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NSLS ANNUAL REPORT 1984

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NATIONAL SYNCHROTRON LIGHT SOURCE
BROOKHAVEN NATIONAL LABORATORY
Associated Universities, Inc.
Upton, Long Island, New York 11973

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FOREWORD

The first comprehensive Annual Report of the National Synchrotron Light Source comes at a time of great activity and forward motion for the facility. In the following pages we outline the management changes that have taken place in the past year, the progress that has been made in the commissioning of the x-ray ring and in the enhanced utilization of the UV ring, together with an extensive discussion of the interesting scientific experiments that have been carried out. These impressive results have required much hard work on the part of the dedicated staff of the NSLS and a considerable creative effort on the part of the users. We look forward to the increasing tempo of work at the NSLS and to a full fruition of the facility in the coming year.

M. Blume
Acting Chairman

II. INTRODUCTION TO THE NSLS

A. Location and Site Plan

The National Synchrotron Light Source is a national user facility supported by the U.S. Department of Energy. It is located on the site of the Brookhaven National Laboratory, about 60 miles east of New York City. The map on page 4 may be used to locate the Laboratory.

The NSLS has two electron storage rings dedicated to the production of UV and X-Ray radiation. These are shown on a plan view of the facility on page 5. The 750 MeV VUV facility has been operating since 1982. The current status and reports of research at the UV ring appear in sections IV, V, and X of this report. The X-Ray storage ring will operate at 2.5 GeV when fully commissioned. At the end of FY84 it was in an early stage of operation at 2.0 GeV, with operation at 2.4 GeV planned during 1985. Complete descriptions of the instrumentation and commissioning of the ring are in sections VI and VII of this report.

A Phase II construction project is underway to expand the NSLS experimental halls and to provide additional laboratory and support areas. The new building will allow more of the NSLS staff to be housed in a common building. In parallel with the conventional construction, a program to design, build, and commission as many as six state-of-the-art beam lines (many on insertion devices) is also part of Phase II. A complete description of the project is in Section IX.

FROM SYRACUSE, BUFFALO,
NORTHERN N.Y., AND CANADA

FROM BOSTON
AND THE NORTHEAST

1 1/2 HOUR RUNNING TIME
CONSULT SCHEDULE

NEW LONDON

LEGEND

AIRFIELDS

- 1 LA GUARDIA
- 2 KENNEDY INT'L.
- 3 LONG ISLAND MACARTHUR

HIGHWAYS

— ALTERNATE
ROUTES

AT L A N T I C O C E A N

APPROACHES TO BROOKHAVEN NATIONAL LABORATORY

— BEST ROUTE FROM NEW YORK CITY

FROM PHILADELPHIA,
WASHINGTON,
THE SOUTHEAST, AND WEST

B. Administration and Staff

The organizational structure of the NSLS Department is shown on page 7. The structure is basically a matrix management scheme with direction of people and dispersal of funds handled in six working sections. Technical direction and policy matters are set by the Accelerator Managers (one person for each of the rings, for the LINAC, and for the beam transport systems) and by the Phase II Construction team. The managers and the Phase II Construction team draw on the resources of the six sections for implementation of their programs.

The Administration Group reports directly to the Chairman and assists with the administrative affairs over the entire Department. Similarly, the Safety Group serves the entire Department.

In addition to this standard organization, the Department uses a number of task force and committee arrangements which are organized on an ad hoc basis to bring particular attention to critical problems. Of special interest during the past year have been the vacuum task force, an injection study task force, a power supply task force, plus workshops on vacuum and RF.

NATIONAL SYNCHROTRON LIGHT SOURCE DEPARTMENT

Chairman: Blum
 Deputy Chairman: Barton
 Department Office: White-DePace
 H.P. Liaison: Flood
 SAVITT: (Batchelor)
 Dickman

ACCELERATOR MANAGER
 Linac: Sheehan, J.
 Booster: Blumberg
 VUV: (Pellegrini)
 X-ray: Kinsky
 Transport: (Batchelor)

Phase II Construction
 Head: Coda
 Secretary: Nelson
 (Hatch), (Larson), (Moncton),
 (Hatch), (Torrano), (Thomlinson),
 Selfer,

ADMINISTRATION
 Head: Foyt
 Secretary: Thiede
 Adams, Fanner, Cragg,
 Jones, Torrano

ELECTRONIC SYSTEMS AND
 OPERATIONAL SECTION
 Head: Batchelor
 Deputy: (Sheehan, J.)
 Secretary: Molondo

ELECTRONIC ENGINEERING: (Kane)
 (Dickman), (Larson), (Newrocky),
 Olsen, Singh, O., (Thomas, M.)

IN CHARGE: Kane
 Ackerman, Blacard, R., (Chou),
 (Catt), D'Almeida, (Fawell),
 (Gale), (Langenbach),
 (McKenzie-Wilson),
 Mueller, Thomas, M.

OPERATIONS: Fawell
 Technical Support: Ramussen
 Operations: Shora
 Morrison, (Catt), Case, Church,
 Brown, Fellen, Garrison,
 James, Hater, Murgatroyd,
 (Hatch), (Ramos), Singh, S.,
 Thomas, S.

ENGINEERING SECTION
 Head: Hatch
 Deputy: (Schuchman)
 Secretary: (Ferreto)

MECHANICAL ENGINEERING: (Hatch)
 Alford, (Ferreto)
 McKenzie-Wilson, Murgatroyd,
 (Schuchman) Shaffer, Woodie

DESIGN/DRAFTING GROUP
 Mechanical Leader: Jordan
 Electrical: Hatch
 Checkers: Choud
 Almay, Bohner, White, Chinn,
 Delano, Callagher, R.,
 Gagliardini, Lehoux, Palo,
 Pajero, Short, Steen,
 Smith, E., Swick, Sec. Det.
 Williams

VACUUM AND ENGINEERING SUPPORT
 Schuchman
 Vacuum Engineer: Forster
 Technical Support: Lebecka

VACUUM GROUP
 Leader: Guder
 DeBoer, Freudenberg, Lange,
 Korn, Lamm, Perill, Smith, C.

MECHANICAL/UTILITIES GROUPS
 Mechanical Leader: McKenna
 Utilities Leader: White
 Survey Leader: (Lebecka)
 Blacard, C., Brock, A.,
 Brock, W., Schwartz,
 Smith, H., Schweier, Mier
 Cunningham, Kern

ACCELERATOR PHYSICS
 Head: Pellegrini
 Secretary: (Thiede)
 (Barton), (Batchelor),
 (Bitter), (Blumberg), (Borok),
 (Cocchini), (Catal), (Culwick),
 (Gentile), (Gonzalez), (Hewitt),
 (Lucco), (Murray), (Newrocky),
 (Sheehan, J.), van Steenberg
 (Vignola), (Hatch), (Hatch), (Hatch)

NUCLEAR RESEARCH:
 Hatch
 Chou,
 (Lamm), (Smith, H.)

DIAGNOSTICS & CONTROLS
 Head: Calayda
 Secretary: (Thiede)
 (Borok), (Calayda),
 (Bitter), (Borok), (Culwick),
 (Newrocky), (Murgatroyd),
 (Sheehan, C.), (Tallent), (Yu)

CONTROLS GROUP: Klein
 Flaminio, Kouda, (Treadwell),
 (Tallent), (Tallent), (Treadwell)

COMPUTER SYSTEMS: Culwick
 DeBovick, Smith, J.,
 Langenbach, Ramussen

MAGNETIC MEASUREMENTS
 Lucco
 (Culwick), (Newrocky)

EXPERIMENTAL PROGRAM SUPPORT
 Head: Thomson
 Secretary: Partero, (Nelson)
 Klatky, Williams

BEAM LINE SUPPORT
 Lucas, Underberg

EXPERIMENTAL AREA OPERATIONS
 Head: Thomson

PET BEAM LINES
 Abramowitz, Bennett, Bloch,
 Bothe, Shu, (Zare)

EXPERIMENTAL TECHNICAL SUPPORT
 Supervisor: Kelly
 Auger, Best, Carlson, Dunn,
 Faughman, Forster,
 Callagher, J., Greene, Kamp

ELECTRICIANS
 Latham: (Moula)

BEAM LINE MAP
 Head: Moncton
 Secretary: (Partero)

Cardoso, Hastings, Laroche,
 Harbeck, Watson

INSTRUMENT DEVELOPMENT
 Overlisen

Lamhard, Van Derlaak

Acting
 as Part Time
 and Coops, CEM, Students
 and Visiting Scientific Staff
 () Additional Assignment
 December 1984

III. USER INTERACTIONS

A. NSLS General Users Meeting/User Representatives

This year's General Users Meeting was held June 4-5, 1984 with 265 registered attendees. Various experimental results from the UV ring were highlighted in the general sessions and there were discussions of the current UV and X-ray storage ring status, the Phase II construction project, and the draft policy for insertion device utilization. During an open house at the NSLS, each UV and X-ray Participating Research Team presented posters on experimental results and displayed their beam line instrumentation.

Elections were held for the NSLS Users Executive Committee members and the User Subgroup Representatives. The current Executive Committee members and Subgroup Representatives are given below:

NSLS Users Executive Committee

Dr. Cullie J. Sparks, Jr. - (615) 574-6996 Metals & Ceramics Division Oak Ridge National Laboratory Oak Ridge, TN 37830 (6/83-6/85)	CHAIRPERSON
Dr. Janos Kirz - (516) 246-8293 Department of Physics State University of New York Stony Brook, NY 11790 (6/82-6/85)	VICE-CHAIRPERSON
Dr. Peter Eisenberger - (201) 730-2838 Corporate Research Science Lab Exxon Research and Eng. Comp. Clinton Township Annandale, NJ 08801 (6/83-6/85)	PAST CHAIRPERSON
Dr. Jerome B. Cohen - (312) 492-3570 Materials Science and Engineering Dept. The Technological Institute Northwestern University Evanston, IL 60201 (6/84-6/86)	
Dr. Philip Coppens - (716) 831-3911 Department of Chemistry State University of New York Buffalo, NY 14214 (6/83-6/85)	

Dr. Paul Cowan - (202) 921-2061
National Bureau of Standards
A141 Physics Blvd.
Gaithersburg, MD 20899 (6/84-6/86)

Dr. Franz J. Himpel - (914) 945-3515
IBM Research Center
P.O. Box 218
Yorktown Heights, NY 10598 (6/84-6/86)

Dr. E. Ward Plummer - (215) 898-8157
Department of Physics
University of Pennsylvania
Philadelphia, PA 19104 (6/83-6/85)

Dr. P. D. Stephens - (516) 246-7950
Department of Physics
State University of New York
Stony Brook, NY 11794 (6/83-6/85)

NSLS User Subgroup Representatives

Dr. John C. Bilello - (516) 246-5983
Dept. of Materials Science
State University of New York
Stony Brook, NY 11794

TOPOGRAPHY

Dr. Wolfgang Eberhardt - (201) 730-2567
Corporate Research Science Lab
EXXON Res. and Eng. Company
Clinton Township, Annandale, NJ 08801

VUV PHOTOEMISSION

Dr. Takeshi Egami - (215) 989-5138
Department of Materials Science
University of Pennsylvania
Philadelphia, PA 19174

ENERGY DISPERSIVE
DIFFRACTION

Dr. G. F. Flynn - (212) 280-4162
Department of Chemistry
315 Havemeyer
Columbia University
New York, NY 10027

TIME RESOLVED
FLUORESCENCE

Dr. Steve Heald - (516) 282-2861
Department of Energy - Bldg. 480
Brookhaven National Laboratory
Upton, NY 11973

EXAFS

Prof. G. Herzog - (201) 932-9601
Department of Chemistry
Douglass College
Rutgers University
New Brunswick, NJ 08903

X-RAY FLUORESCENCE

Dr. C. Denise Caldwell - (203) 436-0824
Department of Physics
Yale University
New Haven, CT 06511

GAS PHASE SPECTROSCOPY/
ATOMIC PHYSICS

Dr. G. L. Liedl - (317) 494-4095
School of Materials Science.
Purdue University
West Lafayette, IN 47907

X-RAY SCATTERING

Dr. A. Kvik - (516) 282-5621
Department of Chemistry
Brookhaven National Laboratory
Upton, NY 11973

X-RAY CRYSTALLOGRAPHY

Dr. Jerome Silverman - (516) 282-5506
NSLS - Bldg. 725A/IBM U6
Brookhaven National Laboratory
Upton, NY 11973

LITHOGRAPHY/MICROSCOPY

Dr. Neville Smith - (201) 582-6422
Bell Laboratories
600 Mountain Avenue
Murray Hill, NJ 07974

SURFACE SCIENCE

At the Meeting a number of concerns were discussed by the User Subgroups and the Executive Committee. As a result of these discussions, the Users Executive Committee (C. Sparks, Jr., Chairman) made several recommendations to the NSLS Management:

1. The criteria considered most important by Users in rating the operating conditions of the rings for useful science are: (a) injection should be reliable, accomplished in reasonable time with the same orbit to 0.1 mm; (b) 2.5 GeV for X-ray ring is crucial to most of the science planned, currents of 100 mA for four hours would produce usable flux for the majority of experiments, but current is less important than the electron energy.

2. The NSLS should make every effort to equip Phase II User laboratories. A user committee should be appointed to consider how the laboratories and equipment are to be maintained.

3. Schedules of projected machine operating modes should be sent to each beam line spokesperson as soon as they are established or revised.

4. A more frequent (~ 4 issues/yr) users newsletter is a desirable means of conveying information. The newsletter could be as simple as xerox copies to reduce the effort required to put out a formal, printed newsletter. In addition to status reports from the NSLS, the newsletter could contain user input such as:

- News from the Users Executive Committee and Subgroup Representatives.
- Experiences of the users in installing beam lines and what to expect.
- The experiences and solutions of the users in obtaining housing: what are the housing needs?
- Gossip column by users of impressions and experiences at the NSLS.
- Letters from the Users proposing ways to improve the scientific productivity at the rings and to enhance the amenities.

5. There should be another announcement to the user community of policy and insertion device parameters to insure that everyone has had a chance to join an insertion device team (this could be included in the newsletter).

On the basis of input received after the General Users Meeting from the User Subgroups and Users Executive Committee, the insertion device policy was revised. The present policy is given below in its entirety.

DRAFT POLICY FOR NSLS INSERTION DEVICE UTILIZATION

Introduction

The existing policy for the instrumentation and utilization of the NSLS storage ring bending magnet ports provides for the design and instrumentation of beam lines by "Participating Research Teams" (PRTs) in addition to beam lines constructed by the NSLS staff for general usage. In return for the development and maintenance of beam lines and the provision of technical assistance to general users using these beam lines, the PRT is given priority usage of their lines for a maximum of 75% of its operational time. General users have access to general user beam lines and to PRT beam lines which are available for at least 25% of their operational time. Non-PRT members are not required to enter into a scientific collaboration as a condition for using a PRT beam line.

PRT and general user proposals are reviewed by the NSLS Program Advisory Committee (PAC). The PRT term is for a maximum of three years.

The PKT term may be renewed on the advice of the PAC, after it has reviewed the PKT's scientific accomplishments and the fulfillment of its obligation to other NSLS users. General users are approved for a specific experiment or for a series of experiments constituting an experimental program.

In the case of insertion device beam lines, it is desirable to enable scientists from outside the NSLS to cooperate in the design, fabrication, and commissioning of beam line instrumentation. Therefore it is proposed that for this purpose "Insertion Device Teams" (IDTs) be established.

The policy governing the use of an insertion device beam line would depend on whether the beam line was built with NSLS funds or with IDT funds:

Insertion Device Teams on NSLS-Funded Beam Lines (Type A IDTs)

For a beam line constructed using NSLS funds, an IDT would be formed under the direction of the NSLS scientist responsible for the insertion device beam line. The IDT term would consist of a two-year commissioning/early operational period followed by a two-year period during which the IDT would have use of the beam line for 25% of its operational time. At the end of this period, the IDT could be renewed for additional two-year terms to continue beam line development or another IDT could be approved to implement new experimental capabilities on the beam line.

The percentage of general user time would increase from 25% during the first two-year period to 75% during subsequent two-year periods. The 25% general user time would become available after the beam line entered an early operational phase.

IDT members would be free to submit general user proposals for experimentation during the 75% general user time.

Insertion Device Teams on IDT-Funded Beam Lines (Type B IDTs)

In cases where an IDT instruments an insertion device and/or a beam line with its own funds, the IDT term would consist of a two-year commissioning/early operational period followed by a two-year period during which the IDT would have use of the beam line for 50% of its operational time. At the end of this period, the IDT could be renewed for an additional two-year period to continue beam line development or another IDT could be approved to implement new experimental capabilities on the beam line.

The percentage of general user time would increase from 25% during the first two-year period to 50% during subsequent two-year periods. The 25% general user time would become available after the beam line entered an early operational phase. IDT members would be free to submit general user proposals for experimentation during the 50% general user time.

Approval for Utilization of NSLS Insertion Devices

There is a Program Advisory Committee (PAC), appointed by the Director of Brookhaven National Laboratory to provide advice on the utilization of the NSLS. The PAC has a broadly based membership consisting of specialists in the relevant scientific disciplines, from outside the laboratory and within.

Among the issues upon which the PAC give advice are:

- (a) priorities for the use of the various insertion devices
- (b) approval of experiments for general users on insertion device beam lines

Proposals for the instrumentation of the NSLS insertion devices by IDTs may be submitted by individuals or groups who wish to form IDTs. The PAC will review these proposals taking into account technical and scientific merit and the fulfillment of obligations to general users.

The terms of Types A and B IDTs have been discussed above and are summarized in tabular form in the chart following this draft policy.

Renewal of terms will be subject to a PAC review of the IDT's performance. Service to general users will be an important consideration in the PAC review.

Non-IDT members will not be required to enter into a scientific collaboration as a condition for using an IDT beam line. Regular insertion device users are encouraged to become members of an IDT by participating in the maintenance or development of experimental facilities. In this sense, IDTs will remain open to new members.

IDT RESPONSIBILITIES

Standing of IDT Members

Upon approval to place instruments on NSLS insertion devices, IDT members will be considered to be members of the NSLS community and will be expected to cooperate fully in assisting general users, in improving operating conditions at the NSLS, and sharing designs for general instrumentation.

Service to Users

1. Type A IDT

The primary responsibility of Type A IDTs is the design, construction and commissioning of beam line instrumentation. The IDT is expected to maintain a file of appropriate information on beam line equipment to permit use by general users. The NSLS is

responsible for maintaining beam line equipment, providing technical assistance to users, and scheduling general users. New IDT Directors will be selected by the NSLS Director in consultation with the NSLS Users Executive and Program Advisory Committees, NSLS User Subgroups and other interested parties.

2. Type B IDT

The IDT is responsible for beam line funding, design, construction, commissioning and maintenance. Also, Type B IDTs are expected to provide liaison and support to general users utilizing the beam line instrumentation that they have implemented. This support includes the maintenance of adequate beam line documentation to permit use by general users. Each IDT will designate an IDT Director who will be responsible for scheduling IDT and general user time on the equipment. New IDT Directors will be selected by the NSLS Director in consultation with IDT members, the NSLS Users Executive and Program Advisory Committees, NSLS User Subgroups, and other interested parties.

Type A IDT Terms/% Usage

Terms	IDT Usage	General User Usage
2 yr. (Commissioning/ Early Operational)	75 % *	25 % *
2 yr.	25 %	75 %
2 yr.**	25 %	75 %

Type B IDT Terms/% Usage

Terms	IDT Usage	General User Usage
2 yr. (Commissioning/ Early Operational)	75 % *	25 % *
2 yr.	50 %	50 %
2 yr.**	50 %	50 %

* 25% general user time begins when beam line is first operational.

** Subject to renewal of IDT by NSLS Program Advisory Committee.

B. General User Proposals

General users are able to perform experiments on an NSLS general user beam line or on a commissioned PRT beam line which is available for use at least 25% of its total operational time. The PRT and general user beam lines are listed in Tables 1 and 2. General user VUV proposals were first solicited in April, 1983 and are presently being accepted without any fixed submission deadlines. A list of approved user VUV proposals is given in Table 3. General user X-ray proposals are reviewed by members of the NSLS Program Advisory Committee and then scheduled.

If general users or PRTs use the NSLS for proprietary research, a full cost recovery fee will be charged for the amount of beam time utilized for proprietary research. The DOE has granted a class waiver of its rights to inventions arising from the use of the NSLS and other DOE facilities by or for third party sponsors.

A limited amount of funds are available to general users under an NSLS-HFBR Faculty Student Support Program. The objective of this program is to make the exciting research capabilities at the NSLS and HFBR accessible to scientists from U.S. institutions of higher education who will have occasion to use these facilities to complement the research program at their home institution. Most of the scientists participating in the program will be members of faculty/student groups in which students will be trained in one of the diverse scientific fields represented at the NSLS and HFBR. The program is designed to defray expenses incurred during exploratory visits to BNL, and while conducting experiments at the NSLS and HFBR. It is aimed at university users having only limited grant support for their research.

Scientists wishing to obtain general user proposal forms, NSLS-HFBR application forms or further information should contact Diane R. Hatton at:

NSLS
Building 510E
Upton, New York 11973
(516) 282-7114

C. List of VUV Users by Beam Line

In Table 4, the VUV Storage Ring users are listed according to beam line. The list includes general users, PRT members, and NSLS staff members. The research results from each beam line are given in the individual activity reports.

Table 1. NSLS UV Beam Lines

<u>Port</u>	<u>Affiliation (Spokesperson)</u>	
U1.	EXXON (Eisenberger)	A) SEXAFS, ARUPS, XPS B) SEXAFS, ARUPS, XPS C) Infra-red Vibr'tnl. Spect.
U3.	LANL/SANDIA/U.CALIF/ LAWRENCE LIVERMORE (Day, Knotek, Gruner, Multhauf)	A) Spectroscopy B) Radiometry
U4.	AT&T BELL LABS (Smith)	A) SEXAFS/ARUPS/XPS B) ARUPS
5FEL	NSLS (Luccio) BNL/AT&T BELL LABS/NSLS (Johnson, Smith, Klaffky)	A) Free Electron Laser Studies B) UPS
U6.	IBM (Wilson)	Lithography
U7.	BNL/SUNY (Strongin, Sham, Jona)	A) ARUPS/XPS/SEXAFS B) ARUPS/XPS/SEXAFS
U8.	IBM (Himpsel)	A) ARUPS B) ARUPS C) EXAFS/SEXAFS D) Microscopy
U9.	NSLS/BNL-CHEM. (Weston) NSLS/BNL-BIO. (Sutherland)	A) Fluorescence Lifetime B) Dichroism/Fluorescence
U10.	TENN/NBS/ORNL (Callicott, Ederer, Arakawa) NSLS (Schuchman)	A) X-Ray Fluorescence B) Vacuum Test Line
U11.	NSLS/BNL-CHEM. (Grover)	Gas Phase Spectroscopy
U12.	PENN/ORNL (Plummer, Jenkins)	A) ARUPS B) ARUPS C) Infra-red Vibr'tnl. Spect.
U14.	NSLS (Williams) NSLS (Hastings)	A) ARUPS/XPS/SEXAFS B) Optics R&D
U15.	NSLS/SUNY (Kirz)	TGM Monochromator/Microscope

ARUPS = angle-resolved ultraviolet photoemission spectroscopy, XPS = X-ray photoemission spectroscopy, EXAFS = extended X-ray absorption fine structure, SEXAFS = surface EXAFS

Table 2. NSLS X-Ray Beam Lines

Port	Affiliation (Spokasperson)	
X 9.	NATIONAL BIOSTRUCTURES RESEARCH RESOURCE (Chance)	A) EXAFS (Biology) B) Scattering
X10.	EXXON (Eisenberger)	A) Scattering B) EXAFS C) Crystallography
X11.	N.C. STATE/CONN./BNL/G.E./U.WASH./MOBIL/ DuPONT/ARGONNE (Sayers, Budnick, Heald Wong, Stern, LaPierre, Stucky, Shenoy)	A) EXAFS B) EXAFS
X12.	NSLS/BNL-BIO. (Schoenborn)	A) Test Line B) Small Angle Scattering C) Protein Crystallography
X13.	NSLS/BNL-CHEM. (Koetzle, Thomlinson) NSLS/BNL PHYSICS/PENN/SUNY/ALLIED CHEM/DuPONT (Cox, Egami, Prewitt, Hasegawa, Stuckey)	A) Crystallography B) Energy Dispersive Diffraction
X14.	ORNL (Sparks)	A) Scattering B) Microprobe
X15.	AT&T BELL LABS (Freeman)	A) Diffraction B) EXAFS
X16.	AT&T BELL LABS	A) Surface Diffraction B) Diffraction B) Diffraction
X18.	MATRIX (Liedl) W.VA/PITT./GULF/ASHLAND/UOP (Montano, Hercules, Lester, Hoggins, Lester)	A) Scattering B) EXAFS
X19.	NSLS (Hastings) NSLS/SUNY (Bilello)	A) EXAFS/SEXAFS/XPS B) Topography
X20.	IBM/MIT (Horn, Birgeneau)	A) Scattering [Low Q Resolution] C) Scattering [High Q Resolution]
X21.	SUNY (Coppens)	A) Scattering B) Small Angle Scattering
X22.	BNL PHYSICS (Moncton)	A) Magnetic Scattering B) High Resolution Scattering C) Surface Scattering
X23.	NBS/NRL (Madden, Kabler)	A1) Interface and Surface Spectroscopy A2) Small Angle Scattering A3) Real Time Topography B) Crystallography
X24.	NBS/NRL (Madden, Kabler)	A) Scattering, XPS B) SEXAFS, UPS/XPS
X26.	U. CHICAGO/BNL (Smith, Jones, Gordon) NIH BIOTECHNOLOGY RESEARCH RESOURCE/BNL APPL. SCI/ CORNELL/TEXAS A&M/U. TENN (Jones, Kostrun, Church, Sellin)	A) Microprobe B) Atomic Physics

Table 3. Approved General User Proposals

Proposal #	Date Received	Title	Spokesperson
83GU-1	06/06/83	"CORE LEVEL EXCITATION AND RELAXATION IN POLYATOMIC MOLECULES"	D. HANSON SUNY - STONY BROOK
83GU-3	08/17/83	"HIGH RESOLUTION SPECTROSCOPY OF C 1s _{1/2} AND N 1s _{1/2} LINES FOR NITROGEN CONTAINING ORGANIC COMPOUNDS ADSORBED ON FLY ASH"	C. STINESPRING, AERODYNE RES.
83GU-4	09/08/83	"PHOTOEMISSION STUDY OF METAL-DOPED β -BORON THERMOELECTRIC MATERIALS"	J. WONG G.E.
83GU-6	09/12/83	"THREE DIMENSIONAL X-RAY MICROSCOPY VIA SOFT X-RAY DIFFRACTION"	D. SAYRE IBM RESEARCH
83GU-7	09/12/83	"STUDIES ON 3p-EXCITED STATES OF ELEMENTS OF THE FIRST TRANSITION SERIES IN COMPOUNDS"	ROBERT G. HAYES U. NOTRE DAME
83GU-10	10/21/83	"FLUORESCENT STUDIES OF SODIUM SALICYLATE"	J. A. R. SAMSON UNIV. OF NEBRASKA
83GU-11	11/7/83	"STUDIES OF THE ELECTRONIC STRUCTURE & EXCITATION PROPERTIES OF VANADIUM-OXYGEN COMPOUNDS WITH TETRAHEDRAL & OCTAHEDRAL V-O COORDINATION. PART I: VANADIUM PENTOXIDE (V ₂ O ₅)"	IRINA M. CURELARU UNIV. OF UTAH
83GU-12	11/09/83	"PHOTOEMISSION PROPERTIES OF COBALT MODIFIED IRON OXIDE"	E. WARD PLUMMER UNIV. OF PENN.
83GU-14	12/16/83	"EFFECT OF SUBSTRATE ON VALENCE OF Yb ADATOMS AS STUDIED BY RESONANT PHOTOEMISSION"	R. D. PARKS POLYTECHNIC INSTITUTE
83GU-15	12/20/83	"TIME-RESOLVED PHOTOCHEMICAL STUDIES USING SYNCHROTRON RADIATION"	C. R. QUICK LOS ALAMOS NATIONAL LAB
84GU-1	01/23/84	"TIME RESOLVED FLUORESCENCE OF MONOMERIC INSULIN"	J.B.A. ROSS MT. SINAI SCH. MED.
84GU-2	02/03/84	"MORPHOLOGICAL AND ELEMENTAL ANALYSIS OF PIGMENT GRANULES OF THE VERTEBRATE RETINA"	B. J. PANESSA SUNY/Stony Brook
84GU-3	03/14/84	"ADSORPTION AND REACTION ON W(100), W(100)-(5x1)-C AND W(100)-(2x1)-O: NEXAFS AND PHOTOEMISSION"	C. M. FRIEND HARVARD
84GU-4	03/30/84	"SOFT X-RAY TESTS OF MULTILAYER COATED OPTICS"	L. GOLUB SMITHSONIAN OBSERVATORY
84GU-5	04/02/84	"DEPENDENCE OF CORE PHOTOFRAGMENTATION PROCESSES ON THE SITE OF CORE EXCITATION"	R. G. HAYES NOTRE DAME
84GU-6	04/16/84	"SURFACE MORPHOLOGY OF CATALYTICALLY INTERESTING INTERMETALLIC COMPOUNDS"	M. denBOER POLYTECHNIC INST.
84GU-7	06/28/84	"SPIN POLARIZED PHOTOELECTRON STUDIES OF MAGNETISM IN SOLIDS (SPEXAFS)"	G. ROTHBERG STEVENS INST. OF TECH.
84GU-8	08/17/84	"RESONANT PHOTOEMISSION STUDY OF THE GROWTH OF CERIUM AND URANIUM CLUSTERS"	R. D. PARKS NEW YORK UNIVERSITY
84GU-9	11/19/84	"A STUDY OF THE EMPTY ELECTRONIC LEVELS OF THE PERFECT AND DEFECT TiO ₂ (110) SURFACES USING CONSTANT INITIAL STATE (CIS) AND CONSTANT FINAL STATE (CFS) MEASUREMENTS"	V. E. HENRICH YALE UNIVERSITY

Table 4. List of VUV Ring Users September, 1982 - October 1, 1984

User	Affiliation	User	Affiliation
<u>Beam Line 4A</u>		<u>Beam Line 7A</u>	
P. Takacs	BNL	M. Strongin	BNL
N. Lucas	BNL	T.K. Sham	BNL
G. Williams	BNL	F. Jona	SUNY/Stony Bk.
		R. Garrett	SUNY/Stony Bk.
		J. Sokolov	SUNY/Stony Bk.
		D. Sondericker	SUNY/Stony Bk.
		S.C. Wu	SUNY/Stony Bk.
		V. Murgai	BNL
		S. Raaen	BNL
		R.G. Carr	SSRL
		M. Ruckman	RPI
		J. Wong	G.E.
		R. Corderman	BNL
		P. Citrin	Bell Labs
		H. Moser	Exxon
		X. Pan	Queens Coll., New York
		C. Friend	Harvard Univ.
		E.K. Baldwin	Harvard Univ.
		S. Hulbert	BNL
		P. Johnson	BNL
		W. Eberhardt	Exxon
<u>Beam Line 4B</u>		<u>Beam Line 8A</u>	
N.V. Smith	Bell Labs		
S. Kevan	Bell Labs		
R. Tung	Bell Labs		
N. Stoffel	Bell Labs		
<u>Beam Line 5FEL A</u>		<u>Beam Line 8B</u>	
C. Pellegrini	BNL	J. Morar	IBM
A. Luccio	BNL	F.R. McFeely	IBM
G. Vignola	ENEA, Centro DiFrascati, Italy	E. Spiller	IBM
L. Yu	BNL	B. Scott	IBM
J. Galayda	BNL	R. Ludeke	IBM
A. vanSteenbergen	BNL	C. Yen	IBM
S. Krinsky	BNL	G. Hughes	IBM
		E.E. Koch	HASYLAB, DESY W. Germany
		G. Hollinger	Inst. of Nuclear Phys., Lyon, France
<u>Beam Line 5FEL B</u>			
P. Johnson	BNL		
N.V. Smith	Bell Labs		
R. Klaffky	BNL		
L. McDonnell	Cork Regional Tech. College, Ireland		
<u>Beam Line 6A</u>			
J. Silverman	IBM		
J. Warlaumont	IBM		
R.A. Lethin	IBM		
J. Barth	IBM		
N. Bobroff	IBM		
D. Nagel	NRL		
H. Kapoor	Univ. of MD		
V. DiMilia	IBM		

Table 4. continued

User	Affiliation	User	Affiliation
<u>Beam Line 9A</u>		<u>Beam Line 9B continued</u>	
R. Weston	BNL	A. Ross	Mt. Sinai
J. Preses	BNL		College of
R. Holroyd	BNL		Medicine
M.A. Wickramaratchi	BNL	D. Robbins	Univ. of KY,
E. Premuzic	BNL		Lexington
J. Gaffney	BNL	J. Olson	Odense Univ.,
D. Spandau	BNL		Denmark
M. Lin	BNL	H. Wyssbrod	Mt. Sinai
C.R. Quick	LANL		College of
G.W. Loge	LANL	E. Stevens	Medicine
J. Tiee	LANL		SUNY/
G. Senum	BNL	E. Morris	Binghamton
H. Kasha	Yale Univ.		MRC/Mill Hill,
R. Larsen	Yale Univ.	D. Mielke	London
E. Martin	Yale Univ.		Columbia
S. Schaftner	Yale Univ.	F. Devlin	University
L. Simonaitis	Yale Univ.		Univ. of So.
R. Bersohn	Columbia Univ.		California
C. Yu	Columbia Univ.	<u>Beam Line 11A</u>	
J. Leventhal	Univ. of MO/ St. Louis	J.R. Grover	BNL
C. Burkhardt	Univ. of MO/ St. Louis	M. White	BNL
W. Garver	Univ. of MO/ St. Louis	R.B. Klemm	BNL
R. Corey	Univ. of MO/ St. Louis	J. Lee	BNL
T. Daulton	Univ. of MO/ St. Louis	E.A. Walters	Univ. of New
D. Earsom	Univ. of MO/ St. Louis	P.F. Fernandez	Mexico
<u>Beam Line 9B</u>		J.K. Newman	Univ. of New
J. Sutherland	BNL		Mexico
B. Laws	BNL	E. Hui	Univ. of New
J. Trunk	BNL		Mexico
D. Monteleone	C.W. Post	C.D. Caldwell	Yale Univ.
B. Lih	Beijing Univ.	Z.M. Goodman	Yale Univ.
J. Mugavero	PRC	<u>Beam Line 14A</u>	
	BNL	G. Williams	BNL
		N. Lucas	BNL
		E.W. Plummer	Univ. of Penn.
		W. Ford	Univ. of Penn.
		R. Didio	Univ. of Penn.

Table 4. continued

User	Affiliation	User	Affiliation
<u>Beam Line 14A continued</u>		<u>Beam Line 15A continued</u>	
C.T. Chen	Univ. of Penn.	W. Ng	SUNY/Stony Bk.
D. Zehner	ORNL	G. Watson	BNL
W. Eberhardt	Exxon	M. Iarocci	BNL
I. Curelaru	Univ. of Utah	H. Kraner	BNL
K.S. Din	Univ. of Utah	J. Pine	Calif. Inst. of Technology
J.S. Chung	Univ. of Utah	D. Sayre	IBM
R. Hayes	Univ. of Notre Dame	M. Howells	Lawrence Berkeley
T.K. Sham	BNL	J. Hastings	BNL
H. Moser	Exxon	L. Beese	IBM
R. Parks	Polytechnic Inst. of NY	R. Feder	IBM
M. denBoer	Polytechnic Inst. of NY	F. Cinotti	BNL
Y.S. Chou	Polytechnic Inst. of NY	T.K. Sham	BNL
Z. Horn	Polytechnic Inst. of NY	W.B. Yun	SUNY/Stony Bk.
G. Rothberg	Stevens Inst. of Technology	R. Haelbich	IBM
K. Choudhary	Stevens Inst. of Technology	R. Rosser	Imperial Coll. London
M. Knotek	Sandia Lab	P. Charalambas	Queen Elizabeth College, London
T. Michalske	Sandia Lab	B. Panessa- Warren	SUNY/Stony Bk.
W. Smith	Sandia Lab	E. McGarvey	SUNY/Stony Bk.
L. Sorroche	Sandia Lab	K. Jones	BNL
S. Spiak	Sandia Lab		
R. Garrett	SUNY/Stony Bk.		
C. Capasso	Univ. of Fla.		
F. Sette	Bell Labs		
J. Stöhr	Exxon		
S. Anderson	SUNY/Stony Bk.		
D. Hanson	SUNY/Stony Bk.		
S. Raaen	Polytechnic Inst. of NY		
<u>Beam Line 15A</u>			
J. Kirz	SUNY/Stony Bk.		
H. Rarback	BNL		
J. Kenney	SUNY/Stony Bk.		
B.X. Yang	SUNY/Stony Bk.		

IV. VUV RESEARCH OPERATIONS

GENERAL

During FY1984 the VUV research community enjoyed continuous operation of the VUV ring with improvements in source size, lifetime, stored current, and reliability. Performance data are summarized in Table I on a year-by-year basis. During the year there were two planned shutdowns, in late December and for the month of March. In the March shutdown the booster energy was raised to 750 MeV providing "at energy" injection. Due to the fact that the NSLS was designed to be the first large high brightness ring with beam line acceptances matched to it, this became vitally important since subtle orbit changes of the order of 0.1 mm began to be noticed as the vertical source size reduced towards its design value. These changes manifested themselves as wavelength shifts for monochromators using the source as an entrance slit. For others it resulted in losses in intensity. Prior to the March shutdown the magnets had to be cycled around their hysteresis loops to reproduce the fields accurately. This time consuming procedure had not entirely eliminated the problems of orbit irreproducibility.

SHIFTS AVAILABLE

From October through to the end of May, the ring was run from Monday-Friday for two shifts a day, fills being at 05:00, 08:00, 12:00 and 17:00 hours. On average, one day a week was used for studies or maintenance. Sundays were reserved for Free Electron Laser studies usually at lower beam energy. Starting in June, two fills were made available on Saturdays and in August evening fills were added to give 24-hour operation such as that illustrated in Fig. 1. Such current vs. time plots were rather common in September.

Figure 2 summarizes the amount of usable VUV beam since the machine started in 1982. During the year the VUV ring provided between 350 and 400 shifts of beam. Several groups were able to utilize 3 shifts a day operation, others were too small and discussions of optimal use of available beam, including rapid sample switching were held recently. Due to the paucity of sources and the demands for beam time, the community will clearly have to learn to adopt running procedures which take advantage of 24 hour running. Also at this time (late summer) the undulator gap was closed permanently to 28 mm and the undulator photoemission beam line became operational.

BEAM LINES OPERATING

The status of the VUV beam lines as of October 1984 is shown in Table II. At the end of this year there were 13 beam lines operating, with 11 ready for commissioning. A further nine beam lines are already planned, which will result in a total of 32 beam lines on the ring. During the year over 150 scientists were involved with research at the VUV ring.

FUTURE PLANS

The major improvement scheduled is the accurate placement of the ring vacuum chambers. This has become necessary for two reasons. First, there is shadowing by upstream components which make it impossible to illuminate all the new beam lines even if the orbit is modified using the trim magnets. The shadowing exists due to the change in circumference of the VUV ring when it was tuned close to the same frequencies as the booster and x-ray rings. At the time, the chamber alignment was postponed since it was clearly more important to continue operations particularly since no one was affected by it then. The second reason for realigning vacuum chambers is the desire to eliminate the use of the high trim fields, since it is known that these have some impact on orbit stability and reproducibility.

Other improvements which are planned are the implementation of the harmonic cavity to allow higher currents to be accelerated in multibunch mode without bunch/bunch interactions. The ring has a feedback system at present which allows it to operate in three bunch mode up to a few hundred milliamps. In single bunch mode the electron density leads to a reduced lifetime. It is more desirable to operate in 9-bunch mode to reduce the number of electrons per bunch but it is necessary to have each bunch at a different tune to eliminate beam blow up via bunch-bunch interactions in which the image charge caused by the passage of one bunch causes defocusing of a subsequent bunch or bunches.

	OCTOBER 1982	OCTOBER 1983	OCTOBER 1984	DESIGN
MAXIMUM STORED CURRENT	100 mA	300 mA	400 mA	1000 mA
MAXIMUM CURRENT/BUNCH	11 mA	300 mA	400 mA	111 mA
MACHINE ENERGY	750 MeV	750 MeV	750 MeV	700 MeV
SOURCE SIZE (mm) Vertical	1.2	0.7	0.4	0.2*
(FWHM at 100 mA) Horizontal	1.5	1.1	0.8	0.7*
LIFETIME (at 100 mA)	20 min.	2 hrs.	3 hrs.	4 hrs.

*Design values somewhat higher than these numbers at the higher beam energy and the machine tune currently used. Thus, horizontally the beam size is as design, vertically it is within a factor of two.

Table I. Summary of NSLS VUV Ring Performance Year-by-Year

Port	Beam Line	Affiliation	Usable Spare mrad/s	Mono.	Status/Comments
1	A B C	Exxon	None	ERG TGM Infra-red	Ready for commissioning Jan 1985 Planned - under procurement Planned - under procurement
2		None	90		
3	A B C	Los Alamos/Sandia U. Cal./Livermore	None	ERG N/A N/A	Ready for commissioning 1985 In planning stage In planning stage
4	A B	Bell	None	PGM TGM Infra-red	Recommissioning Jan 1985 Operational Planned
4IR	A	NSLS	None	Interferometer	Planned - under procurement
5FEL	A B	NSLS BNL/Physics	None	NIM TGM	Operational Operational recommissioning when undulator reinstalled
5	A	NSLS	None	None	Operational diagnostic line/ source size monitor
6	A	IBM	45	None	Operational, space problems
7	A	BNL/Physics, Stony Brook	None	PGM TGM Infra-red	Operational Ready for commissioning 1985 Planned, first mirror installed
8	A B C D	IBM	None	TGM TGM Zone Plate Microscope	Operational Operational Under commissioning Under commissioning
9	A B	BNL Chem./NSLS BNL Bio./NSLS	None	NIM NIM	Operational Operational
10	A B	NBS, ORNL NSLS	None	None None	Ready for commissioning 1985 Vacuum test line for NSLS and High Energy Physics
11	A	BNL Chem./NSLS	None	NIM	Operational
12	A B C	U. of Penn.	None	TGM TGM Infra-red	Ready for commissioning 1985 Ready for commissioning 1985 Ready for commissioning 1985
13		None	90		Space problems due to transverse optical klystron line
13TOK	A	NSLS/Bell	None	Soft X-Ray	Planned installation of TOK, January 1986
14	A	NSLS	None	PGM	Operational
15	A	Stony Brook/NSLS	80	TGM	Operational, space problems
16		None	90		Machine interference problems
Operational - 13, Ready for Commissioning - 11, Planned - 8, TOTAL - 32					

Table II. Status of beam lines on the VUV ring at the National Synchrotron Light Source as of October 1984.

Fig. 1. Current versus time plot for the National Synchrotron Light Source VUV ring for 21st September 1984. Beam current is in milliamperes.

Fig. 2. Amount of beam available for users at the National Synchrotron Light Source VUV ring since start up in 1982. First ever stored beam was in December 1981. Major events are also indicated.

V. VUV RING STUDIES

During 1984 the VUV Ring performance has been improved in terms of maximum current, lifetime, and vertical beam emittance. Longitudinal coupled-bunch beam instabilities have been controlled by means of a resonant feedback system, allowing normal ring operation with three-bunches and larger current. An undulator, originally built for the Free Electron Laser Experiment, has been put into operation as an insertion device, providing radiation to an undulator beam line as part of the normal ring operation.

During October, November, and December the ring has been shutdown, simultaneously with the Booster and X-ray Ring, to improve the vacuum system and to add a number of new radiation ports and beam lines. During this shutdown the vacuum chamber, its ports, and the quadrupole and sextupoles magnets in the ring have been realigned, to provide a larger radiation fan from all ports and a better beam orbit in the ring. The ring is scheduled to restart operation at the end of January 1985.

A list of present beam parameters is given in Table 1.

Table 1. VUV Parameters as of December 1984

Energy	750 MeV
Beam current	
Maximum 1-bunch	400 mA
Maximum 3-bunches	380 mA
Horizontal emittance	$\sim 1.5 \times 10^{-7}$ mrad
Vertical emittance	$\leq 1.0 \times 10^{-9}$ mrad
Beam lifetime (at 100 mA)	~ 3 hours
Average charging rate, 3-bunches	10 mA/minute

The current limit for single-bunch operation has been increased during 1984 from about 300 mA to 400 mA, by a better control of the RF cavity tuner position and by increasing the horizontal and vertical chromaticity. Multi-bunch operation has always been limited by a coupled-bunch longitudinal instability. The threshold for this instability was about 2 mA at 600 MeV and has been increased to about 20 mA by reducing the Q of resonant modes in the RF cavity (by insertion of damping antenna). The installation of a resonant longitudinal feed-back system, capable of controlling three bunches, has allowed storage of up to 380 mA without any appearance of coherent motion.

The present limit to 380 mA for three bunches is still produced by an interaction between the beam and one transverse mode in the RF cavity, that

produces a transverse coherent instability. The resonant frequency of this mode depends upon the position of the cavity tuner, a plunger cylinder entering the cavity radially, which is current dependent. We are currently studying modes to avoid this transverse resonance affecting the beam, including a more accurate and stable control of the cavity temperature which should become operational at the beginning of 1985.

The single-bunch current limit is not yet completely understood and might be due partly to the lifetime reduction with current produced by the increase in gas pressure and by the Touschek effect.

The single-bunch operation minimizes the ion trapping effect on the vertical beam size, which remains practically unchanged up to the largest current value. With three-bunches one can still observe a vertical size increase at large current, on the order of 300 mA. We have also been able to control the vertical beam size by means of skew quadrupoles. Using these quadrupoles it has been possible to reduce the horizontal-vertical coupling to a value of about 1% emittance ratio. In this condition one is limited by the resolution of our beam size measuring apparatus, introduced by diffraction effects, so that the 1% value of the coupling is really an upper limit.

The effect of vertical beam size on lifetime, demonstrating the importance of the Touschek effect contribution, is shown in Fig. 1. At currents greater than 100 mA the Touschek effect starts to reduce the beam lifetime. This also shows the importance of being able to use a large number of bunches, to obtain a large average current and long lifetime.

The increase of bunch length versus current (microwave instability) has also been observed and measured. Since a number of modifications are being made in the vacuum chambers, we are planning to repeat these measurements in 1985.

A variable gap undulator, built as part of the Free Electron Laser experiment, has been operated at a gap of 28 mm, corresponding to a peak magnetic field on axis of about 2 kG and an undulator parameter $K = 0.95$ (r.m.s. value). After matching the ring to the undulator by varying the current in the two adjacent quadrupole doublets, so that both the vertical and horizontal tune remained unchanged, and correcting the closed orbit to make it equal to the one with the undulator fully open, it has been possible to inject in the ring with no reduction in the injection rate or beam lifetime. In this conditions the main effect of the undulator on the beam was to increase the horizontal-vertical coupling; this increase was corrected by the skew quadrupoles, leaving the vertical emittance unchanged.

Undulator radiation has been observed at full machine energy, 750 MeV. Detailed spectral measurements have been done at 250 MeV (see Fig. 2), as part of the Free Electron Laser Experiment. By studying the effect of the undulator on the beam at low energy, it has been observed

Fig. 1. VUV Beam Lifetime: August 30, 1984

that the undulator magnetic field contains a nonlinear sextupole term which might limit the ring dynamic aperture at low energy or very small gap. In addition, during the shutdown it has been observed that part of the beam chamber in the undulator was damaged. As a result, the undulator has been temporarily removed from the ring, to do the necessary corrections and we will reinstall it as soon as possible.

Fig. 2 . Undulator Spectrum vs Energy at $\Lambda = 3511 \text{ \AA}$

A number of new beam lines have been added to the ring during 1984. With the increasing number of lines it has become more difficult to provide good illumination to all ports. This has led to a re-examination of the vacuum chamber and port geometry in the ring, during the fall shutdown resulting in a realignment of the whole system. In addition, during the same shutdown, a ring bakeout and ion glow discharge of the distributed

pumps has been done, together with the addition of more vacuum diagnostics. During 1984, the operation of the sublimation pump system was improved, making it possible to refresh these pumps biweekly and leading to an improvement in vacuum conditions and beam lifetime.

A synchrotron tune splitting RF cavity, operating at a frequency of about 235 MHz, has been added to the ring. This cavity should stabilize a nine-bunch beam against longitudinal coupled-bunch instabilities and will become operational during 1985, increasing the ring flexibility of multi-bunch operation.

The ring diagnostic equipment has also been improved. A beam scraper has been added and a bunch killer (to eliminate small unwanted bunches), has been installed.

With operation at a smaller vertical beam size the stability of the beam orbit has become more critical and a program has been started to address this problem. In particular, work has started on the design of a feed-back system to stabilize the beam position at all ports, including the design of the power amplifiers, the study of hysteresis effect in the beam steering magnets, and the algorithm to provide independent control of beam position and angle at all beam lines. Implementation of this system should start in 1985.

VI. X-RAY COMMISSIONING

During the last year, significant progress has been made in the commissioning of the X-ray ring. Currents of 50 mA have been stored at an energy of 2 GeV with lifetimes of more than one hour. At 20 mA the lifetime is about three hours. From June through mid-September 1984, the alignment of beam lines at 11 radiation ports was carried out and the operating electron orbit at 2 GeV properly illuminated all of these ports. Alignment of beamlines at the remaining four ports will take place in December after the fall shutdown. A second RF system is being installed during this shutdown in order to increase the operating energy from 2 GeV to 2.4 GeV. The design energy of 2.5 GeV will later be achieved by installing a third RF system.

The effort in the X-ray commissioning has been about equally divided between beam studies and hardware improvements. Back in October 1983, the injection rate was about 2 mA/min and a maximum current of 15 mA was achieved. At that time all of the instrumented radiation ports X9 through X16, and X18 through X24 were observed, and the incomplete illumination of the ports was diagnosed as being due to improper placement of the vacuum chambers in the dipole magnets. The upstream corner of the slot in the chamber is the aperture on the outside of the radiation fan, and in some dipoles the chambers were off by as much as a centimeter.

The X-ray ring was shut down from October 10 through December 7, 1983. During this shutdown, the vacuum chambers were moved to their proper locations in the dipole magnets. The front-ends were realigned and the in-tunnel work on the front-end safety systems was completed. The bakeout system for the vacuum chamber was wired-up, and the ring was baked out. Additional sputter-ion and sublimation pumps were installed, as were a new synchrotron light monitor, beam scrapers for lifetime measurements, and radiation monitors.

In December beam was run again and it was verified that the radiation ports were now properly illuminated. Improving the injection rate was given the highest priority in January and February 1984. A peak injection rate of 6 mA/min was obtained, and a maximum current of 50 mA in a single-bunch was achieved. In February, injection rates of 2 mA/min and charging to 30 mA were routine.

The beam lifetime at 1.7 GeV was found to be 20 min at 20 mA and 60 min at 5 mA. Using the beam scrapers, we checked that the transverse aperture was roughly that expected from design, and we observed that the dependence of the lifetime on the distance of the scrapers to the beam was quadratic, as expected from Coulomb scattering off of the residual gas. Based on these observations, upgrading the vacuum system was given high priority.

Following the recommendation of a Vacuum Workshop held at the NSLS at the end of January, a rigorous bakeout of the X-ray ring was carried out during a shutdown extending from February 24 through April 11, 1984. Sublimation pumps were added at the front ends of the even numbered beam lines, and all ion pumps, distributed pumps, and sublimation pumps were conditioned during the bakeout.

During the spring and early summer of 1984, acceleration took place to 1.7 GeV. Then, after a resonant coupling between the RF power amplifier and the ring cavity was diagnosed and eliminated, the operating energy was increased to 2 GeV in July. The bakeout of the X-ray ring resulted in an increase in the beam lifetime by about a factor of ten. This improvement took place gradually during the running period, with lifetimes of more than one hour being achieved for currents of 50 mA at 2 GeV. A maximum current of 130 mA has been accumulated at injection energy (750 MeV) and on several occasions 100 mA has been accelerated to 2 GeV with an observed lifetime of 40 min.

Increasing the lifetime of the stored beam is clearly one of our most important objectives, and based upon beam observations to be made in January 1985, we may schedule a shutdown early in the spring of 1985 for work on the vacuum system. Installation of additional sublimation pumps could take place at that time, and an Argon glow discharge of the distributed ion pumps is contemplated. Valves to isolate a second RF straight section would be installed to allow the future installation of a third RF cavity without affecting the vacuum in the rest of the ring.

In conclusion, our major short-term goals are: (1) to increase the operating energy to 2.4 GeV and later to 2.5 GeV, (2) to carry out the alignment of the beam lines at the four remaining radiation ports, (3) to gradually increase the percentage of running time allocated to usage of the photon beams relative to machine studies, and (4) to diagnose the present limitations on the electron beam lifetime and to carry out work to improve the lifetime. We expect that during the next year the experimental program utilizing the X-ray photon beams will be very productive, and cooperation between the NSLS staff and the experimental users will allow the continued development of the X-ray storage ring in parallel with an active experimental program.

VII. X-RAY RESEARCH OPERATIONS

The past fiscal year, FY1984, saw the first periods of what can be termed x-ray beam line operations. By this is meant dedicated periods during which an x-ray beam was available to users for experimental purposes. Although through FY1984 no experiments were performed, 22 beam lines were successfully illuminated with radiation, alignment performed, and safety systems brought near to full operation on 20 lines. The effort by the NSLS beam line operations staff, the mechanical and vacuum groups, the PRT staff members and the full cooperation of the NSLS machine operations group is summarized in Table I.

The four shutdown periods were blocks of time during which extensive installation work of front ends and safety system hardware inside the shield wall could occur. Altogether, about 15 weeks were devoted to these efforts in parallel with machine shutdown work. The FY1984 shutdown periods were characterized by front end installation, vacuum conditioning, retrofitting, and safety operation commissioning. The operations periods, which totaled about 37 weeks, were intended for machine commissioning, front end alignment, photon observations outside the shield wall, and possible experiments. To meet these goals as efficiently as possible, the operations mode often consisted of a 6 a.m. to 5 p.m. period during which beam line front end work or beam observations had priority over machine work. This operation mode was successful and, as Tables I and II show, allowed the completion of essentially all x-ray front ends.

There were three major tasks completed which were unscheduled in early planning. In late 1983 the retrofit of the front end safety shutters for installation of adequate photon absorbers was completed. That work was intended to make the safety shutters stop all photons (direct and scattered) when in a closed position. They should, therefore, be useful as both bremsstrahlung and photon shutters for hutch access, particularly important on white radiation lines where there are no downstream photon shutters.

The early observation of photons at the front end locations indicated that the storage ring vacuum exit chambers were improperly aligned. The photon fans were all rotated toward the ring, in some cases causing severe interferences of hardware with building supports. A detailed calculation and survey of the proper locations was carried out, and finally in November 1983, the chambers were repositioned. Subsequent photon observations proved the accuracy of these movements. Only X23 and X24, thus far, have not had the light where the survey indicates. To correct these discrepancies, the X24 front end was moved in August 1984 and X23 was moved in October 1984.

The installation and alignment of the front ends proceeded very well up through the March 1984 shutdown period. At that time bakeouts of the installed units was started and it soon became clear that a significant problem with vacuum integrity existed. Following the bakeouts, many of the shutter units leaked at the 13 1/4" flanges. The problem proved to be not correctable on the installed units. The decision was made to bake and vacuum check all units and any that failed were removed from the ring. A long, in depth program was carried out, with input from SSRL personnel, to redesign the flange supports, bolts, and gaskets used. As Table I shows, the first five retrofitted front ends were installed and tested by the middle of August, and the last four units have been installed during October and November 1984. All retrofitted units are performing very well. The seven front ends which did not leak and which were left in the ring are performing very well also.

Throughout the year the vacuum performance and instrumentation of the front ends and beam lines continued to upgrade. A rigid set of requirements was established for acceptance of front ends which involved residual gas analyzer scans as well as total pressure limits. In order for a front end to be opened to the storage ring, or a beam line to a front end, all requirements had to be met. These procedures worked well, and no vacuum events occurred which compromised ring vacuum during all of the 22 beam line commissioning efforts.

One of the most underestimated items on the experimental floor was the effort required for the design, construction, installation, and commissioning of the complex safety systems and beam line control systems. The NSLS no longer is unaware of these requirements and has over the past two years installed 20 complete systems on the x-ray beam lines, has another 18 partially constructed and installed, and is presently retrofitting all VUV beam lines with new, properly interlocked control systems. These safety systems allow a very high degree of user control and freedom from facility personnel intervention for all normal beam line operations. Both personnel and machine protection interlocks are included in the package, as well as easy coupling to beam line device signals. Although no beam line on the x-ray ring is yet fully commissioned, the NSLS expects all 20 of the first lines to quickly become stand alone commissioned lines in early 1985.

The radiation fans which were observed on the 22 beam lines from 11 ports (see Table III for complete details) were almost all within a milliradian of the expected values in both center position and width. Thus, the year ended with 22 lines ready to begin experimental program in FY 1985 after an initial observation period. Beams were actually brought into experimental hutches on X10A, X13A, X16C, and X18A and monochromatic beams were produced on X13B and X18A. The final four beam ports of the initial 15 which will be opened early in 1985 are listed in Table III. FY1985 will also see the beginning of construction of the experimental facilities for beam ports X1 - X8. For completeness, Table IV lists those beam ports and the status of planning for the programs to be carried out. It should be pointed out that beam ports X2, X4, X6, X27, and X28 remain unassigned and are available for future instrumentation.

Table I. X-Ray Beam Lines - Operations FY1984

October, November '83	Shutdown	<ul style="list-style-type: none"> - Storage ring chamber adjustments - Safety shutter retrofit - Safety systems installed in sawteeth
December '83, January,	Operations	<ul style="list-style-type: none"> - Radiation observed upstream of front ends - Survey and alignment of front ends - Beam line surveys
March '84	Shutdown	<ul style="list-style-type: none"> - Front end installation - Bakeout of front ends
April, May, June, July '84	Operations	<ul style="list-style-type: none"> - Front ends vacuum conditioned - Leaking front ends removed for retrofit - Reinstall X23 - Observation of photons outside shield wall on ports 12, 13, 15, 16, 18, 23, 24
August '84	Shutdown	<ul style="list-style-type: none"> - Install retrofitted front ends on ports 10, 11, 21, 22 - Realign front end on X24
August, September '84	Operations	<ul style="list-style-type: none"> - Observation of photons outside shield wall on ports 10, 11, 13, 21, 22
October '84	Shutdown	<ul style="list-style-type: none"> - Install and vacuum condition front ends on ports 9, 14, 19, 20

Table II. X-Ray Beam Lines - Summary

X-Ray Ports	Operational September 1984	11
	Planned 1985	5
	Future	12
Beam Lines	Commissioning 1985	29
	Planned	17
Safety Systems	Ready September 1984	20
	Partially Completed	18
	Future	8

Table III. X-Ray Beam Lines - Operational Status 11/29/84

Port	Beam Line	Affiliation	Research Program	First Photons	Safety System	Comments
X9	A	National Biostructures Research Resource	EXAFS	—	Partial	Ready 1985
	B		Scattering	—	Partial	
X10	A	Exxon	Scattering	9/11/84	Ready	White beam into hutch 9/14/84
	B		EXAFS	—	Partial	
	C		Crystallography	9/11/84	Partial	
X11	A	NC State/Conn./BNL/U. Wash/Mobil/Dupont/ANL	EXAFS	9/10/84	Ready	
	B		EXAFS	9/10/84	Partial	
X12	A	NSLS	Test Line	—	Partial	
	B	NSLS/BNL Biology	Small Angle Scattering	7/27/84	Ready	
	C	BNL Biology	Protein Crystallography	7/27/84	Ready	
X13	A	NSLS/BNL Physics/Penn/SUNY/Allied Chemical/Dupont/Carnegie Institute/Union Carbide	Energy Dispersive Diffraction	12/16/82	Ready	Si powder spectrum in hutch 6/1/84
	B	NSLS/BNL Chemistry	Crystallography	9/12/84	Ready	Monochromatic light 9/14/84
X14	A	ORNL	Scattering	—	Ready	Ready 1985
	B		Microprobe	—	Partial	
X15	A	Bell Labs	Diffraction	6/12/84	Ready	
	B		EXAFS	6/12/84	Partial	
X16	A	Bell Labs	Surface Diffraction	6/8/84	Ready	
	B		Diffraction	—	Partial	
	C		Diffraction	6/8/84	Ready	White beam into hutch 7/12/84
X17	A	NSLS	Scattering/Angiography	—	Partial	Phase II superconducting wiggler - installation 1985-1986
	B	Unassigned	Wiggler Side Station	—	—	

Table III. X-Ray Beam Lines - Operational Status 11/29/84 (continued)

Port	Beam Line	Affiliation	Research Program	First Photons	Safety System	Comments
X18	A	Matrix (Purdue)	Scattering	5/25/84	Ready	Monochromatic light 7/12/84
	B	W.Va./Pitt./Gulf/Ashland/UOP	EXAFS	—	Partial	
X19	A	NSLS	EXAFS	—	Ready	Ready 1985
	C	NSLS/SUNY	Topography	—	Ready	Ready 1985
X20	A	IBM/MIT	Scattering (Low Q Resolution)	—	Ready	Ready 1985
	C		Scattering (High Q Resolution)	—	Ready	Ready 1985
X21	A	SUNY	Scattering	9/14/84	Ready	
	B		Small Angle Scattering	9/14/84	Partial	
X22	A	BNL Physics	Magnetic Scattering	9/14/84	Partial	
	B		High Resolution Scattering	9/14/84	Ready	
	C		Surface Scattering	9/14/84	Partial	
X23	A1	NBS	Interface and Surface Spectroscopy		Partial	
	A2	NBS	Small Angle Scattering	7/12/84	Ready	
	A3	NBS	Real Time Topography		Partial	
	B	NRL	Crystallography	7/13/84	Ready	
X24	A	NBS	Scattering, XPS	5/23/84	Ready	
	C	NRL	SEXAFS, UPS/XPS	5/23/84	Ready	
X25	A	NSLS	High Q Resolution Scattering	—	Partial	Phase II - hybrid wiggler installation 1985-1986
X26	A	NSF Geochemistry Project/ U. Chicago	Microprobe	—	Partial	Installation 1985-1986
	B	NIH Biotechnology Research Resource/BNL Appl. Sci./ Cornell/Texas A&M/U. Tenn.	Atomic Physics	—	Partial	

Table IV. X-Ray Beam Lines - Future Beam Port Plans

Port	Beam Line	Affiliation	Research Program	Comments
X1	A	NSLS	Microscopy/Holography	Phase II soft x-ray undulator - installation 1985-1986
	B		Spectroscopy	
X2	Unassigned			
X3	Future location of X21 program			
X4	Unassigned			
X5	A	BNL Physics	LEGS (Laser Electron Gamma Source)	Installation 1985-1986
			Compton Backscattering Nuclear Physics	
X6	Unassigned			
X7	Future location of X13 program			
X8	A C	LANL	EXAFS/Scattering	Installation 1985-1986
			Soft X-Ray EXAFS/Photoemission	
X27	Unassigned			
X28	Unassigned			

VIII. RESEARCH AND DEVELOPMENT

The research and development activities of the NSLS are divided between work carried out directly by the NSLS and the support activities in the Instrumentation division. The combination provides a strong base for instrument development and optical surface evaluation, the key parts to optimal utilization of the VUV and X-Ray storage rings. These activities are reported by topic in the following:

PIEZOELECTRIC TRANSLATORS

Many of the critical adjustments of optical components are made using piezoelectric translators. Until recently these have been confined to non ultra-high vacuum environments which has limited their use. A simple UHV compatible translator has been developed by T. Oversluizen at the NSLS which is being used in a variety of NSLS developed instruments. A typical device provides 10 μm of translation at working pressures of 1×10^{-10} Torr.

X-RAY MONOCHROMATOR DEVELOPMENT

The UHV monochromator developed in collaboration with the National Bureau of Standards has been installed on a branch line of the NSLS VUV beam line U-14 and performance tests have been carried out. The development of this instrument has involved the piezoelectric translators described above which are the critical components in the insitu adjustment of the two crystal monochromator. Using a lever multiplication scheme a total angular scan of 1/3 of a degree can be accomplished with arc second resolution for aligning the two crystals with respect to one another. The other critical component to successful operation of the monochromator is the ability to pre-align the crystals prior to mounting in the UHV environment and facilities to do this have been developed. Preliminary gas phase absorption studies on sulfur containing compounds indicate the exciting possibilities this instrument can provide once it is in full operation on the x-ray ring.

IMAGE QUALITY STUDIES

Image quality studies were conducted on the plane grating monochromator (PGM) on beam line U4 using visible light to assess the instrument's performance and predict its performance at shorter wavelengths. Zero scans were made using laser pinhole sources at 632.8 nm and 442 nm and also using the actual SR source through a blue filter. Comparisons between the laser scans and the actual source are shown in Fig. 1. The crosses are the data from the actual source whose FWHM is wider than that from the laser (circles) on this range 3 scan.

A physical optics diffraction integral model was developed to analyze the results of the PGM scans. The model computes the effect of wavefront errors on the observed visible wavelength diffraction image and allows one to estimate the magnitude of gross surface figure and slope errors in the data. System performance at shorter wavelengths can then be predicted. This technique has been used to analyze visible images from the PGM system and from the PGM collimator mirror alone, and has also been used to test the performance of the mirror bender and assess the quality of the mirror surface on the Oak Ridge National Lab x-ray beam line X-14. Sensitivity to surface slope error is about 1 arc second using visible wavelength sources.

OPTICAL SURFACE CHARACTERIZATION

A WYKO profiling microscope (NCP-1000, 10x) has been placed into operation in the Instrumentation division under the direction of Dr. Peter Takacs as the first element in a planned optical-component laboratory in support of the NSLS. This instrument is capable of measuring the height of an optical surface at 1024 points along a 1.33 mm linear profile with a precision of 1 Angstrom. Measured data are analyzed on an on-line HP 9836 computer to give a variety of profile parameters for research and quality-control applications. The measurements are non-contacting, easily set-up, and the entire cycle, from sample delivery to hard-copy output, can be completed within five minutes.

To expand the capabilities of the WYKO profilometer, an extensive software package was developed under the direction of Dr. Eugene L. Church, with the assistance of Dr. Peter Z. Takacs and a summer student, Howard Sporn, to perform a complete analysis of the surface profile. The new profile measurements contain information about surface figure and finish. These are separated in the analysis by fitting a least-squares quadratic to the data; the figure information is then contained in the polynomial coefficients, while the finish information lies in the fluctuations of the measured data about the fitted curve. For example, radii of up to 100 meters (sag depth = 22 Angstroms or more can be measured in this way, depending on the degree of surface finish and this method of measuring the curvature of large-radius mirrors has been shown to be in good agreement with interferometric techniques.

The WYKO facility has been used for a variety of ongoing service measurements for Light Source and outside users, as well as a basis for several research papers on surface metrology and statistical estimation. Examples of the surface profile (Fig. 2a, 3a) and power spectral density (Fig. 2b, 3b) for two single point diamond turned surfaces are shown. One is very smooth (2a, 2b) with an rms roughness of less than 10 Å, while the other (3a, 3b) shows considerable grain structure.

A survey of the diamond machining industry was conducted to assess the current state-of-the-art in the single point diamond turning (SPDT) technology. Samples were solicited from a number of manufacturers and the quality of each surface was measured using the WYKO profilometer and our own software package. Results indicate that the surface quality is greatly affected by the choice of substrate material: aluminum 6061 produces a very rough machined surface owing to its intrinsic grain structure, while electroplated copper and electroless nickel produce very smooth surfaces.

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Fig. 1

Fig. 2a

Fig. 2b

Fig. 3a

Fig. 3b

IX. NSLS PHASE II CONSTRUCTION PROJECT

INTRODUCTION

October 1983 was the first month of what was expected to be a 36 month program to increase the space available to NSLS users and staff, and provide six advanced concept beam lines. The project cost was authorized at \$19.7 million. In August 1984, the Department of Energy directed that \$2.6 million of second year construction funds (FY1986) be deferred to the fourth year.

The impact on the design and construction of the building addition is expected to be minimal. Experimental beam lines will be delayed from 8 to 12 months. However, it should be pointed out that even without the extended program, there was the likelihood of some delays in the beam line construction program because of competition for manpower in commissioning the X-Ray storage ring. The costs associated with deferred spending and maintaining part of the staff for an additional year will raise the project cost to \$21.87 million.

SCOPE

With the level of experimental activity in the X-Ray area expected to reach that of the VUV storage ring in the near future, it is evident that users will be adversely affected by lack of laboratories and space for set-up and support. NSLS staff members are now dispersed in a number of locations which reduces the efficiency of our operation. Perhaps most importantly, the demand for new beam lines requires that we move about 30 technicians and supervisors from space they now occupy on the X-Ray experimental floor to make way for new beam lines.

The objectives of the NSLS Phase II construction project are to:

- Increase building area by approximately 52,000 ft² for laboratories, experimental support areas, and integrated work and office space for NSLS staff.
- Design and build up to six state of the art beam lines with emphasis on wiggler and undulator insertions.

Using recommendations from the Users Executive Committee, the NSLS Department Chairman approved the following beam lines:

- High Energy Material Science and Angiography Beam Line using a superconducting wiggler (X17).
- High Q Resolution Beam Line having a hybrid wiggler (X25).

- Microscopy and Holography Beam Line with a SmCo_5 undulator (X1)
- Infrared Beam Line (IR4)
- High E Resolution Beam Line with a hybrid wiggler (X21)
- Soft X-ray Spectroscopy Beam Line with multipole wiggler (U13)

The change from a three to a four year construction program will not affect the scope of work.

BUILDING ADDITION

A major design effort was started by our architect-engineer in December 1983 with close collaboration from NSLS and BNL's Plant Engineering and Safety and Environmental Protection Divisions. The user community gave valuable input on laboratory requirements and other support facilities. Our architect is Abramowitz-Harris-Kingsland and the engineer is Ammann & Whitney, both of New York City. The schedule calls for bids for the building contract to be opened in mid-January 1985, and groundbreaking by early March of the same year.

The NSLS existing building contains about 66,000 ft^2 on the first floor and 8,000 ft^2 on the second. Figure 1 shows the 29,000 ft^2 addition to the first floor. The dotted lines indicate the present perimeter of the building. Of the 29,000 ft^2 , the VUV floor will expand about 5,000 ft^2 adding space on two sides of the ring. The X-Ray experimental floor will grow by 9,000 ft^2 for experimental support. The remaining 15,000 ft^2 will be devoted to support space and building services.

Five new laboratories will be added to the four existing ones. These include laboratories for materials science, x-ray instrumentation, crystal alignment, chemistry, and human angiography. The existing laboratories will be used for biological sciences and one will be a general purpose VUV laboratory. A clean room, equipped with HEPA filtration, several dark rooms and an electronics instrumentation laboratory will be available to users. Finally, we are providing several "quiet" areas adjacent to the X-Ray and VUV floors and a lunchroom/kitchen combination which are intended for use by beam line experimental groups.

There are several other features of interest. A tunnel will connect the first floor of the new addition to valuable space in the basement of Building 535, giving convenient access to a machine shop, metrology laboratory and vacuum and mechanical support areas. A new truck entry will give additional access to the experimental area and take some of the traffic away from the existing truck entry. A two-ton, overhead crane will cover part of the X-Ray support area near the truck entry. A receiving and storage complex near the existing truck entry is expected to handle packages and equipment without congestion on the experimental floor.

Figure 2 is the second floor plan. The existing second floor, shown in the lower center portion of the figure, connects to the new second floor which is located above the expanded VUV area and over part of the expanded X-Ray area. The combined second floor is U-shaped with provision to connect the two legs of the "U" in the future.

The 23,000 ft² of new space will contain offices and work areas for NSLS staff members and for some visitors. It is expected that users will have offices and laboratories available on the third floor of Physics in space now occupied by the NSLS staff. The second floor will contain a new, enlarged seminar room. The present seminar room will become a library. Two new staircases and a new elevator will connect floors at strategic locations so that traffic moving around the perimeter of the experimental floors should be substantially reduced.

We expect some interferences with the operation of the facility during the building expansion program. This will occur from interruption of water and power during tie-in, and from vibration, noise and dirt during excavation and breaking through existing concrete foundation walls. Our plan is to erect temporary insulated dustproof partitions inside the foundation walls where cut-throughs will occur. Then, virtually all construction work will be confined to outside the building. The concrete walls will be cut with diamond saws to reduce dirt, vibration and noise. It was originally planned to coordinate the heavy construction work with a major shutdown of the storage ring(s) in order to reduce the impact on the experimental program. Since the work requiring heavy equipment will take place in the spring of 1985, it is now unlikely that a planned shutdown of the facility will take place because of the desire to operate the X-ray storage ring at that time. Nevertheless, every effort will be made to minimize adverse effects of the construction on the on-going program.

EXPERIMENTAL BEAM LINES

As previously noted, the Phase II construction program includes six experimental beam lines. All, with the exception of the infrared line on the VUV ring, will utilize insertion devices installed on long straight sections of the storage rings. The six beam lines are listed, along with the type of insertion device in Table 1, and their locations shown in Figure 3. Two of the six lines will be at the VUV storage ring and the remainder at the X-ray storage ring. Among the latter group, X17 terminates in an angiography laboratory located in the expanded area of the building.

The photon spectrum of x-ray insertion devices is given in Figure 4. The four beam lines above the horizontal line in Table 1, are currently under design or construction. Conceptual design reports have been prepared for each of the four describing scientific and engineering parameters. Design of the two beam lines below the line (X21, U13), will not begin until next year.

Figure 2. Second Floor Plan Phase II

Table 1. NLS Phase II Experimental Beam Lines

Beam Line	Insertion Device	Peak Power kW/mrad ²	Energy Range keV	Program
(X17) High Energy Material Science and Angiography	High Field S.C. Wiggler 5 poles @ 5T, 2 @ 2.5T 17.4 cm period Fixed Gap	3.21	10-100 (variable for material sci.) 33 (dual for angiography)	Crystallography EXAFS Topography Angiography
(X25) High Q Resolution Scattering (High Brightness Source)	Hybrid Wiggler SmCo ₅ /Vanadium Permadr Poles 12 cm period Variable Gap	3.53 @ 1.1T 6.42 @ 2.0T	1 - 16	Surface Structural Probe, Phase Transitions, Magnetic Scattering
(X1) Microscopy & Holography (Bright, Coherent Source)	Undulator SmCo ₅ /Iron Poles Variable Gap	2.98 @ K = 2.6	0.25 - 3.5	Imaging Biological Samples
(IR4) Infrared (High Brightness, Large Aperture Source)	WV Bending Magnet Brightness: 1000 x black body @ 2000 K	0.4 kW/cm ² on 1st optic	.04 - 10 ⁻⁶	Surface Vibrational Structure, Relax- ation Effects in Semi-conductors
(X21) High E Resolution	Hybrid Wiggler SmCo ₅ /Vanadium Permadr Poles 12 cm period Variable Gap	3.53 @ 1.1T 6.42 @ 2.0T	1 - 16	Inelastic Scattering
(U13) Soft X-Ray Spectroscopy	Multipole Wiggler		0.1 - 2	Transverse Optical Klystron Experiment

Figure 3. Phase II Beam Lines

Figure 4

Front Ends & Exit Chambers

Much of the design effort on X17, X1 and X25 has been concentrated on learning how to handle the extremely intense radiation beams. A study of the power densities in the insertion device beams shows that even for undulators, peak powers of $1\text{--}6\text{ kW/cm}^2$ occur. Wherever the beam can strike front end components, a detailed thermal analysis was carried out using a finite element computer code. For example, a 6° grazing angle is required on a water-cooled Cu absorber at a distance of nine meters from the source to reduce the thermal stress and increase the fatigue lifetime to acceptable limits. On other surfaces, such as beam splitting stops, an angle of 2° was found to be required.

It is necessary on X17 to bring the white beam through a Be window. Using a design worked out at LBL and SSRL, a series of thin pyrolytic graphite foils are used to absorb low energy radiation which, in turn, radiates the energy as heat. In addition, an Xe gas filter is used during angiography experiments at 33 keV to reduce the power on the angiography monochromator by a factor of five, while only reducing flux at the iodine K-edge by a factor of two.

Figure 5 is the front end assembly that receives its beam from the SmCo₅ undulator at Port X1.

Figure 5. X1 Front End

Figure 6 shows a typical component in the front end with grazing angle absorbers. The absorbing element in this case is a rectangular copper bus bar with an internal water cooled channel.

Figure 6. Beam Defining Aperture
for X1 Front End

In order to insure that the photon beam does not destroy the exit chamber, several techniques will be employed: first, vertical electron beam scrapers will be installed to limit the vertical angular deviations of the synchrotron beam to ± 3 mrad. Second, the exit chambers have been completely redesigned with properly water cooled surfaces and a larger vertical slot for the beam. Third, active feedback on the photon beam position will be obtained from beam position monitors. The monitors have vertical tungsten blades which emit a photoemission current when struck by the photon beam. A difference signal between the blades above and below the beam can be calibrated to give beam position. This concept has been successfully used on Beam Line VI at SSRL.

X17 - Material Sciences and Coronary Angiography

The high field superconducting wiggler magnet parameters are given in Table 1. It has been designed, constructed and partially tested and is expected to be installed in the fall of 1985.

Due to vacuum chamber and magnet constraints, only 15 mrad of the total 48 mrad of horizontal radiation is available. The central 5 mrad is to be instrumented for Phase II and must serve programs in EXAFS, crystallography, high pressure, topography, and human coronary angiography. The material research programs will share an experimental area inside the present building at about 30 m from the source. For 25% of the time, however, the 5 mrad beam will be brought through the hutch into the new angiography laboratory.

The beam line optics, i.e. focusing monochromator, for the materials research is now under development at the NSLS. It will be a two-crystal device, initially nonfocusing, but will advance to a focusing geometry as experience is gained. It will be tunable from 10 keV to as high as 100 keV, with scan ranges of 1 keV. The horizontal collection angle and focusing properties are unknown at the present time.

For the angiography program, optics are being built now for use with the current experimental program at the Stanford Synchrotron Radiation Laboratory. The dual energy monochromator, focusing systems, timing slits, data acquisition systems, etc. will be upgraded continuously and eventually either brought to the NSLS or constructed for use specifically at the NSLS.

The front end hardware has been designed to not only allow the 5 mrad central beam out, but also a fan of radiation continuously variable from 0 to approximately 3 mrad on each side. Proposals for the use of these side beams are being solicited, but the rather difficult geometry involved limits the types of viable proposals. It is conceivable that on one side a white beam can be developed, and on the other side, a fixed single energy monochromatic line.

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X-25 High Q Resolution Scattering Beam Line

The x-ray intensity levels associated with NSLS bending magnet beam lines will be inadequate for many frontier areas of structural physics research. Fortunately, intensity levels may be increased by factors of 10 to 100 using short-period, permanent-magnet wigglers which are uniquely suited to installation in NSLS straight sections. Examples of such programs that need a high intensity source are studies of incompletely ordered hydrocarbon monolayers reconstructed on modulated monolayers, atomic clusters, magnetic scattering, and Wigner lattice systems.

The hybrid wiggler for this beam line will be of the permanent magnet construction. The 15 period magnet will have SmCo_5 magnets and Vanadium Permadrur poles. One feature of this device will be the variable gap chamber which will have a gap continuously variable from 1 cm (on axis field 2T, $E_c = 8.3$ keV) to 2.2 cm (on axis field 1.1T, $E_c = 4.58$ keV). This places the peak energy of the photon beams in the energy range 1-16 keV. The photon spectrum is shown in Figure 4. Note the extremely high intensity of the beam relative to the arc source.

The design value for the resolution, $\Delta Q/Q \sim \Delta E/E \sim 10^{-4}$ will be achieved by a combination mirror/monochromator system. The monochromator will be the same basic design as the two-crystal system to be developed for the X17 line. The proposed focusing system is based on the ideas of the Kirkpatrick-Baez microscope and multilayer reflectors to achieve a high throughput-small aberration optical system. The first element will be a horizontal focusing reflector, coated with multilayers of tungsten and carbon to take the high heat load from the beam. The second element, the

vertical focusing Pt coated mirror, the Be window, and the monochromator will thus see very low power levels. A research and development program is necessary to prove the technologies.

X1 - Holography and Microscopy Beam Line

This beam line is designed primarily for soft x-ray imaging experiments. These include forms of microscopy, holography, diffraction, etc.

For imaging experiments it is necessary to have beams of sufficient spatial and temporal coherence. In the absence of a naturally coherent source like a laser we must select the coherent part of the output of a non-coherent source. The spatially coherent part is selected by using a pinhole which subtends an angle at the source equal to the source's coherence angle. This accepts only a small fraction ($<0.1\%$) of the total emission angle. The flux emitted into the coherence solid angle can be shown to be proportional to the brightness. Hence, the need for a high brightness source. Temporal coherence is achieved by the use of monochromators. The coherence length ($\lambda^2/\Delta\lambda$) of the radiation is determined by the monochromator resolution ($\Delta\lambda$). The required values of this differ for different experiments so a flexible monochromator is needed which optimizes flux for both modest resolution ($\lambda/\Delta\lambda \sim 200-400$ for microscopy) and high resolution ($\lambda/\Delta\lambda > 1000$ for some types of holography).

To get the highest brightness source with the required wavelength coverage we use an undulator, which can be tuned so that the region 0.25-0.65 keV is covered fully by the first harmonic for a 2.5 GeV storage ring energy. This device also covers a much wider range with high flux using higher harmonics: up to 3.5 keV at half maximum flux for 2.5 GeV.

It is interesting to note that although the total power produced by the magnet is small since the horizontal angle is only 0.43-0.88 mrad, the power density on axis is $\sim 3 \text{ kW/mrad}^2$. Thus, many of the thermal designs for apertures, chambers, and optics are equivalent to those for the X17 high field wiggler.

The X1 beam line will be divided in two by a splitting mirror which passes the central beam to a 100 μ diameter pinhole to give a high brightness coherent beam. The pinhole follows the splitting mirror so it receives the full power density but only 20% of the total power.

The splitting mirror is a flat, horizontally deflecting mirror large enough to accept the whole beam. It allows the central beam through and deflects the remaining beam at 5° . This beam will be used for soft x-ray spectroscopy where the coherence of the radiation is not important. The mirror will be water cooled, electroless nickel plated copper. A detailed engineering study has been performed to develop this grazing incidence high power mirror which controls thermal distortions.

IR4 - Infrared Beam Line

The only Phase II beam line not associated with an insertion device is the infrared beam line to be placed near beam port U4 on the NSLS VUV ring. The primary design goal is to extract 90 mrad horizontally by 90 mrad vertically of radiation and transport it to an accessible 1:1 focus. It is required that wavelengths up to 1 mm be brought to the experiments. The large acceptance angle is needed to preserve the source brightness at the long wavelengths where diffraction would be significant.

A great deal of design effort has been expended on several unique problems: extraction of the large aperture beam from the storage ring, design of a beam line to bring the radiation up to a platform experimental area, and optical devices. The design extracts the beam downstream of the standard 5° and 22° ports at 33.5° to a first mirror, thence through a series of mirrors up to an experimental station at a mezzanine level.

The optical design is controlled by (a) high power loadings on the first mirror (b) the need to transport the beam out of and away from the ring without interference with existing ports (c) diffraction and (d) the desire only to have pure horizontal or pure vertical deflections of the beam for polarization control.

As with the insertion device lines, thermal loading in the optics is a problem, especially the first mirror M1. The total power in the mirror is 224 W but the power density at the center is 481 W/cm^2 . M1 is a plane mirror that will be cooled and may be made of silicon carbide. A careful thermal distribution analysis is being done to study the cooling techniques, and to understand the tolerance of the long wavelengths to thermally induced figure changes. M2 is also a plane mirror, 550 mm above M1 and the M1,M2 combination is designed to be inserted (or extracted) as a prealigned pair without breaking machine vacuum. The M1,M2 "periscope" sends the beam back along in the "upstream" direction of the electron beam to an ellipsoidal mirror, M3 which deflects the beam horizontally by 90° (p-polarization) onto the experimental floor where it is intercepted by plane mirror M4. M4 deflects the beam vertically to M5 which is a focusing mirror identical to M3. Thus, an image of the source with a magnification of 0.9 is produced (primary focus) between M4 and M5 which is remagnified to give a 1:1 image (secondary focus) near the window, 1550 mm from M5.

X21 - High E Resolution Scattering

The High E Resolution Beam Line will be developed in order to establish a program for inelastic x-ray scattering, ultimately with energy resolution $\Delta E/E \sim 10^{-7}$ in the $E = 10 \text{ keV}$ range. The use of x-ray inelastic scattering, as a technique complementary to neutron inelastic scattering, will provide, for example a powerful tool for studying surface excitations. The magnetic insertion device for X21 will be essentially the same as the permanent-magnet, hybrid-wiggler with variable gap discussed earlier for the X25 program. It's high brightness in the 1-16 keV range

will provide the necessary flux for the inelastic scattering experiments. Various optical schemes have been advanced, but the design is still at an early stage of development.

U13 - High Resolution Soft X-Ray Spectroscopy (TOK)

The soft x-ray scattering beam line will be developed as a separate beam line on the VUV port used for the Transverse Optical Klystron experiment. The magnetic device for this port will be designed and developed specifically for the TOK program. The scientific goal is to establish a beam line for high resolution scattering in the 0.1-2 keV energy range. As with X21, the U13 beam line is at a preliminary stage.

SCHEDULE, COSTS, ORGANIZATION

Figure 7 is a bar graph showing the impact of extending the construction program to four years. The reduction of available funds for beam line components in FY1985 will delay their completion to the extent indicated by the dashed line. As noted earlier in this report, the building construction is not expected to be delayed more than six weeks.

NSLS II SCHEDULE
IMPACT OF FOUR YEAR VS. THREE YEAR PROGRAM

Figure 7

Project cost estimates by major category are given in Figure 8. The building will cost about \$0.5 million more than beam lines. This is offset by the greater cost of Engineering, Design and Inspection (ED&I) for experimental beam line components. It can be seen that the average cost of a Phase II beam line (hardware plus design) will be \$1.75 million.

NSLS II BUDGET ESTIMATE			
(Four Year Construction Plan)			
(November, 1984)			
			<u>\$ x 1000</u>
• CONVENTIONAL CONSTRUCTION			7877
• BEAM LINES			7403
• ED & I			
Conventional Construction	1009		
Beam Lines	3069		4078
• CONTINGENCY			
Conventional Construction	850 (10.9%)		
Beam Lines	1662 (25.4%)		<u>2512</u>
			\$21,870

Figure 8

The NSLS staff is a matrix organization made up from groups within the NSLS Department, several Divisions of the Laboratory and the support of the architect and engineer's forces. Lines of responsibility are shown in Figure 9. Figure 10 lists the personnel involved with beam line design.

For each beam line there is a Principal Scientist and Principal Engineer who are responsible for concept, reduction to practice, schedule and cost controls. Consulting scientists, most from outside organizations, have made and continue to make important contributions to the design. In addition, a large group of supporting staff and others are working on components or analyses that affect more than one beam line.

NSLS PHASE II CONSTRUCTION ORGANIZATION

Figure 9

Personnel Associated with NSLS II Beam Line Design

Others

Alforque Avery (LBL) Hoyer (LBL) Sharma Ulc	Thermal Analysis
---	------------------

Larson	Controls
--------	----------

Oversluizen Ulc	Monochromators
--------------------	----------------

Krinsky Galayda Halbach (LBL) Luccio Pellegrini van Steenberg Yu	Insertions & Chamber- Machine Interfaces
--	---

Takacs	Optical Design
--------	----------------

Schuchman Foerster	Vacuum
-----------------------	--------

Jordan Brite DeLeo LeDoux Onsrud Palo Pjerov Short Siemon Stoeber	Detail Design
--	---------------

Figure 10

X. REPORTS OF RESEARCH AT THE NSLS

This section contains the reports of research carried out at the NSLS storage rings during the 1984 Fiscal Year. Most of the contributions have been specifically written for this annual report by the experimenters. Their efforts are greatly appreciated by the Annual Report Staff. All of the papers this year are for work done on the VUV ring. They are presented by beam line and are arranged alphabetically by first author. The Table of Contents is also arranged by beam line and first author. A listing of all NSLS users from September 1982 to October 1984 can be found in Section III.

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Metal-Insulator Transition on the Ge(001) Surface

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The (001) surfaces of germanium and silicon are prototypical examples of systems possessing a strong, short range reconstruction accompanied by a longer range weaker ordering. The short range interaction is generally accepted to involve asymmetric dimerization of nearest neighboring surface atoms.¹ The energetics involved are hence those of chemical bond formation. If this were the only ordering present, a (2×1) surface unit cell would result. Various reports of larger unit cells ($p(2 \times 2)$, $c(2 \times 2)$, $c(4 \times 2)$) have usually been explained in terms of longer range, energetically weaker ordering of neighboring dimers.²⁻⁴ Recently, total-energy surface slab calculations have been combined with renormalization group techniques to predict a phase transition at $\sim 200\text{K}$ on both surfaces from a low temperature phase in which the dimers are ordered to a high temperature phase in which the dimer bond is preserved but the dimers are randomly oriented.⁵ Such a transition was subsequently observed by LEED.⁶

We report here high resolution angle-resolved photoemission (ARP) experiments which indicate that this transition is accompanied by a metal-insulator transition.⁷ This is demonstrated in Fig. 1. The left panel shows ARP energy distribution curves collected at normal emission in the vicinity of the Fermi level (E_F) at various sample temperatures. At room temperature, a distinct peak at E_F is observed; as nearly as we can tell, the surface is metallic. The peak gradually disappears as the temperature is lowered, leaving a semiconducting surface for $T \lesssim 100\text{K}$. The right panel of the figure shows LEED profiles at the corresponding temperatures in an azimuth which includes a (1×1) beam, a (2×1) beam, and a $c(4 \times 2)$ beam (the 00 , $1\frac{1}{2}$, and $\frac{1}{2}$, $\frac{1}{4}$ beams, respectively). The metal-insulator transition is simultaneous with the observed dramatic sharpening of the $c(4 \times 2)$ beam.

Perhaps the most novel aspect of the metallic peak is its angular behavior. The intensity is sharply peaked within a few degrees of the surface normal. We argue that the metallic peak is associated with disorder-induced defect states pushed into the gap. This angular character is a reflection of the real-space extent of these states. The simplest lattice excitation is the flipping of one dimer. This is shown schematically in Figure 2 in the plane of the dimer axis. The direction of disordering is known to be along such a chain of dimers from atom-scattering studies. In the $c(4 \times 2)$ structure, the orientation

Figure 1. Left panel: EDC's of the Ge(001) valence band at $h\nu = 20 \text{ eV}$ in the vicinity of E_F at normal emission for various sample temperatures.

Right panel: Corresponding LEED profiles extending from the (00) beam to the $(1\frac{1}{2})$ beam. Gradual appearance of a sharp beam at $2.2 \text{\AA}^{-1}$ is indicative of the transition to an ordered $c(4 \times 2)$ state.

Figure 2. Schematic of the Ge(001) surface dimers in the normal $c(4 \times 2)$ configuration and the dimer-flipped configuration.

of the dimers alternates so that a simple dimer flip orients three neighboring dimers in the same direction. There are two useful observations to be made

here. The first is that 3 lattice spacings is approximately the real-space extent required to explain our angle- or momentum-space intensity profile. Second, the surface-atom dangling bonds not associated with dimerization are well-placed for pairing with neighboring dimers in the $c(4 \times 2)$ structure, but much less well-oriented in the dimer-flipped orientation. It is likely that a state would be pushed into the gap in the latter case. Further calculations will be required to determine whether a simple dimer flip is sufficient to explain our observations or whether a more collective mode is necessary.

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Surface States on Simple Metal Surfaces

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The existence of electronic states localized at nominally clean metal surfaces has long been a subject of interest.¹ The accurate characterization of such states continues to be an active area of experimental and theoretical work. In the past year, using high-resolution synchrotron radiation based angle-resolved photoemission (ARP), we have nearly doubled the number of known surface states on a few simple metal surfaces. In addition, very accurate 2-dimensional energy dispersion relations have been measured and compared to the latest self-consistent calculations. A summary of these results is given in Table I.

TABLE I

Surface	Symmetry	<u>Experiment</u>		<u>Theory</u>		Reference
		E_B	m^*/m_e	E_B	m^*/m_e	
Cu(001)	$\bar{X}_1$	0.06(1)	.16(2)	.07	.20	3, 4, 5
Cu(001)	$\bar{X}_2$	4.62(3)	.70(2)	4.10	.63	4, 5
Cu(011)	$\bar{Y}_1$	4.72(5)	nm			4
Ag(111)	$\bar{\Gamma}_1$	5.10(5)	1.18(2)			6
Al(111)	$\bar{\Gamma}_1$	4.56(4)	1.03(1)	4.68		7, 8
Al(111)	K_{14}	0.7(1)		0.90		7, 8

In addition to the simple existence, symmetry, and energy dispersion of such states, we have been attempting to provide a further characterization of the surface state wave function in terms of its decay length and oscillation frequency normal to the surface. Simple tight-binding² and nearly-free-electron⁷ theories have been derived to allow estimates of such quantities using experimental results. We prefer here to use a more intuitive approach. A long decay length implies a sharply peaked frequency spectrum normal to the surface. Neglecting many interesting and important effects, ARP intensities are roughly given by the Fourier transform of the initial state wave function. This peaked momentum distribution thus implies visibility over a narrow range of final state momenta, hence, a narrow range of photon energies. Alternatively, a state with a very short decay length, e.g., one localized to the first layer, will be observed over a very wide range of photon

Fig. 1. Energy distribution curves collected for emission normal to an Al(111) surface

Fig. 2. Energy distribution curves of Cu(001) collected at the $\bar{M}$ point of the surface Brillouin zone

energies. Results for phototypical extreme examples are shown in fig. 1 for Al(111) and fig. 2 for Cu(001). The former has a surface state located at $\bar{\Gamma}$ at $4.56 \pm 0.4 \text{ eV}$ binding energy with a decay length estimated to be in excess of $50 \text{ \AA}$. The state is observable with significant intensity over a photon energy range of only 5-10 eV near $h\nu = 53 \text{ eV}$. Cu(001) possesses a Tamm surface state located at $\bar{M}$ with 1.8 eV binding energy.⁹ Calculations have predicted that this state is localized nearly 100% to the surface layer.⁵ Consequently, the state's intensity relative to that of the bulk feature at 2.0 eV from which it is split off is nearly constant over a wide range of photon energy.

Interesting comparisons can be made to a similar state at $\bar{M}$ of Ag(001). This is predicted to be highly localized to the outermost layer as well.^{10,11} Our experimental results, shown in fig. 3, are at variance with this prediction. The surface state-to-bulk feature intensity ratio varies by a factor of 3. This is intermediate between the Al(111) and Cu(001) extremes, and implies significant bulk penetration. The $\bar{M}$ point on (001) face-centered-cubic surfaces projects from the X-W-X line of the bulk Brillouin zone. The surface state splits from the rather flat uppermost d-band along this line. The simple tight-binding theory indicates that the flatter this bulk band is,

Fig. 3. Energy distribution curves collected at the $\bar{M}$ point of Ag(001). As in fig. 2, the high lying peak is a surface state, while the lower one is a bulk feature. Note the significant intensity oscillations near $h\nu = 35$ eV.

the smaller is the surface state decay length. Hence, endowing this bulk band with a width in excess of that used in the calculation phenomenologically explains our experimental findings. The calculation is non-relativistic, and the spin-orbit interaction does perturb the bulk band near X significantly. This indicates a novel effect of such relativistic corrections on surface state character.

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ANGLE RESOLVED PHOTOEMISSION STUDIES OF ELECTRONIC STRUCTURE

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Angle resolved photoelectron spectroscopy (ARPES) is an effective technique for determining the valence electronic structure of ordered two- and three-dimensional systems. We present summaries of two ARPES studies performed at the U4 beamline of the NSLS UUV ring. This beamline is comprised of a 6-meter toroidal grating monochromator and a high-resolution hemispherical photoelectron-energy analyzer in an ultrahigh vacuum chamber.

ORDERED Cu OVERLAYERS ON Ag(001)

The electronic structure of thin layers of metals can differ substantially from that of the bulk metal. These differences arise both from the two-dimensional (2D) nature of the electronic states in these films and from the influence of surface and interface effects upon the electrostatic potential seen by the electrons. Recent experiments have demonstrated the important role that the band width and energy of valence *d*-bands play in the chemical reactivity and surface magnetism of thin films. The factors controlling these *d*-band parameters are not well understood theoretically. We performed ARPES measurements of the *d*-band electronic structure of copper films 1 to 6 atomic layers thick grown on the (001) face of silver. By comparing ARPES spectra taken on different thicknesses of Cu with the corresponding spectra for clean Ag surfaces it was possible to differentiate between Cu- and Ag-derived electronic states. In Fig. 1 the features denoted by tick-marks originate from Cu3*d* orbitals. The remaining features are due to the Ag substrate. By measuring the energy of the ARPES features as a function of emission angle we deduce portions of the 2D band structure of the Cu monolayer on Ag(001) as illustrated in Figure 2. The various symbols in Fig. 2 represent measured energies of the photoemission features, while the curves drawn through the data are qualitatively similar to band structure calculations for an ideal unsupported copper monolayer. The theoretical band structure had to be stretched substantially and placed slightly lower in energy to allow the close fit to the ARPES data shown in Fig. 2.

After these empirical corrections the resulting bandstructure is closer in width and energy to that of bulk Cu. It is hoped that state-of-the-art band structure calculations which treat the Cu-Ag hybridization interaction and charge transfer in a self-consistent manner would lead to closer agreement with our results without empirical corrections.

Fig. 1. ARPES spectra of 0 to 6 monolayers (ML) of Cu at 30 eV photon energy.

Fig. 2. Two-dimensional band structure of a Cu monolayer derived from ARPES measurements. Hatched region represents Ag 4d continuum.

CHARGE-DENSITY-WAVE PHASE TRANSITION IN TiSe_2

TiSe_2 is a layered compound which undergoes a charge density wave (CDW) phase transition below 200K which doubles the length of the unit cell along all crystal axes. This doubling of the periodicity allows a direct interaction between $\text{Se}4p$ states at the center of the hexagonal Brillouin zone (BZ) and $\text{Ti}3d$ states at the edge of the BZ. The energy of this interaction is thought to be a driving force for the CDW transition. The details of various models of the CDW therefore depend critically upon the relative energies of the $4p$ and $3d$ bands. Band structure calculations and earlier ARPES studies have given various results varying from a ~ 1 electron volt (eV) gap between p and d bands to similar magnitude $p-d$ band overlap.

We performed photon energy dependent ARPES measurements of TiSe_2 above and below the transition temperature to more precisely determine the band lineup. Both the $\text{Se}4p$ bands which form the valence band maximum and the $\text{Ti}3d$ bands which form the conduction band minimum show some dispersion with photon energy. We find that at the extremes of this dispersion the two bands do not overlap appreciably in either the CDW or normal phases. This is illustrated in Fig. 3 where the maximum of the dispersion of the $\text{Se}4p$ bands is compared to the $\text{Ti}3d$ minimum energy. They are nearly degenerate, but a small semiconducting gap ($\sim .02$ eV) is suggested by our ARPES results. This contradicts the commonly held view that TiSe_2 has a ~ 0.2 eV semimetallic overlap. Our results have important implications for current efforts to develop a microscopic theory of the TiSe_2 CDW phase.

Fig. 3. Dispersion of two $\text{Se}4p$ bands which form the valence band maximum. The $\text{Ti}3d$ conduction band minimum is indicated.

Beam Line U5: (FEL and Diagnostic Line)

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The beam line #5 in the VUV storage ring includes two beam lines: the Free Electron Laser (FEL) line and a beam diagnostic line.*

The Free Electron Laser Beam Line

This line extends from one of the straight sections of the VUV ring, where the permanent magnet undulator is installed. At the present time, there are three stations on this line: (1) upstream and (2) downstream of the ring straight for the FEL experiment, and (3) midway downstream to use the undulator as a source of monochromatic radiation in the far ultraviolet. This latter station is described elsewhere in this report, by P. Johnson.

The FEL beam line was designed to carry on an experiment of production of coherent radiation in the visible-to-ultraviolet region of the spectrum. An amplifier and a laser oscillator are being studied.

For the amplifier, a CW Argon-Ion laser is being used together with a variable gap, 38 period permanent magnet undulator. The laser is located in the FEL downstream station hutch; its beam propagates counter the direction of motion of the electrons in the VUV straight, along a line two meters above the electron orbit plane. In the upstream station hutch the laser beam is deflected downwards and then steered into the storage ring. There, the laser beam is propagated collinear with the electron beam.

The undulator has been described in the literature. It was installed on the ring early in 1983 and systematic tests were performed during the summer of 1984.

Undulator radiation has been observed. Color rings showed up also with the undulator gap wide open (residual field of few hundred gauss) due to interference. We used these rings to determine the position of the electron beam, in agreement with readings from the pick-up electrodes, and to align the laser with the electron beam.

For the oscillator experiment a 17 meter long cavity with concave mirrors was also prepared and aligned.

*The scientific staff responsible for studies on the FEL line included: J. Galayda, Y. Hirai (at an earlier stage), A. Luccio, C. Pellegrini, A. van Steenberg, G. Vignola, L.H. Yu. The diagnostic line was set up by A. Luccio and L.H. Yu.

The spectrum of the undulator in a spectral region suitable for FEL operation was also measured through a scanning pinhole (Fig. 1). The fundamental line showed a relative width $\Delta\lambda/\lambda \approx 2.8\%$ at 355 nm, to be compared with the theoretical value of $1/38 \approx 2.6\%$. A small side peak on the low frequency side was also observed, indicating the presence of some distortions in the electron orbit through the undulator.

Fig. 1. Undulator Spectrum at 250 MeV

Higher harmonics in the undulator spectrum, up to the 7th, were also observed, but no quantitative measurements were attempted.

The Diagnostic Line

This line contains a polished Molybdenum mirror in vacuum, which deflects the synchrotron radiation from a bending magnet upwards through a

window. A second mirror in air deflects the light horizontally and a system of three lenses and a beam splitter forms two images of the arc source on detectors, with magnification 1.4:1.

Detectors are diode arrays with 256 elements on 25.4 μm centers, placed along a vertical and a horizontal line, to measure source dimensions, vertical and horizontal respectively.

Beam dimension measurement errors are due to: diffraction, errors in lens positioning, spatial resolution of the diode array and errors due to arc extension of the source. The optical set-up was chosen so to make all these errors comparable (≈ 0.025 mm).

Fig. 2 shows a typical beam profile measurement at 750 MeV with the undulator gap at 28 mm (undulator r.m.s. parameter $\kappa \approx 1$).

Fig. 2. Typical Beam Size Monitor Output.

Undulator based beamline studies on U5

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An undulator is expected to produce an intense flux of photons into a highly collimated beam and further show characteristic harmonics at wavelengths given by¹

$$\lambda = \frac{\lambda_0}{2n\gamma^2} (1 + K^2) \quad n = 1, 2, 3, \dots$$

Here λ_0 is the magnetic period, K is the magnetic strength parameter related to the magnetic field strength, and γ the stored electron beam energy.

At normal operating energies (750 MeV) the FEL undulator installed on the NSLS UV ring is therefore expected to have a fundamental harmonic at wavelength $\lambda = 300\text{\AA}$ for magnetic strength parameter $K = 1$.

We have constructed a simple beamline to allow measurements of the absolute photon flux available from this device at wavelengths in the long wavelength tail of the fundamental. The central element of this beamline shown in Fig. 1 is a small² monochromator based on the chromatic aberration properties of a LiF lens.² This lens focuses different wavelengths at different points along the optical axis and monochromatization is achieved by moving the lens to focus different wavelengths onto a fixed 200 μm wide exit slit.

Photoelectron spectroscopy was carried out with a CMA; photoelectrons being ejected from a freshly evaporated gold surface. Examination of a typical series of EDC's recorded on this system and shown in Fig. 2 allows measurements of the bandwidth of the monochromator to be made. By then measuring the total yield of electrons from the surface and comparing³ with previously published electron yield measurements from the same surface³ it is possible to obtain the total flux of photons from the undulator source. In a 3% bandwidth we measure a photon flux of $\approx 3.5 \times 10^{15}$ photons/sec/amp of stored current. This is less than the theoretical value⁴ of 8×10^{15} photons/sec/1% bandwidth/amp but may well reflect the misalignments of the stored electron beam in the undulator and consequent misalignments in the optical system. Steps are being taken in the current shutdown to correct these problems.

There has been much discussion in the literature as to the effects of beam damage in undulator based beamlines. In the present experiments the

photon flux from the undulator was deflected into the monochromator by a flat copper mirror. After three months of operation this mirror was found to have visible signs of carbon build up. However, it is felt that this was probably due to the proximity of the mirror to the front end where the pressure frequently rose into the mid 10^{-9} torr range.

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Fig. 1 Layout of the apparatus, based on a LiF-lens monochromator used for measuring the total photon flux.

Fig. 2 Measured EDC's from evaporated gold as a function of photon energy.

X-RAY LITHOGRAPHY -- BEAMLINE U6

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OBJECTIVES

Over the last decade there have been remarkable advances in the manufacture of integrated circuits. In 1974, the smallest features being replicated in production were about $4.0\text{ }\mu\text{m}$ wide; by now (1984) they have shrunk to $1.0\text{ }\mu\text{m}$ wide. At this size, however, it has become increasingly difficult to progress to smaller features because of the blurring caused by diffraction of the UV light used to expose the photoresist on the silicon wafers. Although there are techniques being developed to extend conventional optical lithography to smaller dimensions, they are difficult and costly. An alternative approach is to use X-rays, which, because of their much shorter wavelength, promise better resolution than can be obtained by today's methods.

The primary goal of our work is to develop a system to use synchrotron radiation for X-ray lithography. Synchrotron radiation has two major advantages over conventional X-ray sources: the radiation is collimated, and it is orders of magnitude more intense. We therefore believe that a storage ring source will allow the best possible resolution with reasonable throughput.

THE BEAMLINE

There are two fundamental problems which must be solved for X-ray lithography using synchrotron radiation. First, the wafer must be exposed in a non-UHV atmosphere, and second, the radiation must be made uniform over an area of several square centimeters at the wafer plane. The beamline, shown in Figure 1, uses a beryllium window to separate the exposure chamber from the UHV part of the beamline and the storage ring. To achieve uniform illumination an oscillating mirror is used to scan the beam up and down on the wafer. The remaining beamline elements relate primarily to vacuum protection. A more detailed discussion may be found elsewhere (1,2).

Fig. 1. Assembly drawing of beamline.

EXPERIMENTAL PROGRAM

We have concentrated our efforts for the past year on characterizing different aspects of the lithography process and improving our beamline and control system. In particular, we have looked at these issues:

Calibrations: We have studied different techniques for real-time measurement of the incident flux. At present, the best method we have found is to simply integrate the electron beam current in the ring over time. However, changes in the orbit of the beam require frequent re-calibration of the relationship between current and flux. To calibrate, we have used a commercially available dosimeter film (3) to measure the absolute flux for a given integrated current.

Uniformity/Intensity: There is an obvious trade-off between the size of the illuminated area and the intensity of radiation striking the wafer. To increase the intensity, we use a cylindrical scanning mirror, which serves to further collimate the radiation and results in approximately a factor of 3 increase over what would be obtained with a planar mirror. One drawback, however, is that the beam reflected from such a mirror is curved, which requires significant overscanning of the exposed area in order to achieve uniformity. The trade-off between area and intensity is therefore non-trivial. Using dosimeter film, we have been able to measure the uniformity of illumination for different mirror motions. For an area 2" high and about 2" wide, we have obtained illumination uniform to $\pm 7\%$, while for an area only 1" high we have obtained nearly four times as much flux with illumination uniform to $\pm 6\%$. With 200 mA of stored beam current at 750 MeV, the power densities transmitted through the mask to the wafer are about 3.0 and 11.5 mW/cm² for these two motions respectively, giving exposure times of about 180 seconds and 45 seconds in a resist with a sensitivity of 450 J/cm³, such as terpolymer (see below). A contour plot of the uniformity for the 2" high motion is shown in Figure 2. Note that most of the non-uniformity is from left to right rather than up and down, which indicates that the uniformity is limited not by the motion of the mirror but by either a non-uniform coating on the mirror or non-uniform thickness of the beryllium window.

Fig. 2. Contour plot of the incident intensity distribution at the wafer plane. The maximum value is set to 100% and contour lines for 90, 80, 70, 60, and 50% are plotted. The exposed area is about 2" high.

1/4 μm gaps with 3/4 μm pitch
Fig. 3. Pattern showing 0.25 μm gaps and 0.5 μm lines in 1.2 μm thick terpolymer resist, exposed with 450 J/cm³.

Resists: We have studied a variety of resists to determine their sensitivity and resolution. In general, positive resists such as PMMA and terpolymer have been found to have better resolution than negative resists, although negative resists are generally much more sensitive. The smallest features we have been able to replicate are 0.25 μm wide, as shown in Figure 3. The resolution is probably limited by the pattern on the mask.

In addition, we have worked with J. Corelli and his students from the Rensselaer Polytechnic Institute on a project to increase the sensitivity of PMMA by several orders of magnitude while turning it into a negative resist (4). After exposure, a monomer of acrylic acid is grafted on to the exposed resist, which dramatically alters the solubility. Negative tone features as small as 1 μm have been replicated with doses only 1/1000 of those normally used for PMMA.

Spectrum Measurements: Working with David Nagel of the Naval Research Laboratory, we have taken data to measure the spectra of radiation coming through the beryllium window as well as through different mask substrate materials. The measurement technique uses a bent crystal spectrograph to diffract the different wavelengths to different positions on X-ray sensitive film (5).

ACKNOWLEDGMENTS

We wish to thank the members of the Chip Lithography group at the Watson Research Center for their contributions to so many aspects of this work. We also wish to thank the staff of the National Synchrotron Light Source for their cooperation in providing us with an X-ray source, and to acknowledge DARPA, who provided partial support for this work under contract number N00014-82-C-2094.

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**Fragmentation of Small Molecules
Following Soft X-Ray Absorption Near the Carbon K-Edge**

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The absorption of soft-X-ray photons by C 1s electrons in CO, as well as in a number of aliphatic and aromatic hydrocarbons and their derivatives has been studied by carbon K-edge absorption spectroscopy at the U7 beamline in the ion yield mode. It is found that the absorption process results in ionic fragmentation of the original molecules. The fragmentation pattern changes whether the C1s electron gets ionized or excited into a Rydberg-like orbital, or into an unfilled molecular orbital, or into a quasibound resonance state. Moreover, the fragmentation occurs specifically around the site of the carbon atom where the bound (atomic) to bound (molecular orbital) transition takes place. Based on these observations one might consider the use of tunable soft X-ray to produce the heretofore uninvestigated excited states and to induce photochemistry or to selectively break large organic molecules. The latter has very interesting implications in photon-stimulated desorption from surfaces, Biology and Lithography.

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Figure 1 shows the spectra of our fragmentation results of acetone $[(CH_3)_2CO]$, a molecule containing chemically inequivalent C atoms. While the methyl carbon CH_3- is saturated bonded, the carbonyl carbon $C=O$ remains unsaturated and has considerable unoccupied p character at the carbon site. This results in different ionization threshold for the two different C atoms shown in Figure 1a where the higher threshold is for the carbonyl carbon. Since saturated hydrocarbons do not often display an intense π^* resonance, only the carbon atom in the CO group is expected to give rise to the π^* excitation. The most striking observation in Figure 1 is the presence of π^* resonance in the C^+ and O^+ yield but not in CH_3^+ yield and the H^+ . This result strongly indicates that the π^* excitation causes the molecule to break locally, leading to C^+ and O^+ and presumably neutral CH_3 groups. This effect may have very important future applications.^{3,4}

Figure 1. Total ion yield and fragment ion yields of acetone near the carbon K-edge. The zero of each curve is indicated by tick marks on the vertical scale. The ionization limits shown in (a) are ESCA results.

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Core Level Shifts and Electronic Structure of Cu_3Au

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Introduction

This work was motivated by a desire to understand the effects of geometry and charge transfers between the constituents of an alloy on its electronic structure. Alloys, together with small metal particles, are known to be very good catalysts for a number of chemical reactions, but very little is known about the atomic and electronic structures of their surfaces. This photoemission study of the $\{100\}$ and $\{111\}$ surfaces of Cu_3Au was undertaken in conjunction with LEED (low energy electron diffraction) and AES (Auger electron spectroscopy) structural studies of Cu_3Au and Ni_3Al which are being performed at Stony Brook. This work has established that the $\{100\}$ surfaces of these A_3B -type ordered alloys consists of 50% A and 50% B, with the second layer being 100% A, while the $\{111\}$ surfaces always have 75% A and 25% B.

Experiment and Results

On U7 we have studied the valence bands and core levels of the $\{100\}$ and the $\{111\}$ surfaces of Cu_3Au . We have found significant changes both with respect to pure Au and Cu and with respect to emission from the surface versus the bulk in the alloys.

The bulk Au 4f core levels in the alloys have a 0.3 eV higher binding energy than in pure Au. In the alloys the surface Au 4f core levels are shifted towards lower binding energy by 0.41 eV on the $\{100\}$ surface, and by 0.37 on the $\{111\}$ surface, whereas the surface-bulk splitting in pure Au is 0.32 eV. These results were obtained by fitting two Lorentzian line shapes to the Au 4f $7/2$ peak, as illustrated in Fig. 1.

Surprisingly, however, the Au 5d levels are not shifted from bulk to surface, contrary to accepted theories of surface-core-level shifts on noble metals. These theories do not take into account changes in the valence-band configuration between an alloy and the corresponding pure metals and between surface and bulk. However, we found evidence for the fact that the d-electron density is smaller in the alloy than in pure Au, and for the fact that this same density is larger on the surface than in the bulk.

Fig. 1 Au 4f_{7/2} core level peaks showing deconvolution into surface (lower binding energy) and bulk contributions. The top peak is from pure gold, while the lower is from the Cu₃Au {100} surface.

Discussion and Conclusion

The connection between the Au 5d configuration and the observed core level shifts may be summarized as follows. In Cu₃Au, as in all Au alloys studied to date, there is a substantial flow of s-like charge from Cu to Au.² This would normally result in reduced Au core level binding energies; however another consequence of this charge transfer is an increase in s-d hybridization at the Au sites and corresponding depletion of the 5d-electron density. We can see this depletion directly from our valence-band spectra, as mentioned above, and we can further identify the 5d_{5/2} peak as the one that exhibits the depletion. The d-electron depletion causes an increase in binding energy of the 4f core levels, and this explains the observed shift of these levels in the alloy with respect to pure Au. Furthermore, the reduced number of Cu neighbors on the alloy surfaces explains why the s-charge transfer is

smaller, the d-charge depletion smaller and hence the 4f-core-level binding energy smaller than in the bulk, as observed experimentally. Thus, we believe that the direct observation of the changes in valence-electron configuration upon alloying is very significant. It indicates, among other things, the importance and usefulness of synchrotron radiation in revealing details of the valence-band structure in alloys and interfaces.

This work will be extended in the future to studies of other alloy systems, e.g. Ni_3Al and metal overlayers.

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Angle Resolved Photoemission and Band Structure of Cu_3Au

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Introduction

For the purpose of determining the band structure, its difference from the band structure of the constituents and the extent of the agreement with band-structure calculations, we undertook a study of normal photoelectric emission from $\text{Cu}_3\text{Au}\{001\}$ and $\text{Cu}_3\text{Au}\{111\}$ as a function of photon energy. The following reports the preliminary results of this investigation.

Results and Discussion

Photoemission energy distribution curves were measured at normal emission from the $\{100\}$ and $\{111\}$ surfaces of Cu_3Au alloys. Fig. 1 shows spectra measured with photon energies in the range 14-22 eV from the $\{111\}$ surface.

Comparison of our results with those of Knapp et al.¹ for $\text{Cu}\{100\}$ and $\text{Cu}\{111\}$ and Stöhr et al.² for Cu and Au surfaces reveals many similarities and a few subtle differences. The dispersion of the Cu 3d band is very much the same in $\text{Cu}_3\text{Au}\{001\}$ and $\{111\}$ as in the corresponding Cu surfaces, but the relative magnitudes of the $3d_{3/2}$ and the $3d_{5/2}$ peaks are different. The dispersion of the s-p band is different in Cu_3Au and Cu, the former being in agreement with the calculated band structure.³ Close scrutiny of the conduction band seems to reveal that in both the $\{001\}$ and the $\{111\}$ surface of Cu_3Au the character of this band is more like the Au 6s than the Cu 4s. We plan to plot the band structure as determined from our experiments and test the calculations of Skriver and Lengkeek.

We have also observed a surface state at normal emission on the $\{111\}$ surface of Cu_3Au , corresponding to the Cu $\{111\}$ surface state.⁴ The alloy surface state has been observed once previously using a resonance lamp by Jordan and Sokal.⁵ By varying the photon energy at normal emission we were able to confirm the two dimensional nature of the surface feature (Fig. 1). The peak also disappeared when the sample was exposed to oxygen. Taken together these results are strong evidence that the observed feature is indeed a surface state.

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Fig. 1 Normal emission valence band spectra of Cu_3Au {111}.

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Photon Energy Dependent Branching Ratios of the Inner Valence Satellites in the Photoemission of Solid Ethylene

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Our measurements of the photoelectron branching ratios of the outer and inner valence emission of solid ethylene (C_2H_4) as a function of photon energy between 40 eV and 200 eV have enabled us to identify the various photoemission lines. Whereas the single particle picture is valid for photoemission from the outer valence orbitals, the excitation of the innermost valence orbital of ethylene (C 2s derived, $2a_g$ symmetry) is accompanied by a "shake-up" satellite. Ethylene, along with acetylene, is the simplest hydrocarbon that exhibits significant shake-up structure.

The experiments were performed on beamline U7A using a plane grating monochromator.¹ Fig. 1 shows photoelectron EDC's at various photon energies between $h\nu = 40$ eV and $h\nu = 200$ eV for a $\approx 30\text{\AA}$ thick film of ethylene condensed onto a liquid He-cooled cryostat. At this film thickness, the binding energies were observed to be referenced to the local vacuum level.

In agreement with theory,² the inner valence orbital emission line at 18.7 eV binding energy has largely single hole character $(2a_u)^{-1}$, whereas the two lines at 23.2 eV and 26.9 eV, we believe, are unresolved doublets containing various amounts of $(2a_g)^{-1}$, $(2a_u)^{-1}(1b_{2u})^{-1}(1b_{3g})$, $(1b_{2u})^{-2}(4a_g)$, and $(1b_{2u})^{-2}(5a_g)$ character. As shown in Fig. 2, the branching ratios of these two doublets show the same dependence on photon energy, which is distinctly different from the cross sectional behavior of the 18.7 eV singlet. Further, the oscillatory nature of the branching ratios for the 23.2 eV and 26.9 eV features indicates interference effects between the different possible excitation channels.

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Fig. 1. Photoelectron EDCs of a thin film of solid ethylene (C_2H_4) as a function of photon energy. The binding energies are obtained by referencing the $1b_{2u}$ feature to gas phase results. S_1 and S_2 label the satellite features under discussion.

Fig. 2. Branching ratio of the outer valence orbitals and the three distinct features in the photoemission of the inner valence region of C_2H_4 versus photon energy. The corresponding values for gas phase C_2H_4 measured with a Y Mg X-ray source are shown also (x).

Studies of Gd Clusters on Carbon: The Question of Initial State or Final State Effects

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Introduction

In recent work the question of whether the core levels of metal clusters are shifted due to initial state effects, or whether instead the final state configuration of the cluster is the major source of the core level shift, still remains unsettled. Part of this problem involves the intrinsic difficulty of devising an experiment which unambiguously distinguishes between final state effects and initial state effects.

As an example of an initial state effect we consider the levels of very small clusters of Pd in tunneling contact with a metal, Nb, substrate, but not actually touching. In this case the cluster states are referenced to the substrate vacuum level, and since the affinity level in the small cluster can be above the Fermi level of the metal substrate, charge cannot flow from the substrate to the particle to equilibrate Fermi levels. We argue that in this case the system is not in equilibrium and the vacuum level serves as the reference level. It is only when the particle size increases enough so that charge can be transferred that thermodynamic equilibrium is attained and the Fermi level becomes the reference level. Experiments on this system are consistent with this interpretation.

In the case of particles on graphite, a subject of great interest, the situation may be either similar or in fact different. If the initial levels in the cluster were aligned with the vacuum level, the observed shifts could be explained by the change in the initial state level as equilibrium is established between the cluster and the substrate in much the same way as the above situation. Or, on the other hand it is possible that because of the poor conductivity of the graphite, charge transfer between the substrate and cluster is ineffective and a charge is left on the cluster, i.e. a final state charging effect as suggested by Wertheim, et al.²

To design an experiment which could distinguish between initial state alignment and a final state core level shift due to electrostatic charging, we have made measurements on clusters of Gd on Nb metal and on both thin carbon layers and thick carbon layers. The main point of this experiment is that Gd has a much smaller work function than the carbon substrate. If initial state alignment with the vacuum level determines

the core level shifts it would be expected that the initial Gd levels would be at lower binding energy than in bulk Gd and would move to higher binding energy, i.e. more towards the bulk levels, as the cluster size increased. Whereas if Coulomb effects due to the photoemission process were important, it would be expected that the core levels would shift to lower binding energy as the clusters were made larger.

Experimental

The experiments were done by sputtering carbon on a Nb surface, after which Gd was evaporated onto the carbon layer. Both the work function and the Gd f states could be monitored in these experiments by valence band photoemission measurements at 60 eV. The evaporations were done at a pressure of about 3×10^{-10} Torr, at an evaporation rate of about a monolayer in two minutes, which was somewhat marginal for a reactive material such as Gd. However, both the work function results and the differences of the core level shifts on pure metal, thin carbon, and thick carbon all imply that oxygen was not a serious problem. Auger spectra were used to estimate the amount of Gd that was deposited in the different cases.

In Fig. 1 we summarize the data showing the shift in the Gd f levels and the work function on various substrates. In all cases the f levels are seen to shift towards the Fermi level (lower binding energy) as the amount of Gd was increased. Furthermore in both cases the work function decreases as more Gd is added.

Discussion

It is clear from all the data that the smallest Gd clusters are shifted to the highest binding energies, and in addition the initial Gd levels of the smallest particles are deeper than the bulk levels. Furthermore, the shift gets greater as one goes from metal to thin carbon, to thick carbon, where the shift is about 1 eV. At the same time the binding energies are decreasing with increased coverage, the work function is becoming smaller. As mentioned previously, this can only be true if this is caused by a final state effect. The smaller shifts on thin carbon layers also support this view. Clearly as the layer gets thin enough so that electrons from the metal substrate can neutralize the charge on the cluster, a smaller core level shift would be expected. If one was only concerned with the alignment of the initial state vacuum levels this would not be expected, and the experiments conclusively show the existence of a final state charging effect.

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Studies of Gd Clusters on Carbon, V. Murgai, S. Raaen, M. Strongin, and P. Citrin, to be submitted to Phys. Rev. Letters.

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Fig. 1 Shift of Gd 4f level and work function as a function of coverage for thick C substrates, thin carbon, and niobium. The binding energy scale means higher binding energies for the smallest Gd coverage.

Core Level Shifts of Pt Clusters in SiO_2 : The Transition from Metallic to Insulating Behavior

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Introduction

In these measurements the core level shifts and valence band features of Pt in an SiO_2 matrix were determined as a function of Pt concentration. At a Pt fraction of about 0.6 the Pt resistance changes by two orders of magnitude. This is presumably a percolation transition where continuous Pt paths do not exist below this concentration. The experiments described investigate changes in the valence band and core levels as one goes from metallic to insulating behavior.

Experimental

The measurements were performed by sputtering from a dual source which had one Pt target and one Si target, with oxygen added to the argon sputter gas. This deposition yielded an inhomogeneous composition along the sapphire substrate. One end of the substrate was Pt rich and the other end was SiO_2 rich, with various compositions in between. In this way both the valence band spectra and the core levels could be plotted against composition. In previous work on Pd dispersed in SiO_2 prepared in a similar way¹ only the valence bands were measured.

Results

Valence band spectra are shown in Fig. 1, and illustrate both the metallic regime and the insulating regime as one goes along the slide. The caption gives concentrations at the various positions. Fig. 2 shows characteristic Pt 4f levels at both the metallic and insulating ends, and finally in Fig. 3 both the valence band and core level shifts are shown as a function of concentration.

An interesting feature of the results is that there is very little variation in the photoemission results in Fig. 3, in the regime where the resistance of the film changes two orders of magnitude. In fact, the large core level shifts are seen to occur at Pt fractions below ≈ 0.3 . This can be understood by realizing that at the concentration where the percolation transition occurs very little happens to the local order and there are still probably large Pt agglomerates. It is only at lower concentration that the

Pt particles become independent of one another, and small enough so that when a photoelectron is emitted from a particle the charge cannot be neutralized in a time comparable to a photoemission event and a significant Coulomb shift is observed, i.e. there is a charge left on the particle² and the levels are shifted to higher binding energies by e^2/r , the Coulomb energy. Hence the photoemission results are sensitive to local order and charge transfer between individual grains, whereas resistivity measurements are affected when the long range connectivity is destroyed.

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Publications from this work:

Core Level Shifts of Pt Clusters in SiO₂, V. Murgai, S. Raaen, M. Strongin, R. Garrett, and P. Citrin, to be submitted to Phys. Rev.

Fig. 1 Valence band spectrum at $h\nu = 60$ V for Pt in SiO₂. Curve (a) Pt concentration ≈ 0.1 , (b) Pt fraction ≈ 0.2 , and (c) Pt fraction ≈ 0.78 (metallic regime).

Fig. 2 Core level spectra of Pt 4f levels: a) Pt fraction ≈ 0.125 , b) Pt fraction ≈ 0.78 .

Fig. 3 Dependence of $N(E_F)$ and Pt core levels on Pt concentration. Subtract 5 eV from scale on Pt core level spectra to get position relative to E_F .

Photon Desorption Studies of Synchrotron Materials

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Preliminary photodesorption studies have been made on an aluminum alloy¹ used as the chamber material at NSLS. The studies were made for different cleaning procedures and after different sputtering procedures. One of the cleaning processes employed common solvents such as acetone and then alcohol, and the other treatment employed a more complex recipe² which included a NaOH etch. Before this second treatment the samples were also polished. The desorption experiments were done by inserting the samples into the U7 beamline before the plane grating monochromator. Hence the samples were in the direct white beam. In Fig. 1 Auger spectra are shown for a solvent cleaned Al sample which is Ar sputtered for various times. Other spectra for hydrogen sputtering and oxygen sputtering show similar removal of carbon.

In Fig. 2 we show photodesorption data. The angles in the figure are the approximate angle between the sample and the beam. For the solvent cleaned case, Fig. 2a does not emphasize adequately the very rapid desorption of impurities from the surface. There was in general a long line to a Turbo-pump during photodesorption and the gas was slowly pumped away at a rate of ~ 10 l/sec. The large gas loads from the sample illustrated in 2(a) necessitated closing the front end shutter to lower the pressure, indicated by the rapid drops in pressure. Although the pressure in the irradiation region reached the 10^{-7} Torr regime, the pressure at the front end was only in the low 10^{-9} Torr range. This is because of the large pressure drop down the beamline plus the much greater pumping speed at the front end of the line, ~ 500 l/s, compared to about 10 l/s in the irradiation regime. The fact that the gas was pumped so slowly in the irradiation regime gave some worries about readsorption of gas in the 10^{-7} Torr range. A later version of this apparatus has a much higher pumping speed in the irradiation region. Fig. 2b shows the desorption curve for the better cleaning treatment and less initial desorption is evident. We emphasize that the shutter was not closed here as in Fig. 2a and the pressure rise was not nearly as rapid indicating much less desorption. CO_2 was also negligible in this run, showing less hydrocarbons. Figs. 2c and d illustrate the results of a hydrogen glow discharge on the solvent cleaned sample and oxygen glow discharge on the etch cleaning procedure are shown. The hydrogen discharged solvent cleaned sample shows a great reduction in CO , CH_4 and CO_2 . The oxygen discharge treatment shows reduction of CO and CH_4 but there is some increase in CO_2 .

It is clear that the combination of sample polishing and an etch cleaning procedure shows less photodesorbed hydrocarbons than solvent cleaning, and it is clear that glow discharge cleaning reduces the overall hydrocarbons that can photodesorb. However it is somewhat surprising that surfaces which appear clean by Auger spectroscopy can still desorb significant amounts of CO . It is certainly possible that this carbon which is photodesorbed comes from a more extended region at the surface than is sampled during Auger analysis.

We are grateful to Alistair Mathewson for helpful discussions of CO desorption from Al samples during photodesorption and J. C. Schuchman for his advice during the course of these experiments.

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1. The synchrotron alloy composition was Mg 0.4-0.8%, Si 0.3-97%, Fe 0.3%, Cu 0.05%, Mn 0.1%, Cr 0.05%, Zn 0.2%, Ti 0.1%, with Al as the balance.
2. This treatment consisted of polishing, ultrasonic cleaning with Vythane, followed by detergent treatment, rinse, caustic etch, rinse, acetone treatment, rinse and bake to 250°F.

Fig. 1 Auger spectrum of solvent cleaned Al alloy before and after Ar glow discharge. Peak in Al region indicates Al₂O₃.

Fig. 2 Photodesorption curves for Al alloy. Angles indicate angle between sample and beam. Upper solid curve hydrogen, --- CO, --CO₂, lower solid curve is CH₄. a) solvent cleaned before hydrogen glow discharge, not polished, b) treatment described in reference (2) before oxygen discharge, c) cleaning same as a - effect of hydrogen discharge, d) cleaning same as b - effect of oxygen discharge.

The Adsorption of Carbon Monoxide on Palladium Films

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Careful studies of the growth of palladium overlayers on a Ta(110) substrate¹ show that in the region of one monolayer coverage there is a reduction in the density of states at the Fermi level, a characteristic of the noble metals. Representative photoemission spectra from these different coverages are shown in Fig. 1.

Carbon monoxide is found to adsorb molecularly on the thicker Palladium films which grow parallel to the (111) direction, in agreement with earlier studies of adsorption on Pd(111) crystals. However at room temperature no adsorption is found to occur on a Palladium monolayer.²

We have now performed studies of carbon monoxide adsorption of these palladium monolayers cooled to liquid nitrogen temperatures. We find that at the lower temperatures, carbon monoxide is adsorbed and that the photoemission spectra have a similar structure to those recorded from carbon monoxide adsorption on the noble metals.³

In Fig. 2 we compare the photoemission spectra observed for carbon monoxide adsorbed at liquid nitrogen temperatures on the Palladium monolayers and on the thicker palladium films. Both spectra show features that may be interpreted in terms of electron excitation from molecular orbitals associated with the CO, namely the 4σ , 1π , 5σ orbitals. On the Palladium monolayer the peaks are found to move to higher binding energies reflecting the reduced screening of the hole left in the photoemission process.

In addition to these features another peak is observed on the Palladium monolayer system, which because of its cross-sectional behavior and similarity to other systems is identified with many-body excitation or "shake-up" structure. "Shake-up" peaks originate when following the primary excitation of the photoelectron the valence electrons of the system readjust to screen the photo-induced hole.

Similar "shake-up" structure is observed when carbon monoxide is adsorbed at liquid nitrogen temperatures on copper (111)³ surfaces and is evidence of a weaker band or reduced filling of the unoccupied $2\pi^*$ level of the CO molecule.

In conclusion the present experiments demonstrate the noble metal characteristics of the palladium monolayer in contrast to thicker palladium films.

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Fig. 1 Angle integrated photoemission spectra obtained from Ta(110) surface for various coverages of Pd. n is the estimated Pd coverage in monolayers.

Fig. 2 a) Saturation CO coverage on a thick (>3ML) Pd(111)-like film at liquid nitrogen temperature. b) Saturation CO coverage (~6L) on a commensurate Pd monolayer at liquid nitrogen temperature.

Ni, Pd, and Pt Overlayers on Ta(110)

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1 Introduction

Initial work on Pd overlayers grown on Nb showed that the single monolayer had chemical properties¹ that are different from either the bulk overlayer metal itself, or the substrate. These changed properties included reduced hydrogen dissociation and reduced CO adsorption.² The dramatic changes were correlated with drastic changes in the density of states near E_F . The work presented here extends this work to layers of Ni and Pt, and besides the photon energy dependence of the valence band structure, fairly extensive studies were made of core level spectra. There were two significant features of the core level results. First in the case of Pd on Ta we were able to demonstrate that Pd layers prepared by deposition, and by heating a thicker layer to leave a stable "monolayer" structure, were actually somewhat different. This is with comparable LEED spectra and valence band spectra. Second, in the case of Pt where there are sharp 4f levels it was possible to analyze both the substrate (Ta 4f) core level shifts in addition to the overlayer shifts and from this and the valence band spectra some estimate could be made of the bonding energy of the surface layer. Actually a third feature of the work involves shifts in the satellite structure with layer thickness. Besides the shift of the valence band features to higher binding energy, we find that the satellite feature shifts farther than the valence band.

Valence Band Features

Valence band spectra of the three overlayer systems showed that the hybridized d-bands formed by the addition of the overlayer always appear below E_F . This is true for Pd layers prepared both by deposition and by heating a thicker layer until a stable "monolayer" remained. In the case of Ni layers heating to produce a stable surface compound yields a C(2x2) structure, and d-states farther below E_F than the deposited layer. In Fig. 1 it can be seen that at higher photon energies there is a relative decrease in the states at E_F compared to the features at about -3 eV. Since the Ta cross section decreases more strongly than Pd, these measurements show that the states at E_F are essentially Ta like.

Core Level Features

In Fig. 2, Ta 4f levels are shown for pure Ta(110), for a deposited Pd layer, and for a thermally stabilized layer. It can be seen from the data that the deposited layer has more of the bulk Ta features than the thermally stabilized layer. This would imply that there is Pd in a more extended region than just a top layer in the thermally stabilized layer.

In Fig. 3 core level shifts are shown for a Pt layer on Ta(110). The data shows a shift from 0.2 ML to 0.4 ML and then little shift to 1 ML. We interpret this as islanding of the Pt at about 0.4 ML with growth of these islands to one layer. Together with the Ta(110) 4f level shifts with a Pt overlayer, and the shift in the valence band spectra, some estimate can be made of the Pt-Ta binding energy. Using the analysis of Oelhafen³, which assumes small charge transfer, and the separation of Pt and Ta d levels, we estimate a heat of formation of about -1.8 eV.

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Fig. 1 Energy distribution curves for Pd monolayer on Ta(110) produced by thermal stabilization. Note: the virtual absence of states at E_F for spectra taken at $h\nu = 80$ and 100 eV.

Fig. 2 Ta 4f core levels for (a) clean Ta(110), (b) approximate monolayer Pd coverage, and (c) thermally stabilized Pd "monolayer" on Ta(110) at $h\nu = 60$ eV.

Fig. 3 The Pt 4f_{7/2} and 4f_{5/2} photoelectron energy distributions for various Pt coverages on Ta(110). (a) Pt(111) film, (b) 0.2 ML, (c) 0.4 ML, (d) 0.6 ML, (e) 0.8 ML, (f) 1 ML.

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Studies of the Ta(110) Surface and Hydrogen on Ta(110)

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Introduction

The properties of hydrogen on metal surfaces besides being of intrinsic scientific interest, are also important to any understanding of hydrogen uptake in metals. Before the hydrogen features themselves can be studied, there must be some understanding of the features of the clean Ta(110) surface, and various measurements have been made of Ta(110) in normal photoemission.

Clean Ta

The general features of the normal exit photoemission measurements¹ for Ta(110) are shown in Fig. 1. The composite peak that appears near E_F represents a high density of filled states and is similar to that observed in Nb. The main feature at -0.4 eV is due to a pocket of Σ_1 states below E_F . The feature near E_F has a shoulder at -1.1 eV which becomes visible at lower photon energies. There is also a broad feature about 3-5 eV below E_F which becomes visible in EDCs taken at 25 and 30 eV. Further features in the spectra can be understood by recognizing that calculations show a high density of unoccupied states about 13 eV above E_F . For a photon energy of about 18 eV one would expect to see a feature near 5 eV. This is indeed seen in Fig. 1. Furthermore as the photon energy is increased this feature can be seen to shift to higher binding energies.

Other features in the data are the dip in photoemission intensity at ≈ 2.5 eV which can be understood to be due to the calculated band gap between the Σ_1 band and the Σ_2 band.

Although not shown clearly in Fig. 1 an analysis of the data near E_F clearly shows a separate state at -1.1 eV. Examination of the Ta band structure suggests that emission from the N_2 point is responsible for this peak. However the emission at N_2 arises from d_{xy} orbitals which should not contribute to the photoemission signal. It is possible that spin-orbit effects in a high Z metal like Ta can produce hybridized states which no longer have pure Σ_1 or Σ_2 symmetry and can thereby account for the state at -1.1 eV.

Hydrogen on Ta

The data for hydrogen on Ta is summarized in Fig. 2. The peak at -6.5 eV represents the hydrogen-tantalum bonding orbital, and a similar feature occurs on Nb and other transition metals. A second sharper feature occurs at -2.2 eV. A plot of the normalized data in Fig. 3 shows that this feature has the same relative cross section of the Ta 5d valence bands. This is of some

interest since a similar feature observed for hydrogen on Ti(0001) has been attributed by Feibelman and co-workers² to an anti-bonding level, whereas the Ta-like cross section dependence observed here also makes it plausible that this could be a Ta surface state pulled down in energy. Further work will be necessary to distinguish between these possibilities. It is also worth noting that the data of Fig. 3 show the feature at -1.1 eV mentioned above.

Another interesting aspect of this peak is that there is no dispersion with energy in normal photoemission. This implies that the hydrogen layer is two dimensional and is therefore only a few monolayers thick.

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Fig. 1 Plot of intensity at normal exit vs. initial state energy for Ta(110) at photon energies of 14, 16, 18, 20, 25, and 30 eV.

Fig. 2 Energy distribution curves for Ta(110) + 15 LH₂. Plot of intensity at normal exit vs. initial state energy for saturation hydrogen coverage photon energies of 14, 16, 18, 20, 25, and 30 eV.

Fig. 3 Plot of normalized valence band intensity at normal exit vs. initial state energy for 15 LH₂ at photon energies of 14, 16, 18, 20, 25, and 30 eV.

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Carbon K-Edge X-Ray Absorption Spectroscopic Studies of Structure and Electronic Properties of Hydrocarbons Adsorbed on Ni Crystal Surfaces

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Using the Plane Grating Monochromator of the U7A beamline at the National Synchrotron Light Source (NSLS), we have studied the carbon K-edge x-ray absorption spectra of a large number of hydrocarbon molecules and their derivatives adsorbed on Ni single-crystal surfaces (Ni(111), Ni(110) and Ni(100)). The molecules studied include saturated hydrocarbons C_2H_6 and C_6H_{12} , and unsaturated ones C_2H_4 , C_2H_2 , C_6H_6 , C_6H_{10} , C_5H_5N and C_5H_5S . Under the experimental conditions (room temperature, saturated surface), it is found that all the C K-edge Near Edge X-ray Absorption Fine Structures (NEXAFS) of the surface species exhibit the $1s \rightarrow \pi^*$ and $1s \rightarrow \sigma$ shape resonances characteristic of unsaturated molecules although an intense $1s \rightarrow \pi^*$ transition is not seen in the gas phase spectra for the saturated alkanes.¹ Some of the adsorbates also exhibit polarization dependent behavior in their C K-edge absorption coefficient.

In the case of adsorption of ethylene and acetylene on a Ni(111) surface², for example, we found that at 300 K the spectra exhibit both π^* and σ resonances. The polarization dependence of the π^* resonance shows an increasing π^* enhancement as the angle of incidence goes more grazing while the opposite trend is observed for the σ resonance (Fig. 1). From these results, we infer that the adsorbed species has an unsaturated carbon-carbon bond, regardless of whether the adsorbate was C_2H_2 or C_2H_4 , and that the molecular axis of the adsorbed species is parallel to the surface.

Semiquantitative information can also be obtained from these data based on some theoretical³ and empirical considerations.⁴ From the

Fig. 1 C K-Edge NEXAFS Spectra of C_2H_4 on $Ni(III)$ at 300 °K at Various Polarizations

position of the σ resonance relative to the threshold, it is immediately apparent that the carbon-carbon bond is lengthened upon adsorption. A comparison of our data with the correlation of Stöhr et al.⁵ gives a bond length of 1.47 ± 0.04 Å (1.34 Å and 1.21 Å for gas phase C_2H_4 and C_2H_2 ,

respectively) for the "C₂" species adsorbed on Ni(III) surface. This observation indicates that the adsorption process favors the breaking of the carbon-carbon bond.

Detailed analysis on other systems are now in progress.

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Photoemission Study of Metal-Doped β -Boron
Thermoelectric Materials

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In the period August 13 to 17, we were assigned ten shifts on beam line U-7 to perform photoemission measurements of V-doped Boron materials. All the beam time, however, was consumed in detecting leaks in the experimental chamber. After all possible leaks were mended, the background pressure was still high and our beam time was up. A major leak in the monochromator section was later detected by Myron's group.

We hope to obtain 'usable' beam time to perform our experiments in the future.

Oxidation of GaAs(110) cleaved surface

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The oxidation of the GaAs(110) surface has been the subject of considerable attention in both experimental and theoretical investigations(1-6). Despite the large number of studies there has not been any direct or conclusive evidence in support of a particular oxidation mechanism. A variety of models have been proposed in attempts to explain the experimental results however, in the case of photoemission studies, these explanations have to some degree been limited by the spectral resolution of the original data. In this report we present the first results of a high resolution photoelectron spectroscopy study of cleaved GaAs(110) surfaces exposed to oxygen carried out on the IBM beam line at the Light Source. The good overall resolution of less than 0.2 eV for the gallium and arsenic 3d core levels and 0.7 eV for the oxygen 1s made possible the identification of a number of chemically shifted components not previously resolved. We also utilized the tunability of the synchrotron radiation to obtain spectra with predominantly surface or bulk features. These results necessitate a major revision of current ideas about the oxidation mechanism for this surface.

Photoemission spectra of both the Ga and As 3d core levels reveal a multicomponent substructure which increases in complexity with oxygen exposures over the range $10E6 - 10E14$ L (Langmuirs). The spectral evolution of the As-3d core level with exposure, taken with maximum surface sensitivity, is shown in Fig.1. No significant changes in line shape are observed until exposures of $10E6$ L. With increasing exposure a sequential set of four shifted components are observed which are attributed to single through fourfold coordinated bond formation to oxygen. Both bulk and surface-sensitive core spectra reveal a nearly equally intense oxide substructure, which indicates that contrary to previous notions subsurface oxidation is the dominant mechanism throughout the exposure range. The effects of oxidation on the Ga-3d core level were apparent for exposures of $10E4$ L (<0.1 monolayer), and two oxide components were evident for each exposure.

A detailed investigation of the oxygen 1s core level displays a striking dependence of the overall width and make up of the peak on the quality of the cleaved surface. On a highly perfect surface where the sticking coefficient for oxygen is low, the 1s peak is broad throughout the exposure range investigated. Decomposition of spectra into individual peaks, as illustrated in Fig.2(a), consistently indicates three components, two of which, separated by 1eV, have been tentatively assigned to gallium and arsenic oxides, the third peak, shifted by an additional 1.4eV to higher binding energy, to a surface oxide. Although there is no significant increase in the amount of oxygen on the surface over this exposure range, bulk oxidation is occurring as determined from the bulk sensitive Ga and As 3d core levels.

Fig.1 Spectral decomposition of the surface sensitive As-3d spectra for indicated exposures. Dots are experimental data. $h\nu = 590\text{eV}$.

The oxidation of a highly stepped surface dramatically differs from the above observations as illustrated in Fig.2b. Initially the oxygen 1s peak is substantially narrower than on the previous surface but increasing coverage leads to a broadening of the peak with developing substructure as observed on the well cleaved surface. It would appear that at least during the early stages of oxidation the major products of the interaction of oxygen with the surface are gallium oxides. However bulk sensitive studies of the Ga and As core levels indicate that bulk oxidation occurs for both elements at these coverages and at a faster rate than on the good cleave for a comparable exposure. It therefore seems plausible, as has been suggested previously (6), that bulk oxidation nucleates and proceeds at extended cleavage induced

Fig.2 Spectral decomposition of the surface sensitive O-1s core level, (a) for a highly perfect surface, (b) for a stepped surface, coverages as indicated. Dots are the experimental data. $h\nu = 590\text{eV}$.

defects. The most reactive species at these defect sites appears to be gallium which is consistent with some previous studies (2,8). Subsequent surface oxidation at higher coverages gives rise to arsenic and surface oxide components as observed on the previous cleave.

The results confirm recent studies (7) favoring a combined inhomogeneous surface and bulk oxidation of GaAs for submonolayer coverages, in contrast to a strict (4) or even homogeneous (5) surface oxidation.

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Polyimide and the Polymer-Metal Interaction

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Understanding how metal films adhere to polymer surfaces is a task of great interest and importance to the semiconductor packaging industry. The types of chemical and physical interactions which occur at the interface determine the strength and stability of the metal-polymer bond. Earlier work (1-5) has included several ESCA and UPS studies of clean and metal coated polyimide (fig.1). The individual components in photoemission spectra for carbon, oxygen and nitrogen 1s core levels have been tentatively assigned and changes with metal coverage indicate that while Cu does not form chemical bonds with the polymer surface, Cr does.

Fig. 1: Structure of the polyimide monomer, with oxydianiline (ODA) and pyromellitic dianhydride (PMDA) parts noted.

The use of synchrotron radiation for photoemission spectroscopy at the U8 Beamline at NSLS allows us several significant advantages over laboratory ESCA for studying this system. First, a resolution of 0.5-1.0 eV allows for a more accurate assignment and monitoring of peak positions and intensities as a function of metal coverage. Second, photon energy tunability makes a certain amount of depth profiling possible. We have also used the photon energy tunability for recording the Near Edge X-ray Absorption Fine Structure (NEXAFS) of carbon, nitrogen, oxygen and metal edges by collecting the total yield of photoelectrons. Spectra were taken before and after annealing the polyimide at 320 C under UHV conditions and after successive evaporations of copper and chromium metals.

Fig.2 shows the carbon, oxygen and nitrogen 1s NEXAFS spectra for clean, annealed polyimide. Recent work by J. Stohr and coworkers (6) finds that the sigma shape resonance from a pair of atoms varies linearly with the internuclear distance between them. By evaluating the energy position of the sigma shape resonances relative to ionization potentials, tentative assignments have been made for peaks in the C and O spectra. Sharper, lower energy peaks have been assigned to pi resonances. The accompanying table shows these assignments. Assignment

of the remaining peaks is ongoing and may require the study of simpler model compounds.

Fig. 2: C1s, O1s and N1s NEXAFS spectra of polyimide

Carbon 1s			Oxygen 1s			Nitrogen 1s		
Energy (eV)	Assignment	Bond	Energy (eV) ^a	Assignment	Bond	Energy (eV) ^a	Assignment	Bond
285.2	π^*	H-C=C	533	π^*	C=O	402.5	(possible Rydberg 3p)	
287(shldr)	π^*	C=C-C=O	543	σ^*	C-O-C	405	(possible Rydberg 4p)	
287.4	π^*	C=O	546	σ^*	C=O	408	(possible shake-up state)	
289.2	σ^*	C-O, C-N	(possible shake-up states in broad peak)			411	σ^*	N-C=C
292.0	σ^*	C-C=O				415	σ^*	N-C=O
295.3	σ^*	N-C=O						
305	σ^*	C=C-H						

^aEnergy scale is not calibrated

Table 1: Assignments for C, O and N NEXAFS spectra.

Fig.3a shows a sequence of C1s photoemission peaks for increasing amounts of Cu evaporated on polyimide. The three peaks for the clean, annealed polyimide have been assigned in the past to carbonyl carbon atoms (289 eV binding energy), aromatic ring carbon atoms bonded to atoms other than hydrogen and all those in the PMDA aromatic ring (286 eV), and CDA aromatic ring carbon atoms bonded to hydrogen (285 eV). As Cu is deposited the first and second peaks decrease dramatically. After the final evaporation, a total thickness of about 15Å, there is no evidence of the first and only a small amount of the second peak left. This implies that the Cu atoms may sit over preferred sites on the polymer surface. There is also no evidence of any shift in binding energy due to the formation of a chemical bond between the metal and polymer. Fig.3b, however, shows significant shifts in C1s peak positions as Cr is deposited. Again, the first and second peaks

decrease, but a fourth peak appears, indicating the presence of carbon atoms with reduced 1s binding energies.

Fig.3: Cls core level peaks from polyimide, clean (1) and with increasing coverages of a) Cu and b) Cr. Curve 5 in b) shows the effect of annealing on the Cr exposure shown in curve 4.

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Investigations of the Etching Chemistry of Electronic Materials

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The production of VLSI devices involves the fabrication of silicon substrates with micron-scale anisotropic features incorporating a number of distinct materials, such as silicon regions of various electrical properties, grown or deposited insulating layers, and metallizations. Currently, a variety of plasma-based processes are used to achieve the requisite level of profile control. A common feature of these methods is that the reaction is effected by radical and ionic species in a fluoro-carbon plasma. From a mechanistic standpoint, all of these schemes are exceedingly complex, as a large number of bonds must be broken and formed as the reaction proceeds. Furthermore, a complete and unambiguous accounting of the relative efficacy of plasma species for the etching of any particular material has yet to be given. It is therefore hardly surprising that our knowledge of the fundamental processes underlying this important technology remains rudimentary.

In order to begin to investigate some of the mechanisms involved in etching reactions, we have conducted a series of experiments probing the interaction between fluorine atoms (supplied by the dissociative chemisorption of XeF_2) and surfaces of silicon. This provides a logical model system as it is the simplest (in terms of the variety of reactants) in which the volatile fluoride products are actually produced.

The experiments were performed by exposing the clean substrates, either (111) wafers or ingots for cleaving, to XeF_2 in a special dosing chamber using methods described in detail elsewhere (1). The samples were then transferred into the spectrometer chamber through a double vacuum lock after pumping away the residual XeF_2 . High resolution core level spectra were obtained by means of a two-dimensional display type photoemission spectrometer operating in conjunction with a three-meter toroidal grating monochromator situated at beam line UV-8 at NSLS. This facility enables high resolution photoemission experiments to be performed with photon energies between 5 and 140 eV. Such an excitation energy range is amply sufficient for the study of the sharp Si 2p core levels. (The display photoemission spectrometer has since been moved to operate in conjunction with the new 6m/10m TGM, which provides usable photon fluxes from 5 eV to greater than 800 eV for photoemission experiments and extends to above 1000 eV for absorption measurements.) The experiments were performed in two distinct regimes, which we designate as the regimes of chemisorption and steady-state reaction respectively. The former refers to low exposures and monolayer coverages, in which the reaction has not proceeded to product formation, while the latter were performed under conditions known to result in at least 10000 Å of etching.

For the chemisorption regime, typical results are shown in fig 1. This figure shows the result of exposing a Si(111) 7x7 surface to approximately 50 Langmuirs of XeF₂. The silicon 2p core level spectrum develops three equally spaced satellite peaks spaced slightly more than 1 eV apart. These are assigned to mono-, di-, and trifluorosilyl species respectively (1). The total coverage is about 1 monolayer.

Fig. 1

Figure 2 shows the result of exposing a similarly prepared clean surface to 3×10^{-3} Torr of XeF₂ for ten minutes, conditions known to result in substantial etching. Under these conditions the amount of fluorosilyl species present on the sample is greatly increased, and their distribution is strongly altered. Several conclusions concerning the nature of this reaction can be drawn from these results. The most significant of these is that the reaction does not proceed by stripping the surface away a monolayer at a time, but rather by the formation of an highly fluorinated intermediate reaction phase. It is difficult at this time to say much about the nature of this phase except that the distribution of fluorosilyl functionalities shows that it is not polymeric and that it exhibits poor connectivity. The further reaction of SiF₃ groups within this reaction phase also appears to be an important bottleneck in the overall reaction.

Fig. 2

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High Resolution Photoemission investigation: The Oxidation of W

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High resolution photoemission measurements of surface oxide layers on tungsten has revealed a set of well resolved core level shifts characteristic of individual metal oxidation states. Measurement and analysis of this type of data can provide specific and quantitative chemical information about surface oxides. Such information should be particularly useful in characterizing the disordered systems characteristic of applied surface physics where clarity of interpretation is very important.

The formation of bonds between transition metals and strongly electronegative elements such as oxygen and fluorine results in charge transfer with the effect of shifting the metal core electron binding energies. The magnitude of such shifts depends primarily on two factors; the amount of charge transfer and the screening ability of the metals electrons. The size of core-level shifts tend to increase with additional charge transfer and be decreased by screening. In the case of tungsten the amount of screening should be a function of oxygen content since the oxygen ties up free electrons which are effective at screening. A continuous change in the tungsten core level shifts is observed with increasing oxygen content i.e. as the screening changes from that characteristic of a metal "screened" to that characteristic of an insulator "unscreened". In similar studies of bond formation between fluorine and silicon no measurable change in the core level shifts with increasing fluorine content was observed which is consistent with this interpretation since to a first approximation the silicon provides an "unscreened" environment both before and after fluorination.

Although in principle it should be possible to perform first principle calculations to determine the magnitude of core level shifts associated with the various oxidation states, such calculations are very tedious and have not proven themselves to be entirely reliable. We have instead chosen to look at model compounds such as WO_2 and WO_3 where the tungsten oxidation states are known. These shifts are then compared to those found in the surface oxides. This approach has proven entirely satisfactory, providing a clear and convincing interpretation of the core level shifts observed.

The W surface oxidation was performed primarily on high purity 0.001 inch thick foil which could be heated resistively. The foil surface was prepared first by heating in oxygen to burn off carbon and then flashing to temperatures high enough to desorb all the oxygen. The surface was then oxidized in UHV chamber by slowly reducing the temperature from about 900 °C to room temperature while in an ambient of $10E-5$ Torr of oxygen. Smaller oxygen coverages were obtained by heating this surface to progressively higher temperatures. Figure 1 shows the six W spectra arranged from bottom to top in order of increasing oxygen

Fig.1 The W-4f core levels for increasing oxygen exposures with WO₂ and WO₃ at the top for comparison.

content with the WO₂ and WO₃ at the top. Figure 2 shows a full size decomposition of the most heavily oxidized W foil from figure 1. Each of the four subcomponents in figure 2 is represented by a dashed line. The solid line running through the data points is the sum of the dashed lines plus a linear background. Since each of the individual components is itself made up of three peaks; 4f_{7/2}, 4f_{5/2}, 4f_{3/2} and each of these peaks has associated with it a secondary electron tail which is proportional to the integral under the peak, one must endeavor to use all physically available information to reduce the number of free variables. The spectra in figure 1 should be thought of as a set. A suitable decomposition should work on all the spectra with the important parameters (peak positions, widths, tail proportionality) either not changing or changing in a smooth and consistent manner from spectrum to spectrum. Only then can one be confident in the physical relevance of the decomposition.

Decomposition of the W surface oxide spectra reveal three distinct oxide phases. The two with the largest shifts can be immediately identified with oxidation states of +6 by comparison with the WO₃ and +4 by comparison with the WO₂. The remaining peak with a shift which is

Fig.2 Spectral decomposition of W-4f for most heavily oxidized surface.

	Bulk	+2	+4	+6
Oxidized Foil	84.2 %	9.8	6.0	
Oxidized Foil	55.1	27.5	17.4	
Oxidized Foil	48.2	35.5	16.3	
Oxidized Foil	42.2	37.9	10.9	9.0
Oxidized Foil	38.8	37.3	9.3	14.6

Table 1. Percent of the total signal for bulk and oxidation states of W in order of decreasing oxygen content.

very nearly half the +4 shift can then be safely assumed to be +2 i.e. equivalent to WO. Trends in the relative signal strengths of each oxide component as the sample is heated to progressively higher temperatures are displayed in Table 1. Upon the first heating the amount of WO3 drops dramatically while the amounts of the other components stay constant within the experimental accuracy. After the second heating the WO3 is completely gone. The WO is still about the same but the WO2 has increased considerably. One can conclude from this that some of the WO3 has been converted into WO2 during the previous heating and desorption cycle. After the next heating the WO has decreased dramatically with only little change in the WO2. In the last heating phase the WO2 and WO seem to have found a stable equilibrium and are both reduced by the same amount suggesting that the most stable surface oxide phase is a phase intermediate between WO and WO2.

PHOTOIONIZATION OF LASER-EXCITED SODIUM ATOMS
USING SYNCHROTRON RADIATION

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One of the most important interactions in nature is the absorption of electromagnetic energy by an atom. This absorption produces either an energetically excited atom or a positive ion and a free electron (or electrons). Experiments designed to study these bound-bound and bound-free transitions have been conducted for many years; the early results, especially those associated with bound-bound transitions, provided the impetus for the development of quantum physics. By now a great deal has been learned about bound-bound transitions, in both emission and absorption. In fact the energies of the most important of the discrete states of almost all atoms and many of their ions are accurately known.¹ However, although experiments designed to study bound-free absorptions have been conducted for nearly one hundred years, thorough studies of photoionization of only a relatively few atoms have been carried out.^{2,3} This is due largely to the lack of stable continuous sources of radiation covering the wavelengths corresponding to the range of atomic ionization potentials, $\sim 500\text{-}3000\text{\AA}$ (24.6-4.3 eV); this range must be extended to even higher energies if inner shell ionization is to be investigated. However, the relatively recent availability of synchrotron radiation and laser light has made it possible to perform a great many new experiments of fundamental interest. This activity has been accompanied by coeval advances in theoretical treatments of photoionization.⁴

The work being performed in this project is directed toward providing new information on atomic photoionization. By directly detecting mass identified ionic products we avoid many of the experimental problems, such as spurious effects introduced by contamination of the atomic sample by impurities, that have plagued previous investigations.² In fact we have already published results of our first experiments.⁵ In this work photoionization of ground state magnesium atoms was investigated at photon energies near the first ionization threshold, that corresponding to removal of one 3s electron. This work was of particular interest because states in which both 3s electrons were excited (by a single photon) were observed. The energies of these doubly excited states are in excess of the 3s ionization potential so that autoionization of these discrete states imbedded in the ionization continuum was directly observed.

Although we intend to continue to study photoionization of ground state atoms, particularly those interesting cases for which discrepancies

between theory and experiment exist, a major thrust of this project is examination of photoionization of state-selected excited atoms. In particular we have been studying photoionization of excited sodium atoms, $\text{Na}(3p)$, in which the selective excitation is accomplished by irradiating a beam of sodium atoms with light from a cw dye laser tuned to one of the D-lines. These laser-excited atoms are then photoionized by synchrotron light and the ion production studied over a wide range of energy of ionizing radiation. This technique thus exploits the unique features of both laser light (intense monochromatic beams) and synchrotron radiation (broadband tunability).

Figure 1 shows our first data; the observed threshold at 4083Å establishes that indeed this signal results from photoionization of $\text{Na}(3p)$. The small maximum between 2000Å and 2500Å is the signal from photoionization of the unexcited (ground state) atoms, present in the laser-irradiated beam. Comparison of these preliminary data with theoretical treatments⁶ of this process indicates excellent agreement. Further work on this problem is in progress.

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Fig. 1. Na^+ signal vs. wavelength of synchrotron light.

Applications of Tunable VUV Radiation

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Synchrotron radiation in the 110-140 nm wavelength region has been used to produce electronically excited gas-phase radicals via photofragmentation of suitable radical precursors. To date, most of our effort has been directed towards the investigation of the photophysical properties of two different species: 1) C_2H (C_2D) radicals, which are an important hydrocarbon combustion intermediate and yet their spectroscopy is poorly understood, and 2) CF_3 radicals, which are of interest in a variety of chemical systems such as atmospheric chemistry, where they have been implicated in the stratospheric ozone depletion problem, and semiconductor device fabrication, where they are used as chemical etching ingredients. A brief summary of the experimental results obtained for each of these two radicals is given below.

I. C_2H

Electronically excited C_2H (C_2D) radicals (C_2H^*) have been produced by VUV photolysis of C_2H_2 (C_2D_2). The tunability of the synchrotron source has been exploited to obtain the relative C_2H^* production as a function of incident wavelength. Investigations of the C_2H^* emission spectrum revealed that it is much broader than previously reported, extending from about 400 nm to at least 950 nm and possibly even further towards the infrared. Furthermore, the emission spectrum is a function of the photolysis wavelength. In simplistic terms, the emission spectrum shifts towards the blue as the incident wavelength decreases. Accurate C_2H^* fluorescence lifetime analysis was not possible because the observed lifetime (a few μs) was much longer than the time between synchrotron pulses (18.9-170.1 ns).

II. CF_3

VUV synchrotron radiation was used to produce electronically excited CF_3 radicals (CF_3^*) by photolysis of CF_3Cl , CF_3Br , and CF_3I .¹ The collision free fluorescence lifetime of both the uv and visible emission bands of CF_3 was measured using a time-resolved photon counting system. The quenching rates of the uv and visible band emission by CF_3 precursor molecules was also determined. A summary of the lifetime and quenching rate measurements is shown in Table I. The visible emission quenching rate for the case of CF_3Br is not shown because the Stern-Volmer plot showed non-linear behavior for this case. The reason for such non-linear behavior is not understood at this time.

TABLE I

CF ₃ Precursor	Photolysis Wavelength ^a	Ultraviolet Emission Lifetime ^b	Ultraviolet Emission Quenching Rate ^c	Visible Emission Lifetime	Visible Emission Quenching Rate ^c
CF ₃ Cl	115.8	14-17	1-2 x 10 ⁷	14-17	1-3 x 10 ⁷
CF ₃ Br	125.4	14-17	2-3 x 10 ⁷	14-17	--- ^d
CF ₃ I	133.9	14-17	3-5 x 10 ⁷	14-17	3-6 x 10 ⁷

^aWavelength in nm^bLifetimes in ns^cIn units of s⁻¹ torr⁻¹^dSee text for explanationReferences

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Reflectance Measurements of Aluminum Coatings at 200 - 500 nm

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The U9A beam line of NSLS equipped with a monochromator was used to measure the reflectance of mirror samples in the 200 - 500 nm wavelength range. This was done in conjunction with the construction of a Cherenkov detector for BNL - Yale AGS Experiment 780 (Search for rare decay modes of the neutral kaon) which is approved for a run in 1985, as a complement to tests done in the AGS test beam and optical tests at 337 nm using a nitrogen laser. The utmost efficiency of the Cherenkov counter is crucial for the success of the experiment, and it was therefore mandatory to assure that its light gathering power at the short-wavelength end of the range tested be as close to the design value as possible. The tests were very successful in that they helped us to select a thin aluminized mylar with close to 90% reflectance, and pointed out a problem which exists with a certain type of katadioptric mirrors on which the reflective layer had been (poorly) deposited for us by an industrial enterprise.

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UV-VUV CIRCULAR DICHROISM SPECTROMETER

An attachment to the National Synchrotron Light Source (NSLS) beamline U9A, was designed and constructed for the spectroscopic study of optically active compounds using circular dichroism (CD) in the vacuum ultra violet (VUV) region. The current design has entailed the construction of three separate 8"-Conflat flange modules in which were separately mounted the photo elastic modulator (PEM), sample cell, and photomultiplier tube (PMT). All three are mounted in the experimental chamber on beamline U9A. Figure 1 shows the orientation of each of these Conflat flange modules.

Synchrotron radiation which is highly linearly polarized upon extraction from the ring, enters a mirror box and passes through a LiF window which separates the ultra high vacuum VUV synchrotron ring from the experimental system vacuum. After exiting the LiF window the beam enters the monochromator and is then focused into the experimental chamber. The linearly polarized, monochromatic light passes through a CaF₂ quarter-wave photoelastic modulator (PEM) which alternately produces right- and left-handed circularly polarized light at a 50 kHz frequency. The PEM power

Figure 1

supply simultaneously supplies a 50 kHz reference signal to a lock-in amplifier. The modulated circularly polarized light enters the sample cell and the differential absorption of the left- and right-handed components by the optically active compound under study gives rise to a 50 kHz ac signal. This signal is superimposed on a much larger dc signal due to the total light striking the PMT. To extract the small CD ac signal, the dc voltage supplying the photomultiplier tube (PMT) is controlled and maintained by an automatic gain control feedback circuit,¹ which automatically extracts and amplifies the 50 kHz ac signal. This is accomplished by feedback loop to the photomultiplier high voltage supply which compensates source dc variations due to sample absorption and light source variability. This system automatically normalized the CD signal with respect to the total absorption of the sample. The entire system has been completely interfaced with the VAX computer system at U9A, so as to provide for automatic scanning and acquisition of the CD data.

Initial transmission data indicates that at a maximum resolution of .18 nm at a few torr of sample pressure the CD system is capable of obtaining VUV and VUV CD spectra between 135 nm and 300 nm. Simple use of other PMTs will allow spectra to be extended in the visible. VUV spectra have been obtained for a variety of compounds including (+)-carvone, (-)- β -pinene, (+)- α -pinene, trans-pinane, cis-pinane and (+)-3-methylcyclopentanone (MCP). The (+)-3 MCP is in good agreement with previously published data.^{2,3} Future plans include using this system as a chromatographic monitor to selectively detect optically active compounds.

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The Lifetime of the Fluorescent Excited State of Solid, Liquid and Vapor Phase Cyclohexane

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The fluorescence from saturated hydrocarbons was discovered by Hirayama and Lipsky (1). Following the work by Lipsky and coworkers, a number of other investigations, most of which concern lifetime measurements, have been carried out towards the understanding of the photophysical behavior of saturated hydrocarbons. In early work, the fluorescence lifetimes were estimated by fluorescence quenching and energy transfer measurements. These values are very inaccurate and better direct measurements were reported later. In some of these studies, it was found that the lifetimes of some saturated hydrocarbon liquids are temperature dependent, and the lifetimes of some hydrocarbons in the vapor phase are wavelength dependent. Even though the results obtained by direct methods agree with each other for some hydrocarbons, they differ significantly for some others, mainly for cyclohexane. One of the reasons for the discrepancies among these values could be due to variations in experimental conditions such as temperature and excitation energy, and another reason could be the difficulty of evaluating the short lifetime of a very weak emitter. In the present studies, therefore, the lifetime of cyclohexane in the liquid and solid phases was determined under known experimental conditions by systematically varying the temperature and the excitation energy and in the gas phase by varying the excitation energy.

Synchrotron radiation coming through the LiF window on beam line U9A was wavelength resolved by a 0.5 m Seya-Namioka monochromator equipped with a 1200 groove/mm grating. Under our conditions, the bandpass of the excitation beam is 16.7 nm. The beam was focused into the outer sample chamber, which is a stainless steel six-way cross. The entire beam line beyond the LiF window (including the monochromator) was maintained at a vacuum better than 10^{-6} torr. The sample cell for liquids was made of aluminum and had a LiF window mounted with an indium O-ring. The cell was connected to a temperature controller and the temperature of the cell was measured with a thermocouple. The cell was placed in such a way that the LiF window surface makes an incident angle of about 60° with the excitation beam and the fluorescence from the front surface was observed at a right angle to the excitation. Care was taken to avoid reflection of the incident beam into the detection photomultiplier. The sample cell for vapor phase experiments was a simple box shaped cell with four LiF windows. The fluorescence was observed normal to the excitation beam.

The fluorescence from the samples was passed through a narrow bandpass filter (for cyclohexane, a filter peaking at 214 nm with FWHM 10 nm).

Temperature Dependence in Liquid and Solid Cyclohexane

The freezing point of liquid cyclohexane is 6.54°C. The temperature of the sample was varied between +59°C to -49°C. Both the fluorescence intensity and the lifetime increase as the temperature decreases. The increase in fluorescence intensity with decrease in temperature is in agreement with a previous observation.²

The decay rates of some excited liquid saturated hydrocarbons (both linear and cyclic) were found to consist of two processes; a temperature-dependent Arrhenius-type process and a temperature-independent process. It is quite clear that the cyclohexane data closely resemble the behavior shown by alkanes.

Wavelength Dependence in Liquid Cyclohexane

These data were taken at $10^\circ \pm 2^\circ\text{C}$. This temperature was chosen since the fluorescence intensity is higher than at 25°C and cyclohexane still remains a liquid. When the excitation wavelength was changed from 130 nm to 180 nm in 10 nm increments, the lifetime changed from 0.97 ns to 1.03 ns. However, since our measurements have a maximum error of ± 0.05 ns, a definite conclusion cannot be drawn based on these measurements. In any case, the wavelength dependence of lifetime of excited liquid cyclohexane is very weak.

Wavelength Dependence in Cyclohexane Vapor

The experiments were carried out in near collision-free conditions at $25 \pm 2^\circ\text{C}$. The data show that the lifetime of the cyclohexane vapor is strongly wavelength dependent.

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VUV Optical Properties of Cadmium Dimethyl

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When photodissociating a molecular beam of $\text{Cd}(\text{CH}_3)_2$ with 193 nm light from an excimer laser intense $\text{Cd}(^3\text{P}_1 + ^1\text{S}_0)$ emission was seen at 326.1 nm. However the 6.42 eV energy of the photon was somewhat less than the 6.93 eV required for the reaction:

This paradox could be resolved by assuming either that the published thermochemical data was in error or that the excimer laser had effected a two photon transition. Radiation from the synchrotron, a weak source compared to the excimer was shown to produce no measurable emission from $\text{Cd}(\text{CH}_3)_2$ over the range 250-150 nm. At the higher energies in this range, some of the excited states reached must correlate with $\text{Cd}(^3\text{P}_1)$. The fact that this state is not observed implies highly efficient potential curve hopping i.e. internal quenching. A rough vuv absorption spectrum was measured.

Photodissociation of Vinyl Cyanide

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H. Okabe showed some time ago that one could determine the bond energies of cyanides by measuring the threshold energy for the process:

In other words the upper limit determined in this process is close to the true value. Okabe applies this scheme to molecules in which $R = I, Cl, Br, H$ and CH_3 .

We were interested in the process:

If the minimum energy for this reaction could be measured, the heat of formation of the vinyl radical could be determined using the known heats of formation of the CN radical and the parent vinyl cyanide. Unfortunately in the wave length region 200-105 nm no emission was seen from vinyl cyanide. (Okabe had previously observed an exceedingly weak emission excited by 121.6 nm light.) Similar negative results were obtained for phenyl cyanide, C_6H_5CN but for CH_3CN complete agreement with Okabe's data was obtained. Our conclusion is that just as with $Cd(CH_3)_2$ there is very efficient internal quenching of the excited state. An alternative explanation is that photodissociation of vinyl cyanide in the vuv produces HCN molecules but not CN radicals.

Each of the above two experiments took three working days at the light source.

Preliminary Studies on the Acetylcholine Receptor by Vacuum Ultra-Violet Circular Dichroism Spectroscopy

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We have performed circular dichroism (CD) spectroscopic studies on the acetylcholine receptor (AChR) using conventional instrumentation (1). This instrumentation has allowed us to reach a wavelength minimum of about 200 nanometers (nm). Vacuum ultra-violet (VUV) CD studies of the AChR will be useful because the low wavelength data provided is more sensitive than the higher (greater than 200 nm) wavelength data available from conventional CD instrumentation (2).

VUV-CD spectroscopy was performed on reconstituted vesicle samples of purified AChR. The purpose of these preliminary trials was to ascertain whether the sample was amenable to VUV-CD and whether low (170-180 nm) wavelengths could be reached.

Spectra were obtained for this sample, but the absorbing components of the sample buffer prevented the desired low wavelengths from being attained. After optimization of the buffer system, and with the use of Gray cells (3) of various pathlengths, it is expected that low wavelength data collection will be possible.

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U9B: Ultraviolet Biophysics

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Station U9B has two spectrometers that exploit different features of synchrotron radiation. A vacuum spectrometer is devoted to circular dichroism and magnetic circular dichroism; it operates in the spectral range from 160 to 1600 nm. The second spectrometer uses the time structure of the synchrotron beam to measure fluorescence lifetimes and anisotropy. A rotatable mirror directs the photon beam to one or the other spectrometers.

The vacuum spectrometer was used to measure the circular dichroism of DNA's and proteins. John Sutherland, JoAnn Mugavero and John Trunk (BNL-Biology) studied the solution structure of repeating sequence nucleic acid copolymers (synthetic DNA's). A CD band near 200 nm was found to be diagnostic for the handedness of the DNA double helix. Conformation of poly(dA-dC).poly(dG-dT) [A = adenine, C = cytosine, G = guanine and T = thymine] and poly(dA-dT).poly(dA-dT) were shown to form right-handed double helices even though CD at longer wavelengths (recorded with conventional spectrometers) had been interpreted by other workers as suggesting a left-handed helix. The addition of a thermo-regulated sample holder permitted improved short wavelength penetration, reduced problems of bubble formation in short pathlength samples and sharpened spectral bands.

Experiments on the solution structure of poly(dG-dC).poly(dG-dC) covalently modified by the carcinogen acetylaminofluorine (AAF) and the mutagen mitomycin C (MC) were carried out in collaboration with Regina Santella (Columbia P. and S.) and Maria Tomasz (Hunter College, CUNY) respectively. Based on the criterion of vacuum ultraviolet CD the AAF modified dG-dC was found to be in a left-handed, Z-type double helix, while the MC modified dG-dC is a right-handed, B-type helix. The conventional CD ($\lambda > 200$ nm) indicated that both the AAF and MC caused poly(dG-dC) to assume a left-handed double helix. Other less direct evidence supports the conclusion that the MC complex is right handed (Tomasz et al., PNAS 80, 2874-2878; 1983). This is the fourth example in which vacuum ultraviolet CD has proven a better indication of helical type than the longer wavelength conventional CD.

Circular dichroism was used to study the structure of proteins in three separate series of experiments. In a collaboration with John Olson (Odense University, Denmark), the circular dichroism of the 1300 nm band of photooxidized photosynthetic reaction centers from Rhodospseudomonas viridis was measured. The large CD/absorption ratio of 10^{-3} confirmed that this 1300 band has significant singlet-to-triplet character. Eugene Stevens (SUNY-Binghamton) and Edwin Morris (MRC, Mill Hill) studied the CD of the glycoprotein fibronectin both in solution and in dry films to probe conformational transitions induced by heparin binding. Donna Mielke (Columbia University) tested the feasibility of measuring the CD of the acetylcholine

receptor protein in a lipid environment.

A 2.3 T electromagnet attached to the vacuum spectrometer was commissioned. In collaboration with Bo-hai Lin (BNL and Biophysics Institute, Beijing) the magnetic circular dichroism (MCD) of thymine and cytosine was measured. Two new transitions were found for both molecules between 180 and 220 nm. The information about the number and directions of the transition dipoles provided by MCD is critical for proper interpretation of the CD of DNA and RNA.

The fluorescence lifetime spectrometer became fully functional in 1984. A gating circuit was built to eliminate artifacts in the fast timing electronics (Laws et al., Rev. Sci. Instrum. 55, 1564-1568; 1984). William Laws (BNL, Biology) and J.B.A. Ross (Mt. Sinai School of Medicine) started a systematic survey of the lifetimes of the amino acid tyrosine and a large number of chemically related compounds. Their results will provide information on the solution conformation of peptide hormones such as insulin.

The Effects of Autoionization on the Alignment of $\text{Cd}^+(4d^9 5s^2, ^2D_{5/2})$

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The benchmark process for photoionization-induced alignment in atoms is the fluorescence decay of the excited "d"-hole states of Cd^+ . Fluorescence polarization measurements, from which alignment is derived, have been made at the He I (2,3) and Ne II (3) resonance lines, and recently, Kronast et al. (4) covered the region from threshold for $^2D_{5/2}$ production at 705.2 Å to 400 Å. Although these authors see evidence for the presence of doubly excited autoionizing resonances, a detailed study of the variation of alignment through an autoionizing resonance has not been made. It is just such a measurement which we report here.

The process which we observe can be written

and we measure the linear polarization of the fluorescence at 4416 Å. A crossed-beam apparatus is used with fluorescence detection at right angles to the intersection of the two beams. The Cd vapor is produced in a two-chamber oven, and radiation from the 4m normal incidence monochromator on beamline U-11 is the photoexcitation source. Fluorescence is wavelength and polarization selected before detection by a photomultiplier tube operating in the counting mode. The polarization of the fluorescence is defined as $P = (I_{||} - I_{\perp}) / (I_{||} + I_{\perp})$, where $I_{||}$ and $I_{\perp}$ are fluorescence intensities linearly polarized parallel and perpendicular to the direction of the linear polarization of the synchrotron radiation.

The results of the fluorescence measurements are shown in Fig. 1. The upper portion is a recording of the total polarization independent 4416 Å fluorescence intensity. This excitation spectrum is equivalent to the relative partial photoionization cross section of the $\text{Cd}^+ ^2D_{5/2}$ state. The theoretical results of Johnson et al. (5) are given in the lower curve. The overall agreement between theory and experiment is quite good, although the calculation underestimates the strengths of the 5f and 6f resonances.

Figure 2 gives the polarization which has been corrected for all systematic polarization shifts. It is apparent from the figure that cross section minima in the resonance profile are associated with marked

Fig. 1 Partial photoionization cross section of the $2D_{5/2}$ state of Cd^+ from threshold to 670 Å: —●— experimental relative cross section (left vertical scale) obtained from fluorescence measurements; — theoretical absolute cross section (right vertical scale) (4) convoluted with a Gaussian slit function of 1.0 Å half-width.

Fig. 2 Linear polarization of the fluorescence for the process $Cd^+(2D_{5/2}) + Cd^+(2P_{3/2}) + \gamma'(4416 \text{ Å})$ from threshold to 680 Å: —●— experiment; x— theoretical results (4) and convoluted to reflect 1.0 Å excitation bandwidth. Bottom curve is the experimental $2D_{5/2}$ partial cross section reproduced from Fig. 1.

decreases in the polarization of the emitted radiation. Further, it is at the resonance peak positions in the $2D_{5/2}$ cross section that the polarization tends to its most negative values. However, a comparison between experiment and theory shows poor agreement, as theory fails to reproduce the observed variations in the linear polarization.

A striking feature of Fig. 2 is the perturbing effect of the nf series. These transitions are only weakly visible in the $2D_{5/2}$ partial cross section, whereas the influence of the lower members of the nf series on the polarization is comparable to that of the np series.

The alignment parameter over the spectral region of interest is shown in Fig. 3. The variation of the alignment across the autoionizing resonance follows the variation of the linear polarization but is much more pronounced.

Fig. 3 Alignment of the $2D_{5/2}$ excited state of Cd^+ from threshold to 680 Å. The magnitude of the variation of the polarization is less than that of the alignment, due to the effects of the final $2P_{3/2}$ ionic state on the polarization.

For the $2D_{5/2}$ state, the one alignment parameter does not provide adequate information to extract individual $\sigma(jm)$ partial cross sections. The fact that the alignment is positive over the entire spectral region, however, indicates that there is enhanced population in the $|m| = 5/2$ levels. Hence, the effect of the autoionizing resonances is to decrease the alignment, or equivalently, the $|m| = 5/2$ population at their cross section minima.

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Application of Vacuum Ultraviolet Photon Beams to
Transients Produced by Discharge-Flow Tube Sources:
Photoionization Efficiency Spectrum of $O_2(^1\Delta_g)$

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The photoionization spectrum of a $^1\Delta_g$ oxygen was measured previously only over the limited range from its threshold at 11.09 eV up to the threshold for the ionization of the $O_2(X^3\Sigma_g^-)$ ground state at 12.071 eV. However, the availability of monochromatic photon beams of high intensity at the National Synchrotron Light Source and the development of efficient spectrum-stripping techniques now make it feasible to observe the photoionization of a $^1\Delta_g$ oxygen in the presence of ground state oxygen. Therefore a wider span of photon energies can be covered than was heretofore possible. Also, the investigation of a transient species such as $O_2(a^1\Delta_g)$ serves as a demonstration of the application of discharge flow tube techniques at synchrotron light beam lines to measure thermochemical properties and spectra of the radicals and highly reactive molecular fragments that are significant intermediates in flow tube studies of fast chemical reactions in the gas phase.

A molecular beam containing $O_2(a^1\Delta_g)$ was established by collimation of a jet expansion of a microwave-discharged mixture of 1.6 torr of helium and 0.12 torr of oxygen. Under these conditions about 20% of the molecular oxygen in the beam was present as $O_2(a^1\Delta_g)$. This molecular beam crossed the photon beam from the monochromator in the ion-extraction zone of a quadrupole mass spectrometer equipped with a channeltron detector set up to count individual ions. The photon intensity was monitored with a sodium salicylate fluorescent screen plus photomultiplier tube combination. Using a 1200-grooves mm^{-1} laminar grating the photoionization efficiency for the production of O_2^+ ions was measured at wavelengths from 550 to 1210 Å in first order radiation at a resolution of 3 Å, and in selected wavelength regions in second order at a resolution of 1.5 Å. (For wavelengths greater than 1050 Å in first order a 0.2-cm lithium fluoride filter was inserted to remove second and higher order radiation.) The same measurements were repeated with the discharge turned off, and the latter spectra were normalized to the former using prominent lines in the spectrum¹ of $O_2(X^3\Sigma_g^-)$ that do not also appear in the spectrum of $O_2(a^1\Delta_g)$. Spectra attributable to $O_2(a^1\Delta_g)$ alone were then obtained by subtraction.

The observation of a sharp onset at 1118 Å (11.09 eV) plus a spectrum in the threshold region that is identical to that in the literature²

identified the stripped spectrum as that of $O_2(a^1\Delta_g)$. A careful search indicated that metastable $O_2(b^1\Sigma_g^+)$ was not also present, because no onset could be seen at the expected wavelength of 1188 Å (10.43 eV) and in fact no signal at all, above the low background due to the scattered light, could be seen up to 10.9 eV.

The highly congested first order photoionization spectrum at wavelengths below 1000 Å (above 12.4 eV) is displayed in Fig. 1.

Fig. 1. Photoionization spectrum of $O_2(a^1\Delta_g)$ in first order.

Fig. 2. Spectrum of the 16 eV peak in second order (the abscissa values should be multiplied by 2).

The most obvious feature is a complex peak at 16.0 eV, and there are two very conspicuous lines at 14.10 and 14.34 eV. Abrupt drop-offs in the general trend of the gross structure in the higher energy portion of the spectrum suggest that convergence of Rydberg series may be occurring near 18.9, 19.3, 20.9 and 22.3 eV. Two progressions can be seen in the region from 15.7 to 16.6 eV, detailed in Fig. 2, characterized by constant spacings of 672 cm^{-1} and 981 cm^{-1} . Another five-line progression, of spacing 949 cm^{-1} , is evident in the region from 18.2 to 18.8 eV.

The prominent broad peak at 16.0 eV, corresponding to an excitation energy of 17.0 eV in the oxygen molecule when the 0.98 eV excitation energy of the $a^1\Delta_g$ state is added, matches in width and relative strength a similarly spectacular feature at 16.9 eV in the photoionization of ground state $O_2(X^3\Sigma_g^-)$. The latter peak is seen at high resolution¹ to be a broad peak upon which numerous much lower lines are superimposed, and this appears also to be true for the peak in $O_2(a^1\Delta_g)$. The possible Rydberg state convergences would correspond to ionic states near 7.8, 8.2, 9.8 and 11.2 eV. Three of these energies are close to known states of O_2^+ , viz. $D^2\Delta_g$ at 7.78 eV, $B^2\Sigma_g^-$ at 8.27 eV, and a $^2\Pi_u$ state at 11.16 eV.³ It is significant that all three states are doublets, because photoionization of $O_2(a^1\Delta_g)$ to produce ionic states of quartet and higher multiplicity is forbidden. The two progressions near 16 eV have properties consistent with their interpretation as vibrational states of members of Rydberg series converging on either the $C^2\Phi_u$ or the $D^2\Delta_g$ ionic state, because they give principal quantum numbers of 3 or 4 when the quantum defect is in a reasonable range of 0.6 to 1.8, while the known characteristic vibrational energies of the ionic states are 970 and 940 cm^{-1} respectively.⁴ Convergence to $D^2\Delta_g$ might be a preferred choice for the series characterized by the close spacing of 672 cm^{-1} (A in Fig. 2) because its configuration⁵ $\sigma_g^1\pi_u^4\pi_g^2$ suggests the likelihood of a weakened force constant in the lower members of a Rydberg series. Since nearly all of the fundamental vibrational energies of the excited states of the O_2^+ ions fall in the range³ of 898 to 1197 cm^{-1} , the progression near 18.5 eV could also represent one term of a Rydberg series.

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Measurement of the Dissociation Energies of Gas Phase Neutral Dimers by a Photoionization Technique

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A knowledge of the dissociation energies of weak polyatomic heterodimers in the gas phase provides extremely important information for the study of long range intermolecular forces, which study is crucial if chemical reactivity is to be understood in detail. Unfortunately, very few such dissociation energies are known because the measurements have been very difficult. To help alleviate this problem a photoionization technique has been developed for making these measurements that is proving to be fast, unambiguous, sensitive, accurate, and reasonably general.

The dissociation energy $D(A \cdot B)$ of the dimer $A \cdot B$ is just the difference between $P_{A,AB}$, the threshold energy for the dissociative photoionization process $A \cdot B + h\nu \rightarrow A^+ + B + e$, and I_A , the ionization energy of A, the partner of lower ionization potential; i.e., $D(A \cdot B) = P_{A,AB} - I_A$. To measure $P_{A,AB}$ a subtractive technique is used. The target dimer $A \cdot B$ is formed in a molecular beam by collimation of a jet expansion of mixed A and B gas or vapor. This beam is crossed by the photon beam from the monochromator, and, using a quadrupole mass spectrometer and a channeltron ion detector, the wavelength-dependent efficiency for the production of A^+ is measured. The proportions and pressure of the A,B mixture are adjusted so that the production efficiency is composed mainly of contributions from the ionization of uncombined A and the dissociative ionization of $A \cdot B$. A second measurement is made of a molecular beam containing A alone. The second spectrum is normalized to the first at energies just above the ionization energy I_A of A, and the two spectra are subtracted. The result is the desired spectrum for the dissociative photoionization process in its threshold region. A small correction is sometimes necessary for the contribution to the first spectrum of A^+ from the dissociative ionization of $A \cdot A$, but is easily determined by an ancillary measurement similar to that already described. In addition, the dissociation energy of the ionic dimer, $D([A \cdot B]^+)$, can be determined whenever the ionization potential I_{AB} of the dimer $A \cdot B$ can be measured, via the difference $D([A \cdot B]^+) = P_{A,AB} - I_{AB}$.

Two efficiency spectra for dissociative photoionization are shown in Figs. 1 and 2, showing that the threshold functions are often remarkably linear. The thresholds and their associated uncertainties are determined by minimization of the calculated values of chi-square per degree of freedom for assumed straight lines to find the best lines through the data

Figs. 1 and 2. Efficiency function for the production of $C_6H_6^+$ from $C_6H_6 \cdot SO_2$ (left) and $C_6H_6 \cdot HCl$ (right). The arrow shows I_A for C_6H_6 . The value of $P_{A,AB}$ is taken to be the intercept of the best straight line through the data.

beyond a given rejection level. Table 1 lists the measurements that have been made.

The agreement of the results of this work with data obtained by other techniques is excellent. The striking linearity of the threshold functions for dissociative photoionization results from the step-function behavior of the photoionization efficiency function of the monomer A. The ground state of A^+ splits into a band when its partner B becomes loosely associated, because this association creates new vibrational modes having low fundamental frequencies. The one big step function associated with the single ionic ground state in A^+ then becomes a series of small, unresolved step functions associated with the band in $(A \cdot B)^+$ that are manifested in first approximation as a straight line. Above the dissociation energy of

Table 1. Measured Dissociation Energies (kcal mol⁻¹)

Dimer	D _T	D ₀ ^a	D ₀ (Literature)
$\underline{t}\text{-C}_4\text{H}_8\cdot\text{SO}_2$	3.54 ± 0.18	3.73 ± 0.21	3.79 ± 0.17 ^b
$(\underline{t}\text{-C}_4\text{H}_8\cdot\text{SO}_2)^+$	---	2.3 ± 1.1	---
$(\underline{t}\text{-C}_4\text{H}_8)_2$	2.8 ± 1.1	2.8 ± 1.1	---
$1,3\text{-C}_4\text{H}_6\cdot\text{SO}_2$	2.83 ± 0.44	---	---
$(\text{C}_4\text{H}_6\cdot\text{SO}_2)^+$	3.3 ± 0.9	---	---
$\text{C}_6\text{H}_6\cdot\text{SO}_2$	4.00 ± 0.20	4.26 ± 0.24	---
$\text{C}_6\text{H}_6\cdot\text{HCl}$	4.71 ± 0.11	4.74 ± 0.12	5.40 or 1.95 ^c
$(\text{C}_6\text{H}_6\cdot\text{HCl})^+$	---	7.3 ± 1.2	---
$1,3\text{-C}_3\text{H}_5\text{Br}\cdot\text{HCl}$	2.09 ± 0.35	---	---
$(1,3\text{-C}_3\text{H}_5\text{Br})_2$	1.41 ± 0.35	---	---

^aD₀ values for 0° K are corrected from the values D_T measured at beam temperatures T that ranged from 18 to 48 °K.

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(A·B)⁺ this straight line appears as the efficiency function for the production of A⁺. The dissociation energies of the ionic heterodimers are remarkably small compared to those of all the known ionic homodimers (> 10 kcal mol⁻¹), a phenomenon that has been ascribed to a substantial binding contribution arising from delocalization of the odd electron in the ionic homodimers, while the net charge remains localized on the moiety of lower ionization potential in the ionic heterodimers.^{1,2}

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Energy Flow in van der Waals Molecules

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INTRODUCTION

Energy disposal in isolated molecules and during collisions between molecules is fundamental to chemical processes. In this experiment we use the high brightness of the synchrotron radiation from the stored electron beam of NSLS to probe energy flow in van der Waals molecules. These species are generally dimeric clusters of molecules bound together only by long range attractive forces collectively known as van der Waals forces. In many respects they resemble chemical reagents frozen at the stage of formation of collision complexes. This is a particularly significant stage at which to interrupt a chemical reaction and to probe the energy flow. We describe the results of three on energy migration in loosely bound systems.

NONSTATISTICAL BEHAVIOR IN DISSOCIATIVE PHOTOIONIZATION

A basic assumption of RRKM theory of unimolecular decomposition is rapid intramolecular vibrational relaxation (IVR). Many attempts have been made to find molecules in which IVR is inefficient, but save for a few exceptions, there has been little success (1). Van der Waals complexes offer interesting prospect since in certain respects the partners of these complexes behave as independent species (2). We have now demonstrated that the weak coupling of the moieties of a van der Waals complex may impose a bottleneck to vibrational energy relaxation (3).

The experiment involves the dissociative photoionization of the van der Waals complex of trans-1,3-butadiene and SO_2 , $\text{C}_4\text{H}_6 \cdot \text{SO}_2$. First, the molecular ion is produced by direct photoionization $\text{C}_4\text{H}_6 \cdot \text{SO}_2 + h\nu \rightarrow \text{C}_4\text{H}_6 \cdot \text{SO}_2^+ + e$ which is followed by dissociation: $\text{C}_4\text{H}_6 \cdot \text{SO}_2^+ \rightarrow \text{C}_4\text{H}_6^+ + \text{SO}_2$, or $\text{C}_4\text{H}_6 \cdot \text{SO}_2^+ \rightarrow \text{C}_4\text{H}_6 \cdot \text{SO}^+ + \text{O}$. At 584 Å the production ratio of $\text{C}_4\text{H}_6 \cdot \text{SO}^+ / \text{C}_4\text{H}_6^+$ from $\text{C}_4\text{H}_6 \cdot \text{SO}_2$ is 2×10^{-3} . It seems surprising that the highly excited dimer ion $\text{C}_4\text{H}_6 \cdot \text{SO}_2^+$ has an appreciable probability to undergo dissociation by breaking an S-O chemical bond instead of the much weaker van der Waals bond. An RRKM calculation of the production ratio of $\text{C}_4\text{H}_6 \cdot \text{SO}^+ / \text{C}_4\text{H}_6^+$ by unimolecular decomposition of $\text{C}_4\text{H}_6 \cdot \text{SO}_2^+$ confirms this. That is, the energy deposited in the SO_2 moiety remains localized long enough for fragmentation of the strong bond to occur. The violent process of ionic fragmentation in a species may take place without breaking a delicate bond in the same complex. This example is not unique.

INTRAMOLECULAR ELECTRONIC ENERGY TRANSFER IN PHOTOIONIZATION

The geometry of the weak complex between benzene and hydrogen chloride is such that the HCl is, on the average, perpendicular to the benzene ring and on the benzene C_6 axis, with the hydrogen atom closer to the ring than the chlorine atom (4). We have used the recently developed technique of dissociative photoionization of the cluster (5) to measure its dissociation energy to be 4.74 ± 0.12 kcal mol⁻¹ at 0 K. The photoion efficiency function for the process $C_6H_6 \cdot HCl + h\nu \rightarrow (C_6H_6 \cdot HCl)^+ + e$ was determined in the vicinity of the ionization onset (Fig. 1). This onset is characterized by a very weak rise at 1357 ± 7 Å or 9.14 ± 0.05 eV. The weak onset is due to highly unfavorable Franck-Condon factors for direct ionization.

Fig. 1. Threshold PIE curve for the production of $(C_6H_6 \cdot HCl)^+$ over the range 1290-1380 Å.

The photoionization efficiency function in Fig. 1 reflects several important phenomena. First, direct ionization of the complex in which an electron is ejected from the highest filled molecular orbital of benzene results in a positively charged aromatic ring immediately adjacent to the positive end of the dipolar HCl molecule. The configuration of lowest energy of this ion is that with the dipole in the opposite direction. The large geometric modifications for adiabatic ionization ($C_6H_6 \cdot HCl + h\nu \rightarrow C_6H_6 \cdot ClH + e$) are responsible for the observed small Franck-Condon factors. As the photon energy rises to the point where transitions with much more favorable Franck-Condon factors become possible, the photoionization efficiency function rises more rapidly, giving the appearance of an onset. This occurs in the vicinity of 1310 Å.

Second, in the region of lower photon energies than the strong onset there is evidence for autoionization processes. The structures that appear at about 1323 Å and 1344 Å have no parallel in the photoionization spectrum of benzene. It is tempting to correlate these peaks with the prominent absorption band in HCl due to the $b^3\Pi_1$ state. It appears that in the molecular field of its benzene partner the HCl moiety retains enough individuality to predominate in a state(s) of the complex near the energy of its own $b^3\Pi_1$ state. Unlike HCl ($b^3\Pi_1$) the resulting state(s) of the complex is autoionizing because it lies above the ionization potential. It is interesting that in this hypothesis the incident photon appears to be absorbed by the HCl moiety while the electron is ejected from its C_6H_6 partner, suggesting rapid E→E transfer of a significant amount of energy across the weak C_6H_6 -HCl bond.

GAS PHASE HEAT OF FORMATION AND STRUCTURE OF $C_6H_6Cl^+$.

Photofragmentation of appropriate van der Waals cluster molecules offers the intriguing possibility of synthesis of many important ionic reaction intermediates. For example, photofragmentation of $C_6H_6 \cdot HCl$ may proceed as follows: $C_6H_6 \cdot HCl + h\nu \rightarrow C_6H_6Cl^+ + H + e$ where $C_6H_6Cl^+$ is isoelectronic with the long-postulated Wheland intermediate (6) for electrophilic chlorination of benzene. Very little is known about the thermochemistry of these ions in the gas phase or about the dynamics of this reaction. We have now been able to observe this ion, $C_6H_6Cl^+$ ($m/e = 113$) and to determine its onset as 834 ± 5 Å (14.86 ± 0.09 eV). This leads to an apparent $\Delta H_{f,0}^\circ(C_6H_6Cl^+) = 281 \pm 2$ kcal mol^{-1} . It is important to know whether this standard heat of formation is compatible with structures proposed for electrophilic substitution intermediates.

Detailed consideration of possible ionic structures shows that none of the protonated chlorobenzenes, that is, protonation at *o*, *m*, *p*, or *ipso* positions to chlorine, can be reasonably expected to have heats of formation as large as our measured value. Also, heats of formation of open chain ions with the empirical formula $C_6H_6Cl^+$ lie 30–60 kcal mol^{-1} higher than the 281 kcal mol^{-1} determined at NSLS. Several options remain to account for the apparent heat of formation of $C_6H_6Cl^+$. The most viable appears to be that the ion is formed from an excited state of HCl that would be everywhere repulsive except for the existence of a bound state of the proper multiplicity in the vicinity which results in a shallow potential well formed by the avoided curve crossing. Consequently, $C_6H_6Cl^+$ is an electronically excited species, held in a metastable state for at least 10^{-5} s, and not the classical Wheland intermediate.

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Photoelectron Spectroscopy of Autoionizing Rydberg States in Small Molecules

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Unlike Rydberg series involving promotion of the outermost valence electron, Rydberg states resulting from excitations of deeper lying valence orbitals usually lie above the ionization potential. Although the latter belong to the neutral excited state manifold, such "super-excited" Rydberg levels are likely to interact with the degenerate ionization continuum, leading to the well-known phenomenon of autoionization. Autoionizing Rydberg and non-Rydberg resonances have been identified and characterized for a large number of molecules by photoabsorption and photoionization (integrated) measurements. Their effect on the internal energy distribution of the resulting ions, however, has been difficult to study due to the lack of suitably intense laboratory light sources (below 1000 Å) required for such detailed measurements. It is the aim of the present work to systematically measure the decay of selectively excited autoionizing Rydberg states in small molecules through use of photoelectron spectroscopy and the intense, tunable, narrow-band radiation from the U-11 beam line. Such data provide the basis for understanding the complex interaction between the molecular ion core and photoexcited electron, which is responsible for the autoionization process.

The experimental apparatus is shown in Fig. 1. The photoelectron spectrometer features a fully rotatable, high resolution, hemispherical electron energy analyzer and a differentially pumped capillary light guide that channels the ionizing radiation (1000 Å-350 Å) to the sample point while providing a highly effective gas barrier.

Initial measurements focussed on the decay of electronically autoionizing Rydberg series in two sets of related molecules, the hydrogen halides (HCl and HBr) and the valence isoelectronic triatomics CO₂, N₂O and OCS. In the hydrogen halides, excitation of Rydberg states converging to the excited $A^2\Sigma^+$ state of the ion resulted in large variations in the vibrational state distribution of the $X^2\Pi$ ground ionic state to which they decay. An example of such a "resonant" photoelectron spectrum is shown in Fig. 2.

Although the observed high vibrational excitation of the HX^+ ion is consistent with a substantial difference in geometry between the Rydberg and $X^2\Pi$ states, comparison with theoretical spectra employing the Franck-Condon approximation suggests that such interpretations are qualitative at best.

For the linear triatomics CO₂, N₂O and OCS other effects involving multiple electronic decay channels and additional vibrational degrees of freedom were investigated. In all three molecules, constant ionic state scans over the Rydberg series converging to the $C^2\Sigma(g)(\sigma(g))^{-1}$ ionic

Fig. 1. Schematic of photoelectron spectrometer.

Fig. 2. The vibrationally resolved photoelectron spectrum of the $X^2\Pi$ state of HCl^+ following resonant excitation of the $4s\sigma$, $v = 1$ Rydberg state at $\lambda = 792.7 \text{ \AA}$. v' refers to the vibrational levels of the $X^2\Pi$ ionic state. The dashed lines are the normalized vibrational intensities at photon energies not coincident with a resonance.

state, suggest that $np\pi(u)$ Rydberg levels decay preferentially to the $2\Sigma(u)(\sigma(u))^{-1}$ ionic state while the decay of the $np\sigma(u)$ levels strongly favors the $X^2\Pi_g(\pi_g)^{-1}$ ionic ground state. Furthermore, the energy-dependent resonance profiles in the total parent ion yield and in the individual ionic state decay channels are in some instances quite different. This is illustrated in Fig. 3. One observes that the $4p\sigma_u$ resonance in CO_2 results in an overall absorption maximum in the CO_2^+ ion yield and a cross section minimum or "window" in the $X^2\Pi_g$ vibrationless final state channel.

Fig. 3. Comparison of the CO_2^+ yield and intensity of the $X^2\Pi_g(000)$ vibronic level of CO_2^+ in the spectral region leading to the $C^2\Sigma_g^+(000)$ limit at $\lambda = 639.4 \text{ \AA}$.

Spectra of this type lead to direct conclusions concerning the coupling strength between Rydberg series of particular symmetries and the available continuum channels.

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Deexcitation Electron Spectroscopy of Free and Coordinated CO

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The resonant absorption behavior of free and co-ordinated molecules can be readily measured with tunable soft x-ray sources. To study the electronic details of the molecule-substrate interaction, the de-excitation of molecules that have been resonantly excited can also be monitored. Deexcitation electron spectroscopy (DES) is the analysis of electrons emitted following the decay from a resonantly excited neutral state, and is complementary to photoemission (PES) and Auger (AES) spectroscopies(1). This new technique is well-suited to the study of valence-charge redistribution and excited-state lifetimes in molecules. We have used DES to compare the decay channels of resonantly excited CO in two configurations: strongly bound in the carbonyl complex $\text{Cr}(\text{CO})_6$, and weakly adsorbed on $\text{Cu}(110)$. The DES spectra of these two systems show large intensity variations characteristic of the bonding configurations. The 1π - 3π splitting of CO following the $\text{C}_{1s} \rightarrow 2\pi$ transition can also be measured by a comparison of DES with PES.

The experiments were performed using the plane grating monochromator of line U14A, with a measured resolution at the C k-edge of 2 eV. $\text{Cr}(\text{CO})_6$ and CO were adsorbed at 95K onto a Au foil and $\text{Cu}(110)$ crystal, respectively. Resonant absorption energies were measured by monitoring the carbon KVV Auger yield as a function of photon energy, and absorption and energy distribution curves were measured with a CMA.

The absorption spectrum of CO in the energy region of C_{1s} ionization is dominated by the $\text{C}_{1s} \rightarrow 2\pi$ excitation, which occurs at 287.3 eV in the gas phase(1). Our DES initial state is therefore represented by a hole in the C_{1s} shell and an electron in the previously unoccupied 2π level, leaving the molecule in the 1π configuration. The final states in DES and PES are the excited states of singly ionized CO, so that binding energies from both techniques can be directly compared. DES necessarily emphasizes two-hole, 2π states, but single hole states can also be seen if the 2π electron is an active participant in the decay. This is the case for the CO-systems described here(1).

Fig. 1 compares DES spectra of free CO(1), $\text{Cr}(\text{CO})_6$, and CO on $\text{Cu}(110)$. A PES spectrum of $\text{Cr}(\text{CO})_6$, taken at a photon energy well below resonance, is also shown. In comparing gas phase CO to $\text{Cr}(\text{CO})_6$ one notes: (1) the one-hole peaks are still visible for $\text{Cr}(\text{CO})_6$, but their energy positions and relative intensities are quite different than for free CO, (2) the 4σ peak in the $\text{Cr}(\text{CO})_6$ DES is at 17.8 eV binding energy compared to 19.8 in the

Fig. 1 BINDING ENERGY (eV)

gas phase, (3) the 5σ and 1π levels have become nearly degenerate in DES as they do in PES, (4) the intensity ratio of the 4σ peak to the $1\pi+5\sigma$ increases to ~ 1.4 in $\text{Cr}(\text{CO})_6$ compared to ~ 0.1 for CO, (5) AES for $\text{Cr}(\text{CO})_6$ (2-not shown) has exactly the same structure as DES except it is shifted by 9 eV in binding energy. The reduction of the binding energy of the 4σ level when CO is strongly bound is a result of final state screening of the photoinduced hole. Since DES and PES agree in energy for these states, the final configuration for DES is screened CO, i.e. an excited neutral. The dramatic change in the intensity ratio of the 4σ to $1\pi+5\sigma$ is a result of the strong Cr-CO bond perturbing the valence charge distribution of the CO. It is interesting to note that DES from $\text{Cr}(\text{CO})_6$ is very similar to AES results for the strongly bonded CO on $\text{Ni}(100)$ (3).

The top set of curves in Fig. 1 are the DES and AES spectra of weakly chemisorbed CO on $\text{Cu}(110)$. The single hole states (4σ and $1\pi+5\sigma$) are more pronounced than for $\text{Cr}(\text{CO})_6$. The intensity ratio of the 4σ to $1\pi+5\sigma$ (~ 0.6) is intermediate between the gas phase and $\text{Cr}(\text{CO})_6$ values. The most important observation is that, except for intensity variations, the DES spectrum is identical to the AES spectrum.

The AES of molecules adsorbed on metal surfaces is really DES because the metal screens the holes induced by the original ionization or by the subsequent decay. This fact is immediately applicable to a determination of the time scale of these processes. The similarity of the AES and DES from CO on $\text{Cu}(110)$ indicates that the deexcitation is slow compared to the life time of the excited hole configurations. That is, the excited configurations with a C_{1s} hole created by ionization all relax into the completely screened state before an electron decay occurs. We show below that the satellite lines observed in valence PES of CO on Cu are absent in DES (and AES), and therefore the final state of DES is also a screened state.

The intensity ratio of the 4σ to $1\pi+5\sigma$ single hole states

in the DES of CO on Cu is ~ 0.6 compared to ~ 0.1 for gas phase CO. To understand this trend, the generalized valence bond method has been used to calculate charge contours for CO in various valence hole and excited neutral configurations(1). By considering the overlap of various screened final states with a C_{1s} hole initial state, the results indicate that the 4σ intensity should be relatively larger for CO on the metal than in the gas phase. Thus, the relative intensities of DES single-hole peaks contain valuable information about the interaction and bonding between the metal surface and the CO molecule.

Figure 2

An indication of the perturbation of the CO valence charge density by the metal is contained in the $1\Pi-3\Pi$ splitting of neutral CO with a C_{1s} hole. Fig. 2 compares a PES spectrum taken at $h\nu = 35$ eV with the DES spectrum of CO on Cu(110). The CO 4σ and its satellite appear at 11.8 and 13.5 eV in the PES scan. The Cu d-band in the DES is excited by direct photoemission, but direct photoemission from the CO valence orbitals is too weak to see. Two observations are striking. First, there are no satellite lines for the DES spectrum, which is consistent with our argument that the deexcitation process is adiabatic. Secondly, the DES peaks do not line up with the PES peaks. This can be explained if the excited 2Π

electron can couple readily with the unoccupied states of the metal. When the 2Π electron hops onto a metal atom, the metal furnishes an electron to screen the C_{1s} hole. This new electron is in the lower energy 3Π state. In other words, the 1Π decays to the 3Π state before there is an electronic decay of the C_{1s} hole. The shift in the screened peaks between the DES and PES in Fig. 2 is the $1\Pi-3\Pi$ splitting of CO on Cu(110), or ~ 1.0 eV (compared to 1.45 eV for gas phase CO(19)).

To conclude, we would like to emphasize that DES highlights features that are sensitive to the degree of metal-molecule bonding, namely (1) changes in single hole state relative intensity, and (2) variations in multiplet splitting. Thus, DES should prove to be a valuable technique in the study of gas-solid interactions.

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Surface Sensitive Photoemission EXAFS: A New Structural Tool

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A new technique for surface EXAFS has been developed [1,2]. In this technique the absorption fine structure is observed by monitoring the photoelectrons emitted from core levels as a function of photon energy. The surface sensitivity is achieved by detecting elastic photoelectrons that escape to the vacuum from a few atomic layers near the surface. EXAFS from Mn 3p and F 2s outer core levels in MnF_2 were measured, the results were compared with transmission EXAFS from Mn 1s core level and good agreement was found. This development is significant because: (1) Almost all elements have suitable core levels of low binding energy. (2) Since photopeaks from adjacent core levels do not cross as the photon energy is varied, the limitations imposed on other surface EXAFS techniques by this interference is removed. Auger electrons, which have fixed kinetic energies and so can cross photopeaks, will generally have low energies if they originate from outer core levels and be unlikely to appear in the EXAFS region of kinetic energies, i.e., in excess of about 50 eV. (3) VUV light is used, which greatly extends the useable range of photon energies. (4) More than one element in a solid may be studied with the same monochromator.

The experiments were carried out on the VUV beam line U14A at NSLS. The measurements were done on the Mn 3p and F 2s outer core levels in MnF_2 by constant initial state spectroscopy (CIS) in which the height of each photopeak was monitored in a photon energy range 90-280 eV. Photoemission EXAFS requires an angular averaging of the photoelectron signal over a 4π solid angle so that all diffraction effects cancel out except those due to backscattering [3]. The angular averaging was achieved by using a polycrystalline sample and a cylindrical mirror analyser as the measuring device which integrates the signal over a 2π azimuth. The photon flux was measured by monitoring the total electron yield collected by a channel electron multiplier, from a high transmission grid coated with LiF in a side arm attached to the experimental chamber in a vacuum of low 10^{-7} T. MnF_2 thin films were vapor-deposited in an ultrahigh vacuum preparation chamber and the measurements were done in $\leq 10^{-10}$ T vacuum. In addition, some transmission EXAFS data were acquired on the Mn 1s core level in MnF_2 in a photon energy range 6400-7400 eV for comparison of results. The transmission EXAFS experiments were done at SSRL.

Both the transmission and photoemission EXAFS data were analyzed by conventional Fourier transform methods. The background removal was done by spline fit using the IMSL subroutine ICSFKU [4]. Cubic spline functions with four fixed knots were found to describe the background well for both photoemission and transmission EXAFS data. In addition, the pre-edge absorption was removed in the transmission case. The oscillations were filtered out and normalized to the fitted background to obtain $\chi(k)$ [5]. The experimental $\chi(k)$ were Fourier transformed using the amplitude and phase function data of Teo and Lee [6], with their definition of phase function, applying the Lee and Beni method [5] and the nearest neighbor distances were determined directly from the peak positions in the absolute part of the Fourier transforms, i.e., abs. $F(R)$. Figs. 1a-c show $\chi(k)$ weighed by k^3 for the 1s, 3p and 2s cases, respectively. For these plots the threshold energy, E_0 , was arbitrarily taken to be 6537 eV, the binding energy of the Mn 1s core level, and 48 and 28 eV, respectively the binding energies of the Mn 3p and F 2s levels relative to the valence band edge. Figures 1d-f show the

Fig. 1. EXAFS function $k^3\chi(k)$ vs. electron wavevector $k[\text{\AA}^{-1}]$ and Fourier Transform $F(R)$ vs. $R[\text{\AA}]$. Solid line Abs. $F(R)$, dashed line - IM. $F(R)$. (a,d) Mn 1s. (b,e) Mn 3p. (c,f) F 2s.

magnitude and the negative part of the imaginary part of $F(R)$ for the respective Mn 1s, Mn 3p and F 2s EXAFS signals obtained with amplitude and phase function data of Teo and Lee and the parameter E_0 was optimized in each case for peak A. Since no calculated absorber phase shifts are avail-

able yet for the 3p core levels the 2p values were used. For F 2s the 1s values were used. Peak A occurs at 2.11, 2.09 and 2.13 Å, respectively, and these results on the nearest neighbor distance agree with an accuracy of 0.03 Å with the known crystal structure of MnF_2 [7]. Peaks B and C in the figures represent some average values of more than one near neighbor distances.

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STUDIES OF THE ELECTRONIC STRUCTURE AND EXCITATION PROPERTIES OF
VANADIUM-OXYGEN COMPOUNDS WITH TETRAHEDRAL AND OCTAHEDRAL V-O
COORDINATION. PART I: VANADIUM PENTOXIDE

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Vanadium-oxygen compounds are the subject of active current interest because of their remarkable physico-chemical properties, including luminescence, catalytic activity, and high or highly anisotropic conductivity.

We have started the investigation of vanadium pentoxide as the first part of a larger project devoted to studies of five series of oxides, vanadates, and bronzes. Characteristic for all these materials is the enclosure of vanadium atoms within rigid oxygen cages with tetrahedral or octahedral V-O coordination. In different compounds, the more or less deformed V-O basic units may join corners and/or sides to form pairs, chains, layers, or tunnels. Our previous XPS, EELS, and APS studies have revealed large final state many-body effects in the highly localized excited configurations of the VO_n ionic clusters [1-4]. The present synchrotron radiation photoemission experiment is particularly interesting. Tuning through edges and detecting the decay products of various final state configurations should provide important information on the structure of orbitals and the excitation dynamics.

The main objectives of the present study are: a) to gain insight into the detailed electronic structure, bonding characteristics, and excitation properties of the studied materials; b) to evaluate the photoionization cross sections of valence and shallow levels in the energy range from 20 to 200 eV; and c) to study the phase instability of non-stoichiometric or open-structure compounds caused by particle (electron and/or ion) bombardment.

During the time allocated to this project, preliminary experiments on vanadium pentoxide were performed, to test and complete some of our earlier data obtained on polycrystalline V_2O_5 powder material at HASYLAB-DESY, Hamburg, Germany. The present measurements were done on Beam-line U14 A of the NSLS 750 MeV VUV Ring equipped with a plane grating monochromator and a double-pass cylindrical mirror analyzer. Single crystals of V_2O_5 of very good quality were crushed and mounted on the sample holder either as a dried alcohol suspension, or as small crystal chunks embedded in elemental indium. Both the valence band and shallow electron level regions were explored. If pure and stoichiometric, V_2O_5 should be a perfect insulator with a rather large

(2.5 eV) band gap, because the 3d-derived electronic states should be empty. Irradiation-induced reduction of V_2O_5 to the lower oxide V_6O_{13} has earlier been observed in LEED [5], EELS [6], APS [7], and AES [8]. Our synchrotron radiation photoemission experiment indicates that this phase transition is also present in photon irradiation at incident energies of the order of 102 eV, and is observed as the appearance of new electronic states in the gap, accompanied by changes of the 3p-core level structure.

Two major problems surfaced during the experiment. One is related to sample preparation. The samples deposited as dried alcohol suspensions may be covered by an organic overlayer whose photodesorption may alter the spectra, interfering with the photo-induced phase transition of the sample. Ion bombardment could not be used for cleaning purposes because of the anticipated damaging effect of ions. The second problem is related to the occurrence of severe charging effects during the photoemission experiment, as manifested in an instability of the recorded spectra.

In our future work, we plan to prepare clean sample surfaces by cleaving in-situ single crystals of V_2O_5 , and to try charging compensation by using an electron flood gun. Correct evaluations of photoemission cross sections in our future measurements will benefit from an improved current stability of the electron beam in the ring.

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PHOTOEMISSION STUDIES OF I-II, I-III INTERMETALLIC COMPOUNDS
WITH B32 (Zintl) STRUCTURE. PART I: LiAl

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The I-II, I-III intermetallic compounds with B32 (Zintl) structure [1] have recently attracted considerable interest because one of the members of this family (LiAl) is a promising candidate for an electrode material in high energy density (lithium-sulfur) batteries [2,3]. In addition, these materials are useful as solid blankets for nuclear reactors [4]. The experimental and theoretical data obtained so far for these materials raise a number of problems that warrant a thorough consideration, among which: a) the conductivity behavior (metallic in I-II compounds and p-type in I-III compounds), b) the finite vacancy concentration in I-III compounds even at low temperatures, and c) the discrepancies between the results of different band structure calculations, and their poor agreement with the reported experimental data.

We have recently initiated a systematic experimental study of the electronic structure of the occupied and empty states of representative compounds in the I-II and I-III series by using the complementary information provided by a number of electron and x-ray spectroscopies, including XPS, EELS, AES, APS, and synchrotron radiation photoelectron and yield spectroscopies.

The objectives of the synchrotron radiation experiment are: a) to map the occupied (valence and shallow) and empty electronic level distributions of the investigated samples, b) to evaluate the effects of non-stoichiometry on the electronic structure of "real", defect-lattice I-III materials, and c) to study the dynamic behavior of electron excitations over a range of incident photon energies (20-200 eV) that contain characteristic edges of the selected samples.

During the time allocated to this project, preliminary experiments on LiAl were performed on Beam-line U14 A of the NSLS 750 MeV VUV Ring. The polycrystalline, single phase LiAl sample material was obtained from Argonne National Laboratory (courtesy of Dr. Sherman Susman). A clean sample surface was prepared by fracturing the sample in-situ in the measuring chamber at a base pressure of about 10^{-10} torr. The photoelectron spectra were measured by using the plane grating monochromator of the U14 A beam-line and the double pass cylindrical mirror analyser, with a typical resolution of about 0.3 eV at 20 eV and 0.8 eV at 300 eV. Complete sets of EDC, CIS, and CFS spectra were recorded. Data analysis is currently in progress. In the limited time available for this experiment, only one sample material could be

investigated. Although no significant surface contamination was observed, we plan to repeat the measurements on freshly prepared sample surfaces, and to minimize the total surface exposure by restricting the measurements to selected spectra indicated by a detailed analysis of the data obtained in the pilot experiment reported here.

Future work will also extend our studies to other intermetallic compounds in the I-II, and I-III Zintl series.

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Photon Stimulated Desorption of Ions from Polymer Surfaces

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The desorption of ions from solid molecular films following deep valence or core level excitation using synchrotron radiation has been reported for a few relatively small molecules.¹⁻⁵ Using the instrumentation on beamline U14A, we have obtained the first results for the case of polymers. Detailed studies were made of thin films of polystyrene and polyethylene, which were characterized by ion and electron yield spectra in the region of the carbon K edge.

Core electron orbitals are highly localized on specific atoms in a molecule, and the differences in core electron binding energies for different atoms are sufficiently large to selectively excite different elements comprising a molecule or even the same element in different chemical environments in the molecule. An exciting prospect is the possibility that specific bonds can be formed or broken by the activation of selected atoms. This point motivated the present research, following the discovery that ionization of a deep valence C-H bonding orbital in solid methanol multilayers results in desorption of H⁺ due almost exclusively to C-H bond rupture.^{2,6} In addition, different final states can be reached with potentially different chemical consequences. These states include configurations with the core electron excited to an antibonding valence orbital, a Rydberg orbital, a shape resonance, or the ionization continuum.

We found that creation of a core hole via the pi* resonance of the benzene ring in polystyrene does not result in bond rupture and ion desorption, whereas excitation at slightly higher energies (about 4%) does. Although 280 eV or more of energy is deposited by a single photon, the subsequent relaxation and chemistry depends upon the nature of the initial excited state. At present, this observation has several explanations. Core holes in molecules containing light elements primarily decay via Auger processes. It is thought that bond rupture and ion desorption can occur if the resulting two hole final state is localized.⁷⁻⁹ The two hole state, in the benzene ring, may be delocalized due to shielding effects, or because the pi system is delocalized and the holes are not constrained to be

associated with only a pair of atoms. It also is possible for the π^* resonance to decay predominantly to a singly charged ion which will have a photochemistry different from that for the doubly charged ions created by excitation above the K edge. Auger decay of the π^* resonance may not rupture C-H bonds effectively, and the multiple coordination of carbon, the rapid dissipation of electronic and vibrational energy, and the reneutralization of desorbing ions may preclude observation of C^+ and heavier ions.

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Resonant Valence-band Photoemission and
h ν Dependent 3p Photoemission of MnF₂

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This experiment was a preliminary part of a project which is concerned primarily with the h ν dependence of 3p photoemission in transition-element compounds. The primary objective of the work is to seek evidence for the presence of satellite structures in 3p photoemission (1).

Examination of the resonance valence-band photoemission was undertaken because of the considerable recent interest in this phenomenon in compounds (2-4) and because of the idea that the resonant part of the balance photoemission amplitude should be concentrated more in the ligand field states (that is, more in the states which are described in first approximation as d states) the more ionic the system (2).

Figure 1 shows the shallow valence region of MnF₂ with h ν = 57 eV. The feature near 12.3 eV B.E. contains both the final states associated with ionization from the t_{2g} and e_g orbitals which are primarily 3d. The broad feature in the region 14-17 eV B.E. contains various final states which arise from ionization from one of the orbitals which are composed primarily of F2p atomic orbitals.

Figure 2, which synthesizes the results on resonant valence photoemission of MnF₂, shows corrected CIS spectra at binding energies of 12.3 eV, 15.0 eV and 16.5 eV. Observed CIS spectra were corrected for the h ν dependence of the secondary electron yield by measuring the CIS spectrum at 22 eV binding energy, at which binding energy only secondary electrons appear, and by scaling the 22 eV CIS by the ratio of intensity of secondary electrons at the various kinetic energies corresponding to binding energies of 22 eV, 16.5 eV, 15.0 eV and 12.3 eV when excited by radiation with h ν = 51 eV (the resonance maximum).

As one sees, the resonance is localized essentially exclusively in the 12.3 eV binding energy feature. The change of intensity in the other feature is only some 10% of that of the 12.3 eV feature. The resonance in MnF₂ is somewhat more concentrated in the states which are thought of as metal d states than is the case with MnCl₂ (4). In MnCl₂ the various kinds of final states are not as well separated as in MnF₂ and the whole valence region resonates fairly strongly. There is, as well, a resonant satellite which has an intensity comparable with that of the metal 3d features at resonance.

Fig. 1. Shallow valence region of MnF_2 . $h\nu = 57$ eV

Fig. 2. CIS spectra of various shallow valence features of MnF_2 . For details, see text.

These results are, in general, as expected for a very ionic MnF_2 and a considerably less ionic MnCl_2 .

The 3p photoelectron spectrum of MnF_2 is expected to be essentially free of the satellite structures which are predicted to appear in NiCl_4^{-2} , because MnF_2 is very ionic. The behavior of the 3p photoelectron spectrum as $h\nu$ is varied suggests changes in the relative intensities of various features but the results are not unambiguous.

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Resonant Photoemission Studies of f-Electron Systems Performed on Station U14

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The study of the behavior of f-electrons in the early rare earths and early actinides has become an area of strong current interest. This results from (1) the anomalous nature of the 4f instability in mixed valent Ce-based systems, which appears to fail outside the usual promotional model description of mixed valence [1], and (2) the recent discovery of superconductivity in several Ce- and U-based, so-called heavy fermion systems, where the effective mass of the electrons responsible for the superconductivity is of order 200 times the free electron mass [2-4]. f-Derived photoemission experiments allow one to observe the response of the electronic system to the presence of a 4f hole, this being of particular interest in the rare earths because of the Coulomb disturbance created by the deep core 4f hole. Moreover, these experiments reveal the juxtaposition of f-states and valence band states and allow the probing of hybridization effects between the f-electrons and conduction or ligand electrons.

The use of a synchrotron light source allows one to employ Fano resonances which enhance the f-derived features [5], thereby allowing isolation of f-derived features from other features in the valence band. It is convenient to employ resonances at the 4d threshold in rare earth systems and at the 5d threshold in actinide systems, where the corresponding excitations are respectively

$$4d^{10}4f^n \rightarrow 4d^9 4f^{n+1} \rightarrow 4d^{10}4f^{n-1} + e_{4f}$$

and

$$5d^{10}5f^n \rightarrow 5d^9 5f^{n+1} \rightarrow 5d^{10}5f^{n-1} + e_{5f}$$

The power of this approach is illustrated in Fig. 1, where on-resonance, off-resonance and difference spectra (the latter emphasizing f-derived features) are shown for the three known heavy fermion superconductors. For $CeCu_2Si_2$ and UPt_3 , where emission from the transition metal d-band swamps the spectrum at most photon energies, it is necessary to employ the resonance in order to obtain even a qualitative view of the f-emission. The spectra in Fig. 1 fail to exhibit the extremely high density of electronic states at E_F suggested by low temperature experiments [2-4], because of instrumental resolution (~ 0.5 eV) and, at least for $CeCu_2Si_2$, possibly because of lifetime effects.

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On the other hand, the spectra in Fig. 1 allow inferences to be drawn about the hybridization between the f-electrons and the valence band electrons as discussed in Ref. [6].

Of particular interest in Ce-based systems is the two-peaked structure always present in the 4f spectrum, as seen for CeCu_2Si_2 in Fig. 1. The promotional model of mixed valence requires for Ce-based systems a single feature located at or near E_F (see, e.g., Ref. [7]). A series of experiments performed on Station U14 focused on the anomalous 4f-derived photoemission spectra of Ce-based systems; and, in the process, it was discovered quite unexpectedly that the two-peaked spectra were present as well in Pr- and Nd-based systems, a discovery that has brought new illumination to the problem of the 4f-instability in Ce-based systems. In these studies it was demonstrated that the small binding energy feature is not linked to the Fermi energy as formerly thought, but rather with the large binding energy feature, since the energy separation of the two features remains approximately constant as the two features move to higher binding energies in going from Ce to Pr to Nd. Consequently, the small binding energy feature has been identified as a 4f hole screened by a localized electron (mostly of 5d character), such localization being induced by the strong Coulomb field generated by the 4f hole, an idea postulated by Liu and Ho [8], and put on a more comprehensive theoretical basis by Riseborough [9]. This result, as well as explaining the nature of the high energy excitations in Ce-based systems, suggests that local screening is important as well in the mixed valent ground state [10].

Fig. 1. Energy distribution curves taken on-resonance and off-resonance and the difference spectra (which highlight f-derived emission) for three systems. (From Ref. [6]).

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Contact X-ray Microscopy of Biological Materials

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In contact X-ray microscopy, X-rays pass through the biological sample and expose an underlying X-ray sensitive material (photo-resist), producing an image that reflects the photon absorbance within the specimen. Because this absorbance is a function of the energy of the incident X-rays, tuneable synchrotron radiation can be used to vary the contrast in X-ray images, accentuating regions of different chemical composition. The technique is capable of resolution of the order of 100 Å.

Progress has been made toward automating the data collection process. A sample holder was developed that enables up to 28 different samples to be exposed sequentially. The X-ray wavelength and exposure for each sample can be pre-programmed and the experiment run under control of a microcomputer.

Preliminary experiments have been made to assess the feasibility of using contact X-ray microscopy to determine the distribution of elements (differential absorption microanalysis) within biological samples. In principle, differences between images of samples exposed to wavelengths slightly above and slightly below the absorption edge of an element could be used to indicate the distribution and concentration of the element. The inorganic calcium phosphate phase of bone was studied in the region of calcium L absorption edge making use of the absorption spectrum determined by Kenney et al. (1). Samples were exposed to wavelengths between 34.9 Å and 35.9 Å in 0.1 Å steps. A pair of images of bone above and below the calcium absorption edge is shown in figure 1. Images have been digitized and are in the process of being scaled and analyzed. In a similar study images obtained near the carbon absorption edge are being used to study the organic collagen phase of bone.

Differential absorption microanalysis requires that the elements be quite concentrated (of the order of 1% by weight (2)) in order that the differences be above the level of the noise. For most biological material elemental analysis would be limited to C, N, and O. Preliminary studies of muscle, platelets, ribosomes and lymphocytes have been made over these edges to determine appropriate exposures and experimental conditions. Differences in contrast have been observed which may be correlated not only with elemental distribution, but also with the location of protein and lipid within the biological sample.

We would like to acknowledge the assistance of Mr. Waiman Ng for automation of the data collection, Dr. Francoise Cinotti for providing bone samples, and Dr. Janos Kirz and the group at U15 for their continued help.

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Figure 1

Contact X-ray micrographs of a thin (2000 Å) section of human skull tissue taken at two wavelengths in the neighborhood of the calcium L absorption edge. Figure (A) shows sample exposed using X-rays with 35.2 Å wavelength and (B) shows sample exposed at 35.3 Å wavelength. Regions of high photon absorbance appear dark in the prints (magnification 3470 X). The differences between the two pictures should largely be due to the calcium absorption.

X-Ray Holography Experiments on the U15 Beam Line

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For many years scientists have tried to make a new and unique microscope by recording a hologram in the X-ray region and reconstructing it with visible light. This would be expected to give the superb, instant three dimensional picture typical of the holographic method plus the special information gathering properties of the x-ray probe. Under suitable conditions the magnification of the device should naturally be the ratio of the x-ray to visible light wavelength.

Up to the present time most of the hopes for this type of microscopy have never been realized due mainly to the poor coherence properties of microfocus x-ray tubes and other available sources. With the present rapid improvement of synchrotron radiation sources, the introduction of dedicated storage rings, and the demonstration of undulators in the soft x-ray region, we now have sources of vastly greater coherent power and correspondingly improved possibilities for holographic microscopy. We are, therefore, reopening the questions associated with this technique and have begun making holograms using the U15 beam line. Our initial aim is to equal or surpass the performance (especially resolution) achieved in earlier experiments¹ and to try to demonstrate that our understanding of x-ray holography is correct. To this end we have made holograms of various objects, mostly rather simple, so that there would be some possibility of comparison with theory.

So far, we have made mainly Gabor holograms using a pinhole as the coherent source and photographic film as the recording medium. An example of a Gabor hologram and its visible light reconstruction² is shown in Fig. 1. We have also recently made other types of holograms: Fourier Transform, Lloyds mirror, and holograms of real biological objects; we are still analyzing the results. The biological holograms appear to be very good.

Our conclusions so far on this program of holography, which is the first to use a storage ring source, are as follow:

- (1) The fringe patterns we record are consistent with classical holographic theory³.

¹S. Aoki, et al, Jap. J. Appl. Phys. 13, 9, 1385 (1974)

²M.R. Howells, M. Iarocci, manuscript in preparation

³See for example, G.A. Tyler and B.J. Thompson Optica Acta 23, 685 (1976)

- (2) The resolution we have achieved ($\sim 1\mu\text{m}$ in the best case) is somewhat better than the best recorded previously¹ with x-ray holography.
- (3) The limit of resolution of our present method (Gabor holograms with photographic film and reconstruction with visible light) is about $.2 - .4\mu\text{m}$ and should soon be reached. The next step will be to use either resist plus digital reconstruction or Fourier Transform holography.
- (4) The exposure times and total fluences used in these experiments are consistent with our calculations⁴. We therefore believe that our calculations of the performance expected from an undulator experiment are realistic, namely $300\text{\AA}$ resolution at $300\mu\text{m}$ working distance in Gabor geometry with a one hour exposure.

⁴M.R. Howells in X-ray Microscopy, eds. G. Schmahl and D. Rudolf, Springer Series in Optical Sciences Vol. 43, Springer Verlag, Berlin, 1984.

Figure 1

Figure 2

Hologram (Figure 1) and reconstruction (Figure 2) of amosite asbestos fibre of width $0.5 - 2.0 \mu\text{m}$. Hologram parameters: recording wavelength $31\text{\AA}$, working distance 29mm , medium Agfa 8E56HD, time one hour; Reconstruction: wavelength $4416\text{\AA}$, working distance 0.9mm , holographic magnification 1.75, photographic magnification for 35mm frame 100.

Scanning Soft X-Ray Microscopy on the U15 Beam Line

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Soft x-rays are well suited to the imaging of biological materials. We have developed the instrumentation for scanning microscopy and applied the apparatus to the study of a variety of specimens.

The basic optical element in the microscope is a Fresnel zoneplate, fabricated for us at IBM by D. Kern and his group using electron beam lithography techniques (1). This zoneplate is used to focus the x-ray beam to a $0.2\mu\text{m}$ spot. The specimen is mechanically scanned past this spot, while the x-rays transmitted through it are detected by a flow proportional counter. The output from the counter is used to form the image, a map of the specimen absorptivity. Figure 1 is a schematic diagram of the apparatus.

Fig. 1. Schematic diagram of the scanning microscope (not to scale).

Soft x-rays in the 31 Å - 36 Å range easily penetrate a few millimeters of air as well as the water present in biological specimens. The organic matter in the specimens is more opaque to these photons, however, providing a contrast mechanism for imaging unstained materials. Our apparatus is designed to perform with the specimen in an atmospheric environment.

* Work supported in part by the National Science Foundation.

The microscope is built to operate as a user oriented facility for biologists and biomedical investigators. So far we have worked with the following scientists:

- Professor James Hamos, Neurobiology, SUNY, Stony Brook, imaging of neural tissue from the visual pathway of the cat.
- Professor Ed Lattman, Biophysics, Johns Hopkins Medical School, imaging of human chromosomes.
- Professor Jerry Pine, Physics, California Institute of Technology, imaging of neuron cultures.

Another application of the instrument is in elemental mapping. Comparison of two images, taken above and below the absorption edge of the element to be mapped, provides the information for quantitative microanalysis. As a first example, to demonstrate the use of the technique, we determined the distribution of calcium in sections of human bone. This work, carried out in collaboration with Dr. W. Thomlinson of the NSLS and Dr. G. Schidlowsky of the Brookhaven Medical Department has demonstrated that the instrument is capable of mapping at a resolution of 0.2 μm . Figure 2 illustrates the process, and the kind of image that results.

Fig. 2. X-ray images of a 0.2 μm thick section of human skull tissue.

- A. Image at 35.5 $\text{\AA}$ where calcium is highly absorptive. Stronger absorption is indicated by darker shades.
- B. Same specimen imaged at 35.8 $\text{\AA}$.
- A-B. Calcium map formed by difference of first two images. Higher concentration is mapped to lighter shades.

Gas Phase Spectroscopy in the Soft X-ray Region on the U15 Beamline

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The U15 beamline operates with a toroidal grating monochromator. It delivers beam in the 300eV -1200eV range, with a typical bandwidth of 1/300. The experimental station is isolated from the storage ring by a 1500 A thick aluminum contamination barrier. These characteristics make it attractive to use the beamline for spectroscopy near the nitrogen and oxygen absorption edges, especially for specimens which are either gaseous or are incompatible with ultrahigh vacuum systems for other reasons.

We have developed the hardware and the software to collect near edge and EXAFS spectra of gases in three ways:

- 1/ transmission
- 2/ ion yield
- 3/ scintillation

During the development of the system we have collected data on a variety of materials, such as oxygen, carbon dioxide, water vapor, and ethyl alcohol. We have studied the "thickness effect" (1), and the relationship between the three types of spectra obtained. The spectra obtained on carbon dioxide are shown on the Figure. The structure near the oxygen edge is in qualitative agreement with results obtained by other groups (2). Structure at higher energies is suggestive of EXAFS. The analysis is in progress, and a report on the data collection methods is in preparation.

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Figure 1. Carbon dioxide spectra in the 500 eV - 1000 eV range. The three curves correspond to ion yield (top), gas scintillation (middle), and absorption (bottom).

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