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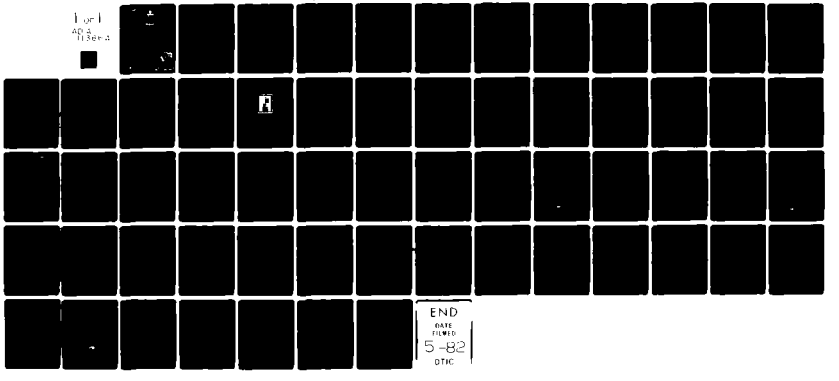

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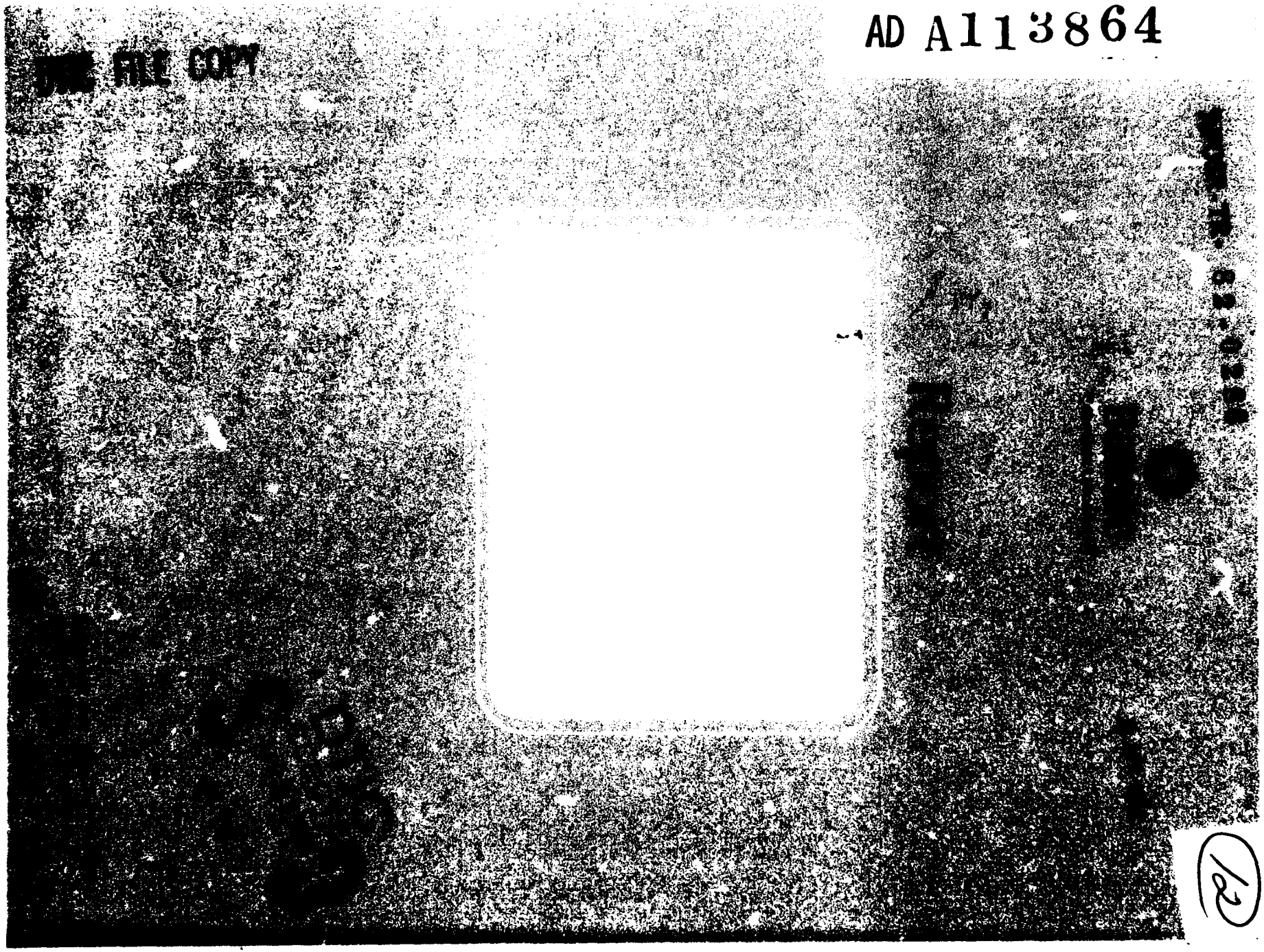

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FINAL RESEARCH REPORT

on

CHEMICAL STRUCTURE BY LASER-PRODUCED X-RAYS

to

U. S. AIR FORCE
OFFICE OF SCIENTIFIC RESEARCH

April 2, 1982

Project Team: R. E. Schwerzel, H. M. Epstein, P. J. Mallozzi, B. E. Campbell, and R. G. Jung

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505 King Avenue
Columbus, OH 43210

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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The research conducted under this grant has successfully proven the feasibility of using laser-produced x-rays to perform EXAFS experiments, and has led to the demonstration that well-resolved EXAFS spectra of light elements (such as aluminum and magnesium) can be obtained using a single multi-nanosecond pulse of laser-produced x-rays. In addition, this research has led to the development of the "flash-EXAFS" technique, in which the transient structural changes which occur upon thermal or optical excitation of a sample can be studied in

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real time (on a nanosecond time scale) by exploiting the short pulse characteristics of laser-EXAFS. It is realistic to say that an entirely new chapter in the history of structural analysis has been begun by this work, as the detailed structures of transient species can now be probed on a time scale never before possible.

PROJECT SUMMARY

The technique of Extended X-Ray Absorption Fine Structure (EXAFS) spectroscopy has become an increasingly important tool in recent years for the study of chemical structure in samples which lack long-range order, such as amorphous solids, catalysts, solutions of biologically important materials, and gases. These studies have gained impetus in recent years by virtue of the availability of synchrotron radiation, which provides a continuous and intense spectrum of the soft x-rays required for EXAFS. A synchrotron, however, is an expensive, cumbersome source of x-rays, to which scientists must travel in order to perform their experiments. A laser x-ray source, on the other hand, is relatively compact, inexpensive, and simple to operate and maintain. Furthermore, there are a variety of novel EXAFS experiments which are inherently beyond the capabilities of synchrotron radiation sources. These experiments, which require short pulse widths and intense fluxes of low-energy (<5 keV) x-rays, are ideally sited to laser-produced x-rays.

The research conducted under this grant has successfully proven the feasibility of using laser-produced x-rays to perform EXAFS experiments, and has led to the demonstration that well-resolved EXAFS spectra of light elements (such as aluminum and magnesium) can be obtained using a single multi-nanosecond pulse of laser-produced x-rays. In addition, this research has led to the development of the "flash-EXAFS" technique, in which the transient structural changes which occur upon thermal or optical excitation of a sample can be studied in real time (on a nanosecond time scale) by exploiting the short pulse characteristics of laser-EXAFS. It is realistic to say that an entirely new chapter in the history of structural analysis has been begun by this work, as the detailed structures of transient species can now be probed on a time scale never before possible.

Much research remains to be done, as is true of any new techniques. A wide range of flash-EXAFS experiments can be conceived which are

of utmost scientific importance, and which may have ultimate practical value to the Air Force, as well. Among these are studies of the transient structural changes which occur in photo-excited organic and organometallic compounds (important with regard to such systems as photosynthesis, dye degradation, and camoflage paint deterioration) and those which occur in flash-melted metals and alloys (important with regard to the study of laser effects on structural materials in missiles and aircraft). In addition, there remains a need for continued refinement of the laser-EXAFS technique itself, particularly with respect to the upgrading of the laser and detector systems, and further improvements in the data-analysis software. It is our hope that this research can be carried out in the not-too-distant future, so as to ensure continued improvement in the utility of this most promising new technique.

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INTRODUCTION

The problem of determining the identities and the exact spatial arrangement of the atoms surrounding any particular atom in a molecule is extremely important, and is fundamental to understanding the chemical structure of any type of liquid, gas, or solid. In the case of materials with long-range order, such as perfect crystals, this information can often by obtained with X-ray or particle beam diffraction techniques. The diffraction techniques rely on the fact that, in a perfect lattice, all of the atoms will reside at fixed, periodic distances from any given atom, and that this periodicity will be retained regardless of how far one moves within the lattice from the atom in question.

For materials without such long-range order, the diffraction techniques are far less useful; one can determine local configurations in this way only for relatively simple molecules composed of a single element. Considerable insight on more complicated molecules can be gained from optical spectroscopy and magnetic resonance techniques. However,

these techniques suffer from the drawback of providing only indirect evidence, from which the structural parameters of interest for any given molecule must be calculated or inferred.

A powerful new structural analysis technique, involving the use of "soft" X-rays (with energies of roughly 0.1 to 20 KeV), has recently been developed. This technique, known as EXAFS (Extended X-ray Absorption Fine-Structure) Spectroscopy, can provide direct structural information on complex materials which lack long-range order, and promises to revolutionize the analysis of chemical structure.

The essential features of EXAFS spectroscopy are depicted schematically in Figure 1. In EXAFS, the local configuration in the

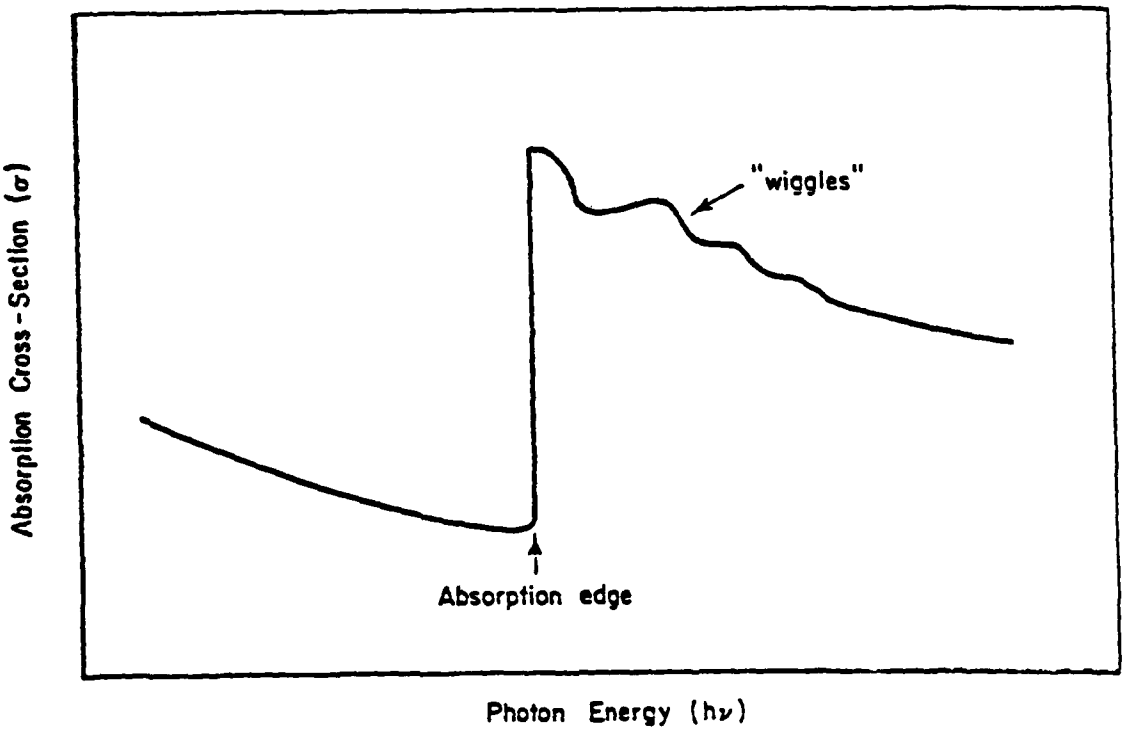

FIGURE 1. SCHEMATIC ILLUSTRATION OF AN EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) SPECTRUM

vicinity of a given atom embedded in a solid, liquid, or gas molecule is indicated by the tiny "wiggles" on the X-ray absorption edge of that atom. Because this fine structure is caused by the scattering of photoelectrons from neighboring atoms, the mathematical analysis of the fine structure provides direct information about the positions of these atoms. EXAFS is thus capable of revealing the actual distances from the x-ray absorbing atom to its nearest neighbors and can, in addition, provide information about the chemical identities of its nearest neighbors.

Chemical structure research with EXAFS has been limited in the past by the lack of suitably intense sources of soft X-rays. This deficiency is now being remedied to some extent by the increasing availability of synchrontron radiation, which has recently been harnessed in a number of X-ray test facilities throughout the world.[1] However, synchrotron radiation is unlikely to be fully satisfactory as a X-ray source due to the enormous size and expense of the required facilities, and the corresponding need for most researchers to perform their experiments at remote locations.

The best hope for providing a relatively small, inexpensive, and transportable X-ray source for EXAFS research lies in the further development of laser-produced X-rays. High-powered laser pulses can provide high intensity X-rays with continuously tuneable wavelengths, as required for EXAFS. The additional feature that the x-rays are produced in a single, intense, ultrashort burst that can be synchronized readily with optical or electrical excitation of the sample provides a new capability: the ability to easily perform fast-kinetic experiments on short-lived excited electronic states of molecules, reactive chemical intermediates, and transient phase changes in excited materials.

The research described in this report has been conducted because of Battelle's belief that an adequate, and perhaps nearly ideal, source of soft X-rays is now available at Battelle's Columbus Laboratories. Laser pulses from neodymium-doped-glass lasers have been converted into X-rays at Battelle with efficiencies ranging from 10 to 30 percent,[2,3]

and the laser-generated X-rays have been used in the past to produce soft X-ray radiographs.(3) The technique used for generating the X-rays involves vaporizing and ionizing material at the surface of a solid target with an approximately 1-joule, approximately 10-nanosecond prepulse, and laser heating the resulting low-temperature plasma to the multikilovolt regime with a 10 to 100-joule, approximately 1-nanosecond main pulse via the inverse bremsstrahlung absorption process. The prepulse strikes a 100- to 200-micron diameter focal spot at an incident intensity of about 10^{11} w/cm^2, whereas the main pulse strikes it at about 10^{14} w/cm^2. The X-rays are produced int the plasma by bremsstrahlung, recombination radiation, and line radiation. More than 20 joules of X-rays, with energies between .3 and 1.5 keV, have been produced in this way in a single beam, multinanosecond laser shot.(3)

Because the laser system required for this purpose is far smaller and less expensive to set up and operate than a synchrotron X-ray source, Battelle feels that the successful demonstration of EXAFS measurements using laser-produced X-rays, as described in this report, could revolutionize the study of molecular structure by making the advanced X-ray techniques that are currently employed only at synchrotron facilities accessible to a large number of organizations which might otherwise be precluded from the use of the limited number of synchrotron facilities available. It also allows the performance of novel EXAFS experiments which are inherently beyond the capabilities of synchrotron radiation sources or rotating-anode x-ray generators.

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Program Objectives

The overall objective of this research program has been to critically evaluate the feasibility of using laser-produced X-rays for the elucidation of chemical structures by means of EXAFS spectroscopy. In performing this research, emphasis has been placed on the following tasks:

- Implementation and Improvement of Laser-EXAFS Capabilities - including modifications to the X-ray sample handling area and data acquisition system at Battelle's laser facility, and the acquisition of the necessary computer software for the deconvolution and interpretation of EXAFS data. The objective of this task have been to acquire state-of-the-art capabilities for performing and interpreting EXAFS experiments at Battelle.

- System Verification and Optimization - with the objective of demonstrating that Battelle's laser facility is capable of reproducing published EXAFS spectra on several well-characterized samples, including at least one sample which has been previously studied using synchrotron radiation.

- Scientific Utilization of the Modified Laser Facility - with the objective of utilizing the EXAFS capabilities developed

in the course of the proposed program for the study of samples of current scientific interest, such as structural kinetic studies of optically excited molecules and reactive intermediates, the analysis of novel alloys and catalysts, and studies of the behavior of rapidly solidifying materials.

The results which have been obtained during the course of the program are described in detail in the follow manuscripts.

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LASER-PRODUCED PLASMAS AS AN ALTERNATIVE X-RAY SOURCE FOR SYNCHROTRON RADIATION RESEARCH AND FOR MICRORADIOGRAPHY

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505 King Avenue, Columbus, Ohio 43201

ABSTRACT

The radiation from plasmas produced by the interaction of a pulsed laser and a solid target can be made to fall in the soft x-ray regime. The x-rays can serve as an alternative to the increasingly important synchrotron radiation facilities for a variety of techniques such as Extended X-ray Absorption Fine-Structure Spectroscopy and X-ray Lithography. In addition, the x-rays are of special interest for general microradiography of thin samples.

I. An Alternative X-Ray Source For Synchrotron Radiation Research

In recent years, synchrotron radiation has evolved from a laboratory curiosity to the foundation of a technique widely exploited by physicists, chemists, and biologists. (1) Among the research areas explored with synchrotron radiation are the investigation of chemical structure by means of EXAFS (Extended X-ray Absorption Fine Structure) and ESCA (Electron Spectroscopy for Chemical Analysis) techniques, and the replication of sub-micrometer linewidth patterns by an x-ray lithographic technique. (1) The purpose of this paper is to discuss how these and other applications of synchrotron radiation might be performed with a laser-plasma x-ray source. Because the laser system is far smaller and less expensive than a synchrotron, it is felt that laser-produced x-rays could make the x-ray techniques that are currently employed only at synchrotron facilities accessible to a large number of organizations which might otherwise be precluded from the use of the limited number of

synchrotron facilities available. In addition, laser-produced x-rays would allow the performance of novel x-ray experiments which are inherently beyond the capabilities of synchrotron radiation sources, particularly those which make use of the short, intense pulse structure of laser-produced x-rays for fast-kinetic studies.

X-Ray Lithography. It is well established that x-ray lithography is an effective means for replicating sub-micrometer linewidth patterns. (2) Besides replicating test patterns, the technique has been used to fabricate surface acoustic wave devices, bubble domain devices, pn diodes, bipolar transitors, and MOS transitors. The basic concept of x-ray lithography is to use the smaller wavelength of an x-ray source instead of the long wavelength of an ultraviolet source. This essentially eliminates the diffraction limitation of the ultraviolet source. With this eliminated, x-ray lithography is capable of producing line patterns with an "error" or "replication accuracy", δ, of 1000 Å. Patterns this small are near the theoretical limit for microcircuit fabrication.

Many difficult problems must be solved before small geometry circuit manufacture by x-ray lithography becomes a commercial reality. The two main obstacles appear to be (a) alignment of the mask with respect to the wafer, and (b) development of an adequate x-ray source.

Recent work by Austin, Smith, and Flanders suggests that the problem of mask alignment is well on its way to solution. (3) These authors have developed a new laser interferometric technique that in principle should be capable of aligning masks relative to wafers with a superposition precision of 100 Å. The technique is compatible with x-ray lithography, and is adaptable to automation.

It should be noted that the second problem, development of an adequate x-ray source, is also solvable, primarily because of work performed at Battelle. (4,5) Experiments have been performed at Battelle in which a COP photoresist was exposed a distance of 20 centimeters from a laser plasma x-ray source. (5) The basic experimental configuration is shown in Figure 1. The x-rays passed through a mask consisting of a relatively transparent layer of silicon, 3 or 4 microns thick, on which a relatively opaque layer of gold, shaped in a circuit pattern, was arrayed. The mask to wafer separation was 30 microns. Four laser shots were required to expose the photoresist at 20 centimeters. At 10 centimeters, a single laser shot sufficed. Pattern replication was perfectly faithful within the limits of optical microscopy, as shown in Figure 2.

The technique used for generating the x-rays involves vaporizing and ionizing material at the surface of a solid target with an approximately 1-joule, approximately 10-nanosecond prepulse, and laser

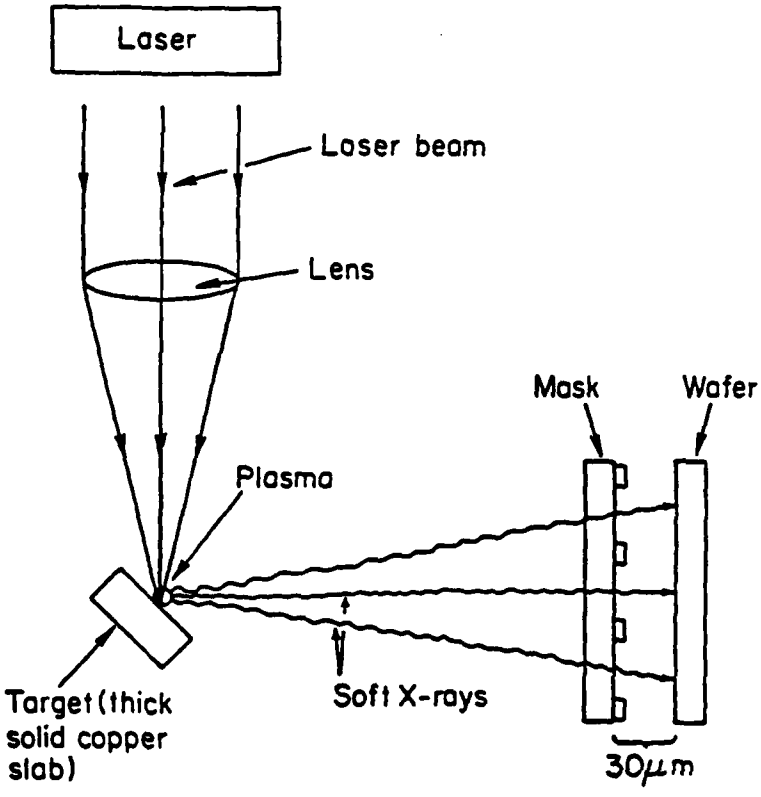

FIGURE 1. BASIC EXPERIMENTAL CONFIGURATION USED FOR X-RAY LITHOGRAPHY APPLICATION. LASER BEAM IS FOCUSED BY A LENS ONTO A SOLID COPPER TARGET AND PRODUCES A PLASMA. X-RAYS GENERATED BY THE PLASMA PASS THROUGH A MASK AND EXPOSE A PHOTORESIST-COATED WAFER.

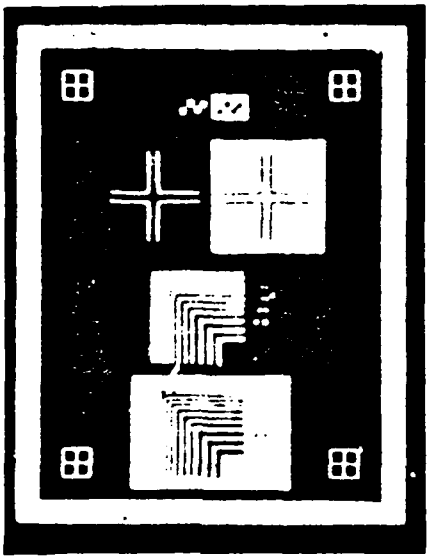

FIGURE 2. TYPICAL LITHOGRAPHIC PATTERN MADE WITH LASER-PRODUCED X-RAYS.

heating the resulting low-temperature plasma to the multi-kilovolt regime with a 10 to 100-joule, approximately 1 nanosecond main pulse via the inverse bremsstrahlung absorption process. The prepulse strikes a 100- to 200-micron diameter focal spot at an incident intensity of about 10^{11} W/cm^2, whereas the main pulse strikes it at about 10^{14} W/cm^2. The x-rays are produced in the plasma by bremsstrahlung, recombination radiation, and line radiation. More than 20 joules of x-rays, with energies between 0.3 and 1.5 keV, have been produced in this way in a single beam, multinanosecond laser shot.(4)

Chemical Structure. Two powerful new structural analysis techniques, both involving the use of "soft" x-rays (with energies of roughly 0.1 to 10 keV), have recently been developed. Because these techniques can provide direct structural information on complex materials which lack long-range order, they promise to revolutionize the analysis of chemical structure.

One of these techniques is known as EXAFS. The essential features of EXAFS spectroscopy are schematically depicted in Figure 3. In EXAFS, the local configuration in the vicinity of a given atom embedded in a solid, liquid, or gas molecule is indicated by the tiny "wiggles" on the x-ray absorption curve of that atom. Because this fine structure is caused by the scattering of photo-electrons from the neighboring atoms, the mathematical analysis of the fine structure provides direct information about the positions of these atoms. The other technique, which is schematically depicted in Figure 4, is a refinement of ESCA. In the ESCA approach, a highly monochromatic beam of x-rays strikes the surface of the sample, and the energy spectrum of the photoelectrons ejected from the surface is measured. The configuration in the vicinity of a given atom is indicated by the energy shifts in the photoelectron spectrum relative to the energy of an electron ejected from the same type of atom in free space.

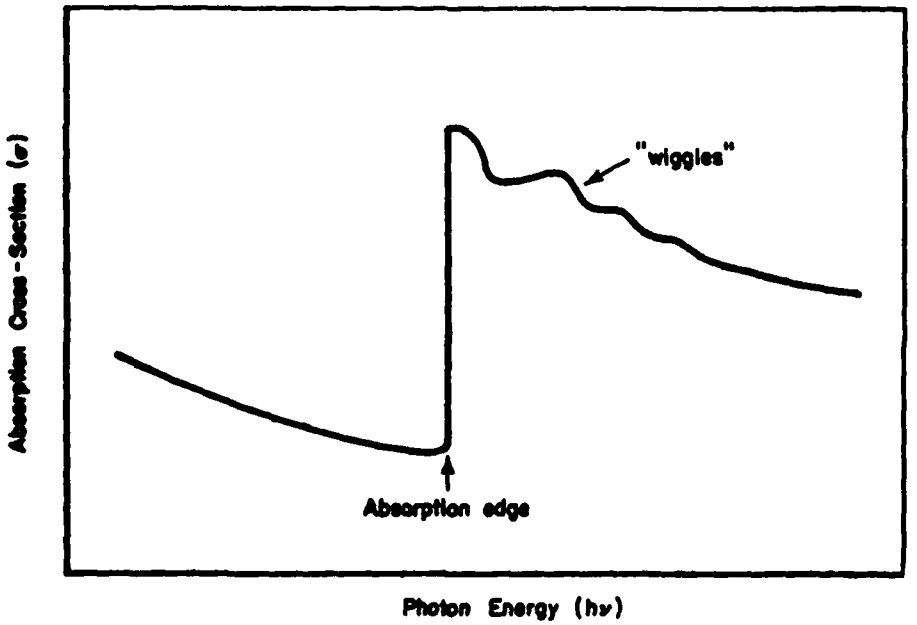

FIGURE 3. SCHEMATIC ILLUSTRATION OF AN EXTENDED X-RAY ABSORPTION FINE STRUCTURE (EXAFS) SPECTRUM.

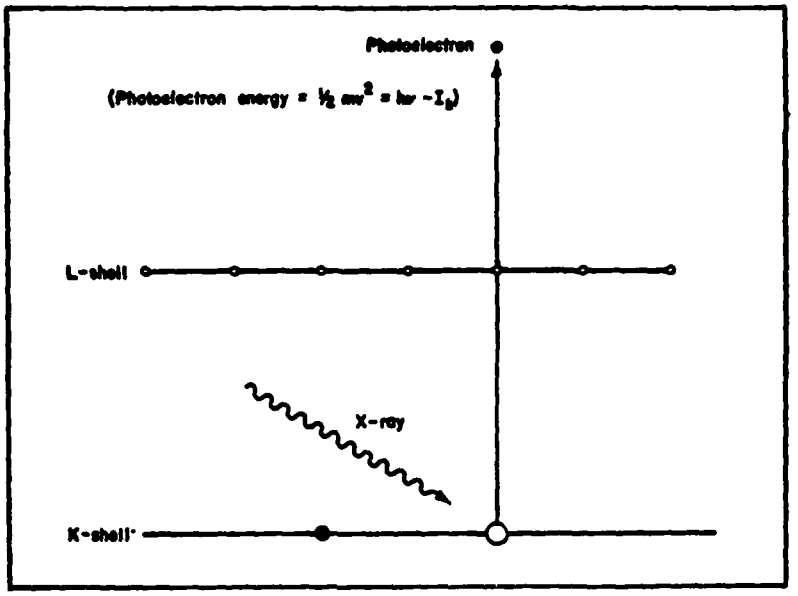

FIGURE 4. SCHEMATIC ILLUSTRATION OF ELECTRON SPECTROSCOPY FOR CHEMICAL ANALYSIS (ESCA).

It would be useful to compare laser x-rays with synchrotron x-rays, particularly from the point of view of performing EXAFS and ESCA experiments.

Synchrotron facilities harnessed for x-ray research typically deliver a time-average, broad-band x-ray power of several watts in a well collimated 1 mm diameter beam. They can therefore deliver 10 joules of more-or-less CW x-rays to a sample in a time interval of several seconds. This is about the same number of joules that are radiated into 2π steradians in a few nanoseconds by an approximately 100 μm diameter laser plasma x-ray source. It should be noted that the laser-produced x-rays are concentrated in a much narrower spectral band than the synchrotron x-rays.

A major treatise could be written concerning the relative utility of laser-produced x-rays and synchrotron x-rays for various research purposes. In general, the two sources are rather different, and their relative utility depends on the particular application one has in mind. There is little question, however, that the laser x-ray source can play an absolutely unique role in fast time-resolved EXAFS studies. This is most easily seen on contemplation of laser-produced

x-ray spectra taken with a bent crystal spectrometer. These spectra can be taken with a single multinanosecond x-ray exposure and the optical density of the film used in these experiments indicates that the number of photons in the intense spectral lines is in excess of 10^8 per eV. This suggests that a signal-to-noise ratio of $\sqrt{10^8} = 10^4$ may be ultimately realized in fast kinetic EXAFS studies. Resolution such as this on a nanosecond time scale is inherently beyond the capability of synchrotron beams.

II. Microradiography With a Laser Plasma X-Ray Source

X-rays emitted from laser generated plasmas are a unique source for microradiographic analysis of thin samples. Among their advantages over conventional sources are: (1) typical pulse widths of nanoseconds or less can stop almost any motion; (2) strong emission in the 100's of eV to the few keV range provide excellent contrast; (3) emissions of 10's of joules per pulse produce flash exposures intense enough for sub-micron resolution in typical contact radiograph configurations; (4) the small x-ray source size, ~100 micrometers, reduces penmubra effects; and (5) the approximate exponential decay of the output in the range of 1 to several keV is useful in the quantitative analysis of radiographs.

A laser plasma x-ray source emits both spectral lines and bremsstrahlung radiation, (6,7,8) with a pronounced grouping of L lines in the vicinity of $h\nu \approx 1$ keV for targets in the atomic number range of ~25-30. However, samples thicker than ~10 micrometers H_2O severely attenuate the lines, and the plasma bremsstrahlung spectral shape,

$$\phi(h\nu) \propto \exp(-h\nu/KT) \quad ,$$

is dominant. ($h\nu$ is the photon energy and KT is the plasma temperature.) For specimens thicker than ~4 mm H_2O, the effective plasma temperature begins to increase because of a small component of higher energy radiation. The energy density, E_f, absorbed in a photographic emulsion after transmission through a specimen of thickness, x, and absorption cross section, α, is

$$E_f \approx c_1/2\pi r^2 \int_o^\infty S(h\nu) \exp[-\alpha x - h\nu/KT] dh\nu \quad j/cm^2 \quad ,$$

where $S(h\nu)$ is the film spectral sensitivity and r is the source-film distance. The Battelle laser can produce about 10 j of x-rays in a 2π solid angle at an equivalent temperature of ~1 keV. For a 100 j laser pulse, $c_1 = 10$.

For low atomic number material in an energy range where attenuation is dominated by the photoelectric absorption,

$$\alpha \approx c_2 \, (h\nu)^{-3}$$

Since the x-ray emission from the plasma source falls off exponentially with increasing energy while the x-ray transmissivity of the specimen falls off rapidly with decreasing energy, the resultant x-rays absorbed in the film, R(hν), form a very narrow energy band as seen in Figure 5. (If an absorption edge lies within the R(hν) peak a differential absorption analysis would be applicable instead of the technique described here.) These x-rays can be considered as approximately monoenergetic with an equivalent energy $(h\nu)_m$ corresponding to the peak of R(hν), which depends only on the thickness and composition of the specimen for a given film and source.

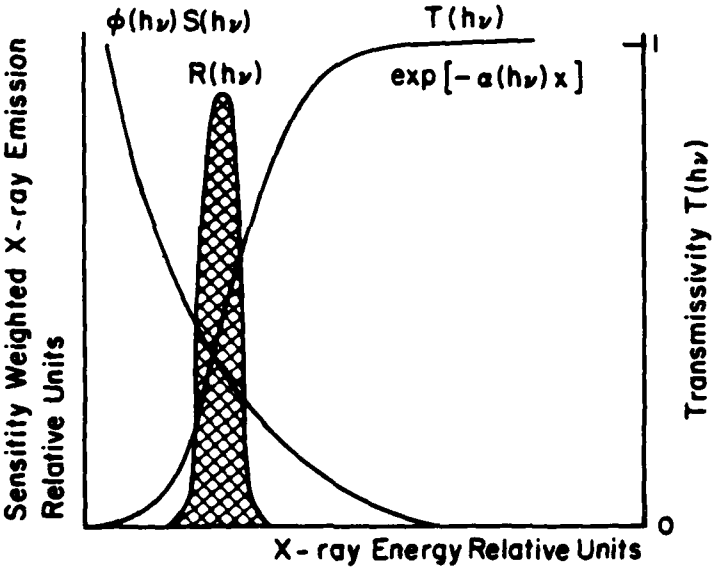

FIGURE 5. EFFECT OF X-RAY SPECTRUM ϕ, DETECTOR SENSITIVITY S, AND FOIL TRANSMISSIVITY ON DETECTOR RESPONSE R.

Any quantitative analysis requires information on the sensivity function S(hν) of the film. (9) The thick emulsion films absorb essentially all of the incident x-rays between ~1 and 5 to 10 keV. Below ~1 keV, the coating over the emulsion is sufficiently absorbing to reduce the sensitivity, and above ~5 keV transmission becomes important. However, the peak of R(hν) lies in the ~1-5 keV range for a wide range of thin sample radiography applications, and this case is worth analyzing carefully.

For constant $S(h\nu)$, the equivalent energy is given by

$$(h\nu)_m = [3c_2x(KT)]^{1/4} \quad .$$

Because of the sharply peaked integrand, E_f can be evaluated by the saddle point method. For KT = 1 keV,

$$E_f \approx 2.280\ r^{-2}\ (c_2x)^{1/8} \exp\ [-1.76\ (c_2x)^{1/4}] \quad j/cm^2 \quad .$$

Any change in absorption cross section, density, or thickness will cause a change in E_f, and the resultant energy contrast is given by

$$C = |dE_f/d(c_2x))E_f^{-1}\Delta(c_2x)| \approx 0.44\ (c_2x)^{-3/4}\ \Delta(c_2x) \quad .$$

Commonly, we wish to determine the absorption cross section of a small inclusion of thickness, t, to evaluate its composition. In the linear range of the film,

$$D \approx \gamma \log E_f$$

and

$$\Delta D/\gamma \approx 0.19\ (c_2x)^{-3/4} t\Delta c_2 \quad .$$

By taking the difference in optical density, D, between the inclusion and the immediately adjacent region, the change in c_2 can be determined. This method has been used to find the salt concentration of small ducts in thin biological specimens, for example.

Resolution. The quality of a contact microradiograph is determined by *several factors(10):* (1) *geometric resolution*, (2) blurring due to motion, (3) diffraction limitations, (4) mottling due to statistical fluctuations, and (5) grain size and noise limitation of the film. The effect of (2) and (3) can generally be neglected for most laser-plasma x-ray applications. In a "contact" microradiograph, the resolvable diameter based only on geometry is given by(11)

$$R_s = D_s\ell/r \quad ,$$

where ℓ is the distance between film and specimen (limited by the specimen thickness), and D_s and r the source diameter and distance.

Statistical fluctuations impose a limit on the resolvable diameter given by

$$R_s = 2.5 \ / \ C\sqrt{n} \quad ,$$

where n is the fluence in photons/cm^2 on the film. Considering both geometry and statistics, we can chose a distance to yield an optimum resolution

$$R_{opt} = 4.0 \times 10^{-3} D_s^{1/3} c_2^{0.27} x^{0.60} \exp[0.29(c_2 x)^{1/4}] (\Delta c_2)^{-1/3}$$

as seen in Figure 6.

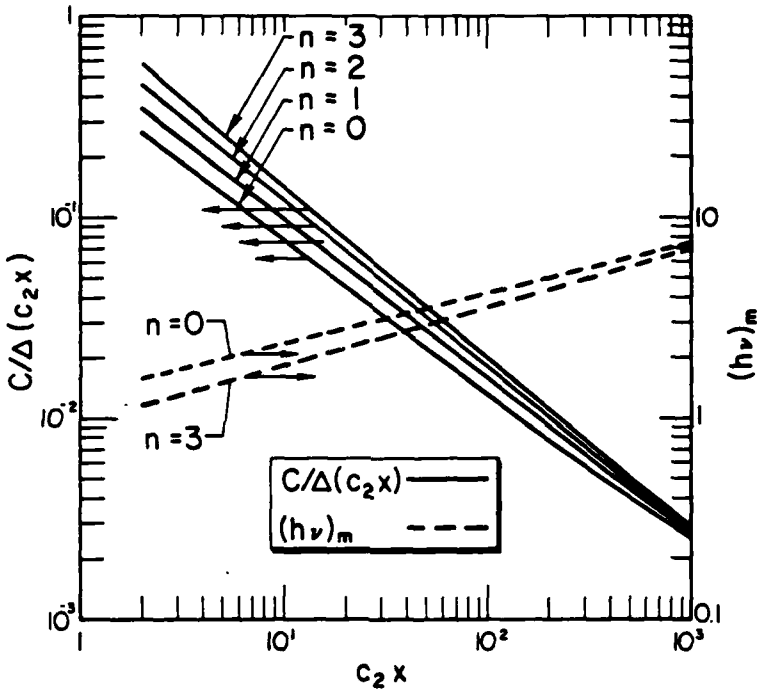

FIGURE 6. CONTRAST AND EFFECTIVE X-RAY ENERGY AS A FUNCTION OF THE ABSORPTION THICKNESS PARAMETER c_2x.

In most x-ray film, both the sensitivity and resolution are determined by silver halide grain size. An increase in grain size produces an increase in sensitivity and a decrease in resolution. The sensitivity is roughly proportional to the area of the grain while the resolving power is inversely proportional to the grain diameter. The limit on resolution imposed by the film grain is of the same order of magnitude as that imposed by statistical fluctuations. The resolution for maximum contrast, C = 1, and exposures to an optical density of ~1 are shown for several films in Table 1.

When the graininess of the film is taken into account, R_{opt} is increased by about an order of magnitude. Contrasts below about .01 are difficult to resolve because of the signal to noise ratios of typical films, but statistical averaging can help reduce this limitation.

TABLE 1. RESOLUTION AND SENSITIVITY FOR VARIOUS KODAK FILMS

Film Type	Resolution C = 1 (lines/mm)	Exposure D = 1 at 2 keV ($ergs/cm^2$)
NS 2T	25	0.1
SO 424	1250	100
RAR 2490	160	2
RAR 2497		
649	4000	500
Type M	50	0.2

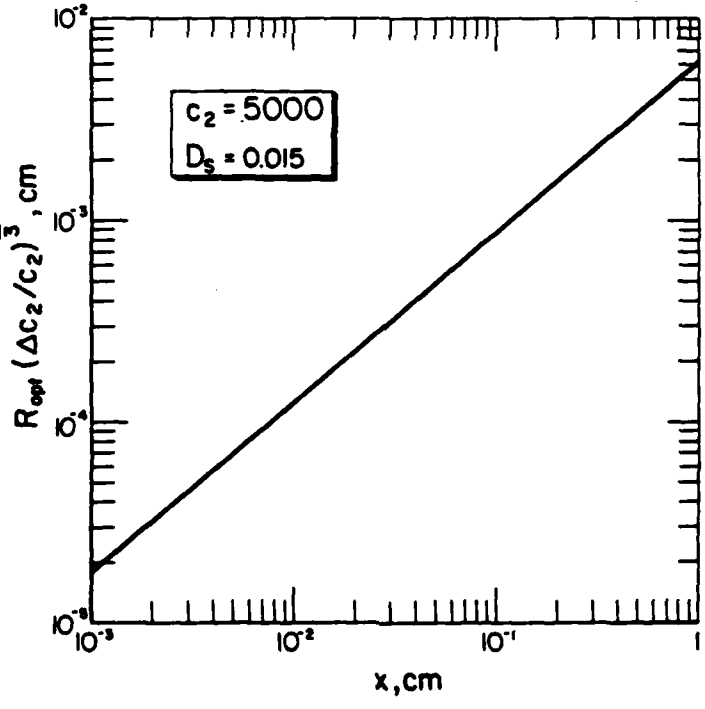

FIGURE 7. MINIMUM RESOLVABLE DIAMETER VS. THICKNESS OF WATER WITH PERFECT RECORDING MEDIA.

For x-ray energies at which the sensitive emulsion of a film becomes significantly transmissive, the films exhibit a strong spectral sensitivity. Thin emulsions will have a sensitivity given by

$$S(h\nu) \propto (h\nu)^{-3} \quad ,$$

if no silver absorption edges appear in the $R(h\nu)$ peak. In case silver absorption edges are present or the film is in the transition region between thick and thin, $S(h\nu)$ can usually be adequately approximated by

$$S(h\nu) \propto (h\nu)^{-n} \quad .$$

It can be seen from Figure 7 that $(h\nu)_m$ is not a strong function of the choice of n, and that the effect of n on contrast is not large. Thus, precise characterizations of the films is unnecessary.

ACKNOWLEDGMENTS

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SCIENCE

Laser-EXAFS: Fast Extended X-ray Absorption Fine Structure Spectroscopy with a Single Pulse of Laser-Produced X-rays

P. J. Mallozzi, R. E. Schwerzel, H. M. Epstein, and B. E. Campbell

Laser-EXAFS: Fast Extended X-ray Absorption Fine Structure Spectroscopy with a Single Pulse of Laser-Produced X-rays

Abstract. *The extended x-ray absorption fine structure (EXAFS) spectrum of aluminum has been measured with a nanosecond pulse of soft x-rays generated by a laser-produced plasma. This technique provides a practical alternative to synchrotron radiation for the acquisition of EXAFS data. It also provides a unique capability for the analysis of molecular structure in highly transient chemical species.*

Determining the identities and exact spatial arrangement of the atoms surrounding any particular atom in a molecule is fundamental to understanding the properties of any type of liquid, gas, or solid. In the case of materials with long-range order, such as perfect crystals, this information can often be obtained with x-ray or particle beam diffraction techniques. Such diffraction techniques rely on the fact that all of the atoms in a perfect lattice reside at fixed, periodic distances from any given atom, and that this periodicity is retained regardless of how far one moves within the lattice from the atom in question.

For materials without long-range order, the diffraction techniques are far less useful; one can determine local configurations in this way only for relatively simple molecules composed of a single element. For more complicated molecules, considerable insight can often be gained from optical spectroscopy and magnetic resonance techniques. However, these techniques have the drawback of providing only indirect evidence, from which the structural parameters of interest for a molecule must be inferred.

Many of these limitations can be overcome with the recently developed technique of extended x-ray absorption fine structure (EXAFS) spectroscopy (*1*, *2*). In EXAFS spectroscopy, the x-ray absorption coefficient of a material is measured as a function of energy from the *K* edge or *L* edge of a specific element in the material to as far as 1000 eV above the edge. The absorption of x-rays by the element is accompanied by the ejection of photoelectrons, which can be scattered from neighboring atoms. Backscattering of these photoelectrons from atoms in the immediate vicinity of the absorbing atom gives rise to a periodic "wiggle" structure in the x-ray absorption spectrum (*1*, *3*, *4*). By analyzing this wiggle structure above the absorption

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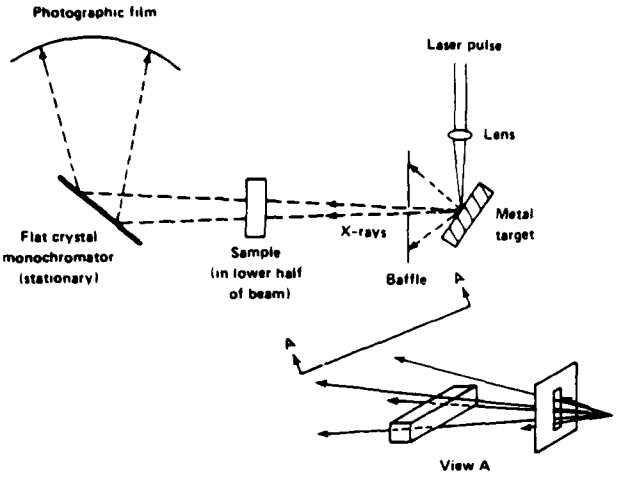

Fig. 1. Schematic top view of laser-EXAFS experimental configuration showing (*View A*) the positioning of the sample in the x-ray beam.

edge of a particular element, information can be obtained about the spatial arrangement of atoms in the immediate vicinity of the absorbing species. Since only the nearby atoms are involved, long-range order is not required; therefore, the EXAFS technique can be applied to the study of a broad class of materials, including liquids, gases, and amorphous or crystalline solids.

In the past, chemical structure research with the EXAFS technique has been limited by the lack of suitably intense sources of x-rays. This deficiency is now being remedied to some extent by the increasing availability of synchrotron radiation, which is being harnessed in a number of x-ray test facilities throughout the world (*5*). Certain types of EXAFS experiments, however, cannot be performed easily with synchrotron x-ray sources. Most significant, perhaps, are experiments designed to analyze highly transient structures such as chemically reactive intermediates or the excited electronic states of molecules. These experiments could be carried out if it were possible to obtain a complete EXAFS spectrum with a single, intense, short pulse of x-rays synchronized with the optical or electrical excitation of the sample. Previous work in our laboratories has indicated that laser-produced plasmas should be nearly ideal x-ray sources for experiments of this type (*6*).

We report here that it is possible to obtain well-resolved EXAFS spectra of light elements (atomic numbers up to about 40) with a single pulse of soft x-rays produced with a neodymium-doped-glass laser. The basic experimental configuration is shown in Fig. 1. In a typical experiment, an infrared laser pulse with an energy of approximately 100 J and a pulse width of approximately $3\frac{1}{2}$ nsec (full width at half-maximum) is focused onto a solid metal slab target, thereby creating a surface plasma and raising it to the kilovolt temperature regime by means of the inverse bremsstrahlung absorption process. The laser pulse strikes a focal spot 100 to 200 μm in diameter at an incident intensity of about 10^{14} W/cm^2. The resulting x-ray spectrum is dispersed by Bragg reflection from a flat KAP (potassium acid phthalate) crystal and recorded on photographic film. The position and range of the recorded spectrum can be varied easily by adjusting the size and position of the dispersing crystal. As shown in Fig. 1, the system is so arranged that the thin-film sample occupies half of the x-ray beam. The reflected (diffracted) x-rays thus form a double image on the photographic film, with the reference portion of the reflected beam striking the top half and the sample portion of the beam striking the lower half of the film. In this way, the entire spectrum is recorded at once, using a single laser pulse. The EXAFS spectrum can easily be extracted from the data since the incident and transmitted x-ray intensities are known for each wavelength.

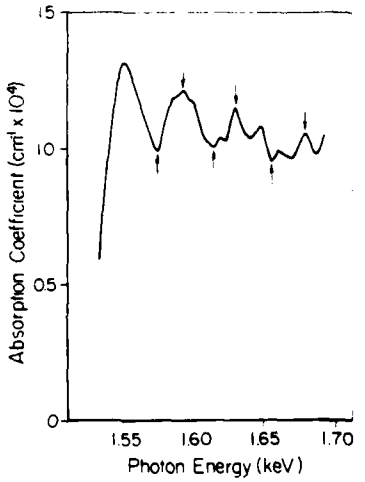

Fig. 2. Laser-EXAFS spectrum of aluminum foil.

We used film because the need to record the entire spectrum in a few nanoseconds rules out detectors based on the counting of individual photons. Film is the simplest alternative and, when evaluated by digital densitometer techniques, is capable of high resolution and contrast discrimination. With proper choice of film type, grain size, exposure, and data handling, it is possible to obtain results approaching the statistical limit allowed by the incident x-ray photon fluence. Because the photographic film is a nonlinear recording medium, it is necessary to multiply the measured optical densities by a known response factor to determine the absolute x-ray flux at each wavelength. This data handling is done with an on-line minicomputer.

The capabilities of this technique are illustrated by the laser-EXAFS spectrum, shown in Fig. 2, of a thin (2.0 μm) foil of aluminum (*7*). This spectrum is representative of our results to date and was obtained with the x-rays produced by a single laser pulse incident on an iron slab target. Iron was chosen as the target material because it produced mainly continuum emission in the vicinity of the aluminum *K* edge. The same EXAFS spectrum was obtained when the sample was exposed to a pulse of x-rays produced by a copper laser target, showing that the results obtained by this technique are independent of the target material, at least for targets with relatively smooth x-ray emission in the vicinity of the absorption edge being studied.

The measured spectrum can be interpreted on the basis of the generally accepted formula for EXAFS (*1*)

$$\chi(k) = \frac{m}{4\pi\hbar^2 k} \sum_j \frac{N_j}{R_j^2} f_j(2k) \exp\left(\frac{-2R}{l}\right) \times \sin[2kR_j + 2\delta_j(k)] \exp(-2k^2\sigma_j^2) \quad (1)$$

Here $\chi(k)$ is the fractional modulation of the absorption coefficient due to EXAFS: $\chi(k) = (\mu - \mu_0)/\mu_0$, where μ_0 is the absorption coefficient for a single atom in a vacuum. The quantity $k = [0.262467(E - E_{edge})]^{1/2}$ is the photoelectron wave vector in reciprocal angstroms, where E is energy in electron volts; m is the electron mass; $\hbar$ is Planck's constant; N_j is the number of atoms scattering at the distance R_j; $f_j(2k)$ is the electron scattering matrix in the backward direction for atoms at R_j; l is the mean free path of the electron; $\exp(-2\sigma_j^2k^2)$ is a Debye-Waller factor due to thermal vibrations or static disorder with root-mean-square fluctuations σ_j; and $\sin[2kR_j + 2\delta_j(k)]$ is the si-

nusoidal interference term, $\delta_1(k)$ being the phase shift. A full analysis of the spectrum on the basis of Eq. 1 requires the use of computer-assisted Fourier transform techniques (*1*, *2*). However, it is more illustrative for the present purpose to employ a straightforward graphical technique (*1*) to deduce the nearest-neighbor distance.

The graphical technique is based on the fact that the EXAFS curve is usually dominated by scattering from the nearest neighbor. This is especially true of the positions of the principal maxima and minima, which are determined mainly by the first sine term in Eq. 1, namely $\sin[2kR_1 + 2\delta_1(k)]$. If δ_1 is linear in k, then $\delta_1 = \alpha_1 k + \beta_1$, and the argument of the sine term takes the form $2k(R_1 - \alpha_1) + 2\beta_1$. The approximate positions of the maxima and the minima of the EXAFS curve are thus given by

$$n\pi = 2k(R_1 - \alpha_1) + 2\beta_1 \qquad (2)$$

where $n = 0, 2, 4, \ldots$ for maxima and $1, 3, 5, \ldots$ for minima. A plot of n against k for the dominant maxima and minima of the EXAFS spectrum shown in Fig. 2 is given in Fig. 3 with $k = 0$ taken to correspond to the inflection point, $E_{k\,\text{edge}} = 1552$ eV, of the measured x-ray absorption coefficient. The points closely fit a straight line with a slope $(2/\pi)(R_1 - \alpha_1)$ of 1.7 Å. This leads to the basic result $(R_1 - \alpha_1) \approx 2.6$Å. Since $R_1 >> \alpha_1$ (α_1 is typically a few tenths of an angstrom), this result is in good agreement with the known nearest-neighbor distance of 2.86 Å for the aluminum face-centered-cubic lattice (*8*).

The spectrum presented in Fig. 2 is noteworthy for several reasons. It illustrates the capability of the laser-EXAFS technique to record EXAFS spectra of light elements with absorption edges below about 3 keV, which are difficult to study with other x-ray sources. The technique is particularly suitable at present for the study of *K*-edge EXAFS spectra of the elements from carbon to sulfur and of *L*-edge EXAFS spectra of the elements from sulfur to molybdenum. More important, however, the complete laser-EXAFS spectrum presented in Fig. 2 was obtained in only a few nanoseconds with a single pulse of laser-produced x-rays. This represents a dramatic improvement in the speed and ease of obtaining EXAFS data compared to what is possible with other known x-ray sources. The technique also makes possible the measurement of "flash-EXAFS" spectra of transient species having lifetimes of a few nanoseconds or less. Thus, with this technique it may soon be possible to make "snapshots" or "movies" of the structural changes that occur in molecules when they are excited by optical or other means. If this proves to be the case, laser-EXAFS will have provided an important new dimension to the study of chemical structure by x-ray absorption techniques.

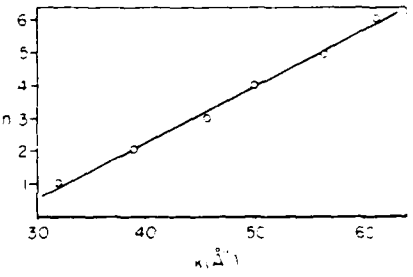

Fig. 3. Graph of n versus k for aluminum. The points correspond to the features indicated by arrows in Fig. 2.

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Laboratory EXAFS Facilities-1980

(University of Washington Workshop)

Edited by
Edward A. Stern
University of Washington

American Institute of Physics
New York **1980**

FOREWORD

This Proceedings is the outcome of a "Workshop on Laboratory EXAFS Facilities and Their Relation to Synchrotron Radiation Sources" held in Seattle, Washington, April 28-30, 1980. The Workshop was held to evaluate the capabilities of Extended X-ray Absorption Fine Structure (EXAFS) facilities using conventional bremstrahlung sources, which are suited for use in one's own laboratory, and to assess their relationship to the EXAFS facilities at national synchrotron radiation sources.

In the last decade, after it was shown that EXAFS can be utilized to obtain information on the atomic arrangement of materials*, EXAFS measurements have experienced a phenomenal growth. The feature of EXAFS that makes it attractive is its capability to measure the atomic arrangement around a chosen atom type independent of whether the material is crystalline or not. This new technique has made feasible structure determination on systems that were not amenable to the more standard techniques.

The demand to do EXAFS measurements gave an impetus to the development of synchrotron radiation sources. At the sources, EXAFS facilities were constructed and instrumentation developed which greatly facilitated the measurements. The EXAFS facilities at the Stanford Synchrotron Radiation Laboratory, the first of such facilities, made accessible EXAFS measurements to the general scientific community leading to a spectacular growth in the application of the technique. As the scientific community became acquainted in this manner to the usefulness of EXAFS the demand quickly outstripped the available facilities. For this and other reasons described in the Proceedings there began a trend to develop techniques for doing EXAFS measurements in the laboratory reviving a technology that had almost disappeared. The 1930's saw the development of the basic technology being used today. However, the modern instruments described in the Proceedings take full advantage of computer technology and modern electronics which give them capabilities that would make the originators of the technology envious.

It seemed appropriate to convene a workshop to make a studied effort to evaluate the relationship between laboratory and synchrotron radiation EXAFS facilities and to assess what may be their relative strengths and weaknesses. These questions are ones that may face many research groups and funding officials in industry, universities, and government, as the assessment is made of how to invest both time and funds in the growing field of EXAFS. Both technical and policy questions are involved. The two questions are dependent on one another and it seemed appropriate to discuss both at the same meeting.

*D.E. Sayers, E.A. Stern, F. Lytle, Phys. Rev. Letters 27, 1204 (1971).

To that purpose many of the people active in the field of EXAFS, were invited to participate. The list of the attendees is given in the Appendix. As can be noted, the spectrum covered both those in research and those influential in policy making. A summary of the conclusions from the Workshop is presented in the next section.

The Workshop was organized into a series of plenary presentations where the present state of the various elements of a laboratory EXAFS facility were given. Chapters 1 to 7 cover these presentations. Then four separate workshops were convened to cover the topics of Sources, Crystals and Focusing, Detectors, and Hardware and Software, chaired by B. R. Stults, D. W. Berreman, D. Sandstrom and P. Georgopoulos, respectively. The presentations of these workshops summarized by their respective chairmen and contributions by panel members and others are given in Chapters 8 to 11. The final presentation of the Workshop considered the "Relation of Roles of EXAFS Facilities in Laboratory and at Synchrotron Radiation Sources" and also constitutes the last chapter of the Proceedings, Chapter 12.

Inherent in the nature of a Proceedings is the problem of the continuity and coherence of the various contributions. The author giving his presentation has to make some assumptions of the topics that will or will not be covered by the other authors. This inevitably leads to repetition in some areas and gaps in others. To help overcome this problem I have taken the liberty of adding a more generous number of editor's notes than is usually the case for a Proceedings. To distinguish the editor's notes from those of the authors', they are referred to by lower case superscripts starting from the end of the alphabet and going backwards. I hope this ordering does not reflect on the notes' contents but it assures that the reference is unique and will not be confused with that of any of the authors. The contributions are divided into chapters and the editor's notes referenced in each chapter are placed at the end of that chapter.

The convening of the Workshop would not have been possible without the generous financial help of Battelle Seminars and Conferences, Seattle, Washington, and the Monsanto Company. Dr. B. R. Stults is particularly deserving of thanks for arranging the support from the Monsanto Company. The initial encouragement and support of Provost George Beckmann and Dean Ronald Geballe of the University of Washington were the essential catalysts that led to the organizing activities which are culminating in these Proceedings.

It would have not been possible to have organized the Workshop and these Proceedings without the help of many people. First, the members of the program committee gave very wise and important advice besides contributing substantially to the Workshop by their participation. They are: John Baldeschwieler, Arthur Bienenstock, Gabrielle Cohen, Gordon Knapp, and B. R. Stults. I also want to give thanks to Donald Sandstrom for his particular helpfulness and to other

chairmen of the individual workshops Dwight Berreman and P. Georgopoulos. My graduate students, associates and post docs were leaned on particularly heavily because of their close proximity. I am appreciative not only of their important help and participation but also by their willingness to be helpful. They are: Charles Bouldin, Grant Bunker, Edward Keller, Kyung-Ha Kim, Kun-quan Lu, Yaacov Azoulay, Bruce Bunker, and W. T. Elam. Mitzie Johnson deserves a special thanks. She handled the administrative details and typed the corrections to the Proceedings helping to organize them into their final form. She managed to get married during the same time, though the Workshop takes no credit or responsibility for that. Finally, I am pleased to express my appreciation to the participants of the Workshop, a list of which is presented in the Appendix, whose contributions, lively interest and discussions constituted the essential element in making the Workshop the success that it was.

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SUMMARY

The Workshop showed that it is possible to build a laboratory EXAFS facility using a fixed anode bremstrahlung x-ray generator with a photon flux of around 1-3 x 10^6 photons/sec in the resolution bandwidth of about 5 eV. Such a facility at the University of Washington using Si(400) monochromating crystals was demonstrated at the Workshop. With the innovations suggested at the conference, in particular, the development of improved detectors as suggested by Y. Yacoby, and crystals better matched to the resolution width, the intensity could be increased by perhaps a factor of 10. With the use of rotating anode sources in place of the fixed anode another factor of 15 can be attained. Thus it appears possible to build laboratory EXAFS facilities with effective intensities above 10^8 photon/sec in a resolution width of 5 eV. These intensities are all quite suitable for measuring EXAFS spectra in concentrated samples, and the highest intensities which the future generation of laboratory EXAFS facilities may attain are competitive with that at the present generation of synchrotron sources. Although the future generation of synchrotron radiation sources will be several orders of magnitude more intense, it was generally agreed that the intensities presently available in laboratory EXAFS facilities make them completely competitive for measurements on concentrated samples and moderately dilute ones. The synchrotron sources have decided advantages in measuring very dilute samples, higher energy resolution, polarization effects, and the high energy spectrum above 20 KeV. At the moment the soft x-ray region of EXAFS measurements is exclusively being covered by synchrotron sources but the ongoing improvement of electron energy loss instrumentation in electron microscopes described in Chapter 6 may open up this region to laboratory EXAFS study.

The possibility of building an EXAFS facility under $100,000 using fixed anode sources makes quite practical the possibility of a large growth in the number of such laboratory facilities. This may have the consequence of concentrating the routine EXAFS measurements in the laboratory, freeing synchrotron sources for the more difficult ones. The growth of the number of laboratory EXAFS facilities should increase the quality of the research in the field by stimulating better training of researchers and innovativeness in the field, both in the laboratory and at the synchrotron radiation sources.

E.A. Stern

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LASER-EXAFS: LABORATORY EXAFS WITH A NANOSECOND PULSE OF LASER-PRODUCED X-RAYS

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ABSTRACT

Laser-produced x-rays are a promising alternative to synchrotron radiation for the measurement of EXAFS spectra. Experiments to date indicate that K-edge EXAFS spectra of elements with atomic numbers up to about Z=20, and L-edge spectra of elements with atomic numbers up to about Z=40, can be obtained with a single nanosecond pulse of x-rays emitted by a laser-produced plasma. The technique shows promise of providing single-shot EXAFS spectra for the remaining elements as well, with the use of advanced laser systems that are available today. The x-ray pulse can be synchronized easily with an external optical or electrical perturbation of the sample, thereby providing a unique capability for recording EXAFS spectra of highly transient species having lifetimes the order of a nanosecond.

INTRODUCTION

We have recently shown that well-resolved EXAFS spectra of light elements (e.g., aluminum and magnesium) can be obtained with a single nanosecond pulse of soft x-rays emitted by a laser-produced plasma.[1,2] In these experiments, a pulse of infrared light from a neodymium-doped glass laser is focused onto a metal target chosen on the basis of its ability to emit continuum x-rays in the vicinity of the absorption edge to be studied.

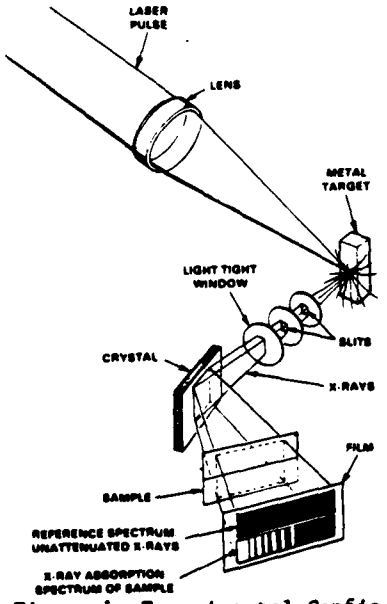

Figure 1. Experimental Configuration for Laser-EXAFS

The laser pulse produces a surface plasma which serves as a point source of x-rays having a pulse width comparable to that of the laser; i.e., on the order of a nanosecond. The x-rays are passed through a light tight shield and beam-shaping slits, and are then dispersed from a flat crystal, typically composed of KAP or RAP. The basic experimental configuration is shown schematically in Figure 1. The entire sample and reference

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spectra are recorded simultaneously, so that chemical structure information can be obtained from data produced with a single laser shot. We have chosen to use photographic film and computerized video densitometry for this purpose in our experiments to date, but anticipate that solid-state detector arrays will be used in the near future.

DISCUSSION

The present capabilities of the laser-EXAFS technique are illustrated by the spectrum shown below in Figure 2. This spectrum was obtained with a laser pulse of approximately 100 joules and a pulse width of approximately 3-1/2 nanoseconds focused to a 100- to 200- micrometer diameter spot on an iron slab target at an incident intensity of about 10^{14} watts/cm^2. In analyzing the data, the energy spectrum was divided into 5-electron-volt energy intervals. The number of photons that struck the film after passage through the sample was approximately 10^6 per energy interval. In principal, this allows an interval to interval contrast of $1/N^{1/2} = 10^{-3}$, or approximately 0.1 percent. This makes possible the measurement of flash-EXAFS spectra of transient species having lifetimes on the order of a nanosecond, provided the sample is concentrated. To measure flash-EXAFS spectra of the highly dilute samples that are generally of interest in biology and surface science, it will be necessary to increase the number of photons recorded per energy interval about ten to a hundredfold. It appears that this may be possible either by improving the output of continuum radiation from the laser plasma source, or by achieving better utilization of the x-rays that are already produced by employing an array of appropriately curved large crystals. Both approaches are being explored in our laboratory, and appear promising. If these experiments prove successful, flash-EXAFS studies of dilute samples will become feasible with laboratory equipment of modest cost.

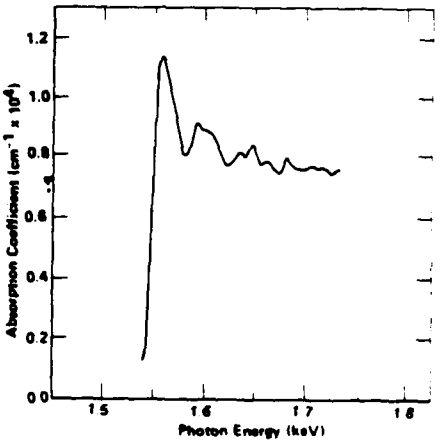

FIGURE 2. LASER-EXAFS SPECTRUM OF ALUMINUM

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Fast extended-x-ray-absorption-fine-structure spectroscopy with a laser-produced x-ray pulse

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Extended-x-ray-absorption-fine-structure (EXAFS) spectra of aluminum and magnesium have been measured with single nanosecond pulses of soft x rays generated by laser-produced plasmas. This technique provides a practical alternative to synchrotron radiation for the acquisition of EXAFS data for elements having atomic numbers up to 40. It also provides a unique capability for the analysis of molecular structure in highly transient chemical species.

I. INTRODUCTION

The extended x-ray-absorption-fine-structure (EXAFS) technique is a powerful new tool for studying molecular structure. EXAFS provides information on the identities and spatial arrangement of the atoms in any type of solid, liquid, or gas, even those composed of highly complex molecules. In the EXAFS technique, the x-ray absorption coefficient of a material is measured as a function of energy from the K edge or L edge of a specific element in the material to as far as 1000 eV above the edge.[1,2] The absorption of x rays by the element is accompanied by the ejection of photoelectrons, which can be scattered from neighboring atoms. Backscattering of these photoelectrons from atoms in the immediate vicinity of the absorbing atom gives rise to a periodic "wiggle" structure in the x-ray absorption spectrum.[1,3,4] By analyzing this wiggle structure above the absorption edge of a particular element, information can be obtained about the spatial arrangement of atoms in the immediate vicinity of the absorbing species. Since only the nearby atoms are involved, long-range order is not required; therefore, the EXAFS technique can be applied to the study of a broad class of materials, including liquids, gases, and amorphous or crystalline solids.

Conceptually, the EXAFS phenomenon may be described in the following manner. The wave function of the photoelectron (the final state of the x-ray-absorption transition) consists of an outgoing part and a scattered part, which overlap near the origin, where the wave function of the initial (bound) state of the electron is concentrated. The overlap produces an interference which is either constructive or destructive, depending on the wave number

$$k = 2\pi/\lambda = 1/\hbar\,[2m(E - E_{edge})]^{1/2}$$

of the photoelectron. When the interference is constructive, the increased amplitude near the origin results in an enhanced absorption coefficient. When the interference is destructive, the absorption coefficient is diminished. Thus, the relative phase relationship between the outgoing and incoming photoelectrons is changed by varying the photon energy of the incident x-rays, causing a periodic modulation in the absorption coefficient. The modulation can be interpreted on the basis that each atom (or shell of atoms) surrounding the absorbing atom will contribute a single modulated sine wave in k to the absorption coefficient.

In the past, chemical-structure research with the EXAFS technique has been limited by the lack of suitably intense sources of x rays. This deficiency is now being remedied to some extent by the increasing availability of synchrotron radiation, which is being harnessed in a number of x-ray test facilities throughout the world.[5] There are certain types of EXAFS experiments, however, which cannot be performed easily with synchrotron x-ray sources. Most significant, perhaps, are those experiments which are designed to analyze highly transient structures such as chemically reactive intermediates or the excited electronic states of molecules. These experiments could be carried out if it were possible to obtain a complete EXAFS spectrum with a single, intense, short pulse of x rays synchronized with the optical or electrical excitation of the sample.

Previous work in our laboratories has indicated that laser-produced plasmas should be nearly ideal x ray sources for fast kinetic studies of this type.[6] Indeed, we have recently reported the first experimental demonstration of the feasibility of performing EXAFS measurements with laser-produced x rays.[7] These experiments show that it is possible to obtain well-resolved EXAFS spectra of light elements (atomic numbers ranging up to about 40) with a single nanosecond pulse of soft x rays produced with a neodymium-doped-glass laser. In the present paper we discuss in detail the techniques and results of our experiments to date.

II. GENERAL TECHNIQUE AND MAIN RESULT

The basic experimental configuration used in the experiments is shown in Fig. 1. In a typical experiment, an infrared laser pulse with an energy of approximately 100 J and a pulse width of approximately 3.5 ns (full width at half maximum) is focused onto a solid metal slab target, thereby creating a surface plasma and raising it to the kilovolt temperature regime by means of the inverse bremsstrahlung absorption process. The laser pulse strikes a 100- to 200-μm diameter focal spot at an incident intensity of about 10^{14} W/cm^2. The resulting x-ray spectrum is dispersed by Bragg reflection from a flat crystal and recorded on photographic film. The position and range of the recorded spectrum can be varied easily by adjusting the size and position of the dispersing crystal as desired. As Fig. 1 indicates, the system is so arranged that the thin-film sample occupies one-half of the x-ray beam. The reflected (diffracted) x rays thus form a double image on the photographic film, with the reference portion of the reflected beam striking the top half of the film and the sample portion of the beam striking the lower half of the film. In this way, the entire spectrum is recorded at once using a single laser pulse. The absorption (EXAFS) spectrum can easily be extracted from the data since both the incident and transmitted x-ray intensities are known for each wavelength.

We have chosen to use film because the need to record the entire spectrum in a few nanoseconds rules out detectors based on the counting of individual photons. Film is the simplest alternative and, when evaluated by digital densitometer techniques, is capable of high resolution and contrast discrimination. With proper choice of film type, grain size, exposure, and data handling, it is possible to obtain results approaching the statistical limit allowed by the incident x-ray photon fluence. Because the photographic film is a nonlinear recording medium, it is necessary to multiply the measured optical densities by a known response factor to determine the absolute x-ray flux at each wavelength. This numerical data handling is done with an online minicomputer.

The capabilities of this technique are illustrated by the K-edge laser-EXAFS spectra shown in Figs. 2 and 3, taken with aluminum and magnesium samples.[8] These spectra are representative of our results to date, and each was obtained with the x rays produced by a single laser pulse incident on a metal slab target. The target used for the aluminum EXAFS spectrum was iron, whereas the target used for the magnesium spectrum was chromium. These target materials produce mainly continuum emission in the vicinity of the K edges they were used to study. Line radiation increases the probable error in data reduction, and should be avoided as much as possible. A KAP (potassium acid phthalate) crystal was used to obtain the aluminum spectrum, and a RAP (rubidium acid phthalate) crystal was used for the magnesium spectrum.

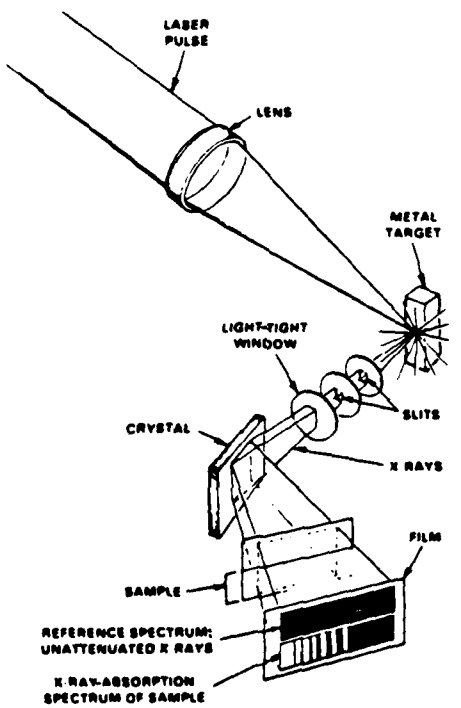

FIG. 1. Schematic view of laser-EXAFS experimental configuration.

III. EXPERIMENTAL APPARATUS AND METHOD

In this section, questions relating to targets, crystals, samples, and other features of the tech-

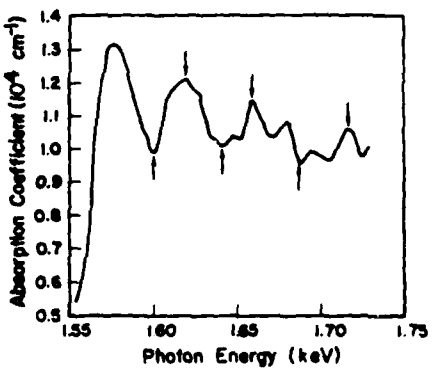

FIG. 2. Laser-EXAFS spectrum of aluminum foil.

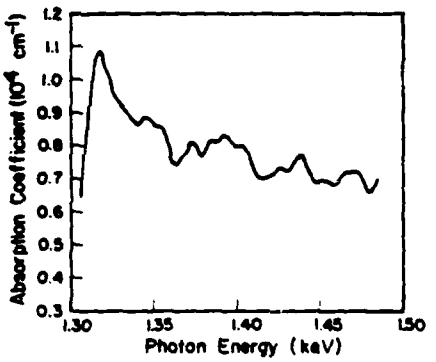

FIG. 3. Laser-EXAFS spectrum of magnesium film.

nique will be discussed in more detail. For clarity, specific data will be given only for the aluminum measurements. The discussion will converge on an evaluation of the potential sensitivity of the technique under the actual operating conditions of the experiment.

Aside from the laser and beam-focusing apparatus, which have already been discussed, the basic experimental apparatus consists of a modified General Electric XRD-7 vacuum x-ray spectrometer with the x-ray tube replaced by the laser-plasma x-ray source. The laser target is mounted on a remotely controlled XYZ translation stage to permit a change of targets or target position in the vacuum. The crystal angle is also remotely controlled and can be adjusted in the vacuum.

The iron target used to produce the aluminum EXAFS spectrum emits both continuum and line radiation. The lines above $h\nu \simeq 1$ keV are bunched into an L group, which lies mostly below 1.5 keV, and a K group, which lies above about 5 keV. The region between 1.5 and 5 keV is mostly continuum radiation with a characteristic plasma bremsstrahlung temperature of approximately 800 eV. For the purpose of planning experiments, using the experimental parameters and configuration described earlier, the following formula for this continuum radiation has proved useful:

$$I(h\nu) = \frac{0.025}{2\pi R^2} \exp\left(\frac{-h\nu}{800}\right), \qquad (1)$$

expressed in units of J/eV cm^2, where R is the distance from the x-ray source (laser target) to an observer, and $h\nu$ is the photon energy in eV. It should be noted that the K edge of aluminum ($E_K = 1560$ eV) lies in the most intense portion of the iron continuum, just above the iron L group. This method of matching target with sample seems reasonable when studying x-ray edges in the 1–2-keV regime, e.g., when studying K edges of elements with atomic numbers $Z \simeq 10$–20 and L edges of elements with atomic numbers $Z \simeq 20$–40. It appears that the appropriate targets for such studies have atomic numbers in the range $Z \simeq 20$–30.

The KAP crystal used to disperse the x rays in the aluminum EXAFS experiments was 1 cm wide and 2.5 cm long, and was located approximately 10 cm from the x-ray source. The x rays are reflected from the crystal according to the formula $2d \sin\theta = m\lambda$, where θ is the Bragg angle, i.e., the angle of incidence measured with respect to the crystal plane. Since the $2d$ spacing of KAP is 26.64 Å, $\theta \simeq 17°$ for first-order reflection ($m = 1$) of x rays at the K edge of the aluminum sample. The rocking-curve width (i.e., the full width at half maximum of the intensity versus angle profile for monochromatic x rays) of the crystal at this angle is 1.2×10^{-4} rad, corresponding to an energy spread $\Delta h\nu \simeq 0.6$ eV. The reflection efficiency at the peak of the rocking curve at this angle is about 5%.

The data given above may be used to calculate the number of photons per eV that strike the film. This quantity can then be used to evaluate the sensitivity with which the x-ray absorption coefficient can be measured. A convenient starting point for the calculation is Eq. (1). This formula tells us that the x-ray fluence at the KAP crystal, which is located at a distance $R = 10$ cm from the x-ray source, in the energy region just above the K edge (i.e., just above $h\nu \simeq 1560$ eV), is

$$0.025 \times 1/(2\pi 10^2) \exp(-1560/800) = 5.7 \times 10^{-6} \text{ J/eV cm}^2,$$

or

$$(5.7 \times 10^{-6})(6 \times 10^{18})1/1560 = 2.2 \times 10^{10} \text{ photons/eV cm}^2.$$

To obtain the number of photons per eV that are reflected from the crystal, we multiply this number by the area of a narrow rectangle whose length is equal to the width of the crystal (1 cm) and whose width is R times the rocking-curve width (1.2×10^{-4} rad), and also multiply it by the reflection efficiency (0.05) of the crystal. We thus arrive at the result

$$(2.2 \times 10^{10})[(1)(10)(1.2 \times 10^{-4})]0.05 \simeq 1.3 \times 10^6$$

photons/eV for the number of photons reflected from the crystal.

The figure 1.3×10^6 ignores attenuation through the sample, which is approximately 2 x-ray mean free paths thick. What really matters in determining the sensitivity of the absorption-coefficient measurement is the number of photons that strike

the film after passage through the sample. This number is readily calculated to be $(1.3\times10^6)1/e^2 = 2\times10^5$ photons/eV.

In analyzing the data, the energy spectrum was divided into 5-eV energy intervals. There are therefore approximately $5(2\times10^5)=10^6$ photons in each energy interval. In principle, this allows an interval-to-interval contrast of $\Delta N/N = 1/N^{1/2} \simeq 10^{-3}$, or approximately 0.1%.

It should be remarked that the reason for using a sample thickness of two mean free paths is that this optimizes the contrast obtainable with a given sized energy interval. It should also be noted, for future reference, that two mean free paths optimize the resolution obtainable at a given contrast level.

The photographic film used to record the EXAFS spectra shown in Figs. 2 and 3 is Kodak NS-2T. This film was chosen because, under the particular conditions of these experiments, the data are produced in the "linear" range of the film, where the optical density is proportional to the log of the exposure. In order to minimize the effect of film nonlinearity, the "reference" portion of the x-ray beam reflected from the crystal is passed through a thin layer of Mylar whose thickness is adjusted to produce the same average exposure as the "sample" portion of the beam. Analysis of the film record was performed automatically with a video digitizer, which serves as a computerized densitometer. The wavelength calibration of the film record is accomplished by noting where well known x-ray lines generated by focusing the laser beam onto selected targets lie, and interpolating between them.

IV. ANALYSIS OF RESULTS

A convenient starting point for interpreting EXAFS spectra is the generally accepted formula[1]

$$\chi(k) = \frac{m}{4\pi\hbar^2 k}\sum_j \frac{N_j}{R_j^2} t_j(2k)\exp\left(\frac{-2R_j}{l}\right) \times \sin[2kR_j + 2\delta_j(k)]\exp(-2k^2\sigma_j^2). \quad (2)$$

Here $\chi(k)$ is the fractional modulation of the absorption coefficient due to EXAFS: $\chi(k) = (\mu-\mu_0)/\mu_0$, where μ_0 is the absorption coefficient for a single atom in a vacuum. The quantity

$$k = [0.262\,467(E - E_{\text{edge}})]^{1/2}$$

is the photoelectron wave vector in reciprocal angstroms, where E is energy in electron volts, m is the electron mass, $\hbar$ is Planck's constant, N_j is the number of atoms scattering at the distance R_j, $t_j(2k)$ is the electron scattering matrix in the backward direction for atoms at R_j, l is the mean free path of the electron, $\exp(-2\sigma_j^2k^2)$ is a Debye-Waller factor due to thermal vibrations or static disorder with root-mean-square fluctuations σ_j, and $\sin[2kR_j + 2\delta_j(k)]$ is the sinusoidal interference term, $\delta_j(k)$ being the phase shift.

A full analysis of EXAFS spectra on the basis of Eq. (2) requires the use of computer-assisted Fourier-transform techniques.[1,2] However, it is more illustrative for the present purpose to employ a straightforward graphical technique[1] to deduce the nearest-neighbor distance. This will be done for the aluminium edge shown in Fig. 2.

The graphical technique which we employ is based on Eq. (2) and stems from the fact that the EXAFS curve is usually dominated by scattering from the nearest neighbors. This is especially true of the positions of the principal maxima and minima, which are determined mainly by the first sine term in Eq. (2), namely, $\sin[2kR_1 + 2\delta_1(k)]$. If δ_1 is linear in k, then $\delta_1 = \alpha_1 k + \beta_1$, and the argument of the sine term takes the form $2k(R_1 - \alpha_1) + 2\beta_1$. The approximate positions of the maxima and the minima of the EXAFS curve are thus given by

$$n\pi = 2k(R_1 - \alpha_1) + 2\beta_1, \quad (3)$$

where $n = 0, 2, 4, \ldots$ for maxima and $1, 3, 5, \ldots$ for minima. A plot of n against k for the dominant maxima and minima of the EXAFS spectrum as shown in Fig. 2 is given in Fig. 4, with $k=0$ taken to correspond to the inflection point, $E_{k=0} = 1552$ eV, of the measured x-ray absorption coefficient. The points closely fit a straight line with a slope $(2/\pi)(R_1 - \alpha_1)$ of 1.7 Å. This leads to the basic result $(R_1 - \alpha_1) \simeq 2.6$ Å. Since $R_1 \gg \alpha_1$ (α_1 is typically a few tenths of an angstrom), this result is in good agreement with the known nearest-neighbor distance of 2.86 Å for the aluminum fcc lattice.[9]

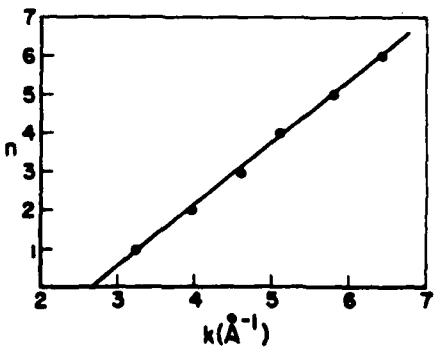

FIG. 4. Graph of n vs k for aluminum. The points correspond to the features indicated by arrows in Fig. 2.

The spectra presented in Figs. 2 and 3 are noteworthy for several reasons. They illustrate the capability of the laser-EXAFS technique to record EXAFS spectra of light elements with absorption edges below about 3 keV, which are difficult to study with other x-ray sources. The technique is particularly suitable at present for the study of K-edge EXAFS spectra of the elements from carbon to sulfur and of L-edge EXAFS spectra of the elements from sulfur to molybdenum. More important, however, the complete laser-EXAFS spectra presented in Figs. 2 and 3 were each obtained in only a few nanoseconds with a single pulse of laser-produced x rays. This represents a dramatic improvement in the speed and ease of obtaining EXAFS data compared to what is possible with other known x-ray sources. The technique also makes possible the measurement of "flash-EXAFS" spectra of transient species having lifetimes of a few nanoseconds or less. Thus, with this technique it may soon be possible to make "snapshots" or "movies" of the structural changes that occur in molecules when they are excited by optical or other means. This capability is provided almost automatically by the pulsed nature of the laser-EXAFS measurement. Experiments along these lines are presently underway in our laboratory, and will be reported shortly.

ACKNOWLEDGMENTS

This work was supported by the U. S. Air Force Office of Scientific Research and Battelle Memorial Institute, Corporate Technical Development.

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Flash-EXAFS for Structural Analysis of Transient Species: Rapidly Melting Aluminum

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ABSTRACT

Extended x-ray absorption fine structure (EXAFS) spectra of solid and flash-melted Al films have been measured simultaneously with a single nanosecond pulse of x-rays emitted from a laser produced plasma. The results constitute the direct observation of a degree of local order in rapidly melting Al. This "flash-EXAFS" technique is thus demonstrated to be useful for the study of dynamic structual changes on the nanosecond time scale.

The extended x-ray absorption fine structure (EXAFS) technique has become recognized in recent years as a versatile tool for studying structure of materials at the atomic level. EXAFS can provide information about the identities and spatial arrangement of the atoms in any type of solid, liquid, or gas, even those composed of highly complex molecules. In the EXAFS technique, the x-ray absorption coefficient of a material is measured as a function of energy from the K edge or L edge of a specific element in the material to as far as 1000 eV above the edge.[1,2] The absorption of x-rays by the element is accompanied by the ejection of photoelectrons, which can be scattered from neighboring atoms. Backscattering of these photoelectrons from atoms in the immediate vicinity of the absorbing atom gives rise to a periodic "wiggle" structure in the x-ray absorption spectrum.[1-4] By analyzing this wiggle structure above the absorption edge of a particular element, information can be obtained about the spatial arrangment of atoms in the immediate vicinity of the absorbing species. Since only the nearby atoms are involved, long-range order is not required; therefore, the EXAFS technique can be applied to the study of a broad class of materials, including liquids, gases and amorphous or crystalline solids.

Previous work in our laboratories has indicated that laser-produced plasmas should be nearly ideal x-ray sources for fast EXAFS studies of transient structural phenomena, and has resulted in the first experimental demonstration of the feasibility of performing EXAFS measurements with laser-produced x-rays.[5-7] These experiments have shown that it is possible to obtain well-resolved EXAFS spectra of light ele-

ments with a single, nanosecond pulse of soft x-rays, produced with a neodymium-doped-glass laser. We refer to this technique as laser-EXAFS, and have described the experimental configuration for performing these experiments in a previous paper.[7]

The fast time scale provided by the laser-EXAFS technique makes it well suited to the study of transient species produced by optical or thermal excitation of the sample. One may envision a variety of species of interest which could, in principle, be studied in this way; these include the photoexcited triplet electronic states of molecules, radicals or ions produced by flash excitation of a reactive sample, and the observation of transient phase changes.

A particularly significant application of thermally induced phase changes is the rapid solidification of certain metallic systems. Amorphous materials are a consequence of very rapid cooling rates, of the order of 10^{6}°C/sec. Studies of the physical properties of various amorphous metals indicate that their properties are closely related to their thermal history. Thus changes in structure during the critical stages of formation of the solid material are particularly interesting. The possibility of following nearest neighbor changes with time during solidification, annealing or melting provides a potentially new tool in the understanding of amorphous materials.

As the beginning step in a series of experiments designed to study the laser-EXAFS spectra of a variety of transient samples, we report here the first observation of a transient phase change in real time by means of EXAFS spectroscopy. Battelle's laser-EXAFS facility was used to

both melt a zone of the sample and interrogate it with an x-ray pulse. A thin (ca. 2 μm) aluminum foil was chosen for these initial experiments because of our prior experience in performing static laser-EXAFS experiments with this material. This experiment is of particular significance because it demonstrates conclusively that laser-EXAFS can detect and help characterize transient structural changes on a multi-nanosecond time scale.

Experimental Section

The basic experimental configuration used in the experiments is shown in Figure 1. In a typical experiment, an infrared laser pulse with an energy of approximately 100J and pulse width of 1.5ns (full width at half maximum) is focused on a solid metal slab target (typically composed of iron or copper), thereby creating a surface plasma and raising it to the kilovolt temperature regime by means of the inverse bremsstrahlung process. The laser pulse strikes a 100-200 μm diameter focal spot an an incident intensity of about $2 \times 10^{14} W/cm^2$. The resulting x-ray spectrum is dispersed by Bragg reflection from a flat crystal and recorded on photographic film.

As Figure 1 indicates, the thin film sample occupies two thirds of the x-ray beam. The remaining 1/3 of the x-ray beam forms the reference spectrum on the photographic film. An infrared prepulse of 30ns width, which has been chipped off the main laser pulse is focused with a cylindrical lens onto a rectangular region comprising about 1/2 of the

width the thin film sample, causing melting of the sample in this area a few tens of ns before the interrogating x-ray pulse arrives. Thus, the reflected (diffracted) x-rays form a triple image on the photographic film, with the reference portion on the top 1/3, the melted sample portion on the middle 1/3 and the solid sample portion on the bottom 1/3. In this way all of the spectra required in an experiment are recorded simultaneously using a single laser pulse. The absorption (EXAFS) spectra of both the solid and melted areas of the sample can easily be extracted from the data since both the incident and transmitted x-ray intensities are known for each wavelength.

To insure that the entire sample is melted, and none of the sample is vaporized, the duration of the infrared prepulse should exceed the thermal diffusion time through the thin film sample. On the other hand, the time lapse between melting and interrogation must be short enough that the molten film maintains its integrity. The approximate relaxation time, τ, for temperature equilibration in a slab is $l^2/4K$, where l is the thickness of the slab and K is its thermal diffusivity (defined as $K = k/c\rho$ where k is the thermal conductivity, c the specific heat, and ρ the density). Thus, a delay of greater than 10ns is needed to produce a reasonably uniform temperature in a 2 m thick Al foil. Since the thermal conductivity of molten Al is about a factor of 3 lower than that of the solid, a heating pulse width of 20-30 ns is needed to ensure complete melting without vaporization.

Because the entire x-ray spectrum must be recorded in a very short time, the detector should have a time-integrating array capability.

Solid state spectra array systems[8] and slow sweep vidicon systems[9] can be used for this purpose. However, we have chosen to use film because of its ready availability and versatility. When film is evaluated by digital densitometer techniques, it is capable of high resolution and contrast discrimination. With proper choice of film type, grain size, exposure and data handling, it is possible to obtain results within an order of magnitude of the statistical limit allowed by the incident x-ray fluence. Because the photographic film is a nonlinear recording medium, it is necessary to multiply the measured optical density by a known response factor to determine the absolute x-ray flux at each wavelength. This numerical data handling is performed by an on-line computer; the same computer also does the background subtraction and Fourier transform calculations.

Results and Discussion

The capability of this technique for time-dependent EXAFS is illustrated in Figure 2, which shows simultaneous absorption spectra of a solid and molten Al foil 2 μm thick. The major set of peaks, attributable to the solid Al structure, are strongly attenuated in the laser-EXAFS spectrum of the molten zone. Some small residual peaks remain essentially unattenuated. These are tentatively attributed to the aluminum oxide surface layers on the foil. The prepulse used to melt the Al foil in this experiment was 30 ns FWHM and contained sufficient energy to melt but not to vaporize the foil. The interrogating pulse was 1.5ns FWHM and was delayed approximately 30ns from the peak of the prepulse. The laser target

used for these studies was iron, a material which produces mainly continuous emission in the vicinity above the K-edge of aluminum. Line radiation increases the probable error in data reduction and is avoided as much as possible. A RAP (rubidium acid phthalate) crystal was used to disperse the x-ray spectrum in these experiments.

The data from Figure 2 were analyzed in k-space within the range $2<k<10$ with a modified Fourier transform procedure, using k^3 weighting of the EXAFS spectrum and a third-order polynomial background subtraction routine. The transformed data are presented in Figure 3. For the crystalline sample, peaks corresponding to the known first, second, and possibly third shell Al-Al distances can be observed. While the data are somewhat noisy, the accuracy of these results (Table 1) serves to confirm the utility of the laser-EXAFS technique for materials in this atomic weight range.

The salient observation is that the amplitude modulation (in R space) of the transformed data for the molten zone is attenuated significantly relative to that of the crystalline zone. This is clear confirmation that melting was achieved with the extended prepulse, and is consistent with the results obtained by others in EXAFS studies of liquid metals.[10] The fact that EXAFS oscillations can still be observed at all (Figure 2b) indicates that a degree of local order is retained in the melt, at least within the 30 ns duration of the experiment; it might be expected that the EXAFS would wash out nearly completely if a random distribution of nearest-neighbor distances had been produced. It is perhaps signifi-

cant that the EXAFS spectra of liquid Ga and several other metals retain a high degree of structure which is nearly identical to that of the solid elements.[10] These molten metals are thought not to be simple hard-sphere liquids, and in the case of liquid Ga, at least, the presence of loosely associated diatomic species has been suggested.[11] Since Al is in the same family of the periodic table as is Ga, it may be that similar dimers occur in the Al melt, at least on a very short time scale.

Conclusion

In summary, the results obtained here provide evidence for residual local structure in rapidly melting Al, perhaps similar to that previously observed by others in liquid Ga. More generally, we have demonstrated that the fast-kinetic laser-EXAFS technique is capable of studying dynamic structural changes of transient samples on a multi-nanosecond time scale, and have recorded the first real-time EXAFS observation of a transient phase change.

Acknowledgements

The Fourier-transform program used in this work was based on a data-analysis software package kindly provided to us by Prof. K. O. Hodgson (Stanford University). Valuable assistance with data reduction was provided by Mr. Jeffery Gulcher. This work was supported by the U.S. Air Force Office of Scientific Research and the Battelle Development Corporation.

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TABLE 1. COMPARISON OF CRYSTALLOGRAPHIC AND FLASH-EXAFS RESULTS FOR CRYSTALLINE AND MOLTEN ALUMINUM

	Al - Al Distance (Angstroms)	
Shell	Crystalline Al (X-ray Diffraction)[a]	Crystalline Al (This Work)
First Shell	2.88	2.9
Second Shell	4.04	4.1
Third Shell	5.76	5.5

(a) American Institute of Physics Handbook, 2nd Ed., p. 9-4, Gray, D. E., ed., McGraw-Hill, Inc., New York (1963).

FIGURE CAPTIONS

Figure 1. Schematic view of flash-EXAFS experimental configuration.

Figure 2. Laser-EXAFS spectra of solid (top) and flash-melted (bottom) zones of aluminum film.

Figure 3. Fourier-transformed laser-EXAFS data from Figure 2, showing inter-atomic distances calculated for solid (top) and flash-melted (bottom) aluminum.

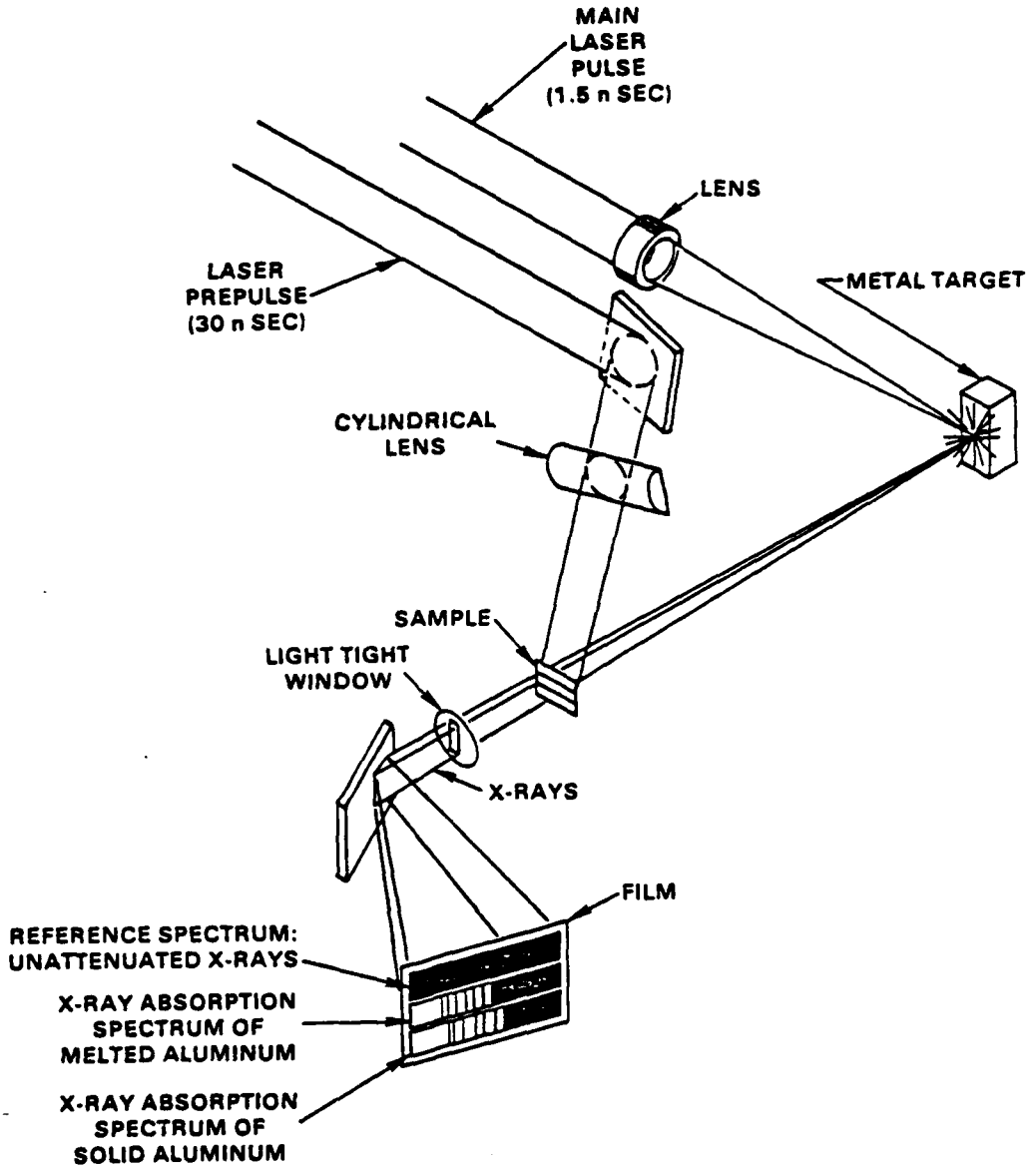
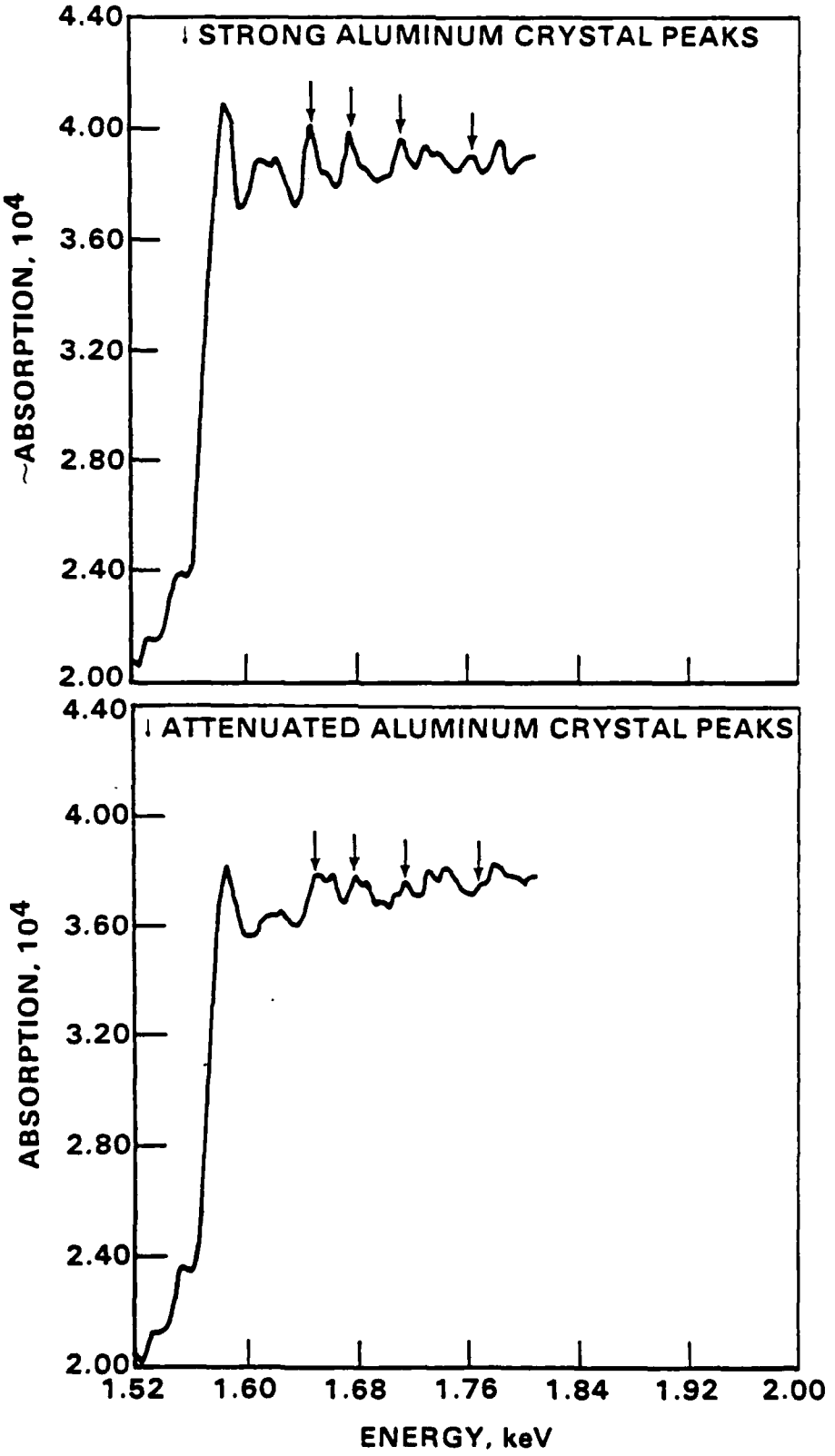
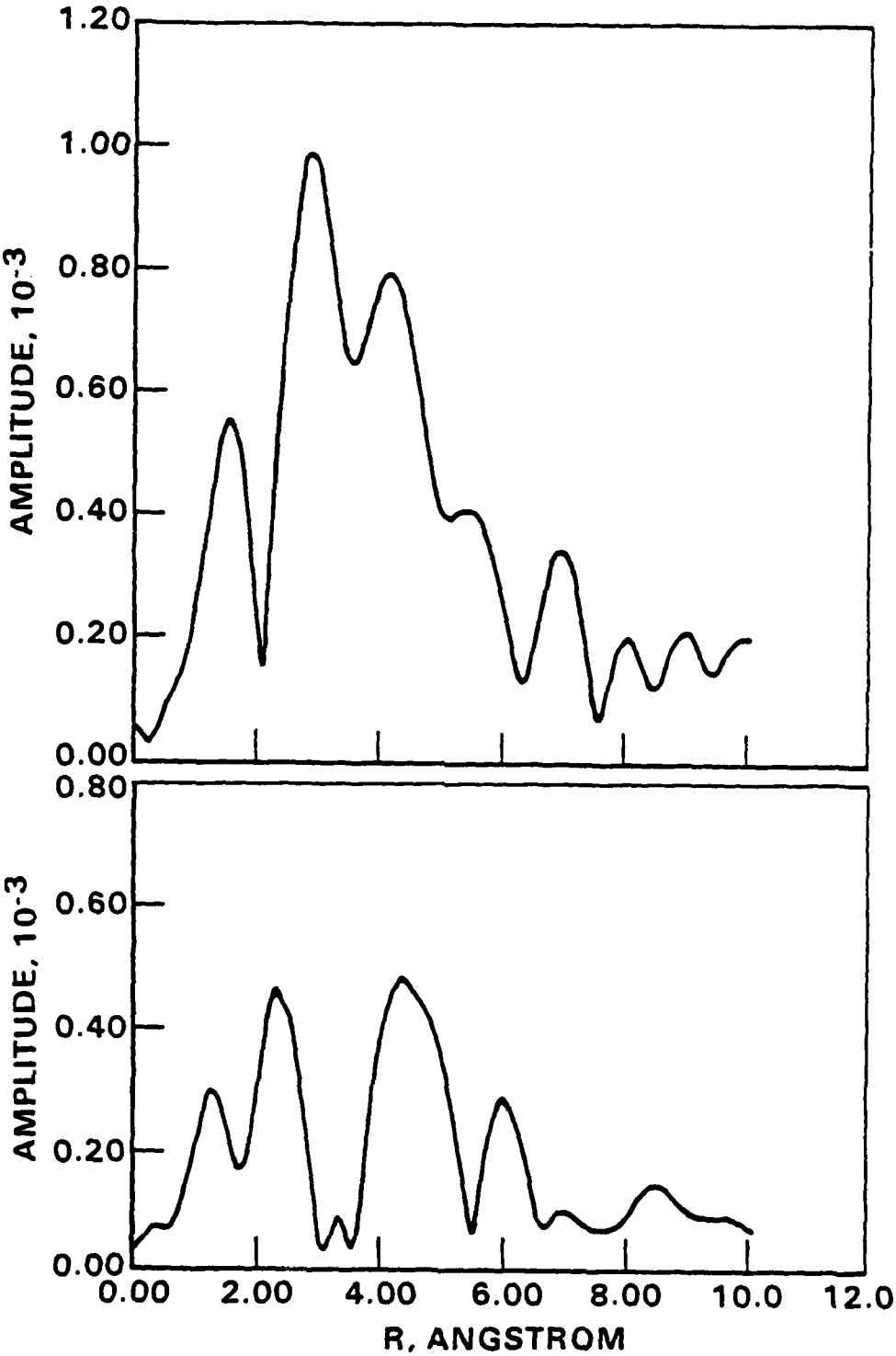


FIG. 1 (EPSTEIN / SCHWARTZ : ELECTRODES)


↓ STRONG ALUMINUM CRYSTAL PEAKS
~ABSORPTION, 10^4
4.40
4.00
3.60
3.20
2.80
2.40
2.00
↓ ATTENUATED ALUMINUM CRYSTAL PEAKS
ABSORPTION, 10^4
4.40
4.00
3.60
3.20
2.80
2.40
2.00
1.52
1.60
1.68
1.76
1.84
1.92
2.00
ENERGY, keV


1.20
1.00
0.80
0.60
0.40
0.20
0.00
AMPLITUDE, 10-3
0.80
0.60
0.40
0.20
0.00
AMPLITUDE, 10-3
0.00
2.00
4.00
6.00
8.00
10.0
12.0
R, ANGSTROM

RECOMMENDATIONS FOR FUTURE RESEARCH

On the basis of the research performed to date, it seems clear that laser-EXAFS is now well established as a viable tool for the study of chemical structure in a variety of materials under both static and transient conditions. The laser-EXAFS technique thus makes possible a number of new studies of major scientific importance (and possible relevance to Air Force goals). Among these are the following key experimental areas:

- Flash-EXAFS Studies of Rapidly Melted Metals and Alloys. As the last manuscript in this report indicates, we have now demonstrated that flash-EXAFS spectra of laser-melted metals can be obtained in real time. This provides a new and powerful tool for studying the dynamics of the melting and resolidification process, as EXAFS spectra can be obtained at a variety of delay times after the melting pulse of infrared laser radiation has hit the sample. This area is particularly relevant to both the growing interest in rapidly cooled amorphous metals and the contemplated use of lasers as defensive weapons.

- Laser-EXAFS Studies of Catalysts. The detailed structures of many catalysts used for chemical synthesis or petroleum refining are known only poorly, if at all. For those catalysts which contain light elements within the range of laser-EXAFS, it should be possible to elucidate both the structure of the catalyst itself and (with suitable fluorescence detection techniques) the structure of reactive species adsorbed to the surface of the catalyst material.

- Flash-EXAFS Studies of Photosynthesis and Other Photochemical Reactions. In flash-EXAFS, there exists a unique tool for

- Flash-EXAFS Studies of Photosynthesis and Other Photochemical Reactions. In flash-EXAFS, there exists a unique tool for probing the dynamic structural changes that occur when molecules are excited to upper electronic states by the absorption of visible or ultraviolet light. This information is of crucial importance, not only to understanding the details of the photosynthetic process, but to understanding the photophysics and photochemistry of many other materials (including dyes and pigments) as well.

- Laser-EXAFS Studies of Metalloenzymes and Proteins . An area of crucial importance in the diagnosis of certain metabolic diseases is the comparative study of the structure of active sites in certain metallo-enzymes obtained from healthy individuals and from patients afflicted with the disease. While these studies are presently beyond the capabilities of laser-EXAFS because the enzymes are highly dilute in the x-ray absorbing metal atoms (leading to serve signal-to-noise problems), we anticipate that future improvements in the laser-EXAFS technique will make these experiments feasible.

In addition to those fields of study, there are many aspects of the laser-EXAFS technique that are in need of further development. Chief among these are: the laser system itself, which should be replaced by a less cumbersome, more efficient laser system; the detector system, which should be modified to permit the use of solid-state photodiode arrays for both transmission and front-surface EXAFS measurements; and the data analysis software, which should be improved to permit the use of additional techniques for background removal and extraction of the EXAFS signal.

It is Battelle's hope that experiments of the type outlined

above can be initiated in the not-too-distant future. We remain committed to the further development and utilization of the laser-EXAFS technique, and hope to remain in the forefront of this most exciting new field of science.