somewhat smaller reference lists were used and all single excitations from the reference space CI were retained. The molecules lie in the *yz* plane with the *z* axis oriented along the CH bond. Electric field gradients and hyperfine coupling parameters are given in the principal axis systems.

Discussion

EPR work by McBride and Merrill on the related benzoyloxyl radical, $C_6H_5CO_2\cdot$, argues in favor of a $^2B_2$ ground state with equal C–O bond lengths. Their reported spin properties are generally in good agreement with our theoretical results for $^2B_2$ formyloxyl in Table V. The 52° angle between the two-fold rotation axis of the molecule and the local magnetic axis on oxygen, calculated at the CI level, is in excellent accord with their experimental result. The computed anistropic hyperfine parameters for ^{13}C are all somewhat too small in absolute magnitude, compared with the experimental values. For instance, converting the $^2B_2$ entries in Table V to gauss gives −3.29, 2.87, and 0.41 in the local *x*, *y*, and *z* directions, compared to −3.86, 3.08, and 0.78 obtained experimentally for benzyloxyl. The calculated ^{17}O anisotropic hyperfine splittings in gauss are 27.3, 27.8, and −55.1, which are all larger than those (19, 22, and −40) measured experimentally for benzoyloxyl.

The spin properties reported for benzoyloxyl by McBride and Merrill suggest a $^2B_2$ ground state for this radical, in agreement with our DZP SDQ-CI calculations on formyloxyl. Nevertheless, with a surface as flat as that which we compute for formlyloxyl, a phenyl substituent effect on the equilibrium geometry observed for benzoyloxyl should be considered.

Whether $^2B_2$ is a minimum or a transition state, connecting two A′ minima with unequal bond lengths, depends critically on the vertical energy separation of the $^2A_1$ state that can be mixed with $^2B_2$ by asymmetric distortion of the CO bond lengths. Since these two states differ in the occupancy of an MO ($6a_1$ in formyloxyl) that has appreciable density on the substituent group in acyloxyl radicals ($R-CO_2\cdot$), a substituent effect on the preferred geometry of the lowest σ state seems possible.

Because calculations on benzoyloxyl of the same quality as those we carried out on formyloxyl were out of the question for us, we investigated the occurrence of a σ substutuent effect by comparing the $^2B_2$–$^2A_1$ energy difference in the two radicals. Calculations were performed at the RHF level with the Dunning [3s,2p/2s] basis set. The optimal geometry in $^2B_2$ of formyloxyl was used for the OCO portion of both radicals, and a standard benzene geometry was assumed for the phenyl group in benzoyloxyl. Figure 8 shows the singly occupied b_2 orbital in the $^2B_2$ state of benzoyloxyl, along with some geometry parameters.

At the RHF level of theory the computed $^2B_2$–$^2A_1$ energy difference is 33.6 kcal/mol compared to 31.4 kcal/mol in formyloxyl. The larger energy difference found in benzyloxyl would tend to favor a C_{2v} ground state more in this radical than in formyloxyl. However, the near identity of these two numbers provides no evidence of the operation of a significant σ substituent effect. Thus, the finding of a $^2B_2$ ground state for benzoyloxyl furnishes experimental support for our prediction of the same C_{2v} σ ground state for formyloxyl.

Acknowledgment. The authors thank the National Science Foundation for partial support of this research.

Registry No. HCO_2, 16499-21-1.

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

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Received January 19, 1982

Abstract: Extended X-ray absorption fine structure (EXAFS) spectra of solid and flash-melted Al films have been measured simultaneosly 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 structural 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 the 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, one can obtain information 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.

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]

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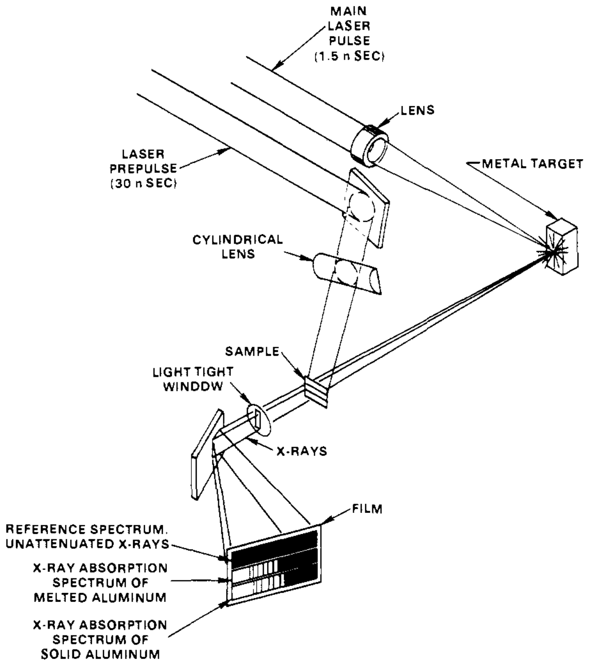

Figure 1. Schematic view of flash-EXAFS experimental configuration.

These experiments have shown that it is possible to obtain well-resolved EXAFS spectra of light elements 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 that 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/s. 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 makes laser-EXAFS a potentially new tool for 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 multinanosecond 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 100 J and pulse width of 1.5 ns (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 at an incident intensity of about 2×10^{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 third of the X-ray beam forms the reference spectrum on the photographic film. An infrared prepulse of 30 ns width, and containing about 120 mJ of infrared energy, which has been chipped off the main laser pulse is focused with a cylindrical lens onto a rectangular region comprising about half of the width of the thin-film sample, causing melting of the sample of this area a few tens of nanoseconds before the interrogating X-ray pulses arrives. Thus, the reflected (diffracted) X-rays form a triple image on the photographic film, with the reference portion on the top third, the melted sample portion on the middle third, and the solid sample portion on the bottom third. In this way all of the spectra required in an experiment are recorded simultaneously by 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 that 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 10 ns is needed to produce a reasonably uniform temperature in a 2-μm-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. We estimate that to completely melt the zone affected by the prepulse (which was focused to a strip about 10 mm × 1 mm in size), approximately 60–65 mJ of energy would be required. Since the prepulse carried about 120 mJ of energy, the sample should have been melted completely (but not vaporized), given the efficient absorption of 1.06-μm Nd:glass laser radiation by aluminum.

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 spectral 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 the solid and molten Al foil. The major absorption peaks, attributable to the solid Al structure,[6,7,10] 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,[10] which may also be responsible for the subtle differences between the published EXAFS spectra of solid aluminum.[6,7,10]

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, as noted above. The interrogating pulse was 1.5-ns fwhm and was delayed approximately 30 ns from the peak of the prepulse. The laser target used for these studies was iron,

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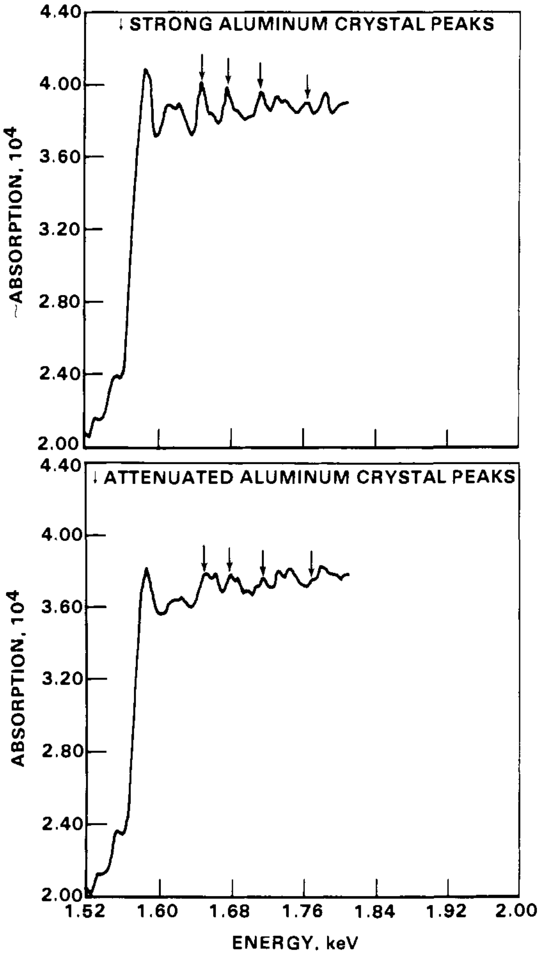

Figure 2. Laser-EXAFS spectra of solid (top) and flash-melted (bottom) zones of aluminum film.

Table I. Comparison of Crystallographic and Flash-EXAFS Results for Crystalline and Molten Aluminum

	crystalline Al-Al distance, Å	
shell	X-ray diffraction[a]	this work
first	2.86	2.9
second	4.04	4.1

[a] American Institute of Physics Handbook, 2nd Ed.; Gray, D. E., Ed.; McGraw-Hill: New York, 1963; p 9-4.

a material that produces mainly continuous emission of 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, by 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 and second shell Al–Al distances can be observed. While the data are somewhat noisy and are not corrected for phase shift (which typically shifts the peaks in R space by a few tenths of an angstrom), the overall accuracy of these results (Table I) serves to confirm the utility of the laser-EXAFS technique for materials in this atomic weight range.

The salient observations are 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 and that the major peak is shifted to a greater distance in the melt. 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.[11] The fact that EXAFS oscillations can still be observed at all (Figure 2, bottom) 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 significant that the EXAFS spectra of liquid Ga and several other metals retain a high degree of structure that is nearly identical with that of the solid elements.[11] 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.[12] 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.

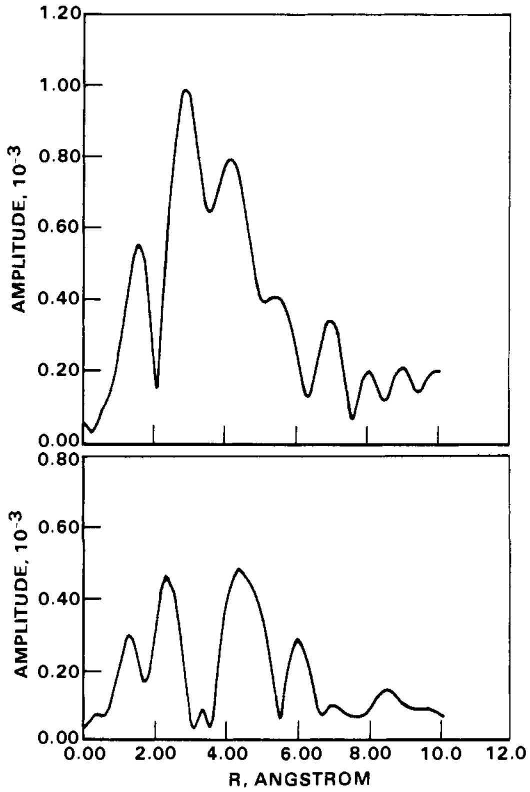

Figure 3. Fourier-transformed laser-EXAFS data from Figure 2, showing interatomic distances calculated for solid (top) and flash-melted (bottom) aluminum.

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 multinanosecond time scale and have recorded the first real-time EXAFS observation of a transient phase change.

Acknowledgment. The Fourier-transform program used in this work was based on a data-analysis softwares package kindly provided to us by Prof. K. O. Hodgson (Stanford University). Valuable assistance with data reduction was provided by 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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