**CRYOGENICS AT THE UNIVERSITY OF VIRGINIA**

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**ABSTRACT**
See reverse side.
20. ABSTRACT

This is the final report on a contract which has provided helium gas for the Liquid Helium Facility at the University of Virginia. This facility is equipped with a Collins helium liquifier and recovery system and supplies liquid helium for a wide variety of research requiring cryogenic techniques in the Departments of Physics and Chemistry and in the School of Engineering and Applied Science. The largest use is centered on solid state and low temperature physics research connected with electronic properties of materials, superconductivity, magnetism, electronic devices and liquid helium. In addition a number of instruments operating at liquid helium temperatures are used for a broader range of research in many departments and at the National Radio Astronomy Laboratory. Seventeen faculty members presently use liquid helium as a major part of their research programs and others utilize instruments and cryostats on an available basis for some aspects of their research.

Brief summaries of research assisted by this ONR support are given below together with listings of recent publications reporting results of the research.
INTRODUCTION

This is the final report on contract N00017-75-C-0845 which has provided helium gas for the Liquid Helium Facility at the University of Virginia. This facility is equipped with a Collins helium liquifier and recovery system and supplies liquid helium for a wide variety of research requiring cryogenic techniques in the Departments of Physics and Chemistry and in the School of Engineering and Applied Science. The largest use is centered on solid state and low temperature physics research connected with electronic properties of materials, superconductivity, magnetism, electronic devices and liquid helium. In addition a number of instruments operating at liquid helium temperatures are used for a broader range of research in many departments and at the National Radio Astronomy Laboratory. Seventeen faculty members presently use liquid helium as a major part of their research programs and others utilize instruments and cryostats on an available basis for some aspects of their research.

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SUMMARIES

1. Magnetic Studies of Transition Metal Ions Coordinated to Proteins and to Prosthetic Groups - Arthur S. Brill, Department of Physics

   Interactions among transition metal ions, (e.g. iron, copper), protein and prosthetic groups, and water are being studied experimentally by means of magnetic and optical techniques. Spectroscopic and other properties of the ions obtained from these measurements are being used to develop quantum mechanical models of electronic structure which include the effects of symmetry and covalency. The determination of hyperfine interactions, including
effects upon linewidth, are used to identify neighboring atoms and to estimate distances necessary in describing the geometric structures of metal ion binding sites. This information is expected to contribute to our understanding of those features of certain metal ions, and of protein and prosthetic groups, which are important for biological function.

Recent Publications:


2. Electronic Properties of Metals and Alloys in High Magnetic Fields - Robert V. Coleman, Department of Physics

Measurements of quantum oscillatory phenomena at high magnetic fields are being made on single crystals of layer structure dichalcogenides and trichalcogenides. DC transport measurements including Hall effect, magnetoresistance and superconducting anisotropy are also being carried out. Both Shubnikov de Haas and de Haas van Alphen oscillations are being measured using ac modulation and harmonic detection. These techniques are being extended for use on the high field Bitter solenoids at the National Magnet Laboratory. Charge density wave formation in the chalcogenides are being studied and the effects of organic intercalation and pressure on the CDW are being followed by measuring the quantum oscillatory phenomena. DC susceptibility, Hall effect and magnetoresistance as a function of temperature are also being used to correlate results with CDW formation. The various types of transport measurement are also being
made on the ferromagnetic metals iron and cobalt with possible extension to ferromagnetic alloys.

Recent Publications:


3. **Spectroscopy of Surface Adsorbed Molecules** - Robert V. Coleman, Department of Physics

Inelastic electron tunneling spectroscopy (IETS) is being used to study the vibrational spectra of molecules adsorbed on oxide surfaces. Selected studies covering the entire range of molecular weight is being undertaken, although special emphasis is put on substituted ring compounds of light to intermediate weight. Analysis of the IETS spectra and mode intensities are used to study surface reactions involving specific substituents, changes in the surface interactions due to substitution, bond polarizabilities, orientation on the surface, electron-phonon coupling strength, charge state, and molecular symmetry on the surface. In order to aid in this vibrational mode analysis experiments using low energy electron diffraction (LEED) and X-ray photoemission (XPS-ESCA) will be developed on the same molecule-substrate systems to give complementary information on orientation and chemical state of the adsorbed molecules. Applications of IETS techniques to molecular-surface interactions, photochemistry, UV radiation damage, trace analysis and molecular structure analysis will be explored.

**Recent Publications:**


4. **Experiments Using Weakly Linked Superconductors** - Bascom S. Deaver, Jr., Department of Physics

The objectives of the research are to investigate some fundamental
properties of superconductors and to use weakly linked superconductors for new types of measurements. The research includes studies of fluxoid quantization in unusual materials and geometries and several types of measurements to investigate the kinematics of the Josephson oscillations in superconducting weak links. Also magnetic measurements with superconducting devices to achieve high sensitivity and fast response time are being used to study the unusual magnetic properties of sodium-ammonia solutions and to observe optically induced paramagnetism in amorphous semiconductors.

Recent Publications:


R. Rifkin, D. A. Vincent, P. K. Hansma and B. S. Deaver, Jr., "Detailed Measurements of the Response of an rf SQUID in the Regime \( \Phi_o/2\pi \), IEEE Transactions on Magnetics MAG-11, 873.


5. Superconducting Electronics - Bascom S. Deaver, Jr., Department of Physics and Robert J. Mattauch, Department of Electrical Engineering

This research is concerned with superconducting devices using the Josephson effects for millimeter wave mixing and for potential new types of infrared detectors and optically controlled fast digital devices. Work is being done on two topics: 1. Fabrication, characterization and testing of variable thickness superconducting microbridges as mixers at frequencies greater than 100 GHz. 2. Studies of Josephson devices fabricated on semiconductor substrates, particularly of the interaction of the Josephson oscillations with impurity levels and collective modes at the superconductor-semiconductor interface. This work involves a close collaboration between the Semiconductor Devices Laboratory directed by Professor R. Mattauch of the Electrical Engineering Department and the low temperature physics research group directed by Professor B. Deaver of the Physics Department.

Mattauch and his colleagues have developed and manufacture the best
available Schottky barrier mixers for the 100-200 GHz range. They supply them to the National Radio Astronomy Observatory (NRAO), Jet Propulsion Laboratory and other laboratories around the world for radio astronomy, molecular spectroscopy associated with atmospheric and stratospheric research and millimeter wave communications. They have demonstrated expertise in microcircuit design and development and in the fabrication and production of devices for users.

For more than ten years the group directed by Deaver has been studying the physics of Josephson devices. They have fabricated and tested nearly every type of weakly linked superconductor with recent emphasis on Nb thin film bridges, characterized them by dc, rf and microwave measurements, have worked extensively with the various models for Josephson devices, and originated a simple phenomenological model for the frequency dependence of the Josephson current in weak links. They are using a variety of Josephson devices for studying the magnetic properties of materials, and are developing the technique of I-V spectroscopy for studying the interaction of a weak link with its surroundings.

During the last two years an informal collaboration has evolved between the two groups to bring their combined expertise to bear on attempting to produce Josephson mixers with characteristics superior to those of Schottky devices.

The potential of I-V spectroscopy made possible by on-line data processing is being applied to investigate the extremely interesting possibilities offered by the interaction of a Josephson device with a semiconductor substrate and for studying the interaction between the superconductor and semiconductor surfaces. Again this research depends on close collaboration between the two groups both for fabrication and
for their combined skills with the physics of semiconductors and superconductors.

Recent Publications:


6. Superconducting Susceptometry System - Bascom S. Deaver, Jr., Department of Physics and Ekkehard Sinn, Department of Chemistry

Superconducting devices are now making possible many new types of magnetic measurements, and recently general purpose instruments using them have become available for measuring the magnetic properties of materials. Several major items of equipment are being added to a new superconducting susceptometer to create a system with superlative characteristics of sensitivity, response time, versatility, and capacity for high productivity. The system is being used in a cooperative effort between groups in Physics and Chemistry for work on several important current research topics including the relationship between structure and magnetism in some compounds containing two or a few transition metal atoms, a search for cooperative phenomena in polymeric complexes with various metal atoms and in conjugated organic compounds, observation of magnetic changes during chemical reactions, and a new type of spectroscopy of excited states by measuring optically excited paramagnetism using a tunable laser.
Recent Publications:


7. Properties of Liquid \(^{4}\)He - George B. Hess, Department of Physics

On account of the possibility of internal counterflow, a complete thermodynamic description of liquid \(^{4}\)He II must include a third independent variable such as \(w^2\), where \(\dot{w} = \dot{v}_s - \dot{v}_n\) is the difference between the superfluid and normal fluid velocity. The dependence of the fractional superfluid density \(\rho_s/\rho\) on \(w^2\) is an independent equation of state, and cannot be inferred from thermodynamic data for \(w=0\). We have recently obtained the first experimental data on the dependence of \(\rho_s\) on \(w^2\), by studying the amplitude dependence of the resonant frequency of a Helmholtz resonator in the regime of vortex-free superfluid flow. We are making a systematic study of this dependence, particularly in the region near the transition temperature \(T_\lambda\), where problems remain in the theory of the superfluid density.

Recent Publications:


8. **Superconducting Particle Detector** - Robert R. Humphris, School of Engineering and Applied Science

A superconducting low-energy thin film particle detector is being developed. Detecting surfaces are fabricated by depositing a niobium or tin-indium film on a glass cover slide and scratching or etching to obtain a \( \sim 1 \) micron strip. At a point just below the \( T_c \) and at current densities near \( I_c \), pulses due to neutral or charged Ar and He particles have been observed. Particle energies are from 150 eV to 800 eV with a detector response of near 100% efficiency.

**Recent Publications:**


9. **Cold Balance** - Robert R. Humphris, School of Engineering and Applied Science

AC losses in superconducting magnets are being investigated in the U.Va. "Cold Balance" facility, sponsored by NASA-LRC. A previous investigation at this facility indicated using very low winding densities in order to obtain low ac losses in gradient coils wound of multifilamentary composite superconductors. Scaling laws are currently being examined by testing large gradient-type coils in an attempt to improve the economic possibility of large-scale wind tunnels utilizing magnetic suspension techniques.

**Recent Publications:**

10. Nonequilibrium Superconductivity—James L. Paterson, Department of Physics

A series of experiments is being done on nonequilibrium superconductivity using thin-film, double tunnel junctions. These experiments measure the quasiparticle energy distribution and chart this distribution as the degree of nonequilibrium (generated by dc tunnel injection) increases. In the weakly-perturbed regime these experiments provide elastic and inelastic branch-mixing times and inelastic scattering times as a function of both energy and temperature. In the strongly-perturbed regime we seek explanations for the recently observed new effects, a first order phase transition and two energy gaps, in the center film.

Recent Publications:


"Energy Dependence of the Branch-mixing Time in Sn-In Alloys," to be published.

"Nonequilibrium Effects in Double Tunnel Junctions," to be published.

11. Magneto-Optical Studies—Paul N. Schatz, Department of Chemistry

We have for some years used magnetic circular dichroism (MCD) spectroscopy to study the electronic structure of relatively simple molecules and ions in solutions and in crystals. This technique has proved a powerful tool which, when used with absorption spectroscopy, is able to give a great deal of additional information about the assignments of transitions, the symmetries and magnetic moments of ground and excited
states, and the magnitudes and nature of vibronic, spin-orbit, inter- and intra-molecular couplings.

In MCD (which is the absorption manifestation of the Faraday effect), one measures the differential absorption of left and right circularly polarized light \((c_L - c_R)\) in the presence of a longitudinal magnetic field. For some time it has been clear that the emission analog of the MCD technique has great potential as a spectroscopic and molecular structure probe. We refer to the phenomenon as magnetic circularly polarized emission (MCPE). Relatively little MCPE work has appeared to date, but there is a rapidly growing interest in this field.

The Chemistry Department, University of Virginia, has a multi-purpose emission spectrometer which, in CPE mode, can measure luminescence dissymmetry factors \([(I_L - I_R)/(I_L + I_R)]\) as small as \(1 \times 10^{-5}\). Furthermore, we are currently setting up a departmental Moletron laser system (UV-14 N\(_2\) laser, DL-14 dye laser, Tektronix ultra high speed transient recorder). Finally, in addition to conventional superconducting solenoids, we have a top-loading split-coil superconducting solenoid and continuous flow cryostat system which permits the "injection" of matrix isolated samples into the magnetic field in such a way that the sample at no time warms above 15° K.

Recent Publications:


P. N. Schatz, "MCD Spectra of Charge-Transfer Transitions: Octahedral Ir\(^{4+}\)," Proceedings of the NATO Advanced Study Institute of Electronic States of


12. Spin State Crossovers of New Spin States - Ekkehard Sinn, Department of Chemistry

High spin ± low spin crossover equilibria occur in many octahedral complexes of iron(III) (S = 1⁺  S = 5₂), iron (II) (S = 0 ± S = 2) and cobalt (II) (S = 1⁺  S = 1₂), and are of considerable biological and physical interest.
The magnetic, spectroscopic and structural properties of such compounds are extremely sensitive to chemical modification, temperature, pressure, counter anions (in the case of cationic complexes), and occluded solvent molecules (either occluded in the lattice or involved in hydrogen bonding with ligand atoms). Intermediate spin states ($S = \frac{3}{2}$ for iron(III) and $S = 1$ for iron(II)) have occasionally been suggested, though only limited supporting evidence was available. The recent unexpected and unprecedented observation of apparent $S = \frac{3}{2}$ states in an $S = \frac{5}{2} \pm S = \frac{3}{2}$ equilibrium in iron dithiocarbamate complexes for which crystal structures were determined (though not at the temperatures where the intermediate spin state predominates), lends weight to the postulate of intermediate spin states in regular six coordinated iron complexes. Preliminary ISR measurements now provide further support. In each case where the molecular structures are known, the observation of $S = \frac{3}{2}$ states coincides with solvent-to-ligand hydrogen bonding.

We are seeking new spin state equilibria and of intermediate spin states as ground or low-lying excited states, and the nature, mechanism and rate of interconversion of the participating spin states in the equilibria, by combining various techniques: bulk magnetic susceptibility, magnetic anisotropy, photon-induced excited state magnetic susceptibility, and solution magnetic susceptibility measurements, and Mössbauer, ESR and NMR spectroscopy, all as a function of temperature; and variable-pressure infrared spectroscopy. The conditions leading to low-lying or ground intermediate spin states are also being investigated. We use solution magnetic susceptibility as a function of pressure (when solubility in a suitable solvent is high enough), and variable-temperature X-ray crystallography
(when suitable single crystals are available), to determine the structural effects of changing the spin state, and relate the structural effects of changing the spin state, and relate the structural properties to the rate and nature of spin interconversion.

Recent Publications:


E. J. Cukauskas, B. S. Deaver, Jr., and E. Sinn, "High Spin—Low Spin Crossover and Antiferromagnetic Interactions in Tris (1-pyrrolidinecarboxy- dithioato) iron (III) and the 4-morpholine (FeM) and dibutyl analogs, effect of recrystallization solvent and crystal structure of FeM nitrobenzene," J. of Chem. Phys. 67, 1257-1266 (1977).

13. Relation between Structure and Magnetism of Poly-nuclear Complexes —Ekkehard Sinn, Department of Chemistry

This involves detailed investigation of the relation between the magnetic interactions and structure of bi- and poly-nuclear transition metal complexes. These investigations will not only improve structural predictions made from magnetic properties and vice versa, but will also permit the elucidation of the mechanism of the magnetic coupling, the rejection or improvement of existing models, and, ultimately, the formulation of an overall model for the magnetism in such systems.

Using the "Metal Complexes as Ligands" method and related (and other unrelated) synthetic procedures, devised and refined by Sinn, it is possible to make polynuclear antiferromagnetic (and some ferromagnetic) systems almost to order (and further improvements seem possible) for the examination of various structural and magnetic problems. Further studies along these lines are being performed using magnetochemistry and X-ray crystallography as the main tools. The results will be interpreted in terms of specific structural features (such as metal environment, metal-ligand-metal
bridging angle, orientation of principal planes) with the intent of solving or contributing to the solutions of the problems outlined.

Recent Publications:

E. M. Boge, D. P. Freyberg, E. Kokot, G. M. Mockler and E. Sinn, "Five- and Six-Coordinated Cobalt(II), Nickel(II), Copper(II) and Zinc(II) Complexes of the Pentadentate Schiff Base Ligands NN'-Bis[(2-hydroxy-5-Y-phenyl)phenylmethylene]-4-azaheptane-1,7-diamine (Y = Chloro or Methyl) and NN'-Bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine", Inorg. Chem., 16, 1655 (1977).


E. J. Cukauskas, B. S. Deaver, Jr. and E. Sinn, "High Spin = Low Spin Crossover and Antiferromagnetic Interactions in Tris(1-Pyrrolidinocarbodithioato)Iron(III) and the 4-Morpholine (FeH) and Dibutyl Analogs, Effect of Recrystallization Solvent, and the Crystal Structure of FeH.Nitrobenzene", J. Chem. Phys., 67, 1257 (1977).


E. Sinn, P. G. Sim, E. V. Dose, M. F. Tweedle and L. J. Wilson, "Electronic and Molecular Structure of Variable-Spin Iron(III) Chelates with Hexadentate Ligands Derived from Triethylenetetramine and β-Diketones or
Salicylaldehyde. Spin State Dependent Crystal and Molecular Structures of
[Fe(acac)₂trien]PF₆ (S = ½), [Fe(acacCl)₂trien]PF₆ (S = ½), [Fe(sal)₂trien]Cl·2H₂O (S = ½) and [Fe(sal)₃trien]NO₃·H₂O (S = ½)," J. Amer. Chem. Soc., in press.

P. G. Sim and E. Sinn, "Synthesis and Crystal Structure of Tris[1-(2-
avo2yl)-2-azabuten-4-yl]amineiron(III), [Fe(pyrol₃tren)]," Inorg. Chem., in press.