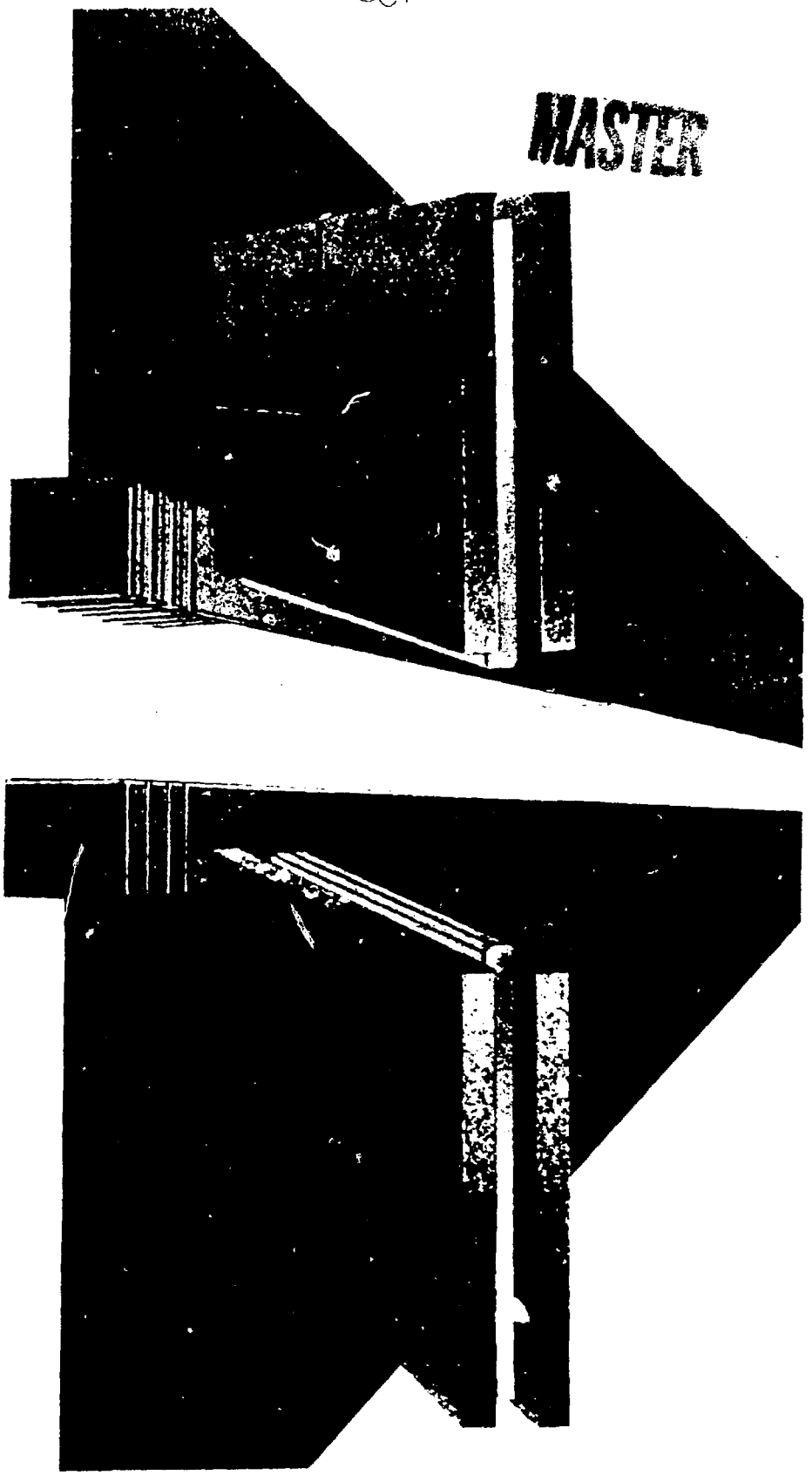
CONF-851255--3

DE86 015172

CONF-851255--3

MASTER

Report of the Workshop on the Scientific Case of a 6-GeV Synchrotron Source



December 9–11, 1985

U.S. Department of Energy
Office of Basic Energy Sciences
Division of Materials Sciences
Washington, D.C. 20545

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

REPORT OF THE WORKSHOP

ON THE SCIENTIFIC CASE FOR A

6 GeV SYNCHROTRON SOURCE

Argonne National Laboratory
Argonne, Illinois

9-11 December 1985

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

CONTENTS

Page

Introduction.....ii

I. Scattering

Macromolecular Crystallography.....I-1
Surface Structures.....-23
Wide Angle X-Ray Scattering.....-28
High Pressure Studies.....-35
Energy Dispersive Diffraction.....-41
Diffuse Scattering.....-46
Dynamical Diffraction.....-50
Topography.....-54
Small Angle Scattering.....-58
X-ray Inelastic Scattering.....-70
Magnetic X-ray Scattering.....-77

II. Spectroscopy

X-Ray Absorption Techniques.....II-1
Soft X-Rays.....-6
X-ray Microprobe Characterization of Materials.....-18
Proposal for a 4.1 KeV Submicron Microprobe.....-29

III. Other Matters of Interest

Time-Resolved Phenomena.....III-1
Angiography.....-3
Detectors.....-8
Atomic Physics.....-18
Data Collection and Computational Requirements.....-22

APPENDIX A - Workshop Agenda.....A-1
APPENDIX B - List of Attendees.....B-1

X-RAY MICROPROBE CHARACTERIZATION OF MATERIALS: THE CASE FOR UNDULATORS ON ADVANCED STORAGE RINGS

C.J. Sparks, Oak Ridge National Laboratory
G.E. Ice, Oak Ridge National Laboratory

ABSTRACT

The unique properties of X-rays offer many advantages over electrons and other charged particles for the microcharacterization of materials. X-rays are more efficient in exciting characteristic X-ray fluorescence and produce higher fluorescent signals to backgrounds than obtained with electrons. Detectable limits for X-rays are a few parts per billion and are 10^{-3} to 10^{-5} less than obtained with electrons. Energy deposition in the sample by X-rays is 10^{-3} to 10^{-4} less than for electrons for the same detectable concentration. High-brightness storage rings, especially in the 6 GeV class with undulators, will be approximately 10^{3} brighter in the X-ray energy range from 5 keV to 35 keV than existing storage rings and provide for X-ray microprobes that are as bright as the most advanced electron probes. Such X-ray microprobes will produce unprecedented low levels of detection in diffraction, EXAFS, Auger, and photoelectron spectoscopies for both chemical characterization and elemental identificaiton. These major improvements in microcharacterization capabilities will have wide-ranging ramifications not only in materials science but also in physics, chemistry, geochemistry, biology, and medicine.

I. INTRODUCTION

Efforts to obtain micro-diffraction and micro-elemental analysis to understand the properties of matter have been made since the early part of this century when the first X-ray probes were constructed. Conferences have been held on the design and application of X-ray microprobe sources.[1] In the early 1950s, there was an upsurge in interest in microanalytical methods. Microprobes with electrons to bombard the sample quickly became the instrument of choice for microcharacterization. Electrons could easily be focused to spot sizes less than 1μm-diam with enormous intensities compared to X-ray sources. Though X-ray excitations give a much better signal to background, their generation required electron bombardment of a metal target with X-rays emitted into 4π srad which then had to be gathered and focused to a small spot with inefficient X-ray optics. With the commercial availability of high-intensity and high-resolution electron microprobes, the unique properties of photons could not overcome the lack of intenstiy from their weak sources. Interest in X-rays as an excitation source for microprobe analysis faded, leaving electrons as the dominant microprobe source. It is a conservative estimate that 1200 to 2500 electron probes currently are being used for microcharacterization of matter in the United States. This represents an investment of $1 billion or more in instrumentation alone. The wide usage of analytical microprobes is well documented in the several yearly conferences and journals of the electron microscopy and microprobe societies and attests to the great emphasis being placed by the scientific community on the need for microstructural characterization of matter.

With the advent of electron storage rings, an intense source of X-rays has become available. The energy spectrum in the hard X-ray region is 10^4 to 10^5 times more brilliant than our conventional X-ray sources (2 kw to 60 kw

dissipated by electrons impinging on metal targets). In fact, with magnetic devices especially suited for extracting the radiation from proposed new high-brightness storage rings, the brightness in units of photons or particles s^{-1} mm^{-2} $mrad^{-2}$ is 10^{19} and approaches that for the most advanced electron probes having field-emission electron guns.[2] To achieve this brightness for the energy range from 2 keV to 35 keV requires undulators on low-emittance electron storage rings in the 6 GeV energy range. This energy range covers the electron energy levels of the K- and/or L-shells for all the atoms and is most useful for fluorescent and diffraction analysis. Present X-ray storage rings (NSLS at Brookhaven; SPEAR at SSRL, Stanford; CESAR at CHESS, Cornell) are about 10^{-3} to 10^{-4} less bright in this energy range.

The improved brightness of a 6 GeV ring with undulators offers major advantages over present storage rings. Scientists will be able to study the chemical composition, geometrical arrangements of the atoms, and electronic structure at unprecedented low levels of concentration. The chemical identity of the elemental composition of matter is a prerequisite to their synthesis, and knowledge of the geometrical arrangement and chemical bonding of the atoms is fundamental to understanding the basic physical and chemical behavior of materials. Much of our progress in the design of materials has come by trial and error. But the science of materials has advanced rapidly in recent years and microcharacterization techniques have made a major contribution providing both chemical identity and geometrical information about the atoms. Yet modern technology is making increasing demands on materials for better performance in terms of their electrical characteristics and under the most adverse environments of high temperature, corrosive atmosphere, and intense radiation fields. More stringent requirements are being placed on the control of manufacturing methods including tightening restrictions on impurity levels,

on structure and compositional variations, on presence of minor phases, and on controlling interfaces.[3-5] The behavior of grain boundaries and other interfaces can determine if a material is ductile and has toughness or is brittle and unreliable for use in structural applications. Minor amounts of second phases can improve the strength of materials or make them unfit for service. Segregation of trace elements to interfaces and second phases can have dramatic effects on the properties of materials. Synergistic effects among trace elements is observed but poorly understood. Concentrations are often below present detectable limits for non-destructive analysis and improved microcharacterization methods are needed. The construction of X-ray microprobes on new high-brightness storage rings will produce unique microcharacterization capabilities unmatched by any other method.

As electron microprobes have clearly dominated the field of microcharacterization, the merits of the use of X-rays for excitation of the sample will be compared to electrons. There are many possible applications where microcharacterization is important to advancing our understanding of materials properties. For more extensive information, the reader should refer to the electron microscopy and microprobe literature.

II. DETECTION LIMITS WITH X-RAYS VERSUS ELECTRONS

A standard definition of the minimum detectable mass fraction [6] based on Poisson counting statistics for 95% confidence in detection is

$$\text{Minimum Detectable Mass Fraction (MDMF)} = 3.29\ C_z(N_b)^{1/2}/N_s, \quad (1)$$

where C_z is the mass fraction of element Z, N_b the background counts, and N_s the counts in the signal. To evaluate Eq. (1), we need to know the fluorescent cross sections to calculate the number of events in the signal and

to evaluate the background. An extensive literature review on this subject provides the information for the evaluation.[7] The number of characteristic fluorescent events is typically 10 to 200 times larger for X-ray excitation than for the same number of electrons. The fluorescent signal to background is approximately 10^4 times larger for X-ray excitation than for electron excitation. This extremely favorable property of X-rays derives from the fact that about 90% or more of the incident X-ray energy is dissipated by ionization of the inner shells. In contrast, only 0.1% of the energy dissipated by electrons gives rise to the fluorescent radiation of interest. Much of their energy is consumed by interactions with the least-bound outer-shell electrons. The deceleration of the incident electrons in the target produces Bremsstrahlung radiation which is responsible for most of the background beneath the fluorescent signals of interest.

We find that 10^{-3} fewer X-rays than electrons are required for the same MDMF. In terms of energy deposited, electron energies from 20 keV to 100 keV usually exceed by three to ten times the ionization energy of the bound electron. X-ray energies can be chosen to lie just above the ionization energy (2 keV to 33 keV). As 10^3 more electrons with energies from three to ten times those of X-rays are required for the same MDMF, the energy deposited by electrons is 3×10^3 to 10^4 times that deposited by X-rays in thick targets. For thin targets most of the incident electron energy is transmitted, but even less incident X-ray energy is absorbed. In air-dried blood cells and 8 μm-thick tissue sections [8] exposed to synchrotron radiation and charged particles, X-ray fluences 10^2 to 10^3 times greater were required to produce similar damage. X-radiation damage to the samples may be orders of magnitude less than the comparison made on the basis of energy deposition alone. Thus with X-ray excitation we have the important choice of being able

to either lower the detectable limits for the same fluences or to reduce the radiation damage and heat deposited in the sample for the same MDMF. Since heating and radiation damage of organic samples is of primary concern in modern electron probes, X-rays offer major improvements.

III. X-RAY INTENSITIES FROM UNDULATORS ON HIGH-BRIGHTNESS STORAGE RINGS

With the proposed X-ray intensities from undulators on high-brightness storage rings (see other sections of this document and SSRL Report 83/01 and NSLS Report, Planned Evolution of NSLS, October 1983 and ANL-85-69, October 1985), fluxes are predicted to be on the order of 10^{15} X-rays s^{-1} in an energy bandwidth, $\Delta E/E$, of 0.1%. Projections of an electron source size in the storage ring of $2\sigma_x$ = 0.8 mm and $2\sigma_y$ = 0.14 mm and divergences of 0.01 mrad in both the horizontal and vertical planes for undulators produce a brilliance approaching 10^{20} X-rays s^{-1} mm^{-2} $mrad^{-2}$ in a 2σ bandwidth of the undulator. Considerations of the X-ray-focusing optics[7,9,10] have shown that demagnifications of 100:1 are feasible with about 25% reflection efficiencies. Because of the small divergence of undulator radiation, X-ray optics can intercept the entire emittance and both focus and monochromate with high efficiency. This small divergence lessens the demands on the optics since only a small area of the optic is illuminated. We base our arguments for the intensities obtainable for an X-ray microprobe on a demagnification of 100:1. A demagnification of 100:1 results in a probe size of about 2 x 8 μm^2, and further reduction is achieved by pinholes in heavy metal foils. The predicted intensities are given in Table I. Comparisons are made with those from the brightest storage ring now in operation and the most intense electron microprobe sources. A gain of 1.4 x 10^4 in intensity per eV is obtained over present low-emittance rings. In addition, undulators in comparison to superconducting wigglers peak

the energy in narrow bandwidths reducing the heat load on X-ray optics. At 10 eV energy bandwidths, the brilliance of undulators will match that available from the most advanced electron probes. Though undulators peak the intensity at harmonic energy intervals, energies ranging from 2 keV to 40 keV are available in either the first or second harmonic. When only discrete X-ray energies are selectable from undulators, then 2, 4, 10, 18, and 35 keV or similar energies are acceptable for most microprobes fluorescent and diffraction analysis.[7] For fluorescent excitation, energy spreads of $\Delta E/E$ = 1 are acceptable.[7] For diffraction analysis of the compounds present, a $\Delta E/E = 10^{-2}$ to 10^{-3} is required. For microprobe EXAFS analysis and photoelectron spectroscopy, $\Delta E/E$ should be 10^{-4} to 10^{-5}. These energy resolutions can be achieved with presently available nearly perfect crystals, and the microprobe energy resolution tailored to meet the experimental needs of a variety of applications.

IV. SPATIAL RESOLUTION

Inherently, X-ray excitation for microprobe analysis offers the highest spatial resolution in thick samples of any radiation because the low-scattering cross sections of X-rays limit the lateral spreading of the probe. Though electron field-emission sources are much smaller (approaching 10 Å-diam) and are focused to diameters of atomic dimension, lateral spreading of the electrons in matter produce interaction regions of about 1 μm-diam in thick samples.[11] Electron-probe analysis of ferrous materials having specimen thicknesses of 1000 Å to 2000 Å produce an interaction region of approximately 500 Å-diam even though the incident probe diameter is much less. Diffraction limits may keep the useful X-ray probe diameter to 500 Å and greater.[10] An X-ray microprobe with a beam diameter of 500 Å to 1 μm

would compete favorably with the spatial resolution of electron microprobes in a great majority of the samples of interest. For extremely thin particles and films (≤1000 Å), the electron microprobe has spacial resolutions ranging from a few angstrom to a few hundred angstroms. Although 500 Å-diam appears feasible for an X-ray microprobe, it is not a fundamental limit. In a 500 Å-diam probe, the diffraction-limited divergence angle is 5 mrad for 12 keV X-rays but only 0.2 mrad for 100 keV electrons. This places a limit of 10 μm to the depth of beam penetration in the sample before divergence of the X-ray beam in the sample exceeds the intended probe size.

TABLE I. Comparison of X-ray Microprobe Intensities from 6 GeV Ring

	14 keV X-rays 2.5 GeV, 500 mA wiggler, NSLS	14 keV X-rays 6GeV, 200 mA undulator	100 keV e^- Electron microprobe field emission[a]
Brilliance Photons or Electrons s^{-1} mm^2 $mrad^2$ 0.1% BW	10^{16}[b]	10^{19}[b,c]	3×10^{19}
Intensity P or e^-/Area sec	$\frac{5 \times 10^{12}}{10\ \mu m^2\ s\ 280\ eV}$	$\frac{2 \times 10^{15}}{10\ \mu m^2\ s\ 10\ eV}$	
	$\frac{5 \times 10^{11}}{\mu m^2\ s\ 280\ eV}$	$\frac{1 \times 10^{14}}{\mu m^2\ s\ 10\ eV}$	$\frac{6 \times 10^{13}}{\mu m^2\ s\ eV}$[e]
	$\frac{1 \times 10^{9}}{500\ A^2\ s\ 280\ eV}$	$\frac{3 \times 10^{11}}{500\ A^2\ s\ 10\ eV}$	$\frac{6 \times 10^{11}}{500\ A\ s\ eV}$
			$\frac{6 \times 10^{9}}{30\ A^2\ s\ eV}$
			$\frac{10^{7}}{4\ A^2 s\ eV}$

[a] Zaluzec, N.J., 1979; "Quantitative X-ray Microanalysis: Instrumental Considerations and Applications to Materials Science," Chapter 4, pp. 121-167 in Introduction to Analytical Electron Microscopy, J.J. Hern, J.I. Goldstein, and D.C. Joy, eds. New York: Plenum Press.

[b] National Synchrotron Light Source, Planned Evolution of NSLS, October 1983.

[c] Stanford Synchrotron Radiation Laboratory, SSRL Report 83/01.

[d] Argonne National Laboratory, An Overview of the Characteristics of the 6 GeV Synchrotron Radiation: A Preliminary Guide for Users, ANL 85-69, Oct. 1985.

[e] LaB_6 electron source.

TABLE II. Comparison of the Characteristics of the Proposed X-ray Microprobe with Those of the Most Advanced Electron Mictoprobes for Fluorescent Chemical Analysis

Characteristics	X-rays	Electrons
Minimum detectable mass fraction s^{-1} for 1 μm-diam probe	0.01 ppm	50 ppm
Minimum detectable mass s^{-1} for 500 Å probe	250 atoms	10,000 atoms
Minimum spatial resolution (samples ≥ 1 μm thick)	~500 Å	10^3 to 10^4 Å
Minimum spatial resolution (samples 100 Å to 2000 Å thick)	~500 Å	10 to 500 Å
Number of electrons and X-rays for the same MDMF	1	10^3
Number of energy units deposited in thick targets for same MDMF	1	10^3 to 10^4
Operating atmosphere	air, gas, water, vapors	vacuum
Relative signal to background (contrast)	10^4	1
Accuracy for quantitative analysis { similar standards	~1%	~10%
Accuracy for quantitative analysis { pure element standards	~5%	>10%
Relative fluorescent cross section	10 to 200	1
Relative thick-target fluorescent yields	10 to 150	1
Charge collection on electrically insulating samples	negligible	must be coated with conducting film

REFERENCES

1. Cosslett, V.E., A. Engström, and H.H. Pattee, Jr., eds. 1957, "X-ray Microscopy and Microradiography," New York, Academic Press, Inc.

2. Zaluzec, N.J., 1979, "Quantitative X-ray Microanalysis: Instrumental Consideration and Applications to Materials Science," Chapter 4, pp. 121-167 in Introduction to Analytical Electron Microscopy, J.J. Hern, J.I. Goldstein, and D.C. Joy, eds. New York, Plenum Press.

3. Kriege, O.H. and J.Y. Marks, 1976, "Nonuniform Distribution (both Micro and Macro) of Trace Elements in High-temperature Alloys," pp. 1017-1022 in National Bureau of Standards Special Publication 422, Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis, Vol. II, P.D. LaFleur, ed. Washington, D.C.: U.S. Government Printing Office.

4. Davis, C.M., 1976, "Trace Element Analysis of Nickel and Nickel-base Alloys - A Review of Current Methods," pp. 1005-1016 in National Bureau of Standards Special Publication 422, Accuracy in Trace Analysis: Sampling, Sample Handling, Analysis, Vol. II, P.D. LaFleur, ed. Washington, D.C.: U.S. Government Printing Office.

5. Hondros, E.D. and M.P. Seah, 1977, "Segregation to Interfaces," International Metals Review 22:262-301.

6. Currie, L.A., 1968, "Limits for Qualitative Detections and Quantitative Determination," Anal. Chem. 40:586-593.

7. Sparks, C.J., Jr., 1980, "X-ray Fluorescence Microprobe for Chemical Analysis," Chapter 14, pp. 459-512 in Synchrotron Radiation Research, H. Winick and S. Doniach, eds. New York: Plenum Press.

8. Slatkin, D.N., A.L. Hanson, K.W. Jones, H.W. Kramer, and J.B. Warren 1984, "Damage to Air-Dried Human Blood Cells and Tissue Sections by Synchrotron Radiation," Brookhaven National Laboratory Report BNL-34555.

9. Howells, M.R. and J.B. Hastings, 1983, "Design Considerations for an X-ray Microprobe," Nucl. Instr. and Meth. 208:379-386.

10. Ice, G.E. and C.J. Sparks, Jr., 1984, "Focusing Optics for a Synchrotron X-radiation Microprobe," Nucl. Instr. and Meth. In press.

11. Goldstein, J.I., 1979, "Principles of Thin Film X-ray Microanalysis," Chapter 3, pp. 83-120 in Introduction to Analytical Electron Microscopy, J.J. Hern, J.I. Goldstein, and D.C. Joy, eds., New York: Plenum Press.