Published in final edited form as:

Rev Sci Instrum. 2016 November ; 87(11): 11E305. doi:10.1063/1.4959918.

High resolution spectrometer for extended x-ray absorption fine structure measurements in the 6 keV to 15 keV energy range

J. F. Seely^{1,a)}, L. T. Hudson², Albert Henins², and U. Feldman¹

¹Artep Inc., 2922 Excelsior Springs Court, Ellicott City, Maryland 21042, USA

²National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, USA

Abstract

A Cauchois transmission-crystal spectrometer has been developed with high crystal resolving power in the 6 keV–15 keV energy range and sufficient sensitivity to record single-shot spectra from the Lawrence Livermore National Laboratory (LLNL) Titan laser and other comparable or more energetic lasers. The spectrometer capabilities were tested by recording the W L transitions from a laboratory source and the extended x-ray absorption fine structure (EXAFS) spectrum through a Cu foil.

I. Introduction

Using reflection crystal spectrometers, it has been shown that the temperature, density, and local structure of shock-compressed metal foils (V, Ti, and Fe) can be determined from the K edge extended x-ray fine structure (EXAFS) spectra.^{1–3} In order to extend this technique to substantially higher atomic number elements and higher energies, and to avoid the small crystal grazing angles and alignment difficulties associated with reflection crystals, an efficient and compact transmission crystal spectrometer is well suited to the task. We report the laboratory development of such a spectrometer that is similar in design and operation to a spectrometer that has successfully recorded single-shot spectra at the Titan laser facility.⁴ The spectrometer resolving power was tested by recording the W L transitions from a laboratory source, and the EXAFS spectrum through a Cu foil was recorded.

The crystal chosen in the present work was a 100 μm thick quartz plate cylindrically bent on a form having 500 mm radius of curvature. In the Cauchois configuration, the source is on the convex side of the crystal and the spectral lines are focused on the Rowland circle on the opposite side of the crystal. The Rowland circle has diameter equal to the crystal bending radius (500 mm), and the image plate detector was placed on the Rowland circle.

As illustrated in Fig. 1, the spectrometer utilizes a quartz transmission crystal that is cut with the (100) planes perpendicular to the crystal surface. Asymmetric diffraction is employed using the (302) planes that have an angle of 27.69° from the (100) planes (and from the

^{a)}Author to whom correspondence should be addressed. Electronic mail: seelyjf@gmail.com.

Note: Contributed paper, published as part of the Proceedings of the 21st Topical Conference on High-Temperature Plasma Diagnostics, Madison, Wisconsin, USA, June 2016.

normal to the crystal surface). The crystal alignment is accomplished using a three-step procedure that is described in more detail in Ref. 4: (1) an alignment laser points to the center of the x-ray source, and the crystal is positioned on a precision rotation stage so that the alignment beam is back-reflected from the center of the crystal. (2) The crystal is rotated to the Bragg angle θ corresponding to the central energy E of the desired spectral range, $\sin \theta = hc/2dE$, where $2d = 0.2512$ nm is the (302) lattice spacing, and the spectrometer slit aperture and the detector are centered on the reflected alignment beam. (3) The crystal is rotated by an additional angle equal to the (302) “asymmetry” angle ($\alpha = 27.69^\circ$) to an angle of $\theta + \alpha$ measured from the alignment laser beam.

In this crystal orientation, the central diffracted ray having energy E emerges from the back surface of the crystal with angle $\theta - \alpha$ from the normal to the crystal surface. As Cauchois first pointed out in 1932,⁵ if this angle is small ($\theta \approx \alpha$), then the spectral line broadening associated with the cylindrical bending of the crystal and the source size is small and can be made comparable to the crystal's rocking curve width (or integrated reflectivity). In addition, the broadening associated with the crystal thickness decreases in proportion to the thickness.⁶ Thus the optimum spectral broadening and resolving power are achieved by selecting the $2d$ and α parameters of the asymmetric diffraction planes so that the desired central energy is diffracted nearly perpendicular to the back crystal surface ($\theta \approx \alpha$) of a thin crystal. The 8.980 keV Cu K edge energy is diffracted by the quartz (302) planes with Bragg angle 33.35° , the diffracted ray has angle 5.66° to the crystal normal, and this angle is sufficiently small so that the dominant broadening mechanism is crystal thickness.

II. High-Resolution Spectra

Using the crystal optic described above, high resolution spectra were recorded using an electron-bombarded industrial W x-ray tube. A $12.7 \mu\text{m}$ thick Cu foil was placed at the spectrometer slit aperture (located between the crystal and the detector) and covered the lower half of the slit. Figure 2 shows the resulting spectra that are centered on the Cu K edge energy 8.9805 keV.⁷ The upper (unattenuated) and the lower (attenuated) spectra derived from a single image-plate exposure are shown in Fig. 2. The W source conditions were 100 kV peak kilovoltage, 10 mA current, 1 mm source width, and 2 mm source height. The source to crystal distance was 25 cm, and the exposure time on a Fuji TR image plate was 6 min. Appearing in the spectra are the W $L\alpha$ and $L\beta$ lines. The Cu K EXAFS features span a 400 eV range above the Cu K edge that is free of spectral lines. In this energy range, the Cu foil absorbs the bremsstrahlung continuum from the W anode that has been dispersed by the crystal's (302) planes with the largest absorption coefficient occurring just above the K edge and diminishing at higher energies.

Also present in Fig. 2 is the weak Cu $K\beta_1$ line, and this line as well as weak Cu $K\alpha$ lines appears in all spectra covering those lines and is caused by the fluorescence of Cu parts inside the x-ray tube. A property of the Cauchois spectrometer is that all spectral lines from an extended source are focused on the Rowland circle with the same dispersion. The energy scale was established using the W L and Cu $K\beta_1$ transition energies (indicated by the vertical lines in Fig. 2) as energy fiducials.⁷

In spectra recorded without the Cu filter and with source to crystal distances varying from 25 cm to 150 cm, Voigt profiles were fitted (using the least squares technique) to the two strongest W L lines on either sides of the Cu K edge, the $L\alpha_1$ and $L\beta_1$ lines, and the FWHM values of the Lorentzian and Gaussian components were determined. For each spectral line, the natural lifetime width (from Ref. 8) was subtracted from the fitted Lorentzian width, $6.51 \text{ eV} \pm 0.65 \text{ eV}$ for the $L\alpha_1$ transition and $6.52 \text{ eV} \pm 0.65 \text{ eV}$ for the $L\beta_1$ transition. The Lorentzian and Gaussian widths resulting from the spatial resolution of the TR image plate from Ref. 9, corresponding to $0.58 \text{ eV} \pm 0.1 \text{ eV}$ Lorentzian and $0.66 \text{ eV} \pm 0.1 \text{ eV}$ Gaussian at the Cu K edge, were removed from the fitted Lorentzian and Gaussian widths. The resulting widths are shown in Fig. 3. The resulting Lorentzian average width is zero within the uncertainties (primarily from the natural widths). The resulting Gaussian widths are independent of the source-to-crystal distance and have an average value $1.92 \text{ eV} \pm 0.10 \text{ eV}$ at a 1-sigma statistical confidence level. This indicates that the intrinsic crystal broadening, after removal of the natural and detector broadenings, is Gaussian in shape with $1.92 \text{ eV} \pm 0.10 \text{ eV}$ FWHM. Dividing by the 27 eV/mm dispersion, this corresponds to $71 \text{ }\mu\text{m}$ on the detector and to an angle of $1.4 \times 10^{-4} \text{ rad}$ at the 500 mm detector distance. Comparison with the various broadening mechanisms of the Cauchois spectrometer in the asymmetric diffraction configuration indicates that the intrinsic crystal broadening primarily results from the $100 \text{ }\mu\text{m}$ thickness of the crystal.⁶

Shown in Fig. 4 is the Cu K absorption coefficient $\ln[(C_o - C_b)/(C - C_b)]$, where C and C_o are the digitized count levels with and without the Cu foil and C_b is the background level. The background level, caused by undispersed radiation reaching the detector that has been scattered by the crystal and the slit aperture as well as by the copper foil, is an important aspect of the data analysis. The background level was chosen so that the absorption coefficients below and above the K edge agree with those calculated using the NIST Cu attenuation cross sections and the $12.7 \text{ }\mu\text{m}$ thickness of the Cu foil.¹⁰ The energy scale in the K edge region was primarily established by the nearby Cu $K\beta_1$ transition energy $8905.413 \text{ eV} \pm 0.038 \text{ eV}$ (Ref. 7) and with $\pm 0.1 \text{ eV}$ Voigt profile fitting 1-sigma uncertainty.

The absorption coefficient curve shown in Fig. 4 was smoothed by a lowpass Fourier transform filter that removed the high-frequency noise on the scale of the $17.2 \text{ }\mu\text{m}$ image plate digitization step. The K edge energy, measured from the first inflection point on the absorption curve, was 8979.25 eV with $\pm 0.1 \text{ eV}$ fitting uncertainty and additional $\pm 0.14 \text{ eV}$ uncertainty from the Cu $K\beta_1$ energy fiducial. This value is in agreement with the tabulated value $8980.5 \text{ eV} \pm 1.0 \text{ eV}$ (Ref. 7) and is outside the very small uncertainty quoted in Ref. 11, $8980.48 \text{ eV} \pm 0.02 \text{ eV}$, measured using a Cu foil cooled to 77 K .

We note that the small absorption dip at 8983.6 eV in Fig. 4 arises from transitions to states having pure $4p$ symmetry in the polycrystalline Cu foil,¹² and this feature is absent in the absorption curve of Cu vapor.¹³ The resolution of this feature is further confirmation of the high resolving power of the present spectrometer.

III. Exafs Spectrum

Shown in Fig. 5 is the normalized EXAFS spectrum plotted as a function of the electron wave number $k = [2m_e(E - E_0)/(\hbar/2\pi)^2]^{1/2}$, where $E_0 = 8979.25$ eV is the Cu K edge energy. The EXAFS spectrum has the usual appearance of damped oscillations having increasing period with wave number.¹² The oscillations result from the interference of the outgoing photoelectron and the electron scattered from neighboring atoms. To a first order approximation that neglects phase change and other effects along the electron path, the distance to the neighboring atoms can be calculated by taking the Fourier transform of the EXAFS spectrum $\chi(k)$,

$$\text{FT}(R) = \frac{1}{\sqrt{2\pi}} \int_{k_{\min}}^{k_{\max}} k^n \chi(k) e^{i2kR} dk,$$

where R is the atomic range parameter. The result is shown in Fig. 6 where the peaks indicate the range parameters from the absorbing atom to the first four shells of atoms. The presently derived range parameter to the first shell is $2.19 \text{ \AA} + 0.10 \text{ \AA}$, and this statistical uncertainty is in agreement with the value $2.25 \text{ \AA}$ (indicated by the vertical line in Fig. 6) in room-temperature polycrystalline face-centered cubic Cu derived using synchrotron radiation and more sophisticated EXAFS analysis software.¹²

The present Cu EXAFS spectra are in agreement with spectra recorded by a Cauchois spectrometer utilizing a mica crystal bent to 400 mm radius of curvature and recorded on photographic film.¹⁴ Owing to the low sensitivity of photographic film, the exposure times were 2–3 h compared to the present 6 min exposure time on the TR image plate. Because of the larger 2d spacing of the mica crystal ($2d = 1.984$ nm), the dispersion was 80 eV/mm and inferior to the present 27 eV/mm dispersion at the Cu K edge. However, the spatial resolution of the photographic film was higher than for the TR image plate used here, approximately $10 \text{ }\mu\text{m}$ versus $40 \text{ }\mu\text{m}$, and the spectral resolutions of the two spectrometers are comparable.

When recording the W L spectra from the same laboratory source, the present spectrometer utilizing diffraction from the (302) planes of a quartz (100) transmission crystal has exposure time (6 min on the TR image plate) comparable to a previous spectrometer utilizing diffraction from the (301) planes of a quartz (101) transmission crystal.⁴ The later spectrometer recorded well-exposed spectra from single shots of the Titan laser, indicating the present higher resolution spectrometer has the capability to record single-shot spectra from the Titan and comparable or higher energy lasers. This enables the recording of high-resolution single-shot EXAFS spectra from warm dense matter using the Titan and comparable or higher energy lasers. We note that the noise level is apparent in the oscillations having $k > 7 \text{ \AA}^{-1}$ in Fig. 5 while the distance to the first shell of neighboring Cu atoms (see Fig. 6) is primarily determined by the oscillations having k in the range $3 \text{ \AA}^{-1}$ – $7 \text{ \AA}^{-1}$ which have low noise level, and it is the first shell of atoms that is of most interest in the EXAFS analysis of warm dense matter which has low long-range order.

The technique of utilizing internal planes that diffract near normal to the exit surface of a transmission crystal to achieve minimal spectral broadening can be extended to higher energies by selection of asymmetric planes that have smaller 2d spacings resulting in diffraction nearly perpendicular to the back crystal surface ($\theta \approx \alpha$).¹⁵

Acknowledgments

Fuji TR image plate is used in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the U.S. government, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

References

1. Yaakobi B, et al. Phys Rev Lett. 2004; 92:095504. [PubMed: 15089486]
2. Ping Y, et al. Phys Rev Lett. 2013; 111:065501. [PubMed: 23971582]
3. Cho BI, et al. Sci Rep. 2016; 6:18843. [PubMed: 26733236]
4. Seely JF, et al. Rev Sci Instrum. 2016; 87:053101. [PubMed: 27250386]
5. Cauchois Y. J Phys Radium. 1932; 3:320.
6. Cauchois, Y., Bonnelle, C. Atomic Inner-Shell Processes. Crasemann, B., editor. Vol. II. Academic Press; New York: 1975.
7. Deslattes R, et al. Rev Mod Phys. 2003; 75:35.
8. Campbell J, Papp T. At Data Nucl Data Tables. 2001; 77:1.
9. Seely JF, et al. J Phys B. 2014; 47:115004.
10. Chantler, CT., et al. www.nist.gov/pml/data/ffast/index.cfm
11. Kraft S, et al. Rev Sci Instrum. 1996; 67:681.
12. Gaur A, et al. Proc Indian Natl Sci Acad. 2013; 79:921.
13. Arp U, et al. J Phys B: At, Mol Opt Phys. 1993; 26:4381.
14. Johari A, et al. Indian J Pure Appl Phys. 2011; 49:308.
15. Seely JF, et al. Opt Lett. 2014; 39:6839. [PubMed: 25503010]

Fig. 1.
Schematic of the crystal alignment.

Fig. 2.
Spectra centered on the Cu K edge.

Fig. 3.
Intrinsic crystal spectral line widths.

Fig. 4.
Cu K absorption coefficient.

Fig. 5.
Cu K edge EXAFS spectrum.

Fig. 6.
Atomic shell range parameter.