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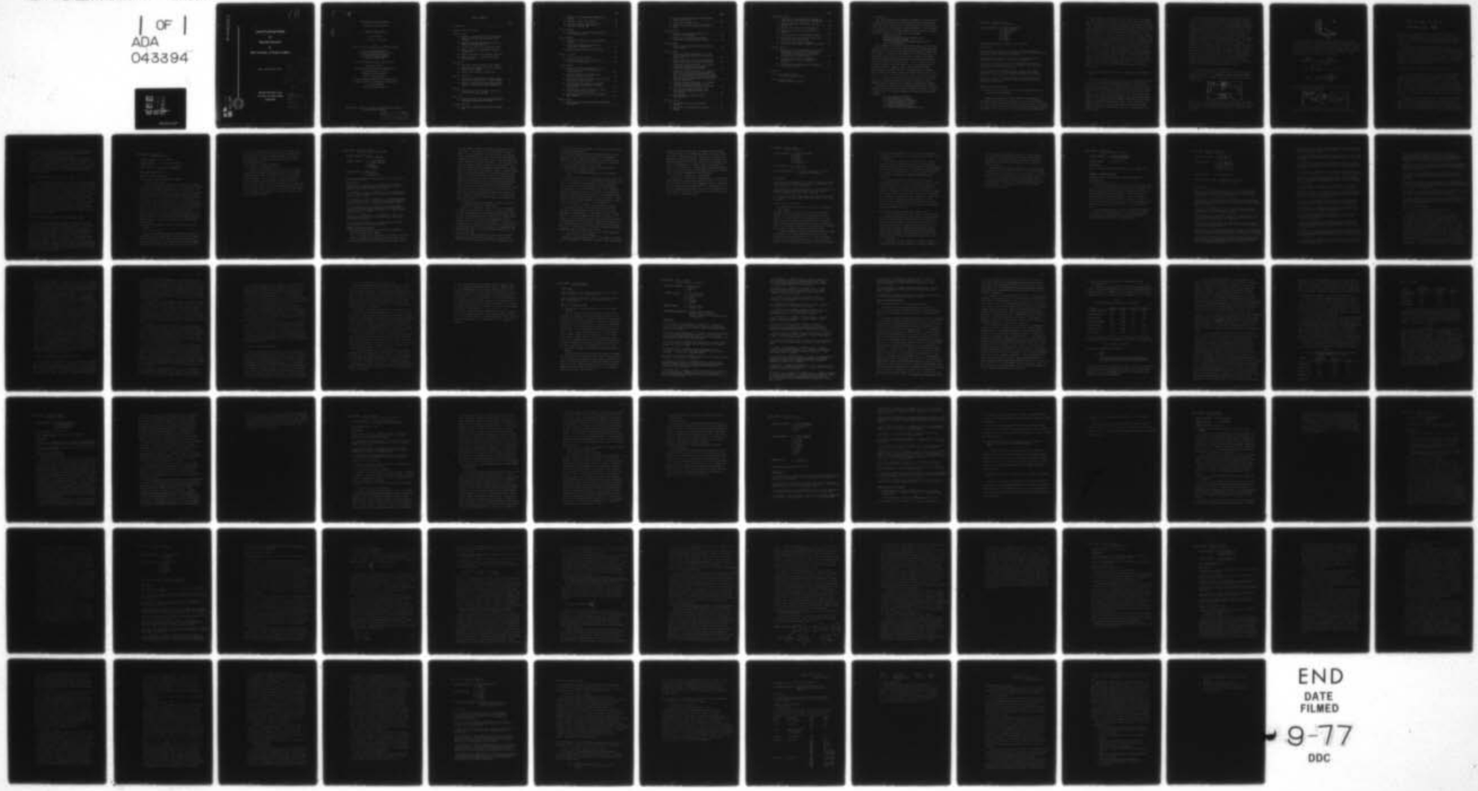

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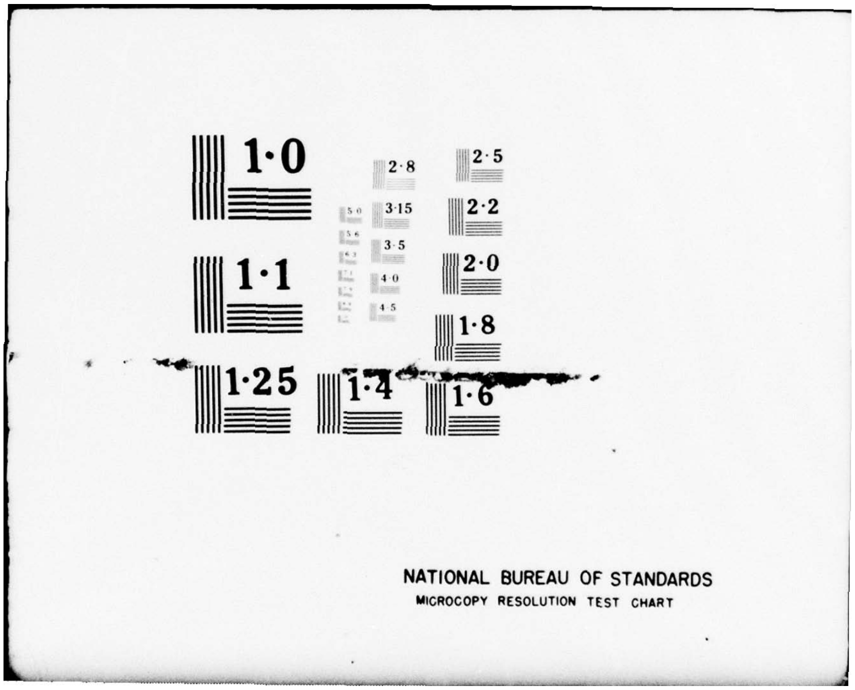
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Materials Research Center
University of North Carolina
Chapel Hill

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THE UNIVERSITY OF NORTH CAROLINA

Chapel Hill, North Carolina

TECHNICAL PROGRESS REPORT

for the period

1 June 1976 - 31 May 1977

on
Research Activities in the Field of Materials Science

with core-support from the
Materials Research Laboratory Section
Division of Materials Research
of the National Science Foundation
under grant DMR 7203024

and with individual project support from the

Army Research Office

National Aeronautics and Space Administration

National Institutes of Health

National Science Foundation

Office of Naval Research

Southern Carolina Department of Natural Resources

U. S. Energy Research and Development Administration

U. S. Gypsum Company

University Research Council

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I. Introduction

This report comprises brief summaries of materials research projects at the University of North Carolina at Chapel Hill for the year ending 31 May 1977. It is submitted to the Materials Research Laboratory Section of the National Science Foundation, Grant DMR 7203024. It also includes descriptions of materials research supported by other agencies, including the following agencies of the United States Government.

Army Research Office
National Aeronautics and Space Administration
National Institute of Health
U. S. Energy Research and Development Administration
Office of Naval Research

The following pages contain brief reports of progress in the various research programs. In cases where work has reached the publication stage, the abstract is often quoted. The summaries are arranged alphabetically by the name of the principal investigator, as it is felt that this is the most probable way in which the report would be consulted. The reader should note, however, that Materials Research at Carolina has been especially encouraged in three unified areas. *Chemically Modified Surfaces* are being developed by different routes but in a collaborative way by Professors Richard C. Jarnagin, Thomas J. Meyer, Earl N. Mitchell, Royce W. Murray and David G. Whitten. Professors William E. Hatfield, Derek J. Hodgson, and Thomas J. Meyer are concerned with *Molecular Design, Synthesis and Characterization of High Conductivity Materials.* *Defects in Ionic Solids* engage the attention of Professors Richard P. Buck, Sang-il Choi, James H. Crawford, David E. Dunn, John P. Hernandez, J. Ross Macdonald, Judith B. Moody, Dietrich Schroeer, and Lawrence M. Slifkin.

This report was prepared by the Materials Research Center of the University which operates the core program of materials research. The Center is administered by an Exeuctive Committee which consists of the following members:

Charles S. Smith, Jr., Director
D. E. Dunn, Professor of Geology
W. E. Hatfield, Professor of Chemistry
J. R. Macdonald, Professor of Physics
T. J. Meyer, Professor of Chemistry
E. N. Mitchell, Professor of Physics
D. F. Taylor, Professor of Operative Dentistry

Faculty Member: Richard P. Buck
Professor of Chemistry

Graduate Students:	
	D.E. Hackleman (MRL-NSF)
	D.E. Mathis (MRL-NSF)
	C.E. Rechsteiner
	T.R. Brumleve
	F.S. Stover
	H.S. Gold
	R.K. Rhodes
	R.R. Walters

Other Supporting Agency: National Science Foundation

Publications:

H.S. Gold, C.E. Rechsteiner, and R.P. Buck, "Generalized Spectral Decomposition Method Applied to Infrared, Ultraviolet, and Atomic Emission Spectroscopy", Anal. Chem., 48, 1540 (1976).

D.E. Mathis and R.P. Buck, "A High Speed Cross Correlator for Broad Band Impedance Measurements", Anal. Chem., 48, 2033 (1976).

R.P. Buck, D.E. Mathis, and R.K. Rhodes, "Impedance Measurements on Purified Silver Chloride Crystals", J. Electroanal. Chem. Interfacial Electrochem., accepted for publication.

C.E. Rechsteiner, D.E. Mathis, M.M. Bursey, and R.P. Buck, "Novel Inexpensive Device for the Electrochemical Generation of Metallic Emitters for Field Desorption", Biomed. Mass Spectrom., 4, 52 (1977).

R.P. Buck, " 'n'-Type Non-Ideality Applied to Acid Errors of Glass Membrane Electrodes", J.Electroanal. Chem. Interfacial Electrochem., accepted for publication.

Summary of Research Activities:

(1) Impedance and Time Constants of Silver Halide Single Crystals and Pressed Pellets (NSF,NSF-MRL)

Impedance measurements are made on purified, vacancy doped and interstitial doped silver bromide crystals of thicknesses from 0.061 cm to 0.260 cm using constant ionic strength solution contacts at temperatures from 20°C to 35°C. Results characterize the macroscopic transport properties from 316KHz to 0.01 Hz and at d.c. In all cases the high frequency limit resistive component of the impedance, R_∞, is equal to the d.c. resistance R_o. This result indicates rapid ion exchange at the surfaces and neither Warburg diffusion nor surface kinetic-limitation of transport. As expected R_∞ is a function of charge carrier concentration, which depends on extrinsic dopant concentration over the temperature range measured. For pure crystals the resistance, R_∞, is linearly dependent on crystal thickness, δ, while thickness correlation could not be tested for the doped crystals as dopant level was not uniform. The geometric capacitance for all crystals, C_g, is linear with δ^{-1}. The dimensionless dielectric constant, κ, calculated from C_g and crystal dimensions, is 13.9 ± 0.7. The electric relaxation time, τ_{el}, defined as the product $R_\infty C_g$, at 25°C is found to be 50 ± 3 μsec for pure crystals, 1 to 4 μsec for the Cd^{2+} doped crystals and 12 to 66 μsec for the S^{2-} doped crystals. Temperature dependence of R_∞ allows determination of crystal transport activation energies. For pure and Cd^{2+} doped crystals a value of 0.33 ± 0.02 eV is found. For the S^{2-} doped crystals values from 0.48 to 0.28 eV are found. The parameter α, in the non- ideal Cole-Cole representation of impedance plane arcs, is 0.96 ± 0.01 for purified crystals, 0.93 ± 0.03 for Cd^{2+} doped, and 0.92 ± 0.02 for S^{2-} doped crystals.

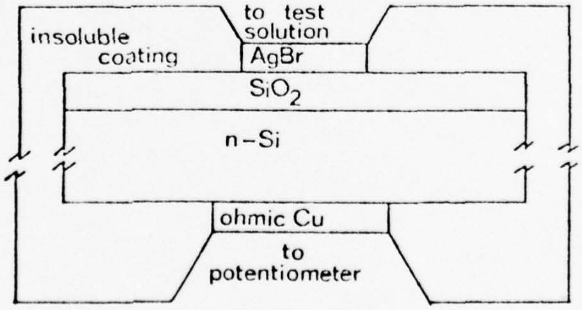
(2) Broad Band Impedance Measurements of Liquid Membrane Cells (NSF-MRL, NSF)

Significant improvement in the band pass of d.c. coupled lock-in detectors used for phase-sensitive impedance measurements has been achieved through the use of state of the art CMOS analog gate-integrated circuits. Instrumentation incorporating an improved detector measures AC cell admittance from 10^{-3} Hz to 1 MHz over an impedance range from 10^2 ohms to 10^{11} ohms (the latter limit being attained only at lower frequencies) thereby eliminating the need for several instruments to span this frequency range. Accuracy of the new instrument above 100KHz was demonstrated by measuring a simple RC circuit and comparing the results to those obtained from a commercial RF bridge. An illustrative application requiring the full frequency range is the kinetic characterization of support materials for liquid membranes.

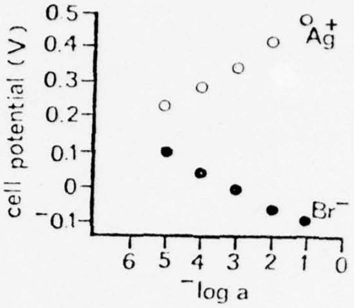
The self-balancing wide-band impedance bridge discussed above has been applied to the study of the electrical properties of a liquid ion exchanger. The Aliquat-3365-nitrate (a quaternary ammonium salt)/nitrobenzene ion exchanger used in nitrate selective electrodes was studied to elucidate the mechanistics of transport in these electrodes. Bulk resistances and geometric capacitances were measured as a function of frequency for varying temperatures and exchanger ion concentrations enabling the calculation of the following parameters: E_a (the transport activation barrier), K_F (the ion pair formation constant), ε (the bulk dielectric constant) and ΔG, ΔH and ΔS for ion pair formation. The influence of trace amounts of water in the liquid exchanger phase on these parameters has been investigated and was shown to decrease κ_F but not affect transport activation barriers. In addition, incorporation of the ion exchanger into polymeric matrices such as PVC has no measurable effect on the transport properties and it was demonstrated that such electrode membrane supports act largely as a matrix for voids which contain the exchanger. This work is currently in the final stages and will be written up and submitted for publication shortly.

(3) Ion Selective Field Effect Transistors (NSF)

Through vacuum deposition of 100 nm layers of AgBr on thin silicon dioxide films (5 nm - 1.3 μm) prepared on silicon substrates through thermal oxidization, a "sandwich" $Si|SiO_2|AgBr$ ion-sensitive electrode has been prepared.



The analysis of over 200 preparations of these devices has shown them to provide stable, rapid-response potentiometric relationships for component ion activities in aqueous solutions, referenced to a saturated calomel electrode.



Limiting high d.c. impedances, from impedance-frequency responses, and external charge-activity measurements, indicate a displacement current (field effect) as the probable cause of electrochemical response. Implications of the mechanism (invoking Volta potential arguments) on the process of potential generation and potential communication shall be analyzed diagramatically and theoretically. For the cell:

(left) (right)

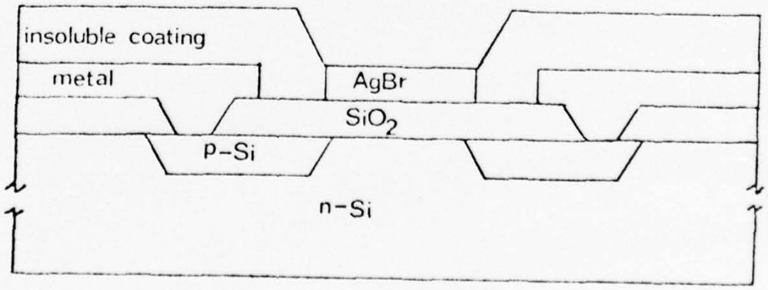
Cu|reference|Test Solution|AgBr|SiO_2|Si|Cu

$$\Delta V = \phi^{right} - \phi^{left} ;$$

$$= -\alpha_e^{Si} + \alpha_e^{Ag} + \phi_{Ag|Ag^+} + \Delta\phi_J - \Delta\phi_{ref}, \text{ where}$$

$$\phi_{Ag|Ag^+} = \phi^\circ_{Ag\ Ag^+} + \frac{RT}{F} \ln \left(\frac{a^{left}_{Ag^+}}{a^{right}_{Ag^+}} \right)$$

The extension of these principles to devices of the form (Ion Selective Field Effect Transistors)



is straightforward, and leads to a current response (in the unsaturated mode of

$$I \propto V_G - V_T + \phi'_{Ag|Ag^+} - \Delta\Delta\phi_J - \frac{V_D}{2} \quad ; \text{ or}$$

$$I \propto (\text{constant}) + \phi_{Ag|Ag^+} - \phi^{\text{min}}_{Ag|Ag^+} \quad .$$

for constant V_G (external bias) and V_D (drain-source voltage). The threshold potential, $\phi^{\text{min}}_{Ag|Ag^+}$, necessary to initiate channel conduction is alterable by changing V_G, hence the threshold concentration of component ion necessary in solution to initiate conduction in the ISFET is externally alterable.

By changing the selective material deposited on the SiO_2, most currently available ion selective electrodes can be made both less perturbing to the observed system and extremely small in size. Present technology allows for the manufacture of these devices on the order of tens of microns in diameter. The rapid response, due to their operation by a field effect, combined with small physical size and less perturbation, leads to a microelectrode alternative to current practices.

(4) Noise Analysis of Electrochemical Systems (NSF-MRL,NSF)

The electronic measurement system for characterizing the frequency spectrum of electrochemical noise has been modified by the addition of impedance converting voltage follower amplifiers at the input of the system through the use of battery power. This was necessary in order to remove the damping effect of the coaxial cables attached to the experimental cell. Initial studies of resistor noise has left several questions unanswered, as the observations and theory of expected results do not yet correspond well. Theoretical analysis of these problems is one area of main interest.

The modification of software in order to allow the system to record data sequentially on magnetic tape, and to allow FORTRAN to utilize the magnetic tapes on the in-house Raytheon 706 computer has provided a system which is as fast in data handling capabilities as the IBM 360 system previously used for the correlation analysis. Comparison of FFT and standard

Fourier transform techniques is in progress, with the current feeling that the FFT may provide less information than the standard Fourier analysis due to the binary nature of its operation.

The construction of a water-jacketed cell housing and associated components has been completed, and with the system now functional, it is expected that experimental results on actual chemical systems are in order. The necessity of determining exactly what the system response is without a chemical system included is not to be overlooked, and this study is currently in progress.

(5) Computer Treatment of Spectroscopic Data (NSF)

A generalized algorithm for symmetric and asymmetric Gaussian deconvolution of spectral data is presented. Quantitative and qualitative applications in infrared, ultraviolet, and atomic emission spectroscopy are outlined in terms of general utility. The limitations and scope of curve fitting in general, and with regard to the current algorithm, are considered. For frequently encountered situations, use of Gaussian and bi-Gaussian parameters is shown to result in sufficient computational accuracy. For the first time, computerized deconvolution is used to improve the apparent resolution in atomic spectroscopy. Deconvolution of weak interligand transfer bands in near infrared spectra of ruthenium dimers is reported. Electronic spectra of a series of ruthenium bis- bipy complexes have been deconvoluted and interpreted.

(6) Digital Simulation of Liquid Ion-Exchange Membranes (NSF)

Results of digital simulation of partially associated liquid ion-exchange membranes with varying site mobility are presented. The membrane is assumed to be ideally permselective and completely electroneutral. The bathing solutions correspond to the biionic case with one complexing and one non-complexing counterion. Selectivity toward the associated counterion, as computed from biionic potentials, is compared with changes in the site and complex mobility. The decrease in the selectivity with decreasing site mobility is found to arise from changes in both interfacial and diffusional potential components. Examination of concentration profiles and internal electric field strengths leads to descriptions of the process by which the selectivity is altered.

Faculty Member: Sang-il Choi
Professor of Physics

Research Associate: W. M. Lee (NSF)

Graduate Student: F. N. Sonnichsen (MRL-NSF)

Degrees Granted: W. M. Lee, Ph.D. (Chemistry)
T. Takeuchi, Ph.D. (MRL-NSF)

Other Supporting Agency: NSF

Summary of Research Activities:

(1) Superionic Conductor, $RbAg_4I_5$; NSF, MRL-NSF
T. Takeuchi and S. Choi

In order to understand the dynamics of the cation Ag^+ in $RbAg_4I_5$, we calculated the potential energy curves of a Ag^+ ion along the paths connecting the crystallographically non-equivalent Ag^+ sites. The crystal structure by S. Geller was used and the energy terms included were Ewald coulomb energy, Born-Mayer repulsive energy, and polarization energy. In total 125 unit cells were considered and Rb^+ and I^- ions were assumed to form rigid lattices. It was found that the most probable paths for Ag^+ ion diffusion are along the path connecting Ag(I) and Ag(II) and along the path connecting Ag(II) and Ag(III). It was also found that the smallest energy barrier is about 0.1 eV, which is very close to the value experimentally obtained by G. G. Bentle. Using the energy curves, vibrational frequencies were estimated and found to be in reasonable agreement with Raman frequencies reported by others. This work was reported at the APS-Washington meeting (1977).

(2) Adsorption and Transport of Ions on β-Alumina Surfaces; NSF, MRL-NSF
W. M. Lee and S. Choi

Although a considerable progress in understanding of large ionic conductivity in beta-alumina single crystals has been made, adsorption and transport of ions on crystal surfaces has not received much attention. For the purpose of understanding such surface pehnomena, potential energy of ions at some sites and along lines connecting such sites on beta-alumina crystal surfaces are calculated. The calculation is strictly classical and includes Coulomb potential energy, polarization energy and repulsive energy. This work is still in progress. Partial results were reported at the APS-San Diego meeting (1977).

(3) Mixed Cation β-Aluminas; NSF-MRL-NSF

J. C. Wang, D. F. Picket, and S. Choi

A calculation method similar to the one used by us for "pure" β-aluminas has been applied to study the effects of K^+ and doubly charged impurities such as Sr^{2+} and Zn^{2+} on the ionic conduction in Na beta-alumina. It is shown that all these ions prefer to occupy Beevers-Ross sites alone, and the conductivities are expected to be lower than that of the pure material in all these cases. The extra energy needed for a K^+ ion to form a pair with a Na^+ ion, instead of being alone, is about 0.09 eV. The case of a Na^+ impurity in K beta-alumina is also analyzed. This work was reported at the APS-San Diego meeting (1977).

Faculty Member: James H. Crawford, Jr.
Professor of Physics and Chairman

Research Associates: Q. Kim
K. H. Lee (MRL-NSF)

Graduate Students: F. J. James (MRL-NSF)
G. S. White (MRL-NSF)
H. Berger
D. Eisenberg
G. E. Matthews

Degrees Granted: H. Berger, M.S.
F. J. James, M.S.
G. E. Matthews, Ph.D.

Other Supporting Agencies: ERDA and University Research Council

Publications:

M. Ikeya and J. H. Crawford, Jr., "Recombination Luminescence in Alkali Halides Doped with Monovalent Cations, $(V_k + e)_A$-Type Emission," Phys. Stat. Sol. (b), 79, 559 (1977).

G. E. Matthews, Jr. and J. H. Crawford, Jr., "Ionic-Thermocurrent Study of the Dipole Relaxation and Equilibrium in Gd-Doped SrF_2," Phys. Rev. B15, 55 (1977).

J. H. Crawford, Jr. and G. E. Matthews, Jr., "Equilibrium between Type I and Type II M^{3+}-F_i^- Complexes in Alkaline Earth Fluorides," Accepted for publication in J. de Physique, Colloque C7, 1977.

J. H. Crawford, Jr. and G. E. Matthews, Jr., "A Defect Model to Account for Non-Locally Compensated Trivalent Rare Earth Ions in Fluorite Crystals," Accepted for publication in J. Semiconductors and Insulators, Vol. 1, 1977.

K. H. Lee, G. E. Holmberg and J. H. Crawford, Jr., "Optical and ESR Studies of Hole Centers in γ-Irradiated Al_2O_3," Phys. Stat. Sol. (a) 39, 669 (1977).

K. H. Lee and J. H. Crawford, Jr., "Electron Centers in Single-Crystal Al_2O_3," Phys. Rev. B15, 4065 (1977).

Summary of Research Activities:

(1) The Structure and Stability of Impurity-Defect Complexes in Alkaline Earth Fluorides; USERDA.

A. G. E. Matthews, Jr.: Configurations of Dipoles in SrF_2:Gd^{3+}.

From the assumption that equilibration between nearest (Type I) and next-neighbor (Type II) M^{3+}-F_i^- dipoles occurs without loss of the total number of dipoles, the ratio of dipole moments can be calculated. It was found that the ratio of Type II to Type I moments is 2.4 as compared to 1.73 expected from the unrelaxed point ion configuration. This ratio has recently been confirmed by Sherstkov and co-workers [Soviet Physics, Solid State 18, 1526 (1977)] using field perturbed ESR methods. It was also found that the Type II dipole stability increases with increasing M^{3+} ionic radius in agreement with the prediction and ESR evidence of Brown et al. [J. Chem. Phys. 50, 891 (1969)]. Finally, a careful examination of the ratio of area under the thermal depolarization (ITC) peak for Type I dipoles in CaF_2 to that for the peak previously thought to be Type II as a function of equilibration temperature reveals that these peaks are not in thermal equilibrium with each other. Also the ratio of their areas is not systematically influenced by the ionic radii of the M^{3+} as was found for SrF_2. These facts together with the observation that the area under the so-called Type II peak in CaF_2 increases greater than linearly with M^{3+} concentration all indicate that in CaF_2 it is not associated with a next-nearest M^{3+}-F_i^- dipole but rather with some more complex dipolar cluster.

B. H. Berger, Q. Kim, G. E. Matthews: Destruction of Defects in CaF_2:M^{3+} and CaF_2:M^{3+} Doped with H^-.

Exposure to γ-radiation in a 10^4 Ci ^{137}Cs source is observed to change the concentration of a variety of dipoles in CaF_2:M^{3+}. The Type I relaxation peak first increases in area and then slowly declines as would be expected as isolated M^{3+} first capture mobile H-centers to form M^{3+}-F_i^- dipoles and subsequently as M^{3+}-F_i^- dipoles capture F^- vacancies to form isolated M^{3+}. The defects responsible for the so-called Type II peak are more strongly affected by irradiation and the initial concentration is restored only upon annealing above 360K. In crystals doped with both M^{3+} and H^- two effects are observed.

(a) The M^{3+}-H_i^- complex analogous to the Type I dipole decreases drastically with irradiation which supports the view that the M^{3+}-H_i^- captures an F^- vacancy created by the irradiation to form a $M^{3+}-H_s^-$ complex with C_{3v} symmetry. This defect has been detected by infra-red spectroscopy.

(b) The $M^{3+}-F_i^-$ dipole concentration also decreases and at a rate much greater than observed in the crystals not containing H^-. Again this is due to the copious supply of F^- vacancies produced by the action of radiation on the substitutional H^- to form vacancies and interstitial H atoms or H_2 molecules.

(2) Radiation Damage, Defects and Defect-Impurity Complexes in Refractory Oxides, MRL-NSF and URC.

A. K. H. Lee: Recombination Luminescence in X-Irradiated MgO.

Exposure of MgO to x-rays at 90K produces two luminescence bands, one at 5.1 eV and one at 3.3 eV. Preirradiation at room temperature, such as to develop the V-band absorption, strongly enhances the 5.1 eV emission at 90K. The enhancement decays upon standing at room temperature in at least two stages and the first stage has a half-life comparable to that of the V_{OH} center at room temperature. Introducing deep electron trapping centers by either impurity addition or deformation strongly attenuates the 5.1 eV emission. These results are consistent with emission resulting from electron capture at holes on V-type centers, i.e. $O^- + e^-$ recombination.

B. K. H. Lee and F. J. James: Electron Centers in Al_2O_3.

Studies have been made of the thermal stability and optical bleaching of absorption bands in Al_2O_3 produced by fast neutron bombardment in the NCSU reactor. Irradiation into the 6.1 eV band causes it to decrease in amplitude and enhances the bands at 5.4, 4.8 and 4.1 eV. Excitation into these latter bands causes bleaching of them and growth of the 6.1 eV band. Polarization of emission at 3.75 eV induced by 4.8 eV excitation is consistent with the assignment of the 4.8 eV band to the F^+ center and other evidence supports assignment of the 6.1 eV band to the F center.

C. G. S. White, W. D. Key, and K. H. Lee: Thermal Stimulated Conductivity in Al_2O_3 and $MgAl_2O_4$.

Exposure of Al_2O_3 and $MgAl_2O_4$ to ^{137}Cs γ-rays results in TSC peaks at several temperatures. In unoxidized crystals of MgO two peaks are observed at 130°C and 214°C, where as oxidized crystals (1200°C for several hours in air) exhibit four peaks (112°C, 130°C, 158°C and 214°C). Previous work in this laboratory has associated these peaks with V^-, $V^=$ and V^-_{OH} centers. Quantitative correlation of the absorption amplitudes of the V-type bands with the conductivity has led to the determination of the lower limit of hole mobility in Al_2O_3: $\mu_h \geq 10^{-3} cm^2$/volt sec. $MgAl_2O_4$ exhibits similar TSC behavior and a very strong TSC peak at 70°C overlaps room temperature producing a long-lived room temperature radio-conductivity.

D. K. H. Lee: Irradiation of Ga Doped MgO.

Gallium enters the MgO lattice substitutionally in the trivalent state. Exposure to γ-rays produces absorption bands at 4.15 eV and 3.32 eV and also results in a new paramagnetic defect as revealed by ESR. The ESR signal arises from a Ga^{2+} in an octahedral site. Optical and thermal bleaching indicate that the 3.3 eV band is associated with Ga^{2+} and the 4.15 eV band is due to the Ga^{1+} which have been reduced by the radiation field.

Faculty Member: David E. Dunn
Professor of Geology

Graduate Students:
- J. D. Dunning (NSF-MRL)
- M. K. Carr
- M. Donaldson
- W. L. Huf
- W. L. Lewis
- N. Muangnoicharoen

Degrees Granted:
- W. L. Huf, M.S.
- W. L. Lewis, Ph.D.

Other Supporting Agencies: Southern Carolina Dept. of Natural Resources, U.S. Gypsum Co.

Publications:

L. W. Lewis and D. E. Dunn, "Effect of Aqueous Surfactants on Crack Propagation Rate in Orthoquartzite," Geol. Soc. America, Abstracts with Programs, v. 8, n. 7, p. 978 (1976).

S. A. Moller and D. E. Dunn, "Constraints on Time of Paleozoic Plate Collision, Southern Appalachian Orogen," Geol. Soc. America, Abstracts with Programs, v. 9, n. 2, p. 168 (1977).

D. E. Dunn and W. L. Huf, "Reduced Tensile Strength of Orthoquartzite at Zero Zeta-Potential," EOS, Trans. Amer. Geophys. Un., v. 58, n. 6, (1977).

Summary of Research Activities:

Environment-Sensitive Fracture Processes in Polycrystalline SiO_2; NSF-MRL.

Rehbinder's hypothesis of reduced surface-free-energy causing reduction in fracture strength has been examined in two very different experimental modes. The experimental data, for shear failure in biaxial compression (Lewis and Dunn) and for tensile failure in hydrofracturing (Dunn and Huf), show no correlation with surface free energy but a significant correlation with zeta-potential. There follows the abstract cited above by Lewis and Dunn.

Cylindrical samples of Crab Orchard Sandstone (Pottsville Group of Pennsylvanian age) having approximately 5% porosity were saturated with various concentrations of the cationic detergent, dodecyl trimethyl ammonium bromide (DTAB), resulting in positive, negative, and zero ζ-potentials. Comparison samples were saturated with distilled deionized water (ζ=-32), the anionic surfactant sodium dodecyl sulfate (SDS, ζ=-41), nonionic Triton X-100 (ζ=-30), and ambient air.

All tests were conducted at a constant effective confining pressure of 0.5 kb, room temperature, and a static axial load equivalent to 94% of the dry or saturated brittle fracture strength, well above the onset of dilatancy. The dependent variable measured was the time, from imposition of static load, required for microcrack growth and coalescence to produce through-going shear fractures.

Dry samples supported the load more than two orders of magnitude longer than any of those saturated with liquids. Samples saturated with DTAB at ζ=0 failed 44% to 49% sooner than water saturated samples. Failure time is inversely proportional to negative ζ, regardless of liquid (H_2O, SDS, Triton X-100, and DTAB). This result correlates with Westwood's concept that ζ=0 should produce maximum brittlization, but not with Rehbinder's concept that increased solution concentration lowers surface free energy. Positive ζ values (DTAB only) resulted in erratic failure times, all of which were greater than ζ=0, and apparently fit neither the Westwood or Rehbinder theories.

There follows the abstract cited above by Dunn and Huf.

Fifty-seven thick walled, hollow cylinders of orthoquartzite were hydrofractured under static axial load and confining pressure of 850 and 250 bars (85 and 25 MPa), respectively, simulating a depth of burial of 4000m for rock with a Poisson's ratio ≈ 0.3. Pressurization rate of the hydrofracturing fluid was 11 bars s^{-1}, and the fluids used were distilled de-ionized water or various concentrations of dodecyl trimethyl ammonium bromide (DTAB) in dilute aqueous solution. Zeta-potentials (ζ) for fluids varied between -40mv (10^{-5}N DTAB) and +60mv (10^{-2}N DTAB), with ζ=0 at 2.5×10^{-4}N DTAB.

Hydrofracture "tensile strength" was calculated from the pressure data and the sample dimensions, assuming no penetration of the fluid into the sample. The validity of this assumption was verified by nineteen diametral tests which yielded a tensile strength only 3.6% greater than the hydrofracture calculation, a difference which is within one standard error of the mean for the data involved.

Mean hydrofracture "tensile strengths" for all fluids having $\zeta \neq 0$ show no significant variation; but at $\zeta = 0$ the tensile strength is reduced 58%. A two-tailed test of the distribution of the means yields a probability >99.9% that the tensile strength reduction at $\zeta = 0$ is real. These results tend to confirm Westwood's theory of chemo-mechanical weakening at $\zeta = 0$ rather than Rehbinder's surface free energy theory. A commercial application in jet-cutting technology may be feasible.

Faculty Member: Kian S. Dy
Associate Professor of Physics

Graduate Students: J. F. Lancaster (MRL-NSF)
T. L. Spratlin (MRL-NSF)

Degrees Granted: J. F. Lancaster, Ph.D.

Publications:

K. S. Dy, "Generalized Friedel Sum Rule," accepted by Phys. Stat. Sol.

Summary of Research Activities:

Bond-Orbital Model for Disordered Tetrahedrally-Coordinated Semiconductors;

James Lancaster and K. S. Dy

A set of closed-form expressions for the electronic energy eigenvalues of Group IV semiconductors is derived. These expressions are valid for any tetrahedral network with six-membered rings only. The model Hamiltonian used is a variation of the bond-orbital model of Harrison and where tetrahedral clusters of bonds are treated as units and nearest-cluster interactions are taken into account. The results show that the band structure and its pressure dependence can be explained quite well in this model with only a few matrix elements.

We also consider the effect of Group IV substitutional impurities on the energy level distribution. In the bond-orbital model, the problem can be reduced into an effective Hamiltonian model, where the band structure effect are included exactly.

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Publications:

E.D. Estes, R.P. Scaringe, W.E. Hatfield, and D.J. Hodgson, "Synthesis and Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimer Di-μ-methoxo-bis[bis(3-chloro-2,4-pentanedionato) chromium(III)", Inorg. Chem., 15, 1179 (1976).

V.T. Kalinnikov, Y.V. Rakitin, V.H. Crawford, and W.E. Hatfield, "Near One-Dimensional Antiferromagnetism in Oxovanadium Carboxylates $VO(OOCR)_2$", American Institute of Physics Conference Proceedings, H.C. Wolfe, Editor, Number 34, 205 (1976).

D.B. Losee, K.T. McGregor, W.E. Estes, and W.E. Hatfield, "1,3-Propanediammonium Tetrachloromanganate(II); A canted Quasi Two-Dimensional Antiferromagnet", Phys. Rev., B14, 4100 (1976).

H.W. Richardson, J.R. Wasson, W.E. Hatfield, E.V. Brown, and A.C. Plasz, "Spectral and Magnetic Properties of Copper(II) 1,5-Naphthyridine-1,5-Dioxide Complexes", Inorg. Chem., 15, 2916 (1976).

H.W. Richardson, J.R. Wasson, and W.E. Hatfield, "Spectral and Magnetic Properties of Copper(II) Furoate and Copper(II) Thiophene-2-carboxylate", J. Mol. Structure, 35, 83 (1977).

D.W. Phelps, D.B. Losee, W.E. Hatfield, and D.J. Hodgson, "Two-Dimensional Magnetic Systems: The Structural and Magnetic Characterization of Bis(propylene-1,3-diammonium) Tetrachlorocuprate(II)", Inorg. Chem., 15, 3147 (1976).

R.P. Scaringe, W.E. Hatfield, and D.J. Hodgson, "Magnetic and Structural Characterization of the Chromium(III) Dimer Sodium Di-μ-hydroxobis[bis-(oxolato)chromate(III)] Hexahydrate, $Na_4[Cr(C_2O_4)_2OH]_2 \cdot 6H_2O$", Inorg. Chim Acta, (Accepted for publication).

H.W. Richardson, J.R. Wasson, and W.E. Hatfield, "On the Superexchange Mechanism in Polymeric Diamine-Bridged Copper(II) Complexes. Part II.", Inorg. Chem., 16, 484 (1977).

J.R. Wasson, J.W. Hall, H.W. Richardson, and W.E. Hatfield, "Imidazolium, Nicotinium, and Quinidinium Tetrachlorocuprates(II)", Inorg. Chem., 16, 458 (1977).

J.R. Wasson, H.W. Richardson, and W.E. Hatfield, "Magnetic Properties of Linear Chain Compounds: Copper(II) Complexes with 2-(o-hydroxyphenyl)-benzoxazole and -benzothiazole", J. Inorg. Nucl. Chem., (accepted for publication).

V.H. Crawford, W.E. Hatfield, and R.E. Tapscott, "Magnetic Studies of Vanadyl(IV) Tartrate Dimers", J. Mol. Structure, (accepted for publication).

R.F. Drake, R.P. Scaringe, D.J. Hodgson, and W.E. Hatfield, "Magnetic Studies on the Nitrate and Bromide Salts of the Cation Di-μ-hydroxobis-[di(1,10-phenanthroline)chromium(III)]$^{4+}$", Inorg. Chim, Acta, (accepted for publication).

V.H. Crawford and W.E. Hatfield, "Magnetic Properties of $Na_2[Cu(d,l\text{-}tartrate)]_2 \cdot 10H_2O$", J. Mol. Structure, (accepted for publication).

H.W. Richardson, J.R. Wasson, W.E. Estes, and W.E. Hatfield, "Spectral and Magnetic Properties of Linear-Chain Aminoacid Complexes of Copper(II)-Bis(d,l-α-aminobutyrato)- and Bis(l-asparaginato)copper(II)", Inorg. Chim. Acta, (accepted for publication).

J.W. Hall, W.E. Estes,E.D. Estes, R.P. Scaringe, and W.E. Hatfield, "The Magnetic Susceptibility of the Chloro(2-diethylaminoethanolato)-copper(II) Tetramer", Inorg. Chem., (accepted for publication).

W.E. Hatfield, H.W. Richardson, and J.R. Wasson, "Unexpectedly Large Spin-Spin Coupling in a Sulfur Bridged Copper(II) Compound", Inorg. Nucl. Chem. Letters, (accepted for publication).

V.H. Crawford and W.E. Hatfield, "Exchange Interactions in Halide-Braidged Chains of Copper(II), $Cu(R\text{-}pyridine)_2X_2$", Inorg. Chem., (accepted for publication).

J.R. Wasson, D.M. Klassen, H.W. Richardson, and W.E. Hatfield, "Low Symmetry Copper(II) Complexes: Spectral Properties of Dihalo-2,6-di(2'-quinolyl)pyridine copper(II) Complexes", Inorg. Chem., (accepted for publication).

D.B. Brown, J.W. Hall, M.F. Scott, and W.E. Hatfield, "Magnetic Exchange Interaction in the Chloro-Bridged Copper(II) Complex, N,N,N',N'-tetramethylethylenediammonium Hexachlorodicuprate(II)", Inorg. Chem.,(accepted for publication).

J.R. Wasson, H.W. Richardson, and W.E. Hatfield, "Electronic Structure of Pseudotetrahedral Copper(II) Schiff Base Complexes, Z. Naturforsch., (accepted for publication).

E.D. Estes, R.P. Scaringe, W.E. Hatfield, and D.J. Hodgson, "The Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimers Di-μ-Methoxy-bis[bis(3-bromo-2,4-pentanedionato)-chromium(III)] and Di-μ-Ethoxy-bis[bis(3-bromo-2,4-pentanedionato)-chromium(III)]", Inorg. Chem., (accepted for publication).

S.J. Cline, R.P. Scaringe, W.E. Hatfield, and D.J. Hodgson, "Structural and Magnetic Properties of Di-μ-hydroxobis[bis(ethylenediamine)chromium-(III)] Dithionate, $[Cr(en)_2OH]_2(S_2O_6)_2$", J. Chem. Soc., Dalton Trans., (accepted for publication).

Yu. V. Rakitin, V.T. Kalinnikov, and W.E. Hatfield, "Magnetic and Thermodynamic Properties of Heisenberg Open Finite Chains. I. Susceptibility in Zero Field", Phys. Status Solidi (b), (accepted for publication).

R.P. Scaringe, W.E. Hatfield, and D.J.Hodgson, "A Ferromagnetically-coupled Chromium(III) Dimer: Synthesis, Structure and Magnetic Properties of Sodium Di-μ-hydroxobis[bis(malonato)chromate(III)] Pentahydrate, Inorg. Chem., (accepted for publication).

Yu. V. Rakitin, V.T. Kalinnikov, and W.E. Hatfield, "Magnetic and Thermodynamic Properties of Heisenberg Open Finite Chains: II. Specific Heat", Phys. Status Solidi (b), (accepted for publication).

D.B. Brown, V.H. Crawford, J.W. Hall, and W.E. Hatfield, "Standards for Magnetic Measurements: A Comparison and a Proposal for the Use of Tetramethylethylenediammonium Tetrachlorocuprate(II)", J. Phys. Chem., (accepted for publication).

Summary of Research Activities:

(1) Studies on Two-Dimensional Compounds (NSF-MRL,NSF)

The magnetic susceptibilities of single crystals of 1,3-propanediammonium tetrachloromanganate(II), $(NH_2CH_2CH_2CH_2NH_3)MnCl_4$, have been measured from 4.2 to 220°K. High-field magnetization measurements below the transition temperature are reported. In moderate magnetic fields, the material undergoes a transition to an antiferromagnetic state at $T_N = 43.6°K$ with the b axis being the preferred axis. Near-zero-field susceptibility measurements below T_N reveal a more complex behavior suggestive of a canted spin system since net moments are observed along the b and c axes. High-field magnetization measurements along the preferred axis reveal a spin-flop transition at $H_{SF} = 24.2$ kOe. The data below T_N can be qualitatively accounted for by considering a model based on Dzyaloshinsky-Moriya interactions being included in the Hamiltonian. A plausible arrangement of the sublattice moments is suggested based on the known crystal structure. Above 50°K the susceptibilities are isotropic and reflect the quasi-two-dimensional nature of the complex. Analysis of the high-temperature series expansions reveals the intralayer exchange constant to be $|J/k| = 4.6$ K.

The crystal structure and magnetic properties of the compound bis(propylene-1,3-diammonium) tetrachlorocuprate, $[H_3NC_3H_6NH_3]CuCl_4$, have been determined. The material crystallizes in the orthorhombic space group Pnma($D_{2h}{}^{16}$) with four formula units in a cell of dimensions a = 7.200 (2), b = 18.246(6), and c = 7.451 (2) Å. Least-squares refinement of 1209 independent reflections has led to a final R factor (on F) of 0.036. The structure consists of tetragonally distorted $[CuCl_6]^{2-}$ units which are chlorobridged to form a two-dimensional layer. Within the two-dimensional network there are two short copper-chloride bond distances of 2.275 (4) Å and two long Cu-Cl distances of 2.946 (4) Å. There are two copper-chloride bonds nearly perpendicular to the bridged network with distances of 2.314 (4) Å. The intralayer bond angles at copper are 87.70 (2) and 92.30 (2)° with the Cu-Cl-Cu bridging angle being 165.70 (4)°. The chlorocuprate sheet is puckered as a result of hydrogen bonding to the propylene-1,3-diammonium ions which lie between the layers. Magnetic susceptibility data collected on powdered and single-crystal samples revealed two-dimensional magnetic interactions with J/k = 15.4 K above the three-dimensional ordering temperature of 13.5 K. In the ordered state the preferred direction of the spins is along c (perhaps with some canting) with the next preferred direction apparently perpendicular to the layer. This unusual result reflects the small interlayer separation of 9.123 (3) Å.

2. Studies on One-Dimensional Compounds (NSF,NSF-MRL)

The spin levels, the dependencies of the effective magnetic moments μ_{eff}, and the spin specific heat C_m as functions of kT/J for open linear Heisenberg chains with individual ion spins S_i of 1/2 to 5/2 and length $N \leq 11$ have been calculated. A comparison of the results with other well known models has been made. The magnetic susceptibility and EPR spectra of oxovanadium carboxylates $VO(OOCR)_2$ ($R = CH_3$, CH_2Cl, $CHCl_2$, CCl_3, $C(CH_3)_3$, C_2H_5, C_3H_7, C_4H_9, and C_6H_{13}) have been studied, and the data have been interpreted in terms of the calculations. The results suggest that the chains contain approximately 50 monomeric subunits. The magnetic susceptibility data for all the compounds are consistent with the Heisenberg model for antiferromagnetic linear chains with a small antiferromagnetic interchain interaction and the presence of a small amount of monomeric impurities.

The di-N-oxide of 1,5-naphthyridine has been prepared and coordination compounds with copper(II) chloride, bromide, and nitrate have been prepared. Infrared, electronic, and electron paramagnetic resonance spectroscopies have been used to determine the binding properties of the ligand and anions. Magnetic susceptibilities support antiferromagnetic exchange through the extended π system of the heterocyclic ligand. The magnetic data can be fit to the isotropic Heisenberg model for linear chains with $S = 1/2$ coupled magnetic ions with $J \simeq -3.5\ cm^{-1}$ in all three complexes.

The magnetic susceptibility behavior of the copper(II) complexes of 2-(o-hydroxyphenyl)benzoxazole and 2-(o-hydroxyphenyl)benzothiazole has been examined over the temperature range 2-77°K. Despite established linear chain structure both complexes exhibit negligible spin exchange coupling. The present work provides additional support of an earlier conclusion that out-of-plane copper-oxygen distances of 2.8Å or greater are too long to transmit spin-spin interactions.

The electronic structures of the linear-chain aminoacid complexes, bis(ℓ-asparaginato)copper(II), $Cu(aspg)_2$, and bis(d,ℓ-α-aminobutyrato)-copper(II), $Cu(aba)_2$, have been elucidated using variable temperature magnetic susceptibility measurements and electronic and electron paramagnetic resonance (EPR) spectroscopy. Despite established linear chain structures, no evidence was found for metal-metal spin exchange coupling to 1.8°K. EPR spectra demonstrated that metal-ligand covalency is minimal. The g- and hyperfine anisotropy of copper(II)-doped $Cd(aspg)_2$ were completely resolved.

The magnetic and spectral properties of a series of substituted pyridine complexes of copper(II) chloride and of copper(II) bromide have been determined. The bases used include 3-methyl-, 3-ethyl-, 4-methyl-

4-ethyl-, and 4-vinyl pyridine. All compounds except Cu(4-methylpyridine)$_2$Cl$_2$ exhibit Heisenberg chain-like magnetic behavior with the exchange integrals for the bromo complexes being approximately twice that observed for the chloro complexes. The J values ranged from -22.3 cm^{-1} for Cu(3-ethylpyridine)$_2$Br$_2$ to -6.7 cm^{-1} for Cu(4-ethylpyridine)$_2$Cl$_2$ may be interpreted in terms of an laternating chain model with the ratio of the exchange coupling constants for a given copper(II) ion with its two nearest neighbors in the chain being 0.6.

Calculations of spin levels and effective magnetic moments as functions of reduced temperature, $\mu_{eff}(kT/J)$, have been carried out for Heisenberg open finite chains with ion spins of 1/2 to 5/2 containing up to 11 subunits ($N \leq 11$). Some relationships useful in interpretation of experimental results are considered. A detailed comparison of the results with literature data is given.

Calculations of spin specific heat, C_M', as a function of reduced temperature, kT/J, have been carried out for Heisenberg open finite chains containing up to 11 ions ($N \leq 11$) with spins S_i of 1/2 to 5/2 on the basis of the model described in the preceding communication. Characteristic features of the $C_M'(kT/J)$ curves corresponding to various S_i and N values are discussed. These can be used in interpretation of experimental temperature dependences of C_M' for the respective ferro- and antiferromagnetic chains.

3. Studies on Dimers (NSF, NSF-MRL)

Magnetic susceptibility and structural data for two additional di-μ-hydroxo-bridged copper(II) complexes are now available. The new data support the linear correlation between the singlet-triplet splitting, 2J, and the Cu-O-Cu bridge angle which has been observed. Magnetic susceptibility data for [Cu(bpy)OH]$_2$(ClO$_4$)$_2$(bpy = 2,2'-bipyridine), for [Cu(tmen)OH]$_2$(ClO$_4$)$_2$ (tmen = N,N,N',N'-tetramethylethylenediamine), and for one complex for which there are no structural data, [Cu(tmpd)OH]$_2$-(ClO$_4$)$_2$ Itmpd = N,N,N',N'-tetramethyl-o phenylenediamine), yield 2J values of 93, -360, and 130 cm^{-1}, respectively. The complexes exhibit triplet-state EPR spectra, and the infrared spectra have been analyzed in terms of the coordination of the perchlorate ion.

Anhydrous copper(II) furoate and copper(II) thiophene-2-carboxylate have been synthesized. They are formulated as dimeric species with four carboxylate bridges. The thiophene and furan moieties give rise to polymeric structures. Electron spin resonance spectra and magnetic susceptibility measurements show that the dimers have a singlet ground state and a thermally populated triplet state. The exchange coupling constants, 2J, are -322 and -312 cm^{-1} for the furoate and thiophene-2-carboxylate complexes, respectively. The electronic and infrared spectra are also discussed.

Imadizolium, nicotinium, and quinidinium tetrachlorocuprate(II) salts have been prepared and characterized spectroscopically. Magnetic susceptibility studies show that nicotinium tetrachlorocuprate exhibits Curie-Weiss law. Remarkably, imidazolium tetrachlorocuprate(II) exhibits magnetic susceptibility behavior consistent with a dimeric formulation of the complex. The complex has a "dimer" electronic transition at 2.52 μm^{-1} which has been interpreted on the basis of molecular orbital calculations. The novel imidazolium complex is formulated as (imidazolium)$_4$$Cu_2Cl_8$ and is thought to be stabilized by hydrogen bonding.

Magnetic susceptibilities have been measured for the sulfur-bridged dimeric copper(II) complex, dichloro-(1H+-thiocarbonohydrazidium-NS)-copper(II) chloride in the temperature range 4.2 to 140°K. The data reflect an antiferromagnetic interaction and may be fit by the Van Vleck singlet-triplet splitting is remarkable in view of the long copper-sulfur bridging bond distances of 2.27 and 3.31 Å.

The magnetic properties of the compound N,N,N',N'-tetramethylenediammonium hexachlorodicuprate(II), $[tmenH_2]Cu_2Cl_6$, were determined in the temperature range 8-80°K and the data reflect an antiferromagnetic exchange interaction with an exchange energy, 2J, of -33.7 cm^{-1} with $g = 2.12$. From a comparison of the spectral and magnetic properties of $[tmenH_2]Cu_2Cl_6$ with those of $KCuCl_3$ it is proposed that the bimetallic $Cu_2Cl_6^{2-}$ unit is present in the new compound and that interdimer interactions are negligible.

4. Molecular Design of High Conductivity Materials (NSF-MRL, ONR)

The 1,4-diaminoanthraquinone (DAAQ) compounds: $2DAAQ \cdot 3I_2$, $DAAQ \cdot CuCl_2$ and $3DAAQ \cdot 2CuBr_2$ have been prepared and characterized. The compound 2 phenothiazine$\cdot 3I_2$ has also been reinvestigated. The solid state conductivities of compressed powders have been investigated by a DC method as a function of temperature. The activation energies for semiconduction (eV) for $2DAAQ \cdot 3I_2$, $DAAQ \cdot CuCl_2$ and $3DAAQ \cdot 2CuBr_2$ have been determined to be 0.053, 0.039, and 0.055, respectively. Electron paramagnetic resonance spectra and magnetic susceptibility measurements as a function of temperature have been measured. The cyclic voltametry of various diaminoanthraquinones in acetonitrile indicates that the semiconducting properties of the DAAQ compounds are related to the ease and reversibility of oxidation-reduction. Related diamonanthraquinone compounds, e.g., $1,5\text{-}DAAQ \cdot CuCl_2$, have been found to be insulators.

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Publications:

John P. Hernandez, "Self-trapping of ortho-positronium in dense fluid helium," Phys. Rev. A 14, 1579 (1975).

John P. Hernandez, "Variational treatment of disordered systems with correlations," Phys. Rev. B (to be published in the May 15, 1977 issue).

Summary of Research Activity:

(1) Self-trapping of ortho-positronium in dense fluid helium; MRL-NSF

Previous theoretical work by the author, on electron self-trapping, is extended to positronium in helium. Results are obtained for several values of the positronium-helium s-wave scattering length (a), in order to determine the validity of published analyses of data on the dependence of the ortho-positronium annihilation rate on the average density and temperature of its fluid helium host. It is concluded that the recently reported value of $^1Z_{eff} = 0.129 \pm 0.006$ is not "contaminated" by self-trapping effects or models, while the value reported for $a = 0.77 \pm 0.04$ Å results from an invalid analysis. It is suggested that a value for a in the neighborhood of 0.8 Å may be reasonably inferred from available experimental data and the calculations presented here, but that the precision of this determination is not very high.

(2) Variational treatment of disordered systems with correlations; MRL-NSF

The variational procedure, developed and applied by Luttinger, for partition function of a particle interacting with a disordered set of scatterers may be applied to treat systems in which the disorder is characterized by general correlations among the positions of the scatterers. Explicit formulas are developed for arbitrary temperature, short-ranged scattering potential, and correlations among the positions of the scatterers.

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Publications

V. H. Crawford, H. W. Richardson, J. R. Wasson, D. J. Hodgson, and W. E. Hatfield, "Relationship between the Singlet-Triplet Splitting and the Cu-O-Cu Bridge Angle in Hydroxo-Bridged Copper Dimers," Inorg. Chem., 15, 2107 (1976).

D. W. Phelps, W. H. Goodman, and D. J. Hodgson, "Structural Characterization of Bis[dibromo(N,N-dimethylethylenediamine)-copper(II)] and Bis[dichloro(N,N-dimethylethylenediamine)copper(II)], $[Cu(dmen)Br_2]_2$ and $[Cu(dmen)Cl_2]_2$," Inorg. Chem., 15, 2266 (1976).

L. G. Purnell and D. J. Hodgson, "N(3) Coordination by a Purine Analog: The Crystal Structure of Trichloro(8-azaadeninium)zinc(II)," Biochim. Biophys. Acta, 447, 117 (1976).

P. de Meester and D. J. Hodgson, "Oxidative Decarboxylation of a Tripeptide: The Reaction of Copper(II) Hydroxide and Glycyclglycyl-L-histidine," J. Am. Chem. Soc., 98, 7086 (1976).

D. J. Hodgson, "Structural and Magnetic Properties of Binuclear Copper(II) Complexes," Inorg. Chem., 15, 3174 (1976).

D. W. Phelps, D. B. Losee, W. E. Hatfield, and D. J. Hodgson, "Two-Dimensional Magnetic Systems: The Structural and Magnetic Characterization of Bis(propylene-1,3-diammonium)Tetrachlorocuprate(II)," Inorg. Chem., 15, 3147 (1976).

P. de Meester and D. J. Hodgson, "A Model for the Binding of D-Penicillamine in Living Systems: Synthesis and Structure of L-histidinyl-D-penicillaminatocobalt(III) Monohydrate, $[Co(L\text{-}his)(D\text{-}pen)]\cdot H_2O$," J. Am. Chem. Soc., 99, 101 (1977).

R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, "Magnetic and Structural Characterization of the Chromium(III) Dimer Sodium Di-μ-hydroxobis[bis(oxalato)chromate(III)] Hexahydrate, $Na_4[Cr(C_2O_4)_2OH]_2\cdot 6H_2O$," Inorg. Chim. Acta, in press.

P. de Meester, D. J. Hodgson, H. C. Freeman, and C. J. Moore, "Tridentate Coordination by L-Cysteine Dianion: Crystal and Molecular Structure of Sodium Bis(L-Cysteinato)chromate(III) Dihydrate," Inorg. Chem., in press.

A. L. Shoemaker and D. J. Hodgson, "Structure of 7-Methyl-8-azaadenine: A Crystallographic and Molecular Orbital Study," J. Am. Chem. Soc., in press.

D. J. Hodgson, "The Stereochemistry of Metal Complexes of Nucleic Acid Constituents," J. Am. Chem. Soc., in press.

L. G. Purnell and D. J. Hodgson, "Interaction of Metal Ions with 8-Azapurines III. Synthesis and Structure of Trichloro(8-azaadeninium)Zinc(II), J. Am. Chem. Soc., in press.

L. G. Purnell and D. J. Hodgson, "^{13}C Nuclear Magnetic Resonance Study of Purines and 8-Azapurines in Aqueous Medium," Organic Magnetic Resonance, in press.

H. M. Helis, P. de Meester, and D. J. Hodgson, "Binding of Penicillamine to Toxic Metal Ions: Synthesis and Structure of Potassium (D-penicillaminato)(L-penicillaminato)cobaltate(III) Dihydrate, $K[Co(D\text{-pen})(L\text{-pen})]\cdot 2H_2O$," J. Am. Chem. Soc., in press.

P. de Meester and D. J. Hodgson, "Synthesis and Structural Characterization of L-histidinyl-D-penicillaminatochromium(III) Monohydrate," J. Chem. Soc. Dalton Trans, in press.

R. B. Wilson, P. de Meester, and D. J. Hodgson, "Structural Characterization of Bis(L-methionato)zinc(II), $Zn(L\text{-met})_2$," Inorg. Chem., in press.

S. J. Cline, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, "Structural and Magnetic Properties of Di-μ-hydroxobis[bis(ethylenediamine)chromium(III)] Dithionate, $[Cr(en)_2OH]_2(S_2O_6)_2$," J. Chem. Soc. Dalton. Trans., in press.

R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson, "A Ferromagnetically-Coupled Chromium(III) Dimer: Synthesis, Structure, and Magnetic Properties of Sodium Di-μ-hydroxobis[bis(malonato)chromate(III)] Pentahydrate," Inorg. Chem., in press.

P. Singh and D. J. Hodgson, "8-Azaadenosine: Crystal Structure of Its Monohydrate and Conformational Analysis for Rotation Around the Glycosyl Bond," J. Am. Chem. Soc., in press.

E. D. Estes, R. P. Scaringe, W. E. Hatfield, and D. J. Hodgson "Structural and Magnetic Characterization of the Alkoxo-Bridged Chromium(III) Dimers Di-μ-Methoxybis[bis(3-bromo-2,4-pentanedionato)chromium(III)] and Di-μ-Ethoxybis[bis(3-bromo-2,4-pentanedionato)chromium(III)]," Inorg. Chem, in press.

R. F. Drake, R. P. Scaringe, D. J. Hodgson, and W. E. Hatfield, "Magnetic Studies on the Nitrate and Bromide Salts of the Cation Di-μ-hydroxobis[di(1,10-phenanthroline)chromium(III)]$^{4+}$," Inorg. Chim. Acta, in press.

P. de Meester and D. J. Hodgson, "The Crystal and Molecular Structure of Glycyl-L-histidinylglycinatocopper(II) Di-hemi-hydrate," Acta Cryst., in press.

P. Singh and D. J. Hodgson, "The Solid-State Conformation and Structure of Formycin B Hydrochloride," Acta Cryst., in press.

Summary of Research Activities

(1) Metal-Metal Interactions in Chain Polymers; NSF-MRL

We have been successful in synthesizing and characterizing a variety of chain polymers of copper(II), all of which possess properties which are both surprising and revealing in terms of long-range interactions.

The complex dibromo[2-(2-aminomethyl)pyridine]copper(II), $CuC_6H_8N_2Br_2$, has been synthesized, and the crystal structures of this complex and of dibromo(2-methyl-1,2-diaminopropane)copper(II), $CuC_4H_{12}N_2Br_2$, have been determined. The aminomethylpyridine complex crystallizes in the monoclinic space group $P2_1/m$, with two formula units in a cell of dimensions *a* = 8.222(15), *b* = 6.372(13), *c* = 9.883(18) Å and β = 116.3(1)°, with observed and calculated densities of 2.51 and 2.43 gcm^{-3}, respectively. The structure has been refined by full-matrix least-squares to a final value of the conventional R-factor (on F) of 0.046 based on 763 independent observations. The diaminopropane complex crystallizes in the orthrhombic space group Pnma, with four formula units in a cell of dimensions *a* = 20.276(28), *b* = 6.208(3), and *c* = 7.058(3) Å and observed and calculated densities of 2.33 and 2.330 gcm^{-3}, respectively. The structure has been refined a final value of R of 0.039 based on 669 intensities. In both complexes, the formula unit is constrained to lie in a crystallographic mirror plane, which is the *ac*-plane in both cases. For the 2-methyl-1,2-diaminopropane complex, this brings about a disorder of three of the four carbon atoms. Both structures consist of infinite dibromo-bridged chains, in which one bromide ligand serves to propagate the chain in both directions while the other is not involved in the chain; thus, one bromide is coordinated to three copper atoms while the other is coordinated to only one. *This form of chain is unique.* The geometry about each copper center is distorted octahedral, with two _cis_ nitrogen atoms and two bromides in the plane and the weaker chain-propagating bromide interactions out of the plane. The Cu-Cu separations in the two chains are 3.737(6) Å and 3.866(2) Å for the aminomethylpyridine and diaminopropane complexes, respectively, with associated Cu-Br-Cu bridging angles of 80.77(4)° and 87.56(3)°, respectively.

The structure of the thiazole complex dichlorobis(thiazole)copper(II), $Cu(thz)_2Cl_2$, is more usual in that the complex consists of square planar units linked by chloride bridges so that the structure of each chain is quite similar to that of the pyridine complex $Cu(py)_2Cl_2$. The arrangement of the chains in the crystal is quite different from that in the pyridine complex, however, since in the latter the square planar units are all parallel while in the thiazole complex the angle between the normals to the planes in adjacent chains is 78°. Consequently, the e.p.r. spectral properties of the thiazole complex are unique, and this observation demonstrates conclusively that electronic effects in these complexes are transmitted between the chains as well as along them.

Further compelling evidence for the significance of long-range non-bonded interactions is provided by our study of the adeninium complex $[Cu(AdH)_2Cl_2]Cl_2$. The complex crystallizes in the space group C2/c of the monoclinic system with the cell dimensions being $\underline{a}$ = 18.117(4), $\underline{b}$ = 8.576(1), $\underline{c}$ = 11.814(4) Å and β = 114.29(1)° with Z = 4. The copper atom is roughly tetrahedrally coordinated and lies on a crystallographic two-fold axis with the four coordination sites being occupied by two chloride ligands with a Cu-Cl distance of 2.228(1) Å and by the N(9) atoms of two adeninium cations with a Cu-N(9) distance of 2.012(2) Å. The cationic purine is protonated at N(1) and N(7). There are weak Cl···Cl interactions of length 3.755(2) Å which link the monomeric units into zig-zag polymeric chains with a Cu-Cl···Cl angle of 169.23(7)°. The corresponding Br···Br contacts are calculated to be 3.791 Å. These ligand-ligand contacts support Heisenberg linear chain antiferromagnetism with $J_{Cl} = -7.6\ cm^{-1}$ and $J_{Br} = -36.5\ cm^{-1}$. This is a remarkable result in view of the long Cl···Cl and Br···Br distances, and demonstrates that these "weak" interactions are of great magnetic significance in the solid state.

(2) Structural and Magnetic Properties of Chromium(III) Dimers;
NSF (Chemistry).

The data which we have obtained on di-hydroxo-bridged chromium(III) dimers of the type $[Cr(L)_2OH]_2^{n+}$ (where L is again a bidentate ligand) are presented in Table I; examination of these data shows that (unlike the copper analogs) there is clearly no linear dependence of J on ϕ. Because in many complexes of this type it is necessary to modify the exchange Hamiltonian by including a second-order term (biquadratic exchange), <u>i.e.</u>

Table I

Structural and Magnetic Properties of $[CrL_2(OH)]_2^{n+}$

Complex	ϕ(deg.)	Cr-Cr(Å)	2J(cm^{-1})	ΔE(cm^{-1})
$[Cr(en)_2OH]_2Cl_2(ClO_4)_2$	103.42	3.059	-26.8	-26.8
$[Cr(phen)_2OH]_2Cl_4$	102.7	3.008	-55.5	-50.3
$[Cr(phen)_2OH]_2I_4$	102.1	2.986	-43.8	-53.6
$[Cr(dipic)(OH_2)OH]_2$	100.7	2.999	-14	-14
$Na_4[Cr(ox)_2OH]_2$	99.6	3.006	-0.6	-0.6
$Na_4[Cr(mal)_2OH]_2$	99.3	3.000	+2.2	+2.2
$[Cr(gly)_2OH]_2$	98.2	2.974	-7.4	-10.0

$$H_{ex} = -2J\vec{S}_1\cdot\vec{S}_2 - j(\vec{S}_1\cdot\vec{S}_2)^2$$

the Van Vleck equation can be written as

$$\chi_m = \frac{Ng^2\beta^2}{kT} \times \left\{\frac{2e^{(2J-6.5j)/kT} + 10e^{(6J-13.5j)/kT} + 28e^{(12J-9j)/kT}}{1 + 3e^{(2J-6.5j)/kT} + 5e^{(6J-13.5j)/kT} + 7e^{(12J-9j)/kT}}\right\}$$

and the singlet-triplet splitting (ΔE in Table I) is 2J-6.5j. Correlations should more properly be made between ΔE (rather than J) and structural features, but it is also apparent that there is no linear relationship between ΔE and ϕ for these complexes.

The reason for this apparent (but not actual) breakdown of the scheme which we had earlier proposed for the interactions in copper(II) dimers is readily seen. In the case of copper(II), we were able to restrict our attention to the $\underline{\sigma}$-system, since the only unpaired spin resides in $\underline{\sigma}$-orbitals. In six-coordinate chromium(III) complexes, however, the unpaired spin is in the t_{2g}-type orbitals, which have components both in the bridging plane and perpendicular to it. Hence, this system allows us to generalize our molecular orbital scheme; the result obtained for copper(II) dimers is a special case of this anticipated result. It should be noted however, that to the extent that the metal-oxygen bridging bonds are of equal length in all of these complexes (for any given metal), the basic hypothesis holds: *The magnetic behavior of dimers of these general types is determined principally by the M-O-M brdiging angle*, ϕ. In the case of six-coordinate systems (e.g. chromium(III) complexes) we have the simplifying feature that the value of τ is forced by the constraints of the pseudo-octahedral geometry to be approximately zero in all cases; consequently, this term is not a factor in the studies under discussion here. I have recently developed an extension of our original model which accounts for the observed properties of chromium(III) dimers.

We are also synthesizing and studying alkoxo-bridged complexes of the type $[Cr(L)_2OR]_2^{n+}$, and have completed our characterizations of three such complexes. Professor L.J. Theriot has devised a more general synthetic route than our own, which was merely an extension of the procedure of Kasuga, and he has generously donated samples of more of these complexes. These alkoxo-bridged dimers are of great value in examining our present correlation, since they allow us to vary the electron density at the bridge. The effect of increasing the electron density at the bridge is to raise the energies of the orbitals ϕ_1, ϕ_2, ϕ_3 and ϕ_5 (remembering that these are the antibonding combinations) and leave ϕ_4 and ϕ_6 unaffected since they contain no bridging character. Thus, to a first approximation, $(E_2-E_1)^2$ is unaffected (assuming similar energy shifts for oxygen p_x and p_y), while $(E_4-E_3)^2$ and $(E_6-E_5)^2$ both increase with increasing electron density at the bridge. Therefore, we expect an increase in the antiferromagnetic interaction with increasing electron density at the bridging atom. We find that the complexes $[Cr(3\text{-}Cl\text{-}acac)_2\text{-}OCH_3]_2$, $[Cr(3\text{-}Br\text{-}acac)_2OCH_3]$, and $[Cr(3\text{-}Br\text{-}acac)_2OC_2H_5]_2$ all have approximately the same ϕ value ($101.5 \pm 0.4°$), but that ΔE for the ethoxy complex ($-17.9\ \text{cm}^{-1}$) has approximately twice the magnitude found for the methoxy complexes ($-9\ \text{cm}^{-1}$). Since ethanol is a weaker acid than methanol, there is greater electron density at the ethoxy oxygen atom; hence, the observed result is entirely consistent with our prediction. This is the strongest experimental evidence of this type ever reported.

(3) Halogen-Bridged Complexes of Copper(II); NSF (Chemistry)

The magnetic coupling in halogen-bridged complexes of copper(II) is more complicated than the hydroxo-systems because of the presence, in the former, of relatively low-lying ligand d-orbitals which can interact with the metal orbitals. A further complication, which we did not anticipate, arises from our discovery that complexes of the types $CuLX_2$ (where L is a bidentate ligand) or CuA_2X_2 (where A is unidentate) show an amazingly wide variety of geometries.

The tetragonal pyramidal dimers are the easiest class to understand, in part because this geometry is most readily comprehended in the light of our previous molecular orbital schemes, and also because data for these complexes are more prevelant at present, with three dibromo-bridged and five dichloro-bridged structures available. These tetragonal pyramidal complexes are, of course, of the out-of-plane type, so in this situation the bridging framework is not in the x,y-plane of the copper atoms; one bridging ligand is axial to a given copper atom, and the other is equatorial. Since the unpaired spin is in the base planes of the molecule, any exchange interactions are expected to be weak.

The available data for these types of dimers (the majority, but not all, of which are from our laboratories) are summarized in Table II.

Table II

Structural and Magnetic Properties of Tetragonal Pyramidal Halogen-bridged Copper(II) Dimers

Complex	Cu-X'(Å) (out-of-plane) (d)	Bridge Angle (ϕ)	J (cm^{-1})
$[Cu(DMG)Cl_2]_2$	2.698	88.0	+3.1
$[Cu(pic)_2Cl_2]_2$	3.37	101.4	-3.7
$[Cu(tmen)Cl_2]_2$	3.147	96.8	-2.5
$[Cu(dmen)Cl_2]_2$	2.734	86.13	-1.0

(continued)

Table II (continued)

Complex	Cu-X'(Å) (out-of-plane) (d)	Bridge Angle (ϕ)	J (cm^{-1})
$[Cu(9Me6MP)Cl_2]_2$	2.737	88.17	-
$[Cu(pic)_2Br_2]_2$	3.872	100.4	-2.5
$[Cu(tmen)Br_2]_2$	3.20	95.6	-2.0
$[Cu(dmen)Br_2]_2$	2.868	83.71	-1.0

If our previous concepts were correct, we would predict that at bridging angles near 90° the ground state would be the triplet, but that as we deform the system (in either direction) we should begin to see singlet ground states. It is apparent, unfortunately, that there is another variable here - the out-of-plane Cu-X' distance, d. We anticipate, therefore, that we can write

$$J = f(\phi,d)$$

since, obviously, an increased value of d will attenuate the overlap and decrease the magnitude of J. But while the magnitude of J is a function of both ϕ and d, the sign of J should be a function of ϕ only, with the ϕ-dependence described above. We obviously have only a limited number of data, but it is true that (at present) all complexes with bridge angles between 87 and 93° have triplet ground states, while all complexes with bridge angles outside of this window have singlet ground states. The data, then, are consistent with our prediction, although the availability of only one complex with a triplet ground state diminishes their reliability as a test of our theory. Moreover, the precise nature of the dependence of J on d remains to be discovered. Presumably, from the above discussion, J is dependent on $\Delta\phi$ [i.e., $|90°-\phi|$] and on d^{-n}, where n need not be integral and may itself be a function of d. We shall need more data to unravel this problem.

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Degrees Granted: W. McLean, Ph.D.

Other Supporting Agency: National Science Foundation

Publications:

W. McLean, L. G. Pedersen, and R. C. Jarnagin, "Alkyl-Metal Surface Complexes: Methyl and Lithium," J. Chem. Phys. 65, 2491-2500 (1976).

W. McLean, "Lithium Surface Complexes," University of Microfilms, Ann Arbor, Michigan (1977).

Summary of Research Activities:

(1) Surface Complexes; NSF--MRL

Experimental studies of surface complexes formed on evaporated lithium films have been continued. The structure of transient lithium peroxides like species formed on lithium surfaces is sought. These species may be involved in formation of epoxides and may serve as polymerization catalysts. The relative rates of reaction of surface with H_2O, O_2, and N_2 have been observed at room temperature. Several features in the ultraviolet photoelectron spectrum of lithium plus water have been clearly identified with surface OH^- (3.7 eV below E_f assigned $1b_1$ and 5.7 eV below E_f assigned $2a_1$). Additional features have been tentatively identified as contributed by a peroxide-like entity (very strong peak at 5.3 eV below E_f plus other peaks at greater binding energy). Additional collection of electron spectra, calculations of electronic levels for assumed species, and observations of $^{18}O_2$ adsorption and desorption are in progress to clarify the tentative identifications.

(2) Nonlinear Photoionization of Donors in Fluids and Liquids; NSF

The molecular features of donor and the collective molecular behavior of solvent that cause and control solvent induced release of electrons from photo-excited donor molecules into the quasi-free electron states of neopentane and tetramethyl silane are sought. Three methods for study of the phenomenon are being developed; a) variation of fluid density from gas-like to liquid-like values; b) comparison in the same donor of direct electron ejection via multiphoton ionization with induced electron release from states excited below the ionization potential, and c) comparison of photoionization by a common mechanism for simple diatomic and monatomic electron donors to photoionization from large polyatomic species with both classes of molecules contained in similar media.

During the past year we have confirmed, with modified experimental arrangement, selected results that had been previously obtained. Development, construction, and testing of an operational test cell for work in super critical fluids is now virtually complete. Instrumentation for measurement of picoampere current in test cell at 200°C and 200 atm has been completed. Instrumentation for pressure testing after each cell refilling has been completed. Testing of cell under operational conditions is 70% complete.

Implementation of pulsed laser techniques to assist in understanding the dynamics of solvent induced electron release has been partly completed. A laser oscillator has been reworked from use with ruby to use with Nd^{3+}: glass. A pulse switchout and slicer has been secured but appropriate frequency multiplying crystals have not yet been received.

We have successfully demonstrated resonantly enhanced multiphoton ionization from donor molecules possessing sharp but well separated transitions and have shown the direct multiphoton ionization to be weakly influenced by a 1000-fold increase in fluid density. Quantitative studies of the effect are in progress. A similar resonantly enhanced multiphoton ionization has been observed in the tetra-alkyl-p-phenylenediamie donors. In these substances the states at the one quantum level, where the resonance is presumed to originate, are inhomogeneously broadened by their internal motions. The strength of the resonant enhancement in this case was somewhat surprising and is yet to be quantitatively examined. We believe that this observation demonstrates, as originally proposed, that multiple photon ionization should be very useful as a tool to examine contrasts between medium induced charge release from bound excited states and genuine electron ejection where both processes originate from a common donor in similar environment.

Faculty Member: J. Ross Macdonald
William R. Kenan, Jr. Professor of Physics

Research Associates: J. A. Garber (NSF, MRL-NSF)
D. R. Franceschetti (NSF, MRL-NSF)

Other Supporting Agency: NSF

Publications:

D. R. Franceschetti and J. R. Macdonald, Comment on "Theory and Analyses of the A.C. Characteristics of Defect Thin Film Insulators," J. Appl. Phys. 47, 4222 (1976).

J. R. Macdonald, D. R. Franceschetti, and R. Meaudre, "Electrical Response of Materials with Recombining Space Charge," accepted by J. Phys. C: Solid State.

D. R. Franceschetti and J. R. Macdonald, "Electrode Kinetics, Equivalent Circuits and System Characterization: Small-signal Conditions," accepted by J. Electroanal. Chem.

D. R. Franceschetti, "On Recombination Kinetics in Theories of Small-signal Electrical Response," accepted by J. Appl. Phys.

Summary of Research Activities:

(1) Comment on "Theory and Analyses of the A.C. Characteristics of Defect Thin-film Insulators"; NSF

D. R. Franceschetti and J. R. Macdonald

A theory of metal-insulator-metal thin films proposed by Nadkarni and Simmons is examined in relation to earlier treatments. Attention is drawn to approximations inherent in the theory and physical processes not considered by the authors.

(2) Electrical Response of Materials with Recombining Space Charge; NSF

J. R. Macdonald and D. R. Franceschetti

The small-signal transient and sinusoidal steady state responses to a material with generation and recombination (G/R) of charge were examined. Explicit consideration was given to systems in which immobile positive charge and mobile negative charge arises from the dissociation of intrinsic or donor centers and recombines bimolecularly. The mobile charge was allowed to react at the electrodes. An exact solution for the steady state admittance of the system was obtained, along with exact and approximate equivalent circuits. Simple approximate equivalent circuits, made up entirely of frequency-independent elements, whose relations to basic material properties were determined in cases of interest, were found to approximate the exact admittance to better than one per cent for all frequencies and for realistic G/R conditions in the completely blocking situation. Similar accuracy was obtained for partly blocking conditions provided G/R and electrode reaction time constants were well separated. The approximate equivalent circuits, which represent a more accurate and simpler solution of the system than available heretofore and are thus appropriate for data analysis, lead to a transient response made up of the sum of two exponential decays. Conditions were considered for the appearance of appreciable G/R effects in either admittance or in transient current decay after a small step function of voltage is applied to the system. It was concluded that for ionic conductors and for many electronic semiconducting materials recombination times will be sufficiently short that only minor G/R effects will be apparent.

(3) Equivalent Circuits and System Characterization: Small-signal Conditions; NSF

J. R. Macdonald

The small-signal steady-state response around the point of zero charge of an electrode/material system was examined for an unsupported electrolyte (material) with two species of charge carrier of arbitrary mobilities and valence numbers and with arbitrary intrinsic/extrinsic conduction character, taking full account of bulk, electrode reaction, sequential adsorption, and diffusion processes. The exact solution of the transport equations for generalized Chang-Jaffé single point boundary conditions was compared with the responses of a variety of plausible equivalent circuits, using a complex least squares fitting technique. A new, hierarchical circuit was found which closely reproduces the exact results when charge of one sign is completely blocked without adsorption, except for some of the cases in which diffusion and reaction effects interfere with each other. The circuit is composed of frequency-independent lumped capacitances and resistances separately identified with bulk, reaction, and adsorption/reaction processes and a single, finite-length, Warburg-like impedance for diffusion effects. Relations between the circuit elements and microscopic electrode/material parameters were found and apply irrespective of the time-frequency overlap between bulk, reaction, and adsorption processes. It was also found that the reaction and adsorption resistances and the adsorption capacitance are all strongly interrelated. The circuit may be used with simultaneous nonlinear least squares fitting of the real and imaginary parts of experimental impedance data to obtain estimates of the values of circuit elements and thus of the microscopic parameters characterizing the electrode/material system.

(4) Electrode Reaction Kinetics as a Boundary Value Problem: Small-signal Conditions; MRL-NSF, NSF

D. R. Franceschetti and J. R. Macdonald

The relationship of small-signal response for overpotential-dependent electrode kinetics to that obtained for Chang-Jaffé boundary conditions was examined in detail. The reaction resistance and adsorption capacitance were found to be formally identical for Butler-Volmer (or Butler-Volmer-like) and Chang-Jaffé conditions. In the dc limit these quantities were found to remain unchanged, for the boundary conditions just mentioned, when a supporting electrolyte is added. A transformation of variables method was devised which permits one to determine the small-signal impedance of an electrode/material system with general overpotential-dependent first-order electrode reaction kinetics from a compact-layer model for the small signal overpotential and the small signal response obtained for Chang-Jaffé boundary conditions. Exact impedance results were determined for the case of a single species of mobile charge carrier. Analysis of this case indicates that the overpotential dependence of the boundary conditions has negligible effect on the small-signal response unless the cell is of microscopic thickness or the Debye length is comparable to the compact layer thickness and the electrode reaction is slow.

(5) Recombination Kinetics in Theories of Small-signal Electrical Response; NSF

D. R. Franceschetti

It was found that small signal electrical response results obtained for generation-recombination or trapping rate laws appropriate to a neutral center dissociation-association mechanism encompass the electrical response to be expected for other frequently encountered generation-recombination or trapping rate laws under a wide range of conditions. Expressions were found relating the rate constants in such kinetic expressions to various definitions of charge carrier lifetimes in semiconductors and ionic conductors.

(6) Numerical Simulation of Electrical Response; NSF, MRL-NSF

D. R. Franceschetti

Computer algorithms were developed for the simulation of large signal transient electrical response. In the large-signal case the equations of charge transport are in general too complicated, owing to their nonlinearity, for exact analytic solution, but lend themselves readily to numerical solution by finite difference algorithms. At the time of this report working versions of a fully implicit and partially implicit (modified Crank Nicholson) computer program have been achieved. These programs, which allow variable step spacing in both position and time, are currently being optimized and compared for accuracy and economy of operation.

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Publications:

A. R. Guiterrez, D. G. Whitten, and T. J. Meyer, "Competition Between Energy Transfer and Electron Transfer in the Photosensitization Process," *Molec. Photochem.*, 7, 349 (1976).

W. L. Bowden, T. J. Meyer, and W. F. Little, "Nitrosoarene Complexes of Ruthenium. Nitrosation of Activated Aromatic Compounds by the Coordinated Nitrosyl Group", *J. Am. Chem. Soc.*, 98, 444 (1976).

R. W. Callahan and T. J. Meyer, "Intervalence Transfer in the Mixed-Valence Ion $(\mathrm{bipy})_2\mathrm{ClRu(pyz)RuCl(bipy)}_2^{3+}$", *Chem. Phys. Lett.*, 39, 82 (1976).

R. C. Young, D. G. Whitten, and T. J. Meyer, "Electron Transfer Quenching of Excited States of Metal Complexes", *J. Am. Chem. Soc.*, 98, 286 (1976).

M. J. Powers, D. J. Salmon, R. W. Callahan, and T. J. Meyer, "The Role of Distance in Electron Transfer in Solution. Experimental Verification of the Hush-Marcus Theory Using Mixed-Valence Complexes", *J. Am. Chem. Soc.*, 98, 6731 (1976).

F. R. Keene, R. C. Young, and T. J. Meyer, "Measurement of Rates of Electron Transfer Between $Ru(bpy)_3^{3+}$ and $Fe(phen)_3^{2+}$, and Between $Ru(phen)_3^{3+}$ and $Ru(bpy)_3^{2+}$ by Differential Excitation Flash Photolysis", *J. Am. Chem. Soc.*, in press.

R. W. Callahan, F. R. Keene, D. J. Salmon, and T. J. Meyer, "Intervalence Transfer and Electron Transfer in the Mixed-Valence Ion $[(bpy)_2ClRu(pyz)RuCl(bpy)_2]^{3+}$", *J. Am. Chem. Soc.*, 99, 1064 (1977).

C. P. Anderson, J. L. Hughey, IV, and T. J. Meyer, "Photochemistry of $Mn_2(CO)_{10}$", *J. Organometal. Chem.*, 125, 49 (1977).

W. L. Bowden, G. M. Brown, E. M. Gupton, W. F. Little, and T. J. Meyer, "Electron Transfer in Diazonium Complexes of Ruthenium", *Inorg. Chem.*, 16, 213 (1977).

C. P. Anderson, R. C. Young, D. J. Salmon, and T. J. Meyer, "Photochemical Generation of $Ru(bpy)_3^{+}$ and O_2^{-}", *J. Am. Chem. Soc.*, 99, 1980 (1977).

Trin-Toan, B. K. Teo, J. A. Ferguson, L. F. Dahl, and T. J. Meyer, "Electrochemical Synthesis and Structure of the Tetrameric cyclopentadienyliron Sulfide Dication, $[Fe_4(\underline{h}^5-C_5H_5)_4(\mu_3-S)_4]^{2+}$. A Metal Cluster Bonding Description of the Electrochemically Reversible $[Fe_4(\underline{h}-C_5H_5)_4]^n$ System (μ = -1 to +3)", *J. Am. Chem. Soc.*, 99, 408 (1977).

W. L. Bowden, W. F. Little, and T. J. Meyer, "Diazotization of Aromatic Amines by Ruthenium Nitrosyl Complexes", *J. Am. Chem. Soc.*, in press.

R. W. Callahan and T. J. Meyer, "Reversible Electron Transfer in Ruthenium Nitrosyl Complexes," *Inorg. Chem.*, 16, 574 (1977).

F. R. Keene, D. J. Salmon, and T. J. Meyer, "Nitro Complexes of Ruthenium(III) as Oxidation Catalysts. Chemically-Catalyzed, Net Electrochemical Oxidation of Triphenylphosphine", *J. Am. Chem. Soc.*, in press.

F. R. Keene, D. J. Salmon, and T. J. Meyer, "Disproportionation at the Ligand in Nitro Complexes of Ruthenium(III)", *J. Am. Chem. Soc.*, in press.

Summary of Research Activities:

(1) Redox Catalysis Using Transition Metal Complexes. F. R. Keene, B. P. Sullivan, D. J. Salmon, B. A. Moyer, J. A. Baumann, N. Henis. (NSF-MRL, NSF)

Ruthenium(III)-nitro complexes like $[\overset{III}{Ru}(bpy)_2(NO_2)py]^{2+}$ (bpy is 2,2'-bipyridine) have been found to act as oxidation catalysts for the electrochemically driven conversions of phosphines to phosphine oxides, sulfides to sulfoxides, aldehydes to acids, and aromatic compounds to phenols and quinones.

Oxidation of $[Ru(bpy)_2(py)H_2O]^{2+}$ by Ce(IV) occurs first to Ru(III) and then to the peroxo complex $[(bpy)_2(py)RuO_2Ru(py)(bpy)_2]^{4+}$. The peroxo ion appears to have the chemically exploitable property of acting as a Ru(IV) oxyl oxidation agent.

(2) Electron Transfer Processes of Metal Complex Excited States. R. C. Young, C. P. Anderson, H. Sprintschnik, J. Nagle.
(NSF)

It has been shown that the excited states of metal complexes can undergo both oxidative and reductive quenching even including examples of non-emitting excited states. The CT excited state $Ru(bpy)_3^{2+*}$ is thermodynamically capable of both oxidizing and reducing water at pH 7 and some progress has been made in the photocatalyzed splitting of water using related complexes.

(3) Mixed-Valence Polymers. B. P. Sullivan, M. J. Powers, J. A. Baumann.
(ARO)

Insight has been gained into the nature of metal-metal interactions between ruthenium ions in mixed-valence dimers with regard to the influence of both bridging and non-bridging ligands. We are currently turning back to the preparation of polymeric complexes where polymer design is based on the insight gained.

(4) Immobilized and Surface-Attached Complexes. H. W. Sprintschnik.
(NSF)

Studies on the surface and polymer attachment chemistry of metal bipyridine complexes has been initiated. The chemistry is based on forming chemical linkages in reactions between ligand-attached acylhalide groups and -OH or $-NH_2$ groups.

Faculty Member: Earl N. Mitchell
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Graduate Student: T. C. Ma (MRL-NSF)

Summary of Research Activities:

(1) Studies of the Electrical Properties of Polymeric Films; MRL-NSF

The project to study the feasibility of making photovoltaic devices (solar cells) using polymeric films is being phased out. The films studied showed conductivities which were quite low and hence would have to be quite thin to be useful. Films thin enough to be contenders for such an application exhibited breakdown characteristics similar to other polymeric films or were shorted. Efforts to discover the source of the presumed nonuniformities in the material which caused the breakdown were unsuccessful.

It was established that the surfaces of the polymeric films were heated substantially when metal electrodes were evaporated onto them. Most of this heating came from the evaporated metal but some radiant heating also occurred if the evaporation was long enough.

However, it has not been possible to make films of the proper thickness and breakdown characteristics in order to determine if the heating is the cause of the presumed nonuniformity in the films.

(2) Studies of the Electrical and Optical Properties of Conducting Glass; MRL-NSF

A project to study chemically modified electrodes for electrocatalysis applications continues in the Chemistry Department at UNC as part of the CMS thrust. Conducting glasses are important as intermediate inert conductors in such studies. If conducting glasses could be attached to certain metal electrodes significant improvements could be achieved especially in so far as geometry is concerned.

A program has been started to try to make conducting (NESA type) glasses using the technique of RF reactive sputtering. Tin oxide glasses have been prepared by Electron Beam evaporators and resistive heating. However, these glasses show absorption in the visible part of the spectrum indicating the presence of defects in the films which could be attributed to oxygen deficiencies.

It is expected that films made by RF sputtering will not show such defects since composition can be controlled more precisely. Doping should prove relatively simple since this can be controlled by electrode composition.

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J. Monrad

Other Supporting Agencies: National Science Foundation,
University Research Council

Publications:

J. B. Moody, "Serpentinization: A Review," Lithos, 9, 125 (1976).

J. B. Moody, "An Experimental Study on the Serpentinization of Iron-Bearing Olivines," Can. Mineral., 14, 462 (1976).

J. B. Moody, "Implications of Laumontite Stability on the Evaluation of Fault Capability," Geol. Soc. America, Abstracts with Programs, 9, 168 (1977).

J. B. Moody and M. L. Sykes, "Pyrophyllite and Associated Low Grade Metamorphism in Southern Appalachians," Geol. Assoc. Canada, Program with Abstracts, 2, 37 (1977).

Summary of Research Activities: (MRL-NSF)

Optical and transmission electron microscopic (TEM) observations were done on the nature of the sliding surface of Crab Orchard orthoquartzite subjected to sliding friction experiments (Hayes, 1975; Dunn & Hayes, 1975) at a constant strain rate of 2.5×10^{-5} sec^{-1} with variation in pore fluid chemistry (water and dodecyl trimethyl ammonium bromide, DTAB). X-ray, optical, TEM and scanning electron microscopy (SEM) observations were also made on the gouge produced in the experiments.

Measurements on doubly-polished, etched thin sections cut perpendicular to the sliding surface determined the nature of the sliding surface, the number of plucked-out grains, disaggregrated grains and intragranular cracks for a constant distance along the sliding surface. All of the tested samples have a decreased number of disaggregrated grains and an increased number of intragranular cracks compared to the untested samples. For a constant confining pressure (P_c) of 500 bars without any pore pressure (P_p), the optical measurements show the same results whether the sample was wet (saturated with water or DTAB) or dry: an increased axial displacement increases the number of intragranular cracks. Addition of a P_p (250 bars) at constant P_c decreases the number of intragranular cracks for the same axial displacement. Two DTAB samples with P_c = 500 bars, P_p = 250 bars showed a decreased number of intragranular cracks with increased axial displacement. The number of pluckouts and disaggregrated grains are related to the stickslip behavior during the experiment, i.e., the magnitude of the force necessary to produce slip and the magnitude of the stress drops with increased axial displacement. Two correlations were observed: (1) the number of pluckouts decreased with increased axial displacement for the dry and water samples with P_c = 500 bars, P_p = 0, and (2) the number of disaggregrated grains decreases with magnitude of force necessary to produce the stick-slip behavior.

No variation in subgrain boundaries, dislocation density or nature of the dislocations was found in the TEM observations of foils made from doubly-polished thin sections. The high dislocation density of the untested samples ($10^{-8} - 10^{9}/cm^{2}$) precluded any determination of increased dislocation density in the experimental samples. However, a parallel alignment of the dislocations was noted in some of the experimental samples.

The possibility of the presence of glass in the gouge is indicated in the presence of an amorphous material in the TEM which would not give a diffraction pattern. Optical and SEM observations of the gouge showed considerable variation in the size, shape, and welding of the gouge fragments, which can be related to the experimental conditions. The unit cell parameters of quartz in the gouge did not show any variation nor was the presence of an amorphous material detected in the X-ray results.

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Other Supporting Agency: NSF Chemistry Division
Office of Naval Research

Publications:

C. M. Elliott and R. W. Murray, "Chemically Modified Carbon Electrodes," Anal. Chem., 48, 1247 (1976).

P. R. Moses and R. W. Murray, "Chemically Modified Electrodes. III. SnO_2 and TiO_2 Electrodes Bearing an Electroactive Reagent," J. Amer. Chem. Soc., 98, 7435 (1976).

L. T. Mimms, M. A. McKnight and R. W. Murray, "Spectrophotometric Study of Coverage and Acid-Base Equilibrium of a Chemically Bonded Base," Anal. Chim. Acta, in press.

D. F. Untereker, J. C. Lennox, L. M. Wier, P. R. Moses and R. W. Murray, "Chemically Modified Electrodes. IV. Evidence for Formation of Monolayers of Bonded Organosilane Reagents," J. Electroanal. Chem., 77, 393 (1977).

D. G. Davis and R. W. Murray, "Surface Electrochemistry of Iron Porphyrins and Iron on Tin Oxide Electrodes," Anal. Chem., 49, 194 (1977).

B. Firth, L. L. Miller, M. Mitani, T. Rogers, J. C. Lennox and R. W. Murray, "Anodic and Cathodic Reactions on a Chemically Modified Edge Surface of Graphite," J. Amer. Chem. Soc., 98, 8271 (1976).

P. R. Moses and R. W. Murray, "Chemically Modified Electrodes. V. Covalent Binding of a Reversible Electrode Reactant to RuO_2 Electrodes," J. Electroanal. Chem., 77, 393 (1977).

J. R. Lenhard and R. W. Murray, "Chemically Modified Electrodes. VII. Covalent Bonding of a Reversible Electrode Reactant to Pt Electrodes Using an Organosilane Reagent," J. Electroanal. Chem., 78, 0000 (1977).

J. C. Lennox and R. W. Murray, "Chemically Modified Electrodes. VI. Binding and Reversible Electrochemistry of Tetra(Aminophenyl)Porphyrin on Glassy Carbon," 78, 0000 (1977).

Summary of Research Activities:

Chemically Modified Electrodes - New Materials and a New Approach to Electrocatalysis

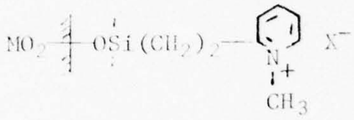
The basic idea in chemically modified electrodes is to covalently bond a monomolecular or submonomolecular assembly of molecules to an electrode surface. A thesis of the research, which was begun in 1974, is that this covalent bonding can be accomplished by predictive principles of solid state synthesis, that ESCA can be used to analyze and characterize the composition and structure of the surface-synthesized monolayers, and that the chemical and electrochemical properties of bound molecular monolayers, and thus the chemical and electrochemical properties of the electrode surface, would to a first approximation be the same as those of analogous free molecular species in solution. To the extent that these theses are true, we believe that it will be possible to tailor-make electrocatalytic surfaces. This capability would have enormous technological implications.

Thus far our pursuit of the above ideas has met a substantial success in the protocol of experiments designed to explore it, and our anticipations of the research thesis have thus far proven correct. Other researchers in academic and industrial locations share our optimism that chemically modified electrode surfaces represents an exceedingly interesting and useful area of electrochemical research and potential electrochemical technology. Since our initial publication in 1975 on chemically modified SnO_2 electrodes, sixteen other research groups have begun research programs on the chemical modification of metal oxide electrodes (four of these in direct collaboration with us). Five other research groups, and ourselves, are also carrying out research on chemically modified carbon surfaces.

Much of the background for this report has been presented in the previous year's discussion to which the reader is referred for numerous background details. Much of the significant work which was conducted during the present year has been implanted in the year's publications and the following discussion of research progress is organized for convenience by publication.

(I) Chemically Modified Electrodes. III. SnO_2 and TiO_2 Electrodes Bearing an Electroactive Reagent (NSF)

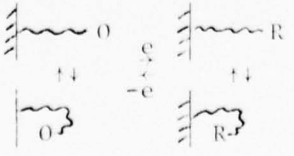
We have previously established that metal oxide electrodes such as SnO_2 and TiO_2 could be silanized with an organosilane containing a pyridine functionality. We established that this pyridine functionality could be methylated, producing the surface structure



where M = Sn, Ti (1)

It proved possible to observe the chemically irreversible reduction of the methylpyridinium functionality on these surfaces, which occur at an electrode potential approximately the same as the solution form of methylpyridinium. The quantity of electrochemically reactive material approximated a molecular monolayer. It proved possible to follow the course of solid state synthesis of the surface methylpyridinium, and its electrochemical reactivity, by ESCA. Also, ion exchange of the surface counterion (X^-) could be followed by ESCA.

Although the electrochemical reaction observed in this case was chemically irreversible, these observations were extremely significant because they constitute the first unambiguous demonstration of an electrochemically reactive molecule covalently bound to an electrode surface. Note that the molecular chain connecting the electrode to the methylpyridinium site is electronically insulating, which raises the question of the mechanism of electron transfer. Two mechanisms can be proposed. (i) A long-range transfer of the electron (tunneling), and (ii) A sterically free motion of the connecting chain so that the molecular orbitals of the methylpyridinium species come into frequent overlap with those of the electrode surface. The latter model is referred to as the "floppy model," introduced by us, and is schematically illustrated in the following equation.

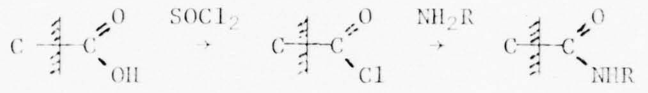


(2)

The observation of electrochemical reactivity in Equation 1 simply proved that one of the two mechanisms could be operative, but provides no insights into which.

(2) Anodic and Cathodic Reactions on a Chemically Modified Edge Surface of Graphite (NSF, ONR)

This paper was a result of a joint project with Professor L. Miller of Colorado State University. Professor Miller had succeeded in attaching chiral amino acid esters to carbon surfaces by, ostensibly, the following chemistry



(3)

The electrodes prepared by Miller exhibit an enantiomorphic selectivity in electrode reactions, which is of some interest in organic electrosynthesis. We conceived of an experiment using highly oriented pyrolytic graphite (HOPG), in which Reaction 3 should occur predominantly on the basal plane edges of the graphitic crystal. In agreement with this prediction, ESCA and chiral electroactivity observations showed a higher population of the "R" groups on the basal plane edge as compared to the basal plane face. This experiment was an important demonstration that the coupling chemistry Miller observes is dependent on a reaction such as that in Reaction 3 and not on strong, irreversible chemisorption, which is a persistent technical problem in working with carbon electrodes.

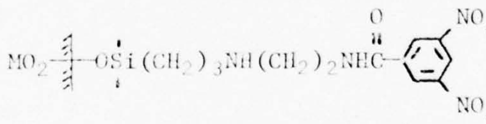
(3) Chemically Modified Electrodes. IV. Evidence for Formation of Monolayers of Bonded Organosilane Reagents (NSF, MRL-NSF)

Much of our chemical modification work on metal oxide electrodes is based on organosilane reactions with the metal oxide, in which it is extremely important that the formation of siloxane polymers be avoided. We desire a known stereochemical relationship between the organosilane functional groupings and the electrode surface in order to understand, in a fundamental way, the electron transfer processes. In this paper, we gathered a variety of evidence from previous and recent research to demonstrate that under properly anhydrous and mild silanization reaction conditions, monolayers and submonolayers of organosilanes can be formed on metal oxide surfaces. The evidence gathered included electrochemical coverage data, coverage data based on optical absorbance of bound chromophores, ESCA, and reaction conditions. The data is not sufficiently precise to exclude the occasional formation of a few percent of polymeric material on the electrode surfaces, but definitely rules out the general presence of gross layers of polymer structures.

Silanization reactions have been used extremely widely, especially on silica surfaces. Many silanization reactions are deliberately conducted under conditions leading to surface polymer formation. Others are conducted under conditions in which monolayer formation is sought. We've found that the literature on silica silanizations contained, in fact, very little definitive evidence for an ability to form silane monolayers. The evidence we gather from chemically modified electrode work should apply to silica surfaces.

(4) Chemically Modified Electrodes. V. Covalent Binding of a Reversible Electrode Reactant to RuO_2 Electrodes, Chemically Modified Electrodes. VII. Covalent Bonding of a Reversible Electrode Reactant to Pt Electrodes Using an Organosilane Reagent (MRL-NSF, NSF)

The surface bound redox couple in Reaction 1 above is chemically irreversible. For electrocatalytic applications, it is desirable to develop an ability to synthesize surface redox groupings which are chemically stable in multiple oxidation states. Previous work had demonstrated that the following structure could be prepared on SnO_2 electrodes



(4)

Inexplicably, the electrochemical reduction of the nitroaromatic functionality is chemically irreversible for both the surface-bound form of Equation 4 and for the analogous solution form. This gave us an impetus to develop new metal oxide electrode substrates. The two publications indicated describe two new metal oxide materials for chemical modification. Approximately ten others are on tap for organosilane modification work.

In paper Number V we demonstrated that the reactions which led to the structure in Equation 4 on SnO_2 also proceeded satisfactorily on RuO_2 films on Ti electrode backing. The electrochemical properties of the RuO_2 electrodes in non-aqueous solvents are excellent, and we established that the surface structure in Equation 4 gave two chemically reversible surface waves in DMSO solvent, in which the dinitroaromatic is reduced to first its anion radical, and then to its dianion. We obtained analogous results, but with the expected single reduction wave. for the 3-nitroaromatic and 4-nitroaromatic variants. We established that the formal potentials for the surface redox couples were within 100 mv. of the solution potentials. This provides the first example of a covalently bonded *chemically reversible* redox couple. The electrochemical data indicated binding of an approximate monolayer. The surface synthetic and electrochemical data were appropriately supplemented and verified by ESCA information.

In paper Number VII, we sought the favorable electrochemical properties of platinum electrodes through reasoning that PtO is easily formed in aqueous acid, and is reductively fairly stable in non-aqueous solvents. We found that Pt electrodes covered with a monolayer of PtO could be readily silanized and subsequently amidized to form a structure such as that in Equation 4 above. The PtOSi bonds proved to be chemically quite stable and are furthermore very resistant to reduction in a variety of non-aqueous solvents. The electrochemical observations obtained on the chemically modified PtO electrodes completely paralleled those on the RuO_2 electrodes. This provided a beautiful demonstration of the predictability of the surface redox chemistry which can be achieved with chemically modified surfaces.

(5) Chemically Modified Electrodes. VI. Binding and Reversible Electrochemistry of Tetra(Aminophenyl)Porphyrin on Glassy Carbon (ONR)

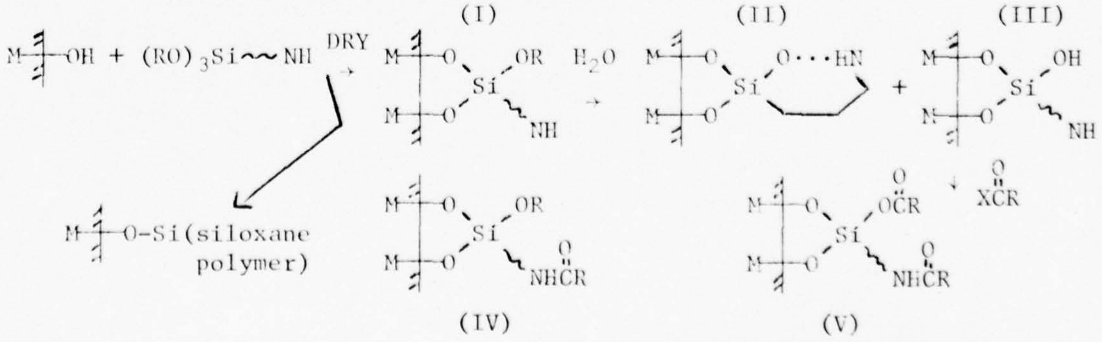
We previously reported that carbon electrodes could be chemically modified with organosilanes. We continued research on these reactions for a period and determined that the organosilane functionalities on carbon electrodes were variously either unreactive or too unstable to be useful for chemical modification of carbon. We therefore set aside the silanization approach to carbon chemical modification and turned to Reaction 3, introduced by Miller, but chose vitreous carbon as the electrode substrate. The choice of vitreous carbon was important from the standpoint of ultimately avoiding much interfering adsorption phenomena. An extended series of experiments proved necessary to dissect the intricacies of inducing Reaction 3 to proceed in a routine manner. We have achieved a more-or-less routine reaction sequence in which

'R" is an aminotetraphenylporphyrin. We are able to observe the electrochemistry of the aminotetraphenylporphyrin reduction to its anion radical and dianion on this chemically modified vitreous carbon surface. The tetraphenylporphyrin electrochemistry is chemically and electrochemically reversible and a combination of a control and ESCA experiments provided a conclusive proof that the coupling of the tetraphenylporphyrin to the vitreous carbon was via the amide bond linkage and not through absorption. This example provides the first example of a reversible redox function immobilized on a carbon electrode.

Inasmuch as the tetraphenylporphyrin moiety bound to vitreous carbon contains no metal, it was of interest to investigate the <u>in situ</u> metallization of the porphyrin in an attempt to prepare a family of immobilized metalloporphyrins. Inasmuch as metalloporphyrins are known electrocatalysts for a variety of electrode reactions, we have focussed a series of experiments in this direction. In this paper, we show that a Co(II) can be readily inserted into the tetraphenylporphyrin ring, and the electrochemistry of the Co(II → I) reaction can be observed in a chemically and electrochemically reversible manner. For both the tetraphenylporphyrin and its metallized variant, the potentials of the surface redox process and the analogous solution species are quite similar to one another. This observation of thermodynamic similarity of surface-coupled redox functions with analogous solution functions, plus the observations noted above on metal oxide electrodes, makes our thesis of predictive redox surfaces more than a simple hypothesis.

(6) ESCA and Electrochemical Studies of the Silanization of Metal Oxide Electrodes (NSF, MRL-NSF)

Through an extended series of experiments largely based on ESCA observations, we have evolved a model for alkylamine silane reactions on metal oxide electrodes which is shown below



The salient features of this model are: (i) Silanization under anhydrous conditions, and maintenance of anhydrous conditions in the post-silanization state can yield structures in which "dangling" (uncoupled) alkoxy groups remain intact (Structure I). (ii) Reaction of Structure I under anhydrous conditions with an amidization reagent yields Structure IV, which is the form yielding the "cleanest" electrochemical behavior of the functionality "R." (iii) Contact of Structure I with moist air or water washing, inactivate the portion of the alkylamine group toward further reaction, most likely by formation of a cyclical, hydrogen-bonded structure such as II. Some of the amine groups remain reactive (III), and these can undergo amidization reactions with a reagent in a similar manner to such groups in Structure I. However, the SiOH groups can also apparently enter into coupling reactions when acid chloride reagents are used to yield silicate esters as shown in Structure V. These esters are not highly stable in the chemical sense, but do give rise to observable electrochemical features which complicate the overall interpretation of electrochemical behavior.

A detailed picture of surface silanization chemistry such as this is important both from the standpoint of reaction strategy in preparing chemically modified electrodes, but also from the standpoint of understanding silanization chemistry in other areas. Silanization reactions are used in a very widespread way, including composites, in pharmaceutical preparations, in bonded chromatographic phases, in organic solid state synthesis, and in enzyme engineering. Our study is the most detailed ESCA application to date to silanize surfaces. A manuscript describing the scheme in Reaction 5 is in preparation.

(7) Stereochemistry of Electron Transfer Reactions (NSF)

As noted above the question of the electron transfer mechanism is a very important one, and two models can be presented. One of these is the "floppy model" as expressed in Reaction 2. The floppy model is amenable to stereochemical investigation through preparation of surface structures in which the O/R groupings are attached bifunctionally, e.g. attached to more than one alkylamine silane chain. In order to establish the appropriate chain length, we carried out a set of "molecular ruler experiments" using a bifunctional reagent and an ESCA element tagging scheme which demonstrated that in the series

$ClCO(CH_2)_nCOCl$, a chain length corresponding to n = 0 is too short for 2-site coupling, where there is a chain of length for n = 4 yields approximately 50% bifunctional coupling. This "molecular ruler experiment" (which is being prepared for publication) gives insight to the proper choice of bifunctional redox reagents to employ an investigation of the stereochemistry of electron transfer. We are now in the course of carrying out experiments with ferrocene and tetrathiofulvalene which contain either one or multiple carboxylic acid groups for amidization-coupling to alkylamine silane surfaces. Preliminary indications are that bifunctional coupling occurs with the TFF molecule, which yields a surface structure of sufficient rigidity that electron transfer with the electrode surface does not take place. This preliminary data provides strong circumstantial evidence for the validity, and necessity, of the "floppy model," Reaction 2. The stereochemical features of chemically modified electrode surfaces will see intensive attention over the next research year.

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Graduate Student: C. S. Kuo (MRL-NSF)

Publications:

D. Schroeer and R. L. Lambe, "Mössbauer Linewidth for Eu^{2+} as an Impurity," Bull. Am. Phys. Soc. 22, 471 (1977).

D. Schroeer, "Moessbauer Studies of Rare-Earths in CaF_2," Bull. Am. Phys. Soc. 22, 494 (1977).

Summary of Research Activities:

(1) The Diamagnetic Dilution of Hematite; MRL-NSF.

Changes in the Morin transition temperature in α-Fe_2O_3 doped with Co has been measured. The relative influences of magnetic dilution and of electrostatic lattice-spacing changes can be separated.

(2) Rare-Earths in Alkali-Earth Difluorides; MRL-NSF.

The Moessbauer linewidth of Eu^{2+} as an impurity dopant increases monotonically with decreasing doping level. This line broadening is due to relaxation effects induced by spin-spin interactions. This relationship can be calibrated for any given host matrix. Then, if the europium is homogeneously distributed throughout a host matrix, the observed linewidth can be used to determine the doping level. Alternatively, if the doping level is known, then the linewidth can give information about the extent of europium clustering in non-homogeneous samples, as during annealing processes. The possibilities of this linewidth-analysis technique will be illustrated by the example of Eu doped into CaF_2.

The Moessbauer isomer shifts of Eu^{151} in SrF_2 and BaF_2 have been studied as a function of doping level. The observed effects are not due to electrostatic effects in the lattice but rather due to different oxygen-stabilized europium-defect configurations.

Oxygen-stabilized trivalent dysprosium defect configurations have been observed for Dy^{161} in CaF_2.

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L. Cain (MRL-NSF)
G. Holmberg (MRL-NSF)

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S. Horan (MRL-NSF, NSF)

Other Supporting Agency: NSF

Publications:

G. Holmberg and L. Slifkin, "ESR of Ni^{2+} in AgCl and AgBr," accepted by J. Phys. C: Solid State.

A. Batra and L. Slifkin, "Point Defects in the Silver Halides," accepted by Jnl. de Physique.

L. Slifkin, "Diffusion et Conductivité dans les Cristaux Ioniques Simples," Proc. 19th Coll. de Métallurgie (to appear, 1977).

A. Batra and L. Slifkin, "A Study of the High-Temperature Transport Anomaly in AgBr, by Diffusion of Na Tracer," accepted by J. Phys. Chem. Solids.

L. Slifkin, "Saclay Conference on Diffusion in Condensed Media," ONR-London Conference Report C-33-76 (1976).

L. Slifkin and J. Shulman, "Lattice Defects in Ionic Crystals: Rept. of the 1976 Berlin Conference, ONR-London Conference Report C-37-76 (1976).

Summary of Research Activities:

(1) Single vacancies and vacancy pairs in AgBr -- a reanalysis of the earlier data; MRL-NSF, NSF.

A. Batra and L. Slifkin

The data on self-diffusion of ^{82}Br in pure and heavily-doped AgBr were previously analyzed, using the Aboagye-Friauf temperature-dependent activation energy for the formation of a Frenkel defect $H_f(T)$, to obtain contributions to anion mass transport by single vacancies and vacancy pairs. The analysis indicated virtually no contribution from the pairs at high temperatures! More reliable $H_f(T)$ have now been obtained from our own data on sodium-diffusion in intrinsic AgBr, and the use of these values gave Arrhenius-type contributions for both single vacancies and vacancy pairs over the temperature range 360-410°C. The activation energy, 1.70 eV, and pre-exponential factor 447 cm^2/sec for the pairs appear normal. The corresponding values of 3.47 eV and 1.1×10^{16} cm^2/sec for the single vacancies are certainly anomalous, and one is tempted to associate this unusual behavior with the extensive Frenkel disorder present in AgBr at high temperatures. At this time, however, this phenomenon still remains a puzzle.

(2) Diffusion and ionic conductivity - AgCl:In; MRL-NSF, NSF

A. Batra and L. Slifkin

The study on the diffusion of indium in AgCl had yielded an activation energy of 1.04 eV and a pre-exponential factor of 3.6×10^{-2} cm^2/sec below about 385°C, and 1.19 eV and 5.1×10^{-1} cm^2/sec above. The activation energy in the lower-temperature region agreed with that obtained by Frisch et al. (Ber. Bunsenges Phys. Chem. 77, 513 (1973)), although their diffusion coefficients are a factor of two lower.

The question that has to be answered is whether indium diffuses in a divalent or a trivalent charged state. For this purpose, ionic conductivity as a function of temperature was measured on two samples. The effects of precipitation became evident at about 160°C for the sample containing about 90 ppm of indium (chemical analysis value by Johnson-Matthey). This result contrasts with the room-temperature solubility of 250 ppm reported by Frisch et al. These authors also claim the indium ion to be divalent. There is not a long enough association region in our data to determine a good value for the association energy, but if one fits the meagre data available to the conventional Lidiard-Debye-Huckel model involving divalent cations, a value of approximately 0.31 eV may be obtained for the solute-vacancy binding energy. This value is about the same as that for other divalent cations in AgCl. It would therefore indicate that either indium is present as the divalent ion or else that a second vacancy is in equilibrium with a In^{3+}-vacancy complex.

(3) Diffusion of yttrium in AgCl; MRL-NSF, NSF.

A. Batra and L. Slifkin

In a search for a cation which diffuses as a trivalent ion in AgCl, yttrium was tried. This ion has been claimed by others to diffuse as Y^{3+} in NaCl. Initial runs with an ambient atmosphere of chlorine proved unsuccessful, presumably due to the formation of an oxychloride of yttrium. However, runs in hydrogen chloride resulted in significant tracer penetration. The data were obtained over the temperature range 377-443°C. The penetration plots, excepting that at the highest temperature, showed an initial turn-up which became progressively worse as the diffusion temperature was lowered. This might have been caused by the low solubility of yttrium in AgCl. However, the long gaussian tail regions in the penetration plots for the data reported here give satisfactory values for the diffusion coefficients. An activation energy of 0.92 eV and pre-exponential factor of 10^{-2} cm^2/sec were obtained. The activation energy here is similar to that for the divalent alkaline-earth ions. Alternatively, if yttrium diffuses as Y^{3+}, the increase in the solute migration energy could have been compensated by the large Y^{3+}-vacancy binding energy.

(4) Frenkel Defects in Mixed Silver Halides; MRL-NSF.

L. S. Cain, H. Manning, and L. Slifkin

The ionic conductivities of mixed AgCl/AgBr, AgBr/AgI, and AgCl/AgI crystals are being measured. The major interests of this study are the dependence of the conductivity and the energies of formation and migration of the native Frenkel defects on composition. These parameters will be obtained by computer analysis of the conductivity as a function of temperature for each crystal. Results will hopefully show how the local lattice strains in the solid solution specimens may affect the above defect parameters.

Measurements on a complete set of mixed AgBr/AgCl crystals have been completed. The two terminal constituents as well as samples with 20, 40, 50, 60, and 80 mole % AgCl have been measured from 300°C to -50°C. The high temperature conductivity decreases monotonically with concentration on going from AgBr to AgCl. Preliminary analysis of the slope of the high temperature (intrinsic) portion of $\ln(\sigma T)$ versus 1000/T indicates that the activation energy is constant for AgCl concentrations to 40 mole % in AgBr, while for higher AgCl concentrations this quantity begins to grow, changing by a total of about 20%. More precise values, as well as values for the individual enthalpies, will be obtained from the computer analysis of the results.

Measurements of the conductivity of mixed AgBr/AgI and AgCl/AgI are also underway. Crystals of AgBr and AgCl with less than 2 mole % AgI will be investigated for the same effects mentioned above. Preliminary measurements of AgBr/AgI samples of 7.5 mole % AgI show an extrinsic conductivity higher by two orders of magnitude than that of pure AgBr at room temperature. Such large effects cannot possibly be due to impurities. The conductivities at high T (250°C), on the other hand, are similar in magnitude to those of AgBr. The conductivity of a 2 mole % AgI sample has the same order of magnitude as that of AgBr both at room and high temperatures. All these conductivities are history-dependent, presumably due to the aggregation or precipitation of the AgI, since we are above the solubility limit of room temperature.

(5) Ionic Conductivity of Beta-Alumina; MRL-NSF

L. S. Cain and L. Slifkin

Experiments are underway to measure the effects of various compositional and microstructural parameters on ion transport in the superionic conductor beta alumina. Ionic conductivity measurements are being performed on single crystal and polycrystal specimens as a function of temperature, frequency, mobile cation composition, and preparation history. The studies actually involve the measurement of the complex electrical impedance. From these dispersion curves we hope to (1) investigate the changes in conductivity caused by mixed mobile cations, i.e., Na-K and Na-Ag, in order to check the theories of ion transport in these materials; and (2) determine the effect of grain size and other parameters due to preparation history. The equipment necessary to begin these measurements is now available and single crystals and polycrystals are on order. Preliminary measurements on medium-density polycrystal samples have indicated that (1) ion exchange is feasible only with very dense samples, (2) measurements of the bulk electrical properties must be done at very high frequencies, (3) the conductivity of sintered samples is two to three orders of magnitude below that of single crystals, and (4) a difference in ideal density of 0.15% causes a difference of two orders of magnitude in the conductivity.

(6) ESR Studies of Defects in Silver Halides and Insulating Oxides; MRL-NSF, NSF

G. E. Holmberg and L. M. Slifkin

In AgCl:Ni at 4 K a narrow line was observed in our earlier work which was superimposed on the 110 G width isotropic ESR line from divalent nickel in a substitutional site without a nearby charge compensating vacancy (octahedral symmetry). This narrow line was not observed at low microwave powers, but increased rapidly in amplitude with microwave power at high microwave power levels, which suggested that it was due to a double quantum transition between $M_S = \pm 1$ states of the nickel ion. We have analyzed superhyperfine structure present on this line and find that the structure is consistent with a nickel interacting with six nearest neighbor chlorine nuclei. The superhyperfine structure for H along [100], [111], and [110] can be fit by adding a term to the nickel spin Hamiltonian: $\sum_{n=1}^{6} [A^n S_z I_z^n + B^n(S_x I_x^n + S_y I_y^n) - g_n \beta_N H \cdot I^n]$ where A^n is approximately 7.35 G and B^n is approximately 2.4 G for ^{35}Cl. Orton *et al.* (Phys. Rev. Lett. 4, 128 (1968)) observed a double quantum transition in MgO:Ni in an octahedral site but saw no resolved superfine structure since the nearest neighbors were oxygen ions with no nuclear spin. In the AgCl:Ni case the nearest neighbor chlorines have a nuclear spin and thereby have superhyperfine interactions with the nickel ion. However, these interactions are larger than expected; a molecular orbital analysis of the nickel-chlorine interactions is being carried out to determine why this is the case. To our knowledge, this is the first observation of resolved superhyperfine structure in a double quantum transition.

Electron and hole trapping experiments have been performed on AgCl:Hg, AgCl:Fe, AgCl:Pd, AgCl:Sn, AgCl:Pb, and AgBr:Pb. In the case of AgCl:Hg, an unexplained ESR signal is developed on illumination with blue light near -100°C. Experiments will be performed to determine if this signal is from Hg^+. Studies on electron and hole trapping at reduced temperatures by AgCl:Fe have been reported by three other research groups, but their results were somewhat contradictory. We are performing additional experiments to try to sort out the discrepancies. A recent paper on AgCl:Pd showed that Pd^{2+} can act as an electron or hole trap in different temperature regions. The behavior of AgCl:Pd near room temperature was not reported, whereas we find that AgCl:Pd exhibits some peculiar photoconductive effects there, depending on the treatment of the sample. We will try to relate these photoconductive effects to minority-carrier trapping by Pd^{2+} ions. So far, electron and hole trapping investigations on AgCl:Sn, AgCl:Pb, and AgBr:Pb have yielded no evidence of the dopant changing to a paramagnetic valence state upon illumination of the sample with blue light.

In conjunction with K. H. Lee of Crawford's group, a new paramagnetic defect, developed when MgO:Ga is subjected to gamma-irradiation, has been shown to be Ga^{2+} in an octahedral site. An accurate analysis is underway, but a preliminary estimate places the Fermi contact interaction between the Gallium 4s electron and its own nucleus at approximately 8.5 GHz for ^{69}Ga.

(7) Internal Friction Study of Impurity-Dislocation Interactions in AgBr; NSF, MRL-NSF

S. Horan and L. Slifkin

We are continuing an internal friction study of the dislocation-defect interactions in single crystals of silver bromide doped with precise, small amounts of cadmium and strontium. During the last year, we have systematically investigated anomalies in the response of the strontium-doped crystals to small harmonic stresses. For limited ranges of temperature (37-100°C.) and impurity concentration (75 ppm and less), we have been able to induce discontinuities in the internal friction and Young's modulus as a function of stress and temperature. Such discontinuities are without precedent.

Present theories postulate dislocation oscillations analogous to a vibrating string within a viscous medium. Impurities and other defects bound to the dislocation provide nodal points ("pins") which can be activated thermally or by applied stress. In general pins are capable of diffusion normal and parallel to the dislocation core. Strontium is an unusual impurity since it has high mobility in AgBr and presumably a high binding energy to dislocations as well. Therefore it is possible that strontium-containing pins would segregate to dislocations and would preferentially migrate along dislocations for form strontium-rich pinning aggregates.

Concurrent ionic conductivity measurements of samples containing 50 ppm Sr impurity or less suggest the formation of aggregates. Long-term monitoring of strain-independent internal friction suggests an increase over time at all temperatures, in spite of intermittent annealing which lowers the total dislocation density of the specimen. These data are consistent with formation of Sr aggregates. Superimposed on this background there may be two phases of equilibrium dislocation-pin structure, each of which is stable over a characteristic stress-temperature range.

Within the accuracy of the present experiment, the change in decrement with strain amplitude is discontinuous and is accompanied by a discontinuous change in the Young's modulus. Extensive data on the temperature, stress, and hysteresis characteristics of the discontinuity indicate a discontinuous change in the distribution and a simultaneous reduction in the number of pins along the dislocation core. These data are consistent with a model predicting a critical condition for pin aggregation.

Further investigations of this effect are now underway to determine response of the discontinuity to variation in the ratio of total impurity content to total dislocation density.

Faculty Member: David G. Whitten
Professor of Chemistry

Research Associates: G. Sprintschnik (MRL-NSF)
F. R. Hopf
P. R. Worsham

Graduate Students: P. J. DeLaive
R. E. Jerry
J. M. Smith
B. E. Horsey
R. H. Schmehl

Other Supporting Agencies: National Science Foundation
National Institutes of Health
U. S. Army Research Office

Publications:

D. G. Whitten, F. R. Hopf, F. H. Quina, G. Sprintschnik and H. W. Sprintschnik, "Photochemistry of Organic Chromophores Incorporated into Fatty Acid Monolayers," J. Am. Chem. Soc., accepted for publication.

F. A. Carroll and D. G. Whitten, "Multiplicity of the Reacting State in the Photoaddition of Carbon Tetrachloride to Anthracene," J. Phys. Chem., 80, 2046 (1976).

J. Bolt, F. H. Quina and D. G. Whitten, "Solid State Photodimerization of Surfactant Esters of Cinnamic Acid," Tetrahedron Letters, 30, 2595-98 (1976).

F. R. Hopf and D. G. Whitten, "Photochemical Reactions in Organized Monolayer Assemblies. 5. Photochemical and Thermal Reactions of Reactive Intermediates Formed by Ligand Photoejection in Ruthenium Porphyrins," J. Am. Chem. Soc., 98, 7422 (1976).

F. H. Quina and D. G. Whitten, "Photochemical Reactions in Organized Monolayer Assemblies. 4. Photodimerization, Photoisomerization, and Excimer Formation with Surfactant Olefins and Dienes in Monolayer Assemblies, Crystals, and Micelles," J. Am. Chem. Soc., 99, 877 (1977).

G. Sprintschnik, H. W. Sprintschnik, P. P. Kirsch, and D. G. Whitten, "Preparation and Photochemical Reactivity of Surfactant Ruthenium(II) Complexes in Monolayer Assemblies and at Water-Solid Interfaces, J. Am. Chem. Soc., accepted for publication.

Summary of Research Activities

(1) Photochemistry at Monolayer-Solution Interfaces: Photochemistry of Surfactant Metal Complexes in Monolayer Assemblies and at a Monolayer-Solution Interface; NSF-MRL, National Institutes of Health.

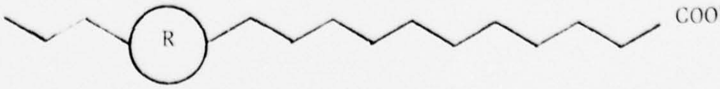
G. Sprintschnik and D. G. Whitten

The synthesis of several surfactant analogs of tris (2,2'-bipyridine)ruthenium(II)$^{2+}$ has been developed. The photochemical reactivity of these surfactant complexes has been investigated in spread films, monolayer assemblies, micelles and at a monolayer assembly-water interface. It has been found that highly purified samples of the dioctadecyl ester of (4,4'-dicarboxy-2,2'-bipyridine)bis(2,2'-bipyridine) ruthenium(II)$^{2+}$ are inactive as catalysts for the photocleavage of water in monolayer assemblies. This is contrary to our previous findings which employed a sample of the surfactant complex which has now been shown to contain several impurities, including other surfactant ruthenium(II) complexes. We have found that the properties of films and monolayer assemblies of these complexes are quite sample sensitive even when different samples of high indicated purity are employed. The failure of the highly purified complex to serve as a catalyst appears partially due to a light-induced destruction of assemblies irradiated in contact with water which is due at least in part to a photohydrolysis of the ester group.

(2) Photochemistry of Organic Chromophores Incorporated into Fatty Acid Monolayers; National Institutes of Health, National Science Foundation.

R. Jerry, P. Worsham, M. Richter, and D. G. Whitten

The synthesis of several photochemically and spectroscopically active hydrocarbon groups and sulfur complex incorporated into a surfactant fatty acid derivative has been developed. Most of the molecules have the structure indicated below:



where the reactive group, R, is incorporated into the hydrophobic portion of a surfactant molecule. The photochemistry of these molecules is being investigated in several organized media including monolayer film and assemblies and micelles. In collaboration with Professor R. W. Murray the "ESCA" of several surfaces coated with monolayers of these substances is being examined.

(3) Photochemistry of Hydrophobic Metal Complexes in Solution; National Science Foundation, National Institutes of Health.

P. J. DeLaive and D. G. Whitten

In connection with the studies outlined in (1) above several metal complexes (mostly ruthenium(II)) have been prepared in which the charged complex is effectively completely surrounded by a hydrophobic shield. These complexes are water insoluble but quite soluble in polar and non-polar organic solvents. The light-induced electron transfer reactions of several of these complexes have been studied. Quenching of the complex excited states by both electron donors and electron acceptors has been observed. However, the rates are in several cases somewhat slower, especially when positively charged quenchers are used and the hydrophobic groups are large. In a few cases the back reactions following light induced electron transfer are slowed down so that high energy products can be stored. These reactions appear quite promising as a means of converting light energy into high energy but isolable chemical products.

Crystal Growth Facility
Supervisor: L. M. Slifkin
Professor of Physics

Personnel: Charles B. Childs, Manager (MRL-NSF)

Other Supporting Agency: National Aeronautics and Space Administration, Langley Research Center

Publication:

C. B. Childs, "High Purity Silver Bromide Crystals Containing Less than Several Parts per Billion of Iodide," accepted by J. Crystal Growth.

Summary of Research Activities:

(1) Silver Halides

A variety of pure and specially doped silver halide crystals have been grown for various studies. The table below shows the distribution of these crystals during 1 June 1976-31 May 1977.

Person	Institution	Crystal	Dopant
Buck, R.	UNC, Chemistry	AgBr	Ag_2S
Cain, L.	UNC, Physics	AgBr	AgI
		AgCl	AgI
Corish, J.	University College Dublin, Republic of Ireland	AgBr	Cd
Eachus, R.	Eastman Kodak Co.	AgBr	None
Holmberg, G.	UNC, Physics	AgBr	Ni + I
		AgBr	Pb
		AgBr	Ni + Pb
		AgCl	Fe + Ni
		AgCl	Ni + Pb
		AgCl	Pb
		AgCl	Sn (30 ppm)
		AgCl	Sn (400 ppm)
		AgCl	Sn (500 ppm)
Horan, S.	UNC, Physics	AgBr	Cd (100 ppm)
		AgBr	Cd (440 ppm)
		AgBr	Ni
		AgBr	Sr (20 ppm)
		AgBr	Sr (30 ppm)
		AgBr	None

Person	Institution	Crystal	Dopant
Nicklow, R.	Oak Ridge National Laboratory	AgBr (2 of)	None

(2) Potassium Bromide

Four potassium bromide crystals have been grown by the Czochralski method using a rotation rate of 3 rev/min and a pulling rate of 1 cm/hour. Each crystal had a mass of ∿ 60-70 gms, a length of ∿ 10-12 cm and a cross section of ∿ 2 cm^2. The pure crystals had an OH^- content less than the minimum detection limit of ∿ 0.6×10^{-9} mole fraction. These crystals were grown for research by the group headed by J. Crawford.

Thin Film Facility
Supervisor: Earl N. Mitchell
Professor of Physics

Summary of Research Activities:

This facility provides sample preparation facilities for general thin film work in the departments involved in the MRC program.

This facility at the present time contains the following major items of equipment:

(1) One Hitachi HU 11A electron microscope, (2) Two consolidated CV-14 evaporation facilities, (3) One Ultek 12-inch ultrahigh vacuum evaporation facility, (4) One Veeco Ga-4 gas analyzer, (5) One CVE-14 evaporation facility, (6) One MICRO-MATIC precision wafering machine, (7) One Veeco electron beam evaporation facility, (8) One Talysurf 4 Surface Profiler, (9) One EAI - .5 KW, 13.56 Mhz RF sputtering power supply.

Instrumental capabilities are available for the fabrication and evaluation of thin films of most inorganic materials that can be made by avaporation in vacuum. Films (either polycrystal or single crystal) have been made by evaporation from heated boats and filaments or by electron bombardment of the source material. The most experience has been accumulated with metal films (tin, lead, silver, gold, nickel, iron, aluminum, chromium and indium for example) but several insulators have been fabricated (SnO_2, SiO_2, MgF_2, and $Pb(NO_3)_2$ for example). The capability of fabricating films by RF sputtering has been added. This unit is being used for form organic films by RF polymerization and to form thin films of conducting glasses.

Specimens have been fabricated on a variety of substrates though the metals, alkali halides, glass, quartz, mica, and carbon have been used most frequently. Specimens of thicknesses ranging from about 50 angstroms to 200,000 angstroms have been fabricated.

Structural evaluation has been performed using electron microscopy, electron diffraction, x-ray diffraction and resistivity measurements. Surface quality has been evaluated using multiple beam interferometry, optical microscope techniques, and surface profile techniques. Specimen thickness has been determined by direct weighing, multiple beam interferometry, and surface profile measurements.

Many different film structures for research applications have been fabricated of a wide variety of materials. Some of them expressed in terms of function are: mirrors, nuclear targets, specimens for channeling studies, quartz transducer electrodes, experimental tunnel diodes, minigrid electrodes for electrochemical studies, conduction electrodes for organic films, particle detector electrodes, diffraction grating coatings, Mössbauer samples, thin films for electron photoemission studies of adulterated surfaces, polymeric films for photovoltaic studies, evaporated thermocouples.

This past year considerable effort has been expended in making polymeric films of tetramethylsilane (TMS) by RF polymerization of the monomer in a mixture of argon and the monomer. This unit has also been used to prepare prototype samples of conducting (NESA) glasses. The principal local interest in these glasses is related to surface catalysis studies performed in the Chemistry Department.

Other specific activities which have occurred this past year are enumerated below:

1. Electrode preparation for superconductivity studies.
2. Films of lanthanium copper and lanthanum gold for superconductivity studies.
3. Mo, Te and Pb isotope targets on carbon for nuclear studies.
4. Preparation and evaluation of tin oxide glasses.
5. Vapor plating of ion cyclotron resonance cells for mass spectrometry of organic molecules.
6. Consultant to chemists on preparation of clean lithium films.
7. Shadow casting and replication for electron microscope studies of polymers.
8. Preparation of metal halides by evaporation.
9. Electron microscope evaluation of silver halide microcrystals.

10. Evaporation of Li films using a Knudsen cell.
11. Electron beam preparation of films of SiO_2, SnO_2, and Mo.
12. Preparation of oxygen doped Al films.
13. Consultation on the preparation of Al-Pb tunnel junctions for inelastic electron tunneling studies of organic molecules.