



# 14<sup>th</sup> Meeting of the Benelux EPR Group

## Program and Abstracts



University of Leuven  
Department of Physics and Astronomy  
Department of Interface Chemistry

Campus Library Arenberg  
3001 Leuven-Heverlee

19 May 2006

# Organization

Andre Stesmans  
*Department of Physics and Astronomy*

# Backing

Robert Schoonheydt  
*Department of Interface Chemistry*  
Peter Gast  
*Leiden Department of Molecular Physics*

**14<sup>th</sup> Meeting of the Benelux EPR Group**  
**University of Leuven – May 19, 2006**

- 10.00      *Registration + poster display + coffee*
- 10.30      *Welcome*
- 10.35 **Electron Paramagnetic Resonance study of rare earth activated K2YF5 thermoluminescent phosphors**      O1  
*Frank Loncke, H. Vrielinck, P. Matthys, and F. Callens*  
*Department of Solid State Sciences, University of Ghent*
- 11.00 **Interactions between single wall carbon nanotubes and organic molecules studied by EPR**      O2  
*Sofie Cambré, W. Wenseleers, and E. Goovaerts*  
*Exp. Condensed Matter Physics group, Physics Department, University of Antwerp*
- 11.25 **Mechanisms and consequences of differences in radical generating capacity of the air polluting component particulate matter (PM) as detected by ESR spectroscopy**      O3  
*Jacob Jan Briede, J.G. Hogervorst, J.C.S. Kleinjans, T.M.C.M. de Kok*  
*Department of Health Risk Analysis and Toxicology, Maastricht University*
- 11.50 **ESR dating of sedimentary quartz**      O4  
*Koen Beerten<sup>a</sup>, A. Stesmans<sup>b</sup>, and U. Radtke<sup>a</sup>*  
*<sup>a</sup>Geographisches Institut der Universität zu Köln, Köln, Germany*  
*<sup>b</sup>Department of Physics and Astronomy, University of Leuven*
- 12.15      *Lunch and group picture*
- 14.00 **Revealing the differences in the heme pocket structure of ferric human Cygb and tomato hemoglobin**      O5  
*A. Iulia Ioanitescu<sup>1</sup>, S. Van Doorslaer<sup>1</sup>, B. Endeward<sup>2</sup>, S. Dewilde<sup>3</sup>, and L. Moens<sup>3</sup>*  
*<sup>1</sup>Departments of Physics and <sup>3</sup>Biomedical Sciences, University of Antwerp,*  
*<sup>2</sup>Inst. for Phys. and Theor. Chemistry, JW Goethe University, Frankfurt am Main*
- 14.25 **Reduction enhances yields of in-vivo trapping of nitric oxide.**      O6  
*Anatoly Vanin<sup>1</sup> and E. van Faassen<sup>2</sup>*  
*<sup>1</sup>Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia*  
*<sup>2</sup>Debye Institute, Interface Physics, Utrecht University*
- 14.50 **EPR characterization of the iron-sulfur clusters in the hybrid-cluster protein of Pyrococcus furiosus**      O7  
*Peter-Leon Hagedoorn*  
*Department of Biotechnology, University of Technology, Delft*
- 15.15      *Coffee break — poster session*

- 15.40 **A multi-frequency EPR study of Co(II)S<sub>4</sub> coordination** O8  
Sergey Milikisyants<sup>a</sup>, D. Maganas<sup>a</sup>, H. Blok<sup>a</sup>, P. Gast<sup>a</sup>, A. Grigoropoulos<sup>b</sup>,  
P. Kyritsis<sup>b</sup>, G. Pneumatikakis<sup>b</sup>, J.M.A. Rijnbeek<sup>a</sup>, S. Sottini<sup>a</sup>, E.J.J. Groenen<sup>a</sup>  
<sup>a</sup>*Department of Molecular Physics, Leiden University*  
<sup>b</sup>*Department of Chemistry, University of Athens, Greece*
- 16.05 **Electron spin resonance probing of fundamental point defects in  
nm-sized silica particles** O9  
Katrijn Clémer, A. Stesmans, and V. V. Afanas'ev  
*Department of Physics and Astronomy, University of Leuven*
- 16.30 **Electron and chlorine interstitials trapping at Fe<sup>2+</sup> impurity ions in  
chlorinated SrCl<sub>2</sub> crystals** O10  
Daniela Ghica<sup>1</sup>, S. Nistor<sup>1</sup>, H. Vrielinck<sup>2</sup>, F. Callens<sup>2</sup>, E. Goovaerts<sup>3</sup>, D. Schoemaker<sup>3</sup>  
<sup>1</sup>*National Institute for Materials Physics, Bucharest, Romania*  
<sup>2</sup>*Department of Solid State Science, University of Ghent*  
<sup>3</sup>*Department of Physics, University of Antwerp*
- 16.55 *General discussion and closing remarks*
- 17.00 *Poster session with drinks in the cloister (corridor; ground floor)*

## Poster presentations

- EPR investigation of Gd<sup>3+</sup> doping impurity in PbWO<sub>4</sub> scintillating crystals** P1  
Mariana Stefan<sup>1</sup>, S. V. Nistor<sup>1</sup>, E. Goovaerts<sup>2</sup>, M. Nikl<sup>3</sup>, and P. Bohacek<sup>3</sup>  
<sup>1</sup>National Institute for Materials Physics, Bucharest, Romania; <sup>2</sup>Department of Physics, University of Antwerp; <sup>3</sup>Institute of Physics AS CR, Prague, Czech Republic
- EPR study of formation of hemoglobin - nitric oxide adduct in whole mouse blood: influence of caveolin-1 genetic deletion** P2  
Irina Lobysheva, C. Dessy, O. Feron, B. Gallez, and J.-L. Balligand  
Unit of Pharmacology and Therapeutics, University of Louvain Medical School
- Electron Magnetic Resonance Study of Radiation-Induced Defects in Sucrose Single Crystals: an Overview** P3  
Hendrik De Cooman<sup>1,2</sup>, G. Vanhaelewyn<sup>1</sup>, E. Pauwels<sup>2</sup>, F. Callens<sup>1</sup>, M. Waroquier<sup>2</sup>  
<sup>1</sup>Dept. of Solid State Sciences, and <sup>2</sup>Center for Molecular Modeling, University of Ghent
- Optical and EPR spectroscopy in low band gap/fullerene derivative blends** P4  
Aranzazu Aguirre<sup>1</sup>, G. Janssen<sup>1</sup>, E. Goovaerts<sup>1</sup>, K. Colladet<sup>3</sup>, L. Lutsen<sup>2</sup>, D. Vanderzande<sup>3</sup>  
<sup>1</sup>Department of Physics - CDE, University of Antwerp; <sup>2</sup>IMEC, IMOMEC division, Diepenbeek; <sup>3</sup>Institute for Materials Research (IMO), Hasselt University, Diepenbeek
- Inherent point defects in tensile strained (100)Si/SiO<sub>2</sub> structures probed by electron spin resonance** P5  
Pieter Somers, V. V. Afanas'ev, and A. Stesmans  
Department of Physics and Astronomy, University of Leuven
- Comparison of ferric E7Q neuroglobin with the aquomet form of horse heart myoglobin using advanced pulsed EPR techniques** P6  
Florin Trandafir<sup>1</sup>, M. Fittipaldi<sup>1</sup>, S. Dewilde<sup>2</sup>, L. Moens<sup>2</sup>, S. Van Doorslaer<sup>1</sup>  
Departments of Physics<sup>1</sup> and Biomedical Science<sup>2</sup>, University of Antwerp
- Electron spin resonance analysis of Si nanocrystals embedded in an SiO<sub>2</sub> matrix** P7  
Mihaela Jivanescu, A. Stesmans, S. Godefroo, and M. Hayne  
Department of Physics and Astronomy, University of Leuven
- Characterization of heterogeneous mesoporous catalysts using electron paramagnetic resonance** P8  
Sepideh Zamani<sup>1</sup>, A. Hanu<sup>2</sup>, P. Cool<sup>2</sup>, and S. Van Doorslaer<sup>1</sup>  
Departments of Physics<sup>1</sup> and Chemistry<sup>2</sup>, University of Antwerp
- Multifrequency ESR of nominally pure, amber coloured superhard cubic boron nitride crystals** P9  
Sergiu V. Nistor<sup>1</sup>, D. Ghica<sup>1</sup>, M. Stefan<sup>1</sup>, A. Bouwen<sup>2</sup>, and E. Goovaerts<sup>2</sup>  
<sup>1</sup>National Institute for Materials Physics, Bucharest, Romania; <sup>2</sup>Department of Physics, CDE, University of Antwerp
- Donor-Acceptor pairs in the Confined Structure of ZnO Nanocrystals** P10  
Serguei B. Orlinskii<sup>1</sup>, H. Blok<sup>1</sup>, J. Schmidt<sup>1</sup>, P. G. Baranov<sup>2</sup>, C. Donegá<sup>3</sup>, A. Meijerink<sup>3</sup>  
<sup>1</sup>Department of Molecular Physics, Huygens Laboratory, Leiden University  
<sup>2</sup>A.F. Ioffe Physico-Technical Institute, RAS, St. Petersburg, Russia; <sup>3</sup>Debye Institute, Utrecht University

**EPR analysis of a new Cobalt Salen Complex: Cobalt Jacobsen's Catalyst**

P11

Evi Vinck<sup>1</sup>, S. Van Doorslaer<sup>1</sup>, R. Tucker<sup>2</sup>, D. M. Murphy<sup>2</sup>, and I. A. Fallis<sup>2</sup>.

<sup>1</sup>*Department of Physics, University of Antwerp;*

<sup>2</sup>*Department of Chemistry, Cardiff University, Wales, UK*

**An EPR study of the exchange interaction between two Cu(II)-ions in protein dimers connected by different linkers**

P12

Sergey Milikisyants<sup>1</sup>, T. de Jongh<sup>2</sup>, R. van den Nieuwendijk<sup>2</sup>, M. Overhand<sup>2</sup>,  
G. Canters<sup>b</sup>, Martina Huber<sup>1</sup>

<sup>1</sup>*Department of Molecular Physics, Leiden University*

## **Oral contributions**

GAP

↳ St. Andrews

O1

## Electron Paramagnetic Resonance study of rare earth activated $K_2YF_5$ thermoluminescent phosphors

F. Loncke, H. Vrielinck, P. Matthys and F. Callens

*Department of Solid State Sciences, Ghent University, Krijgslaan 281 – S1, B-9000 Gent, Belgium, Frank.Loncke@UGent.Be*

As promising new candidates for thermoluminescence (TL) dosimetry,  $K_2YF_5$  crystals singly doped with rare earth (RE) ions are of increasing interest. TL phosphors based on these materials show relatively high sensitivity to ionising radiation and low fading. For some  $K_2YF_5:RE$  combinations, the shape of the TL glow curves depends on the type ( $\alpha$ ,  $\beta$  or  $\gamma$  - rays) of radiation, which offers possibilities for discriminating mixed radiation fields [1-3].  $RE^{3+}$  ions can substitute for  $Y^{3+}$  without charge compensation or strong distortion, since the radii of host and dopant ion are similar. The fact that high concentrations can be attained, will not only increase the number of luminescence activator centres, but may also contribute to the formation of new types of traps. In addition, from a fundamental point of view, the  $K_2YF_5$  host offers the opportunity of studying  $RE^{3+}$  ions in the less frequently encountered hepta-coordination.

In this contribution we report the first results of our Electron Paramagnetic Resonance (EPR) and Electron Nuclear Double Resonance (ENDOR) study on as grown  $K_2YF_5$  crystals (orthorhombic symmetry, space group  $Pna2_1$ ), doped with  $Ce^{3+}$ ,  $Dy^{3+}$  and  $Tb^{3+}$ . With these spectroscopic techniques one can determine in detail the microscopic structure of dopant related and radiation induced defects. The EPR spectra reveal that the crystals contain  $Gd^{3+}$  as unintentional impurity. In  $K_2YF_5:Ce^{3+}$  crystals with low dopant concentration, one  $Ce^{3+}$  centre is observed, with monoclinic symmetry. The ENDOR spectra corresponding to this centre are due to interactions with the nearest  $^{19}F$  shells. The magnetic resonance characteristics are correlated with structural properties of the dopant site known from X-ray diffraction [4].

### References

- [1] "Effect of  $Pr^{3+}$  concentration on thermoluminescence from  $K_2Y_{1-x}Pr_xF_5$  crystals", J. Marcazzo, M. Santiago, E. Caselli, N. Nariyama and N. M. Khaidukov, *Opt. Mater.* 26 (1), 65-70 (2004).
- [2] "Initial thermoluminescent dosimetry experience with  $K_2YF_5$  materials using beta and X-ray sources", D. McLean, J. Varas and N. M. Khaidukov, *Radiat. Phys. Chem.* 71 (3-4), 995-996 (2004).
- [3] "Thermoluminescence response of  $K_2YF_5:Tb^{3+}$  crystals to photon radiation fields", L. O. Faria, D. Lo, H. W. Kui, N. M. Khaidukov and M. S. Nogueira, *Radiat. Prot. Dosim.* 112 (3), 435-438 (2004).
- [4] "Crystallographic structure of  $K_2YF_5$ ", Y.A. Kharitonov, Y.A. Gorbunov and B.A. Maksimov, *Kristallografiya* 28, 1031 (1983)

→  $Er^{3+}$  en  $Dy^{3+}$  ook uitmeten!



## Interactions between single wall carbon nanotubes and organic molecules studied by EPR.

S. Cambré, W. Wenseleers, E. Goovaerts

*Experimental condensed matter physics group. Physics department. University of Antwerp. Universiteitsplein1, B-2610 Antwerp (Belgium)*

Carbon nanotubes are very promising materials for organic electronics due to their unique mechanical, electronic and optical properties. Composites of carbon nanotubes with organic molecules are very interesting for use in organic optoelectronic devices. The organic molecules can interact with the surface of the carbon nanotubes by  $\pi$ -stacking interactions and induce an energy or charge transfer after optical excitation. Another possibility is to encapsulate the molecules inside the carbon nanotubes to induce an amphoteric doping. [1]

In this study we use EPR in combination with resonant Raman scattering, absorption and fluorescence spectroscopy to characterize composites of paramagnetic organic molecules and carbon nanotubes. By using the recently developed technique to solubilize single wall carbon nanotubes in water using bile salts as surfactants [2], we can also study the interaction of individual carbon nanotubes with the molecules.

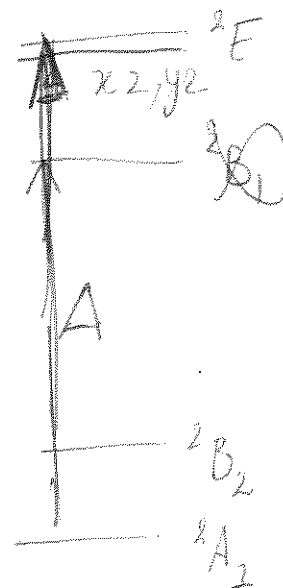
We found that for composites of carbon nanotubes with Cu(II) di-acetylacetonate and a Co(II) porphyrine a significant part of the paramagnetic molecules are insensitive to environmental changes which shows that these molecules are protected by the nanotubes. This is consistent with the encapsulation of the molecules inside the carbon nanotubes.

In addition the fluorescence of the porphyrins in the composites is strongly quenched and time resolved measurements indicate a short decay component, showing that there is an energy or charge transfer between the porphyrins and the carbon nanotubes.

- [1] T. Takenobu *et al.*, *Stable and controlled amphoteric doping by encapsulation of organic molecules inside carbon nanotubes*, Nature materials 2, 683 (2003)  
 [2] W. Wenseleers *et al.*, *Efficient Isolation and solubilization of pristine single-walled nanotubes in bile salt micelles*, Adv. Funct. Mater. 14, 1105 (2004)

*Time-resolved measurements in ps range*

*Lower symmetry  
or higher symmetry*



## **Mechanisms and consequences of differences in radical generating capacity of the air polluting component particulate matter (PM) as detected by ESR spectroscopy.**

Briede JJ, Hogervorst JG, Kleinjans JCS, de Kok TMCM

*Department of Health Risk Analysis and Toxicology, Faculty of Health Sciences, Nutrition and Toxicology Research Institute Maastricht (NUTRIM), Maastricht University, Maastricht, The Netherlands.*

The last decade much attention has been paid to negative health effects of air pollution by elevated ambient particulate matter (PM). Epidemiological studies show that exposure to increased levels of PM are associated with lung and cardiovascular diseases. The formation of reactive oxygen species (ROS) is thought to play an important role in the induction and development of these diseases. We developed an improved electron spin (ESR) spectroscopy-based method to quantify the ROS generating capacity (RGC) of PM. ROS formation was measured directly on the PM-sampled filters after addition of ascorbic acid and the spin trap DMPO. With this method we showed that there was a clear relationship between RGC and lung function of children in the age of 8 – 13 years old. Furthermore, the RGC correlated with the concentration of (carcinogenic) polycyclic aromatic hydrocarbons (PAHs) in ambient PM samples taken in Maastricht (the Netherlands), Teplice and Prachtice (Czech Republic) and Augsburg (Germany). Recent research showed that specific PM-associated oxygenated PAHs, especially the PAH monoketones, correlated with PM-induced ROS formation. Altogether, with this ESR-based method much more insight was gained into the mechanism by which PM induced ROS formation causing adverse health effects.

de Kok TM, Hogervorst JG, Briede JJ, van Herwijnen MH, Maas LM, Moonen EJ, Drieste HA, Kleinjans JC. Genotoxicity and physicochemical characteristics of traffic-related ambient particulate matter. *Environ Mol Mutagen.* (2005) 46 71-80

Briede JJ, De Kok TM, Hogervorst JG, Moonen EJ, Op Den Camp CL, Kleinjans JC. Development and application of an electron spin resonance spectrometry method for the determination of oxygen free radical formation by particulate matter. *Environ Sci Technol.* (2005) 39 8420-6.

Hogervorst JG, de Kok TM, Briede JJ, Wesseling G, Kleinjans JC, van Schayck CP. Relationship between Radical Generation by Urban Ambient Particulate Matter and Pulmonary Function of School Children. *J Toxicol Environ Health A.* 2006 69 245-62.

SiO<sub>2</sub>: Ti-H  
Ti-Li } single crystal

## ESR dating of sedimentary quartz

K. Beerten<sup>a,\*</sup>, A. Stesmans<sup>b</sup>, and U. Radtke<sup>a</sup>

<sup>a</sup> Geographisches Institut der Universität zu Köln, Albertus-Magnus-Platz, 50923 Köln, Germany.

<sup>b</sup> Departement Natuurkunde en Sterrenkunde, Katholieke Universiteit Leuven, Celestijnenlaan 200 D, 3001 Leuven, Belgium.

\* Corresponding author: kbeerten@uni-koeln.de

During the past decades, ESR spectroscopy has become an important tool in earth science to estimate the age of various geological events. One of these is the sedimentation age, or burial time, of sedimentary quartz grains. Sediments contain crucial information on past environmental changes, and determining their burial time may help to assess the age of such changes. A well-known example is the timing of glacial and interglacial periods during the last million years.

Several ESR-active centres in natural quartz are known to be useful for estimating the burial time of sediments. These ESR centres are impurity-related defect sites, consisting of an impurity-atom (Al, Ti or Ge) substituting for Si in the SiO<sub>2</sub> network. They can be activated by ionising radiation, thereby trapping an electron or a hole, and can be passivated by the UV-component of (simulated) sunlight. The passivation mechanism occurs in nature by exposure to solar UV-irradiation during transport (by water or wind) of the quartz grains prior to burial, a process which is referred to as sunlight bleaching. After burial, the ESR centres are activated again due to ionising radiation from U, Th and K in the surrounding sediment. As such, the ESR centres can be used to determine the radioactive dose (the equivalent dose,  $D_e$ ), that the quartz grains had received during burial. If also the rate is known at which the radioactive dose (the dose rate,  $D$ ) was absorbed during burial, the burial time and thus the sedimentation age can be determined. The simplified age equation can thus be written as  $t = D_e/D$ . The equivalent dose is determined by comparing the natural ESR intensity with the artificially induced ESR intensity. The dose rate is usually determined by gamma-spectroscopy or inductively coupled plasma mass spectrometry (ICP-MS) analysis.

The underlying assumption of the ESR dating method is that all the relevant ESR centres were totally bleached prior to burial, thereby resetting the geological clock to zero. If this is not the case, residual doses will generate an ESR signal which is too high. In such case, the ESR age will be an *overestimate* relative to the real geological age of the event. Conversely, the ESR-activated defect sites should be stable enough in time to ensure that the targeted geological period can be entirely covered. If not, the ESR signal will be too low in which case the ESR age will be an *underestimate* relative to the real age.

Here we will show several case studies to illustrate the potential and problems of ESR dating of sediments. The samples were taken from a variety of sedimentary deposits from Africa, Australia and Europe with an age between 0 and 2000 ka (2 million years). Results from single grains (Q-band) and multiple grain samples (X-band) will be presented and confronted with (independent) age control. This cross-check is crucial in the validation of the applied method, and it shows that ESR dating is a promising tool which may help to understand the geological evolution of the earth over the last few million years.

Al, Ti, Ge centres  
bleached @ ambient light UV-sun  
Ti-Li  
or H

## Revealing the differences in the heme pocket structure of ferric human Cygb and tomato hemoglobin

A. Iulia Ioanitescu<sup>1</sup>, S. Van Doorslaer<sup>1</sup>, B. Endeward<sup>2</sup>, S. Dewilde<sup>3</sup>, L. Moens<sup>3</sup>

Departments of Physics<sup>1</sup> and Biomedical Sciences<sup>3</sup>, University of Antwerp,  
Antwerp, Belgium,  
Institute for Physical and Theoretical Chemistry, JW Goethe University,  
Frankfurt am Main, Germany<sup>2</sup>

The ferric form of two recently discovered proteins, human Cygb (CYGB) and tomato SOLLy GLB1 hemoglobins, were studied by means of different spectroscopic techniques, mainly EPR. In addition, the  $\Delta$ Cys mutant of CYGB (Cys $\rightarrow$ Ser) was analysed and compared with the wt form. Combined UV/Vis, resonance-Raman and CW-EPR measurements reveal that the ferric forms, for the both proteins, show predominantly a bis-histidine legation (F8His-Fe<sup>3+</sup>-E7His). This differs from the known forms of vertebrate hemoglobins and myoglobins. Moreover, for CYGB, this contrasts with one of the X-ray studies [<sup>#</sup>], which highlighted the presence of an alternate conformation, leading to penta- and hexa-coordinated species in the same proportion. Pulsed EPR techniques were used to study the low-spin ferric forms of the proteins. Although the used methodology was essentially the same for the two proteins, additional S-band HYSORE measurements were needed in the case of ferric CYGB for which a substantially larger g anisotropy and g strain is found than for ferric SOLLy GLB1. Using these methods, we were able to determine the orientation of the histidine planes, and the hyperfine and nuclear quadrupole couplings of the heme and histidine nitrogens. Essential differences between the two proteins could be identified. Furthermore, our present EPR study on ferric Cygb allows solving an existing ambiguity between two X-ray studies.

<sup>#</sup> De Sanctis D., Dewilde S., Pesce A., Moens L., Ascenzi P., Hankeln T., Burmester T., and Bolognesi M. (2004) *J. Mol. Biol.* **336**, 917-927

**Reduction enhances yields of in-vivo trapping of nitric oxide.**Anatoly Vanin<sup>1</sup> and Ernst van Faassen<sup>2</sup><sup>1</sup> Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia<sup>2</sup> Debye Institute, section Interface Physics, Utrecht University, Netherlands.

Iron dithiocarbamate complexes [1] are widely used for spin trapping of nitric oxide radicals in liquids and heterogenous biological materials like plants, mammalian tissue homogenates or biopts. The iron atom of the dithiocarbamate-complexes strongly binds the NO ligand to form a stable mononitrosyl iron complex (MNIC). In reduced charge state, the NO-Fe<sup>2+</sup>-dithiocarbamate adduct is paramagnetic (S=1/2) and may be quantified with EPR at 77 K or at room temperature. In ferric state the complex is EPR silent. The yield of paramagnetic MNIC provides a lower bound on the quantity of endogenous NO.

We have investigated the trapping pathways in a range of biological systems, from cultured cells, plants, living lab animals to tissue-biopts. Our main conclusions are

1. the majority of NO is trapped by ferric iron-dithiocarbamate complexes and remains EPR silent [2].
2. a significant fraction of trapped NO may be lost by subsequent reaction with strong oxidants like superoxide [3].

The first effect was always found to be significant in any biological system we considered. The second depended on the presence of superoxide in the system, and may vary with tissue type and SOD status. Both effects make that quantification of the yields of NO trapping experiments with EPR seriously underestimates the true NO production.

The first problem is addressed if the population of ferric MNIC is reduced to paramagnetic ferrous state by a reductor like dithionite. This reduction is carried out ex vivo and greatly enhances [2] the yields of paramagnetic MNIC, typically by a factor 3-4. As a bonus, the reduction also eliminates the overlapping EPR spectrum from Cu<sup>2+</sup>-dithiocarbamate complexes that are usually found in biological samples.

The second problem may be addressed by a sophisticated ABC trapping protocol [1]. With ABC the yields of paramagnetic MNIC are enhanced by artificially removing the superoxide from the living test animal or cell culture. The superoxide may be removed by suppletion of a known quantity of exogeneous MNIC-DETC complexes.

Both methods can be combined to get better estimates on the total endogenous NO production in biological systems, from cultured cells, plants, living lab animals to tissue biopts.

[1] A. Vanin, A. Huisman and E. van Faassen, *Iron dithiocarbamate as spin trap for nitric oxide detection: Pitfalls and successes*. Meth.Enzym. 359 (2002) 27-42.

[2] A. Vanin, A. Poltorakov, V. Mikoyan, L. Kubrina and E. van Faassen, *Why iron-dithiocarbamates ensure detection of nitric oxide in cells and tissues*. Nitric Oxide, in press.

[3] A. Vanin, A. Huisman, E. Stroes, F. de Ruijter, T. Rabelink and E. van Faassen, *Antioxidant capacity of MNIC complexes: Implications for nitric oxide trapping*. Free Rad. Biol. Med. 30 (2001) 813 - 824.

## EPR characterization of the iron-sulfur clusters in the hybrid-cluster protein of *Pyrococcus furiosus*

Peter-Leon Hagedoorn

Department of Biotechnology, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands

The hybrid cluster protein (HCP) was previously known as prismane protein. It was not until the discovery of its crystal structure that it was realized that it did not contain a [6Fe-6S] prismane cluster, but instead two iron-sulfur clusters: one [4Fe-4S] cubane cluster and one [4Fe-2S-2O] hybrid cluster (1). The hybrid cluster can accept three electrons. Genes encoding HCP have been identified on the genomes of organisms throughout all three kingdoms of life: eukarya, bacteria and archaea. All organisms that contain HCP have in common that they are (facultative) anaerobic micro-organisms. To date no physiological role for the HCP has been identified. Although an *in-vitro* viologen dependent hydroxylamine reduction activity has been established (2).

The HCP from the hyperthermophilic archaeon *Pyrococcus furiosus* was cloned and expressed in *E. coli*. The recombinant protein was partially expressed as a thermostable soluble protein with partial incorporation of iron-sulfur clusters. In general [4Fe-4S]<sup>+</sup> clusters in proteins exhibit EPR spectra corresponding to pure S=1/2, pure S=3/2, or a physical mixture of S=1/2 and S=3/2. Only in two cases, Fe-hydrogenase and the HCP from *Desulfovibrio* species, a spin-admixed ground state S=3/2 of a [4Fe-4S]<sup>+</sup> cluster has been observed (3). EPR spectroscopy of *P. furiosus* HCP showed evidence of a spin-admixed ground state S=3/2 of a [4Fe-4S]<sup>+</sup> cluster and an additional iron-sulfur cluster of unknown nature. The cubane of *P. furiosus* HCP is likely coordinated by a CXXC-X<sub>7</sub>-C-X<sub>5</sub>-C motif, which is similar to the CXXC-X<sub>8</sub>-C-X<sub>5</sub>-C motif of the *Desulfovibrio desulfuricans* and *Desulfovibrio vulgaris* HCPs. *E. coli* HCP has a CXXC-X<sub>11</sub>-C-X<sub>6</sub>-C motif which coordinates a [2Fe-2S] cluster (4). The truncation of ca. 100 amino acids, which is common in all archaeal HCPs, has no effect on the hydroxylamine reductase activity. This is the first hybrid cluster protein from the archaeal kingdom to be studied. Furthermore this is the first thermostable HCP that has been characterized.

1. Arendsen, A. F., et al. (1998) *J. Biol. Inorg. Chem.* 3, 81-95.
2. Wolfe, M. T., et al. (2002) *J. Bacteriol.* 184, 5898-5902.
3. Hagen, W. R., et al. (1998) *J. Chem. Soc., Faraday Trans.* 94, 2969-2973.
4. van den Berg, W. A., et al. (2000) *Eur. J. Biochem.* 267, 666-676.

tetrahedral coord

$\uparrow$   $^4A_2$  ground state like  $G^{3+}$  octa  
O8

## A multi-frequency EPR study of Co(II)S<sub>4</sub> coordination

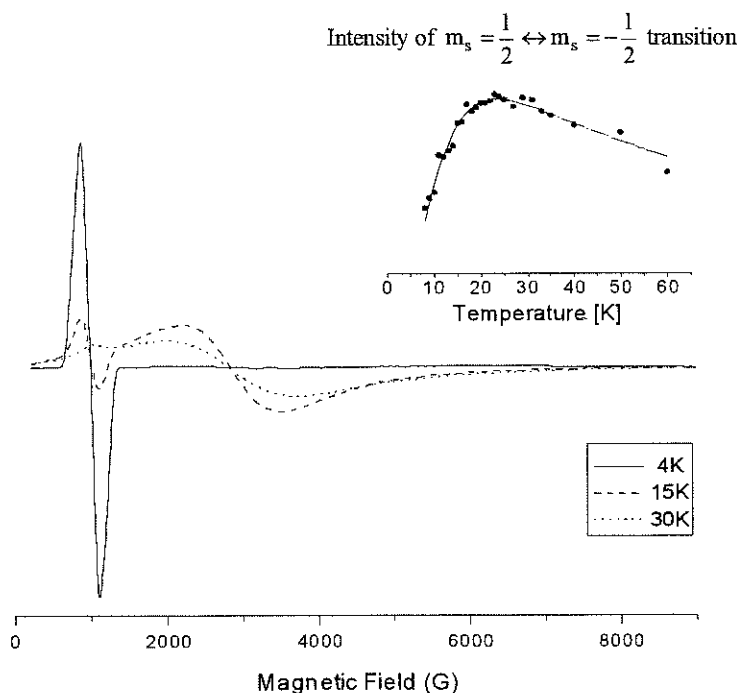
S. Milikisyants<sup>a</sup>, D. Maganas<sup>a</sup>, H. Blok<sup>a</sup>, P. Gast<sup>a</sup>, A. Grigoropoulos<sup>b</sup>, P. Kyritsis<sup>b</sup>, G. Pneumatikakis<sup>b</sup>, J.M.A. Rijnbeek<sup>a</sup>, S. Sottini<sup>a</sup>, E.J.J. Groenen<sup>a</sup>

<sup>a</sup>Department of Molecular Physics, Leiden University, The Netherlands

<sup>b</sup>Department of Chemistry, University of Athens, Greece

Extensive crystallographic studies during the last few years have revealed the existence of M-S bonds in the active site of many metalloenzymes, most prominently with the transition metals M=Fe, Ni, Cu, Zn, Mo, W. Besides these metals, one should also consider Co, since it has recently been shown that the enzyme ATP sulfurylase is a metalloenzyme containing Co(II) and Zn(II) in its active site. Moreover, to enable spectroscopic and magnetic investigations, Zn(II)- or Cd(II)-containing active sites of enzymes are frequently reconstituted with Co(II). The relevance of cobalt-sulfur coordination for biological systems has prompted us to synthesize and investigate by EPR and ENDOR model complexes of cobalt with sulfur-containing bidentate ligands LH of the type R<sub>2</sub>PSNHPSR<sub>2</sub>' where R, R' = phenyl, isopropyl.

The large zero-field splitting of divalent cobalt ( $S = \frac{3}{2}$ ) calls for a multi-frequency approach. We report cw and pulsed EPR experiments at X-, W-, and J-band, from room temperature down to liquid-helium temperatures. We have investigated solutions, powders and crystals of complexes in (pseudo-)tetrahedral geometry. In order to decrease the linewidth (increase the resolution), use has been made of diluted samples in which cobalt is largely replaced by zinc, which is EPR silent. Based on the zero-field splitting and the anisotropy of both the g matrix and the cobalt hyperfine interaction, we will discuss the electronic structure of the cobalt coordination. In addition, we will indicate the possibilities of future ENDOR experiments, which aim at the quantitative analysis of the covalent character of the cobalt-ligand interaction.



X-band cw-EPR of Co[Ph<sub>2</sub>P(S)NP(S)Ph<sub>2</sub>]<sub>2</sub>

## ELECTRON SPIN PROBING OF FUNDAMENTAL POINT DEFECTS IN NM-SIZED SILICA PARTICLES

K. Clémer, A. Stesmans and V. V. Afanas'ev

*University of Leuven, Department of Physics and Astronomy, 3001 Leuven, Belgium*

Results are presented of a first successful observation by electron spin resonance (ESR) of fundamental point defects in fumed  $\sim 7$ -nm sized silica nanoparticles. This includes the prototypical E' center ( $\bullet\text{Si}\equiv\text{O}_3$ ), the peroxyradical ( $\equiv\text{Si}-\text{O}-\text{O}\bullet$ ), the methyl radical, EX, and a newly observed center of axial symmetry ( $g_{\parallel}=2.0041$ ,  $g_{\perp}=2.0027$ ). This is accomplished through K- and Q- band ESR following 10-eV irradiation used to photo-dissociate H from passivated defects. Their analysis provides access to the structure of the nanoscale-on atomic level, herewith opening another field for analysis of the nanoparticle world. To assess specific physico-chemical structural aspects of the particles, the defect centers have been monitored as a function of thermal treatment in vacuum in the range 850-1175 °C.

In this way the presence of two systems of E' centers is revealed. The first one exhibits ESR parameters very similar to those of the familiar E' $_{\gamma}$  center encountered in bulk fused silica, while the second bath exhibits an altered zero crossing g value and line shape, attributed to variations in local structure. While the first E' system most likely resides in the core regions of the nanoparticles, the second system is confined to the outer SiO<sub>2</sub> layers exposing a structurally different, possibly more strained nature than bulk glassy SiO<sub>2</sub>. Probing of fundamental point defects in nm-sized silica particles thus reveals structural variations and non-uniformity, indicative of a structure different from bulk material. The observed narrowing of the optical bandgap is probably related to these structural modifications of the SiO<sub>2</sub> network. In contrast with previous deductions from optical studies<sup>1</sup>, the inferred upper limit of the density of all defects observed suggests that the OHCs cannot be kept responsible for the latter effect.

<sup>1</sup>I. S. Altman, D. Lee, J. D. Chung, J. Song, and M. Choi, Phys. Rev. B **63**, 161402 (R)



## Electron and chlorine interstitials trapping at $\text{Fe}^{2+}$ impurity ions in chlorinated $\text{SrCl}_2$ crystals

D. Ghica, S. V. Nistor, H. Vrielinck, F. Callens, E. Goovaerts, and D. Schoemaker

X-ray irradiation of  $\text{SrCl}_2:\text{Fe}^{2+}$  crystals grown in an inert atmosphere produces only a cubic hole-trapped  $\text{Fe}^{3+}$  center. When  $\text{SrCl}_2:\text{Fe}$  crystals are grown in a chlorine atmosphere (*chlorinated*), several primary electron and hole trapped ( $\text{Fe}^+$  and  $\text{Fe}^{3+}$ , respectively) paramagnetic centers with non-cubic symmetry are formed besides the cubic  $\text{Fe}^{3+}$  center, by short X-ray irradiation at low temperatures (80 K) of the crystal. These paramagnetic centers have been previously studied by magnetic resonance (EPR, ENDOR) spectroscopy [1 – 4]. Because the resulting  $\text{Fe}^+$  and  $\text{Fe}^{3+}$  centers were produced by short irradiation at temperatures where no significant ionic movement is present, it is expected that precursor  $\text{Fe}^{2+}$  centers with similar structure/symmetry were present in the as-grown crystal.

Further annealing treatments, at temperatures higher than 200 K, of such irradiated crystals results in the annealing/conversion of some of the primary  $\text{Fe}^+$  paramagnetic centers in new, secondary  $\text{Fe}^+$ -type paramagnetic centers. Recent EPR investigations show [5] that the secondary  $\text{Fe}^+$  centers formation is determined by the presence and thermally activated movement of the interstitial chlorine ions towards the  $\text{Fe}^+$  ion. Both precursor  $\text{Fe}^{2+}$  and resulting  $\text{Fe}^+$  paramagnetic centers are perturbed by these native  $\text{Cl}^-$  interstitials which were inserted in the crystal lattice during the crystal growth in a chlorine atmosphere.

### References

- [1] S. V. Nistor, M. Stefan, and D. Schoemaker, *Phys. Status Solidi B* **214**, 229 (1999).
- [2] S. V. Nistor, D. P. Lazar, H. Kaess and D. Schoemaker, *Sol. State Comm.* **104**, 521 (1997).
- [3] H. Vrielinck, F. Callens, P. Matthys, S. V. Nistor, D. Ghica, and D. Schoemaker, *Phys. Rev. B* **64**, 024405 (2001).
- [4] D. Ghica, S. V. Nistor, H. Vrielinck, F. Callens, and D. Schoemaker, *Phys. Rev. B* **70**, 024105 (2004).
- [5] D. Ghica, S. V. Nistor, E. Goovaerts, D. Schoemaker, H. Vrielinck, F. Callens, *Phys. Rev. B* (2006) – accepted.

$\text{Fe}^+$  (II) in *Prun* in PRB.

## **Poster contributions**

**EPR investigation of Gd<sup>3+</sup> doping impurity in PbWO<sub>4</sub> scintillating crystals**M Stefan<sup>1</sup>, S V Nistor<sup>1</sup>, E Goovaerts<sup>2</sup>, M Nikl<sup>3</sup> and P Bohacek<sup>3</sup>

<sup>1</sup>) *National Institute for Materials Physics, POB MG-7 Magurele-Bucharest, RO-077125, Romania*

<sup>2</sup>) *Department of Physics, University of Antwerp, Campus Drie Eiken, Universiteitsplein 1, BE-2610 Antwerp, Belgium*

<sup>3</sup>) *Institute of Physics AS CR, Cukrovarnicka 10, 16200 Prague 6, Czech Republic*

Lead tungstate – PbWO<sub>4</sub> (PWO) is presently one of the most studied materials in the scintillator oriented research, due to its approved applications in the detectors of high-energy physics accelerators as well as in other domains. The quest to improve the scintillating properties has resulted in the discovery of several types of dopants able to efficiently compensate/suppress the intrinsic trapping states in the forbidden gap of PWO. A dopant of choice is Gd<sup>3+</sup>, which was found to determine faster scintillation and photoluminescence response, suppression of the deep trap states and increase of the radiation resistance and transmission in the 350 to 500 nm range [1].

In order to shed light on the mechanisms responsible for the observed changes, we performed extensive X-band (9.5 GHz) electron paramagnetic resonance (EPR) studies in a wide temperature range (1.5 to 293 K), on Gd<sup>3+</sup> doped PbWO<sub>4</sub> single crystals.

The Gd<sup>3+</sup> ions were found to substitute the host Pb<sup>2+</sup> ions, with charge compensation at distance. The temperature variation of the zero field splitting parameters was explained by the presence of a local vibrational mode with frequency  $\omega = 3.1 \times 10^{13} \text{ rad}\cdot\text{s}^{-1}$ , 3.5 times larger than in the case of the resonant mode observed for the Mn<sup>2+</sup> impurities [2]. The broadening of the EPR lines was also investigated and explained in terms of spin-lattice relaxation and the presence of local stress.

[1] S. Baccaro, P. Bohacek, A. Cecilia, A. Cemmi, S. Croci, I. Dafinei, M. Diemoz, P. Fabeni, M. Ishii, M. Kobayashi, M. Martini, E. Mihokova, M. Montecchi, M. Nikl, G. Organtini, G. P. Pazzi, Y. Usuki and A. Vedda, *Phys. Status Solidi (a)* 179 (2000) 445.

[2] M. Stefan, S. V. Nistor, E. Goovaerts, M. Nikl and P. Bohacek, *J. Phys.: Condens. Matter* 17 (2005) 719.

## **EPR study of formation of hemoglobin - nitric oxide adduct in whole mouse blood: influence of caveolin-1 genetic deletion.**

**Irina Lobysheva, Chantal Dessy, Olivier Feron, Bernard Gallez, and Jean-Luc Balligand**

*Unit of Pharmacology and Therapeutics, University of Louvain Medical School, 53 Mounier, 1200 Brussels, Belgium; [Irina.Lobysheva@mint.ucl.ac.be](mailto:Irina.Lobysheva@mint.ucl.ac.be)*

Nitric oxide (NO) produced from L-arginine by different NO synthase isoforms (NOS) is involved in various physiological processes, including the regulation of the cardiovascular, immune, and nervous systems. Although endothelial NOS (eNOS) is a recognized key regulator of blood pressure, the assessment of its activity *in vivo* remains a challenge. The half-life of molecular NO is short and different indirect methods have been used to assay its concentration. In circulating blood, a reaction of NO with haemoglobin is predominant. Measurement of paramagnetic hemoglobin-nitric oxide adducts (HbNO) in whole blood by the EPR method can give unique information on systemic, circulating NO levels.

We studied the EPR signal of pentacoordinated nitrosyl Hb (T-form, deoxy-like) in whole blood of mice obtained directly from the right ventricular cavity. Blood samples were immediately frozen in calibrated tubes for EPR measurements at a temperature of 77K.

The EPR spectrum of whole blood is represented by superposition of the EPR signals from different paramagnetic centers in the  $g = 2$  region. Analysis of the pentacoordinated HbNO level was done after digital subtraction of the EPR signal of serum ceruloplasmin and multiple EPR signals of free radical species with  $g = 2$ . The EPR signal of ceruloplasmin was recorded in plasma sample after centrifugation of whole mouse blood (3 000Xg, 5 minutes). The EPR signal of free radical species was obtained by subtraction of the plasma EPR signal (with the small free radical component) from the EPR signal of the whole blood of mice treated with L-NAME (a NOS inhibitor), in which the Hb-NO signal was absent. The level of HbNO was assayed by comparison of the peak-to-peak amplitude of the first component of three hfs lines with similar components obtained from the HbNO standards synthesized by mixing of whole mouse blood with a NO donor in anaerobic conditions. Relative values of HbNO levels was converted into concentrations with references to EPR standard (1 mM Cu-EDTA complex prepared in ratio 1:5 and frozen in water solution with 30% glycerin). We used identical EPR parameters and compared the double integrated area of the EPR signals.

Using this methodology we studied the influence of genetic deletion of one eNOS allosteric regulator, caveolin-1 (cav1) on vascular nitric oxide circulation in blood, measured as Hb-NO derivative. We observed that the circulating Hb-NO level was significantly higher in cav1<sup>-/-</sup> mice (KO) compared with wild type (WT) mice (up to 0.81 +/- 0.12  $\mu$ M, n = 8, in comparison with 0.43 +/- 0.10  $\mu$ M, n = 9), and was strikingly reduced upon 5-day treatment with L-NAME in drinking water (to 0.15 +/- 0.05  $\mu$ M for KO mice and 0.02 +/- 0.02  $\mu$ M for WT mice).

The relationship between the eNOS activity and the HbNO level in blood was studied in caveolin-1 KO mice injected with L-NAME. We obtained time-dependent decrease of HbNO level after L-NAME injection. The HbNO level was decreased down to 62% after 30 minutes and to 10.9 +/- 4.0% of the initial level in blood sampled after 120 minutes.

These data demonstrate the validation of the EPR methodology for the evaluation of NO bioavailability and its applicability to validate paradigms on eNOS regulation *in vivo*.

Kleine  $\beta$ -koppelingen  $\rightarrow$  aanwezigheid van elektronegatief  
"ligand"  $Q=0$  of 20. P3

## Electron Magnetic Resonance Study of Radiation-Induced Defects in Sucrose Single Crystals: an Overview

H. De Cooman<sup>\*#a</sup>, G. Vanhaelewyn<sup>\*b</sup>, E. Pauwels<sup>#b</sup>, F. Callens<sup>\*</sup> and M. Waroquier<sup>#</sup>

<sup>\*</sup>Department of Solid State Sciences, Ghent University,  
Krijgslaan 281-S1, B-9000 Gent, Belgium

<sup>#</sup>Center for Molecular Modeling, Ghent University,  
Proeftuinstraat 86, B-9000 Gent, Belgium

<sup>a</sup>Research Assistant of the Research Foundation - Flanders (FWO - Vlaanderen)

<sup>b</sup>Postdoctoral Fellow of the Research Foundation - Flanders (FWO - Vlaanderen)

The study of radiation-induced defects in sugar single crystals is of major importance for dosimetry purposes as well as in the radiation chemistry of DNA. Sucrose (or table sugar) is of particular interest as a nuclear emergency dosimeter because of its widespread use, its radiation sensitivity, the stability of the induced radicals [1,2], and its considerable linear dose response interval (up to  $10^4$  Gy) [3]. It can also be regarded as a valid model system for the desoxyribose sugar unit in DNA since the sucrose building blocks (fructose and glucose) are chemically similar to desoxyribose.

Electron magnetic resonance (EMR) techniques have already been applied to study the radiation-induced defects in several sugars, often with considerable success. However, these kind of radicals constitute challenging research objects because irradiation generally gives rise to a large variety of radicals, resulting in strongly composite spectra. Consequently, still little is known, despite all efforts, about the identity of the primary sugar radicals and final stable products. Furthermore, even less is known about the radical formation and transformation mechanisms involved.

Fortunately, EMR experimentalists have recently found a new ally in their efforts to model sugar radical structures: Density Functional Theory (DFT) calculations. Due to the enormous increase in computer power and the construction of more accurate density functionals in the last few years, DFT calculations have gradually evolved into a powerful tool to help clarify, interpret and explain experimental results. Very recently this synergy led to the first positive identification of a ring-opened radical structure in X-irradiated  $\beta$ -D-fructose [4].

In the past, radiation-induced radicals in sucrose have been investigated by means of EMR techniques by a number of researchers. Although some radical models were proposed [5], none could be convincingly validated. Furthermore, measurements at 60 K [6] and at room temperature [5] seem to give completely different results. To our knowledge, no DFT calculations have been performed as yet on sucrose.

In the present poster a summary is given of the experimental results obtained so far on radiation-induced radicals in sucrose single crystals and powders. Own measurements are compared with results reported in EMR literature. Finally, a further course of experimental (EMR) and theoretical (DFT) research is outlined.

1. T. Nakajima, Health Physics 55, 951 (1988).
2. T. Nakajima, Appl. Radiat. Isot. 46, 819 (1995).
3. F. Americo, M. Silveira and O. Baffa, Appl. Radiat. Isot. 46, 827 (1995).
4. G.C.A.M. Vanhaelewyn, E. Pauwels, F.J. Callens, M. Waroquier, E. Sagstuen and Paul F.A.E. Matthys, J. Phys. Chem. 110 (6), 2147 (2006).
5. E. Sagstuen, A. Lund, O. Awadelkarim, M. Lindgren and J. Westerling, J. Phys. Chem., 90, 5584 (1986).
6. G. Vanhaelewyn, J. Sadlo, F. Callens, W. Mondelaers, D. De Frenne and P. Matthys, Appl. Radiat. Isot. 52, 1221 (2000).

## Optical and EPR spectroscopy in low band gap/fullerene derivative blends.

A. Aguirre<sup>1,\*</sup>, G. Janssen<sup>1</sup>, E. Goovaerts<sup>1</sup>, K. Colladet<sup>3</sup>, L. Lutsen<sup>2</sup>, D. Vanderzande<sup>3</sup>

(1) Department of Physics - CDE, University of Antwerp, Universiteitsplein 1, B-2610 Antwerpen, Belgium.

(2) IMEC, IMOMEK division, Wetenschapspark 1, B-3590 Diepenbeek, Belgium.

(3) Hasselt University, Institute for Materials Research (IMO) Division of Chemistry, Agoralaan, Bld. D, B-3590 Diepenbeek, Belgium.

There is a considerable demand in photovoltaic applications for new conjugated polymers absorbing at longer wavelengths to obtain an improved overlap with the solar spectrum.

A newly synthesized low band-gap conjugated polymer, with a bis-(1-cyano-2-thienylvinylene)phenylene base structure, has been successfully prepared. The optical properties of both the pure compound and blends with the fullerene derivative PCBM as acceptor, were investigated by absorption and fluorescence spectroscopy as well as picosecond time-resolved laser spectroscopy. The optical techniques were combined with light-induced electron paramagnetic resonance (LI EPR) to evaluate the efficiency of the charge transfer processes in these blends.

In these blends, efficient photo induced charge transfer is demonstrated by LI EPR measurements and quenching of the photoluminescence. The still low efficiencies found for the solar cells are therefore attributed to other factors, such as low charge mobilities or band mismatch.

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\* Corresponding author: aranzazu.aguirre@ua.ac.be

## **Inherent point defects in tensile strained (100)Si/SiO<sub>2</sub> structures probed by electron spin resonance.**

Piet Somers, A. Stesmans, and V. V. Afanas'ev

*Department of Physics, University of Leuven, Celestijnenlaan 200D, 3001 Leuven, Belgium*

The application of biaxial tensile strained-Si (sSi) layers is known to result in a substantial improvement (up to >100%) of the carrier mobility ( $\mu$ ) in inverted channels of Si-based complementary metal-oxide-semiconductor (CMOS) structures. As presently understood this strain would improve the electron mobility through the reduction of intervalley scattering and carrier effective mass as a result of lifting of the six-fold degeneracy of the Si conduction band minima. However, there appears to be some deficiency in the quantitative theoretical understanding of the enhanced mobility, at least in some cases, suggesting an additional effect. In a recent theoretical work, the origin of the lack in understanding was tentatively traced down to an interface (surface) related effect. The current work addresses this issue from the side of inherently occurring point defects at the crucial Si/SiO<sub>2</sub> interface as probed by electron spin resonance.

Electron spin resonance studies are reported on (100)Si/SiO<sub>2</sub> entities grown by thermal oxidation at 790°C (1.1atm O<sub>2</sub>) of biaxial tensile strained(100)Si (sSi) layers epitaxially grown on relaxed virtual substrates, with main focus on P<sub>b</sub>-type interface defects, in particular the electrically detrimental P<sub>b0</sub> variant. In the as-grown state a significant decrease (>50%) in interface defect density compared to the standard unstrained (100)Si/SiO<sub>2</sub> interface was observed. As compared to the latter, this inherent decrease in electrically active interface trap density establishes sSi/SiO<sub>2</sub> as a superior device entity for all electrical properties in which (near)interface traps may play a detrimental role. For one, it may be an additional reason for the commonly reported mobility enhancement in strained silicon inversion layers and the reduction in 1/f noise. The data also confirm the admitted relationship between inherent incorporation of the P<sub>b</sub> related interface defects and the Si/SiO<sub>2</sub> interface mismatch.

## Comparison of ferric E7Q neuroglobin with the aquomet form of horse heart myoglobin using advanced pulsed EPR techniques

F. Trandafir<sup>1</sup>, M. Fittipaldi<sup>1</sup>, S. Dewilde<sup>2</sup>, L. Moens<sup>2</sup>, S. Van Doorslaer<sup>1</sup>  
Departments of Physics<sup>1</sup> and Biomedical Science<sup>2</sup>, University of Antwerp

The function and structure of the nerve globin, neuroglobin, is still a matter of debate. The E7 histidine residue is shown to play a crucial role in controlling exogeneous ligand binding to the heme. Here, we present a pulsed EPR study of the ferric form of the E7-Gln mutant of neuroglobin. The mutant is found to be in a high-spin state ( $S=5/2$ ).

In a first part, we outline a new pulsed-EPR methodology allowing for a thorough analysis of high-spin ferric heme systems in frozen solutions. Different X-band HYSCORE schemes were used to study the hyperfine and nuclear quadrupole couplings of the porphyrin and the histidine nitrogens. In parallel, W-band ELDOR-detected NMR analyses were performed to corroborate these data. For the first time, the interaction with the remote nitrogen of the proximal histidine could be determined. Furthermore, signals stemming from a hyperfine interaction with a  $^{13}\text{C}$  nucleus could be identified in the HYSCORE spectra. In order to unravel in detail the proton hyperfine couplings, aquometmyoglobin in a deuterated buffer was investigated.

In a second part, the same approach is applied to the E7-Gln mutant of neuroglobin, and the results will be compared to those obtained for the neuroglobin mutant.



## Electron spin resonance analysis of Si nanocrystals embedded in an SiO<sub>2</sub> matrix

Mihaela Jivanescu, A. Stesmans, S. Godefroo, and M. Hayne

*Department of Physics and Astronomy, University of Leuven, Celestijnenlaan 200 D, B-3001 Leuven, Belgium*

Electron spin resonance (ESR) is used to analyze Si nanocrystals with diameters of ~2 nm formed within an SiO<sub>2</sub> matrix after high temperature (~1100°C) annealing-induced phase separation of SiO/SiO<sub>2</sub> superstructures. The latter were obtained by reactive evaporation of SiO powders in oxygen ambient onto p-Si wafers. These structures exhibit photoluminescence (PL): When excited with a number of lines between 351.1 and 363.8 nm of an argon ion laser the samples show PL spectra with a peak in the 1.4 - 1.6 eV range with a typical line width of 250 - 350 meV. The origin of this PL is an already long ongoing dispute. Both quantum confinement and influence of defects have been proposed as the possible origin of the PL and so far there appears no convincing evidence, let alone conclusion. In fact, both mechanisms might be operative simultaneously.

In an attempt to further insight, we have performed extensive ESR measurements with the view to address this controversial matter from the defect side. ESR studies were performed both on as received samples and after subjection to different types of illumination within the UV spectral range 180-700 nm (150 W Xe arc lamp) in order to compare and investigate the influence on the density of occurring point defects. One of the illuminations was similar to the one applied for the PL investigations.

Various types of SiO<sub>2</sub>-specific inherent point defects were observed in substantial numbers, implying the SiO<sub>2</sub>-specific E'<sub>γ</sub> and EX centers, the disordered Si-specific D line, and Si/SiO<sub>2</sub> interface-specific P<sub>b</sub>-type centers. The D and P<sub>b</sub>-type centers are observed in the as grown samples and remain largely unchanged upon subsequent irradiation. This indicates the SiO/SiO<sub>2</sub> superstructure is H-lean as could be expected from the high-temperature anneal in pure N<sub>2</sub>. The EX and E'<sub>γ</sub> centers only appear after irradiation.

A main task is to infer where these defects exactly reside in the sample as they may pertain to various locations within the SiO/SiO<sub>2</sub> superstructures with embedded Si nanoparticles. As a general finding, it appears the phase-separated SiO/SiO<sub>2</sub> superstructures are beset with a substantial density of inherent point defects, the potential effect of which on the PL behavior is to be envisioned.

## Characterization of heterogeneous mesoporous catalysts using electron paramagnetic resonance

S.Zamani<sup>1</sup>, A. Hanu<sup>2</sup>, P. Cool<sup>2</sup>, S. Van Doorslaer<sup>1</sup>

*Departments of Physics<sup>1</sup> and Chemistry<sup>2</sup>, University of Antwerp, Universiteitsplein 1, B-2610 Wilrijk, Belgium*

Since 1992, a wide variety of mesoporous materials (siliceous and non-siliceous) have gained growing interest, in order to overcome the limits in accessibility and applicability encountered for microporous zeolites. A lot of research has been done to activate mesoporous materials, like MCM-41, with various transition metals in order to obtain large pore catalysts allowing high diffusion rates and a catalytic activity for bulky molecules. Here we present an electron paramagnetic resonance (EPR) study of the incorporation of vanadyl in MCM-41 via different chemical routes. The samples form the precursors of the final catalysts. Vanadyl ( $\text{VO}^{2+}$ ) species are paramagnetic and therefore EPR active. It will be shown how important information about the mobility and incorporation mechanism of the vanadyl species in the mesoporous systems can be revealed by the use of continuous wave and 2-dimensional pulsed EPR spectroscopy.

## Multifrequency ESR of nominally pure, amber coloured superhard cubic boron nitride crystals

S. V. Nistor\*, D. Ghica\*, M. Stefan\*, A. Bouwen\*\* and E. Goovaerts\*\*

\* National Institute for Materials Physics, P.O. Box MG-7 Magurele-Bucuresti,  
RO-077125 Romania

\*\* Department of Physics-CDE, University of Antwerp, Universiteitsplein 1,  
Antwerpen(Wilrijk), BE-2610 Belgium

Cubic boron nitride (c-BN) with sphalerite structure (F43m,  $a_0=0.3615\text{nm}$ ) exhibits exceptional structural and electronic properties. Besides extreme hardness (the second after diamond), high thermal conductivity, high melting point, low reactivity and a very large band-gap ( $\sim 6.2\text{ eV}$ ), c-BN can be relatively easily *p*- and *n*-type doped. The demonstration of *p-n* junctions and UV-light emitting diodes with unchanged characteristics of up to 900K [1] points to c-BN as an exceptional semiconductor for electro-optical devices operating in extreme conditions. Although the exact nature of the simultaneous *n*- and *p*-type conductivities is not well understood, the formation of point defects seems to be the essential factor. However, until recently the presence and properties of point defects in c-BN has been practically unknown.

Electron Spin Resonance (ESR) is the best method for identification and characterization of paramagnetic point defects in insulators and semiconductors. Because c-BN is usually available in sub millimeter sized, crystalline superabrasive powders, the best approach is to combine low (X-band) frequency ESR measurements on such powder samples with high (W-band) frequency measurements on oriented single crystallites selected from the same powder sample. Such studies, performed in a broad temperature range, which combine the high absolute sensitivity and broad microwave powers range of the X-band measurements with anisotropy studies with very high spectral resolution, on oriented single crystals in the W-band, have already resulted in the unambiguous identification of the D-type point defects in nominally pure, dark colored c-BN superabrasive powders grown with boron excess [2,3].

We shall present here recent results of similar multifrequency ESR investigations on amber colored, large grained c-BN superabrasive powders, which resulted in the identification of a new family of paramagnetic centers called the A-type centers. It will be also shown that a strong variation in their concentrations is induced by low temperature illumination with UV-VIS light. The resulting information offers new insights into the presence and properties of local states in the band gap of semiconducting c-BN.

### References

- [1] T. Taniguchi, S. Koizumi, K. Watanabe, I. Sakaguchi, T. Sekiguchi and S. Yamaoka, *Diam. & Rel. Mater.* **12**, 1098 (2003) and references cited therein.
- [2] S. V. Nistor, M. Stefan, D. Schoemaker and G. Dinca, *Sol. State Comm.* **115**, 39 (2000)
- [3] S. V. Nistor, M. Stefan, E. Goovaerts, A. Bouwen, D. Schoemaker and G. Dinca, *Diam. & Rel. Mater.* **10**, 1408-1411 (2001).

## Donor-Acceptor pairs in the Confined Structure of ZnO Nanocrystals

Serguei B. Orlinskii, Hubert Blok and Jan Schmidt

*Department of Molecular Physics, Huygens Laboratory, Leiden University, Post Office Box 9504, 2300 RA Leiden, The Netherlands*

Pavel G. Baranov

*A.F. Ioffe Physico-Technical Institute, RAS, 194021 St Petersburg, Russia*

Celso de Mello Donegá and Andries Meijerink

*Debye Institute, Utrecht University, Utrecht, The Netherlands*

The Electron Paramagnetic Resonance signal of an exchange-coupled pair consisting of a shallow interstitial Li donor and a deep Na-related acceptor has been identified in ZnO nanocrystals with radii smaller than 1.5 nm. From Electron Nuclear Double Resonance experiments it is concluded that the deep Na-related acceptor is located at the interface of the ZnO core and the Zn(OH)<sub>2</sub> capping layer, while the Li donor is in the ZnO core.

## EPR analysis of a new Cobalt Salen Complex: Cobalt Jacobsen's Catalyst

Evi Vinck<sup>1</sup>, Sabine Van Doorslaer<sup>1</sup>, Richard Tucker<sup>2</sup>, Damien M. Murphy<sup>2</sup>, and Ian A. Fallis<sup>2</sup>.

<sup>1</sup>University of Antwerp, Department of Physics, Universiteitsplein 1, 2610 Wilrijk, Belgium

<sup>2</sup>Cardiff University, Department of Chemistry, Cardiff CF10 3TB, Wales, UK

Cobalt salen related systems have a wide range of applications: they are widely used as catalysts for the oxygenation of organic molecules; they can act as antiviral agents, due to their ability to interact with proteins and nucleic acids; and they have been used to mimic biological co-factors, such as cobalamin. Recently, E. Jacobsen *et al.* discovered a new Cobalt salen catalyst (**1**) (Cobalt Jacobsen), which can be used for the hydrolytic kinetic resolution (HKR) of terminal epoxides and the enantioselective catalytic ring opening of meso epoxides [1]. The HKR technique is widely used to produce epoxides and diols with a high enantioselectivity (around 98 %) and a high chemical yield. The synthesis of the cobalt Jacobsen's complex occurs in two steps. In the first step cobalt salen complex (**2**) is synthesized which is subsequently activated (to **1**) by exposure to air and addition of acetic acid. In this work, we present an analysis of both cobalt salen complexes (**1** and **2**), by means of CW and pulsed Electron Paramagnetic Resonance (EPR). The *g* and cobalt hyperfine values of the non-activated complex **2** show that we are dealing with a low-spin Co(II) complex with a  $|yz, ^2A_2\rangle$  ground state. The X- and W-band EPR spectra of the activated complex **1** bear the characteristics of an organic radical interacting with a cobalt nucleus. X-band HYSCORE experiments reveal the hyperfine and nuclear-quadrupole couplings of the nearest nitrogens. Large changes are observed in both the nitrogen and proton HYSCORE spectra upon activation of the complex. The EPR data will be discussed in function of the electronic structure of both complexes and related to known work on Co(II) complexes.

### References:

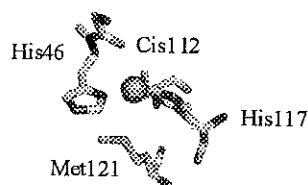
- [1] Tokunaga, M.; Larrow, J.F.; Kakiuchi, F.; Jacobsen, E.N., *Science*, 277, 936 (1997)

## An EPR study of the exchange interaction between two Cu(II)-ions in protein dimers connected by different linkers

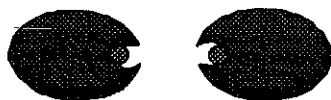
Sergey Milikisyants<sup>a)</sup>, Thyra de Jongh<sup>b)</sup>, Rian van den Nieuwendijk<sup>b)</sup>, Mark Overhand<sup>b)</sup>, Gerard Canters<sup>b)</sup>, Martina Huber<sup>a)</sup>

<sup>a)</sup>Department of Molecular Physics, Leiden University, P.O. Box 9504 2300 RA Leiden, The Netherlands.

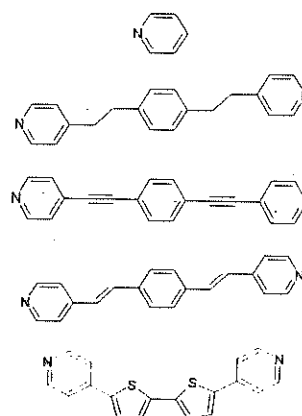
We study the exchange interaction between two protein-based Cu(II) ( $S=1/2$ ) centers linked by organic molecules (linkers). We want to determine, if the interaction is sufficiently strong (distance between Cu centers  $\approx 1.6$  nm) to be resolved in cw-x-band EPR spectra and how it depends on the linker structure.



Copper site of azurin



Dimer



Linkers

To set up the system, a blue copper protein (azurin) was modified. The His117 ligand (see Fig.) was replaced by glycine (azurin H117G) to create a solvent exposed aperture. A pyridine or pyridine based ligands can coordinate to the copper at the former position of His117. Thus, the linkers (see Fig.) can connect proteins creating dimers. Different linkers were analyzed, varying in electronic as well as chemical structure.

## List of attendees

**Prof. Dr. Guy Adriaenssens**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
guy.adriaenssens@fys.kuleuven.be

**Dr. Jacob Jan Briede**  
Department of Health Risk Analysis & Toxicology  
Faculty of Health Sciences  
Maastricht University  
PO Box 616  
6200 MD Maastricht, The Netherlands  
J.Briede@GRAT.unimaas.nl

**Prof. Dr. Valery Afanas'ev**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
valeri.afanasiev@fys.kuleuven.be

**Prof. Dr. Freddy Callens**  
Department of Solid State Sciences  
Ghent University  
Krijgslaan 281 /S1  
B-9000 Gent, Belgium  
Freddy.callens@ugent.be

**Aranzazu Aguirre**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
Aranzazu.Aguirre@ua.ac.be

**Sofie Cambre**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
sofie.cambre@ua.ac.be

**Ajaz Ahmad**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics  
University of Antwerp  
ijaz.ahmad@ua.ac.be

**Katrijn Clémer**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D, 3001 Leuven  
katrijn.clemer@fys.kuleuven.be

**Dr. Koen Beerten**  
Geographisches Institute der Universität zu Köln  
Albertus-Magnus-Platz  
50923 Köln, Germany  
Koen.Beerten@geo.kuleuven.be

**Hendrik De Cooman**  
University of Ghent  
Krijgslaan 281-S1  
9000 Ghent, Belgium  
Hendrik.DeCooman@UGent.be

**Huib Blok**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
huib@molphys.leidenuniv.nl

**Dr. Jelena Culin**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
Jelena.Culin@ua.ac.be

**Prof. Dr. Peter Gast**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
gast@molphys.leidenuniv.nl

**Daniela Ghica**  
National Institute for Materials Physics  
PO Box MG 7, Magurele-Bucuresti  
Romania 077125  
Daniela.Ghica@ua.ac.be

**Prof. Dr. Etienne Goovaerts**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
Etienne.Goovaerts@ua.ac.be

**Prof. Dr. Edgar J.J. Groenen**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
egroenen@molphys.leidenuniv.nl

**Martina Huber**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
mhuber@molphys.leidenuniv.nl

**Peter L. Hagedoorn**  
Kluyver Department of Biotechnology  
Julianalaan 67  
2628 BC Delft, The Netherlands  
P.L.Hagedoorn@tnw.tudelft.nl

**A. Iulia Ioanitescu**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
Iulia.Ioanitescu@ua.ac.be

**Mihaela Jivanescu**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
mihaela.jivanescu@fys.kuleuven.be

**Irina Lobysheva**  
University of Louvain (UCL) Medical School  
Unit of Pharmacology & Therapeutics  
Avenue E. Mounier, 53  
B-1200 Brussels  
Irina.Lobysheva@mint.ucl.ac.be

**Frank Loncke**  
Department of Solid State Sciences  
Ghent university  
Krijgslaan 281 /S1  
B-9000-Gent, Belgium  
frank.loncke@ugent.be

**Dimitris Maganas**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
dimitris@molphys.leidenuniv.nl

**Sergey Milkisyant**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
sergey@molphys.leidenuniv.nl

**Alidin Niztayev**  
Kluyver Laboratory  
Dept. of Biology, TU Delft  
Julianalaan 67  
2628 BC Delft, The Netherlands  
magiclamp33@hotmail.com

**Dr. Vasile Sergiu Nistor**  
National Institute for Materials Physics  
PO Box MG 7, Magurele-Bucuresti  
Romania 077125  
snistor@infim.ro



**Sergei B. Orlinskii**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
orlinski@molphys.leidenuniv.nl

**Ewald Pauwels**  
Center for Molecular Modeling  
Universiteit Gent  
Proeftuinstraat 86  
9000 Gent  
ewald.pauwels@UGent.be

**Marc Penders**  
BRUKER Belgium NV  
Kolonel Bourg straat 124 bus 1  
1140 EVERE  
Marc.Penders@bruker.be

**Jorrit Rijnbeek**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
rijnbeek@molphys.leidenuniv.nl

**Mathieu Salès**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
Mathieu.sales@fys.kuleuven.be

**Francesco Scarpelli**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
scarpelli@molphys.leidenuniv.nl

**Sheron Shamuilia**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
sheron.schamuillia@fys.kuleuven.be

**Jan Schmidt**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
mat@molphys.leidenuniv.nl

**Prof. Dr. Robert Schoonheydt**  
Center for Surface Science and Catalysis  
Dept. of Interface Chemistry, Univ. of Leuven  
Kasteelpark Arenberg 23  
3001 Leuven  
Robert.schoonheydt@be

**Dr. Mariana Stefan**  
National Institute for Materials Physics  
105 bis Atomistilor Street, PO Box MG-7  
077125 Bucharest -Margurele  
Romania  
mstefan@infim.ro

**Prof. Dr. Andre Stesmans**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
andre.stesmans@fys.kuleuven.be

**Piet Somers**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
3001 Leuven  
pieter.somers@fys.kuleuven.be

**Florin Trandafir**  
Experimental Condensed Matter Physics (ECM)  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
Florin.Trandafir@ua.ac.be

**Barry van der Meer**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
vdmeer@molphys.leidenuniv.nl

**Prof. Dr. Sabine Van Doorslaer**  
University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
Sabine.VanDoorslaer@ua.ac.be

**Henk Vrielinck**  
Department of Solid State Science  
University of Ghent  
Krijgslaan 281 /S1  
B-9000 Gent, Belgium  
henk.vrielinck@ugent.be

**Ernst van Faassen**  
Debye Institute, Section Interface Physics  
University of Utrecht  
E.E.H.vanFaassen@phys.uu.nl

**Prof. Dr. Jozef Witters**  
University of Leuven  
Dept. of Physics and Astronomy  
Celestijnenlaan 200 D  
BE 3001 Leuven  
jef.witters@fys.kuleuven.be

**Jörn Venderbos**  
Leiden Inst. Physics, University of Leiden,  
PO Box 9405, 2300 RA Leiden,  
The Netherlands  
j.w.f.venderbos@umail.leidenuniv.nl

**Sepideh Zamani**  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Antwerpen, Belgium  
Sepideh.Zamani@ua.ac.be

**Evi Vinck**  
Department of Physics, University of Antwerp  
Universiteitsplein 1  
B-2610 Wilrijk, Belgium  
evi.vinck@ua.ac.be