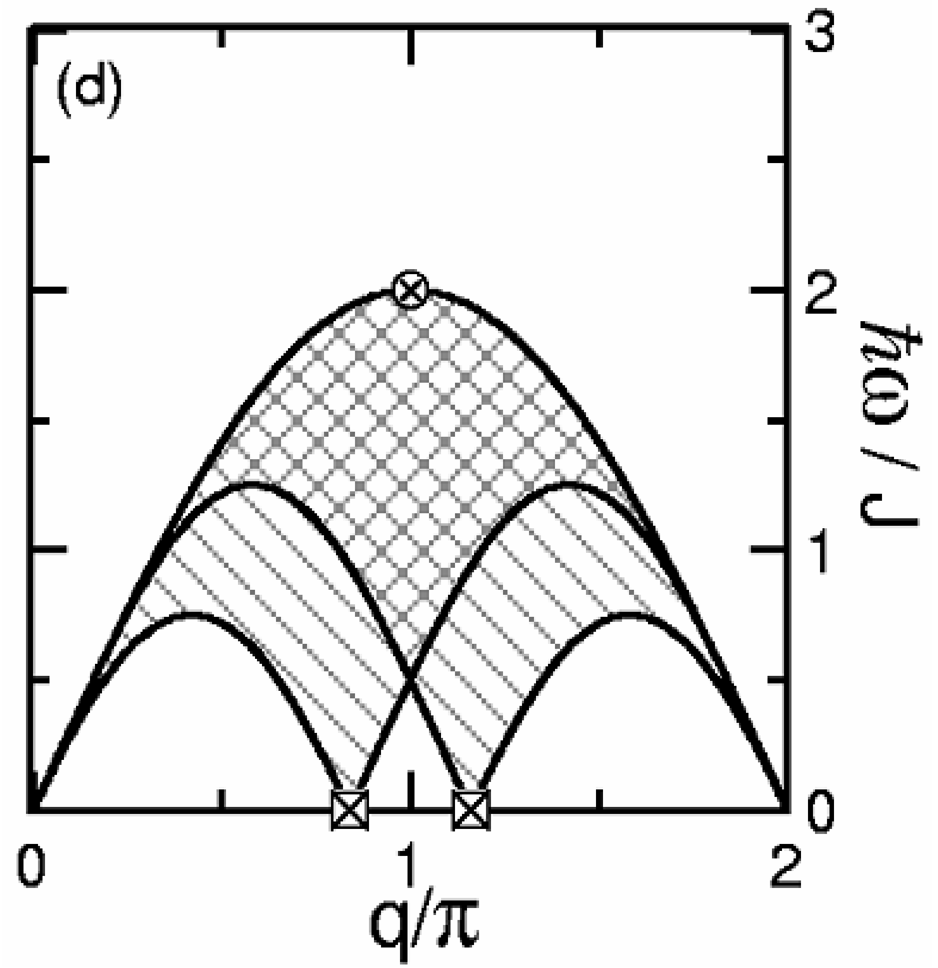


$$H = \sum_n \left(J\mathbf{S}_n \cdot \mathbf{S}_{n+1} - g\mu_B H S^z \right)$$

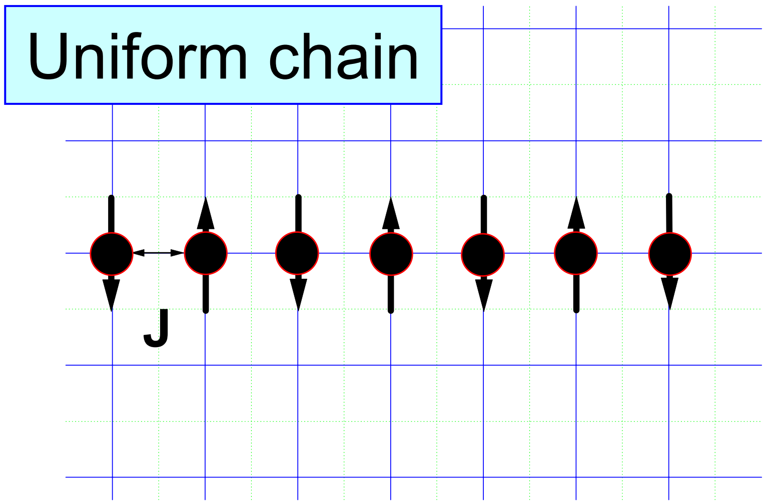
Inelastic neutron scattering in S=1/2 Heisenberg chain Cu-PyzN

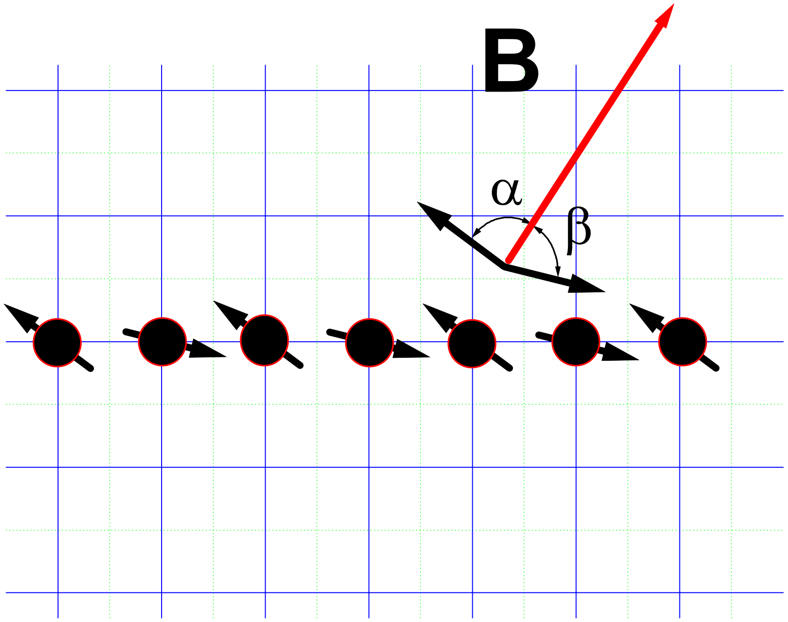


Stone et al. PRL 91, 037205 (2003)



S=1/2 Heisenberg chain with alternating g-factor or DM interaction





Alternating *g*-DM chain: field-induced staggered momentum:

(i) resulting field is superposition of field-induced staggered and applied field ⟹ field-induced gap!

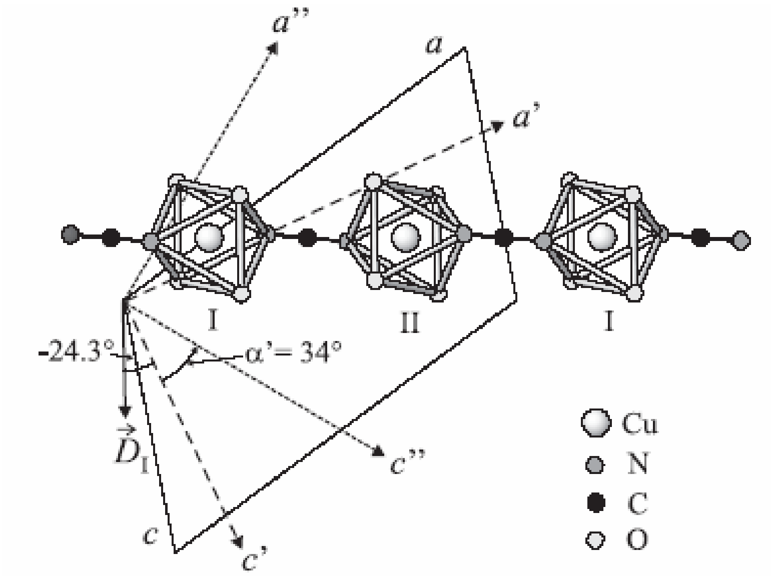
(ii) anisotropy

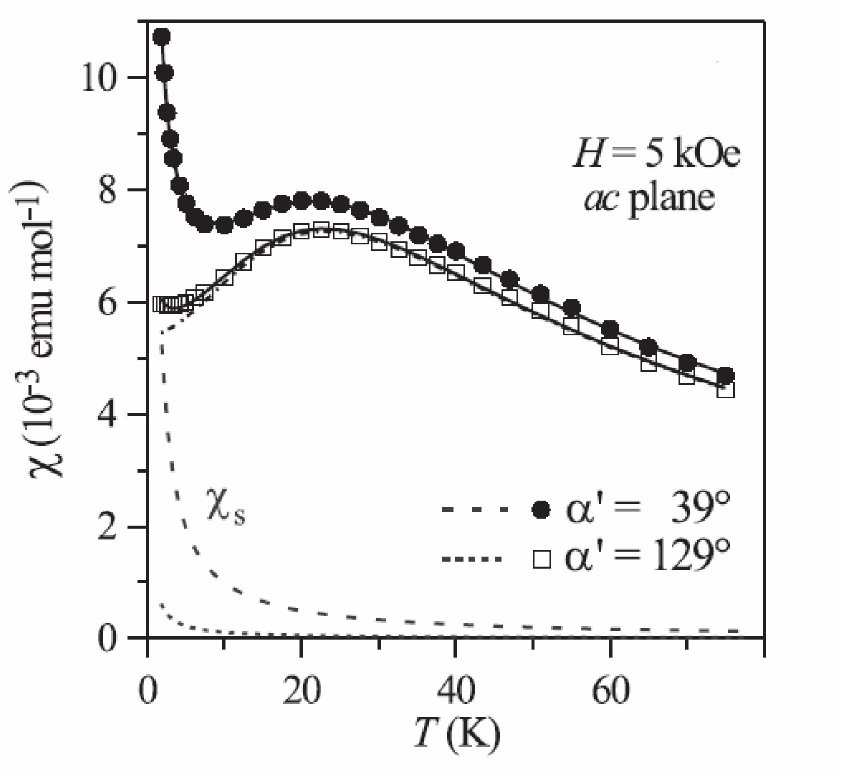
Staggered-field effect in Copper Pyrimidine Dinitrate

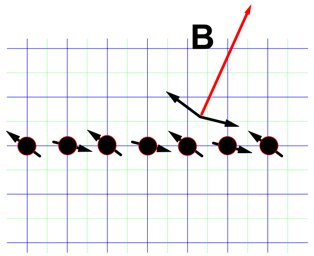
Chem. formula:

$[\mathrm{PM\ Cu(NO_3)_2x(H_20)_2}]_n$

Spin-spin interaction: J = 36 K







R. Feyerherm et al. J. Phys. Cond. Matt. 12, 9200 (2000)

Cu-PM: linewidth vs temperature

$$\Delta H = \eta_0 + FzH\,\mathrm{Im}(G),$$

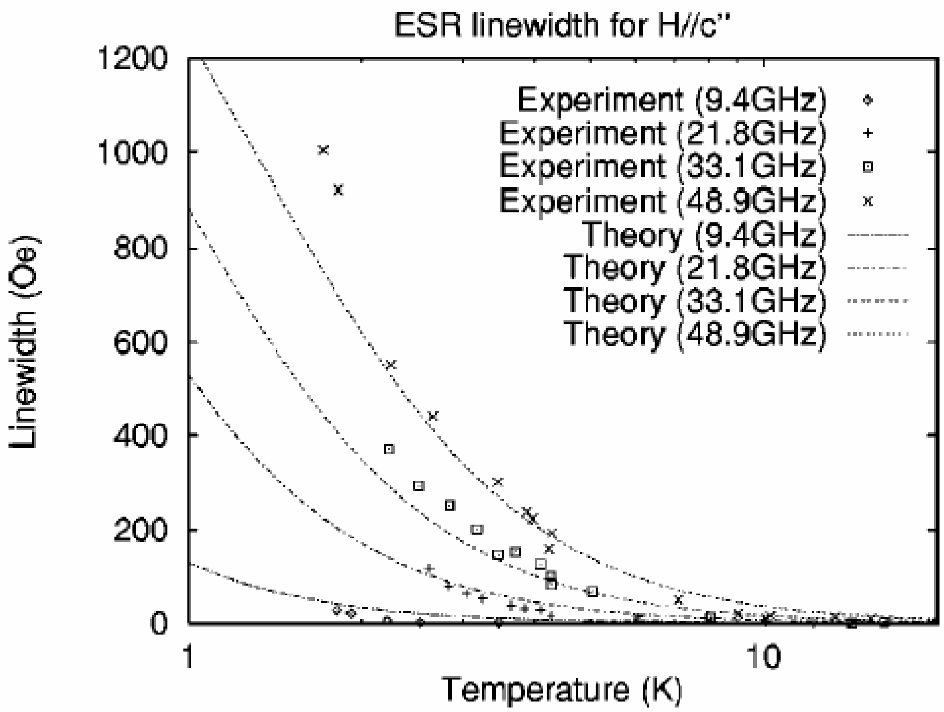
Cu-PM: *g*-factor vs temperature

$$\Delta g = Fz[z - \mathrm{Re}(G)],$$

where $z = \Gamma(\frac{1}{4})/\Gamma(\frac{3}{4})$ and $\Gamma(x)$ denotes the gamma function, and

$$G(H,T) = \Gamma\left(\frac{1}{4} - i\frac{g\mu_B H}{2\pi T}\right)/\Gamma\left(\frac{3}{4} - i\frac{g\mu_B H}{2\pi T}\right),$$

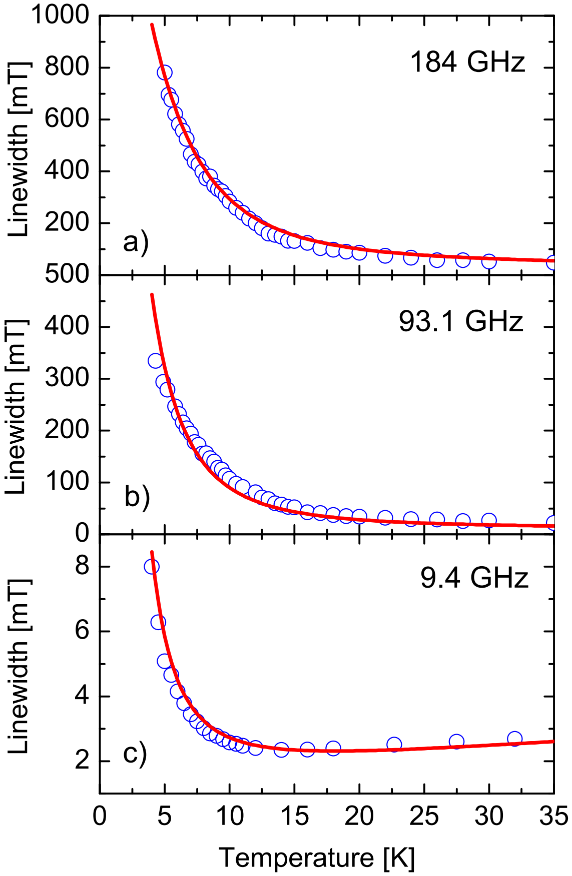
$$F(H,T) = c^2\sqrt{\pi/128}(J/T)\ln^{1/2}(\lambda J/T).$$

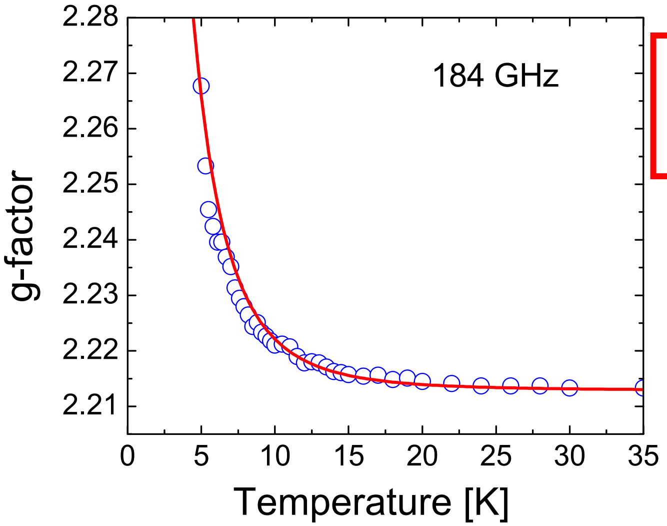


Oshikawa and Affleck, PRB 65, 134410 (2002)

Influence of the field-induced staggered moment on ESR line-width and g-factor shift

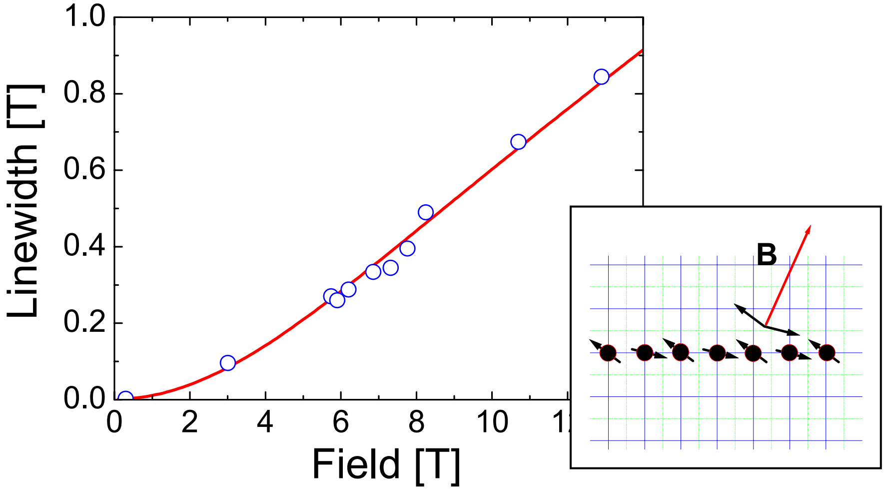
S.Z et al., PRL 95, 017207 (2005)





c = 0.08

h~cH



Effective spin Hamiltonian: uniform + staggered field

$$\mathrm{H}_{\mathrm{eff}} = \sum_n \left(J\,\tilde{\mathbf{S}}_n \cdot \tilde{\mathbf{S}}_{n+1} - \tilde{H}\tilde{S}_n^z - h_s \left(-1\right)^n \tilde{S}_n^x \right)$$

Spin operators can be represented through a phase field $\tilde{\phi}\left(x,t\right)$ relative to incommensurate quasi-long-range order with Lagrangian density

$$\mathrm{L} = \tfrac{1}{2}\left[\left(\partial_t\tilde{\phi}\right)^2 - \left(\partial_x\tilde{\phi}\right)^2\right] + Ch_s \cos\left(2\pi R\left(H\right)\tilde{\phi}\right)$$

This is sine-Gordon model with interaction term proportional to h_s
Spectrum consists of

- Solitons, anti-solitons $$\Delta_s = J\frac{2\Gamma(\xi/2)v_F}{\sqrt{\pi}\Gamma[(1+\xi)/2]}\left[\frac{g\mu_B H}{Jv_F}\frac{\pi\Gamma[1/(1+\xi)]cA_x}{2\Gamma[\xi/(1+\xi)]}\right]^{(1+\xi)/2}$$
- Bound states (breathers) $$\Delta_n = 2\Delta_s \sin(n\pi\xi/2)$$

Oshikawa and Affleck, PRB 62, 9200 (2000)
Essler et al., PRB 68, 064410 (2003)

The Sine-Gordon equation

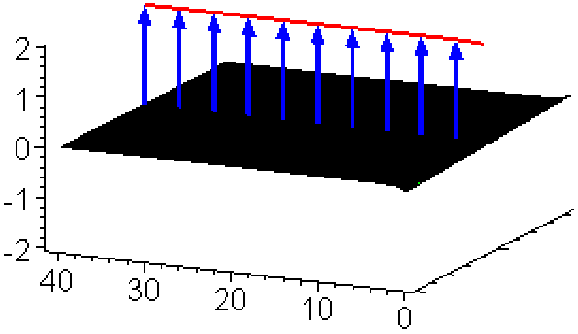
$$\left(\frac{\partial^2}{\partial t^2}\phi(x,t)\right)-\left(\frac{\partial^2}{\partial x^2}\phi(x,t)\right)+\sin(\phi(x,t))=0$$

can be solved exactly:

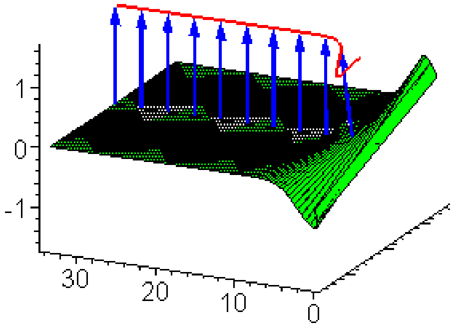
soliton, antisoliton and

soliton-antisoliton bound states (breathers).

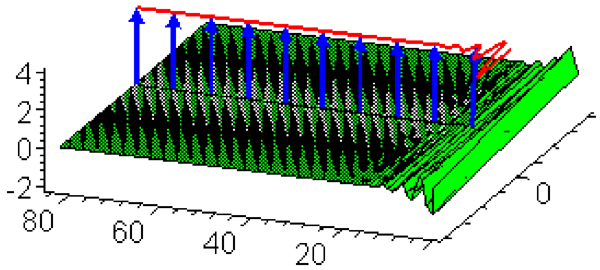
Kink



Large amplitude Breather



Small amplitude Breather



Andrey E. Miroshnichenko, aem124@rsphysse.anu.edu.au,

Effective spin Hamiltonian: uniform + staggered field

$$\mathrm{H}_{\mathrm{eff}} = \sum_n \left(J\,\tilde{\mathbf{S}}_n \cdot \tilde{\mathbf{S}}_{n+1} - \tilde{H}\tilde{S}^z_n - h_s \left(-1\right)^n \tilde{S}^x_n \right)$$

Spin operators can be represented through a phase field $\tilde{\phi}\left(x,t\right)$ relative to incommensurate quasi-long-range order with Lagrangian density

$$\mathrm{L} = \tfrac{1}{2}\left[\left(\partial_t\tilde{\phi}\right)^2 - \left(\partial_x\tilde{\phi}\right)^2\right] + Ch_s \cos\left(2\pi R\left(H\right)\tilde{\phi}\right)$$

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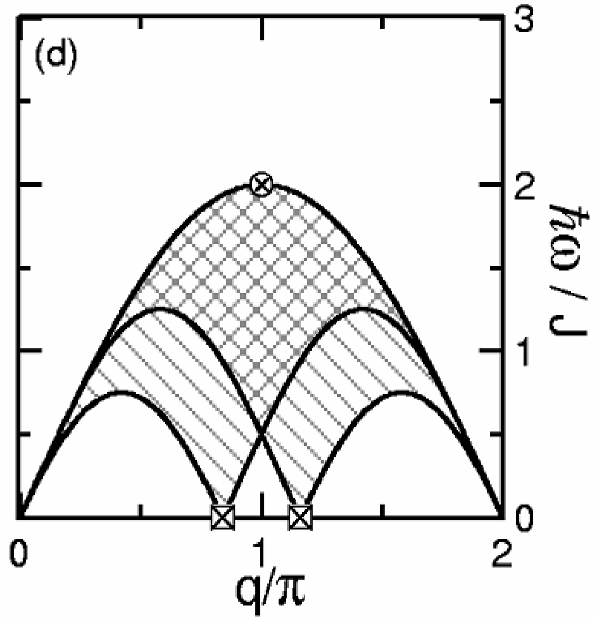
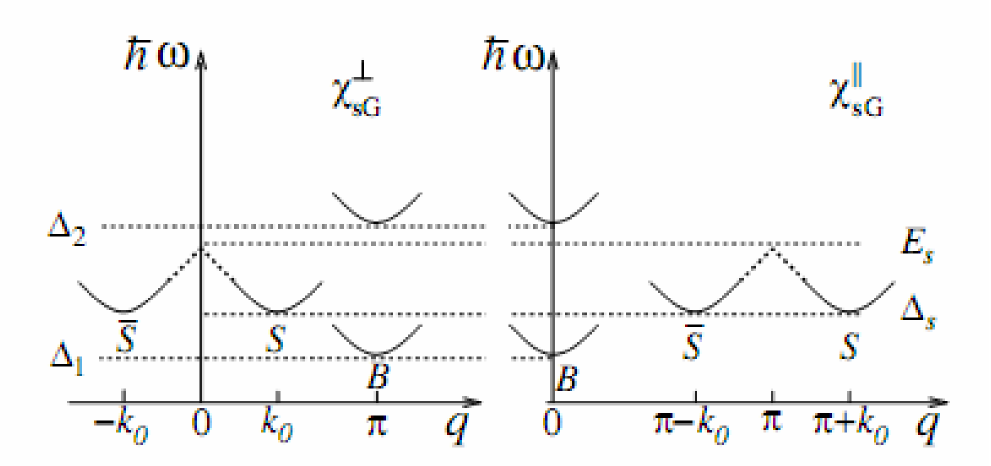
Oshikawa and Affleck, PRB 62, 9200 (2000)
Essler et al., PRB 68, 064410 (2003)

Effect of the staggered field



→



Broken translation symmetry due to alternating g-tensor and DM interaction

→

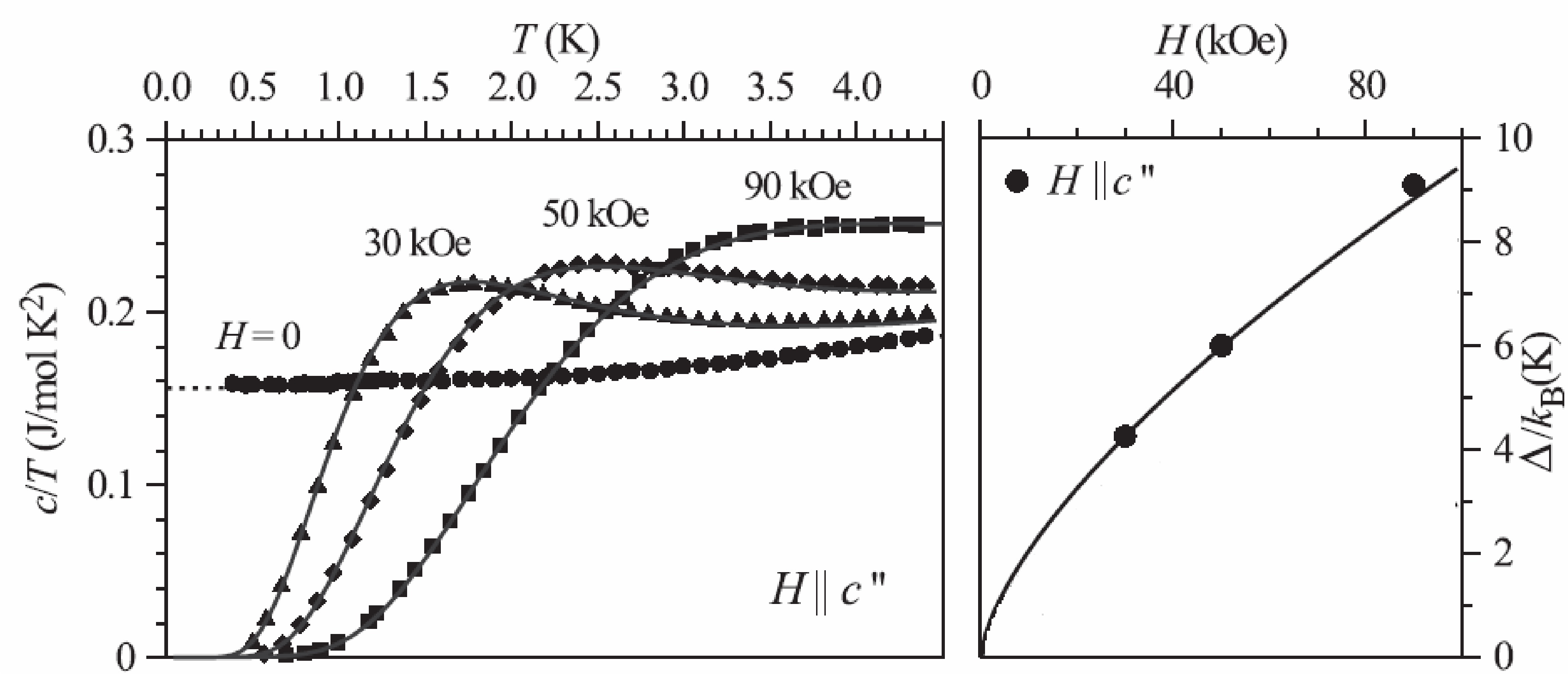
Staggered magnetization

→

Field-induced gap and soliton-breather excitations!

Field-induced gap in Copper Pyrimidine Dinitrate

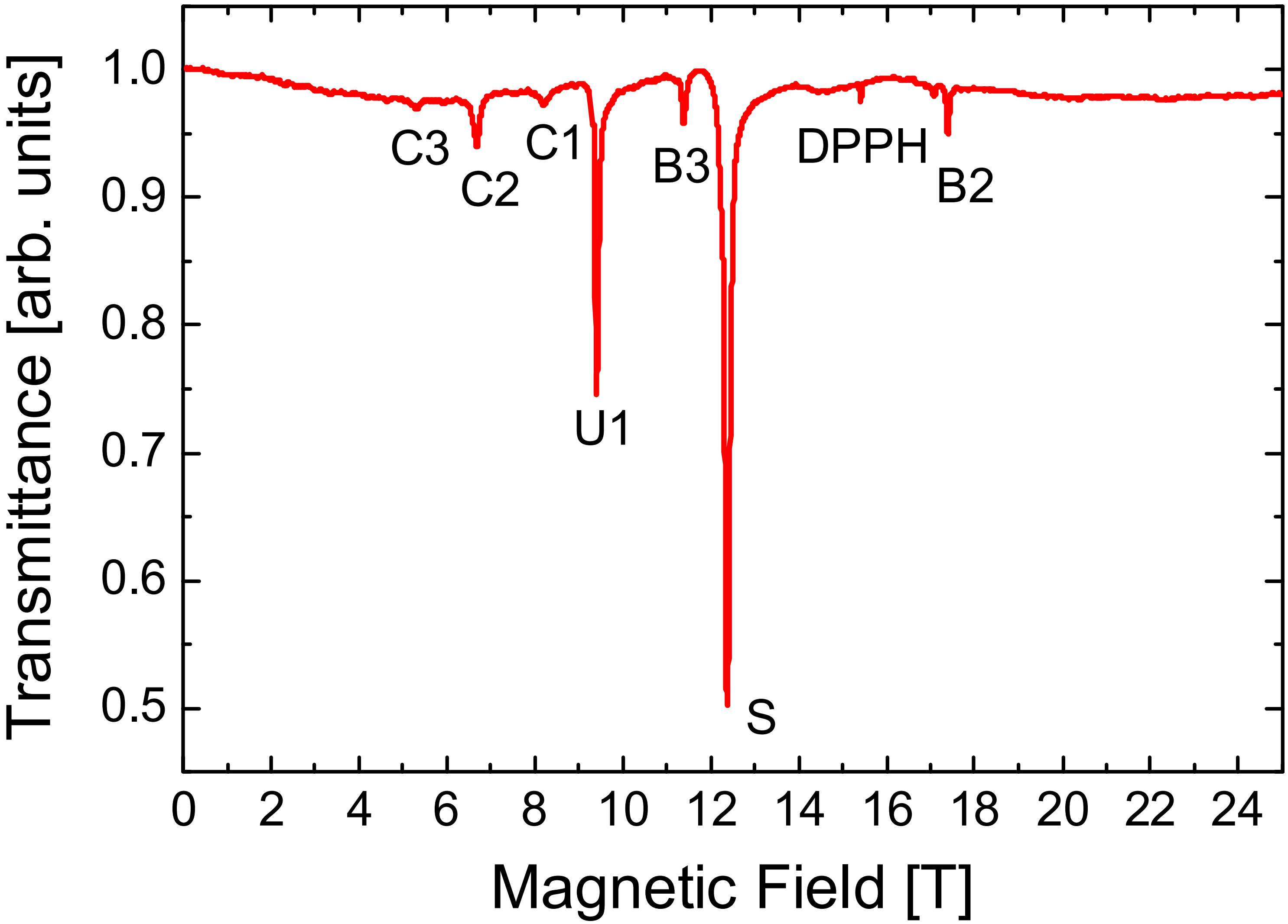
R. Feyerherm et al. J. Phys. Cond. Matt. 12, 9200 (2000)

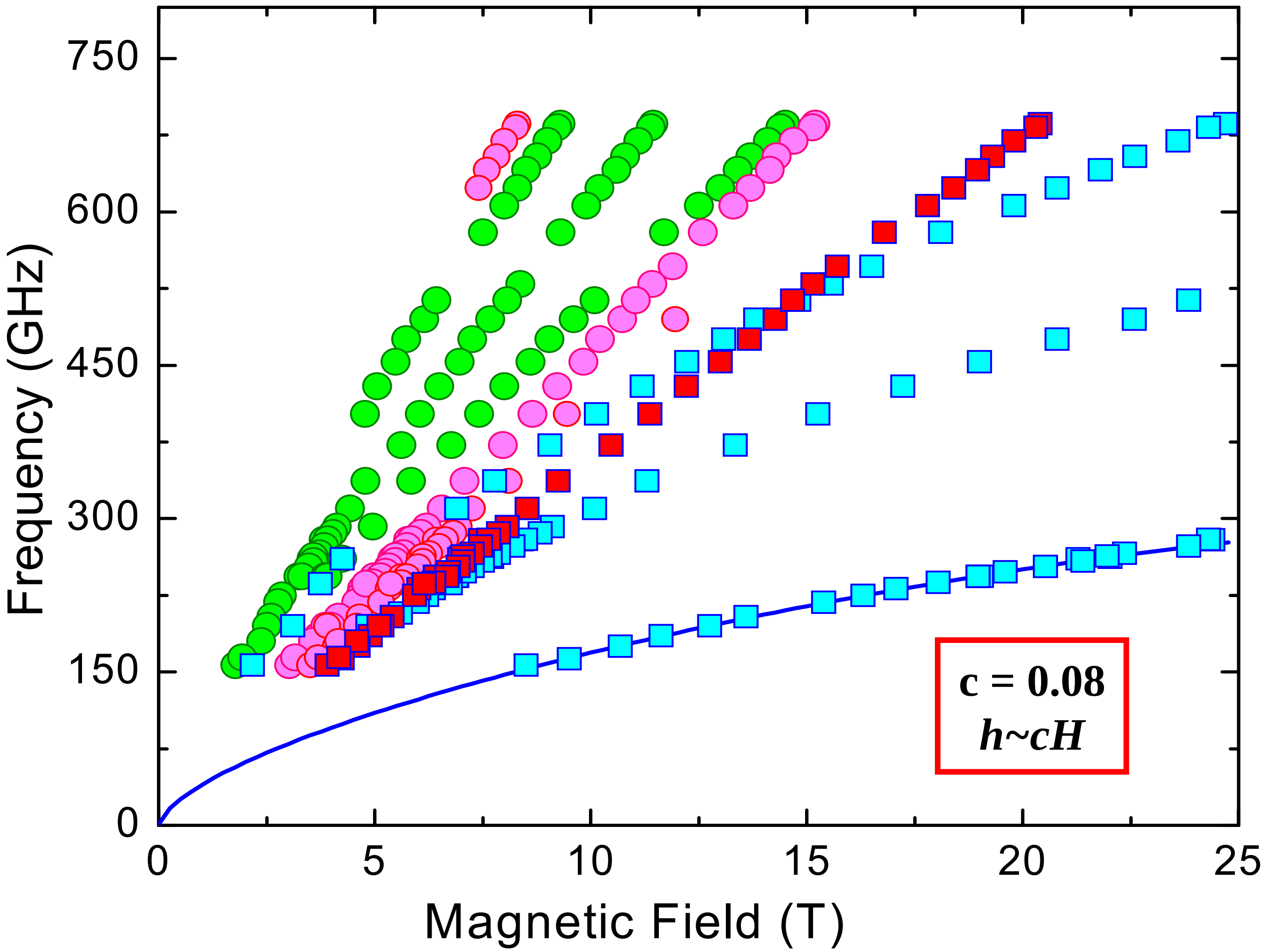


Should we try to probe the gap DIRECTLY?

25 T ESR facility in Tallahassee, USA

429.3 GHz, 1.4 K


Transmittance [arb. units]
1.0
0.9
0.8
0.7
0.6
0.5
Magnetic Field [T]
0
2
4
6
8
10
12
14
16
18
20
22
24
C3
C2
C1
U1
B3
S
DPPH
B2

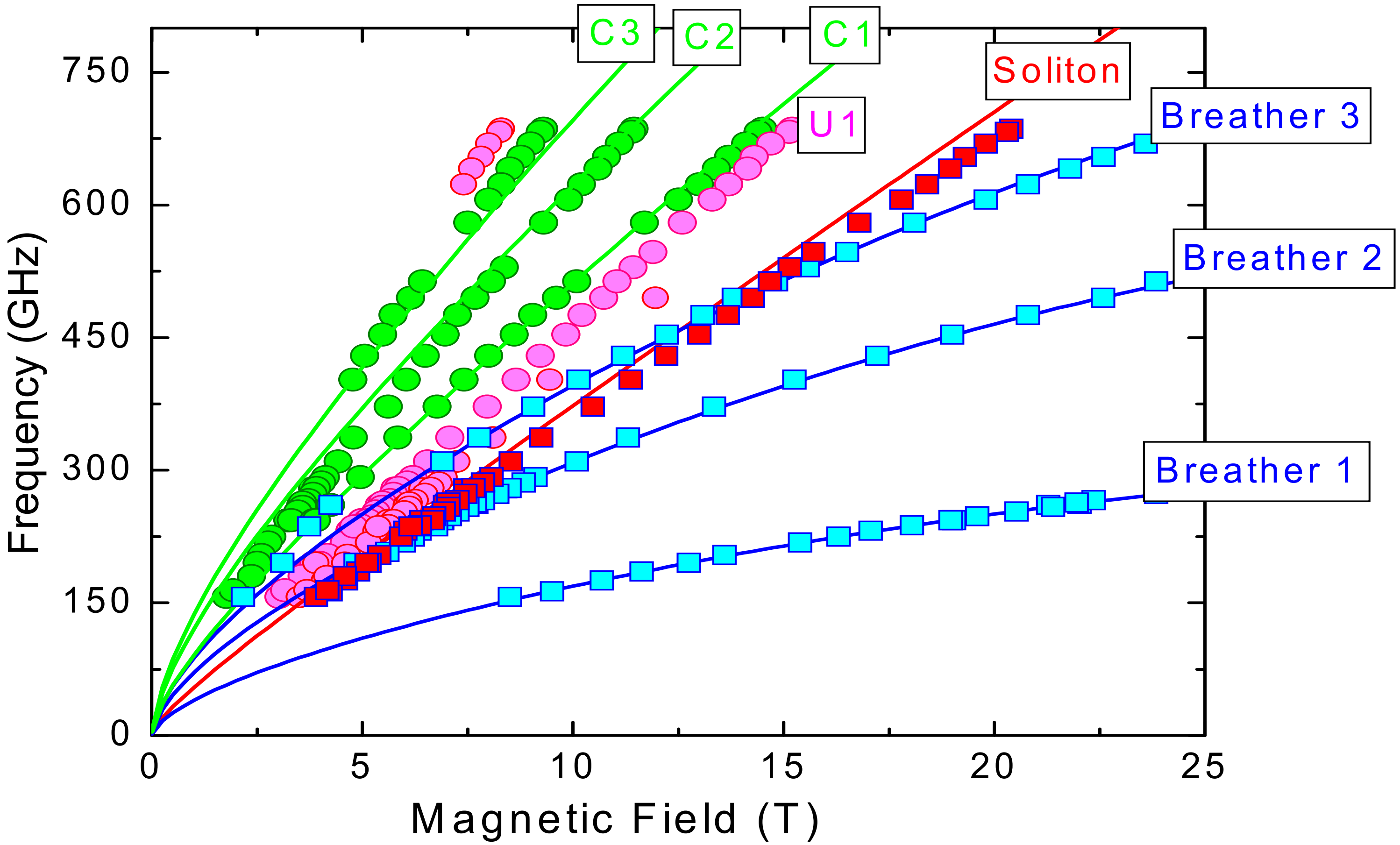


Oshikawa and Affleck, PRL 79, 2883 (1997)
Essler, PRB 59, 14376 (1999)
Affleck and Oshikawa, PRB 60, 1038 (1999); ibid. 62, 9200 (2000)

$$\Delta_s = J\frac{2\Gamma(\frac{\xi}{2})v_F}{\sqrt{\pi}\Gamma(\frac{1+\xi}{2})}\left[\frac{g\mu_B H}{Jv_F}\frac{\pi\Gamma(\frac{1}{1+\xi})\textcircled{c}A_x}{2\Gamma(\frac{\xi}{1+\xi})}\right]^{\frac{1+\xi}{2}}$$

$$\Delta_n = 2\Delta_s \sin(n\pi\xi/2)$$

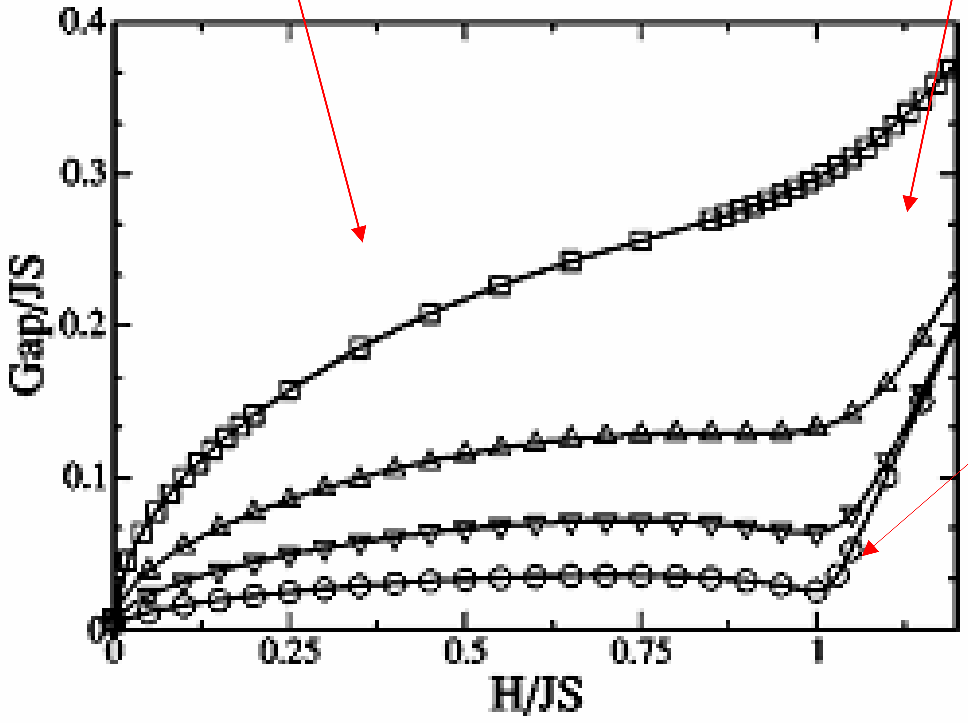
S.Z. et al., PRL. ***93****, 027201 (2004)*



A complete set of solutions of the sine-Gordon equation for a quantum spin chain - soliton and three breathers - has been observed. Excellent agreement with the theory.

What happens in higher magnetic fields?

Transition into fully spin-polarized phase. Magnetization and the gap behavior.



Sine-Gordon phase
SOLITONS & BREATHERS

Fully spin-polarized phase
MAGNONS

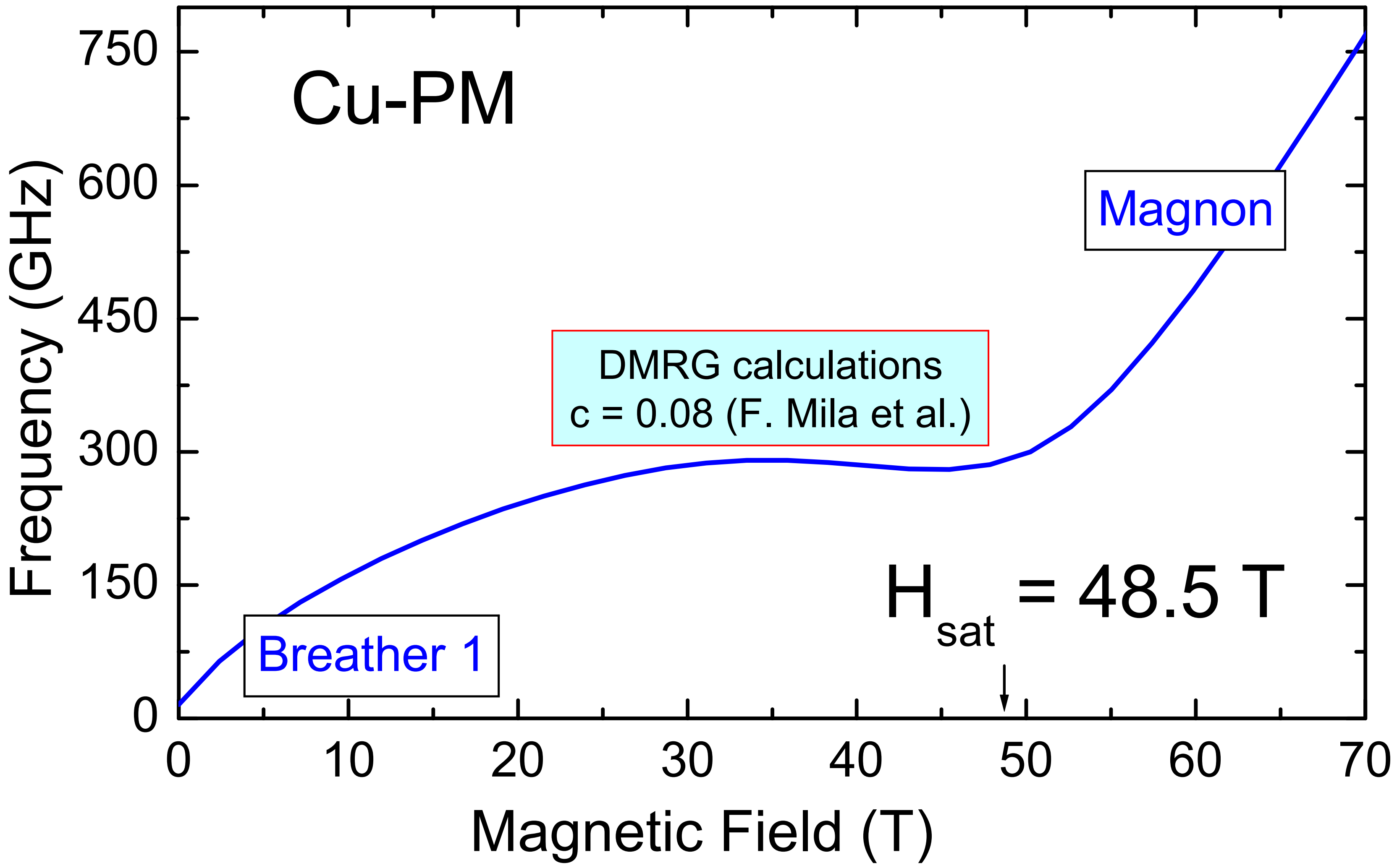
No further development of the transverse staggered magnetization.
Growing of the longitudinal magnetization - a dip

H_{sat} = 48.5 T
(for Cu-PM)

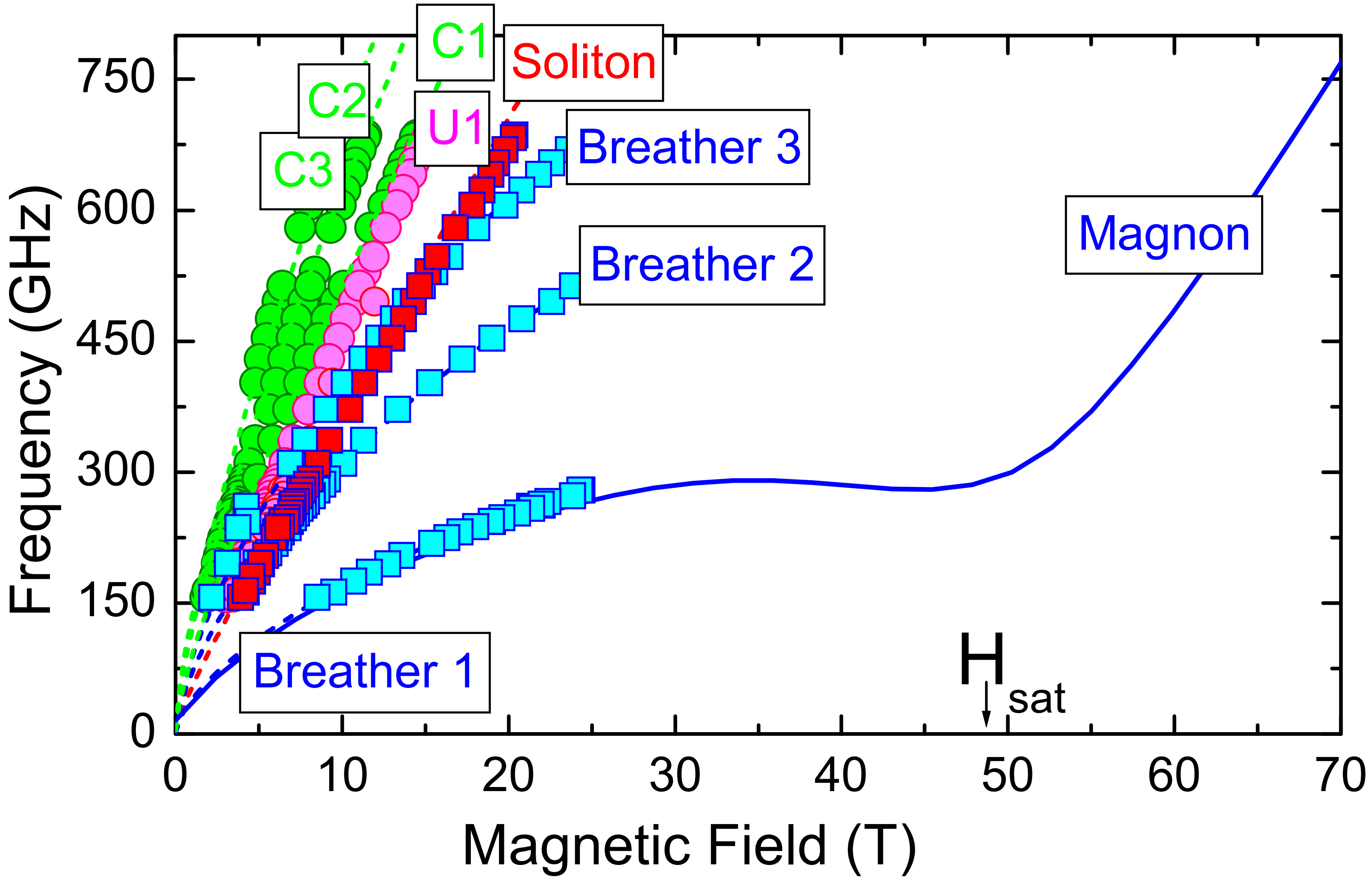
Fouet et al., 70, 174427 (2004)

H_{sat}

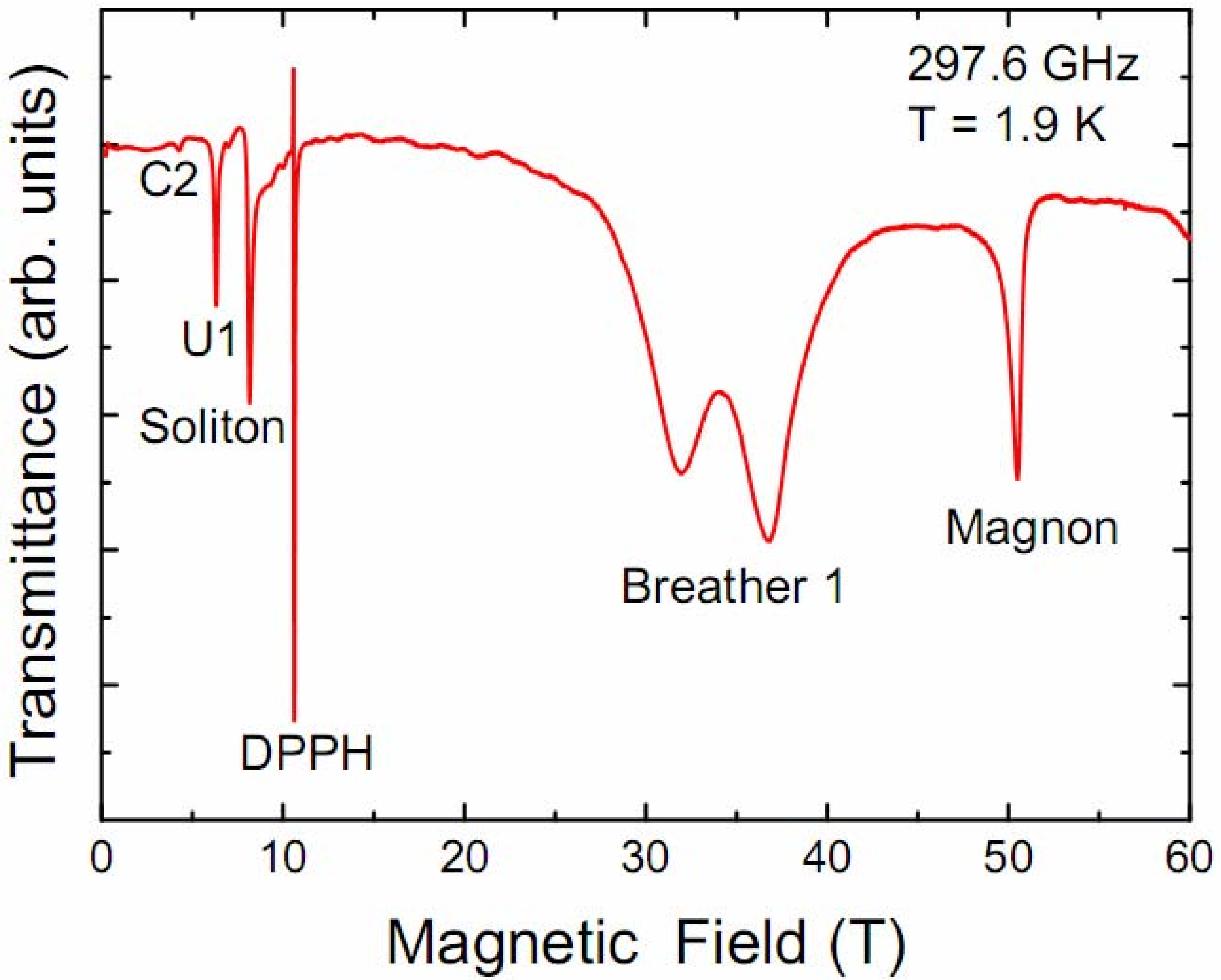
Transition into fully spin-polarized phase. Field-induced gap behavior (calculations).



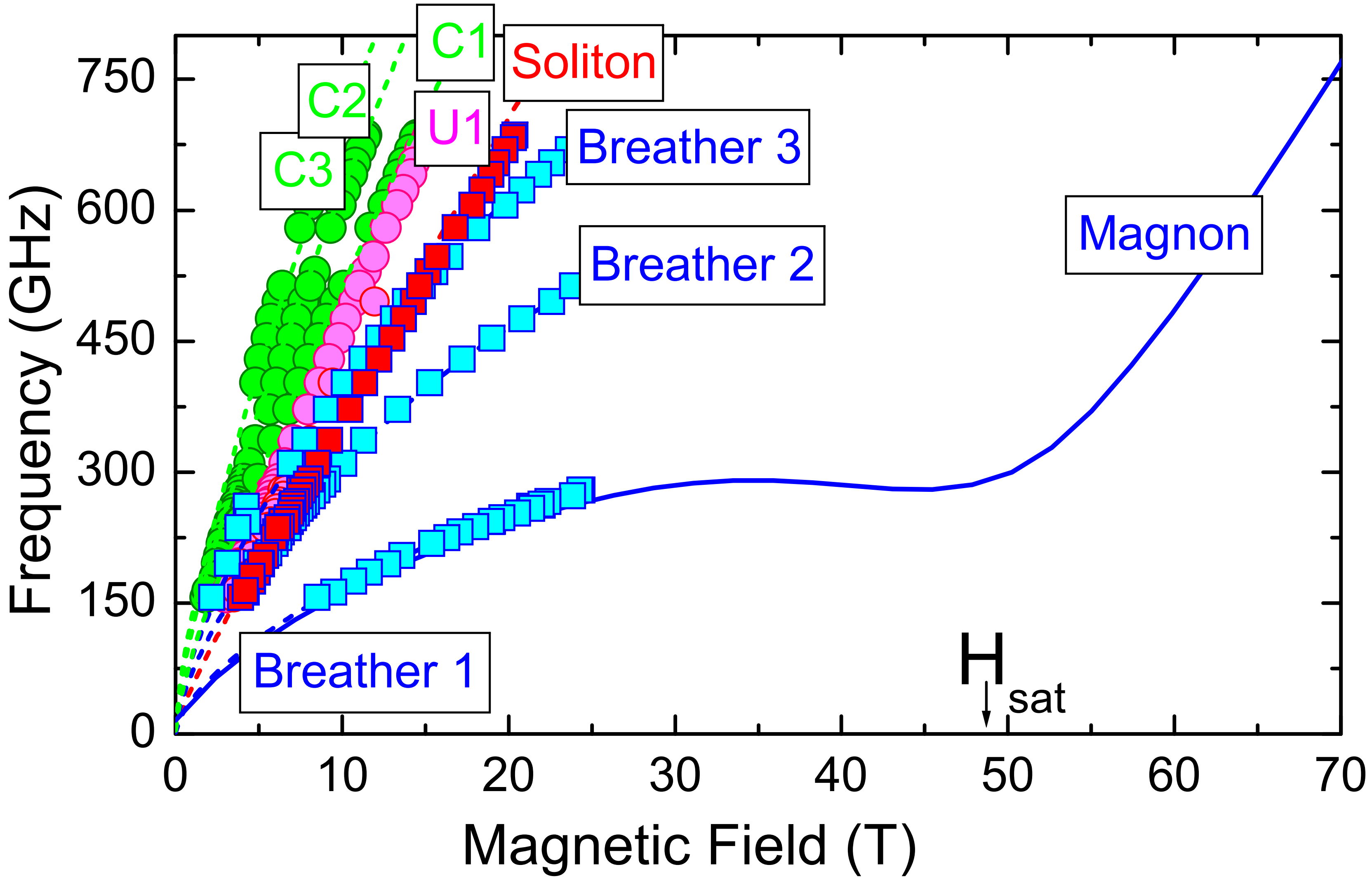
Blue line: theoretical predictions



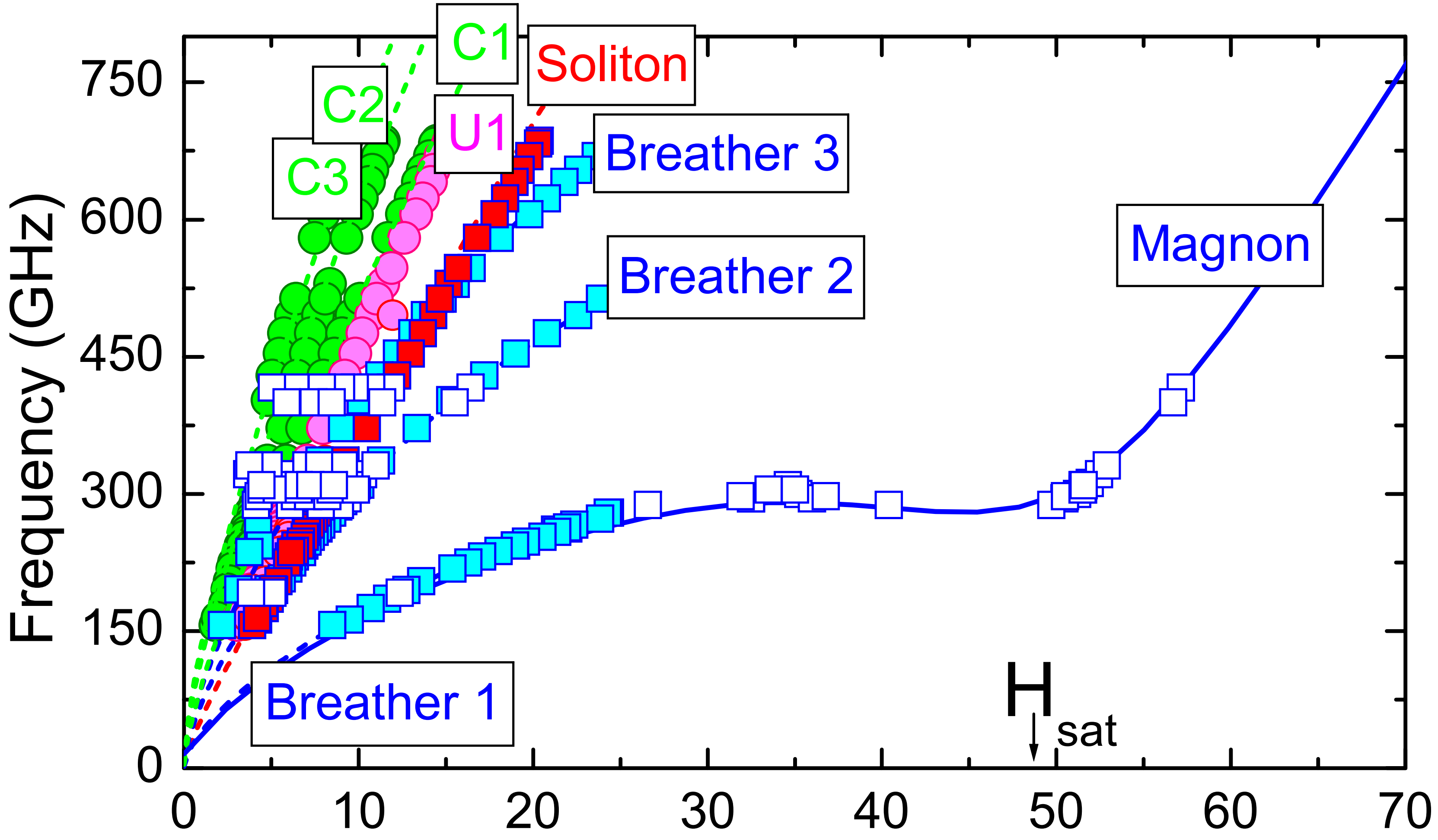
ESR in Cu-PM in pulsed magnetic fields



Blue line: theoretical predictions



Open symbols: pulsed-field results



S.Z. et al., PRB 83, 060409(R), 2011

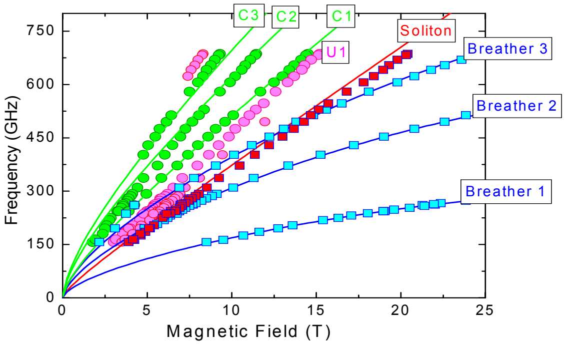
1. The universality of the sine-Gordon formalism has been demonstrated, this time for quantum spin chains.

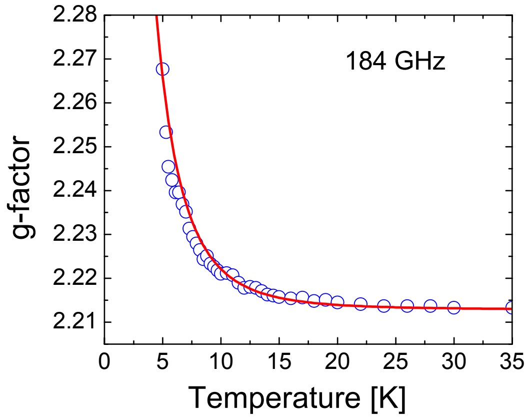
2. Complete set of solutions of the sine-Gordon equation for a quantum spin chain - soliton and three breathers - has been observed

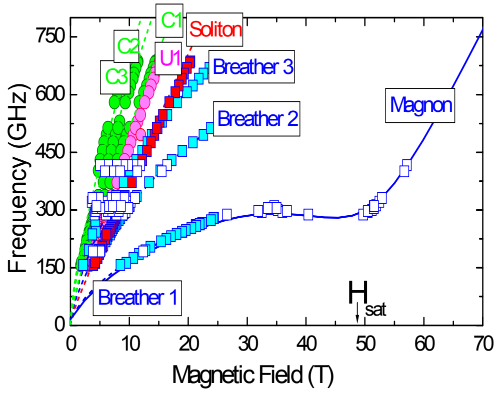
3. Characteristic ESR parameter behavior (line-width, resonance field shift) at the spinon-soliton crossover has been observed.

4. The soliton-magnon crossover has been observed in Cu-PM for the first time.

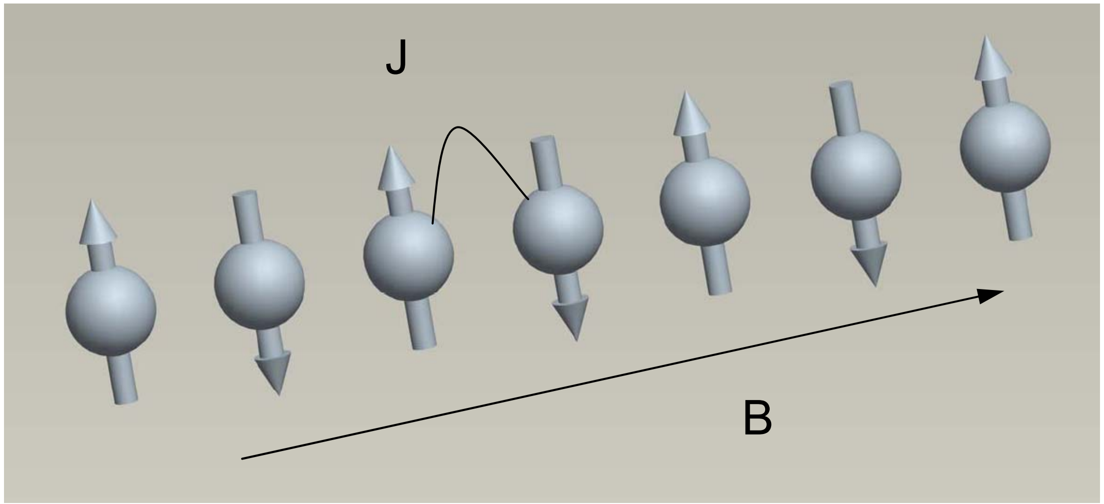
5. All the obtained data were described using the same set of spin-Hamiltonian parameters. Excellent agreement with theory was obtained.





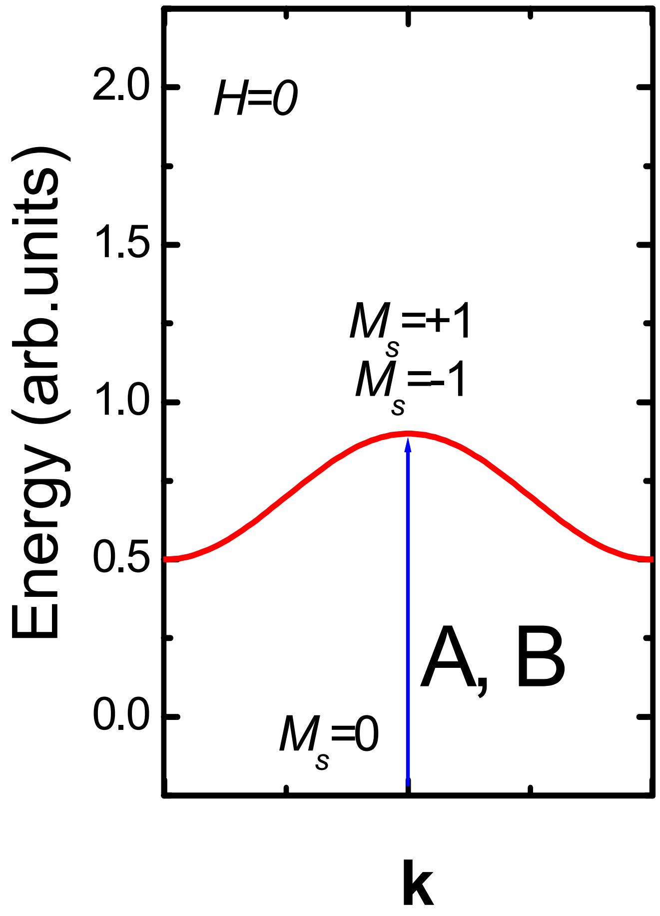


High-field ESR in the large-D spin-chain system DTN

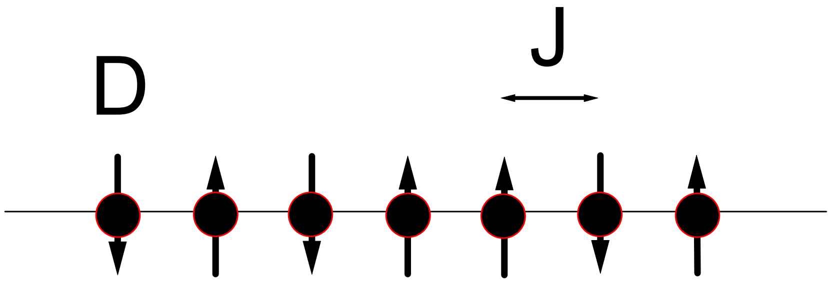


1. *S.A. Zvyagin, J. Wosnitza, C. D. Batista, M. Tsukamoto, N. Kawashima, J. Krzystek, V. S. Zapf, M. Jaime, N. F. Oliveira, Jr.,and A. Paduan-Filho, Magnetic excitations in the spin-1 anisotropic Heisenberg antiferromagnetic chain System NiCl2-4SC(NH2)2, PRL 98, 047205 (2007)*
2. *C. Psaroudaki, S.A. Zvyagin, J. Krzystek, A. Paduan-Filho, X. Zotos, and N. Papanicolaou, Magnetic excitations in the spin-1 anisotropic antiferromagnet NiCl(2)-4SC(NH(2))(2), PRB 85, 014412 (2011)*

Excitation dispersion of S=1 large-D chain systems.

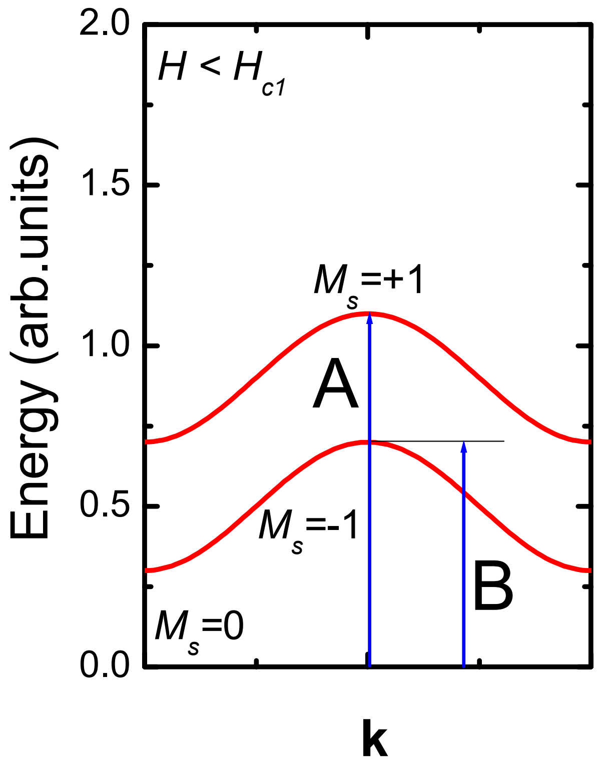


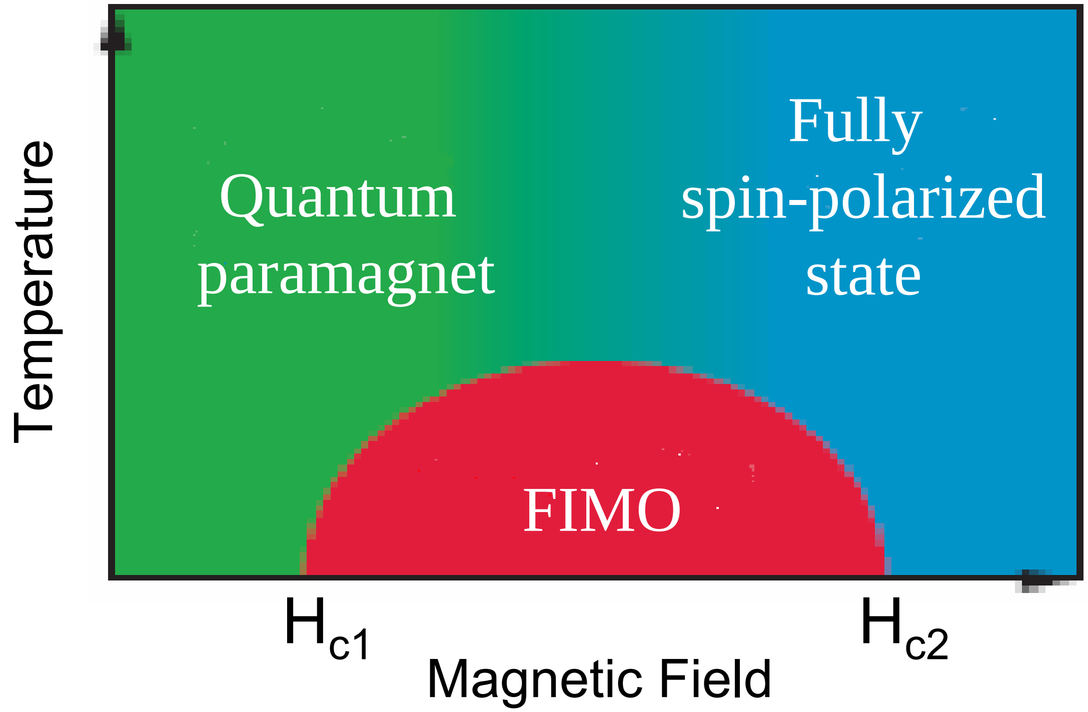
$$\mathcal{H} = \sum_{\mathbf{j},\nu} J_\nu \mathbf{S}_{\mathbf{j}} \cdot \mathbf{S}_{\mathbf{j}+e_\nu} + \sum_{\mathbf{j}} [D(S^z_{\mathbf{j}})^2 + g\mu_B H S^z_{\mathbf{j}}]$$

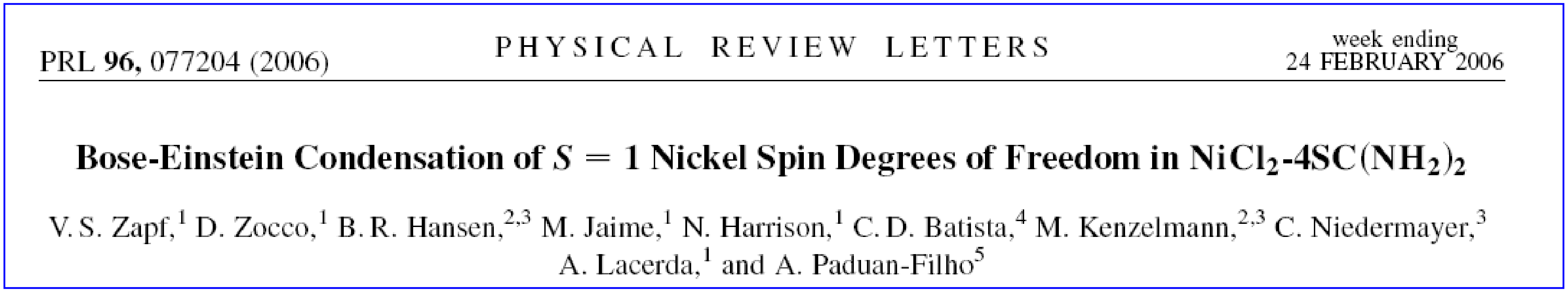


S=1 D/J > 1

… in applied magnetic field.

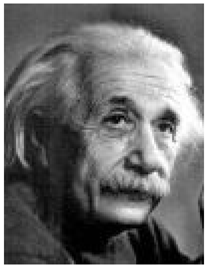





PRL **96,** 077204 (2006) PHYSICAL REVIEW LETTERS week ending 24 FEBRUARY 2006

Bose-Einstein Condensation of $S = 1$ Nickel Spin Degrees of Freedom in $NiCl_2$-$4SC(NH_2)_2$

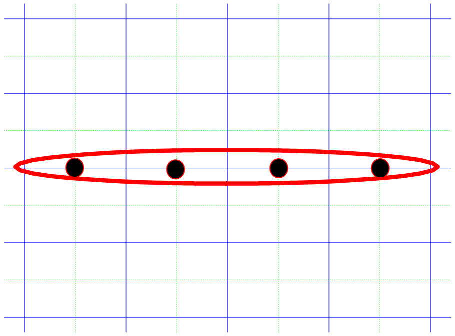
V. S. Zapf,[1] D. Zocco,[1] B. R. Hansen,[2,3] M. Jaime,[1] N. Harrison,[1] C. D. Batista,[4] M. Kenzelmann,[2,3] C. Niedermayer,[3]
A. Lacerda,[1] and A. Paduan-Filho[5]



S.N. Bose, Z. Phys. 26, 178 (1924); A. Einstein, Sitzungsber. Kgl. Preuss. Akad. Wiss. 1924, 261 (1924)

A. Einstein S. Bose

For uniform (and ideal) gas of identical particles (bosons) of a mass m, when the de Broglie wavelength $\lambda_{dB} = (2\pi \hbar^2/mk_B T)^{1/2}$



becomes comparable to the mean interparticle separation, a macroscopic fraction of the gas can be "condensed" into the single lowest quantum state with the wavefunction coherent on the macroscopic scale.

An important condition for realization of BEC is a presence of U1 symmetry.

Debates on FIMP as Magnon BEC

- ☐ There is interaction between quasi-particles even in the "ideal-gas" phase

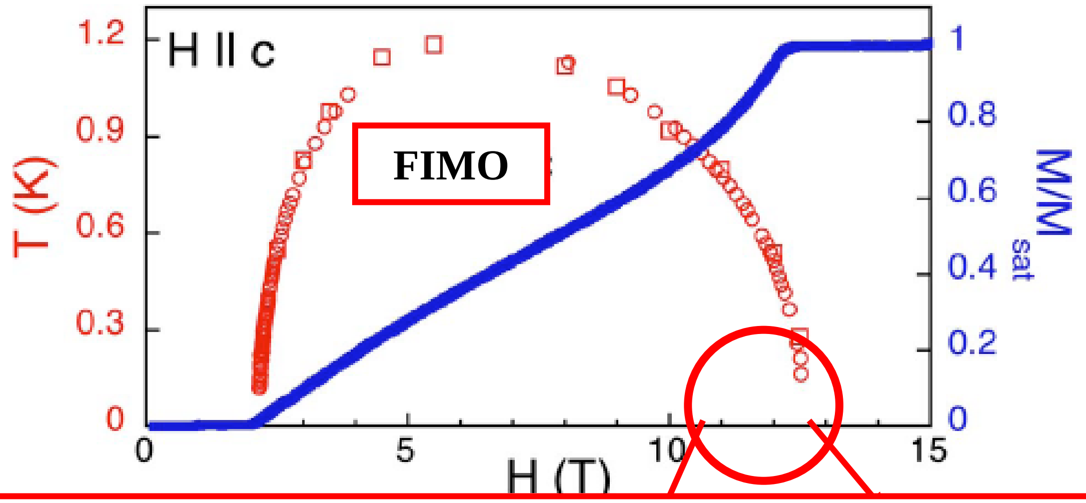
- ☐ The U1 symmetry is always broken by crystal field effects (particularly important at very low T)

- ☐ Number of magnons is not conserved, i.e., real chemical potential is zero

The employment of BEC formalism for description of FIMO is possible, but with some serious remarks

DTN: remaining questions

1. Contradiction between the experimentally observed second critical field ($H_{c2}^{\text{Experiment}}$ = 12.6 T) and the calculated one (H_{c2}^{Theory} = 10.85 T)

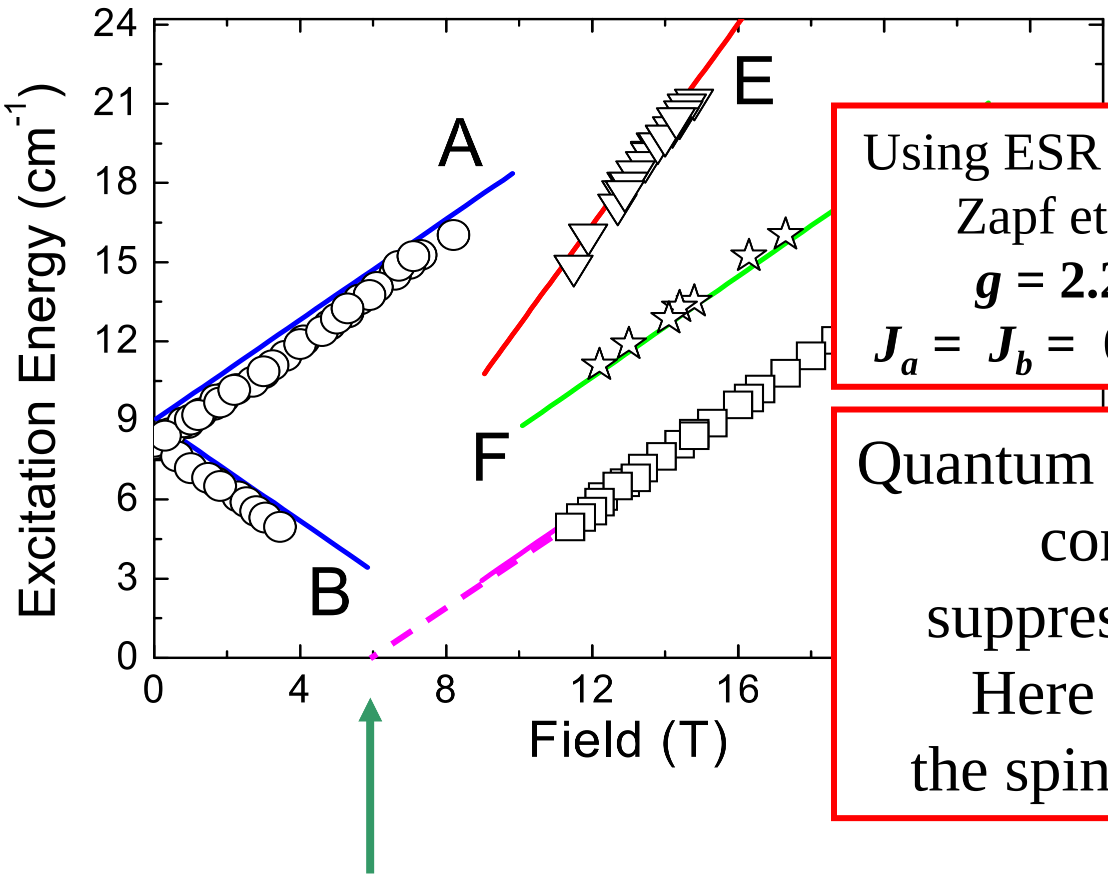


The calculations were done using the generalized spin-wave theory. The generalized spin-wave theory does not account for quantum fluctuations…

Let us go to fully spin-polarized state, where the quantum fluctuations are suppressed completely!

T = 1.6 K

S.Z. et al., PRL 98, 047205 (2007)



Using ESR and INS data from Zapf et al., PRL 2006

$\mathbf{g = 2.26, D = 8.9\ K}$

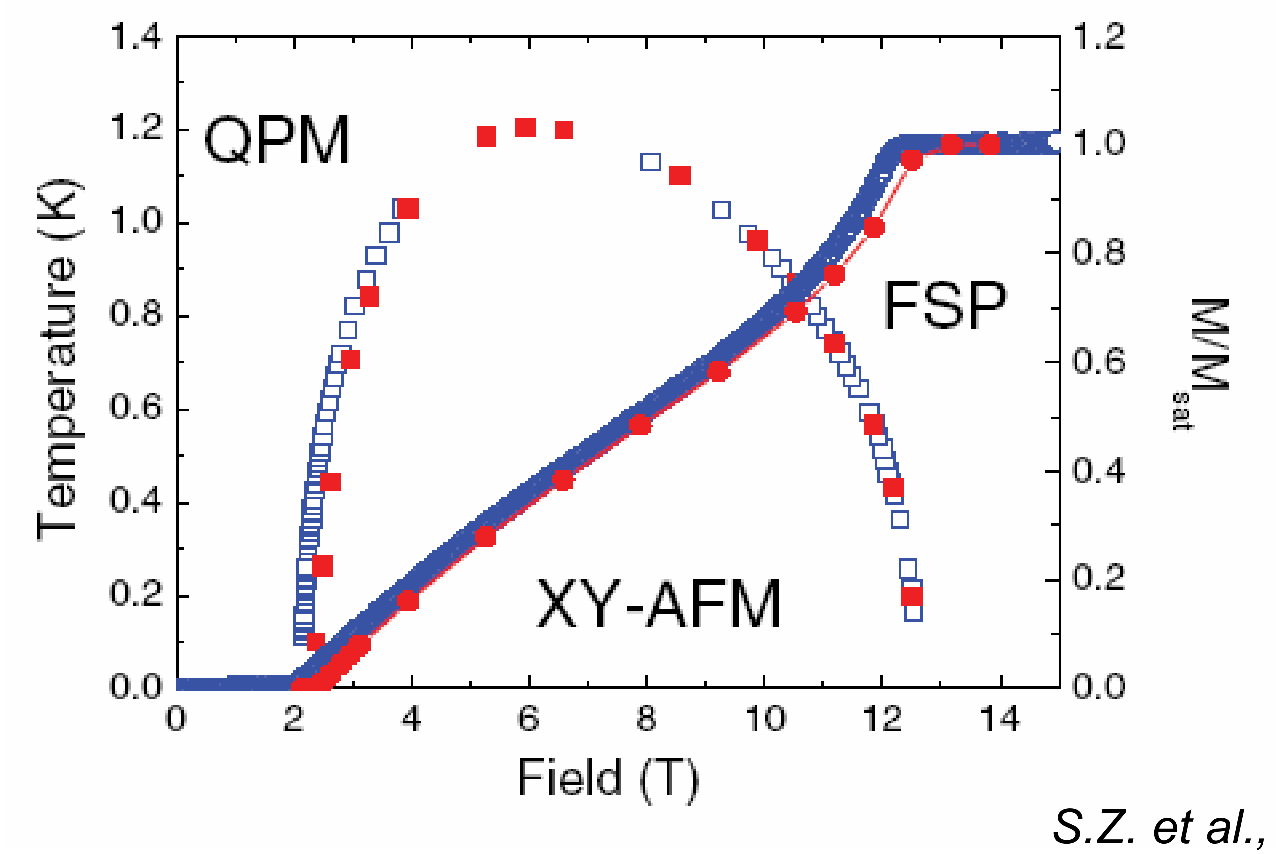
$\mathbf{J_a = J_b = 0.18\ K, J_c = 2.2\ K}$

Quantum fluctuations are completely suppressed by field. Here we can use the spin-wave theory!

$D = g\mu_B H = 8.9\ K$

Let us use new parameters and see how it works!

Phase Diagram and magnetization in DTN
(experiment + theory)



Experiment
Quantum Monte Carlo calculations

S.Z. et al., PRL 98, 047205 (2007)

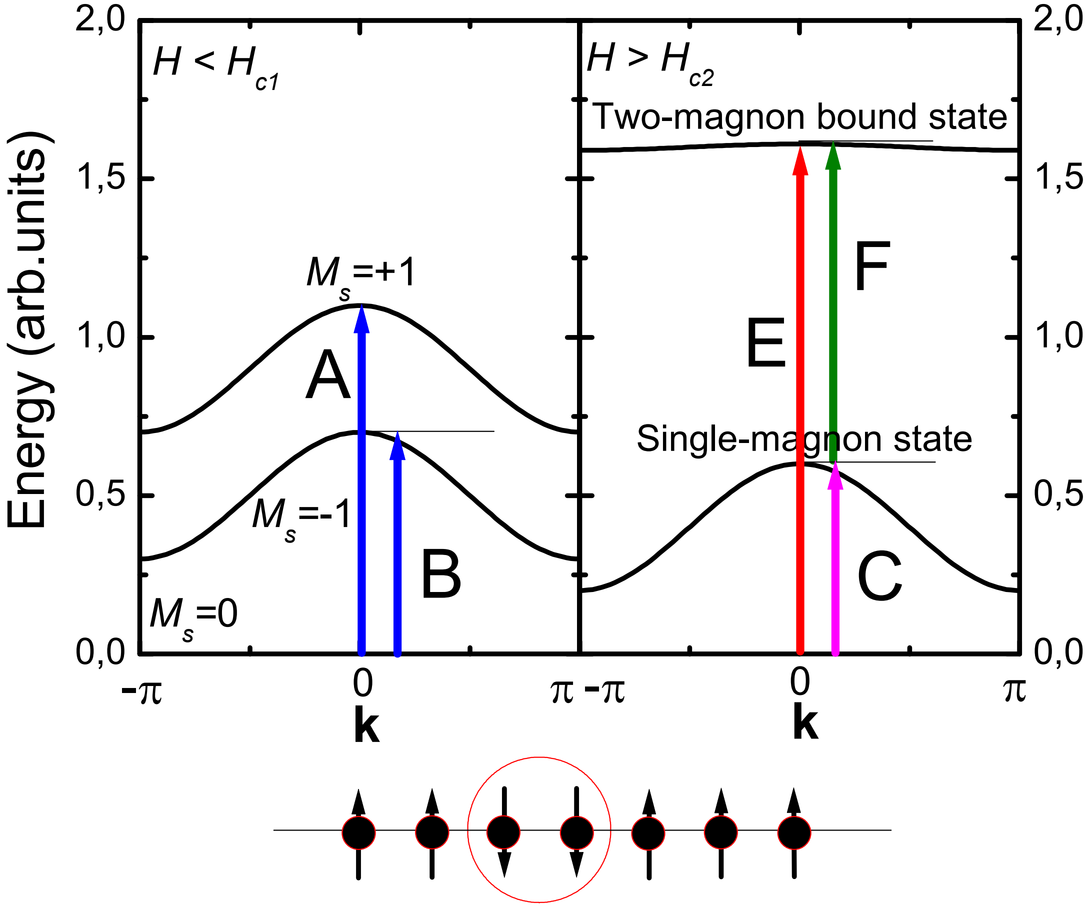
Excellent agreement between theory and experiment!

Microscopic picture

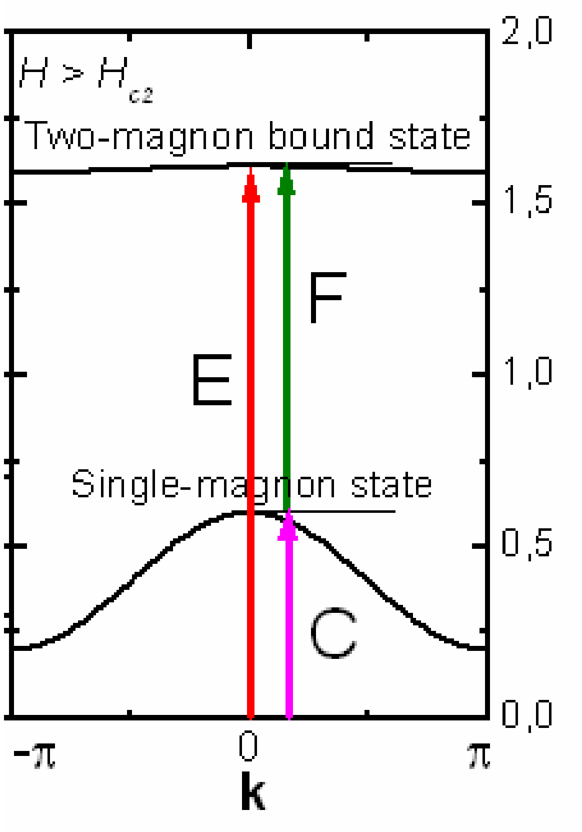
Simultaneous flip of two spins from neighboring sites;
localized due to strong plane anisotropy

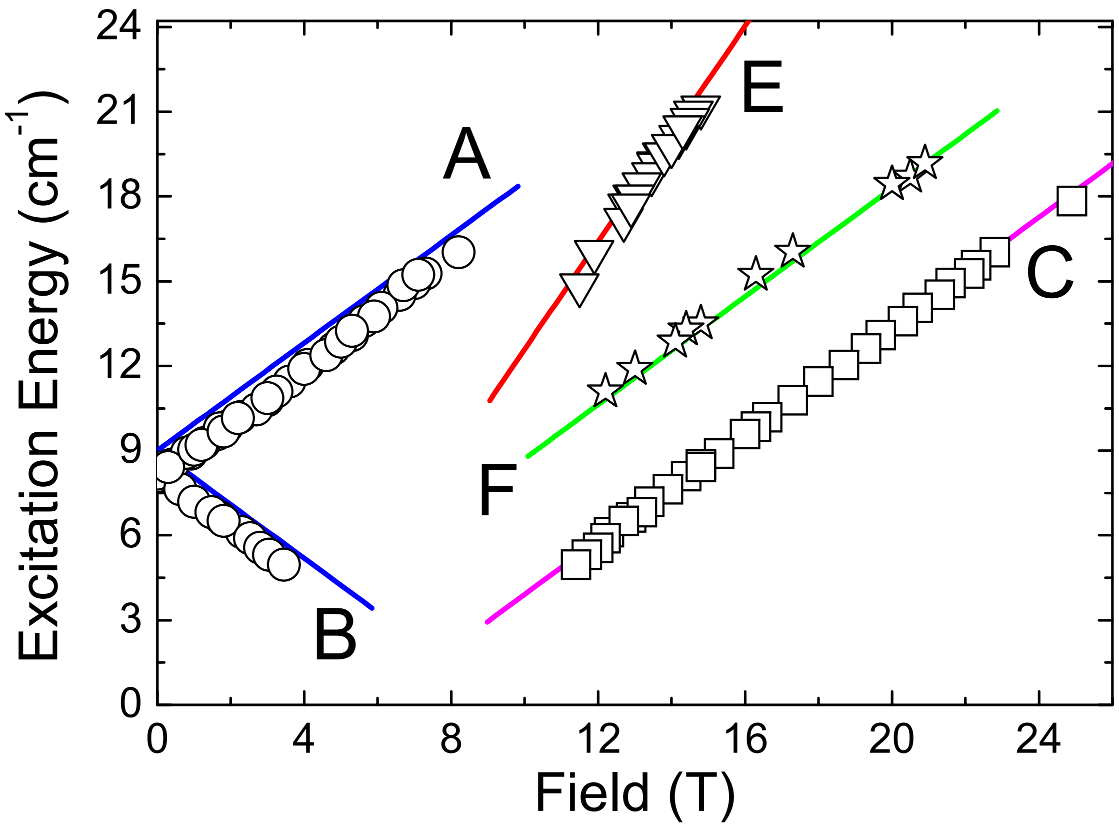
Two-magnon bound states in anisotropic chains.

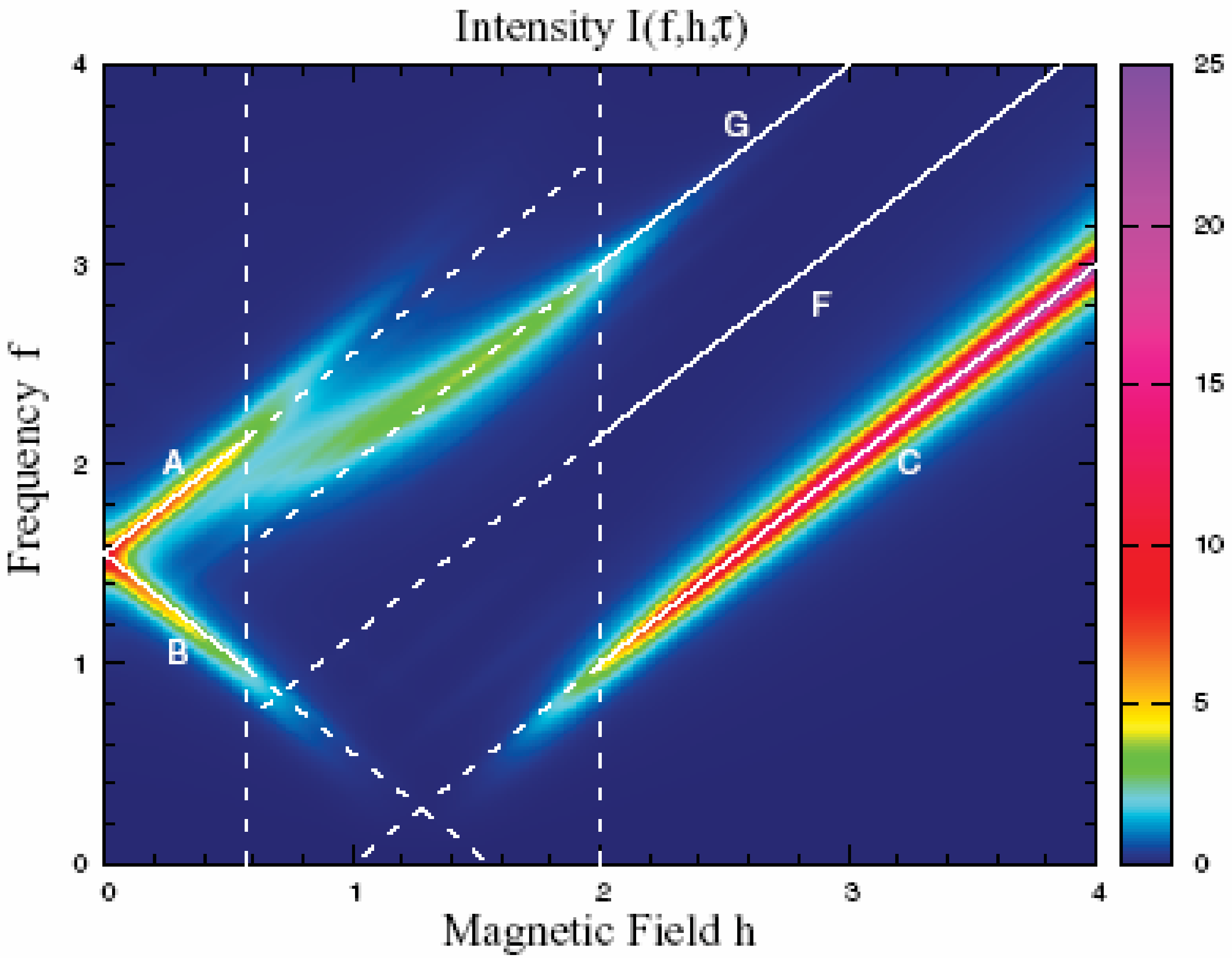
Predicted by Silberglitt and Torrance: PRB 2, 772 (1970)
For Large-D systems by Papanicolaou: PRB 56, 8786 (1997)



First conclusive observation of single-ion bound states

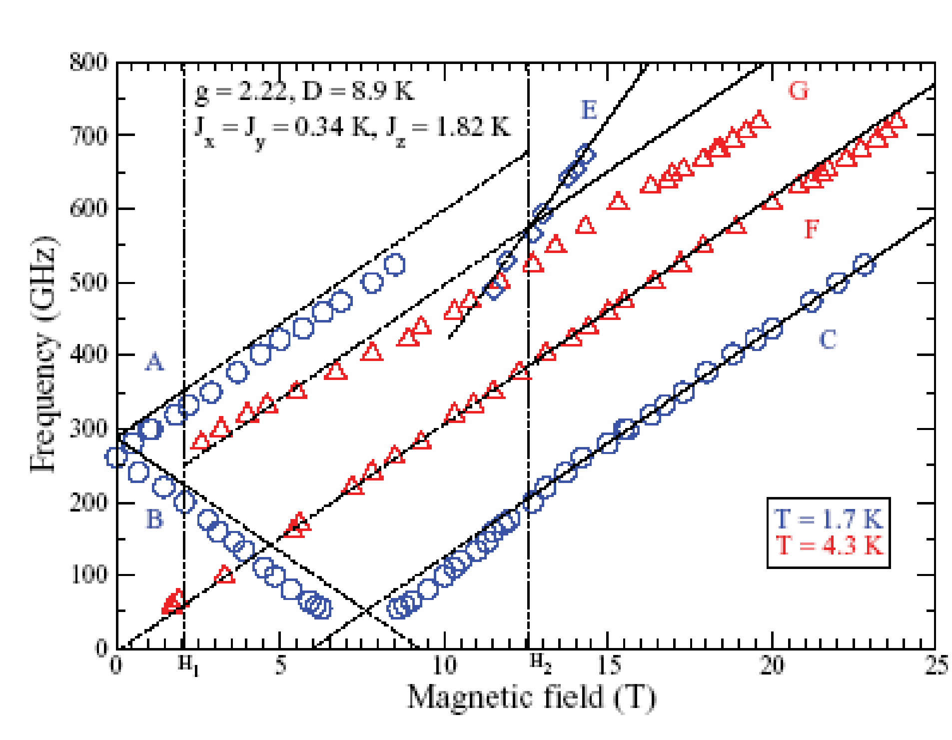




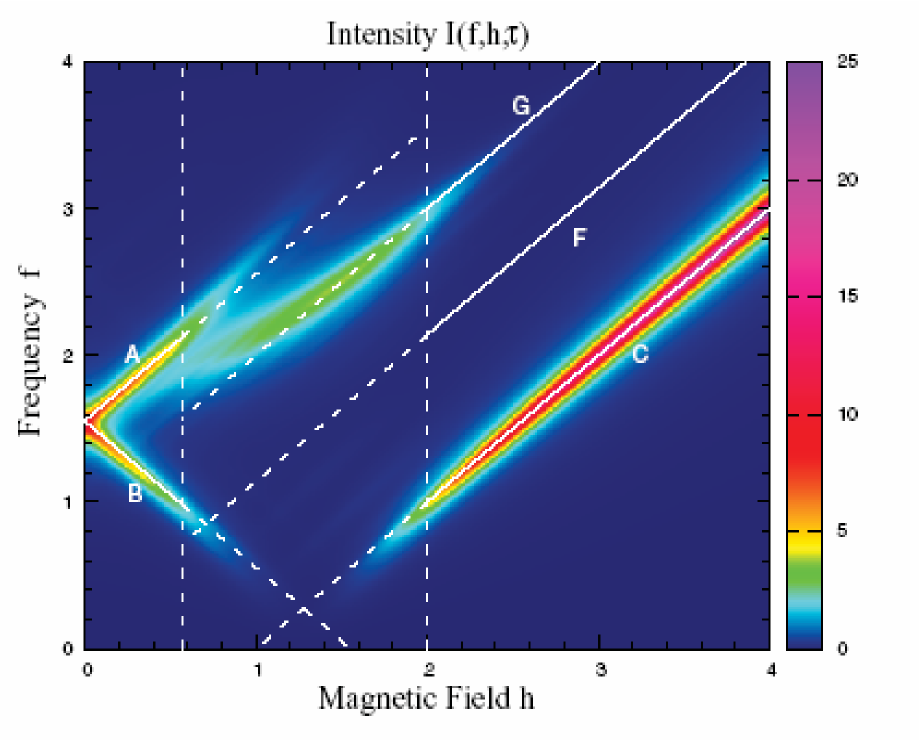


Psaroudaki et al., PRB 85, 014412 (2011)

Experiment



Theory by C.P.



1. Revised set of the spin-Hamiltonian parameters has been obtained
2. Works nicely describing low-T magnetization and the phase diagram of DTN
3. First conclusive observation and description of single-ion bound states in large-D spin system

Thank you for your attention!