Laser Spectroscopy

Electronic transitions in solids are inhomogeneously broadened through the variation of local fields: each optical centre has a different local environment, even in well defined single crystals, due to imperfections and isotope distributions. The energy of an electronic transition depends on the local field, and thus varies over a range reflecting its distribution. Typical inhomogeneous widths of excitations in crystals are of the order of magnitude of 30 GHz (=1 cm^{-1}) respectively, whereas the homogeneous width can approach the limit imposed by the excited state lifetime and be as narrow as 100 Hz (=$3x10^{-9}$ cm^{-1}) at liquid helium temperatures.

Laser based techniques such as spectral hole-burning, fluorescence line narrowing and coherent transient spectroscopy, can overcome the inhomogeneous broadening and extremely narrow features can be measured. The main goal of the Laser Spectroscopy research group is to apply laser based techniques to chemically interesting system, including X-ray storage phosphors, nanoparticles and transition metal ions at extreme dilutions. Besides of delivering valuable results for a better understanding of electronic structure in the solid state, the prevailing driving force behind these spectroscopic studies are the potential applications in data storage and signal processing. Although conventional semiconductor based electronics and magnetic storage are the dominating technologies today, the ever increasing demands for high capacity, high speed storage and processing warrants investigations into optical computing and optical data storage. We are convinced that conventional technologies will be superseded by all-optical technology over the next decades.

Zhiqiang Liu, PhD student within the Australian Synchrotron, Melbourne.

Members

Academic Staff:

Assoc. Prof. Hans Riesen (Group Leader) (h.riesen@adfa.edu.au)
Dr phil.-nat., lic. phil.-nat. (*University of Berne, Switzerland*)

Visiting Fellow:

Captain Brendan Hayward

Research Assistant:

Tracy Massil

Research Students:

Zhiqiang Liu - Research Topic - Spectroscopy of Sm(III) activated X-ray storage phosphors

Baran Yildirim - Research Topic - Optical properties of transition metal ions in nanocrystalline wide-bandgap semiconductors

Current Honours Students:

Rees Davies

Phillip Russell

Recent Honours Student:

Thomas Monks-Corrigan – Exploration of hyperfine interaction within manganese (IV) doped corundum, 2007-2008.

Research Collaborators:

Emeritus Prof. S. Campbell (PEMS, UNSW@ADFA)

Prof. A. Hauser (University of Geneva, Switzerland)

Prof. G. Kearley (Braggs Institute, ANSTO)

Prof. E. Krausz (The Australian National University, Canberra)

Prof. N. B. Manson (The Australian National University, Canberra)

Prof. M. Mizuno (Kanazawa University, Japan)

Prof. A. D. Rae (Research School of Chemistry, The Australian National University)

Prof. A. Rebane (Montanna State University, Bozeman, USA)

Assoc. Prof. M. Stevens-Kalceff (School of Physics, UNSW, Sydney)

Dr A. Szabo (National Research Council of Canada - originator of modern laser spectroscopy of the solid state including FLN and hole-burning spectroscopy)

Current Research

Hans Riesen and his team are interested in a wide range of problems, ranging from applied research, such as X-ray storage phosphors, to very fundamental problems such as coherent transients, and "slow and stopped light" in transition metal doped systems.

The group has currently three major thrusts:

- The full development of the samarium based X-ray storage phosphors which have a significant chance to replace current personal radiation monitoring systems worldwide. UNSW has a spin-off company, Dosimetry & Imaging Pty Ltd, that commercializes this development. The technology can also be used for real time monitoring of doses administered in radiation therapy, and in medical imaging such as dental X-ray diagnostics and mammography. In particular for the latter, there is an urgent need to reduce X-ray dose.
- Optical and electronic properties of transition metal doped wide bandgap semiconductors are investigated by modern laser spectroscopy and a range of synchrotron based techniques such as XANES and XAFS. Some of the investigated materials have significant potential for applications in photovoltaic and electroluminescent devices.

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- We are continuing our quest in very high resolution laser spectroscopy of transition metal ions in the solid state. In particular we are pursuing frequency-switched coherent transients and slow light effects in hole-burning media.

Research Highlight

Associate Professor Hans Riesen has had a study of spectral hole burning selected as an Editor's Choice paper for publication in ***Chemical Physics Letters***. The paper is titled 'Transient spectral hole-burning studies of the R_2 line in ruby'. The paper's authors are **Hans Riesen**, **Nicolas Riesen**; **Nathan Schubert** and **Alex Szabo**. Nicolas Riesen was a Visiting Fellow in the School of PEMS from December 2007 to January 2008; Nathan Schubert was a CDF student who graduated in 2008 from UNSW@ ADFA; and Alex Szabo is the originator of high resolution spectroscopy of the solid state.

Recent Achievements/Recent Research

Hans Riesen, **Stewart Campbell** and Dr Gordon Kearley (ANSTO) were awarded a total of 16 days of beamtime on two instruments at the Berlin Neutron Scattering Centre (BENSC). Their projects were entitled: "Spectral Hole-Burning - Neutron spin-echo studies of water flips in $NaMgAl(oxalate)_3{\cdot}9H_2O$" and "Structure of $NaMgAl(oxalate)_3{\cdot}9H_2O$ - an extraordinary spectral hole-burning host". Stewart and Gordon Kearley travelled to Berlin in October 2008 to conduct the experiments.

These experiments will shed light on an interesting phenomenon discovered in PEMS by Joe Hughes and Hans Riesen: partial deuteration of $NaMgAl(oxalate)_3{\cdot}9H_2O/Cr(III)$ yields a 1000-fold increase in the quantum efficiency of spectral hole-burning in an electronic transition of chromium(III).

Zhiqiang Liu, PhD student operating the power X-ray diffraction beamline at the Australian Synchrotron, Melbourne.

PhD student **Zhiqiang Liu**, who is supervised by **Hans Riesen**, was selected to represent UNSW at the inaugural Australian Synchrotron Winter School. The inaugural Australian Synchrotron Science Winter School held from the 13-16 July, 2009 is a comprehensive 4 day program which has been developed with the aim of building knowledge of synchrotron techniques and providing hands-on practical experience for young researchers. The programme held at the Australian Synchrotron allowed hands-on beamline experiments together with a structured set of lectures by leading experts in the field. Students were guided through the process of data collection by experienced beamline scientists, and learnt about sample mounting, data acquisition and interpretation of the results.

Hans Riesen, Tracy Massil and **Zhiqiang Liu** have also recently carried out some Powder X-ray Diffraction studies at the Australian Synchrotron in Melbourne. Access to beam time is awarded on a competitive basis. Hans and his co-workers were very impressed by both the quality of the facilities and their organisation.

Student Research

Optical properties of transition metal ions in nanocrystalline wide-band gap semiconductors

Baran Yildirim (b.yildirim@student.adfa.edu.au) PhD

Field of Study: Photonics

In general, the aim of the study is to understand the optical and electronic properties of transition metal ions in wide-band gap semiconductors as a function of crystallite size. We started to examine some optical properties of Co^{2+} ions in $LiGa_5O_8$ nanocrystalline powders; there are both octahedral and tetrahedral sites in this lattice. It is assumed that the Co^{2+} ions can enter the crystal lattice in both sites during the combustion reaction. In order to validate this and understand the charge transfer mechanism, spectral hole-burning studies were performed in nano-powders and single crystals. The nanocrystals are to be examined in different hosts such as glasses and glass ceramics. Additionally, XANES (X-Ray Absorption Near Edge Structure) and XAFS (X-Ray Absorption Fine Structure) measurements are to be done at the Australian Synchroton in order to quantify the Co^{2+} ions in tetrahedral and octahedral sites. This material has some potential for photovoltaic applications; one of our motivations for this research project. We will continue conducting a systematic study of the optical properties of a range of transition metal ions incorporated into oxide nanocrystals.

Spectroscopy of Samarium(III) activated x-ray storage phosphors

Zhiqiang Liu (z.liu@student.adfa.edu.au) PhD

Field of Study: Chemistry

My research is based on a recent invention of a highly efficient samarium(III) activated X-ray storage phosphor by Hans Riesen and his team. This phosphor has many applications in medical X-ray imaging and radiology, potentially reducing the harmful X-ray dose for patients. It can also be used in personal radiation monitoring. In contrast to current commercial X-ray storage phosphors, the samarium (III) activated phosphor allows an accumulative and repetitive readout of the X-ray exposure by very narrow f-f photoexcited luminescence. My project will mainly focus on detailed investigations of the storage mechanism of the samarium(III) activated phosphor by a range of modern techniques such as laser spectroscopy (spectral hole-burning and fluorescence line narrowing), scanning and transmission electron microscopy,

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synchrotron powder diffraction and X-ray absorption experiments. Conventional spectroscopy techniques such as fluorescence, reflection, and Raman and ESR will also be employed in the project. Ultimately, we hope to gain a full understanding of the storage mechanism which may enable the design of other samarium(III) activated materials with even higher storage efficiencies.

PhD Opportunities and Scholarships

Possible PhD projects include:

- Systematic studies of dephasing processes and host-guest interactions in transition metal and rare earth compounds. In order to gain a better understanding of the dependence of dephasing processes on the structural properties of the guest and the host, the temperature dependence of the homogeneous linewidth of transition metal and rare earth complexes will be studied in a range of hosts
- Optically detected NMR in coordination compounds. This project has a significant potential to overcome the shortcomings of conventional NMR spectroscopy of coordination compounds with paramagnetic centres.
- Optimising the properties of novel X-rays storage phosphors. This project would take advantage of our recent discovery of a highly effective X-ray storage phosphor.

If you are interested in a PhD or Masters by Research in Laser Spectroscopy:

Contact:
Associate Professor Hans Riesen (h.riesen@adfa.edu.au)

Major Facilities

State of the art laser lab that is fully functional. Lab gear includes:

- Janis/Sumitomo SHI-4.5 closed-cycle refrigerator for optical work between 2.5 K and 300K.
- Janis liquid helium immersion cryostat with optical access.
- Large frame Argon laser Spectra Physics Stabilite.
- State of the art spectrometers and interferometers (Spex and Burleigh Instruments).
- Temperature and current controlled diode lasers (various manufacturers).
- Wavemeter (Coherent).
- Several external cavity diode lasers.

Publications

In Press

Journal - Refereed

Liu, Z., Massil, T. & **Riesen, H.,** in press, Spectral hole-burning properties of Sm^{2+} ions generated by X-rays in BaFCl: Sm^{3+} nanocrystals, HBSM 2009, ***Physics Procedia.***

Riesen, H., **Badek, K.** & Stevens-Kalceff, M., Correlation of inhomogeneous broadening with particle size probed by $^2E \rightarrow {}^4A_2$ luminescence in nanocrystalline $ZnAl_2O_4$/Co(II), submitted to ***Chemical Physics Letters.***

Riesen, H., Szabo, A., in press, Probing hyperfine interactions in ^{53}Cr(III) doped Al_2O_3 by spectral hole-burning in low magnetic fields, HBSM 2009, ***Physics Procedia.***

Yildirim, B. & **Riesen, H.**, in press, Spectral hole-burning properties of $LiGa_5O_8:Co^{2+}$ Nanocrystallites, HBSM 2009, ***Physics Procedia***.

2009 publications

Journal - Refereed

Riesen H., **Riesen N.**, **Schubert N.** & Szabo A., 2009, Transient spectral hole-burning studies of the R_2 line in ruby, ***Chemical Physics Letters,*** 475, 1-3, 10-14, doi:10.1016/j.cplett.2009.04.074.

Patent

Riesen, H., Massil, T. & **Liu, Z.,** 2009, ***Core-Shell Nanophosphors for Radiation Storage and Methods***, Australian Provisional Patent application.

Riesen, H. & Piper, K., ***Apparatus and Method for Detecting and Monitoring Radiation***, 2009, International PCT Application, World Intellectual Property Organization, Publication No WO 2009/052568.

Conference –Paper

Neely, A., Yesil, A., **Riesen, H.** & Odam, J., 2009, In-flight mapping of heating on a hypersonic nose cone, ***16th AIAA/DLR/DGLR International Space Planes and Hypersonic Systems and Technologies Conference,*** 19-22 October 2009, Bremen, Germany.

Conference - Poster

Liu, Z., Massil, T. & **Riesen, H.,** 2009, Spectral hole-burning properties of Sm^{2+} ions generated by X-rays in BaFCl: Sm^{3+} nanocrystals, ***10th International Meeting on Hole Burning, Single Molecule, and Related Spectroscopies: Science Applications,*** 22-27 June 2009, Palm Cove, Australia.

Riesen, H. & Szabo, A., 2009, Probing hyperfine interactions in ^{53}Cr(III) doped Al_2O_3 by spectral hole-burning in low magnetic fields. ***10th International Meeting on Hole Burning, Single Molecule, and Related Spectroscopies: Science Applications***, 22-27 June 2009, Palm Cove, Australia.

Wright, J., Ujhazy, A., Riesen, H. & Dicey, B.B., 2009, Characterizing a new technology for external personnel dosimetry, ***54th Annual Meeting of the Health Physics Society,*** 12-16 July 2009, Minneapolis, Minnesota, USA.

Yildirim, B. & **Riesen, H.,** 2009, Spectral hole-burning properties of $LiGa_5O_8:Co^{2+}$ Nanocrystallites, ***10th International Meeting on Hole Burning, Single Molecule, and Related Spectroscopies: Science Applications***, 22-27 June 2009, Palm Cove, Australia.

2008 publications

Journal - Refereed

Riesen, H.A., 2008, On the $6A_1 \leftarrow {}^4T_1$ luminescence of Fe^{3+} in disordered nanocrystalline $LiGa_5O_8$ prepared by a combustion reaction, ***Chemical Physics Letters***, 461(4-6), 218-221, doi:10.1016/j.cplett.2008.07.016.

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Riesen, H.A. & Dubicki, L., 2008, Probing the R Lines in Tris(acetylacetonato) Chromium(III) and Tris(3-bromo-acetylacetonato) Chromium(III) by Luminescence and Excitation Line Narrowing Spectroscopy, ***Journal of Physical Chemistry A***, 112(41), 10287-10293, doi: 10.1021/jp805831a.

Riesen, H.A. & Rae, A.D., 2008, Revisiting the crystal structure and thermal properties of $NaMgAl(oxalate)_3$ $9H_2O/Cr(III)$: An extraordinary spectral hole-burning material, ***Journal of the Royal Chemical Society, Dalton Transactions,*** 35, 4717-4722, doi: 10.1039/b802559b.

Patent

Riesen, H. & **Piper, K.**, 2008, *Apparatus and Method for Detecting and Monitoring Radiation*, Australian Provisional Patent Application No AU2008905332.

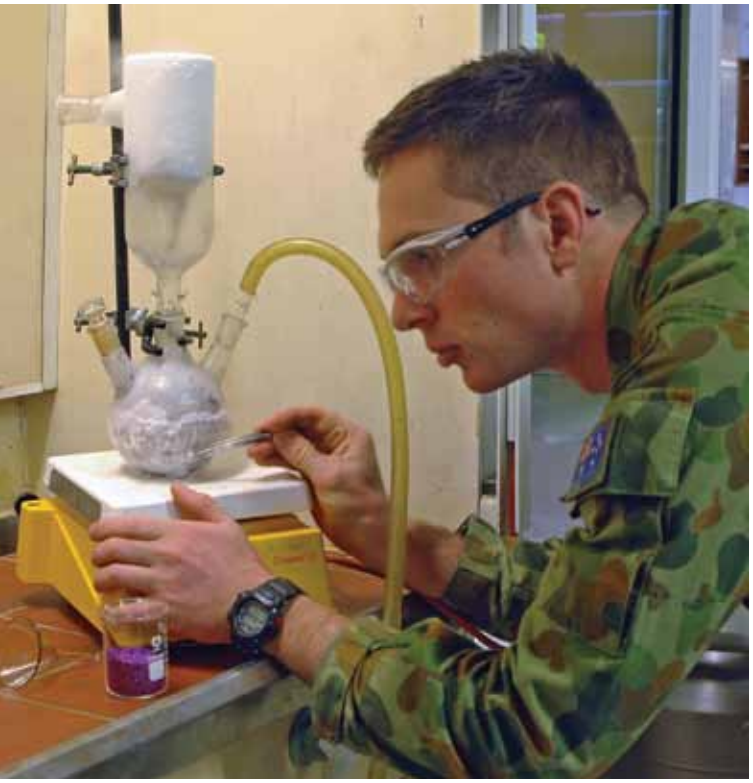
Grants

External Grants

H. Riesen, Highly efficient X-ray storage phosphor for medical and scientific imaging, ARC Discovery Project, 2007-2009: $270,000.

A. Neely & **H. Riesen**, Thermal paints for hypersonic flight-tests, US Department of Airforce, Asian Office of Aerospace Research and Development, 2009: $35,000.

H. Riesen, High resolution powder X-ray diffraction studies of X-ray storage phosphors based on core shell nanoparticles, Australian Synchrotron Access Program, 2009: $1,400.



Honours student Rees Davies working in the laboratory.

S. Campbell, K. Kearley & **H. Riesen**, Spectral hole burning - Neutron spin-echo studies of water flips in NaMgA $(oxalate)_3$. $9H_2O$, Structure of $NaMgAl(oxalate)_3$. $9H_2O$ - an extraordinary spectral hole-burning host, Access to Major Research Facilities Programme, 2008: $11,800.

UNSW Grants

H. Riesen, S. Campbell & W.G. Jackson, Light-induced water flips in crystals: high density optical storage at the molecular level, UNSW Silverstar scheme, 2008: $20,000.

Service

Hans Riesen is acting on two editorial boards of international journals and regularly reviews articles for several journals of high international standing.

Hans was one of the organizers ***of HBSM 2009*** in Palm Cove near Cairns, and acts as an editor of the conference proceedings that will appear in special issues of the ***Journal of Luminescence and Physics Procedia.***

Hans is also the Research Coordinator of PEMS.