

Ohio's Supercomputers, Network, and Computational Chemistry



Case Western Reserve University
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Ohio Supercomputer Center

Ohio Academic Resources Network



Provides supercomputer and network access for all universities and colleges in the state.

Located in Columbus, operated by the Ohio State University

OSC Computers

Originally one large Cray vector machine.

More recently, several machines of various architectures.

	cpu's	memory	disk
Cray X1	64 vector	128 GB	11.2 TB
Pentium 4 Cluster	512	4 GB each	80 GB each
Itanium 2 Cluster	520	4-12 GB each	80 GB each
SGI Altix	3(16 It.) + (32 It.)	32-64 GB	60-400 GB
Sun 6800 (being phased out)	24	48 GB	500 GB
Mass Storage System			450 TB



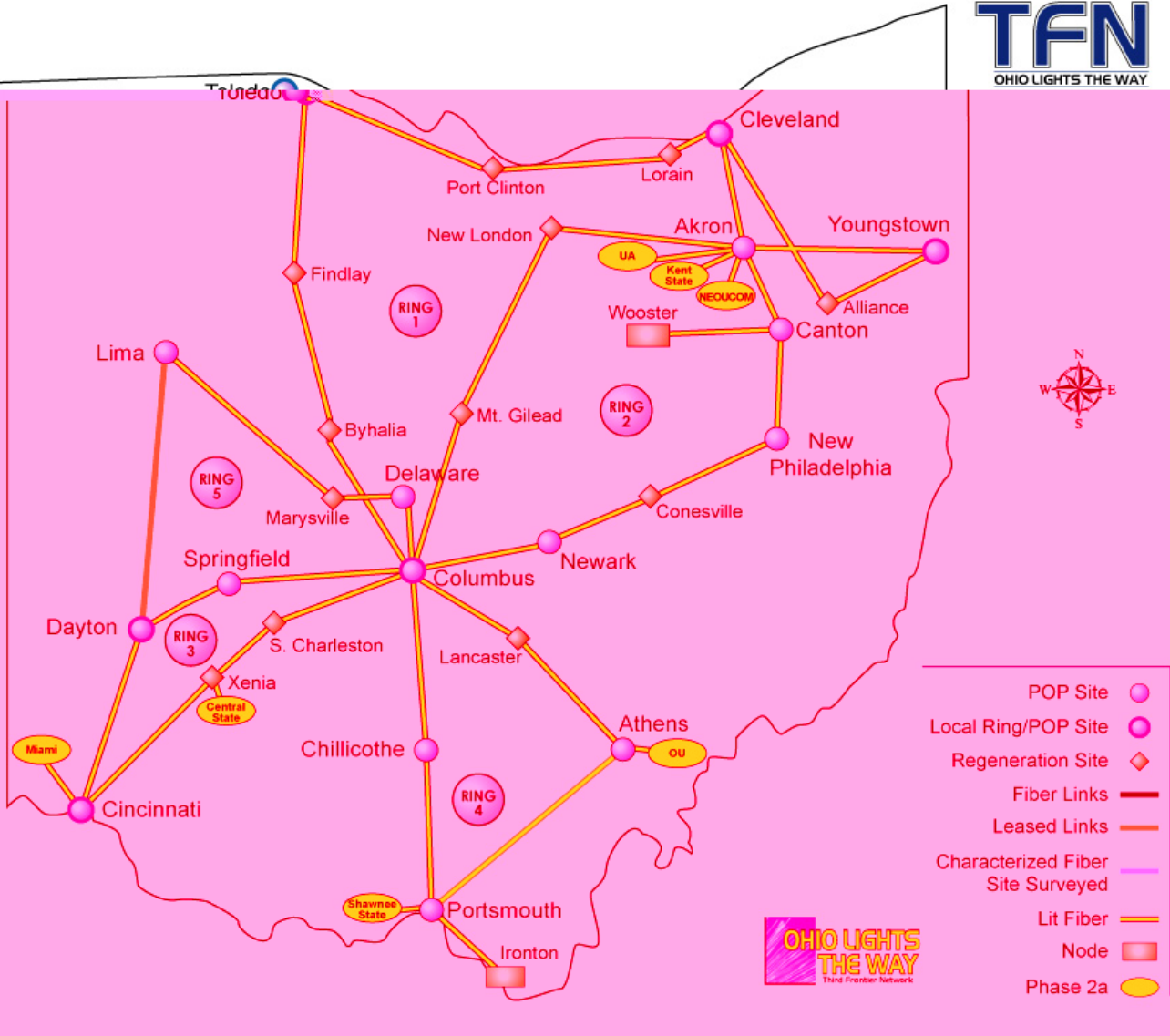
Cluster Ohio Program

Clusters of commodity cpu's – need to replace cpu's about every two years.

Break up old cluster (256-512 cpu's) into smaller clusters (32 cpu's) and give them to individual research groups around state for use for another two years or so. Provide all basic software by statewide site license.

TFN Network Map

TFN
OHIO LIGHTS THE WAY

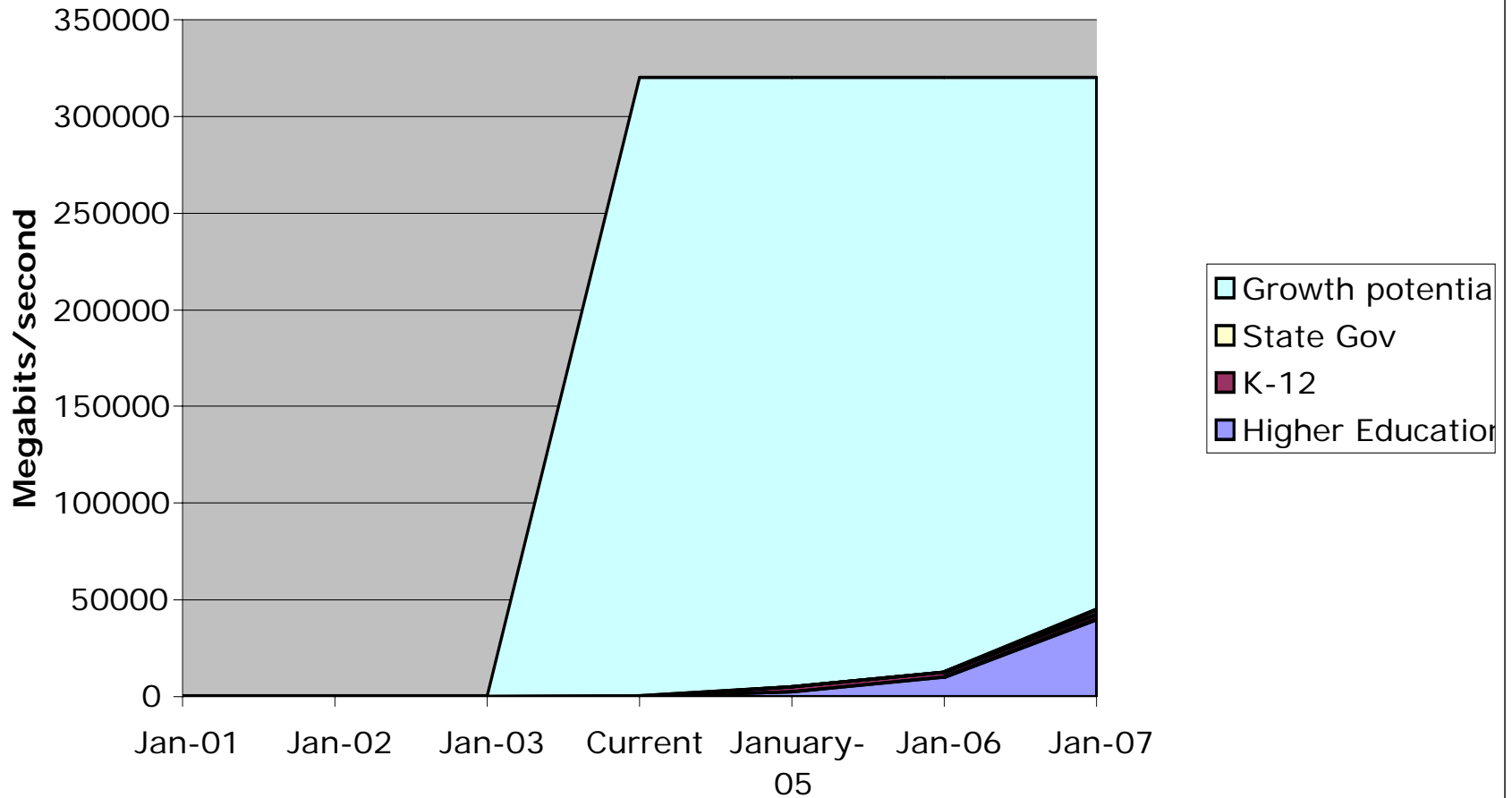


- POP Site
- Local Ring/POP Site
- Regeneration Site
- Fiber Links
- Leased Links
- Characterized Fiber
- Site Surveyed
- Lit Fiber
- Node
- Phase 2a



TFN Capacity

TFN Capacity and Use



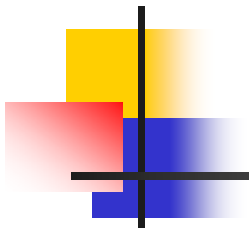


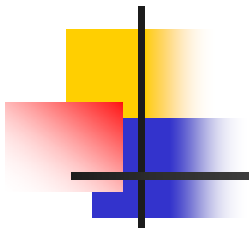
Green Fluorescence of UO_2^{2+}

Uranyl ion: UO_2^{2+}

Linear ion, most stable chemical form of uranium when air, water are present.

Usually complexed with 4-6 ligands in solution or crystals







Discovery of Uranium

Major Ag mine in Bohemia, south side of Erzgebirge, St. Joachimsthal

Ag coins called

Joachimsthaler → thaler ↓
daler → dollar

Also found was an unidentified black ore, pitchblende.

Martin H. Klaproth

1789

School of Mines, School of Artillery

Berlin

Had already discovered other elements.

Concluded that pitchblende contained a new metallic element. Named it uranium after the recently discovered planet.

Chem. Ann. Freunde Naturl. 1789, No. 2, 387-403



Martin H. Klaproth



Optical Properties of U Compounds

Studied optical properties of a yellow Bohemian glass, (canary glass, known to contain U)

Absorption: blue

Reflection: yellow

“internal dispersion”

George G. Stokes

1852

Cambridge University

Optical studies of emitted light from many substances, including

canary glass

several U minerals

several uranyl salts

Stated (Stokes') Law (rephrased)

Emitted light has lower frequency than absorbed light.

Coined new word for emitted light

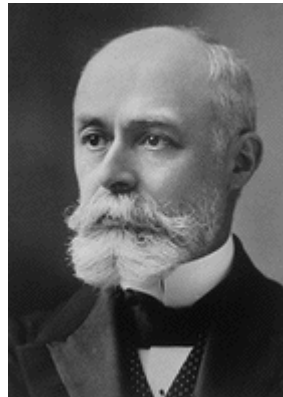
fluorspar + opalescence



A. Henri Becquerel

1896
Paris

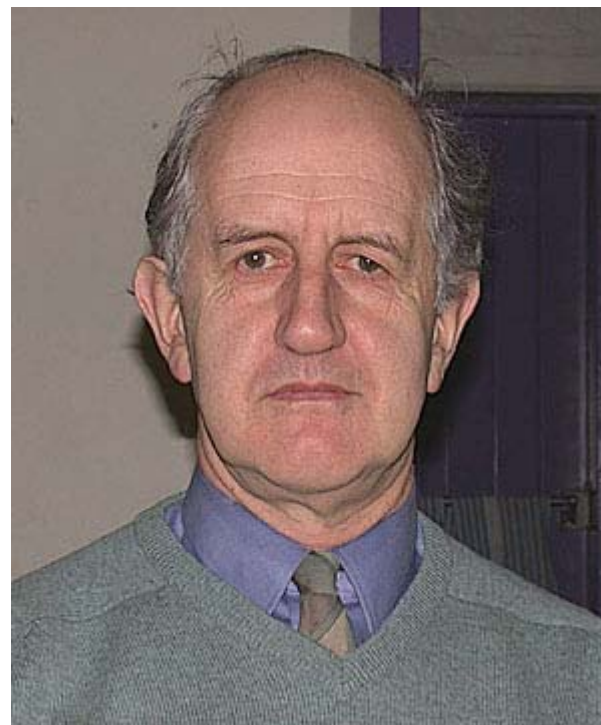
Experiments suggested by discovery of x-rays by Röntgen in 1895. Found that $K_2UO_2(SO_4)_2$ fogged a photographic plate. Awarded Nobel prize for radioactivity with M. Curie and P. Curie.



Detailed Study of Uranyl Spectroscopy – Assignment of transitions by Orbital and Spin Angular Momentum Quantum Numbers.

Robert Denning
Oxford University
Late 1970's

single crystals
very low temperatures
polarized light



Review Paper

Struct. Bonding (Berlin) 1992, 79, 215-277



Relativistic Theory and Quantum Mechanics applied to Chemistry

Computational methods based on Schrödinger Equation and Dirac Equation with various approximations.

Solutions to these equations are wave functions and energies, where wave functions give the probability distributions for finding electrons and nuclei.

One-electron wave functions – orbitals

Molecular orbitals – MOs

Atomic orbitals – AOs

Many-electron wave functions are built from products of MOs according to the Pauli Principle



Linear Expansions lead to Matrix Formulations

AOs – use Gaussian radial functions, angular functions

MOs – linear combinations of AOs

(typical length 10^2)

Antisymmetrized products of MOs and spin functions -
Configuration State Functions (CSFs)

Many-electron wave function –

linear combination of CSFs

(typical length 10^7)



Most Computationally Intensive Step

Extract modest number (typical number 10^1) of the lowest eigenvalues, with eigenvectors, of $10^7 \times 10^7$ real, symmetric, sparse matrix.

Matrix is not stored as such

Davidson Method (Iterative)

From initial approximate vectors, form matrix-vector products, using stored precursor quantities rather than matrix elements.

Many details. Many control parameters. Has been done in parallel.
Basis of Columbus programs.

- I. I. Shavitt – Ohio State, retired
- II. R. Shepard – Argonne National Laboratory
- III. H. Lischka – Univ. Vienna
- IV. T. Müller - Jülich



Energy Terms in Molecules

Non-relativistic:

1. kinetic energy
2. electrostatic

Relativistic:

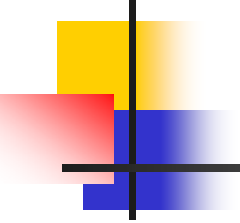
1. dependence of mass on speed
2. Darwin term
3. spin-orbit interaction
4. other (often ignored)

Conserved Quantities in Linear Molecules
(Constants of Motion)

Angular Momentum Components along the axis

1. orbital
2. spin
3. total

Uranyl Electronic States



	Orbital	Spin	Total (Ang. Mom.)
_____	3	0	3
_____	3	1	4
_____	mixed	mixed	3
_____	mixed	mixed	2
_____	mixed	mixed	3
_____	mixed	mixed	2
_____	2	-1	1

_____	0	0	0

green

Uranyl Electronic Energies (in cm^{-1})

Computed

$\text{Cs}_2\text{UO}_2\text{Cl}_4$

$\text{CsUO}_2(\text{NO}_3)_3$

31,710

29,412

31,262

27,983

27,738

29,618

26,118

26,222

27,062

23,902

22,578

23,474

22,628

22,051

22,786

21,421

20,861

21,694

20,719

20,096

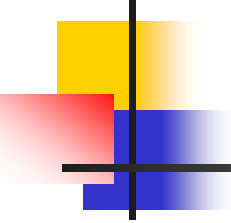
21,090

0

0

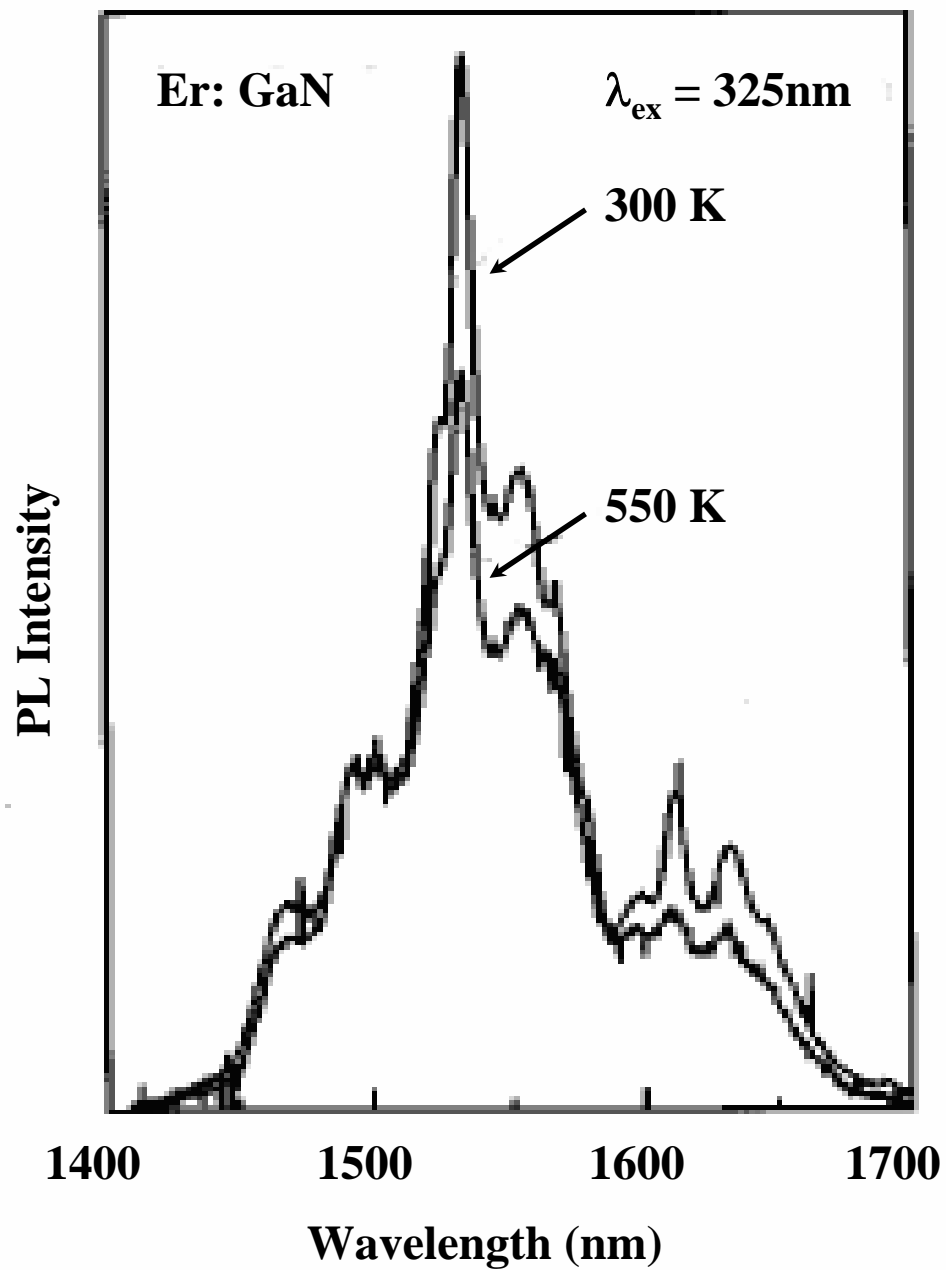
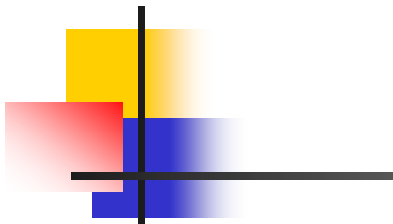
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J. Phys. Chem. A, 1999, 103, 6880-6886



Near-Infrared Photoluminescence
Of Er^{3+} doped into GaN
1540 nm

(Transmission region of optical fibers)



M. Thaik *et al.*, APL, 1997



Crystal Field

GaN exists in two crystal structures
zinc blende, wurzite

Theoretical estimate of $\Delta E_{\text{zinc blende-wurzite}} = 1 \text{ kJ/mol}$

1st shell: 4 N³⁻ ions

2nd shell: 12 Ga³⁺ ions

etc.

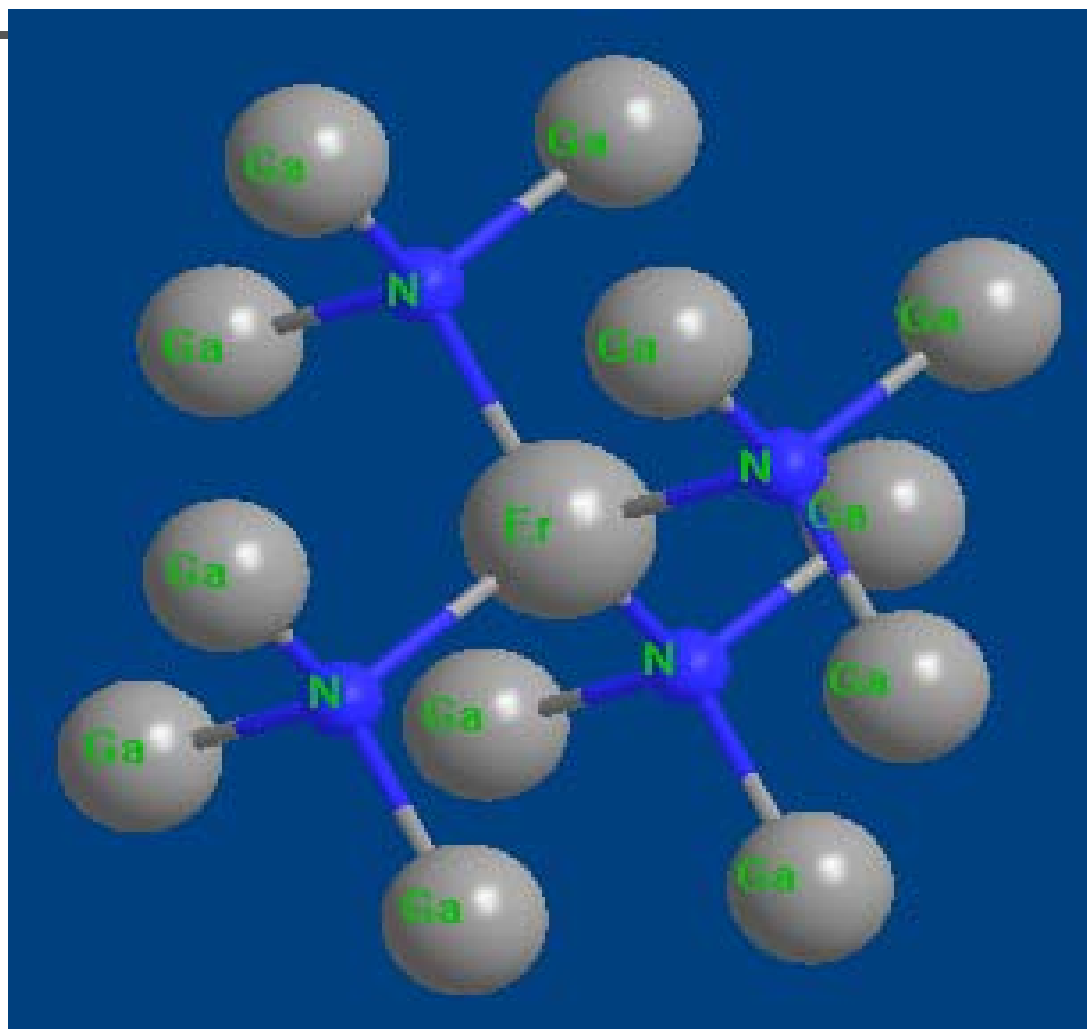
Results show little difference between the two crystal forms

Ionic Cluster

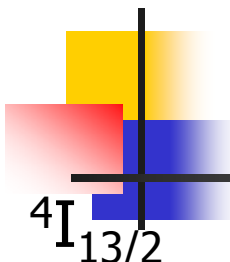
- Ionic Crystal Cluster Building
- Add shells by distance from the central ion
- Add shells until results converge
- Prefer clusters with smaller overall charge

<u>Cluster</u>	<u>No. atoms</u>
Er^{3+}	1
Er N_4^{9-}	5
$\text{Er N}_4 \text{Ga}_{12}^{27+}$	17
$\text{Er N}_4 \text{Ga}_{12} \text{N}_{12}^{9-}$	29
$\text{Er N}_4 \text{Ga}_{12} \text{N}_{12} \text{Ga}_6^{9+}$	35

$\text{ErN}_4\text{Ga}_{12}^{27+}$ T_d Cluster

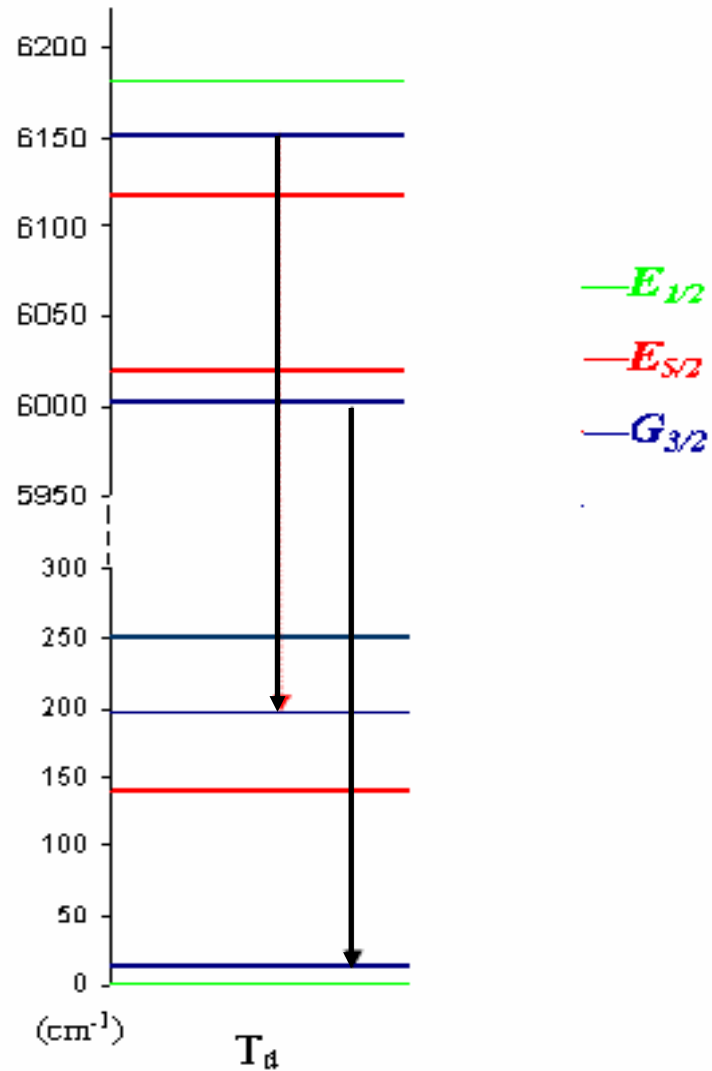


Relative Cluster Energy Levels (cm⁻¹)



		29 atoms	35 atoms
${}^4\text{I}_{13/2}$	$\text{E}_{1/2}$	6137.55	6159.12
	$\text{G}_{3/2}$	6117.12	6135.64
	$\text{E}_{5/2}$	6090.93	6104.59
	$\text{E}_{5/2}$	6009.36	6016.82
	$\text{G}_{3/2}$	5990.28	5994.71
${}^4\text{I}_{15/2}$	$\text{G}_{3/2}$	215.00	238.31
	$\text{G}_{3/2}$	196.71	212.71
	$\text{E}_{5/2}$	33.49	49.11
	$\text{G}_{3/2}$	18.63	22.13
	$\text{E}_{1/2}$	0.00	0.00

Most Intense Transitions





Comparing to the Spectrum

Need to know the initial populations of the upper sublevels.

Photoluminescence initiated by excitation to higher energy levels.

Range of upper levels = 164.41cm^{-1}

Range of lower levels = 238.31cm^{-1}

kT at 300K = 209cm^{-1}

Simplest reasonable assumption is that all upper levels are populated equally



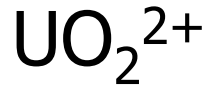
Conclusions

Calculations give a reasonable account of the splittings and intensities. Thus more detailed information on this spectrum is now available.

Use of larger clusters, other improvements, will yield better accuracy.

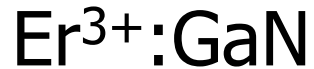
Collaborators

Columbus Programs: many people



Zhiyong Zhang

(now on support staff in materials research at Stanford University)



Yang Yang

(continuing studies at Univ. Wisconsin)

Research Grants

U.S. Department of Energy, Office of Basic Energy Sciences

Other Projects

with computer scientists, astronomers and possibly medical people

1. Application of Tensor Contraction Engine.

Program to write programs for efficient computation of tensor expressions

Written in JAVA and PYTHON

Writes well-optimized programs to evaluate defined expressions

Can test different formulations in a few days rather than a few months.

Many applied to coupled-cluster theory in chemistry.

2. X-ray spectroscopy applied to medicine.

Calculate positions of resonances for possible use in narrow-band x-ray treatments.