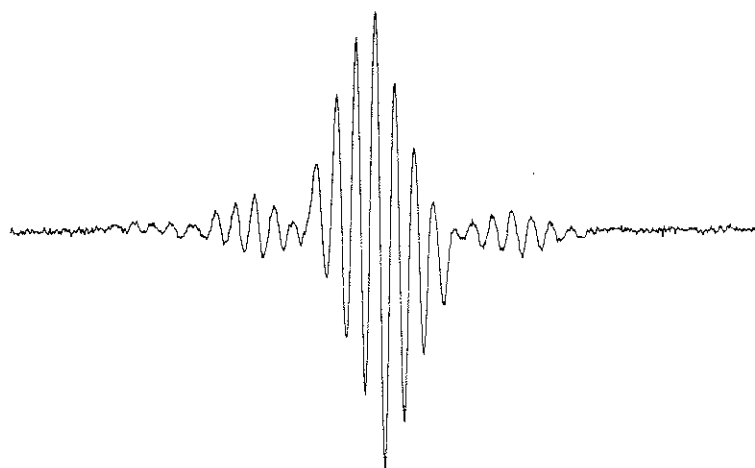
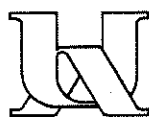


Sixth Meeting of the Benelux EPR Society

Program Book of Abstracts List of Participants



April 24, 1998

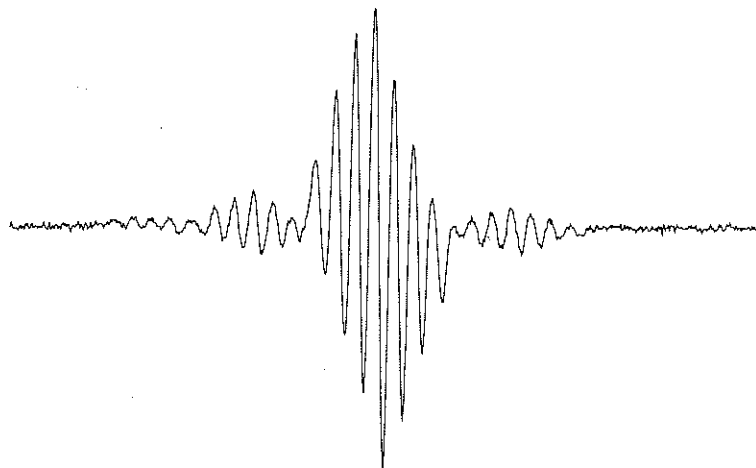


University of Antwerp (UIA)
Department of Physics (building N)
Universiteitsplein 1
Antwerp - Belgium



Sixth Meeting of the Benelux EPR Society

Program Book of Abstracts List of Participants



Organizing committee:

D. Schoemaker

A. Bouwen

E. Goovaerts

S.V. Nistor

P. Gast



Scientific Program

9.00-10.00h: Registration, setup of posters, settlement membership fee, coffee bar.

10.00h: Welcome and introduction by D. Schoemaker, chairman.

Oral presentations

10.10h: P.J.M. van Kan, University of Nijmegen,

'Multi-frequency EPR spectroscopy of myoglobin. Spectral effects for high-spin ferric ion at high magnetic fields.'

10.40h: **Invited lecture by T. Prisner**, University of Frankfurt,

'The challenges of high-frequency EPR and ENDOR'

11.30h: A. van Duijn-Arnold, University of Leiden,

'High-frequency EPR studies of shallow and deep boron acceptors in 6H-SiC'

12.00h: H. Vercammen, University of Antwerp,

'A 9.5 GHz and 95 GHz ESR study of a Rh²⁺ dimer center in NaCl single crystals: Discrimination between g-anisotropy and fine-structure terms'

12.30h: Lunch

14.00h: S. de Vries, Technical University of Delft,

'Novel molybdopterin radical and its interaction with an oxidized [2Fe - 2S]-center'

14.30h: I.V. Borovykh, University of Leiden,

'Photoselection in ESP spectra of photosynthetic reaction centers'

15.00h: coffee break

15.20h: B. Gallez, University of Louvain - UCL,

'The challenges of low-frequency EPR and in-vivo EPR'

15.50h: M.W. Polm, Wageningen Agricultural University,

'EPR and ODMR of hemoglobin hybrids'

16.20h: X.L.R. Dauw, University of Leiden,

'Triplet state dynamics of C₇₀: W-band versus X-band EPR'

16.50h: General meeting of the Benelux EPR Society

17.15h: Poster session, coffee

Closing reception and sandwiches till 19.00h

Multi-frequency EPR spectroscopy of myoglobin.
Spectral effects for high-spin ferric ion at high magnetic fields.

Paul J.M. van Kan¹, Eric van der Horst², Eduard J. Reijerse¹,

P. Jan M. van Bentum² and Wilfred R. Hagen¹

¹*Department of Molecular Spectroscopy and* ²*High-Field Magnet Laboratory*
University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands

The paramagnetism of transition metal ions in proteins frequently results in spin systems with $S > 1/2$. Experimentally, complications arise if the total spin quantum number becomes an integer value. In some cases even half-integer spin systems yield very limited information if the internal interactions that do not depend on the magnetic field are large compared to the Zeeman energy.

One particular class of examples of the latter case is formed by metalloproteins with ferric ion as a cofactor. In weak ligand fields this ion adapts a spin state with $S = 5/2$. The zero-field splittings are in the order of a few wavenumbers, thereby exceeding the Zeeman energy by an order of magnitude in common EPR experiments. Consequently, one would like to apply EPR spectroscopy to such high-spin systems at higher frequencies than the traditional X- and Q-bands and exploit the extra amount of information that theoretically can be gained from spectra obtained when an increasing number of transitions from the spin system with $S > 1/2$ become allowed. Moreover, a spectral resolution enhancement can be expected when the field-swept spectra extend over a wider field range. The latter expectation, however, is only justified if the spectral linewidth due to the statistical distribution of the g -value and zero-field splitting does not increase more than linearly with increasing microwave frequency. It is therefore important to find out if resolution enhancement really occurs experimentally in the spectra of metalloproteins when high-frequency EPR is applied as a method.

We report the result of a series of EPR experiments performed at microwave frequencies from 1 to 285 GHz on the $S = 5/2$ ferric ion in metmyoglobin. Two important phenomena occur upon increasing the frequency. Firstly, the effective g_{\perp} -value decreases notably as the Zeeman energy approaches the value of D , the zero-field splitting. Secondly, the linewidth of the spectra increases anomalously above 130 GHz. The dependence of observed linewidth on the microwave frequency shows three distinct phases. At low frequencies, broadening by unresolved hyperfine splittings is dominant. It is shown that from X-band frequencies onwards, a distribution in the value of g_{\perp} and D causes the measured dependence of linewidth on frequency. The implications of this experiment for the study of randomly distributed spin systems at high frequencies are discussed.

The challenges of high-frequency EPR and ENDOR

*Thomas F. Prisner, Martin Rohrer, Klaus Möbius**

Institut of physical chemistry, Johann-Wolfgang Goethe University Frankfurt

* Insitut of physics, Freie Universität Berlin

High-frequency EPR has proven its value with a number of applications in different fields like semiconductor physics, solid state physics, biochemistry and chemistry. These applications from several laboratories were mostly done with cw-microwave irradiation. Cw-high frequency EPR spectrometers exist up to frequencies of 600 GHz with high sensitivity and good performance, as demonstrated from these laboratories. In many cases these applications take advantage of an increased spectral resolution at higher magnetic field strengths by resolving the anisotropy of the g-matrix in disordered samples. To achieve a maximum in sensitivity is not trivial even for cw-EPR applications at high frequencies, because of the microwave source phase noise, microphonics and sample handling difficulties. More information on the spin system can be obtained by pulsed experiments and by double resonance experiments as ENDOR. In this case the resolved g-matrix can be used to obtain orientation selected hyperfine couplings and to investigate anisotropic motions. It is most difficult to obtain enough microwave power for pulsed EPR and ENDOR applications, especially above frequencies of 140 GHz. This is true despite the fact that the conversion factors of the microwave resonators become much better at these high frequencies because of small cavity volume. New spectrometer designs at 360 GHz (cw) and 180 GHz (pulsed) and there extensions to ENDOR spectroscopy will be discussed together with some applications of pulsed and cw EPR spectroscopy on proteins at 95 GHz.

HIGH-FREQUENCY EPR STUDIES OF SHALLOW AND DEEP BORON ACCEPTORS IN 6H-SiC

A. van Duijn-Arnold¹, T. Matsumoto², O.G. Poluektov³, T. Ikoma⁴ and P.G. Baranov⁵,
J. Schmidt¹

¹Huygens Laboratory, University of Leiden, P.O. Box 9504, 2300 RA Leiden, the Netherlands

²Nagaoka University of Technology, Niigata, 940-21, Japan

³Institute of Chemical Physics, Russian Academy of Sciences, Moscow, Russia

⁴Institute for Chemical Reaction Science, Tohoku University, Sendai 980-77, Japan

⁵A.F. Ioffe Physico-Technical Institute, St Petersburg, Russia

Key Words: EPR, Acceptors, SiC

Boron is known to produce shallow and deep acceptors in SiC. The shallow boron acceptor (ionization energy ~ 350 meV) has been studied extensively in the last 30 years and the theoretical model for its geometric and electronic structure has been reinterpreted several times. EPR experiments on a ¹³C-enriched 6H-SiC crystal established that B replaces Si and that it occupies 3 sites with equal probability: two quasi cubic (k_1 and k_2) and one hexagonal (hex) [1]. In the model proposed by Zubatov et al. [1] the main spin density was located in the dangling bond of a C atom along the B-C connection line. In more recent publications [2-4] a new description was given on the basis of ENDOR and ODMR investigations. In this model the valence electron is donated to B by a neighbouring C atom thus forming a $B_{Si}^- - C^+$ bond. The unpaired electron of C^+ is uniformly distributed among the three back bonds. The authors call this model the boron-induced carbon acceptor.

EPR and ENDOR spectroscopy at 95 GHz on the shallow B acceptor in a ¹³C-enriched 6H-SiC crystal has allowed us to measure accurately the g-tensors of the 13 magnetically inequivalent B sites. Moreover we have measured the hyperfine tensors of the ¹¹B, and ¹³C nuclear spin of the neighbouring C atom. From the results we conclude that the main density of the unpaired electron is located on the B-C bond as originally suggested by Zubatov et al. [1]. From a ²⁹Si and ¹³C ENDOR study it is further concluded that 60-70% of the spin density is distributed in the crystal with a Bohr radius of 2.2 Å, a value in reasonable agreement with effective-mass theory [5].

The deep B acceptor (ionization energy ~ 600 meV) in 6H-SiC has also been studied by EPR and ENDOR spectroscopy at 95 GHz. In particular the ENDOR results on ¹¹B support the model proposed by Baranov et al. [6-8] in which the deep B-acceptor consists of a B-vacancy pair. This model explains in a consistent way all EPR and ENDOR data [9].

References

1. A.G. Zubatov, I.M. Zaritskii, S.N. Lukin, E.N. Mokhov and V.G. Stepanov, *Sov. Phys. Solid. State* **27** (1985) 197.
2. R. Müller, M. Feege, S. Greulich-Weber and J.-M. Spaeth, *Semicond. Sci. Technol.* **8** (1993) 1377.
3. J. Reinke, R. Müller, M. Feege, S. Greulich-Weber and J.-M. Spaeth, *Mat. Sci. Forum* **143-147** (1994) 63.
4. F.J. Adrian, S. Greulich-Weber, J.-M. Spaeth, *Solid State Comm.* **94** (1995) 41.
5. T. Matsumoto, O.G. Poluektov, E.N. Mokhov, P.G. Baranov and J. Schmidt, *Phys. Rev. B* **55** (1997) 2219.
6. P.G. Baranov, E.N. Mokhov, A. Hofstaetter, A. Scharmann, *J.E.T.P.* **63** (1996) 848.
7. P.G. Baranov and E.N. Mokhov, *Semicond. Sci. Technol.* **11** (1996) 489.
8. P.G. Baranov, I.V. Ilyin and E.N. Mokhov, *Solid State Comm.* **100** (1996) 371.
9. A. v. Duijn-Arnold, T. Ikoma, O.G. Poluektov, P.G. Baranov, E.N. Mokhov and J. Schmidt, *Phys. Rev. B* **57** (1998) 1607.

A 9.5 GHz and 95 GHz ESR study of a Rh^{2+} dimer center in NaCl single crystals: Discriminating between g -anisotropy and fine-structure terms

H. Vercammen, E. Goovaerts, H. Käß, A. Bouwen, D. Schoemaker

*University of Antwerp – UIA, Department of Physics,
Universiteitsplein 1, B-2610 Antwerpen, Belgium*

Recently, a new ESR spectrum in Bridgman-grown NaCl single crystals was ascribed to a Rh^{2+} dimer center¹. This spectrum measured in the X-band is buried under more intense lines of the $\text{Rh}^{2+}\cdot 1\text{Vac}^+$ center ($\text{Vac}^+ = \text{Na}^+$ vacancy) and is only visible for a limited range of field orientations. The identification was based on a simulation of the available data using identical orthorhombic g tensors for both spins $S_1 = S_2 = 1/2$, with two principal axes (x and y) along $\langle 110 \rangle$ directions parallel and perpendicular to the $\text{Rh}^{2+}\text{--}\text{Rh}^{2+}$ axis (see Figure 1), taking into account the dipolar interaction between the spins.

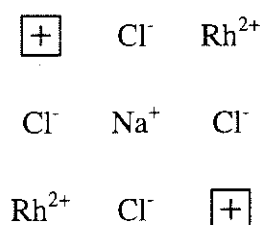


Figure 1 Model of the Rh^{2+} dimer in NaCl

We present high-frequency (W-band: 95 GHz) measurements that confirm the defect identification as a dimer, but demonstrate that a different spin-Hamiltonian analysis is required. The dimer spectrum can now be observed for a wider range of field orientations, distinguishable from the monomer spectra on which they were superimposed in the X-band measurements. A simulation² of the dimer spectrum for the W-band, using the spin-Hamiltonian of ref. 1, is in contradiction with our experimental data. Indeed, the assumed g -anisotropy in the xy -plane would yield a large increase of the absolute line splittings from X- to W-band, while the observed splittings in the perpendicular spectrum have hardly changed. This immediately demonstrates that the observed angular dependence in the xy -plane originates from a field-independent term in the Hamiltonian, namely the spin-spin interaction, $\mathbf{S}_1 \cdot \mathbf{D} \cdot \mathbf{S}_2$. The X- and W-band data can be simultaneously described by an axial or near-to-axial g tensor, similar to the case of $\text{Rh}^{2+}\cdot 2\text{Vac}^+$ center³, if one takes a more general form of the fine-structure tensor \mathbf{D} , not a purely dipolar interaction.

These results show that through ESR-measurements at two very different frequencies one can discriminate efficiently between field-dependent and field-independent interactions in the spin Hamiltonian and avoid ambiguities in spectral assignments.

¹ S. Schweizer, J.-M. Spaeth, *J. Phys. Chem. Solids* **58**, 859 (1997).

² Computer Program EPR-NMR (Department of Chemistry, University of Saskatchewan, Canada, 1995).

³ M. Zdravkova, H. Vrielinck, F. Callens, E. Boesman, H. Vercammen, D. Schoemaker, *J. Appl. Phys.* **82**, 2476 (1997).

Novel Molybdopterin Radical And Its Interaction With An Oxidized [2Fe-2S] Center

Dion M.A.M. Luykx, Johannes A. Duine and Simon de Vries*

Department of Microbiology and Enzymology, Delft University of Technology, Julianalaan 67, 2628 BC Delft, The Netherlands

The EPR spectra of three different molybdoprotein aldehyde dehydrogenases, one purified from *Comamonas testosteroni* and two purified from *Amycolatopsis methanolica* showed in their oxidized state a novel type of signal. These three enzymes contain two different [2Fe-2S] centers, one flavin and one molybdopterin cytosin dinucleotide as cofactors all of which are expected to be EPR silent in the oxidized state. The new EPR signal is isotropic with $g = 2.004$ both at X-band and Q-band frequencies, consists of six partially resolved lines and shows Curie temperature behaviour suggesting that the signal is due to an organic radical with $S = 1/2$. The EPR spectra of *Comamonas testosteroni* aldehyde dehydrogenase obtained after cultivation in media containing $^{15}\text{NH}_4\text{Cl}$ and/or after substitution of H_2O for D_2O show the presence of both nitrogen and proton hyperfine interactions. Simulations of the spectra of the four possible isotope combinations yield a single set of hyperfine coupling constants. The electron spin shows hyperfine interaction with a single $I = 1$ (0.9 mT) ascribed to a N-nucleus, with a single $I = 1/2$ (1.5 mT) ascribed to one non-exchangeable H-nucleus and with two, exchangeable, identical $I = 1/2$ spins (0.6 mT), ascribed to two identical exchangeable protons. Taken together, the observations and simulations rule out amino-acid residues or flavin as the origin of the radical. The values of the various hyperfine coupling constants are consistent with the properties expected for a molybdenum(VI)-trihydropterin radical in which the N5-atom is engaged in two hydrogen bonding interactions with the protein. The majority of the electron (spin) density of the radical is located at and around the N5-atom and at the proton bound to the C6-atom of the pterin ring.

The EPR spectrum of the molybdopterin radical broadens above 65K and is no longer detectable above 168K indicating that it is not magnetically isolated. The linebroadening is ascribed to cross-relaxation with a nearby, rapidly relaxing, oxidized [2Fe-2S]-center involving its magnetic $S = 1$ excited state in this process. The molybdenum(VI)-trihydropterin radical and the pterin moiety are suggested to fulfil a role in mediating internal electron transfer between the molybdenum atom and the nearby iron-sulphur cluster.

Photoselection in ESP spectra of photosynthetic reaction centers

I.V. Borovykh, I.B. Klenina*, P. Gast, A.J. Hoff
and I.I. Proskuryakov*

Department of Biophysics, Huygens Laboratory, Leiden State University, The Netherlands.

* Institute of Soil Science and Photosynthesis RAS, Pushchino, Russia.

The first relatively stable stage of photoinduced electron transfer in reaction centers (RCs) of many photosynthetic bacteria is $P^+Q_A^-$. As early as 1977 (Hoff et al. FEBS Lett. **73**, 185), it was reported that when the normally present magnetic interaction between Q_A^- and paramagnetic Fe^{2+} ion is disrupted, an electron spin-polarised (ESP) photoinduced signal may be detected using time-resolved EPR. This ESP signal was subsequently attributed to the state $P^+Q_A^-$, which since 1987 (Hore et al. Chem. Phys. Lett. **137**, 495., Closs et al. J. Phys. Chem. **91**, 3592) is considered as a spin-correlated radical pair (RP2). In principle, a wealth of information about the spatial arrangement of the P^+ and Q_A^- cofactors in RCs may be derived from a simulation of the spin-polarised signal.

Recently we observed that the shape of the RP2 signal strongly depends on the wavelength of excitation laser flash. The observed dependence of the ESP signal of RP2 in Zn^{2+} - substituted RCs of *Rb. sphaeroides* R26 arises due to the effect of photoselection by plane-polarised laser light, as proved by rotating the polarization plane of the excitation light parallel and perpendicular to the magnetic field of the spectrometer. Simulation of the RP2 spectra obtained with 90° - rotation of the polarization plane yields the relative orientation of the RP components with high reliability and precision. The photoselection-ESP enables studies on structural organisation of systems other than bacterial RCs.

The challenges of low-frequency EPR and in-vivo EPR

B. Gallez, C. Baudelet, B. Jordan, R. Debuyst.

Laboratory of Medicinal Chemistry and Radiopharmacy
Laboratory of Biomedical Magnetic Resonance
University of Louvain, B-1200 Brussels, Belgium

Although the technique is now more than 50 years old, only very recently has Electron Paramagnetic Resonance (EPR) become widely used for the study of functioning tissues and intact animals. The main reason for the limited applications in the past was the problem of high non resonant dielectric loss of the exciting frequency (usually in the microwave range) due to the high content of water in biological samples. Because of this phenomenon, the penetration depth of the most commonly applied frequency (9-10 Ghz) (X-Band) is less than 1 mm and therefore only suitable for in vitro samples localized in capillaries or flat cells. The development of spectrometers working at lower frequencies during the last few years now makes it possible to conduct in vivo measurements on a variety of animals and isolated organs. These advances have been facilitated by the development of new resonators with higher sensitivity and appropriate stability for in vivo applications. As a consequence it now becomes feasible to use EPR to obtain new insights into complex aspects of pathophysiology, physiology and pharmacy.

The ability to report on local conditions non invasively is an especially important advantage of in vivo EPR. Although the level of naturally occurring free radicals is too low for direct detection in vivo under physiological circumstances, this potential limitation can be exploited by adding paramagnetic probes (spin labels, charcoal particles) to the system, which then provide very specific sources of the EPR signals. Information can then be obtained in vivo such as microviscosity, polarity, partial pressure of oxygen, and pH. It also may be possible to obtain information on reactive species indirectly, using spin trapping techniques.

The aim of this presentation will be to present an overview of the current status and possible applications in the near future for in vivo EPR. We will focus on our research activity in the development of methods for the measurement of the partial pressure of oxygen (pO₂). Recent progress made in our laboratory, or in collaboration of the group of H.M. Swartz (Dartmouth Medical School, USA) will be presented.

EPR and ODMR of hemoglobin hybrids

M. Polm

Wageningen Agricultural University, Department of Molecular Physics, P.O. Box 8128, 6700 ET Wageningen, the Netherlands

Time resolved fluorescence detected magnetic resonance (FDMR) has been applied at 4.2 K to the three triplet spin levels of the lowest triplet state of the ZN- and Mg-protoporphyrin (Zn-/Mg-PP) centres in the Zn- and Mg-substituted met-hemoglobins hybrids $Zn_2Fe_2(III)Hb$ and $Mg_2Fe_2(III)Hb$, respectively. The results show enhanced decay rate constants for the triplet spin levels as compared to those of their fully substituted analogues Zn_4Hb and Mg_4Hb . The results can be explained by spin-lattice relaxation between the triplet spin levels induced by a fluctuating magnetic dipole interaction with the distant Fe(III)PP centres.

At 4.2 K the Fe(III) spin behaves as a fictitious spin $S=1/2$. It can be shown, that the time dependent interactions of $S=5/2$, $m_s=1/2$ with the triplet spin-levels cause relaxation between the x and z, and the y and z triplet spin levels only.

Triplet-State Dynamics of C_{70} : W-band versus X-band EPR

X.L.R. Dauw, O.G. Poluektov, J.B.M. Warntjes, M.V. Bronsveld, and E.J.J. Groenen
Centre for the Study of Excited States of Molecules
Huygens Laboratory,
University of Leiden,
P.O. Box 9504,
2300 RA Leiden, The Netherlands

Electron-spin-echo experiments at 9 and 95 GHz on the triplet state of C_{70} in glassy matrices are presented. For C_{70} the study of the decay of the electron-spin echo as a function of the time after laser excitation has allowed a complete description of the distinct population and decay of the substates of the lowest triplet state at 1.2K. The use of 95 GHz microwaves was found to be crucial. At 9 GHz information is limited because the echo decay is dominated by one sublevel leading to mono-exponential decays at all magnetic fields. At 95 GHz a more informative behaviour has been observed, analysis of which reveals the significance of $\Delta M_s=2$ spin-lattice relaxation at this microwave frequency which reflects the pseudo-rotation of the C_{70} molecule in the triplet state about its long axis on the time scale of microseconds at 1.2K. In addition, the triplet fine-structure parameter D and the relative populating probabilities and decay rates of the triplet sublevels will be discussed.

Posters

- P1 : B. Weckhuyzen, University of Leuven,
'EPR as a tool to study preferential adsorption and mobility of transition metal ions on inorganic oxides'
- P2 : A. Priem, University of Nijmegen,
'g-Strain and dipolar broadening studied by high-frequency EPR'
- P3 : E. van der Horst, University of Nijmegen,
'Phase sensitive MM-wave ESR'
- P4 : G. Vanhaelewyn, University of Ghent,
'An EPR spectrum-decomposition study of irradiated alanine'
- P5 : M. Zdravkova, University of Ghent,
'EPR and ENDOR study of NaCl single crystals doped with Na₂IrCl₆'
- P6 : H. Vrielinck, University of Ghent,
'Identification of a Rh⁺ center in x-irradiated solution-grown NaCl:Rh³⁺ with ENDOR'
- P7 : H. Vrielinck, University of Ghent,
'ENDOR study of cubic transition metal complexes in NaCl'
- P8 : S. Nistor, Institute of Materials Physics, Bucharest, and University of Antwerp,
'Electron and hole trapping in doped PbCl₂ crystals'
- P9 : S. Nistor, Institute of Materials Physics, Bucharest, and University of Antwerp,
'Chlorination induced changes in electron/hole trapping properties of Fe²⁺ ions in cubic SrCl₂:Fe crystals'
- P10 : H. Vercammen, University of Antwerp,
'ESR study of rhodium centers in solution-grown NaCl single crystals'
- P11 : W. Geens, University of Antwerp,
'Comparative ODMR study of recombination processes in poly-phenylene-vinylene trimer blends and polymers[⊙]
- P12 : G. Maresch, Bruker Germany and Belgium,
'High-resolution spectroscopy of manganese ions in calcite and related minerals by W-band EPR'
- P13 : M. Stefan, Institute of Atomic Physics, Bucharest,
'ESR of paramagnetic Tl⁰ and Tl²⁺ centers in ferroelectric Rb₂ZnCl₄ crystals'
- P14 : D. Vandenbroucke, Agfa-Gevaert NV, Antwerp,
'The nanomaterial research network feeding the technological development at Agfa'
- P15 : J. Michalik, Institute of Nuclear Chemistry and Technology, Warsaw,
'ESR and optical studies on silver clusters in sodalites and zeolites rho'

EPR as a tool to study preferential adsorption and mobility of transition metal ions on inorganic oxides

R. Ramachandra Rao, Bart Schoofs, Gabriela Catana,
Bert M. Weckhuysen and Robert A. Schoonheydt

*Centrum voor Oppervlaktechemie en Katalyse, Departement Interfasechemie,
K.U.Leuven, Kardinaal Mercierlaan 92, 3001 Heverlee, Belgium*

Knowledge of the mobility of transition metal ions such as Cr^{n+} and V^{n+} on the surface of inorganic oxides is important for the following reasons : (1) Cr^{6+} - and V^{5+} -ions are environmental and health hazards and (2) supported chromium or vanadium oxides are industrially important catalysts e.g. ethylene polymerization (Cr/SiO_2) and selective catalytic reduction of NO_x with NH_3 (V/TiO_2) [1,2].

When two inorganic oxides are in competition for transition metal ions, the latter may selectively go to the oxide with which it has the strongest affinity. It is this competition that is reported in this study [3,4]. Spectroscopic fingerprints of V^{4+} (d^1) and Cr^{5+} (d^1) are used to evaluate the preference of these ions for oxides and its mobility. Silica, alumina and zeolites were chosen as inorganic oxides because the different coordination environments of V^{4+} and Cr^{5+} on these supports can be distinguished by EPR.

It will be shown that both V^{4+} and Cr^{5+} are mobile under hydrated and dehydrated conditions, and preferentially migrate from silica to alumina, and to a lesser extent, to the zeolite. No migration is observed from alumina to zeolite or silica, and the observed preference sequences are discussed in relation to the properties of the inorganic oxides. It seems that EPR is an excellent method to study preference sequences of transition metal ions in inorganic oxides.

References

- (1) Bert M. Weckhuysen, Israel E. Wachs and Robert Schoonheydt. Surface chemistry and spectroscopy of chromium in inorganic oxides. *Chem. Rev.* 1996, **96**, 3327.
- (2) Israel E. Wachs, Bert M. Weckhuysen. Structure and reactivity of surface vanadium oxide species on oxide supports. *Appl. Catal. A : General* 1997, **157**, 67.
- (3) Bert M. Weckhuysen, Bart Schoofs and Robert Schoonheydt. Mobility of chromium in inorganic oxides : spectroscopic fingerprinting of oxidation states and coordination environments. *J. Chem. Soc. Faraday Trans.* 1997, **93**, 2117.
- (4) Gabriela Catana, R. Ramachandra Rao, Bert M. Weckhuysen, Pascal Van Der Voort, Etienne Vansant and Robert A. Schoonheydt. Supported Vanadium Oxide Catalysts : Quantitative Spectroscopy, Preferential Adsorption and Mobility. submitted for publication.

G-strain and dipolar broadening studied by high-frequency EPR

A.H. Priem, A.A.K. Klaassen, E.J. Reijerse, W.R. Hagen

High Frequency EPR is often used to obtain better g -resolution in $S=1/2$ -systems. Also, at higher frequencies the dipolar and exchange contributions are much smaller. EPR studies of paramagnetic species at conventional EPR frequencies often suffer from dipolar broadening due to these effects. This can be overcome by diluting the paramagnetic species in a diamagnetic host, but is not always possible.

A complication when going to higher microwave frequencies is g -strain broadening, which is proportional to the magnetic field. In this case, the higher microwave frequency will not result in a better g -resolution. However, it is not known where the optimum between dipolar broadening and g -strain broadening lies, *i.e.* which frequency is 'high enough'.

In this study, a number of Cr(V) compounds were prepared and measured at three different EPR-frequencies. These compounds, of the type M_3CrO_8 , where $M=Li, Na, K$ or Rb , have an unpaired electron which occupies the $3d$ atomic orbital on Cr. An earlier study by Cage *et al*¹ showed a completely resolved g -tensor for all compounds at 375 GHz. This study shows that optimum g -resolution can be obtained at much lower frequencies.

¹Journal of Magnetic Resonance, **124**,495,1997

Phase sensitive MM-wave ESR

E. van der Horst, P.J.M. van Bentum, J.A.A.J. Perenboom

Katholieke Universiteit Nijmegen, Toernooiveld 1, 6525ED Nijmegen, the Netherlands

We present the progress of a high frequency ESR spectrometer which is under development as part of the high magnetic field facility in Nijmegen. ESR at high frequencies benefits from a better absolute g -value resolution and the ability to measure systems with high zero field splittings. We will present the results of various innovative techniques to open the 1 THz range for ESR spectroscopy, such as phase sensitive heterodyne multi frequency detection and quasi optics. We present preliminary results for a number of test samples c.g. Magnesiumoxide, Calciumformiate, bio-chemical samples such as myoglobin, integer spin systems e.g. Ni (II), single crystal manganates and II-VI semiconductors. It is expected that the ESR facility will be available to external users at the second half of 1998 for CW operation up to 285 GHz. Extension to higher frequencies and pulsed operation is under evaluation.

AN EPR SPECTRUM DECOMPOSITION STUDY OF IRRADIATED ALANINE

G. Vanhaelewyn^{1#}, W. Mondelaers², F. Callens^{1*}

¹University of Ghent
Laboratory for Crystallography and Study of the Solid State,
Krijgslaan 281-S1, B-9000 Gent, Belgium

²University of Ghent
Department of Subatomic and Radiation Physics,
Proeftuinstraat 86, B-9000 Gent, Belgium

[#]Research Assistant of the Fund for Scientific Research - Flanders (Belgium)
(F.W.O.)

^{*}Research Director of the Fund for Scientific Research - Flanders (Belgium) (F.W.O.)

Polycrystalline samples of the amino acid α -alanine have been irradiated with an X-ray beam from a 15 MeV linear electron accelerator at both room temperature (RT) and higher temperatures. The EPR spectra from RT-irradiated alanine powder are dominated by the well-known RT-stable alanine radical $\text{CH}_3\text{C}^{\bullet}\text{HCOOH}$. Upon heating of RT-irradiated alanine powder, using a high temperature X-band EPR cavity, a strong decay of the RT-stable alanine radical was observed. Spectrum features recently ascribed to a second stable radical in irradiated alanine at RT [1], become more pronounced upon heating, providing a quasi-experimental isolation of this second alanine radical.

A multi variate statistical method called MLCFA (Maximum Likelihood Common Factor Analysis) was applied in combination with the high temperature cavity in order to determine the number of components in irradiated alanine powder which behave differently as a function of temperature. A previous MLCFA study applied to a dose series of alanine spectra, clearly demonstrated the compositeness of the powder spectra [2]. Furthermore the EPR components isolated from single crystal studies, will be compared with those found by using the high temperature cavity and applying MLCFA on heated and non-heated X-irradiated alanine powder.

- [1] E. Sagstuen, E. O. Hole, S. R. Haugedal and W. H. Nelson, "Alanine Radicals: Structure Determination by EPR and ENDOR of Single Crystal X-irradiated at 295 K", J. Phys. Chem., 101, 9763-9772, 1997.
- [2] F. Callens, K. Van Laere, W. Mondelaers, P. Matthys and E. Boesman, "A study of the Composite Character of the ESR Spectrum of Alanine", Appl. Radiat. Isot., 47, 1241-1250, 1996.

EPR and ENDOR study of NaCl single crystals doped with Na_2IrCl_6

M. Zdravkova[#], K. Sabbe, F. Callens*, P. Matthys

*Laboratory for Crystallography and Study of the Solid State,
Krijgslaan 281-S1, B-9000 Gent, Belgium*

Bridgman-grown NaCl single crystals doped with Na_2IrCl_6 do not show an EPR spectrum before irradiation. This indicates that Ir is reduced during the dopant procedure to diamagnetic Ir^{3+} . X-irradiation of the crystals produces paramagnetic Ir centers in which the iridium ion may have different valent states.

After irradiation at liquid nitrogen temperature one axial Ir^{2+} defect is formed. This defect is assigned to a $(\text{IrCl}_6)^{4-}$ complex associated with two sodium ion vacancies. After short anneal at 180 K this defect is transformed into another Ir^{2+} complex with lower g values, most probably by losing one vacancy. At the same time a second paramagnetic center is formed.

A comparative X- and Q-band EPR study reveals that during the irradiation at room temperature at least three different paramagnetic Ir defects are formed: orthorhombic and axial Ir^{2+} and axial Ir^{4+} . The latter two defects are more stable and can be found long time after the irradiation. They can also be observed in the crystal, irradiated at liquid nitrogen and annealed to room temperature.

X-band and Q-band ENDOR measurements are in progress in order to propose and/or confirm a structural model for these defects.

[#] On leave from the Institute of Catalysis, Academy of Sciences, 1113 Sofia, Bulgaria

* Research Director of the Fund for Scientific Research - Flanders, (Belgium)

Identification of a Rh^+ centre in x-irradiated solution-grown $\text{NaCl}:\text{Rh}^{3+}$ with ENDOR

H. Vrielinck, F. Callens, M. Zdravkova# and P. Matthys*
Laboratory for Crystallography and Study of the Solid State
Krijgslaan 281 - S1, B-9000 Gent (Belgium)

Rh^{3+} acts as a deep electron trap in AgCl and is routinely used to increase contrast and decrease sensitivity of photographic emulsions. In a recent ENDOR study,¹ it has been shown that solution-grown $\text{NaCl}:\text{Rh}^{3+}$ single crystals may act as relevant model systems for similarly doped AgCl microcrystals in photographic emulsions. Three stable paramagnetic rhodium related centres are produced after x-irradiation at room temperature of these single crystals. Two of these have earlier been identified as Rh^{2+} centred complexes.¹ For the third centre an intense ENDOR spectrum was observed at temperatures below 15 K, although no EPR spectrum was detected.

In the present study this centre is identified as a RhCl_6^{5-} complex substituting for NaCl_6^{5-} . The central Rh^+ ion has a d^8 configuration which leads to a centre with effective spin $S=1$. This is confirmed by the observation of a $\Delta M_S=2$ transition in the EPR spectrum. The ENDOR angular variation shows that the complex has cubic symmetry. From repeated irradiations at 77 K followed by thermal pulse annealing, the formation mechanism of this centre is deduced.

¹ M. Zdravkova, H. Vrielinck, F. Callens, E. Boesman, H. Vercammen and D. Schoemaker, *J. Appl. Phys.* **82** (5), 2476-2482 (1997)

* Research director of the Fund for Scientific Research - Flanders (Belgium)

On leave from the Institute of Catalysis, Academia of Sciences, Sofia, Bulgaria

ENDOR study of cubic transition metal complexes in NaCl

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

Laboratory for Crystallography and Study of the Solid State

Krijgslaan 281, B-9000 Gent (Belgium)

Cubic Fe^+ , Ru^+ and Rh^+ complexes, doped in NaCl single crystals, were studied with ENDOR spectroscopy. The Fe^+ and Ru^+ centres have a d^7 configuration in an intermediate cubic crystal field. This leads to an isotropic g factor near $g = 13/3$. The Rh^+ centre has a $4d^8$ configuration, with effective spin $S = 1$.

For the three centres studied, the equivalence of the six nearest Cl ions is demonstrated by the angular dependence of their ENDOR resonances. In the ENDOR spectrum of the Ru^+ and the Rh^+ centres, an isotropic hyperfine interaction (self ENDOR) and interactions with the fourth shell Na nuclei are also observed. In this way the ENDOR results effectively support the cubic symmetry of the centres.

* Research director of the Fund for Scientific Research - Flanders (Belgium)

ELECTRON AND HOLE TRAPPING IN PbCl_2 CRYSTALS

S.V. Nistor*, M. Stefan *, E. Goovaerts and D. Schoemaker****

* Institute of Atomic Physics (N.I.M.P), POB MG-7 Magurele, 76900
Bucuresti, Romania

** Physics Department, University of Antwerp (U.I.A.) 2610 Antwerp(Wilrijk),
Belgium

Crystalline lead halides exhibit strong photoluminescence under UV excitation at low temperatures and photochemical changes resulting in the formation of colloidal lead and desorption of halogen at higher temperatures. Paramagnetic centres, resulting from primary processes associated with the recombination/trapping of the electrons and holes produced by low temperature irradiation, are to be expected. The early identification of the ESR spectra around $g \sim 2$, as being due to trapped electron Pb^+ and Pb_2^{3+} centres [1], are inconsistent with more recent, extensive ESR studies [2] on such centres in alkali halides.

In order to gain a better insight into the processes involving the electron-hole pairs produced by irradiation/illumination we performed ESR and optical spectroscopy studies on PbCl_2 single crystals doped with 0.1 and 0.2 mol% TlCl , x-ray irradiated (tungsten cathode, 50kV, 50mA) at 80K and further pulse annealed at various temperatures, up to RT.

Changes in both ESR and optical absorption/emission spectra have been observed as a function of the thallium content in the as grown crystals and of the pulse annealing temperature after low temperature x-ray irradiation. Besides the ESR spectra of the self-trapped electron (STEL) and dimer $(\text{PbTl})^{2+}$ centres [3,4], several anisotropic lines have been observed in the x-ray irradiated crystals with relative intensity depending on the thallium content in the as grown crystal. The quantitative analysis of the line positions angular dependence in the three main crystal planes led to the identification of new monomer and dimer type of thallium trapped-electron centres. Changes in both ESR and optical spectra have been observed in the 120-140K temperature range, attributed to the thermally induced movement of vacancies lying next to the paramagnetic centres and to the thermally induced release of electron /holes.

Based on the production properties of the identified trapped electron centres in such crystals we found that the early reported A-centre [1] does exhibit production properties characteristic of a trapped-hole centre. The quantitative analysis of the low temperature ESR spectra angular dependence obtained by rotating the magnetic field in the three main crystal planes suggests a superposition of ESR spectra from V_k -type hole-self trapped centres with different g - and A - tensors principal values and main axes. Such paramagnetic centres seem to result from the presence of molecular Cl_2^- defects with different intramolecular separation and orientation of the molecular axes, resulting from holes being self-trapped at pairs of neighbouring Cl^- lattice ions. Contrary to the simple cubic alkali halides, the PbCl_2 lattice has several pairs of neighbouring Cl^- ions with slightly different separations and orientation of the intranuclear

axis, which explains the above model. It is worthwhile mentioning that the present results seem to represent the firstly reported case of an ionic compound exhibiting both electron and hole self-trapping properties.

[1]. W. C. De Gruijter and J Kerksen, J. Solid State Comm. **5**, 467 (1972).

[2]. S. Nistor and D. Schoemaker, Phys. Stat. Sol. (b) **190**, 339 (1995).

[3]. S. V. Nistor, E. Goovaerts and D. Schoemaker, Phys. Rev. **B48**, 9575 (1993)

[4]. S. V. Nistor, E. Goovaerts and D. Schoemaker, Phys. Rev. **B57**, 1 (1998)

CHLORINATION INDUCED CHANGES IN ELECTRON/HOLE TRAPPING PROPERTIES OF Fe^{2+} IONS IN CUBIC $\text{SrCl}_2\text{:Fe}$ CRYSTALS

S.V. Nistor*, E. Goovaerts, A. Bouwen** and D. Schoemaker****

* Institute of Atomic Physics (N.I.M.P), 76900 Bucuresti Magurele, Romania

** Physics Department, University of Antwerp (U.I.A.) B-2610 Antwerpen, Belgium

It is shown that SrCl_2 crystals grown in a chlorine atmosphere, with 0.1% Fe added in the melt, exhibit after x-ray irradiation at 80K, besides trapped-hole Fe^{3+} centres with cubic symmetry previously reported [1] in crystals grown in vacuum, an Fe^{3+} centre with axial $\langle 111 \rangle$ symmetry [2], as well as additional trapped-electron Fe^+ centres.

The ESR studies performed in the X(9 GHz) and W(95 GHz) microwave frequency bands lead to the identification of two main trapped-electron centres, called $\text{Fe}^+(\text{I})$ and $\text{Fe}^+(\text{II})$, both with axial $\langle 100 \rangle$ local symmetry but different spin Hamiltonian (SH) parameters and production properties.

The concentration of the $\text{Fe}^+(\text{I})$ centres, produced in small amounts by x-ray irradiation at 80K in the as grown crystals, increases about an order of magnitude in samples firstly quenched at RT after being annealed for 5 to 10 minutes at 700K. The resulting $\text{Fe}^+(\text{I})$ centres are extremely stable, at least up to 700K. Their ESR lines are visible in the X-band below $T = 120\text{K}$.

The $\text{Fe}^+(\text{II})$ centres exhibit a different behaviour. Produced by X-ray irradiation at 77 K, their concentration does not depend on the previous thermal history of the sample. They are unstable at RT and their ESR lines are visible in the X-band below $T = 15\text{K}$.

After our knowledge this is the first reported ESR study of a Fe^+ (d^7) ion in a fluorite type lattice with bivalent cations. The ESR spectrum results from the magnetically induced transitions inside the fourfold spin-degenerate ${}^4A_{2g}$ lowest lying state of the free-ion 4F ground term [3], split by a local tetragonal distortion in two Kramers doublets separated by $2D = 6B_2^0$. From the angular dependence of line positions in the X-band and observations of transitions in the upper doublet it has been possible to determine directly, for the first time, the full spin Hamiltonian parameters of the $S = 3/2$ system. The results are in excellent agreement with the W-band ESR spectra.

It seems very likely that in both centres cation impurities are located in the nearest neighbour empty cube of lattice anions along a tetragonal $\langle 100 \rangle$ axis. Such impurities, which seem to be natural K^+ or Na^+ impurities from the SrCl_2 material, are responsible for the local tetragonal crystal field, as well as for the electron trapping properties of the precursor Fe^{2+} ions. To explain the observed aggregation properties of the $\text{Fe}^+(\text{I})$ precursor, the presence of a neighbouring charge compensating vacancy has to be considered as well.

- [1]. J. M. De Siebenthal, D. Nicolin and H. Bill, Chem. Phys. Lett. **58**, 317 (1978)
- [2]. S. V. Nistor, D.P. Lazar, H. Kass and D. Schoemaker, Solid State Comm. **104**, 521 (1997)
- [3]. A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford, 1970.

ESR study of rhodium centers in solution-grown NaCl single crystals

H. Vercammen and D. Schoemaker

*University of Antwerp, Department of Physics,
Universiteitsplein 1, B-2610 Antwerpen, Belgium*

H. Vrielinck and F. Callens

*University of Gent, Department of Physics,
Krijgslaan 281/S1, 9000 Gent, Belgium*

Recent ESR-measurements on rhodium doped AgCl microcrystals¹ show that Rh^{3+} is a good electron trap and forms Rh^{2+} . The electron trapping and detrapping properties are largely influenced by the molecular structure of the Rh^{3+} complex. Because characterization of the molecular structure is not a trivial task in a powder of microcrystals², one has to fall back on model systems. In this case these are macroscopic single crystals: either grown from the melt or from solution. In this work rhodium doped solution-grown NaCl single crystals are studied.

The $[\text{RhCl}_6]^{4-}$ center in solution-grown NaCl was already investigated³. The analysis showed that the center is in the low spin d^7 configuration, where the electron is mainly localized in the $4d_{z^2}$ orbital of the rhodium ion. The symmetry of both \mathbf{g} en \mathbf{A} tensors at 77K is axial, along a $\langle 001 \rangle$ direction. Analogous results were obtained for Bridgman-grown AgCl crystals³. In another work⁴ orthorhombic \mathbf{g} en \mathbf{A} tensors were found for the rhodium center in AgCl at 20K, however no comparable axial spectrum was detected at 77K.

NaCl single crystals were grown from a saturated aqueous solution, which contains about 0.6 % $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$. After x -irradiation at 77K, the nearly-axial spectrum, of the so-called O(I) spectrum was observed at 20K. The principal axes of the \mathbf{g} tensor are oriented along $\langle 110 \rangle$, $\langle \bar{1}10 \rangle$ en $\langle 001 \rangle$ with $g_x \approx g_y$. After annealing to about 190K, the O(I) center is partially converted to another, orthorhombic center, O(II). The principal axes for this center coincide with the cubic axes of the crystal. After a long pulse anneal to 300K, the O(II) is converted to a large extent to the RTAX center. This center possesses axial symmetry along $\langle 001 \rangle$. The g_x en g_y or g_{\perp} values and g_z or g_{\parallel} values of all three centers are comparable.

The change in symmetry is attributed to vacancy diffusion. Before irradiation the Rh^{3+} center is supposed to be fully charge compensated, i.e., with two cation vacancies. After irradiation at 77K and electron capture, one extra charge is present for the O(I) center. This center easily loses one vacancy at higher temperatures, while it converts to O(II). Apparently, the remaining vacancy will diffuse away after a long period at 300K, where the O(II) is being converted to RTAX⁵, which is no longer (locally) compensated. This is contrasted by the dominant rhodium center in Bridgman grown NaCl which is O(II)⁶.

¹ H. Vercammen, T. Ceulemans, D. Schoemaker, P. Moens, D. Vandenbroucke, *Proceedings of the 49th Annual Conference of IS&T*, Minneapolis, Minnesota, 1996, p.54.

² P. Moens, H. Vercammen, D. Vandenbroucke, F. Callens, D. Schoemaker, *ibidem*, p. 56.

³ J.R. Shock and M. T. Rogers, *J. Chem. Phys.* **62**, 2640 (1975).

⁴ M.T. Olm, J.R. Niklas, J.M. Spaeth, M.C.R. Symons, *Phys. Rev. B* **38**, 4343 (1988).

⁵ M. Zdravkova, H. Vrielinck, F. Callens, E. Boesman, H. Vercammen, D. Schoemaker, *J. Appl. Phys.* **82**, 2476 (1997).

⁶ S. Schweizer, J.-M. Spaeth, *J. Phys. Chem. Solids* **58**, 859 (1997).

Comparative ODMR study of recombination processes in polyphenylene-vinylene trimer blends and polymers

W. Geens, V. Dyakonov, E. Goovaerts, H. J. Geise*, W. Tachelet*
Physics Department, *Chemistry Department, University of Antwerp (U.I.A.)

In recent years conjugated polymers (CP) have been shown to exhibit exciting features that make them attractive for optoelectronic applications. To use CP in electroluminescent devices, efforts are still necessary to improve their luminescence efficiency. Photoinduced charge transfer (CT) must be prevented because it leads to the dissociation of the primary photogenerated singlet excitons (SE), which are responsible for the light emission. This can be done by using polymer blends, in which CP are embedded into a non-conjugated matrix. Further, by using oligomers one can also control the colour and structural properties of the films.

In this contribution we compare X-band ODMR experiments performed on films of PPV and different PPV-based trimers in a polystyrene (PS) matrix. ODMR is known to be sensitive to the CT states. By monitoring the photoluminescence (PL) from PPV, three different PL-enhancing features were found in ODMR: i) a "narrow" line (FWHM = 1.5mT, $g = 2$); ii) a broad powder spectrum (130mT); iii) a "half-field" signal ($g \approx 4$).

The origin of the ODMR signals in CP is controversial. In one model [1] the resonant microwaves influence the non-radiative recombination path via spin-dependent SE quenching. Another model [2] considers the radiative recombination or triplet-triplet annihilation path as the origin of ODMR. In this model CT polaron pairs (or interchain CT-excitons) are responsible for ODMR, and the triplet recombination channel is operative. In this work we found that, in spite of a very strong PL, the ESR induced changes of PL are weaker by more than one order of magnitude in all trimer blends used, which is in agreement with the CT origin of ODMR.

The scenario may look as follows: under photoexcitation the SE's and CT-excitons are generated. Since CT states are ESR active, the resonant microwaves increase the rate of the generation of intrachain triplet excitons, which annihilate in a second order reaction and contribute to the PL. This process results in the "narrow" signal. The resonant microwave transitions between magnetic sublevels of annihilating excitons may also result in an enhancement of the SE emission, which was observed as the powder pattern and half-field signal.

In summary, we compared PL and ODMR spectra on polymer films and trimer/PS blends. The observations support the CT nature of the "narrow" ODMR signal. The CT processes in trimer-blends is significantly suppressed by the presence of the non-conjugated PS matrix.

[1] Z. V. Vardeny *et al.*, *Mol. Cryst. Liq. Cryst.*, **256**, 465 (1994).

[2] V. Dyakonov *et al.*, in *Inorganic and Organic Electroluminescence*, 129 (1996).

High-Resolution Spectroscopy of Manganese Ions in Calcite and Related Minerals by W-Band EPR

G.G. Maresch, Bruker Analytik GmbH, Rheinstetten, Germany

High-frequency EPR spectrometers provide outstanding resolution and sensitivity [1]. With EPR instruments operating at W-band with a microwave frequency of 94 GHz even small concentrations of electron spins can be examined with high precision. The resonance frequency is approximately ten times higher than the frequency used in standard EPR spectrometers. In many cases this increases spectroscopic resolution by a factor of ten. This enhancement in resolution and sensitivity is needed for many chemical and biological applications.

Manganese ions occur naturally in calcite and similar minerals. Marble deposits are the origin of calcite which is the basis for calcium oxide. Manganese is found even in highly purified calcium oxide. Due to the high crystal symmetry of the manganese sites there is no evidence of a contribution by zero-field splittings. The individual linewidths are smaller than one Gauss. In comparison, manganese ions in many other materials have a zero-field contribution to the Hamiltonian as big as several GHz [2]. The large zero-field splittings result in spectral widths in the Tesla range. As an example this is shown in EPR spectra from manganese ions in ammonium chloride powder. The X-band EPR spectrum is directly compared to the W-band spectrum.

The narrow linewidths of manganese and other impurities in calcium oxide powders allow pulsed EPR studies over a wide temperature range. The manganese lines are detected at 90 K with a minimum linewidth of 300 mG. In addition to the manganese signals, electron-spin echoes are obtained from a free radical like defect. At low temperatures the signals from the free radicals become dominant. The line which is structureless at room temperature splits into three lines at 10 K.

With the assumption that the g-factor is independent of the magnetic field, the narrow manganese lines are used for magnetic field calibration [3]. A similar system, Mn in MgO has been used for this purpose [4]. High-frequency EPR spectroscopy provides such a high resolution that the precision of g-factor measurements is pushed upward by one order of magnitude.

[1] Ya.S. Lebedev, in "Modern Pulsed and Continuous-Wave ESR", L. Kevan and M.K. Bowman, eds., Wiley 1990.

[2] J.W.H. Schreurs, J. Chem. Phys. 69 (1978) 2151.

[3] O.J. Rubio, P. Munoz, O.J. Boldu, Y. Chen, and M.M. Abraham, J. Chem. Phys. 70 (1979) 633.

[4] O. Burghaus, M. Rohrer, T. Grötzinger, M. Plato, and K. Möbius, Meas. Sci. Technol. 3 (1992) 765.

ESR OF PARAMAGNETIC Tl^0 AND Tl^{2+} CENTRES IN
FERROELECTRIC Rb_2ZnCl_4 CRYSTALS

M. Stefan^{*}, S.V. Nistor^{*} and D. Schoemaker^{**}

^{*}Institute of Atomic Physics (NIMP), POB MG-7 Magurele, 76900
Bucharest, Romania

^{**}Physics Department, University of Antwerp (UIA), 2610 Antwerp (Wilrijk),
Belgium

Not too many data are available in the literature concerning the irradiation effects in pure/doped Rb_2ZnCl_4 crystals [1-3], although this system presents a great deal of interest due to its multiple structural phase transitions (SPT) i.e., from a normal orthorhombic ($Pm\bar{c}n$) paraelectric phase to an incommensurate phase at $T_1 = 303$ K, followed by a transition to a commensurate orthorhombic ($P2_1cn$) ferroelectric phase at $T_{c1} = 192$ K and to a monoclinic ($C1c1$) ferroelectric one at $T_{c2} = 74$ K.

We report here the results of an ESR study on Rb_2ZnCl_4 crystals doped in the melt with 0.2mol% $TlCl$. The anisotropic ESR spectra, observed after x-ray irradiation at 80 K in the two low temperature ferroelectric phases, exhibit, besides the already reported V_k centres [1], additional transitions attributed to Tl^{2+} - type [4] and Tl^0 - type centres [5]. Changes into ESR spectra, observed above 120 K, during pulse-annealing experiments, have been attributed to the movement of vacancies around the Tl^{2+} ions.

The average values of the spin-Hamiltonian parameters around 90 K for the $Tl^0(6s^26p^1)$ centres are $g_{\parallel} \sim 1.842$, $g_{\perp} \sim 1.535$, $A_{\parallel} \sim 0.3333$ T and $A_{\perp} \sim -0.1905$ T. The resulting $\rho = 0.1061$ T and $A_p = 0.0416$ T, anisotropic and isotropic hf contributions, respectively, strongly support the presence of an odd crystal field, associated to a lack of inversion symmetry at the Tl site. For the $Tl^{2+}(6s^1)$ centres the average spin-Hamiltonian parameters at the same temperature are $g \sim 2.005$ and $A \sim 3.67$ T. By cooling the crystals below T_{c2} additional line splittings were observed for both centres, explained by the lattice symmetry lowering effect. Accurate spin-Hamiltonian parameters for each centre exhibiting local rhombic symmetry have been obtained by computer fitting procedures.

During crystal growth the Tl^+ ions are supposed to enter the crystal lattice substitutionally at cation sites. The two different centres, Tl^0 and Tl^{2+} , may originate from different locations of the precursor Tl^+ ions, at Rb^+ and Zn^{2+} sites respectively, with/without neighbouring charge compensating vacancies.

An important result of the present study consists in the identification of the Tl^0 and Tl^{2+} centres as new, sensitive paramagnetic probes for investigating SPT and vacancy dynamics in these crystals.

- [1]. F. J. Lopez and A. Martin, Phys. Rev. **B 38**, 6392 (1988)
- [2]. S.V. Nistor, A. Bouwen and D. Schoemaker, Phys. Stat. Sol. (b) **189**, 345 (1995)
- [3]. M. Stefan, S.V. Nistor, N. M. Grecu and D. Schoemaker, Phys. Stat. Sol. (b) **202**, 999

(1997)

[4]. S. V. Nistor, D. Schoemaker and I. Ursu, Phys. Stat. Sol. (b) **185**, 9
(1994)

[5]. E. Goovaerts, J. Andriessen, S. V. Nistor and D. Schoemaker, Phys.
Rev. **B 24**, 29

(1981)

The Nanomaterial Research Network Feeding the Technological Development at AGFA.

D. Vandenbroucke[#], R. DeKeyser, Agfa-Gevaert N.V., R&D, PRO/AgX-3140, Septestraat 27, B.-2640 Mortsel, Belgium.

In imaging materials, the characteristic photochemical properties of silver halides are exploited to realize high light efficiencies and high image qualities. The nanostructuring of various silver halides in microcrystals, the incorporation of intentionally designed point defects in one or various zones of the nano-sized AgX phases in a single microcrystal, the formation of mesoscopic phases on the crystal surface and a supra-molecular organization of organic compounds in nano-phases on the crystal surfaces are major tools in the design of AgX based imaging materials for specific applications.

In order to optimize the technology to produce these nano-materials in large-scale batches in a homogenous way and in order to realize fast innovation in the design of new materials, appropriate characterization technologies and know-how are indispensable. Analytical technique such as e.g. an automated cryo-nanoprobe STEM-EDX technique, are applied in order to characterize to homogeneity of the nanostructuring intra and inter crystal. Physical and photophysical properties of the silver halide and of ionic defects in the silver halides are investigated by transient microwave absorption techniques operating at 9.3 GHz and 36 GHz and by magnetic resonance techniques such as EPR and ENDOR and related techniques operating at 9.3 GHz, 36 GHz and 95 GHz. Surface organization is controlled by local probe techniques such STM, PSTM or using analytical techniques as e.g. TOF-SIMS.

The development of specialized characterization technologies is stimulated to realize acceleration in the innovation of imaging materials. This synergy is the result of a coordinated effort of a network of local experts bringing in their advanced technologies and a focused interface in basic oriented application groups.

[#] Tel. : 00 32 3 444.31.40, Fax : 00 32 3 444.33.47, Email : VDBROUCKE@TWI.AGFA.BE

ESR and Optical Studies on Silver Clusters in Sodalites and Zeolites Rho

J. Michalik¹, J. Sad^{3o1}, T. Kodaira², S. Shimomura³ and H. Yamada³

¹*Institute of Nuclear Chemistry and Technology, 03-195 Warsaw, Poland*

²*National Institute for Research in Inorganic Materials, Tsukuba, Ibaraki
305, Japan*

³*National Institute for Advanced Interdisciplinary Research, Tsukuba,
Ibaraki 305, Japan*

There is an increasing interest to develop the new nanomaterials for electronics, optics and heterogeneous catalysis. Zeolite frameworks offer excellent conditions for the stabilization of nanoparticles with uniform nuclearity and shape. Silver ions were deemed to be suitable guests because of their great tendency to be exchanged into zeolites and their ease of reduction which is often accompanied by cluster formation.

The main goal of present study was to correlate the ESR and optical data for small, cationic silver clusters in zeolites. To achieve this goal the clusters have to be relatively stable at RT because the optical measurements cannot be carried out at low temperature. Therefore we focused on two systems: 1. AgCs-rho zeolite in which unique stability of Ag_4^{3+} clusters was discovered earlier¹ and 2. Ag-oxalatosodalite, in which recently we stabilized at RT Ag_5^{n+} cluster. Pentameric silver is represented by ESR isotropic sextet with $A_{\text{iso}} = 92 \text{ G}$ and $g_{\text{iso}} = 1.987$. Unirradiated samples of dehydrated zeolites are ESR silent, whereas diffuse reflectance spectra show weak absorption peaks associated with silver clusters with maxima at 270 nm for AgCs-rho and at 380 nm for Ag-oxalatosodalite. After irradiation at RT the intensity of these peaks increases, but no new absorption appears. The ESR measurements of the same samples reveal the spectra of tetrameric silver cluster in rho zeolite and pentameric cluster in sodalite. By comparison of the optical and ESR results we conclude that silver agglomeration proceeds during zeolite dehydration. As a result of autoreduction and migration of silver atoms and cations

diamagnetic clusters are formed - tetrameric in AgCs-rho characterized by absorption with maximum at $\lambda=270$ nm and pentameric in Ag-oxalatosodalite ($\lambda=380$ nm). Paramagnetic clusters Ag_4^{3+} and Ag_5^{n+} are formed from diamagnetic species by electron capture or abstraction during radiolysis. Diffuse reflectance spectra suggest that absorption maxima for diamagnetic and paramagnetic clusters with the same nuclearity do not differ much.

1. J. Michalik, J.Sad³o, J-S. Yu, L. Kevan *Colloids and Surface A*, 115, 239 (1996)

LIST OF PARTICIPANTS

Christine **Baudelet**
Université Catholique de Louvain (CMFA)
Avenue Emmanuel Mounier 73-40
1200 Brussels
Belgium
E-mail: baudelet@cmfa.ucl.ac.be

Igor **Borovykh**
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands

Prof. August **Bouwen**
Department of Physics
University of Antwerp (UIA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202453
Fax: +32-3-8202245
E-mail: abouwen@uia.ua.ac.be

Prof. Freddy **Callens**
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium
E-mail: Freddy.Callens@rug.ac.be

Prof. Jan **Ceulemans**
KU Leuven
Celestijnenlaan 200-F
3001 Heverlee
Belgium
E-mail:
jan.ceulemans@chem.kuleuven.ac.be

Dr. Tom **Ceulemans**
Department of Physics
University of Antwerp (UIA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202454
Fax: +32-3-8202245
E-mail: ceuleman@uia.ua.ac.be

Pegie **Cool**
Inorganic Chemistry
University of Antwerp (UIA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202354
Fax: +32-3-8202374
E-mail: cool@uia.ua.ac.be

Xavier L.R. **Dauw**
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
E-mail: Xavier@molphys.LeidenUniv.nl

Prof. Engbert **de Boer**
University of Nijmegen
Vinkenlaan 18
65DICK Malden
The Netherlands
E-mail: edeboer@sci.kun.nl

Prof. René **Debuyst**
Université Catholique de Louvain (INAN)
Chemin du Cyclotron 2
1348 Louvain-la-Neuve
Belgium
Debuyst@inan.ucl.ac.be

Prof. Simon de Vries
Technische Universiteit Delft
Julianalaan 67
2628 BC Delft
The Netherlands
E-mail: s.devries@STM.TUDELFT.NL

Prof. Peter Gast
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
GAST@RULHL1.LEIDENUNIV.NL
Prof. Etienne Goovaerts
Department of Physics
University of Antwerp (UIA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202446
Fax: +32-3-8202245
E-mail: goovaert@uia.ua.ac.be

Prof. Arnold J. Hoff
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
HOFF@RULHL1.LEIDENUNIV.NL

Prof. Machalik Jacek
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium

Hanno Kaess
Institut für Physikalische Chemie III
Technical University of Darmstadt
Petersenstrasse 20
64287 Darmstadt
Germany
Tel.: +49-6151-16-2998
Fax: +49-6151-16-4347
E-mail: kaess@hrzpub.tu-darmstadt.de
hk@pc07.pc.chemie.tu-darmstadt.de

Prof. Bernard Gallez
Laboratory of Medicinal Chemistry and
Radiopharmacy
Catholic University of Louvain
Avenue Mounier 73.40
1200 Brussels
Belgium
Tel.: +32-2-7647348
Fax: +32-2-7647363
E-mail: Gallez@cmfa.ucl.ac.be

Wim Geens
IMEC
Kapeldreef 75
3001 Leuven
Belgium
E-mail: geens@imec.be
Prof. W.R. Hagen
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: hagen@sci.kun.nl

Drs. Bob Hulsebosch
Biophysics Department Leiden
Niels Bohrweg 2
2300 RA Leiden
The Netherlands
E-mail: ESR@RULHL1.LEIDENUNIV.NL

Sadlo Jarek
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium

Adri A.K. Klaassen
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: Adri.Klaassen@sci.kun.nl

Dr. Günther **Maresch**
Bruker Institute
Silberstreifen
76287 Rheinsletten
Germany
E-mail: ggm@bruker.de

Dr. Sergiu V. **Nistor**
Institute of Atomic Physics
National Institute of Materials Physics
POB MG 6 Magurele
R-76900 Bucuresti
Romania
Tel.: +40-1-780 5385/1916
Fax: +40-1-4231700
E-mail: snistor@roifa.ifa.ro
snistor@alpha1.infim.ro

Dr. Sergiu V. **Nistor**
Department of Physics
University of Antwerp (UA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202452
Fax: +32-3-8202245
E-mail: nistor@uia.ua.ac.be

Sergei **Pashenko**
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
HOFF@RULHL1.LEIDENUNIV.NL

Marc **Polm**
Department of Molecular Physics
Wageningen Agricultural University
P.O. Box 8128
6700 ET Wageningen
The Netherlands
E-mail: Marc.Polm@foto.mf.wau.nl

Alex **Priem**
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: alexp@sci.kun.nl

Thomas **Prisner**
Institut für Physikalische Chemie der
J.W. Goethe-Universität
Marie-Curie-Strasse 11
60439 Frankfurt/M.
Germany
Tel.: +49-69-798-29449
Fax: +49-69-798-29404
E-mail: prisner@chemie.uni-frankfurt.de

Prof. Iwan **Proskuryakov**
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
pros@biophys.LeidenUniv.nl

Dr. Ramachandra **Rao**
Katholieke Universiteit Leuven
Kardinaal Mercierlaan 92
3001 Heverlee
Belgium

Dr. Ed J. **Reijerse**
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: rey@sci.kun.nl

Kris **Sabbe**
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium
E-mail: Kris.Sabbe@rug.ac.be

Prof. Jan Schmidt
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
E-mail: mat@molphys.LeidenUniv.nl

Prof. Dirk Schoemaker
Department of Physics
University of Antwerp (UIA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202456
Fax: +32-3-8202245
E-mail: schmaker@uia.ua.ac.be

Bart Schoofs
Katholieke Universiteit Leuven
Kardinaal Mercierlaan 92
3001 Heverlee
Belgium
Tel: +32-16-321610
Fax: +32-16-321998
E-mail: bart.schoofs@agr.kuleuven.ac.be

Prof. Robert Schoonheydt
Katholieke Universiteit Leuven
Kardinaal Mercierlaan 92
3001 Heverlee
Belgium
E-mail:
Robert.Schoonheydt@agr.kuleuven.ac.be

Dr. Marianna Stefan
Institute of Atomic Physics
National Institute of Materials Physics
POB MG 6 Magurele
R-76900 Bucuresti
Romania

Wiesiek J. Szweryn
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: wiesiek@scie.kun.nl

Dr. Marianna Stefan
Department of Physics
University of Antwerp (UA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202452
Fax: +32-3-8202245

Ir. Pieter J. van Dam
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: pjvdam@sci.kun.nl

Dr. Dirk Vandenbroucke
Agfa-Gevaert nv
Septestraat 27
6240 Mortsel
E-mail: VDBROUCKE@TWI.AGFA.BE

Eric van der Horst
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: ericvdh@sci.kun.nl

Ankie van Duijn-Arnold
Huygens Laboratory
P.O. Box 9504
2300 RA Leiden
The Netherlands
E-mail: arnold@molphys.LeidenUniv.nl

Gauthier Vanhaelewyn
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium
E-mail: Gauthier.Vanhaelewyn@rug.ac.be

Jouri Van Landeghem
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium
E-mail: jouri.vanlandeghem@rug.ac.be

Dr. Henk Vrielinck
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium
E-mail: Henk.Vrielinck@rug.ac.be

Dr. Bert Weckhuysen
Katholieke Universiteit Leuven
Kardinaal Mercierlaan 92
3001 Heverlee
Belgium
E-mail:
BERT.WECKHUYSEN@AGR.KULEUVEN.
AC.BE

Dr. Paul J.M. van Kan
Department of Physical Chemistry
University of Nijmegen
Toernooiveld 1
6525 ED Nijmegen
The Netherlands
E-mail: vankan@sci.kun.nl

Hans Vercammen
Department of Physics
University of Antwerp (UIA)
Universiteitsplein 1
2610 Wilrijk
Belgium
Tel.: +32-3-8202454
Fax: +32-3-8202245
E-mail: hansver@uia.ua.ac.be

Dr. Stachowicz Waclaw
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium

Dr. Marieta Zdravkova
University of Ghent
Krijgslaan 281-S1
9000 Gent
Belgium
E-mail: Marieta.Zdravkova@rug.ac.be